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An efficient synthesis of indolo[3,2-*a*]carbazoles *via* the novel acid catalyzed reaction of indoles and diaryl-1,2-diones†

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A mild and efficient one pot method for the synthesis of indolo[3,2-*a*]carbazole derivatives by the *para*-toluenesulfonic acid catalyzed condensation of indole with acyclic 1,2-diones is described. With cyclobutene-1,2-diones the reaction afforded indole substituted carbazole derivatives in good yield.

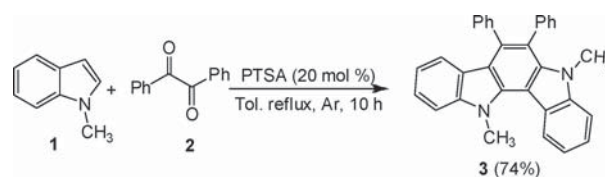
Introduction

The indolocarbazole framework is present in a number of alkaloids which exhibit potent biological activities.¹ *Inter alia*, these include antitumor, antihistaminic and antimicrobial activities.² It is also noteworthy that, by virtue of their thermal stability, intense luminescence and other desirable properties, carbazole derivatives have been widely used in molecular electronics.³ Their potential applications as organic LEDs,⁴ high performance p-channel semiconductors and thin film transistors are also worthy of mention.⁵

Of the five isomeric forms of indolocarbazoles,¹ the [3,2-*a*]carbazole framework has received the least attention, presumably because of its limited access from natural sources and the lack of efficient methods for its synthesis. In this context, the recent one pot synthesis of the related indolo[3,2-*b*]carbazoles is noteworthy.⁶ The first report on the natural occurrence of an indolo[3,2-*a*]carbazole consists of the isolation of acorinazole by Bergman *et al.*, from a marine sponge *Ancorina* species.⁷ In 1951, Tomlinson reported the first synthesis of indolo[3,2-*a*]carbazole by the double Fischer indolization of bis(cyclohexanone)-*m*-phenylenedihydrazone.⁸ Subsequently, Hall and Plant reported another method for the synthesis of indolocarbazole by heating 5-aminotetrahydrocarbazole with 2-chlorocyclohexanone.⁹ In spite of the large amount of work on the synthesis of carbazoles,¹⁰ no direct and efficient method for the synthesis of indolo[3,2-*a*]carbazole derivatives has been reported. In the context of our interest in the chemistry of 1,2-diones¹¹ we surmised that a condensation of these with indole, if successful, would provide a direct route to the synthesis of indolo[3,2-*a*]carbazole. Surprisingly, such a simple protocol has not been reported.

Results and discussion

Against this background, our studies were initiated by heating a solution of benzil and *N*-methylindole in dry toluene under reflux in the presence of *para*-toluenesulfonic acid (20 mol%) for 10 h. The reaction mixture, on processing, afforded a product in 74% yield which was characterized as the indolo[3,2-*a*]carbazole **3** (Scheme 1)



Scheme 1 Reaction of *N*-methyl indole with benzil.

The product was characterized on the basis of spectroscopic data. In the ¹H NMR the two methyl protons resonated at δ 4.51 and 3.28 ppm and, in the ¹³C NMR, the signals at δ 35.7 and 33.2 ppm correspond to the two methyl carbons. The high resolution mass spectrum was also in accordance with the assigned structure. Unambiguous evidence for the structure of the compound **3** was confirmed by single crystal X-ray analysis (Fig. 1)‡

The reaction was investigated with various Lewis and Brønsted acids and the results are shown in Table 1. It appears that PTSA is the best catalyst for the condensation reaction.

The reaction appears to be general with the analogs of benzil and the results are presented in Table 2. Similar reactivity was also observed in the reaction of indole with 2,3-butanedione **21**, but the product **22** was obtained in low yield.

