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Supporting Information

Selective Synthesis of Aryl thioamides and Aryl-α-ketoamides from α-Oxocarboxylic Acids and Tetraalkylthiuram Disulfides: An Unexpected Chemoselectivity from Aryl Sulfonyl Chlorides

Miao Lai, Zhiyong Wu, Yizhi Wang, Ying Zheng and Mingqin Zhao**

Flavors and Fragrance Engineering & Technology Research Center of Henan Province, College of Tobacco Science, Henan Agricultural University, Zhengzhou 450002, P.R. China

smileyongyong062@163.com

zhaomingqin118@126.com

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1. General information

All reactions were carried out under air atmosphere in a dried tube. Chemicals were either purchased or synthesized according to references. All α-oxocarboxylic acids compounds except benzoyl formic acid were prepared according to literature[1]. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. Analytical thin layer chromatography (TLC) was performed on precoated silica gel F_{254} plates. Compounds were visualized by irradiation with UV light (254 nm).

Analytical information: ^{1}H NMR and ^{13}C NMR spectra data were recorded by a BRUKER AVANCE III 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. ^{1}H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ^{13}C NMR chemical shifts are expressed in ppm. Infrared spectra were recorded with a Thermo Scientific Nicolet 6700 FT-IR Spectrometer. HRMS data were obtained using AB SCIEX Triple TOF 5600+ high resolution mass spectrometer (USA). The products listed below were determined by ^{1}H and ^{13}C NMR spectra.

2. General procedure for the preparation of products 3

Under air atmosphere, α-oxocarboxylic acids **1** (0.2 mmol), thiuram disulfides **2** (0.4 mmol, 2.0 equiv.) and KOH (0.4 mmol, 2.0 equiv.) were charged into a 10 mL sealable tube equipped with a magnetic stirring bar. After the addition of DMSO (1.0 mL), the resulting mixture was stirred at 80 °C for 48 h in oil bath. After cooling down, the reaction mixture was quenched with a sat. NH_4Cl solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (elute: petroleum ether-EtOAc) to give the pure product **3** in moderate to good yields.

3. General procedure for the preparation of products 4

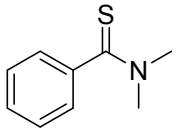
A mixture of α-oxocarboxylic acids **1** (0.2 mmol), thiuram disulfides **2** (0.4 mmol, 2.0 equiv.), KOH (0.4 mmol, 2.0 equiv.), tosyl chloride (0.4 mmol, 2.0 equiv.) and 1.0 mL of 1,4-dioxane was added in a 10 mL sealable tube and stirred at 100 ^{o}C for 24 h under air atmosphere. The progress of the reaction was monitored by thin-layer chromatography. After cooling down, the reaction mixture was quenched with sat. $NaHCO_3$ solution and subsequently extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, and filtered. The residue was evaporated under reduced pressure and purified by flash column chromatography (elute: petroleum ether-EtOAc) to give the pure product **4** in moderate to good yields.

4. References

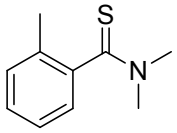
1 a) C. Pimpasri, L. Sumunnee, and S. Yotphan, *Org. Biomol. Chem.* **2017**, *15*, 4320-4327； b) X.

Chen, X. Cui, and Y. Wu, *Org. Lett.* **2016**, *18*, 3722-3725.

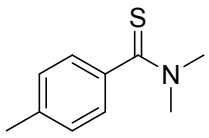
5. Characterization data of the products



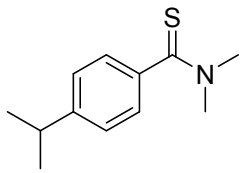
***N,N*-dimethylbenzothioamide (3a):** Purification by column chromatography on silica gel (R_f = 0.40, petroleum ether/ethyl acetate = 3:1) yielded **3a** (29.4 mg, 89%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.37-7.27 (m, 5H), 3.60 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.3, 143.4, 128.6, 128.3, 125.7, 44.2, 43.2; IR(KBr): 3444, 3021, 2930, 1530, 1486, 1454, 1439, 1388, 1315, 1275, 1210, 1139, 999, 917, 763 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{12}NS$: $[M+H]^+$: 166.0690, found: 166.0692.



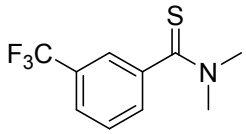
***N,N*,2-trimethylbenzothioamide (3b):** Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 3:1) yielded **3b** (25 mg, 68%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.21-7.15 (m, 3H), 7.13-7.11 (m, 1H), 3.61 (s, 3H), 3.04 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.1, 143.3, 131.5, 130.4, 128.1, 126.2, 125.2, 42.8, 42.2, 18.9; IR(KBr): 2927, 2855, 1517, 1481, 1389, 1294, 1279, 1136, 1043, 993, 883, 794 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{14}NS$: $[M+H]^+$: 180.0847, found: 180.0846.



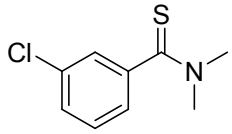
***N,N*,4-trimethylbenzothioamide (3c):** Purification by column chromatography on silica gel (R_f = 0.26, petroleum ether/ethyl acetate = 3:1) yielded **3c** (33.6 mg, 93%) as a light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.21 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.60 (s, 3H), 3.18 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.7, 140.6, 138.7, 128.9, 125.9, 44.2, 43.3, 21.2; IR(KBr): 3444, 2926, 1608, 1503, 1453, 1386, 1289, 1217, 1180, 1045, 994, 883, 822, 616 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{14}NS$: $[M+H]^+$: 180.0847, found: 180.0846.



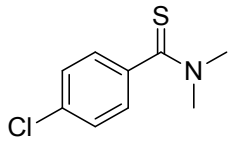
4-isopropyl-*N,N*-dimethylbenzothioamide (3d): Purification by column chromatography on silica gel (R_f = 0.34, petroleum ether/ethyl acetate = 3:1) yielded **3d** (36.5 mg, 87%) as a light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.20-7.16 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.52 (s, 3H), 3.11 (s, 3H), 2.86-2.79 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.7, 149.5, 140.9, 126.3, 125.9, 44.2, 43.3, 33.9, 23.8; IR(KBr): 3443, 3024, 2959, 2926, 2866, 1607, 1523, 1497, 1459, 1393, 1286, 1214, 1140, 1054, 884, 830 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{18}NS$: $[M+H]^+$: 208.1160, found: 208.1161.



***N,N*-dimethyl-3-(trifluoromethyl)benzothioamide (3e):** Purification by column chromatography on silica gel (R_f = 0.32, petroleum ether/ethyl acetate = 3:1) yielded **3e** (24.1 mg, 52%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.59 (t, *J* = 6.4 Hz, 2H), 7.51-7.49 (m, 2H), 3.61 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.2, 143.9, 130.9 (q, *J* = 32.6 Hz), 129.0 (d, *J* = 7.1 Hz), 125.2 (q, *J* = 3.7 Hz), 125.0, 122.6 (q, *J* = 3.8 Hz), 119.6, 44.1, 43.2; IR(KBr): 2935, 1520, 1394, 1335, 1277, 1210, 1167, 1128, 1073, 1015, 909, 805, 701, 671 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}F_3NS$: $[M+Na]^+$: 234.0564, found: 234.0565.

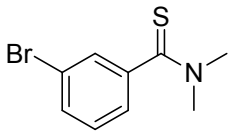


3-chloro-*N,N*-dimethylbenzothioamide (3f): Purification by column chromatography on silica gel (R_f = 0.31, petroleum ether/ethyl acetate = 3:1) yielded **3f** (29.7 mg, 74%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.33-7.30 (m, 3H), 7.19 (td, *J* = 4.7, 2.2 Hz, 1H), 3.61 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.2, 144.8, 134.3, 129.7, 128.6, 125.9, 123.8, 44.1, 43.2; IR(KBr): 2932, 1592, 1565, 1519, 1471, 1391, 1289, 1144, 1078, 1013, 898, 788, 752, 694 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{11}ClNS$: $[M+H]^+$: 200.0301, found: 200.0302.

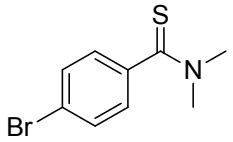


4-chloro-*N,N*-dimethylbenzothioamide (3g): Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **3g** (32 mg, 78%) as a light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.34-7.31 (m, 2H), 7.25 (dd, *J* = 6.6, 2.0 Hz, 2H), 3.59 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.9, 141.7, 134.6, 128.6, 127.3, 44.2, 43.3; IR(KBr): 3443, 3016, 2936, 1590, 1525, 1488, 1394, 1286, 1144, 1089, 1017, 989, 882, 728 cm^{-1}; HRMS

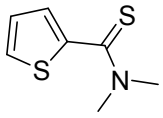
(ESI) calcd. for $C_9H_{11}ClNS$: $[M+H]^+$: 200.0301, found: 200.0300.



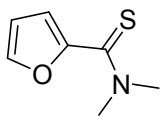
3-bromo-*N,N*-dimethylbenzothioamide (3h): Purification by column chromatography on silica gel (R_f = 0.32, petroleum ether/ethyl acetate = 5:1) yielded **3h** (29.6 mg, 60%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.48-7.44 (m, 2H), 7.25-7.22 (m, 2H), 3.58 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.1, 145.0, 131.5, 129.9, 128.7, 124.3, 122.4, 44.2, 43.2; IR(KBr): 3053, 2931, 1519, 1470, 1391, 1287, 1144, 1051, 995, 877, 786, 728, 694 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{11}BrNS$: $[M+H]^+$: 243.9796, found: 243.9795.



4-bromo-*N,N*-dimethylbenzothioamide (3i): Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **3i** (31.6 mg, 64%) as a light yellow solid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.48 (dt, J = 8.9, 2.3 Hz, 2H), 7.19 (dt, J = 8.9, 2.3 Hz, 2H), 3.58 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.9, 142.1, 131.5, 127.5, 122.7, 44.2, 43.3; IR(KBr): 3424, 3042, 2930, 1527, 1483, 1396, 1289, 1144, 1014, 989, 935, 880, 815 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{11}BrNS$: $[M+H]^+$: 243.9796, found: 243.9798.

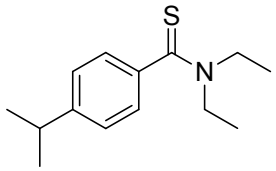


***N,N*-dimethylthiophene-2-carbothioamide (3j):** Purification by column chromatography on silica gel (R_f = 0.34, petroleum ether/ethyl acetate = 3:1) yielded **3j** (18.9 mg, 55%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.32 (dd, J = 5.1, 1.1 Hz, 1H), 7.05 (dd, J = 3.7, 1.1 Hz, 1H), 6.91 (dd, J = 5.1, 3.7 Hz, 1H), 3.51 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.8, 145.2, 129.2, 126.5, 126.4, 44.6, 26.9; IR(KBr): 3419, 3071, 2923, 2851, 1504, 1388, 1354, 1271, 1224, 1127, 1050, 976, 865, 835, 714, 629 cm^{-1}; HRMS (ESI) calcd. for $C_7H_{10}NS_2$: $[M+H]^+$: 172.0255, found: 172.0254.

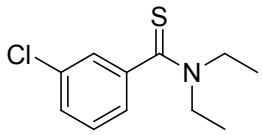


***N,N*-dimethylfuran-2-carbothioamide (3k):** Purification by column chromatography on silica gel (R_f = 0.28, petroleum ether/ethyl acetate = 7:1) yielded **3k** (8.5 mg, 26%) as a light yellow solid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.39 (t, J

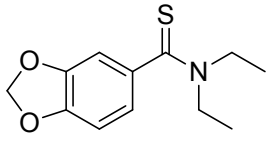
= 0.9 Hz, 1H), 7.02 (dd, *J* = 3.4, 0.5 Hz, 1H), 6.38 (q, *J* = 1.8 Hz, 1H), 3.48 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 199.8, 152.5, 143.2, 117.7, 111.9, 44.4, 44.2; IR(KBr): 3443, 2924, 2852, 1650, 1511, 1465, 1390, 1294, 1141, 1076, 1025, 985, 751 cm^{-1}; HRMS (ESI) calcd. for $C_7H_{10}NOS$: $[M+H]^+$: 156.0483, found: 156.0481.



***N,N*-diethyl-4-isopropylbenzothioamide (3l):** Purification by column chromatography on silica gel (R_f = 0.40, petroleum ether/ethyl acetate = 5:1) yielded **3l** (15.3 mg, 32%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.20 (td, *J* = 8.5, 2.2 Hz, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 2H), 2.95-2.88 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 200.8, 148.8, 141.4, 126.4, 125.1, 47.8, 46.1, 33.9, 23.9, 13.9, 11.3; IR(KBr): 3424, 2959, 2932, 2868, 1922, 1605, 1565, 1491, 1422, 1372, 1317, 1284, 1244, 1190, 1138, 986, 832, 746 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{22}NS$: $[M+H]^+$: 236.1473, found: 236.1472.

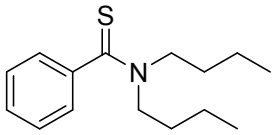


3-chloro-*N,N*-diethylbenzothioamide (3m): Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 5:1) yielded **3m** (25.8 mg, 56%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.30 (d, *J* = 5.2 Hz, 2H), 7.25 (s, 1H), 7.15-7.12 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.46 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.2, 145.2, 134.3, 129.8, 128.1, 125.2, 123.2, 47.9, 46.1, 13.9, 11.2; IR(KBr): 2976, 2934, 1592, 1564, 1497, 1408, 1381, 1285, 1141, 1078, 995, 857, 788 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{15}ClNS$: $[M+H]^+$: 228.0614, found: 228.0612.

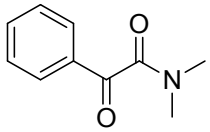


***N,N*-diethylbenzo[*d*][1,3]dioxole-5-carbothioamide (3n):** Purification by column chromatography on silica gel (R_f = 0.35, petroleum ether/ethyl acetate = 5:1) yielded **3n** (13 mg, 25%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 6.78 (dd, *J* = 5.3, 3.6 Hz, 2H), 6.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.99 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.51 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) 199.9, 147.5, 147.4, 137.8, 118.8, 108.1, 106.6, 101.3, 47.9,

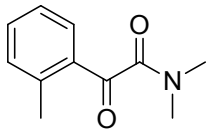
46.2, 13.9, 11.2; IR(KBr): 2977, 2935, 1487, 1364, 1314, 1289, 1244, 1186, 1144, 1128, 1037, 986, 935, 895 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{16}NO_2S$: $[M+H]^+$: 238.0902, found: 238.0903.



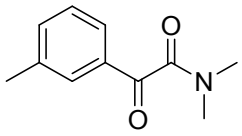
***N,N*-dibutylbenzothioamide (3o):** Purification by column chromatography on silica gel (R_f = 0.40, petroleum ether/ethyl acetate = 3:1) yielded **3o** (10 mg, 20%) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.28-7.20 (m, 3H), 7.15-7.12 (m, 2H), 3.99 (t, *J* = 7.8 Hz, 2H), 3.30 (t, *J* = 7.8 Hz, 2H), 1.79-1.72 (m 2H), 1.50-1.43 (m 2H), 1.37 (q, *J* = 7.5 Hz, 2H), 1.04 (q, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.69 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 200.7, 144.0, 128.3, 128.0, 125.2, 53.3, 51.5, 30.5, 28.1, 20.3, 19.8, 13.9, 13.5; IR(KBr): 3443, 2959, 2932, 2872, 1496, 1482, 1457, 1441, 1422, 1373, 1275, 761, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{24}NS$: $[M+H]^+$: 250.1629, found: 250.1630.



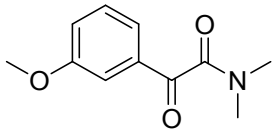
***N,N*-dimethyl-2-oxo-2-phenylacetamide (4a):** Purification by column chromatography on silica gel (R_f = 0.26, petroleum ether/ethyl acetate = 3:1) yielded **4a** (31.5 mg, 89%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.96-7.94 (m, 2H), 7.64 (tt, *J* = 6.9, 1.2 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 3.12 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.8, 167.0, 134.7, 133.1, 129.7, 129.0, 37.0, 34.0; IR(KBr): 3444, 2933, 1681, 1650, 1597, 1450, 1405, 1247, 1146, 994, 882, 726, 683, 643 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{12}NO_2$: $[M+H]^+$: 178.0868, found: 178.0860.



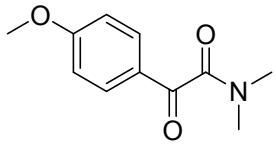
***N,N*-dimethyl-2-oxo-2-(*o*-tolyl)acetamide (4b):** Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4b** (38.2 mg, 51%) as a colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.70-7.68 (m, 1H), 7.50-7.46 (m, 1H), 7.31 (t, *J* = 6.8 Hz, 2H), 3.11 (s, 3H), 2.98 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.7, 167.8, 141.5, 133.7, 132.6, 132.5, 131.6, 126.2, 37.1, 34.1, 21.7; IR(KBr): 3442, 2929, 2851, 1680, 1635, 1457, 1406, 1240, 1157, 1124, 989, 887, 741, 645 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$: 192.1025, found: 192.1021.



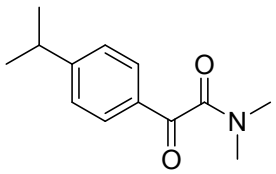
***N,N*-dimethyl-2-oxo-2-(*m*-tolyl)acetamide (4c):** Purification by column chromatography on silica gel (R_f = 0.31, petroleum ether/ethyl acetate = 3:1) yielded **4c** (21.2 mg, 56%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.83 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.11 (s, 3H), 2.95 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.5, 167.3, 145.9, 130.7, 129.8, 129.7, 37.0, 34.0, 21.9; IR(KBr): 3444, 2926, 1646, 1605, 1573, 1406, 1250, 1146, 999, 887, 762, 614 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$: 192.1025, found: 192.1015.



2-(3-methoxyphenyl)-*N,N*-dimethyl-2-oxoacetamide (4d): Purification by column chromatography on silica gel (R_f = 0.28, petroleum ether/ethyl acetate = 3:1) yielded **4d** (22.5 mg, 55%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.50-7.48 (m, 2H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.20-7.17 (m, 1H), 3.87 (s, 3H), 3.12 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.7, 167.0, 160.1, 134.4, 130.1, 122.8, 121.6, 112.8, 55.5, 37.1, 34.0; IR(KBr): 3445, 2928, 1681, 1650, 1597, 1487, 1281, 1261, 1221, 1136, 1045, 1007, 764, 646 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{14}NO_3$: $[M+H]^+$: 208.0974, found: 208.0970.

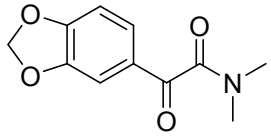


2-(4-methoxyphenyl)-*N,N*-dimethyl-2-oxoacetamide (4e): Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 1:1) yielded **4e** (31.9 mg, 77%) as a light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.91 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.11 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.5, 167.4, 164.8, 132.1, 126.2, 114.3, 55.6, 37.1, 34.0; IR(KBr): 3449, 2925, 1664, 1647, 1603, 1573, 1401, 1263, 1147, 1026, 859, 775, 613 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{14}NO_3$: $[M+H]^+$: 208.0974, found: 208.0960.

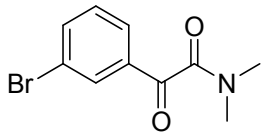


2-(4-isopropylphenyl)-*N,N*-dimethyl-2-oxoacetamide (4f): Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 3:1) yielded

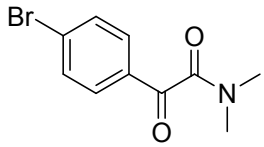
4f (30 mg, 69%) as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.87 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 3.12 (s, 3H), 3.02-2.93 (m, 1H), 2.96 (s, 3H), 1.27 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.5, 167.3, 156.6, 131.0, 129.9, 127.2, 37.1, 34.5, 34.0, 23.6; IR(KBr): 3451, 2963, 2930, 1678, 1648, 1604, 1462, 1414, 1252, 1149, 1057, 996, 782, 715 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{18}NO_2$: $[M+H]^+$: 220.1338, found: 220.1333.



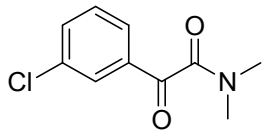
2-(benzo[*d*][1,3]dioxol-5-yl)-*N*,*N*-dimethyl-2-oxoacetamide (4g): Purification by column chromatography on silica gel (R_f = 0.35, petroleum ether/ethyl acetate = 1:1) yielded **4g** (27.8 mg, 63%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.50 (dd, J = 8.1, 1.6 Hz, 1H), 7.42 (d, J = 1.6 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.08 (s, 2H), 3.10 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.1, 167.2, 153.3, 148.6, 127.9, 127.4, 108.4, 108.3, 102.2, 37.1, 34.0; IR(KBr): 3450, 2921, 1638, 1502, 1440, 1265, 1097, 1035, 852, 769, 632 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}NO_4$: $[M+H]^+$: 222.0766, found: 222.0760.



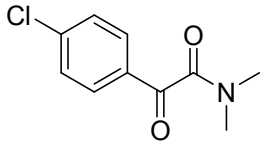
2-(3-bromophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (4h): Purification by column chromatography on silica gel (R_f = 0.32, petroleum ether/ethyl acetate = 3:1) yielded **4h** (34.1 mg, 67%) as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 8.09 (t, J = 1.8 Hz, 1H), 7.88 (dt, J = 7.8, 1.0 Hz, 1H), 7.77 (ddd, J = 8.0, 1.9, 1.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 3.13 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.1, 166.2, 137.5, 134.9, 132.4, 130.6, 128.3, 123.3, 37.1, 34.1; IR(KBr): 3441, 2924, 1757, 1684, 1407, 1241, 1147, 999, 756, 641 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}BrNO_2$: $[M+H]^+$: 255.9973, found: 255.9976.



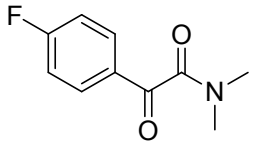
2-(4-bromophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (4i): Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 2:1) yielded **4i** (46.9 mg, 92%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.82 (dd, J = 6.8, 1.7 Hz, 2H), 7.66 (dd, J = 7.0, 1.8 Hz, 2H), 3.12 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.5, 166.4, 132.4, 131.9, 131.1, 130.2, 37.1, 34.1; IR(KBr): 3442, 2933, 1678, 1650, 1586, 1399, 1247, 1146, 1071, 996, 882, 841, 762, 647 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}BrNO_2$: $[M+H]^+$: 255.9973, found: 255.9971.



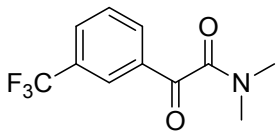
2-(3-chlorophenyl)-*N,N*-dimethyl-2-oxoacetamide (4j): Purification by column chromatography on silica gel (R_f = 0.35, petroleum ether/ethyl acetate = 2:1) yielded **4j** (27.1 mg, 64%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.93 (t, *J* = 1.6 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 3.13 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.2, 166.3, 135.4, 134.7, 134.6, 130.3, 129.5, 127.8, 37.0, 34.1; IR(KBr): 3443, 2931, 1685, 1650, 1573, 1412, 1240, 1149, 1002, 896, 760, 729, 675, 643 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}ClNO_2$: $[M+H]^+$: 212.0478, found: 212.0475.



2-(4-chlorophenyl)-*N,N*-dimethyl-2-oxoacetamide (4k): Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4k** (32.1 mg, 76%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.89 (dt, *J* = 9.0, 2.3 Hz, 2H), 7.49 (dt, *J* = 9.0, 2.3 Hz, 2H), 3.12 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.3, 166.5, 141.3, 131.5, 131.0, 129.4, 37.0, 34.1; IR(KBr): 3443, 2929, 1684, 1651, 1589, 1401, 1249, 1148, 1085, 996, 885, 847, 772 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}ClNO_2$: $[M+H]^+$: 212.0478, found: 212.0479.

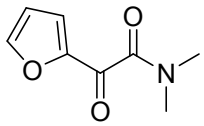


2-(4-fluorophenyl)-*N,N*-dimethyl-2-oxoacetamide (4l): Purification by column chromatography on silica gel (R_f = 0.32, petroleum ether/ethyl acetate = 3:1) yielded **4l** (30 mg, 77%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 8.01-7.97 (m, 2H), 7.21-7.17 (m, 2H), 3.12 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.0, 168.0, 166.0 (d, *J* = 127.8 Hz), 132.5 (d, *J* = 9.8 Hz), 129.6 (d, *J* = 2.8 Hz), 116.3 (d, *J* = 22.2 Hz), 37.1, 34.1; IR(KBr): 3441, 2929, 1674, 1637, 1598, 1507, 1401, 1273, 1234, 1149, 997, 886, 847, 770, 613 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{11}FNO_2$: $[M+H]^+$: 196.0774, found: 196.0756.

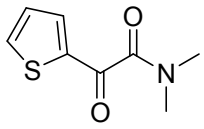


***N,N*-dimethyl-2-oxo-2-(3-(trifluoromethyl)phenyl)acetamide (4m):** Purification by

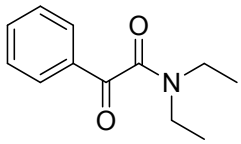
column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4m** (30 mg, 61%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 8.23 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 3.15 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 189.9, 166.0, 133.8, 132.9, 131.8 (q, *J* = 33.1 Hz), 130.9 (q, *J* = 3.5 Hz), 129.7, 126.3 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 270.9 Hz), 37.1, 34.2; IR(KBr): 3425, 2928, 2854, 1689,1651, 1612, 1439, 1407, 1334, 1237, 1171, 1143, 1072, 1002, 765, 695, 654 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{11}F_3NO_2$: $[M+H]^+$: 246.0742, found: 246.0732.



2-(furan-2-yl)-*N,N*-dimethyl-2-oxoacetamide (4n): Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4n** (17.7 mg, 53%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.71 (d, *J* = 0.9 Hz, 1H), 7.37 (d, *J* = 3.6 Hz, 1H), 6.61 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.09 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.5, 165.4, 150.2, 148.7, 122.3, 112.9, 37.2, 34.5; IR(KBr): 3449, 3129, 2923, 2852, 1652, 1568, 1463, 1391, 1302, 1259, 1151, 1029, 999, 773, 658 cm^{-1}; HRMS (ESI) calcd. for $C_8H_{10}NO_3$: $[M+H]^+$: 168.0661, found: 168.0645.

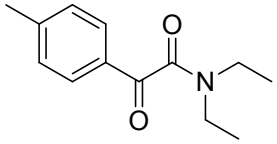


***N,N*-dimethyl-2-oxo-2-(thiophen-2-yl)acetamide (4o):** Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **4o** (36.6 mg, 72%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.82 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.79 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.18 (dd, *J* = 4.8, 4.0 Hz, 1H), 3.10 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 183.5, 165.9, 140.3, 136.4, 136.1, 128.6, 37.3, 34.5; IR(KBr): 3442, 3080, 2927, 1647, 1508, 1407, 1246, 1144, 1053, 965, 842, 746, 643 cm^{-1}; HRMS (ESI) calcd. for $C_8H_{10}NO_2S$: $[M+H]^+$: 184.0432, found: 184.0418.

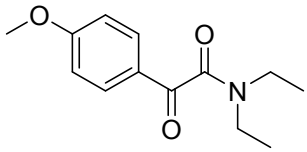


***N,N*-diethyl-2-oxo-2-phenylacetamide (4p):** Purification by column chromatography on silica gel (R_f = 0.35, petroleum ether/ethyl acetate = 8:1) yielded **4p** (24.2 mg, 59%) as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.97-7.95 (m, 2H), 7.68-7.64 (m, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 3.59 (q, *J* = 7.2 Hz, 2H), 3.27 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.6,

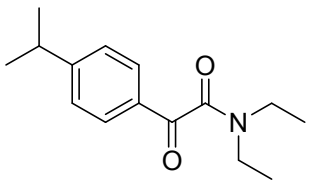
166.7, 134.6, 133.3, 129.6, 128.9, 42.1, 38.8, 14.1, 12.8; IR(KBr): 3443, 2977, 2934, 1681, 1640, 1597, 1449, 1383, 1233, 1146, 856, 721, 689, 632 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{16}NO_2$: $[M+H]^+$: 206.1181, found: 206.1180.



***N,N*-diethyl-2-oxo-2-(*m*-tolyl)acetamide (4q):** Purification by column chromatography on silica gel (R_f = 0.34, petroleum ether/ethyl acetate = 5:1) yielded **4q** (16.2 mg, 37%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.83 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.56 (q, *J* = 7.2 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.4, 166.9, 145.8, 130.9, 129.7, 129.6, 42.1, 38.7, 21.9, 14.1, 12.8; IR(KBr): 3442, 2970, 2931, 1675, 1640, 1605, 1444, 1382, 1238, 1217, 1180, 1147, 1099, 863, 785, 755, 612 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{18}NO_2$: $[M+H]^+$: 220.1338, found: 220.1336.

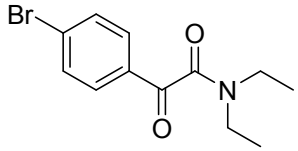


***N,N*-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (4r):** Purification by column chromatography on silica gel (R_f = 0.42, petroleum ether/ethyl acetate = 1:1) yielded **4r** (20.3 mg, 43%) as a colorless solid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.92-7.89 (m, 2H), 6.99-6.95 (m, 2H), 3.89 (s, 3H), 3.55 (q, *J* = 7.2 Hz, 2H), 3.24 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.4, 167.1, 164.7, 132.1, 126.4, 114.3, 55.6, 42.1, 38.7, 14.1, 12.8; IR(KBr): 2975, 2936, 1671, 1644, 1599, 1573, 1511, 1461, 1310, 1266, 1241, 1173, 1144, 1023, 864, 844, 786, 611 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{18}NO_3$: $[M+H]^+$: 236.1287, found: 236.1287.

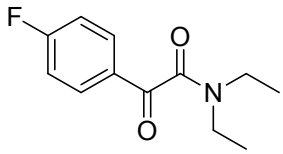


***N,N*-diethyl-2-(4-isopropylphenyl)-2-oxoacetamide (4s):** Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 8:1) yielded **4s** (25.5 mg, 55%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.86 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.56 (q, *J* = 7.2 Hz, 2H), 3.24 (q, *J* = 7.1 Hz, 2H), 3.01-2.95 (m, 1H), 1.30-1.27 (m, 9H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.4, 167.0, 156.4, 131.2, 129.9, 127.1, 42.1, 38.7, 34.5, 23.6, 14.1, 12.8; IR(KBr): 3443, 2966, 2934, 2874, 1678, 1644, 1604, 1462, 1418, 1383,

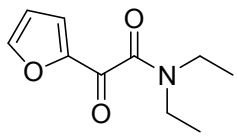
1364, 1235, 1184, 1145, 1057, 866, 785, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{22}NO_2$: $[M+H]^+$: 248.1651, found: 248.1655.



2-(4-bromophenyl)-*N,N*-dibutyl-2-oxoacetamide (4t): Purification by column chromatography on silica gel (R_f = 0.45, petroleum ether/ethyl acetate = 20:1) yielded **4t** (40.6 mg, 60%) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.80 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 3.49 (t, *J* = 7.6 Hz, 2H), 3.14 (t, *J* = 7.7 Hz, 2H), 1.69-1.62 (m, 2H), 1.57-1.49 (m, 2H), 1.41 (q, *J* = 7.5 Hz, 2H), 1.19 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.3, 166.5, 132.3, 132.2, 131.0, 129.9, 47.4, 44.1, 30.7, 29.4, 20.2, 19.8, 13.8, 13.6; IR(KBr): 2960, 2932, 2873, 1684, 1644, 1586, 1459, 1398, 1248, 1208, 1175, 1070, 1011, 944, 765 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{22}BrNNaO_2$: $[M+Na]^+$: 362.0732, found: 362.0731.

