Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2018

Base-promoted ring opening of 3-chlorooxindoles for the construction of 2-aminoarylthioates and their transformation to quinazolin-4(3*H*)-ones

Tej Narayan Poudel, Hari Datta Khanal and Yong Rok Lee*

School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Korea

E-mail: yrlee@yu.ac.kr

Phone: 82-53-810-2529; Fax: 82-53-810-4631

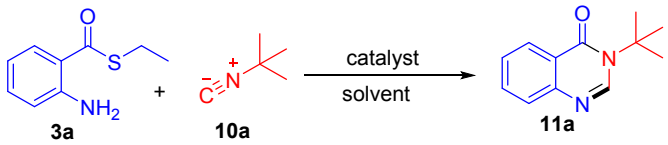
Supplementary Information

Contents

1. Optimization for the formation of quinazolin-4(3*H*)-ones (**11**) S2
2. Characterization data of substrates (**1a-1e**) S2-S3
3. Characterization data of the synthesized compounds (**3-6** and **11**) S3-S10
4. Copies of NMR spectra of substrates (**1a-1e**) S11-S15
5. Copies of NMR spectra of synthesized compounds (**3-6** and **11**) S16-S55
6. Experimental section for fluorescence sensing S56

Optimization of the reaction conditions for the formation of quinazolin-4(3*H*)-ones

Table S1. Optimization of the reaction conditions for the formation of **11a**[a]



S. No.	Catalysts (10 mol%)	Solvents	Condition	Yield (%)
1	-	Toluene	12h, Reflux	-
2	$In(OTf)_3$	Toluene	12h, Reflux	50
3	$In(acac)_3$	Toluene	12h, Reflux	15
4	$Rh_2(OPiv)_4$	Toluene	12h, 80 °C	Trace
5	$Au(PPh_3)CH_3$	Toluene	12h, 80 °C	Trace
6	$Pd(OAc)_2$	Toluene	12h, Reflux	-
7	AgOTf	Toluene	12h, 80 °C	45
8	$Fe(OAc)_3$	Toluene	12h, 80 °C	Trace
9	$Cu(OTf)_2$	Toluene	12h, 80 °C	86
10	$Cu(OTf)_2$	CH_3CN	12h, 80 °C	20
11	$Cu(OTf)_2$	THF	12h, 80 °C	30

[a]Reaction conditions: **3a** (0.27 mmol), **10a** (0.27 mmol), and catalyst (10 mol%) in 3 mL solvent were stirred under nitrogen gas protection.

Characterization data of substrates (1a-1e)

3-Chloroindolin-2-one (1a): ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.79 (1H, s), 7.36 (1H, d, J = 7.4 Hz), 7.29 (1H, t, J = 7.7 Hz), 7.03 (1H, t, J = 7.5 Hz), 6.87 (1H, d, J = 7.8 Hz), 5.57 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.2, 142.4, 130.3, 126.5, 125.6, 122.3, 110.1, 52.2; ATR-IR (neat) 3351, 3150, 1685, 1618, 1466, 1165, 743, 674 cm^{-1}.

3-Chloro-5-methoxyindolin-2-one (1b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (1H, s), 6.97 (1H, s), 6.80 (1H, s), 5.11 (1H, s), 3.77 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 156.3, 134.2, 127.2, 115.5, 112.2, 111.2, 55.8, 52.3; ATR-IR (neat) 3151, 1686, 1479, 1200, 1168, 760, 680, 538 cm^{-1}.

3,5-Dichloroindolin-2-one (1c): ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.91 (1H, s), 7.43 (1H, s), 7.35 (1H, dd, J = 8.3, 2.1 Hz), 6.88 (1H, d, J = 8.3 Hz), 5.58 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.7, 142.1, 130.9, 129.3, 127.0, 126.5, 112.4, 52.5; ATR-IR (neat) 3148, 2098, 1739, 1684, 1473, 1177, 823, 675, 561 cm^{-1}.

3-Chloro-5-fluoroindolin-2-one (1d): ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.81 (1H, s), 7.29 (1H, dd, J = 8.0, 2.1 Hz), 7.18-7.11 (1H, m), 6.89-6.85 (1H, m), 5.59 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.1, 158.1 (J = 236.2 Hz), 138.6, 128.1 (J = 8.7 Hz), 116.7 (J = 23.2 Hz), 113.38 (J = 25.5 Hz), 111.1 (J = 8.2 Hz), 52.0; ATR-IR (neat) 3166, 1685, 1398, 1479, 1177, 757, 690, 540 cm^{-1}.

3-Chloro-5-nitroindolin-2-one (1e): ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.45 (1H, s), 8.21-8.16 (2H, m), 7.04 (1H, d, J = 8.5 Hz), 5.66 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.5, 148.7, 142.4, 127.5, 127.2, 121.2, 110.4, 51.1; ATR-IR (neat) 3308, 1741, 1615, 1327, 1192, 1069, 835, 661 cm^{-1}.

Characterization data of the synthesized compounds

***S*-Ethyl 2-aminobenzothioate (3a):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and ethanethiol **2a** (31 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (65 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 8.4 Hz), 7.20–7.15 (1H, m), 6.61–6.56 (2H, m), 5.70 (2H, s), 2.93 (2H, q, J = 7.5 Hz), 1.25 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 147.7, 234.1, 130.1, 118.5, 117.1, 116.3, 23.1, 14.8; ATR-IR (neat) 3478, 3364, 2967, 2928, 1612, 1576, 1200, 909, 741, 681 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_9H_{11}NOS$: 181.0561. Found: 181.0558.

***S*-Propyl 2-aminobenzothioate (3b):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and propane-1-thiol **2b** (38 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (73 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (1H, d, J = 8.4 Hz), 7.23-7.18 (1H, m), 6.65-6.60 (2H, m), 5.89 (2H, s), 2.93 (2H, t, J = 7.5 Hz), 1.69-1.56 (2H, m), 0.97 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 147.2, 134.1, 130.1, 118.9, 117.3, 116.7, 30.7, 23.0, 13.5; ATR-IR (neat) 3478, 3364, 2962, 2926, 1613, 1579, 1199, 911, 812, 742, 681 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{13}NOS$: 195.0718. Found: 195.0718.

***S*-Butyl 2-aminobenzothioate (3c)**: Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and butane-1-thiol **2c** (45 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (74 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1H, dd, J = 8.7, 1.8 Hz), 7.17 (1H, t, J = 7.2 Hz), 6.59–6.54 (2H, m), 5.75 (2H, s), 2.92 (2H, t, J = 7.2 Hz), 1.58–1.53 (2H, m), 1.40–1.33 (2H, m), 0.86 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 147.7, 134.0, 130.1, 118.5, 117.0, 116.3, 31.6, 28.4, 22.0, 13.6; ATR-IR (neat) 3479, 3365, 2957, 1613, 1578, 1199, 1158, 910, 741, 681 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{15}NOS$: 209.0874. Found: 209.0876.

***S*-Isopropyl 2-aminobenzothioate (3d)**: Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and propane-2-thiol **2d** (38 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (68 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (1H, dd, J = 8.7, 1.5 Hz), 7.16–7.10 (1H, m), 6.56–6.50 (2H, m), 5.71 (2H, s), 3.75–3.61 (1H, m), 1.29 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 147.8, 134.0, 130.0, 118.4, 116.9, 116.1, 34.3, 23.0; ATR-IR (neat) 3477, 3356, 2950, 1612, 1190, 1145, 942, 742, 645 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{13}NOS$: 195.0718. Found: 195.0721.

***S*-(*Tert*-butyl) 2-aminobenzothioate (3e):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and 2-methylpropane-2-thiol **2e** (45 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (54 mg, 52%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (1H, d, J = 8.4 Hz), 7.15 (1H, t, J = 7.2 Hz), 6.57–6.52 (2H, m), 5.64 (2H, s), 1.49 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 147.6, 133.8, 130.0, 119.5, 117.2, 116.3, 47.8, 30.0; ATR-IR (neat) 3472, 3358,

2952, 1614, 1468, 1189, 1154, 930, 742, 647 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{15}NOS$: 209.0874. Found: 209.0875.

***S*-Ethyl 2-amino-5-methoxybenzothioate (3f):** Prepared from 3-chloro-5-methoxyindolin-2-one **1b** (99 mg, 0.5 mmol) and ethanethiol **2a** (31 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (76 mg, 72%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (1H, d, J = 2.7 Hz), 6.92 (1H, dd, J = 8.7, 2.7 Hz), 6.59 (1H, d, J = 9.0 Hz), 5.53 (2H, s), 3.75 (3H, s), 2.98 (2H, q, J = 7.2 Hz), 1.31 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 150.5, 142.4, 123.2, 118.6, 118.4, 112.0, 55.8, 23.3, 14.7; ATR-IR (neat) 3476, 3365, 2930, 1583, 1556, 1167, 949, 838, 677 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{13}NO_2S$: 211.0667. Found: 211.0667.

***S*-Butyl 2-amino-5-methoxybenzothioate (3g):** Prepared from 3-chloro-5-methoxyindolin-2-one **1b** (99 mg, 0.5 mmol) and butane-1-thiol **2c** (45 mg, 0.5 mmol) over 14 h according to the general procedure. The product was obtained as a liquid (81 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (1H, d, J = 2.7 Hz), 6.93 (1H, dd, J = 9.0, 2.7 Hz), 6.61 (1H, d, J = 9.0 Hz), 5.53 (2H, s), 3.76 (3H, s), 3.01 (2H, t, J = 7.5 Hz), 1.66–1.61 (2H, m), 1.48–1.41 (2H, m), 0.93 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 150.8, 142.2, 123.2, 118.9, 118.7, 112.5, 55.9, 31.7, 28.7, 22.0, 13.5; ATR-IR (neat) 3483, 3367, 2927, 1584, 1556, 1492, 1241, 1168, 950, 838 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{17}NO_2S$: 239.0980. Found: 239.0982.

***S*-Isopropyl 2-amino-5-methoxybenzothioate (3h):** Prepared from 3-chloro-5-methoxyindolin-2-one **1b** (99 mg, 0.5 mmol) and propane-2-thiol **2d** (38 mg, 0.5 mmol) over 14 h according to the general procedure. The product was obtained as a liquid (61 mg, 54%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (1H, d, J = 2.7 Hz), 6.92 (1H, dd, J = 8.7, 2.7 Hz), 6.60 (1H, d, J = 9.0 Hz), 5.32 (2H, s), 3.84–3.70 (4H, m), 1.38 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 162.3, 150.8, 142.3, 123.2, 118.9, 118.7, 112.4, 55.9, 34.7, 23.1; ATR-IR (neat) 3478, 3366, 2961, 2924, 2859, 1584, 1492, 1169, 1042, 950, 839 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{15}NO_2S$: 225.0823. Found: 225.0826.

***S*-Ethyl 2-amino-5-chlorobenzothioate (3i):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and ethanethiol **2a** (31 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (78 mg, 72%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1H, d, J = 1.8 Hz), 7.18 (1H, dd, J = 8.7, 2.1 Hz), 6.50 (1H, d, J = 8.7 Hz), 5.77 (2H, s), 2.99 (2H, q, J = 7.2 Hz), 1.30 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 146.2, 134.1, 129.1, 120.7, 119.1, 118.5, 23.4, 14.7; ATR-IR (neat) 3482, 3367, 2960, 2872, 1577, 1188, 32, 818, 647 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_9H_{10}ClNOS$ 215.0172. Found: 215.0174.

***S*-Propyl 2-amino-5-chlorobenzothioate (3j):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and propane-1-thiol **2b** (38 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (75 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (1H, d, J = 2.4 Hz), 7.18 (1H, dd, J = 8.7, 2.4 Hz), 6.58 (1H, d, J = 8.7 Hz), 5.80 (2H, s), 2.97 (2H, t, J = 7.2 Hz), 1.72–1.60 (2H, m), 1.00 (3H, t, , J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 146.1, 134.0, 129.2, 120.8, 119.2, 118.5, 30.8, 22.9, 13.4; ATR-IR (neat) 3480, 3364, 2963, 2930, 1613, 1576, 1480, 1186, 930, 816, 741, 517 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{12}ClNOS$: 229.0328. Found: 229.0326.

***S*-Isopropyl 2-amino-5-chlorobenzothioate (3k):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and propane-2-thiol **2d** (38 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a solid (71 mg, 62%), mp: 44–46 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 2.4 Hz), 7.16 (1H, dd, J = 9.0, 2.4 Hz), 6.56 (1H, d, J = 9.0 Hz), 5.80 (2H, s), 3.78–3.72 (1H, m), 1.37 (6H, d, J = 6.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 146.3, 134.0, 129.2, 120.7, 119.3, 118.5, 34.8, 23.0; ATR-IR (neat) 3454, 3349, 2968, 2926, 2868, 1613, 1544, 1189, 1154, 929, 819, 742, 508 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{12}ClNOS$: 229.0328. Found: 229.0326.

***S*-(*Tert*-butyl) 2-amino-5-chlorobenzothioate (3l):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and 2-methylpropane-2-thiol **2e** (45 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (61 mg, 50%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 2.4 Hz), 7.15 (1H, dd, J = 8.7, 2.4 Hz), 6.57 (1H, d, J = 8.7 Hz), 5.68 (2H, s), 1.54 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 146.0, 133.7, 129.2, 120.6, 120.1, 118.6, 48.3, 29.9; ATR-IR (neat) 3426, 3320, 2959, 2921, 1612, 1580, 1468, 1152, 924, 815, 742, 519 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{14}ClNOS$: 243.0485. Found: 243.0488.

***S*-Ethyl 2-amino-5-fluorobenzothioate (3m):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and ethanethiol **2a** (31 mg, 0.5 mmol) over 8 h according to the general procedure. The product was obtained as a liquid (69 mg, 74%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (1H, dd, J = 9.6, 2.7 Hz), 7.03–6.97 (1H, m), 6.61–6.56 (1H, m), 5.67 (2H, s), 2.98 (2H, q, J = 7.2 Hz), 1.03 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5 (J = 3.0 Hz), 153.7 (J = 234.0 Hz), 144.2, 122.1 (J = 23.2 Hz), 118.3 (J = 7.5 Hz), 118.1 (J = 6.0 Hz), 114.8 (J = 22.5 Hz), 23.4, 14.7; ATR-IR (neat) 3452, 3349, 2965, 1618, 1559, 1486, 1230, 1148, 850, 827, 685 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_9H_{10}FNOS$: 199.0467. Found: 199.0468.

***S*-Propyl 2-amino-5-fluorobenzothioate (3n):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and propane-1-thiol **2b** (38 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (75 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (1H, dd, J = 9.9, 3.0 Hz), 7.02–6.96 (1H, m), 6.59–6.55 (1H m), 5.65 (2H, s), 2.96 (2H, t, J = 6.9 Hz), 1.71–1.59 (2H, m), 0.99 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5 (J = 3.0 Hz), 153.6 (J = 234.0 Hz), 144.3 (J = 1.5 Hz), 122.1 (J = 23.2 Hz), 118.3 (J = 7.5 Hz), 118.1 (J = 5.2 Hz), 114.8 (J = 23.2 Hz), 30.8, 22.9, 13.3; ATR-IR (neat) 3480, 3368, 2964, 2873, 1588, 1557, 1488, 1229, 1146, 965, 842, 524 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{12}FNOS$: 213.0624. Found: 213.0620.

***S*-Butyl 2-amino-5-fluorobenzothioate (3o):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and butane-1-thiol **2c** (45 mg, 0.5 mmol) over 8 h according to the general procedure. The product was obtained as a liquid (77 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (1H, dd, J = 9.9, 3.0 Hz), 7.01–7.00 (1H, m), 6.62–6.57 (1H, m), 5.66 (2H, s), 2.99 (2H, t, J = 7.5 Hz), 1.64–1.56 (2H, m), 1.46–1.38 (2H, m), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6 (J = 3.0 Hz), 153.7 (J = 234.0 Hz), 144.2 (J = 0.75 Hz), 122.1 (J = 23.2 Hz), 118.4 (J = 6.7 Hz), 118.2 (J = 6.0 Hz), 114.9 (J = 23.2 Hz), 31.5, 28.7, 22.0, 13.6; ATR-IR (neat) 3481, 3369, 2958, 2929, 1588, 1557, 1231, 1147, 966, 844, 685, 525 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{14}FNOS$: 227.0780. Found: 227.0782.

***S*-Propyl 2-amino-5-nitrobenzothioate (3p):** Prepared from 3-chloro-5-nitroindolin-2-one **1e** (106 mg, 0.5 mmol) and propane-1-thiol **2b** (38 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a solid (94 mg, 78%), mp: 92–94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (1H, d, J = 2.4 Hz), 8.04 (1H, dd, J = 9.3, 2.7 Hz), 6.66–6.63 (3H, m), 2.97 (2H, t, J = 7.2 Hz), 1.71–1.59 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 152.5, 136.7, 128.8, 127.4, 116.8, 116.5, 31.0, 22.7, 13.3; ATR-IR (neat) 3450, 3338, 1609, 1482, 1312, 1201, 1104, 942, 747, 637 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{12}N_2O_3S$: 240.0569. Found: 240.0567.

***S*-Cyclopentyl 2-aminobenzothioate (4a):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and cyclopentanethiol **2f** (51 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (68 mg, 62%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (1H, dd, J = 8.4, 1.5 Hz), 7.25–7.19 (1H, m), 6.65–6.59 (2H, m), 5.89 (2H, s), 3.85–2.18 (1H, m), 2.18–2.11 (2H, m), 1.76–1.60 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 147.6, 133.9, 130.1, 118.5, 117.0, 116.2, 42.2, 33.2, 24.7; ATR-IR (neat) 3477, 3362, 2955, 2866, 1612, 1578, 1199, 1157, 909, 741, 683 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{15}NOS$: 221.0874. Found: 221.0877.

***S*-Cyclohexyl 2-aminobenzothioate (4b):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and cyclohexanethiol **2g** (58 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (71 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 8.4 Hz), 7.18 (1H, t, J = 7.8 Hz), 6.60–6.57 (2H, m), 5.96 (2H, s), 3.59–3.55 (1H, m), 1.94–1.91 (2H, m), 1.70–1.68 (2H, m), 1.56–1.54 (1H, m), 1.46–1.37 (4H, m), 1.27–1.24 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 147.5, 134.0, 130.1, 119.0, 117.3, 116.6, 42.2, 33.2, 26.1, 25.6; ATR-IR (neat) 3478, 3363, 2927, 2851, 1612, 1578, 1196, 1157, 809, 741, 681, 518 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{17}NOS$: 235.1031. Found: 235.1029.

***S*-Cyclopentyl 2-amino-5-methoxybenzothioate (4c):** Prepared from 3-chloro-5-methoxyindolin-2-one **1b** (99 mg, 0.5 mmol) and cyclopentanethiol **2f** (51 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (82 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (1H, d, J = 3.0 Hz), 6.91 (1H, dd, J = 9.0, 2.7 Hz), 6.61 (1H, d, J = 9.0 Hz), 5.49 (2H, s), 3.87–3.77 (1H, m), 3.75 (3H, s), 2.18–2.08 (2H, m), 1.76–1.65 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 150.5, 142.1, 123.2, 118.8, 118.6, 111.9, 55.8, 42.4, 33.2, 24.7; ATR-IR (neat) 3463, 3360, 2962, 2860, 1586, 1556, 1489, 1164, 1040, 823, 677 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{17}NO_2S$: 251.0980. Found: 251.0982.

***S*-Cyclopentyl 2-amino-5-chlorobenzothioate (4d):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and cyclopentanethiol **2f** (51 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (87 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 2.4 Hz), 7.15 (1H, dd, J = 9.0, 2.4 Hz), 6.56 (1H, d, J = 9.0 Hz), 5.80 (2H, s), 3.84–3.79 (1H, m), 2.17–2.12 (2H, m), 1.74–1.71 (2H, m), 1.65–1.60 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 146.2, 133.9, 129.3, 120.7, 119.3, 118.5, 42.6, 33.2, 24.7; ATR-IR (neat) 3422, 3318, 2955, 2928, 1618, 1468, 1150, 914, 815, 747, 529 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{14}ClNOS$: 255.0485. Found: 255.0487.

***S*-Cyclohexyl 2-amino-5-chlorobenzothioate (4e):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and cyclohexanethiol **2g** (58 mg, 0.5 mmol) over 12 h according to the general

procedure. The product was obtained as a liquid (72 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (1H, d, J = 1.8 Hz), 7.17 (1H, dd, J = 8.4, 2.4 Hz), 6.58 (1H, d, J = 8.4 Hz), 5.88 (2H, s), 3.64–3.61 (1H, m), 1.99–1.97 (2H, m), 1.75–1.73 (2H, m), 1.61–1.59 (1H, m), 1.52–1.42 (4H, m), 1.33–1.28 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.5, 146.2, 134.0, 129.3, 120.8, 119.5, 118.5, 42.5, 33.1, 26.0, 25.6; ATR-IR (neat) 3423, 3325, 2961, 2919, 1614, 1579, 1452, 1160, 918, 817, 738 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{16}ClNOS$: 269.0641. Found: 269.0639.

***S*-Cyclopentyl 2-amino-5-fluorobenzothioate (4f):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and cyclopentanethiol **2f** (51 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (94 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (1H, dd, J = 9.9, 3.0 Hz), 7.03–6.96 (1H, m), 6.62–6.57 (1H, m), 5.67 (2H, s), 3.84–3.77 (1H, m), 2.20–2.10 (2H, m), 1.76–1.55 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4 (J = 3.0 Hz), 153.7 (J = 234.0 Hz), 144.1, 122.0 (J = 24.0 Hz), 118.4, 118.3, 115.0 (J = 23.2 Hz), 42.6, 33.2, 24.7; ATR-IR (neat) 3480, 3366, 2957, 2868, 1588, 1557, 1230, 1147, 966, 845, 686 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{14}FNOS$: 239.0780. Found: 239.0782.

***S*-Cyclohexyl 2-amino-5-fluorobenzothioate (4g):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and cyclohexanethiol **2g** (58 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (83 mg, 65%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (1H, dd, J = 10.2, 3.0 Hz), 7.02–6.98 (1H, m), 6.62–6.60 (1H, m), 5.75 (2H, s), 3.64–3.61 (1H, m), 2.02–1.95 (2H, m), 1.75–1.73 (2H, m), 1.61–1.59 (1H, m), 1.52–1.44 (4H, m), 1.33–1.27 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6 (J = 2.0 Hz), 153.9 (J = 234.4 Hz), 143.9, 122.0 (J = 23.1 Hz), 118.7, 118.5 (J = 6.9 Hz), 115.0 (J = 22.9 Hz), 42.6, 33.1, 26.0, 25.5; ATR-IR (neat) 3479, 3367, 2928, 2852, 1556, 1487, 1229, 1145, 964, 841, 685 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{16}FNOS$: 253.0937. Found: 253.0934.

***S*-Benzyl 2-aminobenzothioate (5a):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and phenylmethanethiol **2h** (62 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (83 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (1H, d, J = 7.8 Hz), 7.31–7.28 (2H, m), 7.25–7.14 (4H, m), 6.59–6.54 (2H, m), 5.83 (2H, s), 4.18 (2H, s); ^{13}C NMR (75 Hz, $CDCl_3$) δ 192.2, 147.8, 137.7, 134.3, 130.1, 128.9, 128.5, 127.1, 118.1, 117.1, 116.4, 33.0; ATR-IR (neat) 3481, 3366, 3027, 1612, 1578, 1550, 1200, 1157, 908, 680 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{13}NOS$: 243.0718. Found: 243.0718.

***S*-(4-(*Tert*-butyl)benzyl) 2-aminobenzothioate (5b):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and (4-(*tert*-butyl)phenyl)methanethiol **2i** (90 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a liquid (97 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (1H, dd, J = 8.4, 1.5 Hz), 7.42–7.36 (4H, m), 7.36–7.27 (1H, m), 6.72–6.67 (2H, m), 5.82 (2H, s), 4.31 (2H, s), 1.38 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 150.0, 147.9, 134.5, 134.2, 130.1, 128.5, 125.4, 118.0, 117.0, 116.2, 34.4, 32.6, 31.2; ATR-IR (neat) 3483, 3367, 2960, 1612, 1579, 1198, 1158, 910, 742, 681, 558 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{21}NOS$: 299.1344. Found: 299.1346.

***S*-(2-chlorobenzyl) 2-aminobenzothioate (5c):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and (2-chlorophenyl)methanethiol **2j** (79 mg, 0.5 mmol) over 12 h according to the general procedure. The product was obtained as a solid (97 mg, 70%), mp: 56–58 °C; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.88 (1H, dd, J = 8.4, 1.6 Hz), 7.55–7.53 (1H, m), 7.40–7.38 (1H, m), 7.29–7.25 (1H, m), 7.23–7.20 (2H, m), 6.67–6.63 (2H, m), 5.86 (2H, s), 4.39 (2H, s), ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 148.1, 135.6, 134.4, 134.2, 131.1, 130.1, 129.5, 128.6, 126.9, 117.9, 117.0, 116.3, 30.8; ATR-IR (neat) 3476, 3356, 1613, 1573, 1549, 1202, 1157, 906, 734 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{12}ClNOS$: 277.0328. Found: 277.0327.

***S*-(4-Chlorobenzyl) 2-aminobenzothioate (5d):** Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and (4-chlorophenyl)methanethiol **2k** (79 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a solid (66 mg, 58%), mp: 71–73 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (1H, dd, J = 8.2, 1.3 Hz), 7. 39–7.34 (4H, m), 7.28–7.25 (1H, m), 6.92 (2H, s), 6.81 (1H, dd, J = 8.4, 0.7 Hz), 6.56–6.53 (1H, m), 4.23 (2H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ 190.4, 149.3, 137.2, 134.5, 131.6, 130.6, 129.4, 128.3, 117.0, 115.8, 114.9, 31.2; ATR-IR (neat) 3488, 3367, 3034, 1634,1576, 1548, 1205, 1160, 912, 844, 510 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{12}ClNOS$: 277.0328. Found: 277.0331.

***S*-Benzyl 2-amino-5-methoxybenzothioate (5e):** Prepared from 3-chloro-5-methoxyindolin-2-one **1b** (99 mg, 0.5 mmol) and phenylmethanethiol **2h** (62 mg, 0.5 mmol) over 14 h according to the general procedure. The product was obtained as a liquid (82 mg, 60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.13 (6H, m), 6.85 (1H, dd, J = 9.0, 2.7 Hz), 6.52 (1H, d, J = 9.0 Hz), 5.45 (2H, s), 4.17 (2H, s), 3.64 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 150.5, 142.5, 137.6, 128.9, 128.5, 127.1, 123.6, 118.7, 117.8, 111.7, 55.7, 33.1; ATR-IR (neat) 3475, 3362, 2924, 1579, 1489, 1237, 1154, 909, 833, 697 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{15}NO_2S$: 273.0823. Found: 273.0822.

***S*-Benzyl 2-amino-5-chlorobenzothioate (5f):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and phenylmethanethiol **2h** (62 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (90 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (1H, d, J = 2.4 Hz), 7.30–7.17 (5H, m), 7.11 (1H, dd, J = 8.7, 2.4 Hz), 6.51 (1H, d, J = 8.7 Hz), 5.75 (2H, s), 4.18 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 146.3, 137.3, 134.3, 129.2, 128.9, 128.6, 127.3, 120.8, 118.6, 118.5, 33.2; ATR-IR (neat) 3483, 3365, 3029, 1612, 1576, 1185, 929, 814, 699, 515 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{12}ClNOS$: 277.0328. Found: 277.0331.

***S*-(4-(*Tert*-butyl)benzyl) 2-amino-5-chlorobenzothioate (5g):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and (4-(*tert*-butyl)phenyl)methanethiol **2i** (90 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a liquid (114 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1H, d, J = 2.1 Hz), 7.34–7.27 (4H, m), 7.18 (1H, dd, J = 8.7, 2.4 Hz), 6.60 (1H, d, J = 8.7 Hz), 5.76 (2H, s), 4.23 (2H, s), 1.29 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 150.3, 146.2, 134.2, 134.1, 129.3, 128.6, 125.5, 121.0, 118.9, 118.6, 34.4, 32.9, 31.3; ATR-IR (neat) 3484, 3367, 2959, 2924, 1577, 1544, 1185, 929, 814, 741 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{20}ClNOS$: 333.0954. Found: 333.0952.

***S*-(4-Chlorobenzyl) 2-amino-5-chlorobenzothioate (5h):** Prepared from 3,5-dichloroindolin-2-one **1c** (101 mg, 0.5 mmol) and (4-chlorophenyl)methanethiol **2k** (79 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a solid (109 mg, 70%), mp: 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (1H, d, J = 2.4 Hz), 7.30–7.26 (4H, m), 7.18 (1H, dd, J = 9.0, 2.4 Hz), 6.59 (1H, d, J = 9.0 Hz), 5.72 (2H, s), 4.19 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 146.5, 136.0, 134.4, 133.0, 130.2, 129.2, 128.7, 120.8, 118.6, 118.5, 32.5; ATR-IR (neat) 3474, 3365,

1610, 1572, 1541, 1186, 930, 806, 741, 638 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{11}Cl_2NOS$: 310.9938. Found: 310.9935.

***S*-(4-(*Tert*-butyl)benzyl) 2-amino-5-fluorobenzothioate (5i):** Prepared from 3-chloro-5-fluoroindolin-2-one **1d** (93 mg, 0.5 mmol) and (4-(*tert*-butyl)phenyl)methanethiol **2i** (90 mg, 0.5 mmol) over 10 h according to the general procedure. The product was obtained as a solid (108 mg, 68%), mp: 52–54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (1H, dd, J = 9.9, 3.0 Hz), 7.34–7.27 (4H, m), 7.05–6.99 (1H, m), 6.64–6.60 (1H, m), 5.66 (2H, s), 4.23 (2H, s), 1.29 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7 (J = 3.0 Hz), 153.8 (J = 234.7 Hz), 150.2, 144.1, 134.1, 128.5, 125.5, 122.3 (J = 23.2 Hz), 118.5 (J = 7.5 Hz), 117.9 (J = 6.0 Hz), 114.9 (J = 23.2 Hz), 34.4, 32.9, 31.2; ATR-IR (neat) 3485, 3454, 3377, 2959, 1585, 1553, 1147, 968, 806, 685 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{20}FNOS$: 317.1250. Found: 317.1252.

3-(Ethylthio)indolin-2-one (6): Prepared from 3-chlorooxindole **1a** (84 mg, 0.5 mmol) and ethanethiol **2a** (31 mg, 0.5 mmol) over 4 h under an argon atmosphere. The product was obtained as a sticky liquid (31 mg, 32%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.71 (1H, s), 7.33 (1H, d, J = 7.8 Hz), 7.20 (1H, t, J = 7.8 Hz), 7.03 (1H, t, J = 6.6 Hz), 6.2 (1H, d, J = 7.8 Hz), 4.29 (1H, s), 2.68–2.63 (1H, m), 2.48–2.42 (1H, m), 1.17 (3H, t, J = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.7, 141.3, 128.8, 126.7, 125.0, 122.7, 110.2, 45.6, 23.6, 14.0; ATR-IR (neat) 3209, 2924, 1698, 1616, 1467, 1325, 1229, 745, 678 cm^{-1}.

3-(*Tert*-butyl)quinazolin-4(3*H*)-one (11a): Prepared from *S*-ethyl 2-aminobenzothioate **3a** (50 mg, 0.27 mmol) and 2-isocyano-2-methylpropane **10a** (23 mg, 0.27 mmol) over 12 h according to the general procedure. The product was obtained as a solid (47 mg, 86%), mp: 76–78 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (1H, s), 8.24 (1H, dd, J = 6.0, 2.1 Hz), 7.69–7.66 (1H, m), 7.63–7.61 (1H, m), 7.43–7.41 (1H, m), 1.71 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 147.2, 143.9, 133.8, 126.8, 126.6, 126.6, 123.0, 60.7, 28.6; ATR-IR (neat) 3013, 1674, 1598, 1472, 1365, 1311, 1188, 1126, 924, 764, 696 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{14}N_2O$: 202.1106. Found: 202.1107.

3-Cyclohexylquinazolin-4(3*H*)-one (11b): Prepared from *S*-ethyl 2-aminobenzothioate **3a** (50 mg, 0.27 mmol) and isocyanocyclohexane **10b** (30 mg, 0.27 mmol) over 10 h according to the general procedure. The product was obtained as a solid (50 mg, 82%), mp: 104–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (1H, d, J = 8.1 Hz), 8.11 (1H, s), 7.74–7.66 (2H, m), 7.46 (1H, t, J = 7.8 Hz), 4.83–4.73 (1H, m), 1.99–1.89 (4H, m), 1.78–1.73 (1H, m), 1.68–1.42 (4H, m), 1.31–1.16 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 147.2, 143.8, 134.1, 127.1, 127.0, 126.9, 121.5, 53.3, 32.5, 25.8, 25.2; ATR-IR (neat) 3065, 2925, 2853, 1662, 1559, 1473, 1328, 1130, 770, 697 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{16}N_2O$: 228.1263. Found: 228.1263.

3-(*Tert*-butyl)-6-methoxyquinazolin-4(3*H*)-one (11c): Prepared from *S*-ethyl 2-amino-5-methoxybenzothioate **3f** (57 mg, 0.27 mmol) and 2-isocyano-2-methylpropane **10a** (23 mg, 0.27 mmol) over 12 h according to the general procedure. The product was obtained as a solid (52 mg, 83%), mp: 106–108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (1H, s), 7.62 (1H, d, J = 2.4 Hz), 7.56 (1H, d, J = 9.0 Hz), 7.28 (1H, dd, J = 9.0, 3.0 Hz), 3.87 (3H, s), 1.72 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 158.5, 141.8, 141.7, 128.2, 124.3, 105.7, 60.7, 55.7, 28.6; ATR-IR (neat) 3099, 2923, 1651, 1491, 1358, 1301, 1217, 1028, 837, 736, 554 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{16}N_2O_2$: 232.1212. Found: 232.1209.