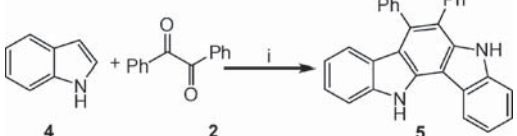
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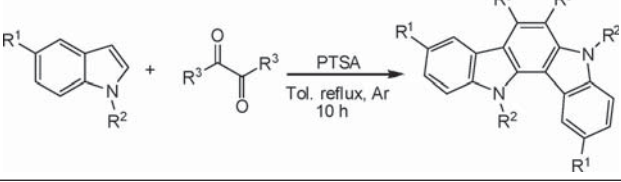
† CCDC reference numbers 658189 and 659431. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b803009j

‡ Crystal data for compound **3**: C₃₂H₂₄N₂, *M*_r = 436.53, triclinic, space group *P*-1, *a* = 9.819(3), *b* = 11.498(3), *c* = 11.946(3) Å, *a* = 68.553(4), *β* = 69.635(4), *γ* = 69.955(4)°, *V* = 1140.4(5) Å³, *Z* = 2, *ρ*_{calcd} = 1.271 g cm⁻³, *μ* = 0.074 mm⁻¹, *T* = 293(2) K, reflections collected = 7966, independent reflections = 3975, *R*_{int} = 0.0295, *R*₁ = 0.0591, *wR*₂ = 0.1389 [*I* > 2σ(*I*)]. CCDC-658189.† These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

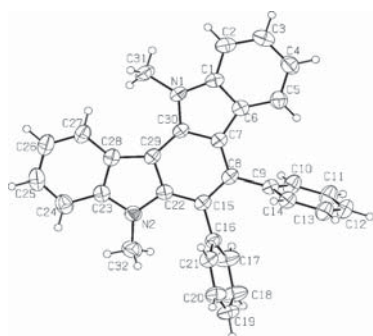
Table 1 Condensation reaction of indole and benzil with different catalysts


Entry	Acids	Mol %	Product %
1	PTSA	20 mol %	62%
2	AuCl ₃	1 mol %	58%
3	Cu(OTf) ₃	20 mol %	57%
4	Yb(OTf) ₃	20 mol %	28%
5	SnCl ₄	20 mol %	29%
6	Sc(OTf) ₃	20 mol %	52%
7	BF ₃ OEt	20 mol %	No reaction

i = catalyst, toluene, reflux, argon, 10 h.

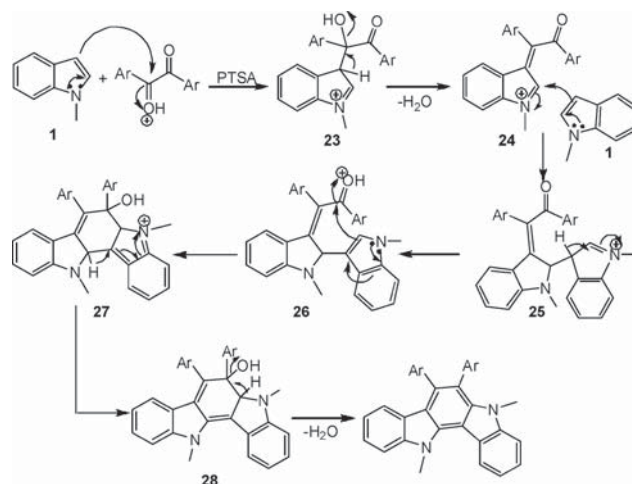
Table 2 Condensation reaction of indole and *N*-substituted indole with various benzils


Entry	R ¹ , R ²	R ³	Product %
1	R ¹ = R ² = H (4)	Phenyl (2)	5 (62)
2	R ¹ = R ² = H (4)	3,4-Dichlorophenyl (6)	7 (76)
3	R ¹ = R ² = H (4)	4-Fluorophenyl (8)	9 (57)
4	R ¹ = H, R ² = CH ₃ (1)	4-Trifluoromethylphenyl (10)	11 (79)
5	R ¹ = H, R ² = CH ₃ (1)	3,4-Dichlorophenyl (6)	12 (67)
6	R ¹ = H, R ² = CH ₃ (1)	4-Bromophenyl (13)	14 (67)
7	R ¹ = H, R ² = allyl (15)	Phenyl (2)	16 (60)
8	R ¹ = H, R ² = ethyl (17)	Phenyl (2)	18 (64)
9	R ¹ = Br, R ² = H (19)	Phenyl (2)	20 (74)
10	R ¹ = R ² = H (4)	Methyl (21)	22 (12)

**Fig. 1** ORTEP diagram for the compound **3** (40% probability factor for the thermal ellipsoids).

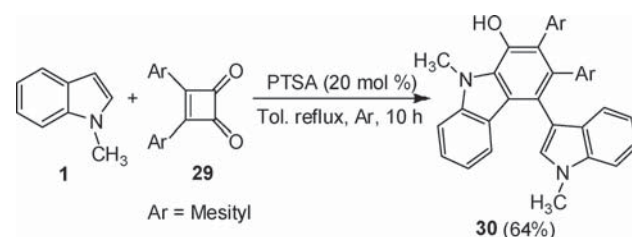
Mechanism

A mechanistic rationalization for the reaction is given in Scheme 2. Indole **1** first reacts with benzil to form the intermediate **23** which loses one molecule of water to form the highly electrophilic species **24**. The latter reacts with another molecule of indole