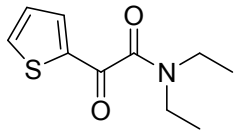


***N,N*-diethyl-2-(4-fluorophenyl)-2-oxoacetamide (4u):** Purification by column chromatography on silica gel (R_f = 0.32, petroleum ether/ethyl acetate = 8:1) yielded **4u** (13.5 mg, 31%) as a light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.98 (td, *J* = 5.4, 2.0 Hz, 2H), 7.18 (t, *J* = 8.6 Hz, 2H), 3.56 (q, *J* = 7.2 Hz, 2H), 3.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 189.9, 167.9, 166.4 (d, *J* = 110.0 Hz), 132.4 (d, *J* = 9.6 Hz), 129.8 (d, *J* = 2.7 Hz), 116.3 (d, *J* = 22.1 Hz), 42.2, 38.9, 14.2, 12.8; IR(KBr): 3447, 2979, 2925, 1682, 1643, 1599, 1508, 1462, 1235, 1145, 1099, 867, 786, 609 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{15}FNO_2$: $[M+H]^+$: 224.1087, found: 224.1086.

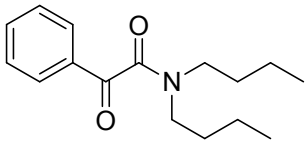


***N,N*-diethyl-2-(furan-2-yl)-2-oxoacetamide (4v):** Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4v** (16.8 mg, 43%) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: 7.70 (d, *J* = 1.0 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 6.60 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.52 (q, *J* = 7.2 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.8, 165.3, 150.3, 148.5, 122.0, 112.8, 42.3, 39.3, 14.2, 12.7; IR(KBr): 3442, 3128, 2979, 2934, 1644, 1568, 1460, 1392, 1262, 1038, 978, 836, 770 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{14}NO_3$: $[M+H]^+$: 196.0974, found:

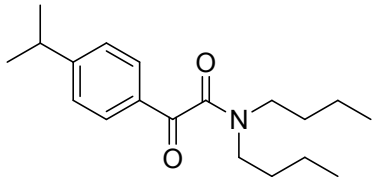
196.0964.



***N,N*-diethyl-2-oxo-2-(thiophen-2-yl)acetamide (4w):** Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 8:1) yielded **4w** (16.3 mg, 39%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.78 (d, *J* = 4.4 Hz, 2H), 7.18 (t, *J* = 4.4 Hz, 1H), 3.53 (q, *J* = 7.2 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 183.7, 165.7, 140.6, 136.1, 135.9, 128.6, 42.4, 39.3, 14.3, 12.7; IR(KBr): 3443, 2978, 2935, 1641, 1409, 1355, 1242, 1145, 1055, 830, 751, 631 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{14}NO_2S$: $[M+H]^+$: 212.0745, found: 212.0741.

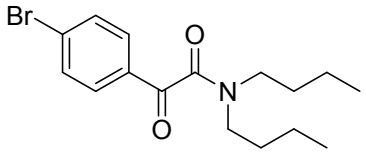


***N,N*-dibutyl-2-oxo-2-phenylacetamide (4x):** Purification by column chromatography on silica gel (R_f = 0.46, petroleum ether/ethyl acetate = 20:1) yielded **4x** (29.2 mg, 46%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.94-7.92 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 3.50 (t, *J* = 7.6 Hz, 2H), 3.15 (t, *J* = 7.7 Hz, 2H), 1.71-1.63 (m, 2H), 1.57-1.50 (m, 2H), 1.42 (q, *J* = 7.5 Hz, 2H), 1.18 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.6, 167.1, 134.5, 133.4, 129.6, 128.9, 47.4, 44.0, 30.6, 29.5, 20.2, 19.8, 13.8, 13.5; IR(KBr): 2960, 2932, 2873, 1682, 1643, 1597, 1449, 1378, 1316, 1247, 1210, 944, 724 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{24}NO_2$: $[M+H]^+$: 262.1807, found: 262.1801.

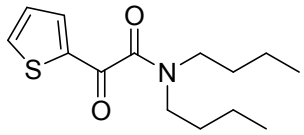


***N,N*-dibutyl-2-(4-isopropylphenyl)-2-oxoacetamide (4y):** Purification by column chromatography on silica gel (R_f = 0.26, petroleum ether/ethyl acetate = 10:1) yielded **4y** (26.8 mg, 44%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.88 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.51 (t, *J* = 7.6 Hz, 2H), 3.16 (t, *J* = 7.7 Hz, 2H), 3.04-2.97 (m, 1H), 1.73-1.65 (m, 2H), 1.60-1.53 (m, 2H), 1.44 (q, *J* = 7.6 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 6H), 1.21 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.4, 167.3, 156.3, 131.3, 129.9, 127.1, 47.4, 44.0, 34.5, 30.6, 29.5, 23.6, 20.3, 19.8, 13.9, 13.6; IR(KBr): 3454, 2961, 2932, 2873, 1679, 1642, 1605, 1462, 1250, 1213, 1182, 1057, 944, 780, 713 cm^{-1};

HRMS (ESI) calcd. for $C_{19}H_{30}NO_2$: $[M+H]^+$: 304.2277, found: 304.2277.



2-(4-bromophenyl)-*N,N*-diethyl-2-oxoacetamide (4z): Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 8:1) yielded **4z** (24.9 mg, 43%) as a light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.81 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.65 (dd, *J* = 6.9, 1.7 Hz, 2H), 3.55 (q, *J* = 7.2 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.3, 166.2, 132.4, 132.1, 131.0, 130.0, 42.1, 39.0, 14.2, 12.8; IR(KBr): 3424, 3062, 2977, 2931, 1678, 1583, 1438, 1340, 1296, 1232, 1214, 1175, 1070, 972, 868 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{15}BrNO_2$: $[M+H]^+$: 284.0286, found: 284.0280.



***N,N*-dibutyl-2-oxo-2-(thiophen-2-yl)acetamide (4a′):** Purification by column chromatography on silica gel (R_f = 0.36, petroleum ether/ethyl acetate = 8:1) yielded **4a′** (20.8 mg, 39%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 7.78-7.76 (m, 2H), 7.17 (dd, *J* = 4.6, 4.1 Hz, 1H), 3.47 (t, *J* = 7.6 Hz, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 1.68-1.61 (m, 2H), 1.60-1.52 (m, 2H), 1.40 (q, *J* = 7.5 Hz, 2H), 1.22 (q, *J* = 7.7 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 183.7, 166.0, 140.7, 136.0, 135.8, 128.5, 47.6, 44.4, 30.8, 29.4, 20.2, 19.8, 13.8, 13.6; IR(KBr): 2960, 2933, 2873, 1643, 1514, 1459, 1410, 1250, 1212, 1145, 1055, 932, 731, 671 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{22}NO_2S$: $[M+H]^+$: 268.1371, found: 268.1376.

6. Single-crystal X-ray structure of 3d

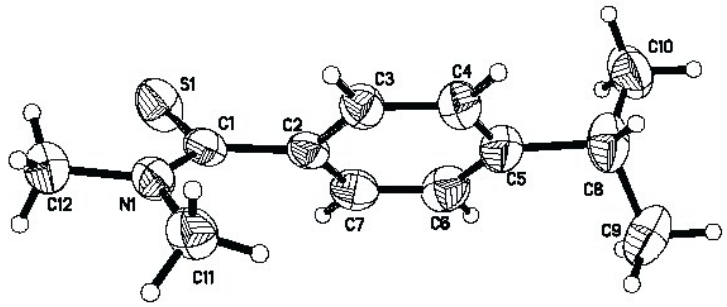


Figure S1. Single-crystal X-ray Structure of 4-Isopropyl-*N,N*-dimethylbenzothioamide **3d**

The structure of **3d** was determined by the X-ray diffraction. Compound **3d** was recrystallized from Dichloromethane/n-Hexane. Further information can be found in

the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1873946.

Table S1 Crystal data and structure refinement for 3d.

Identification code	201809391
Empirical formula	$C_{12}H_{17}NS$
Formula weight	207.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.3585(5)
b/Å	10.9450(11)
c/Å	17.5672(13)
α/°	90
β/°	92.051(7)
γ/°	90
Volume/Å^3	1221.78(18)
Z	4
ρ_{calc}g/cm^3	1.127
μ/mm^{-1}	2.041
F(000)	448.0
Crystal size/mm^3	0.17 × 0.1 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.522 to 134.052
Index ranges	$-5 \le h \le 7$, $-13 \le k \le 12$, $-20 \le l \le 20$
Reflections collected	4465
Independent reflections	2177 [R_{int}= 0.0282, R_{sigma}= 0.0369]
Data/restraints/parameters	2177/13/144
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1= 0.0566, wR_2= 0.1577
Final R indexes [all data]	R_1= 0.0760, wR_2= 0.1751
Largest diff. peak/hole / e Å^{-3}	0.20/-0.26

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 201809391. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	9542(4)	7170(3)	4814.2(14)	62.6(7)
C2	8769(4)	7985(2)	5421.4(14)	58.8(6)
C3	8768(4)	7617(3)	6174.8(15)	68.4(7)
C4	7945(5)	8340(3)	6728.5(17)	80.9(8)

C5	7115(5)	9472(3)	6561(2)	87.3(9)
C6	7107(5)	9839(3)	5815(2)	86.6(8)
C7	7893(5)	9114(3)	5248.7(17)	74.8(8)
C8	6303(10)	10181(5)	7257(3)	89.9(15)
C8A	5980(20)	10546(12)	6919(7)	89.9(15)
C9	7010(16)	11527(7)	7225(5)	118(2)
C9A	7660(40)	11045(16)	7438(12)	118(2)
C10	3860(20)	10109(13)	7225(6)	113(3)
C10A	4490(50)	9940(30)	7479(15)	113(3)
C11	13052(4)	7097(3)	5456.7(19)	82.1(9)
C12	12223(5)	5831(4)	4332(2)	91.4(10)
N1	11473(3)	6725(2)	4879.2(13)	66.8(6)
S1	7884.2(13)	6843.1(11)	4079.5(4)	98.0(4)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 201809391. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	56.0(14)	74.5(16)	57.7(13)	3.1(12)	7.9(10)	-12.1(12)
C2	47.4(11)	67.7(15)	61.5(13)	1.9(11)	3.0(9)	-8.6(11)
C3	74.3(16)	70.0(16)	61.2(14)	3.3(12)	4.8(12)	-0.1(13)
C4	96(2)	81(2)	67.1(16)	-5.7(15)	16.3(14)	-4.2(17)
C5	83.9(19)	82(2)	97.4(17)	-20.4(15)	17.9(16)	-3.3(16)
C6	80.1(19)	67.7(17)	111.8(18)	0.4(16)	1.0(17)	8.7(15)
C7	68.3(16)	78.6(19)	77.2(17)	14.0(15)	-1.2(13)	-4.4(14)
C8	133(4)	80(3)	57(3)	5(2)	1(3)	33(3)
C8A	133(4)	80(3)	57(3)	5(2)	1(3)	33(3)
C9	152(7)	88(5)	112(6)	-34(4)	-11(4)	3(4)
C9A	152(7)	88(5)	112(6)	-34(4)	-11(4)	3(4)
C10	141(10)	94(5)	108(8)	3(5)	57(6)	20(5)
C10A	141(10)	94(5)	108(8)	3(5)	57(6)	20(5)
C11	55.7(14)	104(2)	86.2(19)	-7.0(17)	-1.1(13)	0.6(15)
C12	85(2)	90(2)	101(2)	-17.5(19)	22.1(17)	0.3(17)
N1	58.6(12)	74.5(14)	67.9(13)	-5.0(11)	8.9(9)	-3.9(11)
S1	74.6(5)	154.6(10)	64.3(5)	-21.9(5)	-3.8(3)	-12.2(5)

Table S4 Bond Lengths for 201809391.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.488(4)	C5	C8A	1.526(12)
C1	N1	1.321(4)	C6	C7	1.380(4)

C1	S1	1.676(3)	C8	C9	1.541(11)
C2	C3	1.384(4)	C8	C10	1.553(16)
C2	C7	1.385(4)	C8A	C9A	1.48(2)
C3	C4	1.372(4)	C8A	C10A	1.54(3)
C4	C5	1.374(5)	C11	N1	1.459(4)
C5	C6	1.371(5)	C12	N1	1.463(4)
C5	C8	1.553(6)			

Table S5 Bond Angles for 201809391.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	S1	117.72(19)	C6	C5	C8A	100.6(6)
N1	C1	C2	119.3(2)	C5	C6	C7	122.1(3)
N1	C1	S1	123.0(2)	C6	C7	C2	120.6(3)
C3	C2	C1	121.5(2)	C5	C8	C10	107.8(6)
C3	C2	C7	117.1(3)	C9	C8	C5	110.1(5)
C7	C2	C1	121.3(2)	C9	C8	C10	109.9(7)
C4	C3	C2	121.5(3)	C5	C8A	C10A	103.9(15)
C3	C4	C5	121.4(3)	C9A	C8A	C5	101.4(11)
C4	C5	C8	114.7(4)	C9A	C8A	C10A	102.3(18)
C4	C5	C8A	142.1(6)	C1	N1	C11	124.8(2)
C6	C5	C4	117.2(3)	C1	N1	C12	120.9(3)
C6	C5	C8	128.1(4)	C11	N1	C12	114.3(2)

Table S6 Torsion Angles for 201809391.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-176.3(3)	C5	C6	C7	C2	-1.3(5)
C1	C2	C7	C6	177.4(3)	C6	C5	C8	C9	-43.6(7)
C2	C1	N1	C11	-8.7(4)	C6	C5	C8	C10	76.3(7)
C2	C1	N1	C12	174.2(3)	C6	C5	C8A	C9A	-115.9(12)
C2	C3	C4	C5	-1.0(5)	C6	C5	C8A	C10A	138.1(13)
C3	C2	C7	C6	1.5(4)	C7	C2	C3	C4	-0.4(4)
C3	C4	C5	C6	1.2(5)	C8	C5	C6	C7	179.7(4)
C3	C4	C5	C8	-178.6(4)	C8A	C5	C6	C7	-176.8(6)
C3	C4	C5	C8A	176.0(9)	N1	C1	C2	C3	-56.3(3)
C4	C5	C6	C7	0.0(5)	N1	C1	C2	C7	128.0(3)
C4	C5	C8	C9	136.1(5)	S1	C1	C2	C3	122.9(2)
C4	C5	C8	C10	-104.0(6)	S1	C1	C2	C7	-52.9(3)
C4	C5	C8A	C9A	68.8(16)	S1	C1	N1	C11	172.2(2)
C4	C5	C8A	C10A	-37.1(18)	S1	C1	N1	C12	-4.9(4)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 201809391.

Atom	*x*	*y*	*z*	U(eq)
H3	9337	6861	6309	82
H4	7950	8059	7228	97
H6	6553	10601	5686	104
H7	7834	9386	4747	90
H8	6856	9805	7729	108
H8A	5156	11084	6593	108
H9A	8518	11564	7224	177
H9B	6520	11955	7661	177
H9C	6431	11899	6769	177
H9AA	8234	10401	7754	177
H9AB	7085	11668	7753	177
H9AC	8760	11389	7143	177
H10A	3329	10432	6748	170
H10B	3316	10577	7636	170
H10C	3432	9272	7272	170
H10D	3267	9635	7203	170
H10E	4074	10525	7849	170
H10F	5204	9269	7732	170
H11A	12606	7836	5696	123
H11B	14370	7234	5221	123
H11C	13219	6464	5833	123
H12A	11053	5366	4128	137
H12B	13216	5293	4583	137
H12C	12891	6250	3925	137

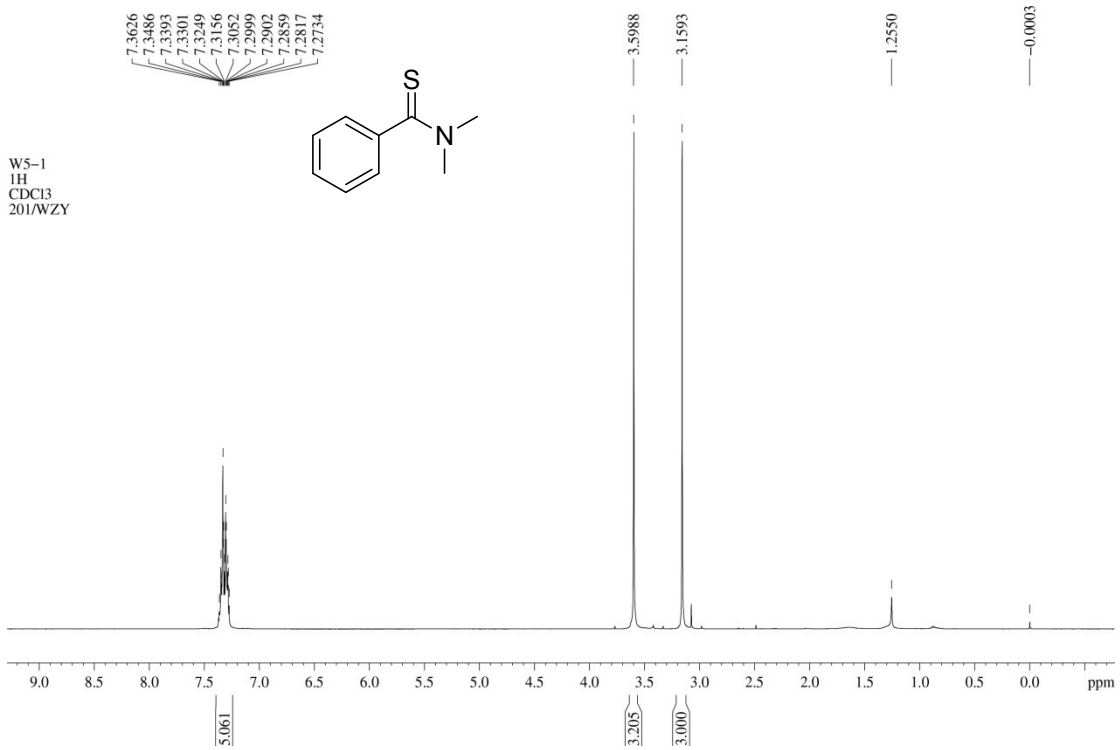
Table S8 Atomic Occupancy for 201809391.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C8	0.677(7)	H8	0.677(7)	C8A	0.323(7)
H8A	0.323(7)	C9	0.677(7)	H9A	0.677(7)
H9B	0.677(7)	H9C	0.677(7)	C9A	0.323(7)
H9AA	0.323(7)	H9AB	0.323(7)	H9AC	0.323(7)
C10	0.677(7)	H10A	0.677(7)	H10B	0.677(7)
H10C	0.677(7)	C10A	0.323(7)	H10D	0.323(7)
H10E	0.323(7)	H10F	0.323(7)		

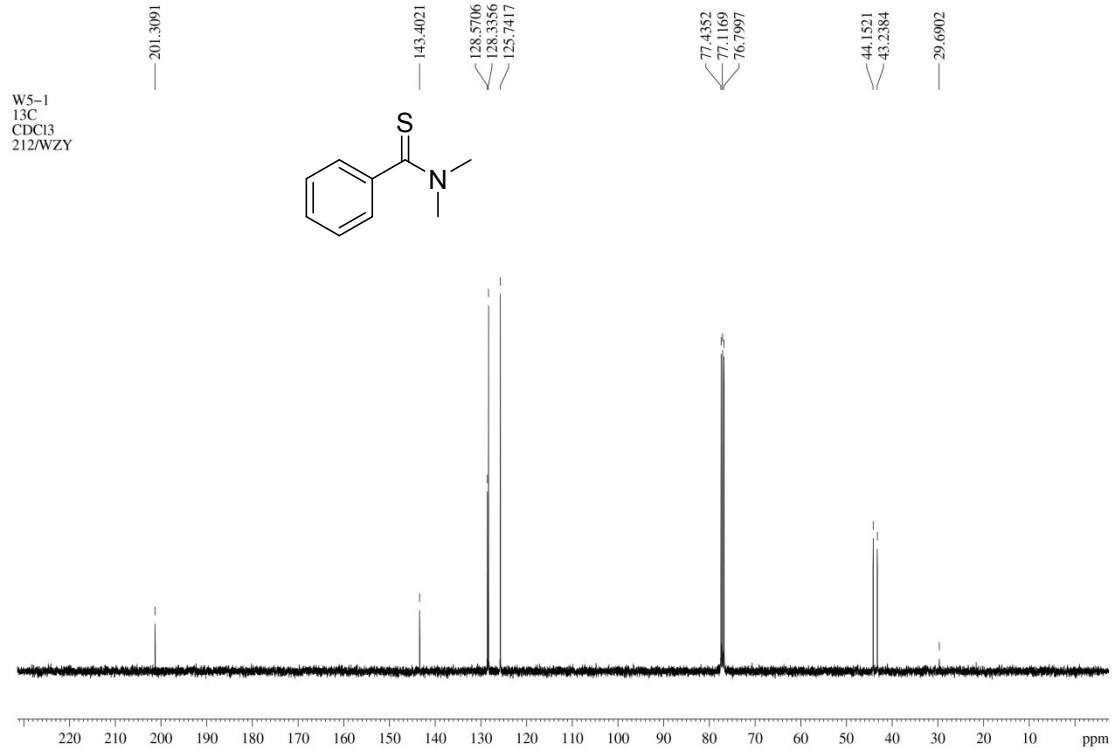
Crystal structure determination of 3d: Crystal Data for $C_{12}H_{17}NS$ (*M* =207.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a*= 6.3585(5) Å, *b* = 10.9450(11) Å, *c*

= 17.5672(13) Å, β = 92.051(7)°, V= 1221.78(18)Å^3, Z = 4, T = 293(2) K, μ(CuKα) = 2.041 mm^{-1}, *Dcalc* = 1.127 g/cm^3, 4465 reflections measured (9.522° ≤ 2Θ ≤ 134.052°), 2177 unique (R_{int} = 0.0282, R_{sigma} = 0.0369) which were used in all calculations. The final R_1 was 0.0566 (I > 2σ(I)) and wR_2 was 0.1751 (all data).

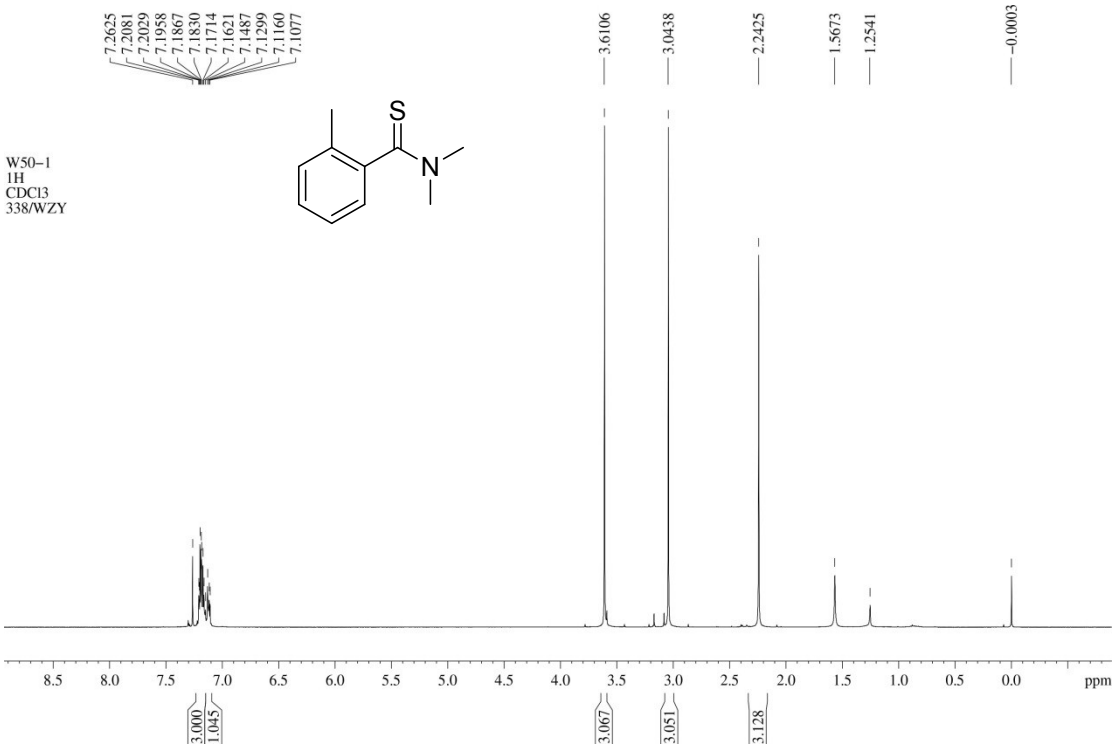
7. Copies of ^{1}H NMR and ^{13}C NMR spectra



