Remote substituent effects on regioselectivity in the Pauson–Khand reaction of 2-substituted norbornenes

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Remote substituent effects on regioselectivity in the Pauson–Khand reaction of 2-substituted norbornenes

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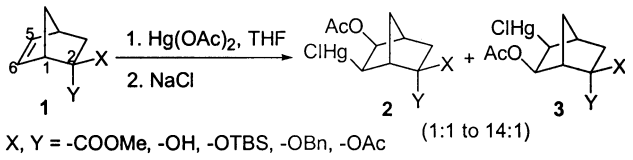
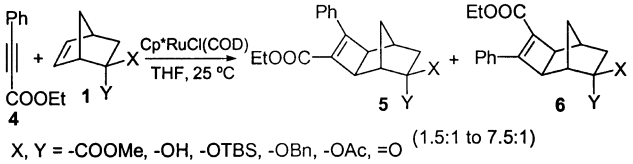
Abstract—The effect of a remote substituent on the regioselectivity in the Pauson–Khand reaction of 2-substituted norbornenes has been investigated. Moderate level of regioselectivity was observed and the regioselectivity increases as the electron-withdrawing power of the remote substituent increases. *exo* Substituents at C-2 of norbornenes generally gave a higher regioselectivity than the *endo* substituents.

1. Introduction

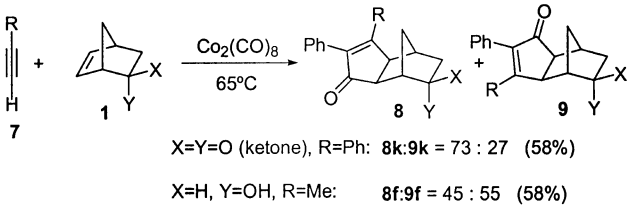
The study on remote stereoelectronic effects in controlling the regio- and stereoselectivities on nucleophilic and electrophilic additions to π-bonds has attracted considerable interest.[1,2] The most common systems for these studies are 7-oxabicyclo[2.2.1]hept-5-ene derivatives,[3–8] 7-norbornanones[9–11] and 7-methylenenorbornanes.[12,13] Less attention has been paid to remote substituent effects on the 2-substituted norbornene system.[14–17] We have recently studied the effect of a remote substituent on the regioselectivity of oxymercuration of 2-substituted norbornenes.[16] Moderate to high levels of regioselectivity were observed with both *exo*- and *endo*-substituents at C-2 of norbornenes (Scheme 1). Examples of remote substituent effects on transition metal-catalyzed cycloadditions are rare in the literature.[7,17–19] We have recently reported the first examples of a remote substituent effect on the regioselectivity of the ruthenium-catalyzed [2+2] cycloadditions of 2-substituted norbornenes.[17] Although our study showed only moderate regioselectivity (1.5:1 to 7.5:1) with various C_2-substituents on norbornene (Scheme 2), it was the first study of this kind and provided important information on long-range electronic effect on Ru-catalyzed [2+2] cycloadditions. Schore and co-workers have reported two isolated examples of remote substituent effects on the regioselectivity of the Co-mediated Pauson–Khand reaction of 2-substituted norbornenes (with X=Y=O, ketone **1k**; and X=H, Y=OH, *endo* alcohol **1f**) and moderate regioselectivities were observed (Scheme 3).[18] As only two different substituents (ketone and *endo* alcohol) were tested in Schore's study, and we noticed from our study on the Ru-catalyzed [2+2] cycloadditions that usually *exo* substituents show stronger remote substituent effects on the regioslectivities in metal-catalyzed cycloadditions, we decided to study the regioselectivity of the Co-mediated Pauson–Khand reaction



Scheme 1. Remote substituent effect on the oxymercuration of 2-substituted norbornenes.



Scheme 2. Ruthenium-catalyzed [2+2] cycloadditions of 2-substituted norbornenes.



Scheme 3. Literature examples of co-catalyzed Pauson–Khand reactions of 2-substituted norbornenes.

Keywords: Pauson–Khand reaction; cycloadditions; transition metal-catalyzed reactions; remote substituent effects; stereoelectronic effects; regioselectivity; norbornenes.

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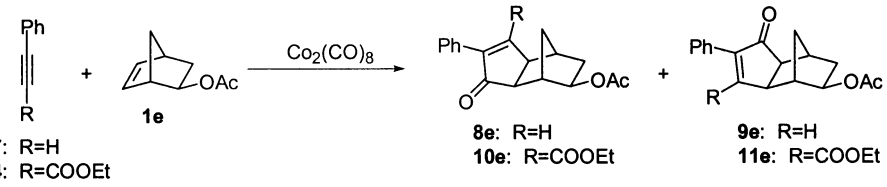
Table 1. Effect of an activator in the Pauson–Khand reactions



Entry	Activator	Solvent	Temperature (°C)	R=H		R=COOEt	
				Yield (%)[a]	**8e/9e**[b]	Yield (%)[a]	**10e/11e**[b]
1	None	$ClCH_2CH_2Cl$	80	–	–	88	52:48
2	Me_3NO	$ClCH_2CH_2Cl$	25	48	50:50	60	62:38
3	$CyNH_2$	$ClCH_2CH_2Cl$	80[c]	29	57:43	77	66:34
4	Me_2S	$ClCH_2CH_2Cl$	25	27	50:50	40[d]	67:33

[a] Isolated yields of pure products after column chromatography.
[b] Measured by intergration on 400 MHz ^{1}H NMR spectra of the crude reaction mixtures.
[c] No reaction was observed at lower temperature.
[d] Took 11 days for the reaction to go to completion, and higher temperature did not improve the rate or the yield of the reaction.

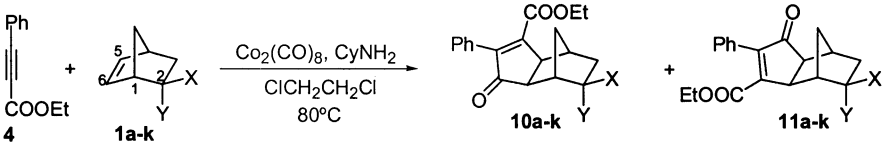
of 2-substituted norbornenes with a broader range of *exo* and *endo* substituents.

2. Results and discussion

In an initial experiment, *exo*-2-substituted norbornene **1e** (X=OAc) reacted with the Co–alkyne complex of alkyne **4** (R=COOEt) in 1,2-dichloroethane at 80°C to provide a mixture of regioisomers **10e** and **11e** in a 52:48 ratio with a combined yield 88% (Table 1, entry 1). As recent development of the Pauson–Khand reaction[20] has shown that both the rate of the reaction and regio- and stereoselectivities could be improved by addition of certain 'activators' such as amine *N*-oxides,[21] amines,[22] and alkyl methyl sulfides,[23] we decided to look at the effect of the addition of trimethylamine *N*-oxide, cyclohexylamine and dimethyl sulfide in the $Co_2(CO)_8$ mediated Pauson–Khand reaction between *exo*-2-substituted norbornene **1e** (X=OAc) and alkyne **4** or **7** (Table 1). With alkyne **4** (R=COOEt), the regioselectivity improved slightly when an activator was used (Table 1, entries 2–4). Although the use of dimethyl sulfide gave the highest regioselectivity (67:33), the rate of this reaction was very slow and the reaction took 11 days to go to completion. On the other hand, the use of cyclohexylamine gave a similar regioselectivity (66:34) with a much better yield and faster reaction time. With terminal alkyne **7**, (R=H) both the yields and the regioselectivities were lower regardless of which activator was used.

