Rhodium-catalysed arylative annulation of 1,4-enynes with arylboronic acids

Takanori Matsuda* and Shoichi Watanuki

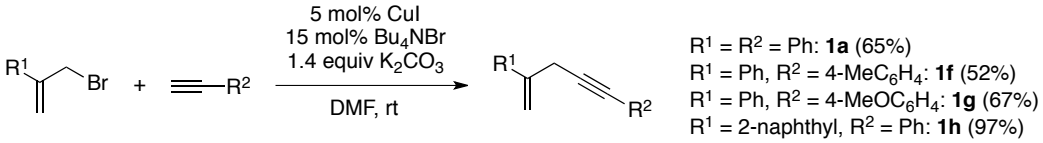
Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Electronic Supplementary Information

General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel® C-200 (75–150 μm). Preparative thin-layer chromatography (TLC) was performed on Wakogel® B-5F. Proton chemical shifts were referenced to residual $CHCl_3$ signal at 7.26 ppm. Carbon chemical shifts were referenced to $CDCl_3$ at 77.0 ppm.

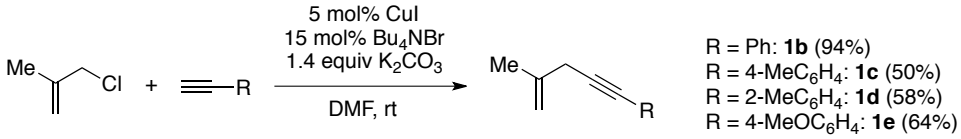
Materials. 1,4-Enynes were prepared according to the literature methods.[1] All other commercially available chemical resources were used as received without further purification.

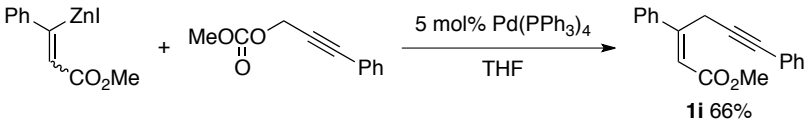
Preparation of 1,4-Enynes.

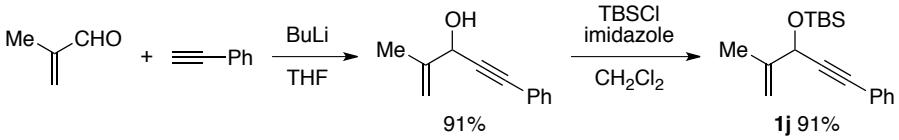


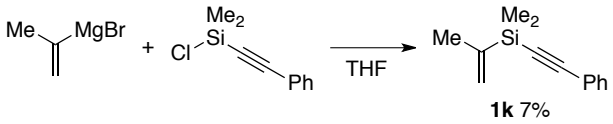
$R^1 = R^2$ = Ph: **1a** (65%)
R^1 = Ph, R^2 = 4-MeC_6H_4: **1f** (52%)
R^1 = Ph, R^2 = 4-$MeOC_6H_4$: **1g** (67%)
R^1 = 2-naphthyl, R^2 = Ph: **1h** (97%)

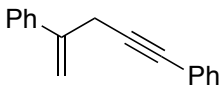
1 (*a*) F. Yang, K.-G. Ji, S.-C. Zhao, S. Ali, Y.-Y. Ye, X.-Y. Liu and Y.-M. Liang, *Chem. Eur. J.*, 2012, **18**, 6470; (*b*) S. Ma and A. Zhang, *J. Org. Chem.*, 2002, **67**, 2287; (*c*) W. Chen, J.-H. Tay, X.-Q. Yu and L. Pu, *J. Org. Chem.*, 2012, **77**, 6215.



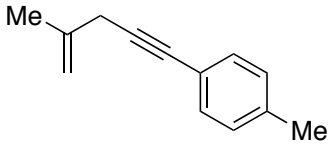




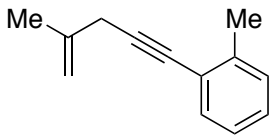




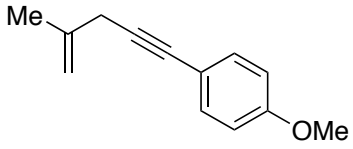
2,5-Diphenylpent-1-en-4-yne (1a): IR (ν/cm^{-1}): 1489, 1435, 903, 756, 694.



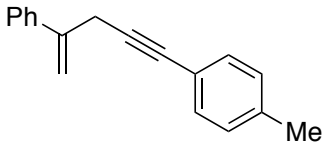
5-(4-Methylphenyl)-2-phenylpent-1-en-4-yne (1c): Colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.86 (s, 3H), 2.34 (s, 3H), 3.12 (s, 2H), 4.88 (s, 1H), 5.09 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.4, 22.2, 28.1, 82.8, 86.2, 111.7, 120.6, 128.9, 131.4, 137.7, 140.7; HRMS (MALDI) calcd for $C_{13}H_{14}Na$ $[M + Na]^+$ 193.0988, found 193.1012; IR (ν/cm^{-1}): 1508, 895, 818.



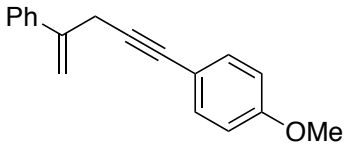
5-(2-Methylphenyl)-2-phenylpent-1-en-4-yne (1d): Colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.88 (s, 3H), 2.45 (s, 3H), 3.19 (s, 2H), 4.88–4.92 (m, 1H), 5.12 (s, 1H), 7.08–7.24 (m, 3H), 7.40 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.8, 22.1, 28.3, 81.7, 90.9, 111.7, 123.5, 125.4, 127.6, 129.3, 131.9, 139.9, 140.7; HRMS (MALDI) calcd for $C_{13}H_{14}Na$ $[M + Na]^+$ 193.0988, found 193.1007; IR (ν/cm^{-1}): 1485, 895, 756.



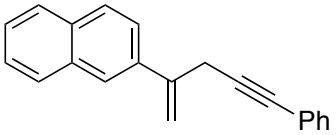
5-(4-Methoxyphenyl)-2-phenylpent-1-en-4-yne (1e): Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.84–1.86 (m, 3H), 3.11 (s, 2H), 3.80 (s, 3H), 4.86–4.89 (m, 1H), 5.08 (s, 1H), 6.79–6.85 (m, 2H), 7.33–7.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.2, 28.2, 55.2, 82.5, 85.4, 111.6, 113.8, 115.9, 132.9, 140.8, 159.1; HRMS (MALDI) calcd for $C_{13}H_{14}NaO$ $[M + Na]^+$ 209.0937, found 209.0919; IR (ν/cm^{-1}): 1508, 1246, 833.



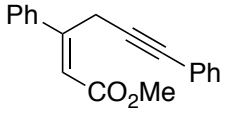
5-(4-Methylphenyl)-2-phenylpent-1-en-4-yne (1f): White solid, mp 68–69 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 2.34 (s, 3H), 3.61 (s, 2H), 5.53–5.59 (m, 2H), 7.10 (d, J = 8.1 Hz, 2H), 7.26–7.40 (m, 5H), 7.46–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 21.4, 25.8, 83.8, 86.1, 113.7, 120.5, 125.8, 127.7, 128.3, 128.9, 131.4, 137.7, 139.9, 142.6; HRMS (ESI) calcd for $C_{18}H_{16}Na$ $[M + Na]^+$ 255.1144, found 255.1142; IR (ν/cm^{-1}): 1504, 903, 818, 771, 702.



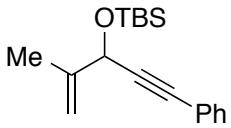
5-(4-Methoxyphenyl)-2-phenylpent-1-en-4-yne (1g): White solid, mp 80–81 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 3.58–3.62 (m, 2H), 3.80 (s, 3H), 5.52–5.58 (m, 2H), 6.80–6.85 (m, 2H), 7.26–7.40 (m, 5H), 7.46–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 25.8, 55.1, 83.5, 85.3, 113.6, 113.8, 115.7, 125.7, 127.7, 128.3, 132.9, 139.9, 142.7, 159.2; HRMS (ESI) calcd for $C_{18}H_{16}NaO$ $[M + Na]^+$ 271.1093, found 271.1094; IR (ν/cm^{-1}): 1504, 1234, 1026, 910, 825, 702.



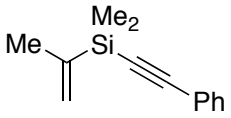
2-(2-Naphthyl)-5-phenylpent-1-en-4-yne (1h): White solid, mp 99–101 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 3.75 (s, 2H), 5.68 (s, 1H), 5.71 (s, 1H), 7.26–7.32 (m, 3H), 7.40–7.53 (m, 4H), 7.65–7.70 (m, 1H), 7.80–7.88 (m, 3H), 7.90–7.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 25.9, 83.8, 86.9, 114.3, 123.6, 124.1, 124.4, 126.0, 126.2, 127.5, 127.8, 127.9, 128.18, 128.24, 131.6, 132.9, 133.2, 137.0, 142.2; HRMS (ESI) calcd for $C_{21}H_{16}Na$ $[M + Na]^+$ 291.1144, found 291.1142; IR (ν/cm^{-1}): 903, 818, 748, 687.



Methyl (*E*)-3,6-diphenylhex-2-en-5-ynoate (1i): Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3H), 4.32 (s, 2H), 6.22 (s, 1H), 7.19–7.29 (m, 4H), 7.38–7.43 (m, 4H), 7.60–7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.2, 51.4, 81.5, 86.6, 117.6, 126.6, 126.9, 127.7, 128.0, 128.5, 129.4, 131.5, 139.8, 153.6, 166.5.



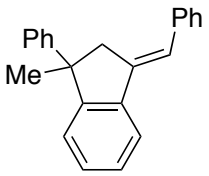
3-[(*tert*-Butyldimethylsilyl)oxy]-2-methyl-5-phenylpent-1-en-4-yne (1j): Colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 3H), 0.20 (s, 3H), 0.95 (s, 9H), 1.89 (s, 3H), 4.91 (s, 1H), 5.00 (s, 1H), 5.21 (s, 1H), 7.27–7.33 (m, 3H), 7.40–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –5.0, –4.6, 18.3, 18.4, 25.8, 67.1, 84.9, 89.2, 111.3, 123.0, 128.18, 128.21, 131.6, 144.6; HRMS (MALDI) calcd for $C_{18}H_{26}NaOSi$ $[M + Na]^+$ 309.1645, found 309.1676; IR (ν/cm^{-1}): 2954, 2854, 1250, 1072, 849, 779.



Dimethyl(isopropenyl)(phenylethynyl)silane (1k): Colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.32 (s, 6H), 1.94 (t, J = 1.5 Hz, 3H), 5.48 (dq, J = 2.7, 1.4 Hz, 1H), 5.67 (dq, J = 3.2, 1.6 Hz, 1H), 7.27–7.33 (m, 3H), 7.44–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –2.1, 22.1, 92.0, 106.1, 123.0, 126.5, 128.2, 128.6, 132.0, 144.8; HRMS (MALDI) calcd for $C_{13}H_{16}NaSi$ $[M + Na]^+$ 223.0913, found 223.0943; IR (ν/cm^{-1}): 2954, 2160, 1250, 926, 841, 779, 756, 687.

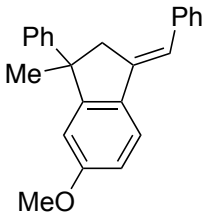
General Procedure for the Rhodium-Catalysed Arylative Annulation of 1,4-Enynes 1 with Arylboronic Acids 2. A Schlenk tube was charged with arylboronic acid **2** (0.300 mmol), $[Rh(OH)(cod)]_2$ (2.5 μmol, 5 mol% Rh), *rac*-BINAP (6.0 μmol), and 1,4-enyne **1** (0.100 mmol) (liquid substrates were added via syringe after 1,4-dioxane). The tube was evacuated and backfilled with nitrogen. 1,4-Dioxane (1.0 mL) and Et_3N (0.150 mmol) were added via syringe through the septum. After heating at 90 °C for the indicated time, the

reaction mixture was filtered through a plug of Florisil® washing with hexane–AcOEt (5:1), and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel to afford the following compounds.



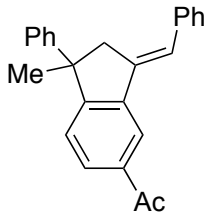
(*E*)-3-Benzylidene-1-methyl-1-phenylindane (3a). The general procedure was followed using **1a** (21.4 mg, 0.098 mmol), **2a** (36.5 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), and 1,4-dioxane (1.0 mL) for 4 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3a** (22.3 mg, 0.075 mmol, 77%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (s, 3H), 3.27 (dd, J = 17.1, 2.4 Hz, 1H), 3.42 (dd, J = 17.0, 2.3 Hz, 1H), 7.01–7.08 (m, 2H), 7.14–7.47 (m, 12H), 7.65–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.2, 50.5, 50.9, 119.8, 120.1, 124.8, 125.9, 126.38, 126.41, 127.2, 128.2, 128.4, 128.5, 128.7, 138.0, 141.6, 141.7, 149.3, 153.5; HRMS (MALDI) calcd for $C_{23}H_{20}Na$ $[M + Na]^+$ 319.1457, found 319.1462.

Asymmetric reaction: **1a** (21.7 mg, 0.099 mmol), **2a** (36.7 mg, 0.301 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.1 mg, 12.2 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane, 4 times) yielded **3a** (21.1 mg, 0.071 mmol, 72%); 92% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 99.9:0.1, 0.3 mL/min, t_{minor} = 37.0 min, t_{major} = 39.2 min). $[\alpha]_D^{23}$ = +79.6 (*c* 0.077, $CHCl_3$).



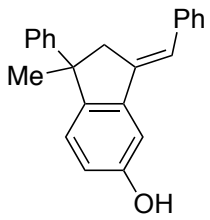
(*E*)-3-Benzylidene-6-methoxy-1-methyl-1-phenylindane (3b). The general procedure was followed using **1a** (21.2 mg, 0.097 mmol), **2b** (45.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), and 1,4-dioxane (1.0 mL) for 2 h. Purification by preparative TLC on silica gel (hexane:AcOEt:toluene = 48:2:1) yielded **3b** (23.1 mg, 0.071 mmol, 73%) as a yellow solid. Mp 128–131 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73 (s, 3H), 3.26 (dd, J = 16.8, 2.4 Hz, 1H), 3.40 (dd, J = 16.8, 2.4 Hz, 1H), 3.76 (s, 3H), 6.53 (d, J = 2.4 Hz, 1H), 6.84–6.90 (m, 2H), 7.13–7.43 (m, 10H), 7.58 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.0, 50.5, 51.3, 55.4, 109.0, 114.2, 117.7, 121.2, 125.9, 126.0, 126.4, 128.21, 128.23, 128.3, 134.5, 138.3, 141.3, 149.1, 155.3, 160.6; HRMS (MALDI) calcd for $C_{24}H_{22}NaO$ $[M + Na]^+$ 349.1563, found 349.1537.

Asymmetric reaction: **1a** (21.8 mg, 0.100 mmol), **2b** (45.5 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt:toluene = 60:2:1, 3 times) yielded **3b** (23.5 mg, 0.072 mmol, 72%); 87% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 98:2, 0.3 mL/min, t_{minor} = 17.6 min, t_{major} = 22.2 min). $[\alpha]_D^{22}$ = +123.9 (*c* 0.14, $CHCl_3$).



(*E*)-5-Acetyl-3-benzylidene-1-methyl-1-phenylindane (3c). The general procedure was followed using **1a** (22.2 mg, 0.102 mmol), **2c** (49.5 mg, 0.302 mmol), $[Rh(OH)(cod)]_2$ (1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), and 1,4-dioxane (1.0 mL) for 3.5 h. Preparative TLC on silica gel (hexane:AcOEt:toluene = 45:5:1) followed by recycling gel permeation chromatography ($CHCl_3$) yielded **3c** (24.3 mg, 0.072 mmol, 71%) as a white solid. Mp 145–154 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (s, 3H), 2.67 (s, 3H), 3.31 (dd, J = 16.8, 2.4 Hz, 1H), 3.46 (dd, J = 17.0, 2.6 Hz, 1H), 7.09–7.48 (m, 12H), 7.83 (dd, J = 8.0, 1.7 Hz, 1H), 8.25 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.9, 27.9, 50.7, 50.9, 120.2, 121.3, 124.9, 126.25, 126.32, 126.9, 128.4, 128.5, 128.7, 128.9, 136.6, 137.6, 140.3, 142.2, 148.4, 158.6, 198.0; HRMS (MALDI) calcd for $C_{24}H_{22}NaO$ $[M + Na]^+$ 361.1563, found 361.1533; IR (ν/cm^{-1}): 1678, 1230, 702.

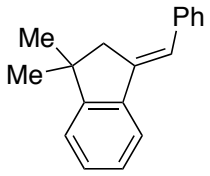
Asymmetric reaction: **1a** (21.8 mg, 0.100 mmol), **2c** (49.2 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt:toluene = 60:6:1, 3 times) yielded **3c** (23.5 mg, 0.069 mmol, 70%); 91% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 99.9:0.1, 1.0 mL/min, t_{minor} = 56.8 min, t_{major} = 61.4 min). $[\alpha]_D^{22}$ = +118.8 (*c* 0.17, $CHCl_3$).



(*E*)-3-Benzylidene-1-methyl-1-phenylindan-5-ol (3d). The general procedure was followed using **1a** (22.3 mg, 0.102 mmol), **2d** (40.8 mg, 0.296 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), and 1,4-dioxane (1.0 mL) for 3 h. Purification by preparative TLC on silica gel ($CHCl_3$) yielded **3d** (18.8 mg, 0.060 mmol,

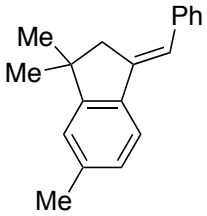
59%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (s, 3H), 3.26 (dd, J = 17.0, 2.3 Hz, 1H), 3.36 (dd, J = 17.0, 2.9 Hz, 1H), 4.25 (s, 1H), 6.70 (dd, J = 7.5, 0.9 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 7.18–7.45 (m, 12H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 25.3, 49.6, 52.1, 113.0, 116.3, 120.6, 126.2, 126.6, 127.0, 128.4, 128.6, 129.1, 129.3, 137.80, 137.84, 141.5, 143.6, 146.9, 152.4; HRMS (MALDI) calcd for $C_{23}H_{20}NaO$ $[M + Na]^+$ 335.1406, found 335.1374; IR (ν/cm^{-1}): 3533, 1589, 1481, 1219, 756, 694.

Asymmetric reaction: **1a** (21.8 mg, 0.100 mmol), **2d** (41.4 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:toluene = 5:1, 4 times, then hexane:AcOEt:toluene = 50:10:1) yielded **3d** (18.8 mg, 0.060 mmol, 61%); 89% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 90:10, 1.0 mL/min, t_{minor} = 7.0 min, t_{major} = 7.9 min). $[\alpha]_D^{22}$ = +154.2 (*c* 0.095, $CHCl_3$).

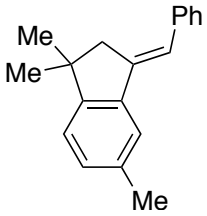


(*E*)-3-Benzylidene-1,1-dimethylindane (3e). The general procedure was followed using **1b** (15.5 mg, 0.099 mmol), **2a** (36.5 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (15.4 mg, 0.152 mmol), and 1,4-dioxane (1.0 mL) for 4 h. Purification by preparative TLC on silica gel (hexane) yielded **3e** (15.5 mg, 0.066 mmol, 67%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 6H), 2.98 (d, J = 2.7 Hz, 2H), 6.96 (t, J = 2.4 Hz, 1H), 7.17–7.41 (m, 8H), 7.55–7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 30.0, 42.9, 47.8, 119.6, 120.1, 122.7, 126.3, 126.8, 128.36, 128.44, 128.5, 138.3, 140.9, 141.9, 154.3; HRMS (MALDI) calcd for $C_{18}H_{18}Na$ $[M + Na]^+$ 257.1301, found 257.1300.

No NOE was observed between the vinylic proton and the methylene protons.

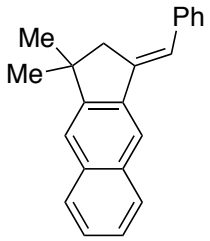


(*E*)-3-Benzylidene-1,1,6-trimethylindane (3f). The general procedure was followed using **1b** (16.3 mg, 0.104 mmol), **2d** (40.6 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.6 mg, 5.8 μmol), Et_3N (15.0 mg, 0.148 mmol), and 1,4-dioxane (1.0 mL) for 3 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3f** (17.1 mg, 0.069 mmol, 66%) as a white solid. Mp 80–86 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (s, 6H), 2.41 (s, 3H), 2.98 (d, J = 2.4 Hz, 2H), 6.92 (t, J = 2.4 Hz, 1H), 7.05–7.30 (m, 4H), 7.35–7.42 (m, 2H), 7.44–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.6, 30.0, 42.7, 48.1, 118.6, 119.9, 123.2, 126.1, 127.9, 128.3, 128.4, 138.3, 138.4, 138.5, 141.9, 154.5; HRMS (MALDI) calcd for $C_{19}H_{20}Na$ $[M + Na]^+$ 271.1457, found 271.1480.

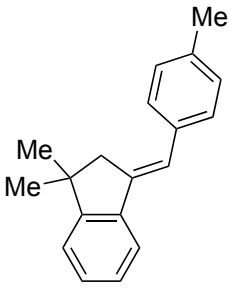


(*E*)-3-Benzylidene-1,1,5-trimethylindane (3g). The general procedure was followed using **1b** (15.5 mg, 0.099 mmol), **2e** (40.5 mg, 0.298 mmol), $[Rh(OH)(cod)]_2$ (1.0 mg, 2.2 μmol, 4.4 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (15.3 mg, 0.151 mmol), and 1,4-dioxane (1.0 mL) for 3 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3g** (11.9 mg, 0.048 mmol, 48%) as a white solid. Mp 73–79 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (s, 6H), 2.39 (s, 3H), 2.97 (d, J = 2.4 Hz,

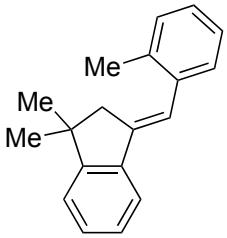
2H), 6.94 (t, J = 2.4 Hz, 1H), 7.06–7.26 (m, 3H), 7.34–7.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.4, 30.1, 42.5, 48.1, 119.3, 120.5, 122.4, 126.2, 128.4, 128.5, 129.5, 136.4, 138.3, 141.1, 142.0, 151.6; HRMS (MALDI) calcd for $C_{19}H_{20}Na$ $[M + Na]^+$ 271.1457, found 271.1489.



