Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition-Metal Free Direct C-H Functionalization of Quinoxalin-2(1*H*)-ones with Oxamic Acids Leading to 3-Carbamoyl Quinoxalin-2(1*H*)-ones

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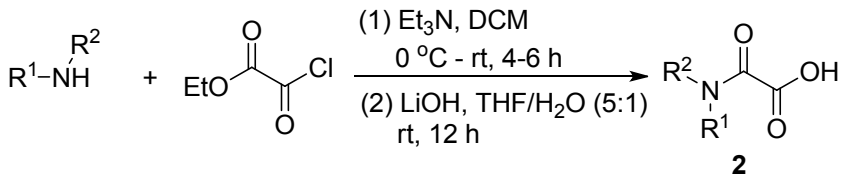
Contents

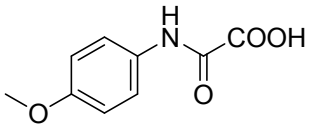
1. General procedure for the preparation of oxamic acids 2a-2u



To a solution of the corresponding aniline or amine (10 mmol) in CH_2Cl_2 (30 mL) was added Et_3N (11 mmol, 1.11g), oxalyl chloride (11 mmol, 1.50 g) was then added to the solution slowly at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4-6 h. The reaction mixture was then treated with 1.0 M HCl (20 mL) and extracted with dichloromethane (3 × 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, directly subjected to hydrolysis.

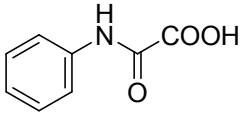
The residue was dissolved in THF (15 mL) and H_2O (5 mL), and LiOH (50 mmol, 4.2 g) was added. After stirring for 6-8 h at room temperature, the basic reaction mixture was washed with dichloromethane (3 × 30 mL). The aqueous phase was separated and acidified with 1.0 M aqueous HCl solution. The resulting mixture was extracted with ethyl acetate (3 × 30 mL) and the combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was recrystallized by CH_2Cl_2/hexanes.

2-((4-Methoxyphenyl)amino)-2-oxoacetic acid (2a)



Colorless powder, mp 134-135 °C; IR (KBr) ν(cm^{-1}): 3352, 3230, 1755, 1678, 1515, 1353, 1253, 1174; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.51 (s, 1H), 7.67 (d, $J_{H\text{-}H}$ = 9.0 Hz, 2H), 6.90 (t, $J_{H\text{-}H}$ = 9.0 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.8 (C=O), 157.8 (C=O), 156.3, 131.4, 122.0 (CH), 114.2 (CH), 55.6 (CH_3).

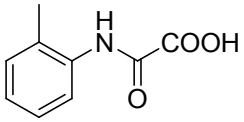
2-Oxo-2-(phenylamino)acetic acid (2b)



Colorless crystal, mp 144-145 °C; IR (KBr) ν(cm^{-1}): 3295, 1763, 1680, 1597, 1545, 1495, 1449, 1345, 1307, 1206; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.72 (s, 1H), 7.79 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H), 7.36 (t, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.14 (t, $J_{H\text{-}H}$ = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.6 (C=O), 157.3

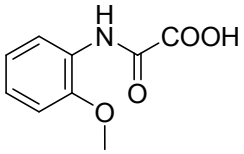
(C=O), 138.1, 129.1 (CH), 125.0 (CH), 120.7 (CH).

2-Oxo-2-(o-tolylamino)acetic acid (2c)



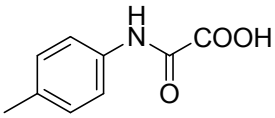
Colorless crystal, mp 111-113 °C; IR (KBr) ν(cm^{-1}): 3257, 2923, 1755, 1680, 1587, 1524, 1347, 1293, 1252, 1212; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.15 (s, 1H), 7.37 (d, $J_{H\text{-}H}$ = 6.9 Hz, 1H), 7.25 (d, $J_{H\text{-}H}$ = 7.6 Hz, 1H), 7.22-7.18 (m, 1H), 7.17-7.13 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.7 (C=O), 157.5 (C=O), 135.4, 133.0, 130.8 (CH), 126.7 (CH), 126.5 (CH), 125.7 (CH), 18.0 (CH_3).

2-((2-Methoxyphenyl)amino)-2-oxoacetic acid (2d)



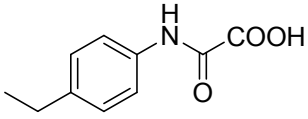
Light yellow crystal, mp 142-143 °C; IR (KBr) ν(cm^{-1}): 3349, 3241, 1757, 1686, 1598, 1540, 1487, 1466, 1344, 1248; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.71 (s, 1H), 8.12 (d, $J_{H\text{-}H}$ = 7.8 Hz, 1H), 7.16-7.09 (m, 2H), 6.98-6.94 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3 (C=O), 157.5 (C=O), 149.2, 126.5, 125.4 (CH), 121.0 (CH), 120.1 (CH), 111.5 (CH), 56.3 (CH_3).

2-Oxo-2-(p-tolylamino)acetic acid (2e)



Colorless crystal, mp >300 °C; IR (KBr) ν(cm^{-1}): 3324, 3229, 1757, 1679, 1511, 1341, 1315, 1199; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.63 (s, 1H), 7.65 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.13 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.7 (C=O), 157.1 (C=O), 135.6, 134.0, 129.5 (CH), 120.7 (CH), 20.9 (CH_3).

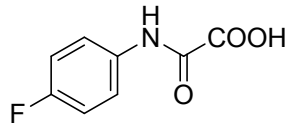
2-((4-Ethylphenyl)amino)-2-oxoacetic acid (2f)



Colorless crystal, mp 119-120 °C; IR (KBr) ν(cm^{-1}): 3300, 2963, 1756, 1682, 1545, 1342, 1308, 1209; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.59 (s, 1H), 7.65 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.17 (d, $J_{H\text{-}H}$ = 8.4

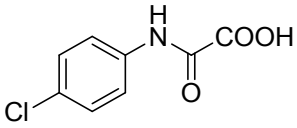
Hz, 2H), 2.56 (q, J_{H-H} = 7.5 Hz, 2H), 1.16 (t, J_{H-H} = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.0 (C=O), 154.7 (C=O), 142.7, 133.1, 128.7 (CH), 120.0 (CH), 28.4 (CH_2), 15.4 (CH_3).

2-((4-Fluorophenyl)amino)-2-oxoacetic acid (2g)



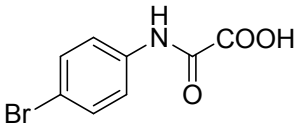
Colorless crystal, mp 141-142 °C; IR (KBr) ν(cm^{-1}): 3634, 3330, 1675, 1550, 1509, 1264, 1240, 1211; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.78 (s, 1H), 7.81-7.77 (m, 2H), 7.21-7.17 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.5 (C=O), 159.1 (d, J_{F-C} = 239.8 Hz), 157.3 (C=O), 134.6, 122.6 (d, J_{F-C} = 7.9 Hz), 115.8 (d, J_{F-C} = 22.2 Hz), ^{19}F NMR (376 MHz, DMSO-d_6)δ: -117.7.

2-((4-Chlorophenyl)amino)-2-oxoacetic acid (2h)



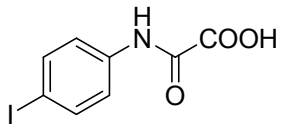
Colorless crystal, mp > 300 °C; IR (KBr) ν(cm^{-1}): 3316, 3229, 1751, 1679, 1492, 1359, 1304, 1206, 1174; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.84 (s, 1H), 7.80 (d, J_{H-H} = 6.9 Hz, 2H), 7.41 (d, J_{H-H} = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3 (C=O), 157.4 (C=O), 137.1, 129.1 (CH), 128.6, 122.3 (CH).

2-((4-Bromophenyl)amino)-2-oxoacetic acid (2i)



Colorless crystal, mp 118-120 °C; IR (KBr) ν(cm^{-1}): 3376, 3279, 1702, 1673, 1586, 1520, 1485; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.74 (s, 1H), 7.74 (dd, J_{H-H} = 7.0 Hz, J_{H-H} = 1.9 Hz, 2H), 7.52 (dd, J_{H-H} = 7.0 Hz, J_{H-H} = 1.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.4 (C=O), 158.8 (C=O), 148.5, 131.9 (CH), 122.4 (CH), 116.4.

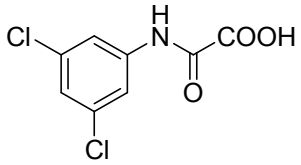
2-((4-Iodophenyl)amino)-2-oxoacetic acid (2j)



Light yellow crystal, mp > 300 °C; IR (KBr) ν(cm^{-1}): 3322, 3229, 1753, 1644, 1339, 1305, 1115; ^{1}H

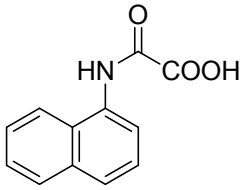
NMR (400 MHz, DMSO-d_6) δ: 10.66 (s, 1H), 7.67 (d, $J_{H\text{-}H}$ = 8.8 Hz, 2H), 7.60 (d, $J_{H\text{-}H}$ = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3 (C=O), 157.4 (C=O), 138.0, 137.8 (CH), 122.9 (CH), 89.0.

2-((3,5-Dichlorophenyl)amino)-2-oxoacetic acid (2k)



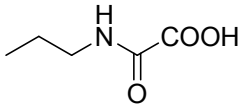
Light yellow crystal, mp 165-167 ^{o}C; IR (KBr) ν(cm^{-1}): 3298, 1733, 1661, 1584, 1544, 1438, 1421, 1172; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.04 (s, 1H), 7.89 (d, $J_{H\text{-}H}$ = 1.8 Hz, 2H), 7.36 (d, $J_{H\text{-}H}$ = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.8 (C=O), 157.6 (C=O), 140.6, 134.5 (CH), 124.2, 118.9 (CH).

2-(Naphthalen-1-ylamino)-2-oxoacetic acid (2l)



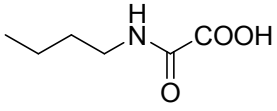
Pale powder, mp 157-158 ^{o}C; IR (KBr) ν(cm^{-1}): 3254, 3049, 1752, 1672, 1533, 1508, 1331, 1228; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.78 (s, 1H), 7.98-7.95 (m, 1H), 7.91 (t, $J_{H\text{-}H}$ = 5.2 Hz, 1H), 7.86 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H), 7.60-7.51 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.8 (C=O), 158.8 (C=O), 134.1, 132.8, 128.7, 128.5 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 125.9 (CH), 123.4 (CH), 123.2 (CH).

2-Oxo-2-(propylamino)acetic acid (2m)



Colorless crystal, mp 76-77 ^{o}C; IR (KBr) ν(cm^{-1}): 3227, 2966, 2936, 2878, 1764, 1666, 1546, 1345, 1241, 1178; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.79 (s, 1H), 3.06 (q, $J_{H\text{-}H}$ = 6.6 Hz, 2H), 1.49-1.40 (m, 2H), 0.81 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.7 (C=O), 158.6 (C=O), 41.1 (CH_2), 22.3 (CH_2), 11.6 (CH_3).

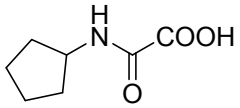
2-(Butylamino)-2-oxoacetic acid (2n)



Colorless crystal, mp 89-90 ^{o}C; IR (KBr) ν(cm^{-1}): 3288, 2953, 2889, 1761, 1675, 1449, 1366, 1343,

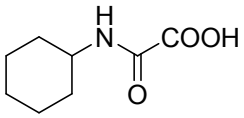
1177; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.79 (s, 1H), 3.10 (q, $J_{H\text{-}H}$ = 6.8 Hz, 2H), 1.46-1.39 (m, 2H), 1.30-1.21 (m, 2H), 0.86 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.7 (C=O), 158.6 (C=O), 39.0 (CH_2), 31.1 (CH_2), 19.9 (CH_2), 14.0 (CH_3).

2-(Cyclopentylamino)-2-oxoacetic acid (2o)



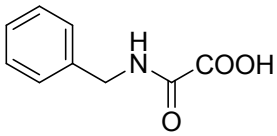
Colorless crystal, mp 120-122 °C; IR (KBr) ν(cm^{-1}): 3272, 2958, 2873, 1759, 1666, 1545,1373, 1335, 1241, 1173; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.68 (d, $J_{H\text{-}H}$ = 7.4 Hz, 1H), 4.04-3.98 (m, 1H), 1.83-1.76 (m, 2H), 1.67-1.61 (m, 2H), 1.52-1.44 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.9 (C=O), 158.7 (C=O), 51.1 (CH), 32.1 (CH_2), 23.9 (CH_2).

2-(cyclohexylamino)-2-oxoacetic acid (2p)



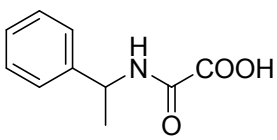
Colorless crystal, mp 118-119 °C; IR (KBr) ν(cm^{-1}): 3277, 2948, 2855, 1760, 1670, 1545, 1448, 1348, 1305, 1249; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.59 (d, $J_{H\text{-}H}$ = 8.2 Hz, 1H), 3.54 (d, $J_{H\text{-}H}$ = 8.2 Hz, 1H), 1.69-1.66 (m, 4H), 1.55 (d, $J_{H\text{-}H}$ = 12.4 Hz, 1H), 1.33-1.18 (m, 4H), 1.08-1.02 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.9 (C=O), 157.9 (C=O), 48.7 (CH), 32.1 (CH_2), 25.4 (CH_2), 25.1 (CH_2).

2-(Benzylamino)-2-oxoacetic acid (2q)



Colorless crystal, mp 145-146 °C; IR (KBr) ν(cm^{-1}): 3287, 1756, 1676, 1551, 1454, 1363, 1344, 1246, 1175; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.31 (t, $J_{H\text{-}H}$ = 6.2 Hz, 1H), 7.34-7.30 (m, 2H), 7.27-7.22 (m, 3H), 4.30 (d, $J_{H\text{-}H}$ = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.7 (C=O), 159.2 (C=O), 139.1, 128.7 (CH), 127.7 (CH), 127.3 (CH), 42.8 (CH_2).

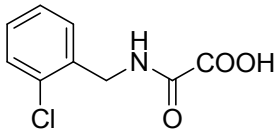
2-Oxo-2-((1-phenylethyl)amino)acetic acid (2r)



Colorless crystal, mp 110-112 °C; IR (KBr) ν(cm^{-1}): 3298, 1765, 1669, 1449, 1362, 1335, 1307,

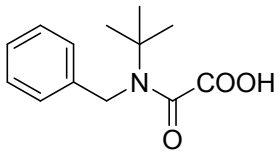
1237; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.18 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1H), 7.36-7.29 (m, 4H), 4.98-4.90 (m, 1H), 1.42 (d, $J_{H\text{-}H}$ = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.9 (C=O), 158.5 (C=O), 144.2, 128.7 (CH), 127.3 (CH), 126.6 (CH), 48.9 (CH), 22.2 (CH_3).

2-((2-Chlorobenzyl)amino)-2-oxoacetic acid (2s)



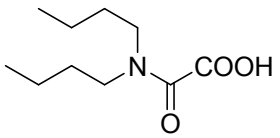
Colorless crystal, mp 145-146 °C; IR (KBr) ν(cm^{-1}): 3477, 3389, 1677, 1546, 1423, 1316, 1256; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.34 (t, $J_{H\text{-}H}$ = 6.0 Hz, 1H), 7.45-7.43 (m, 1H), 7.33-7.28 (m, 3H), 4.40 (d, $J_{H\text{-}H}$ = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.4 (C=O), 159.2 (C=O), 135.7, 132.3, 129.5 (CH), 129.1 (CH), 128.9 (CH), 127.6 (CH), 40.7 (CH_2).

2-(Benzyl(*tert*-butyl)amino)-2-oxoacetic acid (2t)



Colorless crystal, mp 128-130 °C; IR (KBr) ν(cm^{-1}): 3479, 2981, 1730, 1609, 1446, 1360, 1289, 1186; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.38-7.24 (m, 5H), 4.55 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.6 (C=O), 165.4 (C=O), 139.2, 128.8 (CH), 127.5 (CH), 126.9 (CH), 58.0, 49.5 (CH_2), 28.0 (CH_3).

2-(dibutylamino)-2-oxoacetic acid (2u)



Colorless viscous liquid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.24 (d, $J_{H\text{-}H}$ = 7.5 Hz, 2H), 3.18 (d, $J_{H\text{-}H}$ = 7.5 Hz, 2H), 1.54-1.41 (m, 4H), 1.29-1.17 (m, 4H), 0.89-0.83 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.6 (C=O), 163.2 (C=O), 47.2 (CH_2), 43.1 (CH_2), 30.6 (CH_2), 29.2 (CH_2), 19.9 (CH_2), 19.6 (CH_2), 14.0 (CH_3), 13.8 (CH_3).

2. Screening the reaction conditions

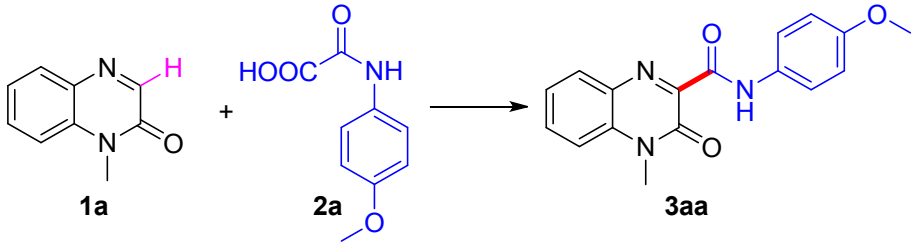


Table S1 Screening the molar ratio of reaction substrates[a]

Entry	The molar ratio of **1a** and **2a**	Yields (%)[b]
1	1:1	73
2	1:1.2	86
3	1:1.5	80
4	1:2	78

[a] Reaction conditions: 1-methylquinoxalin-2(1*H*)-one **1a** (0.2 mmol, 32.0 mg), 2-((4-methoxyphenyl)amino)-2-oxoacetic acid **2a**, $(NH_4)_2S_2O_8$ (0.5 mmol, 114 mg) in 2.0 mL DMSO-H_2O (600:1, v/v) co-solvent at 60 °C for 4.0 h.

[b] Isolated yield.

