

Photoreductive N-N Homocoupling Catalyzed by a Superphotoreductant

Yi-Ping Wang,[†] Zhen-Zhen Guo,[†] Jian-Ping Qu,^{*‡} and Yan-Biao Kang^{*†}

[†]Hefei National Research Center for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

[‡]Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China

E-mail: ybkang@ustc.edu.cn, ias_jpqu@njtech.edu.cn

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1. General Information

All reactions were carried out under atmospheric pressure. Solvents were pre-dried over activated 4Å molecular sieves and heated to reflux over calcium hydride or Mg turnings and iodine crystals (CH₃CN, DCM, Et₃N, THF, DMF, DMSO, DIPA, DIPEA) under nitrogen atmosphere and collected by distillation. Aldehydes and ketones were used with purification as commercially available. Aldehydes, ketones and other chemicals without notes in experimental section were purchased from commercial sources. All reactions were performed with Semi-LED lamps (C35LU-60), the glass reaction tube was placed 1.5 cm away from LEDs. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel or basic aluminum oxide. Chemical yields refer to pure isolated substances. All work-up and purification procedures were carried out with reagent-grade solvents in air. ¹H, ¹⁹F decoupled, ¹³C{¹H} NMR spectra were recorded on a Bruker 400/500 spectrometer; Chemical shifts are reported in δ units relative to CDCl₃ [¹H δ = 7.26, ¹³C δ = 77.16] and DMSO- d^6 [¹H δ = 2.50, ¹³C δ = 39.52]. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). UV-Vis Absorption Spectrum was recorded on a UV-3600 spectrometer. Fluorescence Spectrum was recorded on an F-4600 spectrometer.



Figure S1. Reaction set up. The left picture shows the Schleck tube (inner/outer diameter: 19/22 mm, 2mm glass door, 25mL) used for the photocatalysis. The right picture shows the general reaction setup with light-on, in which six 3 W LEDs ($\lambda_{\text{max}} = 407\text{nm}$) beam were used as the light source. The glass reaction tube was placed 1.5 cm away from LEDs.

2. Optimization of Reaction

Procedure for imine radical homo-coupling: (*E*)-1-(*p*-tolyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (0.5 mmol, 1 equiv), **CBZ6** (x mol%) and reductant (y equiv) were weighed directly into an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (2.5 mL) was added sequentially in the Schlenk tube via syringe. Then the tube was placed 1.5 cm away from LEDs (3 W×6) with an electric fan cooling the reaction, and the reaction mixture was stirred vigorously under the irradiation. After Z h, the tube was removed from the light source. The crude mixture was extracted with DCM (10 mL × 3), then washed with 10 mL NaCl (aq., 1 N). Organic phase was collected and dried under vacuum. The conversion was determined by ¹H NMR technology using nitromethane and *tert*-butyl methyl ether (MTBE) as internal standards.

Table S1. Screening of Reaction Conditions^a

Entry	PC	x(mol%)	y (equiv)	2a (%) ^b
1	CBZ6	2.0	1.2	71 (82 ^d)
2	-	2.0	1.2	33
3	CBZ6	1.0	1.2	60
4	CBZ6	2.0	1.0	59
5	CBZ6	2.0	1.5	61
6	CBZ6	2.0	2.0	58
7 ^c	CBZ6	2.0	2.0	n.r.

^a Conditions: **1a** (0.5 mmol), **CBZ6** (x mol %), HCOONa (y equiv), DMSO (2.5 mL), 18 W LEDs ($\lambda_{\text{max}} = 407 \text{ nm}$), nitrogen atmosphere, about 40 °C. ^b Yield was determined by ¹H NMR analysis using nitromethane and *tert*-butyl methyl ether as internal standards; n.r. = no reaction. ^c Without light. ^d Isolated yield.

Table S2. Screening of Solvent^a

Entry	Solvent	2a (%) ^b
1	MeCN	9
2	EtOAc	9
3	DMF	18
4	DCM	45
5	THF	5

^a Conditions: **1a** (0.5 mmol), **CBZ6** (2 mol %), HCOONa (1.2 equiv), solvent (2.5 mL), 18 W LEDs ($\lambda_{\text{max}} = 407 \text{ nm}$), nitrogen atmosphere, about 40 °C. ^b Yield was determined by ¹H NMR analysis using nitromethane and *tert*-butyl methyl ether as internal standards.

Table S3. Screening of Photocatalyst^a

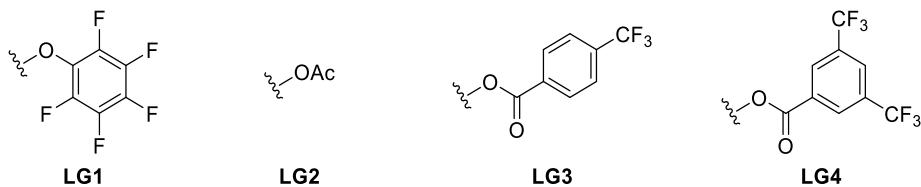
Entry	Photocatalyst	2a (%)^b
1	Ir(ppy)₃	28
2	Ru(bpy)₃Cl₂• 6H₂O	26
3	Rhodamine B	59
4	4CZIPN	68

^a Conditions: **1a** (0.5 mmol), **PC** (2 mol %), HCOONa (1.2 equiv), DMSO (2.5 mL), 18 W LEDs ($\lambda_{\text{max}} = 407 \text{ nm}$), nitrogen atmosphere, about 40 °C. ^b Yield was determined by ¹H NMR analysis using nitromethane and *tert*-butyl methyl ether as internal standards.

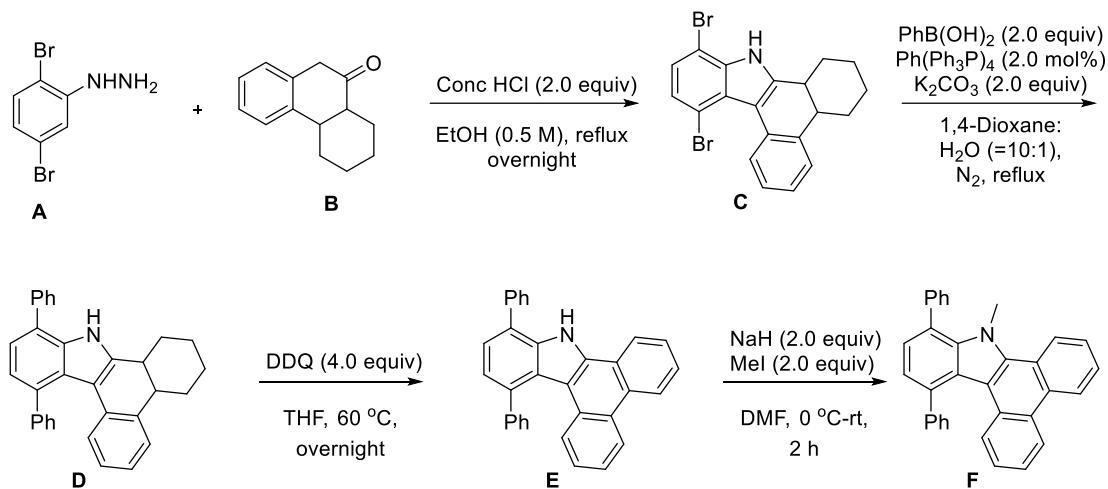
Table S4. Screening of leaving group^a

Entry	LG	2a (%)^b
1	LG1	0
2	LG2	0
3	LG3	8
4	LG4	33

^a Conditions: **1a** (0.5 mmol), **CBZ6** (2 mol %), HCOONa (1.2 equiv), DMSO (2.5 mL), 18 W LEDs ($\lambda_{\text{max}} = 407 \text{ nm}$), nitrogen atmosphere, about 40 °C. ^b Yield was determined by ¹H NMR analysis using nitromethane and *tert*-butyl methyl ether as internal standards.



3. Synthesis of CBZ6



To a stirred solution of (2,5-dibromophenyl)hydrazine (**A**, 20 mmol, 1.0 equiv) and 4b,6,7,8,8a,10-hexahydrophenanthren-9(5H)-one (**B**, 20 mmol, 1.0 equiv) in EtOH (40.0 mL) was dropwise added Conc HCl (40 mmol, 2.0 equiv). The reaction mixture was heated to reflux in an oil bath, stirring overnight. After the disappearance of **A**, the system was adjusted PH to neutral with Na₂CO₃ (1 M aq), extracted by ethyl acetate. Then combined organic layers were washed with water three times, dried over with dry Na₂SO₄, and concentrated under *vacuo* to give the crude compound **C** for the next step. (PS: Starting materials **A** and **B** were purchased from commercial sources.)

Crude intermediate **C** obtained above (20 mmol, 1.0 equiv), PhB(OH)₂ (2.0 equiv), Pd(Ph₃P)₄ (2.0 mol%) and K₂CO₃ (2.0 equiv) were weighed into a 100 mL Schlenk tube. The tube was evacuated and filled with nitrogen (three times). 1,4-dioxane (10 % vol H₂O) were added under nitrogen atmosphere. The reaction mixture was heated to reflux for 24 h in an oil bath. After the disappearance of **C**, the system was extracted by EA. Then combined organic layers were washed with water by three times, dried over with dry Na₂SO₄, and concentrated under *vacuo*. The mixture was filtered through a short pad of silica gel to obtain the crude product **D** (crude ¹H NMR yield: 67%). The crude intermediate was used directly for next step.

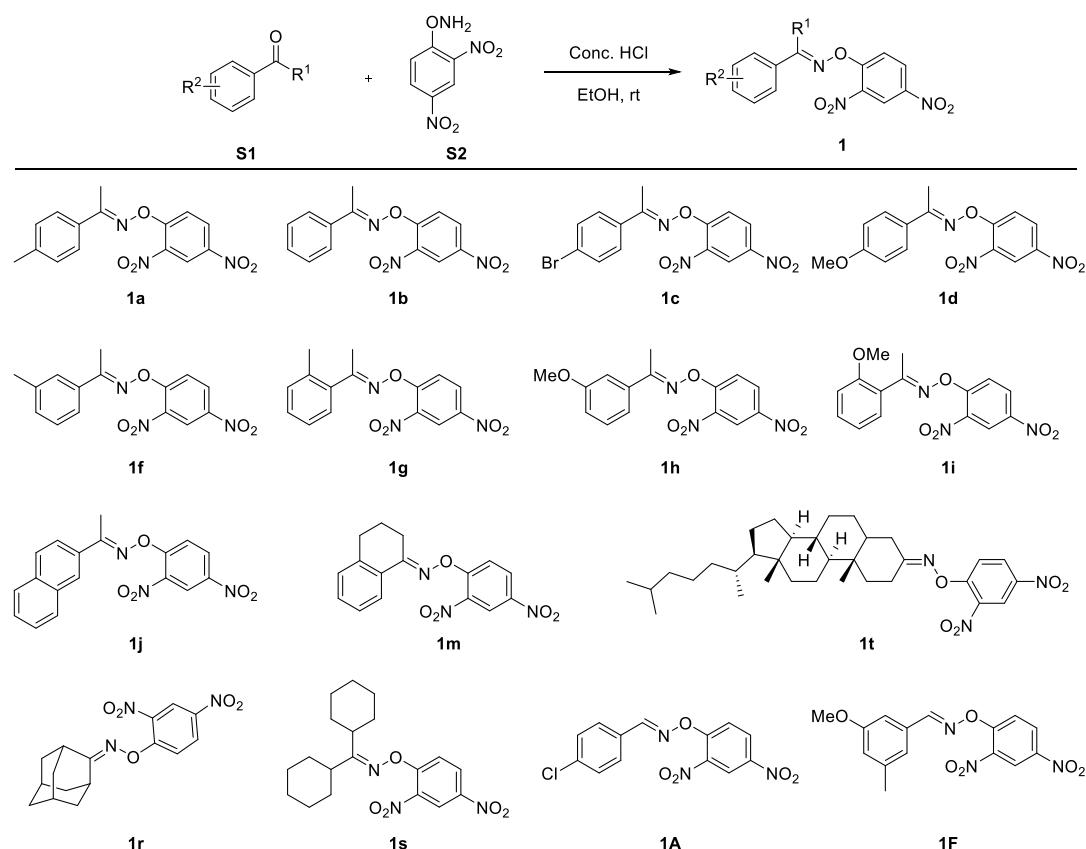
To a stirred solution of crude **D** (20 mmol, 1.0 equiv) in THF (50.0 mL) was added DDQ (3.0 equiv). The reaction mixture was stirred at 60 °C in an oil bath. After the disappearance of **D**, the resulting solution was filtered through Celite and washed with dichloromethane. The combined organic layers were washed by water with three times, dried over with dry Na₂SO₄, and concentrated under *vacuo* to obtain the crude product **E**, which was used directly for next step.

To a stirred solution of **E** (20 mmol, 1 equiv) in DMF (40.0 mL), NaH (60% dispersion in mineral oil, 2.0 equiv) was added portionwise under 0 °C. The solution was stirred at room temperature for 1 h, MeI (2.0 equiv) in DMF was dropwisely added. After the disappearance of **E**, the system was extracted by dichloromethane. Then combined organic layers were washed with water three times, dried over Na₂SO₄, and concentrated under *vacuo* and purified by column chromatography (3.3 g, 90%; over all 38%). ¹H NMR (400 MHz, CDCl₃) δ 8.79 (dd, *J* = 7.1, 3.9 Hz, 1 H), 8.62 (d, *J* = 8.2 Hz, 1 H), 8.42 (dd, *J* = 5.9, 2.1 Hz, 1 H), 7.74 (d, *J* = 7.7 Hz, 2 H), 7.67-7.65 (m, 2 H), 7.58-7.52 (m, 4 H), 7.48-7.38 (m, 3 H), 7.34 (t, *J* = 7.0 Hz, 1 H), 7.20 (d, *J* = 8.2 Hz, 1 H), 6.95 (t, *J* = 7.1 Hz, 1 H), 3.79 (s, 3 H). ¹H NMR data agreed with the literature¹⁹ we reported.

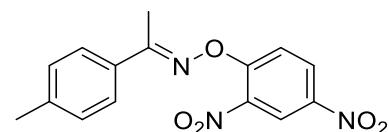
4. Synthesis of 1

4.1 Synthesis of compound 1a-1d, 1f-1j, 1m, 1r-1t, 1A, 1F

General Procedure 1 (GP1) for the condensation of acetophenone or aldehyde with *O*-(2,4-dinitrophenyl)hydroxylamine



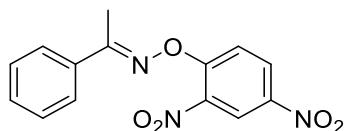
Concentrated HCl (2~3 drops) was added dropwise into a solution of **S2** (0.6 g, 3 mmol, 1.0 equiv) and acetophenone or aldehyde (**S1**, 1.2 equiv) in EtOH (5 mL). The reaction mixture was stirred overnight. After the disappearance of **S1**, 10 mL water was poured into the system. Then solid was separated out, and filtered by Buchner funnel. The solid was washed by petrol and dried under vacuo to give the pure product.



(*E*)-1-(*p*-tolyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (**1a**)

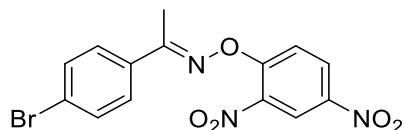
According to the **GP1**, compound **1a** (*Z:E* = 0.1:1) was obtained (88%, 1.35 g) as a

white solid, m.p.: 165.7-169.1 °C. **¹H NMR of Z and E-1a** (400 MHz, CDCl₃): δ 8.91 (d, *J* = 2.7 Hz, 1 H), 8.82 (d, *J* = 2.7 Hz, 0.1 x 1 H, *Z*), 8.45 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.41 (d, *J* = 2.7 Hz, 0.1 x 1 H, *Z*), 8.08 (d, *J* = 9.4 Hz, 1 H), 8.04 (d, *J* = 9.4 Hz, 0.1 x 1 H, *Z*), 7.67 (d, *J* = 8.2 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 0.1 x 2 H, *Z*), 7.30 (d, *J* = 8.2 Hz, 0.1 x 2 H, *Z*), 7.27 (d, *J* = 8.3 Hz, 2H), 2.58 (s, 0.1 x 3 H, *Z*), 2.57 (s, 3 H), 2.42 (s, 3 H), 2.42 (s, 0.1 x 3 H, *Z*). **¹³C{¹H} NMR of Z and E-1a** (100 MHz, CDCl₃): δ 163.5, 157.6, 141.7, 140.8, 136.1, 131.3, 129.7, 129.6, 129.3, 129.1, 128.6, 126.9, 122.3, 122.1, 117.5, 21.58, 14.8. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄N₃O₅⁺ 316.0928, found 316.0933.



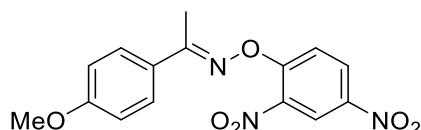
(*E*)-1-phenylethan-1-one *O*-(2,4-dinitrophenyl) oxime (**1b**)¹

According to the **GP1**, compound **1b** was obtained (82%, 0.74 g) as a white solid. **¹H NMR** (400 MHz, DMSO-*d*⁶): δ 8.85 (d, *J* = 2.7 Hz, 1 H), 8.57-8.54 (m, 1 H), 8.11 (d, *J* = 9.3 Hz, 1 H), 7.89-7.87 (m, 2 H), 7.57-7.51 (m, 3 H), 2.55 (s, 3 H).



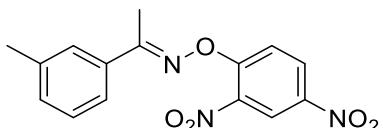
(*E*)-1-(4-bromophenyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (**1c**)²

According to the **GP1**, compound **1c** was obtained (88%, 1.00 g) as a white solid. **¹H NMR** (500 MHz, DMSO-*d*⁶): δ 8.85 (d, *J* = 2.5 Hz, 1 H), 8.56 (dd, *J* = 9.5, 2.5 Hz, 1 H), 8.10 (d, *J* = 9.0 Hz, 1 H), 7.83 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 2.53 (s, 3H).



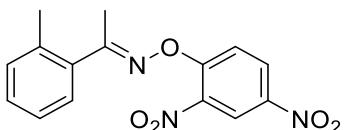
(E)-1-(4-methoxyphenyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1d)

According to the **GP1**, compound **1d** (*Z:E* = 0.2:1) was obtained (99%, 0.98 g) as a white solid, m.p.: 139.5-140.8 °C. **1H NMR** of **Z** and **E-1d** (400 MHz, CDCl₃): 8.91 (d, *J* = 2.7 Hz, 1 H), 8.83 (d, *J* = 2.7 Hz, 0.2 x 1 H, *Z*), 8.44 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.42-8.41 (m, 0.2 x 1 H, *Z*), 8.07 (d, *J* = 9.4 Hz, 1 H), 8.04 (d, *J* = 4.7 Hz, 0.2 x 1 H, *Z*), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 3.0 Hz, 0.2 x 2 H, *Z*), 7.23 (m, 0.2 x 2 H, *Z*), 6.97 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.84 (s, 0.2 x 3 H, *Z*), 2.56 (s, 3 H), 2.53 (s, 0.2 x 3 H, *Z*). **13C{1H} NMR** of **Z** and **E-1d** (100 MHz, CDCl₃): δ 163.0, 162.1, 157.7, 140.7, 136.1, 131.0, 129.5, 128.6, 126.3, 122.3, 117.5, 114.3, 55.6, 14.7. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄N₃O₆⁺ 332.0877 found 332.0880.



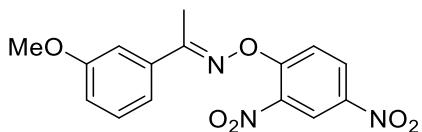
(E)-1-(*m*-tolyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1f)

According to the **GP1**, compound **1f** was obtained (91%, 0.86 g) as a white solid, m.p.: 125.6-126.4 °C. **1H NMR** (500 MHz, CDCl₃): δ 8.92 (d, *J* = 2.7 Hz, 1 H), 8.46 (dd, *J* = 9.3, 2.7 Hz, 1 H), 8.09 (d, *J* = 9.4 Hz, 1 H), 7.57 (d, *J* = 8.7, 2 H), 7.38-7.32 (m, 2 H), 2.58 (s, 3 H), 2.44 (s, 3 H). **13C{1H} NMR** (125 MHz, CDCl₃): δ 163.9, 157.6, 140.9, 138.8, 134.1, 132.0, 129.6, 128.9, 127.6, 122.3, 117.5, 21.6, 145.1. HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₁₅H₁₃NaN₃O₅⁺ 338.0747, found 338.0751.



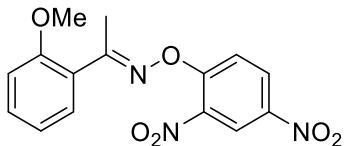
(E)-1-(*o*-tolyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1g)³

According to the **GP1**, compound **1g** was obtained (69%, 0.65 g) as a white solid. **1H NMR** (400 MHz, CDCl₃): δ 8.92 (d, *J* = 2.6 Hz, 1 H), 8.41 (dd, *J* = 9.4, 2.7 Hz, 1 H), 7.93 (d, *J* = 9.4 Hz, 1 H), 7.39-7.27 (m, 4 H), 2.54 (s, 3 H), 2.44 (s, 3 H).



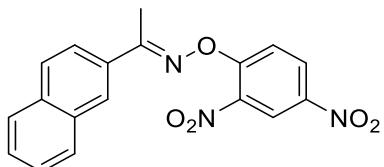
(E)-1-(3-methoxyphenyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1h)

According to the **GP1**, compound **1h** (*Z:E* = 0.1:1) was obtained (93%, 0.92 g) as a white solid, m.p.: 128.2-129.6 °C. **1H NMR** of *Z* and *E*-**1h** (500 MHz, CDCl₃): δ 8.92 (d, *J* = 2.5 Hz, 1 H), 8.81 (d, *J* = 2.7 Hz, 0.1 x 1 H, *Z*), 8.46 (dd, *J* = 9.5, 2.5 Hz, 1 H), 8.42-8.39 (m, 0.1 x 1 H, *Z*), 8.06 (d, *J* = 9.4 Hz, 1 H), 8.02 (d, *J* = 9.4 Hz, 0.1 x 1 H, *Z*), 7.41-7.30 (m, 3 H), 7.14-7.13 (m, 0.1 x 3 H, *Z*), 7.06 (dd, *J* = 7.5, 2.5 Hz, 1 H), 7.01 (d, *J* = 2.5 Hz, 0.1 x 1 H, *Z*), 3.90 (s, 0.1 x 3 H, *Z*), 3.88 (s, 3 H), 2.60 (s, 0.1 x 3 H, *Z*), 2.58 (s, 3 H). **13C{1H} NMR** of *Z* and *E*-**1h** (125 MHz, CDCl₃): δ 163.6, 159.9, 157.5, 141.0, 135.5, 130.0, 129.6, 122.3, 119.5, 117.5, 116.5, 112.8, 55.6, 15.1. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄N₃O₆⁺ 332.0877 found 332.0901.



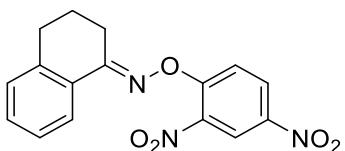
(E)-1-(2-methoxyphenyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1i)

According to the **GP1**, compound **1i** was obtained (93%, 0.92 g) as a white solid, m.p.: 127.9-128.8 °C. **1H NMR** (400 MHz, CDCl₃): δ 8.91 (d, *J* = 2.7 Hz, 1 H), 8.40 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 1 H), 7.48-7.44 (m, 1 H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 1 H), 6.99 (d, *J* = 8.7 Hz, 1 H), 3.89 (s, 3 H), 2.53 (s, 3 H). **13C{1H} NMR** (100 MHz, CDCl₃): δ 166.1, 157.8, 157.6, 140.8, 136.1, 131.9, 129.7, 129.5, 124.4, 122.2, 120.8, 117.6, 111.4, 55.7, 18.1. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄N₃O₆⁺ 332.0877 found 332.0891.



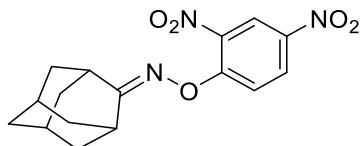
(E)-1-(naphthalen-2-yl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1j)

According to the **GP1**, compound **1j** (*Z:E* = 0.8:1) was obtained (100%, 1.05 g) as a white solid, m.p.: 187.5-188.3 °C. **1H NMR of Z and E-1j** (400 MHz, CDCl₃): δ 8.94 (d, *J* = 2.6 Hz, 1 H), 8.82 (d, *J* = 2.6 Hz, 0.8 x 1 H, *Z*), 8.48 (dd, *J* = 11.7, 2.6 Hz, 1 H), 8.44 (dd, *J* = 9.4, 2.6 Hz, 0.8 x 1 H, *Z*), 8.24 (s, 0.8 x 1 H, *Z*), 8.19 (s, 1 H), 8.15 (d, *J* = 9.2 Hz, 1 H), 8.08 (d, *J* = 9.4 Hz, 0.8 x 1 H, *Z*), 7.99-7.88 (m, 6.5 H), 7.79 (dd, *J* = 8.5, 1.4 Hz, 0.8 x 1 H, *Z*), 7.61-7.56 (m, 3.6 H), 2.71 (s, 3 H), 2.55 (s, 0.8 x 3 H, *Z*). **¹³C{¹H} NMR** peaks is too weak, it can not be obviously detected. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₈H₁₄N₃O₅⁺ 352.0928 found 352.0920.



(E)-3,4-dihydronaphthalen-1(2H)-one O-(2,4-dinitrophenyl) oxime (1m)

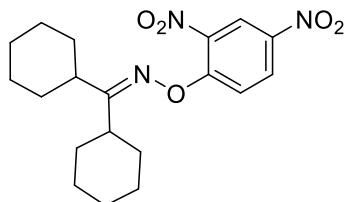
According to the **GP1**, compound **1m** (*Z:E* = 0.11:1) was obtained (81%, 0.80 g) as a white solid, m.p.: 202.9-203.6 °C. **1H NMR of Z and E-1m** (400 MHz, CDCl₃): δ 8.92 (d, *J* = 2.5 Hz, 1 H), 8.88 (d, *J* = 2.6 Hz, 0.11 x 1 H, *Z*), 8.59 (d, *J* = 7.8 Hz, 0.11 x 1 H, *Z*), 8.47 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.11 (m, 2.22 H), 7.42-7.24 (m, 3.33 H), 3.11 (t, *J* = 6.7 Hz, 2 H), 2.99 (t, *J* = 6.5 Hz, 0.11 x 2 H, *Z*), 2.85 (t, *J* = 6.0 Hz, 2 H), 2.76 (t, *J* = 6.2 Hz, 0.11 x 2 H, *Z*), 2.17-2.10 (m, 0.11 x 2 H, *Z*), 2.00-1.94 (m, 2H). **¹³C{¹H} NMR of Z and E-1m** (100 MHz, CDCl₃): δ 162.5, 157.7, 141.6, 140.8, 131.3, 129.6, 129.3, 128.4, 126.8, 125.3, 122.3, 117.5, 29.7, 26.1, 21.4. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₆H₁₄N₃O₅⁺ 328.0928 found 328.0910.



(1r,3r,5R,7S)-adamantan-2-one O-(2,4-dinitrophenyl) oxime (1r)

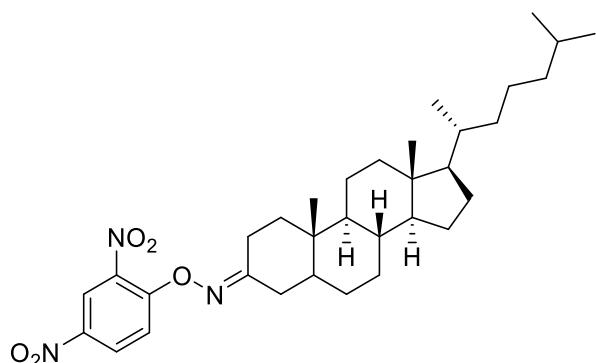
According to the **GP1**, compound **1r** was obtained (89%, 0.88 g) as a white solid. m.p.: 145.1-145.7 °C. **1H NMR** (400 MHz, CDCl₃): δ 8.88 (d, *J* = 2.7 Hz, 1 H), 8.41 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.01 (d, *J* = 9.4 Hz, 1 H), 3.77 (s, 1 H), 2.79 (s, 1 H), 2.12-2.03 (m, 6

H), 1.95-1.91 (m, 6 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 175.6, 158.2, 140.3, 135.9, 129.5, 122.2, 117.3, 39.2, 38.0, 36.2, 36.1, 31.6, 27.5. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₆H₁₈N₃O₅⁺ 332.1241, found 332.1242.



Dicyclohexylmethanone *O*-(2,4-dinitrophenyl) oxime (1s)

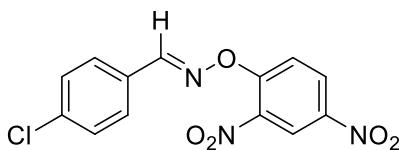
According to the **GP1**, compound **1s** was obtained (95%, 1.07 g) as a white solid, m.p.: 150.0-150.7 °C. **¹H NMR** (500 MHz, CDCl₃): δ 8.88 (d, *J* = 2.7 Hz, 1 H), 8.40 (dd, *J* = 9.4, 2.7 Hz, 1 H), 87.92 (d, *J* = 9.4 Hz, 1 H), 3.04-2.98 (m, 1 H), 2.41-2.35 (m, 1 H), 1.92-1.60 (m, 12 H), 1.48-1.22 (m, 8 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 176.3, 158.1, 140.4, 136.0, 129.4, 122.2, 117.3, 42.3, 41.0, 31.5, 28.6, 26.4, 26.3, 26.0, 25.8. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₉H₂₆N₃O₅⁺ 376.1867, found 376.1879.



(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*,*E*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one *O*-(2,4-dinitrophenyl) oxime (1t)

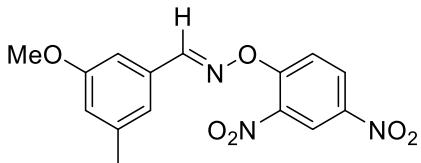
According to the **GP1**, compound **1t** (*Z:E* = 1:1) was obtained (75%, 1.28 g) as a white solid, m.p.: 181.9-183.0 °C. **¹H NMR of Z and E-1t** (400 MHz, CDCl₃): δ 8.87 (d, *J* = 2.3 Hz, 1 H), 8.40 (dd, *J* = 9.3, 2.0 Hz, 1 H), 7.96 (dd, *J* = 9.6, 2.0 Hz, 1 H), 3.44 (d, *J* = 15.2 Hz, 0.5 H), 3.19 (d, *J* = 14.9 Hz, 0.5 H), 2.52-2.08 (m, 4 H), 2.00-1.95 (m, 3 H),

1.84-1.70 (m, 3 H), 1.57-1.45 (m, 4 H), 1.41-1.32 (m, 8 H), 1.25-1.06 (m, 7 H), 1.04-0.95 (s, 4 H), 0.91-0.89 (m, 4 H), 0.86-0.79 (m, 6 H), 0.67 (s, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** of **Z and E-1t** (100 MHz, CDCl_3): δ 169.3, 169.3, 157.9, 140.4, 135.9, 129.5, 122.2, 117.3, 117.2, 56.4, 56.3, 54.0, 53.9, 46.9, 45.9, 42.7, 40.0, 39.6, 38.6, 37.7, 36.3, 36.2, 35.9, 35.5, 34.0, 31.8, 29.9, 28.9, 28.8, 28.3, 28.1, 27.7, 24.3, 23.9, 23.4, 23.0, 22.7, 21.4, 18.8, 12.2, 12.2, 11.7, 11.6. HRMS (ESI) m/z [M+H] $^+$ calcd. for $\text{C}_{33}\text{H}_{49}\text{N}_3\text{O}_5^+$ 568.3745, found 568.3748.



(E)-4-chlorobenzaldehyde O-(2,4-dinitrophenyl) oxime (1A)²

According to the **GP1**, compound **1A** was obtained (82%, 0.79 g) as a white solid. **^1H NMR** (400 MHz, CDCl_3): δ 8.89 (d, $J = 2.7$ Hz, 1 H), 8.63 (s, 1 H), 8.47 (dd, $J = 9.3, 2.8$ Hz, 1 H), 8.02 (d, $J = 9.4$ Hz, 1 H), 7.70 (d, $J = 8.4$ Hz, 2 H), 7.48 (d, $J = 8.5$ Hz, 2 H).

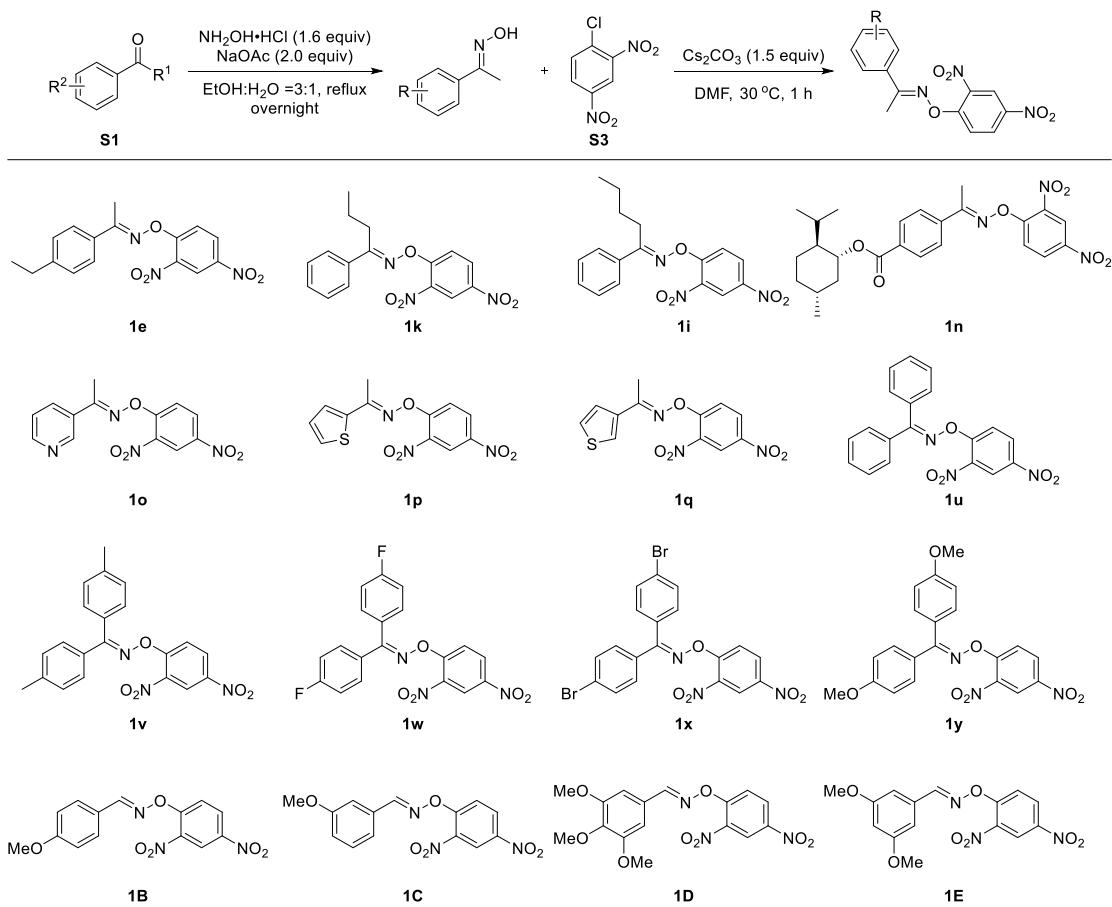


(E)-3-methoxy-5-methylbenzaldehyde O-(2,4-dinitrophenyl) oxime (1F)

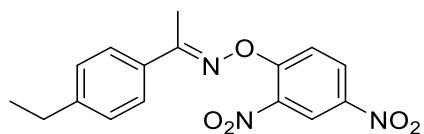
According to the **GP1**, compound **1F** was obtained (75%, 0.75 g) as a white solid, m.p.: 148.5-149.4 °C. **^1H NMR** (500 MHz, CDCl_3): δ 8.88 (d, $J = 2.8$ Hz, 1 H), 8.57 (s, 1 H), 8.46 (dd, $J = 9.4, 2.8$ Hz, 1 H), 8.04 (dd, $J = 9.3$ Hz, 1 H), 7.12 (s, 1 H), 7.08 (s, 1 H), 6.89 (s, 1 H), 3.86 (s, 3 H), 2.40 (s, 3H). **$^{13}\text{C}\{\text{H}\}$ NMR** (125 MHz, CDCl_3): δ 160.1, 157.3, 156.7, 141.1, 140.7, 136.2, 130.4, 129.4, 122.2, 122.1, 119.2, 117.5, 110.1, 55.6, 21.6. HRMS (ESI) m/z [M+H] $^+$ calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_6^+$ 332.0877 found 332.0866.

4.2 Synthesis of compound **1e**, **1k**, **1l**, **1n**, **1o-1q**, **1u-1y**, **1B-1D**, **1E**

General Procedure 2 (GP2) for the S_NAr of oxime with 1-chloro-2,4-dinitrobenzene.

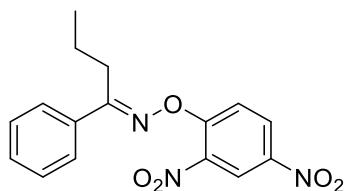


Acetophenone or aldehyde (**S1**, 5.0 mmol, 1.0 equiv), hydroxylamine hydrochloride (0.56 g, 8.0 mmol, 1.6 equiv) and NaOAc (1.36 g, 10 mmol, 2.0 equiv) were weighted into a flask of 100 mL into 20 ml of solvent with three to one ratio of ethanol to water. The reaction was refluxed in an oil bath until the disappearance of **S1**, cooling to the room temperature followed by the addition of 50 mL water. Then the solid was separated out, and filtered by Buchner funnel. The solid was washed by petrol and dried under vacuo to give the oxime pure product. After that, oxime (3 mmol, 1.0 equiv), 2,4-dinitrochlorobenzene (0.61 g, 3.0 mmol, 1.0 equiv) and cesium carbonate (1.5 g, 4.5 mmol, 1.5 equiv) were added into 5 mL DMF, stirring at room temperature for 1 h, then poured into 25 mL water to separate the solid out, and filtered by Buchner funnel. The filter was washed by water and petrol by three times and dried under vacuo to give the target product.



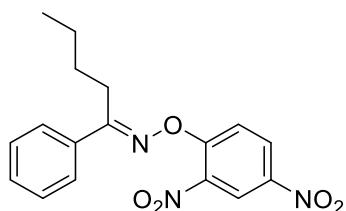
(E)-1-(4-ethylphenyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1e)

According to the **GP2**, compound **1e** was obtained (63%, 0.62 g) as a white solid, m.p.: 121.1-121.8 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.92 (d, *J* = 2.6 Hz, 1 H), 8.45 (dd, *J* = 9.4, 2.6 Hz, 1 H), 8.08 (d, *J* = 9.4 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 2.72 (q, 2 H), 2.58 (s, 3 H), 1.28 (t, *J* = 7.6 Hz, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 163.6, 157.7, 148.0, 140.8, 136.1, 129.6, 128.5, 127.1, 122.3, 117.5, 28.9, 15.5, 14.9. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₆H₁₆N₃O₅⁺ 330.1084, found 330.1055.



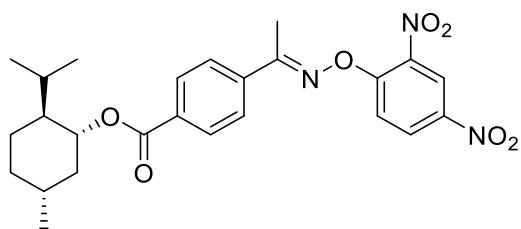
(E)-1-phenylbutan-1-one *O*-(2,4-dinitrophenyl) oxime (1k)

According to the **GP2**, compound **1k** (*Z:E* = 0.03:1) was obtained (81%, 0.80 g) as a white solid, m.p.: 116.2-117.1 °C. **¹H NMR of Z and E-1k** (500 MHz, CDCl₃): δ 8.92 (d, *J* = 2.6 Hz, 1 H), 8.79 (d, *J* = 2.7 Hz, 0.03 x 1 H, *Z*), 8.44 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.43-8.40 (m, 0.03 x 1 H, *Z*), 8.07 (d, *J* = 9.4 Hz, 1 H), 8.00 (d, *J* = 9.4 Hz, 0.03 x 1 H, *Z*), 7.76-7.75 (m, 2 H), 7.53-7.52 (m, 0.03 x 5 H, *Z*), 7.52-7.46 (m, 3 H), 3.03 (t, *J* = 7.7 Hz, 2 H), 2.75 (t, *J* = 7.4 Hz, 0.03 x 2 H, *Z*), 1.74-1.69 (m, 2 H), 1.64-1.60 (m, 0.03 x 2 H, *Z*), 1.05 (t, *J* = 7.3 Hz, 3 H), 1.01 (t, *J* = 7.9 Hz, 0.03 x 3 H, *Z*). **¹³C{¹H} NMR of Z and E-1k** (125 MHz, CDCl₃): δ 167.6, 157.7, 140.9, 136.2, 133.5, 129.5, 127.3, 122.3, 117.5, 30.7, 20.6, 14.3. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₆H₁₆N₃O₅⁺ 330.1084, found 330.1055.



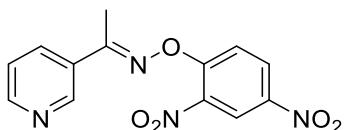
(E)-1-phenylbutan-1-one *O*-(2,4-dinitrophenyl) oxime (1l)

According to the **GP2**, compound **1l** was obtained (80%, 0.82 g) as a yellow solid, m.p.: 87.2-87.5 °C. **1H NMR** (500 MHz, CDCl_3): δ 8.93 (d, $J = 2.7$ Hz, 1 H), 8.45 (dd, $J = 9.4, 2.7$ Hz, 1 H), 8.07 (d, $J = 9.4$ Hz, 1 H), 7.77-7.74 (m, 2 H), 7.53-7.46 (m, 3 H), 3.04 (t, $J = 7.8$ Hz, 2 H), 1.68-1.62 (m, 2 H), 1.51-1.44 (m, 2 H), 0.95 (t, $J = 7.3$ Hz, 3 H). **13C{1H} NMR** (125 MHz, CDCl_3): δ 167.7, 157.7, 140.9, 136.2, 133.5, 131.1, 129.5, 129.0, 127.3, 122.3, 117.5, 29.1, 28.7, 23.0, 13.9.



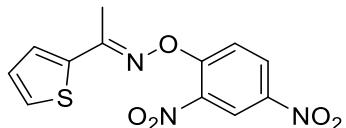
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-1-((2,4-dinitrophenoxy)imino)ethyl)benzoate (1n)

According to the **GP2**, compound **1n** was obtained (75%, 1.09 g) as a white solid, m.p.: 154.9-156.7 °C. **1H NMR** (500 MHz, CDCl_3): δ 8.93-8.92 (m, 1 H), 8.47 (dd, $J = 9.4, 2.5$ Hz, 1 H), 8.13 (d, $J = 8.4$ Hz, 2 H), 8.07 (d, $J = 9.4$ Hz, 1 H), 7.85 (d, $J = 8.4$ Hz, 2 H), 4.99-4.93 (m, 1 H), 2.62 (s, 3 H), 2.14 (d, $J = 11.8$ Hz, 1 H), 1.99-1.81 (m, 1 H), 1.74 (d, $J = 11.5$ Hz, 2 H), 1.61-1.55 (m, 2 H), 1.20-1.08 (m, 2 H), 0.93 (t, $J = 5.3$ Hz, 7 H), 0.81 (d, $J = 6.9$ Hz, 3 H). **13C{1H} NMR** (125 MHz, CDCl_3): δ 165.4, 162.9, 157.3, 141.2, 138.1, 136.3, 133.1, 130.1, 129.6, 127.0, 122.3, 117.5, 75.5, 47.4, 41.0, 34.4, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7, 15.0. HRMS (ESI) m/z [M+H]⁺ calcd. for $\text{C}_{25}\text{H}_{30}\text{N}_3\text{O}_7^+$ 484.2078, found 484.2075.



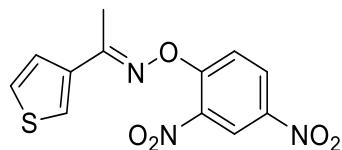
(E)-1-(pyridin-3-yl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1o)

According to the **GP2**, compound **1o** (*Z:E* = 0.06:1) was obtained (85%, 0.77 g) as a white solid, m.p.: 145.9-146.8 °C. **1H NMR of Z and E-1o** (500 MHz, CDCl₃): δ 9.02 (d, *J* = 2.0 Hz, 1 H), 9.00 (s, 0.06 x 1 H, *Z*), 8.93 (d, *J* = 2.7 Hz, 1 H), 8.91 (d, *J* = 2.9 Hz, 0.06 x 1 H, *Z*), 8.75-8.74 (m, 1 H), 8.70 (s, 0.06 x 1 H, *Z*), 8.48 (dd, *J* = 9.4, 2.6 Hz, 1 H), 8.36-8.31 (m, 0.06 x 1 H, *Z*), 8.15-8.12 (m, 0.06 x 2 H, *Z*), 8.09-8.05 (m, 2 H), 7.44-7.39 (m, 1 H), 7.08-7.05 (m, 0.06 x 1 H, *Z*), 2.62 (s, 3 H), 2.61 (s, 0.06 x 3 H, *Z*). **13C{1H} NMR of Z and E-1o** (125 MHz, CDCl₃): δ 161.5, 157.1, 152.0, 148.1, 141.3, 136.3, 134.3, 130.2, 129.6, 123.7, 122.3, 117.4, 14.8. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₃H₁₁N₄O₅⁺ 303.0724, found 303.0723.



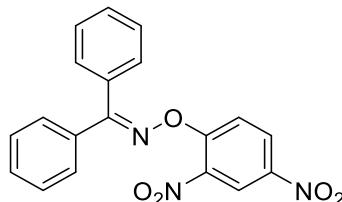
(E)-1-(thiophen-2-yl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1p)

According to the **GP2**, compound **1p** (*Z:E* = 0.6:1) (88%, 0.81 g) as a white solid, m.p.: 116.3-118.2 °C. **1H NMR of Z and E-1p** (500 MHz, CDCl₃): δ 8.91 (d, *J* = 2.5 Hz, 1 H), 8.80 (d, *J* = 2.5 Hz, 0.6 x 1 H, *Z*), 8.48-8.43 (m, 1.6 H), 8.04 (d, *J* = 9.4 Hz, 1.6 H), 7.83 (d, *J* = 3.6 Hz, 0.6 x 1 H, *Z*), 7.71 (d, *J* = 4.9 Hz, 0.6 x 1 H, *Z*), 7.71-7.48 (m, 2 H), 7.20 (t, *J* = 4.3 Hz, 0.6 x 1 H, *Z*), 7.13 (t, *J* = 4.1 Hz, 1 H), 2.60 (s, 3 H), 2.55 (s, 0.6 x 3 H, *Z*). **13C{1H} NMR of Z and E-1p** (125 MHz, CDCl₃): δ 158.9, 157.3, 156.9, 153.6, 141.3, 141.0, 137.0, 136.1, 133.6, 133.3, 131.2, 130.1, 130.0, 129.7, 129.1, 127.8, 127.2, 122.2, 121.6, 118.2, 117.5, 20.5, 14.9. HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₁₂H₉N₃NaO₅S⁺ 330.0155, found 330.0185.



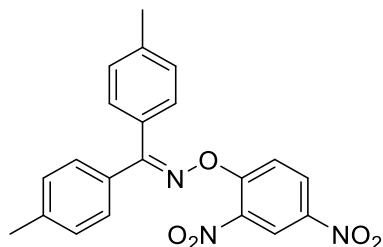
(E)-2-(thiophen-2-yl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (1q)

According to the **GP2**, compound **1q** (*Z:E* = 0.4:1) was obtained (76%, 0.70 g) as a yellow solid. m.p.: 180.0-180.7 °C. **1H NMR of Z and E-1q** (400 MHz, CDCl₃): δ 8.92 (d, *J* = 2.7 Hz, 1 H), 8.89 (d, *J* = 2.7 Hz, 0.4 x 1 H, *Z*), 8.48-8.45 (m, 1.4 H), 8.42-8.41 (m, 0.4 x 1 H, *Z*), 8.12 (d, *J* = 9.4 Hz, 0.4 x 1 H, *Z*), 8.05 (d, *J* = 9.4 Hz, 1 H), 7.76-7.75 (m, 1 H), 7.67-7.66 (m, 0.4 x 1 H, *Z*), 7.58-7.57 (m, 1 H), 7.44-7.41 (m, 1.4 H), 2.57 (s, 3 H), 2.45 (s, 0.4 x 3 H, *Z*). **¹³C{¹H} NMR of Z and E-1q** (100 MHz, CDCl₃): δ 159.2, 157.7, 157.5, 155.1, 140.9, 136.3, 136.1, 132.9, 131.4, 129.6, 129.5, 128.7, 127.6, 127.2, 125.7, 125.3, 122.3, 122.2, 118.1, 117.5, 21.2, 15.1. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₂H₁₀N₃O₅S⁺ 308.0336, found 308.0335.



Diphenylmethanone *O*-(2,4-dinitrophenyl) oxime (1u)⁴

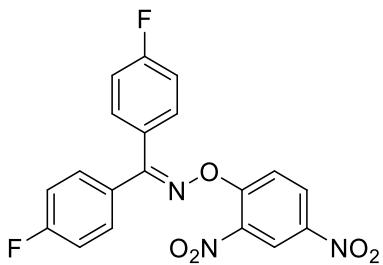
According to the **GP2**, compound **1u** was obtained (100%, 1.09 g) as a white solid. **¹H NMR** (400 MHz, DMSO-*d*⁶): δ 8.78 (d, *J* = 2.5 Hz, 1 H), 8.56 (dd, *J* = 9.4, 2.6 Hz, 1 H), 8.19 (d, *J* = 9.3 Hz, 1 H), 7.66-7.45 (m, 10 H).



Di-p-tolylmethanone *O*-(2,4-dinitrophenyl) oxime (1v)

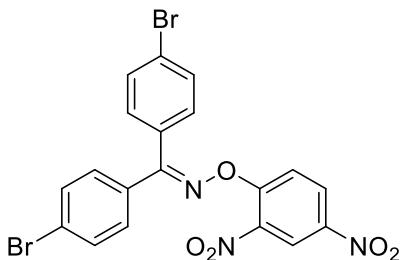
According to the **GP2**, compound **1v** was obtained (87%, 1.02 g) as a white solid, m.p.:

180.0-181.9 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.83 (d, *J* = 2.7 Hz, 1 H), 8.46 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.15 (d, *J* = 9.4 Hz, 1 H), 7.549 (d, *J* = 8.2 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 2.45 (s, 3 H), 2.43 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 165.0, 157.7, 141.8, 140.9, 136.4, 131.9, 130.0, 129.4, 129.3, 129.3, 128.9, 128.5, 122.1, 117.6, 21.7, 21.6. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₂₁H₁₈N₃O₅⁺ 392.1241, found 392.1248.



Bis(4-fluorophenyl)methanone *O*-(2,4-dinitrophenyl) oxime (**1w**)⁵

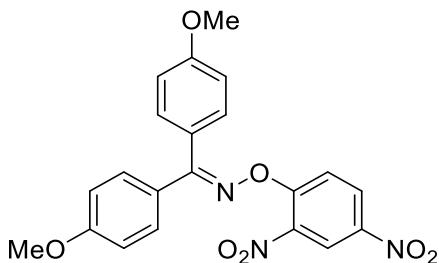
According to the **GP2**, compound **1w** was obtained (82%, 0.98 g) as a white solid. **¹H NMR** (500 MHz, CDCl₃): δ 8.84 (d, *J* = 2.6 Hz, 1 H), 8.47 (dd, *J* = 9.3, 2.6 Hz, 1 H), 8.12 (d, *J* = 9.4 Hz, 1 H), 7.61 (dd, *J* = 8.7, 5.4 Hz, 2 H), 7.50 (dd, *J* = 8.6, 5.3 Hz, 2 H), 7.22 (d, *J* = 8.6 Hz, 2 H), 7.15 (d, *J* = 8.5 Hz, 2 H).



Bis(4-bromophenyl)methanone *O*-(2,4-dinitrophenyl) oxime (**1x**)

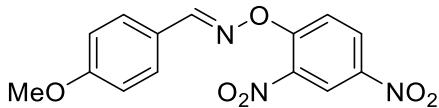
According to the **GP2**, compound **1x** was obtained (96%, 1.50 g) as a white solid, m.p.: 175.9-176.6 °C. **¹H NMR** (500 MHz, CDCl₃): δ 8.84 (d, *J* = 2.5 Hz, 1 H), 8.47 (dd, *J* = 9.3, 2.5 Hz, 1 H), 8.10 (d, *J* = 9.3 Hz, 1 H), 7.67 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 2 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 163.1, 157.0, 141.5, 136.6, 133.0, 132.2, 131.9, 131.4, 130.6, 129.6, 129.4, 126.5, 125.5, 122.1, 117.6. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₁₉H₁₂Br₂N₃O₅⁺

519.9138, found 519.9140.



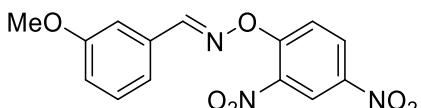
Bis(4-methoxyphenyl)methanone *O*-(2,4-dinitrophenyl) oxime (1y)⁵

According to the **GP2**, compound **1y** was obtained (92%, 1.17 g) as a yellow solid. **¹H NMR** (400 MHz, CDCl₃): δ 8.84 (d, *J* = 2.7 Hz, 1 H), 8.45 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.15 (d, *J* = 9.4 Hz, 1 H), 7.54 (dd, *J* = 6.8, 2.1 Hz, 2 H), 7.48 (dd, *J* = 6.8, 2.1 Hz, 2 H), 7.01 (dd, *J* = 6.8, 2.1 Hz, 2 H), 6.95 (dd, *J* = 6.8, 2.1 Hz, 2 H), 3.89 (s, 3 H), 3.87 (s, 3 H).



(E)-4-methoxybenzaldehyde *O*-(2,4-dinitrophenyl) oxime (1B)⁷

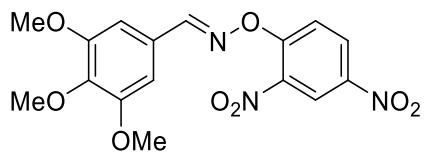
According to the **GP2**, compound **1B** was obtained (76%, 0.72 g) as a white solid. **¹H NMR** (400 MHz, CDCl₃): δ 8.88 (d, *J* = 2.5 Hz, 1 H), 8.59 (s, 1 H), 8.45 (dd, *J* = 9.3, 2.5 Hz, 1 H), 8.04 (d, *J* = 9.1 Hz, 1 H), 7.70 (d, *J* = 8.7 Hz, 2 H), 6.99 (d, *J* = 8.7 Hz, 2 H), 3.88 (s, 3 H).



(E)-3-methoxybenzaldehyde *O*-(2,4-dinitrophenyl) oxime (1C)

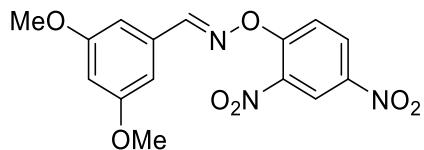
According to the **GP2**, compound **1C** was obtained (53%, 0.50 g) as a white solid, m.p.: 171.2-171.8 °C. **¹H NMR** (500 MHz, CDCl₃): δ 8.87 (d, *J* = 2.6 Hz, 1 H), 8.61 (s, 1 H), 8.46 (dd, *J* = 9.3, 2.6 Hz, 1 H), 8.03 (d, *J* = 9.3 Hz, 1 H), 7.40 (t, *J* = 8.2 Hz, 1 H), 7.29 (t, *J* = 7.0 Hz, 2 H), 7.09-7.07 (m, 1 H), 3.88 (s, 3 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 160.2, 157.2, 156.5, 141.3, 130.8, 130.4, 129.4, 122.1, 121.5, 118.4, 117.5, 112.8,

55.6. HRMS (ESI) m/z [M+H]⁺ calcd. for C₁₄H₁₂N₃O₆⁺ 318.0726, found 318.0715.



(E)-3, 4, 5-trimethoxybenzaldehyde O-(2,4-dinitrophenyl) oxime (1D)

According to the **GP2**, compound **1D** was obtained (76%, 0.86 g) as a white solid, m.p.: 179.4-180.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.86 (d, *J* = 2.7 Hz, 1 H), 8.55 (s, 1 H), 8.46 (dd, *J* = 9.4, 2.7 Hz, 1 H), 8.01 (d, *J* = 9.4 Hz, 1 H), 6.96 (s, 2 H), 3.93 (s, 6 H), 3.92 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 157.2, 156.4, 153.8, 141.7, 141.1, 136.2, 129.4, 124.5, 122.1, 117.4, 105.6, 61.2, 56.4. HRMS (ESI) m/z [M+H]⁺ calcd. for C₁₆H₁₆N₃O₈⁺ 378.0932, found 378.0923.



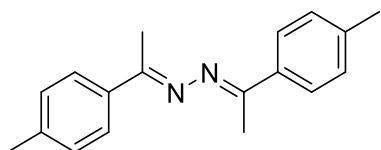
(E)-3, 5-dimethoxybenzaldehyde O-(2,4-dinitrophenyl) oxime (1E)

According to the **GP2**, compound **1E** was obtained (95%, 0.99 g) as a white solid, m.p.: 189.2-190.5 °C. **¹H NMR** (400 MHz, DMSO-d6): 8.93 (s, 1 H), 8.86 (d, *J* = 2.8 Hz, 1 H), 8.55 (dd, *J* = 9.4, 2.8 Hz, 1 H), 8.14 (d, *J* = 9.4 Hz, 1 H), 7.05 (d, *J* = 2.2 Hz, 2 H), 6.72 (t, *J* = 2.2 Hz, 1 H), 3.81 (s, 6 H). **¹³C{¹H} NMR** peaks is too weak to be detected due to the insolubility. HRMS (ESI) m/z [M+H]⁺ calcd. for C₁₅H₁₃N₃O₇⁺ 348.0826, found 348.0827.

5. Synthesis of 2 via the Homo-coupling of 1

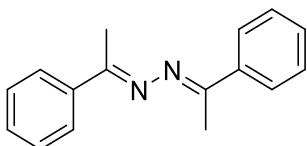
General procedure 3 (GP3): (*E*)-1-(*p*-tolyl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime (0.5 mmol, 1 equiv), **CBZ6** (2 mol%) and HCOONa (1.2 equiv) were weighed directly into an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (2.5 mL) was added sequentially in the Schlenk tube via syringe. Then the tube was placed 1.5 cm away from LEDs (3 W×6) with an electric fan cooling the reaction, and the reaction mixture was stirred vigorously under the irradiation. After 4 h, the tube was removed from the light source. The crude mixture was extracted with DCM (10 mL × 3), then washed with 10 mL NaCl (aq., 1 N). Organic phase was collected and dried under vacuum. The residue was purified by flash chromatography column to give the pure product.

CAUTION: The byproduct 2,4-dinitrophenol is toxic and explosive, handle carefully.



(1*E*,2*E*)-1,2-bis(1-(*p*-tolyl)ethylidene)hydrazine (2a)⁷

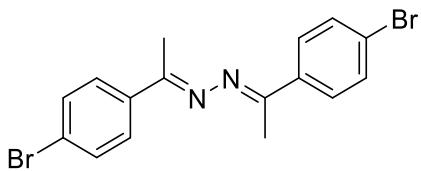
2a was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (54.0 mg, 82% yield). **1H NMR** (500 MHz, CDCl₃): δ 7.82 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 2.41 (s, 3 H), 2.31 (s, 3 H). **13C{1H} NMR** (125 MHz, CDCl₃): δ 157.8, 139.8, 135.8, 129.2, 126.7, 21.5, 15.1.



(1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine (2b)⁷

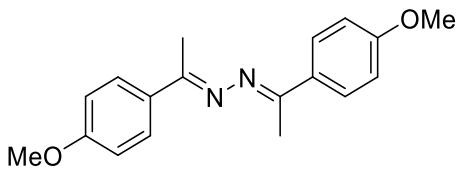
2b was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (42.6 mg, 72% yield). **1H NMR** (400 MHz, CDCl₃): δ 7.95-7.93 (m, 2 H), 7.46-7.44 (m, 3 H), 2.34 (s, 3 H).

$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.8, 138.5, 129.7, 128.5, 126.7, 15.2.



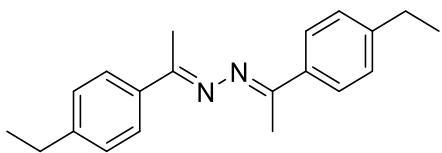
(1*E*,2*E*)-1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine (2c)⁷

2c was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (69.0 mg, 70% yield). **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.78 (d, J = 8.6 Hz, 2 H), 7.55 (d, J = 8.6 Hz, 2 H), 2.30 (s, 3 H). **$^{13}\text{C}\{\text{H}\}$ NMR** (100 MHz, CDCl_3): δ 157.4, 137.3, 131.7, 128.3, 124.3, 15.0.



(1*E*,2*E*)-1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine (2d)⁷

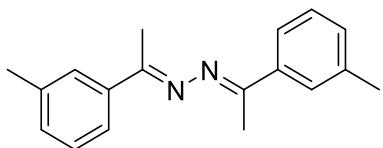
2d was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 50:1:1~20:1:1) to afford a yellow solid (66.0 mg, 89% yield). **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.88 (d, J = 7.1 Hz, 2 H), 6.94 (d, J = 7.0 Hz, 2 H), 3.86 (s, 3 H), 2.33 (s, 3 H). **$^{13}\text{C}\{\text{H}\}$ NMR** (100 MHz, CDCl_3): δ 160.9, 157.9, 131.4, 128.2, 113.7, 55.5, 14.9.



(1*E*,2*E*)-1,2-bis(1-(4-ethylphenyl)ethylidene)hydrazine (2e)

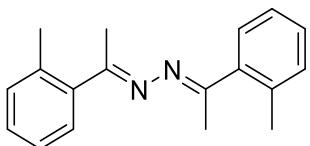
2e was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (54.8 mg, 75% yield), m.p.: 96.9-97.5 °C. **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.85 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 2.70 (q, J = 15.2, 7.6 Hz, 2 H), 2.31 (s, 3 H), 1.28 (t, J = 7.6 Hz, 3 H). **$^{13}\text{C}\{\text{H}\}$**

NMR (100 MHz, CDCl₃): δ 157.8, 146.1, 136.2, 128.0, 126.8, 28.9, 15.6, 15.1.



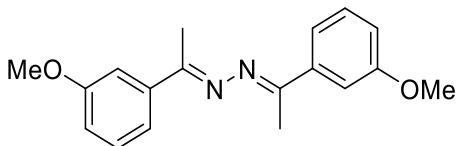
(1E,2E)-1,2-bis(1-(*m*-tolyl) ethylidene)hydrazine (2f)¹⁸

2f was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (60.8 mg, 92% yield). **¹H NMR** (400 MHz, CDCl₃): δ 7.76 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 7.5 Hz, 1 H), 2.43 (s, 3H), 2.31 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 157.6, 138.6, 138.1, 130.5, 128.4, 127.3, 123.9, 21.6, 15.3.



(1E,2E)-1,2-bis(1-(*o*-tolyl) ethylidene)hydrazine (2g)

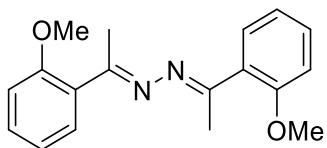
2g was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow liquid (47.6 mg, 72% yield). **¹H NMR** (500 MHz, CDCl₃): δ 7.41-7.39 (m, 1H), 7.32-7.27 (m, 3 H), 2.50 (s, 3H), 2.27 (s, 3 H). **¹³C NMR** (125 MHz, CDCl₃): δ 161.0, 140.0, 135.5, 130.9, 128.5, 128.0, 125.9, 20.7, 19.3.



(1E,2E)-1,2-bis(1-(3-methoxyphenyl)ethylidene)hydrazine (2h)¹⁷

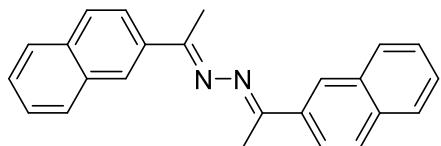
2h was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 50:1:1~20:1:1) to afford a yellow solid (65.9 mg, 89% yield). **¹H NMR** (400 MHz, CDCl₃): δ 7.53 (s, 1 H), 7.46 (d, *J* = 7.2 Hz, 1 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 6.98 (dd, *J* = 8.1, 2.3 Hz, 1 H), 3.88 (s, 3 H), 2.30 (s, 3H). **¹³C{¹H} NMR** (100 MHz,

CDCl_3): δ 159.7, 157.3, 139.9, 129.4, 119.4, 115.7, 111.7, 55.5, 15.3.



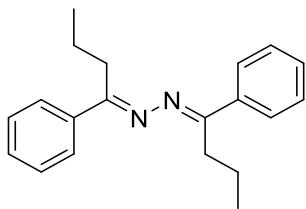
(1*E*,*2E*)-1,2-bis(1-(2-methoxyphenyl)ethylidene)hydrazine (2i)⁷

2i was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 50:1:1~20:1:1) to afford a yellow solid (50.4 mg, 68% yield). **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.55-7.53 (m, 1 H), 7.38-7.33 (m, 1 H), 7.03-6.94 (m, 3 H), 3.86 (s, 3 H), 2.23 (s, 3H). **$^{13}\text{C}\{\text{H}\} \text{NMR}$** (100 MHz, CDCl_3): δ 158.8, 157.6, 130.2, 129.7, 129.65, 120.7, 111.2, 55.6, 18.8.



(1*E*,*2E*)-1,2-bis(1-(naphthalen-2-yl)ethylidene)hydrazine (2j)⁷

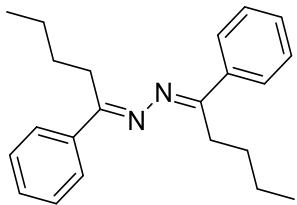
2j was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (63.0 mg, 75% yield). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ 8.27-8.25 (m, 2 H), 7.94-7.87 (m, 3 H), 7.55-7.51 (m, 2H), 2.49 (s, 3 H). **$^{13}\text{C}\{\text{H}\} \text{NMR}$** (125 MHz, CDCl_3): δ 157.8, 136.0, 134.2, 133.2, 128.8, 128.1, 127.8, 127.0, 126.8, 126.5, 124.1, 15.1.



(1*E*,*2E*)-1,2-bis(1-phenylbutylidene)hydrazine (2k)⁷

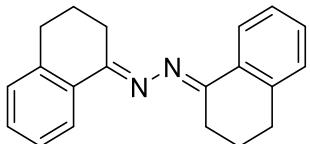
2k was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (66.5 mg, 91% yield). **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.93-7.91 (m, 2 H), 7.46-7.42 (m, 3 H), 2.90 (q, J = 9.6,

7.8 Hz, 2 H), 1.63-1.55 (m, 2 H), 0.98 (t, $J = 7.3$ Hz, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 162.7, 138.0, 129.6, 128.5, 127.1, 30.7, 20.6, 14.6.