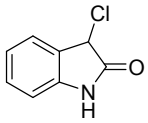
3-(*Tert*-butyl)-6-chloroquinazolin-4(3*H*)-one (11d): Prepared from *S*-ethyl 2-amino-5-chlorobenzothioate (**3i**) (58 mg, 0.27 mmol) and 2-isocyano-2-methylpropane **10a** (23 mg, 0.27 mmol) over 10 h according to the general procedure. The product was obtained as a solid (50 mg, 78%), mp: 120–122 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (1H, s), 8.22 (1H, s), 7.64–7.59 (2H, m), 1.72 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 145.3, 144.2, 134.4, 132.8, 128.2, 126.1, 124.0, 61.3, 28.5; ATR-IR (neat) 2922, 2853, 1672, 1597, 1378, 1315, 1254, 1094, 930, 828 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{13}ClN_2O$: 236.0716. Found: 236.0719.

6-Chloro-3-cyclohexylquinazolin-4(3*H*)-one (11e): Prepared from *S*-ethyl 2-amino-5-chlorobenzothioate (**3i**) (58 mg, 0.27 mmol) and isocyanocyclohexane **10b** (30 mg, 0.27 mmol) over 10 h according to the general procedure. The product was obtained as a solid (50 mg, 70%), mp: 110–112 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (1H, d, J = 1.8 Hz), 8.08 (1H, s), 7.65-7.60 (2H, m), 4.78–4.74 (1H, m), 1.98–1.91 (4H, m), 1.78–1.75 (1H, m), 1.64–1.57 (2H, m), 1.52–1.46 (2H, m), 1.26–1.20 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.6, 145.9, 144.0, 134.5, 132.9, 128.8, 126.3, 122.9, 53.6, 32.5, 25.8, 25.2; ATR-IR (neat) 2935, 2853, 1672, 1600, 1472, 1255, 825, 647, 518 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{15}ClN_2O$: 262.0873. Found: 262.0870.

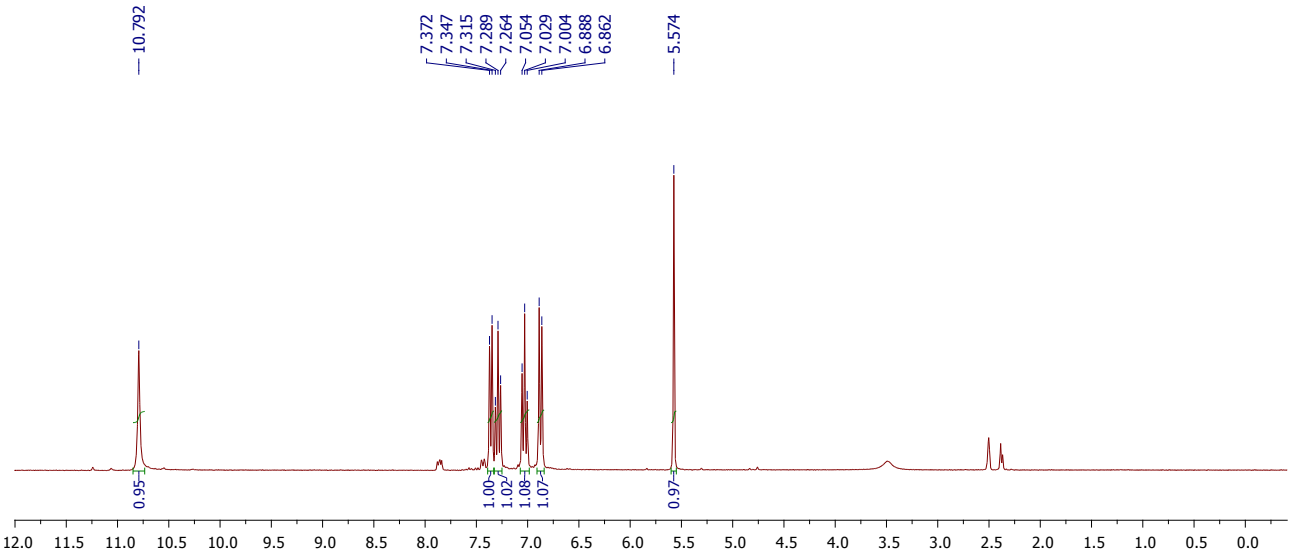
3-(*Tert*-butyl)-6-fluoroquinazolin-4(3*H*)-one (11f): Prepared from *S*-ethyl 2-amino-5-fluorobenzothioate (**3m**) (54 mg, 0.27 mmol) and 2-isocyano-2-methylpropane **10a** (23 mg, 0.27 mmol) over 10 h according to the general procedure. The product was obtained as a solid (48 mg, 80%), mp: 105–107 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (1H, s), 7.88 (1H, dd, J = 8.4, 2.4 Hz), 7.67–7.65 (1H, m), 7.44–7.40 (1H, m), 1.73 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 161.0 (d, J = 247.0 Hz), 143.6, 143.2 (d, J = 2.4 Hz), 128.9 (d, J = 8.1 Hz), 124.3, 122.6 (d, J = 24.1 Hz), 111.5 (d, J = 22.9 Hz), 61.1, 28.6; ATR-IR (neat) 2917, 2849, 1674, 1595, 1457, 1313, 1188, 1115, 825, 740, 605 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{13}FN_2O$: 220.1012. Found: 220.1012.

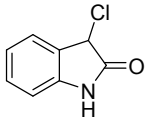
3-Cyclohexyl-6-fluoroquinazolin-4(3*H*)-one (11g): Prepared from *S*-ethyl 2-amino-5-fluorobenzothioate (**3m**) (54 mg, 0.27 mmol) and isocyanocyclohexane **10b** (30 mg, 0.27 mmol) over 10 h according to the general procedure. The product was obtained as a solid (50 mg, 75%), mp: 106–108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (1H, s), 7.86 (1H, dd, J = 9.0, 3.0 Hz), 7.66–7.63 (1H, m), 7.41–7.38 (1H, m), 4.75–4.70 (1H, m), 1.94–1.87 (4H, m), 1.74–1.71 (1H, m), 1.61–1.54 (2H, m), 1.49–1.41 (2H, m), 1.23-1.15 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1 (d, J = 252.4 Hz), 160.2, 143.8, 143.2, 129.5 (d, J = 8.1 Hz), 122.7 (d, J = 24.1 Hz), 111.9, 111.7, 53.6, 32.5, 25.8, 25.2; ATR-IR (neat) 3075, 2928, 2855, 1657, 1483, 1259, 1124, 891, 831, 723, 630 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{15}FN_2O$: 246.1168. Found: 246.1166.

Copies of NMR spectra of substrates (1a-1e)

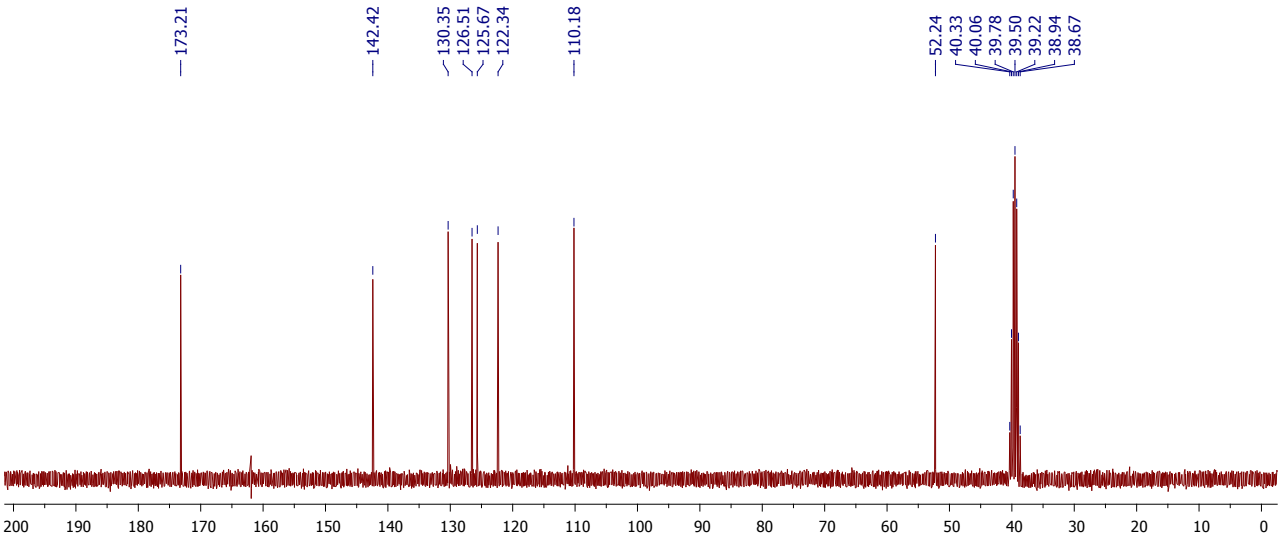


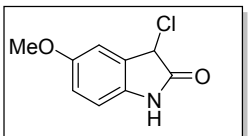
^{1}H NMR of **1a**
(300 MHz, DMSO-d_6)



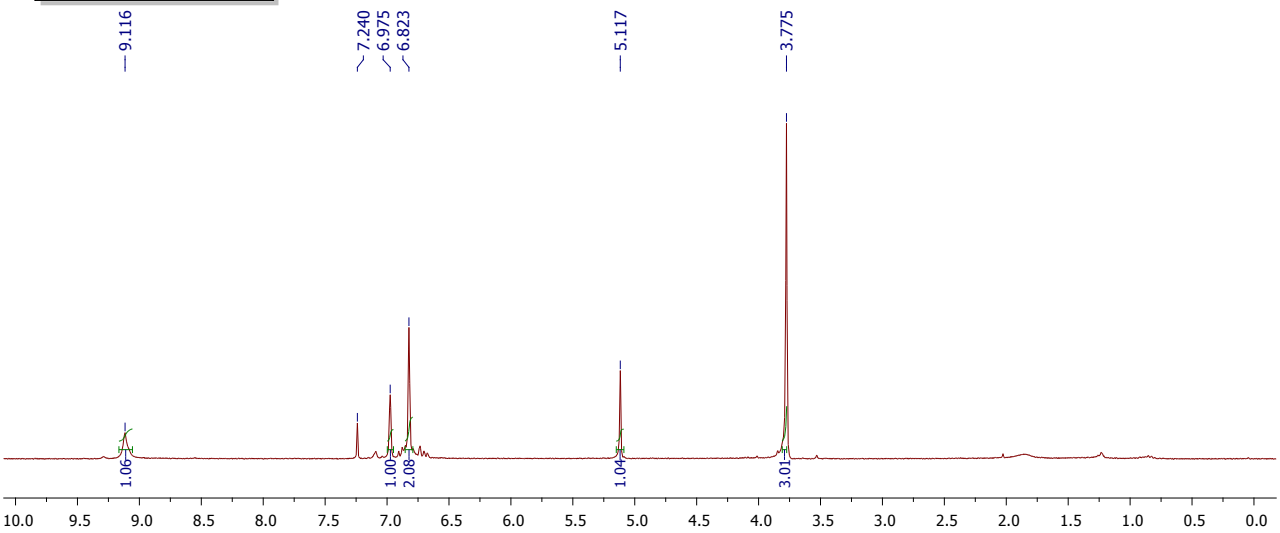


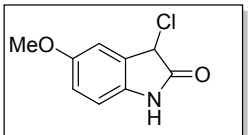
^{13}C NMR of **1a**
(75 MHz, DMSO-d_6)



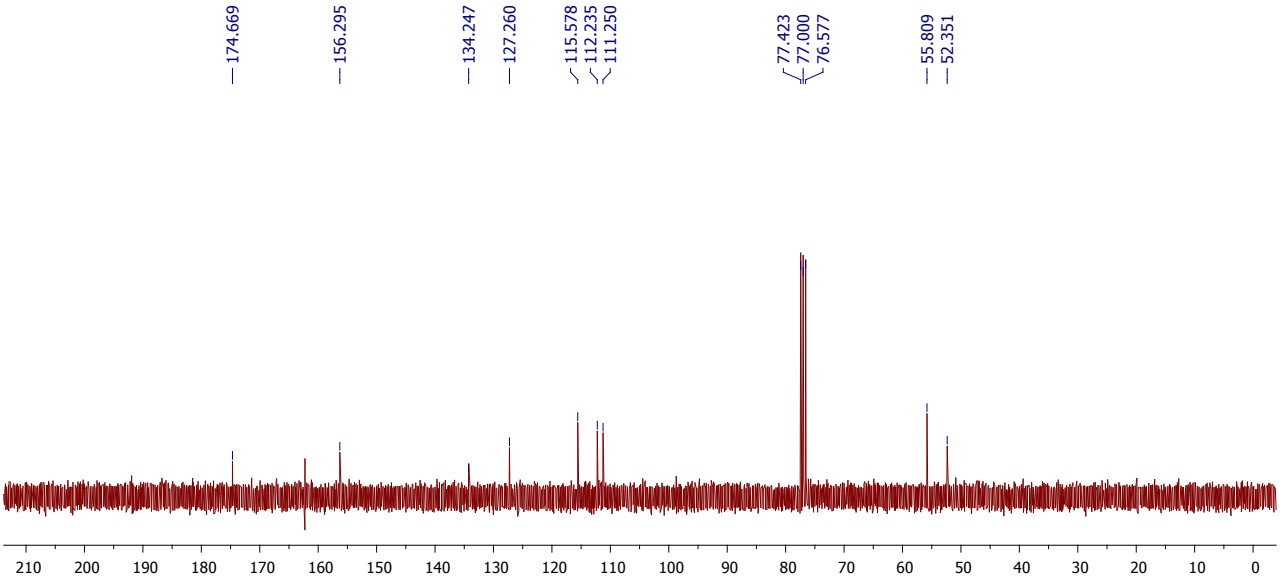


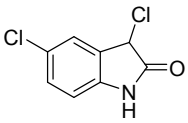
^{1}H NMR of **1b**
(300 MHz, $CDCl_3$)



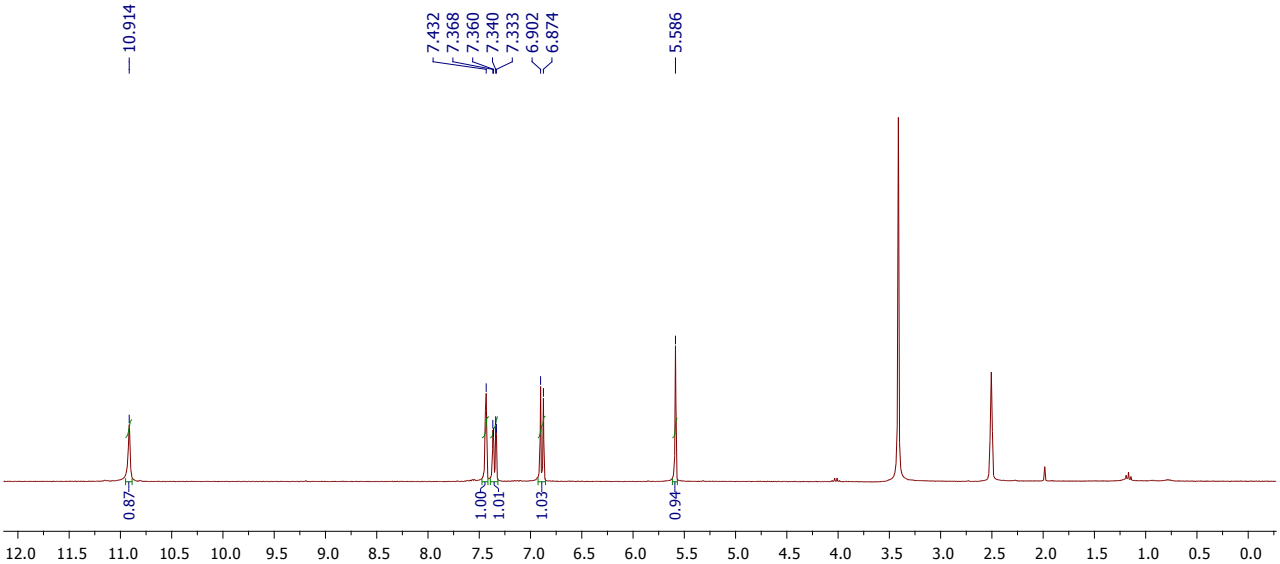


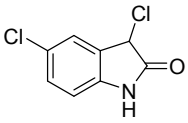
^{13}C NMR of **1b**
(75 MHz, $CDCl_3$)



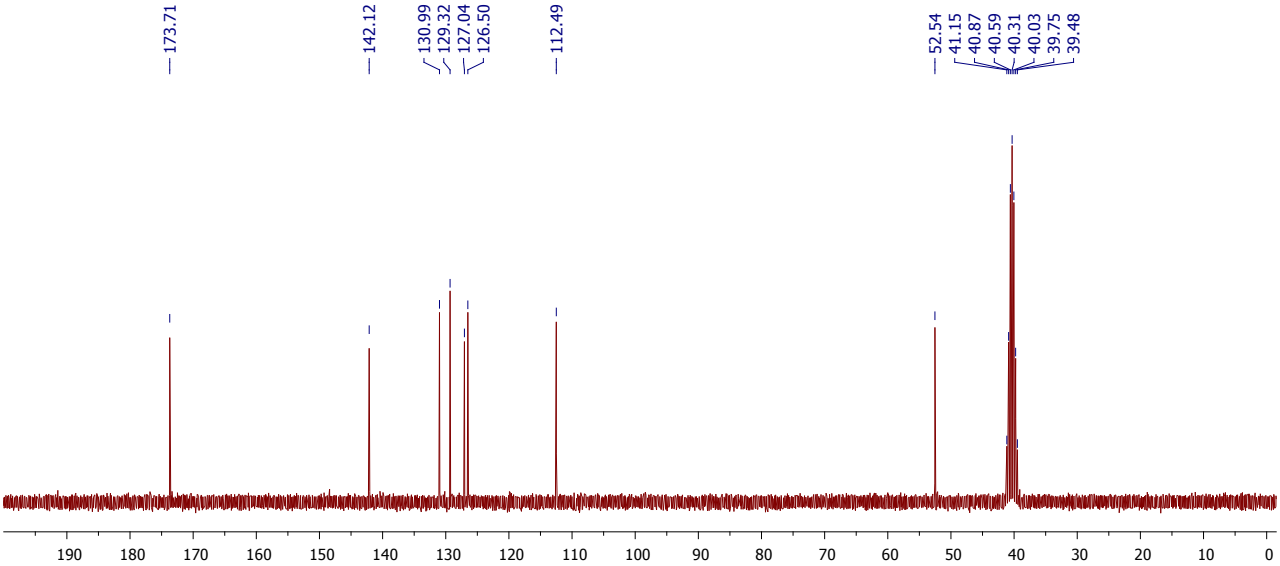


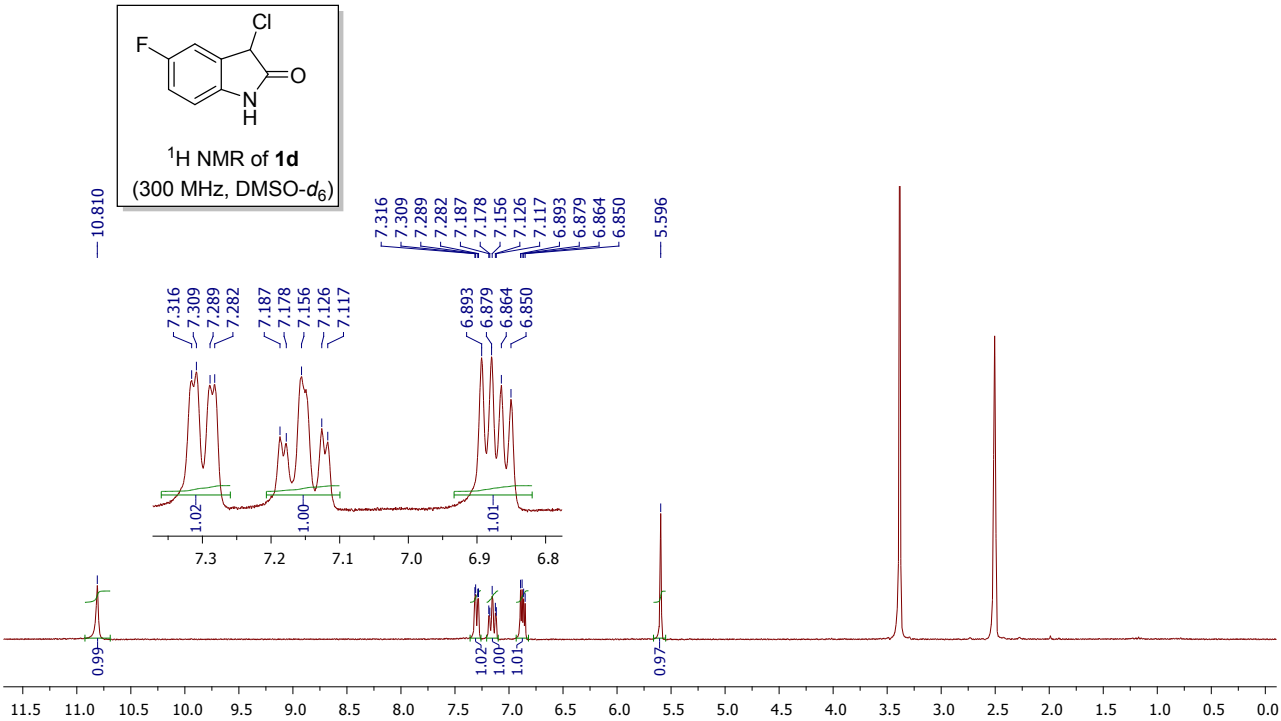
^{1}H NMR of **1c**
(300 MHz, DMSO-d_6)

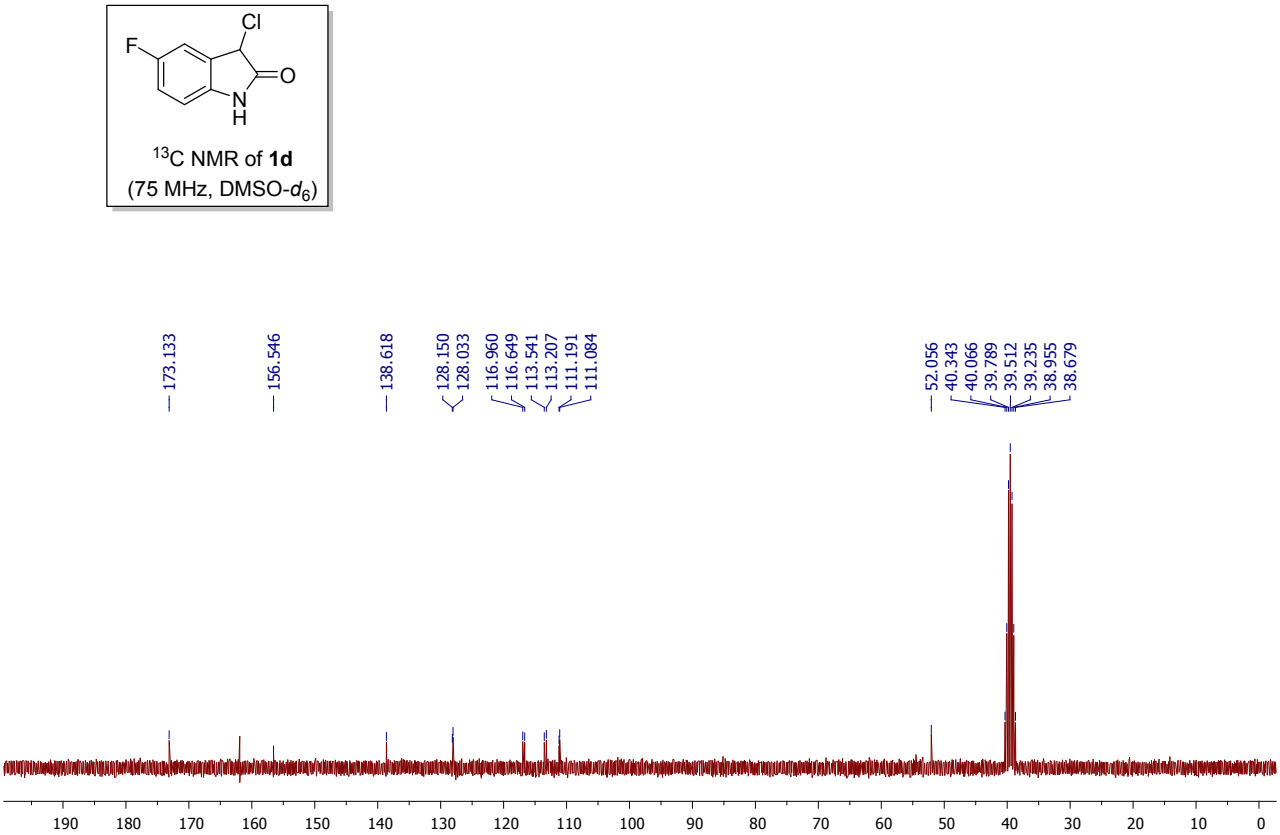


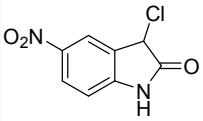


^{13}C NMR of **1c**
(75 MHz, DMSO-d_6)

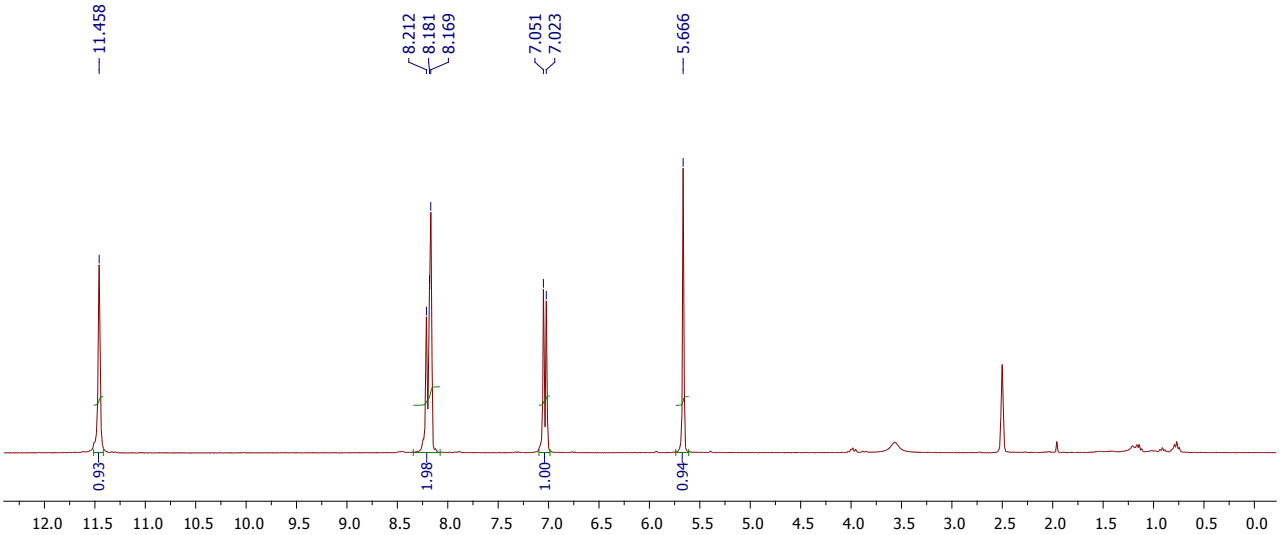


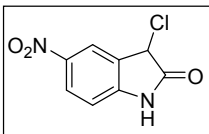

Cl
F
O
N
H
^{1}H NMR of **1d**
(300 MHz, DMSO-d_6)
10.810
7.316
7.309
7.289
7.282
7.187
7.178
7.156
7.126
7.117
6.893
6.879
6.864
6.850
5.596
1.02
1.00
1.01
0.99
0.97


Cl
F
O
N
H
^{13}C NMR of **1d**
(75 MHz, DMSO-d_6)
173.133
156.546
138.618
128.150
128.033
116.960
116.649
113.541
113.207
111.191
111.084
52.056
40.343
40.066
39.789
39.512
39.235
38.955
38.679

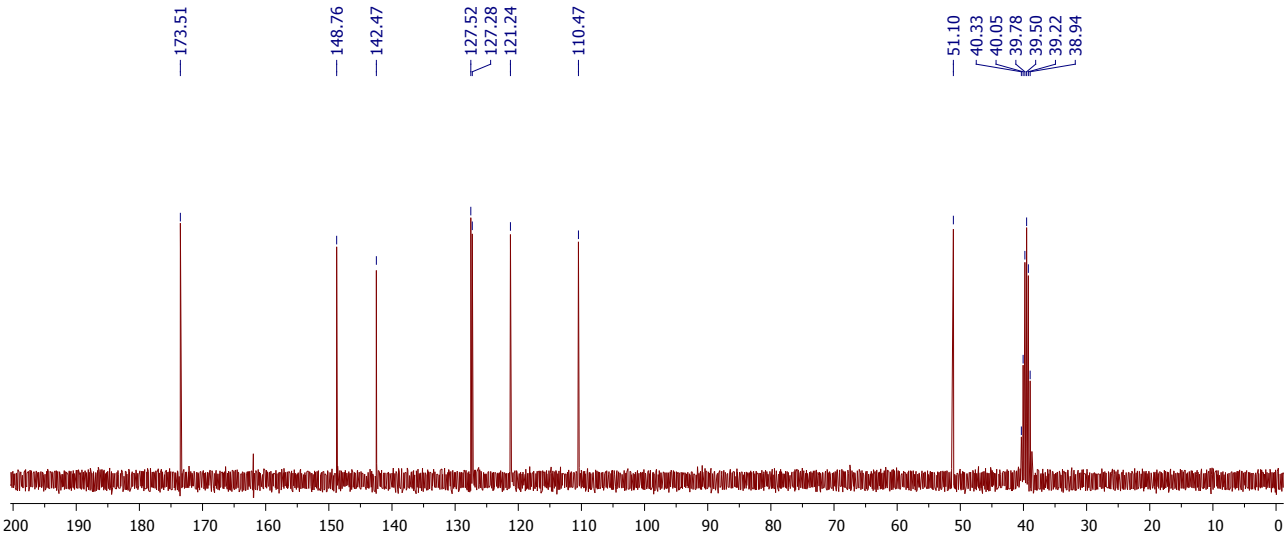


^{1}H NMR of **1e**
(300 MHz, DMSO-d_6)

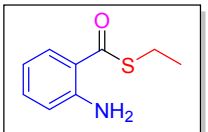




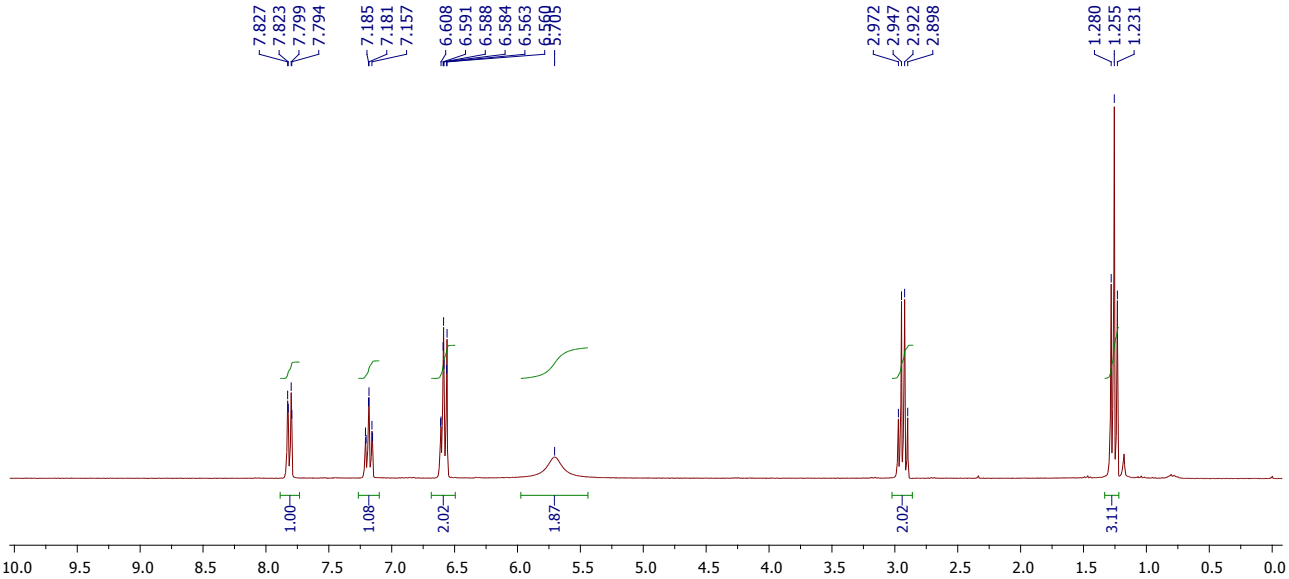
^{13}C NMR of **1e**
(75 MHz, DMSO-d_6)