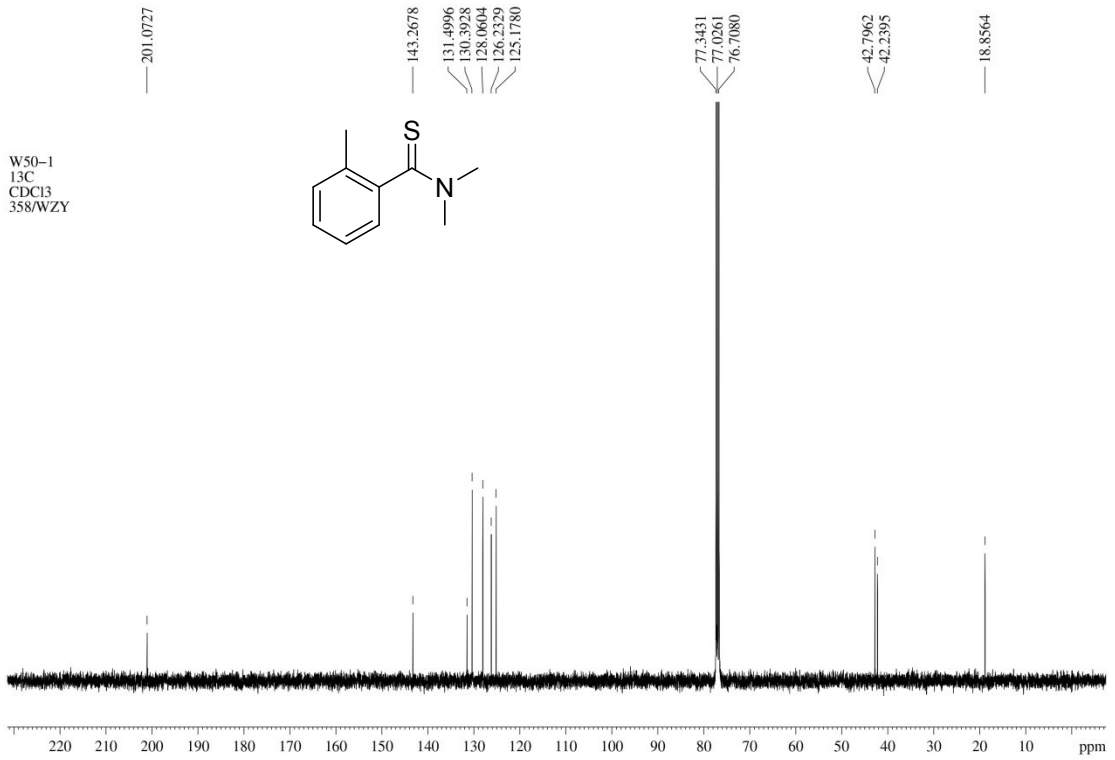
^{1}H NMR spectrum of compound **3a**



^{13}C NMR spectrum of compound **3a**

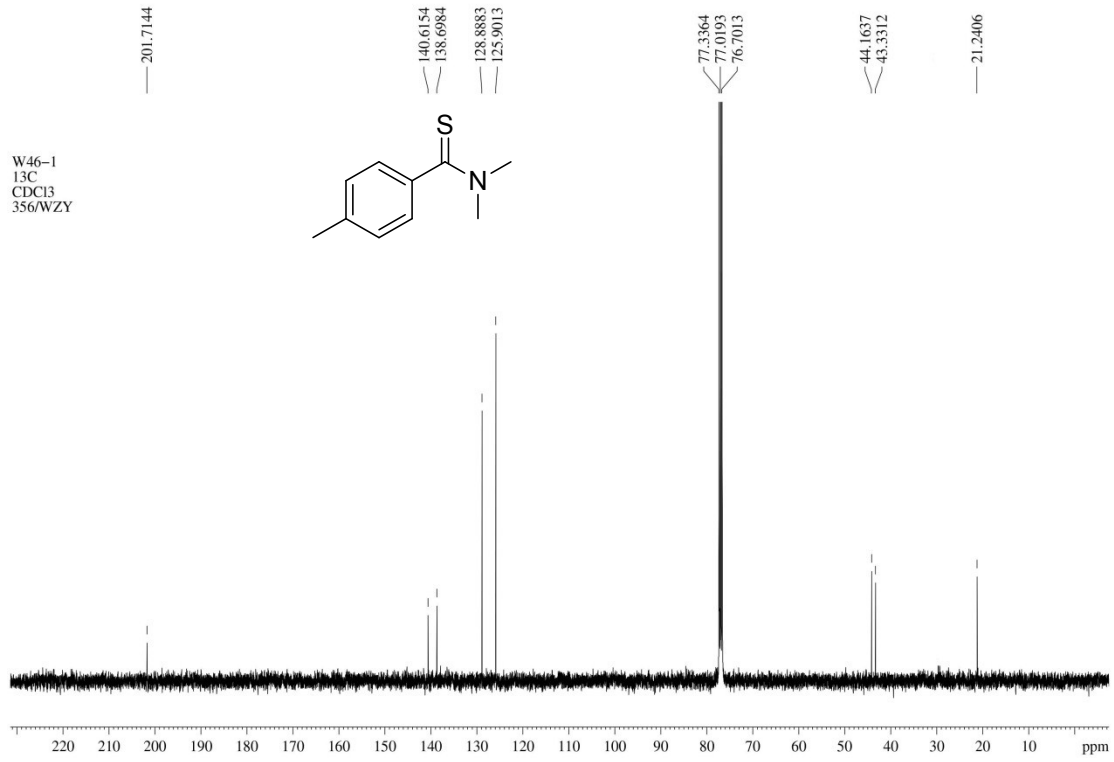


^{1}H NMR spectrum of compound **3b**

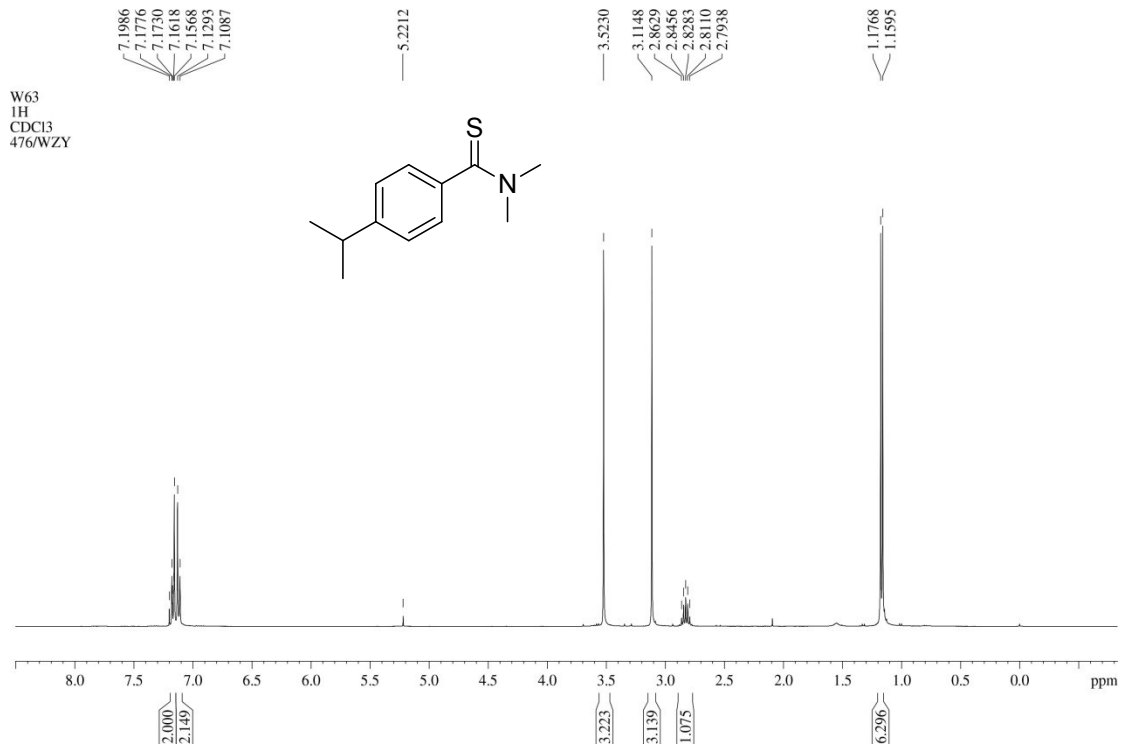


^{13}C NMR spectrum of compound **3b**

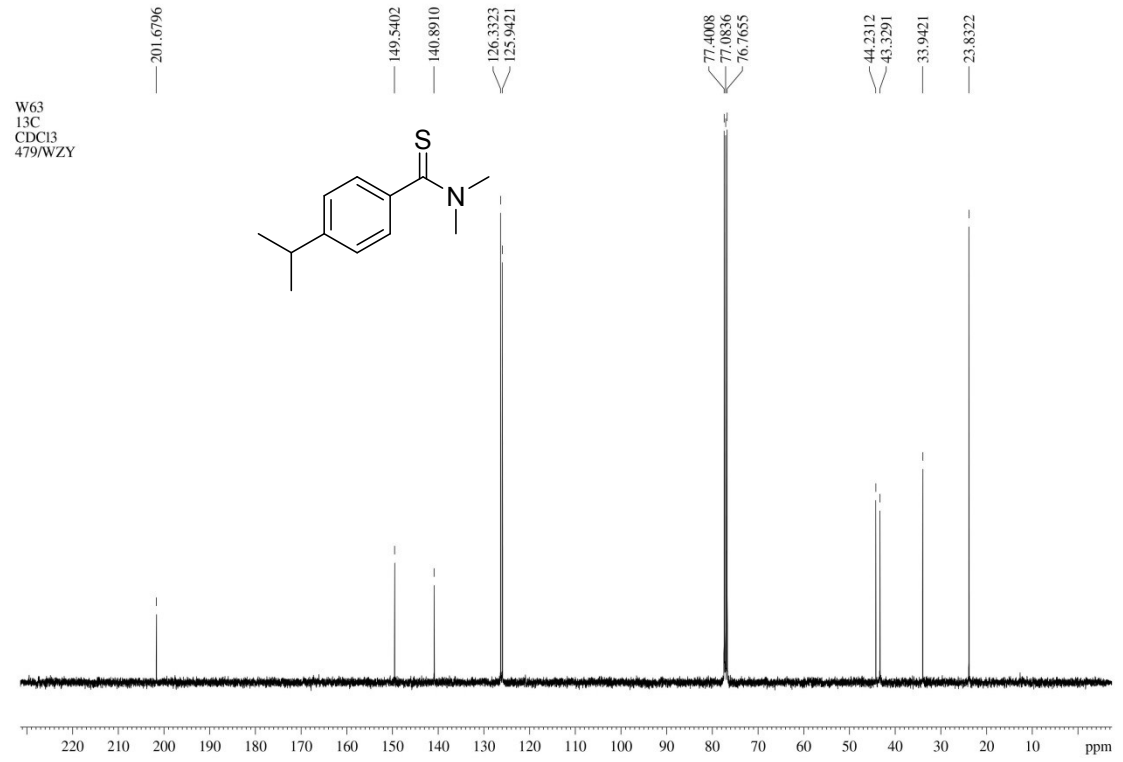
^{1}H NMR spectrum of compound **3c**



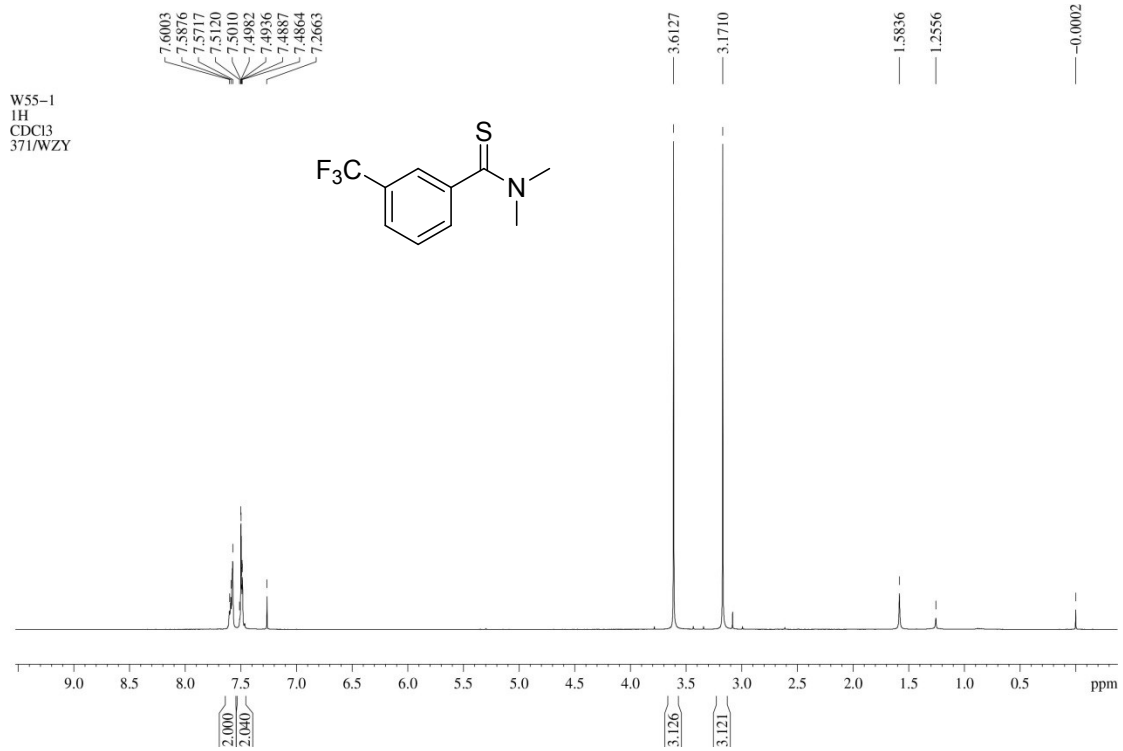
^{13}C NMR spectrum of compound **3c**



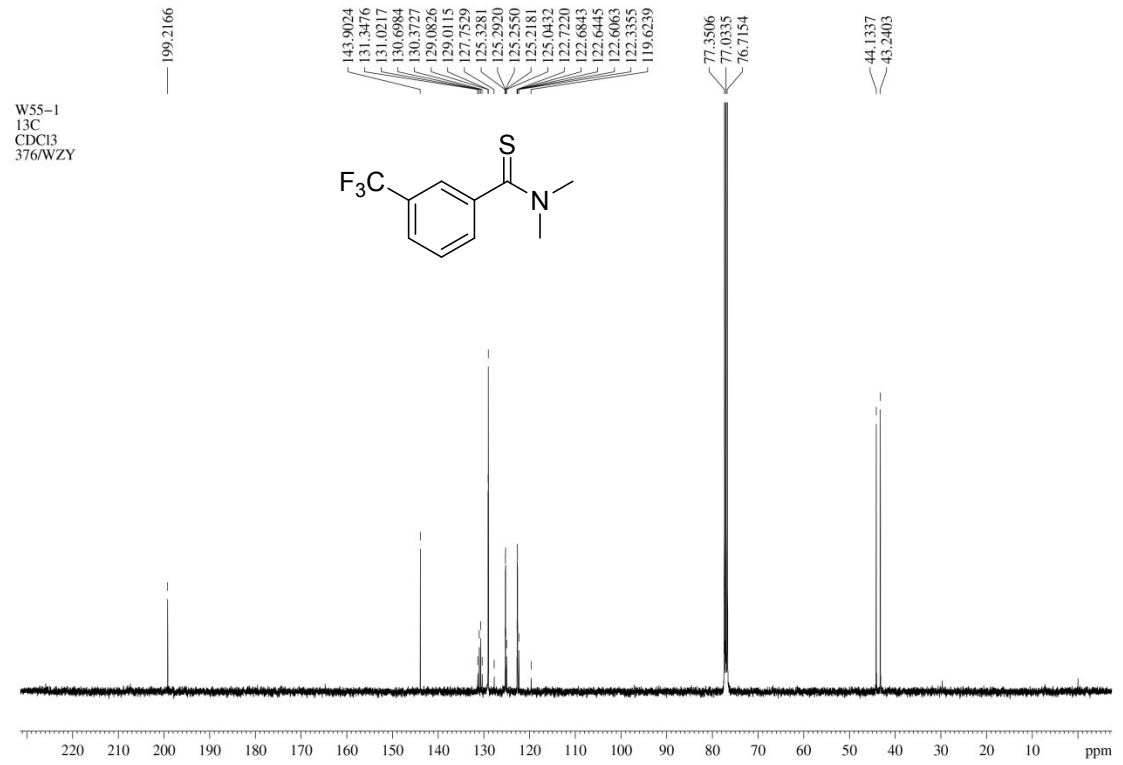
^{1}H NMR spectrum of compound **3d**



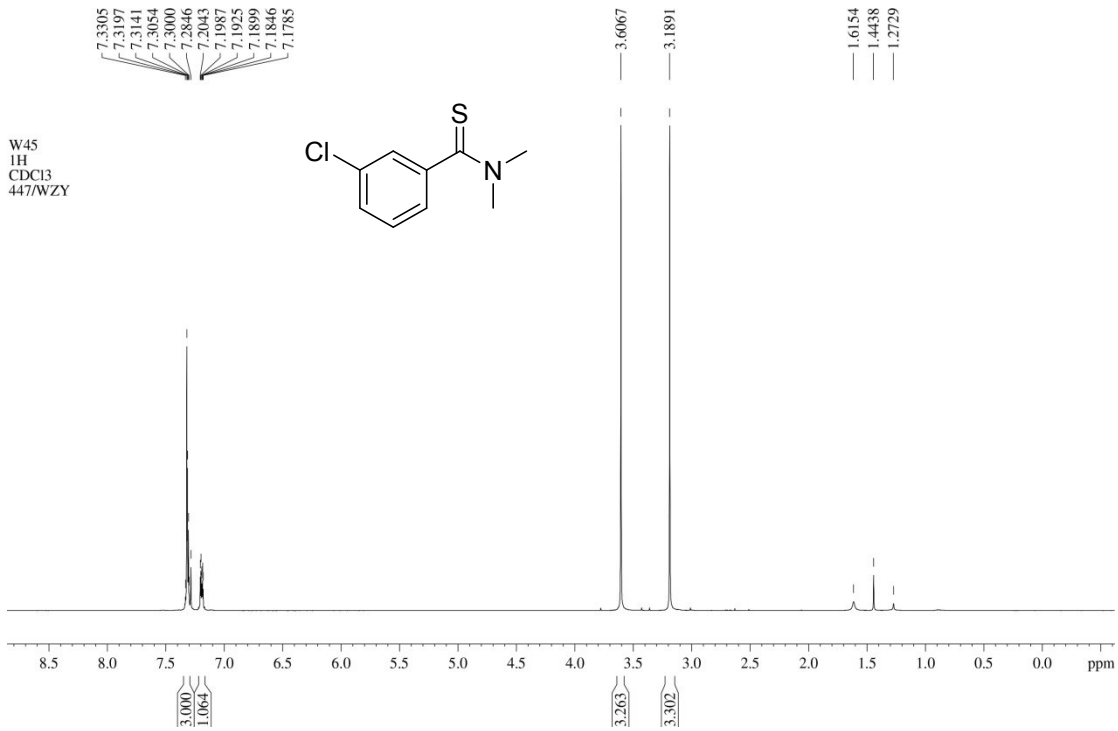
^{13}C NMR spectrum of compound **3d**



^{1}H NMR spectrum of compound **3e**



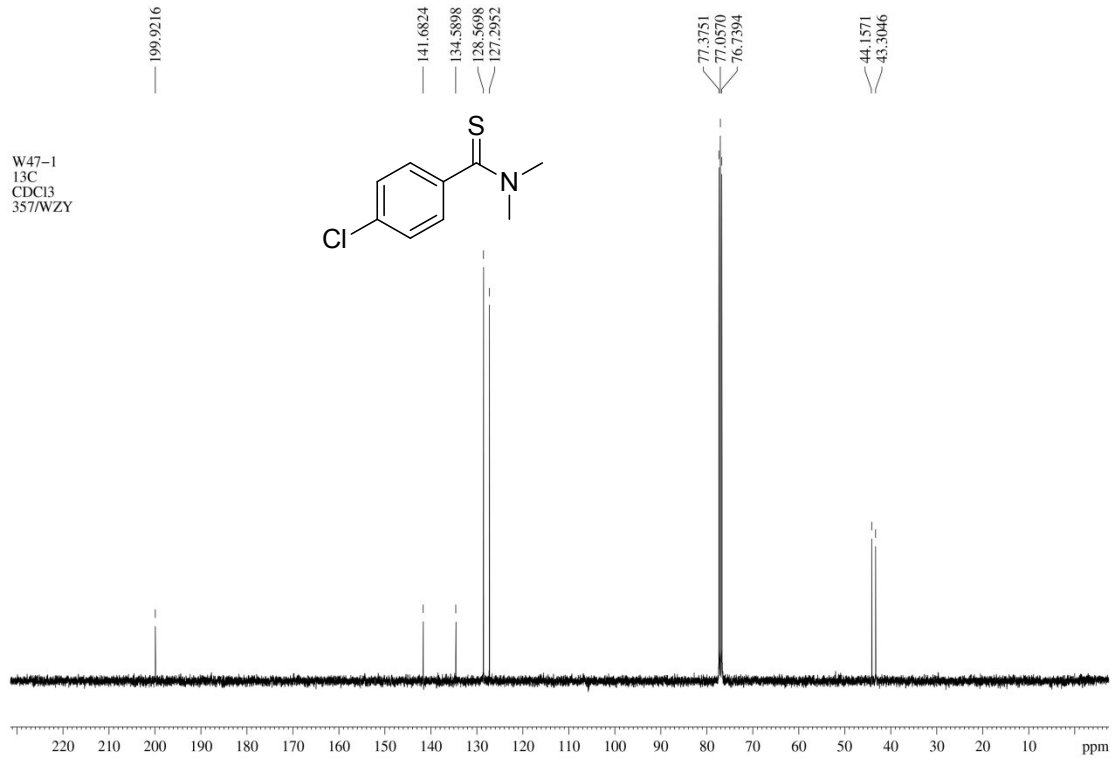
^{13}C NMR spectrum of compound **3e**



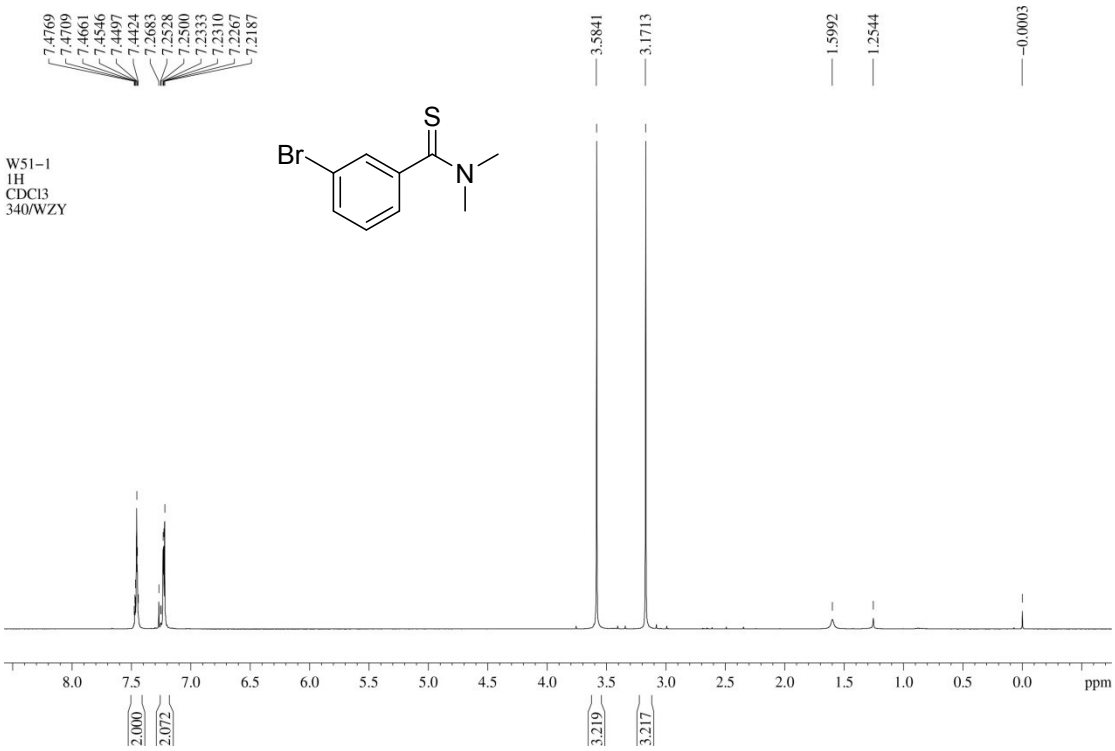
^{1}H NMR spectrum of compound **3f**

^{13}C NMR spectrum of compound **3f**

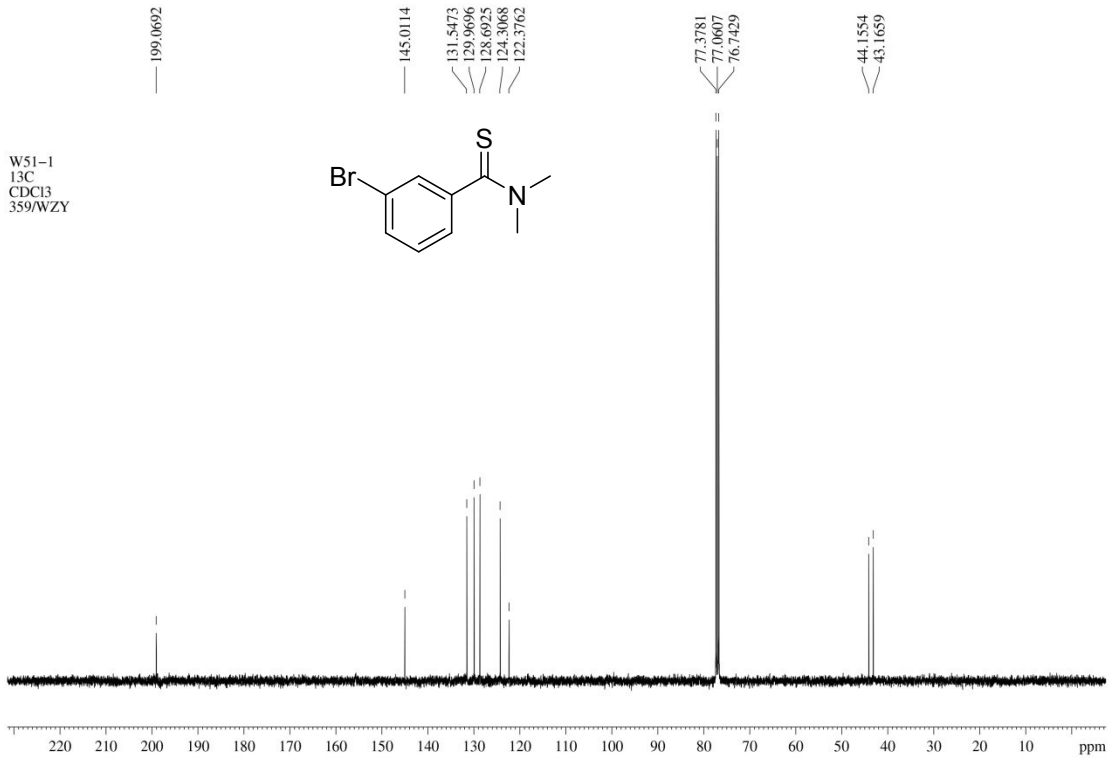
^{1}H NMR spectrum of compound **3g**



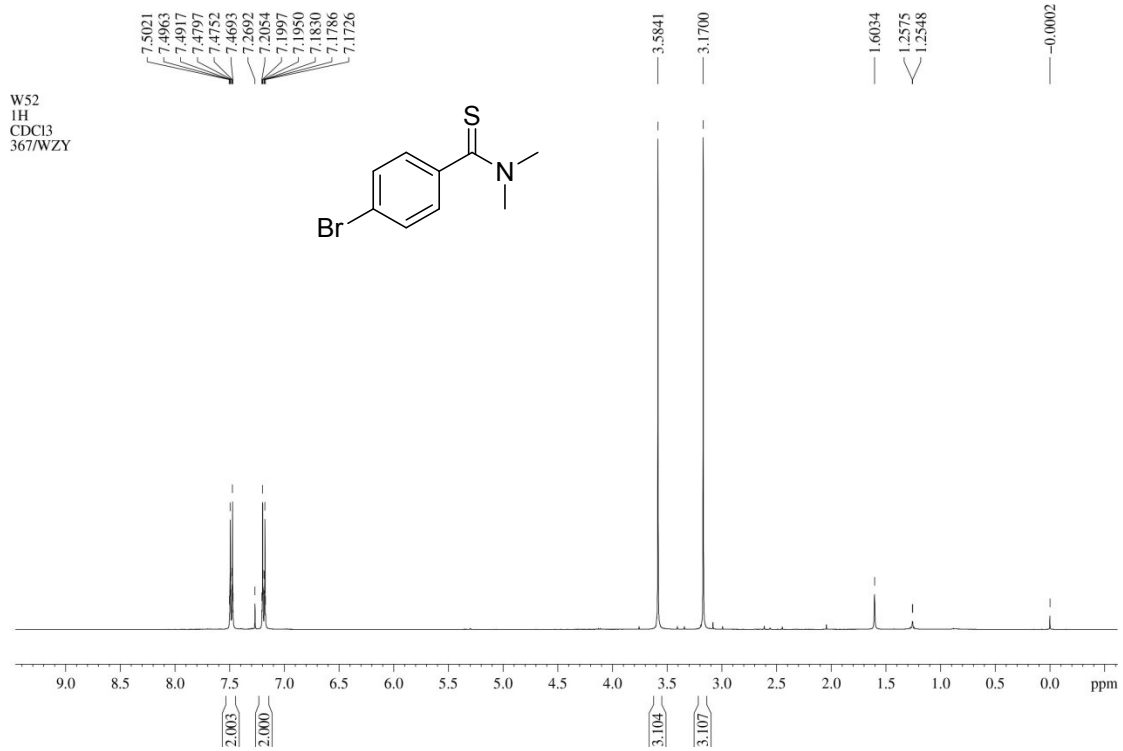
^{13}C NMR spectrum of compound **3g**



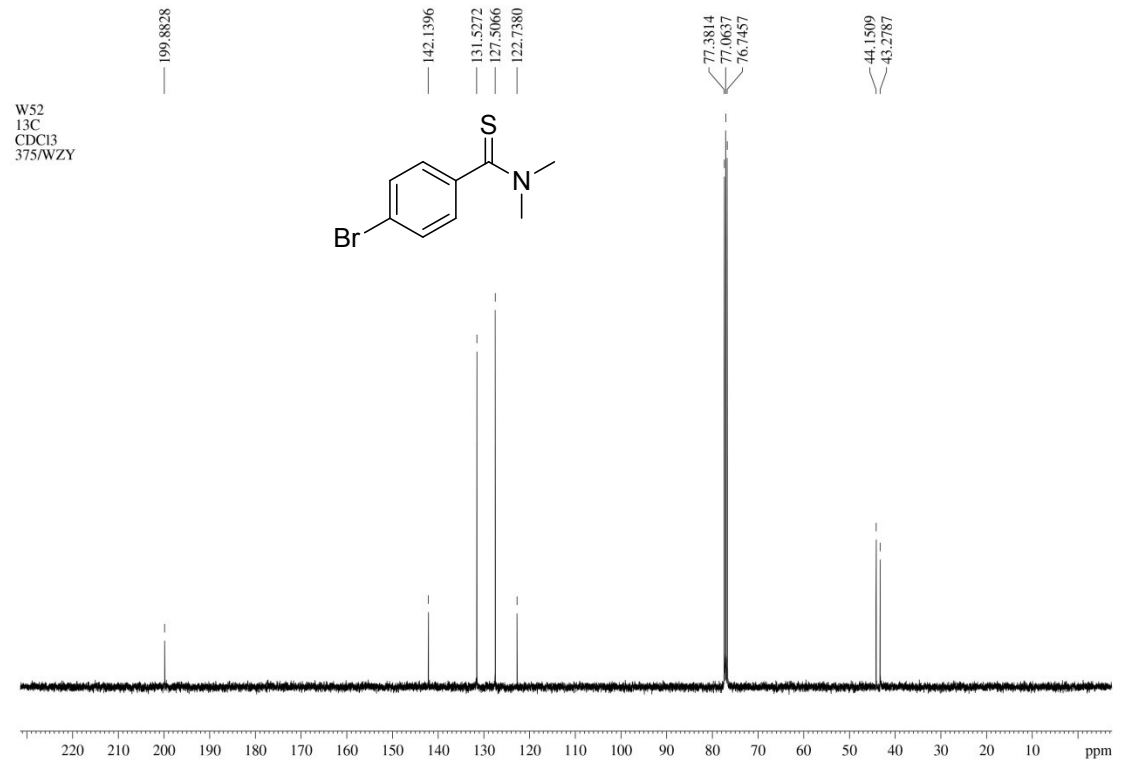