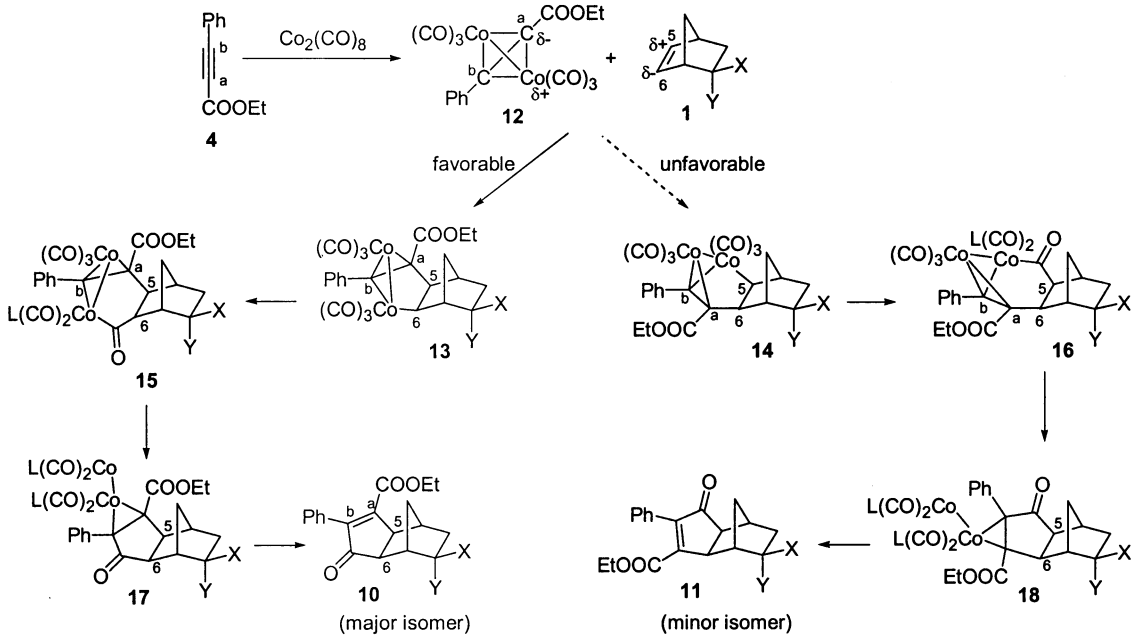
In order to study the remote substitutent effect on the Pauson–Khand reaction with various C_2-substituted norbornenes, *exo*- and *endo*-2-substituted norbornenes **1a–k** were prepared.[16] Table 2 shows the results of the Pauson–Khand reaction between various *exo*- and *endo*-2-substituted norbornenes **1a–k** with alkyne **4**, using cyclohexylamine as an activator in the $Co_2(CO)_8$-mediated Pauson–Khand reaction. The yields of these reactions ranged from moderate to good. Although the regioselectivities were only moderate (50:50 to 74:26), several important trends were observed in this study. First, in all cases, the *exo*-substituents showed a stronger remote effect than the corresponding *endo*-substituents. For example, *exo*-OBn–norbornene **1c** gave a regioselectivity of 62:38 (Table 2, entry 3), whereas the corresponding reaction of *endo*-OBn–norbornene **1h** was non-selective (50:50, Table 2, entry 8). A similar trend was observed in our previous study on the Ru-catalyzed [2+2] cycloadditions of

Table 2. Effect of a remote C_2-substituent on the regioselectivity of the Pauson–Khand reaction of 2-substituted norbornenes



Entry	**1**	*exo*-Substituents (Y=H)			Entry	**1**	*endo*-Substituents (X=H)		
		X	Yield (%)[a]	**10/11**[b]			Y	Yield (%)[a]	**10/11**[b]
1	**1a**	OH	51	55:45	6	**1f**	OH	71	50:50
2	**1b**	OTBS	61	58:42	7	**1g**	OTBS	80	55:45
3	**1c**	OBn	66	62:38	8	**1h**	OBn	71	50:50
4	**1d**	OMEM	71	63:37	9	**1i**	OMEM	81	50:50
5	**1e**	OAc	74	66:34	10	**1j**	OAc	73	50:50
					11	**1k**	X=Y=O (ketone)	43	74:26

[a] Isolated yields of pure products after column chromatography.
[b] Measured by intergration on 400 MHz ^{1}H NMR spectra of the crude reaction mixtures.

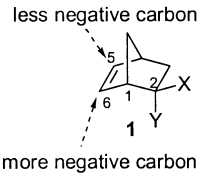


Scheme 4. Explanation on the regiochemistry of the Pauson–Khand reaction of 2-substituented norbornenes.

2-substituted norbornenes.[17] Secondly, the regioselectivity of the Pauson–Khand [2+2+1] cycloadditions of *exo*-2-substituted norbornenes followed the same trend that we observed in the Ru-catalyzed [2+2] cycloadditions, that is: X=OTBS (58:42)<OBn (62:38)<OAc (66:34)<=O (74:26). 2-Norbornenone **1k** showed the strongest remote substituent effect and the highest regioselectivity in both the Pauson–Khand [2+2+1] cycloaddition and Ru-catalyzed [2+2] cycloaddition.

The regiochemistry of the Pauson–Khand reaction has been interpreted on the basis of a combination of electronic and steric factors during the insertion of the alkene component into the C–Co bond of the Co–alkyne complex.[18,20] According to some of our previous theoretical calculations on some 2-substituted norbornenes (see preceding paper), C_6 of 2-substituted **1** is always more 'negative' than C_5 (Scheme 4). In the Co–alkyne complex **12**, the C–Co is polarized in such a way that the C is $\delta-$ and the Co is $\delta+$ (electronegativity: C=2.5 and Co=1.7). Thus, naturally the preferred orientation of addition of the Co–alkyne complex **12** to 2-substituted norbornene **1** should occur with the more negative carbon of the alkene (C_6) attached to the $\delta+$ Co and the less negative carbon of the alkene (C_5) attached to the $\delta-$ C_a to give complex **13**. CO insertion followed by reductive elimination of complex **13** would give the major isomer **10**.

