Supporting Information for

Metal- and Reagent-Free Intramolecular Oxidative Allylic Amination of Tri- and Tetrasubstituted Alkenes

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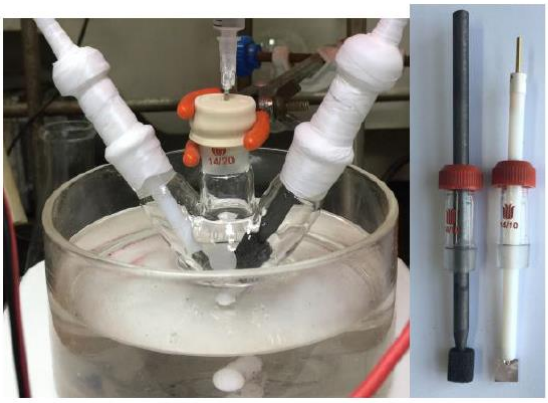
1. General Information

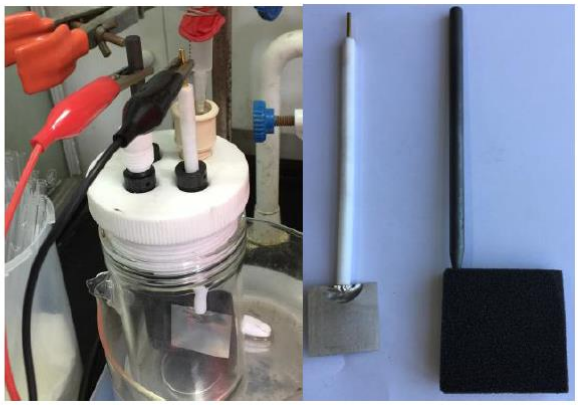
Anhydrous DMA was purchased from Aldrich. Other solvents and commercially available reagents were used without purification. Flash column chromatography was performed with silica gel (230–400 mesh). Cyclic voltammograms were recorded on a CHI 760E potentiostat. NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.2 ppm) for ^{13}C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer. High resolution mass spectra (ESI) were recorded by the instrumentation center of Department of Chemistry, Xiamen University, on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer.

2. General Procedure for the Electrolysis

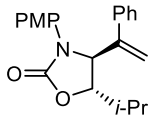
A 10-mL three-necked round-bottomed flask was charged with the substrate (0.3 mmol) and Et_4NPF_6 (0.3 mmol). The flask was equipped with a rubber stopper, a reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm x 1 cm x 1 cm) and a platinum plate (1 cm x 1 cm) cathode and then flushed with argon. DMA (4 mL) and HOAc (0.1 mL) were added. The constant current (10 mA) electrolysis was carried out at 110 °C (oil bath temperature) until complete consumption of the substrate (monitored by TLC or ^{1}H NMR). The reaction mixture was cooled to RT. Saturated $NaHCO_3$ (10 mL), brine (50 mL) and ethyl acetate (20 mL) were added. The phases were separated and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

The 3.2-gram (10 mmol) scale electrolysis of compound **41** was conducted in a 200-mL beaker-type cell described previously[1] with a RVC anode (5 cm x 5 cm x 1.2 cm), a Pt plate cathode (3 cm x 3 cm), and a constant current of 250 mA.

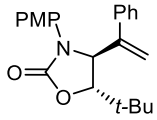




3. Characterization Data for the Cyclization Products

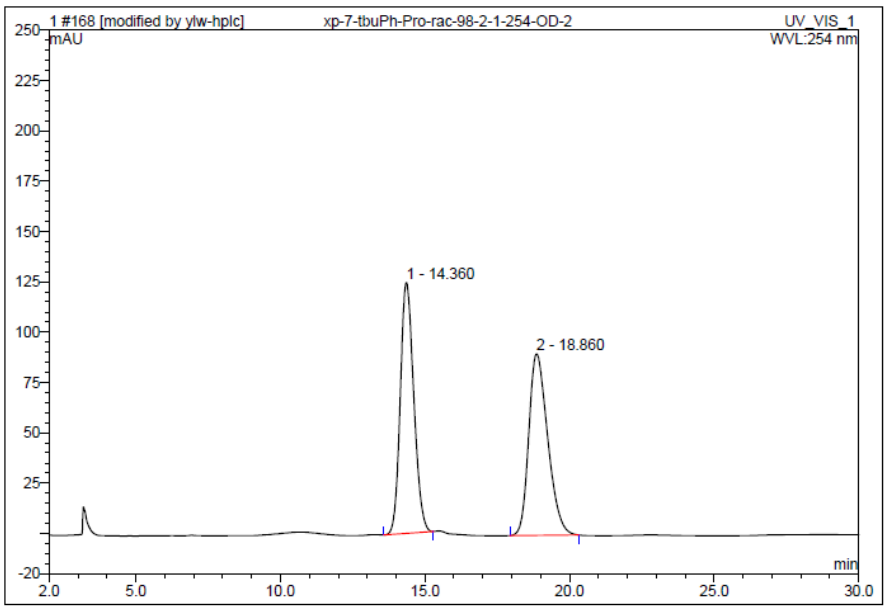


5-Isopropyl-3-(4-methoxyphenyl)-4-(1-phenylvinyl)oxazolidin-2-one (2). Yield = 82%, electricity = 3.0 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.39–7.33 (m, 3H), 7.32–7.27 (m, 2H), 6.92–6.86 (m, 2H), 5.42 (s, 1H), 5.31 (s, 1H), 4.83 (dd, *J* = 4.2, 0.8 Hz, 1H), 4.08 (dd, *J* = 5.5, 4.2 Hz, 1H), 3.78 (s, 3H), 1.97–1.88 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 155.8, 146.0, 138.1, 130.6, 128.9, 128.6, 127.3, 122.5, 117.4, 114.4, 83.4, 64.3, 55.6, 32.8, 17.8, 16.7; IR (neat, cm^{-1}): 2962, 1750, 1514, 1249, 1035, 830; ESI HRMS *m/z* $(M+Na)^+$ calcd 360.1570, obsd 360.1569.

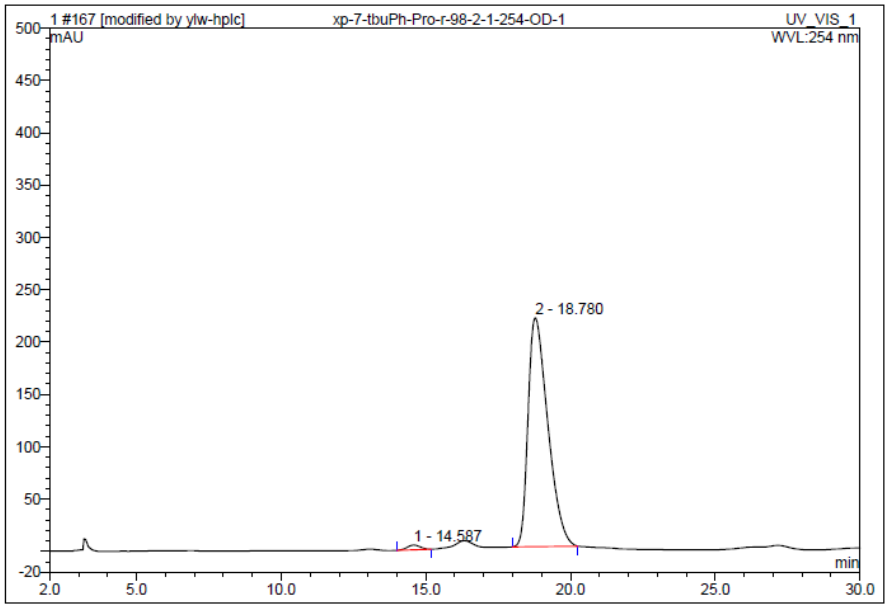


5-Isopropyl-3-(4-methoxyphenyl)-4-(1-phenylvinyl)oxazolidin-2-one (3). Yield = 67%, electricity = 4.0 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.40 (m, 2H), 7.39–7.31 (m, 3H), 7.32–7.26 (m, 2H), 6.93–6.86 (m, 2H), 5.38 (s, 1H), 5.33 (s, 1H), 4.82 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.95 (d, *J* = 3.8 Hz, 1H), 3.78 (s, 3H), 0.90 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 155.9, 146.9, 138.2, 130.5, 128.9, 128.6, 127.6, 122.8, 117.8, 114.5, 86.0, 63.1, 55.6, 34.9, 24.6; IR (neat, cm^{-1}): 2960, 1750, 1514, 1250, 1043, 830; ESI HRMS *m/z* $(M+Na)^+$ calcd 374.1727, obsd 374.1725.

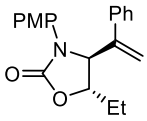
(4*S*,5*S*)-5-(*tert*-Butyl)-3-(4-methoxyphenyl)-4-(1-phenylvinyl)oxazolidin-2-one [(-)-3]. Yield = 72%; $[\alpha]_D^{20}$ = −25.3° (*c* 1.0, $CHCl_3$), 99:1 e.r. (determined by HPLC: Chiralcel OD-H column, 8/92 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; retention time = 14.59 min (minor), 18.78 min (major). The spectral data (NMR, IR, MS) were the same with those of *rac*-**3**.



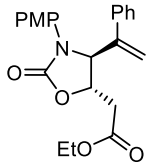
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	14.36	n.a.	124.686	67.393	49.59	n.a.	BMB*
2	18.86	n.a.	90.094	68.499	50.41	n.a.	BMB*
Total:			214.780	135.892	100.00	0.000	



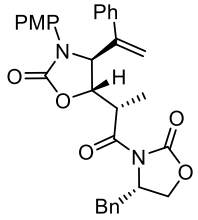
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	14.59	n.a.	4.476	2.323	1.33	n.a.	BMB*
2	18.78	n.a.	218.713	172.875	98.67	n.a.	BMB*
Total:			223.189	175.198	100.00	0.000	



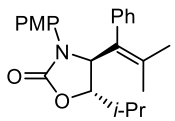
5-Ethyl-3-(4-methoxyphenyl)-4-(1-phenylvinyl)oxazolidin-2-one (4). Yield = 78%, electricity = 3.0 F; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.27 (m, 7H), 6.92–6.84 (m, 2H), 5.44 (s, 1H), 5.30 (s, 1H), 4.87–4.78 (m, 1H), 4.23 (dt, *J* = 7.1, 5.0 Hz, 1H), 3.78 (s, 3H), 1.84–1.70 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 155.7, 145.1, 138.1, 130.7, 129.0, 128.6, 127.0, 122.3, 117.0, 114.4, 80.4, 65.9, 55.6, 28.3, 9.0; IR (neat, cm^{-1}): 2923, 1750, 1513, 1248, 827; ESI HRMS *m/z* $(M+Na)^+$ calcd 346.1416, obsd 346.1414.



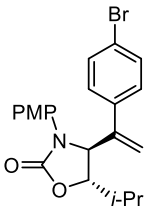
Ethyl 2-(3-(4-methoxyphenyl)-2-oxo-4-(1-phenylvinyl)oxazolidin-5-yl)acetate (5). Yield = 73%，electricity = 3.3 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.27 (m, 7H), 6.91–6.83 (m, 2H), 5.45 (s, 1H), 5.32 (s, 1H), 5.04 (d, *J* = 4.4 Hz, 1H), 4.67 (td, *J* = 6.1, 4.4 Hz, 1H), 4.15–4.02 (m, 2H), 3.78 (s, 3H), 2.82–2.69 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 157.0, 155.1, 144.6, 137.8, 130.3, 129.0, 128.7, 127.1, 122.6, 117.6, 114.4, 75.2, 65.4, 61.4, 55.6, 39.7, 14.2; IR (neat, cm^{-1}): 2922, 1755, 1514, 1258, 750; ESI HRMS *m/z* $(M+Na)^+$ calcd 404.1468, obsd 404.1467.



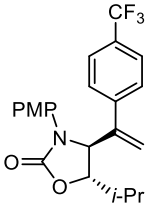
(4*R*,5*S*)-5-((*S*)-1-((*S*)-4-Benzyl-2-oxooxazolidin-3-yl)-1-oxopropan-2-yl)-3-(4-methoxyphenyl)-4-(1-phenylvinyl)oxazolidin-2-one (6). Yield = 85%, electricity = 2.9 F; Colorless solid; Isolated as a 13:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.38 (m, 2H), 7.38–7.24 (m, 8H), 7.17–7.10 (m, 2H), 6.93–6.85 (m, 2H), 5.41 (s, 1H), 5.35 (s, 1H), 5.18 (d, *J* = 4.4 Hz, 1H), 4.53 (dd, *J* = 6.0, 4.4 Hz, 1H), 4.48–4.41 (m, 1H), 4.36–4.28 (m, 1H), 4.16 (t, *J* = 8.3 Hz, 1H), 4.11 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.78 (s, 3H), 3.19 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.75 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 157.4, 155.4, 153.2, 146.0, 138.2, 135.1, 130.1, 129.5, 129.1, 128.9, 128.6, 127.6, 127.4, 123.8, 118.3, 114.5, 79.6, 66.5, 64.4, 55.6, 55.4, 41.1, 37.8, 12.7; IR (neat, cm^{-1}): 2923, 1753, 1692, 1387, 1037, 751; ESI HRMS m/z $(M+Na)^+$ calcd 549.1996, obsd 549.1996.



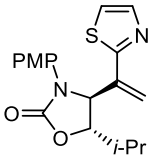
5-Isopropyl-3-(4-methoxyphenyl)-4-(2-methyl-1-phenylprop-1-en-1-yl)oxazolidin-2-one (7). Yield = 63%, electricity = 2.7 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.27–7.24 (m, 3H), 6.95–6.90 (m, 2H), 6.89–6.76 (m, 2H), 5.17 (d, *J* = 5.0 Hz, 1H), 4.13 (t, *J* = 5.3 Hz, 1H), 3.82 (s, 3H), 2.04–1.94 (m, 4H), 1.47 (s, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 155.9, 137.9, 135.5, 132.2, 131.1, 130.0, 128.5, 127.5, 122.8, 114.4, 81.9, 60.5, 55.7, 32.6, 23.5, 20.1, 18.0, 17.0; IR (neat, cm^{-1}): 2926, 1752, 1258, 750; ESI HRMS m/z $(M+Na)^+$ calcd 388.1883, obsd 388.1886.



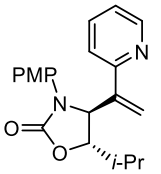
4-(1-(4-Bromophenyl)vinyl)-5-isopropyl-3-(4-methoxyphenyl)oxazolidin-2-one (8). Yield = 77%，electricity = 2.7 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.42–7.37 (m, 2H), 7.19–7.13 (m, 2H), 6.91–6.85 (m, 2H), 5.41 (s, 1H), 5.35 (s, 1H), 4.79 (d, *J* = 4.2 Hz, 1H), 4.05 (dd, *J* = 5.6, 4.2 Hz, 1H), 3.78 (s, 3H), 1.97–1.88 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 155.7, 145.2, 137.0, 132.1, 130.3, 128.9, 122.8, 122.7, 118.3, 114.5, 83.2, 64.4, 55.6, 32.8, 17.8, 16.7; IR (neat, cm^{-1}): 2926, 1752, 1259, 750; ESI HRMS m/z $(M+Na)^+$ calcd 438.0675, obsd 438.0672.



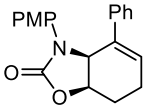
5-Isopropyl-3-(4-methoxyphenyl)-4-(1-(4-(trifluoromethyl)phenyl)vinyl)oxazolidin-2-one (9). Yield = 80%, electricity = 2.7 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.57 (m, 2H), 7.44–7.35 (m, 4H), 6.93–6.84 (m, 2H), 5.48 (s, 1H), 5.44 (s, 1H), 4.84 (d, *J* = 4.2 Hz, 1H), 4.07 (dd, *J* = 5.6, 4.2 Hz, 1H), 3.79 (s, 3H), 2.00–1.91 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 155.6, 145.3, 141.7, 130.7 (q, $J_{C\text{-}F}$ = 32.7 Hz), 130.2, 127.7, 125.9 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.06 (q, $J_{C\text{-}F}$ = 272.1 Hz), 122.7, 119.6, 114.5, 83.2, 64.4, 55.6, 32.8, 17.8, 16.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.72; IR (neat, cm^{-1}): 2926, 1752, 1259, 750; ESI HRMS m/z $(M+Na)^+$ calcd 428.1444, obsd 428.1440.



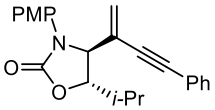
5-Isopropyl-3-(4-methoxyphenyl)-4-(1-(thiazol-2-yl)vinyl)oxazolidin-2-one (10). Yield = 77%, electricity = 2.8 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 3.3 Hz, 1H), 7.44–7.38 (m, 2H), 7.30 (d, *J* = 3.3 Hz, 1H), 6.87–6.81 (m, 2H), 5.92 (d, *J* = 0.9 Hz, 1H), 5.51 (d, *J* = 0.9 Hz, 1H), 5.35 (dd, *J* = 3.6, 0.9 Hz, 1H), 4.23 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.76 (s, 3H), 2.21–2.11 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.03–0.98 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 156.7, 155.9, 143.5, 140.2, 130.4, 121.9, 119.6, 118.7, 114.4, 84.4, 61.7, 55.6, 32.8, 18.3, 16.2; IR (neat, cm^{-1}): 2962, 1751, 1514, 1248, 1038, 830; ESI HRMS m/z $(M+Na)^+$ calcd 367.1087, obsd 367.1090.



5-Isopropyl-3-(4-methoxyphenyl)-4-(1-(pyridin-2-yl)vinyl)oxazolidin-2-one (11). Yield = 56%, electricity = 2.9 F; Light yellow oil; Isolated as a 11:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63–8.56 (m, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.51–7.44 (m, 2H), 7.23 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.86–6.81 (m, 2H), 5.80 (s, 1H), 5.51 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.45 (d, *J* = 0.9 Hz, 1H), 4.17 (dd, *J* = 4.8, 3.5 Hz, 1H), 3.76 (s, 3H), 2.19–2.09 (m, 1H), 1.03–0.98 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 156.1, 155.9, 148.9, 145.3, 136.8, 130.9, 123.1, 121.4, 121.2, 116.6, 114.3, 84.8, 61.1, 55.6, 32.6, 18.3, 16.3; IR (neat, cm^{-1}): 2922, 1748, 1586, 1132, 1076; ESI HRMS m/z $(M+Na)^+$ calcd 361.1523, obsd 361.1523.

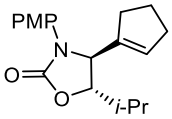


3-(4-Methoxyphenyl)-4-phenyl-3a,6,7,7a-tetrahydrobenzo[*d*]oxazol-2(3*H*)-one (12). Yield = 65%, electricity = 3.5 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02–6.96 (m, 3H), 6.95–6.89 (m, 2H), 6.89–6.82 (m, 2H), 6.54–6.47 (m, 2H), 6.21–6.16 (m, 1H), 5.23–5.20 (m, 1H), 5.15–5.09 (m, 1H), 3.64 (s, 3H), 2.56–2.44 (m, 1H), 2.34–2.21 (m, 2H), 1.93–1.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 157.0, 140.2, 136.1, 131.1, 129.8, 128.0 (2s), 126.9, 126.4, 113.9, 73.7, 57.8, 55.5, 25.5, 20.3; IR (neat, cm^{-1}): 2920, 1740, 1515, 1128, 822; ESI HRMS m/z $(M+Na)^+$ calcd 344.1257, obsd 344.1258.

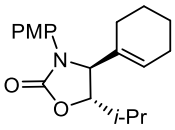


5-Isopropyl-3-(4-methoxyphenyl)-4-(4-phenylbut-1-en-3-yn-2-yl)oxazolidin-2-one (13). Yield = 61%, electricity = 3.4 F; Light yellow oil; Isolated as a 11:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.43 (m, 2H), 7.40–7.30 (m, 5H), 6.91–6.85 (m, 2H), 5.57 (s, 1H), 5.47 (s, 1H), 4.49 (d, *J* = 4.5 Hz, 1H), 4.33 (dd, *J* = 6.1, 4.5 Hz, 1H),

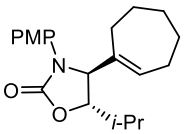
3.78 (s, 3H), 2.10–2.01 (m, 1H), 1.10 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 156.0, 132.0, 130.4, 129.8 129.1, 128.6, 124.5, 124.1, 122.2, 114.5, 93.2, 85.2, 83.0, 65.9, 55.6, 32.7, 17.6, 17.2; IR (neat, cm^{-1}): 2922, 1749, 1457, 1586, 1132, 1076; ESI HRMS m/z $(M+Na)^+$ calcd 384.1570, obsd 384.1571.



4-(Cyclopent-1-en-1-yl)-5-isopropyl-3-(4-methoxyphenyl)oxazolidin-2-one (14). Yield = 63%, electricity = 3.5 F; Light yellow oil; Isolated as a 6.5:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 6.89–6.83 (m, 2H), 5.74–5.68 (m, 1H), 4.67 (d, J = 5.6 Hz, 1H), 4.03 (t, J = 5.6 Hz, 1H), 3.78 (s, 3H), 2.36–2.26 (m, 3H), 2.21–2.11 (m, 1H), 2.02–1.94 (m, 1H), 1.94–1.77 (m, 2H), 1.05 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 155.9, 141.5, 131.2, 130.5, 123.0, 114.3, 82.1, 61.0, 55.6, 32.6, 32.4, 30.3, 23.2, 17.7, 17.0; IR (neat, cm^{-1}): 2960, 1751, 1514, 1375, 1248, 829; ESI HRMS m/z $(M+Na)^+$ calcd 324.1570, obsd 324.1568.

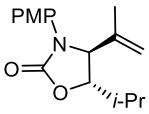


4-(Cyclohex-1-en-1-yl)-5-isopropyl-3-(4-methoxyphenyl)oxazolidin-2-one (15). Yield = 67%, electricity = 3.1 F; Light yellow oil; Isolated as a 6.5:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 6.90–6.84 (m, 2H), 5.76–5.69 (m, 1H), 4.32 (d, J = 5.2 Hz, 1H), 4.02 (t, J = 5.2 Hz, 1H), 3.79 (s, 3H), 2.09–1.91 (m, 4H), 1.90–1.80 (m, 1H), 1.67–1.57 (m, 1H), 1.57–1.47 (m, 3H), 1.04 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 156.0, 135.1, 130.5, 128.1, 123.0, 114.2, 82.3, 66.8, 55.6, 32.6, 25.2, 22.9, 22.3 (2s), 17.8, 16.8; IR (neat, cm^{-1}): 2932, 1750, 1514, 1248, 829, 758; ESI HRMS m/z $(M+Na)^+$ calcd 338.1727, obsd 338.1725.

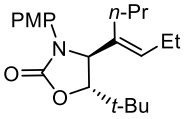


4-(Cyclohept-1-en-1-yl)-5-isopropyl-3-(4-methoxyphenyl)oxazolidin-2-one (16). Yield = 67%, electricity = 2.8 F; Light yellow oil; Isolated as a 10:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 6.89–6.83 (m, 2H), 5.89 (t, J = 6.4 Hz, 1H), 4.39 (d, J = 5.8 Hz, 1H), 3.99 (t, J = 5.8 Hz, 1H), 3.79 (s, 3H), 2.20–2.06 (m, 3H), 2.04–1.93 (m, 2H), 1.74–1.59 (m, 2H), 1.43–1.30 (m, 3H), 1.24–1.15 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 156.2, 140.3, 134.2, 130.2,

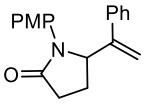
123.7, 114.1, 81.8, 68.5, 55.6, 32.5, 32.4, 28.5, 27.2, 26.7, 26.6, 18.0, 17.1; IR (neat, cm^{-1}): 2924, 1751, 1514, 1248, 1037, 829; ESI HRMS m/z $(M+Na)^+$ calcd 352.1883, obsd 352.1881.



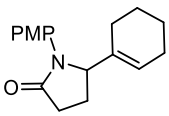
5-Isopropyl-3-(4-methoxyphenyl)-4-(prop-1-en-2-yl)oxazolidin-2-one (17). Yield = 74%, electricity = 2.5 F; Light yellow oil; Isolated as a 8.3:1 mixture of diastereomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.34 (m, 2H), 6.92–6.82 (m, 2H), 5.05 (s, 1H), 5.00–4.98 (m, 1H), 4.45 (d, *J* = 4.7 Hz, 1H), 4.03 (t, *J* = 5.2 Hz, 1H), 2.06–1.94 (m, 1H), 1.70 (s, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 155.8, 142.4, 130.4, 122.7, 116.3, 114.3, 82.0, 66.0, 55.6, 32.7, 17.7, 16.8 (2s); IR (neat, cm^{-1}): 2963，1754, 1514, 1249, 1037, 830; ESI HRMS m/z $(M+Na)^+$ calcd 298.1414, obsd 298.1412.



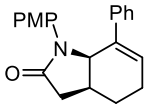
5-(*tert*-Butyl)-4-(hept-3-en-4-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (18). Yield = 68%, electricity = 2.6 F; Light yellow oil; Isolated as a 5.5:1 mixture of *E*/*Z* isomers and only the major isomer was shown. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.33 (m, 2H), 6.90–6.81 (m, 2H), 5.44 (t, *J* = 7.2 Hz, 1H), 4.37 (d, *J* = 3.9 Hz, 1H), 3.91 (d, *J* = 3.9 Hz, 1H), 3.78 (s, 3H), 2.08–1.99 (m, 3H), 1.98–1.89 (m, 1H), 1.46–1.23 (m, 2H), 1.00 (s, 9H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 156.0, 135.9, 133.6, 130.8, 122.5, 114.2, 85.6, 65.0, 55.6, 35.1, 29.1, 24.7, 22.7, 21.4, 14.8, 14.0; IR (neat, cm^{-1}): 2961, 2872, 1748, 830, 753; ESI HRMS m/z $(M+Na)^+$ calcd 368.2196, obsd 368.2195.



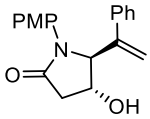
1-(4-Methoxyphenyl)-5-(1-phenylvinyl)pyrrolidin-2-one (19). Yield = 74%, electricity = 4.1 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2H), 7.41–7.30 (m, 5H), 6.91–6.84 (m, 2H), 5.40 (s, 1H), 5.14 (d, *J* = 1.0 Hz, 1H), 5.11 (ddd, *J* = 8.6, 2.7, 1.0 Hz, 1H), 3.78 (s, 3H), 2.65 (dt, *J* = 16.6, 9.4 Hz, 1H), 2.55–2.37 (m, 2H), 1.94 (ddt, *J* = 12.3, 9.3, 2.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 156.8, 146.5, 139.0, 131.8, 128.8, 128.3, 126.6, 123.2, 114.1, 113.8, 63.4, 55.6, 30.8, 25.7; IR (neat, cm^{-1}): 2922, 1695, 1509, 1246, 828; ESI HRMS m/z $(M+Na)^+$ calcd 316.1308, obsd 316.1308.



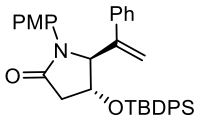
5-(Cyclohex-1-en-1-yl)-1-(4-methoxyphenyl)pyrrolidin-2-one (20). Yield = 55%, electricity = 4.1 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 6.89–6.83 (m, 2H), 5.64–5.57 (m, 1H), 4.50 (dd, *J* = 8.4, 5.0 Hz, 1H), 3.79 (s, 3H), 2.67–2.58 (m, 1H), 2.56–2.47 (m, 1H), 2.33–2.23 (m, 1H), 1.98–1.86 (m, 4H), 1.81–1.73 (m, 1H), 1.64–1.55 (m, 1H), 1.53–1.37 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 157.1, 136.2, 131.4, 125.8, 124.6, 114.0, 66.7, 55.6, 31.5, 25.1, 24.4, 23.5, 22.5 (2s); IR (neat, cm^{-1}): 2927, 1693, 1512, 1247, 829; ESI HRMS m/z $(M+Na)^+$ calcd 294.1465, obsd 294.1465.



1-(4-Methoxyphenyl)-7-phenyl-1,3,3a,4,5,7a-hexahydro-2*H*-indol-2-one (21). Yield = 90%, electricity = 3.5 F; White soild; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01–6.93 (m, 3H), 6.89–6.82 (m, 2H), 6.72–6.64 (m, 2H), 6.52–6.44 (m, 2H), 6.01 (t, *J* = 4.0 Hz, 1H), 5.06 (d, *J* = 5.5 Hz, 1H), 3.65 (s, 3H), 2.82–2.70 (m, 2H), 2.48–2.41 (m, 1H), 2.39–2.23 (m, 2H), 1.88–1.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 158.2, 141.6, 136.8, 131.3, 130.5, 128.9, 127.8, 126.6, 126.5, 113.9, 60.5, 55.5, 37.1, 33.2, 23.9, 23.8; IR (neat, cm^{-1}): 2926, 1697, 1512, 1246, 830; ESI HRMS m/z $(M+Na)^+$ calcd 342.1465, obsd 342.1463.

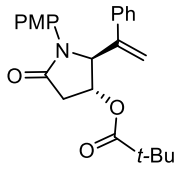


4-Hydroxy-1-(4-methoxyphenyl)-5-(1-phenylvinyl)pyrrolidin-2-one (22). Yield = 53%, electricity = 6.2 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.47–7.42 (m, 2H), 7.41–7.32 (m, 3H), 6.88–6.83 (m, 2H), 5.47 (s, 1H), 5.14 (d, *J* = 1.4 Hz, 1H), 5.03 (s, 1H), 4.21 (d, *J* = 5.6 Hz, 1H), 3.77 (s, 3H), 2.92 (dd, *J* = 17.6, 5.7 Hz, 1H), 2.83 (brs, 1H), 2.43 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 157.0, 143.6, 138.4, 131.6, 129.0, 128.6, 126.4, 123.2, 114.3, 114.1, 73.0, 69.6, 55.6, 40.6; IR (neat, cm^{-1}): 2929, 1674, 1512, 1252, 750; ESI HRMS m/z $(M+Na)^+$ calcd 332.1257, obsd 332.1259.

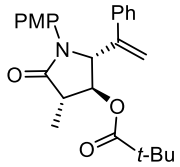


4-((*tert*-Butyldiphenylsilyl)oxy)-1-(4-methoxyphenyl)-5-(1-phenylvinyl)pyrrolidin-2-one (23). Yield = 70%, electricity = 3.6 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.53 (m, 2H), 7.53–7.45 (m, 4H), 7.42–7.36 (m, 2H), 7.33–7.19 (m, 7H), 7.18–7.12 (m, 2H), 6.96–6.88 (m, 2H), 5.29 (s, 1H), 5.10–5.03 (m, 2H), 4.20 (d, *J* = 5.1 Hz, 1H), 3.80 (s, 3H), 2.62 (dd, *J* = 17.2, 5.3 Hz, 1H), 2.36 (d, *J* = 17.2 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 157.0, 144.3, 138.8, 135.9, 135.8, 133.2, 133.0, 132.0, 130.1, 130.0, 128.8, 128.3, 128.0, 127.9, 126.7, 123.3,

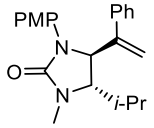
114.8, 114.3, 73.5, 71.2, 55.6, 40.6, 26.9, 19.2; IR (neat, cm^{-1}): 2954, 1704, 1512, 1249, 703; ESI HRMS m/z $(M+Na)^+$ calcd 570.2435, obsd 570.2433.



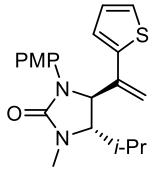
1-(4-Methoxyphenyl)-5-oxo-2-(1-phenylvinyl)pyrrolidin-3-yl pivalate (24). Yield = 78%, electricity = 3.1 F; Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.42–7.33 (m, 5H), 6.93–6.87 (m, 2H), 5.51 (s, 1H), 5.25 (d, *J* = 1.1 Hz, 1H), 5.08 (dt, *J* = 5.9, 1.1 Hz, 1H), 5.04 (s, 1H), 3.79 (s, 3H), 2.97 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.47 (dd, *J* = 18.0, 1.1 Hz, 1H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 171.9, 157.2, 143.5, 138.1, 131.4, 129.0, 128.8, 126.6, 123.2, 115.7, 114.4, 71.5, 69.7, 55.6, 38.9, 37.8, 27.1; IR (neat, cm^{-1}): 2970, 1732, 1706, 1181, 829；ESI HRMS m/z $(M+Na)^+$ calcd 416.1832, obsd 416.1833.



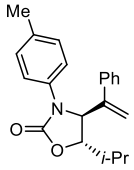
(2*R*,3*S*,4*S*)-1-(4-Methoxyphenyl)-4-methyl-5-oxo-2-(1-phenylvinyl)pyrrolidin-3-yl pivalate (25). Yield = 97%, electricity = 2.5 F; Light yellow oil; Isolated as a 8.3:1 mixture of diastereomers and and only the major isomer was shown. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53–7.48 (m, 2H), 7.37–7.28 (m, 5H), 6.92–6.87 (m, 2H), 5.46 (s, 1H), 5.21 (d, *J* = 1.2 Hz, 1H), 5.10 (dd, *J* = 2.9, 1.1 Hz, 1H), 4.87 (t, *J* = 2.9 Hz, 1H), 3.78 (s, 3H), 2.59 (qd, *J* = 7.6, 3.2 Hz, 1H), 1.38 (d, *J* = 7.7 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 174.7, 157.1, 144.8, 138.2, 131.2, 128.8, 128.6, 126.6, 123.5, 116.0, 114.2, 77.6, 67.3, 55.6, 45.6, 38.8, 27.1, 15.7; IR (neat, cm^{-1}): 2972, 1733, 1705, 1250，1147, 832; ESI HRMS m/z $(M+Na)^+$ calcd 430.1989, obsd 430.1986.



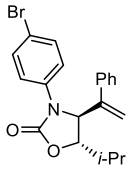
4-Isopropyl-1-(4-methoxyphenyl)-3-methyl-5-(1-phenylvinyl)imidazolidin-2-one (26). Yield = 77%, electricity = 3.6 F; Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.37–7.30 (m, 5H), 6.90–6.84 (m, 2H), 5.29 (s, 1H), 5.24 (s, 1H), 4.55 (d, *J* = 3.2, 0.8 Hz, 1H), 3.77 (s, 3H), 3.13 (t, *J* = 3.2 Hz, 1H), 2.82 (s, 3H), 2.02–1.93 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.73 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 155.6, 147.4, 138.9, 133.1, 128.7, 128.2, 127.6, 121.3, 116.0, 114.2, 65.8, 60.5, 55.6, 29.7, 29.4, 17.6, 15.9; IR (neat, cm^{-1}): 2959, 1700, 1513, 1246, 827; ESI HRMS m/z $(M+Na)^+$ calcd 373.1886, obsd 373.1886.



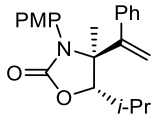
4-Isopropyl-1-(4-methoxyphenyl)-3-methyl-5-(1-(thiophen-2-yl)vinyl)imidazolidin-2-one (27). Yield = 54%, electricity = 3.1 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.25 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.11 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.86–6.80 (m, 2H), 5.49 (s, 1H), 5.19 (s, 1H), 4.52 (d, *J* = 4.1 Hz, 1H), 3.75 (s, 3H), 3.30 (dd, *J* = 4.2, 3.3 Hz, 1H), 2.88 (s, 3H), 2.13–2.05 (m, 1H), 0.96–0.92 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 156.0, 141.0, 140.4, 132.5, 127.5, 125.7, 124.9, 122.4, 115.9, 114.2, 65.5, 61.5, 55.6, 30.0, 29.9, 17.6, 16.4; IR (neat, cm^{-1}): 2959, 1701, 1509, 1242, 828; ESI HRMS m/z $(M+Na)^+$ calcd 379.1451, obsd 379.1452.



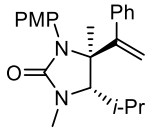
5-Isopropyl-4-(1-phenylvinyl)-3-(*p*-tolyl)oxazolidin-2-one (28). Yield = 77%, electricity = 4.8 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.39–7.29 (m, 5H), 7.18–7.13 (m, 2H), 5.40 (s, 1H), 5.30 (s, 1H), 4.87 (d, *J* = 3.8 Hz, 1H), 4.05 (dd, *J* = 5.4, 3.8 Hz, 1H), 2.31 (s, 3H), 1.96–1.86 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 145.8, 138.2, 135.1, 134.4, 129.8, 128.9, 128.6, 127.3, 120.4, 116.9, 83.4, 63.7, 32.8, 21.0, 17.8, 16.6; IR (neat, cm^{-1}): 2961, 1750, 1515, 1133, 752; ESI HRMS m/z $(M+Na)^+$ calcd 344.1621, obsd 344.1618.



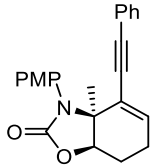
3-(4-Bromophenyl)-5-isopropyl-4-(1-phenylvinyl)oxazolidin-2-one (29). Yield = 71%, electricity = 7.6 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.42 (m, 4H), 7.40–7.34 (m, 3H), 7.31–7.27 (m, 2H), 5.42 (s, 1H), 5.27 (s, 1H), 4.86 (d, *J* = 3.6 Hz, 1H), 4.08 (dd, *J* = 5.4, 3.7 Hz, 1H), 1.97–1.86 (m, 1H), 0.94 (d, *J* = 2.8 Hz, 3H), 0.93 (d, *J* = 2.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 145.4, 137.7, 136.8, 132.2, 129.0, 128.8, 127.2, 121.5, 117.5, 116.9, 83.5, 63.3, 32.7, 17.8, 16.5; IR (neat, cm^{-1}): 2961, 1754, 1493, 1391, 826; ESI HRMS m/z $(M+Na)^+$ calcd 408.0570, obsd 408.0567.



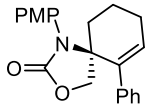
5-Isopropyl-3-(4-methoxyphenyl)-4-methyl-4-(1-phenylvinyl)oxazolidin-2-one (31). Yield = 74%, electricity = 3.3 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.44 (m, 2H), 7.40–7.34 (m, 3H), 7.31–7.24 (m, 2H), 6.90–6.84 (m, 2H), 5.48 (s, 1H), 5.37 (s, 1H), 4.22 (d, *J* = 9.5 Hz, 1H), 3.79 (s, 3H), 2.09–1.99 (m, 1H), 1.44 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 157.2, 149.8, 140.5, 129.1, 128.9, 128.8, 128.3, 128.2, 120.9, 114.2, 85.6, 68.2, 55.6, 28.9, 19.8, 18.6, 17.9; IR (neat, cm^{-1}): 2962, 1704, 1513, 1248, 828; ESI HRMS m/z $(M+Na)^+$ calcd 374.1727, obsd 374.1731.



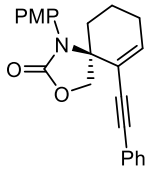
5-Isopropyl-3-(4-methoxyphenyl)-1,4-dimethyl-4-(1-phenylvinyl)imidazolidin-2-one (32). Yield = 66%, electricity = 3.3 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 5H), 7.27–7.24 (m, 2H), 6.89–6.84 (m, 2H), 5.36 (d, *J* = 0.9 Hz, 1H), 5.23 (d, *J* = 0.9 Hz, 1H), 3.79 (s, 3H), 3.30 (d, *J* = 2.3 Hz, 1H), 2.66 (s, 3H), 2.07–1.99 (m, 1H), 1.37 (s, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 157.2, 153.5, 140.8, 130.7, 128.8, 128.3, 127.7, 127.1, 116.7, 114.1, 69.5, 66.0, 55.6, 32.5, 29.3, 22.6, 18.2, 17.3; IR (neat, cm^{-1}): 2964, 1752, 1513, 1250, 830; ESI HRMS m/z $(M+Na)^+$ calcd 387.2043, obsd 387.2045.



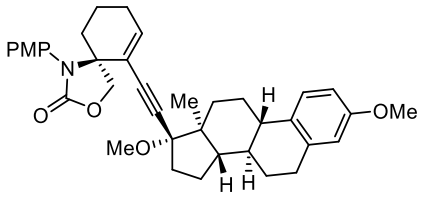
3-(4-Methoxyphenyl)-3a-methyl-4-(phenylethynyl)-3a,6,7,7a-tetrahydrobenzo[*d*]oxazol-2(3*H*)-one (33). Yield = 67%, electricity = 2.9 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.11 (m, 5H), 6.95–6.88 (m, 2H), 6.88–6.79 (m, 2H), 6.43 (dd, *J* = 6.3, 2.8 Hz, 1H), 4.67 (t, *J* = 3.4 Hz, 1H), 3.69 (s, 3H), 2.59–2.46 (m, 1H), 2.37–2.26 (m, 1H), 2.25–2.14 (m, 1H), 1.89–1.77 (m, 1H), 1.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 157.2, 137.5, 131.5, 131.4, 128.3, 128.2, 128.1, 123.3, 122.9, 114.2, 91.9, 87.7, 76.9, 61.8, 55.5, 24.9, 23.4, 20.6; IR (neat, cm^{-1}): 2931, 1752, 1513, 1247, 1057, 759; ESI HRMS m/z $(M+Na)^+$ calcd 382.1414, obsd 382.1415.



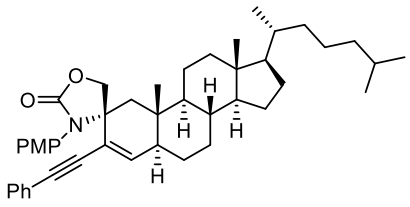
1-(4-Methoxyphenyl)-6-phenyl-3-oxa-1-azaspiro[4.5]dec-6-en-2-one (34). Yield = 48%, electricity = 5.2 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 7.08–7.01 (m, 2H), 6.84–6.78 (m, 2H), 6.14 (t, *J* = 4.0 Hz, 1H), 4.51 (d, *J* = 8.8 Hz, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 2.23–2.09 (m, 3H), 1.92–1.83 (m, 1H), 1.68–1.57 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 157.2, 140.2, 139.9, 133.7, 129.0, 128.9, 128.3, 127.9 (2s), 114.4, 74.4, 63.4, 55.6, 36.4, 25.6, 19.1; IR (neat, cm^{-1}): 2920, 1751, 1513, 1250, 832, 762; ESI HRMS m/z $(M+Na)^+$ calcd 358.1414, obsd 358.1415.



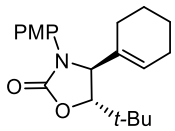
1-(4-Methoxyphenyl)-6-(phenylethynyl)-3-oxa-1-azaspiro[4.5]dec-6-en-2-one (35). Yield = 71%, electricity = 2.8 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.45 (m, 2H), 7.39–7.34 (m, 2H), 7.34–7.28 (m, 3H), 6.92–6.86 (m, 2H), 6.42 (t, *J* = 4.2 Hz, 1H), 4.57 (d, *J* = 8.5 Hz, 1H), 4.25 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 2.15–1.86 (m, 4H), 1.66–1.57 (m, 1H), 1.55–1.48 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 157.7, 140.1, 131.9, 130.1, 128.7, 128.6, 128.4, 124.5, 122.8, 114.7, 91.7, 86.8, 74.3, 64.2, 55.6, 33.5, 25.4, 19.1; IR (neat, cm^{-1}): 2928, 1753, 1513, 1250, 833, 757; ESI HRMS m/z $(M+Na)^+$ calcd 382.1414 obsd 382.1417.



6-(((8*R*,9*S*,13*S*,14*S*,17S)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)-1-(4-methoxyphenyl)-3-oxa-1-azaspiro[4.5]dec-6-en-2-one (36). Yield = 66%, electricity = 3.8 F; Light yellow oil; Isolated as a 1:1 mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.17 (dd, *J* = 8.6, 4.5 Hz, 1H), 6.91–6.81 (m, 2H), 6.69 (dt, *J* = 8.7, 2.7 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 6.38 (dt, *J* = 5.2, 2.8 Hz, 1H), 4.50 (dd, *J* = 8.5, 3.7 Hz, 1H), 4.22 (dd, *J* = 8.5, 4.7 Hz, 1H), 3.76 (2s, 3H), 3.75&3.68 (2s, 3H), 3.42&3.41 (2s, 3H), 2.89–2.72 (m, 2H), 2.36–2.22 (m, 2H), 2.19–1.88 (m, 6H), 1.88–1.65 (m, 5H), 1.60–1.21 (m, 6H), 0.88&0.87 (2s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 158.7, 157.5, 157.0, 140.0, 139.8, 138.2 (2s), 133.0, 132.9, 129.2, 128.8, 128.6 (2s), 126.5 (2s), 124.5, 124.3, 114.6, 114.5, 113.8 (2s), 111.6, 111.5, 92.6, 92.5, 86.5 (2s), 85.3, 85.3, 74.1, 73.9, 64.0, 63.9, 55.6, 55.5, 55.4, 53.7 (2s), 50.0 (2s), 48.1, 48.0, 43.5, 43.4, 39.3 (2s), 37.0, 36.9, 34.6, 34.4, 33.3 (2s), 29.9, 27.2, 26.7, 25.2 (2s), 22.9, 22.8, 19.1, 19.0, 13.0, 12.9; IR (neat, cm^{-1}): 3052, 2932, 1759, 1609, 1393, 831, 754; ESI HRMS m/z $(M+Na)^+$ calcd 604.3033, obsd 604,3034.

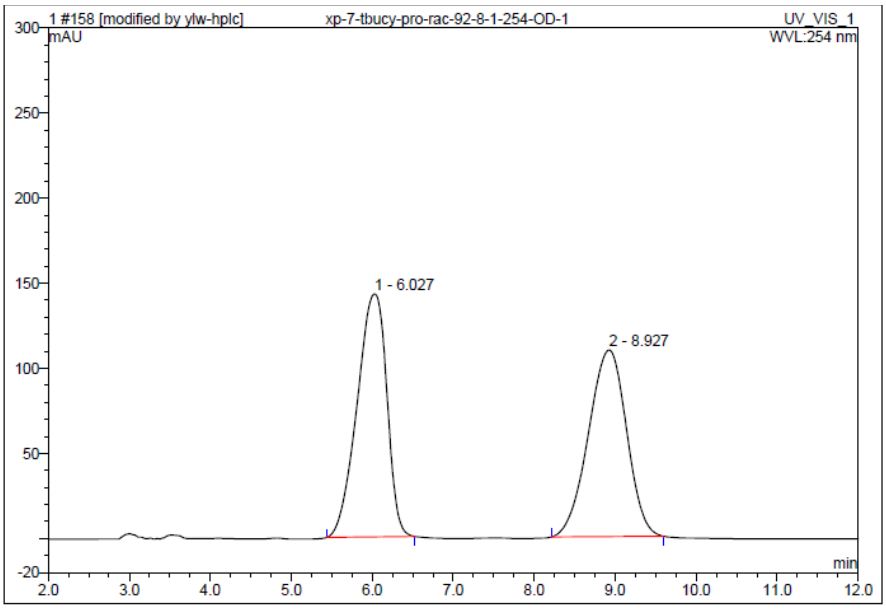


(2*R*,5*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3'-(4-Methoxyphenyl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(phenylethynyl)-1,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydrospiro[cyclopenta[*a*]-phenanthrene-2,4'-oxazolidin]-2'-one (37). The stereochemistry of the newly formed stereogenic center was assigned using a NOESY experiment (see page S85). Yield = 70%, electricity = 4.1 F; Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.45 (m, 2H), 7.37–7.27 (m, 5H), 6.93–6.87 (m, 2H), 6.05 (d, *J* = 2.2 Hz, 1H), 4.65 (d, *J* = 8.7 Hz, 1H), 4.35 (d, *J* = 8.7 Hz, 1H), 3.79 (s, 3H), 2.11 (d, *J* = 13.5 Hz, 1H), 1.98 (dt, *J* = 12.6, 3.3 Hz, 1H), 1.86–1.75 (m, 1H), 1.73–1.62 (m, 3H), 1.56–1.44 (m, 4H), 1.40–1.24 (m, 8H), 1.17–0.95 (m, 8H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.1 Hz, 3H), 0.85 (d, *J* = 2.1 Hz, 3H), 0.83 (s, 3H), 0.73–0.61 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 157.4, 143.8, 131.9, 130.2, 128.6, 128.5, 128.0, 122.9, 122.7, 114.7, 91.7, 86.4, 76.2, 65.6, 56.4, 56.3, 55.6, 52.6, 46.6, 45.8, 42.8, 39.9, 39.7, 37.7, 36.3, 35.9, 34.8, 31.6, 28.3, 28.2, 26.6, 24.2, 24.0, 23.0, 22.7, 21.3, 18.8, 13.8, 12.3; IR (neat, cm^{-1}): 3055, 1759, 1608, 1572, 831, 691; ESI HRMS m/z $(M+Na)^+$ calcd 670.4231, obsd 670.4231.

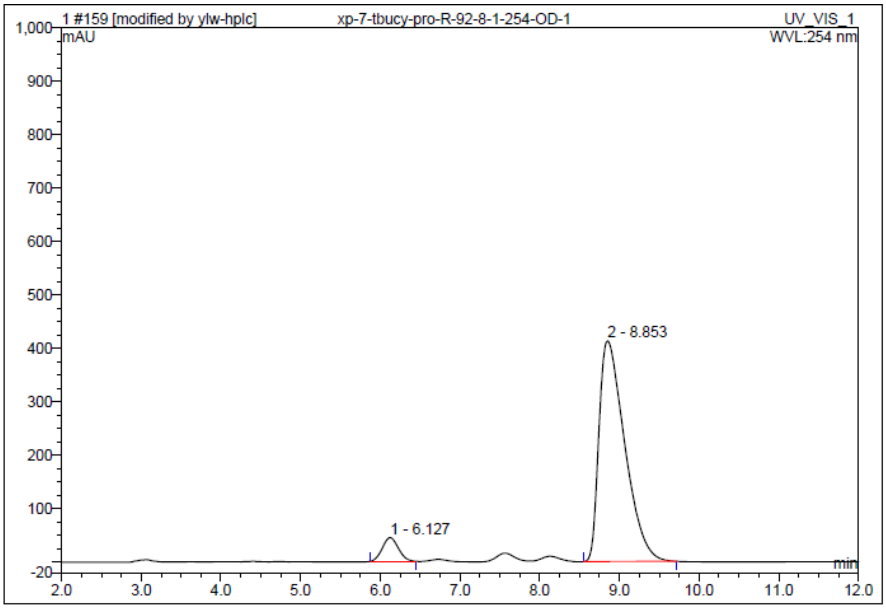


5-(*tert*-Butyl)-4-(cyclohex-1-en-1-yl)-3-(4-methoxyphenyl)oxazolidin-2-one (39). Yield = 76%, electricity = 2.7 F; Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 6.90–6.83 (m, 2H), 5.74–5.69 (m, 1H), 4.35 (d, *J* = 4.2 Hz, 1H), 3.90 (d, *J* = 4.2 Hz, 1H), 3.79 (s, 3H), 2.05–1.93 (m, 3H), 1.92–1.84 (m, 1H), 1.64–1.47 (m, 4H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 156.1, 135.7, 130.6, 127.8, 123.1, 114.3, 85.1, 64.9, 55.6, 35.0, 25.2, 24.7, 22.9, 22.4, 22.3; IR (neat, cm^{-1}): 2930, 1751, 1514, 1398, 1248, 829; ESI HRMS m/z $(M+Na)^+$ calcd 358.1883, obsd 352.1886.

(4*S*,5*R*)-4-(*tert*-Butyl)-5-(cyclohex-1-en-1-yl)-1-(4-methoxyphenyl)pyrrolidin-2-one [(−)-39]. Synthesized from **(+)-38** (99:1 e.r.) in 72% yield as a colorless solid. $[\alpha]_D^{20}$ = −15.0° (*c* 1.0, $CHCl_3$), 94:6 e.r. (determined by HPLC: Chiralcel OD-H column, 2/98 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; retention time = 6.13 min (minor), 8.85 min (major). The spectral data (NMR, IR, MS) were the same with those of *rac*-**39**.

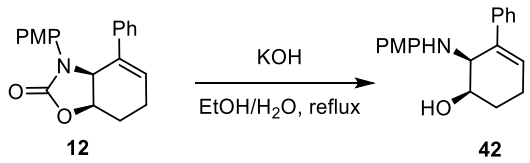


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	6.03	n.a.	142.691	60.653	50.32	n.a.	BMB*
2	8.93	n.a.	109.562	59.879	49.68	n.a.	BMB*
Total:			252.254	120.532	100.00	0.000	



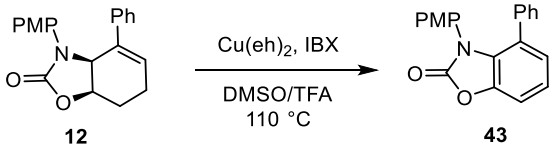
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	6.13	n.a.	44.180	10.302	6.25	n.a.	BMB*
2	8.85	n.a.	412.907	154.635	93.75	n.a.	BMB*
Total:			457.087	164.937	100.00	0.000	

4. Transformations of Products



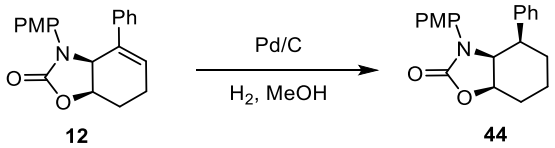
12 42

2-((4-Methoxyphenyl)amino)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-3-ol (42). **12** (0.2 g, 0.62 mmol) was treated with KOH (0.7 g, 12 mmol) in EtOH (20 mL) and H_2O (20 mL) under reflux for 12 h. The reaction mixture was cooled to RT. EtOH was removed under reduced pressure. The leftover aqueous solution was extracted three times with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **42** as a colorless solid (0.15 g, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.15 (m, 5H), 6.76–6.70 (m, 2H), 6.69–6.63 (m, 2H), 6.18 (t, *J* = 4.1 Hz, 1H), 4.42–4.33 (m, 1H), 4.08–3.98 (m, 1H), 3.74 (s, 3H), 3.22 (brs, 1H), 2.67 (d, *J* = 8.5 Hz, 1H), 2.48–2.36 (m, 1H), 1.95–1.86 (m, 1H), 1.83–1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 143.0, 139.5, 137.4, 128.5, 127.9, 127.4, 126.2, 115.9, 114.9, 69.1, 57.2, 55.9, 26.7, 24.4; IR (neat, cm^{-1}): 3385, 2926, 1510, 1240, 821, 753; ESI HRMS m/z $(M+Na)^+$ calcd 318.1465, obsd 318.1462.

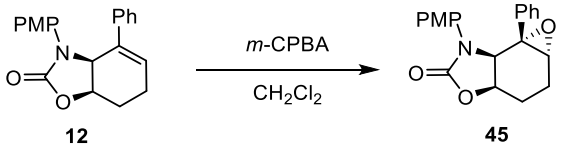


12 43

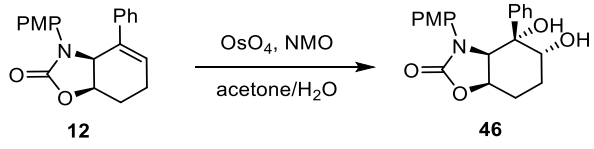
3-(4-Methoxyphenyl)-4-phenylbenzo[*d*]oxazol-2(3*H*)-one (43). The title compound was prepared according to an unpublished procedure of our group. **12** (0.040 g, 0.12 mmol, 1.0 equiv), copper bis(2-ethylhexanoate) (13 mg, 0.04 mmol, 0.3 equiv), and IBX (0.34 g, 1.2 mmol, 10 equiv) were placed in a 10-mL round bottom flask. The flask was flushed with argon. DMSO (1.5 mL) and TFA (1.5 mL) were added. The resulting mixture was heated in an oil bath setting at 110 °C for 8 h. The reaction mixture was cooled to RT. Saturated $NaHCO_3$ (20 mL) and ethyl acetate (20 mL) were added. The phases were separated and the aqueous phase was extracted with ethyl acetate (2 x 20 mL). The combined organic solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **43** as a colorless solid (0.025 g, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.14–7.07 (m, 2H), 7.04–6.98 (m, 2H), 6.94–6.90 (m, 2H), 6.90–6.85 (m, 2H), 6.60–6.55 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 154.5, 143.5, 135.8, 129.1, 128.4, 128.0, 127.6, 127.2, 126.7, 126.6, 126.3, 122.7, 114.1, 109.2, 55.7; IR (neat, cm^{-1}): 2921, 1777, 1514, 1256, 829, 757; ESI HRMS m/z $(M+Na)^+$ calcd 340.0944, obsd 340.0946.



3-(4-Methoxyphenyl)-4-phenylhexahydrobenzo[d]oxazol-2(3H)-one (44). **12** (0.050 g, 0.16 mmol, 1.0 equiv) was dissolved in MeOH (5 mL) under argon atmosphere. 10% Pd/C (0.017 g, 0.016 mmol, 0.1 equiv) was added. The reaction mixture was then stirred for 3 h under hydrogen atmosphere (balloon). The reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **44** as a colorless solid (0.047 g, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00–6.89 (m, 3H), 6.88–6.80 (m, 2H), 6.76–6.69 (m, 2H), 6.52–6.40 (m, 2H), 4.97–4.90 (m, 1H), 4.84–4.75 (m, 1H), 3.68 (s, 3H), 3.07 (dt, *J* = 12.8, 3.5 Hz, 1H), 2.18–1.92 (m, 4H), 1.88–1.77 (m, 1H), 1.73–1.60 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 157.3, 140.3, 130.6, 128.0, 127.8, 126.3, 126.0, 113.9, 74.3, 61.1, 55.6, 42.0, 25.4, 21.2, 18.0; IR (neat, cm^{-1}): 2920, 1749, 1513, 750; ESI HRMS m/z $(M+Na)^+$ calcd 346.1414, obsd 346.1412.

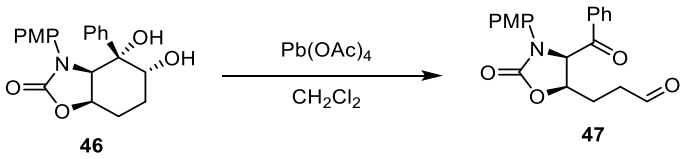


1-(4-Methoxyphenyl)-6a-phenylhexahydrooxireno[2',3':5,6]benzo[1,2-*d*]oxazol-2(1*H*)-one (45). To a solution of **12** (0.040 g, 0.12 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) at 0 °C was added *m*-CPBA (0.043 g, 0.5 mmol, 4.0 equiv). The reaction mixture was warmed to RT and stirred for 8 h. Saturated aqueous $NaHCO_3$ (20 mL) and ethyl acetate (20 mL) were added and the layers were separated. The aqueous phase was extracted twice with ethyl acetate. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **45** as a colorless solid (0.035 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16–7.09 (m, 2H), 7.06–6.96 (m, 3H), 6.86–6.80 (m, 2H), 6.54–6.47 (m, 2H), 4.83–4.79 (m, 1H), 4.75 (dd, *J* = 6.9, 1.3 Hz, 1H), 3.67 (s, 3H), 3.51–3.48 (m, 1H), 2.45–2.37 (m, 1H), 2.21 (dq, *J* = 15.2, 3.6 Hz, 1H), 2.08–1.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 156.1, 136.9, 130.6, 128.5, 128.5, 128.1, 124.2, 113.7, 72.5, 60.4, 59.2, 57.7, 55.6, 18.8, 18.3; IR (neat, cm^{-1}): 2925, 1743, 1248, 824, 759; ESI HRMS m/z $(M+Na)^+$ calcd 360.1206, obsd 360.1201.



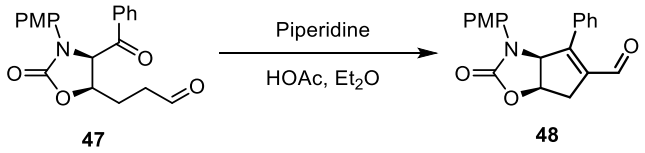
4,5-Dihydroxy-3-(4-methoxyphenyl)-4-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (46). To a solution of **12** (0.32 g, 1.0 mmol, 1.0 equiv) in acetone (30 mL) and H_2O (3 mL) at 0 °C was added

OsO_4 (0.2 M in *t*-BuOH, 0.25 mL, 0.05 equiv), followed by NMO (0.12 g, 1.1 mmol, 1.1 equiv). The reaction mixture was warmed to RT and stirred for 12 h. Saturated aqueous $Na_2S_2O_3$ (40 mL) and ethyl acetate (40 mL) were added and the layers were separated. The aqueous Phase was extracted twice with ethyl acetate. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **46** as a colorless solid (0.30 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.16 (m, 2H), 7.04–6.98 (m, 3H), 6.71–6.63 (m, 2H), 6.48–6.42 (m, 2H), 4.97–4.91 (m, 1H), 4.59–4.52 (m, 2H), 3.67 (s, 3H), 2.94 (s, 1H), 2.49–2.39 (m, 1H), 2.24–2.14 (m, 1H), 2.09–1.95 (m, 2H), 1.88–1.77 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 157.0, 140.3, 130.3, 128.5, 127.9, 127.0, 125.2, 113.8, 76.6, 74.1, 67.5, 64.7, 55.6, 24.2, 23.9； IR (neat, cm^{-1}): 3365, 2920, 1753, 1514, 1247, 830; ESI HRMS m/z $(M+Na)^+$ calcd 378.1312 obsd 378.1311.



46 **47**

3-(4-Benzoyl-3-(4-methoxyphenyl)-2-oxooxazolidin-5-yl)propanal (47). To a solution of **46** (0.25 g, 0.70 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL), was added $Pb(OAc)_4$ (0.38 g, 0.86 mmol, 1.2 equiv). The reaction mixture was stirred for 8 h at RT and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **47** as a colorless solid (0.22 g, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.99–7.93 (m, 2H), 7.70–7.64 (m, 1H), 7.58–7.51 (m, 2H), 7.34–7.29 (m, 2H), 6.86–6.80 (m, 2H), 5.93 (d, *J* = 8.8 Hz, 1H), 5.03 (ddd, *J* = 11.4, 8.8, 2.5 Hz, 1H), 3.74 (s, 3H), 2.79–2.62 (m, 2H), 1.87–1.77 (m, 1H), 1.73–1.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 193.7, 157.4, 155.6, 135.5, 134.9, 130.3, 129.6, 128.4, 123.5, 114.6, 74.0, 63.8, 55.6, 39.6, 23.8; IR (neat, cm^{-1}): 2919, 1754, 1688, 1514, 1077, 831; ESI HRMS m/z $(M+Na)^+$ calcd 376.1155, obsd 376.1152.



47 **48**

3-(4-Methoxyphenyl)-2-oxo-4-phenyl-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*d*]oxazole-5-carbaldehyde (48). The title compound was prepared by following a reported procedure.[2] To a solution of **47** (0.040 g, 0.11 mmol, 1.0 equiv) in Et_2O (5 mL), was added piperidine (0.030 g, 0.33 mmol, 3 equiv). The reaction mixture was stirred for 15 min at RT before the addition of HOAc (0.04 mL, 0.66 mmol, 6 equiv). The reaction mixture was heated for 6 h at 40 °C and then concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **48** as a colorless solid (0.32 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.25–7.20 (m, 1H), 7.19–7.12 (m, 2H), 7.10–7.04 (m, 2H), 6.91–6.84 (m, 2H), 6.61–6.55 (m, 2H), 5.72 (d, *J* = 7.3 Hz, 1H), 5.39–5.32 (m, 1H), 3.69 (s, 3H), 3.24 (d, *J* = 18.6

Hz, 1H), 3.12 (dd, *J* = 18.6, 6.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 158.0, 155.8, 155.7, 138.2, 131.3, 129.7, 129.5, 129.3, 128.5, 126.6, 114.2, 74.9, 71.3, 55.6, 37.2; IR (neat, cm^{-1}): 2920, 1749, 1670, 1514, 1248, 832; ESI HRMS m/z $(M+Na)^+$ calcd 358.1050, obsd 358.1051.

5. X-ray Crystallography

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **31** (cyclohexane/CH_2Cl_2) in a loosely capped vial.

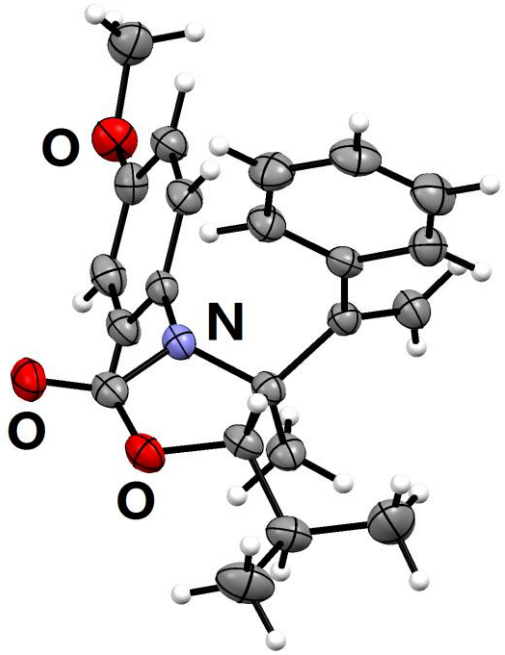


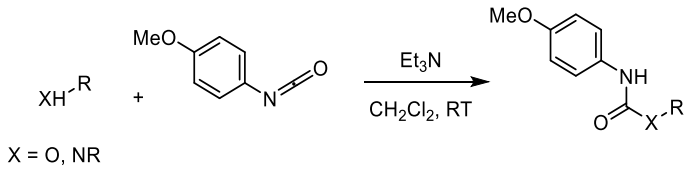
Table S1. Crystal Data and Structure Refinement for 31

Empirical formula	$C_{22}H_{25}NO_3$
Formula weight	351.43
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.193(2)
b/Å	7.1614(13)

c/Å	23.653(4)
α/°	90
β/°	98.978(3)
γ/°	90
Volume/Å^3	1872.6(6)
Z	4
ρ_{calc}g/cm^3	1.247
μ/mm^{-1}	0.082
F(000)	752.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.486 to 57.726
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 9, -31 ≤ l ≤ 30
Reflections collected	15915
Independent reflections	4546 [R_{int} = 0.0261, R_{sigma} = 0.0258]
Data/restraints/parameters	4546/0/247
Goodness-of-fit on F^2	0.941
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1246
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1305
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22

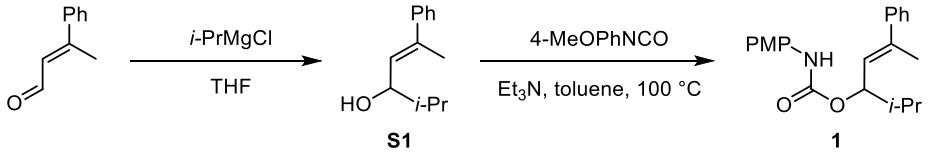
6. Synthesis and Characterization of Substrates

6.1 General Procedure II: Synthesis of Carbamates and Ureas



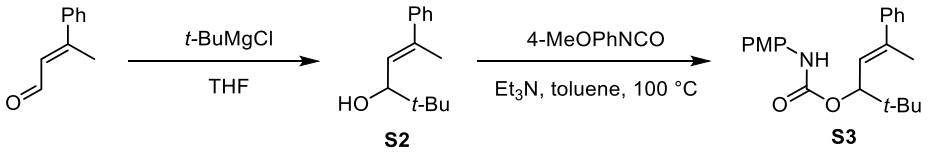
To a solution of the alcohol or amine (1 equiv) in toluene (0.1 M) was added 4-methoxyphenyl isocyanate (1.2 equiv) at RT, followed by Et_3N (2 equiv). The resulting reaction mixture was stirred at 100 °C until complete consumption of the starting material (monitored by TLC). The solvent was removed under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

6.2 Synthesis and Characterization Data for New Substrates



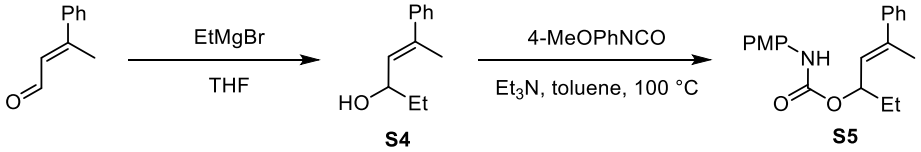
(*E*)-2-methyl-5-phenylhex-4-en-3-ol (S1). To a solution of (*E*)-3-phenylbut-2-enal[3] (3.0 g, 22.7 mmol, 1.0 equiv) in THF (30 mL) at −20 °C was added *i*-PrMgCl (2.0 M in THF, 14 mL, 1.2 equiv) dropwise over 10 min. Upon complete addition, the reaction mixture was stirred for 30 min at −20 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 min. Saturated aqueous NH_4Cl (30 mL) was added to quench the reaction. The resulting mixture was extracted with EtOAc (2 x 50 mL). The combined organic solution was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **S1** as a light yellow oil (2.8 g, 64% yield). The crude product was used in the following step without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.29–7.23 (m, 2H), 7.22–7.15 (m, 1H), 5.71 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.19 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.04 (d, *J* = 1.4 Hz, 3H), 1.80–1.69 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

(*E*)-2-Methyl-5-phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate (1). The title compound was obtained as a colorless solid in 90% yield (2.9 g) starting from **S1** (1.8 g, 9.5 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.34–7.25 (m, 5H), 6.87–6.82 (m, 2H), 6.49 (s, 1H), 5.71 (dq, *J* = 9.5, 1.4 Hz, 1H), 5.49–5.40 (m, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 2.04–1.95 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.7, 153.5, 142.2, 138.6, 132.3, 128.4, 127.5, 125.7, 125.3, 119.7, 113.9, 75.5, 55.2, 32.5, 18.3, 18.0, 16.4; IR (neat, cm^{-1}): 3329, 2961, 1699, 1221, 1031, 828, 759; ESI HRMS m/z $(M+Na)^+$ calcd 362.1727 obsd 362.1727.



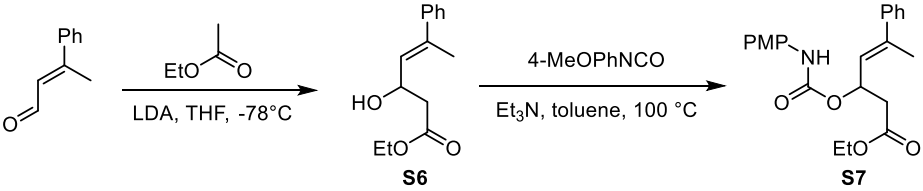
(*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-ol (S2). The title compound was obtained as a light yellow oil (1.2 g, 85% yield) starting from (*E*)-3-phenylbut-2-enal (1.5 g, 10 mmol, 1.0 equiv) and *t*-BuMgCl (1.0 M in THF, 20 mL, 2.0 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S2**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.38 (m, 2H), 7.35–7.30 (m, 2H), 7.28–7.24 (m, 1H), 5.82 (dq, *J* = 9.2, 1.4 Hz, 1H), 4.20 (d, *J* = 9.3 Hz, 1H), 2.11 (d, *J* = 1.3 Hz, 3H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 138.5, 128.4, 128.1, 127.4, 126.1, 76.4, 36.1, 25.8, 16.9; IR (neat, cm^{-1}): 3442, 2954, 1445, 994, 760, 697; ESI HRMS m/z $(M+Na)^+$ calcd 227.1406, obsd 227.1410.

(*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S3). The title compound was obtained as a colorless solid in 61% yield (0.41 g) starting from **S2** (0.4 g, 1.9 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.34–7.29 (m, 3H), 7.27–7.23 (m, 2H), 6.87–6.79 (m, 2H), 6.49 (s, 1H), 5.74 (dq, *J* = 10.0, 1.4 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 2.20 (d, *J* = 1.4 Hz, 3H), 1.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 153.9, 143.5, 140.3, 131.3, 128.4, 127.5, 126.2, 124.1, 120.7, 114.4, 79.0, 55.7, 35.8, 26.0, 17.1; IR (neat, cm^{-1}): 3425, 2954, 1699, 1226, 1029, 838; ESI HRMS m/z $(M+Na)^+$ calcd 376.1883, obsd 376.1882.



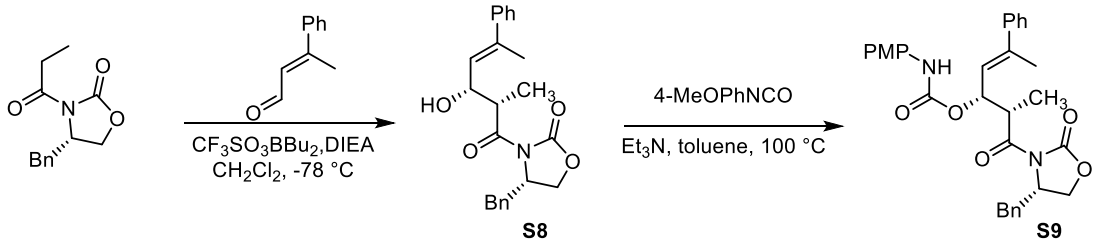
(*E*)-5-Phenylhex-4-en-3-ol (S4). The title compound was obtained as a light yellow oil starting from (*E*)-3-phenylbut-2-enal (1.0 g, 7.0 mmol, 1.0 equiv) and EtMgBr (3.0 M in THF, 3.8 mL, 1.6 equiv) by following the procedure described for the synthesis of **S1**. The crude product was used in the following step without purification.

(*E*)-5-Phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S5) The title compound (1.3 g, 58% yield over two steps) was obtained as a colorless solid starting from **S4** (7.0 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.36 (m, 2H), 7.35–7.19 (m, 5H), 6.88–6.76 (m, 2H), 6.55 (s, 1H), 5.72–5.67 (m, 1H), 5.63–5.55 (m, 1H), 3.76 (s, 3H), 2.17 (s, 3H), 1.88–1.78 (m, 1H), 1.73–1.64 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 153.8, 143.0, 139.2, 131.3, 128.4, 127.5, 126.5, 126.1, 120.7, 114.4, 73.9, 55.6, 28.4, 16.8, 9.7; IR (neat, cm^{-1}): 3328, 2932, 1700, 1214, 827, 757; ESI HRMS m/z $(M+Na)^+$ calcd 348.1570, obsd 348.1570.



Ethyl (*E*)-3-hydroxy-5-phenylhex-4-enoate (S6). To a solution of ethyl acetate (1.2 mL, 12 mmol, 1.0 equiv) in THF (30 mL) at −78 °C was added LDA (2 M in THF, 6.6 mL, 1.1 equiv) dropwise over 30 min. Upon complete addition, the reaction mixture was stirred for 30 min at −78 °C. (*E*)-3-phenylbut-2-enal (1.7 g, 12 mmol, 1.0 equiv) was added dropwise over 10 min. After being stirred for 1 h at −78 °C, the reaction mixture was treated with saturated aqueous NH_4Cl (30 mL), warmed to ambient temperature, and extracted with EtOAc (3 x 50 mL). The combined organic solution was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S6** as a light yellow oil (1.7 g, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.35–7.29 (m, 2H), 7.28–7.23 (m, 1H), 5.78 (dq, *J* = 8.5, 1.4 Hz, 1H), 4.97 (tt, *J* = 8.5, 3.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.96 (d, *J* = 3.7 Hz, 1H), 2.64 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.58 (dd, *J* = 16.2, 4.1 Hz, 1H), 2.12 (d, *J* = 1.4 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 142.8, 138.1, 128.5, 128.4, 127.6, 126.0, 65.8, 61.0, 41.7, 16.6, 14.4; IR (neat, cm^{-1}): 3443, 2982, 1736, 1025, 759, 697; ESI HRMS m/z $(M+Na)^+$ calcd 257.1148 obsd 257.1147.

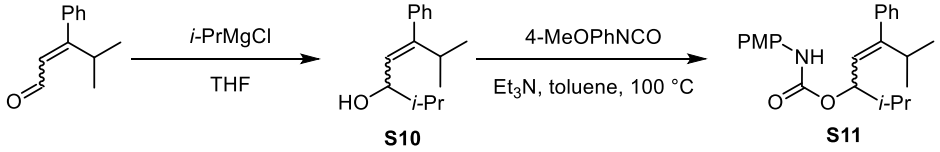
Ethyl (*E*)-3-(((4-methoxyphenyl)carbamoyl)oxy)-5-phenylhex-4-enoate (S7). The title compound was obtained as a light yellow oil in 92% yield (0.60 g) starting from **S6** (1.7 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.35 (m, 2H), 7.35–7.21 (m, 5H), 6.87–6.79 (m, 2H), 6.65–6.50 (m, 1H), 6.09–6.01 (m, 1H), 5.73 (dq, *J* = 9.2, 1.4 Hz, 1H), 4.21–4.10 (m, 2H), 3.76 (s, 3H), 2.84 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.68 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.22 (d, *J* = 1.4 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 156.1, 153.1, 142.7, 140.3, 131.0, 128.4, 127.8, 126.1, 124.9, 120.7, 114.4, 69.0, 60.9, 55.6, 40.5, 16.8, 14.4; IR (neat, cm^{-1}): 3342, 2981, 1734, 1271, 1030; ESI HRMS m/z $(M+Na)^+$ calcd 406.1625, obsd 406.1624.



(*S*)-4-Benzyl-3-((2*S*,3*R*,*E*)-3-hydroxy-2-methyl-5-phenylhex-4-enoyl)oxazolidin-2-one (S8). To a solution of (4*S*)-4-benzyl-3-propanoyl-1,3-oxazolidin-2-one (1.4 g, 6.2 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) at 0 °C was added dibutylboron triflate (1 M in CH_2Cl_2, 6.2 mL, 1.0 equiv) dropwise. Upon complete addition, the reaction mixture was stirred for 15 min at 0 °C and DIEA (1 mL, 6.2 mmol, 1.0 equiv) was added slowly. After being stirred for 30 min at 0 °C, the reaction mixture was cooled to −78 °C. A solution of (*E*)-3-phenylbut-2-enal (1.0 g, 6.8 mmol, 1.1 equiv) in CH_2Cl_2 (20 mL) was added dropwise over 20 min. The resulting mixture was warmed to ambient temperature and stirred for 12 h. The reaction was quenched with 10 mL of pH 7 buffer solution (Na_2PO_4/NaH_2PO_4), followed by hydrogen peroxide (4 mL) and methanol (8 mL). The resulting solution was stirred for 2 h and then concentrated. The residue was diluted with dichloromethane

and washed with saturated $NaHCO_3$ and then brine. The organic phase was dried over $MgSO_4$ and concentrated to afford crude product **S8** as a light yellow oil (1.4 g, 59% yield), which was used in the following step without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2H), 7.36–7.23 (m, 6H), 7.22–7.17 (m, 2H), 5.85 (dq, *J* = 8.4, 1.4 Hz, 1H), 4.91–4.82 (m, 1H), 4.73–4.62 (m, 1H), 4.20–4.12 (m, 2H), 4.06–3.99 (m, 1H), 3.25 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.84–2.69 (m, 2H), 2.11 (d, *J* = 1.4 Hz, 3H), 1.36 (d, *J* = 7.0 Hz, 3H).

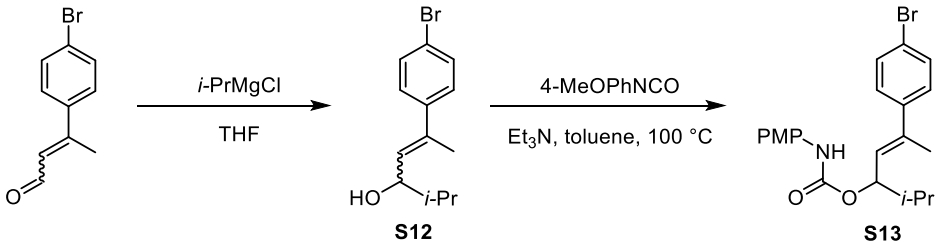
(*2S,3R,E*)-1-((*S*)-4-Benzyl-2-oxooxazolidin-3-yl)-2-methyl-1-oxo-5-phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S9). The title compound was obtained as a light yellow oil in 65% yield (0.36 g) starting from **S8** (0.4 g, 1.0 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.35–7.22 (m, 8H), 7.21–7.15 (m, 2H), 6.86–6.79 (m, 2H), 6.56 (s, 1H), 6.01 (dd, *J* = 9.1, 6.3 Hz, 1H), 5.78 (dq, *J* = 9.1, 1.4 Hz, 1H), 4.59–4.52 (m, 1H), 4.30–4.22 (m, 1H), 4.12 (d, *J* = 5.0 Hz, 2H), 3.77 (s, 3H), 3.25 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.78 (dd, *J* = 13.4, 9.6 Hz, 1H), 2.22 (d, *J* = 1.4 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 156.2, 153.6, 153.4, 142.8, 140.7, 135.4, 131.0, 129.6, 129.1, 128.5, 127.8, 127.5, 126.1, 123.6, 120.9, 114.4, 72.7, 66.4, 55.9, 55.7, 42.5, 38.1, 16.9, 12.6; IR (neat, cm^{-1}): 3346, 2934, 1779, 1701, 1213, 829; ESI HRMS m/z $(M+Na)^+$ calcd 551.2153, obsd 551.2154.



2,6-Dimethyl-5-phenylhept-4-en-3-ol (S10). The title compound was obtained as a light yellow oil (0.46 g, 46% yield) starting from 4-methyl-3-phenylpent-2-enal[4] (0.8 g, 4.6 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.8 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S10** (*E*/*Z* = 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.23 (m, 3H), 7.18–7.14 (m, 0.5H), 7.10–7.05 (m, 1.5H), 5.46 (dd, *J* = 9.5, 1.1 Hz, 0.75H), 5.27 (d, *J* = 9.3 Hz, 0.25H), 4.29 (dd, *J* = 9.2, 6.8 Hz, 0.25H), 3.60 (dd, *J* = 9.5, 6.9 Hz, 0.75H), 3.17–3.06 (m, 0.25H), 2.61–2.50 (m, 0.75H), 1.78–1.71 (m, 0.25H), 1.69–1.59 (m, 0.75H), 1.06 (d, *J* = 6.9 Hz, 0.75H), 1.05–1.00 (m, 6H), 0.94 (d, *J* = 6.9 Hz, 0.75H), 0.86 (d, *J* = 6.7 Hz, 2.25H), 0.82 (d, *J* = 6.9 Hz, 2.25H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 150.3, 142.5, 140.6, 130.1, 128.9, 128.8, 128.0, 127.7, 126.8, 126.7, 125.9, 74.2, 72.9, 36.4, 34.7, 34.4, 29.8, 22.3, 22.0, 21.9, 21.6, 18.6, 18.5 (2s); IR (neat, cm^{-1}): 3374, 2960, 1441, 1011, 703; ESI HRMS m/z $(M+Na)^+$ calcd 241.1563, obsd 241.1561.

2,6-Dimethyl-5-phenylhept-4-en-3-yl (4-methoxyphenyl)carbamate (S11). The title compound (*E*/*Z* = 7:3) was obtained as a light yellow oil in 71% yield (0.48 g) starting from **S10** (0.4 g, 1.8 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.23 (m, 5H), 7.18–7.12 (m, 2H), 6.87–6.81 (m, 2H), 6.49 (s, 0.3H), 6.39 (s, 0.7H), 5.52 (dd, *J* = 9.5, 6.8 Hz, 0.3H), 5.41 (dd, *J* = 9.2, 1.2 Hz, 0.7H), 5.20 (d, *J* = 9.5 Hz, 0.3H), 4.92 (dd, *J* = 9.2, 6.0 Hz, 0.7H), 3.79–3.75 (m, 3H), 3.31–3.19 (m, 0.3H), 2.61–2.51 (m, 0.7H), 1.99–1.88 (m, 0.3H), 1.88–1.76 (m,

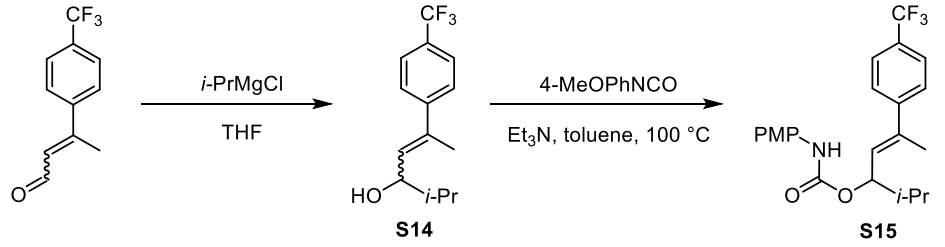
0.7H), 1.10–0.96 (m, 8H), 0.86–0.78 (m, 4H); ^{13}C NMR (126 MHz, CDCl3) δ 156.0, 155.9, 152.0, 151.7, 142.2, 140.2, 131.5, 128.9 (2s), 127.9, 127.6, 126.9, 126.8, 125.7, 121.7, 120.6, 114.4 (2s), 55.7, 36.6, 33.1, 33.0, 29.9, 22.0, 21.8, 21.5, 18.5, 18.4, 18.3, 18.2; IR (neat, cm^{-1}): 3338, 2961, 1701, 1219, 1032; ESI HRMS m/z (M+Na)$^+$ calcd 390.2040, obsd 390.2042.



S12 S13

5-(4-Bromophenyl)-2-methylhex-4-en-3-ol (S12). The title compound was obtained as a light yellow oil (0.67 g, 56% yield) starting from 3-(4-bromophenyl)but-2-enal[5] (0.98 g, 4.5 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.7 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S12** (*E*/*Z* = 13:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.30–7.24 (m, 2H), 5.76 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.24 (dd, *J* = 8.9, 6.6 Hz, 1H), 2.07 (d, *J* = 1.4 Hz, 3H), 1.85–1.75 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 136.9, 131.5, 130.1, 127.7, 121.3, 74.1, 34.8, 18.4, 18.4, 16.6; IR (neat, cm^{-1}): 3375, 2957, 1486, 1077, 820; ESI HRMS m/z (M+Na)$^+$ calcd 291.0355, obsd 291.0355.

(*E*)-5-(4-Bromophenyl)-2-methylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S13). The title compound was obtained as a colorless solid in 86% yield (0.75 g) starting from **S12** (0.56 g, 2.1 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.33–7.23 (m, 4H), 6.87–6.79 (m, 2H), 6.53 (s, 1H), 5.69 (dq, *J* = 9.4, 1.3 Hz, 1H), 5.41 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.77 (s, 3H), 2.15 (d, *J* = 1.4 Hz, 3H), 2.02–1.94 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 153.8, 142.1, 138.7, 131.4, 131.2, 127.8, 125.8, 121.4, 120.7, 114.4, 76.9, 55.7, 33.1, 18.5, 18.2, 16.9; IR (neat, cm^{-1}): 3375, 2957, 1486, 1077, 820; ESI HRMS m/z (M+Na)$^+$ calcd 440.0832, obsd 440.0833.

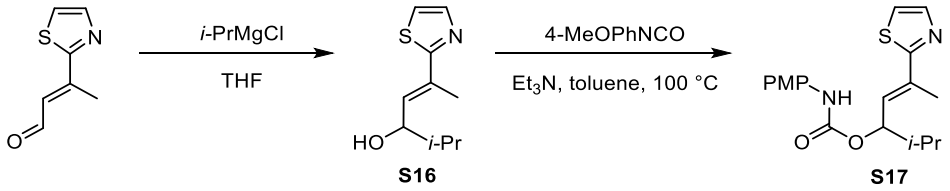


S14 S15

2-Methyl-5-(4-(trifluoromethyl)phenyl)hex-4-en-3-ol (S14). The title compound was obtained as a light yellow oil (0.48 g, 40% yield) starting from 3-(4-bromophenyl)but-2-enal[4] (1.0 g, 4.6 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.8 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl

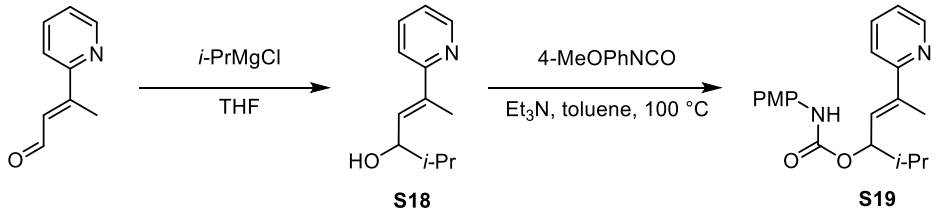
acetate/hexanes to give **S14** (*E*/*Z* = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.55 (m, 2H), 7.52–7.47 (m, 2H), 5.83 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.27 (dd, *J* = 8.9, 6.6 Hz, 1H), 2.11 (d, *J* = 1.4 Hz, 3H), 1.87–1.78 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 136.8, 131.5, 129.4 (q, $J_{C\text{-}F}$ = 32.4 Hz), 126.3, 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 271.7), 121.2, 74.0, 34.8, 18.4, 18.4, 16.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.5; IR (neat, cm^{-1}): 3376, 2961, 1327, 1126, 839; ESI HRMS m/z $(M+Na)^+$ calcd 281.1124, obsd 281.1124.