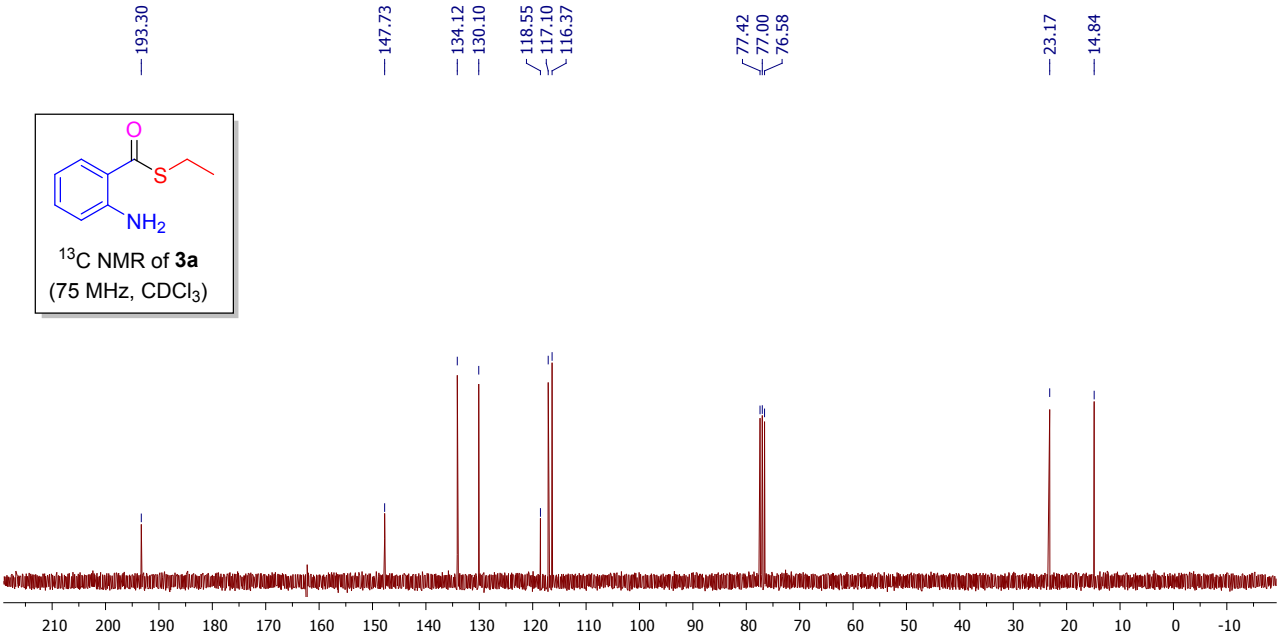


Copies of NMR spectra of synthesized compounds (3, 4, 5, 6 and 11)

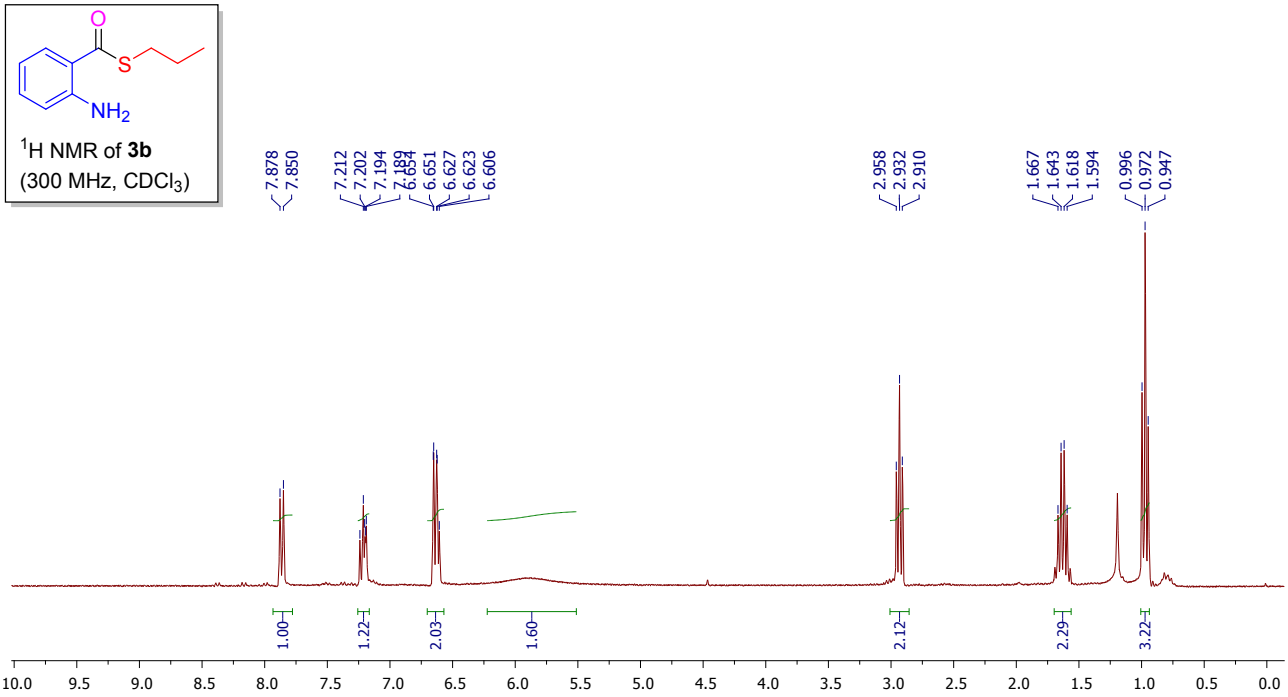


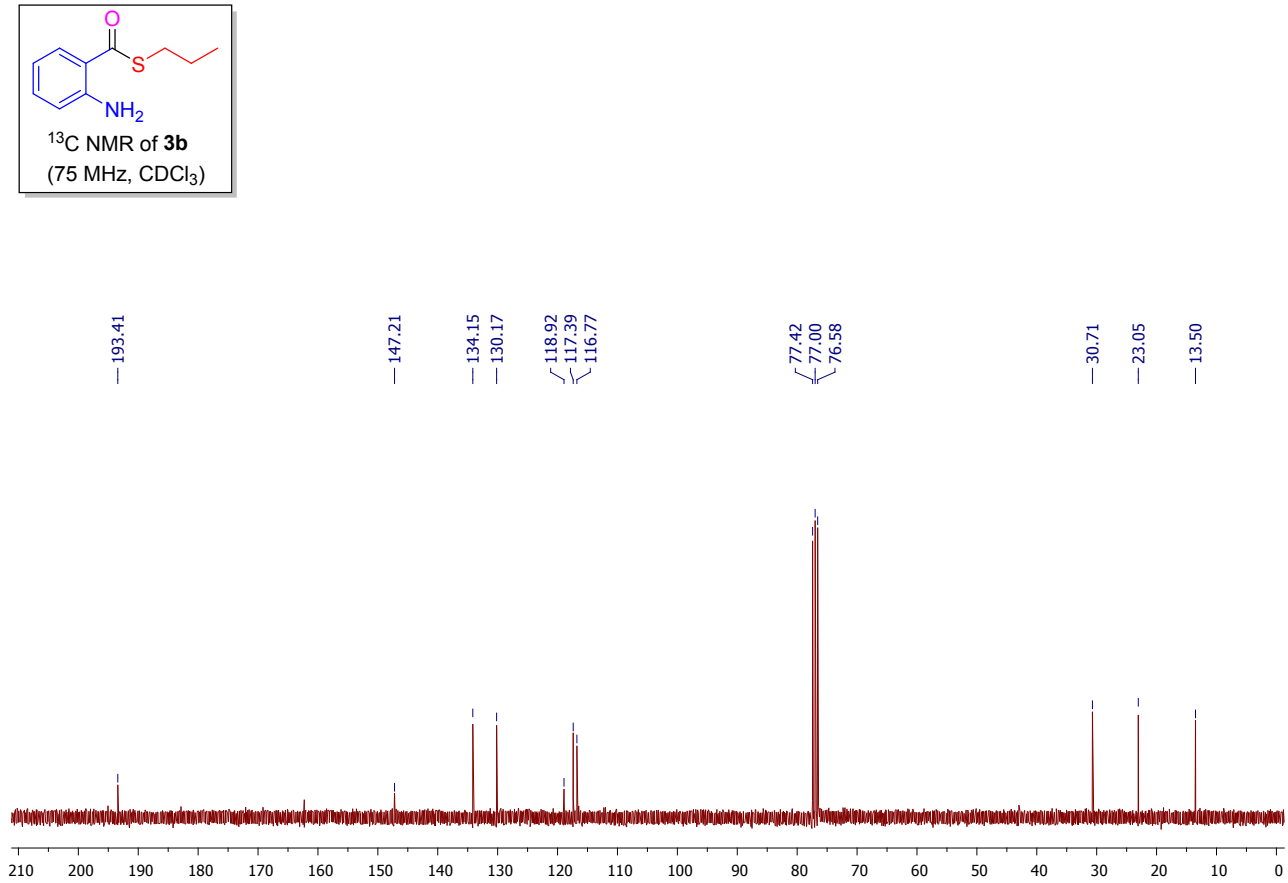
^{1}H NMR of **3a**
(300 MHz, $CDCl_3$)

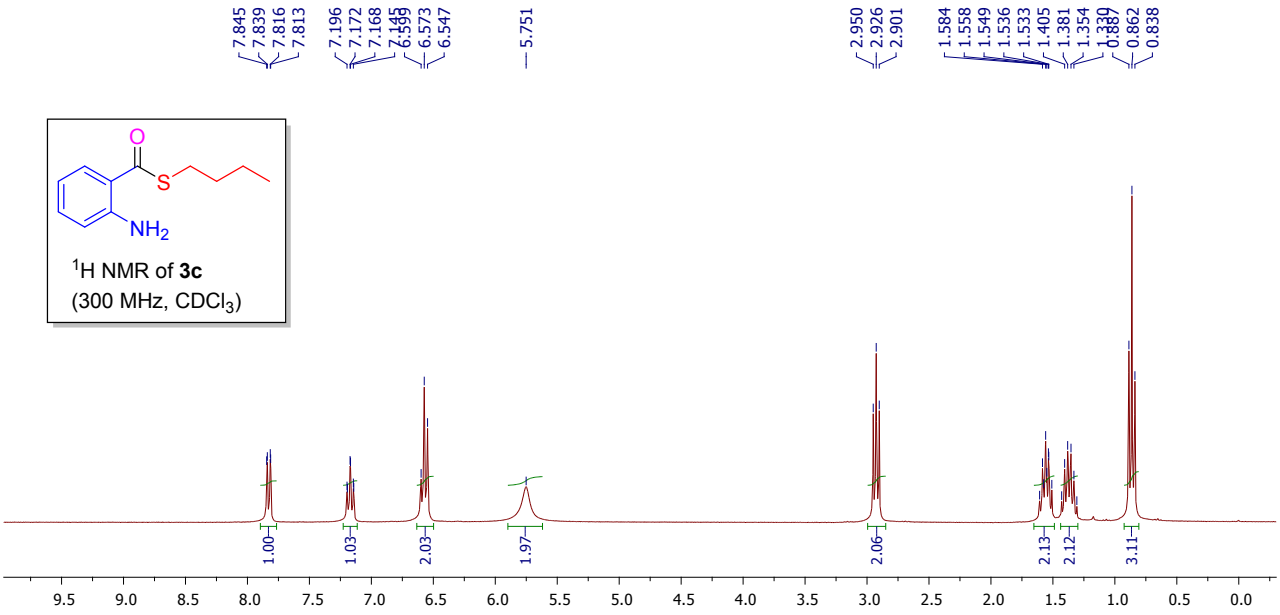




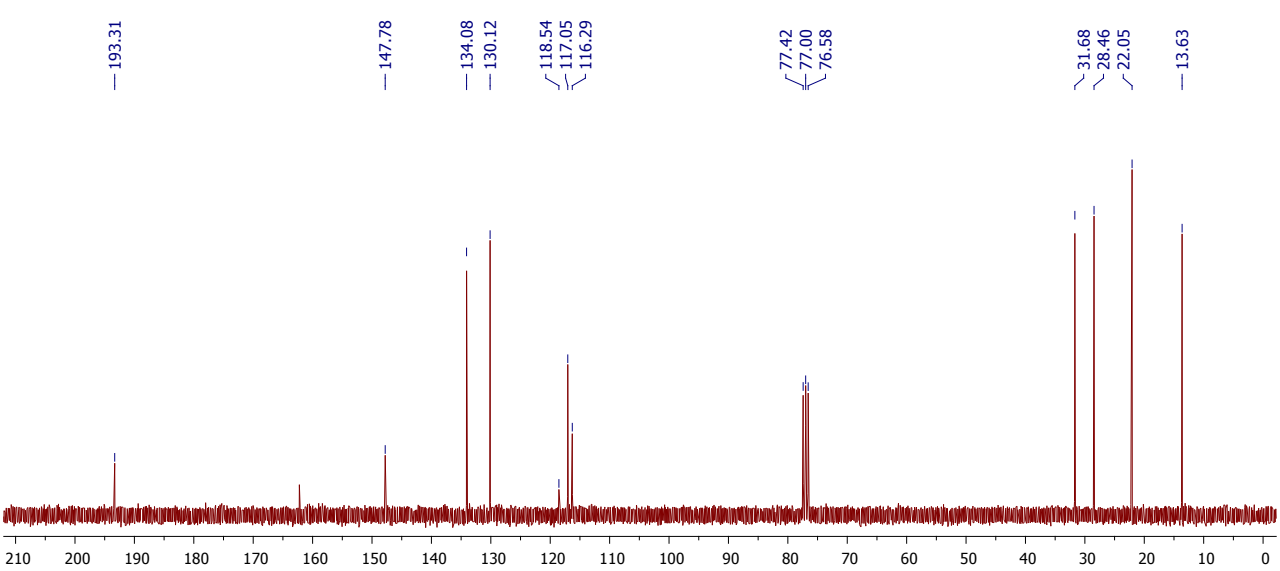
^{13}C NMR of **3a**
(75 MHz, $CDCl_3$)


O
S
NH2
1H NMR of 3b
(300 MHz, CDCl3)
7.878
7.850
7.212
7.202
7.194
6.651
6.627
6.623
6.606
2.958
2.932
2.910
1.667
1.643
1.618
1.594
0.996
0.972
0.947
1.00
1.22
2.03
1.60
2.12
2.29
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

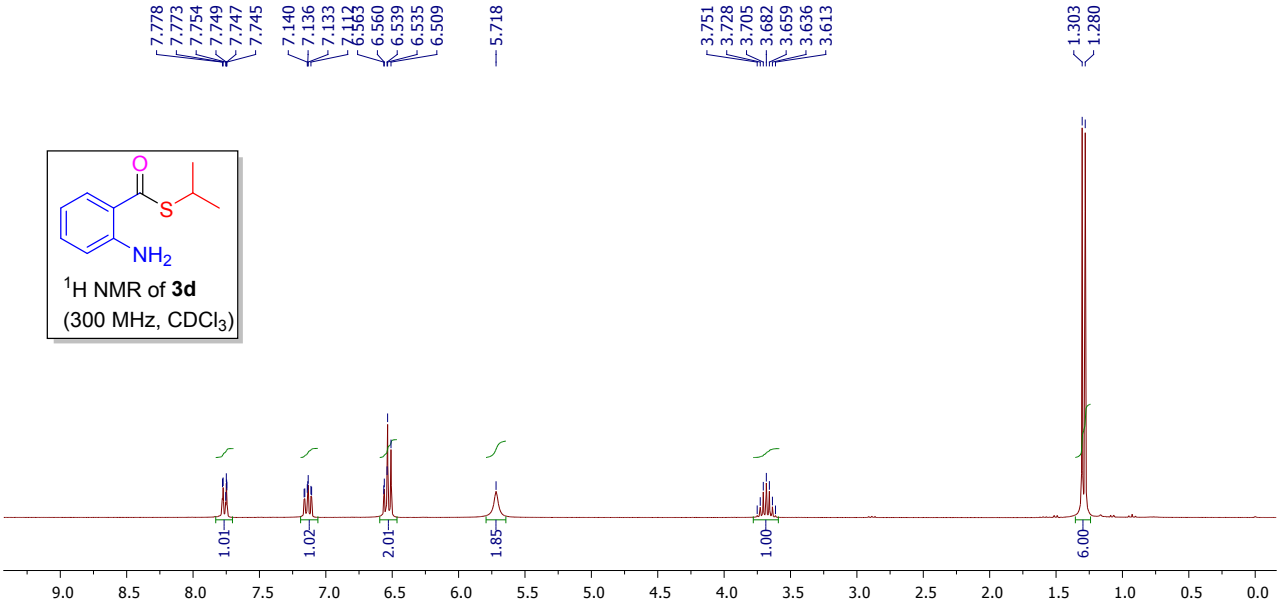

O
S
NH2
13C NMR of 3b
(75 MHz, CDCl3)
193.41
147.21
134.15
130.17
118.92
117.39
116.77
77.42
77.00
76.58
30.71
23.05
13.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



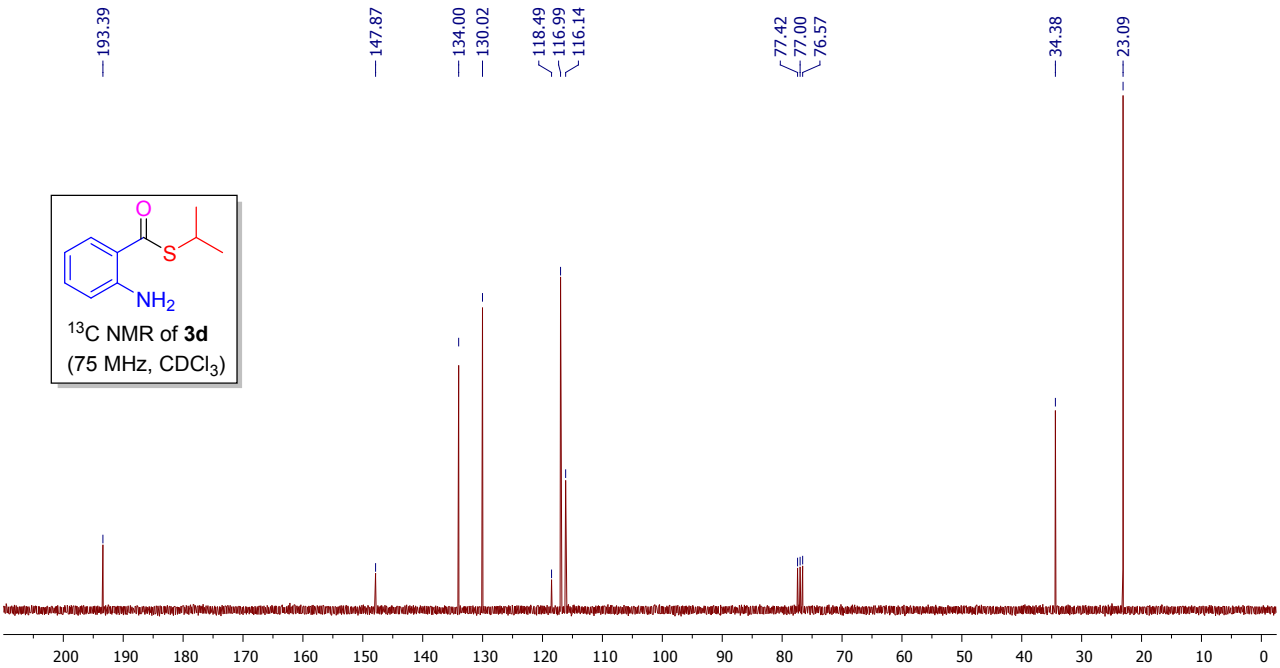
^{1}H NMR of **3c**
(300 MHz, $CDCl_3$)



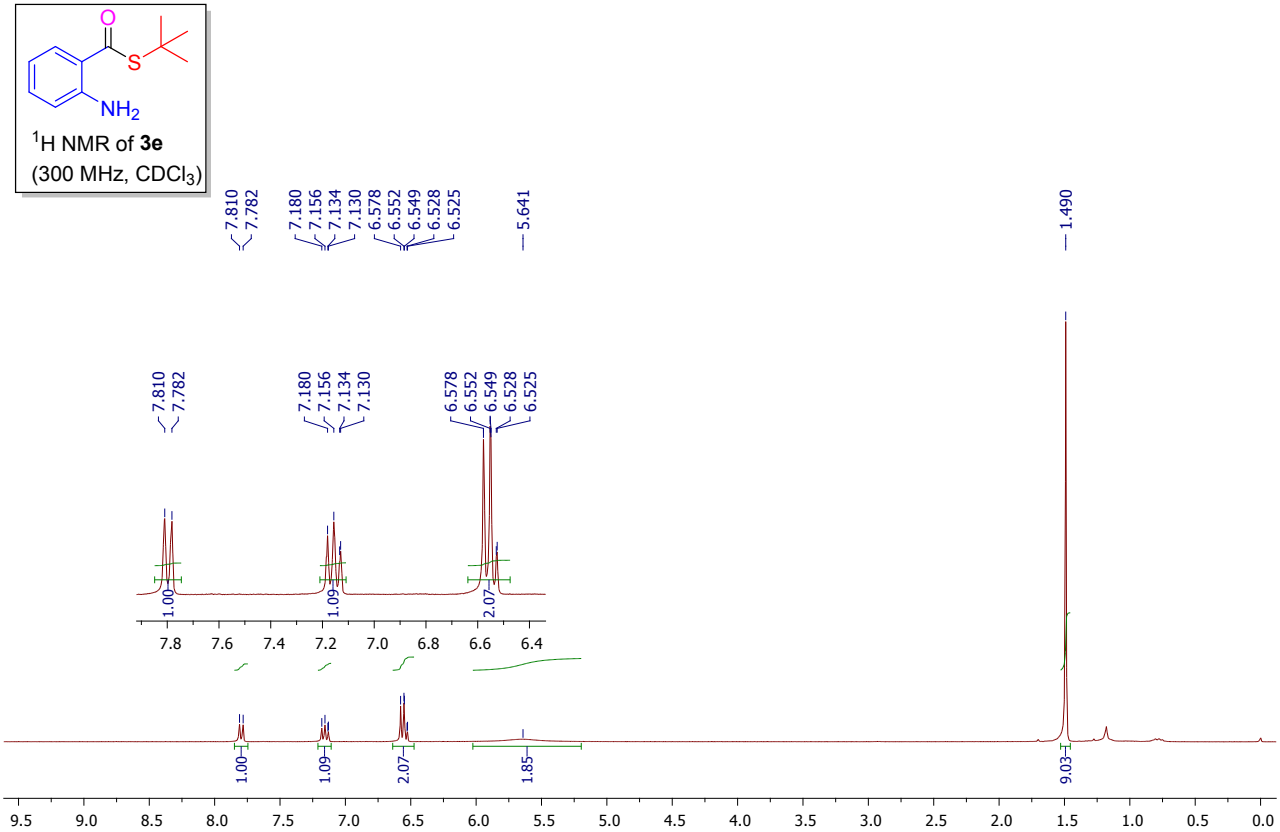
^{13}C NMR of **3c**
(75 MHz, $CDCl_3$)

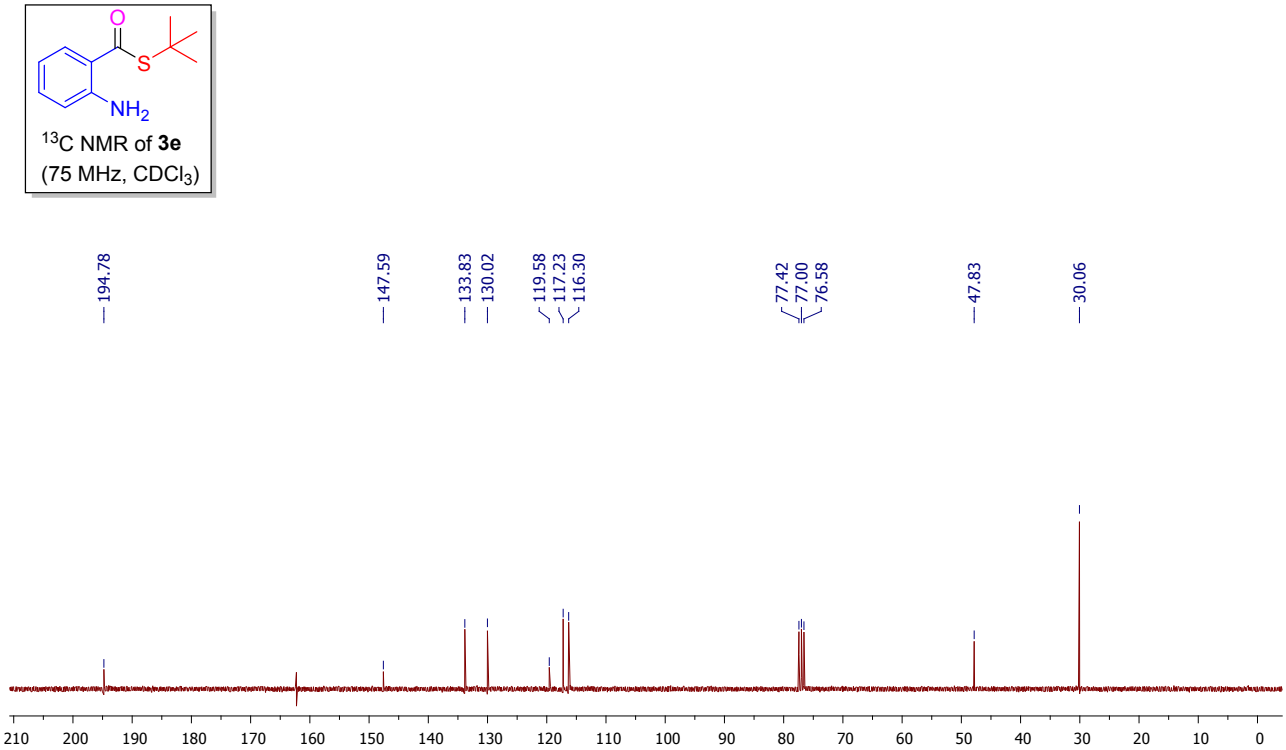


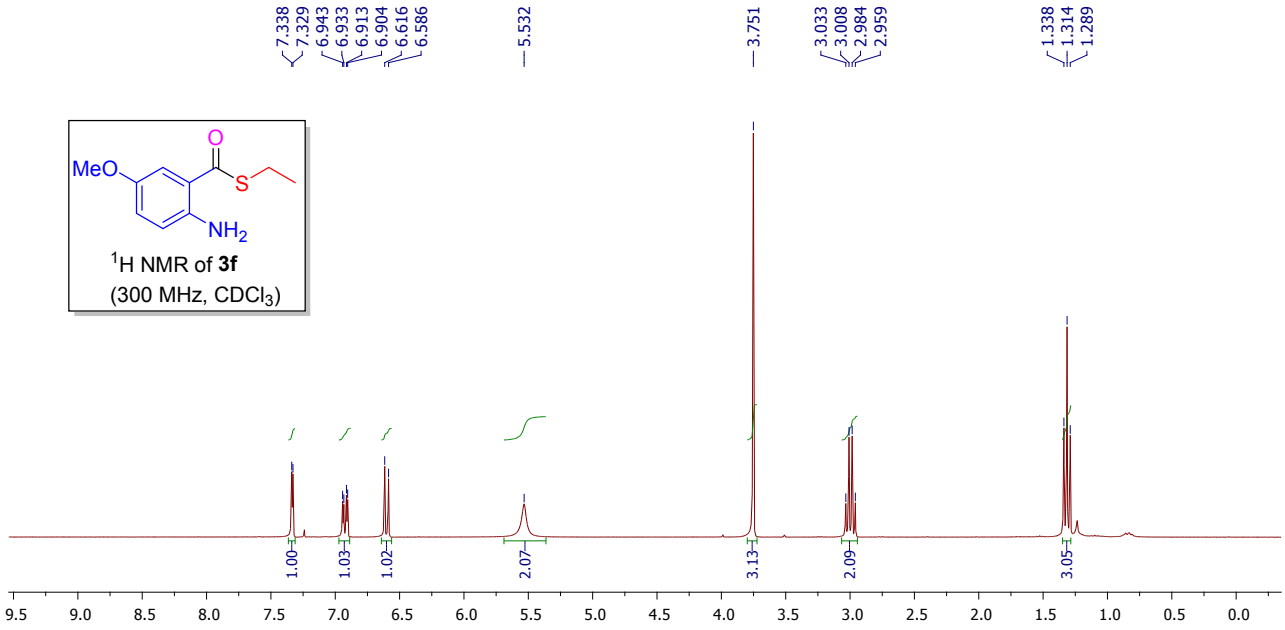
^{1}H NMR of **3d**
(300 MHz, $CDCl_3$)



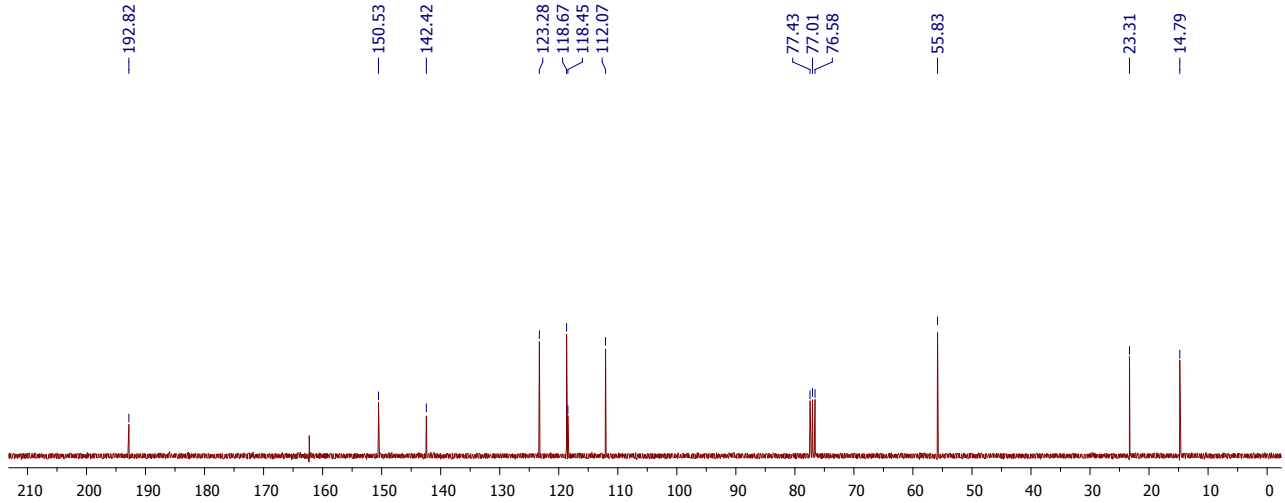
^{13}C NMR of **3d**
(75 MHz, $CDCl_3$)


O
S
NH2
1H NMR of 3e
(300 MHz, CDCl3)
7.810
7.782
7.180
7.156
7.134
7.130
6.578
6.552
6.549
6.528
6.525
5.641
1.490
1.00
1.09
2.07
1.85
9.03

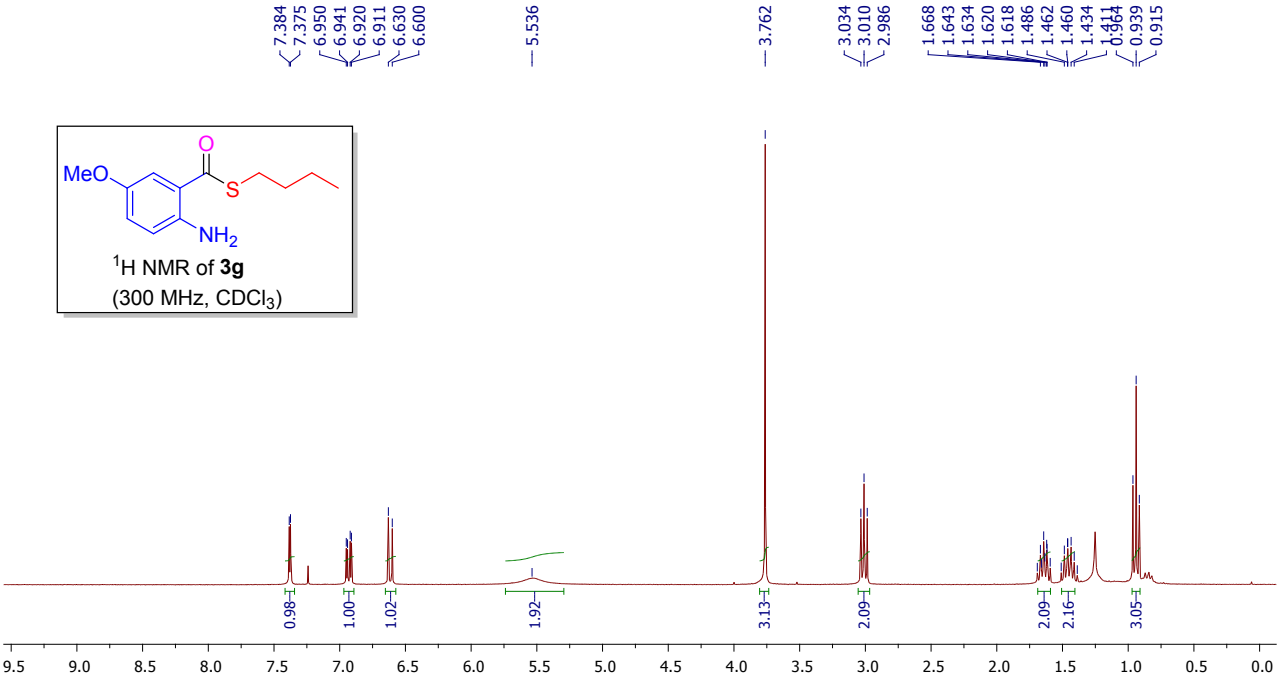

O
S
NH2
13C NMR of 3e
(75 MHz, CDCl3)
194.78
147.59
133.83
130.02
119.58
117.23
116.30
77.42
77.00
76.58
47.83
30.06