^{1}H NMR spectrum of compound **3h**



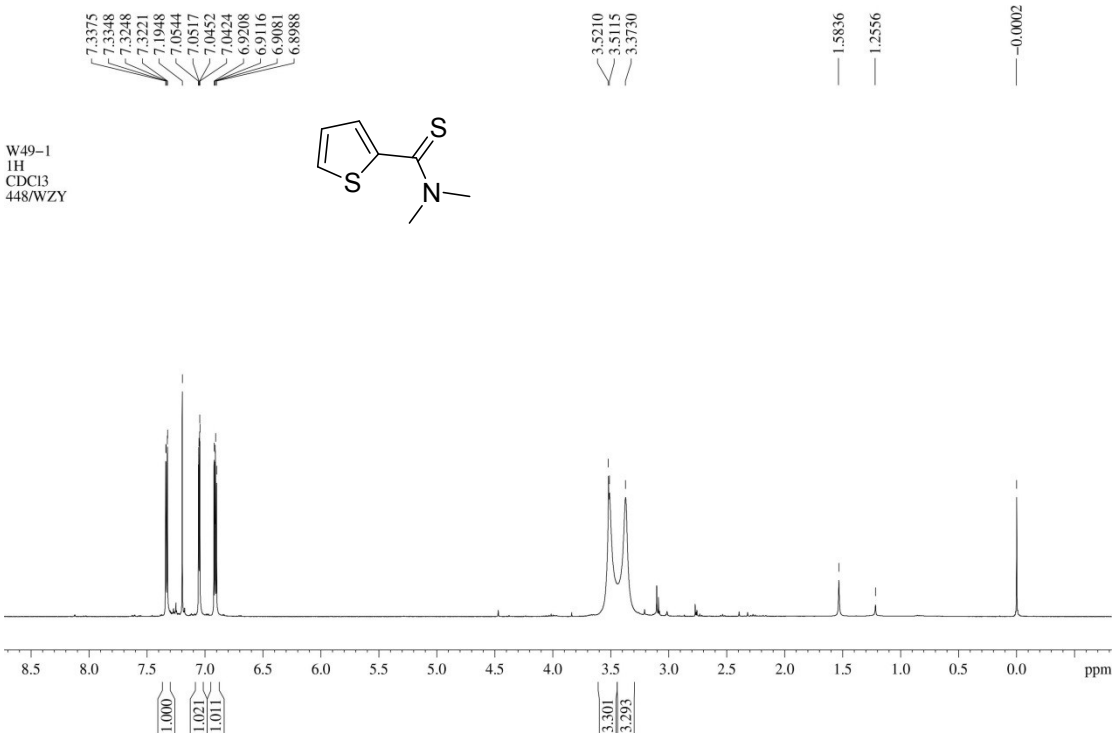
^{13}C NMR spectrum of compound **3h**



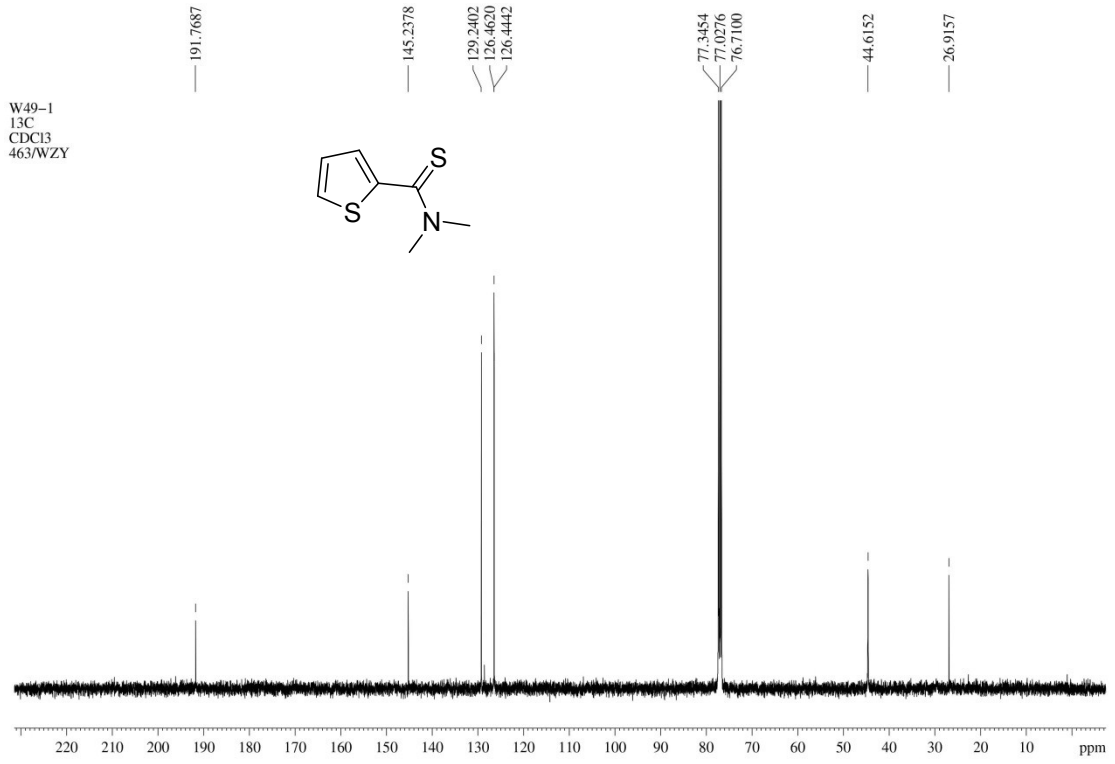
^{1}H NMR spectrum of compound **3i**



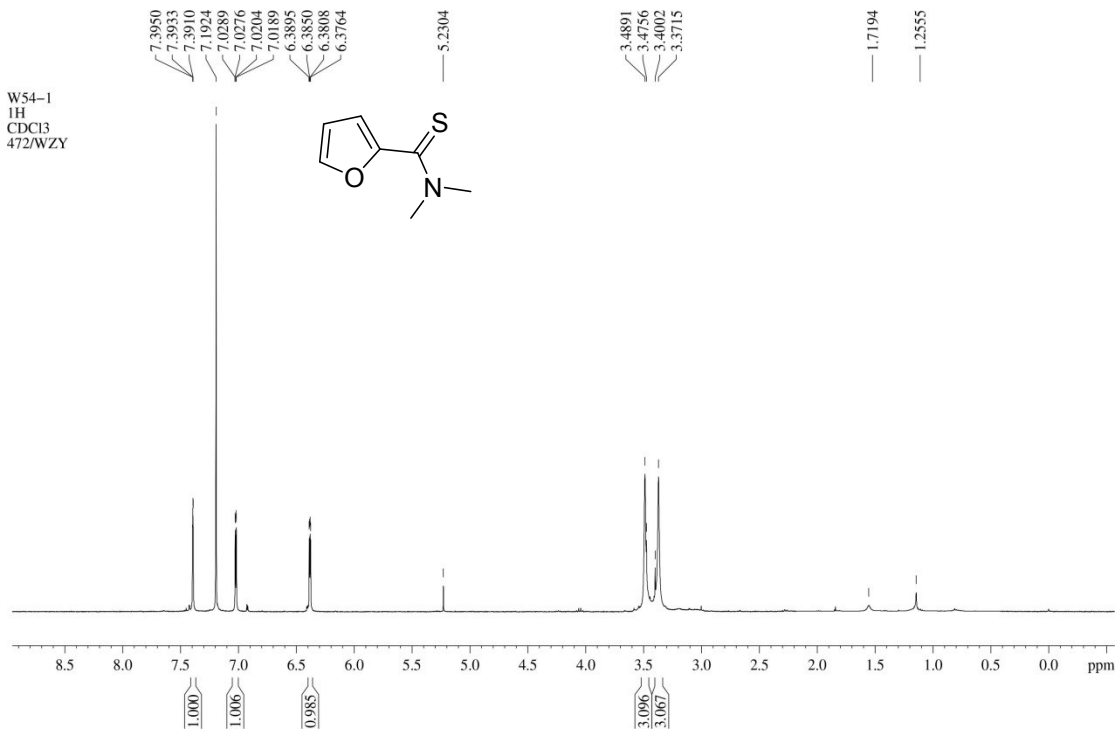
^{13}C NMR spectrum of compound **3i**



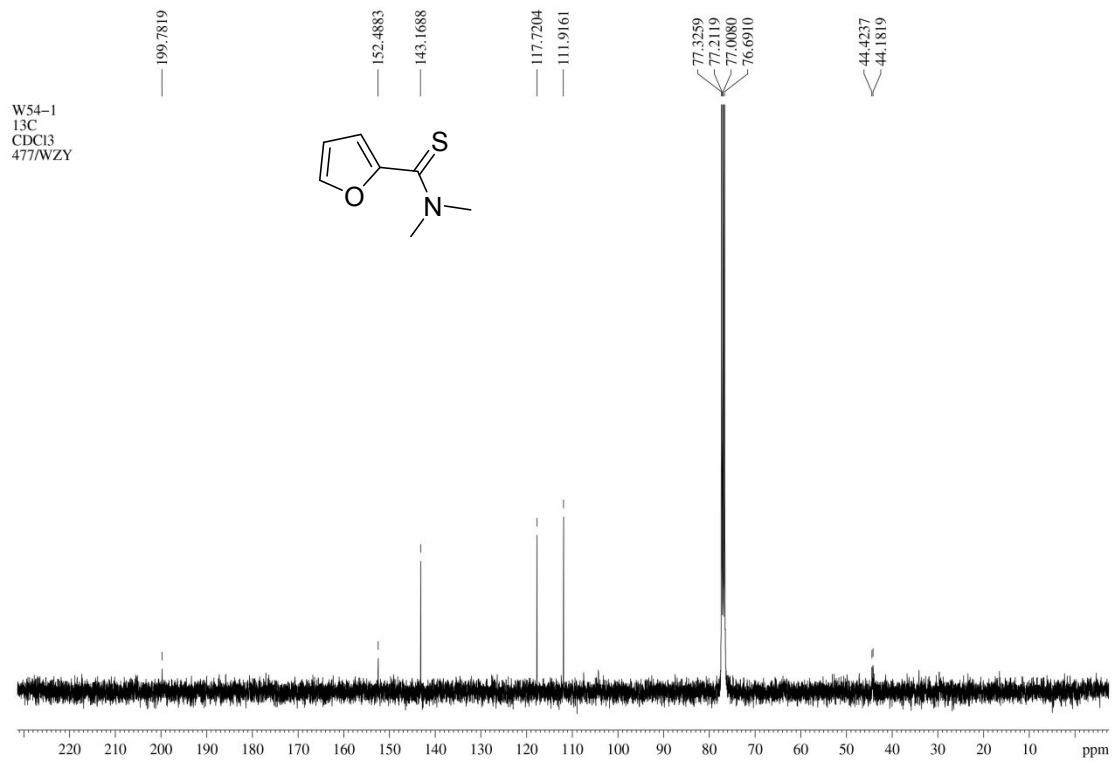
^{1}H NMR spectrum of compound **3j**



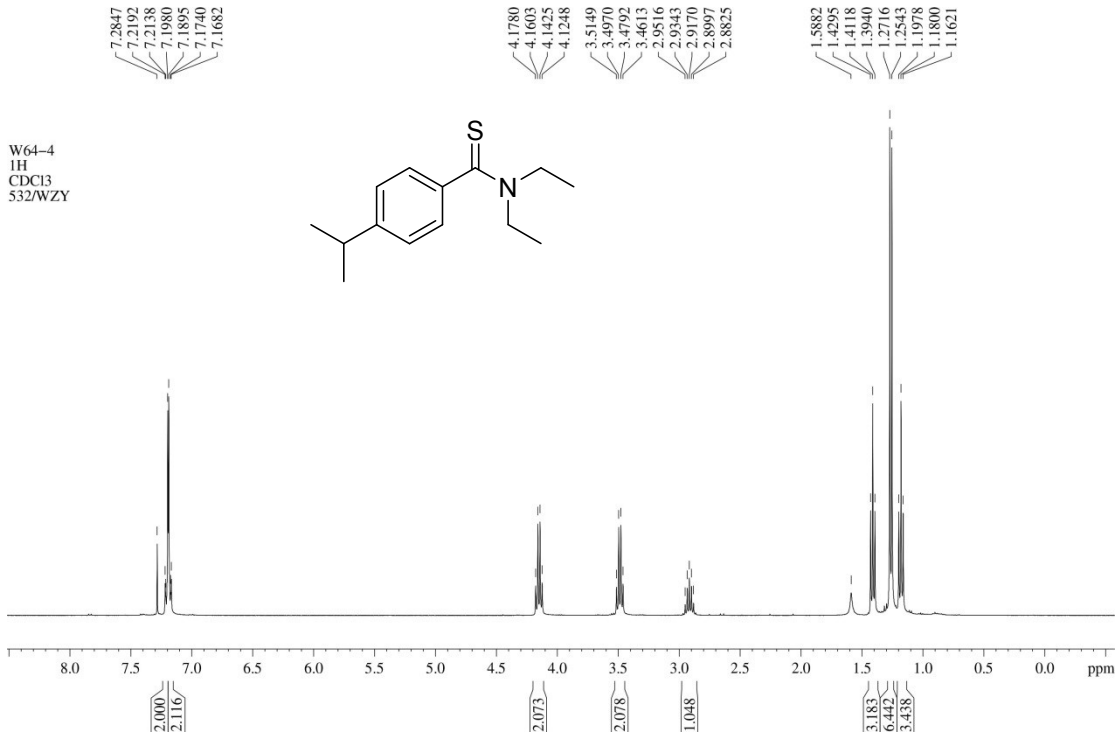
^{13}C NMR spectrum of compound **3j**



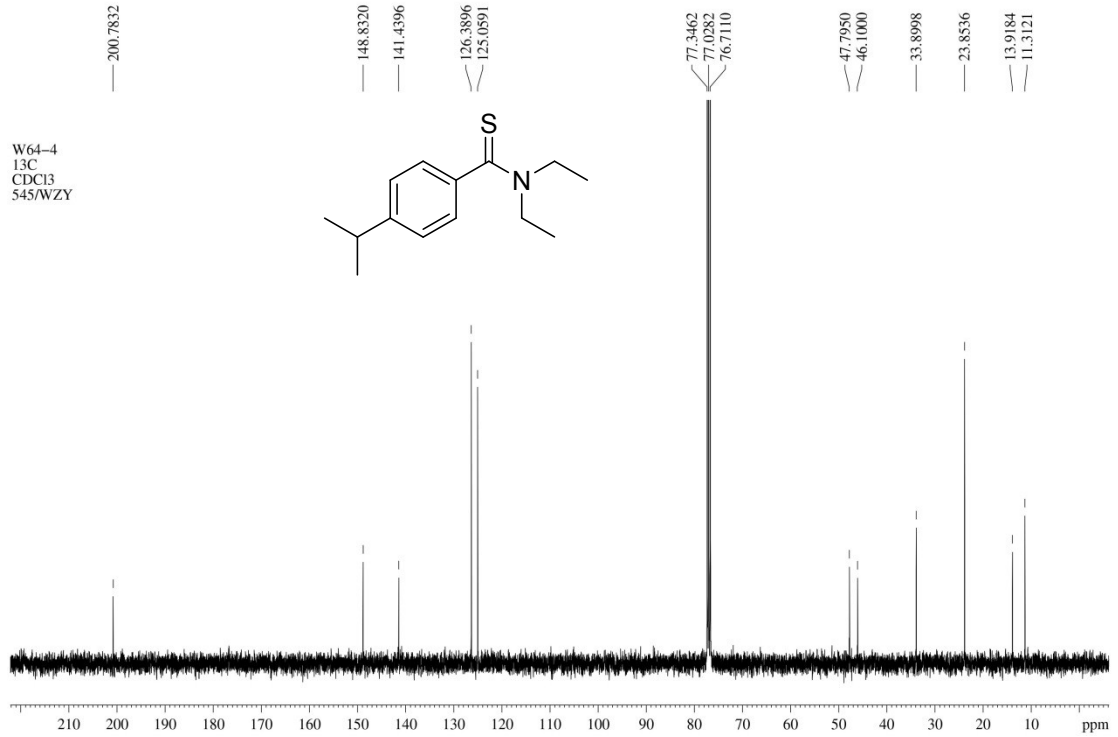
^{1}H NMR spectrum of compound **3k**



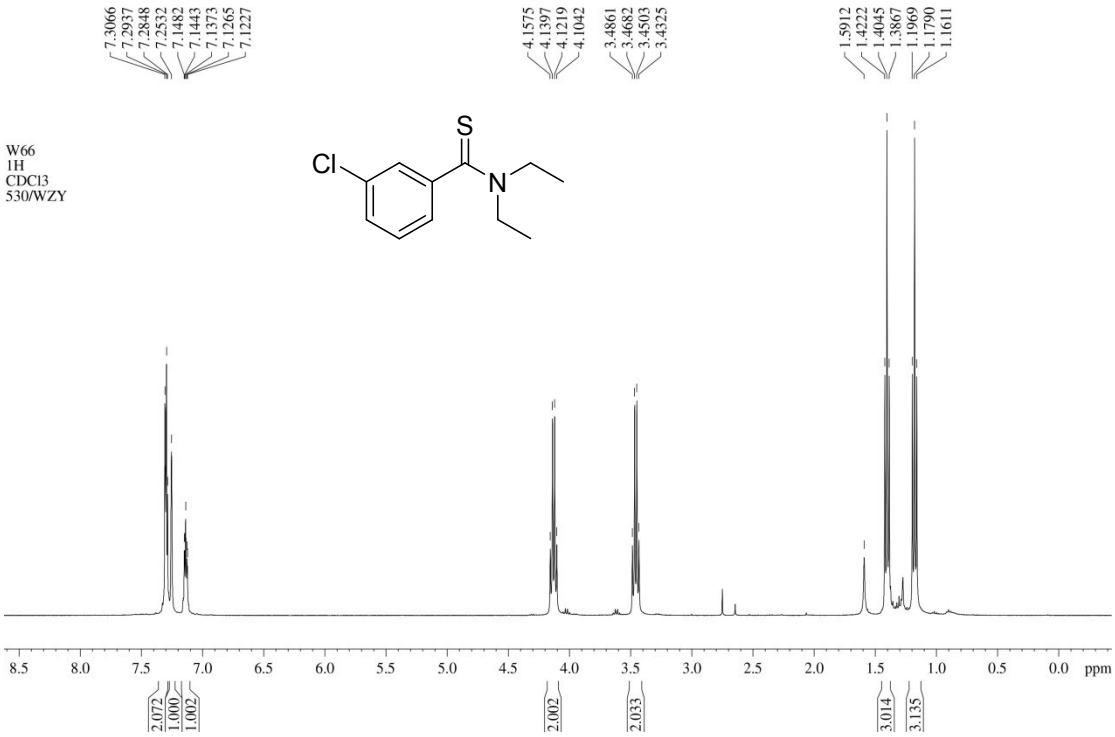
^{13}C NMR spectrum of compound **3k**



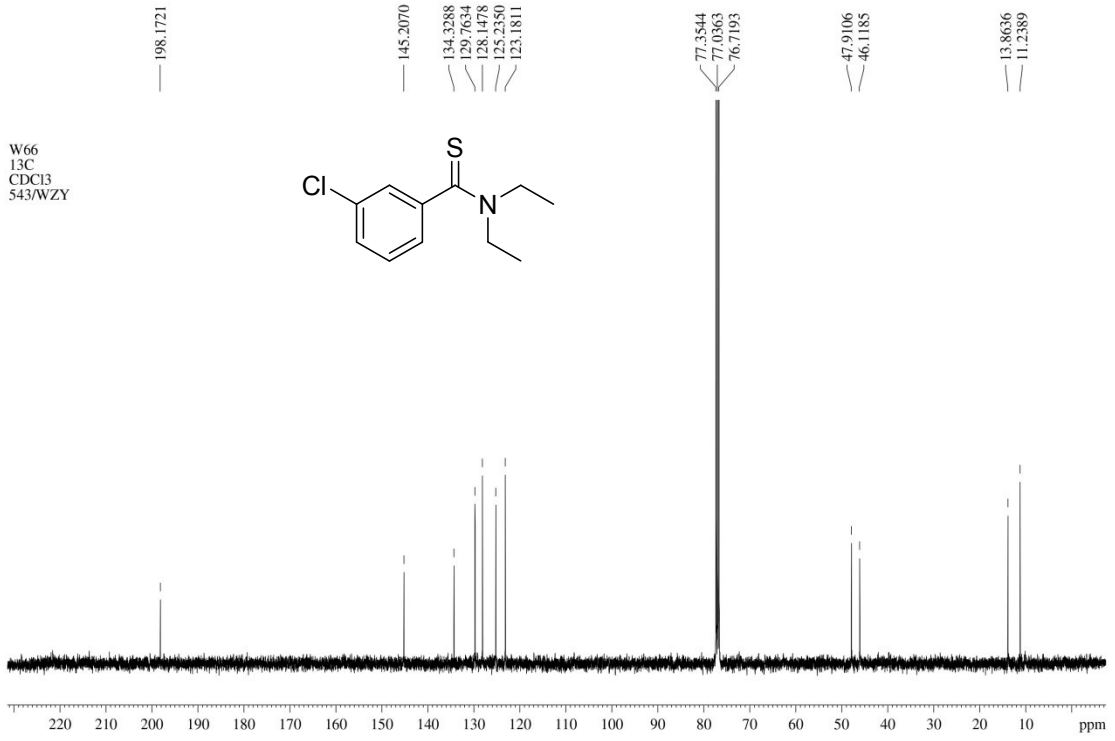
^{1}H NMR spectrum of compound **3l**



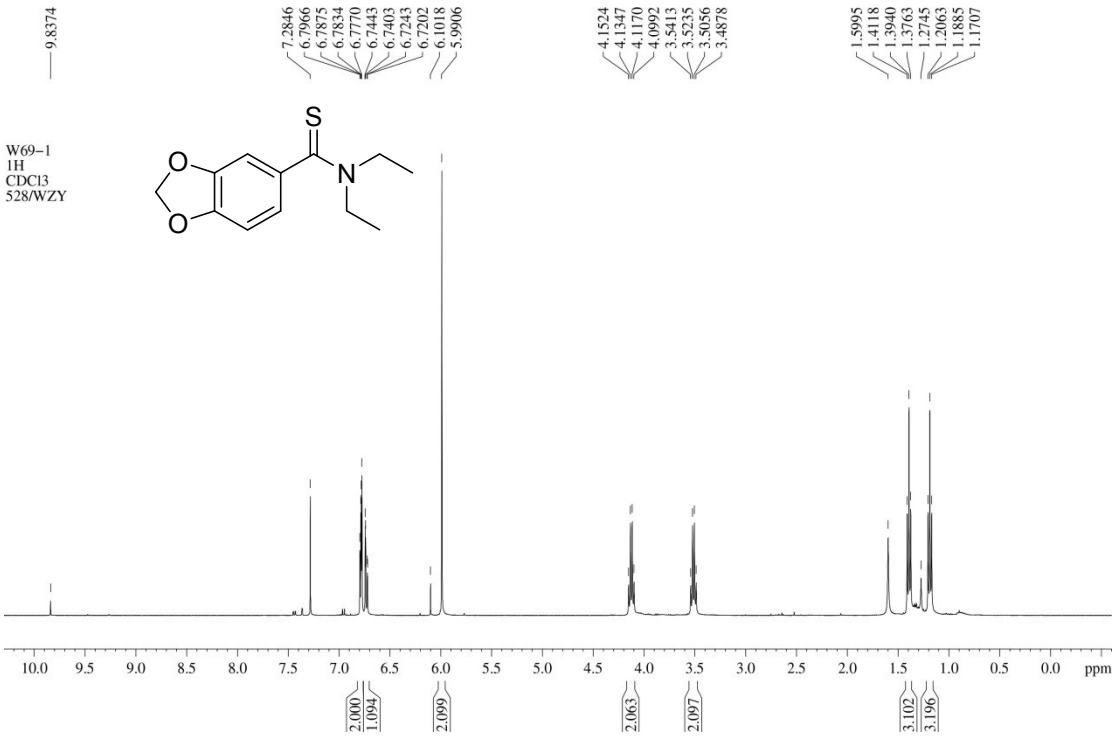
^{13}C NMR spectrum of compound **3l**



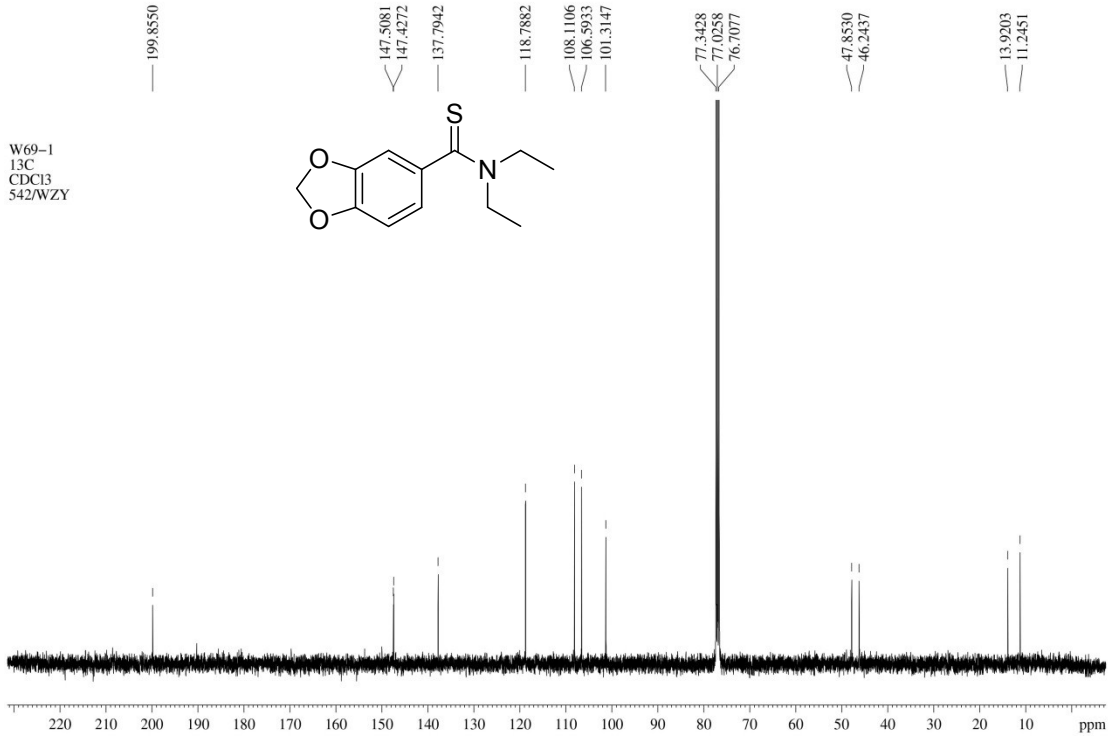
^{1}H NMR spectrum of compound **3m**



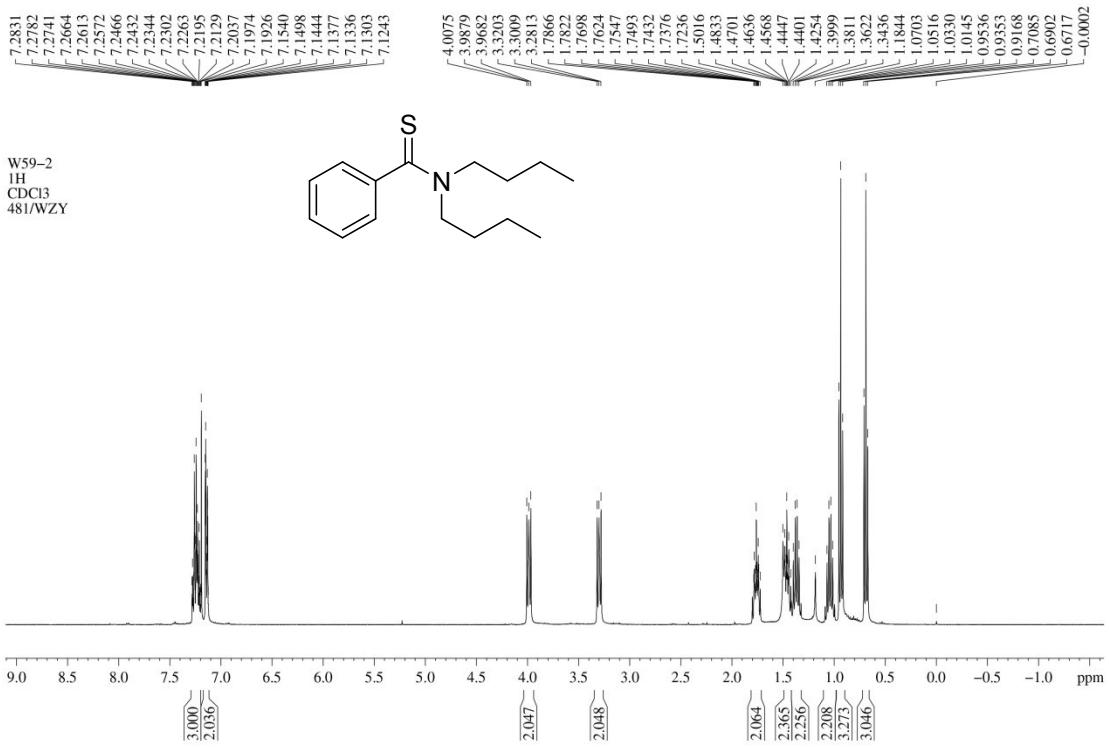
^{13}C NMR spectrum of compound **3m**



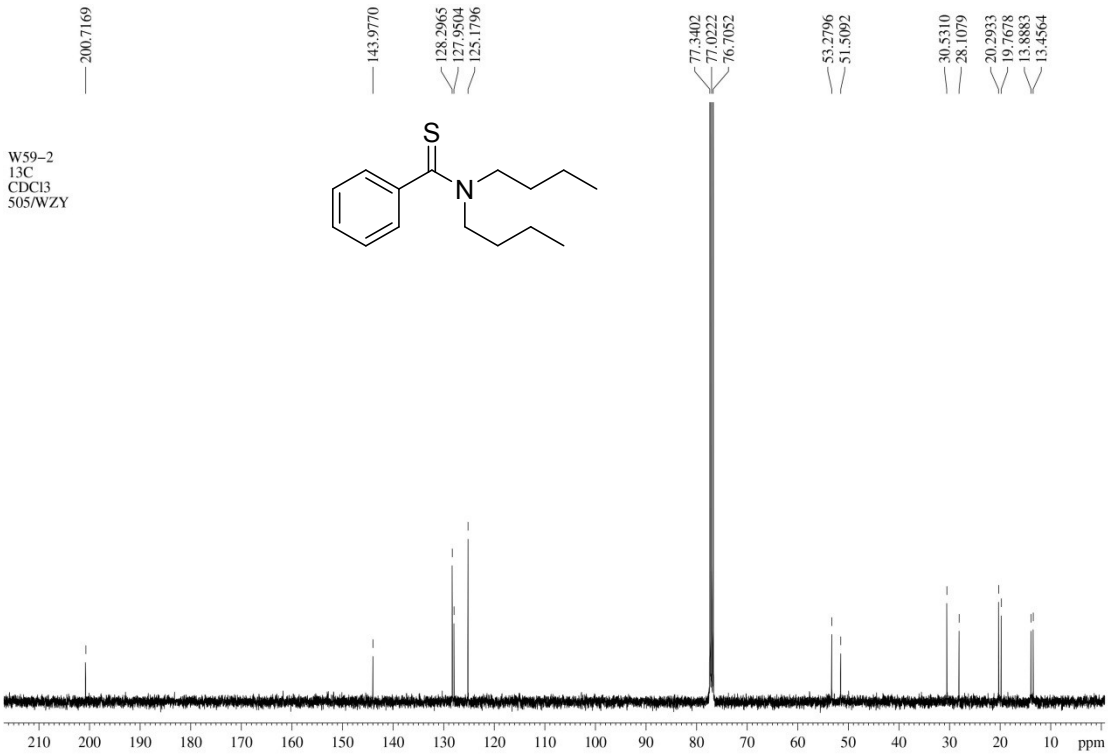
^{1}H NMR spectrum of compound **3n**



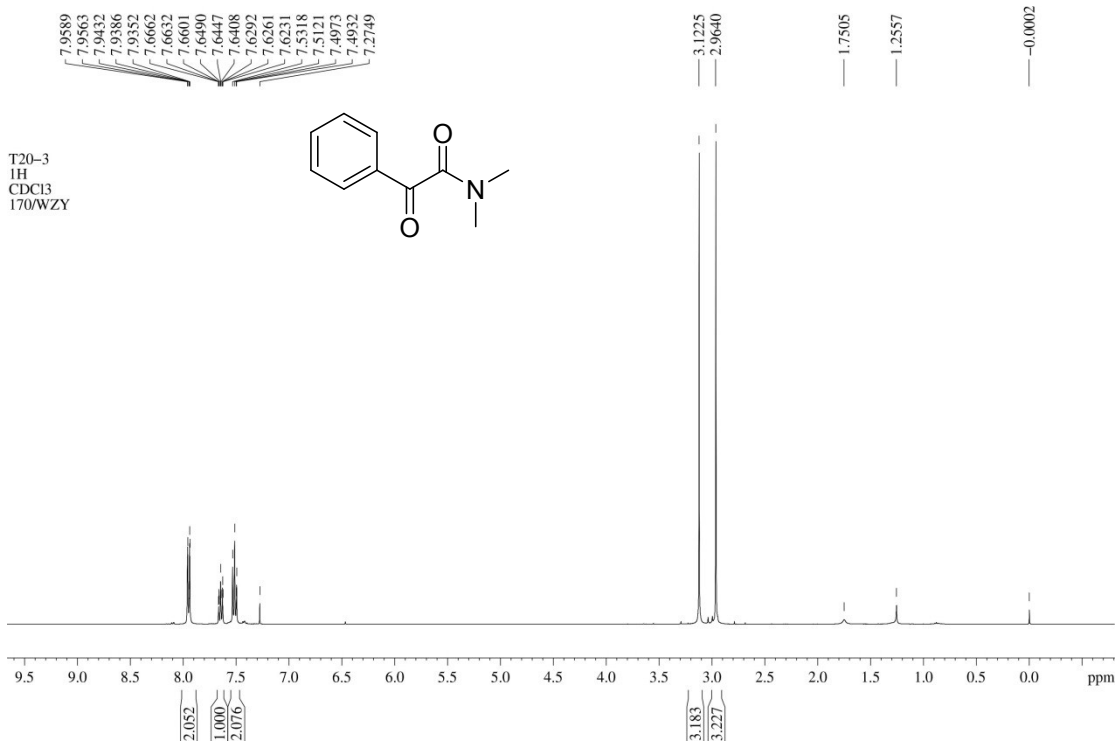