2-Methyl-5-(4-(trifluoromethyl)phenyl)hex-4-en-3-yl (4-methoxyphenyl)carbamate (S15). The title compound was obtained as a light yellow oil in 93% yield (0.59 g) starting from **S14** (0.4 g, 1.5 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.54 (m, 2H), 7.52–7.46 (m, 2H), 7.33–7.26 (m, 2H), 6.87–6.80 (m, 2H), 6.52 (s, 1H), 5.75 (dq, *J* = 9.3, 1.4 Hz, 1H), 5.43 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.77 (s, 3H), 2.20 (d, *J* = 1.4 Hz, 3H), 2.04–1.95 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 153.8, 146.8, 138.7, 131.2, 129.5 (q, $J_{C\text{-}F}$ = 32.4 Hz), 127.3, 126.4, 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.8, 114.4, 76.8, 55.7, 33.1, 18.5, 18.2, 16.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.5; IR (neat, cm^{-1}): 3328, 2962, 1701, 1326, 829; ESI HRMS m/z $(M+Na)^+$ calcd 430.1600, obsd 430.1600.



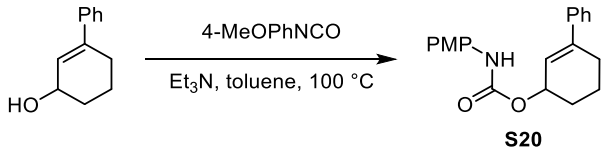
(*E*)-2-Methyl-5-(thiazol-2-yl)hex-4-en-3-ol (S16). The title compound was obtained as a light yellow oil (0.4 g, 52% yield) starting from (*E*)-3-(thiazol-2-yl)but-2-enal (0.6 g, 3.9 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.9 mL, 1.5 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S16**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.3 Hz, 1H), 7.21 (d, *J* = 3.3 Hz, 1H), 6.40 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.29 (dd, *J* = 8.9, 6.6 Hz, 1H), 2.02 (brs, 1H), 1.89–1.79 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 143.1, 133.4, 132.0, 118.3, 73.7, 34.7, 18.3 (2s), 15.7; IR (neat, cm^{-1}): 3377, 2957, 1017, 779; ESI HRMS m/z $(M+Na)^+$ calcd 220.0767, obsd 220.0767.

(*E*)-2-Methyl-5-(thiazol-2-yl)hex-4-en-3-yl (4-methoxyphenyl)carbamate (S17). The title compound was obtained as a colorless solid in 77% yield (0.43 g) starting from **S16** (0.33 g, 1.7 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.3 Hz, 1H), 7.31–7.25 (m, 2H), 7.23 (d, *J* = 3.3 Hz, 1H), 6.87–6.80 (m, 2H), 6.59 (s, 1H), 6.40 (dq, *J* = 9.3, 1.4 Hz, 1H), 5.44 (dd, *J* = 9.3, 6.8 Hz, 1H), 3.77 (s, 3H), 2.31 (d, *J* = 1.4 Hz, 3H), 2.08–1.96 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 156.1, 153.7, 143.3, 133.5, 131.2, 128.7, 120.8, 118.6, 114.4, 76.4, 55.7, 33.0, 18.5, 18.2, 16.1; IR (neat, cm^{-1}): 3321, 2961, 1718, 1220, 829; ESI HRMS m/z $(M+Na)^+$ calcd 369.1243, obsd 369.1244.

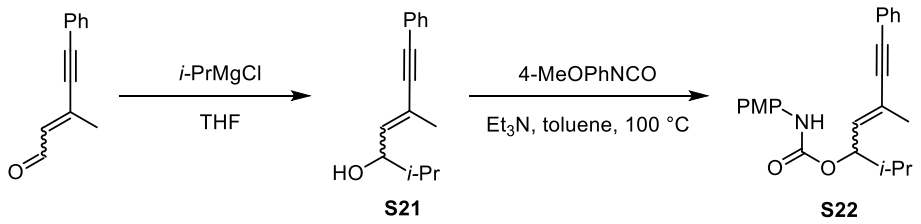


(*E*)-2-Methyl-5-(pyridin-2-yl)hex-4-en-3-ol (S18). The title compound was obtained as a light yellow oil (0.2 g, 26% yield) starting from (*E*)-3-(pyridin-2-yl)but-2-enal[6] (0.6 g, 4.0 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.9 mL, 1.5 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S18**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H), 7.64 (td, *J* = 7.8, 1.9 Hz, 1H), 7.44 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.15 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.31 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.32 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.16 (d, *J* = 1.4 Hz, 3H), 1.94–1.74 (m, 2H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 149.0, 137.3, 136.5, 132.4, 122.1, 120.2, 74.1, 34.8, 18.5, 18.4, 15.2; IR (neat, cm^{-1}): 3377, 2957, 1586, 1017, 779; ESI HRMS m/z $(M+Na)^+$ calcd 314.1202, obsd 314.1203.

(*E*)-2-Methyl-5-(pyridin-2-yl)hex-4-en-3-yl (4-methoxyphenyl)carbamate (S19). The title compound was obtained as a light yellow oil in 99% yield (0.35 g) starting from **S18** (0.2 g, 1.0 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.9 Hz, 1H), 7.43 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.32–7.25 (m, 2H), 7.15 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.85–6.80 (m, 2H), 6.63 (s, 1H), 6.37 (dq, *J* = 9.4, 1.4 Hz, 1H), 5.50 (dd, *J* = 9.4, 6.8 Hz, 1H), 3.76 (s, 3H), 2.25 (d, *J* = 1.4 Hz, 3H), 2.06–1.98 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.7, 154.7, 153.5, 148.8, 137.6, 136.8, 132.3, 127.8, 122.5, 119.9, 119.7, 113.9, 75.5, 55.2, 32.4, 18.2, 18.0, 14.7.; IR (neat, cm^{-1}): 3320, 2960, 1721, 1222, 1031; ESI HRMS m/z $(M+Na)^+$ calcd 363.1679 obsd 363.1681.

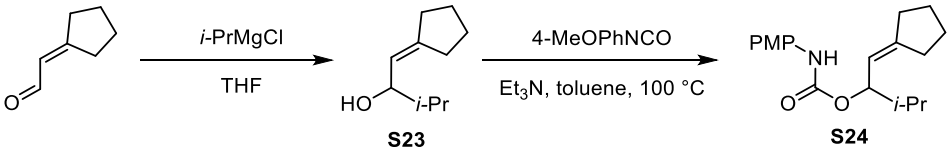


3,4,5,6-Tetrahydro-[1,1'-biphenyl]-3-yl (4-methoxyphenyl)carbamate (S20). The title compound was obtained as a colorless solid in 80% yield (0.65 g) starting from 3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol[7] (0.44 g, 2.5 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.37 (m, 2H), 7.36–7.22 (m, 5H), 6.90–6.78 (m, 2H), 6.55 (s, 1H), 6.20–6.12 (m, 1H), 5.50–5.41 (m, 1H), 3.77 (s, 3H), 2.56–2.47 (m, 1H), 2.44–2.34 (m, 1H), 2.02–1.75 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 153.9, 142.3, 141.2, 131.2, 128.5, 127.8, 125.6, 122.7, 120.7, 114.4, 69.7, 55.7, 28.4, 27.5, 19.6; IR (neat, cm^{-1}): 3322, 2928, 1695, 1513, 1217, 1031, 828; ESI HRMS m/z $(M+Na)^+$ calcd 346.1414, obsd 346.1413.



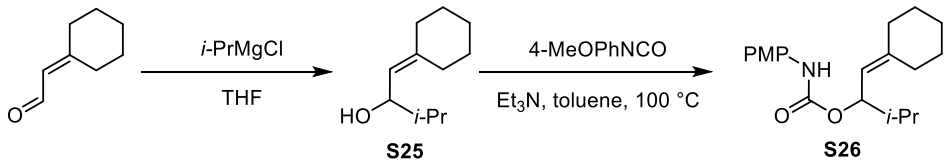
2,5-Dimethyl-7-phenylhept-4-en-6-yn-3-ol (S21). The title compound was obtained as a light yellow oil (0.40 g, 54% yield) starting from 3-methyl-5-phenylpent-2-en-4-ynal[8] (0.59 g, 3.5 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.1 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S21** (*E*/*Z* = 7:3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.35–7.28 (m, 3H), 5.92 (dq, *J* = 9.2, 1.5 Hz, 0.3H), 5.74 (dq, *J* = 8.8, 1.5 Hz, 0.7H), 4.42 (dd, *J* = 8.8, 6.5 Hz, 0.7H), 4.15 (dd, *J* = 9.1, 6.7 Hz, 0.3H), 1.98 (d, *J* = 1.5 Hz, 2.1H), 1.95 (d, *J* = 1.5 Hz, 0.9H), 1.85–1.72 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 2.1H), 0.99 (d, *J* = 6.8 Hz, 0.9H), 0.94 (d, *J* = 6.8 Hz, 2.1H), 0.92 (d, *J* = 6.8 Hz, 0.9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.3, 131.7, 131.6, 128.5, 128.4, 128.3, 123.4 (2s), 121.0, 120.8, 93.9, 91.9, 88.2, 87.7, 76.0, 73.5, 34.5, 34.2, 23.5, 18.5, 18.3 (2s), 18.2 (2s); IR (neat, cm^{-1}): 3383, 2958, 1489, 1014, 755, 690; ESI HRMS m/z $(M+Na)^+$ calcd 237.1250, obsd 237.1251.

2,5-Dimethyl-7-phenylhept-4-en-6-yn-3-yl (4-methoxyphenyl)carbamate (S22). The title compound was obtained as a light yellow oil in 73% yield (0.50 g, *E*/*Z* = 65:35) starting from **S21** (0.4 g, 1.87 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.40 (m, 2H), 7.35–7.26 (m, 5H), 6.87–6.77 (m, 2H), 6.50 (s, 1H), 5.85 (dq, *J* = 9.7, 1.5 Hz, 0.35H), 5.70 (dq, *J* = 8.7, 1.5 Hz, 0.65H), 5.62 (dd, *J* = 8.7, 5.9 Hz, 0.65H), 5.31 (dd, *J* = 9.7, 6.8 Hz, 0.35H), 3.82–3.71 (m, 3H), 2.08–1.91 (m, 4H), 1.02–0.95 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.6, 138.4, 134.0, 131.8, 131.7, 128.4 (2s), 128.3, 123.4 (2s), 122.9, 122.5, 120.6, 114.4, 114.3, 94.7, 91.8, 88.1, 87.9, 78.6, 76.0, 55.7, 33.0, 32.8, 23.5, 18.4, 18.3, 18.1 (2s); IR (neat, cm^{-1}): 3329, 2961, 1704, 1515, 1220, 828; ESI HRMS m/z $(M+Na)^+$ calcd 386.1727, obsd 386.1725.



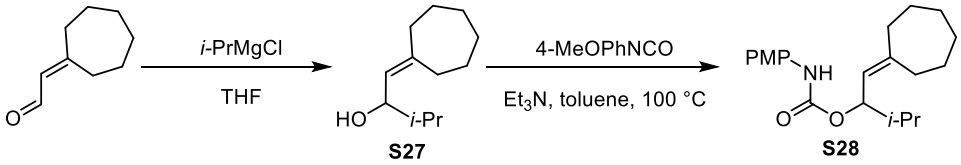
1-Cyclopentylidene-3-methylbutan-2-ol (S23). The title compound was obtained as a light yellow oil (0.25 g, 23% yield) starting from 2-cyclopentylideneacetaldehyde[9] (0.7 g, 7.0 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 4.2 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was used in the following step without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33–5.28 (m, 1H), 3.96 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.39–2.25 (m, 3H), 2.23–2.14 (m, 1H), 1.75–1.58 (m, 5H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

1-Cyclopentylidene-3-methylbutan-2-yl (4-methoxyphenyl)carbamate (S24). The title compound was obtained as a light yellow oil in 56% yield (0.24 g) starting from **S23** (0.44 g, 2.5 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.20 (m, 2H), 6.87–6.78 (m, 2H), 6.48 (s, 1H), 5.29–5.23 (m, 1H), 5.15 (dd, *J* = 9.4, 6.6 Hz, 1H), 3.77 (s, 3H), 2.59–2.49 (m, 1H), 2.33–2.18 (m, 3H), 1.93–1.82 (m, 1H), 1.69–1.58 (m, 4H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 154.0, 149.8, 131.5, 120.7, 117.3, 114.4, 78.6, 55.7, 34.0, 32.8, 29.4, 26.5, 26.2, 18.5, 18.1; IR (neat, cm^{-1}): 3327, 2957, 1701, 1515, 1222, 1032, 828; ESI HRMS m/z $(M+Na)^+$ calcd 326.1727, obsd 326.1729.



1-Cyclohexylidene-3-methylbutan-2-ol (S25). The title compound was obtained as a light yellow oil (0.83 g, 60% yield) starting from 2-cyclopentylideneacetaldehyde[9] (1.0 g, 8.2 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 4.9 mL, 1.2 equiv) by following the procedure described for the synthesis of **S1**. The crude product was used in the following step without purification.

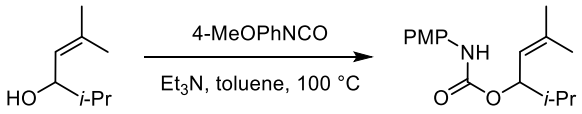
1-Cyclohexylidene-3-methylbutan-2-yl (4-methoxyphenyl)carbamate (S26). The title compound was obtained as a light yellow oil in 66% yield (0.98 g) starting from **S25** (0.80 g, 4.7 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 6.88–6.79 (m, 2H), 6.45 (s, 1H), 5.31 (dd, *J* = 9.4, 6.8 Hz, 1H), 5.09–5.05 (m, 1H), 3.77 (s, 3H), 2.35–2.22 (m, 2H), 2.15–2.04 (m, 2H), 1.91–1.81 (m, 1H), 1.67–1.58 (m, 3H), 1.58–1.48 (m, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.8, 145.8, 131.5, 120.7, 118.8, 114.4, 76.2, 55.7, 37.4, 32.9, 29.9, 28.8, 28.0, 26.9, 18.6, 18.2; IR (neat, cm^{-1}): 3328, 2929, 1700, 1515, 1221, 1032; ESI HRMS m/z $(M+Na)^+$ calcd 340.1883, obsd 340.1882.



1-Cycloheptylidene-3-methylbutan-2-ol (S27). The title compound was obtained as a light yellow oil (1.4 g, 71% yield) starting from 1-cycloheptylidene-3-methylbutan-2-ol[10] (1.4 g, 10.8 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 8.4 mL, 1.5 equiv) by following the procedure described for the synthesis of **S1**. The crude product was used in the following step without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22–5.17 (m, 1H), 4.05 (dd, *J* = 9.1, 6.8 Hz, 1H), 2.34–2.29 (m, 2H), 2.26–2.21 (m, 2H), 1.72–1.46 (m, 9H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

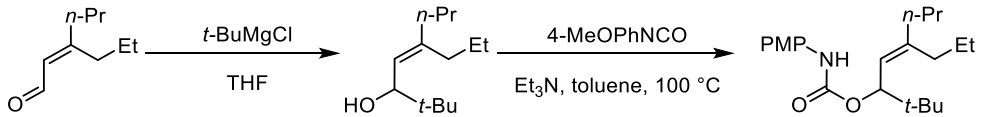
1-Cycloheptylidene-3-methylbutan-2-yl (4-methoxyphenyl)carbamate (S28). The title compound was obtained as a colorless solid in 92% yield (1.2 g) starting from **S27** (0.72 g, 4.0

mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 6.88–6.78 (m, 2H), 6.49 (s, 1H), 5.28 (dd, *J* = 9.6, 6.8 Hz, 1H), 5.15 (dt, *J* = 9.6, 1.3 Hz, 1H), 3.77 (s, 3H), 2.50–2.37 (m, 2H), 2.28–2.19 (m, 2H), 1.91–1.82 (m, 1H), 1.72–1.60 (m, 2H), 1.59–1.44 (m, 6H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.9, 147.6, 131.5, 122.4, 120.6, 114.3, 76.5, 55.7, 38.1, 32.9, 30.6, 29.7, 29.3 (2s), 27.2, 18.6, 18.3; IR (neat, cm^{-1}): 3330, 2924, 1699, 1515, 1222, 1031; ESI HRMS m/z $(M+Na)^+$ calcd 354.2040, obsd 354.2039.



S29

2,5-Dimethylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S29). The title compound was obtained as a colorless solid in 67% yield (3.7 g) starting from 2,5-dimethylhex-4-en-3-ol[11] (2.36 g, 20 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.19 (m, 2H), 6.87–6.79 (m, 2H), 6.50 (s, 1H), 5.25 (dd, *J* = 9.6, 6.8 Hz, 1H), 5.16–5.11 (m, 1H), 3.77 (s, 3H), 1.77–1.75 (m, 1H), 1.76 (d, *J* = 1.4 Hz, 3H), 1.75 (d, *J* = 1.4 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.9, 137.9, 131.5, 122.2, 120.7, 114.4, 77.0, 55.7, 32.9, 26.1, 18.8, 18.5, 18.1; IR (neat, cm^{-1}): 3325, 2961, 1698, 1515, 1222, 1031; ESI HRMS m/z $(M+Na)^+$ calcd 300.1570, obsd 300.1573.

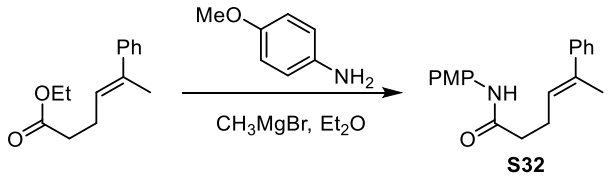


S30 **S31**

2,2-Dimethyl-5-propyloct-4-en-3-ol (S30). The title compound was obtained as a light yellow oil (0.17 g, 25% yield) starting from 3-propylhex-2-enal[12] (0.5 g, 3.5 mmol, 1.0 equiv) and *t*-BuMgBr (1.0 M in THF, 7.0 mL, 2.0 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S30**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28–5.22 (m, 1H), 4.03 (dd, *J* = 9.6, 2.8 Hz, 1H), 2.15–2.07 (m, 1H), 2.07–1.92 (m, 3H), 1.49–1.37 (m, 4H), 0.94–0.86 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 124.8, 75.6, 39.1, 35.2, 32.6, 25.8, 21.9, 21.4, 14.5, 14.1; IR (neat, cm^{-1}): 3361, 2922, 1593, 1461, 1134; ESI HRMS m/z $(M+Na)^+$ calcd 221.1876, obsd 221.1881.

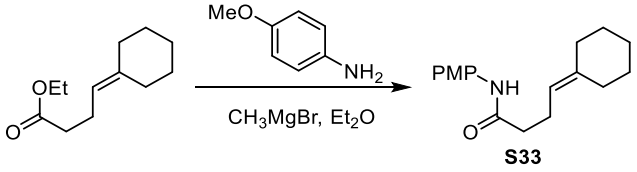
2,2-Dimethyl-5-propyloct-4-en-3-yl (4-methoxyphenyl)carbamate (S31). The title compound was obtained as a colorless solid in 81% yield (0.21 g) starting from **S30** (0.15 g, 0.75 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.24 (m, 2H), 6.87–6.80 (m, 2H), 6.40 (s, 1H), 5.33 (d, *J* = 9.9 Hz, 1H), 5.18 (d, *J* = 9.9 Hz, 1H), 3.78 (s, 3H), 2.22–2.10 (m, 2H), 2.06–1.94 (m, 2H), 1.50–1.36 (m, 4H), 0.95–0.90 (m, 12H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.8, 146.0, 131.6, 120.7 (2s), 114.3, 78.2, 55.7, 38.9, 35.2, 32.8, 26.1, 21.6,

21.3, 14.6, 14.0; IR (neat, cm^{-1}): 3335, 2959, 1700, 1516, 1226; ESI HRMS m/z $(M+Na)^+$ calcd 370.2353, obsd 370.2350.



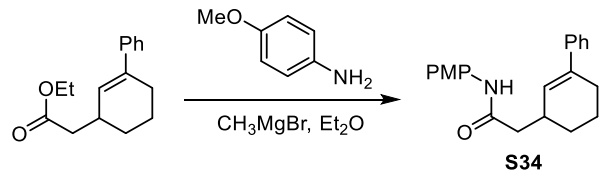
S32

(*E*)-*N*-(4-Methoxyphenyl)-5-phenylhex-4-enamide (S32). To a solution of CH_3MgBr (3.0 M in Et_2O, 1.2 mL, 2.0 equiv) in Et_2O (20 mL) at 0 °C was added a solution of *p*-anisidine (0.45 g, 3.7 mmol, 2.0 equiv) in Et_2O (20 mL) dropwise. Upon complete addition, the reaction mixture was stirred for 10 min at 0 °C before dropwise addition of ethyl (*E*)-5-phenylhex-4-enoate[13] (0.4 g, 1.8 mmol, 1.0 equiv). The reaction mixture was warmed to ambient temperature and stirred for 1 h. Saturated aqueous NH_4Cl (40 mL) was added to quench the reaction. The resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic solution was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to afford **S32** as a colorless solid in 92% yield (0.5 g). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 4H), 7.27–7.22 (m, 1H), 7.20–7.06 (m, 3H), 6.86–6.80 (m, 2H), 5.56–5.44 (m, 1H), 3.77 (s, 3H), 2.44–2.28 (m, 4H), 2.04 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 156.5, 141.7, 138.3, 131.2, 128.4, 128.0, 126.9, 125.5, 121.9, 114.2, 55.6, 37.8, 25.8, 25.4; IR (neat, cm^{-1}): 3281, 2919, 1700, 1077, 827; ESI HRMS m/z $(M+Na)^+$ calcd 318.1465, obsd 318.1464.



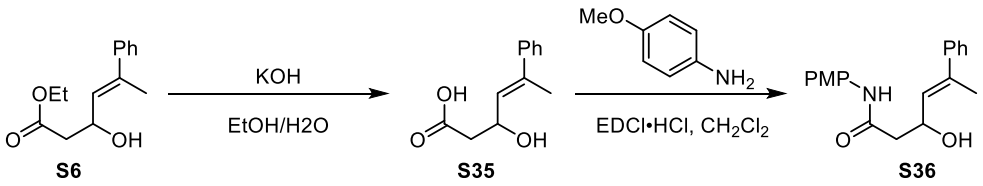
S33

4-Cyclohexylidene-*N*-(4-methoxyphenyl)butanamide (S33). The title compound was obtained as a colorless solid (0.39 g, 84% yield) starting from ethyl 4-cyclohexylidenebutanoate[14] (0.3 g, 1.7 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S32**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46–7.37 (m, 2H), 7.34 (brs, 1H), 6.91–6.79 (m, 2H), 5.11 (t, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 2.45–2.32 (m, 4H), 2.15 (t, *J* = 6.0 Hz, 2H), 2.07 (t, *J* = 5.6 Hz, 2H), 1.59–1.44 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 156.4, 142.0, 131.3, 121.9, 119.4, 114.2, 55.6, 38.1, 37.3, 28.9, 28.8, 27.9, 27.0, 23.6; IR (neat, cm^{-1}): 3301, 2924, 1652, 1527, 1248, 1032, 827; ESI HRMS m/z $(M+Na)^+$ calcd 296.1621, obsd 296.1622.



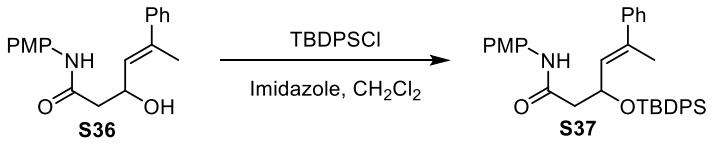
S34

***N*-(4-Methoxyphenyl)-2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)acetamide** (**S34**). The title compound was obtained as a colorless solid (0.26 g, 48% yield) starting from ethyl 2-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)acetate[15] (0.39 g, 1.6 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S32**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.36 (m, 4H), 7.33–7.27 (m, 2H), 7.25–7.20 (m, 2H), 6.91–6.80 (m, 2H), 6.02 (s, 1H), 3.78 (s, 3H), 2.96–2.86 (m, 1H), 2.48–2.29 (m, 4H), 2.01–1.86 (m, 2H), 1.79–1.68 (m, 1H), 1.42–1.31 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 156.6, 142.2, 138.1, 131.1, 128.4, 127.7, 127.1, 125.3, 122.0, 114.3, 55.7, 44.4, 33.7, 28.7, 27.7, 21.8； IR (neat, cm^{-1}): 3286, 2923, 1650, 1509, 1243, 1030, 835; ESI HRMS m/z $(M+Na)^+$ calcd 344.1621, obsd 344.1621.



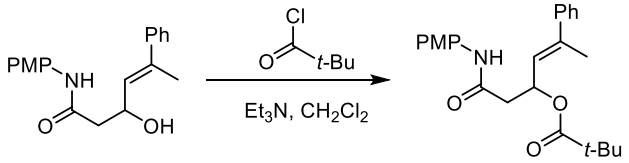
(*E*)-3-Hydroxy-5-phenylhex-4-enoic acid (S35). **S6** (1.2 g, 5.1 mmol, 1.0 equiv) was treated with KOH (1.0 g, 17.8 mmol, 3.5 equiv) in EtOH (50 mL) and H_2O (5 mL) under reflux for 3 h. The reaction mixture was cooled to RT. EtOH was removed under reduced pressure. The leftover aqueous solution was extracted three times with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford **S35** as a colorless solid in 86% yield (0.86 g). The crude product was used in the following step without purification. ^{1}H NMR (500 MHz, CDCl3) δ 7.42–7.38 (m, 2H), 7.36–7.31 (m, 2H), 7.30–7.26 (m, 1H), 5.80 (dq, *J* = 8.3, 1.4 Hz, 1H), 5.00 (td, *J* = 8.3, 4.1 Hz, 1H), 2.72 (dd, *J* = 16.5, 8.3 Hz, 1H), 2.66 (dd, *J* = 16.5, 4.1 Hz, 1H), 2.13 (d, *J* = 1.4 Hz, 3H).

(*E*)-3-Hydroxy-*N*-(4-methoxyphenyl)-5-phenylhex-4-enamide (S36). To a solution of **S35** (0.56 g, 2.7 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added EDCl·HCl (0.62 g, 3.2 mmol, 1.2 equiv), followed by *p*-anisidine (0.4 g, 3.2 mmol, 1.2 equiv). The resulting reaction mixture was stirred at 8 h at RT, diluted with EtOAc, and quenched with 1 N HCl (15 mL). The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with CH_2Cl_2/MeOH to afford **S36** as a colorless solid in 74% yield (0.62 g). ^{1}H NMR (500 MHz, CD_3OD) δ 7.46–7.35 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25–7.18 (m, 1H), 6.91–6.81 (m, 2H), 5.78 (d, *J* = 8.6 Hz, 1H), 5.08–4.99 (m, 1H), 3.76 (s, 3H), 2.68 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.53 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 171.4, 158.0, 144.5, 138.7, 132.7, 130.5, 129.3, 128.3, 126.9, 123.3, 114.9, 67.2, 55.8, 45.9, 16.6; IR (neat, cm^{-1}): 3427, 3303, 2929, 1645, 1035, 814, 692; ESI HRMS m/z $(M+Na)^+$ calcd 334.1414, obsd 334.1414.



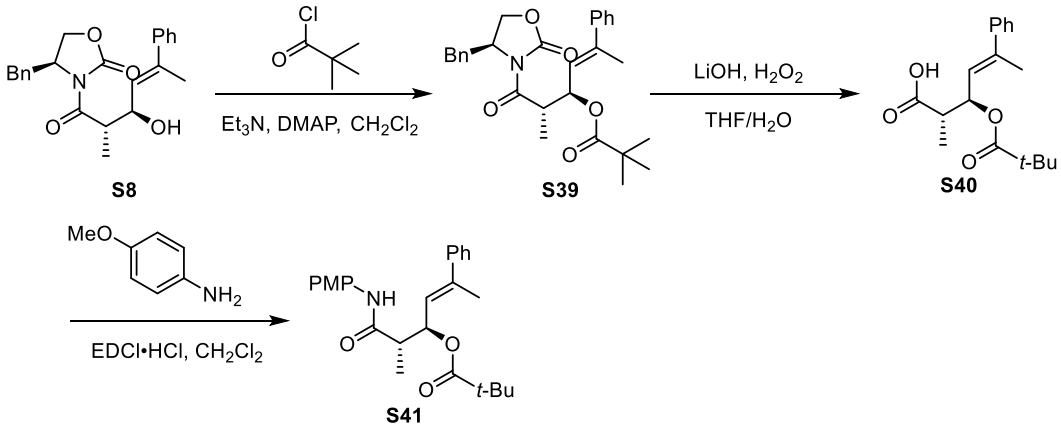
S36 S37

(*E*)-3-((*tert*-Butyldiphenylsilyl)oxy)-*N*-(4-methoxyphenyl)-5-phenylhex-4-enamide (S37). To a solution of **S36** (0.25 g, 0.8 mmol, 1 equiv) in CH_2Cl_2 (15 mL) was added TBDPSCl (0.28 mL, 1.1 mmol, 1.4 equiv) and imidazole (0.080 g, 1.2 mmol, 1.5 equiv). The reaction mixture was stirred at RT for 24 h and quenched with saturated aqueous $NaHCO_3$ (10 mL). The reaction mixture was extracted twice with CH_2Cl_2. The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel chromatography eluting with EtOAc/hexanes provided **S37** as a colorless solid (0.2 g, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.71 (d, *J* = 7.1 Hz, 4H), 7.51–7.29 (m, 8H), 7.24–7.15 (m, 3H), 7.12–7.02 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.80 (d, *J* = 8.8 Hz, 1H), 5.03–4.94 (m, 1H), 3.79 (s, 3H), 2.71 (dd, *J* = 14.7, 4.5 Hz, 1H), 2.56 (dd, *J* = 14.7, 5.9 Hz, 1H), 1.50 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 156.4, 143.0, 136.9, 136.1, 136.0, 133.5, 133.3, 131.4, 130.2, 130.0, 128.7, 128.3, 128.1, 127.8, 127.4, 126.1, 121.8, 114.3, 69.0, 55.7, 46.1, 27.2, 19.5, 16.1; IR (neat, cm^{-1}): 3323, 2928, 1727, 1511, 1280, 826, 701; ESI HRMS m/z $(M+Na)^+$ calcd 572.2591, obsd 572.2590.



S36 S38

(*E*)-1-((4-Methoxyphenyl)amino)-1-oxo-5-phenylhex-4-en-3-yl pivalate (S38). To a solution of **S36** (0.21 g, 0.67 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was added pivaloyl chloride (0.10 mL, 0.81 mmol, 1.2 equiv) and Et_3N (0.18 mL, 1.3 mmol, 2.0 equiv) . The reaction mixture was stirred at RT for 8 h and the solvent was removed under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S38** as a colorless solid in 54% yield (0.14 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.26 (m, 8H), 6.91–6.77 (m, 2H), 6.12–5.97 (m, 1H), 5.80–5.66 (m, 1H), 3.78 (s, 3H), 2.79 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.72 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.26–2.13 (m, 3H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 167.2, 156.7, 142.6, 140.6, 130.9, 128.5, 127.8, 126.2, 124.6, 122.0, 114.4, 69.0, 55.7, 43.5, 39.0, 27.3, 16.9; IR (neat, cm^{-1}): 3354, 2921, 1703, 1678, 1035, 829; ESI HRMS m/z $(M+Na)^+$ calcd 418.1989, obsd 418.1989.

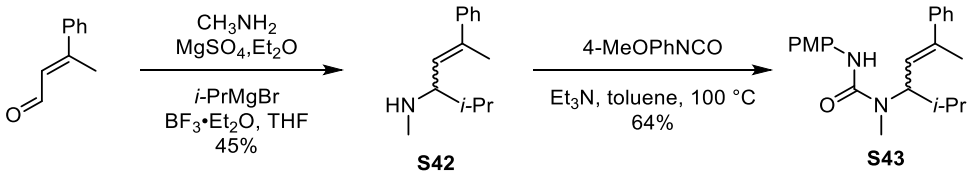


(2*S*,3*R*,*E*)-1-((*S*)-4-Benzyl-2-oxooxazolidin-3-yl)-2-methyl-1-oxo-5-phenylhex-4-en-3-yl pivalate (S39). To a solution of **S8** (0.80 g, 2.1 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added pivaloyl chloride (0.52 mL, 4.2 mmol, 2.0 equiv), Et_3N (1.0 mL, 7.2 mmol, 3.5 equiv) and DMAP (0.25 g, 0.20 mmol, 0.1 equiv). The reaction mixture was stirred at RT for 12 h and diluted with EtOAc, quenched with 1 N HCl (20 mL). The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford **S39** as a light yellow oil (0.8 g, 82% yield). The crude product was used in the following step without purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.35–7.29 (m, 4H), 7.29–7.24 (m, 2H), 7.22–7.17 (m, 2H), 5.96 (dd, *J* = 9.4, 6.5 Hz, 1H), 5.76–5.68 (m, 1H), 4.58–4.50 (m, 1H), 4.26 (t, *J* = 6.7 Hz, 1H), 4.13 (d, *J* = 4.9 Hz, 2H), 3.26 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.78 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.19 (d, *J* = 1.6 Hz, 3H), 1.33 (d, *J* = 6.6 Hz, 3H), 1.21 (s, 9H).

(2*S*,3*R*,*E*)-2-Methyl-5-phenyl-3-(pivaloyloxy)hex-4-enoic acid (S40). To a solution of **S39** (0.8 g, 1.7 mmol, 1.0 equiv) in THF (20 mL) and H_2O (5 mL) was added lithium hydroxide monohydrate (0.14 g, 3.3 mmol, 2.0 equiv) and 30% H_2O_2 (0.7 mL). The reaction mixture was stirred for 2 h at RT. THF was removed under reduced pressure. The excess H_2O_2 was quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL). The reaction mixture was extracted with diethyl ether to remove any neutral organic impurities. The aqueous layer was acidified with 1 N HCl to pH = 2 and then extracted three times with CH_2Cl_2. The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford **S40** as a light yellow oil (0.4 g, 76% yield). The crude product was used in the following step without purification.

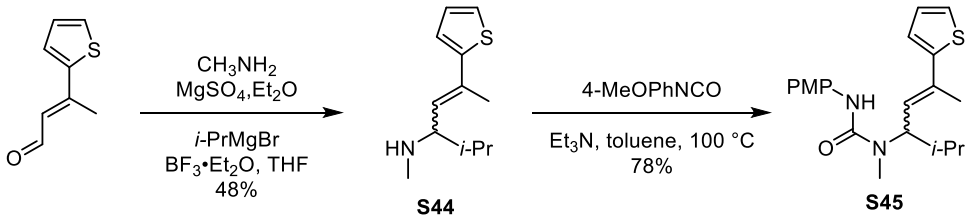
(2*S*,3*R*,*E*)-1-((4-Methoxyphenyl)amino)-2-methyl-1-oxo-5-phenylhex-4-en-3-yl pivalate (S41). The title compound was obtained as a colorless solid in 78% yield (0.27 g) starting from **S40** (0.39 g, 1.6 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S36**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (brs, 1H), 7.38–7.31 (m, 4H), 7.31–7.21 (m, 3H), 6.87–6.76 (m, 2H), 5.80 (dd, *J* = 9.5, 6.5 Hz, 1H), 5.73–5.68 (m, 1H), 3.76 (s, 3H), 2.83–2.75 (m, 1H), 2.17 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 170.8, 156.6, 143.0, 141.8, 130.9,

128.4, 127.7, 126.3, 123.1, 122.1, 114.3, 73.0, 55.6, 46.5, 39.1, 27.4, 17.0, 13.7; IR (neat, cm^{-1}): 3289, 2972, 1727, 1653, 1245, 1153, 828; ESI HRMS m/z $(M+Na)^+$ calcd 432.2145, obsd 432.2142.



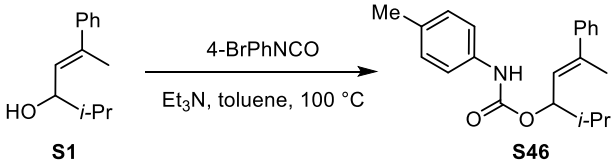
***N*,2-Dimethyl-5-phenylhex-4-en-3-amine (S42)**. To a solution of (*E*)-3-phenylbut-2-enal (1.0 g, 6.8 mmol, 1.0 equiv) in Et_2O (25 mL) was added CH_3NH_2 (2 M in THF, 6 mL, 1.8 equiv). The reaction mixture was stirred for 12 h at RT and filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (20 mL) and cooled to −78 °C. $BF_3{\cdot}Et_2O$ (2.0 mL, 10 mmol, 1.5 equiv) was added. The resulting mixture was stirred for 30 min at the same temperature before treating with *i*-PrMgCl (2.0 M in THF, 6.8 mL, 2.0 equiv). The reaction was stirred at −78 °C for another 30 min and then warmed up to ambient temperature. Saturated aqueous $NaHCO_3$ (40 mL) was added after 1 h to quench the reaction. The resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic solution was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to afford **S42** as a light yellow oil in 45% yield (0.62 g, *E*/*Z* = 5.7:1). ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ 7.46–7.38 (m, 2H), 7.36–7.29 (m, 2H), 7.27–7.22 (m, 1H), 5.57 (d, *J* = 9.7 Hz, 1H), 3.17 (dd, *J* = 9.6, 6.1 Hz, 1H), 2.39 (s, 3H), 2.09 (d, *J* = 1.2 Hz, 3H), 1.83–1.74 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 142.6, 140.3, 137.6, 130.0, 128.4, 128.2, 128.1, 127.0, 126.6, 125.9, 63.9, 63.4, 34.6, 34.4 (2s), 32.9, 26.7, 19.8, 19.6, 18.8, 18.5, 16.8; IR (neat, cm^{-1}): 3358, 2920, 1658, 1469, 758, 697; ESI HRMS m/z $(M+Na)^+$ calcd 226.1566, obsd 226.1567.

3-(4-Methoxyphenyl)-1-methyl-1-(2-methyl-5-phenylhex-4-en-3-yl)urea (S43). The title compound was obtained as a colorless solid in 64% yield (0.4 g, *E*/*Z* = 85:15) starting from **S42** (0.3 g, 1.4 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ 7.42–7.37 (m, 2H), 7.36–7.19 (m, 5H), 6.86–6.80 (m, 2H), 6.23 (s, 1H), 5.71 (dd, *J* = 8.7, 1.3 Hz, 1H), 4.86 (t, *J* = 9.5 Hz, 1H), 3.76 (s, 3H), 2.86 (s, 3H), 2.14 (d, *J* = 1.3 Hz, 3H), 1.94–1.85 (m, 1H), 0.98 (d, *J* = 4.4 Hz, 3H), 0.97 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 155.9, 155.8, 155.5, 143.6, 141.8, 141.3, 140.2, 132.6, 132.5, 128.8, 128.4, 127.8, 127.4 (2s), 126.4, 126.0, 125.5, 122.4, 121.9, 114.2, 114.0, 61.3, 58.3, 55.7, 55.6, 31.6, 31.3, 29.4, 26.4, 20.2, 19.8, 19.6, 19.4, 17.2； IR (neat, cm^{-1}): 3358, 2920, 1658, 1469, 758, 697; ESI HRMS m/z $(M+Na)^+$ calcd 375.2043, obsd 375.2041.

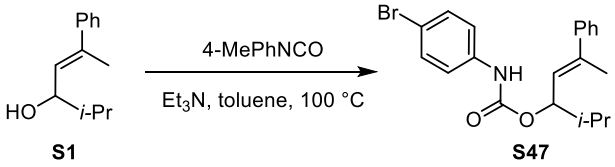


***N*,2-Dimethyl-5-(thiophen-2-yl)hex-4-en-3-amine (S44)**. The title compound was obtained as a light yellow oil 48% yield (0.66 g) starting from (*E*)-3-(thiophen-2-yl)but-2-enal[3] (1.0 g, 6.5 mmol, 1.0 equiv) following the procedure described for the synthesis of **S42**. This compound was used in the following step without purification.

3-(4-Methoxyphenyl)-1-methyl-1-(2-methyl-5-(thiophen-2-yl)hex-4-en-3-yl)urea (S45). The title compound was obtained as a colorless solid in 78% yield (0.4 g, *E*/*Z* = 9:1) starting from **S44** (0.3 g, 1.4 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 1.8H), 7.22–7.17 (m, 0.2H), 7.17–7.10 (m, 1H), 7.07–7.01 (m, 1H), 7.00–6.94 (m, 1H), 6.88–6.74 (m, 2H), 6.17 (s, 1H), 5.87 (d, *J* = 8.9 Hz, 0.9H), 5.58 (d, *J* = 9.8 Hz, 0.1H), 4.87 (t, *J* = 9.5 Hz, 0.9H), 4.45 (t, *J* = 9.4 Hz, 0.1H), 3.77 (s, 2.7H), 3.75 (s, 0.3H), 2.87 (s, 3H), 2.16 (s, 3H), 1.94–1.81 (m, 1H), 1.01–0.91 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 155.9, 147.2, 133.9, 132.4, 127.6, 125.0, 123.9, 123.4, 122.4, 114.3, 58.1, 55.7, 31.5, 29.4, 19.9, 19.5, 17.1; IR (neat, cm^{-1}): 3355, 2958, 1634, 1512, 1235, 824; ESI HRMS m/z $(M+Na)^+$ calcd 381.1607, obsd 381.1606.

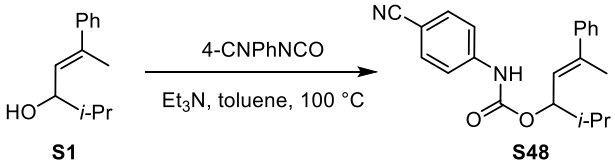


(*E*)-2-Methyl-5-phenylhex-4-en-3-yl p-tolylcarbamate (S46). The title compound was obtained as a colorless solid in 88% yield (0.3 g) starting from **S1** (0.2 g, 1.0 mmol) and 4-MePhNCO (0.16 mL, 1.2 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.35–7.29 (m, 2H), 7.28–7.23 (m, 3H), 7.13–7.05 (m, 2H), 6.53 (s, 1H), 5.71 (dd, *J* = 9.5, 1.4 Hz, 1H), 5.45 (dd, *J* = 9.5, 6.9 Hz, 1H), 2.29 (s, 3H), 2.19 (d, *J* = 1.4 Hz, 3H), 2.05–1.96 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 143.3, 139.9, 135.7, 133.0, 129.7, 128.4, 127.5, 126.1, 125.2, 118.9, 77.5, 33.2, 20.9, 18.6, 18.2, 17.0; IR (neat, cm^{-1}): 3320, 2961, 1698, 1526, 1223, 816; ESI HRMS m/z $(M+Na)^+$ calcd 346.1778, obsd 346.1780.



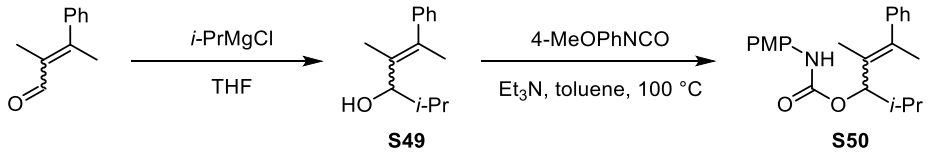
(*E*)-2-Methyl-5-phenylhex-4-en-3-yl (4-bromophenyl)carbamate (S47). The title compound was obtained as a colorless solid in 82% yield (0.5 g) starting from **S1** (0.3 g, 1.6 mmol) and 4-

BrPhNCO (0.37 g, 1.9 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.36 (m, 4H), 7.35–7.25 (m, 5H), 6.63 (s, 1H), 5.73–5.67 (m, 1H), 5.45 (dd, *J* = 9.4, 6.8 Hz, 1H), 2.18 (d, *J* = 1.5 Hz, 3H), 2.04–1.95 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 143.1, 140.1, 137.4, 132.1, 128.4, 127.6, 126.1, 124.9, 120.3, 115.9, 77.1, 33.1, 18.5, 18.2, 17.0; IR (neat, cm^{-1}): 3320, 2962, 1700, 1518, 1220, 758; ESI HRMS m/z $(M+Na)^+$ calcd 410.0726, obsd 410.0725.



S1 **S48**

(*E*)-2-Methyl-5-phenylhex-4-en-3-yl p-tolylcarbamate (S48). The title compound was obtained as a light yellow oil in 71% yield (0.2 g) starting from **S1** (0.16 g, 0.84 mmol) and 4-CNPhNCO (0.15 g, 1.9 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.35–7.29 (m, 2H), 7.28–7.23 (m, 3H), 7.13–7.05 (m, 2H), 6.53 (s, 1H), 5.71 (dd, *J* = 9.5, 1.4 Hz, 1H), 5.45 (dd, *J* = 9.5, 6.9 Hz, 1H), 2.29 (s, 3H), 2.19 (d, *J* = 1.4 Hz, 3H), 2.05–1.96 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 143.3, 139.9, 135.7, 133.0, 129.7, 128.4, 127.5, 126.1, 125.2, 118.9, 76.9, 33.2, 20.9, 18.6, 18.2, 17.0; IR (neat, cm^{-1}): 3320, 2962, 2224, 1733, 1526, 1218, 1042; ESI HRMS m/z $(M+Na)^+$ calcd 357.1573, obsd 357.1570.

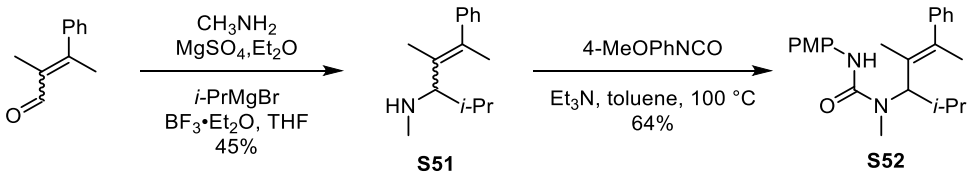


S49 **S50**

2,4-Dimethyl-5-phenylhex-4-en-3-ol (S49). The title compound was obtained as a light yellow oil (0.38 g, 60% yield) starting from 2-methyl-3-phenylbut-2-enal[16] (0.5 g, 3.1 mmol, 1.0 equiv) and *i*-PrMgCl (2.0 M in THF, 2.5 mL, 1.6 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S49** (*E*/*Z* = 1.3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.25–7.19 (m, 1H), 7.13–7.04 (m, 2H), 4.33 (d, *J* = 9.3 Hz, 0.44H), 3.72 (d, *J* = 9.6 Hz, 0.56H), 2.03–1.99 (m, 1.3H), 1.98–1.95 (m, 1.7H), 1.90–1.82 (m, 0.45H), 1.80–1.76 (m, 1.7H), 1.77–1.72 (m, 0.55H), 1.55–1.49 (m, 1.3H), 1.12 (d, *J* = 6.5 Hz, 1.3H), 0.91–0.86 (m, 3H), 0.67 (d, *J* = 6.8 Hz, 1.7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 144.5, 135.4, 134.2, 132.3, 132.1, 128.4 (2s), 128.3, 128.1, 126.3 (2s), 78.3, 77.1, 32.5, 31.7, 21.8, 20.9, 19.8, 19.6, 19.3, 19.0, 13.6, 11.9; IR (neat, cm^{-1}): 3314, 2956, 1491, 1132, 765, 701; ESI HRMS m/z $(M+Na)^+$ calcd 227.1406, obsd 227.1407.

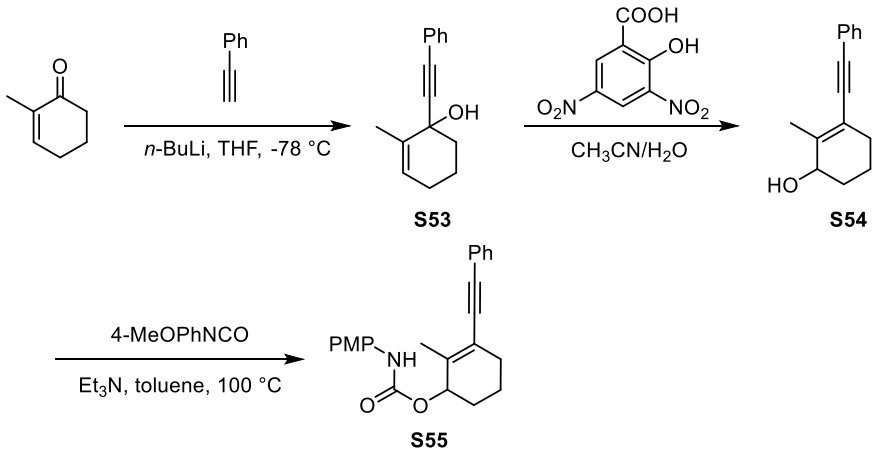
2,4-Dimethyl-5-phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate (S50). The title compound was obtained as a colorless solid in 33% yield (0.12 g, *E*/*Z* = 1.3:1) starting from **S49** (0.26 g, 1.27 mmol, 1.0 equiv) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.27

(m, 4H), 7.25–7.18 (m, 2H), 7.13–7.08 (m, 1H), 6.89–6.81 (m, 2H), 6.49&6.41 (2s, 1H), 5.49 (d, *J* = 9.9 Hz, 0.45H), 5.04 (d, *J* = 9.3 Hz, 0.55H), 3.78 (2s, 3H), 2.12 (d, *J* = 1.6 Hz, 1.3H), 2.08–2.01 (m, 0.45H), 1.97 (d, *J* = 1.2 Hz, 1.7H), 1.91–1.80 (m, 0.55H), 1.77 (s, 1.7H), 1.50 (s, 1.3H), 1.07 (d, *J* = 6.6 Hz, 1.3H), 0.95 (d, *J* = 6.9 Hz, 1.3H), 0.82 (d, *J* = 6.6 Hz, 1.7H), 0.70 (d, *J* = 6.9 Hz, 1.7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 155.8, 153.9, 153.4, 145.1, 143.9, 136.2, 136.0, 131.6, 131.4, 128.6 (2s), 128.4, 128.3, 128.1, 128.0, 126.4, 126.3, 120.6, 114.4, 114.3, 81.2, 80.0, 55.6 (2s),, 31.3, 30.9, 22.1(2s), 19.6, 19.2, 19.1, 18.5, 14.3, 13.1; IR (neat, cm^{-1}): 3336, 2962, 1710, 1218, 1032; ESI HRMS m/z $(M+Na)^+$ calcd 376.1883, obsd 376.1884.



***N*,2,4-Trimethyl-5-phenylhex-4-en-3-amine (S51)**. The title compound was obtained as a light yellow oil (0.36 g, 53% yield) starting from 2-methyl-3-phenylbut-2-enal (0.50 g, 3.1 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S42**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S51** (*E*/*Z* = 1.5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 2H), 7.25–7.19 (m, 1H), 7.12–7.08 (m, 0.80H), 7.06–7.01 (m, 1.2H), 3.70 (brs, 1H), 3.36 (d, *J* = 9.8 Hz, 0.40H), 2.90 (d, *J* = 9.6 Hz, 0.60H), 2.41 (s, 1.2H), 2.31 (s, 1.8H), 2.03–1.97 (m, 3H), 1.80–1.66 (m, 2.8H), 1.41 (q, *J* = 1.5 Hz, 1.2H) 1.12 (d, *J* = 6.5 Hz, 1.2H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 1.8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 144.5, 137.4, 136.7, 129.5, 128.5 (2s), 128.4, (2s), 128.1, 126.3 (2s), 67.7, 67.0, 33.7, 30.9, 30.8, 22.2, 21.1, 20.7, 20.5, 20.2, 20.0, 13.4, 11.9; IR (neat, cm^{-1}): 3363, 2961, 1599, 1465, 1075, 766; ESI HRMS m/z $(M+H)^+$ calcd 218.1903, obsd 218.1904.

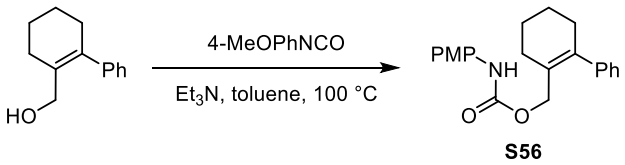
(*E*)-1-(2,4-Dimethyl-5-phenylhex-4-en-3-yl)-3-(4-methoxyphenyl)-1-methylurea (S52). The title compound was obtained as a colorless solid in 33% yield (0.2 g) starting from **S51** (0.41 g, 1.9 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.29–7.21 (m, 3H), 7.13–7.08 (m, 2H), 6.88–6.81 (m, 2H), 6.35 (s, 1H), 4.69 (brs, 1H), 3.78 (s, 3H), 3.03 (s, 3H), 2.21–2.12 (m, 4H), 1.51 (q, *J* = 1.5 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 155.7, 144.9, 135.7, 132.8, 130.9, 128.5, 128.0, 126.5, 121.8, 114.4, 62.4, 55.7, 30.9, 28.5, 21.5, 20.9, 19.8, 15.5; IR (neat, cm^{-1}): 3360, 2919, 1632, 1512, 1234, 826; ESI HRMS m/z $(M+Na)^+$ calcd 389.2199, obsd 389.2201.



2-Methyl-1-(phenylethynyl)cyclohex-2-en-1-ol (S53). To a solution of phenylacetylene (0.6 mL, 5.5 mmol, 1.1 equiv) in THF (20 mL) at −78 °C was added *n*-butyllithium (2.5 M in hexane, 2.2 mL, 1.1 equiv) dropwise over 10 min. Upon complete addition, the reaction mixture was stirred for 30 min at −78 °C. 2-Methylcyclohex-2-en-1-one (0.57 mL, 5 mmol, 1.0 equiv) was added dropwise over 30 min. The reaction mixture was warmed to ambient temperature and stirred for 1 h. Saturated aqueous NH_4Cl (20 mL) was added to quench the reaction. The resulting mixture was extracted three times with EtOAc (3 x 50 mL). The combined organic solution was washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford compound **S53** as a light yellow oil (0.83 g, 78%). The crude product was used in the following step without purification.

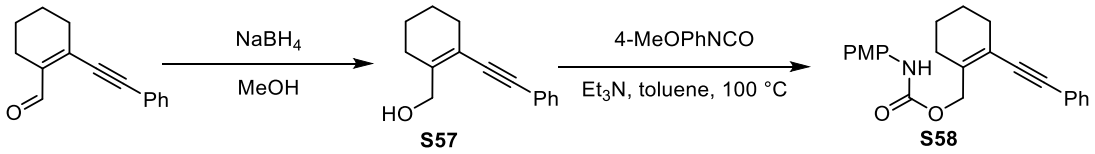
2-Methyl-3-(phenylethynyl)cyclohex-2-en-1-ol (S54). The title compound was prepared by following a reported procedure.[7] To a solution of **S53** (0.4 g, 1.9 mmol, 1.0 equiv) in CH_3CN (25 mL) and H_2O (5 mL) was added 3,5-dinitrosalicylic acid (0.08 g, 0.35 mmol, 0.2 equiv). The reaction mixture was stirred for 2 h at 60 °C, cooled to RT and concentrated under reduced pressure. The residue was diluted with Et_2O and saturated aqueous $NaHCO_3$ (30 mL). The phases were separated and the aqueous phase was extracted twice with Et_2O. The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **S54** as a light yellow oil (0.3 g, 75% yield). The crude product was used in the following step without purification.

2-Methyl-3-(phenylethynyl)cyclohex-2-en-1-yl (4-methoxyphenyl)carbamate (S55). The title compound was obtained as a colorless solid in 87% yield (0.4 g) starting from **S54** (0.27 g, 1.3 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.40 (m, 2H), 7.37–7.26 (m, 5H), 6.91–6.79 (m, 2H), 6.55 (brs, 1H), 5.33 (t, J = 4.5 Hz, 1H), 3.78 (s, 3H), 2.39–2.29 (m, 1H), 2.29–2.18 (m, 1H), 2.02 (s, 3H), 1.97–1.81 (m, 2H), 1.79–1.64 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 153.9, 138.2, 131.6, 131.2, 128.5, 128.3, 123.7, 120.9, 120.7, 114.5, 93.7, 89.2, 71.6, 55.7, 30.2, 29.0, 19.2, 18.5; IR (neat, cm^{-1}): 3323, 2936, 1698, 1515, 1224, 828, 756; ESI HRMS m/z $(M+Na)^+$ calcd 384.1570, obsd 384.1571.



S56

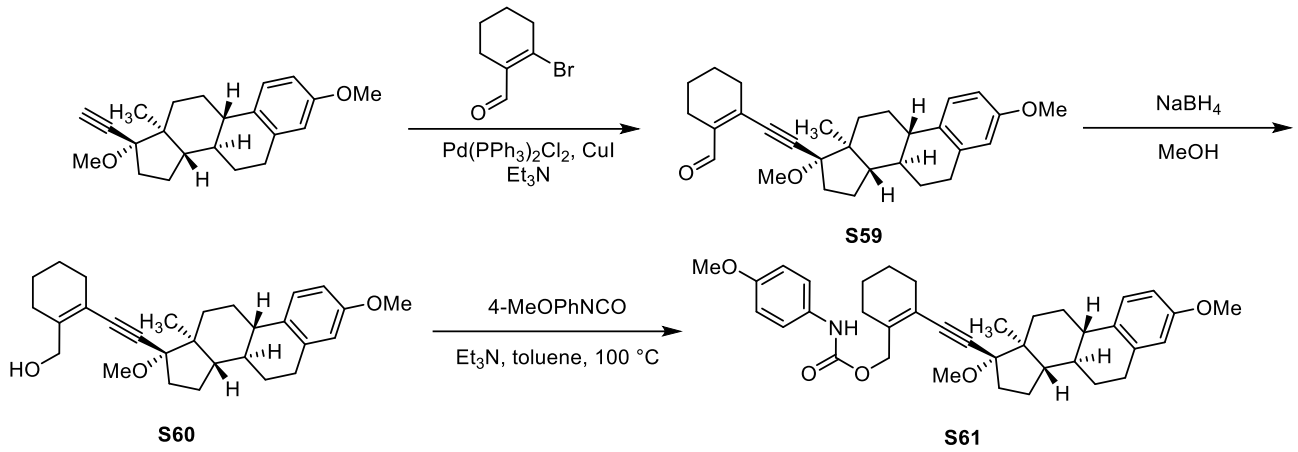
(3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl (4-methoxyphenyl)carbamate (S56). The title compound was obtained as a colorless solid in 78% yield (0.86 g) starting from (3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanol[17] (0.61 g, 3.2 mmol, 1.0 equiv) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.29–7.21 (m, 3H), 7.18–7.12 (m, 2H), 6.86–6.81 (m, 2H), 6.46 (s, 1H), 4.50 (s, 2H), 3.77 (s, 3H), 2.36–2.30 (m, 2H), 2.25–2.16 (m, 2H), 1.79–1.69 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 154.2, 142.6, 139.5, 131.2, 128.5, 128.4, 128.2, 127.0, 120.6, 114.4, 66.6, 55.7, 32.5, 27.3, 23.2, 22.7; IR (neat, cm^{-1}): 3330, 2921, 1694, 1528, 1249, 1055, 824; ESI HRMS m/z $(M+Na)^+$ calcd 360.1570 obsd 360.1571.



S57 **S58**

(2-(Phenylethynyl)cyclohex-1-en-1-yl)methanol (S57). To a solution of 2-(phenylethynyl)cyclohex-1-ene-1-carbaldehyde[18] (0.3 g, 1.38 mmol, 1.0 equiv) in MeOH (20 mL) was adde $NaBH_4$ (78 mg, 2.1 mmol, 1.5 equiv). The reaction mixture was stirred for 1 h at RT and then concentrated under reduced pressure. The residue was diluted with Et_2O and brine (20 mL). The phases were separated and the aqueous phase was extracted twice with Et_2O. The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **S57** as a light yellow oil. The crude product was used in the following step without purification.

(2-(Phenylethynyl)cyclohex-1-en-1-yl)methyl (4-methoxyphenyl)carbamate (S58). The title compound was obtained as a colorless solid (0.31 g, 63% yield over two steps) starting from **S57** (1.38 mmol, 1.0 equiv) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.38 (m, 2H), 7.35–7.22 (m, 5H), 6.88–6.77 (m, 2H), 6.57 (s, 1H), 4.98 (s, 2H), 3.77 (s, 3H), 2.35–2.26 (m, 2H), 2.26–2.15 (m, 2H), 1.72–1.62 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 154.2, 139.5, 131.6, 131.1, 128.4, 128.2, 123.6, 120.8, 120.1, 114.4, 93.3, 88.3, 67.2, 55.7, 30.4, 27.2, 22.3, 22.2; IR (neat, cm^{-1}): 3321, 2930, 1703, 1514, 1218, 1032, 827; ESI HRMS m/z $(M+Na)^+$ calcd 384.1570, obsd 384.1569.

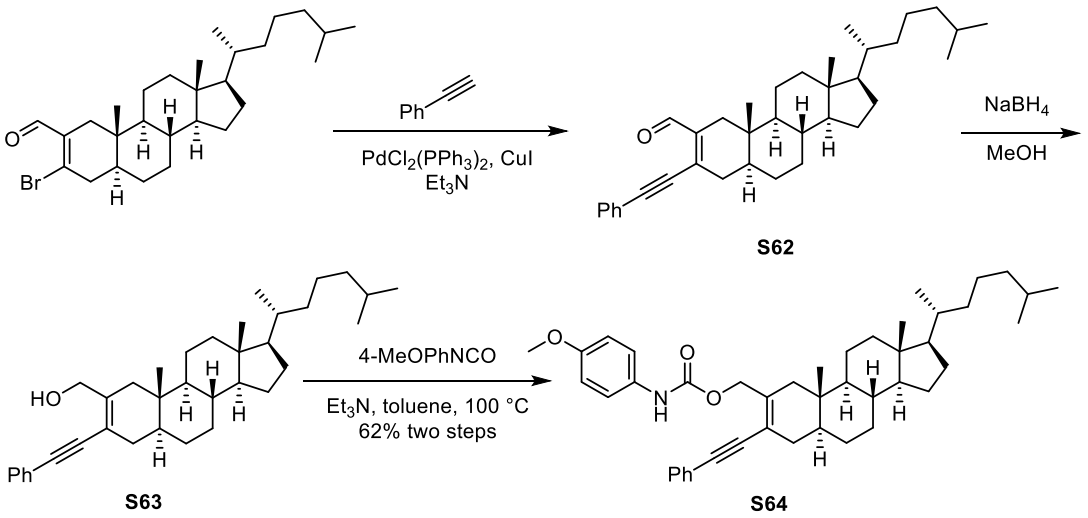


2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)cyclohex-1-ene-1-carbaldehyde (S59). To a solution of 2-bromocyclohex-1-ene-1-carbaldehyde[19] (0.32 g, 1.68 mmol, 1.0 equiv) in Et_3N (20 mL), was added $(PPh_3)_2PdCl_2$ (0.06 g, 0.85 mmol, 0.05 equiv) and ethinylestradiol 3,17-dimethyl ether (0.6 g, 1.85 mmol, 1.1 equiv). The solution was stirred at RT for 15 min before addition of CuI (32 mg, 0.17 mmol, 0.1 equiv). The resulting mixture was stirred at 50 °C for 12 h. The reaction mixture was cooled to RT and filtered through Celite. The filtrate was concentrated under reduced pressure. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S59** in 87% yield (0.63 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 3.77 (s, 3H), 3.42 (s, 3H), 2.91–2.80 (m, 2H), 2.50–2.43 (m, 2H), 2.38–2.16 (m, 5H), 2.06 (ddd, *J* = 13.6, 11.9, 3.8 Hz, 1H), 1.96–1.75 (m, 4H), 1.75–1.62 (m, 5H), 1.55–1.33 (m, 4H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 157.6, 142.7, 140.2, 138.0, 132.5, 126.5, 113.9, 111.7, 100.6, 86.6, 85.2, 55.4, 53.8, 50.4, 48.3, 43.9, 39.4, 36.9, 34.7, 33.0, 30.0, 27.5, 26.7, 23.0, 22.2, 22.0, 21.2, 13.0; IR (neat, cm^{-1}): 2933, 1675, 1500, 1257, 1095, 1040; ESI HRMS m/z $(M+Na)^+$ calcd 455.2557, obsd 455.2557.

(2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)cyclohex-1-en-1-yl)methanol (S60). The title compound was obtained as a light yellow oil starting from **S59** (0.53 g, 1.23 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S57**. The crude product was used in the following step without purification.

(2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)cyclohex-1-en-1-yl)methyl (4-methoxyphenyl)carbamate (S61). The title compound was obtained as a colorless solid in 56% yield of two steps (0.4 g) starting from **S60** (1.23 mmol) by following the General Procedure II. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.79–6.72 (m, 2H), 6.67 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 6.52 (s, 1H), 4.95–4.83 (m, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.41 (s, 3H), 2.89–2.73 (m, 2H), 2.36–2.14 (m, 7H), 2.07–1.95 (m, 2H), 1.90–1.75 (m, 4H), 1.72–1.59 (m, 5H), 1.52–1.31 (m, 4H), 0.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5,

156.0, 153.9, 138.6, 138.1, 132.8, 131.1, 126.5, 120.4, 114.3, 113.9, 111.6, 94.3, 86.9, 86.5, 67.3, 55.6, 55.3, 53.5, 50.0, 48.0, 43.7, 39.4, 37.1, 34.6, 30.7, 30.0, 27.3, 27.3, 26.8, 22.9, 22.3, 22.2, 13.0; IR (neat, cm^{-1}): 3352, 2922, 1696, 1515, 1222, 1034, 828; ESI HRMS m/z $(M+Na)^+$ calcd 606.3190, obsd 606.3194.

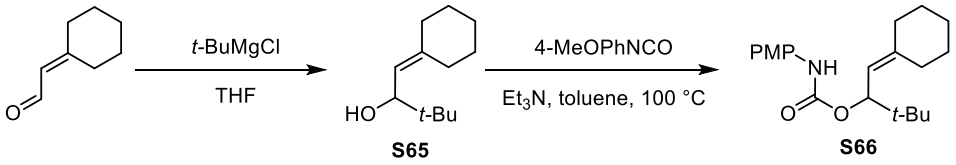


(5*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(phenylethynyl)-2,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-2-carbaldehyde (S62). The title compound was obtained as a colorless solid (1.0 g, 90% yield) starting from the (5α)-3-Bromocholest-2-ene-2-carboxaldehyde[20] (1.1 g, 2.3 mmol, 1.0 equiv) and phenylacetylene (0.3 mL, 2.7 mmol, 1.2 equiv) by following the procedure described for the synthesis of **S59**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.49–7.44 (m, 2H), 7.38–7.31 (m, 3H), 2.57 (d, *J* = 18.3 Hz, 1H), 2.45–2.36 (m, 1H), 2.28–2.18 (m, 1H), 2.00 (dt, *J* = 12.7, 3.4 Hz, 1H), 1.87–1.67 (m, 3H), 1.65–1.49 (m, 4H), 1.47–1.19 (m, 9H), 1.18–0.95 (m, 8H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.87 (d, *J* = 2.2 Hz, 3H), 0.86 (d, *J* = 2.2 Hz, 3H), 0.80–0.73 (m, 1H), 0.72 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 141.9, 139.1, 131.8, 129.3, 128.7, 122.5, 98.8, 86.1, 56.5, 56.4, 53.9, 42.7, 41.3, 40.0, 39.7, 37.2, 36.5, 36.4, 36.0, 35.7, 34.2, 31.7, 28.4, 28.2, 28.1, 24.4, 24.0, 23.0, 22.8, 21.2, 18.9, 12.2, 12.0; IR (neat, cm^{-1}): 293, 1675, 1443, 1222, 756, 689; ESI HRMS m/z $(M+Na)^+$ calcd 521.3754, obsd 521.3753.

((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(phenylethynyl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-2-yl)methanol (S63). The title compound was obtained as a light yellow oil starting from **S62** (1.0 g, 2 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S57**. The crude product was used in the following step without purification.

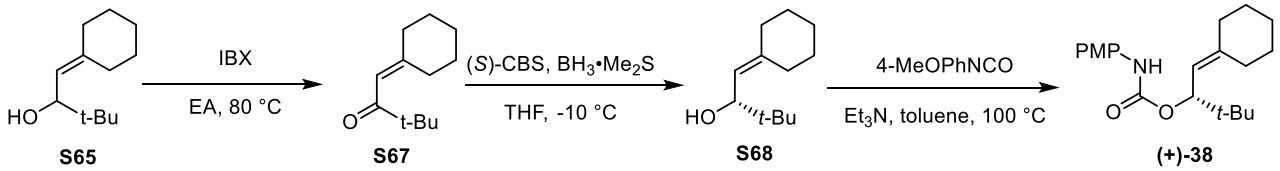
((5*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(phenylethynyl)-2,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-2-yl)methyl (4-methoxyphenyl)carbamate (S64). The title compound was obtained as a colorless solid in 62% yield over two steps (0.8 g) starting from **S63** (2 mmol) by following the General Procedure II. ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.47–7.38 (m, 2H), 7.34–7.22 (m, 5H), 6.90–6.78 (m, 2H), 6.61 (s, 1H), 5.02–4.89 (m, 2H), 3.77 (s, 3H), 2.23–2.13 (m, 2H), 2.07–1.94 (m, 2H), 1.91–1.76 (m, 2H), 1.73–1.64 (m, 1H), 1.63–1.44 (m, 4H), 1.45–1.18 (m, 8H), 1.19–0.94 (m, 8H), 0.94–0.81 (m, 10H), 0.80–0.70 (m, 4H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 154.2, 138.4, 131.6, 131.2, 128.4, 128.2, 123.6, 120.8, 119.0, 114.4, 93.4, 88.0, 67.5, 56.5, 56.4, 55.7, 53.9, 42.6, 41.9, 41.3, 40.1, 39.7, 36.4, 36.0, 35.7, 35.2, 34.7, 31.7, 28.4, 28.3, 28.2, 24.4, 24.0, 23.0, 22.8, 21.3, 18.9, 12.2, 12.1; IR (neat, cm^{-1}): 3353, 2929, 1731, 1514, 1259, 828, 750; ESI HRMS m/z $(M+Na)^+$ calcd 672.4387, obsd 672.4386.



1-Cyclohexylidene-3,3-dimethylbutan-2-ol (S65). The title compound was obtained as a light yellow oil (0.6 g, 40% yield) starting from 2-cyclohexylideneacetaldehyde[9] (1.0 g, 8.2 mmol, 1.0 equiv) and *t*-BuMgCl (1.0 M in THF, 16 mL, 2.0 equiv) by following the procedure described for the synthesis of **S1**. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S65**. The spectral data were consistent with those reported in the literature.[21]

1-Cyclohexylidene-3,3-dimethylbutan-2-yl (4-methoxyphenyl)carbamate (S66). The title compound was obtained as a colorless solid in 74% yield (0.5 g) starting from **S65** (0.4 g, 2.2 mmol) by following the General Procedure II. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.24 (m, 2H), 6.87–6.80 (m, 2H), 6.47 (s, 1H), 5.33–5.28 (m, 1H), 5.14–5.09 (m, 1H), 3.77 (s, 3H), 2.37–2.23 (m, 2H), 2.16–2.04 (m, 2H), 1.67–1.43 (m, 6H), 0.93 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 153.9, 145.9, 131.6, 120.6, 117.5, 114.3, 78.1, 55.7, 37.6, 35.0, 29.8, 28.8, 27.9, 26.9, 26.0; IR (neat, cm^{-1}): 3326, 2930, 1698, 1515, 1227, 1029, 828; ESI HRMS m/z $(M+H)^+$ calcd 354.2040, obsd 354.2041.

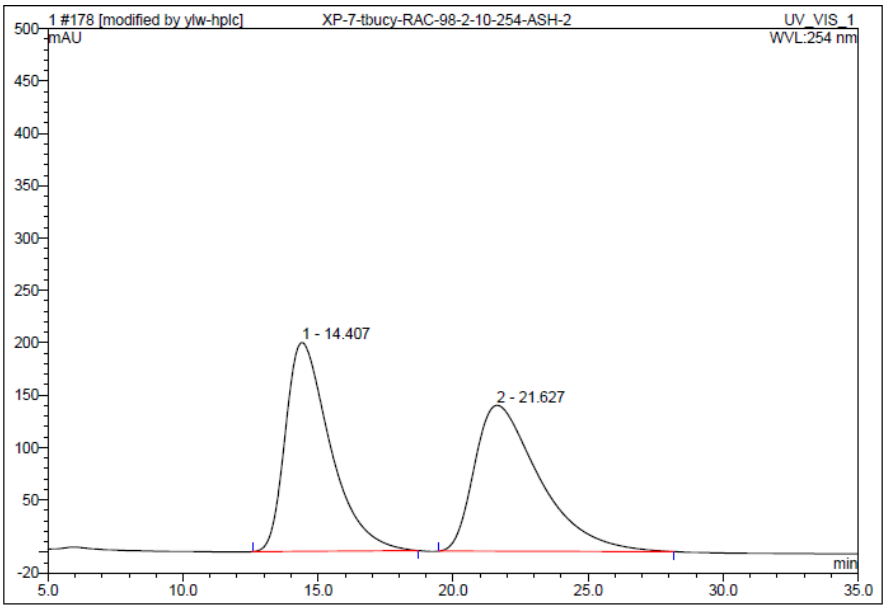


1-Cyclohexylidene-3,3-dimethylbutan-2-one (S67). A suspension of **S65** (1.0 g, 5.5 mmol, 1.0 equiv) and IBX (14.9 g, 16.4 mmol, 3 equiv) in EtOAc (30 mL) was heated to 80 °C and stirred for 5 h. The resulting mixture was cooled to RT, filtered and concentrated under reduced pressure to afford **S67** as a light yellow oil (0.7 g, 70%), which was used in the following step without further purification.

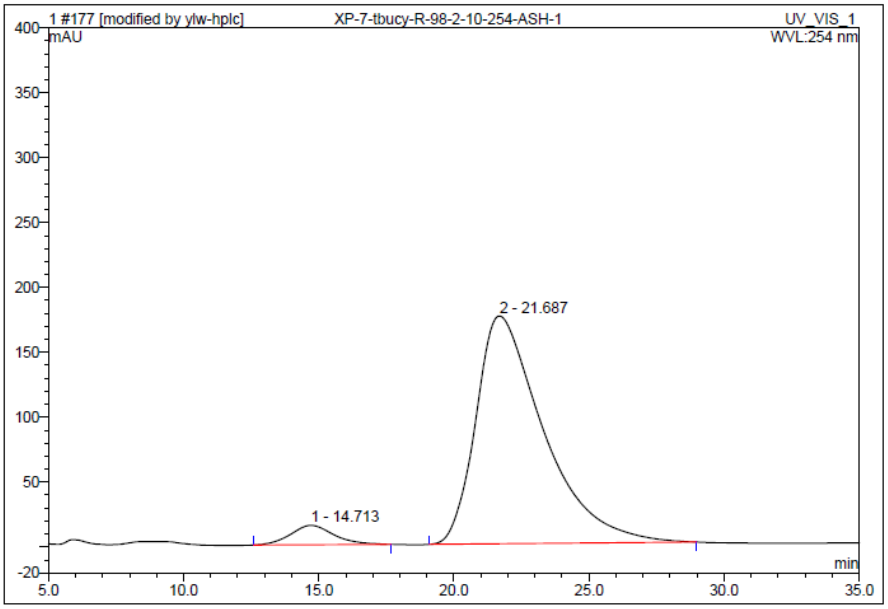
(*R*)-1-Cyclohexylidene-3,3-dimethylbutan-2-ol (S68). The enantioenriched allylic alcohol was prepared by following a reported procedure.[22] To a solution of (*S*)-(-)-2-methyl-CBS-oxazaborolidine (1.0 M in toluene, 3 mL, 1.0 equiv) in THF (20 mL) at −10 °C was added

$BH_3 \cdot Me_2S$ (2.0 M in THF, 3 mL, 2.0 equiv). The reaction mixture was stirred 15 min at at −10 °C before addition of a solution of **S67** (0.54 g, 3 mmol, 1.0 equiv) in THF (20 mL) dropwise over 15 min. The reaction mixture was warmed to ambient temperature, stirred for 1.5 h and then cooled to −78 °C. MeOH (20 mL) was added to quenced the reaction. The reaction mixture was slowly warmed to room temperature, diluted with diethyl ether, and washed with saturated aqueous $NaHCO_3$ and then brine. The organic solution was dried over $MgSO_4$, filtered, and concentratedunder reduced pressure. The crude product was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S68** as a light yellow oil (0.2 g, 37%). The spectral data were consistent with the those reported.[21]

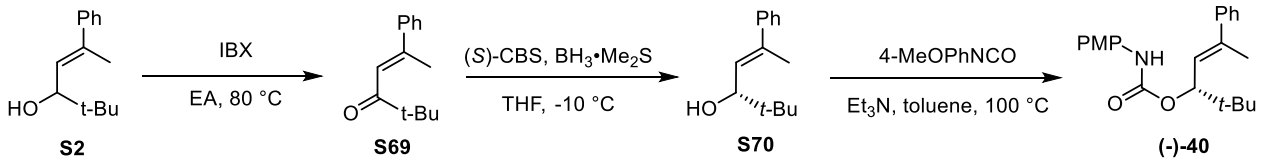
(*R*)-1-Cyclohexylidene-3,3-dimethylbutan-2-yl (4-methoxyphenyl)carbamate ((+)-38). The title compound was obtained as a colorless solid in 77% yield (0.28 g) starting from **S68** (0.2 g, 1.1 mmol) by following the General Procedure II. $[\alpha]_D^{20}$ = +15.3° (*c* 1.0, $CHCl_3$), 95:5 e.r. (determined by HPLC: Chiralcel AS-H column, 2/98 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; retention time = 14.71 min (minor), 21.69 min (major). The spectral data (NMR, IR, MS) were the same with those of *rac*-**S66**.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	14.41	n.a.	199.484	384.741	49.66	n.a.	BMB*
2	21.63	n.a.	139.438	389.975	50.34	n.a.	BMB*
Total:			338.922	774.716	100.00	0.000	



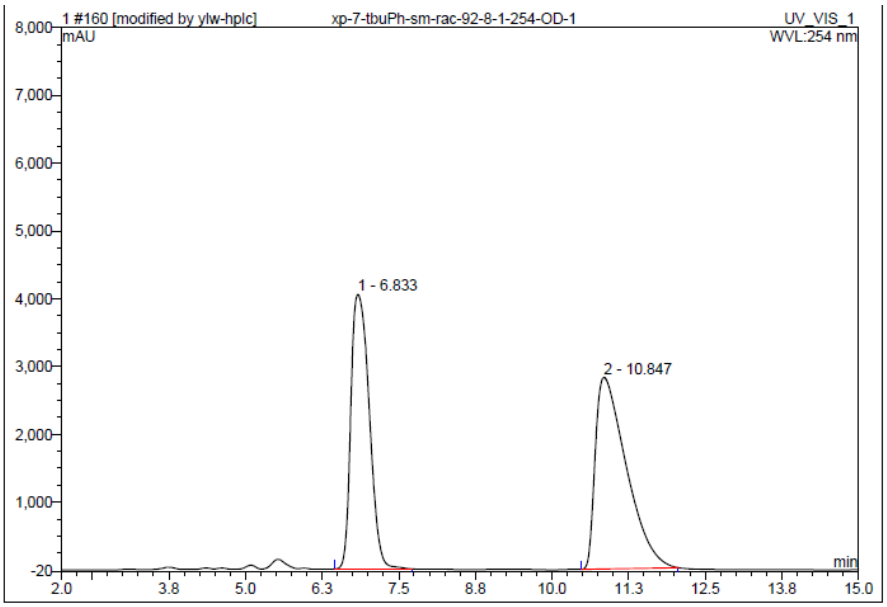
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	14.71	n.a.	14.909	27.684	5.15	n.a.	BMB*
2	21.69	n.a.	175.567	510.232	94.85	n.a.	BMB*
Total:			190.476	537.916	100.00	0.000	



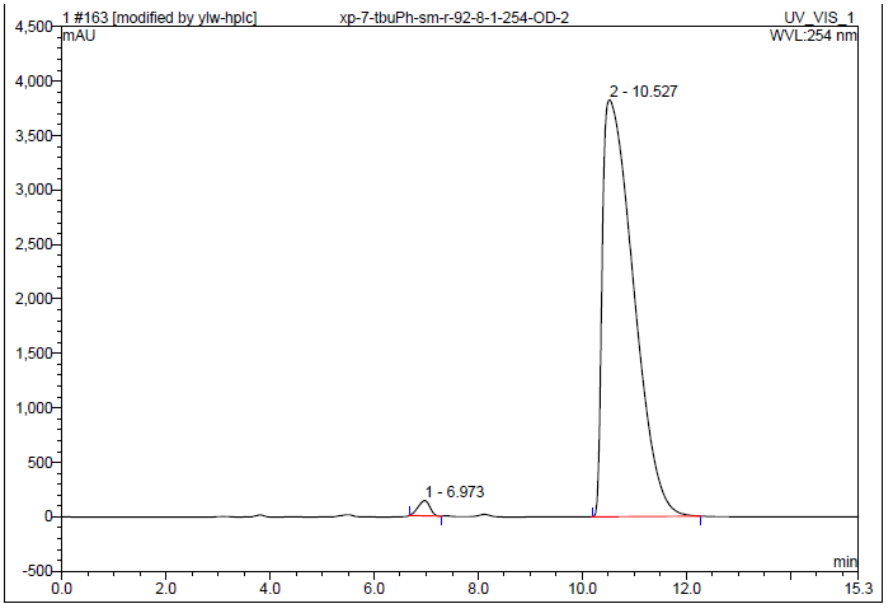
(*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-one (S69). The title compound was obtained as a light yellow oil (0.6 g, 40% yield) starting from **S2** (1.0 g, 4.9 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S67**. The crude product was used in the following step without further purification.

(*R*,*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-ol (S70). The title compound was obtained as a light yellow oil (0.24 g, 60% yield) starting from **S69** (0.4 g, 2.5 mmol, 1.0 equiv) by following the procedure described for the synthesis of **S68**. The spectral data (NMR, IR, MS) were the same with those of *rac*-**S2**.