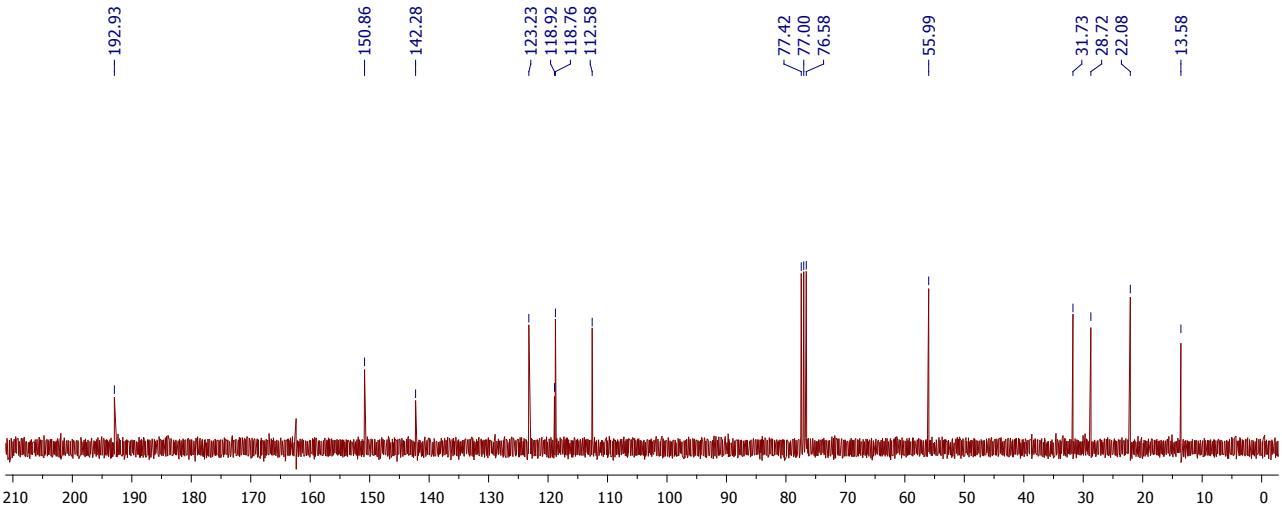
^{1}H NMR of **3f**
(300 MHz, $CDCl_3$)



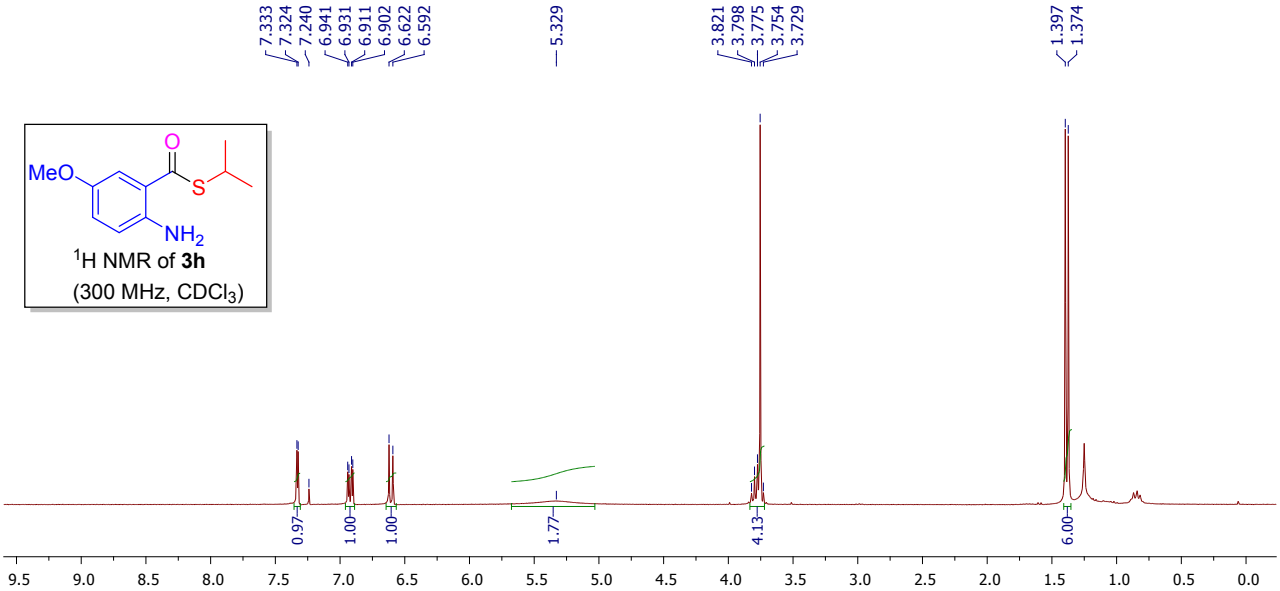
^{13}C NMR of **3f**
(75 MHz, $CDCl_3$)



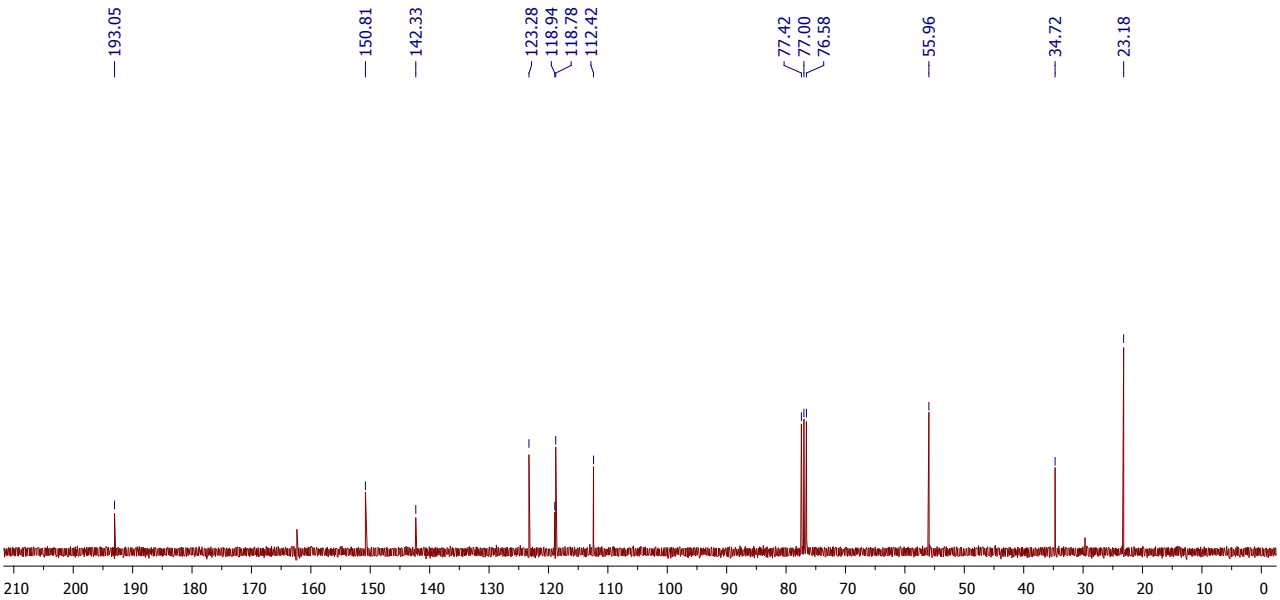
^{1}H NMR of **3g**
(300 MHz, $CDCl_3$)



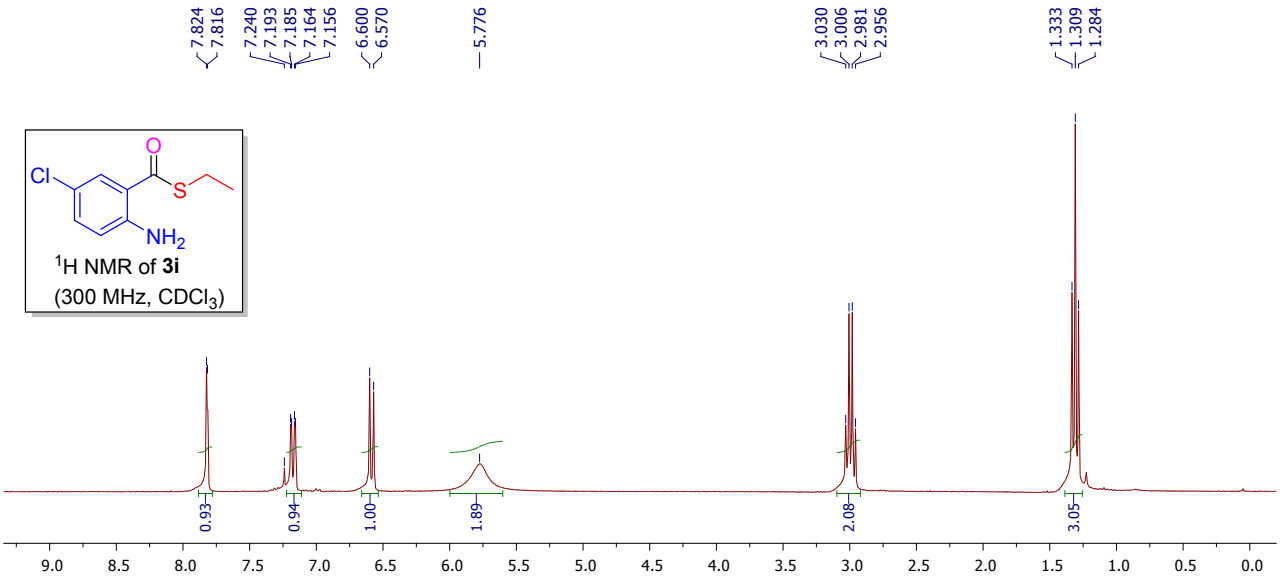
^{13}C NMR of **3g**
(75 MHz, $CDCl_3$)



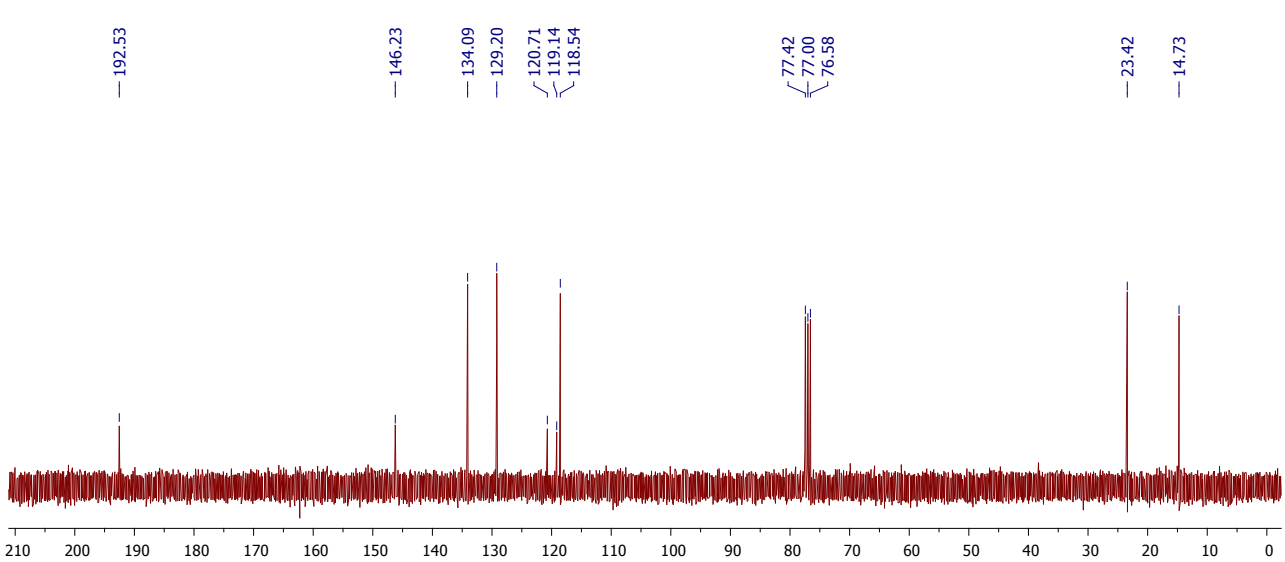
^{1}H NMR of **3h**
(300 MHz, $CDCl_3$)



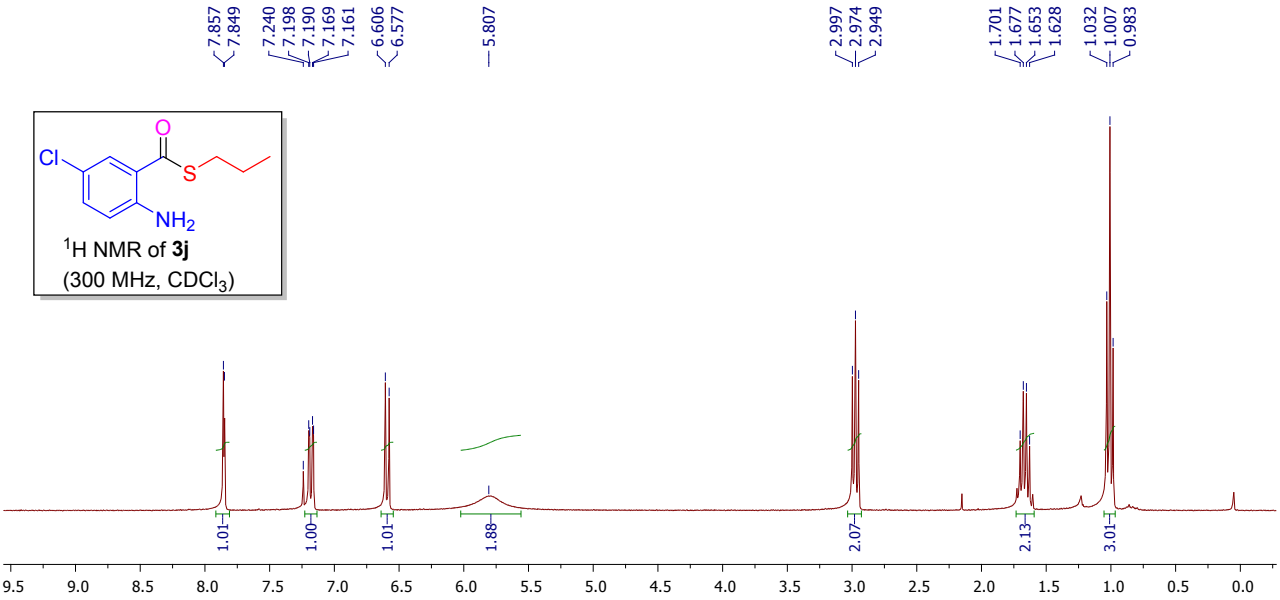
^{13}C NMR of **3h**
(75 MHz, $CDCl_3$)

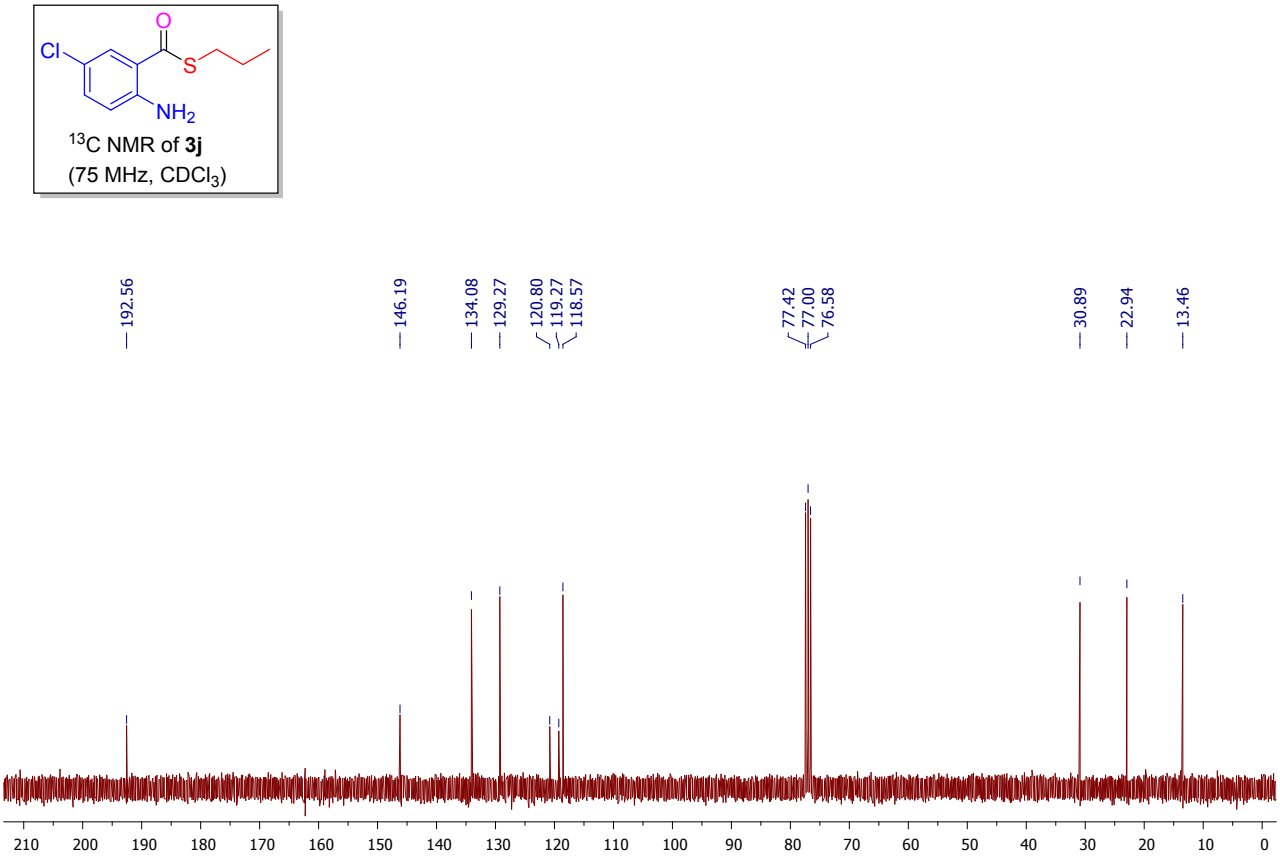


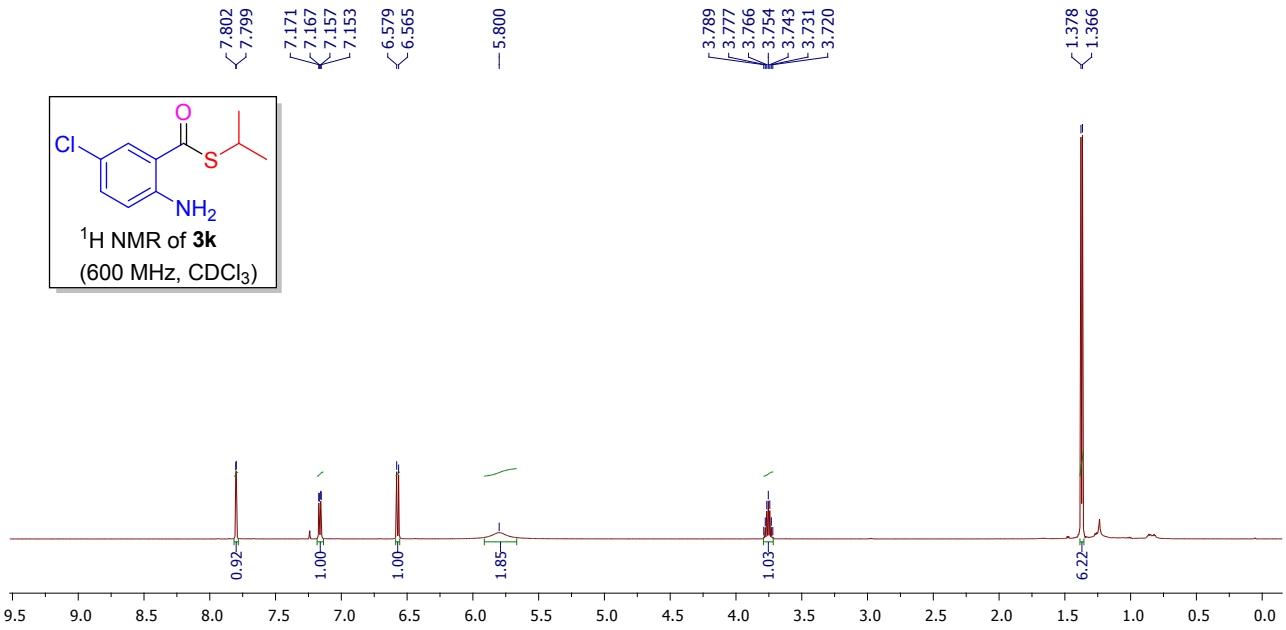
^{1}H NMR of **3i**
(300 MHz, $CDCl_3$)

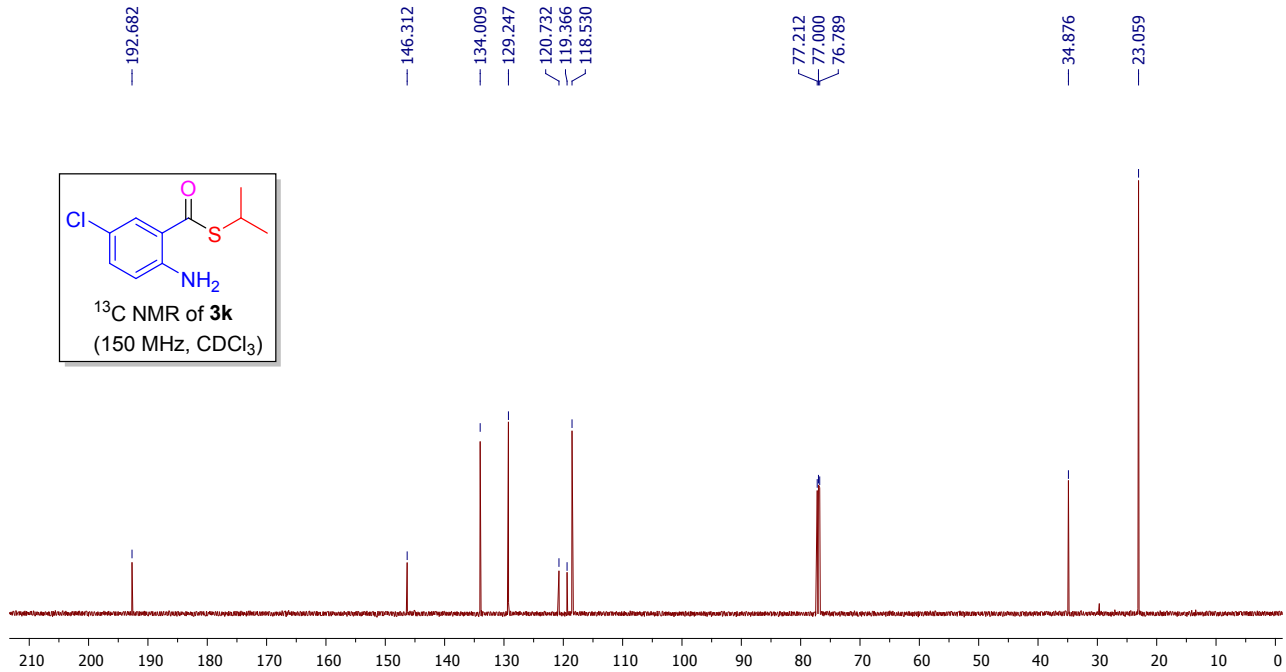


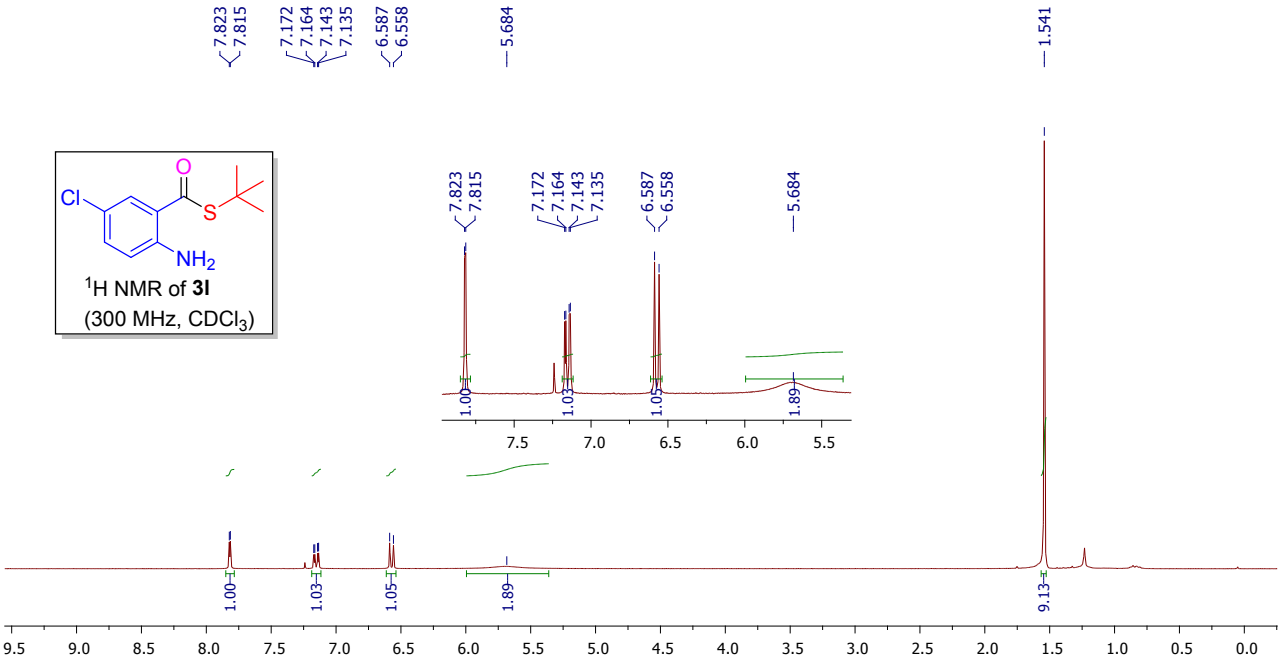
^{13}C NMR of **3i**
(75 MHz, $CDCl_3$)


7.857
7.849
7.240
7.198
7.190
7.169
7.161
6.606
6.577
5.807
2.997
2.974
2.949
1.701
1.677
1.653
1.628
1.032
1.007
0.983
Cl
O
S
NH2
1H NMR of 3j
(300 MHz, CDCl3)
1.01
1.00
1.01
1.88
2.07
2.13
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

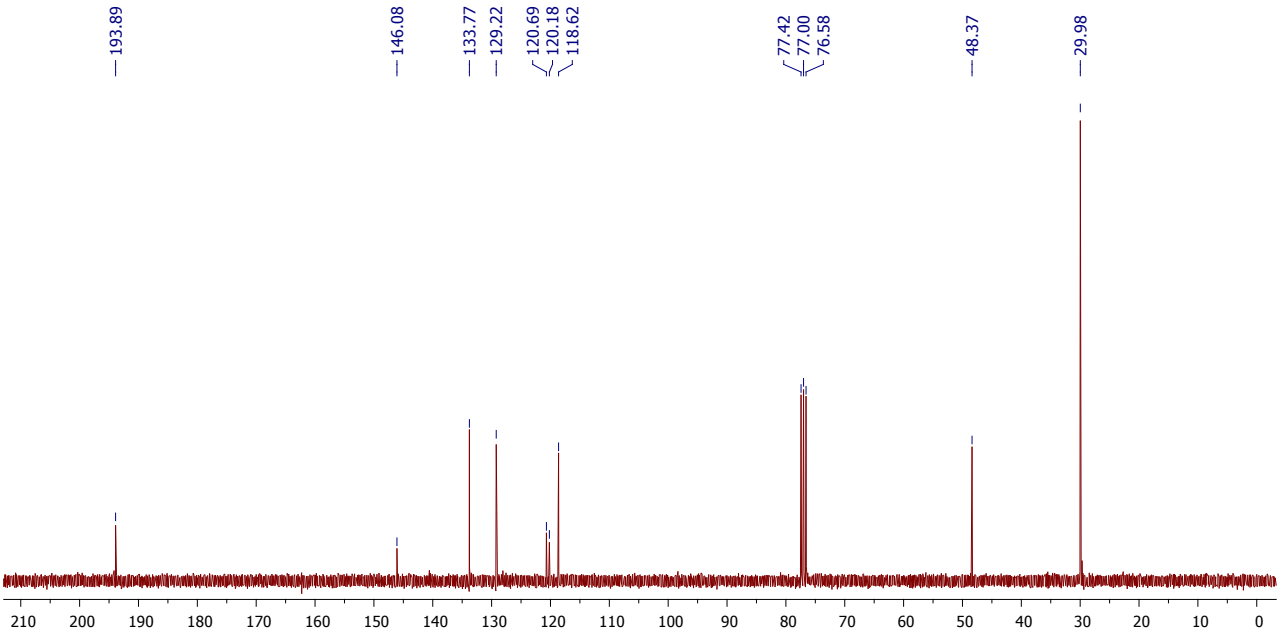

Cl
O
S
NH2
13C NMR of 3j
(75 MHz, CDCl3)
192.56
146.19
134.08
129.27
120.80
119.27
118.57
77.42
77.00
76.58
30.89
22.94
13.46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.802
7.799
7.171
7.167
7.157
7.153
6.579
6.565
5.800
3.789
3.777
3.766
3.754
3.743
3.731
3.720
1.378
1.366
Cl
O
S
NH2
1H NMR of 3k
(600 MHz, CDCl3)
0.92
1.00
1.00
1.85
1.03
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

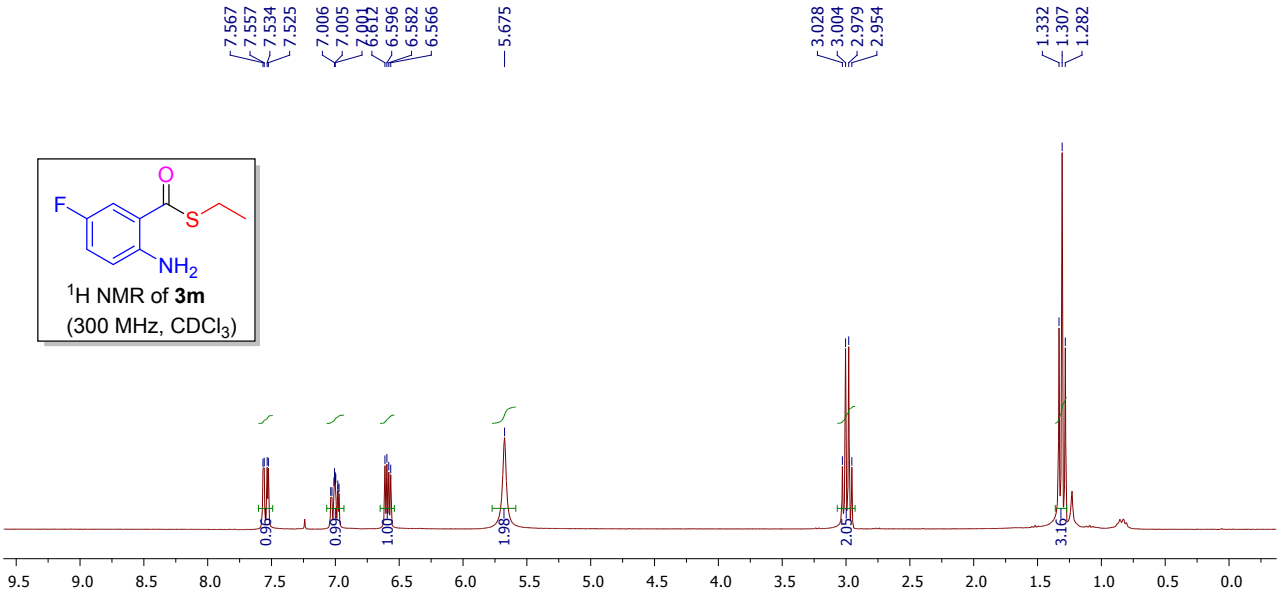

192.682
146.312
134.009
129.247
120.732
119.366
118.530
77.212
77.000
76.789
34.876
23.059
Cl
O
S
NH2
13C NMR of 3k
(150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