^{13}C NMR spectrum of compound **3n**



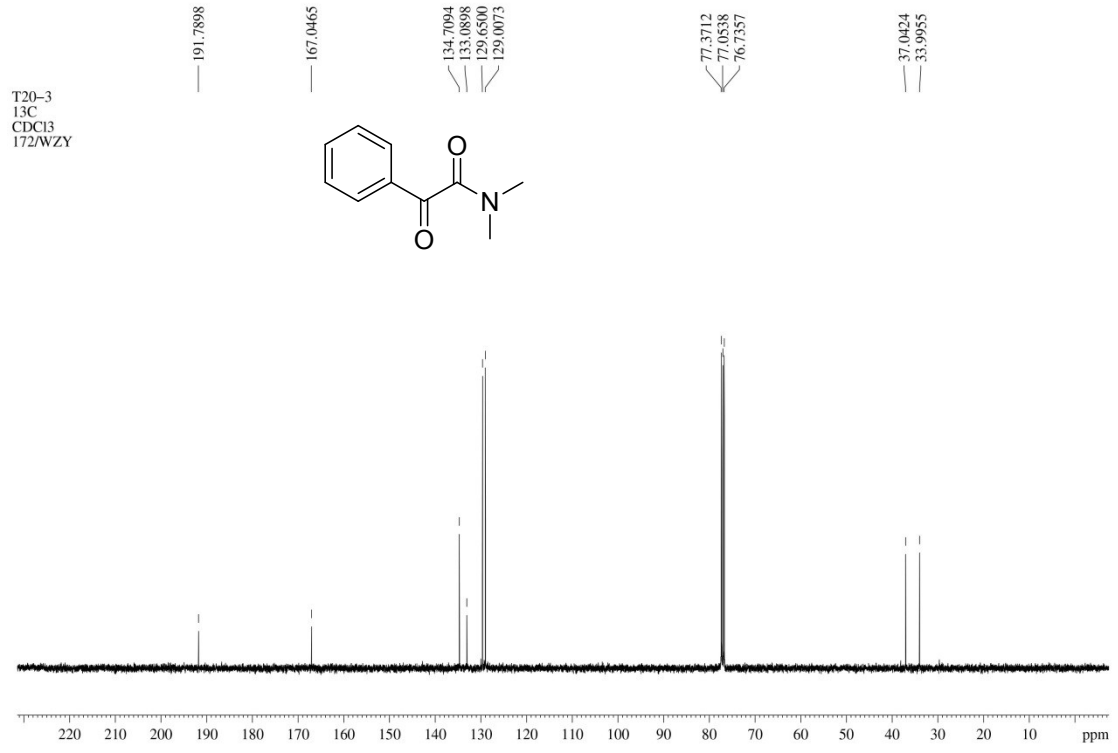
^{1}H NMR spectrum of compound **3o**



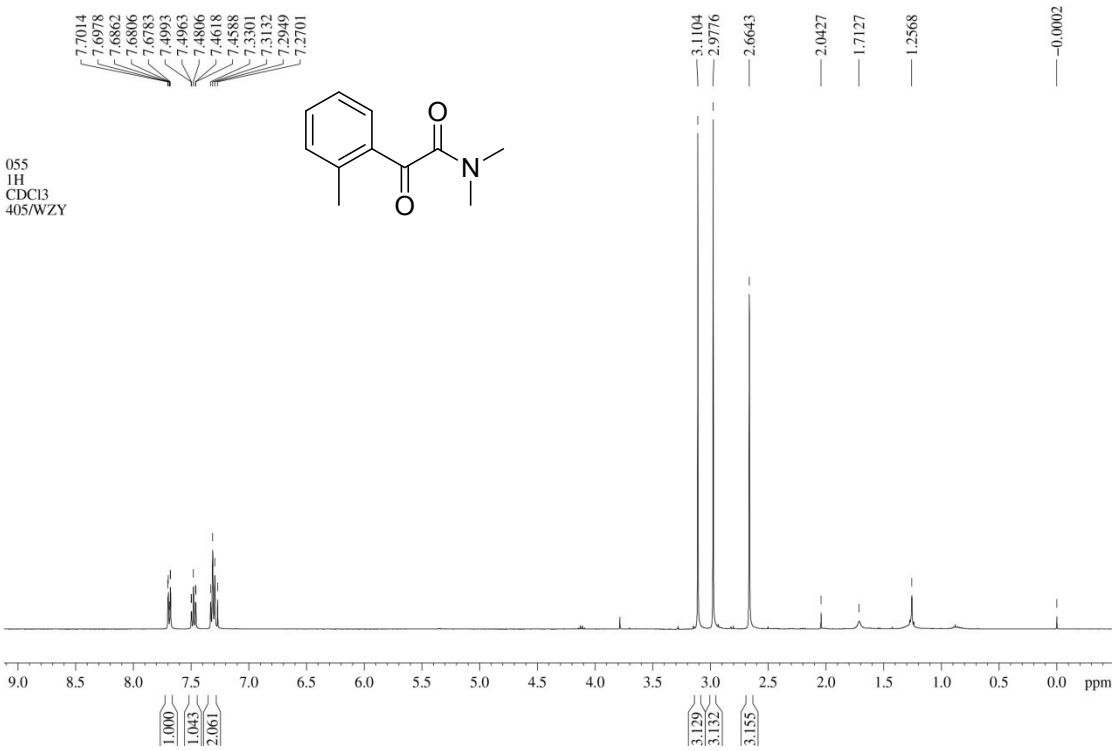
^{13}C NMR spectrum of compound **3o**



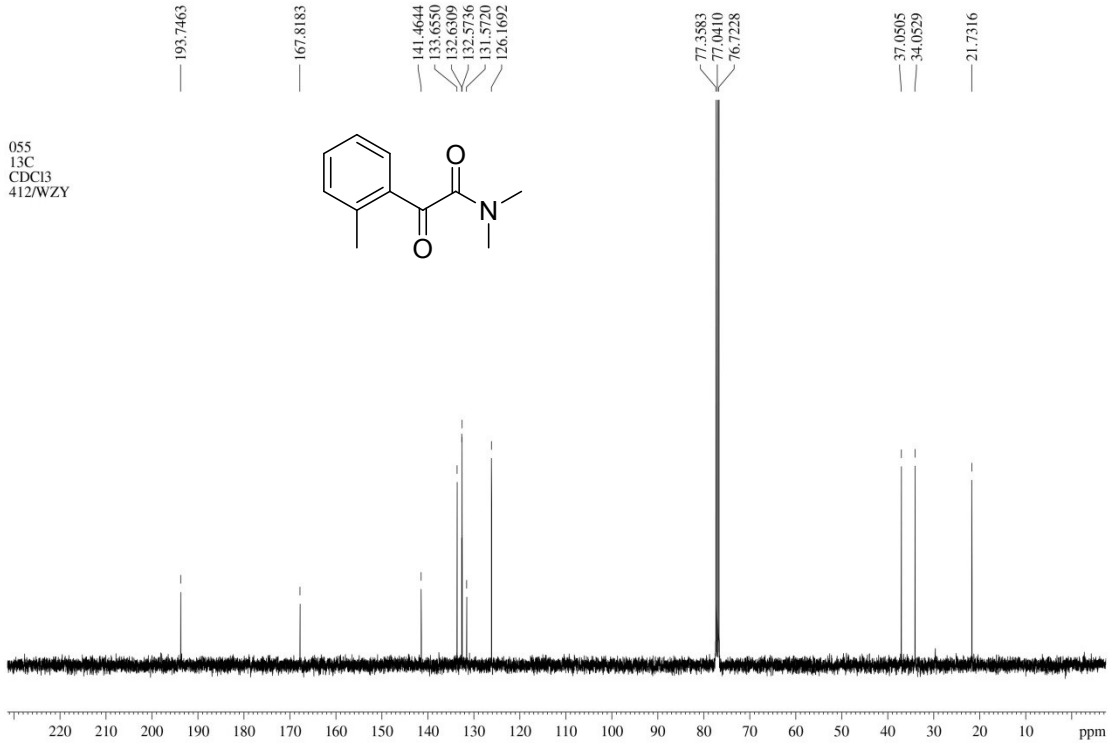
^{1}H NMR spectrum of compound **4a**



^{13}C NMR spectrum of compound **4a**

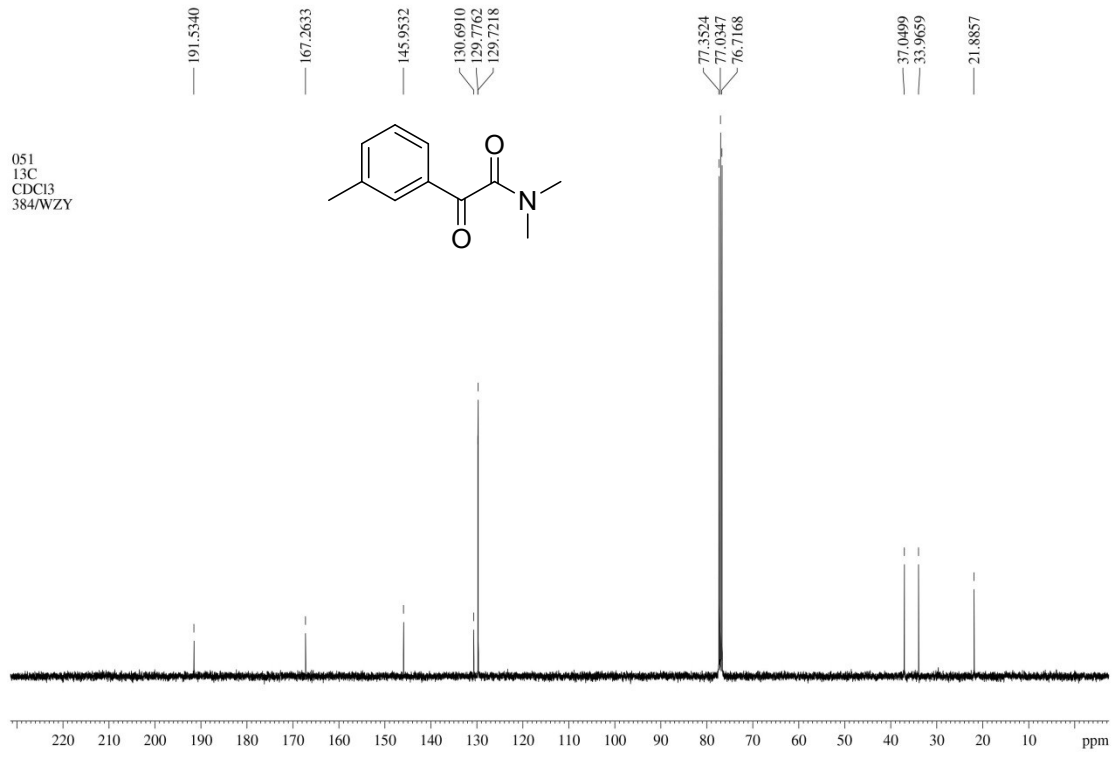


^{1}H NMR spectrum of compound **4b**

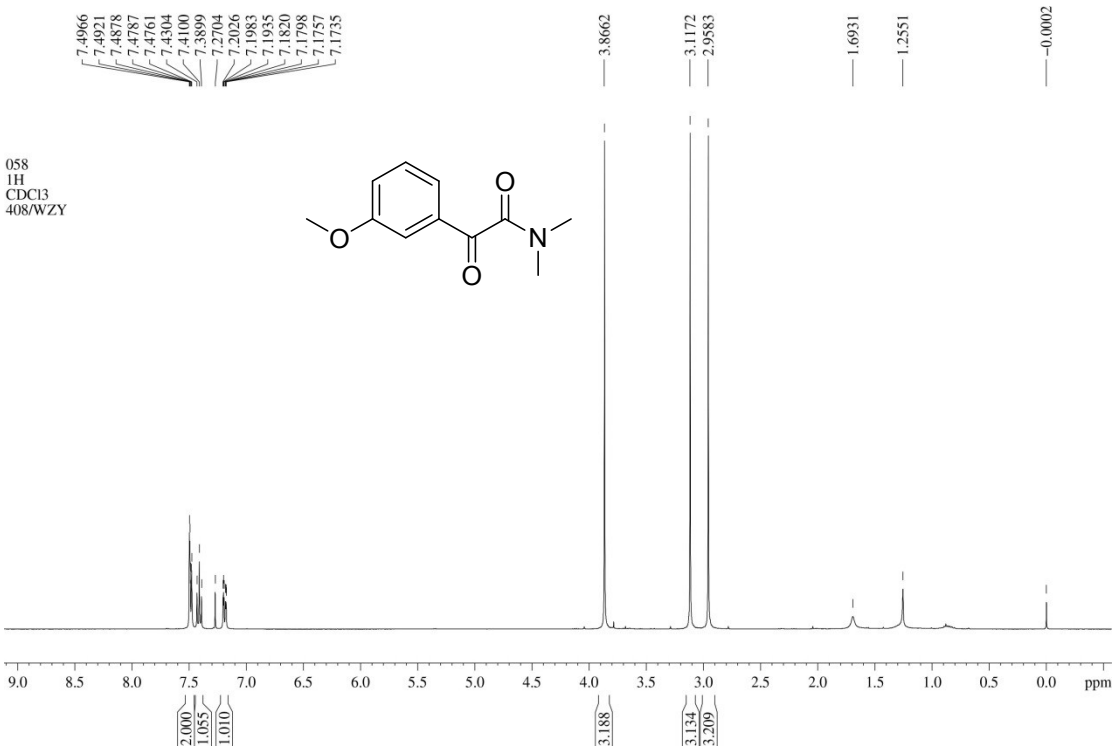


^{13}C NMR spectrum of compound **4b**

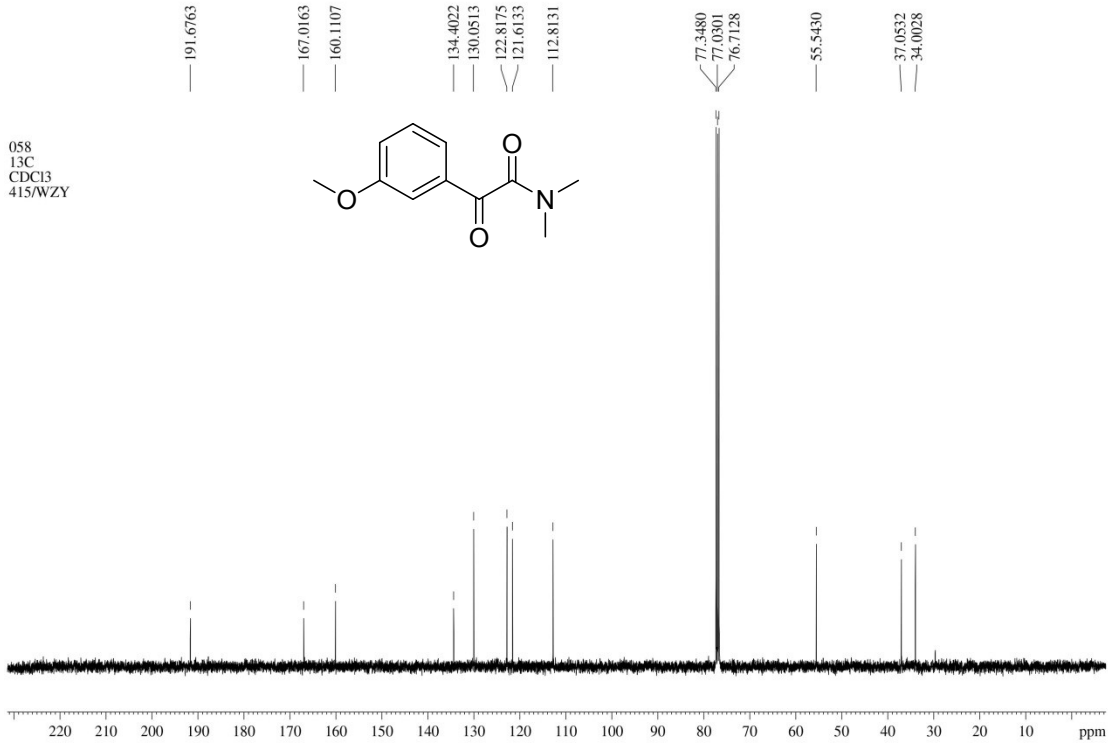
^{1}H NMR spectrum of compound **4c**



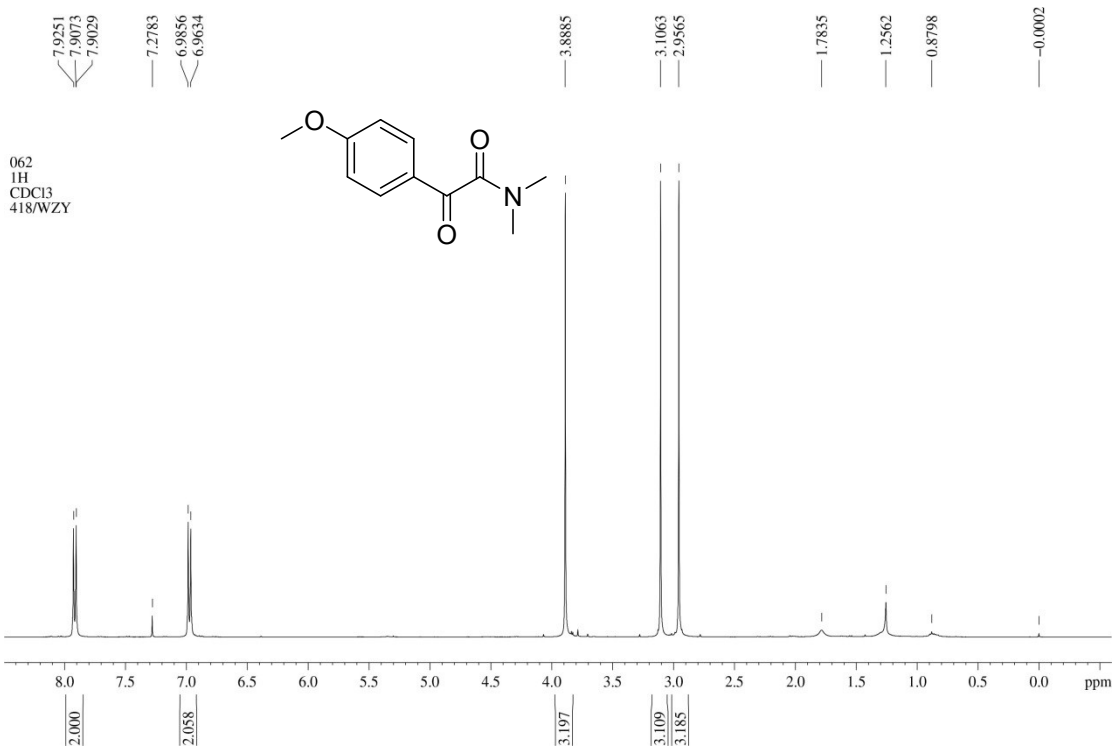
^{13}C NMR spectrum of compound **4c**



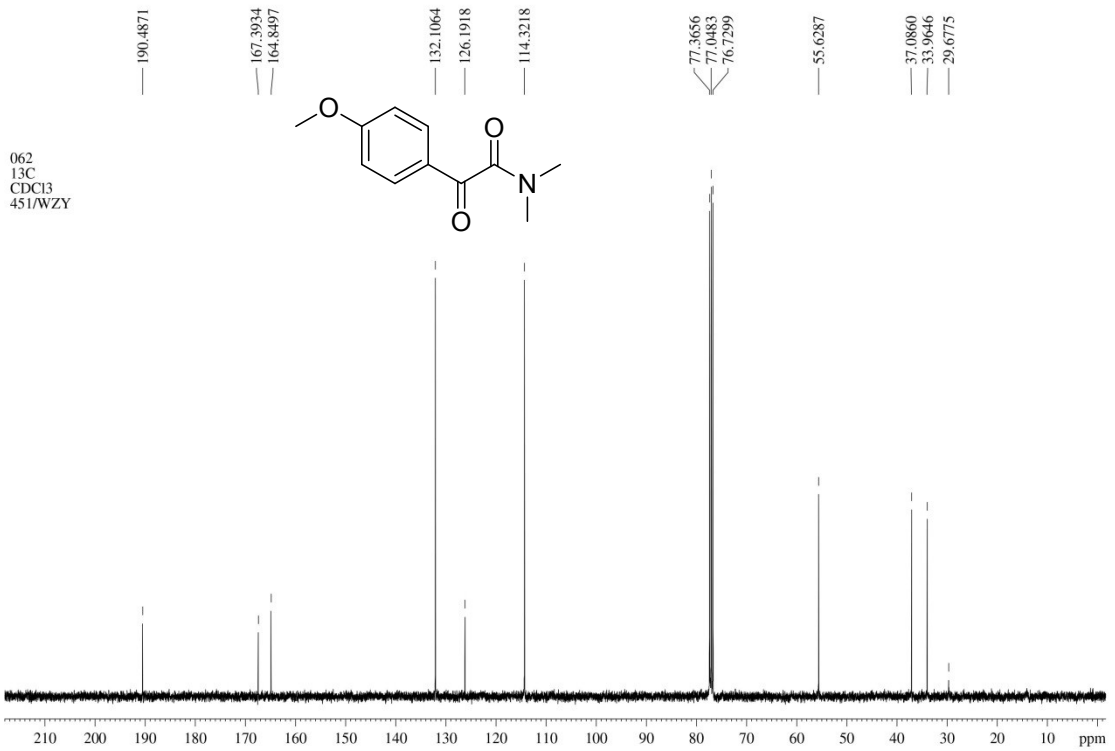
^{1}H NMR spectrum of compound **4d**



^{13}C NMR spectrum of compound **4d**

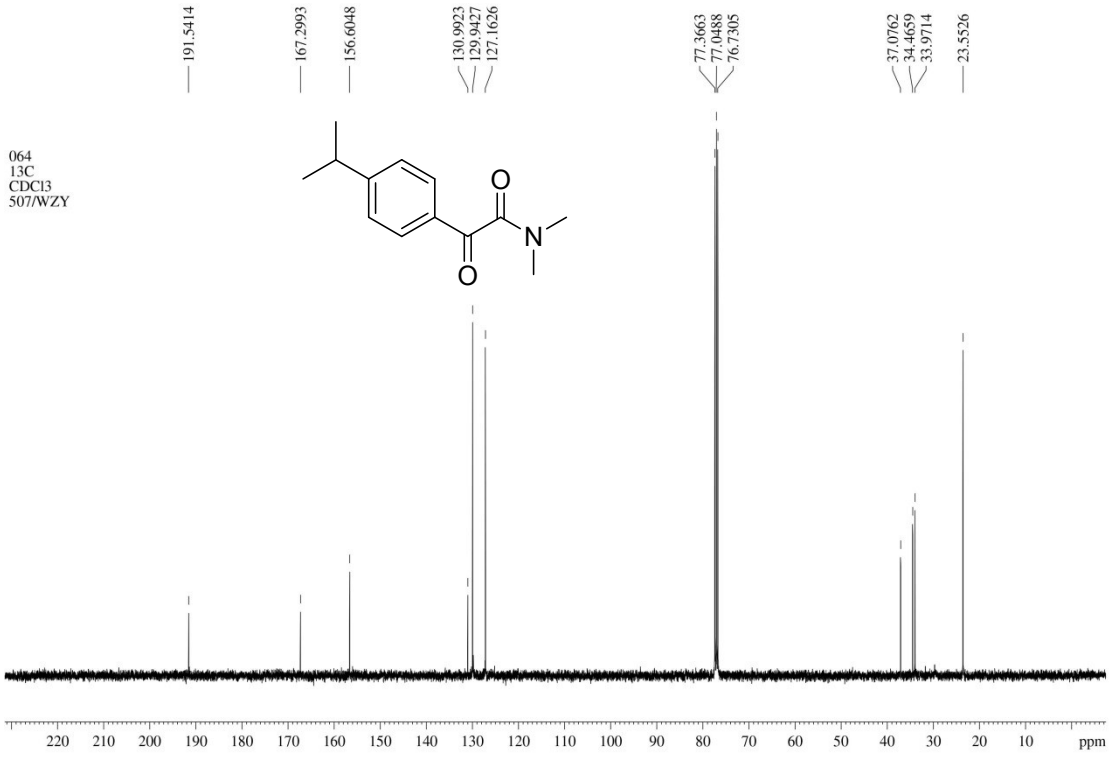


^{1}H NMR spectrum of compound **4e**



^{13}C NMR spectrum of compound **4e**

^{1}H NMR spectrum of compound **4f**

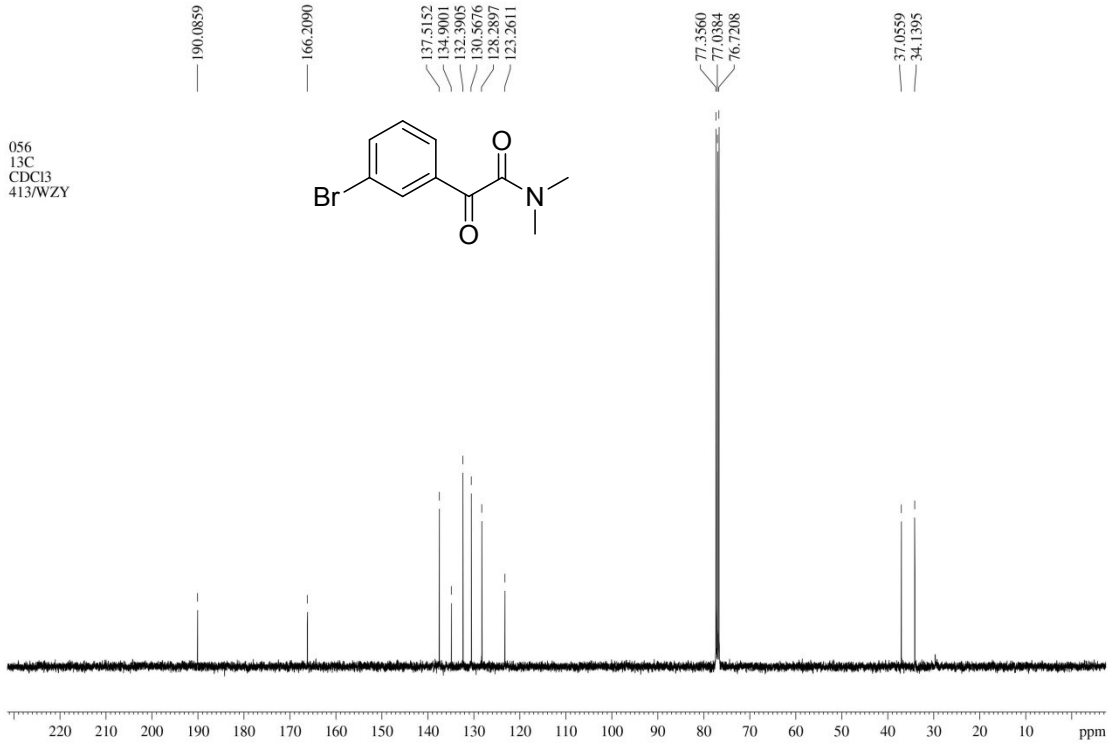


^{13}C NMR spectrum of compound **4f**

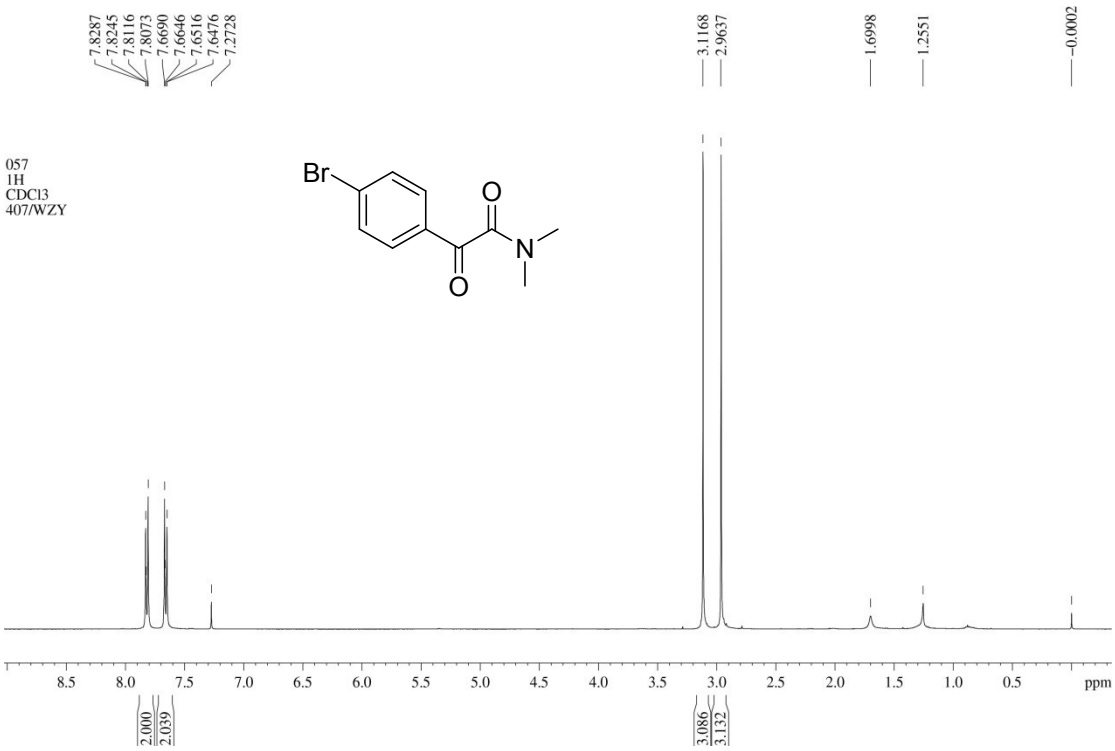
^{1}H NMR spectrum of compound **4g**