3. NMR spectra of compounds **2a-2u**

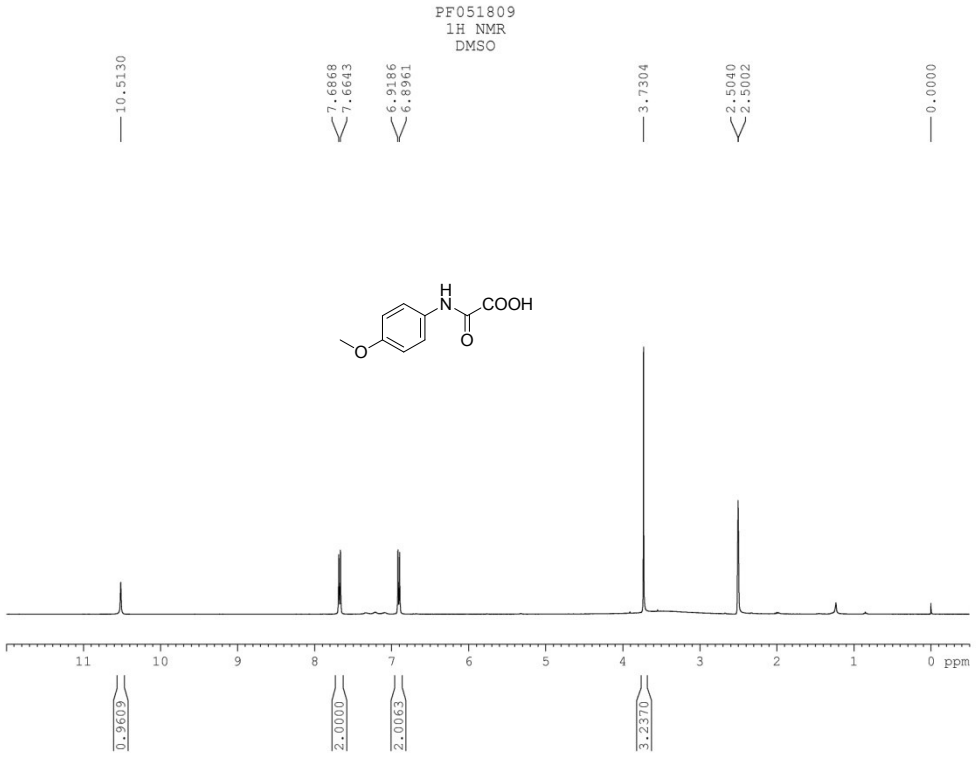


Fig. S1 ^{1}H NMR spectrum of compound **2a**

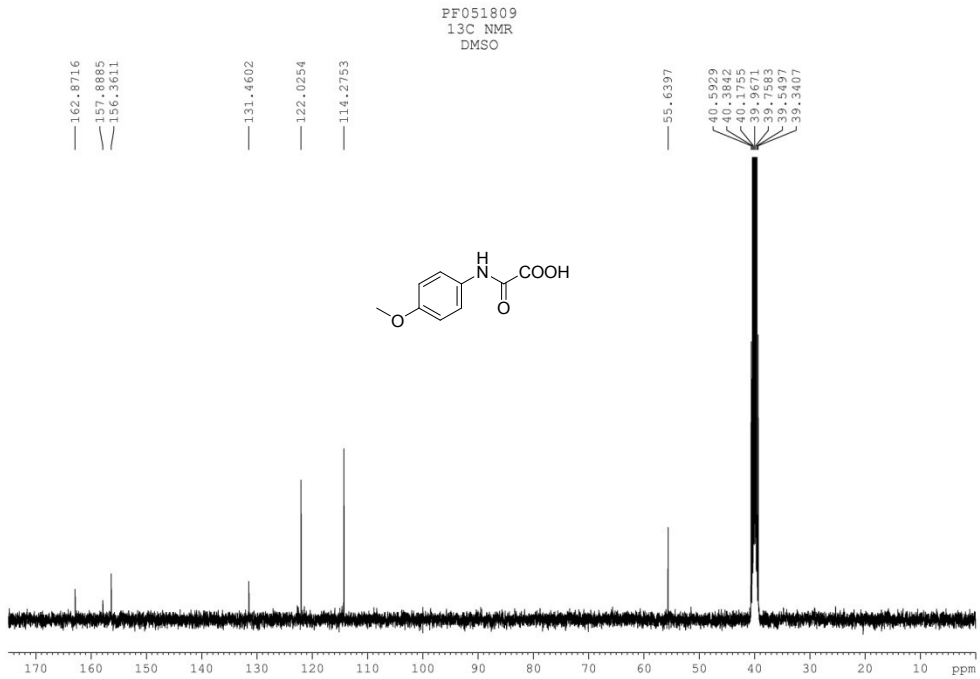


Fig. S2 ^{13}C NMR spectrum of compound **2a**

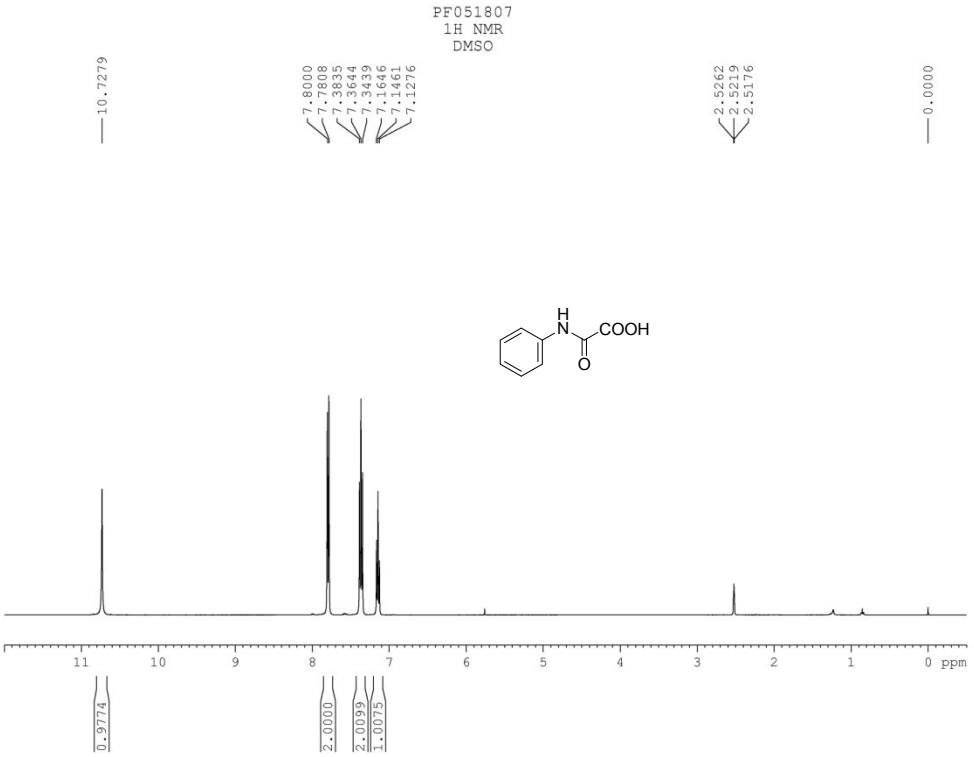


Fig. S3 ^{1}H NMR spectrum of compound **2b**

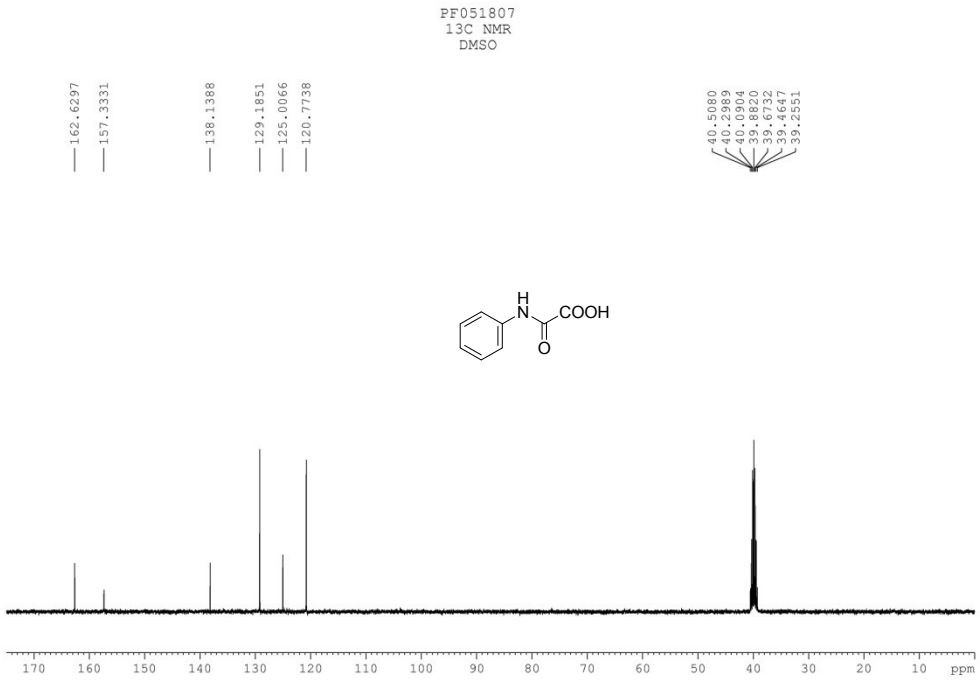


Fig. S4 ^{13}C NMR spectrum of compound **2b**

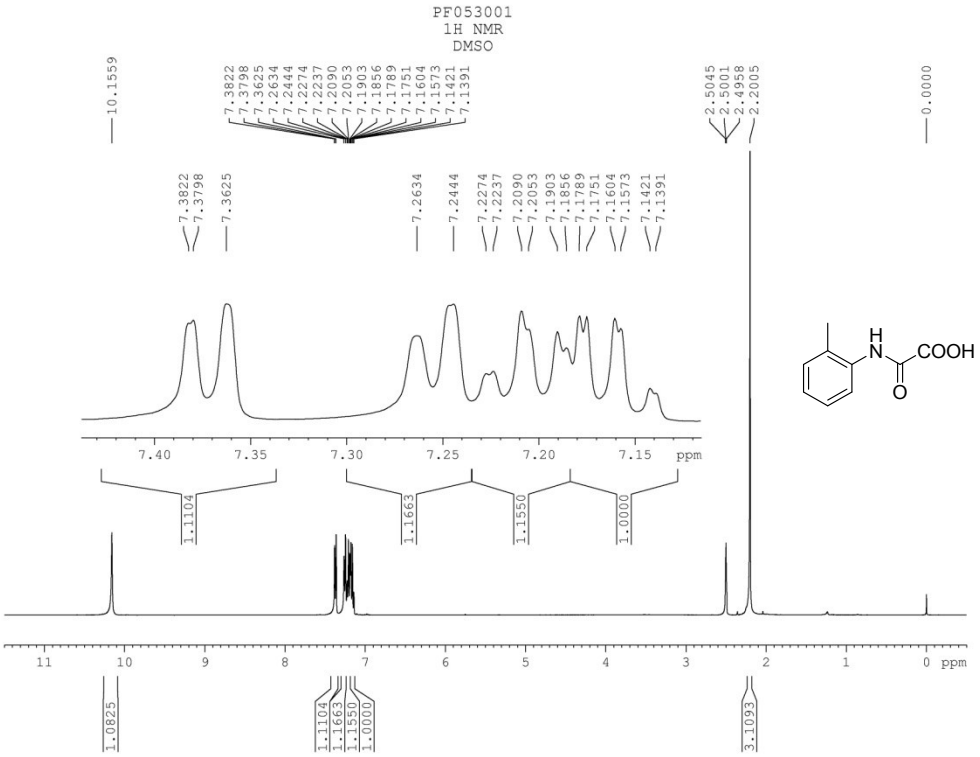


Fig. S5 ^{1}H NMR spectrum of compound **2c**

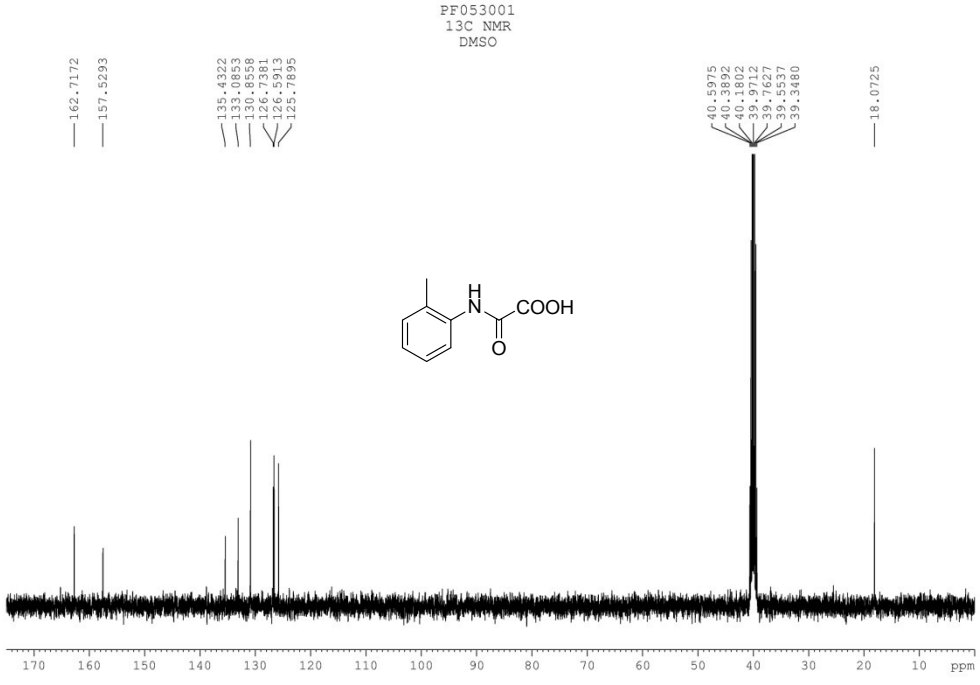


Fig. S6 ^{13}C NMR spectrum of compound **2c**

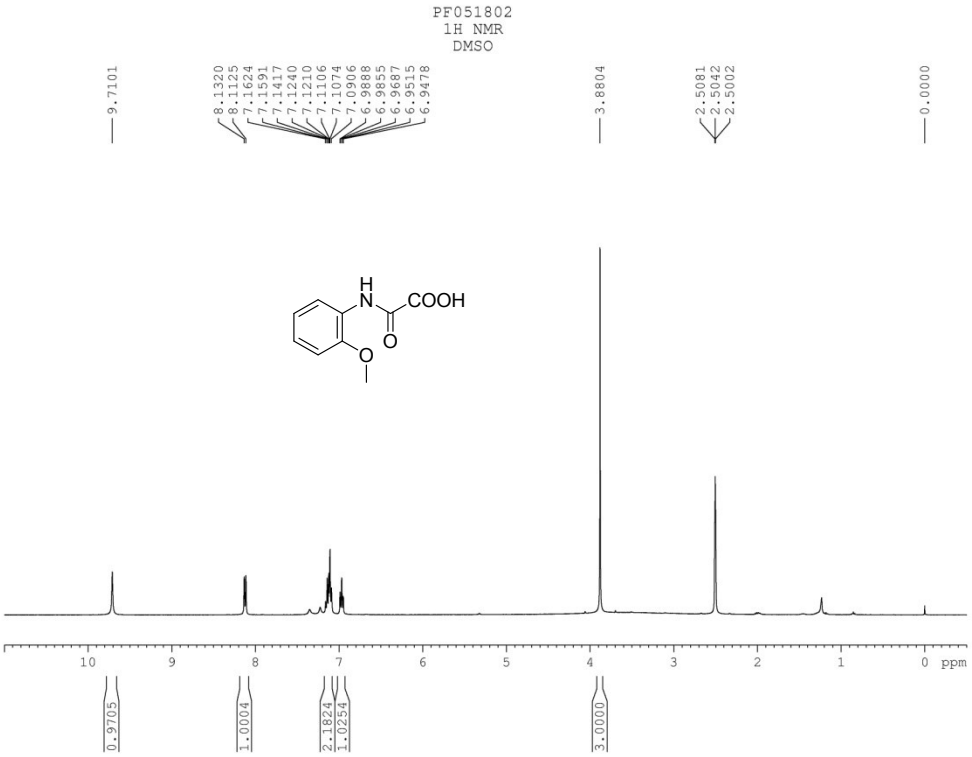


Fig. S7 ^{1}H NMR spectrum of compound **2d**

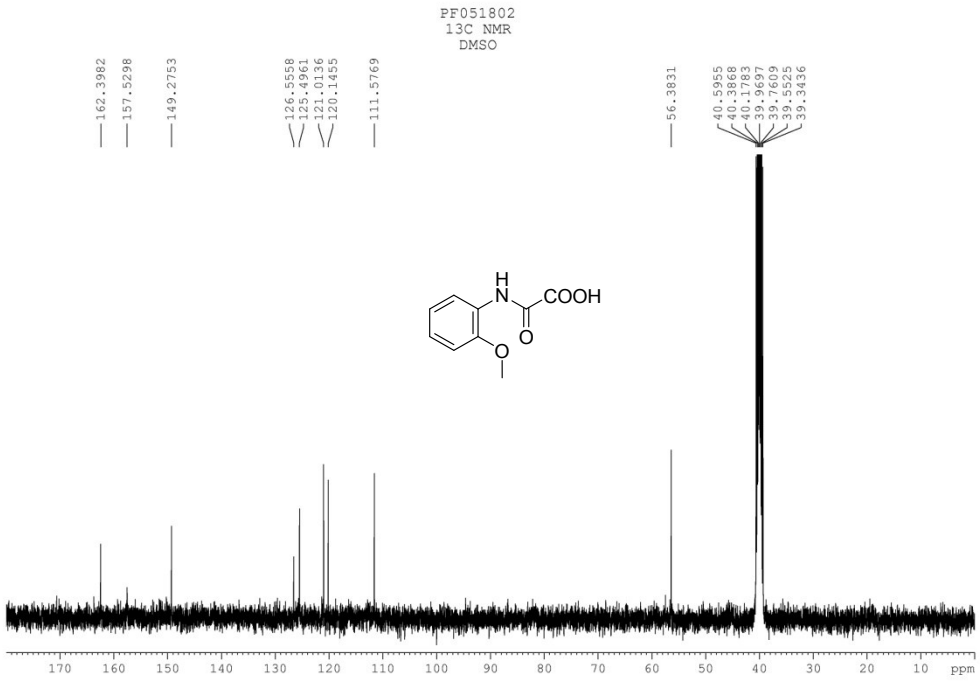


Fig. S8 ^{13}C NMR spectrum of compound **2d**

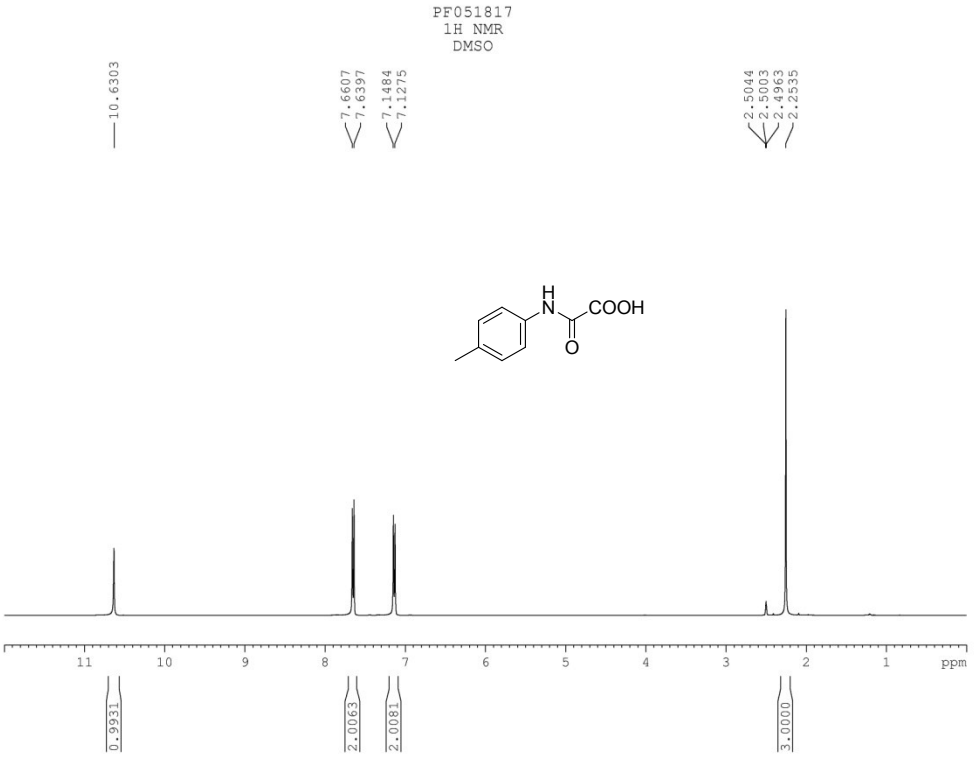


Fig. S9 ^{1}H NMR spectrum of compound **2e**

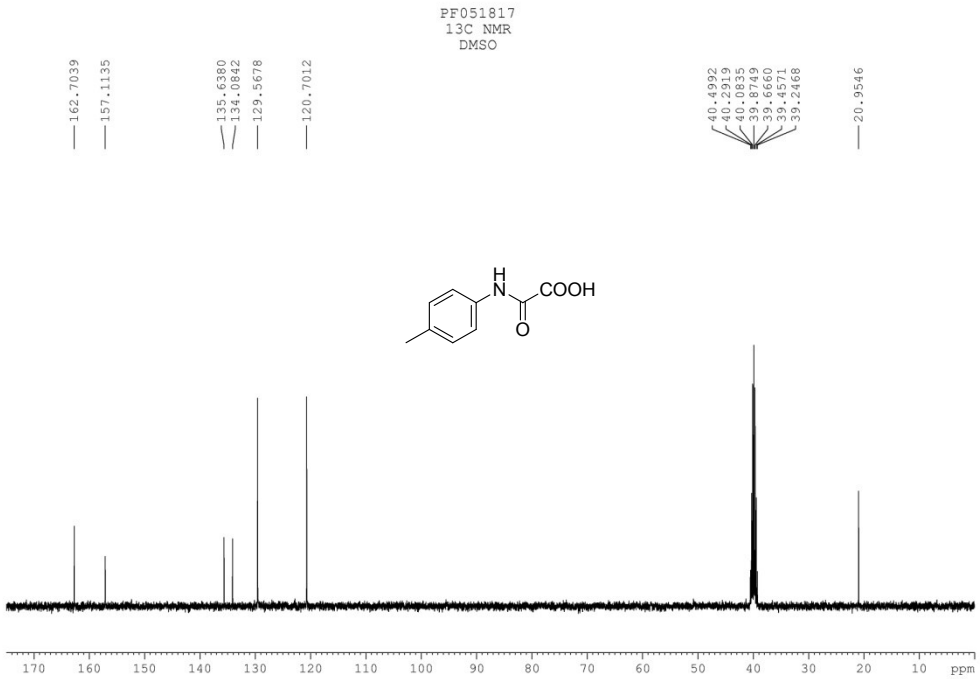


Fig. S10 ^{13}C NMR spectrum of compound **2e**

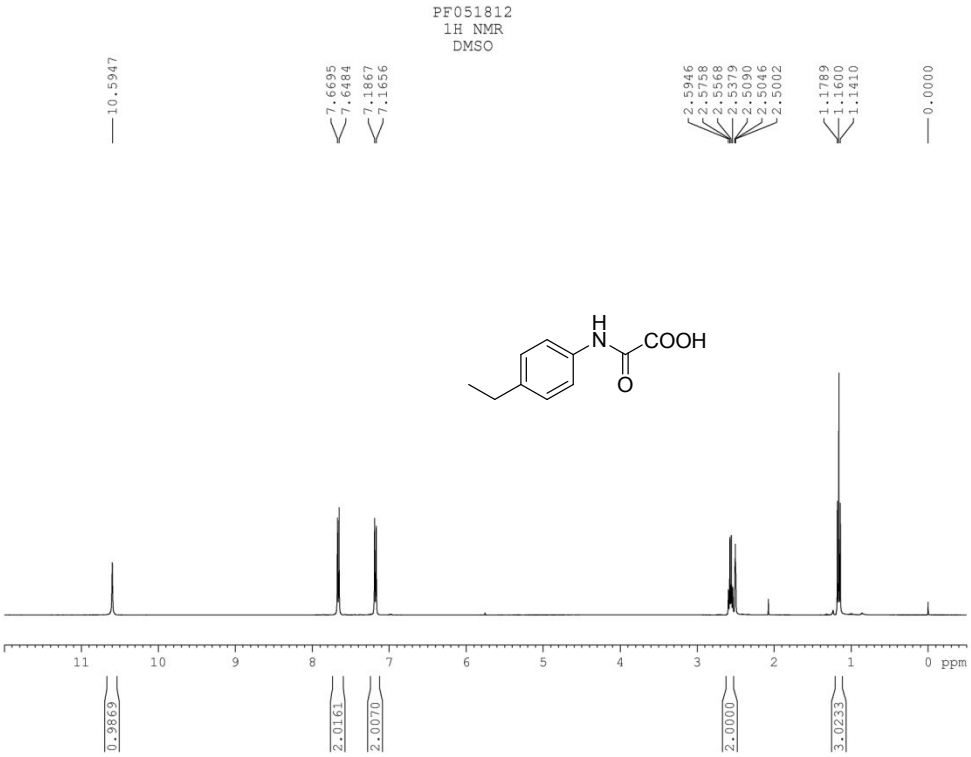


Fig. S11 ^{1}H NMR spectrum of compound **2f**

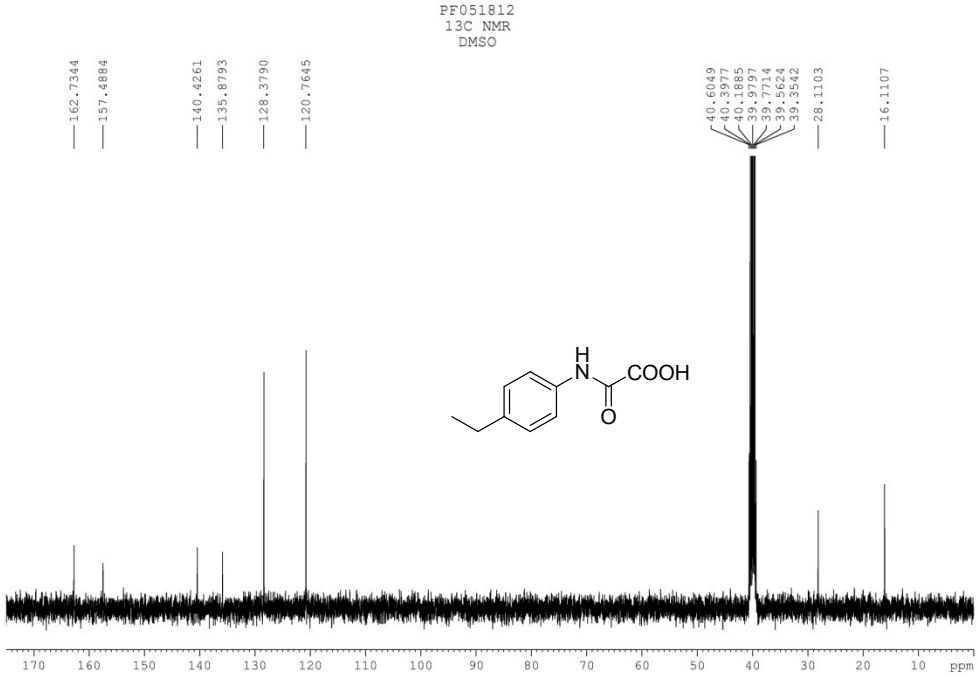


Fig. S12 ^{13}C NMR spectrum of compound **2f**

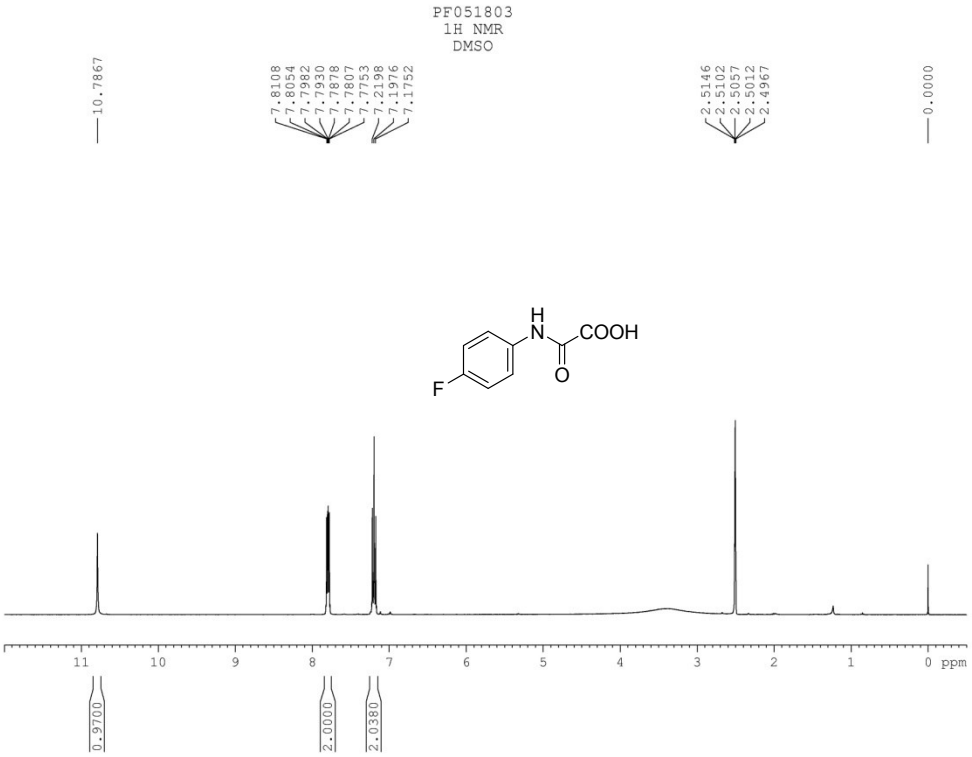


Fig. S13 ^{1}H NMR spectrum of compound **2g**

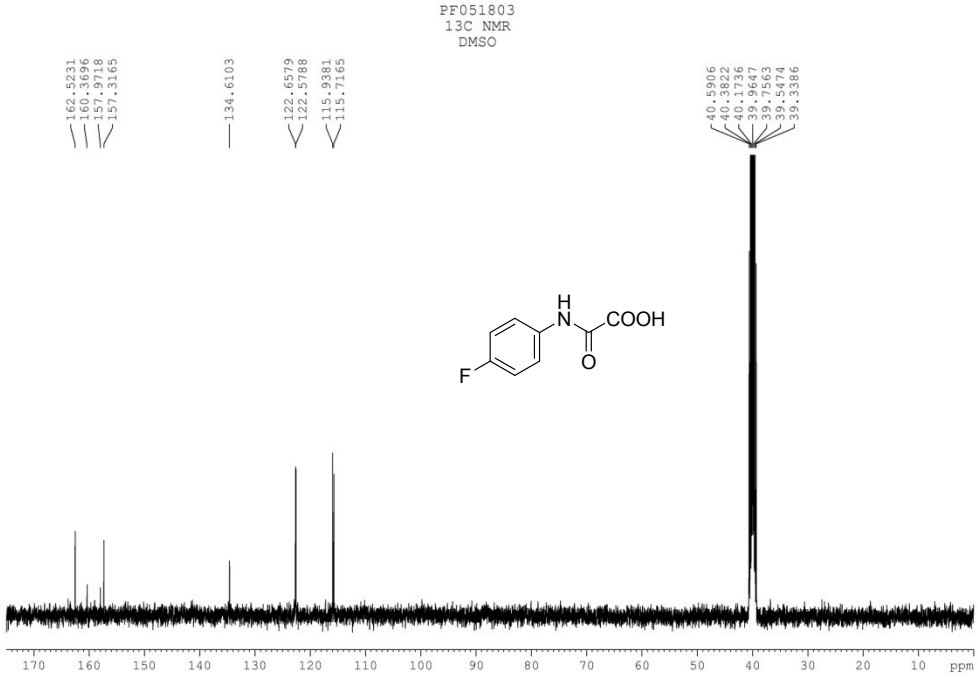


Fig. S14 ^{13}C NMR spectrum of compound **2g**

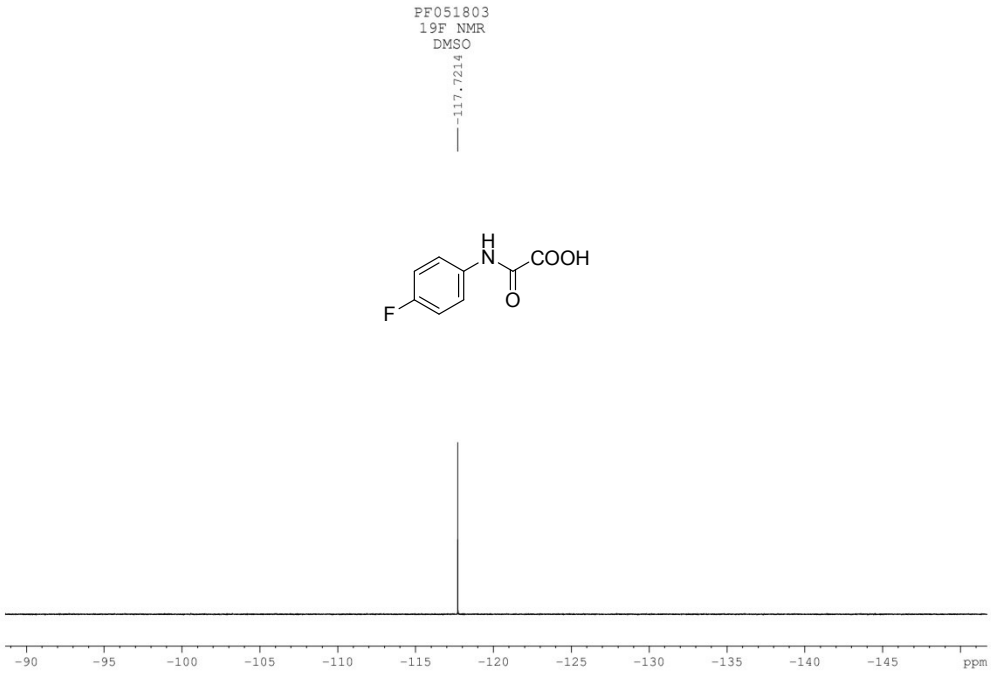


Fig. S15 ^{19}F NMR spectrum of compound **2g**

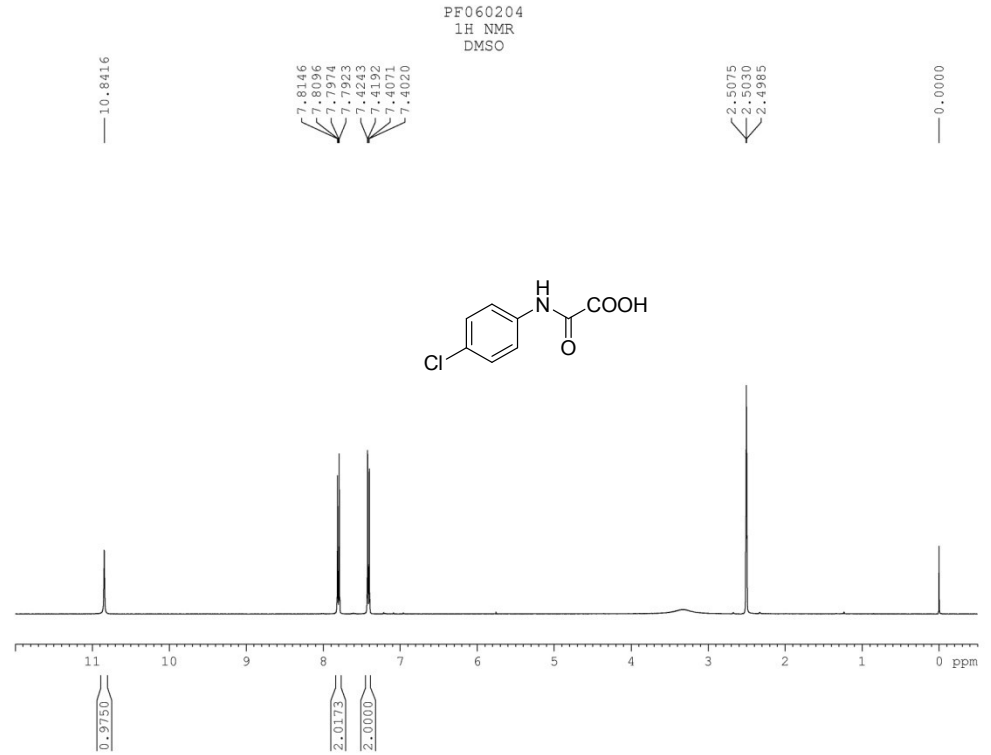


Fig. S16 ^{1}H NMR spectrum of compound **2h**

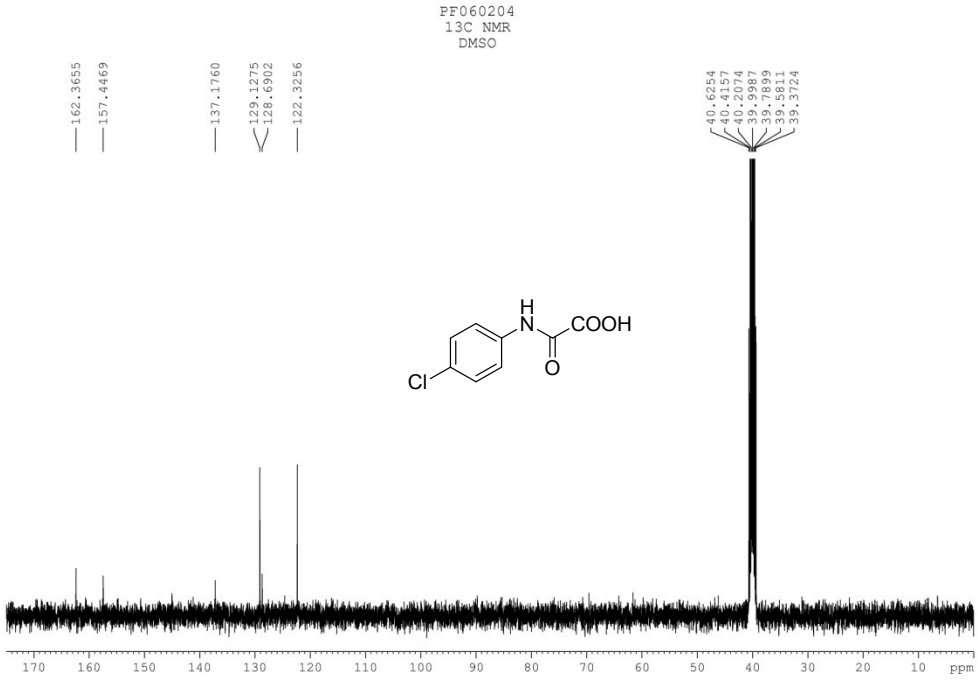


Fig. S17 ^{13}C NMR spectrum of compound **2h**

