Supporting Information for

Synthesis of 4*H*-1,3-benzoxazines via Metal- and Oxidizing Reagent-Free Aromatic C–H Oxygenation

Fan Xu, Xiang-Yang Qian, Yan-Jie Li and Hai-Chao Xu*

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1. General Information

Anhydrous potassium phosphate and tetraethylammonium hexafluorophosphate were purchased from Aldrich. Anhydrous dichloromethane, acetonitrile and tetrahydrofuran were obtained by distillation under argon from calcium hydride and sodium/benzophenone, respectively. Trifluoroacetic acid and triethylamine were commercial available and used without further purification. Flash column chromatography was performed with silica gel (230–400 mesh). 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. The electrodes used for the preparative electrolysis were the same as those previously reported.[1]

2. Procedures for the Electrolysis

General procedure for the electrolysis in batch: A 10 mL three-necked round-bottomed flask was charged with the amide substrate (0.2 mmol) and Et_4NPF_6 (0.2 mmol). The flask was equipped with a reflux condenser, a reticulated vitreous carbon (100 PPI) anode (1.2 cm x 1 cm x 1 cm) and a platinum plate (1 cm x 1 cm) cathode, and flushed with argon. Anhydrous CH_3CN (5 mL) and THF (1 mL) were added. The constant current (10 mA) electrolysis was carried out at 80 °C (oil bath temperature). After complete consumption of the starting amide, the reaction mixture was cooled to rt and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired product.

Procedure for reaction scale up: The amide **1** (1.07 g, 3.4 mmol) and Et_4NPF_6 (95 mg, 0.34 mmol) was dissolved in dry MeCN/THF (5:1, 67 mL) and flowed through the electrochemical microreactor (volume = 250 μL) in a flow rate of 0.3 mL/min (Figure S1). A constant current of 50 mA was employed. The solution was concentrated under reduced pressure on a rotary evaporator. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product **2**.

Parameters of the flow reactor: The anode and cathode are held apart by a fluorinated ethylene propylene (FEP) foil of 250 μm thick. A rectangular reaction channel (total length: 313 mm, width: 3.2 mm) is cut in the FEP foil to give an overall channel volume of 250 μL. The whole device is held together by steel screws and wing nuts.

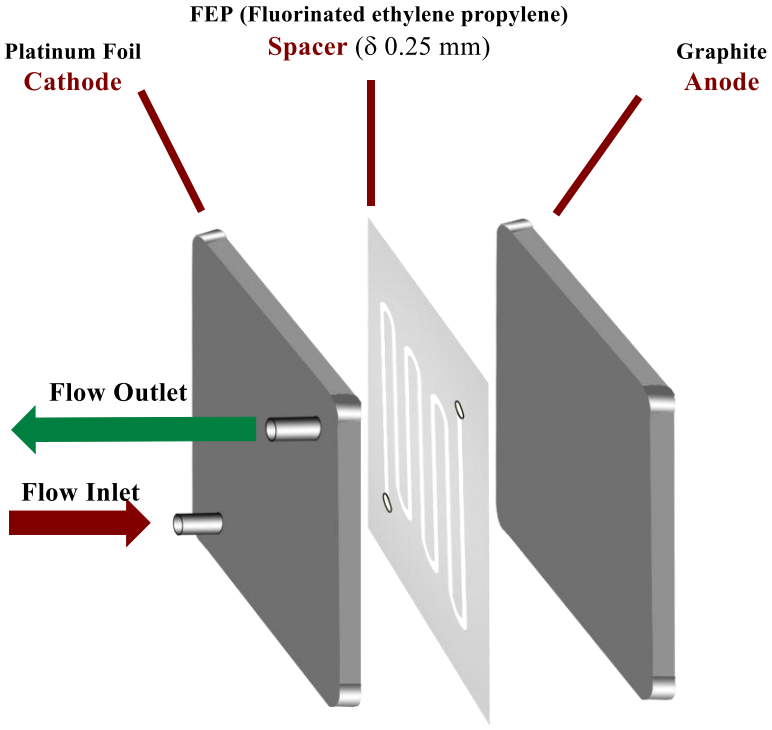
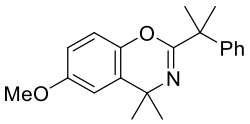
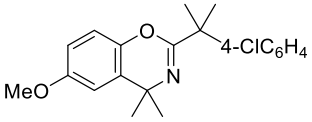


Figure S1. Design of the microreactor.

3. Characterization Data for Electrolysis Products

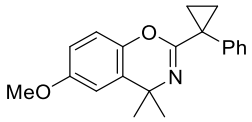


6-Methoxy-4,4-dimethyl-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3]oxazine (2). The title compound contained a regioisomer in a ratio of 15.7:1. Colorless oil; Yield = 63% (40.0 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.24–7.19 (m, 2H), 7.14–7.09 (m, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.59–6.54 (m, 2H), 3.68 (s, 3H), 1.51 (s, 6H), 1.45 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 156.2, 146.5, 142.7, 129.8, 128.3, 126.3, 125.8, 116.0, 112.6, 110.4, 55.8, 52.8, 44.5, 32.3, 27.4. IR (neat, cm^{-1}): 3059, 2972, 1682, 1497, 1092, 699. ESI HRMS *m/z* $(M+H)^+$ calcd 310.1802, obsd 310.1810.

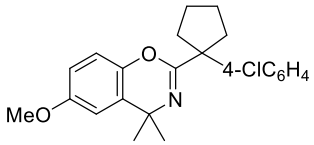


2-(2-(4-Chlorophenyl)propan-2-yl)-6-methoxy-4,4-dimethyl-4*H*-benzo[*e*][1,3] oxazine (3). The title compound contained a regioisomer in a ratio of 13:1. Colorless oil; Yield = 65% (45.3 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.27–7.22 (m, 2H), 6.72 (t, *J* = 1.7 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 2H), 3.76 (s, 3H), 1.57 (s, 6H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.3, 145.0, 142.6, 132.1, 129.7, 128.4, 127.3, 115.9, 112.7, 110.5, 55.8, 52.9, 44.2, 32.3, 27.3. IR (neat, cm^{-1}): 2972, 2929, 1682, 1495, 827. ESI HRMS *m/z* $(M+H)^+$ calcd 344.1412,

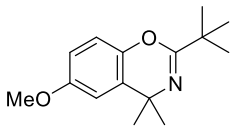
obsd 344.1421[$C_{20}H_{23}{}^{35}ClNO_2$]$^+$.



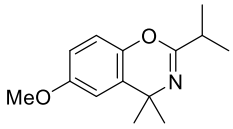
6-Methoxy-4,4-dimethyl-2-(1-phenylcyclopropyl)-4*H*-benzo[*e*][1,3]oxazine (4). Colorless oil; Yield = 69% (42.3 mg); Current = 5.2 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.31–7.26 (m, 2H), 7.23–7.19 (m, 1H), 6.71–6.68 (m, 2H), 6.65 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.76 (s, 3H), 1.51–1.47 (m, 2H), 1.45 (s, 6H), 1.15–1.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 155.8, 142.6, 141.2, 129.7, 129.1, 128.2, 126.6, 116.0, 112.6, 110.4, 55.8, 52.9, 32.2, 28.9, 14.5. IR (neat, cm^{-1}): 2963, 1646, 1507, 1076, 803. ESI HRMS *m/z* (M+Na)$^+$ calcd 330.1465, obsd 330.1479.



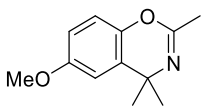
2-(1-(4-Chlorophenyl)cyclopentyl)-6-methoxy-4,4-dimethyl-4*H*-benzo[*e*][1,3] oxazine (5). The title compound contained a regioisomer in a ratio of 11.5:1. Light yellow oil; Yield = 66% (43.4 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.19–7.15 (m, 2H), 6.62–6.55 (m, 3H), 3.68 (s, 3H), 2.64–2.56 (m, 2H), 1.83–1.73 (m, 2H), 1.72–1.61 (m, 4H), 1.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 156.0, 143.7, 142.7, 132.1, 129.5, 128.3, 128.2, 115.9, 112.6, 110.5, 56.6, 55.8, 52.9, 36.3, 32.2, 23.5. IR (neat, cm^{-1}): 2969, 2872, 1682, 1495, 818. ESI HRMS *m/z* (M+H)$^+$ calcd 370.1568, obsd 370.1576 [$C_{22}H_{25}{}^{35}ClNO_2$]$^+$.



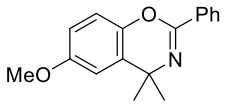
2-(*tert*-Butyl)-6-methoxy-4,4-dimethyl-4*H*-benzo[*e*][1,3]oxazine (6). The title compound contained a regioisomer in a ratio of 6.7:1. Colorless oil; Yield = 43% (21.3 mg); Current = 5.2 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79–6.72 (m, 1H), 6.67–6.59 (m, 2H), 3.71 (s, 3H), 1.37 (s, 6H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 156.2, 142.9, 130.0, 115.8, 112.6, 110.5, 55.8, 52.4, 36.8, 32.2, 27.7. IR (neat, cm^{-1}): 2970, 1683, 1425, 805. ESI HRMS *m/z* (M+H)$^+$ calcd 248.1645, obsd 248.1653.



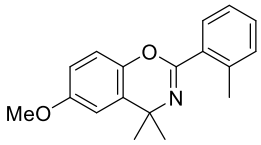
2-Isopropyl-6-methoxy-4,4-dimethyl-4*H*-benzo[*e*][1,3]oxazine (7). The title compound contained a regioisomer in a ratio of 9.4:1. Colorless oil; Yield = 66% (31.9 mg); Current = 4.3 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77–6.73 (m, 1H), 6.66–6.62 (m, 2H), 3.71 (s, 3H), 2.54–2.44 (m, 1H), 1.39 (s, 6H), 1.13 (d, *J* = 6.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 156.3, 142.5, 129.7, 115.9, 112.7, 110.6, 55.8, 52.3, 34.0, 32.4, 19.7. IR (neat, cm^{-1}): 2968, 1653, 1424, 1048, 809. ESI HRMS *m/z* (M+H)$^+$ calcd 234.1489, obsd 234.1488.



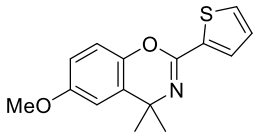
6-Methoxy-2,4,4-trimethyl-4*H*-benzo[*e*][1,3]oxazine (8). The title compound contained a regioisomer in a ratio of 9.4:1. Colorless oil; Yield = 44% (18.0 mg); Current = 4.4 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84–6.80 (m, 1H), 6.75–6.71 (m, 2H), 3.80 (s, 3H), 2.09 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 152.1, 142.1, 129.2, 115.9, 112.9, 110.7, 55.8, 52.6, 32.6, 21.1. IR (neat, cm^{-1}): 2931, 1654, 1509, 1212, 1046. ESI HRMS *m/z* $(M+H)^+$ calcd 206.1176, obsd 206.1180.



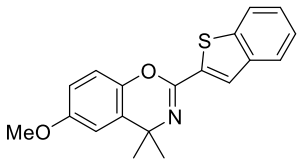
6-Methoxy-4,4-dimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (9). The title compound contained a regioisomer in a ratio of 4.4:1. Colorless oil; Yield = 66% (37.4 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14–8.08 (m, 2H), 7.52–7.42 (m, 3H), 7.02 (dd, *J* = 8.5, 0.7 Hz, 1H), 6.83–6.78 (m, 2H), 3.84 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 150.4, 142.4, 132.9, 130.8, 129.7, 128.3, 127.6, 116.3, 112.9, 110.7, 55.8, 53.2, 32.6. IR (neat, cm^{-1}): 3063, 2970, 2929, 1667, 1297, 695. ESI HRMS *m/z* $(M+H)^+$ calcd 268.1332, obsd 268.1336.



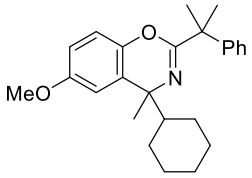
6-Methoxy-4,4-dimethyl-2-(*o*-tolyl)-4*H*-benzo[*e*][1,3]oxazine (10). The title compound contained a regioisomer in a ratio of 9.1:1. Colorless oil; Yield = 68% (38.6 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 (td, *J* = 7.4, 1.5 Hz, 1H), 7.26–7.21 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.80 (d, *J* = 2.9 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.81 (s, 3H), 2.51 (s, 3H), 1.61 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 152.5, 142.4, 137.3, 133.3, 131.0, 129.9, 129.5, 129.1, 125.8, 116.2, 112.9, 110.6, 55.8, 53.5, 32.5, 20.7. IR (neat, cm^{-1}): 3068, 2972, 1660, 1495, 700. ESI HRMS *m/z* $(M+H)^+$ calcd 282.1489, obsd 282.1495.



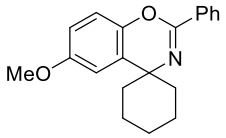
6-Methoxy-4,4-dimethyl-2-(thiophen-2-yl)-4*H*-benzo[*e*][1,3]oxazine (11). The title compound contained a regioisomer in a ratio of 5.1:1. Colorless oil; Yield = 79% (45.8 mg); Current = 6.1 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.32 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.91–6.86 (m, 1H), 6.71–6.65 (m, 2H), 3.73 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 147.2, 142.1, 136.9, 129.7, 129.0, 128.7, 127.4, 116.2, 112.9, 110.7, 55.8, 53.3, 32.4. IR (neat, cm^{-1}): 3074, 2970, 1663, 1496, 710. ESI HRMS *m/z* $(M+H)^+$ calcd 274.0896, obsd 274.0905.



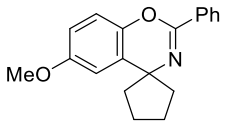
2-(Benzo[*b*]thiophen-2-yl)-6-methoxy-4,4-dimethyl-4*H*-benzo[*e*][1,3]oxazine (12). The title compound contained a regioisomer in a ratio of 4.7:1. Light yellow solid; Yield = 62% (40.5 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86–7.76 (m, 2H), 7.40–7.29 (m, 2H), 7.02–6.96 (m, 1H), 6.80–6.74 (m, 1H), 3.80 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 147.4, 142.0, 141.1, 139.5, 137.1, 125.8, 125.5, 124.7, 124.6, 122.5, 116.2, 113.0, 110.8, 55.8, 53.6, 32.5. IR (neat, cm^{-1}): 3057, 2971, 2926, 1662, 1497, 747. ESI HRMS *m/z* $(M+H)^+$ calcd 324.1053, obsd 324.1046.



4-Cyclohexyl-6-methoxy-4-methyl-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3] oxazine (13). The title compound contained a regioisomer in a ratio of 8.1:1. Colorless oil; Yield = 65% (49.0 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.24–7.17 (m, 2H), 7.15–7.06 (m, 1H), 6.57–6.52 (m, 3H), 3.67 (s, 3H), 1.81–1.67 (m, 2H), 1.61–1.51 (m, 6H), 1.50 (s, 3H), 1.42 (s, 3H), 1.23–0.92 (m, 5H), 0.90–0.78 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 155.9, 146.5, 143.6, 128.2, 128.1, 126.2, 126.0, 115.6, 112.2, 111.1, 58.0, 55.7, 49.9, 44.8, 28.8, 28.0, 27.1, 26.9, 26.7, 26.3. IR (neat, cm^{-1}): 2929, 2850, 1686, 1495, 1132, 765. ESI HRMS *m/z* $(M+H)^+$ calcd 378.2428, obsd 378.2441.

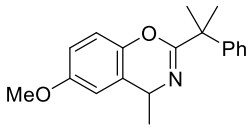


6-Methoxy-2-phenylspiro[benzo[*e*][1,3]oxazine-4,1'-cyclohexane] (14). The title compound contained a regioisomer in a ratio of 4.9:1. Colorless oil; Yield = 61% (37.1 mg); Current = 5.2 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.01 (m, 2H), 7.43–7.31 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.68 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.72 (s, 3H), 2.13–2.01 (m, 2H), 1.82–1.67 (m, 5H), 1.53–1.44 (m, 2H), 1.36–1.25 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 148.8, 143.0, 133.1, 130.7, 130.4, 128.2, 127.6, 116.1, 112.6, 110.4, 55.8, 54.9, 40.6, 26.4, 21.5. IR (neat, cm^{-1}): 3059, 2932, 1672, 1497, 694. ESI HRMS *m/z* $(M+H)^+$ calcd 308.1645, obsd 308.1655.

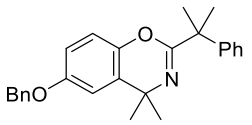


6-Methoxy-2-phenylspiro[benzo[*e*][1,3]oxazine-4,1'-cyclopentane] (15). The title compound contained a regioisomer in a ratio of 6.7:1. Colorless oil; Yield = 57% (34.1 mg); Current = 4.2 *F*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.01 (m, 2H), 7.47–7.35 (m,

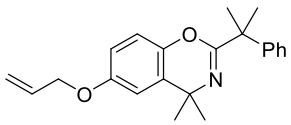
3H), 7.00–6.93 (m, 1H), 6.78–6.72 (m, 2H), 3.79 (s, 3H), 2.18–1.97 (m, 6H), 1.92–1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 149.0, 143.2, 133.0, 130.7, 128.6, 128.2, 127.5, 116.0, 112.8, 110.6, 63.4, 55.8, 45.2, 25.0. IR (neat, cm^{-1}): 2955, 2852, 1670, 1498, 1198, 694. ESI HRMS *m/z* $(M+H)^+$ calcd 294.1489, obsd 294.1497.



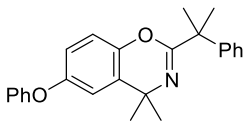
6-Methoxy-4-methyl-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3]oxazine (16). Colorless oil; Yield = 31% (18.2 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.34–7.28 (m, 2H), 7.23–7.18 (m, 1H), 6.66–6.65 (m, 2H), 6.60–6.57 (m, 1H), 4.68 (q, *J* = 6.9 Hz, 1H), 3.75 (s, 3H), 1.60 (s, 3H), 1.60 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 156.4, 146.2, 143.2, 128.4, 126.4, 125.8, 125.7, 116.2, 113.3, 110.6, 55.8, 50.6, 44.8, 27.6, 27.0, 25.5. IR (neat, cm^{-1}): 3254, 2970, 2929, 1635, 1506, 1205, 700. ESI HRMS *m/z* $(M+H)^+$ calcd 296.1645, obsd 196.1649.



6-(Benzyloxy)-4,4-dimethyl-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3]oxazine (17). The title compound contained a regioisomer in a ratio of 14.2:1. Colorless oil; Yield = 65% (50.1 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.26 (m, 6H), 7.25–7.18 (m, 3H), 7.14–7.08 (m, 1H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.62 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.90 (s, 2H), 1.51 (s, 6H), 1.43 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.4, 146.5, 142.9, 137.1, 129.8, 128.7, 128.3, 128.1, 127.7, 126.3, 125.8, 116.0, 113.6, 111.7, 70.7, 52.8, 44.5, 32.3, 27.4. IR (neat, cm^{-1}): 3030, 2966, 1682, 1495, 1091, 806. ESI HRMS *m/z* $(M+H)^+$ calcd 386.2115, obsd 386.2123.

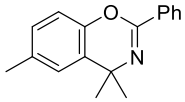


6-(Allyloxy)-4,4-dimethyl-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3]oxazine (18). The title compound contained a regioisomer in a ratio of 14.8:1. Colorless oil; Yield = 53% (35.9 mg); Current = 7.2 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.25–7.18 (m, 2H), 7.14–7.10 (m, 1H), 6.71–6.63 (m, 1H), 6.60–6.51 (m, 2H), 5.95 (m, 1H), 5.32 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.40 (dt, *J* = 5.4, 1.5 Hz, 2H), 1.51 (s, 6H), 1.44 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.2, 146.5, 142.8, 133.5, 129.7, 128.3, 126.3, 125.8, 117.8, 115.9, 113.5, 111.5, 69.5, 52.8, 44.5, 32.3, 27.4. IR (neat, cm^{-1}): 2971, 2927, 1683, 1195, 1076. ESI HRMS *m/z* $(M+H)^+$ calcd 336.1958, obsd 336.1968.

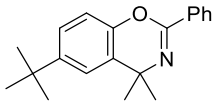


4,4-Dimethyl-6-phenoxy-2-(2-phenylpropan-2-yl)-4*H*-benzo[*e*][1,3]oxazine (19).

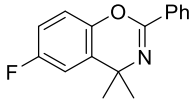
Colorless oil; Yield = 80% (61.5 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.25–7.19 (m, 4H), 7.14–7.10 (m, 1H), 7.01–6.95 (m, 1H), 6.88–6.84 (m, 2H), 6.82 (d, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 1.52 (s, 6H), 1.42 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 158.0, 152.9, 146.3, 144.6, 130.1, 129.8, 128.4, 126.4, 125.8, 122.9, 118.6, 118.0, 116.4, 116.2, 52.8, 44.5, 32.4, 27.3. IR (neat, cm^{-1}): 3060, 2970, 2929, 1685, 1588, 1485, 696. ESI HRMS *m/z* $(M+H)^+$ calcd 372.1958, obsd 372.1968.



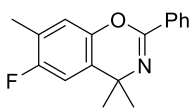
4,4,6-Trimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (20). The title compound contained a regioisomer in a ratio of 1:1. Colorless oil; Yield = 71% (35.6 mg); Current = 5.0 *F*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.05 (m, 4H), 7.60–7.41 (m, 6H), 7.21–7.03 (m, 5H), 6.98 (d, *J* = 8.1 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 1.64 (s, 6H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (2C), 146.5, 146.1, 134.2, 133.0, 132.9, 130.9, 130.8, 129.1, 128.4 (2C), 128.3 (2C), 127.6, 125.7, 124.8, 124.1, 122.8, 115.3, 53.0, 52.8, 32.7, 32.6, 21.2, 15.8. IR (neat, cm^{-1}): 3059, 2970, 1668, 1499, 694. ESI HRMS *m/z* $(M+H)^+$ calcd 252.1383, obsd 252.1392.



6-(*tert*-Butyl)-4,4-dimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (21). The title compound was obtained as a mixture of regioisomers in ratio of 7.7:1. Colorless oil; Yield = 81% (47.4 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.05 (m, 2H), 7.42–7.33 (m, 3H), 7.17–7.13 (m, 1H), 7.10–7.04 (m, 1H), 7.01–6.96 (m, 1H), 1.52 (s, 6H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 146.9, 136.5, 133.1, 130.7, 128.8, 128.4, 127.6, 125.3, 124.1, 123.5, 52.8, 34.9, 33.0, 30.2. IR (neat, cm^{-1}): 3064, 2967, 1676, 694. ESI HRMS *m/z* $(M+H)^+$ calcd 294.1852, obsd 294.1862.

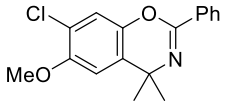


6-Fluoro-4,4-dimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (22). Colorless oil; Yield = 63% (32.8 mg); Current = 6.5 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11–8.04 (m, 2H), 7.51–7.43 (m, 1H), 7.46–7.39 (m, 2H), 7.01 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.95 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.91 (td, *J* = 8.8, 3.0 Hz, 1H), 1.58 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6 (d, $J_{C\text{-}F}$ = 242.1 Hz), 150.2, 144.3 (d, $J_{C\text{-}F}$ = 2.3 Hz), 132.5, 131.0, 130.3 (d, $J_{C\text{-}F}$ = 6.7 Hz), 128.3, 127.6, 116.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 114.6 (d, $J_{C\text{-}F}$ = 23.6 Hz), 111.9 (d, $J_{C\text{-}F}$ = 23.6 Hz), 53.2, 32.5.). ^{19}F NMR (471 MHz, $CDCl_3$) δ −117.8. IR (neat, cm^{-1}): 3064, 2974, 2926, 1672, 1497, 1180, 693. ESI HRMS *m/z* $(M+H)^+$ calcd 256.1132, obsd 256.1142.



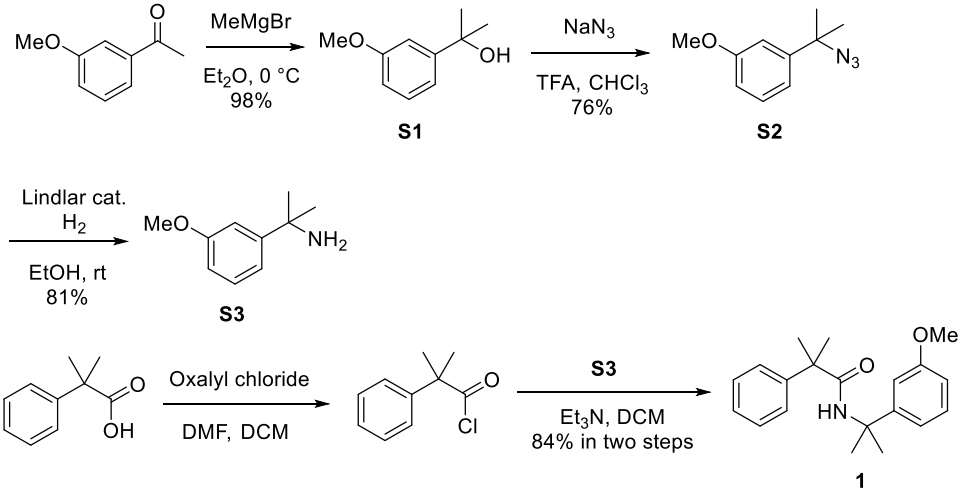
6-Fluoro-4,4,7-trimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (23). The title

compound was obtained as a mixture of regioisomers in ratio of 8.2:1. Colorless oil; Yield = 45% (24.4 mg); Current = 5.2 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.03 (m, 2H), 7.48–7.39 (m, 3H), 6.92–6.84 (m, 2H), 2.26 (d, J = 1.9 Hz, 3H), 1.56 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 241.0 Hz), 150.2, 143.8 (d, $J_{C\text{-}F}$ = 2.2 Hz), 132.6, 130.9, 128.3, 127.6, 127.4 (d, $J_{C\text{-}F}$ = 6.6 Hz), 124.5 (d, $J_{C\text{-}F}$ = 19.5 Hz), 118.0 (d, $J_{C\text{-}F}$ = 4.9 Hz), 111.4 (d, $J_{C\text{-}F}$ = 24.5 Hz), 52.9, 32.6, 14.5 (d, $J_{C\text{-}F}$ = 3.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −117.7 (minor), −122.3 (major). IR (neat, cm^{-1}): 3060, 2971, 1670, 1497, 1065, 694. ESI HRMS *m/z* $(M+H)^+$ calcd 270.1289, obsd 270.1296.



7-Chloro-6-methoxy-4,4-dimethyl-2-phenyl-4*H*-benzo[*e*][1,3]oxazine (24). Colorless oil; Yield = 56% (34.7 mg); Current = 5.8 *F*; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.03 (m, 2H), 7.49–7.39 (m, 3H), 7.12 (s, 1H), 6.77 (s, 1H), 3.90 (s, 3H), 1.59 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 150.0, 142.1, 132.4, 131.0, 128.3, 127.9, 127.6, 121.5, 117.5, 108.8, 56.9, 53.1, 32.5. IR (neat, cm^{-1}): 3066, 2971, 2929, 1668, 1487, 695. ESI HRMS *m/z* $(M+H)^+$ calcd 302.0942, obsd 302.0944 $[C_{17}H_{17}{}^{35}ClNO_2]^+$.

4. Synthesis and Characterization of New Substrates

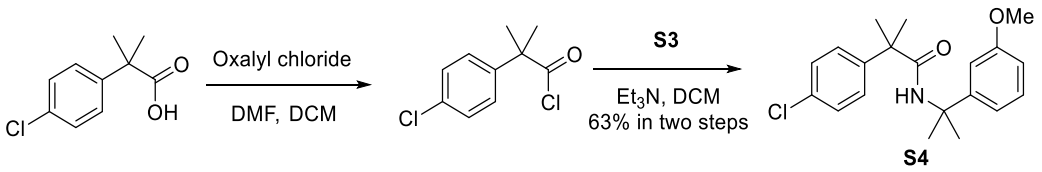


2-(3-Methoxyphenyl)propan-2-ol (S1).[2] To a solution of methylmagnesium bromide (3 M in Et_2O, 44 mL, 1.2 equiv) in dry Et_2O (80 mL) was added a solution of 1-(3-methoxyphenyl)ethan-1-one (16.0 g, 106 mmol, 1 equiv) in Et_2O (20 mL) dropwise at 0 °C. After complete addition, the solution was warmed to rt gradually. Upon complete consumption of ketone (monitored by TLC), saturated NH_4Cl (80 mL) and Et_2O (100 mL) were added. The phases were separated, and the aqueous phase was extracted with Et_2O (80 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 **S1** (17.4 g). Colorless oil; Yield = 98%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.9 Hz, 1H), 7.10–7.01 (m, 2H), 6.78 (dd, J = 8.2, 2.5 Hz, 1H), 3.81 (s, 3H), 1.87 (s, 1H), 1.57 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 151.1, 129.3, 116.9, 111.9, 110.7, 72.6, 55.3, 31.8.

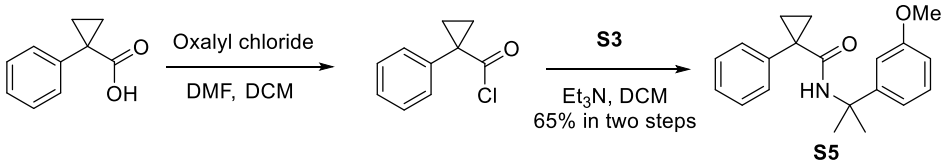
1-(2-Azidopropan-2-yl)-3-methoxybenzene (S2). The title compound was prepared by following a modified procedure in the literature.[3] To a solution of **S1** (5.8 g, 34.9 mmol, 1 equiv) and NaN_3 (5.0 g, 77 mmol, 2.2 equiv) in $CHCl_3$ (180 mL) was added trifluoroacetic acid (14.5 mL, 189 mmol, 5 equiv) at rt. The reaction mixture was stirred at rt until complete consumption of **S1** (monitored by TLC). Saturated aqueous NH_4Cl (80 mL) was added, followed by slow addition of aqueous ammonia (25%) to adjust the pH of the aqueous phase to 7. The phases were separated, and the aqueous phase was extracted with dichloromethane (80 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 **S2** (5.1 g) as colorless oil in 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.04–6.97 (m, 2H), 6.82 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.82 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 146.5, 129.7, 117.6, 112.5, 111.7, 63.8, 55.4, 28.5. IR (neat, cm^{-1}): 2978, 2936, 2101, 1601, 1269, 700. ESI HRMS *m/z* $(M+H)^+$ calcd 192.1131, obsd 192.1128.

2-(3-Methoxyphenyl)propan-2-amine (S3). To a solution of **S2** (2.7 g, 14.1 mmol, 1 equiv) in EtOH (20 mL) was added Lindlar catalyst (5% Pd, 3.0 g, 0.1 equiv). The reaction mixture was stirred at rt under hydrogen atmosphere until complete consumption of **S2**. The mixture was passed through a pad of celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with dichloromethane/methanol to give **S3** (1.9 g). Light yellow oil; Yield = 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 8.2 Hz, 1H), 7.13–7.07 (m, 2H), 6.78 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 3.83 (s, 3H), 1.67 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 152.3, 129.2, 117.2, 111.2, 111.0, 55.2, 52.5, 32.8. IR (neat, cm^{-1}): 3365, 2963, 1601, 1486, 1249, 1049, 702. ESI HRMS *m/z* $(M+H)^+$ calcd 166.1226, obsd 166.1234.

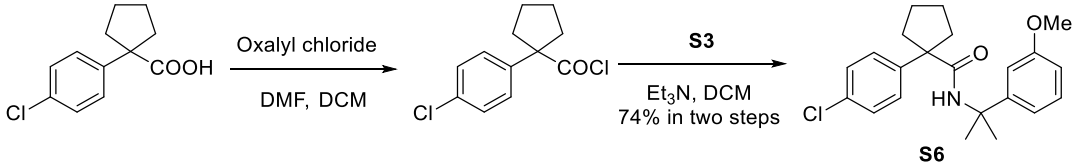
***N*-(2-(3-Methoxyphenyl)propan-2-yl)-2-methyl-2-phenylpropanamide (1).** To a solution of 2-methyl-2-phenylpropanoic acid (3.4 g, 20 mmol, 1.1 equiv) in DCM (30 mL) under argon was added three drops of DMF, oxalyl chloride (1.9 mL, 22 mmol, 1.2 equiv) was then added dropwise. The resulting reaction mixture was stirred at rt for 3 h before being concentrated under reduced pressure. The residue was dissolved in DCM (30 mL) and treated sequentially with a solution of **S3** (3.0 g, 18 mmol, 1 equiv) in DCM (10 mL) and Et_3N (5.0 mL, 36 mmol, 2 equiv). The reaction mixture was stirred at rt until complete consumption of **S3** (monitored by TLC). The solvent was removed under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the title compound (4.7 g). White solid; Yield = 84%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.38 (m, 4H), 7.36–7.29 (m, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.85–6.73 (m, 3H), 5.38 (s, 1H), 3.78 (s, 3H), 1.58 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 159.6, 149.0, 145.6, 129.4, 128.8, 127.1, 126.4, 117.0, 111.7, 111.0, 55.6, 55.2, 47.5, 28.9, 27.1. IR (neat, cm^{-1}): 3319, 2970, 1645, 1520, 1245, 696. ESI HRMS *m/z* $(M+Na)^+$ calcd 334.1778, obsd 334.1786.



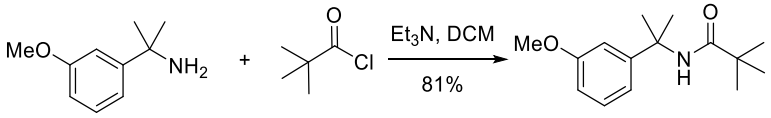
2-(4-Chlorophenyl)-*N*-(2-(3-methoxyphenyl)propan-2-yl)-2-methylpropanamide (S4). The title compound was obtained as a white solid in 63% yield (1.0 g) starting from **S3** (0.78 g, 4.7 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 4H), 7.26–7.18 (m, 1H), 6.85–6.80 (m, 1H), 6.79–6.74 (m, 2H), 5.36 (s, 1H), 3.78 (s, 3H), 1.60 (s, 6H), 1.55 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 159.8, 148.9, 144.3, 133.0, 129.5, 129.0, 127.8, 117.0, 111.7, 111.1, 55.8, 55.2, 47.2, 28.9, 27.1. IR (neat, cm^{-1}): 3426, 3358, 2973, 1671, 1494, 1265, 830. ESI HRMS *m/z* $(M+Na)^+$ calcd 368.1388, obsd 368.1398 $[C_{20}H_{24}{}^{35}ClNNaO_2]^+$.



***N*-(2-(3-Methoxyphenyl)propan-2-yl)-1-phenylcyclopropane-1-carboxamide (S5).** The title compound was obtained as a white solid in 65% yield (2.0 g) starting from **S3** (1.6 g, 9.8 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.41–7.35 (m, 2H), 7.34–7.28 (m, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.84–6.81 (m, 1H), 6.78 (t, J = 2.2 Hz, 1H), 6.72 (dd, J = 8.1, 2.4 Hz, 1H), 5.60 (s, 1H), 3.77 (s, 3H), 1.55–1.51 (m, 8H), 1.01–0.99 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 159.7, 149.1, 140.5, 131.0, 129.4, 129.2, 128.0, 117.0, 111.5, 111.0, 56.0, 55.2, 31.2, 29.3, 15.1. IR (neat, cm^{-1}): 3426, 3003, 2975, 1675, 1502, 1291, 702. ESI HRMS *m/z* $(M+Na)^+$ calcd 332.1621, obsd 332.1630.

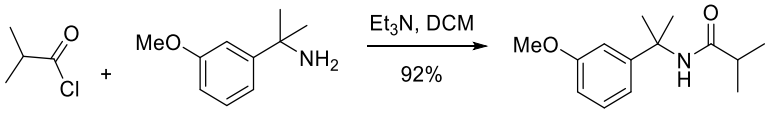


1-(4-Chlorophenyl)-*N*-(2-(3-methoxyphenyl)propan-2-yl)cyclopentane-1-carbox amide (S6). The title compound was obtained as a white solid in 74% yield (1.4 g) starting from **S3** (0.84 g, 5.1 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 4H), 7.20 (t, J = 8.0 Hz, 1H), 6.76 (d, J = 2.2 Hz, 1H), 6.74 (d, J = 2.2 Hz, 1H), 6.69 (t, J = 2.2 Hz, 1H), 5.40 (s, 1H), 3.76 (s, 3H), 2.50–2.40 (m, 2H), 2.00–1.90 (m, 2H), 1.85–1.66 (m, 4H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 159.7, 149.0, 143.3, 132.8, 129.4, 129.0, 128.2, 116.9, 111.7, 111.0, 59.5, 55.7, 55.2, 36.7, 29.0, 24.0. IR (neat, cm^{-1}): 3427, 2958, 1672, 1493, 1266, 699. ESI HRMS *m/z* $(M+Na)^+$ calcd 394.1544, obsd 394.1553 $[C_{22}H_{26}{}^{35}ClNNaO_2]^+$.



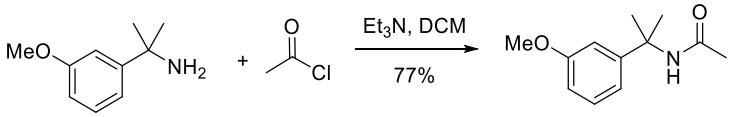
S3 S7

***N*-(2-(3-Methoxyphenyl)propan-2-yl)pivalamide (S7).** To a solution of **S3** (0.84 g, 5.0 mmol, 1 equiv) in DCM (20 mL) was added Et_3N (1.5 mL, 10 mmol, 2 equiv) under argon. Trimethylacetyl chloride (0.70 g, 5.8 mmol, 1.1 equiv) was added dropwise. The mixture was stirred at rt until complete consumption of **S3** (monitored by TLC). The solvent was removed under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product (1.0 g). White solid; Yield = 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.95 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 6.90 (t, *J* = 2.1 Hz, 1H), 6.76 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 5.86 (s, 1H), 3.79 (s, 3H), 1.67 (s, 6H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 159.7, 149.2, 129.5, 117.1, 111.4, 111.3, 55.5, 55.3, 39.1, 29.2, 27.8. IR (neat, cm^{-1}): 3330, 2974, 1645, 1531, 1220, 699. ESI HRMS *m/z* $(M+Na)^+$ calcd 272.1621, obsd 272.1631.



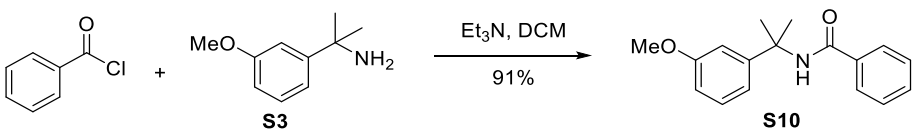
S3 S8

***N*-(2-(3-Methoxyphenyl)propan-2-yl)isobutyramide (S8).** The title compound was obtained as a white solid in 92% yield (0.98 g) starting from **S3** (0.75 g, 4.5 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 1H), 6.96 (ddd, *J* = 7.8, 1.9, 0.9 Hz, 1H), 6.92 (t, *J* = 2.2 Hz, 1H), 6.76 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 5.74 (s, 1H), 3.79 (s, 3H), 2.31 (m, 1H), 1.68 (s, 6H), 1.14 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 159.7, 149.1, 129.5, 117.2, 111.4 (2C), 55.6, 55.3, 36.3, 29.2, 19.8. IR (neat, cm^{-1}): 3289, 3066, 2968, 1652, 1548, 1050, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 258.1465, obsd 258.1472.



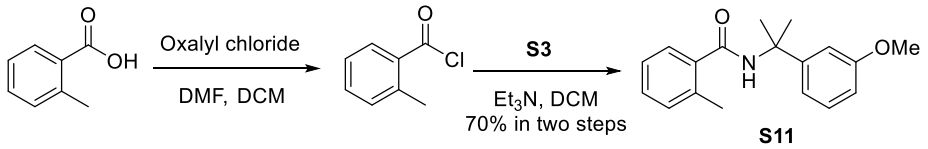
S3 S9

***N*-(2-(3-Methoxyphenyl)propan-2-yl)acetamide (S9).** The title compound was obtained as a colorless solid in 77% yield (0.87 g) starting from **S3** (0.90 g, 5.5 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.97 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 6.93 (t, *J* = 2.2 Hz, 1H), 6.76 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 5.90 (s, 1H), 3.80 (s, 3H), 1.94 (s, 3H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 159.7, 148.8, 129.5, 117.3, 111.7, 111.2, 55.9, 55.3, 29.1, 24.4. IR (neat, cm^{-1}): 3302, 3067, 2974, 2936, 1656, 1547, 1291, 701. ESI HRMS *m/z* $(M+Na)^+$ calcd 230.1151, obsd 230.1159.



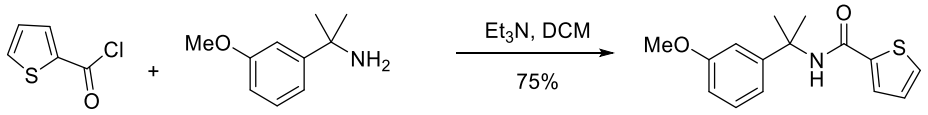
S3 S10

***N*-(2-(3-Methoxyphenyl)propan-2-yl)benzamide (S10).** The title compound was obtained as a white solid in 91% yield (1.1 g) starting from **S3** (0.75 g, 4.5 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.72 (m, 2H), 7.50–7.45 (m, 1H), 7.44–7.37 (m, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.04 (ddd, *J* = 7.8, 1.9, 0.9 Hz, 1H), 7.00 (t, *J* = 2.2 Hz, 1H), 6.78 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.43 (s, 1H), 3.79 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.8, 148.8, 135.5, 131.4, 129.6, 128.6, 126.9, 117.3, 111.7, 111.4, 56.4, 55.3, 29.2. IR (neat, cm^{-1}): 3244, 3058, 1633, 1540, 1049, 692. ESI HRMS *m/z* $(M+Na)^+$ calcd 292.1308, obsd 292.1316.



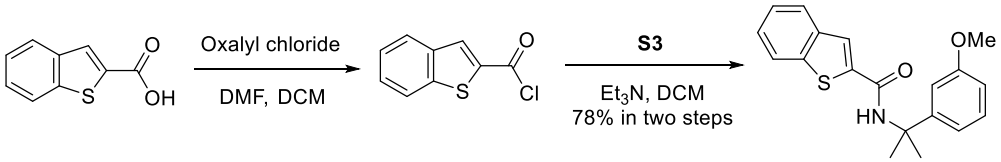
S11

***N*-(2-(3-Methoxyphenyl)propan-2-yl)-2-methylbenzamide (S11).** The title compound was obtained as a light yellow solid in 70% yield (2.1 g) starting from **S3** (1.6 g, 9.6 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 1H), 7.31–7.24 (m, 2H), 7.21–7.16 (m, 2H), 7.08–7.04 (m, 1H), 7.04–7.01 (m, 1H), 6.81–6.77 (m, 1H), 6.04 (s, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 159.8, 148.7, 137.4, 136.1, 131.1, 129.8, 129.6, 126.6, 125.8, 117.3, 111.6, 56.5, 55.3, 29.2, 19.9. IR (neat, cm^{-1}): 3285, 2973, 1648, 1530, 1265, 699. ESI HRMS *m/z* $(M+Na)^+$ calcd 306.1465, obsd 306.1472.



S3 **S12**

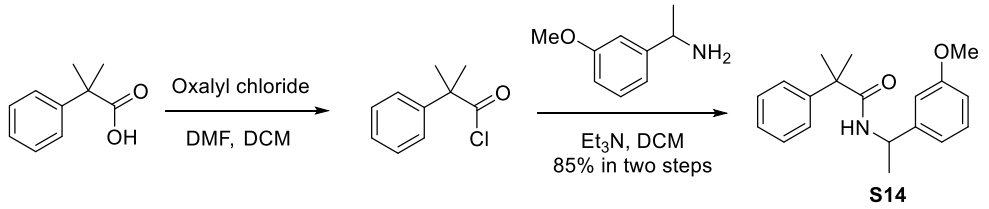
***N*-(2-(3-Methoxyphenyl)propan-2-yl)thiophene-2-carboxamide (S12).** The title compound was obtained as a white solid in 75% yield (0.84 g) starting from **S3** (0.67 g, 4.0 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.45 (m, 1H), 7.44–7.42 (m, 1H), 7.30–7.24 (m, 1H), 7.07–7.02 (m, 2H), 7.00 (t, *J* = 2.2 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.26 (s, 1H), 3.79 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 159.8, 148.7, 140.1, 129.8, 129.7, 127.9, 127.6, 117.3, 111.7, 111.5, 56.7, 55.3, 29.3. IR (neat, cm^{-1}): 3307, 3071, 1626, 1545, 1311, 699. ESI HRMS *m/z* $(M+Na)^+$ calcd 298.0872, obsd 298.0881.



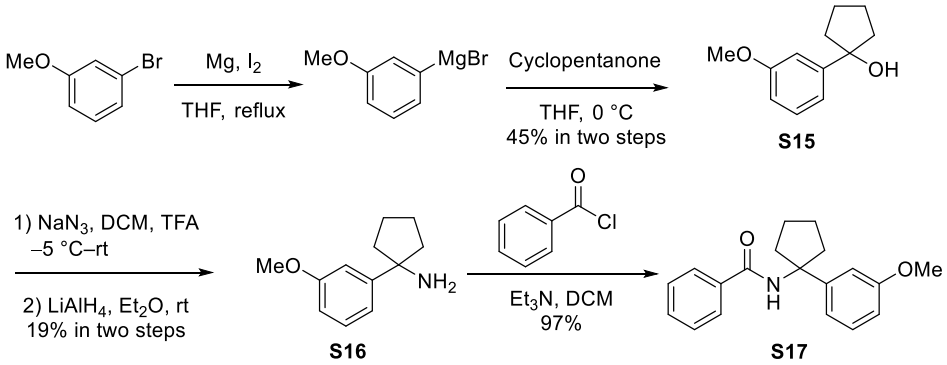
S13

***N*-(2-(3-Methoxyphenyl)propan-2-yl)benzo[*b*]thiophene-2-carboxamide (S13).** The title compound was obtained as a white solid in 78% yield (0.98 g) starting from **S3** (0.64 g, 3.9 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (s, 1H), 8.29 (s, 1H), 8.02–7.92 (m, 2H), 7.49–7.39 (m, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 2.2 Hz, 1H), 6.77

(dd, J = 8.1, 2.5 Hz, 1H), 3.71 (s, 3H), 1.69 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.9, 159.1, 149.5, 140.9, 140.1, 139.3, 129.0, 126.1, 125.1, 124.8, 122.7, 117.1, 111.3, 110.6, 55.7, 54.9, 29.4. IR (neat, cm^{-1}): 3304, 2972, 1625, 1539, 1050, 696. ESI HRMS *m/z* (M+Na)$^+$ calcd 348.1029, obsd 348.1038.



***N*-(1-(3-Methoxyphenyl)ethyl)-2-methyl-2-phenylpropanamide (S14).** The title compound was obtained as a white solid in 85% yield (2.4 g) starting from 1-(3-methoxyphenyl)ethan-1-amine (1.5 g, 9.6 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 4H), 7.33–7.27 (m, 1H), 7.21 (t, J = 7.9 Hz, 1H), 6.83–6.71 (m, 2H), 6.71–6.67 (m, 1H), 5.38 (d, J = 8.0 Hz, 1H), 5.07 (m, 1H), 3.77 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H), 1.35 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 159.8, 145.3, 145.2, 129.6, 128.8, 127.1, 126.5, 118.2, 112.6, 111.7, 55.2, 48.8, 47.1, 27.1 (2C), 21.8. IR (neat, cm^{-1}): 3346, 2972, 1653, 1495, 1256, 699. ESI HRMS *m/z* (M+Na)$^+$ calcd 320.1621, obsd 320.1629.

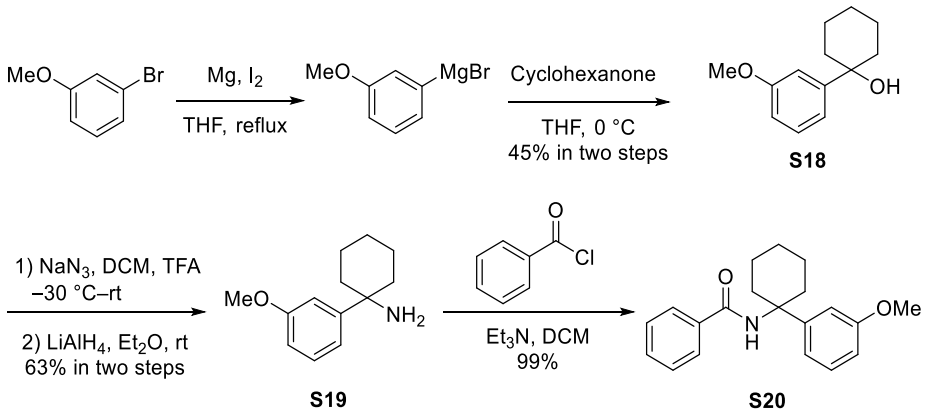


1-(3-Methoxyphenyl)cyclopentan-1-ol (S15). The title compound was prepared by following a modified procedure in the literature.[4] To an oven dried two-necked round bottom flask was added magnesium turnings (1.1 g, 45.0 mmol 1.5 equiv). The flask was equipped with a reflux condenser and flushed with argon before adding I_2 (51 mg, 0.2 mmol) and THF (30 mL). The solution was stirred at rt for 30 min. 1-bromo-3-methoxybenzene (30.0 mmol, 1 equiv) was then added dropwise. The resulting reaction mixture was then refluxed for 2 h and then cooled to rt. The freshly prepared Grignard reagent was transferred by cannula to a round bottom flask. Cyclopentanone (2.6 mL, 30 mmol, 1 equiv) in THF (10 mL) was added to the solution dropwise at 0 °C. The reaction mixture was stirred at rt overnight. Saturated NH_4Cl (50 mL) was added. The phases were separated, and the aqueous phase was extracted with ethyl acetate. 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 the product (2.6 g). Colorless oil; Yield = 45% in two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 1H), 7.12–7.00 (m, 2H), 6.78 (ddd, J = 8.2, 2.6, 1.0 Hz, 1H), 3.81 (s, 3H), 2.02–1.93 (m, 6H), 1.87–1.80 (m, 2H), 1.74 (s,

1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.0, 129.3, 117.6, 112.0, 111.4, 83.6, 55.3, 42.0, 24.0. IR (neat, cm^{-1}): 3443, 2959, 1601, 1287, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 215.1043, obsd 215.1043.

1-(3-Methoxyphenyl)cyclopentan-1-amine (S16). The title compound was prepared by following a modified procedure in the literature.[5] To a solution of **S15** (2.6 g, 13.5 mmol, 1 equiv) and sodium azide (2.0 g, 30 mmol, 2.2 equiv) in CH_2Cl_2 (50 mL) under argon was added a solution of TFA (8.3 mL, 108 mmol, 8 equiv) in CH_2Cl_2 (10 mL) at −5 °C over 15 min. The resulting suspension was stirred at −5 °C until complete consumption of **S15** (monitored by TLC). Saturated NH_4Cl (30 mL) and ammonia solution (25%) was added until the pH of the aqueous phase reached above 7. The phases were separated, and the aqueous phase was extracted with dichloromethane (30 mL). The combined organic solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in Et_2O (50 mL) and treated with $LiAlH_4$ (0.51 g, 13.5 mmol, 1 equiv) in several portions at rt. The reaction mixture was stirred at rt for 3 h. Et_2O, H_2O (0.51 mL), 15% NaOH (0.51 mL), H_2O (1.53 mL) and anhydrous $MgSO_4$ were added sequentially. The mixture was stirred at rt for 30 min and then filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with dichloromethane/ methanol to give the product (0.5 g). Light yellow oil; Yield = 19% in two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 1H), 7.07–6.98 (m, 2H), 6.76 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 3.81 (s, 3H), 2.06–1.74 (m, 8H), 1.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 151.7, 129.3, 117.9, 111.9, 111.1, 64.1, 55.3, 41.6, 23.8. IR (neat, cm^{-1}): 3364, 2956, 2870, 1600, 1050, 701. ESI HRMS *m/z* $(M+Na)^+$ calcd 214.1202, obsd 214.1211.

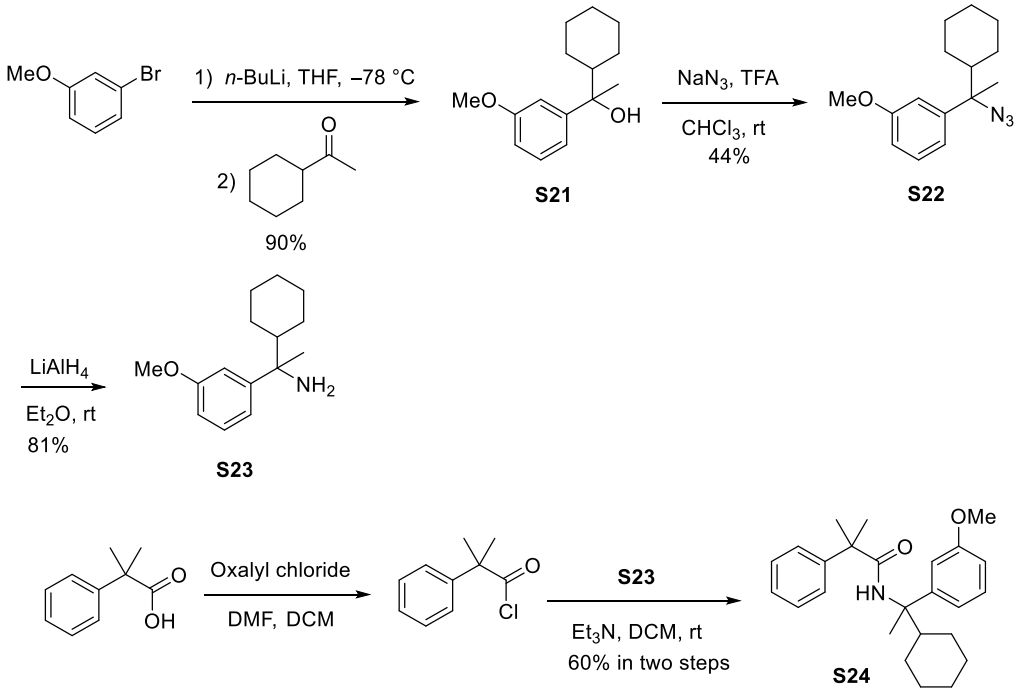
***N*-(1-(3-Methoxyphenyl)cyclopentyl)benzamide (S17).** The title compound was obtained as a light yellow solid in 97% yield (0.69 g) starting from **S16** (0.46 g, 2.4 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.72 (m, 1H), 7.54–7.47 (m, 1H), 7.46–7.38 (m, 2H), 7.29–7.24 (m, 1H), 7.09 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 7.05 (t, *J* = 2.1 Hz, 1H), 6.79 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.44 (s, 1H), 3.81 (s, 3H), 2.58–2.43 (m, 2H), 2.29–2.12 (m, 2H), 1.97–1.80 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.6, 146.9, 135.6, 131.4, 129.2, 128.6, 126.9, 118.3, 112.5, 111.4, 67.1, 55.3, 39.5, 23.5. IR (neat, cm^{-1}): 3261, 3054, 2958, 1633, 1531, 1132, 696. ESI HRMS *m/z* $(M+Na)^+$ calcd 318.1465, obsd 318.1472.



1-(3-Methoxyphenyl)cyclohexan-1-ol (S18).[6] The title compound was obtained as a light yellow oil in 45% yield (2.8 g) starting from 1-bromo-3-methoxybenzene (5.6 g, 30 mmol) by following the procedure described for the synthesis of **S15**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.14–7.07 (m, 2H), 6.81 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.84 (s, 3H), 1.87–1.73 (m, 8H), 1.69–1.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 151.4, 129.3, 117.1, 111.9, 110.9, 73.3, 55.3, 38.9, 25.6, 22.3.

1-(3-Methoxyphenyl)cyclohexan-1-amine (S19). The title compound was obtained as a light yellow oil in 63% yield (1.7 g) starting from **S18** (2.7 g, 13.1 mmol) by following the procedure described for the synthesis of **S16**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.2 Hz, 1H), 7.15–7.09 (m, 2H), 6.79 (ddd, *J* = 8.1, 2.4, 1.1 Hz, 1H), 3.84 (s, 3H), 2.02–1.92 (m, 2H), 1.74–1.55 (m, 9H), 1.41–1.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 152.0, 129.3, 117.7, 111.7, 111.2, 55.3, 54.0, 39.4, 25.9, 22.6. IR (neat, cm^{-1}): 3383, 2932, 2854, 1600, 1246, 701. ESI HRMS *m/z* $(M+H)^+$ calcd 206.1539, obsd 206.1532.

***N*-(1-(3-Methoxyphenyl)cyclohexyl)benzamide (S20).** The title compound was obtained as a white solid in 99% yield (1.5 g) starting from **S19** (0.81 g, 3.9 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.73 (m, 2H), 7.51–7.46 (m, 1H), 7.45–7.39 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 7.01 (t, *J* = 2.1 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.31 (s, 1H), 3.77 (s, 3H), 2.55–2.45 (m, 2H), 1.88 (td, *J* = 13.2, 3.7 Hz, 2H), 1.78–1.69 (m, 3H), 1.66–1.55 (m, 2H), 1.40–1.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 159.7, 148.7, 135.8, 131.4, 129.4, 128.7, 126.9, 117.7, 112.0, 111.3, 58.6, 55.2, 36.3, 25.6, 22.5. IR (neat, cm^{-1}): 3319, 3059, 2933, 1647, 1487, 695. ESI HRMS *m/z* $(M+Na)^+$ calcd 332.1621, obsd 332.1630.



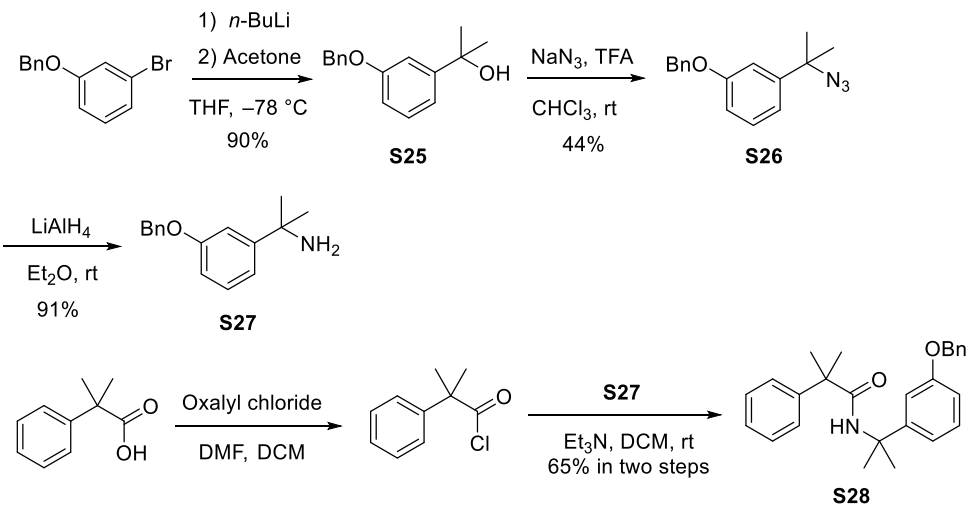
1-Cyclohexyl-1-(3-methoxyphenyl)ethan-1-ol (S21). To a solution of 1-bromo-3-methoxybenzene (5.6 g, 30 mmol, 1.0 equiv) in THF (90 mL) was added *n*-BuLi (14 mL, 33 mmol, 1.1 equiv) dropwise at −78 ˚C. The resulting solution was stirred for 1 h

at the same temperature before adding 1-cyclohexylethan-1-one (4.5 g, 36 mmol, 1.2 equiv) dropwise. The resulting solution was stirred at −78 ˚C for 48 h. Saturated aqueous NH_4Cl (80 mL) and ethyl acetate (100 mL) were added. The phases were separated, and the aqueous phase was extracted with ethyl acetate. The combined organic solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give product (6.3 g). Colorless oil; Yield = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 6.99–6.93 (m, 2H), 6.77–6.74 (m, 1H), 3.80 (s, 3H), 1.79–1.66 (m, 4H), 1.65–1.52 (m, 3H), 1.50 (s, 3H), 1.22–0.92 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 149.9, 128.8, 117.9, 111.7, 111.4, 76.7, 55.3, 49.0, 27.5, 27.3, 26.9, 26.8 (2C), 26.5. IR (neat, cm^{-1}): 3491, 2931, 2852, 1600, 1259, 1046, 703. ESI HRMS *m/z* $(M+Na)^+$ calcd 257.1512, obsd 257.1510.

1-(1-Azido-1-cyclohexylethyl)-3-methoxybenzene (S22). The title compound was obtained as a yellow oil in 44% yield (3.1 g) starting from **S21** (6.3 g, 27 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 1H), 6.94–6.91 (m, 2H), 6.81–6.78 (m, 1H), 3.81 (s, 3H), 1.72–1.68 (m, 2H), 1.65 (s, 3H), 1.62–1.54 (m, 4H), 1.15–0.92 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 145.3, 129.2, 118.7, 112.8, 111.9, 77.4, 70.1, 55.3, 48.9, 27.8, 27.7, 26.6, 26.4, 21.2. IR (neat, cm^{-1}): 3334, 2932, 2853, 2103, 1601, 1261, 705. ESI HRMS *m/z* $(M+Na)^+$ calcd 282.1577, obsd 282.1582.

1-Cyclohexyl-1-(3-methoxyphenyl)ethan-1-amine (S23). To a solution of **S22** (2.3 g, 8.9 mmol, 1.0 equiv) in Et_2O (80 mL) was added $LiAlH_4$ (0.67 g, 17.7 mmol, 2.0 equiv) at rt. The reaction mixture was stirred at rt until complete consumption of **S22** (monitored by TLC). Et_2O, H_2O (0.67 mL), 15% NaOH (0.67 mL), H_2O (2.0 mL) and anhydrous $MgSO_4$ were added sequentially. The resulting mixture was stirred at rt for 30 min and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with dichloromethane/ methanol to give the product (1.7 g). Yellow oil; Yield = 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 1H), 7.01–6.97 (m, 2H), 6.74–6.71 (m, 1H), 3.79 (s, 3H), 1.75–1.57 (m, 4H), 1.54–1.40 (m, 4H), 1.39 (s, 3H), 1.26–0.89 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 151.1, 128.7, 118.1, 112.1, 110.6, 76.8, 57.4, 55.1, 49.4, 27.9, 27.5, 27.4, 26.9, 26.5. IR (neat, cm^{-1}): 3357, 2928, 2851, 1599, 1248, 1049, 703. ESI HRMS *m/z* $(M+Na)^+$ calcd 256.1672, obsd 256.1680.

***N*-(1-Cyclohexyl-1-(3-methoxyphenyl)ethyl)-2-methyl-2-phenylpropanamide (S24).** The title compound was obtained as a yellow oil in 60% yield (1.1 g) starting from **S23** (1.3 g, 5.5 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.40 (m, 4H), 7.34–7.30 (m, 1H), 7.19–7.15 (m, 1H), 6.73–6.65 (m, 3H), 5.43 (s, 1H), 3.76 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H), 1.59 (s, 3H), 1.58–1.54 (m, 2H), 1.38–1.19 (m, 4H), 1.03–0.84 (m, 3H), 0.54–0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176, 159.3, 146.9, 145.5, 128.9, 128.8, 127.2, 126.6, 118.3, 112.3, 111.1, 60.9, 55.2, 49.5, 47.7, 27.5, 27.0 (2C), 26.7, 26.6 (2C), 26.4, 21.6. IR (neat, cm^{-1}): 3434, 3058, 2929, 2854, 1682, 1498, 1260, 702. ESI HRMS *m/z* $(M+Na)^+$ calcd 402.2404, obsd 402.2414.

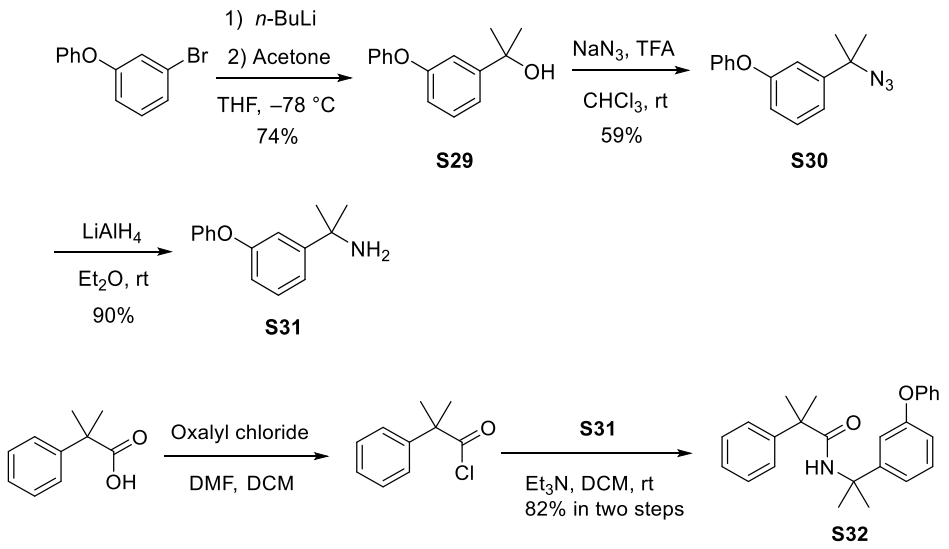


2-(3-(Benzyloxy)phenyl)propan-2-ol (S25).[7] The title compound was prepared according to a procedure in the literature.

1-(2-Azidopropan-2-yl)-3-(benzyloxy)benzene (S26). The title compound was obtained as a colorless oil in 44% yield (1.9 g) starting from **S25** (4.0 g, 16.5 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.32 (m, 6H), 7.18–7.17 (m, 1H), 7.13–7.09 (m, 1H), 6.98–6.95 (m, 1H), 5.14 (s, 2H), 1.69 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.5, 137.0, 129.6, 128.7, 128.1, 127.6, 117.8, 113.3, 112.7, 70.2, 63.8, 28.4. IR (neat, cm^{-1}): 3032, 2978, 2930, 2102, 1600, 1268, 697. ESI HRMS *m/z* $(M+Na)^+$ calcd 290.1264, obsd 290.1267.

2-(3-(Benzyloxy)phenyl)propan-2-amine (S27). The title compound was obtained as a colorless oil in 91% yield (1.6 g) starting from **S26** (1.9 g, 7.1 mmol) by following the procedure described for the synthesis of **S23**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.21 (m, 6H), 7.16–7.14 (m, 1H), 7.09–7.06 (m, 1H), 6.83–6.80 (m, 1H), 5.05 (s, 2H), 1.62 (s, 2H), 1.46 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 152.3, 137.2, 129.2, 128.6, 128.0, 127.6, 117.5, 112.2, 119.4, 70.1, 52.5, 32.8. IR (neat, cm^{-1}): 3365, 3031, 2963, 2925, 1580, 1245, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 264.1359, obsd 264.1367.