**Scheme 2** Proposed mechanism for the formation of indolocarbazole.

and subsequent cyclization and aromatization affords the product **3**. The possibility of the diarylation followed by pinacol-type rearrangement is excluded since it will lead to the formation of only indolo[2,3-*a*]carbazole.

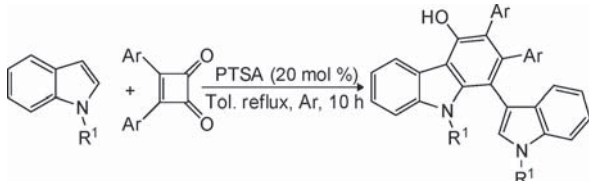
The success of the above reaction prompted us to explore the indole condensation reaction with cyclobutene-1,2-diones. In the event of 3,4-dimesitylcyclobutene-1,2-dione **29** reacting with *N*-methylindole **1** the carbazole derivative **30** was obtained in 64% yield (Scheme 3).

**Scheme 3** Reaction of *N*-methyl indole with cyclobutene-1,2-dione.

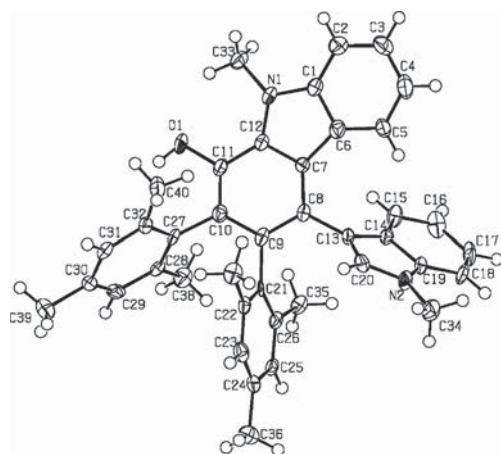
The structure of the product **30** was established on the basis of spectroscopic data. The peak at 3523 cm⁻¹ in the IR is diagnostic of the OH group. In the ¹H NMR the OH proton resonated at δ 5.29 ppm (exchangeable with D₂O) and the two *N*-methyl protons resonated at δ 4.27 and 3.64 ppm. In the ¹³C NMR the signals at δ 29.8 and 29.4 ppm correspond to the two methyl carbons attached to nitrogen. The structure of the compound was finally confirmed by single crystal X-ray analysis (Fig. 2)§

The reaction appears to be general with analogs of cyclobutene-1,2-diones and the results are presented in Table 3.

§ Crystal data for compound **30**: C₄₁H₄₀Cl₂N₂O, *M*_r = 647.65, triclinic, space group *P*-1, *a* = 8.2446(10), *b* = 14.3609(17), *c* = 15.8071(19) Å, *a* = 111.220(2), *β* = 95.001(2), *γ* = 105.513(2)°, *V* = 1645.5(3) Å³, *Z* = 2, *ρ*_{calcd} = 1.307 g cm⁻³, *μ* = 0.234 mm⁻¹, *T* = 100(2) K, reflections collected = 10889, independent reflections = 5147, *R*_{int} = 0.0431, *R*1 = 0.1089, *wR*2 = 0.2814 [*I* > 2 σ(*I*)], GOF = 1.091. CCDC-659431.† These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

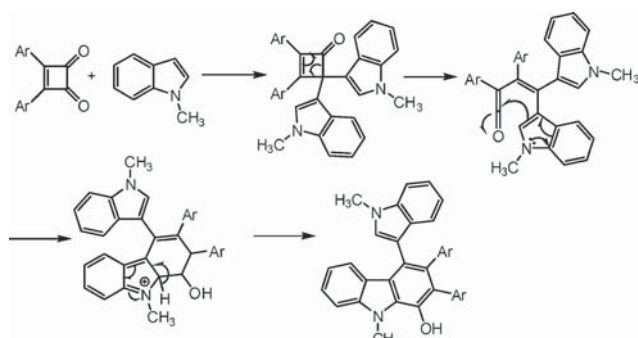
Table 3 Condensation reaction of indole and *N*-substituted indoles with various cyclobutene-1,2-diones