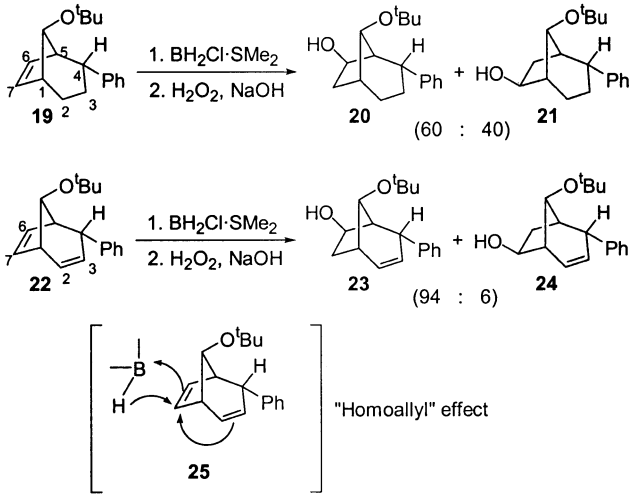
Table 3. Theoretical analysis of the difference in charges between C_5 and C_6 of some the 2-substituted norbornenes



Norbonene	Difference in charges between C_5 and C_6	Observed regioselectivity
1a (X=OH, Y=H)	0.003	55:45
1c (X=OCH_2Ph, Y=H)	0.007[a]	62:38
1e (X=OAc, Y=H)	0.015	66:34
1k (X=Y=O, ketone)	0.003	74:26

[a] X=OCH_3 was used to in the calculation to model the experimentally used OCH_2Ph.

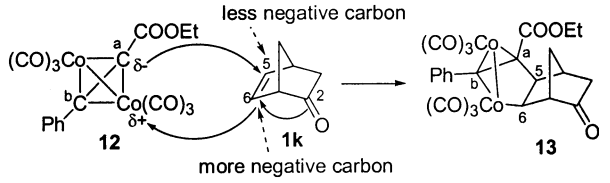
In order to explain the regioselectivity trend in the Pauson–Khand reaction of 2-substituted norbornenes **1** with alkyne **4**, we have performed theoretical calculations on some of the norbornenes using the GAUSSIAN 98 suite of programs (Table 3).[24,25] Natural population analysis shows that the charges on the C_5 and C_6 atoms of the 2-substituted norbornenes **1** are slightly different. One would expect the greater the difference in the charges between C_5 and C_6 in **1**, the higher the regioselectivity. As shown in Table 3, when the substituent X changes from OH to OCH_2Ph to OAc, the difference in charge between C_5 and C_6 increases from 0.003 to 0.007 and to 0.015 and this follows the trend that we observed in the regioselectivity in the Pauson–Khand reaction. For the norbornene **1k** in which the highest regioselectivity (74:26) was observed in the Pauson–Khand reaction, we expect the difference in the charges between C_5 and C_6 would be greater than 0.015. But in fact the charge difference is only 0.003. We believe that norbornene **1k** is a special case and its regioselectivity in the Pauson–Khand reaction not only depends on the through-bond inductive effect of the remote substituent (as in all other cases), the regioselectivity is also controlled by a through-space orbital interaction. This through-space orbital interaction in controlling regioselectivity in addition reaction of bicyclic alkenes have been observed by Danishesky and co-workers (Scheme 5).[26] Hydroboration–oxidation of bicyclic alkene **19** lead to the formation of regiosomers **20** and **21** in a 60:40 ratio. When the C_2–C_3 σ bond is replaced by a π bond (bicyclic alkene **22**), the regioselectivity of the hydroboration increased dramatically to 94:6. Danishesky



Scheme 5. Example of a through-space orbital interaction in controlling regioslectivity in addition reaction of bicyclic alkene system.

explained these results by the 'homoallyl' effect of the through-space orbital interaction (**25**, Scheme 5). A similar through-space orbital interaction in norbornene **1k** may also by effective (Scheme 6) which make C_6 a lot more 'negative' than C_5 and this accounts for the highest regioselectivity in the Pauson–Khand reaction.

The regiochemistry and stereochemistry of the cycloadducts were determined by various NMR techniques. The *exo* stereochemistry of the cycloadducts was proven by the coupling pattern of H^b and H^c in the ^1H NMR spectra (Fig. 1). For example, in **10b**, as the dihedral angles between H^b and H^d, and H^c and H^e in the *exo* cycloadducts are close to 90°, their coupling constants would be very small ($J \sim 0$–2 Hz). For *endo* cycloadducts, the corresponding dihedral angles are approximately 42° and would give coupling constants of ~5 Hz.[27] In all of our cycloadducts, both H^b and H^c are doublets (coupled only with each other but not with H^d or H^e), therefore all the cycloadducts must possess *exo* stereochemistry.[28] Using a combination of several NMR techniques: HCOSY, HSQC and HMBC,[29] all the protons of



Scheme 6. Through-space orbital interaction in norbornene **1k**.

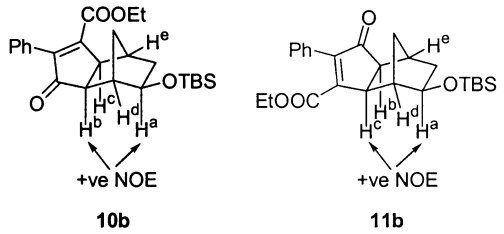


Figure 1. Determination of regiochemistry.

the major and minor regioisomers were well-characterized. The regiochemistry of the cycloadducts was then determined by NMR GOESY experiments (a gradient NOE experiment).[30] For example, in the major regioisomer **10b**, H^a showed +ve NOE effect with H^b and H^d but not with H^c or H^e whereas for the minor isomer **11b**, H^a showed +ve NOE effect with H^c and H^d but not with H^b or H^e.

3. Conclusions

We have investigated the remote substituent effect of the Pauson–Khand reaction of 2-substituted norbornenes. *exo* Substituents always showed a stronger remote effect than the corresponding *endo* substituents. The stronger the electron withdrawing power of the remote substituent, the greater the remote substituent effect. Although the regioselectivities were only moderate, this study provides important information about long-range electronic effects on transition metal-catalyzed cycloadditions.

4. Experimental

4.1. General information

All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherwise stated. Standard column chromatography was performed on 230–400 mesh silica gel (obtained from Silicycle) by use of flash column chromatography techniques.[31] Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer. Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0). High resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by Canadian Microanalytical Service, British Columbia or by Quantitative Technologies, New Jersey.

4.2. Materials

Unless stated otherwise, commercial reagents were used without purification. $Co_2(CO)_8$ was purchased from Strem Chemicals and was stored in a inert atmosphere dry box. THF was purified by distillation from potassium/benzophenone under dry nitrogen. 1,2-Dichloroethane and cyclohexylamine were purified by distillation from 4 Å molecular sieves under dry nitrogen. Norbornenes **1a**–**1c**, **1e**–**1h**, **1j** and **1k**, and alkyne **4** were prepared according to literature procedure.[16,32]

4.2.1. 2-*exo*-Methoxyethoxymethoxybicyclo[2.2.1]hept-5-ene (norbornene 1d). MEMCl (3.90 mL, 34.2 mmol)

was added to a flame-dried flask containing 2-*exo*-norbornenol **1a** (2.43 g, 22.1 mmol) and diisopropylethylamine (5.9 mL, 33.9 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred for 3 d at room temperature. After quenching with water (50 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with water (2×50 mL), brine (50 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give **1d** (2.97 g, 15.0 mmol, 68%) as a clear, transparent liquid. R_f 0.49 (EtOAc/hexanes=1:4); IR (neat) 3062 (m), 2973 (s), 2940 (s), 2882 (s), 2817 (m), 1465 (m), 1362 (m), 1332 (m), 1280 (w), 1240 (m), 1185 (m), 1120 (s), 1050 (s), 1023 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.15 (dd, 1H, J=5.7, 2.8 Hz), 5.90 (dd, 1H, J=5.7, 3.2 Hz), 4.78 (d_{AB}, 1H, J=7.0 Hz), 4.74 (d_{AB}, 1H, J=7.0 Hz), 3.76–3.65 (m, 3H), 3.55 (t, 2H, J=4.6 Hz), 3.38 (s, 3H), 2.86 (s, 1H), 2.78 (s, 1H), 1.65 (d, 1H, J=8.3 Hz), 1.57 (ddd, 1H, J=12.0, 6.9, 2.6 Hz), 1.53 (ddd, 1H, J=8.3, 2.5, 1.6 Hz), 1.35 (ddd, 1H, J=12.0, 3.3, 2.4 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 140.6, 133.1, 94.6, 77.9, 71.7, 66.8, 59.0, 47.2, 45.9, 40.3, 34.6. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found C, 66.38; H, 9.22.