(*R*,*E*)-2,2-Dimethyl-5-phenylhex-4-en-3-yl (4-methoxyphenyl)carbamate ((-)-40). The title compound was obtained as a colorless solid in 89% yield (0.37 g) starting from **S70** (0.24 g, 1.2 mmol) by following the General Procedure II. $[\alpha]_D^{20} = -74.3°$ (*c* 1.0, $CHCl_3$), 99:1 e.r. (determined by HPLC: Chiralcel OD-H column, 8/92 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; retention time = 6.97 min (minor), 10.53 min (major). The spectral data (NMR, IR, MS) were the same with those of *rac*-**S3**.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	6.83	n.a.	4049.959	1406.323	45.95	n.a.	BMB*
2	10.85	n.a.	2827.903	1654.302	54.05	n.a.	BMB*
Total:			6877.863	3060.625	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	6.97	n.a.	139.954	36.550	1.37	n.a.	BMB*
2	10.53	n.a.	3828.714	2640.250	98.63	n.a.	BMB*
Total:			3968.668	2676.799	100.00	0.000	

7. References:

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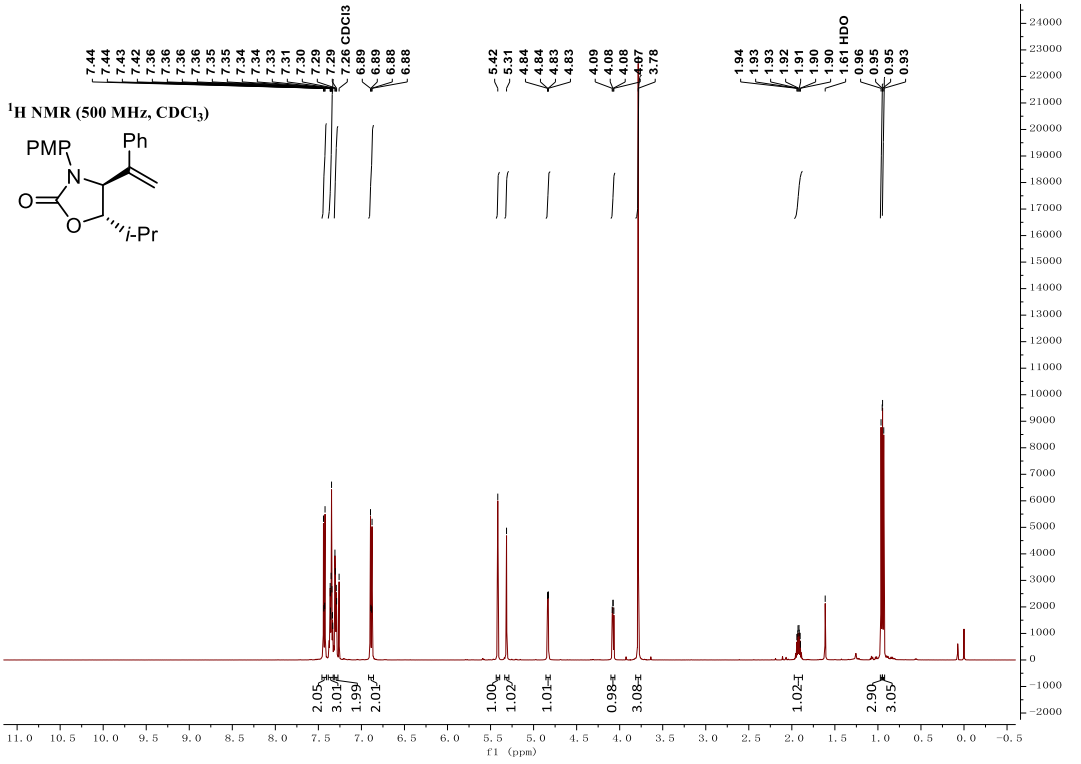
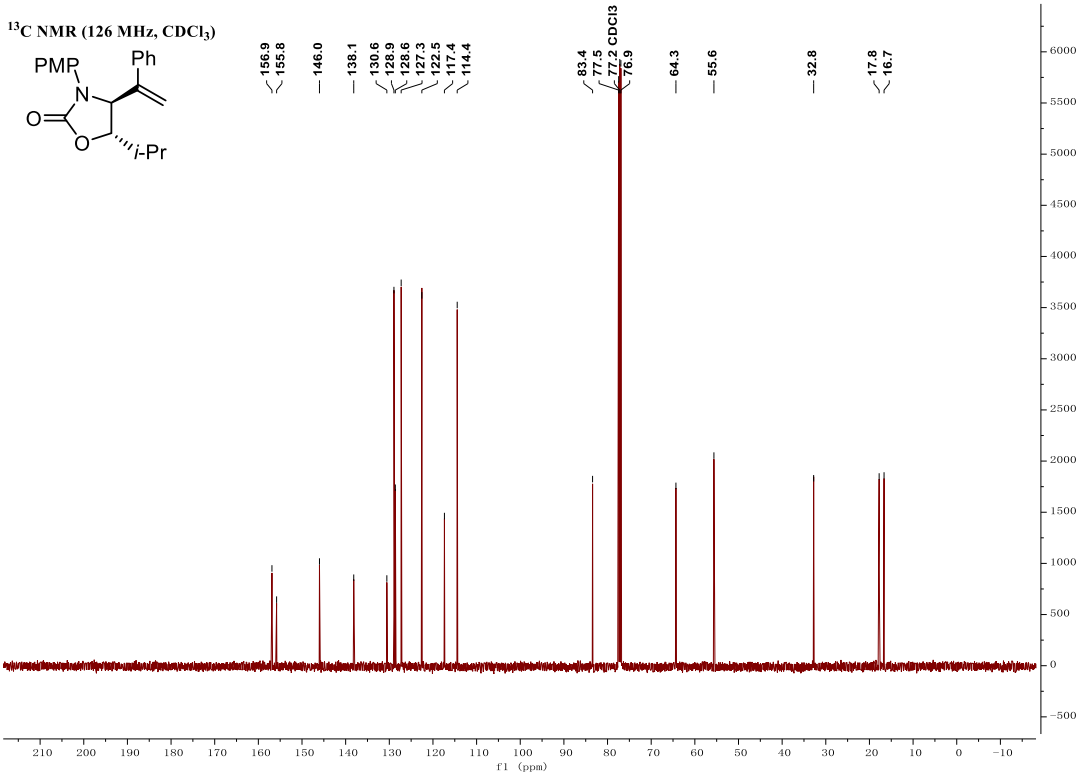
8. NMR Spectra for New Compounds

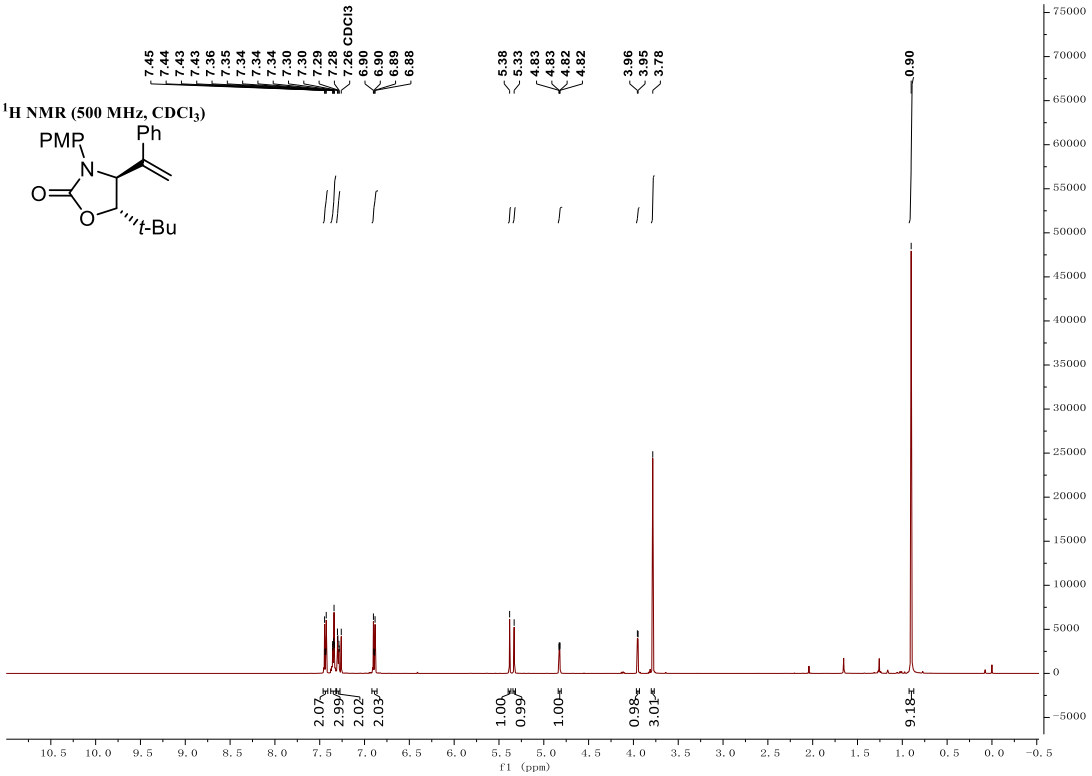
Compound 2


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
Ph
N
O
O
i-Pr
7.44 7.44 7.43 7.42 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.31 7.30 7.29 7.29 7.26 CDCl3 6.89 6.89 6.88 6.88
5.42 5.31 4.84 4.84 4.83 4.83
4.09 4.08 4.08 4.07 3.78
1.94 1.93 1.93 1.92 1.91 1.90 1.90 1.61 HDO 0.96 0.95 0.95 0.93
2.05 3.01 1.99 2.01 1.00 1.02 1.01 0.98 3.08 1.02 2.90 3.05
f1 (ppm)

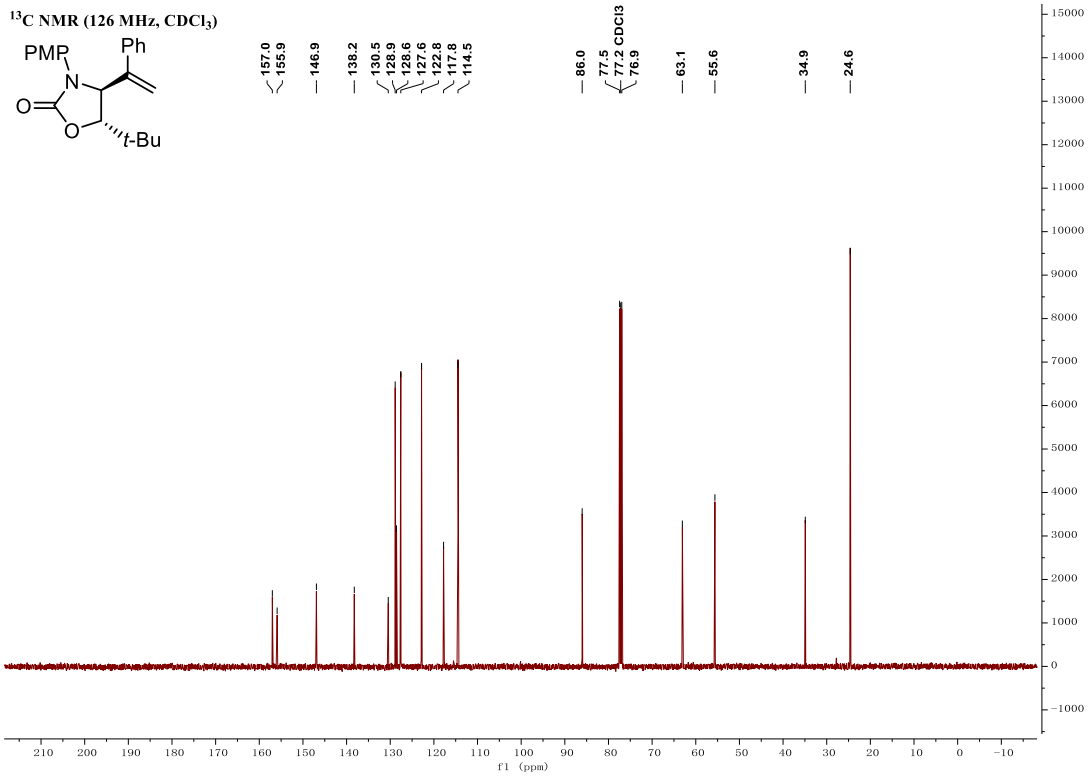

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
Ph
N
O
O
i-Pr
156.9 155.8 146.0 138.1 130.6 128.9 128.6 127.3 122.5 117.4 114.4
83.4 77.5 77.2 CDCl3 76.9 64.3 55.6 32.8 17.8 16.7
f1 (ppm)

Compound 3

^{1}H NMR (500 MHz, $CDCl_3$)

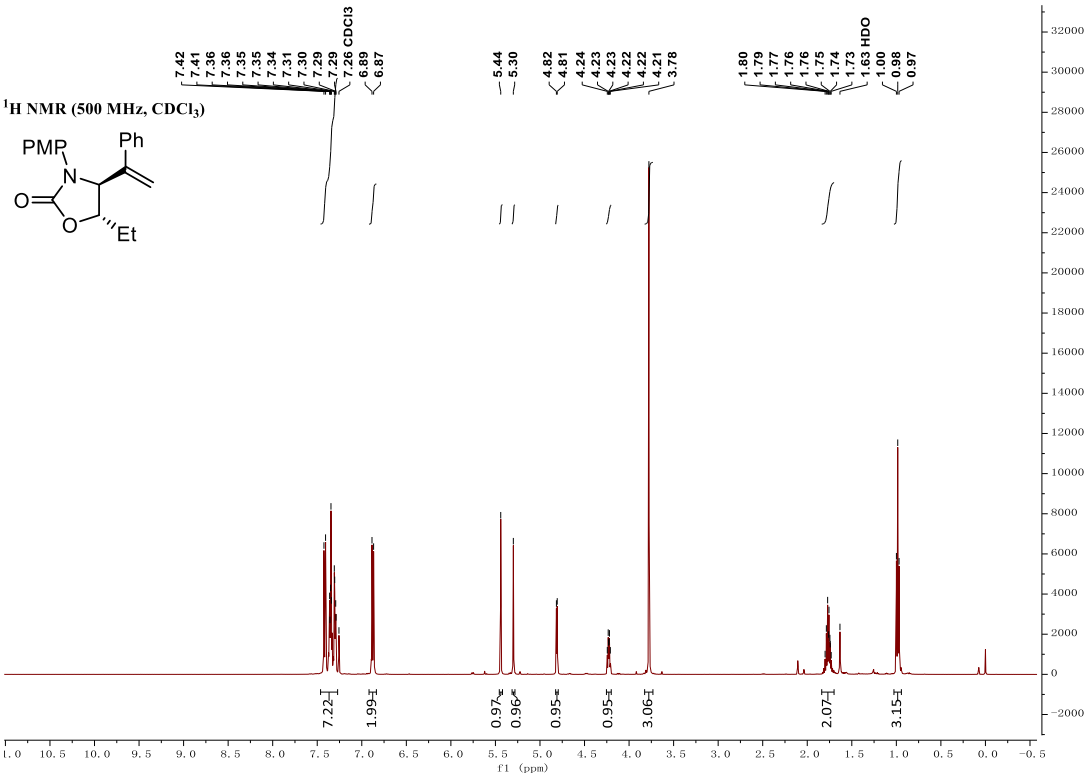


^{13}C NMR (126 MHz, $CDCl_3$)

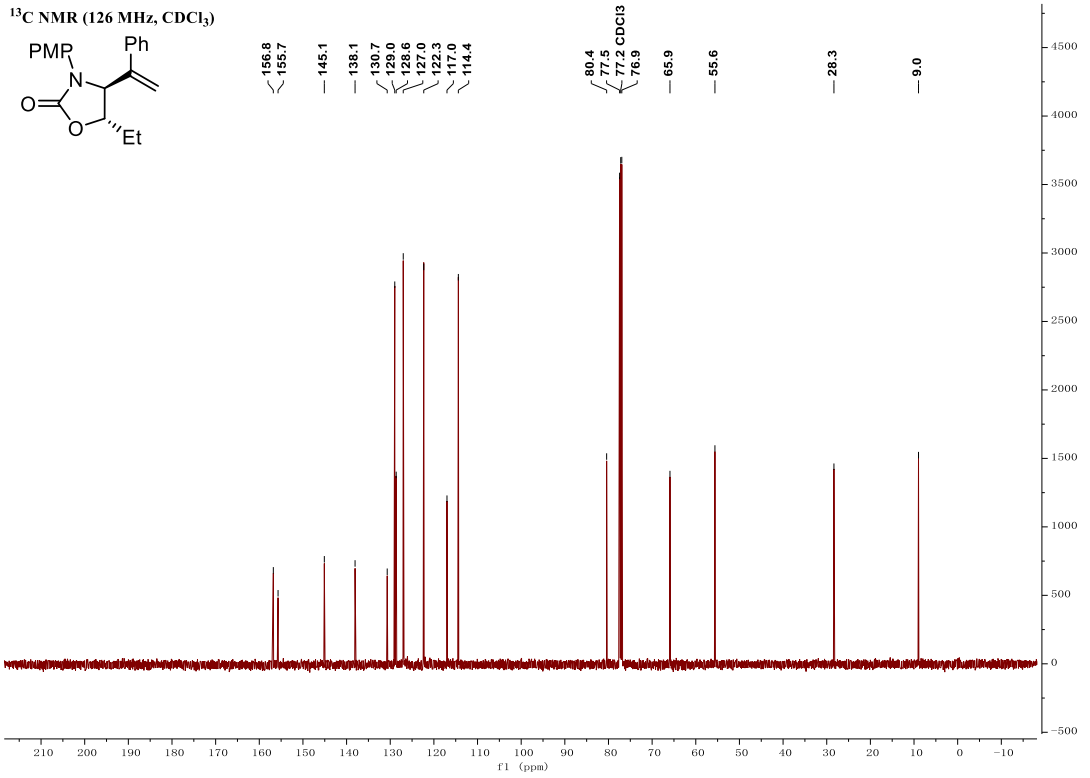


Compound 4

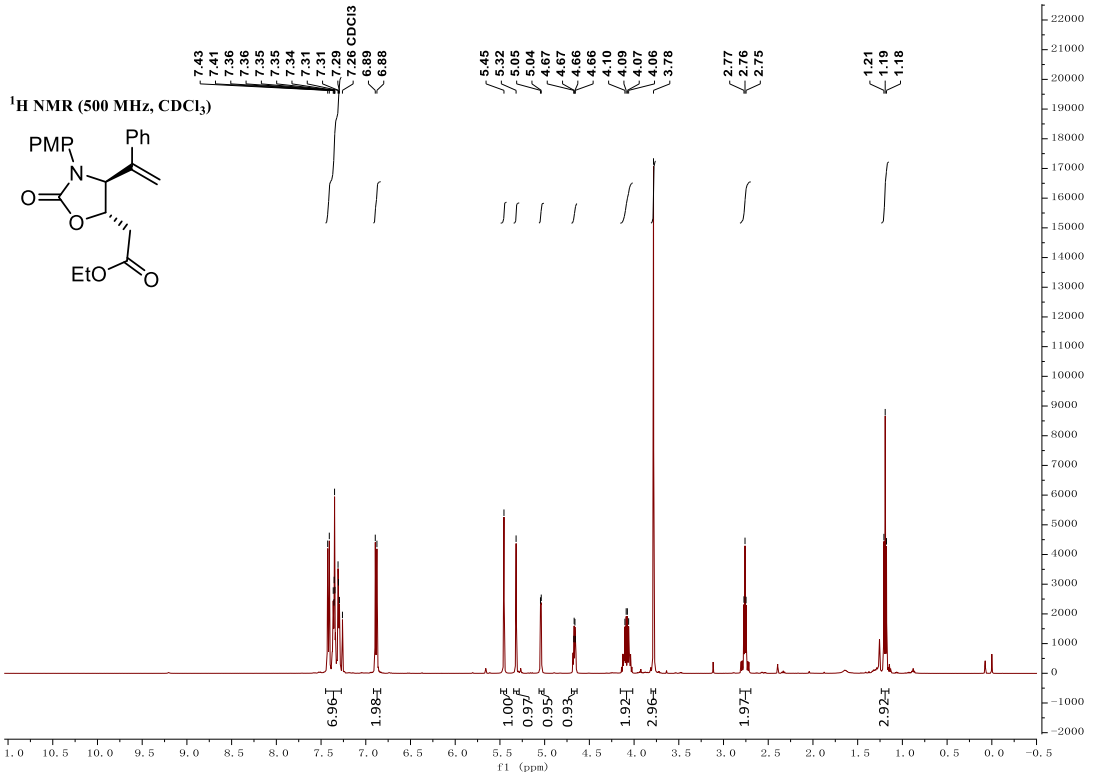
^{1}H NMR (500 MHz, $CDCl_3$)

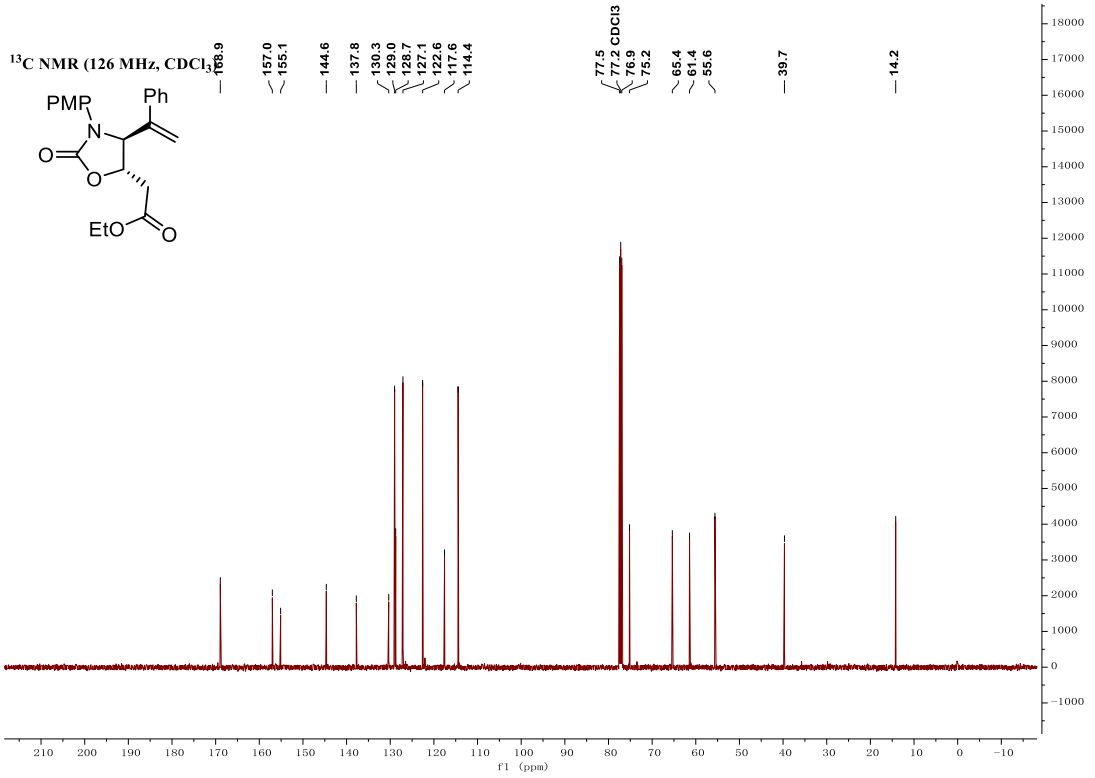


^{13}C NMR (126 MHz, $CDCl_3$)

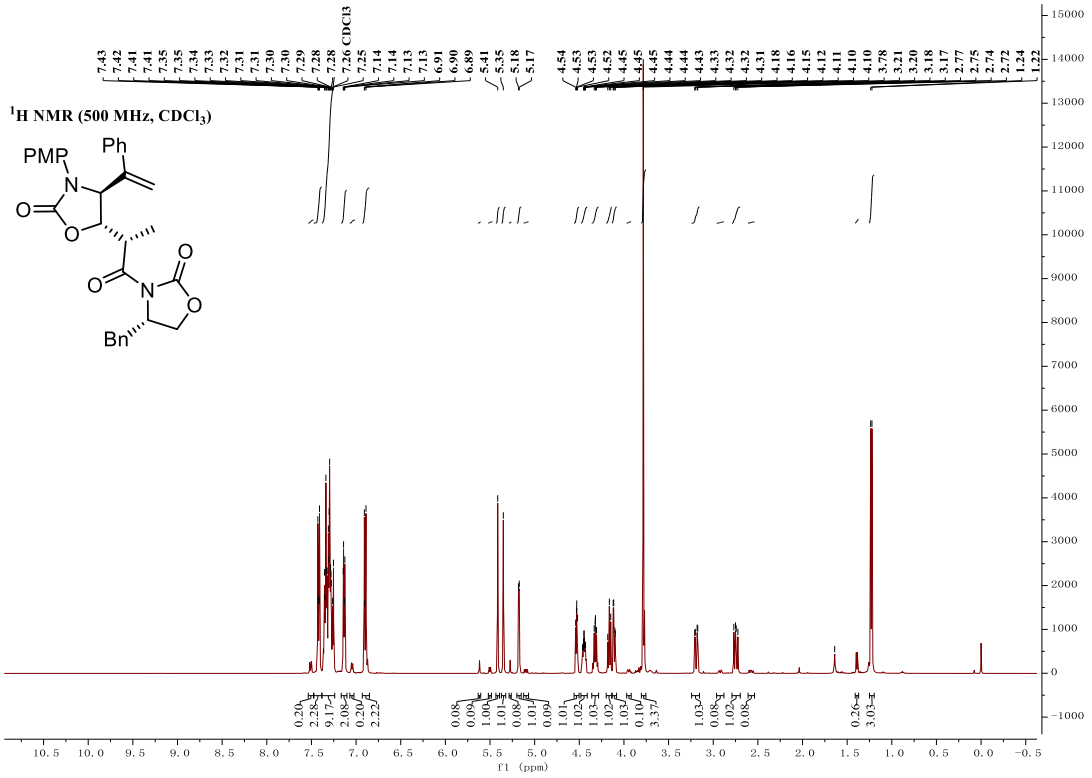


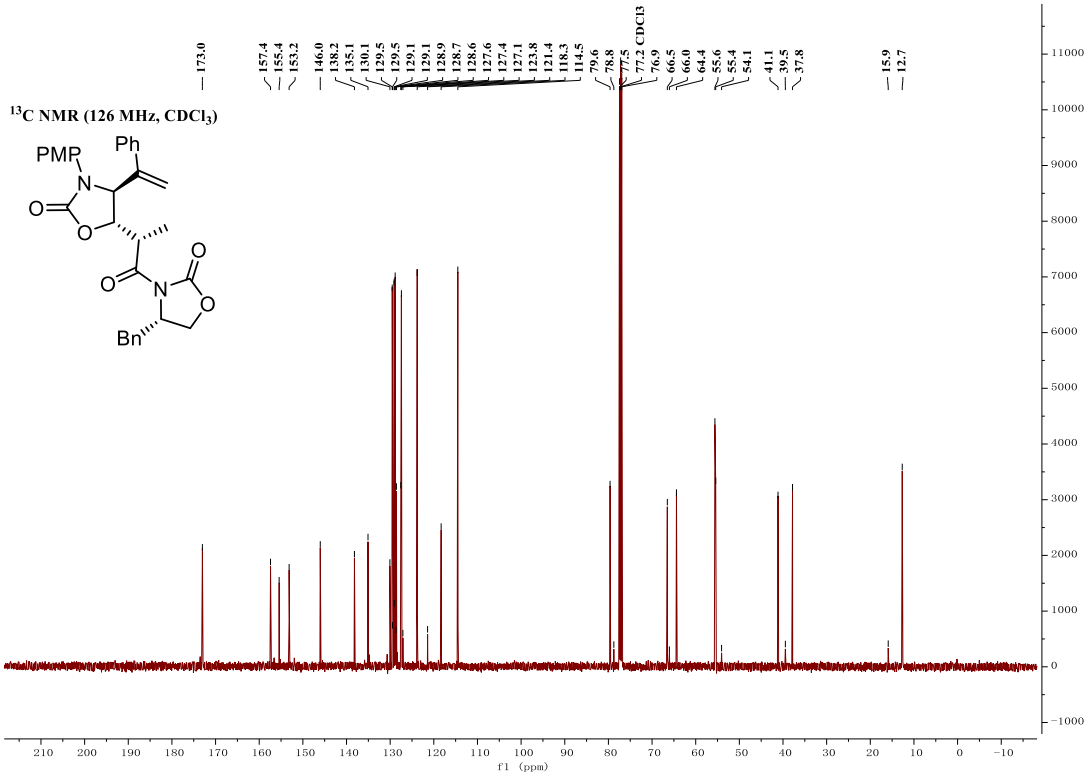
Compound 5


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
Ph
N
O
O
EtO
O
7.43
7.41
7.36
7.35
7.35
7.34
7.31
7.31
7.29
7.26 CDCl3
6.89
6.88
5.45
5.32
5.05
5.04
4.67
4.67
4.66
4.66
4.10
4.09
4.07
4.06
3.78
2.77
2.76
2.75
1.21
1.19
1.18
6.96
1.98
1.00
0.97
0.95
0.93
1.92
2.96
1.97
2.92
f1 (ppm)


^{13}C NMR (126 MHz, $CDCl_3$)
PMP
Ph
N
O
O
EtO
O
168.9
157.0
155.1
144.6
137.8
130.3
129.0
128.7
127.1
122.6
117.6
114.4
77.5
77.2 CDCl3
76.9
75.2
65.4
61.4
55.6
39.7
14.2
f1 (ppm)

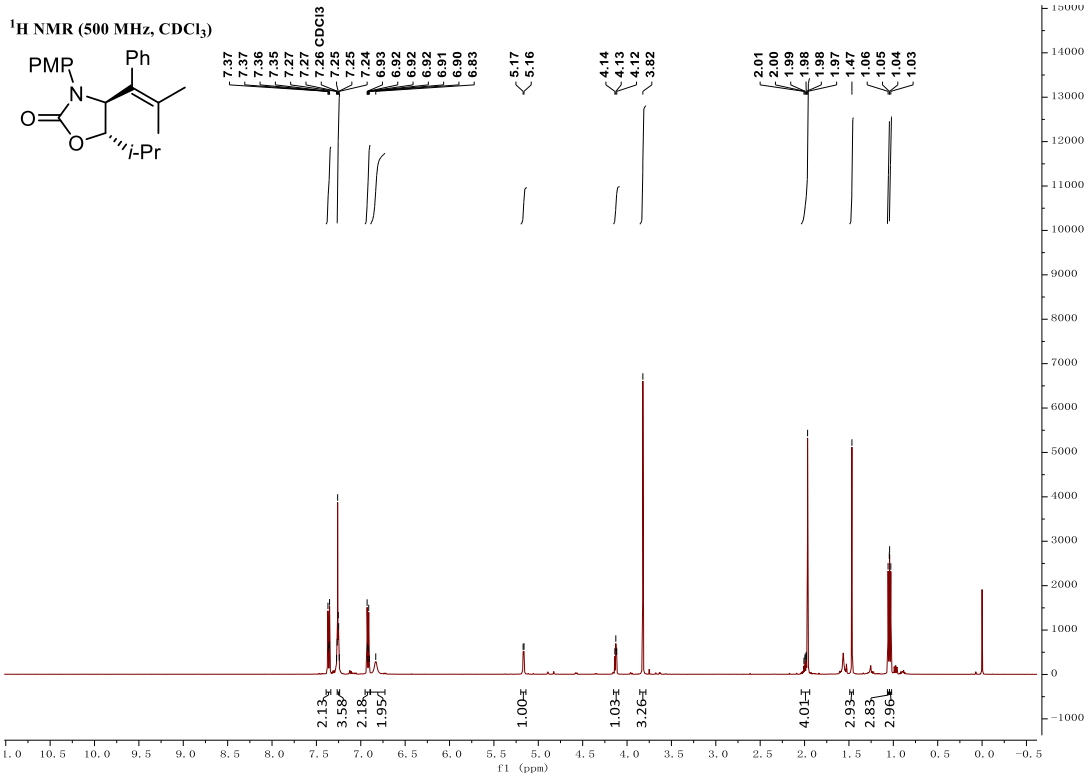
Compound 6


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
Ph
N
O
O
O
N
O
Bn
7.43 7.42 7.41 7.41 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.26 CDCl3 7.25 7.14 7.14 7.13 7.13 6.91 6.90 6.89 5.41 5.35 5.18 5.17
4.54 4.53 4.53 4.52 4.45 4.45 4.45 4.44 4.44 4.43 4.33 4.32 4.31 4.18 4.16 4.15 4.12 4.11 4.10 4.10 3.78 3.21 3.20 3.18 3.17 2.77 2.75 2.74 2.72 1.24 1.22
0.20 2.28 9.17 2.08 0.20 2.22 0.08 0.09 1.00 1.01 0.08 1.01 0.09 1.01 1.02 1.03 1.02 1.03 0.10 3.37 1.03 0.08 1.02 0.08 0.26 3.03
f1 (ppm)

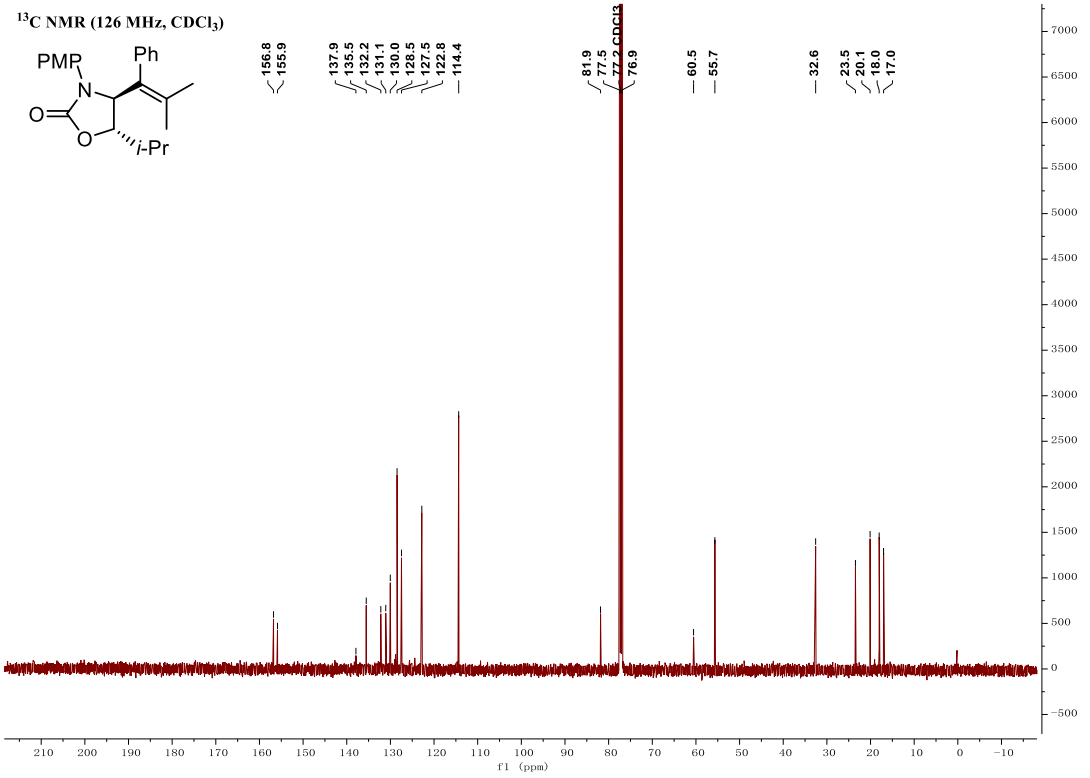

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
Ph
N
O
O
O
N
O
Bn
173.0
157.4 155.4 153.2 146.0 138.2 135.1 130.1 129.5 129.5 129.1 129.1 128.9 128.7 128.6 127.6 127.4 127.1 123.8 121.4 118.3 114.5 79.6 78.8 77.5 77.2 CDCl3 76.9 66.5 66.0 64.4 55.6 55.4 54.1 41.1 39.5 37.8 15.9 12.7
f1 (ppm)

Compound 7

^{1}H NMR (500 MHz, $CDCl_3$)

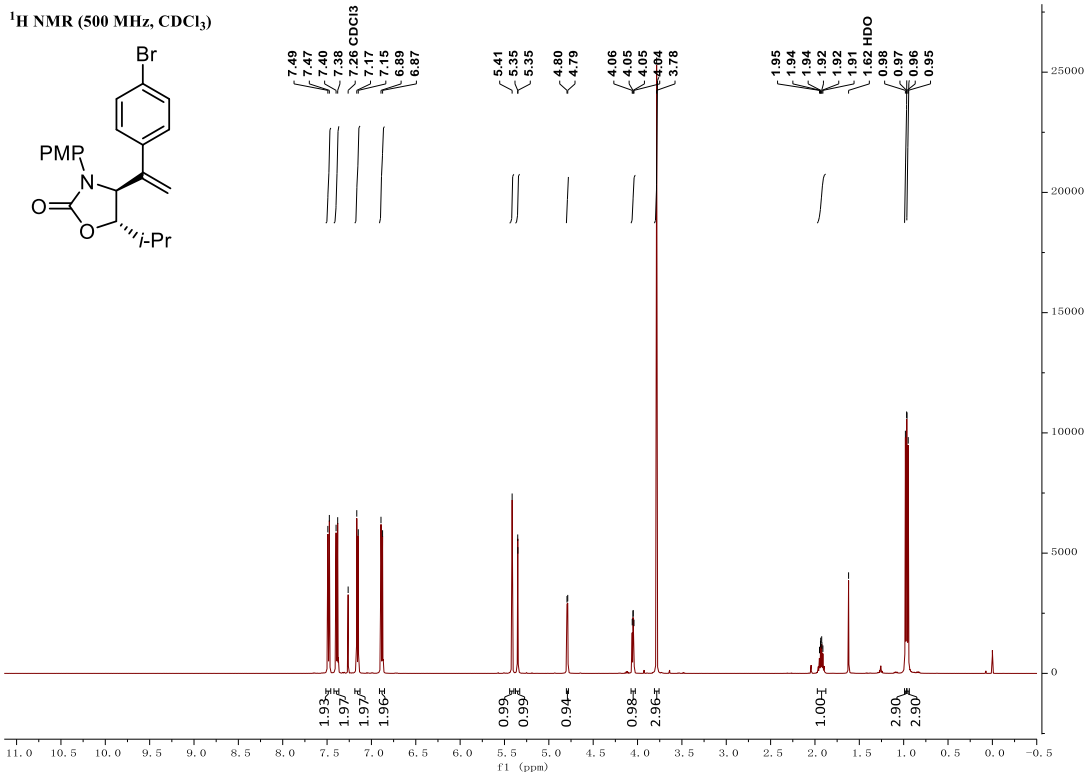


^{13}C NMR (126 MHz, $CDCl_3$)

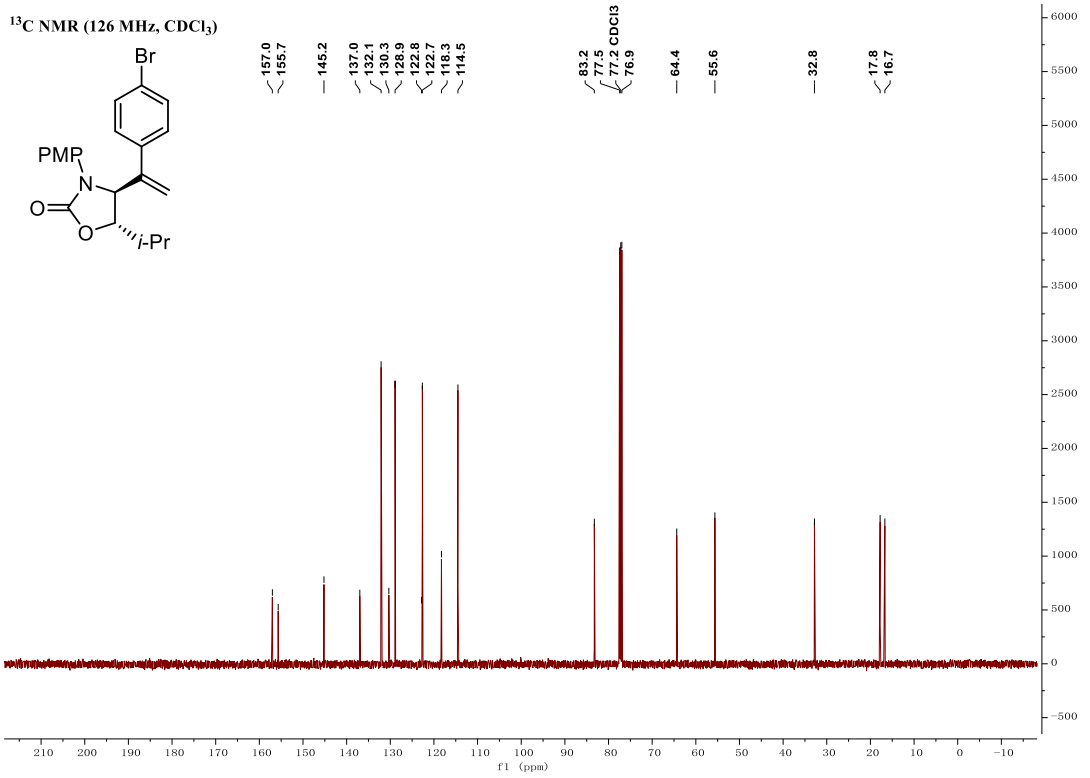


Compound 8

^{1}H NMR (500 MHz, $CDCl_3$)

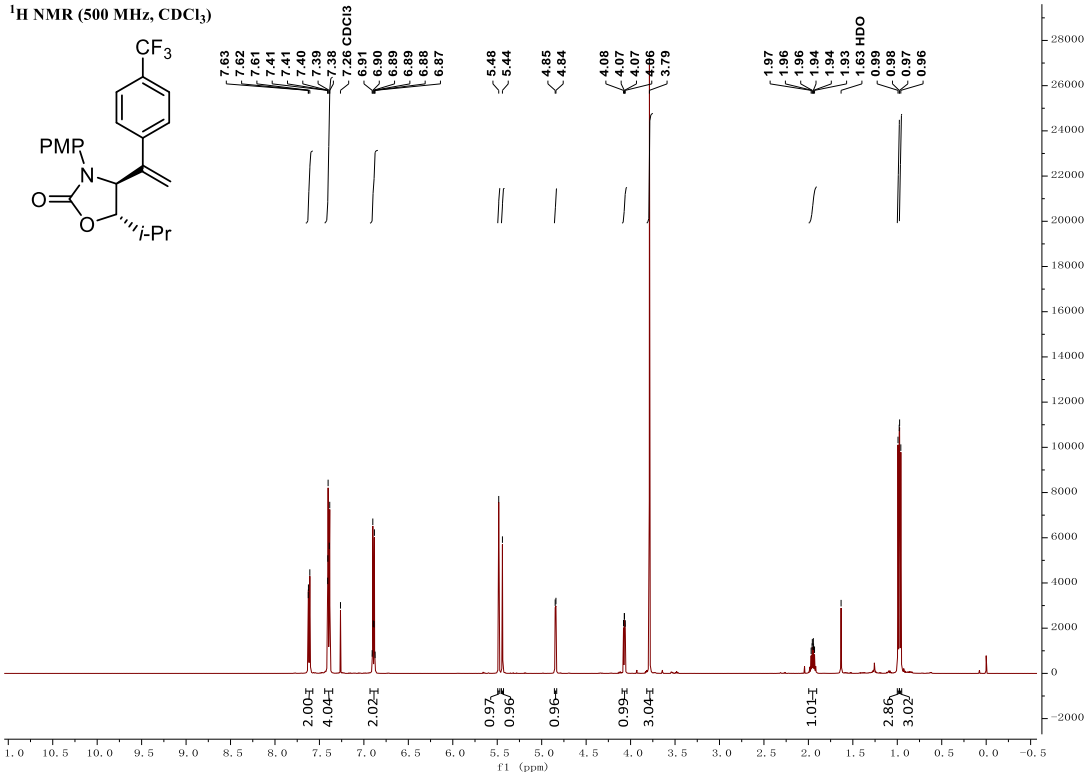


^{13}C NMR (126 MHz, $CDCl_3$)

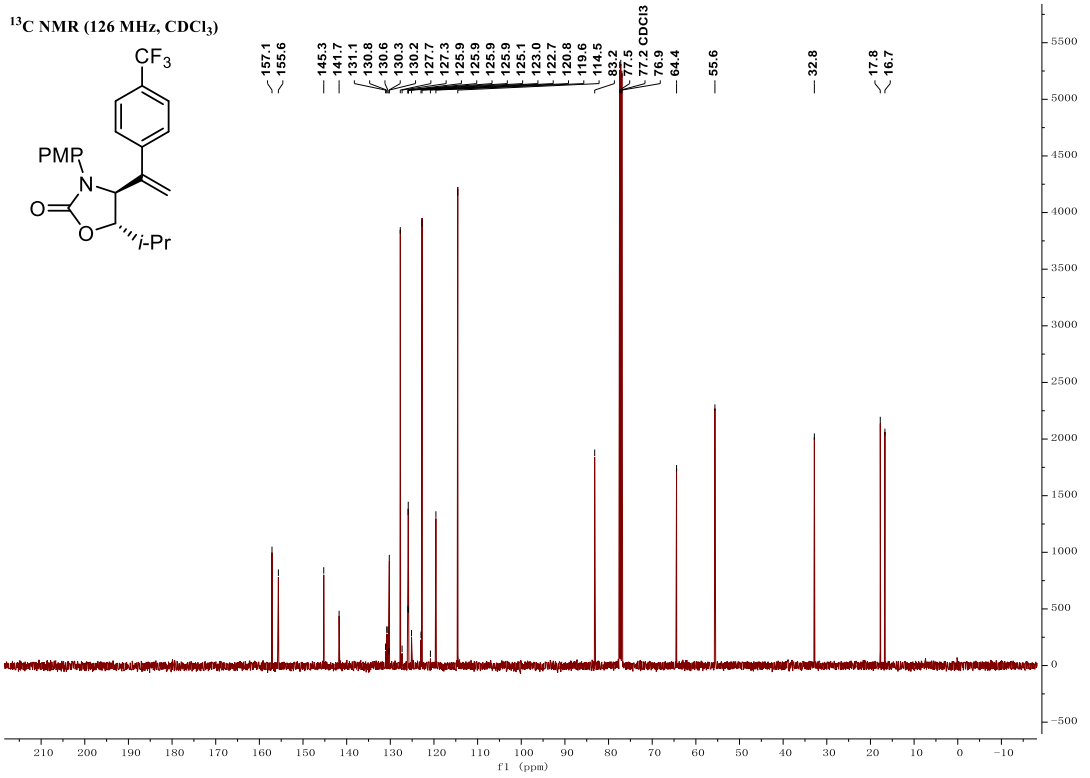


Compound 9

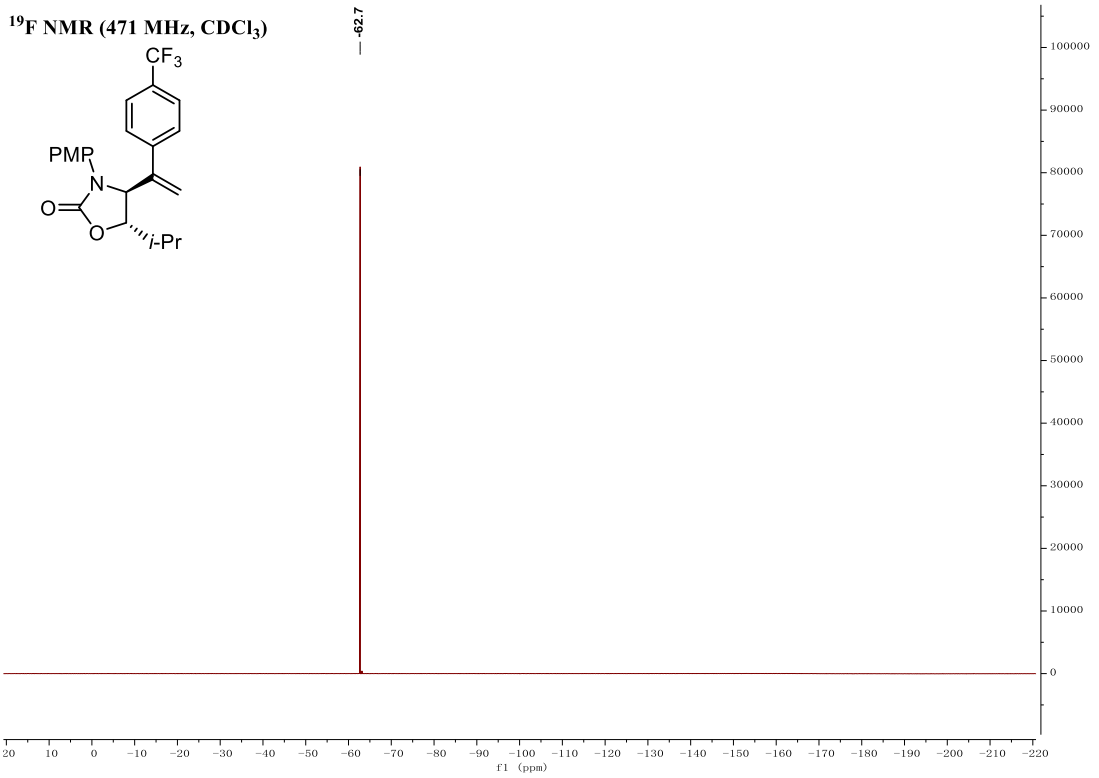
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

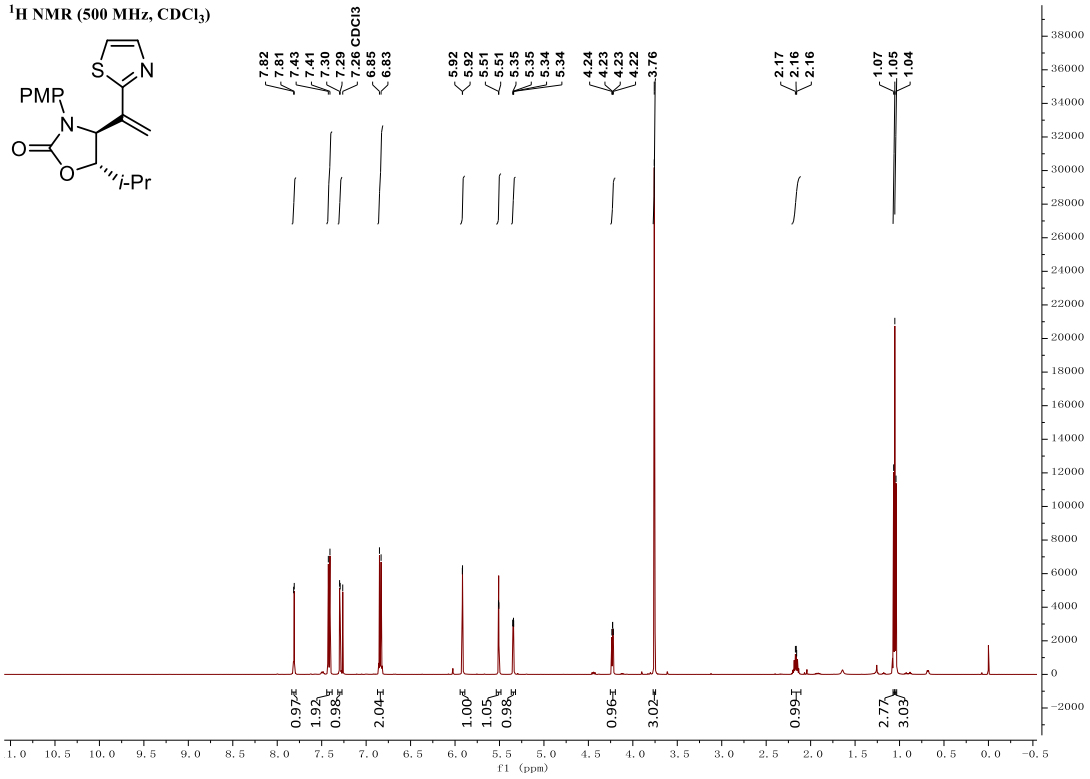


^{19}F NMR (471 MHz, $CDCl_3$)

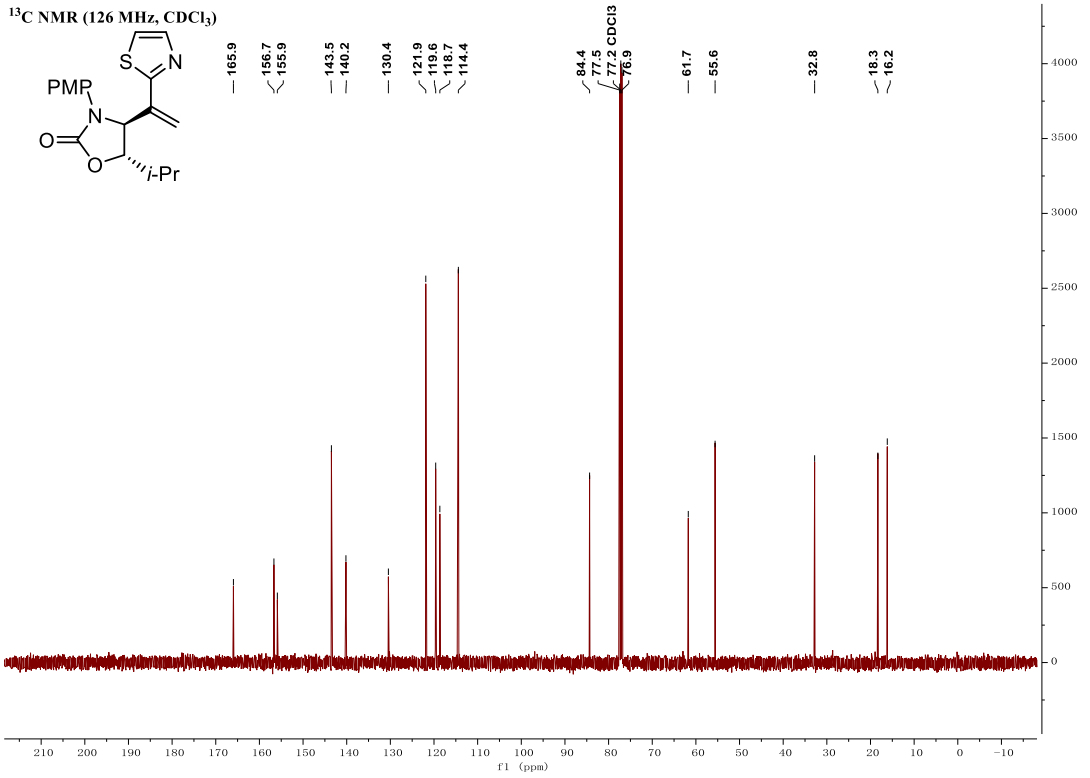


Compound 10

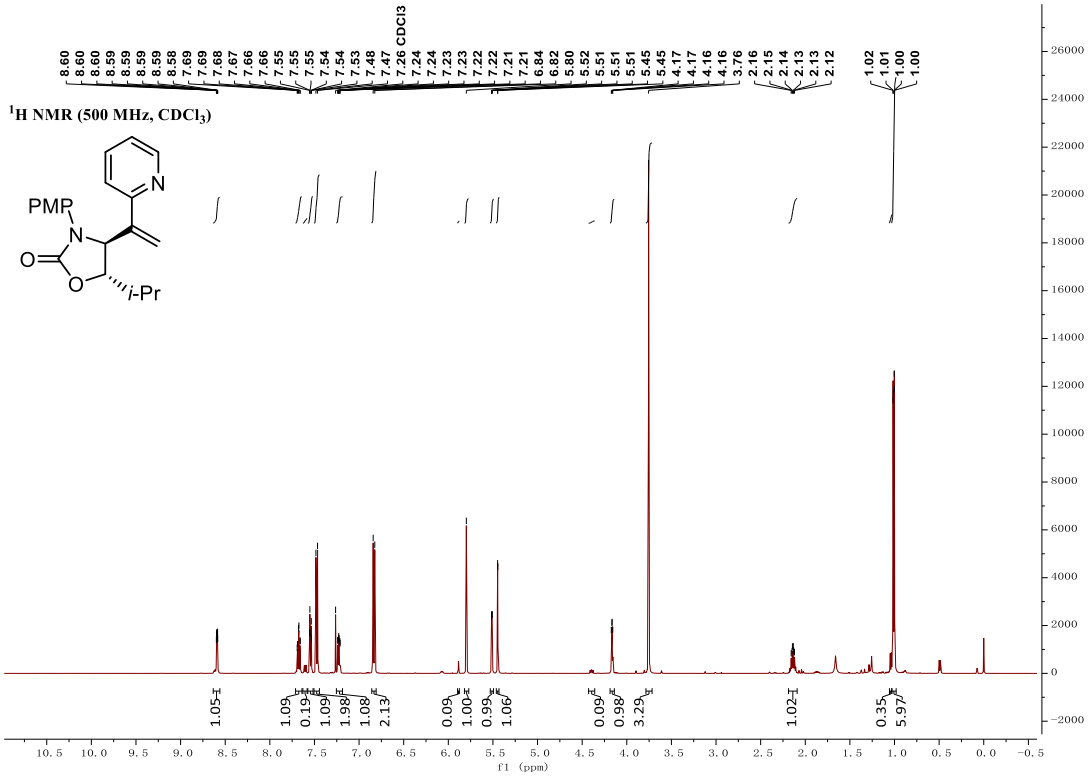
^{1}H NMR (500 MHz, $CDCl_3$)

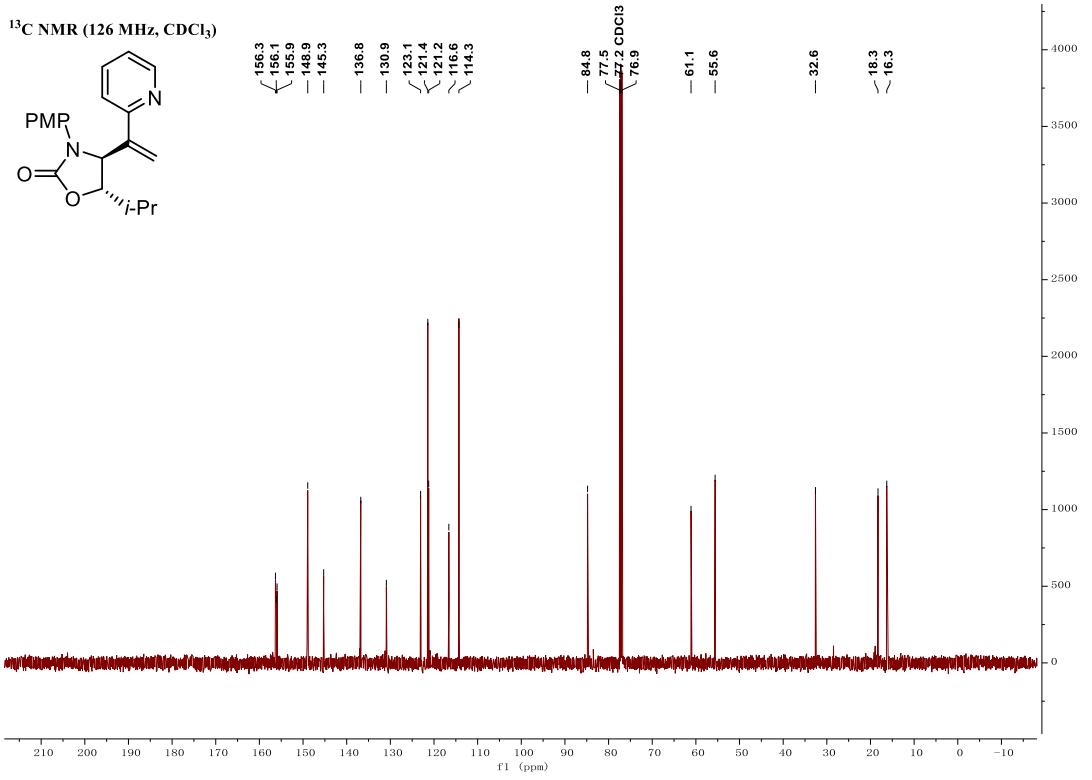


^{13}C NMR (126 MHz, $CDCl_3$)

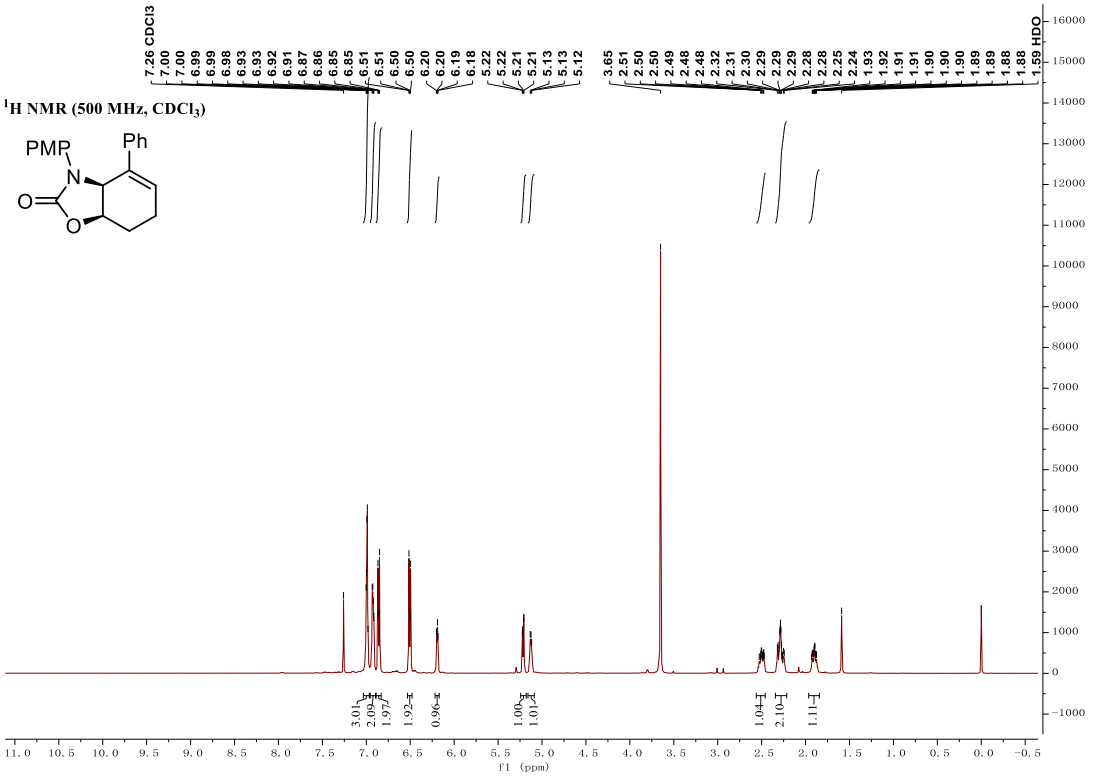


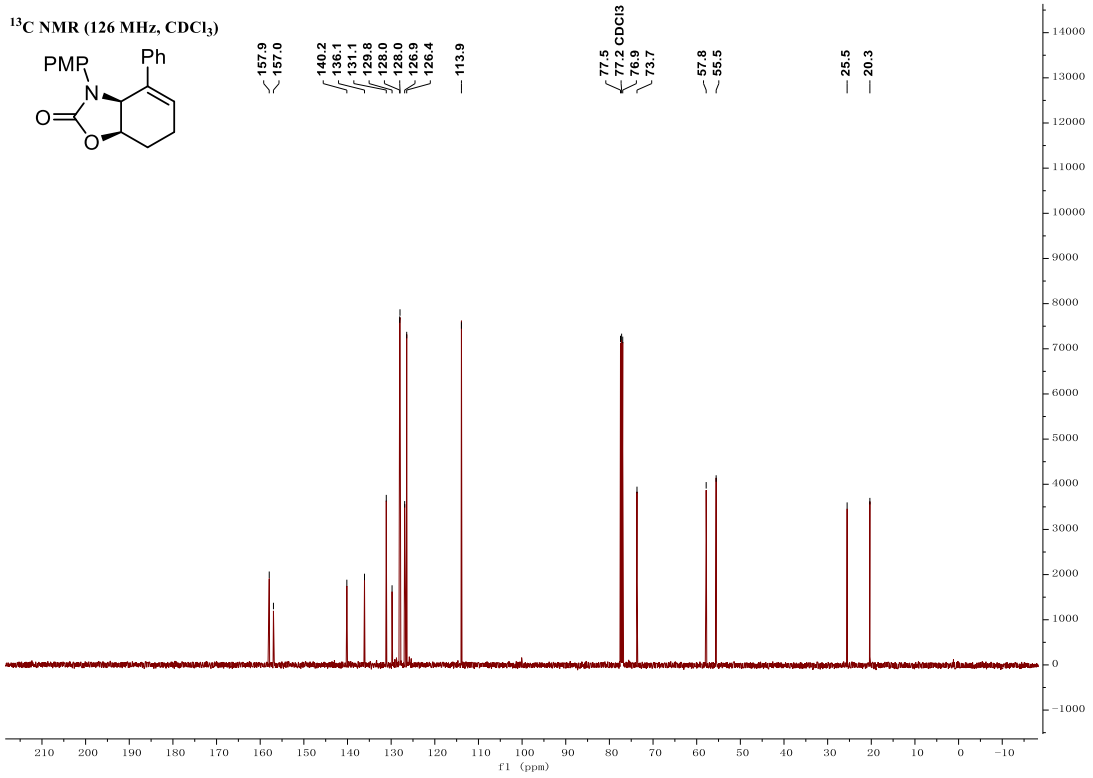
Compound 11


8.60 8.60 8.60 8.59 8.59 8.59 8.59 8.58 7.69 7.69 7.68 7.67 7.66 7.66 7.55 7.55 7.55 7.54 7.54 7.53 7.48 7.47 7.26 CDCl3 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 6.84 6.82 5.80 5.52 5.51 5.51 5.51 5.45 4.17 4.17 4.16 4.16 3.76 2.16 2.15 2.14 2.13 2.13 2.12 1.02 1.01 1.00 1.00
PMP
N
O
O
i-Pr
1.05 1.09 0.19 1.09 1.98 1.08 2.13 0.09 1.00 0.99 1.06 0.09 0.98 3.29 1.02 0.35 5.97
f1 (ppm)

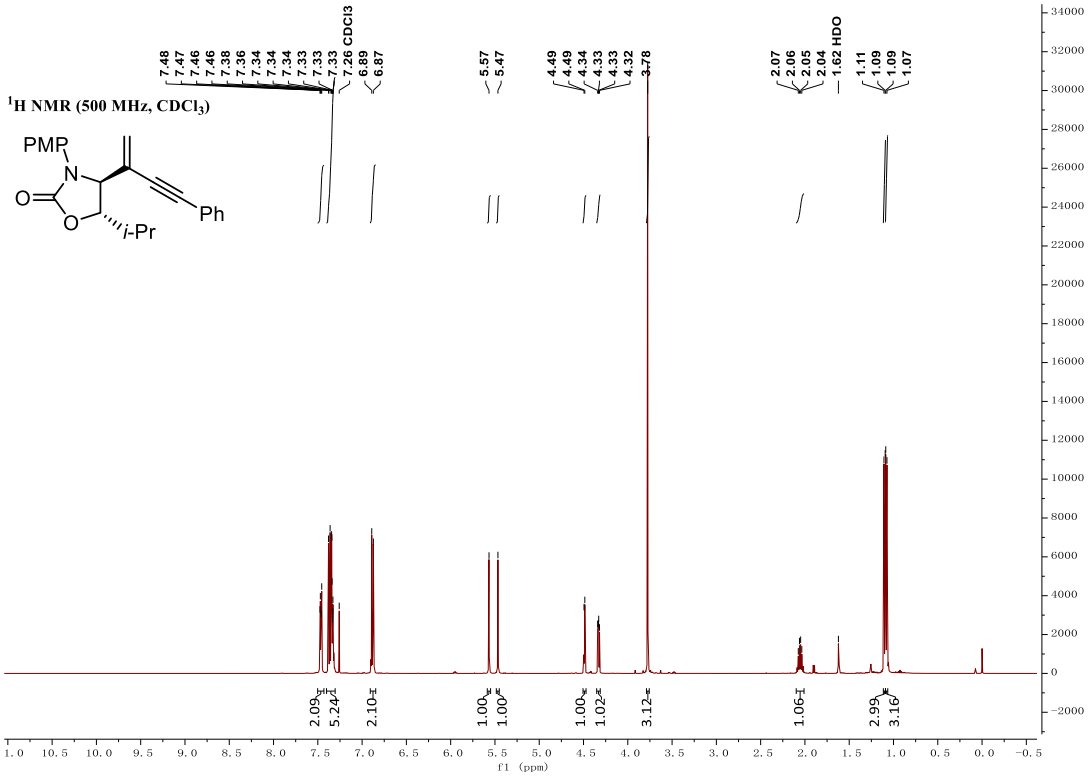

156.3 156.1 155.9 148.9 145.3 136.8 130.9 123.1 121.4 121.2 116.6 114.3 84.8 77.5 77.2 CDCl3 76.9 61.1 55.6 32.6 18.3 16.3
PMP
N
O
O
i-Pr
f1 (ppm)

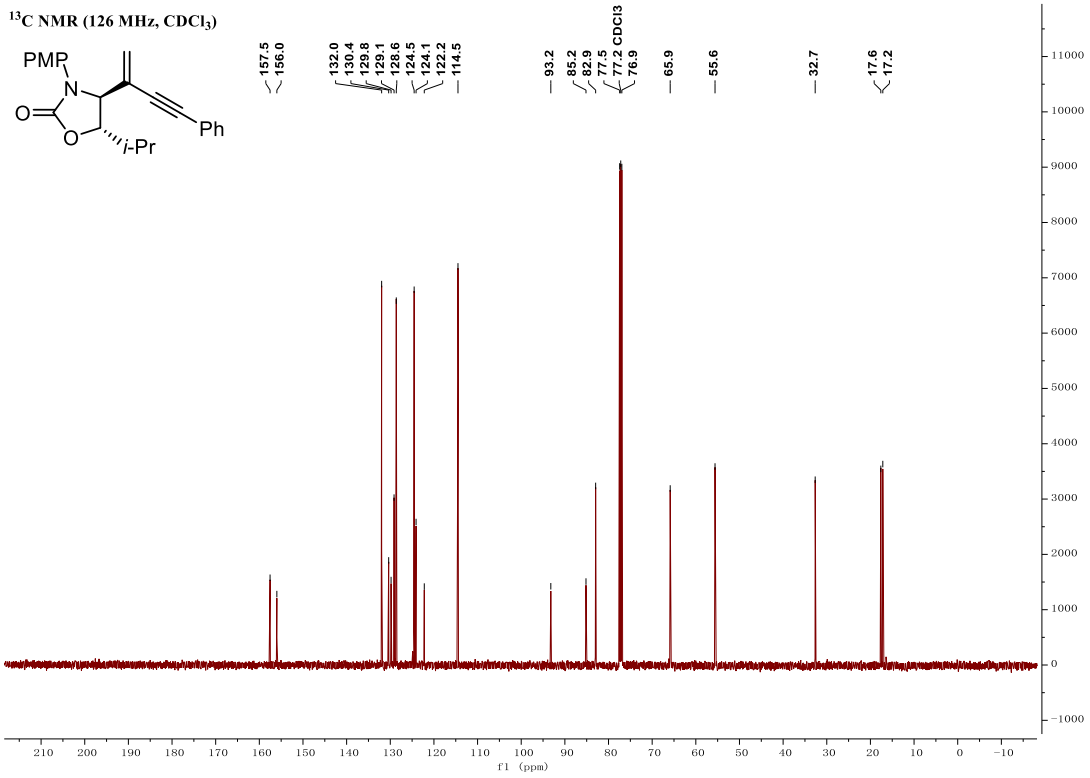
Compound 12


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
Ph
N
O
O
7.26 CDCl3
1.59 HDO
3.01
2.09
1.97
1.92
0.96
1.00
1.01
1.04
2.10
1.11
f1 (ppm)

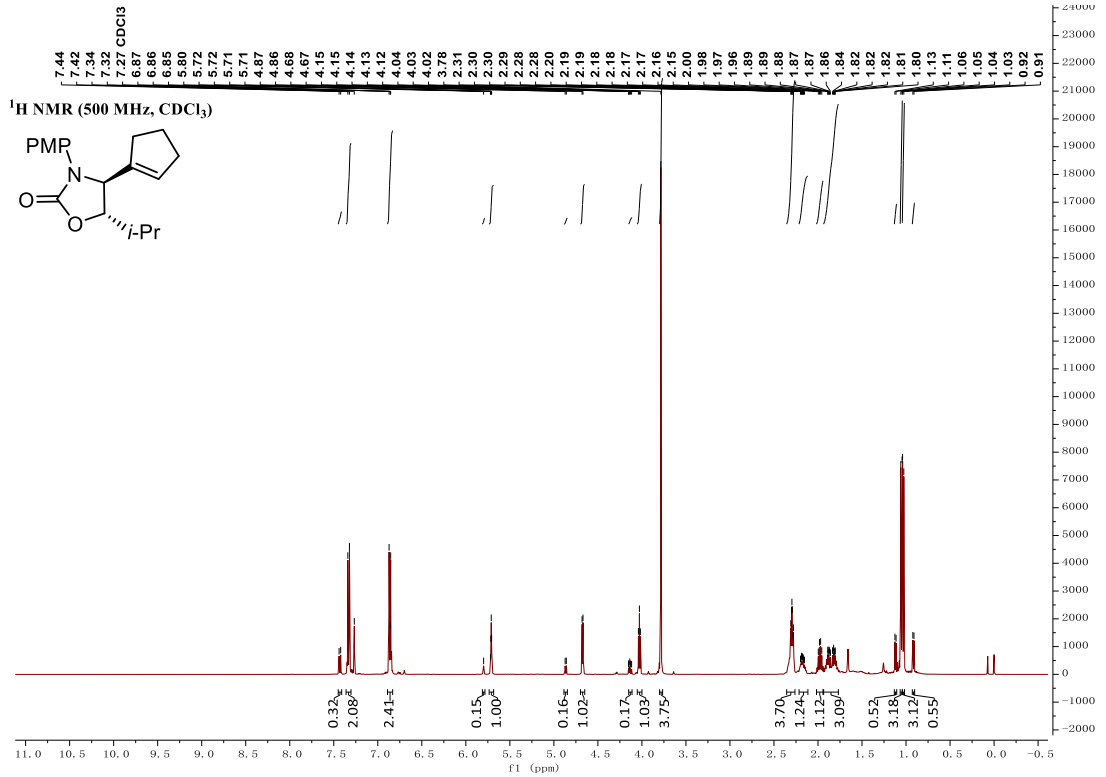

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
Ph
N
O
O
157.9
157.0
140.2
136.1
131.1
129.8
128.0
128.0
126.9
126.4
113.9
77.5
77.2 CDCl3
76.9
73.7
57.8
55.5
25.5
20.3
f1 (ppm)

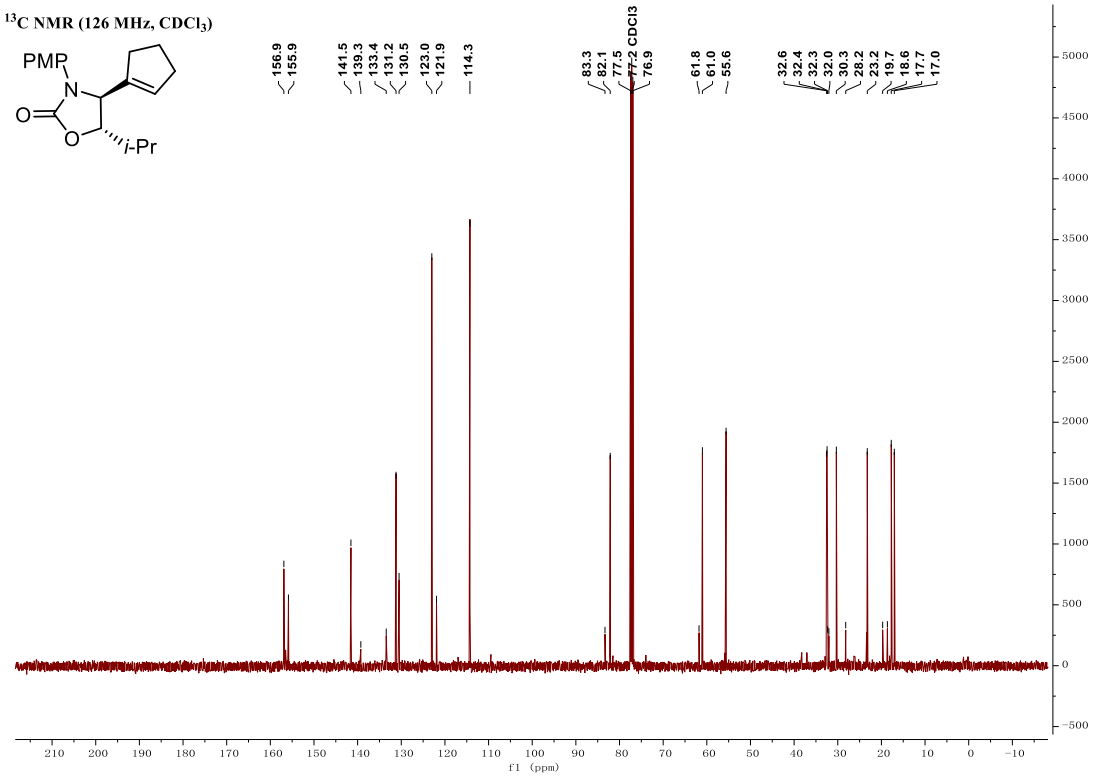
Compound 13


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
Ph
7.48
7.47
7.46
7.46
7.38
7.36
7.34
7.34
7.34
7.33
7.33
7.33
7.26 CDCl3
6.89
6.87
5.57
5.47
4.49
4.49
4.34
4.33
4.33
4.32
3.78
2.07
2.06
2.05
2.04
1.62 HDO
1.11
1.09
1.09
1.07
2.09
5.24
2.10
1.00
1.00
1.00
1.02
3.12
1.06
2.99
3.16
f1 (ppm)

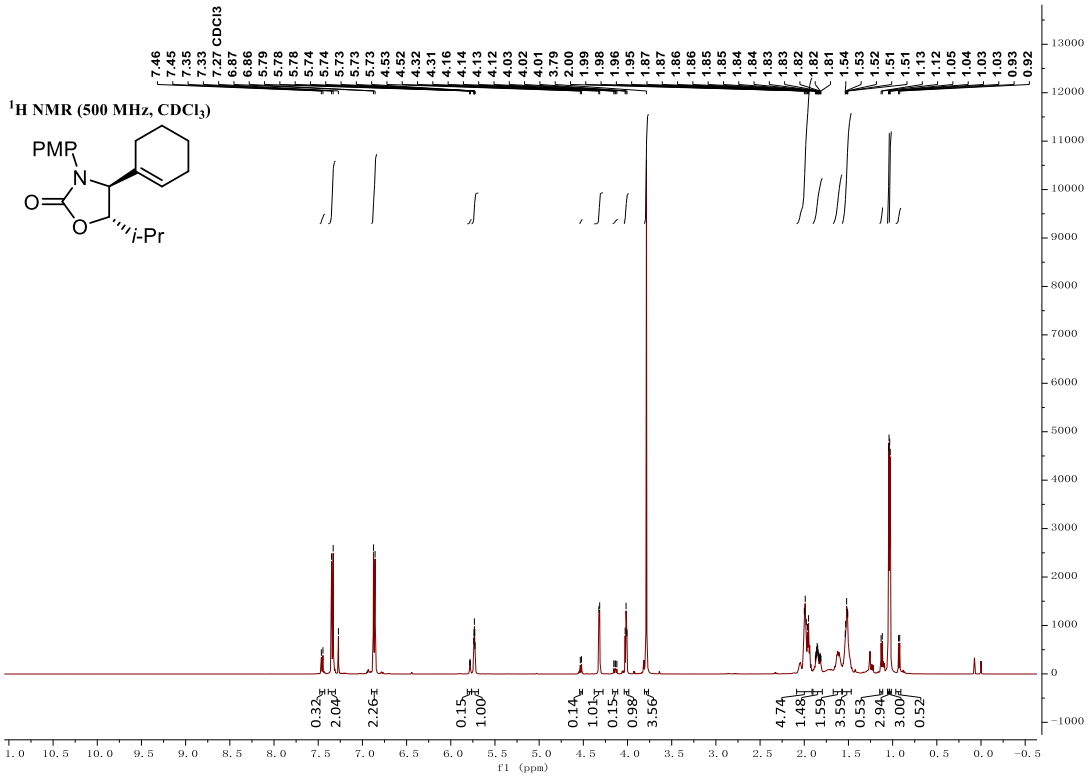

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
Ph
157.5
156.0
132.0
130.4
129.8
129.1
128.6
124.5
124.1
122.2
114.5
93.2
85.2
82.9
77.5
77.2 CDCl3
76.9
65.9
55.6
32.7
17.6
17.2
f1 (ppm)

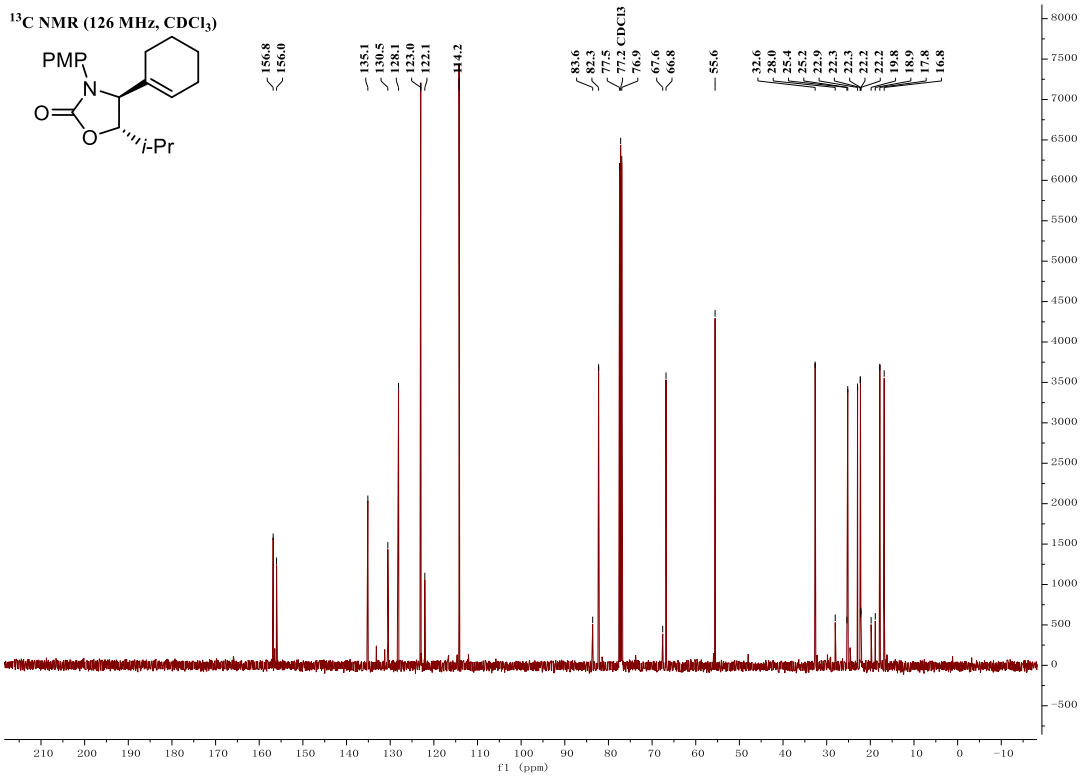
Compound 14


7.44
7.42
7.34
7.32
7.27 CDCl3
6.87
6.86
6.85
5.80
5.72
5.72
5.71
5.71
4.87
4.86
4.68
4.67
4.15
4.15
4.14
4.13
4.12
4.04
4.03
4.02
3.78
2.31
2.30
2.30
2.29
2.28
2.28
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.00
1.98
1.97
1.96
1.89
1.89
1.88
1.87
1.87
1.86
1.84
1.82
1.82
1.82
1.81
1.80
1.13
1.11
1.06
1.05
1.04
1.03
0.92
0.91
1H NMR (500 MHz, CDCl3)
PMP
N
O
O
i-Pr
0.32
2.08
2.41
0.15
1.00
0.16
1.02
0.17
1.03
3.75
3.70
1.24
1.12
3.09
0.52
3.18
3.12
0.55
f1 (ppm)

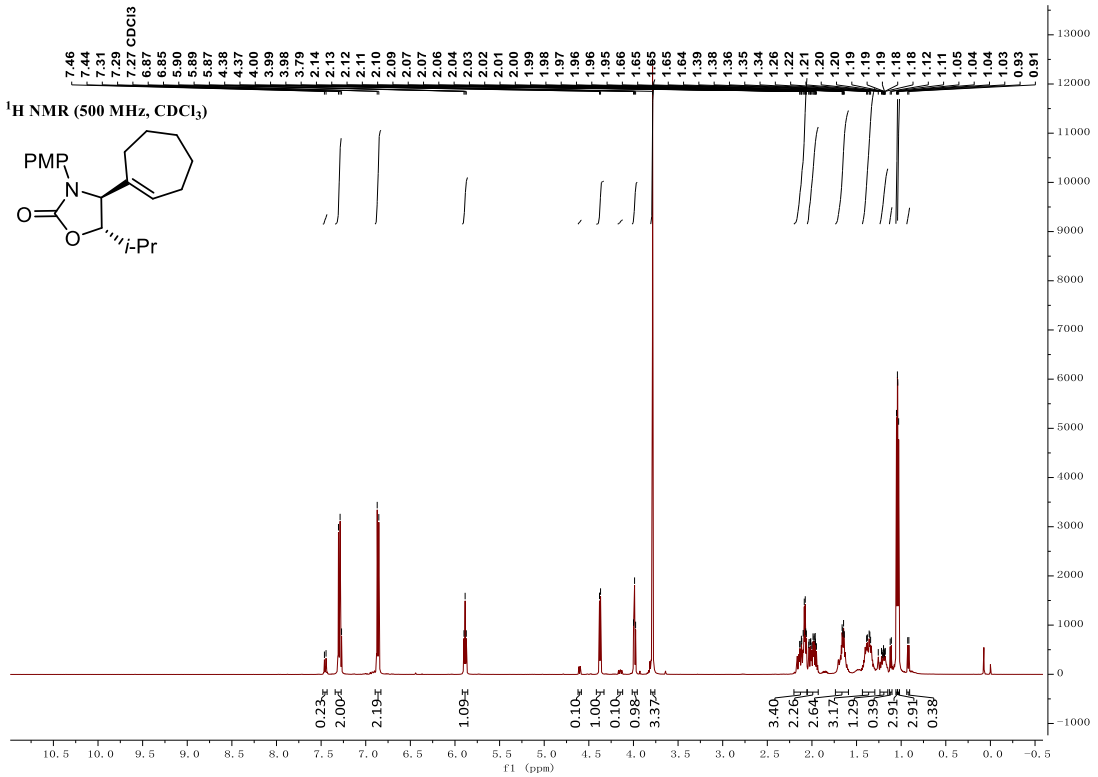

13C NMR (126 MHz, CDCl3)
PMP
N
O
O
i-Pr
156.9
155.9
141.5
139.3
133.4
131.2
130.5
123.0
121.9
114.3
83.3
82.1
77.5
77.2 CDCl3
76.9
61.8
61.0
55.6
32.6
32.4
32.3
32.0
30.3
28.2
23.2
19.7
18.6
17.7
17.0
f1 (ppm)

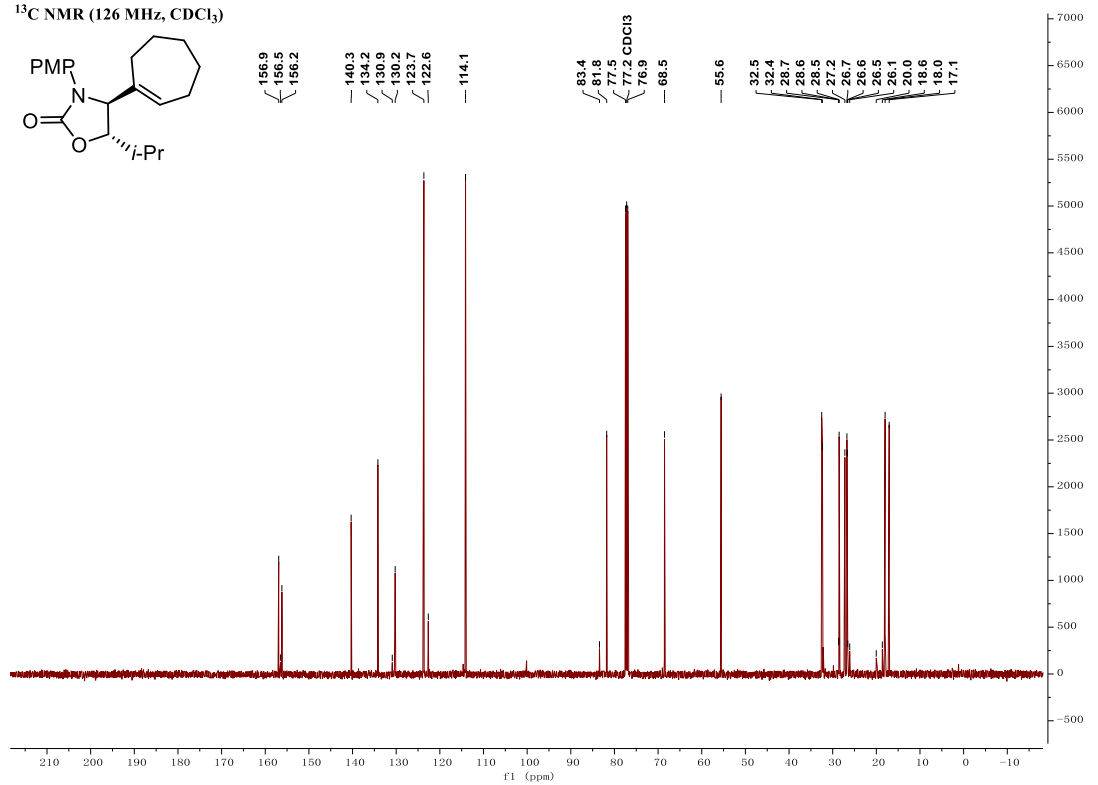
Compound 15


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
7.27 CDCl3
f1 (ppm)


^{13}C NMR (126 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
156.8
156.0
135.1
130.5
128.1
123.0
122.1
114.2
83.6
82.3
77.5
77.2 CDCl3
76.9
67.6
66.8
55.6
32.6
28.0
25.4
25.2
22.9
22.3
22.3
22.2
22.2
19.8
18.9
17.8
16.8
f1 (ppm)

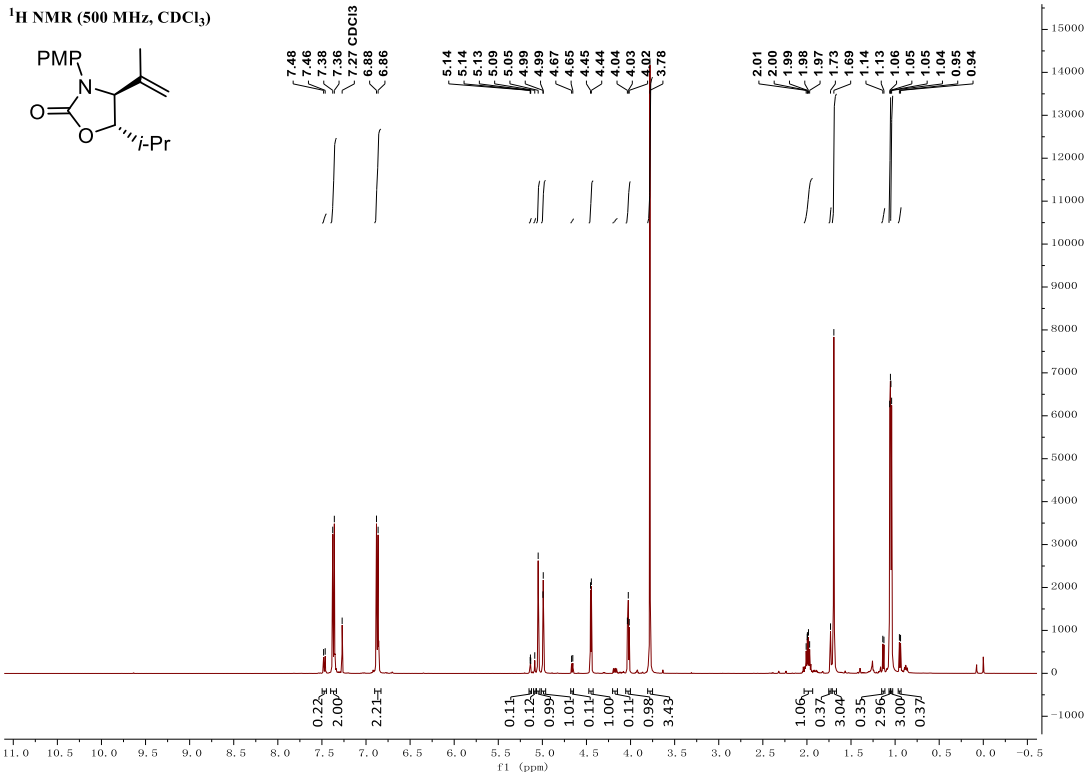
Compound 16


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
7.46 7.44 7.31 7.29 7.27 CDCl3 6.87 6.85 5.90 5.89 5.87 4.38 4.37 4.00 3.99 3.98 3.79 2.14 2.13 2.12 2.11 2.10 2.09 2.07 2.07 2.06 2.04 2.03 2.02 2.01 2.00 1.99 1.98 1.97 1.96 1.96 1.95 1.66 1.65 1.65 1.65 1.64 1.39 1.38 1.36 1.35 1.34 1.26 1.22 1.21 1.20 1.20 1.19 1.19 1.19 1.18 1.18 1.12 1.11 1.05 1.04 1.04 1.03 0.93 0.91
0.23 2.00 2.19 1.09 0.10 1.00 0.10 0.98 3.37 3.40 2.26 2.64 3.17 1.29 0.39 2.91 2.91 0.38
f1 (ppm)