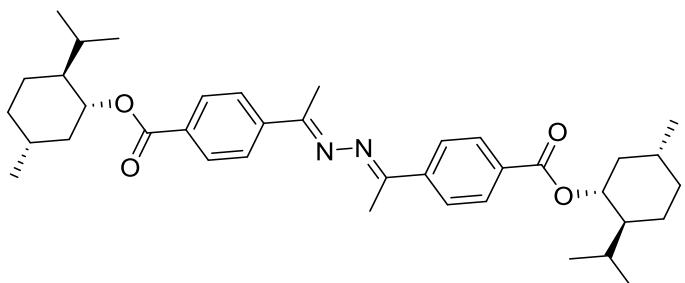
(1E,2E)-1,2-bis(1-phenylbutylidene)hydrazine (2l)

2l was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow liquid (78.5 mg, 94% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.93-7.91 (m, 2 H), 7.46-7.42 (m, 3 H), 2.94-2.91 (m, 2 H), 1.56-1.50 (m, 2 H), 1.43-1.37 (m, 2 H), 0.91 (td, $J = 7.3, 1.6$ Hz, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 162.8, 137.9, 129.6, 128.5, 127.0, 29.2, 28.5, 23.2, 14.0.



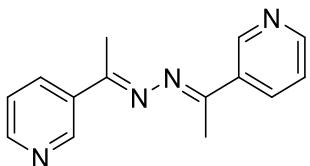
1,2-bis((E)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine (2m)⁷

2m was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (47.0 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.31-8.28 (m, 1 H), 7.32-7.28 (m, 2 H), 7.18-7.16 (m, 1 H), 2.83 (t, $J = 6.0$ Hz, 2 H), 2.77 (t, $J = 6.5$ Hz, 2 H), 1.96-1.90 (m, 2 H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.3, 140.7, 133.1, 129.6, 128.8, 126.5, 125.7, 30.1, 27.5, 22.3.



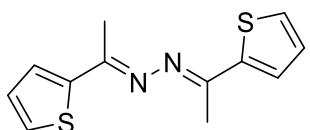
Bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 4,4'-(*(1E,1'E)*-hydrazine-1,2-diylidenebis(ethan-1-yl-1-ylidene))dibenzoate (2n**)**

2n was prepared according to **GP3** by employing 4Å MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (103.6 mg, 69% yield), m.p.: 138.9-140.1 °C. **1H NMR** (400 MHz, CDCl₃): δ 8.10 (d, *J* = 8.4 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 4.99-4.92 (m, 1H), 2.33 (s, 3 H), 2.14 (d, *J* = 11.8 Hz, 1 H), 1.99-1.95 (m, 1H), 1.74 (d, *J* = 11.4 Hz, 1 H), 1.60-1.55 (m, 2H), 1.19-1.08 (m, 2H), 0.98-0.89 (m, 7H), 0.80 (d, *J* = 6.9 Hz, 3 H). **13C{1H} NMR** (100 MHz, CDCl₃): δ 165.8, 157.2, 142.1, 131.8, 129.7, 126.6, 47.4, 41.1, 34.4, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7, 15.3. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₃₈H₅₃N₂O₄⁺ 601.4000, found 601.3998.



(1*E*,2*E*)-1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (2o**)⁷**

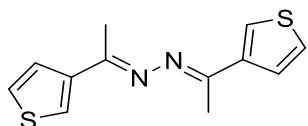
2o was prepared according to **GP3** and purified by flash column chromatography (EA/DCM/MeOH = 1:1:0.2%) to afford a yellow solid (56.0 mg, 94% yield). **1H NMR** (500 MHz, CDCl₃): δ 9.11 (s, 1 H), 8.65 (s, 1 H), 8.21 (dt, *J* = 8.0, 1.7 Hz, 1 H), 7.36 (dd, *J* = 7.9, 4.7 Hz, 1 H), 2.35 (s, 3 H). **13C{1H} NMR** (125 MHz, CDCl₃): δ 157.0, 150.8, 148.3, 134.1, 133.8, 123.4, 15.0.



(1*E*,2*E*)-1,2-bis(1-(thiophen-2-yl)ethylidene)hydrazine (2p**)⁸**

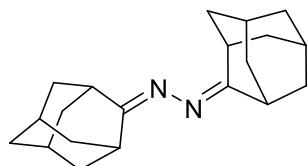
2p was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (44.7 mg, 72% yield). **1H NMR** (500 MHz, CDCl₃): δ 7.41 (dd, *J* = 3.7, 1.1 Hz, 1 H), 7.38 (dd, *J* = 5.1, 1.0 Hz, 1

H), 7.07 (dd, $J = 5.1, 3.7$ Hz, 1 H), 2.45 (s, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 157.4, 144.7, 128.9, 127.7, 127.4, 15.3.



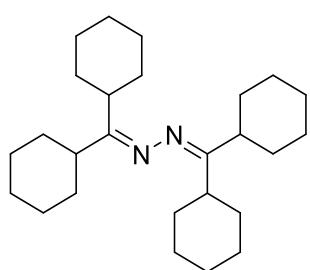
(1E,2E)-1,2-bis(1-(thiophen-3-yl)ethylidene)hydrazine (2q)¹⁶

2q was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (44.1 mg, 71% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.70 (dd, $J = 5.1, 1.1$ Hz, 1 H), 7.64 (dd, $J = 2.9, 1.2$ Hz, 1 H), 7.33 (dd, $J = 5.1, 2.9$ Hz, 1 H), 2.33 (s, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 155.3, 142.2, 126.3, 125.8, 125.1, 15.7.



1,2-di((1R,3R,5R,7S)-adamantan-2-ylidene)hydrazine (2r)⁷

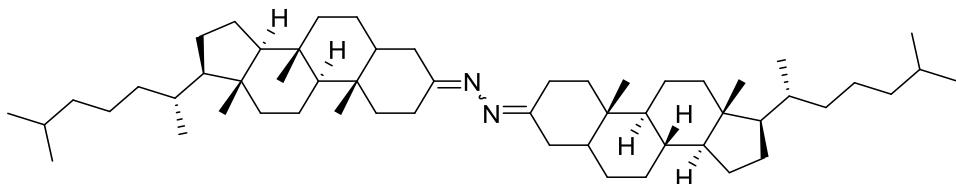
2r was prepared according to **GP3** and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a white solid (74.1 mg, 54% yield). ^1H NMR (400 MHz, CDCl_3): δ 3.26 (s, 1 H), 2.62 (s, 1 H), 2.06-1.76(m, 14 H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.2, 39.7, 39.4, 38.1, 36.7, 31.8, 28.0.



1,2-bis(dicyclohexylmethylene)hydrazine (2s)

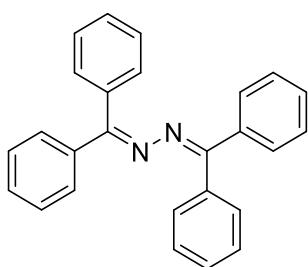
2s was prepared according to **GP3** (12 h) and purified by flash column chromatography (PE/EA/DCM = 100:1:1) to afford a white solid (68.5 mg, 71% yield), m.p.: 103.9-

104.7 °C. **¹H NMR** (400 MHz, CDCl₃): δ 2.85-2.77 (m, 2 H), 2.28-2.20 (m, 2 H), 1.76-1.42(m, 20 H), 1.38-1.15 (m, 20H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 169.1, 41.3, 40.4, 32.2, 28.8, 26.8, 26.3. HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₂₆H₄₄N₂Na⁺ 407.3397, found 407.3397.



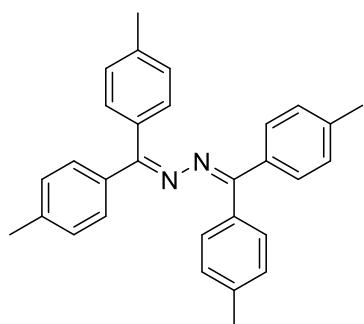
(1*E*,2*E*)-1-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[a]phenanthren-3-ylidene)-2-((8*R*,9*R*,10*S*,13*R*,14*R*,17*R*)-8,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[a]phenanthren-3-ylidene)hydrazine (2t)

2t was prepared according to **GP3** by employing 4 Å MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1). *Z* and *E* (=1:1) of compound **2m** was obtained as a yellow solid (62.7 mg, 32% yield). **¹H NMR** (400 MHz, CDCl₃): δ 3.0-2.96 (m, 0.5 H), 2.77 (d, *J* = 14.1 Hz, 0.5 H), 2.38-2.12 (m, 2H), 1.98-0.67 (m, 42 H), 0.65 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 166.0, 165.9, 165.5, 165.4, 56.5, 56.3, 54.2, 54.0, 54.1, 53.9, 47.3, 47.2, 46.8, 46.1, 46.0, 44.8, 42.7, 40.1, 40.0, 39.6, 39.1, 38.7, 38.3, 38.3, 38.2, 38.1, 36.3, 36.2, 35.9, 35.7, 35.5, 35.5, 31.9, 31.8, 31.5, 30.8, 29.8, 29.1, 29.0, 28.9, 28.4, 28.1, 24.3, 24.1, 23.9, 23.0, 22.7, 21.6, 21.4, 21.3, 18.8, 12.2, 11.7, 11.7, 11.6. HRMS (ESI) *m/z* [M+H]⁺ calcd. for C₅₅H₉₅N₂⁺ 783.7490, found 783.7485.



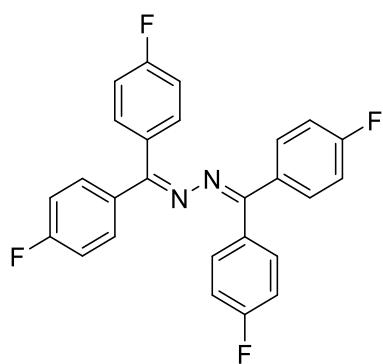
1, 2-bis(diphenylmethylene)hydrazine (2u)⁸

2u was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (90.1 mg, 90% yield). **1H NMR** (400 MHz, CDCl₃): δ 7.51-7.49 (m, 2 H), 7.43-7.28 (m, 8 H). **13C{¹H} NMR** (100 MHz, CDCl₃): δ 159.1, 138.3, 135.6, 129.7, 129.4, 128.8, 128.1, 128.0.



1,2-bis(di-p-tolylmethylene)hydrazine (2v)⁸

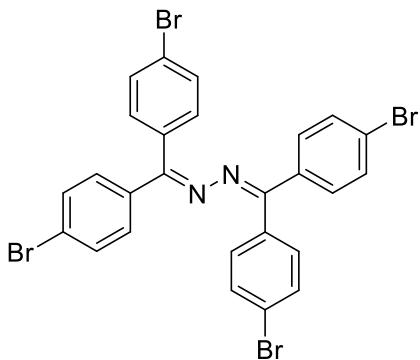
2v was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (99.9 mg, 96% yield). **1H NMR** (400 MHz, CDCl₃): δ 7.41 (dd, *J* = 8.2, 1.2 Hz, 2 H), 7.25 (dd, *J* = 7.7, 1.2 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 2.39 (s, 3 H), 2.35 (s, 2 H). **13C{¹H} NMR** (100 MHz, CDCl₃): δ 159.0, 139.6, 138.5, 136.0, 132.8, 129.7, 128.9, 128.8, 128.5, 21.6, 21.5.



1,2-bis(bis(4-fluorophenyl)methylene)hydrazine (2w)⁸

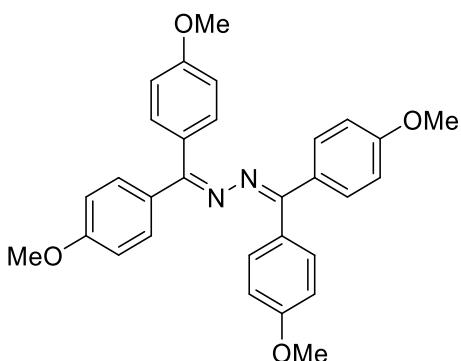
2w was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (96.2 mg, 89% yield). **1H NMR** (500 MHz, CDCl₃): δ 7.49-7.45 (m, 2 H),

7.33-7.30 (m, 2 H), 7.14-7.10 (m, 2 H), 7.02-6.98 (m, 2 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 165.1, 163.9, 163.1, 161.9, 159.0, 134.1 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 8.2 Hz), 131.2 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 8.2 Hz), 115.4 (d, *J* = 19.0 Hz), 115.2 (d, *J* = 18.3 Hz). **¹⁹F NMR** (471 MHz, CDCl₃): δ -110.47, -111.25.



1,2-bis(bis(4-Bromophenyl)methylene)hydrazine (2x)¹⁰

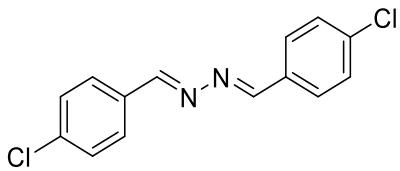
2x was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (167.3 mg, 99% yield). **¹H NMR** (500 MHz, CDCl₃): δ 7.56 (dd, *J* = 6.6, 1.8 Hz, 2 H), 7.45 (dd, *J* = 6.7, 1.8 Hz, 2 H), 7.34-7.32 (m, 2 H), 7.18-7.16 (m, 2 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 159.1, 136.4, 133.7, 131.7, 131.5, 131.1, 130.3, 125.0, 123.6.



1,2-bis(bis(4-Methoxylphenyl)methylene)hydrazine (2y)⁹

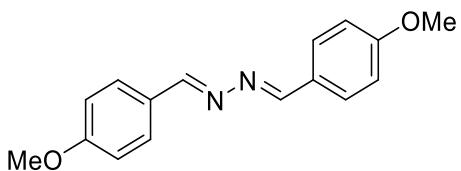
2y was prepared according to **GP3** by employing 2.0 equiv of HCOONa for 5 h and purified by flash column chromatography (PE/EA/DCM = 50:1:1~20:1:1) to afford a yellow solid (118.9 mg, 99% yield). **¹H NMR** (500 MHz, CDCl₃): δ 7.48 (d, *J* = 8.9

Hz, 2 H), 7.33 (d, J = 8.8 Hz, 2 H), 6.91 (d, J = 8.8 Hz, 2 H), 6.82 (d, J = 8.9 Hz, 2 H), 3.84 (s, 3 H), 3.81 (s, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 160.8, 159.8, 159.3, 131.8, 131.6, 130.5, 128.2, 113.5, 113.1, 55.4, 55.4.



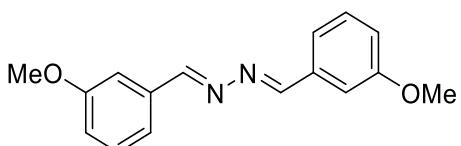
1,2-bis((E) -4-chlorobenzylidene)hydrazine (2A)¹¹

2A was prepared according to **GP3** by employing 4 \AA MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (42.3 mg, 61% yield). ^1H NMR (500 MHz, CDCl_3): δ 8.61 (s, 1 H), 7.78 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 161.2, 137.5, 132.6, 129.9, 129.3.



1,2-bis((E) -4-methoxybenzylidene)hydrazine (2B)¹²

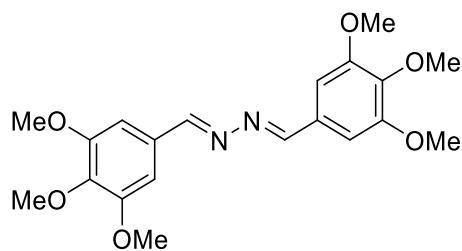
2B was prepared according to **GP3** by employing 4 \AA MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (58.4 mg, 87% yield). ^1H NMR (500 MHz, CDCl_3): δ 8.62 (s, 2 H), 7.78 (d, J = 8.8 Hz, 4 H), 6.96 (d, J = 8.8 Hz, 4 H), 3.86 (s, 3 H), 3.86 (s, 3 H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3): δ 162.1, 161.2, 130.2, 127.1, 114.4, 55.5.



1,2-bis((E) -3-methoxybenzylidene)hydrazine (2C)¹³

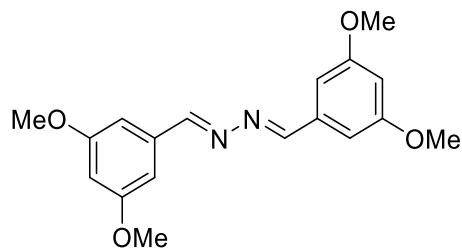
2C was prepared according to **GP3** by employing 4 \AA MS (25 mg) and purified by flash

column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (47.6 mg, 71% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.64 (s, 1 H), 7.45 (d, *J* = 0.8 Hz, 1 H), 7.37-7.36 (m, 2 H), 7.04-7.01 (m, 1 H), 3.88 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 162.1, 160.0, 135.6, 129.9, 122.1, 118.1, 112.1, 55.5.



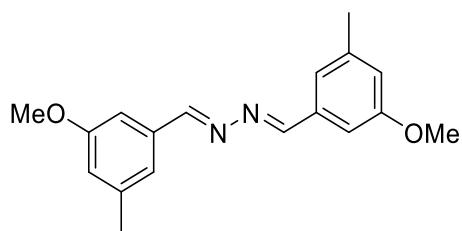
1,2-bis((E)-3,4,5-trimethoxybenzylidene)hydrazine (2D)¹⁴

2D was prepared according to **GP3** by employing 4Å MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (85.4 mg, 88% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.56 (s, 1 H), 7.08 (s, 2 H), 3.93 (s, 6 H), 3.91 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 161.6, 153.6, 141.0, 129.6, 105.7, 61.1, 56.3.



1,2-bis((E)-3, 5-dimethoxybenzylidene)hydrazine (2E)¹⁵

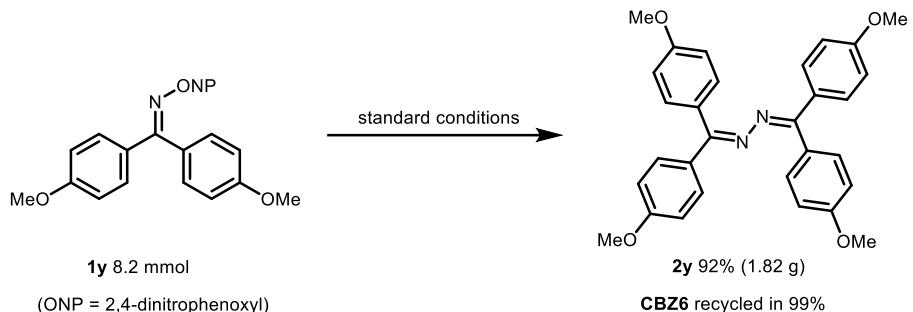
2E was prepared according to **GP3** by employing 4Å MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (82.1 mg, 95% yield). **¹H NMR** (500 MHz, CDCl₃): δ 8.56 (s, 2 H), 6.99 (d, *J* = 1.4 Hz, 2 H), 6.57 (s, 1 H), 3.84 (s, 6 H). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ 162.1, 161.1, 136.0, 106.3, 104.0, 55.6.



1,2-bis((E)-3-methoxy-5-methylbenzylidene)hydrazine (2F)

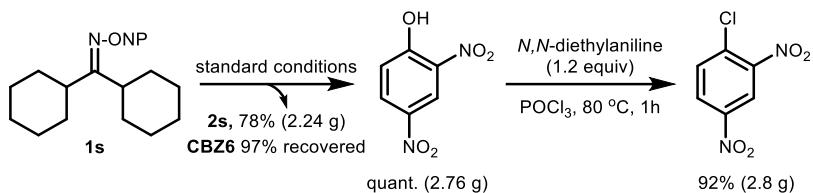
2F was prepared according to **GP3** by employing 4Å MS (25 mg) and purified by flash column chromatography (PE/EA/DCM = 100:1:1~50:1:1) to afford a yellow solid (53.3 mg, 72% yield), m.p.: 97.6-98.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.60 (s, 1 H), 7.72 (d, *J* = 9.6 Hz, 1 H), 6.84 (s, 1 H), 3.86 (s, 3 H), 2.38 (s, 3 H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 162.4, 160.0, 140.1, 135.3, 122.7, 118.8, 109.5, 55.5, 21.5. HRMS (ESI) *m/z* [M+H] calcd. for C₁₈H₂₁N₂O₂ 297.1603, found 297.1616.

6. Gram-scale Reaction



Bis(4-methoxyphenyl)methanone *O*-(2,4-dinitrophenyl) oxime (8.2 mmol, 1 equiv), **CBZ6** (2 mol%) and HCOONa (2.0 equiv) were weighed directly into an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (40 mL) was added sequentially in the Schlenk tube via syringe. Then the tube was placed 1.5 cm away from LEDs (3 W×6), and the reaction mixture was stirred vigorously under the irradiation. After 8 h, the tube was removed from the light source. The crude mixture was extracted with DCM (20 mL × 3), then washed with 50 mL NaCl (aq., 1 N). Organic phase was collected and dried under vacuum. The residue was purified by flash chromatography column to give the pure product (1.82 g, 92%) and **CBZ6** recycled in 99% yield (71 mg).

7. Recycling of ONP-leaving Group



Dicyclohexylmethanone *O*-(2,4-dinitrophenyl) oxime **1s** (15 mmol, 1 equiv), **CBZ6** (2 mol%) and HCOONa (2.0 equiv) were weighed directly into an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (75 mL) was added sequentially in the Schlenk tube via syringe. Then the tube was placed 1.5 cm away from LEDs (3 W×6), and the reaction mixture was stirred vigorously under the irradiation. After 24 h, the tube was removed from the light source and then quenched by addition of water (100 mL). The crude mixture was extracted with Et₂O (20 mL × 3), then washed with 20 mL NaCl (aq., 1 N). Organic phase was collected under vacuum. The residue was purified by flash chromatography column to give the pure product **2s** (2.24 g, 78%) and **CBZ6** recycled in 97% yield (126 mg).

The aqueous layer was added with concentrated HCl to adjust pH of 1.0, extracted with DCM (20 mL × 3). Organic phase was collected, dried with anhydrous Na₂SO₄ and evaporated under vacuum to get the crude product. The residue was purified by recrystallization with EtOH to give 2,4-dinitrophenol as a reddish brown solid. (2.76 g, quant).

According to the reported procedures,²⁰ a 100 mL Schlenk reaction tube was charged with 2,4-dinitrophenol (2.76 g, 15 mmol) and POCl₃ (5.87 mL, 4.2 equiv). *N,N*-diethylaniline (2.69 g, 1.2 equiv) was added dropwise to the reaction mixture under nitrogen atmosphere. Then the reaction tube was heated at 80 °C in an oil bath for 1.5 h. After cooling down to r.t., the resulting solution was dropped into an ice bath, extracted with ethyl acetate. The organic layer was washed with brine, and dried with anhydrous sodium sulfate. The solvent was concentrated in *vacuo* and the residue was purified by flash column chromatography to give 1-chloro-2,4-dinitrobenzene as yellow liquid (2.80 g, 92%).

8. Synthesis of Hydrazine

2a or **2d** (0.25 mmol, 1.0 equiv) and ion-exchange resin (NCK-9) ($C_{\text{hydrogen ion}} \geq 4.7 \text{ mmol/g}$) (212 mg, 4.0 equiv) were weighed into a flask of 25 mL, then added a mixture of 0.5 ml toluene to water (v/v=1:1).

After the reaction mixture was cooled into the room temperature, 3.5 mL H_2O was added and DCM (3 x 3 mL) extracted the mixture. The organic phase was combined and concentrated for the quantification of ketone. The yield of the corresponding ketone was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The hydrazine was quantified by iodimetry using iodine standard solution [GBW(E)081614 ($C_{(1/2 \text{ I}_2)} = 0.1005 \text{ mol/L}$)]. The quantitative yield for hydrazine was determined based on three runs of the reactions.

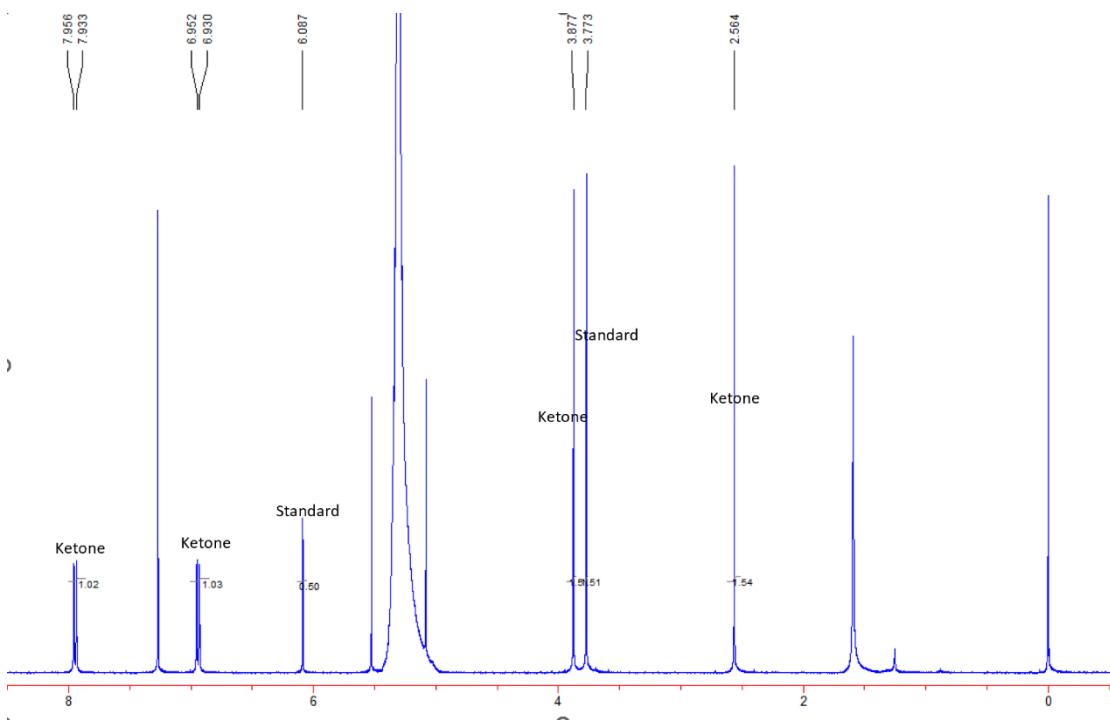


Figure S2. Crude ^1H NMR spectrum of ketone from the hydrolysis of **2d** (0.25 mmol) with 1,3,5-trimethoxybenzene (28 mg) as an internal standard.

9. UV-Vis Absorption Spectra

Test conditions for UV-Vis absorption spectrum and fluorescence spectrum:

Substrate 1a: 6.3 mg dissolved in 20 mL DMSO (0.001 M)

HCOONa: 1.4 mg dissolved in 20 mL DMSO (0.001 M)

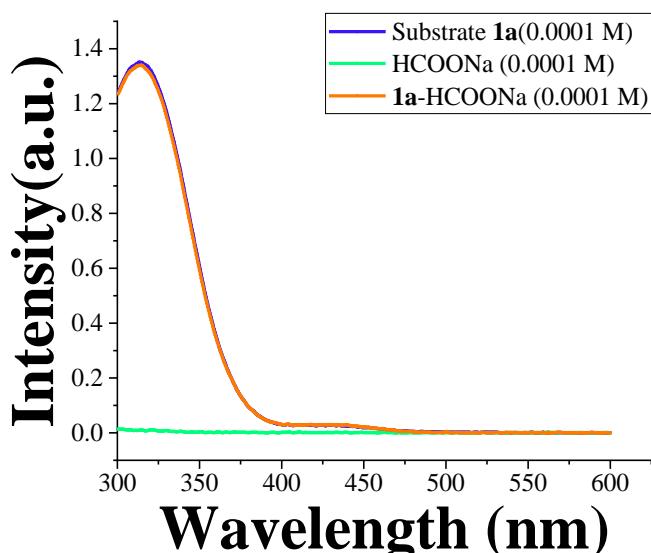


Figure S3. Molar absorptivity spectra of **1a**, HCOONa and **1a**-HCOONa.

Test conditions for quenching reaction:

CBZ6: 4.3 mg dissolved in 10 mL DMSO (0.001 M)

Quencher: 39.41 mg of **1a** dissolved in 20 mL DMSO (0.00625M).

General procedure:

0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, keep the total volume at 2mL, **1a** and DMSO were added as the following table:

Entry	CBZ6	1a	DMSO	Total volume
1	0.5 mL (2.5×10^{-4} M)	0 μ L (0 mM)	1.5 mL	2 mL
2	0.5 mL (2.5×10^{-4} M)	5 μ L (0.015625 mM)	1.495 mL	2 mL
3	0.5 mL (2.5×10^{-4} M)	10 μ L (0.03125 mM)	1.49 mL	2 mL
4	0.5 mL (2.5×10^{-4} M)	15 μ L (0.046875 mM)	1.485 mL	2 mL
5	0.5 mL (2.5×10^{-4} M)	20 μ L (0.0625 mM)	1.48 mL	2 mL

Excitation wavelength: 330 nm

Make and model of fluorescence spectrophotometer:

Make: Hitachi High-Technologies Corporation, Tokyo, Japan

Model: F-4600

10. References

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11. NMR Spectra

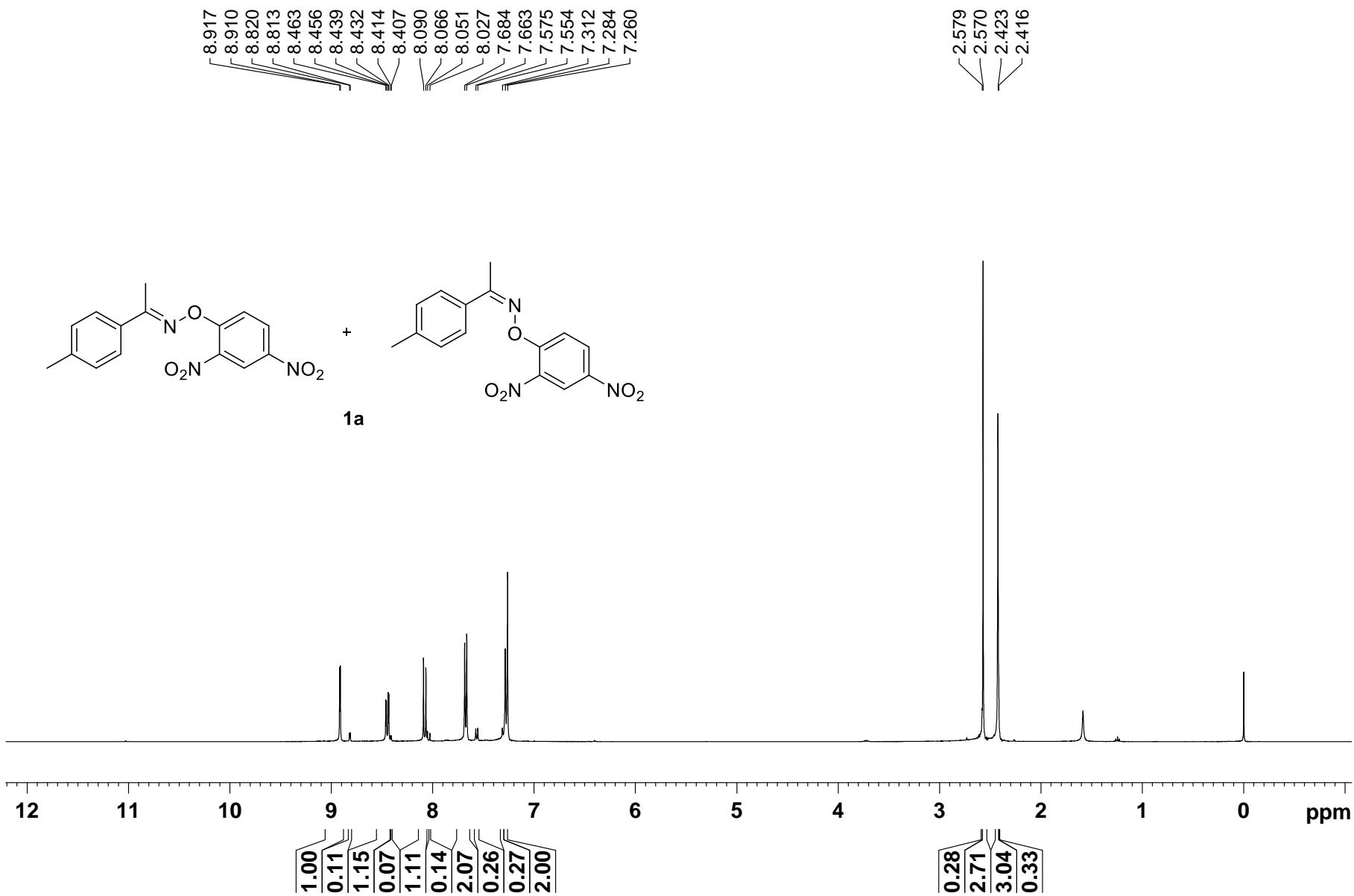


Figure S4. ^1H NMR spectrum of **1a** (CDCl_3 , 400 M).

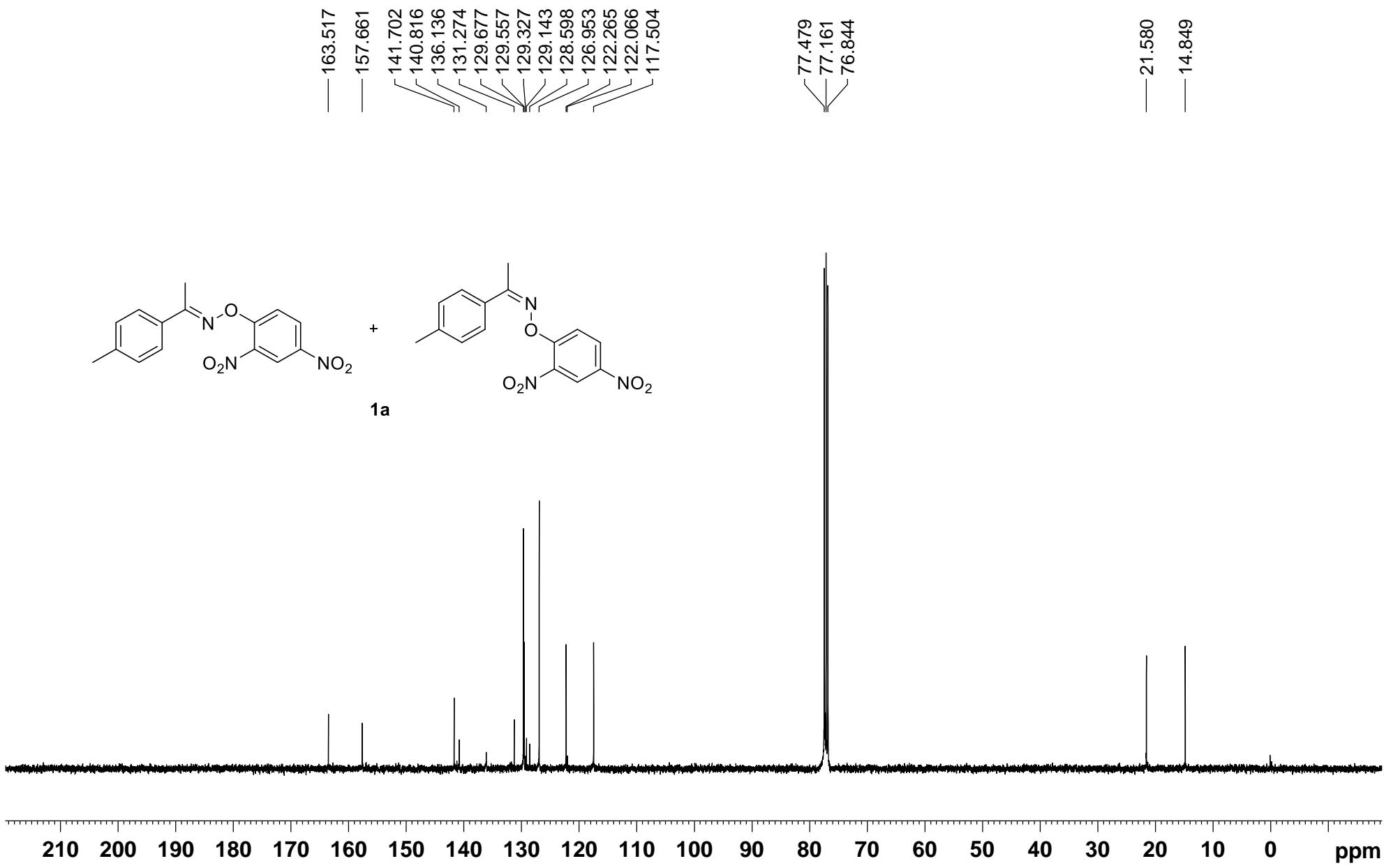


Figure S5. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **1a** (CDCl_3 , 100 M).

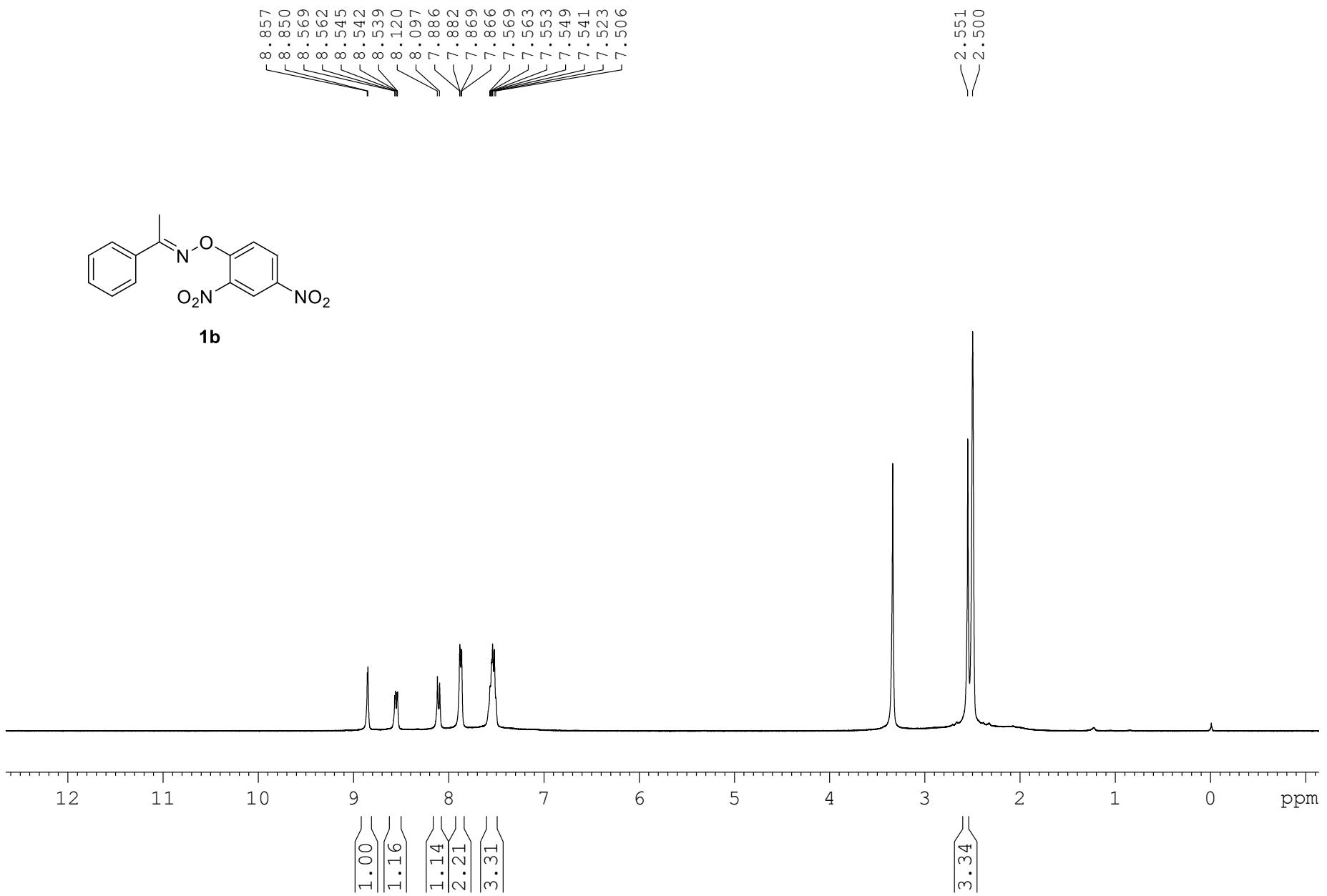


Figure S6. ^1H NMR spectrum of **1b** (DMSO- d^6 , 400 M).

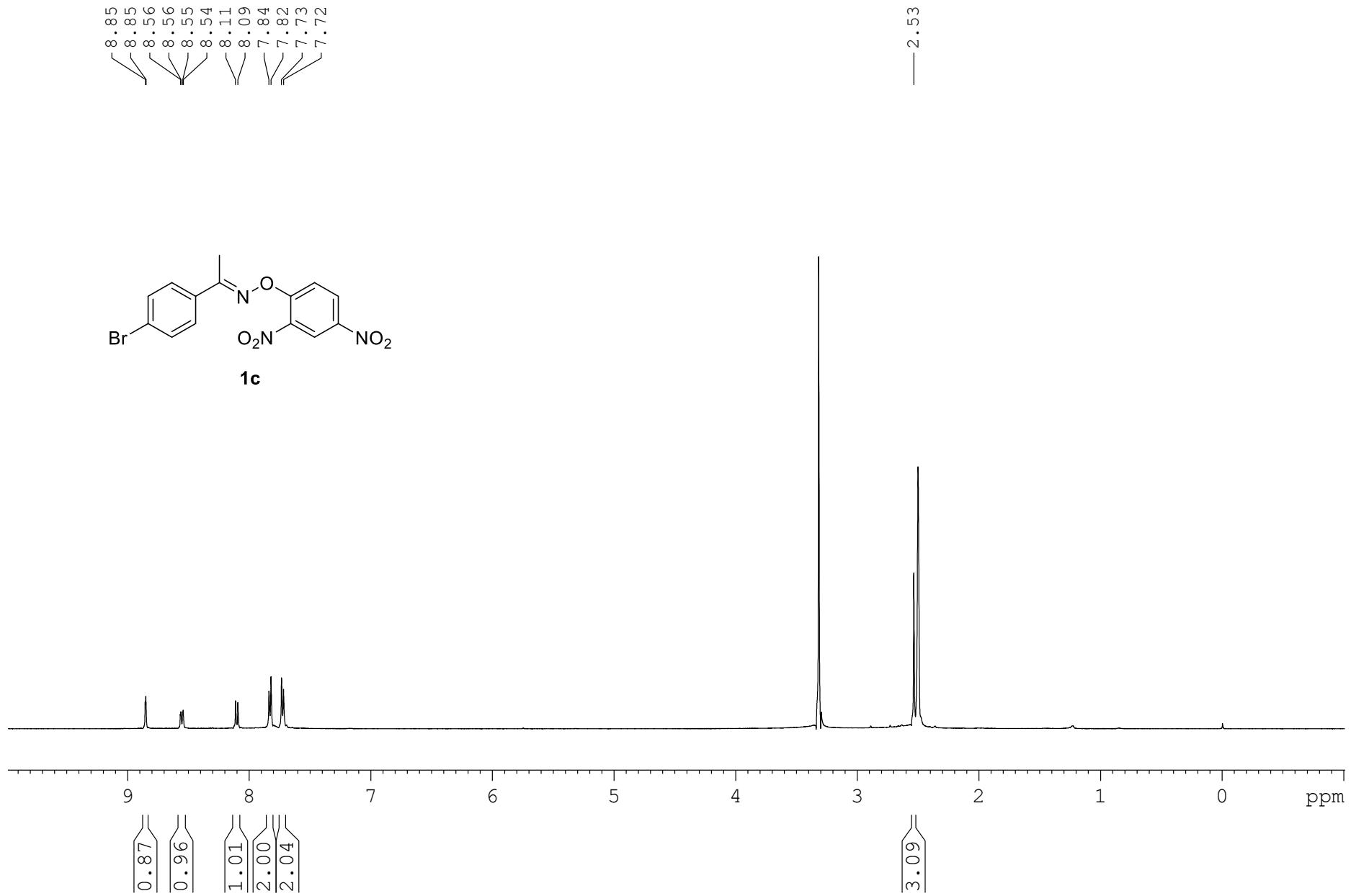


Figure S7. ¹H NMR spectrum of **1c** (DMSO- *d*⁶, 500 M).

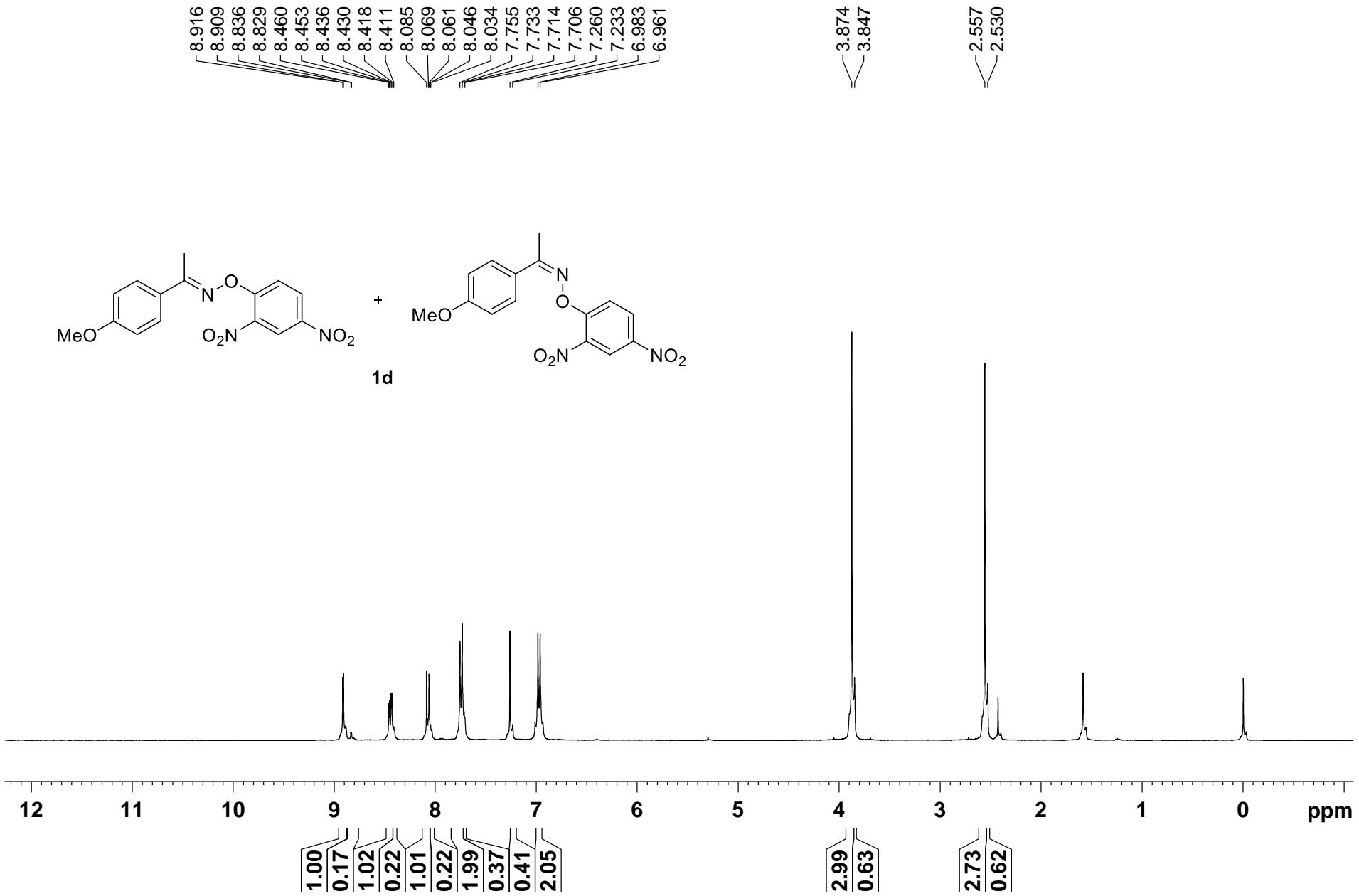


Figure S8. ^1H NMR spectrum of **1d** (CDCl_3 , 400 M).

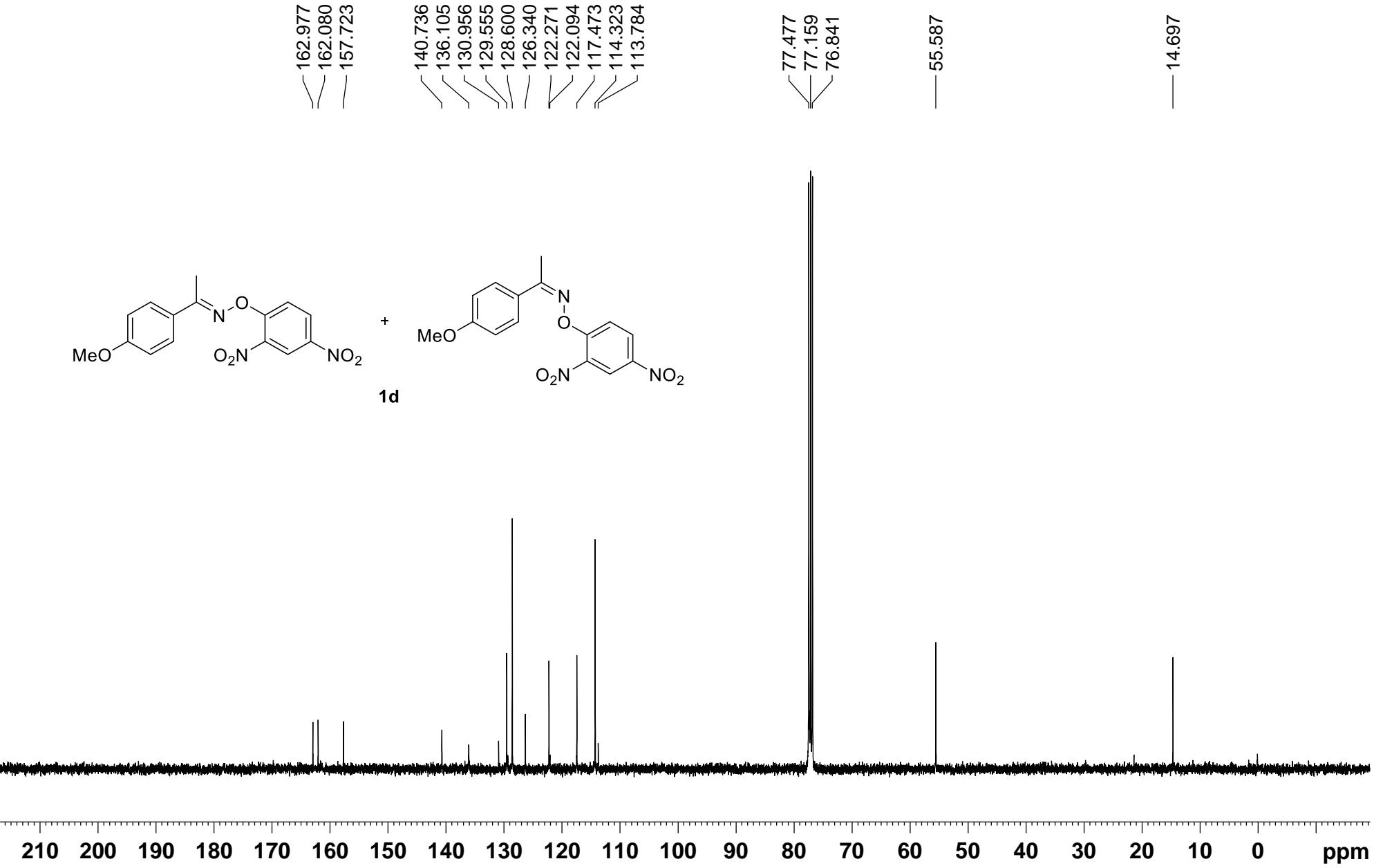


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1d** (CDCl_3 , 100 M).

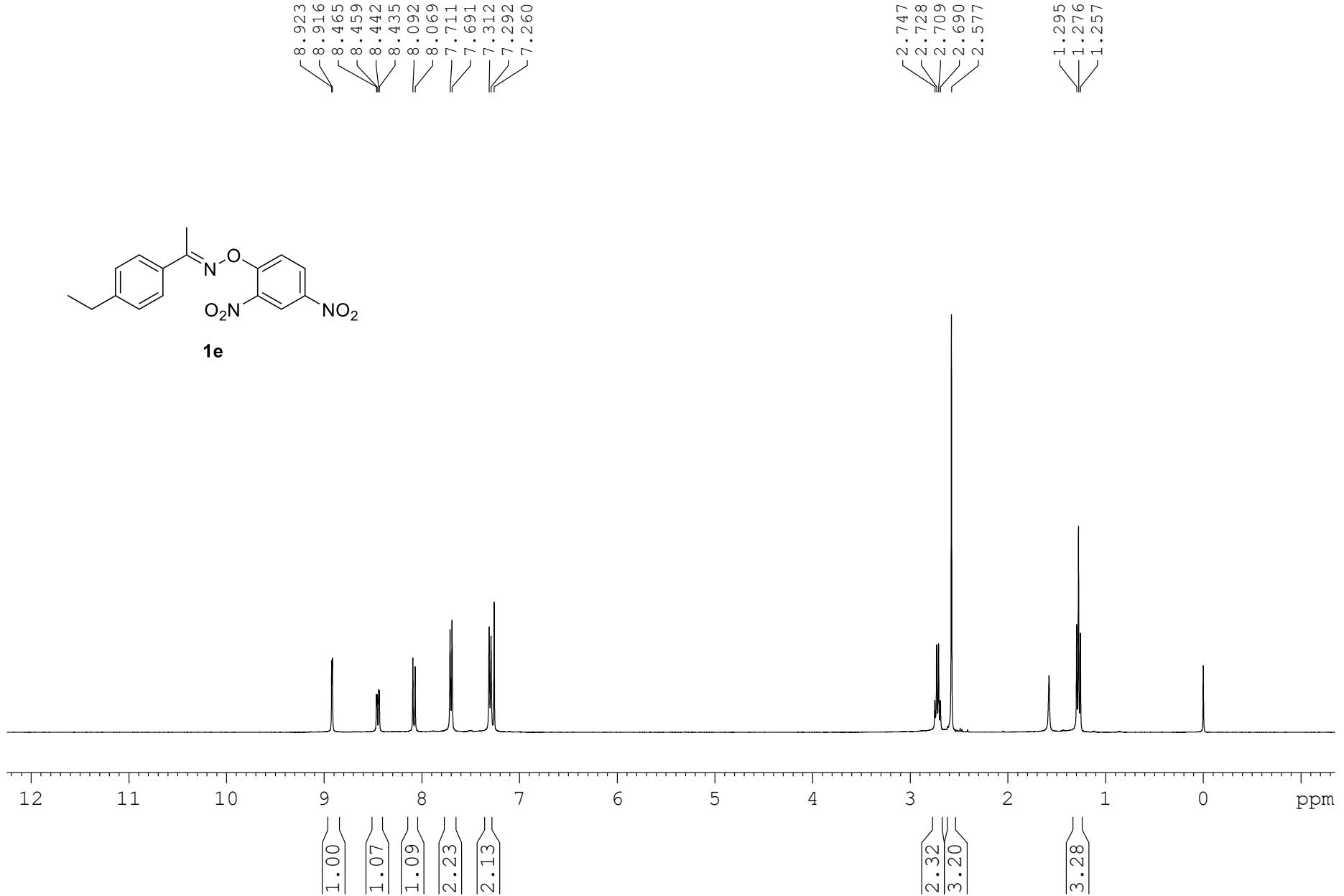
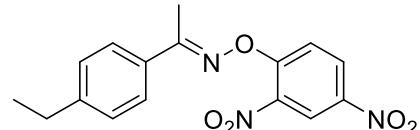


Figure S10. ¹H NMR spectrum of **1e** (CDCl₃, 400 M).



1e

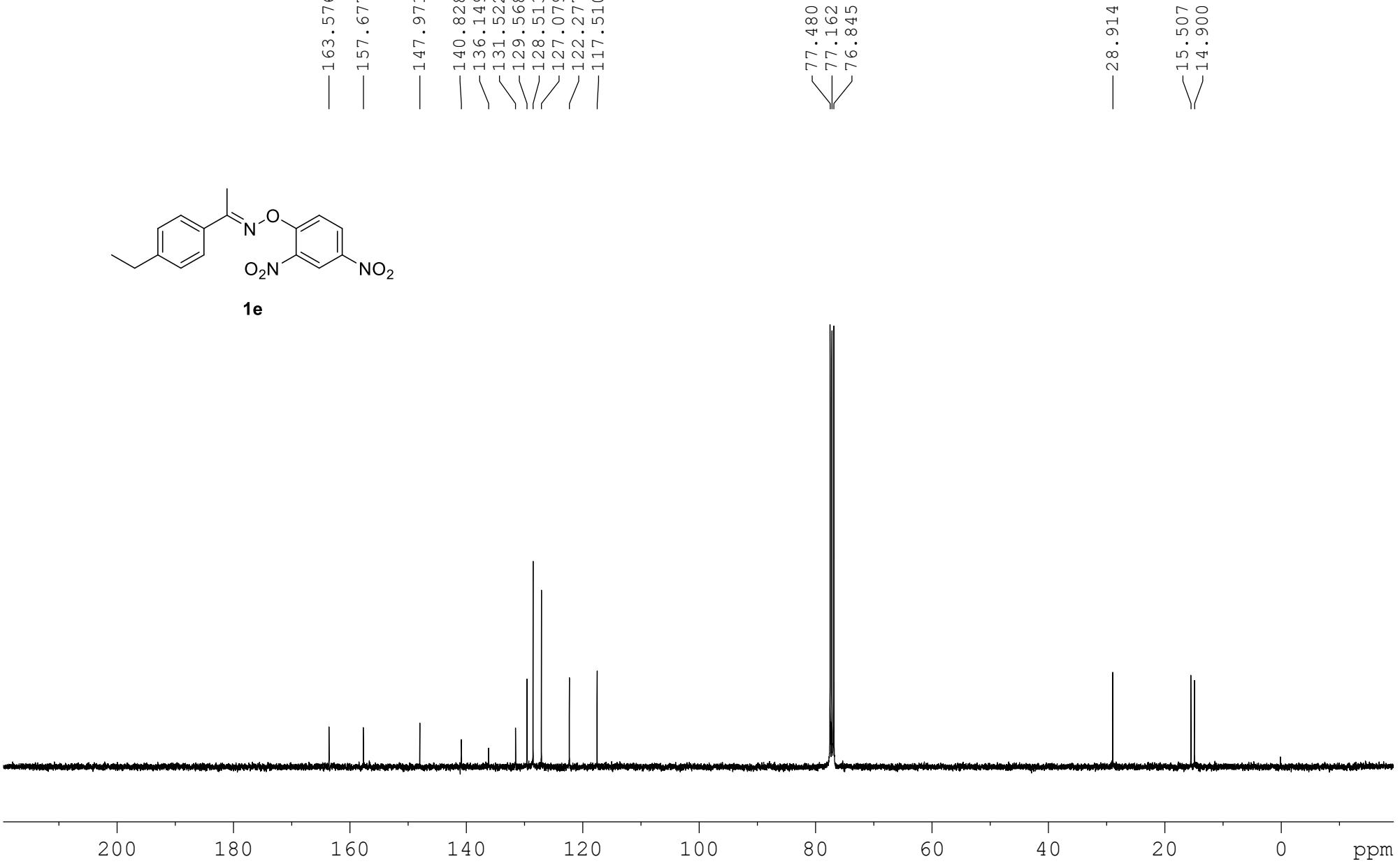


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1e** (CDCl_3 , 100 M).

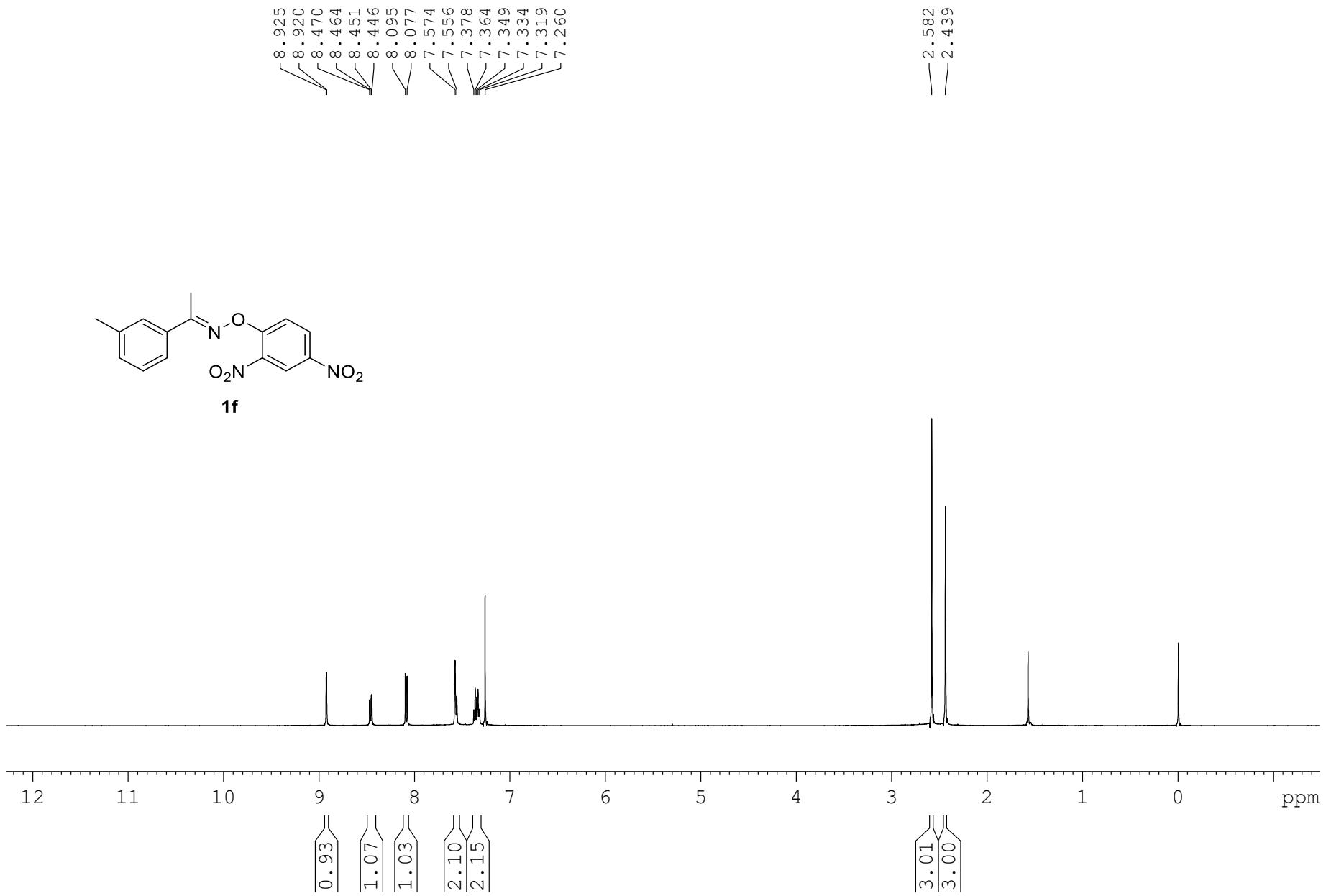


Figure S12. ^1H NMR spectrum of **1f** (CDCl_3 , 500 M).

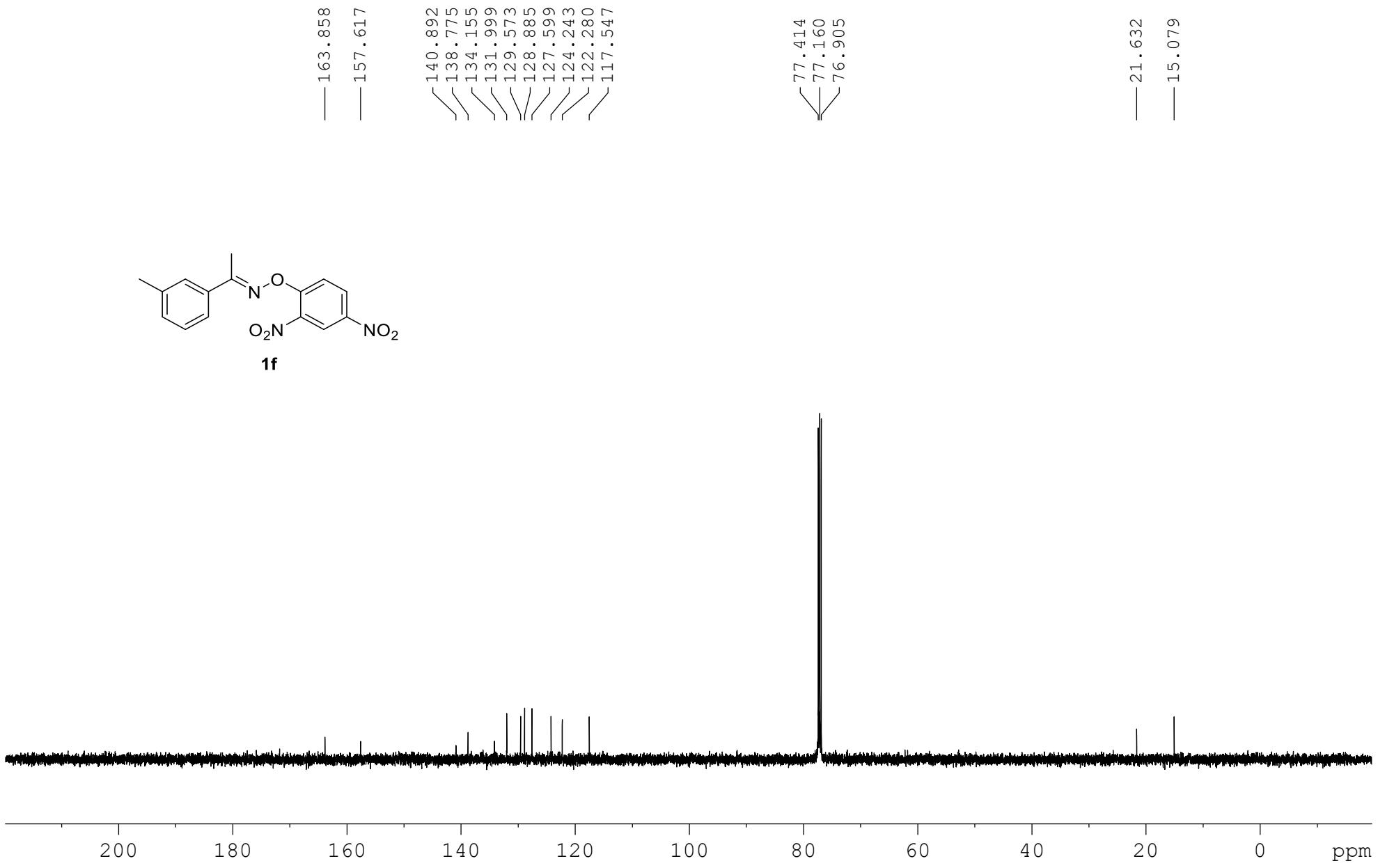


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1f** (CDCl_3 , 125 M).