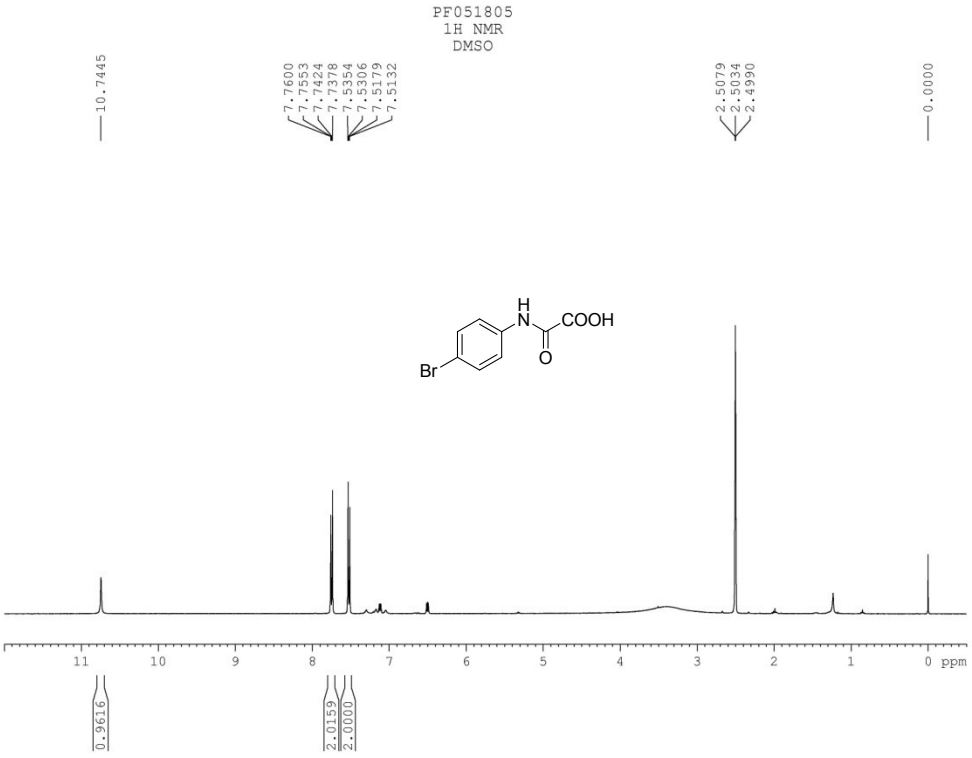


Fig. S18 ^{1}H NMR spectrum of compound **2i**

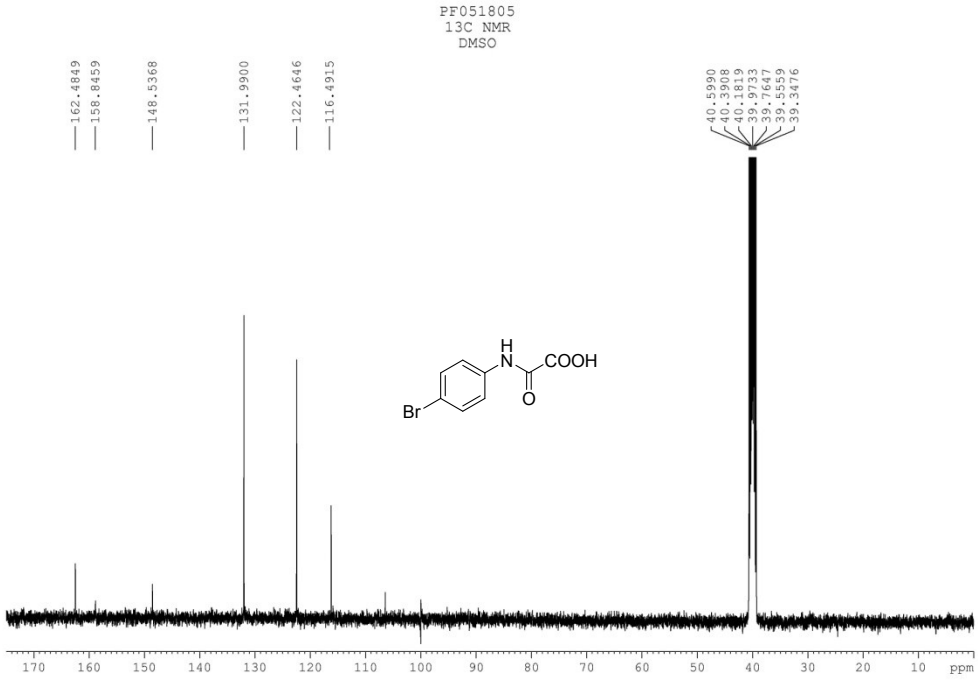


Fig. S19 ^{13}C NMR spectrum of compound **2i**

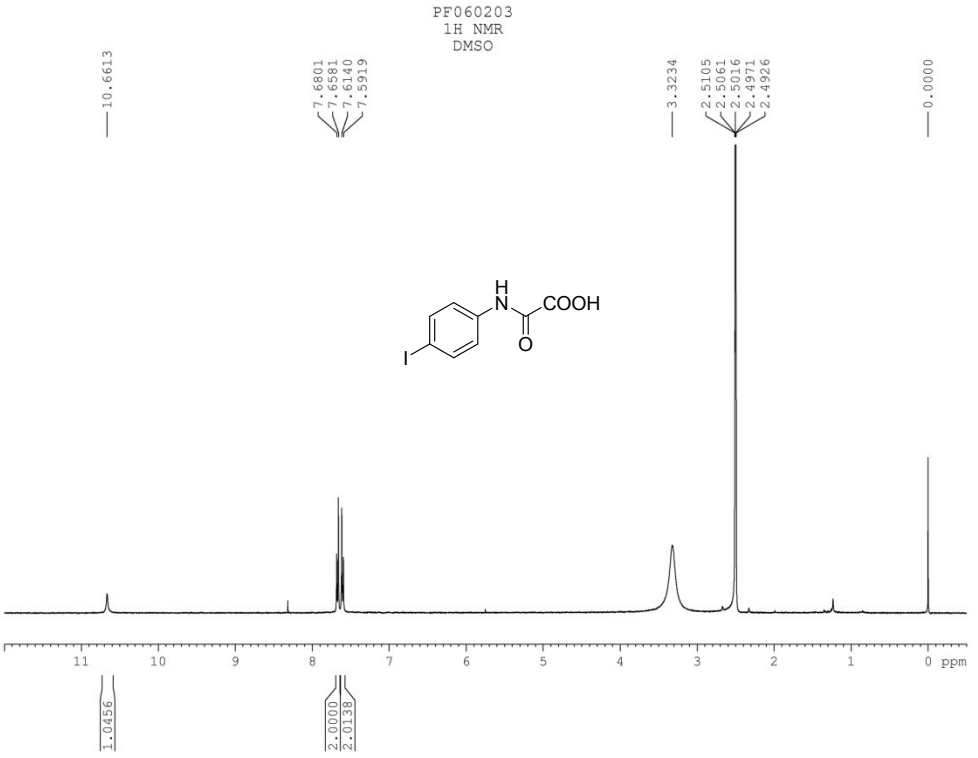


Fig. S20 ^{1}H NMR spectrum of compound **2j**

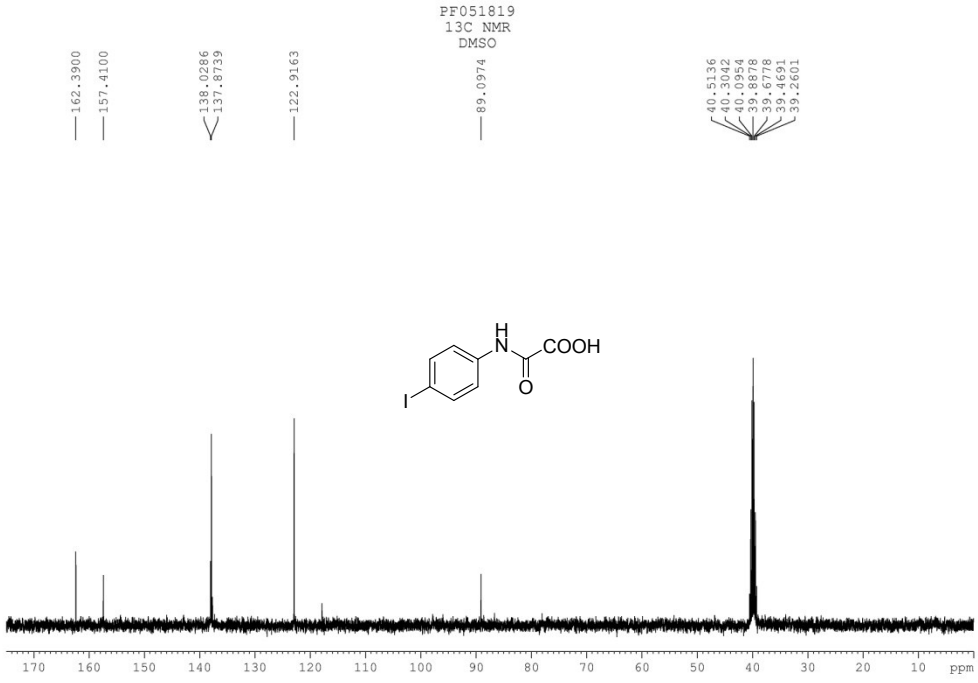


Fig. S21 ^{13}C NMR spectrum of compound **2j**

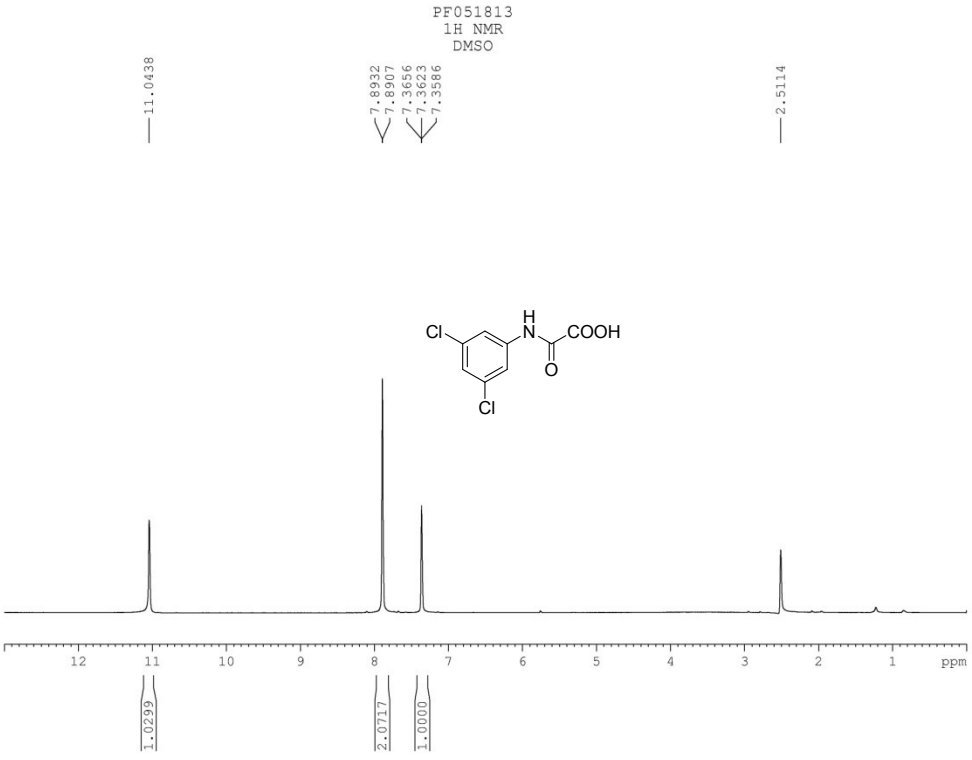


Fig. S22 ^{1}H NMR spectrum of compound **2k**

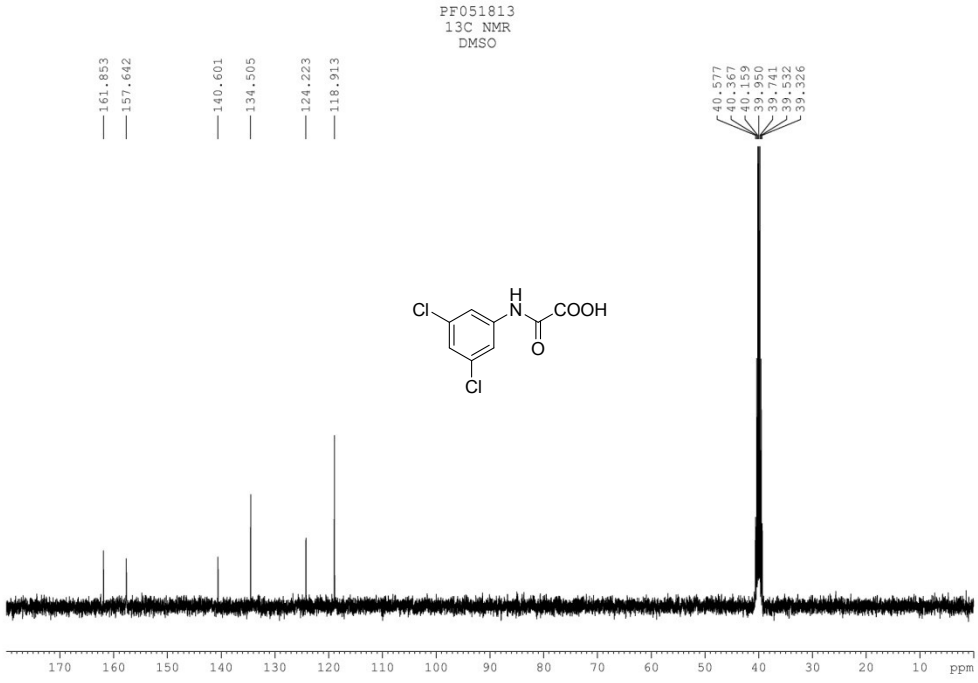


Fig. S23 ^{13}C NMR spectrum of compound **2k**

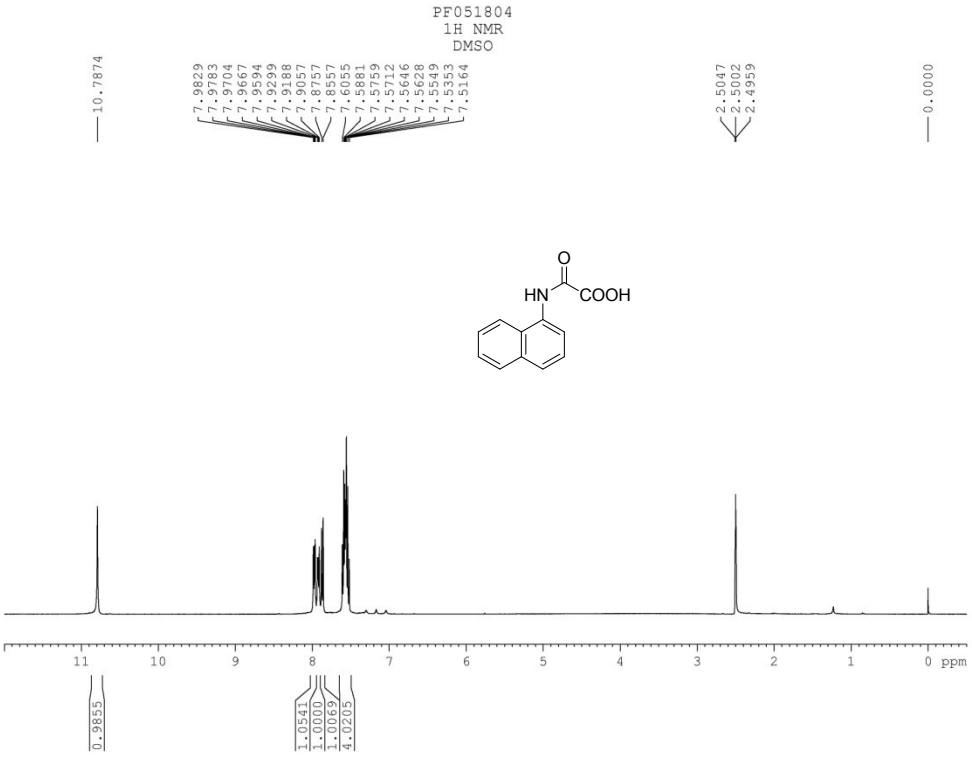


Fig. S24 ^{1}H NMR spectrum of compound **2l**

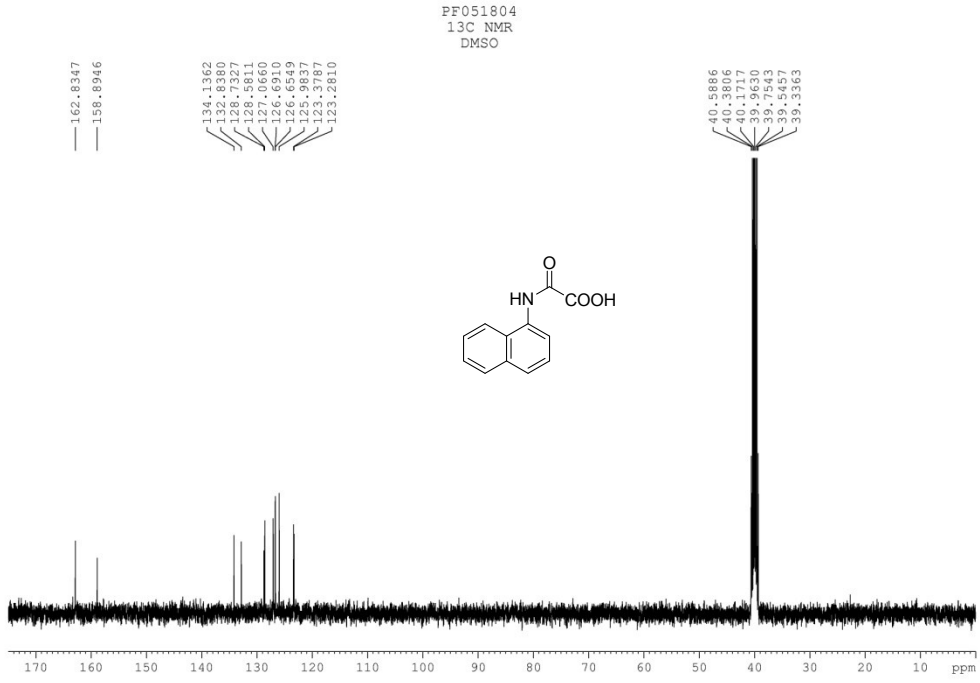


Fig. S25 ^{13}C NMR spectrum of compound **2l**

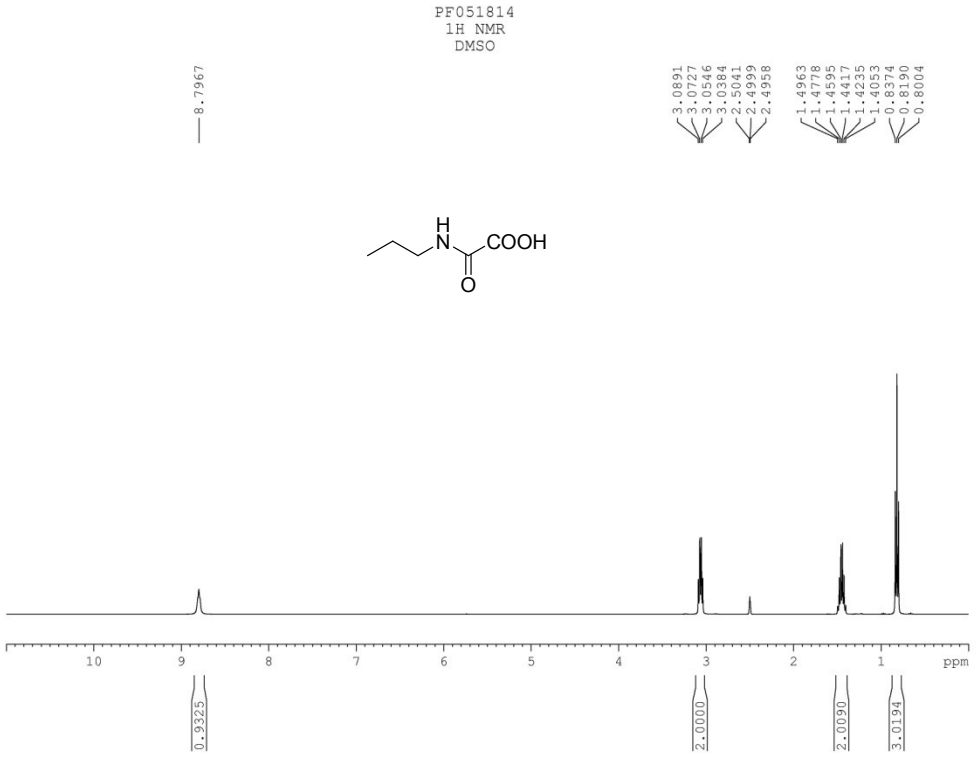


Fig. S26 ^{1}H NMR spectrum of compound **2m**

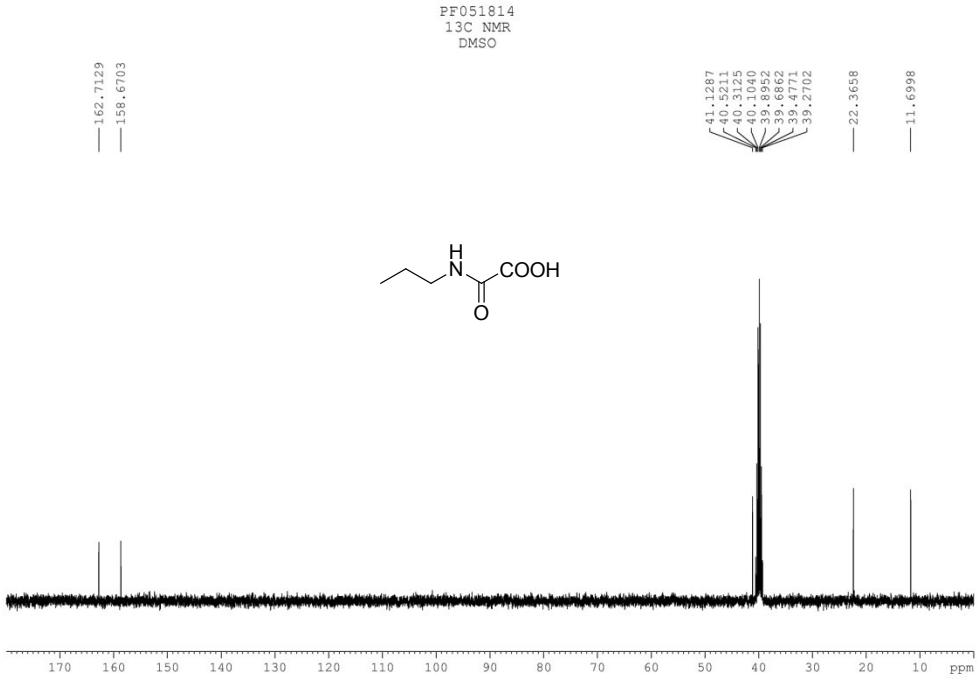


Fig. S27 ^{13}C NMR spectrum of compound **2m**

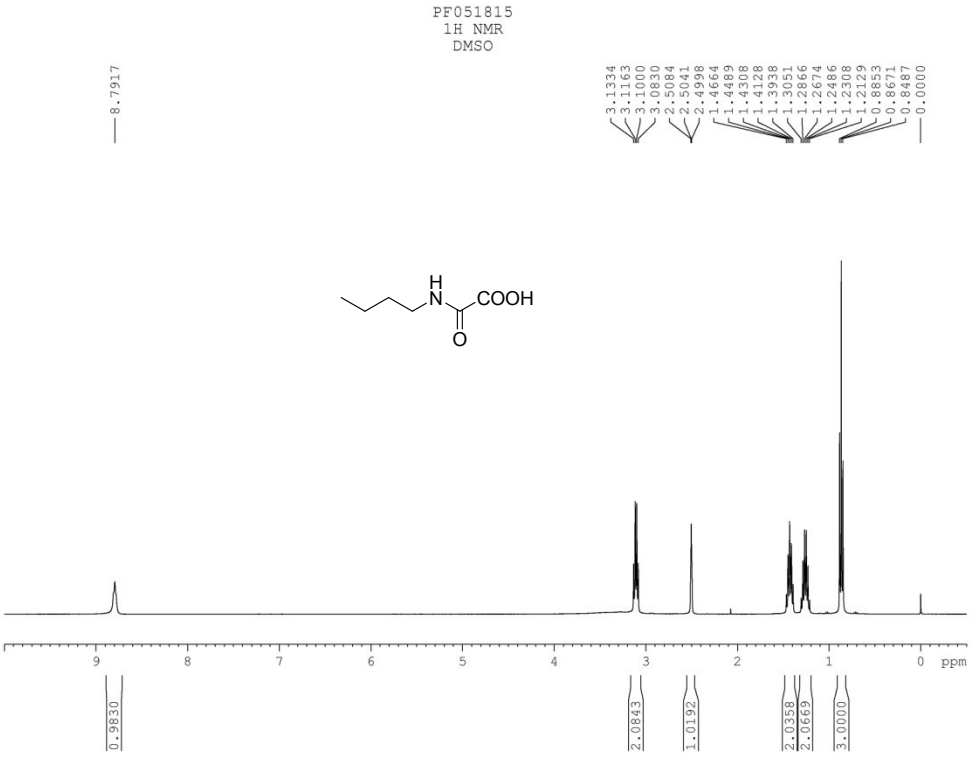


Fig. S28 ^{1}H NMR spectrum of compound **2n**

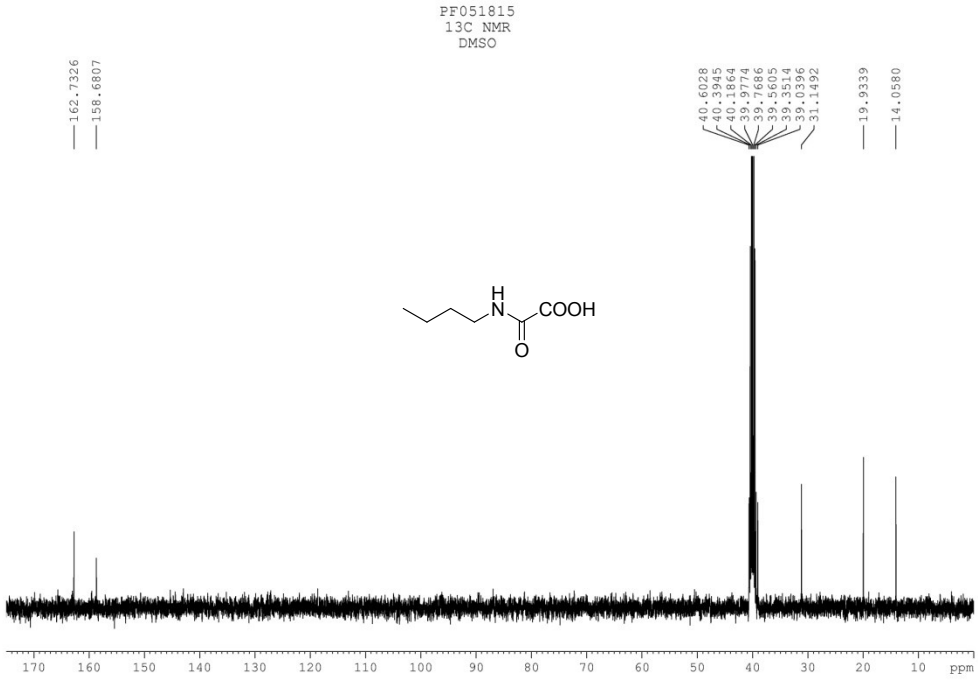


Fig. S29 ^{13}C NMR spectrum of compound **2n**

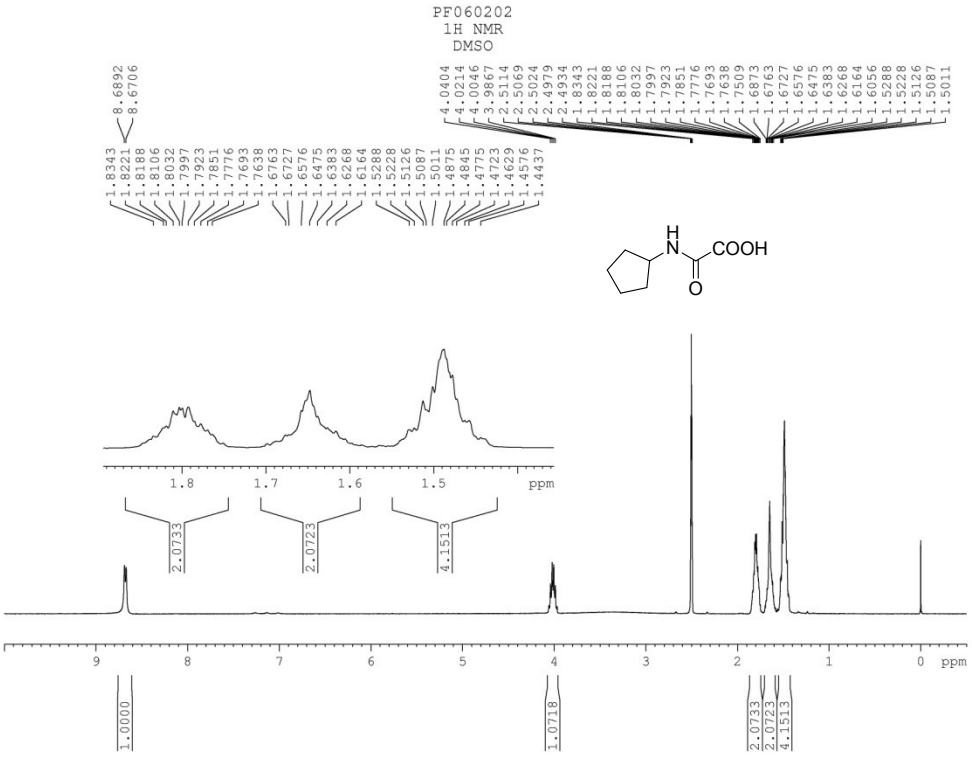


Fig. S30 ^{1}H NMR spectrum of compound **2o**

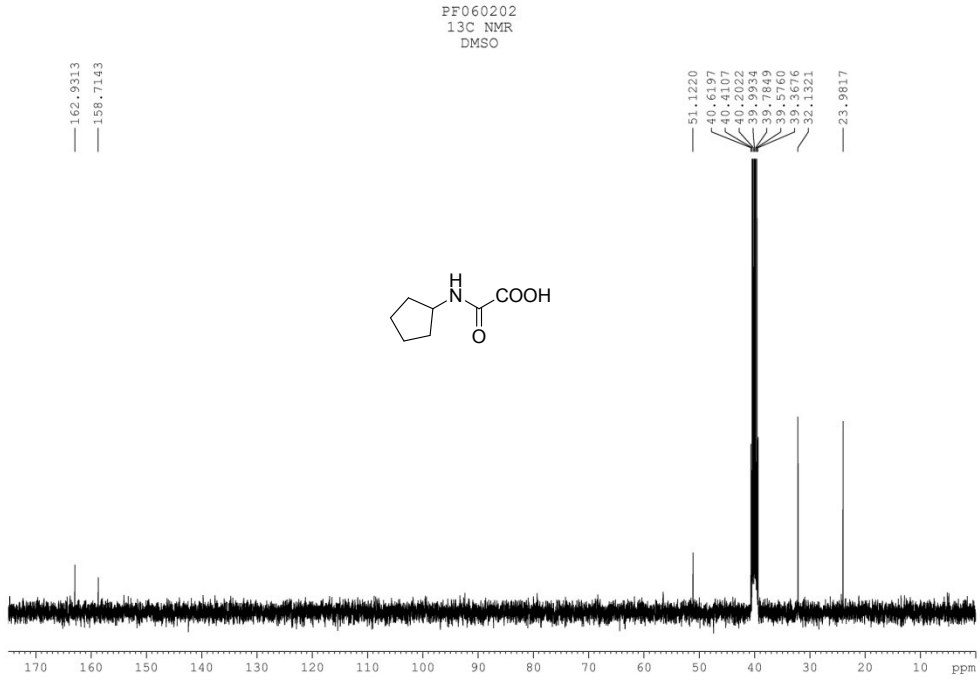


Fig. S31 ^{13}C NMR spectrum of compound **2o**

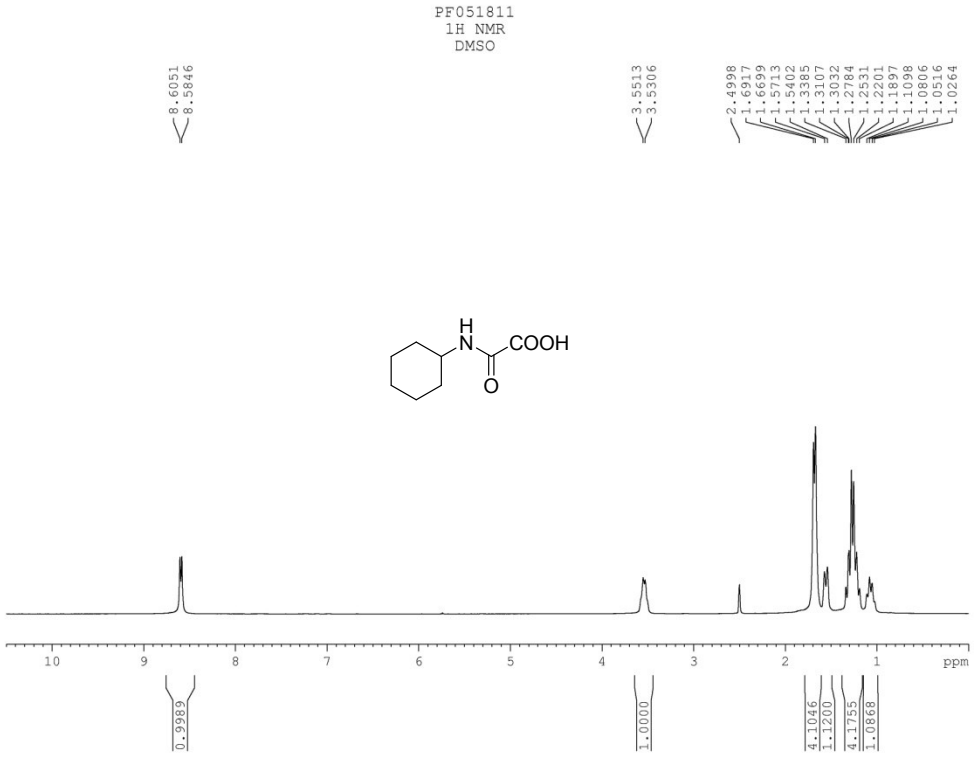


Fig. S32 ^{1}H NMR spectrum of compound **2p**

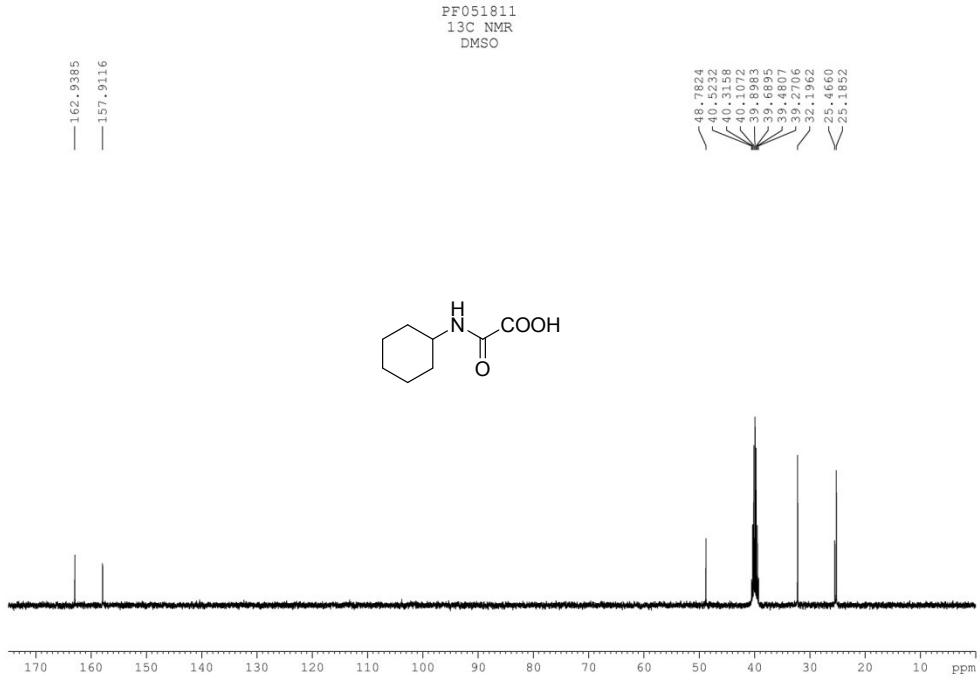


Fig. S33 ^{13}C NMR spectrum of compound **2p**

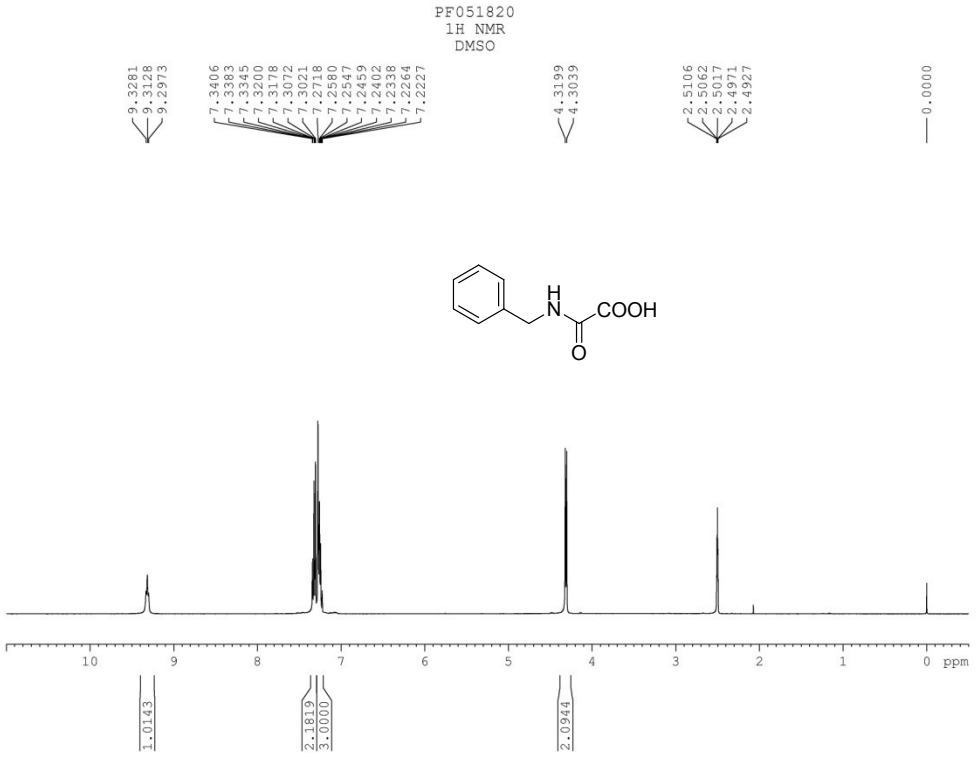


Fig. S34 ^{1}H NMR spectrum of compound **2q**

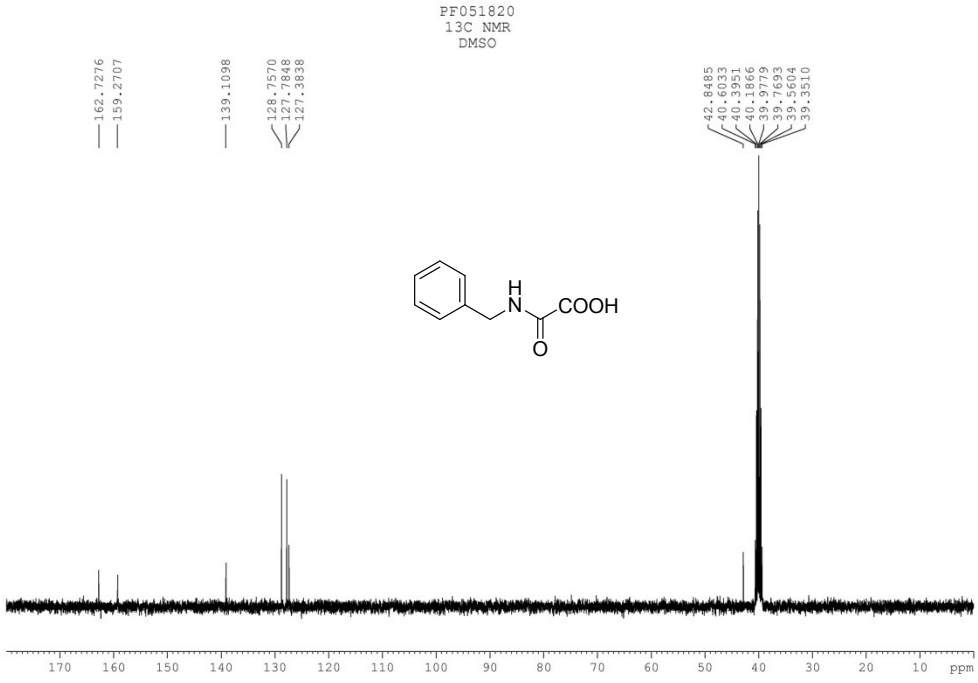