***N*-(2-(3-(Benzyloxy)phenyl)propan-2-yl)-2-methyl-2-phenylpropanamide (S28).** The title compound was obtained as a colorless oil in 65% yield (0.76 g) starting from **S27** (0.73 g, 3.0 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.29 (m, 8H), 7.28–7.21 (m, 1H), 7.26–7.21 (m, 1H), 7.18–7.16 (m, 1H), 6.90–6.75 (m, 3H), 5.36 (s, 1H), 4.96 (s, 2H), 1.54 (s, 6H), 1.53 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 159.0, 149.2, 145.7, 137.3, 129.4, 128.9, 128.7, 128.1, 127.7, 127.1, 126.4, 117.3, 112.7, 112.0, 70.1, 55.7, 47.5, 28.9, 27.1. IR (neat, cm^{-1}): 3424, 3030, 2973, 2929, 1676, 1497, 1265, 699. ESI HRMS *m/z* $(M+Na)^+$ calcd 410.2091, obsd 410.2098.

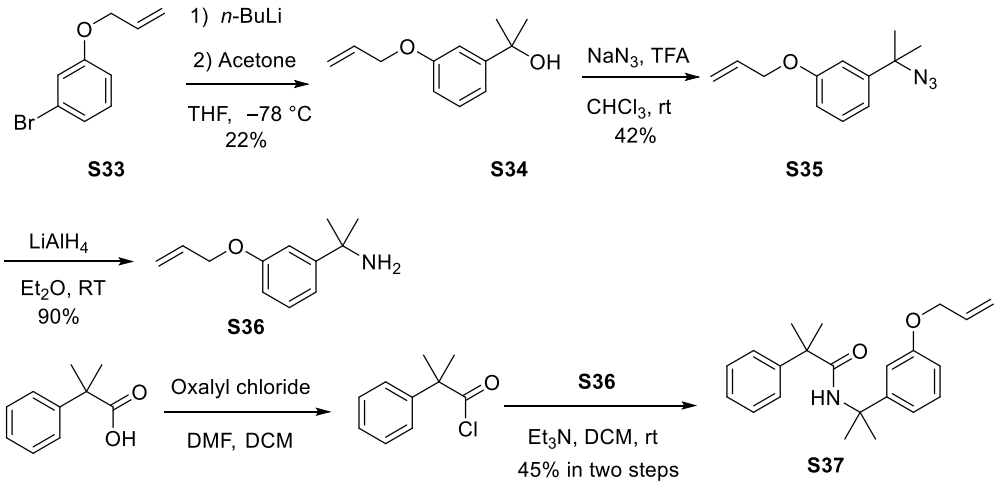


2-(3-Phenoxyphenyl)propan-2-ol (S29). The title compound was obtained as a colorless oil in 74% yield (8.4 g) starting from 1-bromo-3-phenoxybenzene (12.5 g, 50 mmol) by following the procedure described for the synthesis of **S21**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.23 (m, 3H), 7.23–7.14 (m, 2H), 7.14–7.05 (m, 1H), 7.04–6.97 (m, 2H), 6.85 (ddd, *J* = 8.0, 2.4, 1.1 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 157.3, 151.6, 129.8, 129.6, 123.3, 119.5, 118.9, 117.1, 115.5, 72.5, 31.8. IR (neat, cm^{-1}): 3418, 3067, 2975, 1581, 1489, 1227, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 251.1043, obsd 251.1050.

1-(2-Azidopropan-2-yl)-3-phenoxybenzene (S30). The title compound was obtained as a colorless oil in 59% yield (4.5 g) starting from **S29** (6.8 g, 29.8 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.23 (m, 3H), 7.20–7.06 (m, 3H), 7.04–6.97 (m, 2H), 6.89 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 157.2, 147.0, 129.9, 123.5, 120.1, 118.9, 117.7, 116.2, 63.7, 28.4.

2-(3-Phenoxyphenyl)propan-2-amine (S31). The title compound was obtained as a yellow oil in 90% yield (3.5 g) starting from **S30** (4.3 g, 16.9 mmol) by following the procedure described for the synthesis of **S23**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.20 (m, 5H), 7.09–7.05 (m, 1H), 7.01–6.98 (m, 2H), 6.84–6.81 (m, 1H), 1.94 (s, 2H), 1.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 157.1, 152.7, 129.8, 129.5, 123.2, 119.8, 118.8, 116.6, 115.9, 76.9, 52.6, 32.8. IR (neat, cm^{-1}): 3367, 3065, 2964, 1580, 1489, 1240, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 250.1202, obsd 250.1213.

2-Methyl-*N*-(2-(3-phenoxyphenyl)propan-2-yl)-2-phenylpropanamide (S32). The title compound was obtained as a colorless oil in 82% yield (1.5 g) starting from **S30** (1.3 g, 5.5 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 6H), 7.27–7.19 (m, 2H), 7.10 (m, 1H), 7.03–6.93 (m, 3H), 6.90–6.87 (m, 1H), 6.84–6.82 (m, 1H), 5.28 (s, 1H), 1.51 (s, 6H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 157.4, 157.1, 149.4, 145.3, 129.8, 129.6, 128.8, 127.0, 126.3, 123.1, 119.5, 118.8, 117.0, 115.5, 55.3, 47.3, 29.1, 26.9. IR (neat, cm^{-1}): 3424, 3060, 2974, 2930, 1676, 1490, 1226, 698. ESI HRMS *m/z* $(M+Na)^+$ calcd 396.1934, obsd 396.1943.

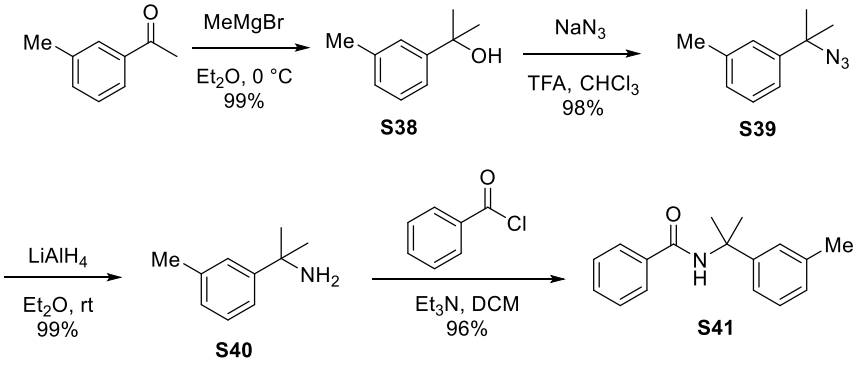


2-(3-(Allyloxy)phenyl)propan-2-ol (S34). The title compound was obtained as a colorless oil in 22% yield (1.5 g) starting from **S33** (7.4 g, 35 mmol) by following the procedure described for the synthesis of **S21**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 1H), 7.07–7.00 (m, 2H), 6.77–6.74 (m, 1H), 6.07–5.98 (m, 1H), 5.38 (dddd, *J* = 17.3,5.2,3.2, 1.6 Hz, 1H), 5.25 (dddd, *J* = 17.3, 5.2, 3.2, 1.6 Hz, 1H), 4.51–4.48 (m, 2H), 2.54 (s, 1H), 1.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 151.0, 133.4, 129.1, 117.5, 117.0, 125.1, 125.0, 111.5, 72.4, 68.7, 31.6. IR (neat, cm^{-1}): 3424, 2976, 2928, 1601, 1485, 1267, 701. ESI HRMS *m/z* $(M+Na)^+$ calcd 215.1043, obsd 215.1042.

1-(Allyloxy)-3-(2-azidopropan-2-yl)benzene (S35). The title compound was obtained as a colorless oil in 42% yield (0.47 g) starting from **S34** (1.0 g, 5.2 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 1H), 7.02–6.99 (m, 2H), 6.82–6.79 (m, 1H), 6.09–6.00 (m, 1H), 5.43 (dddd, *J* = 17.3, 5.2, 3.2, 1.6 Hz, 1H), 5.28 (dddd, *J* = 17.3, 5.2, 3.2, 1.6 Hz, 1H), 4.54–4.52 (m, 2H), 1.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.5, 133.4, 129.6, 117.9, 117.8, 113.3, 112.5, 69.0, 63.8, 28.5.

2-(3-(Allyloxy)phenyl)propan-2-amine (S36). The title compound was obtained as a colorless oil in 90% yield (0.33 g) starting from **S35** (0.42 g, 1.9 mmol) by following the procedure described for the synthesis of **S23**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 1H), 7.12–7.08 (m, 2H), 6.80–6.77 (m, 1H), 6.12–6.03 (m, 1H), 5.46 (dddd, *J* = 17.3,5.2,3.2, 1.6 Hz, 1H), 5.30 (dddd, *J* = 17.3, 5.2, 3.2, 1.6 Hz, 1H), 4.57–4.55 (m, 2H), 2.09 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 152.0, 133.4, 129.1, 117.5, 117.3, 112.0, 111.8, 68.8, 52.5, 32.6.

***N*-(2-(3-(Allyloxy)phenyl)propan-2-yl)-2-methyl-2-phenylpropanamide (S37).** The title compound was obtained as a yellow solid in 45% yield (0.33 g) starting from **S36** (0.3 g, 1.6 mmol) by following the procedure described for the synthesis of **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.37 (m, 4H), 7.36–7.29 (m, 1H), 7.27–7.16 (m, 1H), 6.88–6.72 (m, 3H), 6.07 (ddd, *J* = 16.9, 10.5, 5.2 Hz, 1H), 5.51–5.46 (m, 1H), 5.38 (m, 1H), 5.33–5.20 (s, 1H), 4.49 (dt, *J* = 5.3, 1.5 Hz, 2H), 1.58 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 158.8, 149.1, 145.6, 133.5, 129.4, 128.9, 127.1, 126.4, 117.7, 117.2, 112.5, 111.8, 68.9, 55.7, 47.5, 28.9, 27.1. IR (neat, cm^{-1}): 3424, 3060, 2974, 2929, 1676, 1497, 1265, 700. ESI HRMS *m/z* $(M+Na)^+$ calcd 360.1934, obsd 360.1944.

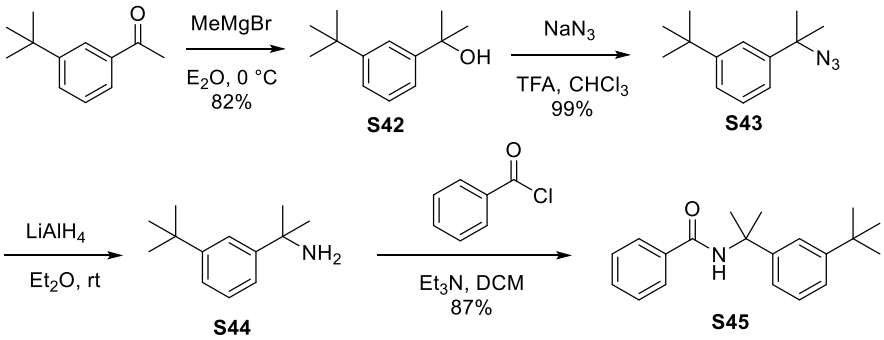


2-(*m*-Tolyl)propan-2-ol (S38).[2] The title compound was obtained as a light yellow oil in 99% yield (4.0 g) starting from 1-(*m*-tolyl)ethan-1-one (4.0 g, 30 mmol) by following the procedure described for the synthesis of **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 1H), 7.32 (dt, *J* = 7.8, 1.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.13–7.08 (m, 1H), 2.42 (s, 3H), 1.99 (s, 1H), 1.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 137.8, 128.2, 127.5, 125.2, 121.5, 72.6, 31.8, 21.7.

1-(2-Azidopropan-2-yl)-3-methylbenzene (S39). The title compound was obtained as a colorless oil in 98% yield (4.6 g) starting from **S38** (4.0 g, 26.8 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 3H), 7.17–7.13 (m, 1H), 2.43 (s, 3H), 1.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 138.2, 128.5, 128.3, 126.0, 122.3, 63.9, 28.5, 21.7. IR (neat, cm^{-1}): 2979, 2928, 2101, 1607, 1246, 704. ESI HRMS *m/z* $(M+H)^+$ calcd 176.1182, obsd 176.1185.

2-(*m*-Tolyl)propan-2-amine (S40). The title compound was obtained as a colorless oil in 99% yield (3.7 g) starting from **S39** (4.4 g, 25.1 mmol) by following the procedure described for the synthesis of **S23**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.36 (m, 1H), 7.35–7.31 (m, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.10–7.05 (m, 1H), 2.41 (s, 3H), 1.61 (s, 2H), 1.52 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 137.7, 128.2, 126.9, 125.5, 121.8, 52.4, 32.9, 21.7. IR (neat, cm^{-1}): 3364, 3023, 2964, 2923, 1606, 1200, 705. ESI HRMS *m/z* $(M+H)^+$ calcd 150.1277, obsd 150.1274.

***N*-(2-(*m*-Tolyl)propan-2-yl)benzamide (S41).** The title compound was obtained as a white solid in 96% yield (1.6 g) starting from **S40** (0.97 g, 6.5 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.68 (m, 1H), 7.52–7.43 (m, 1H), 7.42–7.36 (m, 2H), 7.29–7.19 (m, 3H), 7.10–7.00 (m, 1H), 6.46 (s, 1H), 2.34 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 147.0, 138.0, 135.6, 131.3, 128.6, 128.5, 127.6, 126.9, 125.6, 121.9, 56.3, 29.2, 21.8. IR (neat, cm^{-1}): 3241, 3057, 2969, 1630, 1535, 1191, 687. ESI HRMS *m/z* $(M+Na)^+$ calcd 276.1359, obsd 276.1365.

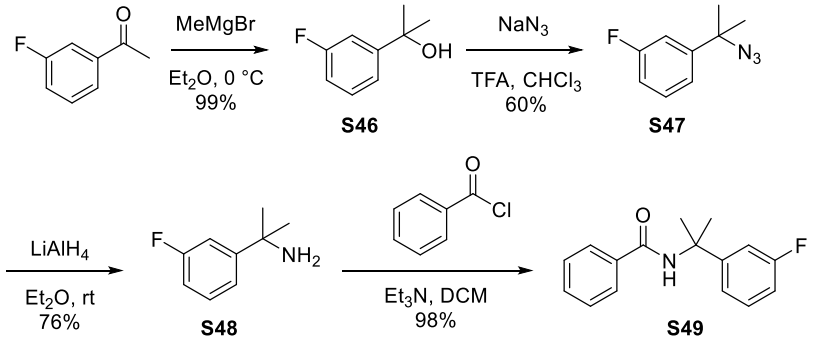


2-(3-(*tert*-Butyl)phenyl)propan-2-ol (S42). The title compound was obtained as a white solid in 82% yield (4.5 g) starting from 1-(3-(*tert*-butyl)phenyl)ethan-1-one (5.0 g, 28.4 mmol) by following the procedure described for the synthesis of **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 1H), 7.34–7.30 (m, 3H), 1.84 (s, 1H), 1.63 (s, 6H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 148.9, 128.0, 123.8, 121.7, 121.4, 72.9, 35.0, 32.0, 31.6. IR (neat, cm^{-1}): 3281, 2960, 1600, 1362, 707. ESI HRMS *m/z* $(M+Na)^+$ calcd 215.1406, obsd 215.1409.

1-(2-Azidopropan-2-yl)-3-(*tert*-butyl)benzene (S43). The title compound was obtained as a light yellow oil in 99% yield (4.9 g) starting from **S42** (4.4 g, 22.9 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.48 (m, 1H), 7.35–7.30 (m, 2H), 7.29–7.25 (m, 1H), 1.68 (s, 6H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 144.4, 128.3, 124.5, 122.3, 122.2, 64.2, 35.0, 31.5, 28.6.

2-(3-(*tert*-Butyl)phenyl)propan-2-amine (S44). The title compound was prepared by following the procedure described for the synthesis of **S23**. The title compound was used in next step without purification.

***N*-(2-(3-(*tert*-Butyl)phenyl)propan-2-yl)benzamide (S45).** The title compound was obtained as a white solid oil in 87% yield (1.3 g) starting from **S44** (0.97 g, 5.1 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.51–7.44 (m, 2H), 7.44–7.36 (m, 2H), 7.31–7.26 (m, 3H), 6.40 (s, 1H), 1.84 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 151.3, 146.7, 135.9, 131.3, 128.7, 128.3, 126.9, 124.0, 122.0, 121.8, 56.8, 34.9, 31.6, 29.2. IR (neat, cm^{-1}): 3246, 3060, 2957, 1634, 1539, 693. ESI HRMS *m/z* $(M+Na)^+$ calcd 318.1828, obsd 318.1835.



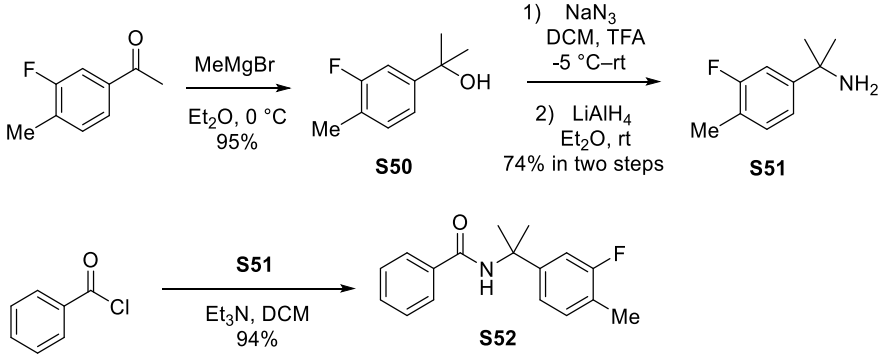
2-(3-Fluorophenyl)propan-2-ol (S46).[3] The title compound was obtained as a colorless oil in 99% yield (4.6 g) starting from 1-(3-fluorophenyl)ethan-1-one (4.1 g, 30 mmol) by following the procedure described for the synthesis of **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.18 (m, 3H), 7.00–6.90 (m, 1H), 2.06 (s, 1H), 1.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 245.0 Hz), 152.1 (d, $J_{C\text{-}F}$ = 6.4 Hz), 129.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 120.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 113.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 111.9 (d, $J_{C\text{-}F}$ = 22.4 Hz), 72.5, 31.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ −113.1.

1-(2-Azidopropan-2-yl)-3-fluorobenzene (S47). The title compound was obtained as a colorless oil in 60% yield (3.2 g) starting from **S46** (4.5 g, 29 mmol) by following the procedure described for the synthesis of **S2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.0, 6.0 Hz, 1H), 7.24 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.18 (dt, *J* = 10.6, 2.1 Hz, 1H),

7.01 (tdd, J = 8.3, 2.6, 1.0 Hz, 1H), 1.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 245.8 Hz), 147.6 (d, $J_{C\text{-}F}$ = 6.6 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.2 Hz), 120.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 114.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 112.7 (d, $J_{C\text{-}F}$ = 22.8 Hz), 63.5, 28.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ −112.4.

2-(3-Fluorophenyl)propan-2-amine (S48). The title compound was obtained as a light yellow oil in 76% yield (2.0 g) starting from **S47** (3.0 g, 16.7 mmol) by following the procedure described for the synthesis of **S23**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.27–7.21 (m, 1H), 6.97–6.89 (m, 1H), 1.65 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 244.8 Hz), 153.4 (d, $J_{C\text{-}F}$ = 6.2 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 120.5 (d, $J_{C\text{-}F}$ = 2.7 Hz), 113.1 (d, $J_{C\text{-}F}$ = 21.2 Hz), 112.2 (d, $J_{C\text{-}F}$ = 22.3 Hz), 52.5 (d, $J_{C\text{-}F}$ = 1.7 Hz), 32.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ −113.3. IR (neat, cm^{-1}): 3369, 3072, 2967, 2928, 1585, 1483, 699. ESI HRMS *m/z* $(M+H)^+$ calcd 154.1027, obsd 154.1034.

***N*-(2-(3-Fluorophenyl)propan-2-yl)benzamide (S49).** The title compound was obtained as a white solid in 98% yield (1.0 g) starting from **S48** (0.61 g, 4.0 mmol) by following the procedure described for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.71 (m, 2H), 7.54–7.44 (m, 1H), 7.47–7.36 (m, 2H), 7.29 (td, J = 8.0, 6.0 Hz, 1H), 7.21 (ddd, J = 7.9, 1.8, 1.1 Hz, 1H), 7.13 (ddd, J = 10.8, 2.5, 1.8 Hz, 1H), 6.92 (tdd, J = 8.3, 2.5, 1.0 Hz, 1H), 6.45 (s, 1H), 1.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 163.1 (d, $J_{C\text{-}F}$ = 245.0 Hz), 149.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 135.3, 131.6, 130.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.7, 127.0, 120.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 113.7 (d, $J_{C\text{-}F}$ = 21.1 Hz), 112.3 (d, $J_{C\text{-}F}$ = 22.5 Hz), 56.1 (d, $J_{C\text{-}F}$ = 1.8 Hz), 29.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ −113.0. IR (neat, cm^{-1}): 3259, 3060, 2982, 1633, 1539, 696. ESI HRMS *m/z* $(M+Na)^+$ calcd 280.1108, obsd 280.1116.

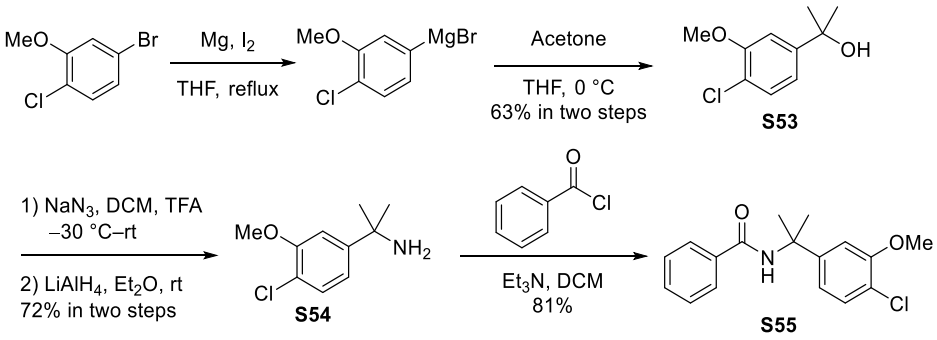


2-(3-Fluoro-4-methylphenyl)propan-2-ol (S50). The title compound was obtained as a colorless oil in 95% yield (2.1 g) starting from 1-(3-fluoro-4-methylphenyl)ethan-1-one (2.0 g, 13.1 mmol) by following the procedure described for the synthesis of **S1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16–7.07 (m, 3H), 2.24 (d, J = 2.0 Hz, 3H), 2.01 (s, 1H), 1.54 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 244.1 Hz), 149.3 (d, $J_{C\text{-}F}$ = 6.4 Hz), 131.2 (d, $J_{C\text{-}F}$ = 5.4 Hz), 123.0 (d, $J_{C\text{-}F}$ = 17.4 Hz), 119.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 111.5 (d, $J_{C\text{-}F}$ = 23.3 Hz), 72.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 31.8, 14.2 (d, $J_{C\text{-}F}$ = 3.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −117.5.

2-(3-Fluoro-4-methylphenyl)propan-2-amine (S51). The title compound was obtained as a light yellow oil in 74% yield (2.0 g) starting from **S50** (2.0 g, 11.9 mmol) by following the procedure described for the synthesis of **S16**. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.18–7.09 (m, 3H), 2.24 (d, J = 1.8 Hz, 3H), 1.61 (s, 2H), 1.46 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 243.7 Hz), 150.6 (d, $J_{C\text{-}F}$ = 6.3 Hz), 131.2 (d, $J_{C\text{-}F}$ = 5.5 Hz), 122.4 (d, $J_{C\text{-}F}$ = 17.3 Hz), 120.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 111.8 (d, $J_{C\text{-}F}$ = 23.1 Hz), 52.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 32.9, 14.2 (d, $J_{C\text{-}F}$ = 3.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −117.6. IR (neat, cm^{-1}): 3367, 2965, 2928, 1503, 1407, 817, 638. ESI HRMS *m/z* $(M+H)^+$ calcd 168.1183, obsd 168.1182.

***N*-(2-(3-Fluoro-4-methylphenyl)propan-2-yl)benzamide (S52).** The title compound was obtained as a white solid in 94% yield (1.4 g) starting from **S51** (0.88 g, 5.3 mmol) by following the procedure described for the synthesis of **S7**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.78–7.70 (m, 2H), 7.52–7.44 (m, 1H), 7.41 (dd, J = 8.3, 6.9 Hz, 2H), 7.17–6.97 (m, 3H), 6.45 (s, 1H), 2.23 (d, J = 1.8 Hz, 3H), 1.77 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 161.4 (d, $J_{C\text{-}F}$ = 243.9 Hz), 146.9 (d, $J_{C\text{-}F}$ = 6.7 Hz), 135.3, 131.5, 131.5 (d, $J_{C\text{-}F}$ = 5.8 Hz), 128.7, 127.0, 123.0 (d, $J_{C\text{-}F}$ = 17.3 Hz), 120.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 111.9 (d, $J_{C\text{-}F}$ = 23.5 Hz), 55.9 (d, $J_{C\text{-}F}$ = 1.7 Hz), 29.4, 14.3 (d, $J_{C\text{-}F}$ = 3.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −117.2. IR (neat, cm^{-1}): 3309, 3058, 2980, 1641, 1532, 1189. ESI HRMS *m/z* $(M+Na)^+$ calcd 294.1265, obsd 294.1273.

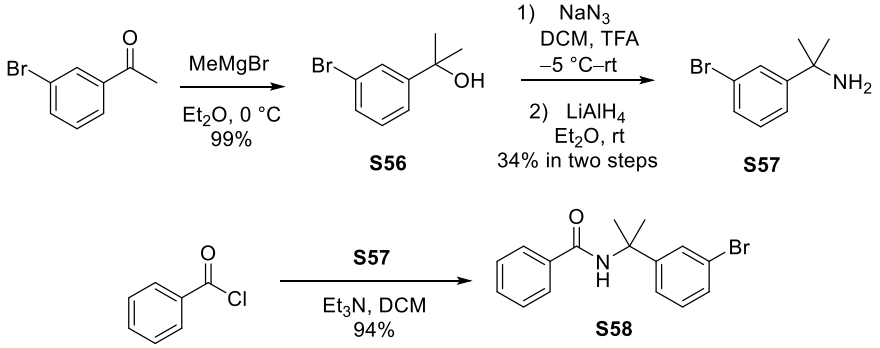


2-(4-Chloro-3-methoxyphenyl)propan-2-ol (S53). The title compound was obtained as a light yellow solid in 63% yield (3.8 g) starting from 4-bromo-1-chloro-2-methoxybenzene (6.6 g, 30 mmol) by following the procedure described for the synthesis of **S15**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.3 Hz, 1H), 7.15 (d, J = 2.1 Hz, 1H), 6.94 (dd, J = 8.2, 2.1 Hz, 1H), 3.92 (s, 3H), 1.86 (s, 1H), 1.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 149.6, 129.8, 120.8, 117.5, 108.9, 72.6, 56.2, 31.9. IR (neat, cm^{-1}): 3424, 2974, 2933, 1578, 1487, 1400, 1058, 709. ESI HRMS *m/z* $(M+Na)^+$ calcd 223.0496, obsd 223.0500 $[C_{10}H_{13}{}^{35}ClNaO_2]^+$.

2-(4-Chloro-3-methoxyphenyl)propan-2-amine (S54). The title compound was obtained as a light yellow oil in 72% yield (2.0 g) starting from **S53** (2.7 g, 13.5 mmol) by following the procedure described for the synthesis of **S16**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 2.1 Hz, 1H), 7.00 (dd, J = 8.3, 2.1 Hz, 1H), 3.92 (s, 3H), 1.69 (br s, 2H), 1.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.7, 129.7, 120.3, 117.9, 109.4, 56.2, 52.6, 33.1. IR (neat, cm^{-1}): 3366, 2965, 1576, 1487, 1057, 708. ESI HRMS *m/z* $(M+H)^+$ calcd 200.0837, obsd 200.0836 $[C_{10}H_{15}{}^{35}ClNO]^+$.

***N*-(2-(4-Chloro-3-methoxyphenyl)propan-2-yl)benzamide (S55).** The title compound was obtained as a white solid in 81% yield (0.66 g) starting from **S54** (0.53 g, 2.7 mmol) by following the procedure described for the synthesis of **S7**. ^1H NMR

(400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.52–7.46 (m, 1H), 7.45–7.38 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.48 (s, 1H), 3.86 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 155.0, 147.2, 135.3, 131.6, 130.1, 128.7, 126.9, 120.9, 117.9, 109.3, 56.2 (2C), 29.5. IR (neat, cm^{-1}): 3311, 3059, 2975, 1644, 1487, 1059, 713. ESI HRMS *m/z* $(M+Na)^+$ calcd 326.0918, obsd 326.0928 $[C_{17}H_{18}{}^{35}ClNNaO_2]^+$.

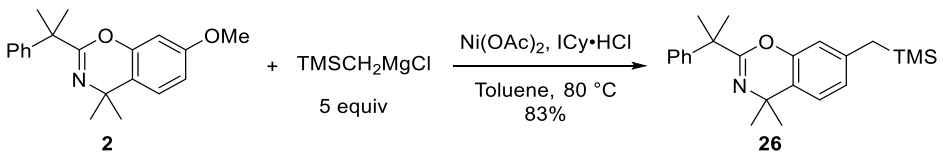


2-(3-Bromophenyl)propan-2-ol (S56).[9] The title compound was obtained as a colorless oil in 99% yield (6.7 g) starting from 1-(3-bromophenyl)ethan-1-one (6.0 g, 30 mmol) by following the procedure described for the synthesis of **S1**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 1.9 Hz, 1H), 7.44–7.36 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 1.92 (s, 1H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 130.0, 129.9, 127.9, 123.2, 122.6, 72.4, 31.8.

2-(3-Bromophenyl)propan-2-amine (S57).[10] The title compound was obtained as a light yellow oil in 34% yield (2.1 g) starting from **S56** (3.6 g, 15.1 mmol) by following the procedure described for the synthesis of **S16**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 1.9 Hz, 1H), 7.42 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.34 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 1.63 (s, 3H), 1.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 129.9, 129.4, 128.3, 123.6, 122.6, 52.5, 32.9.

***N*-(2-(3-Bromophenyl)propan-2-yl)benzamide (S58).** The title compound was obtained as a white solid in 94% yield (1.2 g) starting from **S57** (0.83 g, 3.9 mmol) by following the procedure described for the synthesis of **S7**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.56 (t, *J* = 1.9 Hz, 1H), 7.52–7.46 (m, 1H), 7.45–7.39 (m, 2H), 7.39–7.32 (m, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.45 (s, 1H), 1.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 149.3, 135.2, 131.6, 130.1, 129.9, 128.7, 128.3, 127.0, 123.6, 122.8, 56.0, 29.5. IR (neat, cm^{-1}): 3246, 3056, 2973, 1633, 688. ESI HRMS *m/z* $(M+Na)^+$ calcd 340.0307, 342.0287, obsd 340.0312, 342.0292.

5. Transformation of the Product 2



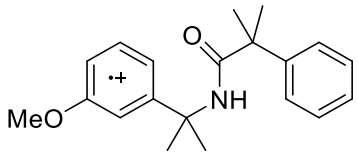
4,4-Dimethyl-2-(2-phenylpropan-2-yl)-7-((trimethylsilyl)methyl)-4*H*-benzo[*e*][1,3] Oxazine (26). To a flame-dried 10 mL round-bottomed flask with a stir bar was added

2 (130 mg, 0.42 mmol, 1 equiv), $Ni(OAc)_2$ (8.2 mg, 0.046 mmol, 0.1 equiv) and ICy·HCl[8] (23 mg, 0.084 mmol, 0.2 equiv) in a glove box, then $TMSCH_2MgCl$ (1.0 M in THF, 2.1 mL, 5 equiv) was added. The flask was capped with a rubber septum and removed from the glove box. The solvent was removed *in vacuo* and the residue was dissolved in toluene (2.0 mL). The resulting reaction mixture was stirred at 80 °C until complete consumption of **2** (monitored by TLC). Saturated aqueous solution of NH_4Cl (5.0 mL) was added to quench the reaction. The phases were separated and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give **26** (127 mg) as a colorless oil (yield = 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.28–7.21 (m, 1H), 6.83 (d, J = 2.1 Hz, 1H), 6.75 (dd, J = 8.3, 2.1 Hz, 1H), 6.61 (d, J = 8.2 Hz, 1H), 2.05 (s, 2H), 1.64 (s, 6H), 1.56 (s, 6H), 0.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 146.6, 145.4, 136.1, 128.3, 128.2, 126.9, 126.3, 125.9, 124.4, 114.9, 52.4, 44.5, 32.6, 27.4, 26.5, −1.8. IR (neat, cm^{-1}): 2967, 2926, 1682, 1493, 847, 696. IR (neat, cm^{-1}): 2967, 2926, 1682, 1493, 847, 696. ESI HRMS *m/z* $(M+H)^+$ calcd 366.2248, obsd 366.2257.

6. Computational Studies

Computational methods: The geometries were optimized in gas phase by M062X functional with 6-31G* basis set for all atoms. Vibrational frequency analysis at the same level was carried out to check the stationary point as minima. Natural orbital ananlysis was performed to examine the single occupied orbital. All the calculations were performed in Gaussian09 package.[11]

Geometries (in Å) and energies (in a.u.).



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C	-1.910122	1.113540	1.103909
C	-3.044413	1.935374	1.021988
C	-0.648966	-1.064933	0.727816
N	0.526639	-0.194656	0.662468
C	0.665515	0.710991	-0.350194
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H	-1.567115	-2.334018	2.235446
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Energies (0K) = -981.699051027

Energies (0K) + ZPE = -981.283257
Enthalpies (298K) = -981.259864

Free Energies (298K) = -981.335212

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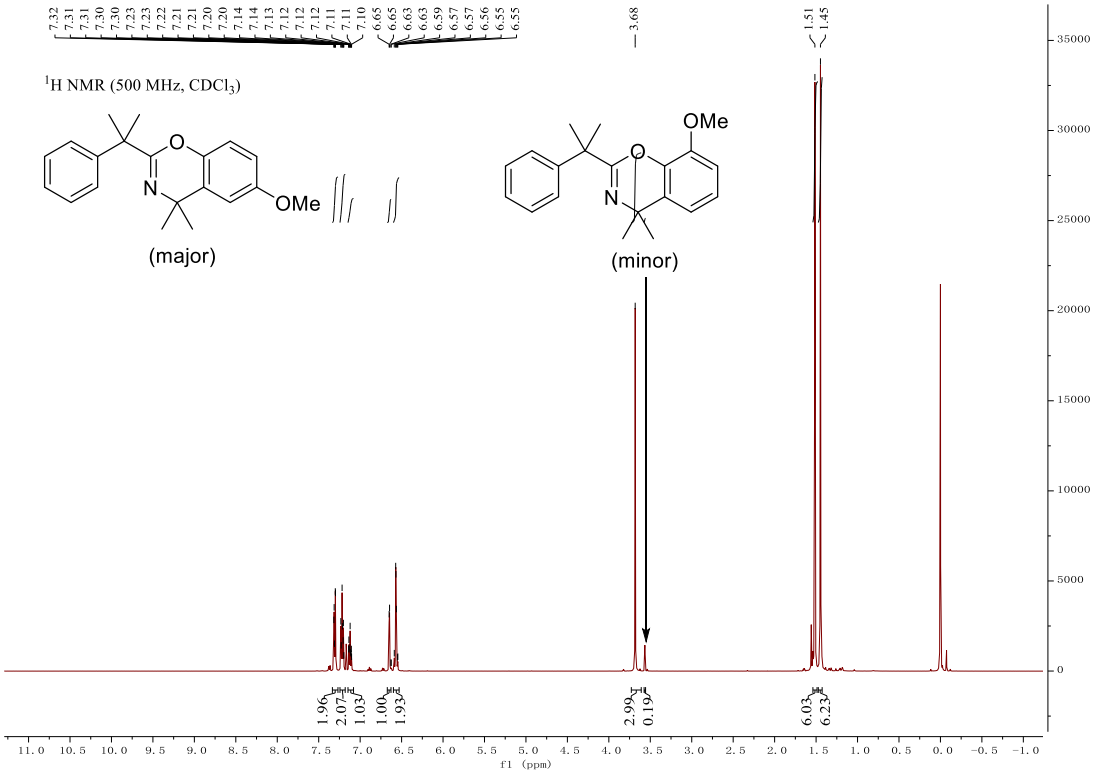
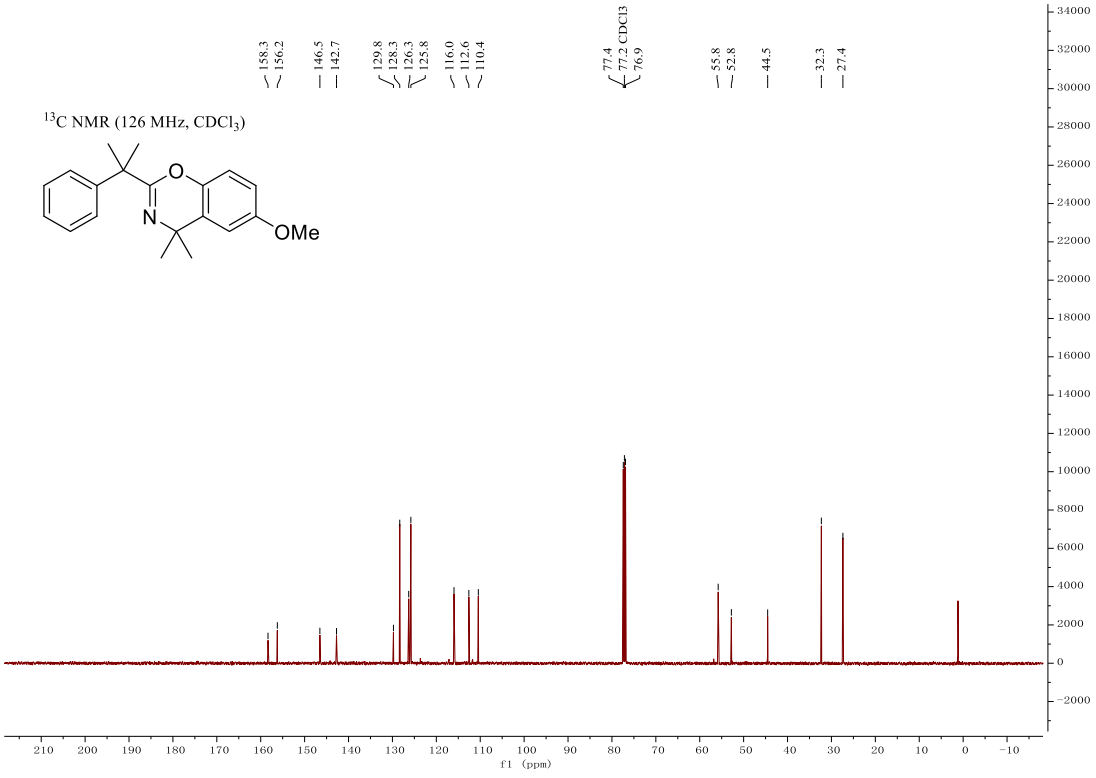
(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

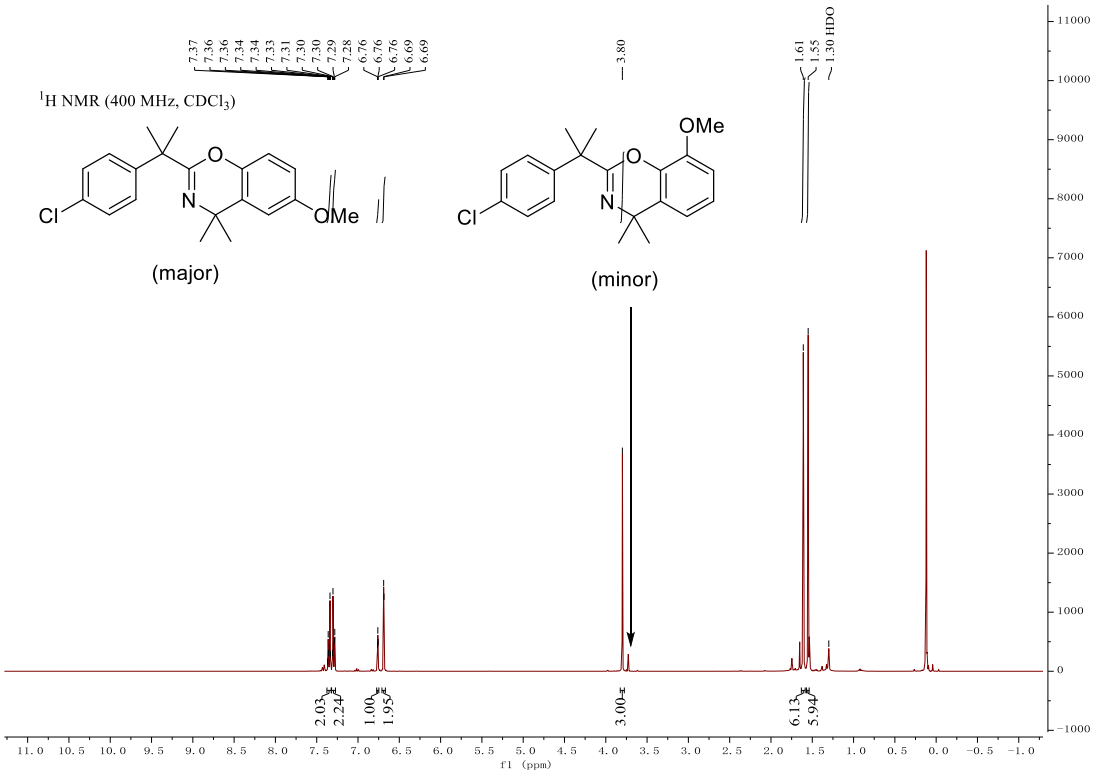
8. NMR Spectra for New Compounds

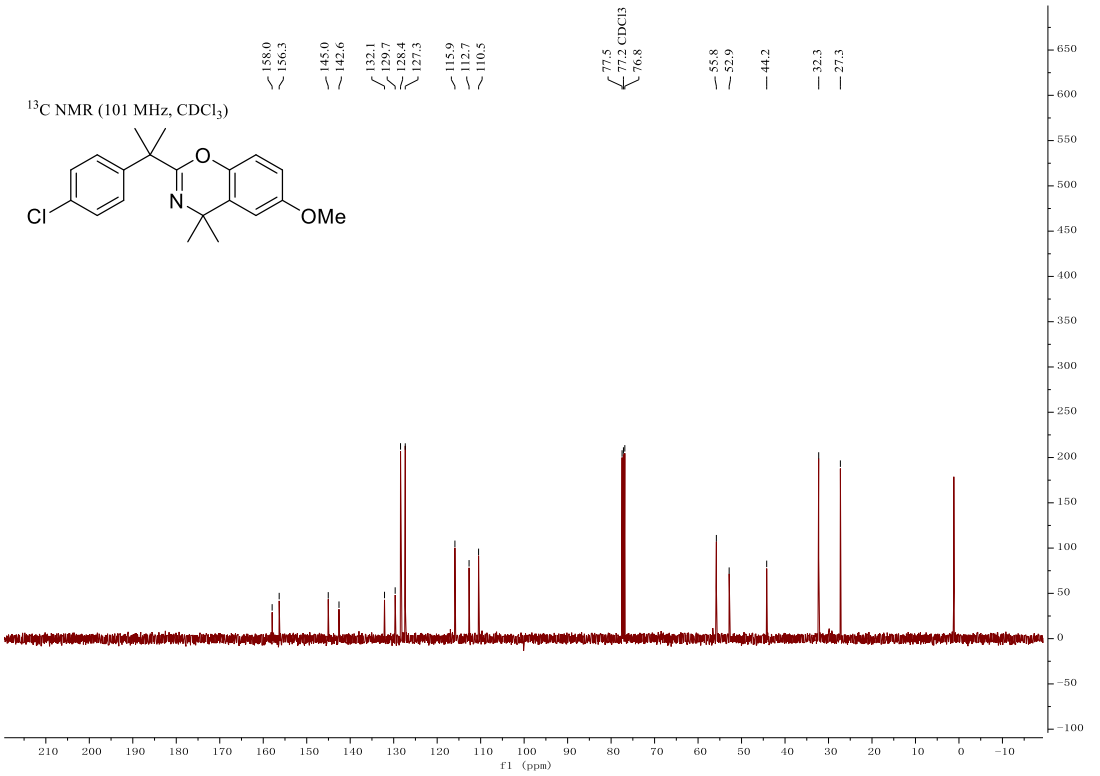
Compound 2



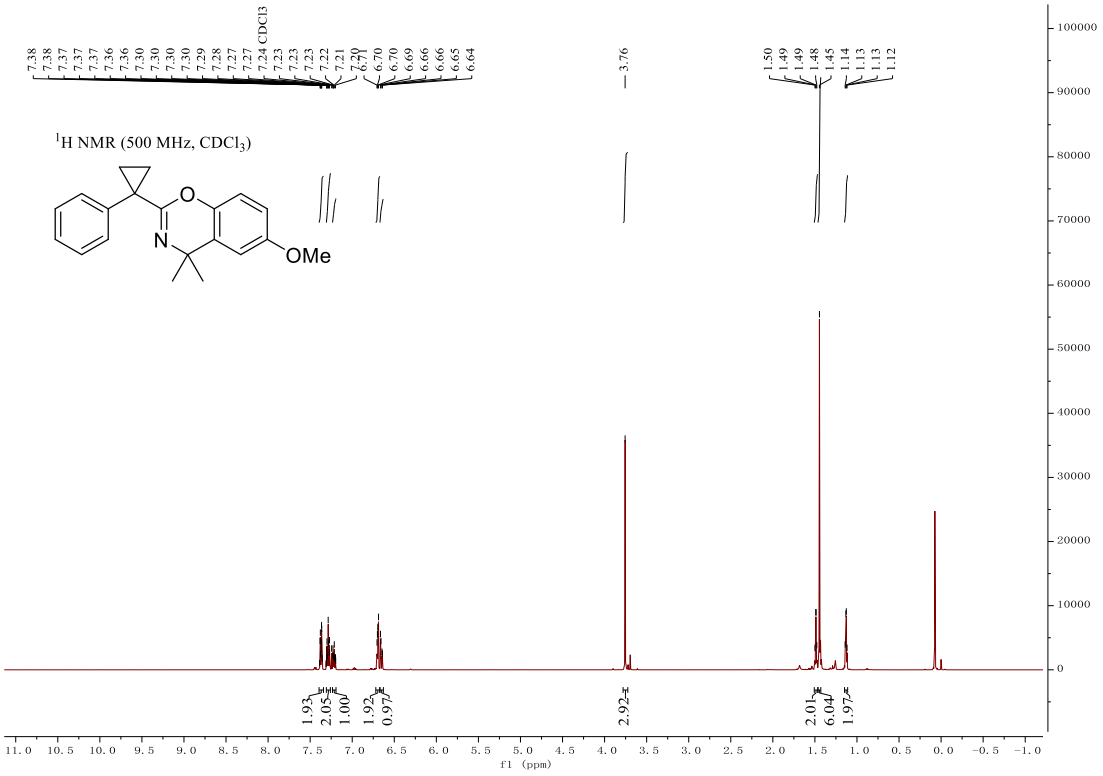


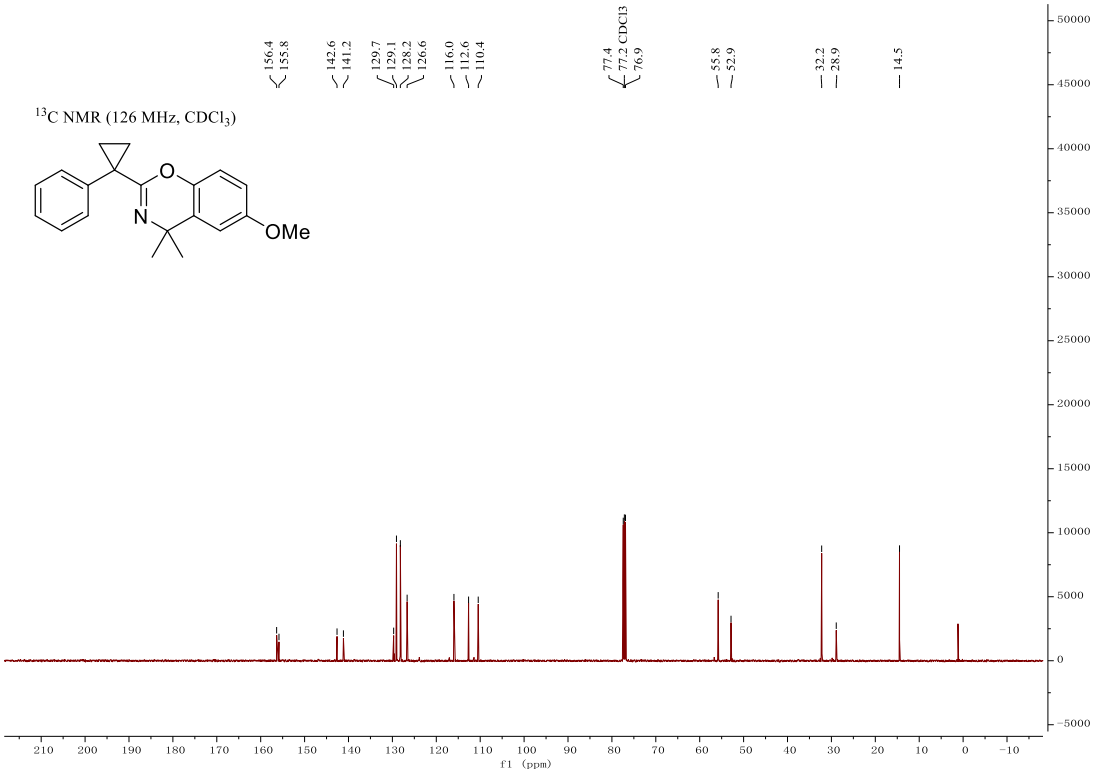
Compound 3


7.37
7.36
7.36
7.34
7.34
7.33
7.31
7.30
7.30
7.29
7.28
6.76
6.76
6.69
6.69
3.80
1.61
1.55
1.30 HDO
^{1}H NMR (400 MHz, $CDCl_3$)
Cl
O
N
OMe
(major)
(minor)
2.03
2.24
1.00
1.95
3.00
6.13
5.94
f1 (ppm)

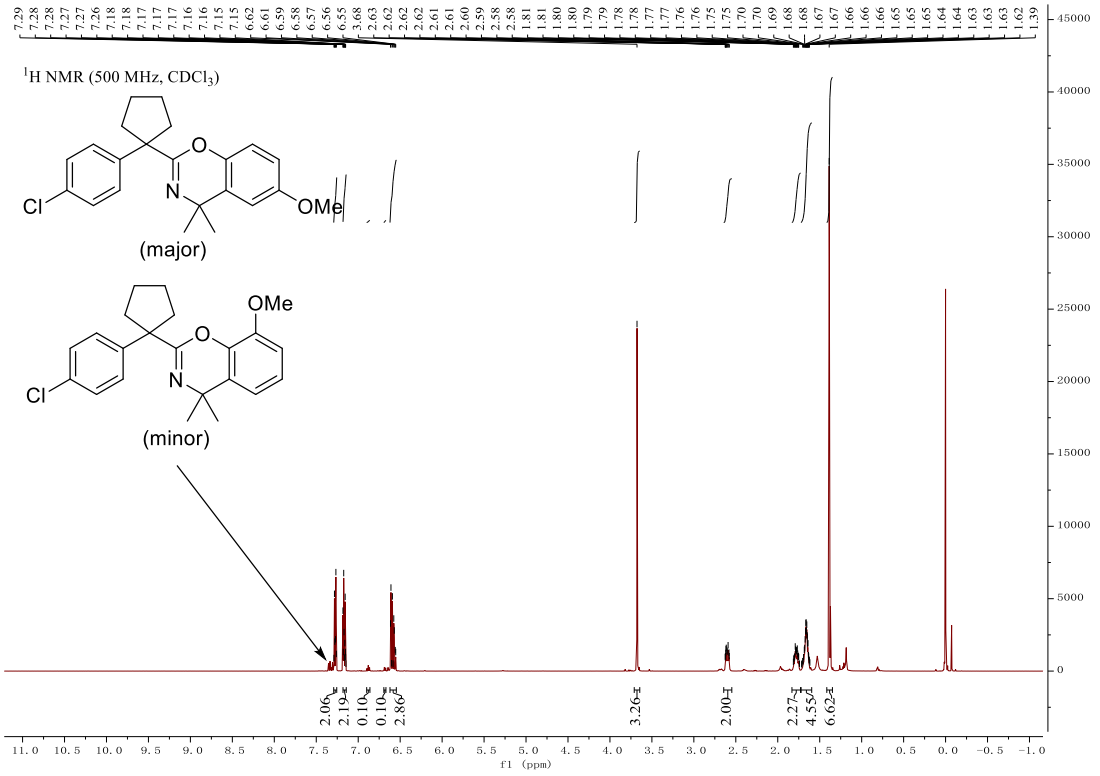

158.0
156.3
145.0
142.6
132.1
129.7
128.4
127.3
115.9
112.7
110.5
77.5
77.2 CDCl3
76.8
55.8
52.9
44.2
32.3
27.3
^{13}C NMR (101 MHz, $CDCl_3$)
Cl
O
N
OMe
f1 (ppm)

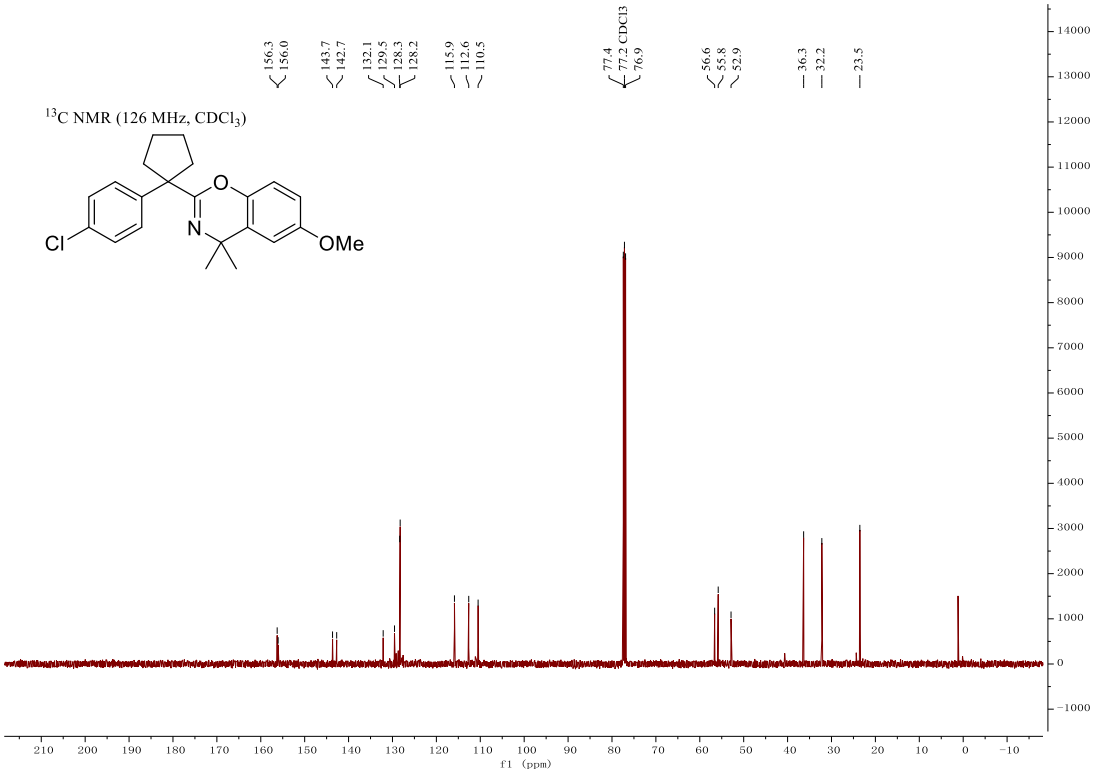
Compound 4


7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.30
7.30
7.30
7.30
7.29
7.28
7.27
7.27
7.24 CDCl3
7.23
7.23
7.23
7.22
7.21
6.70
6.70
6.69
6.66
6.66
6.65
6.64
3.76
1.50
1.49
1.49
1.48
1.45
1.14
1.13
1.13
1.12
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
OMe
1.93
2.05
1.00
1.92
0.97
2.92
2.01
6.04
1.97
f1 (ppm)

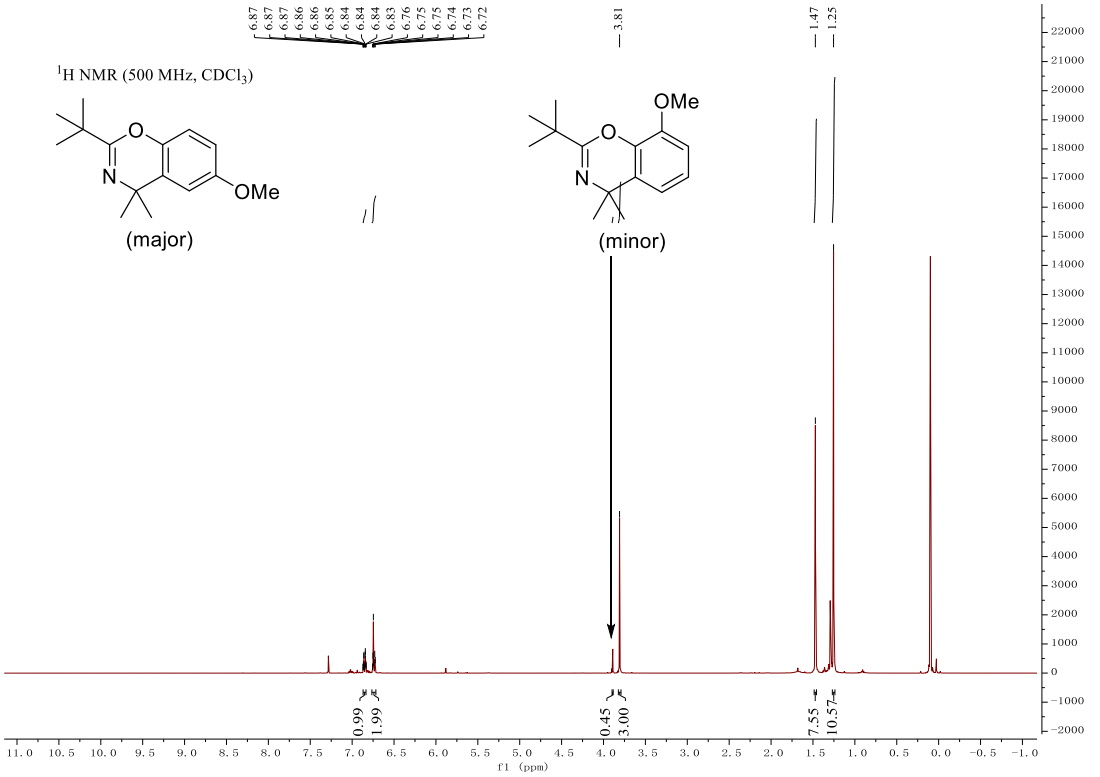

156.4
155.8
142.6
141.2
129.7
129.1
128.2
126.6
116.0
112.6
110.4
77.4
77.2 CDCl3
76.9
55.8
52.9
32.2
28.9
14.5
^{13}C NMR (126 MHz, CDCl$_3$)
O
N
OMe
f1 (ppm)

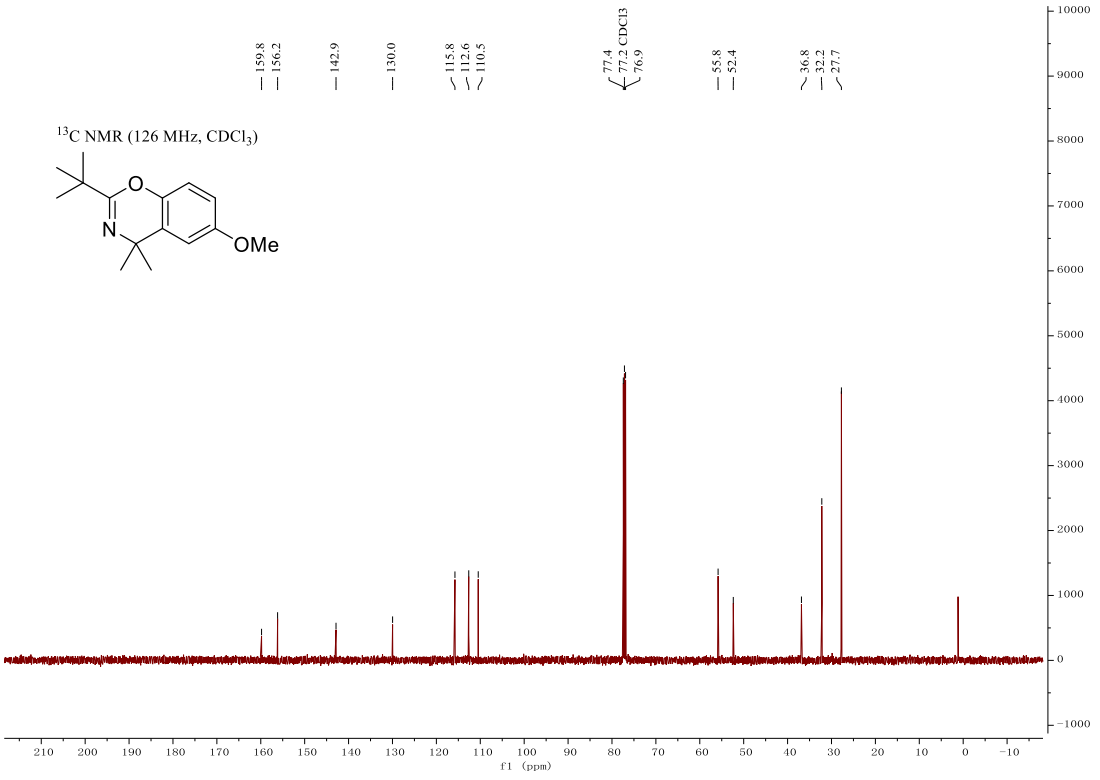
Compound 5


^{1}H NMR (500 MHz, $CDCl_3$)
Cl
O
N
OMe
(major)
OMe
O
N
Cl
(minor)
2.06
2.19
0.10
0.10
2.86
3.26
2.00
2.27
4.55
6.62
f1 (ppm)

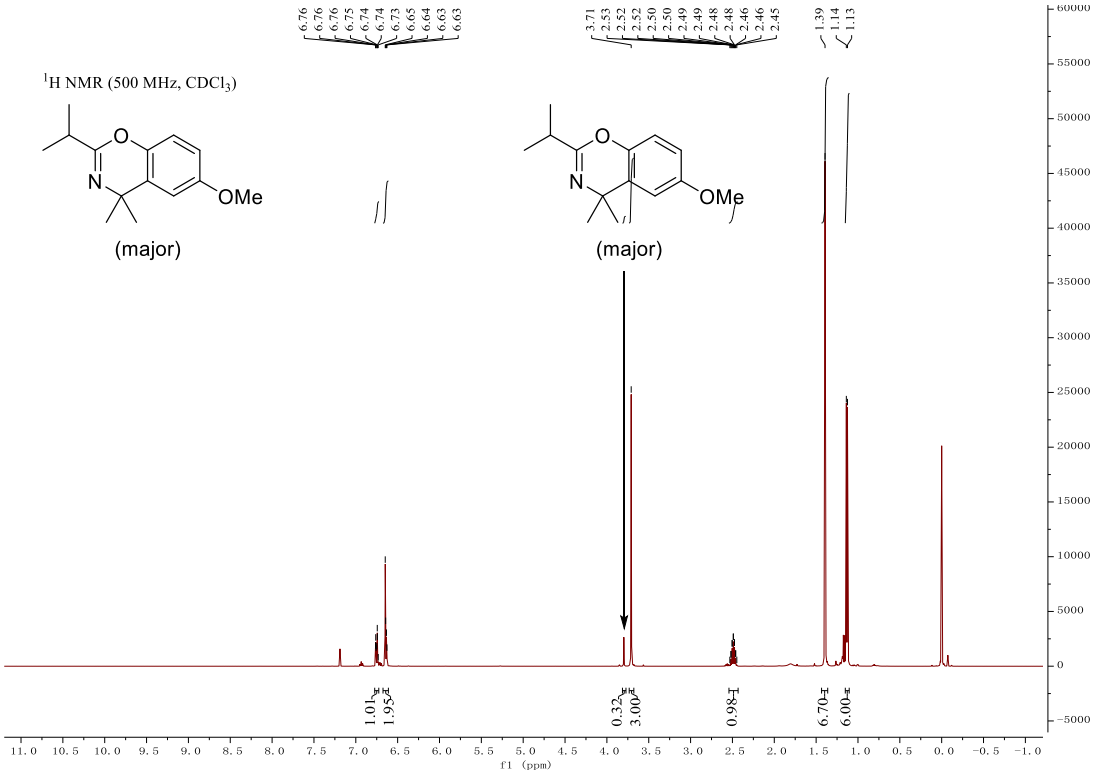

^{13}C NMR (126 MHz, $CDCl_3$)
156.3
156.0
143.7
142.7
132.1
129.5
128.3
128.2
115.9
112.6
110.5
77.4
77.2 CDCl3
76.9
56.6
55.8
52.9
36.3
32.2
23.5
Cl
O
N
OMe
f1 (ppm)

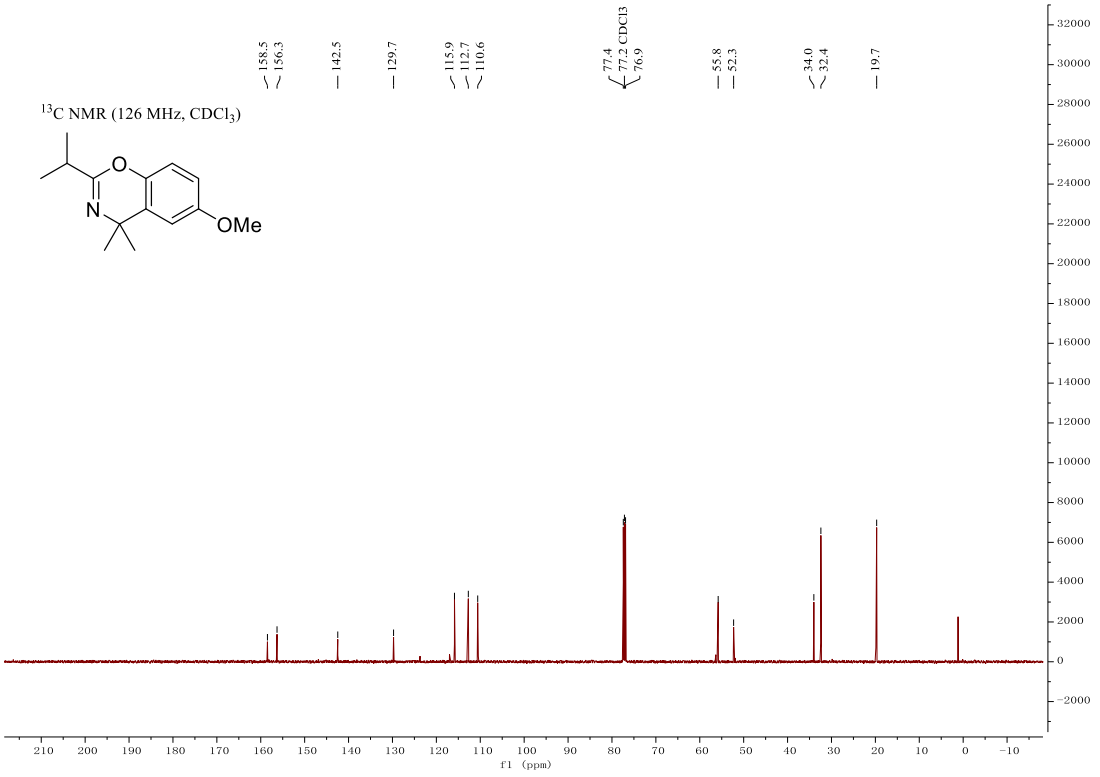
Compound 6


6.87
6.87
6.87
6.86
6.86
6.85
6.84
6.84
6.84
6.83
6.76
6.75
6.75
6.74
6.73
6.72
3.81
1.47
1.25
^{1}H NMR (500 MHz, $CDCl_3$)
OMe
(major)
OMe
(minor)
0.99
1.99
0.45
3.00
7.55
10.57
f1 (ppm)