4.2.2. 2-*endo*-Methoxyethoxymethoxybicyclo[2.2.1]hept-5-ene (norbornene 1i). MEMCl (1.20 mL, 10.5 mmol) was added to a flame-dried flask containing 2-*endo*-norbornenol **1f** (791 mg, 7.18 mmol) and diisopropylethylamine (1.9 mL, 10.9 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 2 d at room temperature. After quenching with water (15 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were washed with water (2×20 mL), brine (20 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give **1i** (815 mg, 4.11 mmol, 57%) as a clear, transparent liquid. R_f 0.43 (EtOAc/hexanes=1:4); IR (neat) 3062 (w), 2971 (s), 2938 (s), 2881 (s), 2817 (m), 1724 (w), 1630 (w), 1573 (w), 1456 (m), 1364 (m), 1256 (m), 1195 (m), 1175 (s), 1124 (s), 1101 (s), 1050 (s), 1025 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.31 (dd, 1H, J=5.4, 3.0 Hz), 5.99 (dd, 1H, J=5.4 3.0 Hz), 4.72 (d_{AB}, 1H, J=6.9 Hz), 4.68 (d_{AB}, 1H, J=6.9 Hz), 4.42 (m, 1H), 3.72–3.61 (m, 2H), 3.56 (d, 1H, J=4.5 Hz), 3.55 (d, 1H, J=4.5 Hz), 3.39 (s, 3H), 3.06 (d, 1H, J=0.6 Hz), 2.77 (d, 1H, J=0.5 Hz), 2.01 (ddd, 1H, J=12.0, 8.1, 3.8 Hz), 1.41 (ddd, 1H, J=8.4, 3.4, 1.8 Hz), 1.23 (d, 1H, J=8.6 Hz), 0.89 (dt, 1H, J=12.1, 3.3 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 138.0, 131.6, 94.6, 77.5, 71.7, 66.8, 58.9, 47.3, 46.0, 42.1, 34.3. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found C, 66.97; H, 9.01.

4.2.3. Pauson–Khand reaction of norbornene 1e with phenylacetylene 7 (Table 1, entry 3). Phenylacetylene (30.0 μL, 0.273 mmol) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.1 mg, 0.261 mmol) in 1,2-dichloroethane (2 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1e** (37.3 mg, 0.245 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 17 h. The solvent was removed by rotary evaporation, then the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **8e** and **9e** (19.9 mg, 0.0705 mmol, 29%, **8e/9e**=57:43 measured by 400 MHz ^1H NMR) as a light orange solid.

8-*exo*-Acetoxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (8e) and 9-*exo*-acetoxy-4-phenyltricyclo[5.2.1.0^{2,6}]-dec-4-ene-3-one (9e). R_f 0.33 (EtOAc/hexanes=1:4); IR (neat) 3055 (m), 2966 (s), 2857 (m,), 1738 (s), 1699 (s), 1656 (m), 1494 (s), 1447 (s), 1378 (s), 1324 (m), 1296 (s), 1244 (s), 1189 (m), 1163 (s), 1133 (m), 1056 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, 2H, J=7.7 Hz), 7.64 (d, 0.57H, J=2.9 Hz), 7.62 (d, 0.43H, J=3.0 Hz), 7.40–7.30 (m, 3H), 4.79 (d, 0.43H, J=7.2Hz), 4.76 (d, 0.57H, J=6.6 Hz), 2.76 (dd, 0.43H, J=4.2, 3.6 Hz), 2.71 (dd, 0.57H, J=4.4, 3.2 Hz), 2.58 (s, 1H), 2.40–2.33 (m, 2H), 2.05 (s, 1.29H), 2.04 (s, 1.71H), 1.97 (ddd, 0.57H, J=13.6, 6.8, 2.2 Hz), 1.90 (ddd, 0.43H, J=13.2, 6.7, 2.0 Hz), 1.64–1.57 (m, 1H), 1.40 (tm, 1H, J=11.4 Hz), 1.14 (tm, 1H, J=12.6 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ major isomer **8e**: 207.2, 170.6, 159.3, 146.7, 131.1, 128.65, 128.4, 127.1, 75.7, 50.1, 46.9, 44.1, 39.5, 37.5, 28.5, 21.2; minor isomer **9e**: 207.7, 170.8, 158.2, 148.2, 132.7, 128.68, 128.4, 127.1, 76.8, 53.9, 43.7, 43.1, 38.23, 38.20, 28.5, 21.3. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found C, 75.73; H, 6.66.

4.2.4. Pauson–Khand reaction of norbornene 1a with acetylene 4 (Table 2, entry 1). A solution of acetylene **4** (43.7 mg, 0.251 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (88.7 mg, 0.259 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1a** (25.5 mg, 0.231 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 17 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:1) to give an inseparable mixture of **10a** and **11a** (36.8 mg, 0.118 mmol, 51%, **10a/11a**=55:45 measured by 400 MHz ^1H NMR) as a clear, transparent liquid.

5-(Ethoxycarbonyl)-8-*exo*-hydroxy-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10a) and 5-(ethoxycarbonyl)-9-*exo*-hydroxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11a). R_f 0.24 (EtOAc/hexanes=2:3); IR (neat, NaCl) 3419 (br. s), 2967 (m), 2251 (w), 1699 (m), 1635 (m), 1446 (w), 1374 (m), 1345 (m), 1234 (m), 1172 (m), 1065 (m), 1019 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.35 (m, 3H), 7.31–7.28 (m, 2H), 4.26–4.16 (m, 2H), 4.05 (d, 0.45H, J=6.1 Hz), 3.98 (d, 0.55H, J=6.3 Hz), 2.92 (d, 1H, J=6.3 Hz), 2.60 (d, 0.45H, J=4.2 Hz), 2.54 (d, 0.55H, J=4.2 Hz), 2.45 (s, 1H), 2.33 (d, 0.45H, J=3.6 Hz), 2.32 (d, 0.55H, J=4.7 Hz), 1.91 (ddd, 0.55H, J=13.4, 6.8, 2.4 Hz), 1.86 (ddd, 0.45H, J=13.3, 6.9, 2.4 Hz), 1.68–1.52

(m, 3H), 1.47 (ddd, 0.45H, J=13.3, 4.1, 2.4 Hz), 1.17 (m, 0.55H), 1.144 (t, 1.65H, J=6.9 Hz), 1.141 (t, 1.35H, J=7.1 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ major isomer **10a**: 208.0, 165.92, 158.5, 148.36, 130.0, 128.8, 128.7, 127.93, 73.2, 61.44, 49.6, 48.1, 47.5, 41.2, 37.4, 27.7, 13.8; minor isomer **11a**: 208.0, 165.89, 157.4, 148.39, 130.1, 128.8, 128.7, 127.91, 74.4, 61.40, 53.0, 46.6, 44.5, 40.9, 38.9, 28.1, 13.8. HRMS calcd. for $C_{19}H_{20}O_4$: m/z 312.1362, found m/z 312.1332.