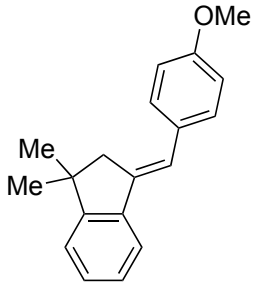
(*E*)-3-Benzylidene-1,1-dimethylbenzo[*f*]indane (3h). The general procedure was followed using **1b** (16.3 mg, 0.104 mmol), **2f** (51.9 mg, 0.302 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (14.8 mg, 0.146 mmol), and 1,4-dioxane (1.0 mL) for 2 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3h** (20.1 mg, 0.071 mmol, 68%) as a white solid. Mp 144–149 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 6H), 3.06 (d, J = 2.7 Hz, 2H), 7.20–7.30 (m, 2H), 7.38–7.46 (m, 4H), 7.49–7.55 (m, 2H), 7.65 (s, 1H), 7.77–7.90 (m, 2H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 30.3, 42.5, 48.2, 118.4, 120.6, 121.0, 125.3, 125.6, 126.5, 127.6, 128.2, 128.4, 128.7, 133.1, 134.3, 138.1, 140.3, 141.1, 152.6; HRMS (MALDI) calcd for $C_{22}H_{20}Na$ $[M + Na]^+$ 307.1457, found 307.1455.



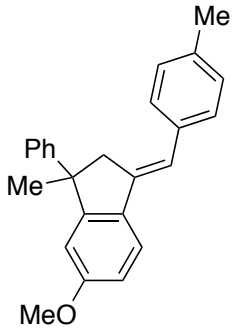
(*E*)-1,1-Dimethyl-3-(4-methylbenzylidene)indane (3i). The general procedure was followed using **1c** (16.7 mg, 0.098 mmol), **2a** (36.4 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.7 mg, 5.9 μmol), Et_3N (15.6 mg, 0.154 mmol), and 1,4-dioxane (1.0 mL) for 2.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3i** (16.5 mg, 0.066 mmol, 68%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 6H), 2.37 (s, 3H), 2.96 (d, J = 2.4 Hz, 2H), 6.93 (t, J = 2.6 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.22–7.27 (m, 3H), 7.36 (d, J = 7.8 Hz, 2H), 7.53–7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.2, 30.0, 42.8, 47.8, 119.5, 120.0, 122.6, 126.8, 128.2, 128.4, 129.1, 135.4, 136.1, 141.0, 141.1, 154.1; HRMS (MALDI) calcd for $C_{19}H_{20}Na$ $[M + Na]^+$ 271.1457, found 271.1449.



(*E*)-1,1-Dimethyl-3-(2-methylbenzylidene)indane (3j). The general procedure was followed using **1d** (16.5 mg, 0.097 mmol), **2a** (36.7 mg, 0.301 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (15.5 mg, 0.153 mmol), and 1,4-dioxane (1.0 mL) for 2.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 42:8:1) yielded **3j** (16.1 mg, 0.065 mmol, 67%) as a white solid. Mp 57–60 °C ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 6H), 2.39 (s, 3H), 2.86 (d, J = 2.4 Hz, 2H), 7.03 (t, J = 2.4 Hz, 1H), 7.12–7.31 (m, 6H), 7.40–7.44 (m, 1H), 7.57–7.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.2, 29.7, 42.6, 47.5, 117.7, 120.2, 122.7, 125.6, 126.6, 126.8, 127.9, 128.4, 130.1, 136.6, 137.1, 140.9, 142.0, 154.4; HRMS (MALDI) calcd for $C_{19}H_{20}Na$ $[M + Na]^+$ 271.1457, found 271.1439.



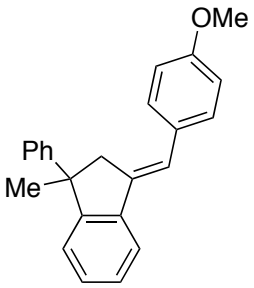
(*E*)-3-(4-Methoxybenzylidene)-1,1-dimethylindane (3k). The general procedure was followed using **1e** (17.8 mg, 0.096 mmol), **2a** (36.5 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.6 mg, 5.8 μmol), Et_3N (15.3 mg, 0.151 mmol), and 1,4-dioxane (1.0 mL) for 2 h. Purification by preparative TLC on silica gel (hexane:AcOEt:toluene = 45:5:1) yielded **3k** (17.4 mg, 0.065 mmol, 69%) as a yellow solid. Mp 88–95 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (s, 6H), 2.96 (d, J = 2.1 Hz, 2H), 3.85 (s, 3H), 6.90–6.98 (m, 3H), 7.22–7.31 (m, 3H), 7.43 (d, J = 8.7 Hz, 2H), 7.53–7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 30.1, 42.8, 47.8, 55.3, 113.8, 119.0, 119.8, 122.6, 126.8, 128.0, 129.7, 131.1, 139.7, 141.2, 153.9, 158.1; HRMS (MALDI) calcd for $C_{19}H_{20}ONa$ $[M + Na]^+$ 287.1406, found 287.1441.



(*E*)-6-Methoxy-1-methyl-3-(4-methylbenzylidene)-1-phenylindane (3l). The general procedure was followed using **1f** (23.2 mg, 0.100 mmol), **2b** (45.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol% Rh), *rac*-BINAP (7.3 mg, 11.7 μmol), and 1,4-dioxane (1.0 mL) for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 60:6:1, 3 times) yielded **3l** (24.5 mg, 0.072 mmol, 72%) as a brown

solid. Mp 119–122 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 1.72 (s, 3H), 2.34 (s, 3H), 3.24 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.38 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.75 (s, 3H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.83–6.89 (m, 2H), 7.11–7.33 (m, 9H), 7.56 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 21.1, 28.0, 50.5, 51.3, 55.4, 109.0, 114.2, 117.6, 121.0, 125.9, 126.4, 128.18, 128.20, 129.1, 134.7, 135.5, 135.8, 140.4, 149.2, 155.1, 160.5; HRMS (ESI) calcd for $C_{25}H_{24}NaO$ [M + Na]$^+$ 363.1719, found 363.1722.

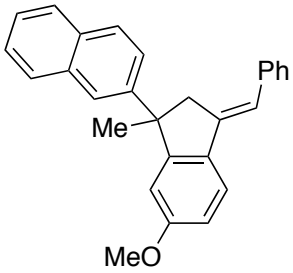
Asymmetric reaction: **1f** (23.2 mg, 0.100 mmol), **2b** (45.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 50:5:1, 2 times) yielded **3l** (25.4 mg, 0.075 mmol, 75%); 84% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 99.5:0.5, 0.3 mL/min, t_{minor} = 30.2 min, t_{major} = 49.2 min). $[\alpha]_D^{22}$ = +107.1 (*c* 0.065, $CHCl_3$).



(*E*)-3-(4-Methoxybenzylidene)-1-methyl-1-phenylindane (3m). The general procedure was followed using **1g** (24.8 mg, 0.100 mmol), **2a** (36.7 mg, 0.301 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol% Rh), *rac*-BINAP (7.5 mg, 12.0 μmol), and 1,4-dioxane (1.0 mL) for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$ = 10:1, 3 times) yielded **3m** (22.9 mg, 0.070 mmol, 70%) as a yellow solid. Mp 99–104 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 1.73 (s, 3H), 3.23 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.38 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.82 (s, 3H), 6.86–6.93 (m, 2H), 6.96–6.99 (m, 1H), 7.01–7.06 (m, 1H), 7.13–7.32 (m, 7H), 7.35–7.41 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ

28.2, 50.5, 50.8, 55.3, 113.9, 119.3, 119.8, 124.7, 125.9, 126.4, 127.1, 128.2, 128.3, 129.8, 130.9, 139.4, 141.8, 149.4, 153.2, 158.2; HRMS (ESI) calcd for $C_{24}H_{22}NaO$ $[M + Na]^+$ 349.1563, found 349.1565.

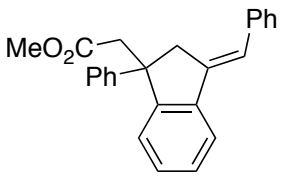
Asymmetric reaction: **1g** (24.8 mg, 0.100 mmol), **2a** (36.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 60:6:1, 3 times) yielded **3m** (20.9 mg, 0.064 mmol, 64%); 90% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 98:2, 0.5 mL/min, t_{major} = 20.4 min, t_{minor} = 23.3 min). $[\alpha]_D^{22}$ = +192.0 (*c* 0.088, $CHCl_3$).



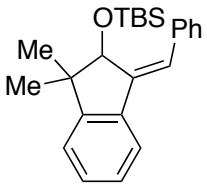
(*E*)-3-Benzylidene-6-methoxy-1-methyl-1-(2-naphthyl)indane (3n). The general procedure was followed using **1h** (28.2 mg, 0.105 mmol), **2b** (45.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol% Rh), *rac*-BINAP (7.4 mg, 11.9 μmol), and 1,4-dioxane (1.0 mL) for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 60:6:1, 3 times) yielded **3n** (26.3 mg, 0.070 mmol, 66%) as a yellow solid. Mp 176–181 °C; ^{1}H NMR ($CDCl_3$, 301 MHz) δ 1.83 (s, 3H), 3.31 (dd, *J* = 17.0, 2.3 Hz, 1H), 3.49 (dd, *J* = 17.0, 2.6 Hz, 1H), 3.73 (s, 3H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.85–6.93 (m, 2H), 7.13–7.21 (m, 1H), 7.25–7.36 (m, 3H), 7.38–7.50 (m, 4H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.75–7.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.6 MHz) δ 28.0, 50.7, 50.9, 55.4, 108.9, 114.5, 117.9, 121.2, 123.9, 125.6, 125.9, 126.00, 126.02, 127.4, 128.0, 128.1,

128.3, 128.4, 131.8, 133.1, 134.6, 138.3, 141.3, 146.3, 155.3, 160.7; HRMS (ESI) calcd for $C_{28}H_{24}NaO$ $[M + Na]^+$ 399.1719, found 399.1722.

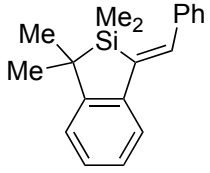
Asymmetric reaction: **1h** (28.2 mg, 0.105 mmol), **2b** (45.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 10 mol%), and (*R*)-MeO-BIPHEP (7.0 mg, 12.0 μmol) were reacted in 1,4-dioxane (1.0 mL) at 90 °C for 3.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 50:5:1, 2 times) yielded **3n** (27.7 mg, 0.074 mmol, 70%); 86% ee determined by HPLC analysis (CHIRALPAK® IB column, hexane:*i*-PrOH = 99.9:0.1, 0.5 mL/min, t_{minor} = 35.7 min, t_{minor} = 39.5 min). $[\alpha]_D^{22}$ = +215.4 (*c* 0.10, $CHCl_3$).



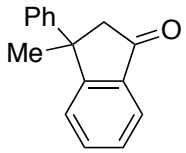
(*E*)-3-Benzylidene-1-(methoxycarbonyl)-1-phenylindane (3o). The general procedure was followed using **1i** (27.3 mg, 0.099 mmol), **2a** (36.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), and 1,4-dioxane (1.0 mL) for 4 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$:toluene = 45:5:1) yielded **3o** (17.9 mg, 0.051 mmol, 51%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.07 (d, *J* = 15.3 Hz, 1H), 3.33 (d, *J* = 15.3 Hz, 1H), 3.51 (s, 3H), 3.54 (dd, *J* = 17.0, 2.3 Hz, 1H), 3.73 (dd, *J* = 17.0, 2.3 Hz, 1H), 7.01 (t, *J* = 2.4 Hz, 1H), 7.12–7.40 (m, 11H), 7.44–7.49 (m, 2H), 7.63–7.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 44.2, 47.9, 51.5, 52.5, 119.8, 120.2, 125.3, 125.9, 126.2, 126.5, 127.7, 128.40, 128.43, 128.5, 128.6, 137.8, 141.1, 142.0, 147.3, 149.8, 171.5; HRMS (MALDI) calcd for $C_{25}H_{22}O_2Na$ $[M + Na]^+$ 377.1512, found 377.1523; IR (ν/cm^{-1}): 1736, 1442, 1165, 910, 764, 694.



(*Z*)-3-Benzylidene-2-[(*tert*-butyldimethylsilyl)oxy]-1,1-dimethylindane (3p). The general procedure was followed using **1j** (28.8 mg, 0.101 mmol), **2a** (36.3 mg, 0.298 mmol), $[Rh(OH)(cod)]_2$ (1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (14.7 mg, 0.145 mmol), and 1,4-dioxane (1.0 mL) for 4.5 h. Purification by preparative TLC on silica gel (hexane) yielded **3p** (18.4 mg, 0.050 mmol, 50%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ –0.66 (s, 3H), –0.18 (s, 3H), 0.81 (s, 9H), 1.06 (s, 3H), 1.42 (s, 3H), 4.83 (s, 1H), 7.03 (s, 1H), 7.19–7.32 (m, 4H), 7.36–7.43 (m, 2H), 7.52–7.56 (m, 1H), 7.60–7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.9, –3.7, 18.6, 20.6, 25.9, 29.9, 47.7, 83.2, 120.6, 122.7, 125.1, 127.0, 127.2, 128.4, 128.7, 129.1, 137.2, 139.8, 143.7, 152.4; HRMS (MALDI) calcd for $C_{24}H_{32}OSiNa$ $[M + Na]^+$ 387.2115, found 387.2131.



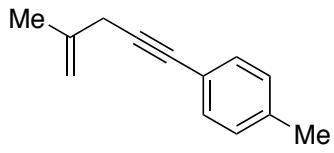
(*Z*)-3-Benzylidene-1,1,2,2-tetramethyl-2-silaindane (3q). The general procedure was followed using **1k** (20.9 mg, 0.104 mmol), **2a** (36.5 mg, 0.299 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol), Et_3N (15.3 mg, 0.151 mmol), and 1,4-dioxane (1.0 mL) for 3 h. Purification by preparative TLC on silica gel (hexane) yielded **3q** (14.2 mg, 0.051 mmol, 49%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 6H), 1.23 (s, 6H), 7.18–7.44 (m, 8H), 7.55–7.60 (m, 1H), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.3, 25.9, 26.1, 121.8, 124.6, 126.3, 127.3, 127.8, 128.06, 128.12, 128.2, 128.9, 136.9, 139.7, 152.8; HRMS (MALDI) calcd for $C_{19}H_{22}NaSi$ $[M + Na]^+$ 301.1383, found 301.1388.

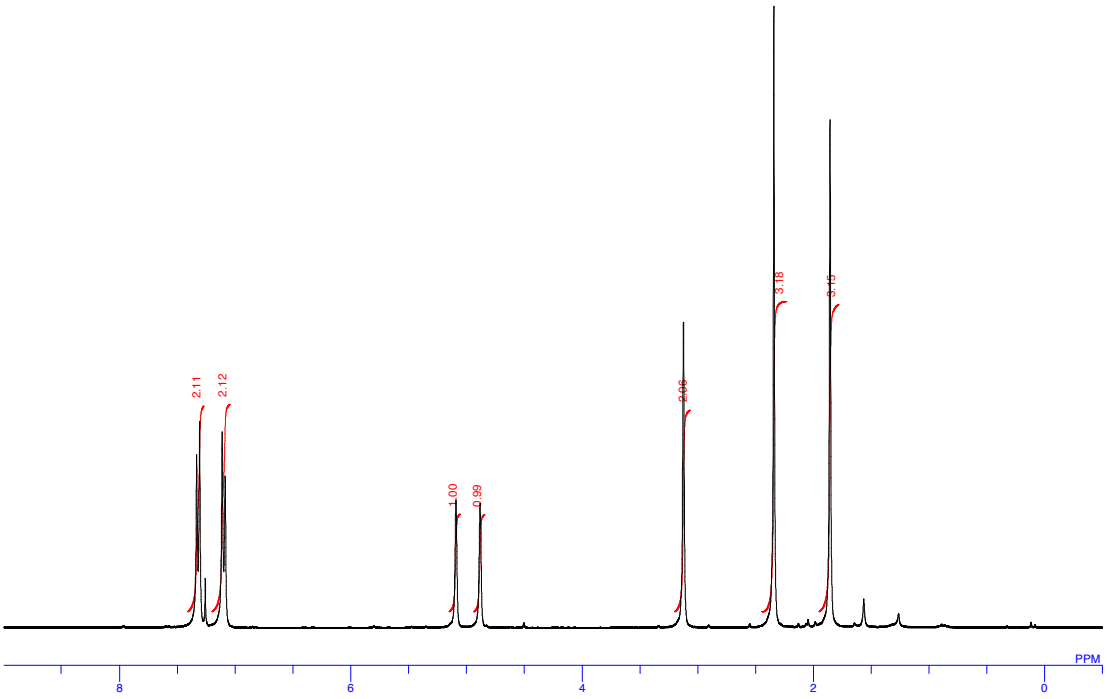


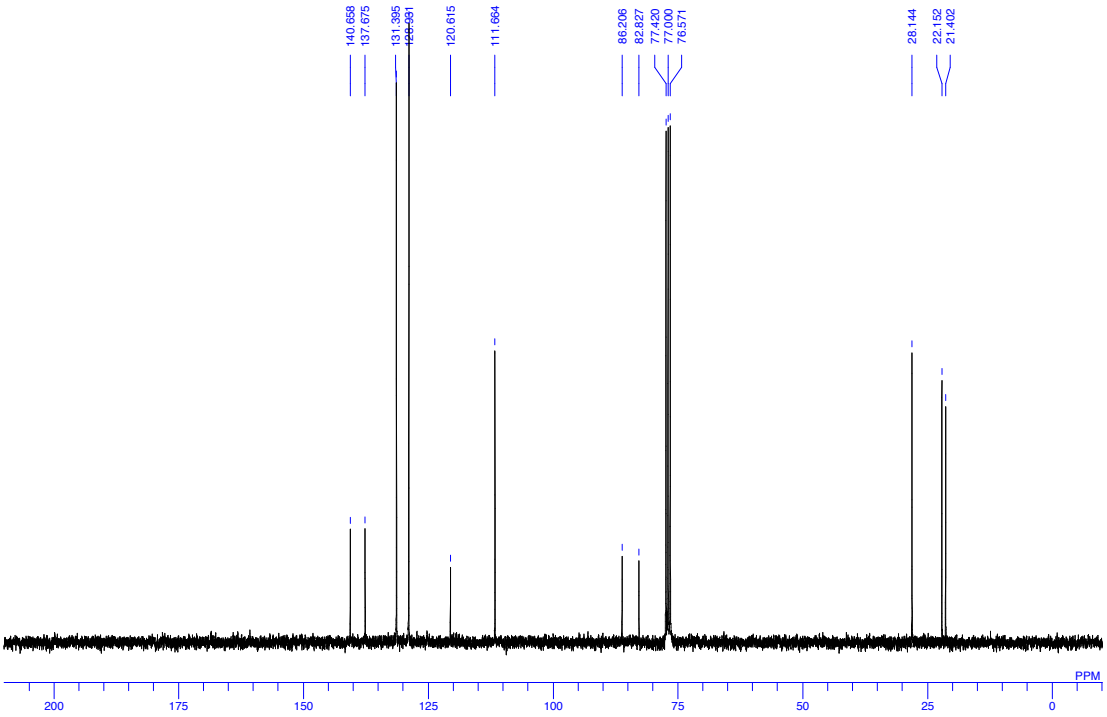
3-Methyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (4). A mixture of **3a** (29.6 mg, 0.100 mmol), 4-iodobenzoic acid (5.0 mg, 0.020 mmol), and Oxone® (123.0 mg) in H_2O–CH_3CN (1:1, 1.0 mL) were heated at 60 °C for 22 h. After cooling to room temperature, water was added to the reaction mixture, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by preparative TLC on silica gel (hexane:AcOEt = 10:1) to afford **4** (13.9 mg, 0.063 mmol, 63%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 301 MHz) δ 1.84 (s, 3H), 2.87 (d, J = 18.9 Hz, 1H), 3.00 (d, J = 18.9 Hz, 1H), 7.15–7.33 (m, 6H), 7.42 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H). The spectral data matched those reported in the literature.[2]

2 T. Matsuda, M. Shigeno, M. Makino and M. Murakami, *Org. Lett.*, 2006, **8**, 3379.

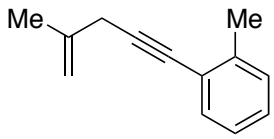
1c

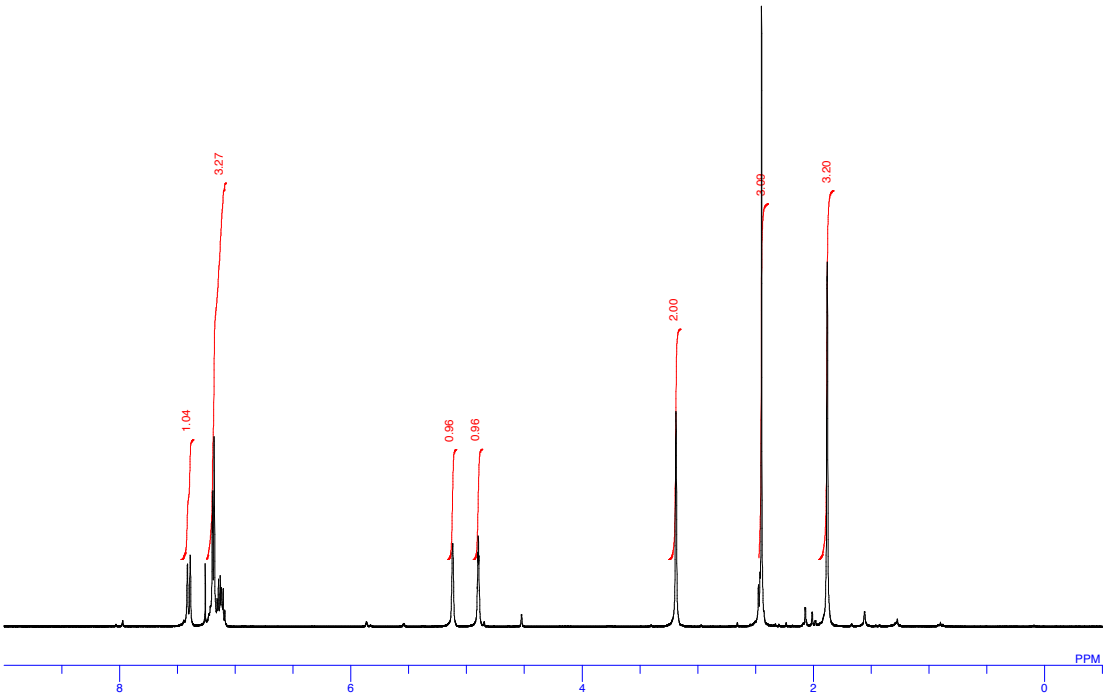

Me
Me

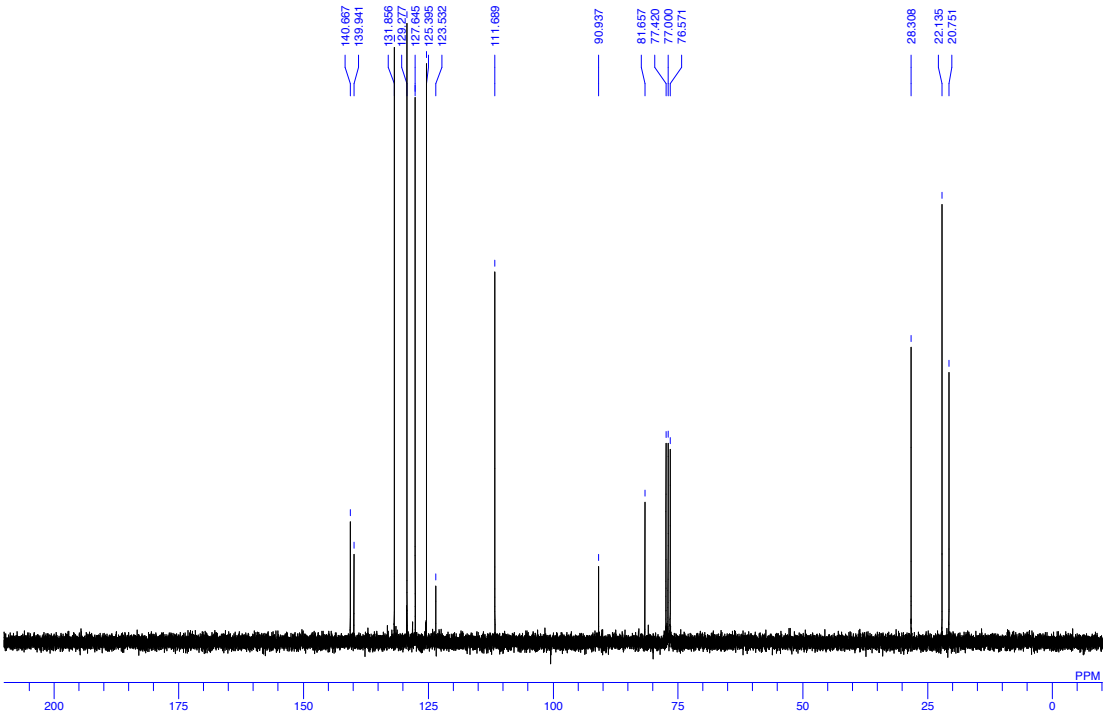

2.11
2.12
1.00
0.99
2.06
3.18
3.15
PPM
8
6
4
2
0


140.658
137.675
131.395
120.615
111.664
86.206
82.827
77.420
77.000
76.571
28.144
22.152
21.402
PPM
200
175
150
125
100
75
50
25
0