^{13}C NMR spectrum of compound **4g**

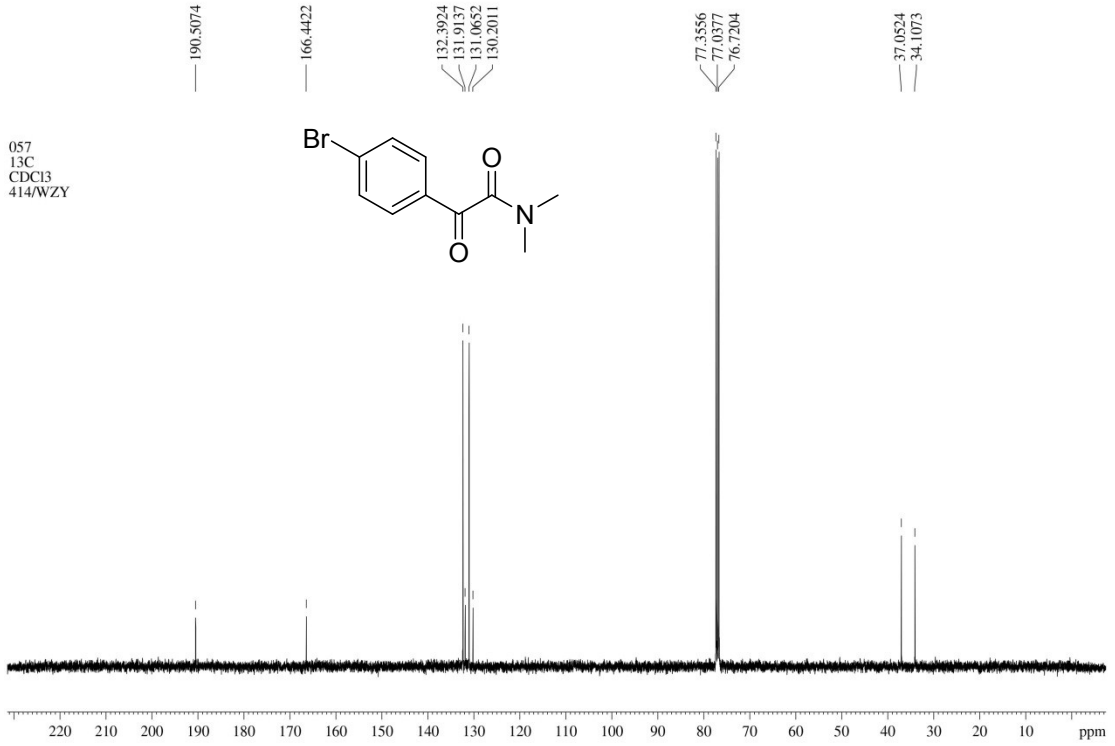
^{1}H NMR spectrum of compound **4h**



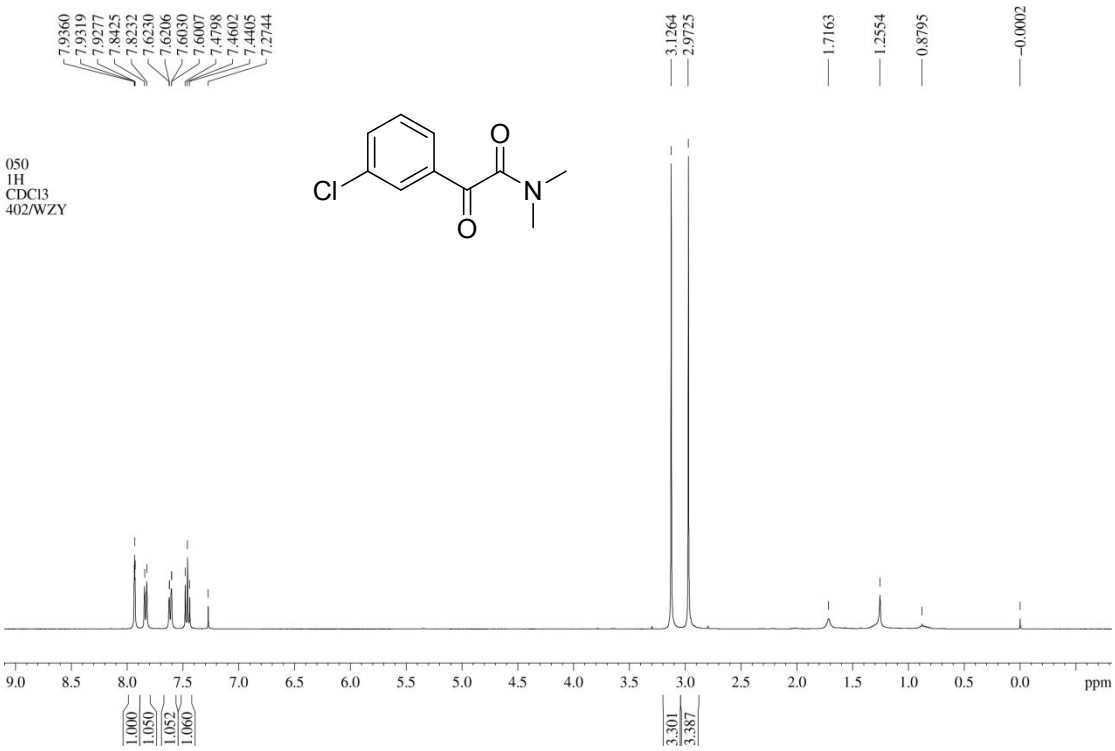
^{13}C NMR spectrum of compound **4h**



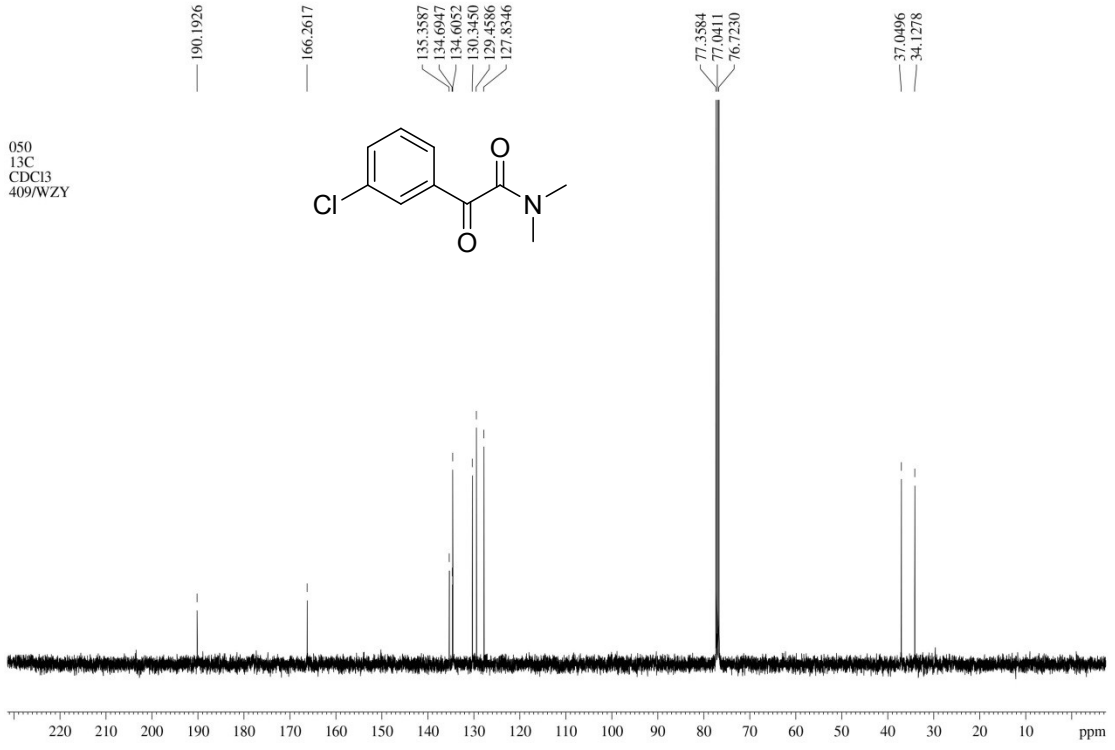
^{1}H NMR spectrum of compound **4i**



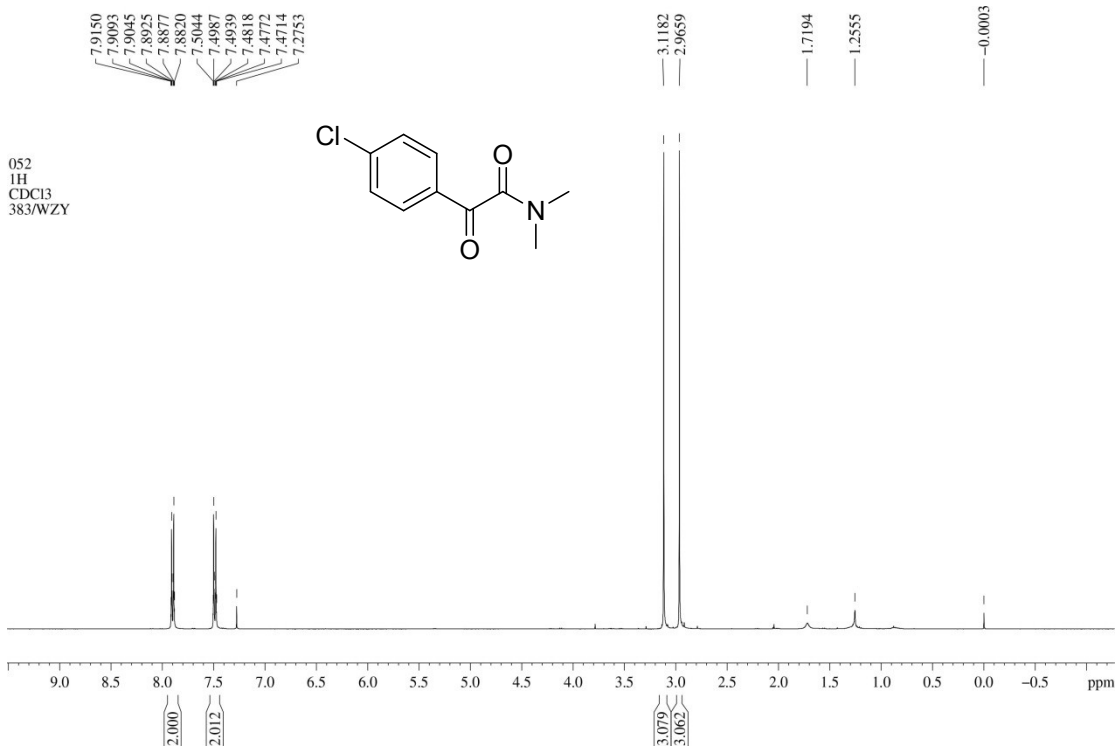
^{13}C NMR spectrum of compound **4i**



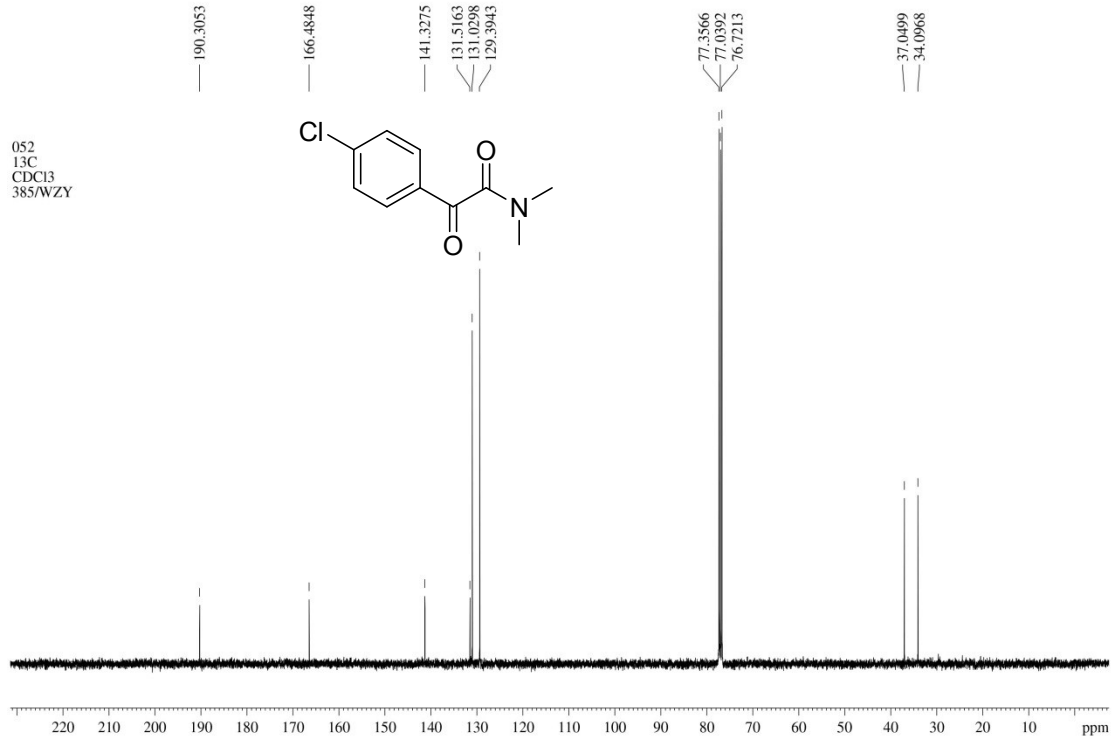
^{1}H NMR spectrum of compound **4j**



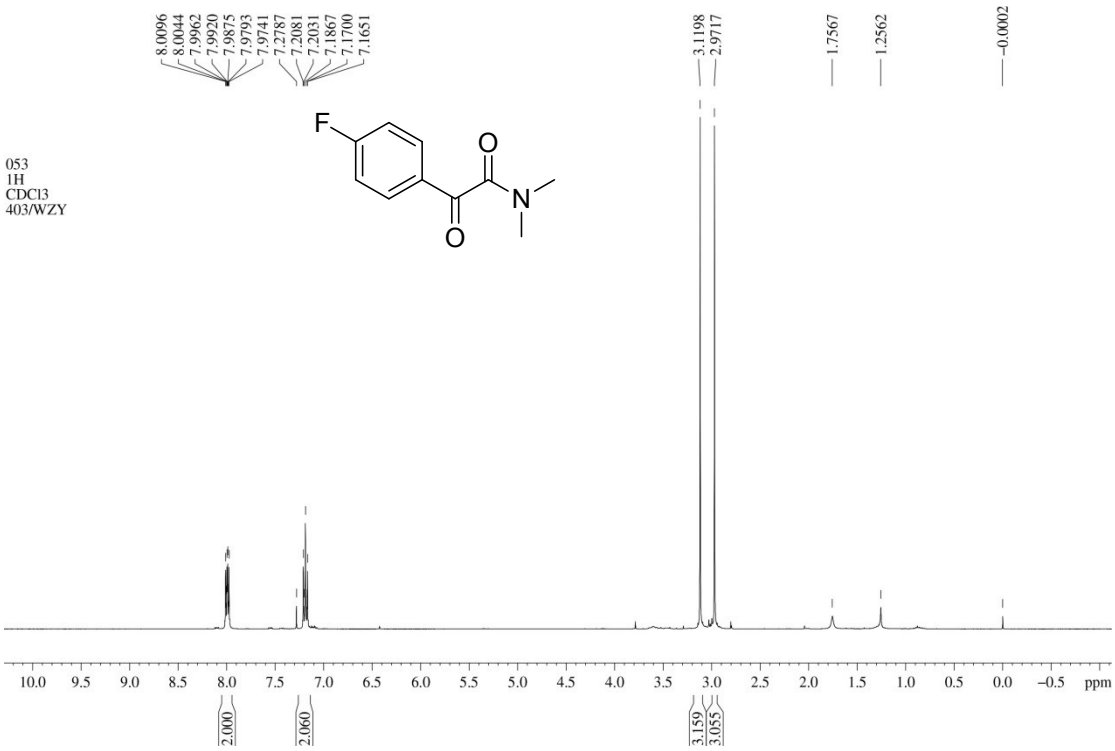
^{13}C NMR spectrum of compound **4j**



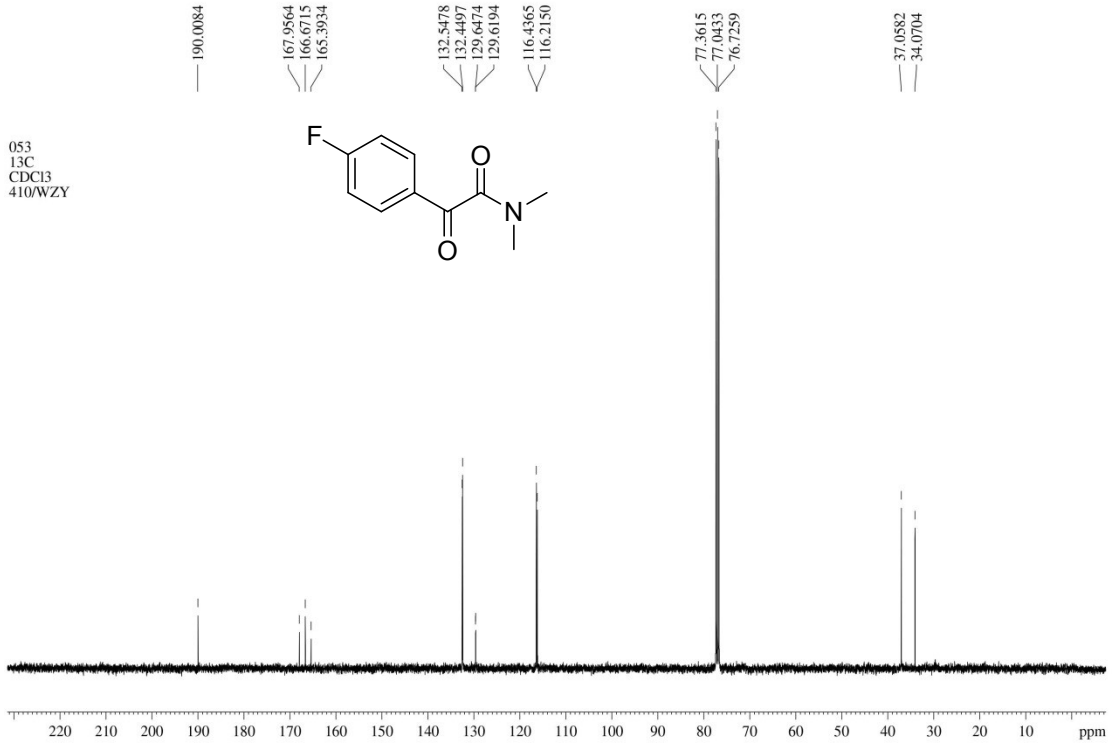
^{1}H NMR spectrum of compound **4k**



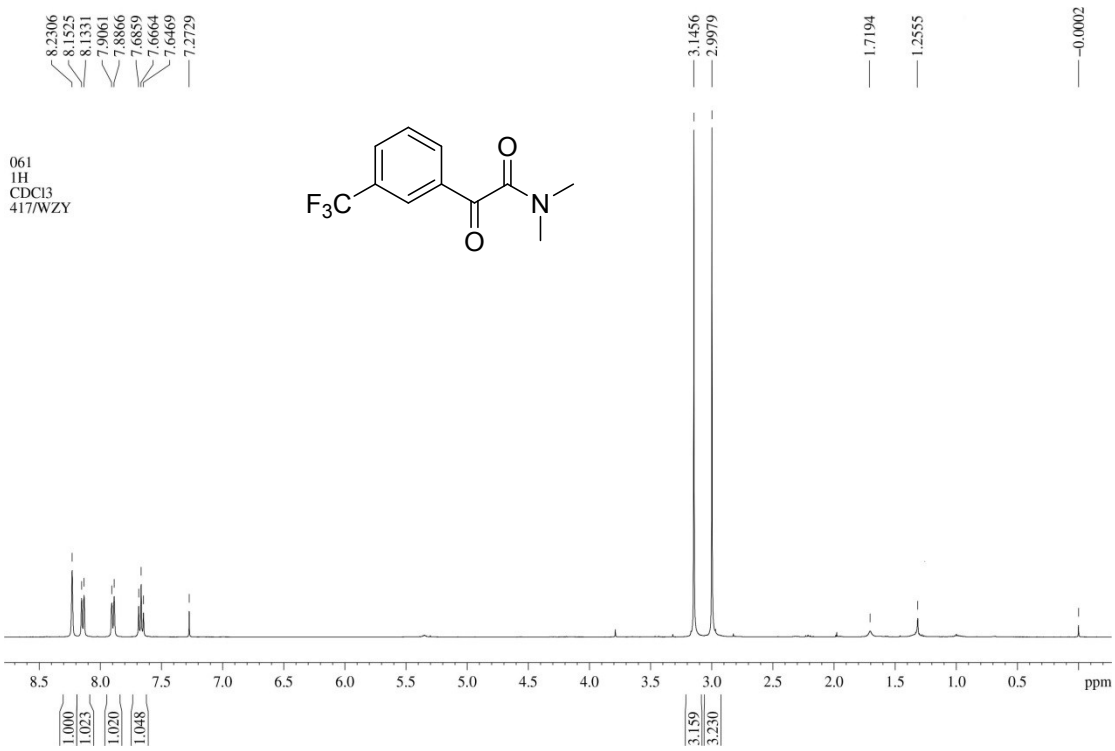
^{13}C NMR spectrum of compound **4k**



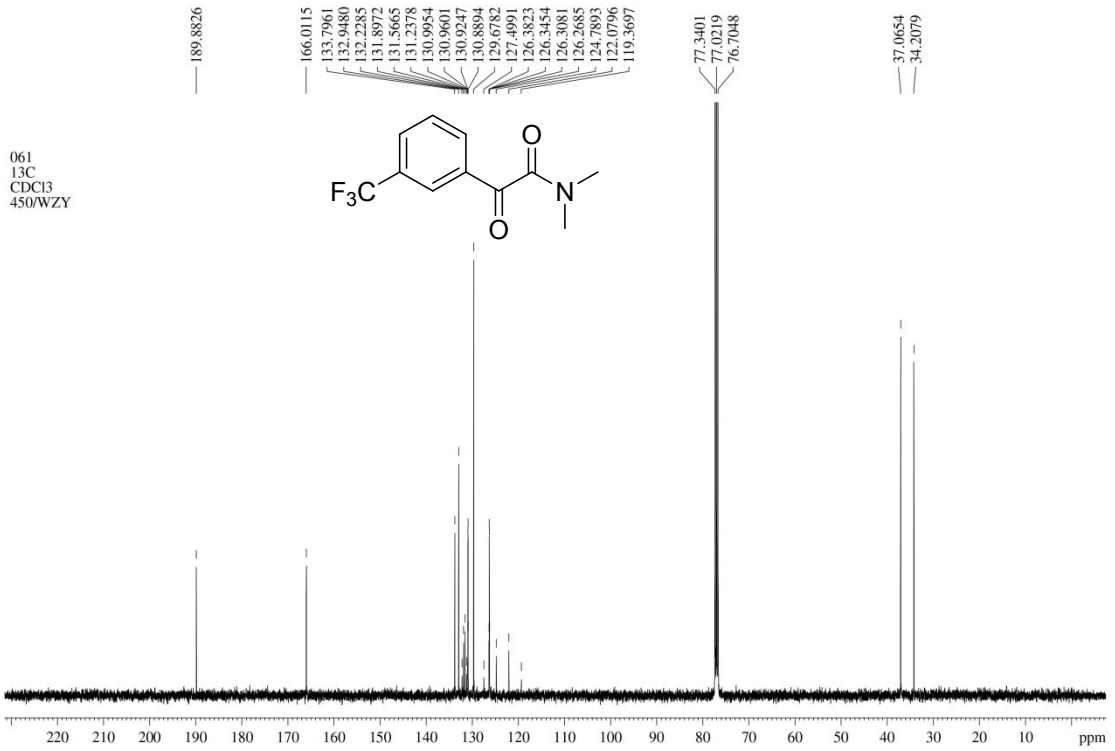
^{1}H NMR spectrum of compound **4l**



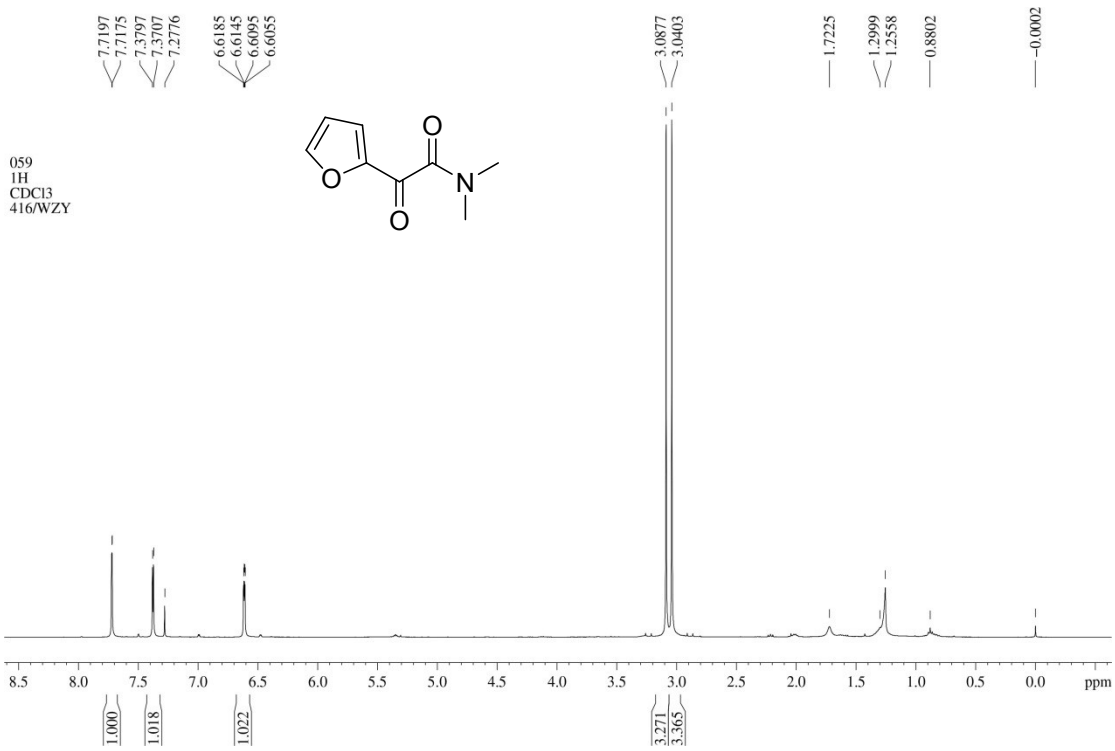
^{13}C NMR spectrum of compound **4l**



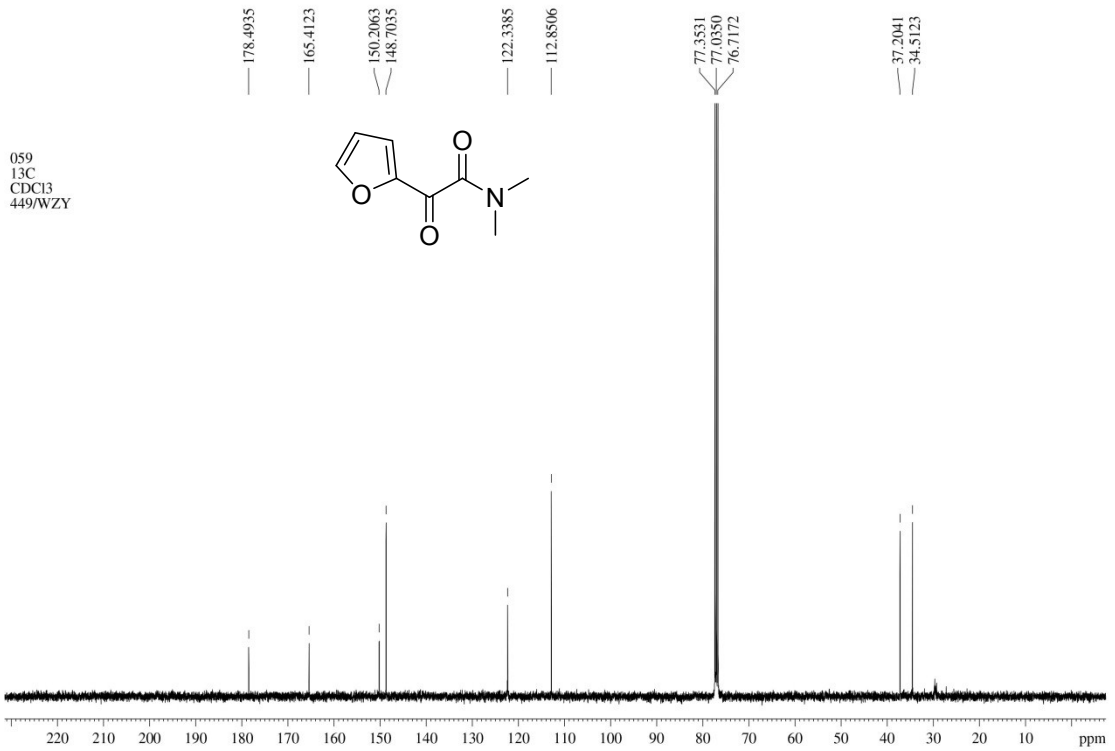
^{1}H NMR spectrum of compound **4m**



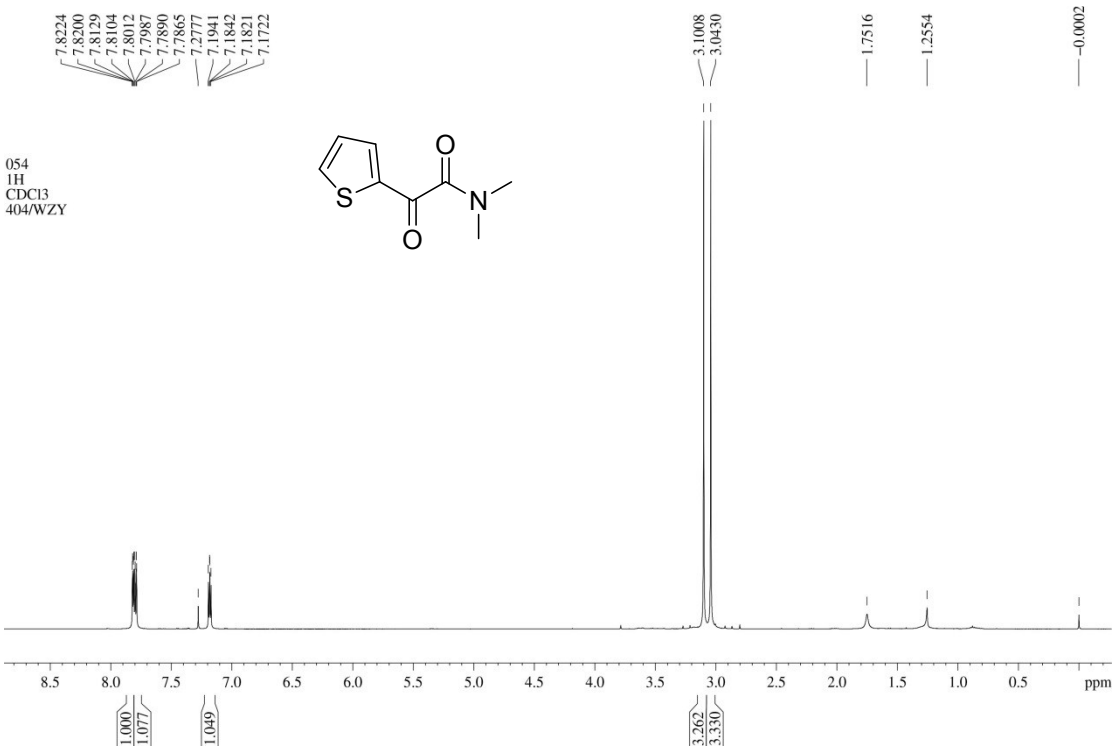
^{13}C NMR spectrum of compound **4m**



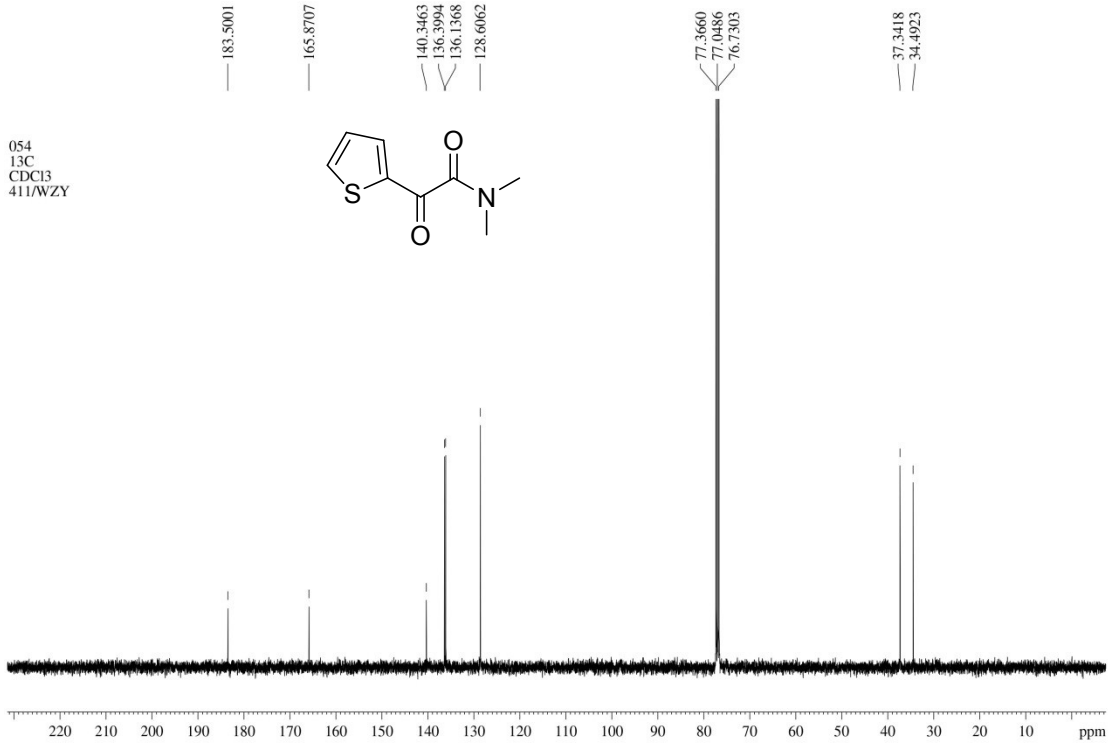