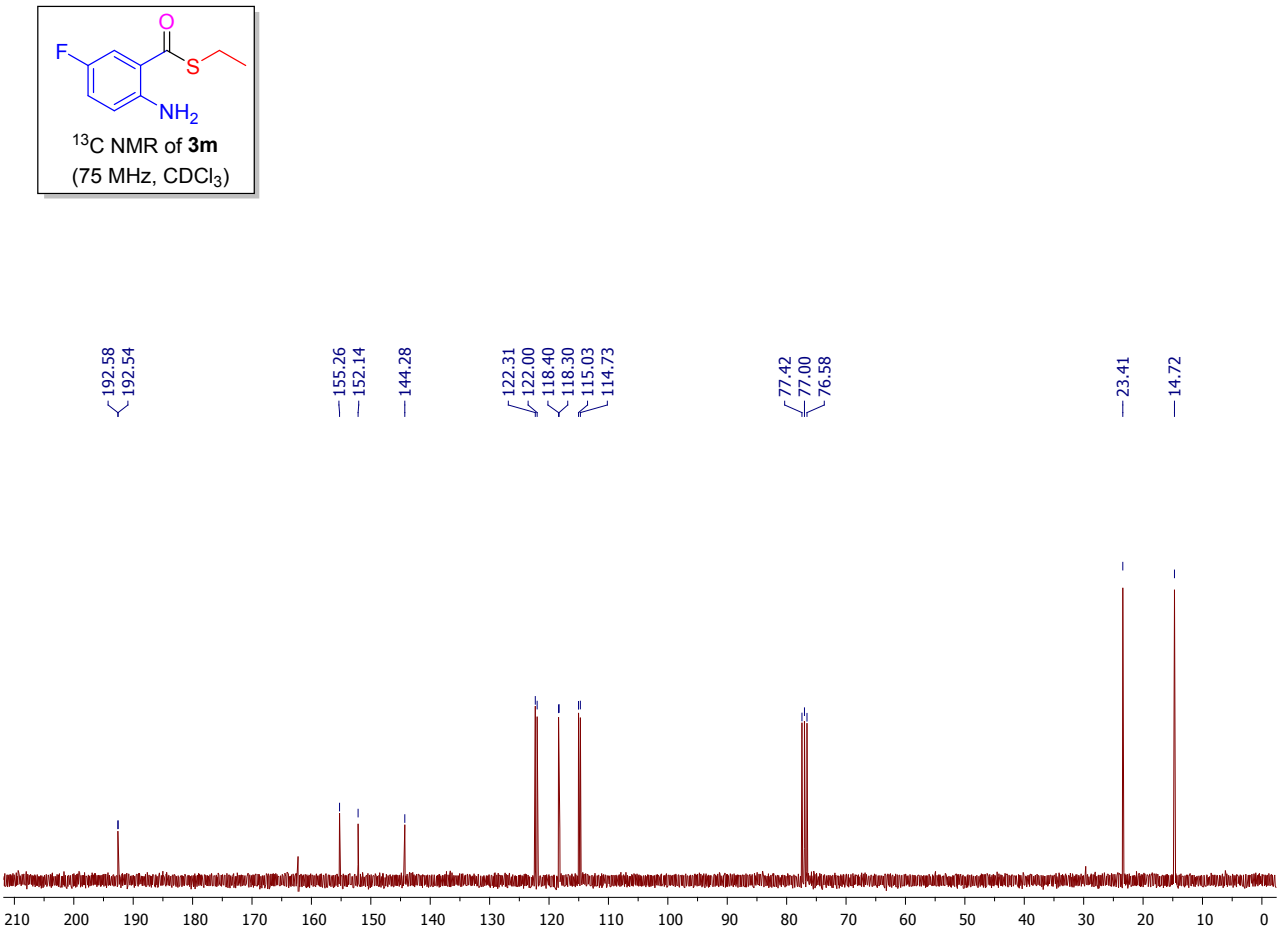


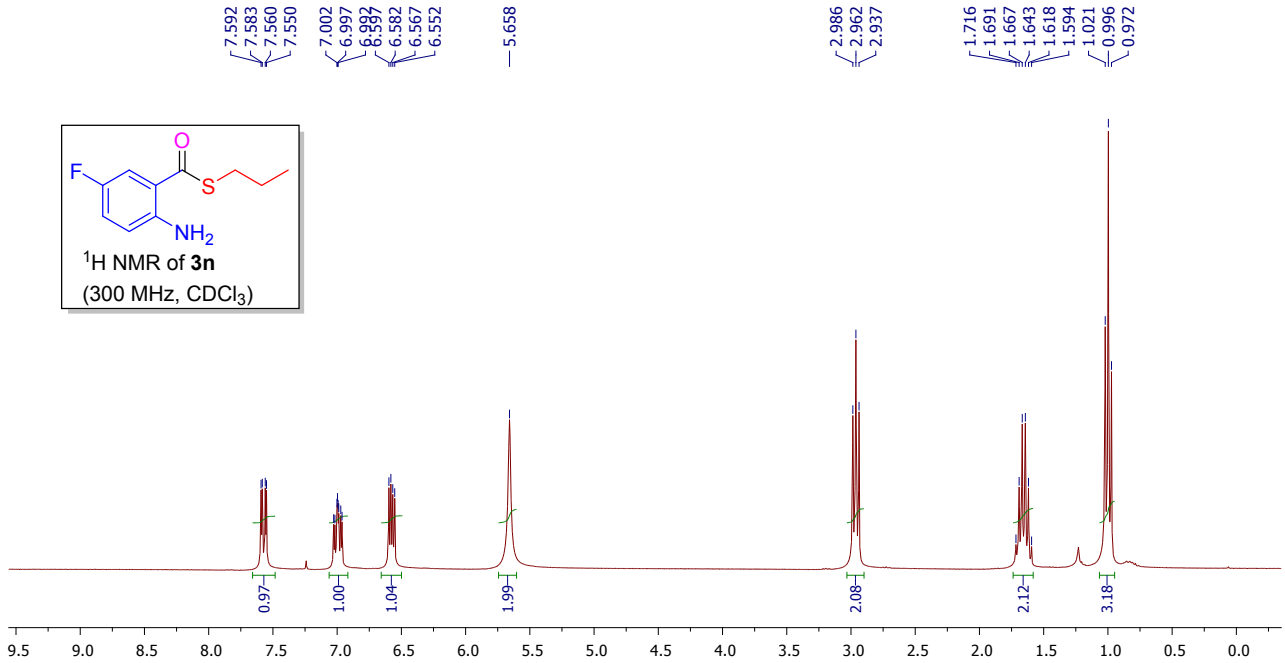
^{1}H NMR of **3l**
(300 MHz, $CDCl_3$)



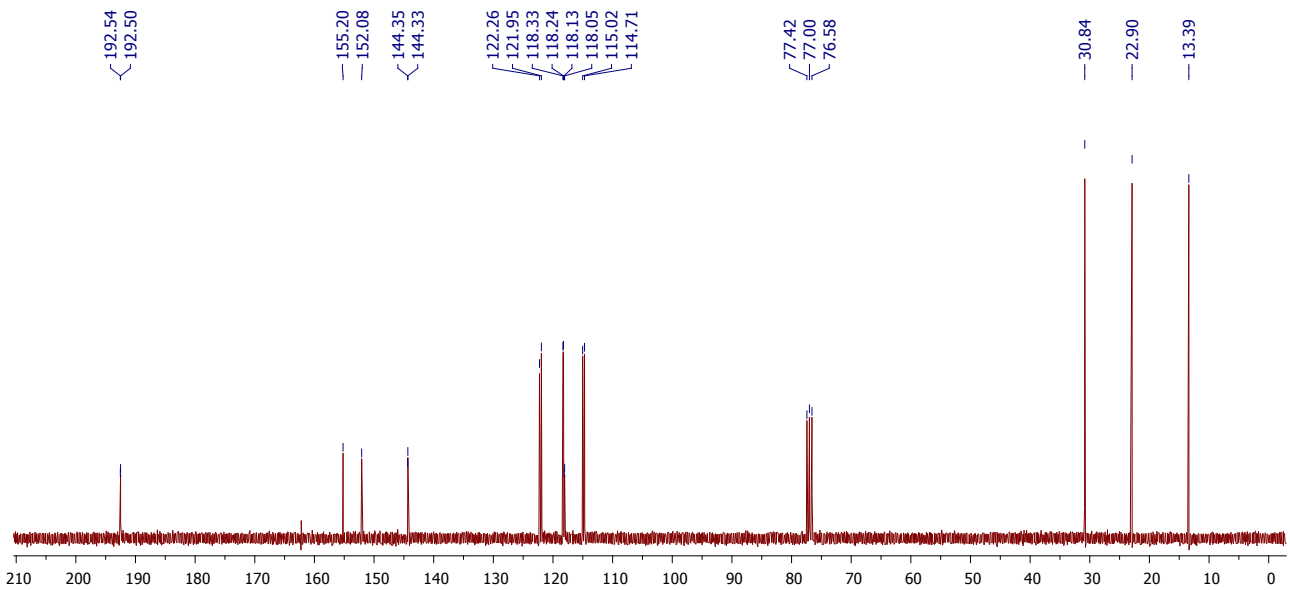
^{13}C NMR of **3l**
(75 MHz, $CDCl_3$)


7.567
7.557
7.534
7.525
7.006
7.005
6.596
6.582
6.566
5.675
3.028
3.004
2.979
2.954
1.332
1.307
1.282
F
O
S
NH2
1H NMR of 3m
(300 MHz, CDCl3)
0.96
0.99
1.00
1.98
2.03
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

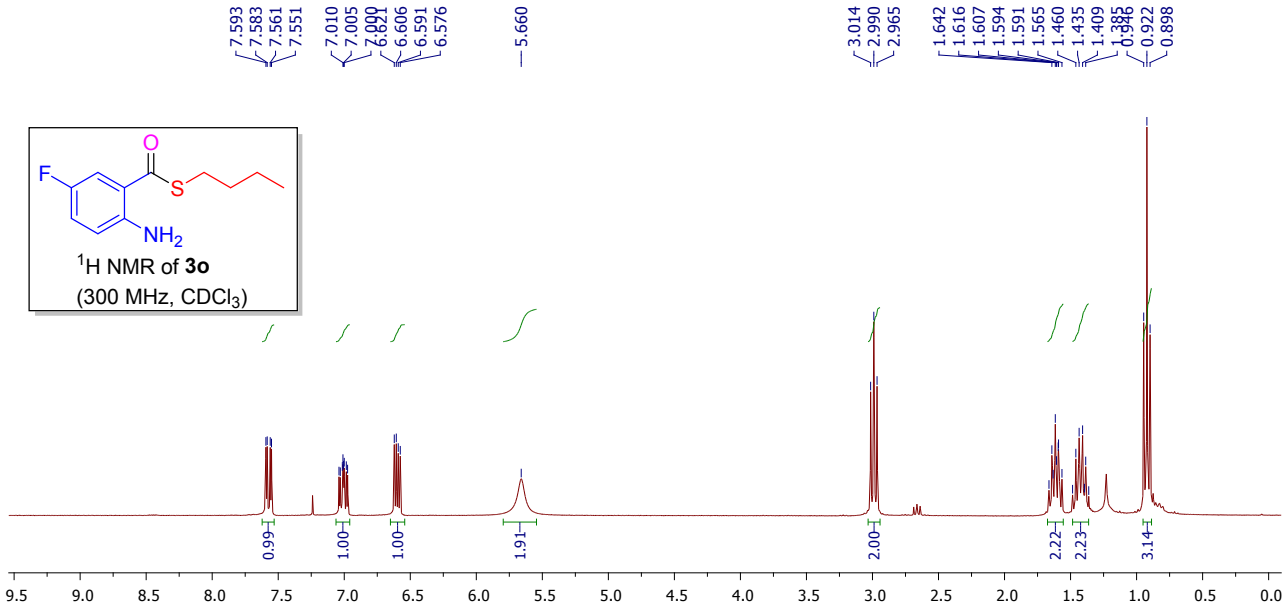

F
O
S
NH2
13C NMR of 3m
(75 MHz, CDCl3)
192.58
192.54
155.26
152.14
144.28
122.31
122.00
118.40
118.30
115.03
114.73
77.42
77.00
76.58
23.41
14.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



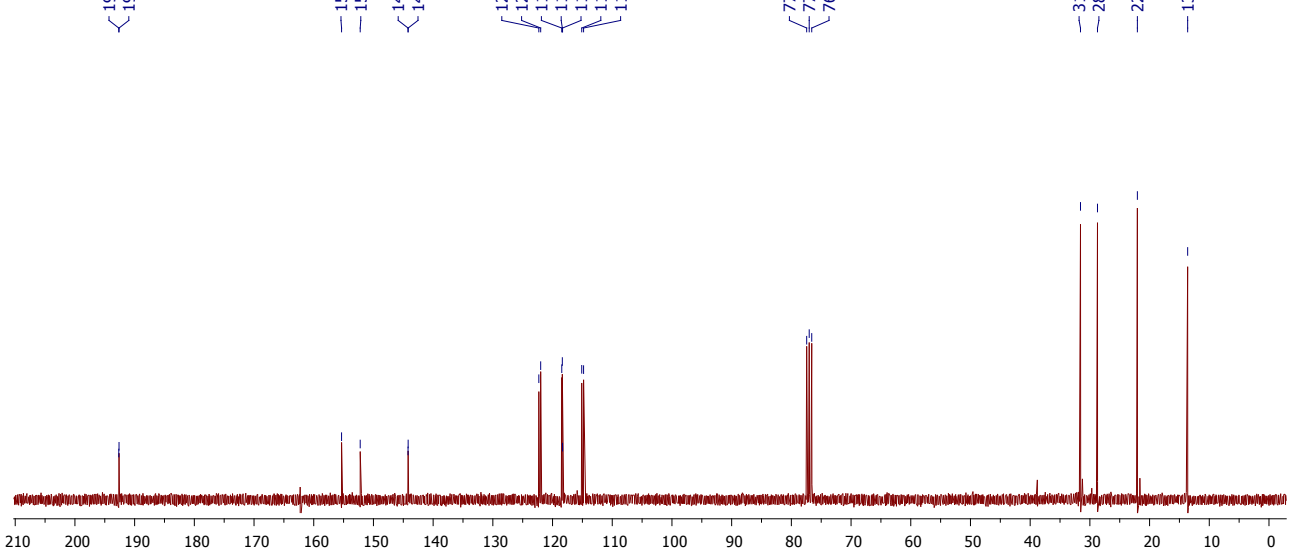
^{1}H NMR of **3n**
(300 MHz, $CDCl_3$)



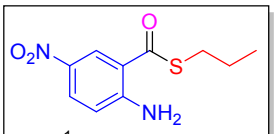
^{13}C NMR of **3n**
(75 MHz, $CDCl_3$)



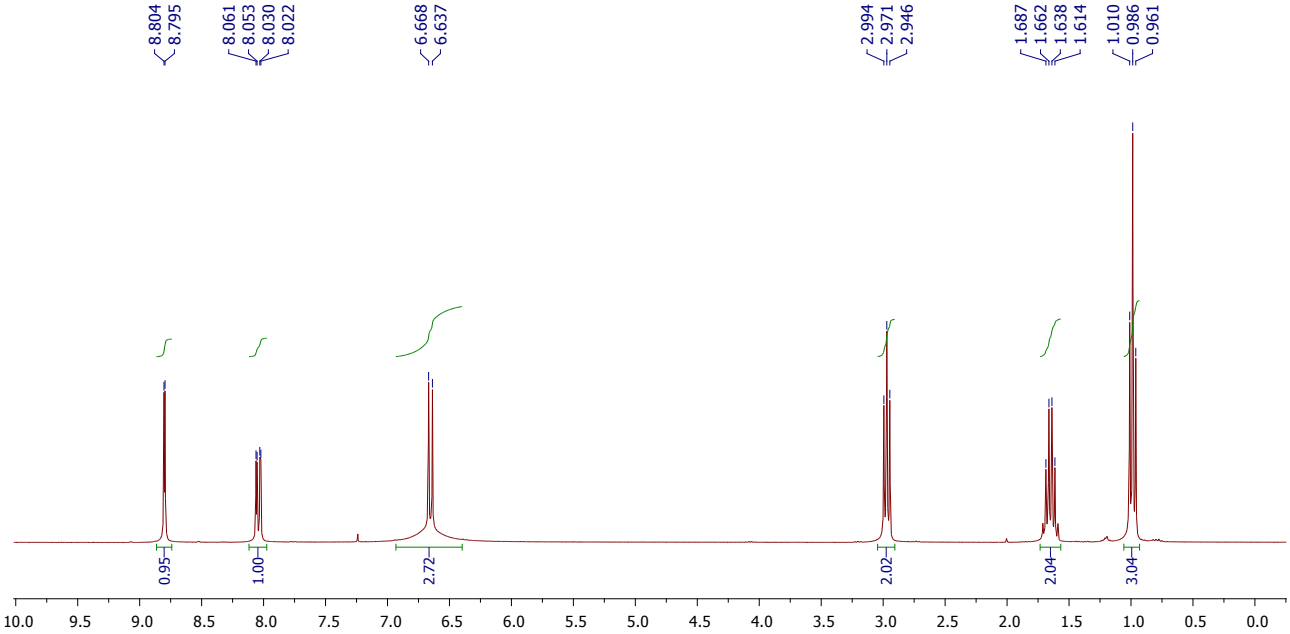
^{1}H NMR of **3o**
(300 MHz, $CDCl_3$)

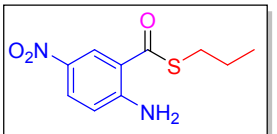


^{13}C NMR of **3o**
(75 MHz, $CDCl_3$)

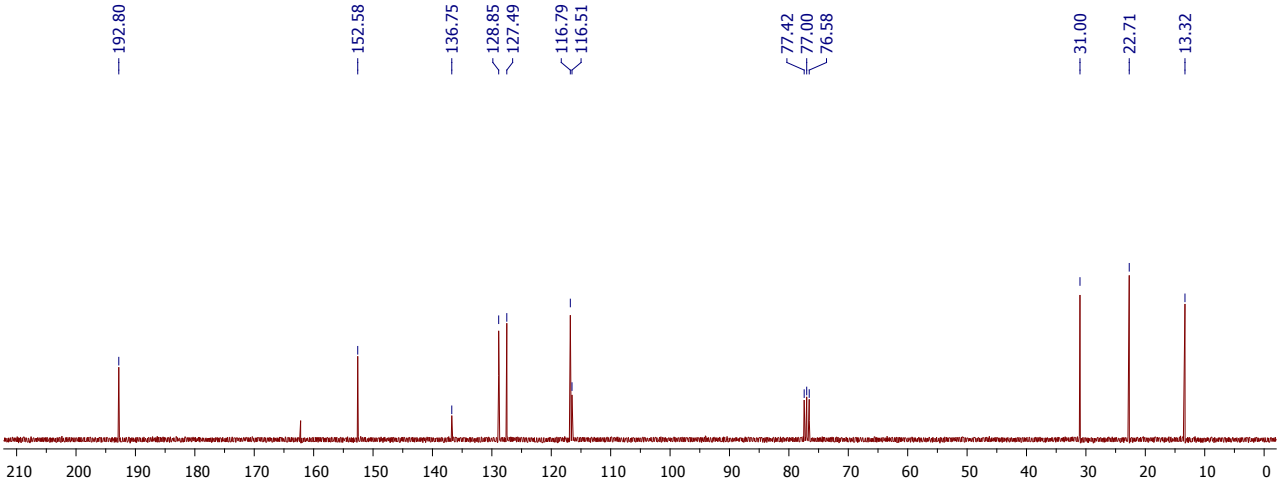


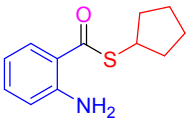
^{1}H NMR of **3p**
(300 MHz, $CDCl_3$)



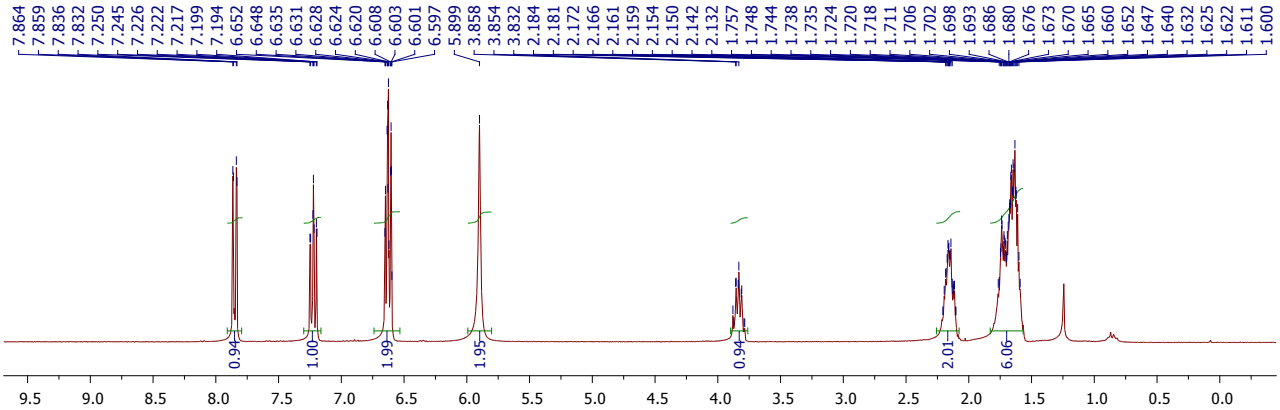


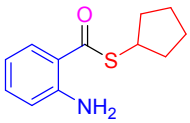
^{13}C NMR of **3p**
(75 MHz, $CDCl_3$)



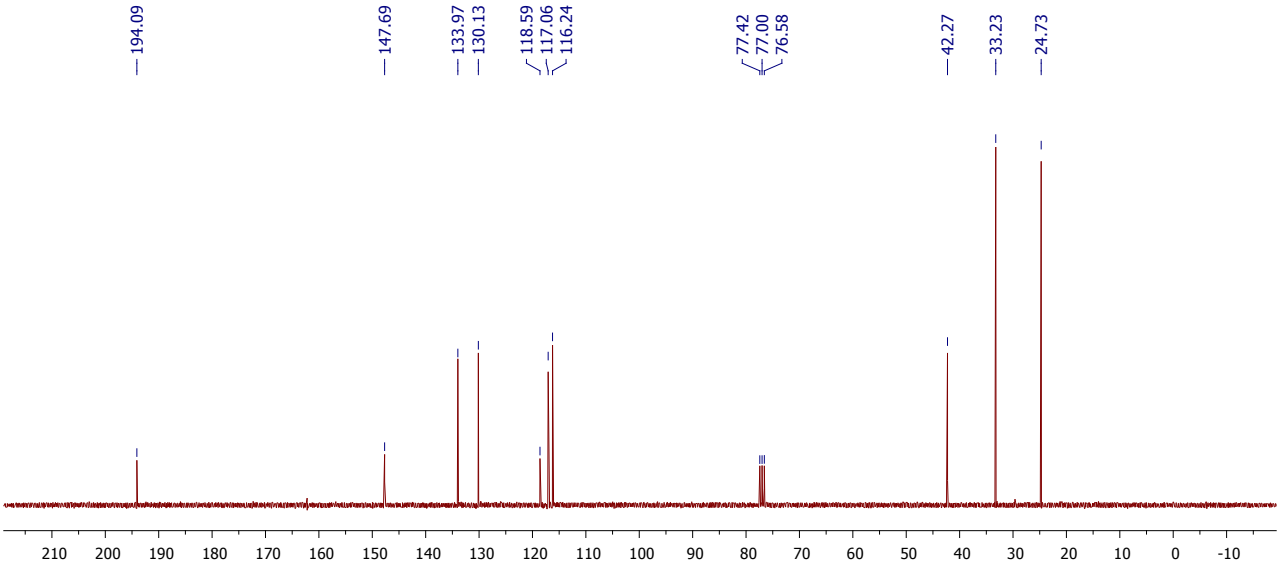


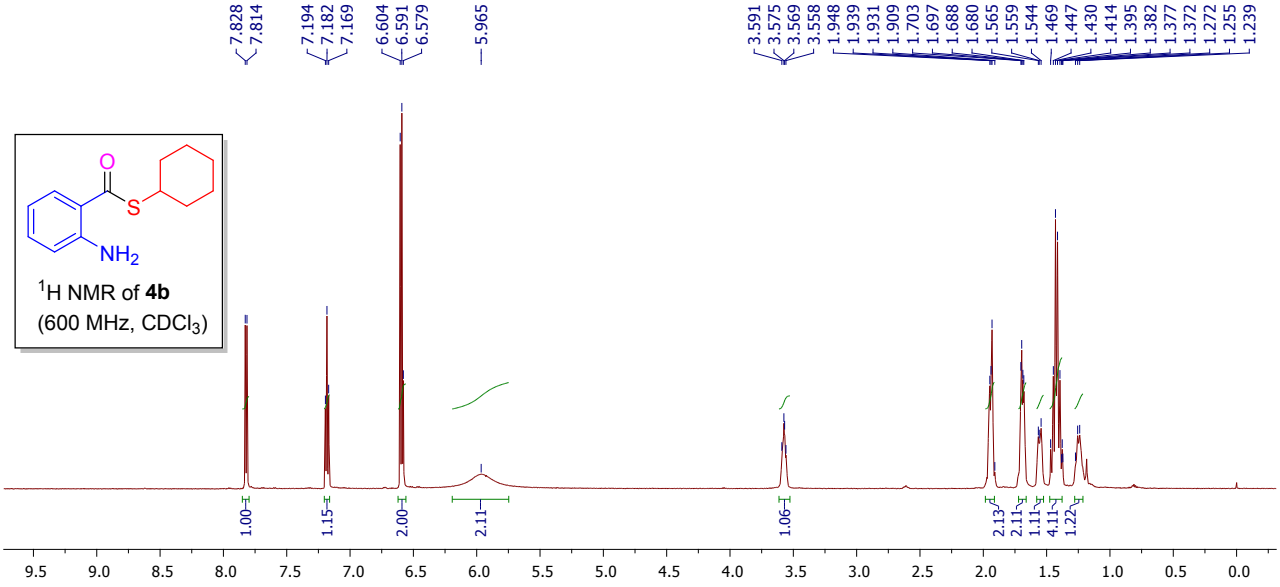
^{1}H NMR of **4a**
(300 MHz, $CDCl_3$)



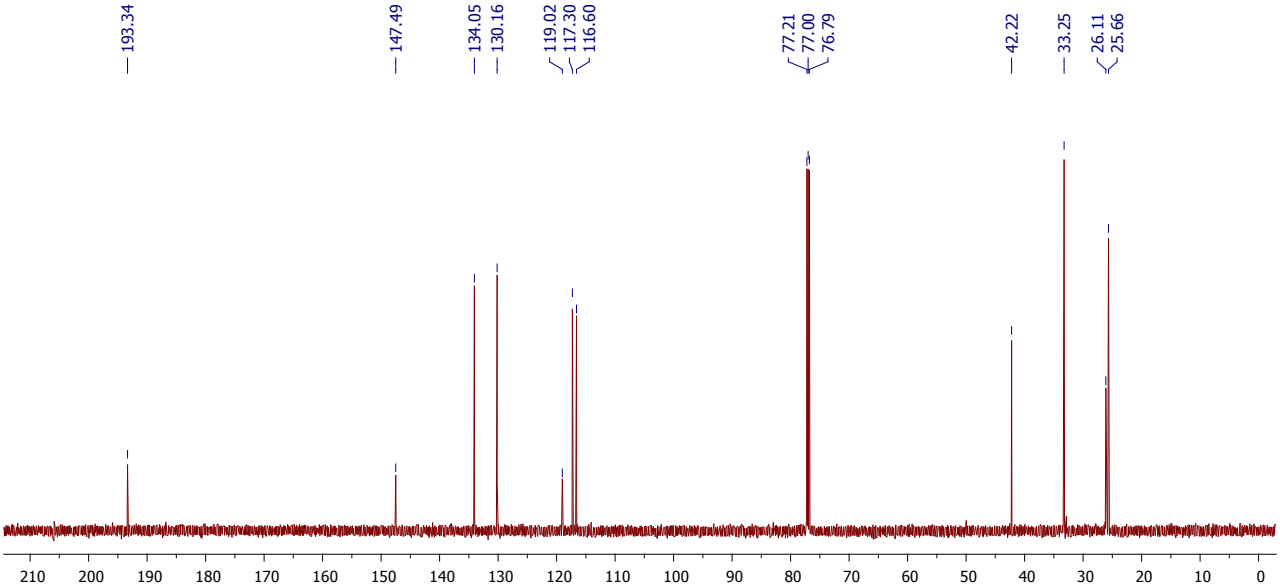


^{13}C NMR of **4a**
(75 MHz, $CDCl_3$)

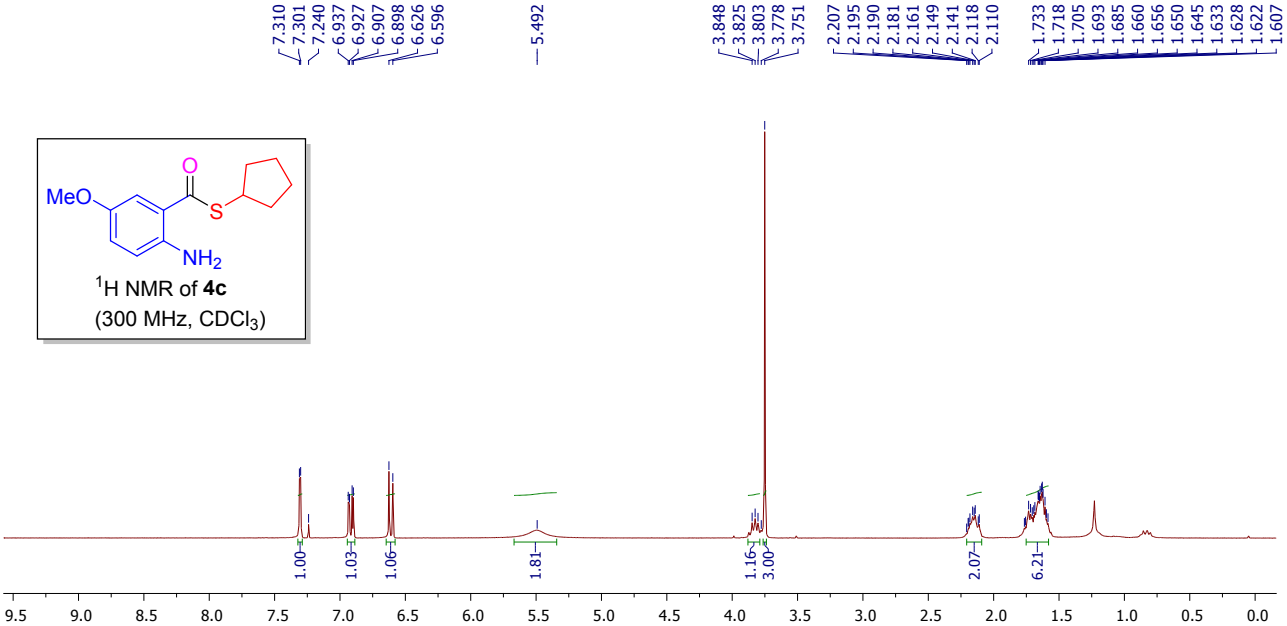




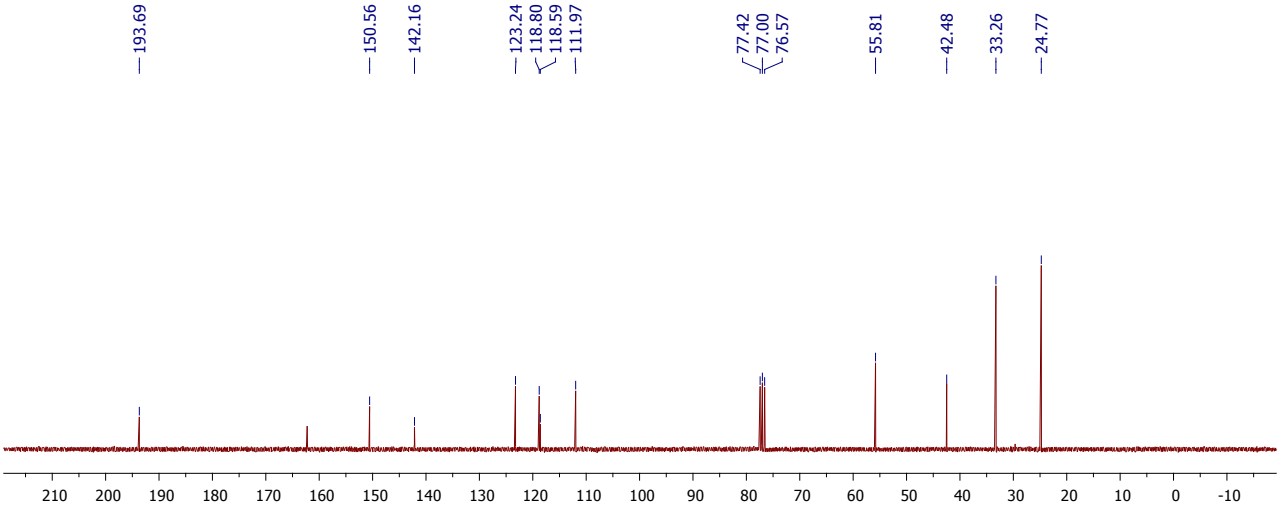
^{1}H NMR of **4b**
(600 MHz, $CDCl_3$)



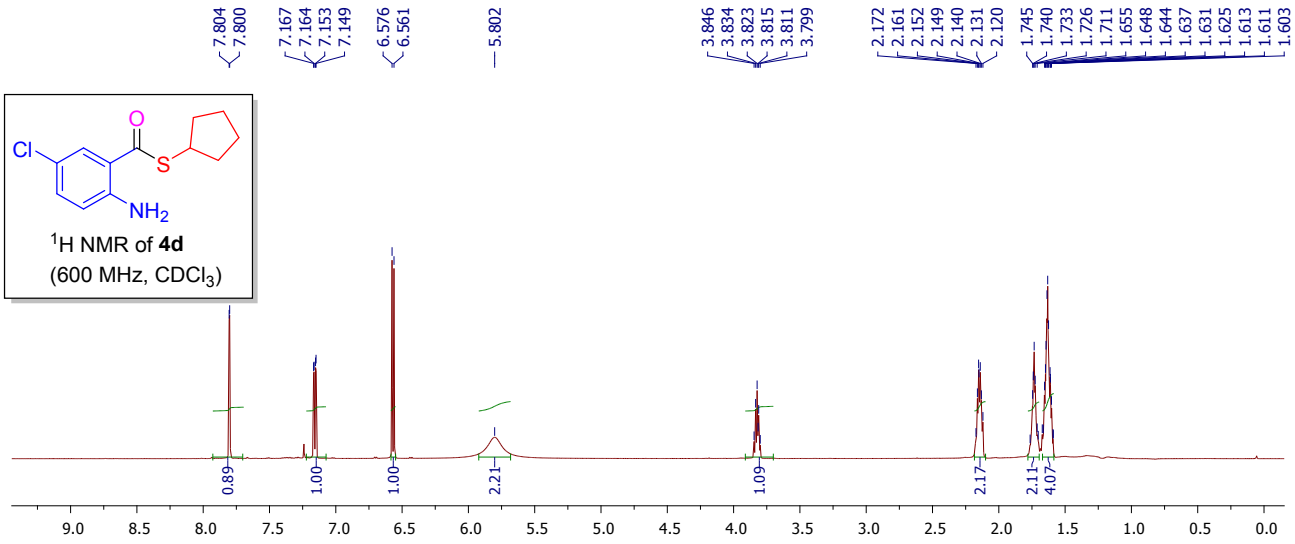
^{13}C NMR of **4b**
(150 MHz, $CDCl_3$)