Entry	R ¹	Ar	Product (%)
1	H (4)	Phenyl (31)	32 (50)
2	Allyl (15)	Mesityl (29)	33 (72)
3	Methyl (1)	Phenyl (31)	34 (75)
4	Allyl (15)	Phenyl (31)	35 (54)
5	Methyl (1)	4-Methylphenyl (36)	37 (52)
6	Ethyl (38)	4-Methylphenyl (36)	39 (62)

**Fig. 2** ORTEP diagram for the compound **30** (30% probability factor for the thermal ellipsoids, lattice dichloromethane molecule is omitted for clarity).

Mechanism

A mechanistic rationalization for the reaction is given in Scheme 4. Presumably, the diarylation of cyclobutene-1,2-dione takes place to form an intermediate which then undergoes ring opening to form the ketene, which conceivably undergoes ring closure and subsequent aromatization to afford the product **30**.

**Scheme 4** Proposed mechanism for the formation of indolylcarbazole.

Conclusions

In conclusion, we have devised a direct and efficient acid catalyzed protocol for the annulation of indole with acyclic 1,2-diones and cyclobutene-1,2-diones, affording indolo[3,2-*a*]carbazoles and indole substituted carbazole derivatives. The experimental simplicity and the mild reaction conditions are noteworthy.

Experimental section

General methods

All reactions were carried out in oven-dried glassware under argon atmosphere. Progress of reaction was monitored by thin layer chromatography (visualization was effected by exposure to UV light or iodine), while purification was effected by silica gel column chromatography. NMR data were collected at room temperature in CDCl₃ or (CD₃)₂SO at an operating frequency of 300 MHz (75 MHz for ¹³C NMR). IR spectra were recorded on Bomem MB series FT-IR spectrophotometer. Melting points were recorded on a Buchi melting point apparatus and are uncorrected. High resolution mass spectra were recorded under EI/HRMS (at 5000 resolution) using JOEL JMS 600H mass spectrometer.

General experimental procedure for the synthesis of carbazole derivatives

To a solution of indole derivatives (2.5 equiv.) and 1,2-diones (1 equiv.) in dry toluene was added 20 mol% of *para*-toluenesulfonic acid under an atmosphere of argon. After refluxing the reaction mixture for 10 h, the solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography (60–120 mesh, hexane–ethyl acetate solvent mixtures) to afford the product as colorless crystalline solid.

Characterization data of 3

Mp: 240–242 °C. IR (KBr) ν_{max} : 3049, 1579, 1500, 1479, 1444, 1417, 1386, 1323, 1255 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-*d*₆): δ 8.59 (d, 1H, *J* = 8.0 Hz), 7.46–7.17 (m, 16H), 6.87 (uneven triplet, 1H, *J*₁ = 7.9 Hz, *J*₂ = 7.1 Hz), 6.48 (d, 1H, *J* = 7.9 Hz), 4.51 (s, 3H), 3.28 (s, 3H). ¹³C NMR (CDCl₃ + DMSO-*d*₆): δ 142.7, 142.1, 140.4, 139.2, 132.6, 130.6, 128.2, 127.5, 126.9, 126.8, 124.9, 124.6, 124.1, 122.9, 121.4, 121.2, 119.6, 119.4, 115.4, 109.4, 109.1, 107.5, 35.7, 33.2. HRMS (EI): calculated: 436.1939; found: 436.1909.

Characterization data of 5

Mp: 320–322 °C. IR (KBr) ν_{max} : 3452, 3402, 1635, 1610, 1462, 1442, 1371, 1327, 1255, 1153, 1022 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-*d*₆): δ 10.46 (bs, 1H), 8.65 (bs, 1H), 8.52 (d, 1H, *J* = 7.5 Hz), 7.60 (d, 1H, *J* = 8.0 Hz), 7.48–7.23 (m, 14H), 6.88 (m, 1H, *J* = 7.1 Hz), 6.80 (d, 1H, *J* = 7.8 Hz). ¹³C NMR ((CD₃)₂CO): δ 141.4, 141.0, 140.5, 139.3, 138.8, 132.3, 131.6, 129.0, 128.8, 127.7, 127.4, 125.2, 124.2, 123.1, 121.7, 120.1, 119.6, 118.7, 115.3. HRMS (EI): calculated: 408.1625; found: 408.1665.