Fig. S35 ^{13}C NMR spectrum of compound **2q**

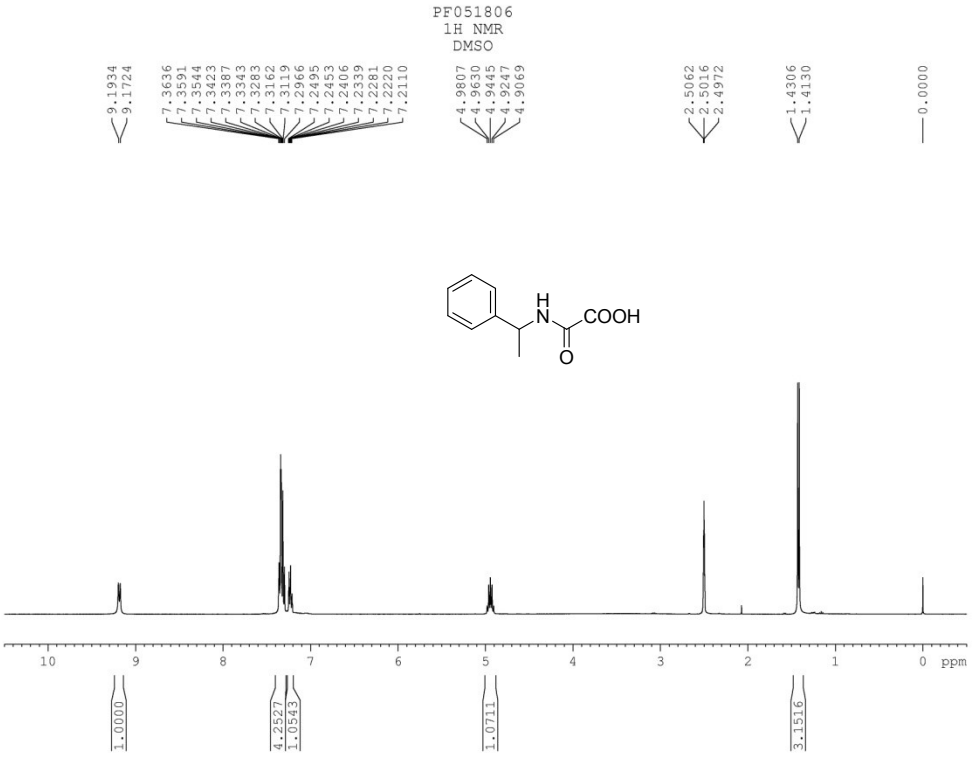


Fig. S36 ^{1}H NMR spectrum of compound **2r**

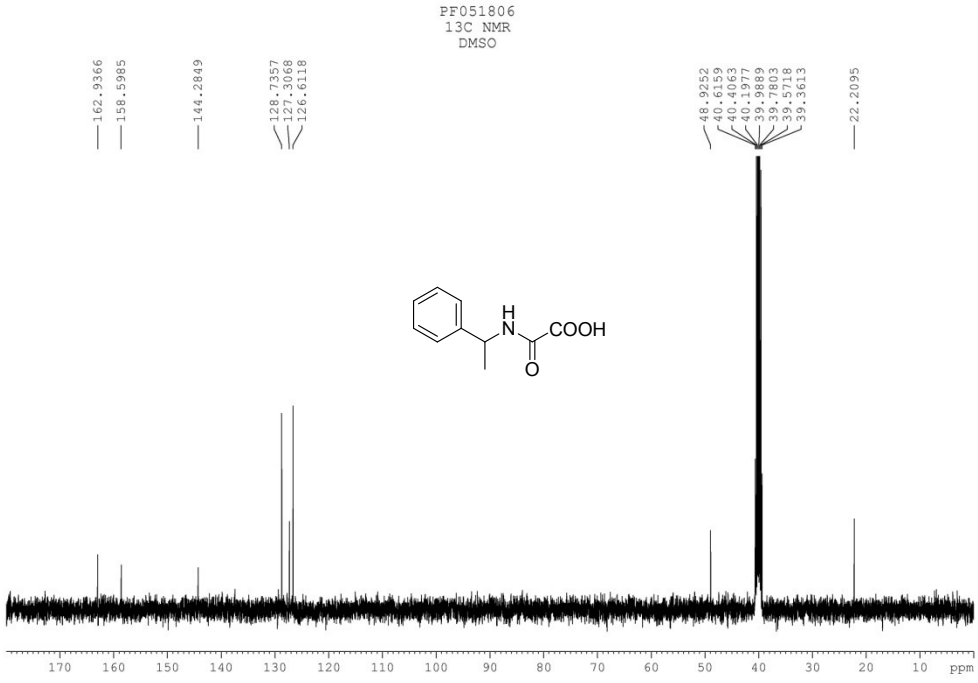


Fig. S37 ^{13}C NMR spectrum of compound **2r**

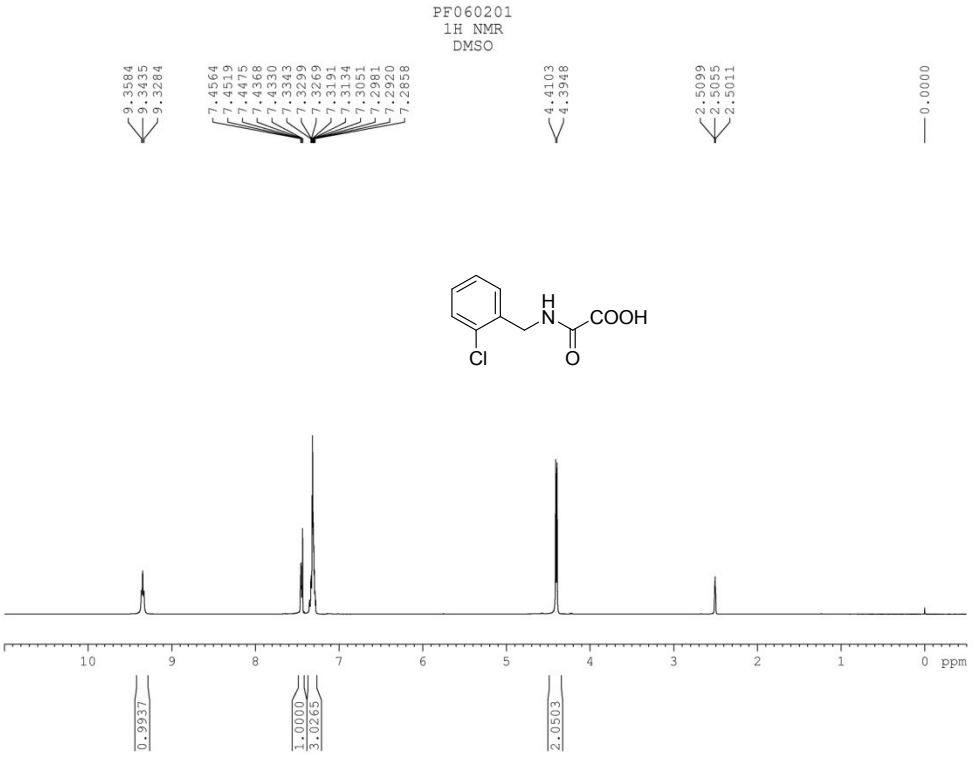


Fig. S38 ^{1}H NMR spectrum of compound **2s**

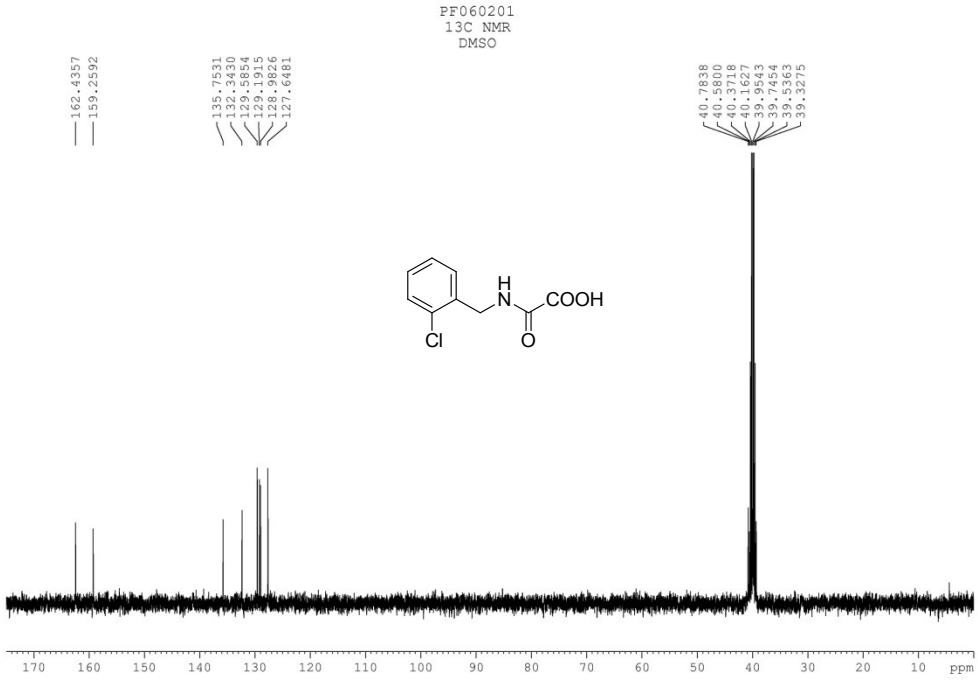


Fig. S39 ^{13}C NMR spectrum of compound **2s**

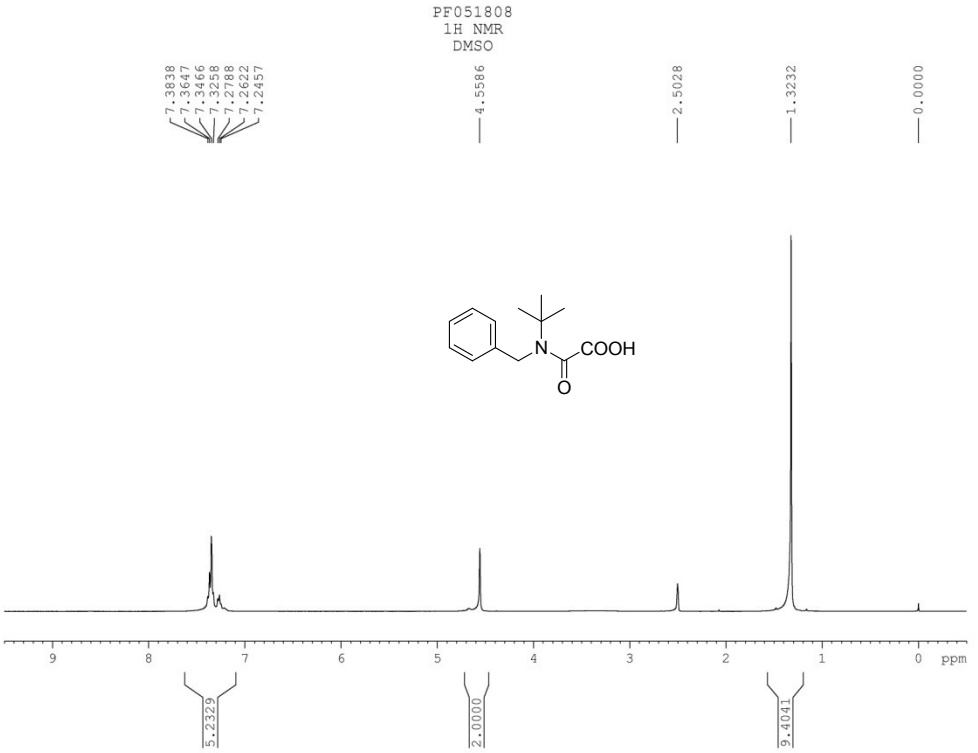


Fig. S40 ^{1}H NMR spectrum of compound **2t**

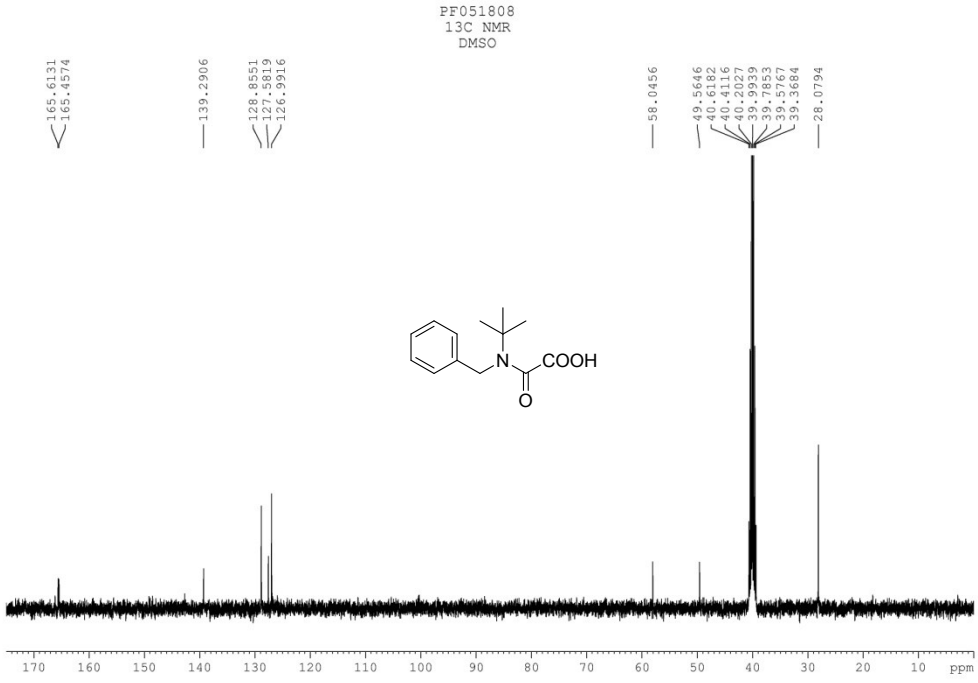


Fig. S41 ^{13}C NMR spectrum of compound **2t**

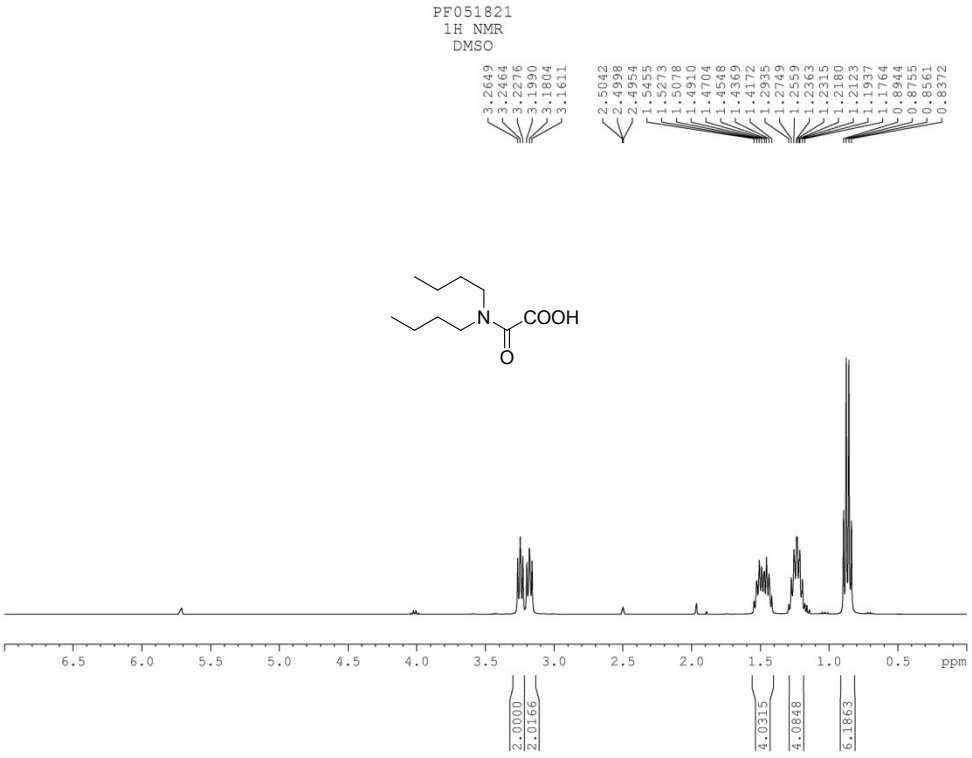


Fig. S42 ^{1}H NMR spectrum of compound **2u**

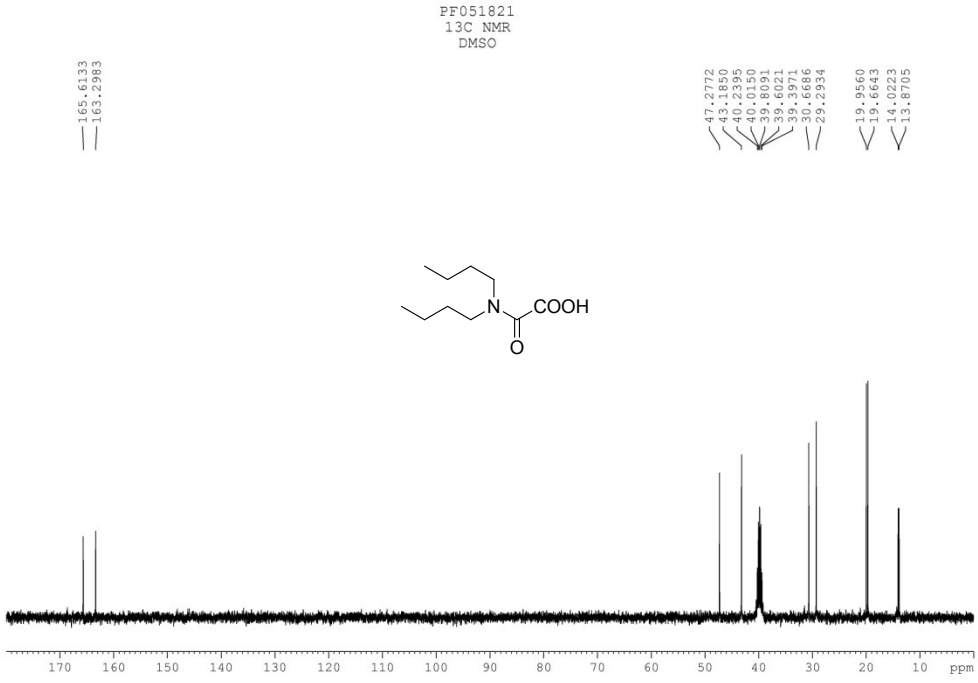


Fig. S43 ^{13}C NMR spectrum of compound **2u**

4. Copies of spectra of products **3aa-3av**, **3bb-3pq** and **4**

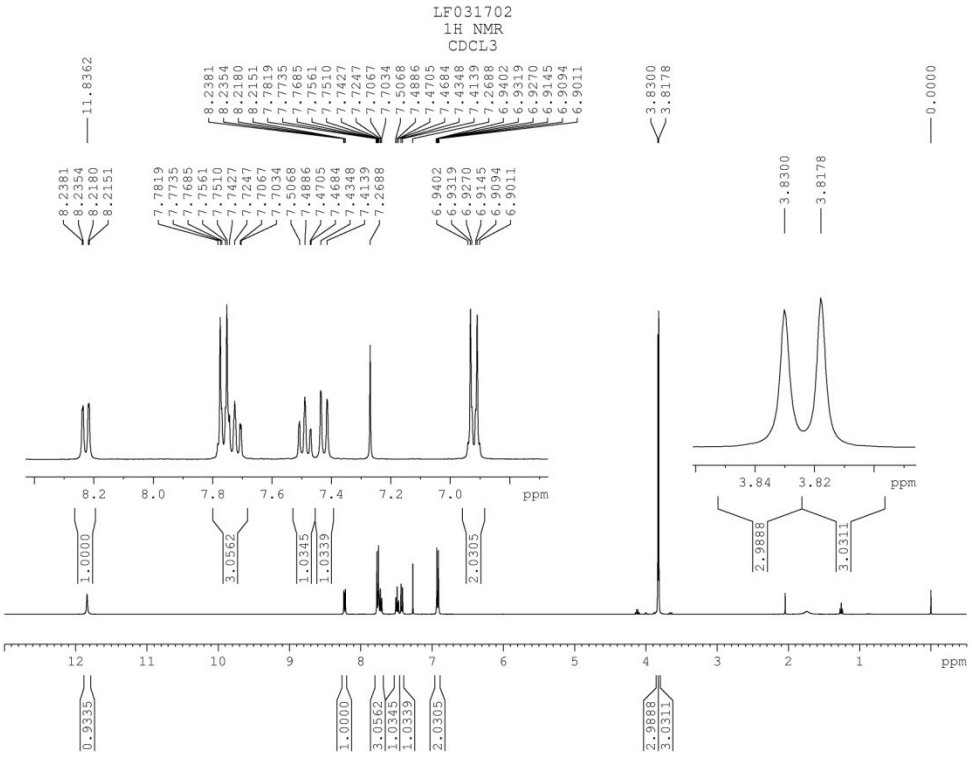


Fig. S44 ^{1}H NMR spectrum of compound **3aa**

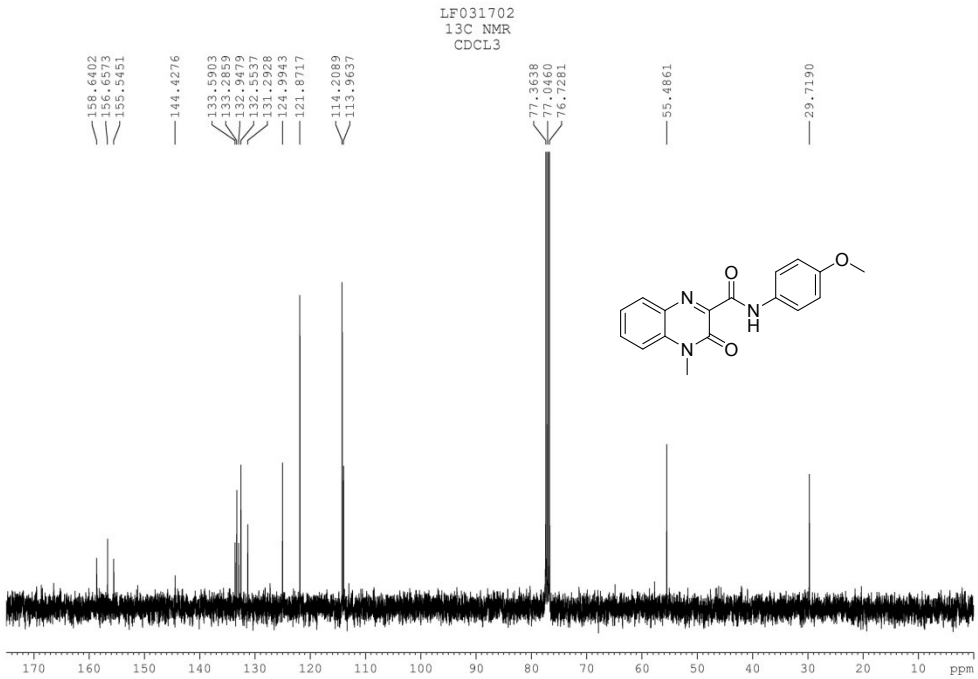


Fig. S45 ^{13}C NMR spectrum of compound **3aa**

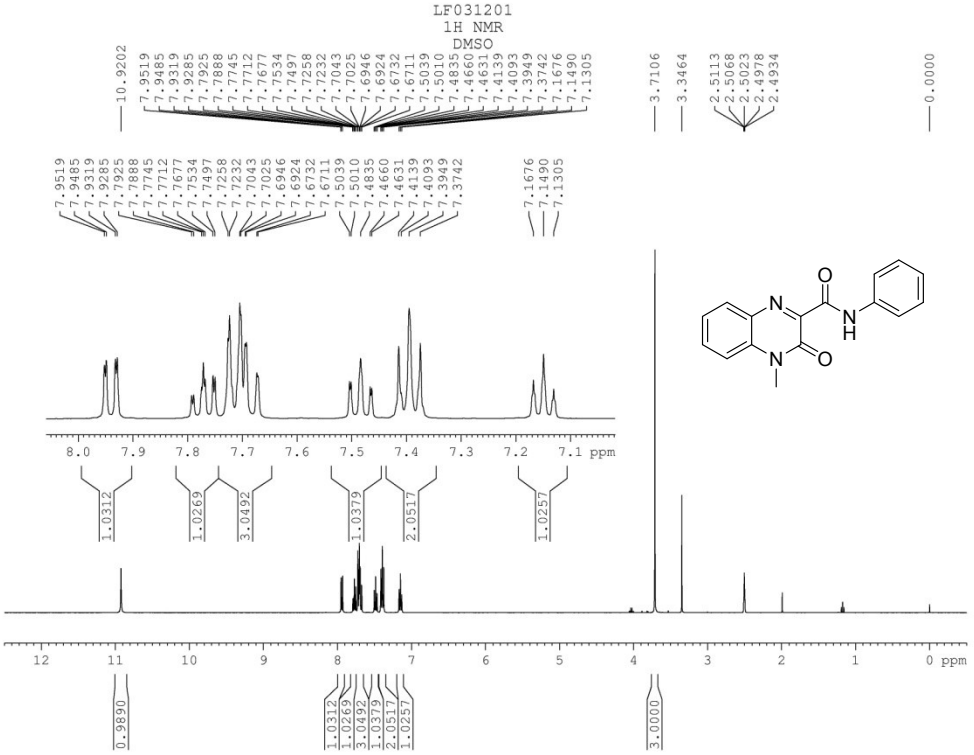


Fig. S46 ^{1}H NMR spectrum of compound **3ab**

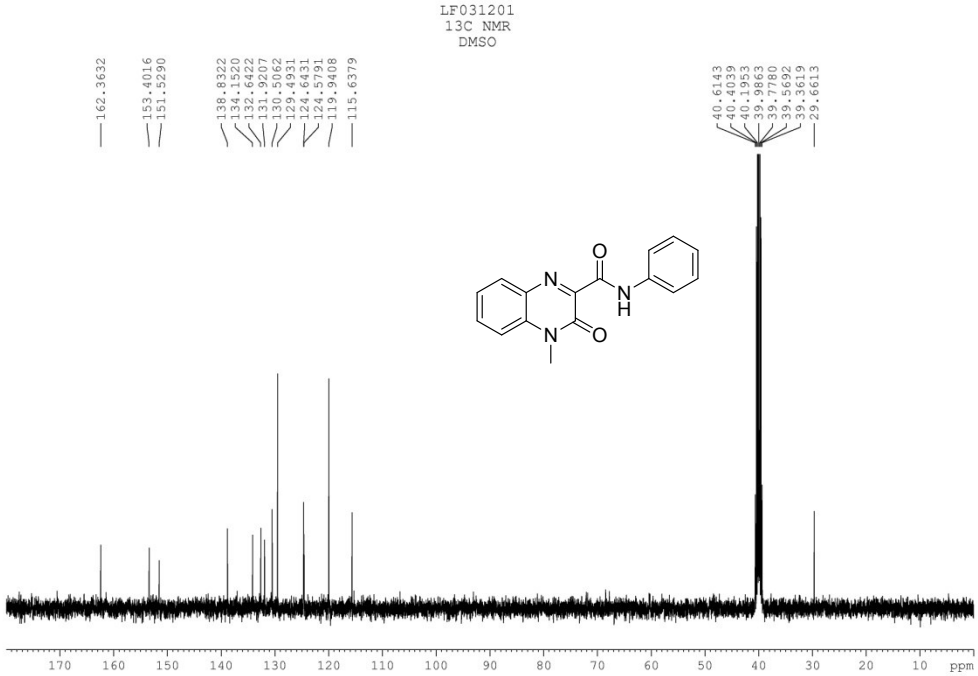


Fig. S47 ^{13}C NMR spectrum of compound **3ab**

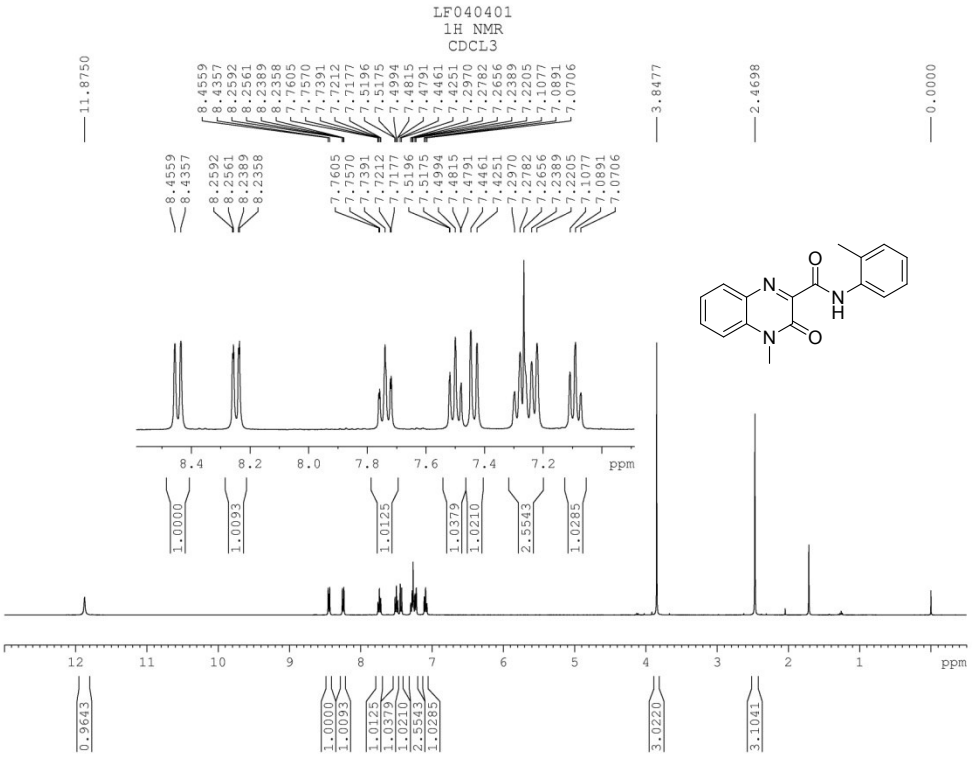


Fig. S48 ^{1}H NMR spectrum of compound **3ac**

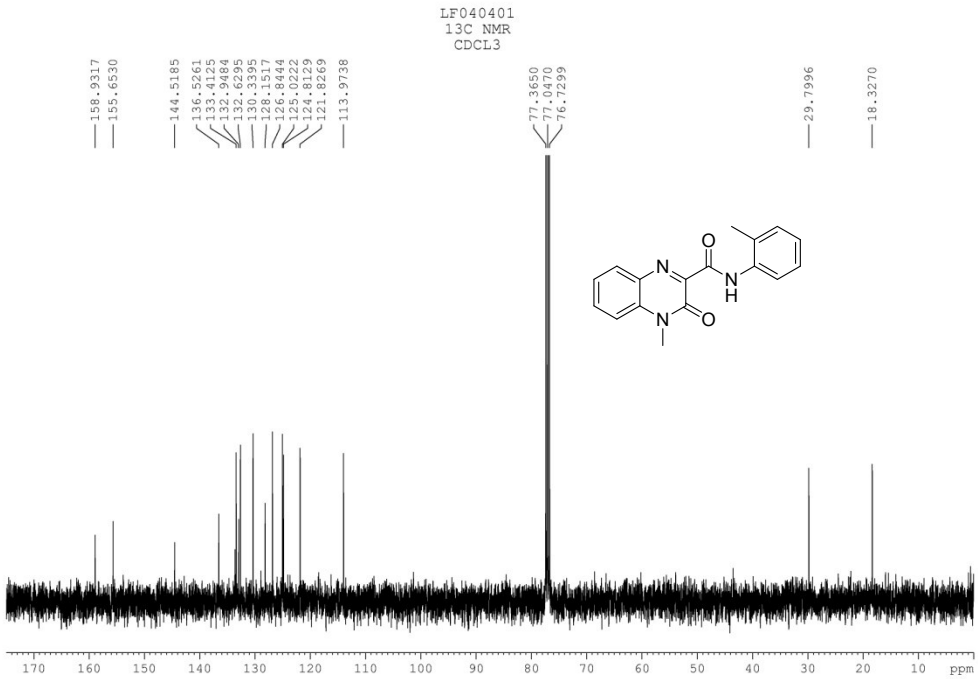


Fig. S49 ^{13}C NMR spectrum of compound **3ac**

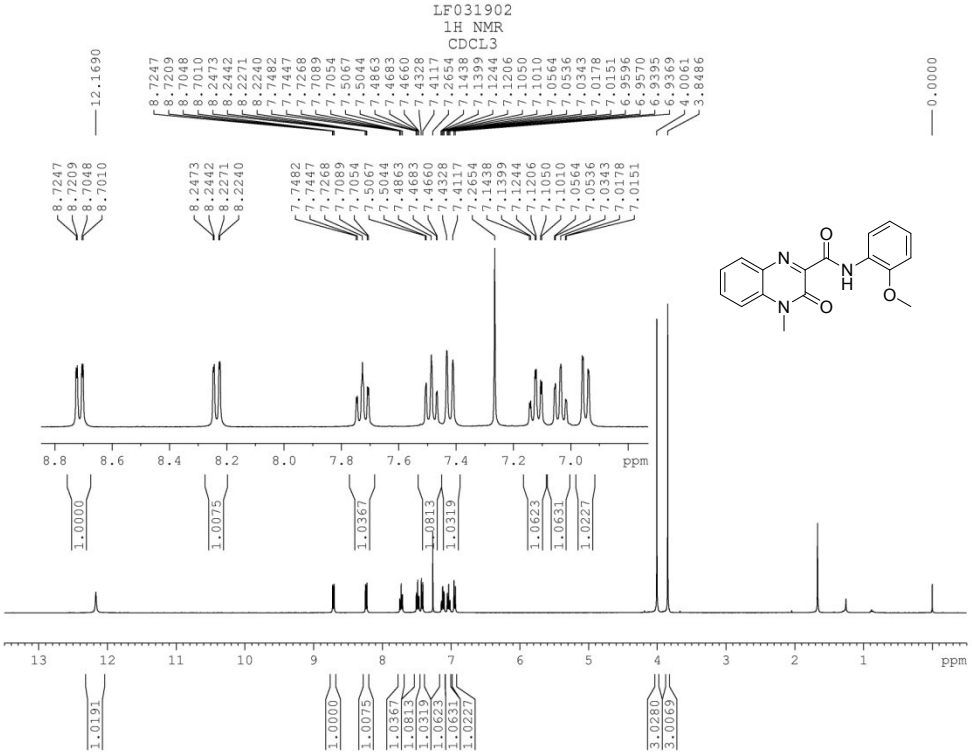


Fig. S50 ^{1}H NMR spectrum of compound **3ad**

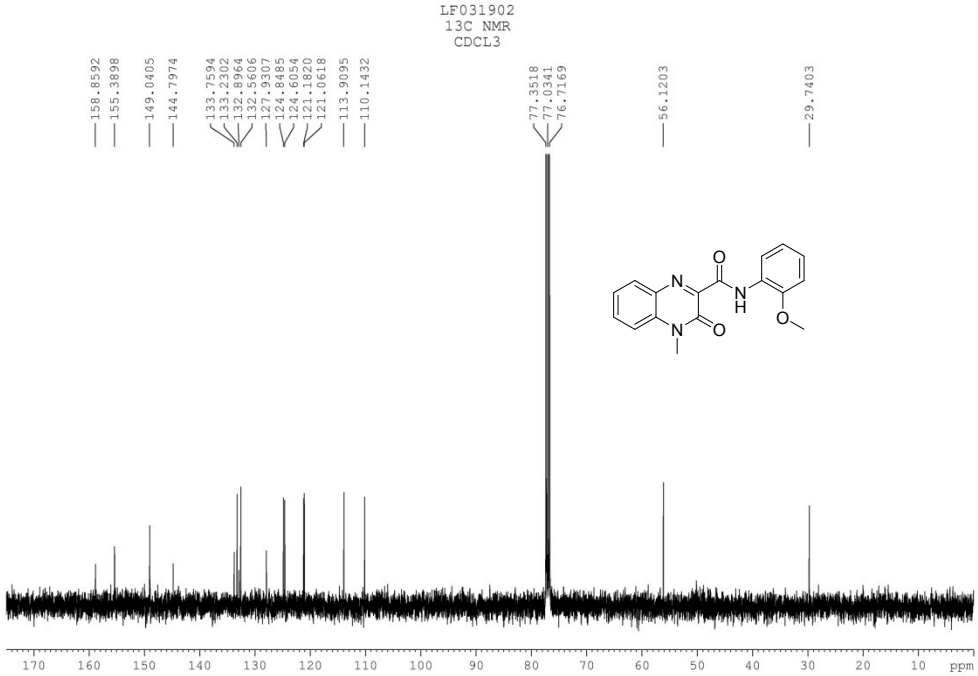


Fig. S51 ^{13}C NMR spectrum of compound **3ad**

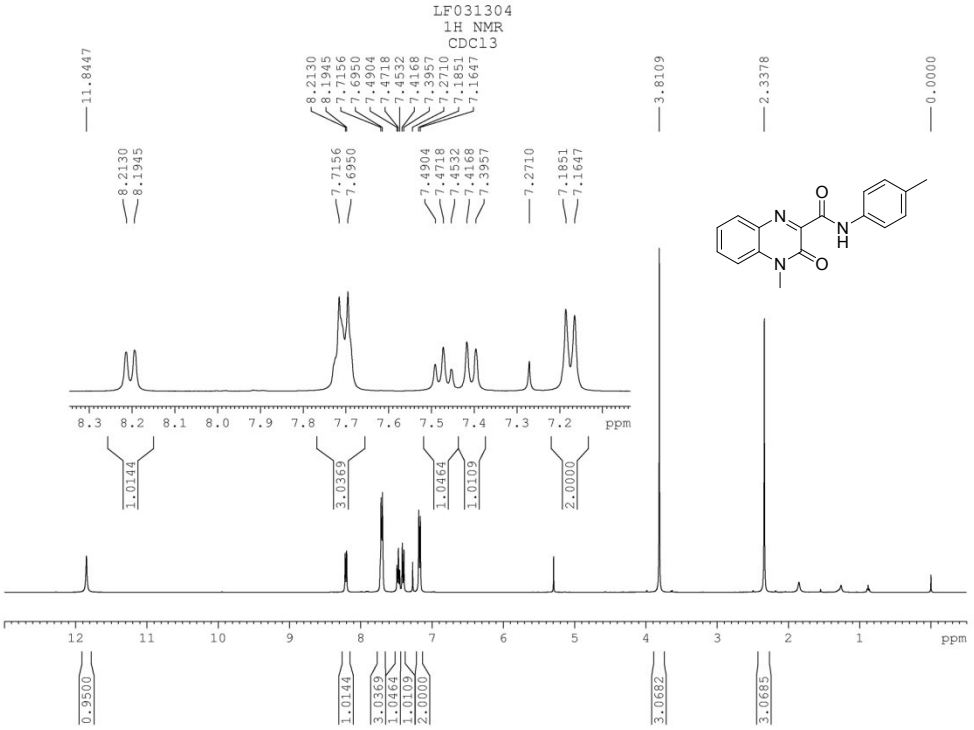