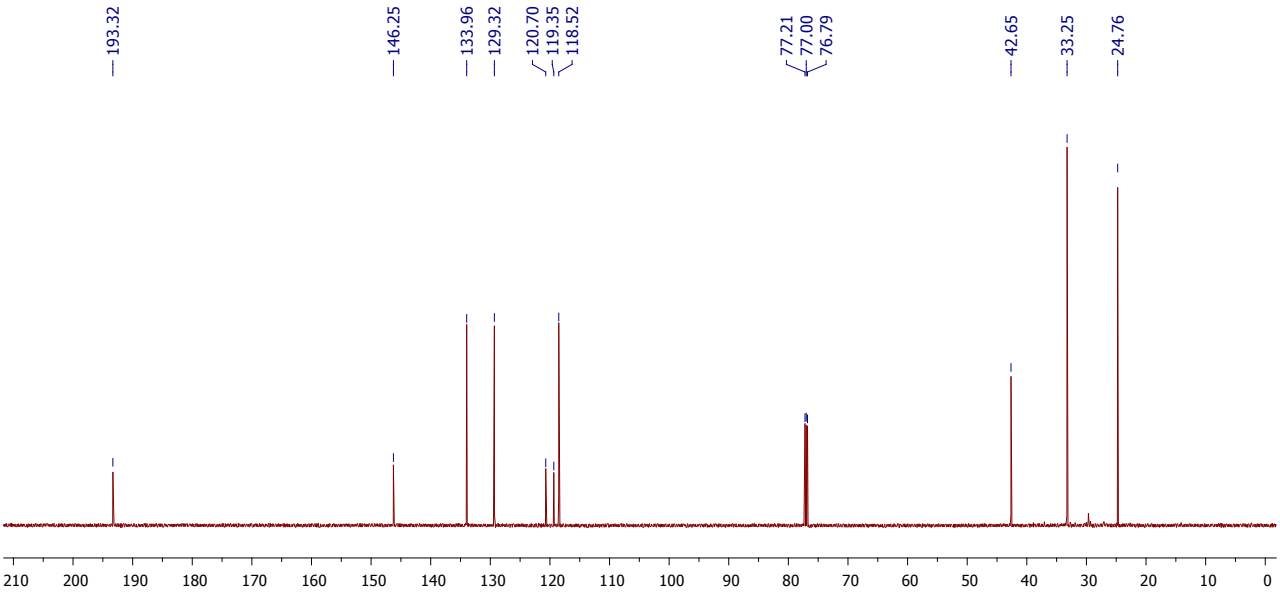


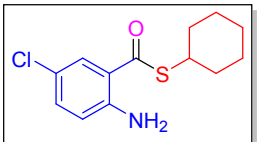
^{1}H NMR of **4c**
(300 MHz, $CDCl_3$)



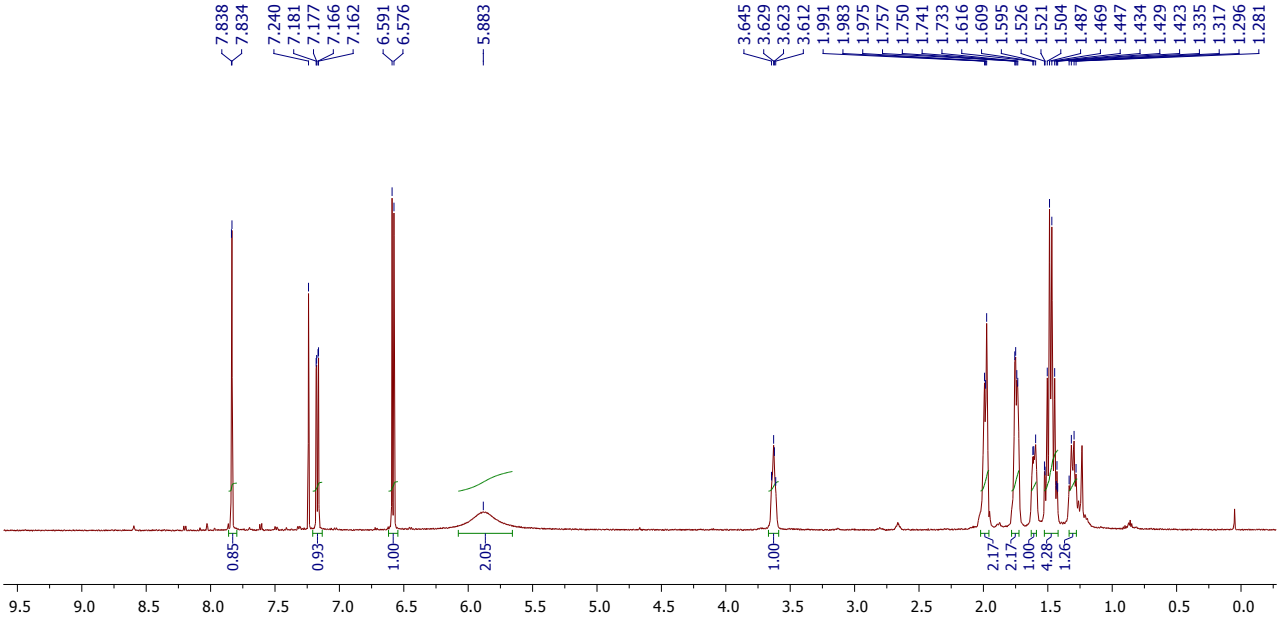
^{13}C NMR of **4c**
(75 MHz, $CDCl_3$)


7.804
7.800
7.167
7.164
7.153
7.149
6.576
6.561
5.802
3.846
3.834
3.823
3.815
3.811
3.799
2.172
2.161
2.152
2.149
2.140
2.131
2.120
1.745
1.740
1.733
1.726
1.711
1.655
1.648
1.644
1.637
1.631
1.625
1.613
1.611
1.603
Cl
O
S
NH2
^{1}H NMR of **4d**
(600 MHz, $CDCl_3$)
0.89
1.00
1.00
2.21
1.09
2.17
2.11
4.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

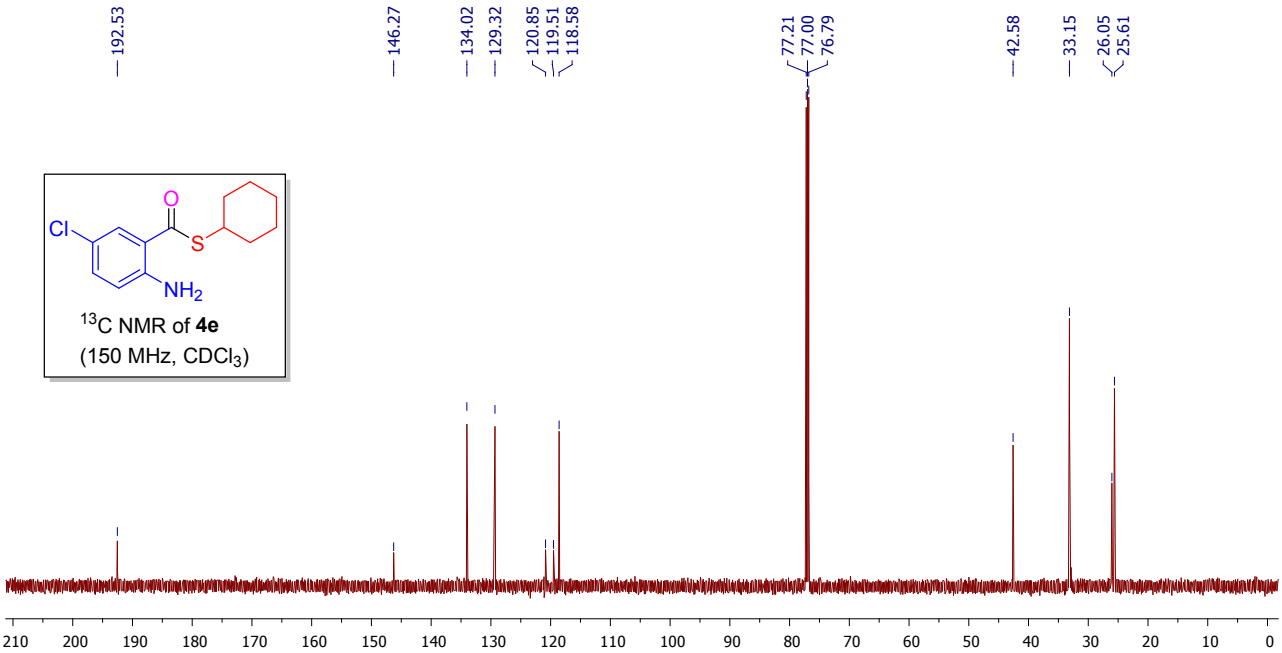

Cl
O
S
NH2
^{13}C NMR of **4d**
(150 MHz, $CDCl_3$)
193.32
146.25
133.96
129.32
120.70
119.35
118.52
77.21
77.00
76.79
42.65
33.25
24.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

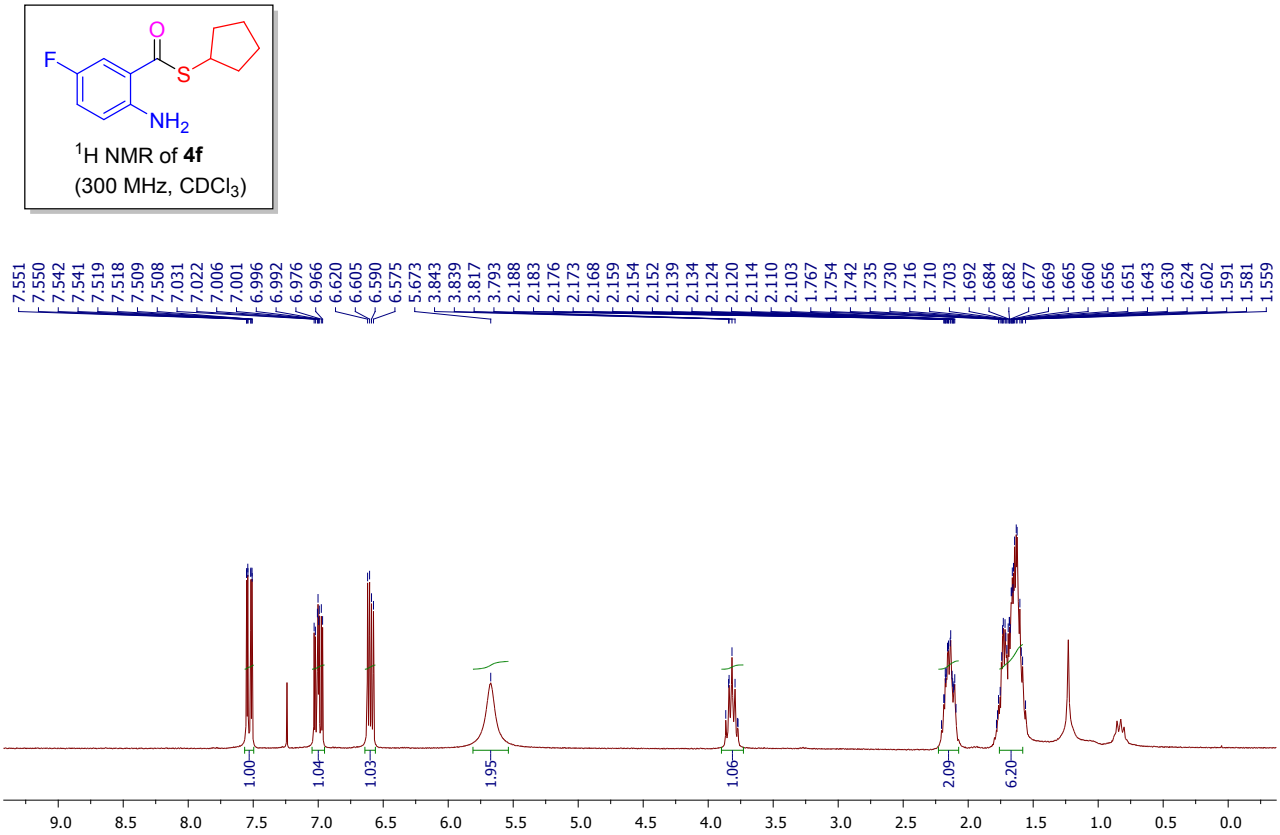


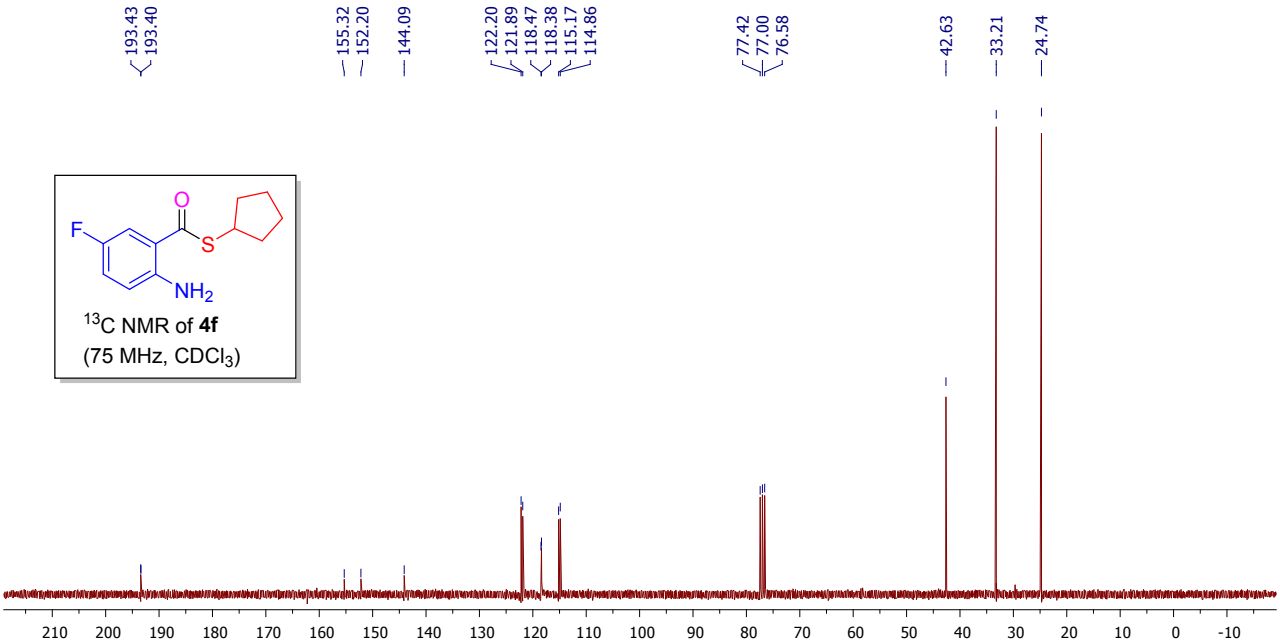
^{1}H NMR of **4e**
(600 MHz, $CDCl_3$)

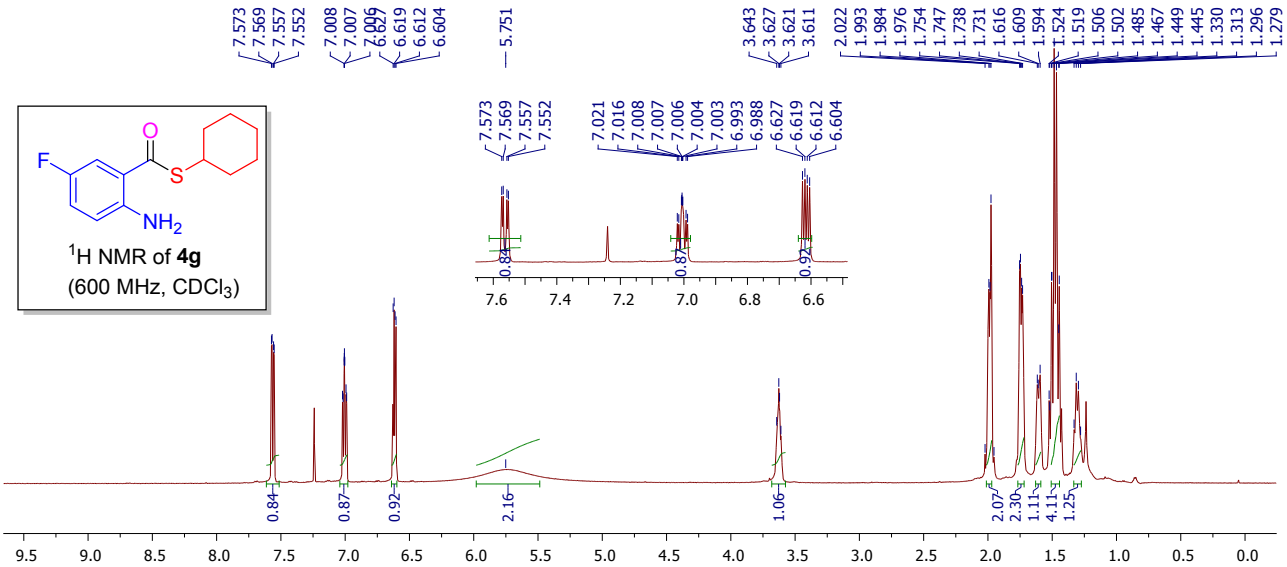


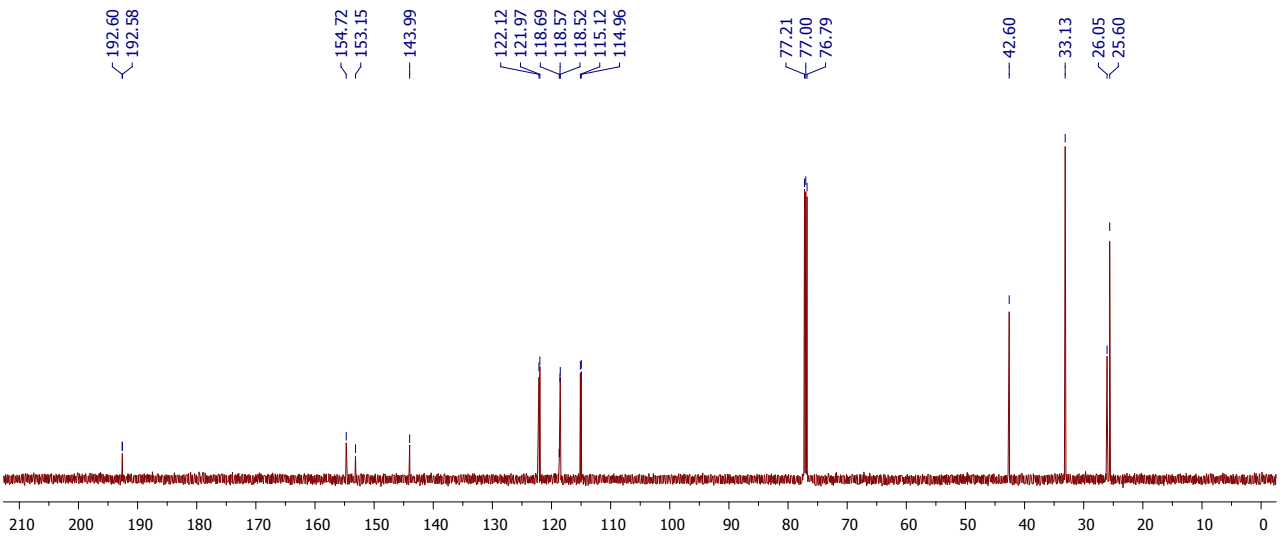
^{13}C NMR of **4e**
(150 MHz, $CDCl_3$)

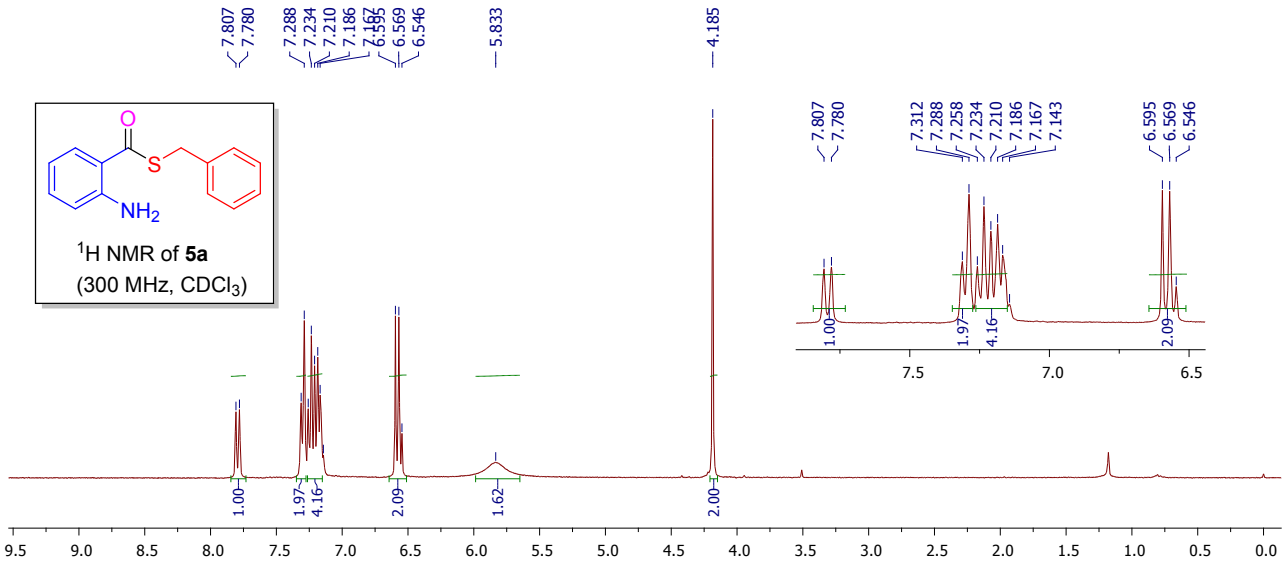


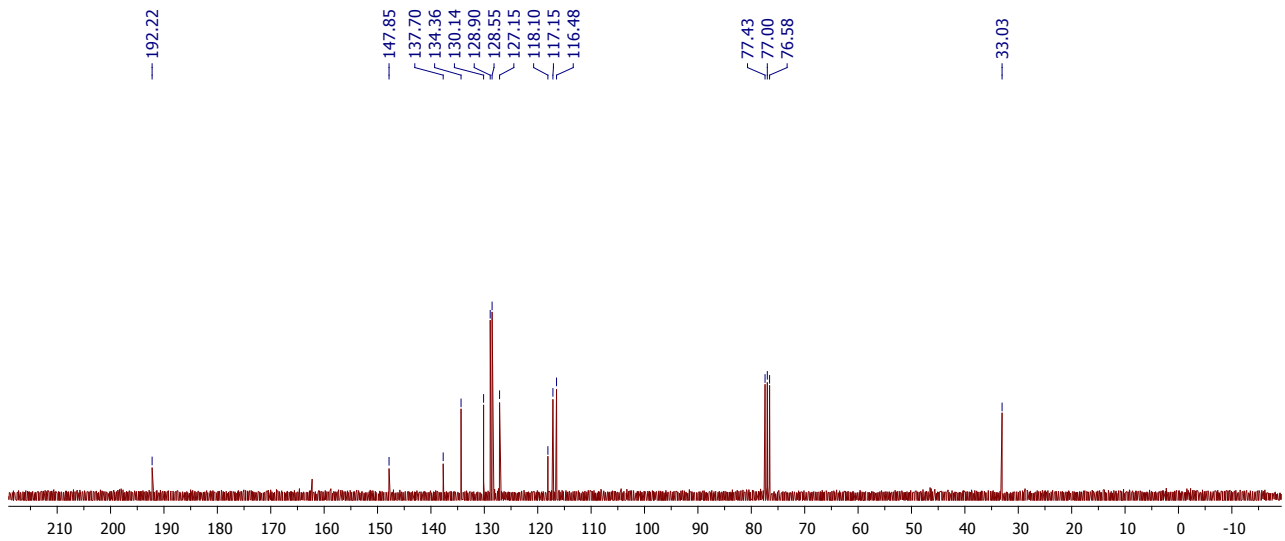

F
O
S
NH2
1H NMR of 4f
(300 MHz, CDCl3)
7.551 7.550 7.542 7.541 7.519 7.518 7.509 7.508 7.031 7.022 7.006 7.001 6.996 6.992 6.976 6.966 6.620 6.605 6.590 6.575 5.673 3.843 3.839 3.817 3.793 2.188 2.183 2.176 2.173 2.168 2.159 2.154 2.152 2.139 2.134 2.124 2.120 2.114 2.110 2.103 1.767 1.754 1.742 1.735 1.730 1.716 1.710 1.703 1.692 1.684 1.682 1.677 1.669 1.665 1.660 1.656 1.651 1.643 1.630 1.624 1.602 1.591 1.581 1.559
1.00 1.04 1.03 1.95 1.06 2.09 6.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

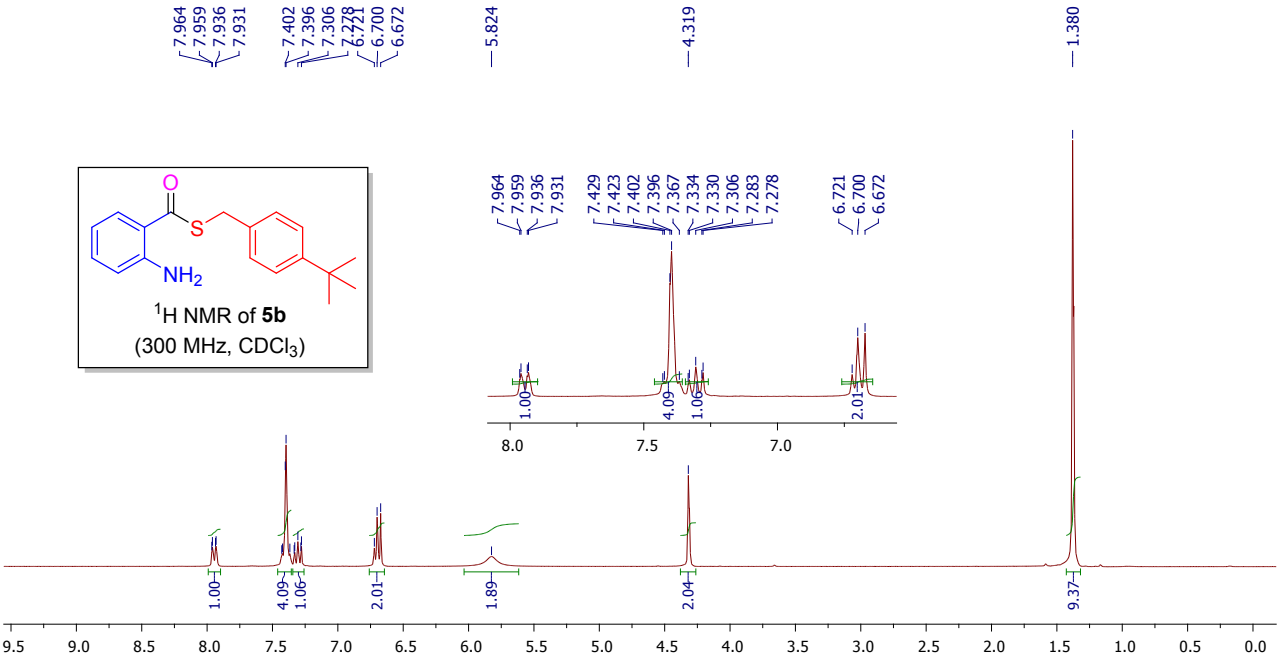

193.43 193.40 155.32 152.20 144.09 122.20 121.89 118.47 118.38 115.17 114.86 77.42 77.00 76.58 42.63 33.21 24.74
F
O
S
NH2
13C NMR of 4f
(75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


F
O
S
NH2
1H NMR of 4g
(600 MHz, CDCl3)

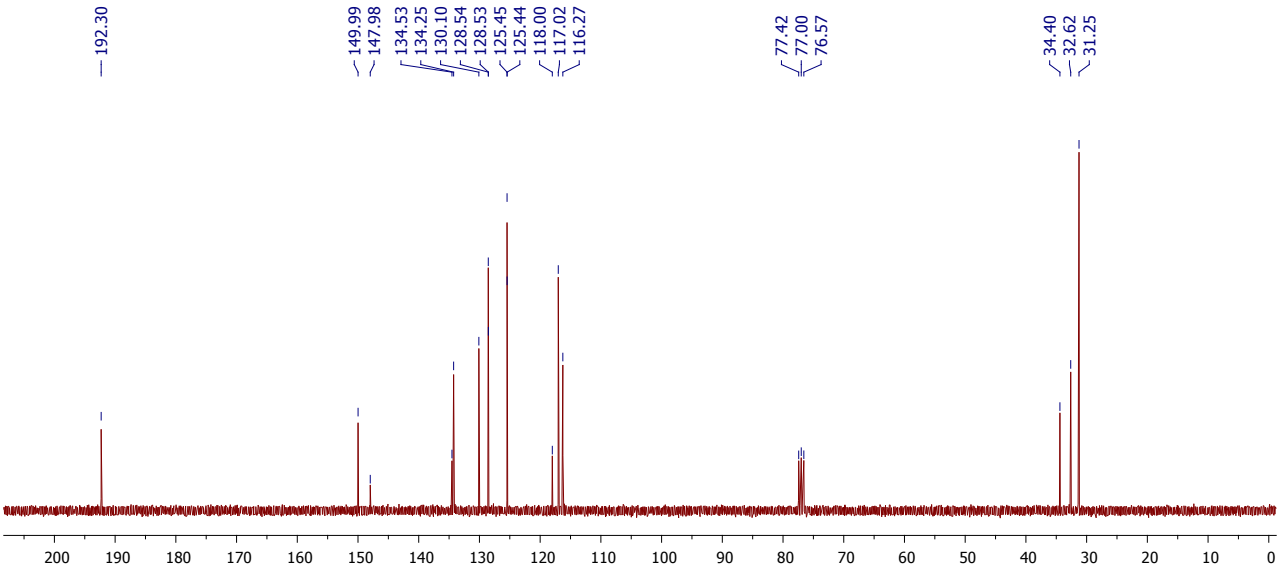

F
O
S
NH2
13C NMR of 4g
(150 MHz, CDCl3)


^{1}H NMR of **5a**
(300 MHz, $CDCl_3$)

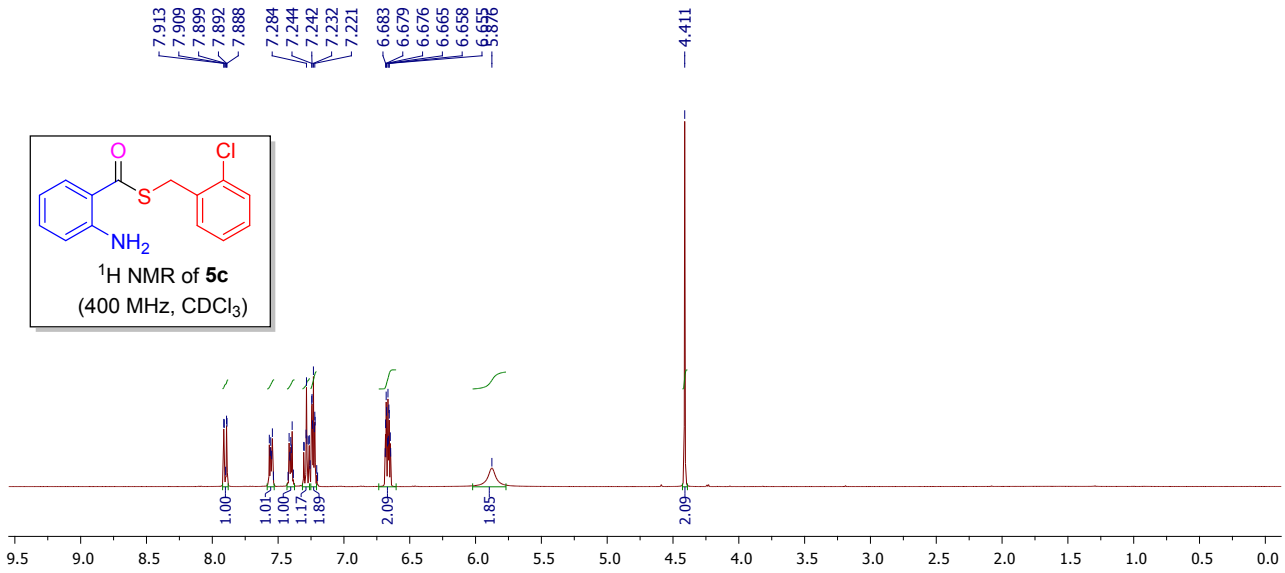

^{13}C NMR of **5a**
(75 MHz, $CDCl_3$)