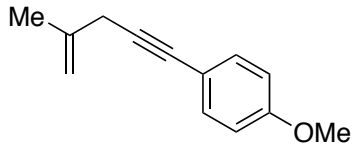
1d

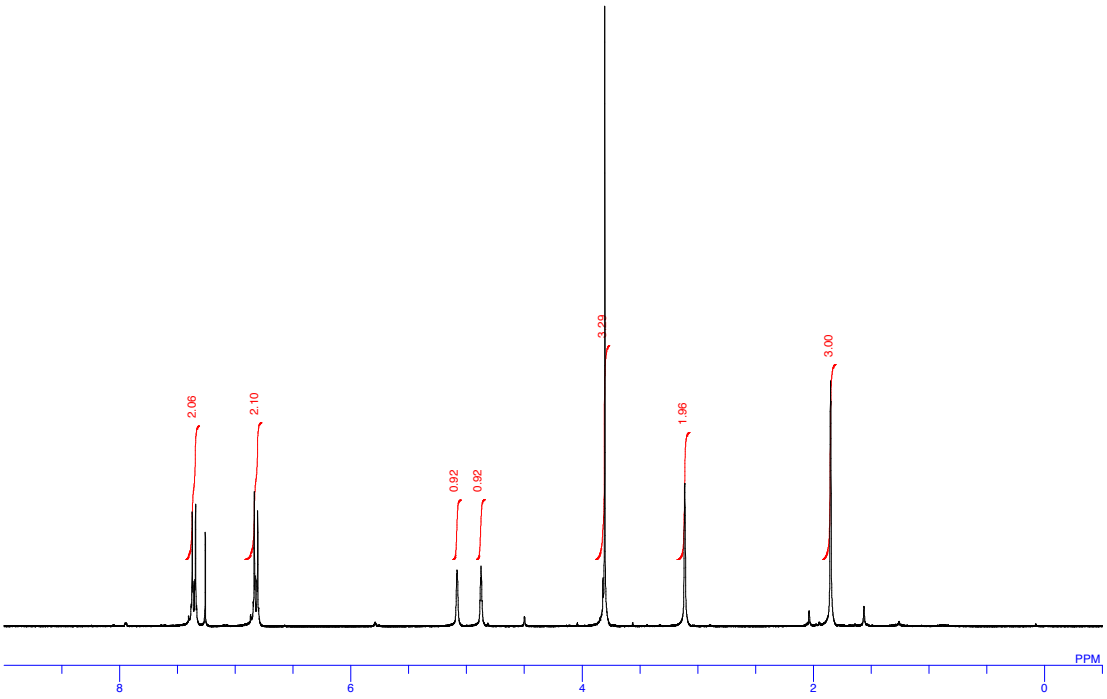

Me
Me

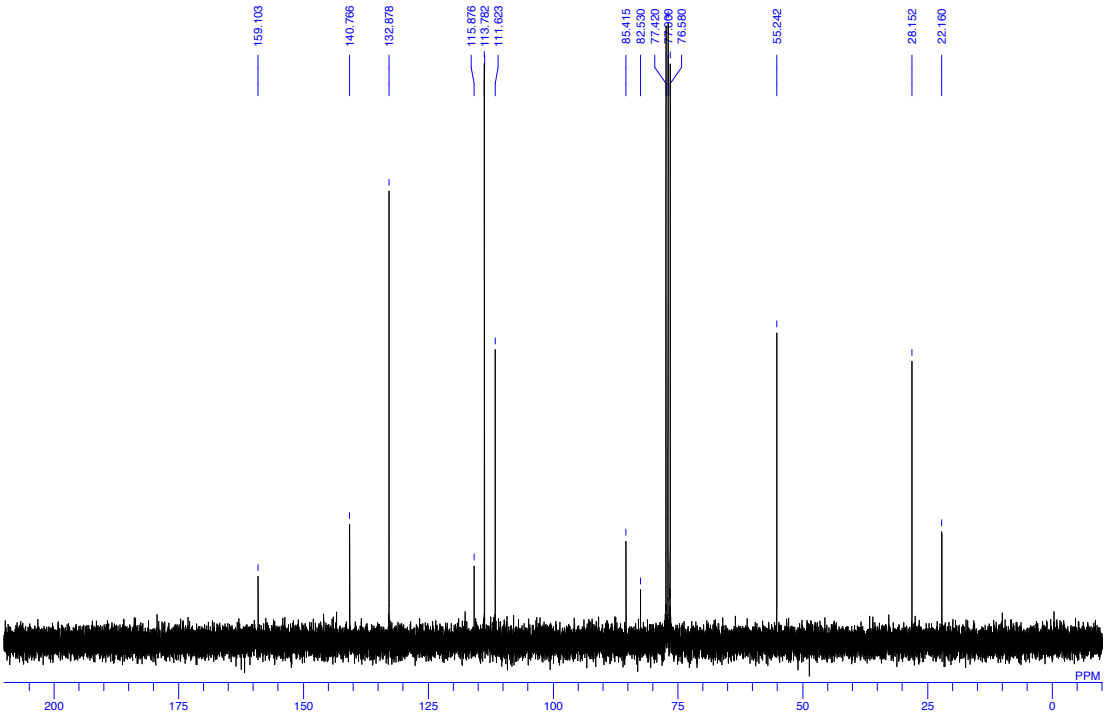

1.04
3.27
0.96
0.96
2.00
3.09
3.20
PPM
8
6
4
2
0


140.667
139.941
131.856
129.277
127.645
125.395
123.532
111.689
90.937
81.657
77.420
77.000
76.571
28.308
22.135
20.751
PPM
200
175
150
125
100
75
50
25
0

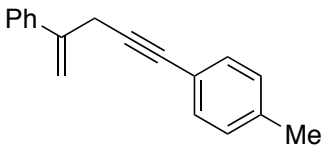
1e

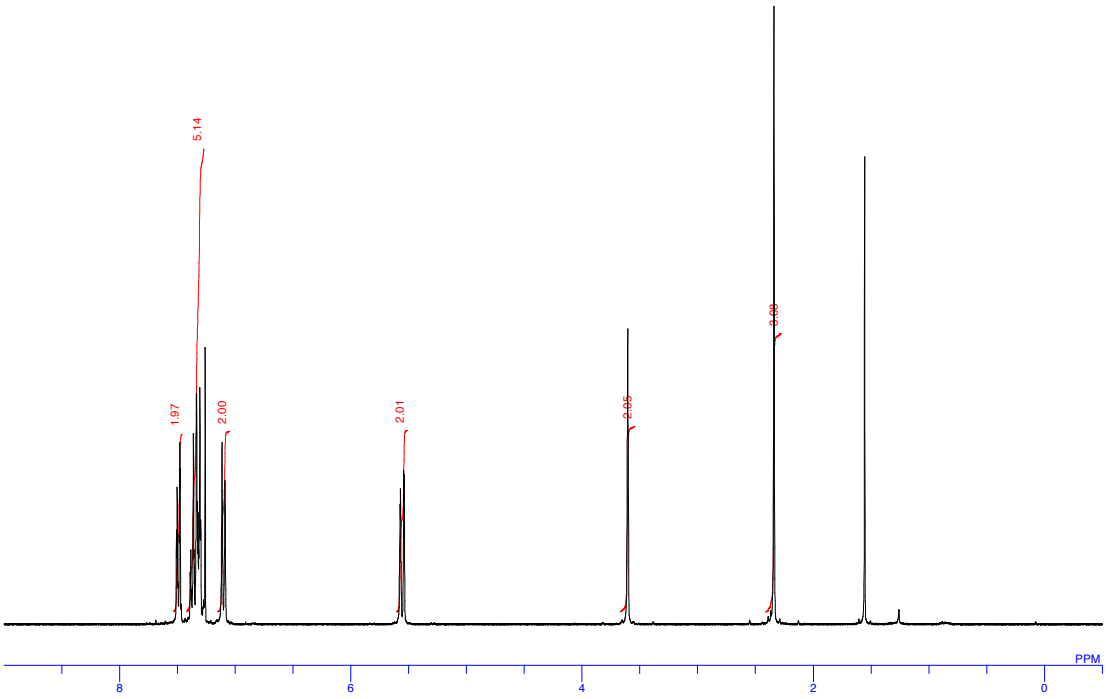

Me
OMe

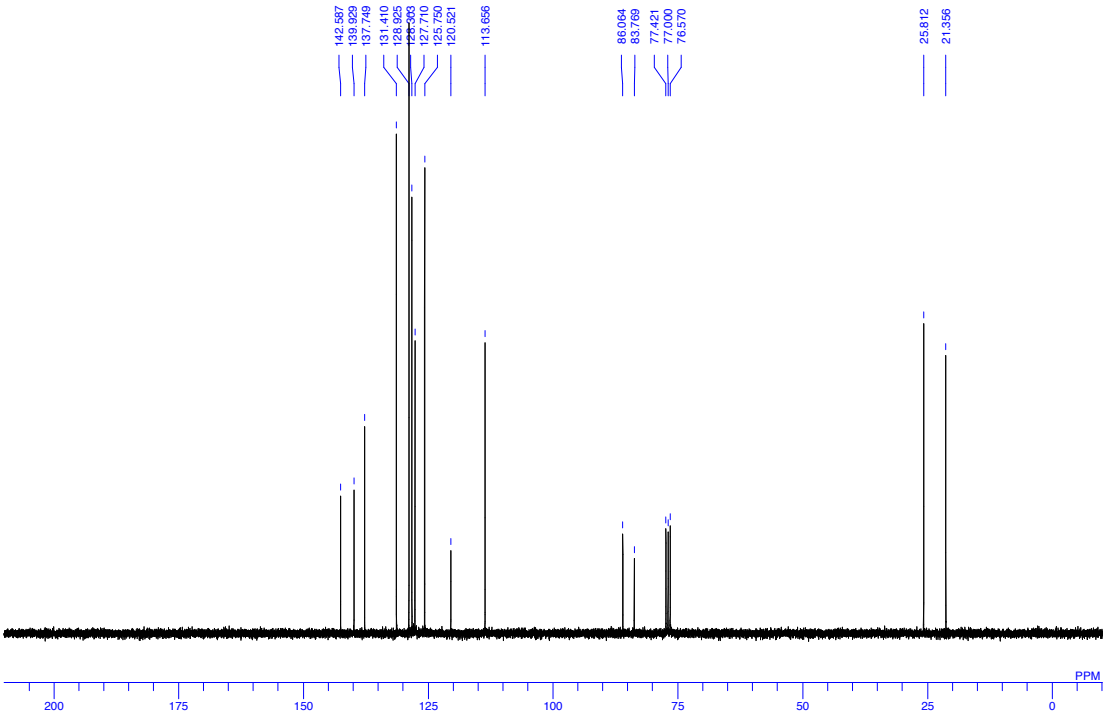

2.06
2.10
0.92
0.92
3.29
1.96
3.00
PPM
8
6
4
2
0


159.103
140.766
132.878
115.876
113.782
111.623
85.415
82.530
77.420
76.580
55.242
28.152
22.160
PPM
200
175
150
125
100
75
50
25
0

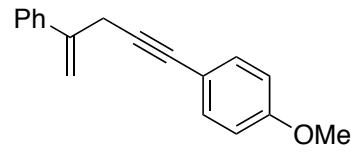
1f

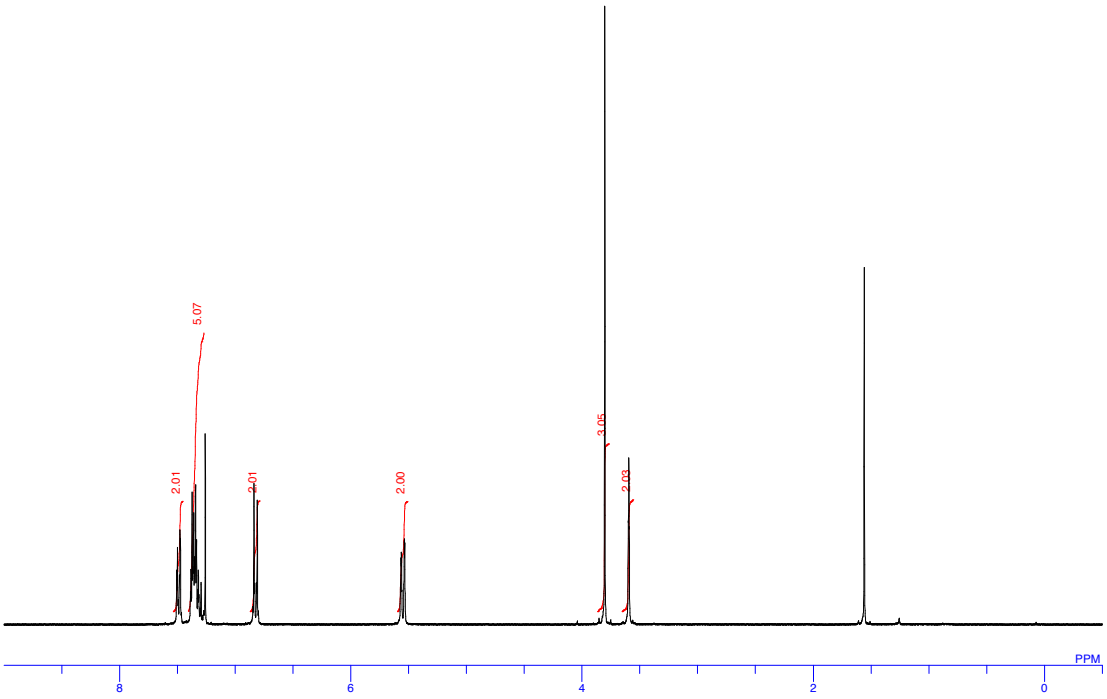

Ph
Me

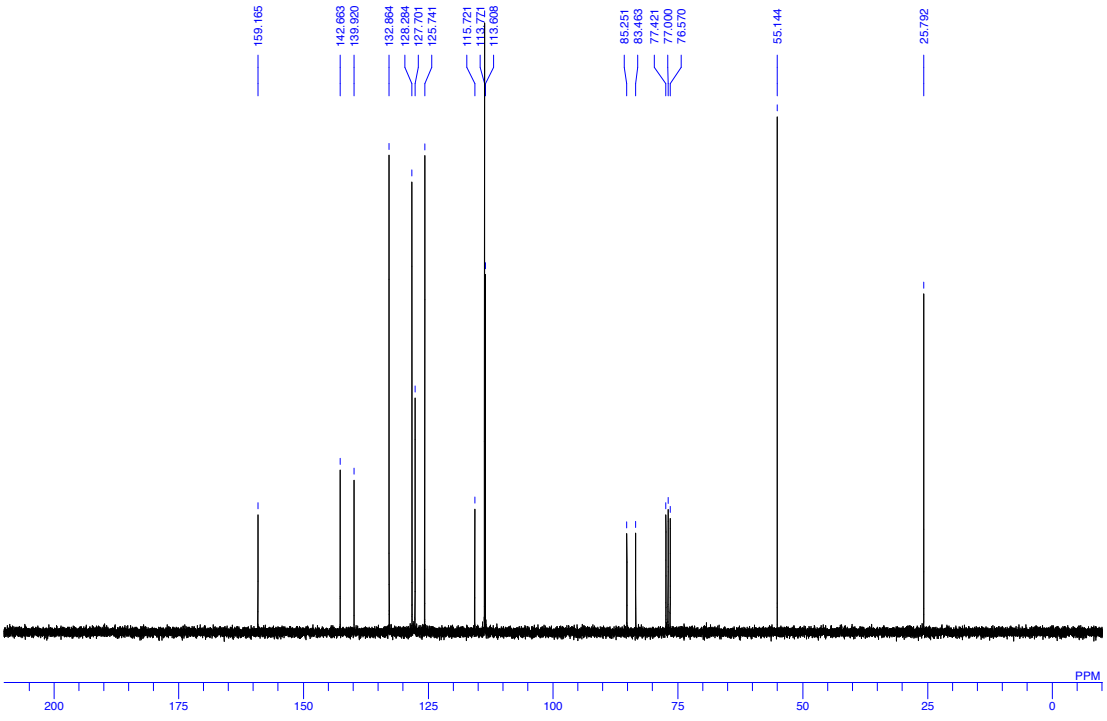

5.14
1.97
2.00
2.01
2.05
3.09
PPM
8
6
4
2
0


142.587
139.929
137.749
131.410
128.925
128.303
127.710
125.750
120.521
113.656
86.064
83.769
77.421
77.000
76.570
25.812
21.356
PPM
200
175
150
125
100
75
50
25
0

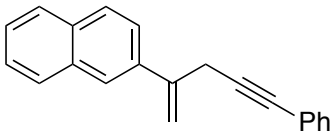
1g

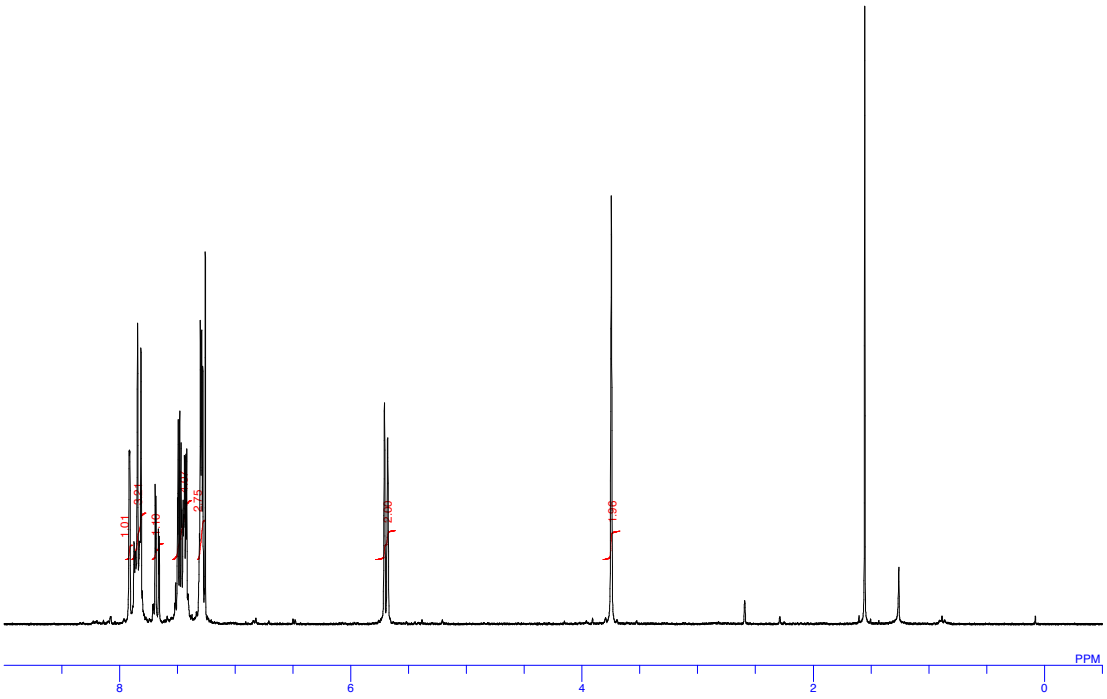

Ph
OMe

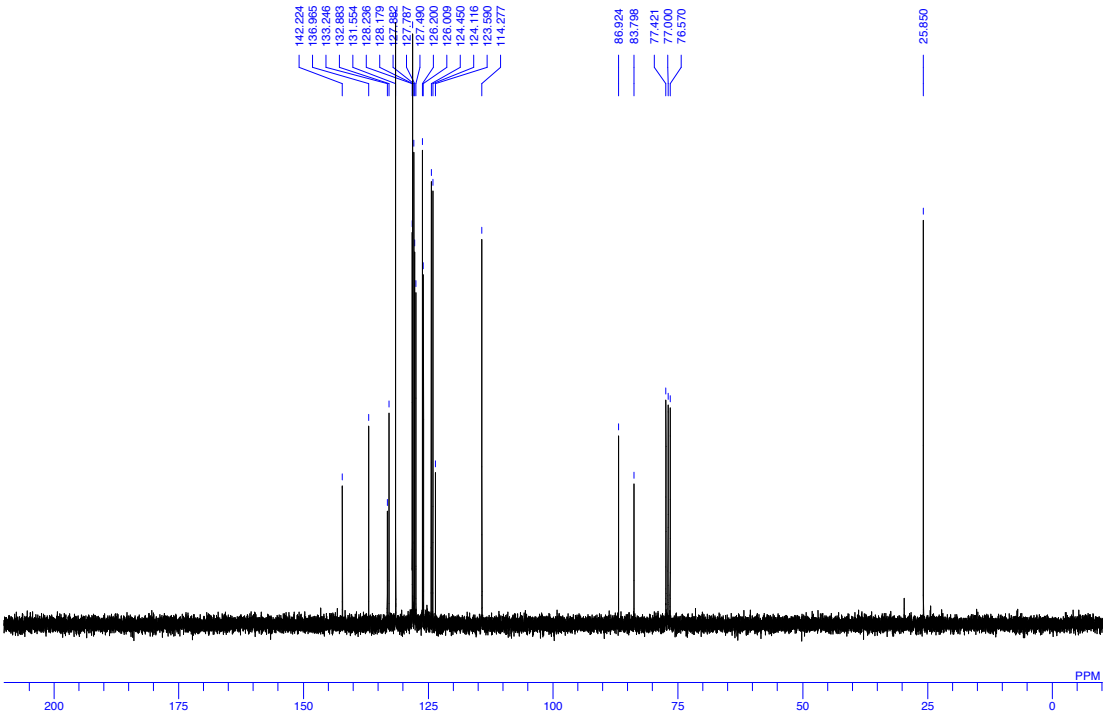

5.07
2.01
2.01
2.00
3.05
2.03
PPM
8
6
4
2
0


159.165
142.663
139.920
132.864
128.284
127.701
125.741
115.721
114.721
113.608
85.251
83.463
77.421
77.000
76.570
55.144
25.792
PPM
200
175
150
125
100
75
50
25
0