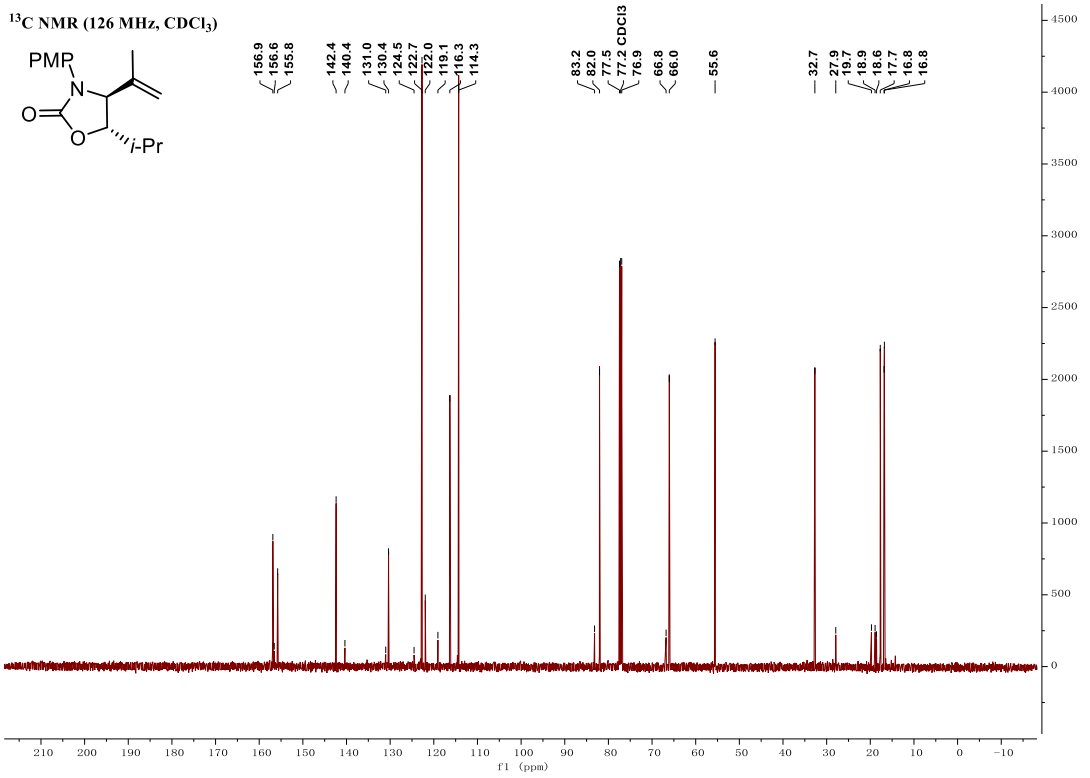

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
N
O
O
i-Pr
156.9 156.5 156.2 140.3 134.2 130.9 130.2 123.7 122.6 114.1 83.4 81.8 77.5 77.2 CDCl3 76.9 68.5 55.6 32.5 32.4 28.7 28.6 28.5 27.2 26.7 26.6 26.5 26.1 20.0 18.6 18.0 17.1
f1 (ppm)

Compound 17

^{1}H NMR (500 MHz, $CDCl_3$)

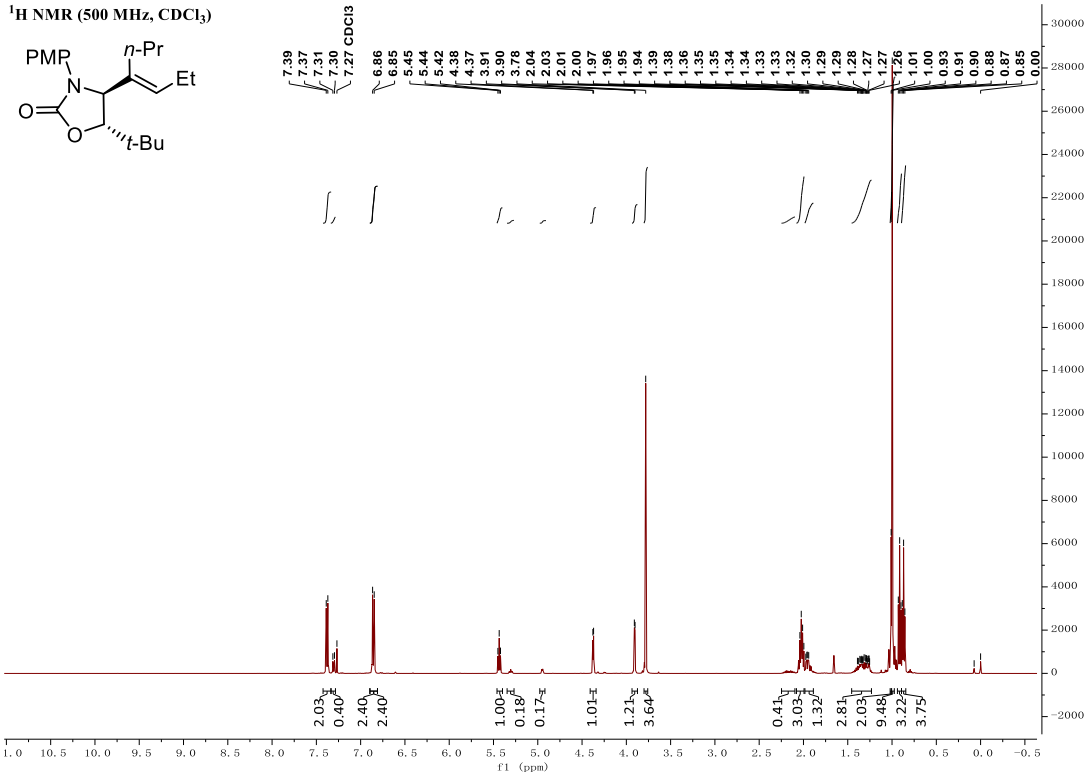


^{13}C NMR (126 MHz, $CDCl_3$)

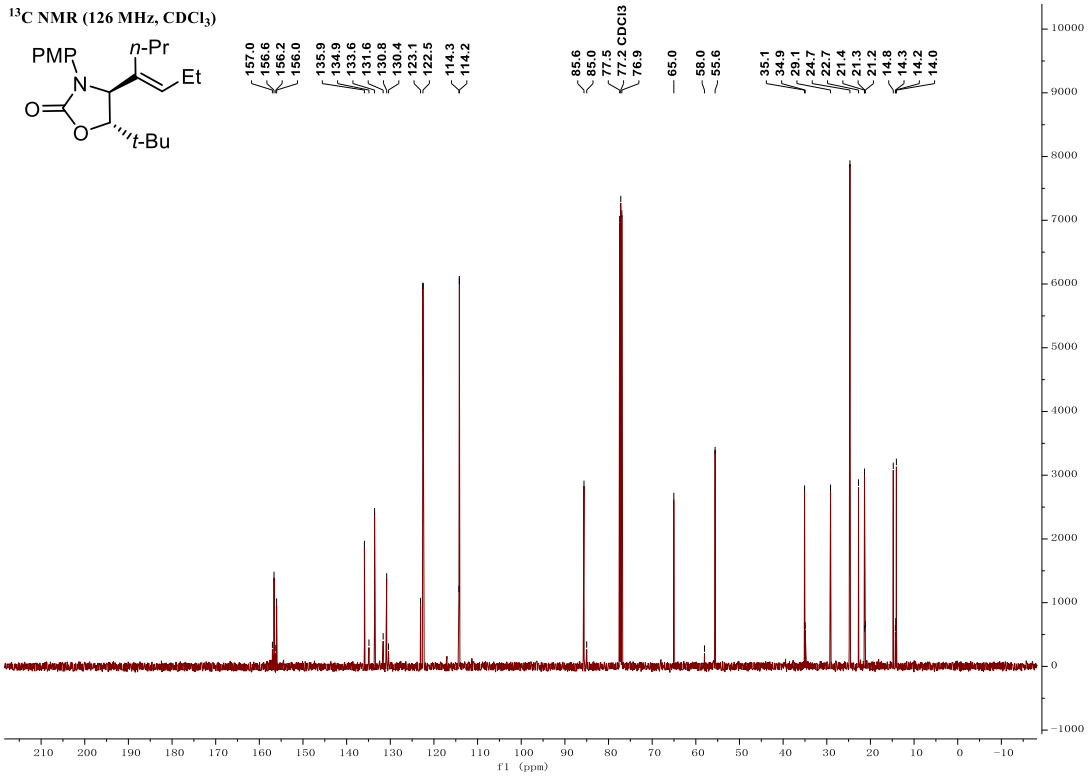


Compound 18

^{1}H NMR (500 MHz, $CDCl_3$)

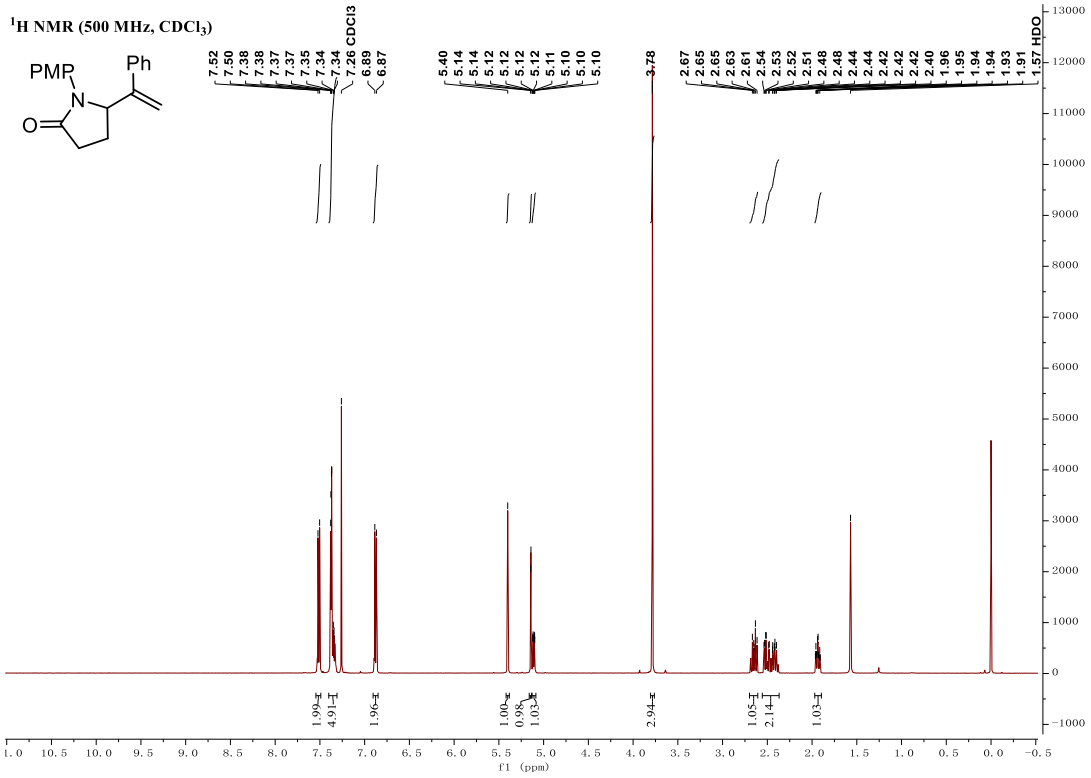


^{13}C NMR (126 MHz, $CDCl_3$)

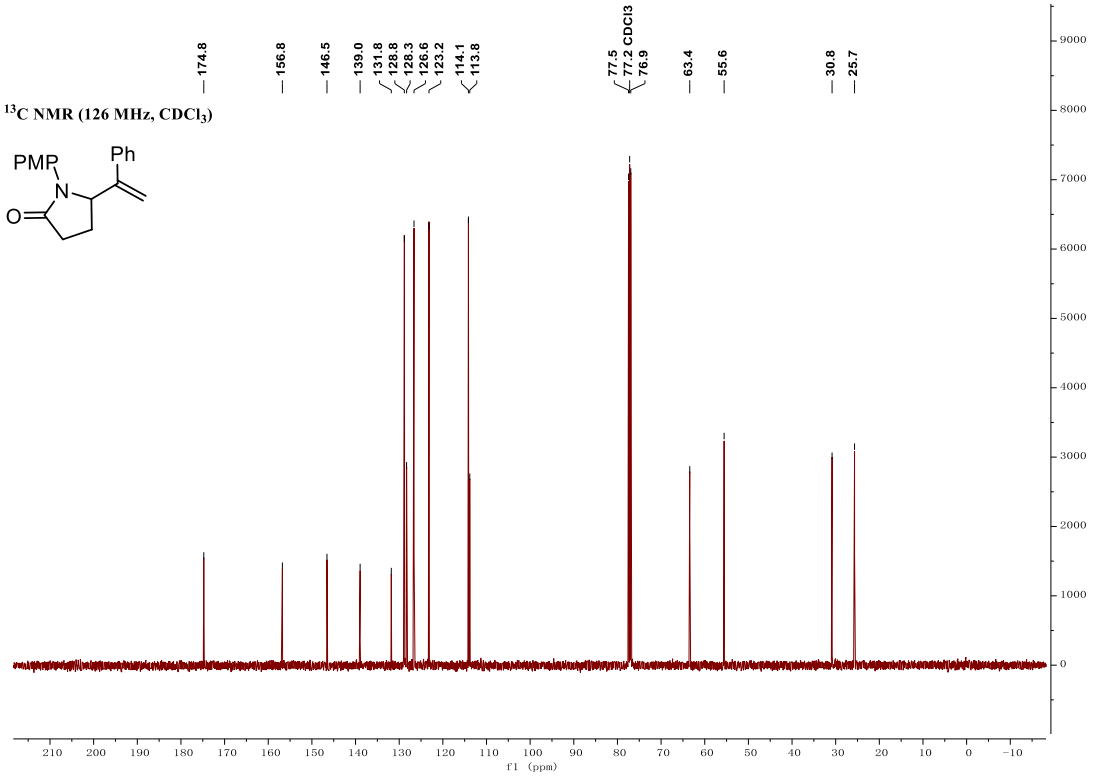


Compound 19

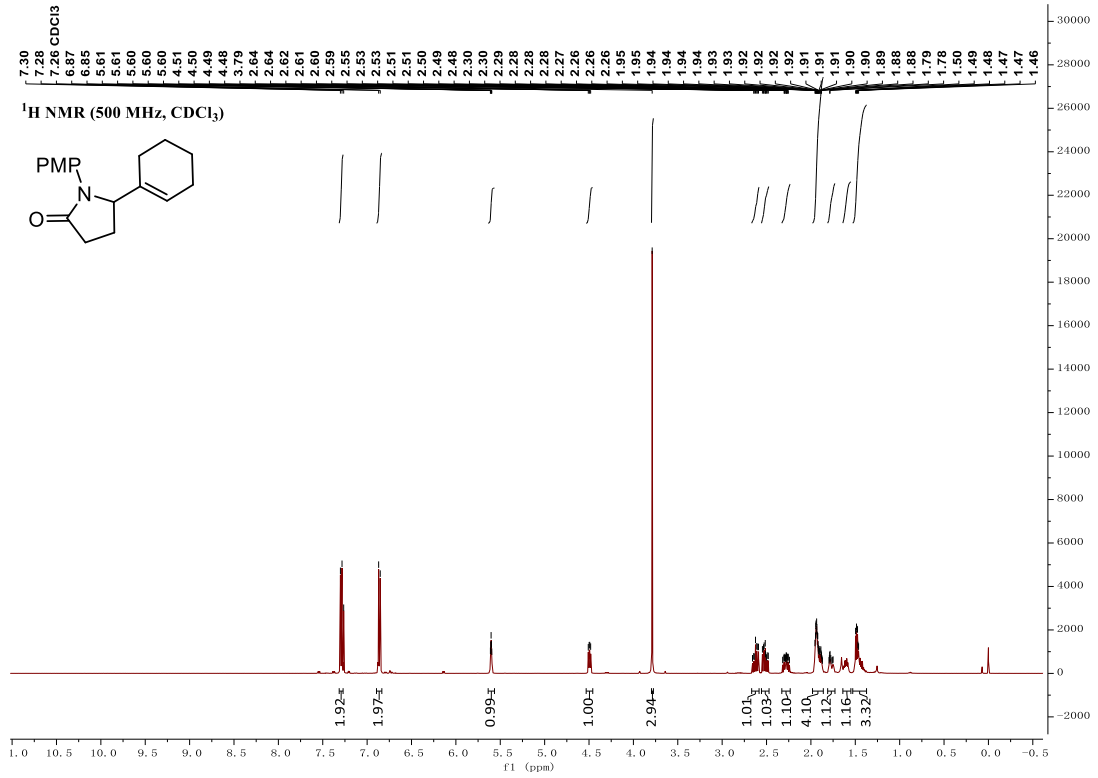
^{1}H NMR (500 MHz, $CDCl_3$)

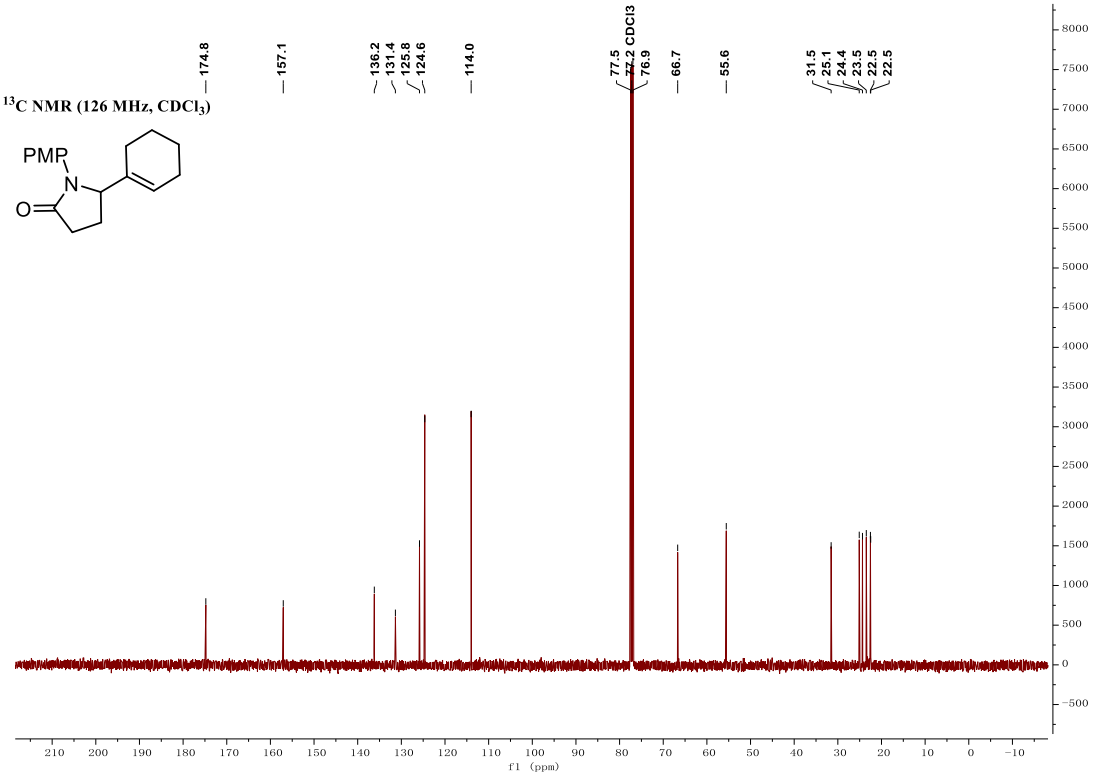


^{13}C NMR (126 MHz, $CDCl_3$)



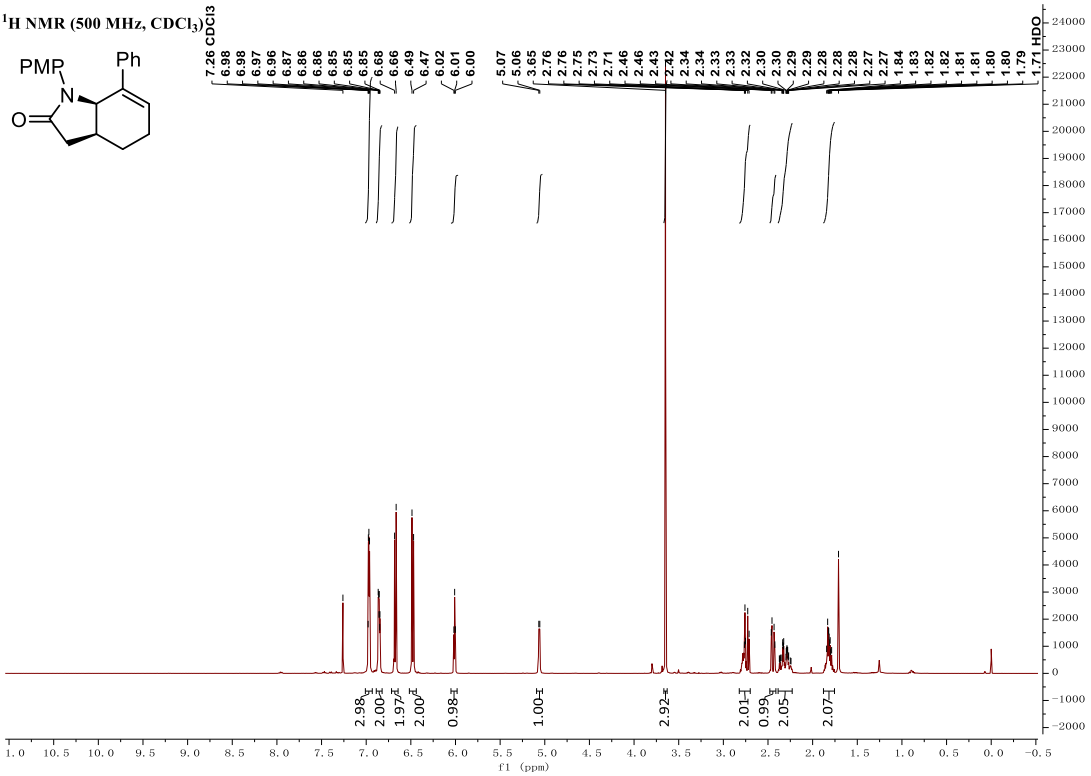
Compound 20


7.30
7.28
7.26 CDCl3
6.87
6.85
5.61
5.61
5.60
5.60
5.60
4.51
4.50
4.49
4.48
3.79
2.64
2.64
2.62
2.61
2.60
2.59
2.55
2.53
2.53
2.51
2.51
2.50
2.49
2.48
2.30
2.30
2.29
2.28
2.28
2.28
2.27
2.26
2.26
2.26
1.95
1.95
1.94
1.94
1.94
1.94
1.93
1.93
1.92
1.92
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.79
1.78
1.50
1.49
1.48
1.47
1.47
1.46
1H NMR (500 MHz, CDCl3)
PMP
N
O
1.92
1.97
0.99
1.00
2.94
1.01
1.03
1.10
4.10
1.12
1.16
3.32
f1 (ppm)

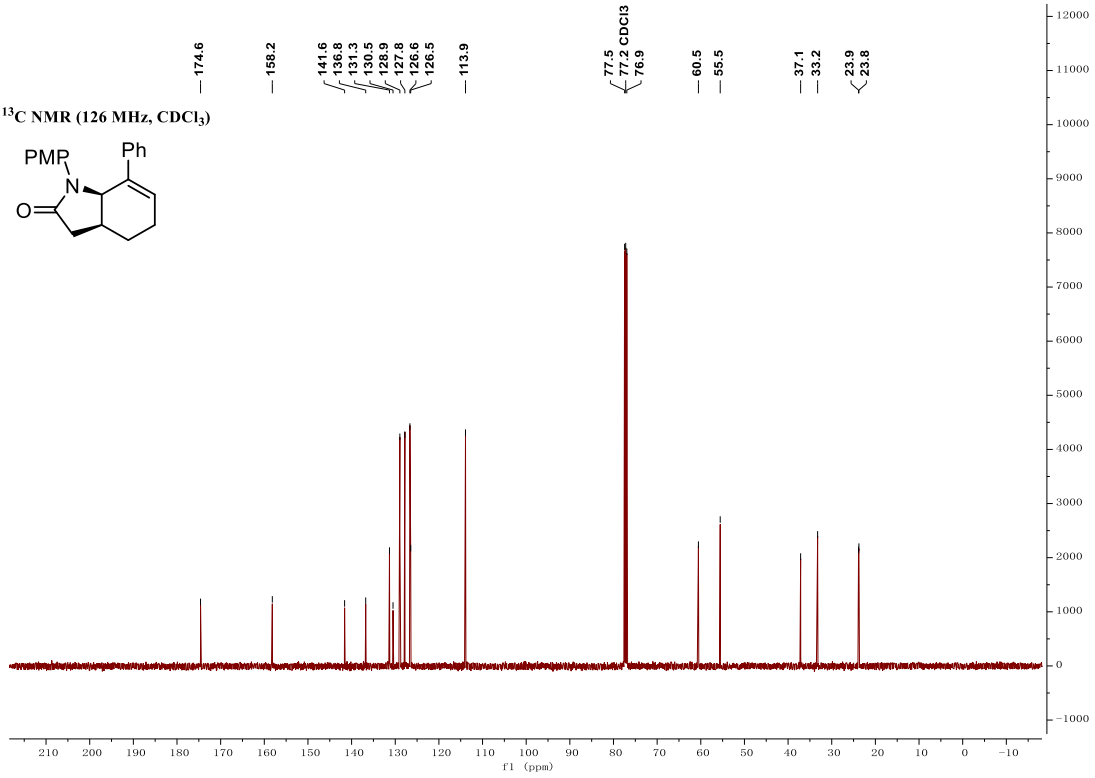

174.8
157.1
136.2
131.4
125.8
124.6
114.0
77.5
77.2 CDCl3
76.9
66.7
55.6
31.5
25.1
24.4
23.5
22.5
22.5
13C NMR (126 MHz, CDCl3)
PMP
N
O
f1 (ppm)

Compound 21

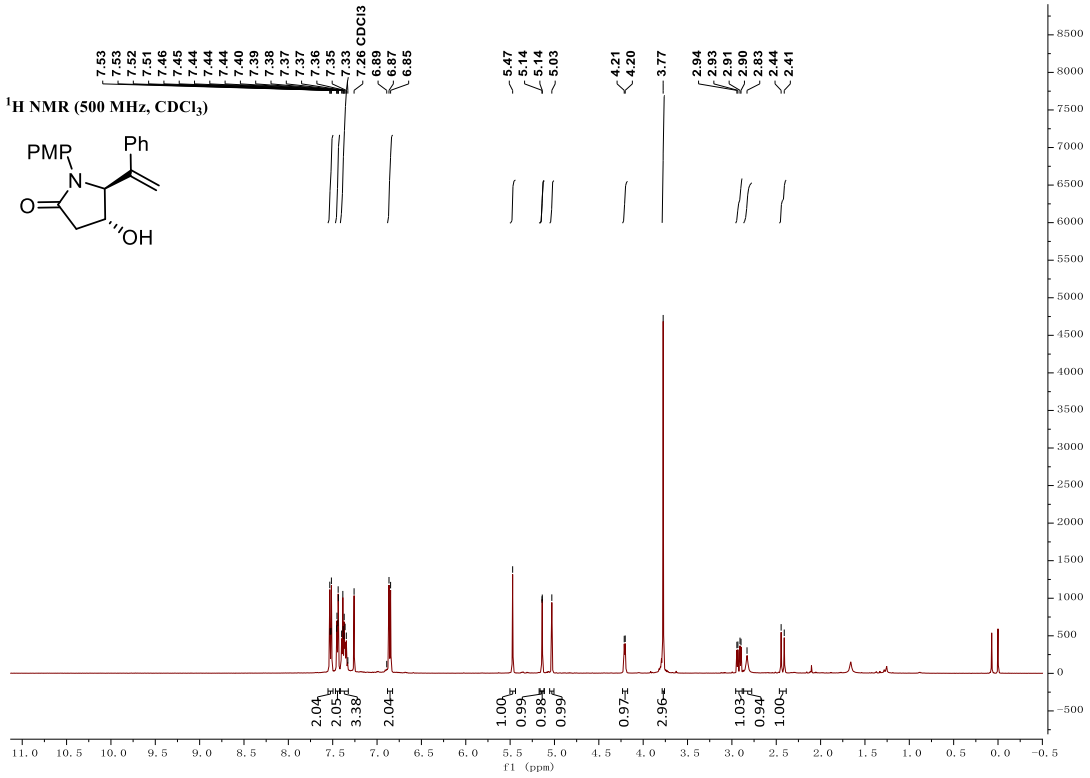
^{1}H NMR (500 MHz, $CDCl_3$)

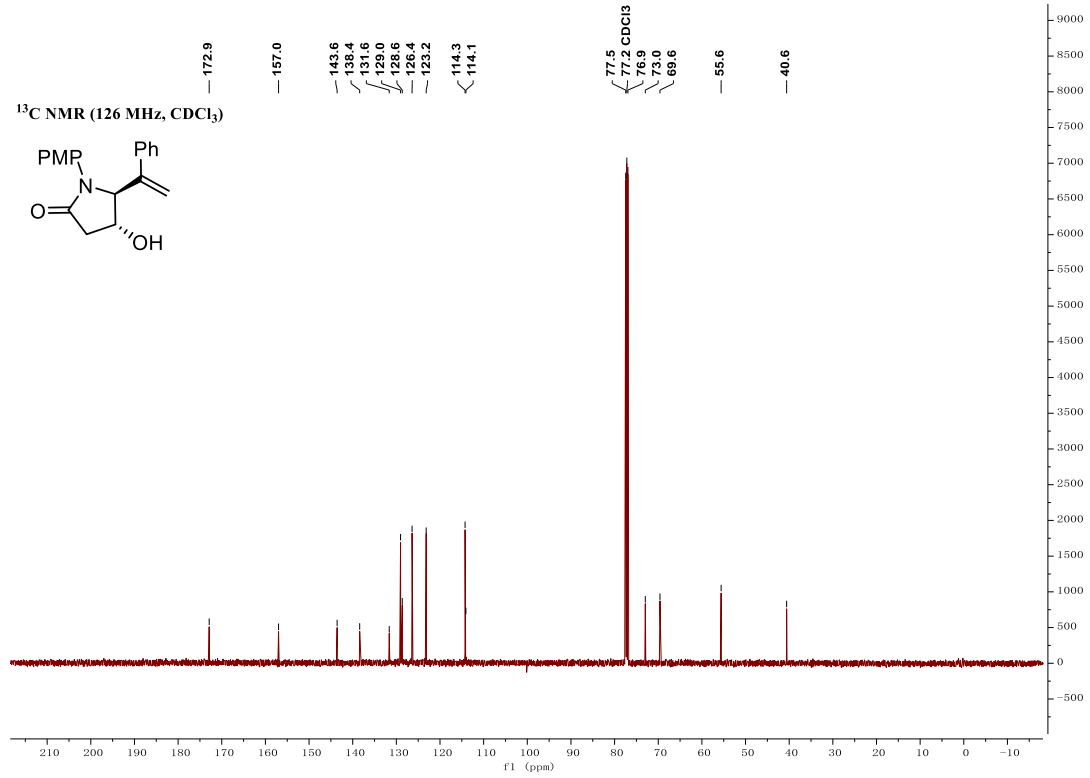


^{13}C NMR (126 MHz, $CDCl_3$)

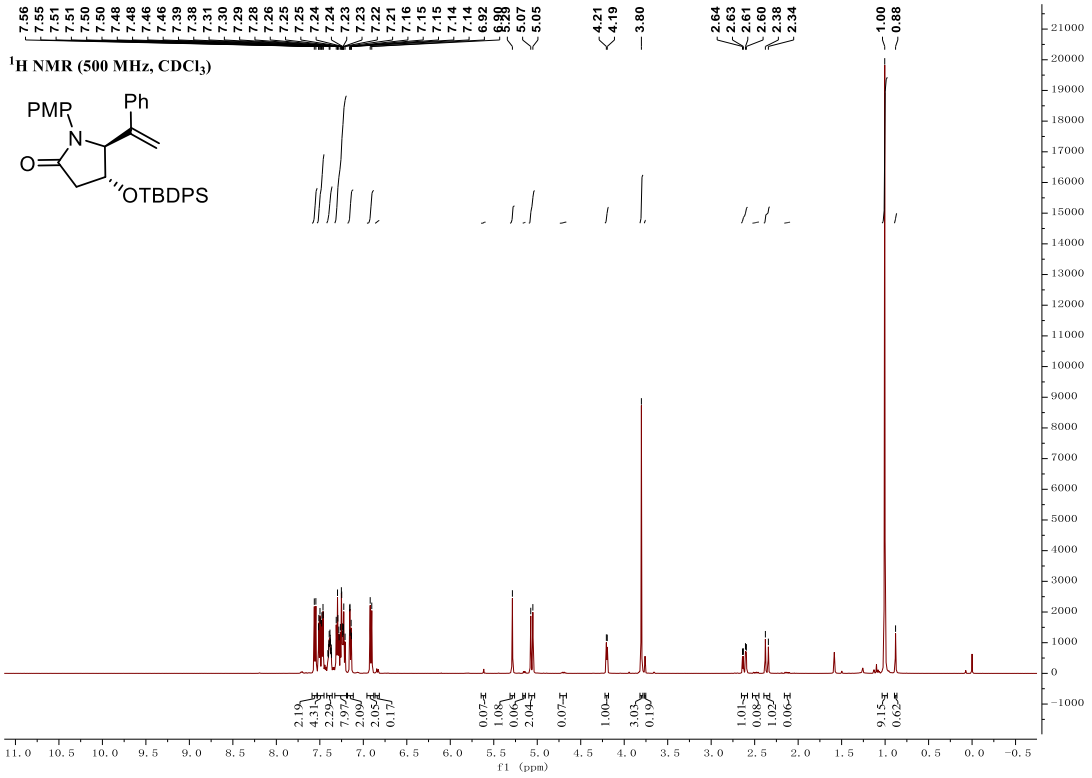


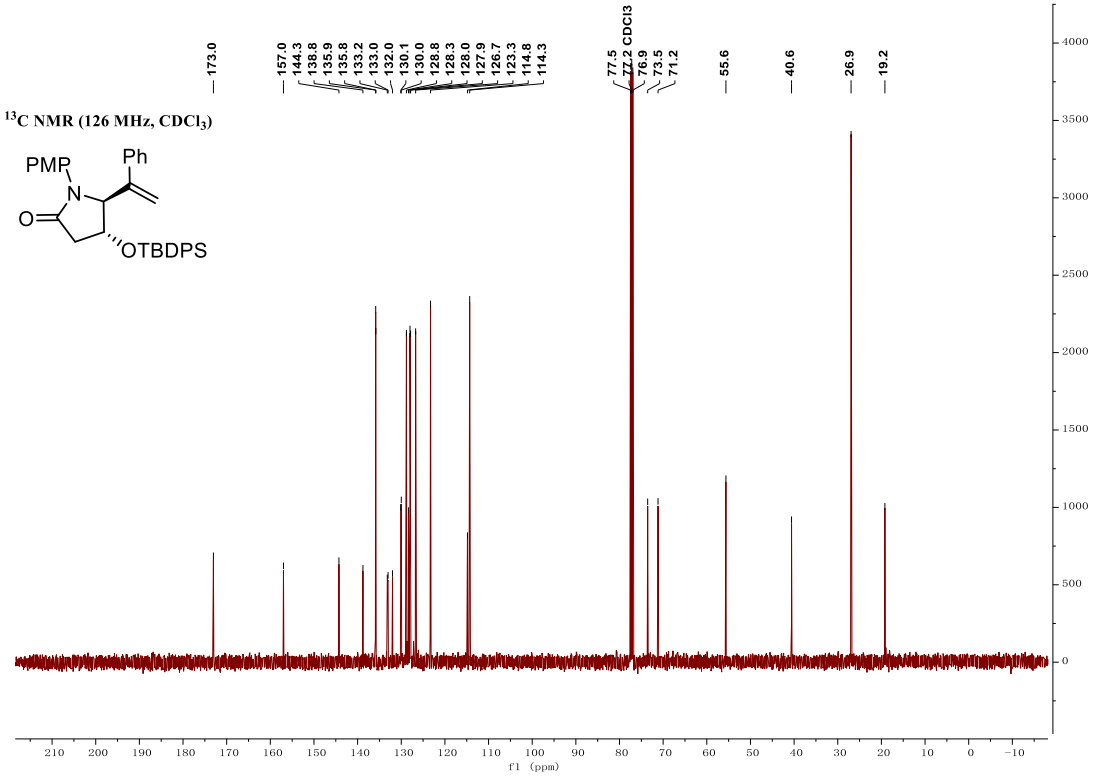
Compound 22


7.53
7.53
7.52
7.51
7.46
7.45
7.44
7.44
7.44
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.33
7.26 CDCl3
6.89
6.87
6.85
5.47
5.14
5.14
5.03
4.21
4.20
3.77
2.94
2.93
2.91
2.90
2.83
2.44
2.41
1H NMR (500 MHz, CDCl3)
PMP
Ph
N
O
OH
2.04
2.05
3.38
2.04
1.00
0.99
0.98
0.99
0.97
2.96
1.03
0.94
1.00
f1 (ppm)


172.9
157.0
143.6
138.4
131.6
129.0
128.6
126.4
123.2
114.3
114.1
77.5
77.2 CDCl3
76.9
73.0
69.6
55.6
40.6
13C NMR (126 MHz, CDCl3)
PMP
Ph
N
O
OH
f1 (ppm)

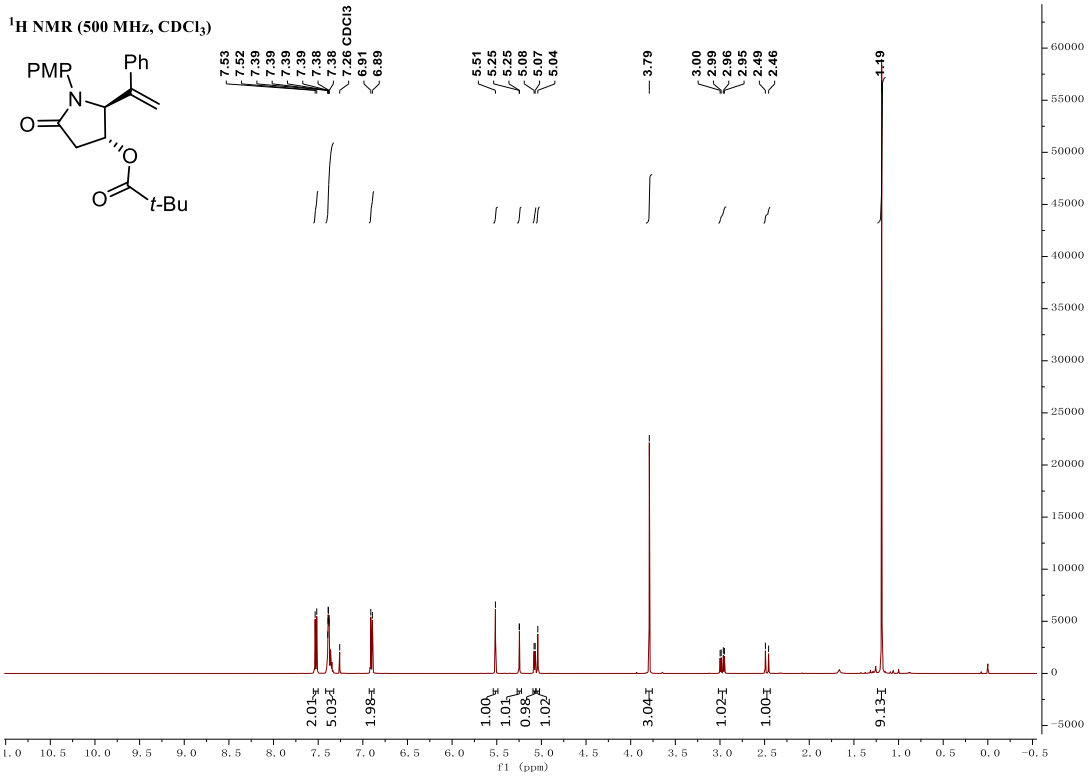
Compound 23


7.56 7.55 7.51 7.51 7.50 7.50 7.48 7.48 7.46 7.46 7.39 7.38 7.31 7.30 7.29 7.28 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.16 7.15 7.15 7.14 7.14 6.92 5.29 5.07 5.05 4.21 4.19 3.80 2.64 2.63 2.61 2.60 2.38 2.34 1.00 0.88
^{1}H NMR (500 MHz, CDCl$_3$)
PMP
Ph
N
O
OTBDPS
2.19 4.31 2.29 7.97 2.09 2.05 0.17 0.07 1.08 0.06 2.04 0.07 1.00 3.03 0.19 1.01 0.08 1.02 0.06 9.15 0.62
f1 (ppm)

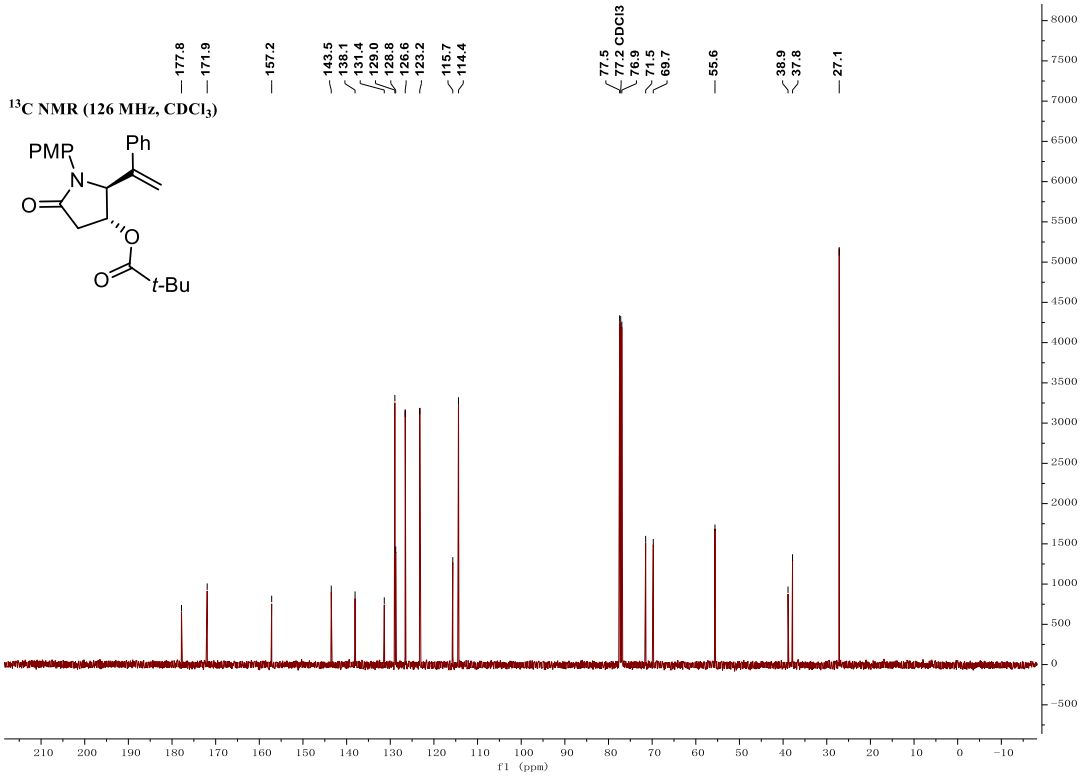

173.0 157.0 144.3 138.8 135.9 135.8 133.2 133.0 132.0 130.1 130.0 128.8 128.3 128.0 127.9 126.7 123.3 114.8 114.3 77.5 77.2 CDCl3 76.9 73.5 71.2 55.6 40.6 26.9 19.2
^{13}C NMR (126 MHz, CDCl$_3$)
PMP
Ph
N
O
OTBDPS
f1 (ppm)

Compound 24

^{1}H NMR (500 MHz, $CDCl_3$)

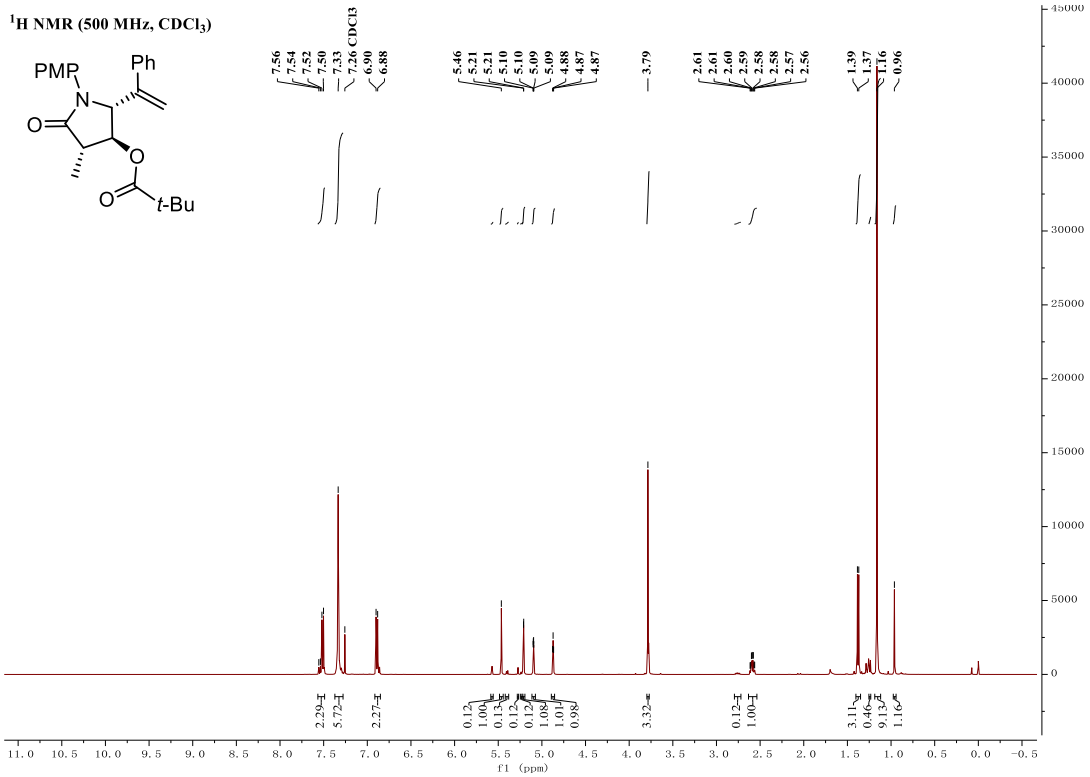


^{13}C NMR (126 MHz, $CDCl_3$)

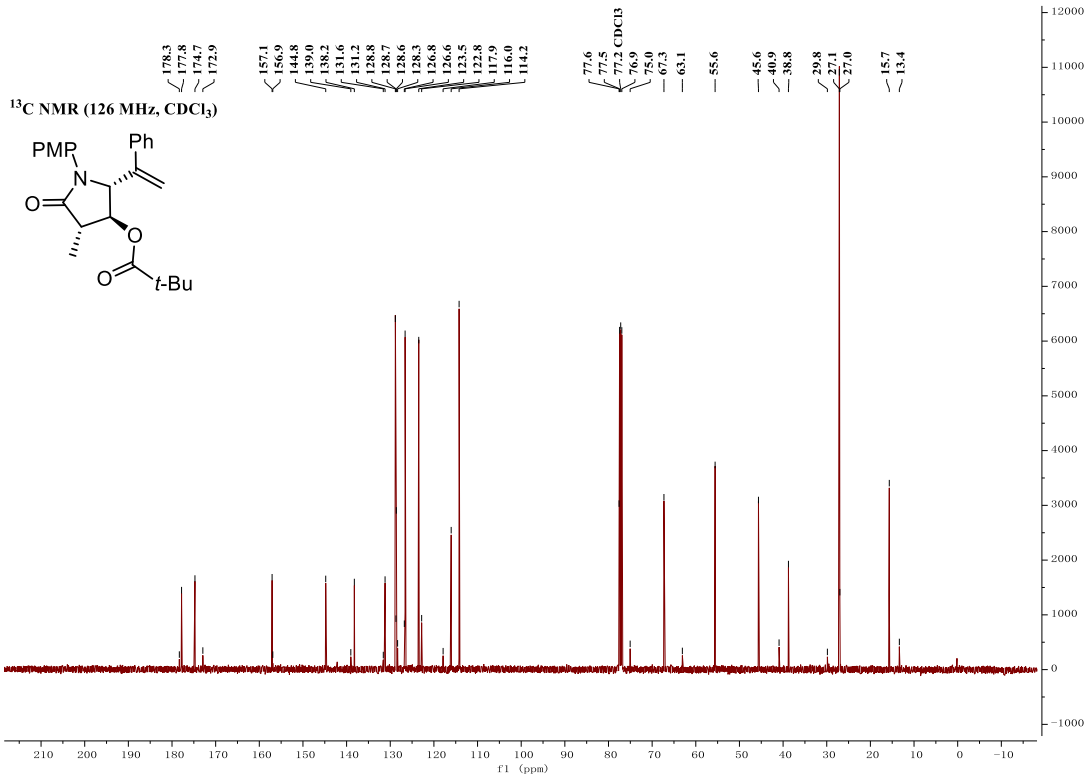


Compound 25

^{1}H NMR (500 MHz, $CDCl_3$)

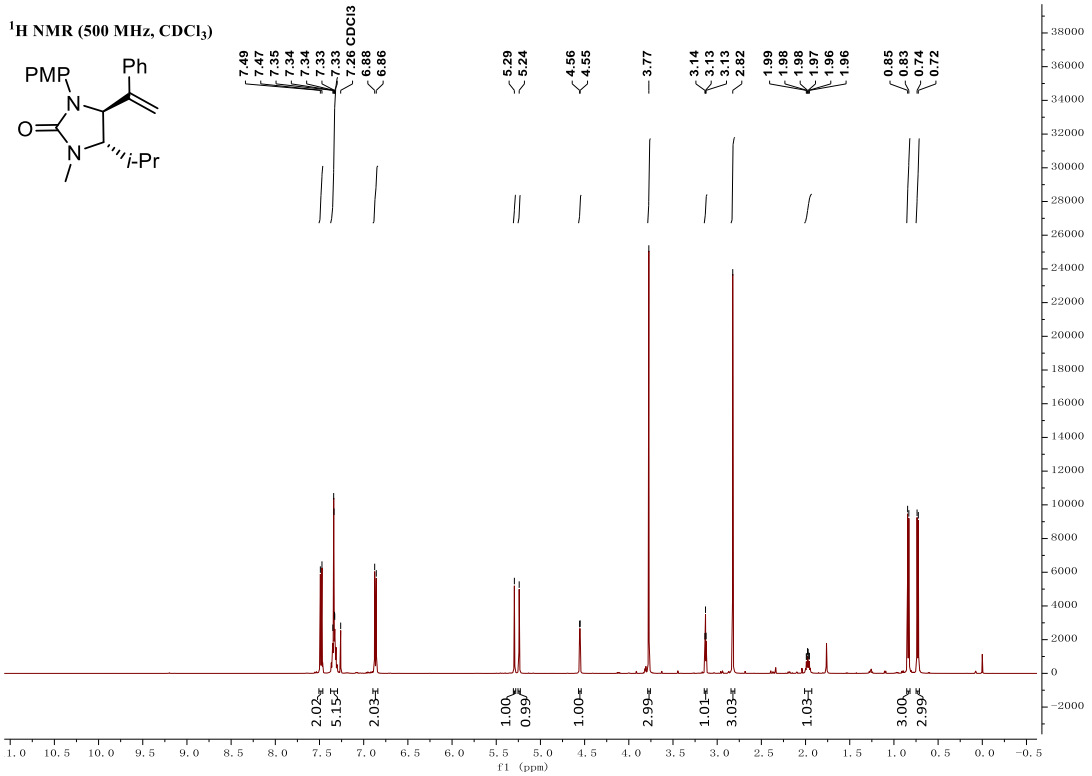


^{13}C NMR (126 MHz, $CDCl_3$)

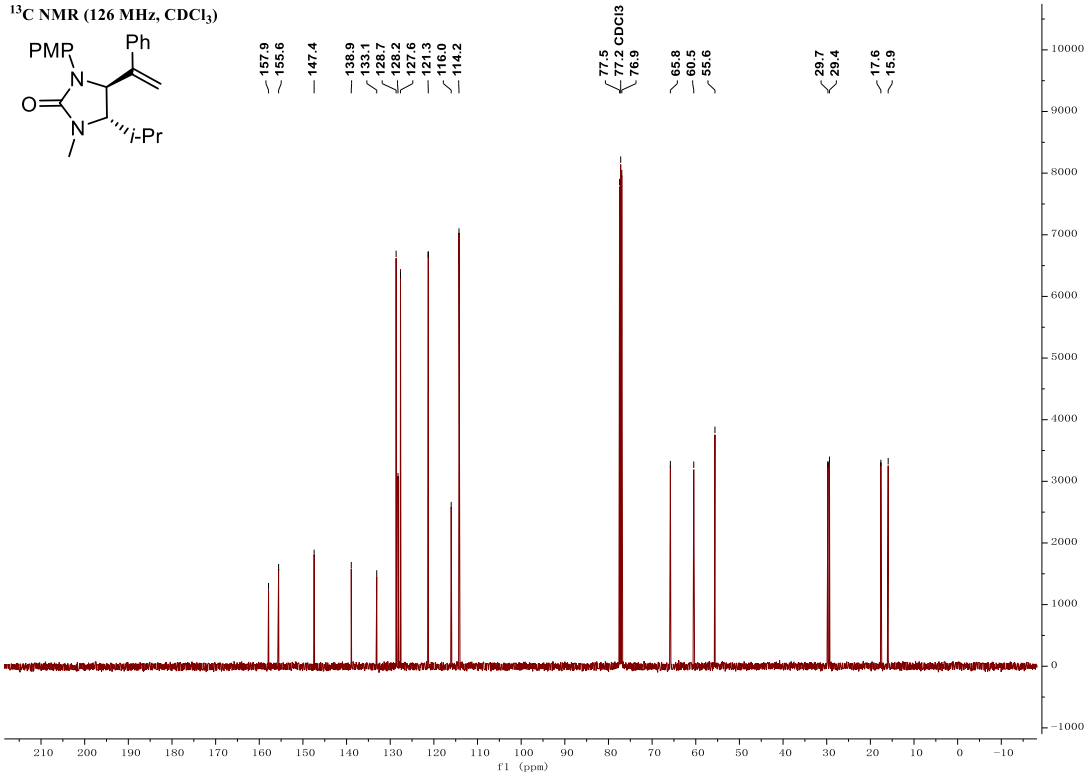


Compound 26

^{1}H NMR (500 MHz, $CDCl_3$)

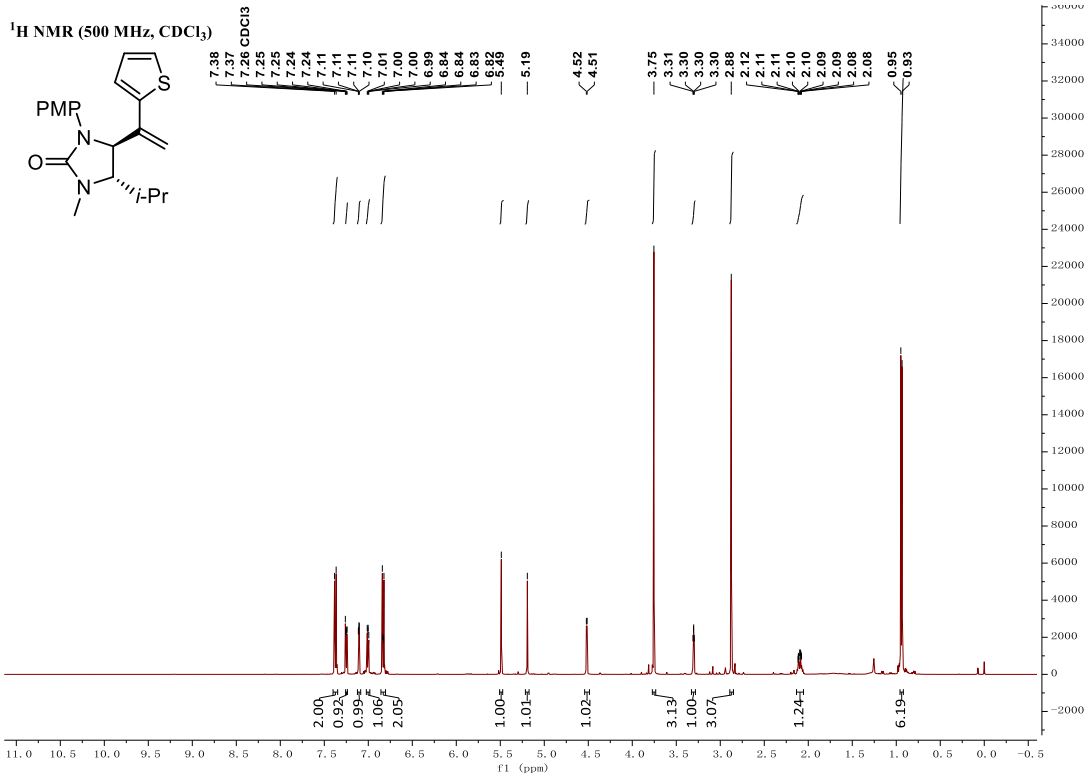


^{13}C NMR (126 MHz, $CDCl_3$)

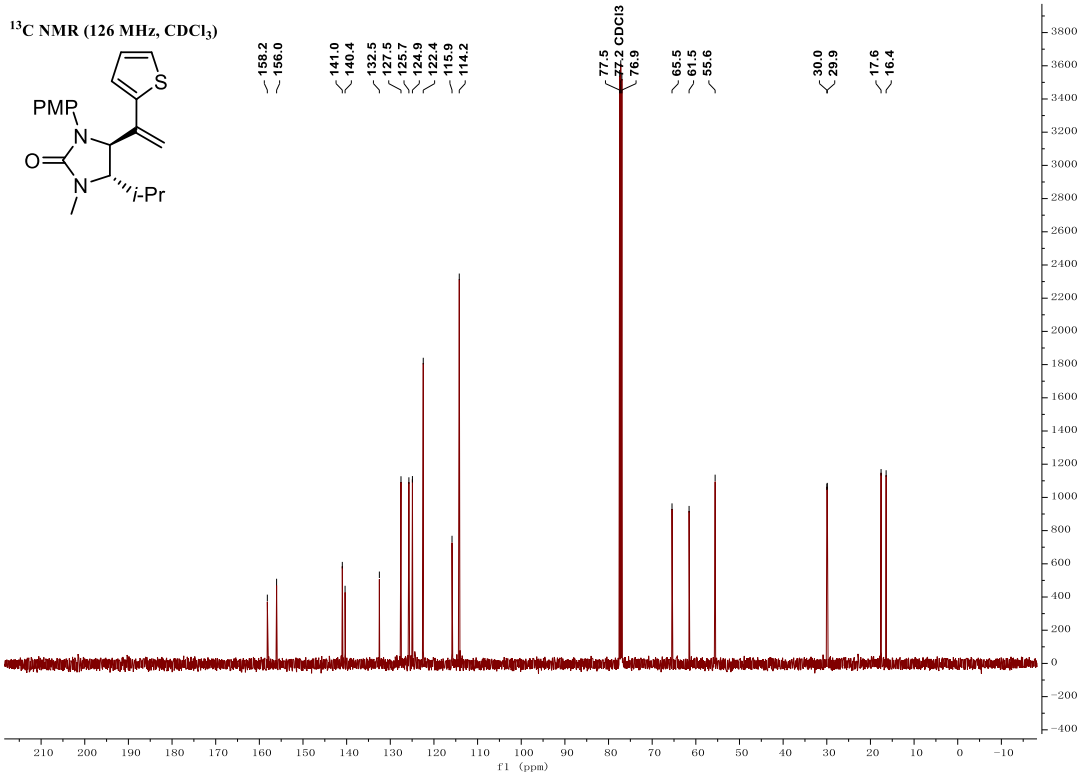


Compound 27

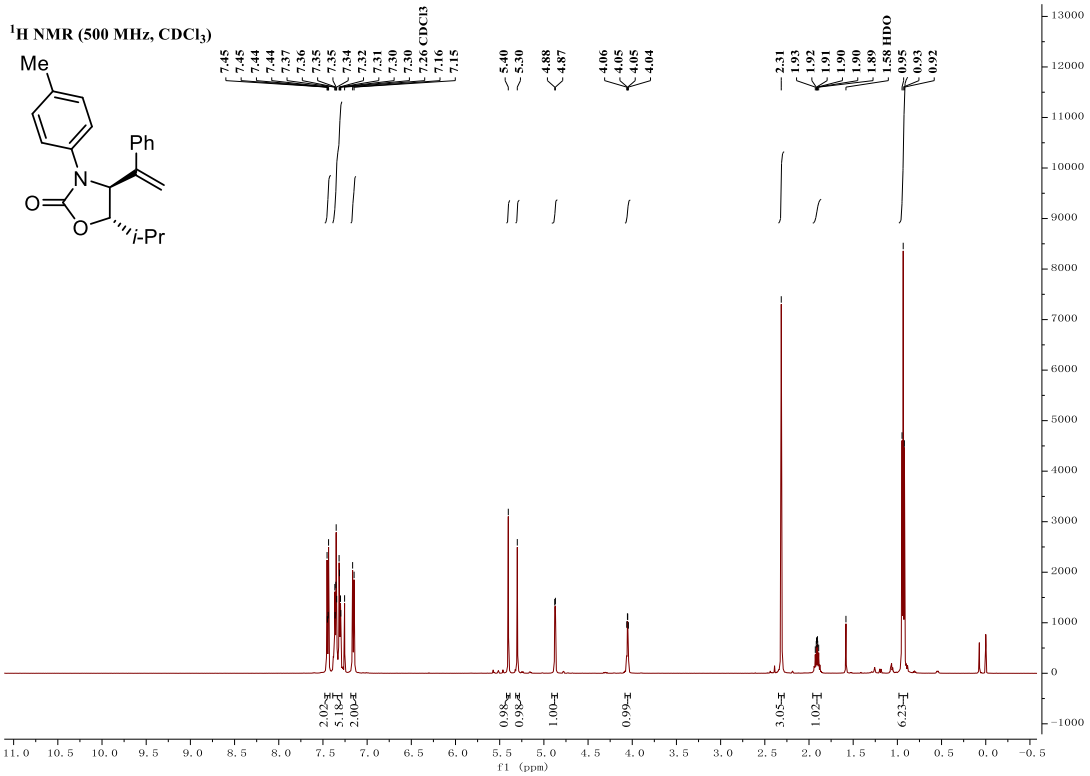
^{1}H NMR (500 MHz, $CDCl_3$)

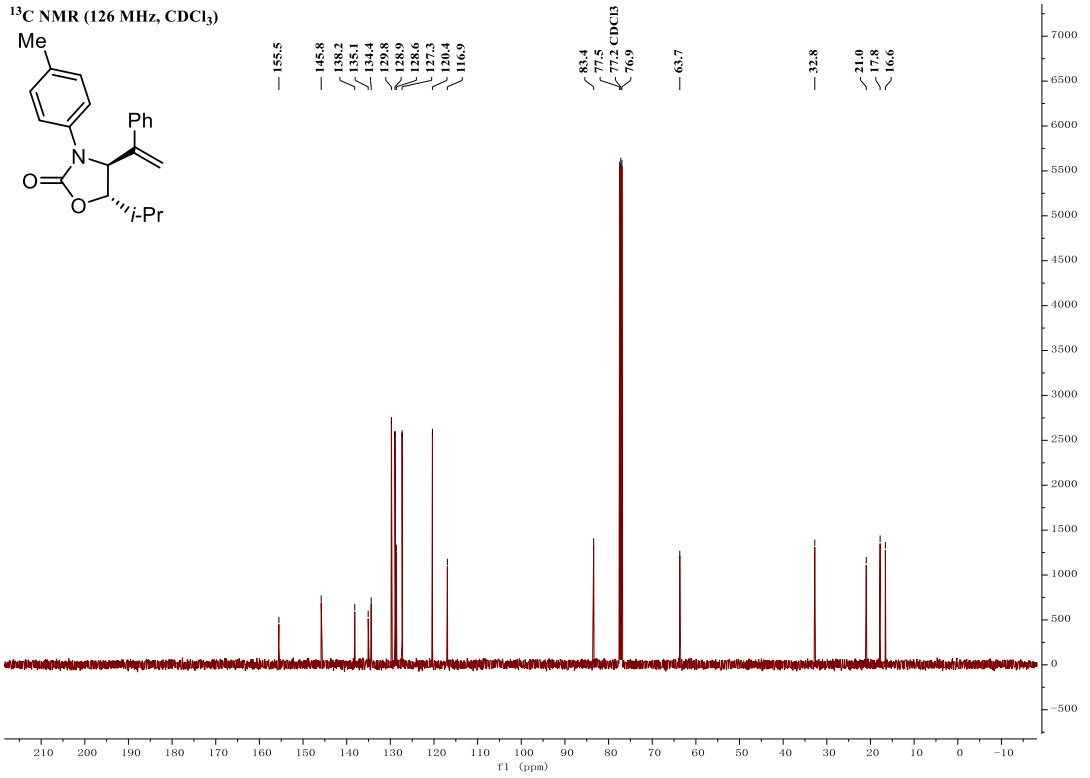


^{13}C NMR (126 MHz, $CDCl_3$)



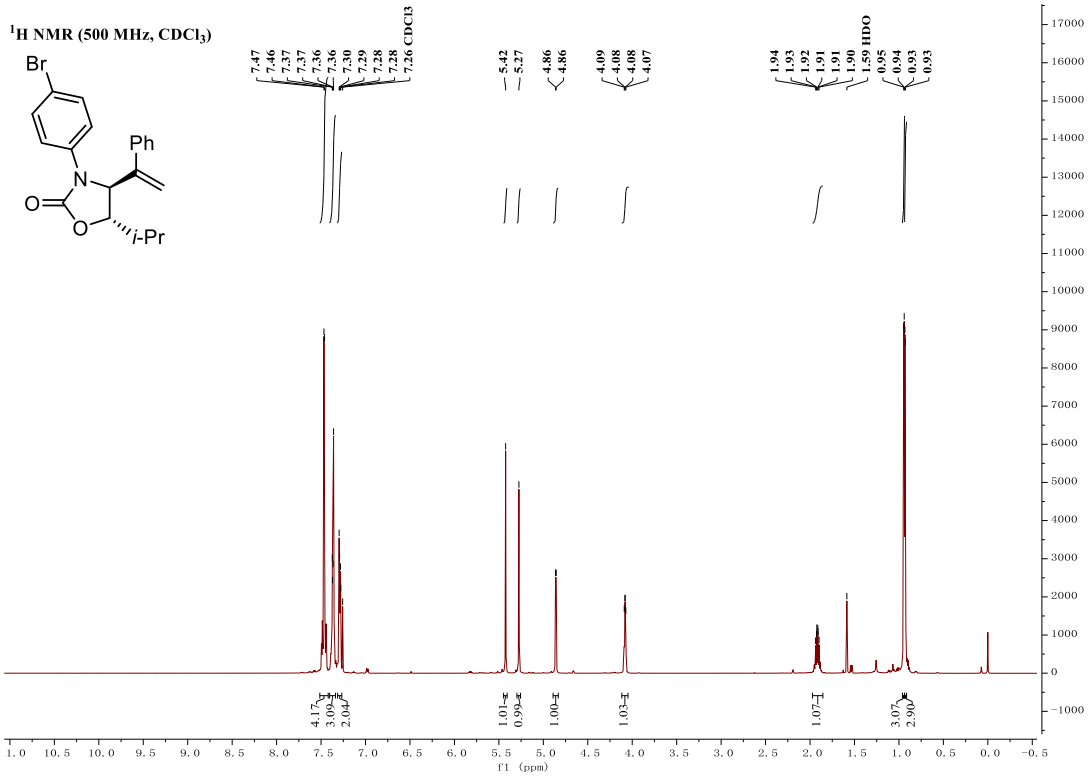
Compound 28


^{1}H NMR (500 MHz, CDCl$_3$)
Me
Ph
N
O
O
i-Pr
7.45
7.45
7.44
7.44
7.37
7.36
7.35
7.35
7.34
7.32
7.31
7.30
7.30
7.26 CDCl3
7.16
7.15
5.40
5.30
4.88
4.87
4.06
4.05
4.05
4.04
2.31
1.93
1.92
1.91
1.90
1.90
1.89
1.58 HDO
0.95
0.93
0.92
2.02
5.18
2.00
0.98
0.98
1.00
0.99
3.05
1.02
6.23
f1 (ppm)

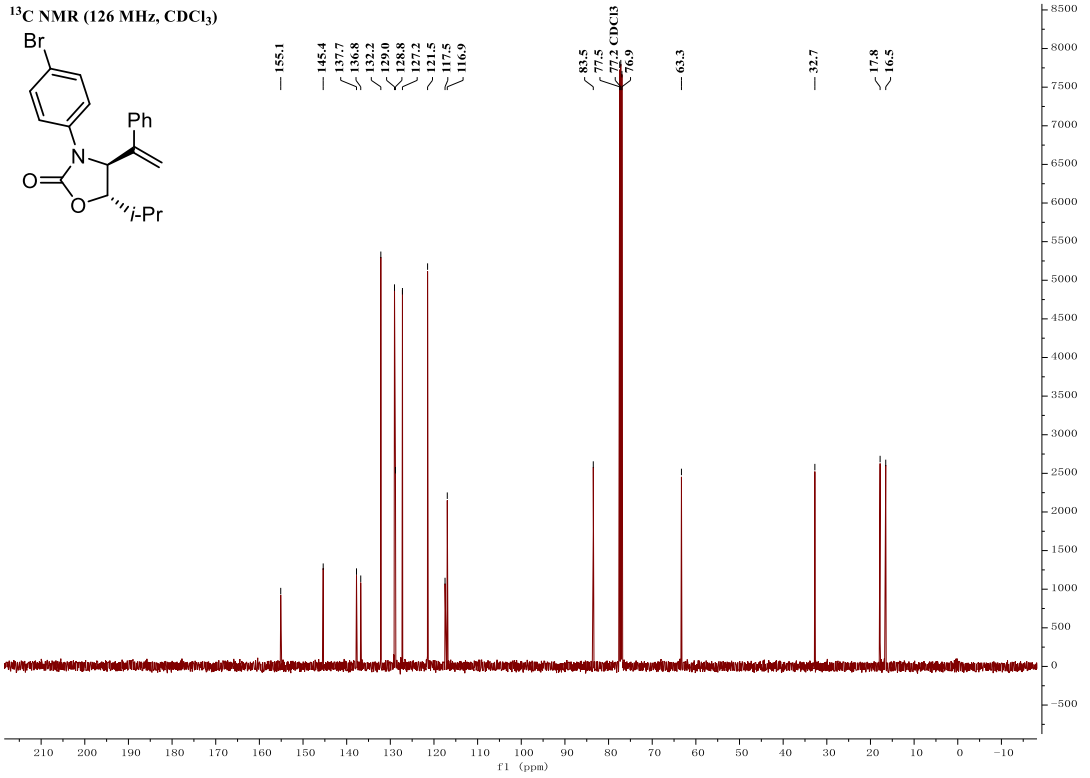

^{13}C NMR (126 MHz, CDCl$_3$)
Me
Ph
N
O
O
i-Pr
155.5
145.8
138.2
135.1
134.4
129.8
128.9
128.6
127.3
120.4
116.9
83.4
77.5
77.2 CDCl3
76.9
63.7
32.8
21.0
17.8
16.6
f1 (ppm)

Compound 29

^{1}H NMR (500 MHz, $CDCl_3$)

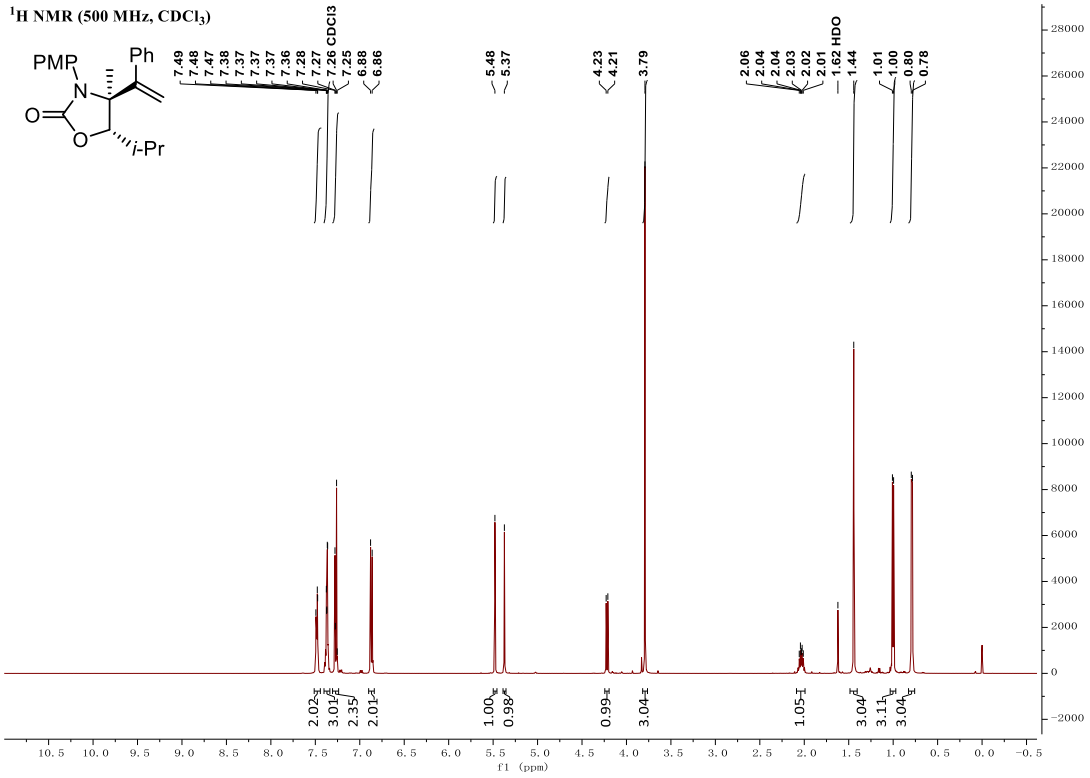


^{13}C NMR (126 MHz, $CDCl_3$)

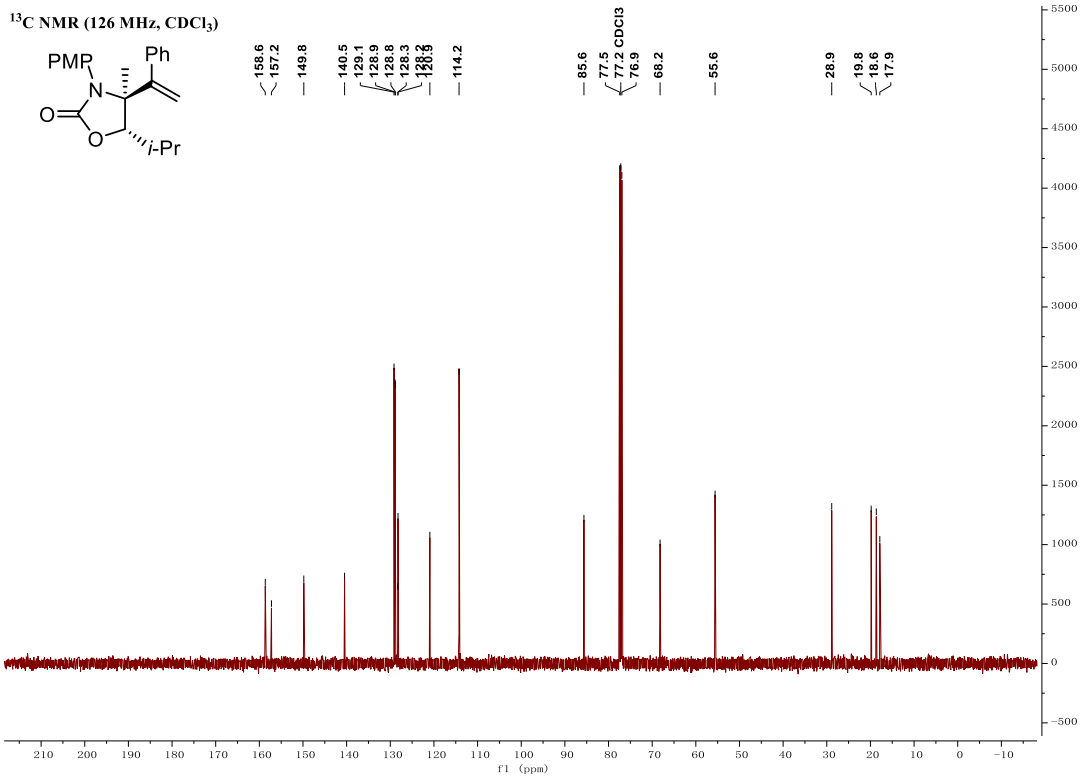


Compound 31

^{1}H NMR (500 MHz, $CDCl_3$)

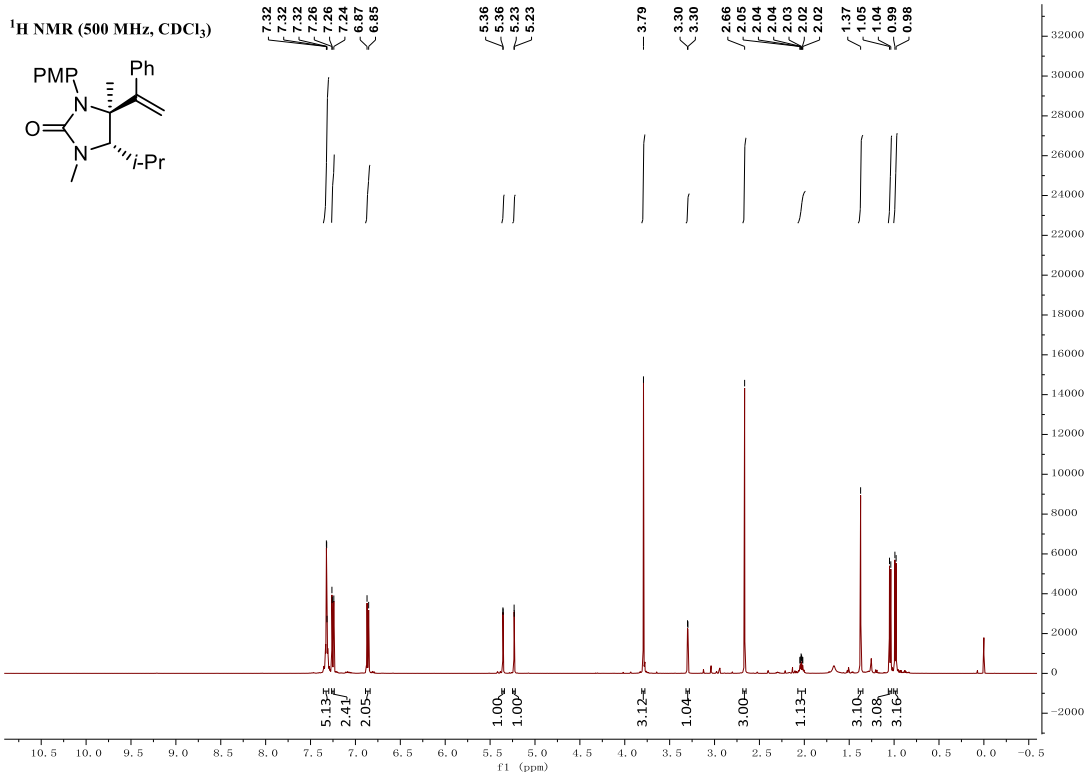


^{13}C NMR (126 MHz, $CDCl_3$)

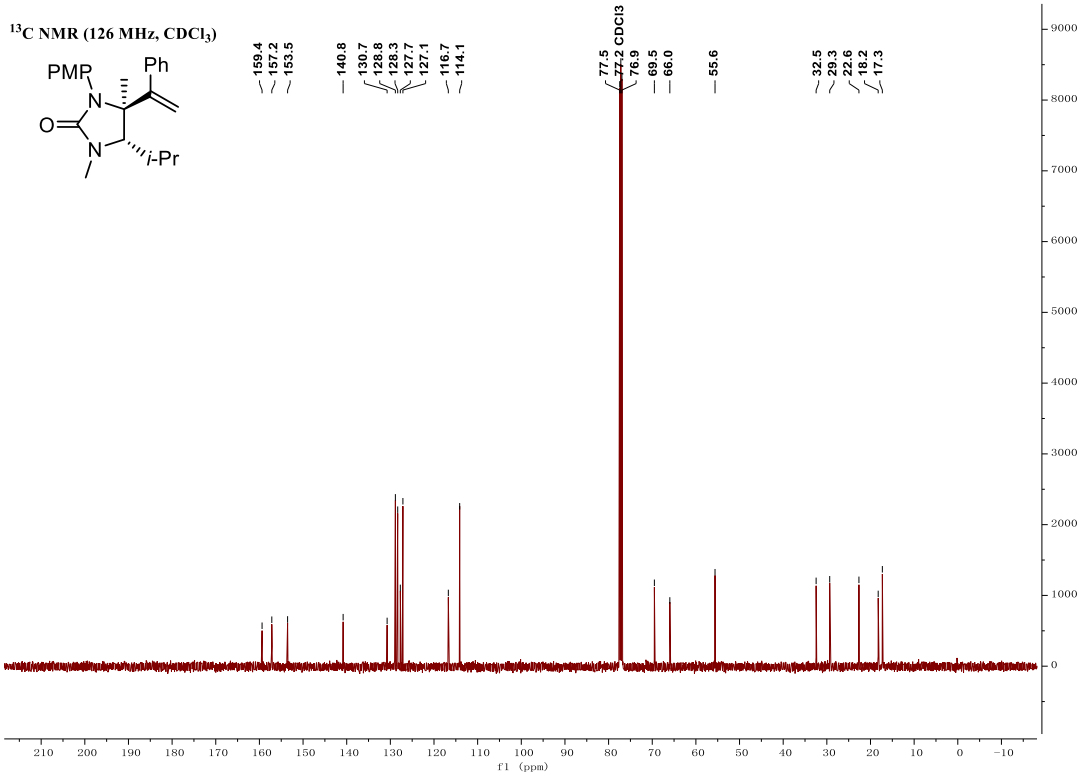


Compound 32

^{1}H NMR (500 MHz, $CDCl_3$)

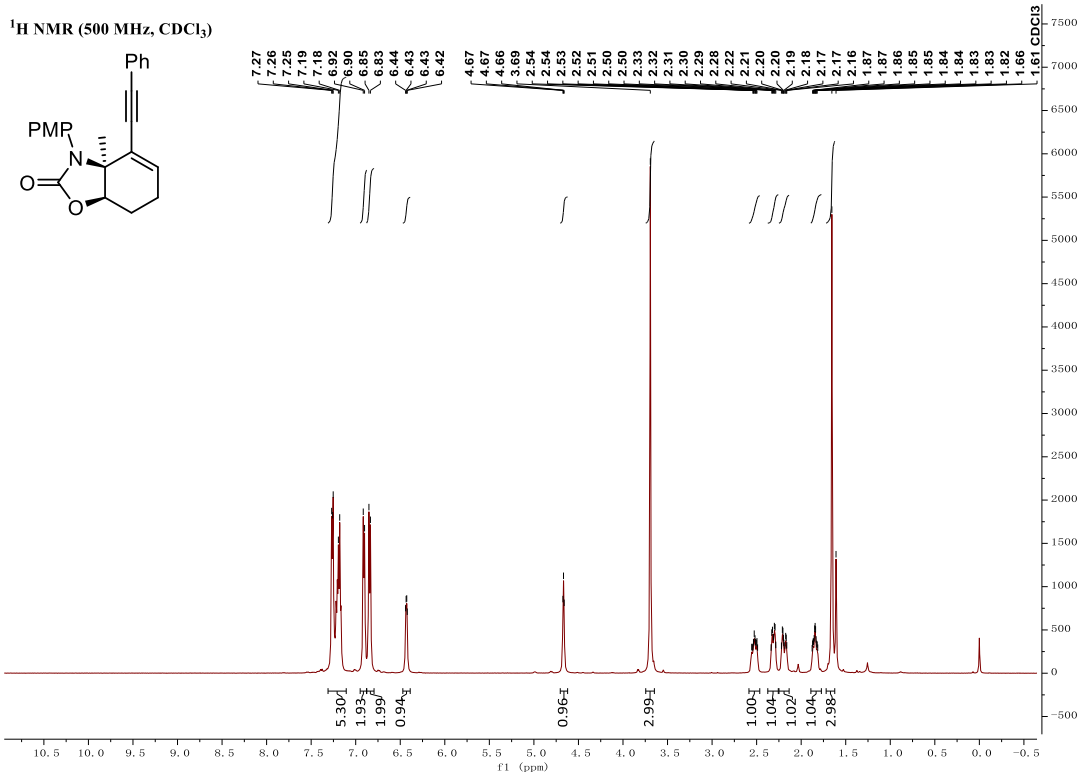


^{13}C NMR (126 MHz, $CDCl_3$)