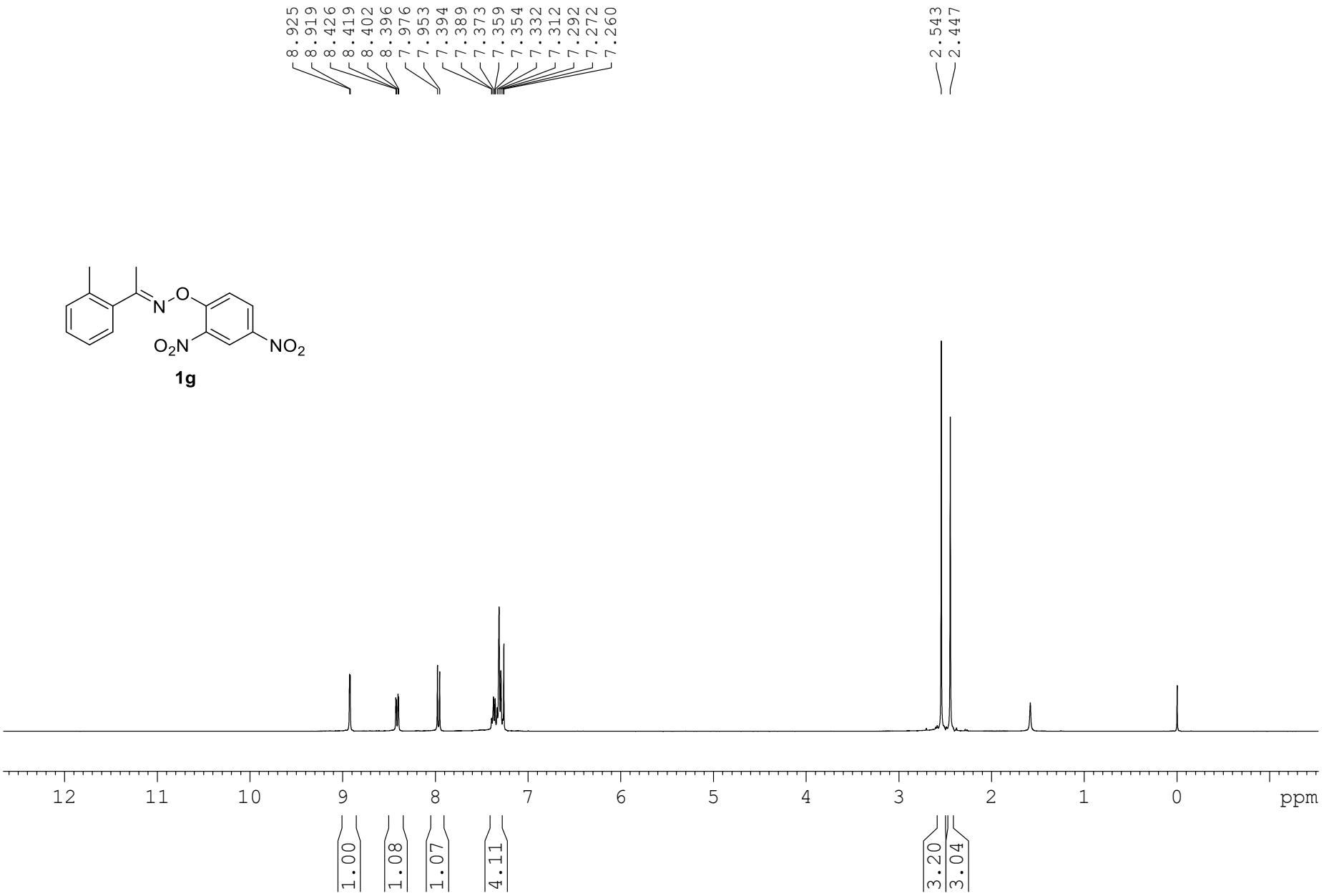


Figure S14. ^1H NMR spectrum of **1g** (CDCl_3 , 400 M).

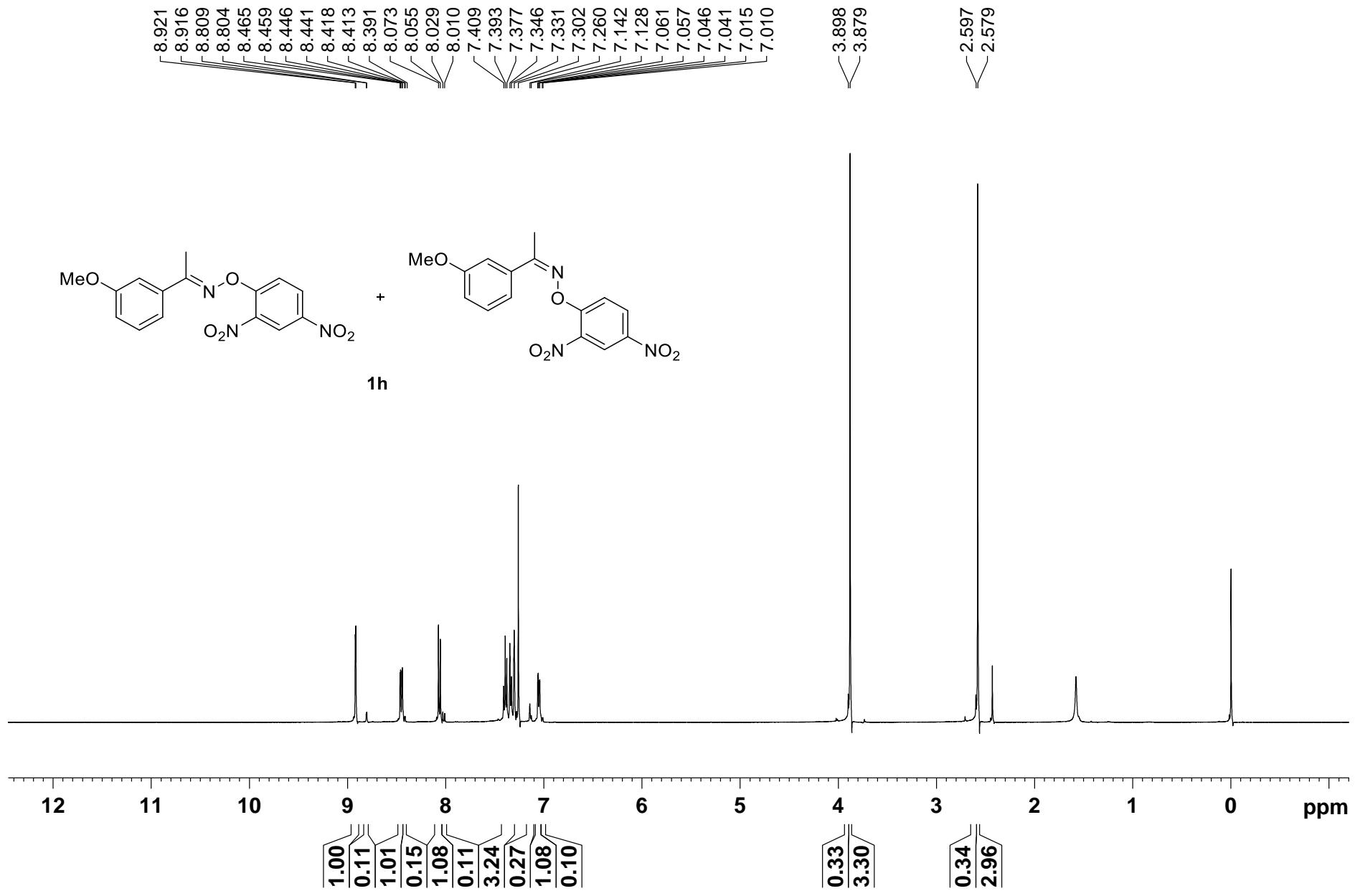


Figure S15. ^1H NMR spectrum of **1h** (CDCl_3 , 500 M).

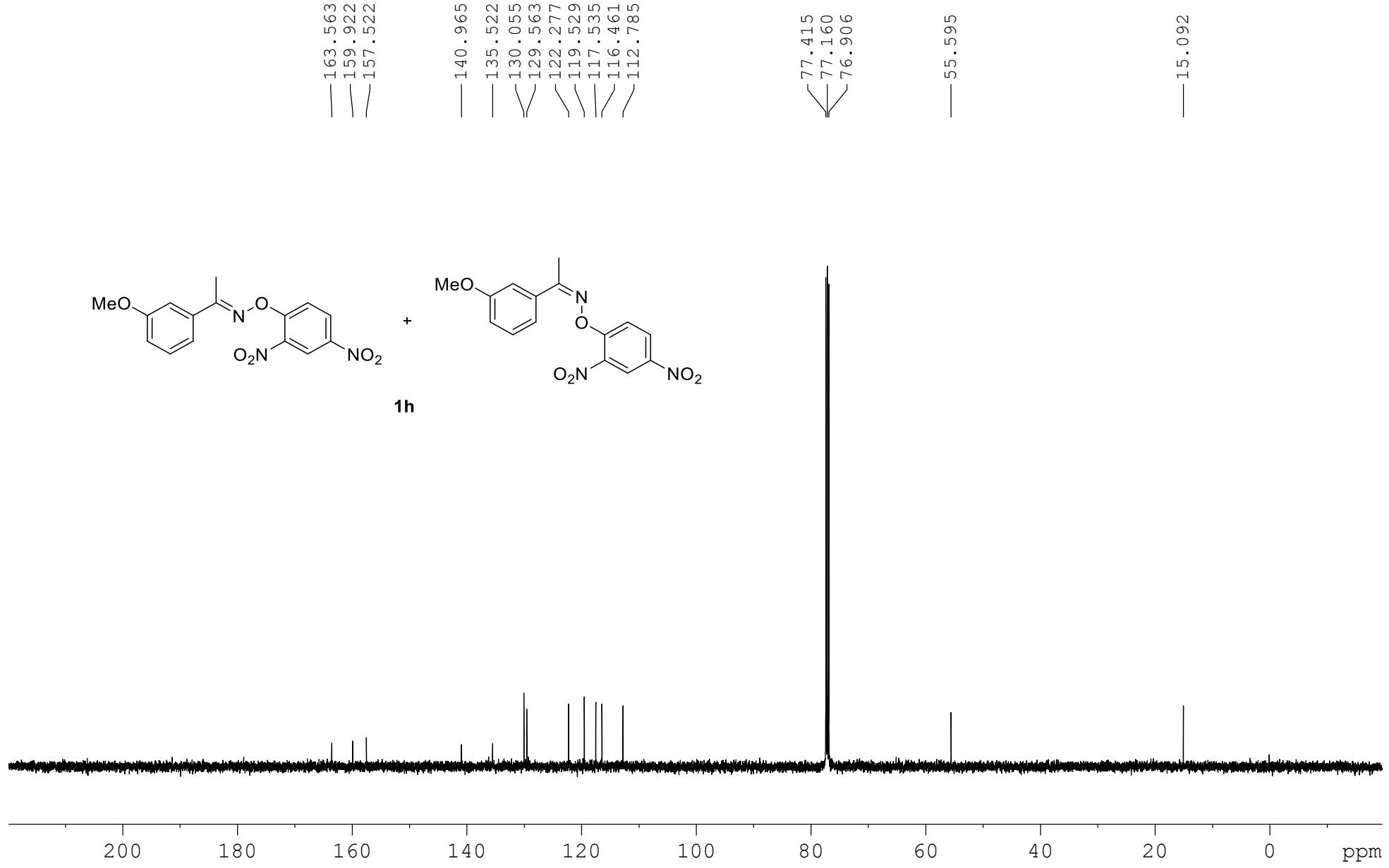


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1h** (CDCl_3 , 125 M).

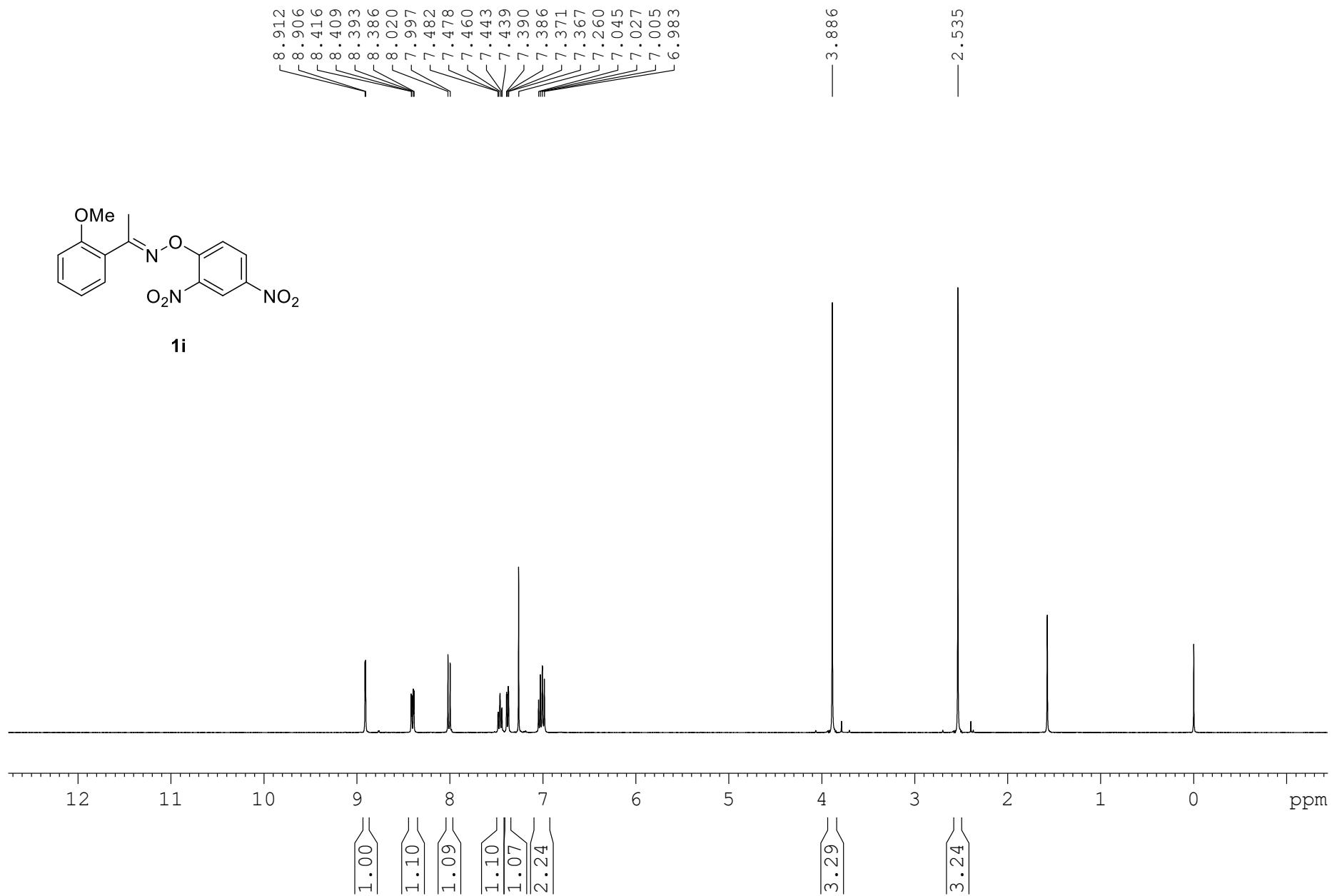


Figure S17. ¹H NMR spectrum of **1i** (CDCl₃, 400 M).

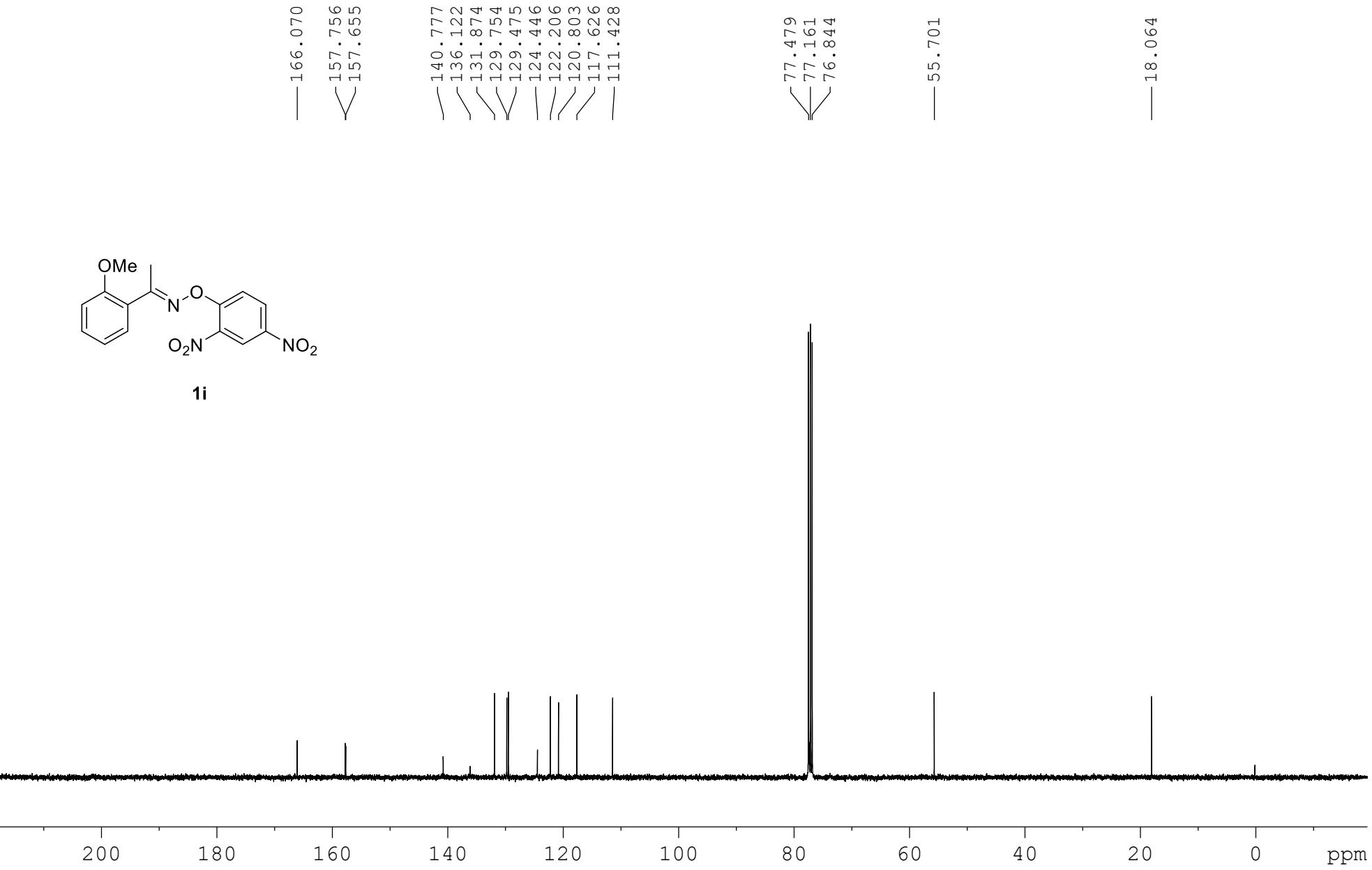


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1i** (CDCl_3 , 100 M).

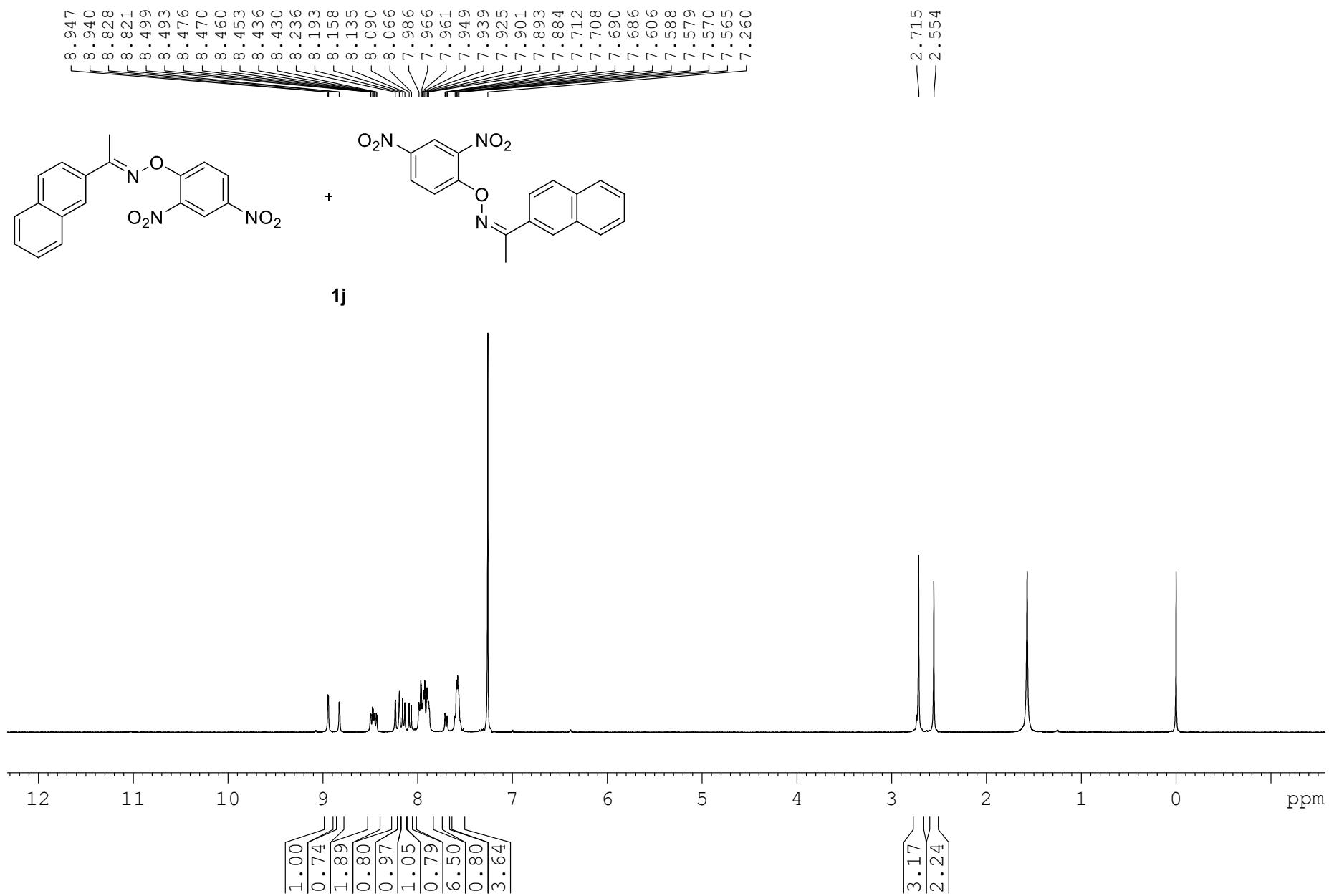


Figure S19. ^1H NMR spectrum of **1j** (CDCl_3 , 400 M).

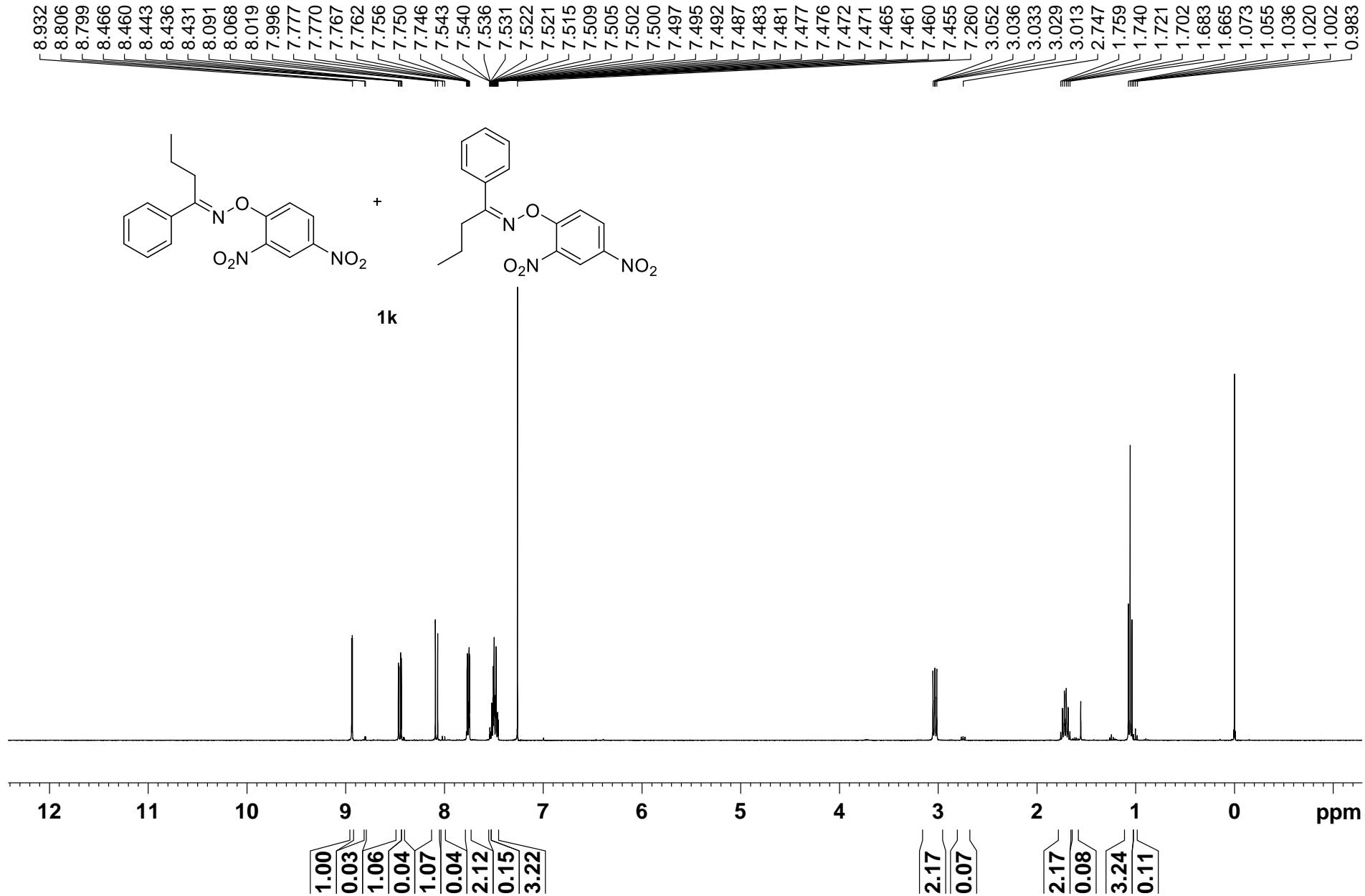


Figure S20. ^1H NMR spectrum of **1k** (CDCl_3 , 500 M).

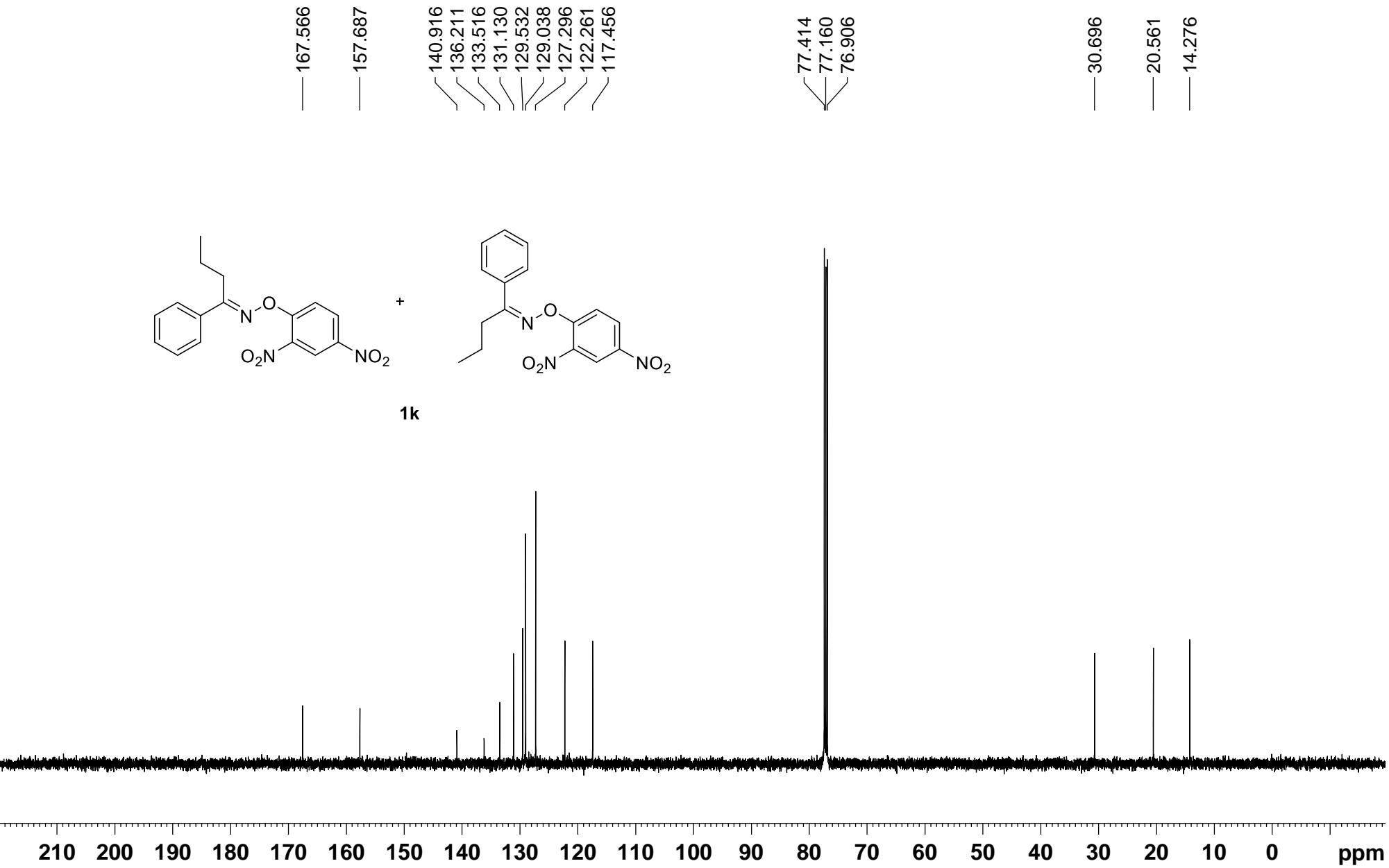


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1k** (CDCl_3 , 125 M).

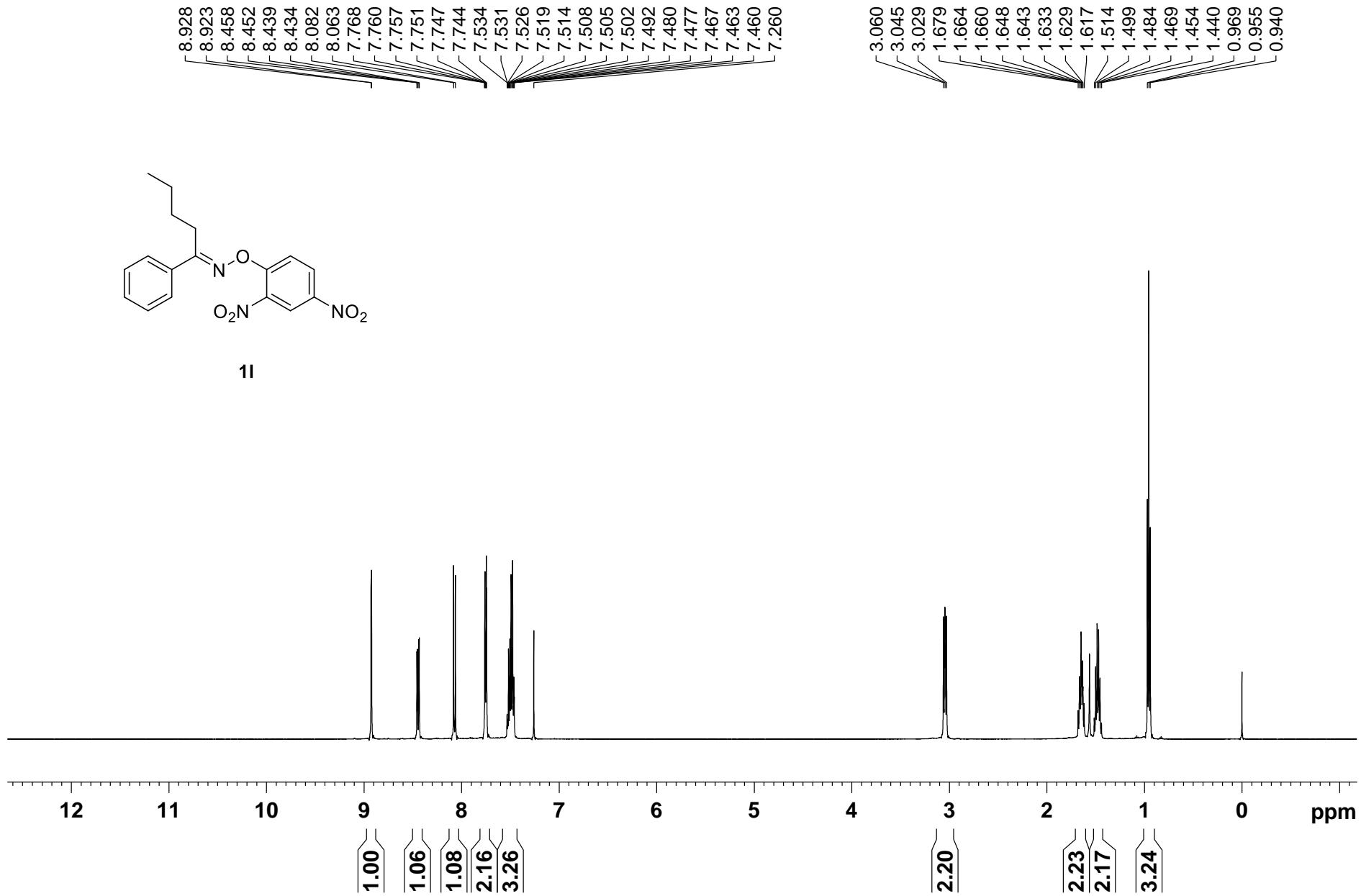


Figure S22. ¹H NMR spectrum of **11** (CDCl₃, 500 M).

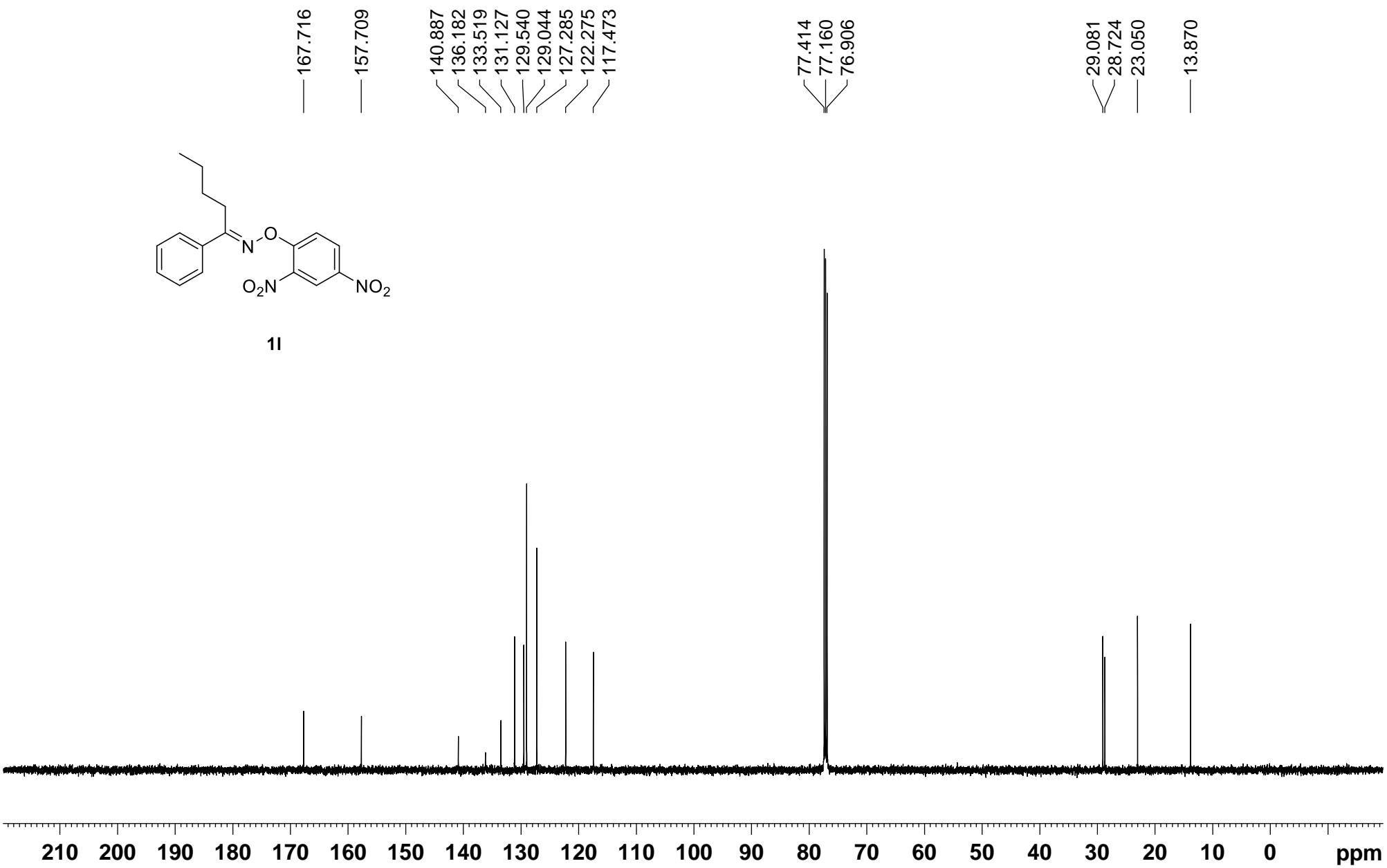


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1I** (CDCl_3 , 125 M).

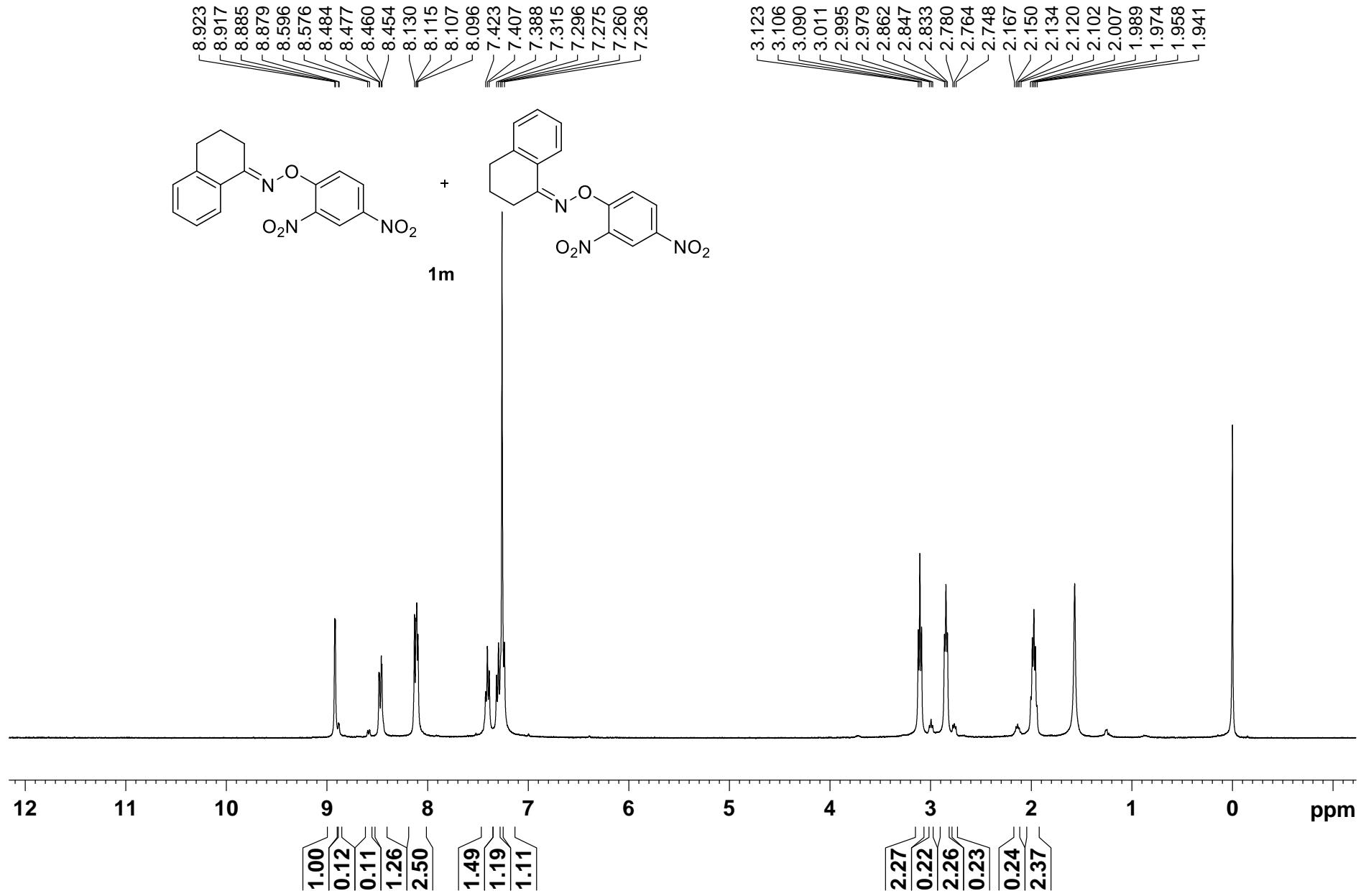


Figure S24. ^1H NMR spectrum of **1m** (CDCl_3 , 400 M).

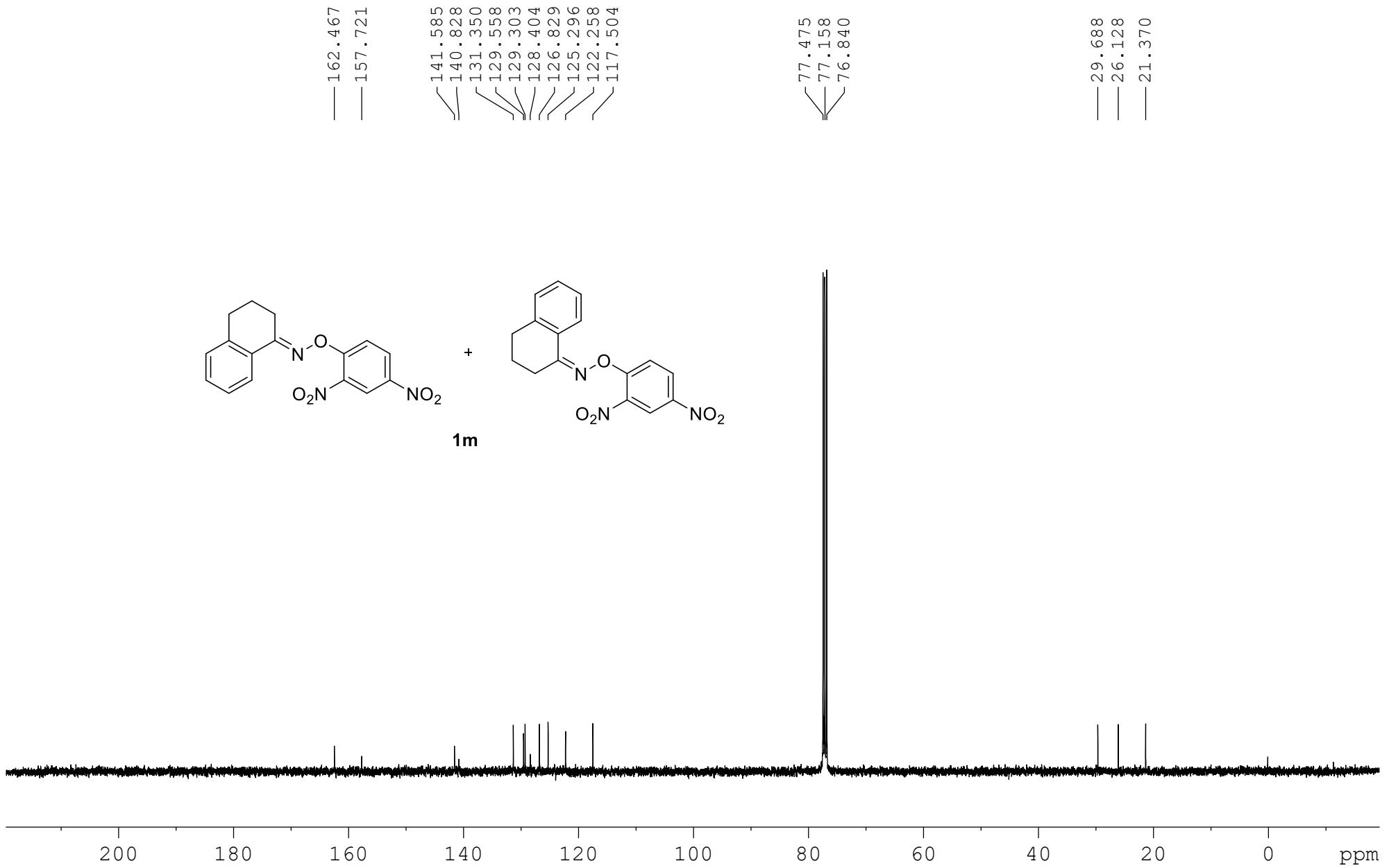


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1m** (CDCl_3 , 100 M).

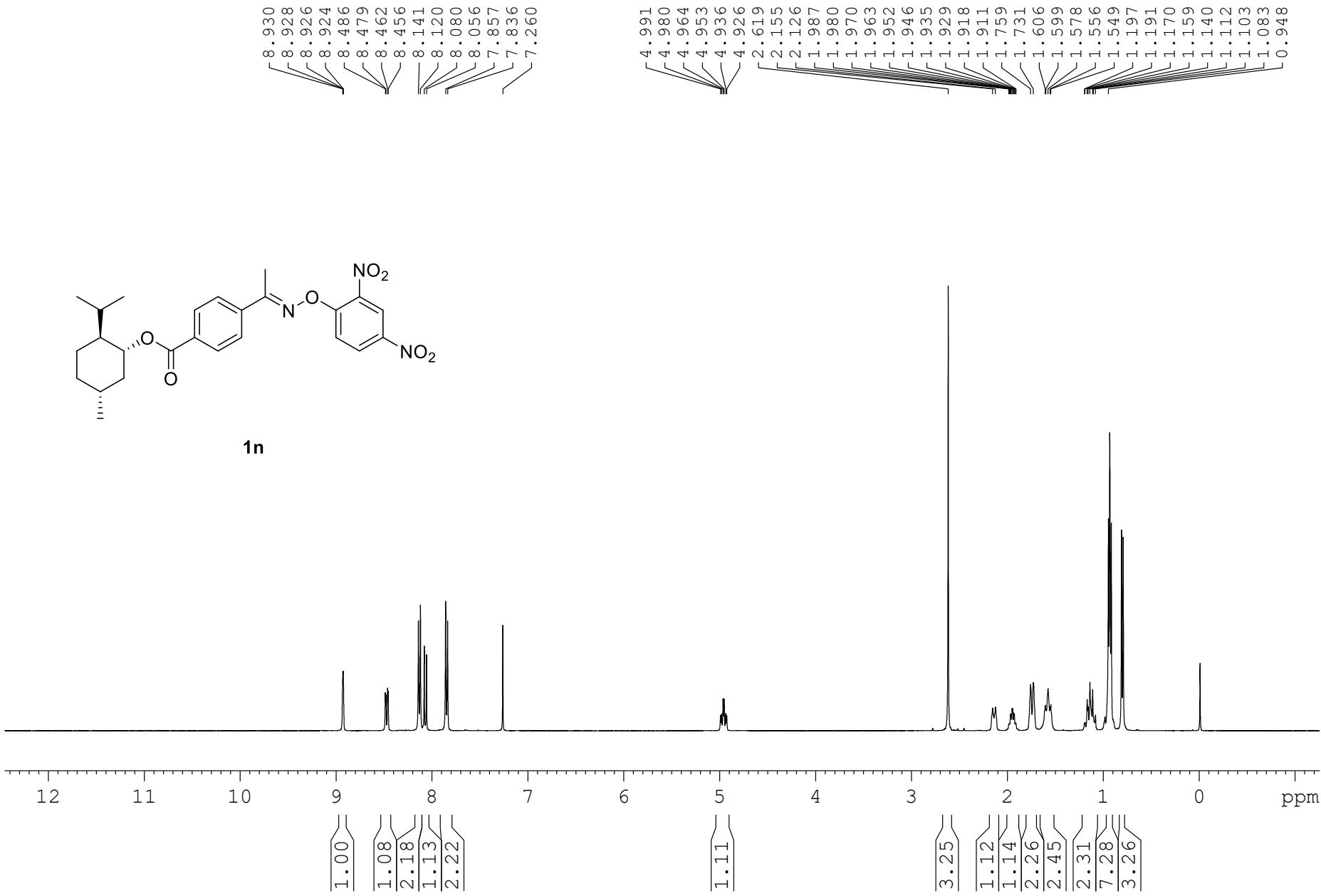


Figure S26. ¹H NMR spectrum of **1n** (CDCl_3 , 500 M).

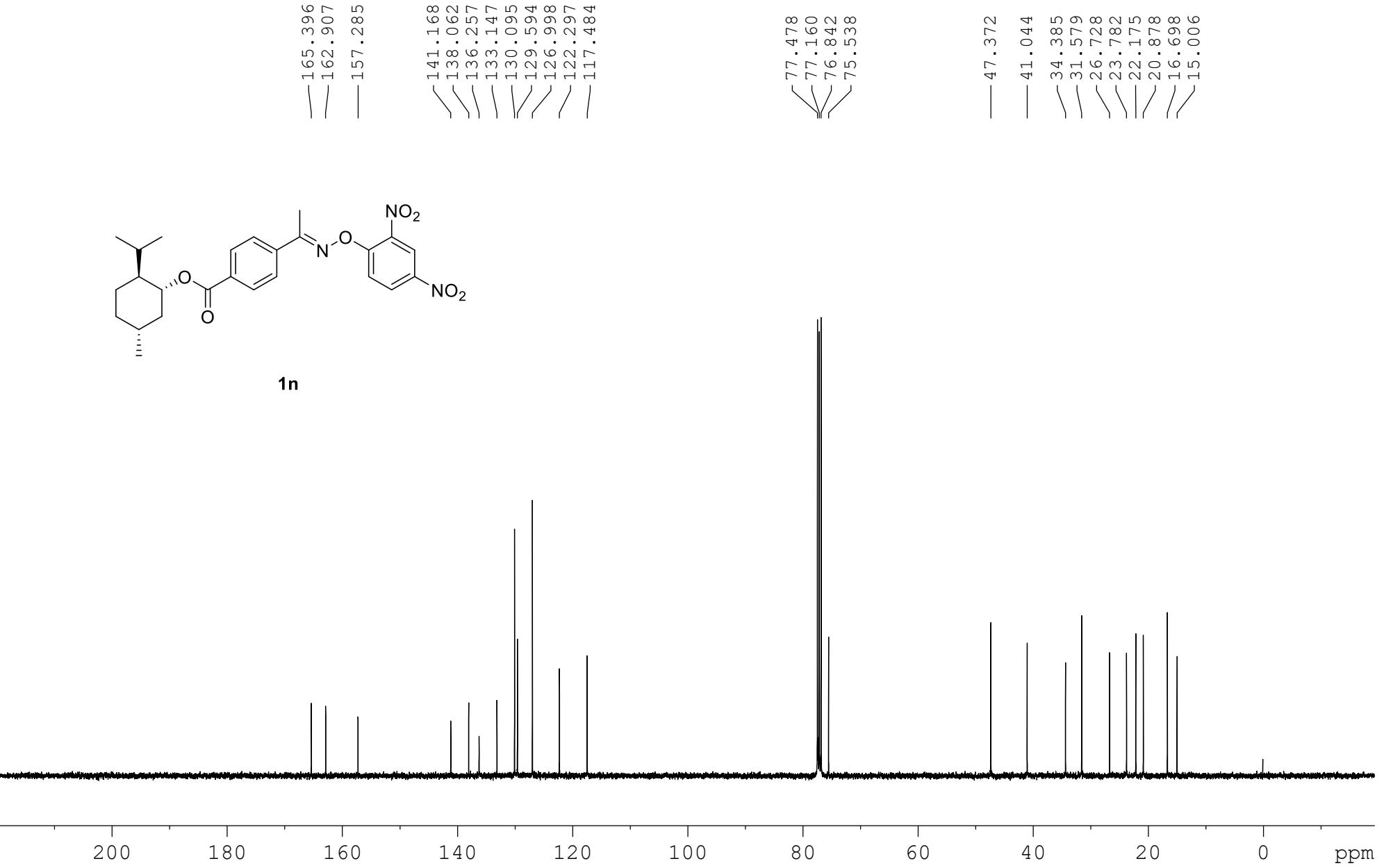


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1n** (CDCl_3 , 125 M).

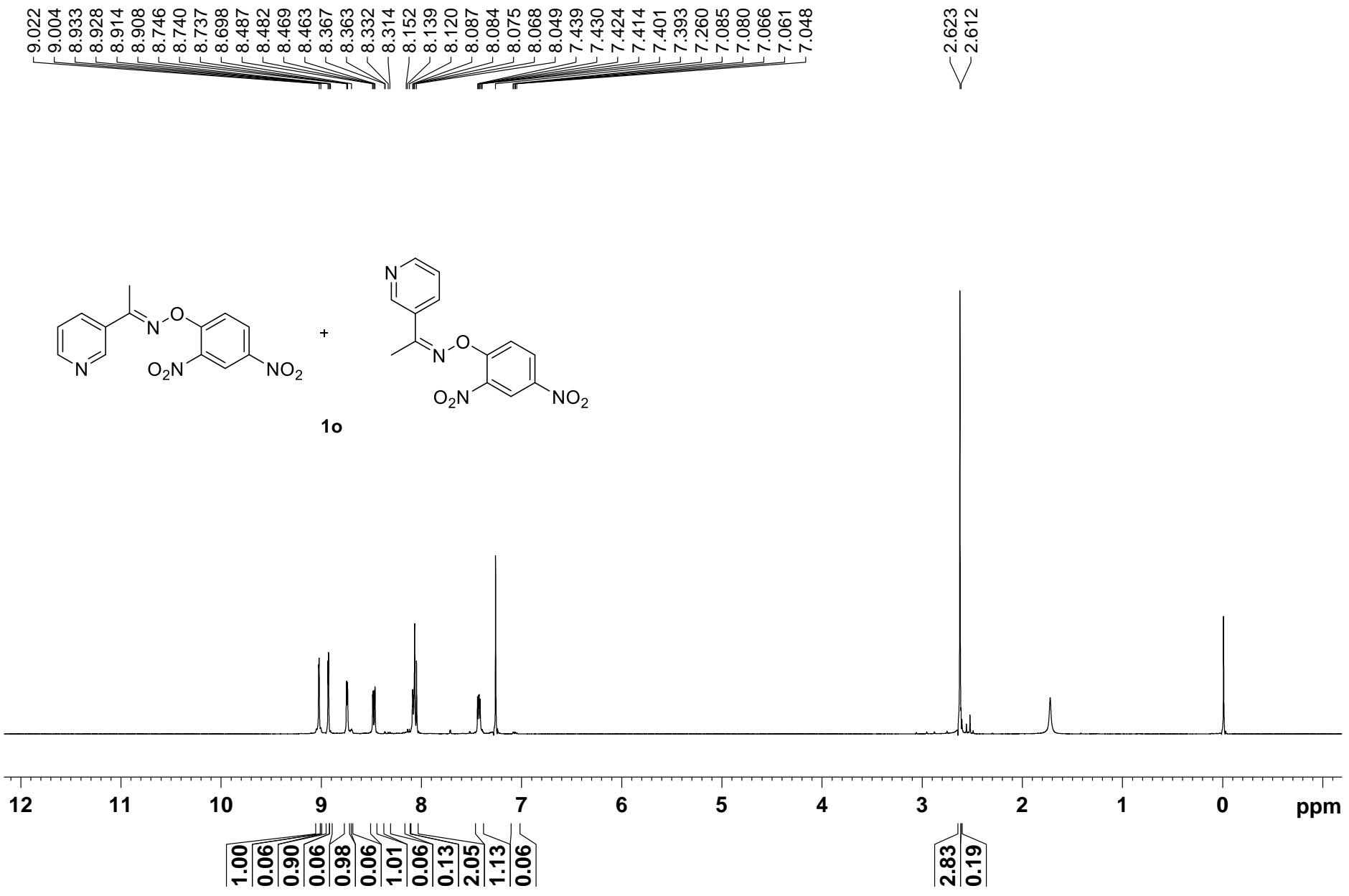


Figure S28. ^1H NMR spectrum of **1o** (CDCl_3 , 500 M).

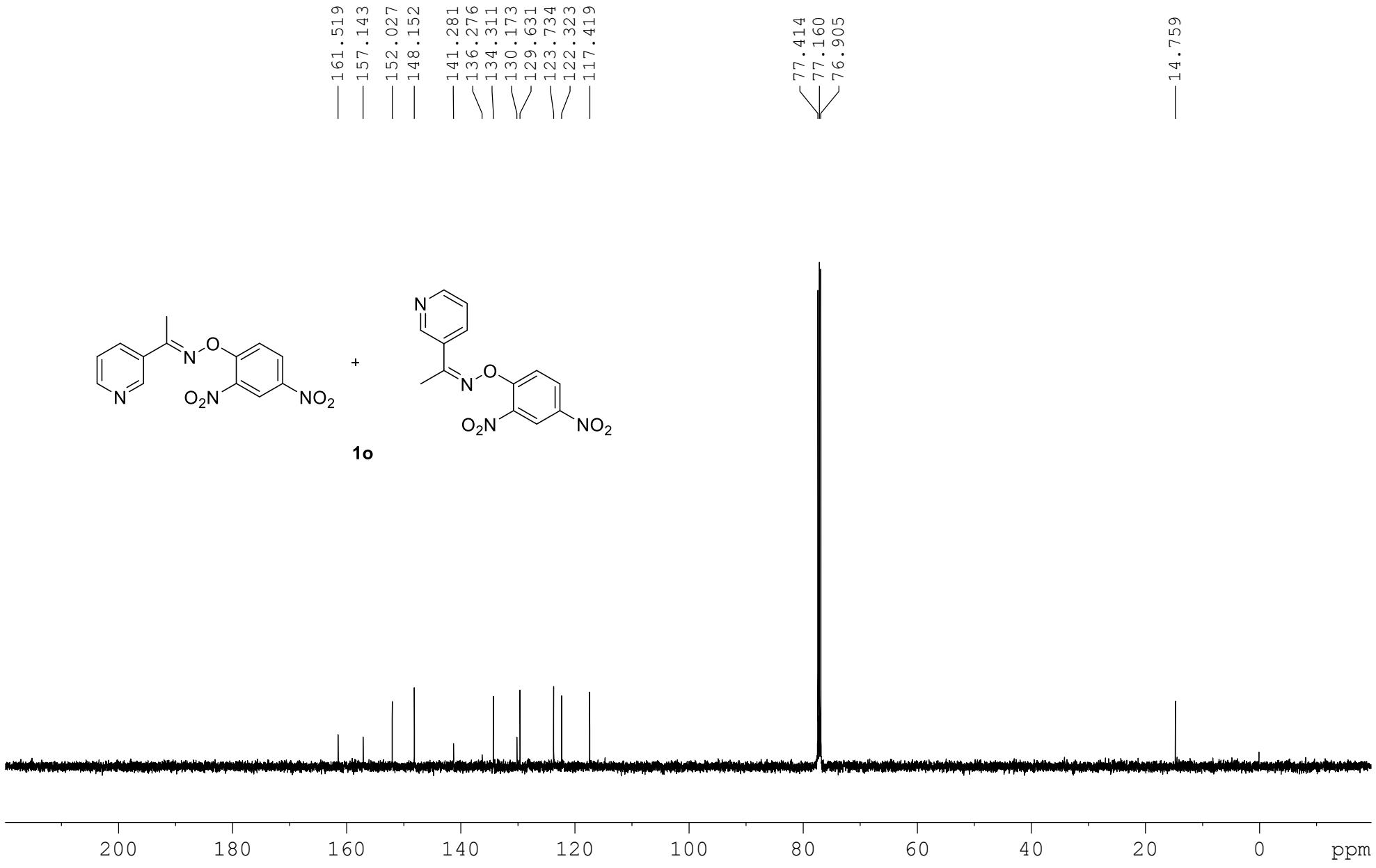


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1o** (CDCl_3 , 125 M).

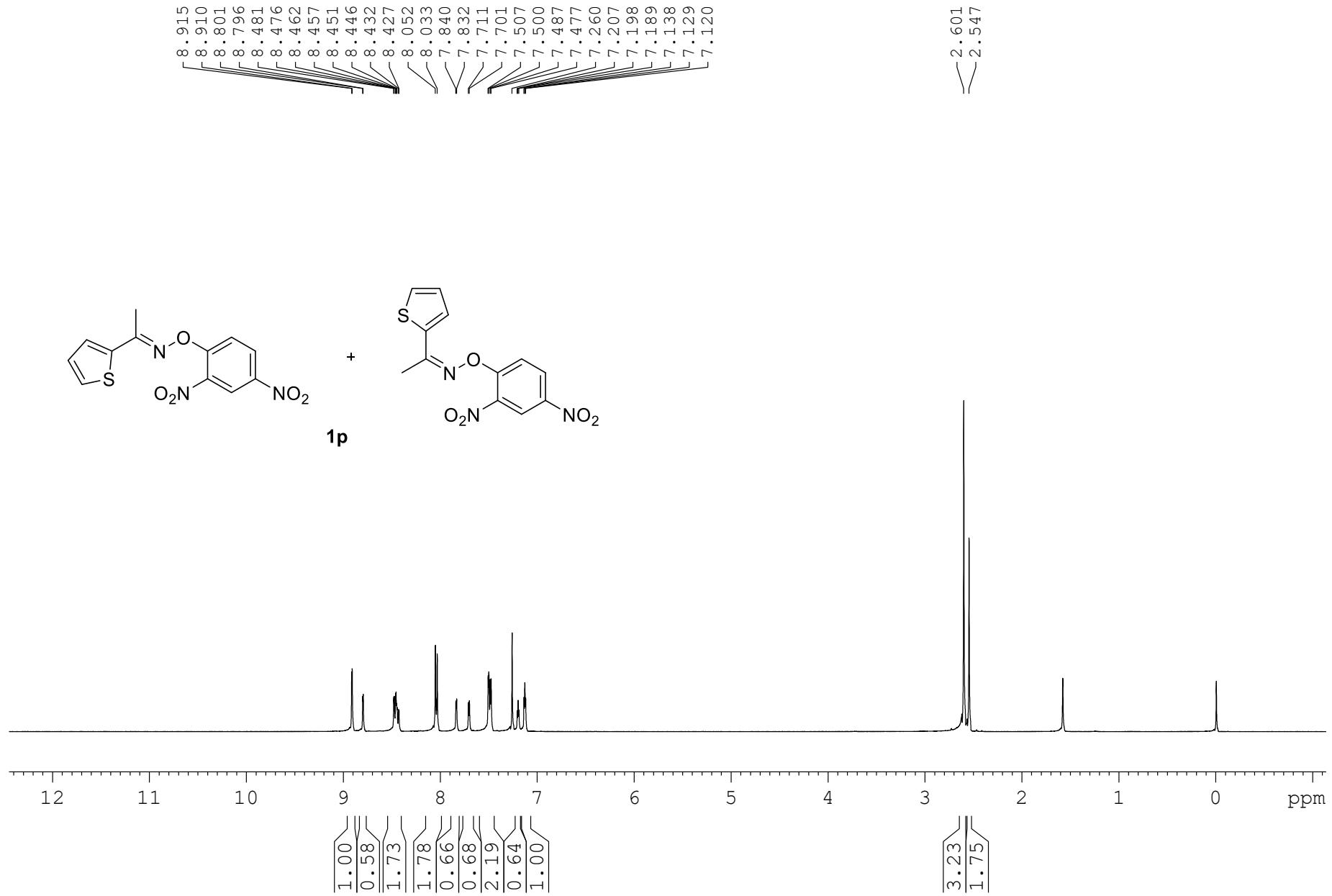


Figure S30. ^1H NMR spectrum of **1p** (CDCl_3 , 500 M).