Characterization data of 12

Mp: 220–221 °C. IR (KBr) ν_{max} : 3053, 2431, 1612, 1548, 1583, 1490, 1469, 1444 cm⁻¹. ¹H NMR (CDCl₃ + DMSO-*d*₆): δ 8.56 (d,

1H, $J = 8.1$ Hz), 7.51–7.23 (m, 9H), 7.08–6.96 (m, 3H), 6.58 (d, 1H, $J = 7.9$ Hz), 4.46 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (CDCl_3 + DMSO- d_6): δ 142.4, 139.7, 133.8, 133.7, 132.3, 131.5, 131.4, 131.3, 130.4, 129.7, 129.6, 129.4, 124.9, 124.4, 123.8, 122.8, 120.8, 120.6, 119.9, 119.7, 109.3, 109.2, 35.5, 33.4. LRMS (FAB): calculated: 572.0831; found: 572.2324.

Characterization data of 16

Mp: 224–226 °C. IR (KBr) ν_{max} : 3080, 2951, 1610, 1589, 1538, 1440, 1400, 1350, 1250 cm^{-1} . ^1H NMR (CDCl_3 + DMSO- d_6): δ 8.44 (d, 1H, $J = 7.7$ Hz), 7.43–7.16 (m, 15H), 6.86 (uneven triplet, 1H, $J_1 = 7.8$ Hz, $J_2 = 7.2$ Hz), 6.59–6.51 (m, 1H), 6.44 (d, 1H, $J = 7.8$ Hz), 5.62–5.43 (m, 5H), 4.93 (d, 1H), 4.58 (d, 1H), 4.37–4.36 (m, 2H). ^{13}C NMR (CDCl_3 + DMSO- d_6): δ 142.4, 141.2, 140.1, 138.4, 137.3, 135.8, 134.5, 133.2, 131.9, 130.4, 127.9, 127.3, 126.9, 124.9, 123.9, 121.2, 119.8, 119.6, 118.5, 115.7, 109.9, 107.5, 49.5, 46.7. HRMS (EI): calculated: 488.2252; found: 488.2252.

Characterization data of 22

Mp: 261–263 °C. IR (KBr) ν_{max} : 3437, 3412, 3049, 1639, 1498, 1458, 1373, 1250, 1100 cm^{-1} . ^1H NMR (CDCl_3 + DMSO- d_6): δ 9.95 (bs, 1H), 9.17 (bs, 1H), 8.36 (d, 1H, $J = 7.6$ Hz), 8.23 (d, 1H, $J = 7.8$ Hz), 7.61 (d, 1H, $J = 7.9$ Hz), 7.54 (d, 1H, $J = 7.9$ Hz), 7.39–7.20 (m, 4H), 2.96 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (DMSO- d_6): δ 139.5, 139.3, 138.9, 132.1, 128.5, 124.2, 122.1, 121.7, 121.1, 120.7, 119.7, 118.9, 113.9, 111.5, 110.3, 110.1, 104.2, 13.4, 13.2. HRMS (EI): calculated: 284.1313; found: 284.1367.

Characterization data of 30

Mp: 255–257 °C. IR (KBr) ν_{max} : 3520, 3053, 2928, 1588, 1532, 1486, 1360, 1210, 1098, 1010 cm^{-1} . ^1H NMR (CDCl_3): δ 7.36–7.25 (m, 5H), 7.13 (uneven triplet, 2H, $J_1 = 8.7$ Hz, $J_2 = 8.4$ Hz), 6.86 (uneven triplet, 2H, $J_1 = 7.2$ Hz, $J_2 = 7.8$ Hz), 6.72 (s, 1H), 6.67 (s, 1H), 6.49 (s, 2H), 6.31 (s, 1H), 5.29 (s, 1H), 4.27 (s, 3H), 3.64 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (CDCl_3): δ 139.6, 137.5, 137.4, 137.3, 136.8, 136.3, 134.4, 130.3, 128.9, 128.7, 127.6, 126.7, 125.1, 123.5, 123.2, 121.6, 120.9, 118.8, 118.3, 113.8, 109.0, 107.9, 29.8, 29.4, 26.9, 21.8, 21.5, 21.1, 20.9, 20.8. LRMS (FAB): calculated: 562.2984; found: 562.78.