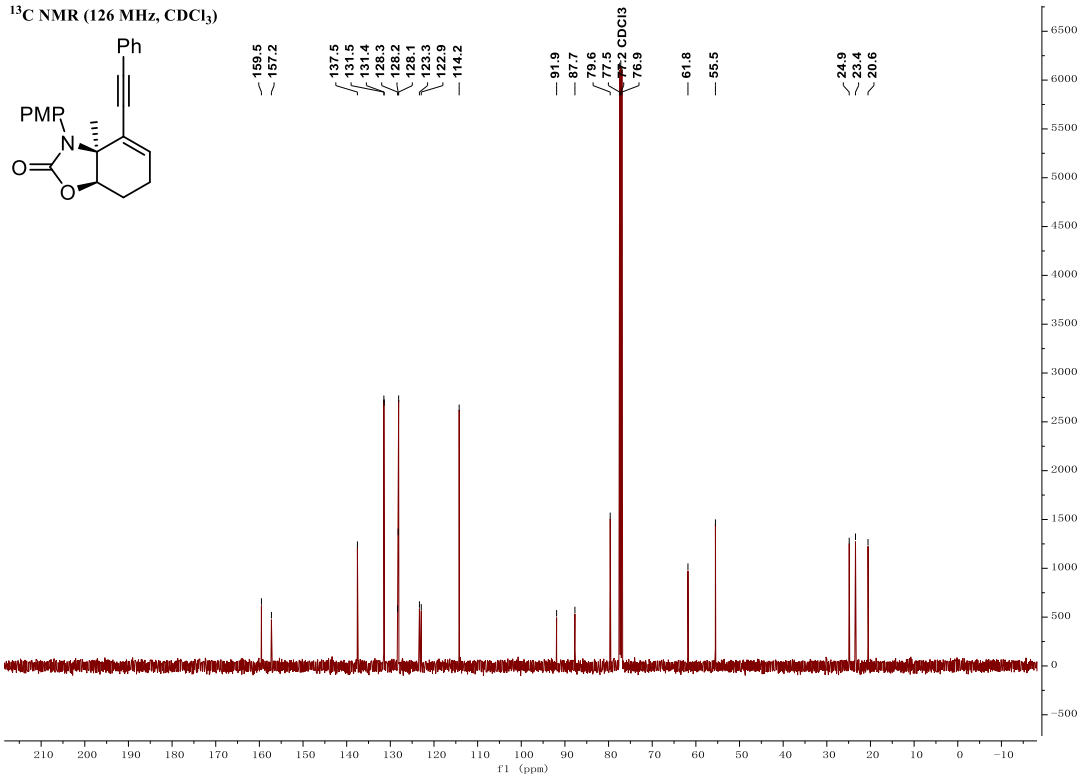


Compound 33

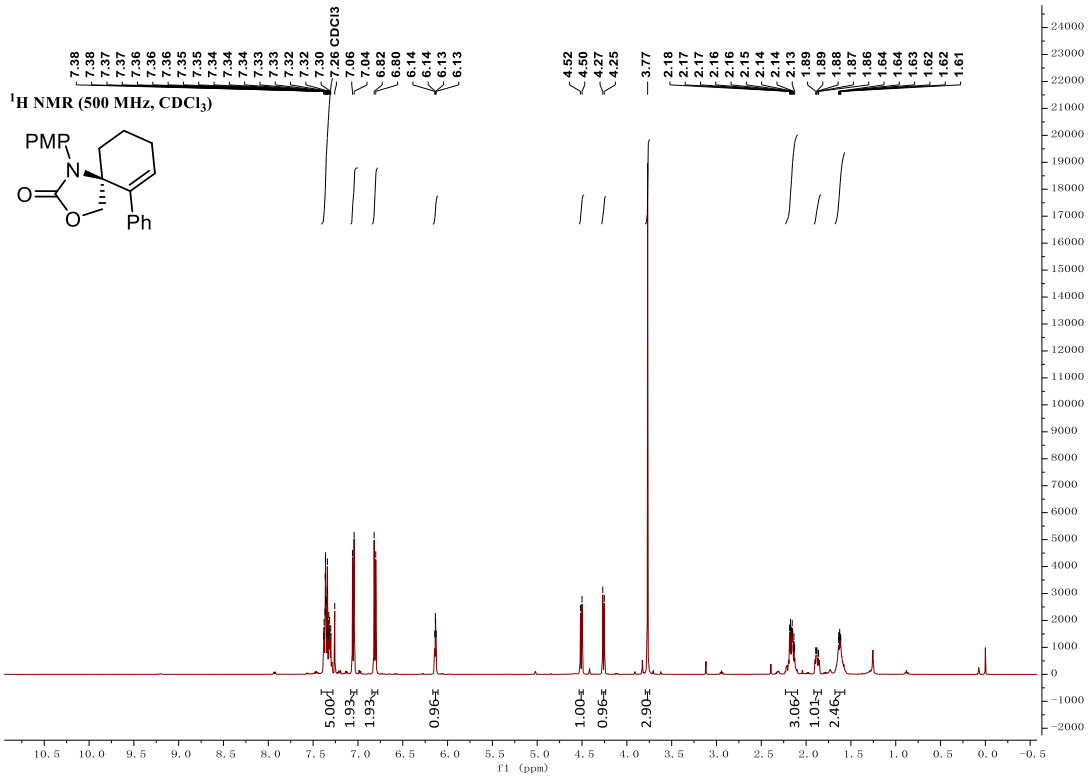
^{1}H NMR (500 MHz, $CDCl_3$)

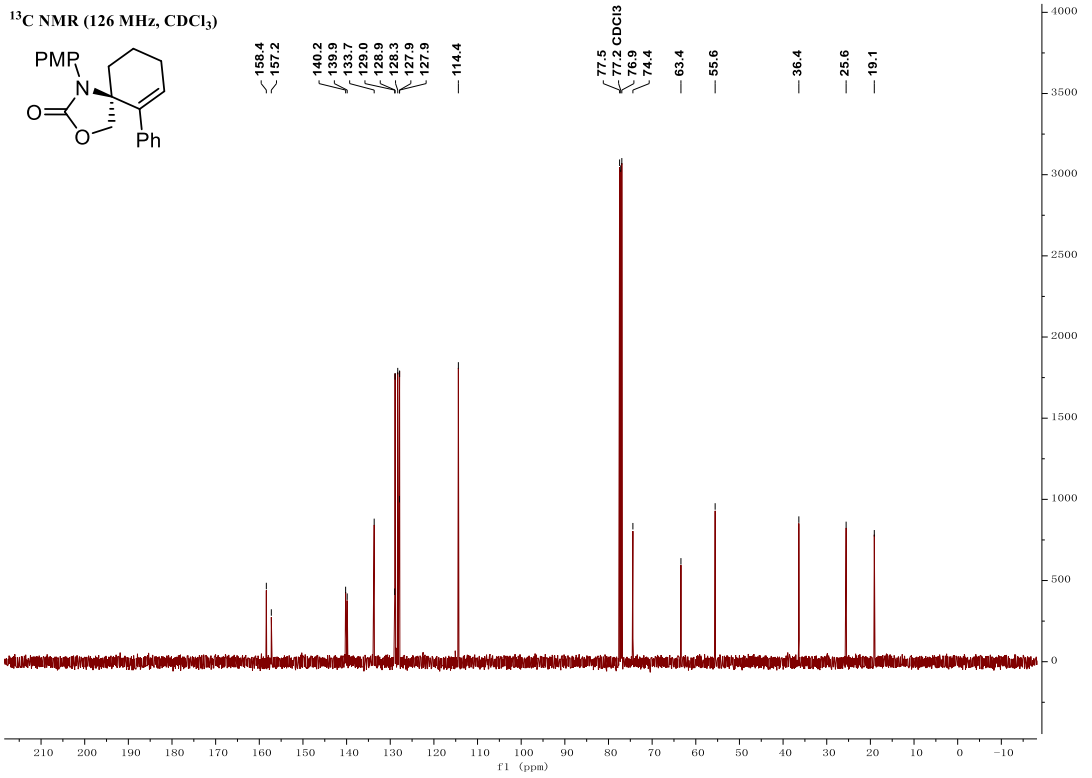


^{13}C NMR (126 MHz, $CDCl_3$)

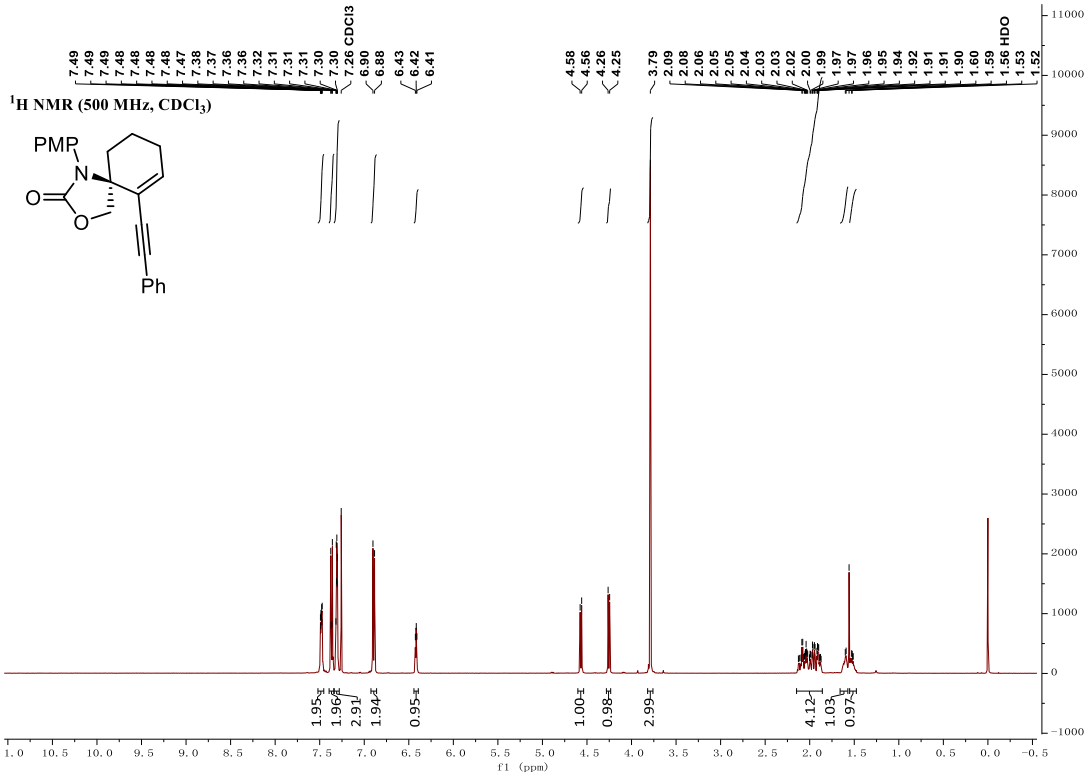


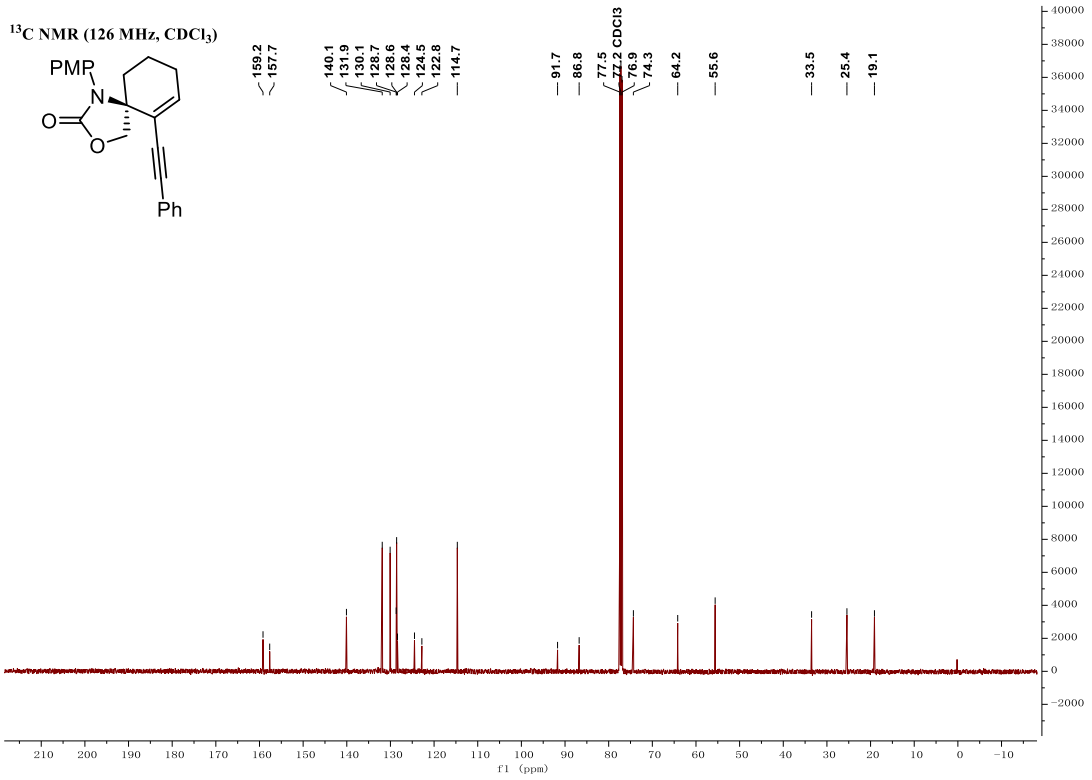
Compound 34


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
N
O
O
Ph
7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.30 7.26 CDCl3 7.06 7.04 6.82 6.80 6.14 6.14 6.13 6.13
4.52 4.50 4.27 4.25 3.77
2.18 2.17 2.17 2.16 2.16 2.15 2.14 2.14 2.13 1.89 1.89 1.88 1.87 1.86 1.64 1.64 1.63 1.62 1.62 1.61
5.00 1.93 1.93 0.96 1.00 0.96 2.90 3.06 1.01 2.46
f1 (ppm)

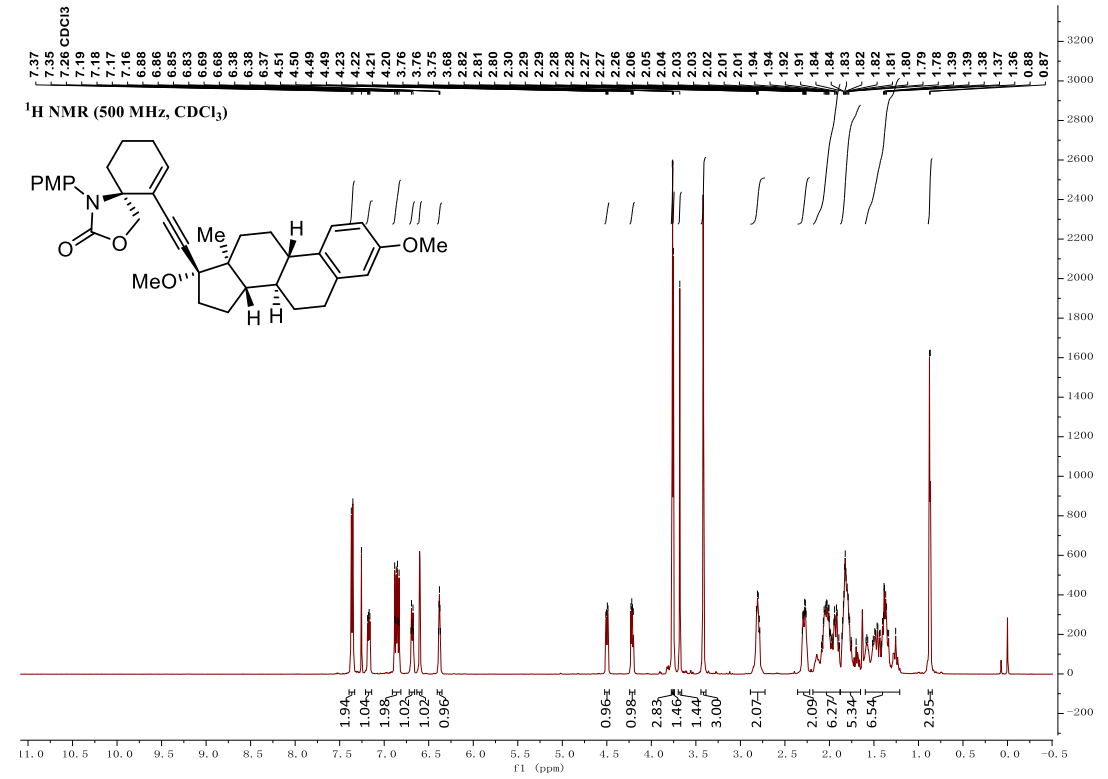

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
N
O
O
Ph
158.4 157.2 140.2 139.9 133.7 129.0 128.9 128.3 127.9 127.9 114.4
77.5 77.2 CDCl3 76.9 74.4 63.4 55.6 36.4 25.6 19.1
f1 (ppm)

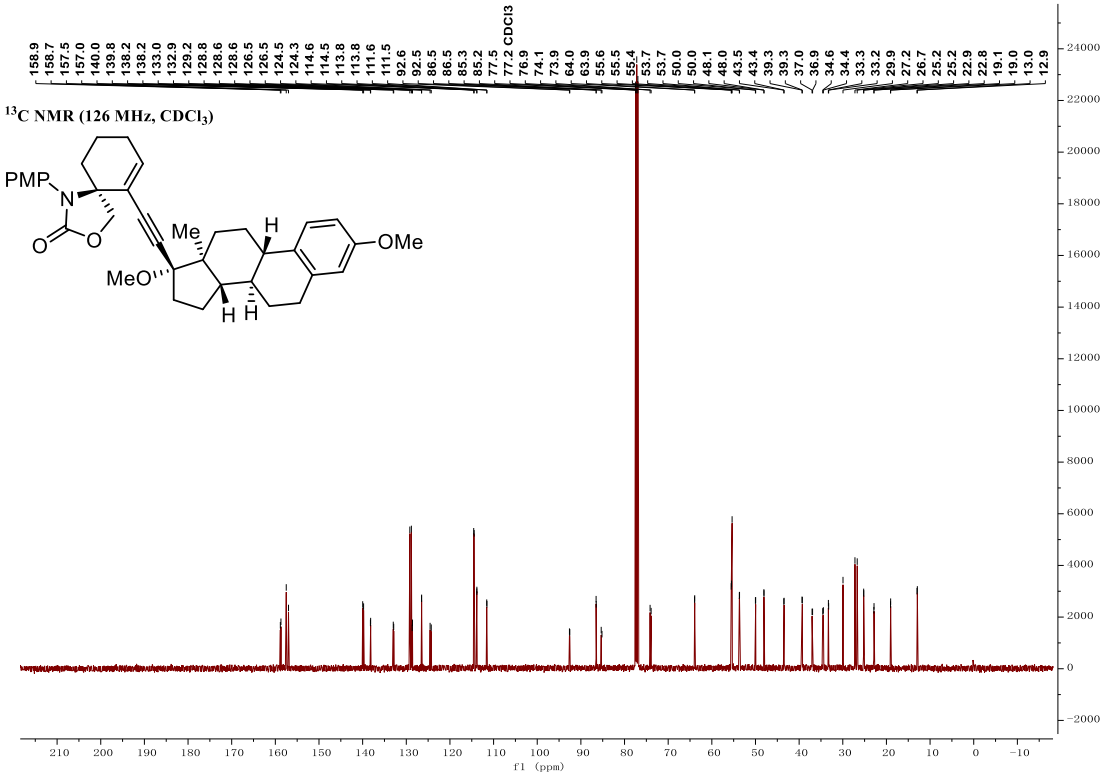
Compound 35


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
N
O
O
Ph
7.49 7.49 7.49 7.48 7.48 7.48 7.47 7.38 7.37 7.36 7.36 7.32 7.31 7.31 7.31 7.30 7.30 7.26 CDCl3 6.90 6.88 6.43 6.42 6.41
4.58 4.56 4.26 4.25 3.79 2.09 2.08 2.06 2.05 2.05 2.04 2.03 2.03 2.02 2.00 1.99 1.97 1.97 1.96 1.95 1.94 1.92 1.91 1.91 1.90 1.60 1.59 1.56 HDO 1.53 1.52
1.95 1.96 2.91 1.94 0.95 1.00 0.98 2.99 4.12 1.03 0.97
f1 (ppm)

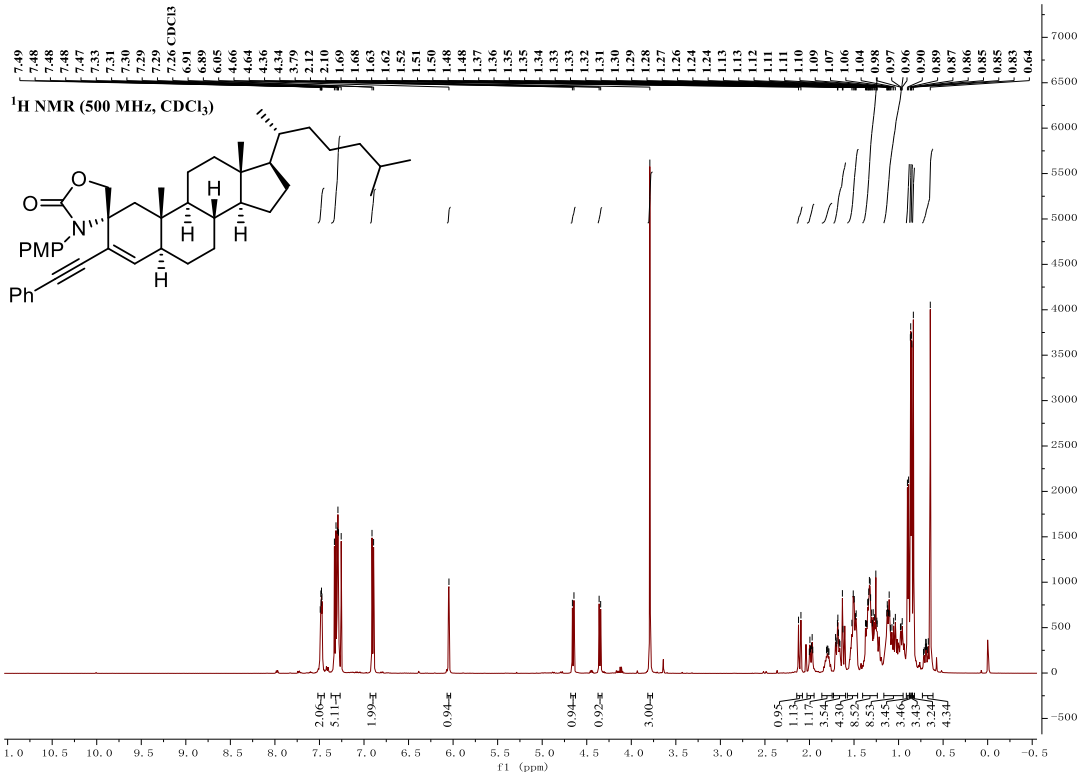

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
N
O
O
Ph
159.2 157.7 140.1 131.9 130.1 128.7 128.6 128.4 124.5 122.8 114.7 91.7 86.8 77.5 77.2 CDCl3 76.9 74.3 64.2 55.6 33.5 25.4 19.1
f1 (ppm)

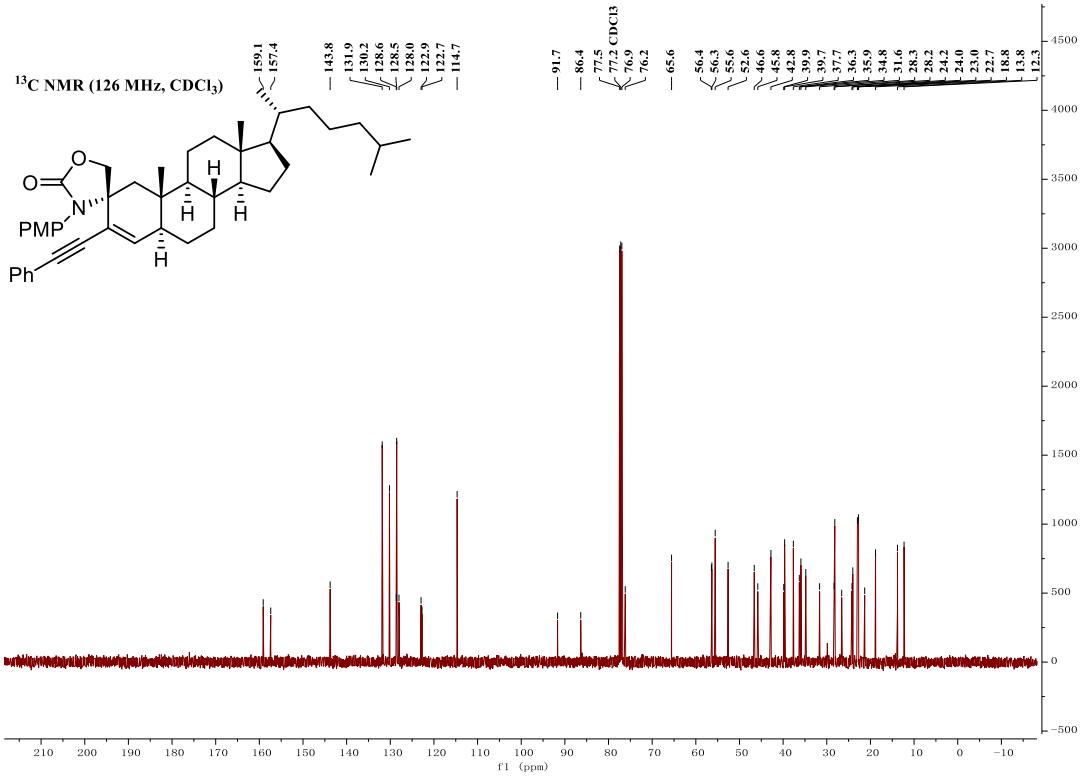
Compound 36

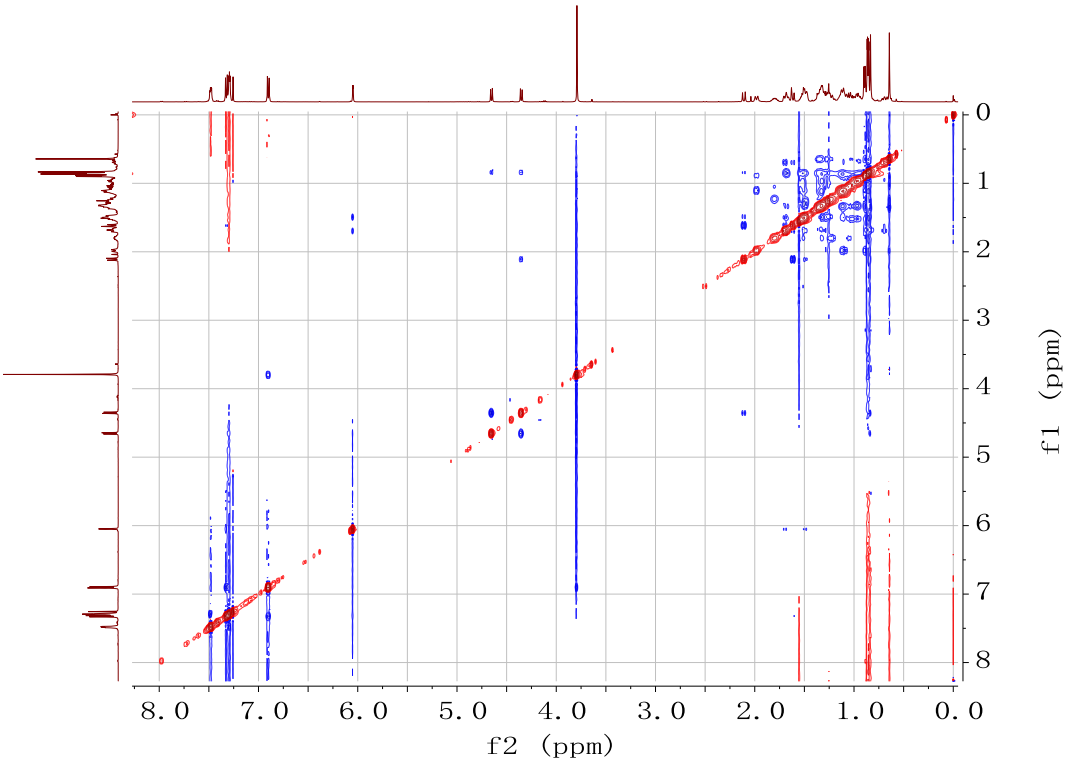

7.37
7.35
7.26 CDCl3
7.19
7.18
7.17
7.16
6.88
6.86
6.85
6.83
6.69
6.68
6.38
6.38
6.37
4.51
4.50
4.49
4.49
4.23
4.22
4.21
4.20
3.76
3.76
3.75
3.68
2.82
2.81
2.80
2.30
2.29
2.29
2.28
2.28
2.27
2.27
2.26
2.06
2.05
2.04
2.03
2.03
2.02
2.01
2.01
1.94
1.94
1.92
1.91
1.84
1.84
1.83
1.82
1.82
1.81
1.80
1.79
1.78
1.39
1.39
1.38
1.37
1.36
0.88
0.87
1H NMR (500 MHz, CDCl3)
PMP
N
O
O
Me
MeO
H
OMe
H
H
1.94
1.04
1.98
1.02
1.02
0.96
0.96
0.98
2.83
1.46
1.44
3.00
2.07
2.09
6.27
5.34
6.54
2.95
f1 (ppm)

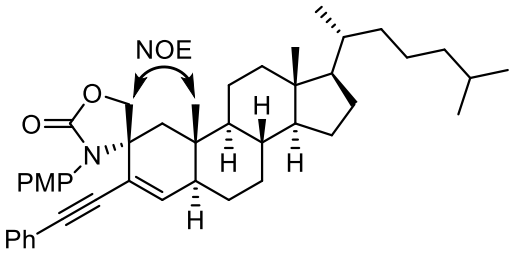

158.9
158.7
157.5
157.0
140.0
139.8
138.2
138.2
133.0
132.9
129.2
128.8
128.6
128.6
126.5
126.5
124.5
124.3
114.6
114.5
113.8
113.8
111.6
111.5
92.6
92.5
86.5
86.5
85.3
85.2
77.5
77.2 CDCl3
76.9
74.1
73.9
64.0
63.9
55.6
55.5
55.4
53.7
53.7
50.0
50.0
48.1
48.0
43.5
43.4
39.3
39.3
37.0
36.9
34.6
34.4
33.3
33.2
29.9
27.2
26.7
25.2
25.2
22.9
22.8
19.1
19.0
13.0
12.9
13C NMR (126 MHz, CDCl3)
PMP
N
O
O
Me
MeO
H
OMe
H
H
f1 (ppm)

Compound 37



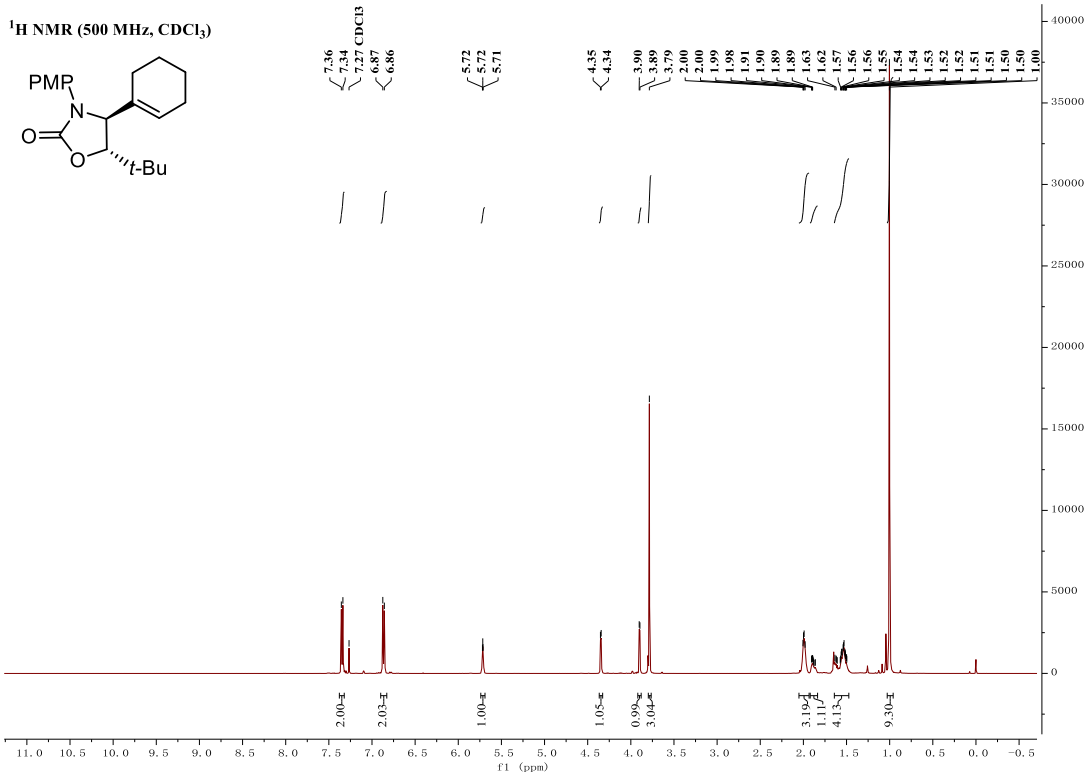



0
1
2
3
4
5
6
7
8
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)

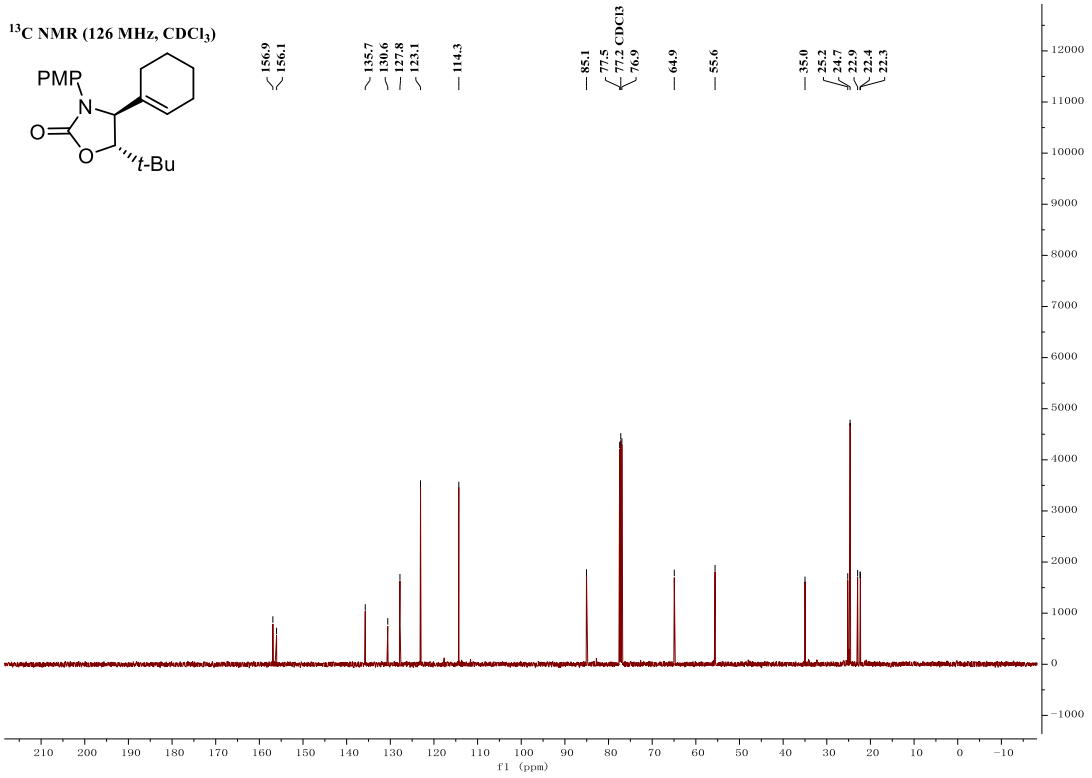

NOE
O
O
N
PMP
Ph
H
H
H
H

Compound 39

^{1}H NMR (500 MHz, $CDCl_3$)

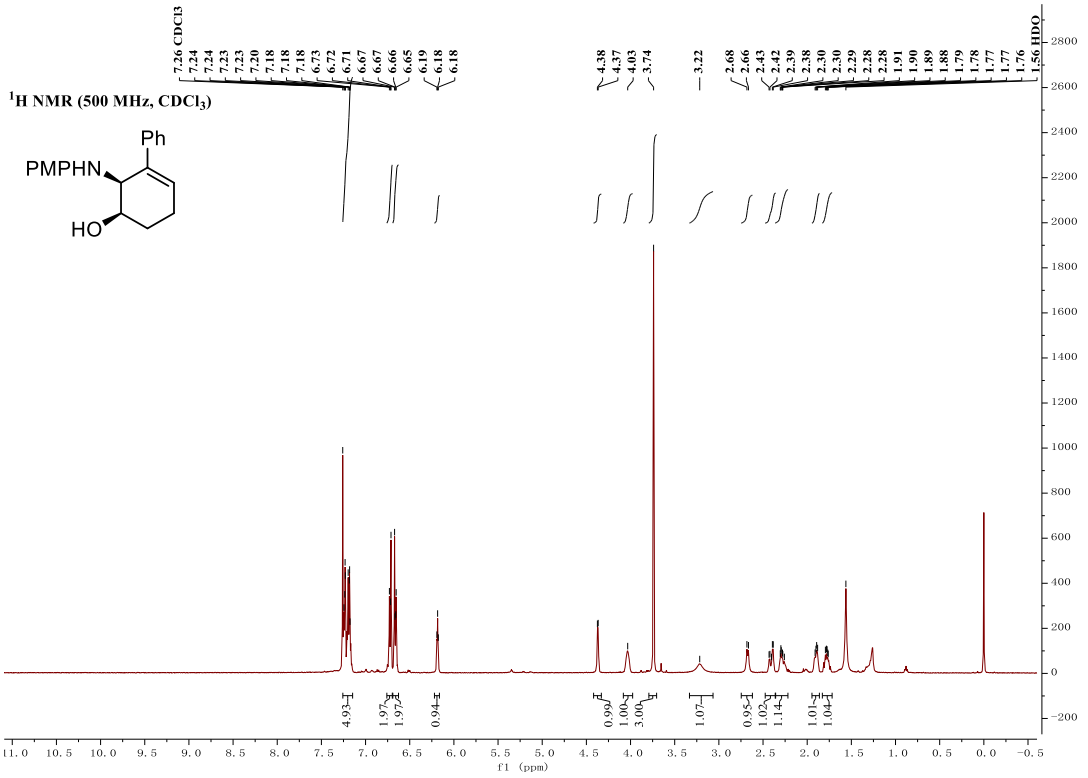


^{13}C NMR (126 MHz, $CDCl_3$)

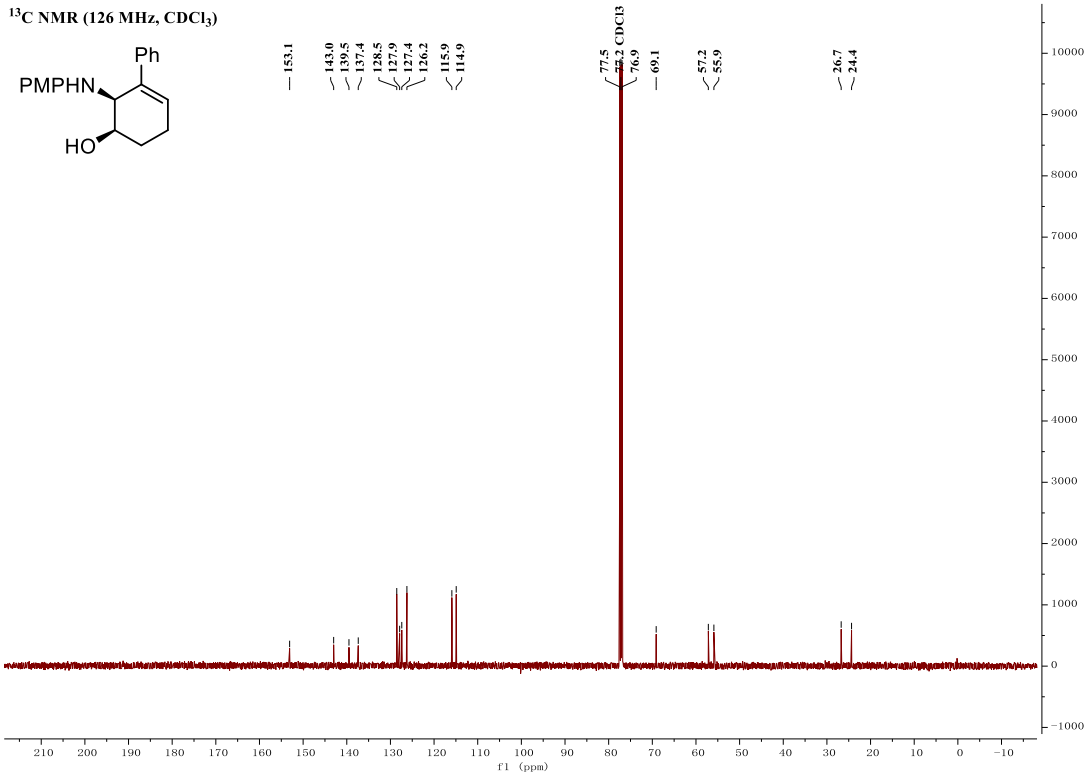


Compound 42

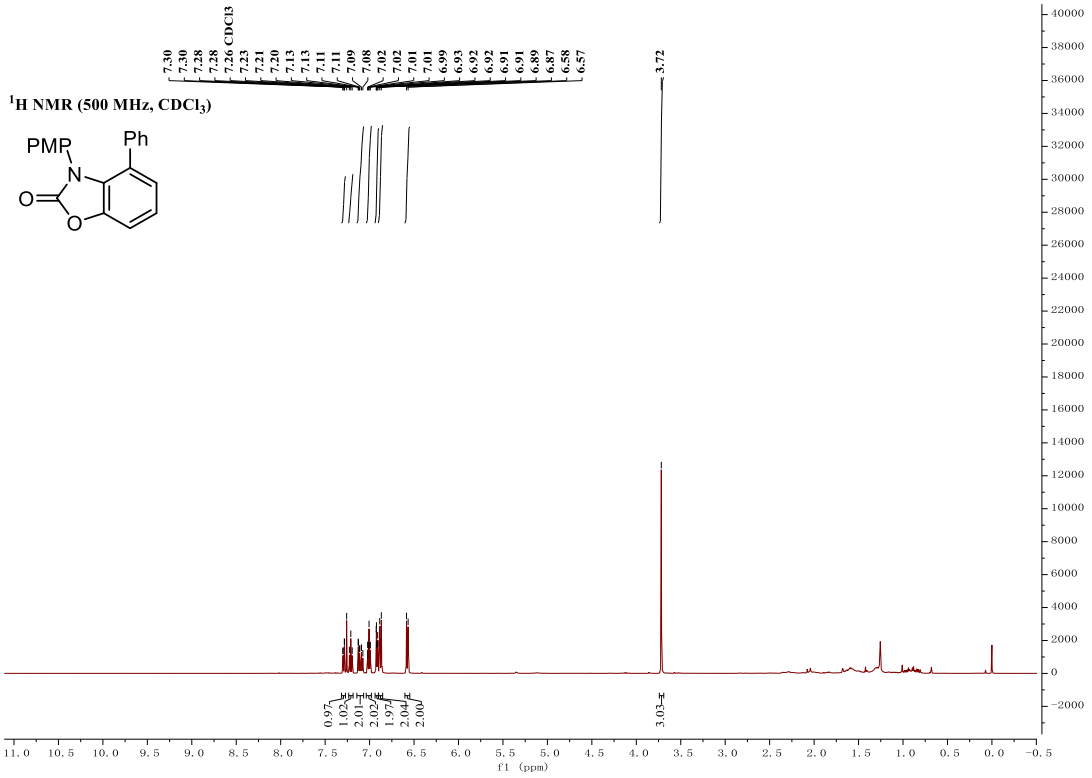
^{1}H NMR (500 MHz, $CDCl_3$)

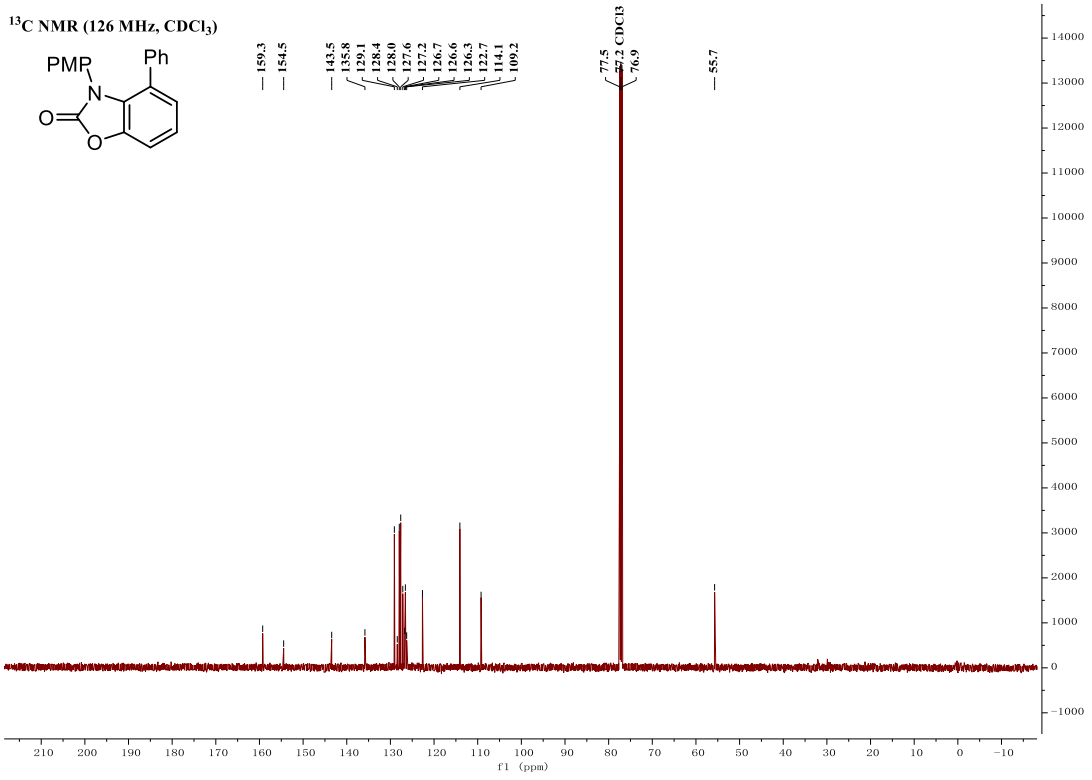


^{13}C NMR (126 MHz, $CDCl_3$)



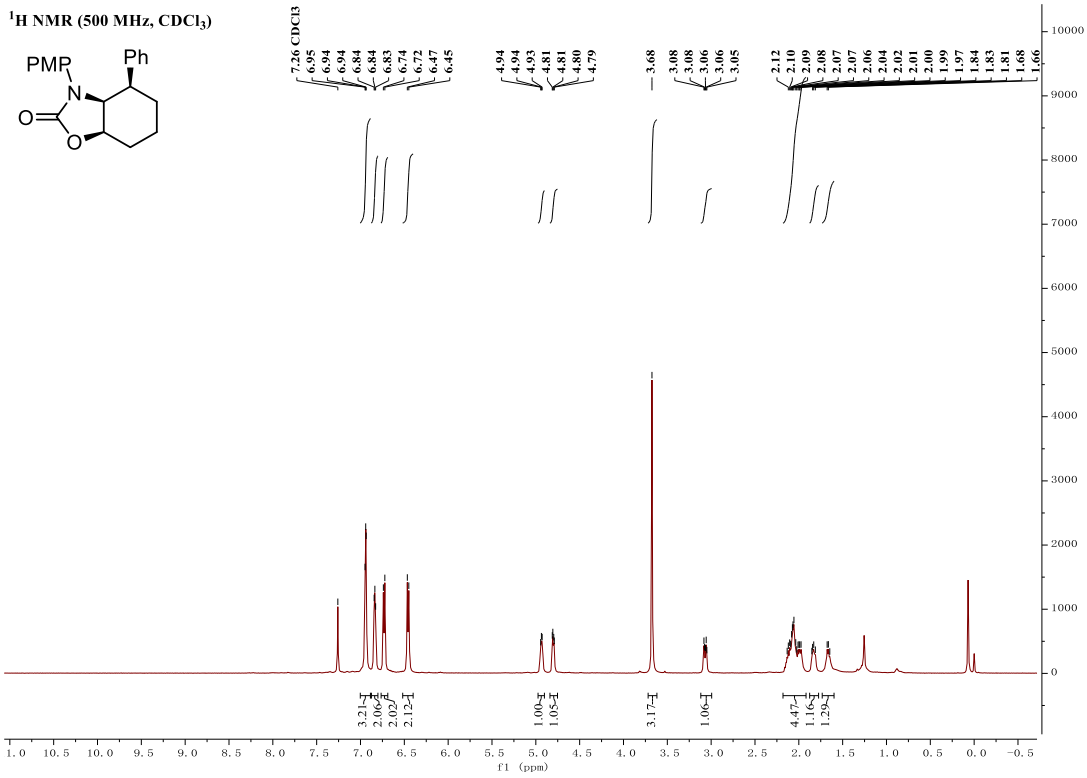
Compound 43


7.30
7.30
7.28
7.28
7.26 CDCl3
7.23
7.21
7.20
7.13
7.13
7.11
7.11
7.09
7.08
7.02
7.02
7.01
7.01
6.99
6.93
6.92
6.92
6.91
6.91
6.89
6.87
6.58
6.57
3.72
0.97
1.02
2.01
2.02
1.97
2.04
2.00
3.03
f1 (ppm)

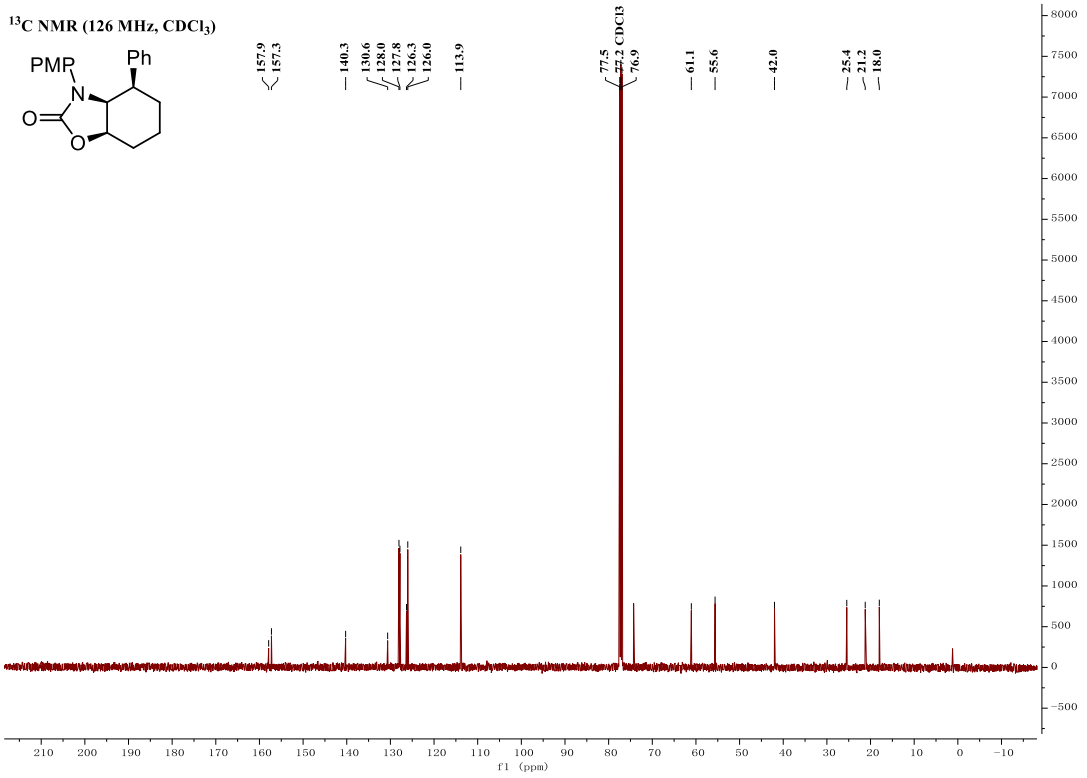

159.3
154.5
143.5
135.8
129.1
128.4
128.0
127.6
127.2
126.7
126.6
126.3
122.7
114.1
109.2
77.5
77.2 CDCl3
76.9
55.7
f1 (ppm)

Compound 44

^{1}H NMR (500 MHz, $CDCl_3$)

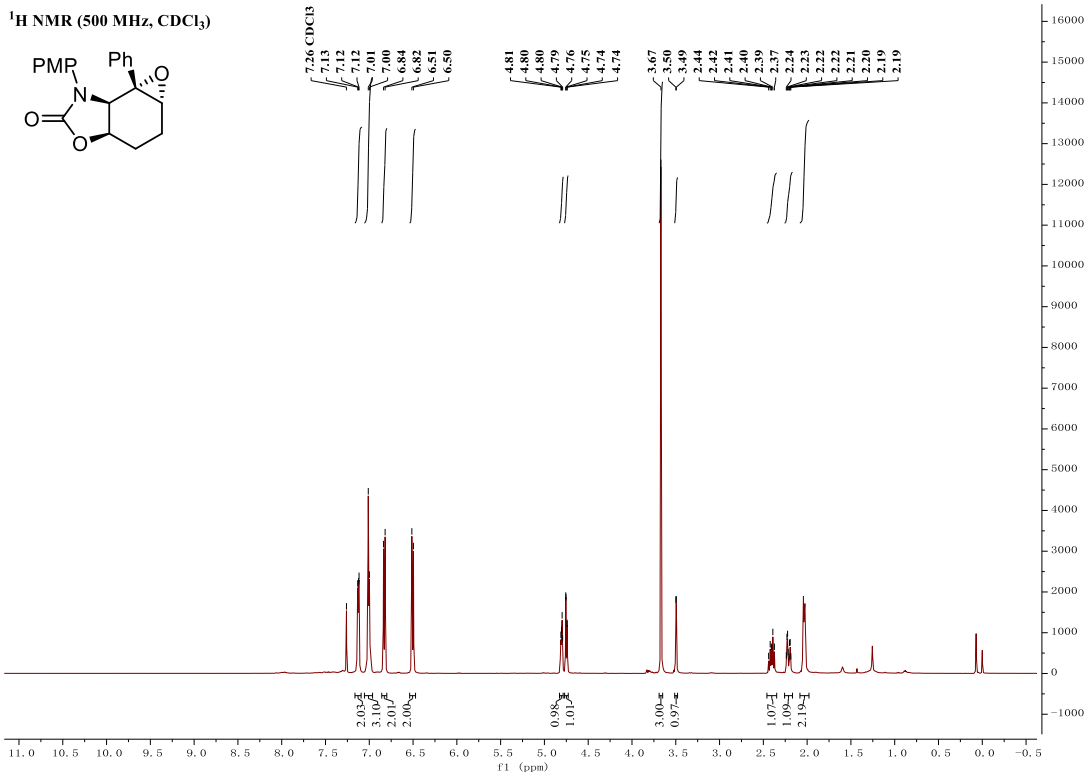


^{13}C NMR (126 MHz, $CDCl_3$)

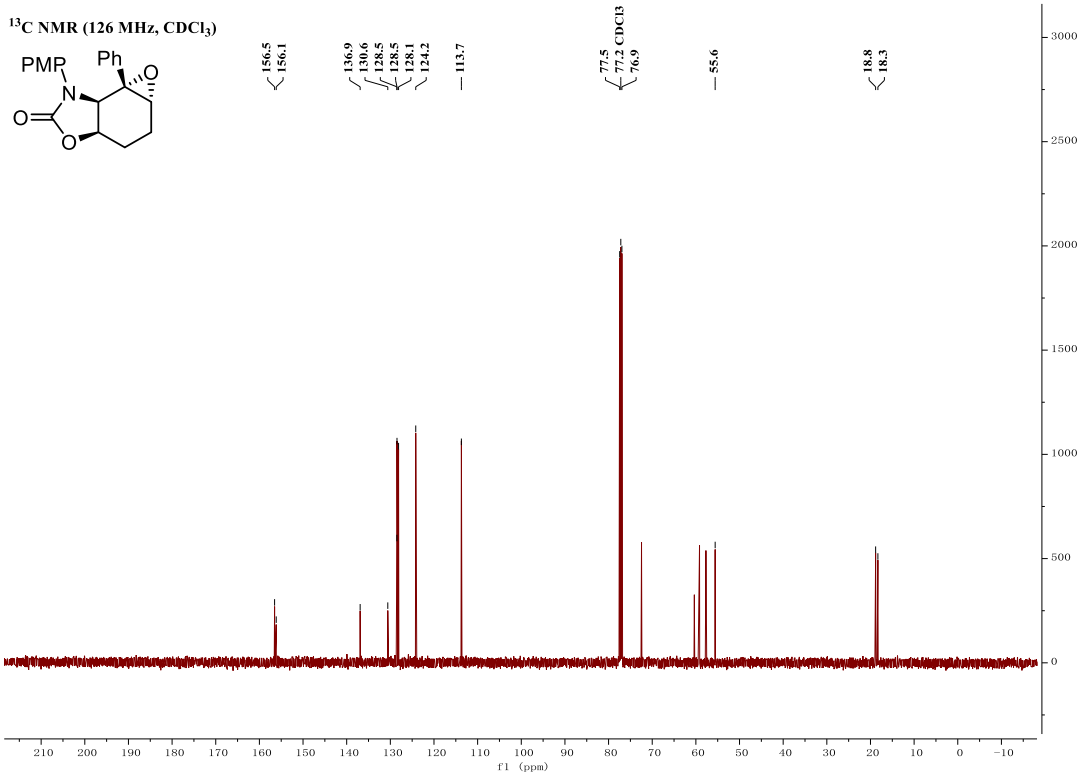


Compound 45

^{1}H NMR (500 MHz, $CDCl_3$)

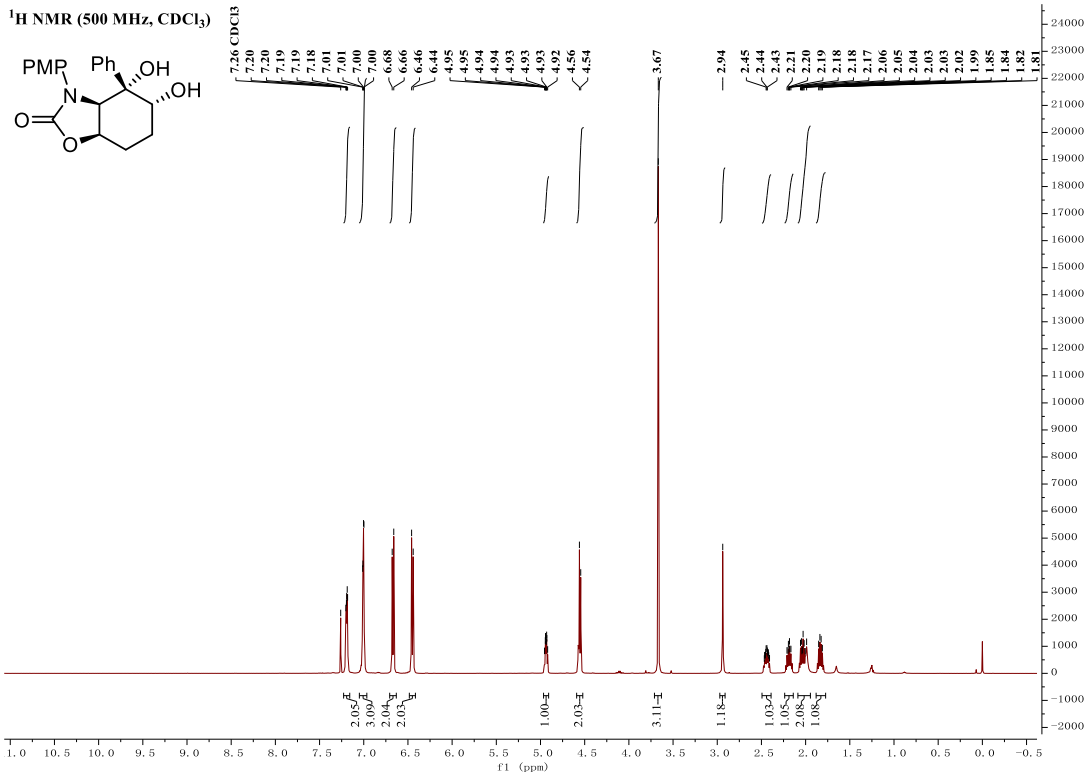


^{13}C NMR (126 MHz, $CDCl_3$)

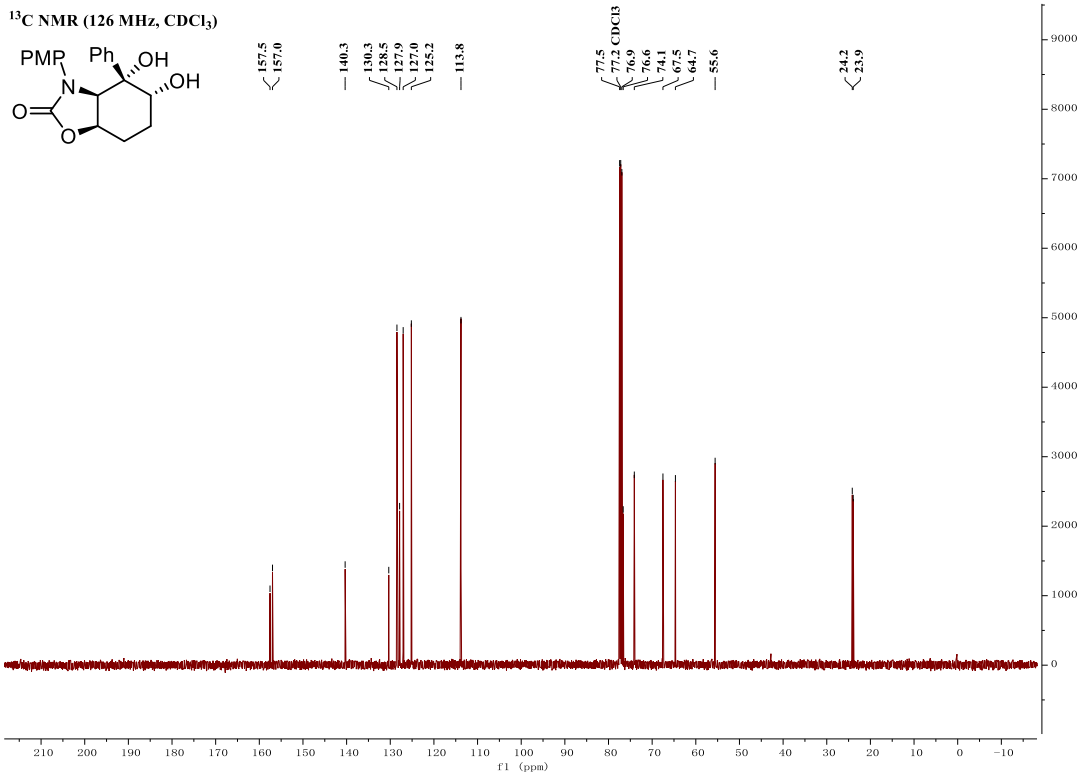


Compound 46

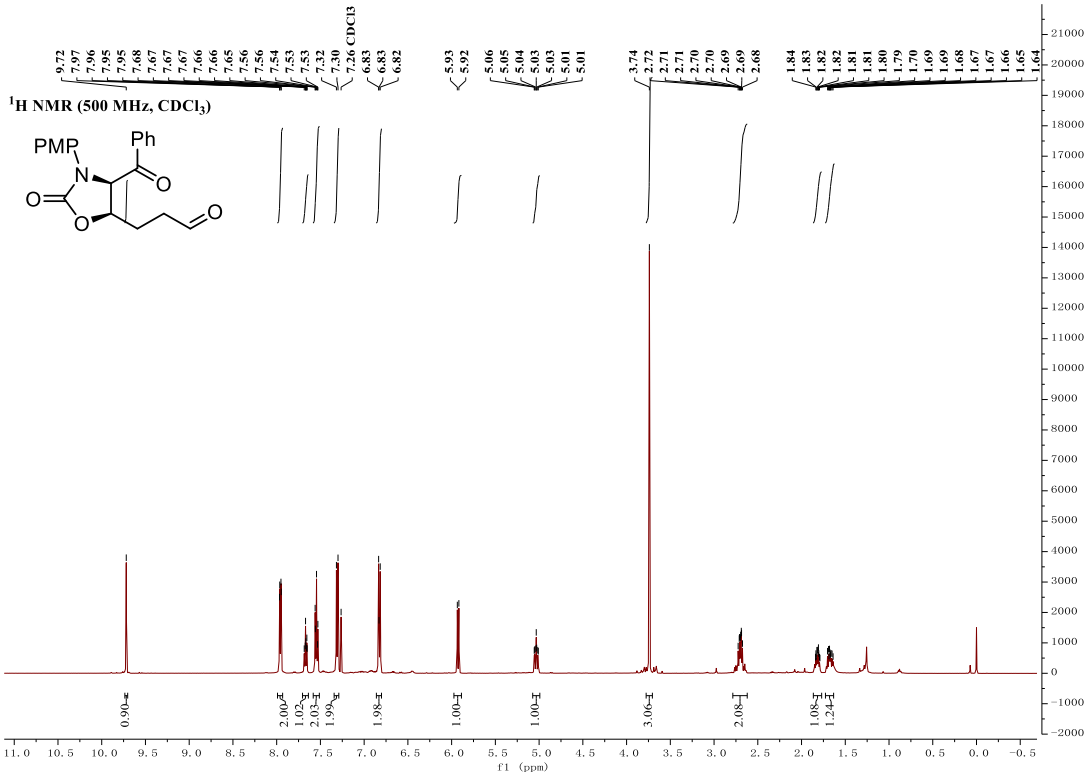
^{1}H NMR (500 MHz, $CDCl_3$)

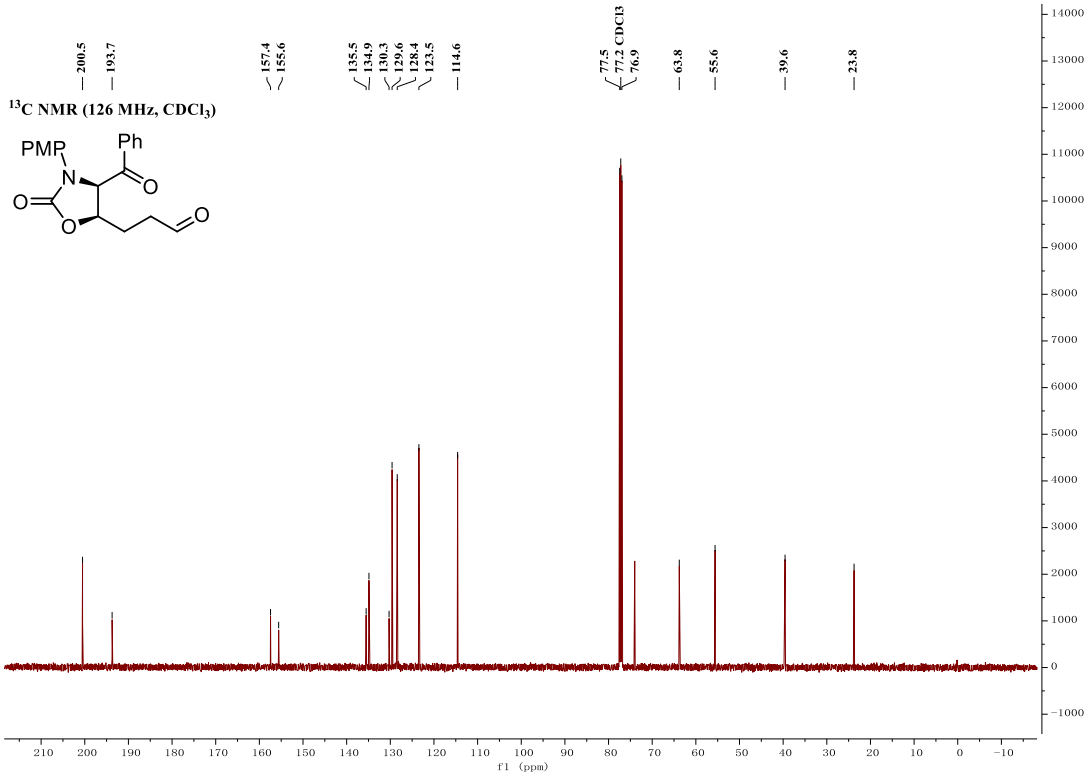


^{13}C NMR (126 MHz, $CDCl_3$)

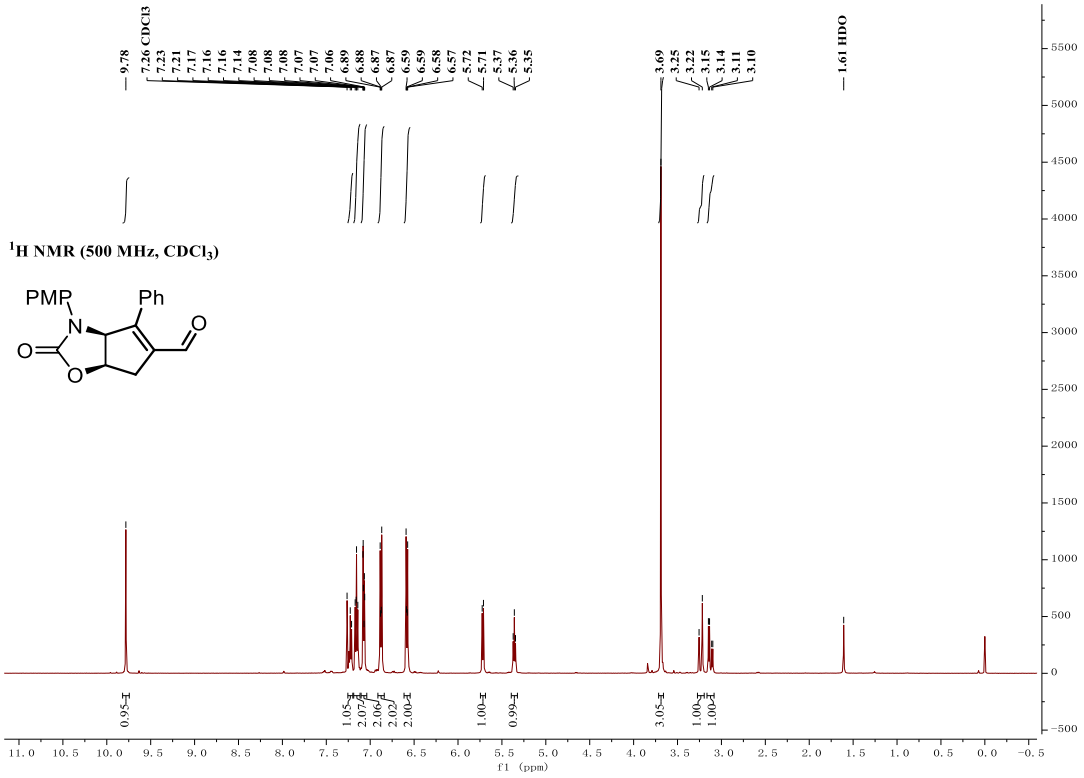


Compound 47

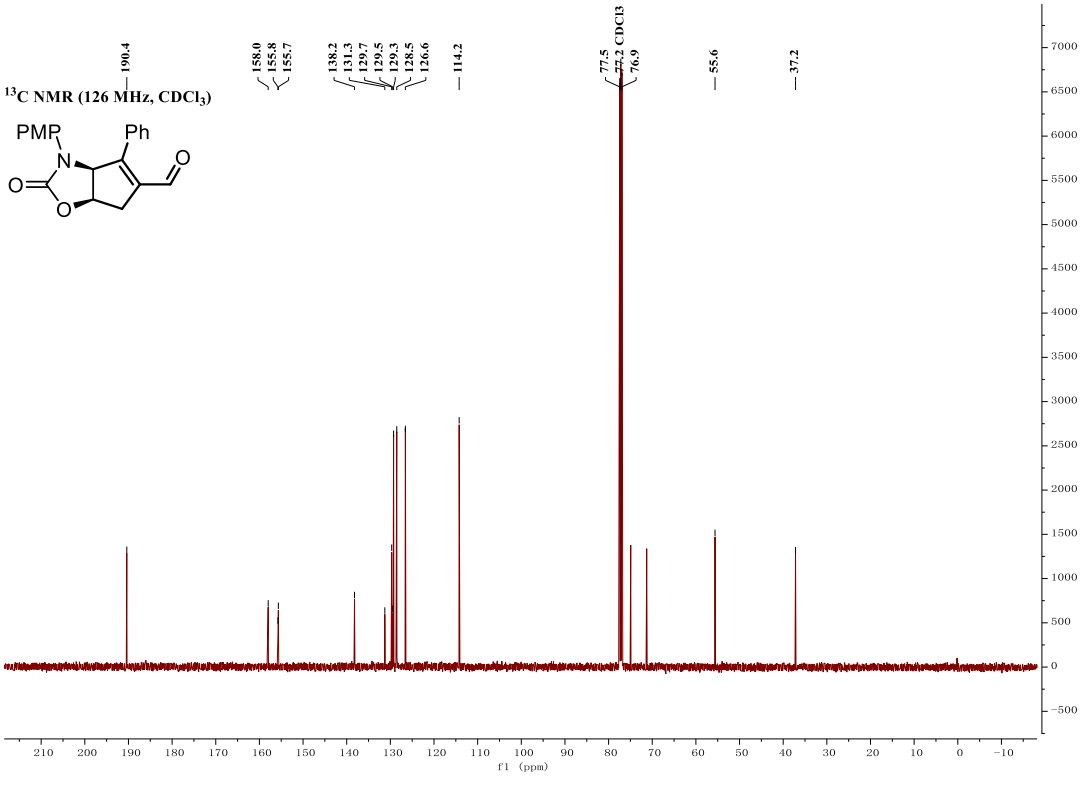

9.72 7.97 7.96 7.95 7.95 7.68 7.67 7.67 7.67 7.66 7.66 7.65 7.56 7.56 7.54 7.53 7.53 7.32 7.30 7.26 CDCl3 6.83 6.83 6.82
5.93 5.92
5.06 5.05 5.04 5.03 5.03 5.01 5.01
3.74 2.72 2.71 2.71 2.70 2.70 2.69 2.69 2.68
1.84 1.83 1.82 1.82 1.81 1.81 1.80 1.79 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.65 1.64
^{1}H NMR (500 MHz, CDCl$_3$)
PMP
Ph
0.90 2.00 1.02 2.03 1.99 1.98 1.00 1.00 3.06 2.08 1.08 1.24
f1 (ppm)


200.5 193.7
157.4 155.6
135.5 134.9 130.3 129.6 128.4 123.5 114.6
77.5 77.2 CDCl3 76.9
63.8 55.6 39.6 23.8
^{13}C NMR (126 MHz, CDCl$_3$)
PMP
Ph
f1 (ppm)

Compound 48

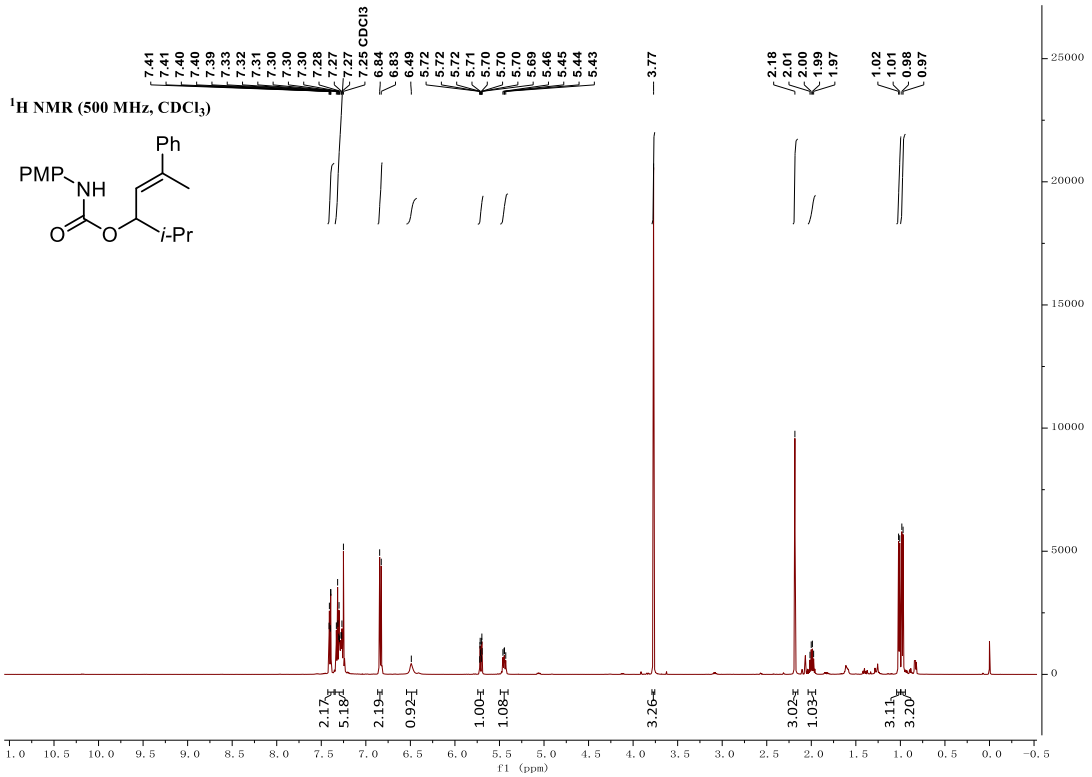


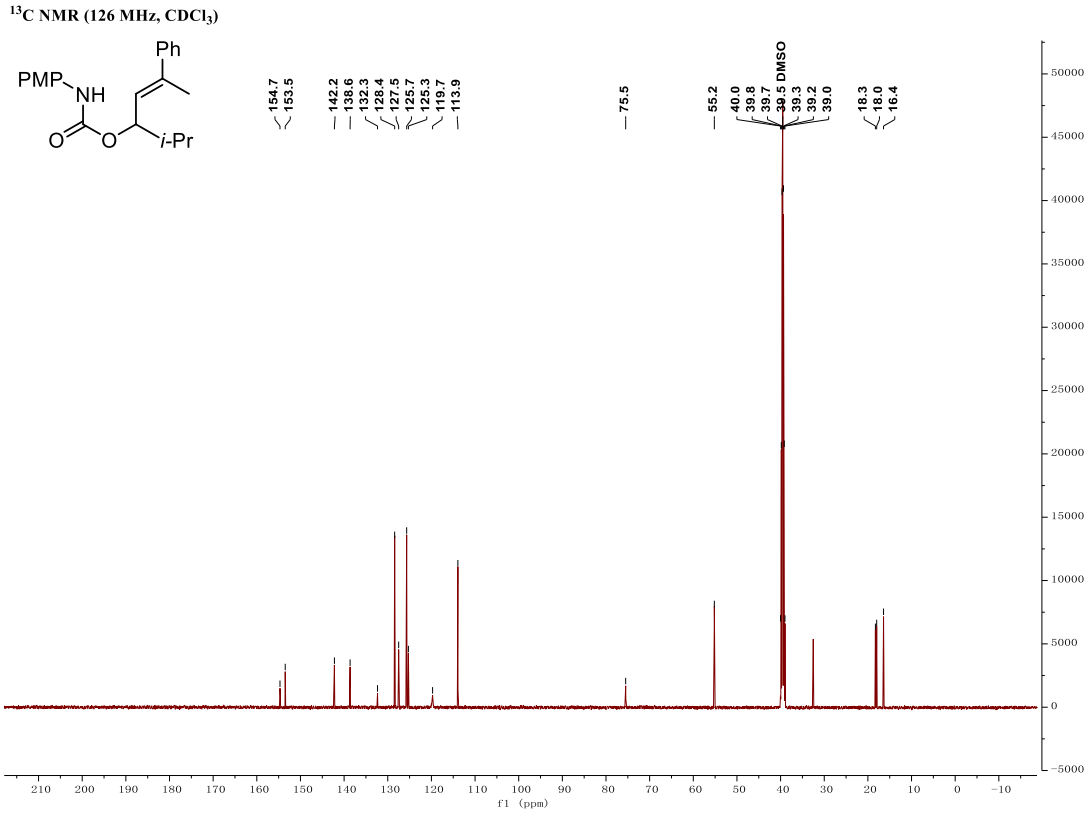
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

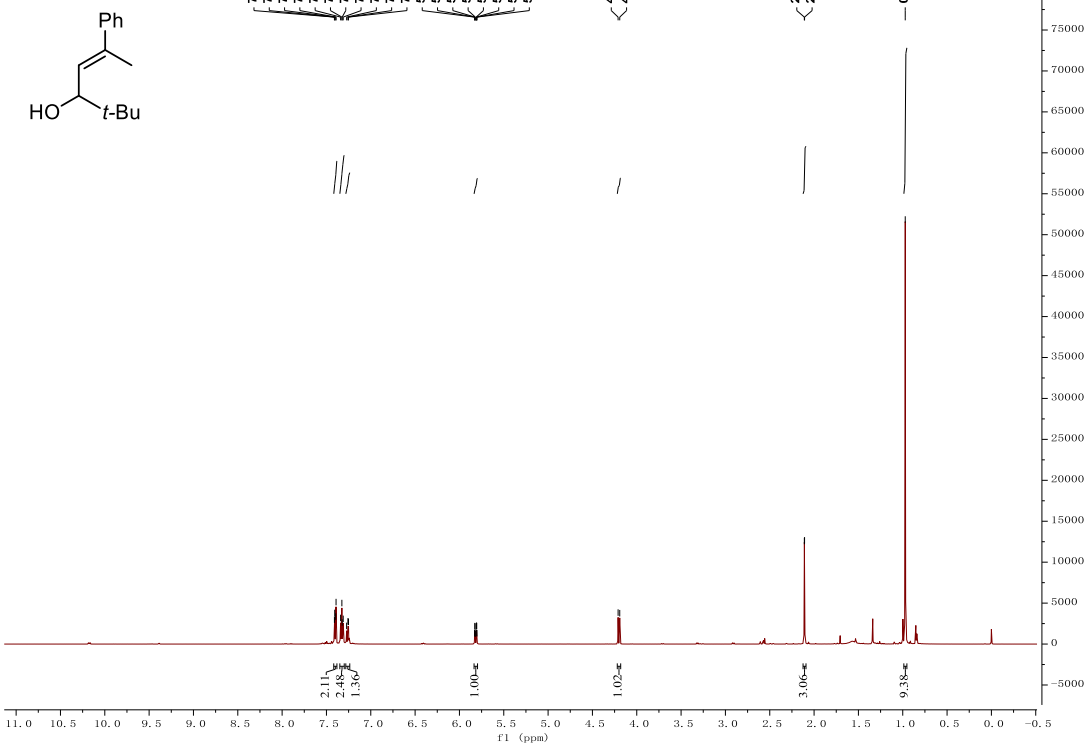
Compound 1


^{1}H NMR (500 MHz, $CDCl_3$)
PMP
NH
O
O
Ph
i-Pr
7.41 7.41 7.40 7.40 7.39 7.33 7.32 7.31 7.30 7.30 7.30 7.28 7.27 7.27 7.25 CDCl3 6.84 6.83 6.49 5.72 5.72 5.72 5.71 5.70 5.70 5.69 5.46 5.45 5.44 5.43 3.77 2.18 2.01 2.00 1.99 1.97 1.02 1.01 0.98 0.97
2.17 5.18 2.19 0.92 1.00 1.08 3.26 3.02 1.03 3.11 3.20
f1 (ppm)

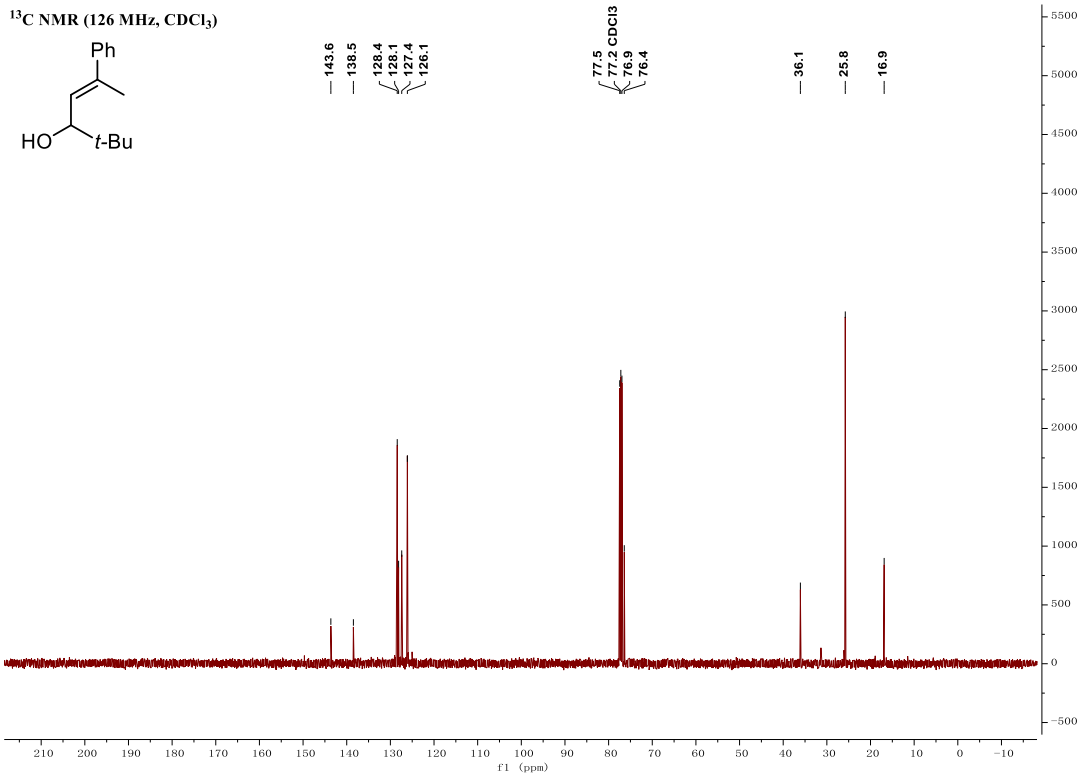

^{13}C NMR (126 MHz, $CDCl_3$)
PMP
NH
O
O
Ph
i-Pr
154.7 153.5 142.2 138.6 132.3 128.4 127.5 125.7 125.3 119.7 113.9 75.5 55.2 40.0 39.8 39.7 39.5 DMSO 39.3 39.2 39.0 18.3 18.0 16.4
f1 (ppm)

Compound S2

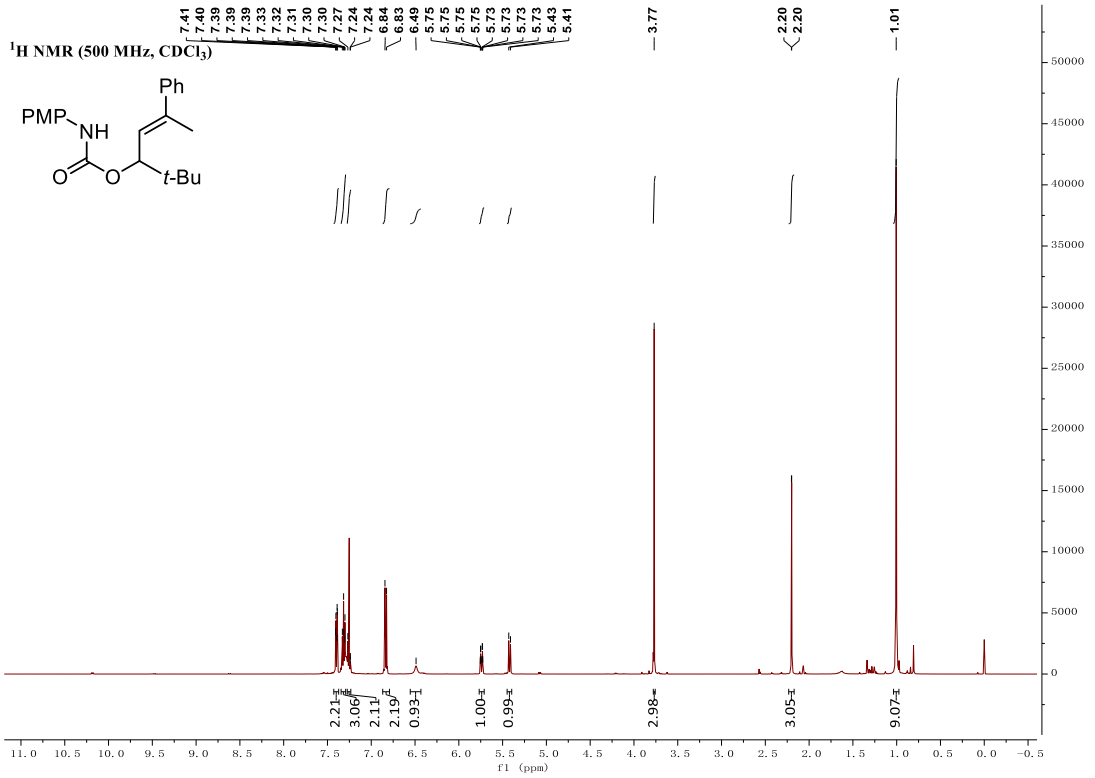
^{1}H NMR (500 MHz, $CDCl_3$)