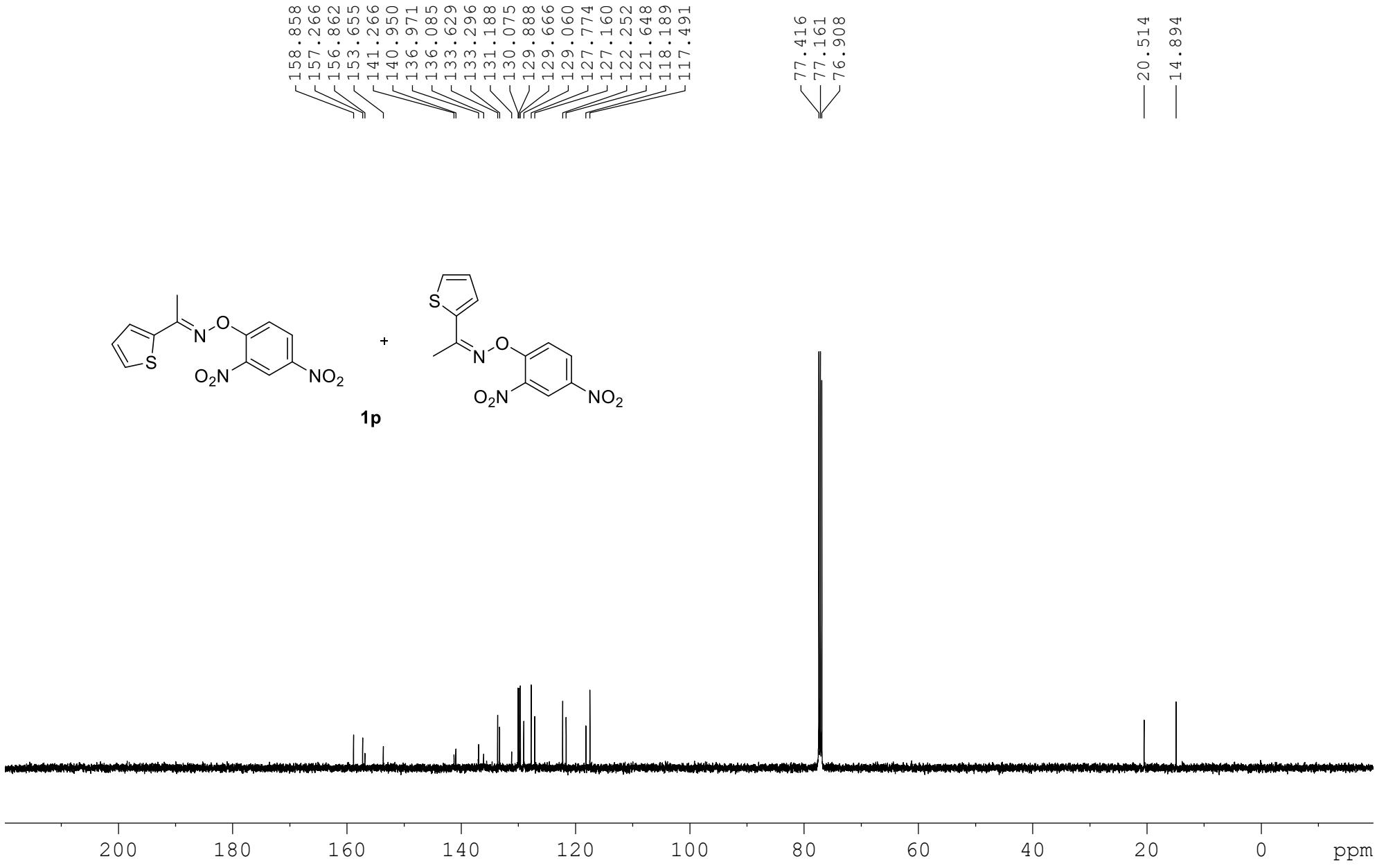


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1p** (CDCl_3 , 125 M).

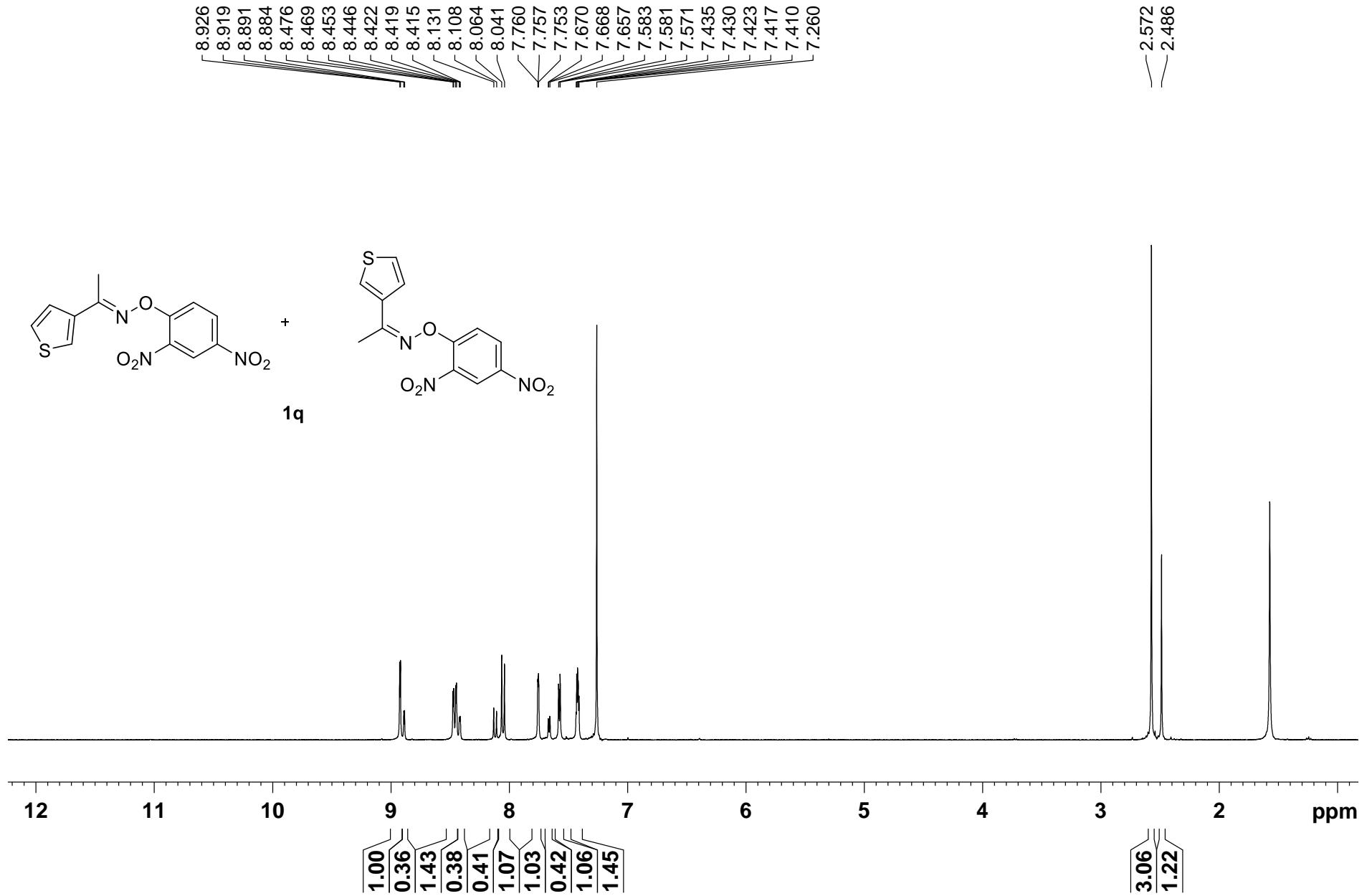


Figure S32. ¹H NMR spectrum of **1q** (CDCl_3 , 400 M).

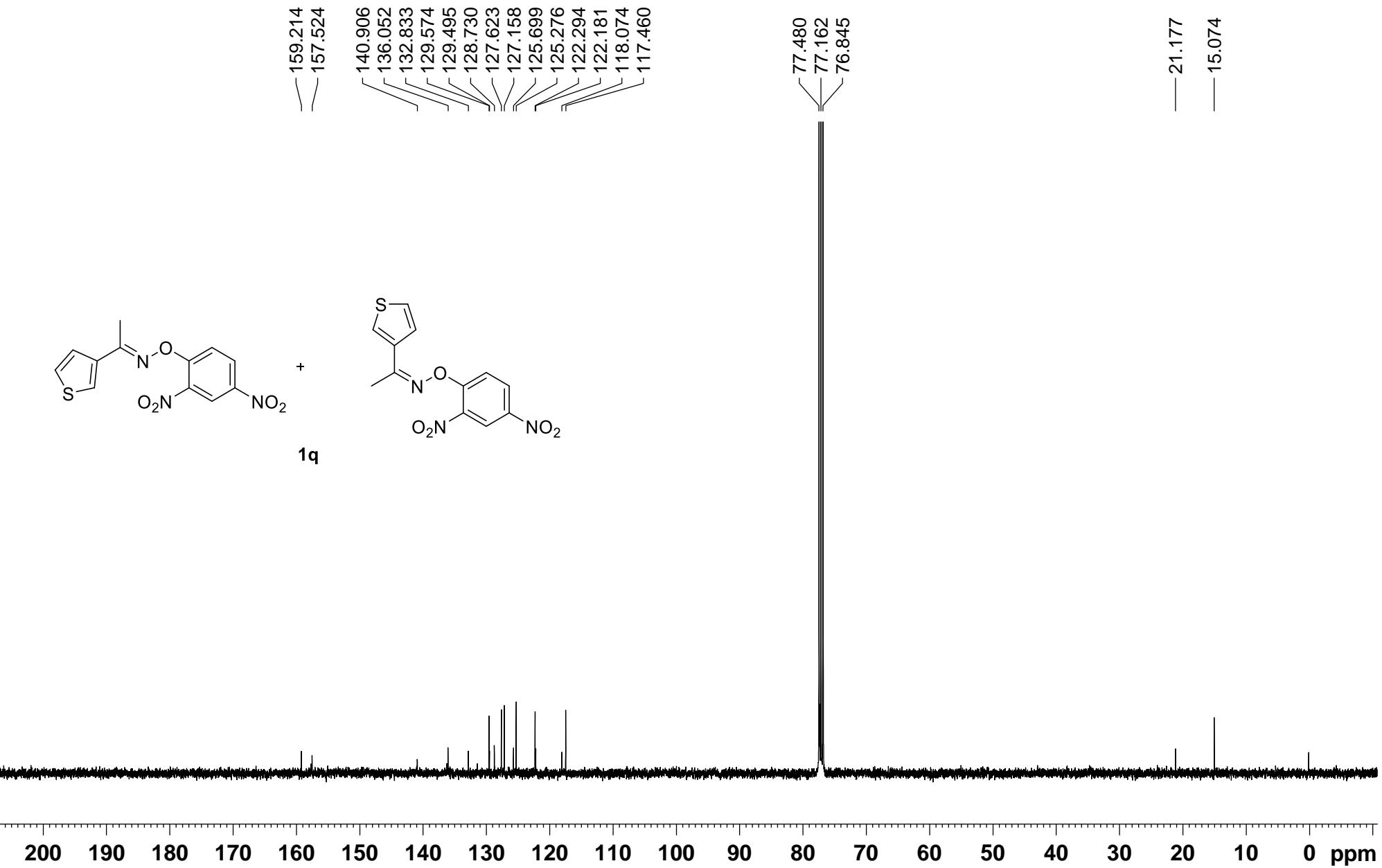


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1q** (CDCl_3 , 100 M).

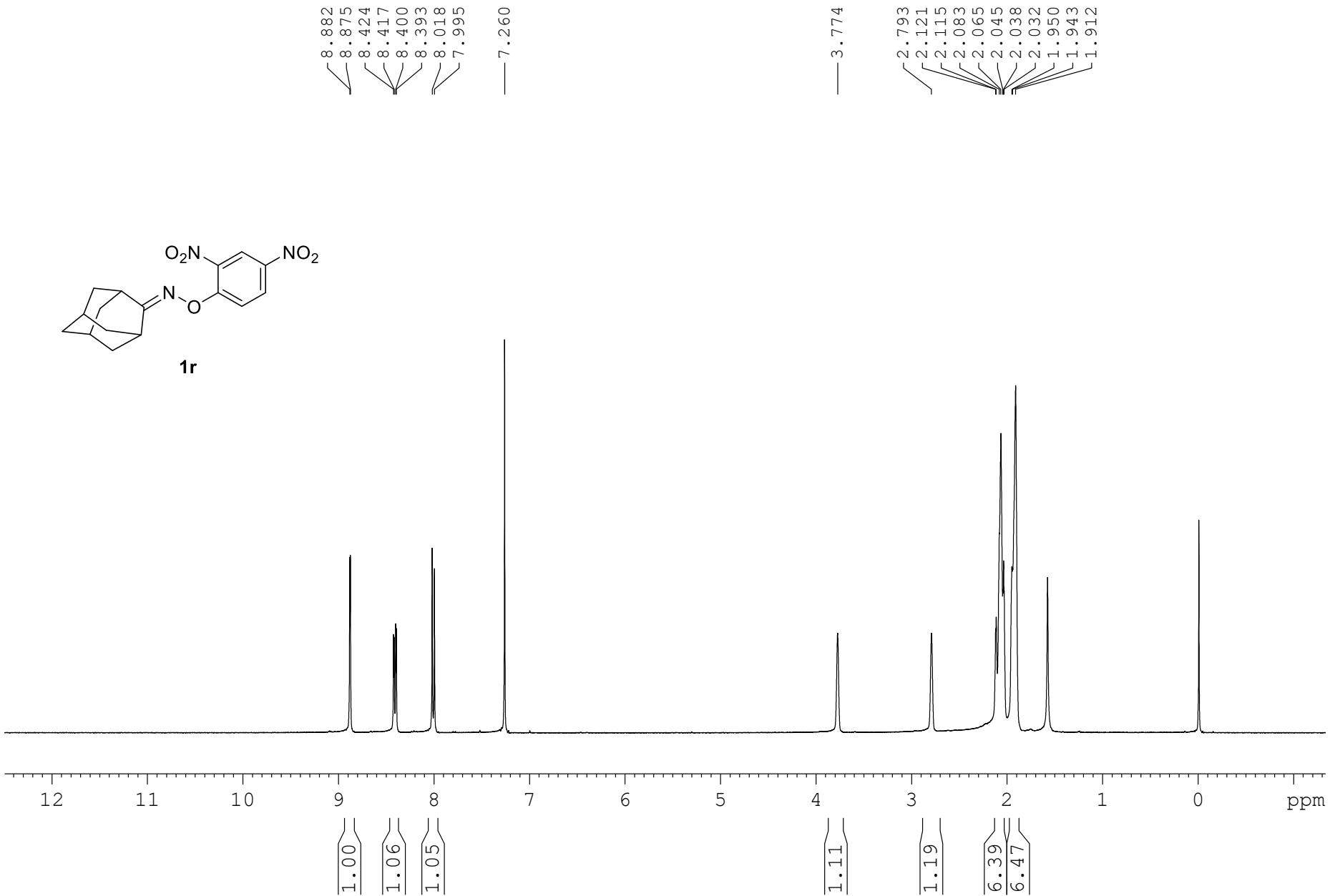


Figure S34. ^1H NMR spectrum of **1r** (CDCl_3 , 400 M).

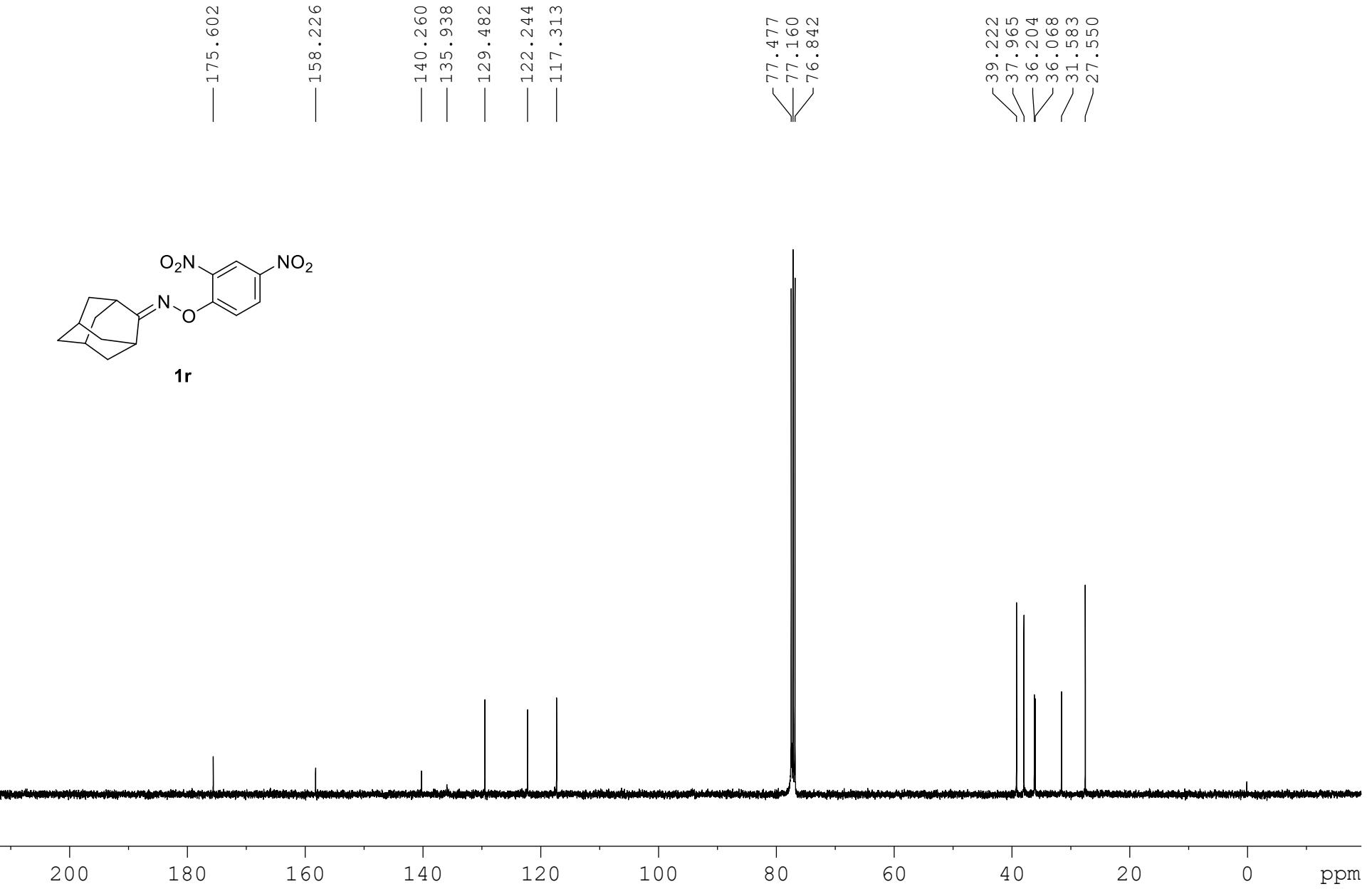


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1r** (CDCl_3 , 100 M).

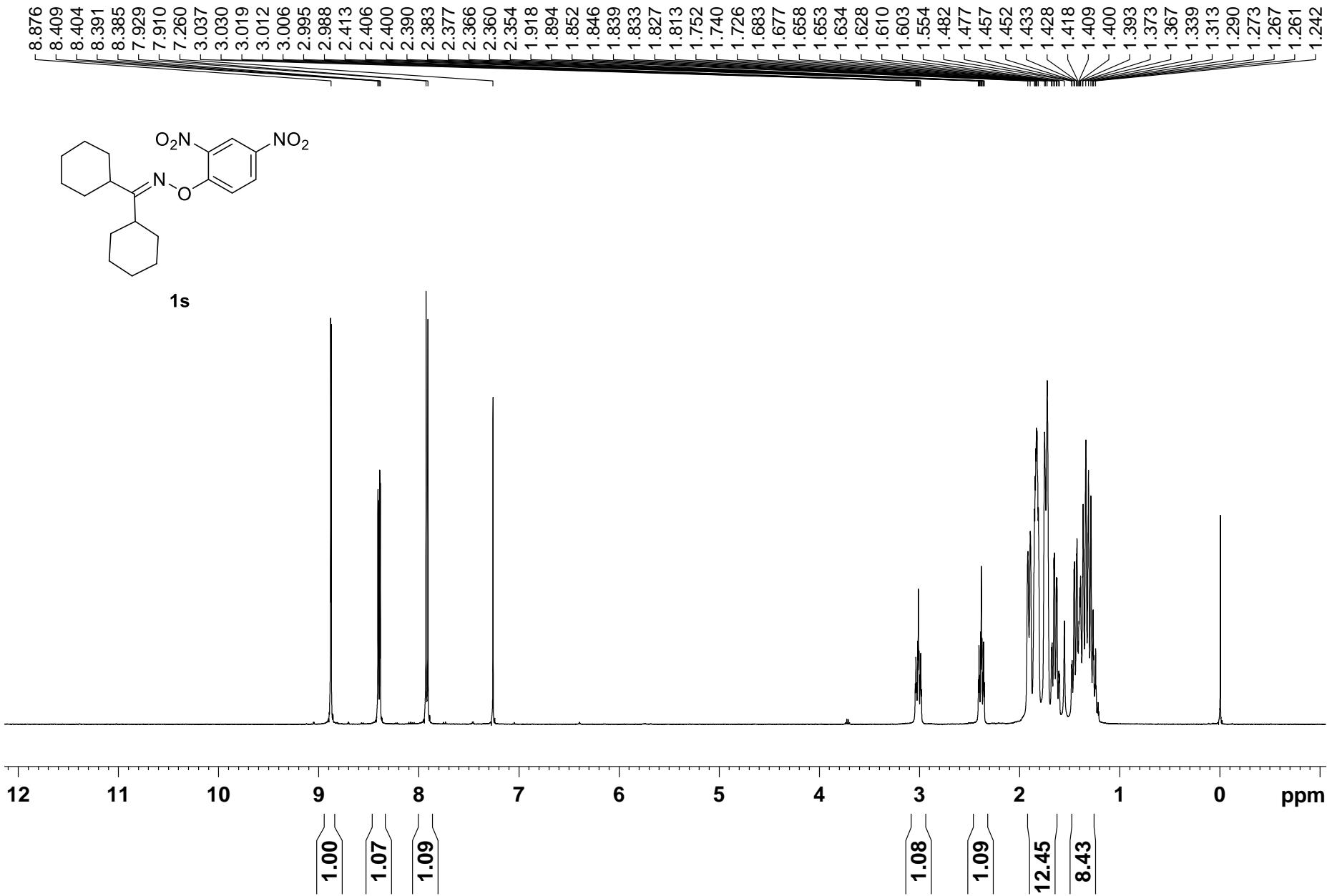


Figure S36. ^1H NMR spectrum of **1s** (CDCl_3 , 500 M).

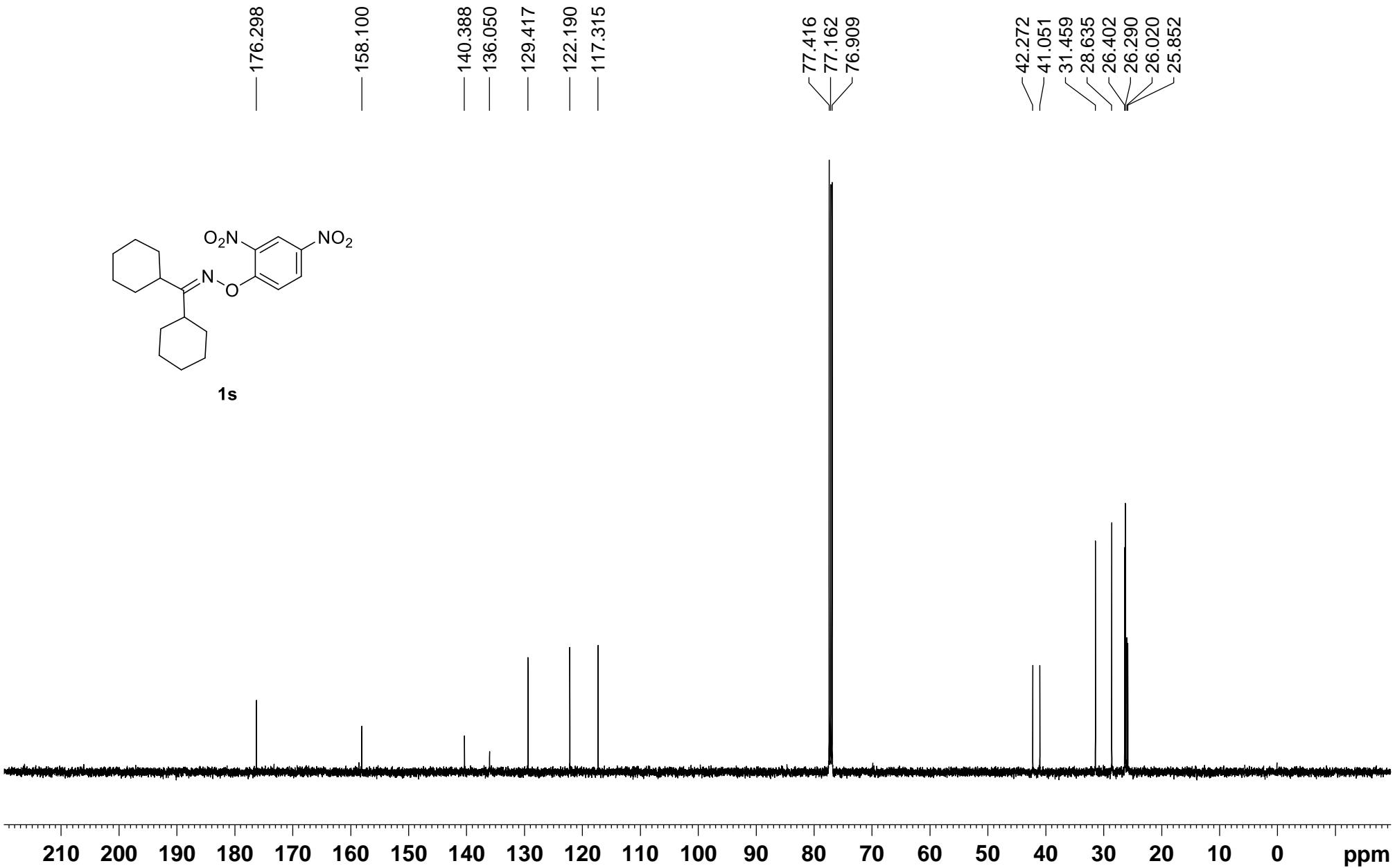


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1s** (CDCl_3 , 125 M).

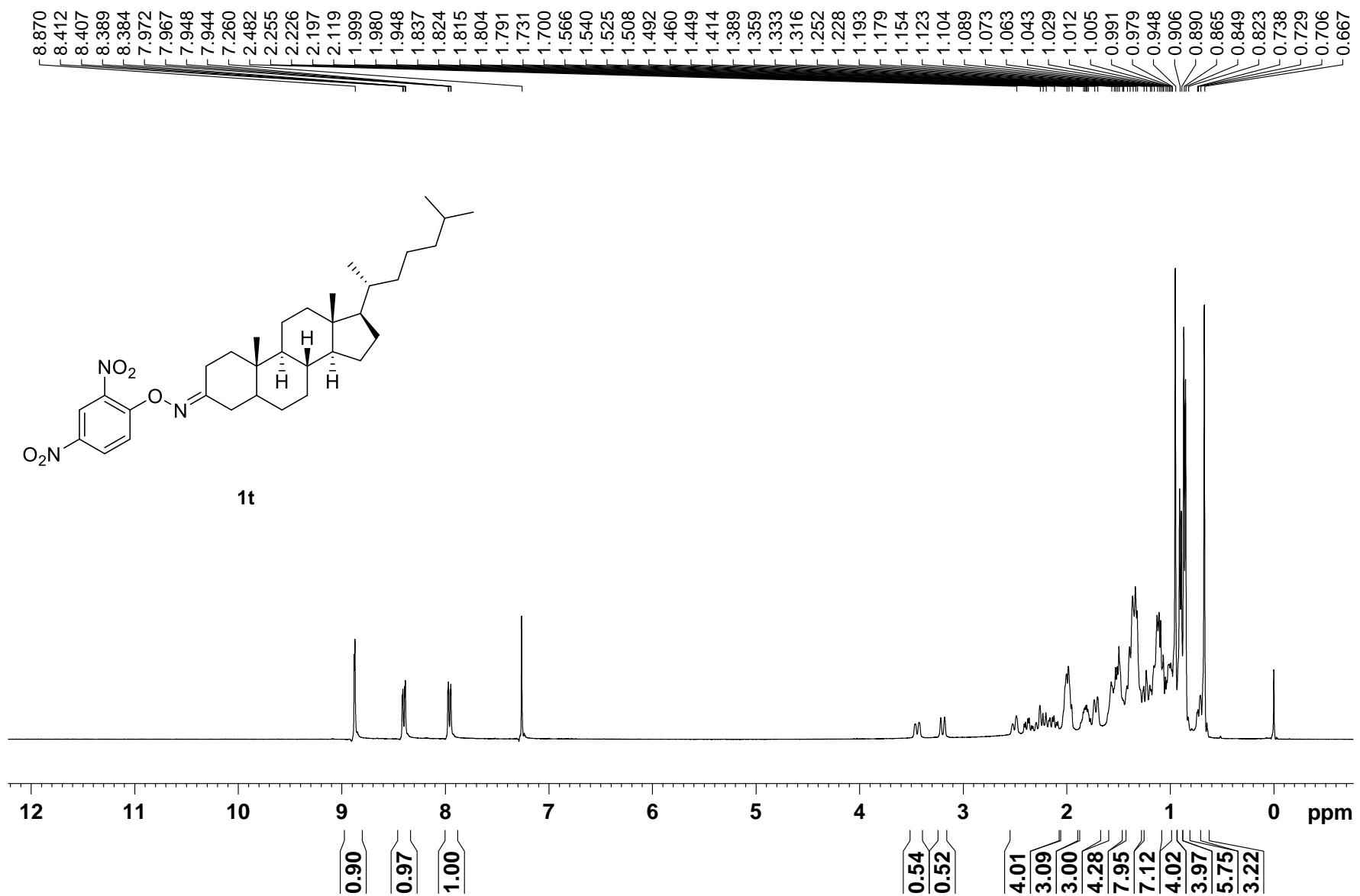


Figure S38. ^1H NMR spectrum of **1t** (CDCl_3 , 400 M).

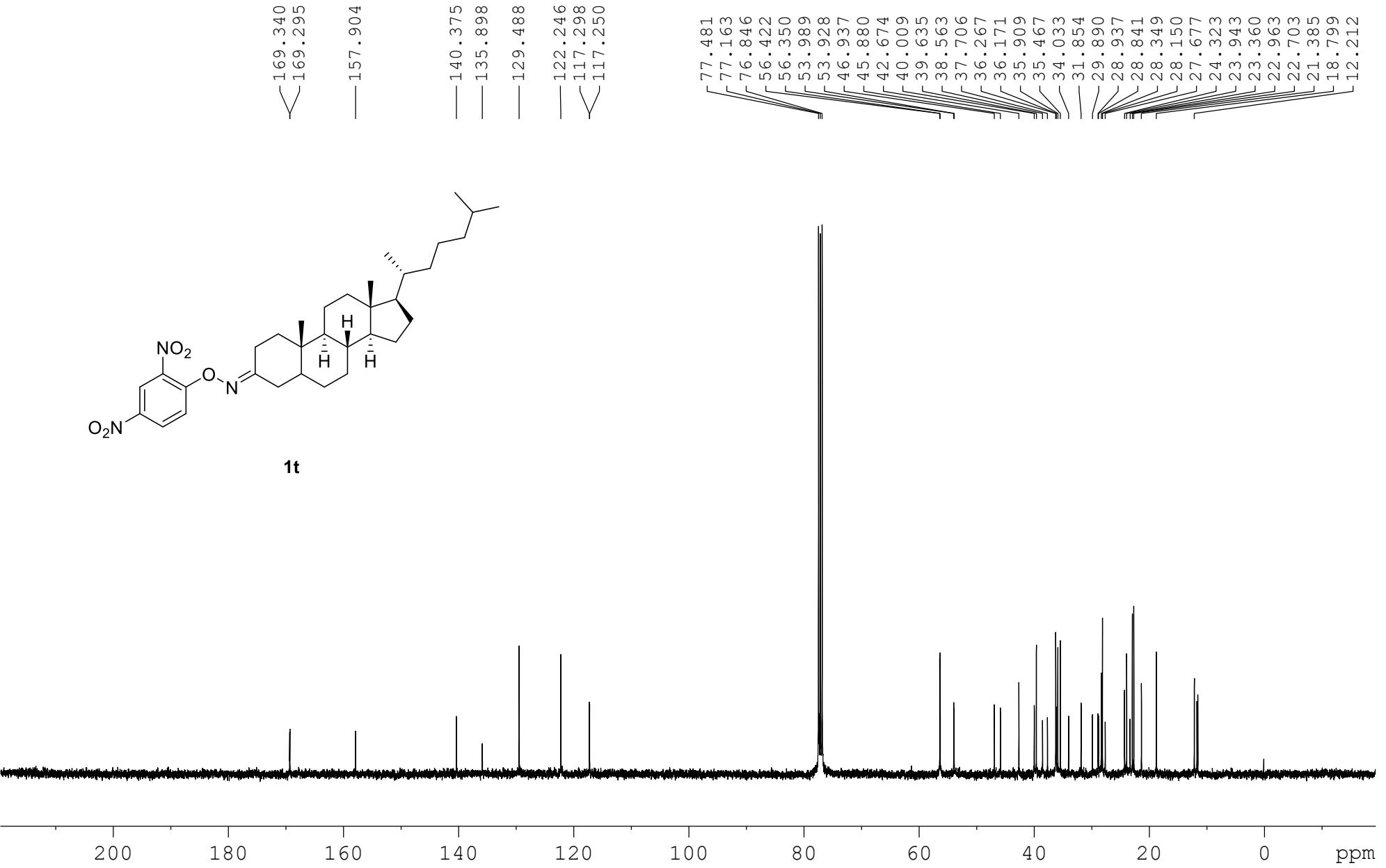


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1t (CDCl_3 , 100 M).**

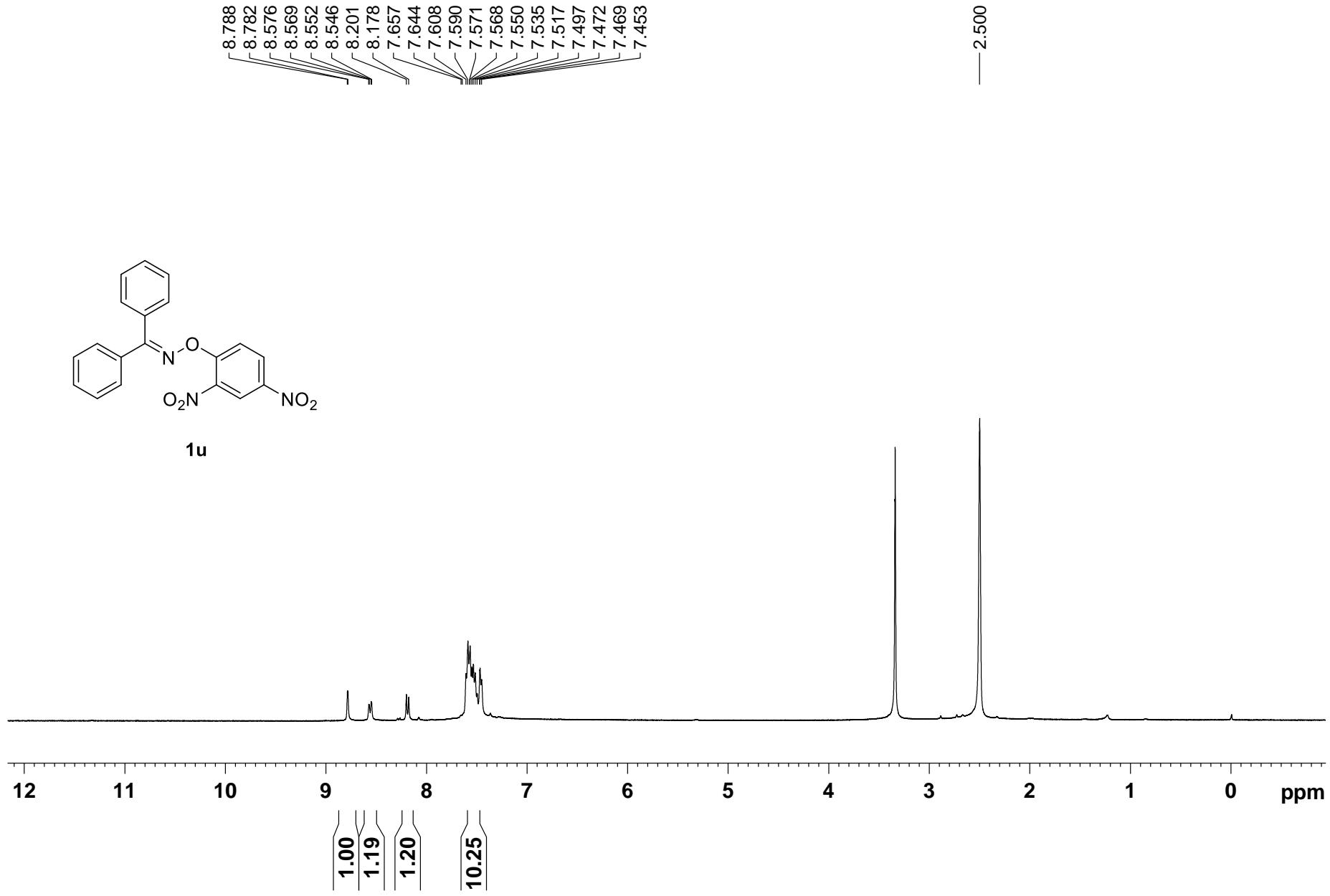


Figure S40. ^1H NMR spectrum of **1u** ($\text{DMSO}-d^6$, 400 M).

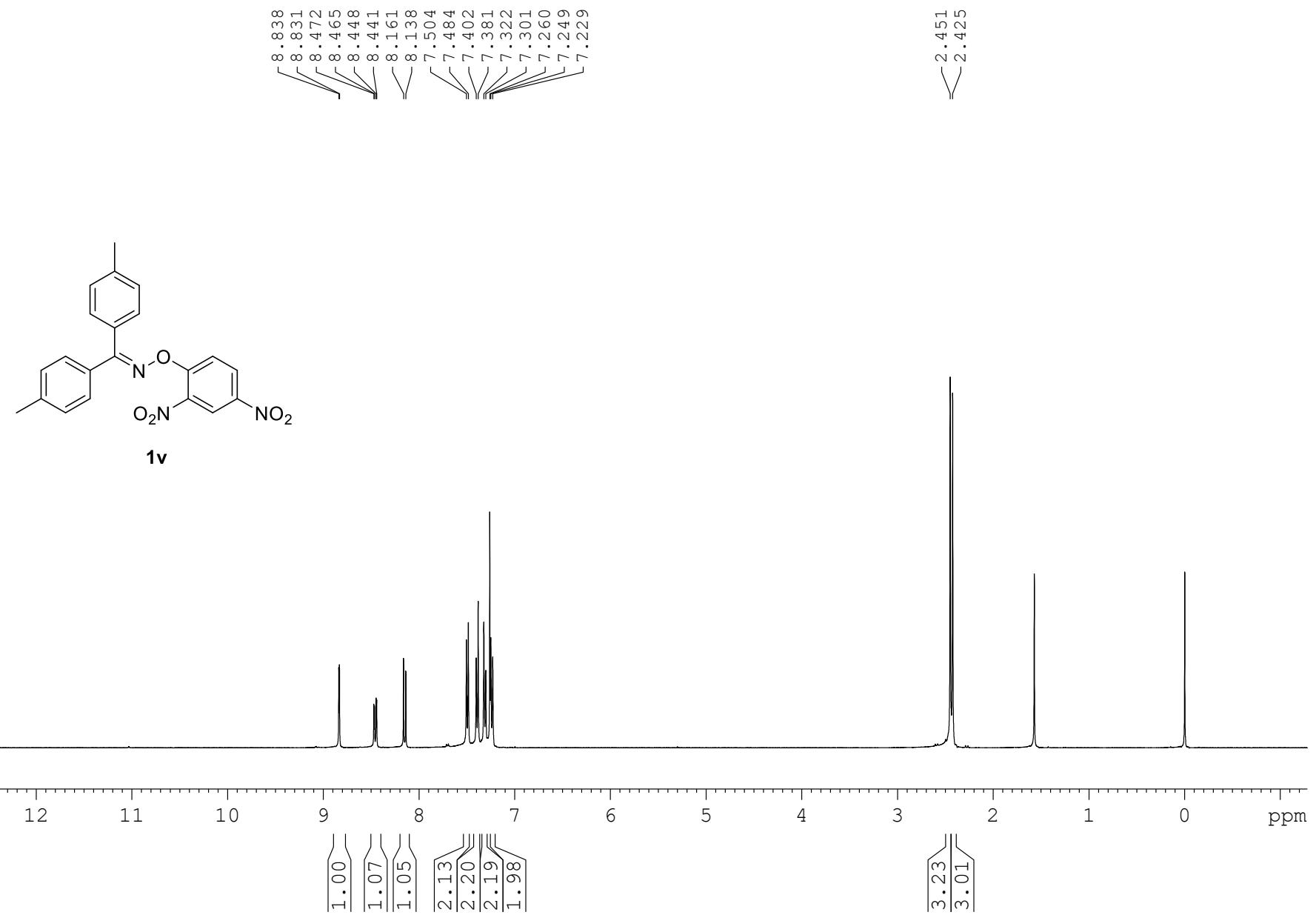


Figure S41. ¹H NMR spectrum of **1v** (CDCl₃, 400 M).

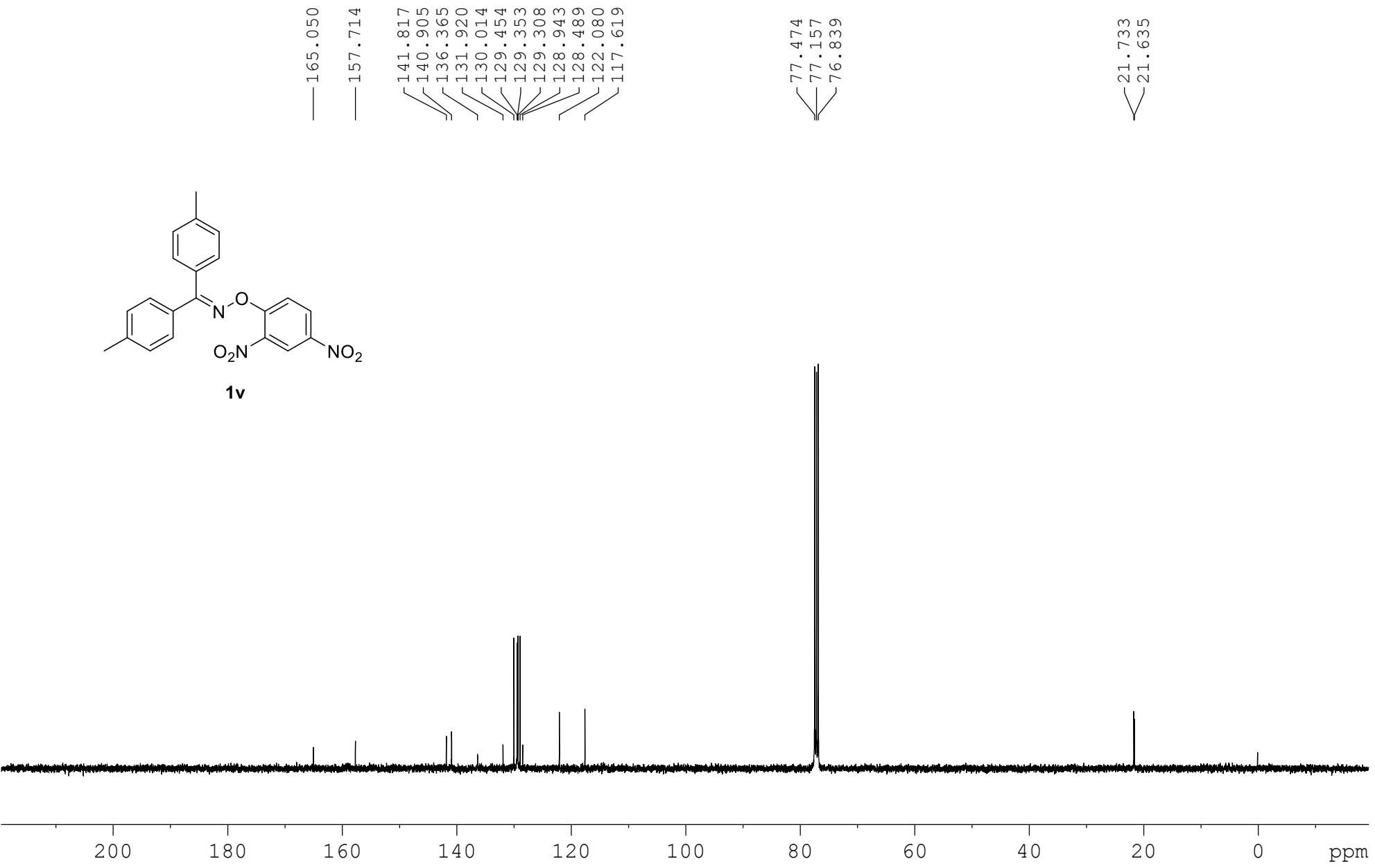


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1v** (CDCl_3 , 100 M).

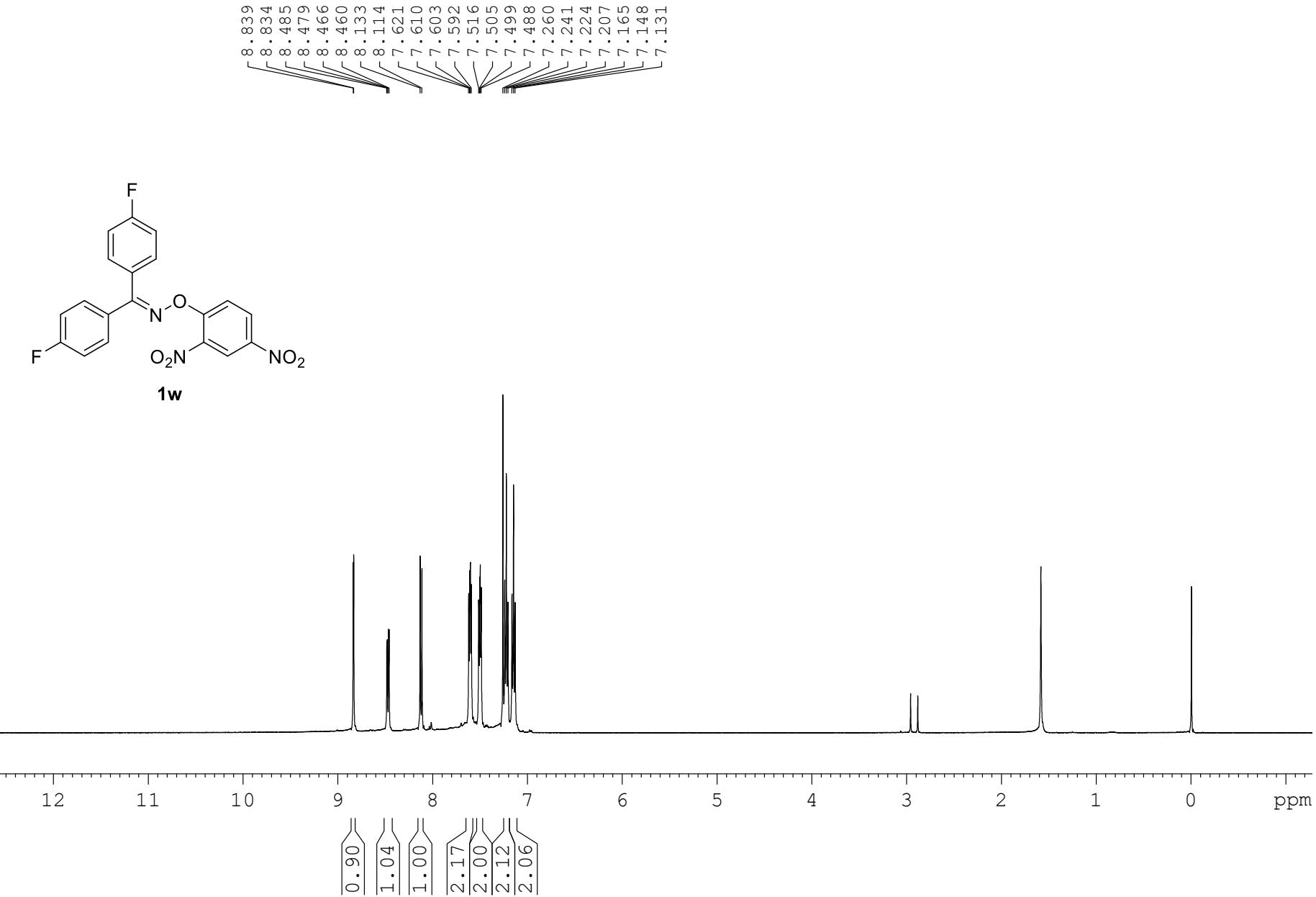


Figure S43. ¹H NMR spectrum of **1w** (CDCl₃, 500 M).

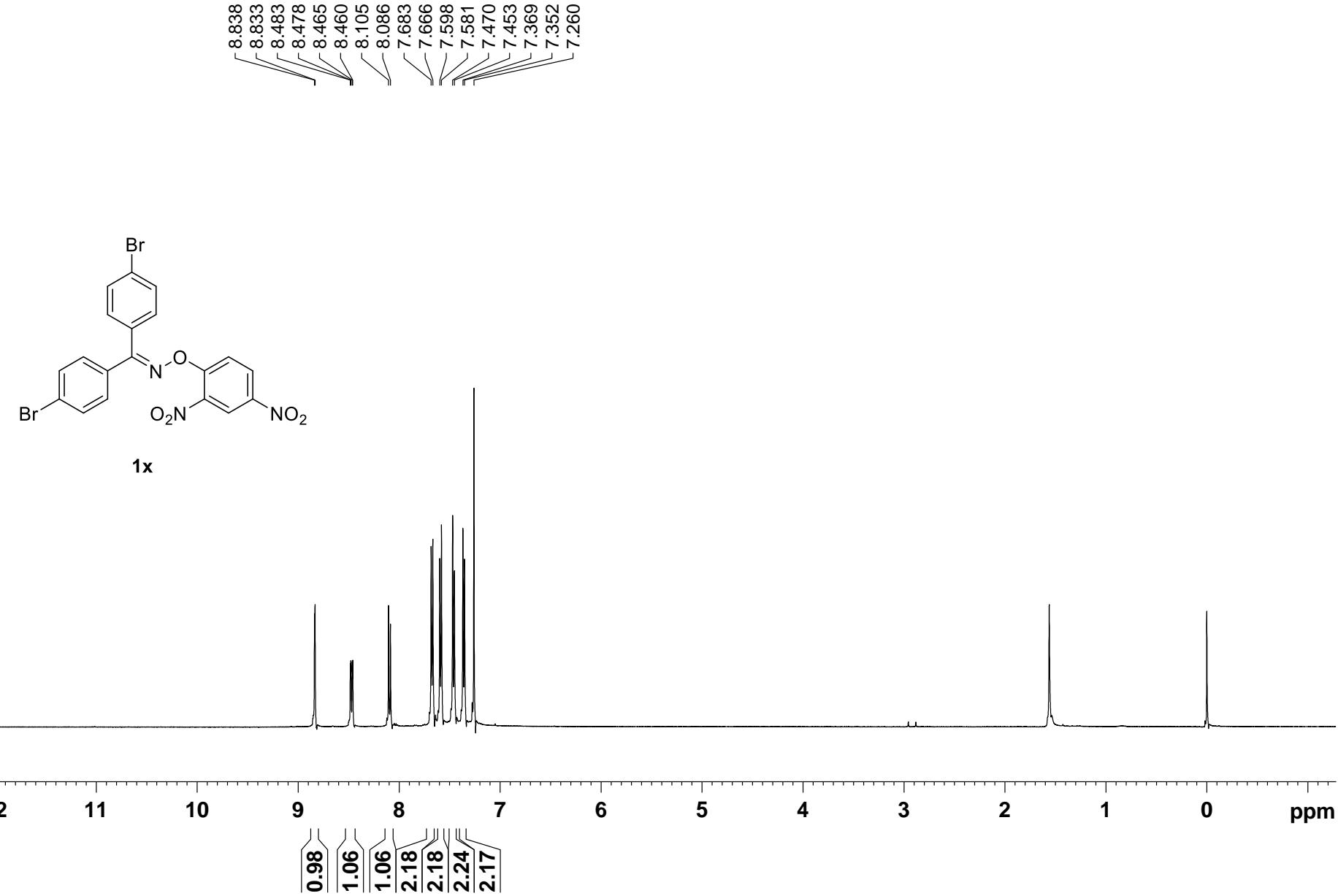


Figure S44. ^1H NMR spectrum of **1x** (CDCl_3 , 500 M).

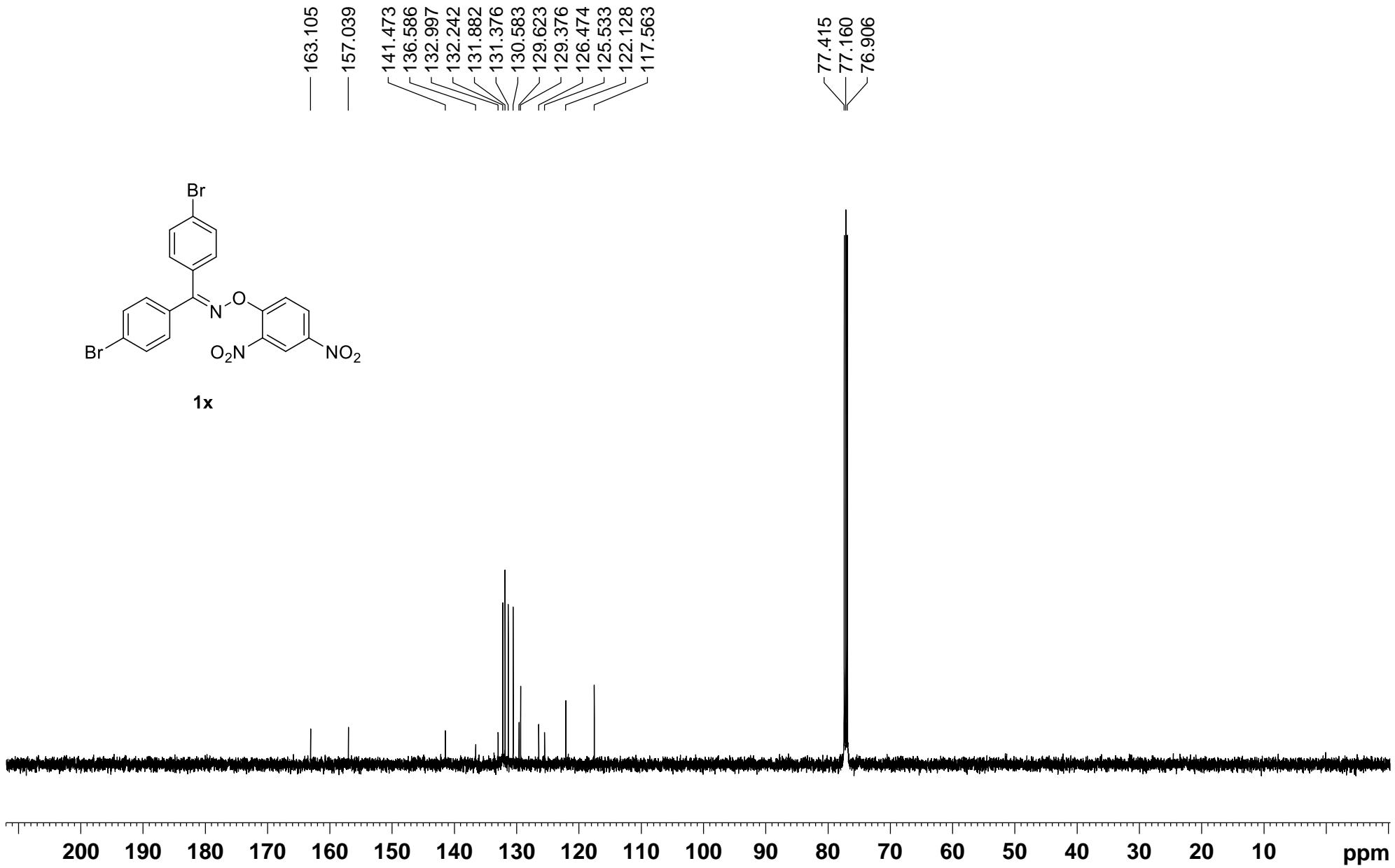
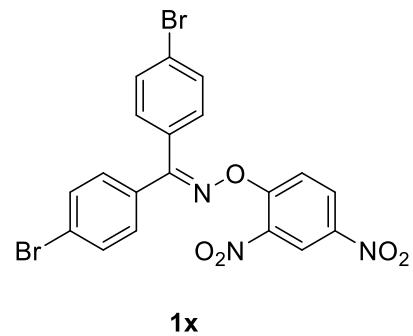


Figure S45. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **1x** (CDCl_3 , 125 M).

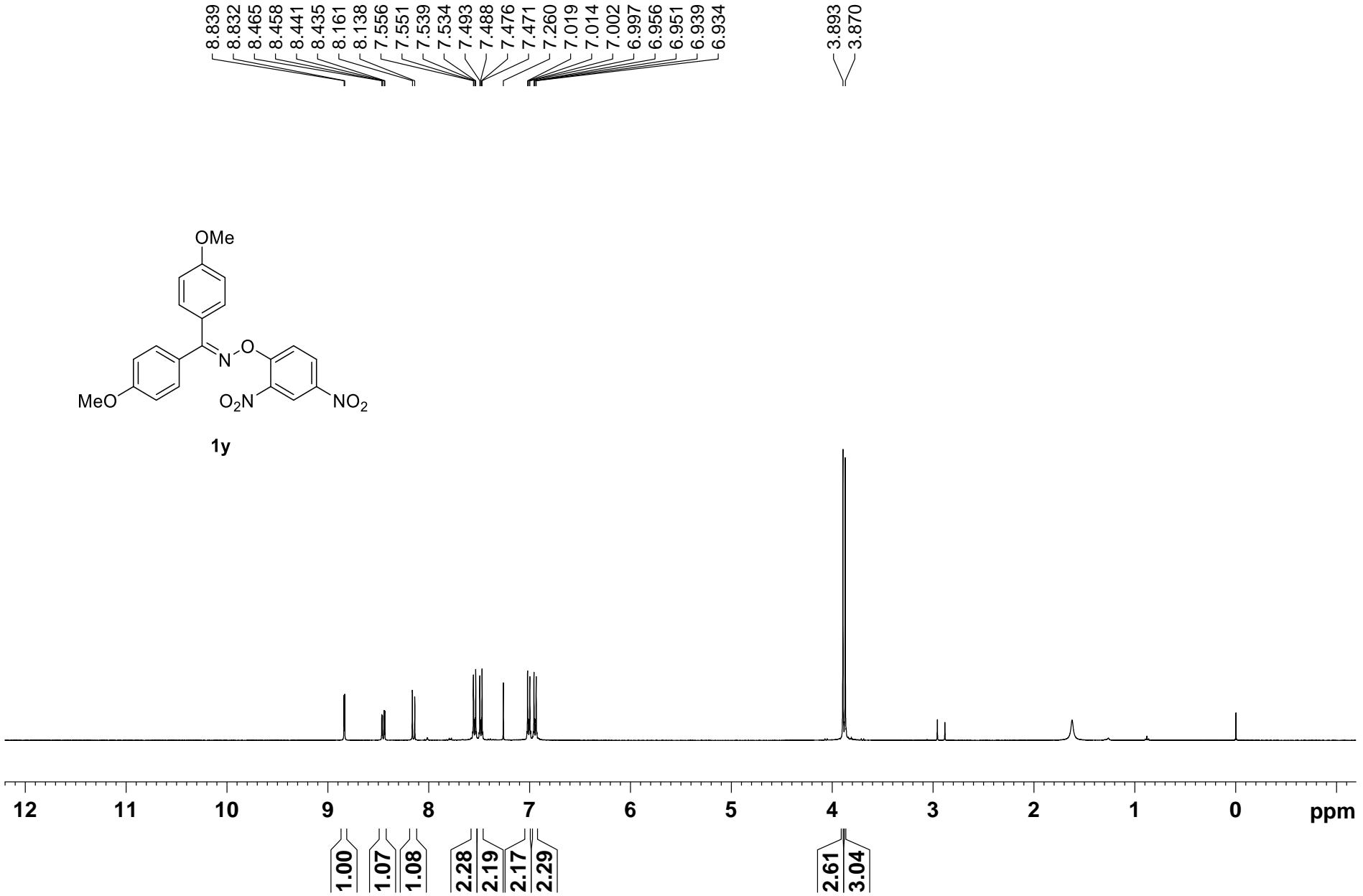


Figure S46. ^1H NMR spectrum of **1y** (CDCl_3 , 500 M).

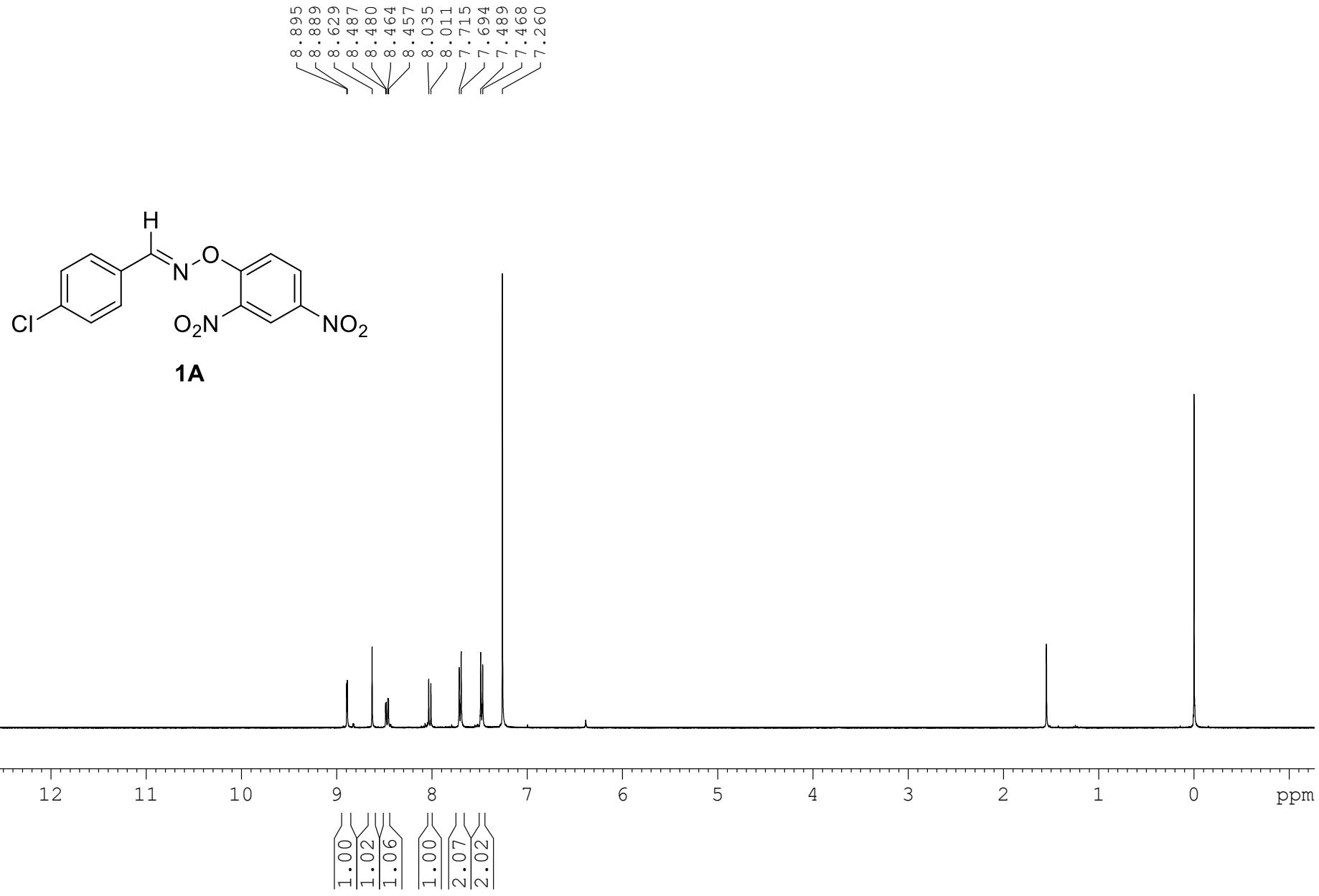


Figure S47. ^1H NMR spectrum of **1A** (CDCl_3 , 400 M).

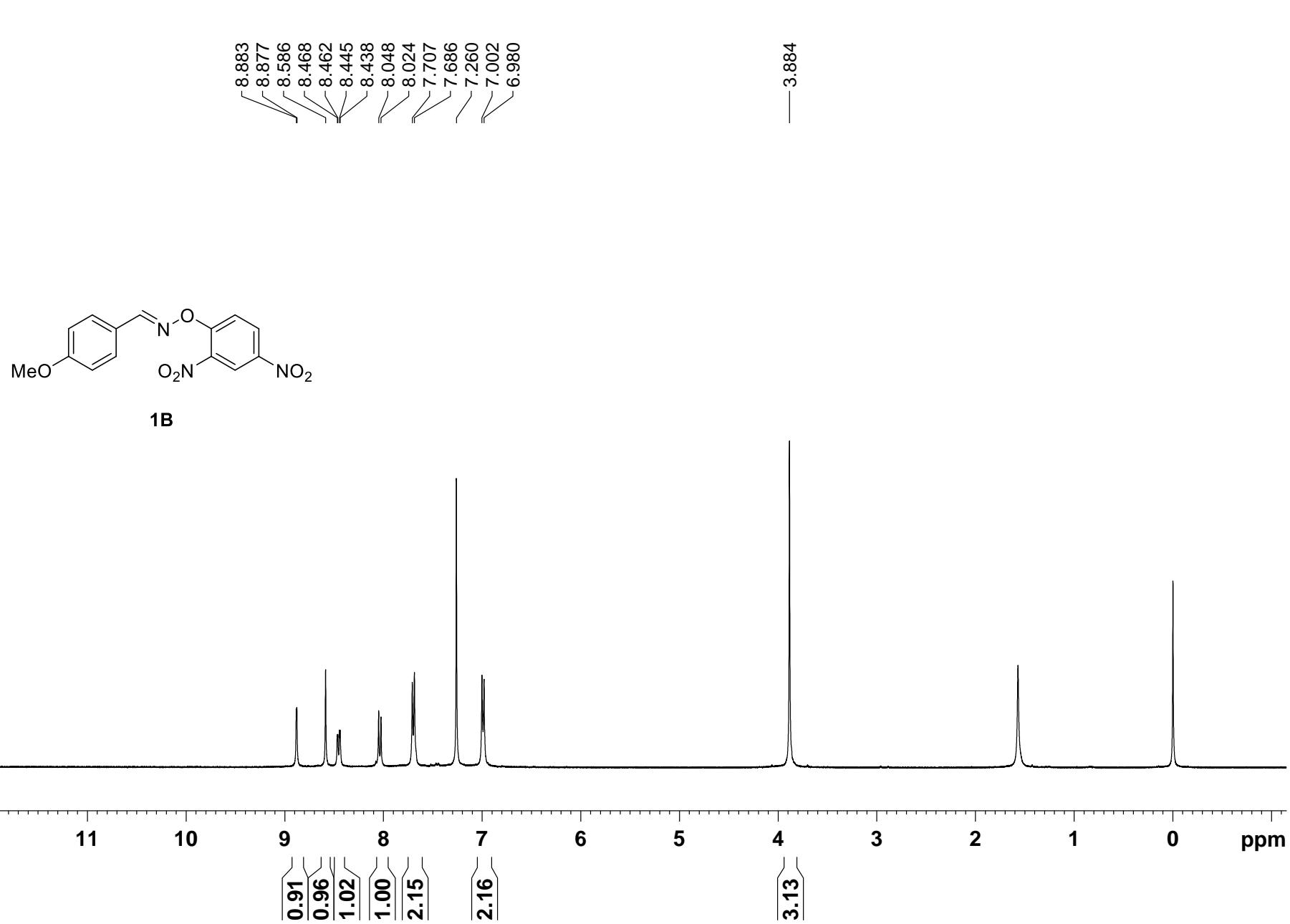


Figure S48. ^1H NMR spectrum of **1B** (CDCl_3 , 400 M).