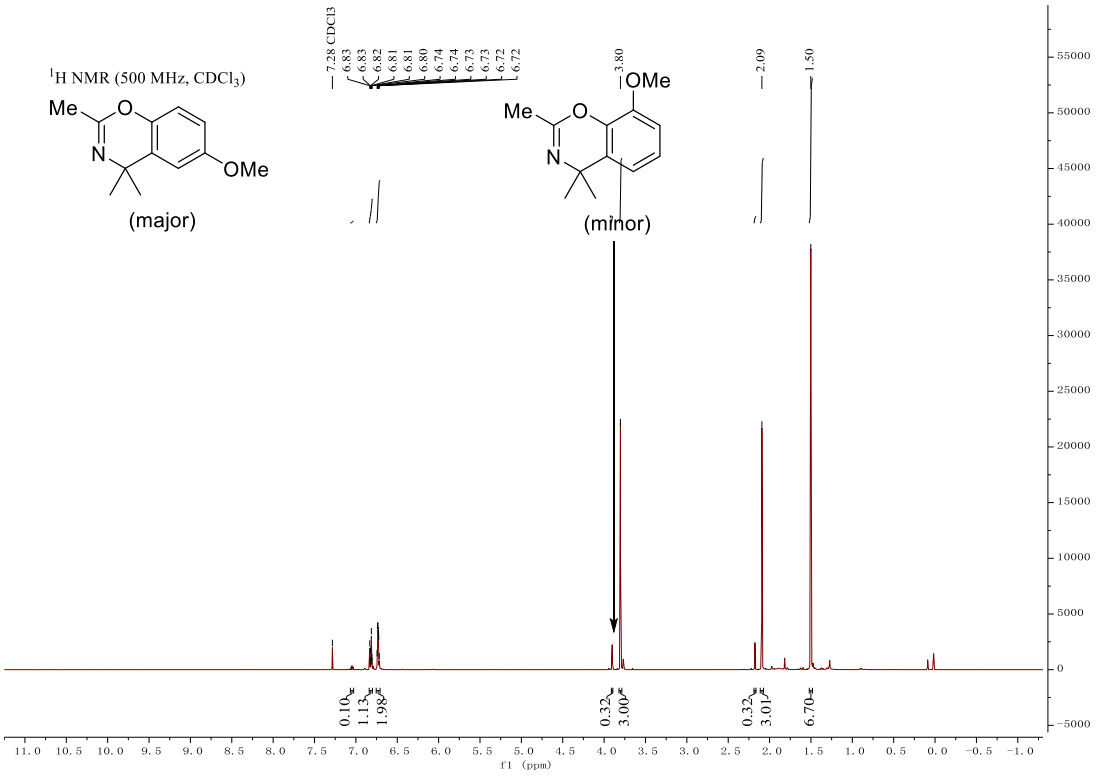

159.8
156.2
142.9
130.0
115.8
112.6
110.5
77.4
77.2 CDCl3
76.9
55.8
52.4
36.8
32.2
27.7
^{13}C NMR (126 MHz, $CDCl_3$)
OMe
f1 (ppm)

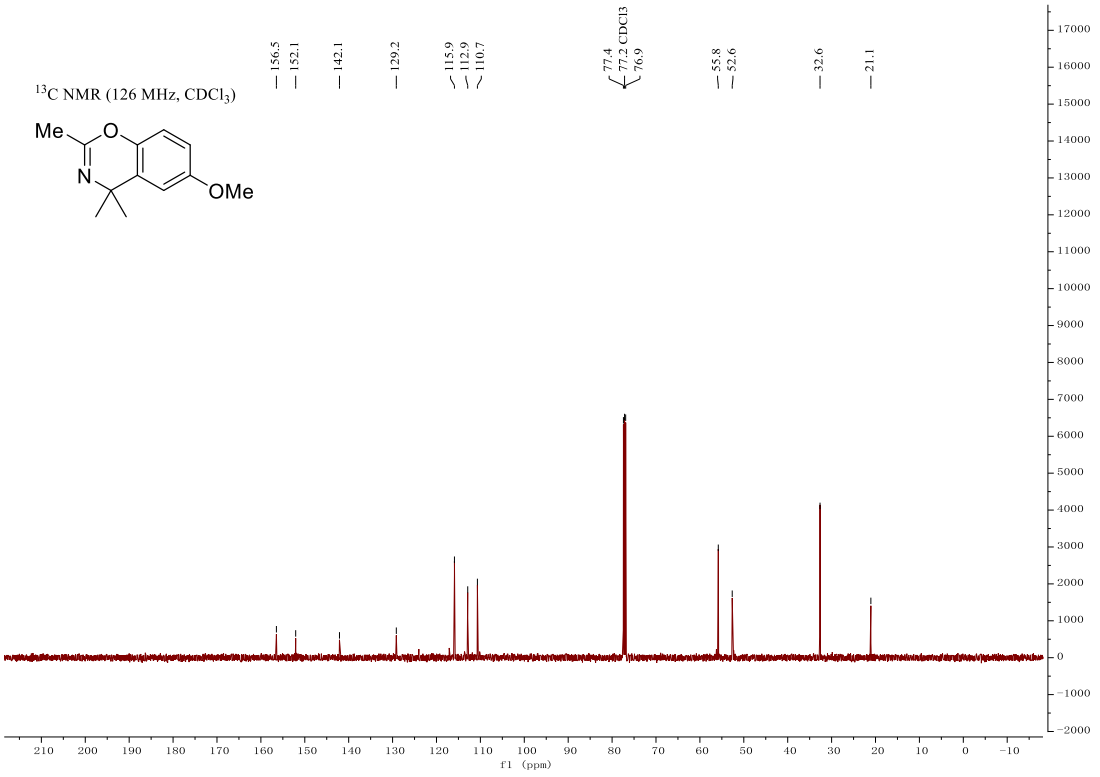
Compound 7


^{1}H NMR (500 MHz, $CDCl_3$)
OMe
(major)
OMe
(major)
6.76
6.76
6.76
6.75
6.74
6.74
6.73
6.65
6.64
6.63
6.63
3.71
2.53
2.52
2.52
2.50
2.50
2.49
2.49
2.48
2.48
2.46
2.46
2.45
1.39
1.14
1.13
1.01
1.95
0.32
3.00
0.98
6.70
6.00
f1 (ppm)

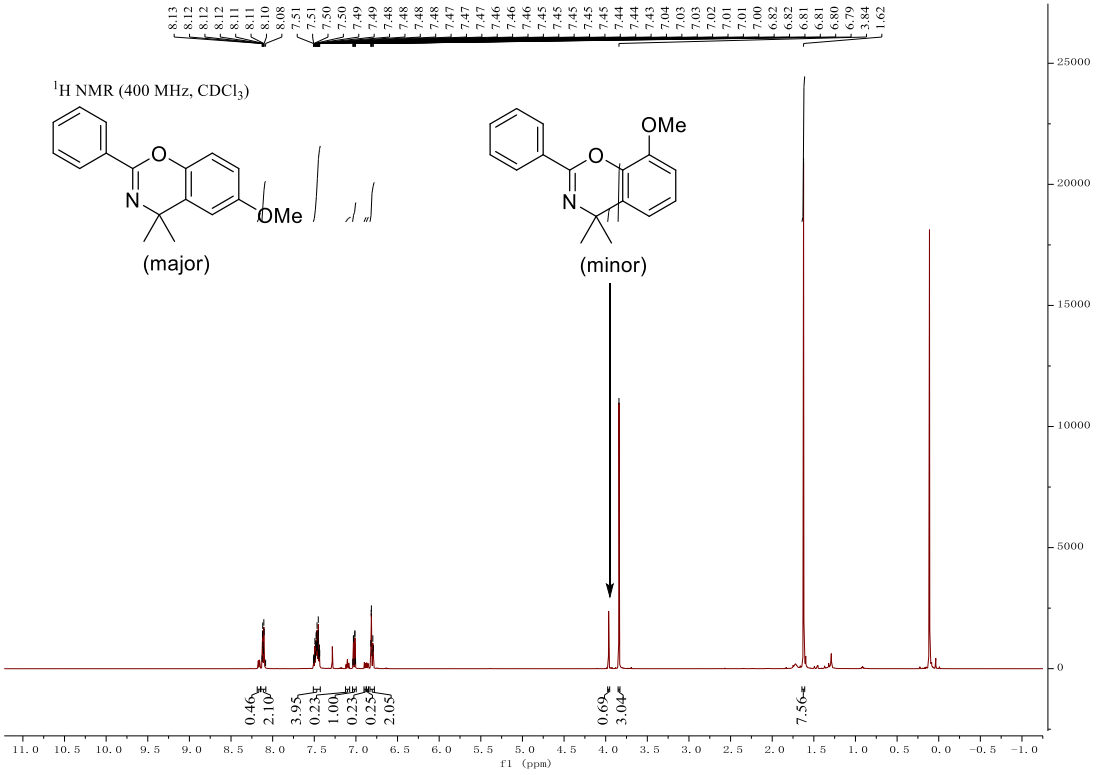

^{13}C NMR (126 MHz, $CDCl_3$)
OMe
158.5
156.3
142.5
129.7
115.9
112.7
110.6
77.4
77.2 CDCl3
76.9
55.8
52.3
34.0
32.4
19.7
f1 (ppm)

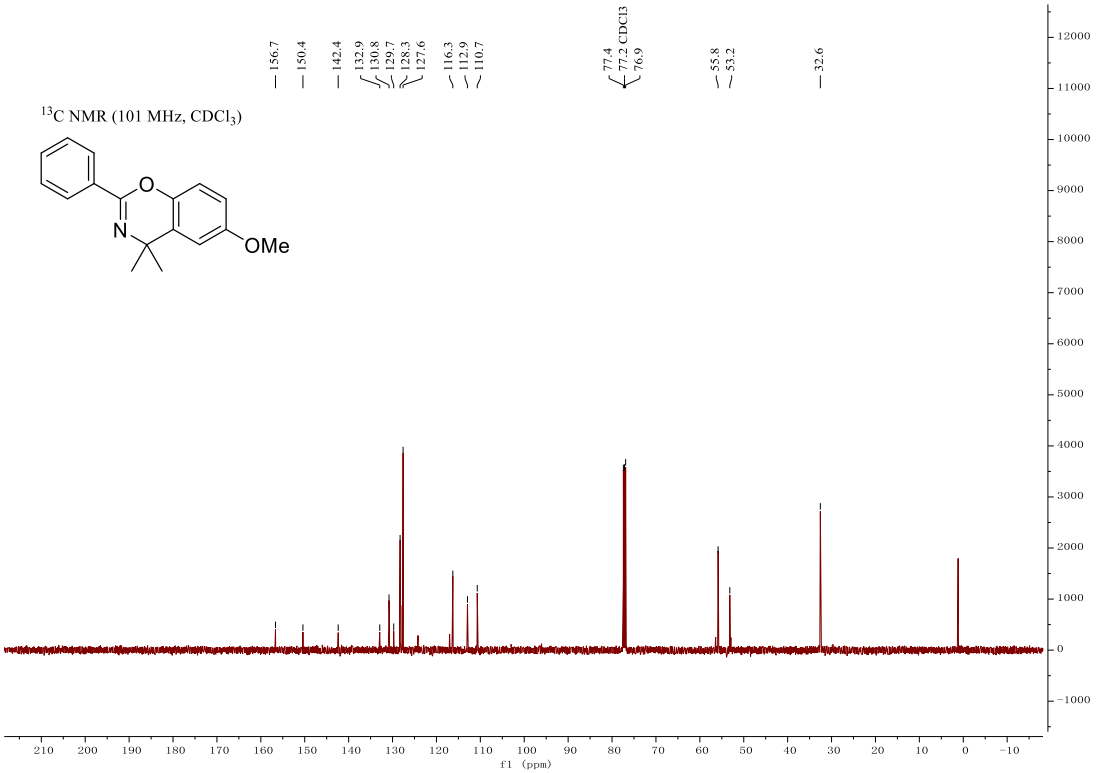
Compound 8


^{1}H NMR (500 MHz, CDCl$_3$)
Me
O
N
OMe
(major)
OMe
(minor)
7.28 CDCl3
6.83
6.82
6.81
6.80
6.74
6.73
6.72
3.80
2.09
1.50
0.10
1.13
1.98
0.32
3.00
0.32
3.01
6.70
f1 (ppm)

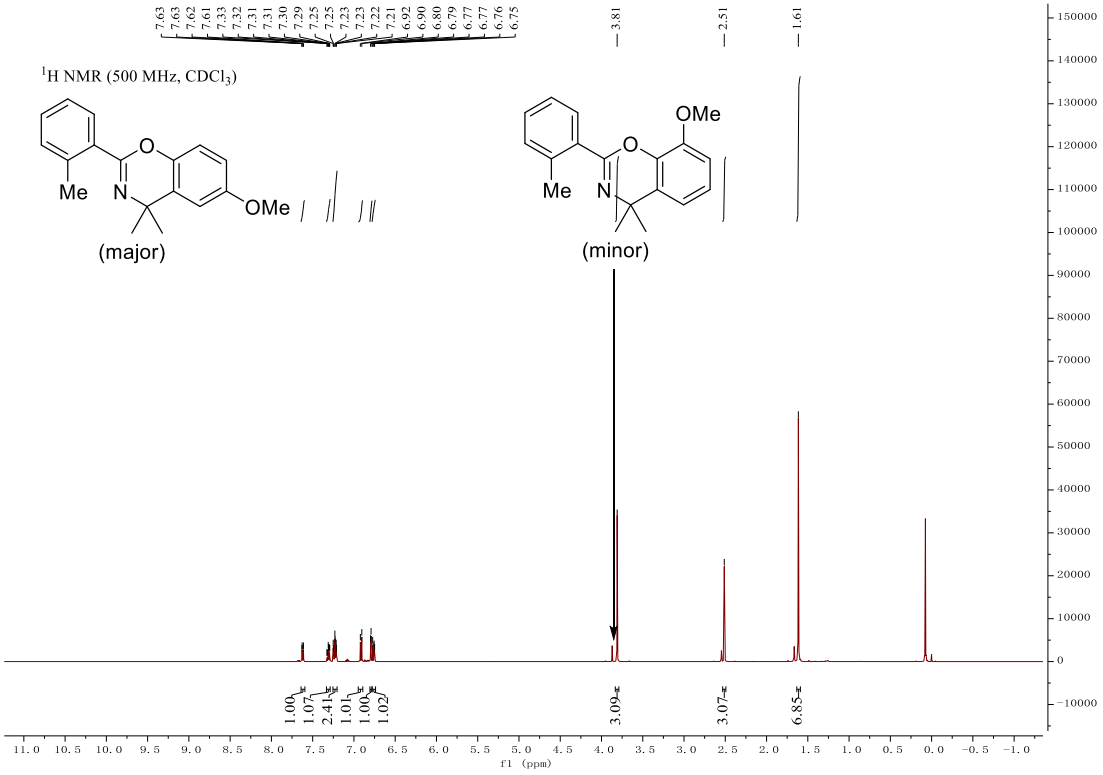

^{13}C NMR (126 MHz, CDCl$_3$)
Me
O
N
OMe
156.5
152.1
142.1
129.2
115.9
112.9
110.7
77.4
77.2 CDCl3
76.9
55.8
52.6
32.6
21.1
f1 (ppm)

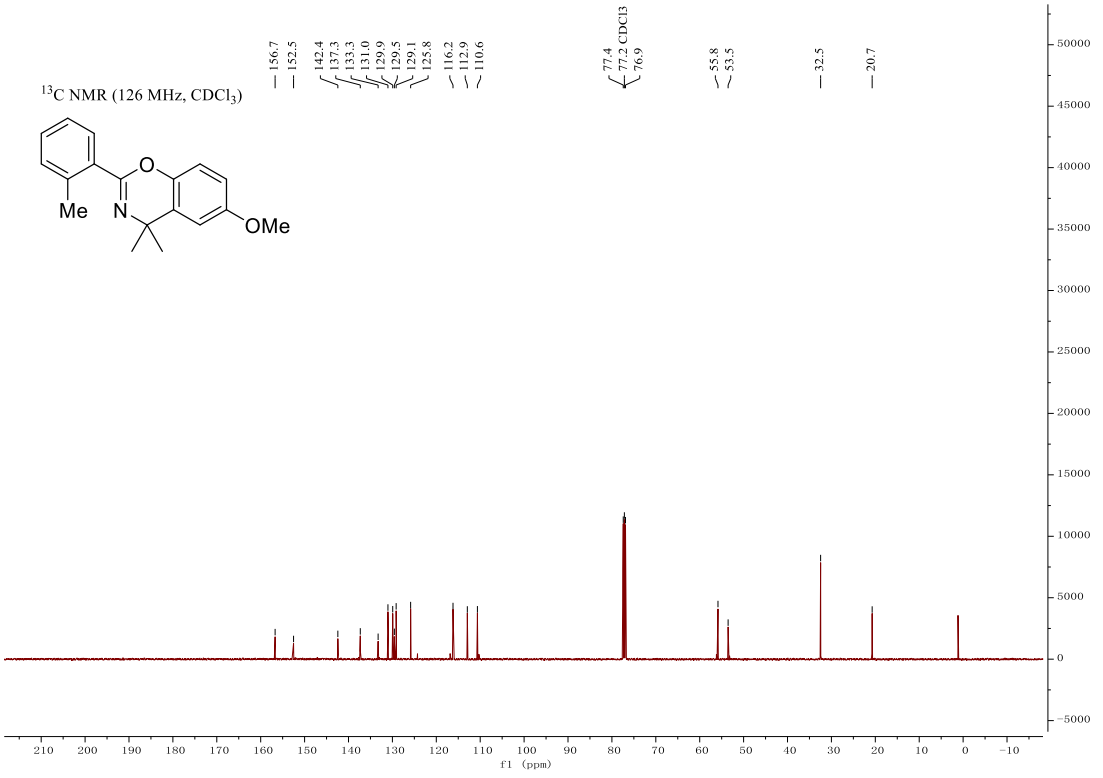
Compound 9


^{1}H NMR (400 MHz, $CDCl_3$)
OMe
(major)
OMe
(minor)
0.46
2.10
3.95
0.23
1.00
0.23
0.25
2.05
0.69
3.04
7.56
f1 (ppm)

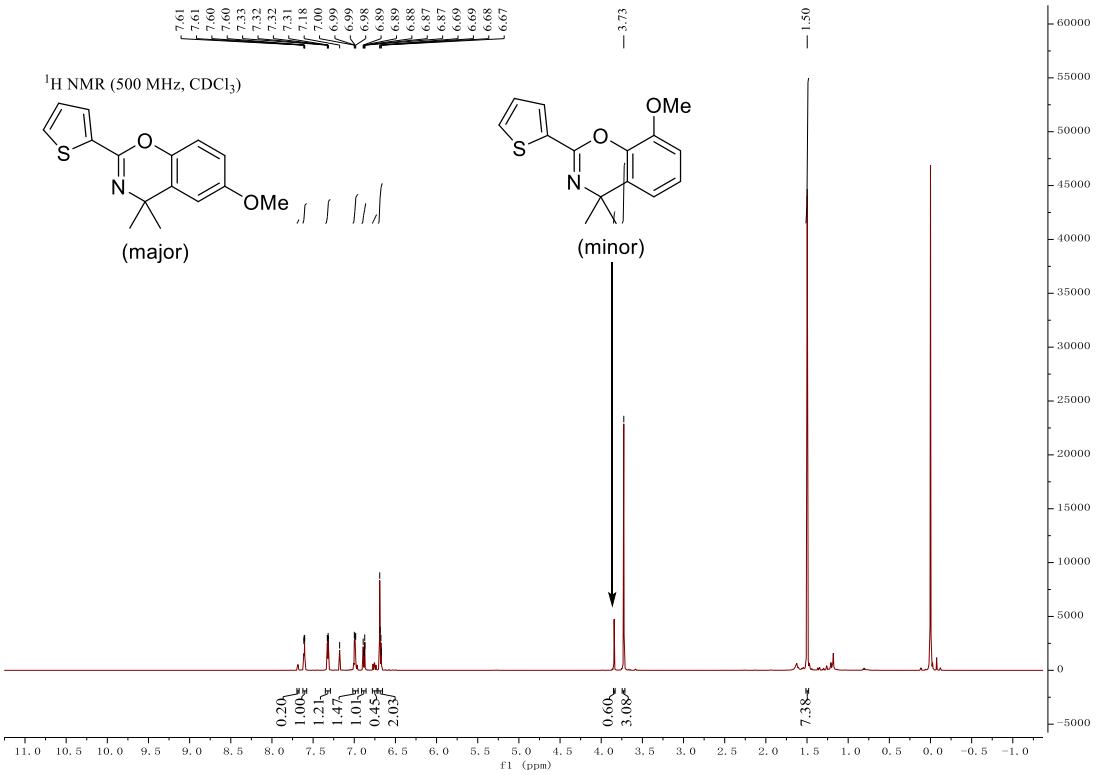

^{13}C NMR (101 MHz, $CDCl_3$)
OMe
156.7
150.4
142.4
132.9
130.8
129.7
128.3
127.6
116.3
112.9
110.7
77.4
77.2 CDCl3
76.9
55.8
53.2
32.6
f1 (ppm)

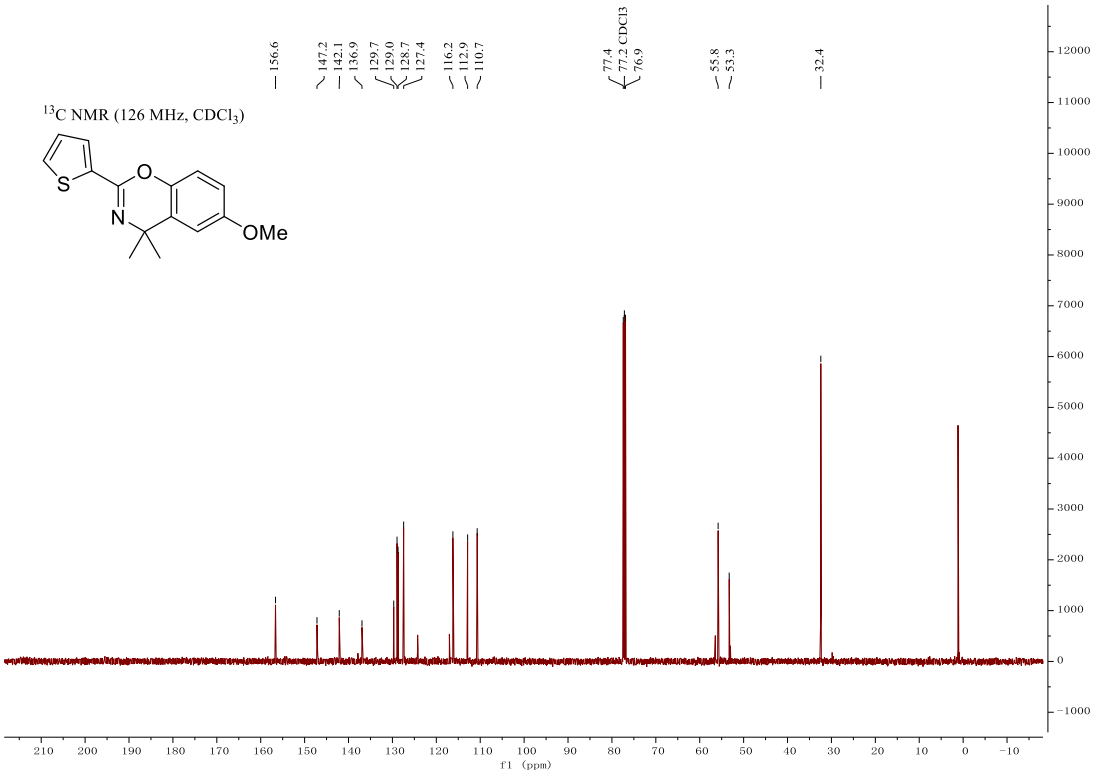
Compound 10


^{1}H NMR (500 MHz, $CDCl_3$)
Me
O
N
OMe
(major)
OMe
Me
O
N
(minor)
7.63 7.63 7.62 7.61 7.33 7.32 7.31 7.31 7.30 7.29 7.25 7.25 7.23 7.23 7.22 7.21 6.92 6.90 6.80 6.79 6.77 6.77 6.76 6.75
3.81
2.51
1.61
1.00 1.07 2.41 1.01 1.00 1.02
3.09
3.07
6.85
f1 (ppm)

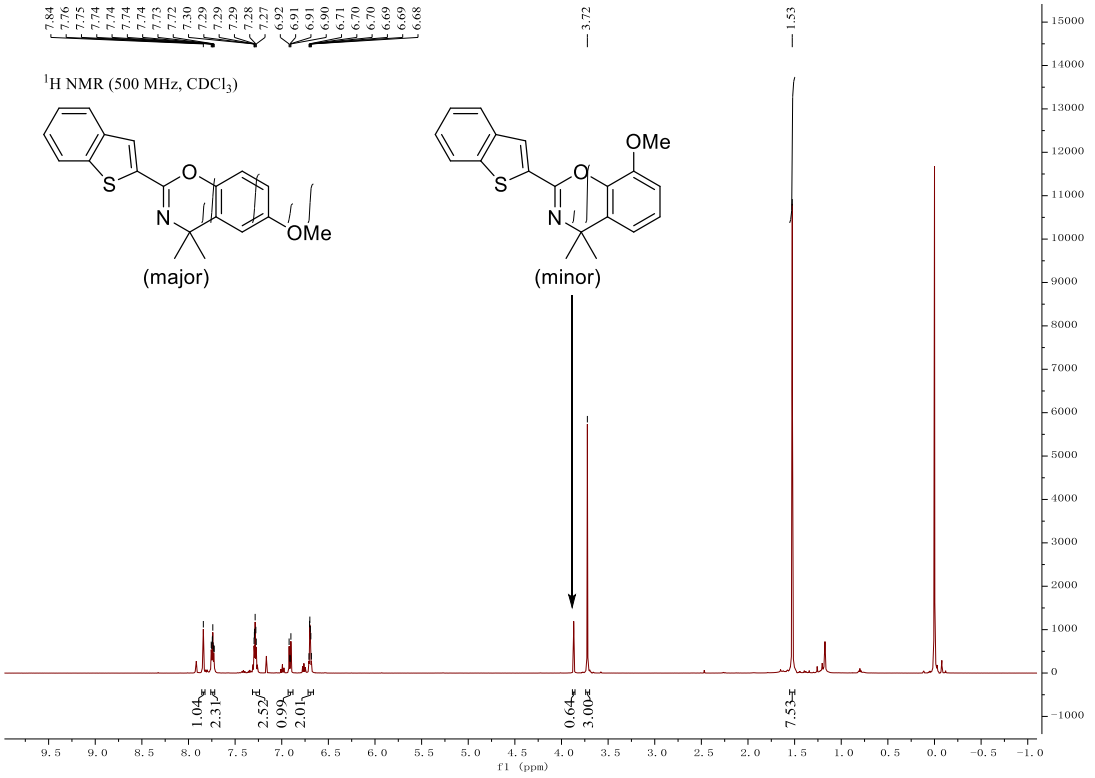

^{13}C NMR (126 MHz, $CDCl_3$)
Me
O
N
OMe
156.7
152.5
142.4
137.3
133.3
131.0
129.9
129.5
129.1
125.8
116.2
112.9
110.6
77.4
77.2 CDCl3
76.9
55.8
53.5
32.5
20.7
f1 (ppm)

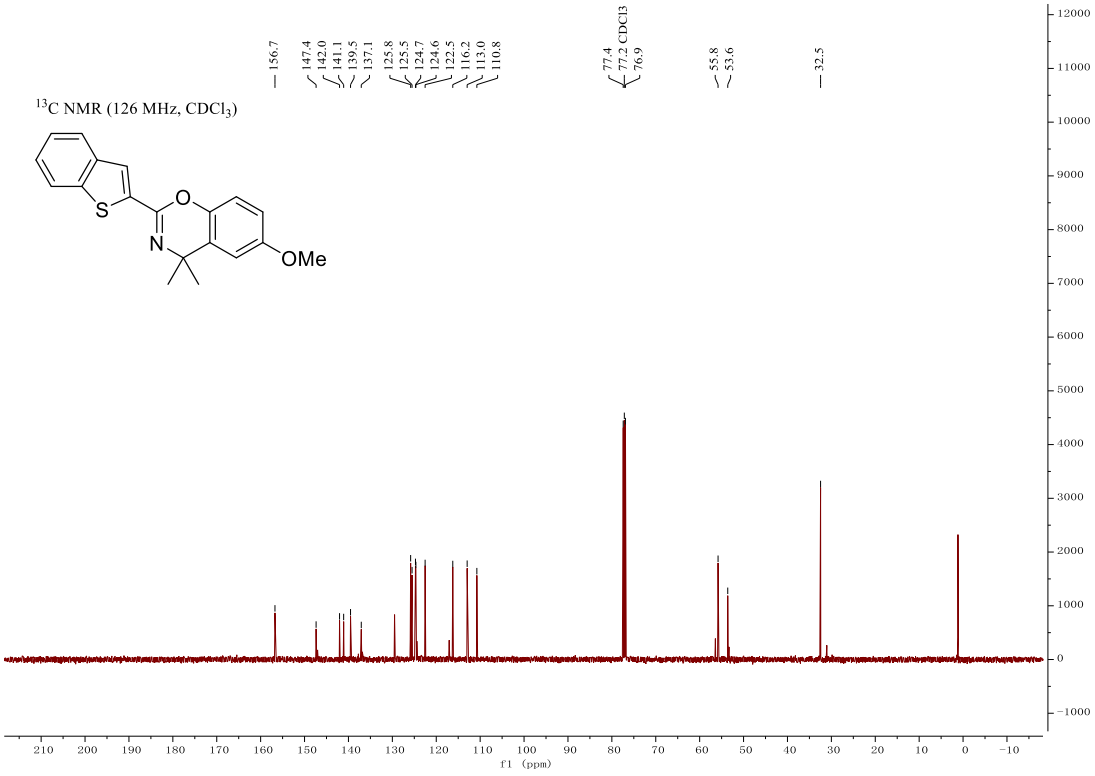
Compound 11


7.61
7.61
7.60
7.60
7.33
7.32
7.31
7.18
7.00
6.99
6.99
6.98
6.89
6.89
6.88
6.87
6.87
6.69
6.69
6.68
6.67
3.73
1.50
^{1}H NMR (500 MHz, $CDCl_3$)
OMe
(major)
OMe
(minor)
0.20
1.00
1.21
1.47
1.01
0.45
2.03
0.60
3.08
7.38
f1 (ppm)

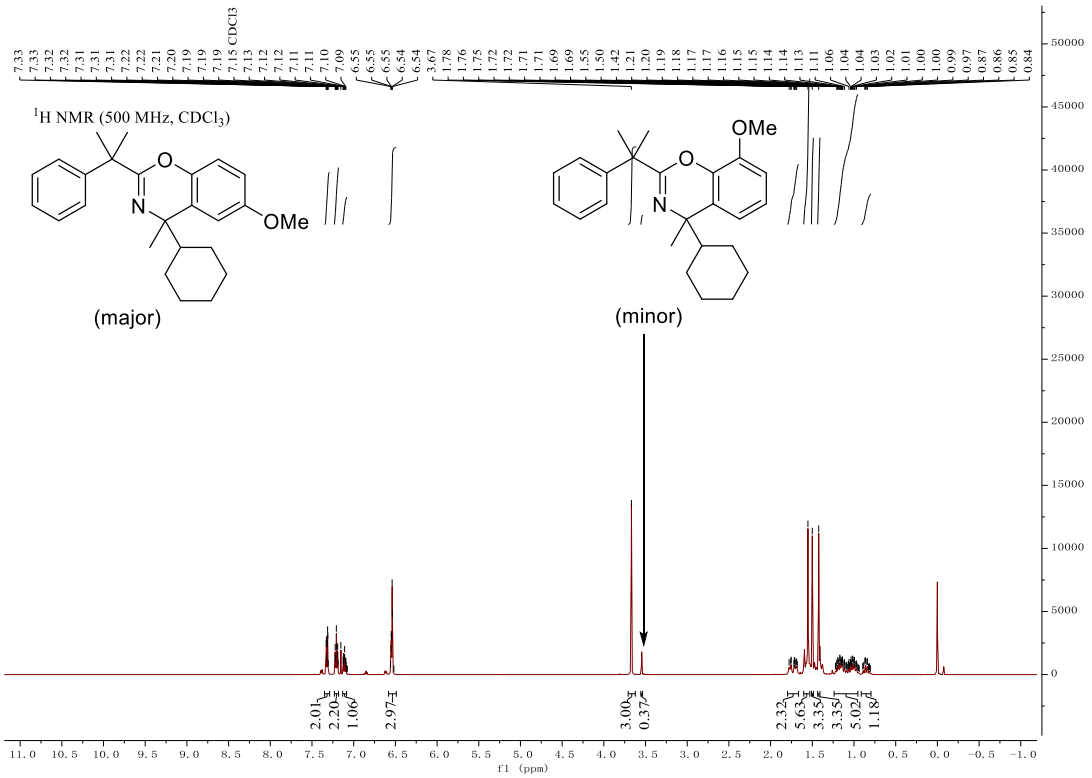

156.6
147.2
142.1
136.9
129.7
129.0
128.7
127.4
116.2
112.9
110.7
77.4
77.2 CDCl3
76.9
55.8
53.3
32.4
^{13}C NMR (126 MHz, $CDCl_3$)
OMe
f1 (ppm)

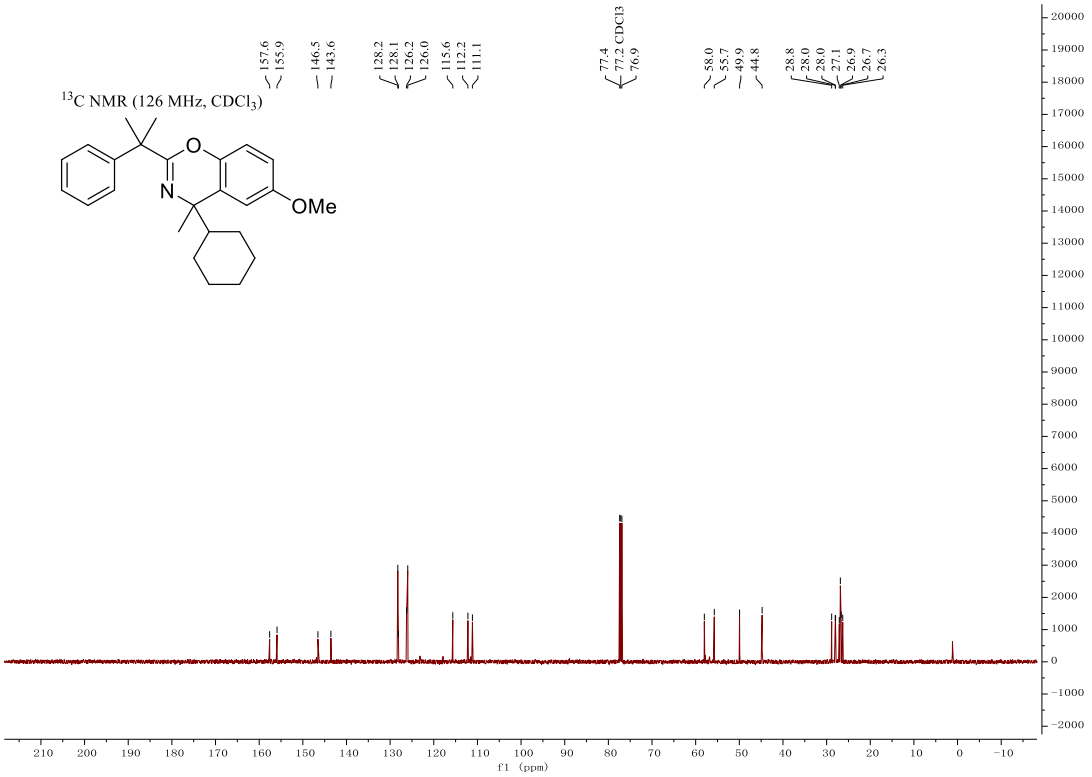
Compound 12


7.84
7.76
7.75
7.74
7.74
7.74
7.73
7.72
7.30
7.29
7.29
7.28
7.27
6.92
6.91
6.91
6.90
6.71
6.70
6.70
6.69
6.69
6.68
3.72
1.53
^{1}H NMR (500 MHz, $CDCl_3$)
O
S
N
OMe
(major)
OMe
(minor)
1.04
2.31
2.52
0.99
2.01
0.64
3.00
7.53
f1 (ppm)

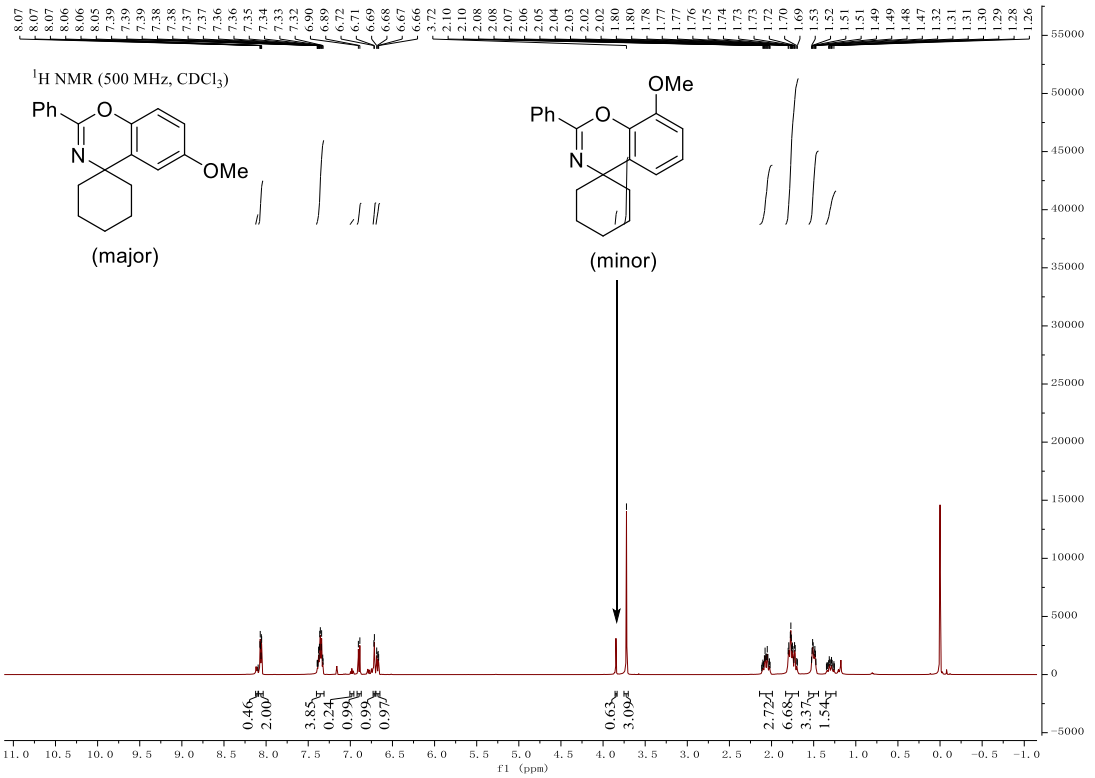

156.7
147.4
142.0
141.1
139.5
137.1
125.8
125.5
124.7
124.6
122.5
116.2
113.0
110.8
77.4
77.2 CDCl3
76.9
55.8
53.6
32.5
^{13}C NMR (126 MHz, $CDCl_3$)
O
S
N
OMe
f1 (ppm)

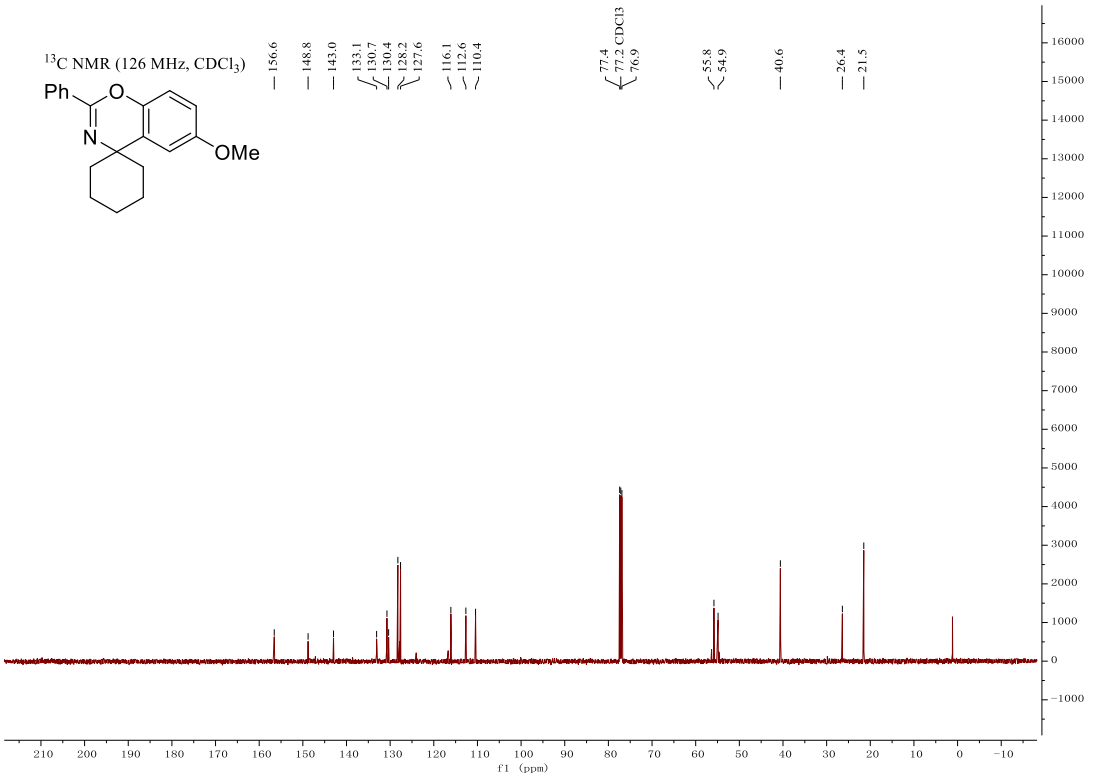
Compound 13


^{1}H NMR (500 MHz, $CDCl_3$)
OMe
(major)
OMe
(minor)
2.01
2.20
1.06
2.97
3.00
0.37
2.32
5.63
3.35
3.35
5.02
1.18
f1 (ppm)

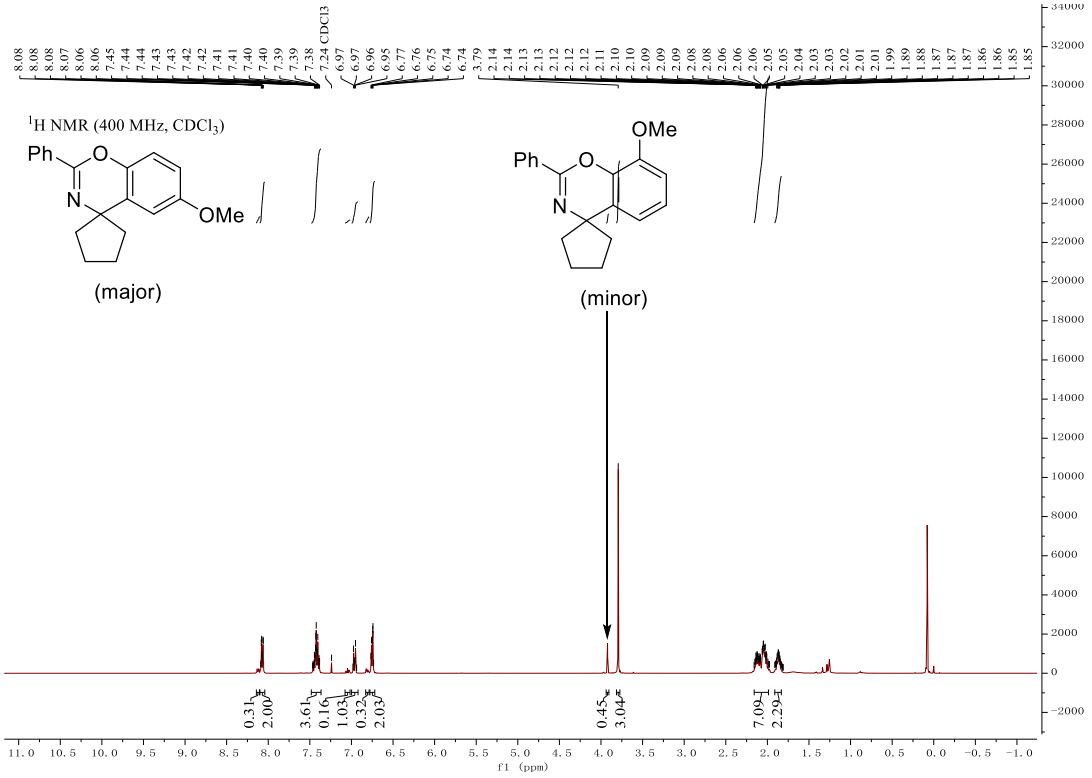

^{13}C NMR (126 MHz, $CDCl_3$)
OMe
157.6
155.9
146.5
143.6
128.2
128.1
126.2
126.0
115.6
112.2
111.1
77.4
77.2 CDCl3
76.9
58.0
55.7
49.9
44.8
28.8
28.0
28.0
27.1
26.9
26.7
26.3
f1 (ppm)

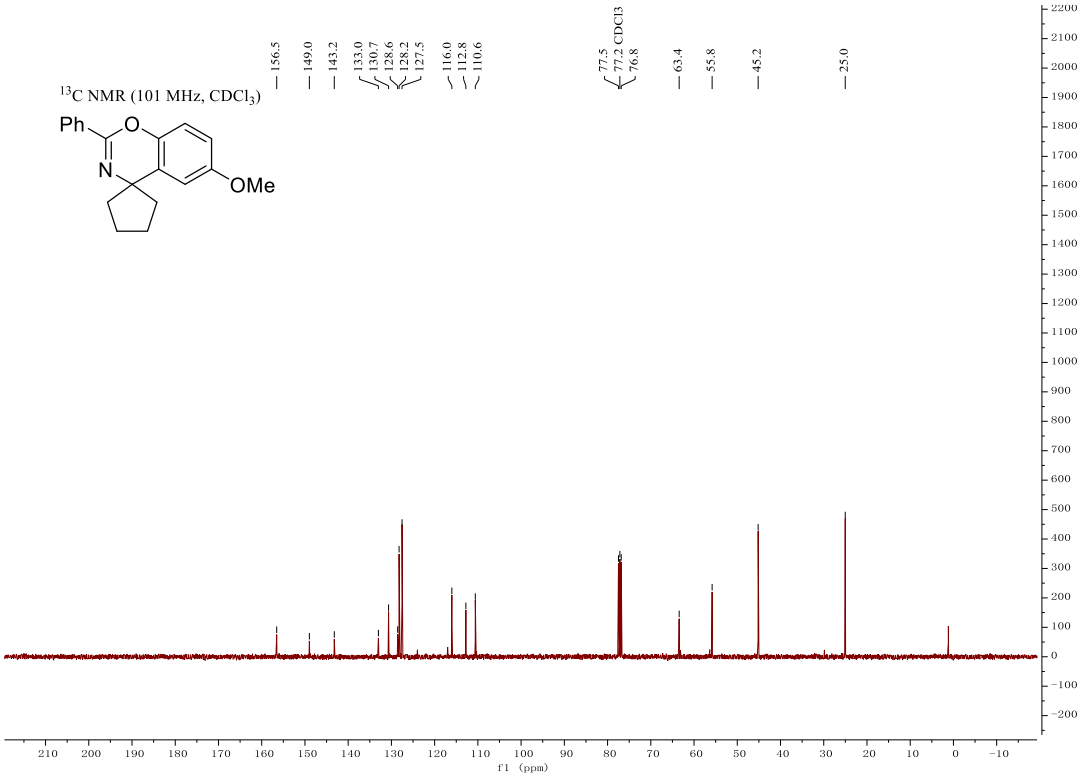
Compound 14


^{1}H NMR (500 MHz, CDCl$_3$)
Ph
O
N
OMe
(major)
(minor)
0.46
2.00
3.85
0.24
0.99
0.99
0.97
0.63
3.09
2.72
6.68
3.37
1.54
f1 (ppm)

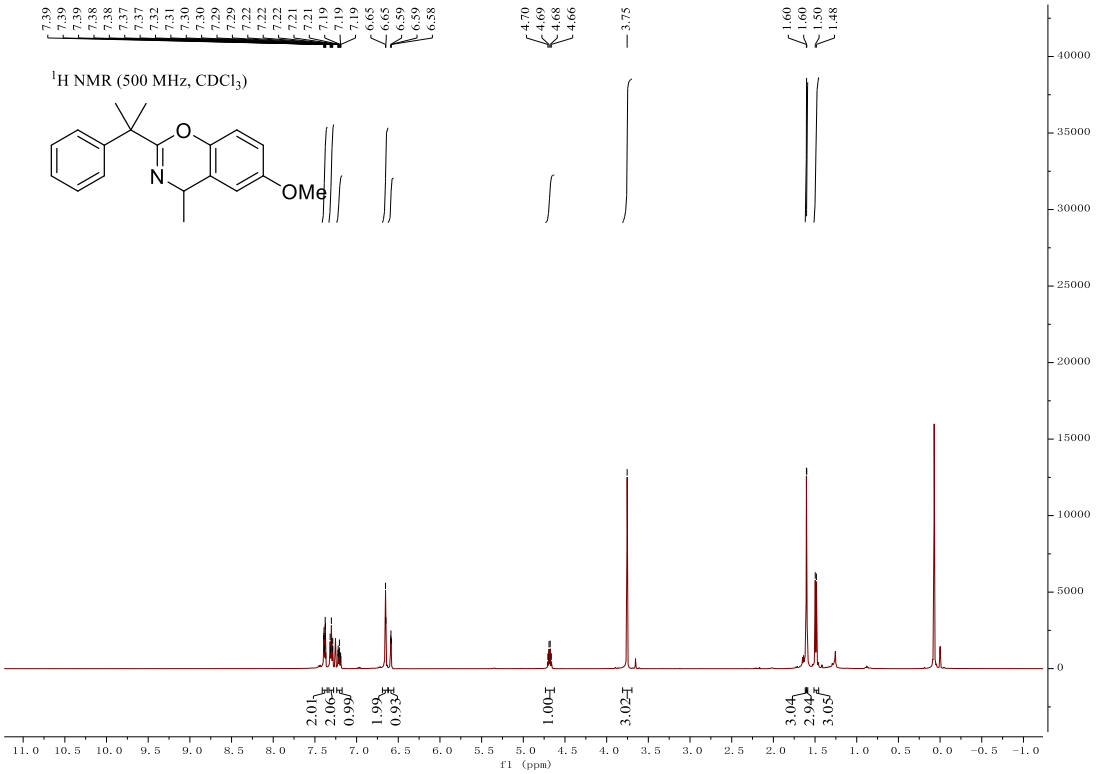

^{13}C NMR (126 MHz, CDCl$_3$)
Ph
O
N
OMe
156.6
148.8
143.0
133.1
130.7
130.4
128.2
127.6
116.1
112.6
110.4
77.4
77.2 CDCl3
76.9
55.8
54.9
40.6
26.4
21.5
f1 (ppm)

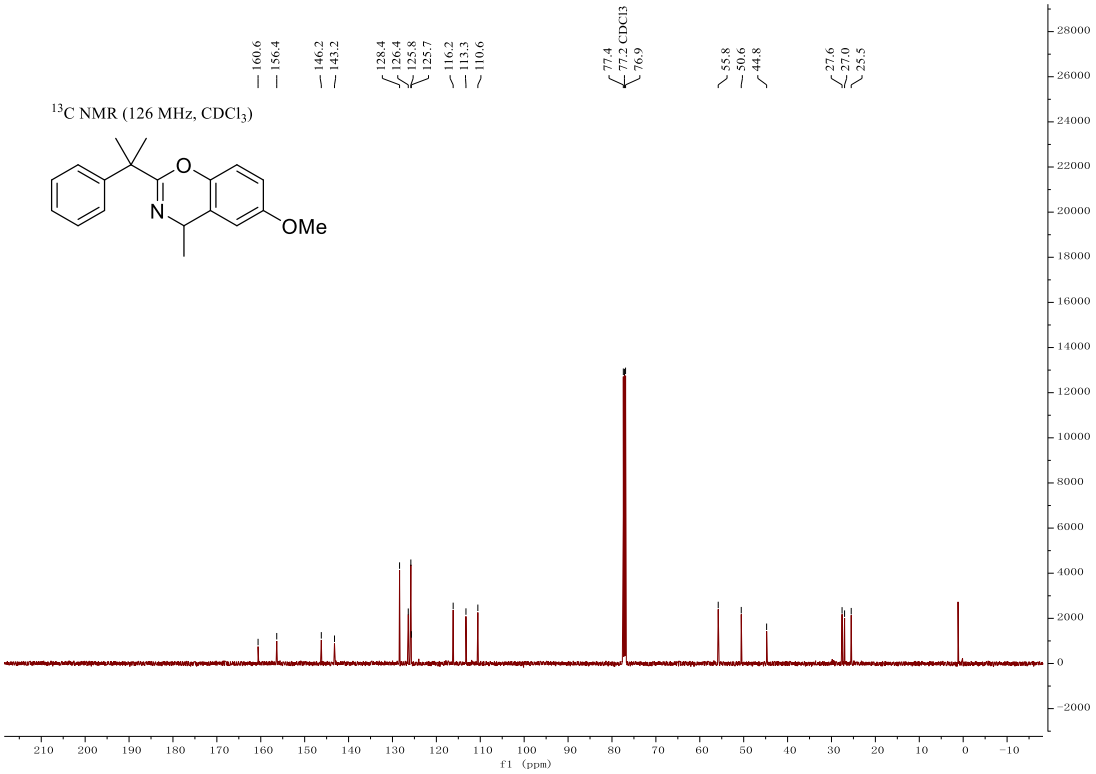
Compound 15


^{1}H NMR (400 MHz, $CDCl_3$)
Ph
O
N
OMe
(major)
OMe
Ph
O
N
(minor)
CDCl3
0.31
2.00
3.61
0.16
1.03
0.32
2.03
0.45
3.04
7.09
2.29
f1 (ppm)

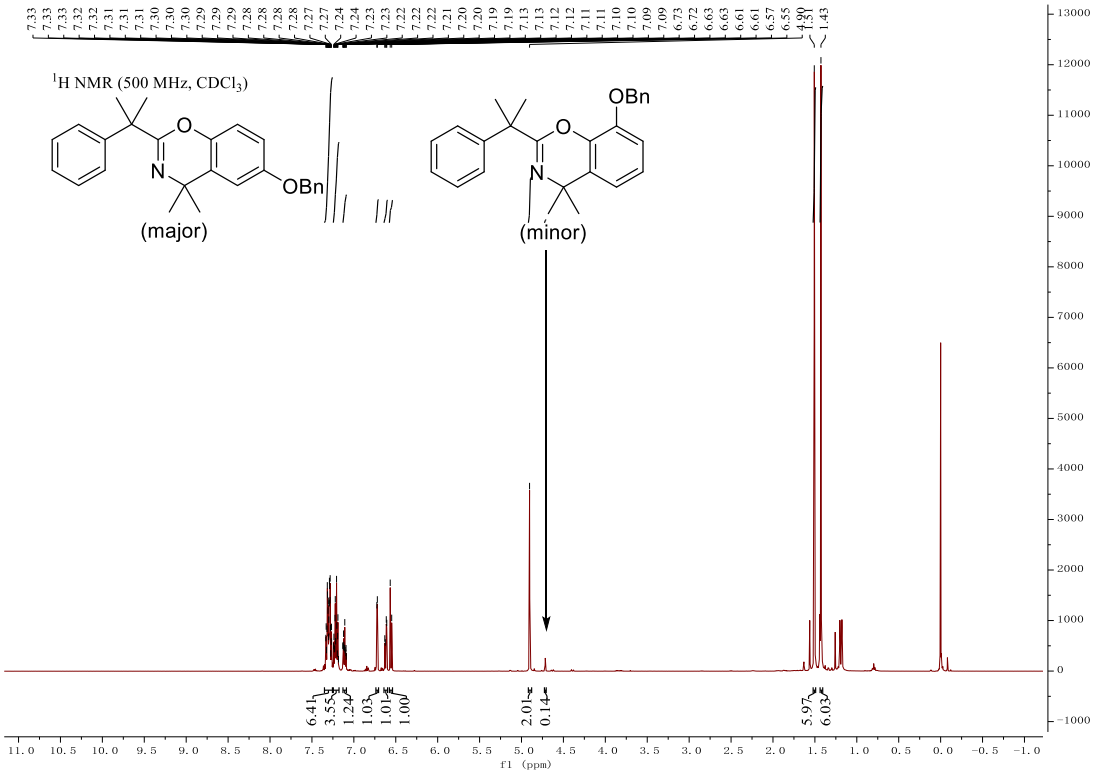

^{13}C NMR (101 MHz, $CDCl_3$)
Ph
O
N
OMe
156.5
149.0
143.2
133.0
130.7
128.6
128.2
127.5
116.0
112.8
110.6
77.5
77.2 CDCl3
76.8
63.4
55.8
45.2
25.0
f1 (ppm)

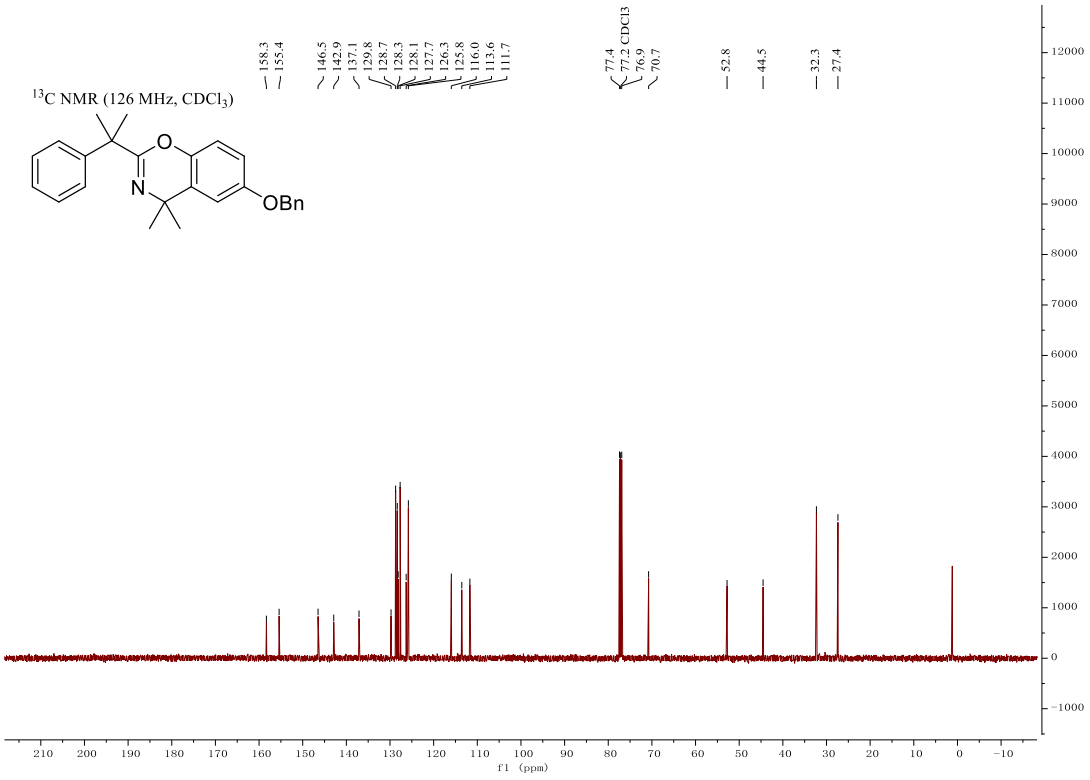
Compound 16


^{1}H NMR (500 MHz, $CDCl_3$)
O
N
OMe
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.32
7.31
7.30
7.30
7.29
7.29
7.22
7.22
7.21
7.21
7.19
7.19
7.19
6.65
6.65
6.59
6.59
6.58
4.70
4.69
4.68
4.66
3.75
1.60
1.60
1.50
1.48
2.01
2.06
0.99
1.99
0.93
1.00
3.02
3.04
2.94
3.05
f1 (ppm)

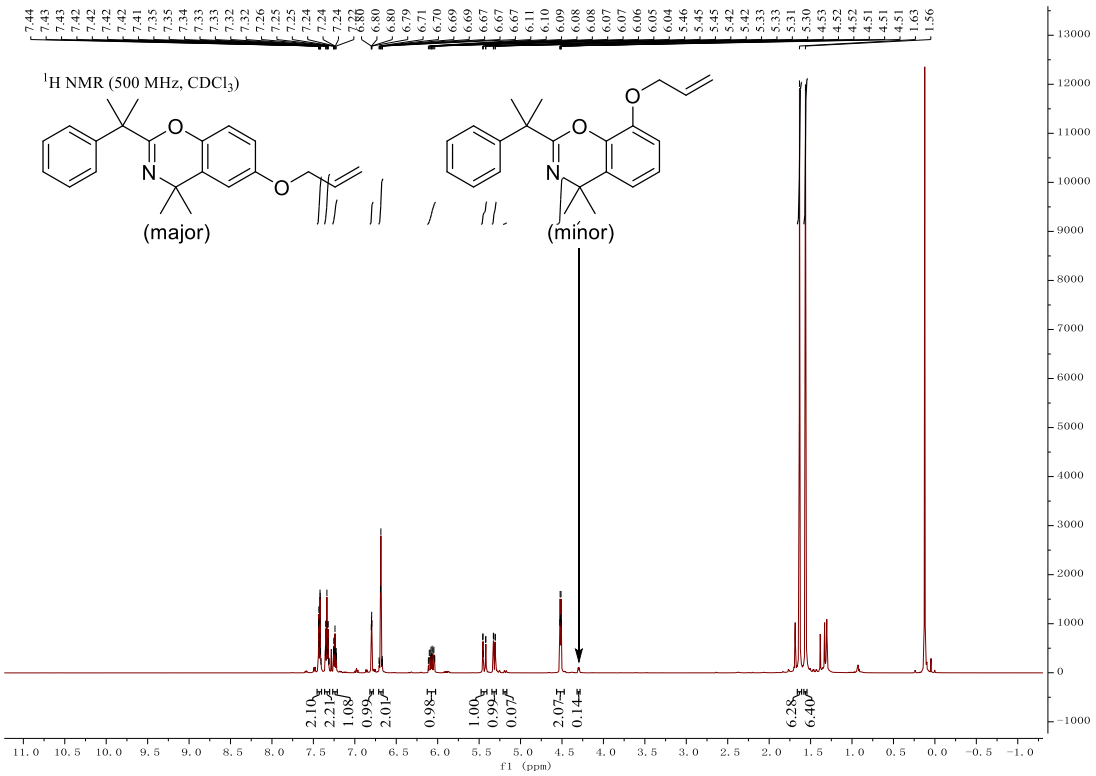

160.6
156.4
146.2
143.2
128.4
126.4
125.8
125.7
116.2
113.3
110.6
77.4
77.2 CDCl3
76.9
55.8
50.6
44.8
27.6
27.0
25.5
13C NMR (126 MHz, CDCl3)
O
N
OMe
f1 (ppm)

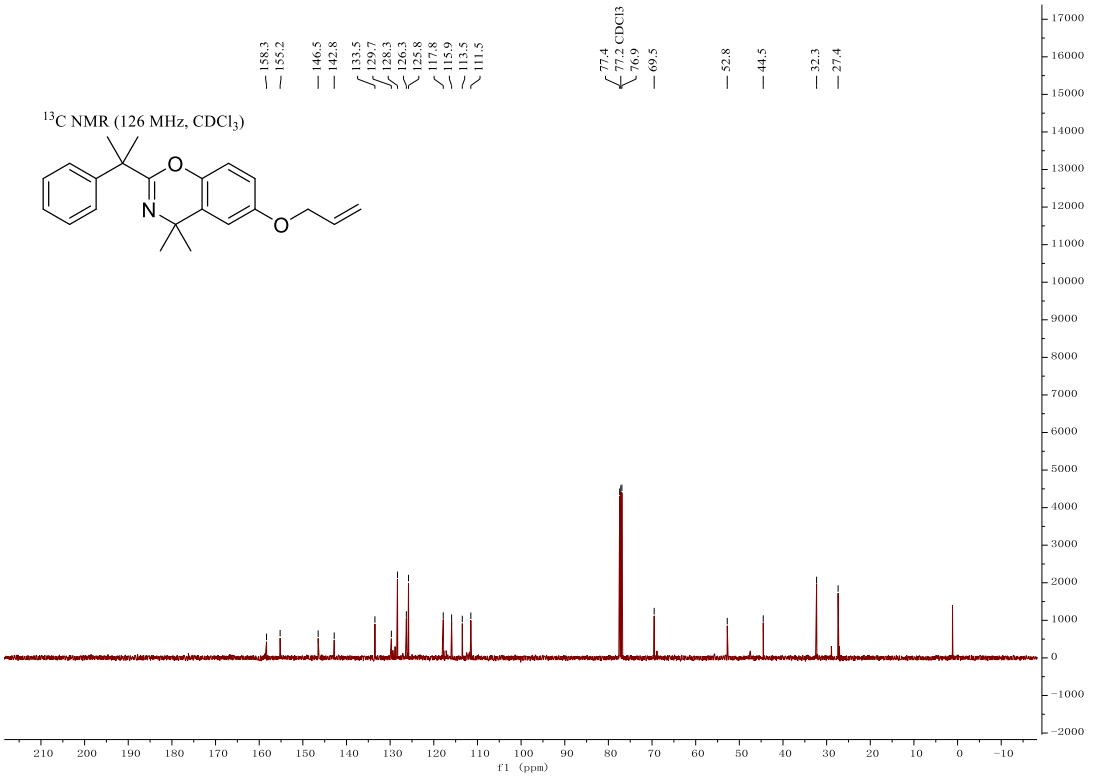
Compound 17


1H NMR (500 MHz, CDCl3)
O
N
OBn
(major)
OBn
O
N
(minor)
6.41
3.55
1.24
1.03
1.01
1.00
2.01
0.14
5.97
6.03
f1 (ppm)