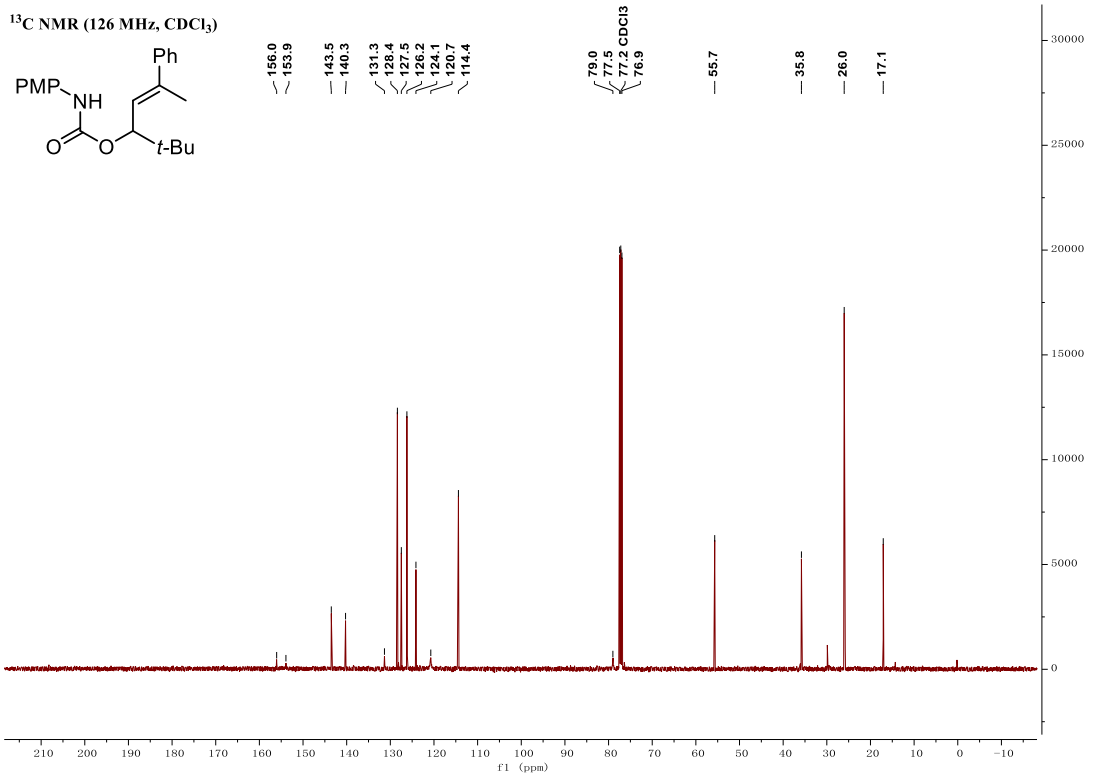


^{13}C NMR (126 MHz, $CDCl_3$)



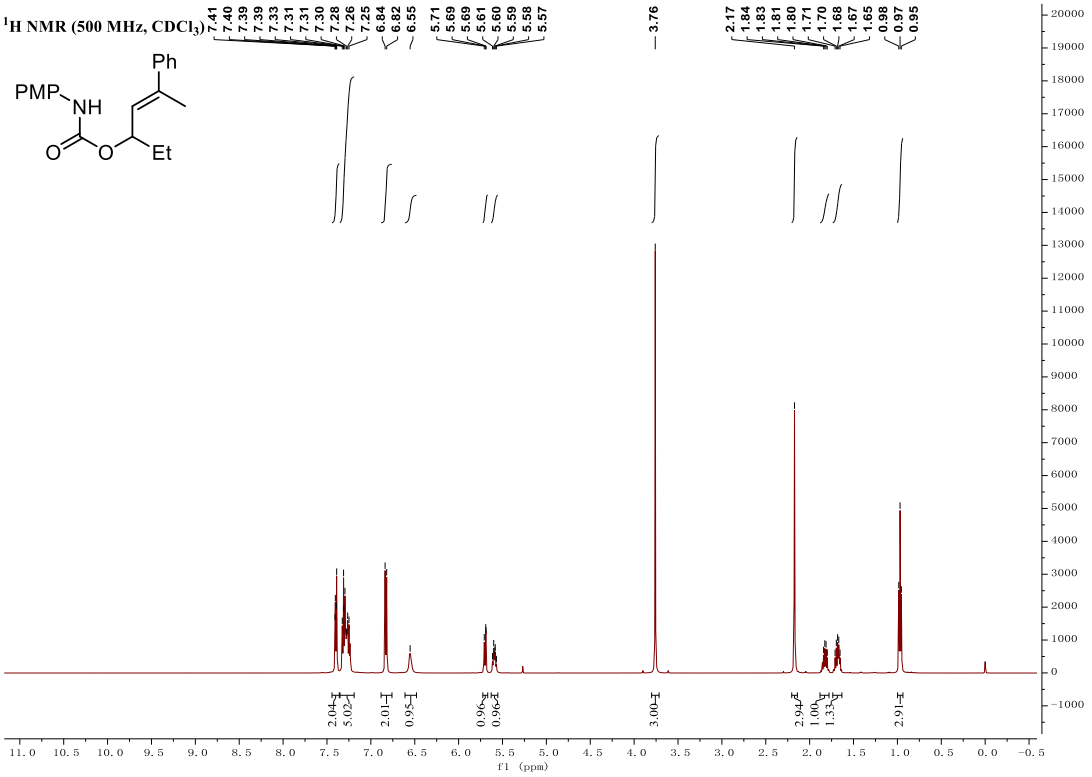
Compound S3


^{1}H NMR (500 MHz, CDCl$_3$)
PMP
NH
O
O
Ph
t-Bu
7.41
7.40
7.39
7.39
7.39
7.33
7.32
7.31
7.30
7.30
7.27
7.24
7.24
6.84
6.83
6.49
5.75
5.75
5.75
5.75
5.73
5.73
5.73
5.73
5.43
5.41
3.77
2.20
2.20
1.01
2.21
3.06
2.11
2.19
0.93
1.00
0.99
2.98
3.05
9.07
f1 (ppm)

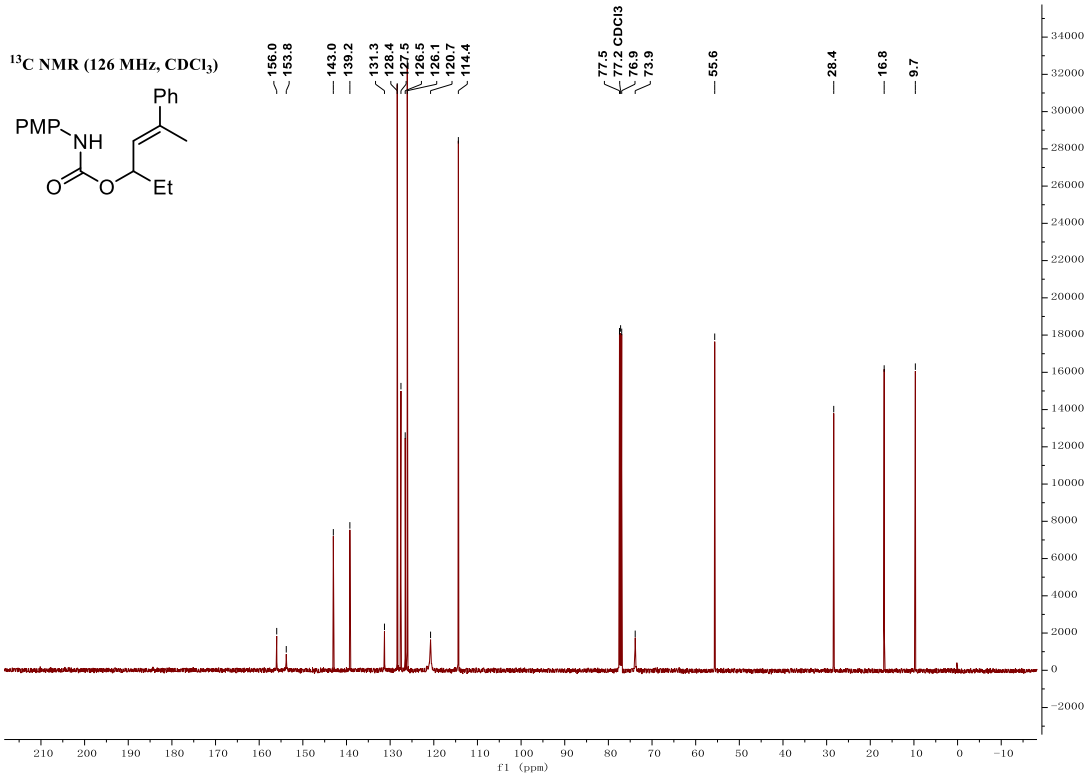

^{13}C NMR (126 MHz, CDCl$_3$)
PMP
NH
O
O
Ph
t-Bu
156.0
153.9
143.5
140.3
131.3
128.4
127.5
126.2
124.1
120.7
114.4
79.0
77.5
77.2 CDCl3
76.9
55.7
35.8
26.0
17.1
f1 (ppm)

Compound S5

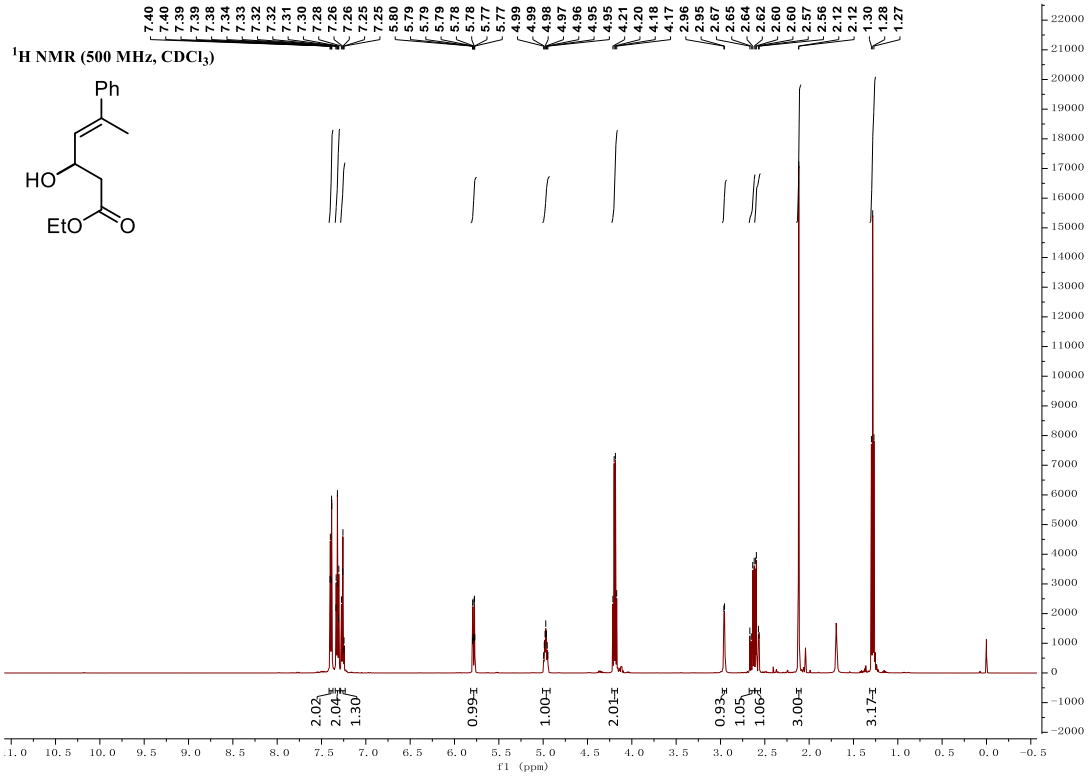
^{1}H NMR (500 MHz, $CDCl_3$)

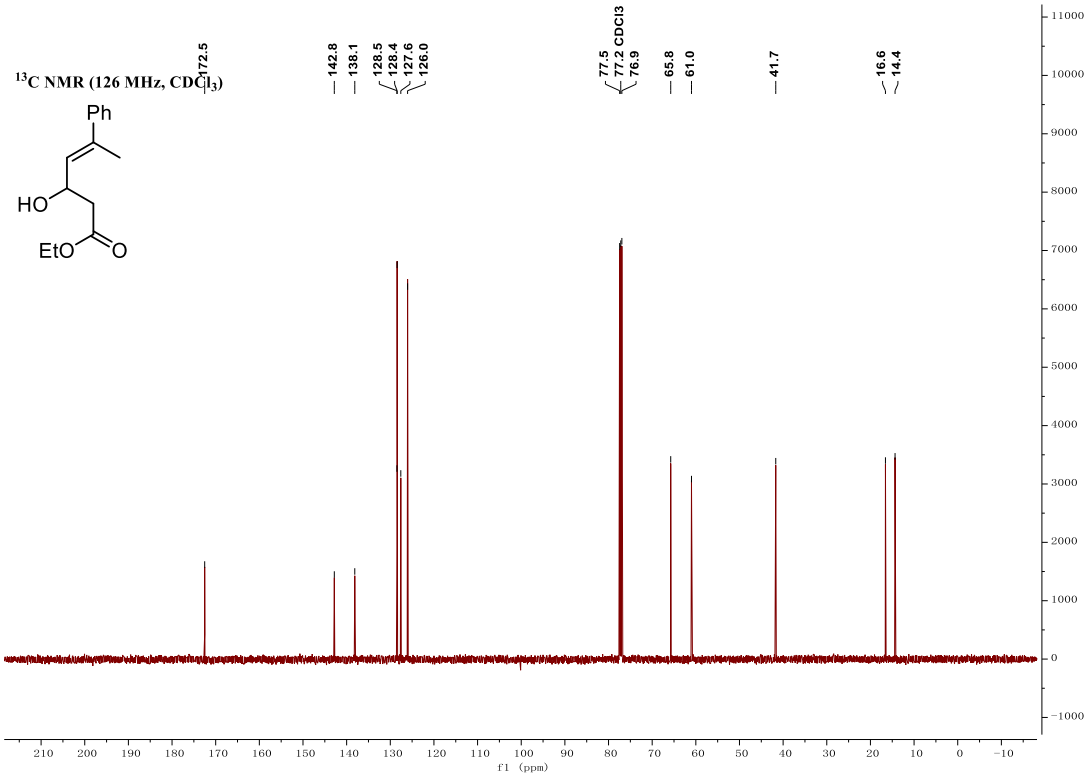


^{13}C NMR (126 MHz, $CDCl_3$)

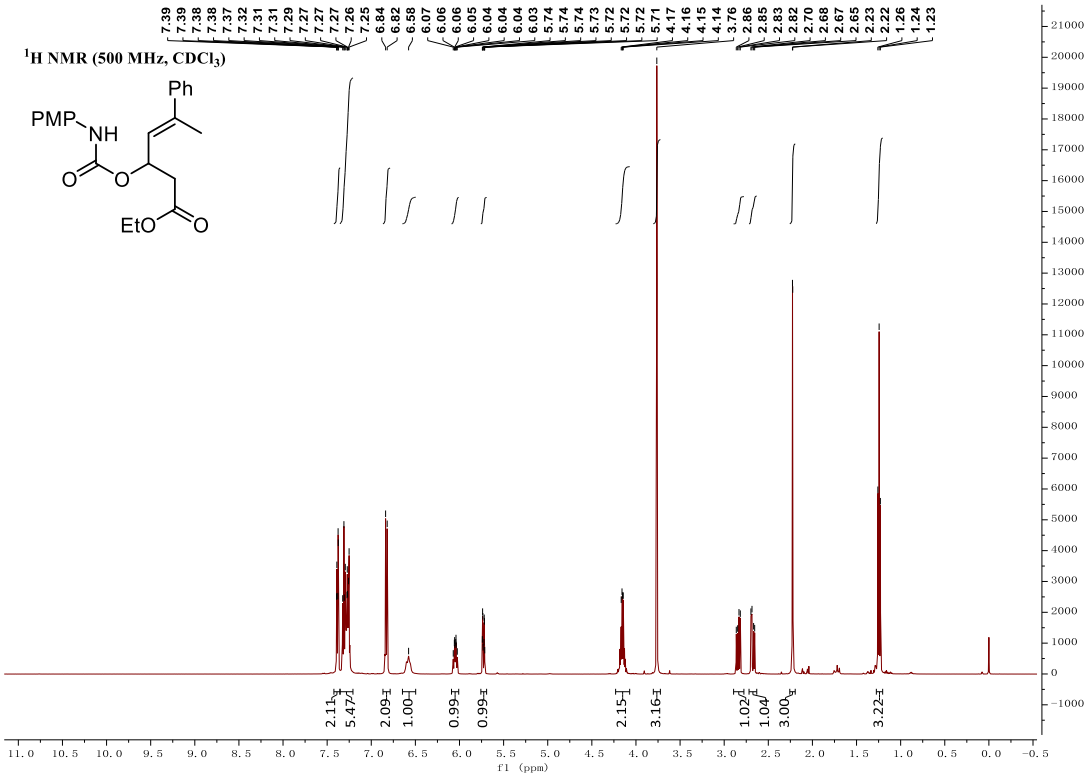


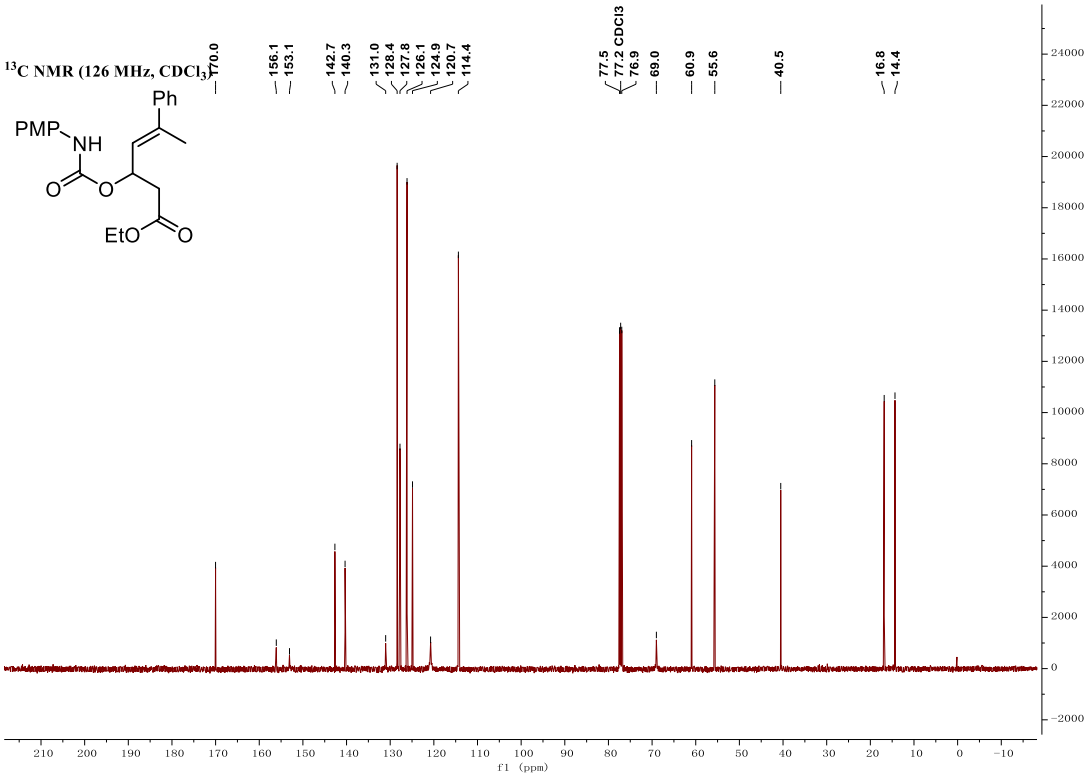
Compound S6


7.40 7.40 7.39 7.39 7.38 7.34 7.33 7.32 7.32 7.31 7.30 7.28 7.26 7.26 7.25 7.25 5.80 5.79 5.79 5.78 5.78 5.77 5.77 4.99 4.98 4.97 4.96 4.95 4.95 4.21 4.20 4.18 4.17 2.96 2.95 2.67 2.65 2.64 2.62 2.60 2.60 2.57 2.56 2.12 2.12 1.30 1.28 1.27
1H NMR (500 MHz, CDCl3)
Ph
HO
EtO
O
2.02 2.04 1.30 0.99 1.00 2.01 0.93 1.05 1.06 3.00 3.17
f1 (ppm)

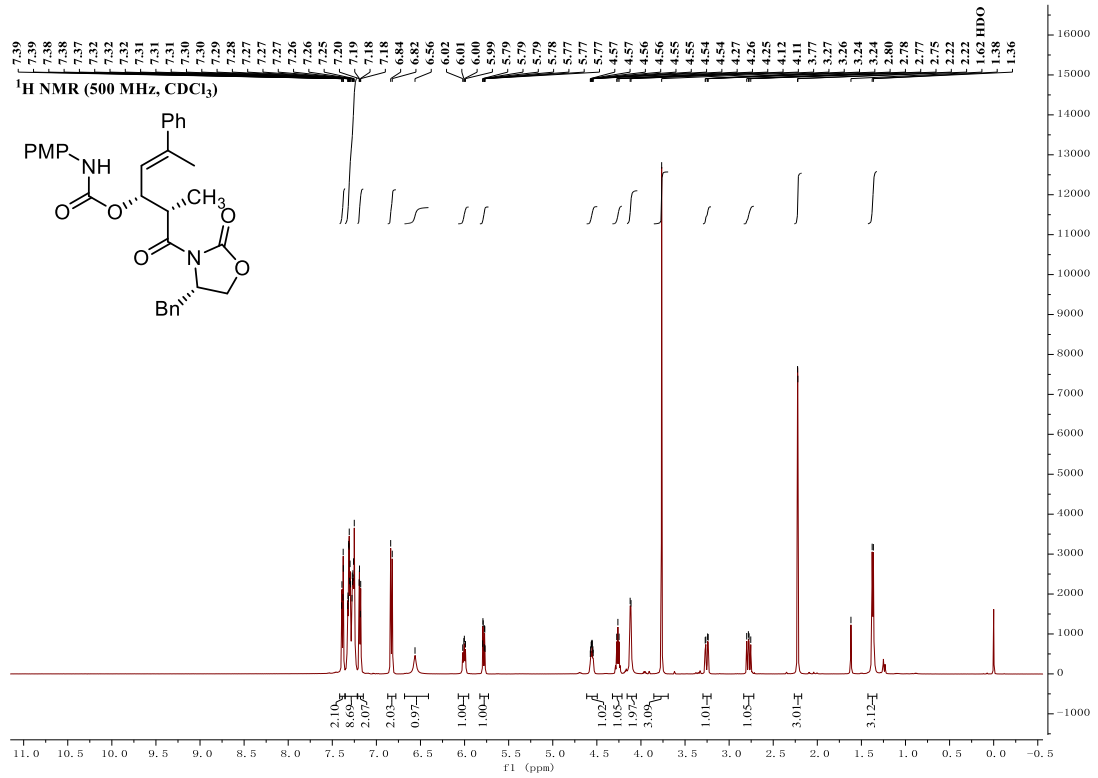

172.5
142.8 138.1 128.5 128.4 127.6 126.0
77.5 77.2 CDCl3 76.9
65.8 61.0 41.7 16.6 14.4
13C NMR (126 MHz, CDCl3)
Ph
HO
EtO
O
f1 (ppm)

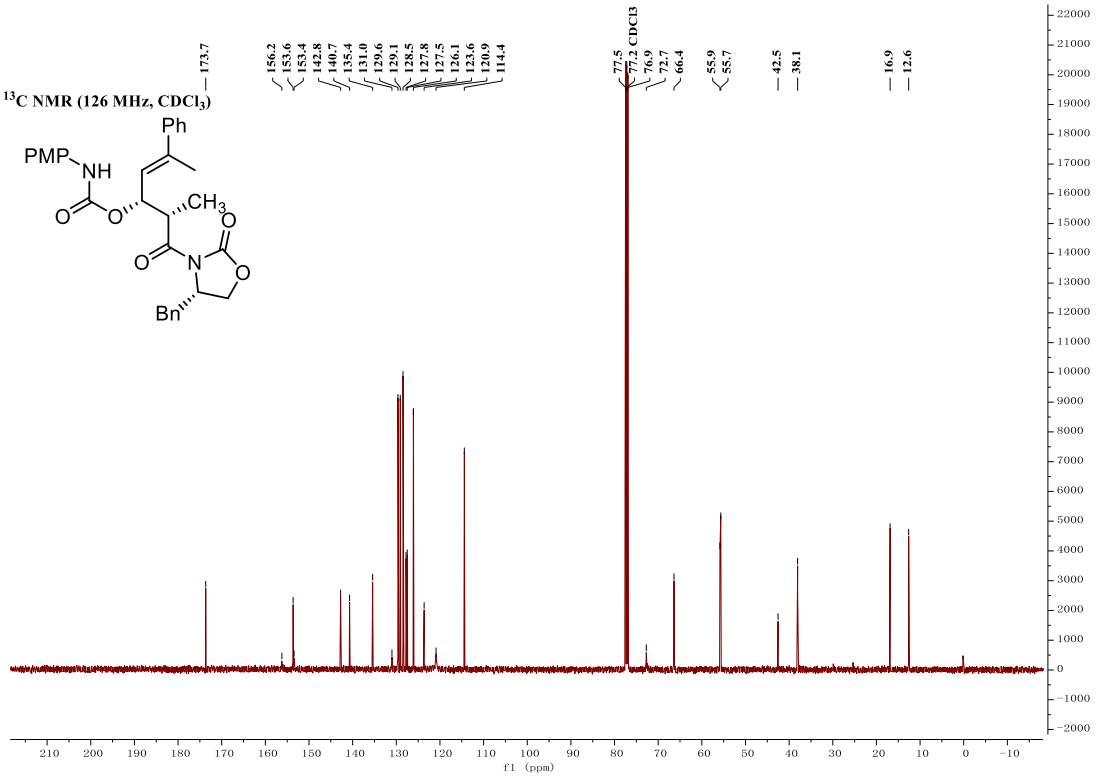
Compound S7


7.39 7.39 7.38 7.38 7.37 7.32 7.31 7.31 7.29 7.27 7.27 7.27 7.26 7.25 6.84 6.82 6.58 6.07 6.06 6.06 6.05 6.04 6.04 6.04 6.03 5.74 5.74 5.74 5.73 5.72 5.72 5.72 5.71 4.17 4.16 4.15 4.14 3.76 2.86 2.85 2.83 2.82 2.70 2.68 2.67 2.65 2.23 2.22 1.26 1.24 1.23
^{1}H NMR (500 MHz, CDCl$_3$)
Ph
PMP
NH
O
O
EtO
O
2.11 5.47 2.09 1.00 0.99 0.99 2.15 3.16 1.02 1.04 3.00 3.22
f1 (ppm)

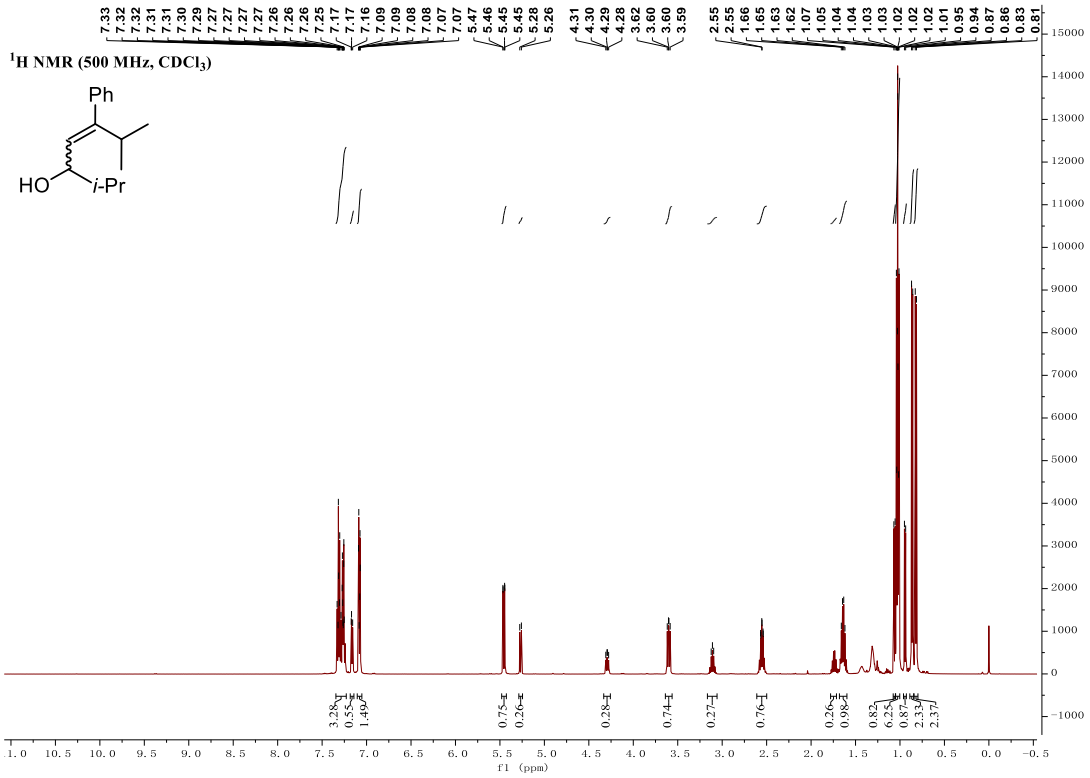

^{13}C NMR (126 MHz, CDCl$_3$)
170.0 156.1 153.1 142.7 140.3 131.0 128.4 127.8 126.1 124.9 120.7 114.4 77.5 77.2 CDCl3 76.9 69.0 60.9 55.6 40.5 16.8 14.4
Ph
PMP
NH
O
O
EtO
O
f1 (ppm)

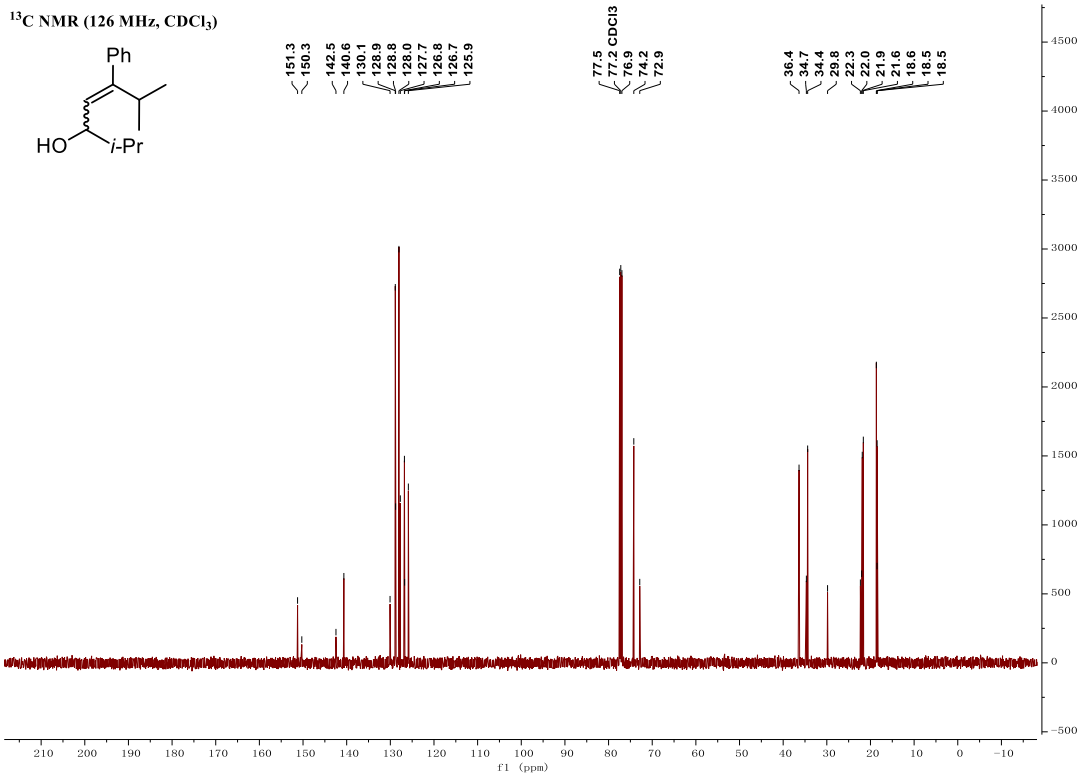
Compound S9


^{1}H NMR (500 MHz, $CDCl_3$)
Ph
PMP
NH
CH_3
Bn
7.39 7.39 7.38 7.38 7.37 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.20 7.19 7.18 7.18 6.84 6.82 6.56 6.02 6.01 6.00 5.99 5.79 5.79 5.79 5.78 5.77 5.77 5.77 4.57 4.57 4.56 4.56 4.55 4.55 4.54 4.54 4.27 4.26 4.25 4.12 4.11 3.77 3.27 3.26 3.24 3.24 2.80 2.78 2.77 2.75 2.22 2.22 1.62 HDO 1.38 1.36
2.10 8.69 2.07 2.03 0.97 1.00 1.00 1.02 1.05 1.97 3.09 1.01 1.05 3.01 3.12
f1 (ppm)

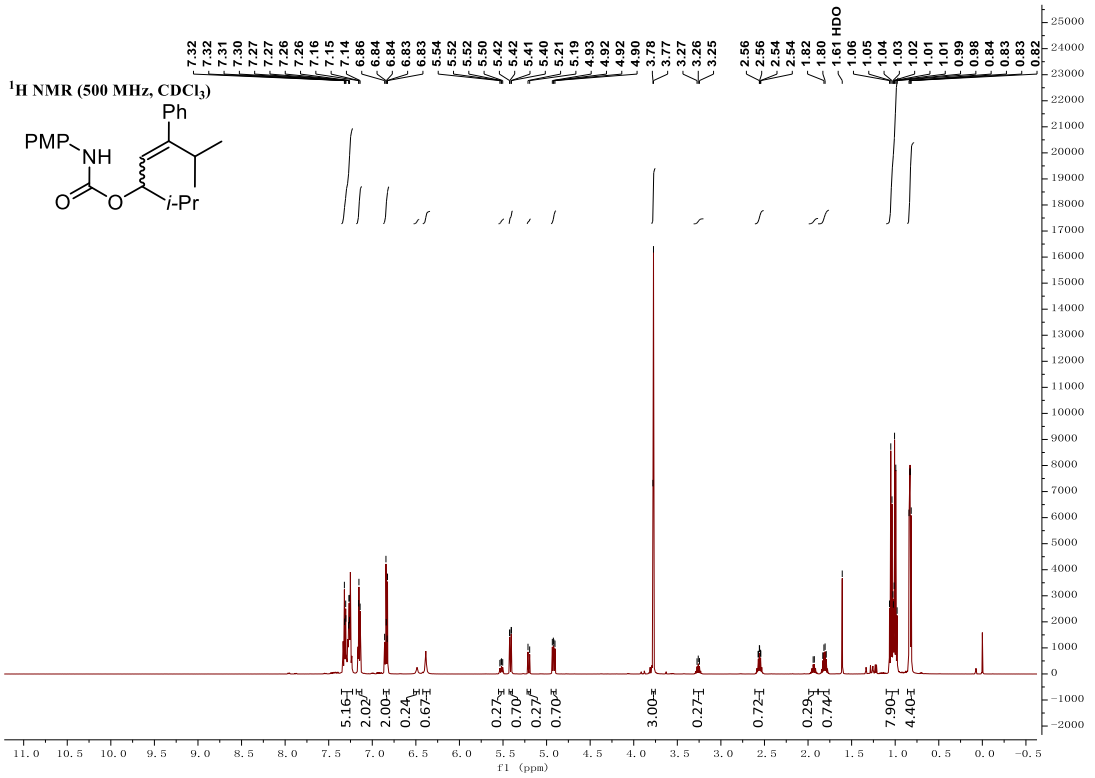

^{13}C NMR (126 MHz, $CDCl_3$)
Ph
PMP
NH
CH_3
Bn
173.7
156.2 153.6 153.4 142.8 140.7 135.4 131.0 129.6 129.1 128.5 127.8 127.5 126.1 123.6 120.9 114.4
77.5 77.2 CDCl3 76.9 72.7 66.4 55.9 55.7 42.5 38.1 16.9 12.6
f1 (ppm)

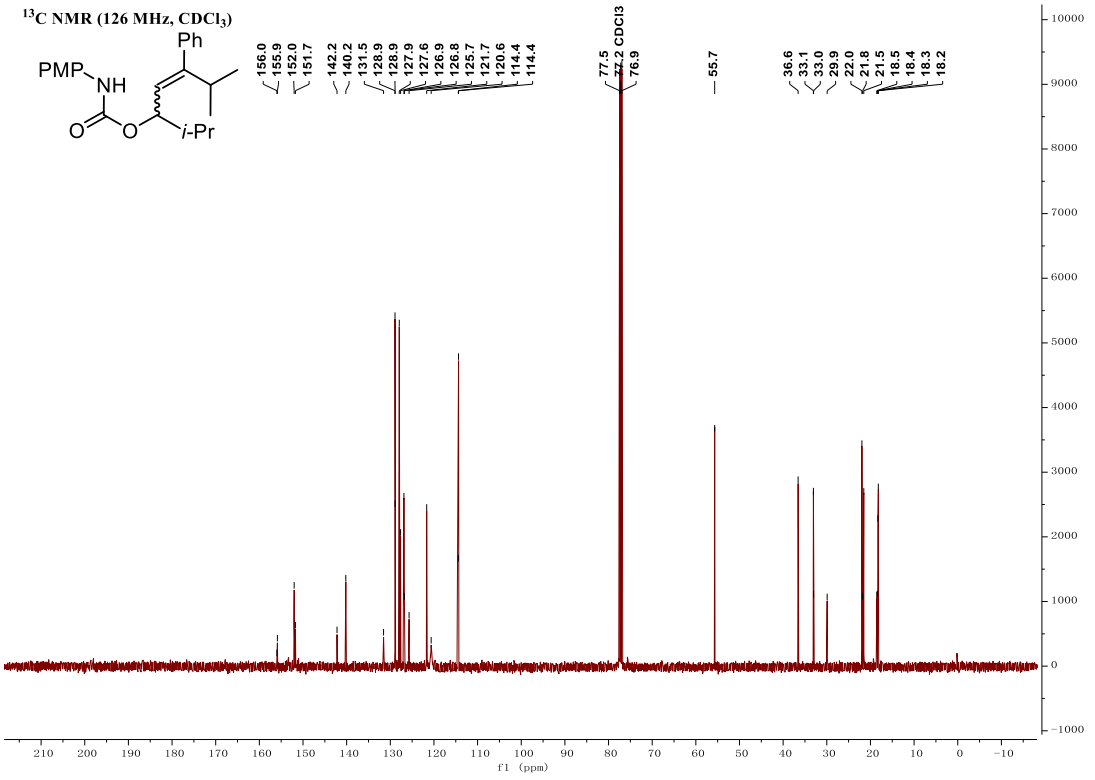
Compound S10





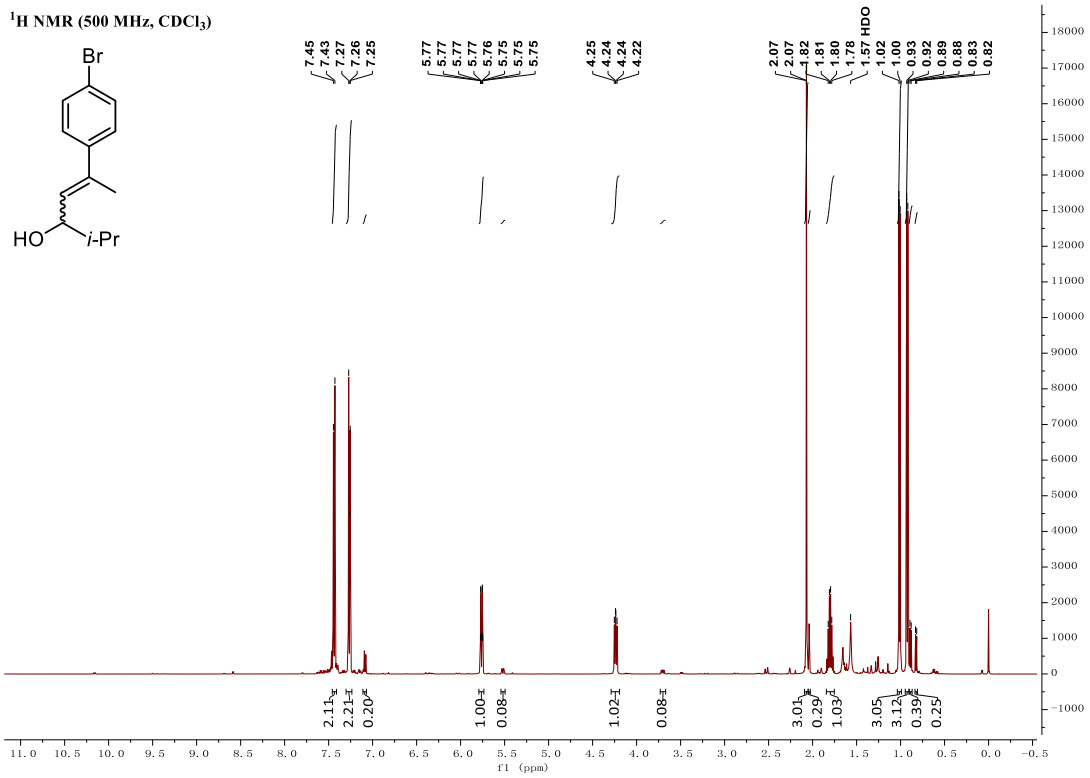
Compound S11



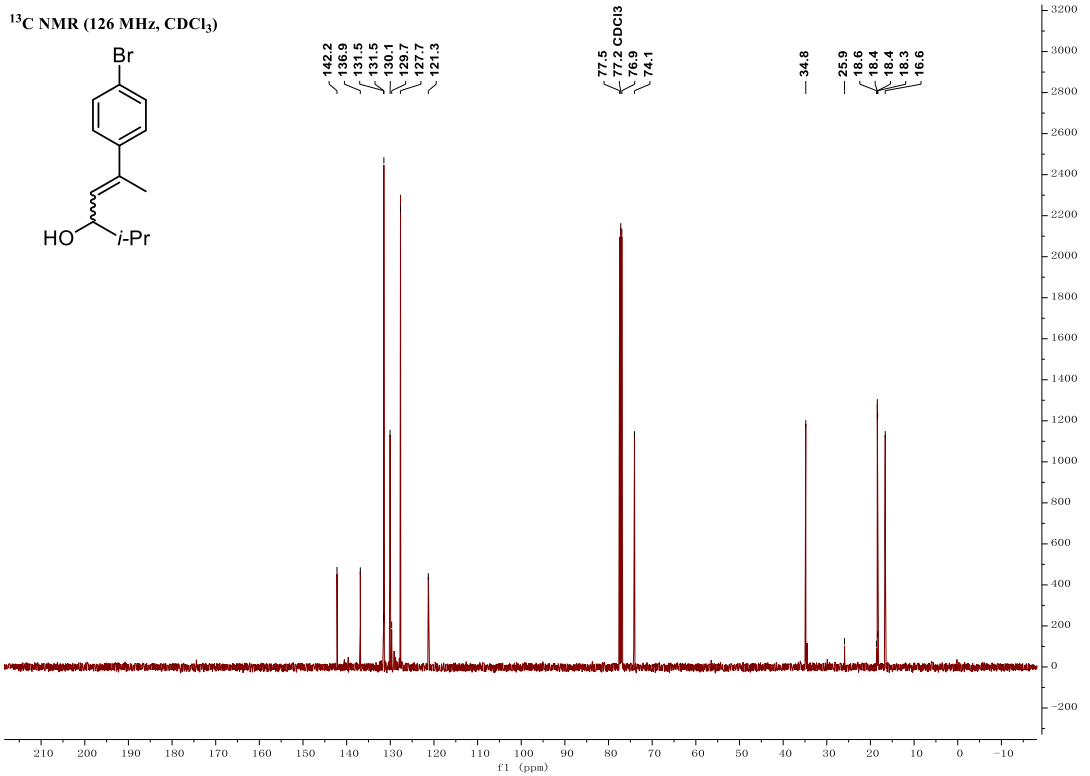


Compound S12

^{1}H NMR (500 MHz, $CDCl_3$)

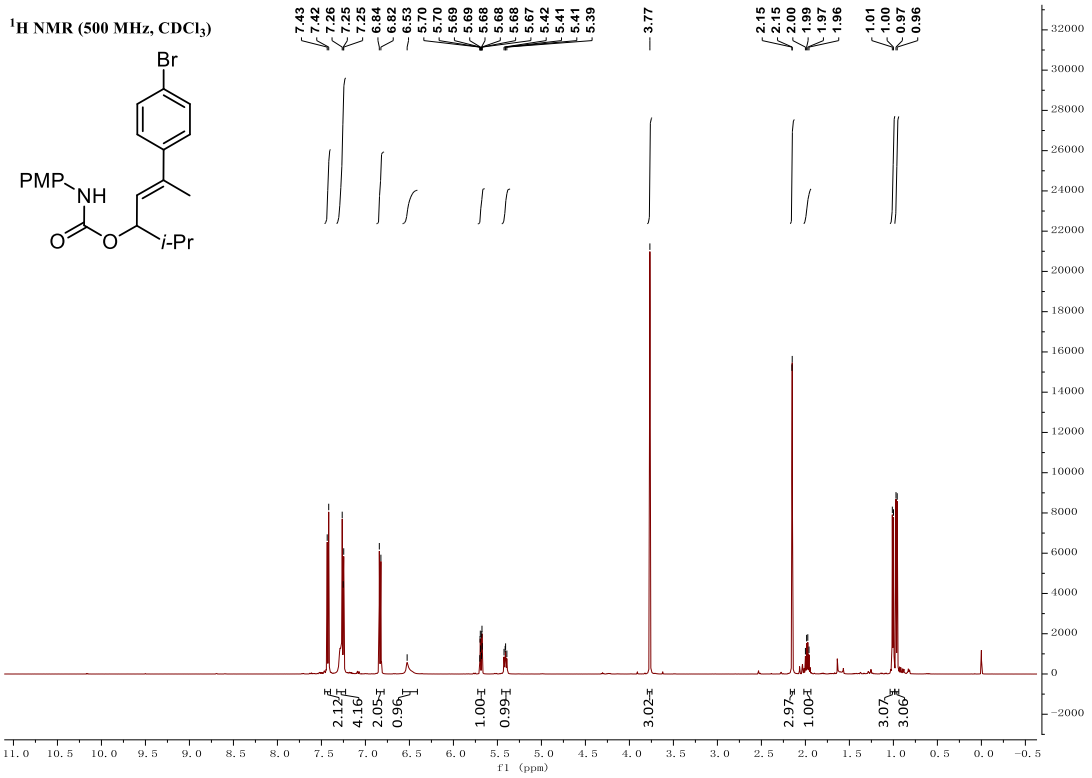


^{13}C NMR (126 MHz, $CDCl_3$)

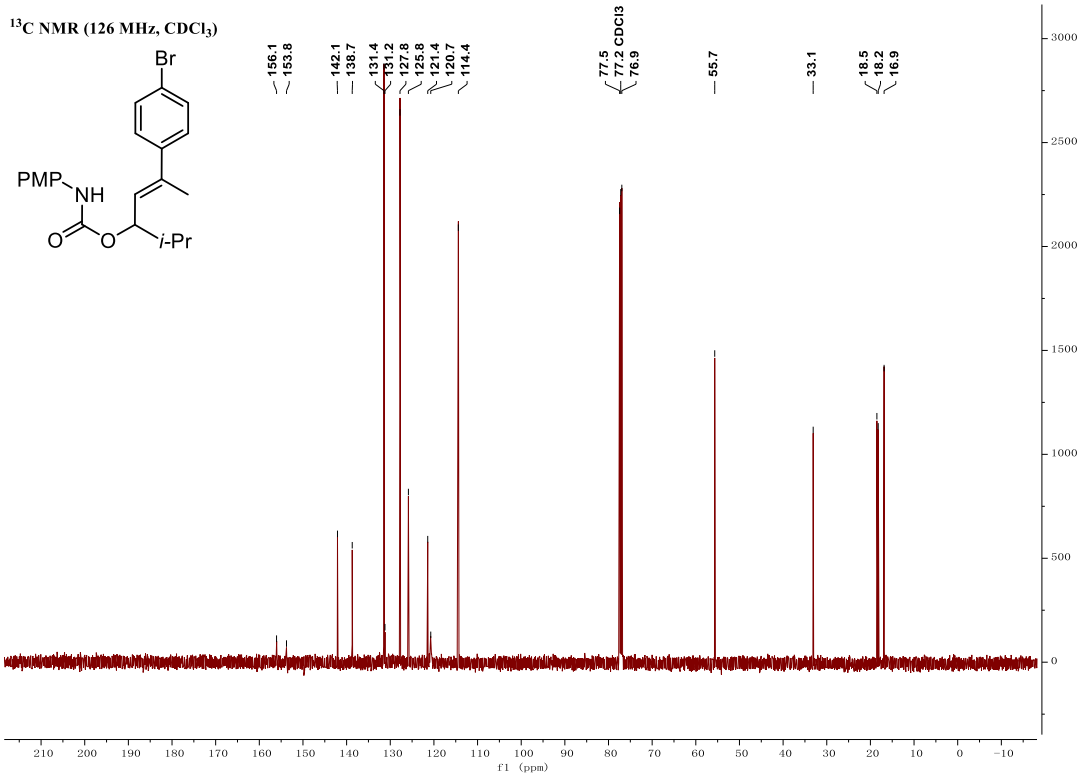


Compound S13

^{1}H NMR (500 MHz, $CDCl_3$)

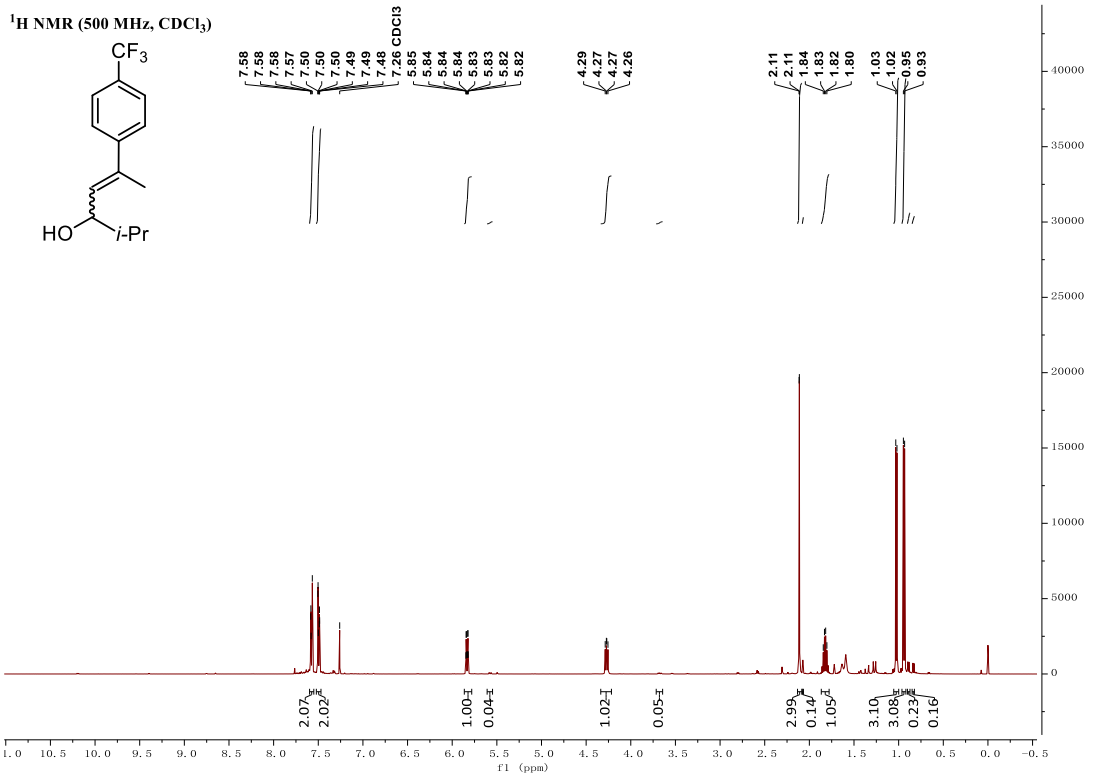


^{13}C NMR (126 MHz, $CDCl_3$)

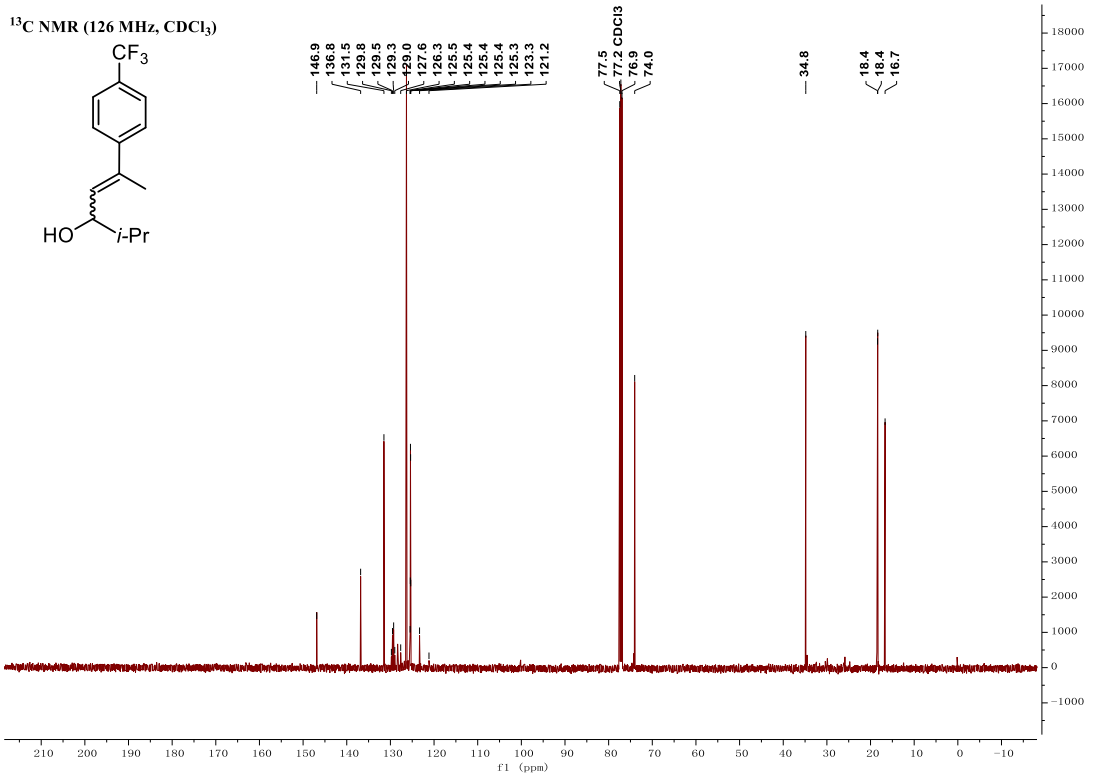


Compound S14

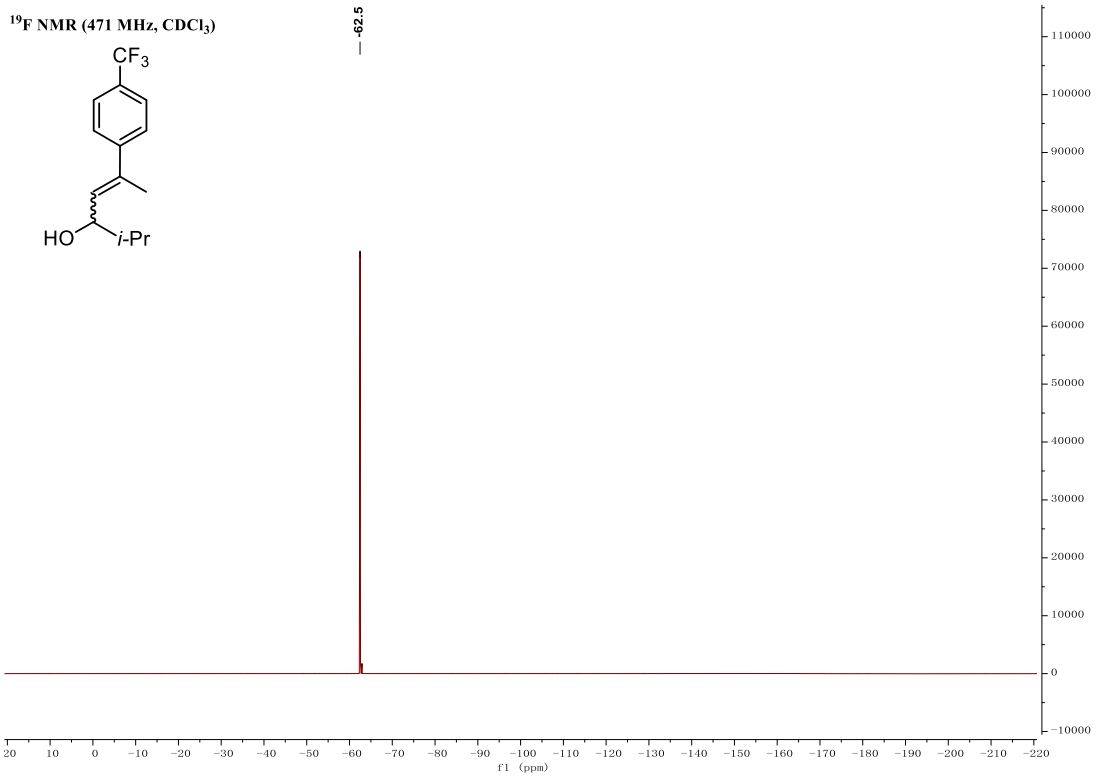
^{1}H NMR (500 MHz, $CDCl_3$)



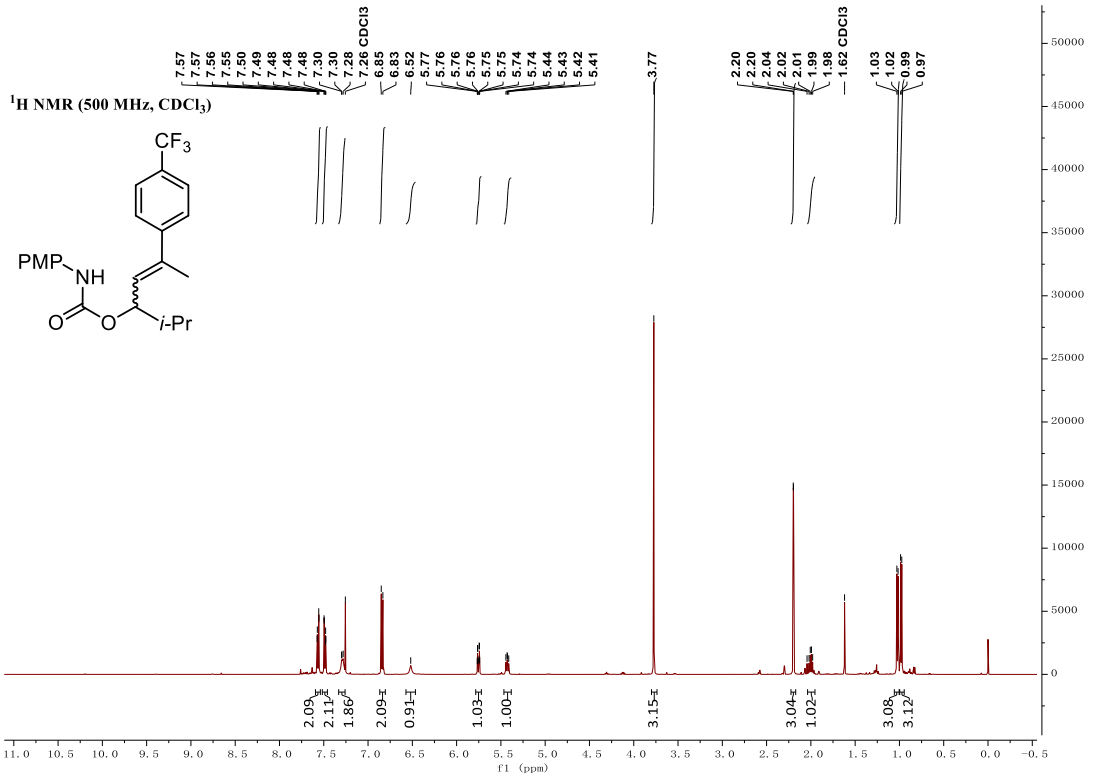
^{13}C NMR (126 MHz, $CDCl_3$)

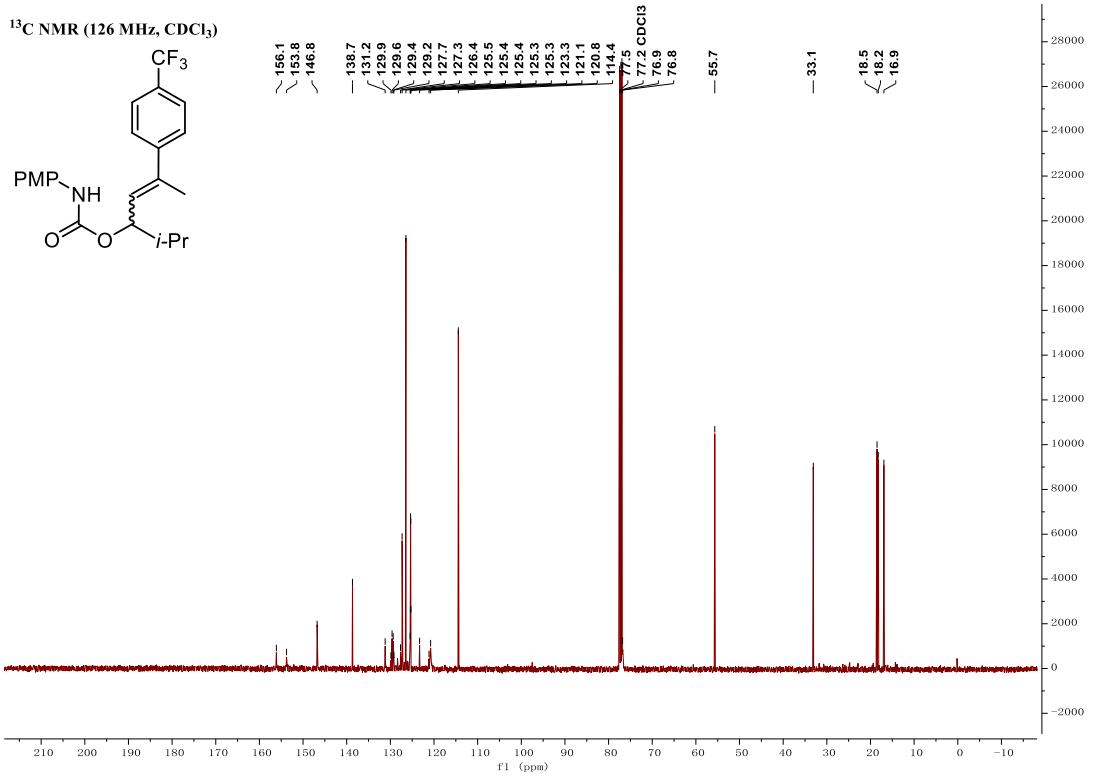


^{19}F NMR (471 MHz, $CDCl_3$)

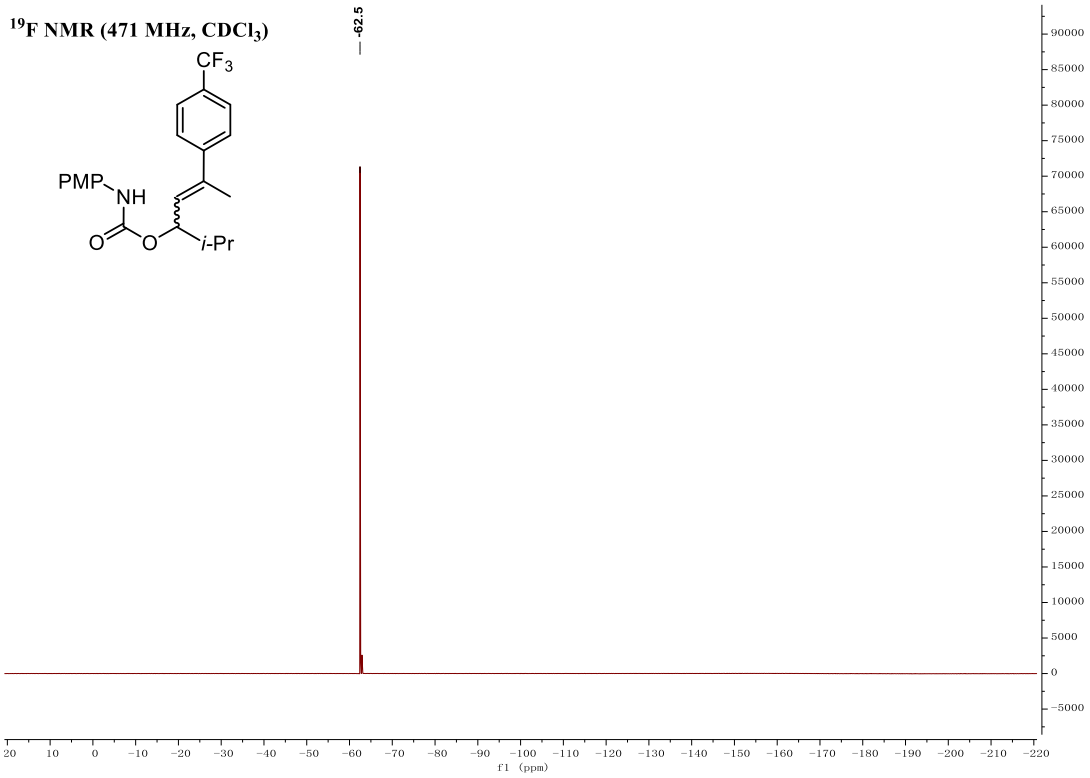


Compound S15



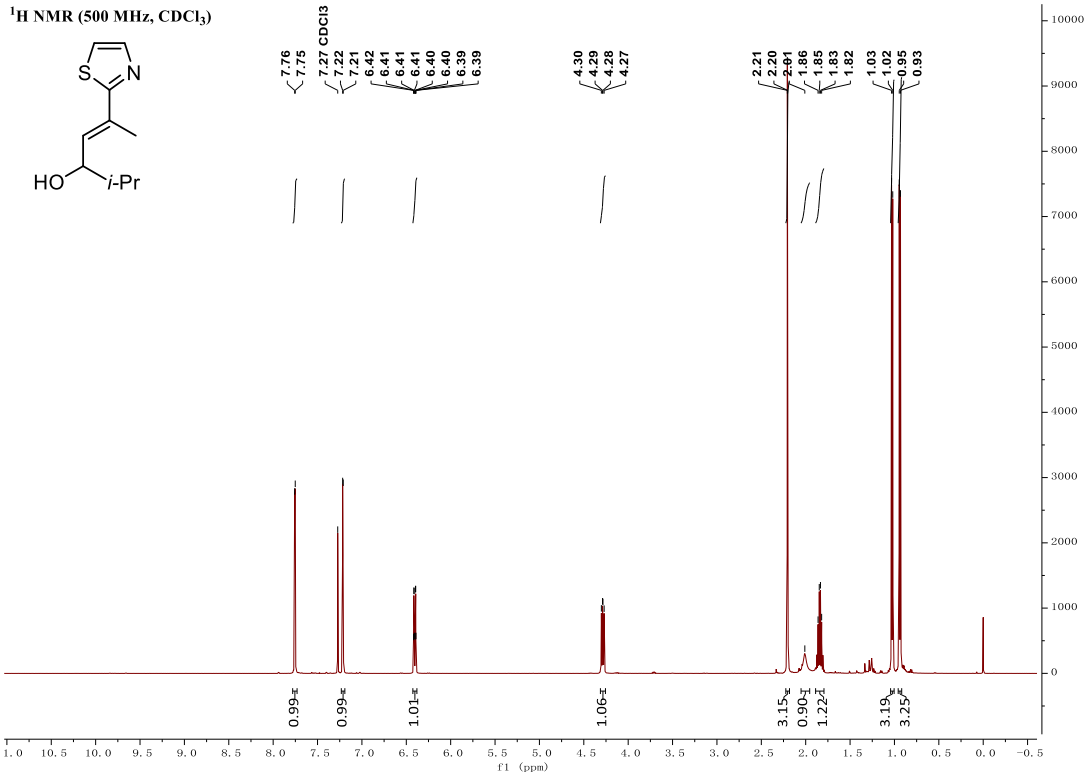


^{19}F NMR (471 MHz, $CDCl_3$)

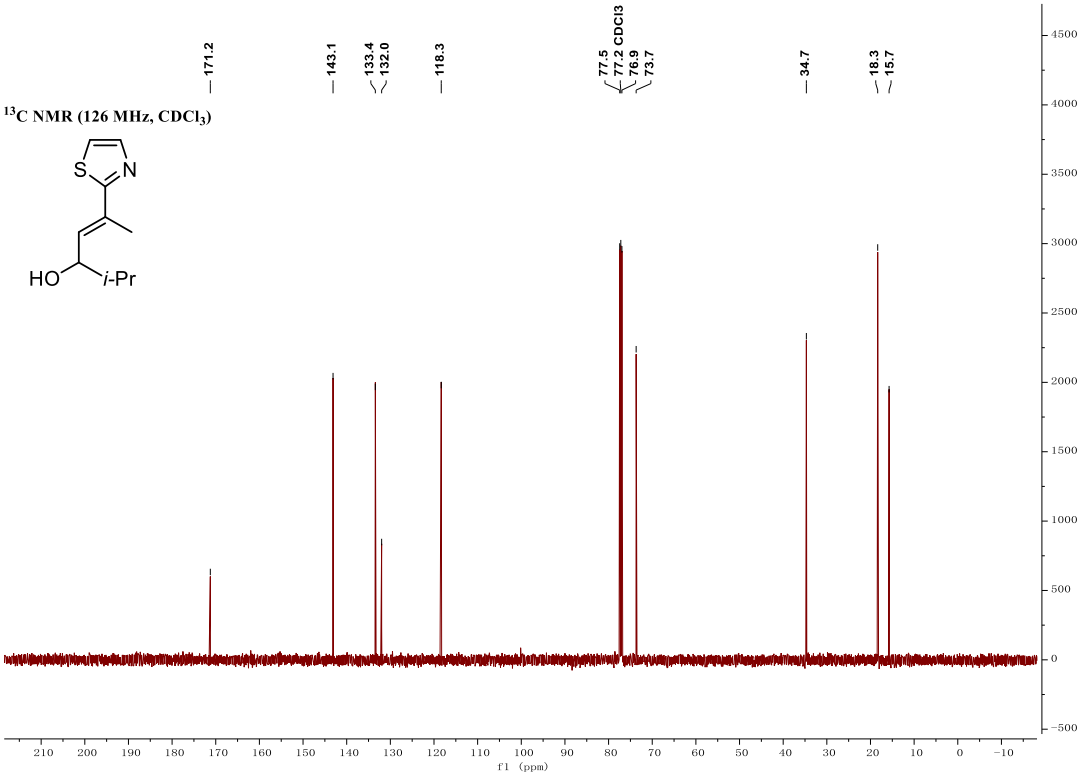


Compound S16

^{1}H NMR (500 MHz, $CDCl_3$)

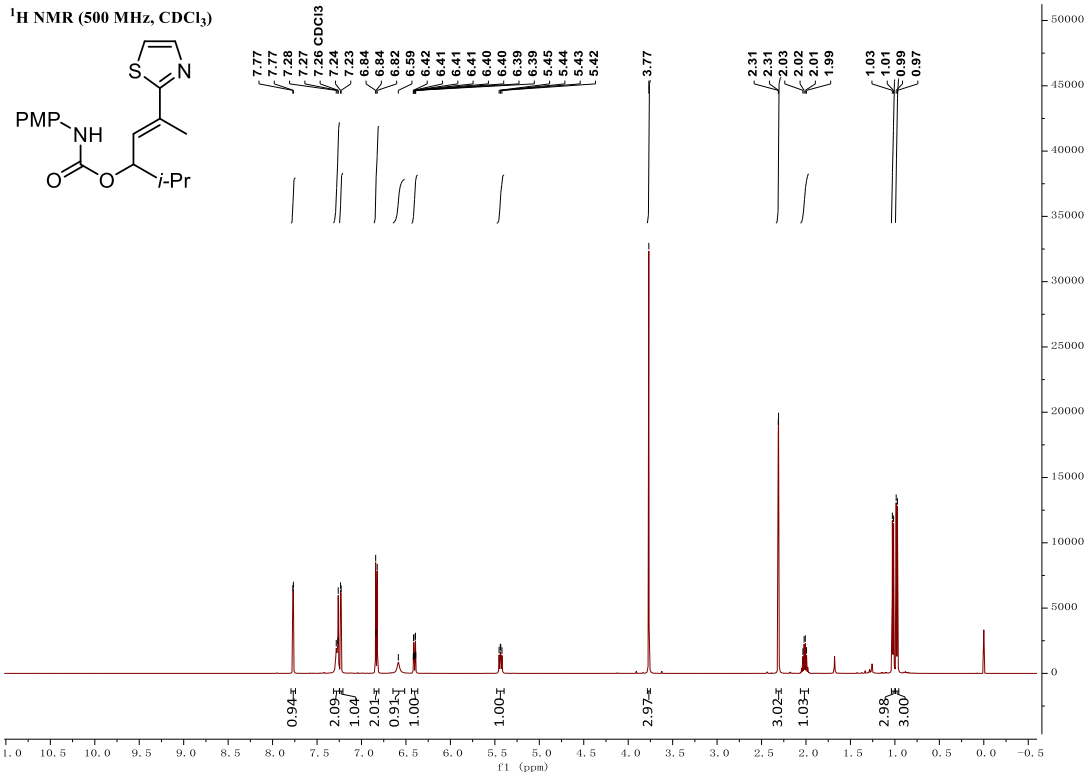


^{13}C NMR (126 MHz, $CDCl_3$)

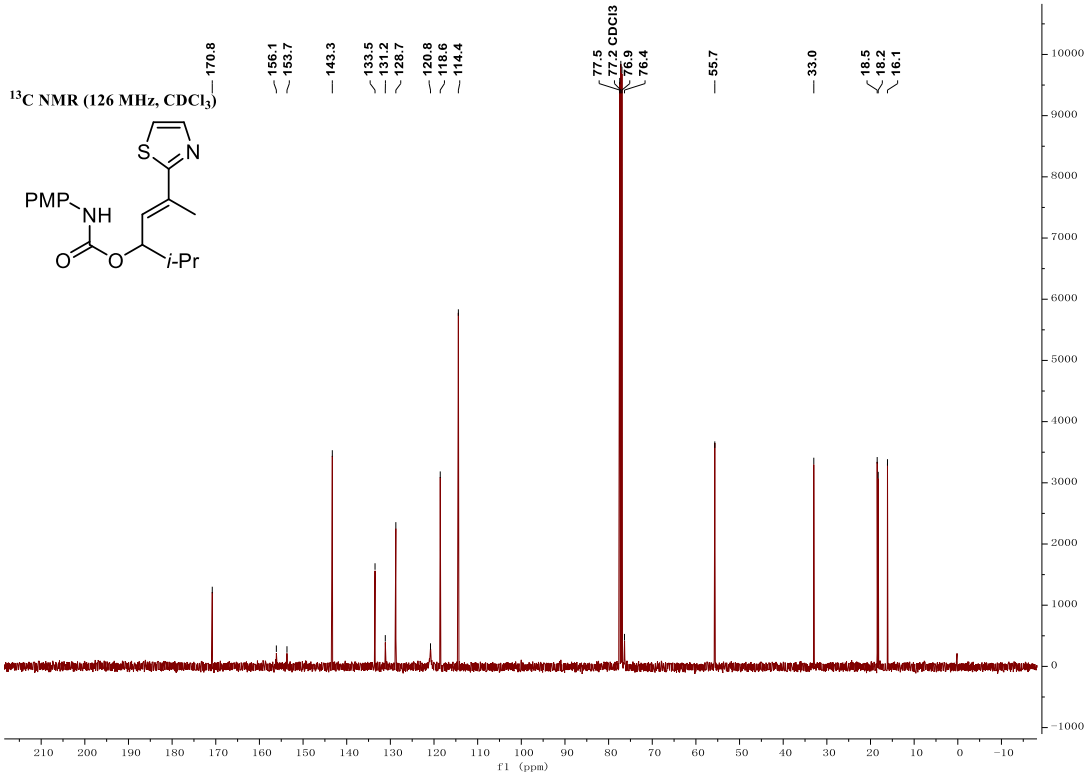


Compound S17

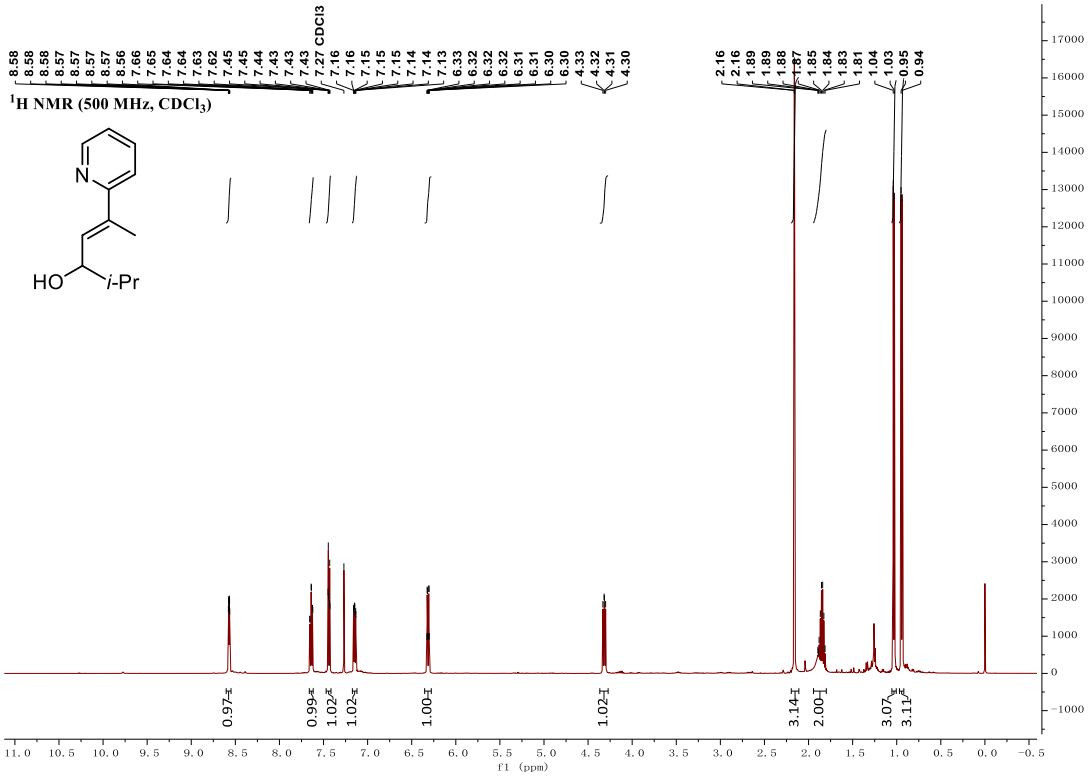
^{1}H NMR (500 MHz, $CDCl_3$)

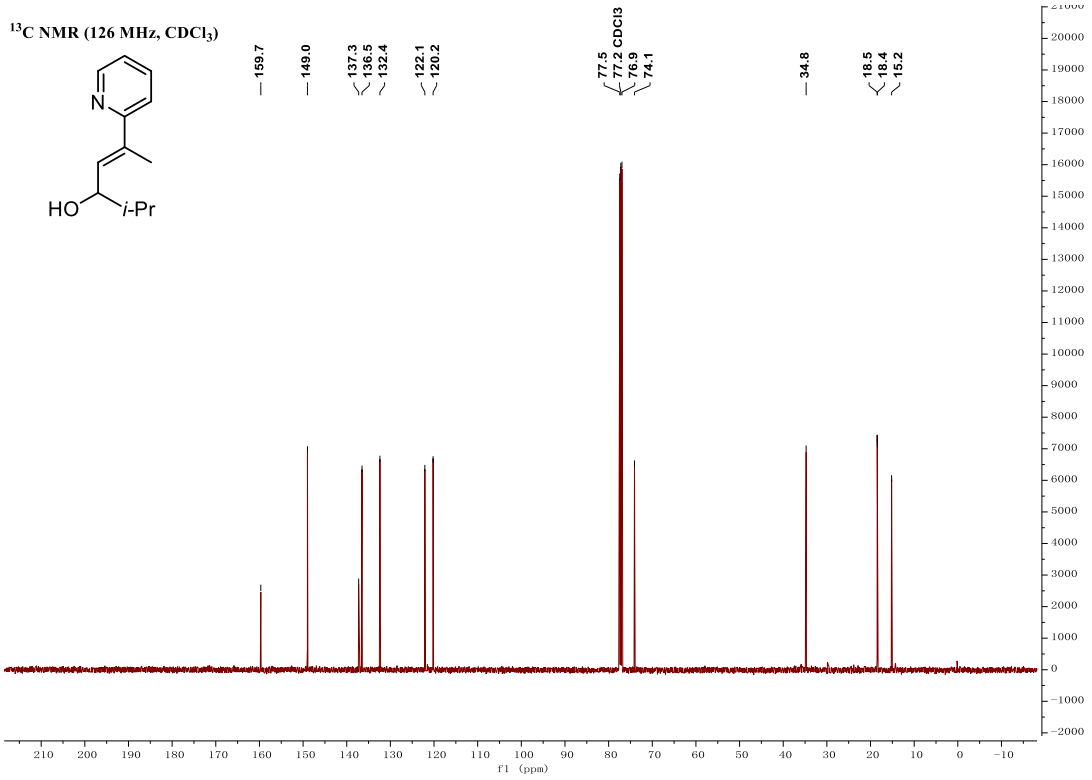


^{13}C NMR (126 MHz, $CDCl_3$)