Fig. S52 ^{1}H NMR spectrum of compound **3ae**

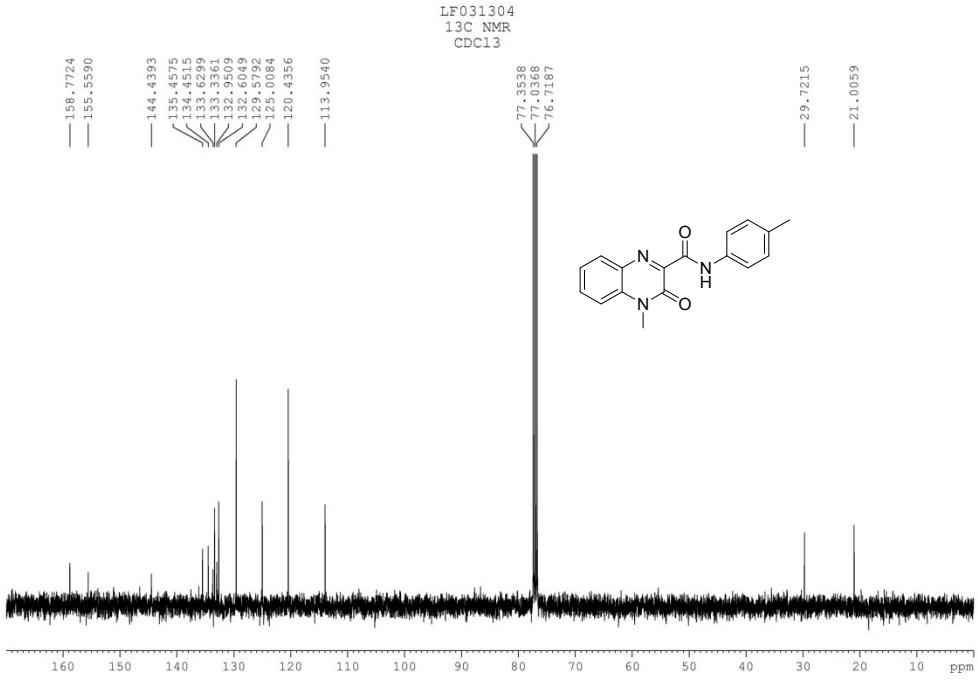


Fig. S53 ^{13}C NMR spectrum of compound **3ae**

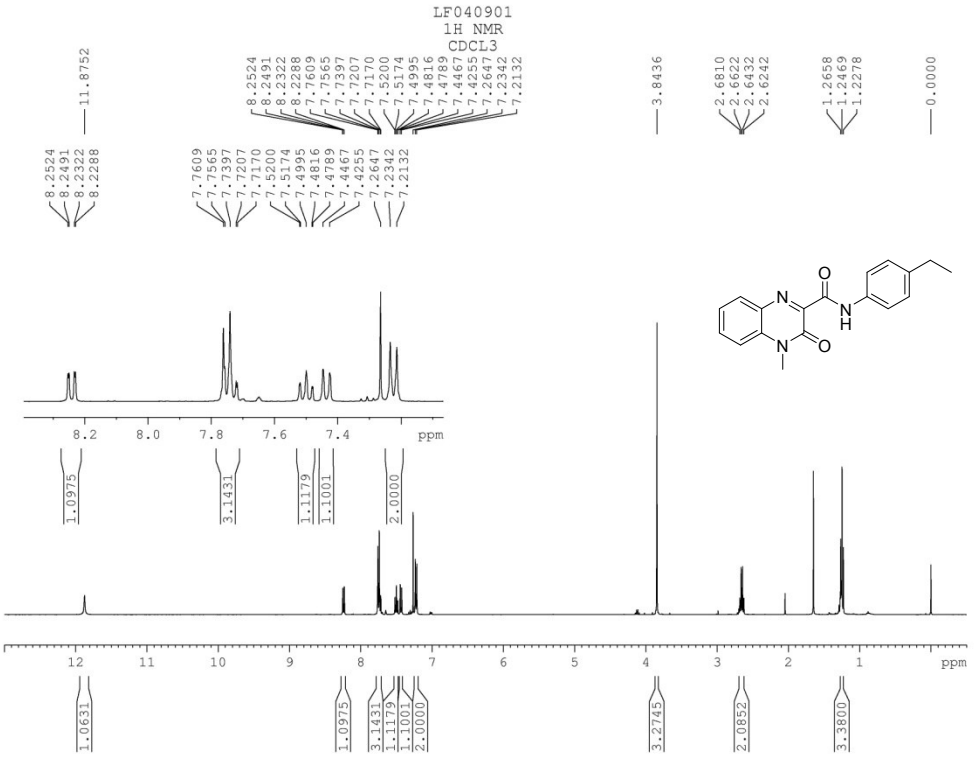


Fig. S54 ^{1}H NMR spectrum of compound **3af**

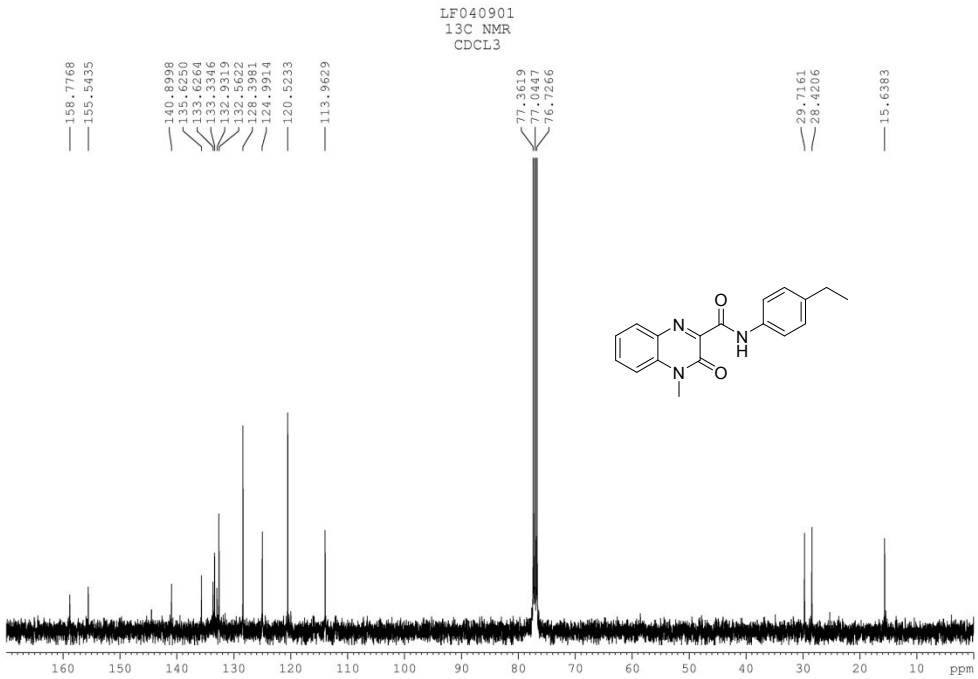


Fig. S55 ^{13}C NMR spectrum of compound **3af**

Fig. S56 ^{1}H NMR spectrum of compound **3ag**

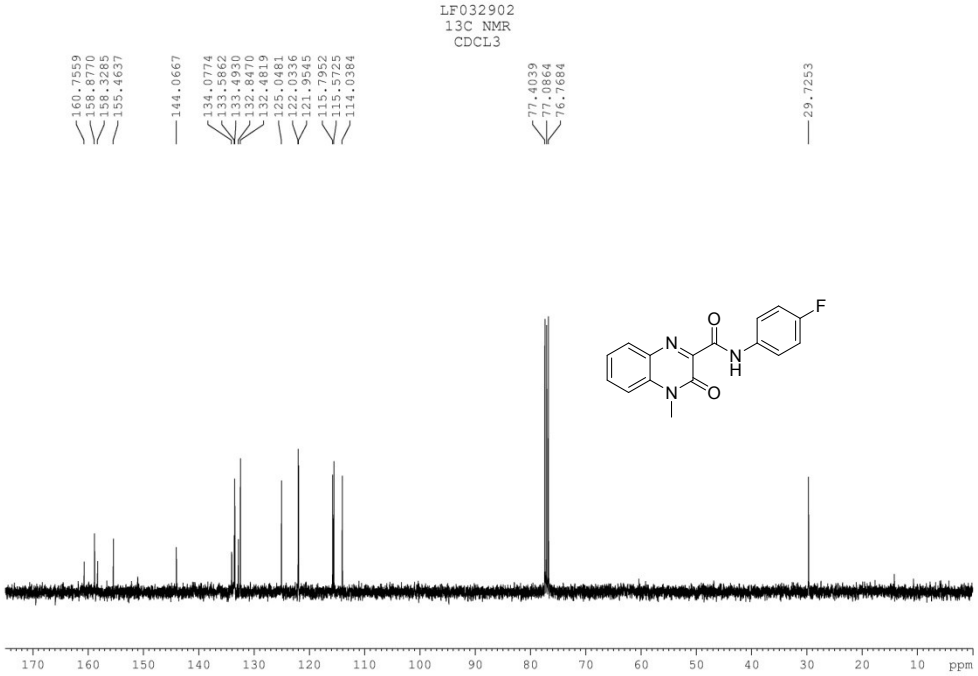


Fig. S57 ^{13}C NMR spectrum of compound **3ag**

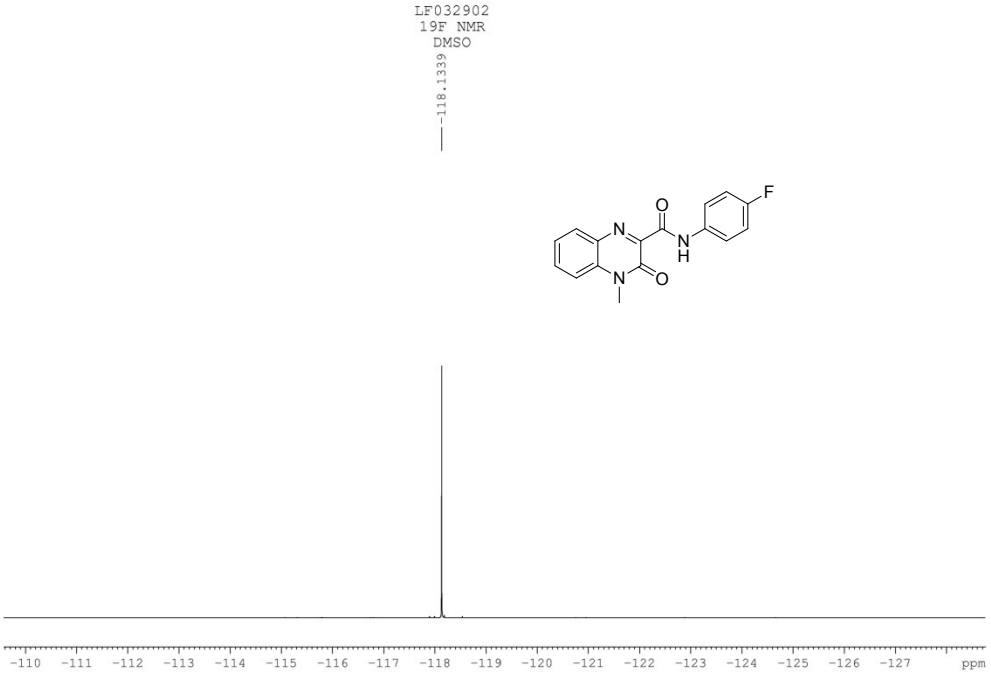


Fig. S58 ^{19}F NMR spectrum of compound **3ag**

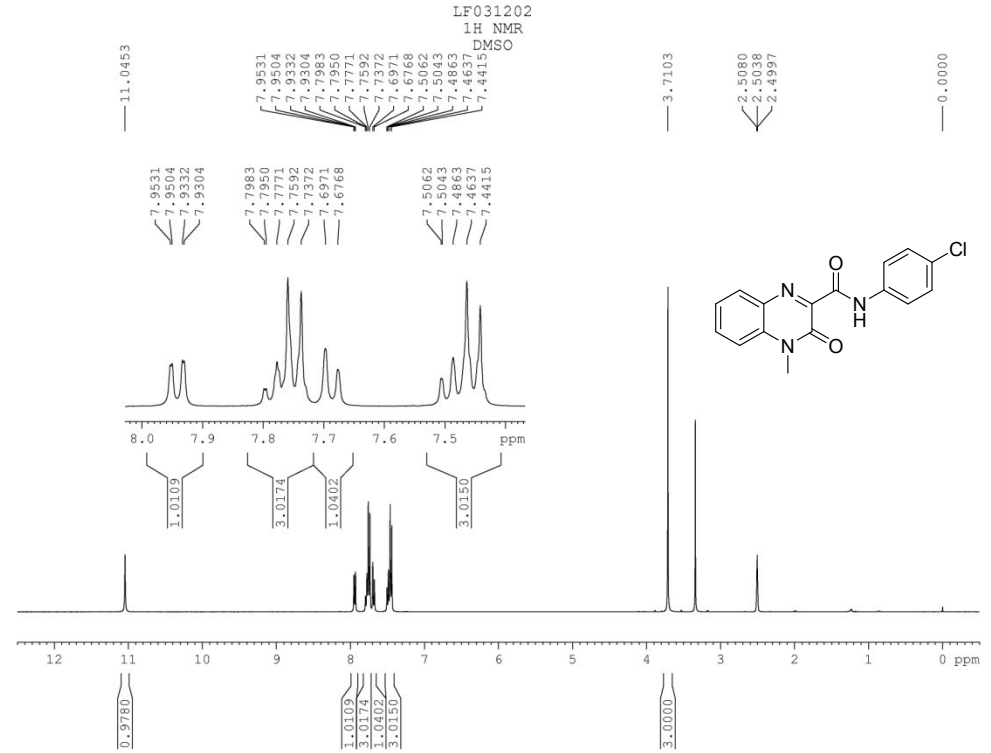


Fig. S59 ^{1}H NMR spectrum of compound **3ah**

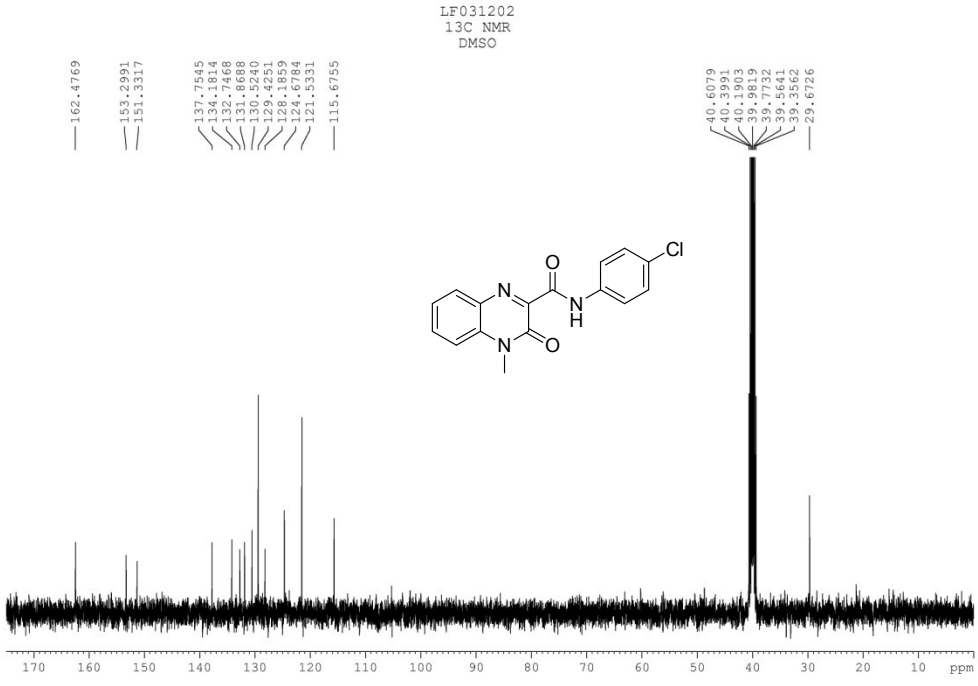


Fig. S60 ^{13}C NMR spectrum of compound **3ah**

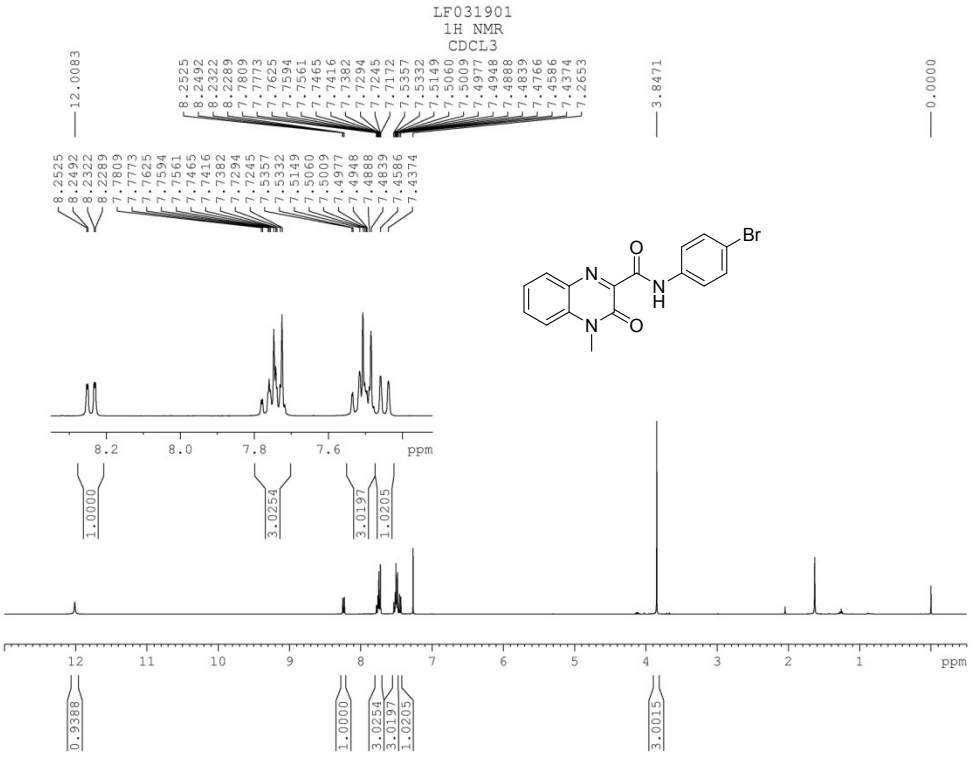


Fig. S61 ^{1}H NMR spectrum of compound **3ai**

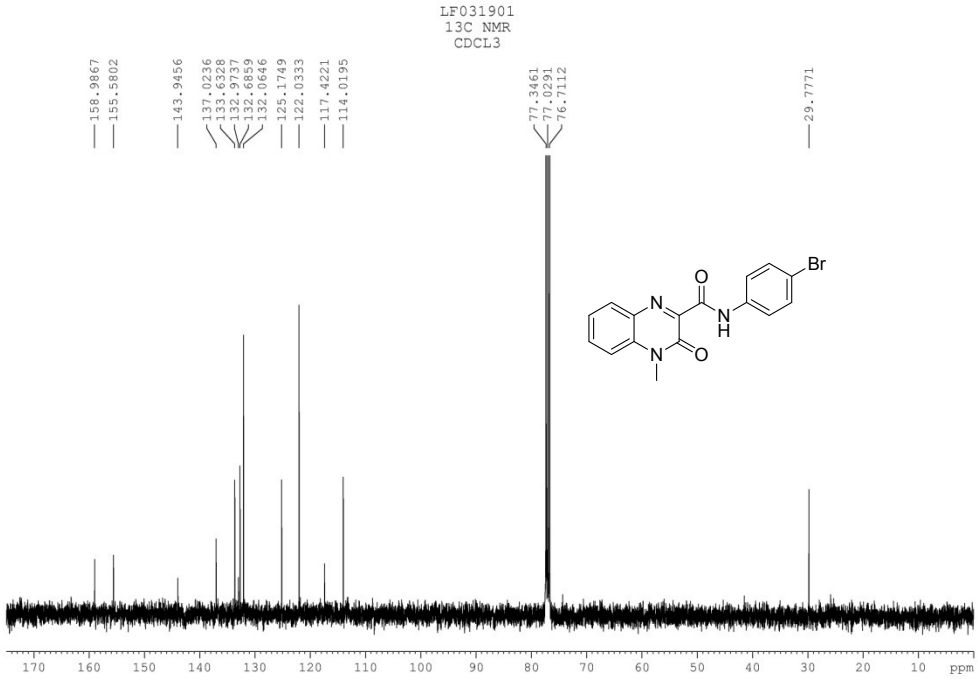


Fig. S62 ^{13}C NMR spectrum of compound **3ai**

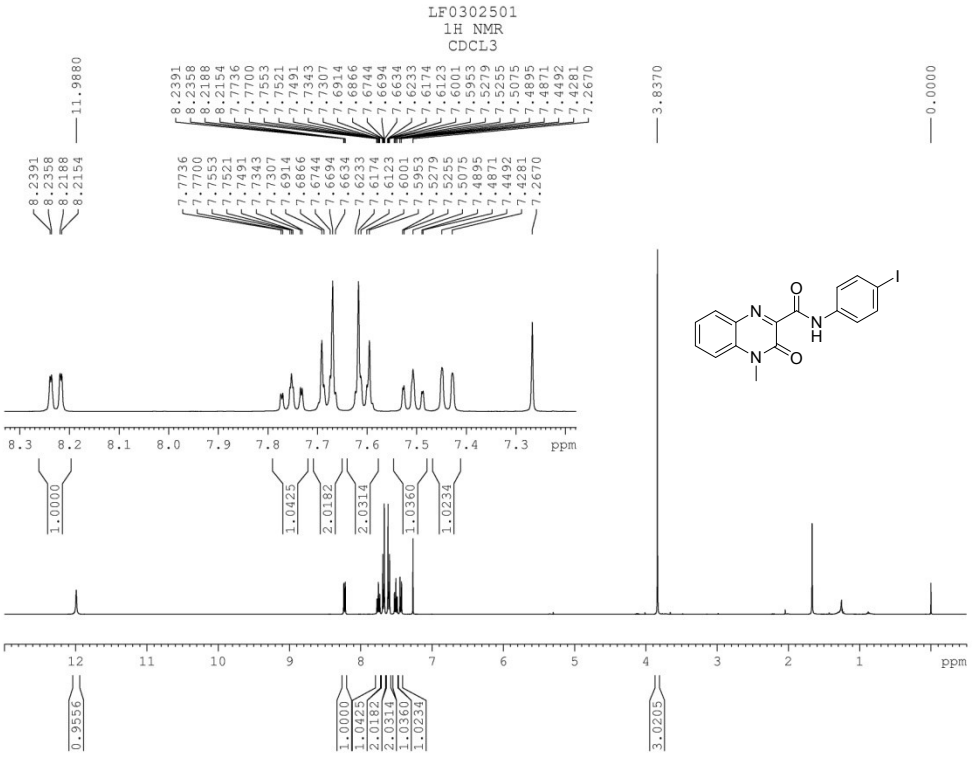


Fig. S63 ^{1}H NMR spectrum of compound **3aj**

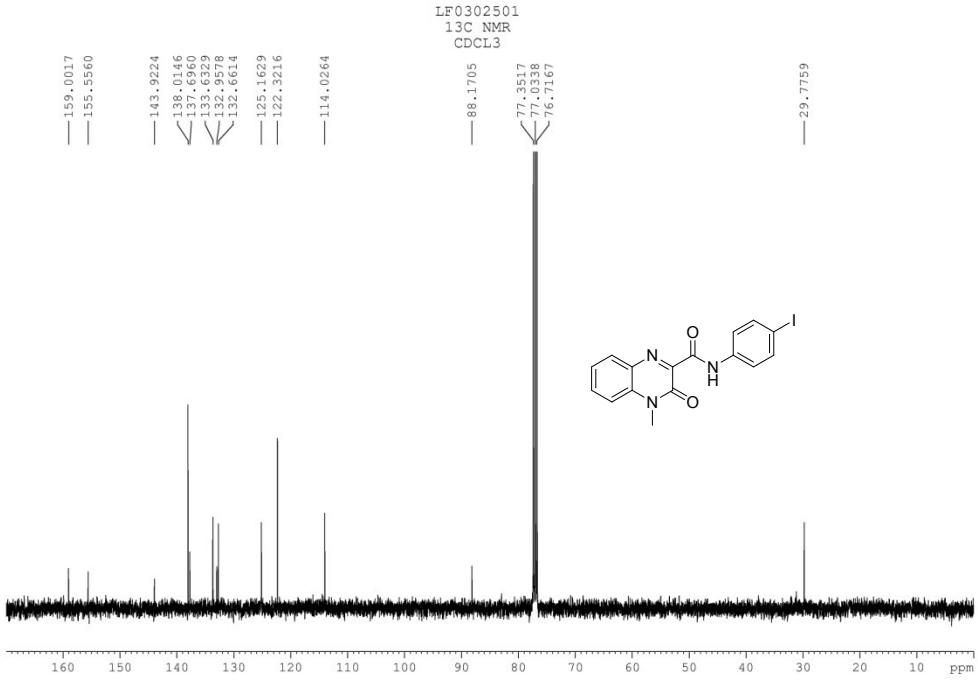


Fig. S64 ^{13}C NMR spectrum of compound **3aj**

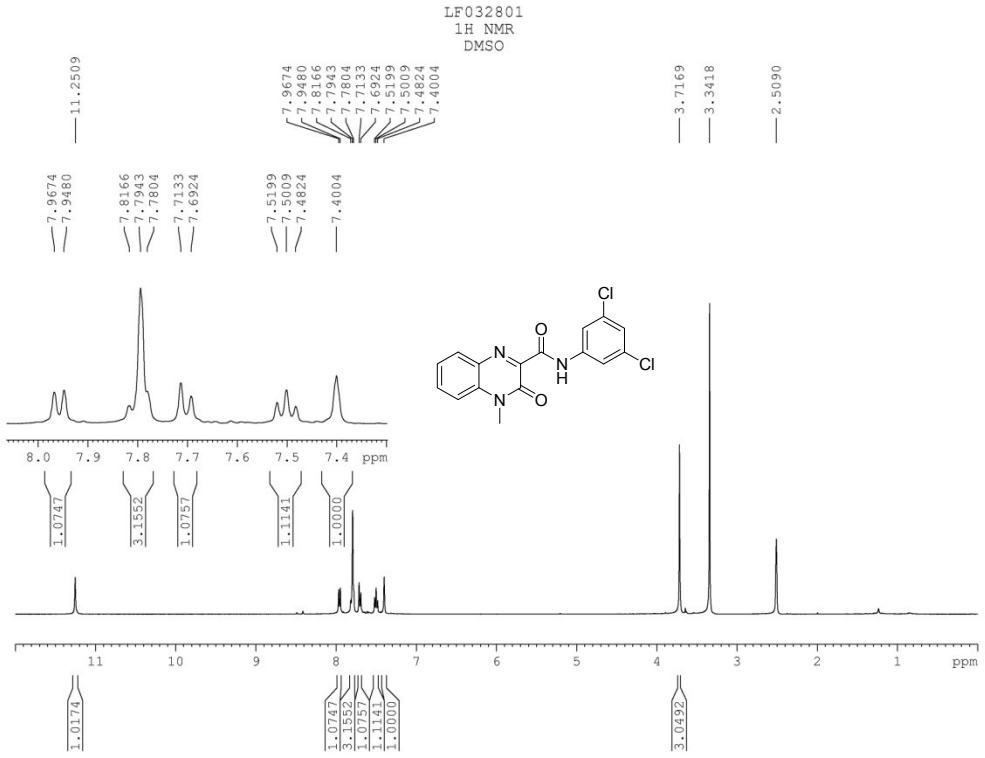


Fig. S65 ^{1}H NMR spectrum of compound **3ak**

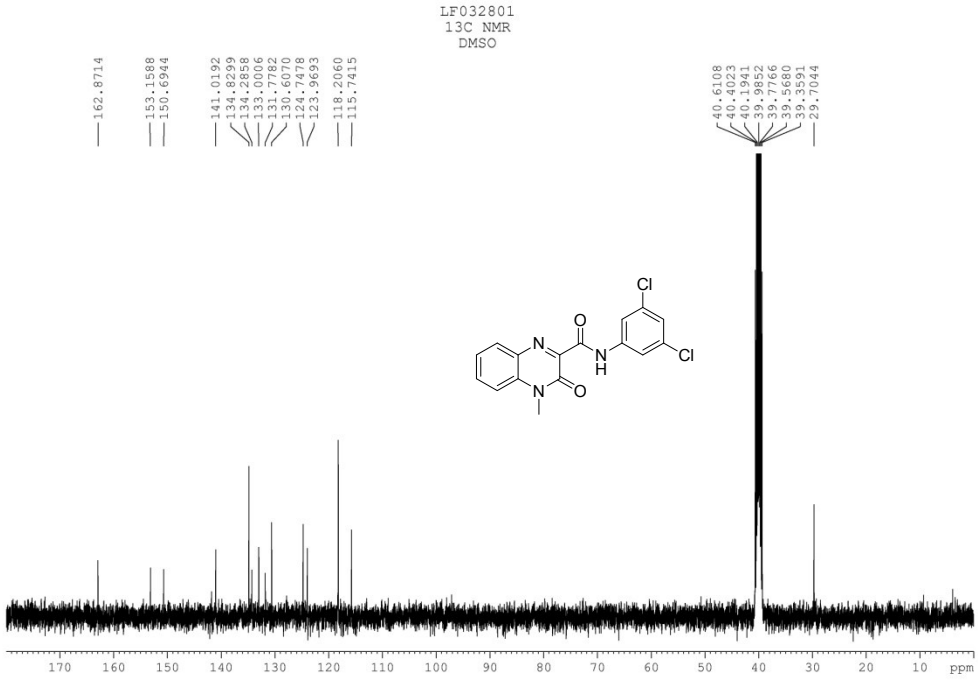


Fig. S66 ^{13}C NMR spectrum of compound **3ak**

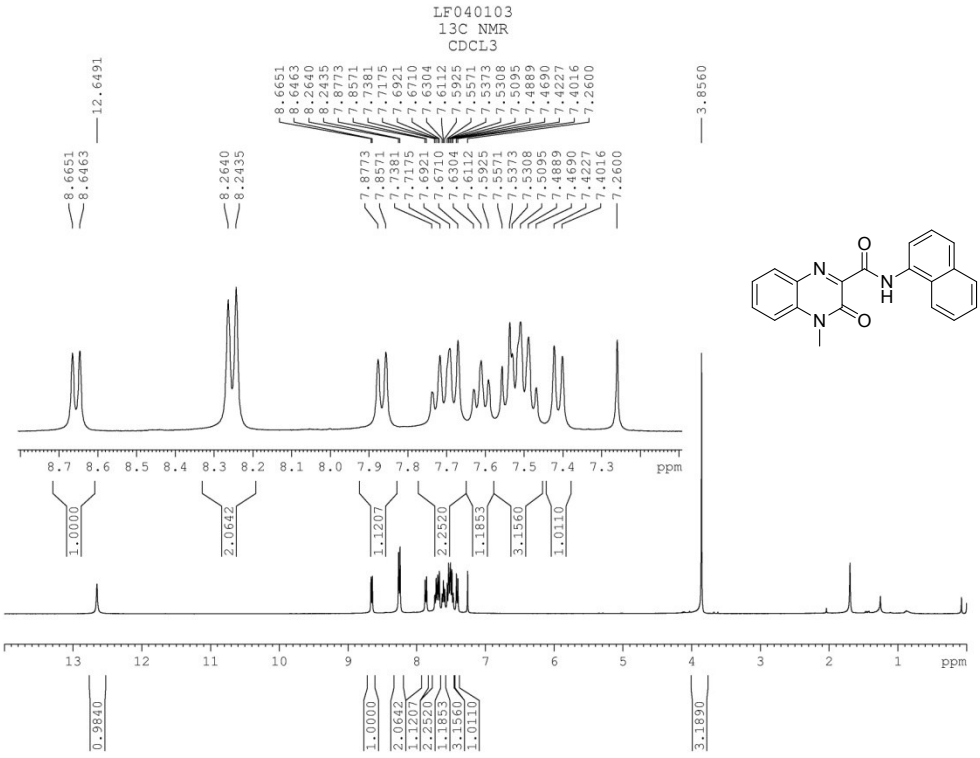


Fig. S67 ^{1}H NMR spectrum of compound **3al**

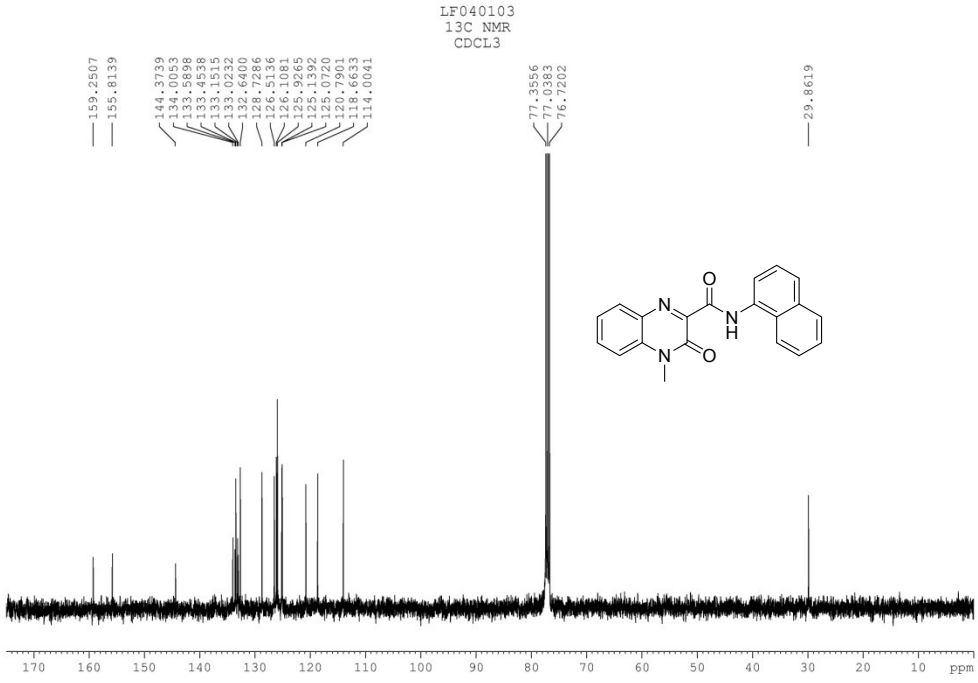


Fig. S68 ^{13}C NMR spectrum of compound **3al**

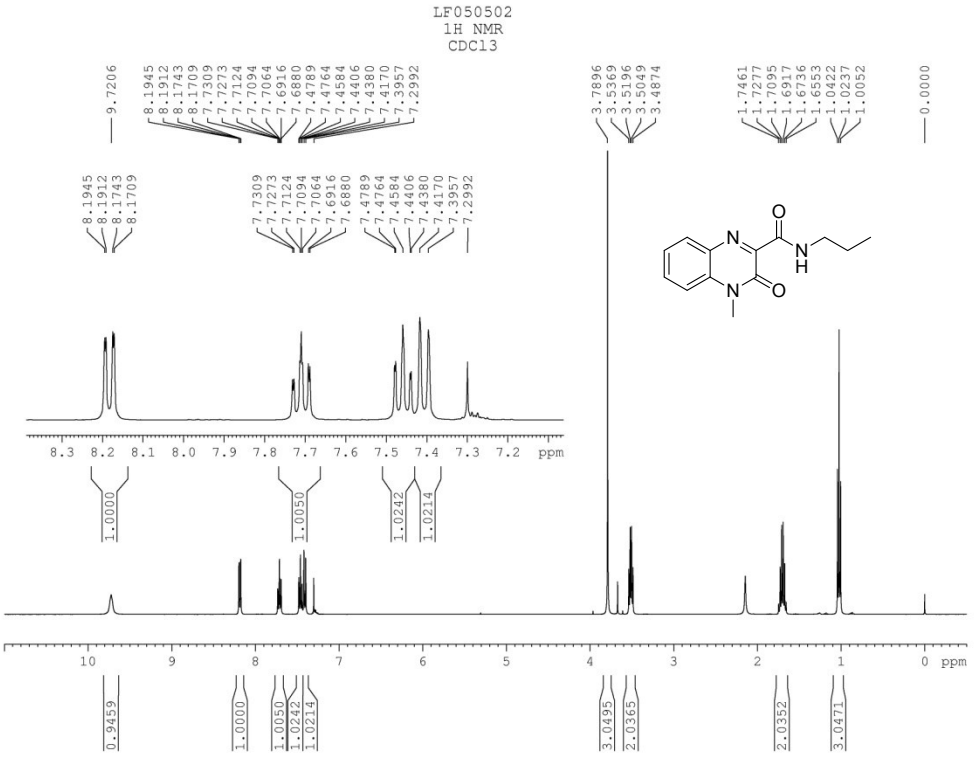


Fig. S69 ^{1}H NMR spectrum of compound **3am**