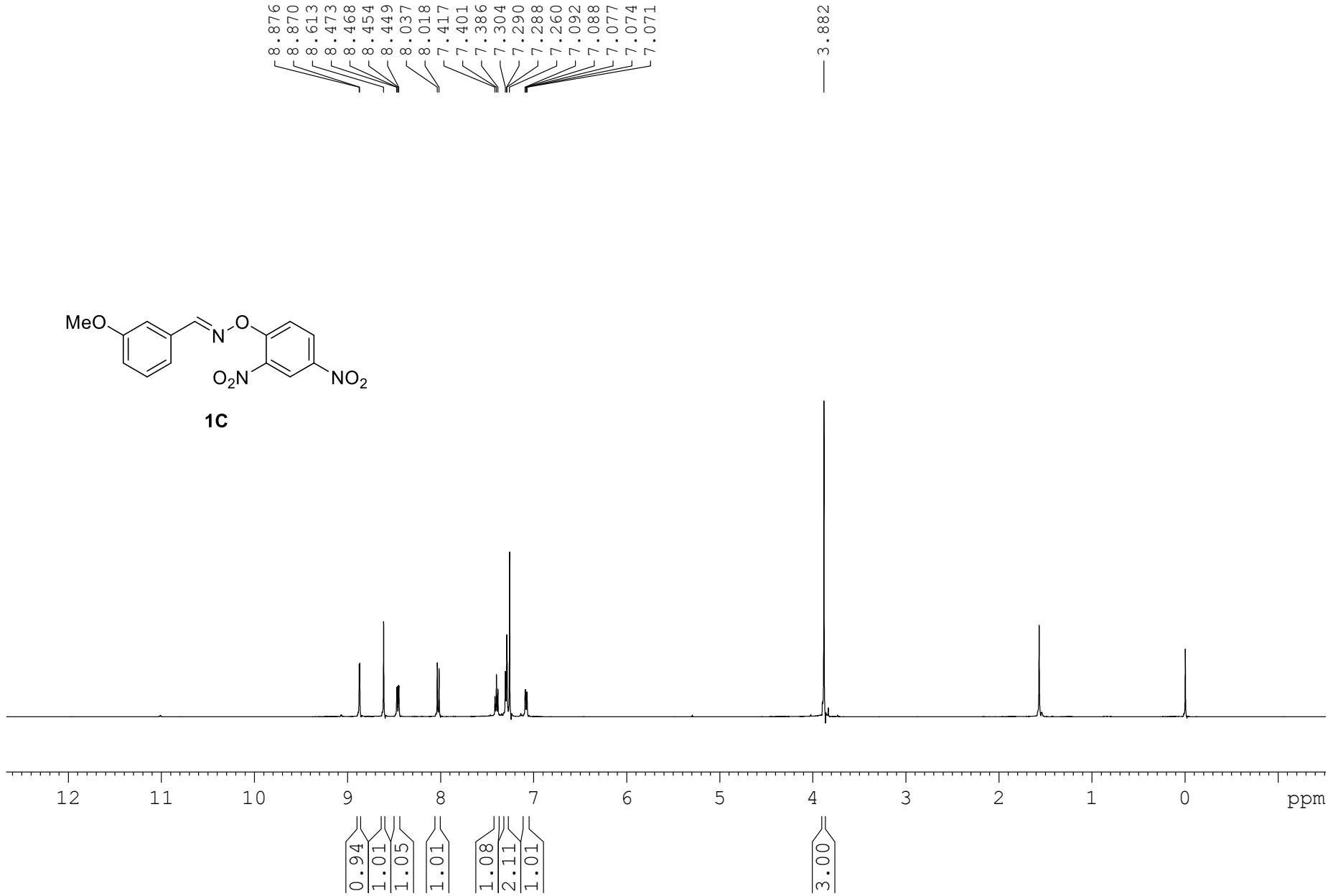


Figure S49. ^1H NMR spectrum of **1C** (CDCl_3 , 500 M).

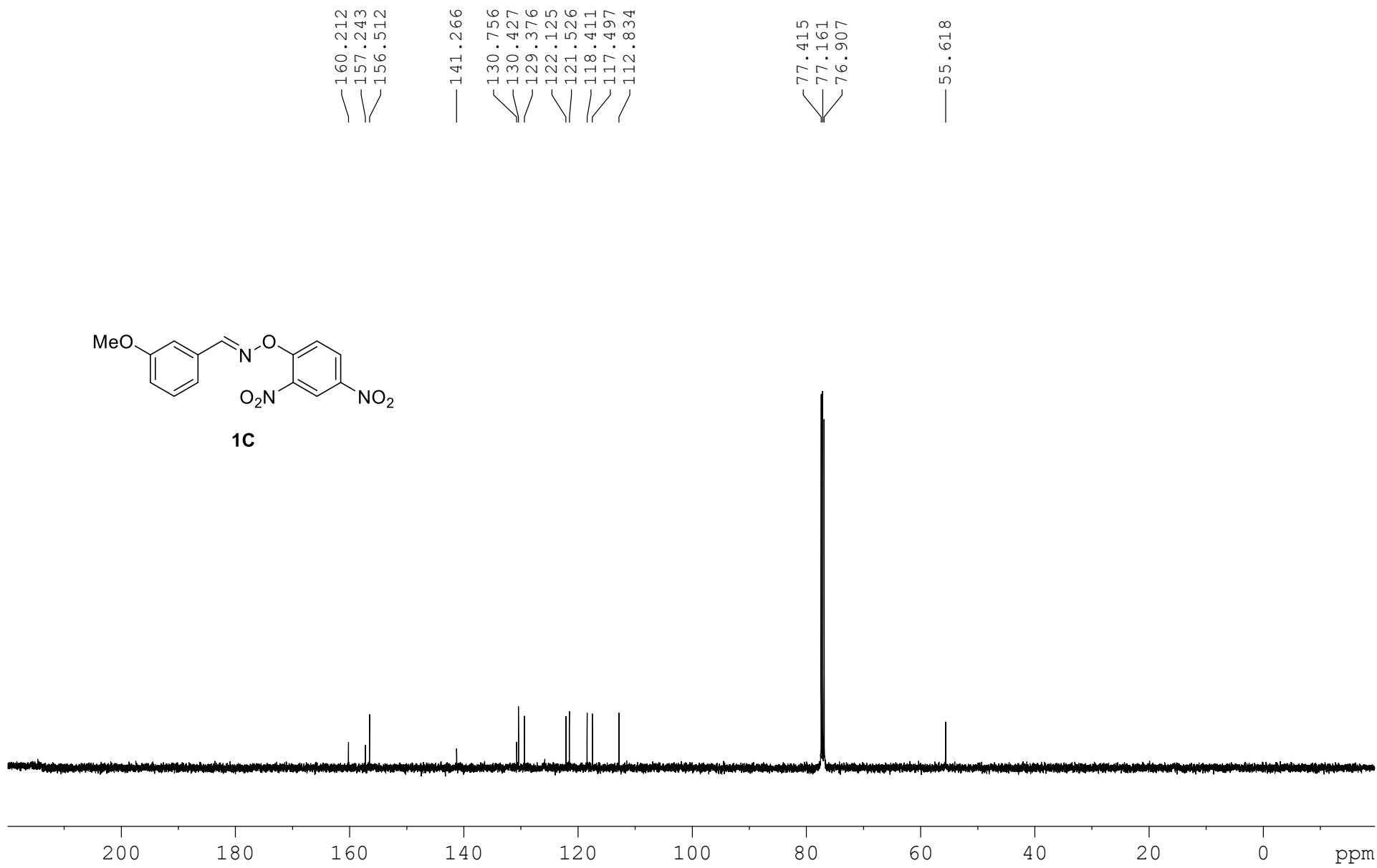
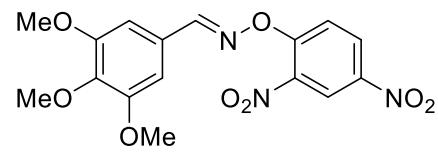


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1C** (CDCl_3 , 125 M).



Figure S51. ¹H NMR spectrum of **1D** (CDCl₃, 400 M).



1D

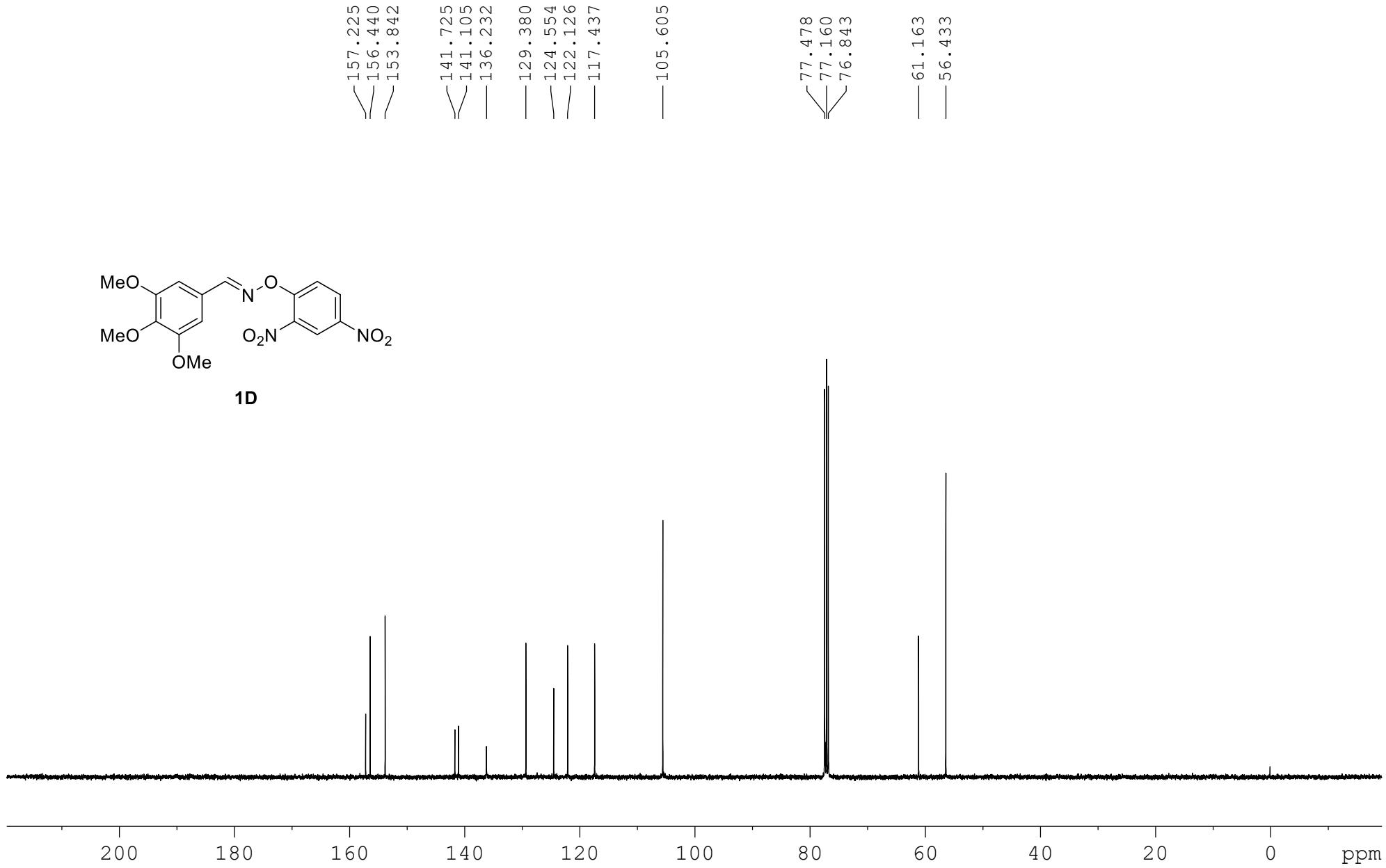


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1D** (CDCl_3 , 100 M).

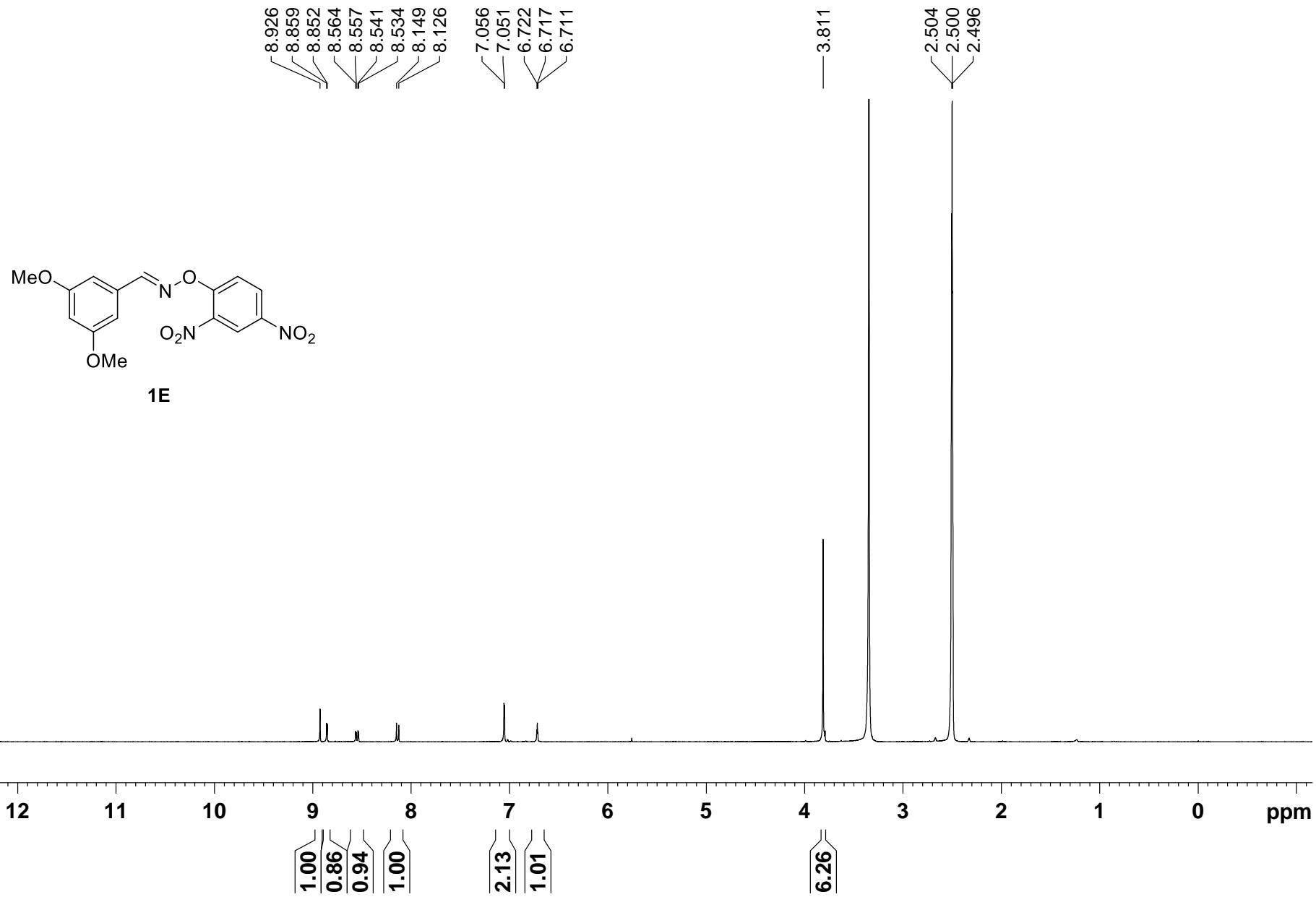


Figure S53. ^1H NMR spectrum of **1E** ($\text{DMSO}-d^6$, 500 M).

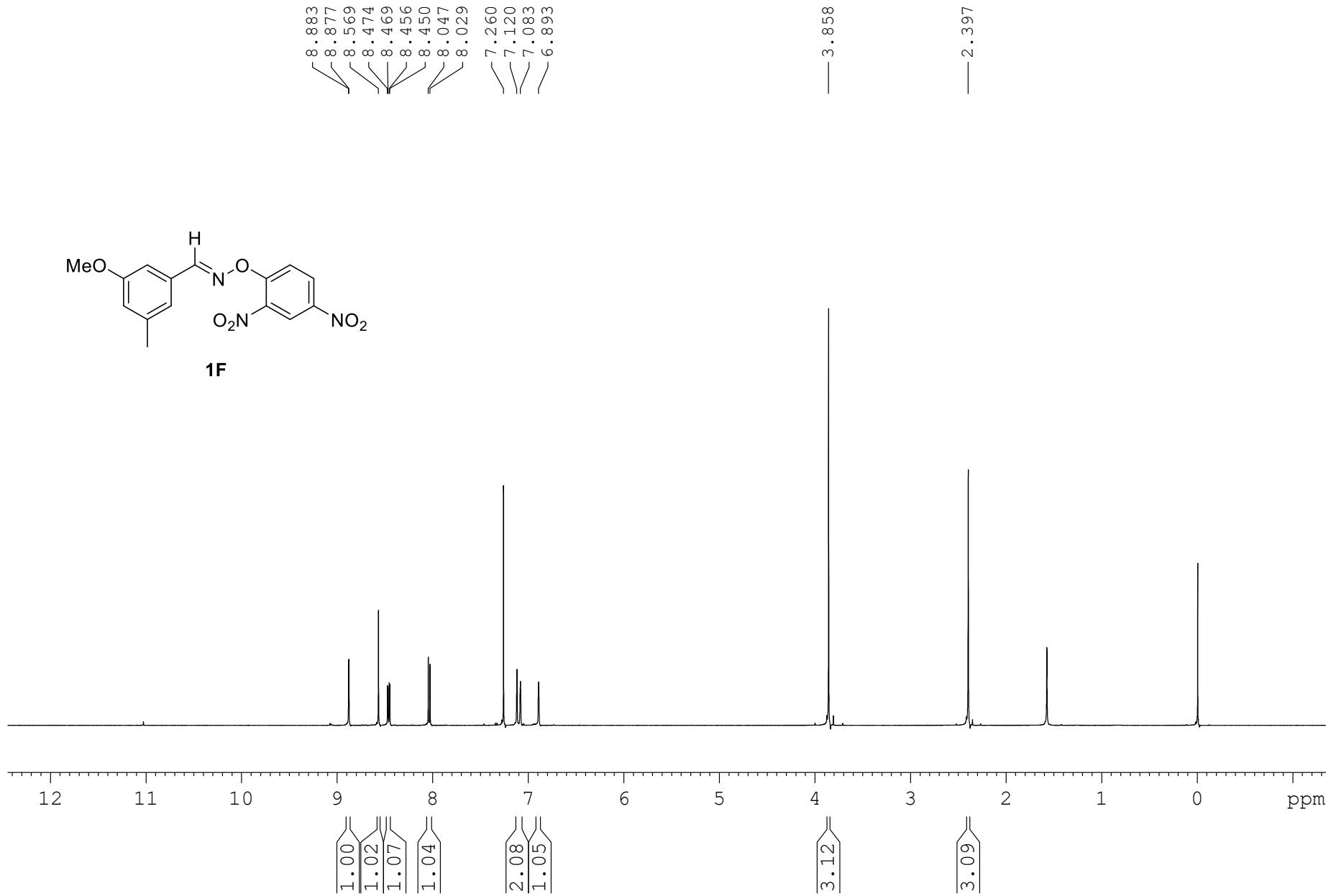
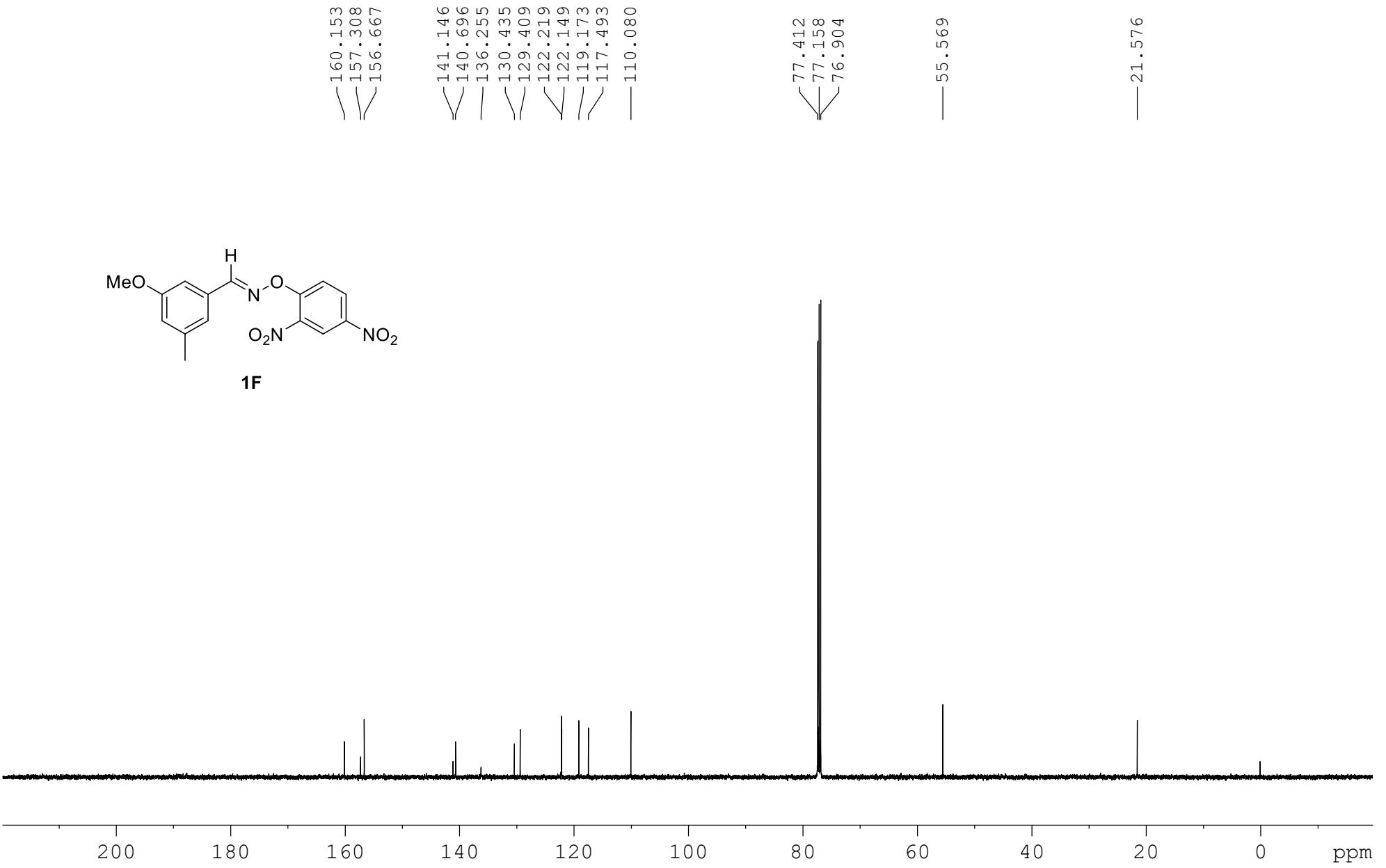
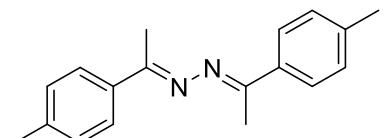


Figure S54. ^1H NMR spectrum of **1F** (CDCl_3 , 500 M).





2a

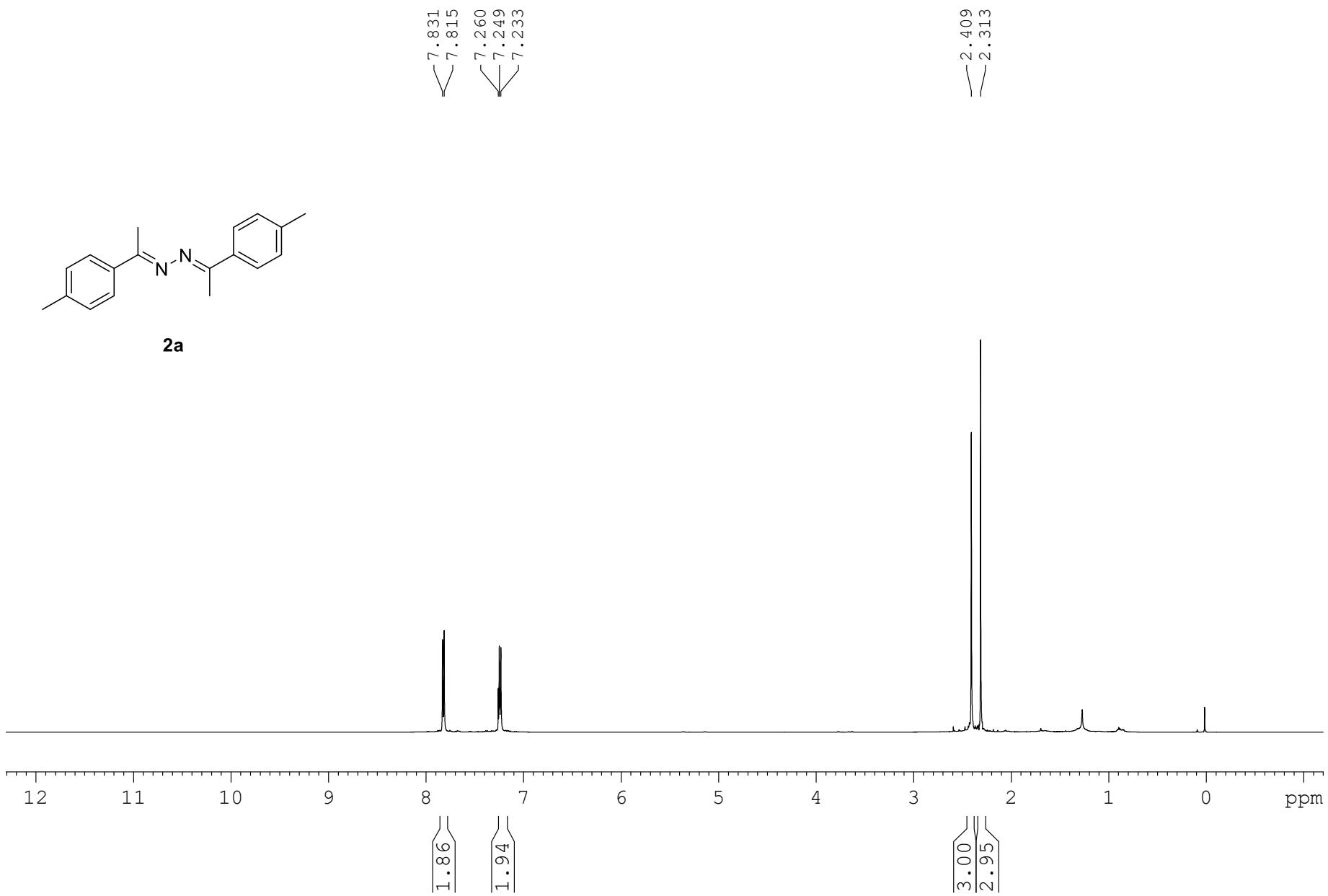


Figure S56. ${}^1\text{H}$ NMR spectrum of **2a** (CDCl_3 , 500 M).

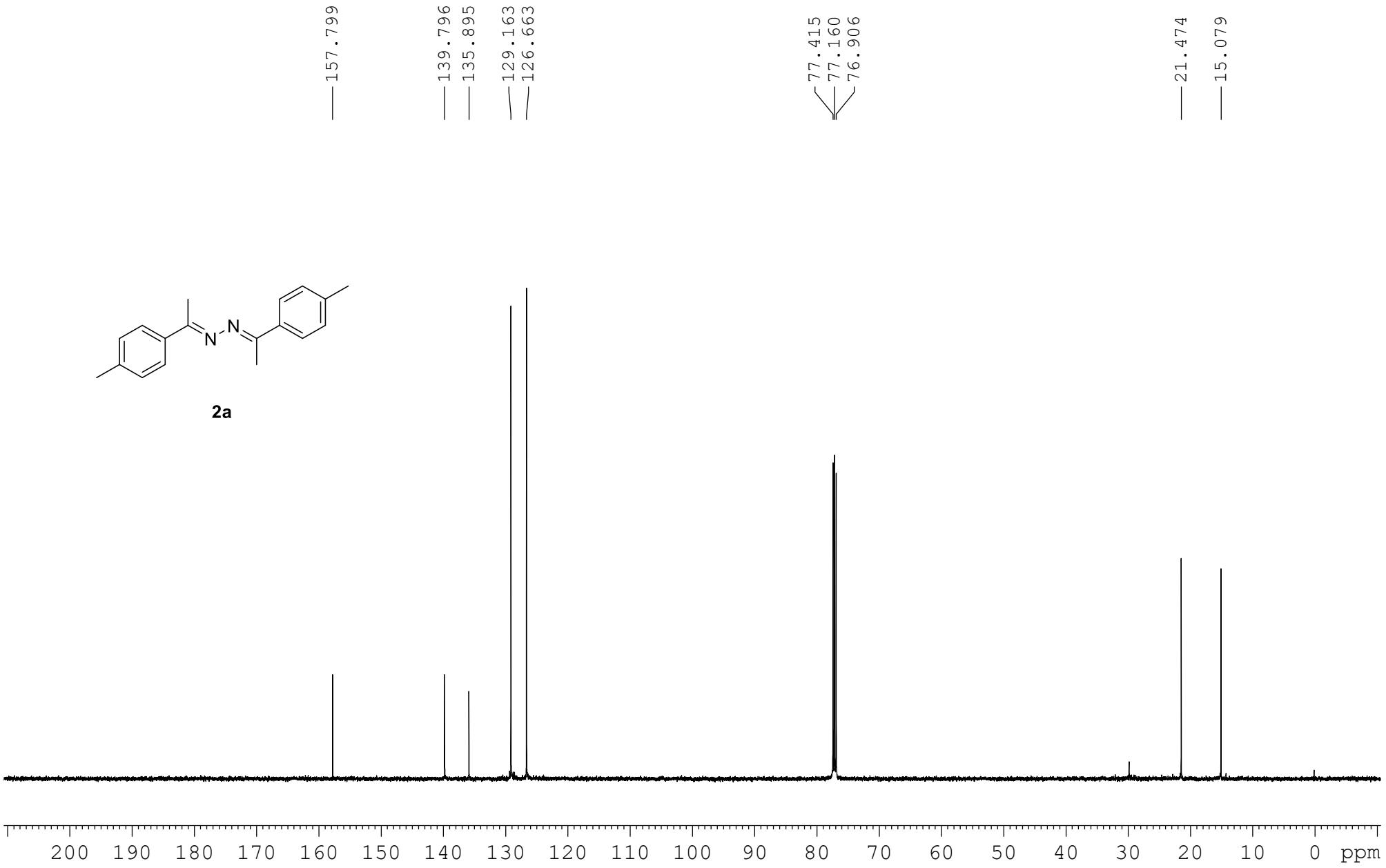
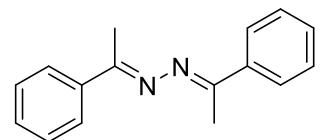


Figure S57. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** (CDCl_3 , 125 M).



2b

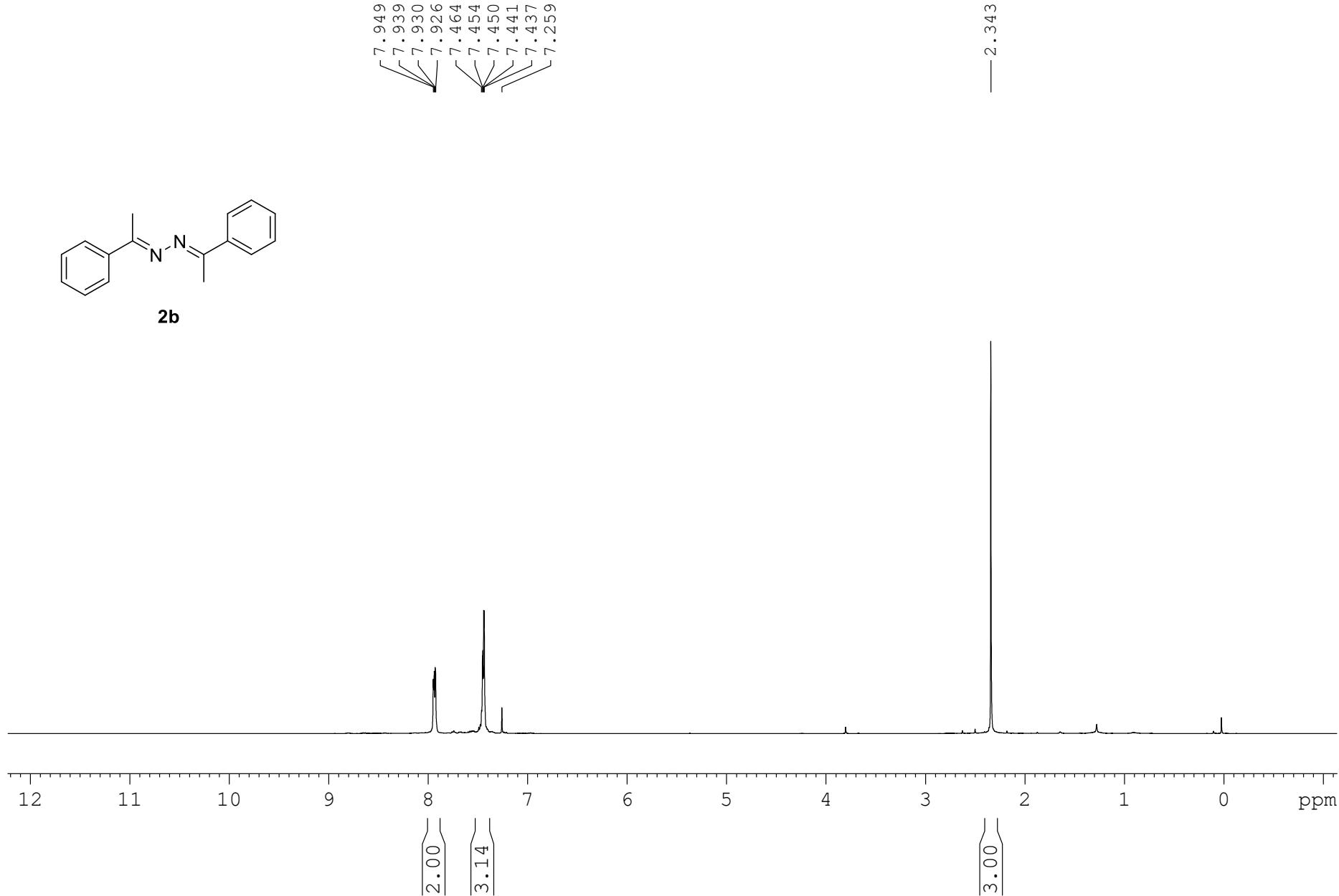


Figure S58. ¹H NMR spectrum of **2b** (CDCl_3 , 400 M).

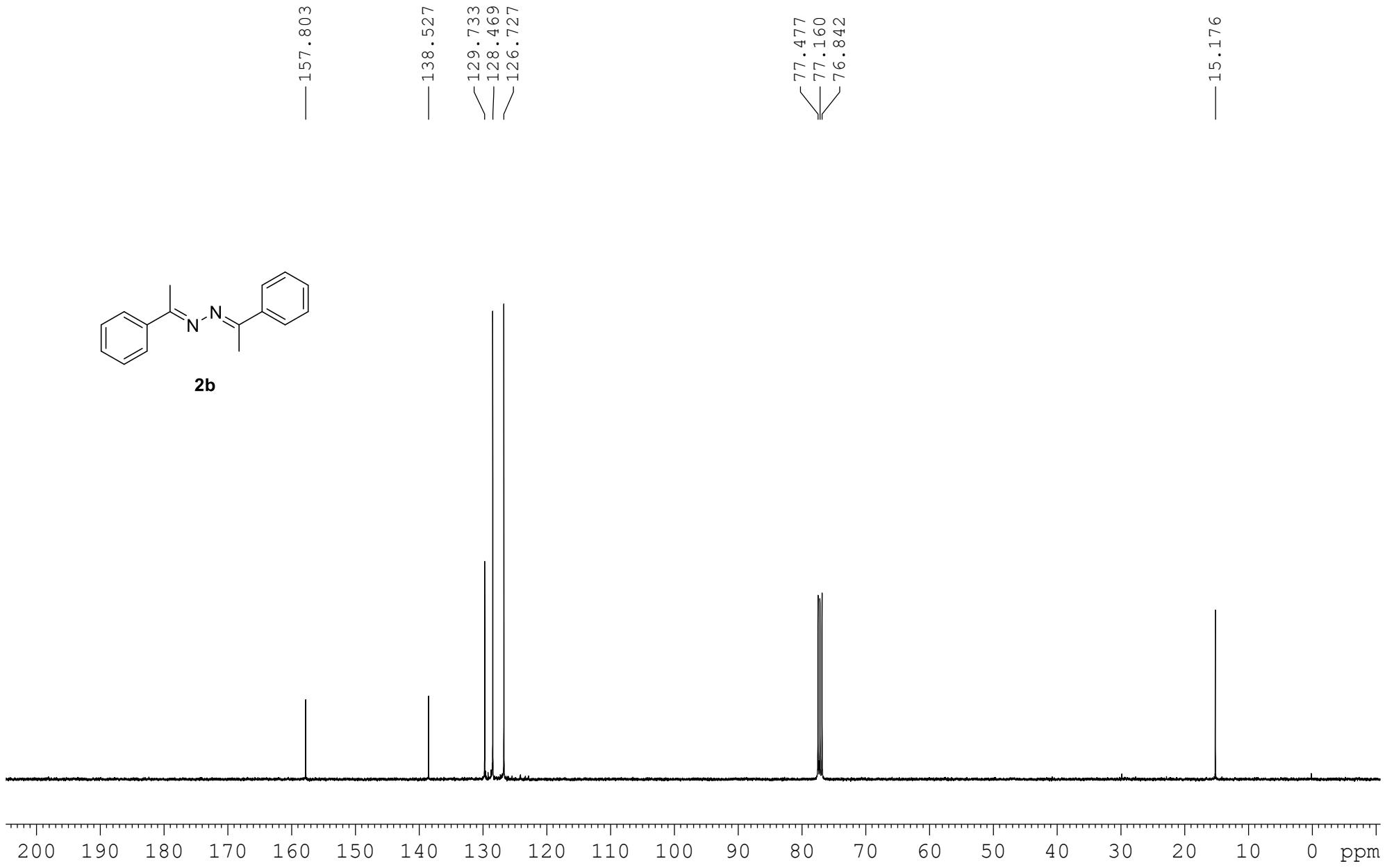


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b** (CDCl_3 , 100 M).

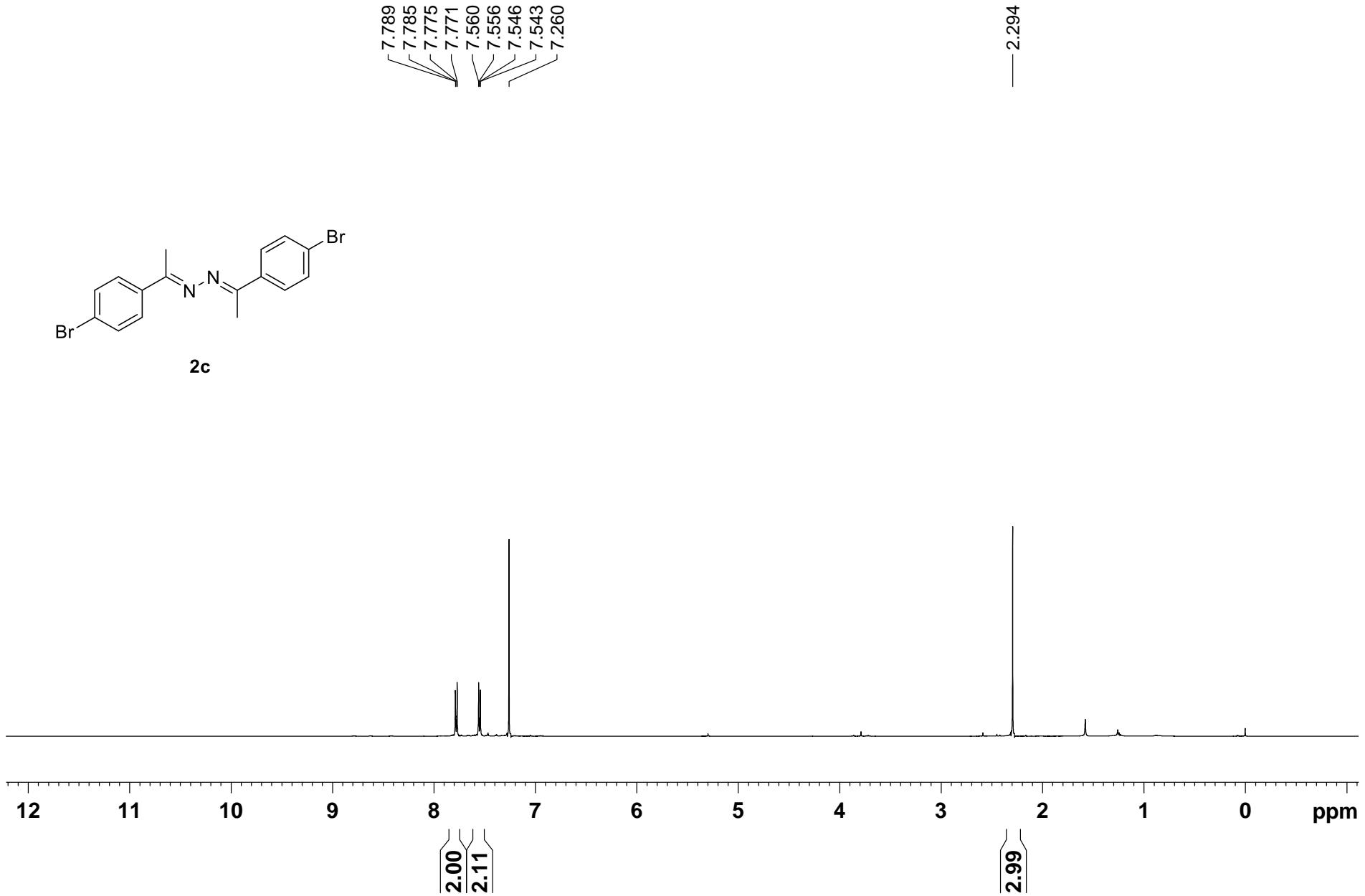
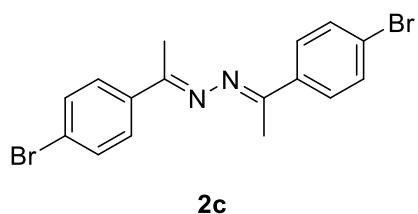


Figure S60. ^1H NMR spectrum of **2c** (CDCl_3 , 400 M).

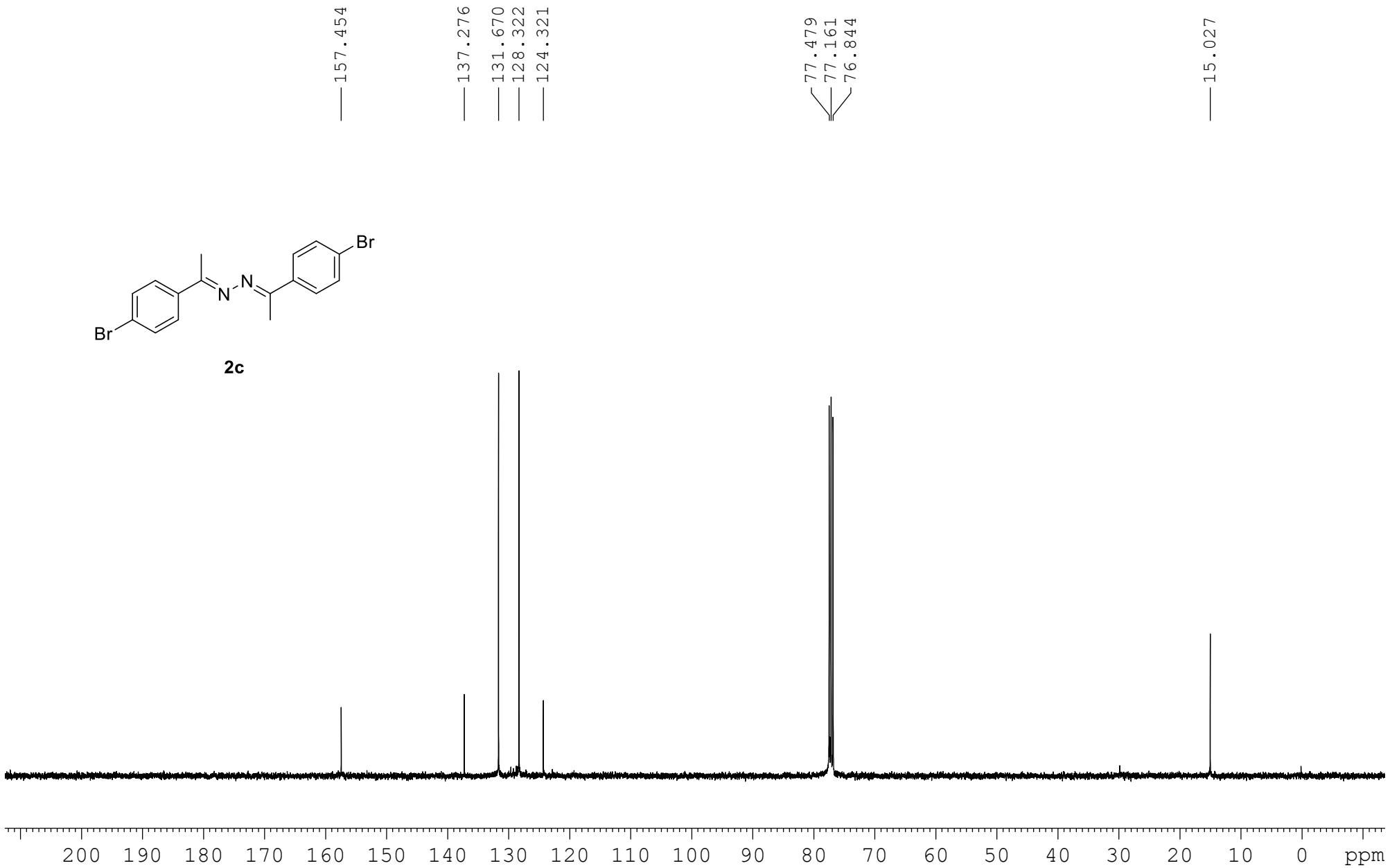


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2c** (CDCl_3 , 100 M).

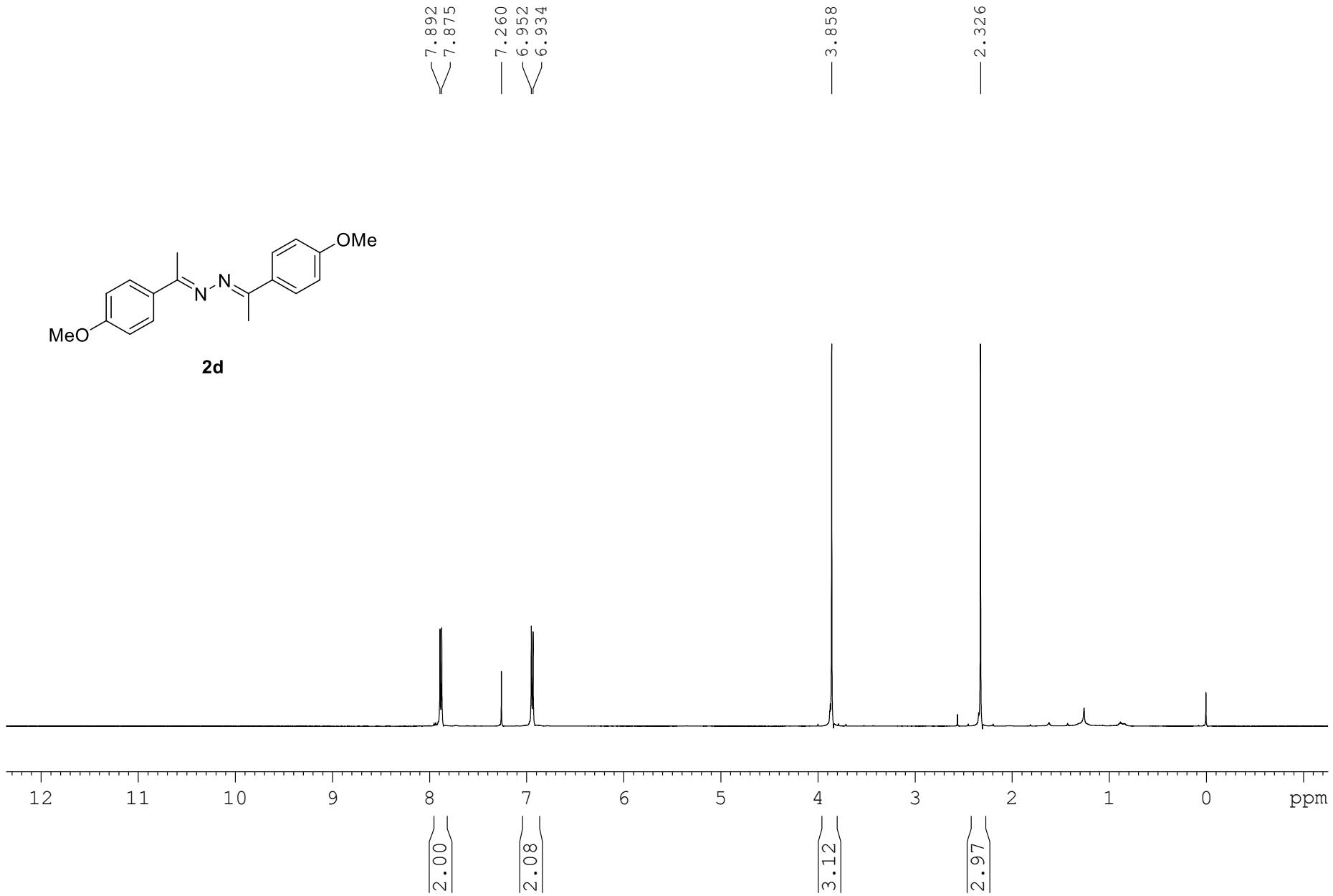
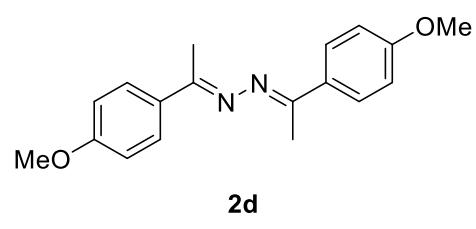


Figure S62. ^1H NMR spectrum of **2d** (CDCl_3 , 400 M).

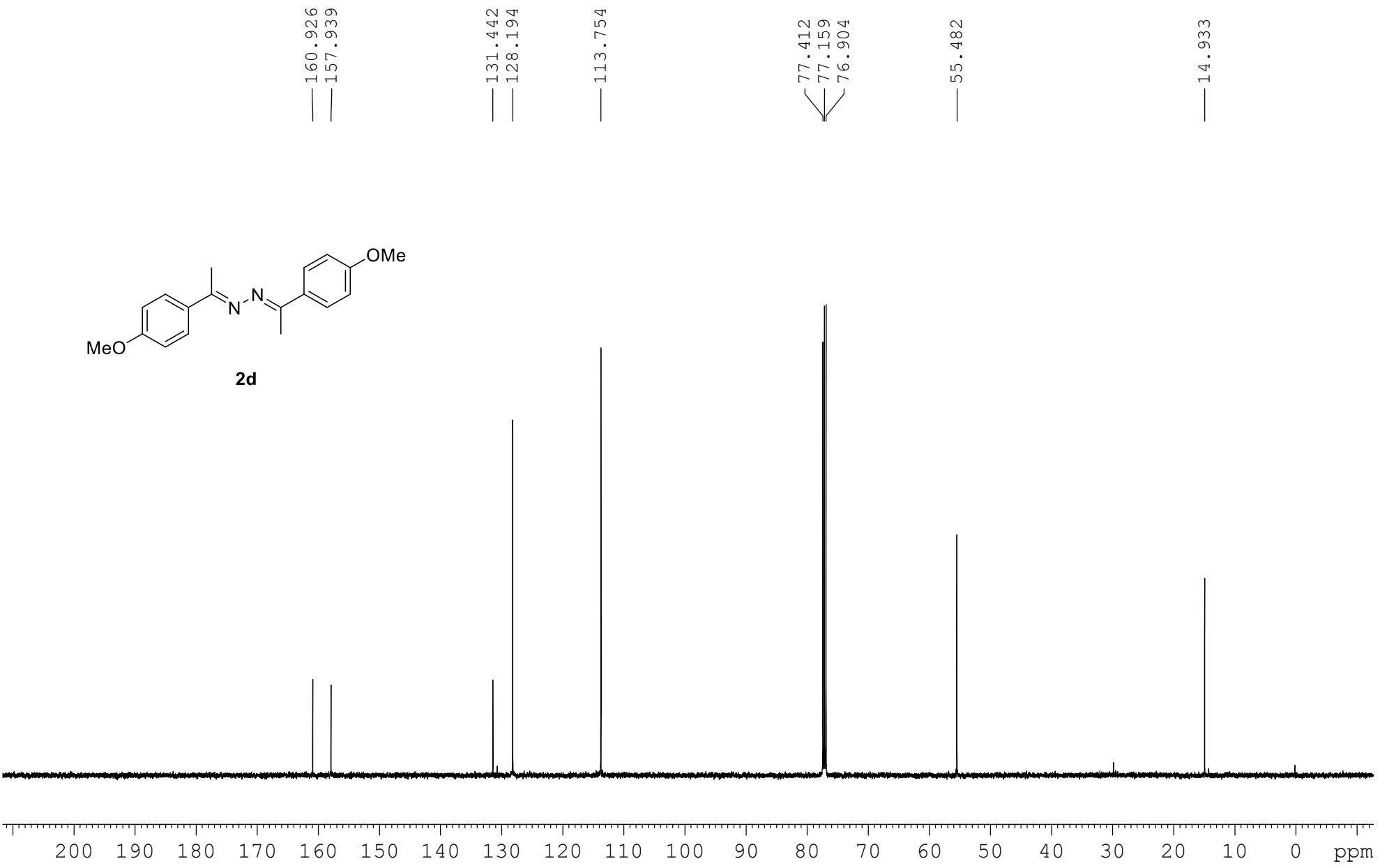


Figure S63. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2d** (CDCl_3 , 100 M).

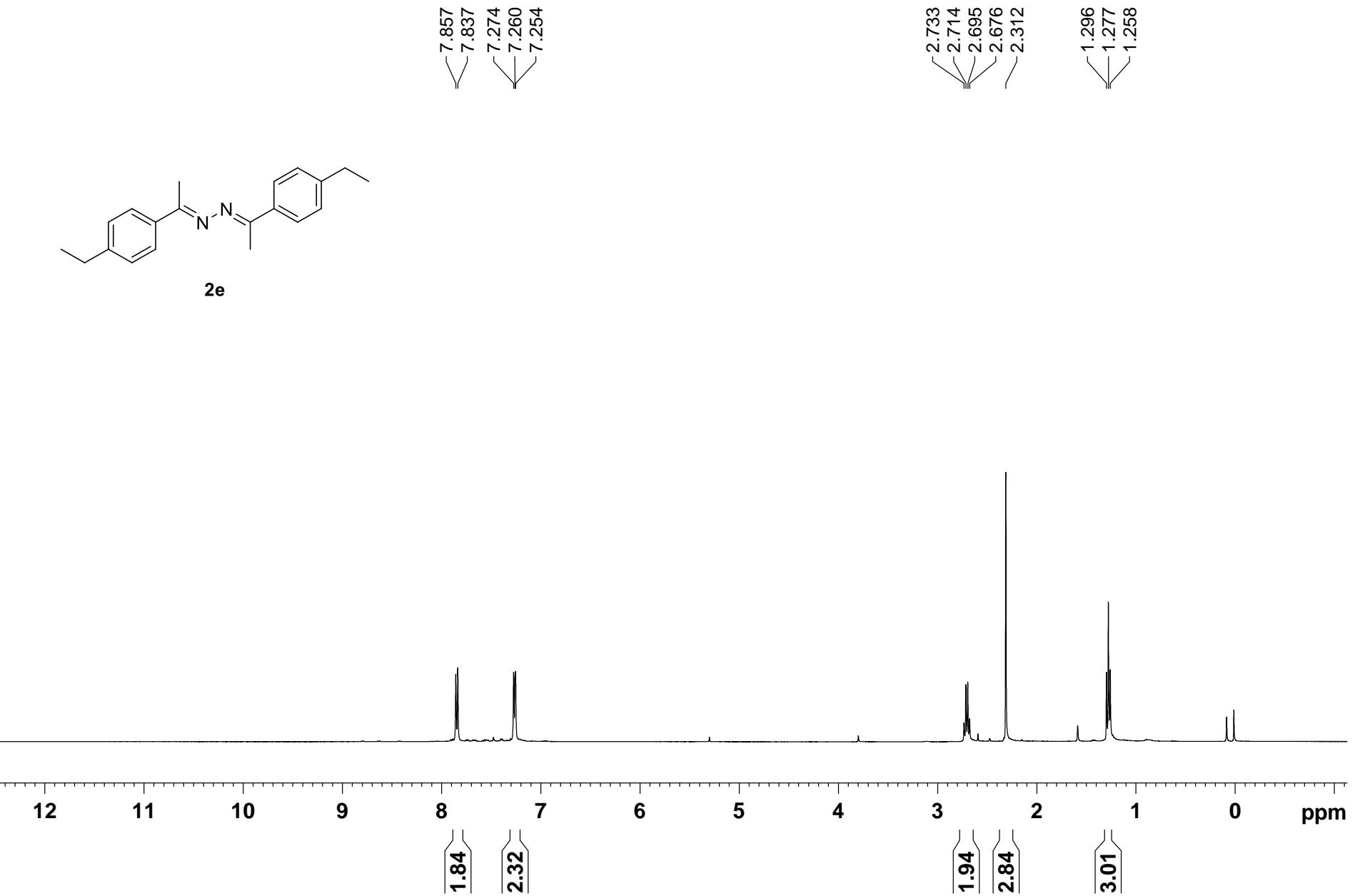


Figure S64. ^1H NMR spectrum of **2e** (CDCl_3 , 400 M).

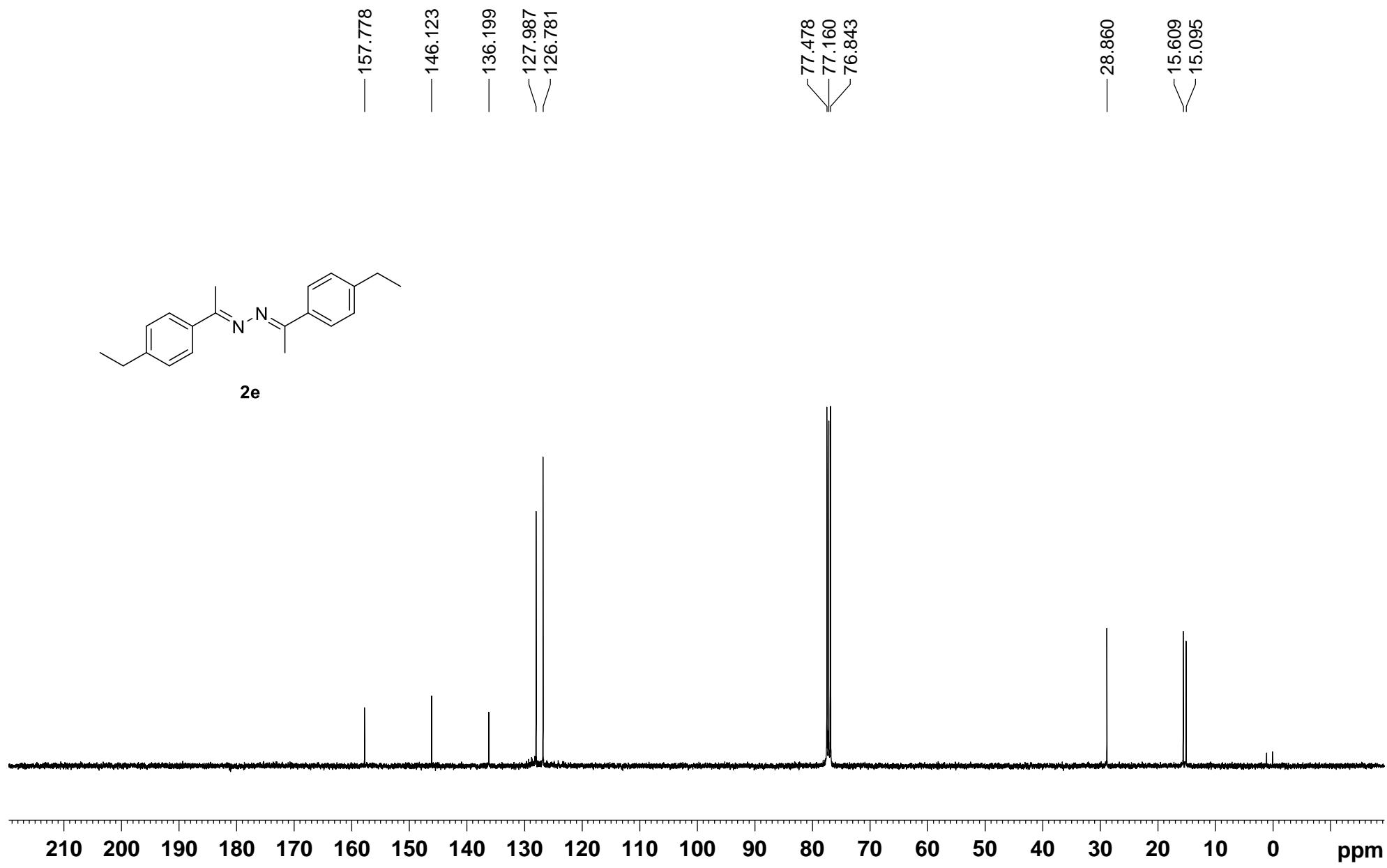


Figure S65. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2e** (CDCl_3 , 100 M).

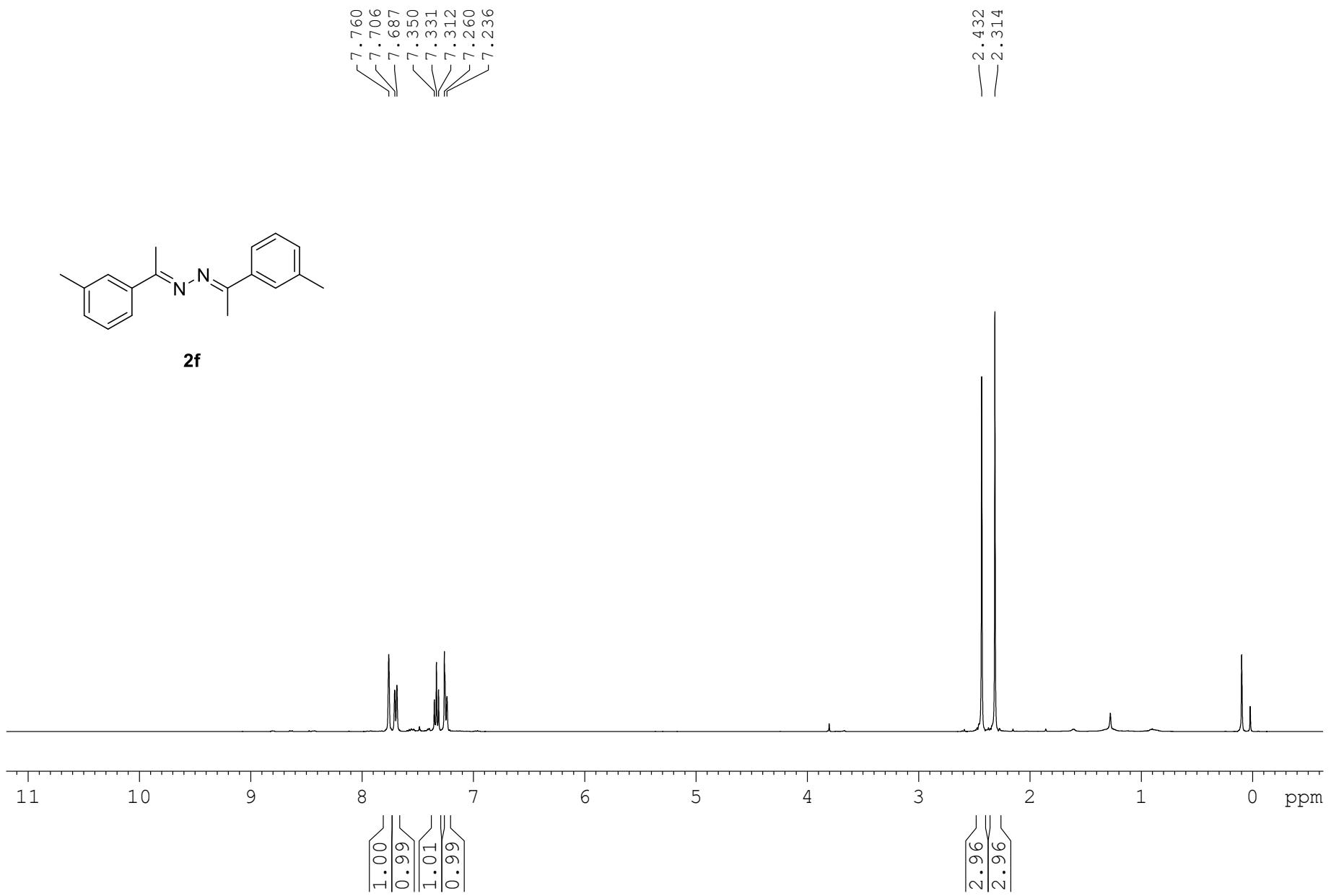


Figure S66. ¹H NMR spectrum of **2f** (CDCl₃, 400 M).