4.2.5. Pauson–Khand reaction of norbornene 1b with acetylene 4 (Table 2, entry 2). A solution of acetylene **4** (41.8 mg, 0.240 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (88.9 mg, 0.260 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1b** (53.4 mg, 0.238 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 22 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **10b** and **11b** (62.3 mg, 0.146 mmol, 61%, **10b/11b**=58:42 measured by 400 MHz ^{1}H NMR) as a light orange, transparent liquid.

5-(Ethoxycarbonyl)-8-*exo*-(*tert*-butyldimethylsilyoxy)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (10b) and 5-(ethoxycarbonyl)-9-*exo*-(*tert*-butyldimethylsilyoxy)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11b). R_f 0.44 (EtOAc/hexanes=1:9); IR (neat, NaCl) 3058 (w), 2956 (s), 2931 (s), 2886 (m), 2857 (s), 1721 (s), 1495 (w), 1472 (m), 1446 (m), 1390 (w), 1373 (m), 1345 (w), 1252 (s), 1172 (s), 1155 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.35 (m, 3H), 7.31–7.28 (m, 2H), 4.26–4.14 (m, 2H), 3.93 (d, 0.42H, J=6.4 Hz), 3.85 (d, 0.58H, J=6.3 Hz), 2.89 (d, 0.58H, J=5.5 Hz), 2.87 (d, 0.42H, J=5.5 Hz), 2.55 (d, 0.42H, J=4.3 Hz), 2.47 (d, 0.58H, J=4.4 Hz), 2.38 (s, 0.58H), 2.36 (s, 0.42H), 2.30 (d, 0.42H, J=5.6 Hz), 2.28 (d, 0.58H, J=5.4 Hz), 1.80 (m, 1H), 1.56–1.51 (m, 1.58H), 1.47 (ddd, 0.42H, J=13.0, 4.4, 2.3 Hz), 1.17 (t, 1.26H, J=7.2 Hz), 1.14 (t, 1.74H, J=7.2 Hz), 1.08 (m, 1H), 0.89 (s, 3.78H), 0.88 (s, 5.22H), 0.084 (s, 1.26H), 0.078 (s, 1.26H), 0.070 (s, 1.74H), 0.06 (s, 1.74H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10b**: 208.1, 166.1, 158.6, 148.7, 130.20, 128.81, 128.7, 127.95, 73.6, 61.4, 49.7, 48.4, 47.6, 42.5, 37.2, 27.8, 25.80, 17.99, 13.8, −4.6(2); minor isomer **11b**: 208.3, 165.7, 157.4, 148.3, 130.17, 128.77, 128.7, 127.91, 74.9, 61.4, 53.4, 46.8, 44.6, 41.9, 38.8, 28.1, 25.83, 18.04, 13.9, −4.71, −4.72. Anal. Calcd for $C_{25}H_{34}O_4Si$: C, 70.38; H, 8.03. Found C, 70.41; H, 8.04.

4.2.6. Pauson–Khand reaction of norbornene 1c with acetylene 4 (Table 2, entry 3). A solution of acetylene **4** (42.0 mg, 0.241 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.3 mg, 0.261 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1c** (49.0 mg, 0.245 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 20 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **10c** and **11c** (64.2 mg, 0.159 mmol, 66%, **10c/11c**=62:38 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid.

8-*exo*-(Benzyloxy)-5-(ethoxycarbonyl)-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10c) and 9-*exo*-(benzyloxy)-5-(ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11c). R_f 0.49 (EtOAc/hexanes=1:4); IR (neat, NaCl) 3033 (w), 2972 (m), 2938 (m), 2882 (m), 2251 (w), 1705 (s), 1496 (m), 1465 (m), 1446 (m), 1373 (m), 1348 (m), 1233 (m), 1173 (s), 1075 (m), 1027 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.27 (m, 10H), 4.61–4.48 (m, 2H), 4.27–4.16 (m, 2H), 3.74 (d, 0.38H, J=5.8 Hz), 3.66 (d, 0.62H, J=6.4 Hz), 2.94 (d, 0.62H, J=5.4 Hz), 2.90 (d, 0.38H, J=5.5 Hz), 2.75 (s, 0.62H), 2.69 (s, 0.38H), 2.61 (d, 0.38H, J=3.9 Hz), 2.54 (d, 0.62H, J=4.3 Hz), 2.35 (d, 0.38H, J=5.4 Hz), 2.29 (d, 0.62H, J=5.4 Hz), 1.86 (ddd, 0.62H, J=13.4, 6.8, 2.0 Hz), 1.81 (ddd, 0.38H, J=13.1, 6.8, 2.0 Hz), 1.71 (ddd, 0.62H, J=13.3, 4.2, 2.5 Hz), 1.64 (ddd, 0.38H, J=13.3, 3.6, 3.3 Hz), 1.58 (s, 0.38H), 1.55 (s, 0.62H), 1.20–1.13 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10c**: 208.0, 165.94, 158.5, 148.3, 138.4, 130.07, 128.70, 128.68, 128.4, 127.94, 127.54, 127.51, 80.3, 70.8, 61.4, 49.7, 48.5, 43.5, 39.1, 37.1, 28.2, 13.8; minor isomer **11c**: 207.9, 165.88, 157.4, 148.4, 138.4, 130.12, 128.8, 128.70, 128.68, 128.4, 127.91, 127.51, 81.5, 70.7, 61.4, 53.4, 44.7, 42.8, 38.6, 38.5, 28.5, 13.8. HRMS Calcd for $C_{26}H_{26}O_4$: m/z 402.1831, found m/z 402.1839.

4.2.7. Pauson–Khand reaction of norbornene 1d with acetylene 4 (Table 2, entry 4). A solution of acetylene **4** (41.5 mg, 0.238 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.0 mg, 0.260 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1d** (47.7 mg, 0.241 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 19 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **10d** and **11d** (67.8 mg, 0.169 mmol, 71%, **10d/11d**=63:37 measured by 400 MHz ^{1}H NMR) as a light yellow semi-solid.