^{1}H NMR spectrum of compound **4n**



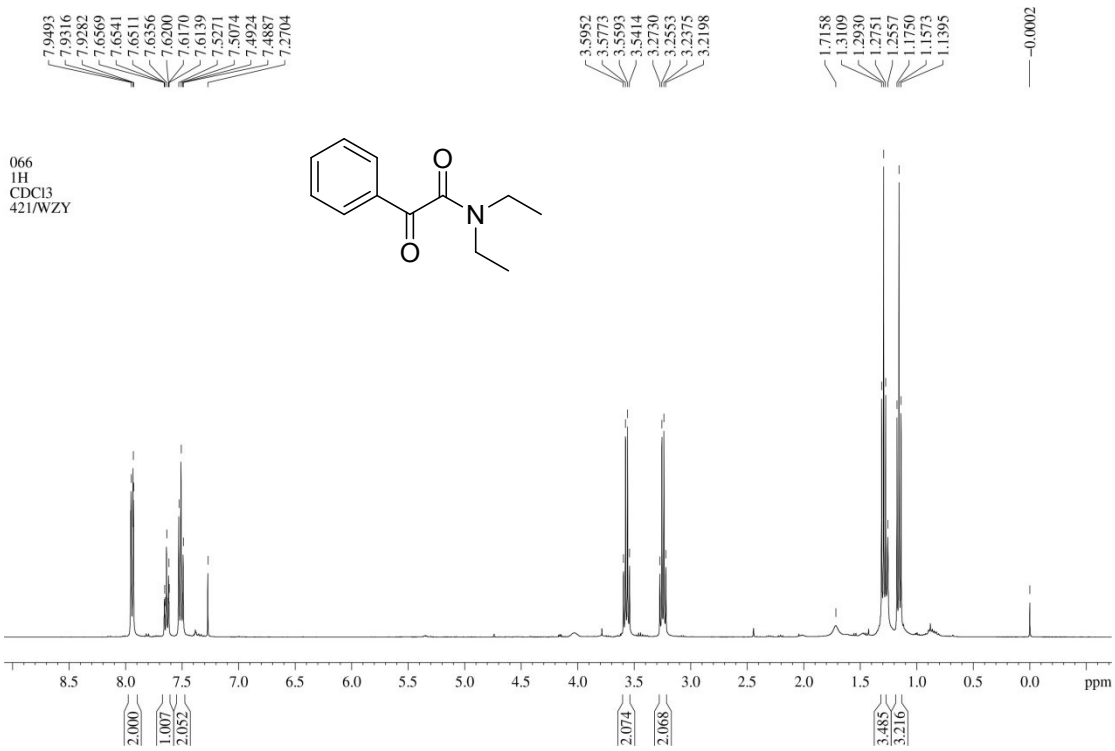
^{13}C NMR spectrum of compound **4n**



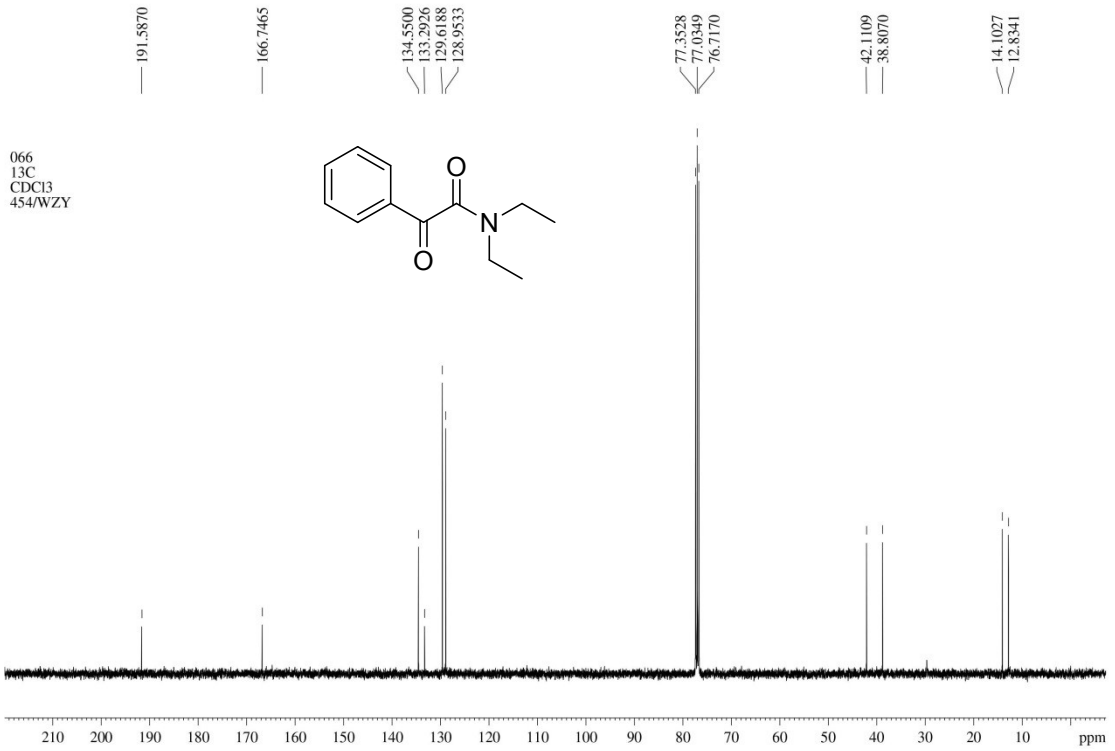
^{1}H NMR spectrum of compound **4o**



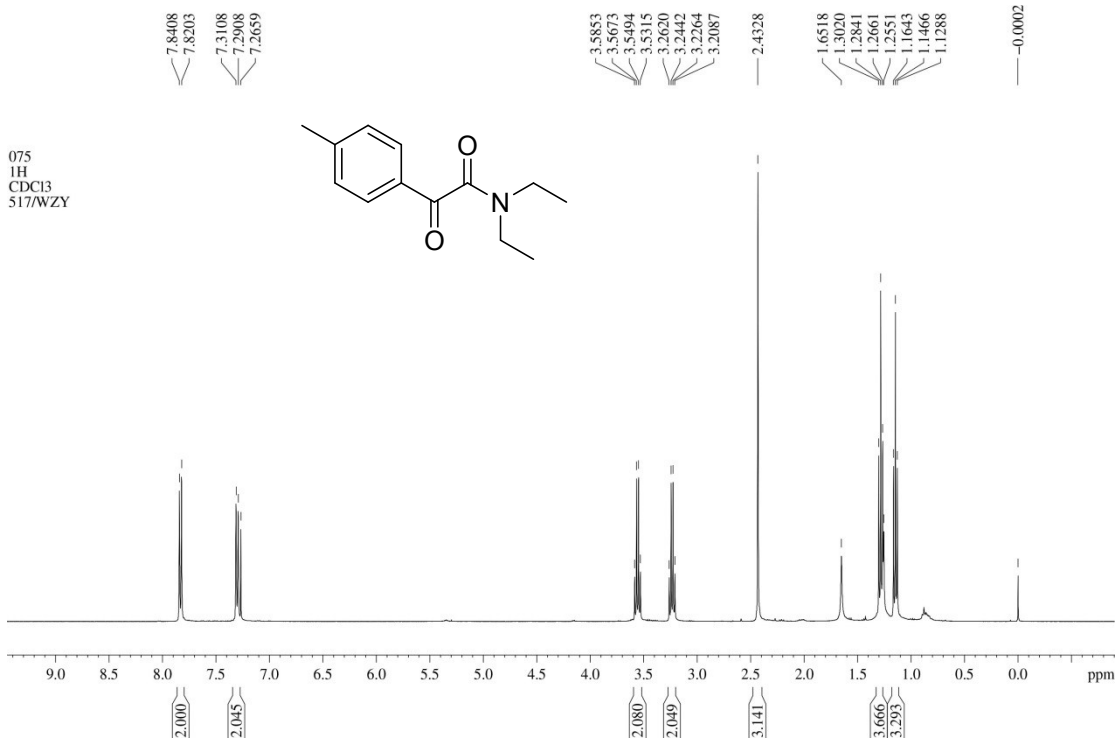
^{13}C NMR spectrum of compound **4o**



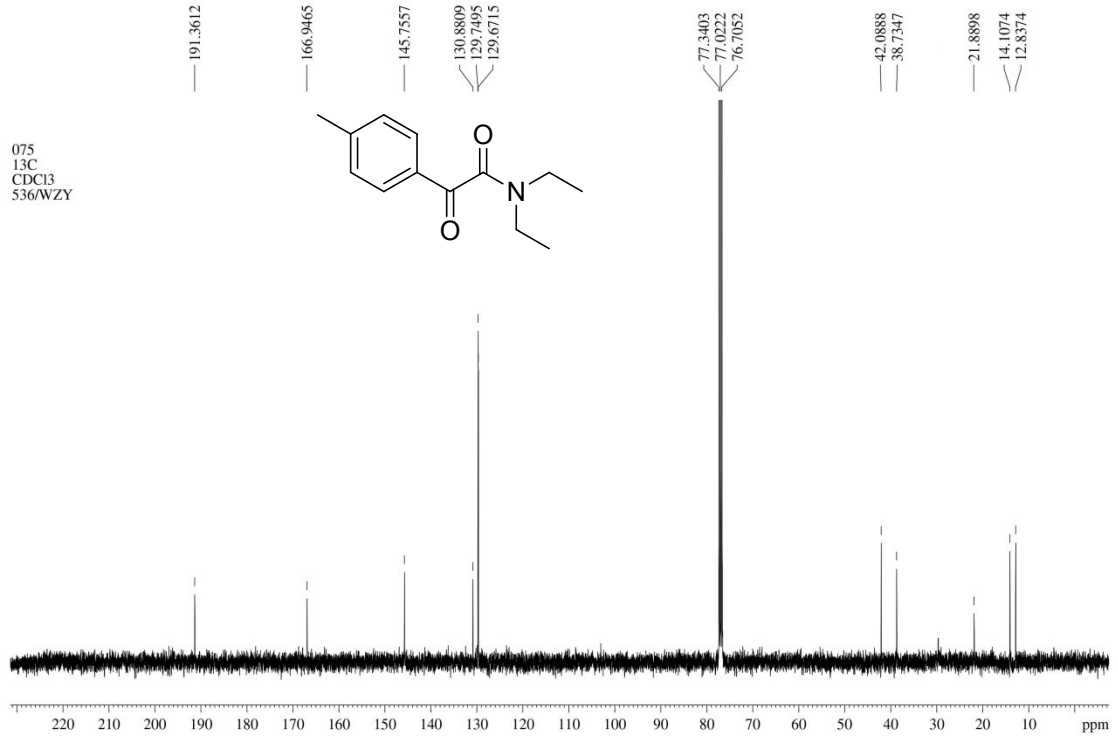
^{1}H NMR spectrum of compound **4p**



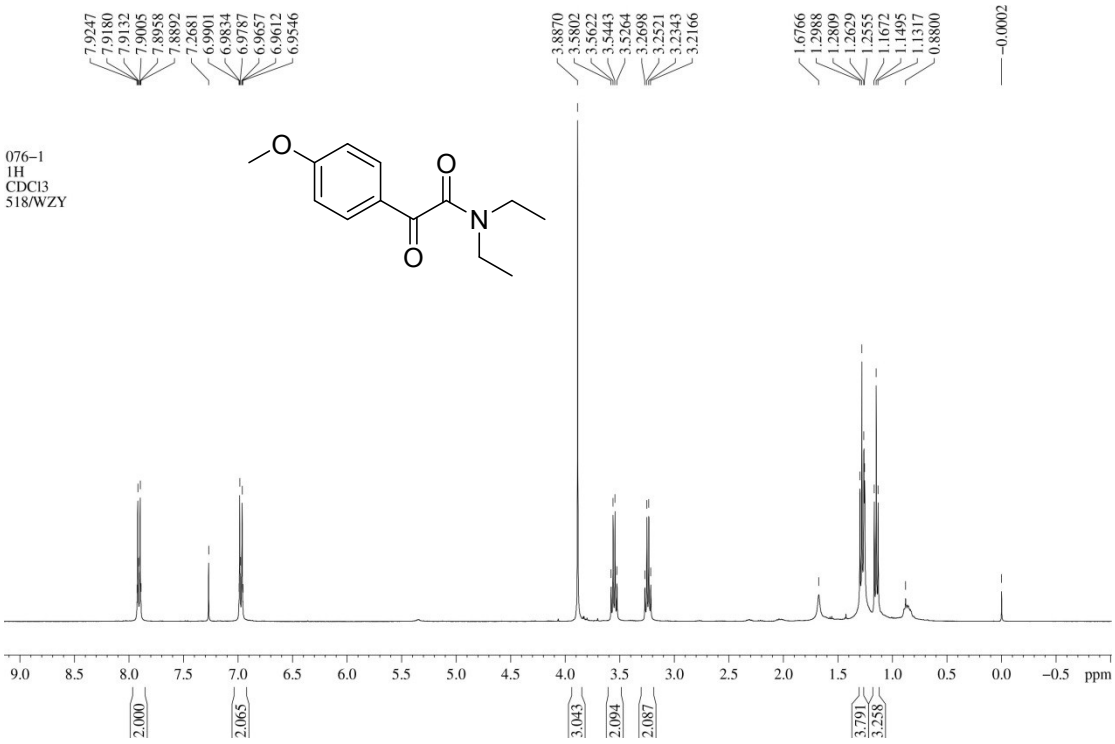
^{13}C NMR spectrum of compound **4p**



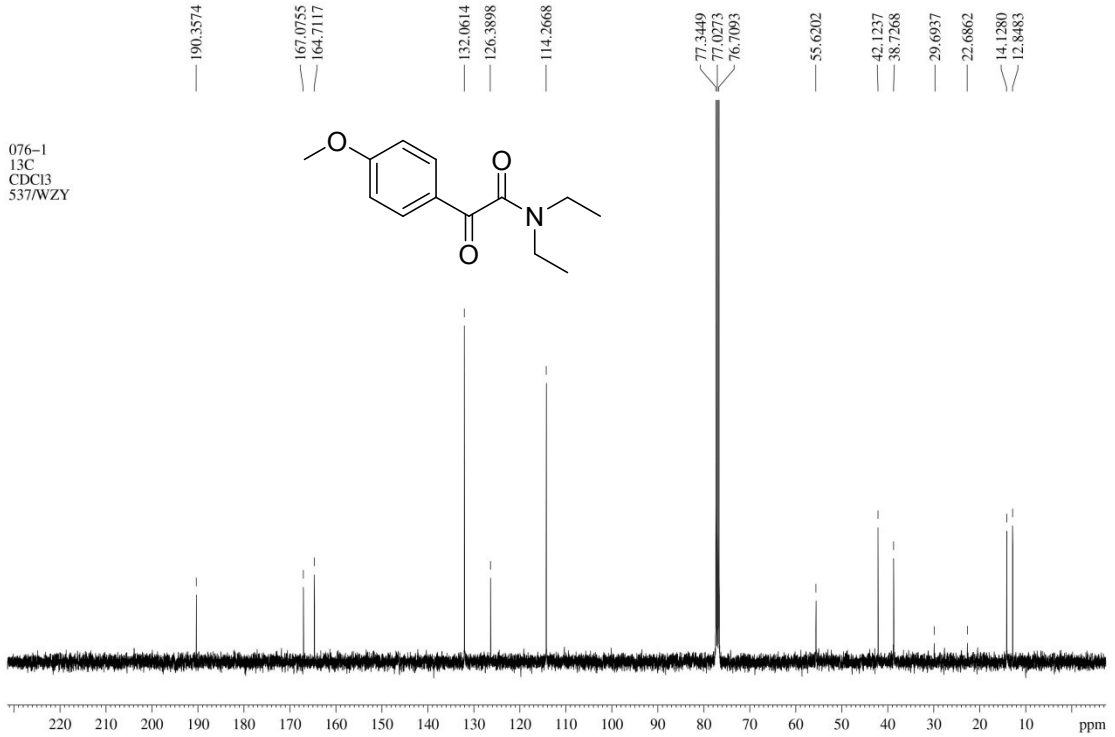
^{1}H NMR spectrum of compound **4q**



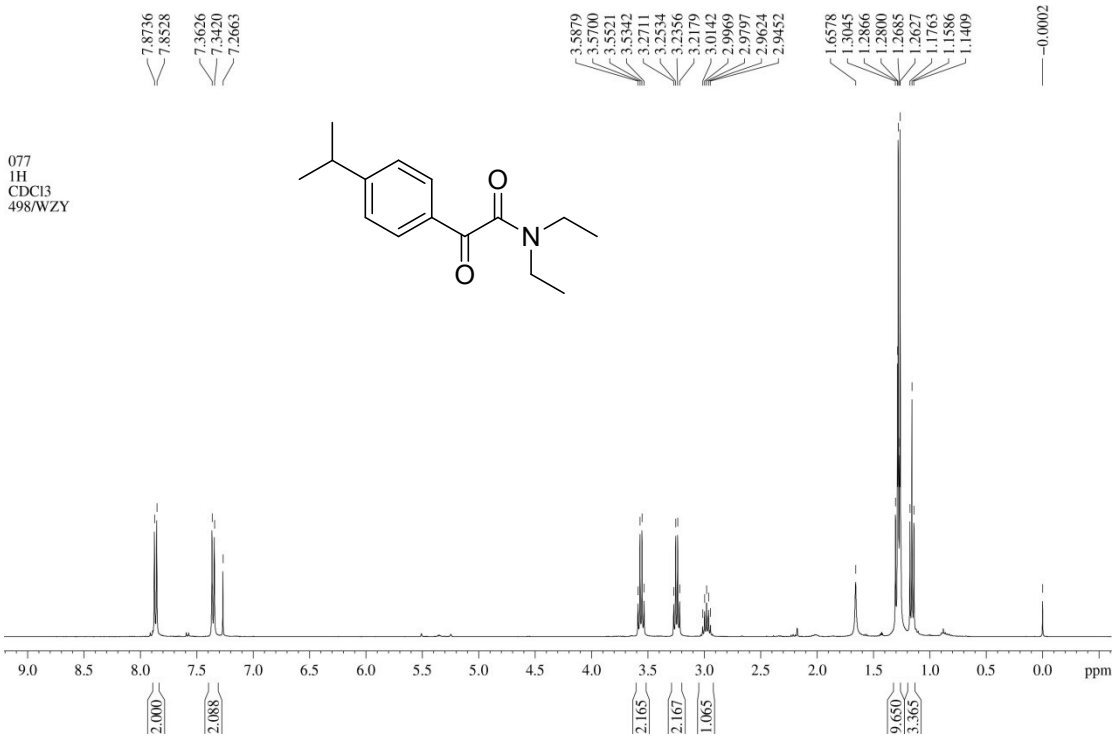
^{13}C NMR spectrum of compound **4q**



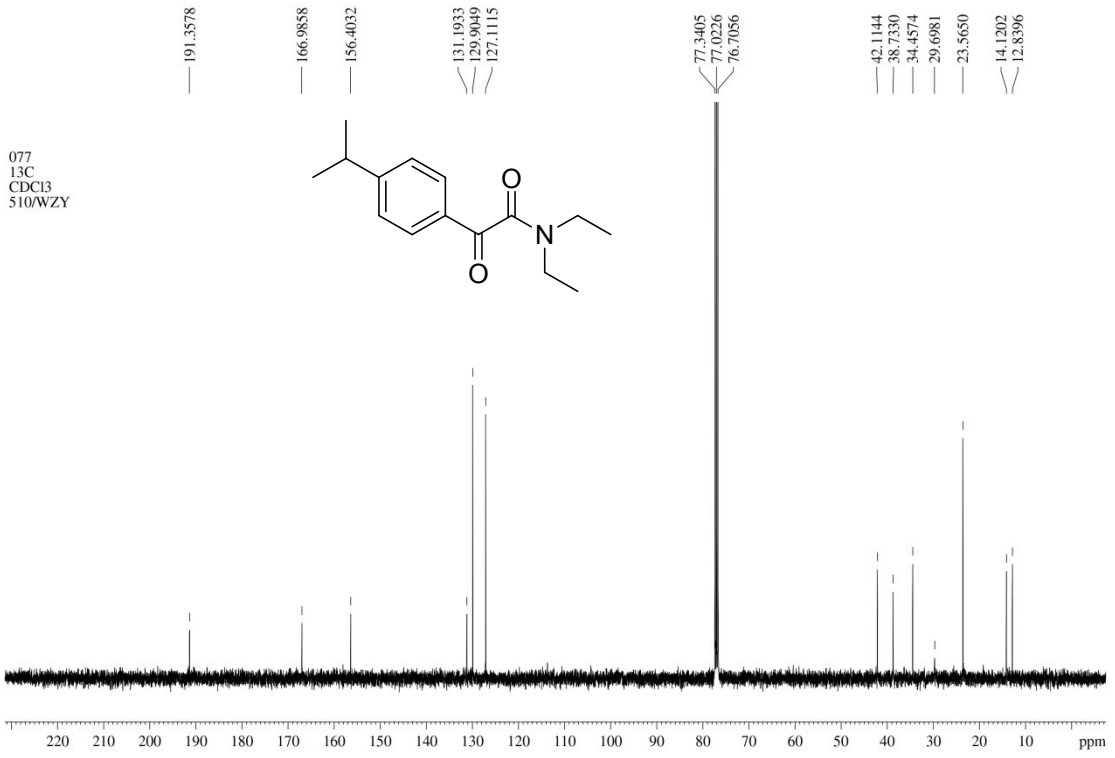
^{1}H NMR spectrum of compound **4r**



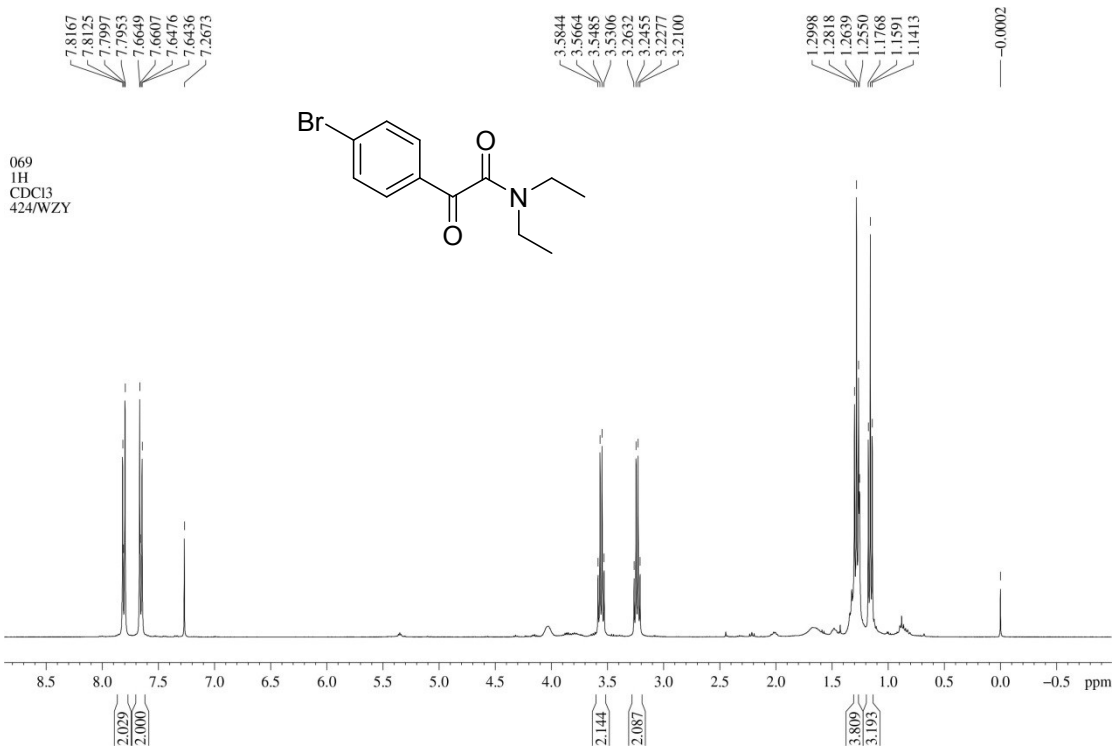
^{13}C NMR spectrum of compound **4r**



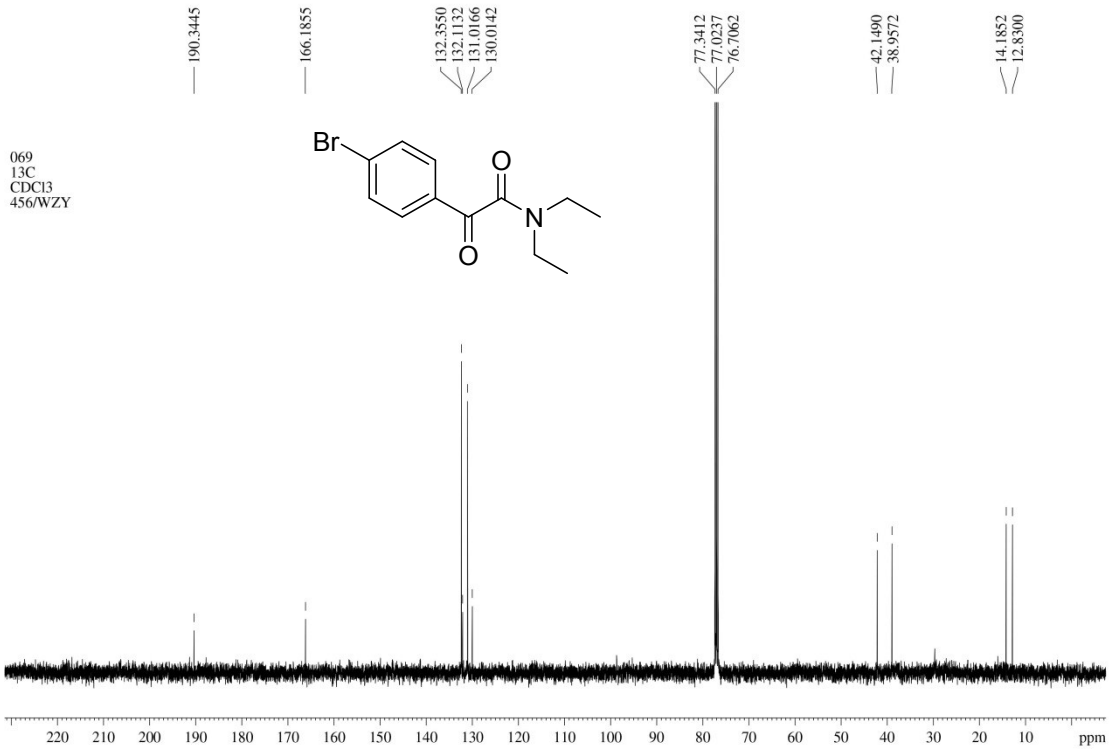
^{1}H NMR spectrum of compound **4s**



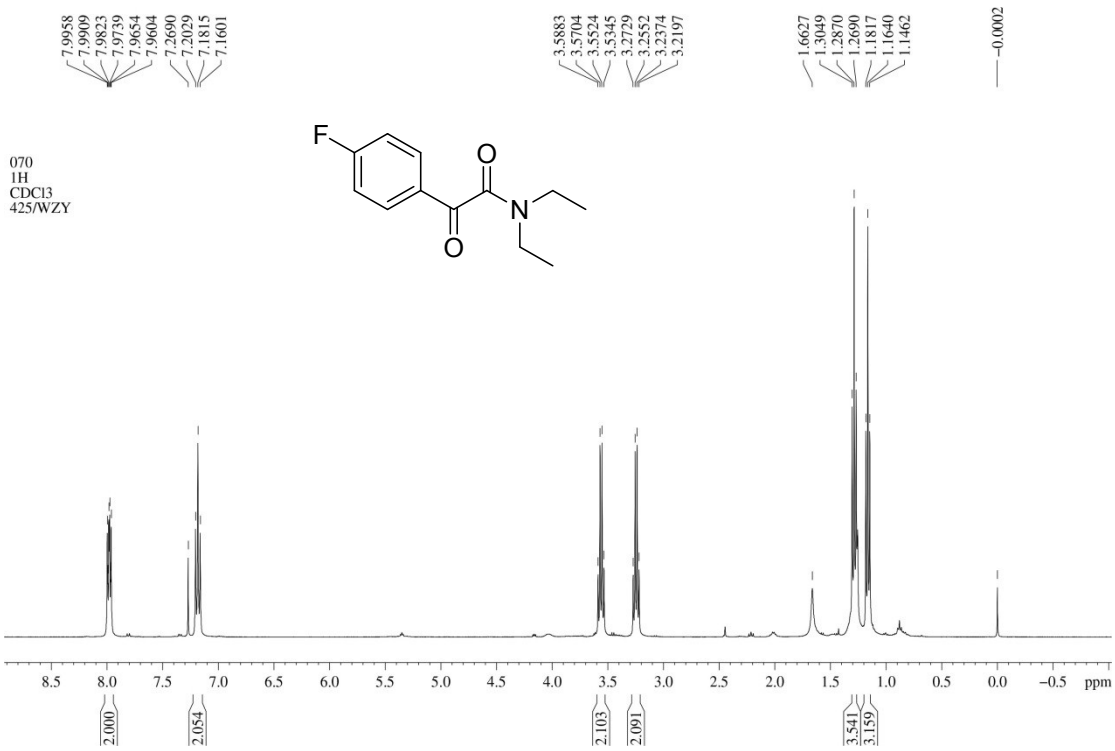
^{13}C NMR spectrum of compound **4s**



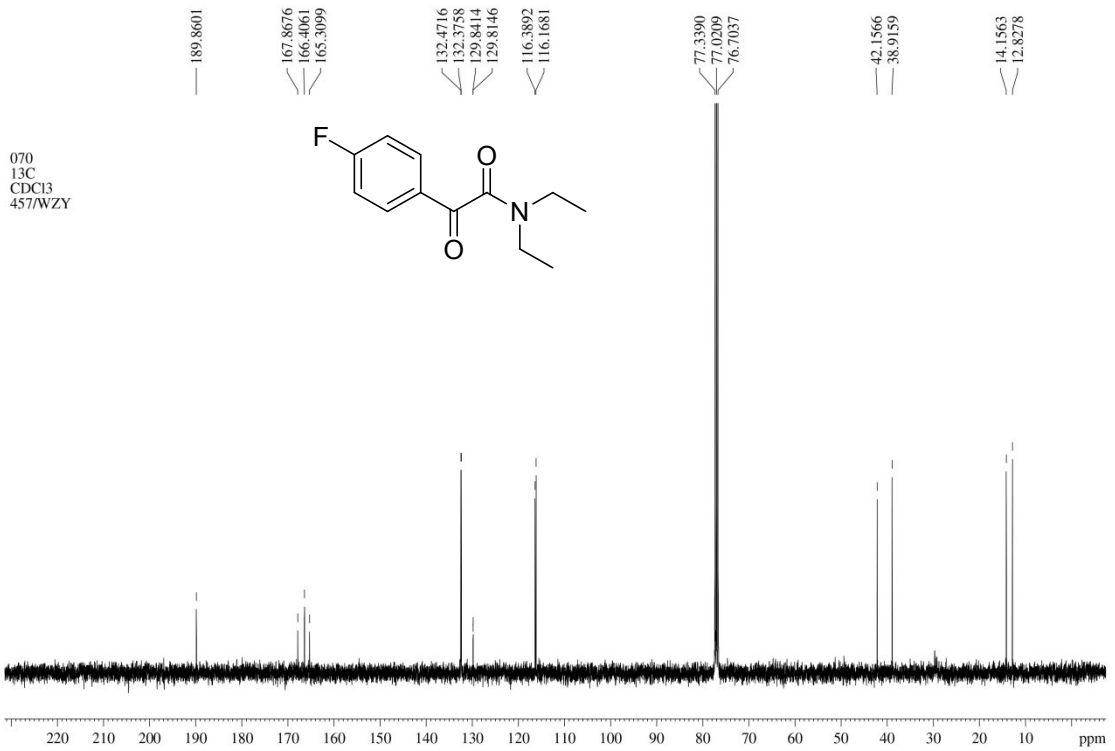
^{1}H NMR spectrum of compound **4t**



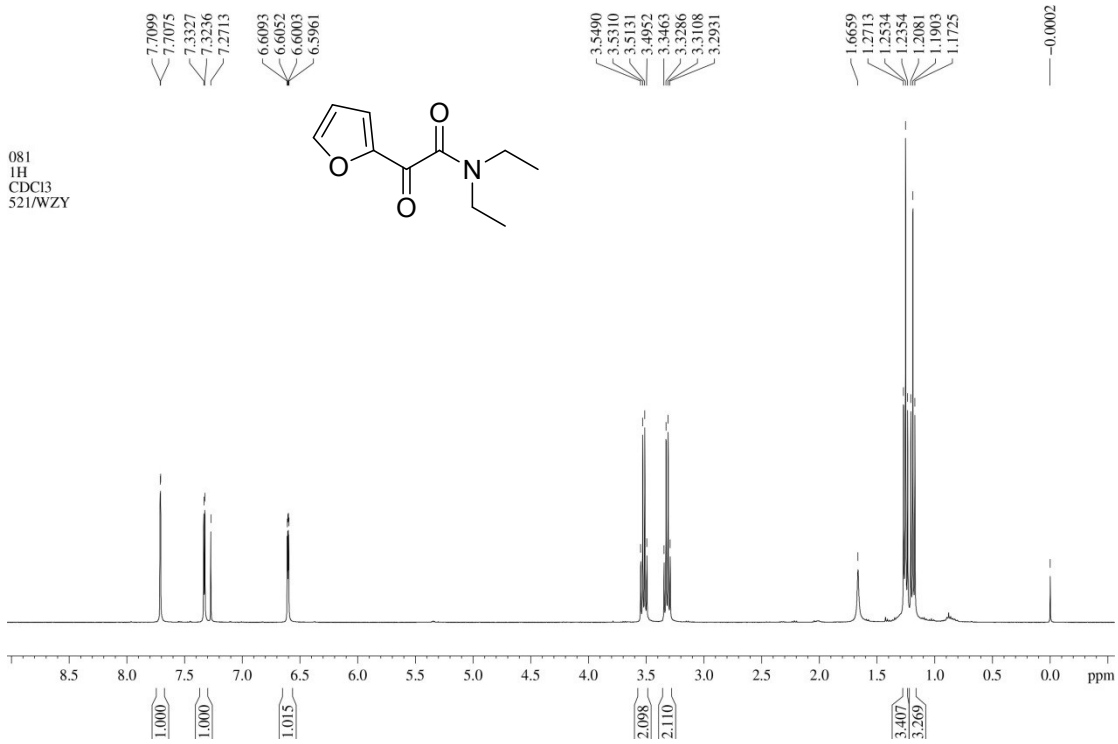