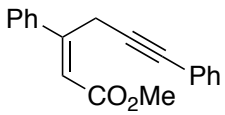
1h

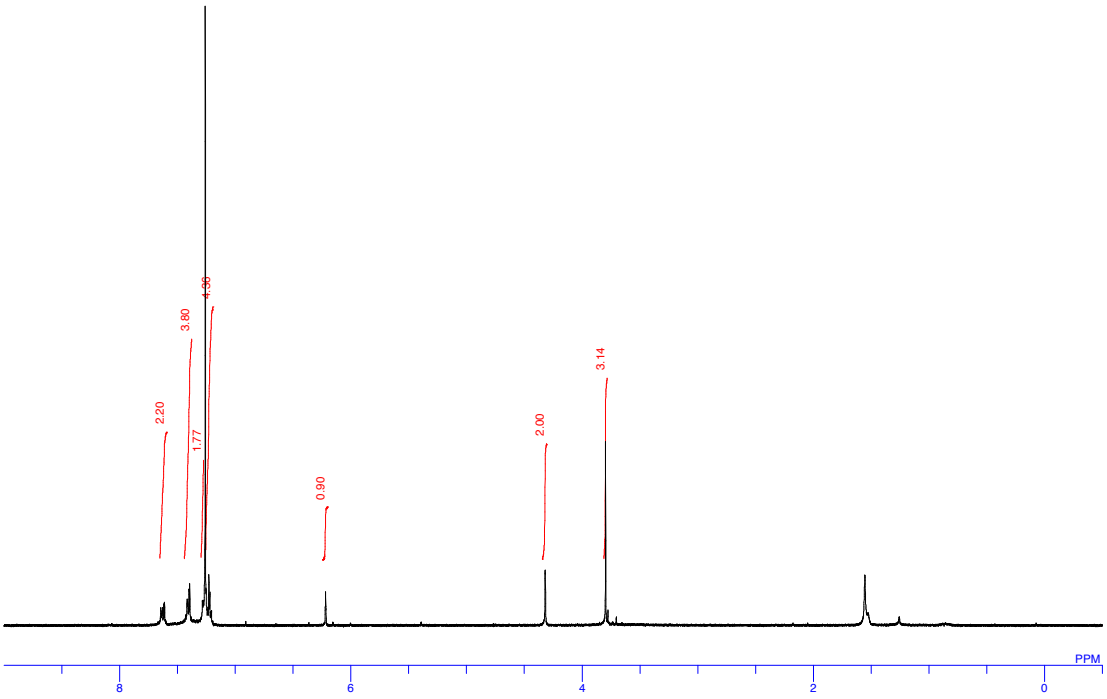

Ph

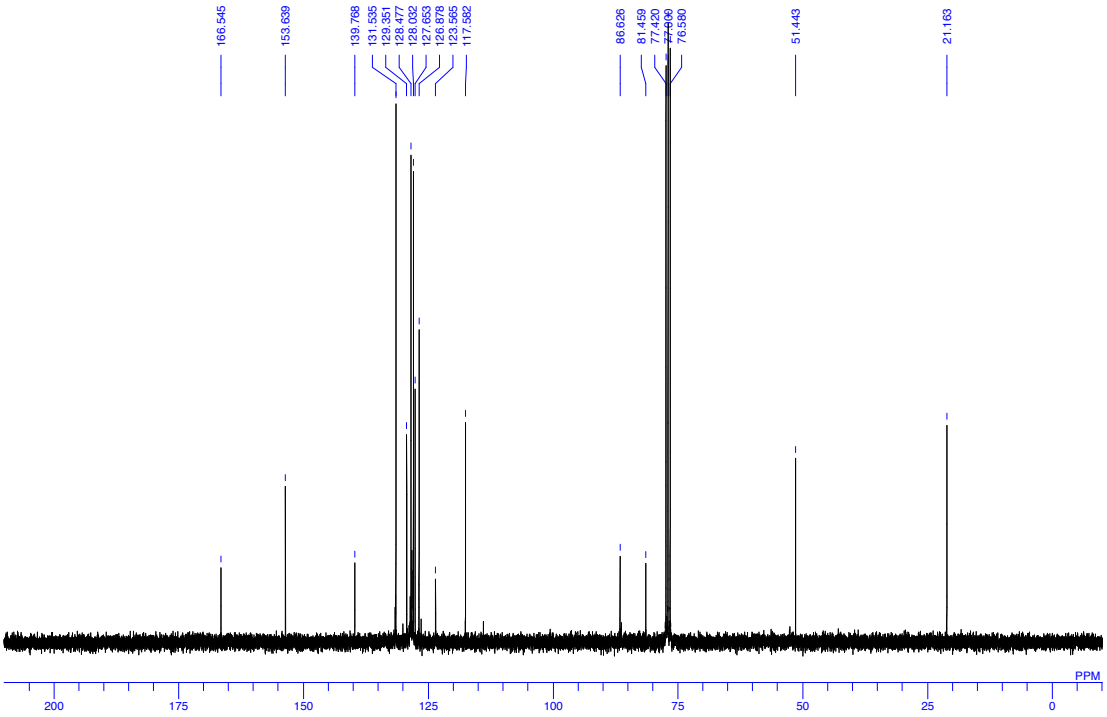

1.01
2.00
1.93
PPM
8
6
4
2
0


142.224
136.965
133.246
132.883
131.554
128.236
128.179
127.892
127.787
127.490
126.200
126.009
124.450
124.116
123.590
114.277
86.924
83.798
77.421
77.000
76.570
25.850
PPM
200
175
150
125
100
75
50
25
0

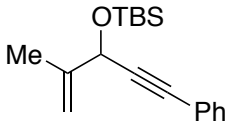
1i

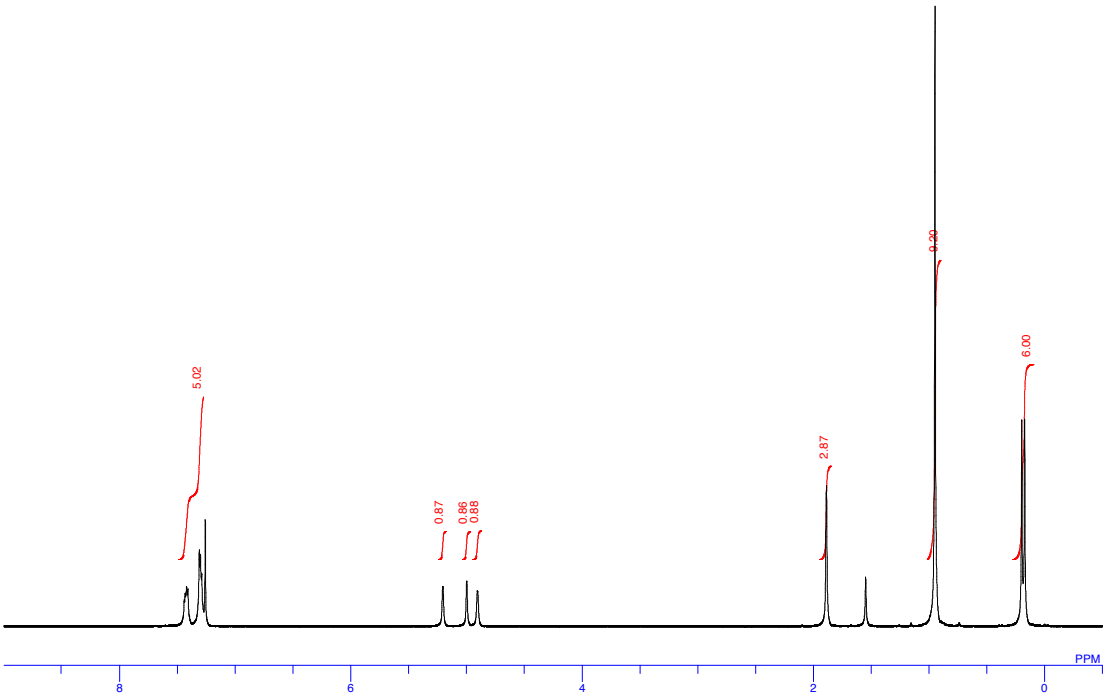

Ph
Ph
CO2Me

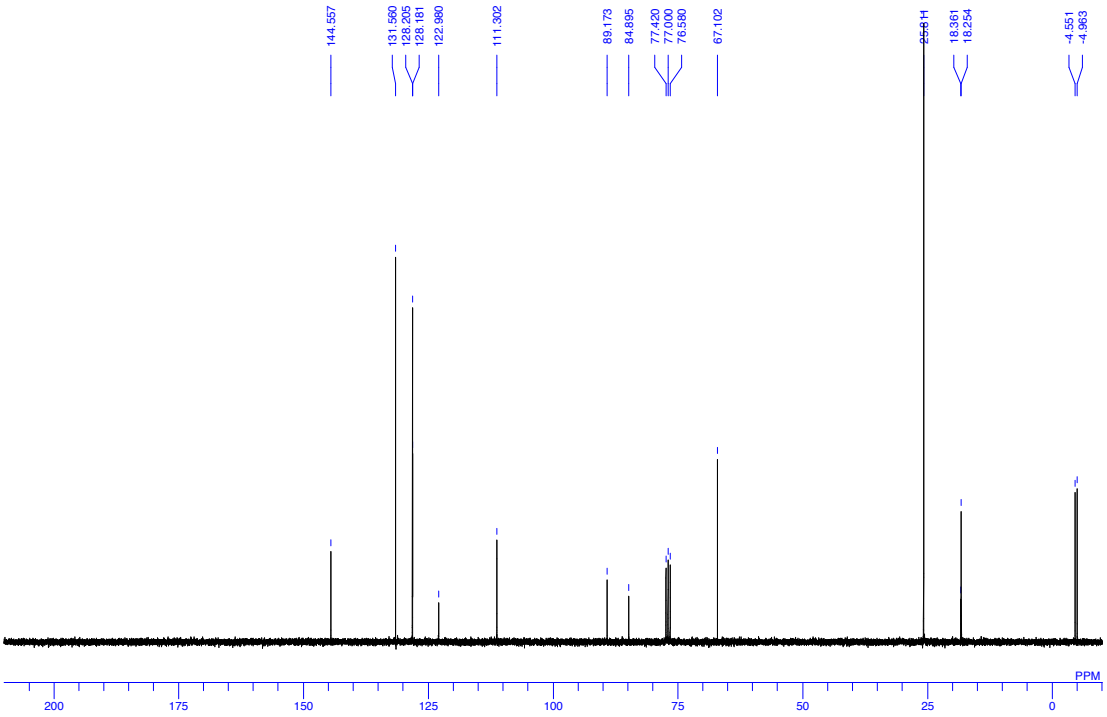

2.20
3.80
4.00
1.77
0.90
2.00
3.14
PPM
8
6
4
2
0


166.545
153.639
139.768
131.535
129.351
128.477
128.032
127.653
126.878
123.565
117.582
86.626
81.459
77.420
76.580
51.443
21.163
PPM
200
175
150
125
100
75
50
25
0

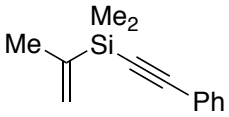
1j

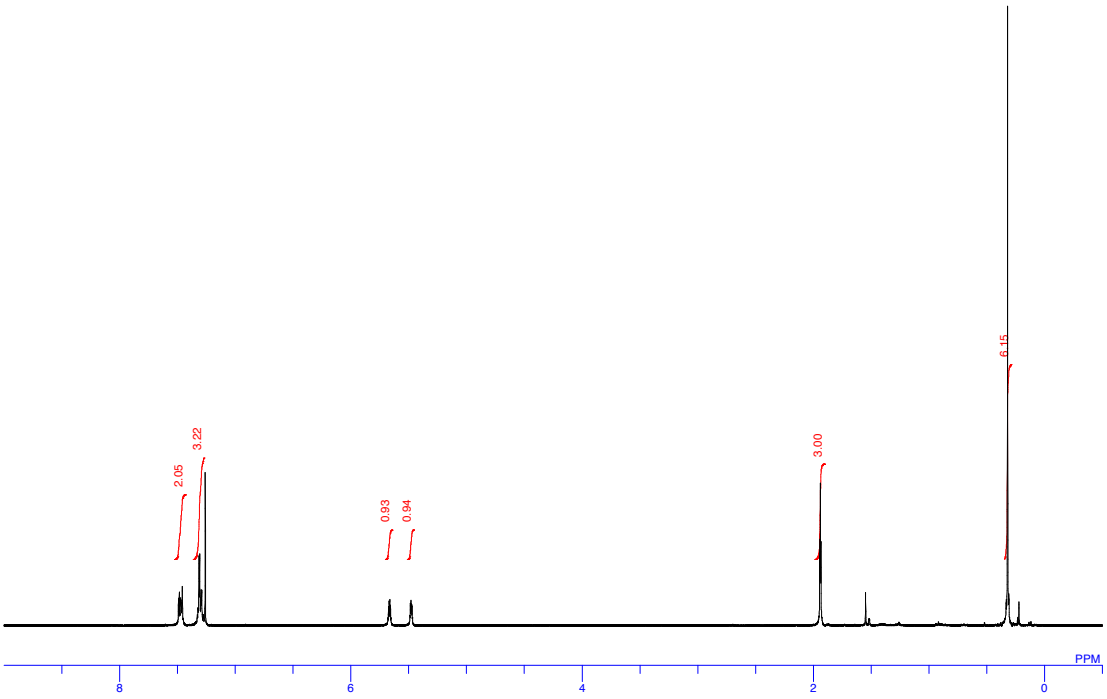

OTBS
Me
Ph

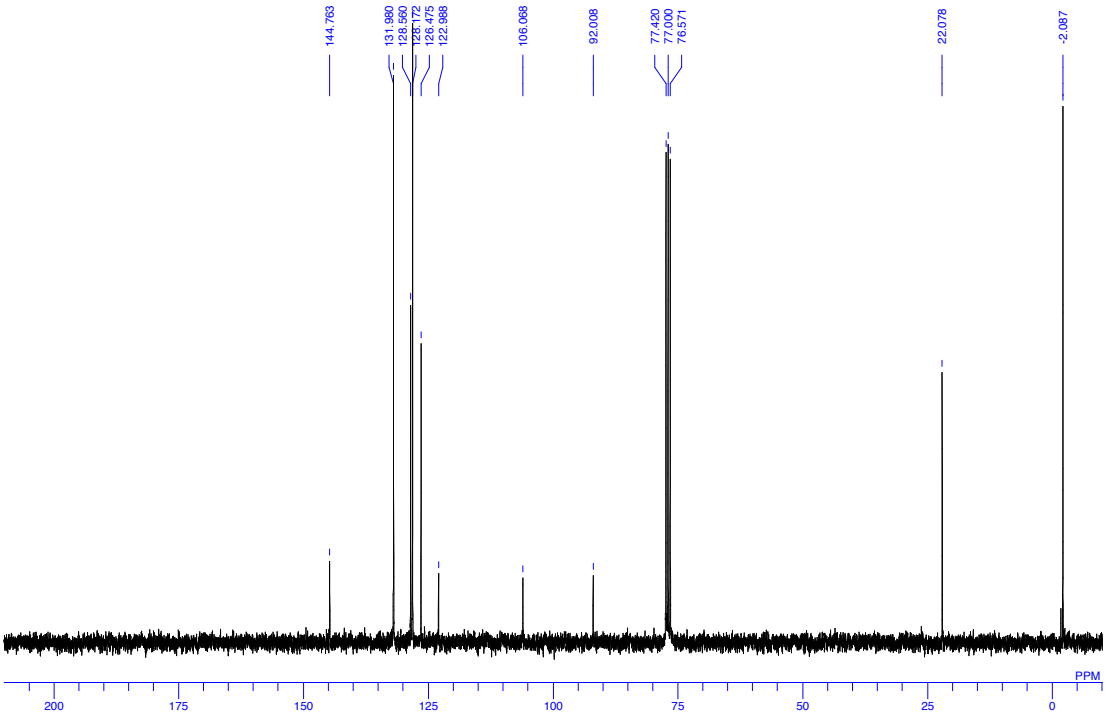

5.02
0.87
0.86
0.88
2.87
9.20
6.00
PPM
8
6
4
2
0


144.557
131.560
128.205
128.181
122.980
111.302
89.173
84.895
77.420
77.000
76.580
67.102
25.811
18.361
18.254
-4.551
-4.963
PPM
200
175
150
125
100
75
50
25
0

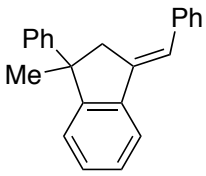
1k

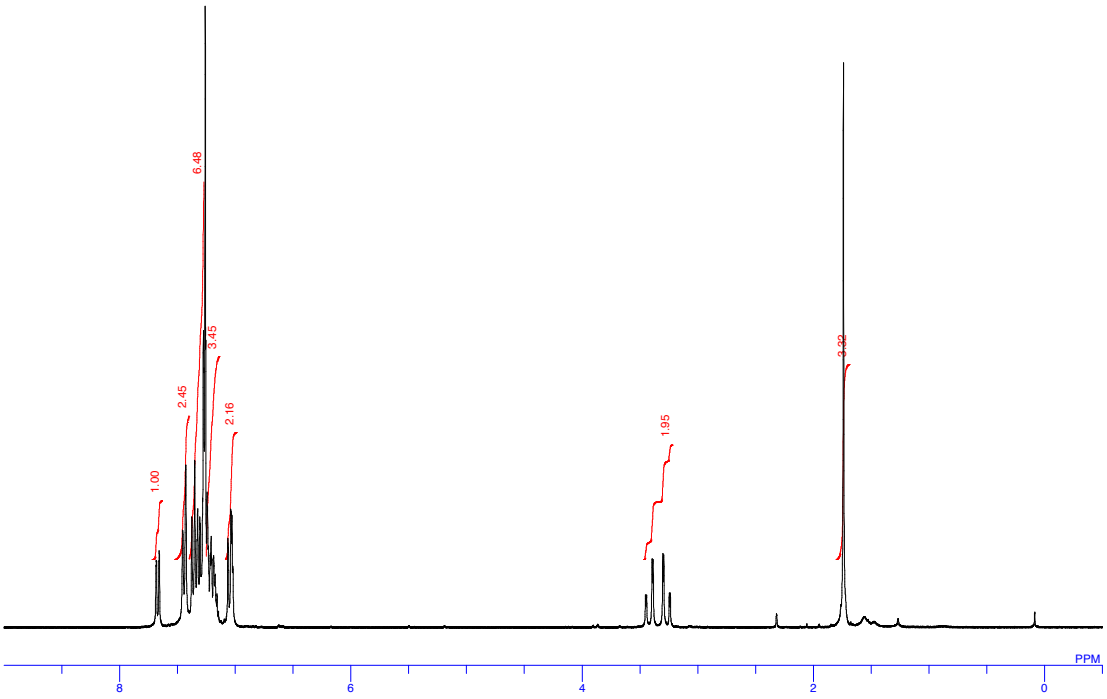

Me2
Si
Me
Ph

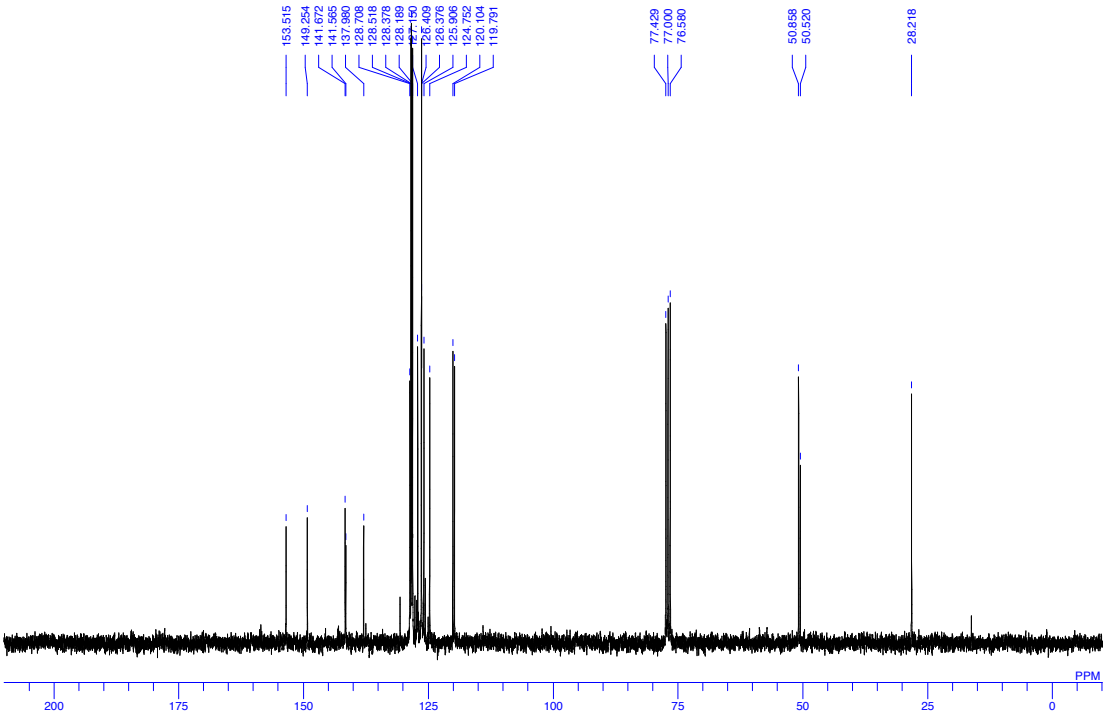

2.05
3.22
0.93
0.94
3.00
6.15
PPM
8
6
4
2
0


144.763
131.980
128.560
128.172
126.475
122.988
106.068
92.008
77.420
77.000
76.571
22.078
-2.087
PPM
200
175
150
125
100
75
50
25
0