5-(Ethoxycarbonyl)-8-*exo*-methoxyethoxymethoxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (10d) and 5-(ethoxycarbonyl)-9-*exo*-methoxyethoxymethoxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11d). R_f 0.50 (EtOAc/hexanes=2:3); IR (neat, NaCl) 3057 (w), 2965 (m), 2937

(m), 2886 (m), 2819 (w), 2250 (w), 1712 (s), 1495 (w), 1446 (m), 1373 (w), 1233 (m), 1176 (m), 1109 (m), 1043 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39–7.35 (m, 3H), 7.31–7.28 (m, 2H), 4.80–4.72 (m, 2H), 4.26–4.16 (m, 2H), 3.94 (d, 0.37H, J=5.9 Hz), 3.87 (d, 0.63H, J=6.6 Hz), 3.74–3.65 (m, 2H), 3.59–3.56 (m, 2H), 3.41 (s, 3H), 2.93 (d, 0.63H, J=5.5 Hz), 2.92 (d, 0.37H, J=5.6 Hz), 2.63 (s, 0.63H), 2.60 (s, 0.63H), 2.53 (s, 0.37H), 2.52 (s, 0.37H), 2.34 (d, 0.37H, J=5.2 Hz), 2.33 (d, 0.63H, J=5.3 Hz), 1.87 (ddd, 0.63H, J=13.4, 7.0, 2.4 Hz), 1.81 (ddd, 0.37H, J=13.4, 7.1, 2.4 Hz), 1.63 (ddd, 0.37H, J=13.5, 4.5, 2.3 Hz), 1.58 (m, 1H), 1.49–1.45 (m, 1H), 1.53 (t, 1.11H, J=7.1 Hz), 1.17 (m, 0.63H), 1.14 (t, 1.89H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10d**: 207.7, 166.0, 158.4, 148.4, 130.1, 128.8, 128.7, 127.9, 94.0, 77.7, 67.0, 61.38, 59.04, 49.6, 48.3, 44.5, 39.1, 37.2, 28.3, 24.9, 13.8; minor isomer **11d**: 207.9, 165.8, 157.5, 148.2, 130.1, 128.8, 128.7, 127.9, 94.1, 78.9, 71.7, 61.41, 59.00, 53.3, 44.6, 43.5, 38.6, 33.9, 28.5, 25.6, 13.8. HRMS Calcd for $C_{23}H_{28}O_6$: m/z 400.1886, found m/z 400.1870.

4.2.8. Pauson–Khand reaction of norbornene 1e with acetylene 4 (Table 2, entry 5). A solution of acetylene **4** (41.7 mg, 0.239 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.7 mg, 0.262 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1e** (41.5 mg, 0.273 mmol) in 1,2-dichloroethane (1 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.5 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 13 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **10e** and **11e** (63.1 mg, 0.178 mmol, 74%, **10e/11e**=66:34 measured by 400 MHz ^1H NMR) as a clear, transparent oil.

8-*exo*-Acetoxy-5-(ethoxycarbonyl)-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10e) and 9-*exo*-acetoxy-5-(ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11e). R_f 0.28 (EtOAc/hexanes=1:4); IR (neat, NaCl) 3058 (w), 2979 (s), 2941 (m), 2254 (m), 1705 (s), 1495 (w), 1467 (w), 1446 (m), 1375 (s), 1295 (m), 1240 (s), 1174 (s), 1118 (w), 1047 (s), 1016 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.35 (m, 3H), 7.32–7.29 (m, 2H), 4.84 (d, 0.34H, J=6.6 Hz), 4.77 (d, 0.66H, J=6.8 Hz), 4.27–4.16 (m, 2H), 3.03 (d, 0.34H, J=5.4 Hz), 2.98 (d, 0.66H, J=5.5 Hz), 2.63 (br. s, 1.66H), 2.58 (d, 0.34H, J=4.4 Hz), 2.43 (d, 0.66H, J=5.4 Hz), 2.39 (d, 0.34H, J=5.6 Hz), 2.043 (s, 1.02H), 2.038 (s, 1.98H), 2.01 (ddd, 0.66H, J=13.8, 7.1, 2.4 Hz), 1.95 (ddd, 0.34H, J=13.7, 7.1, 2.5 Hz), 1.64 (ddd, 0.66H, J=13.8, 4.4, 2.4 Hz), 1.57 (ddd, 0.34H, J=13.7, 3.7, 3.4 Hz), 1.49 (dm, 0.34H, J=1.3 Hz), 1.46 (dm, 0.66H, J=1.3 Hz), 1.24–1.20 (m, 1H), 1.17 (t, 1.02H, J=7.2 Hz), 1.14 (t, 1.98H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10e**: 207.0, 170.45, 165.8, 158.1, 148.50, 129.92, 128.89, 128.7, 127.92, 75.4, 61.4, 49.2, 47.9, 44.5, 39.2, 37.5, 28.7, 21.2, 13.78; minor isomer **11e**: 207.5, 170.47, 165.6, 157.1, 148.53, 129.87, 128.92, 128.7, 127.94, 76.4, 61.5, 52.9, 44.3, 43.7, 38.7, 38.6, 28.9, 21.2, 13.81. Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found C, 71.44; H, 6.09.

4.2.9. Pauson–Khand reaction of norbornene 1f with acetylene 4 (Table 2, entry 6). A solution of acetylene **4** (41.4 mg, 0.238 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (88.8 mg, 0.260 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1f** (29.3 mg, 0.266 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 18 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **10f** and **11f** (53.1 mg, 0.170 mmol, 71%, **10f/11f**=50:50 measured by 400 MHz ^1H NMR) as white crystals.

5-(Ethoxycarbonyl)-8-*endo*-hydroxy-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10f) and 5-(ethoxycarbonyl)-9-*endo*-hydroxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11f). R_f 0.30 (EtOAc/hexanes=2:3); IR (neat, NaCl) 3401 (br. s), 3058 (w), 2960 (s), 2251 (w), 1699 (s), 1650 (m), 1494 (w), 1469 (w), 1446 (m), 1374 (m), 1345 (m), 1302 (m), 1240 (s), 1174 (s), 1142 (s), 1122 (m), 1077 (m), 1007 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.29 (m, 5H), 4.47 (m, 0.5H), 4.36 (m, 0.5H), 4.24–4.14 (m, 2H), 3.79 (d, 0.5H, J=5.5 Hz), 3.20 (d, 0.5H, J=5.4 Hz), 3.14 (d, 0.5H, J=5.4 Hz), 2.59 (d, 0.5H, J=6.4 Hz), 2.58 (s, 0.5H), 2.57 (s, 0.5H), 2.52 (d, 0.5H, J=4.4 Hz), 2.47 (d, 0.5H, J=4.5 Hz), 2.19 (ddd, 0.5H, J=14.7, 9.9, 4.9 Hz), 2.09 (ddd, 0.5H, J=14.4, 9.9, 4.6 Hz), 2.04 (d, 0.5H, J=2.8 Hz), 1.99 (d, 0.5H, J=2.5 Hz), 1.92 (m, 0.5H), 1.68 (ddd, 0.5H, J=13.6, 4.1, 3.5 Hz), 1.26–1.21 (m, 1.5H), 1.14 (t, 1.5H, J=7.1 Hz), 1.13 (t, 1.5H, J=7.1 Hz), 1.07 (m, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.3, 208.7, 166.2, 166.1, 159.4, 158.6, 148.8, 148.6, 130.4, 130.2, 128.8, 128.71, 128.69, 128.65, 127.9, 72.0, 71.3, 61.4, 61.3, 53.7, 48.7, 46.4, 45.6, 44.6, 40.4, 40.2, 38.9, 38.7, 38.2, 31.0, 30.7, 13.80, 13.78. HRMS Calcd for $C_{19}H_{20}O_4$: m/z 312.1362, found m/z 312.1344.