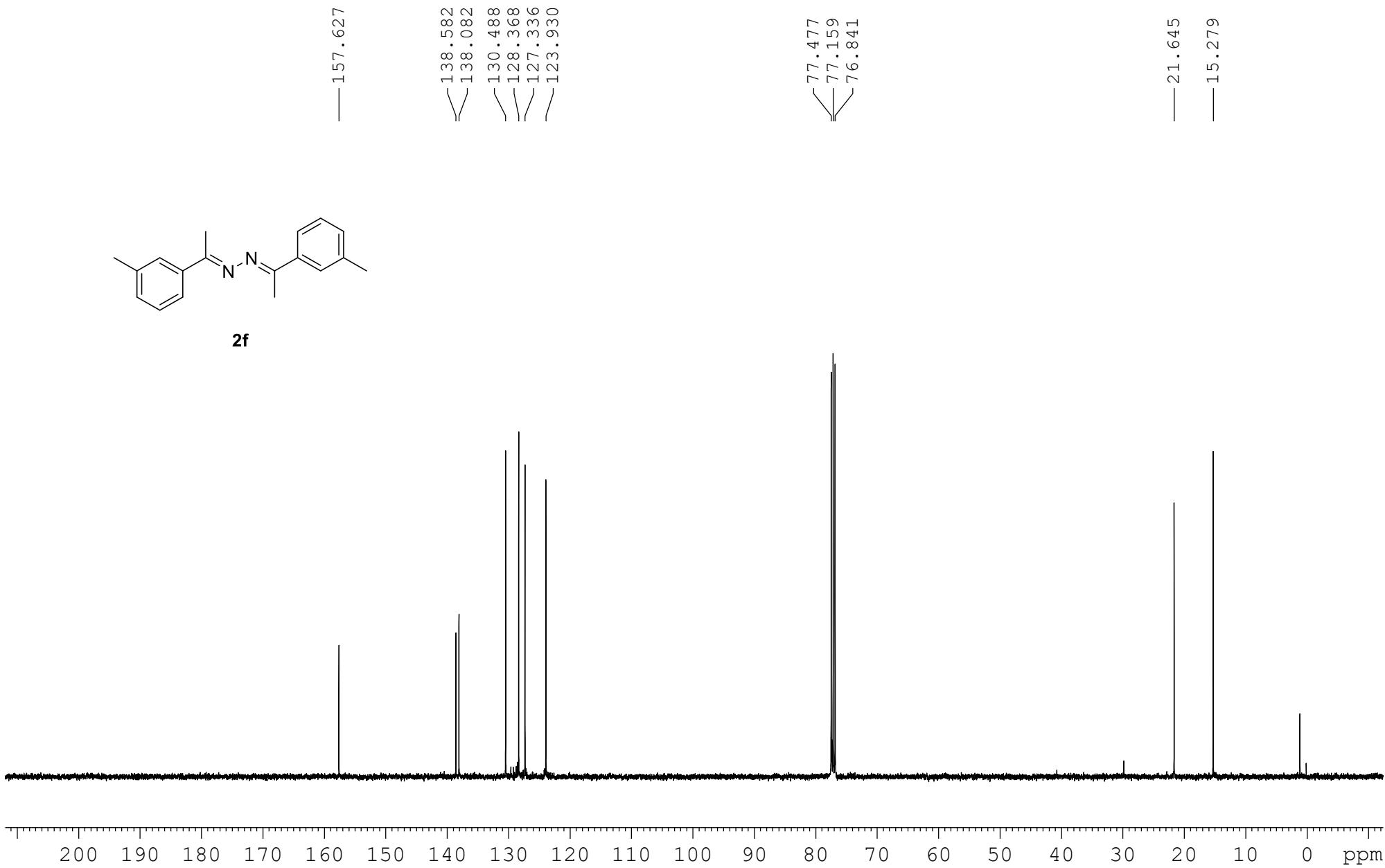
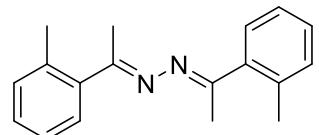


Figure S67. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2f** (CDCl_3 , 100 M).



2g

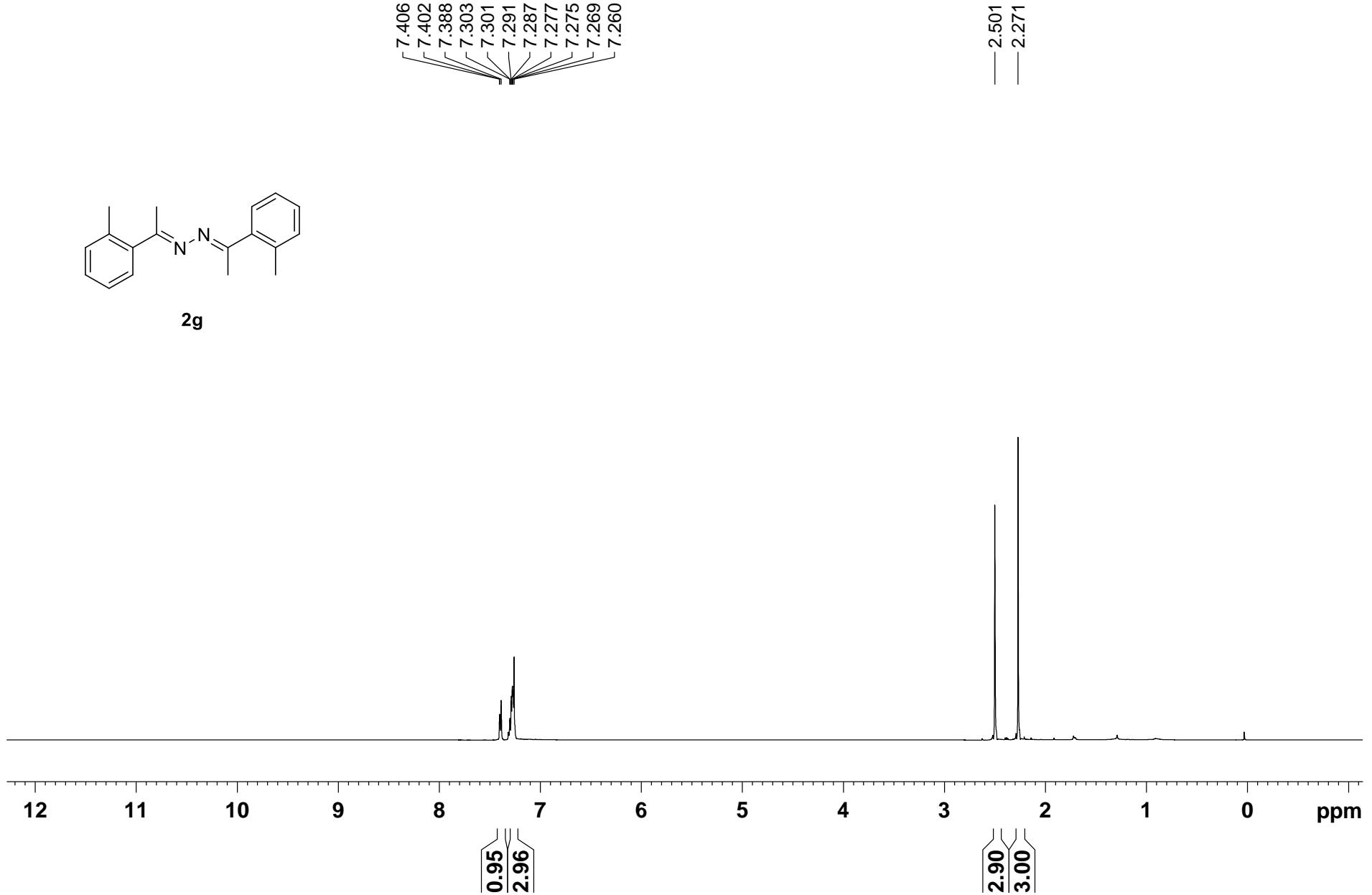


Figure S68. ¹H NMR spectrum of **2g** (CDCl₃, 500 M).

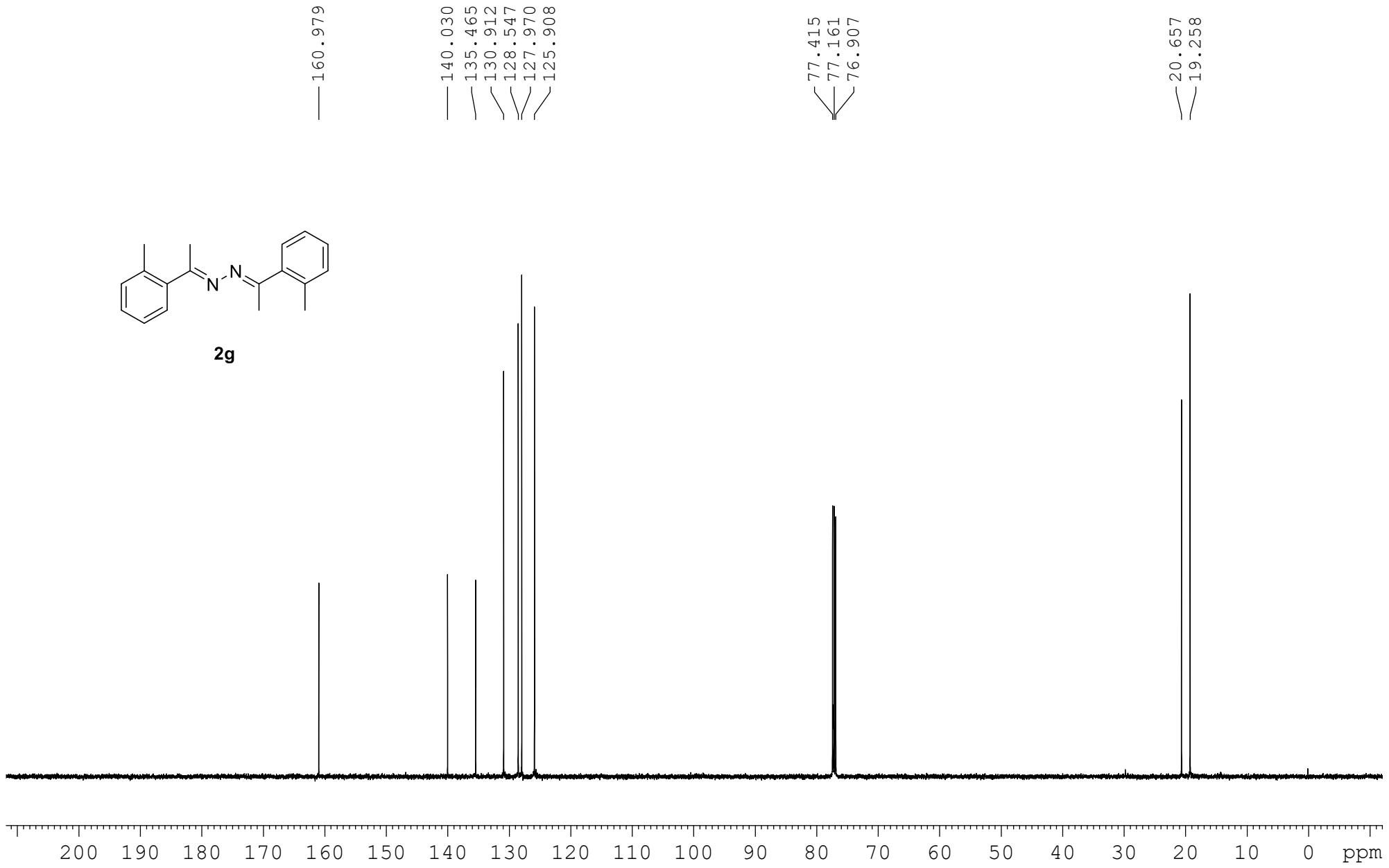


Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2g** (CDCl_3 , 125 M).

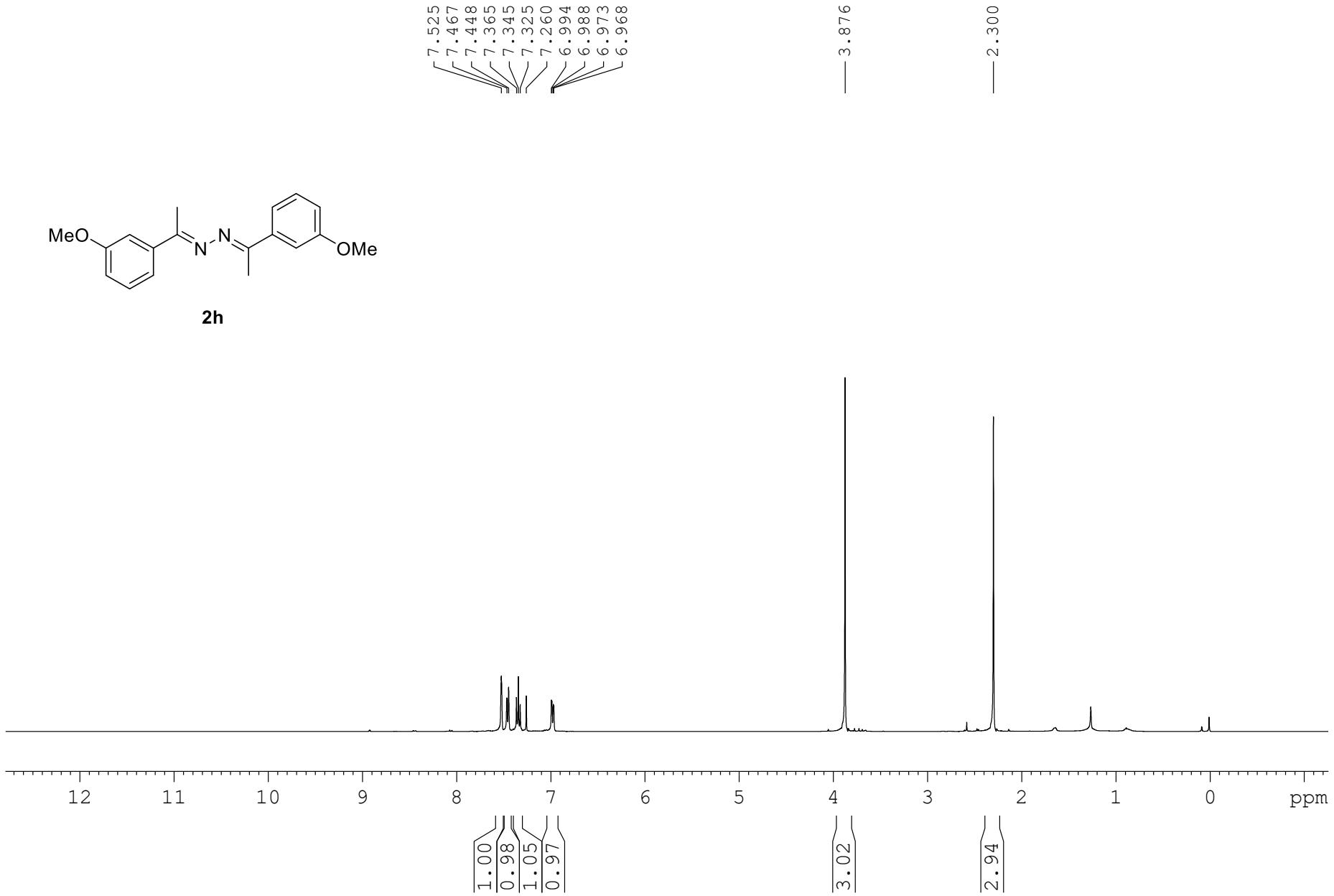
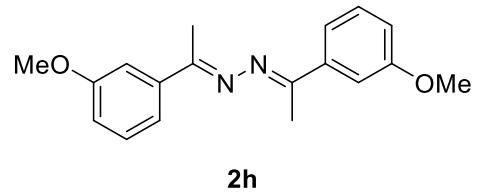


Figure S70. ¹H NMR spectrum of **2h** (CDCl₃, 400 M).

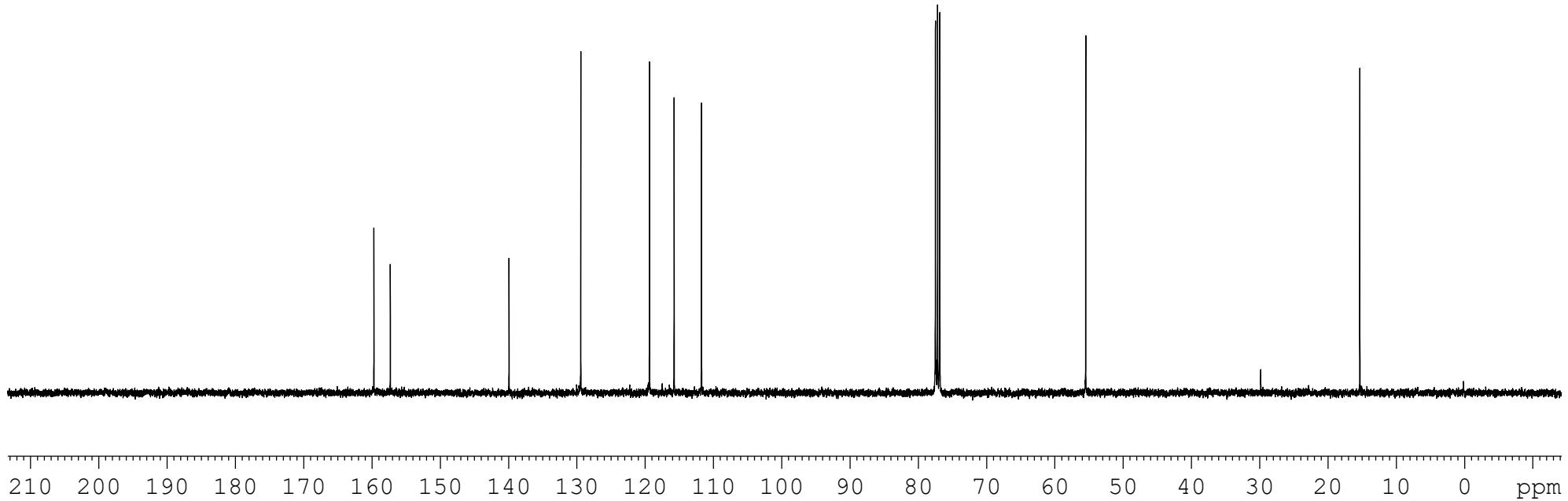
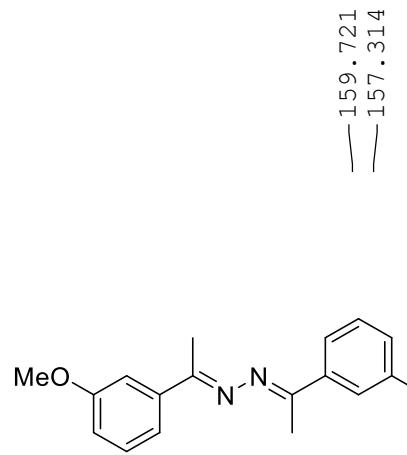
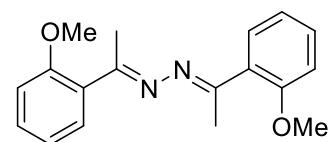


Figure S71. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2h** (CDCl_3 , 100 M).



2i

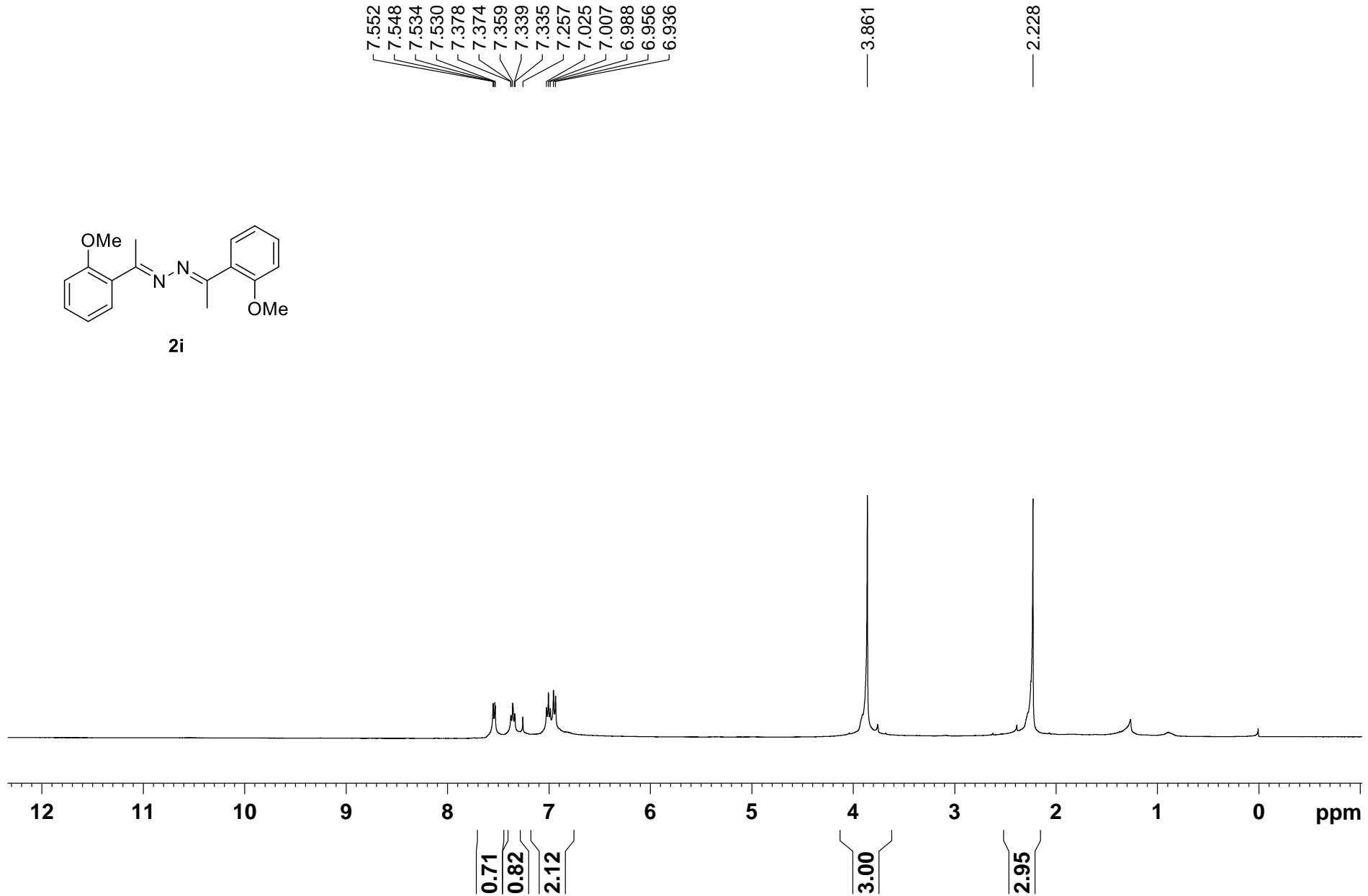


Figure S72. ^1H NMR spectrum of **2i** (CDCl_3 , 400 M).

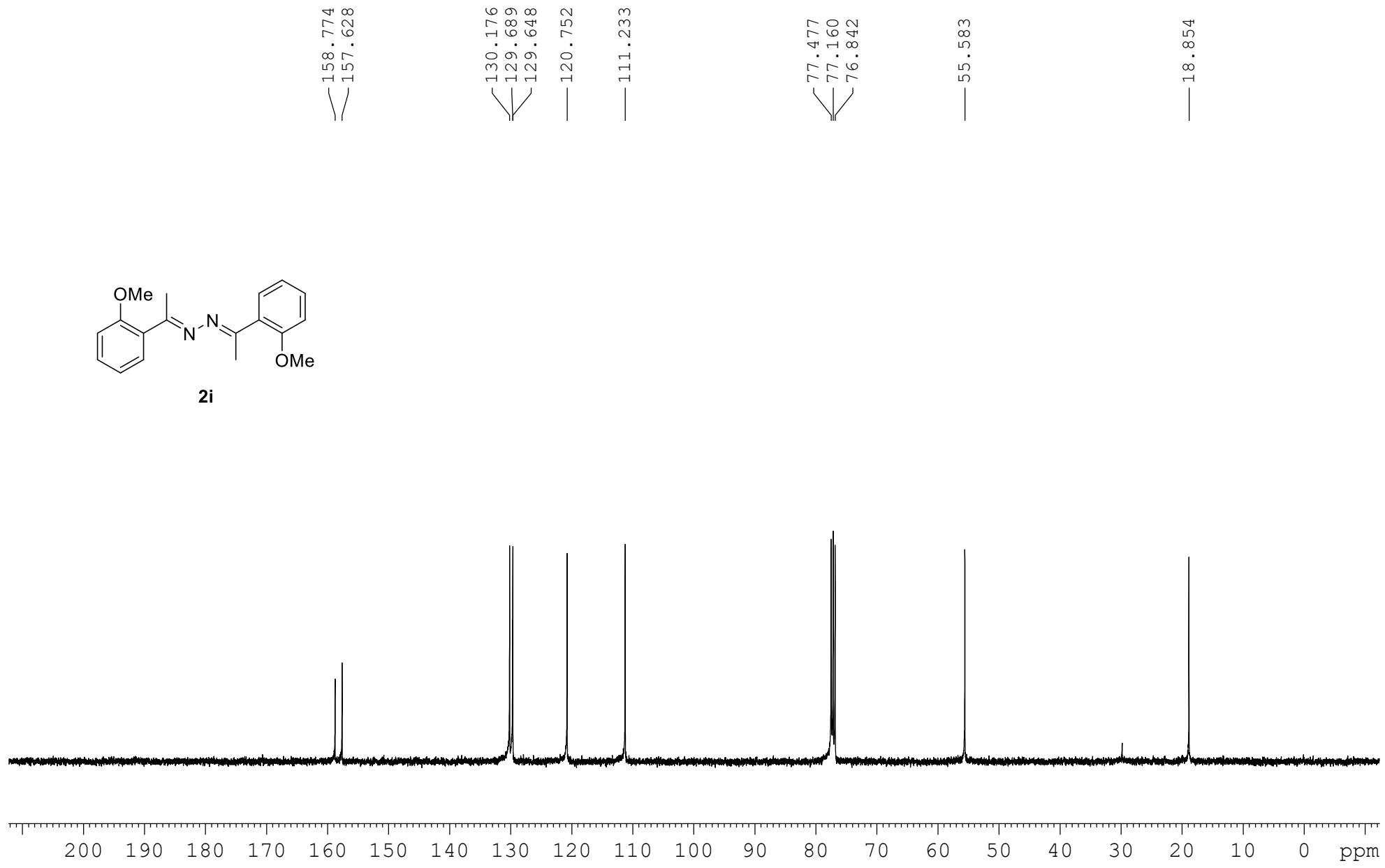
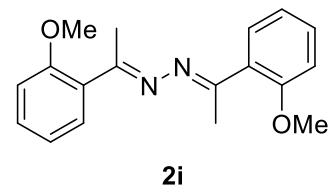


Figure S73. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2i** (CDCl_3 , 100 M).

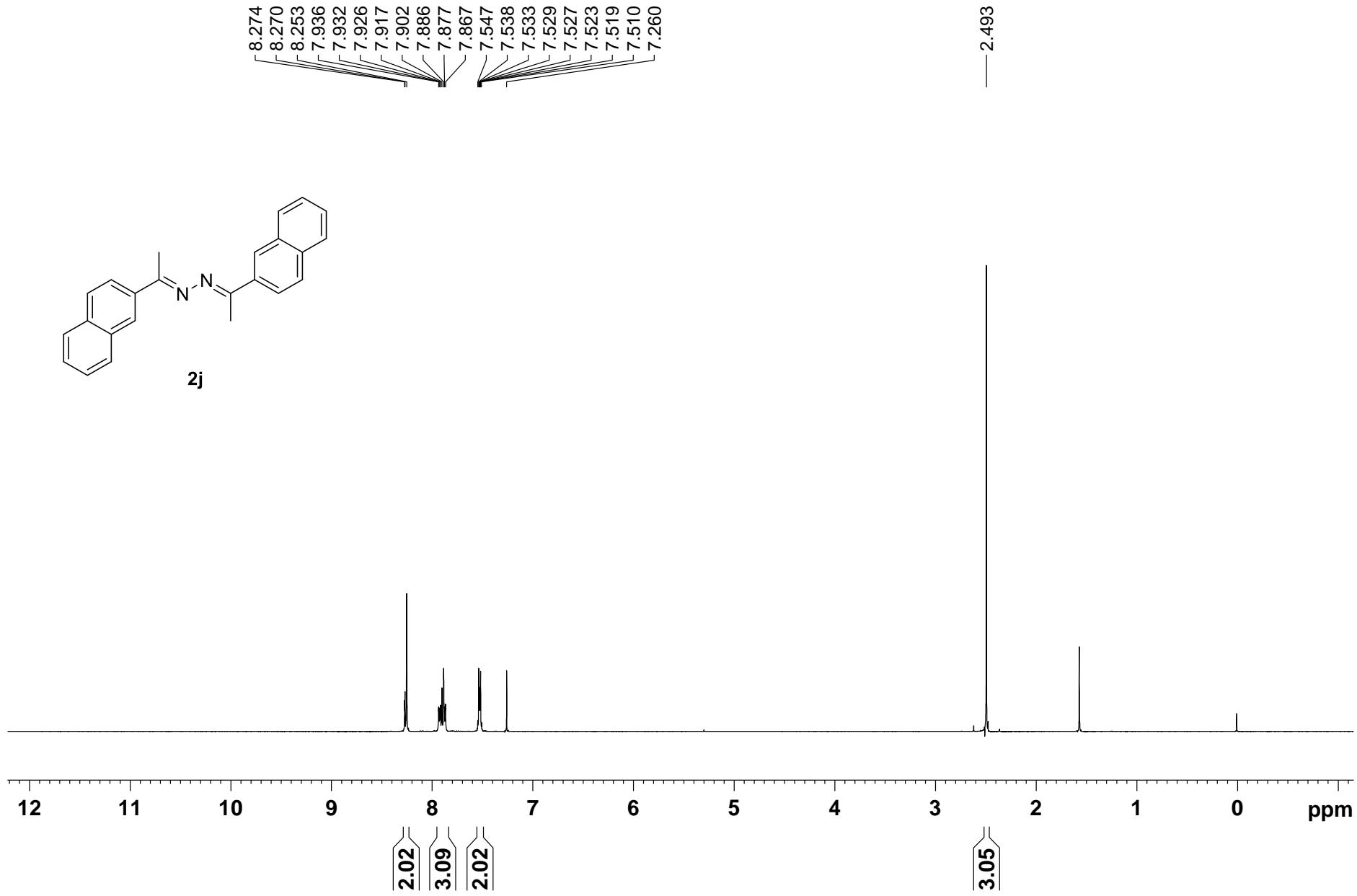


Figure S74. ^1H NMR spectrum of **2j** (CDCl_3 , 500 M).

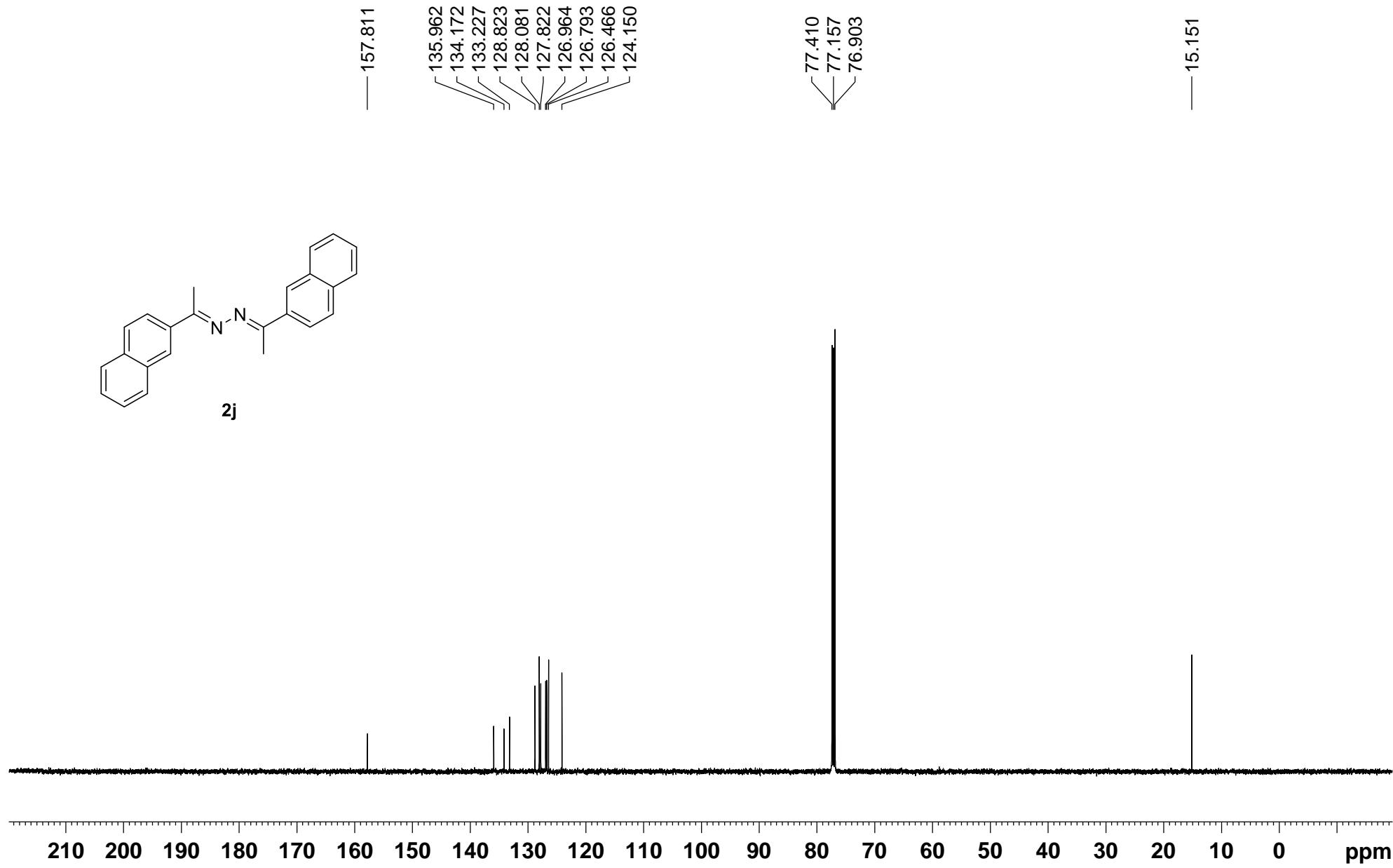


Figure S75. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2j** (CDCl_3 , 125 M).

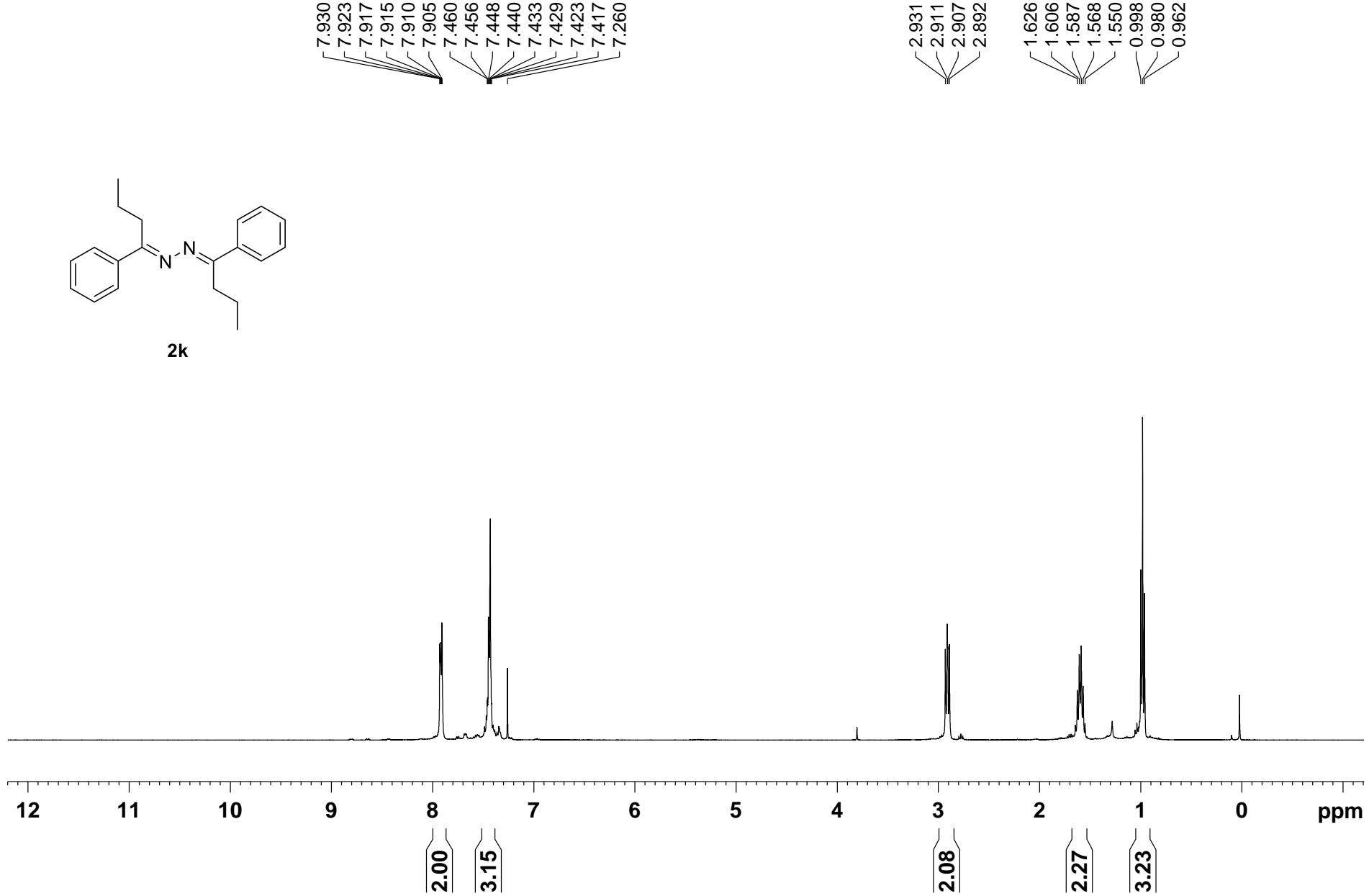
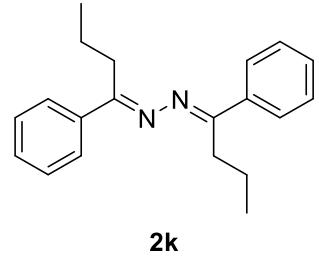


Figure S76. ^1H NMR spectrum of **2k** (CDCl_3 , 400 M).

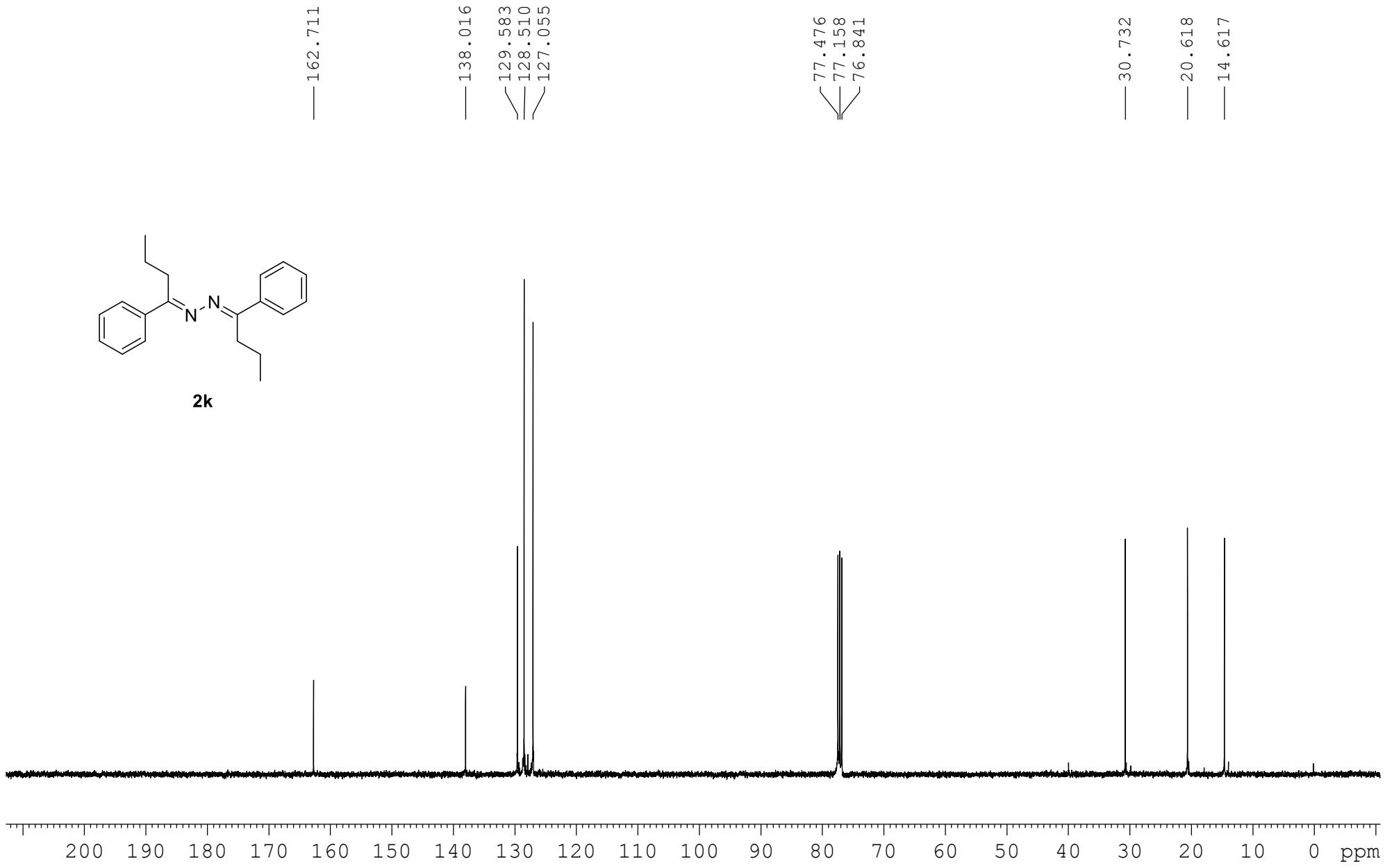


Figure S77. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2k** (CDCl_3 , 100 M).

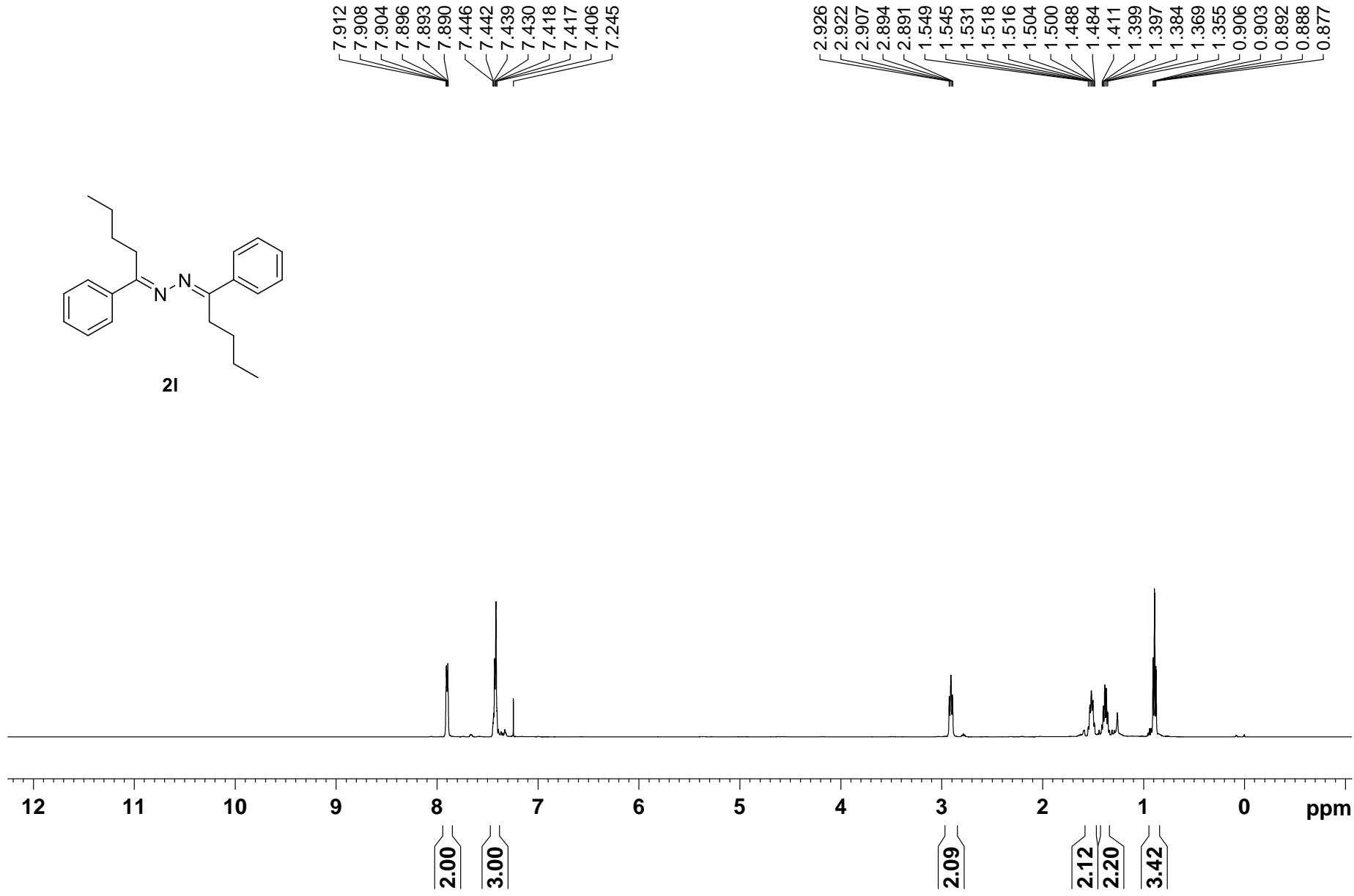


Figure S78. ^1H NMR spectrum of **2l** (CDCl_3 , 500 M).

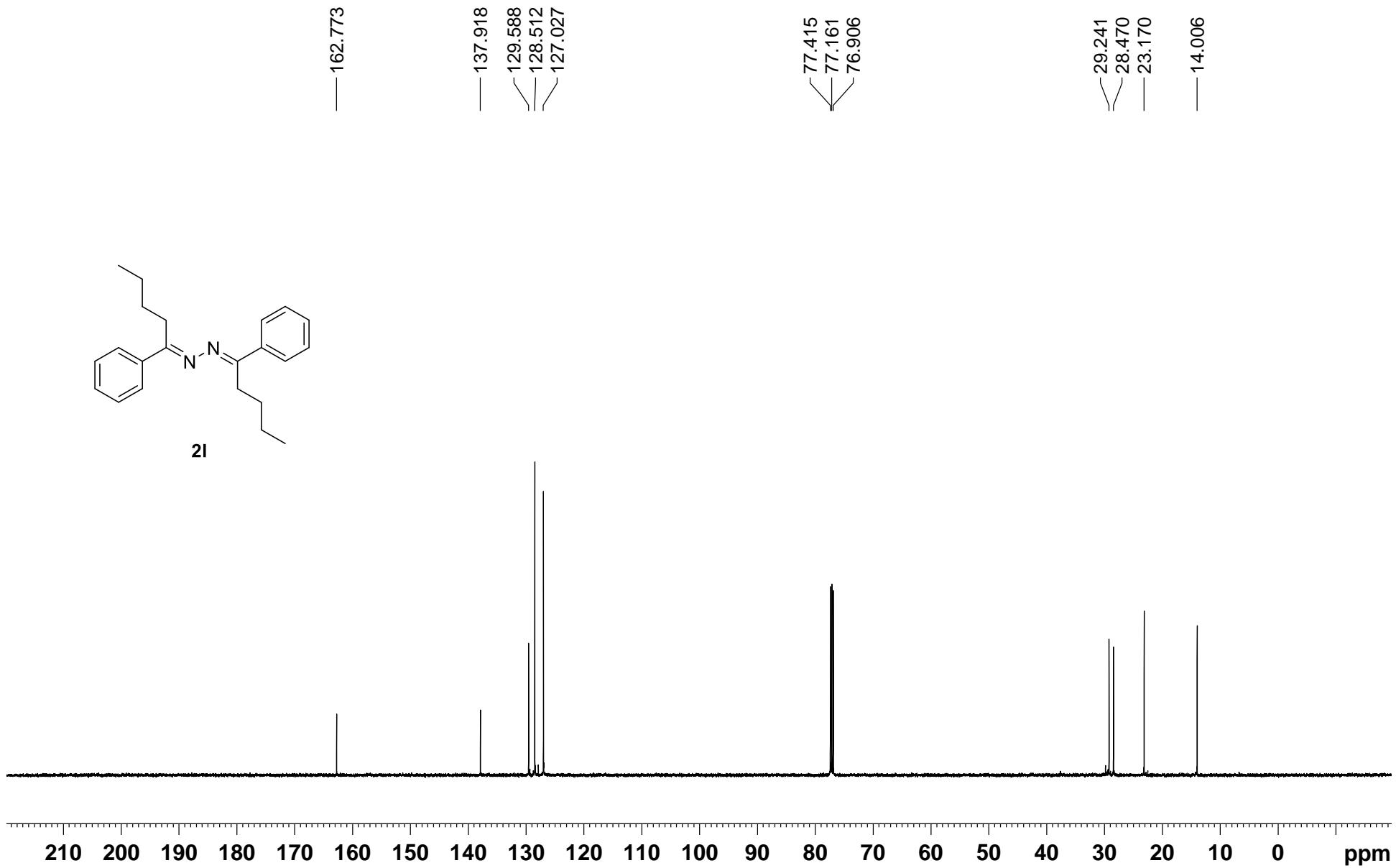


Figure S79. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2l** (CDCl_3 , 125 M).

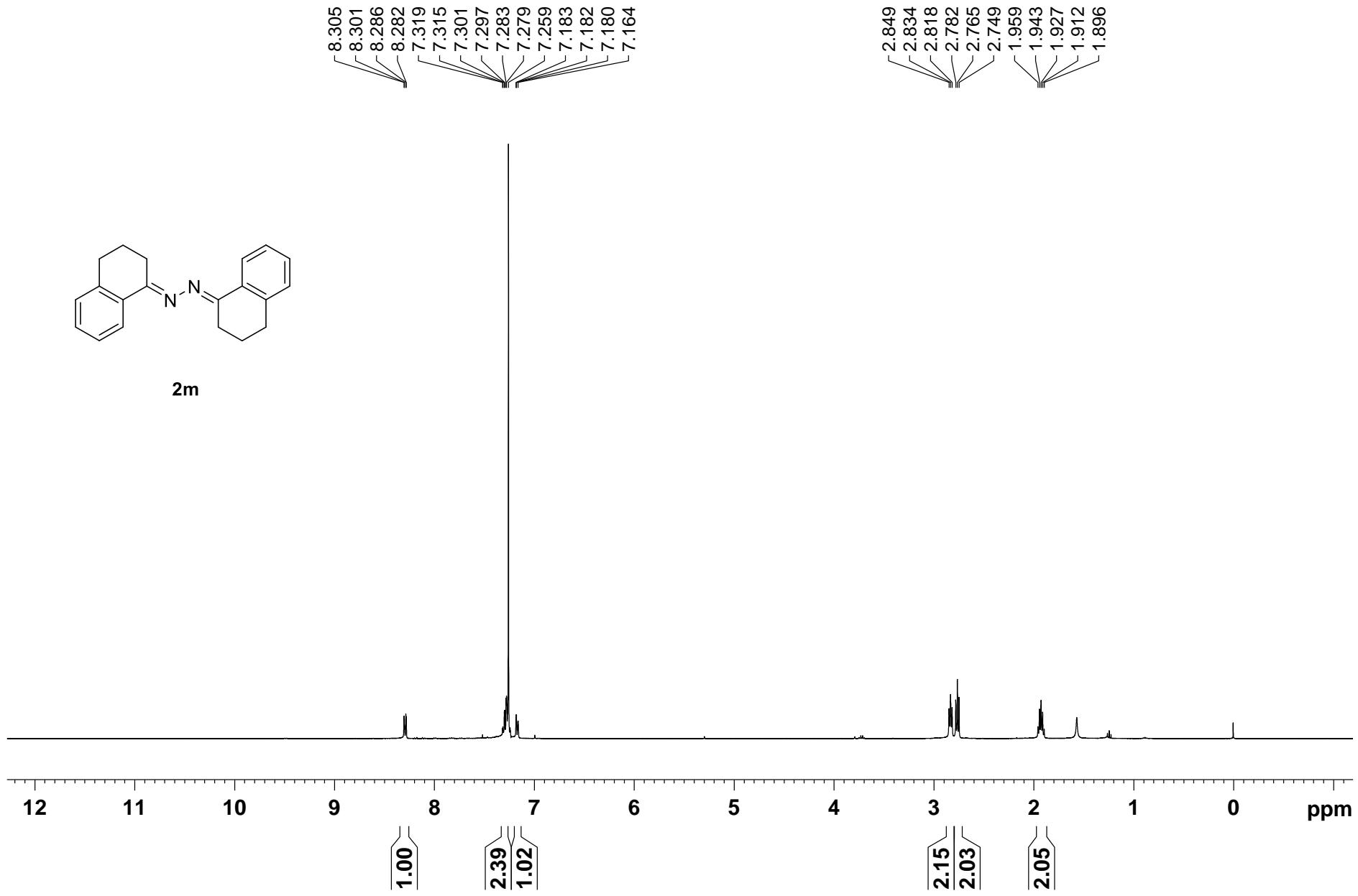


Figure S80. ^1H NMR spectrum of **2m** (CDCl_3 , 400 M).

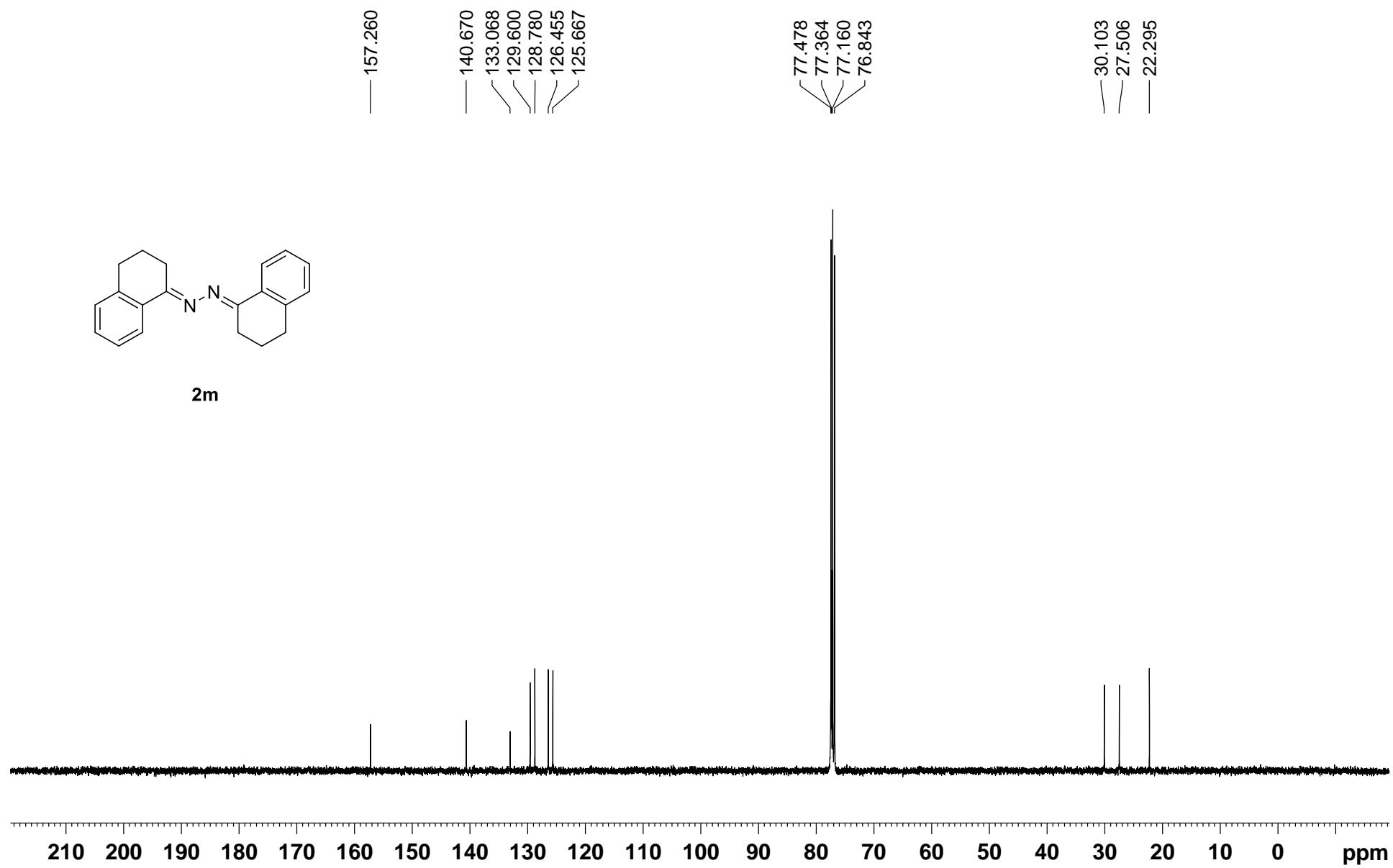
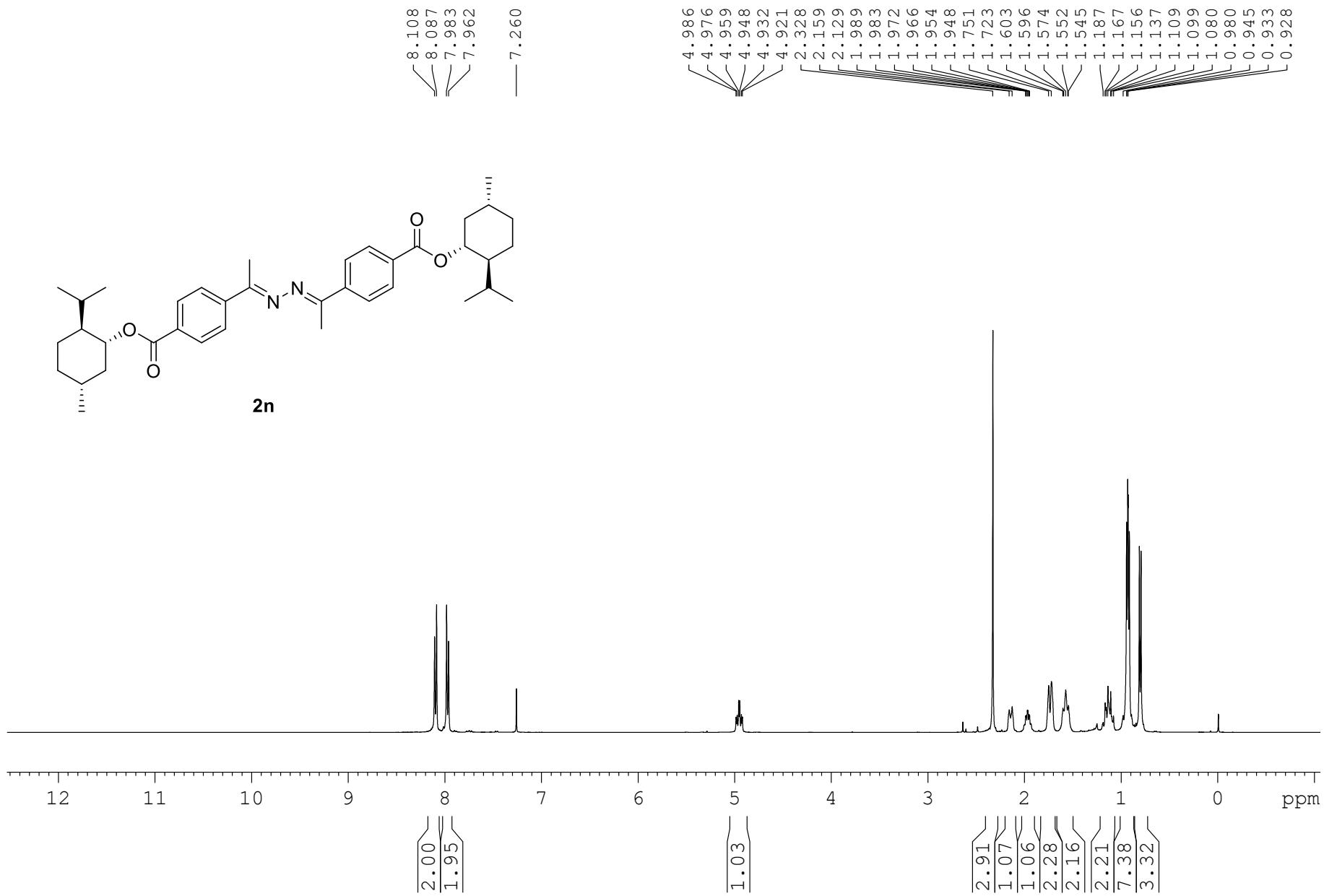


Figure S81. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2m** (CDCl_3 , 100 M).



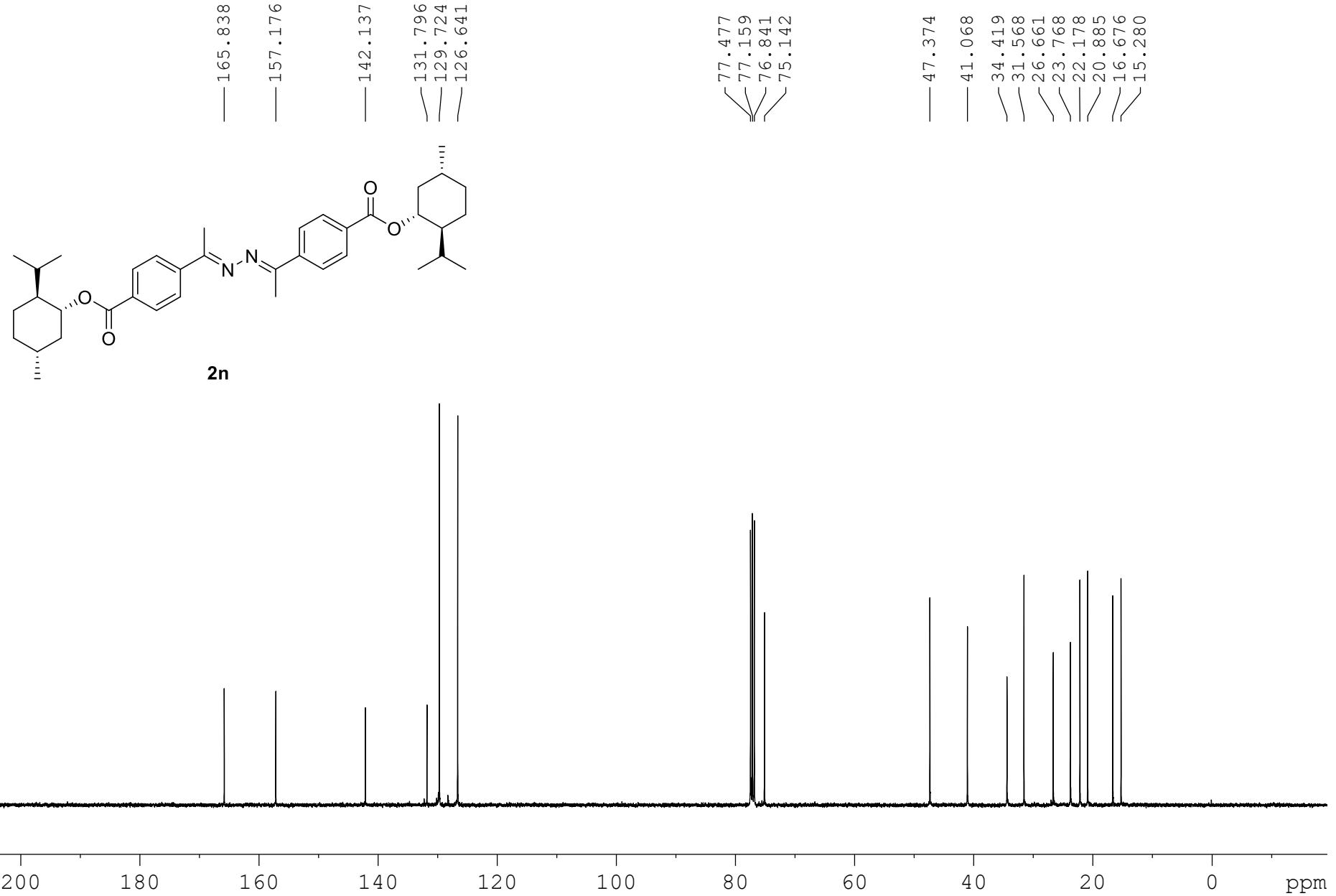


Figure S83. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2n** (CDCl_3 , 100 M).