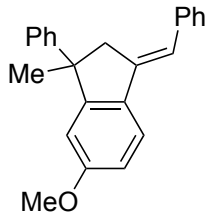
3a

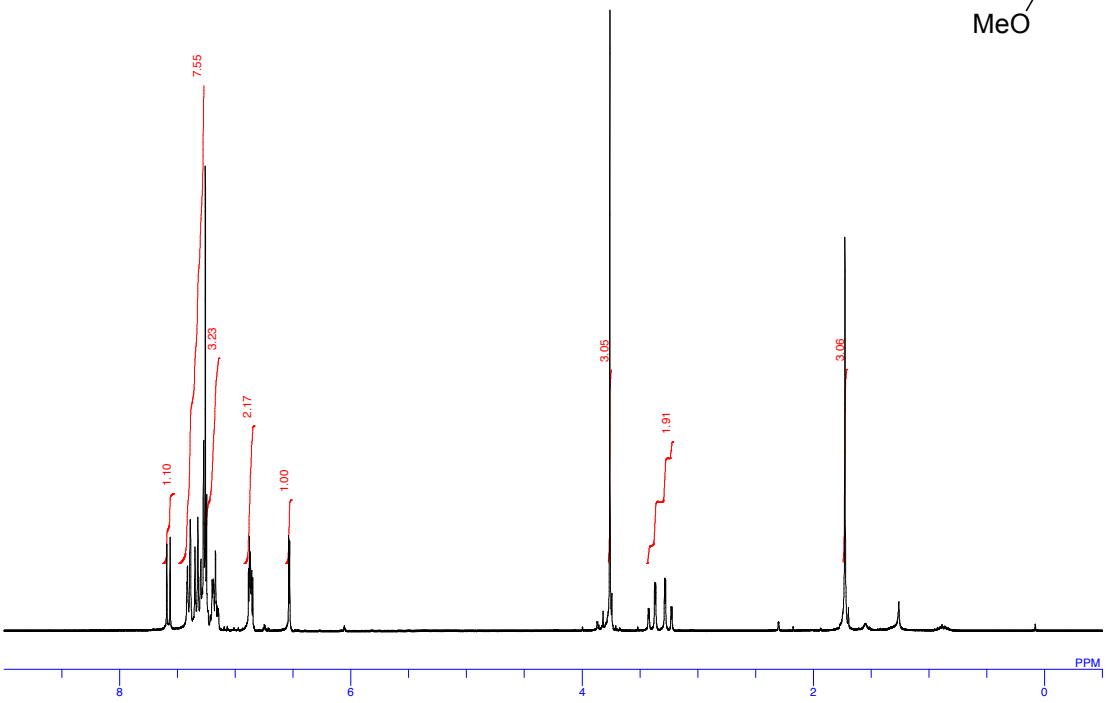

Ph
Ph
Me

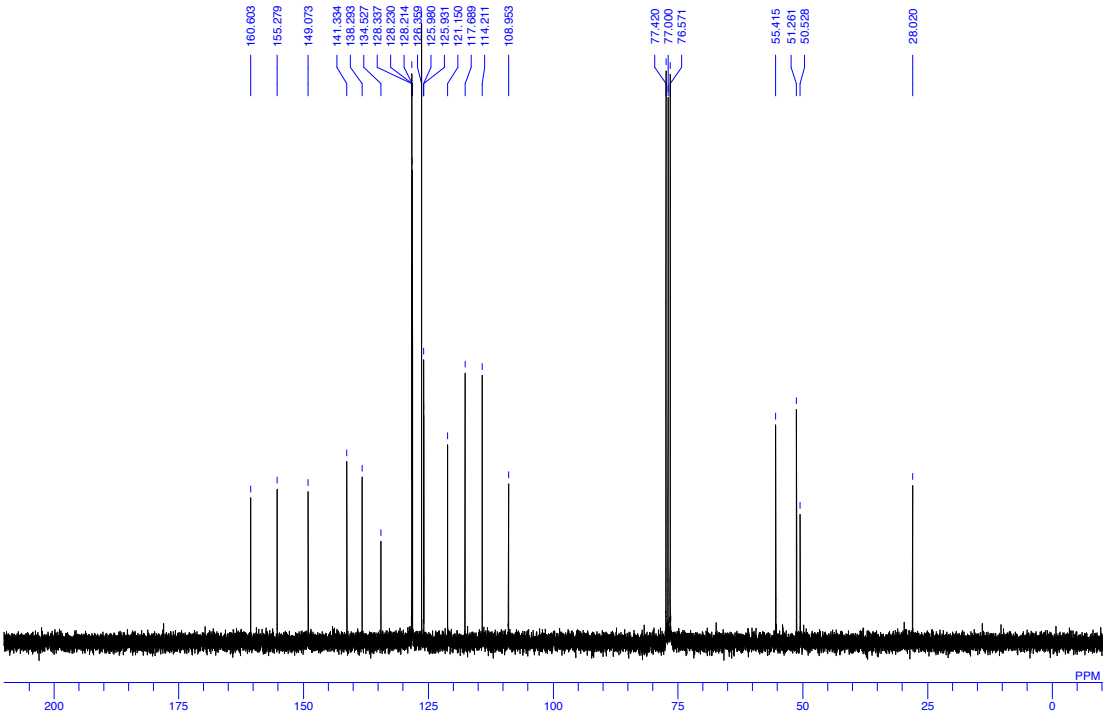

1.00
6.48
2.45
3.45
2.16
1.95
3.32
PPM
8
6
4
2
0


153.515
149.254
141.672
141.565
137.980
128.708
128.518
128.378
128.189
126.409
126.376
125.906
124.752
120.104
119.791
77.429
77.000
76.580
50.858
50.520
28.218
PPM
200
175
150
125
100
75
50
25
0

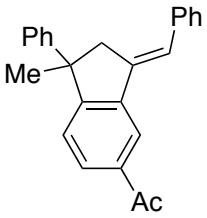
3b

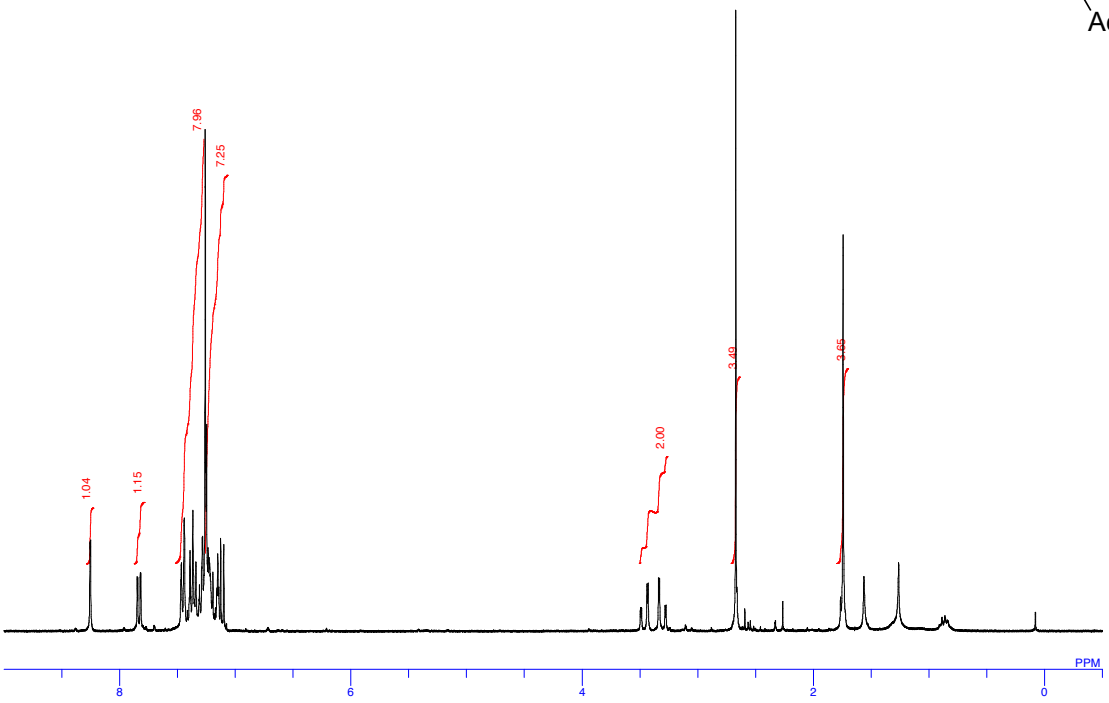

Ph
Ph
Me
MeO

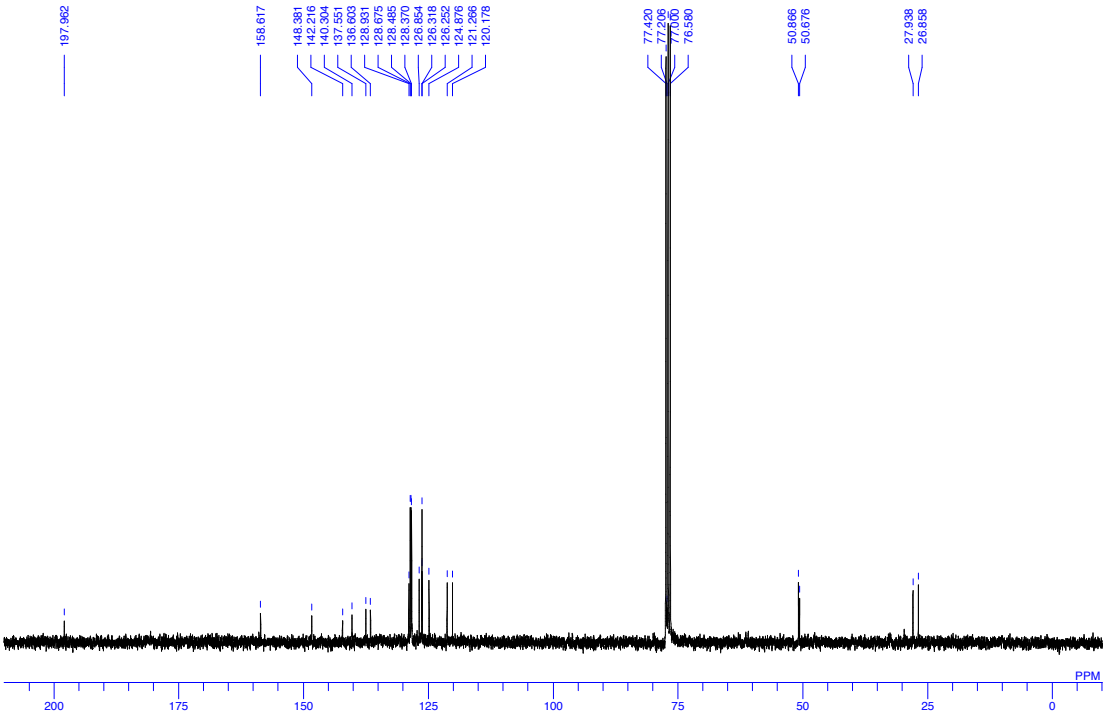

7.55
3.23
2.17
1.10
1.00
3.05
1.91
3.06
PPM
8
6
4
2
0


160.603
155.279
149.073
141.334
138.268
134.527
128.337
128.230
128.214
126.359
125.980
125.931
121.150
117.689
114.211
108.953
77.420
77.000
76.571
55.415
51.261
50.528
28.020
PPM
200
175
150
125
100
75
50
25
0

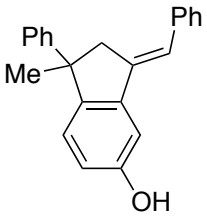
3c

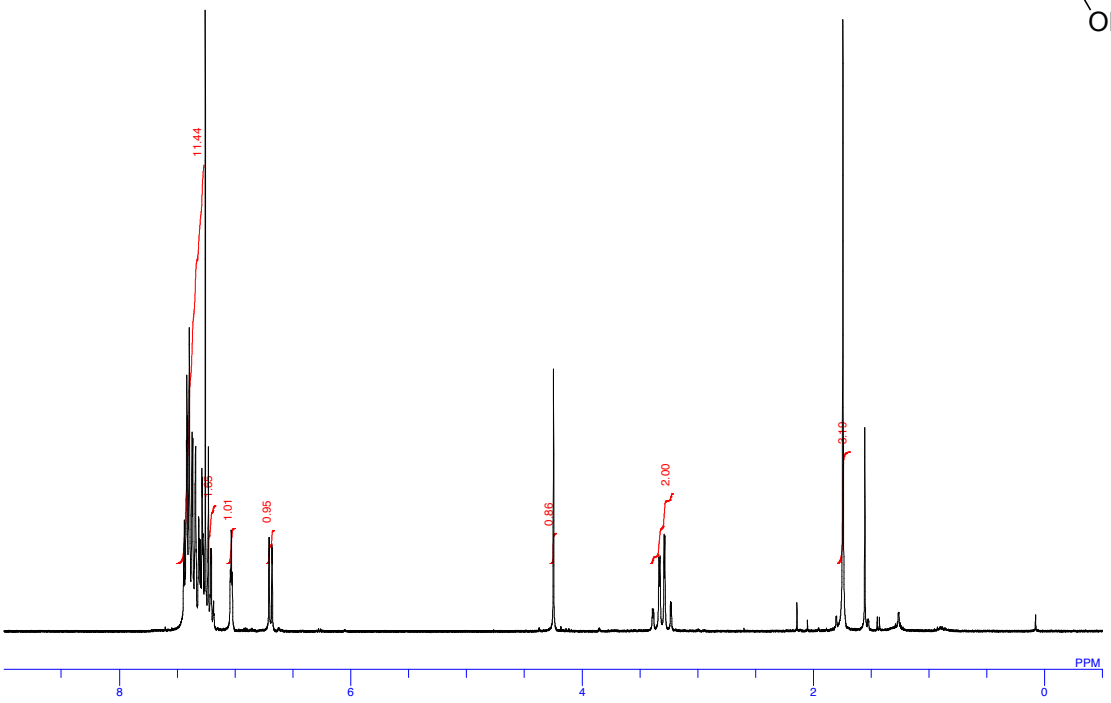

Ph
Ph
Me
Ac

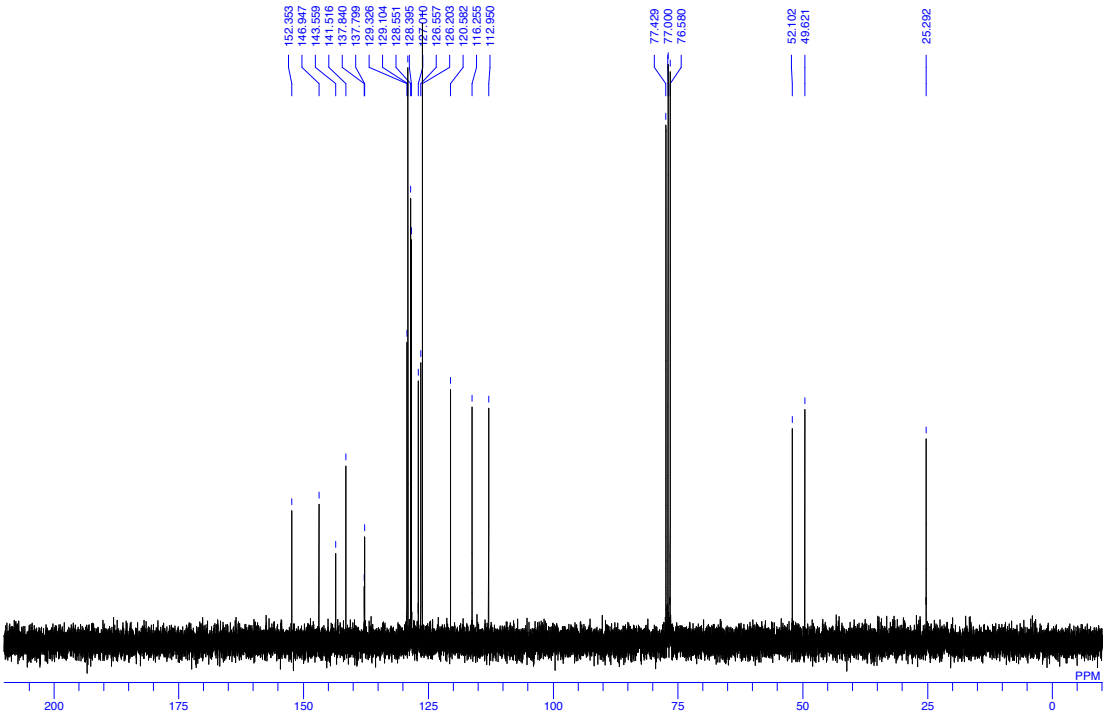

7.96
7.25
1.04
1.15
2.00
3.49
3.65
PPM
8
6
4
2
0


197.962
158.617
148.381
142.216
140.304
137.551
136.603
128.931
128.675
128.485
128.370
126.854
126.318
126.252
124.876
121.266
120.178
77.420
77.206
77.000
76.580
50.866
50.676
27.938
26.858
PPM
200
175
150
125
100
75
50
25
0

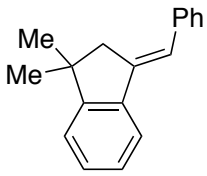
3d

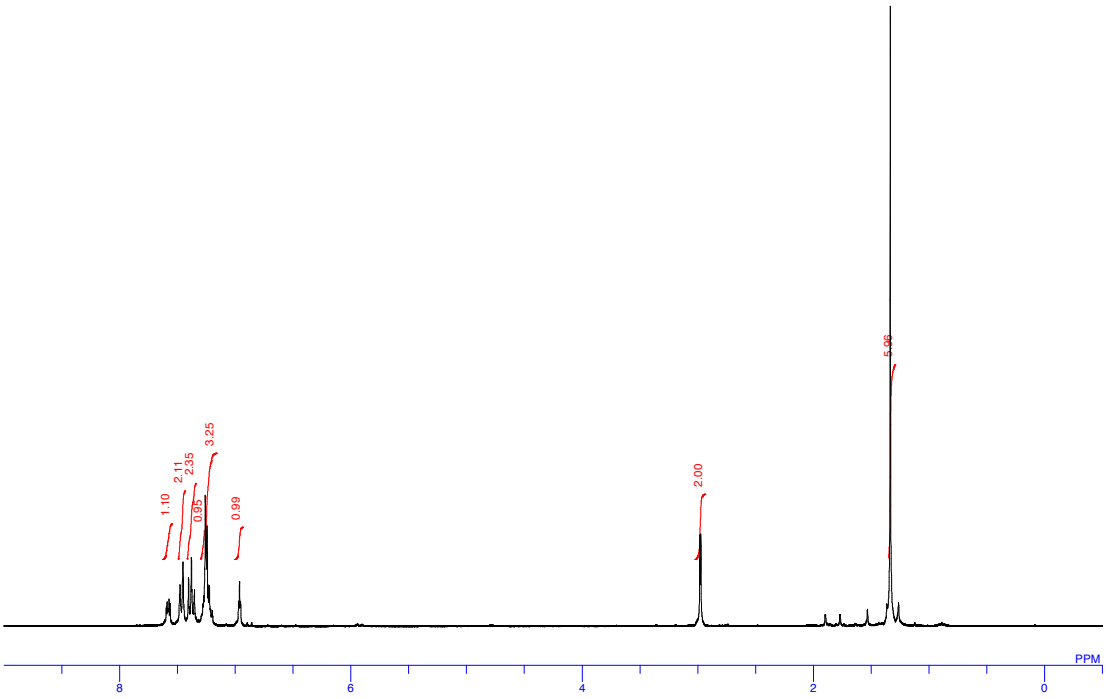

Ph
Ph
Me
OH

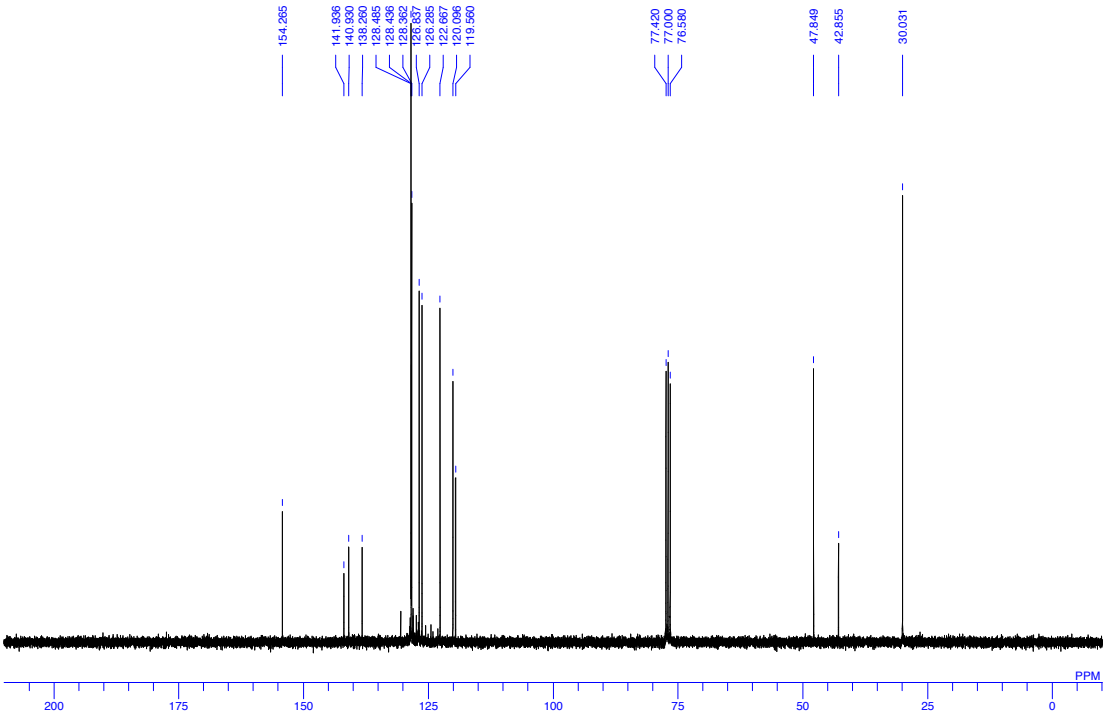

11.44
1.65
1.01
0.95
0.86
2.00
3.10
PPM
8
6
4
2
0


152.353
146.947
143.559
141.516
137.840
137.799
129.326
129.104
128.551
128.395
127.010
126.557
120.693
116.255
112.950
77.429
77.000
76.580
52.102
49.621
25.292
PPM
200
175
150
125
100
75
50
25
0