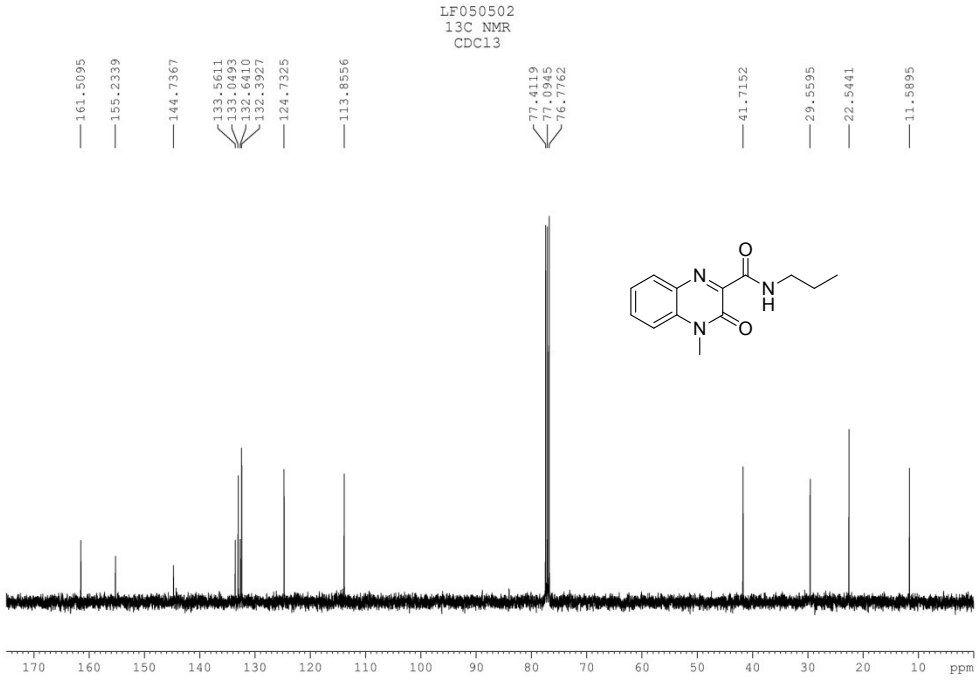


Fig. S70 ^{13}C NMR spectrum of compound **3am**

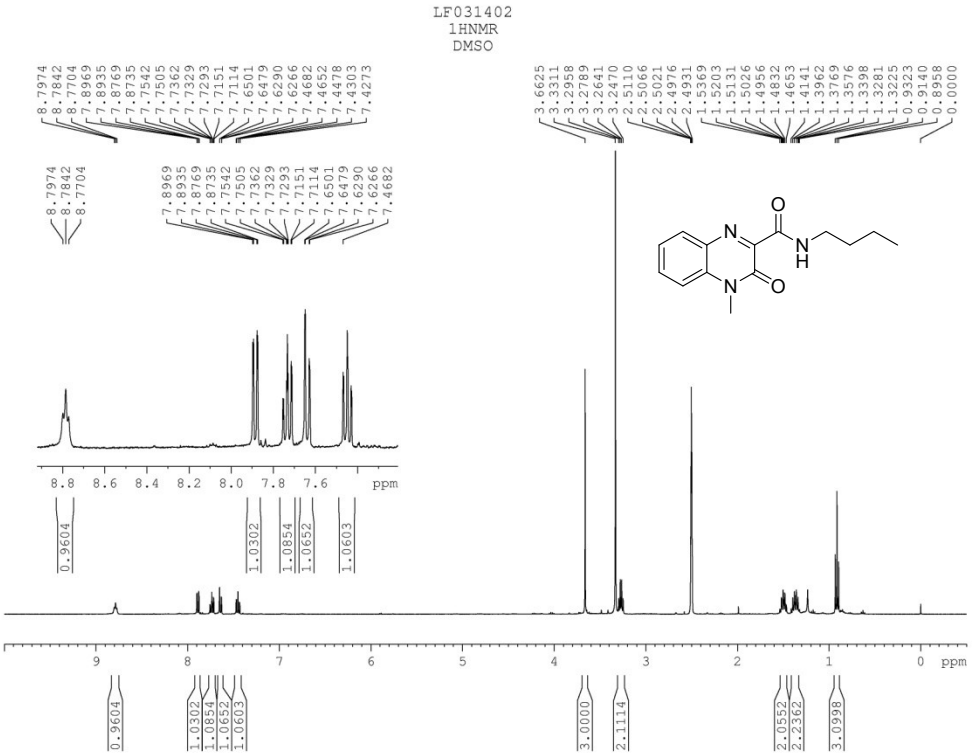


Fig. S71 ^{1}H NMR spectrum of compound **3an**

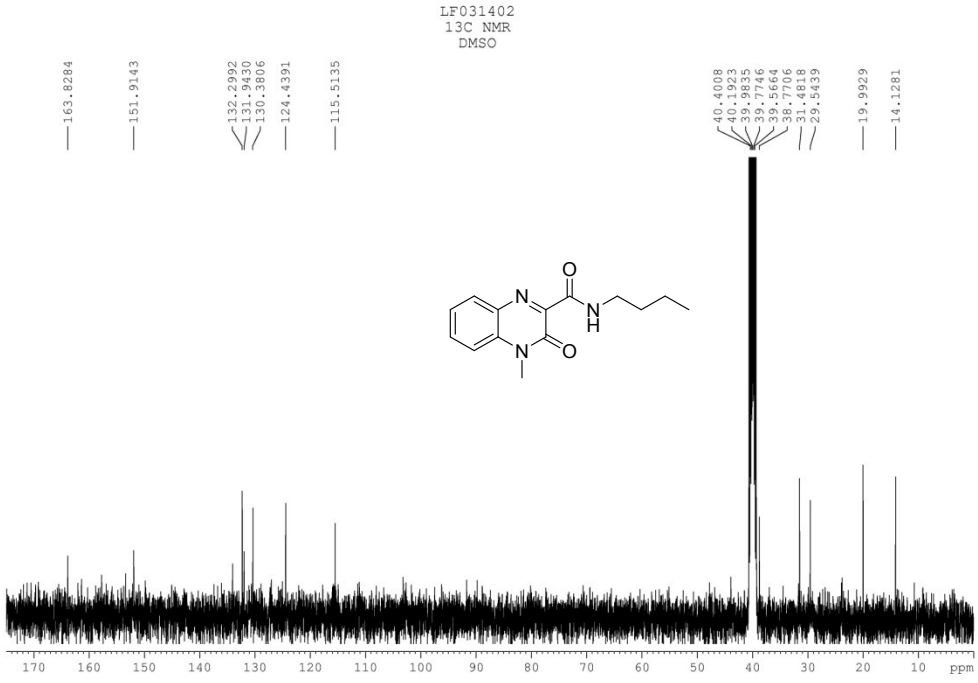


Fig. S72 ^{13}C NMR spectrum of compound **3an**

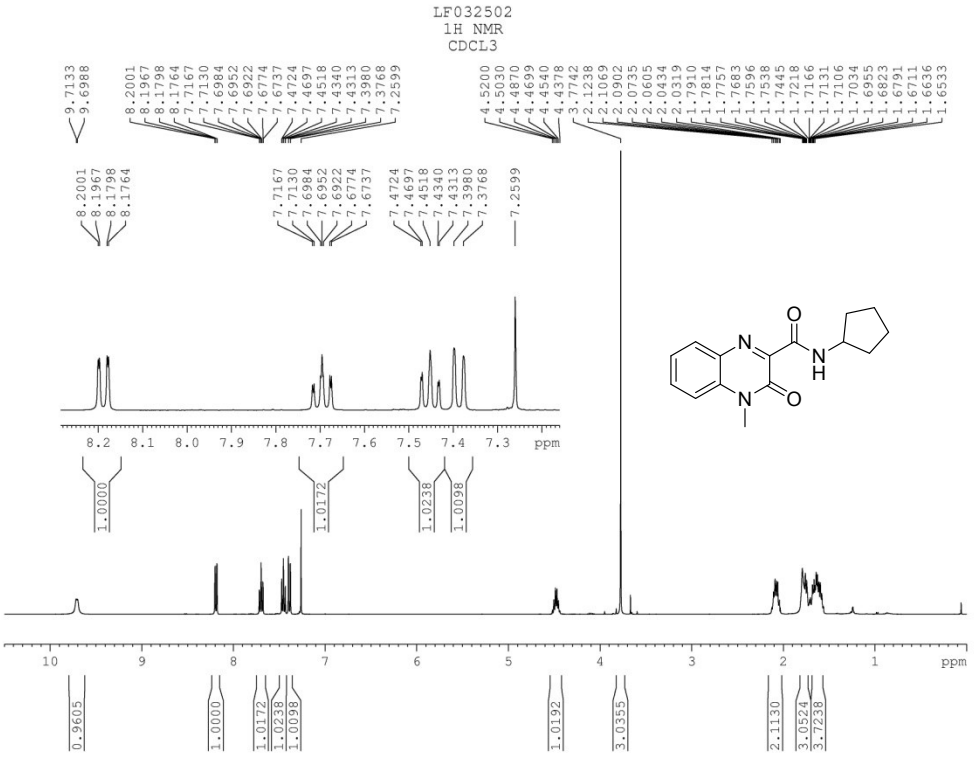


Fig. S73 ^{1}H NMR spectrum of compound **3ao**

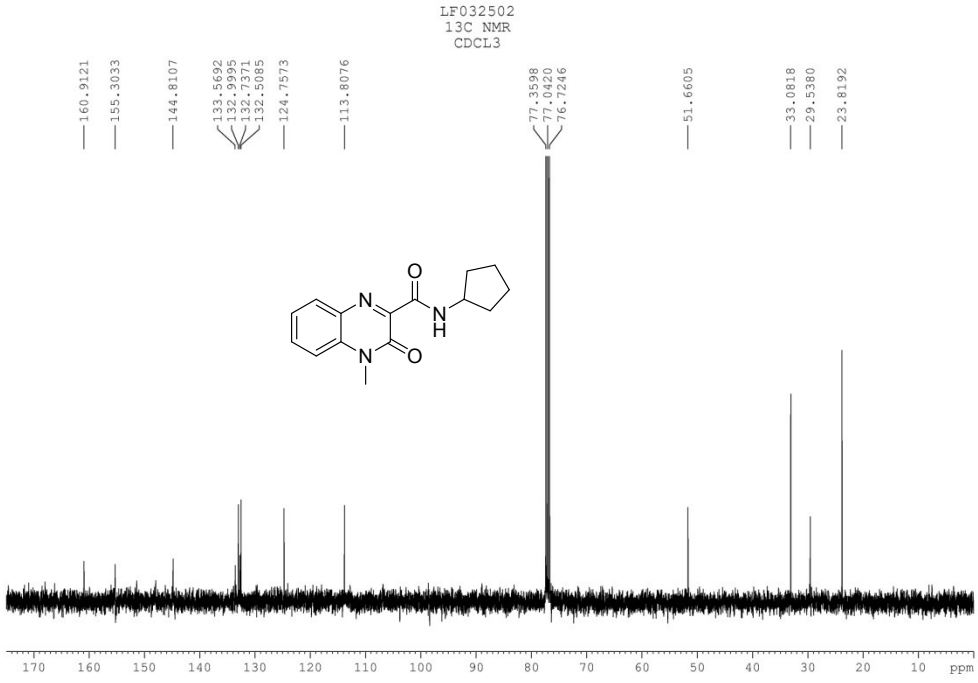


Fig. S74 ^{13}C NMR spectrum of compound **3ao**

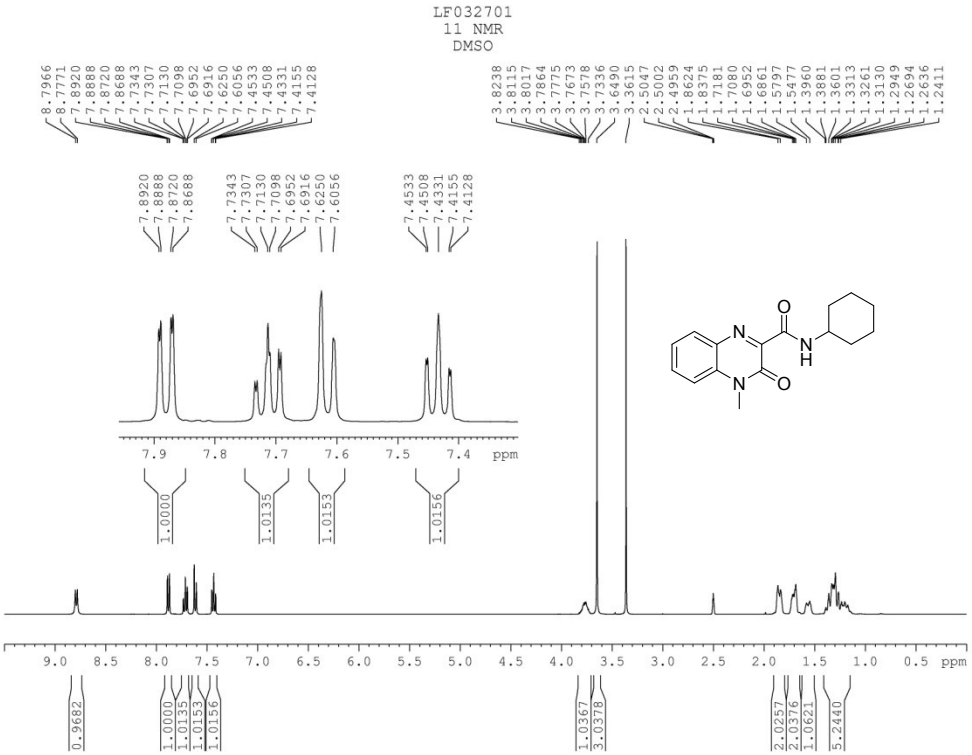


Fig. S75 ^{1}H NMR spectrum of compound **3ap**

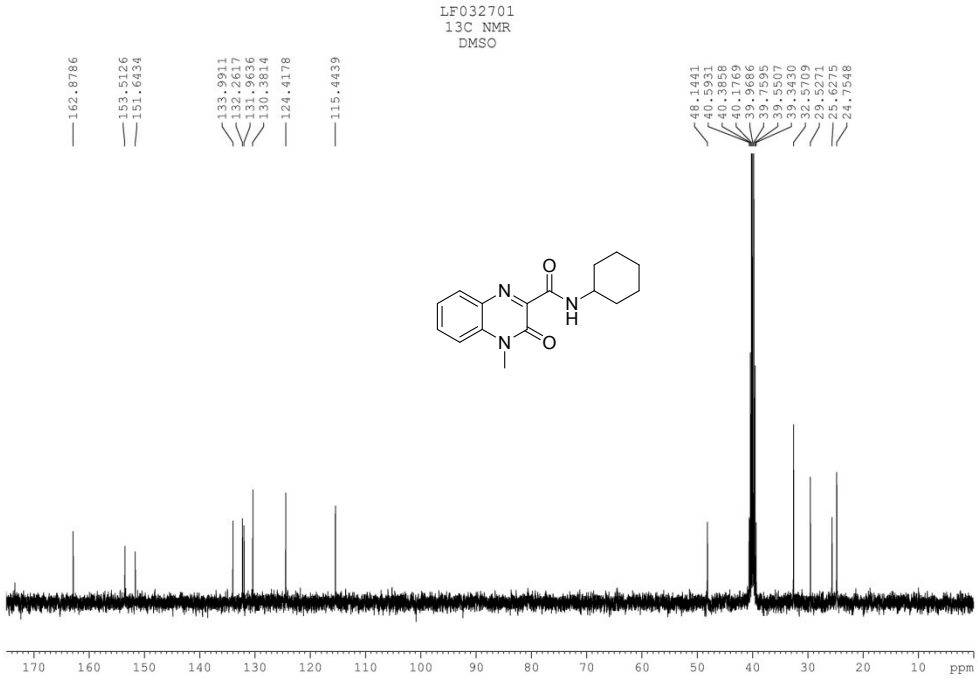


Fig. S76 ^{13}C NMR spectrum of compound **3ap**

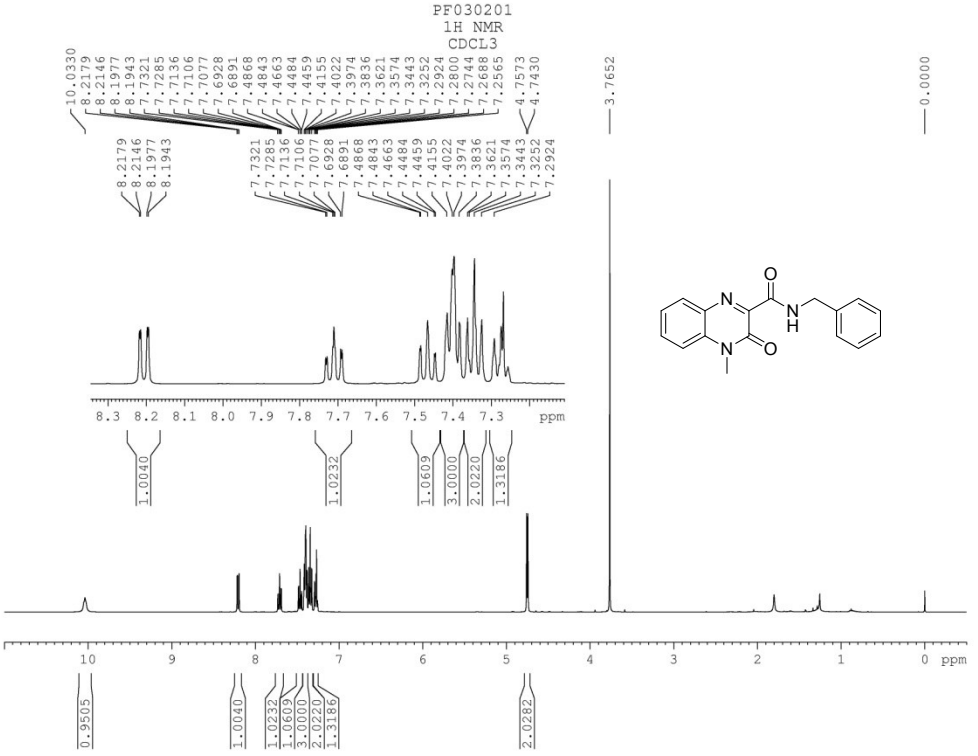


Fig. S77 ^{1}H NMR spectrum of compound **3aq**

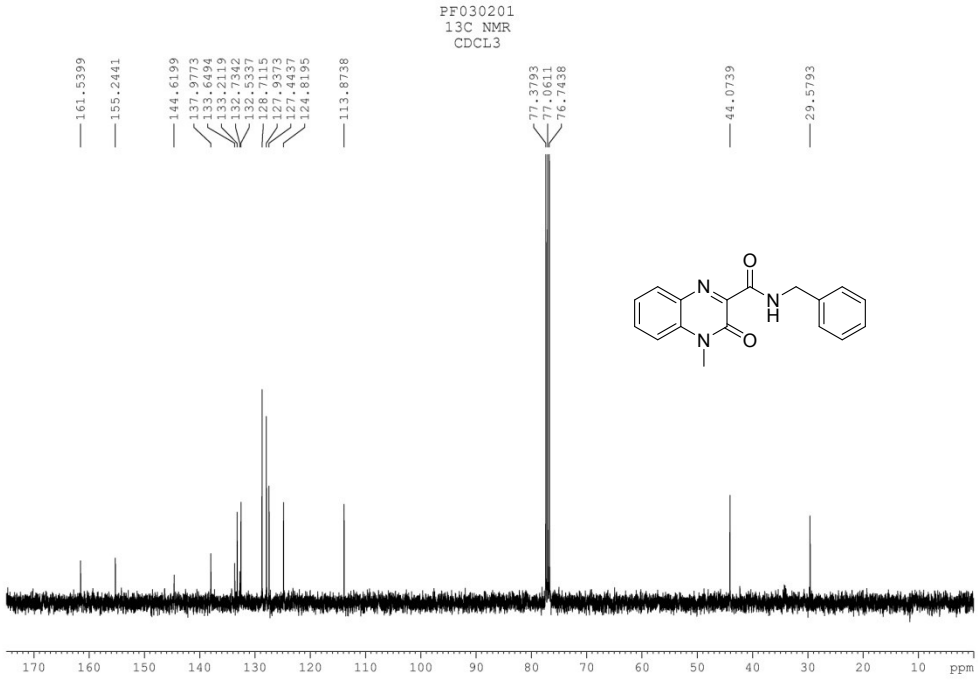


Fig. S78 ^{13}C NMR spectrum of compound **3aq**

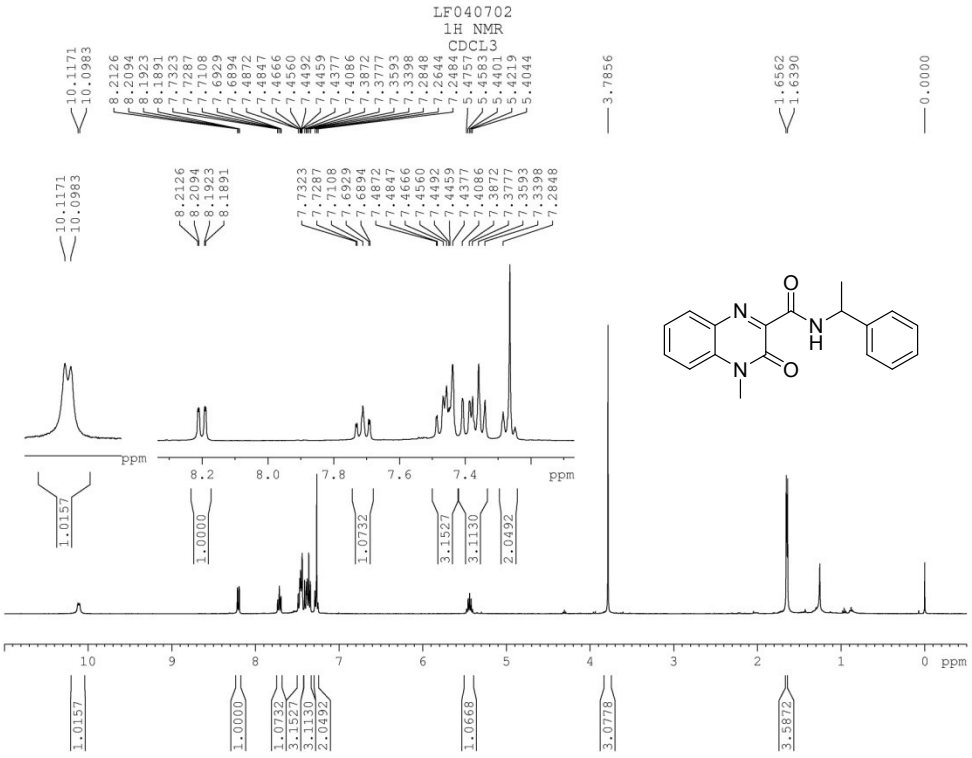


Fig. S79 ^{1}H NMR spectrum of compound **3ar**

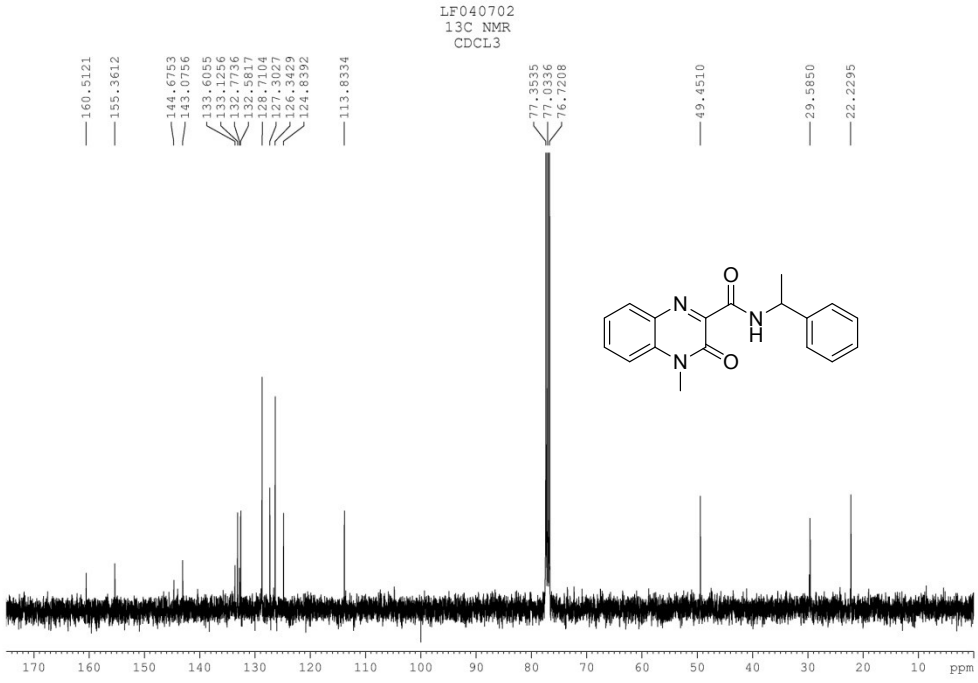


Fig. S80 ^{13}C NMR spectrum of compound **3ar**

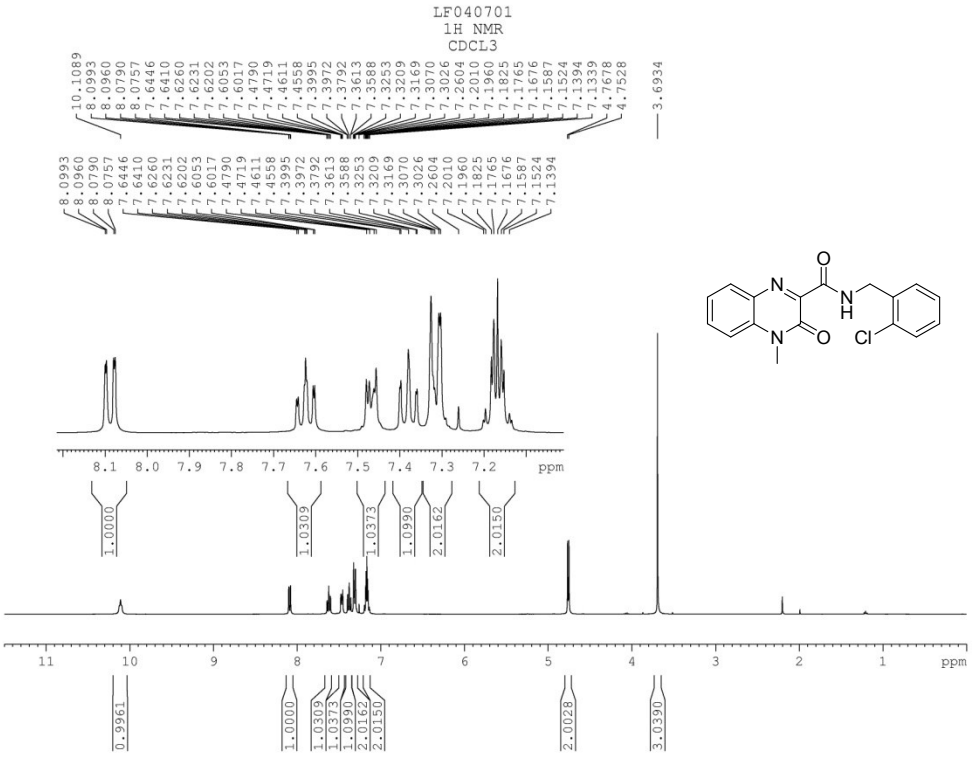


Fig. S81 ^{1}H NMR spectrum of compound **3as**

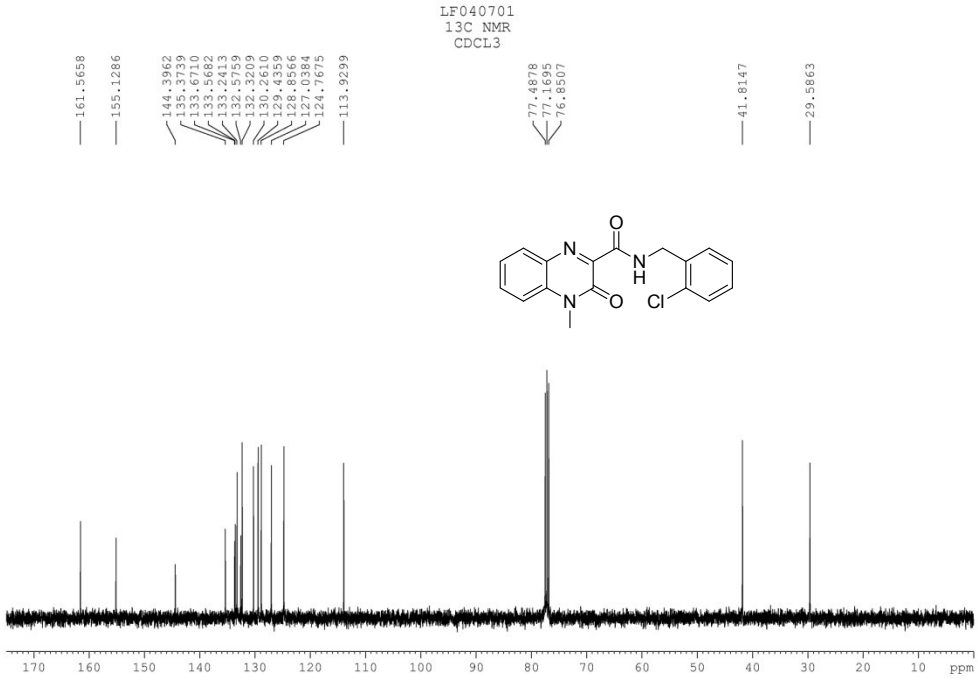


Fig. S82 ^{13}C NMR spectrum of compound **3as**

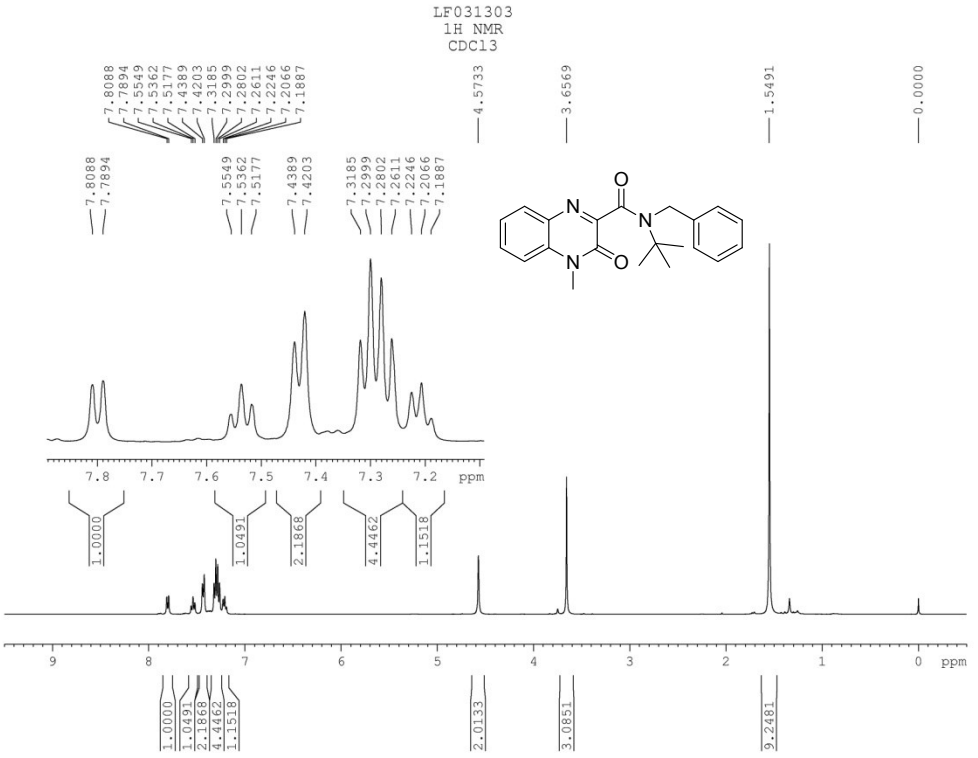


Fig. S83 ^{1}H NMR spectrum of compound **3at**

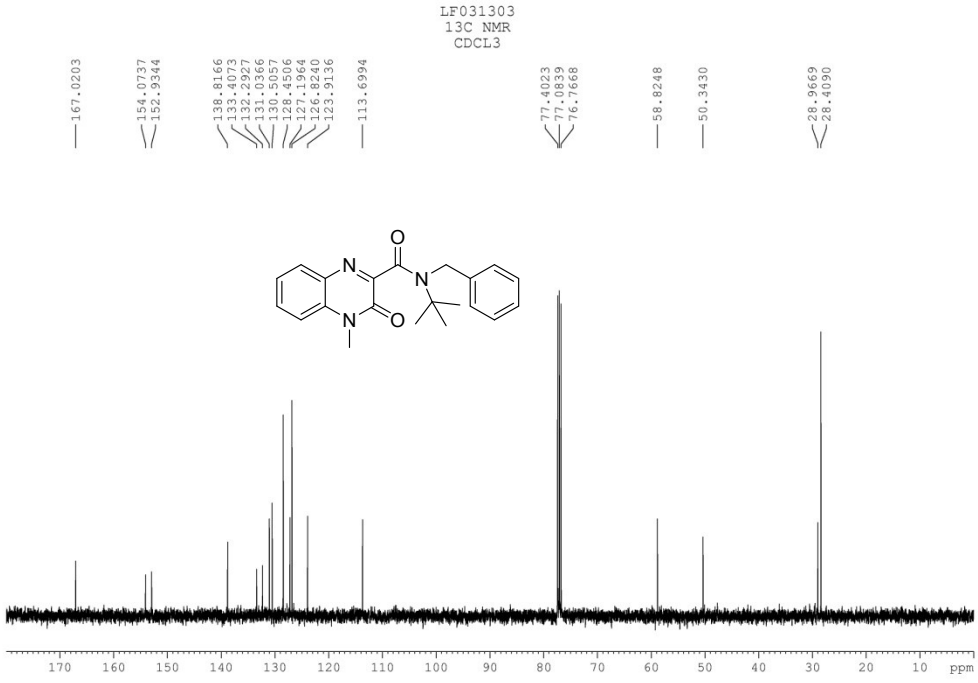


Fig. S84 ^{13}C NMR spectrum of compound **3at**

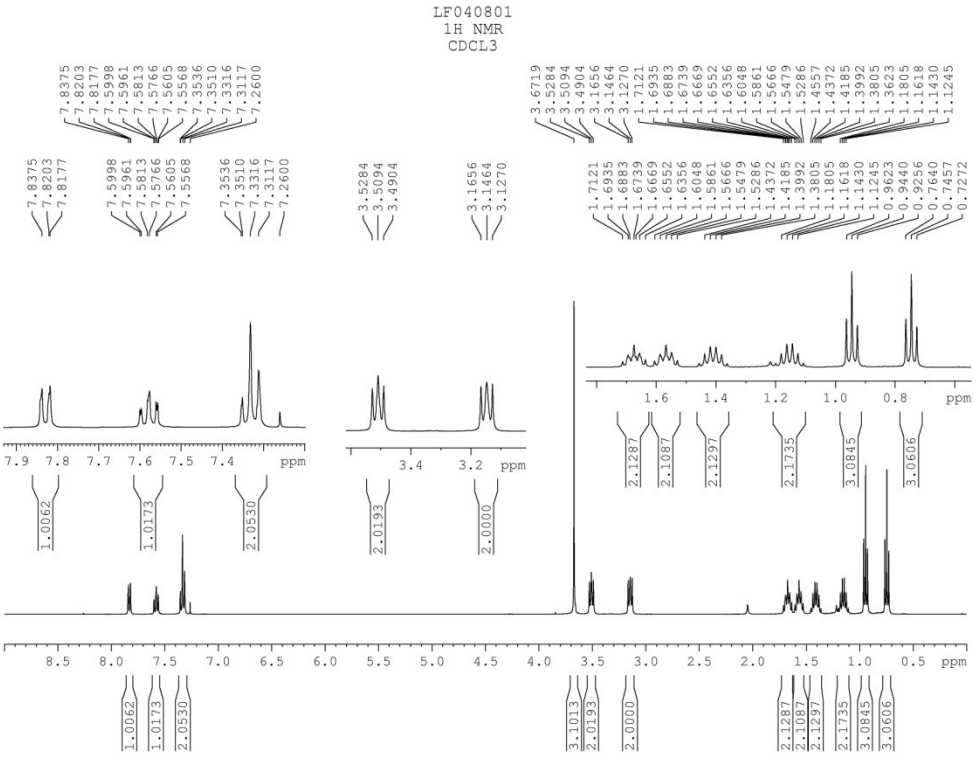


Fig. S85 ^{1}H NMR spectrum of compound **3au**

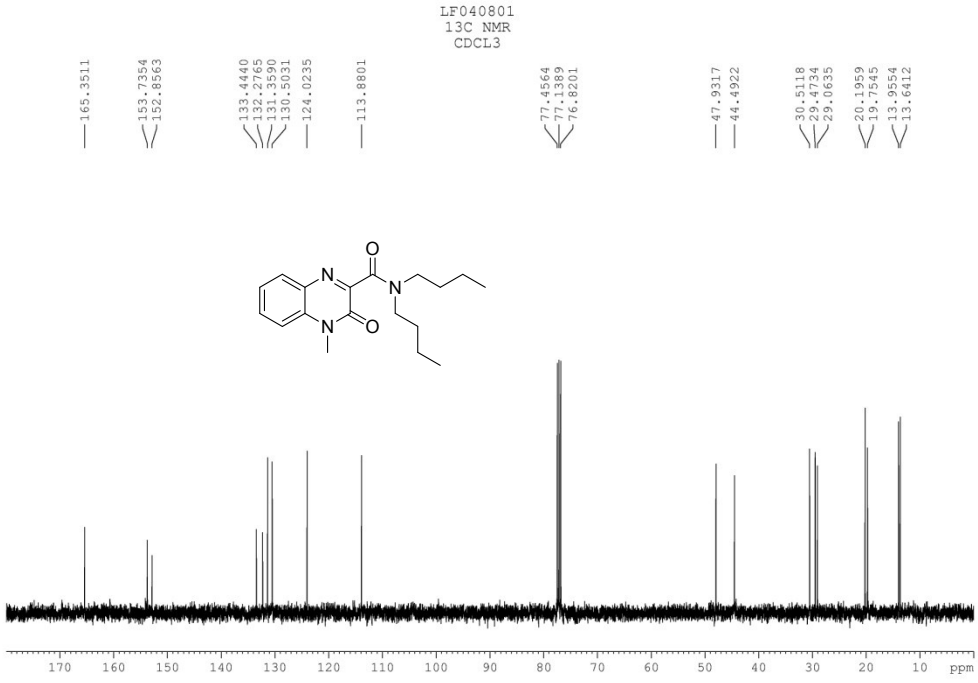


Fig. S86 ^{13}C NMR spectrum of compound **3au**

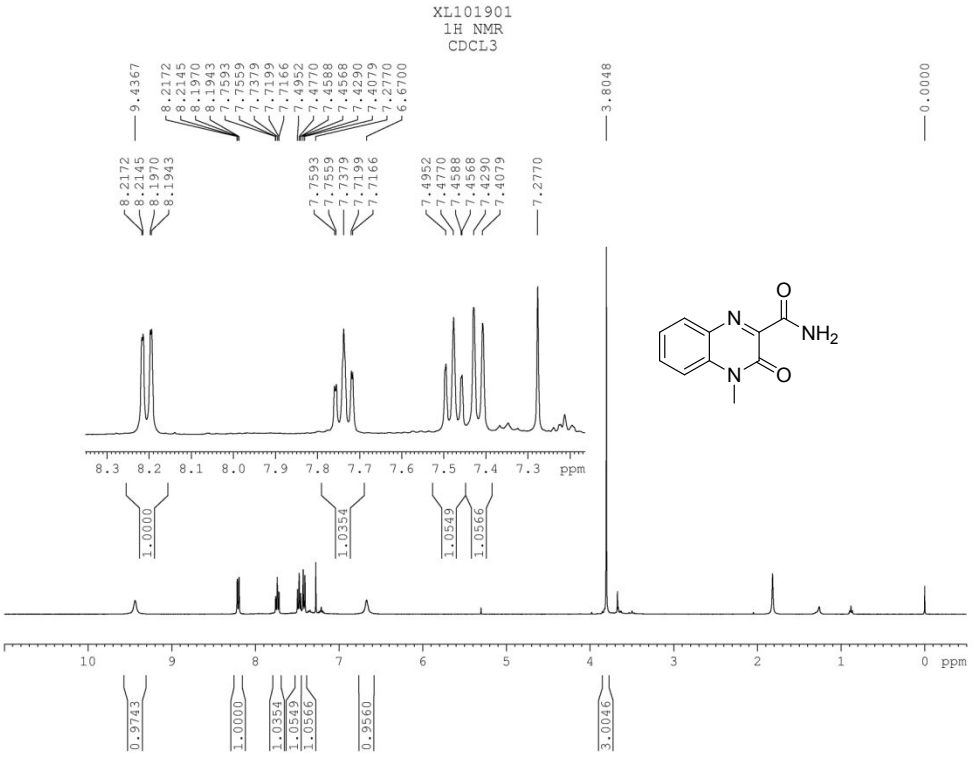