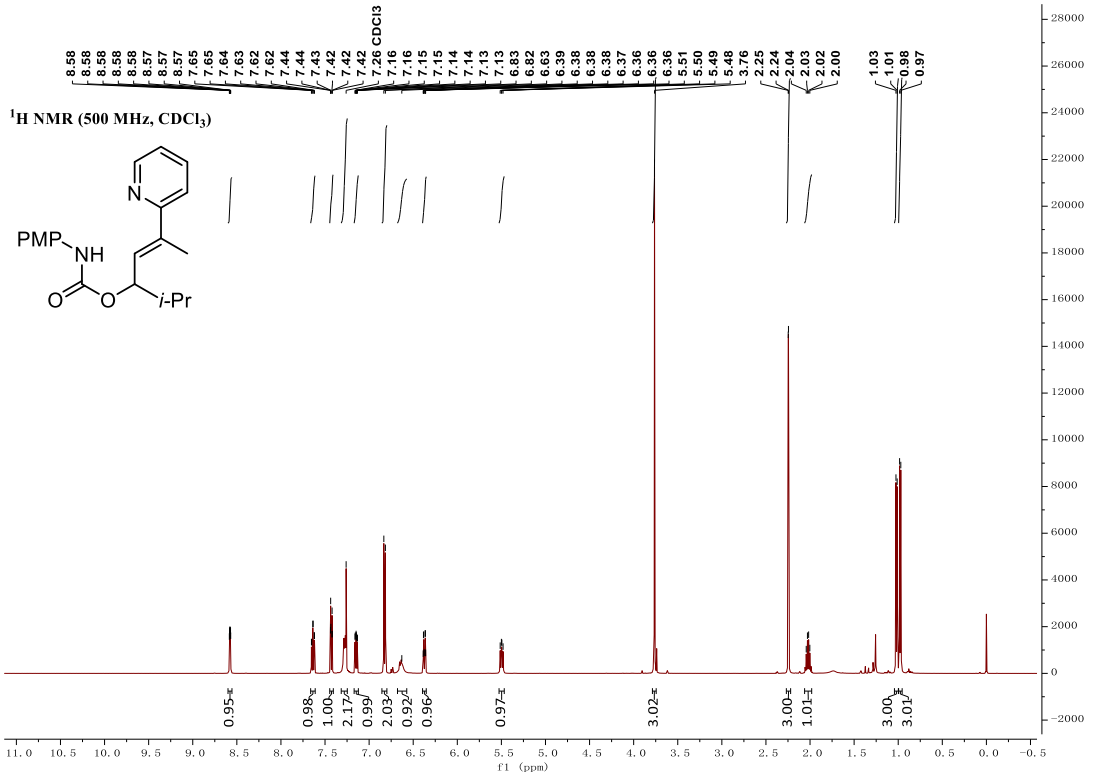


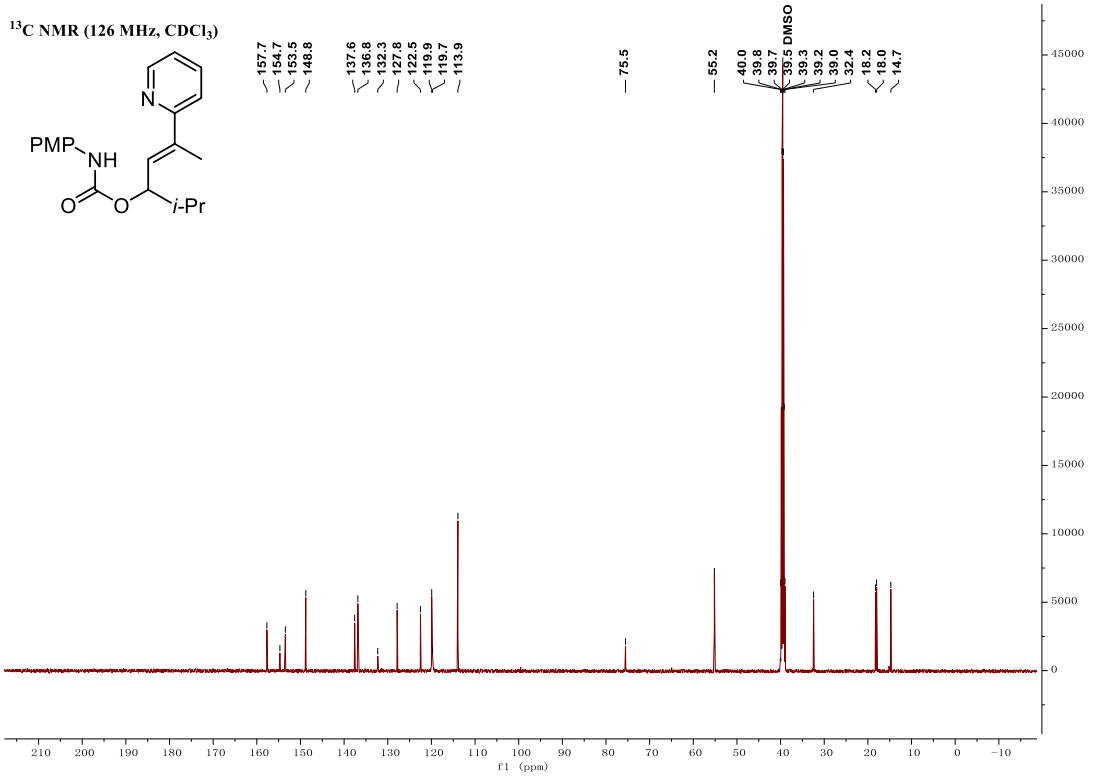
Compound S18



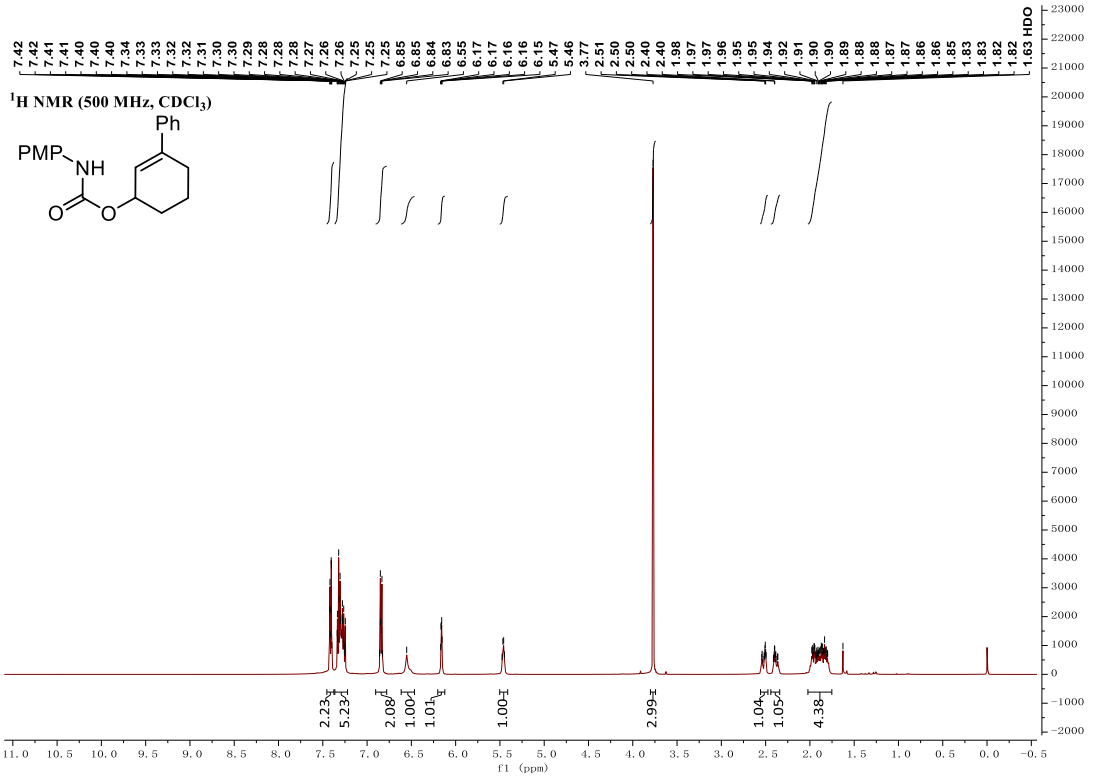


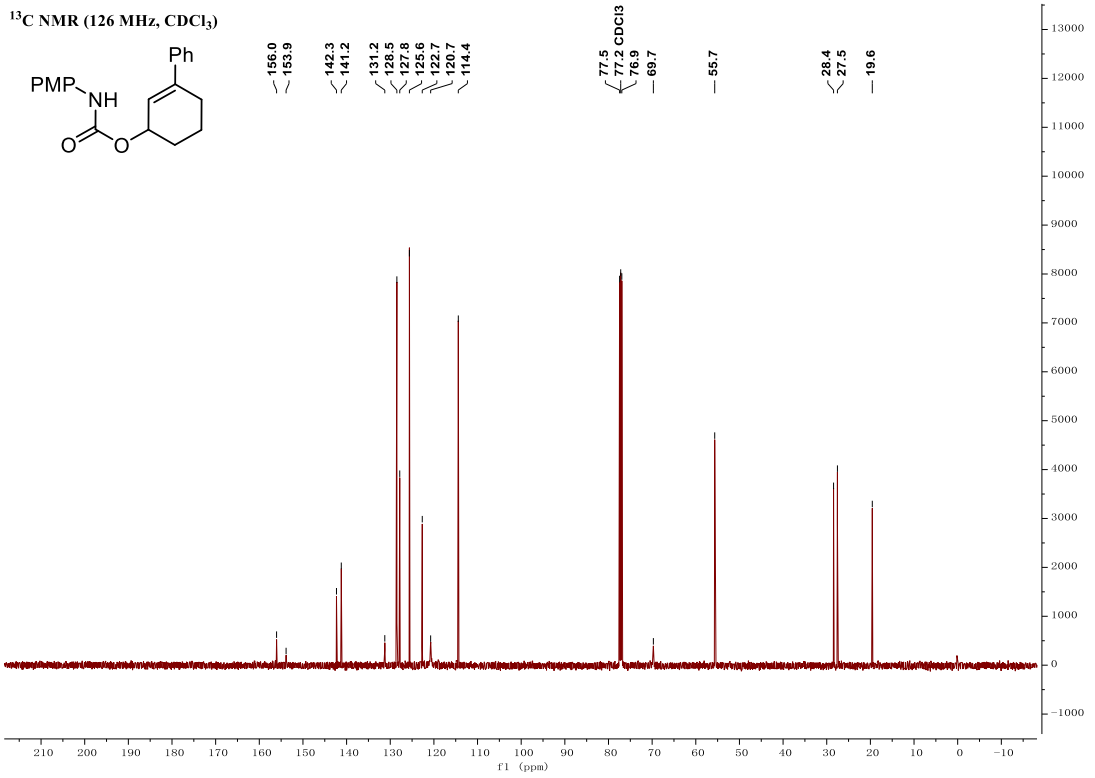
Compound S19



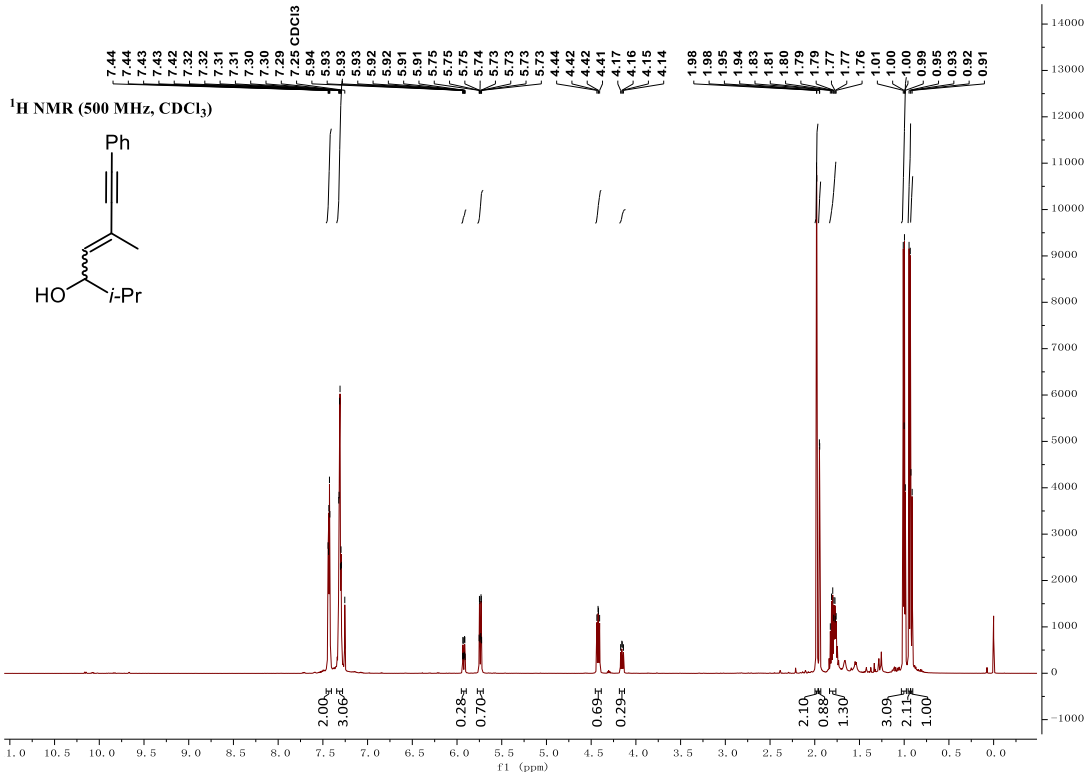


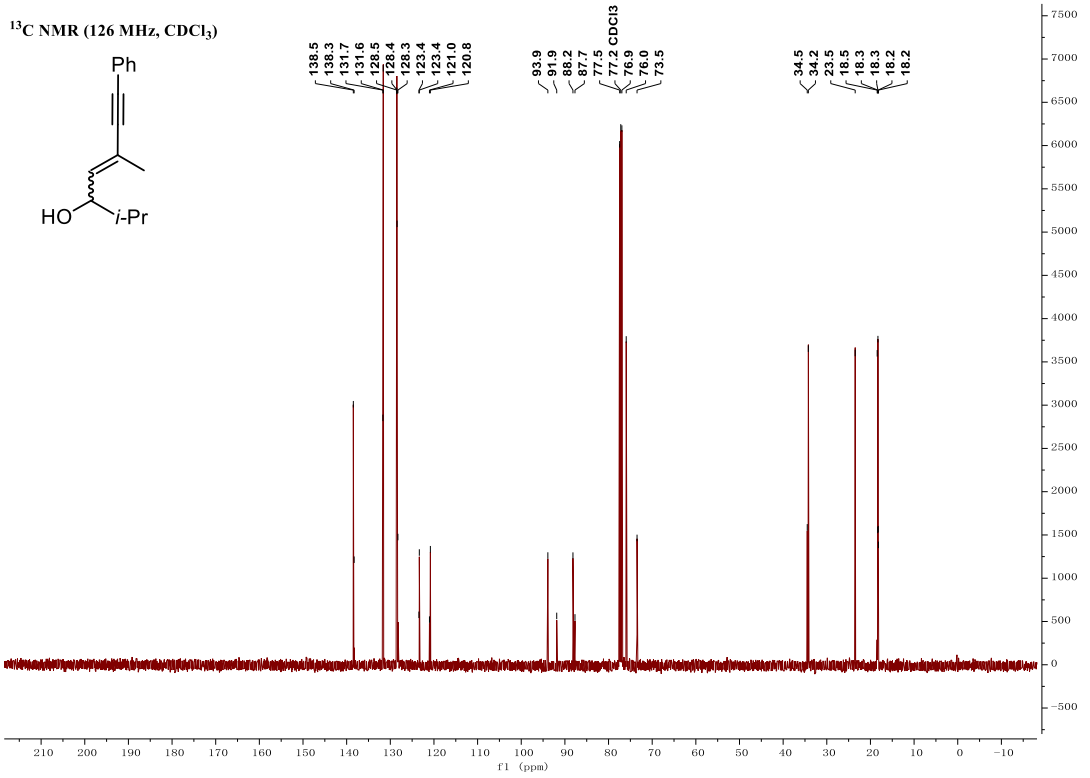
Compound S20



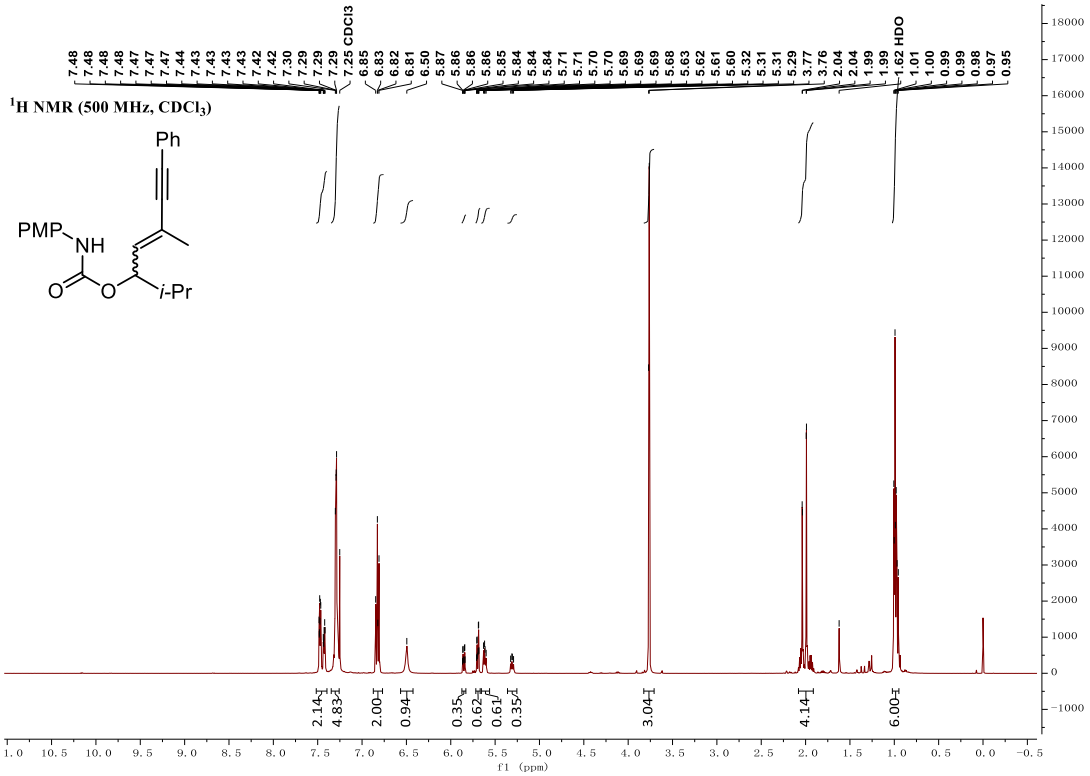


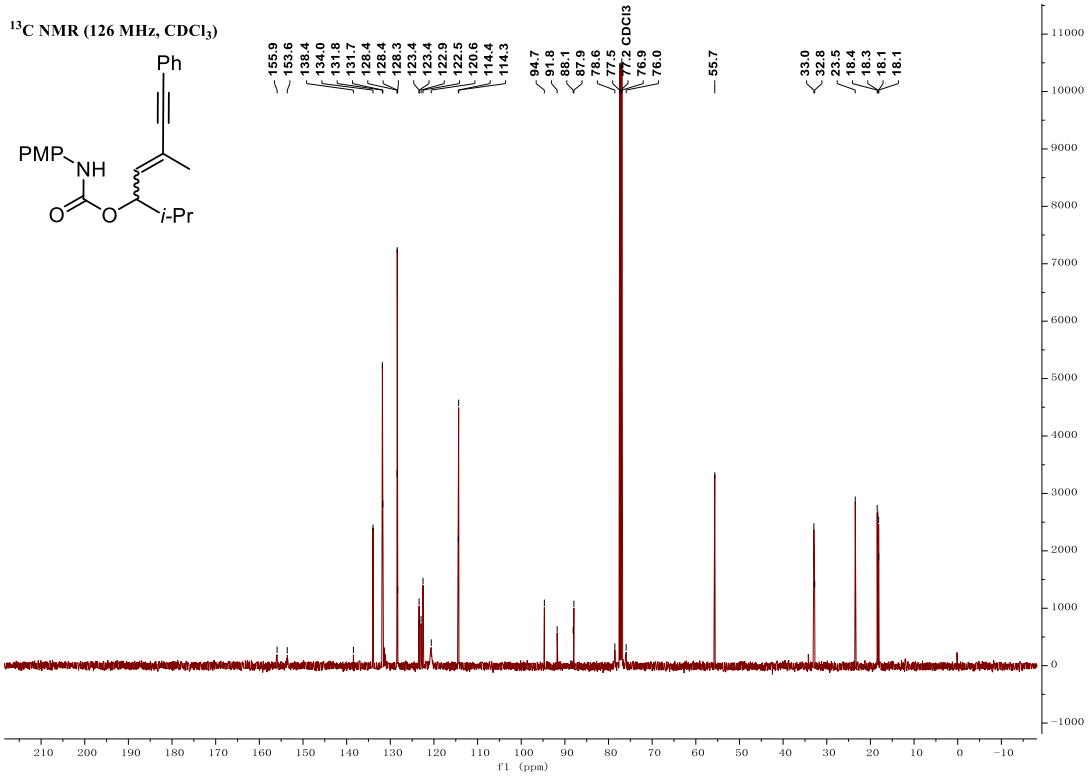
Compound S21



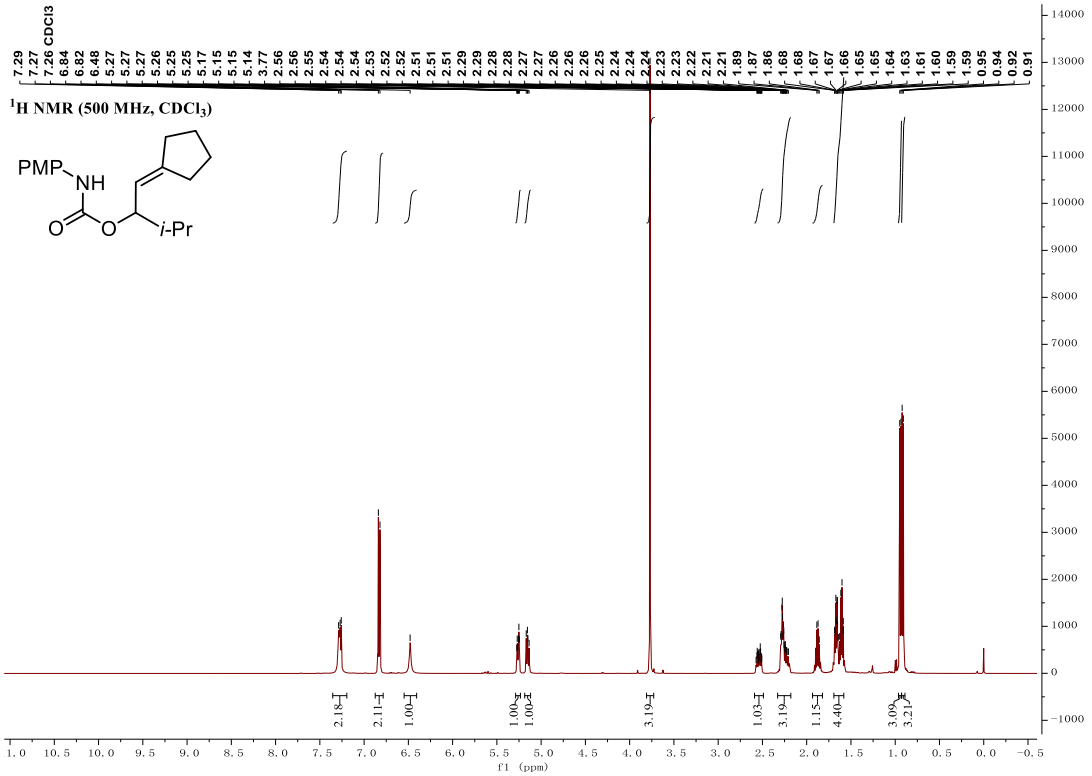


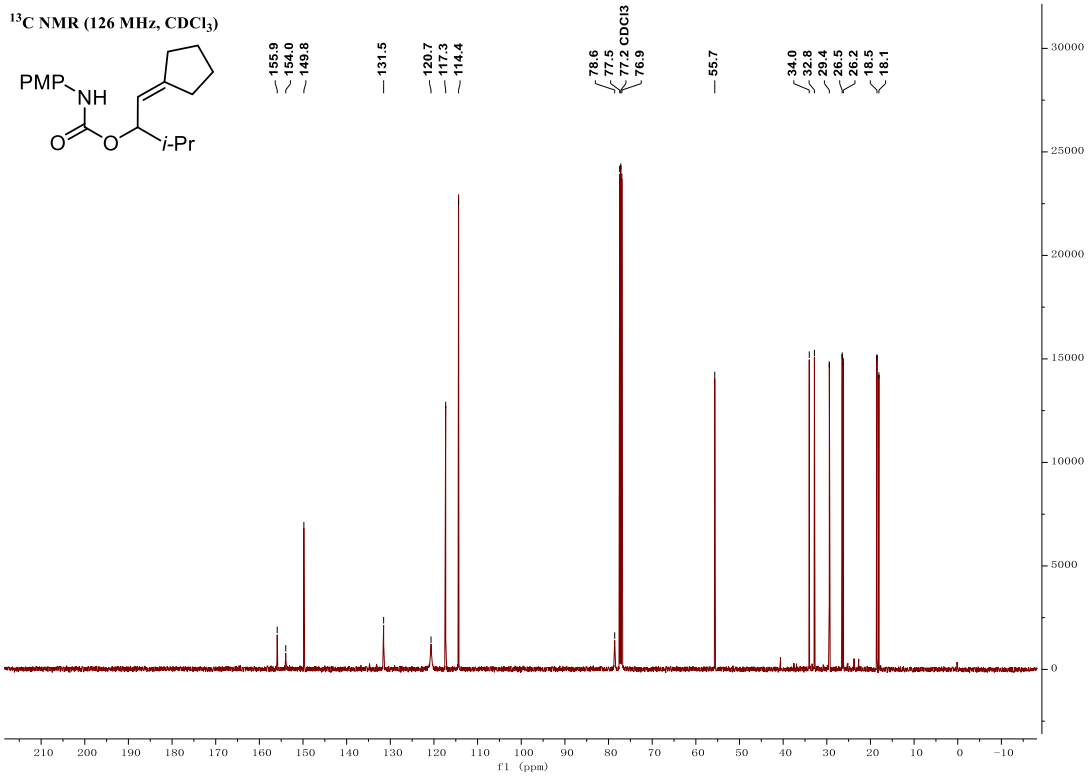
Compound S22



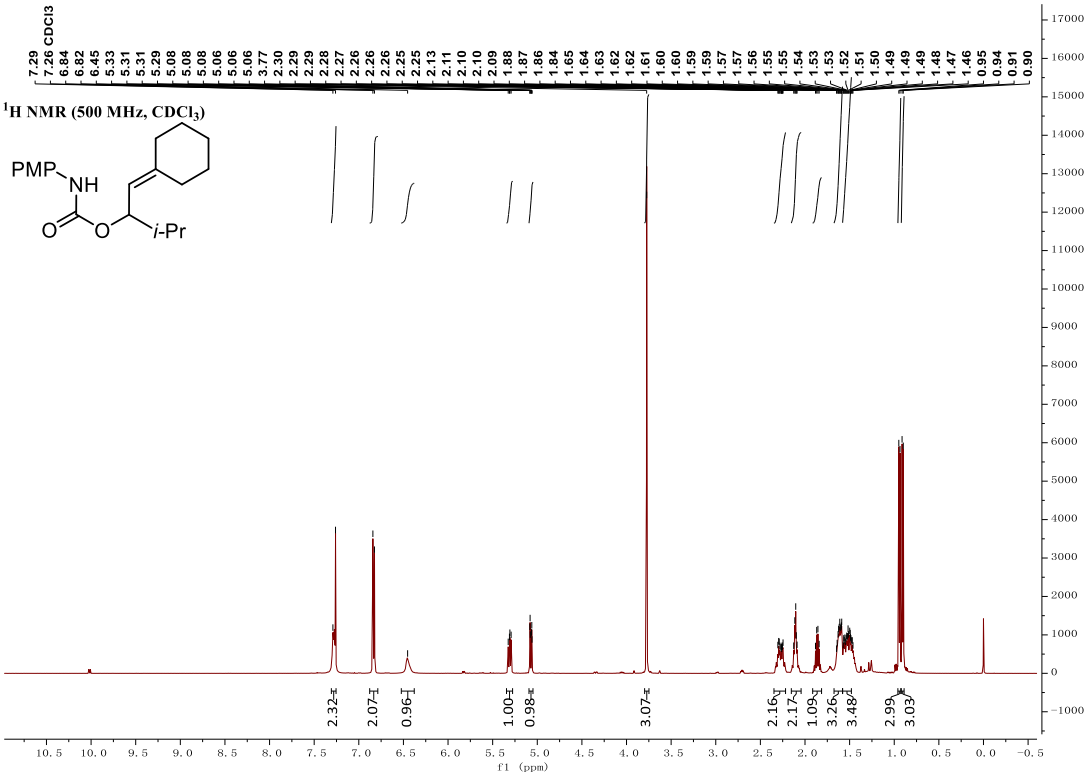


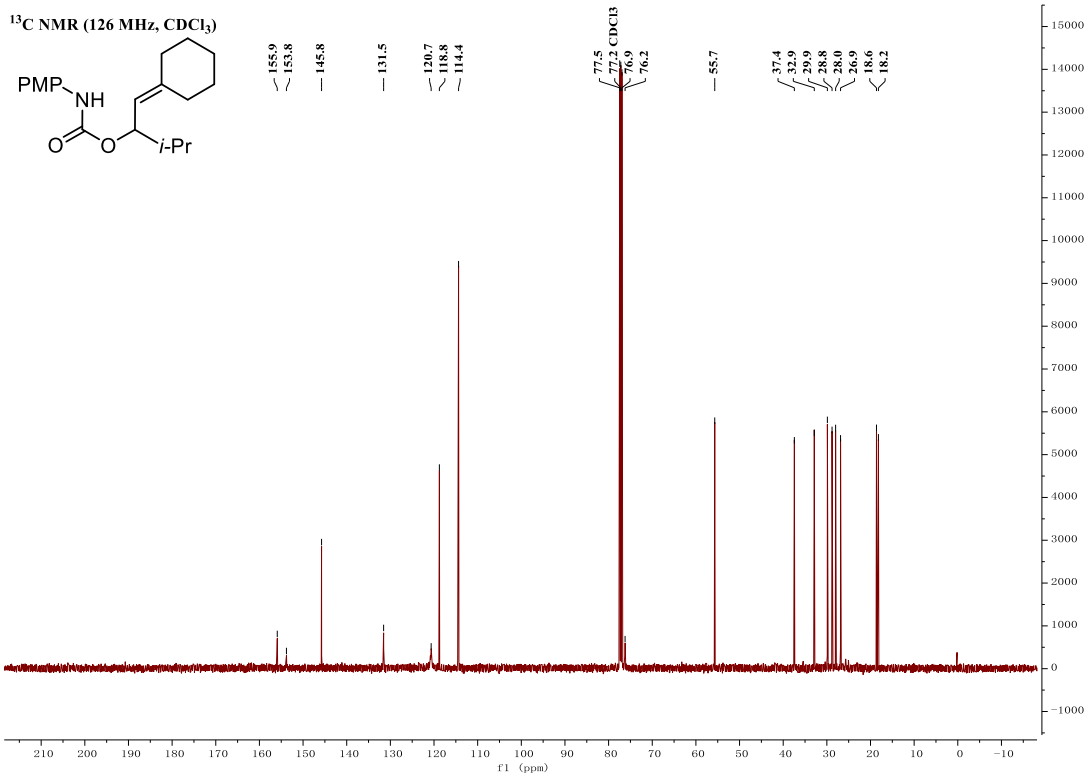
Compound S24



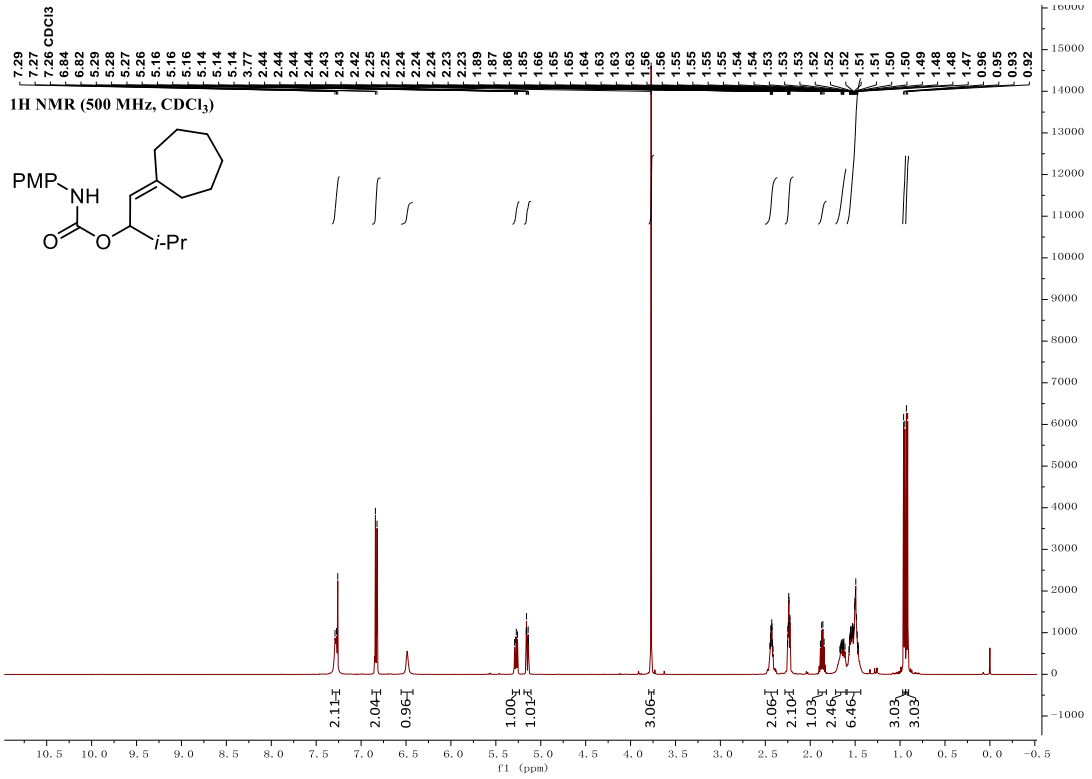


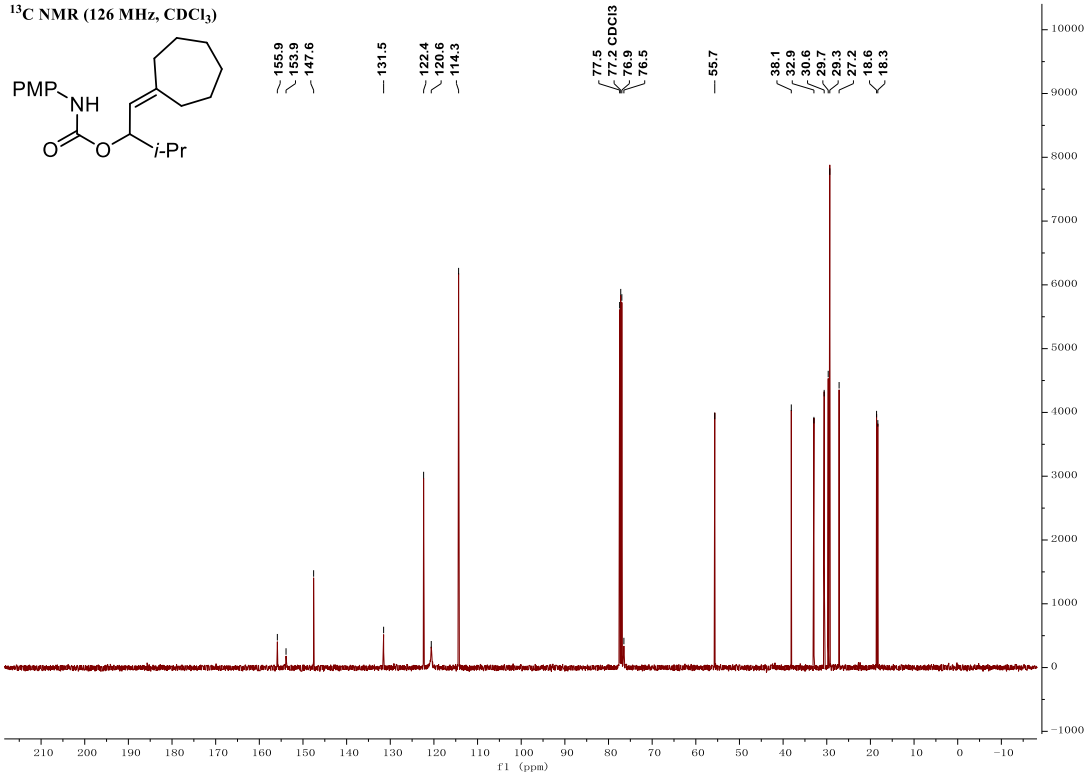
Compound S26





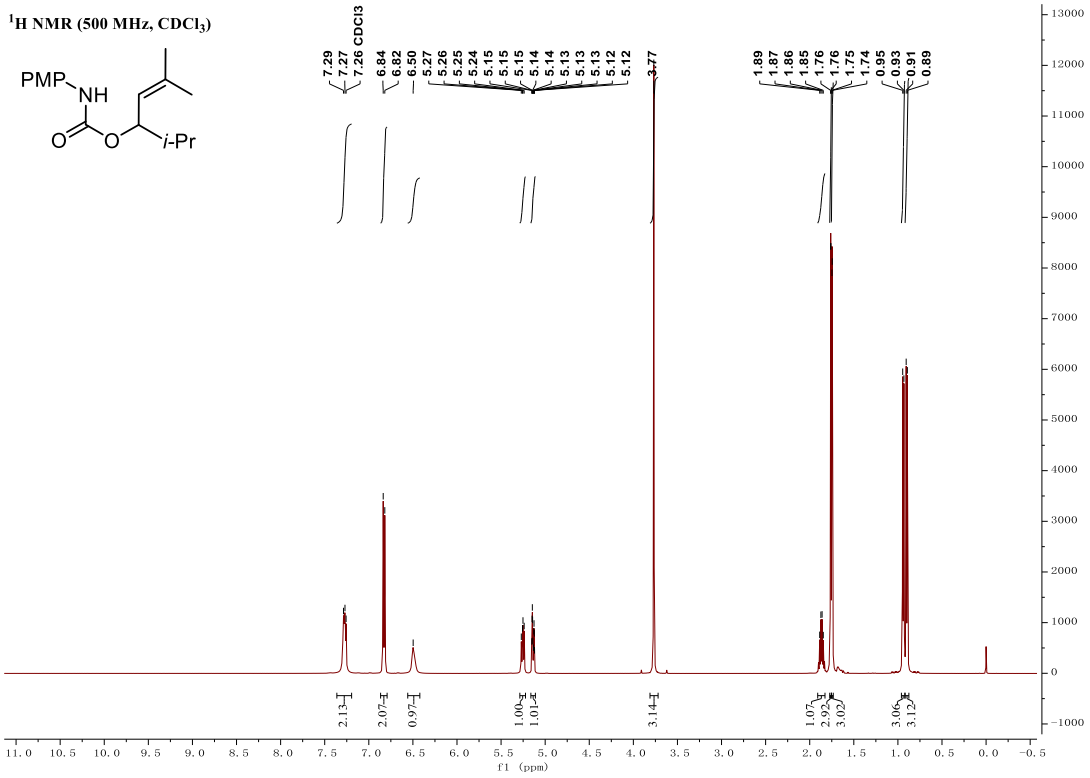
Compound S28



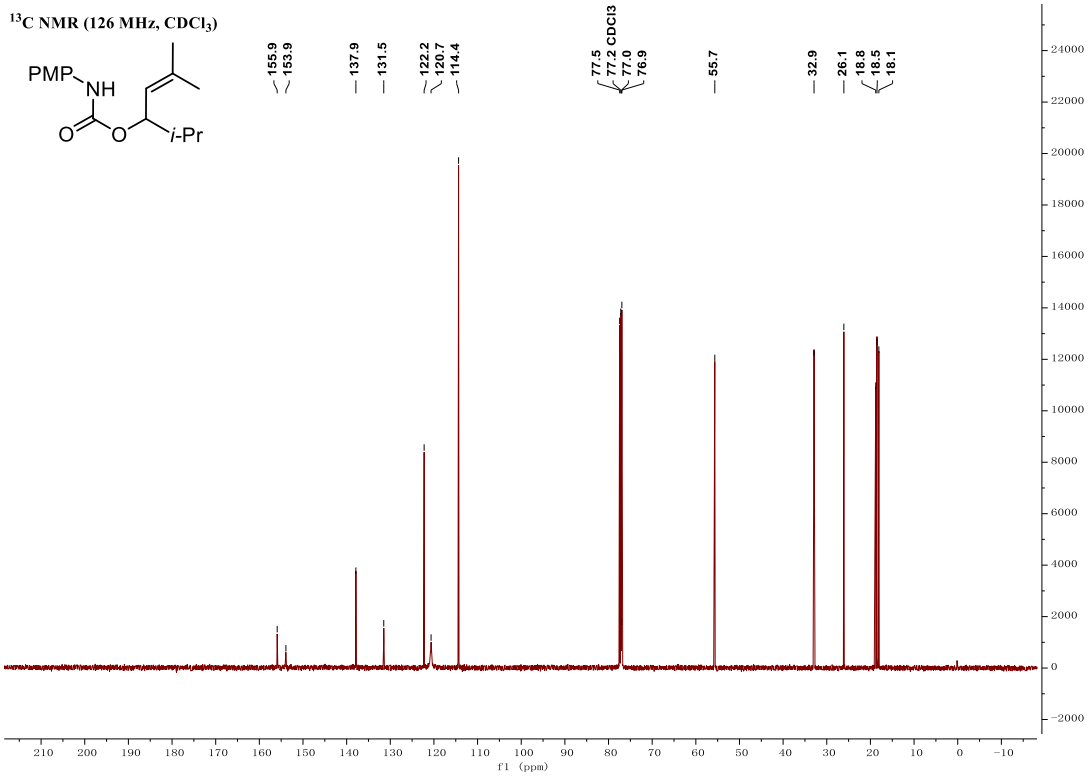


Compound S29

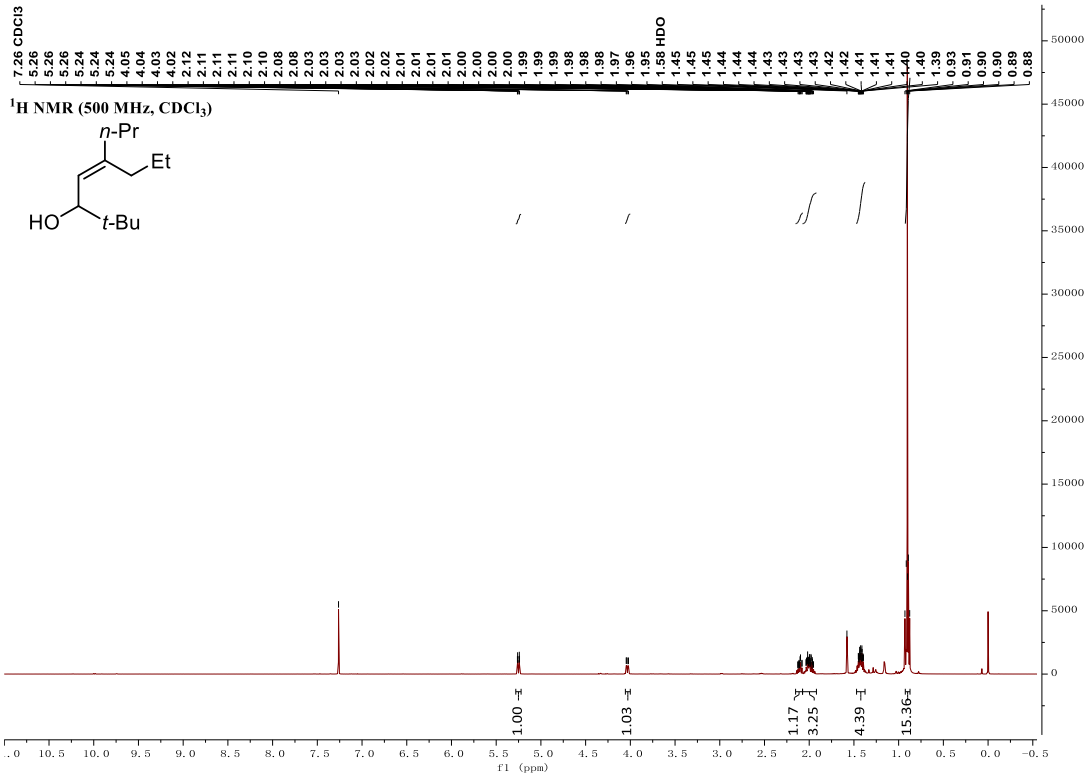
^{1}H NMR (500 MHz, $CDCl_3$)

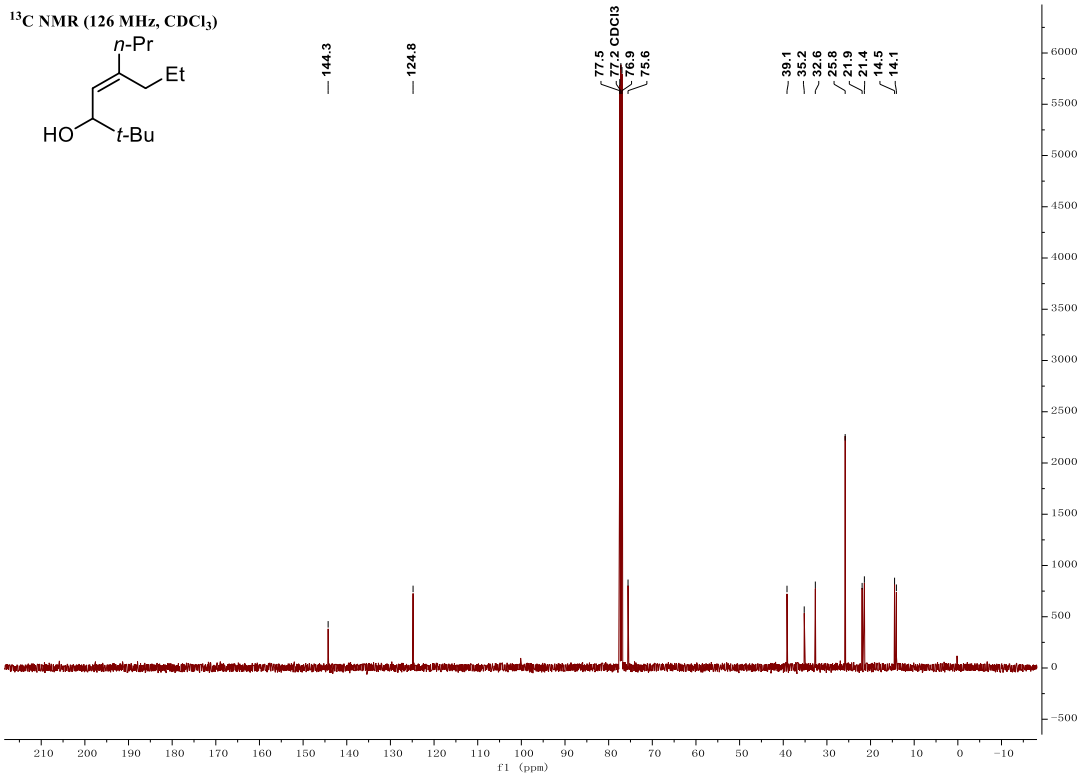


^{13}C NMR (126 MHz, $CDCl_3$)

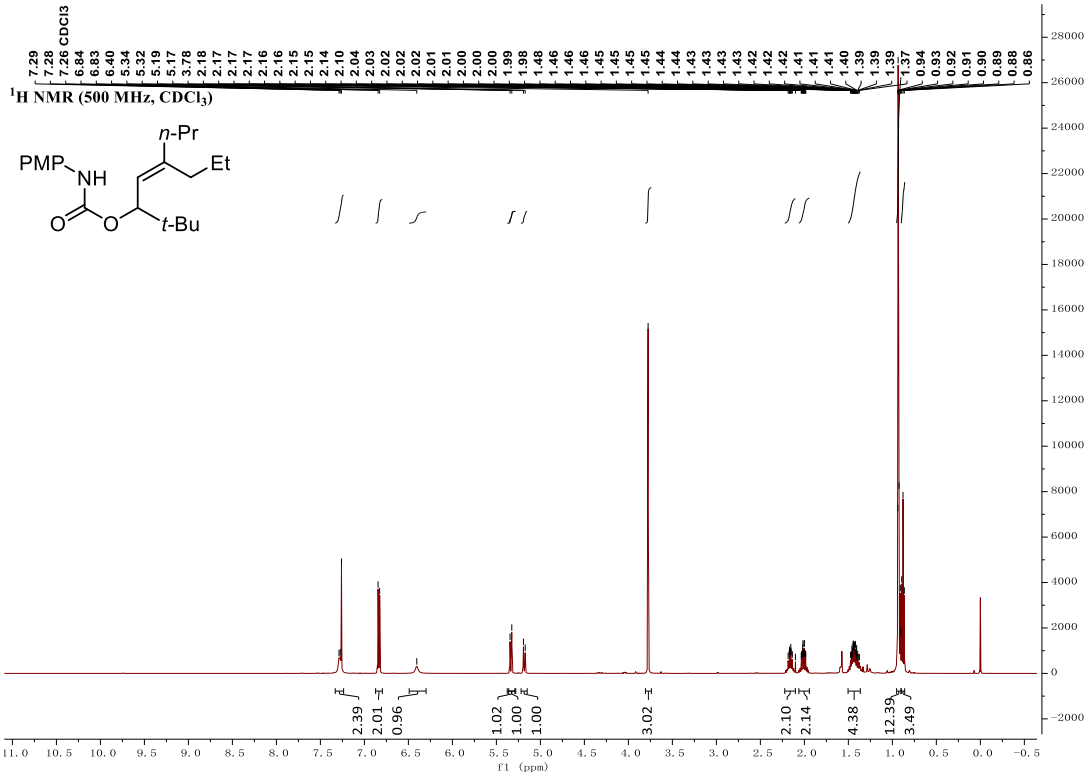


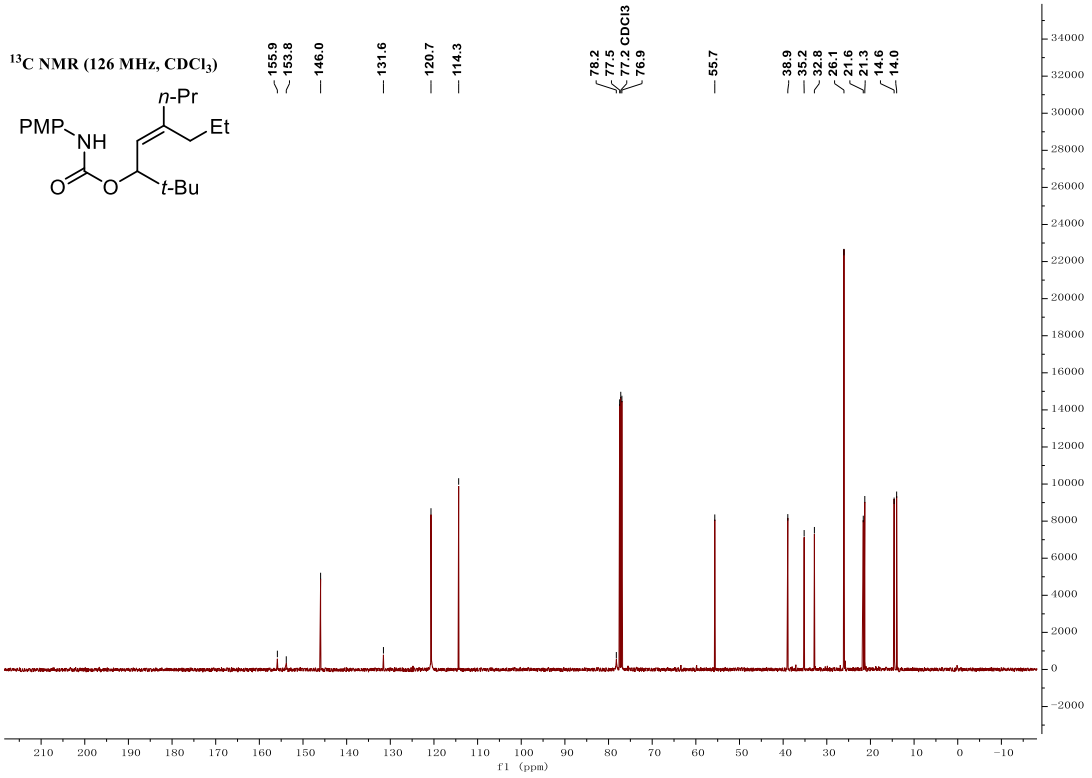
Compound S30





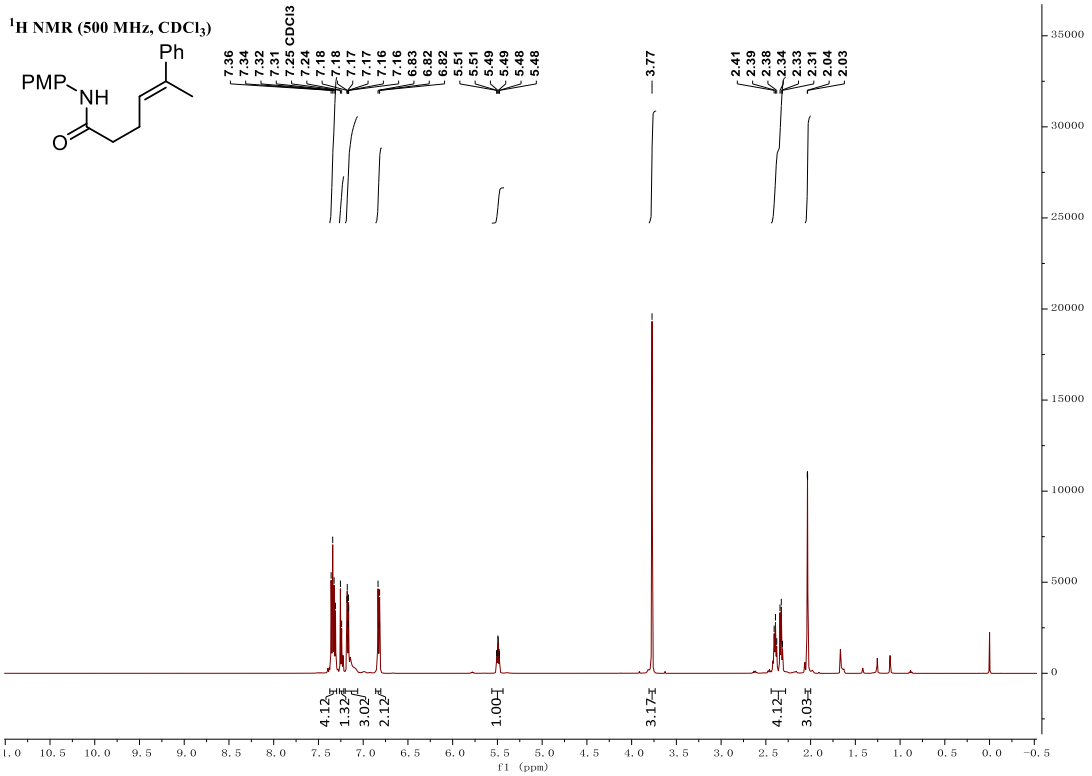
Compound S31



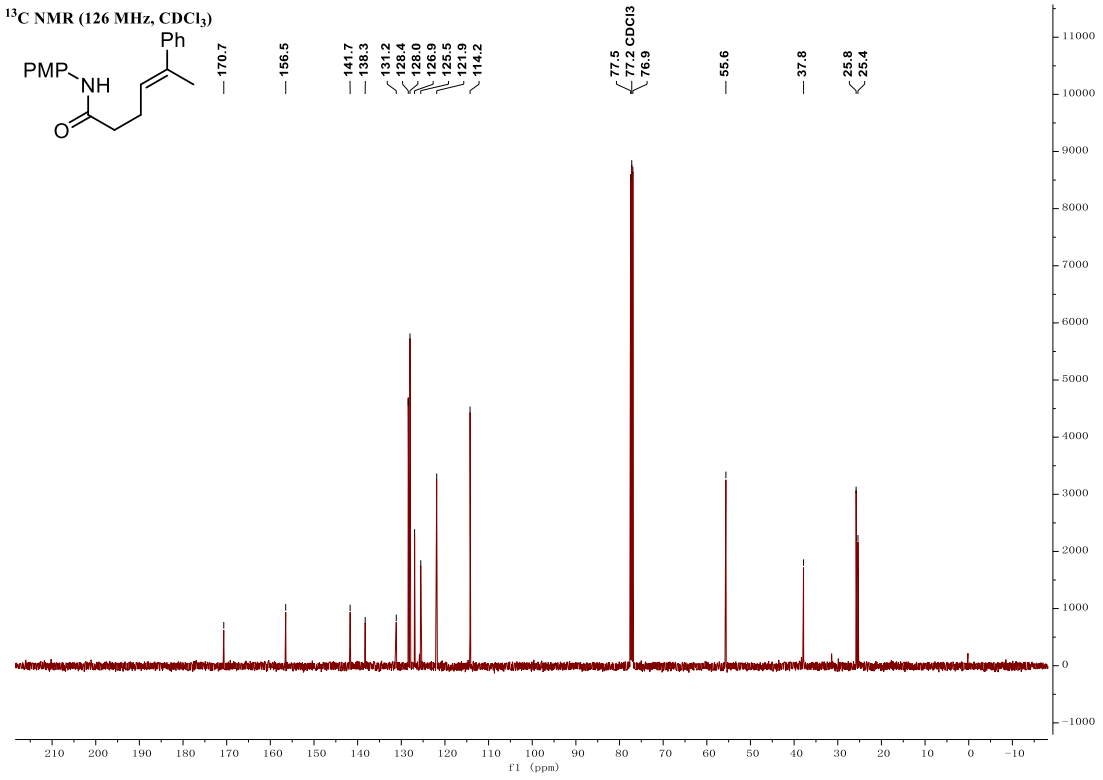


Compound S32

^{1}H NMR (500 MHz, $CDCl_3$)

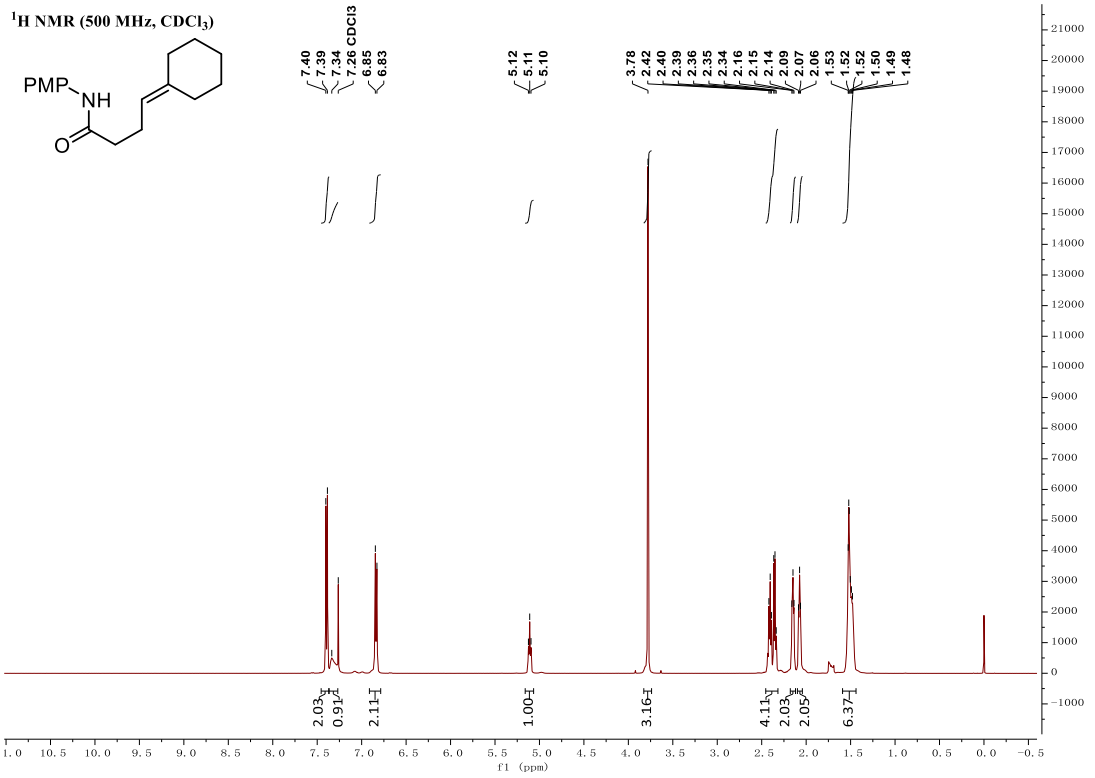


^{13}C NMR (126 MHz, $CDCl_3$)

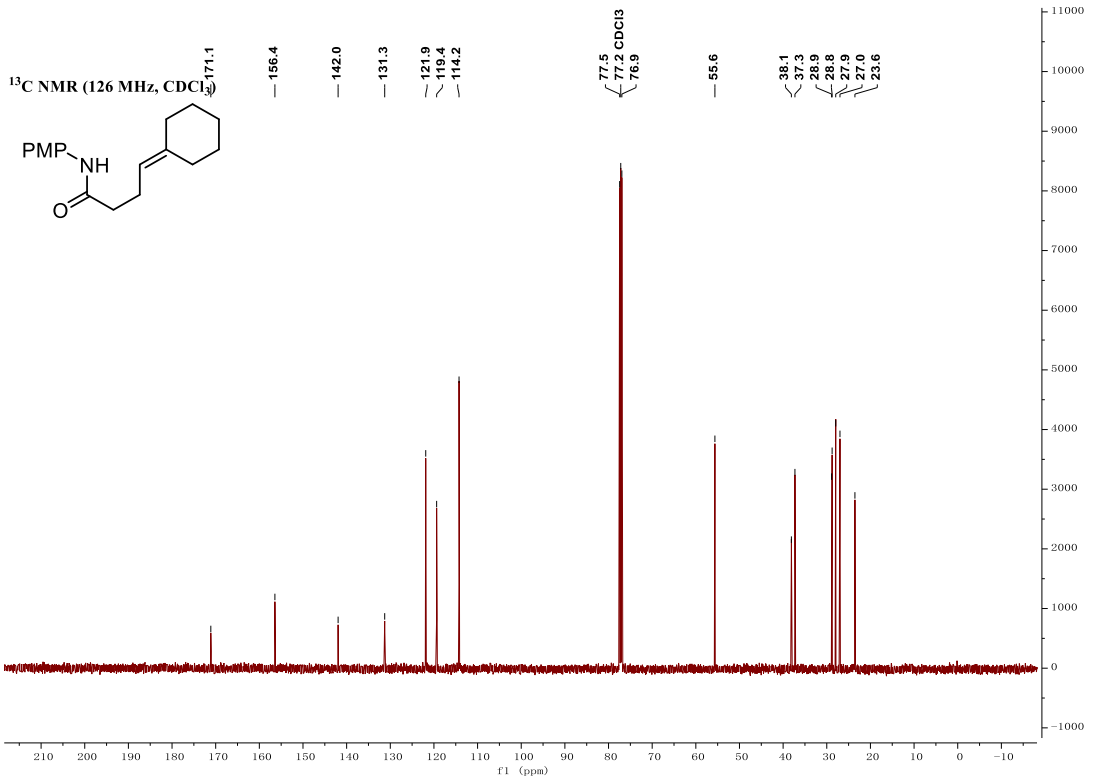


Compound S33

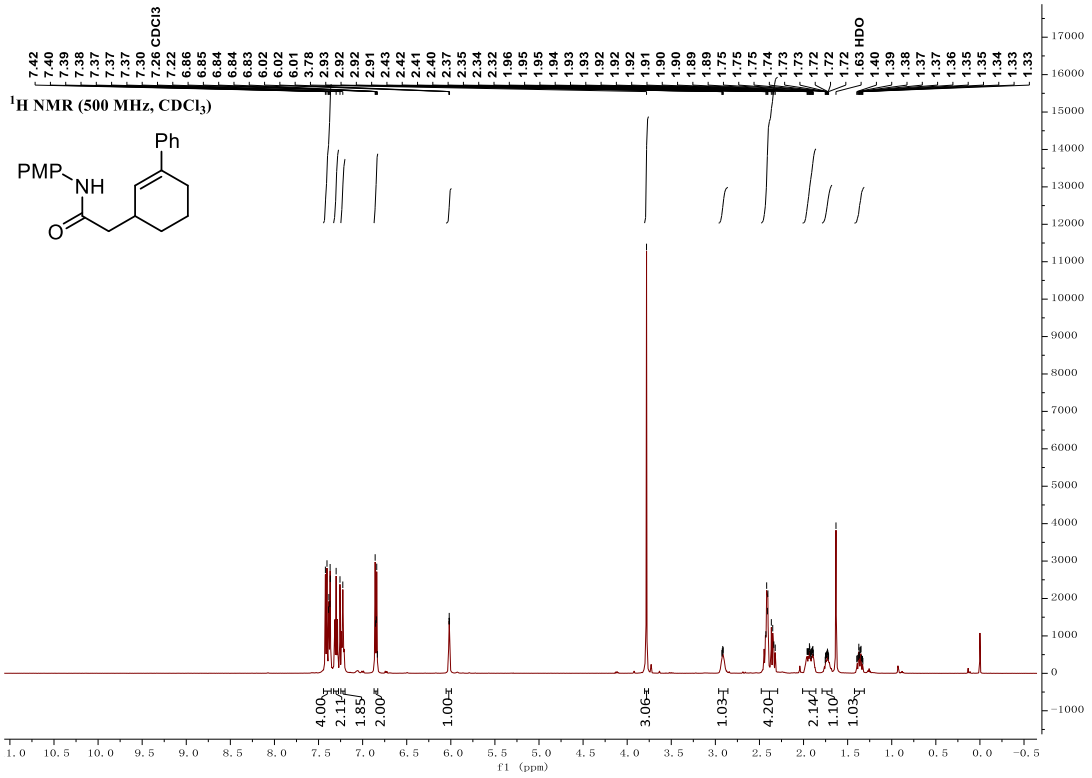
^{1}H NMR (500 MHz, $CDCl_3$)

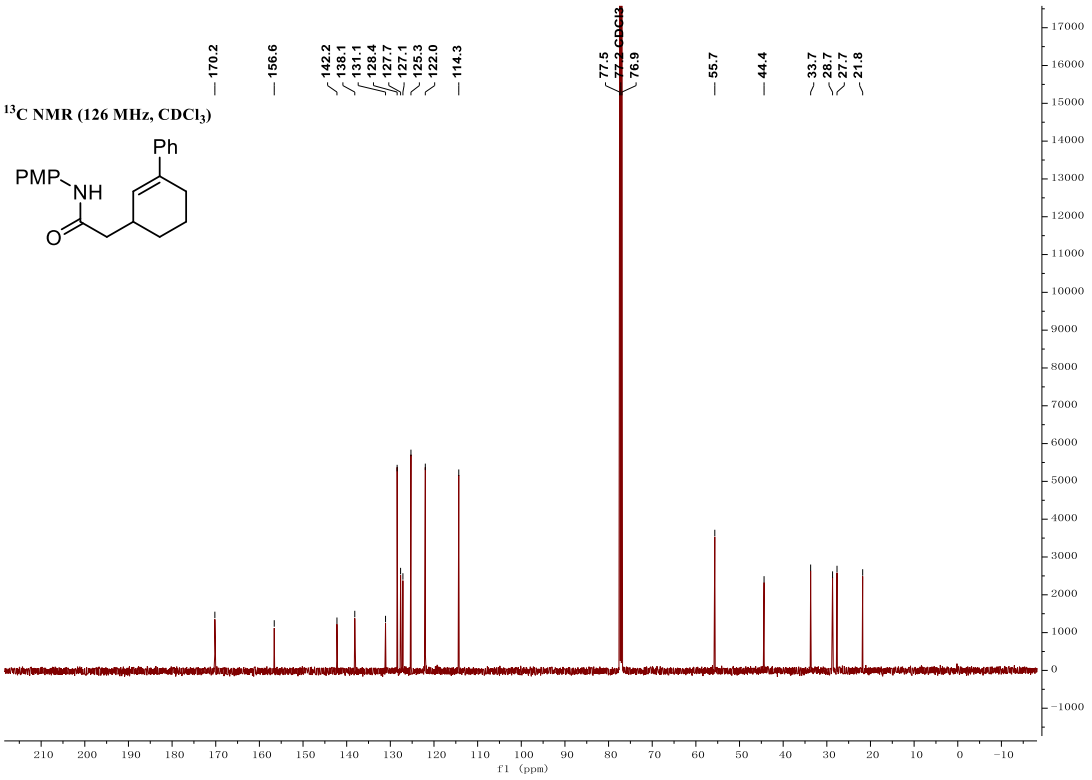


^{13}C NMR (126 MHz, $CDCl_3$)

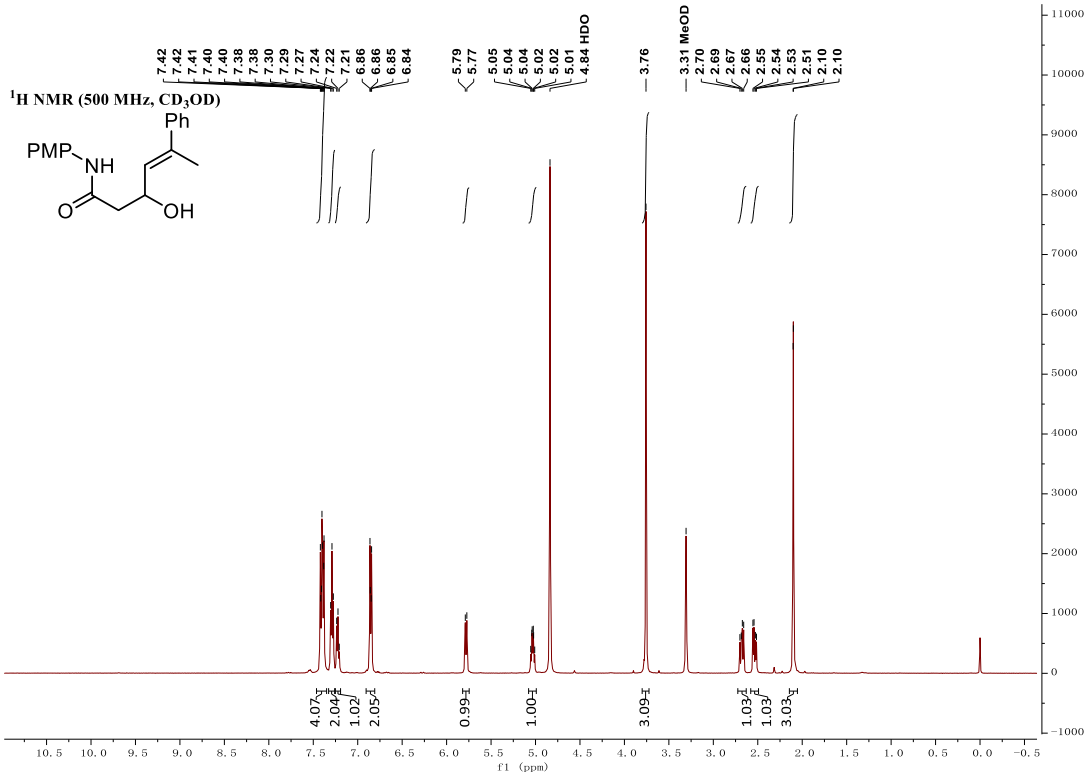


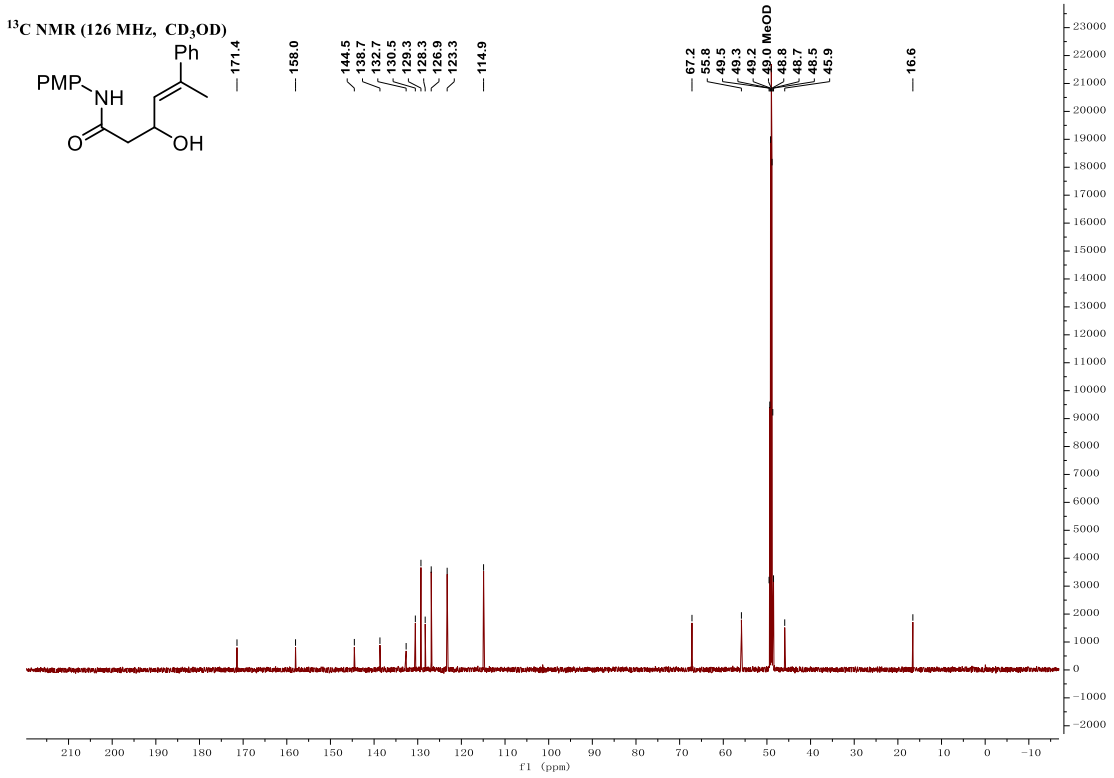
Compound S34





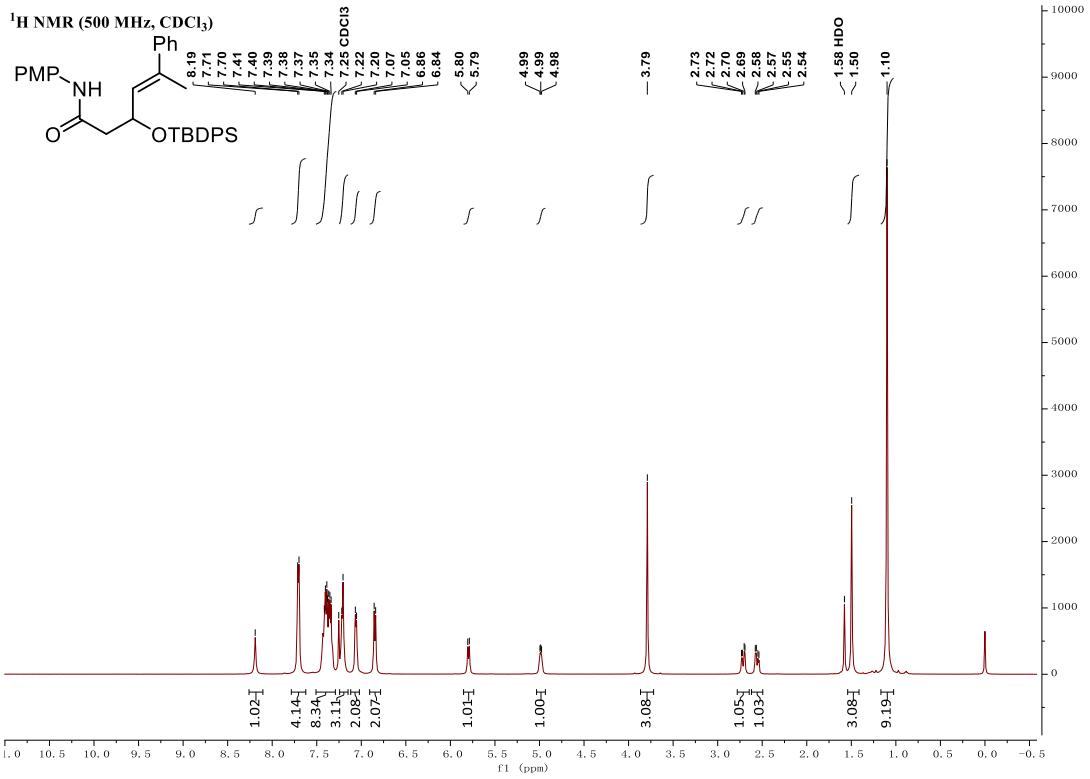
Compound S36



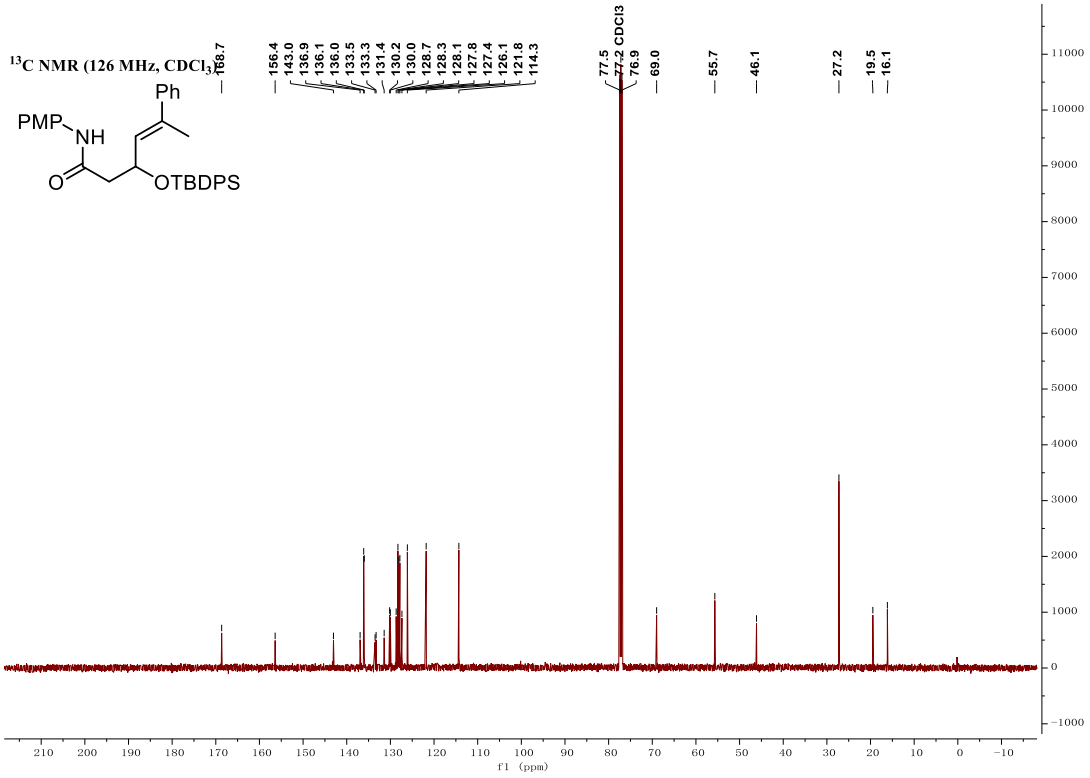


Compound S37

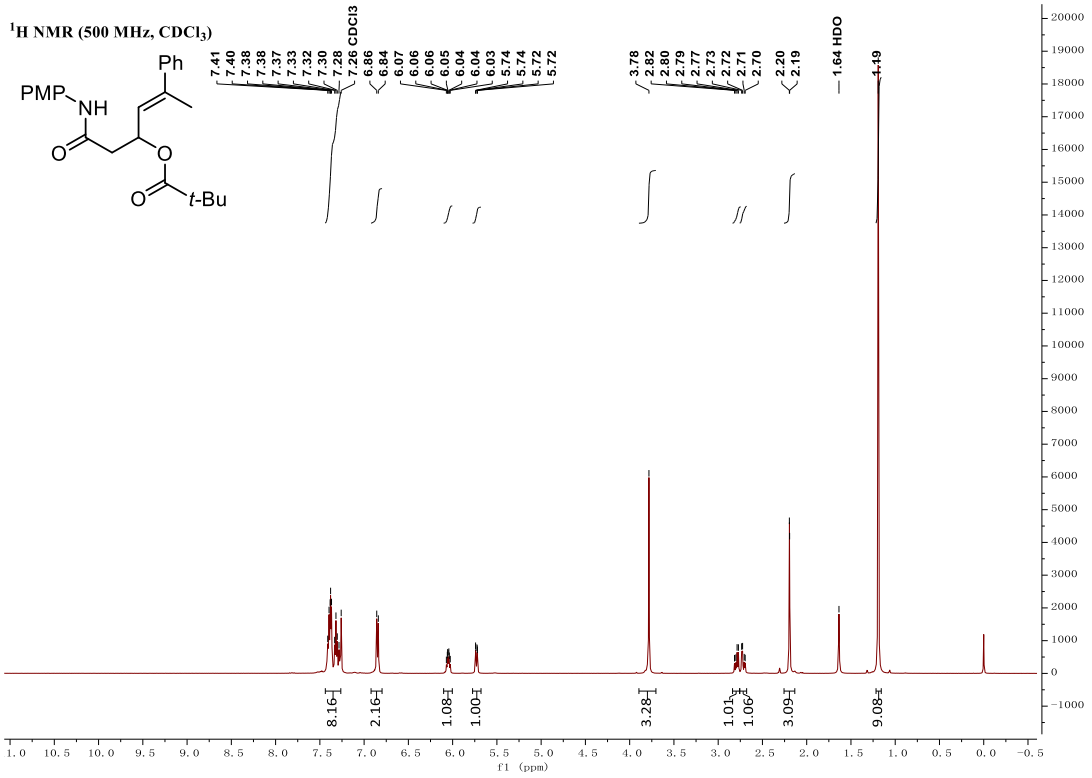
^{1}H NMR (500 MHz, $CDCl_3$)

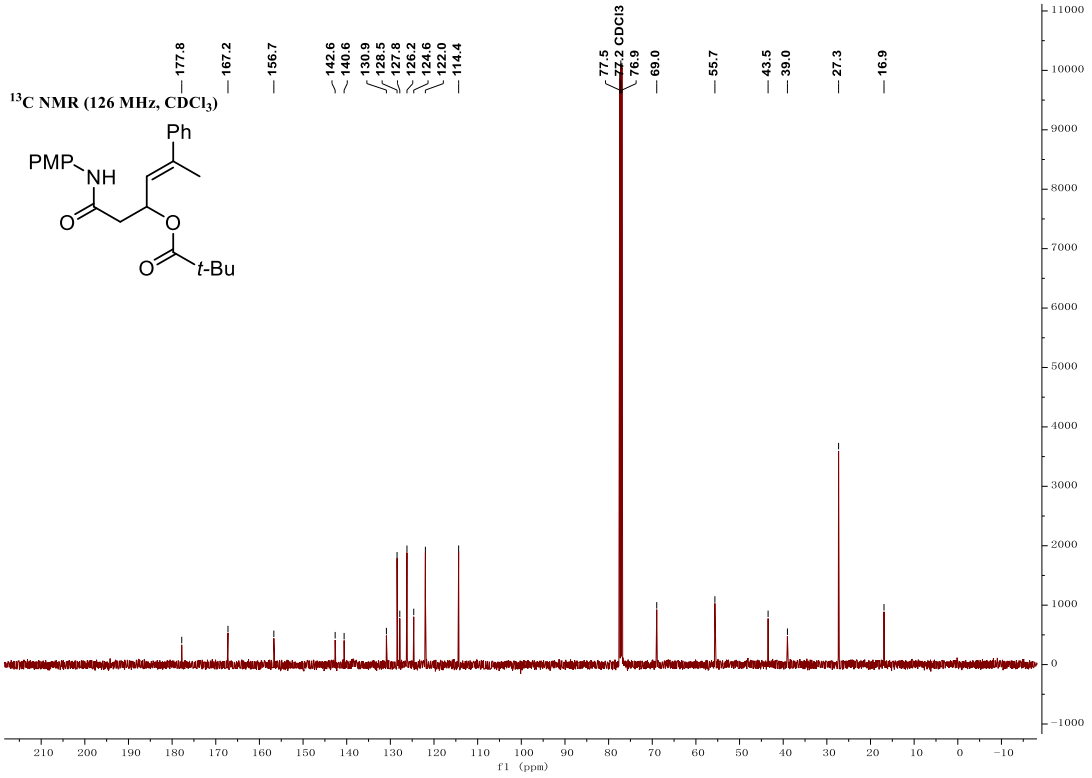


^{13}C NMR (126 MHz, $CDCl_3$)

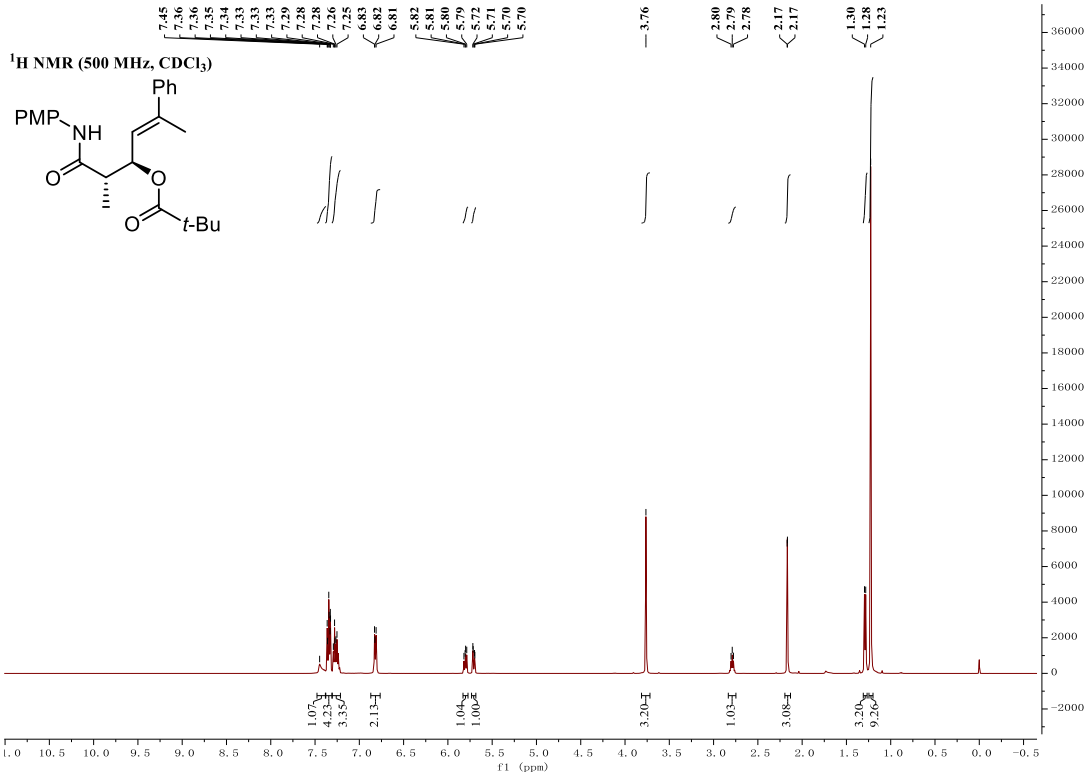


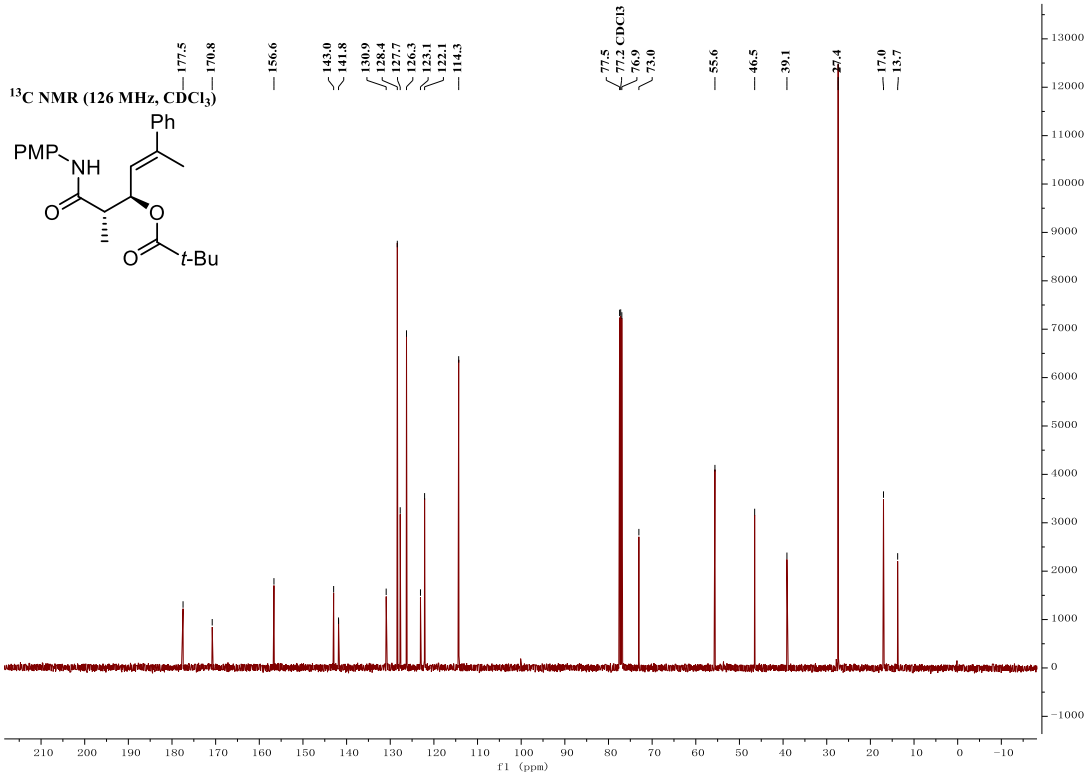
Compound S38





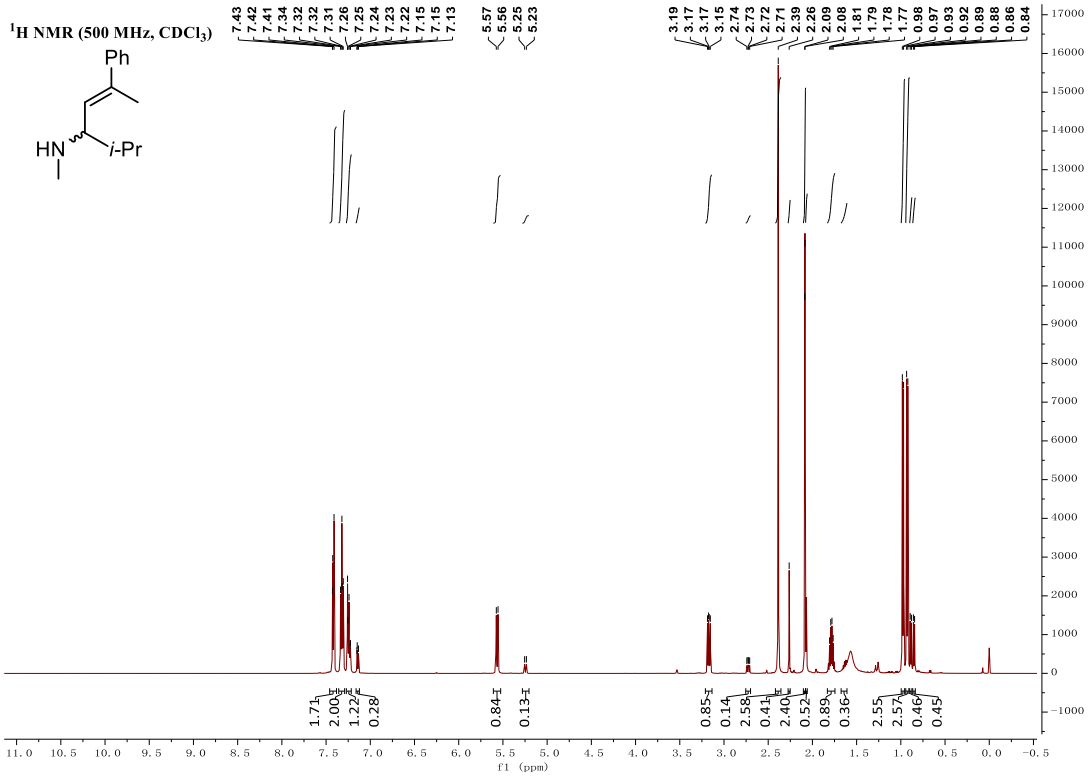
Compound S41



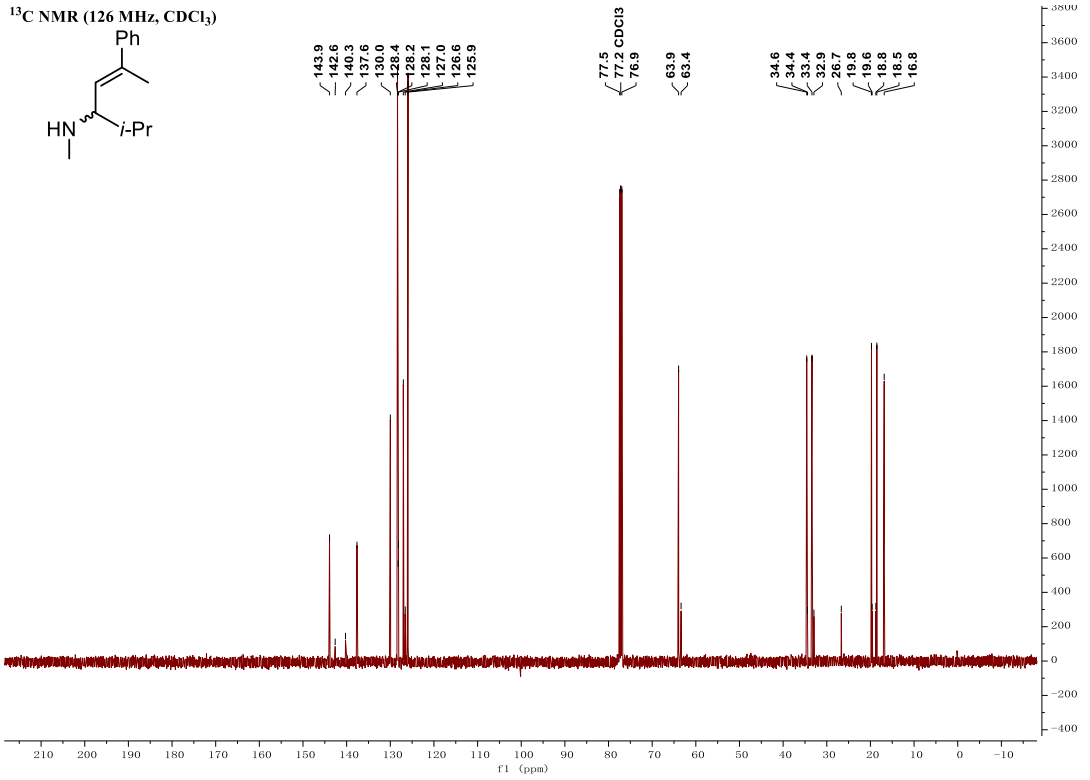


Compound S42

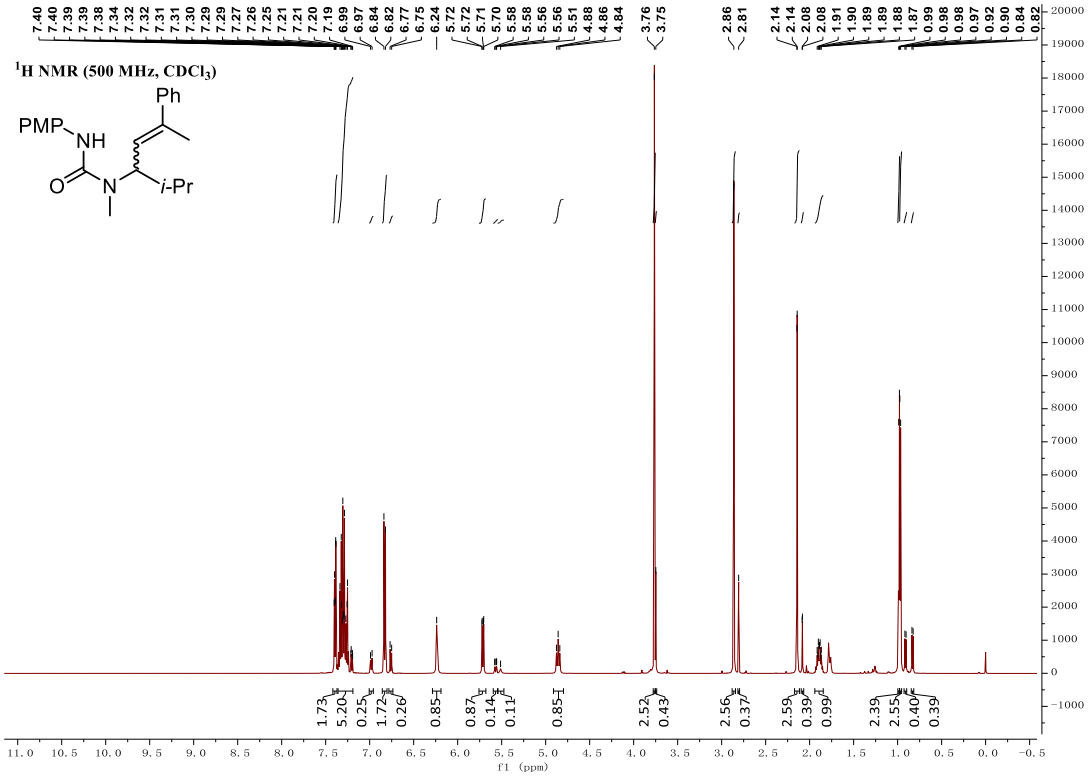
^{1}H NMR (500 MHz, $CDCl_3$)