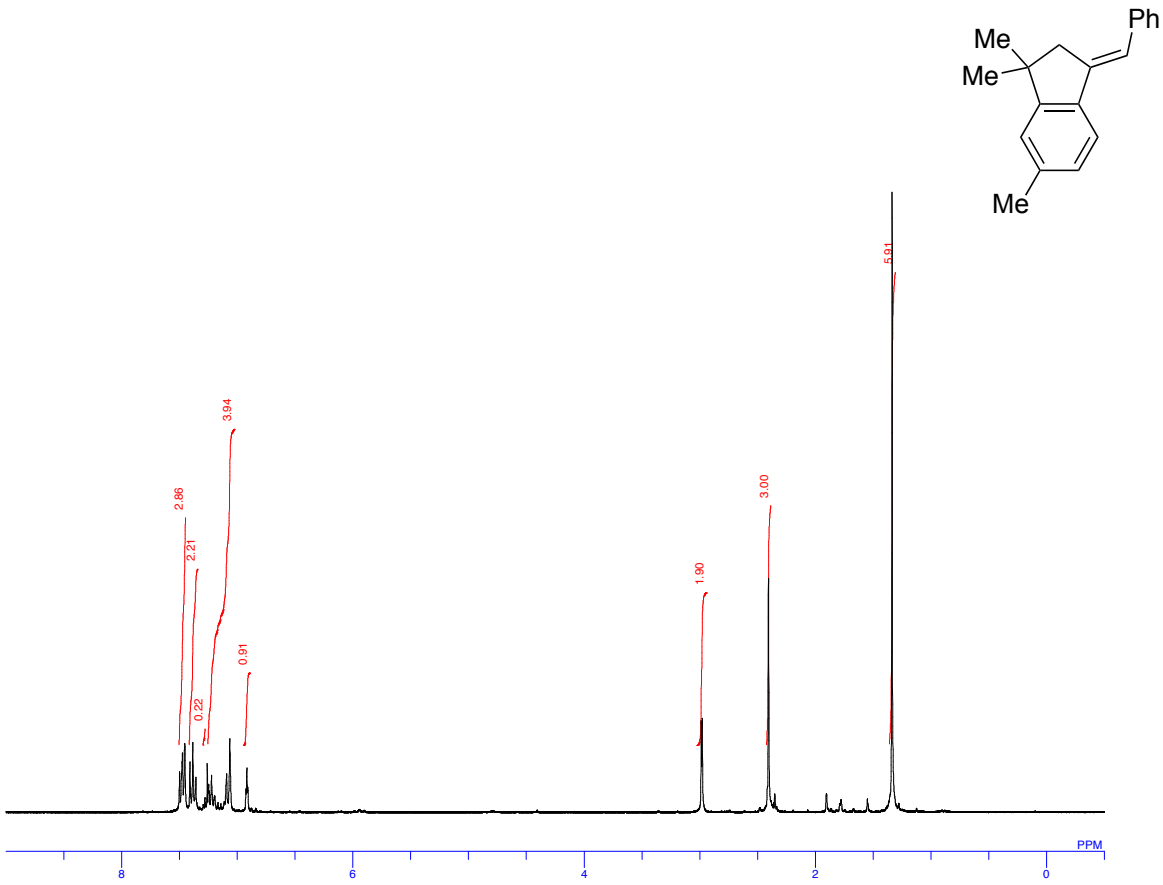
3e

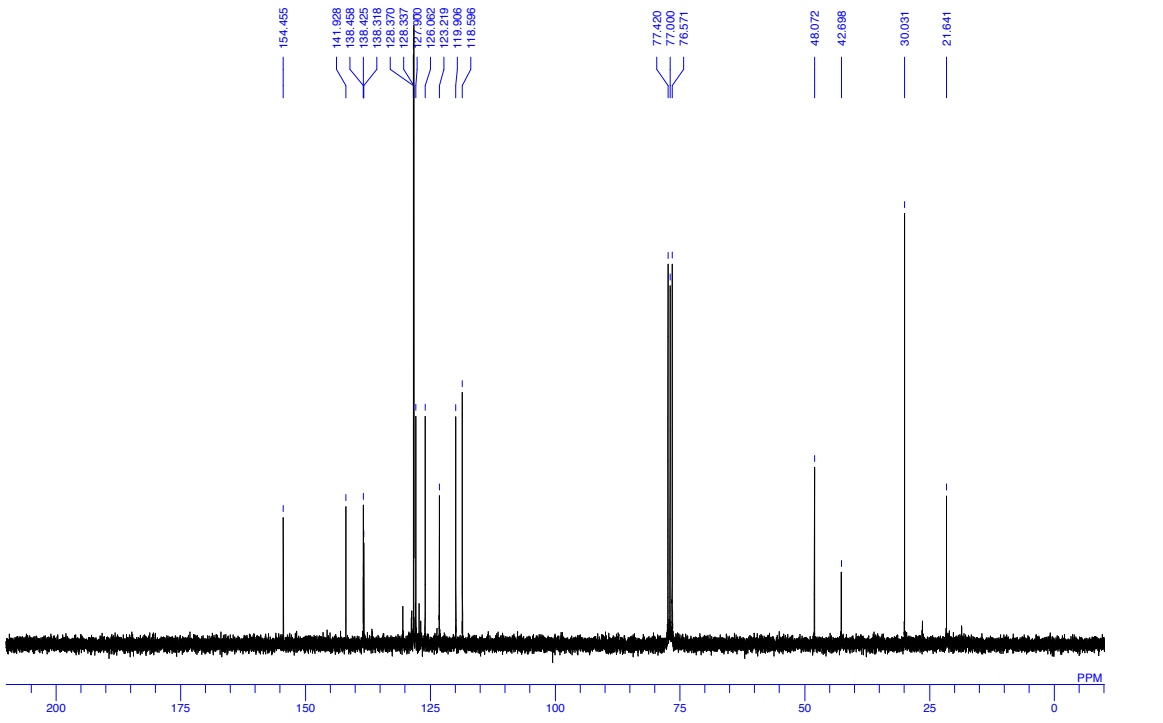

Ph
Me
Me


1.10
2.11
2.35
0.95
3.25
0.99
2.00
5.06
PPM
8
6
4
2
0

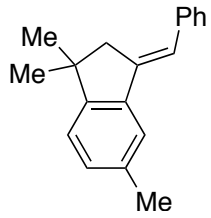

154.265
141.936
140.930
136.260
128.485
128.436
128.362
126.837
126.285
122.667
120.096
119.560
77.420
77.000
76.580
47.849
42.855
30.031
PPM
200
175
150
125
100
75
50
25
0

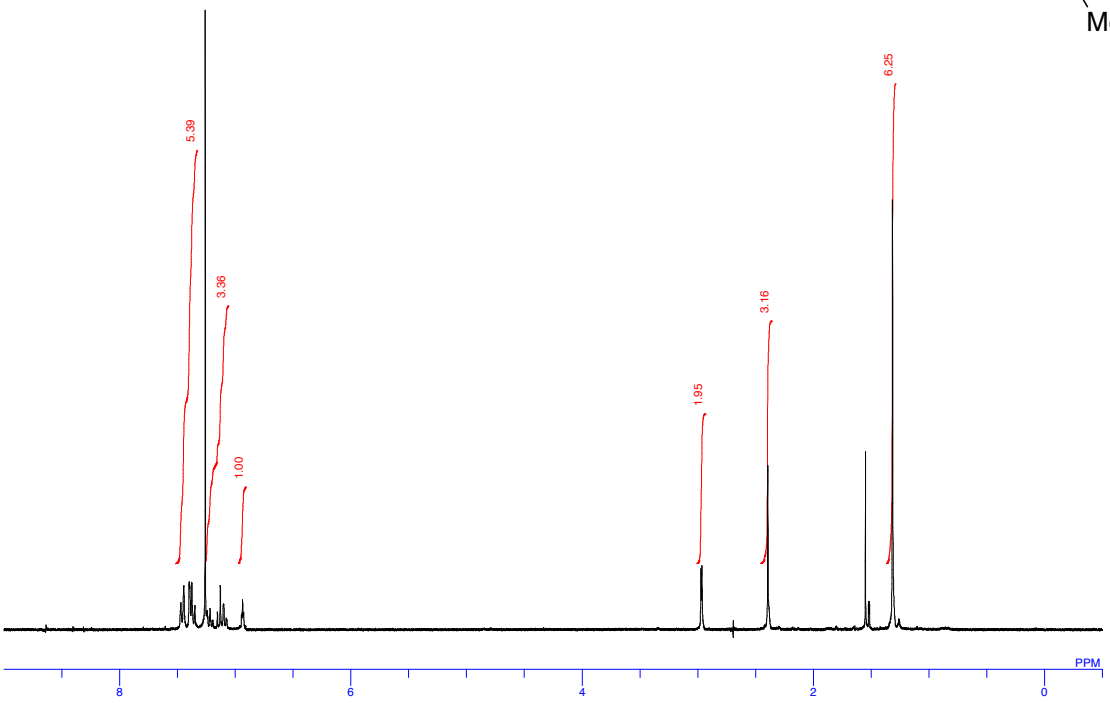
3f

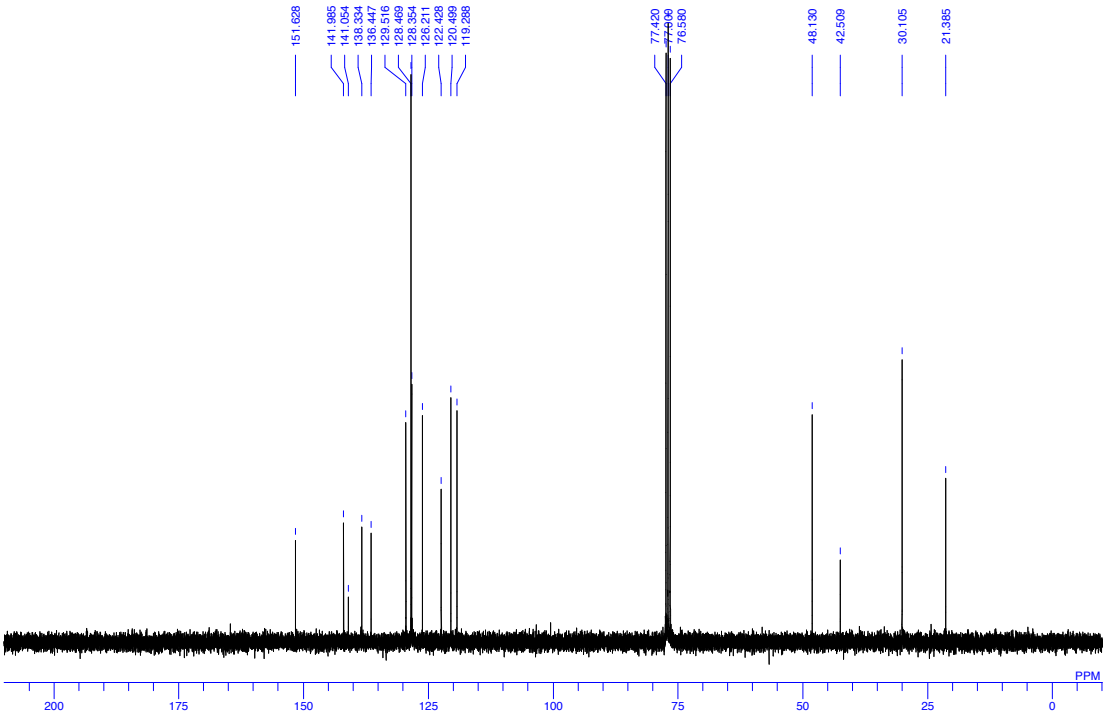

Ph
Me
Me
Me
2.86
2.21
0.22
3.94
0.91
1.90
3.00
5.91
PPM
8
6
4
2
0


154.455
141.928
138.458
138.425
138.318
128.370
128.337
127.300
126.062
123.219
119.906
118.596
77.420
77.000
76.571
48.072
42.698
30.031
21.641
PPM
200
175
150
125
100
75
50
25
0

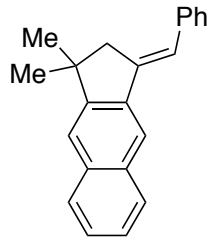
3g

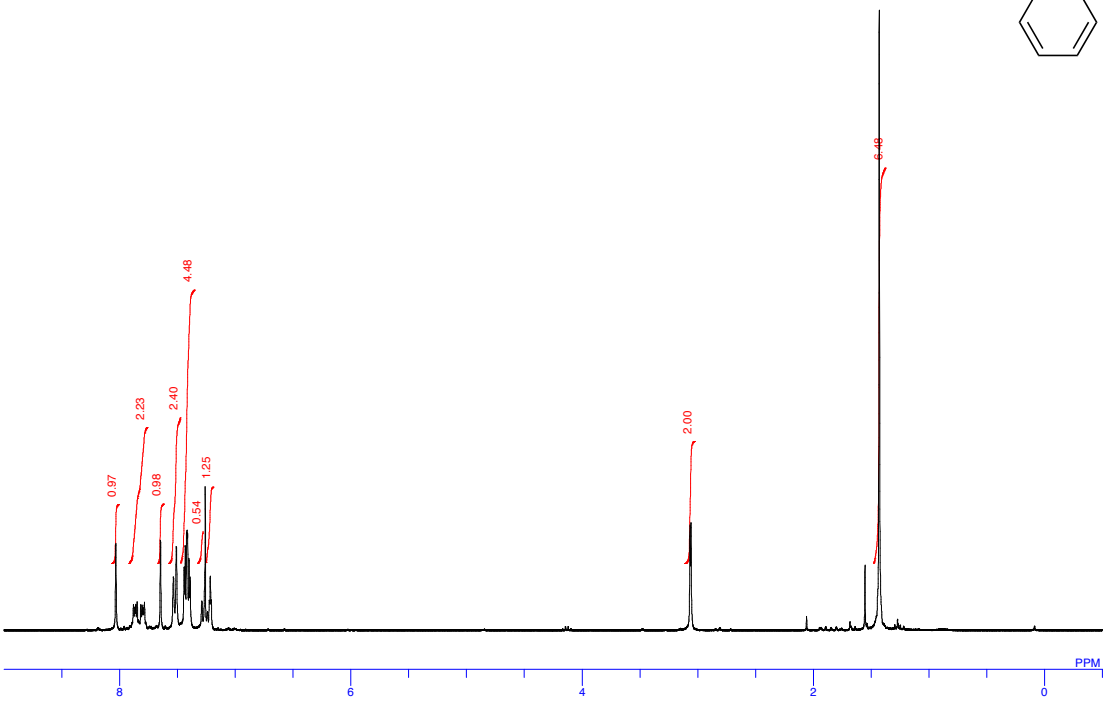

Ph
Me
Me
Me

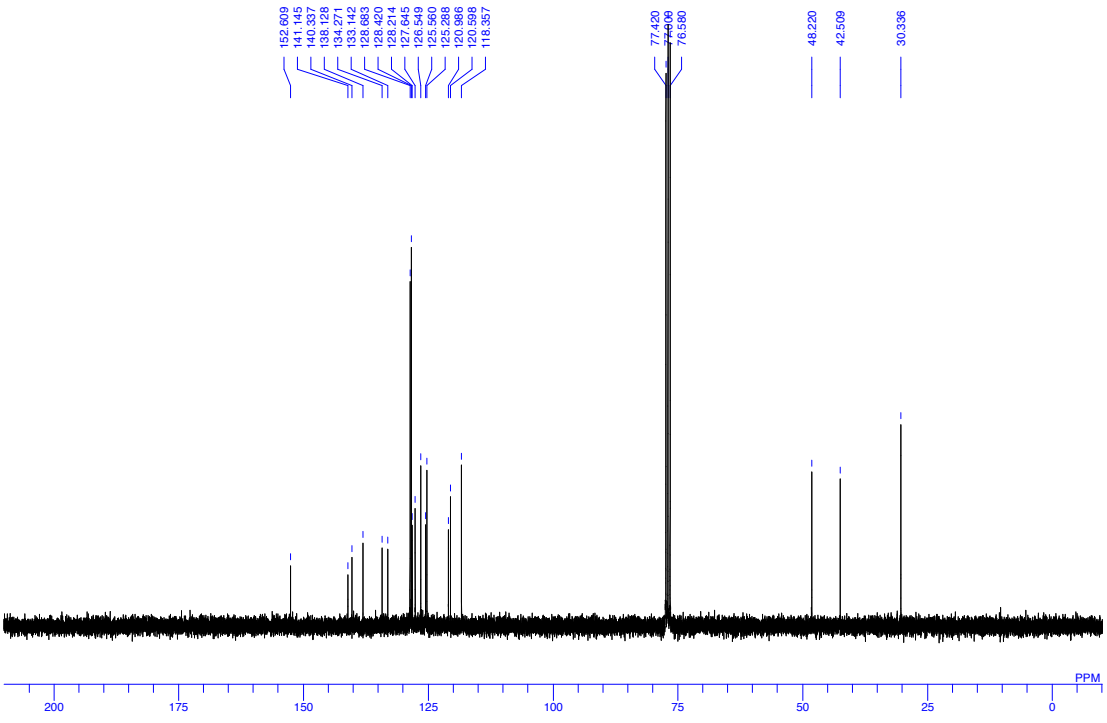

5.39
3.36
1.00
1.95
3.16
6.25
PPM
8
6
4
2
0


151.628
141.985
141.054
138.334
136.447
129.516
128.469
128.354
126.211
122.428
120.499
119.288
77.420
76.580
48.130
42.509
30.105
21.385
PPM
200
175
150
125
100
75
50
25
0

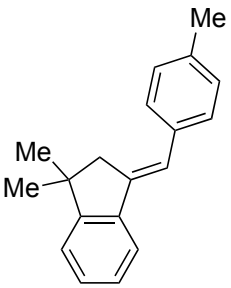
3h

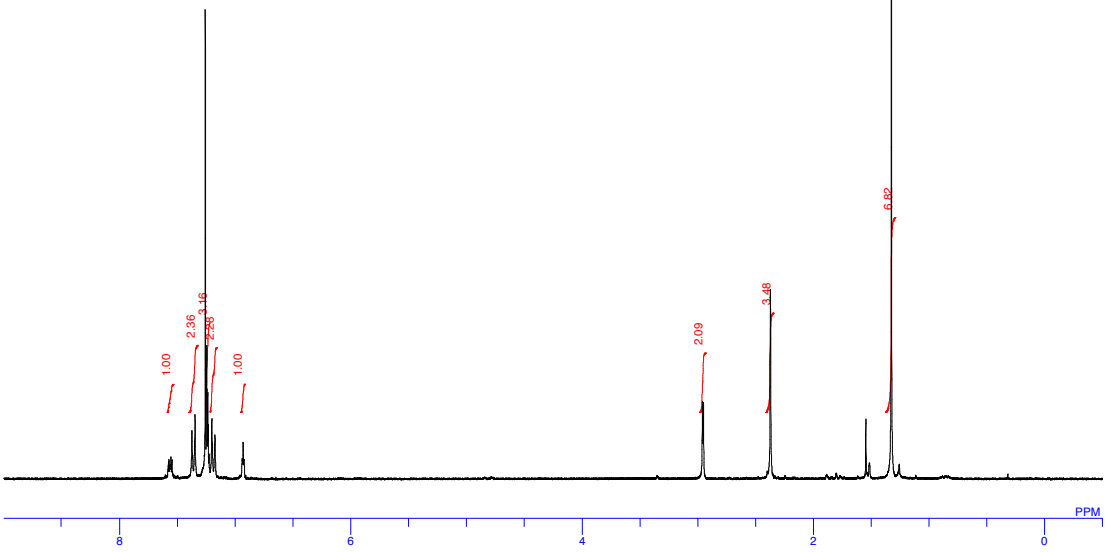

Ph
Me
Me

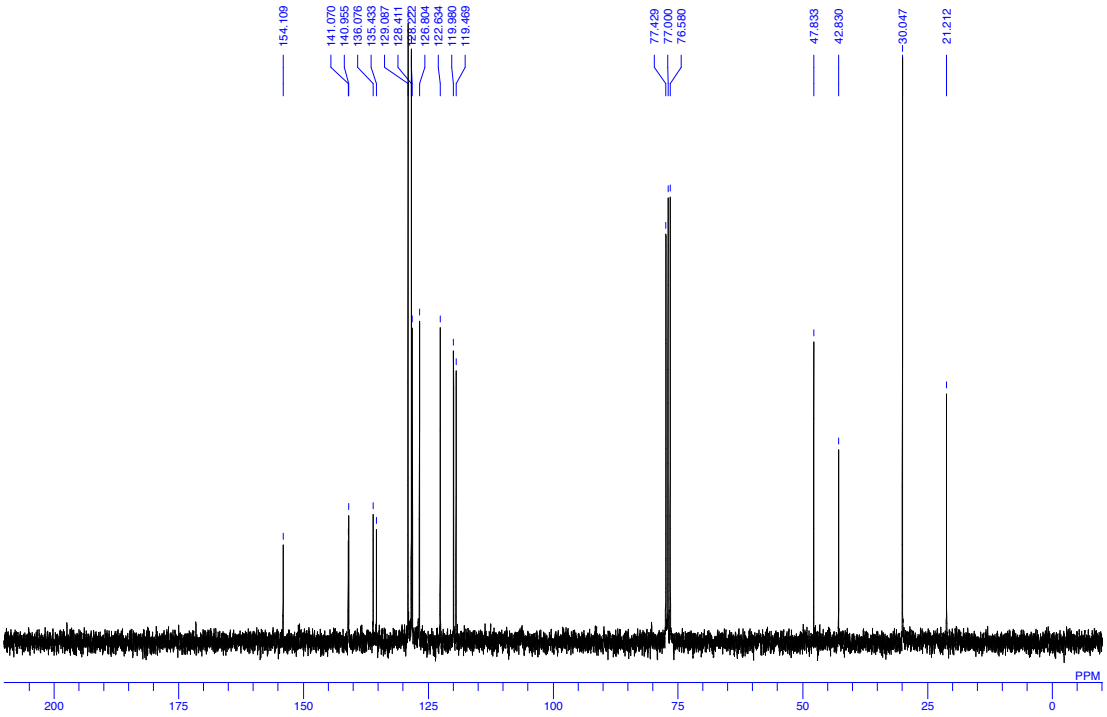

0.97
2.23
0.98
2.40
4.48
0.54
1.25
2.00
6.48
PPM
8
6
4
2
0


152.609
141.145
140.337
138.128
134.271
133.142
128.693
128.420
128.214
127.645
126.549
125.560
125.288
120.986
120.598
118.357
77.420
77.000
76.580
48.220
42.509
30.336
PPM
200
175
150
125
100
75
50
25
0