Fig. S87 ^{1}H NMR spectrum of compound **3av**

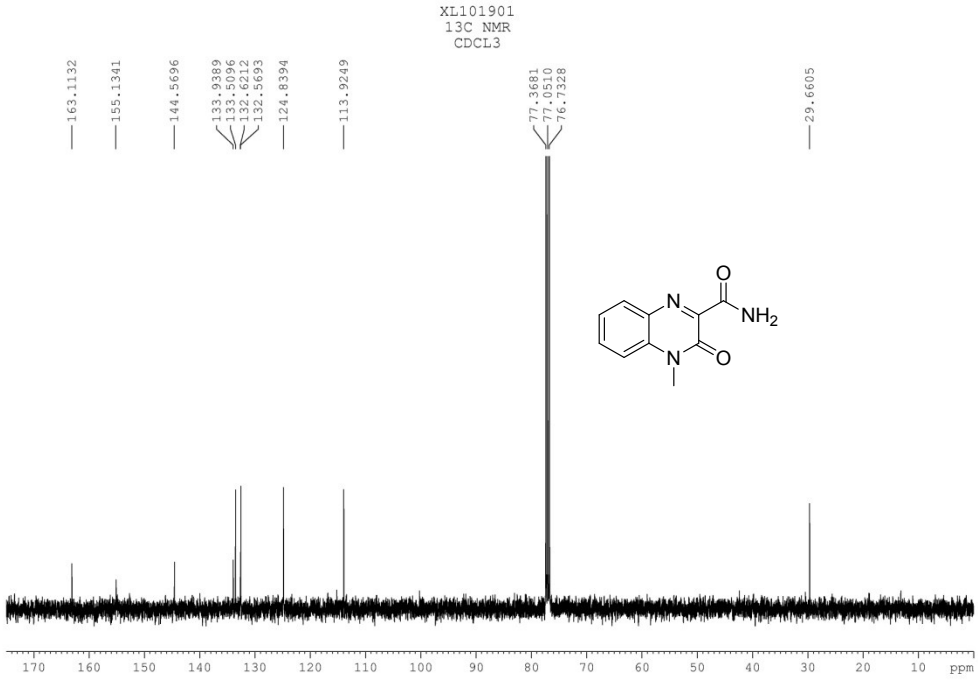


Fig. S88 ^{13}C NMR spectrum of compound **3av**

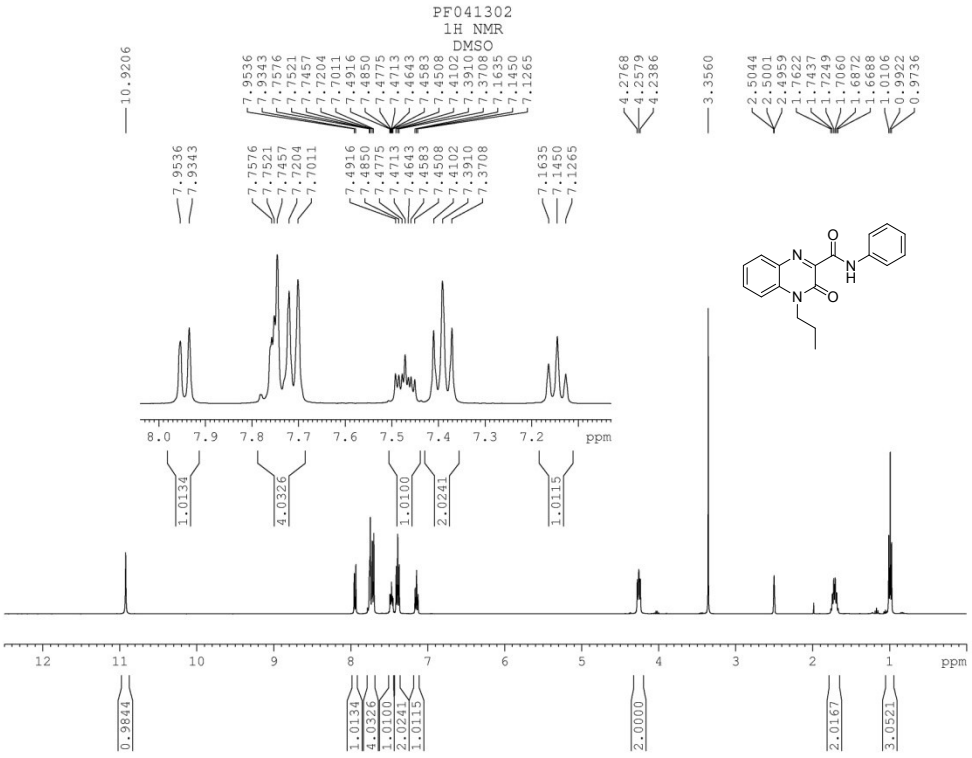


Fig. S89 ^{1}H NMR spectrum of compound **3bb**

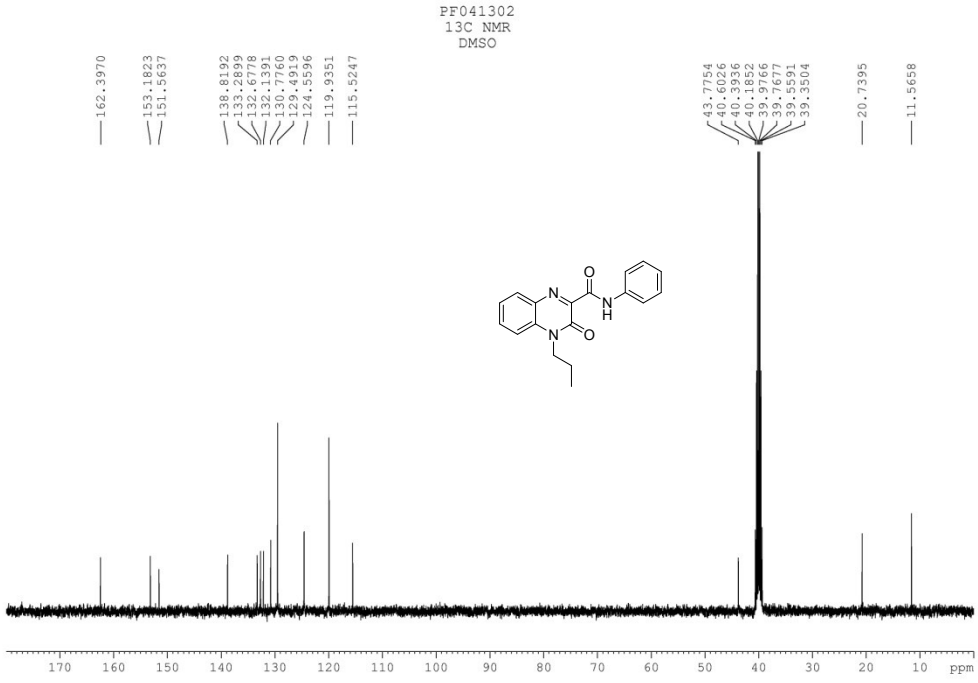


Fig. S90 ^{13}C NMR spectrum of compound **3bb**

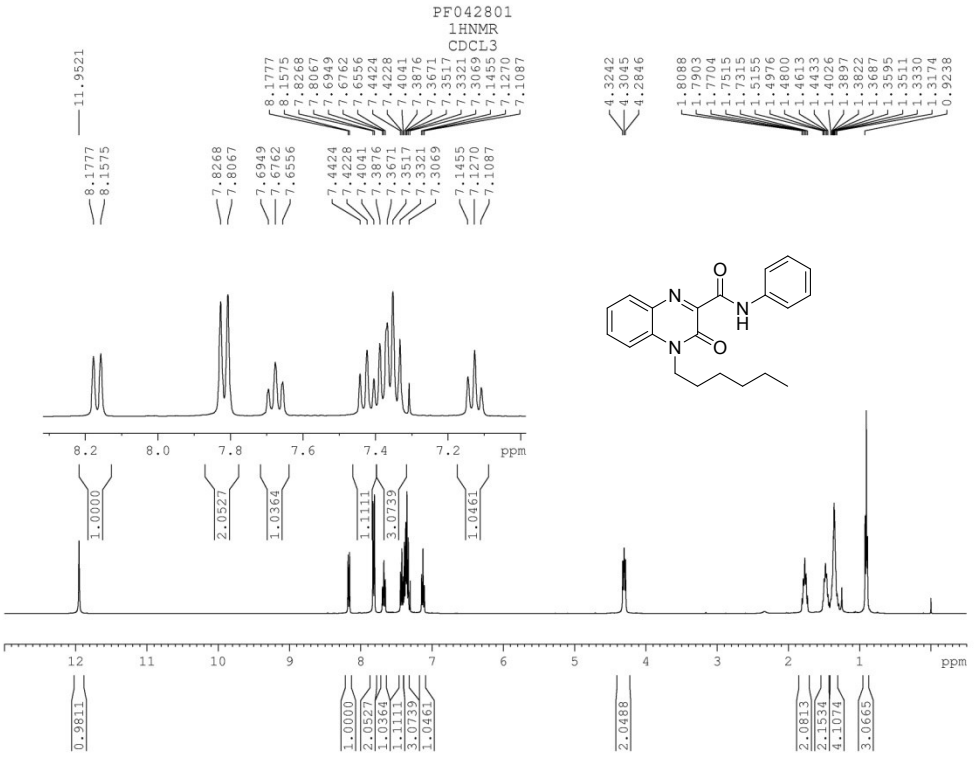


Fig. S91 ^{1}H NMR spectrum of compound **3cb**

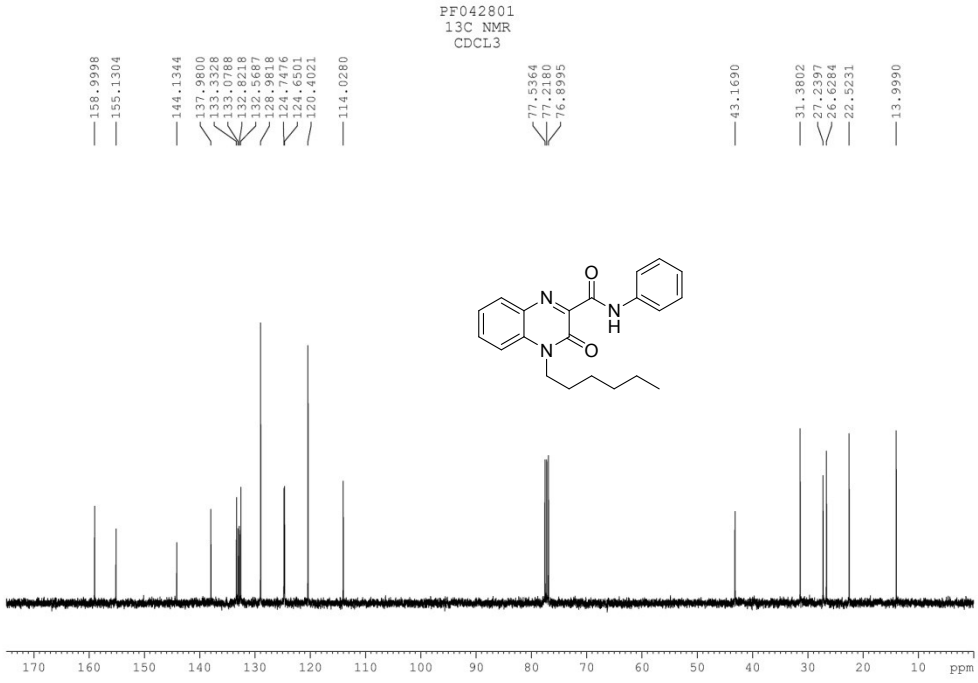


Fig. S92 ^{13}C NMR spectrum of compound **3cb**

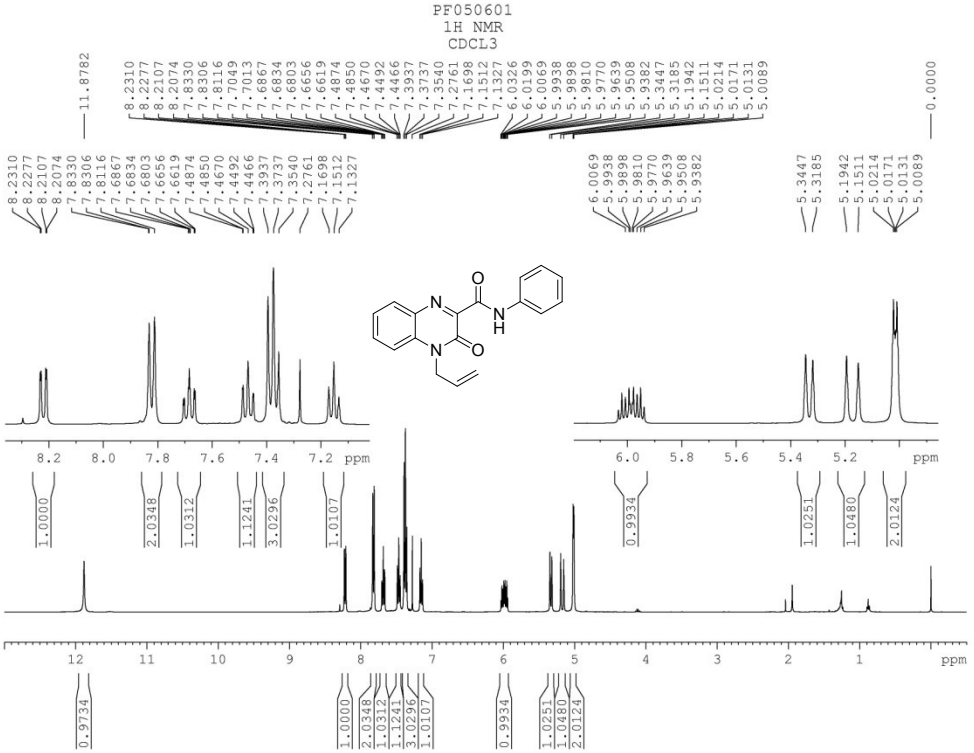


Fig. S93 ^{1}H NMR spectrum of compound **3db**

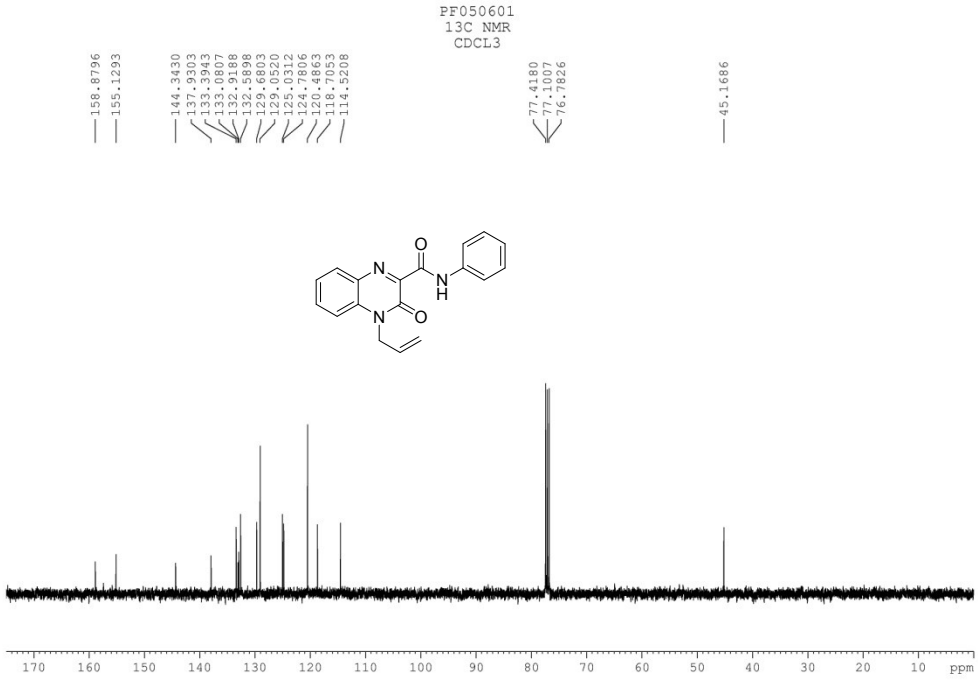


Fig. S94 ^{13}C NMR spectrum of compound **3db**

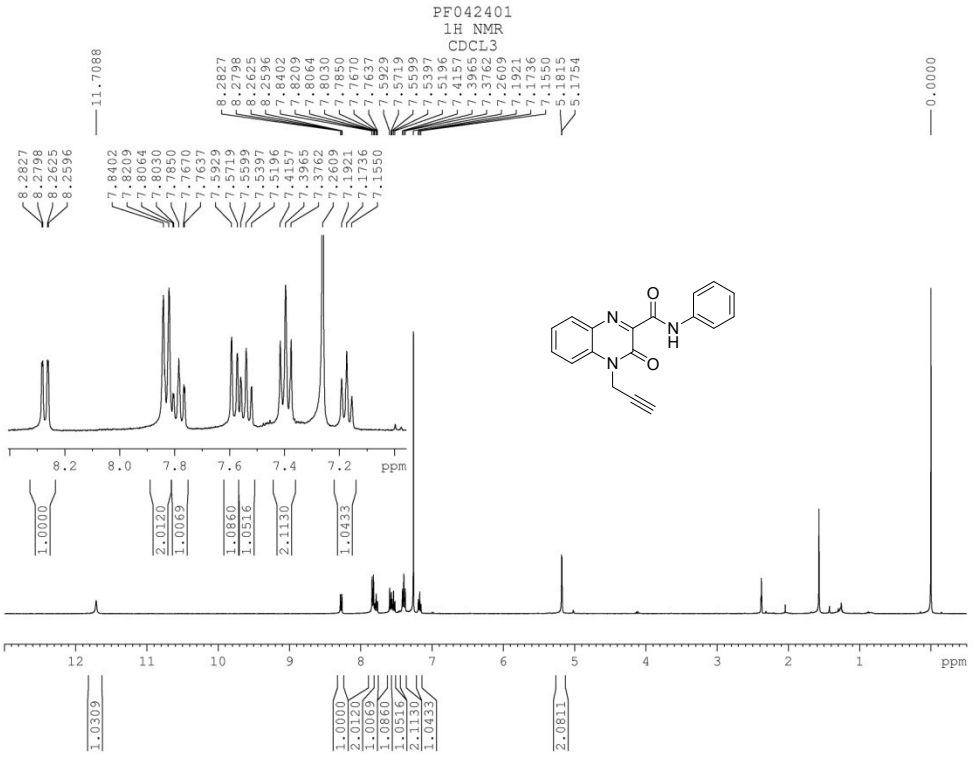


Fig. S95 ^{1}H NMR spectrum of compound **3eb**

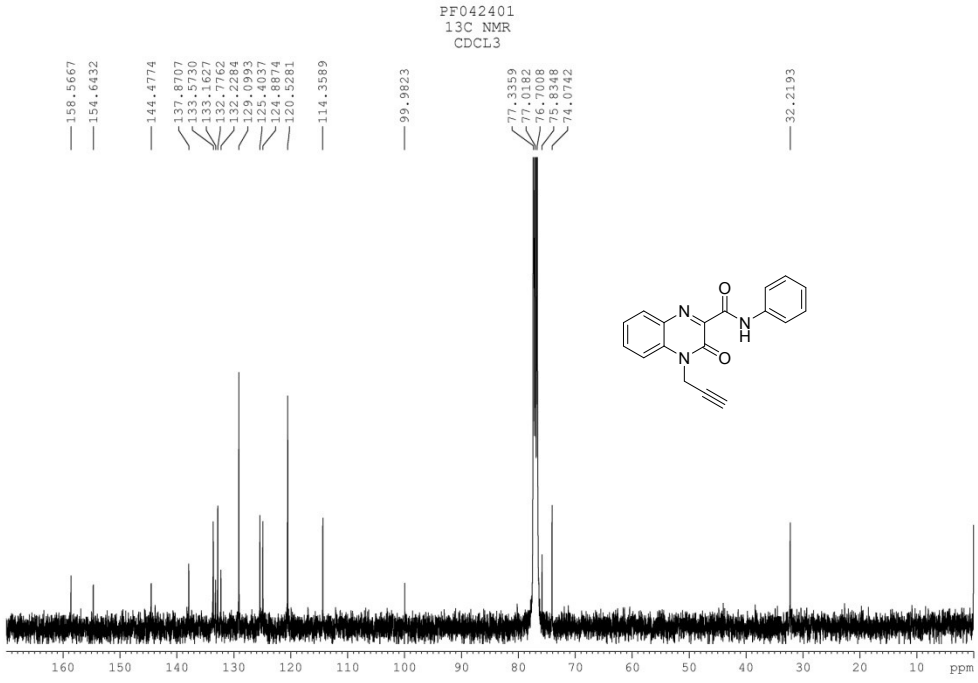


Fig. S96 ^{13}C NMR spectrum of compound **3eb**

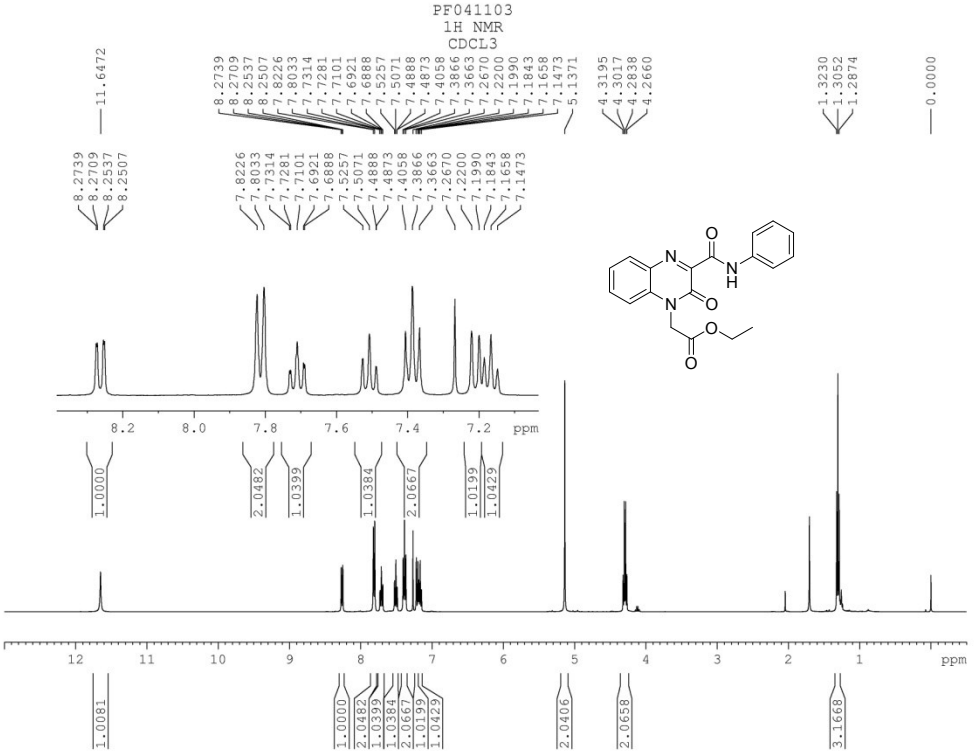


Fig. S97 ^{1}H NMR spectrum of compound **3fb**

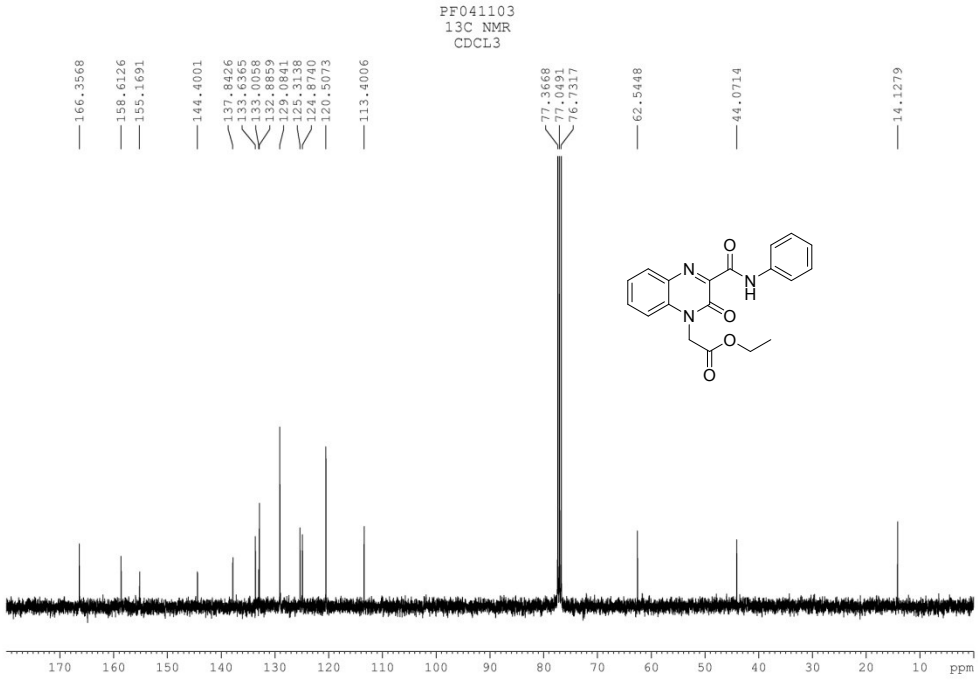


Fig. S98 ^{13}C NMR spectrum of compound **3fb**

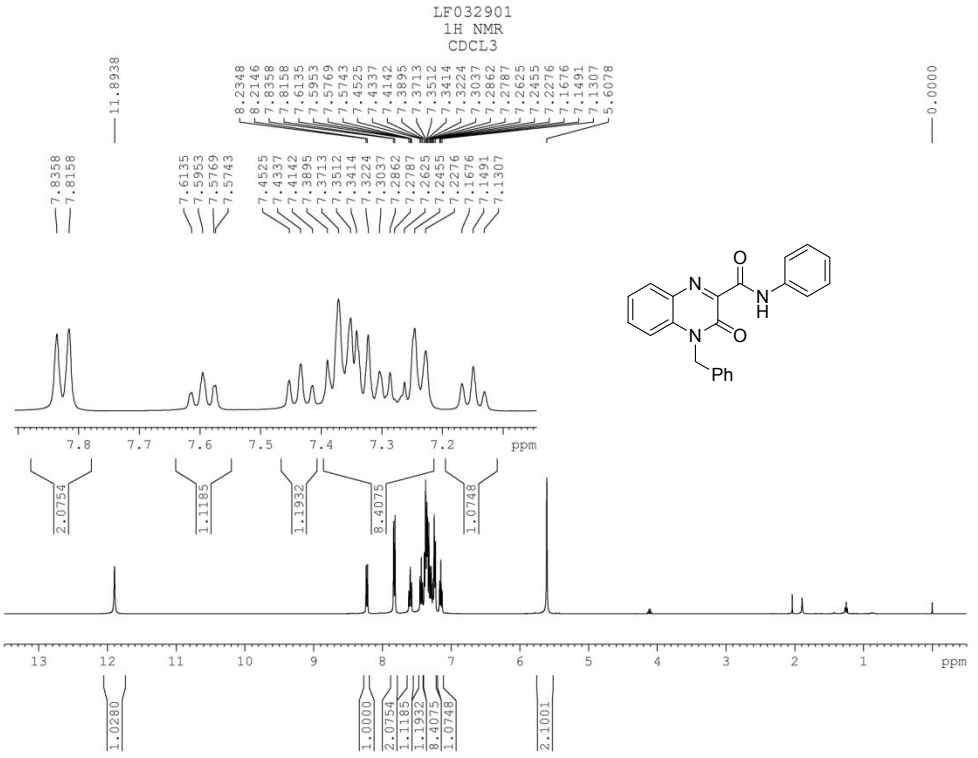


Fig. S99 ^{1}H NMR spectrum of compound **3gb**

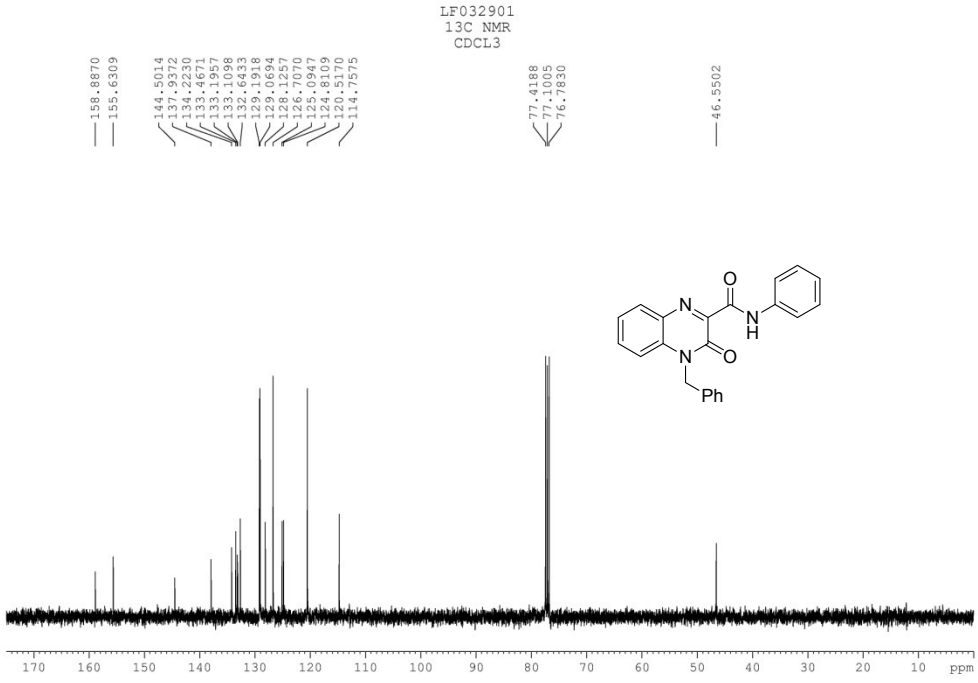


Fig. S100 ^{13}C NMR spectrum of compound **3gb**

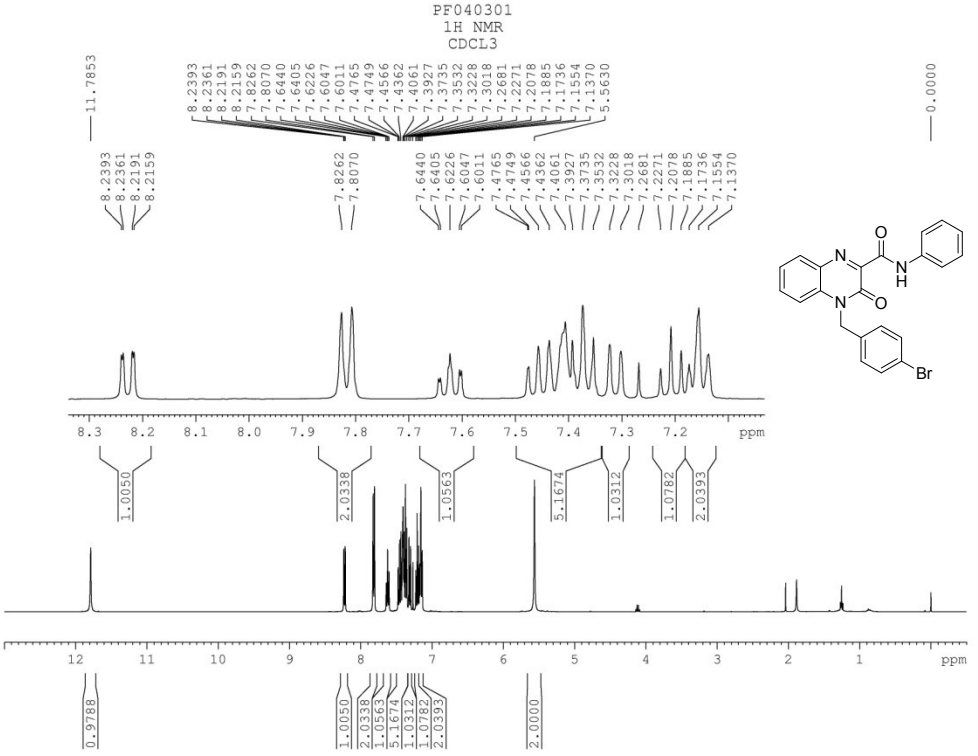


Fig. S101 ^{1}H NMR spectrum of compound **3hb**

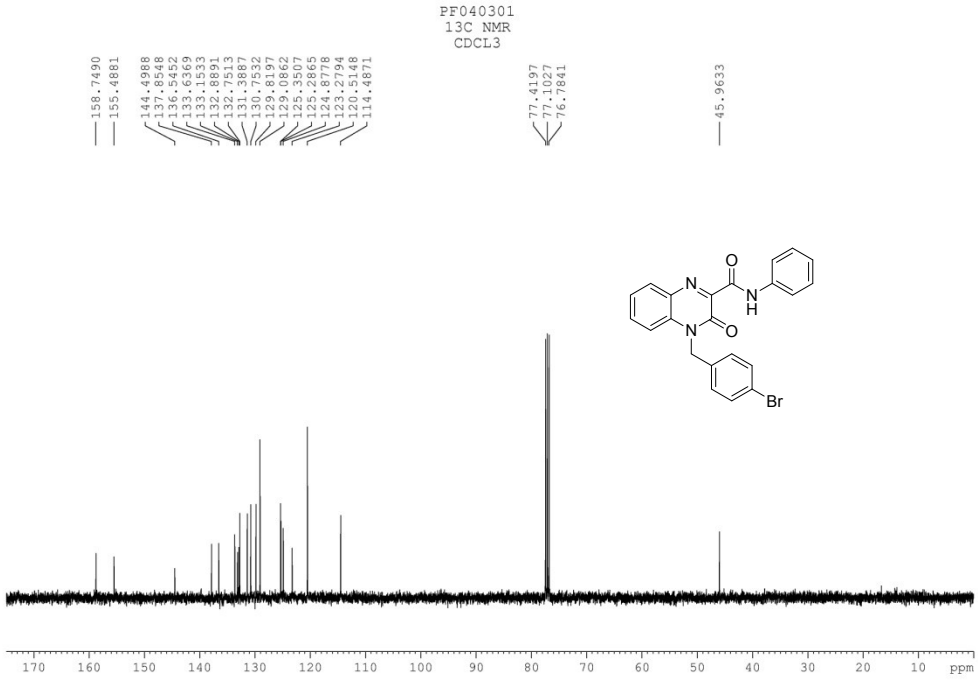


Fig. S102 ^{13}C NMR spectrum of compound **3hb**

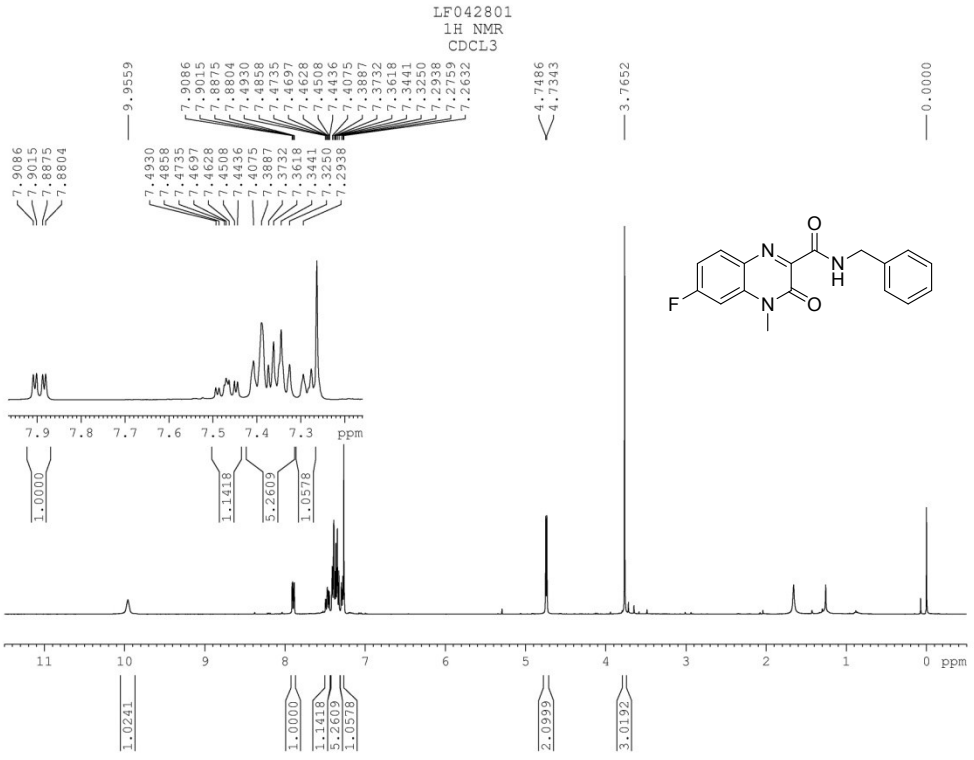


Fig. S103 ^{1}H NMR spectrum of compound **3iq**

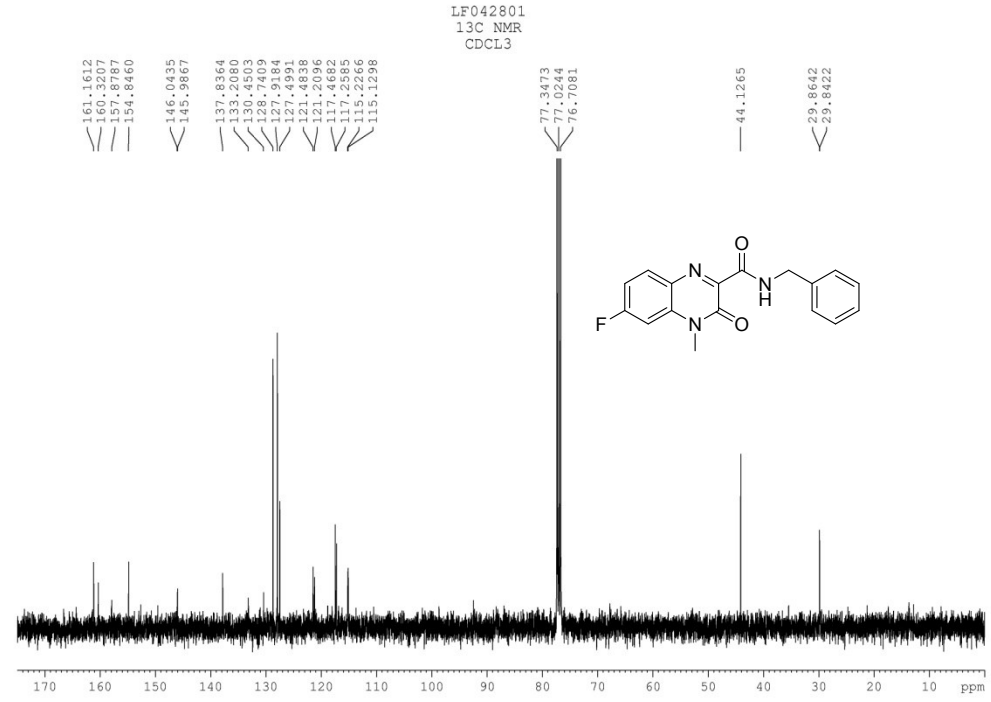


Fig. S104 ^{13}C NMR spectrum of compound **3iq**