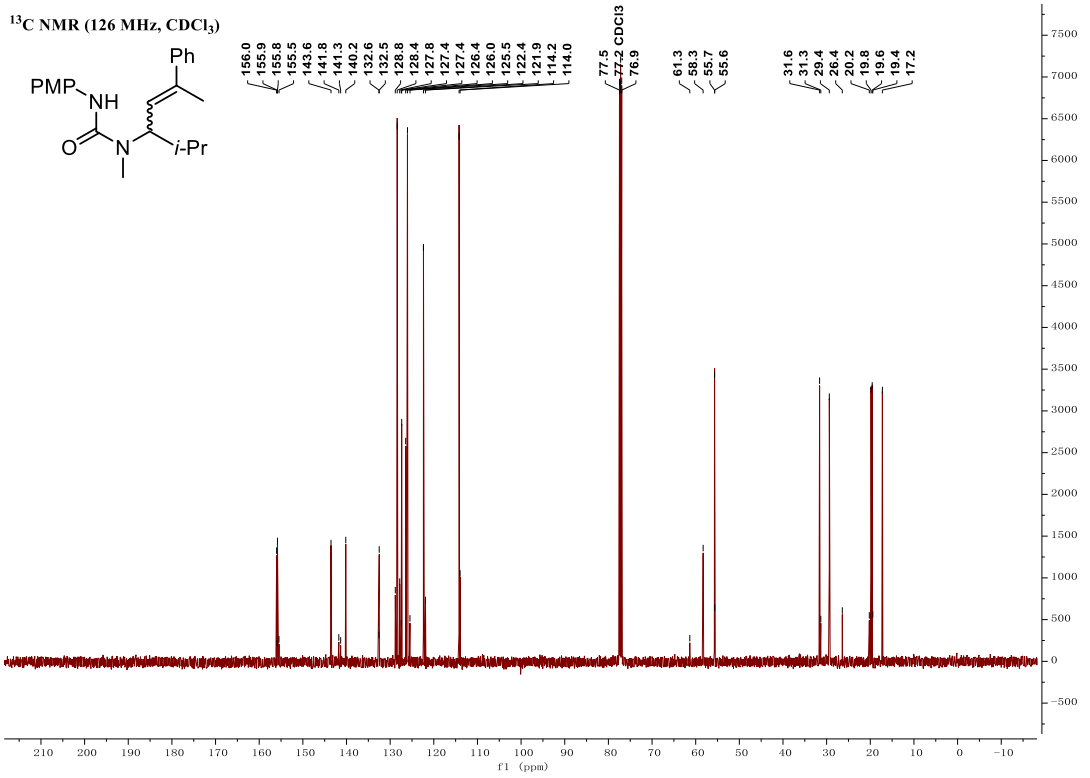


^{13}C NMR (126 MHz, $CDCl_3$)

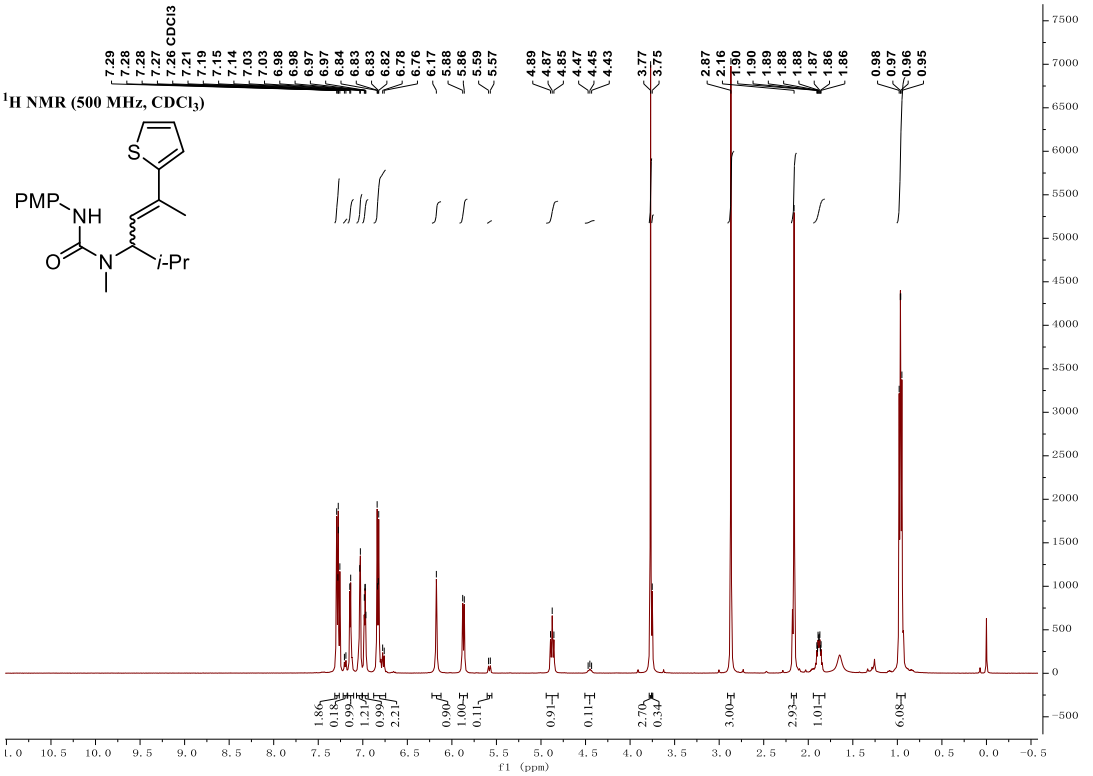


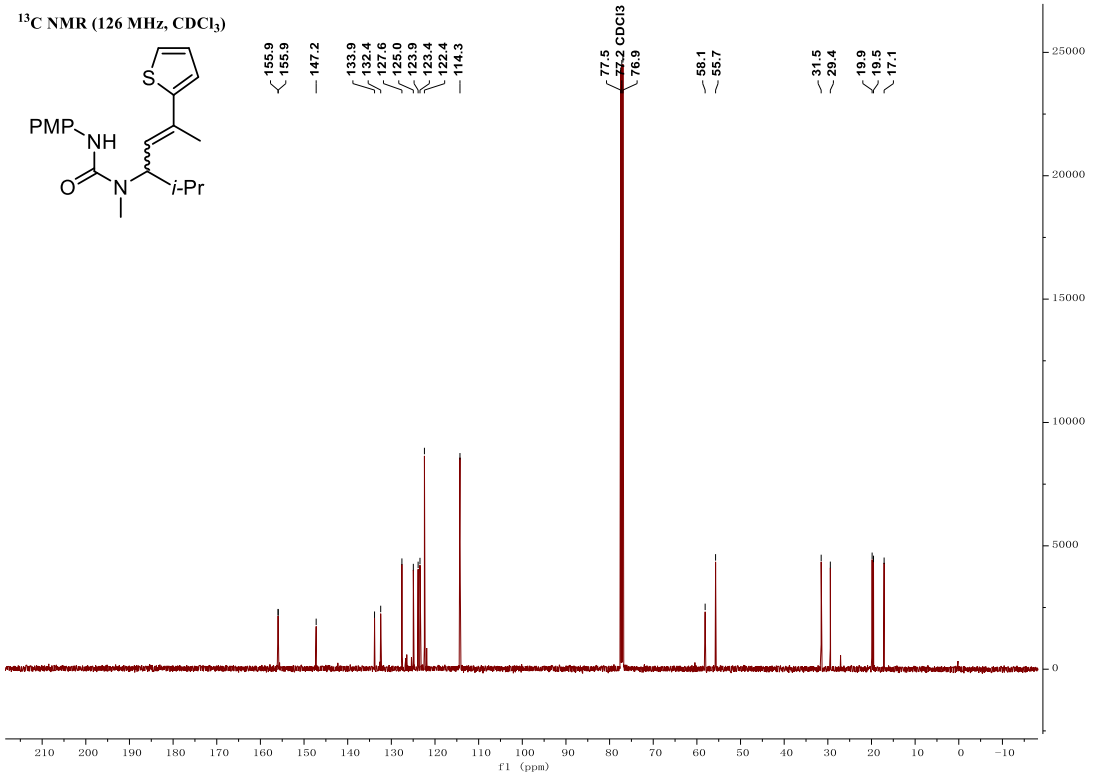
Compound S43



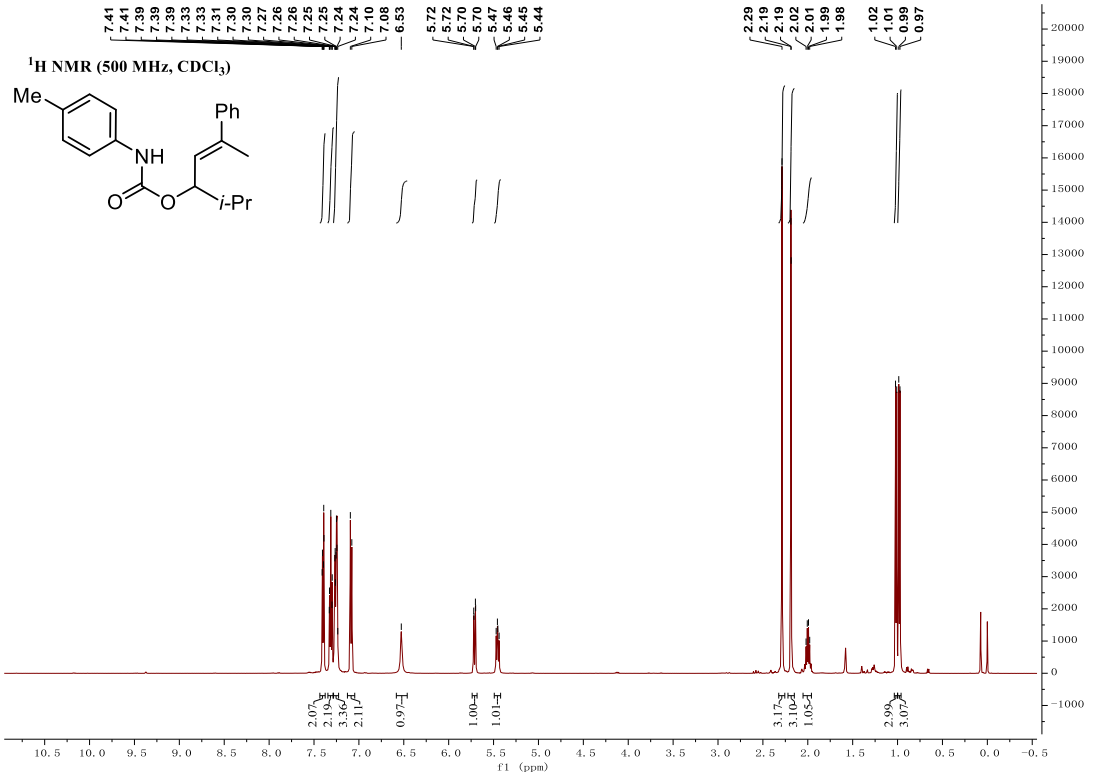


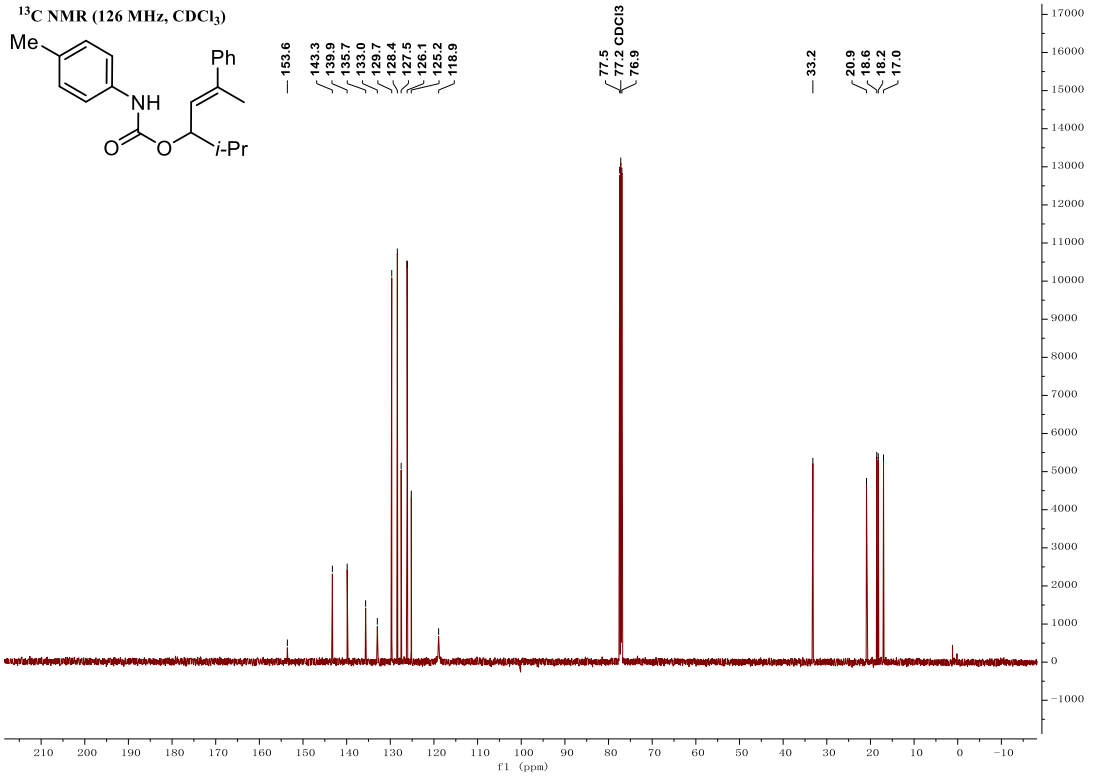
Compound S45



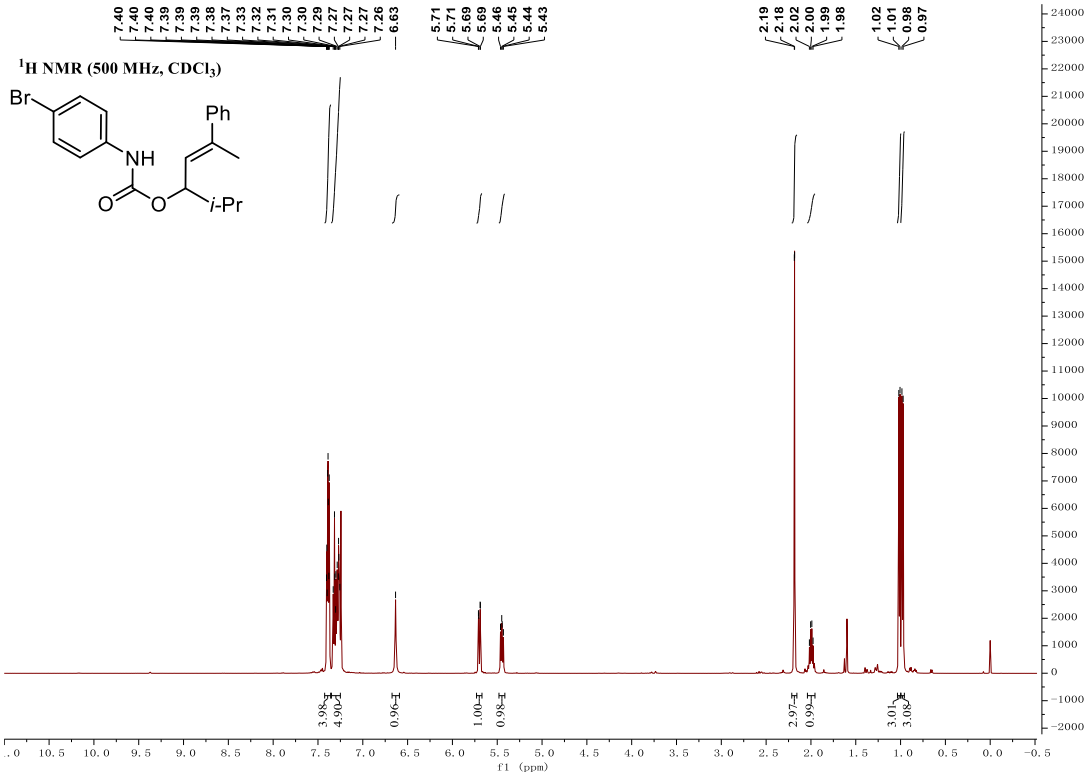


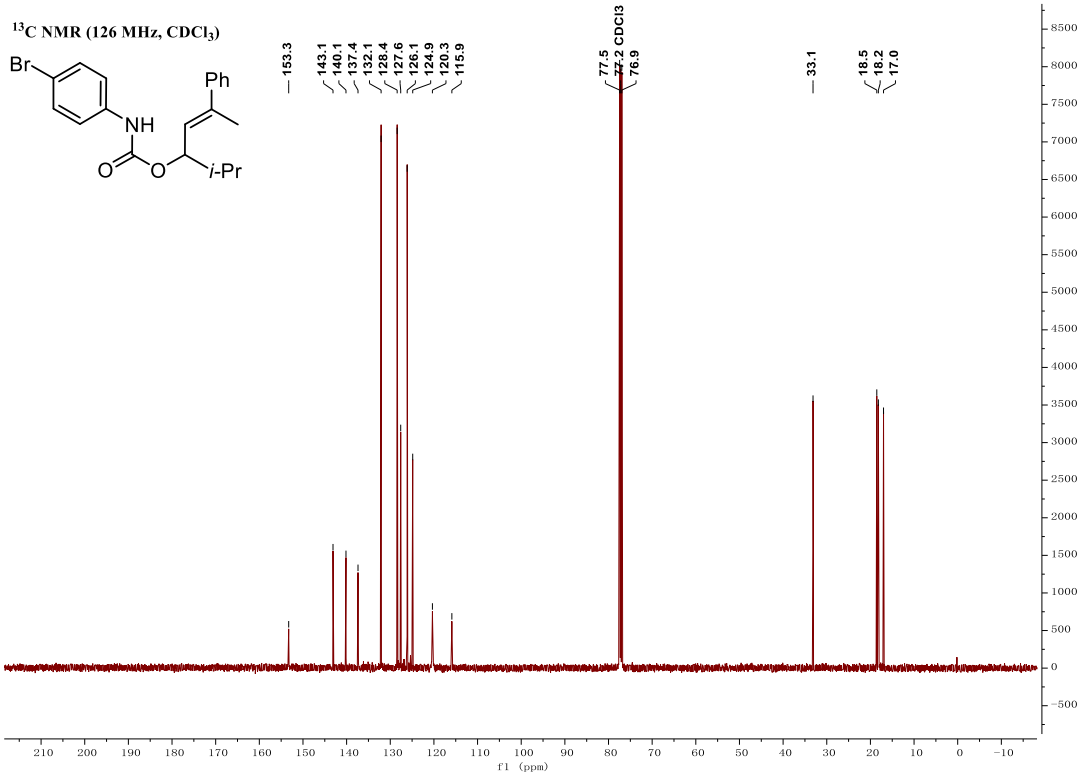
Compound S46



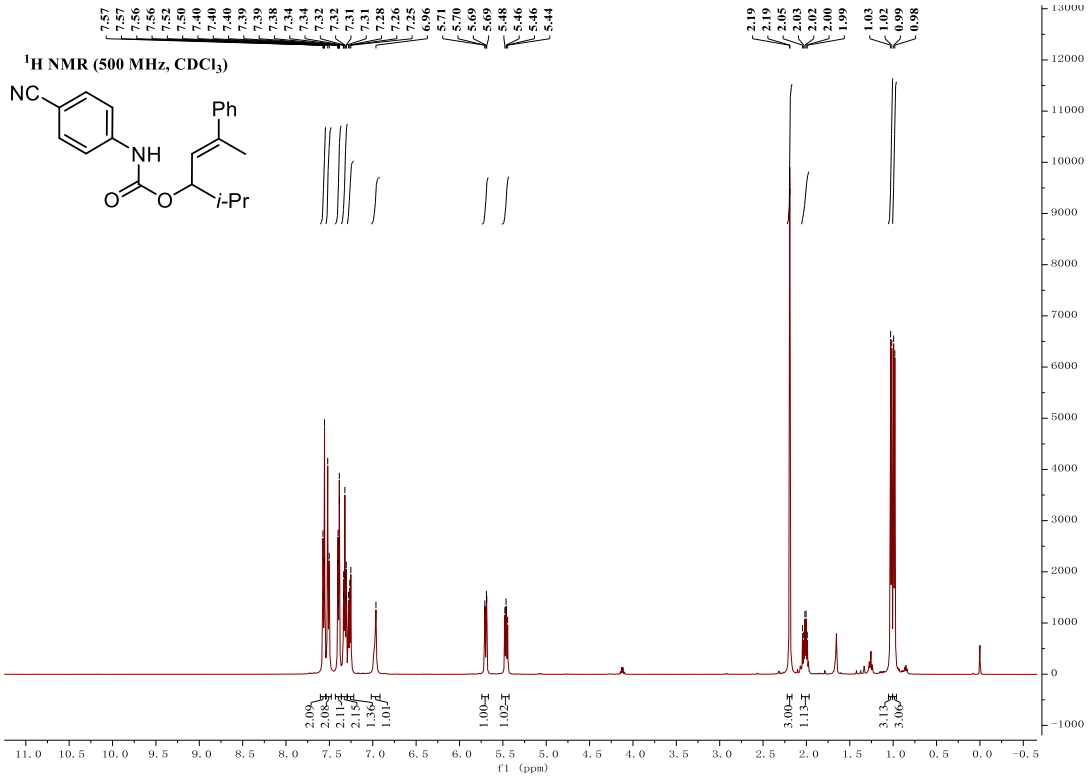


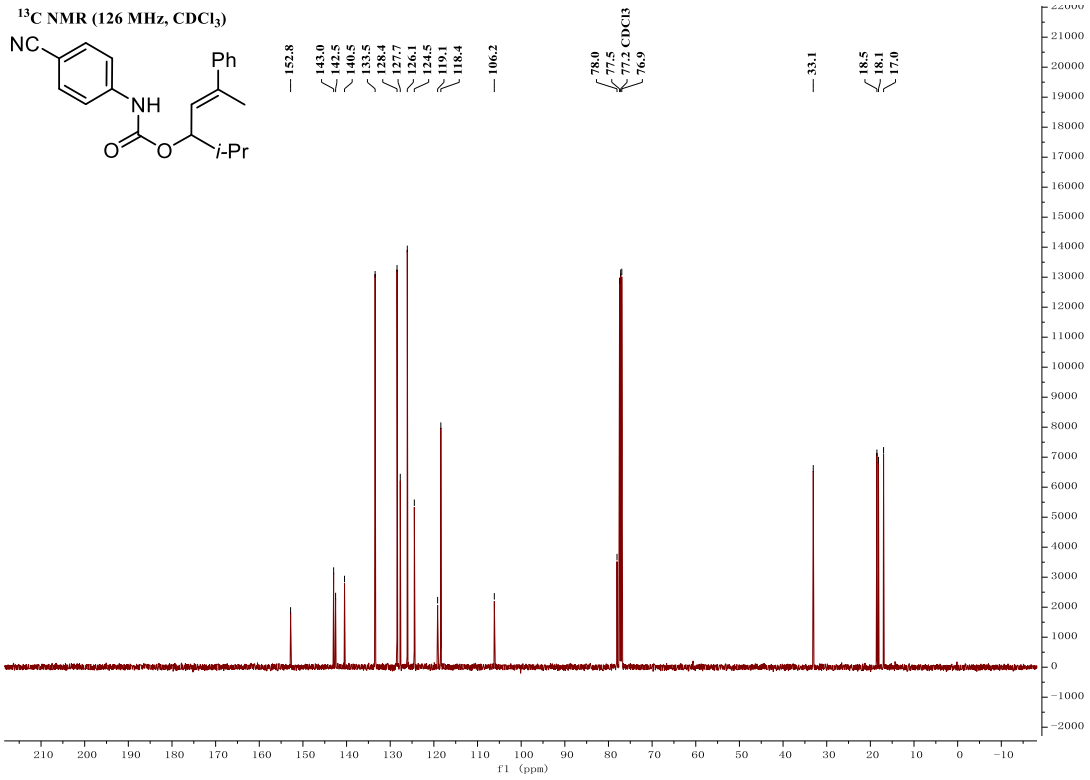
Compound S47



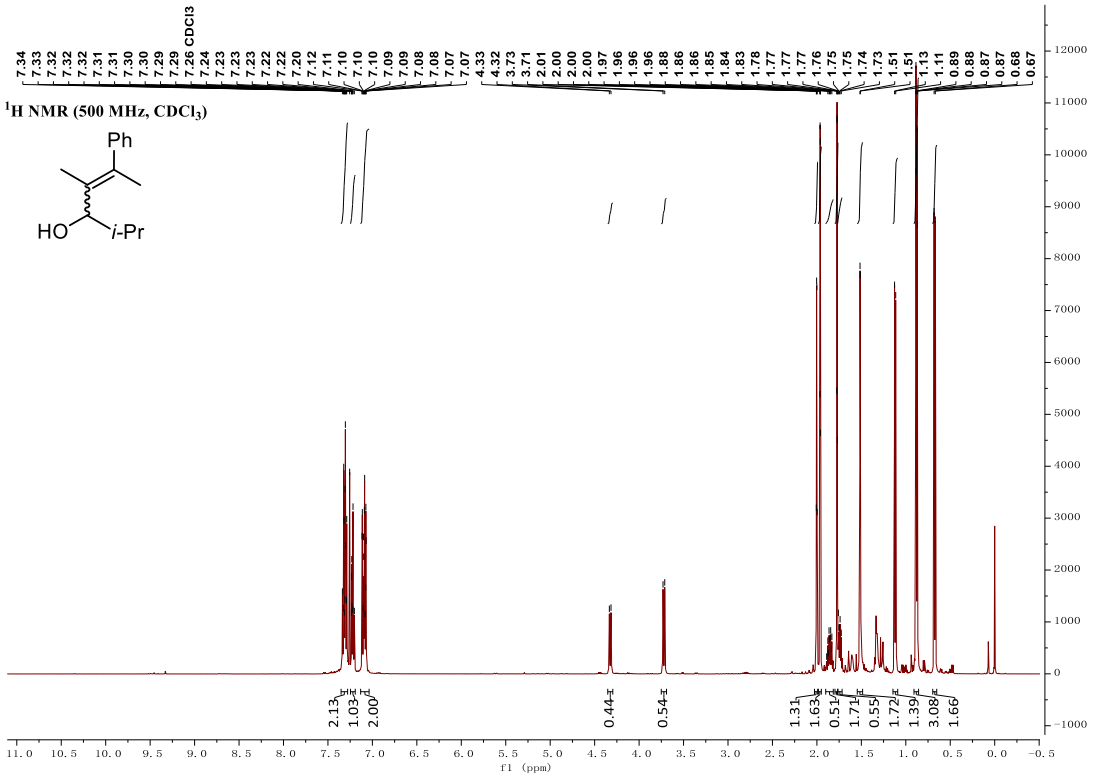


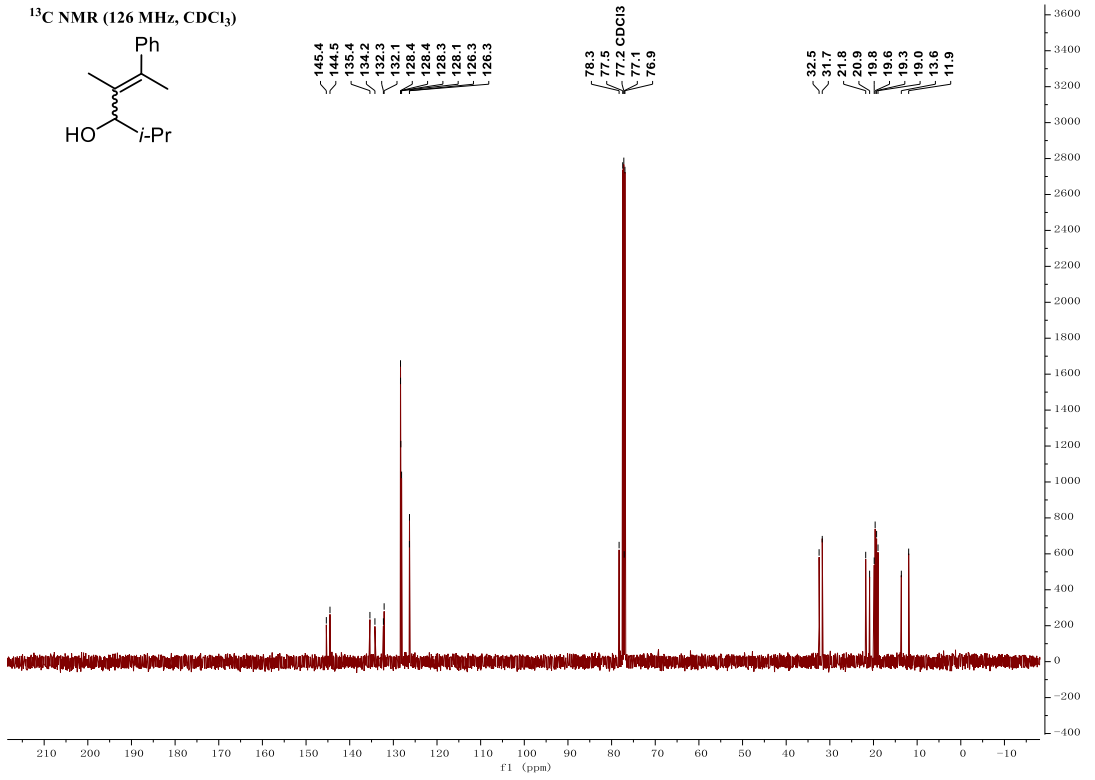
Compound S48



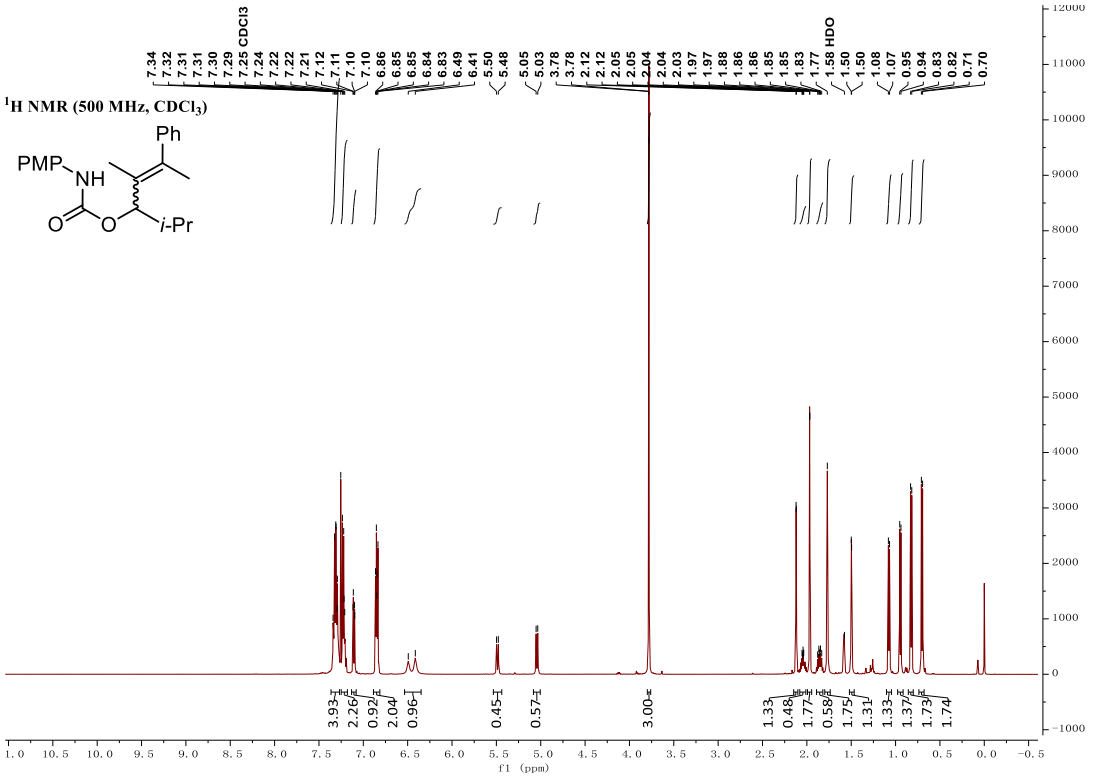


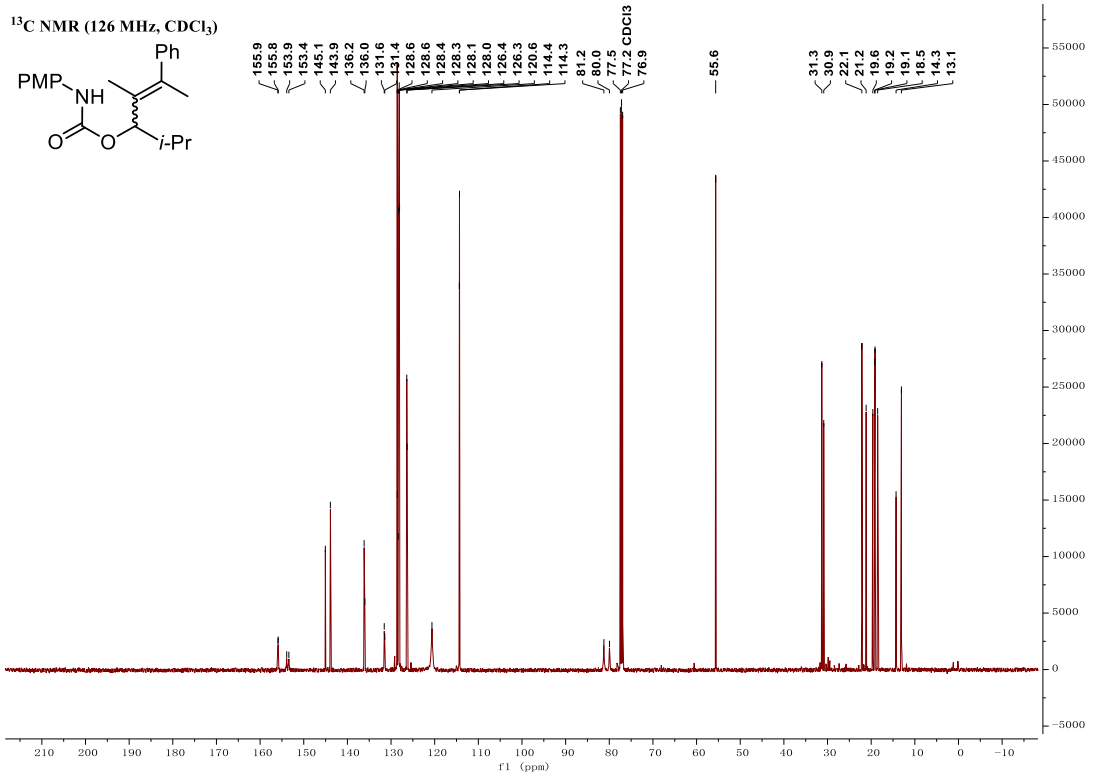
Compound S49



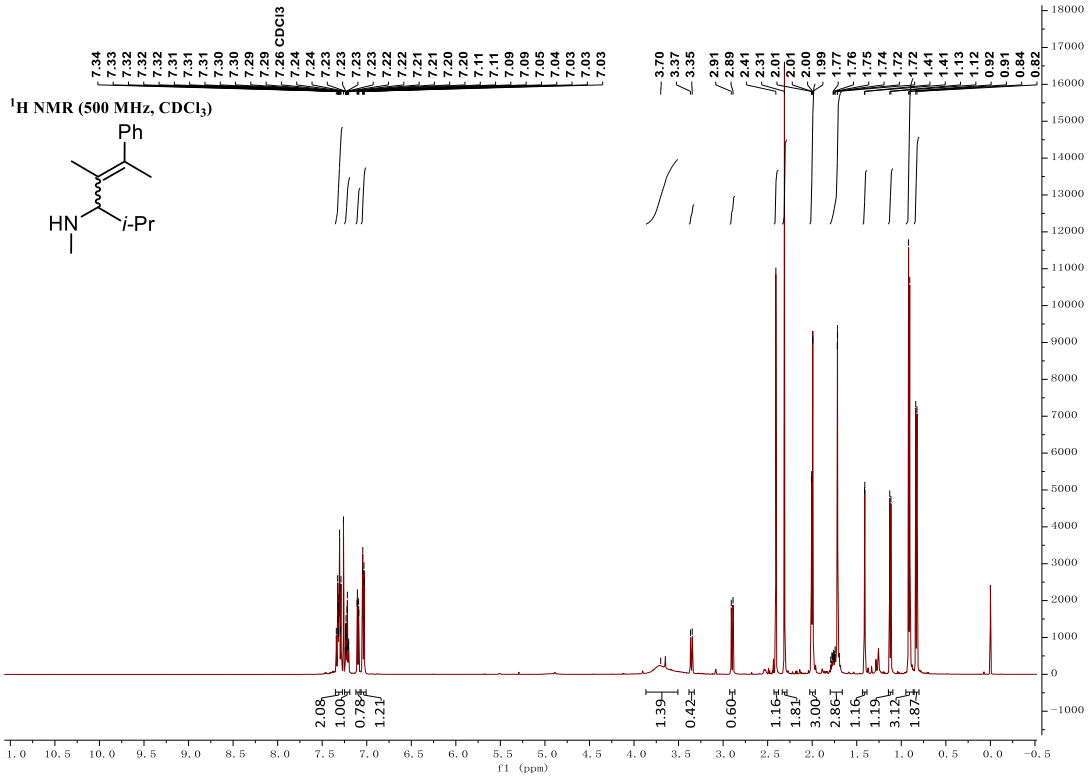


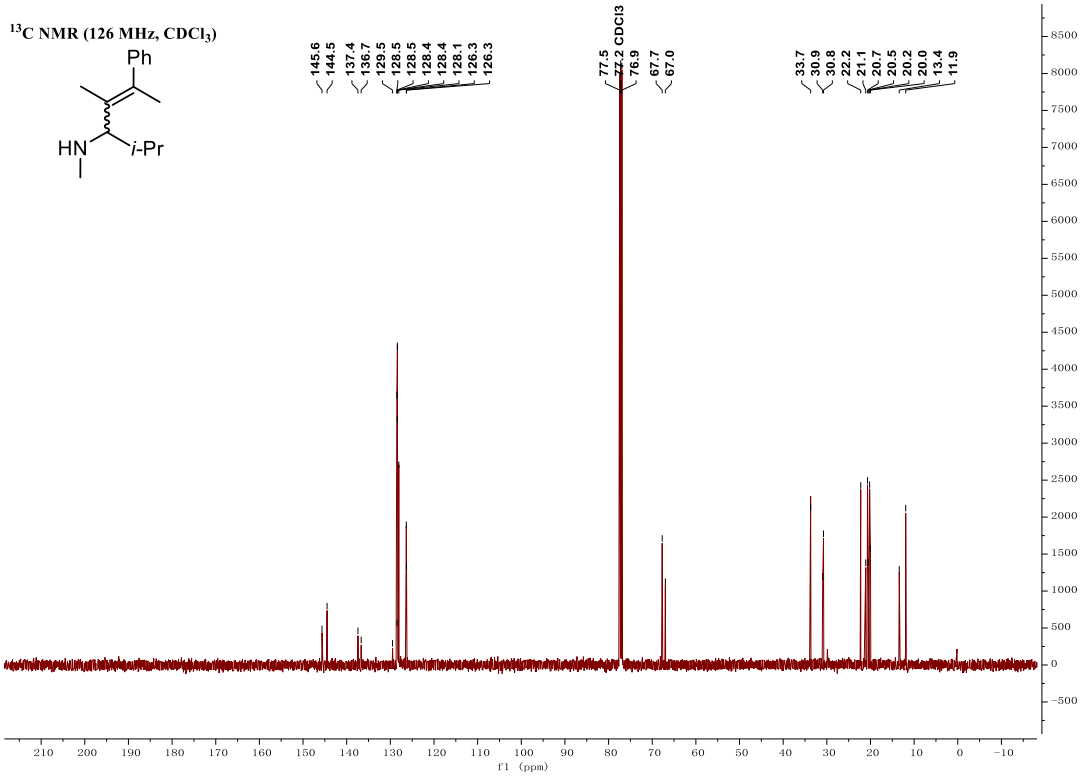
Compound S50



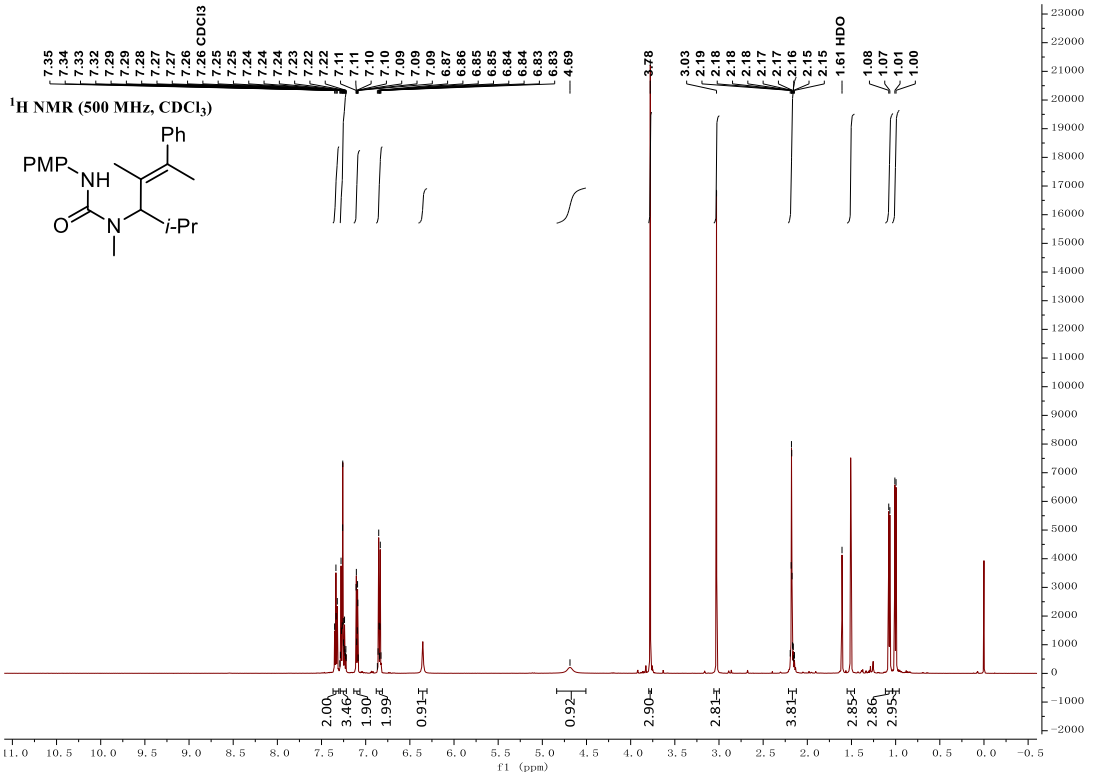


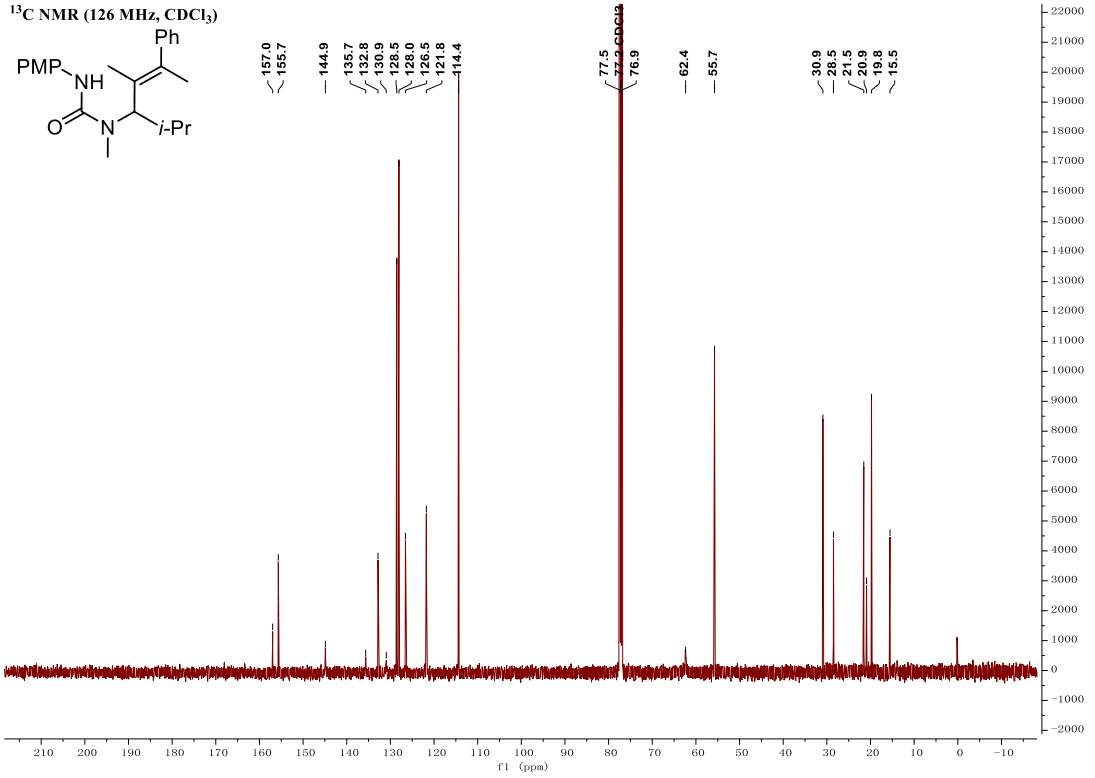
Compound S51



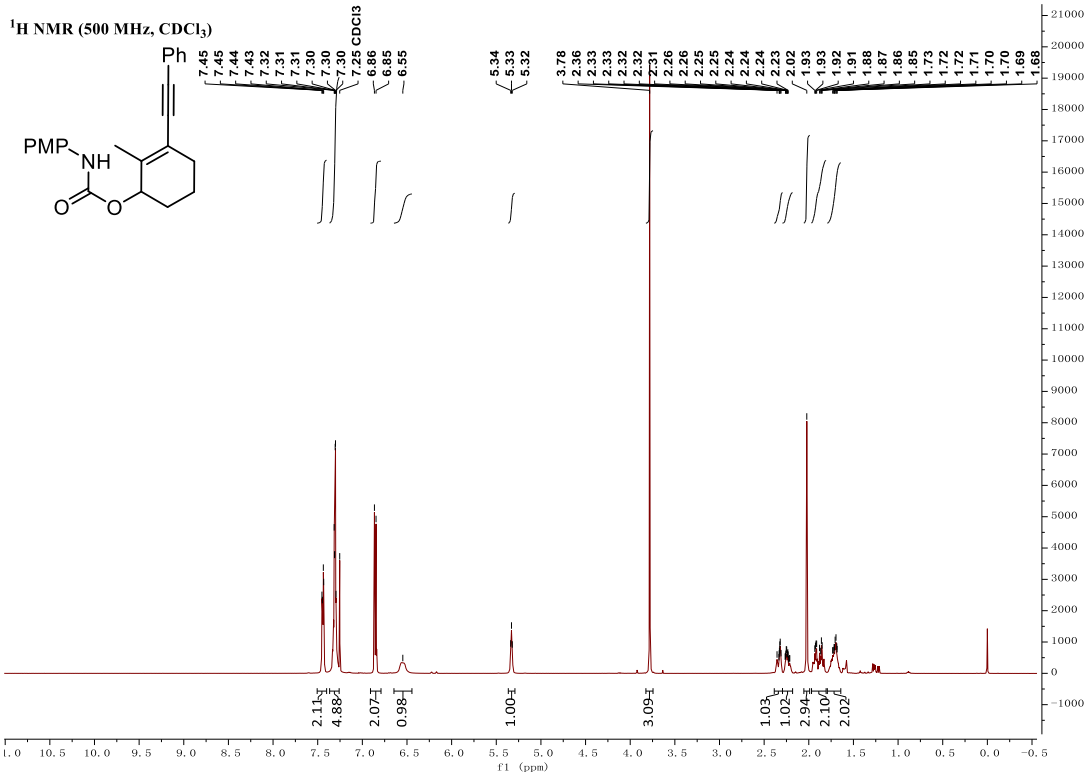


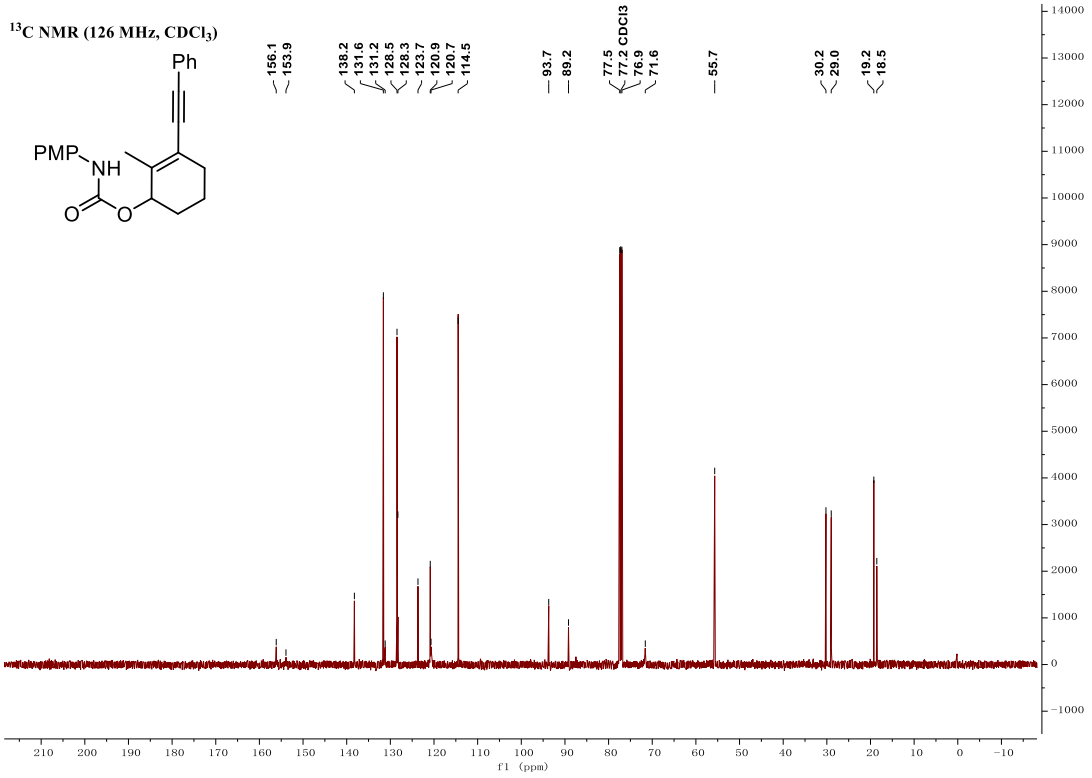
Compound S52



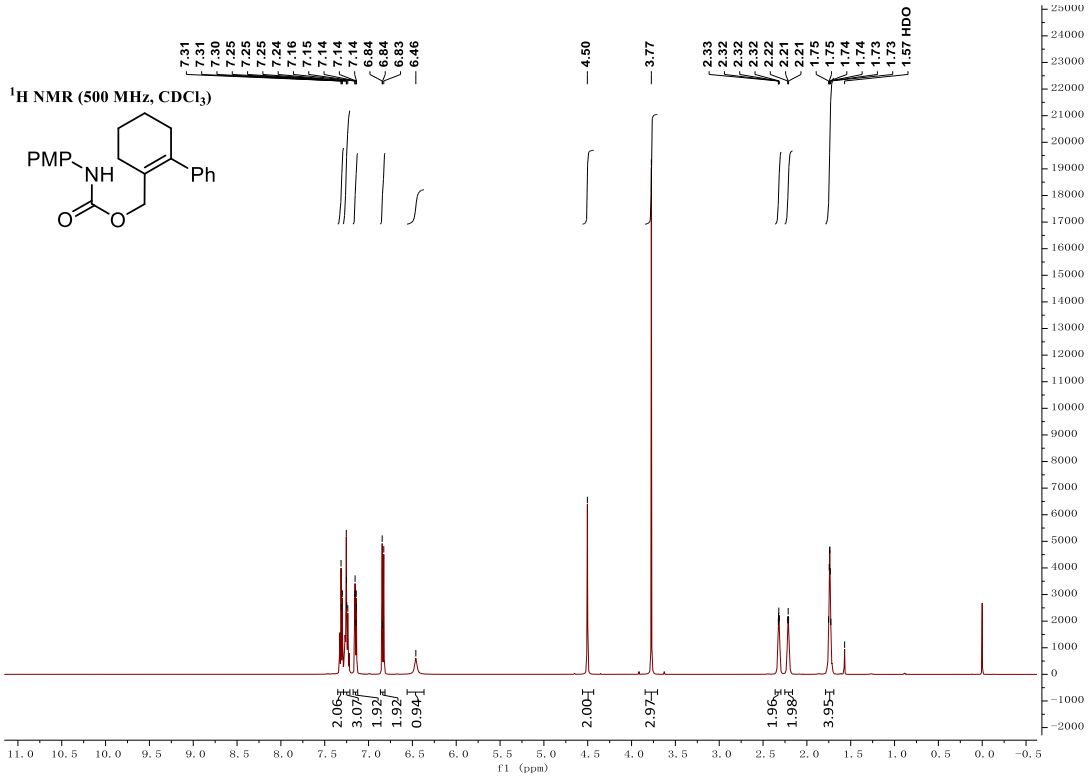


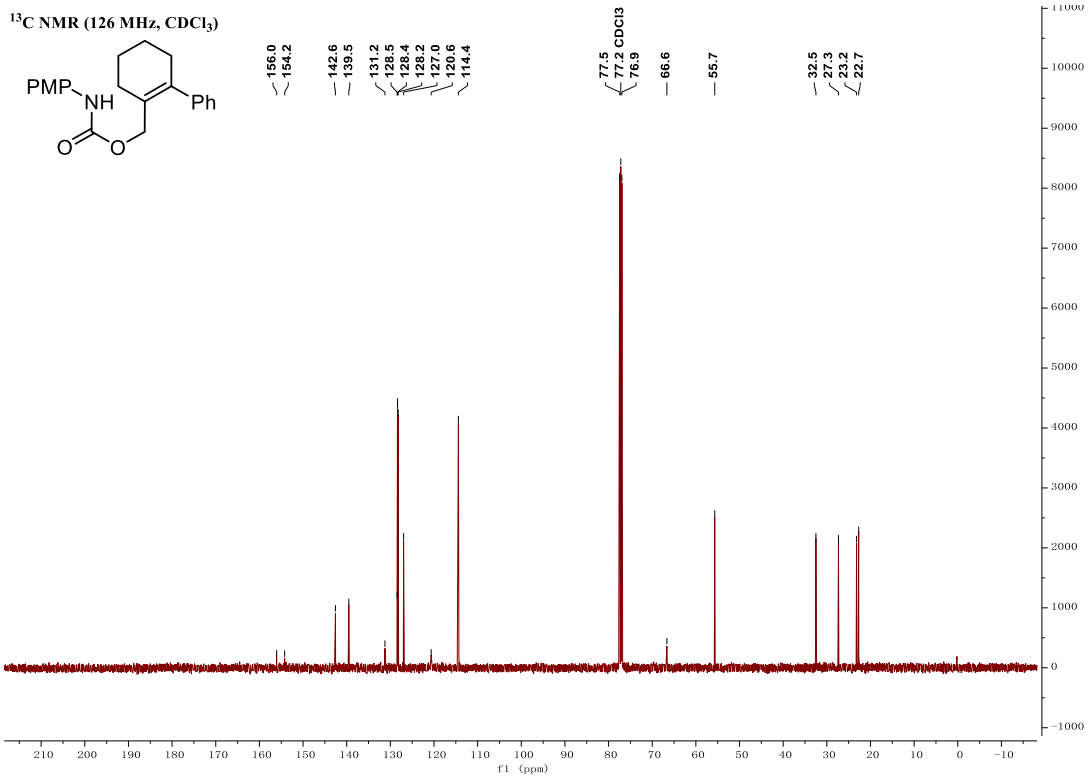
Compound S55



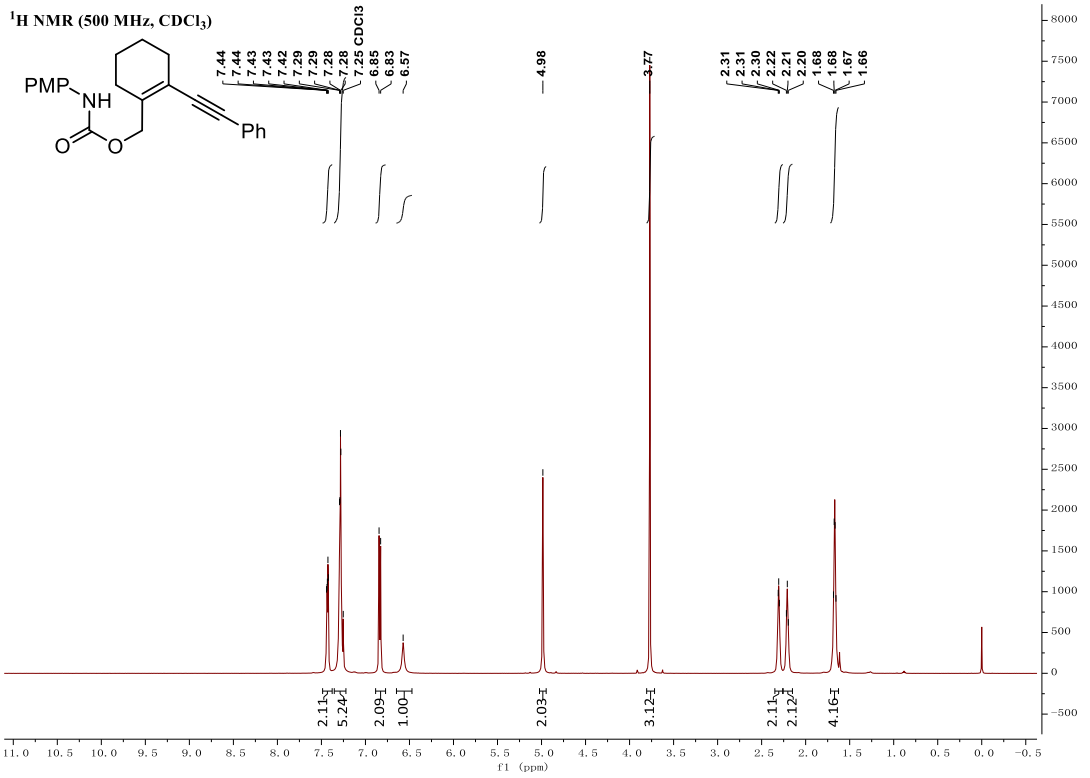


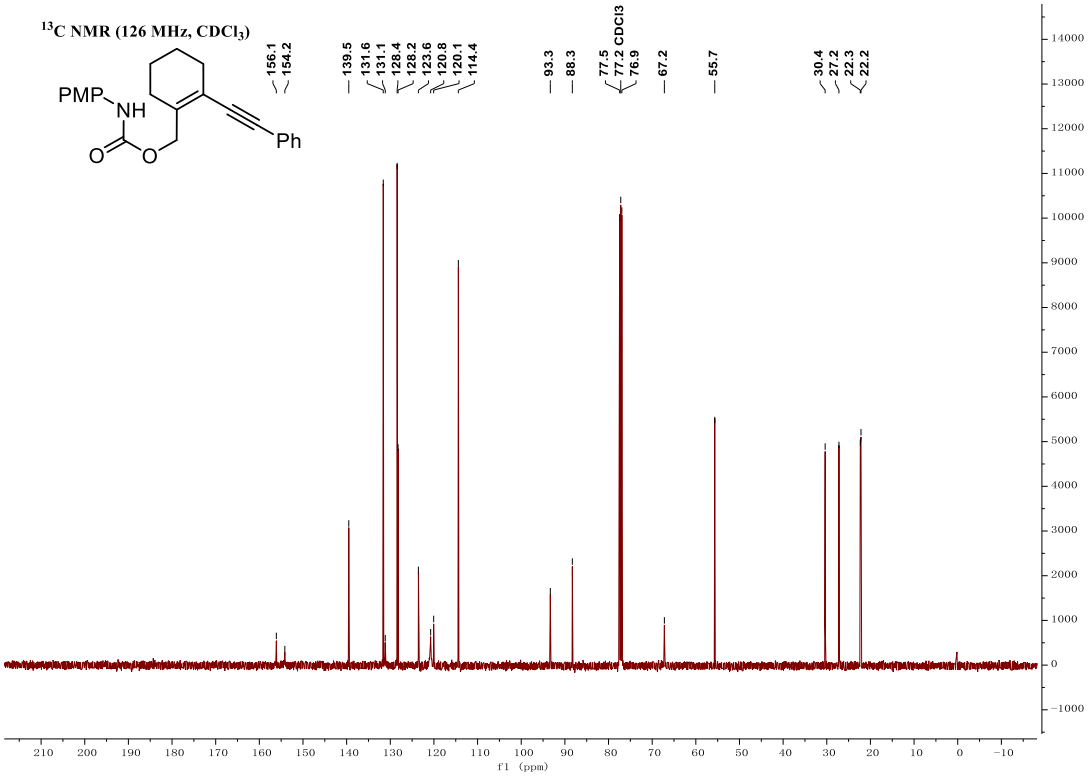
Compound S56



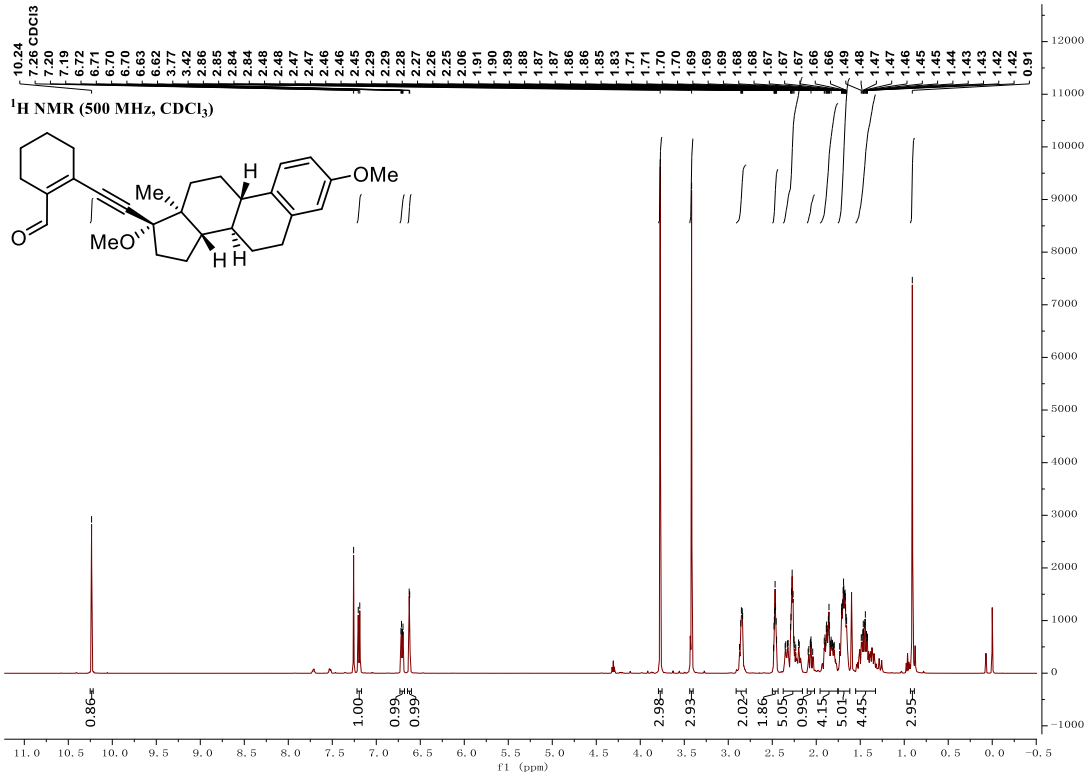


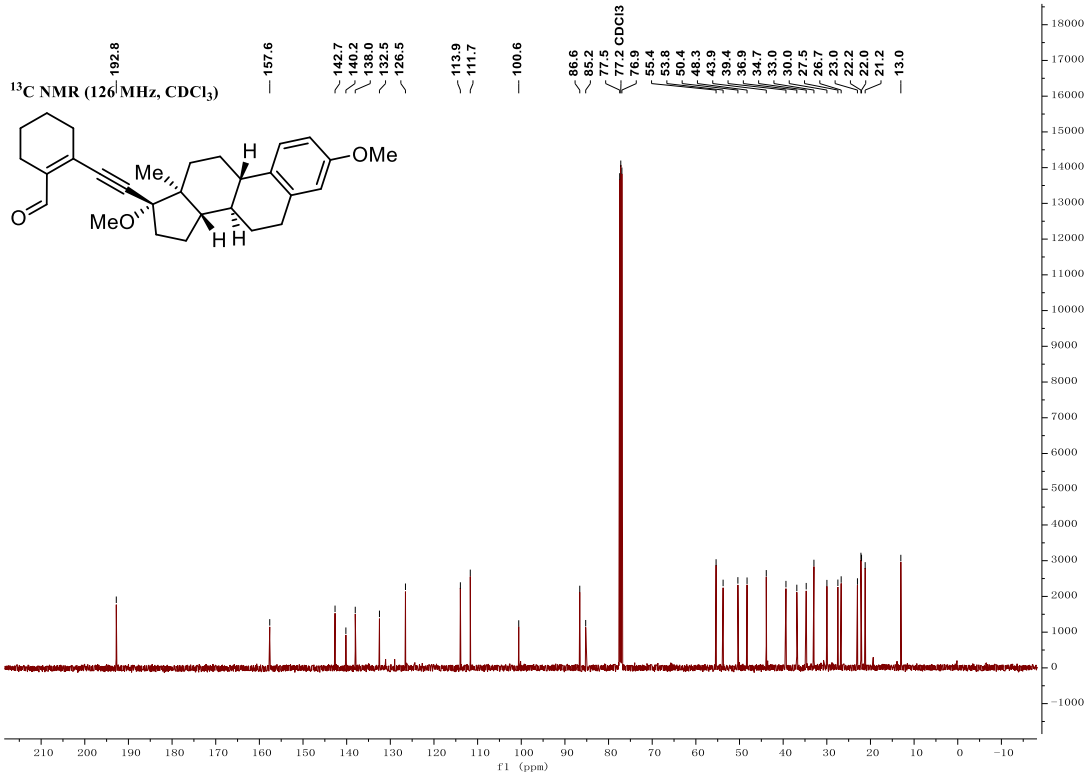
Compound S58



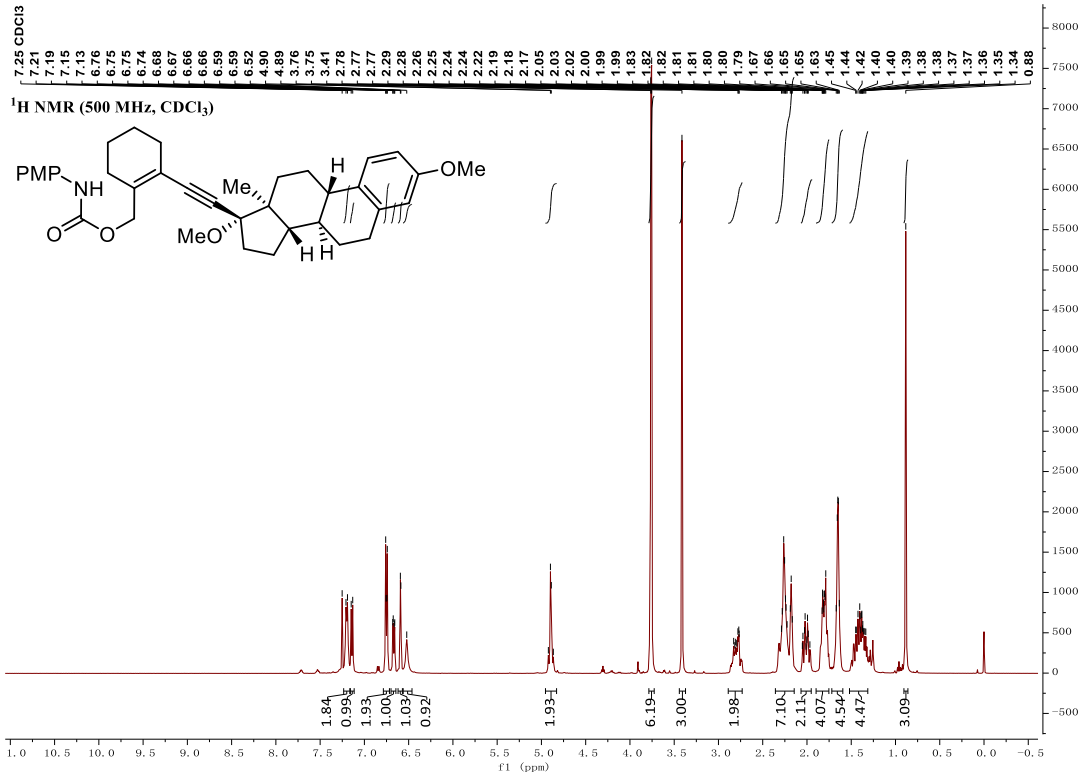


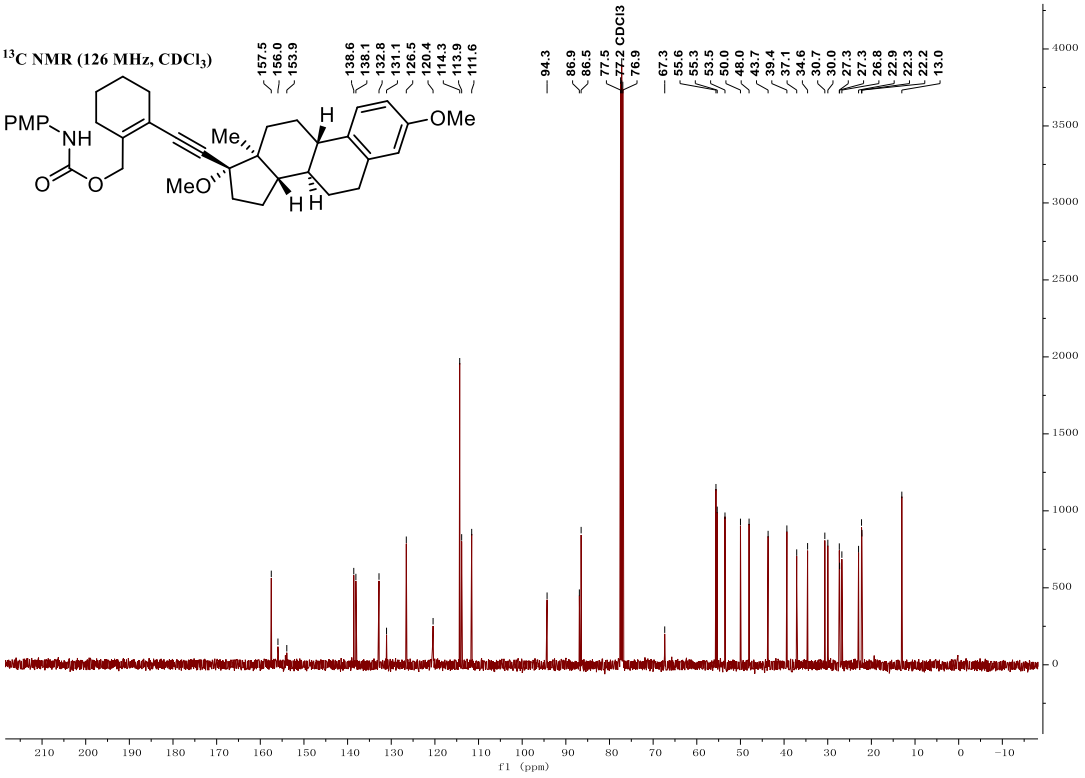
Compound S59



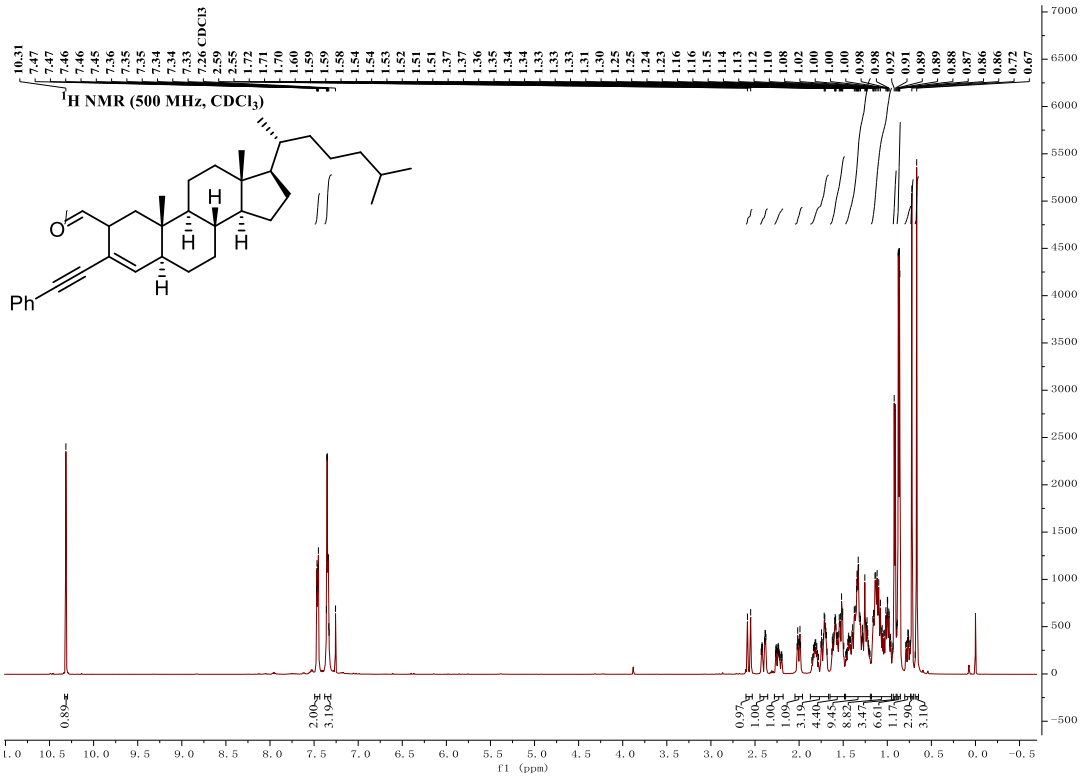


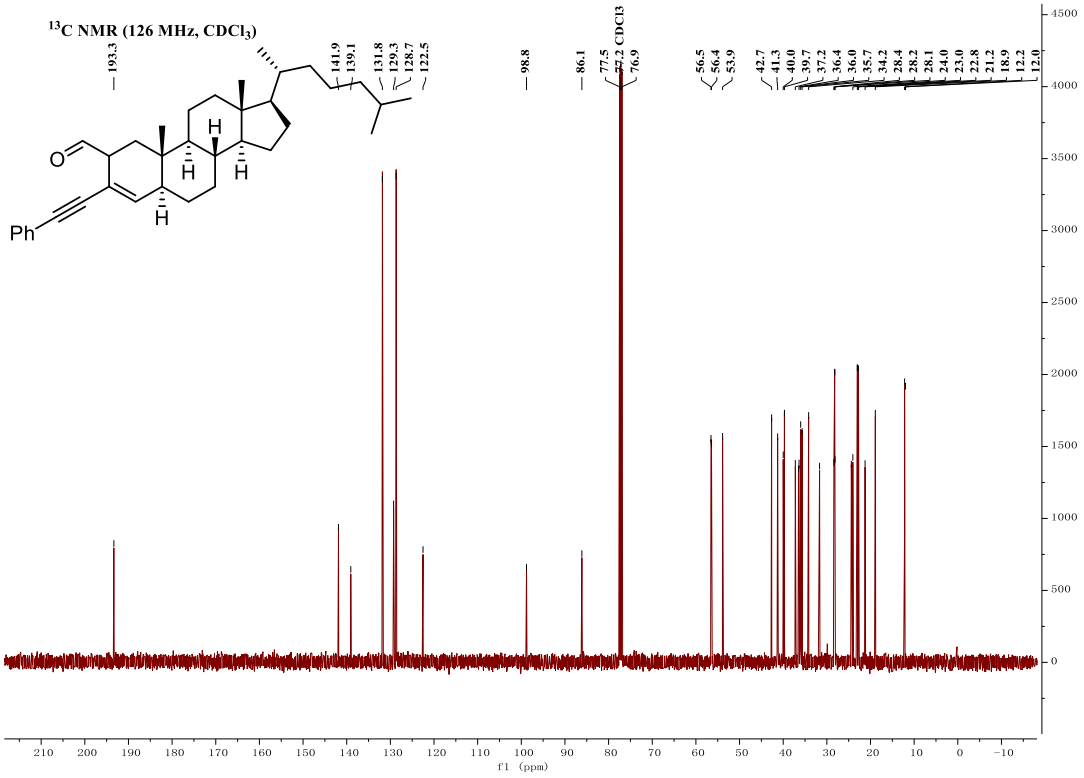
Compound S61



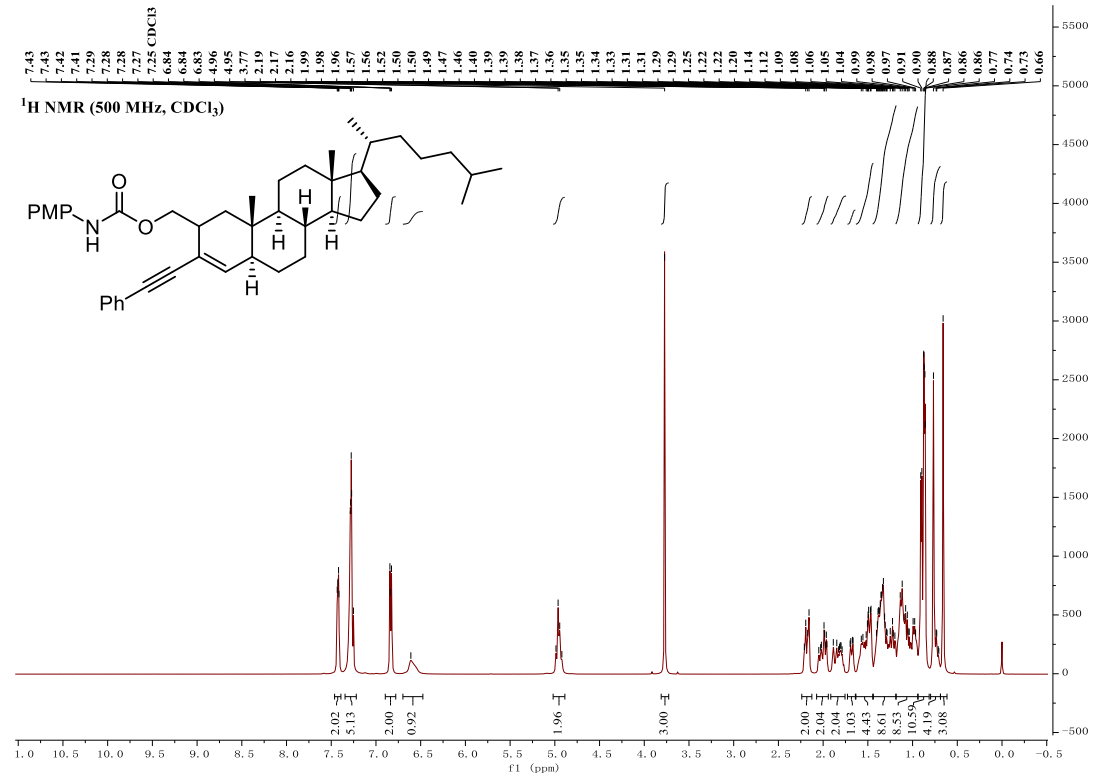


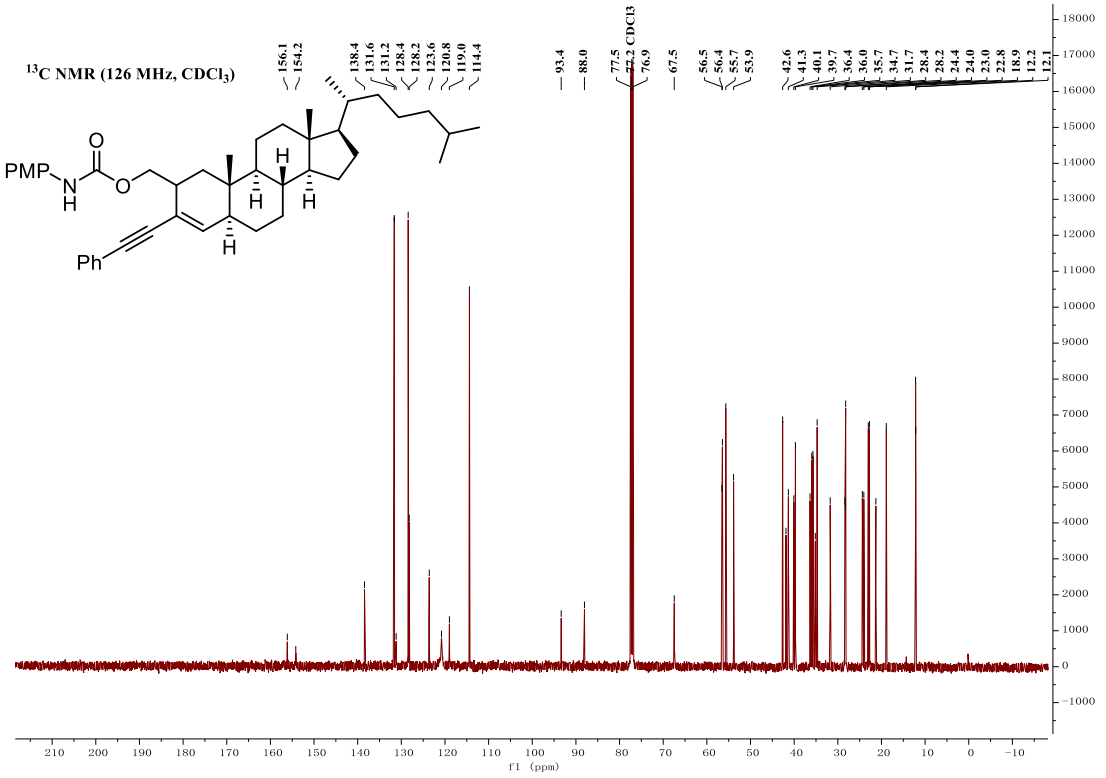
Compound S62





Compound S64





Compound S66