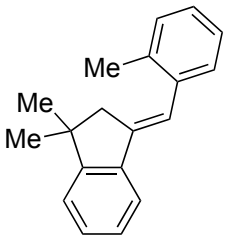
3i

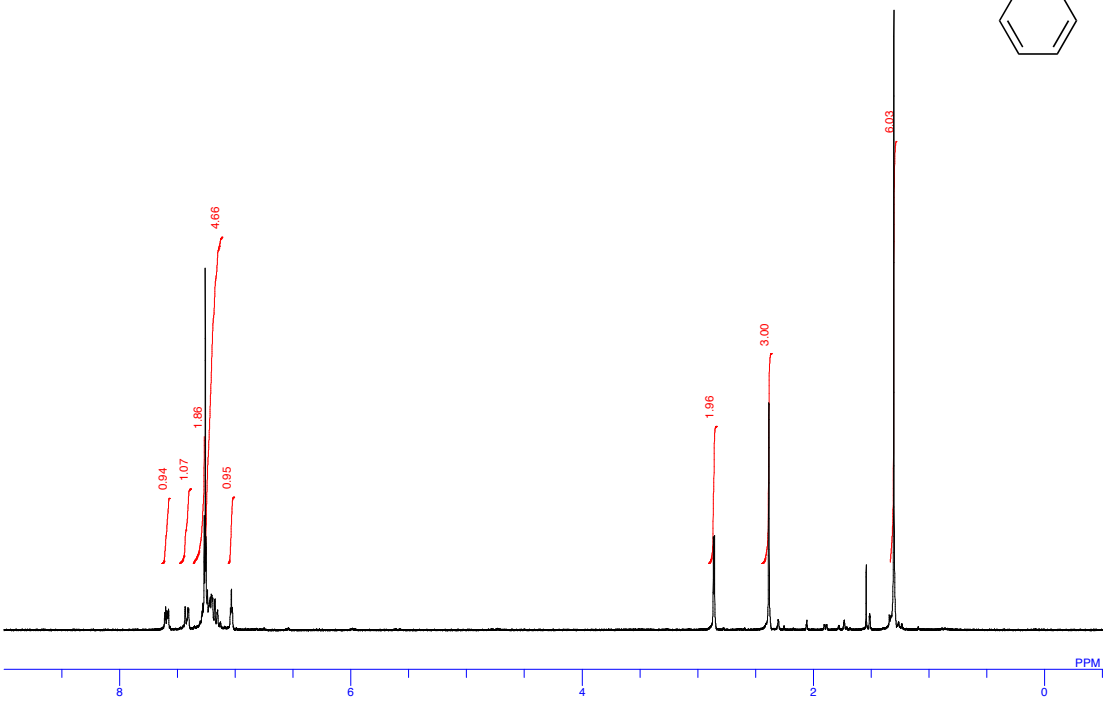

Me
Me
Me

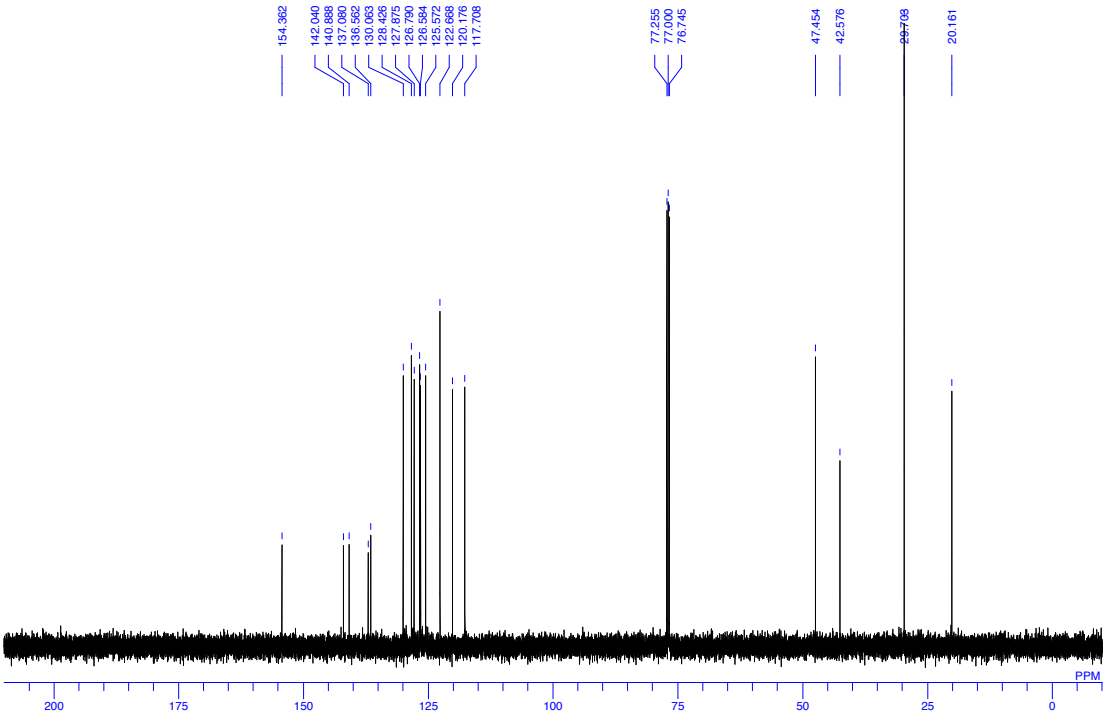

1.00
2.36
3.16
2.28
1.00
2.09
3.48
6.82
PPM
8
6
4
2
0


154.109
141.070
140.955
136.076
135.433
129.087
128.411
126.804
122.634
119.980
119.469
77.429
77.000
76.580
47.833
42.830
30.047
21.212
PPM
200
175
150
125
100
75
50
25
0

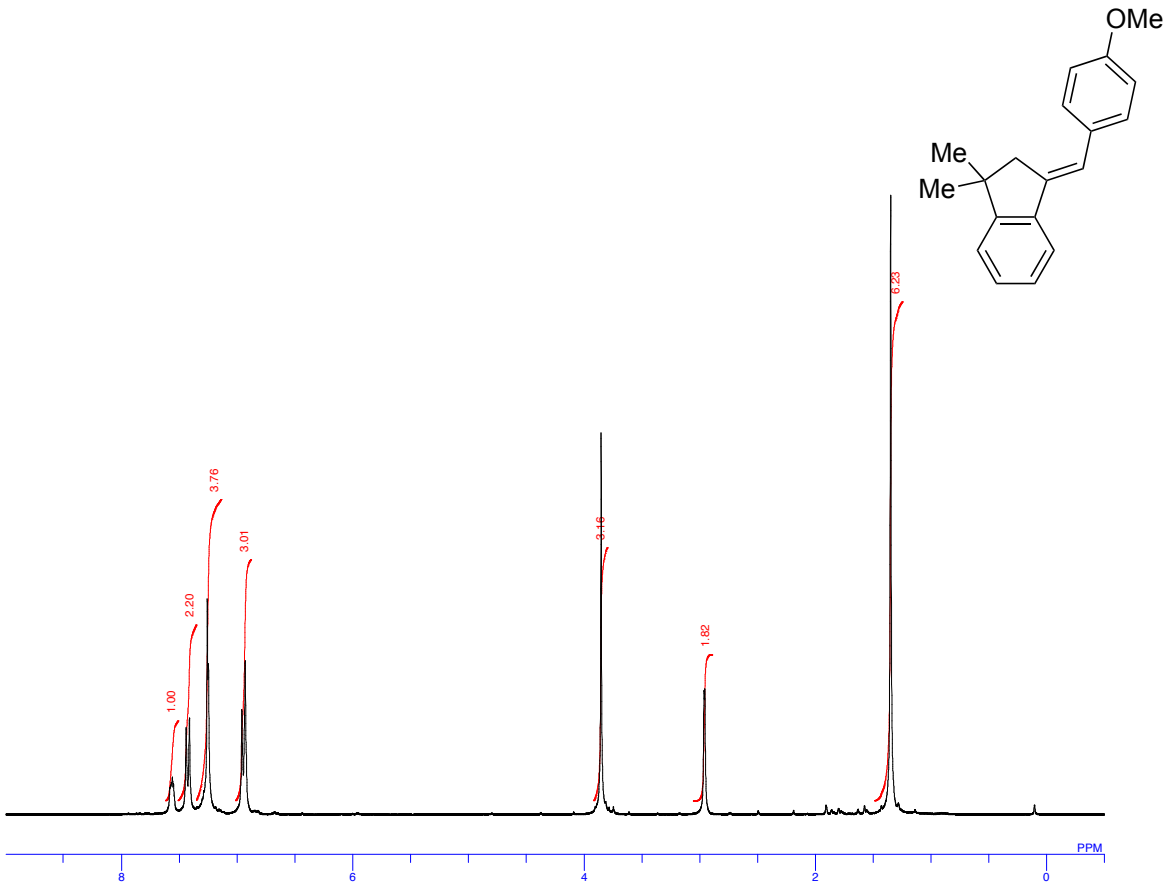
3j

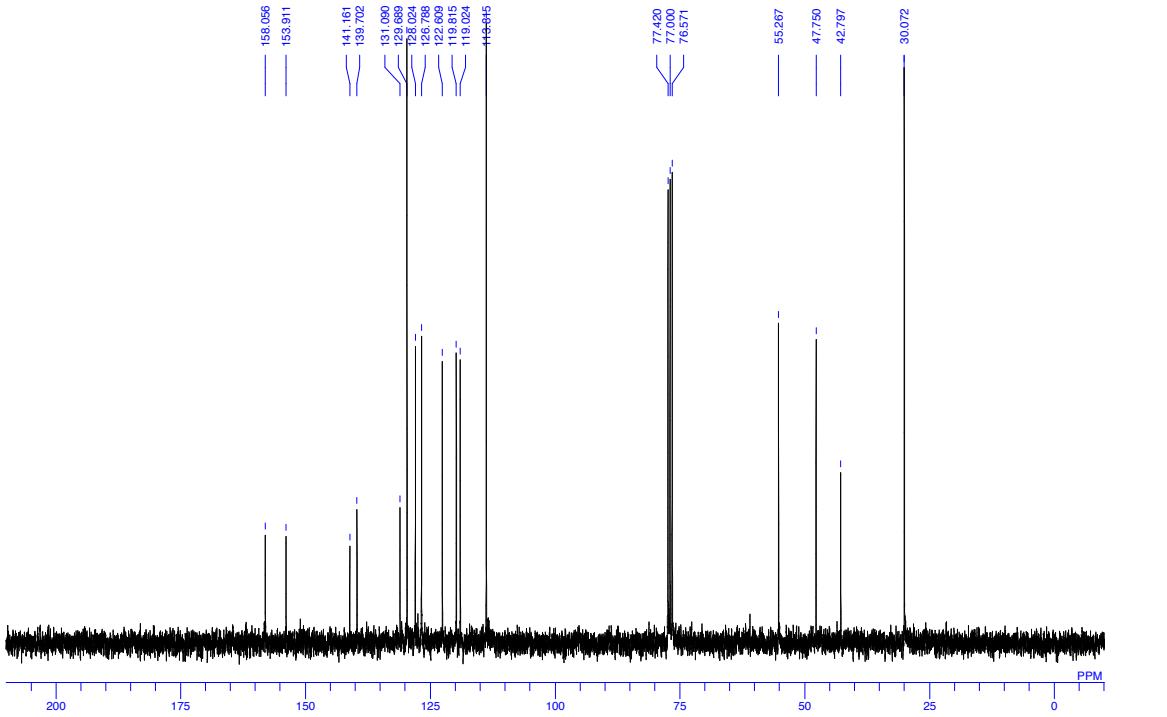

Me
Me
Me


0.94
1.07
1.86
4.66
0.95
1.96
3.00
6.03
PPM
8
6
4
2
0

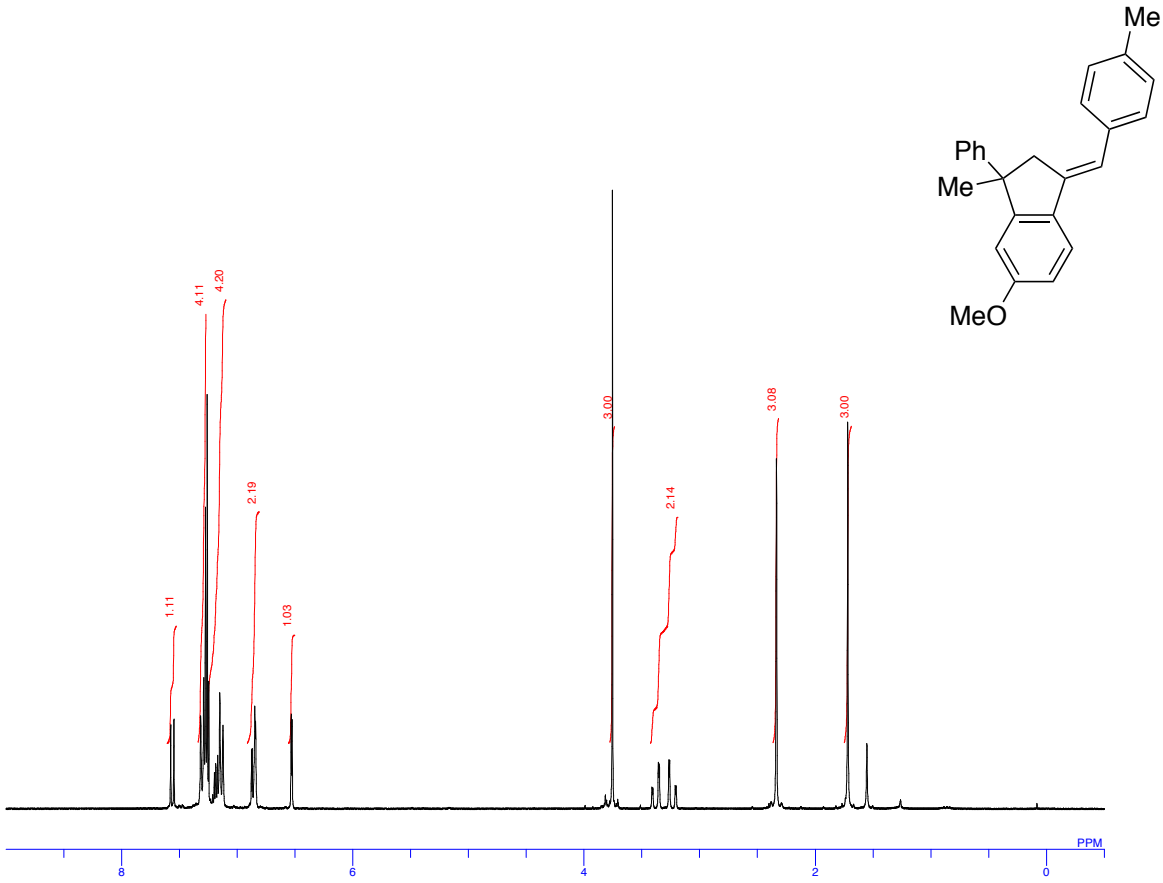

154.362
142.040
140.888
137.080
136.562
130.063
128.426
127.875
126.790
126.584
125.572
122.668
120.176
117.708
77.255
77.000
76.745
47.454
42.576
29.709
20.161
PPM
200
175
150
125
100
75
50
25
0

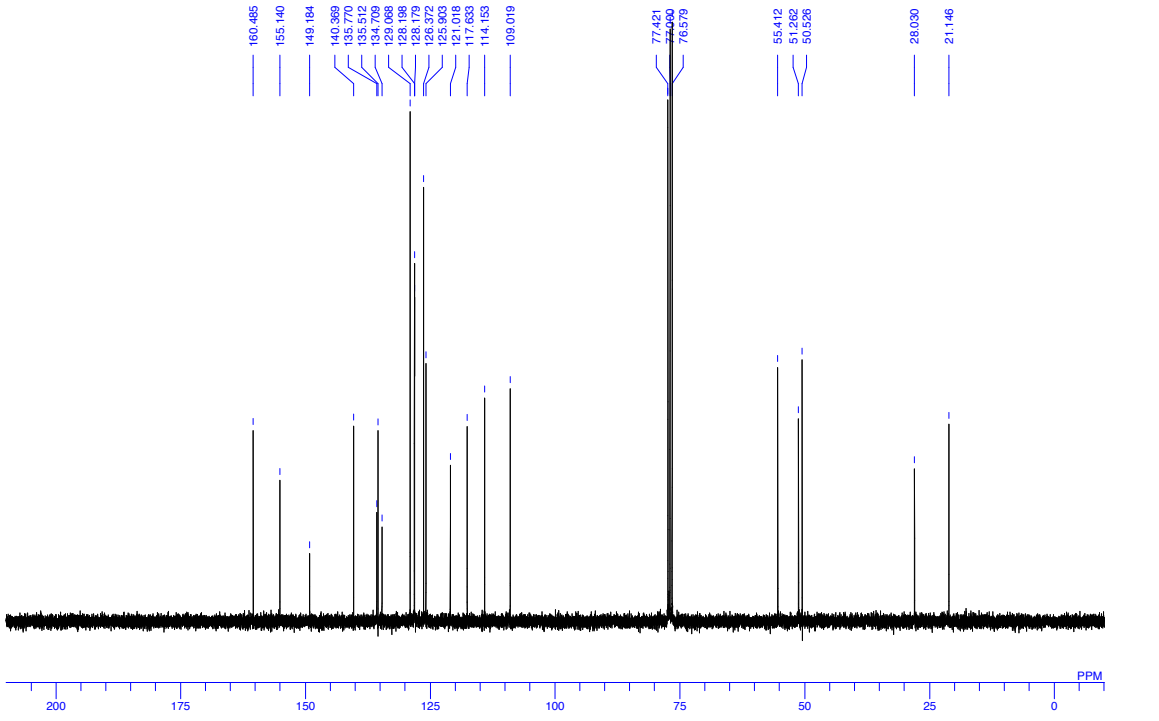
3k


OMe
Me
Me
1.00
2.20
3.76
3.01
8.16
1.82
6.23
PPM
8
6
4
2
0

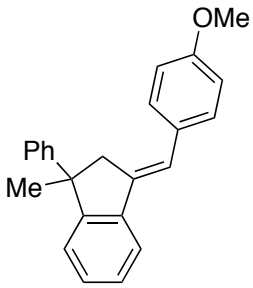

158.056
153.911
141.161
139.702
131.090
129.689
128.024
126.788
122.609
119.815
119.024
113.015
77.420
77.000
76.571
55.267
47.750
42.797
30.072
PPM
200
175
150
125
100
75
50
25
0

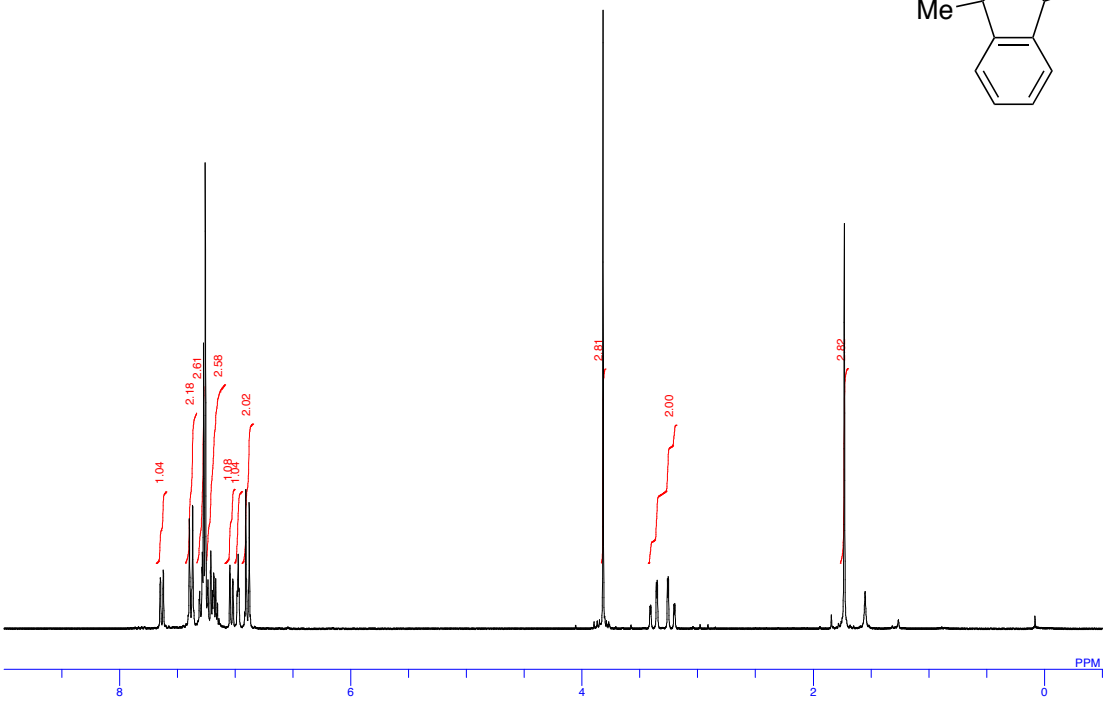
3l

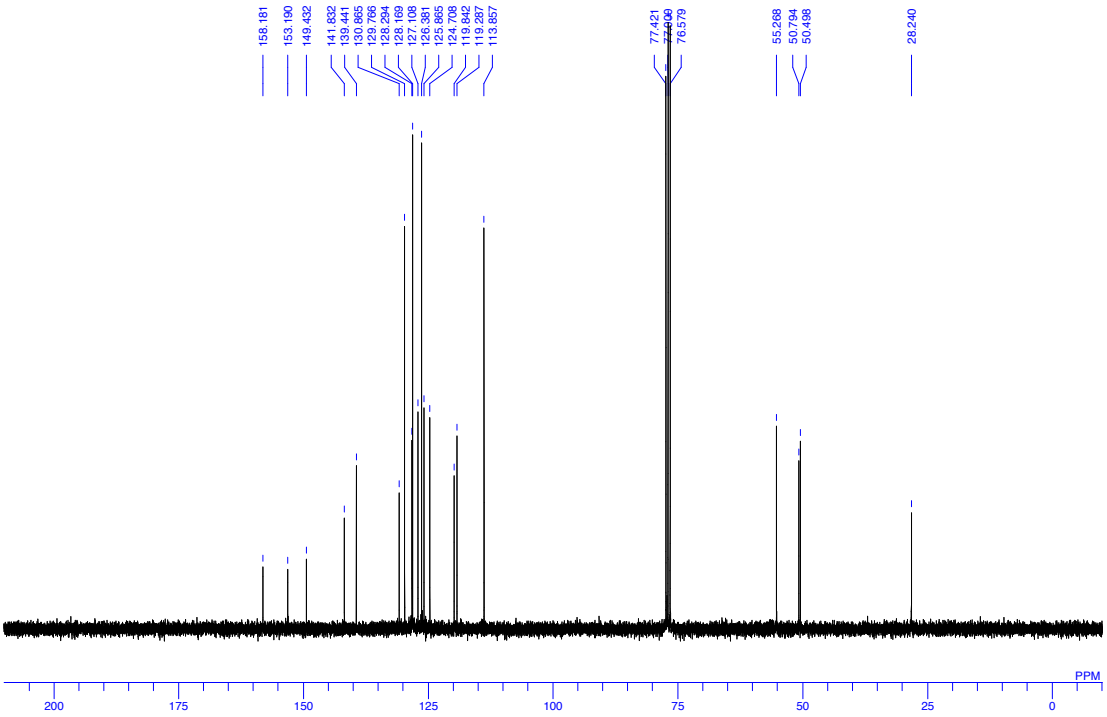

Me
Ph
Me
MeO
1.11
4.11
4.20
2.19
1.03
3.00
2.14
3.08
3.00
PPM
8
6
4
2
0


160.485
155.140
149.184
140.369
135.770
135.512
134.709
129.068
128.198
128.179
126.372
125.903
121.018
117.633
114.153
109.019
77.421
77.000
76.579
55.412
51.262
50.526
28.030
21.146
PPM
200
175
150
125
100
75
50
25
0