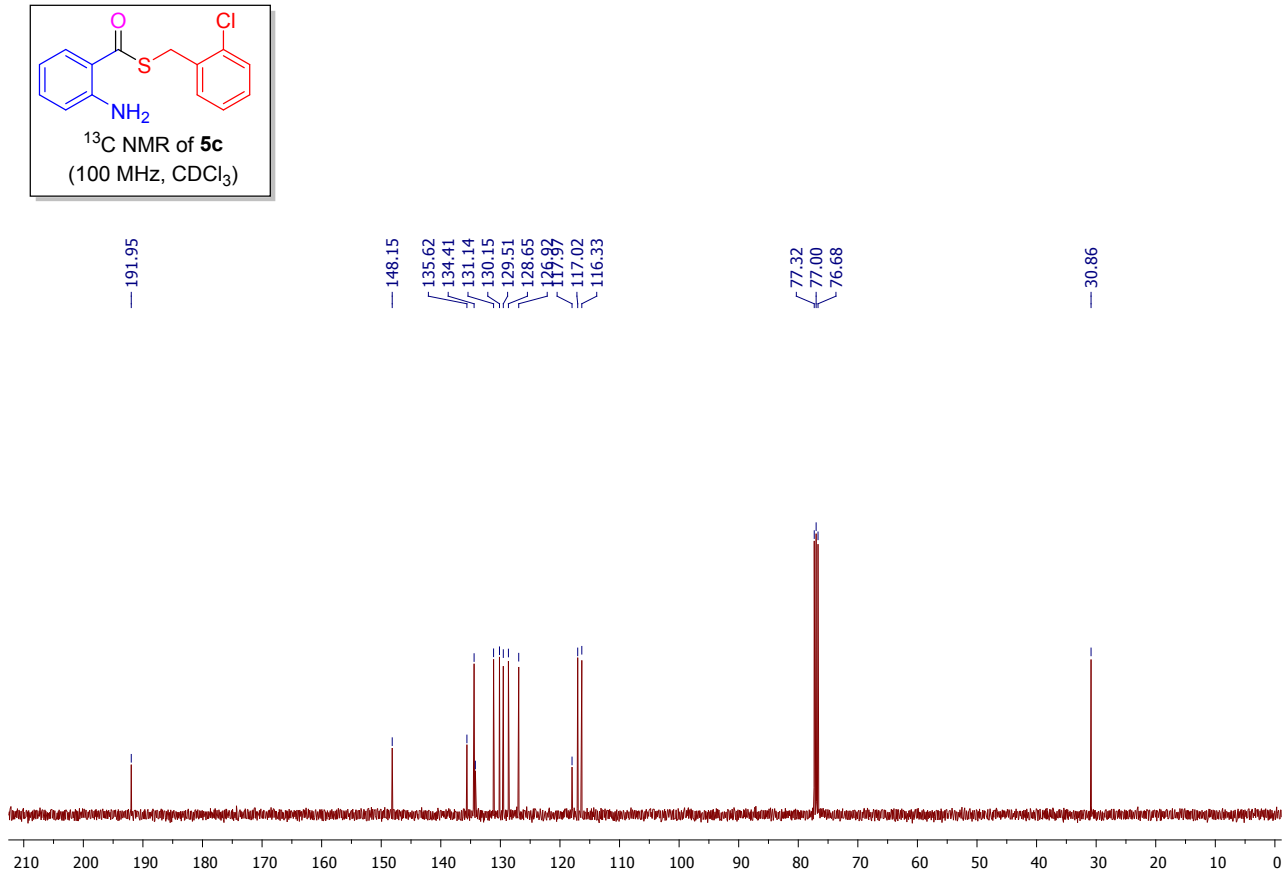


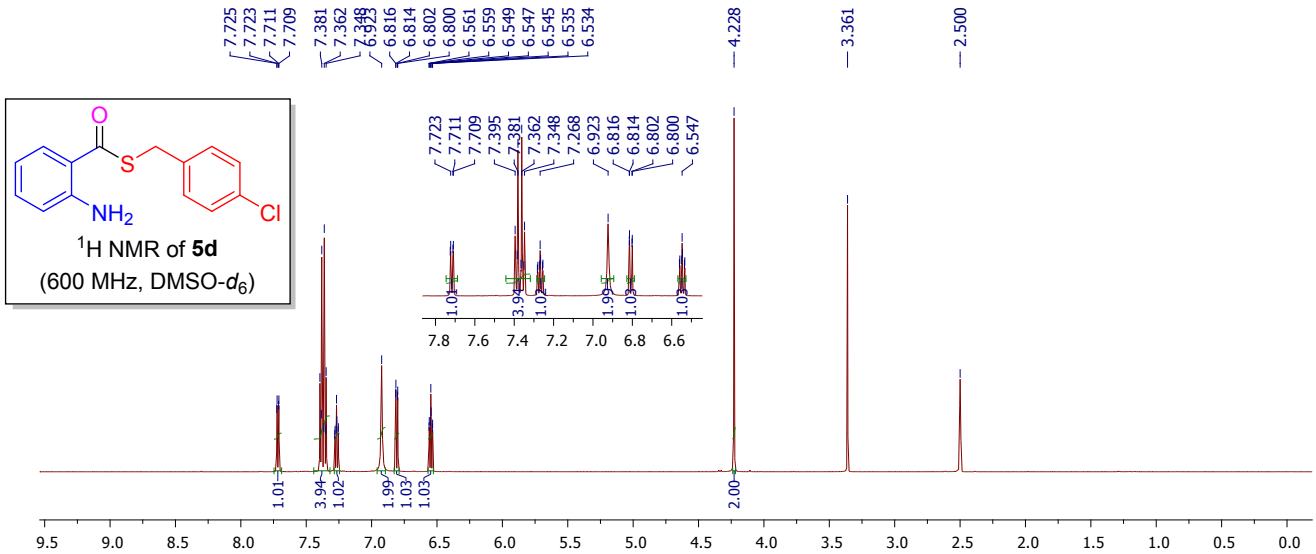
^{1}H NMR of **5b**
(300 MHz, $CDCl_3$)

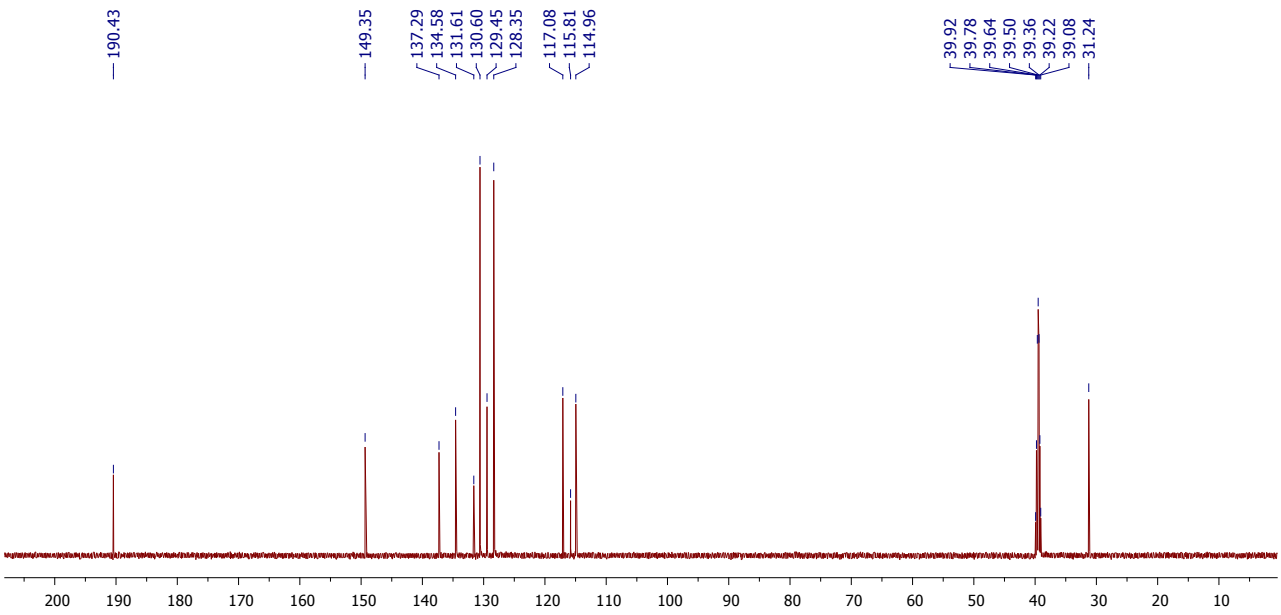


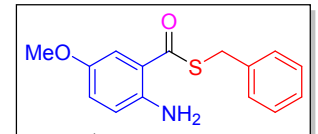
^{13}C NMR of **5b**
(75 MHz, $CDCl_3$)


7.913
7.909
7.899
7.892
7.888
7.284
7.244
7.242
7.232
7.221
6.683
6.679
6.676
6.665
6.658
4.411
O
Cl
S
NH2
1H NMR of 5c
(400 MHz, CDCl3)
1.00
1.01
1.00
1.17
1.89
2.09
1.85
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

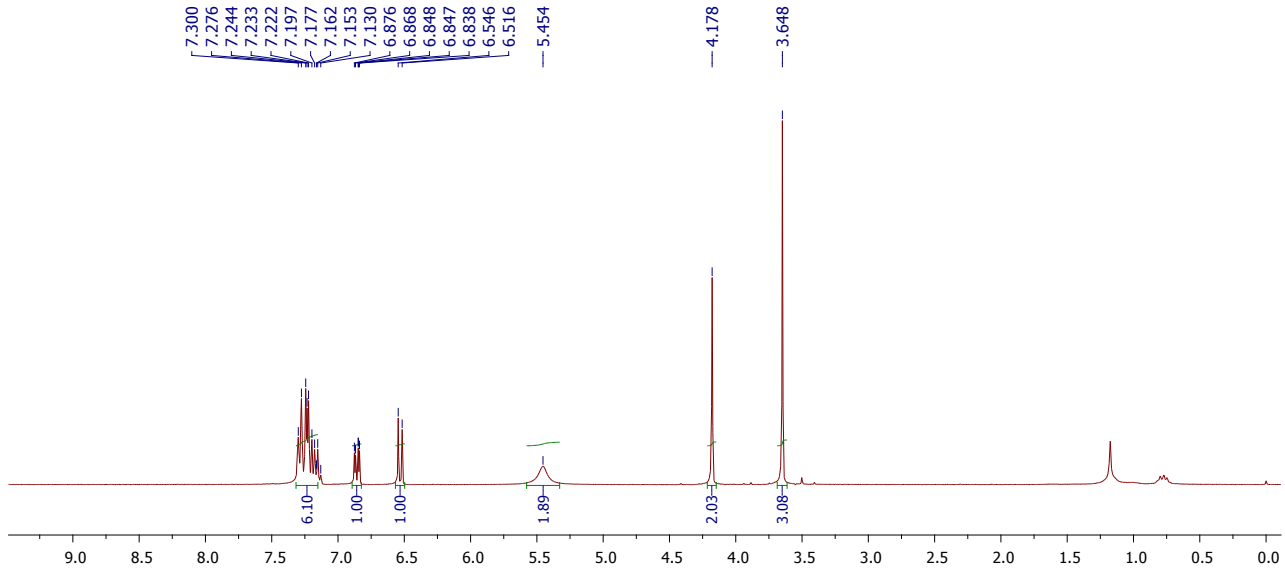

O
Cl
S
NH2
13C NMR of 5c
(100 MHz, CDCl3)
191.95
148.15
135.62
134.41
131.14
130.15
129.51
128.65
117.02
116.33
77.32
77.00
76.68
30.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

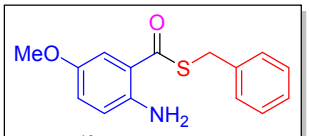

^{1}H NMR of **5d**
(600 MHz, DMSO-d_6)


^{13}C NMR of **5d**
(150 MHz, DMSO-d_6)

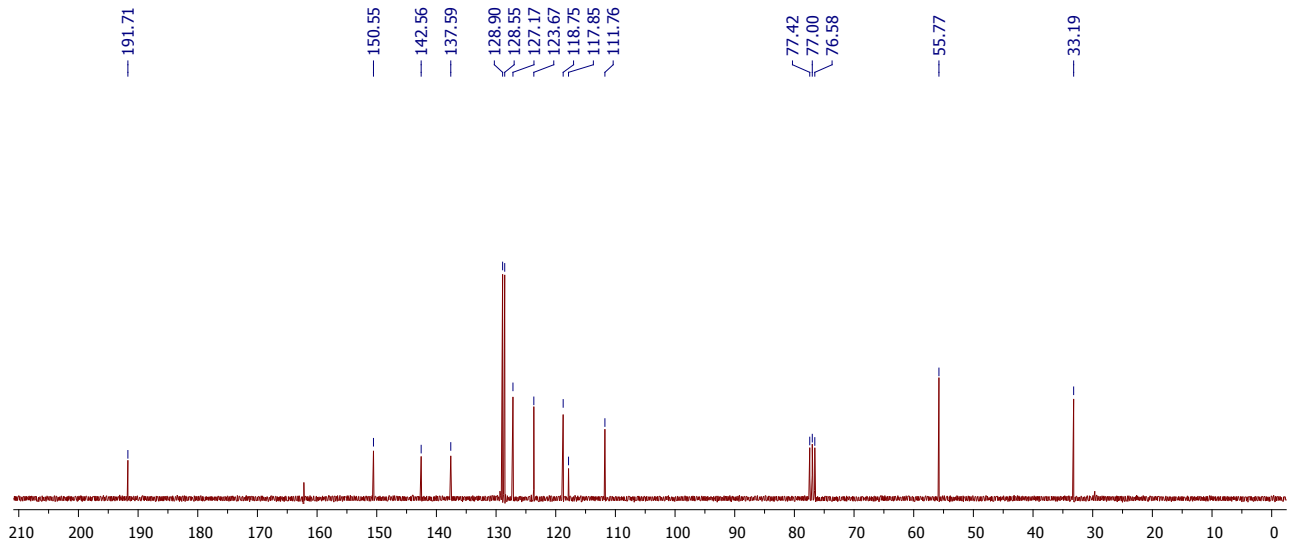


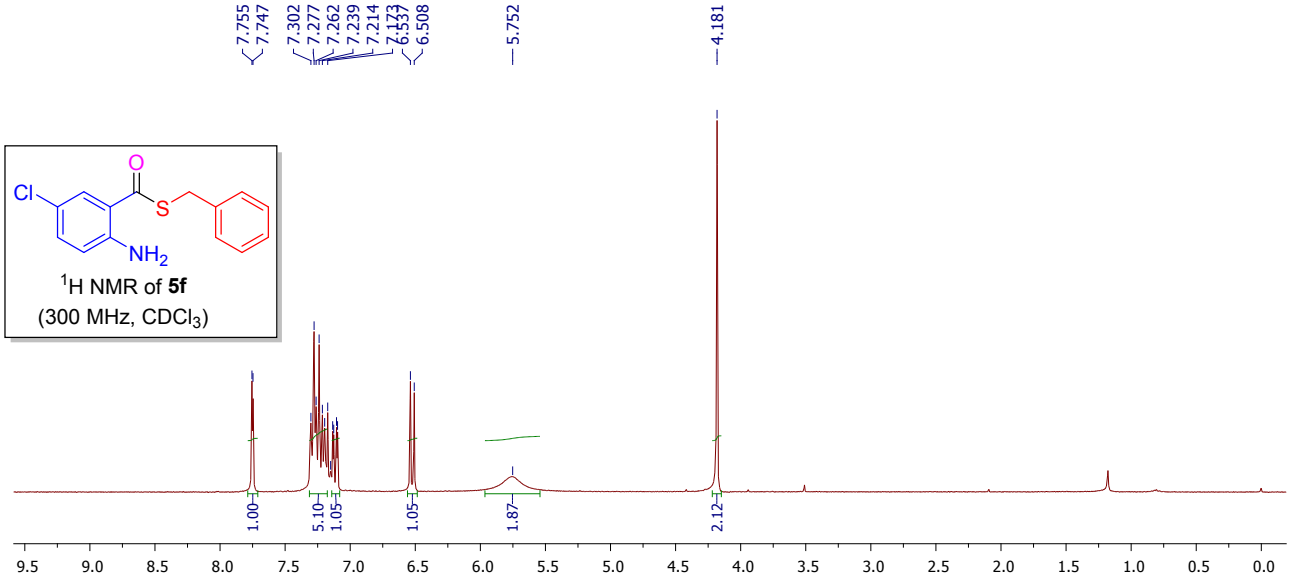
^{1}H NMR of **5e**
(300 MHz, $CDCl_3$)

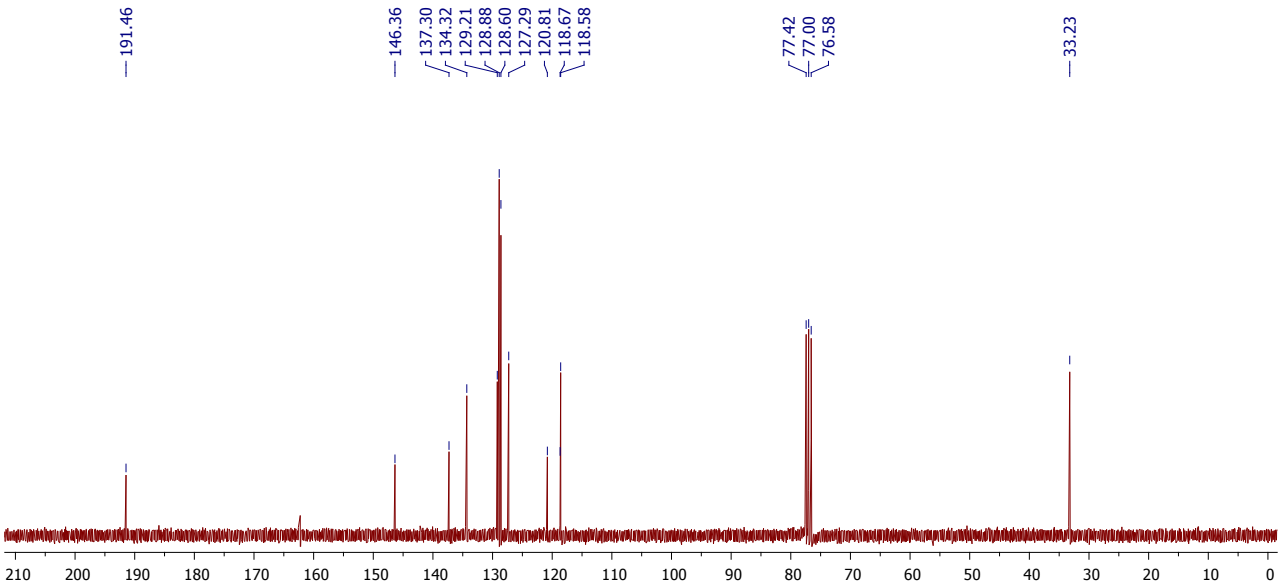


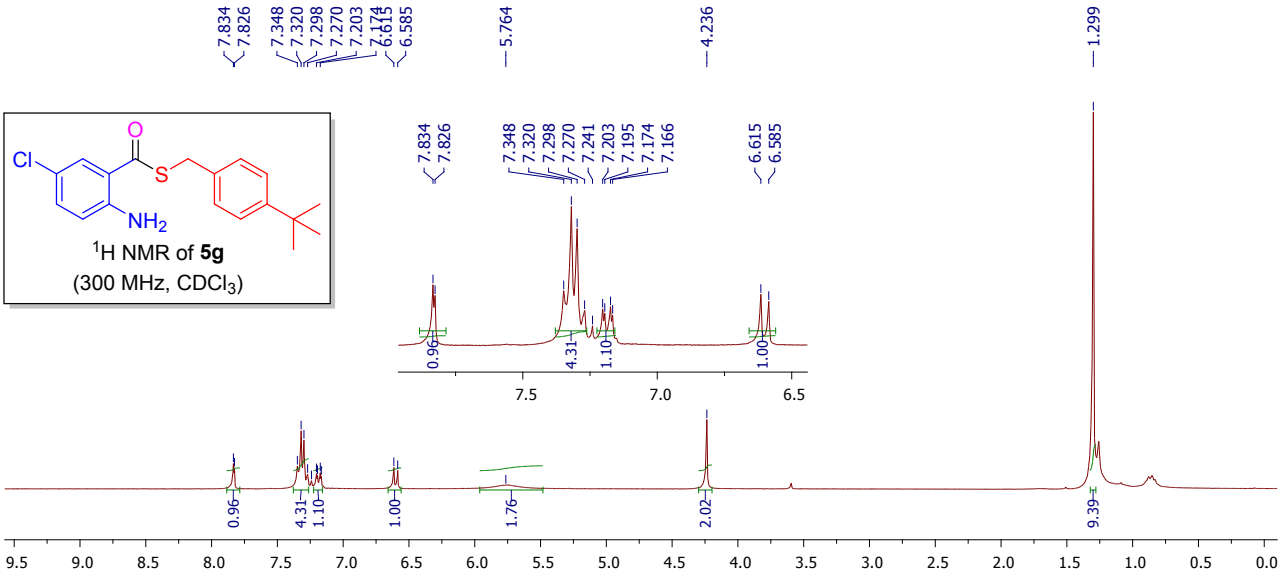


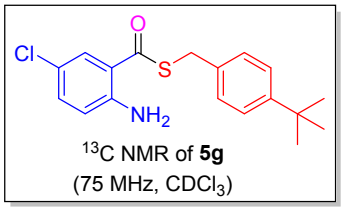
^{13}C NMR of **5e**
(75 MHz, $CDCl_3$)




7.755
7.747
7.302
7.277
7.262
7.239
7.214
7.173
6.537
6.508
5.752
4.181
Cl
O
S
NH2
1H NMR of 5f
(300 MHz, CDCl3)
1.00
5.10
1.05
1.05
1.87
2.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

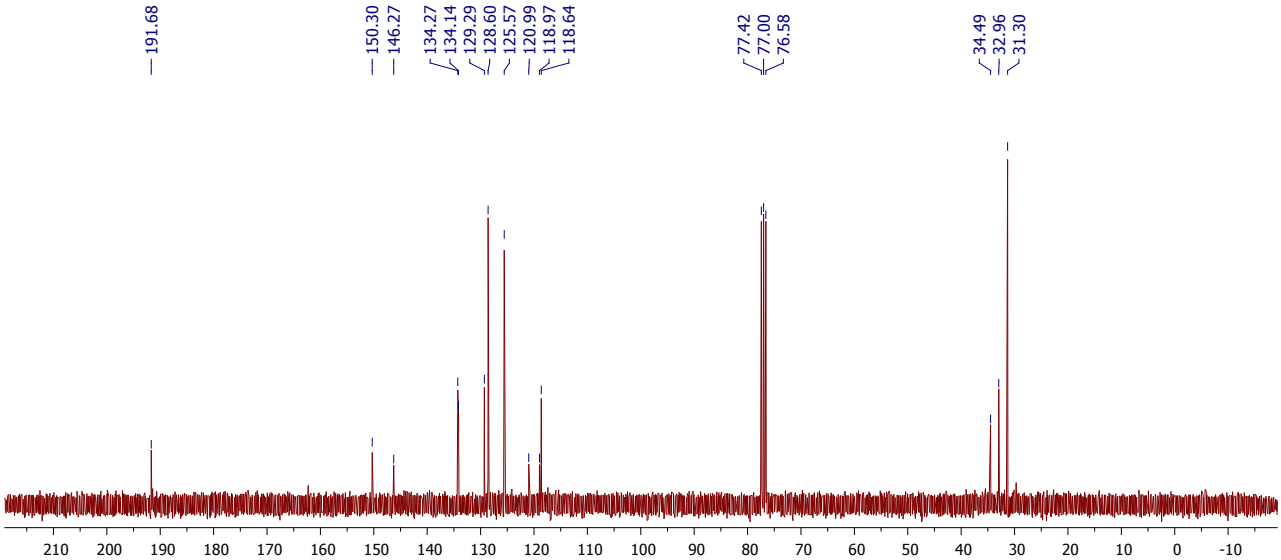

Cl
O
S
NH2
13C NMR of 5f
(75 MHz, CDCl3)
191.46
146.36
137.30
134.32
129.21
128.88
128.60
127.29
120.81
118.67
118.58
77.42
77.00
76.58
33.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

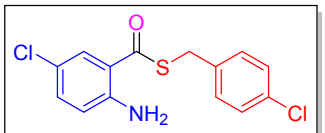




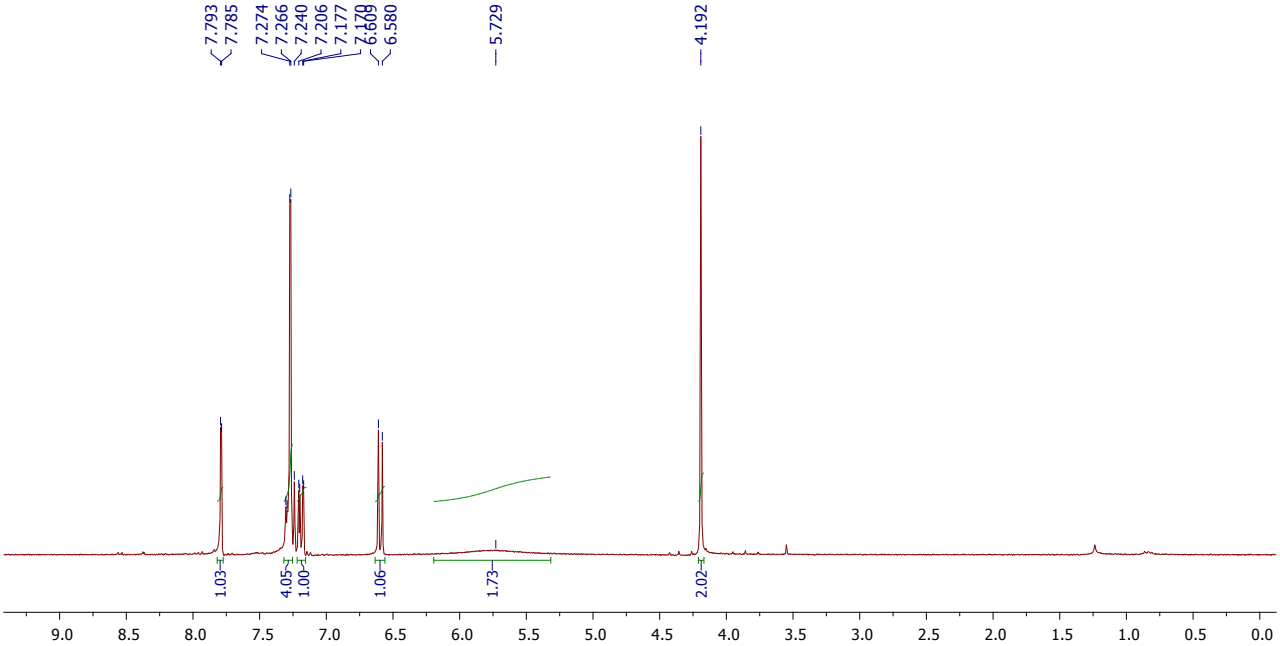
^{1}H NMR of **5g**
(300 MHz, $CDCl_3$)

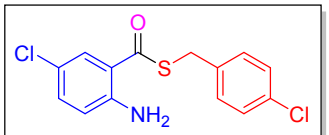
^{13}C NMR of **5g**
(75 MHz, $CDCl_3$)



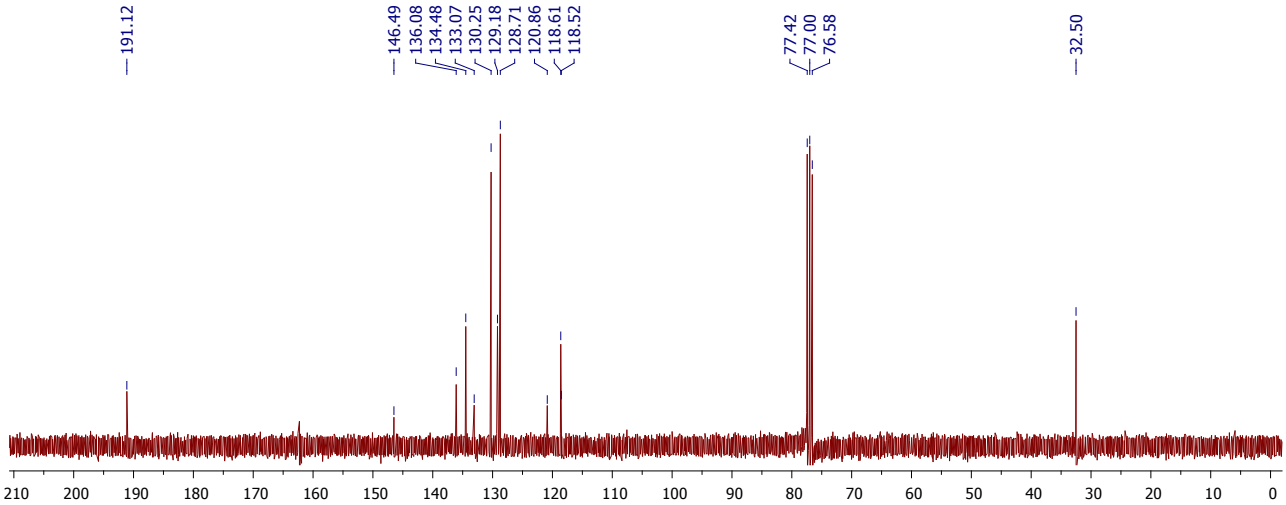


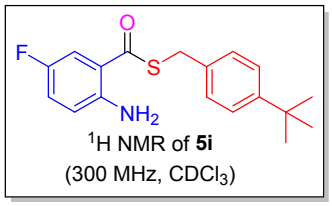
^{1}H NMR of **5h**
(300 MHz, $CDCl_3$)



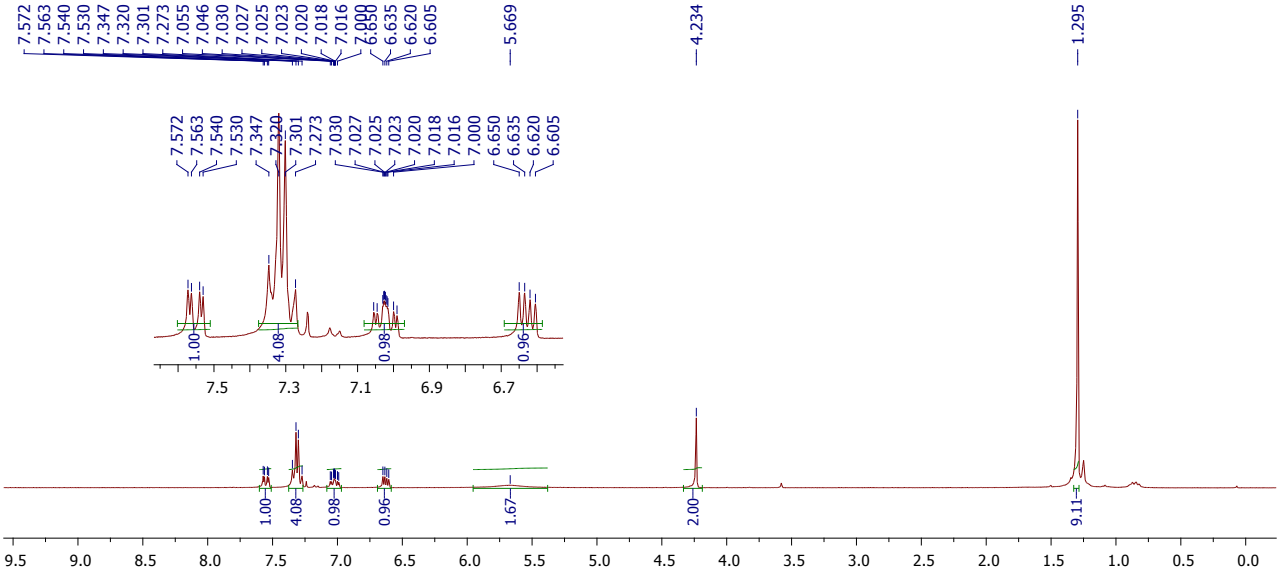


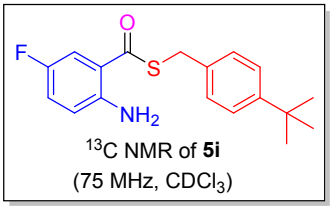
^{13}C NMR of **5h**
(75 MHz, $CDCl_3$)



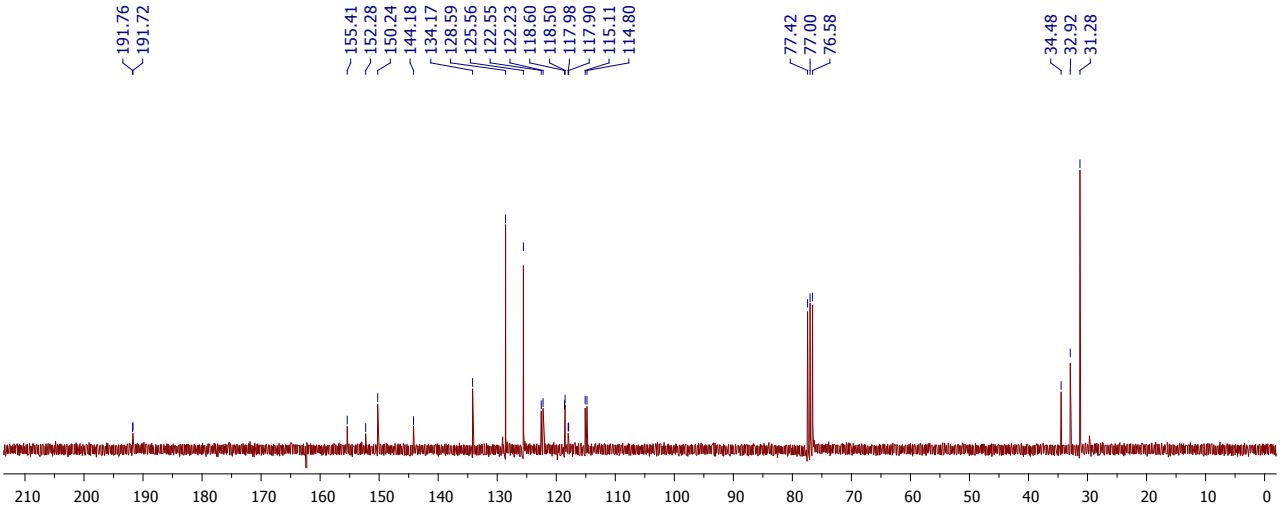


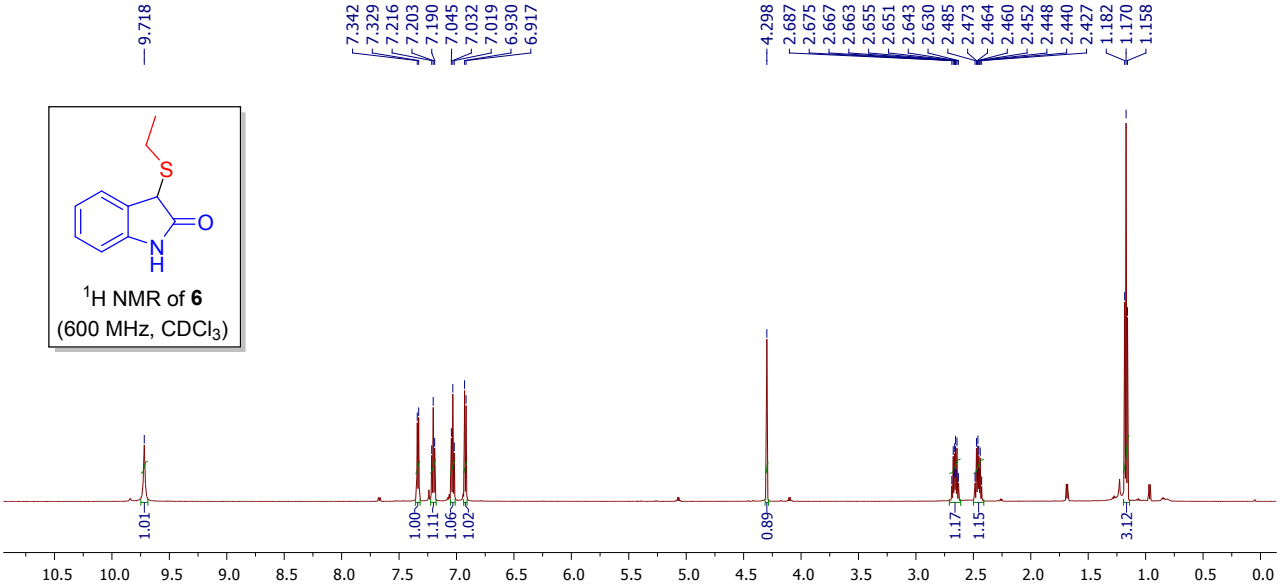
^{1}H NMR of **5i**
(300 MHz, $CDCl_3$)