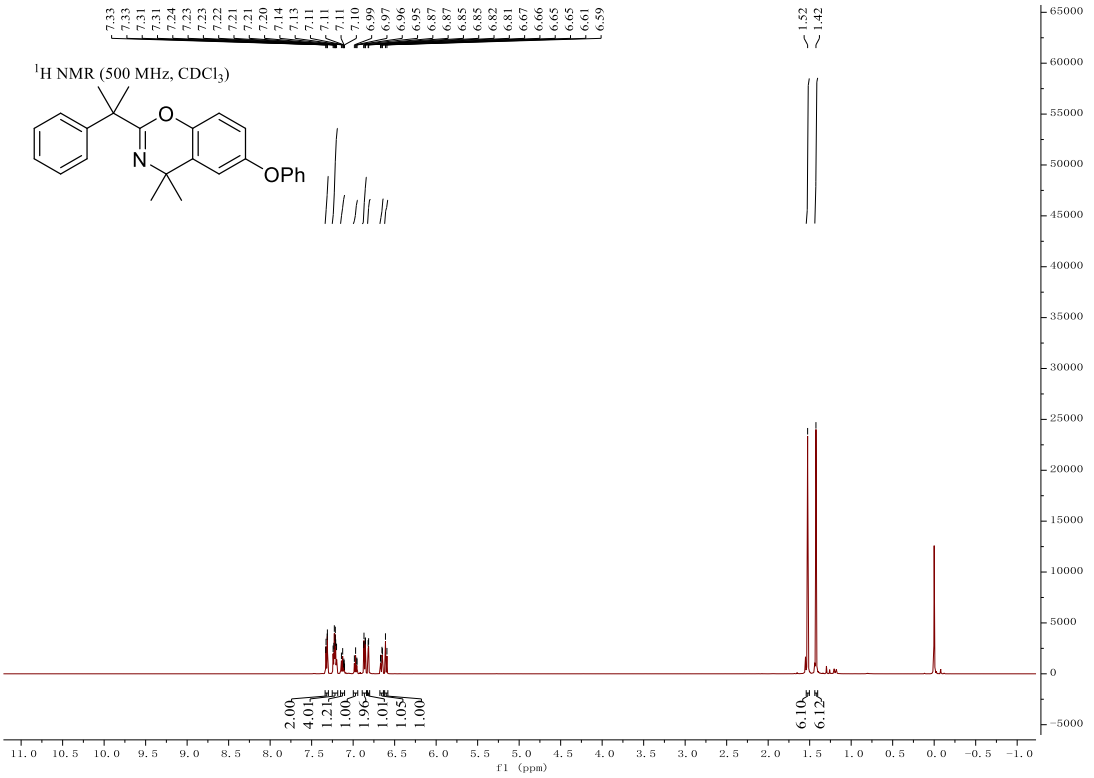

13C NMR (126 MHz, CDCl3)
158.3
155.4
146.5
142.9
137.1
129.8
128.7
128.3
128.1
127.7
126.3
125.8
116.0
113.6
111.7
77.4
77.2 CDCl3
76.9
70.7
52.8
44.5
32.3
27.4
O
N
OBn
f1 (ppm)

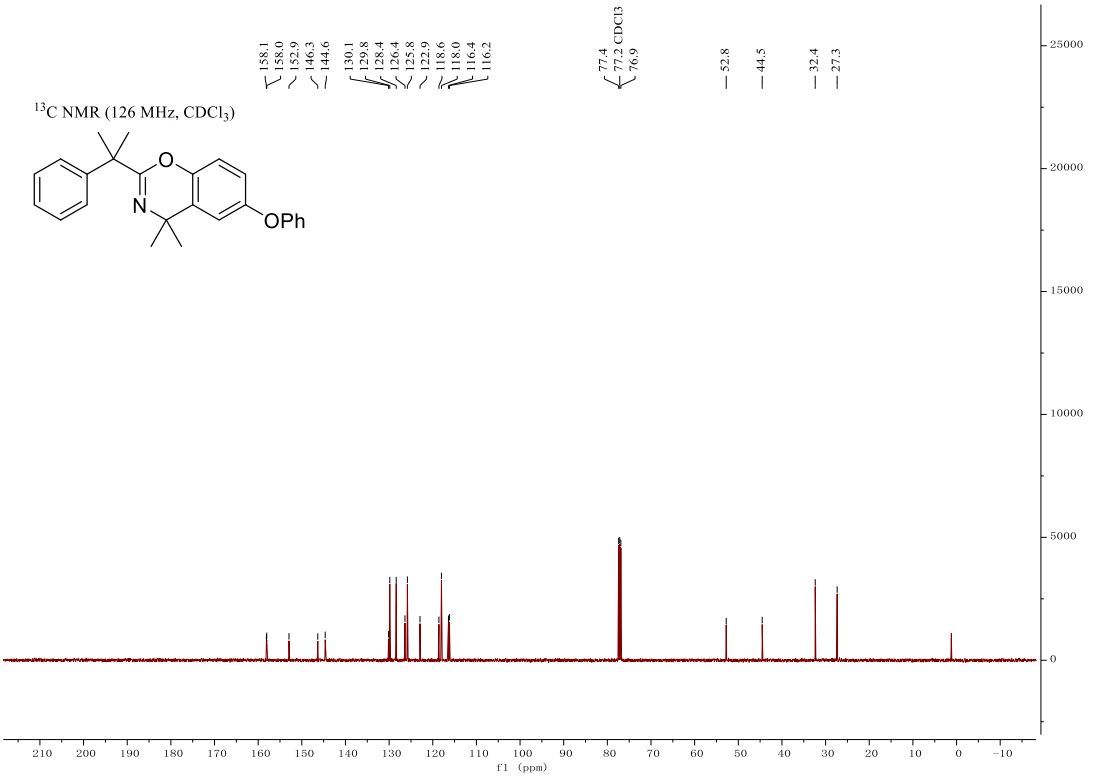
Compound 18


7.44 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.26 7.25 7.25 7.24 7.24 7.24 7.22 6.80 6.80 6.80 6.79 6.71 6.70 6.69 6.69 6.67 6.67 6.67 6.11 6.10 6.09 6.08 6.08 6.07 6.07 6.06 6.05 6.04 5.46 5.45 5.45 5.42 5.33 5.33 5.31 5.30 4.53 4.52 4.52 4.51 4.51 4.51 1.63 1.56
^{1}H NMR (500 MHz, $CDCl_3$)
(major)
(minor)
2.10 2.21 1.08 0.99 2.01 0.98 1.00 0.99 0.07 2.07 0.14 6.28 6.40
f1 (ppm)

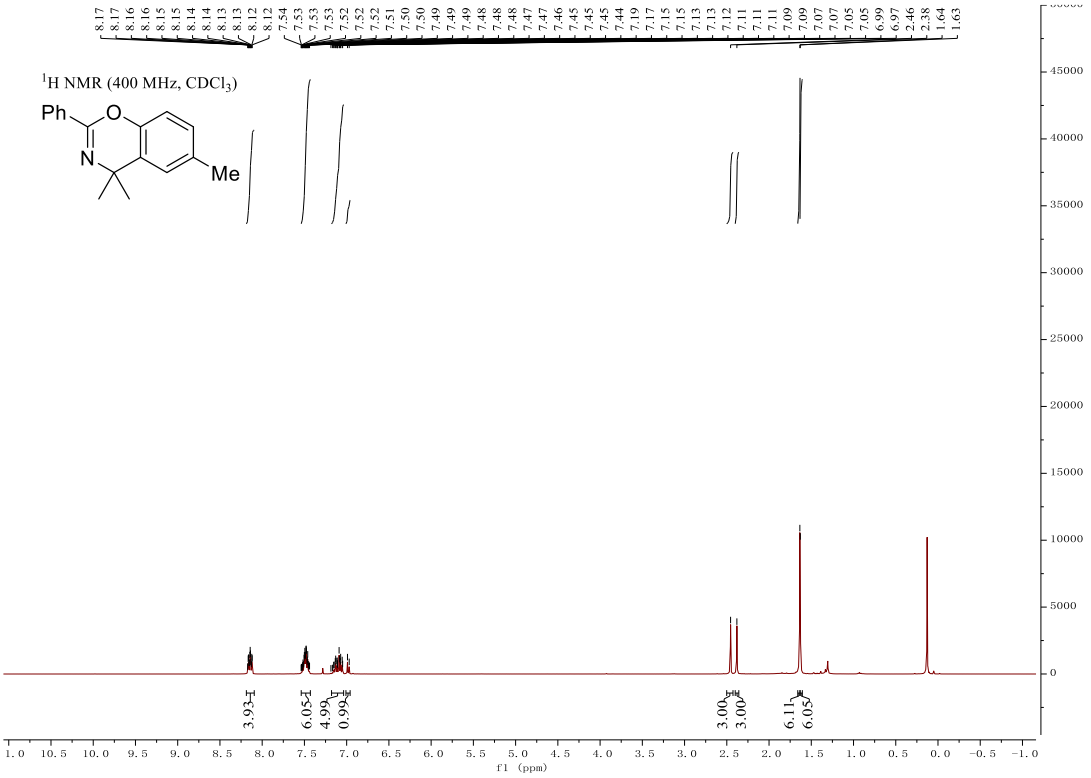

158.3 155.2 146.5 142.8 133.5 129.7 128.3 126.3 125.8 117.8 115.9 113.5 111.5 77.4 77.2 CDCl3 76.9 69.5 52.8 44.5 32.3 27.4
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

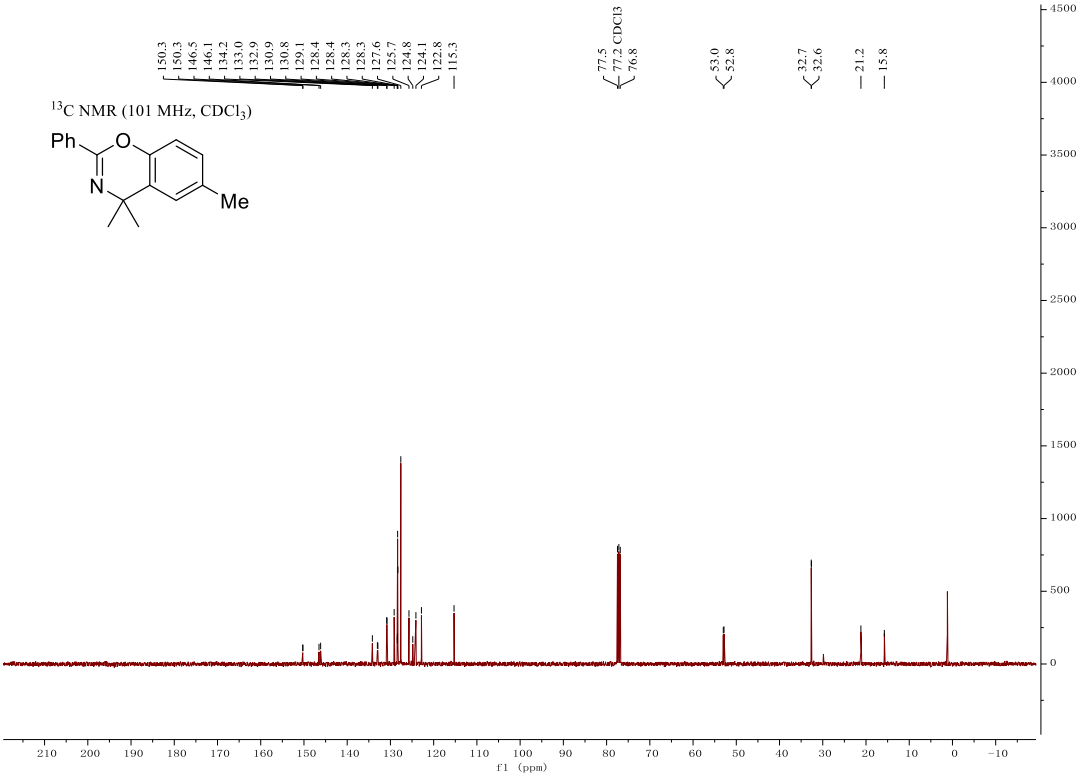
Compound 19



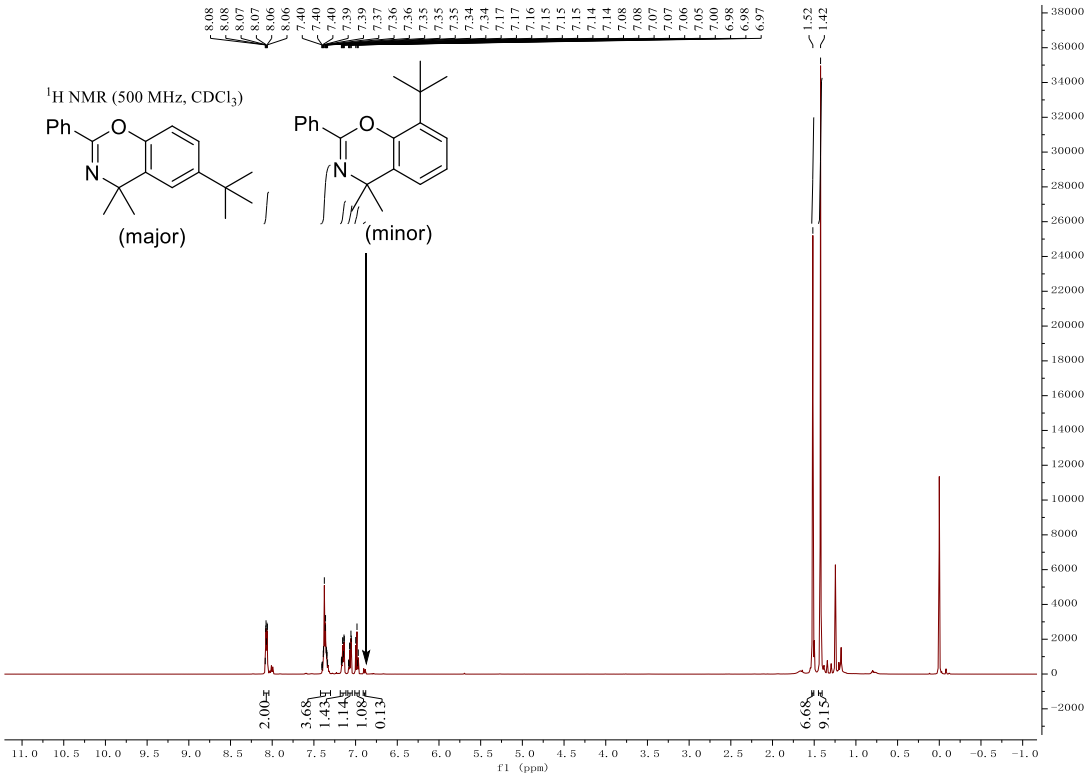


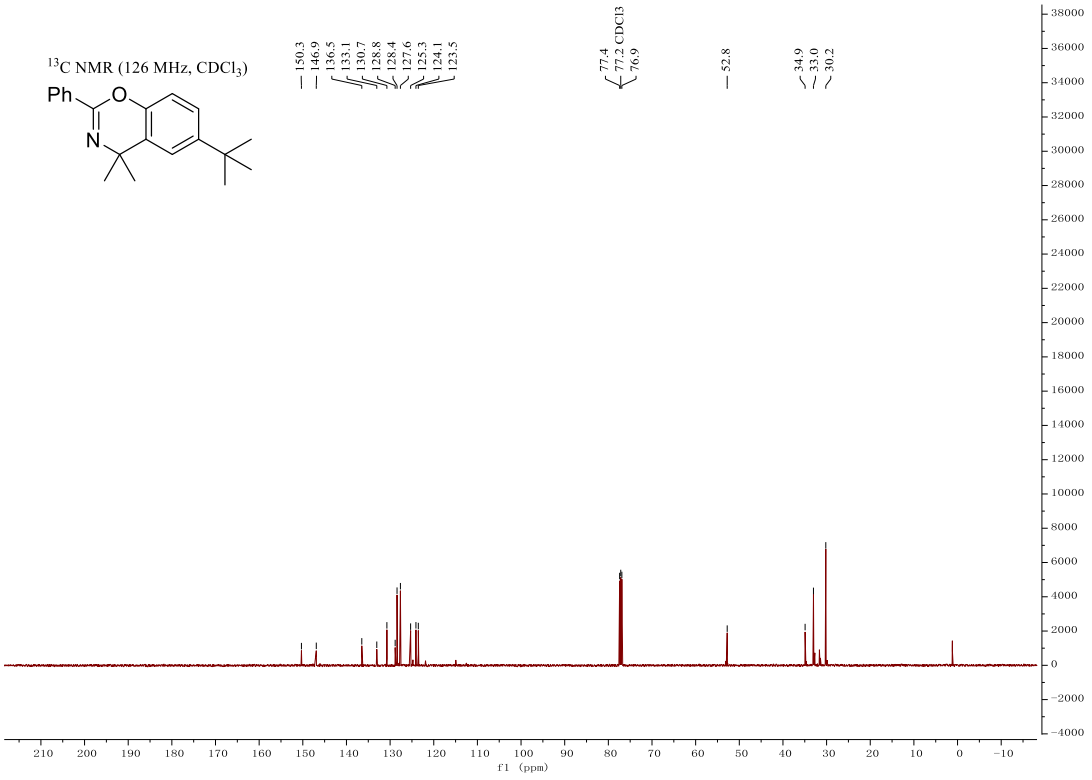
Compound 20


^{1}H NMR (400 MHz, $CDCl_3$)
Ph
O
N
Me
8.17 8.17 8.16 8.16 8.15 8.15 8.14 8.14 8.13 8.13 8.12 8.12 7.54 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.45 7.44 7.19 7.17 7.15 7.15 7.13 7.13 7.12 7.11 7.11 7.11 7.09 7.09 7.07 7.07 7.05 7.05 6.99 6.97 2.46 2.38 1.64 1.63
3.93 6.05 4.99 0.99 3.00 3.00 6.11 6.05
f1 (ppm)

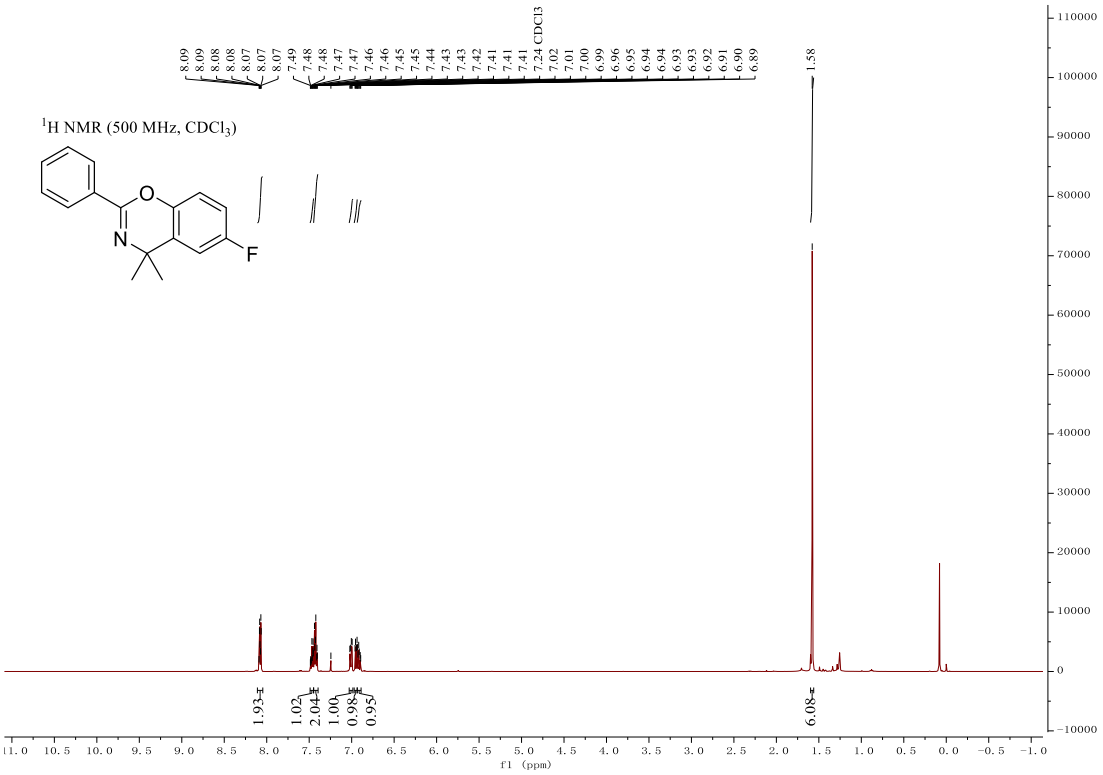

^{13}C NMR (101 MHz, $CDCl_3$)
Ph
O
N
Me
150.3 150.3 146.5 146.1 134.2 133.0 132.9 130.9 130.8 129.1 128.4 128.4 128.3 128.3 127.6 125.7 124.8 124.1 122.8 115.3
77.5 77.2 CDCl3 76.8
53.0 52.8
32.7 32.6
21.2
15.8
f1 (ppm)

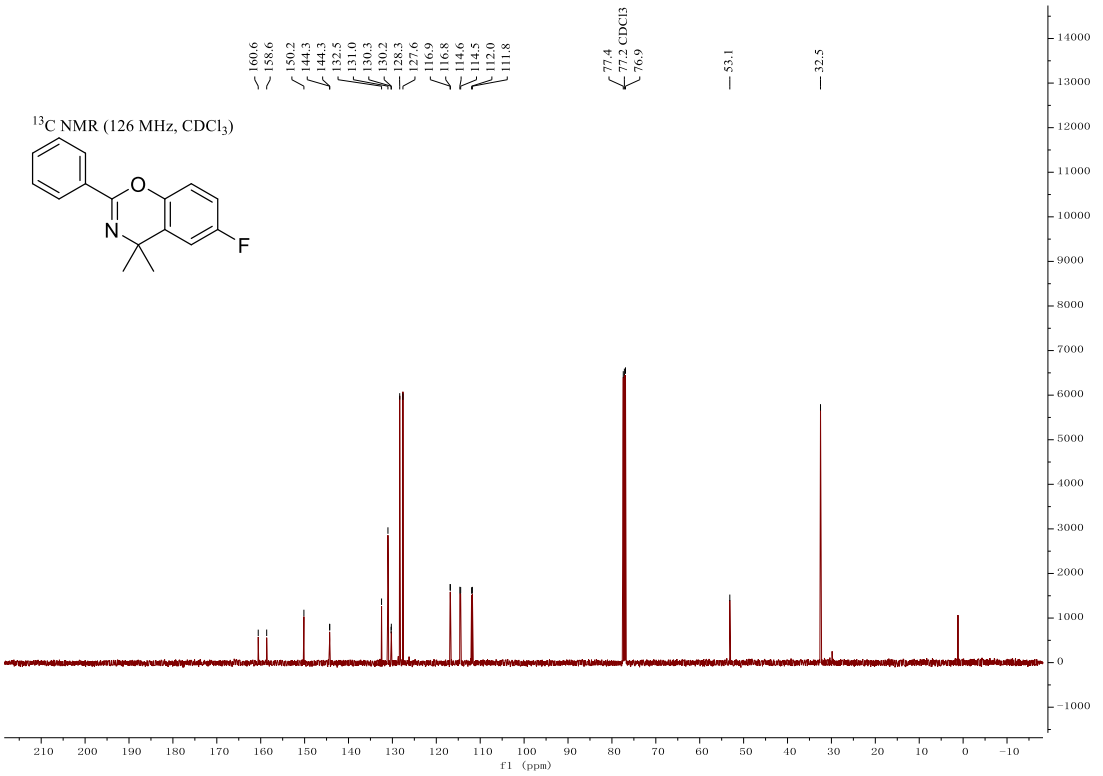
Compound 21


^{1}H NMR (500 MHz, $CDCl_3$)
Ph
O
N
(major)
(minor)
8.08
8.08
8.07
8.07
8.06
8.06
7.40
7.40
7.40
7.39
7.39
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.17
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.08
7.08
7.07
7.07
7.06
7.05
7.00
6.98
6.98
6.97
1.52
1.42
2.00
3.68
1.43
1.14
1.14
1.08
0.13
6.68
9.15
f1 (ppm)

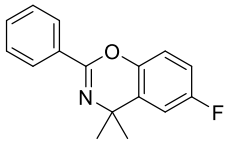

^{13}C NMR (126 MHz, $CDCl_3$)
Ph
O
N
150.3
146.9
136.5
133.1
130.7
128.8
128.4
127.6
125.3
124.1
123.5
77.4
77.2 CDCl3
76.9
52.8
34.9
33.0
30.2
f1 (ppm)

Compound 22


^{1}H NMR (500 MHz, $CDCl_3$)
8.09 8.09 8.08 8.08 8.07 8.07 8.07 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.41 7.24 CDCl3 7.02 7.01 7.00 6.99 6.96 6.95 6.94 6.94 6.93 6.93 6.92 6.91 6.90 6.89
1.58
1.93
1.02
2.04
1.00
0.98
0.95
6.08
O
N
F
f1 (ppm)

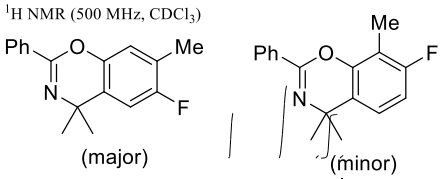

^{13}C NMR (126 MHz, $CDCl_3$)
160.6 158.6 150.2 144.3 144.3 132.5 131.0 130.3 130.2 128.3 127.6 116.9 116.8 114.6 114.5 112.0 111.8
77.4 77.2 CDCl3 76.9
53.1
32.5
O
N
F
f1 (ppm)

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

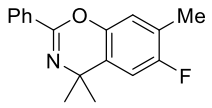


Compound 23

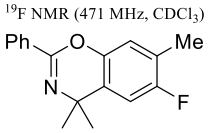
^{1}H NMR (500 MHz, $CDCl_3$)



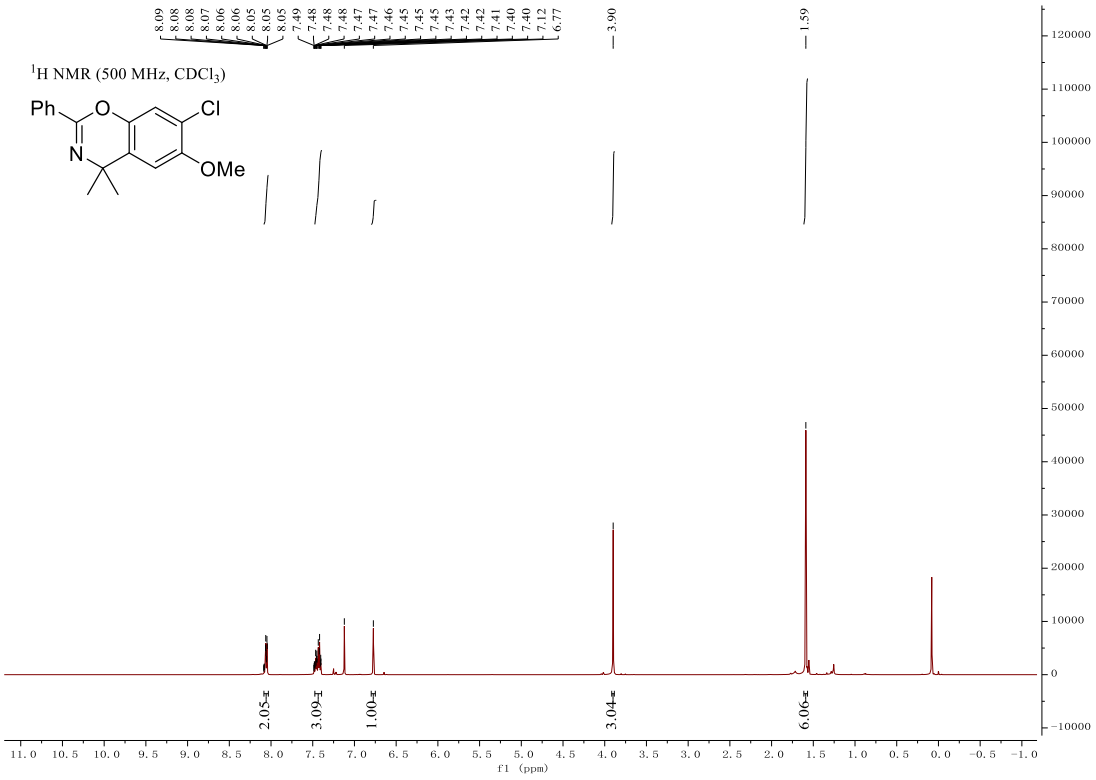
^{13}C NMR (126 MHz, $CDCl_3$)

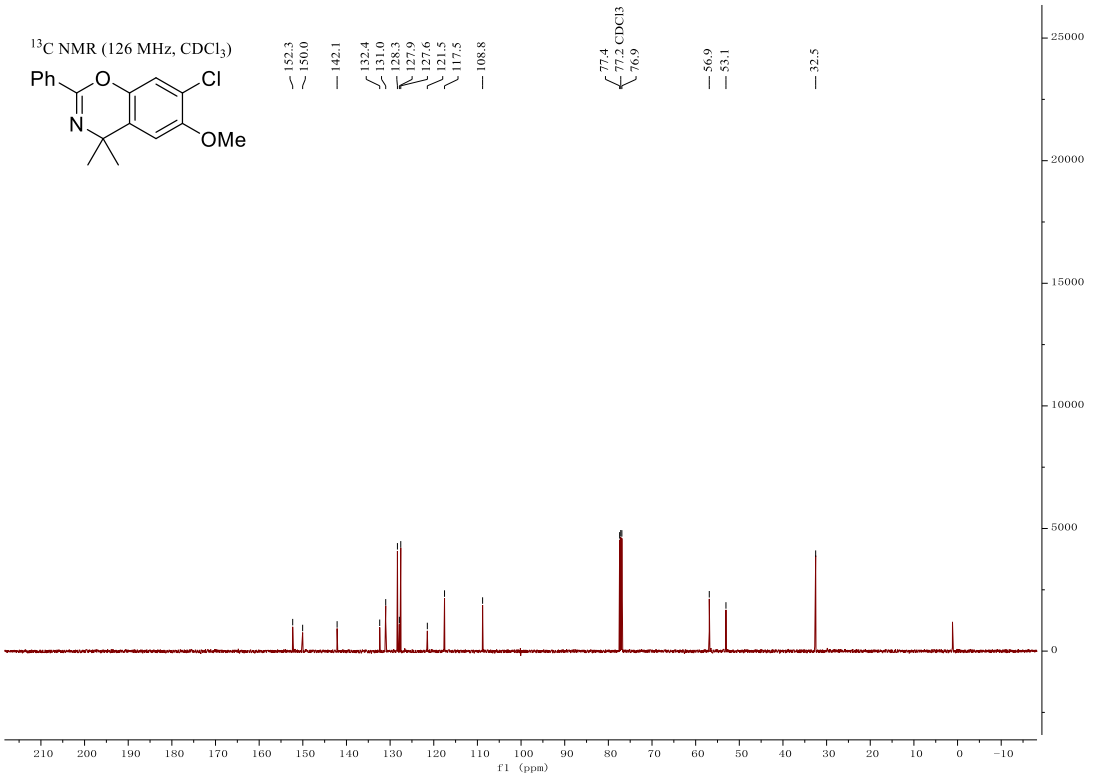


^{19}F NMR (471 MHz, $CDCl_3$)

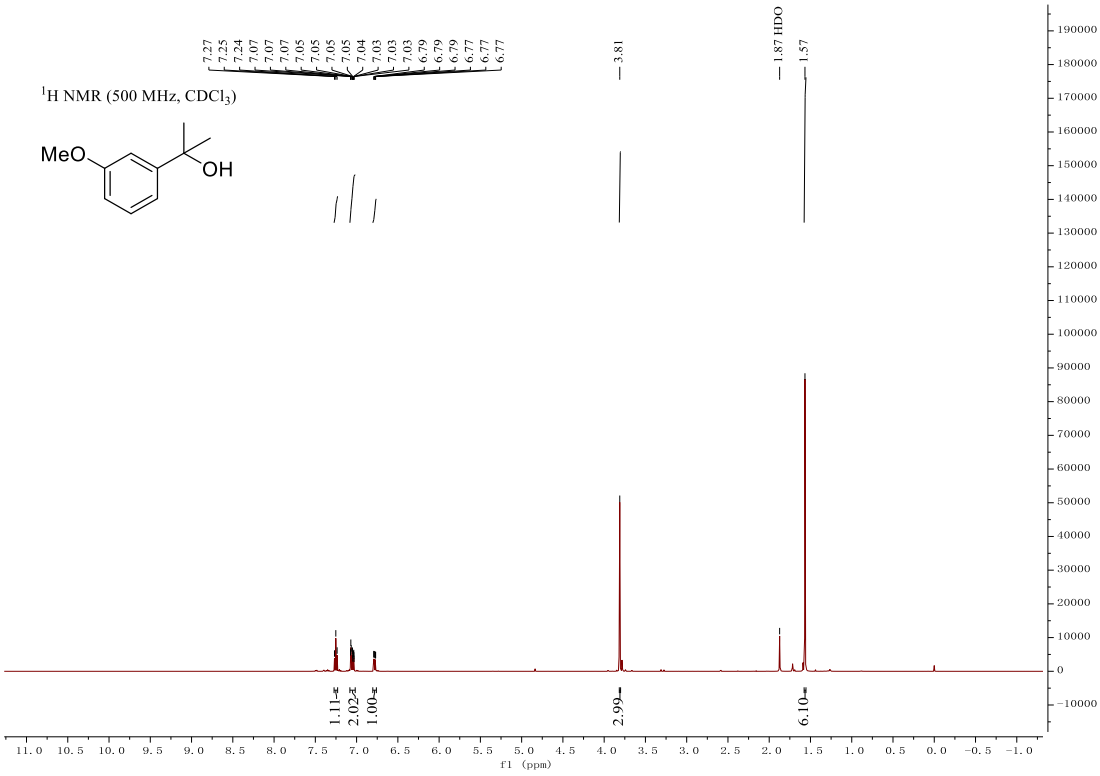


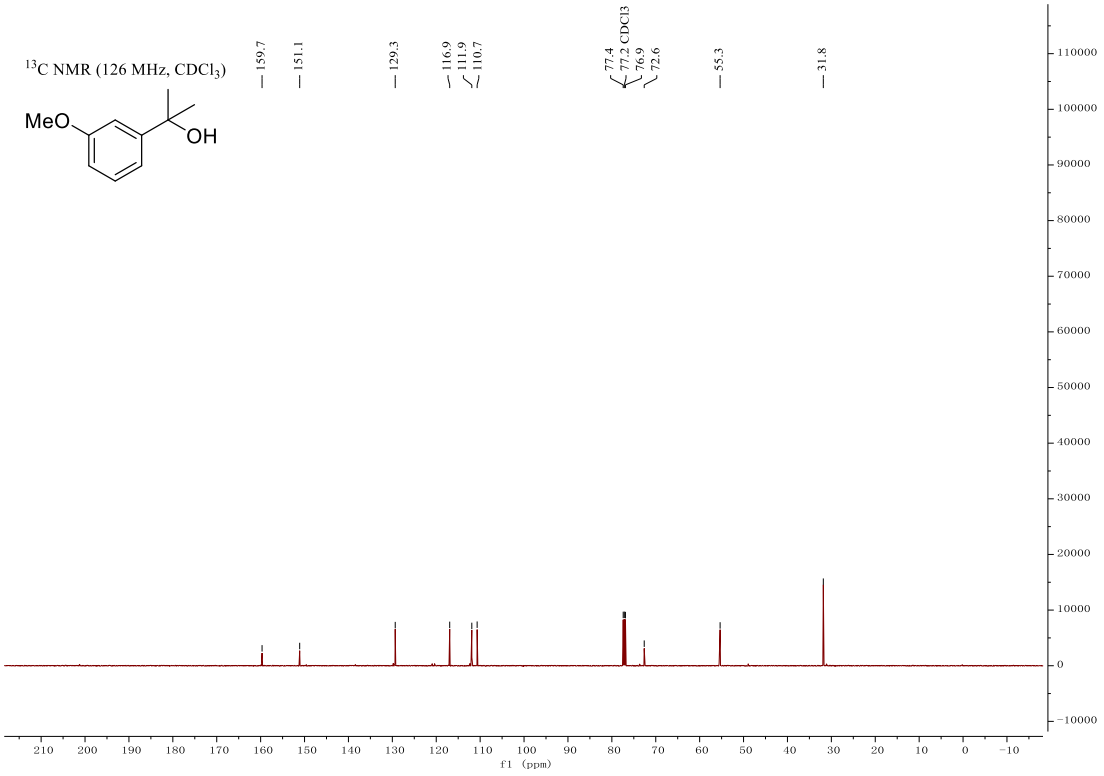
Compound 24


8.09
8.08
8.08
8.07
8.06
8.06
8.05
8.05
8.05
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.45
7.43
7.42
7.42
7.41
7.40
7.40
7.12
6.77
3.90
1.59
^{1}H NMR (500 MHz, CDCl$_3$)
Ph
O
N
Cl
OMe
2.05
3.09
1.00
3.04
6.06
f1 (ppm)

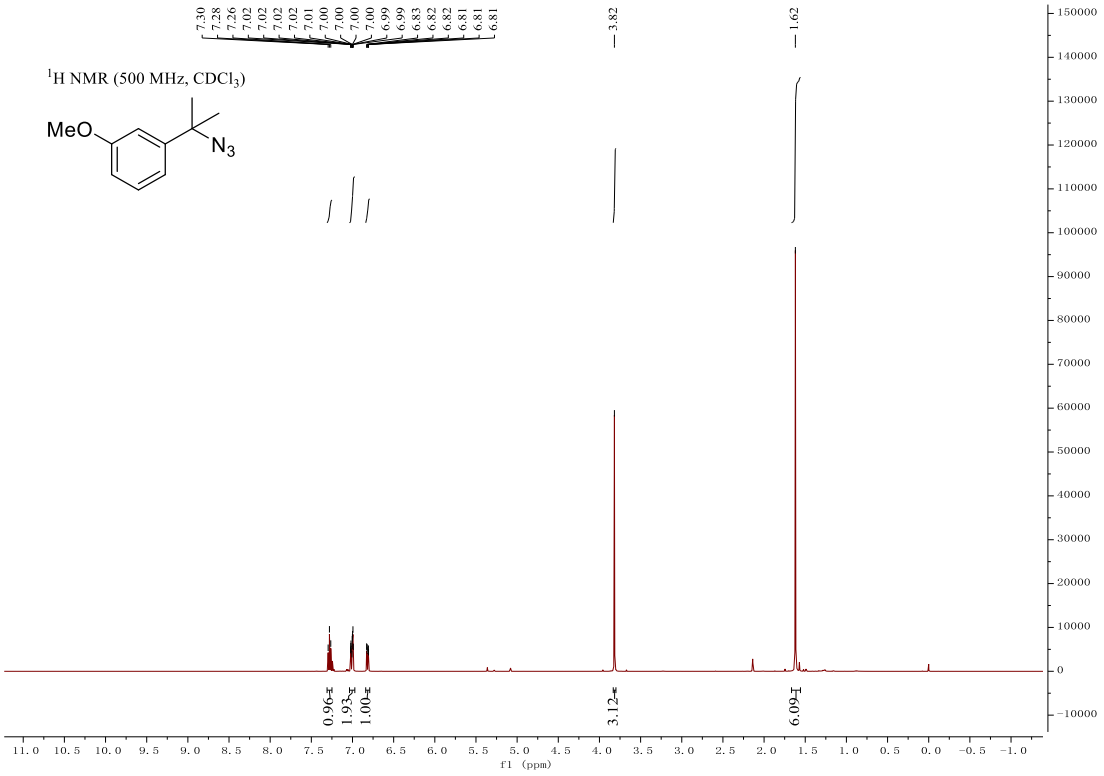

13C NMR (126 MHz, CDCl3)
Ph
O
N
Cl
OMe
152.3
150.0
142.1
132.4
131.0
128.3
127.9
127.6
121.5
117.5
108.8
77.4
77.2 CDCl3
76.9
56.9
53.1
32.5
f1 (ppm)

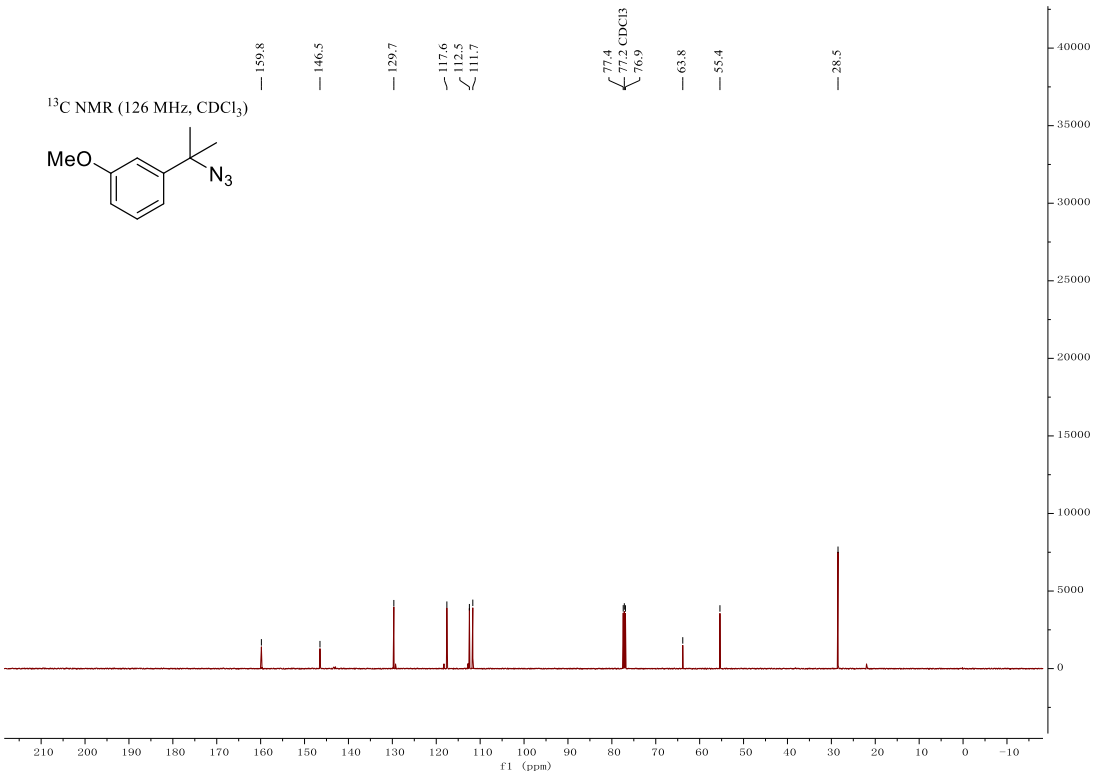
Compound S1


1H NMR (500 MHz, CDCl3)
MeO
OH
7.27
7.25
7.24
7.07
7.07
7.07
7.05
7.05
7.05
7.05
7.04
7.03
7.03
7.03
6.79
6.79
6.79
6.77
6.77
6.77
3.81
1.87 HDO
1.57
1.11
2.02
1.00
2.99
6.10
f1 (ppm)

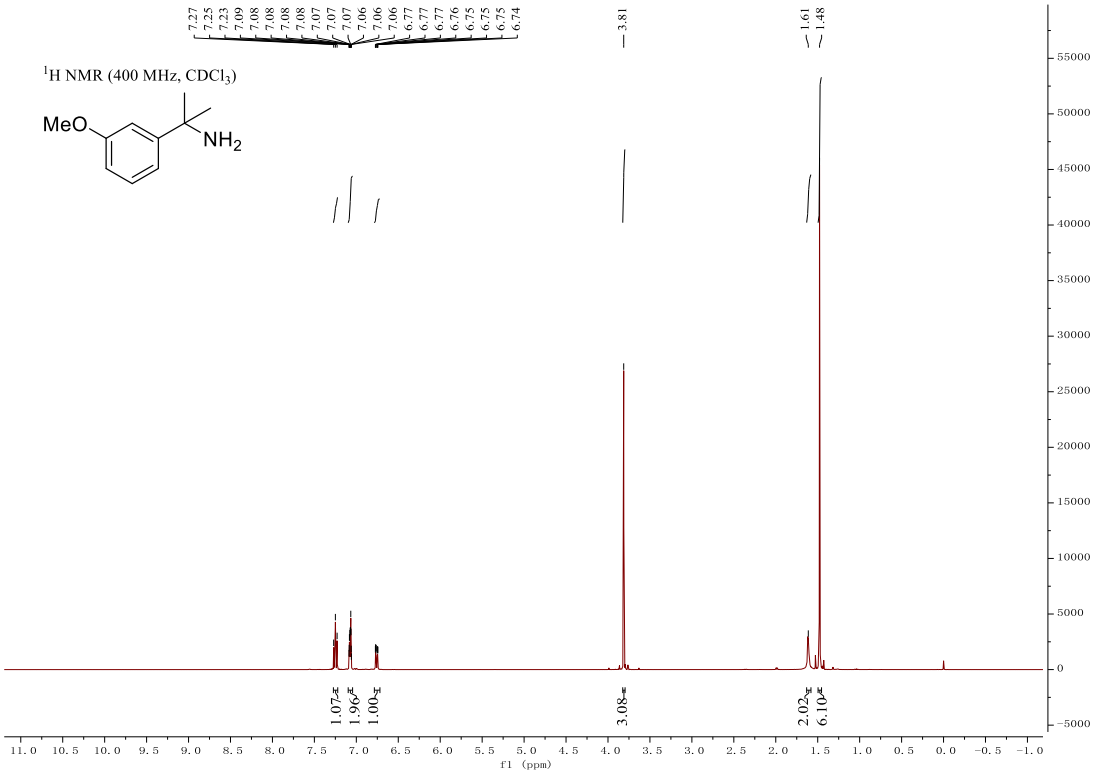

13C NMR (126 MHz, CDCl3)
MeO
OH
159.7
151.1
129.3
116.9
111.9
110.7
77.4
77.2 CDCl3
76.9
72.6
55.3
31.8
f1 (ppm)

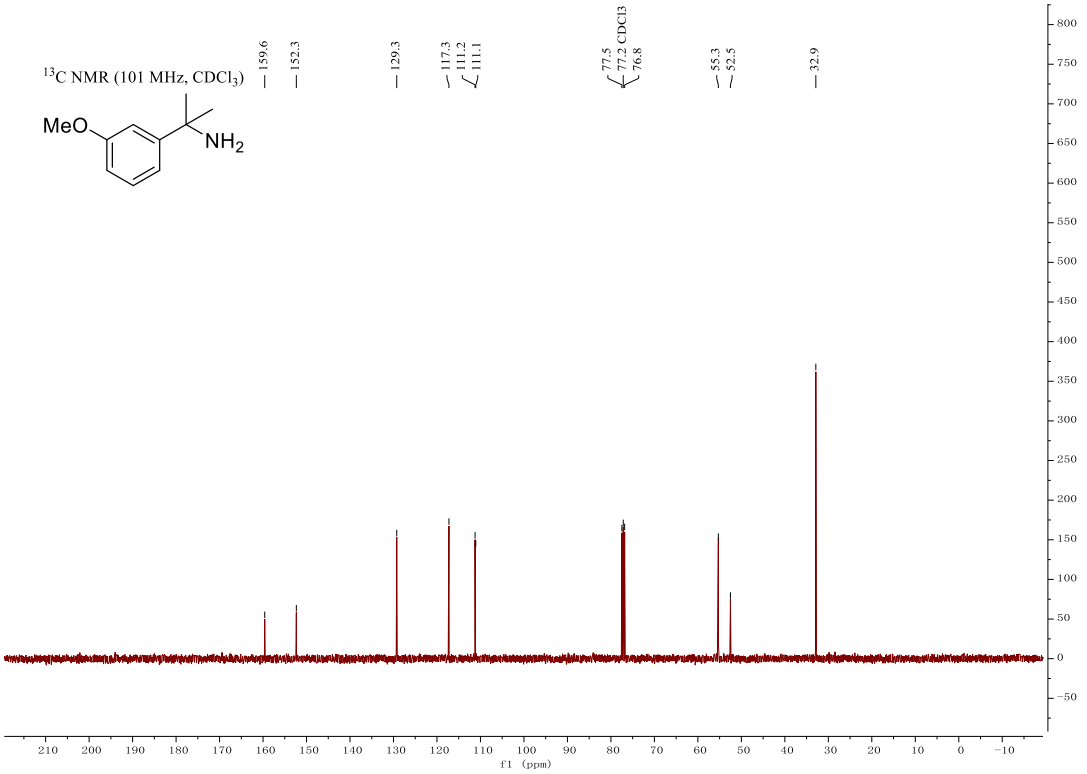
Compound S2


1H NMR (500 MHz, CDCl3)
MeO
N3
7.30
7.28
7.26
7.02
7.02
7.02
7.02
7.01
7.00
7.00
7.00
7.00
6.99
6.99
6.83
6.82
6.82
6.81
6.81
6.81
3.82
1.62
0.96
1.93
1.00
3.12
6.09
f1 (ppm)

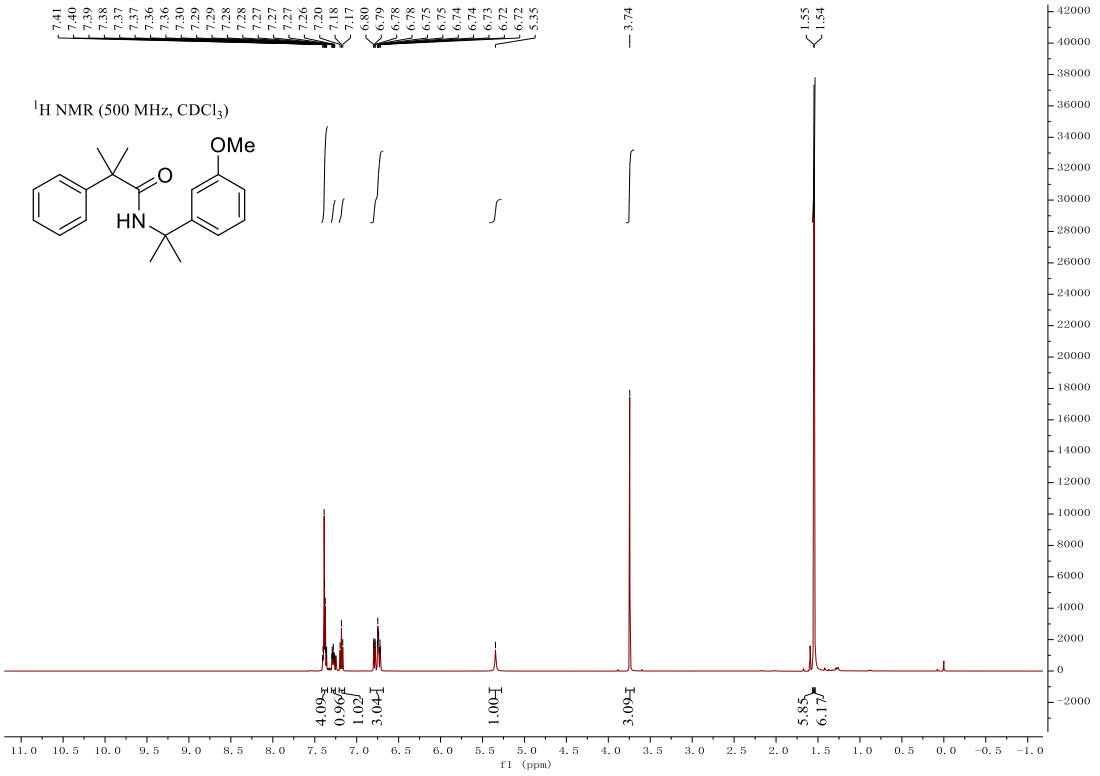

159.8
146.5
129.7
117.6
112.5
111.7
77.4
77.2 CDCl3
76.9
63.8
55.4
28.5
13C NMR (126 MHz, CDCl3)
MeO
N3
f1 (ppm)

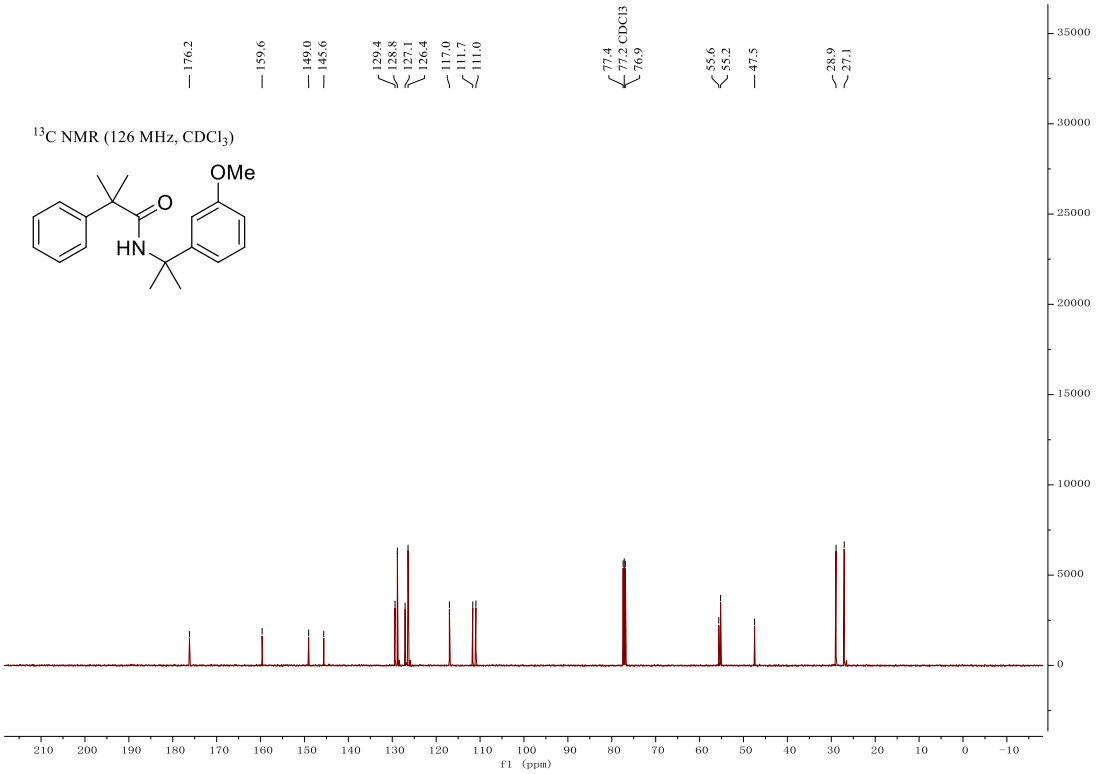
Compound S3


7.27
7.25
7.23
7.09
7.08
7.08
7.08
7.08
7.07
7.07
7.07
7.06
7.06
7.06
6.77
6.77
6.77
6.76
6.75
6.75
6.75
6.74
3.81
1.61
1.48
1H NMR (400 MHz, CDCl3)
MeO
NH2
1.07
1.96
1.00
3.08
2.02
6.10
f1 (ppm)

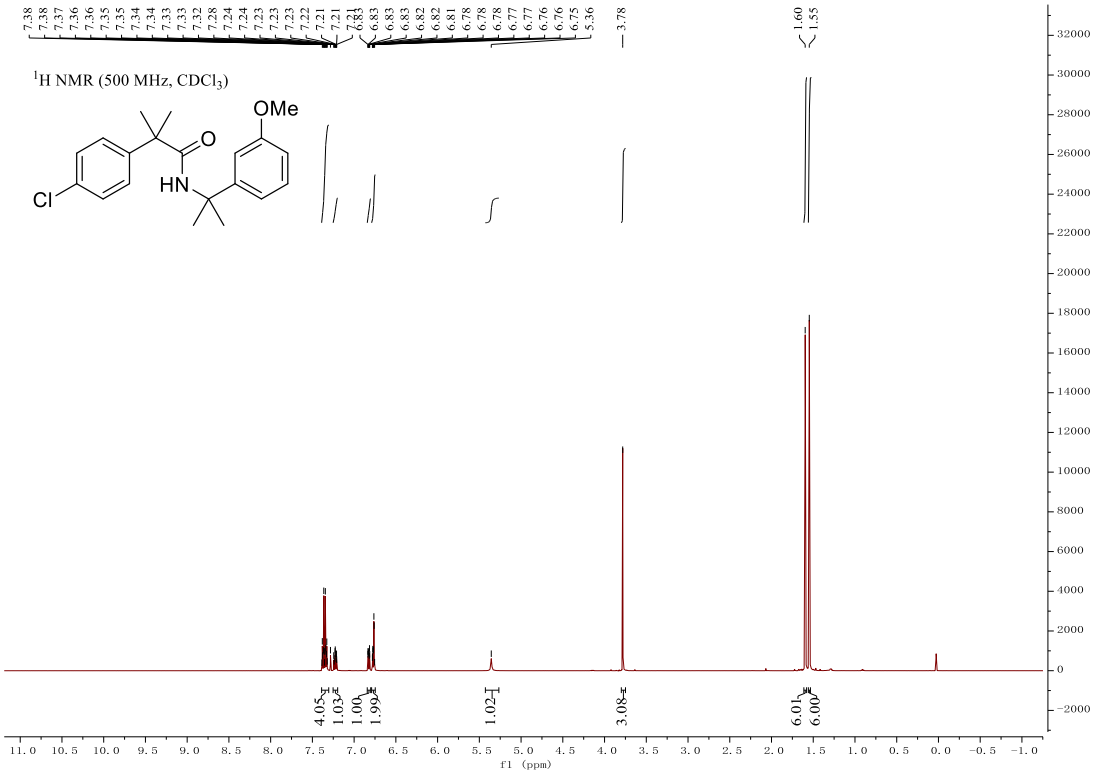

13C NMR (101 MHz, CDCl3)
MeO
NH2
159.6
152.3
129.3
117.3
111.2
111.1
77.5
77.2 CDCl3
76.8
55.3
52.5
32.9
f1 (ppm)

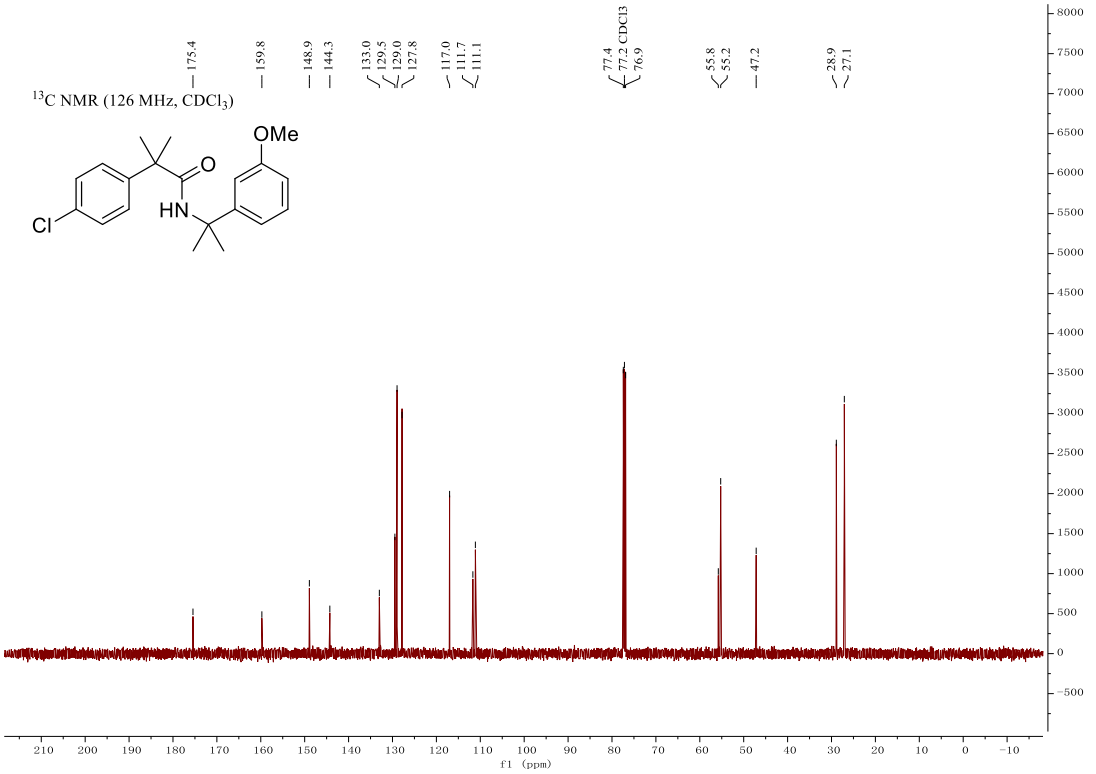
Compound 1


1H NMR (500 MHz, CDCl3)
OMe
O
HN
7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.20
7.18
7.17
6.80
6.79
6.78
6.78
6.75
6.75
6.74
6.74
6.73
6.72
6.72
5.35
3.74
1.55
1.54
4.09
0.96
1.02
3.04
1.00
3.09
5.85
6.17
f1 (ppm)

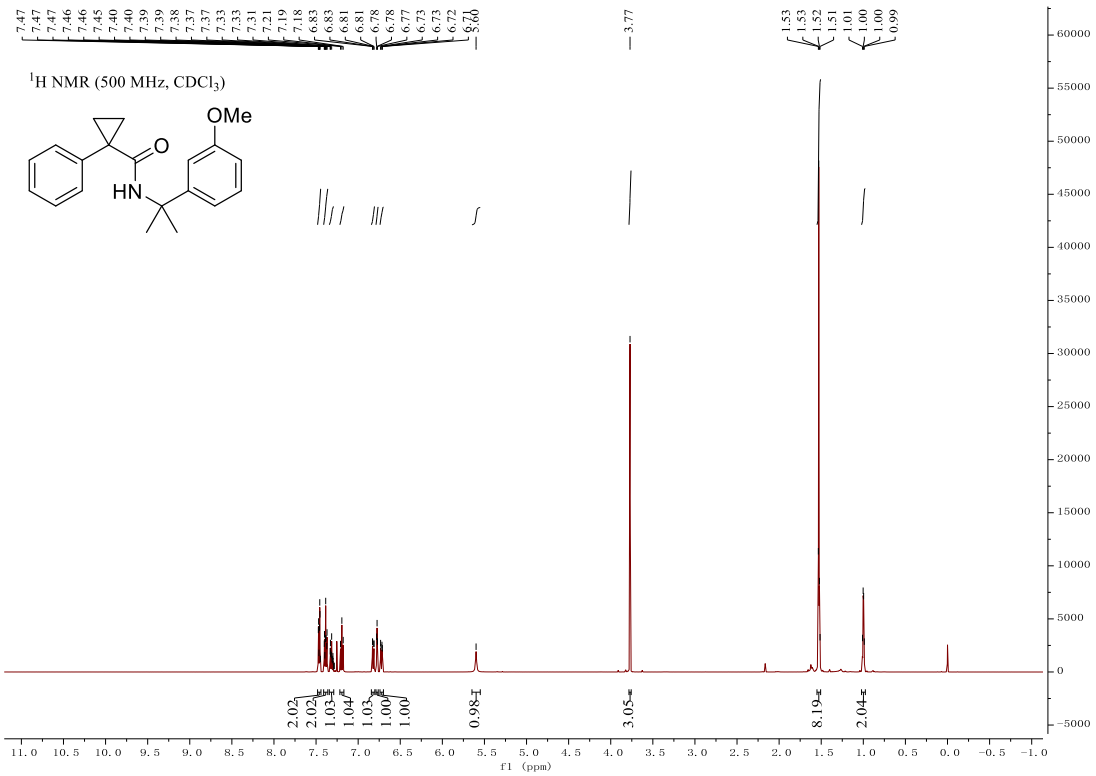

176.2
159.6
149.0
145.6
129.4
128.8
127.1
126.4
117.0
111.7
111.0
77.4
77.2 CDCl3
76.9
55.6
55.2
47.5
28.9
27.1
13C NMR (126 MHz, CDCl3)
OMe
O
HN
f1 (ppm)

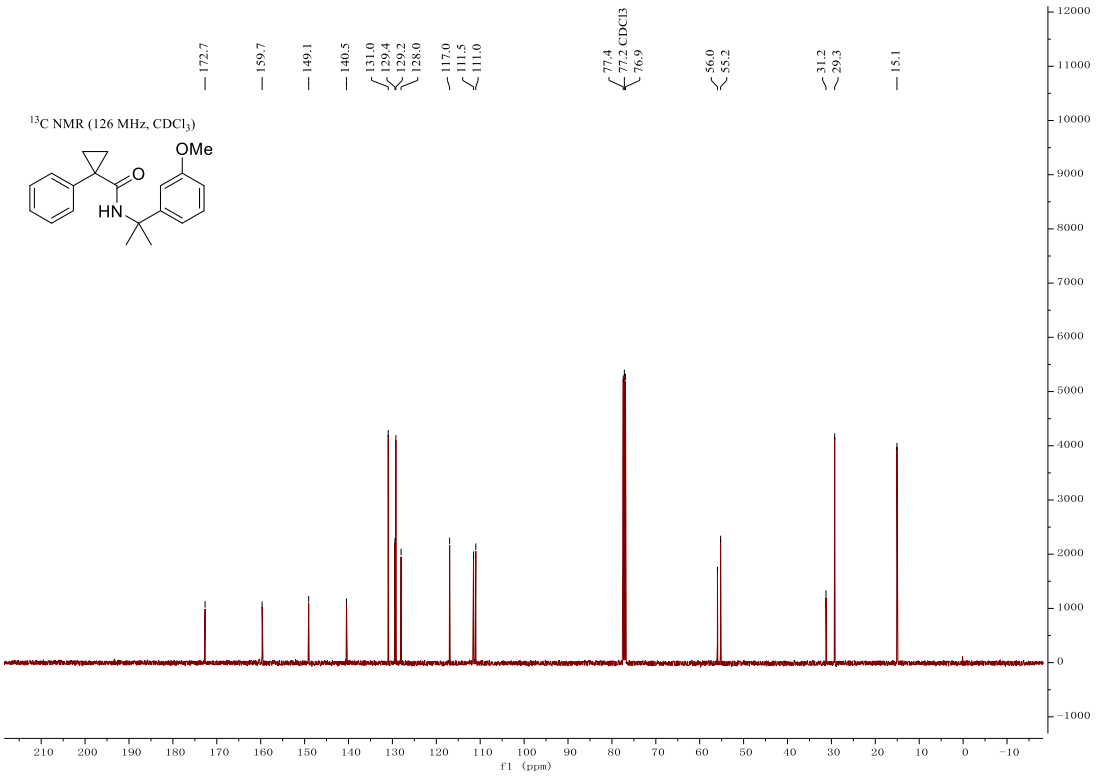
Compound S4


7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.28
7.24
7.24
7.23
7.23
7.23
7.22
7.21
7.21
7.21
6.83
6.83
6.83
6.82
6.82
6.81
6.78
6.78
6.78
6.77
6.77
6.76
6.76
6.75
5.36
3.78
1.60
1.55
1H NMR (500 MHz, CDCl3)
OMe
O
HN
Cl
4.05
1.03
1.00
1.99
1.02
3.08
6.01
6.00
f1 (ppm)