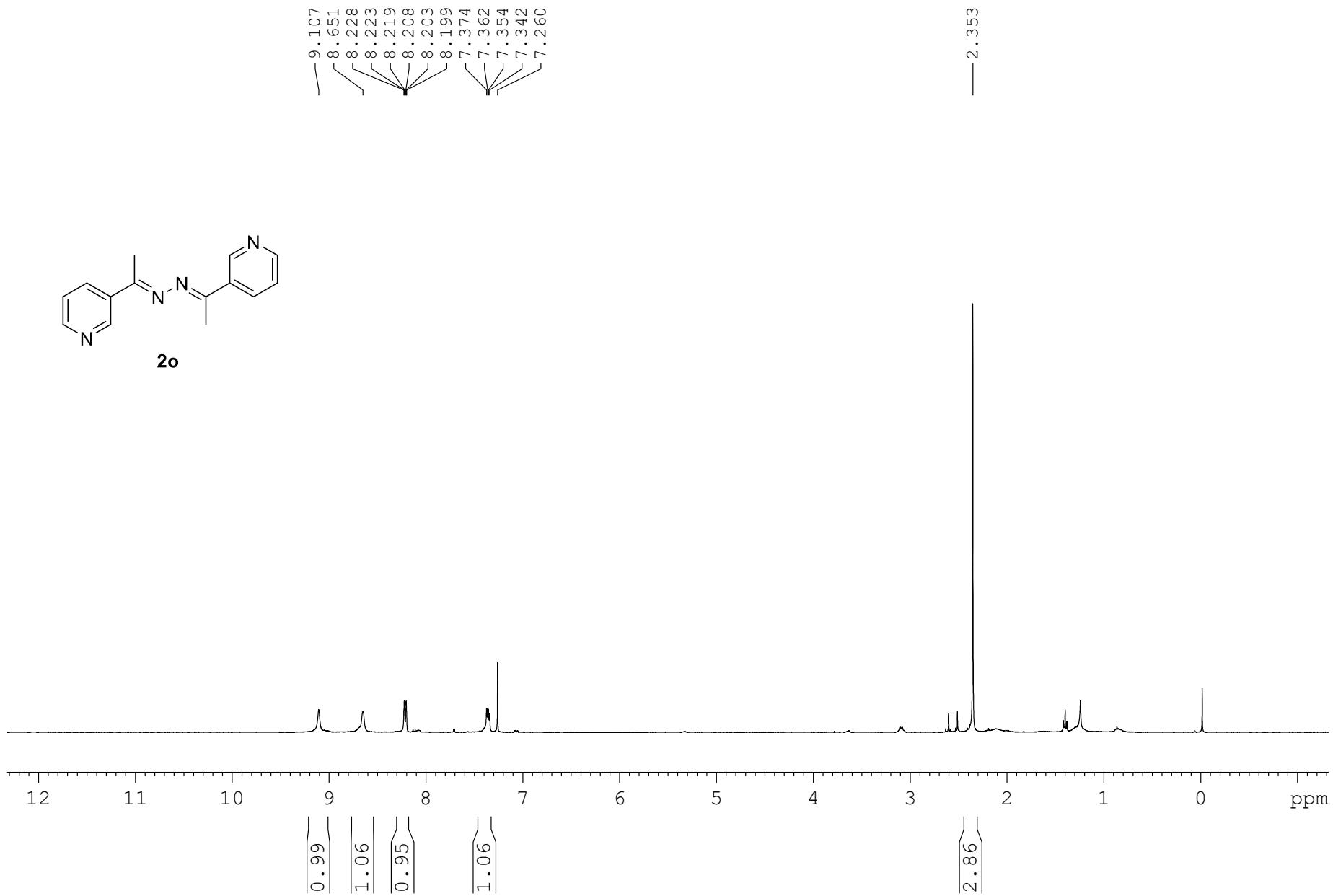
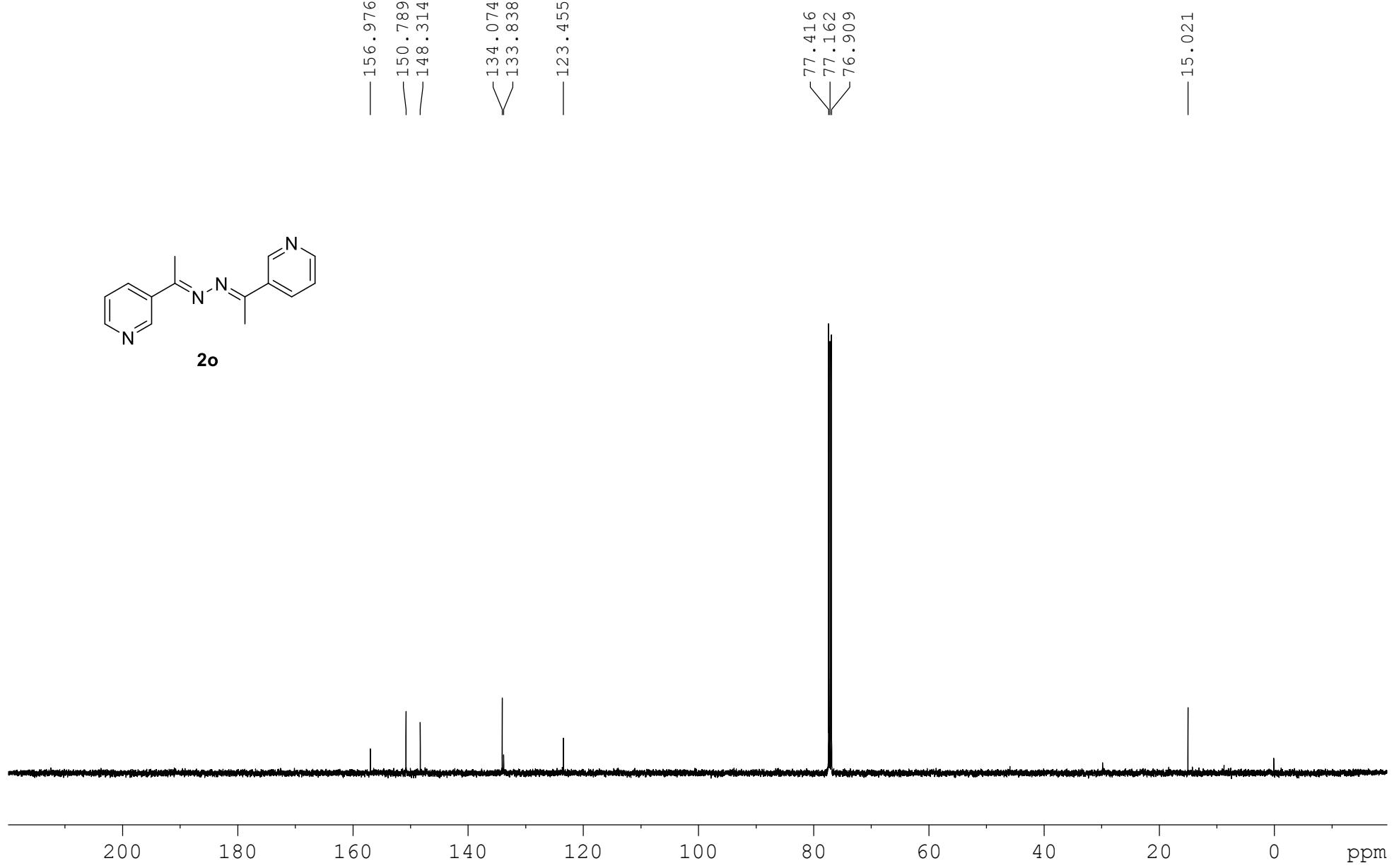


Figure S84. ^1H NMR spectrum of **2o** (CDCl_3 , 500 M).



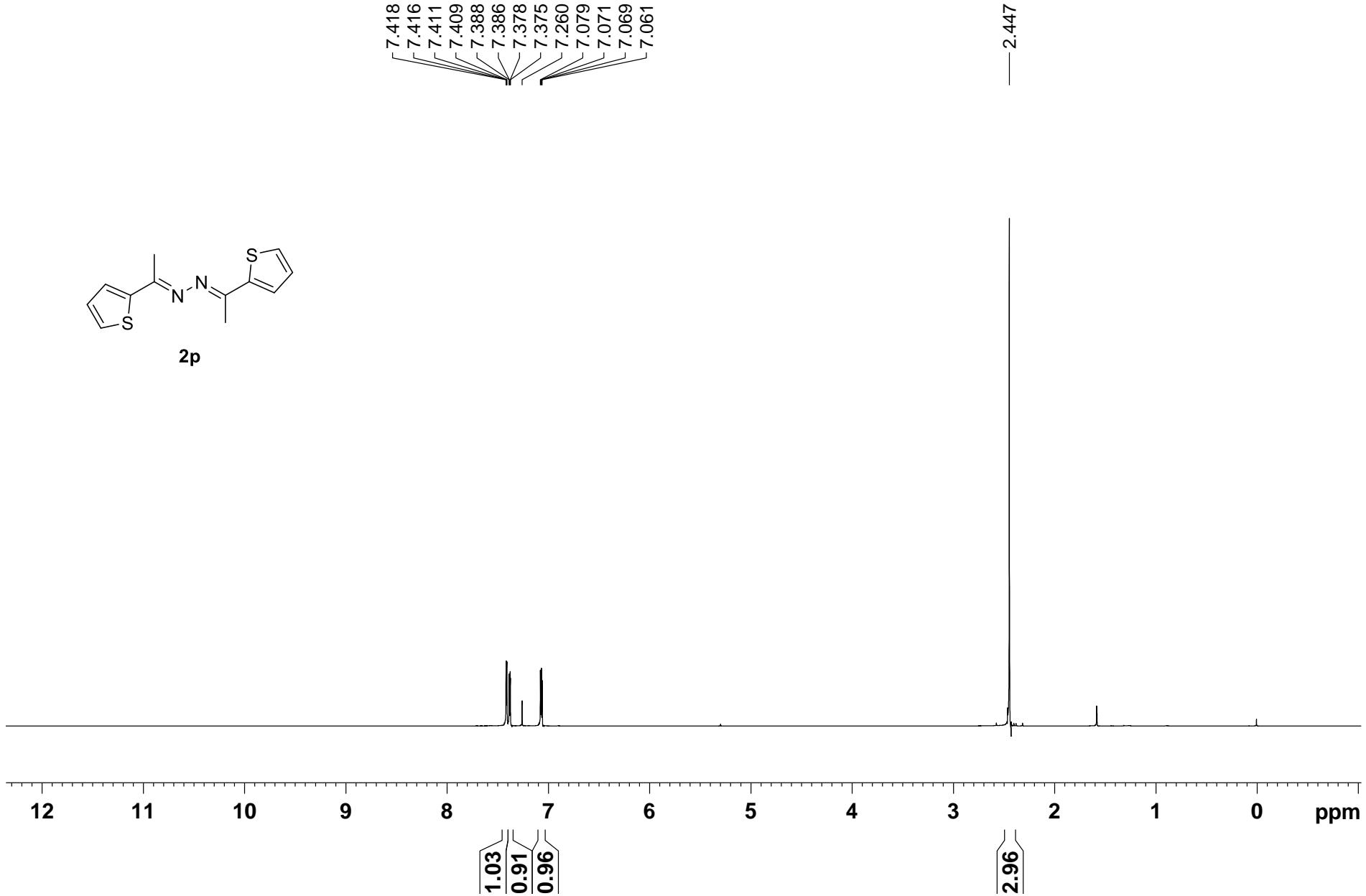


Figure S86. ^1H NMR spectrum of **2p** (CDCl_3 , 500 M).

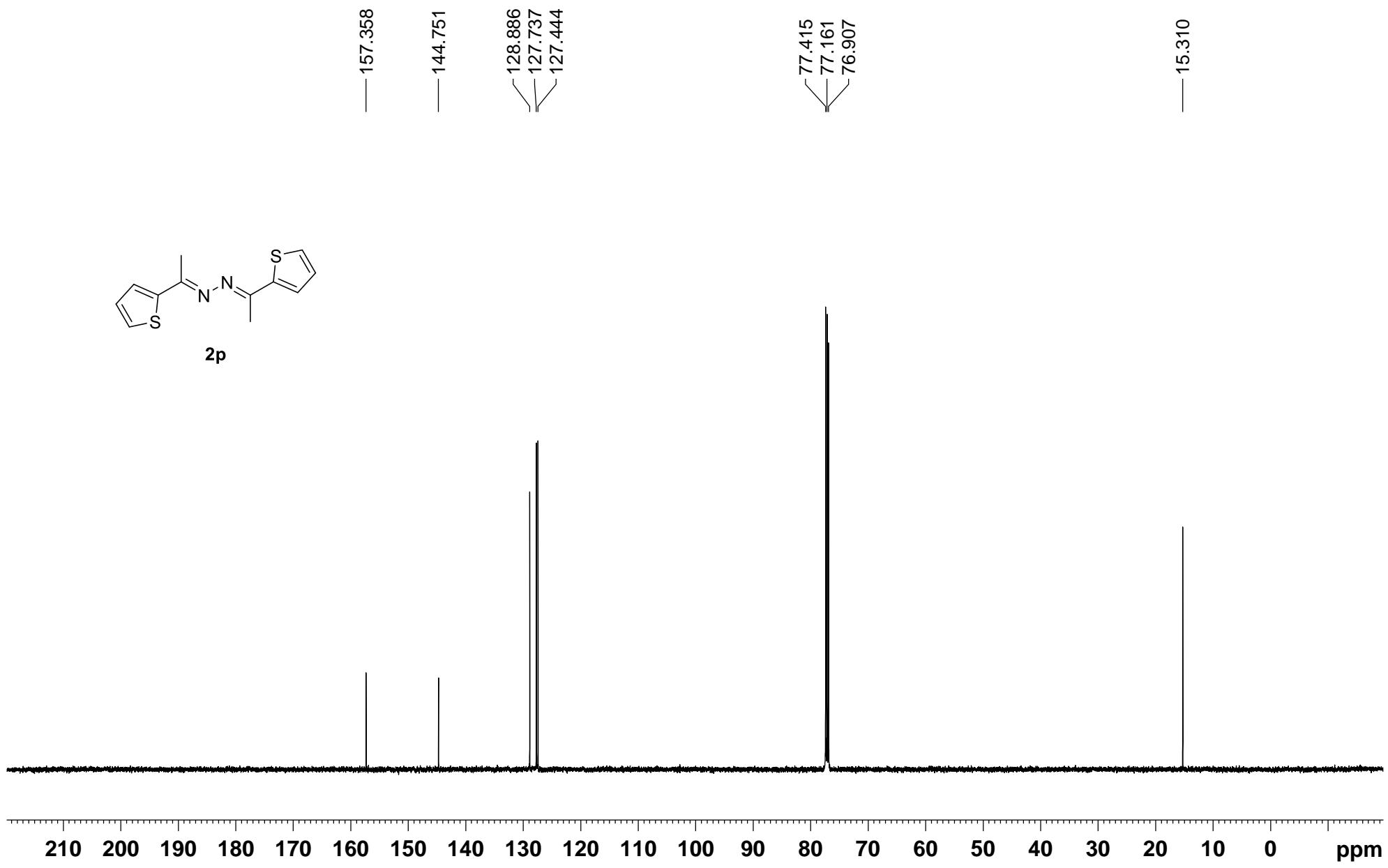


Figure S87. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2p** (CDCl_3 , 125 M).

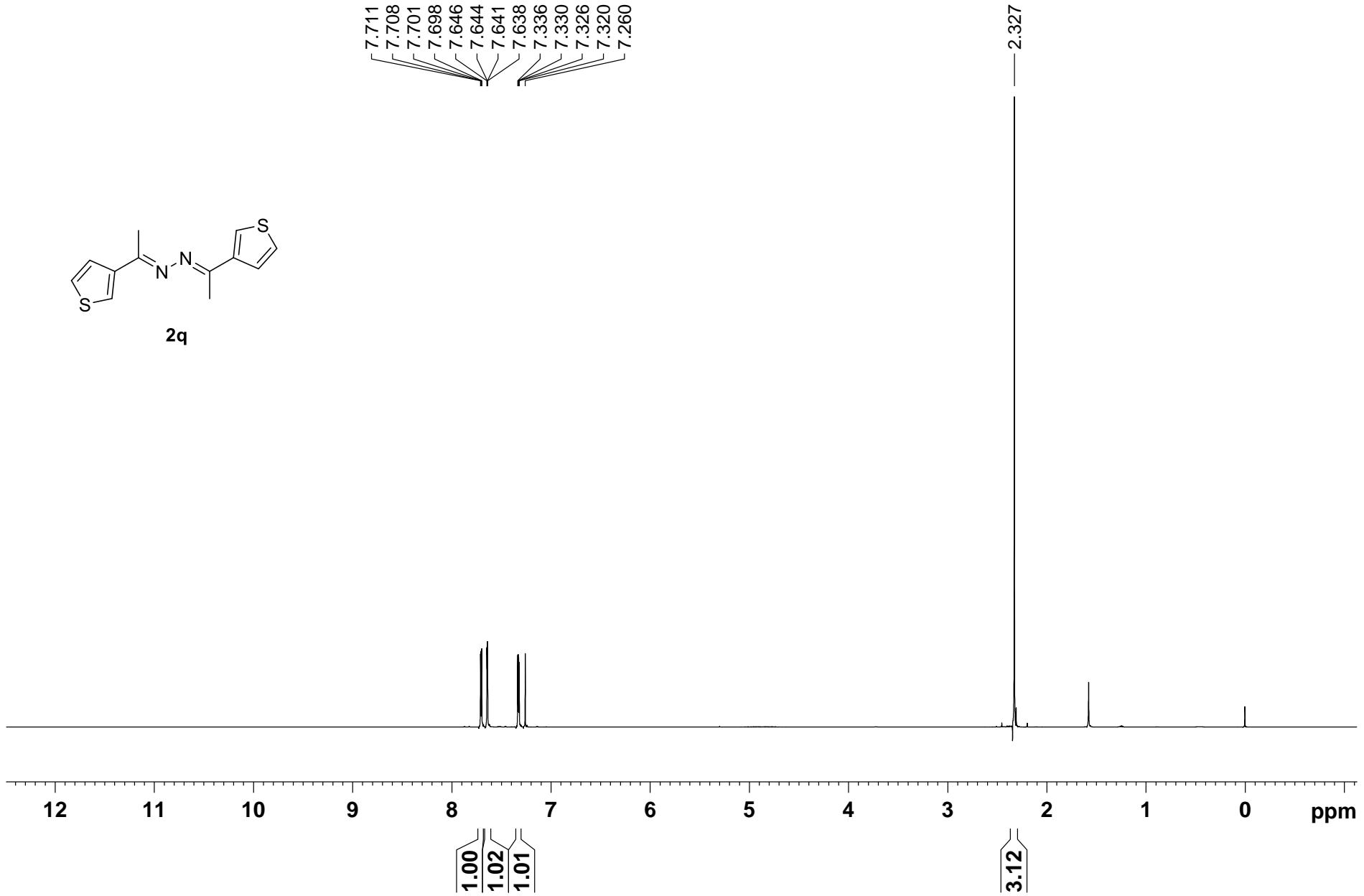


Figure S88. ^1H NMR spectrum of **2q** (CDCl_3 , 500 M).

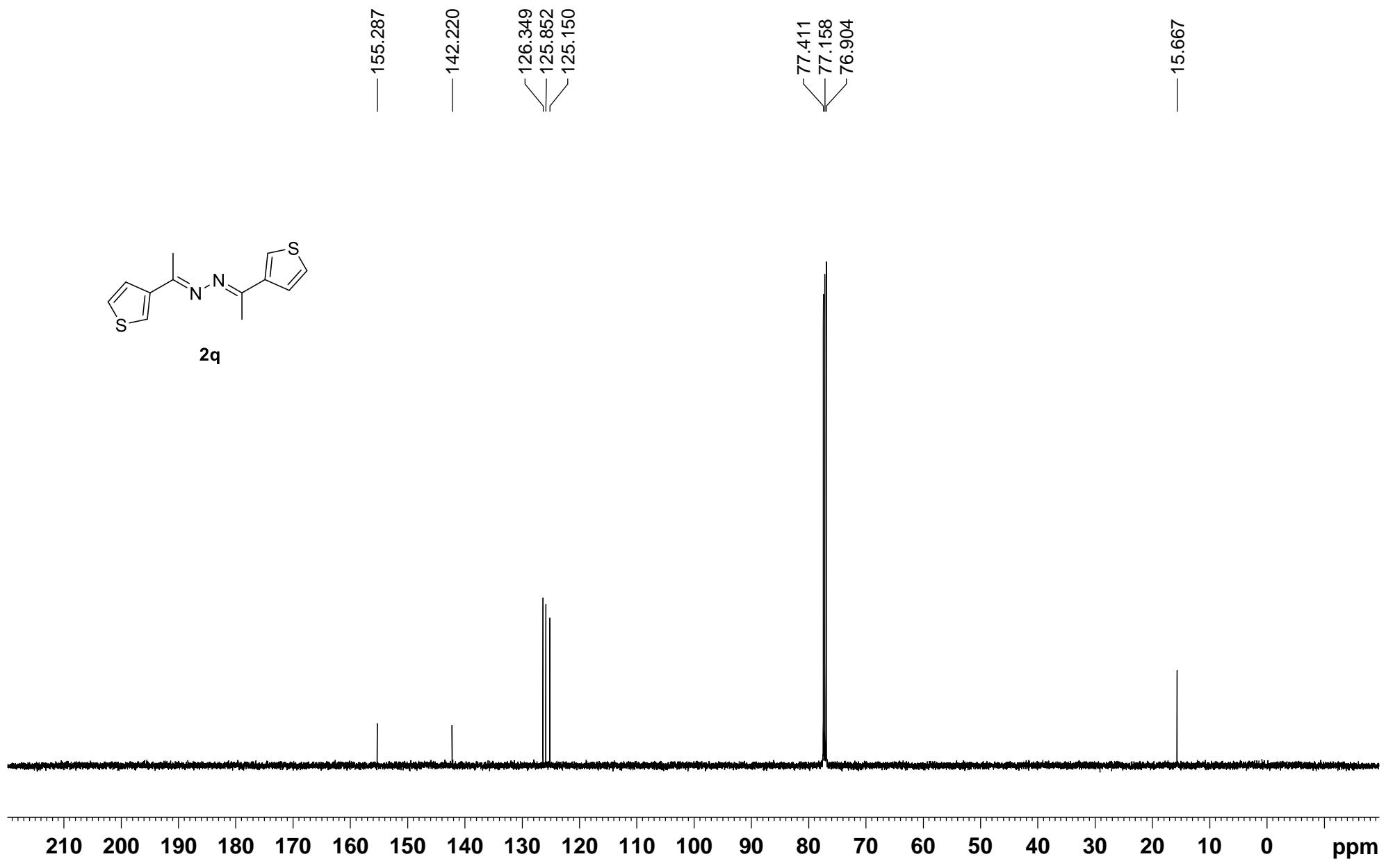


Figure S89. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2q** (CDCl_3 , 125 M).

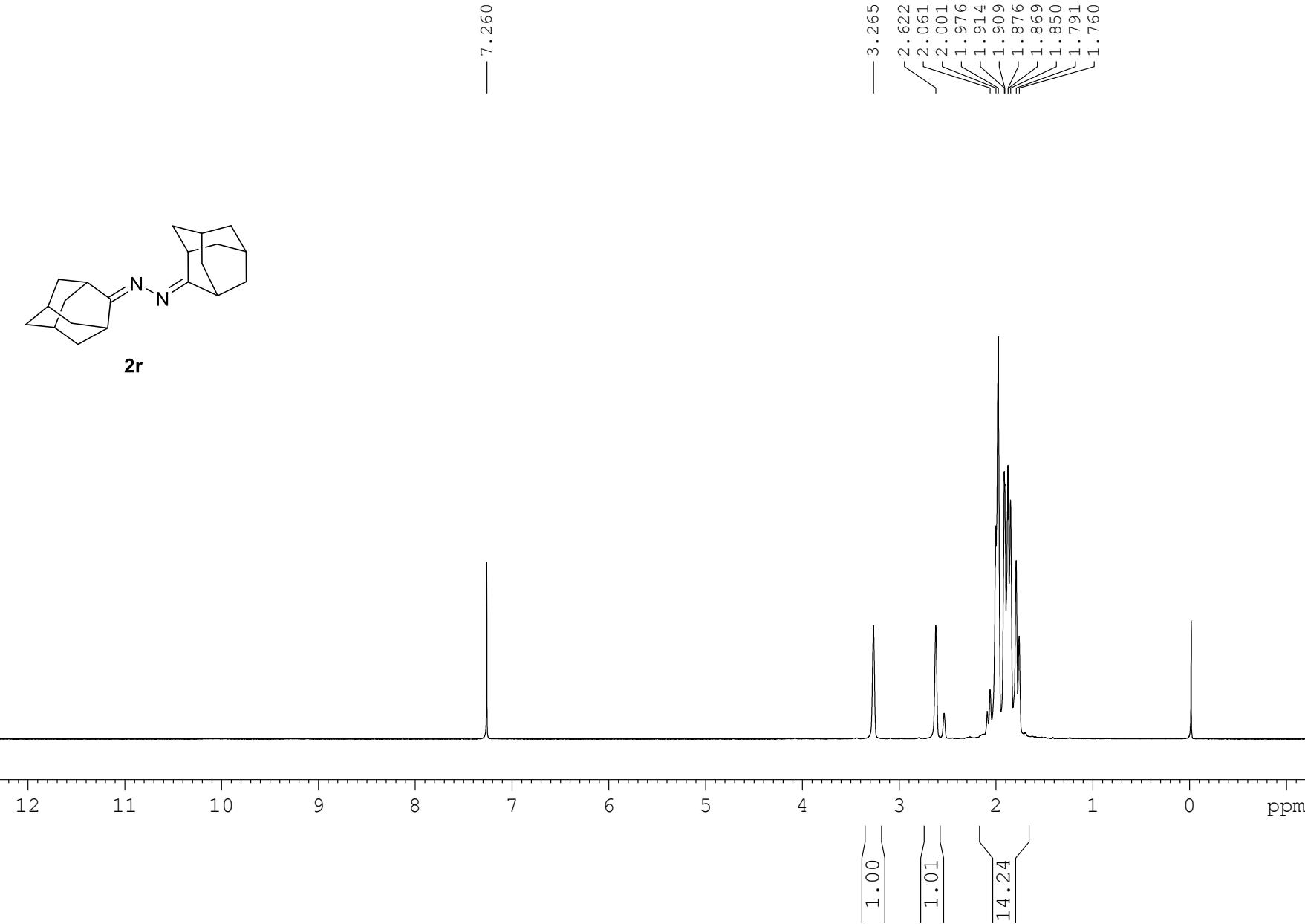


Figure S90. ^1H NMR spectrum of **2r** (CDCl_3 , 400M).

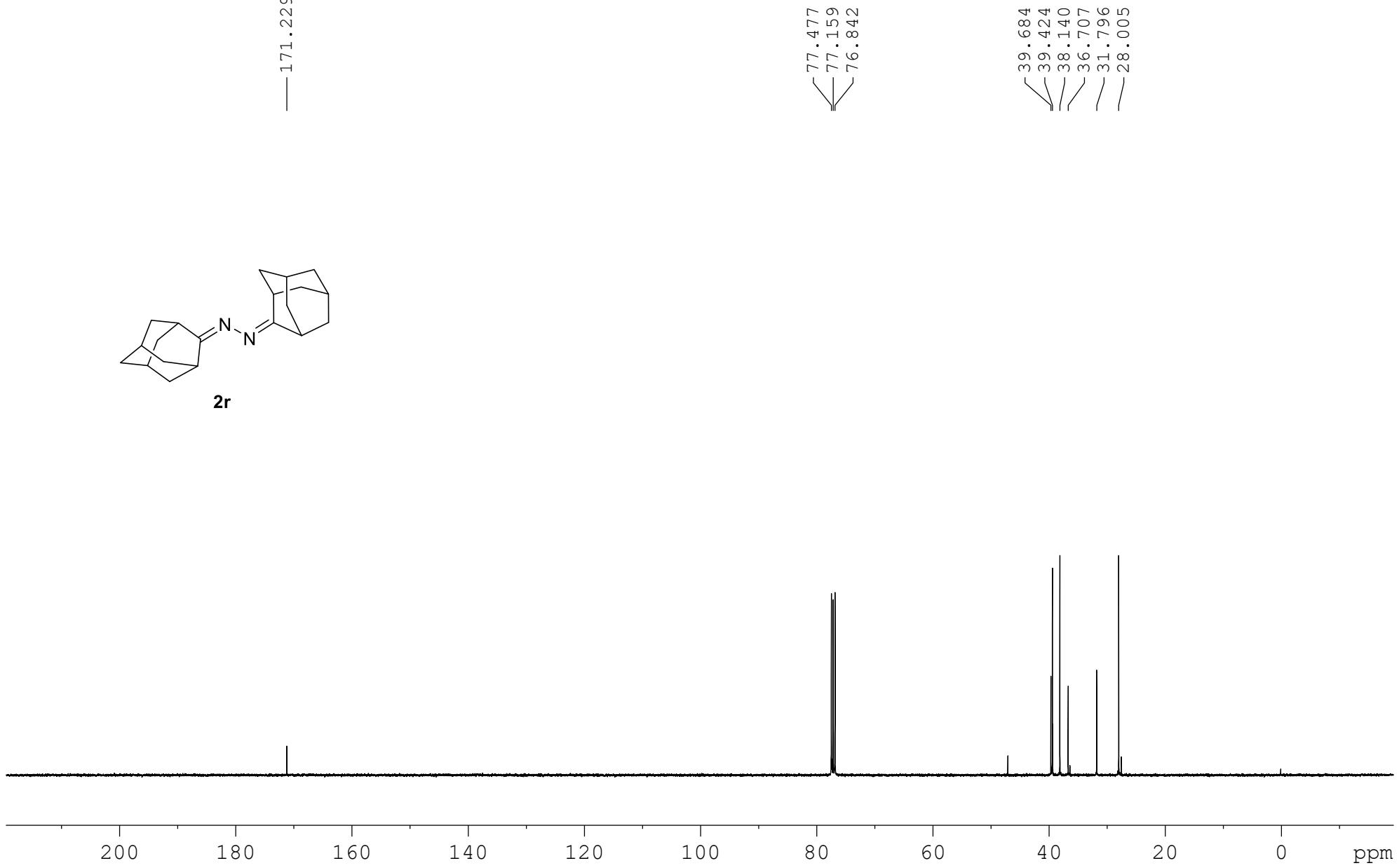
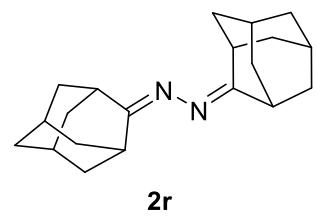


Figure S91. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2r** (CDCl_3 , 100 M).

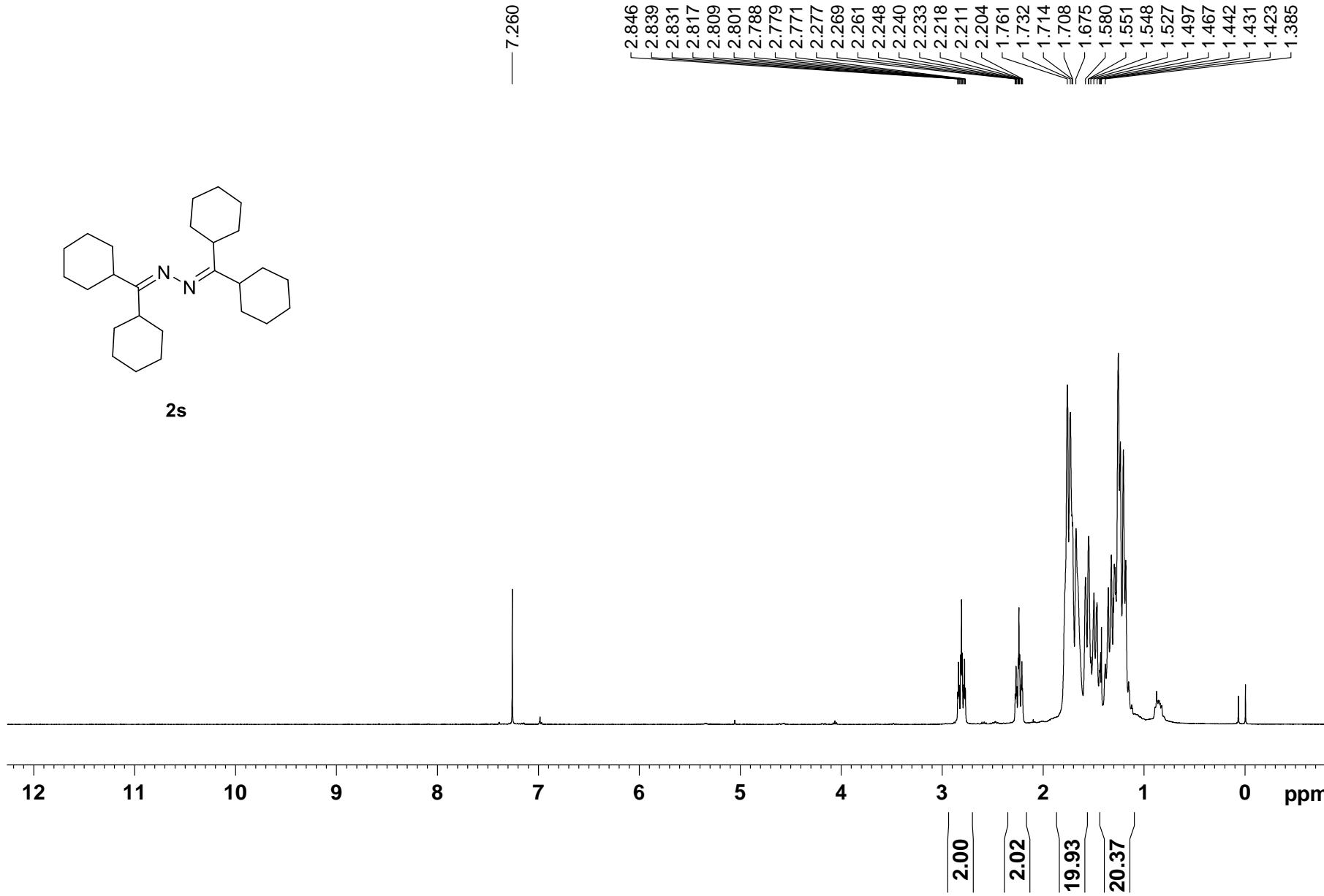
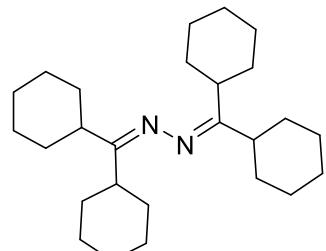


Figure S92. ^1H NMR spectrum of **2s** (CDCl_3 , 400M).



2s

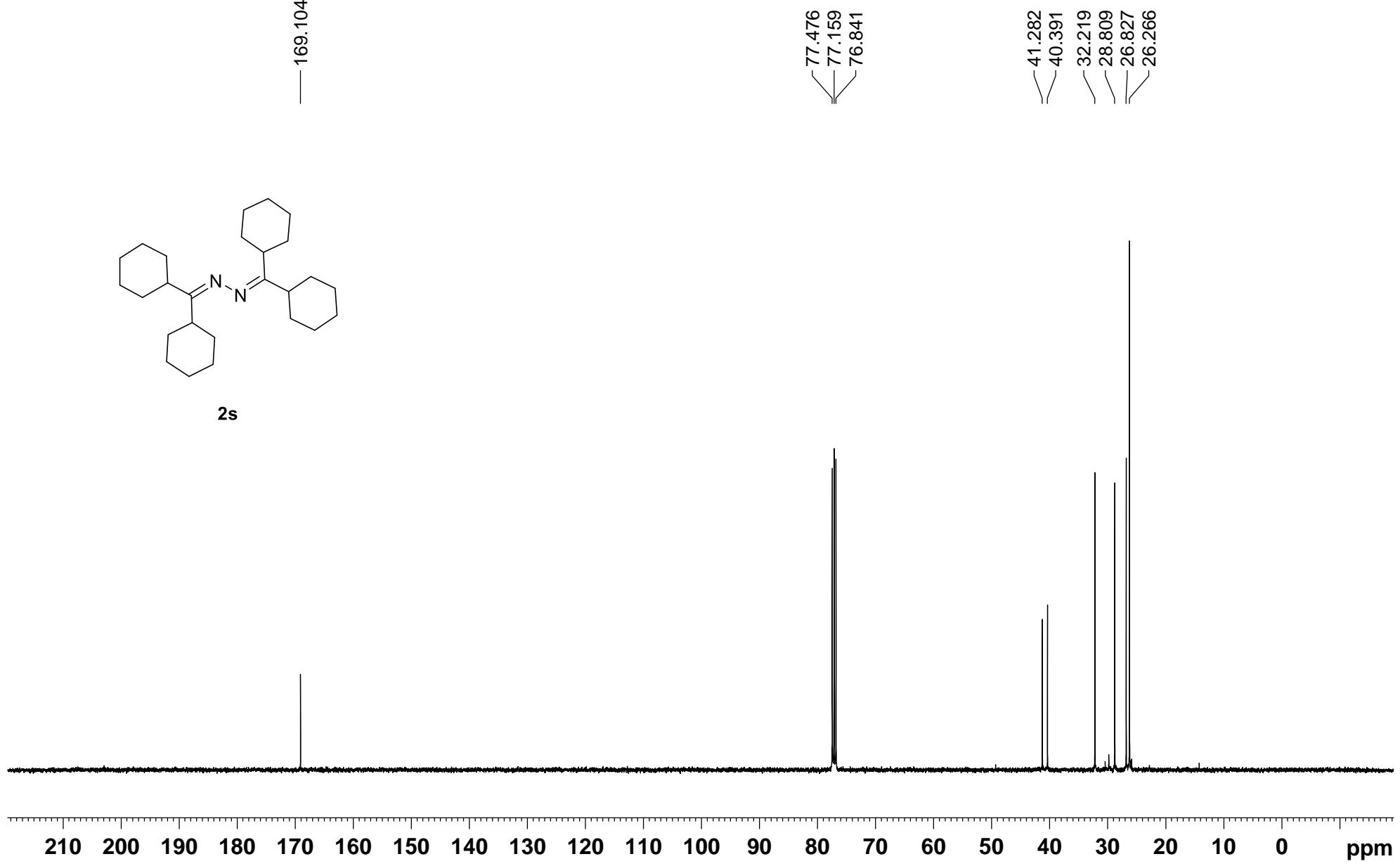


Figure S93. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2s** (CDCl_3 , 100 M).

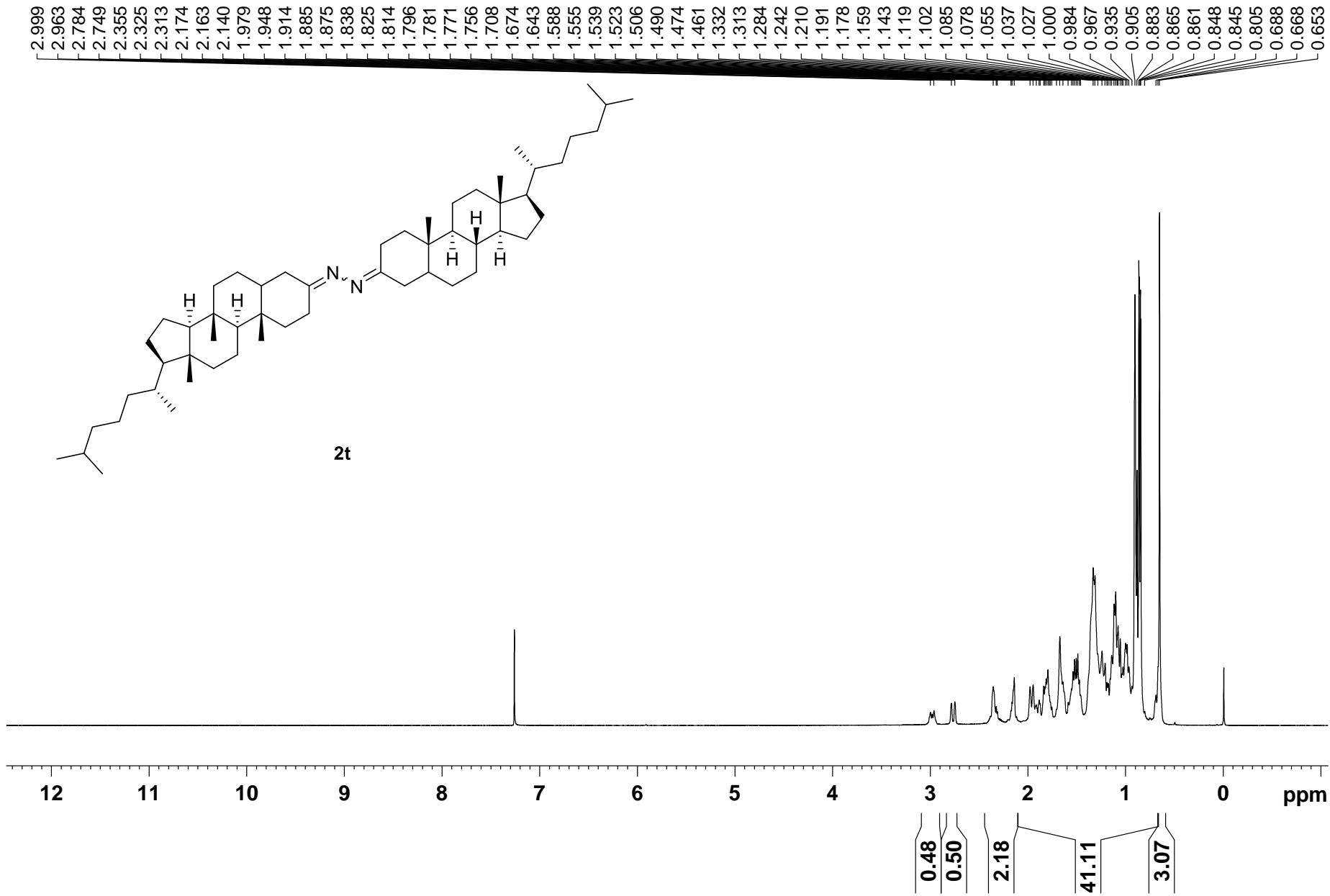


Figure S94. ^1H NMR spectrum of **2t** (CDCl_3 , 400 M).

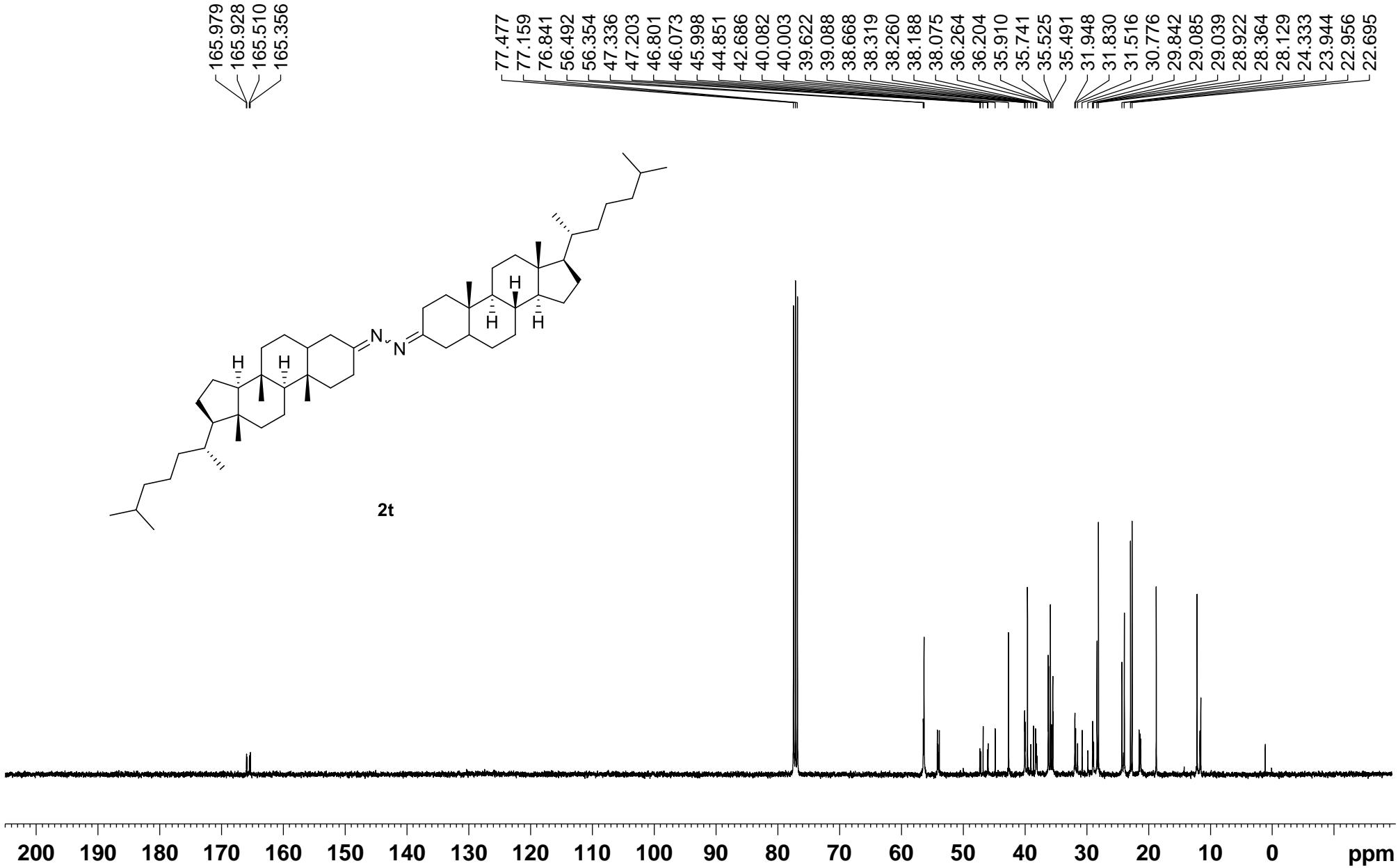
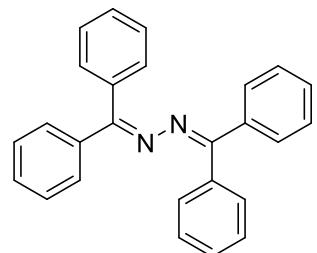


Figure S95. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2t** (CDCl_3 , 100 M).



2u

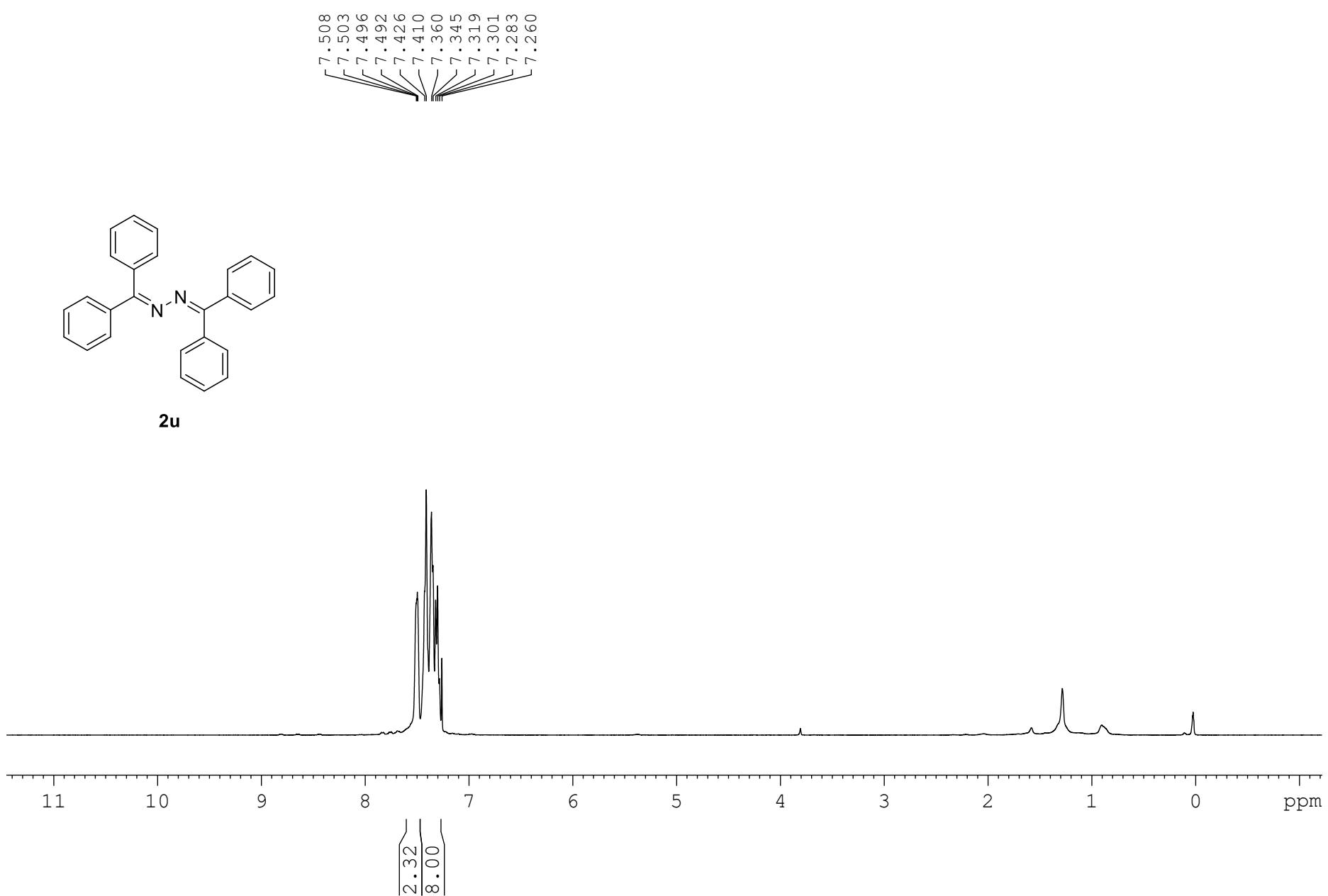


Figure S96. ¹H NMR spectrum of **2u** (CDCl₃, 400 MHz).

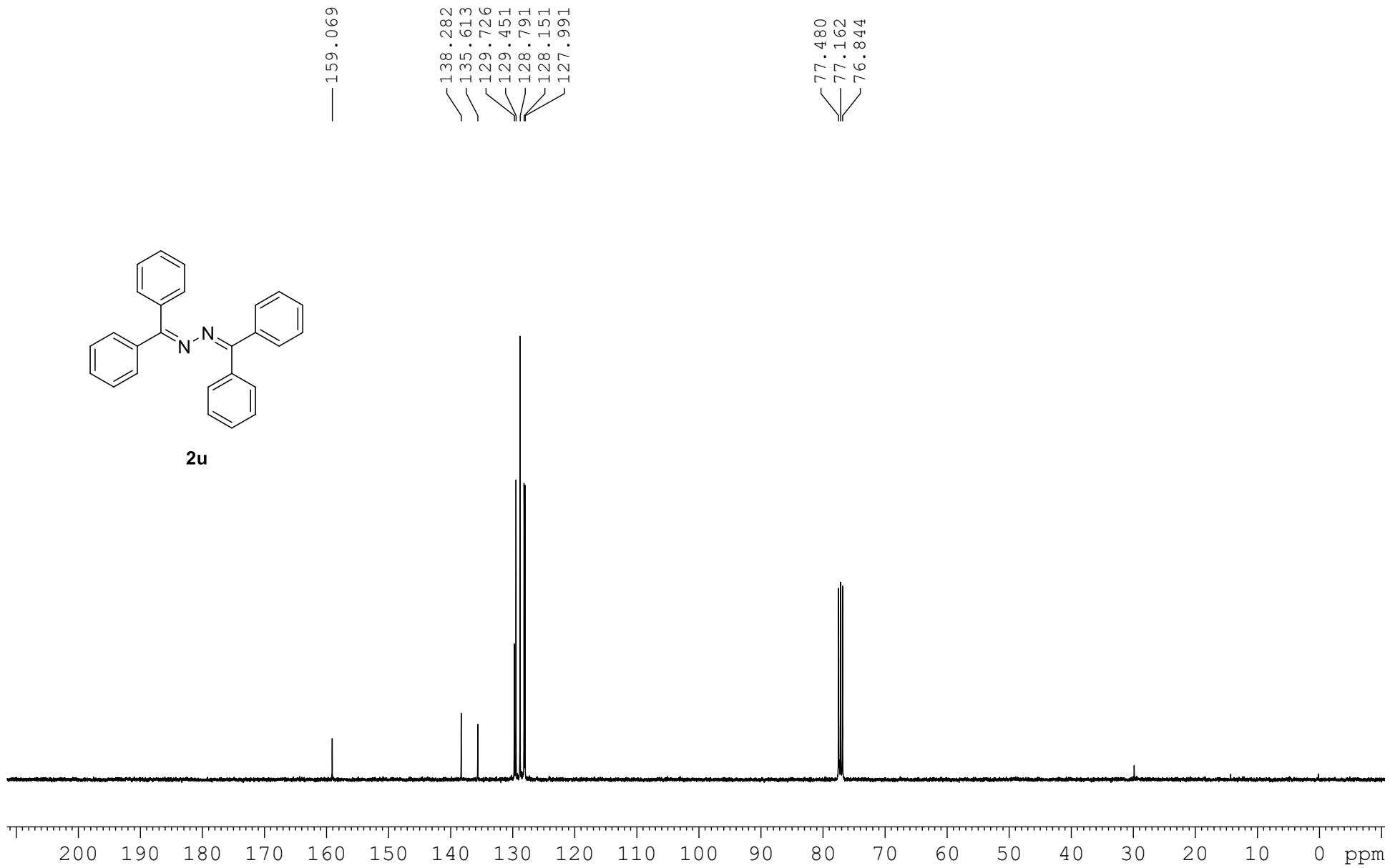


Figure S97. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2u** (CDCl_3 , 100 M).

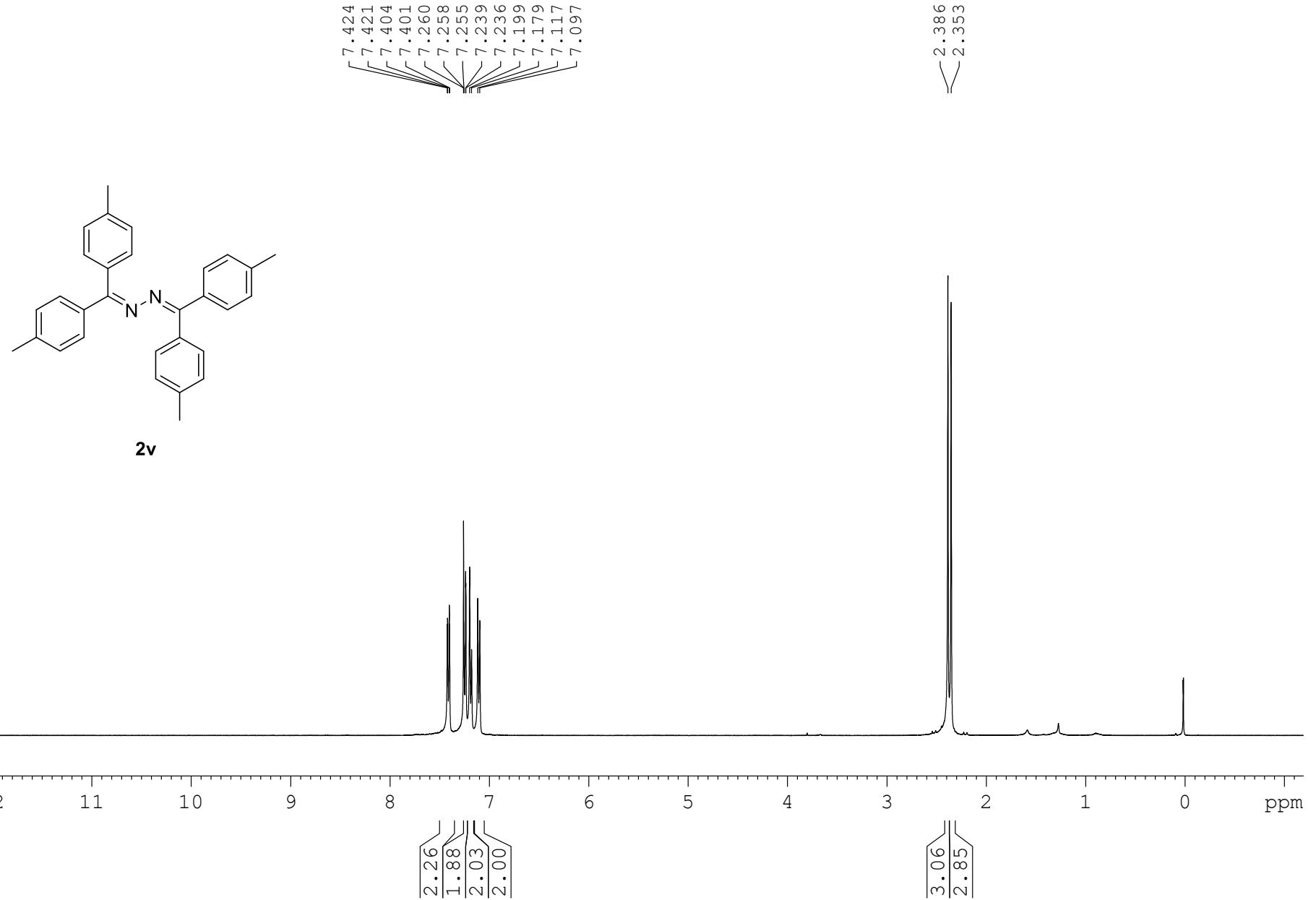


Figure S98. ^1H NMR spectrum of **2v** (CDCl_3 , 400 M).

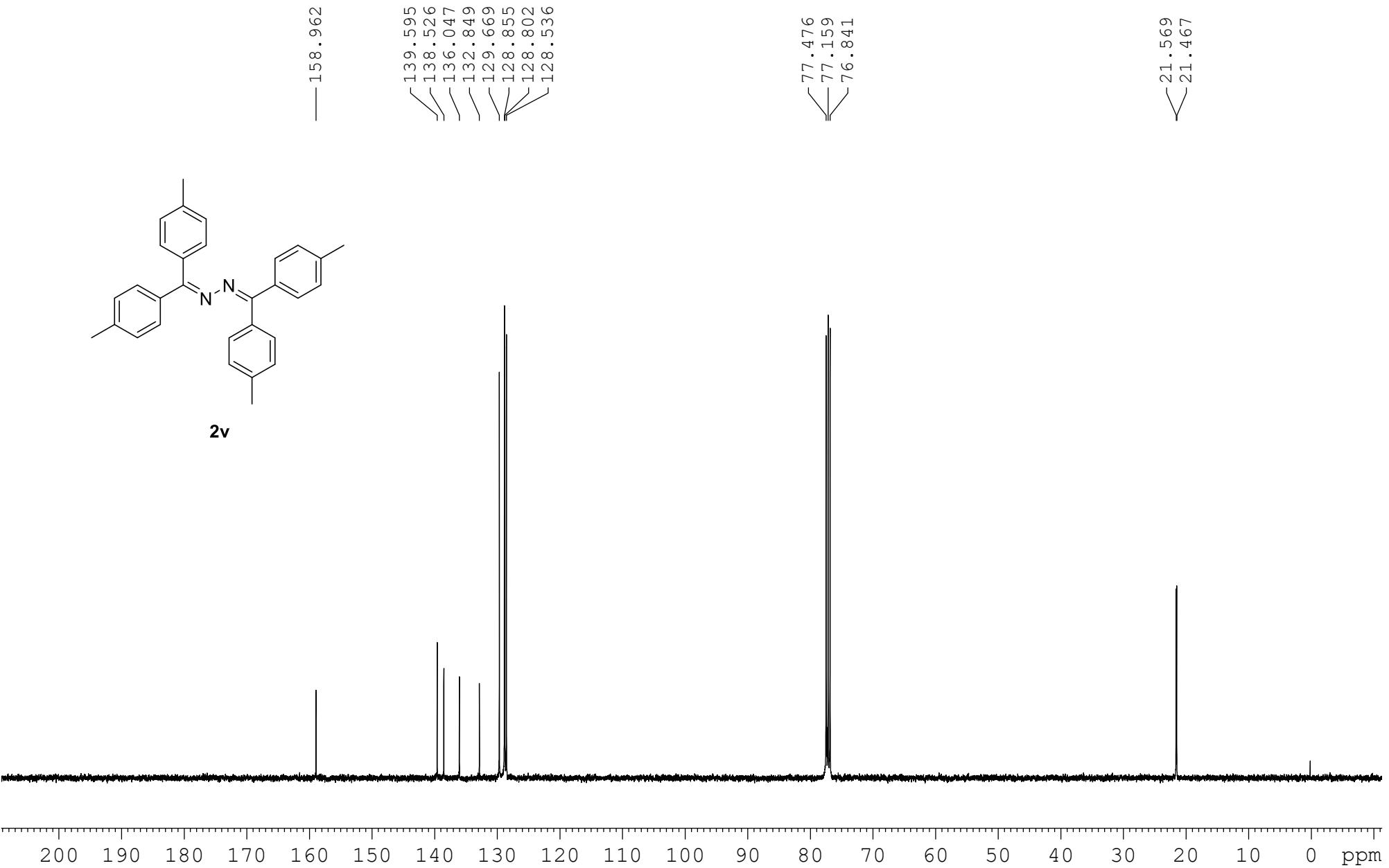


Figure S99. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2v** (CDCl_3 , 100 M).

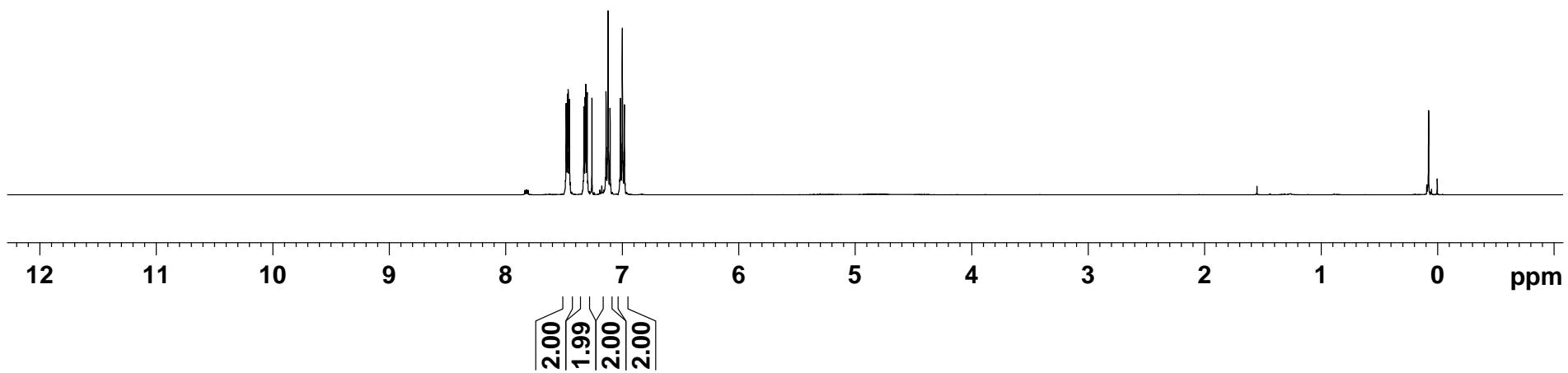
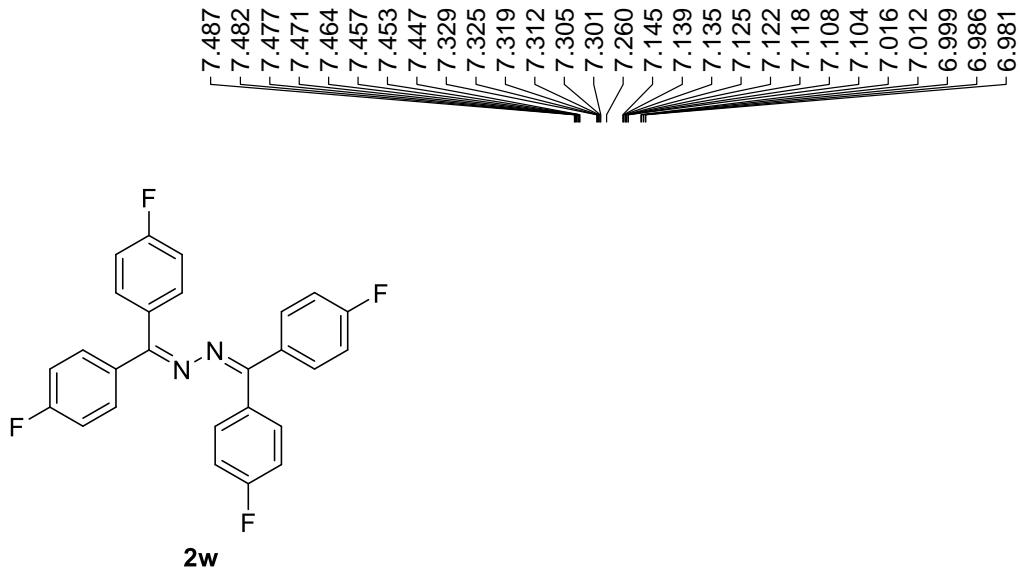


Figure S100. ¹H NMR spectrum of **2w** ($CDCl_3$, 500 M).

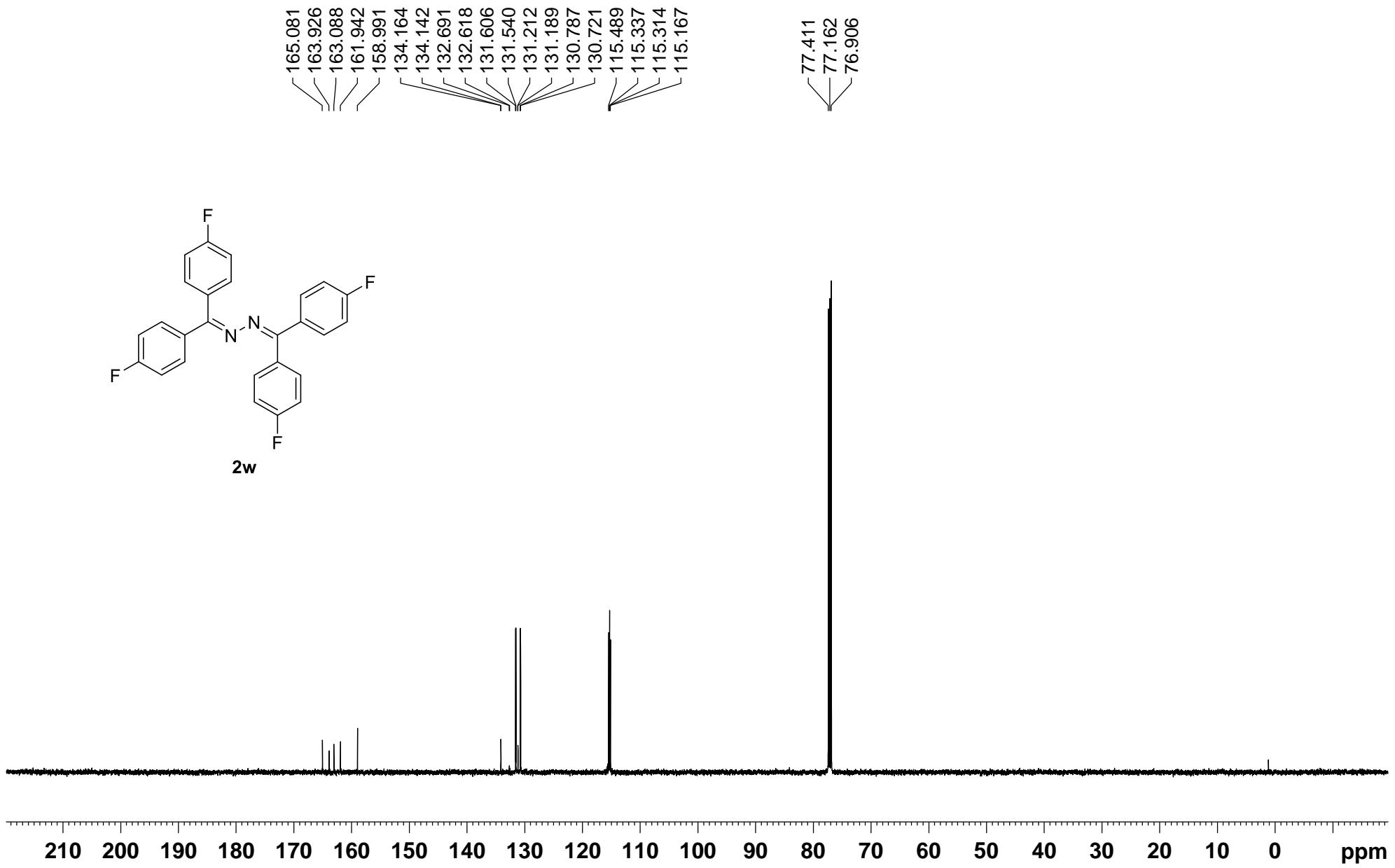
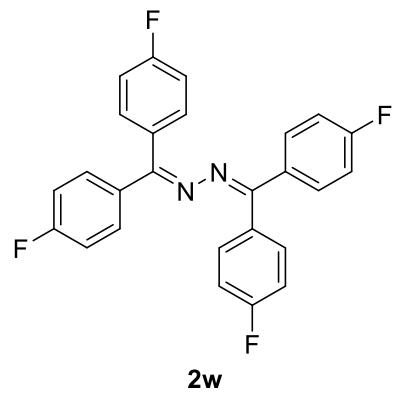


Figure S101. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2w** (CDCl_3 , 125 M).