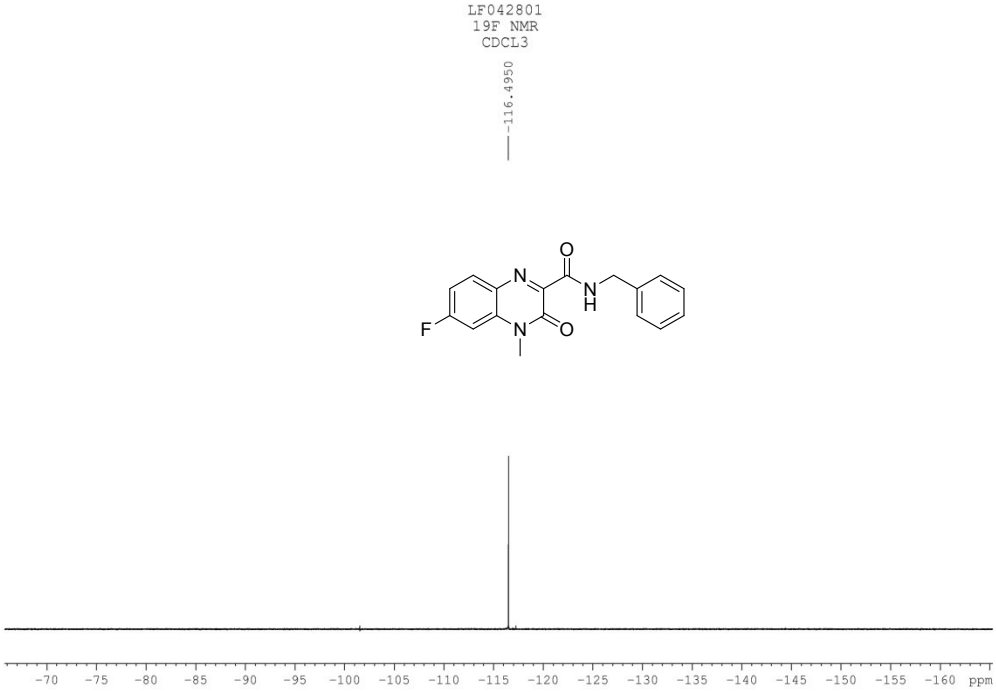


Fig. S105 ^{19}F NMR spectrum of compound **3iq**

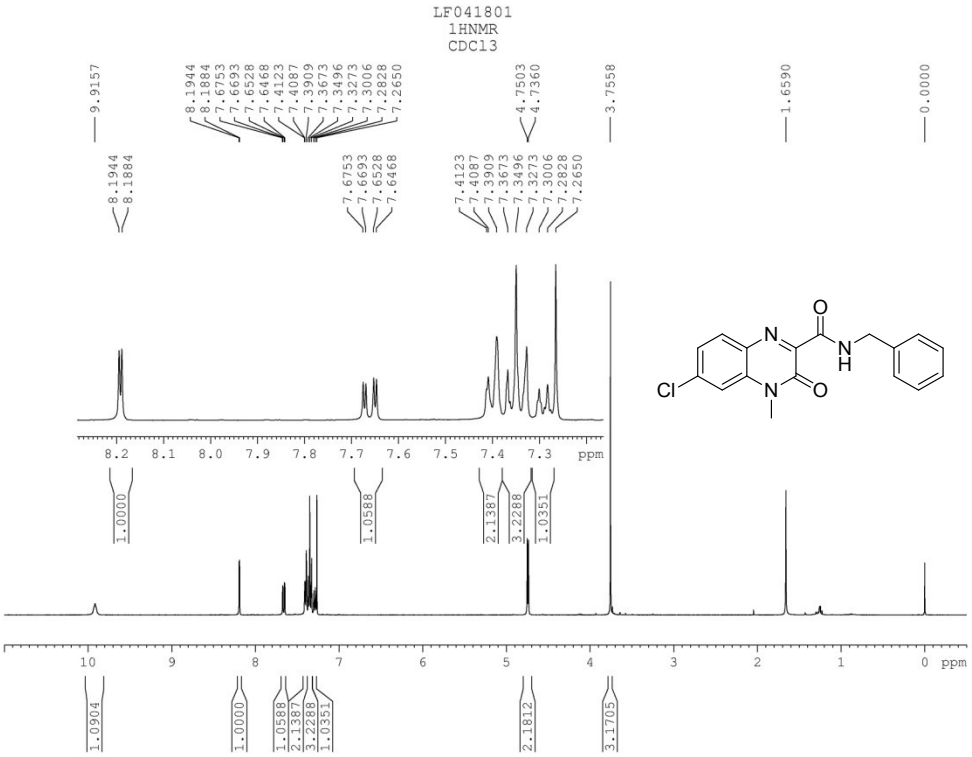


Fig. S106 ^{1}H NMR spectrum of compound **3jq**

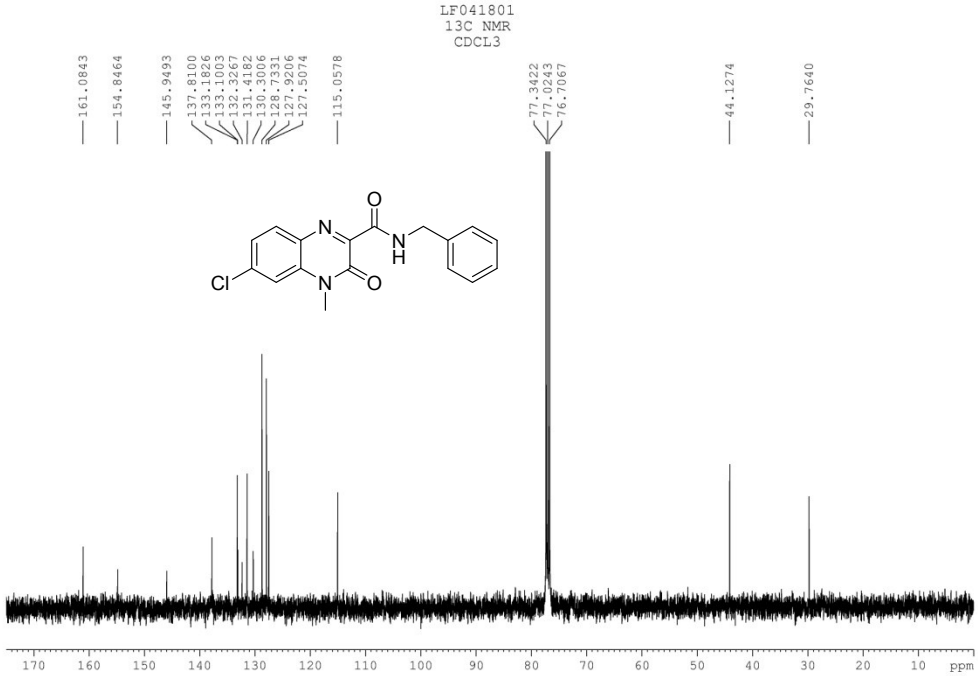


Fig. S107 ^{13}C NMR spectrum of compound **3jq**

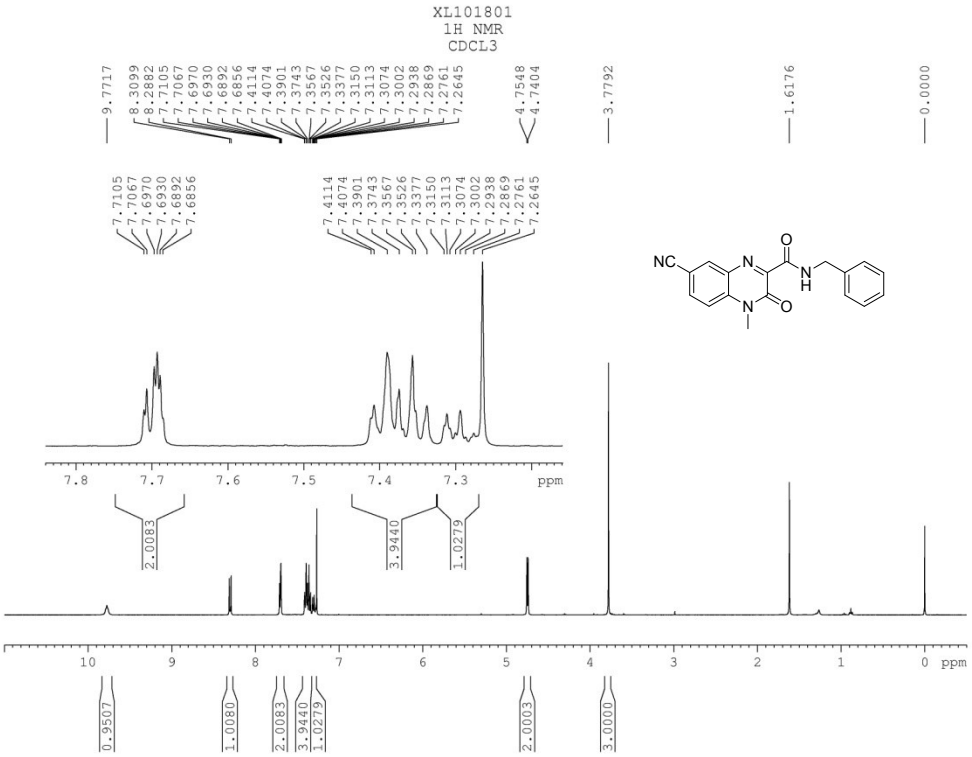


Fig. S108 ^{1}H NMR spectrum of compound **3kq**

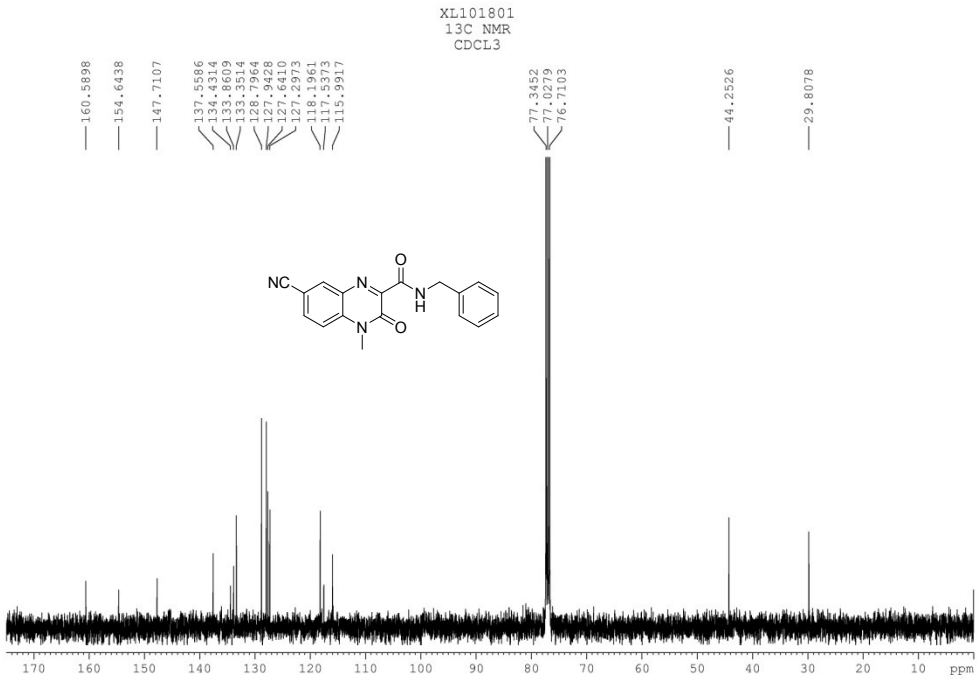


Fig. S109 ^{13}C NMR spectrum of compound **3kq**

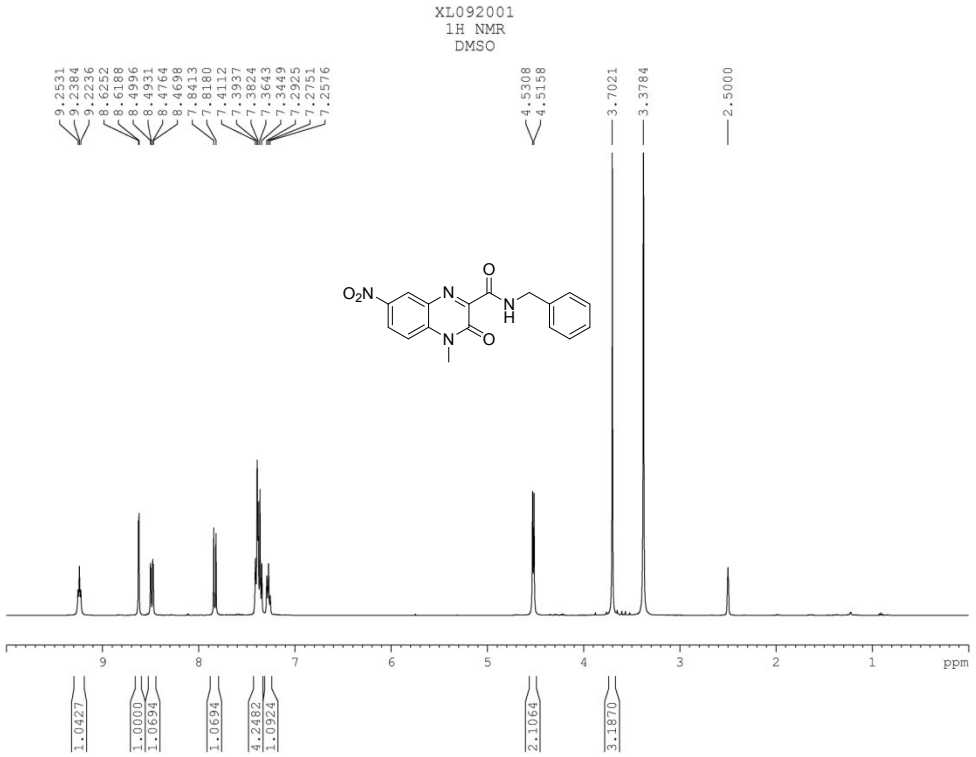


Fig. S110 ^{1}H NMR spectrum of compound **3lq**

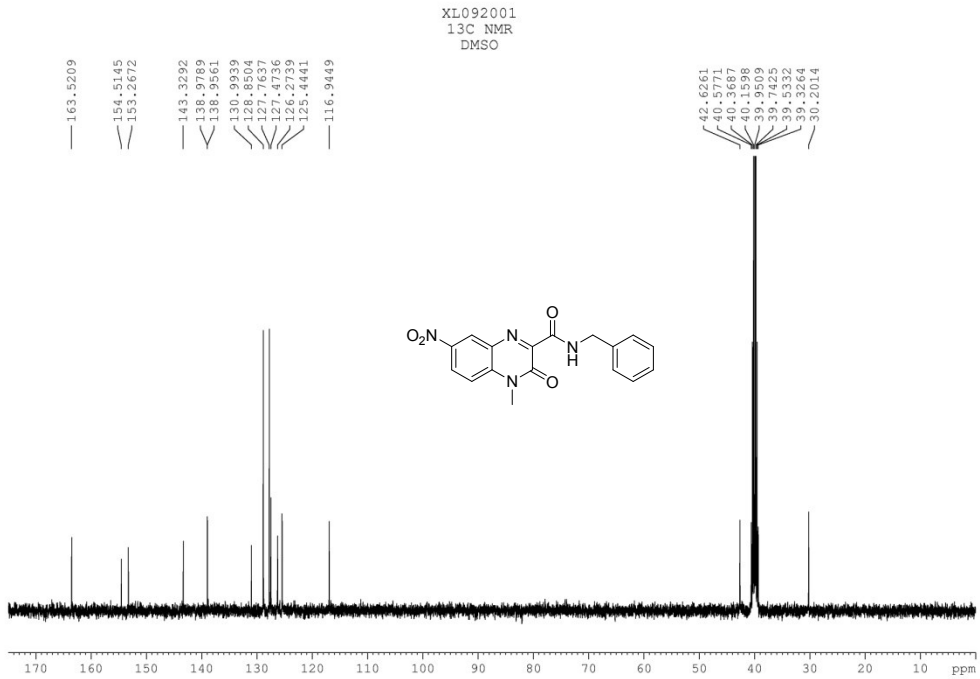


Fig. S111 ^{13}C NMR spectrum of compound **3lq**

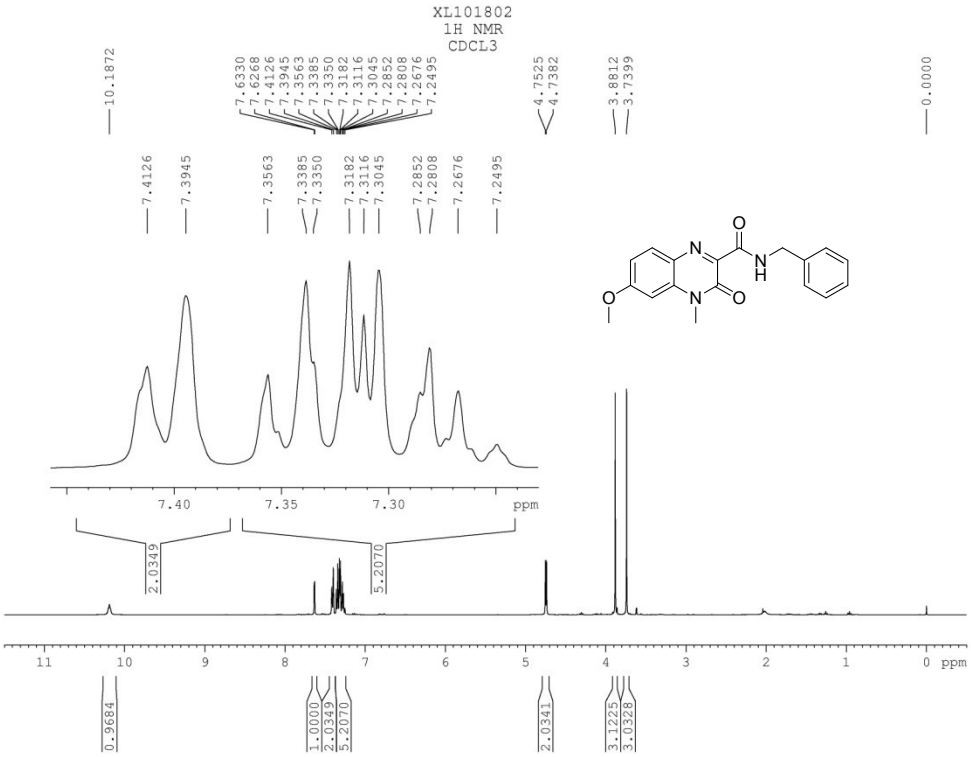


Fig. S112 ^{1}H NMR spectrum of compound **3mq**

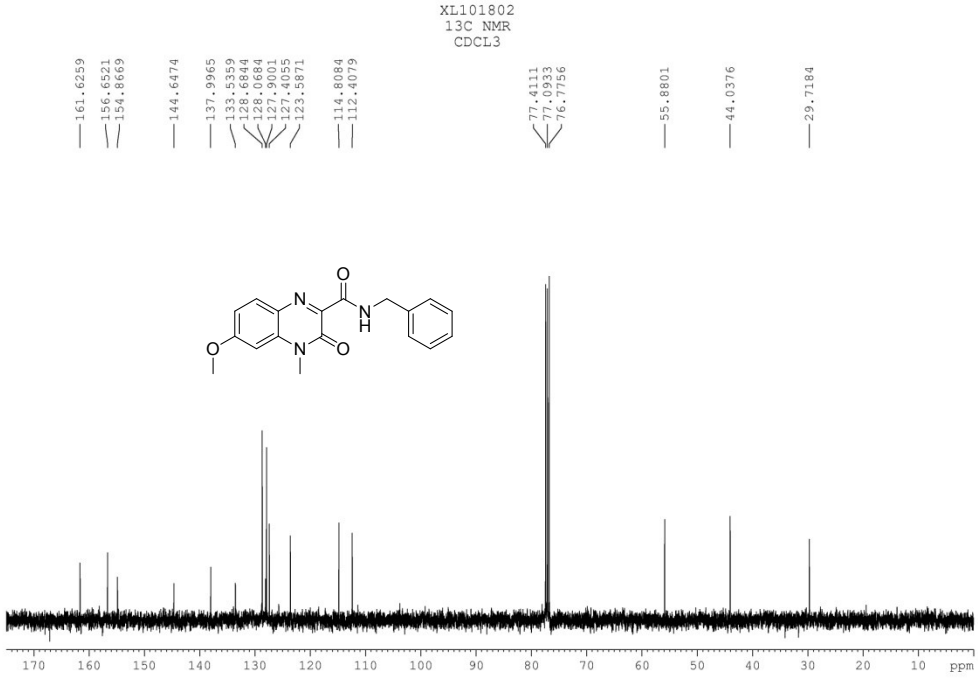


Fig. S113 ^{13}C NMR spectrum of compound **3mq**

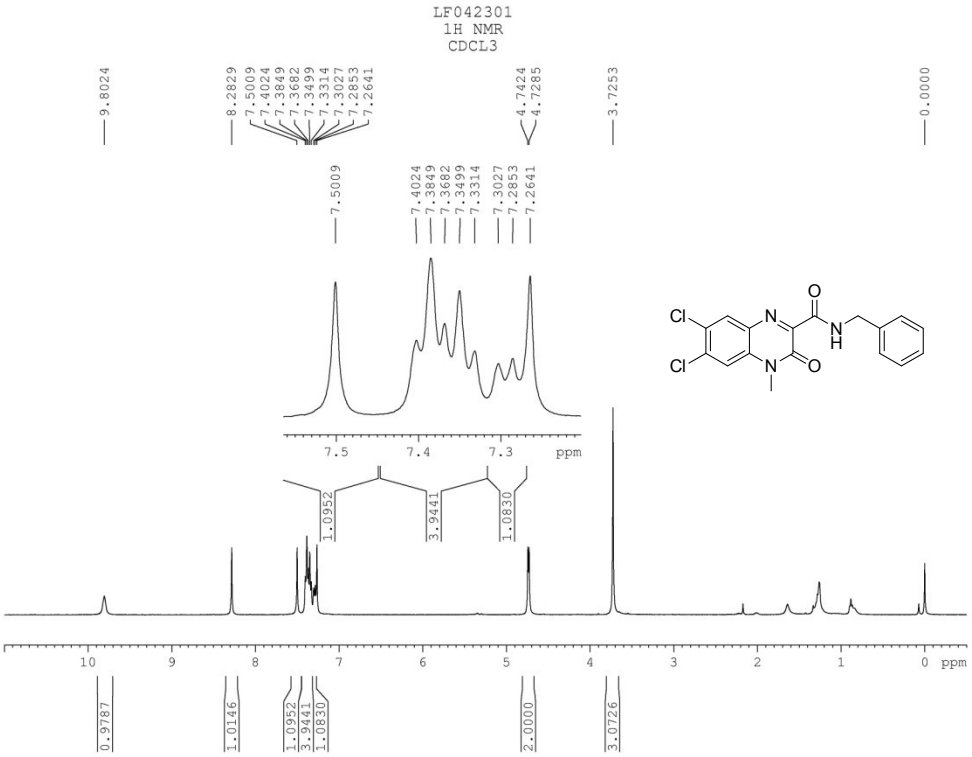


Fig. S114 ^{1}H NMR spectrum of compound **3nq**

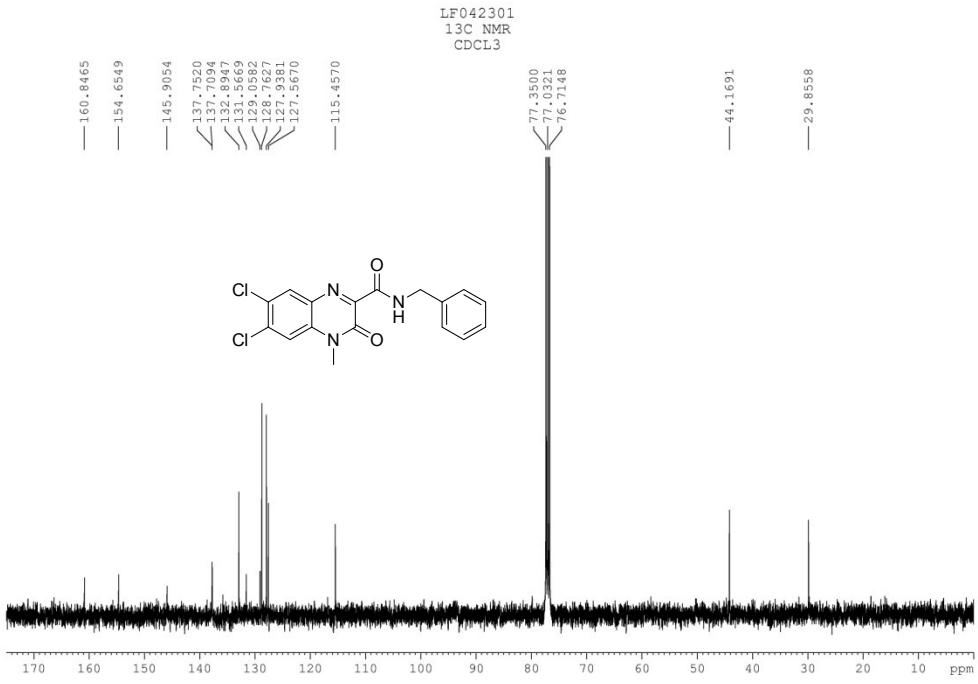


Fig. S115 ^{13}C NMR spectrum of compound **3nq**

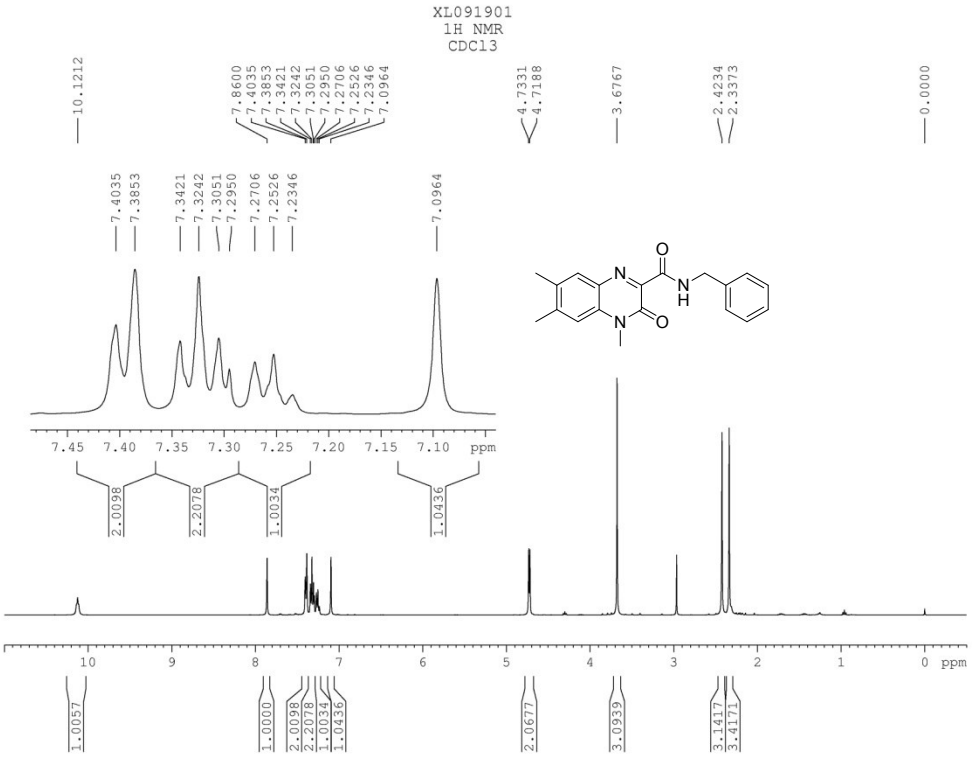


Fig. S116 ^{1}H NMR spectrum of compound **3oq**

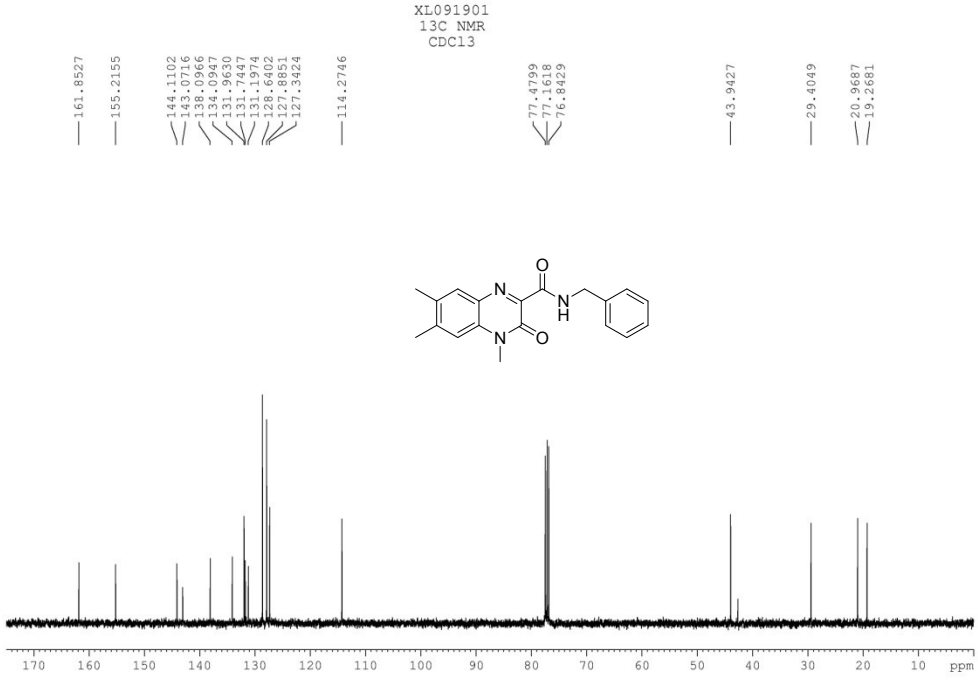


Fig. S117 ^{13}C NMR spectrum of compound **3oq**

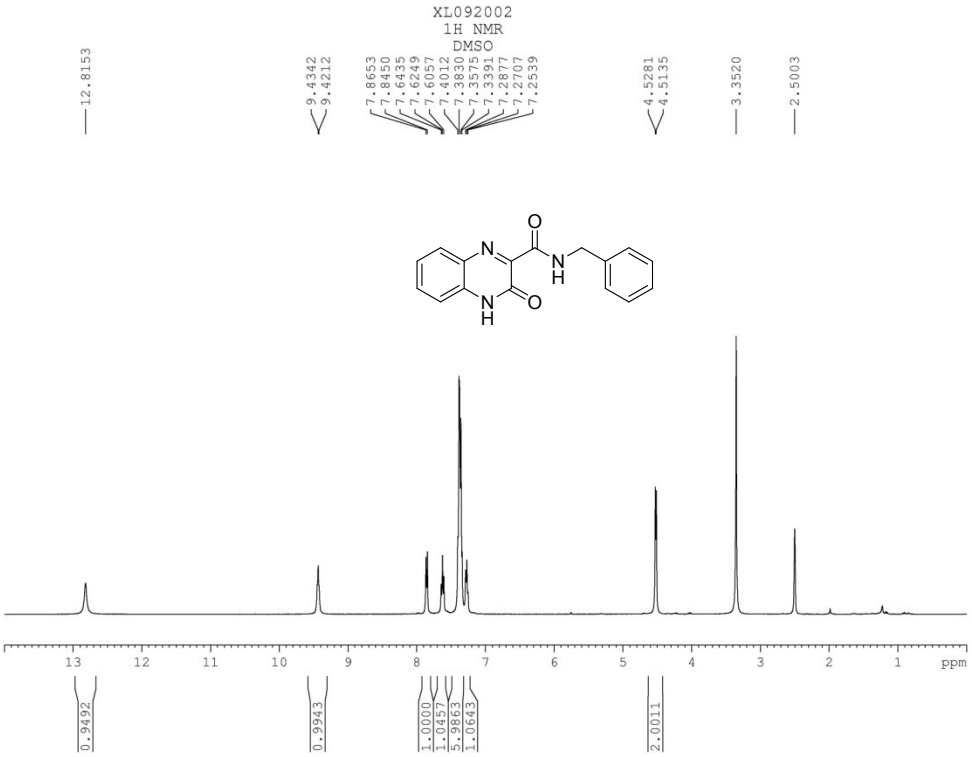


Fig. S118 ^{1}H NMR spectrum of compound **3pq**

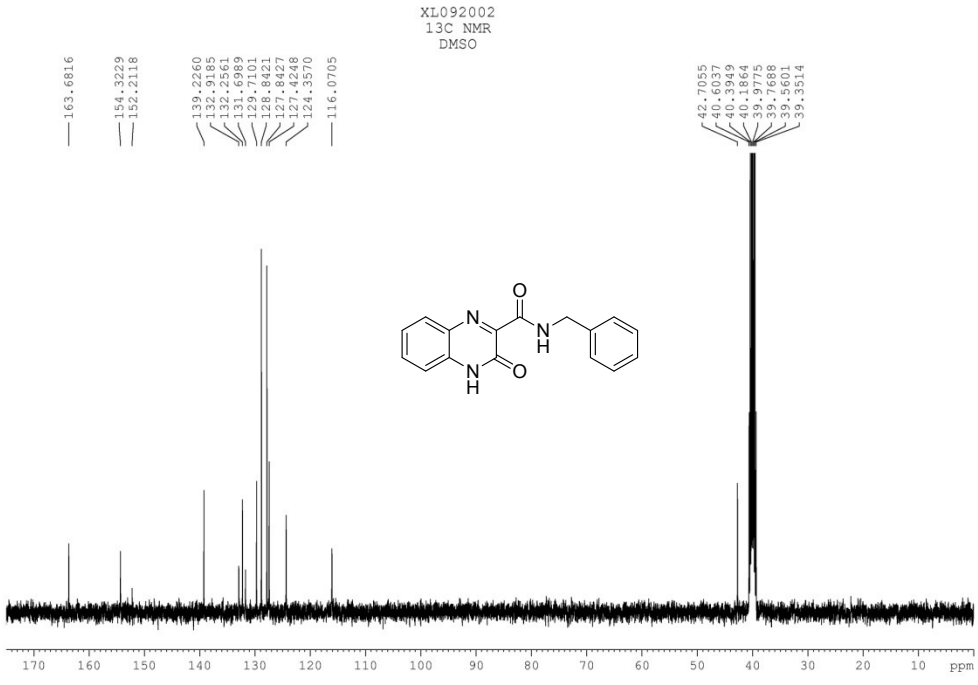


Fig. S119 ^{13}C NMR spectrum of compound **3pq**

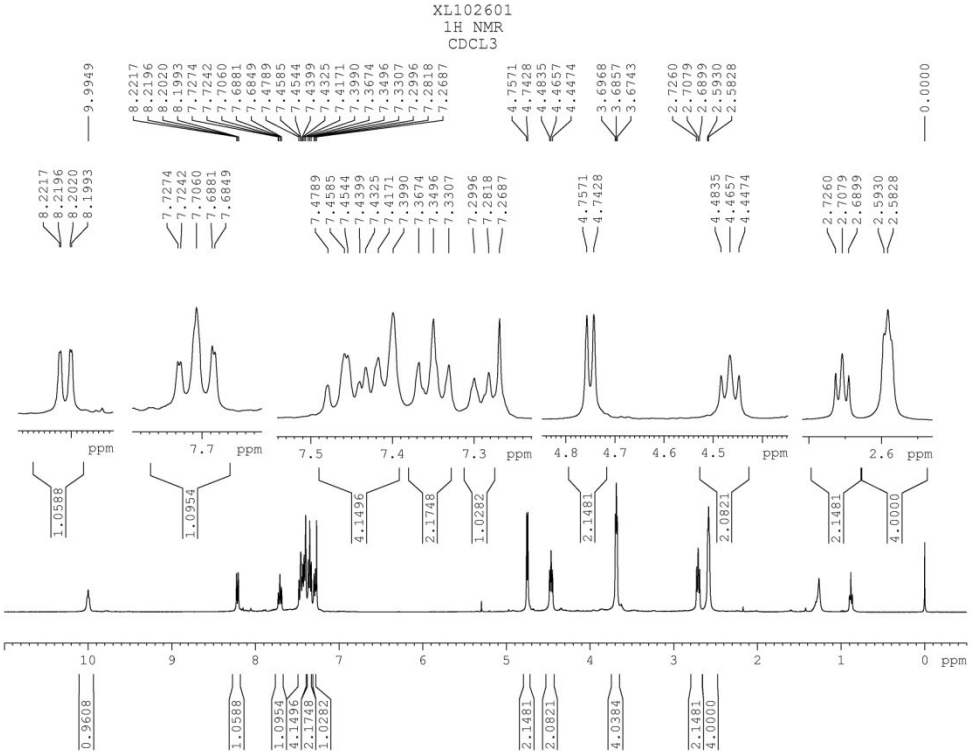


Fig. S120 ^{1}H NMR spectrum of compound **4**

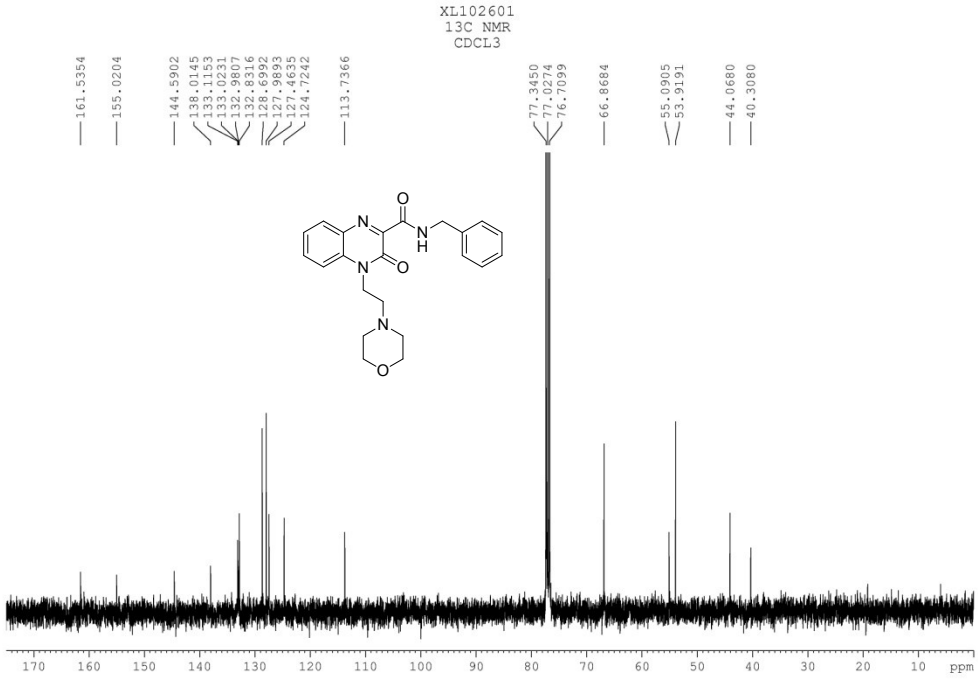


Fig. S121 ^{13}C NMR spectrum of compound **4**