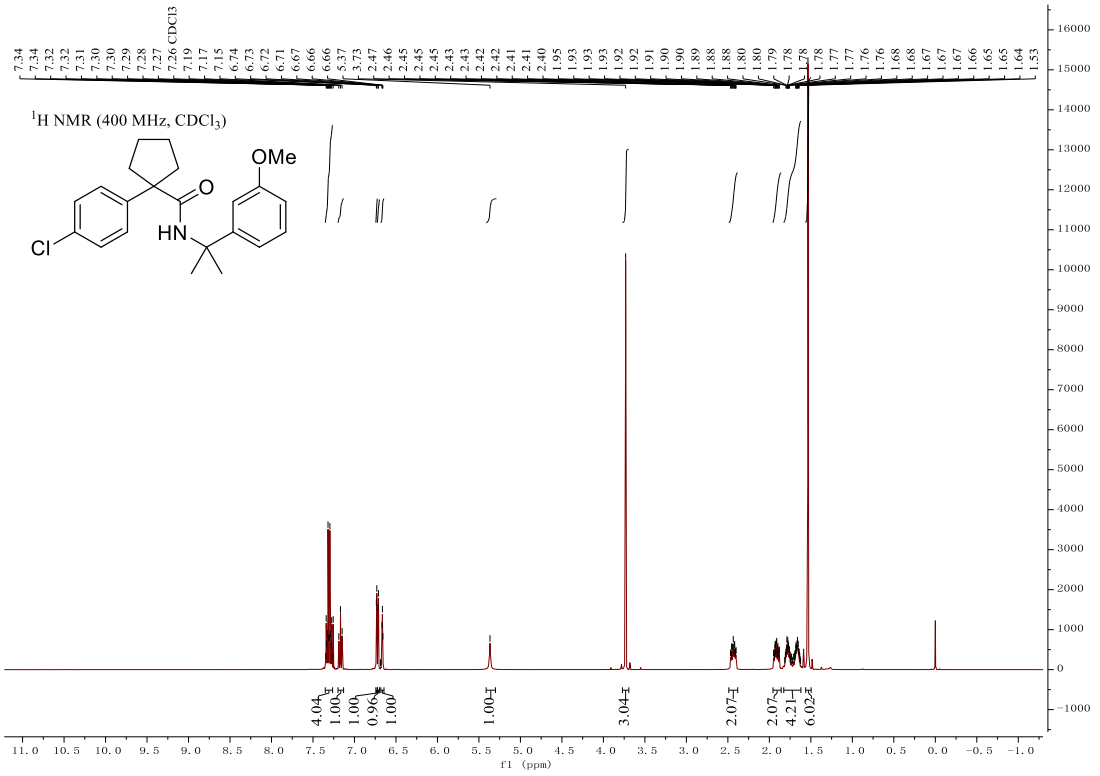

175.4
159.8
148.9
144.3
133.0
129.5
129.0
127.8
117.0
111.7
111.1
77.4
77.2 CDCl3
76.9
55.8
55.2
47.2
28.9
27.1
13C NMR (126 MHz, CDCl3)
OMe
O
HN
Cl
f1 (ppm)

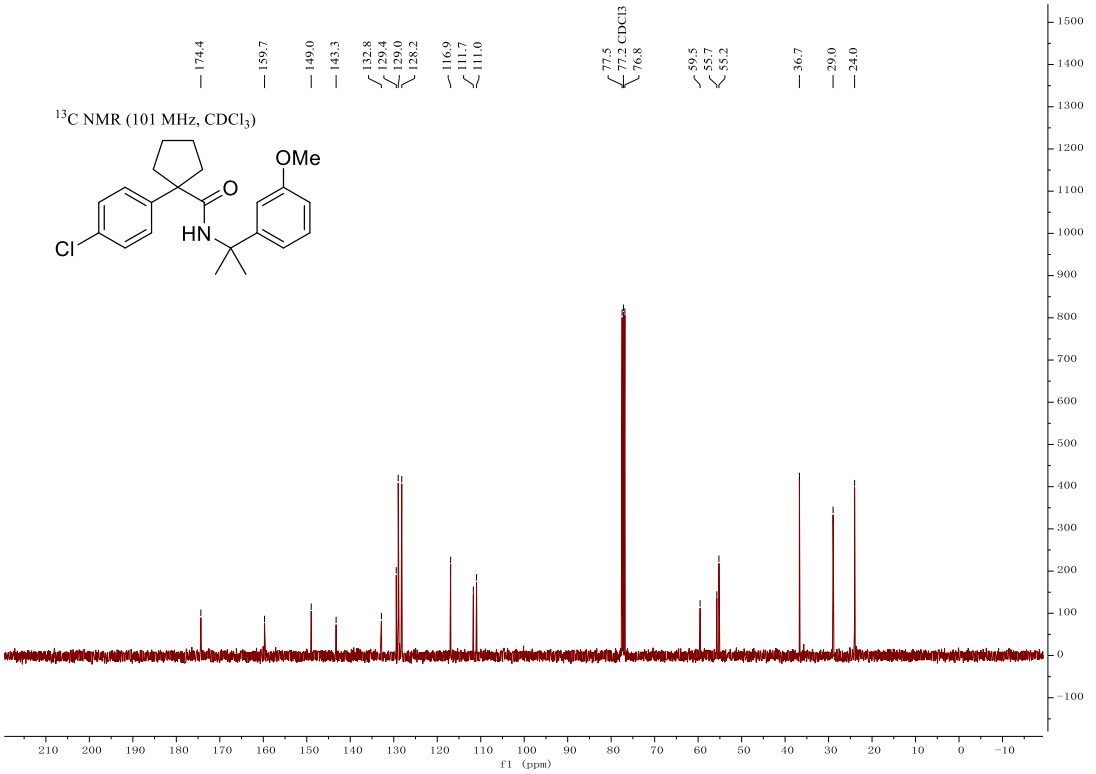
Compound S5


7.47
7.47
7.47
7.46
7.46
7.45
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.33
7.33
7.31
7.21
7.19
7.18
6.83
6.83
6.81
6.81
6.78
6.78
6.77
6.73
6.73
6.72
6.72
5.60
3.77
1.53
1.53
1.52
1.51
1.01
1.00
1.00
0.99
1H NMR (500 MHz, CDCl3)
OMe
O
HN
2.02
2.02
1.03
1.04
1.03
1.00
1.00
0.98
3.05
8.19
2.04
f1 (ppm)

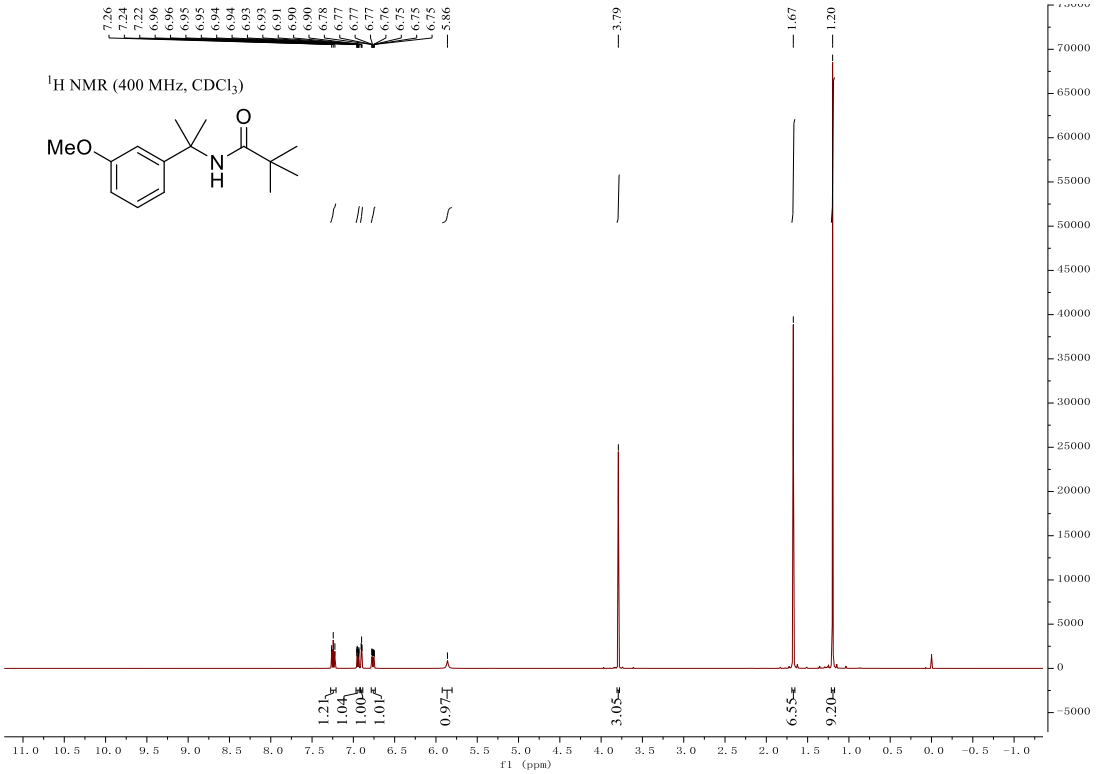

172.7
159.7
149.1
140.5
131.0
129.4
129.2
128.0
117.0
111.5
111.0
77.4
77.2 CDCl3
76.9
56.0
55.2
31.2
29.3
15.1
13C NMR (126 MHz, CDCl3)
OMe
O
HN
f1 (ppm)

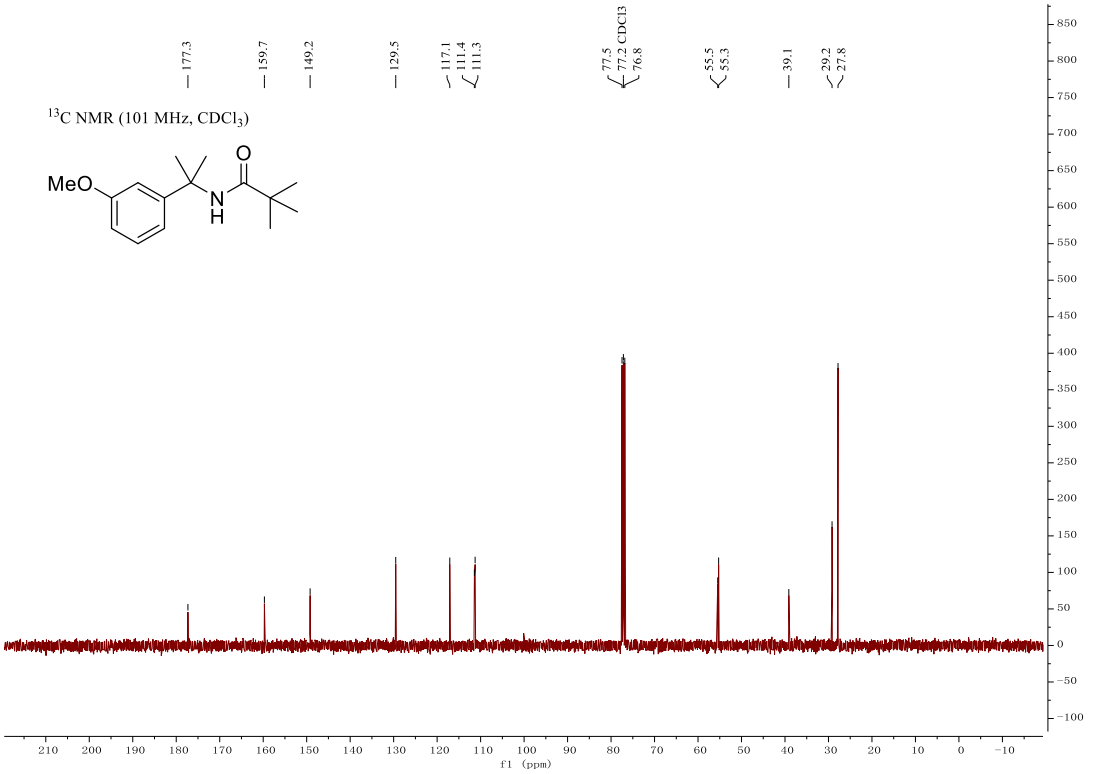
Compound S6


7.26 CDCl3
1H NMR (400 MHz, CDCl3)
OMe
O
HN
Cl
4.04
1.00
1.00
0.96
1.00
1.00
3.04
2.07
2.07
4.21
6.02
f1 (ppm)

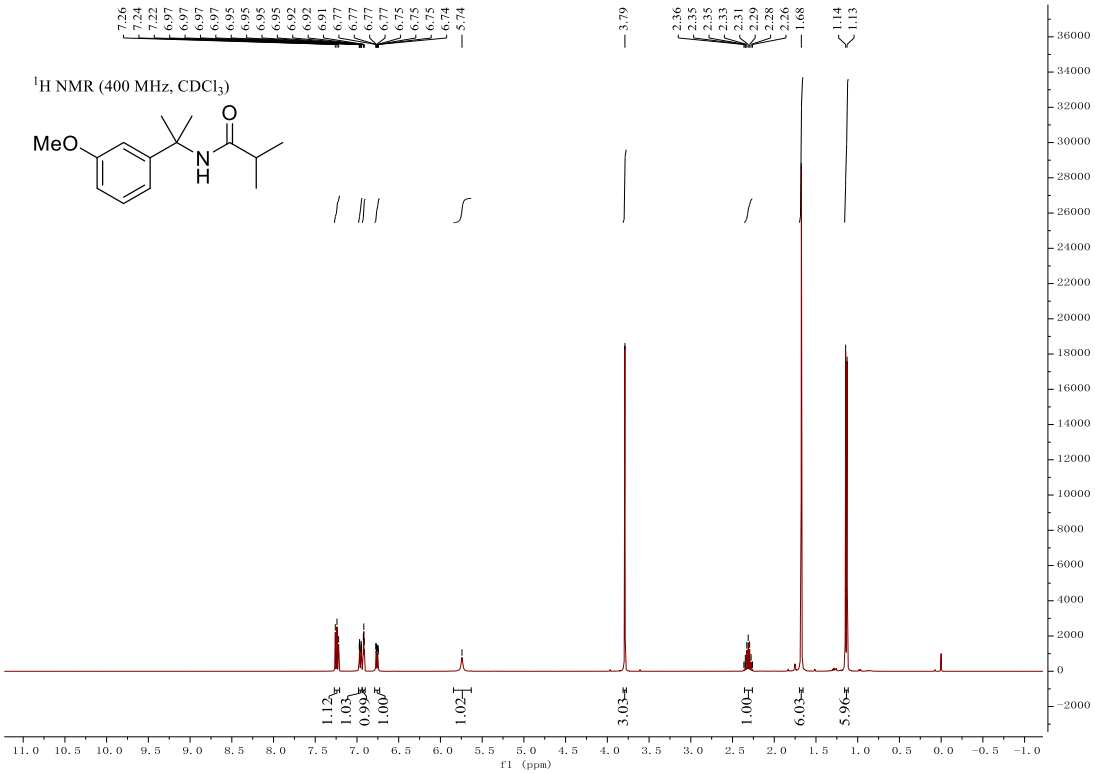

174.4
159.7
149.0
143.3
132.8
129.4
129.0
128.2
116.9
111.7
111.0
77.5
77.2 CDCl3
76.8
59.5
55.7
55.2
36.7
29.0
24.0
13C NMR (101 MHz, CDCl3)
OMe
O
HN
Cl
f1 (ppm)

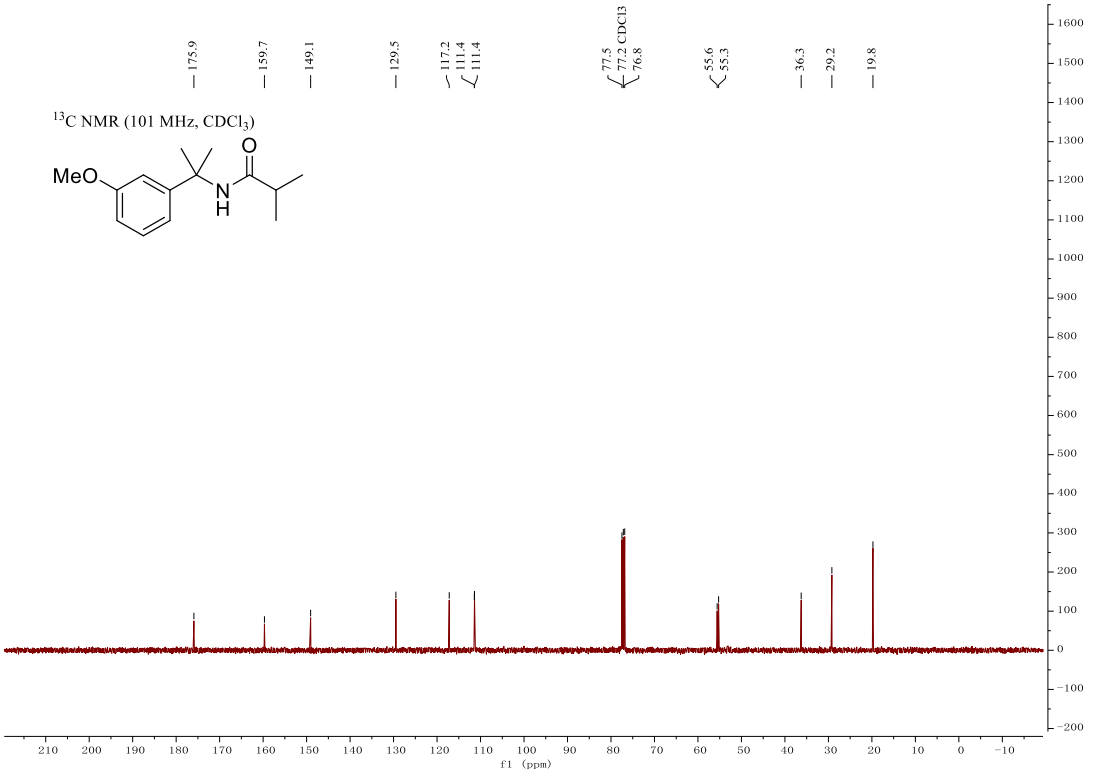
Compound S7


7.26
7.24
7.22
6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.93
6.91
6.90
6.90
6.78
6.77
6.77
6.77
6.76
6.75
6.75
6.75
5.86
3.79
1.67
1.20
1H NMR (400 MHz, CDCl3)
MeO
N
H
O
1.21
1.04
1.00
1.01
0.97
3.05
6.55
9.20
f1 (ppm)

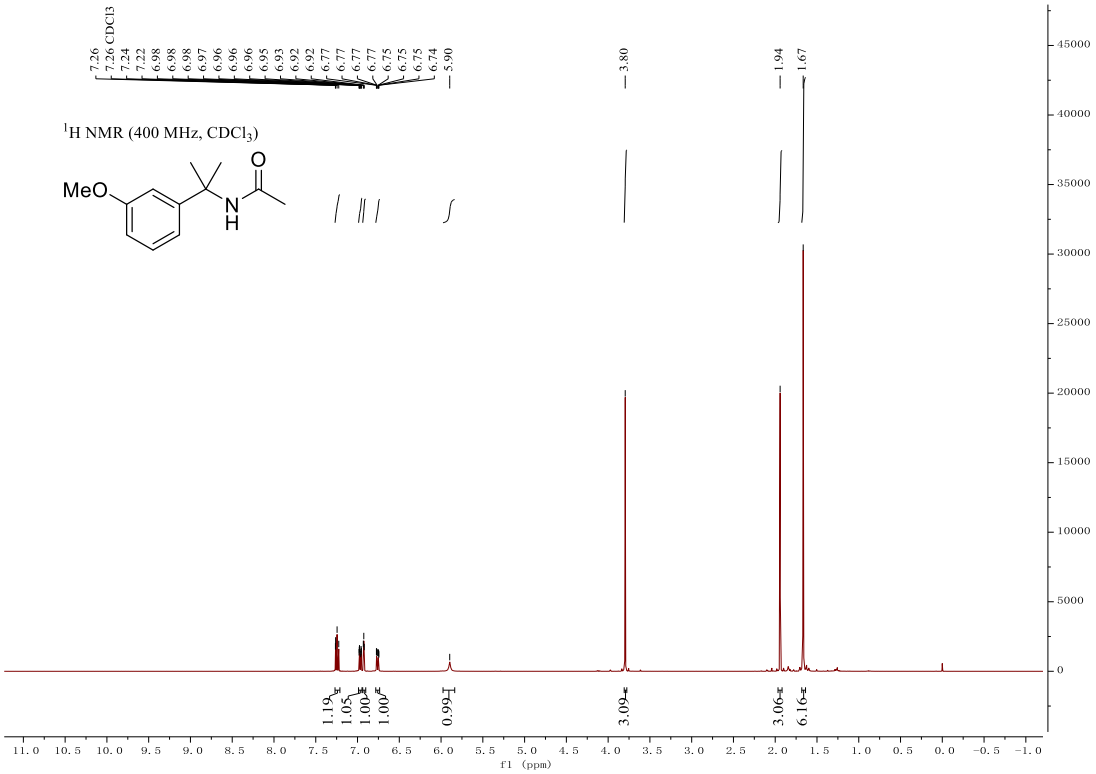

177.3
159.7
149.2
129.5
117.1
111.4
111.3
77.5
77.2 CDCl3
76.8
55.5
55.3
39.1
29.2
27.8
13C NMR (101 MHz, CDCl3)
MeO
N
H
O
f1 (ppm)

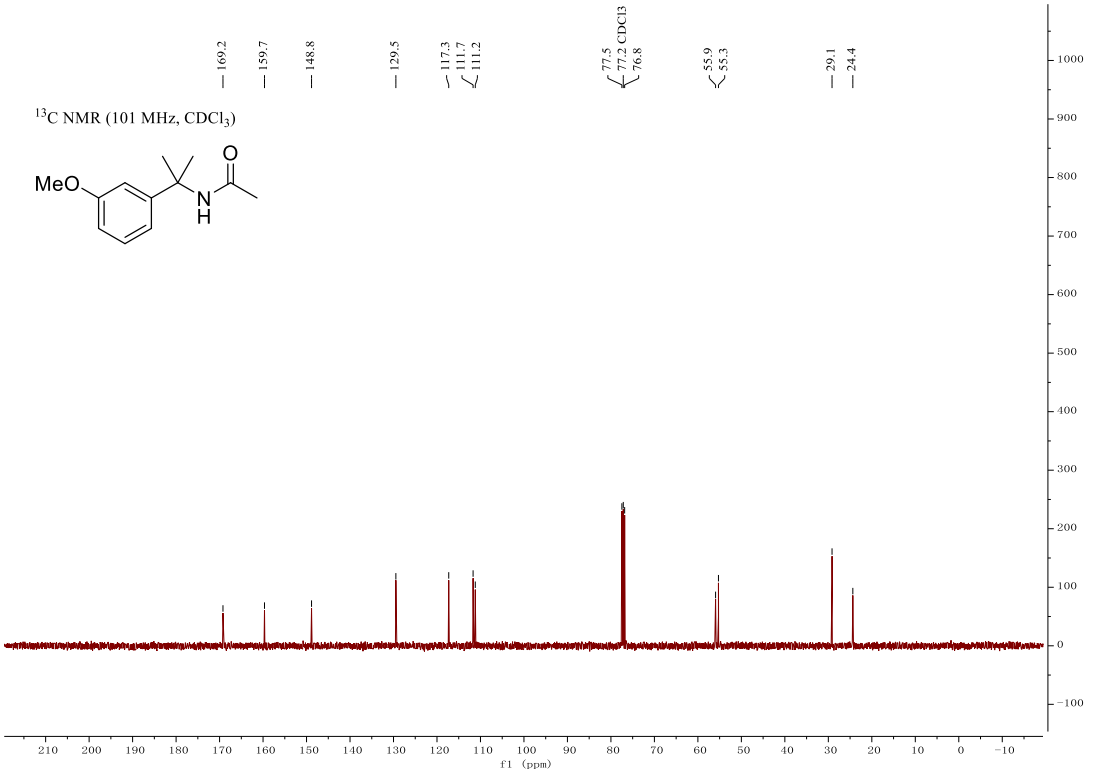
Compound S8


7.26
7.24
7.22
6.97
6.95
6.92
6.91
6.77
6.75
6.74
5.74
3.79
2.36
2.35
2.33
2.31
2.29
2.28
2.26
1.68
1.14
1.13
1H NMR (400 MHz, CDCl3)
MeO
N
H
O
1.12
1.03
0.99
1.00
1.02
3.03
1.00
6.03
5.96
f1 (ppm)

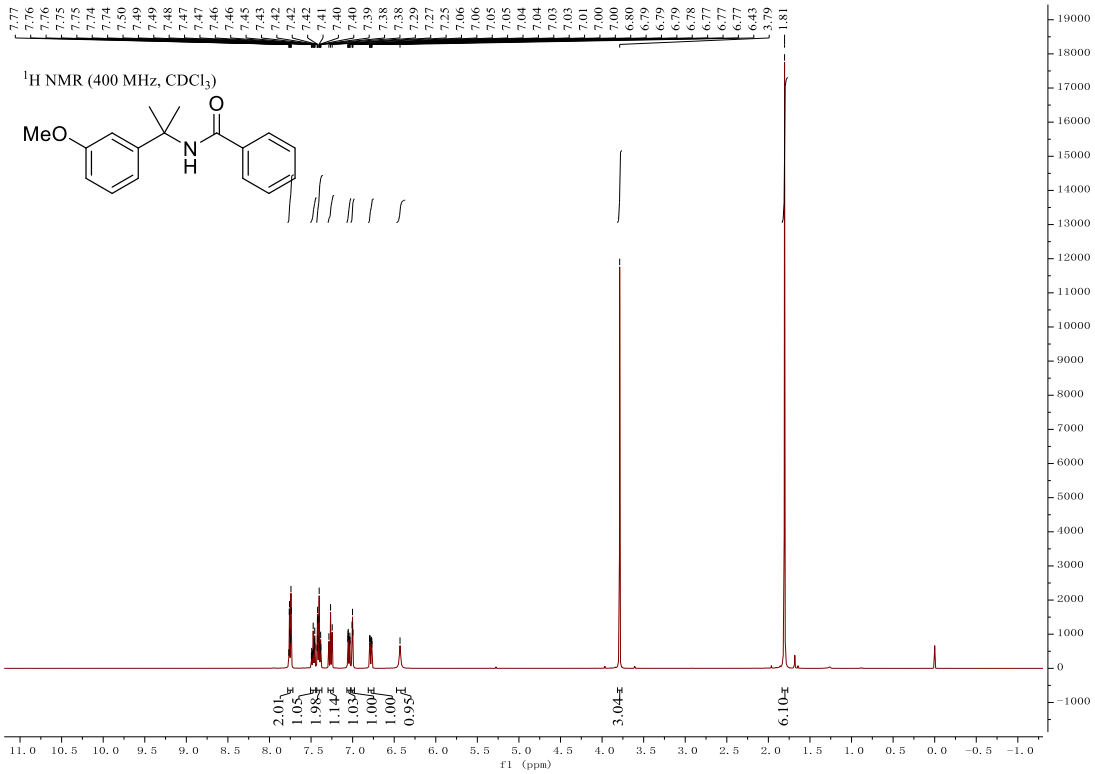

175.9
159.7
149.1
129.5
117.2
111.4
111.4
77.5
77.2 CDCl3
76.8
55.6
55.3
36.3
29.2
19.8
13C NMR (101 MHz, CDCl3)
MeO
N
H
O
f1 (ppm)

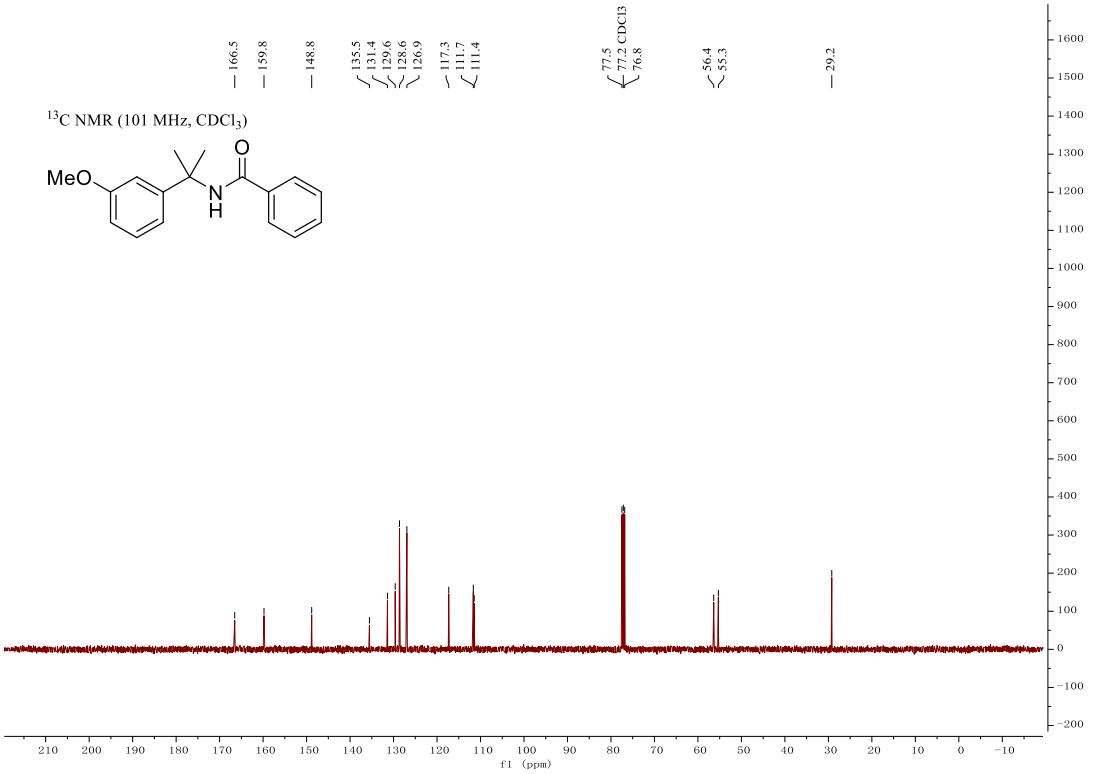
Compound S9


7.26
7.26 CDCl3
7.24
7.22
6.98
6.98
6.98
6.97
6.96
6.96
6.96
6.95
6.93
6.92
6.92
6.77
6.77
6.77
6.75
6.75
6.75
6.74
5.90
3.80
1.94
1.67
1H NMR (400 MHz, CDCl3)
MeO
N
H
O
1.19
1.05
1.00
1.00
0.99
3.09
3.06
6.16
f1 (ppm)