-110.465
-111.247

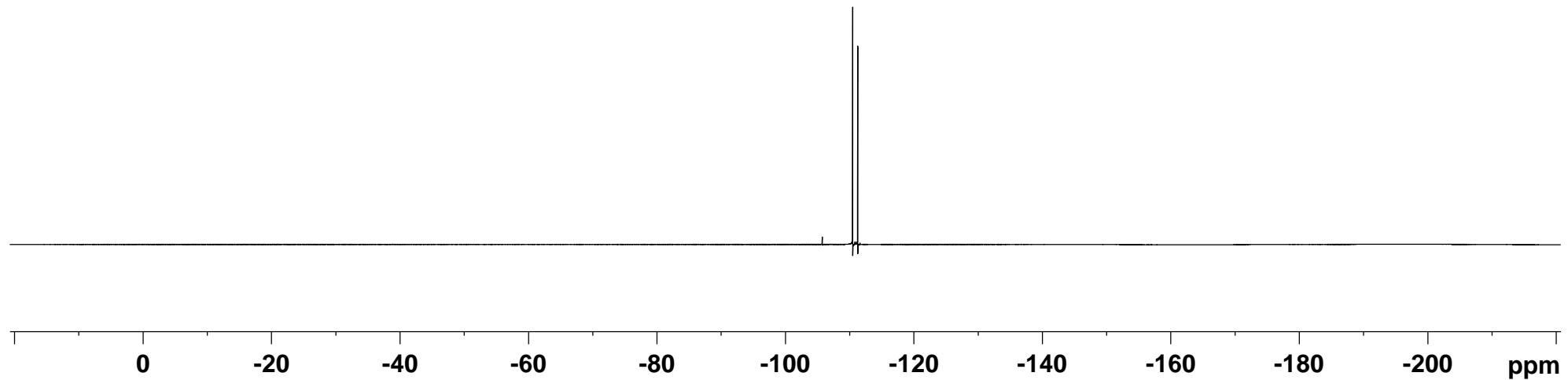


Figure S102. ^{19}F NMR spectrum of **2w** (CDCl_3 , 471 M).

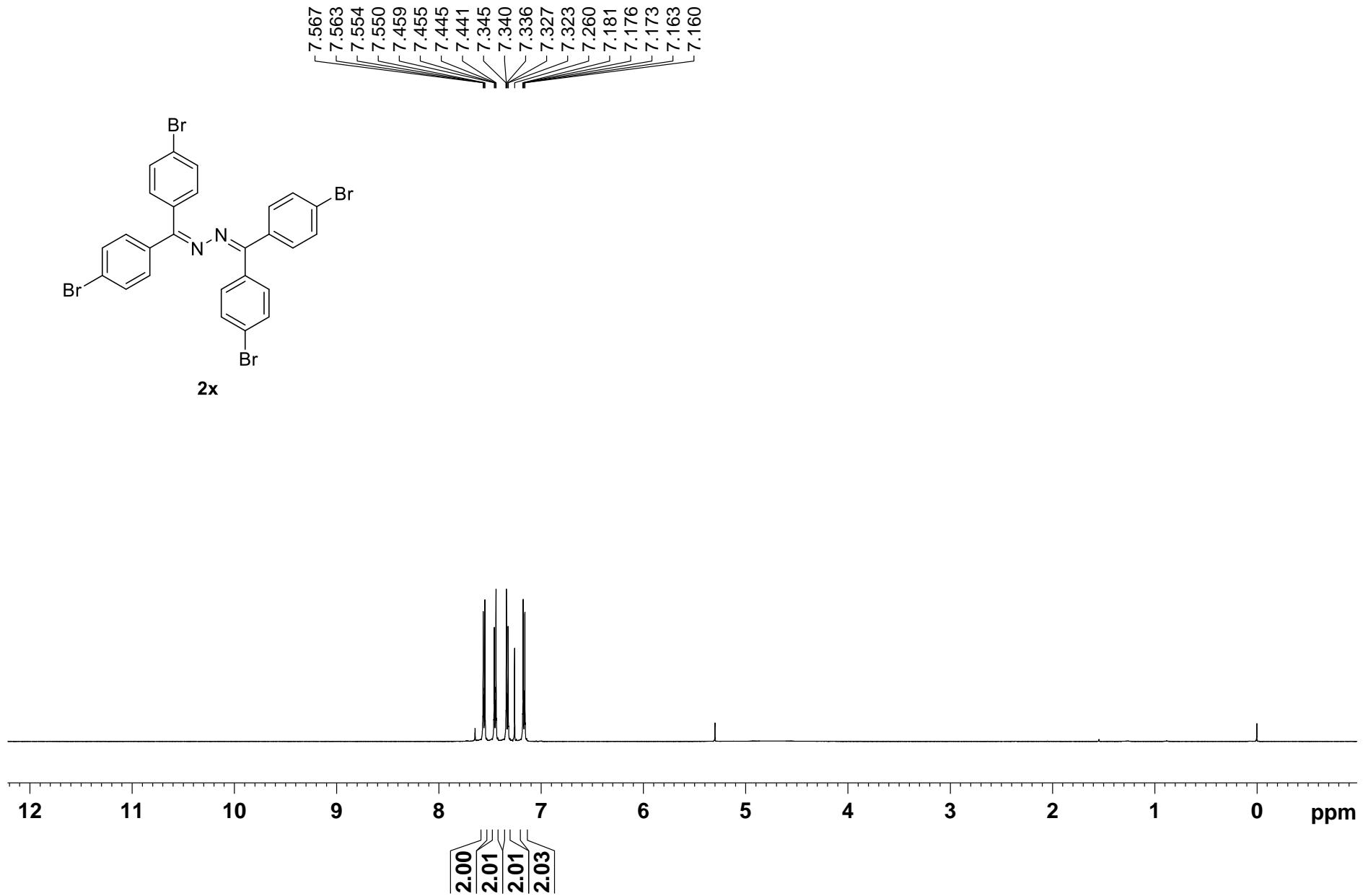
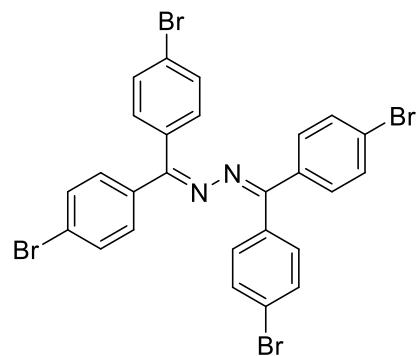


Figure S103. ^1H NMR spectrum of **2x** (CDCl_3 , 500 M).

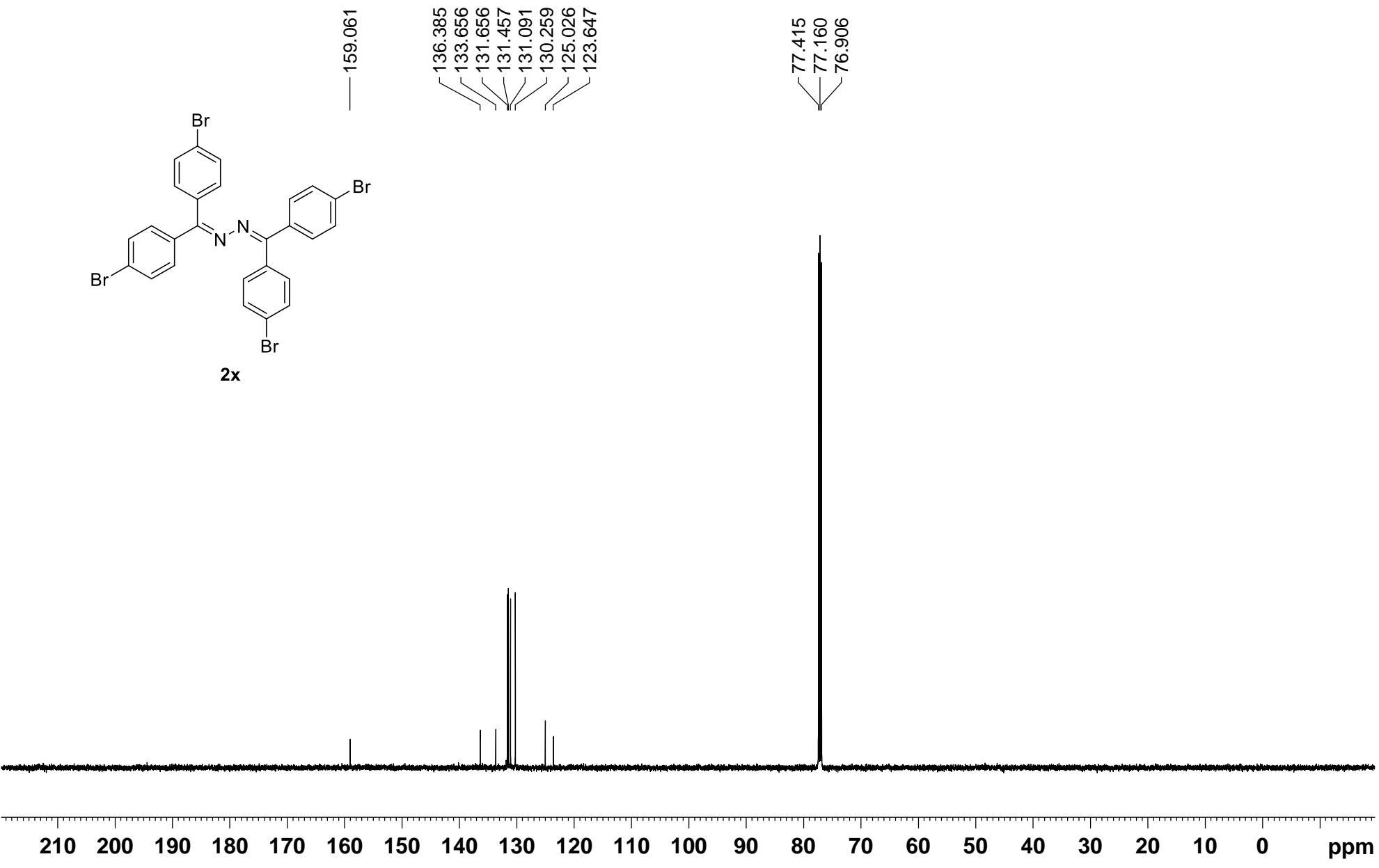


Figure S104. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2x** (CDCl₃, 125 M).

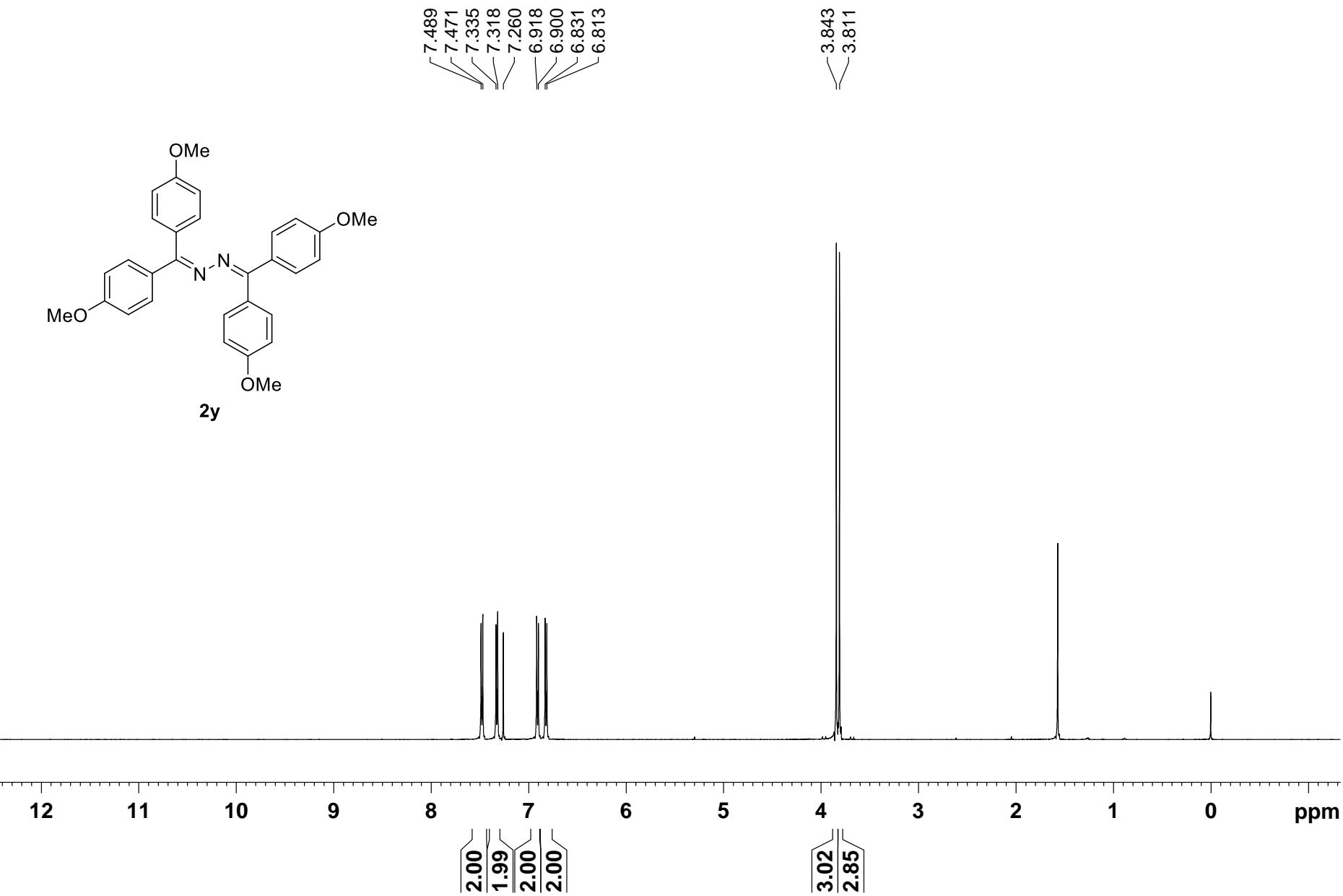


Figure S105. ¹H NMR spectrum of **2y** (CDCl₃, 500 M).

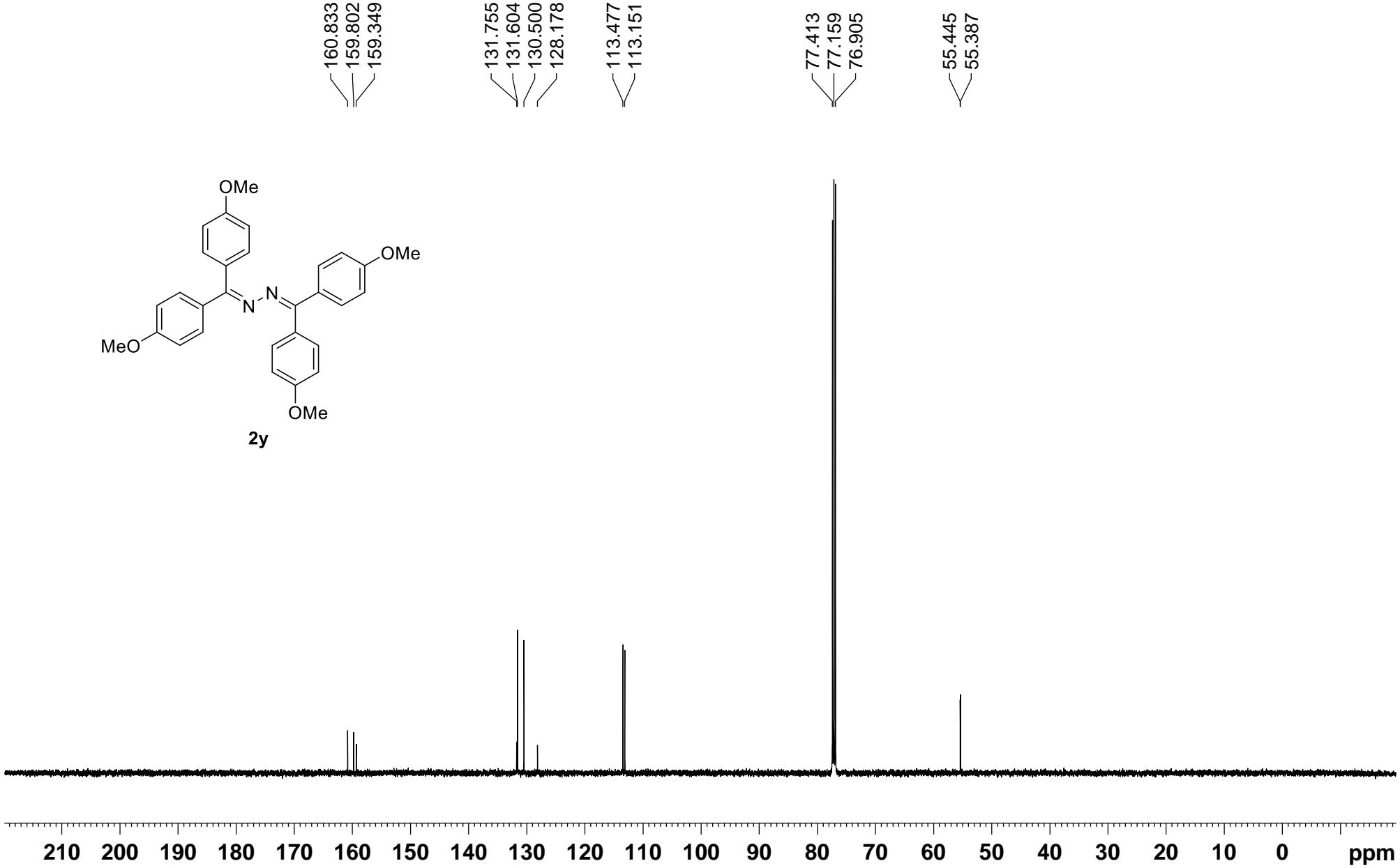
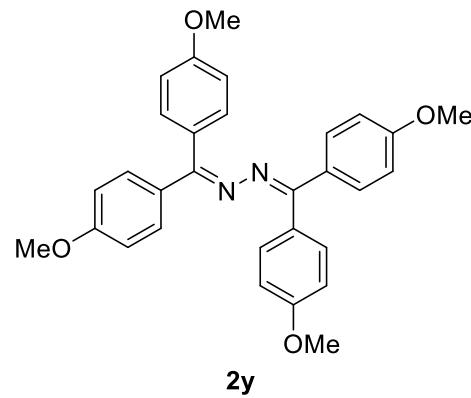


Figure S106. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2y** (CDCl_3 , 125 M).

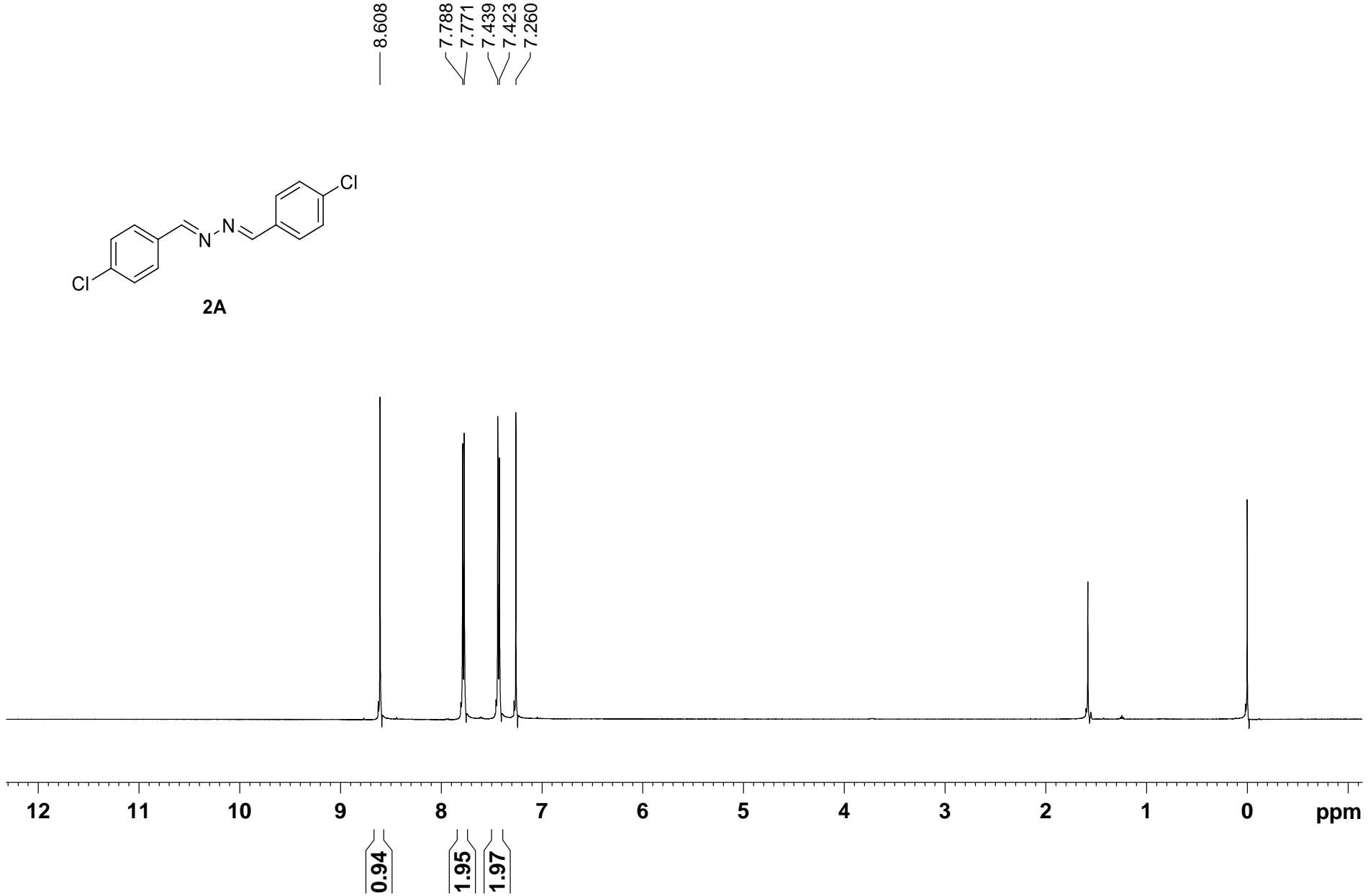
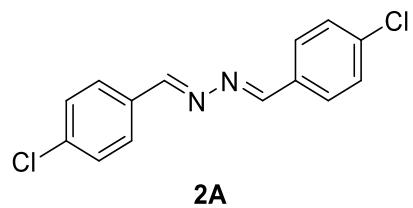


Figure S107. ¹H NMR spectrum of **2A** (CDCl_3 , 500 M).

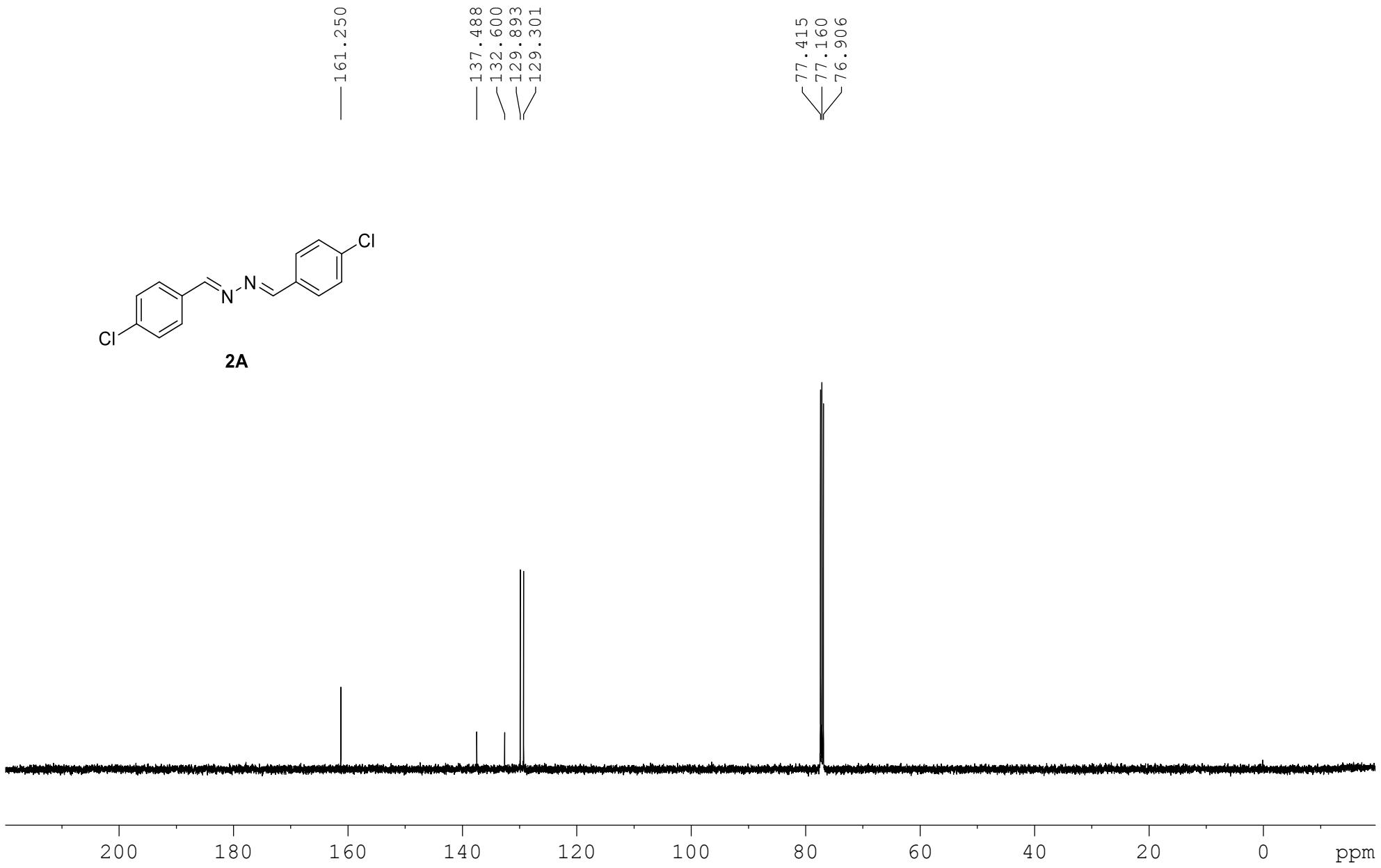
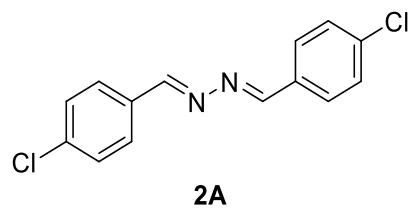


Figure S108. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2A** (CDCl_3 , 125 M).

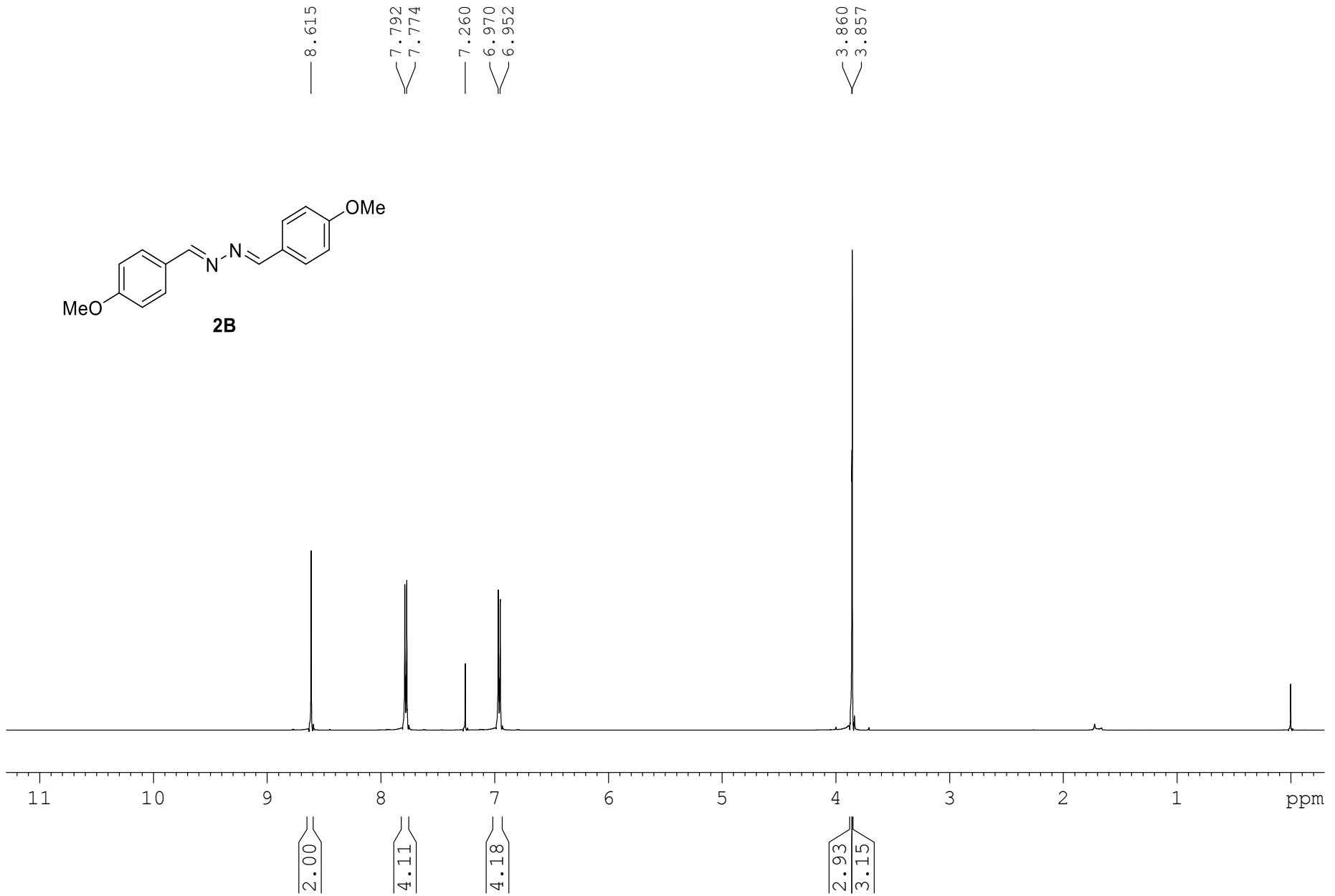


Figure S109. ^1H NMR spectrum of **2B** (CDCl_3 , 500 M).

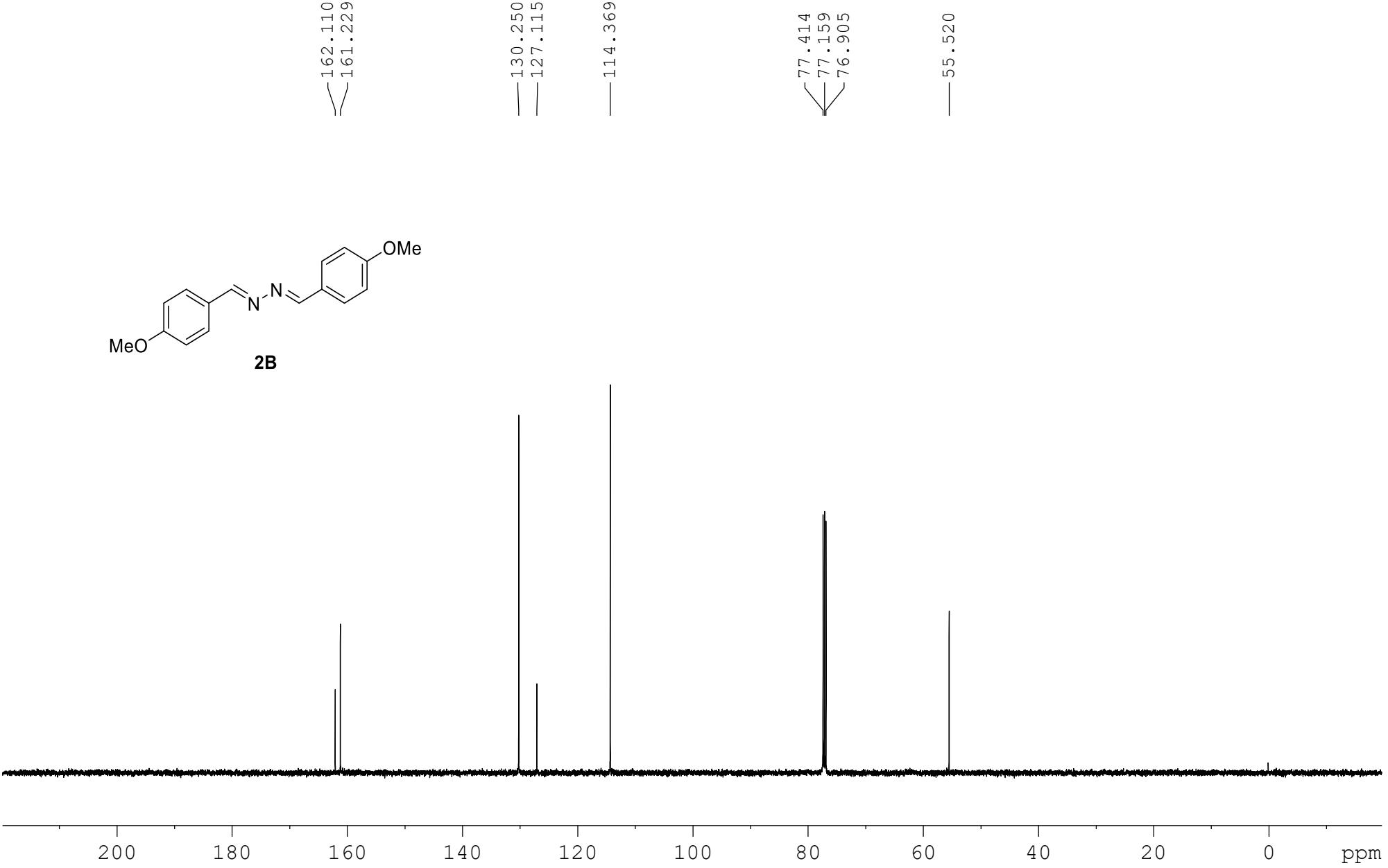
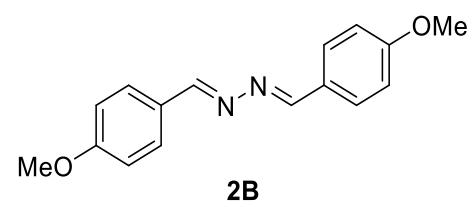


Figure S110. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2B** (CDCl_3 , 125 M).

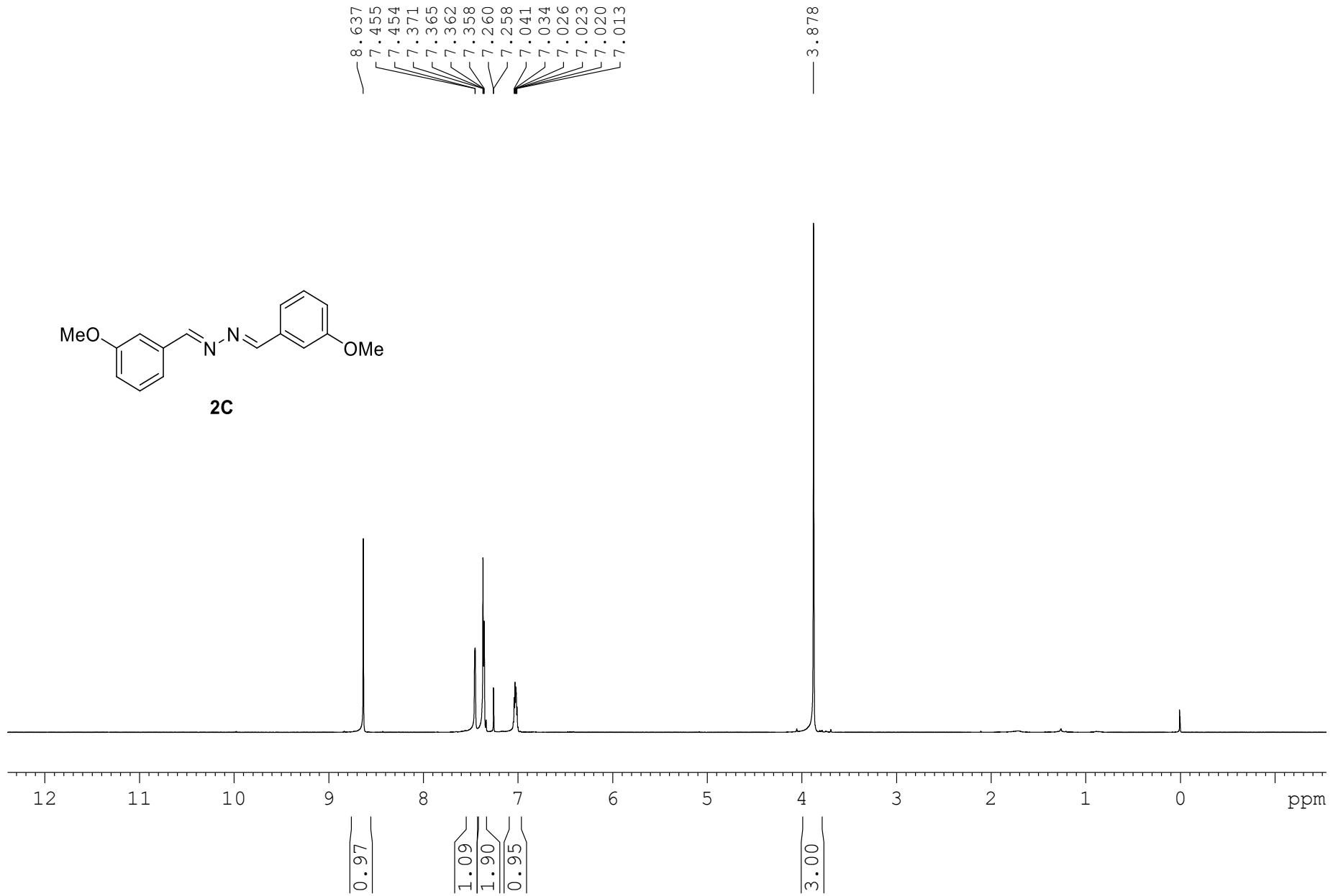
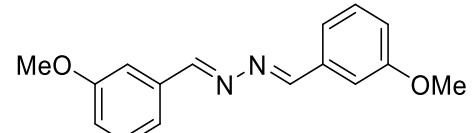


Figure S111. ^1H NMR spectrum of **2C** (CDCl_3 , 400 M).



2C

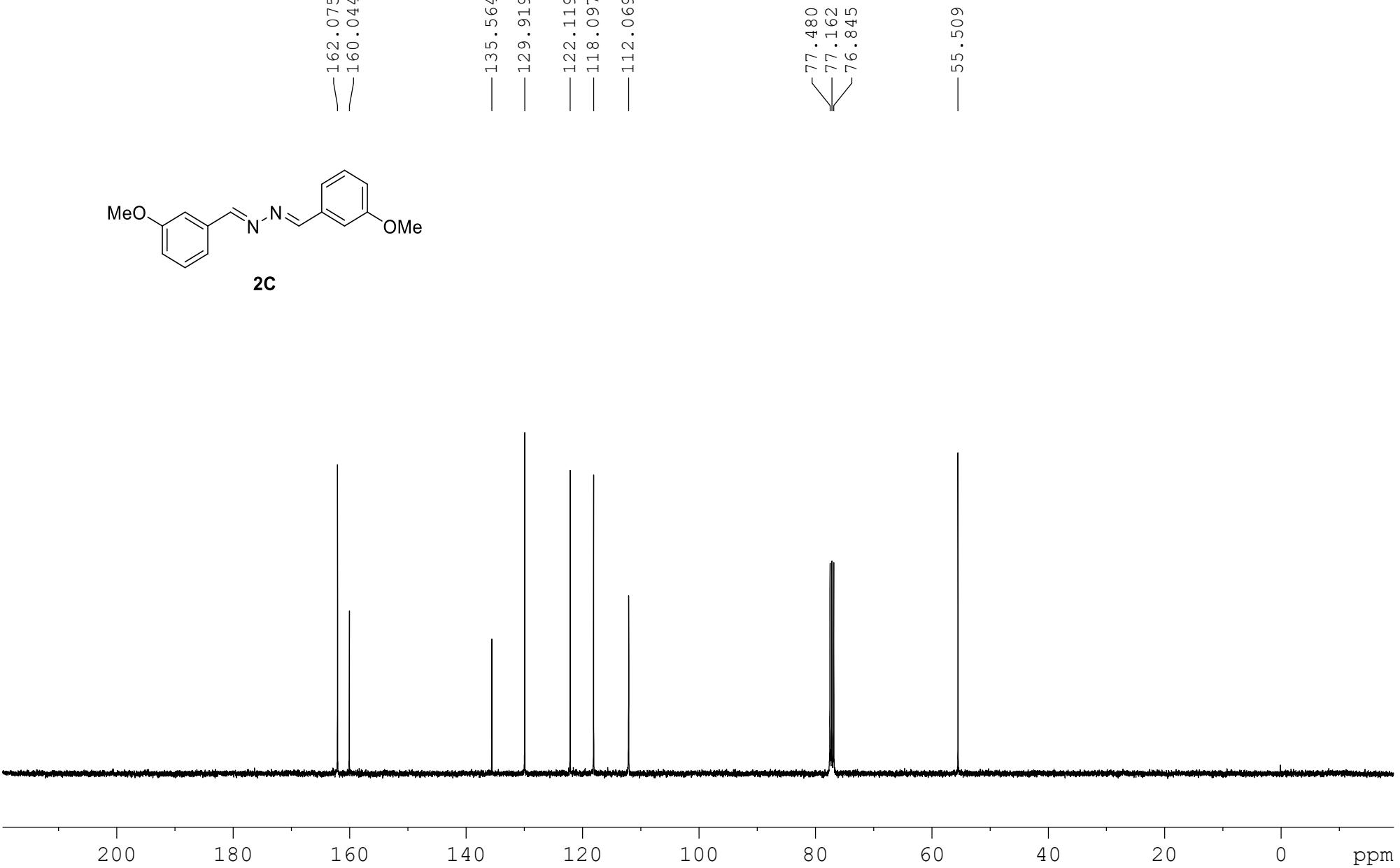


Figure S112. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2C** (CDCl_3 , 100 M).

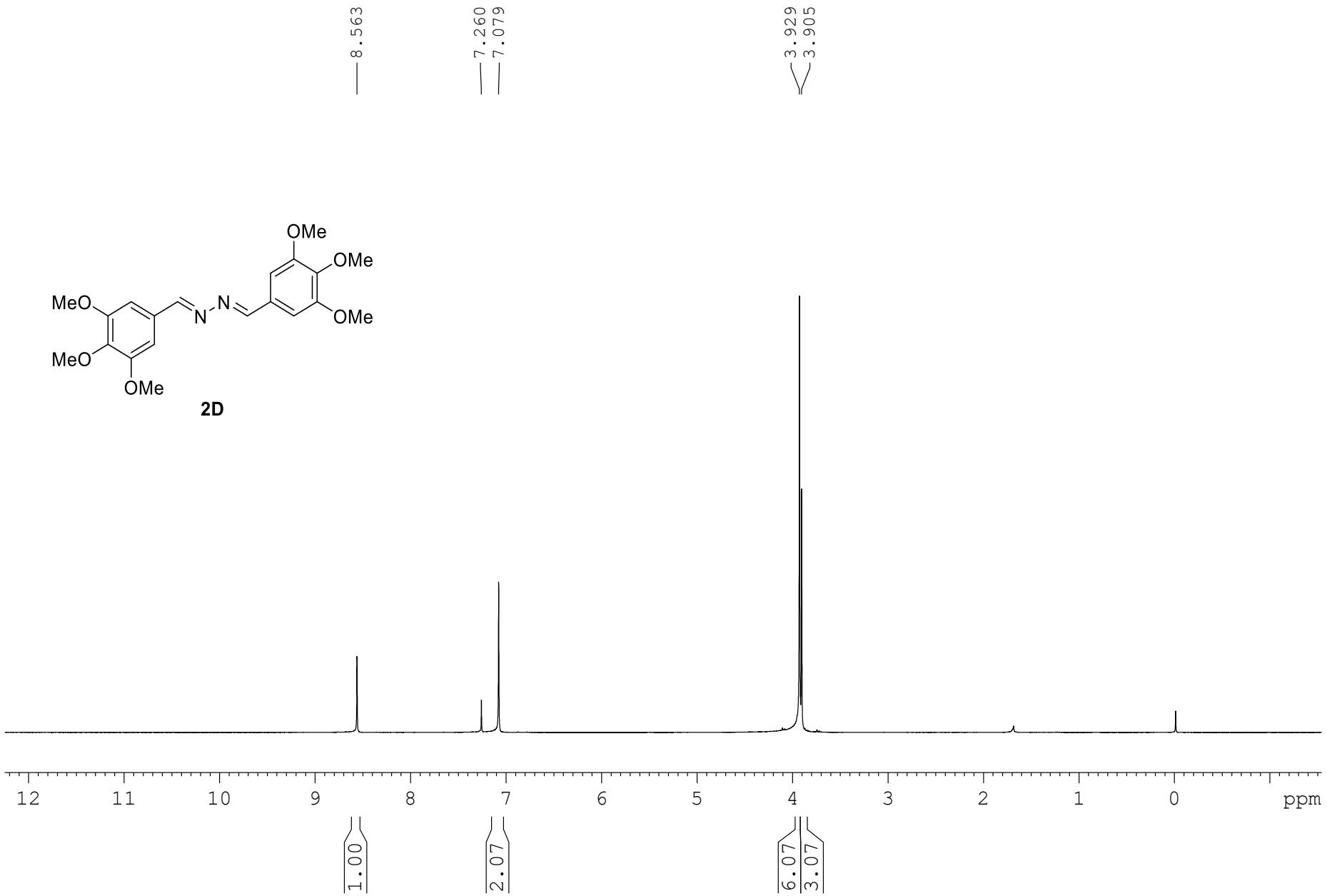


Figure S113. ^1H NMR spectrum of **2D** (CDCl_3 , 400 M).

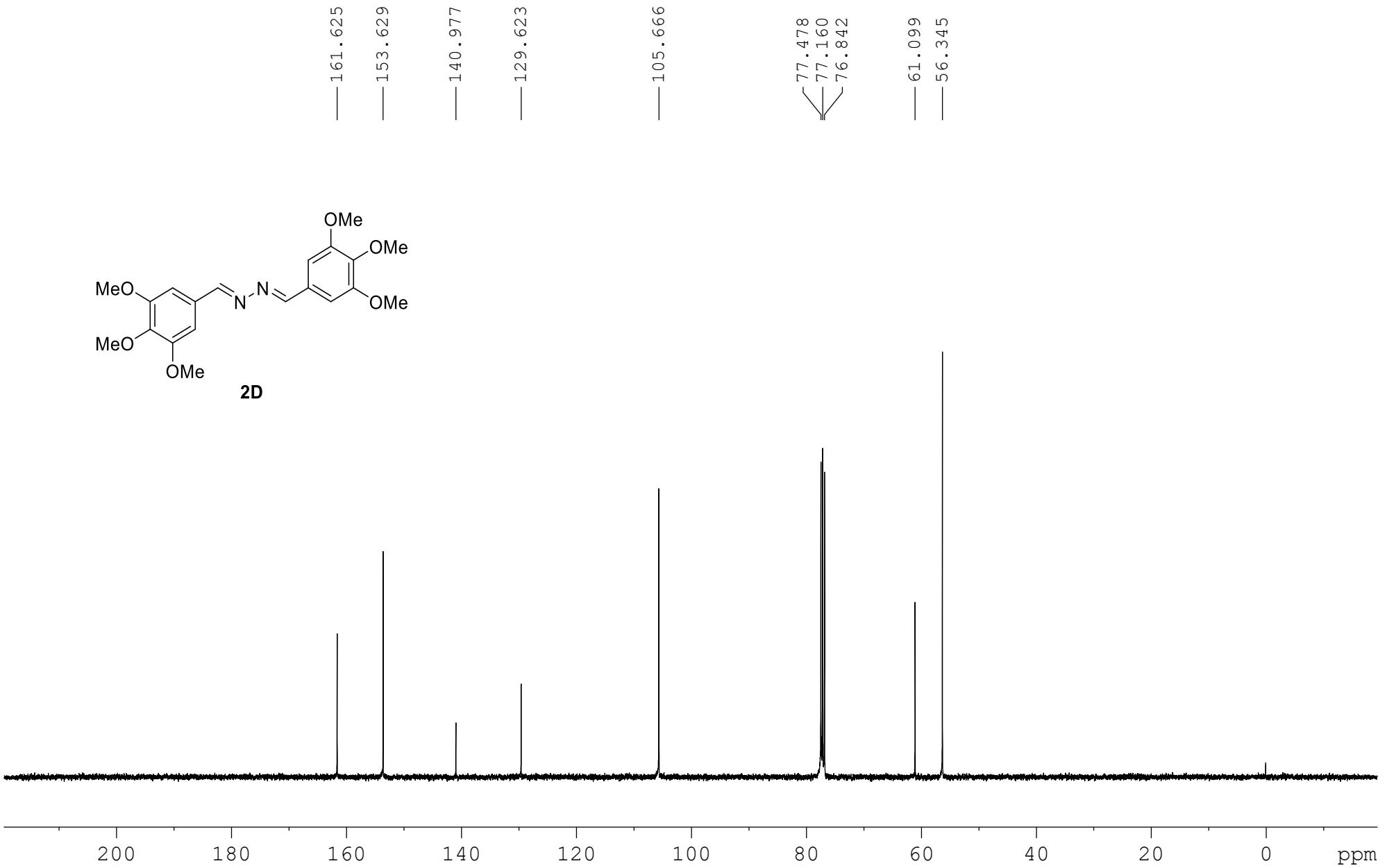
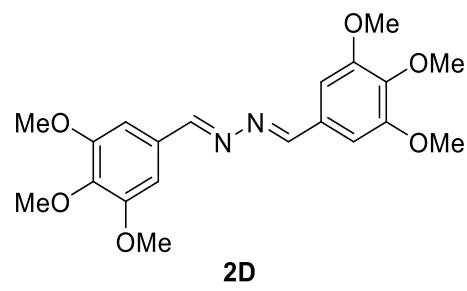


Figure S114. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2D** (CDCl_3 , 100 M).

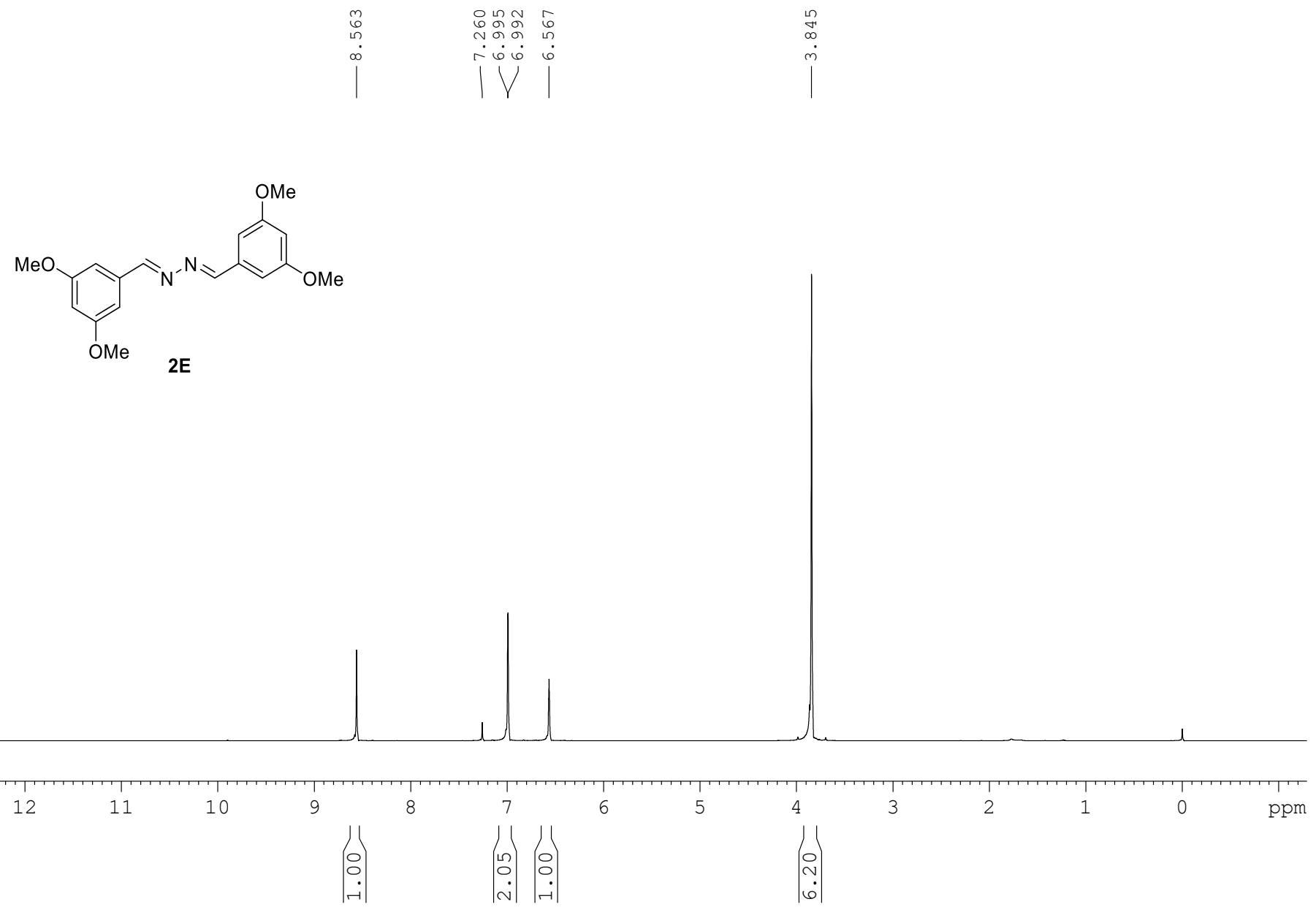


Figure S115. ^1H NMR spectrum of **2E** (CDCl_3 , 500 M).

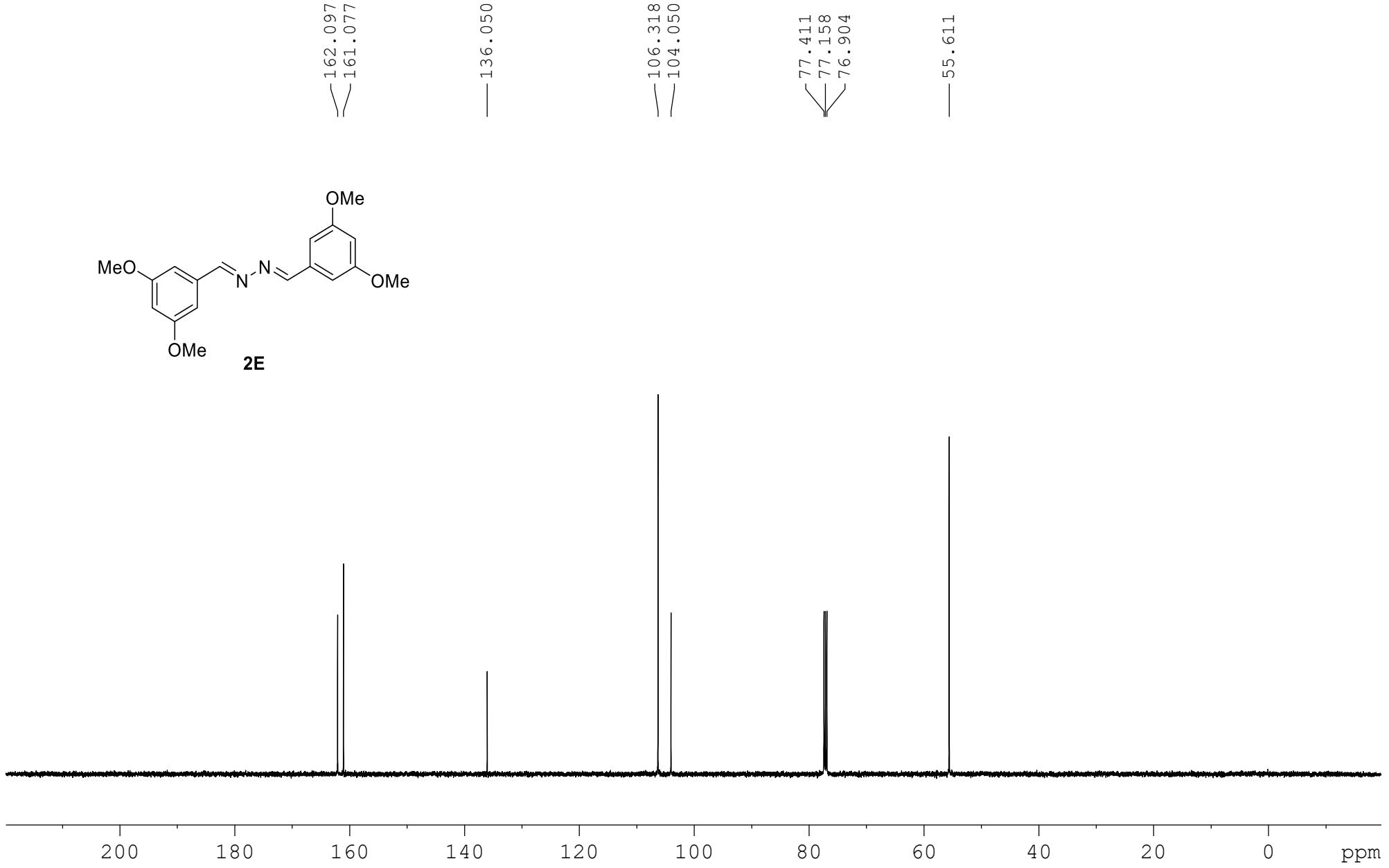
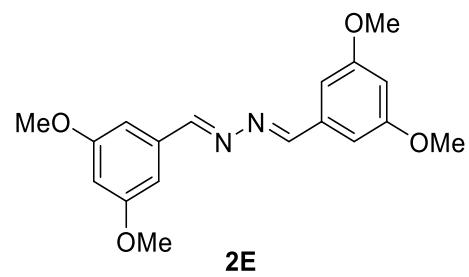


Figure S116. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2E** (CDCl_3 , 125 M).

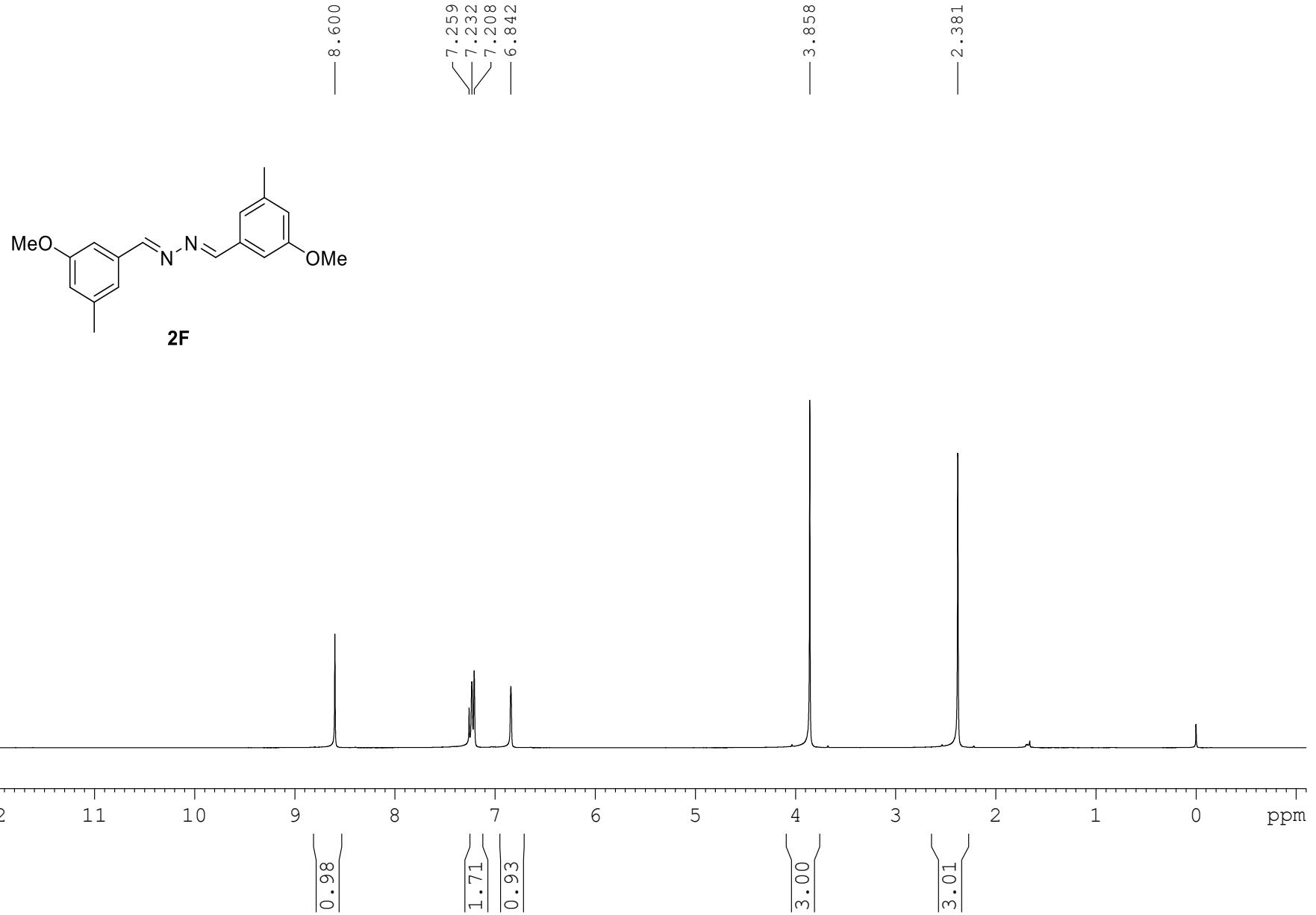
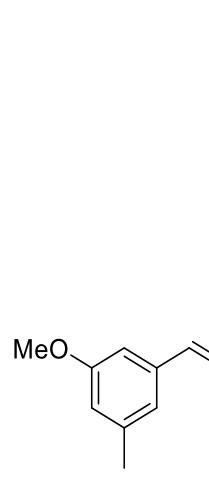


Figure S117. ¹H NMR spectrum of **2F** (CDCl₃, 400 M).



2F

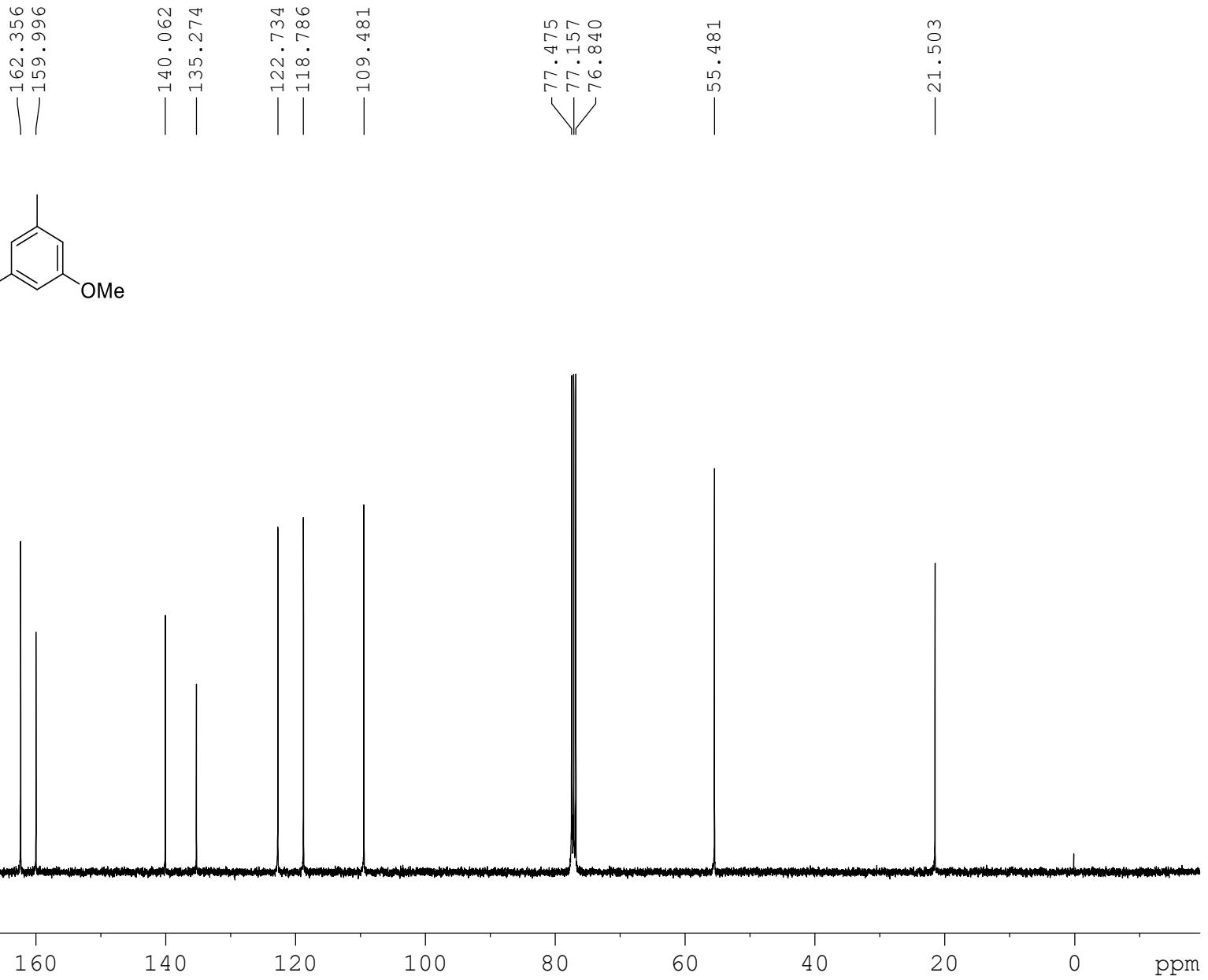


Figure S118. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **2F** (CDCl_3 , 100 M).