^{13}C NMR spectrum of compound **4t**



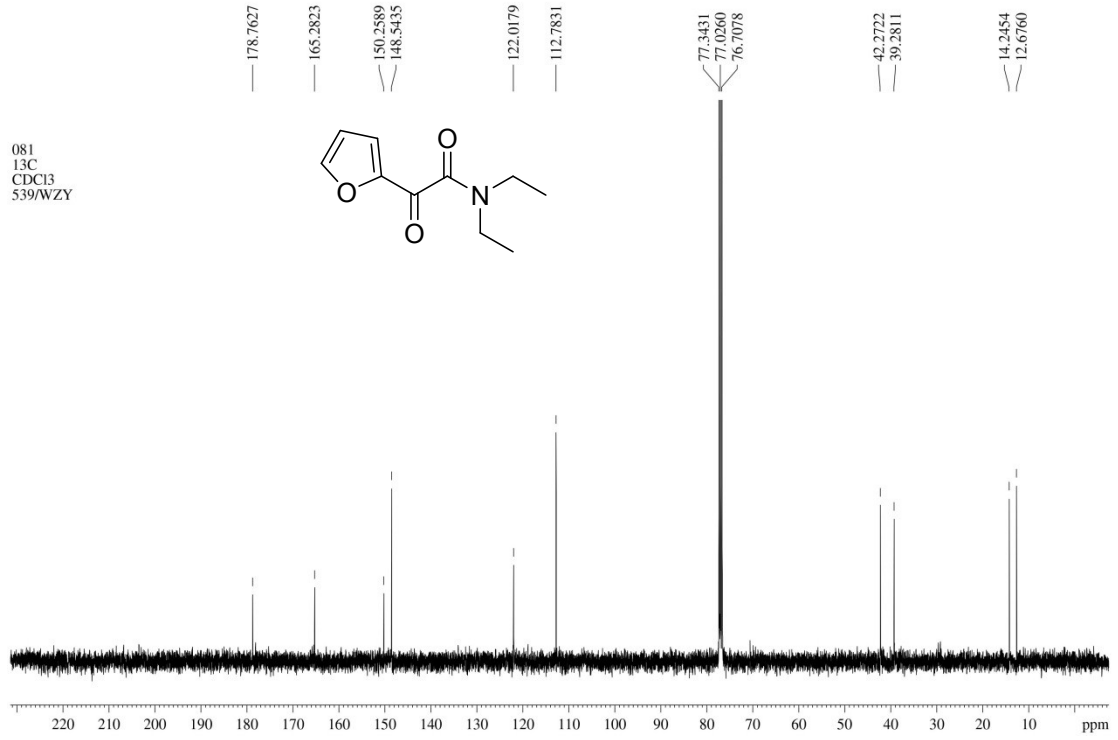
^{1}H NMR spectrum of compound **4u**



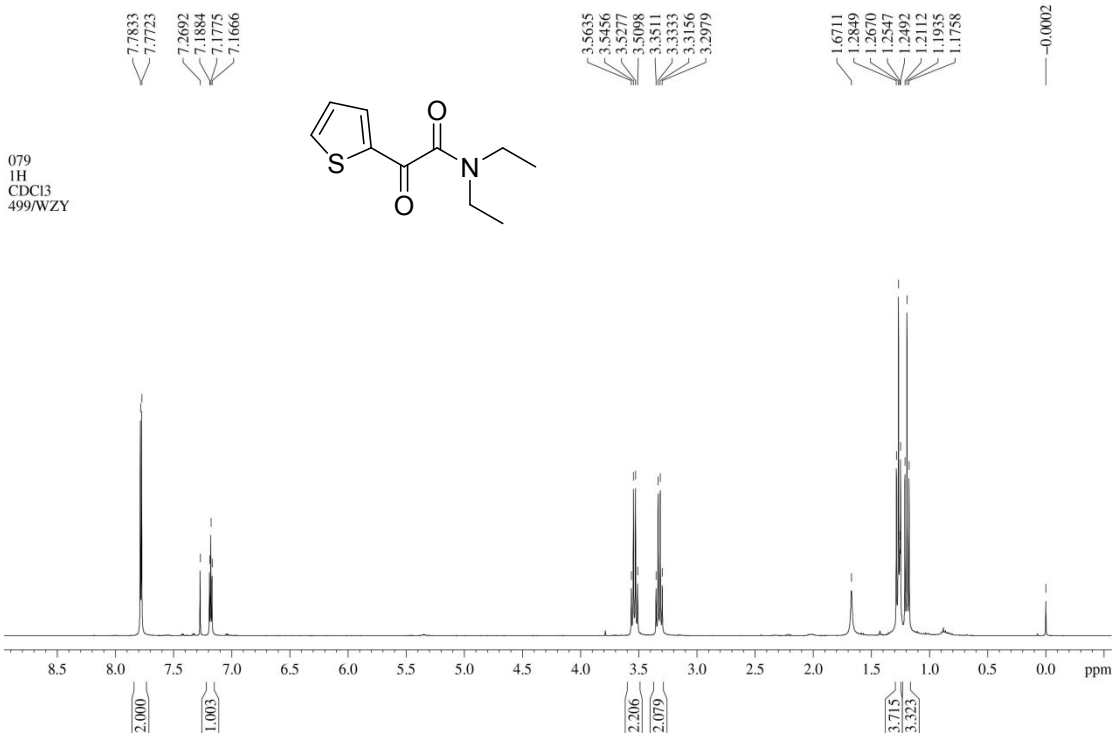
^{13}C NMR spectrum of compound **4u**



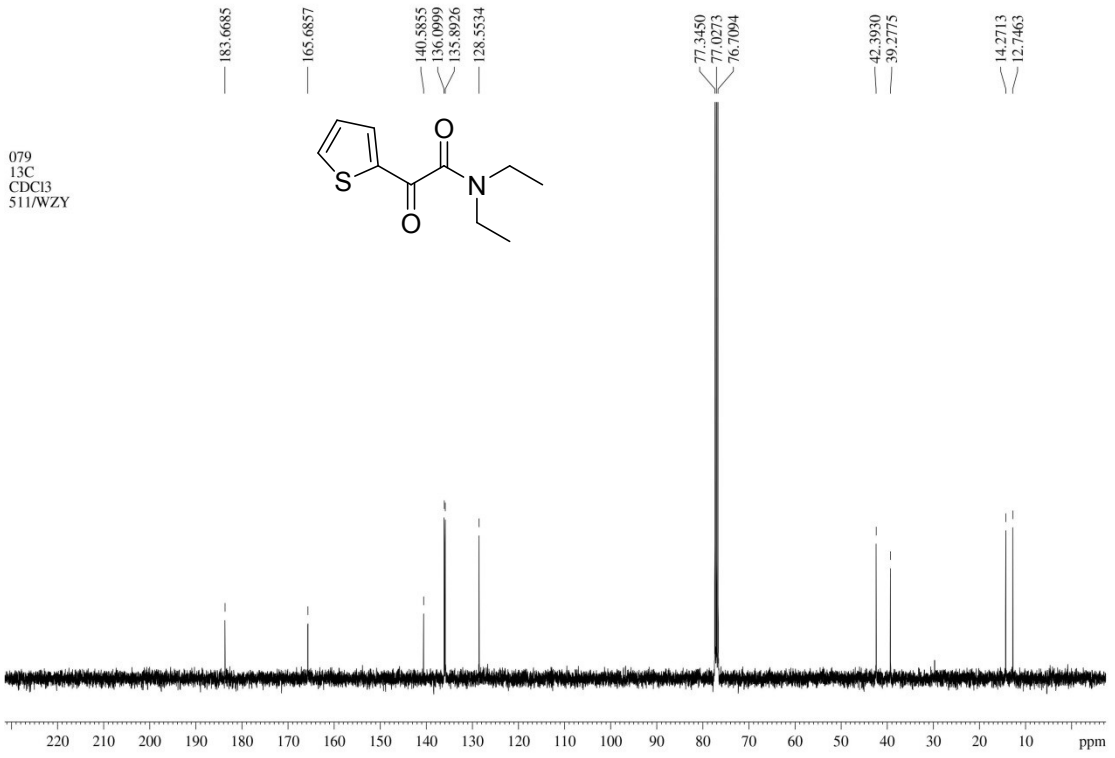
^{1}H NMR spectrum of compound **4v**



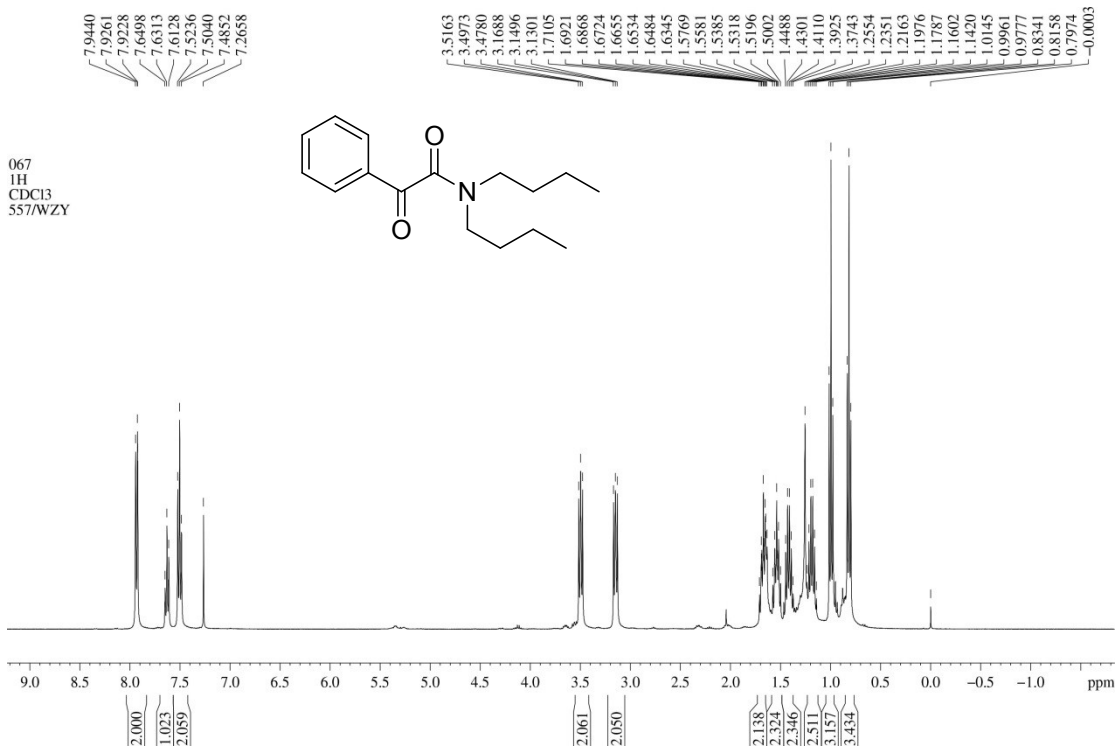
^{13}C NMR spectrum of compound **4v**



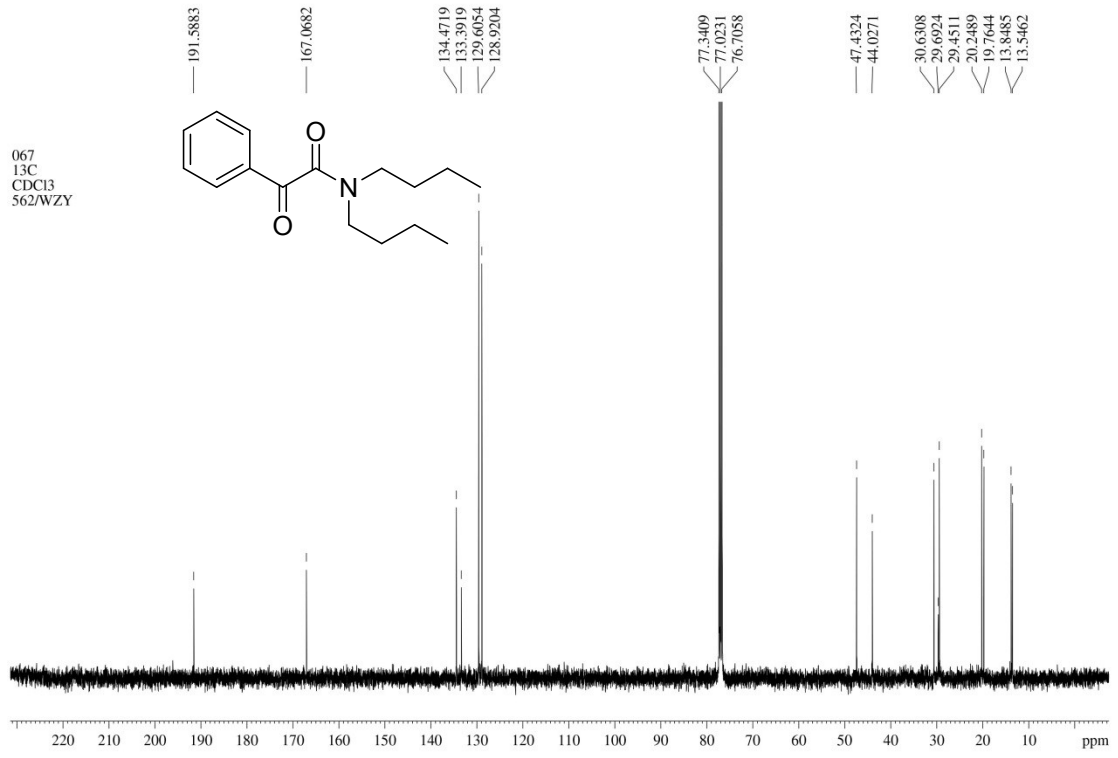
^{1}H NMR spectrum of compound **4w**



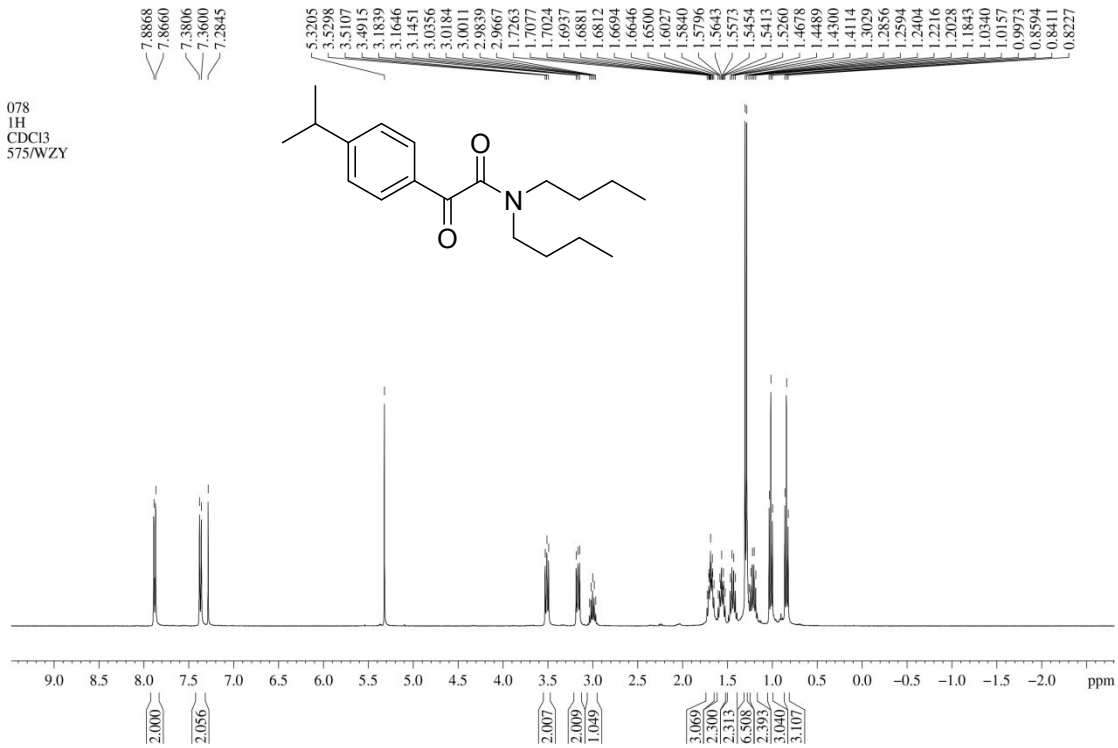
^{13}C NMR spectrum of compound **4w**



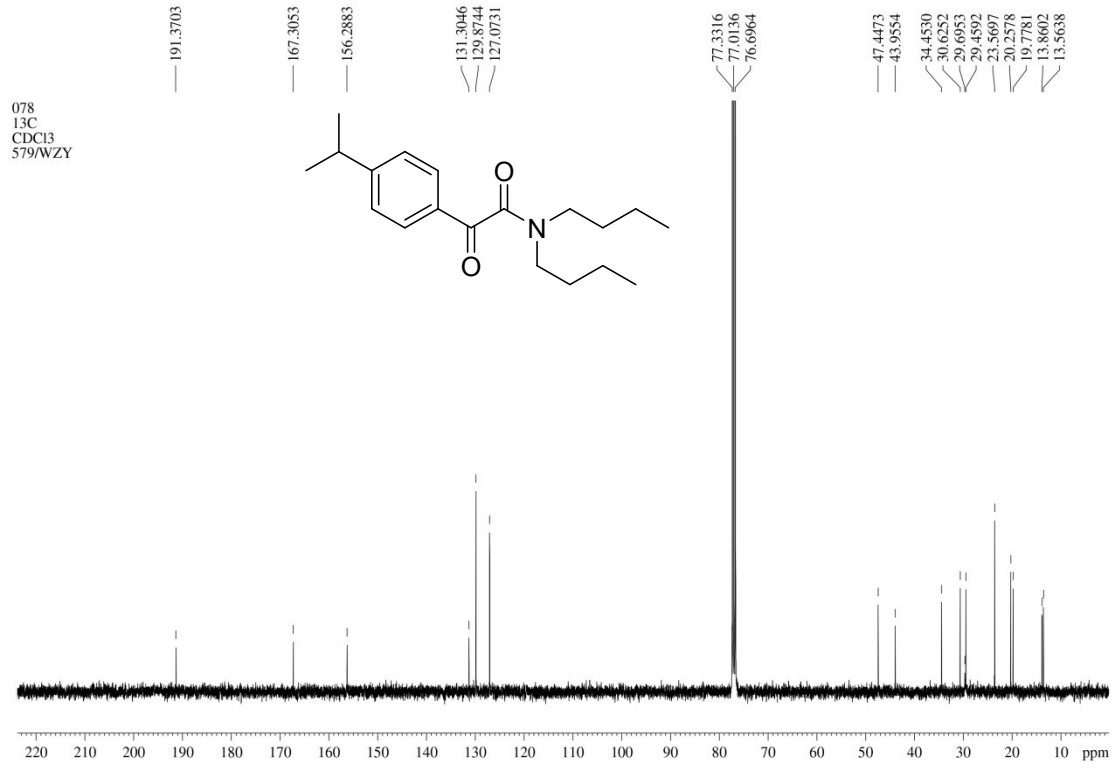
^{1}H NMR spectrum of compound **4x**



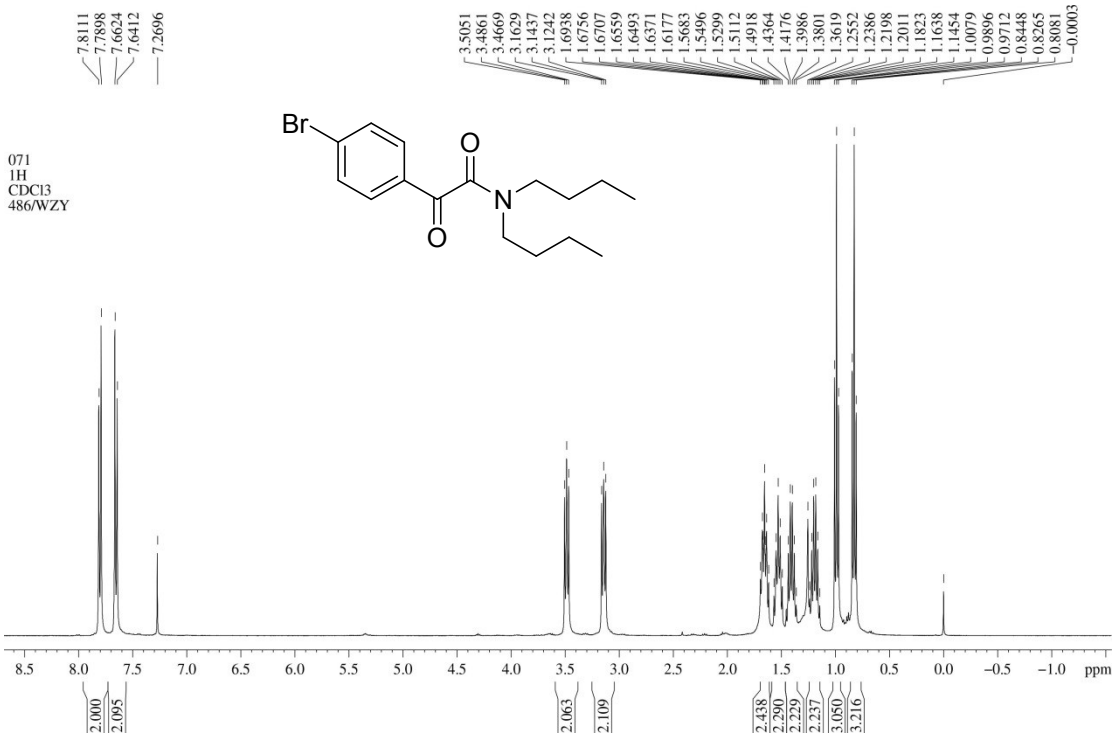
^{13}C NMR spectrum of compound **4x**



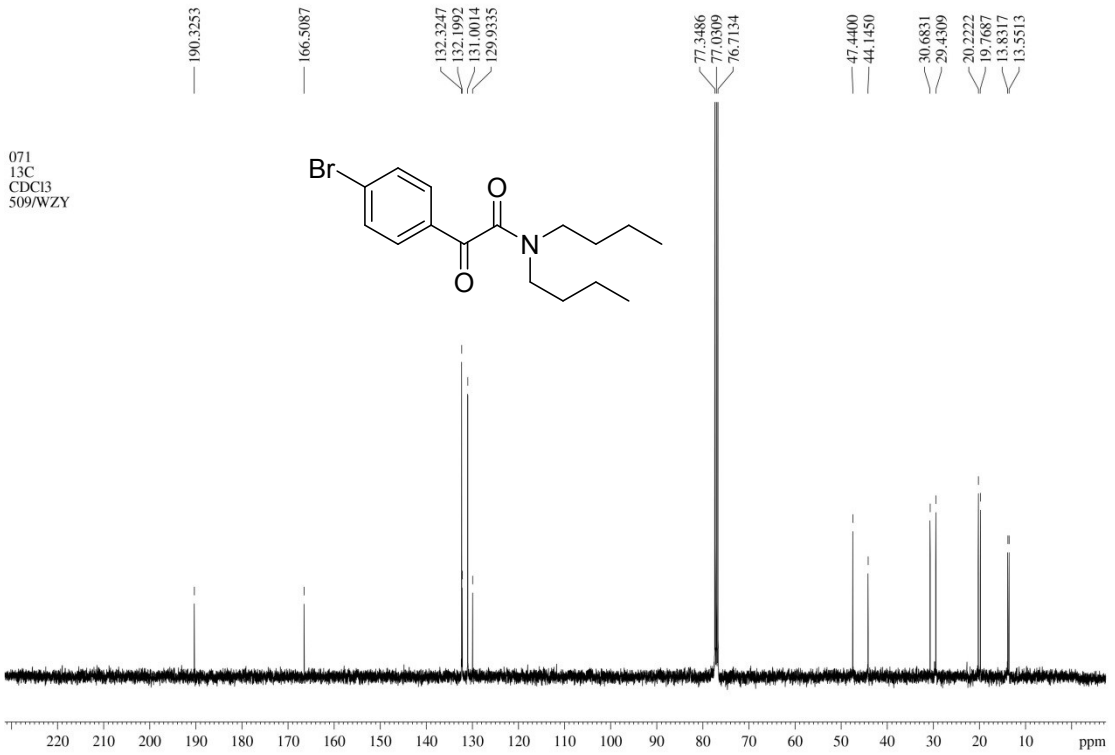
^{1}H NMR spectrum of compound **4y**



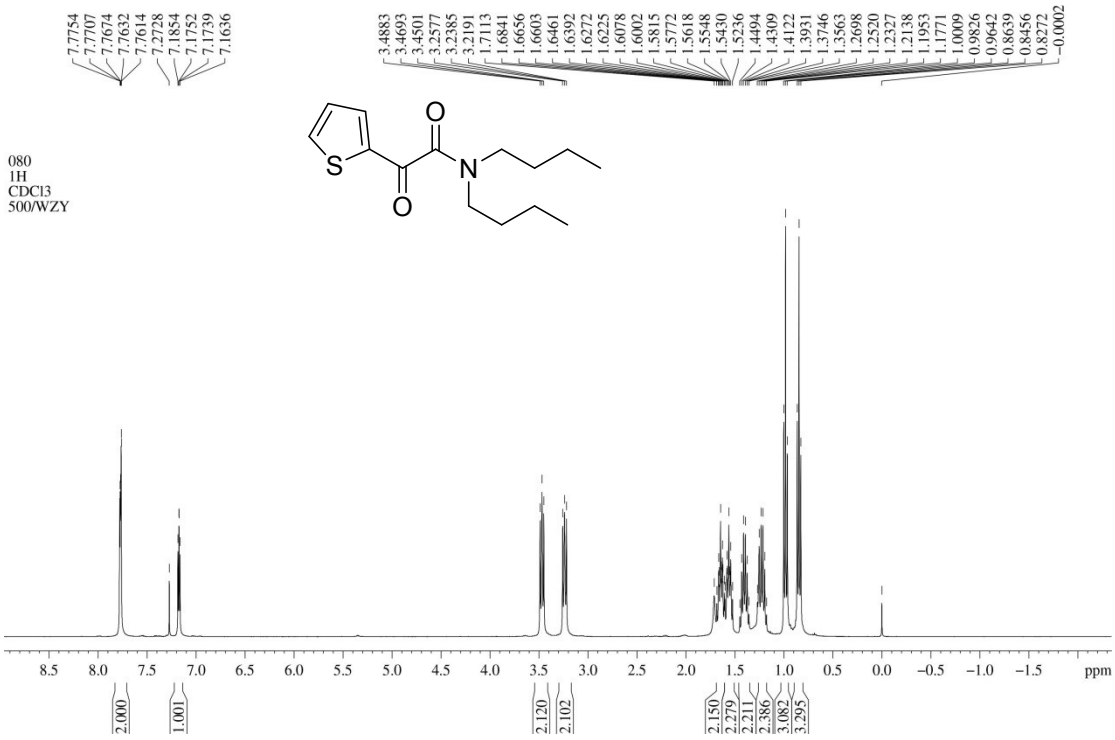
^{13}C NMR spectrum of compound **4y**



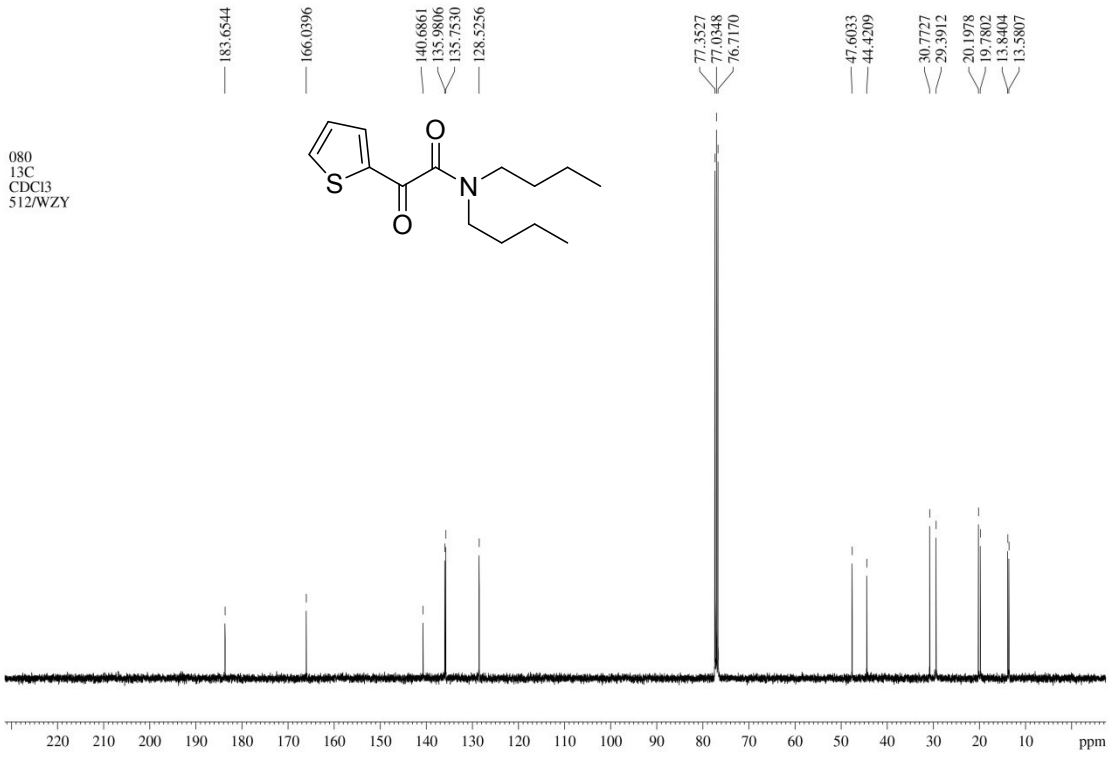
^{1}H NMR spectrum of compound **4z**



^{13}C NMR spectrum of compound **4z**



^{1}H NMR spectrum of compound **4a′**



^{13}C NMR spectrum of compound **4a′**