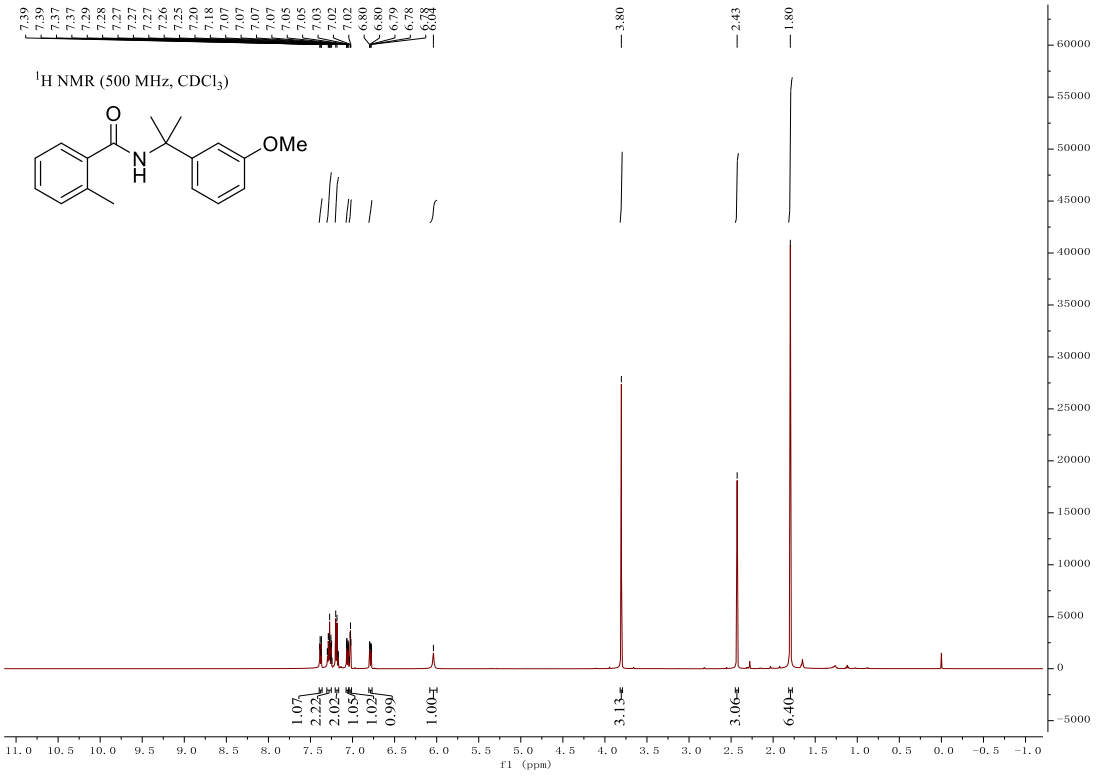


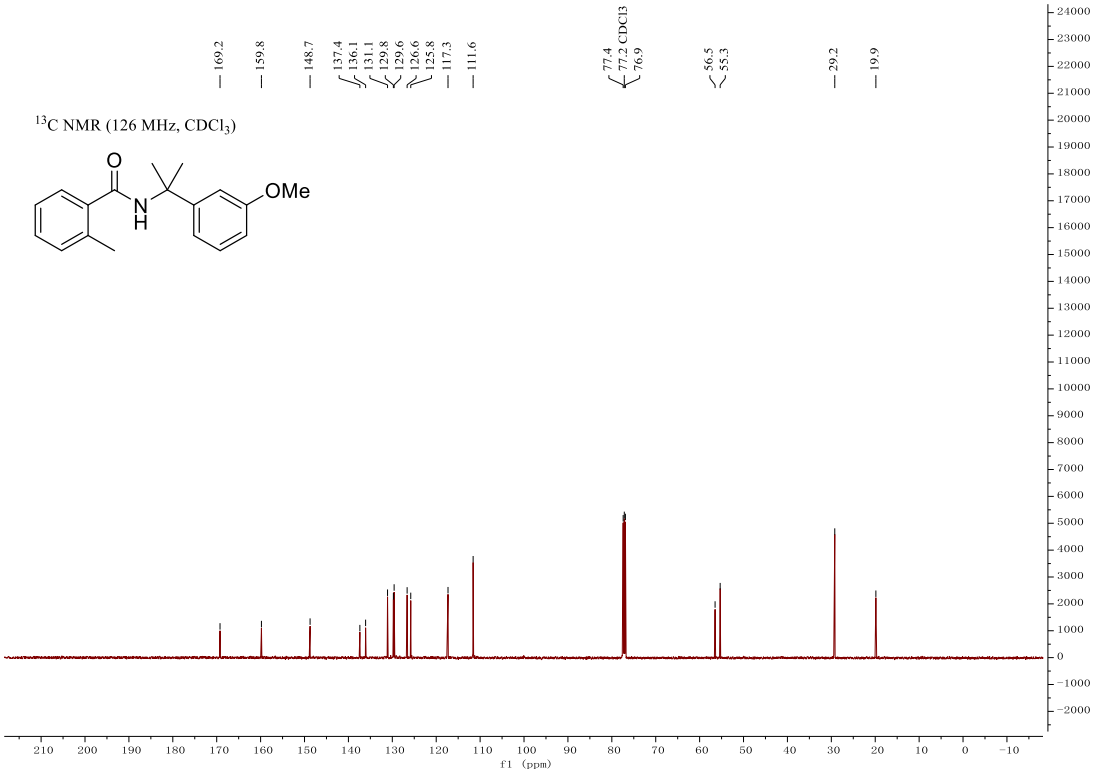
Compound S10



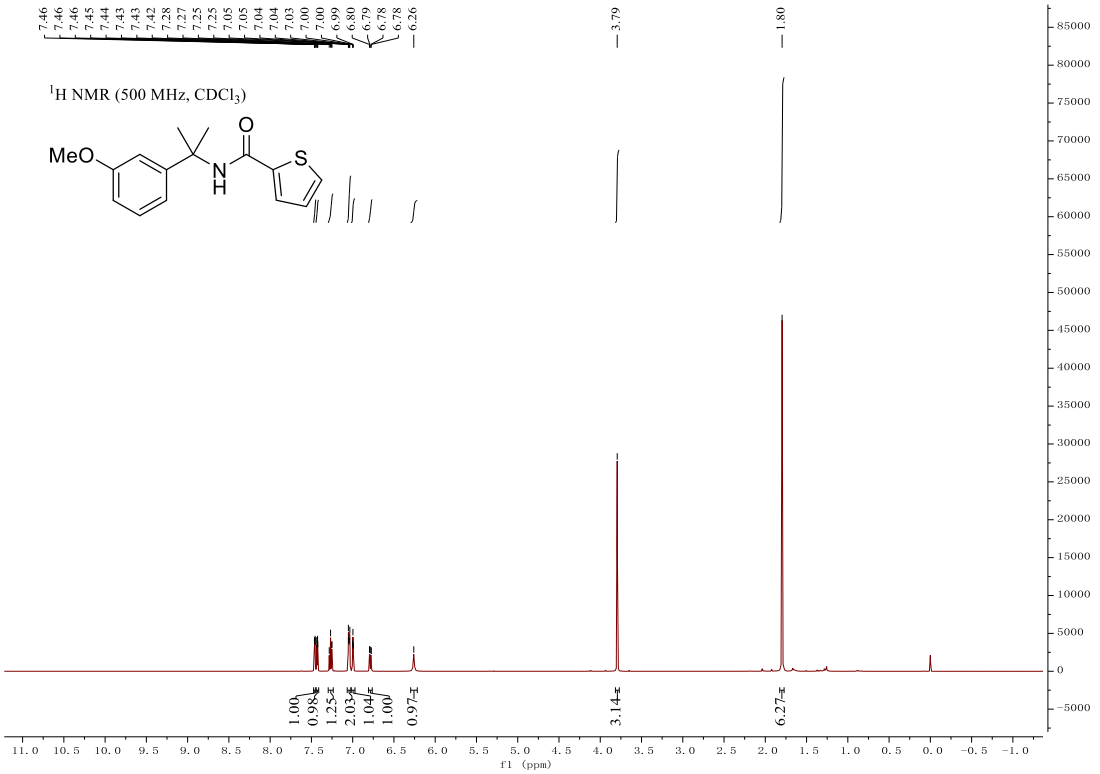


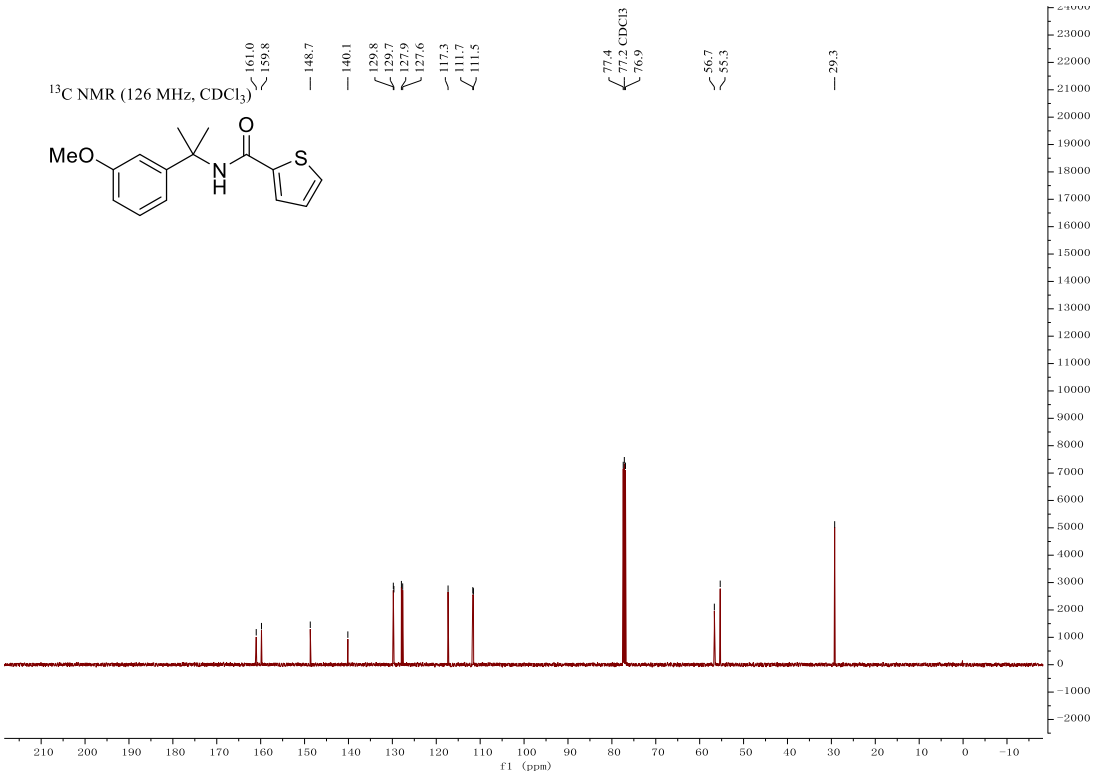
Compound S11



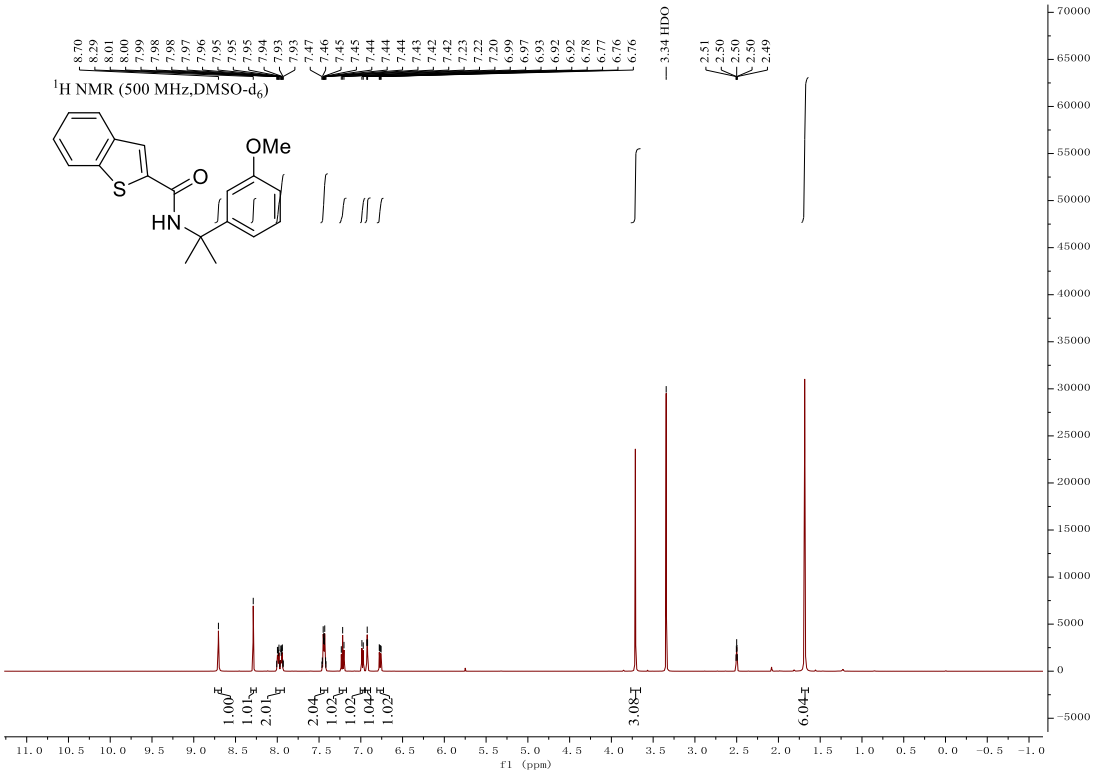


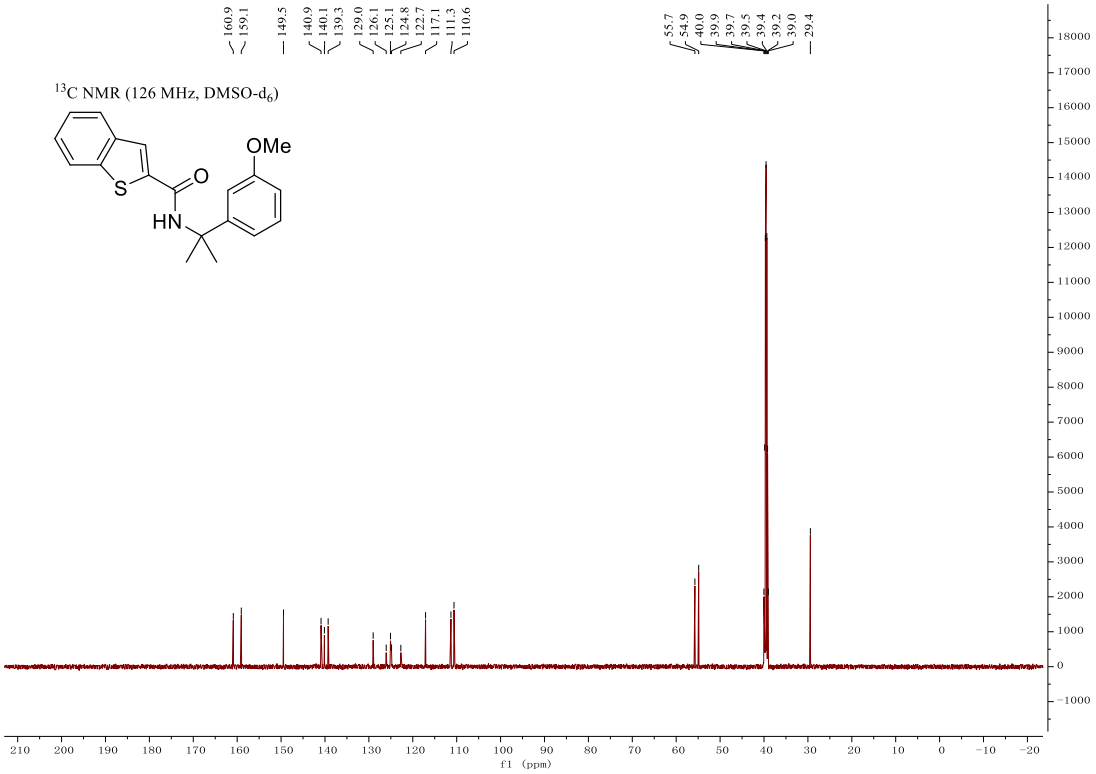
Compound S12



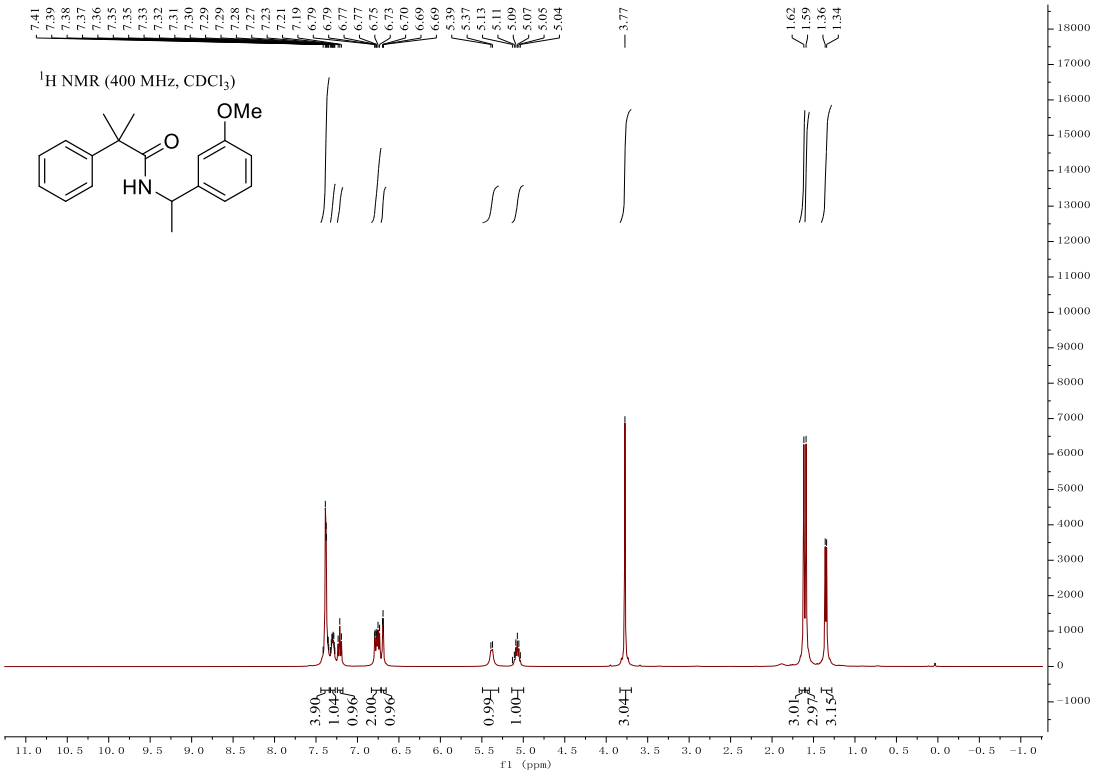


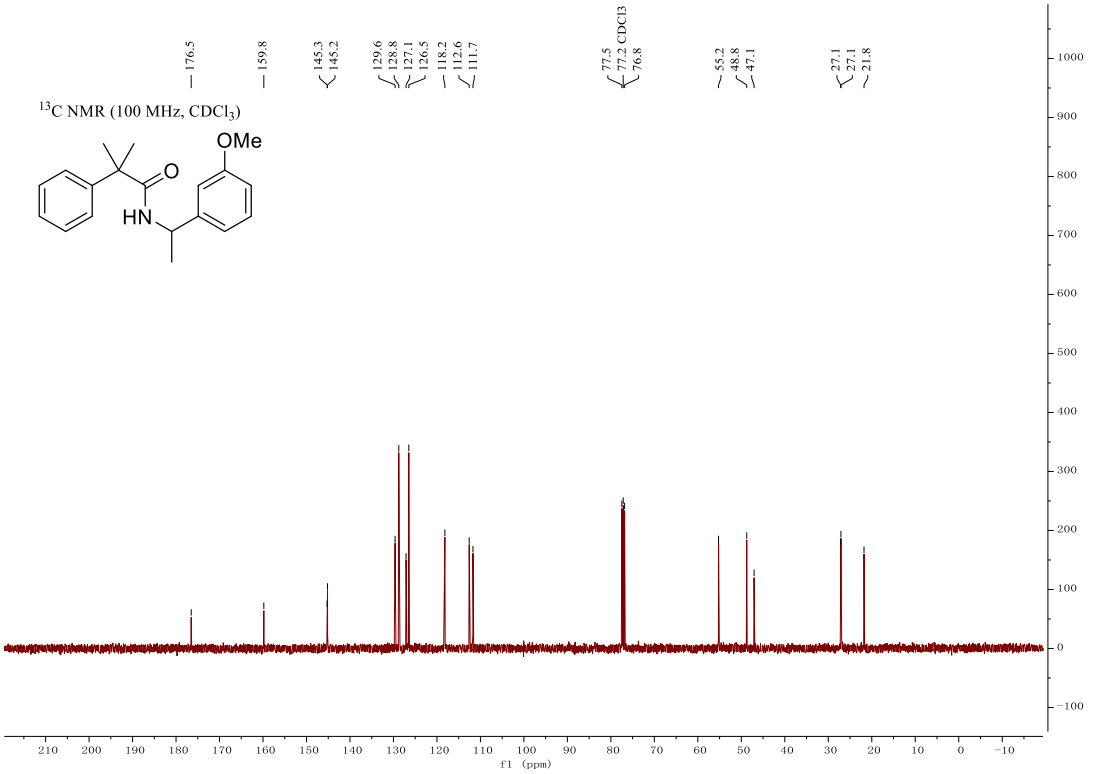
Compound S13



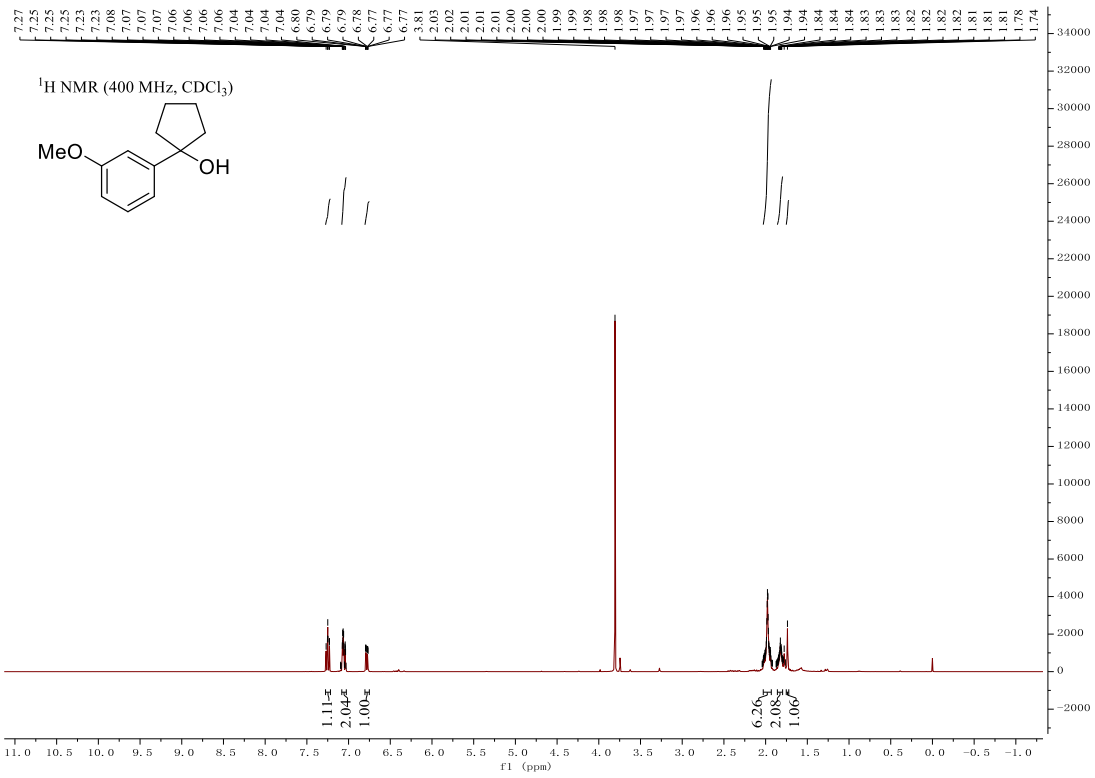


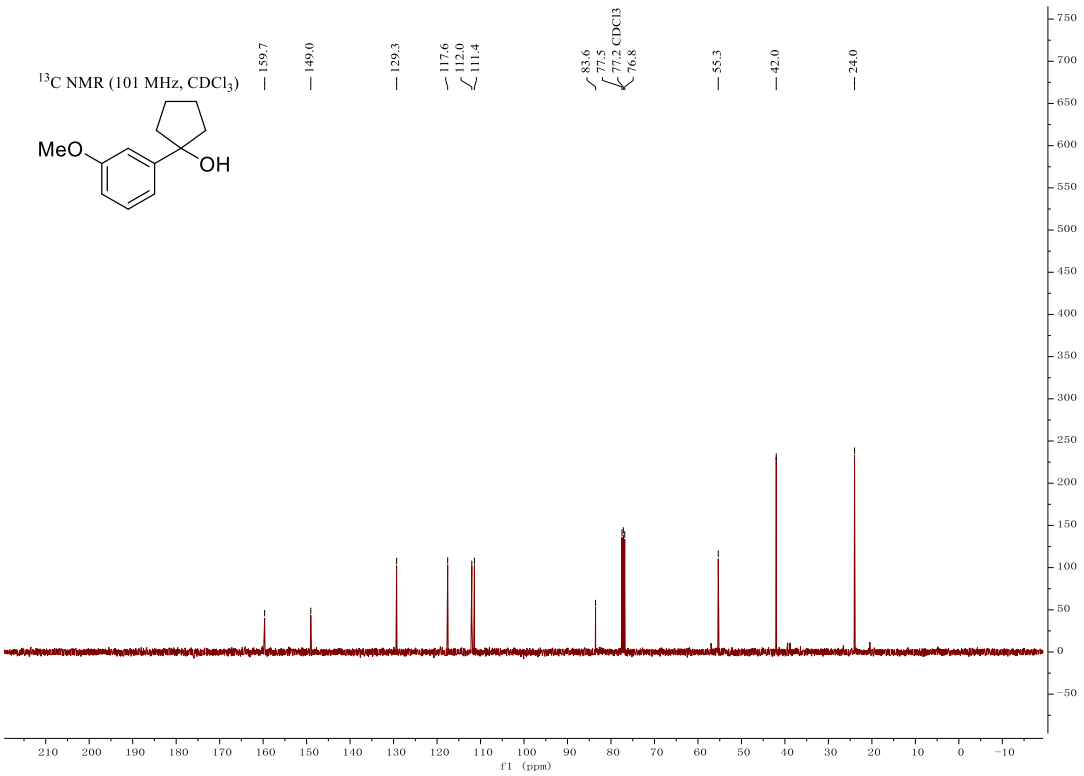
Compound S14



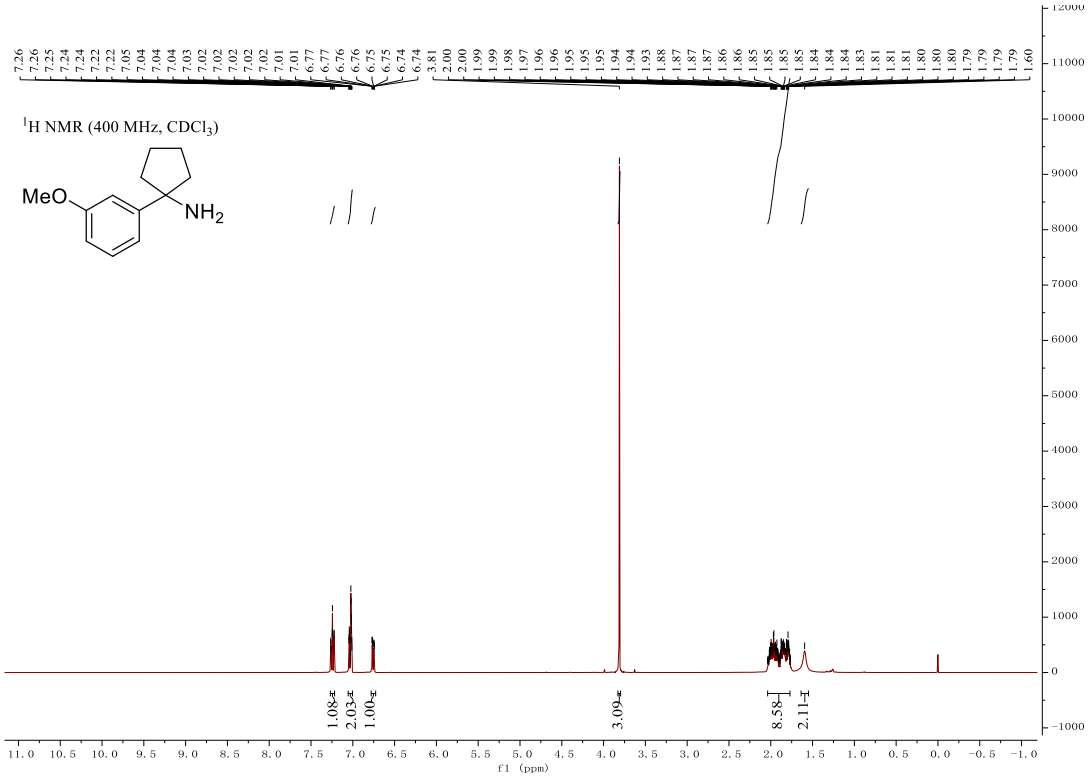


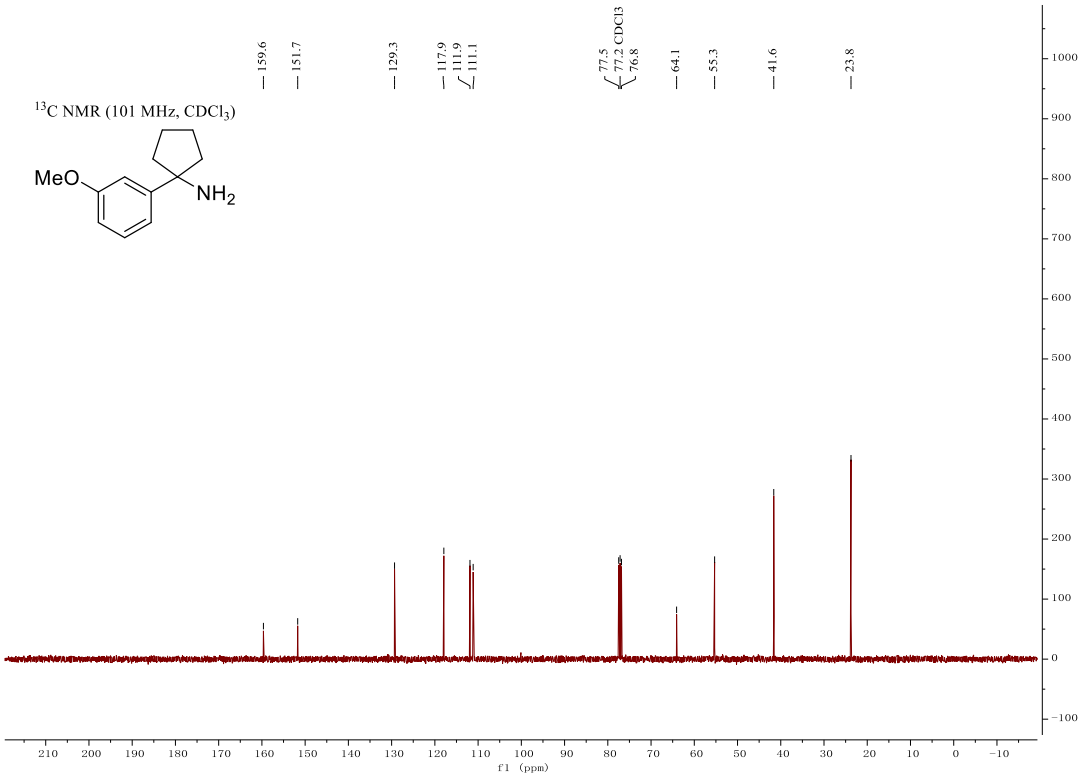
Compound S15



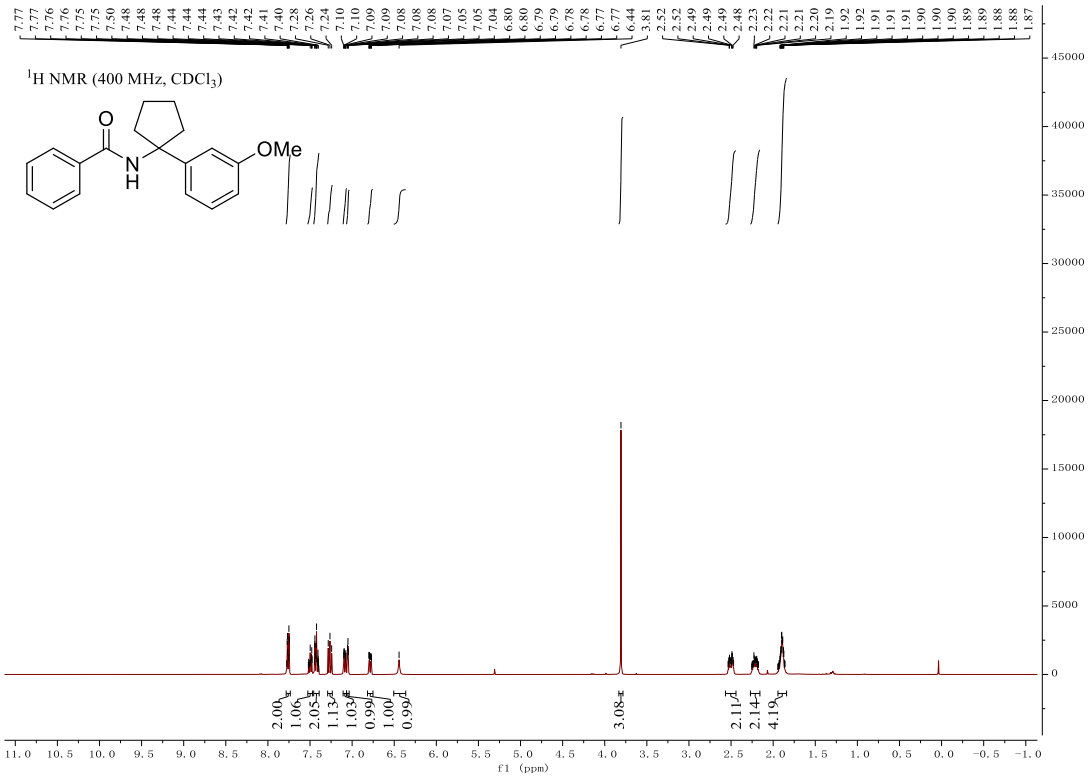


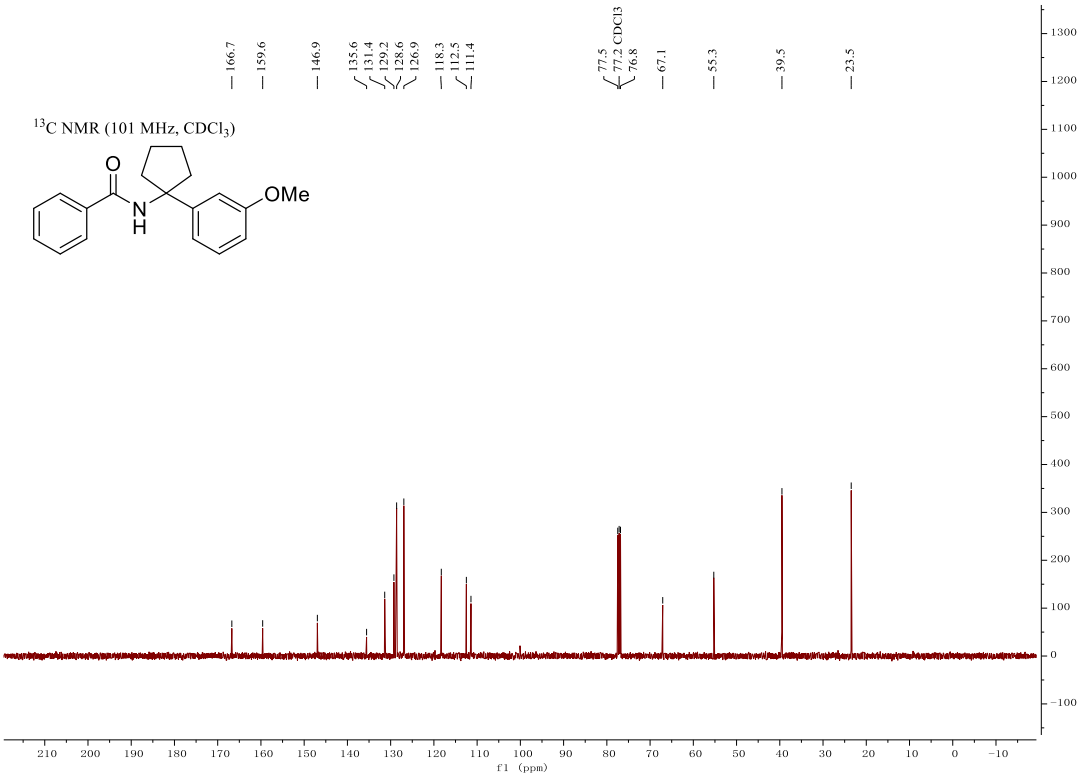
Compound S16



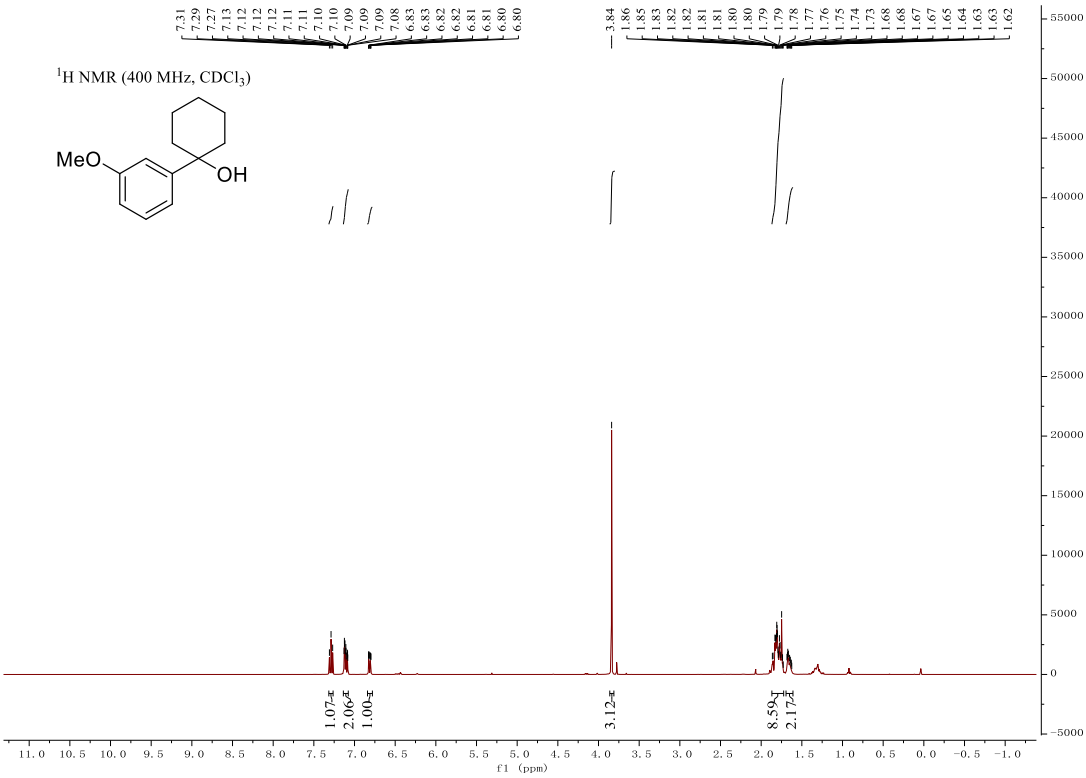


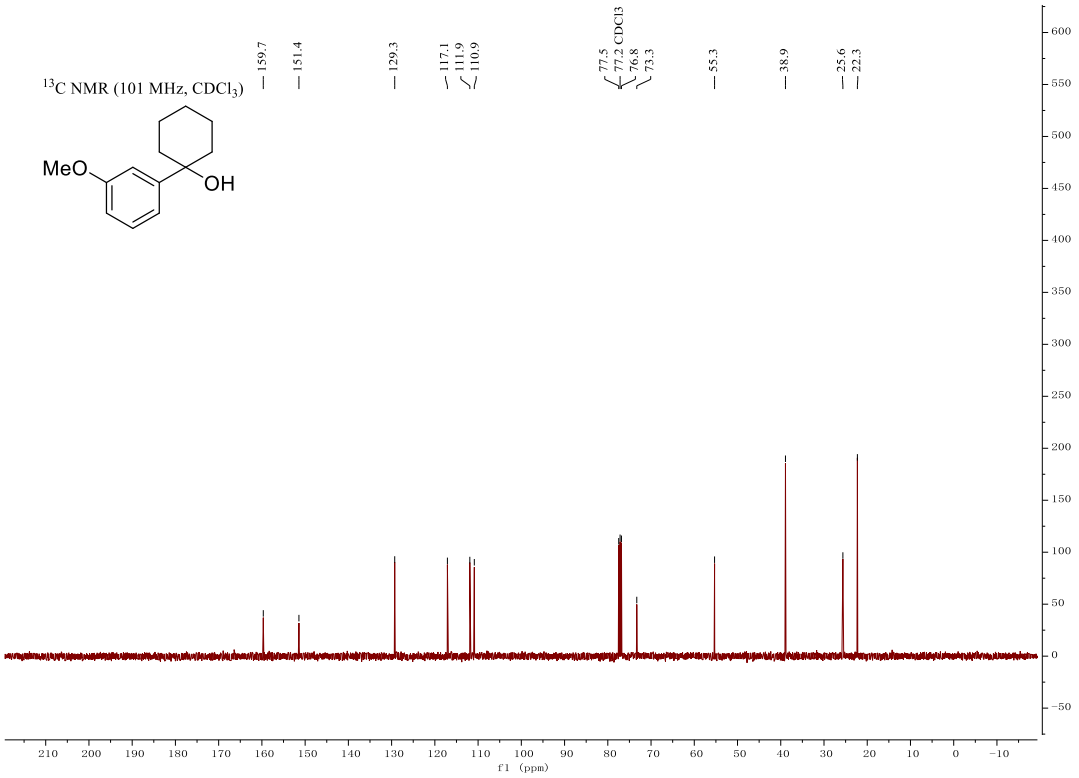
Compound S17



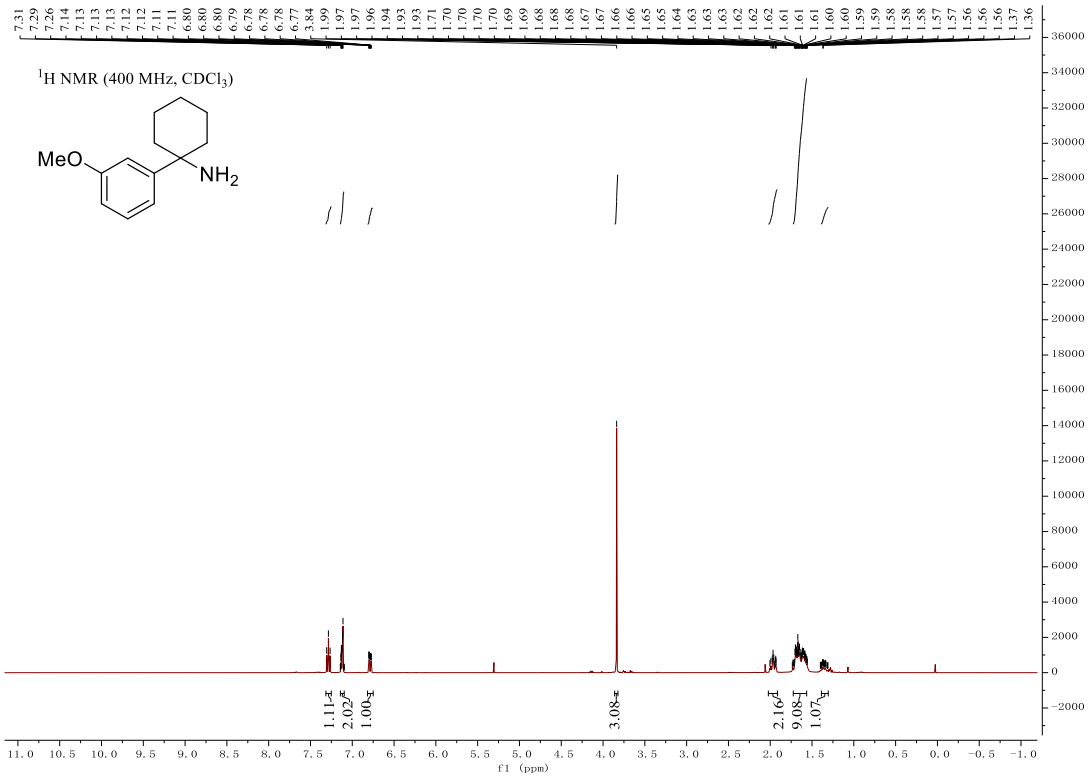


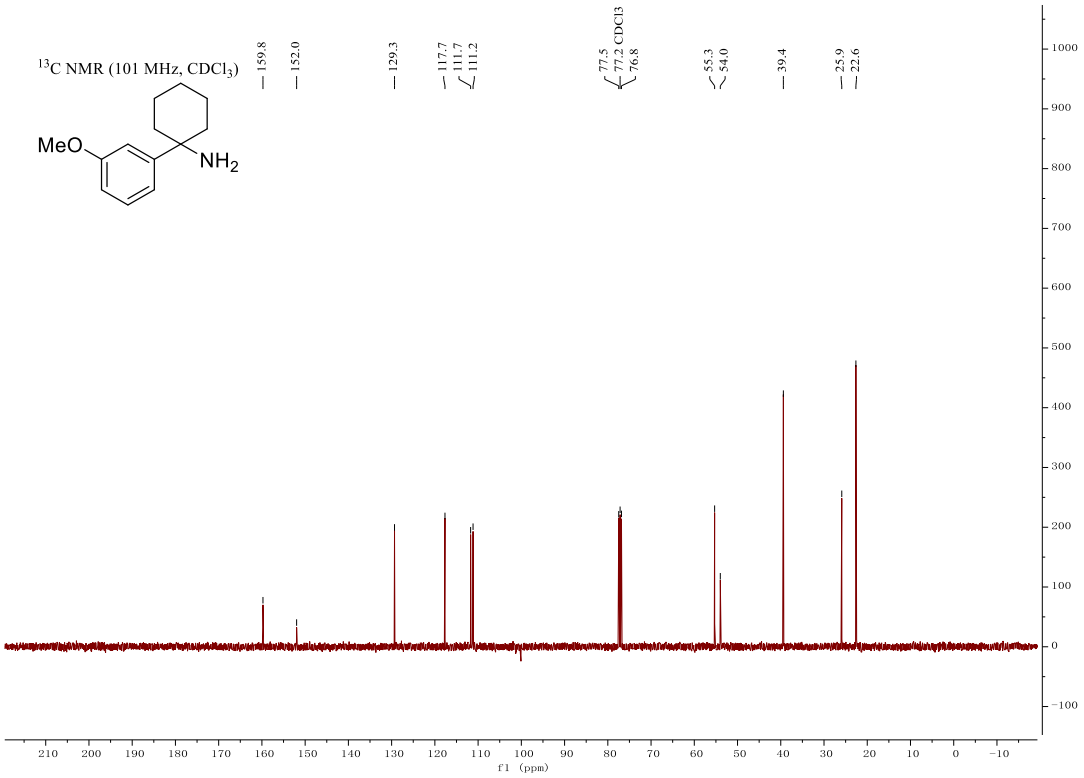
Compound S18



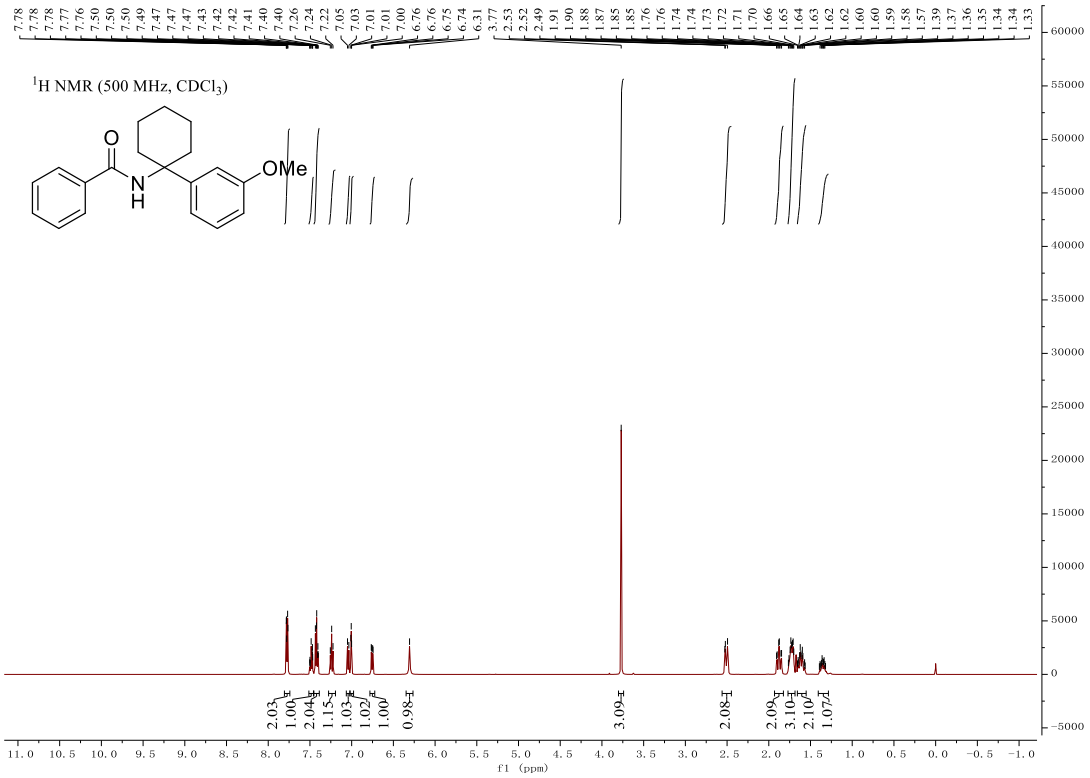


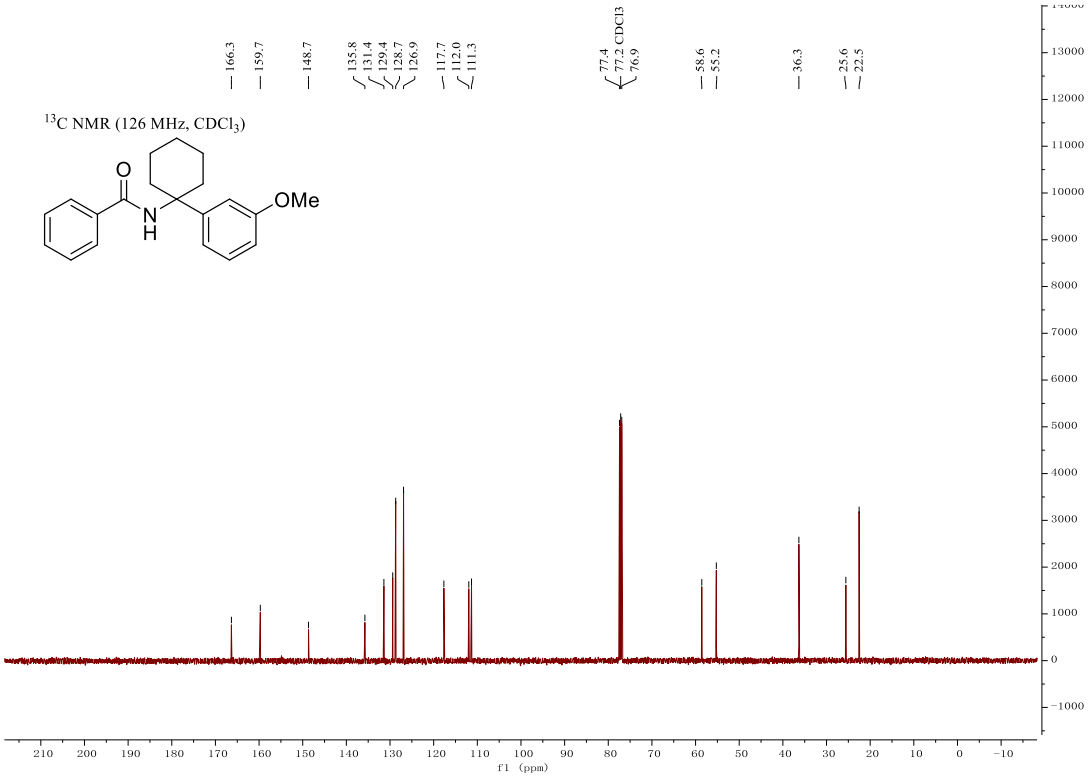
Compound S19



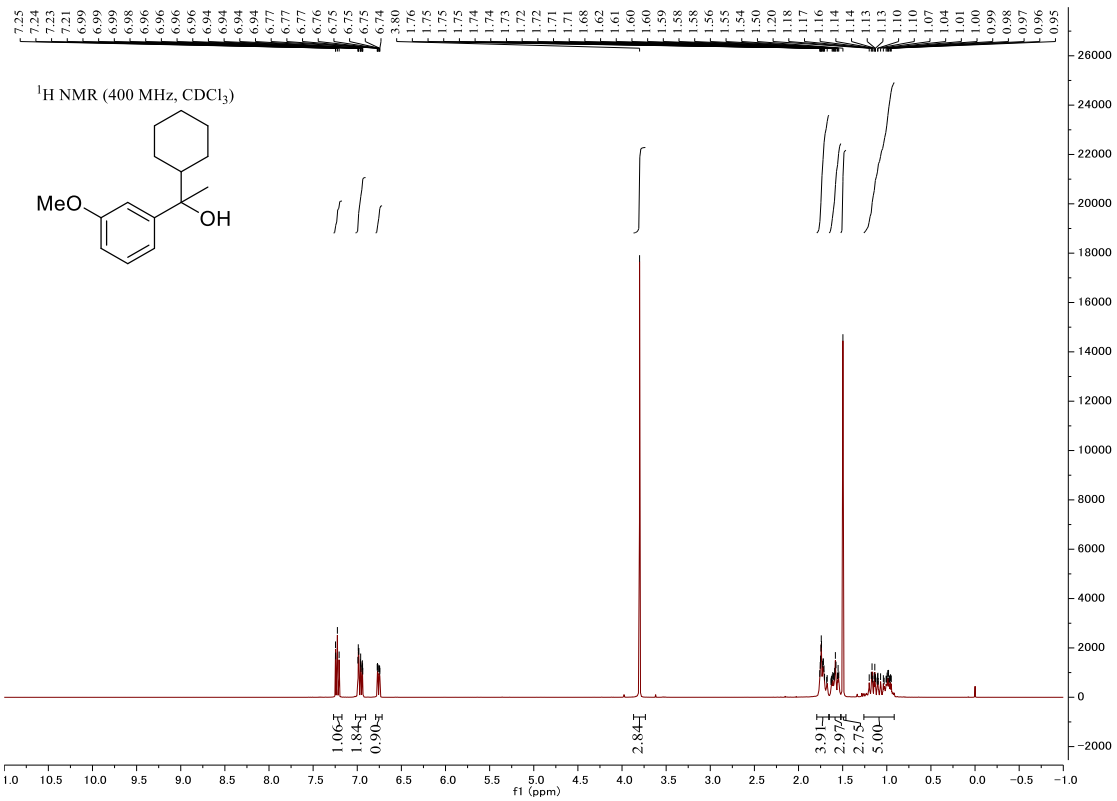


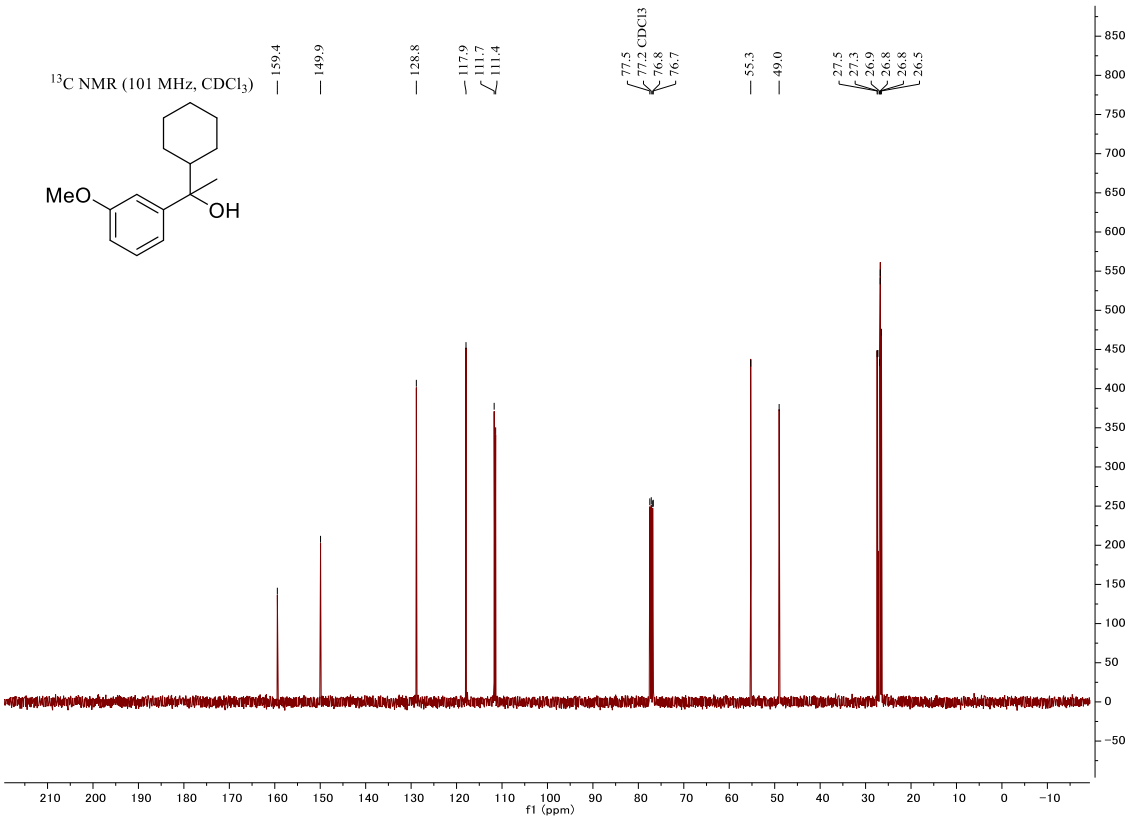
Compound S20



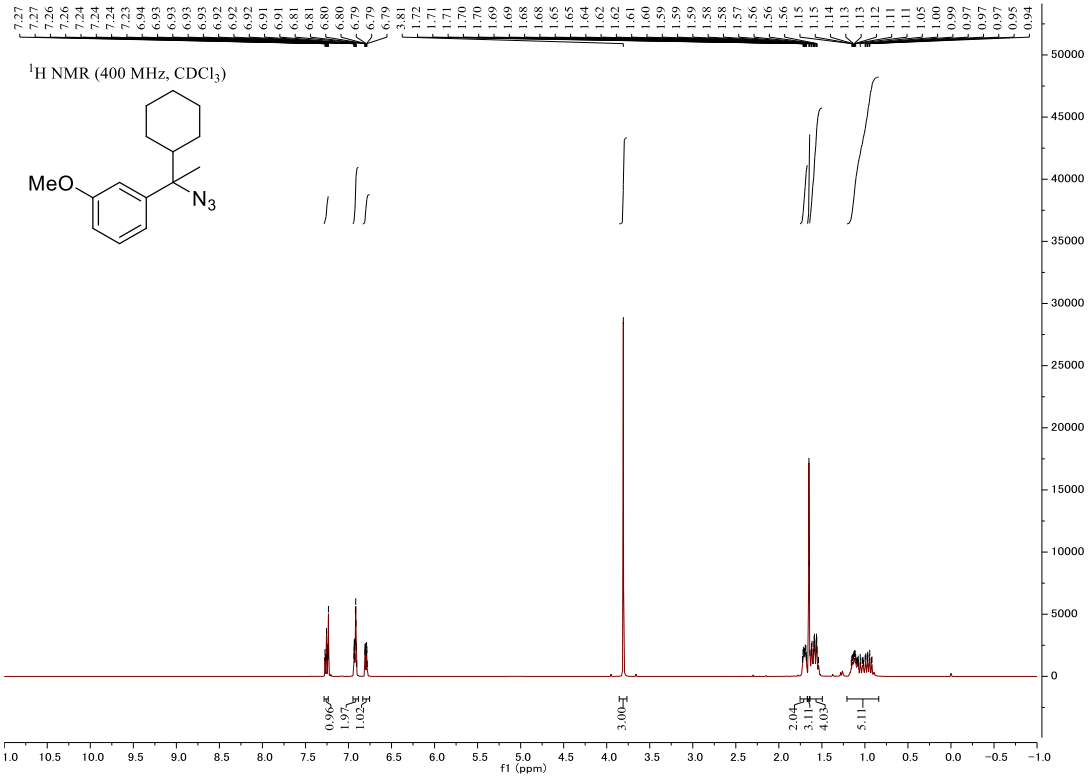


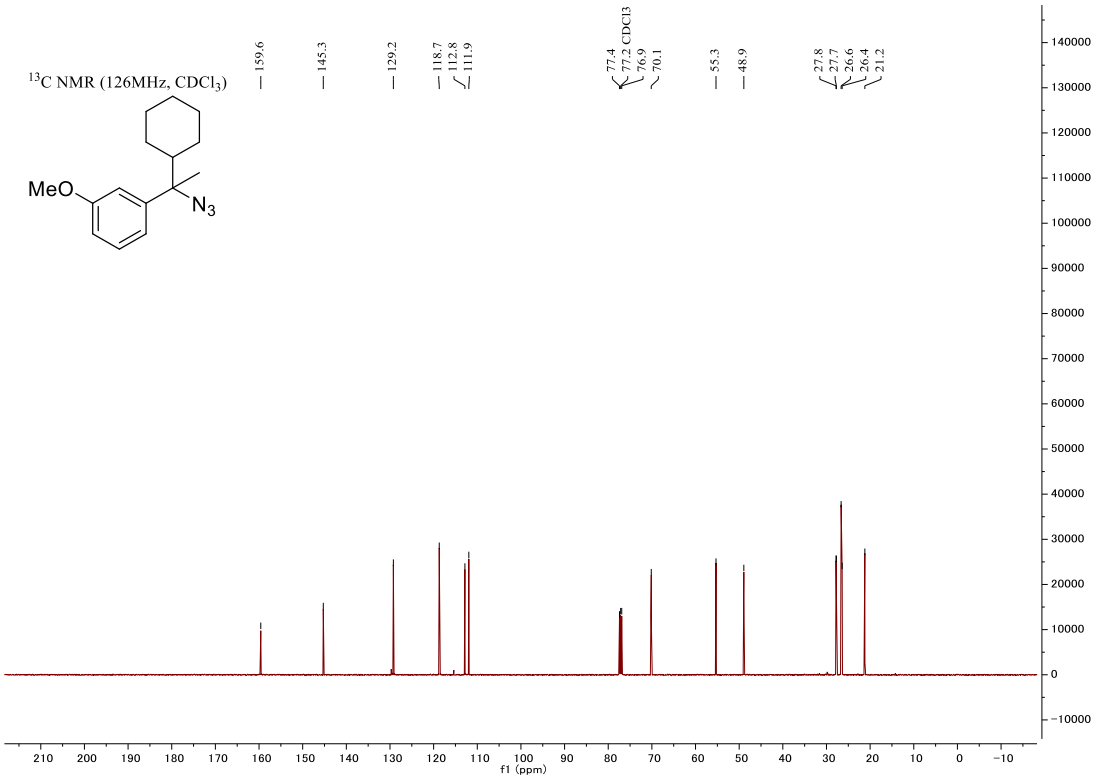
Compound S21



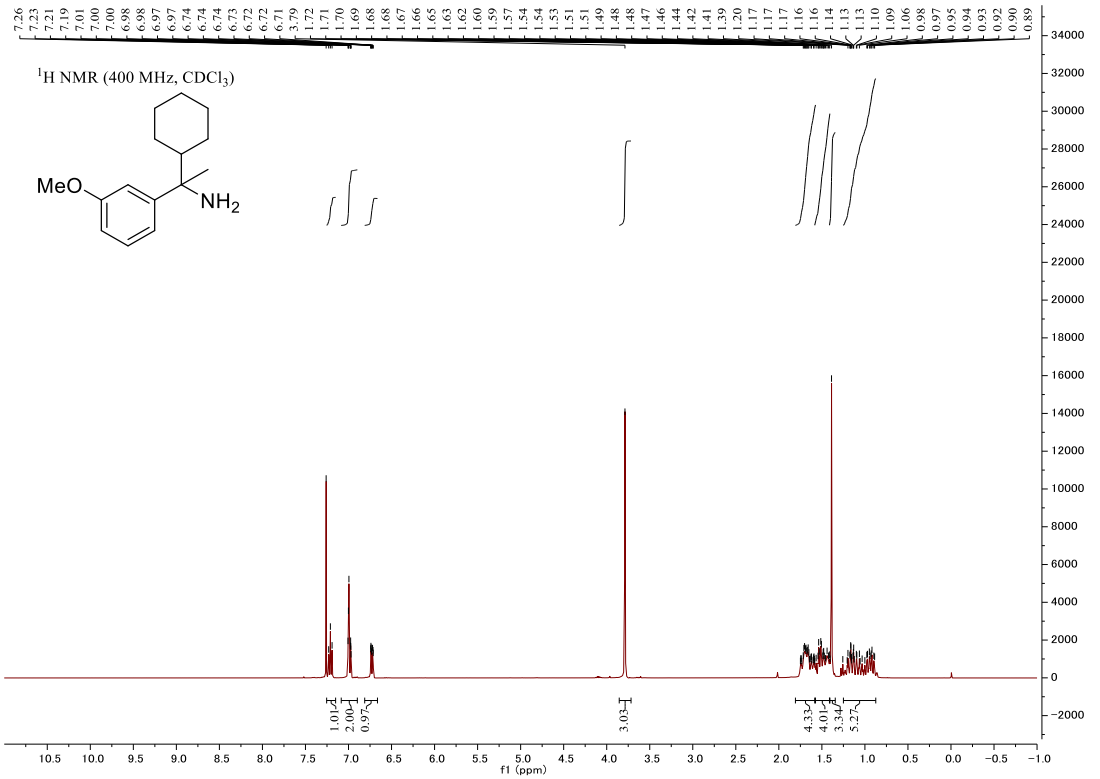


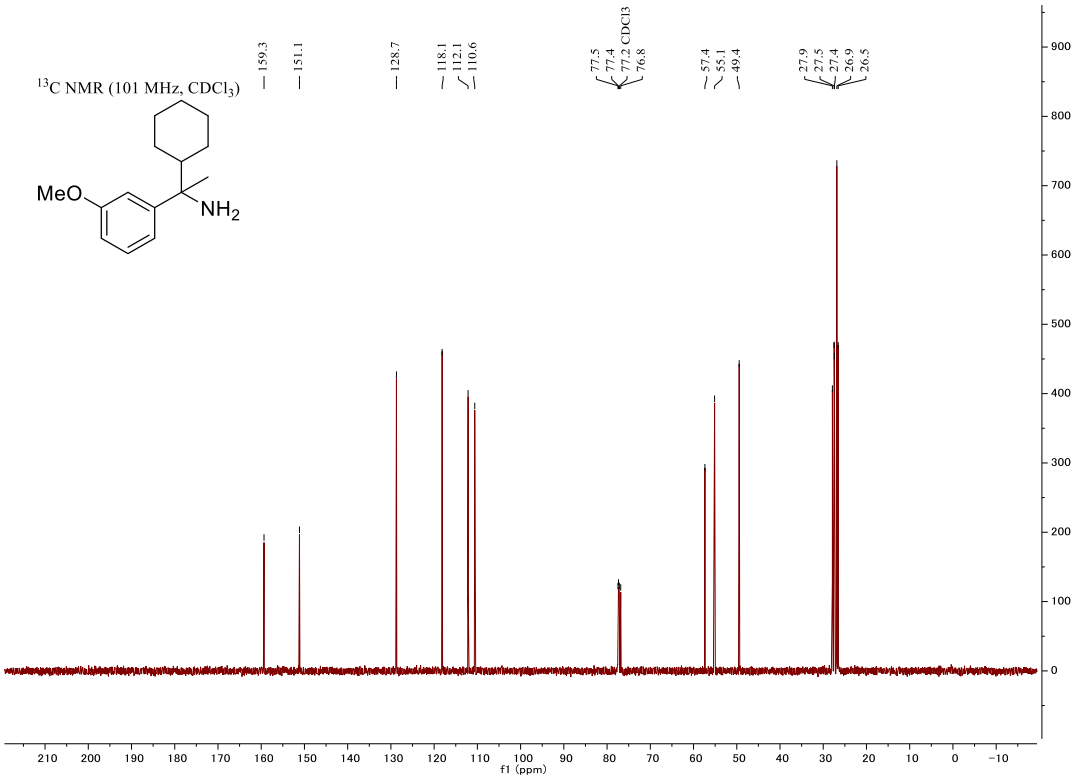
Compound S22



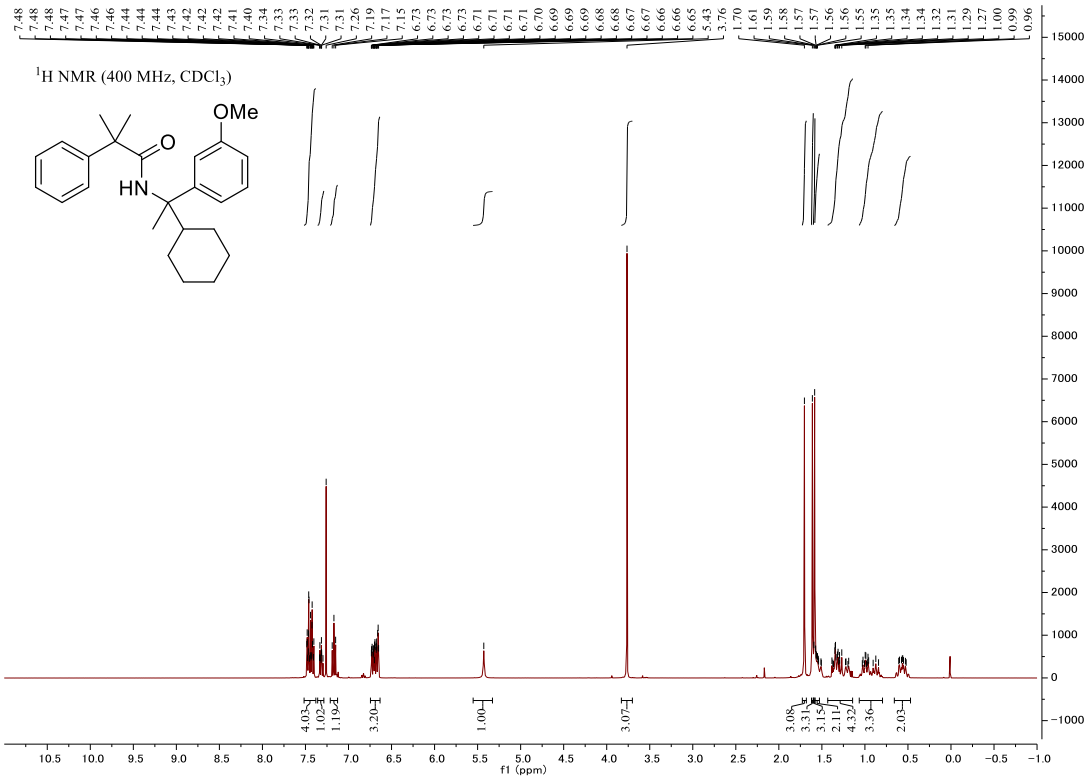


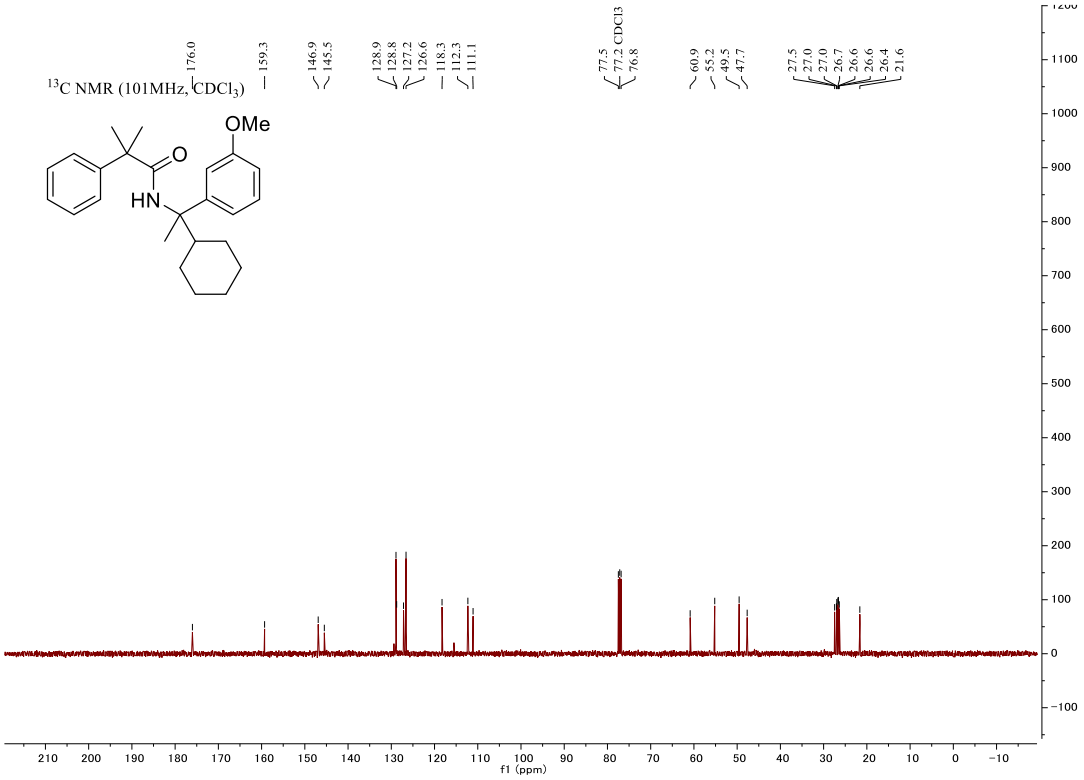
Compound S23



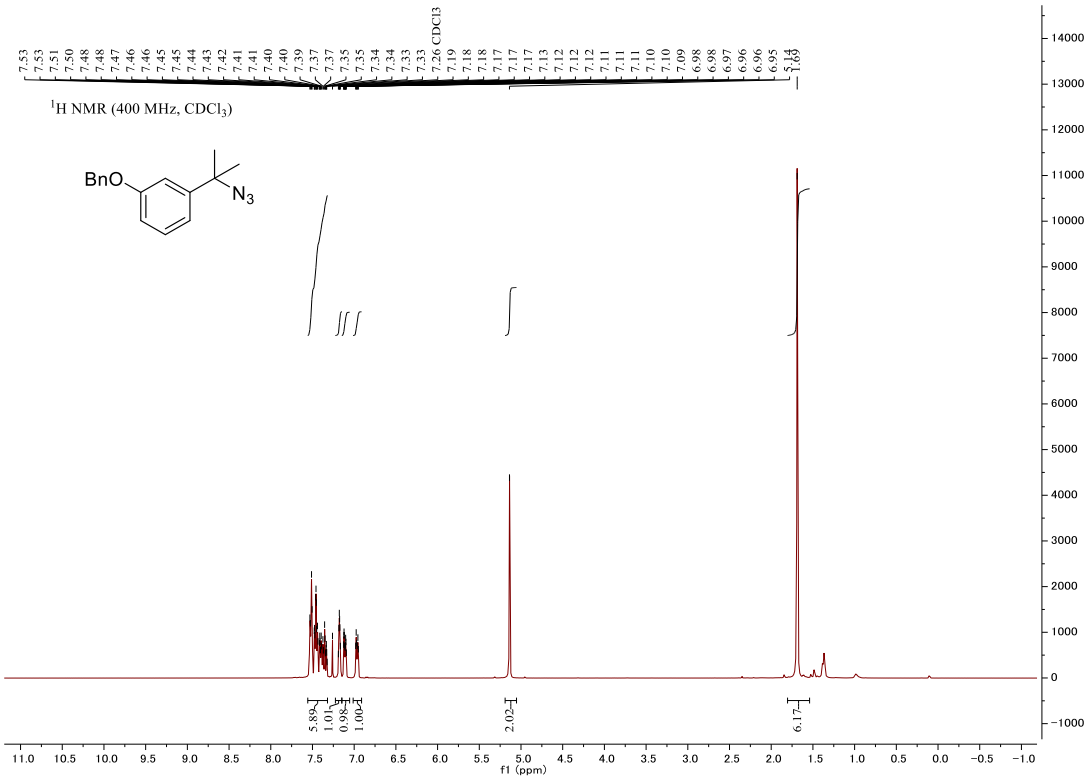


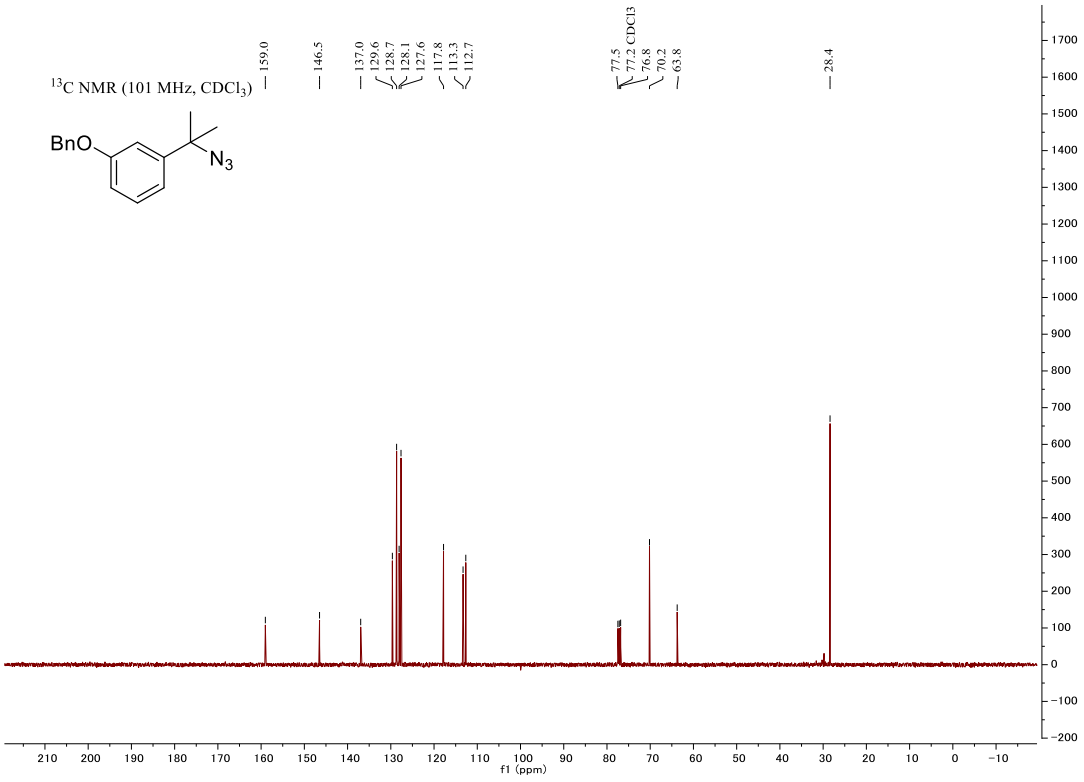
Compound S24



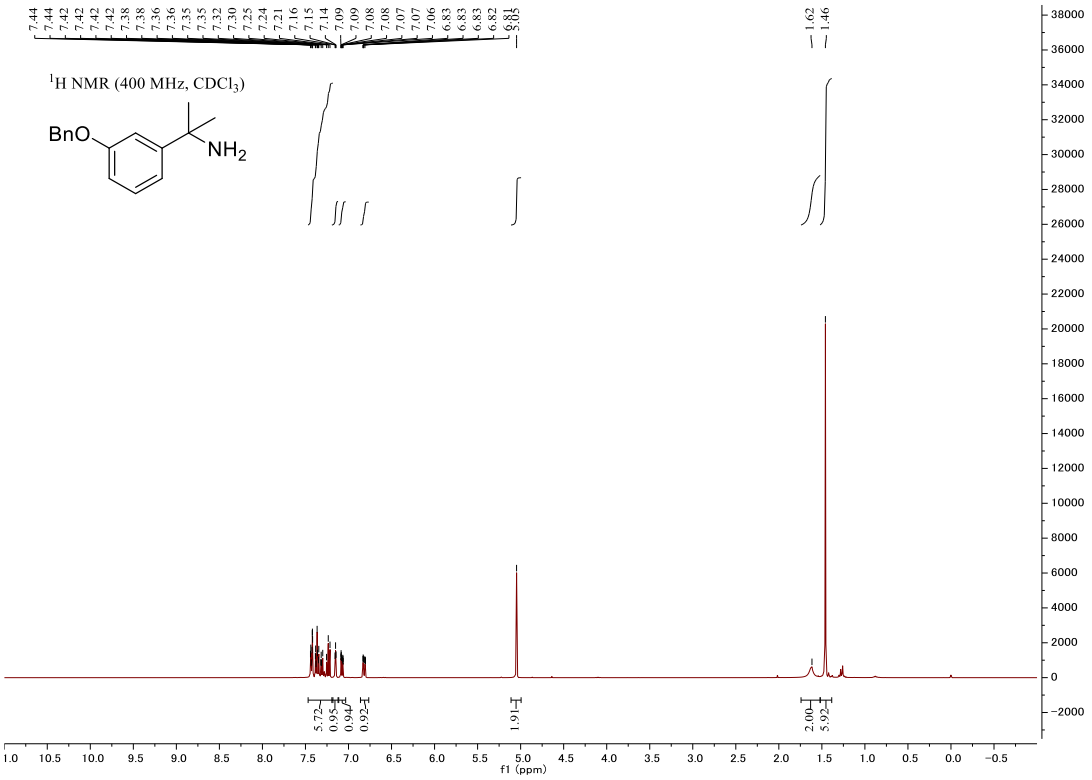


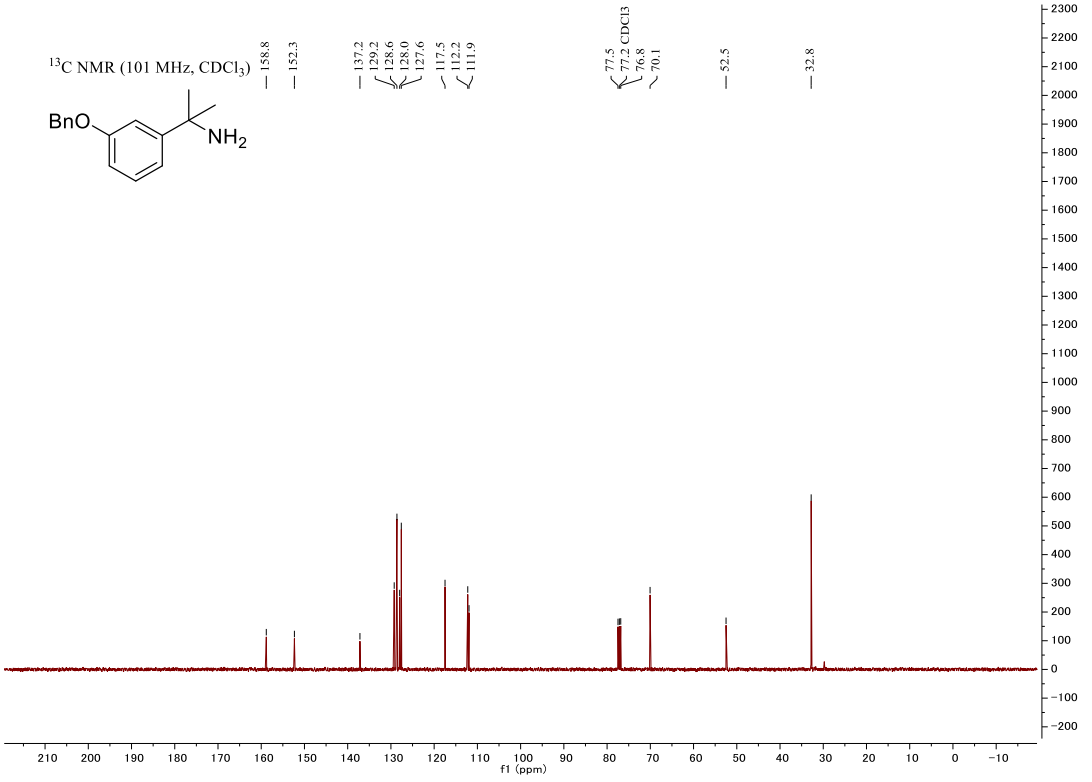
Compound S26



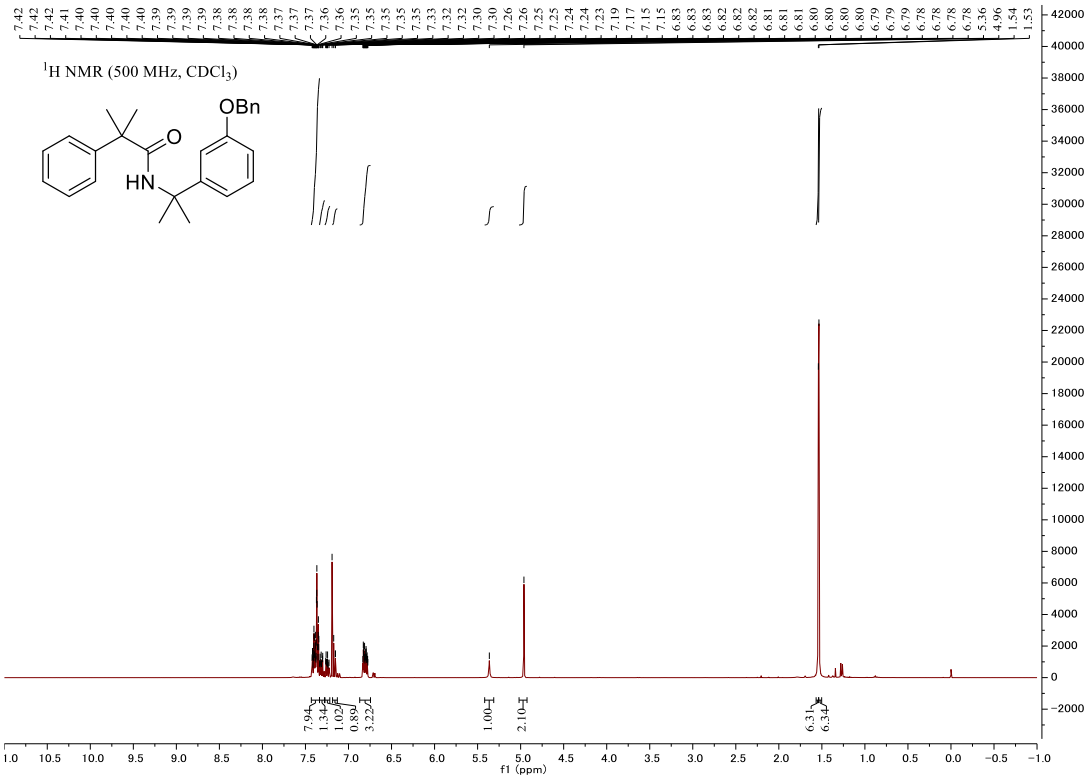


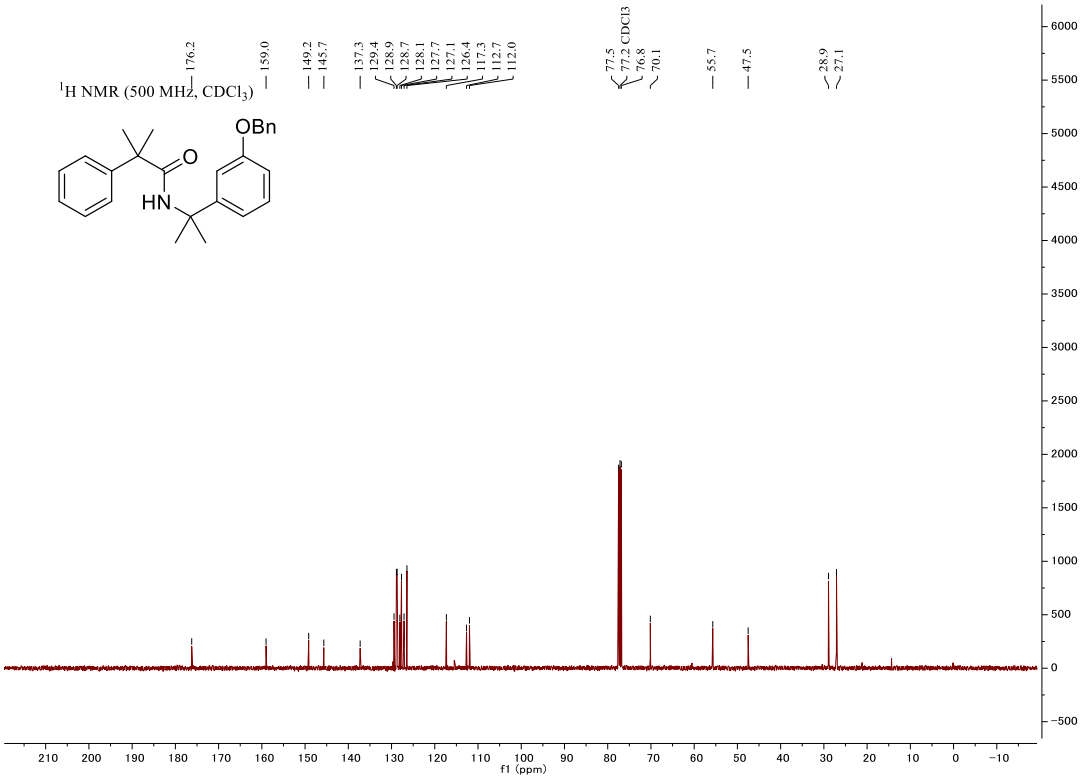
Compound S27



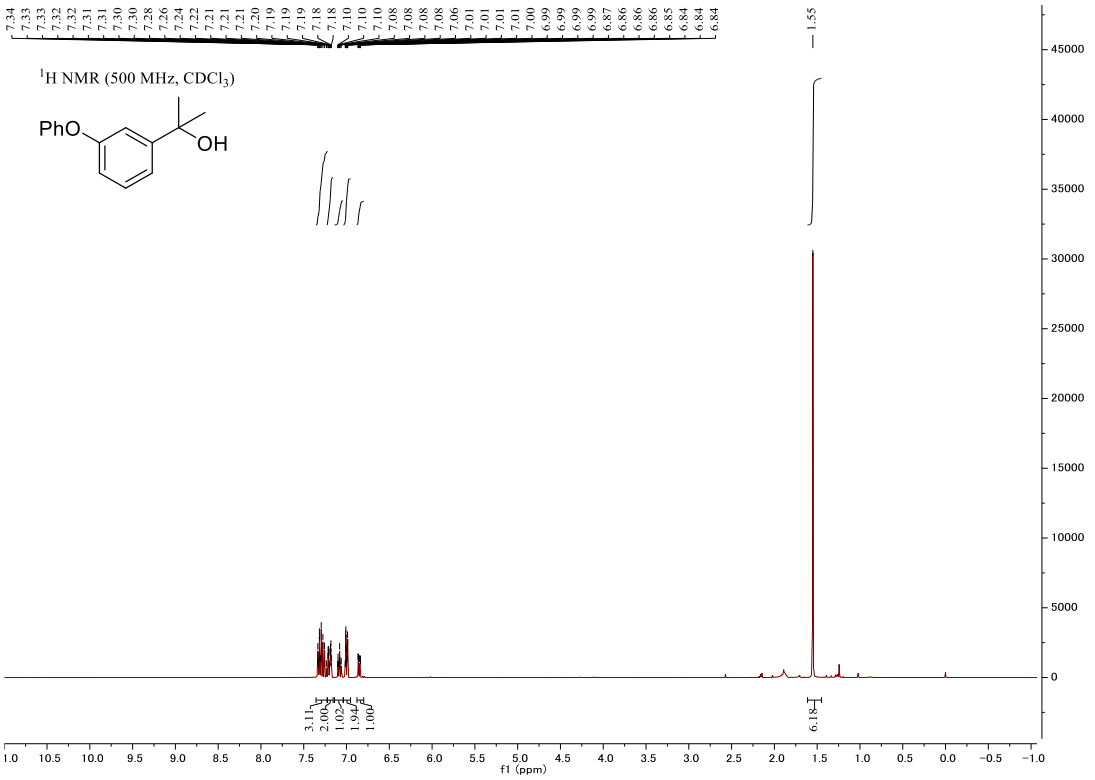


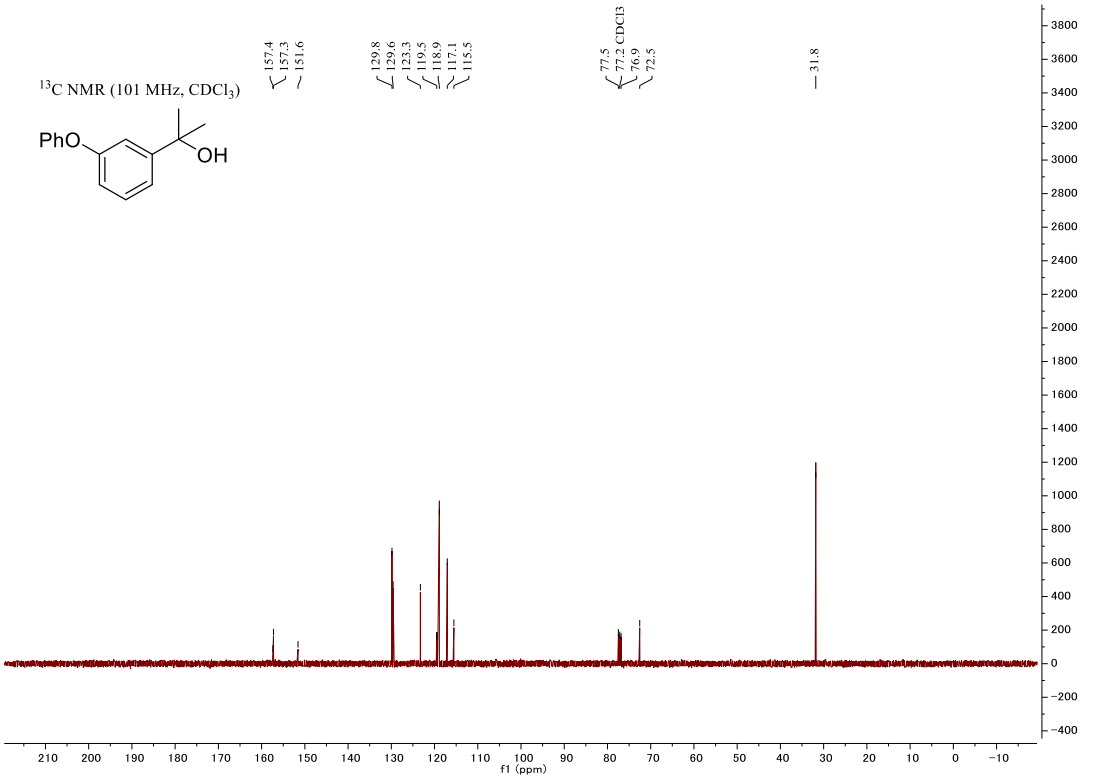
Compound S28



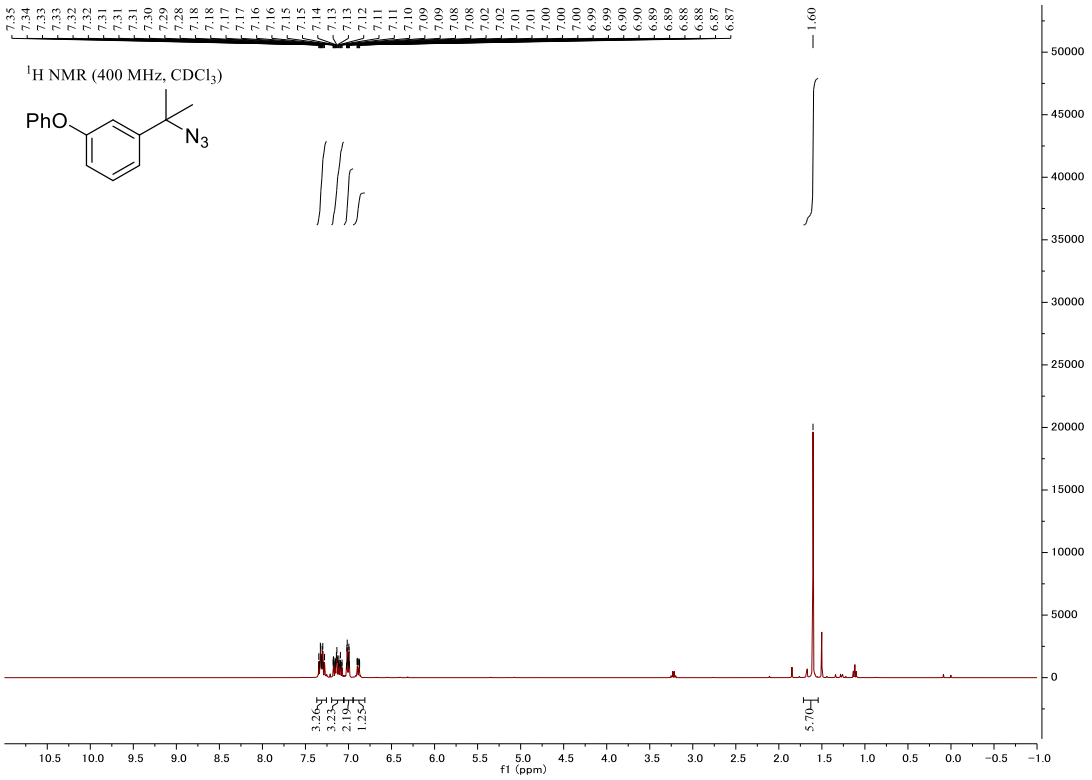


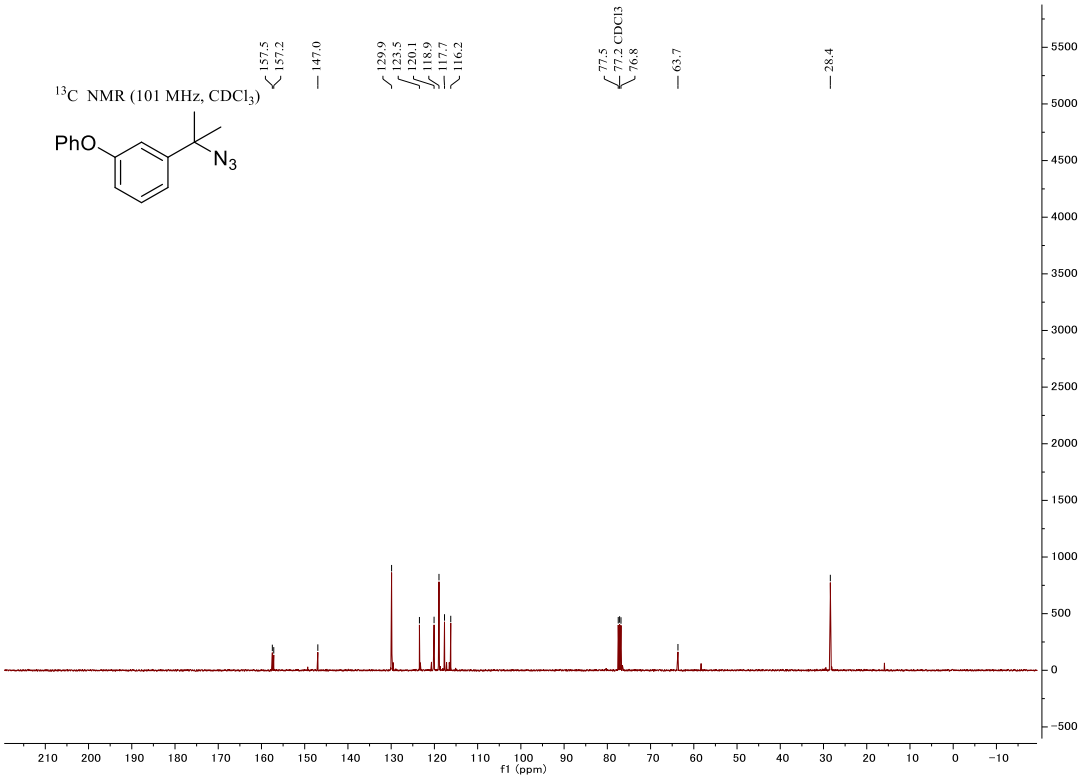
Compound S29



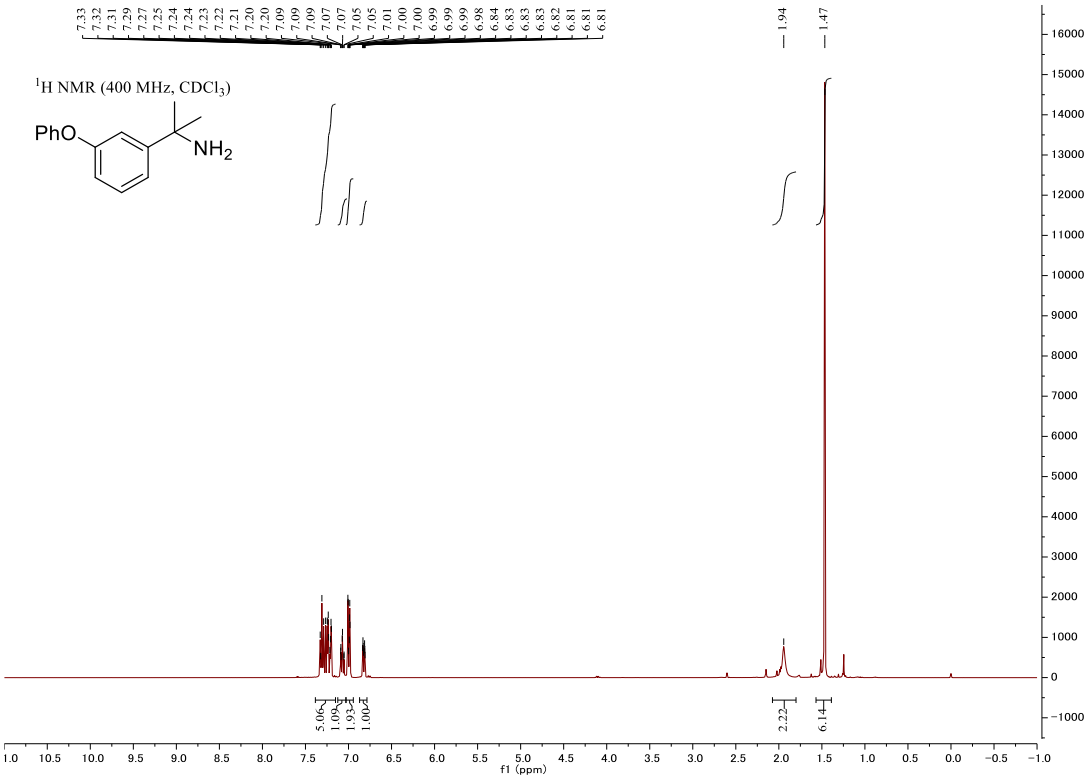


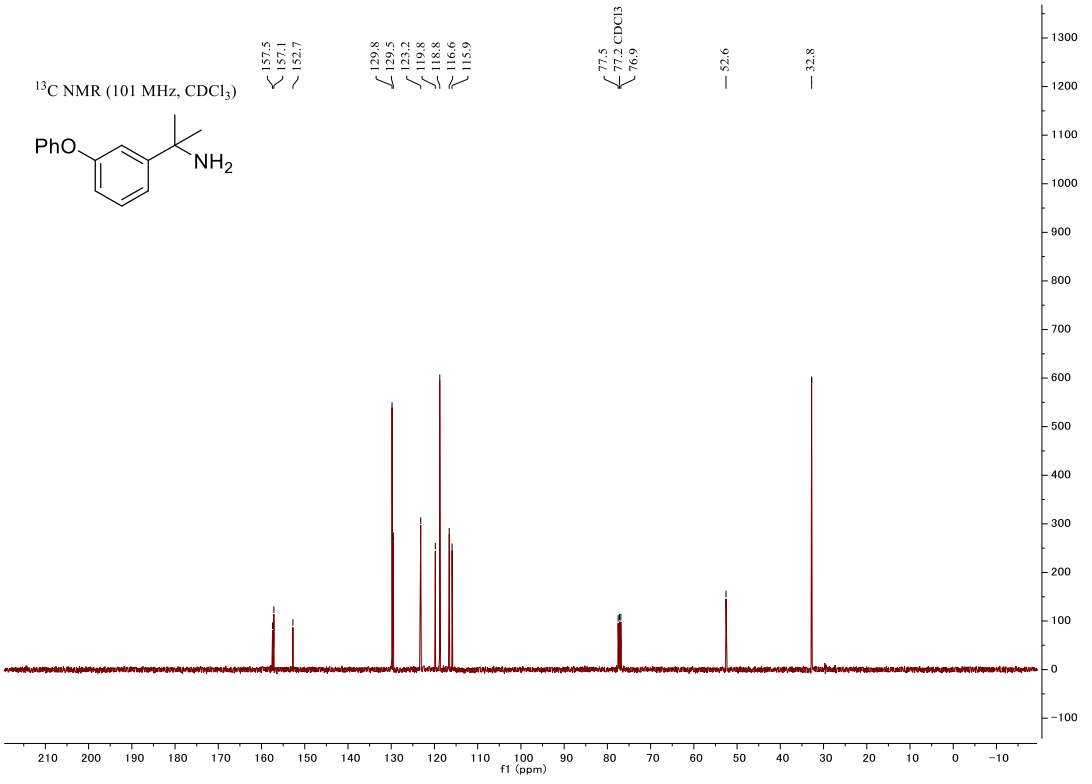
Compound S30



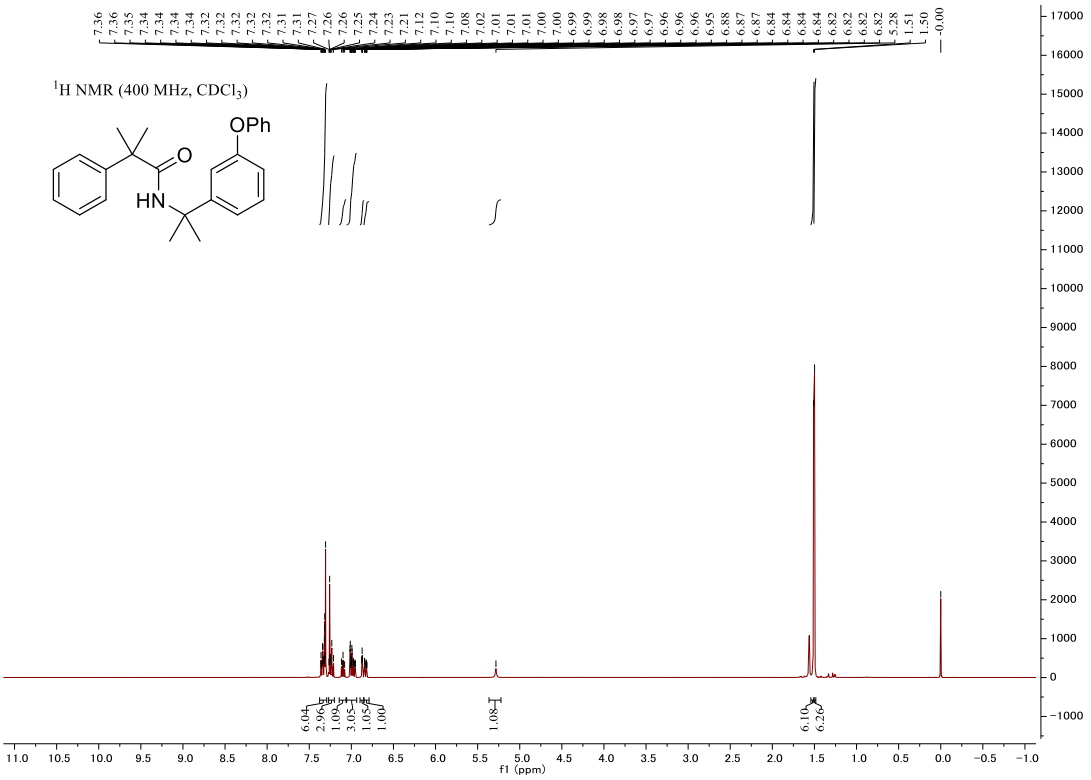