Characterization data of 32

IR (thin film) ν_{max} : 3510, 3419, 3063, 2923, 1590, 1540, 1454, 1316, 1215, 1094, 1012 cm^{-1} . ^1H NMR (CDCl_3): δ 8.39 (bs, 1H), 7.93 (bs, 1H), 7.41–7.14 (m, 11H), 6.86–6.70 (m, 9H), 5.29 (bs, 1H). ^{13}C NMR (CDCl_3): δ 140.8, 135.4, 131.6, 130.9, 128.9, 128.5, 128.3, 127.8, 126.7, 126.3, 125.4, 125.2, 123.9, 122.9, 121.8, 120.5, 119.7, 119.1, 110.9, 110.5. HRMS (EI): calculated: 450.1732; found: 450.1733.

Characterization data of 33

IR (thin film) ν_{max} : 3545, 3075, 2925, 1628, 1568, 1550, 1440, 1420, 1390, 1018 cm^{-1} . ^1H NMR (CDCl_3): δ 7.33–7.11 (m, 5H), 6.89–6.69 (m, 5H), 6.53 (s, 1H), 6.47 (s, 1H), 6.32 (m, 1H), 6.14–6.08 (m, 1H), 5.69–5.64 (m, 1H), 5.49–5.42 (m, 1H), 5.29–5.23 (m, 1H),

5.13–5.05 (m, 2H), 4.90–4.87 (m, 2H), 4.63–4.51 (m, 2H), 4.34 (d, 1H, $J = 17.1$ Hz), 2.22 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (CDCl_3): δ 139.6, 138.4, 137.6, 137.5, 137.3, 134.4, 133.1, 130.3, 129.0, 128.8, 127.8, 127.6, 125.1, 123.6, 121.1, 119.0, 118.5, 115.8, 109.3, 47.9, 47.5. LRMS (FAB): calculated: 614.82; found: 614.94.

Characterization data of 34

Mp: 135–137 °C. IR (KBr) ν_{max} : 3523, 3051, 2929, 1598, 1541, 1481, 1454, 1436, 1386, 1354 cm^{-1} . ^1H NMR (CDCl_3): δ 7.38–7.24 (m, 11H), 7.23–6.73 (m, 8H), 6.55 (s, 1H), 5.20 (s, 1H), 4.26 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (CDCl_3): δ 142.3, 140.9, 132.1, 131.5, 130.8, 129.0, 128.3, 127.4, 126.7, 126.2, 125.3, 125.0, 123.3, 122.9, 121.3, 120.7, 119.1, 118.5, 108.9, 108.1, 32.7, 31.9. HRMS (EI): calculated: 478.1888; found: 478.1835.

Characterization data of 35

IR (thin film) ν_{max} : 3515, 3048, 2935, 1620, 1555, 1490, 1389, 1240, 1110, 1019 cm^{-1} . ^1H NMR (CDCl_3): δ 7.53–7.08 (m, 11H), 6.84–6.72 (m, 8H), multiplet centered around 6.13 (s, 1H), 5.74–5.72 (m, 1H), 5.56 (s, 1H), 5.46–5.29 (m, 2H), 5.17–5.12 (m, 2H), 5.00–4.98 (m, 1H), 4.60–4.55 (m, 3H). ^{13}C NMR (CDCl_3): δ 141.5, 139.6, 136.6, 131.1, 130.8, 130.7, 129.8, 128.1, 127.7, 126.5, 126.3, 125.3, 125.1, 123.5, 122.5, 120.1, 120.0, 118.7, 109.8, 108.9, 108.5, 48.4, 47.6. LRMS (FAB): calculated: 530.66; found: 530.89.

Characterization data of 37

Mp: 218–220 °C. IR (KBr) ν_{max} : 3520, 3053, 2928, 1588, 1532, 1486, 1360, 1210, 1098, 1010 cm^{-1} . ^1H NMR (CDCl_3): δ 7.27–7.15 (m, 7H), 6.97–6.92 (m, 3H), 6.66–6.51 (m, 7H), 5.21 (s, 1H), 4.21 (s, 3H), 3.64 (s, 3H), 2.27 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (CDCl_3): δ 142.3, 138.4, 137.9, 136.8, 136.4, 133.9, 132.9, 131.9, 130.8, 129.9, 129.3, 129.1, 128.1, 124.7, 123.3, 122.9, 121.2, 120.7, 119.1, 118.4, 114.1, 108.9, 32.6, 31.9, 21.2, 21.1. LRMS (FAB): calculated: 506.64; found: 506.90.

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