4.2.10. Pauson–Khand reaction of norbornene 1g with acetylene 4 (Table 2, entry 7). A solution of acetylene **4** (41.7 mg, 0.239 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (88.8 mg, 0.260 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1g** (53.1 mg, 0.237 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 24 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **10g** and **11g** (80.9 mg, 0.190 mmol, 80%, **10g/11g**=55:45

measured by 400 MHz ^{1}H NMR) as a light orange, transparent liquid.

5-(Ethoxycarbonyl)-8-*endo*-(*tert*-butyldimethylsilyoxy)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (10g) and 5-(ethoxycarbonyl)-9-*endo*-(*tert*-butyldimethylsilyoxy)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11g). R_f 0.37 (EtOAc/hexanes=1:19); IR (neat, NaCl) 3058 (w), 2956 (s), 2931 (s), 2886 (s), 2857 (s), 2254 (w), 2100 (m), 2065 (s), 2035 (s), 1797 (w), 1716 (s), 1495 (w), 1471 (s), 1464 (m), 1389 (w), 1372 (m), 1300 (w), 1251 (s), 1144 (s), 1100 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37–7.30 (m, 5H), 4.35 (ddd, 0.45H, J=9.4, 4.2, 3.1 Hz), 4.26–4.14 (m, 2.55H), 3.81 (d, 0.45H, J=5.4 Hz), 3.19 (d, 0.45H, J=5.4 Hz), 3.10 (d, 0.55H, J=5.4 Hz), 2.54–2.47 (m, 2H), 2.43 (d, 0.55H, J=4.2 Hz), 2.09 (ddd, 0.55H, J=12.9, 9.5, 4.8 Hz), 2.00 (ddd, 0.45H, J=13.1, 9.6, 4.5 Hz), 1.18 (t, 1.35H, J=7.1 Hz), 1.20–1.12 (m, 2H), 1.14 (t, 1.65H, J=7.1 Hz), 1.09 (dt, 0.55H, J=13.0, 2.9 Hz), 1.02 (dt, 0.45H, J=12.9, 2.9 Hz), 0.92 (s, 4.05H), 0.90 (s, 4.95H), 0.10 (s, 1.35H), 0.08 (s, 1.65H), 0.074 (s, 1.35H), 0.066 (s, 1.65H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10g**: 210.3, 166.3, 158.4, 148.8, 130.4, 128.73, 128.68, 127.88, 71.5, 61.25, 53.8, 48.7, 46.0, 40.1, 38.9, 30.6, 25.9, 18.05, 13.8, −4.7, −4.8; minor isomer **11g**: 208.9, 166.0, 159.9, 148.5, 130.5, 128.73, 128.68, 127.95, 72.3, 61.23, 46.6, 44.9, 40.5, 40.4, 39.2, 30.3, 25.8, 18.08, 13.9, −4.7, −4.8. HRMS Calcd for $C_{25}H_{34}O_4Si$: m/z 426.2226, found m/z 426.2221.

4.2.11. Pauson–Khand reaction of norbornene 1h with acetylene 4 (Table 2, entry 8). A solution of acetylene **4** (41.8 mg, 0.240 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.6 mg, 0.262 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1h** (46.5 mg, 0.232 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 18 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **10h** and **11h** (65.9 mg, 0.164 mmol, 71%, **10h/11h**=58:42 measured by 400 MHz ^{1}H NMR) as a light orange, transparent liquid.

8-*endo*-(Benzyloxy)-5-(ethoxycarbonyl)-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10h) and 9-*endo*-(benzyloxy)-5-(ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11h). R_f 0.24 (EtOAc/hexanes=1:9); IR (neat, NaCl) 3062 (w), 3032 (w), 2961 (s), 2868 (m), 2251 (w), 1701 (s), 1496 (m), 1454 (m), 1394 (w), 1373 (m), 1347 (m), 1225 (s), 1175 (s), 1146 (s), 1090 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43–7.29 (m, 10H), 4.67 (d_{AB}, 0.5H, J=11.4 Hz), 4.63 (d_{AB}, 0.5H, J=11.8 Hz), 4.47 (d_{AB}, 0.5H, J=11.7 Hz), 4.46 (d_{AB}, 0.5H, J=11.4 Hz), 4.30–4.18 (m, 2H), 4.15 (ddd, 0.5H, J=10.5, 4.0, 3.0 Hz), 4.02 (ddd, 0.5H, J=9.6, 3.8, 3.2 Hz), 3.73 (d, 0.5H, J=5.4 Hz), 3.16 (d, 0.5H, J=5.4 Hz), 3.10 (d, 0.5H, J=5.4 Hz), 2.84 (d, 0.5H, J=3.8 Hz), 2.80 (d, 0.5H, J=3.7 Hz), 2.59 (d, 0.5H, J=5.4 Hz), 2.55 (d, 0.5H, J=4.2 Hz), 2.49 (d, 0.5H, J=4.3 Hz), 2.14 (ddd, 0.5H, J=14.5, 9.8, 4.8 Hz), 2.06 (ddd, 0.5H, J=14.4, 10.1, 4.7 Hz), 1.32–1.15 (m, 3H), 1.17 (t, 1.5H, J=7.2 Hz), 1.15 (t, 1.5H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.8, 208.8, 166.1, 165.7, 158.7, 158.4, 149.4, 148.7, 138.13, 138.06, 130.4, 130.3, 128.8, 128.7, 128.41, 128.36, 127.9, 127.83, 127.81, 127.7, 127.60, 127.57, 78.9, 78.1, 71.2, 71.1, 61.3, 53.7, 48.6, 46.0, 43.3, 41.6, 40.3, 39.8, 38.4, 36.9, 36.2, 30.6, 30.3, 13.84, 13.79. HRMS Calcd for $C_{26}H_{26}O_4$: m/z 402.1831, found m/z 402.1838.

4.2.12. Pauson–Khand reaction of norbornene 1i with acetylene 4 (Table 2, entry 9). A solution of acetylene **4** (41.9 mg, 0.241 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.3 mg, 0.261 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1i** (46.6 mg, 0.235 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 24 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **10i** and **11i** (76.2 mg, 0.190 mmol, 81%, **10i/11i**=50:50 measured by 400 MHz ^{1}H NMR) as a white semi-solid.