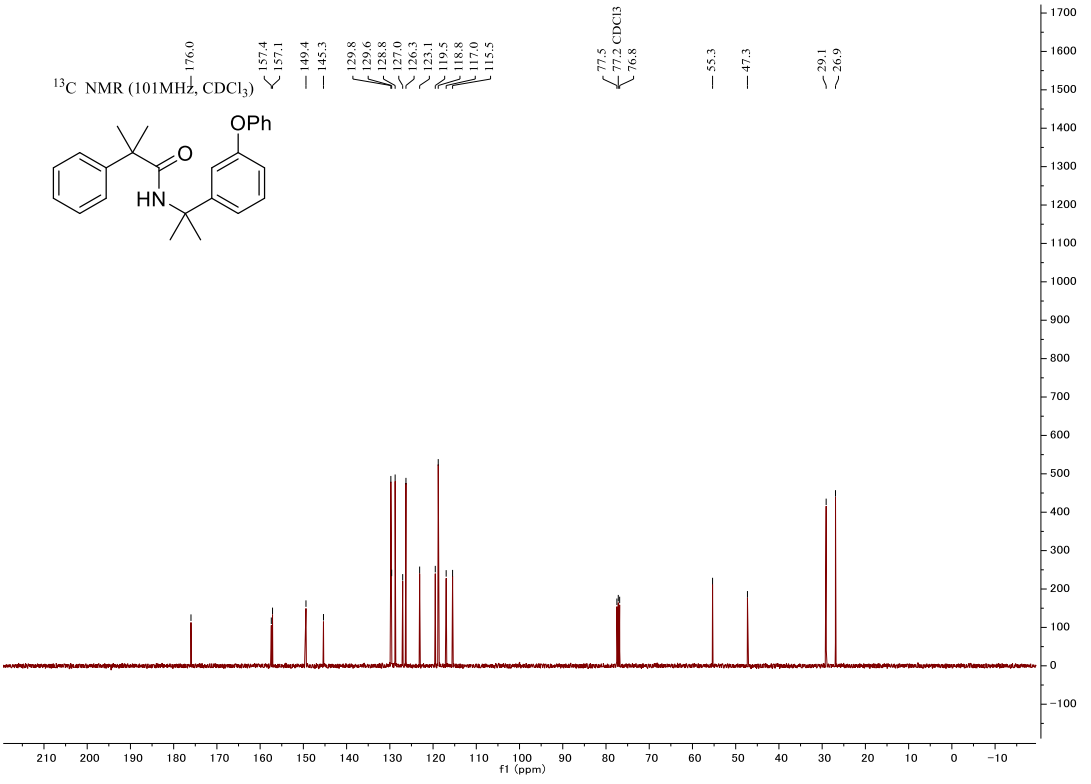
Compound S31



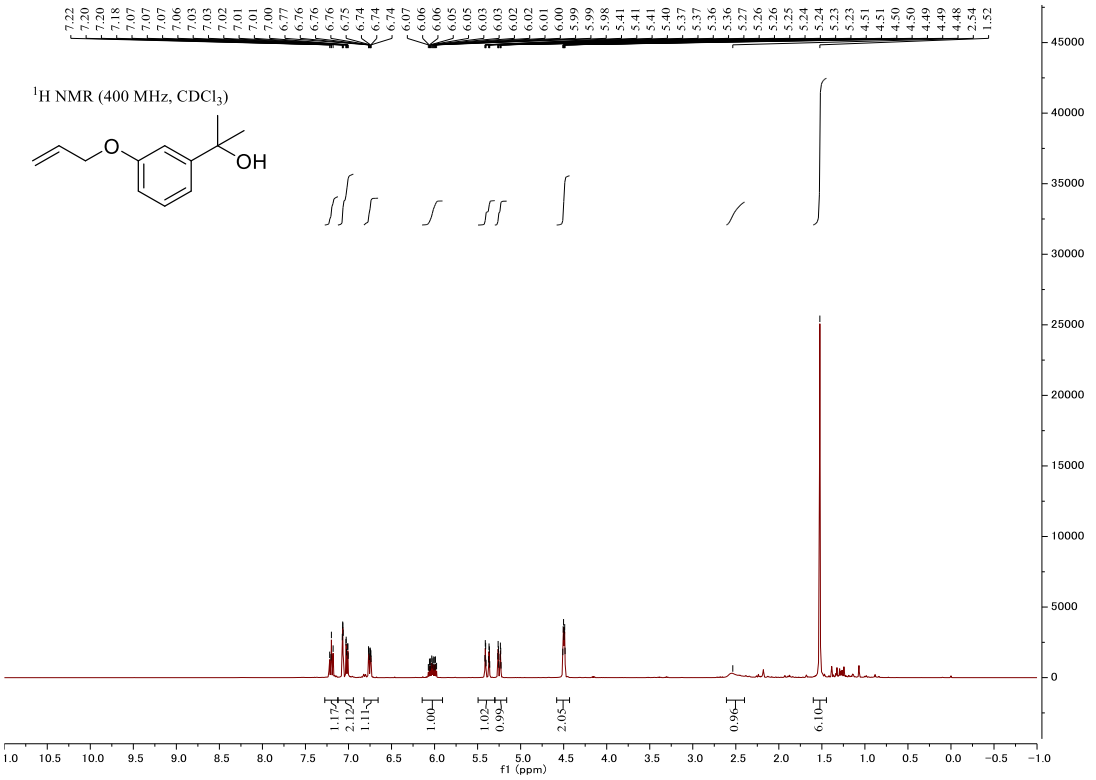


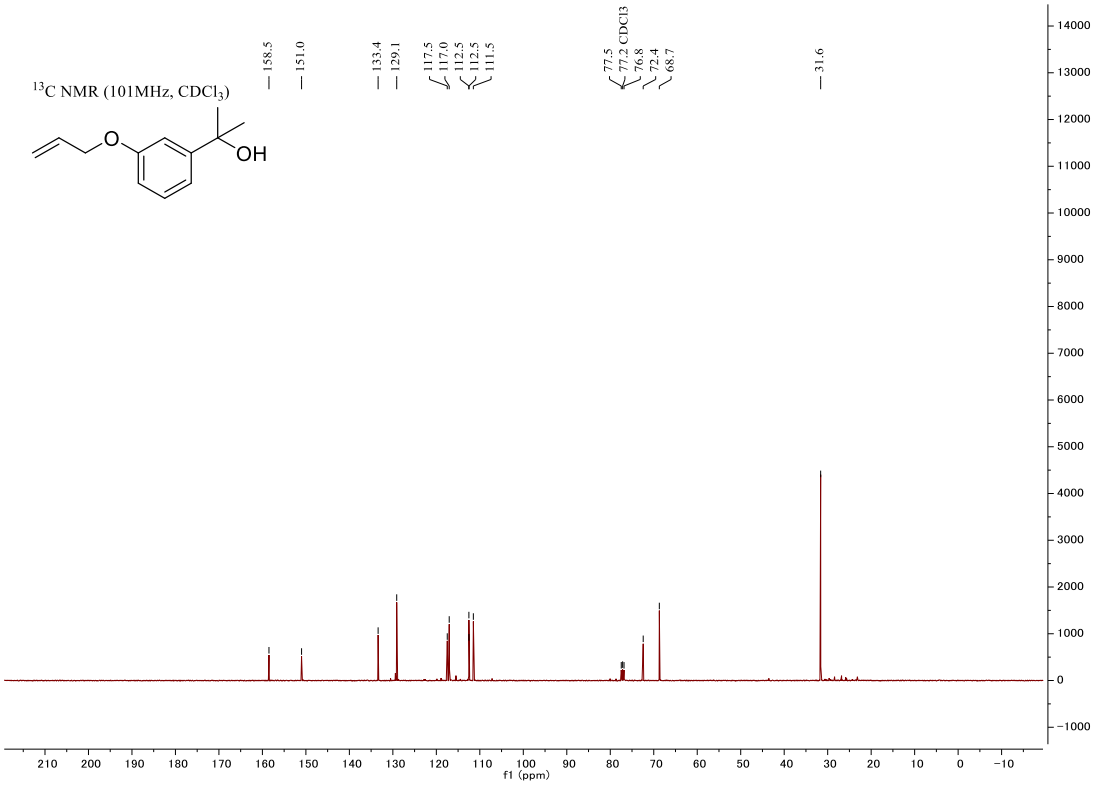
Compound S32



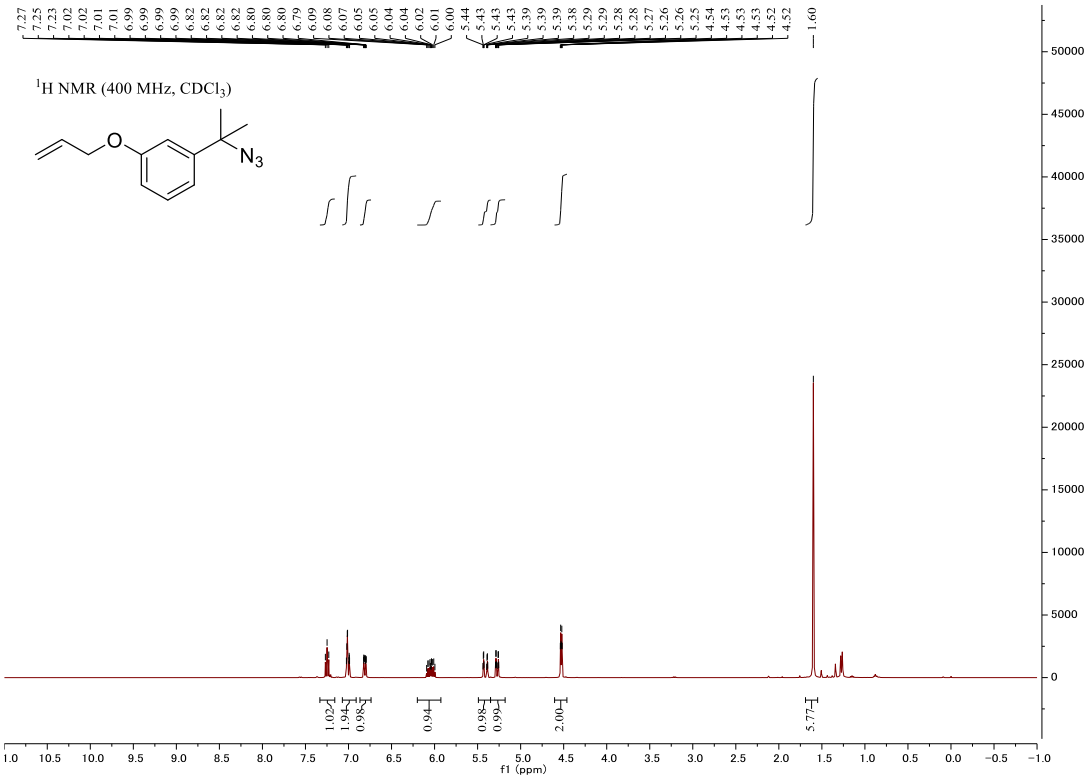


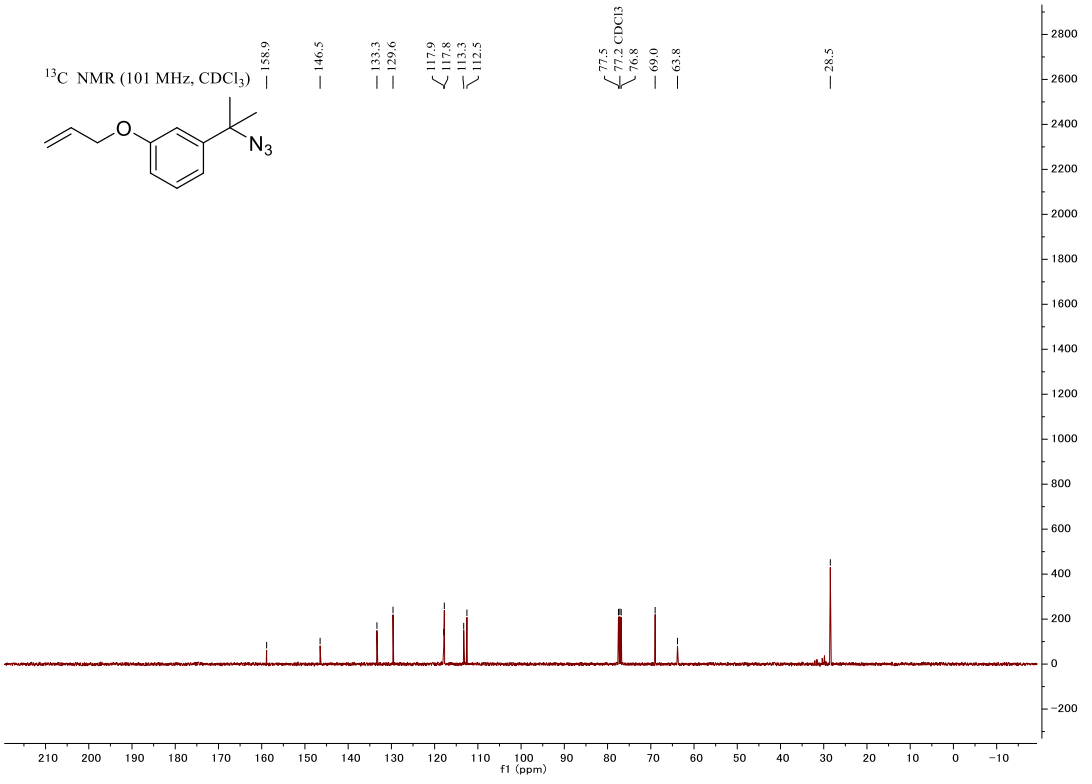
Compound S34



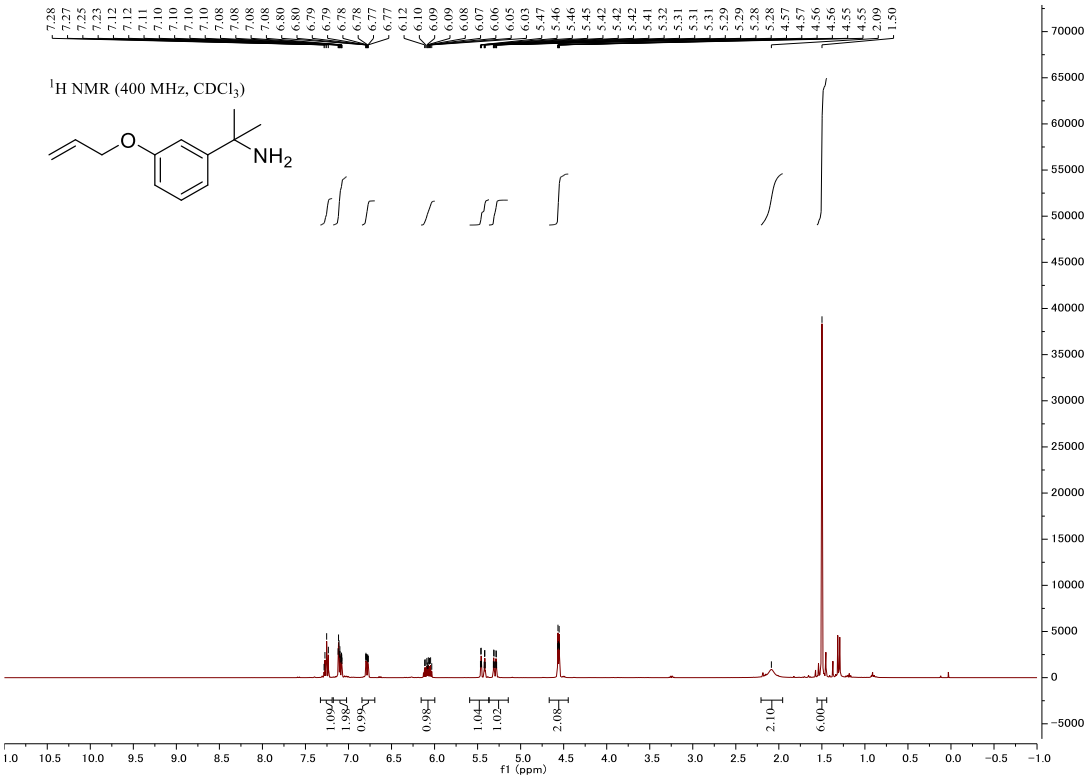


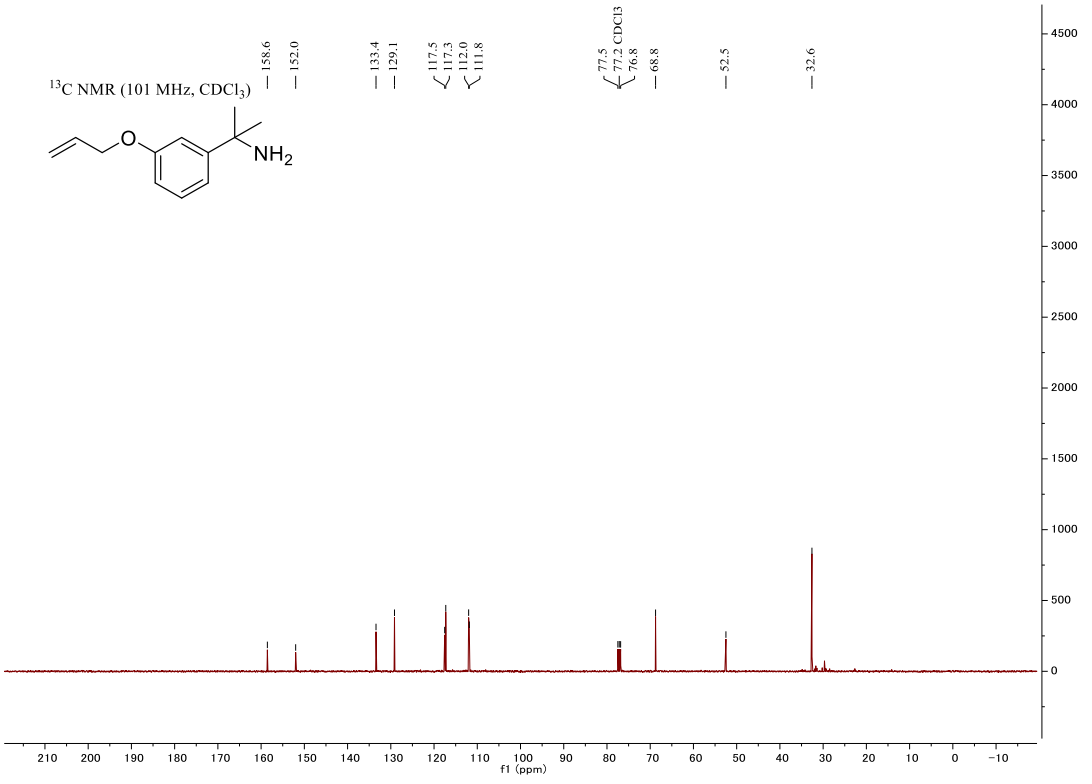
Compound S35



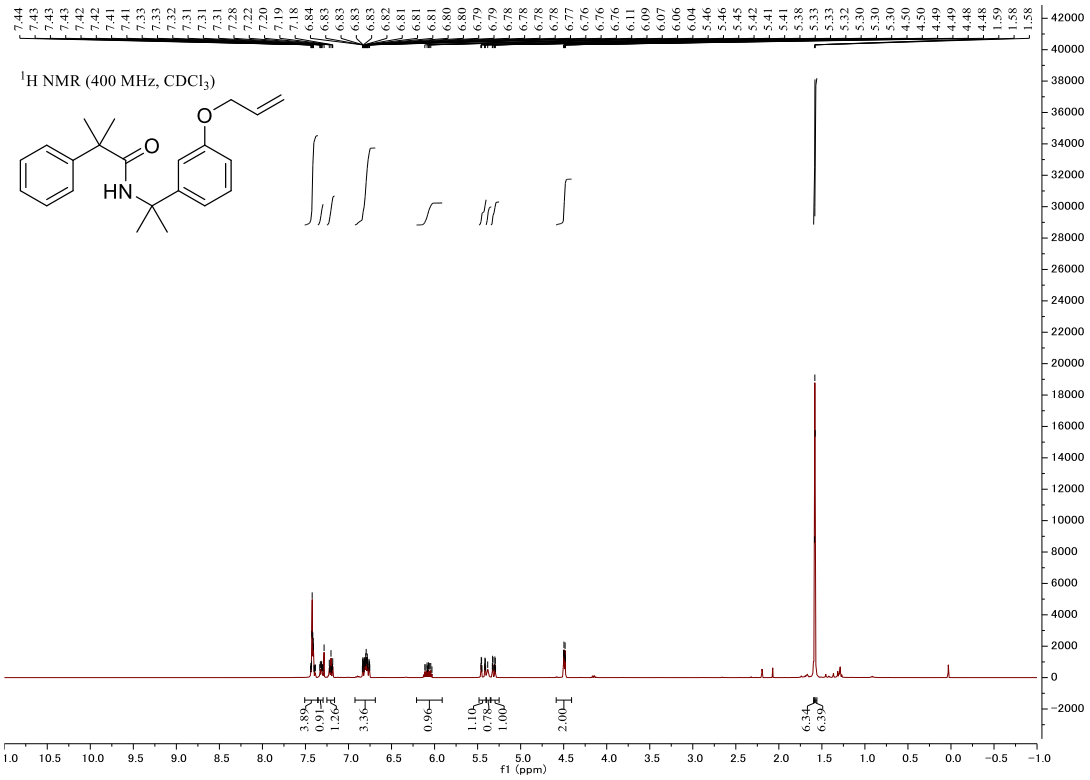


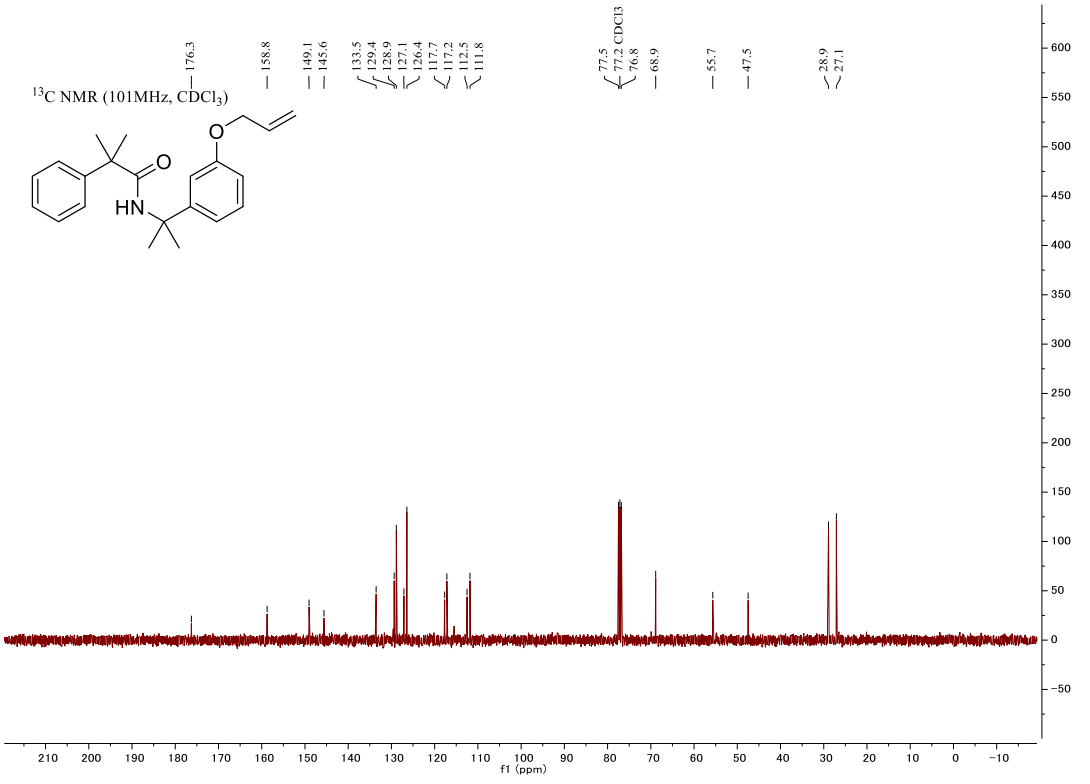
Compound S36



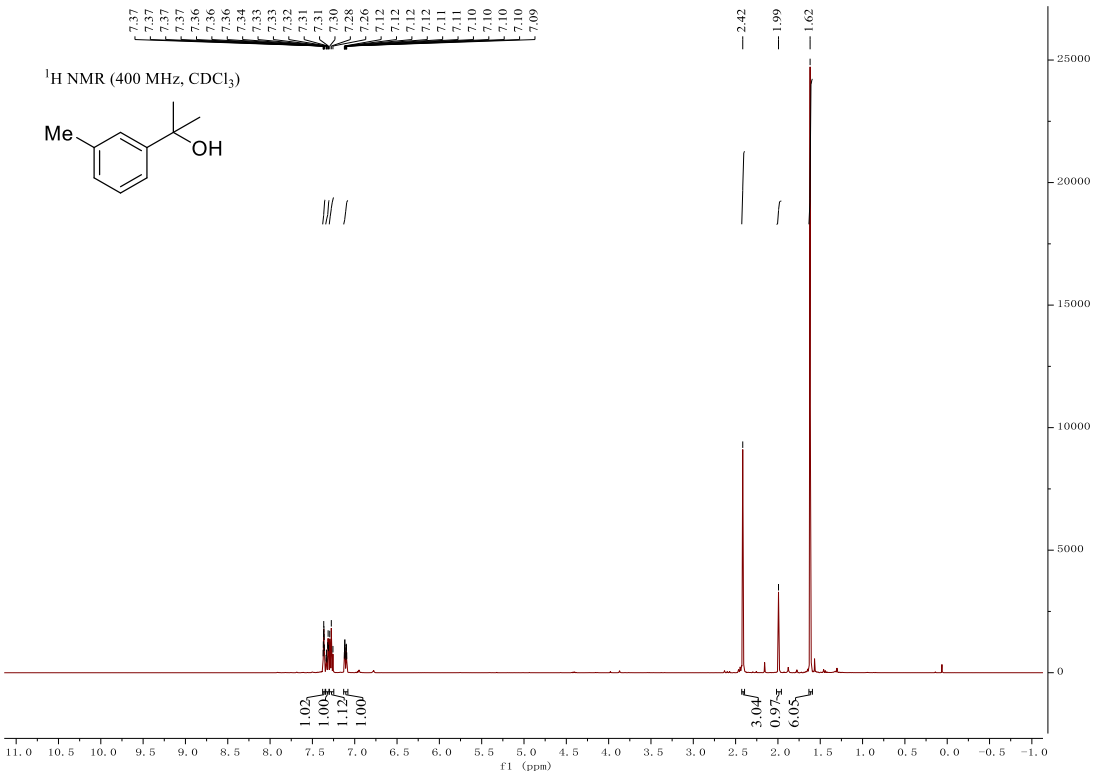


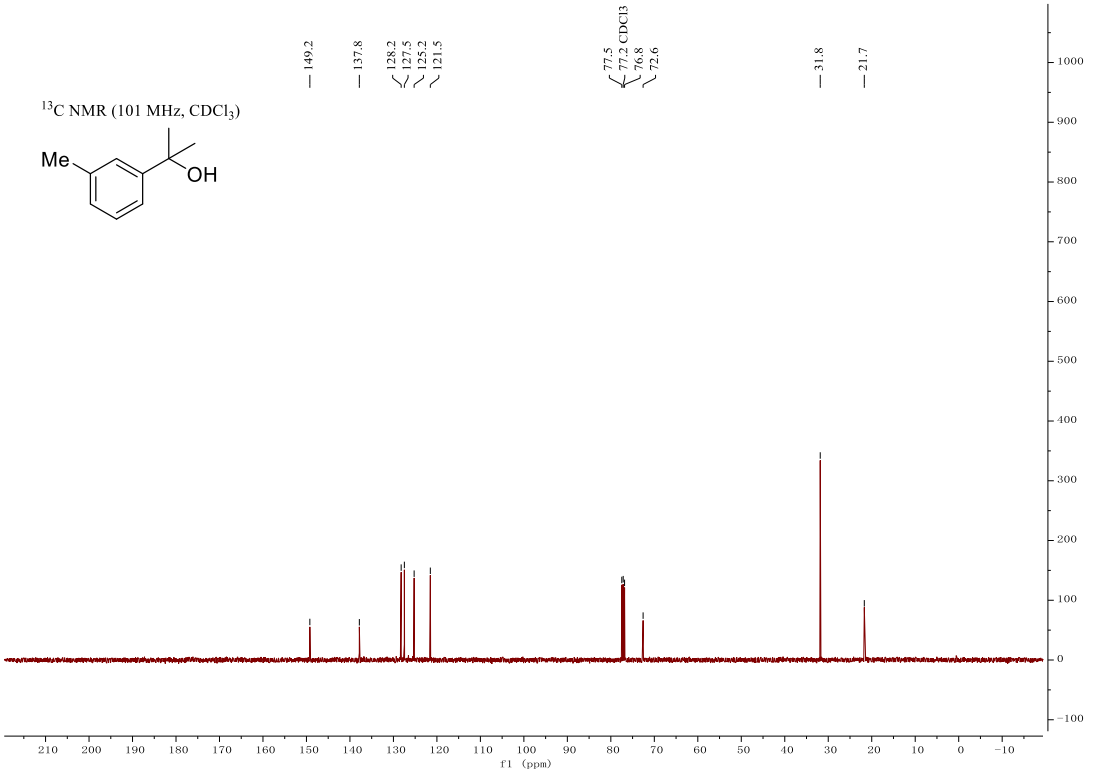
Compound S37



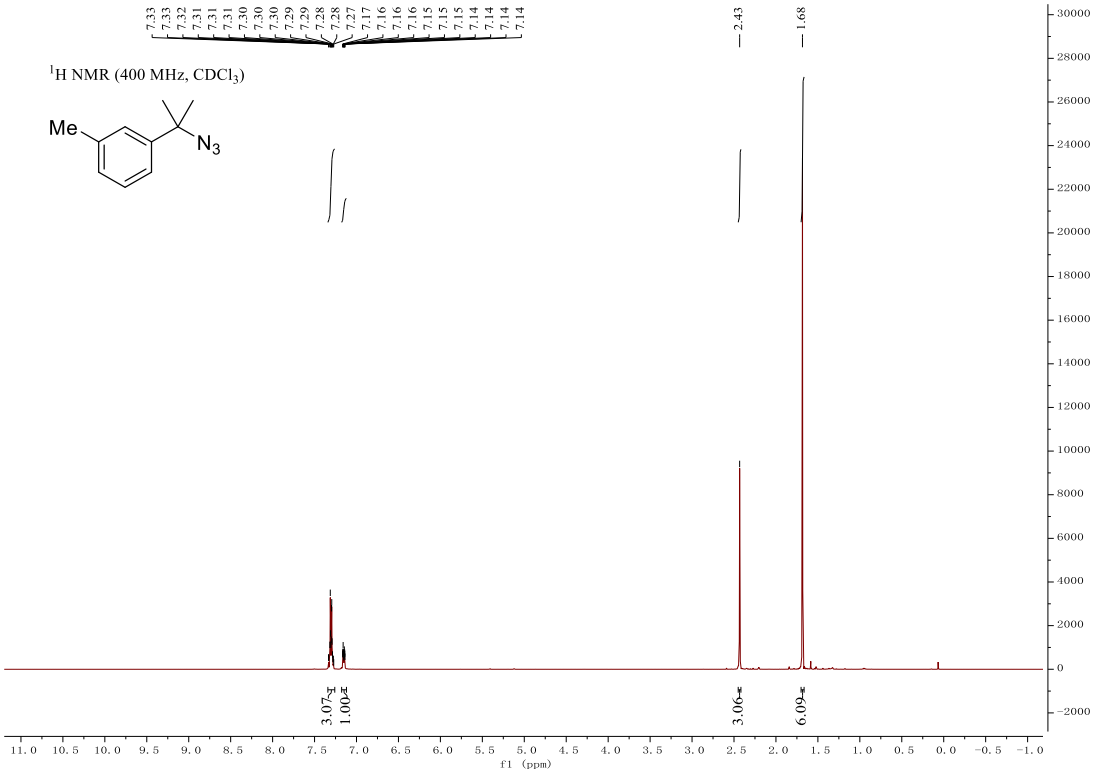


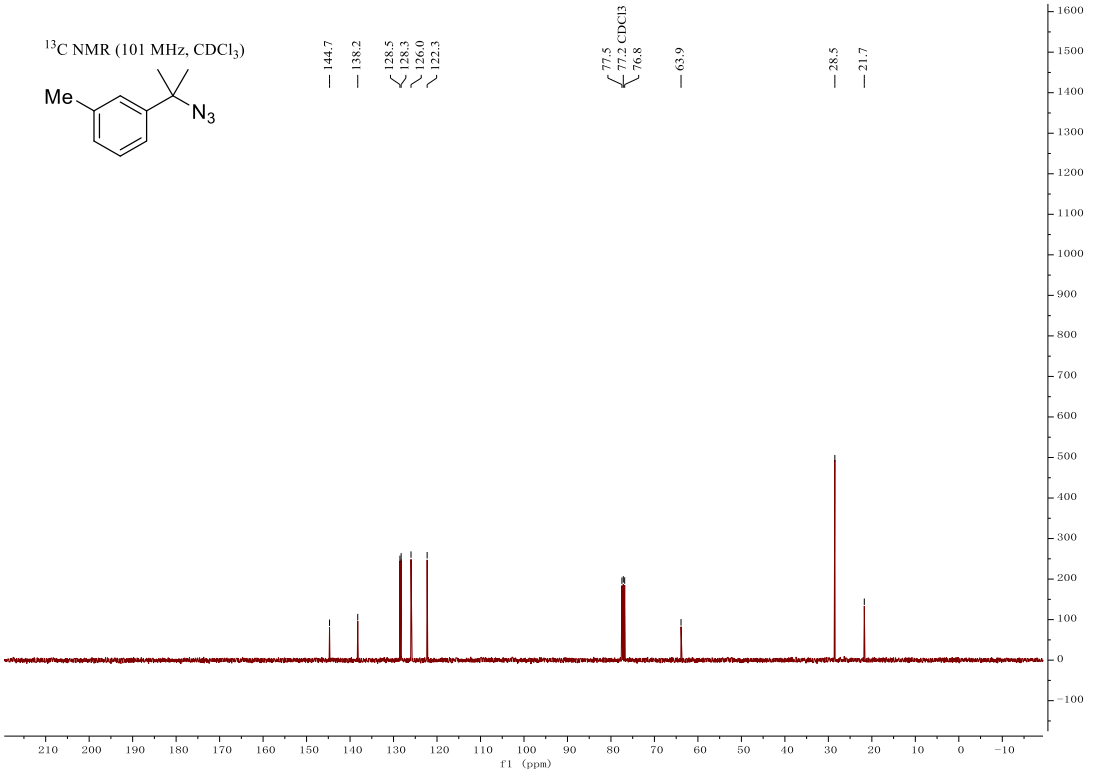
Compound S38



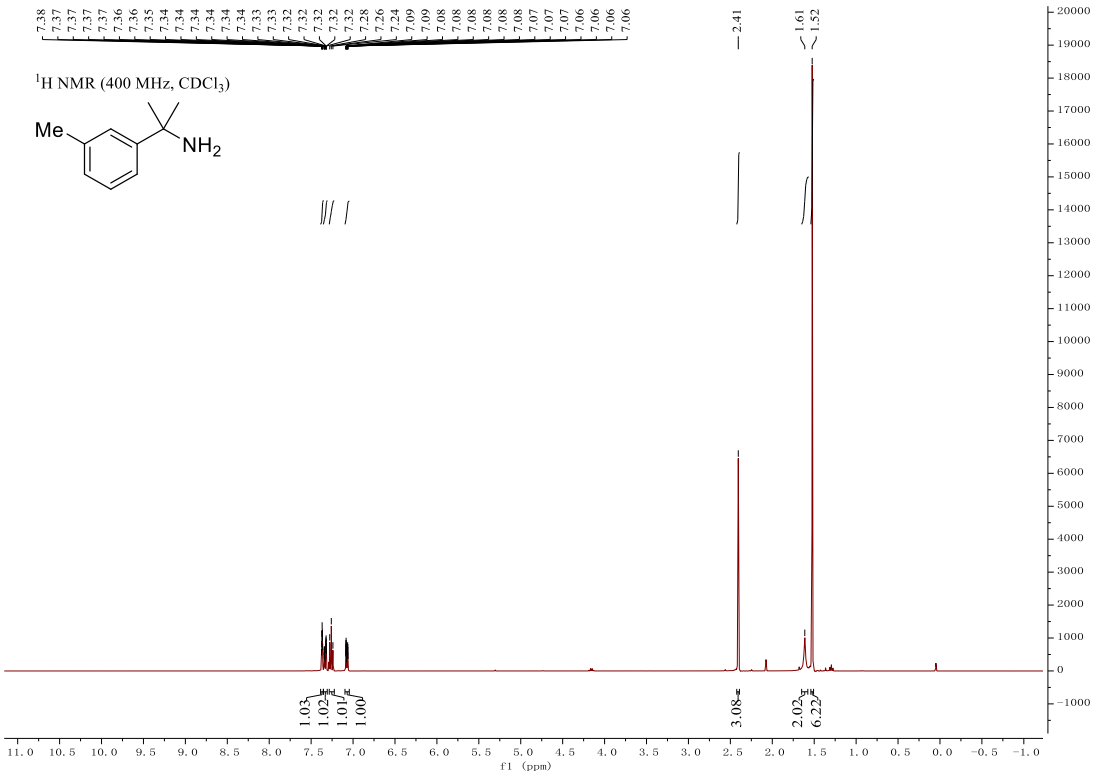


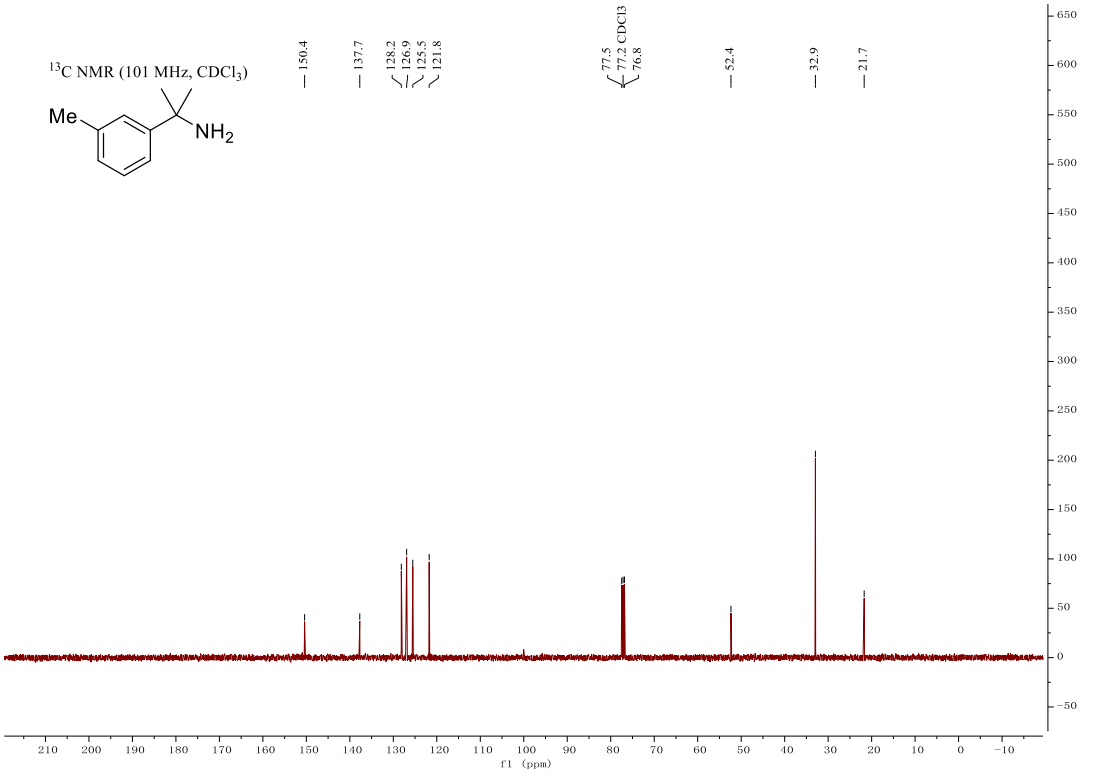
Compound S39



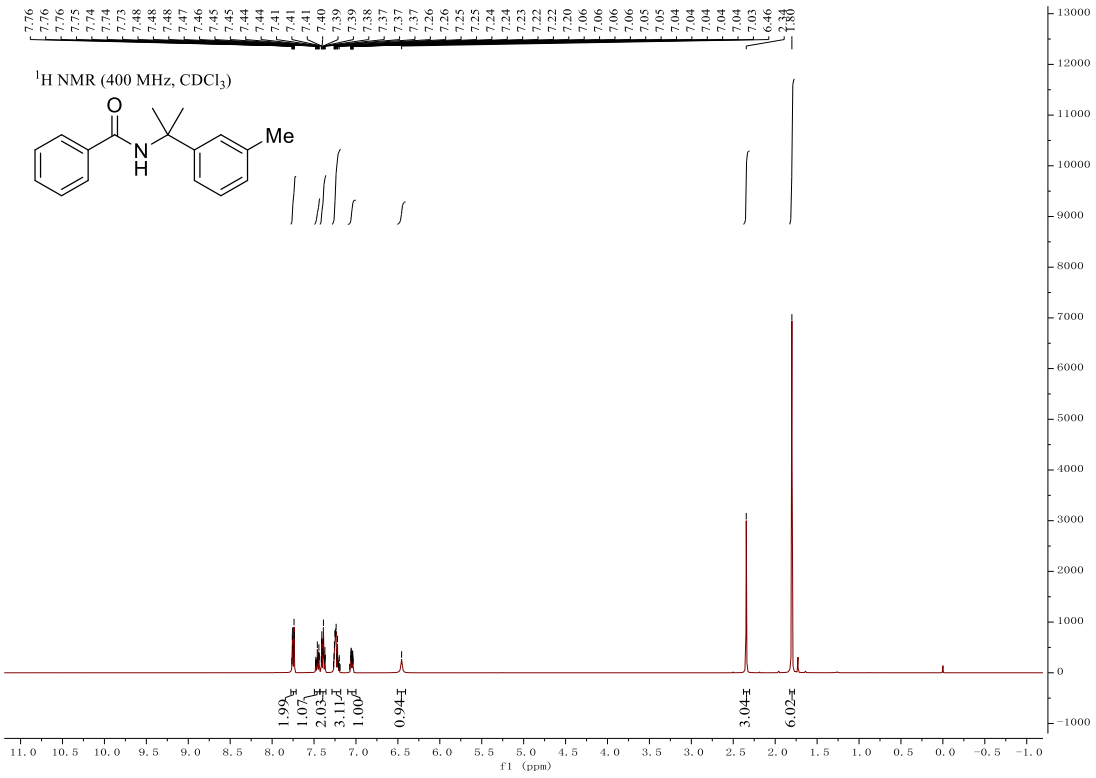


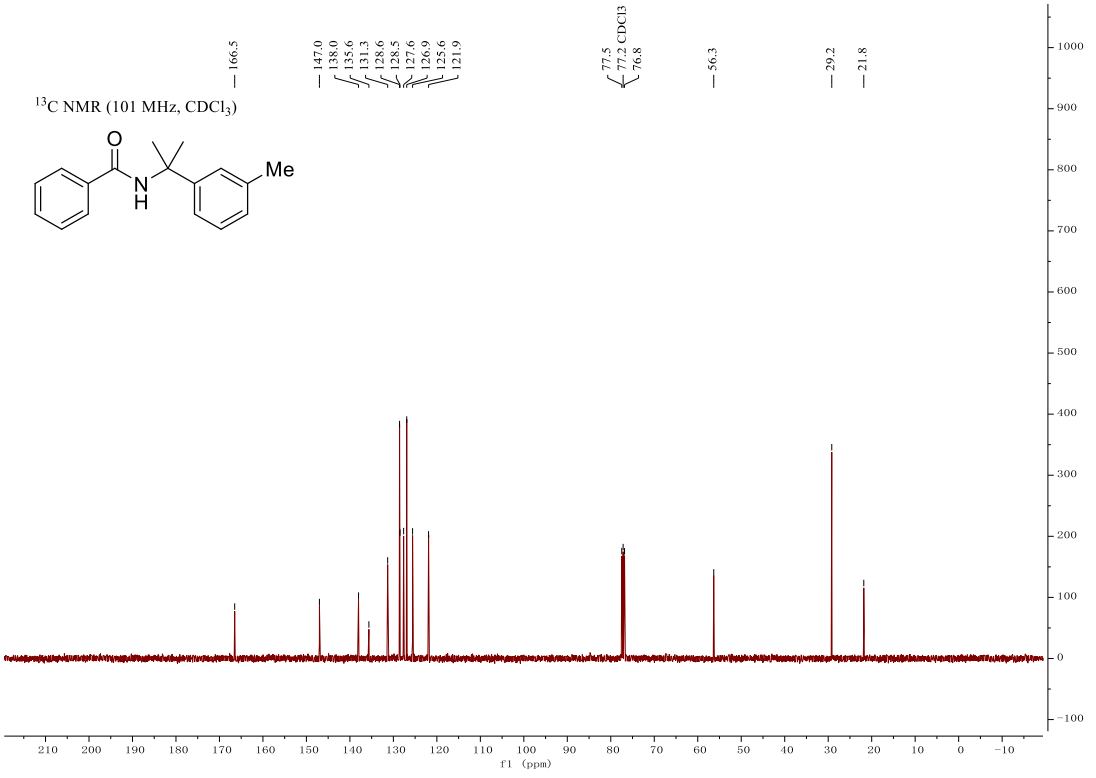
Compound S40



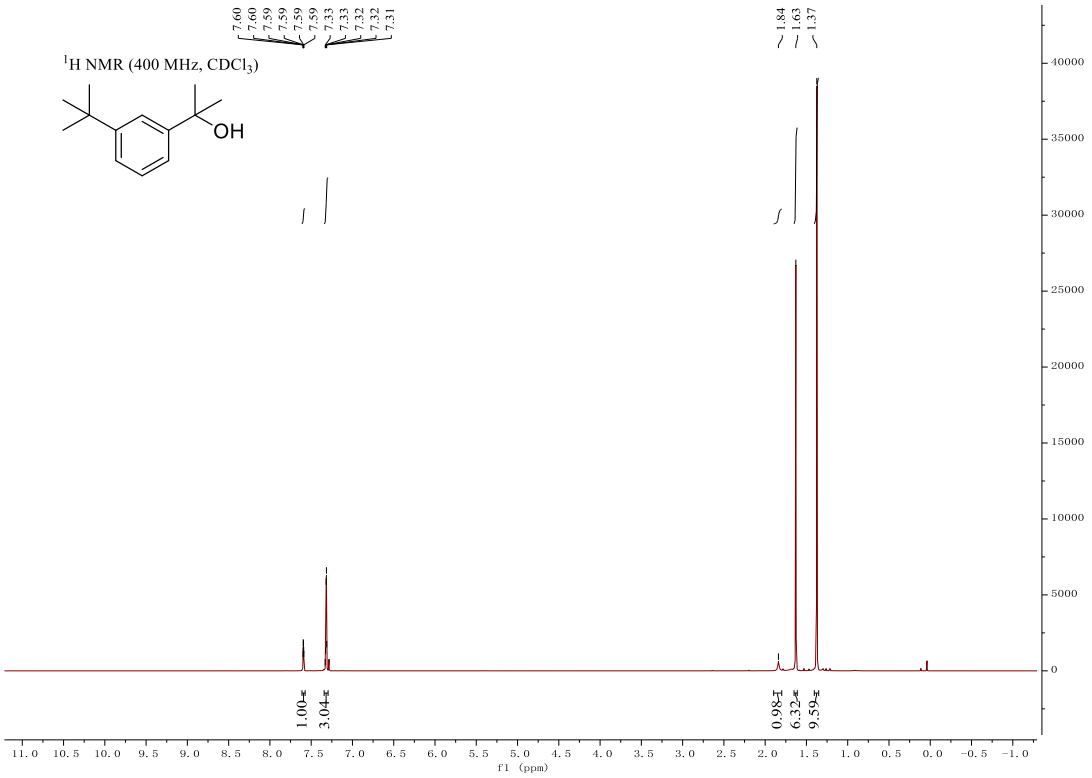


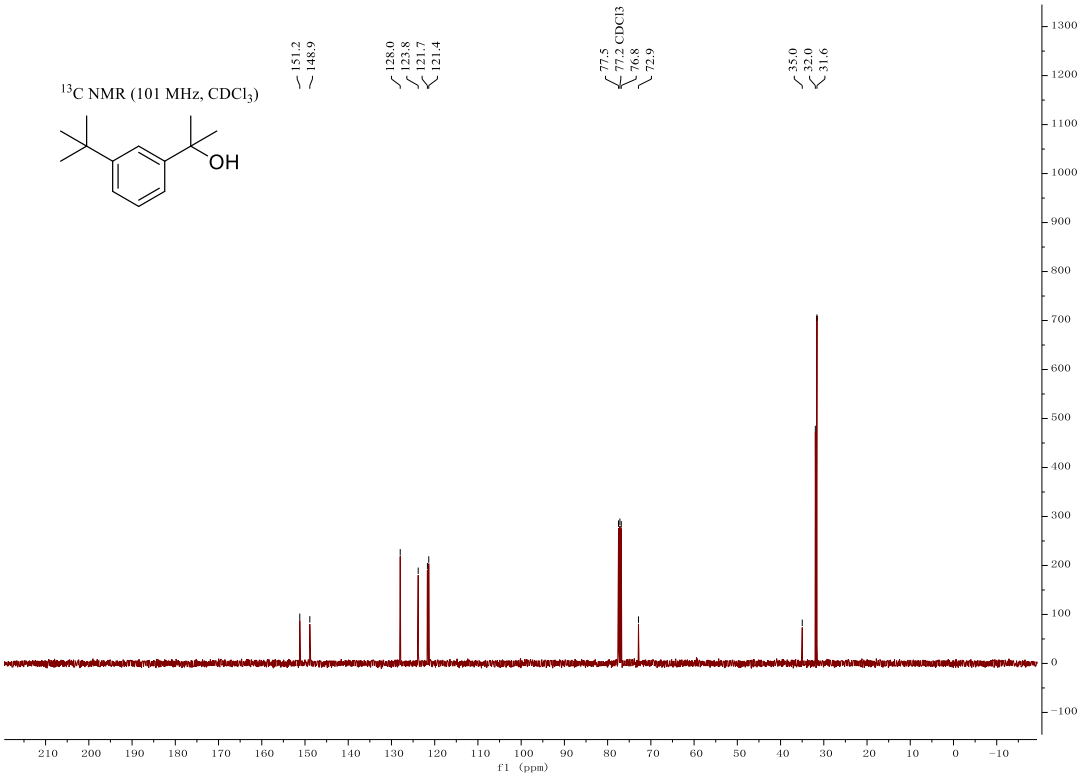
Compound S41



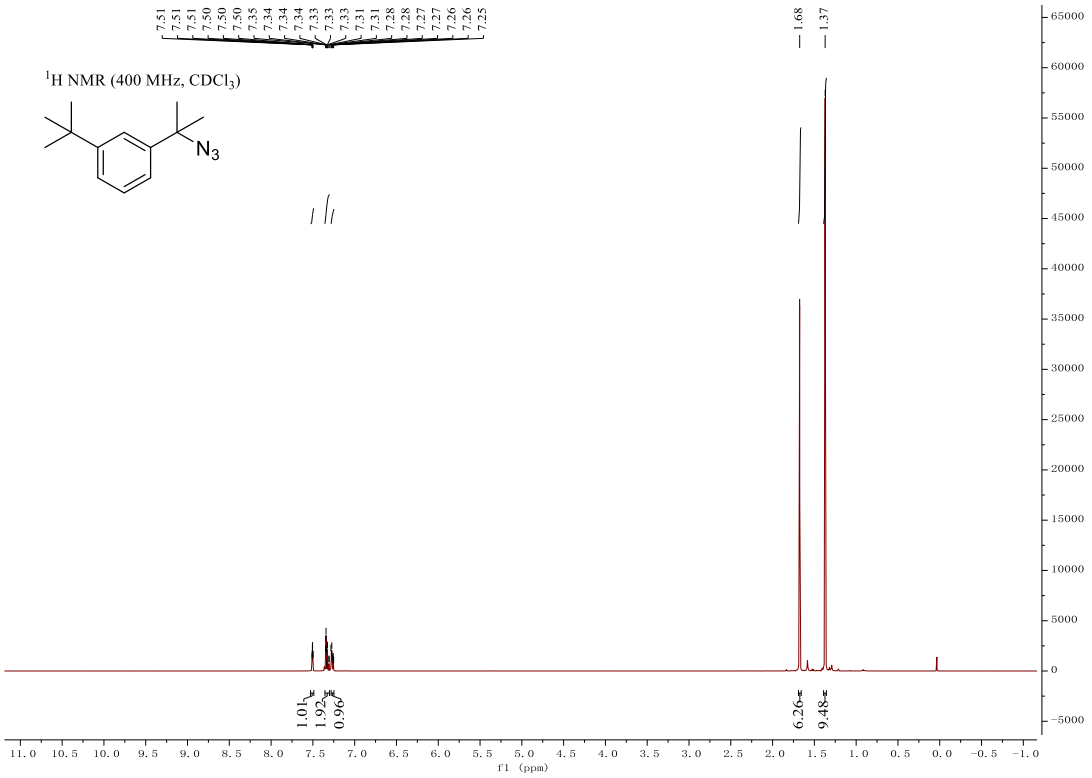


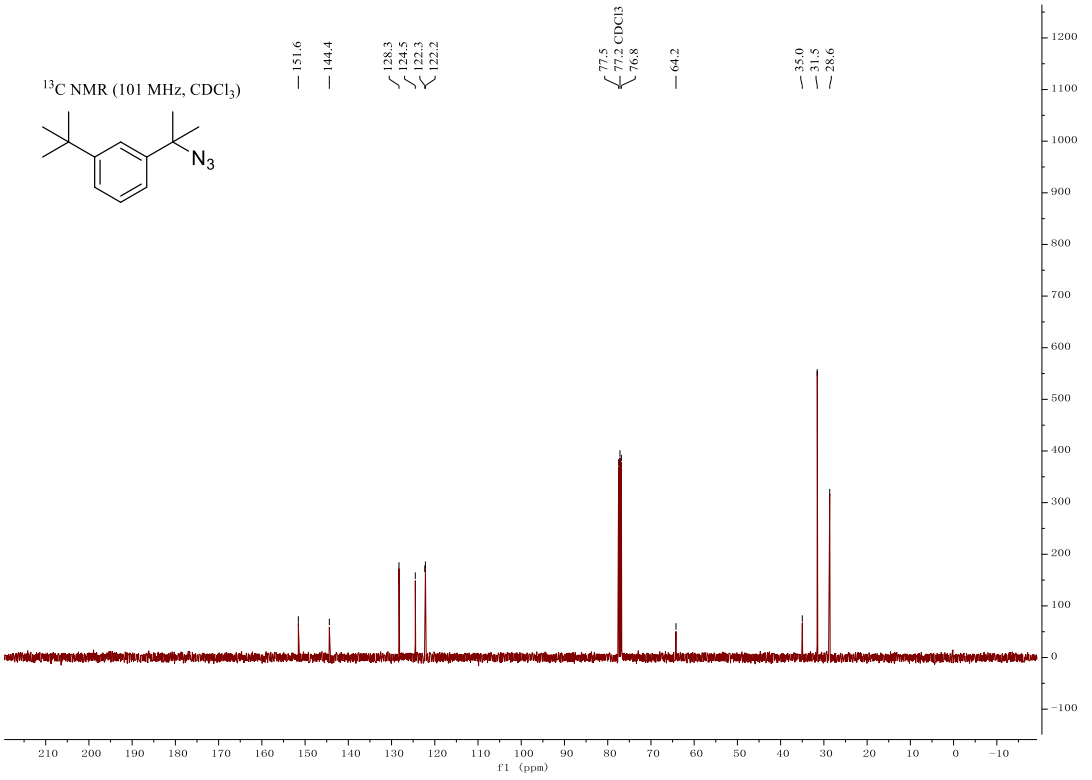
Compound S42



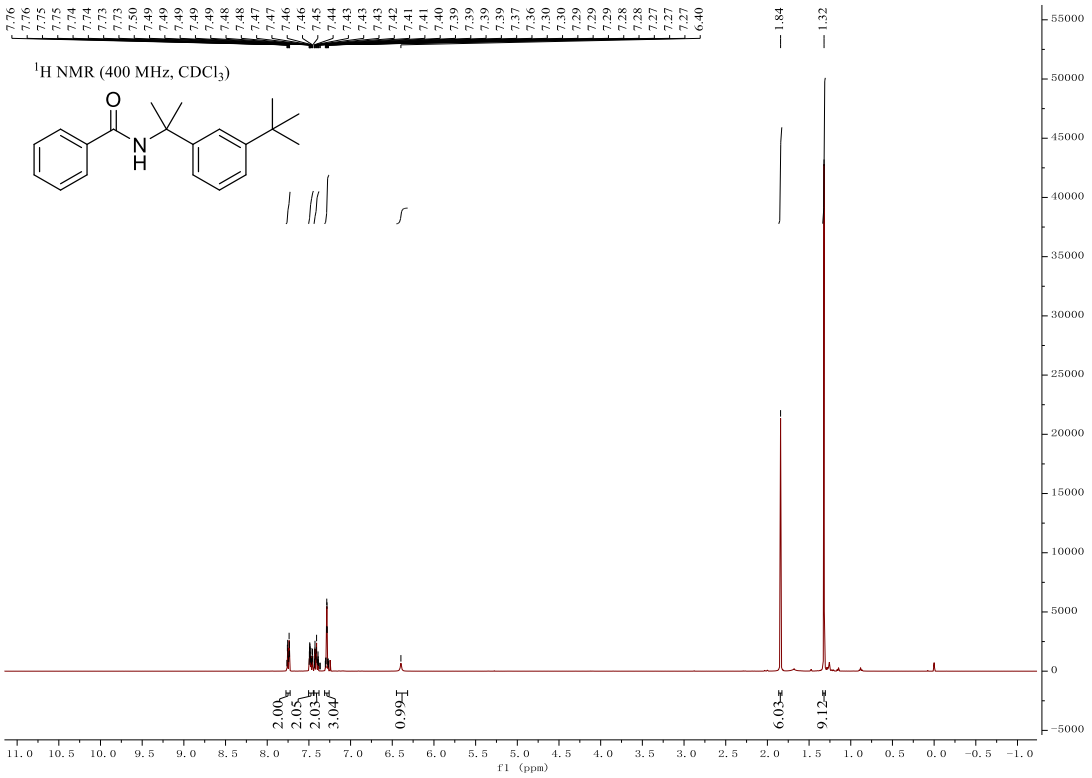


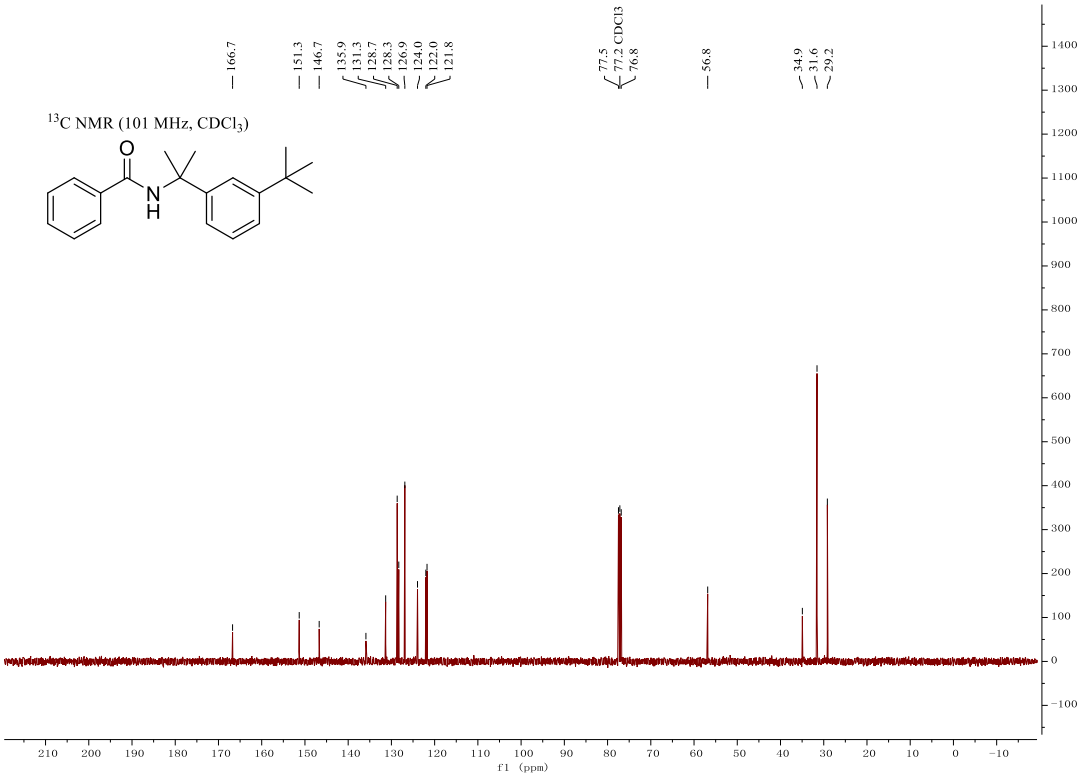
Compound S43



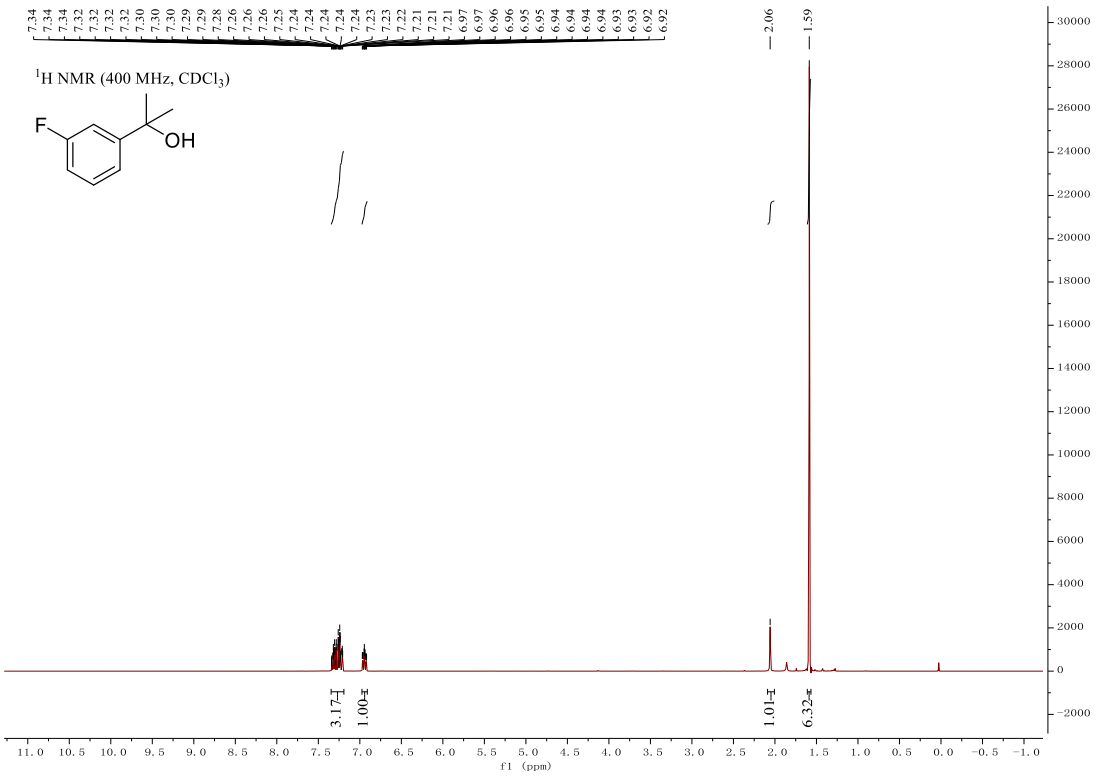


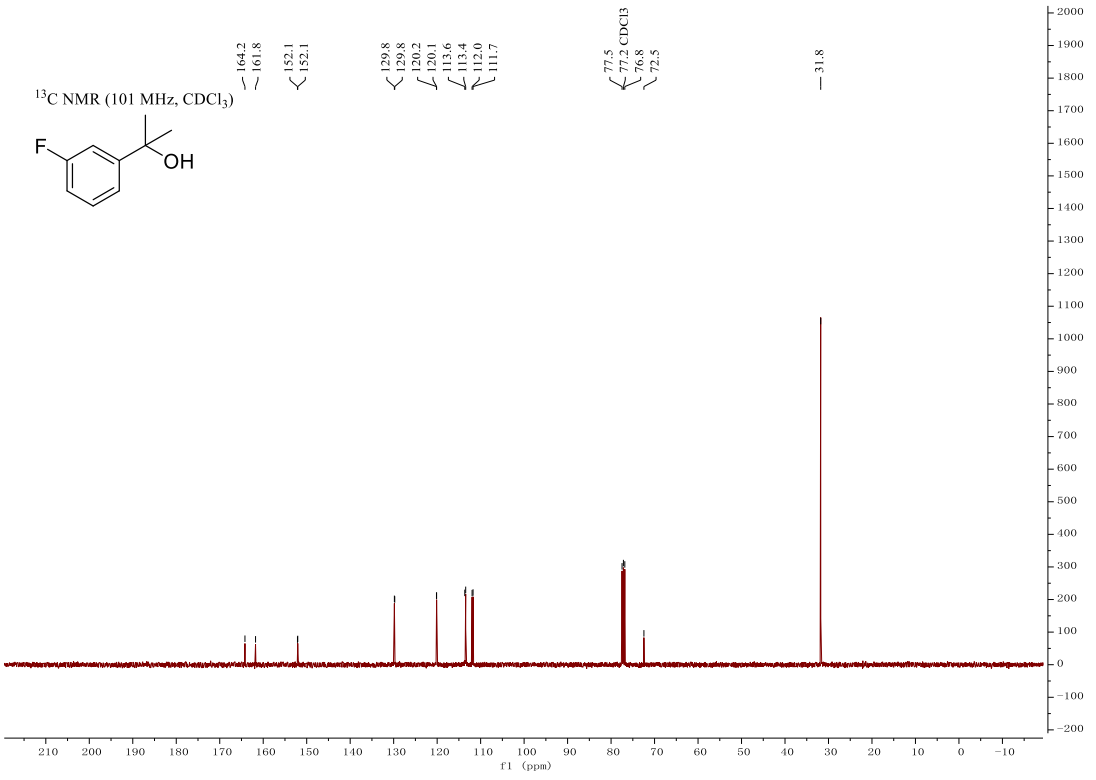
Compound S45

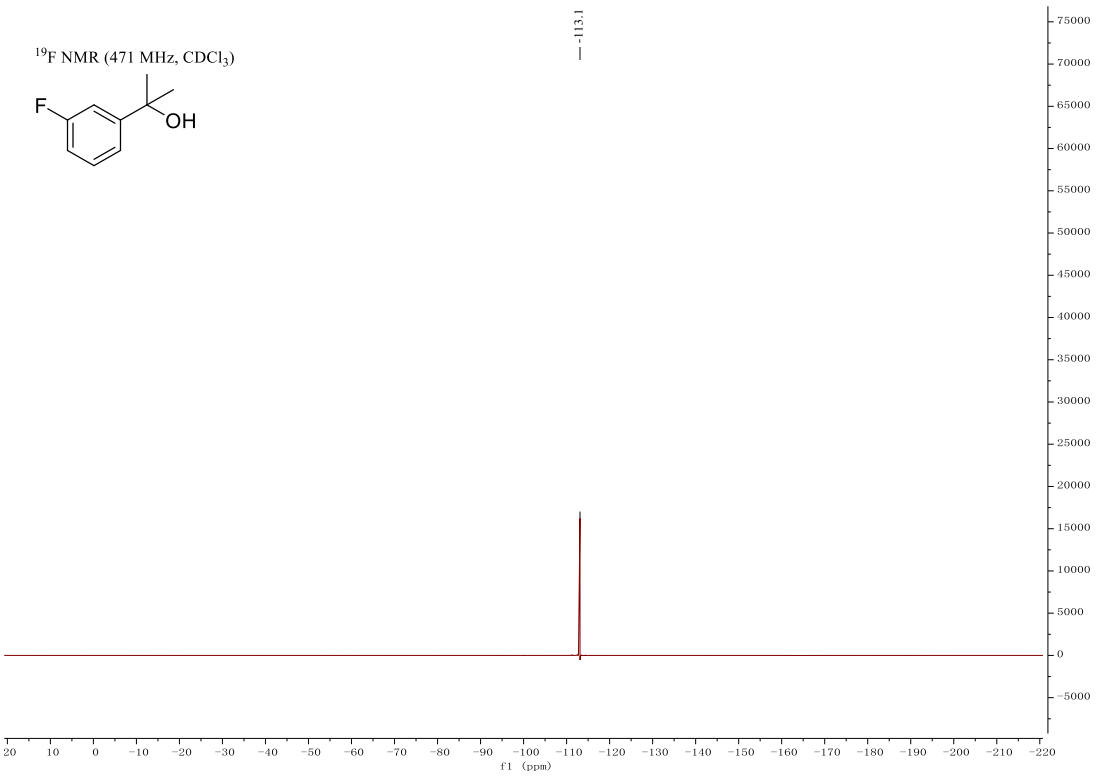




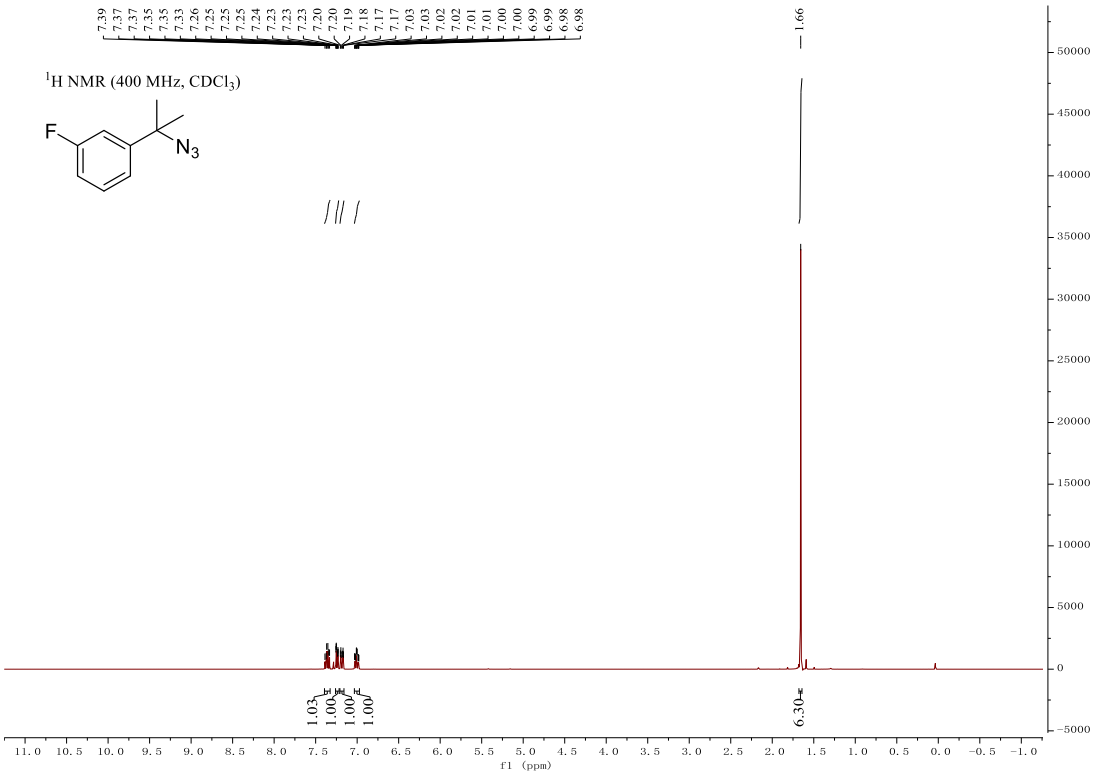
Compound S46


7.34 7.34 7.34 7.32 7.32 7.32 7.30 7.30 7.30 7.29 7.29 7.28 7.26 7.26 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.21 6.97 6.97 6.96 6.96 6.95 6.95 6.94 6.94 6.94 6.94 6.93 6.92 6.92
2.06
1.59
^{1}H NMR (400 MHz, $CDCl_3$)
F
OH
3.17
1.00
1.01
6.32
f1 (ppm)

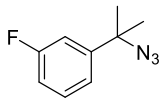

164.2
161.8
152.1
152.1
129.8
129.8
120.2
120.1
113.6
113.4
112.0
111.7
77.5
77.2 CDCl3
76.8
72.5
31.8
^{13}C NMR (101 MHz, $CDCl_3$)
F
OH
f1 (ppm)



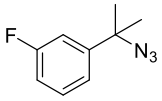
Compound S47



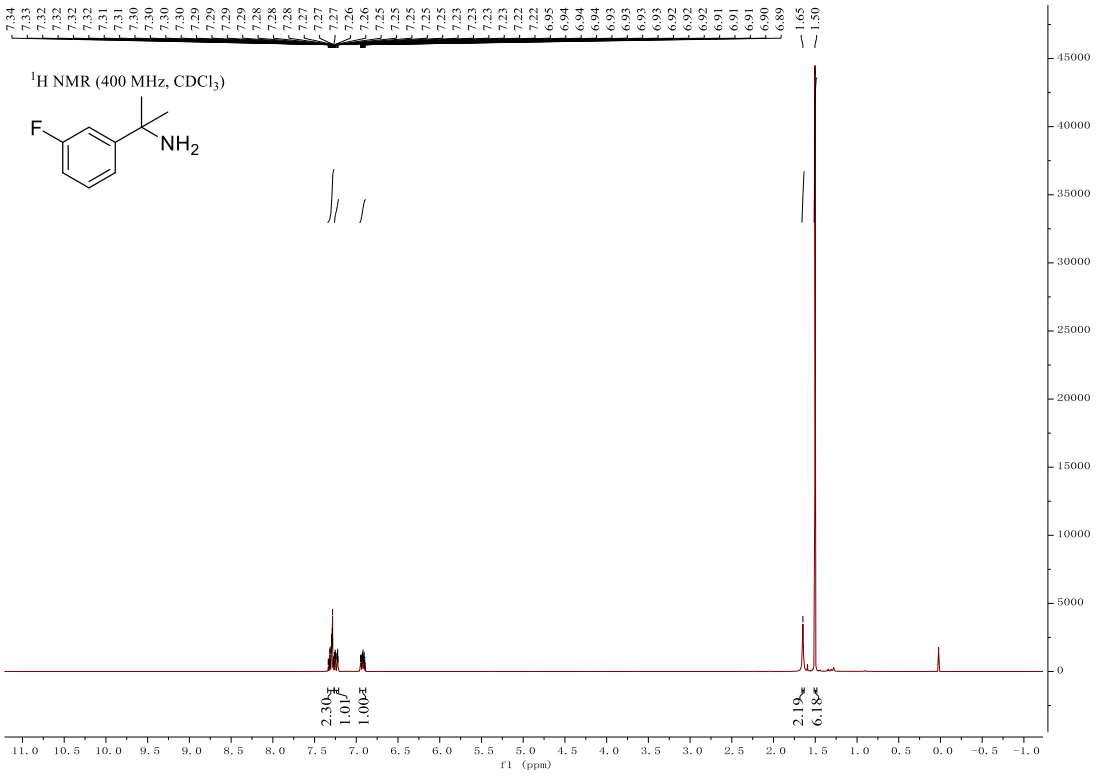
^{13}C NMR (101 MHz, $CDCl_3$)

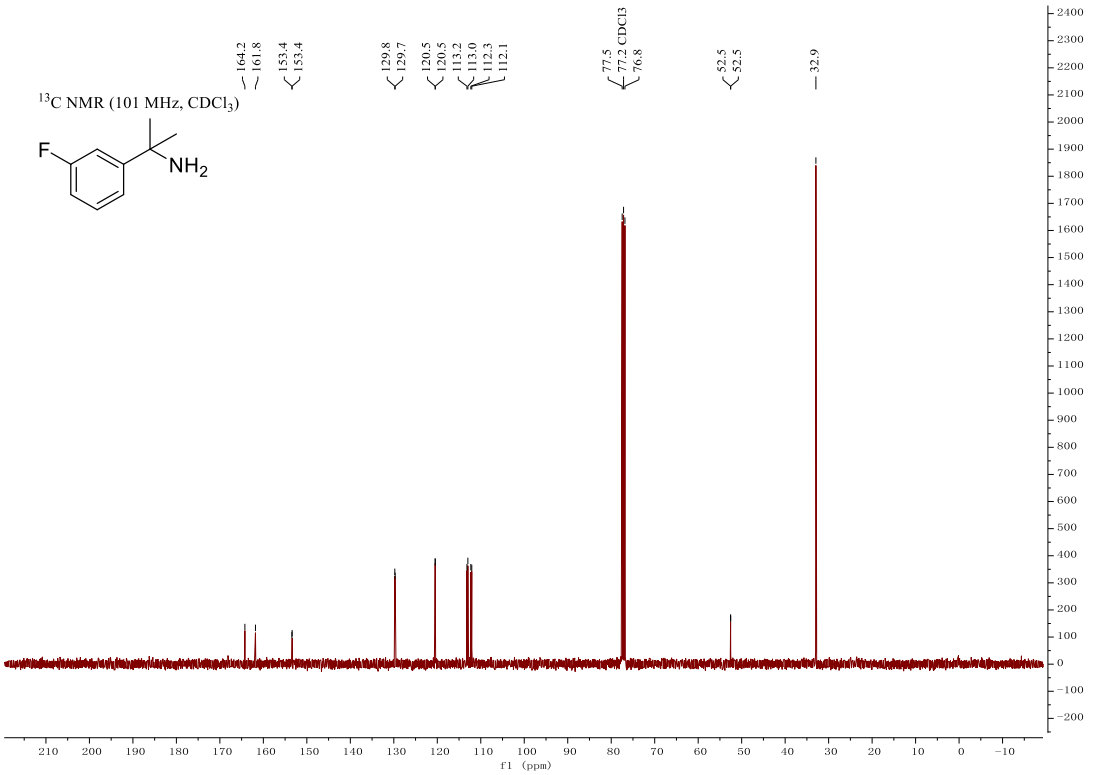