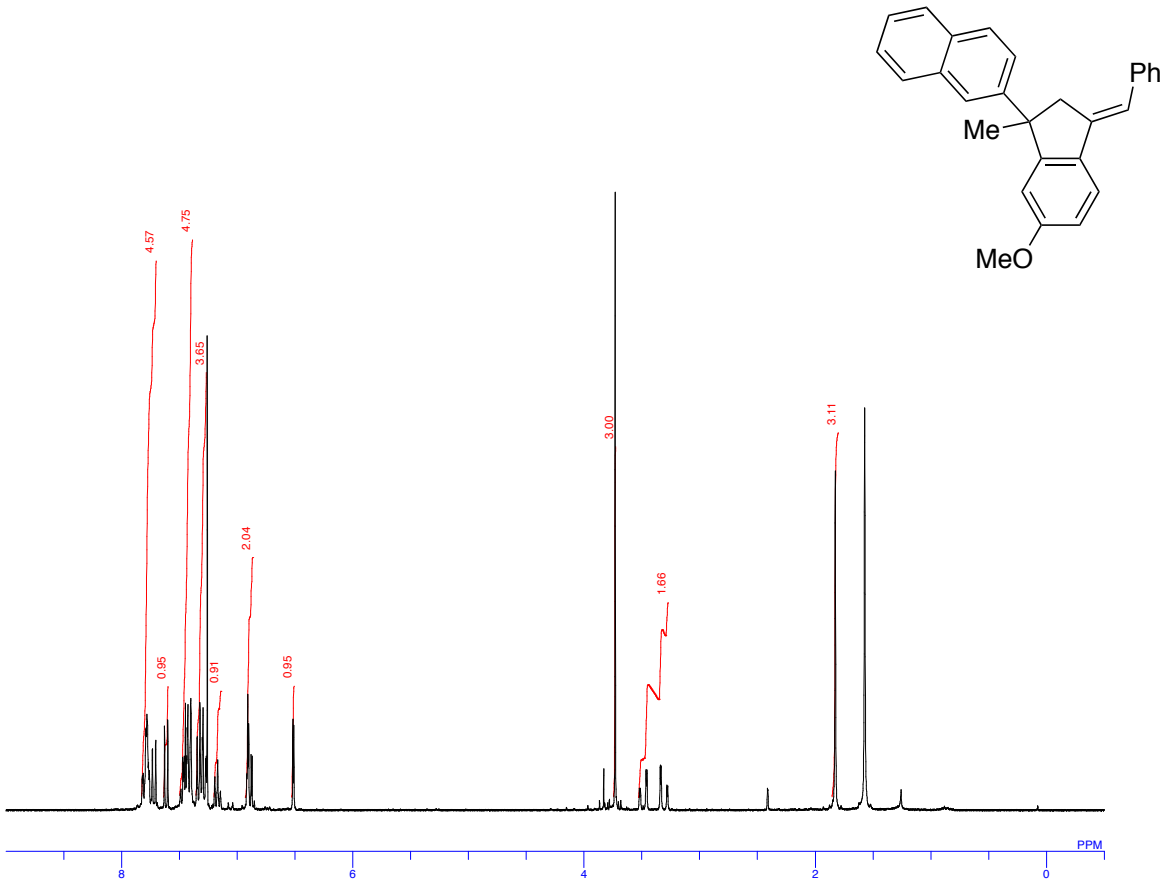
3m

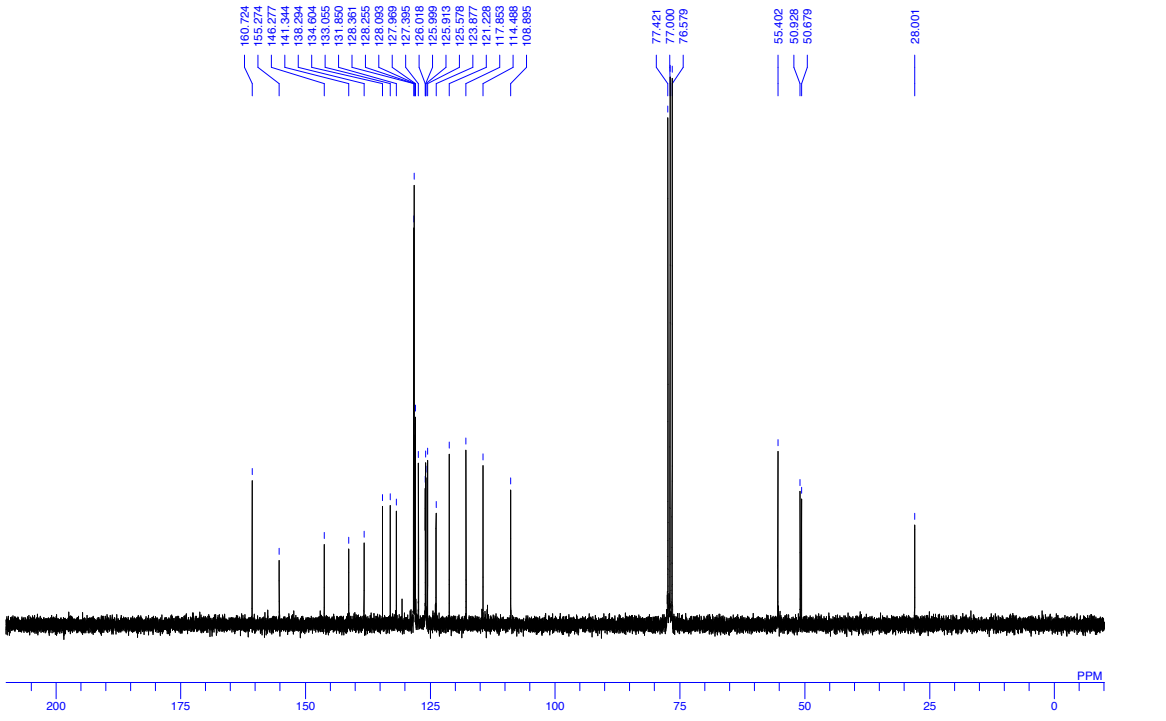

OMe
Ph
Me


1.04
2.18
2.61
2.58
2.02
1.08
1.04
2.81
2.00
2.82
PPM
8
6
4
2
0

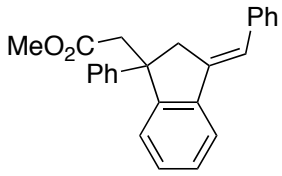

158.181
153.190
149.432
141.832
139.441
130.865
129.766
128.294
128.169
127.108
126.381
125.865
124.708
119.842
119.287
113.857
77.421
77.000
76.579
55.268
50.794
50.498
28.240
PPM
200
175
150
125
100
75
50
25
0

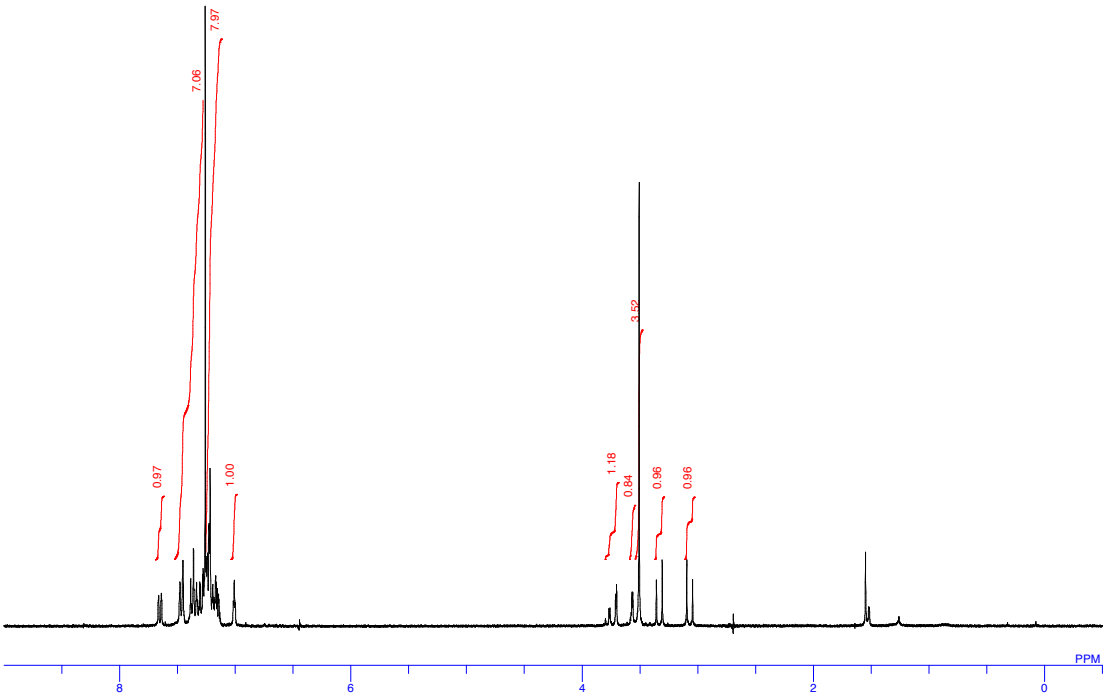
3n

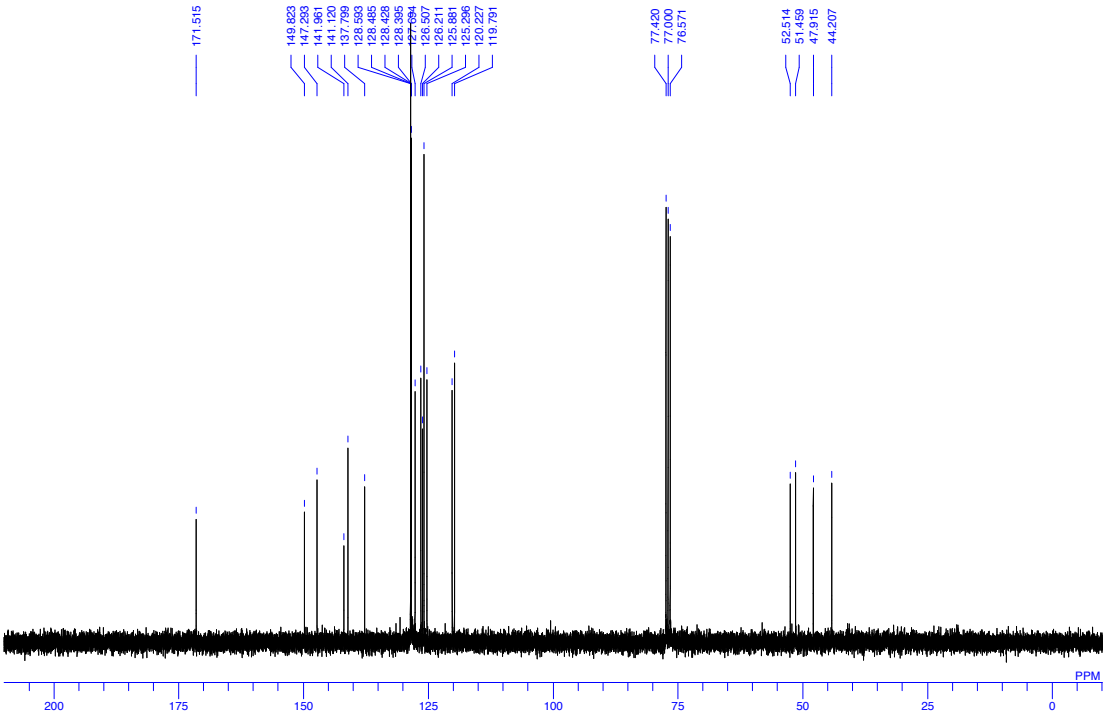

Ph
Me
MeO
4.57
4.75
3.65
0.95
0.91
2.04
0.95
3.00
1.66
3.11
PPM
8
6
4
2
0


160.724
155.274
146.277
141.344
138.284
134.604
133.055
131.850
128.361
128.255
128.093
127.969
127.395
126.018
125.999
125.913
125.578
123.877
121.228
117.853
114.488
108.895
77.421
77.000
76.579
55.402
50.928
50.679
28.001
PPM
200
175
150
125
100
75
50
25
0

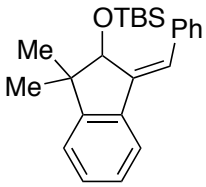
3o

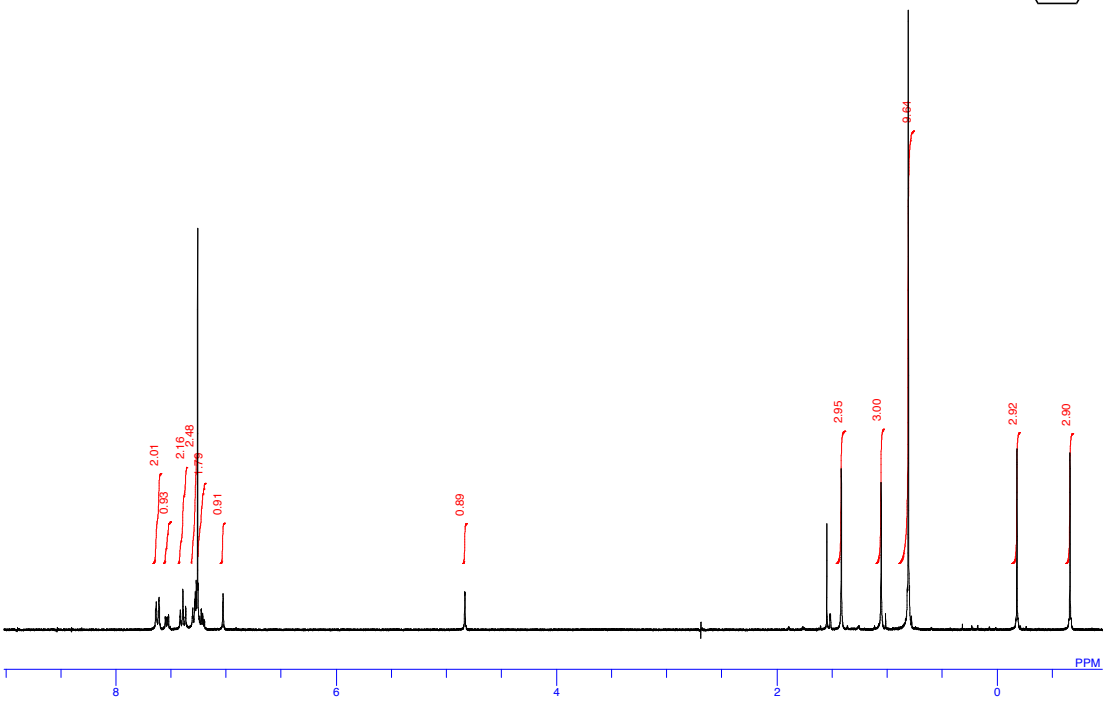

Ph
MeO2C
Ph

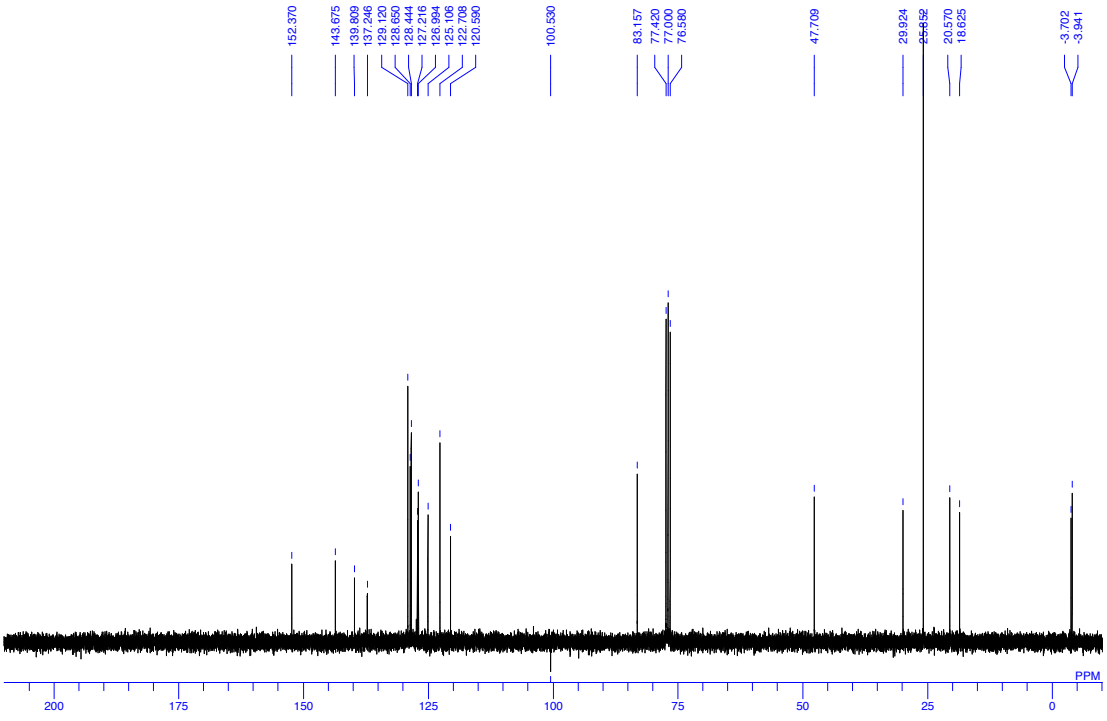

7.97
7.06
3.52
1.18
1.00
0.97
0.84
0.96
0.96
PPM
8
6
4
2
0


171.515
149.823
147.293
141.961
141.120
137.799
128.593
128.485
128.428
128.395
127.084
126.507
126.211
125.881
125.296
120.227
119.791
77.420
77.000
76.571
52.514
51.459
47.915
44.207
PPM
200
175
150
125
100
75
50
25
0

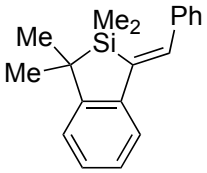
3p

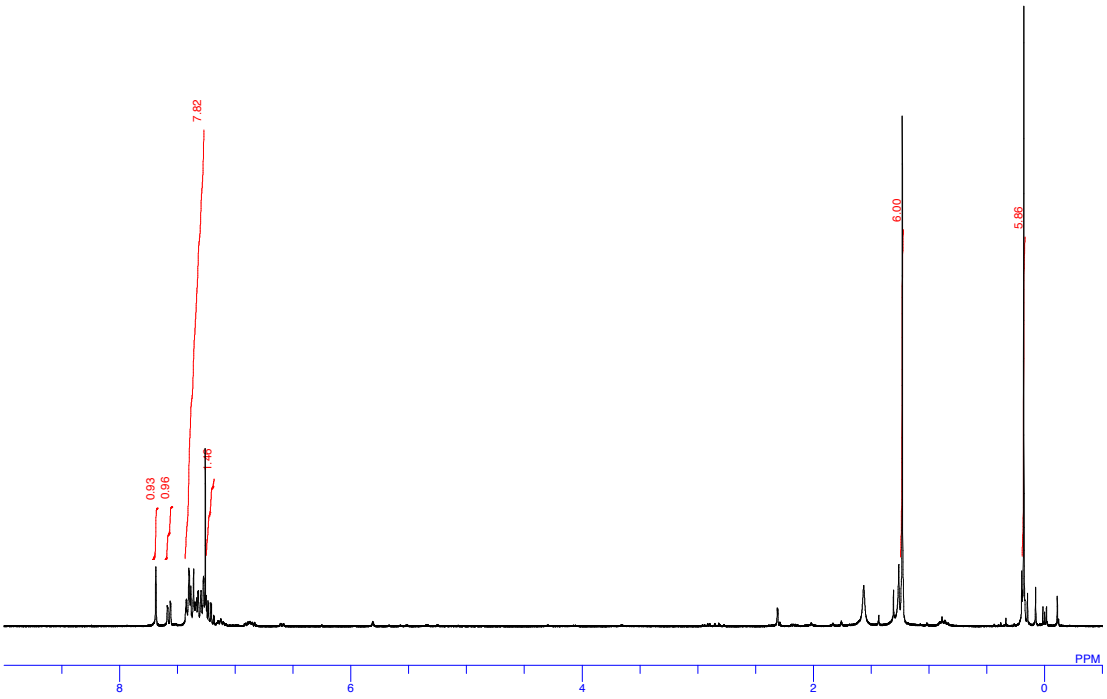

OTBS
Ph
Me
Me

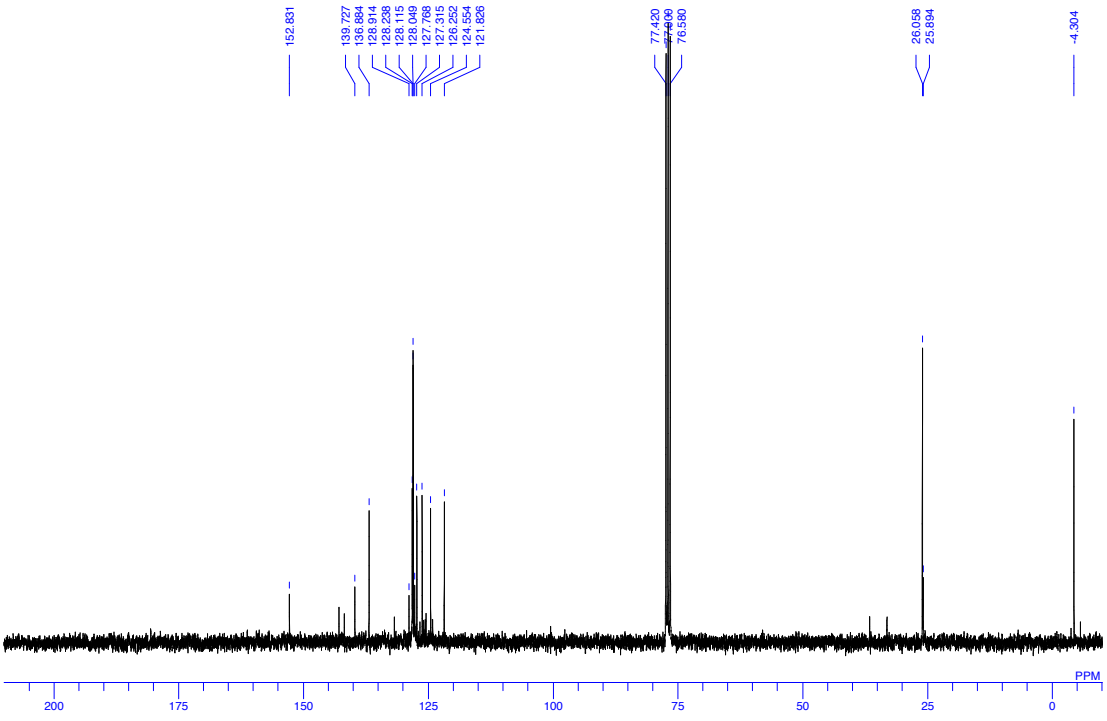

2.01
0.93
2.16
2.48
1.79
0.91
0.89
2.95
3.00
6.84
2.92
2.90
PPM
8
6
4
2
0


152.370
143.675
139.809
137.246
129.120
128.650
128.444
127.216
126.994
125.106
122.708
120.590
100.530
83.157
77.420
77.000
76.580
47.709
29.924
25.652
20.570
18.625
-3.702
-3.941
PPM
200
175
150
125
100
75
50
25
0

3q


Me
Me
Si
Me2
Ph


0.93
0.96
7.82
1.48
6.00
5.86
PPM
8
6
4
2
0


152.831
139.727
136.884
128.914
128.238
128.115
128.049
127.768
127.315
126.252
124.554
121.826
77.420
76.580
26.058
25.894
-4.304
PPM
200
175
150
125
100
75
50
25
0

4