5-(Ethoxycarbonyl)-8-*endo*-methoxyethoxymethoxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (10i) and 5-(ethoxycarbonyl)-9-*endo*-methoxyethoxymethoxy-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11i). R_f 0.15 (EtOAc/hexanes=1:4); IR (neat, NaCl) 3058 (w), 2959 (s), 2938 (s), 2888 (s), 2250 (w), 1794 (w), 1709 (s), 1494 (w), 1446 (m), 1373 (m), 1301 (w), 1241 (s), 1228 (s), 1170 (s), 1105 (s), 1048 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.37 (m, 3H), 7.31–7.28 (m, 2H), 4.82–4.76 (m, 2H), 4.32 (ddd, 0.5H, J=9.8, 4.0, 3.6 Hz), 4.23–4.14 (m, 2.5H), 3.76–3.69 (m, 2H), 3.64 (d, 0.5H, J=5.2 Hz), 3.62–3.55 (m, 2H), 3.399 (s, 1.5H), 3.396 (s, 1.5H), 3.11 (d, 0.5H, J=5.4 Hz), 3.05 (d, 0.5H, J=5.5 Hz), 2.699 (s, 0.5H), 2.697 (s, 0.5H), 2.54 (d, 0.5H, J=5.6 Hz), 2.52 (d, 0.5H, J=5.2 Hz), 2.47 (d, 0.5H, J=4.5 Hz), 2.15 (ddd, 0.5H, J=14.2, 10.5, 4.8 Hz), 2.05 (ddd, 0.5H, J=14.0, 10.2, 4.6 Hz), 1.66 (d, 0.5H, J=6.9 Hz), 1.25–1.17 (m, 2.5H), 1.130 (t, 1.5H, J=7.1 Hz), 1.128 (t, 1.5H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.6, 208.6, 166.1, 165.9, 159.0, 158.3, 148.8, 148.7, 130.3, 130.2, 128.74, 128.72, 128.66, 127.9, 94.8, 94.4, 76.24, 76.20, 71.8, 71.7, 67.2, 61.30, 61.28, 59.0, 53.7, 48.7, 46.1, 44.3, 42.2, 40.6, 39.8, 38.3, 36.7, 36.0, 30.5, 30.2, 13.8. HRMS Calcd for $C_{23}H_{28}O_6$: m/z 400.1886, found m/z 400.1876.

4.2.13. Pauson–Khand reaction of norbornene 1j with acetylene 4 (Table 2, entry 10). A solution of acetylene **4** (42.0 mg, 0.241 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (89.3 mg, 0.261 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1j**

(34.7 mg, 0.228 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 24 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **10j** and **11j** (59.3 mg, 0.167 mmol, 73%, **10j/11j**=50:50 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid.

8-*endo*-Acetoxy-5-(ethoxycarbonyl)-4-phenyltricyclo-[5.2.1.0^{2,6}]dec-4-ene-3-one (10j) and 9-*endo*-acetoxy-5-(ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3-one (11j). R_f 0.23 (EtOAc/hexanes=1:4); IR (neat, NaCl) 3058 (w), 2972 (s), 2255 (w), 1796 (w), 1716 (s), 1494 (w), 1446 (m), 1374 (s), 1301 (m), 1244 (s), 1176 (s), 1154 (s), 1048 (m), 1023 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39–7.36 (m, 3H), 7.32–7.30 (m, 2H), 5.14 (ddd, 0.5H, J=10.1, 4.2, 3.6 Hz), 5.07 (ddd, 0.5H, J=10.0, 4.1, 3.7 Hz), 4.27–4.14 (m, 2H), 3.59 (d, 0.5H, J=5.4 Hz), 3.15 (d, 0.5H, J=5.5 Hz), 3.02 (d, 0.5H, J=5.5 Hz), 2.80 (d, 0.5H, J=4.4 Hz), 2.77 (d, 0.5H, J=4.2 Hz), 2.57 (d, 0.5H, J=6.2 Hz), 2.56 (d, 0.5H, J=6.1 Hz), 2.53 (d, 0.5H, J=4.5 Hz), 2.29 (ddd, 0.5H, J=13.8, 10.0, 4.7 Hz), 2.18 (ddd, 0.5H, J=13.9, 10.1, 4.6 Hz), 2.11 (s, 1.5H), 2.07 (s, 1.5H), 1.63 (m, 0.5H), 1.26–1.19 (m, 2.5H), 1.16 (t, 1.5H, J=7.0 Hz), 1.14 (t, 1.5H, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.8, 208.1, 170.70, 170.67, 165.9, 165.6, 158.3, 158.2, 148.9, 148.8, 130.1, 128.9, 128.7, 127.9, 74.3, 73.3, 61.40, 61.39, 53.3, 48.4, 46.2, 43.6, 42.2, 40.8, 39.7, 38.5, 36.9, 35.9, 30.6, 30.3, 21.1, 13.79, 13.76. HRMS Calcd for $C_{21}H_{22}O_5$: m/z 354.1467, found m/z 354.1466.

4.2.14. Pauson–Khand reaction of norbornene 1k with acetylene 4 (Table 2, entry 11). A solution of acetylene **4** (54.0 mg, 0.310 mmol) in 1,2-dichloroethane (0.5 mL) was added to a flame-dried vial containing $Co_2(CO)_8$ (108 mg, 0.316 mmol) via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). The reaction mixture was stirred at room temperature for 30 min. A solution of norbornene **1k** (33.5 mg, 0.310 mmol) in 1,2-dichloroethane (0.5 mL) was then added to the reaction mixture via a cannula and rinsed with 1,2-dichloroethane (2×0.25 mL). Cyclohexylamine (0.11 mL, 0.962 mmol) was added, and the reaction mixture was stirred at 80°C for 21 h. After quenching with Et_2O (20 mL), the reaction mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **10k** and **11k** (41.7 mg, 0.134 mmol, 43%, **10k/11k**=74:26 measured by 400 MHz ^{1}H NMR) as a light yellow semi-solid.

5-(Ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3,8-dione (10k) and 5-(ethoxycarbonyl)-4-phenyltricyclo[5.2.1.0^{2,6}]dec-4-ene-3,9-dione (11k). R_f 0.52 (EtOAc/hexanes=2:3); IR (neat, NaCl) 3058 (m), 2982 (s), 2937 (s), 2254 (w), 1716 (s), 1494 (w), 1467 (w), 1446 (m), 1408 (w), 1374 (m), 1235 (s), 1163 (s), 1105 (m), 1077 (w), 1020 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.37 (m, 3H), 73.5–7.30 (m, 2H), 4.29–4.17 (m, 2H), 3.36 (d, 0.26H, J=5.5 Hz), 3.31 (d, 0.74H, J=5.5 Hz), 2.99 (d, 0.26H, J=3.4 Hz), 2.96 (d, 0.74H, J=3.4 Hz), 2.94 (s, 0.74H), 2.92 (s, 0.26H), 2.73 (dd, 0.74H, J=5.5, 0.7 Hz), 2.68 (d, 0.26H, J=5.4 Hz), 2.29 (d_{AB}d, 0.74H, J=18.0, 4.6 Hz), 2.22 (d_{AB}d, 0.26H, J=18.0, 4.6 Hz), 2.08 (d_{AB}d, 0.74H, J=18.0, 3.6 Hz), 2.01 (d_{AB}d, 0.26H, J=17.8, 4.1 Hz), 1.67–1.59 (m, 2H), 1.19 (t, 0.78H, J=7.1 Hz), 1.16 (t, 2.22H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ major isomer **10k**: 213.0, 205.2, 165.5, 157.5, 149.5, 129.6, 129.2, 128.71, 128.0, 61.7, 51.9, 47.5, 47.1, 43.6, 37.3, 30.6, 13.79; minor isomer **11k**: 214.1, 205.2, 165.5, 155.6, 148.8, 129.5, 129.3, 128.74, 128.1, 61.8, 52.3, 51.4, 43.14, 43.05, 38.1, 30.8, 13.83. HRMS Calcd for $C_{19}H_{18}O_4$: m/z 310.1205, found m/z 310.1207.

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