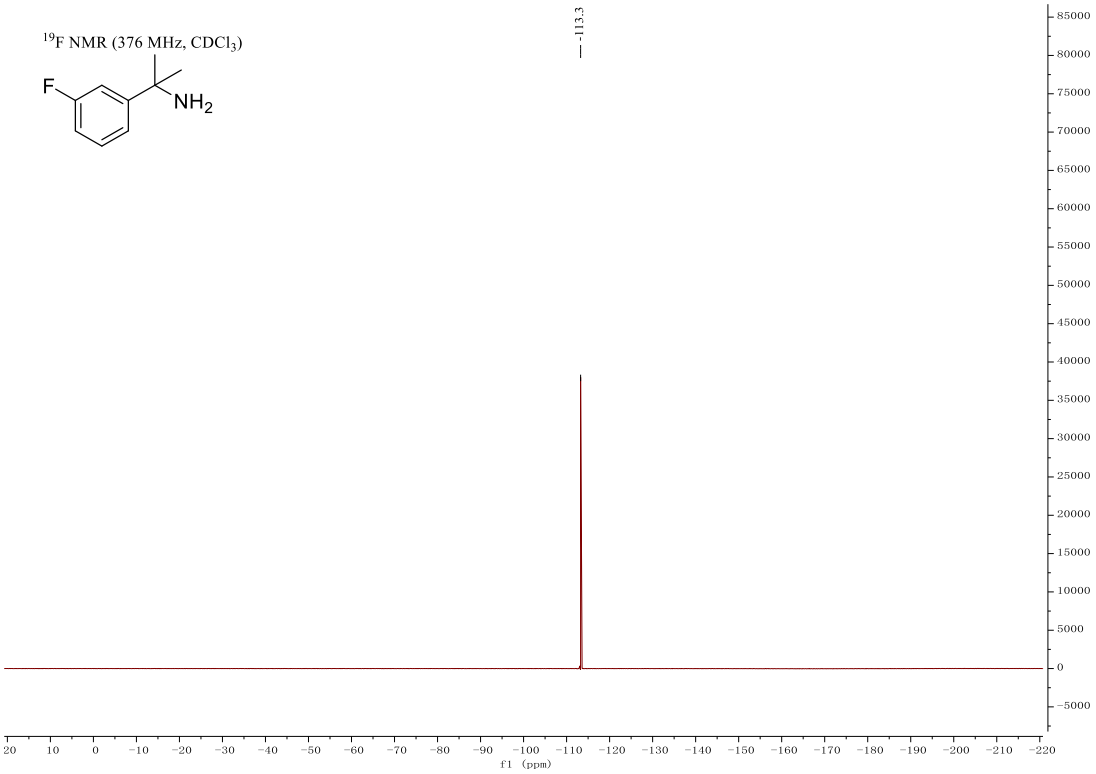
^{19}F NMR (376 MHz, $CDCl_3$)



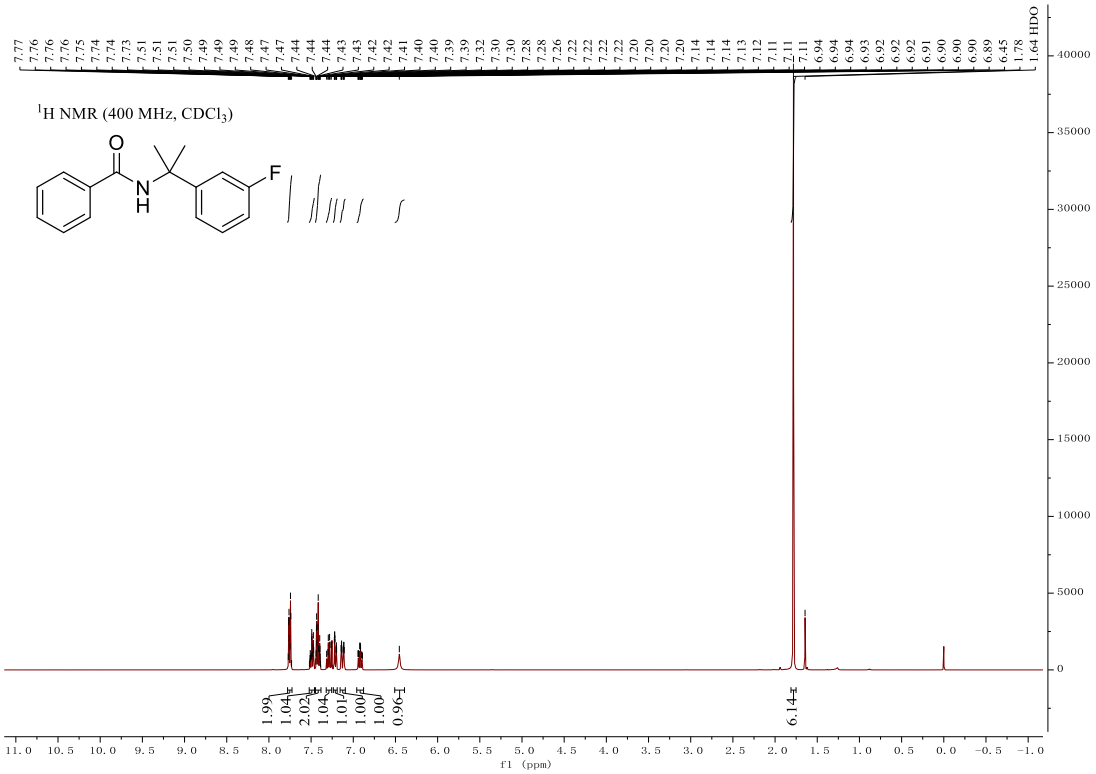
Compound S48



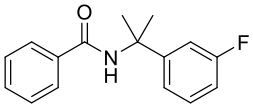




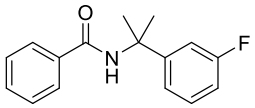
Compound S49



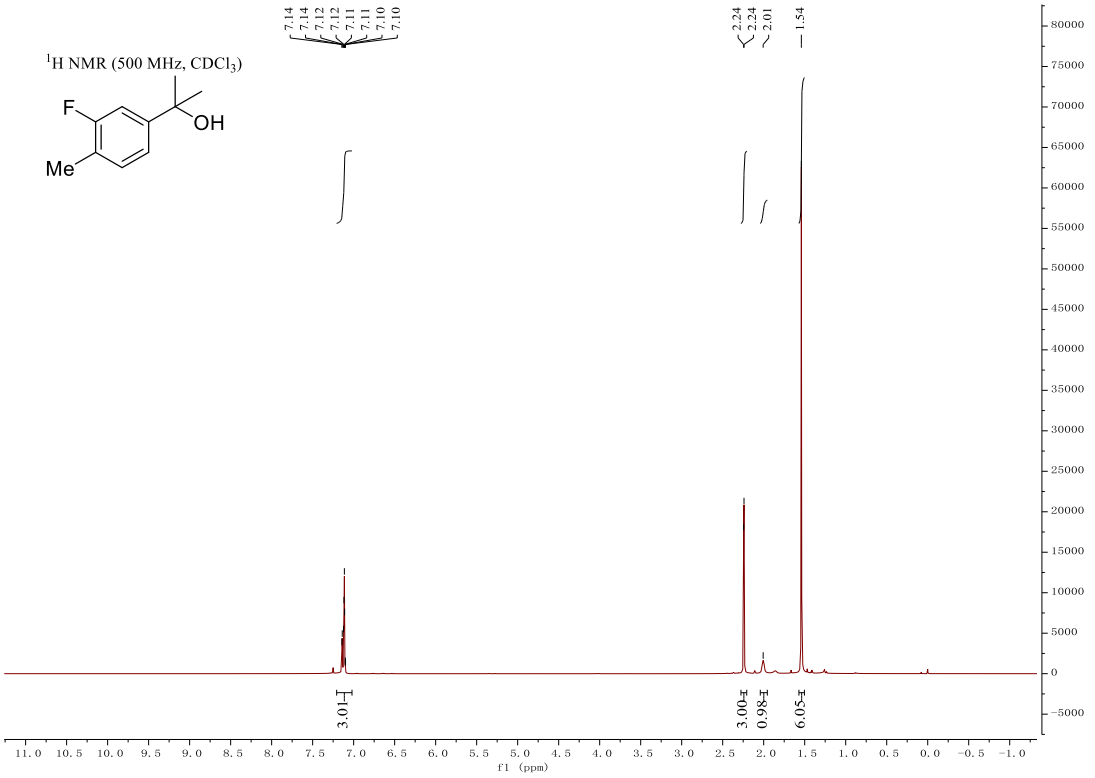
^{13}C NMR (101 MHz, $CDCl_3$)

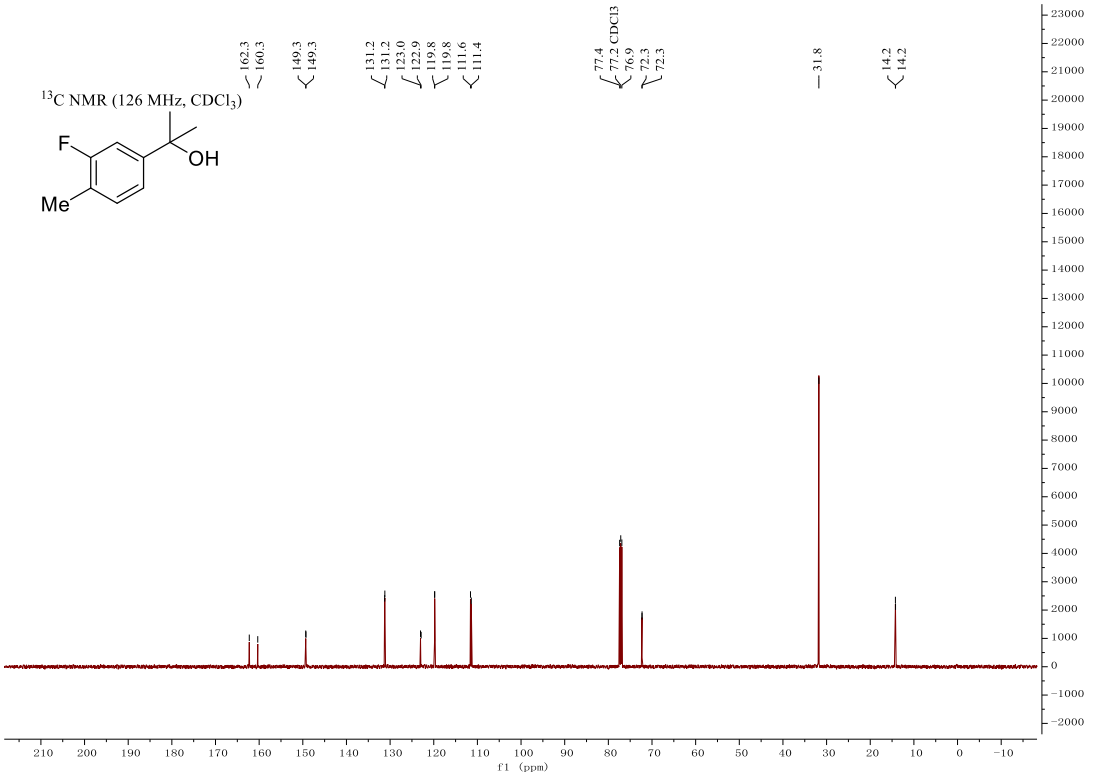


^{19}F NMR (471 MHz, $CDCl_3$)

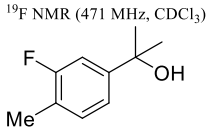


Compound S50



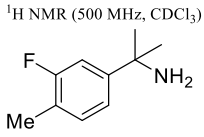


^{19}F NMR (471 MHz, $CDCl_3$)

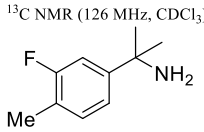


Compound S51

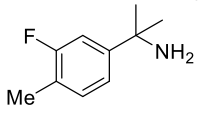
^{1}H NMR (500 MHz, $CDCl_3$)



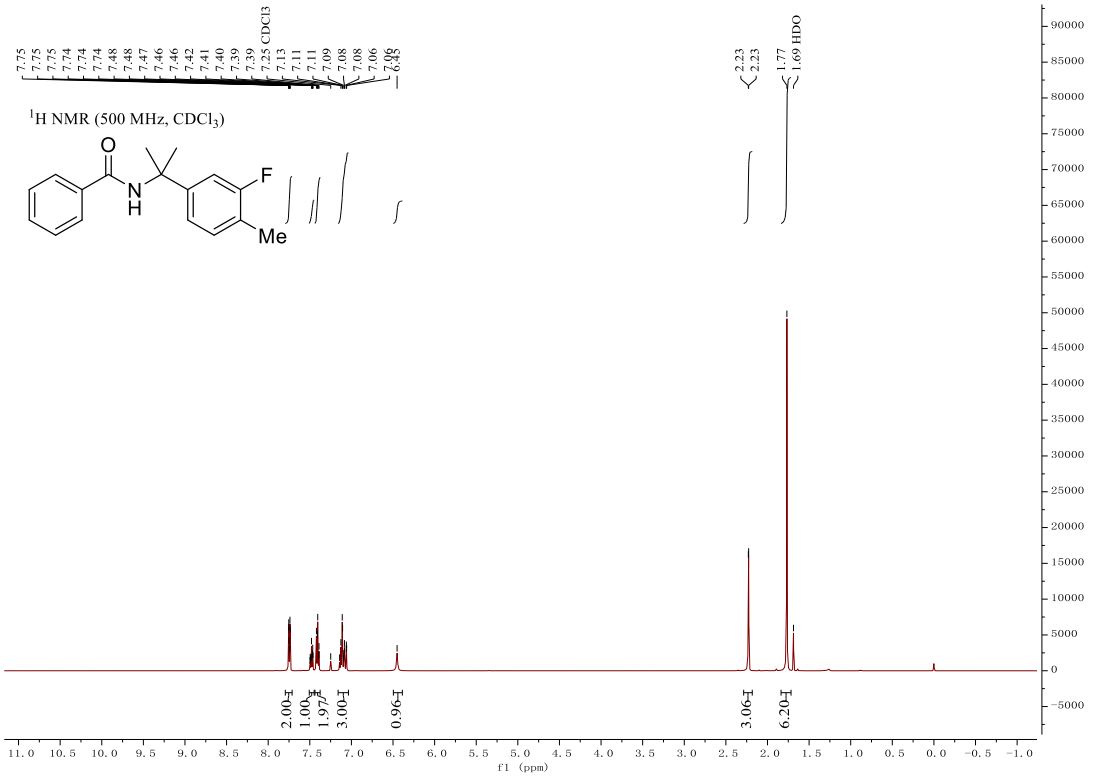
^{13}C NMR (126 MHz, $CDCl_3$)

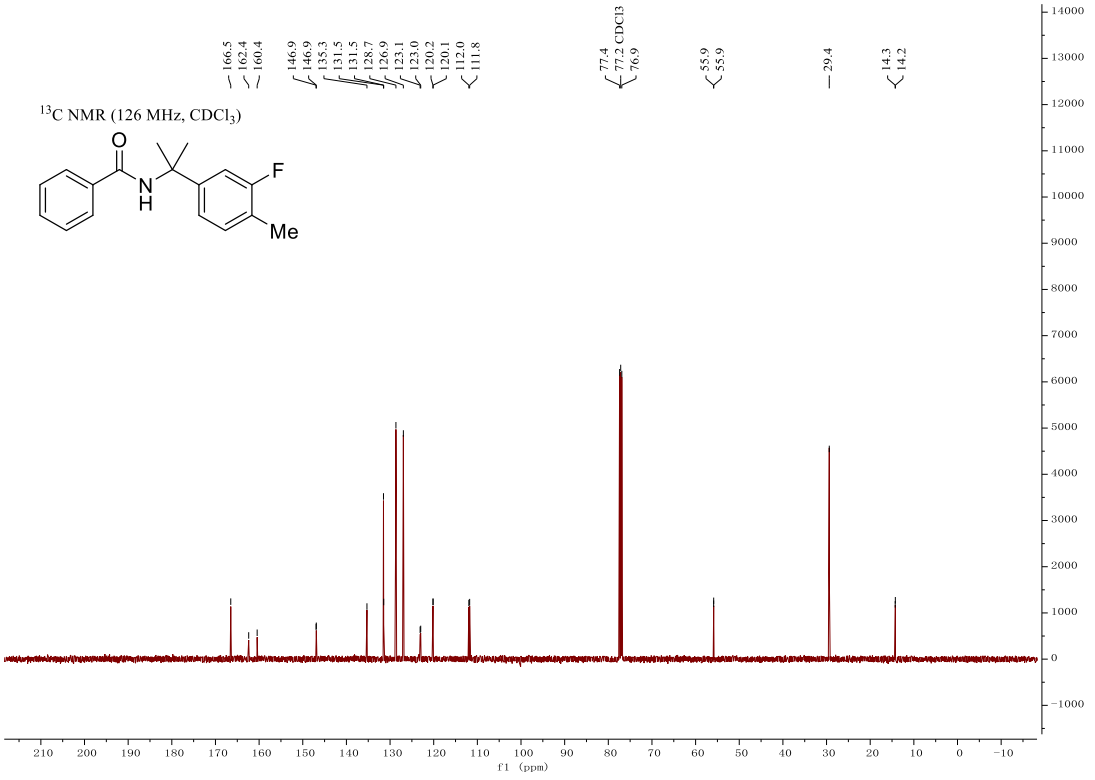


^{19}F NMR (471 MHz, $CDCl_3$)

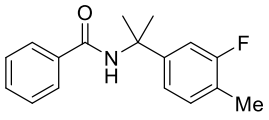


Compound S52



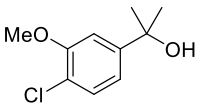


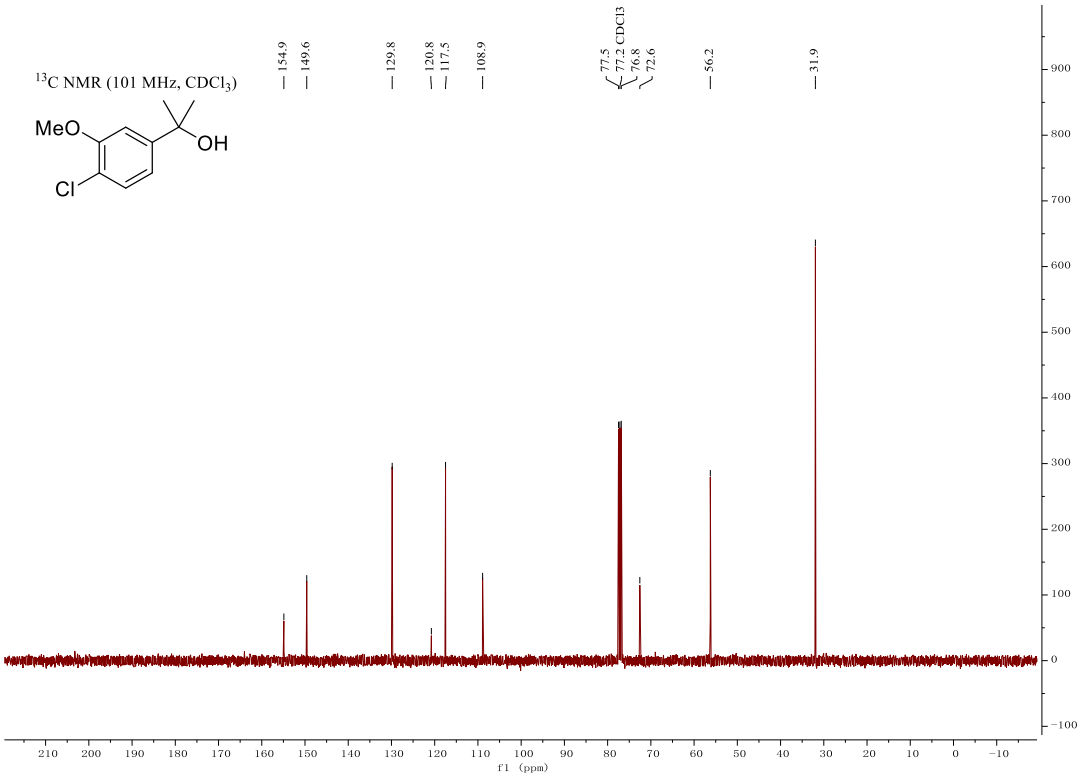
^{19}F NMR (471 MHz, $CDCl_3$)



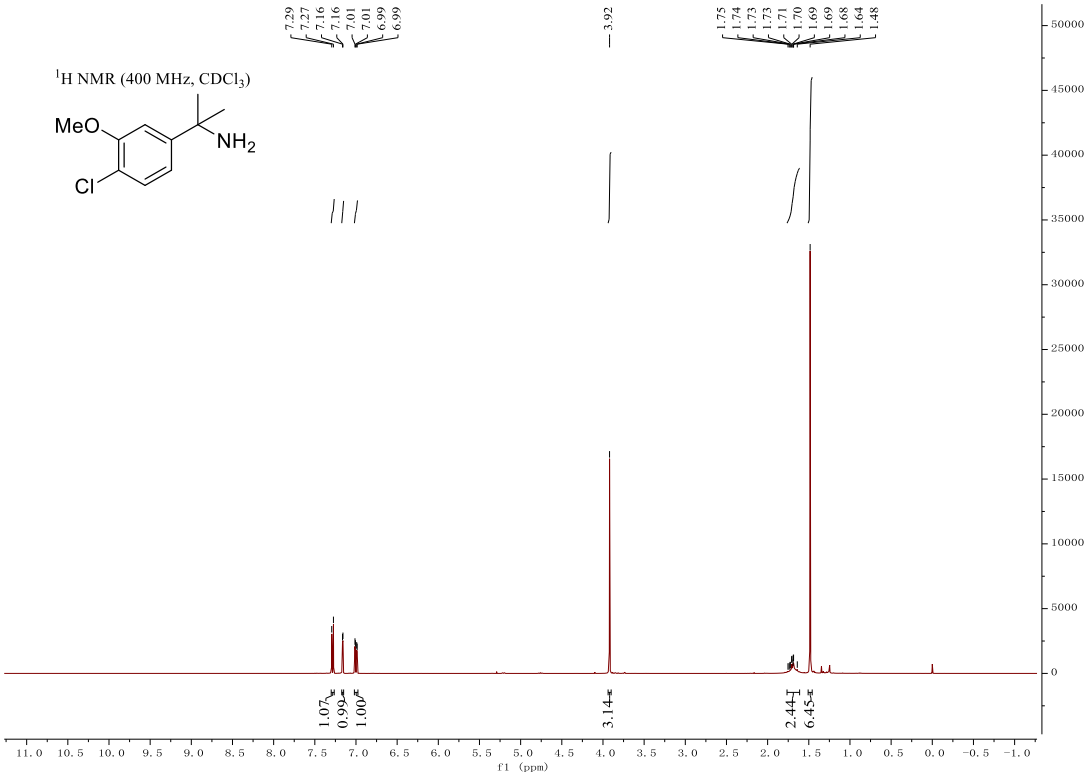
Compound S53

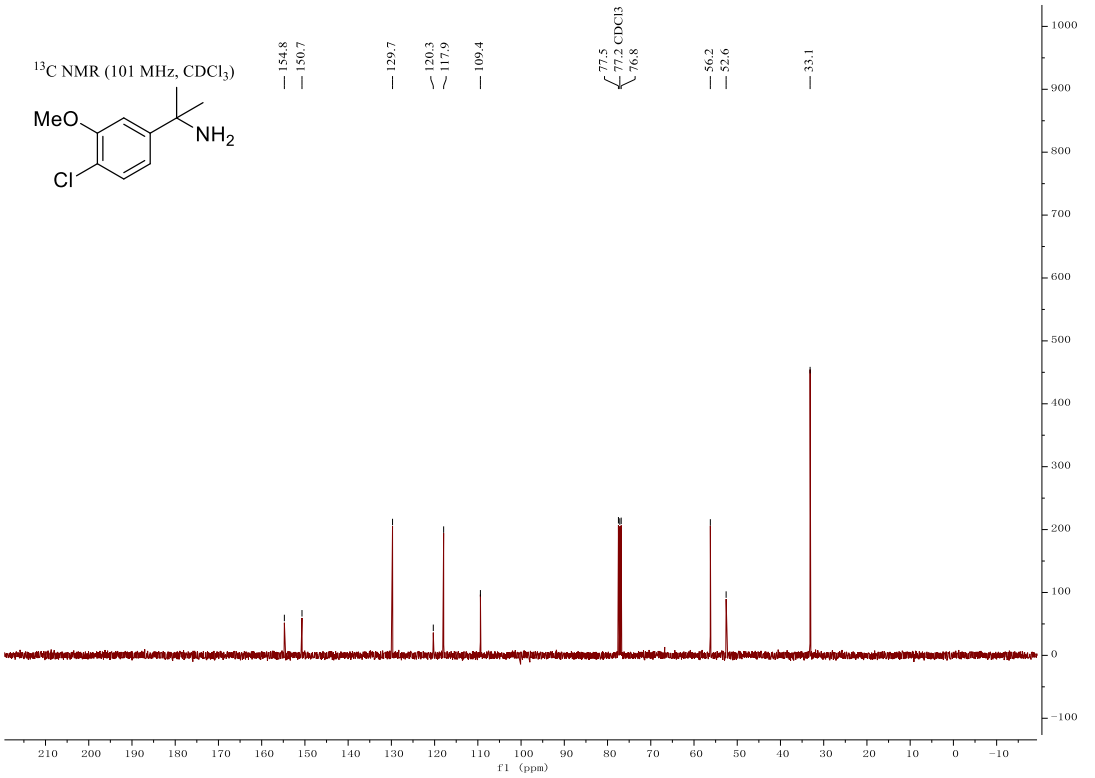
^{1}H NMR (400 MHz, $CDCl_3$)



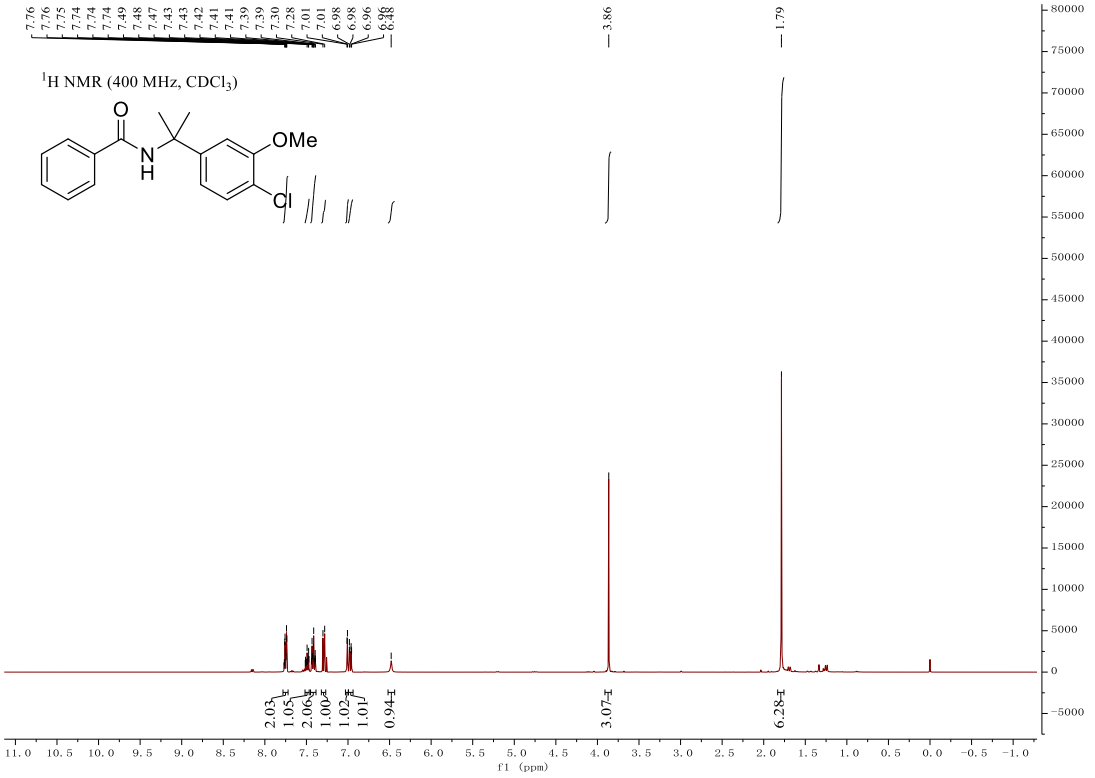


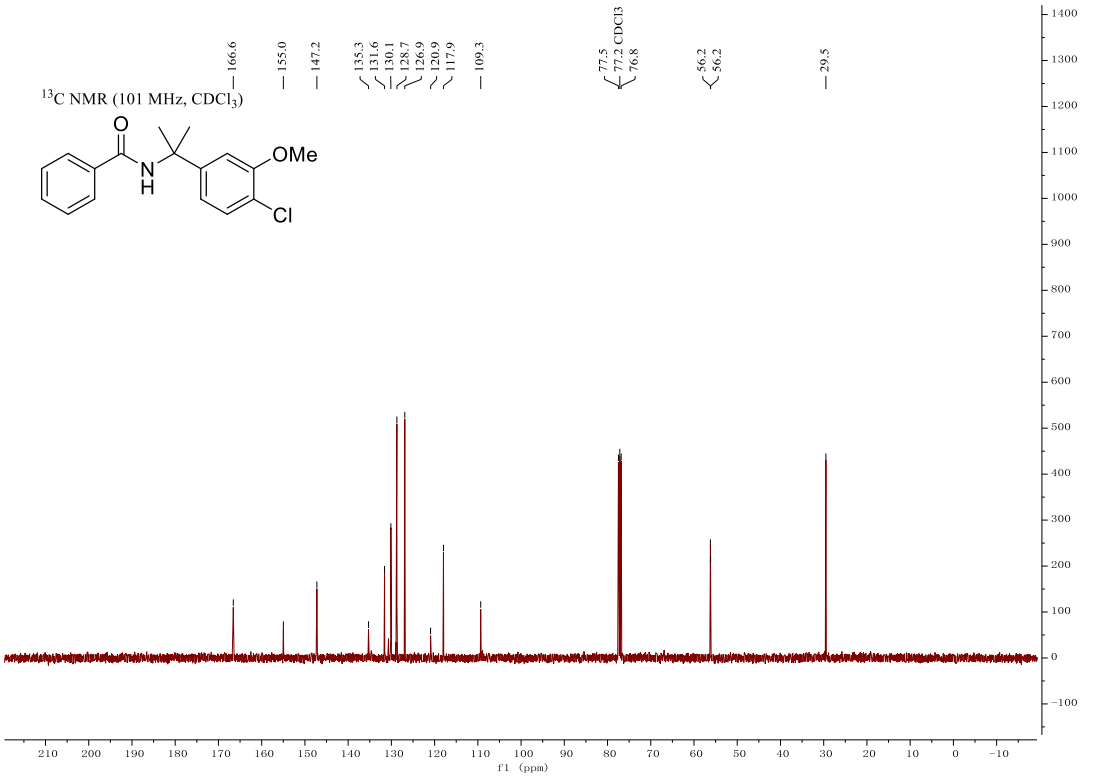
Compound S54



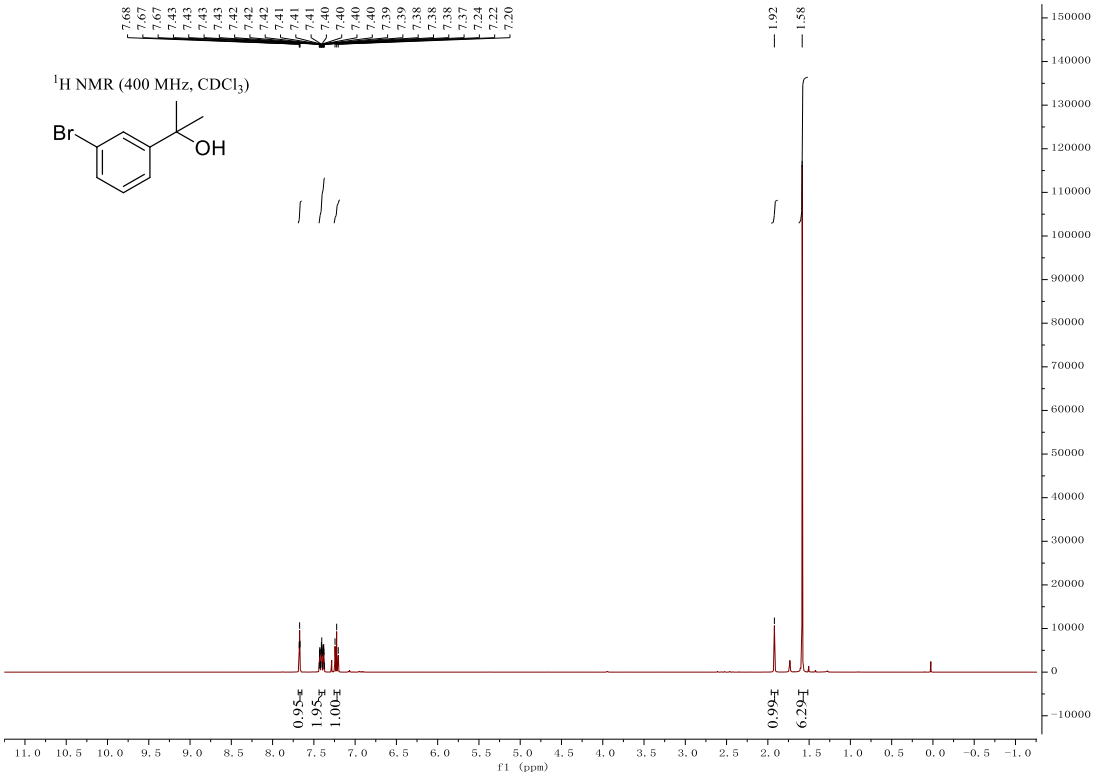


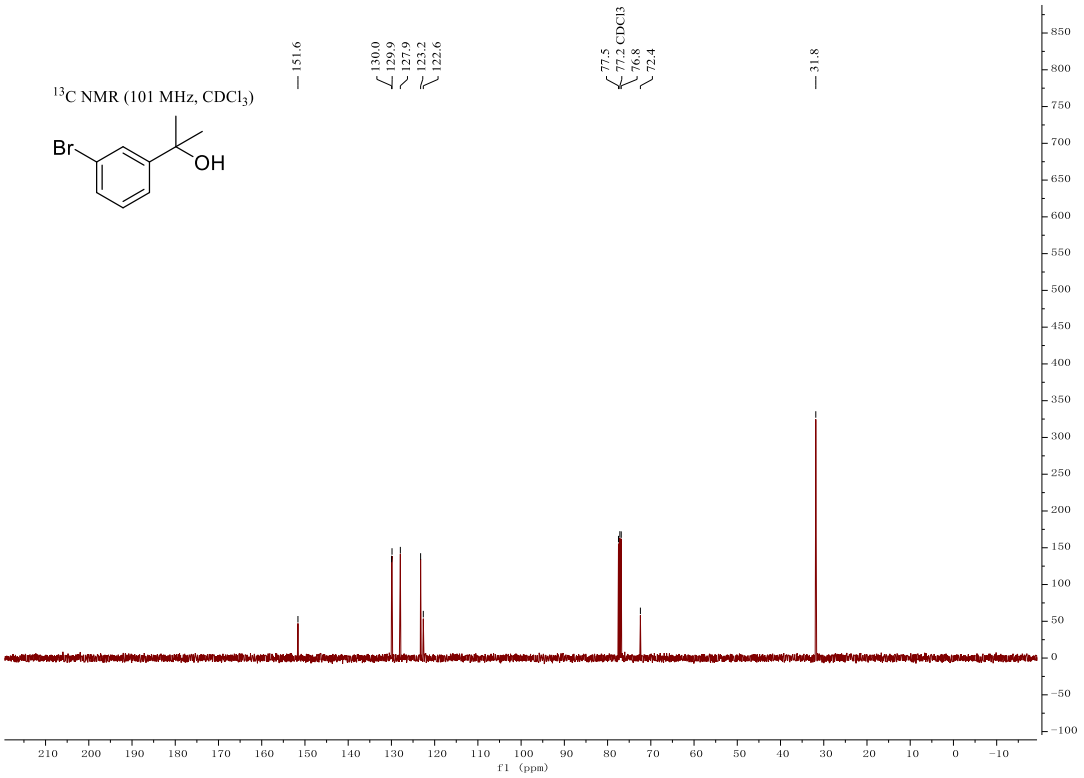
Compound S55



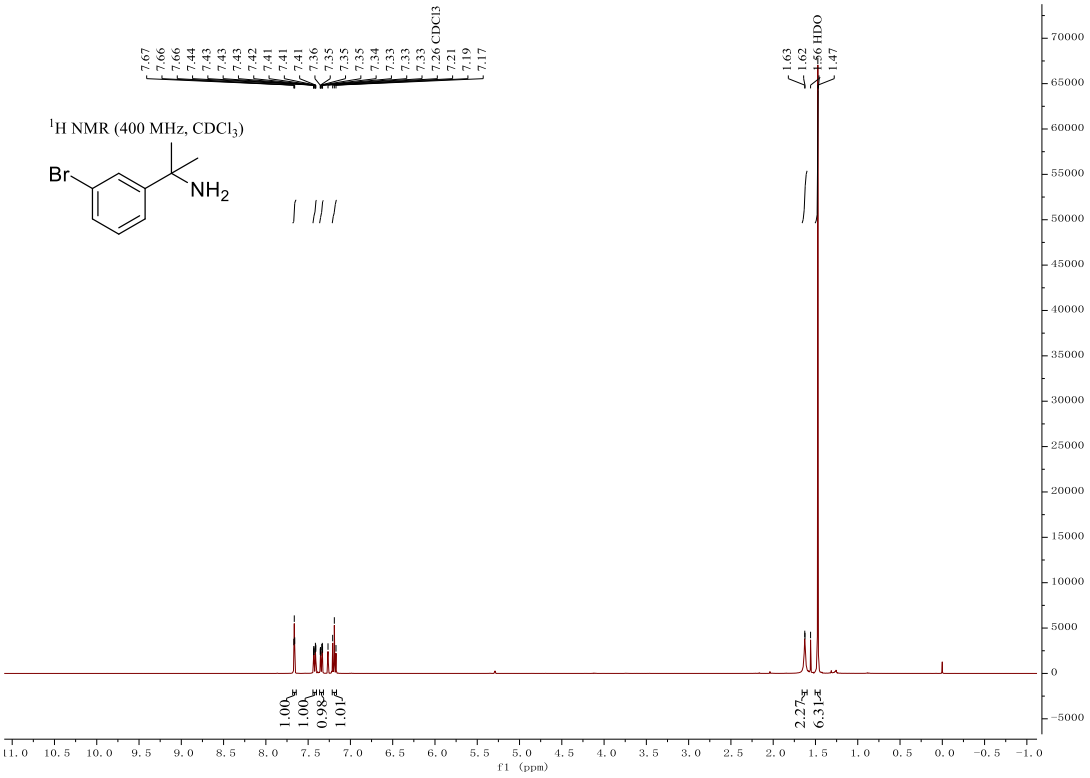


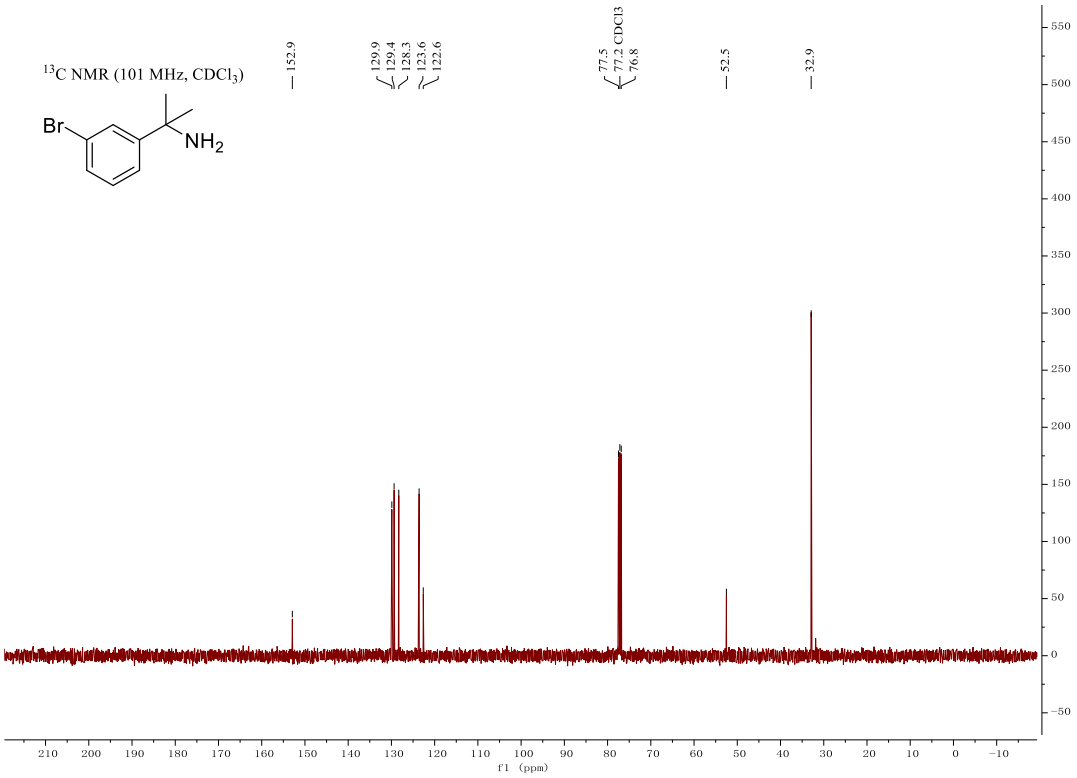
Compound S56



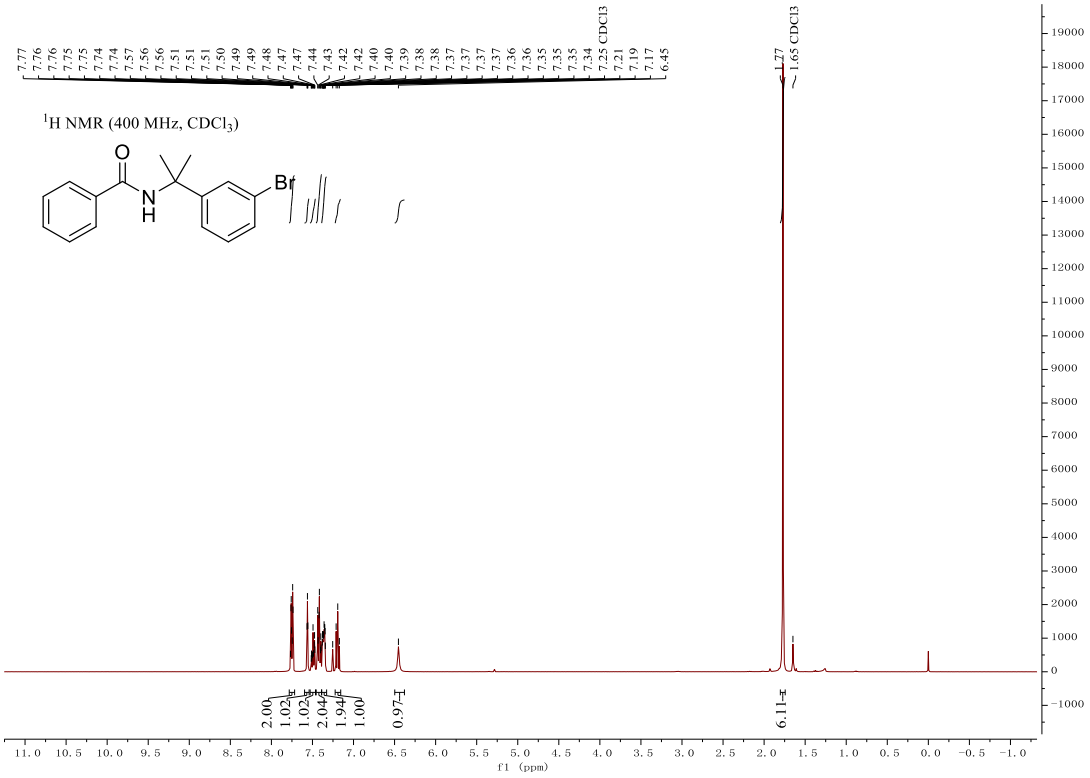


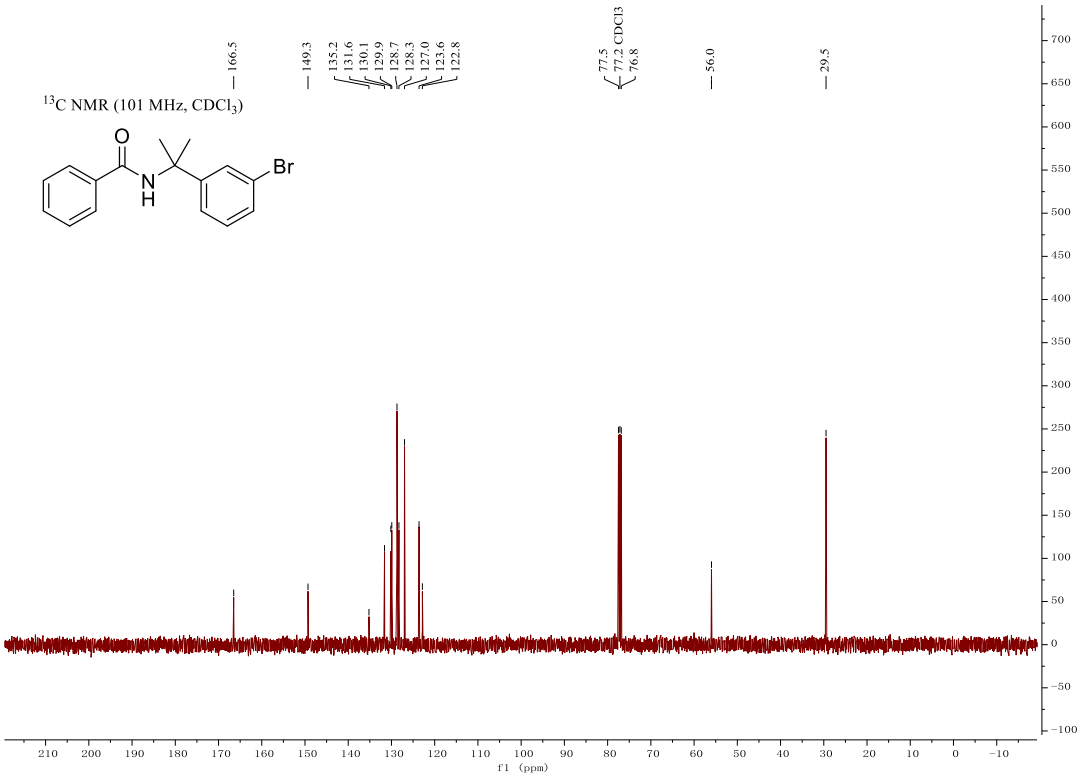
Compound S57



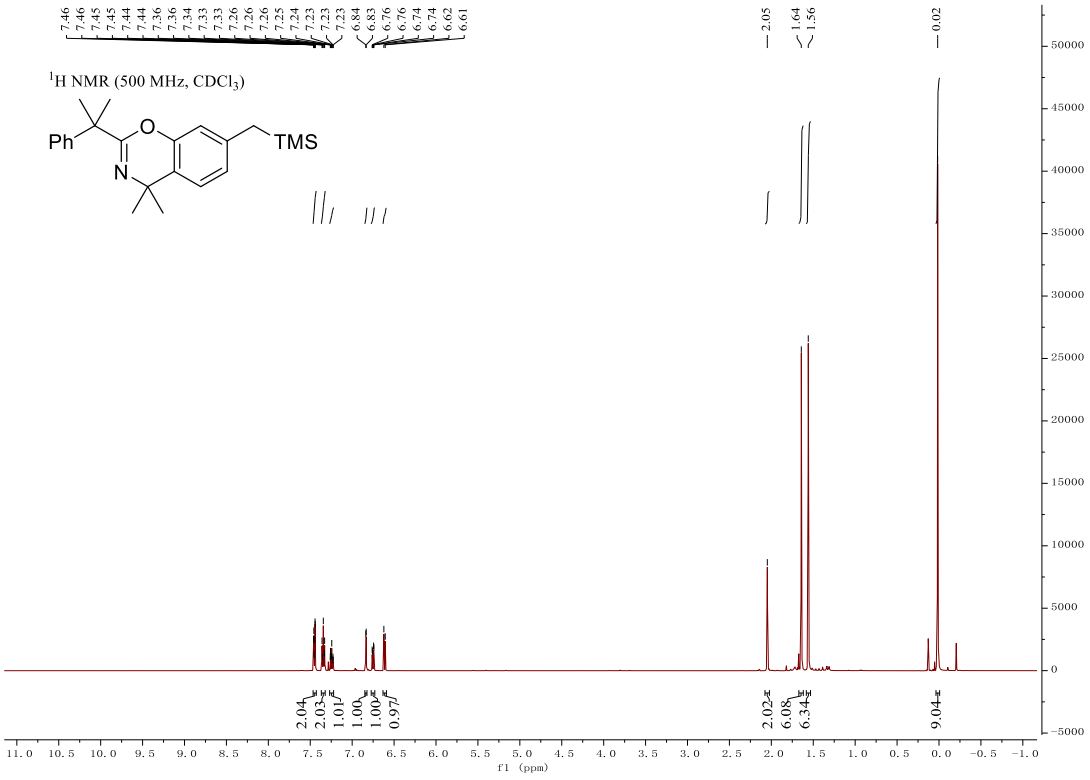


Compound S58




166.5
149.3
135.2
131.6
130.1
129.9
128.7
128.3
127.0
123.6
122.8
77.5
77.2 CDCl3
76.8
56.0
29.5
13C NMR (101 MHz, CDCl3)
O
N
H
Br
f1 (ppm)

Compound 26


7.46
7.46
7.45
7.45
7.44
7.44
7.36
7.36
7.34
7.33
7.33
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.23
6.84
6.83
6.76
6.76
6.74
6.74
6.62
6.61
2.05
1.64
1.56
0.02
1H NMR (500 MHz, CDCl3)
Ph
O
N
TMS
2.04
2.03
1.01
1.00
1.00
0.97
2.02
6.08
6.34
9.04
f1 (ppm)

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