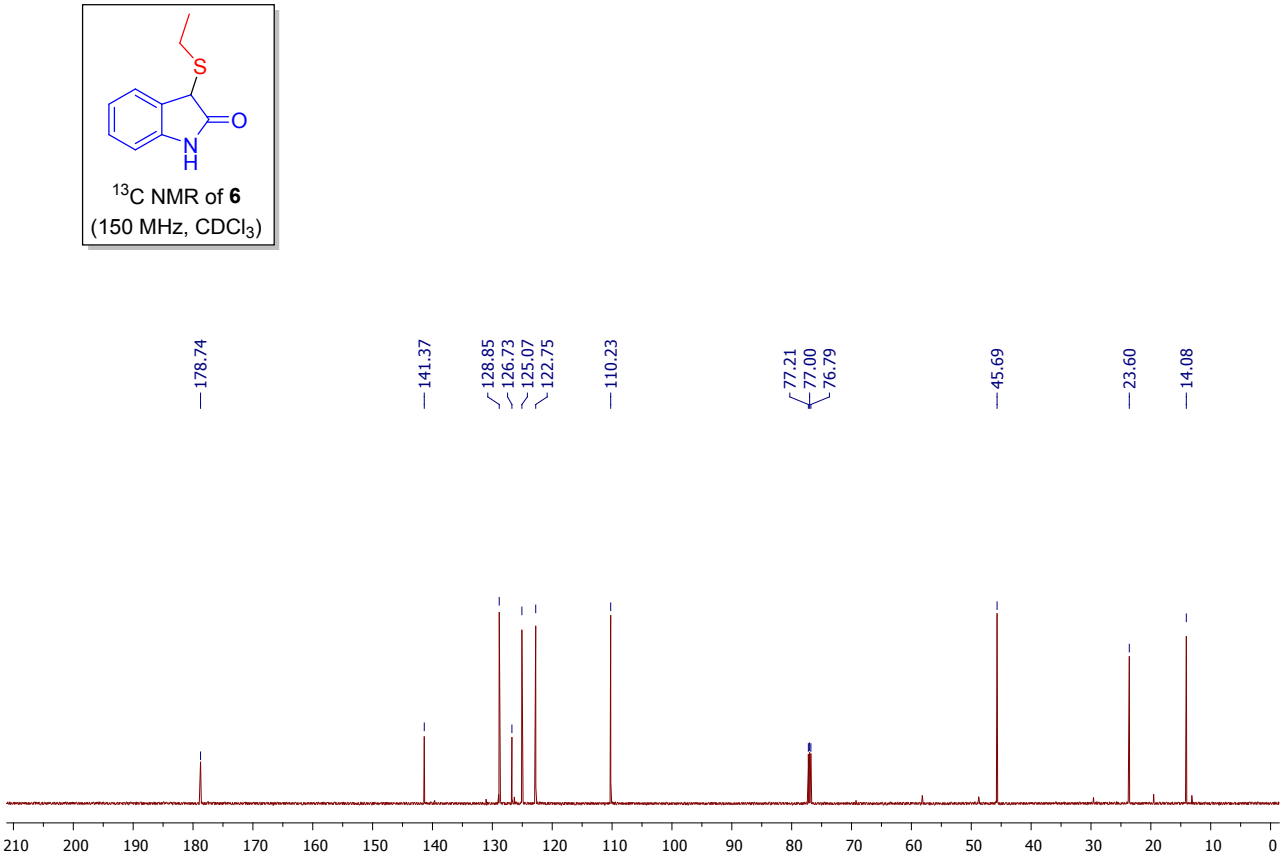


^{13}C NMR of **5i**
(75 MHz, $CDCl_3$)

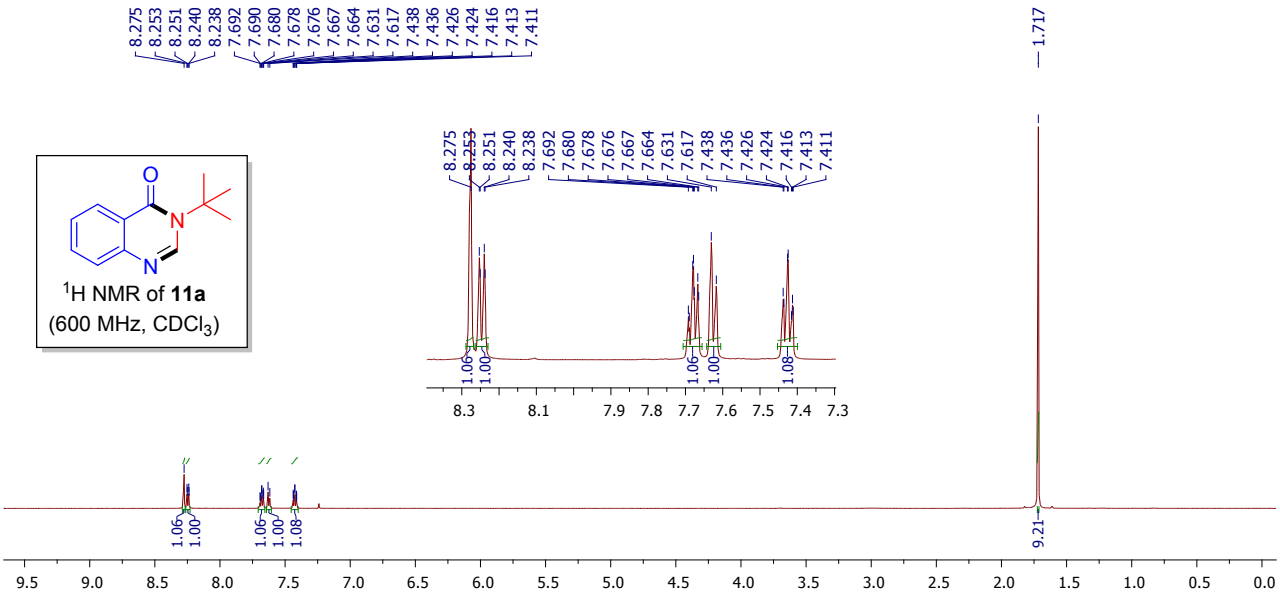




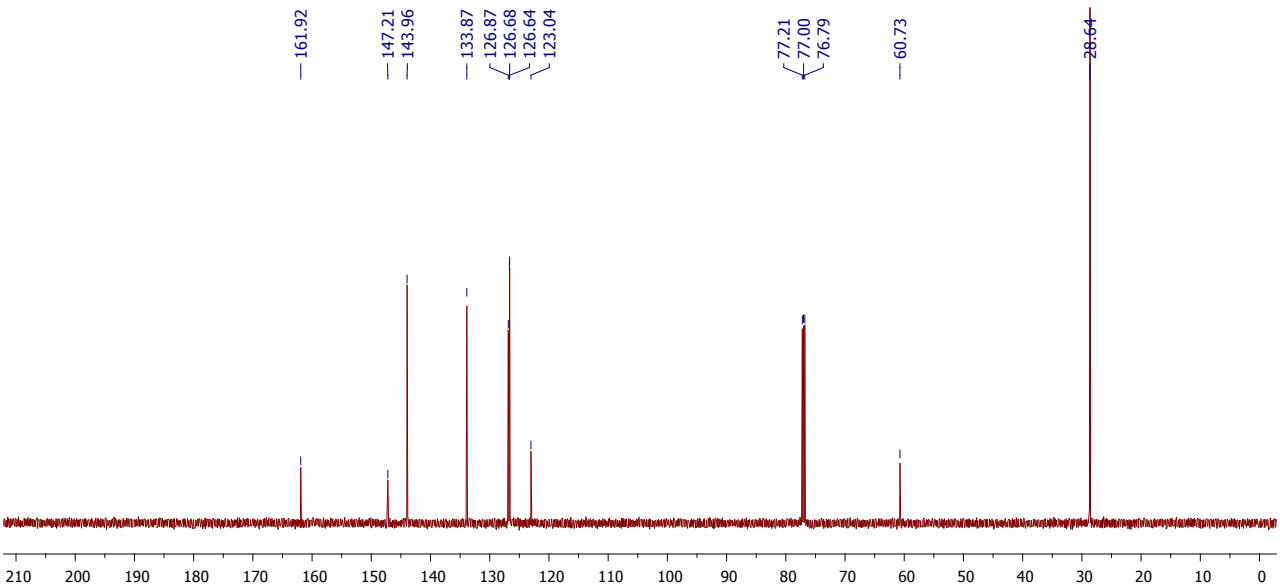
^{1}H NMR of **6**
(600 MHz, $CDCl_3$)



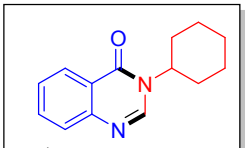
^{13}C NMR of **6**
(150 MHz, $CDCl_3$)



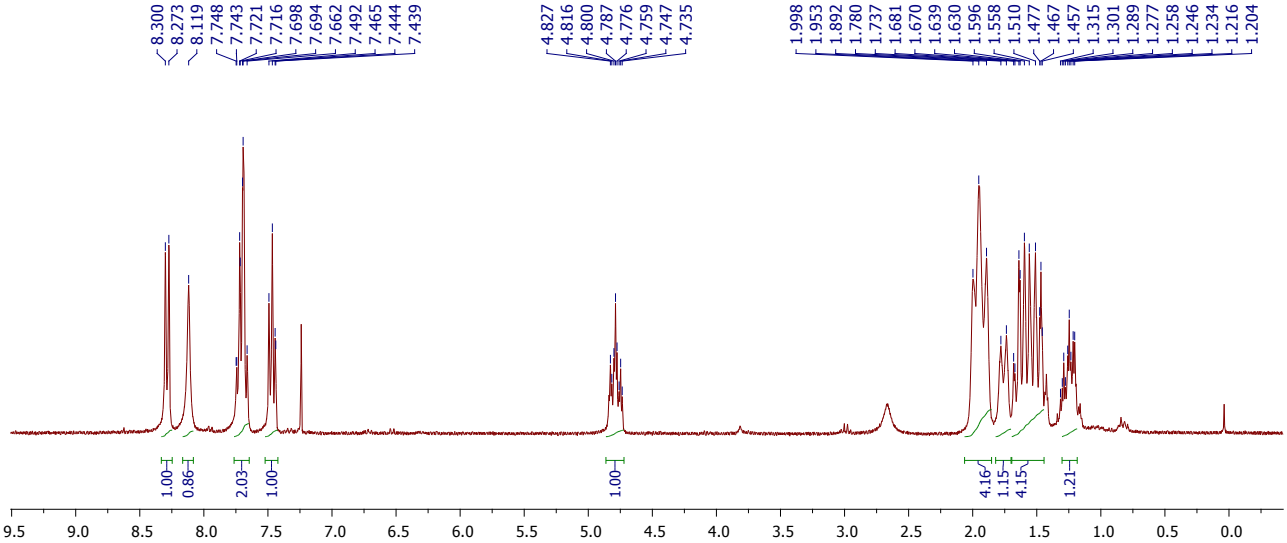
^{1}H NMR of **11a**
(600 MHz, $CDCl_3$)

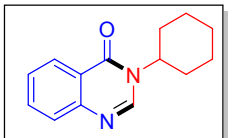


^{13}C NMR of **11a**
(150 MHz, $CDCl_3$)

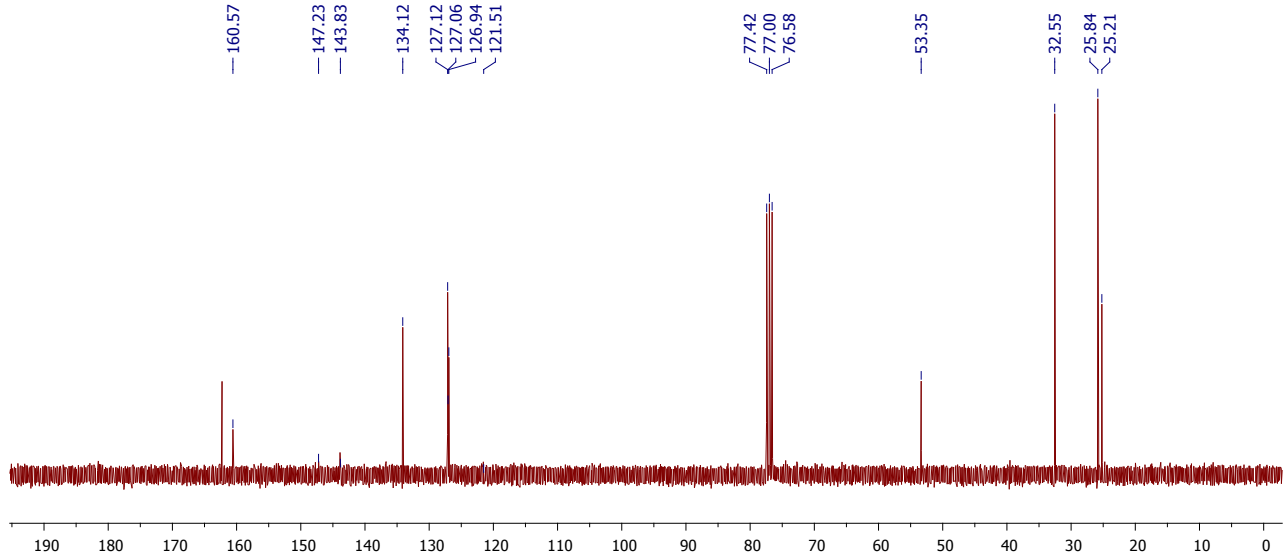


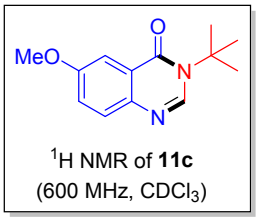
^{1}H NMR of **11b**
(300 MHz, $CDCl_3$)



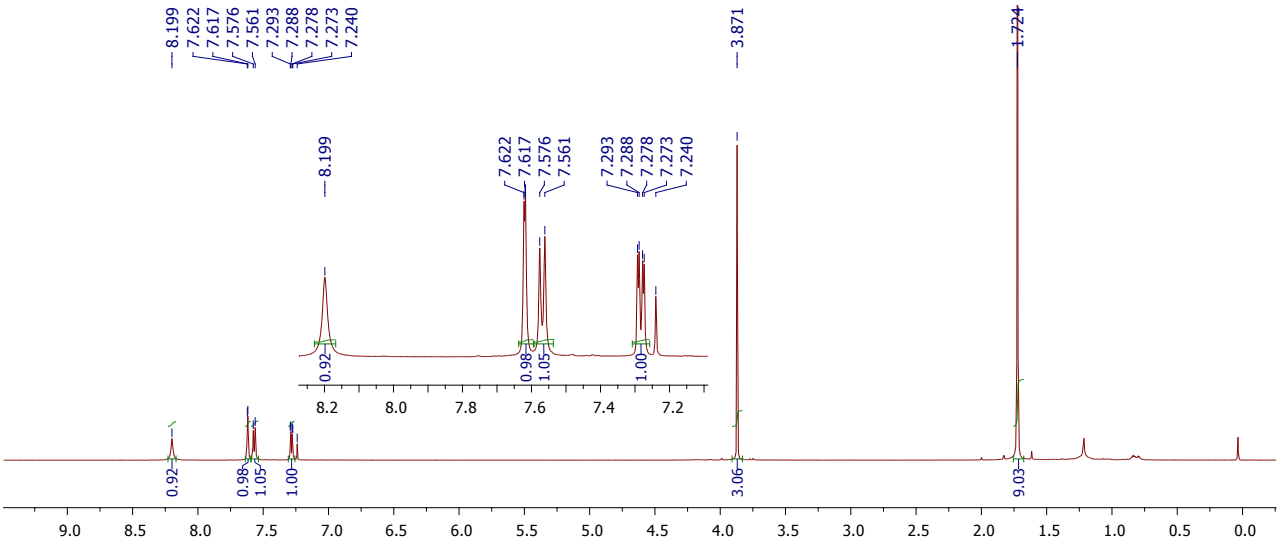


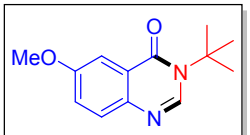
^{13}C NMR of **11b**
(150 MHz, $CDCl_3$)



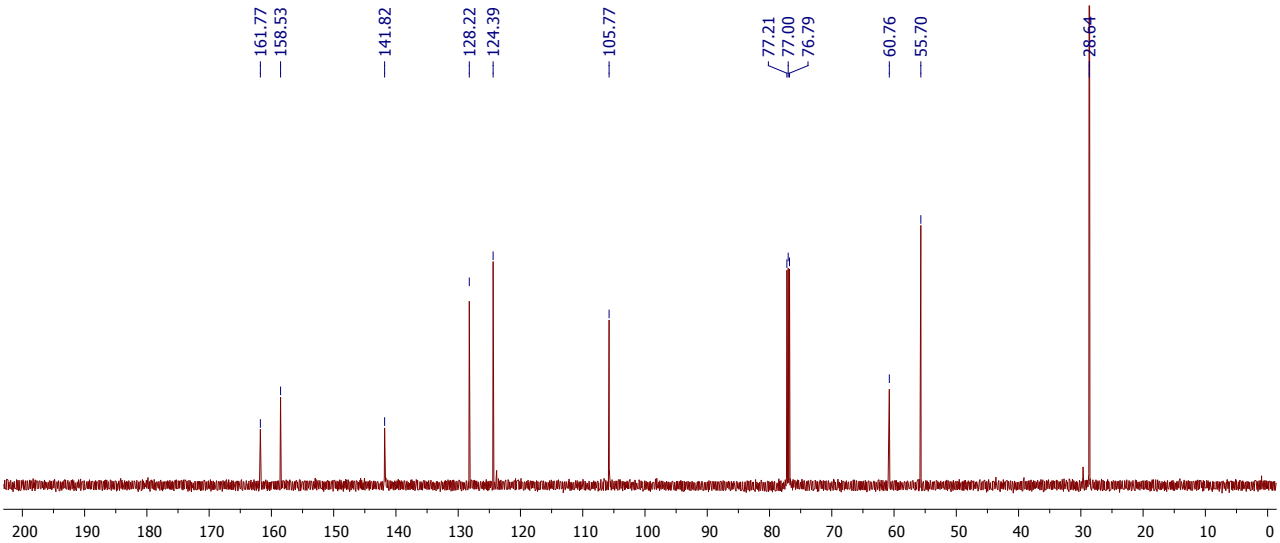


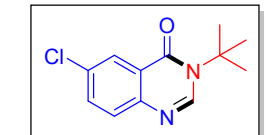
^{1}H NMR of **11c**
(600 MHz, $CDCl_3$)



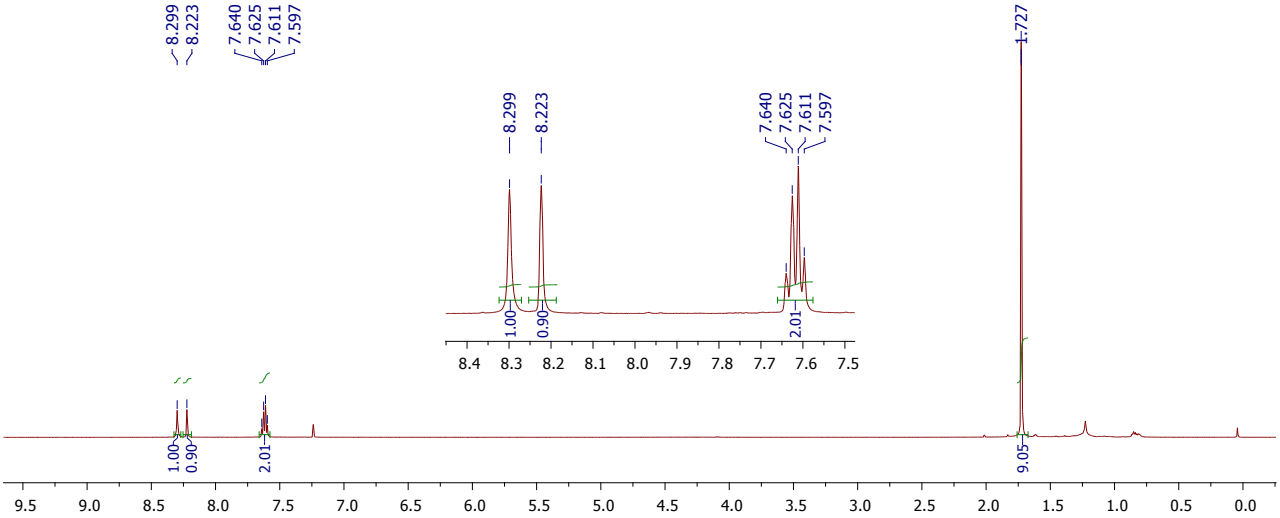


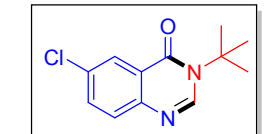
^{13}C NMR of **11c**
(150 MHz, $CDCl_3$)



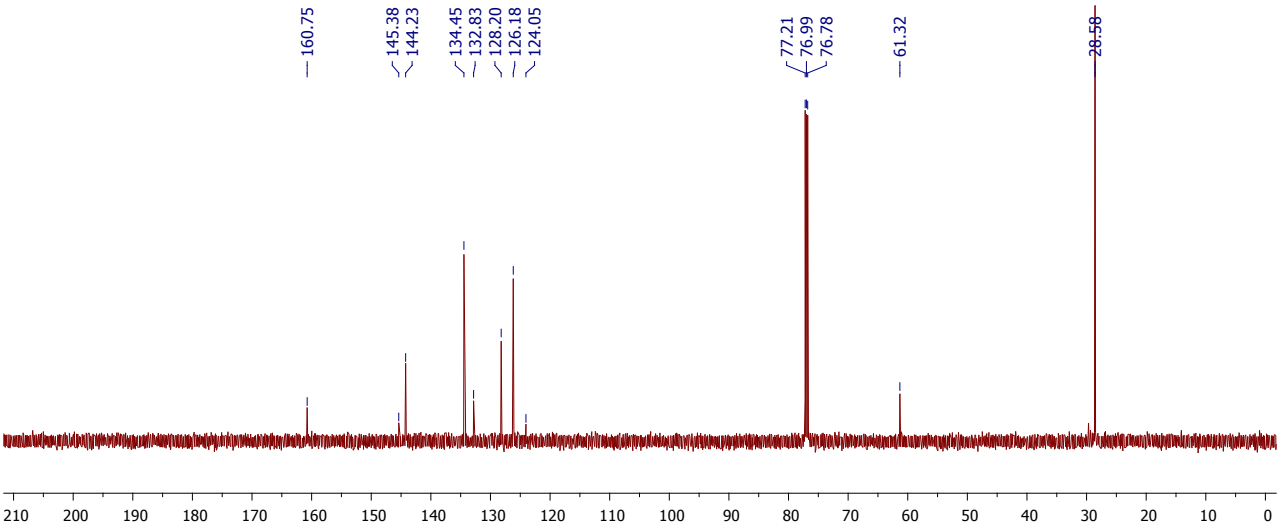


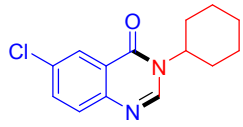
^{1}H NMR of **11d**
(600 MHz, $CDCl_3$)



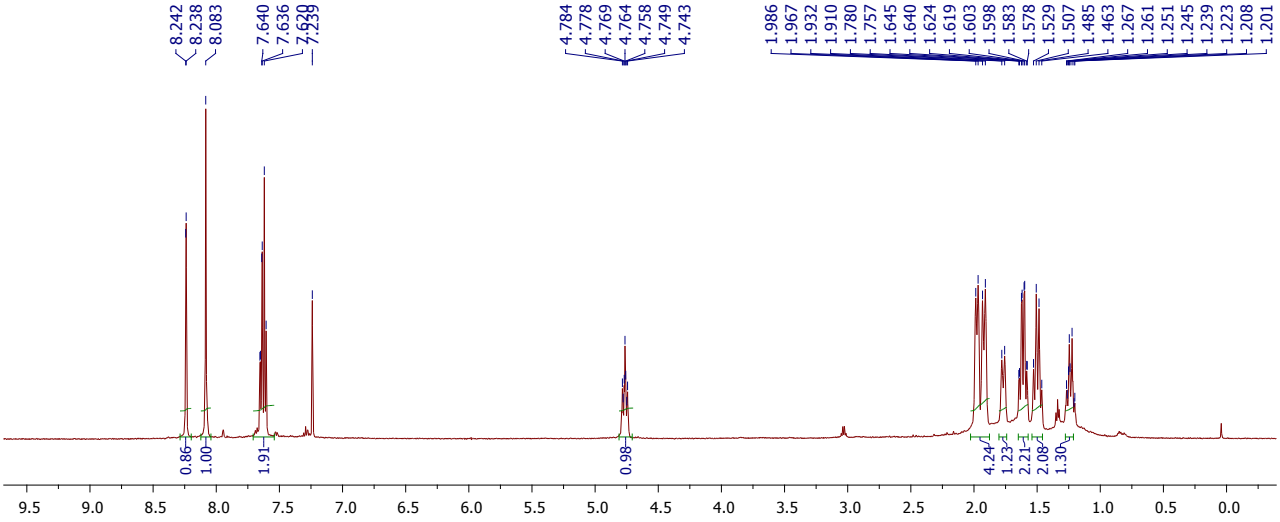


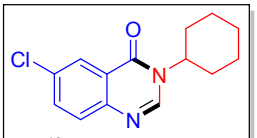
^{13}C NMR of **11d**
(150 MHz, $CDCl_3$)



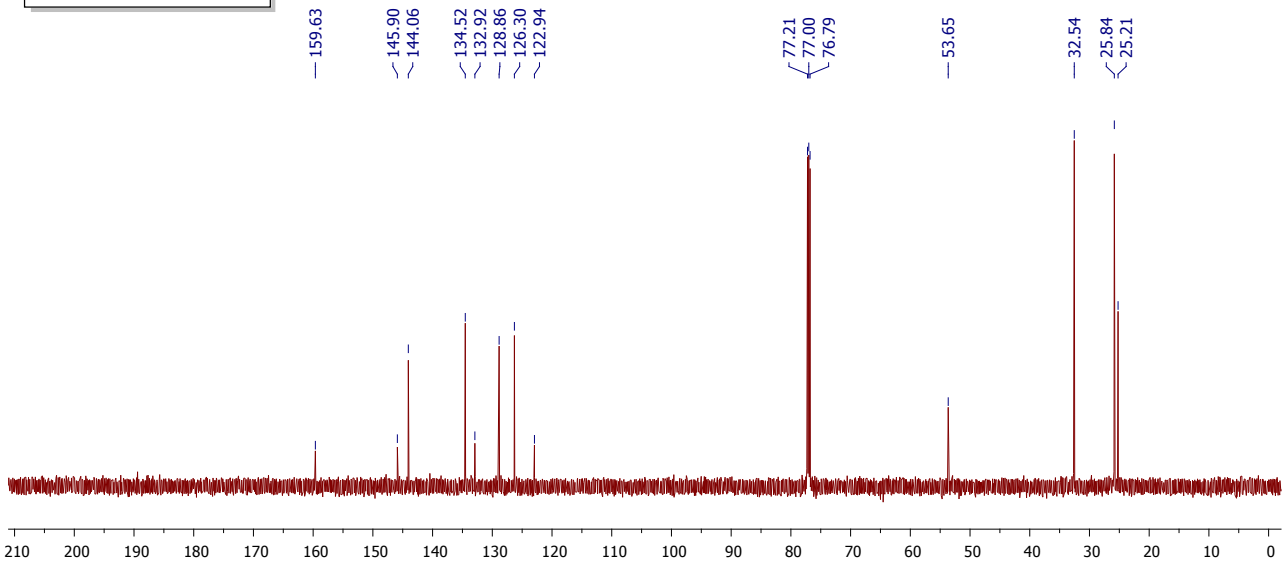


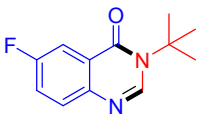
^{1}H NMR of **11e**
(600 MHz, $CDCl_3$)



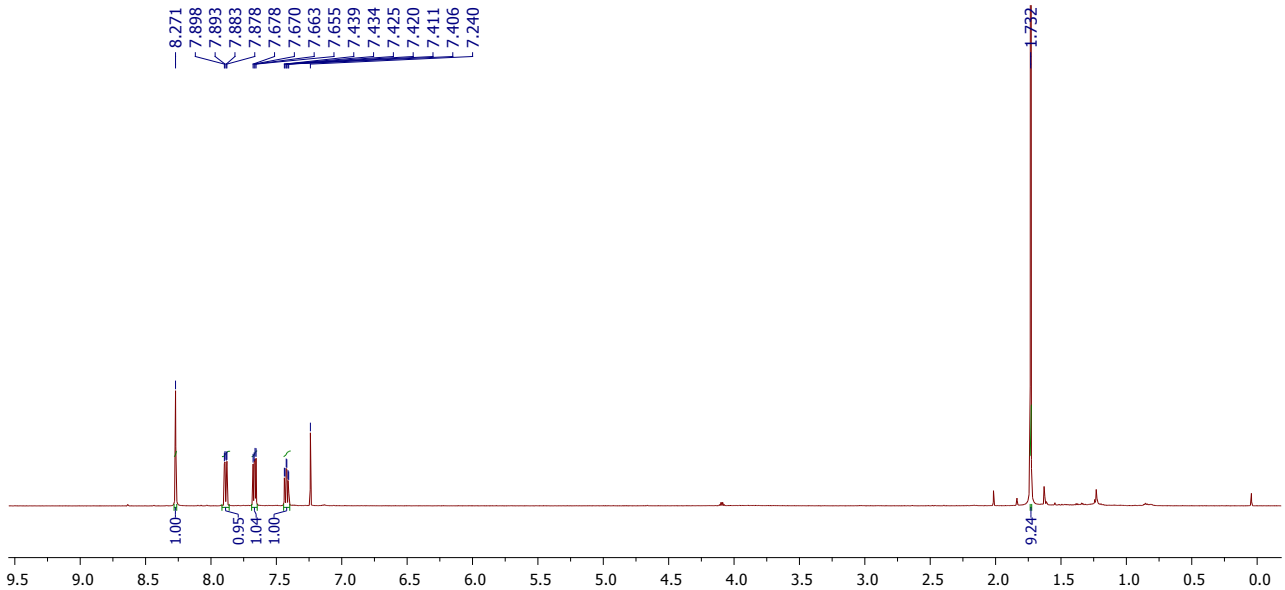


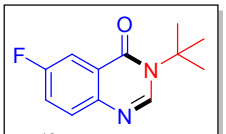
^{13}C NMR of **11e**
(150 MHz, $CDCl_3$)



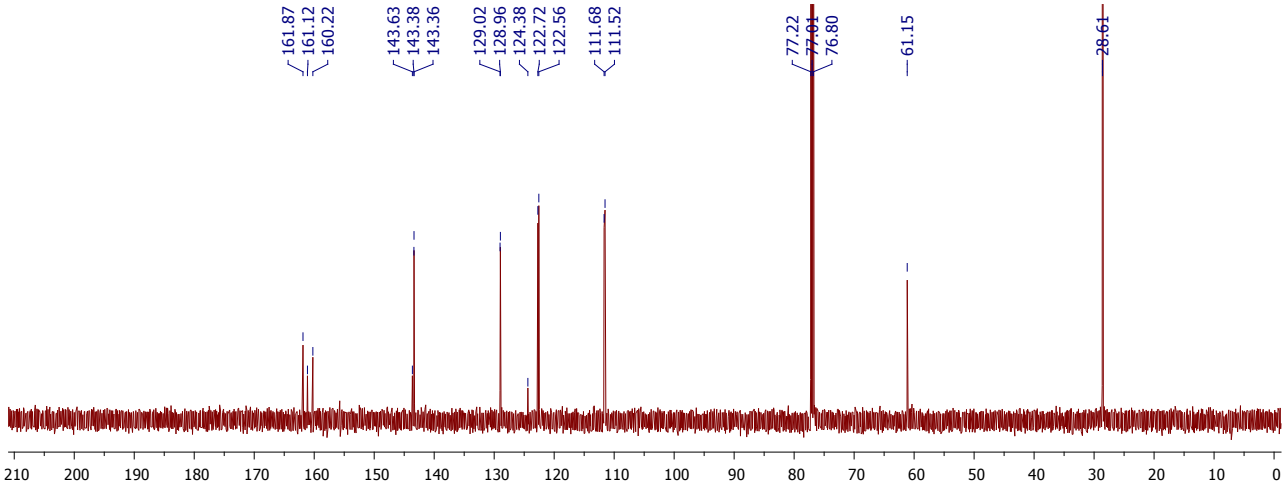


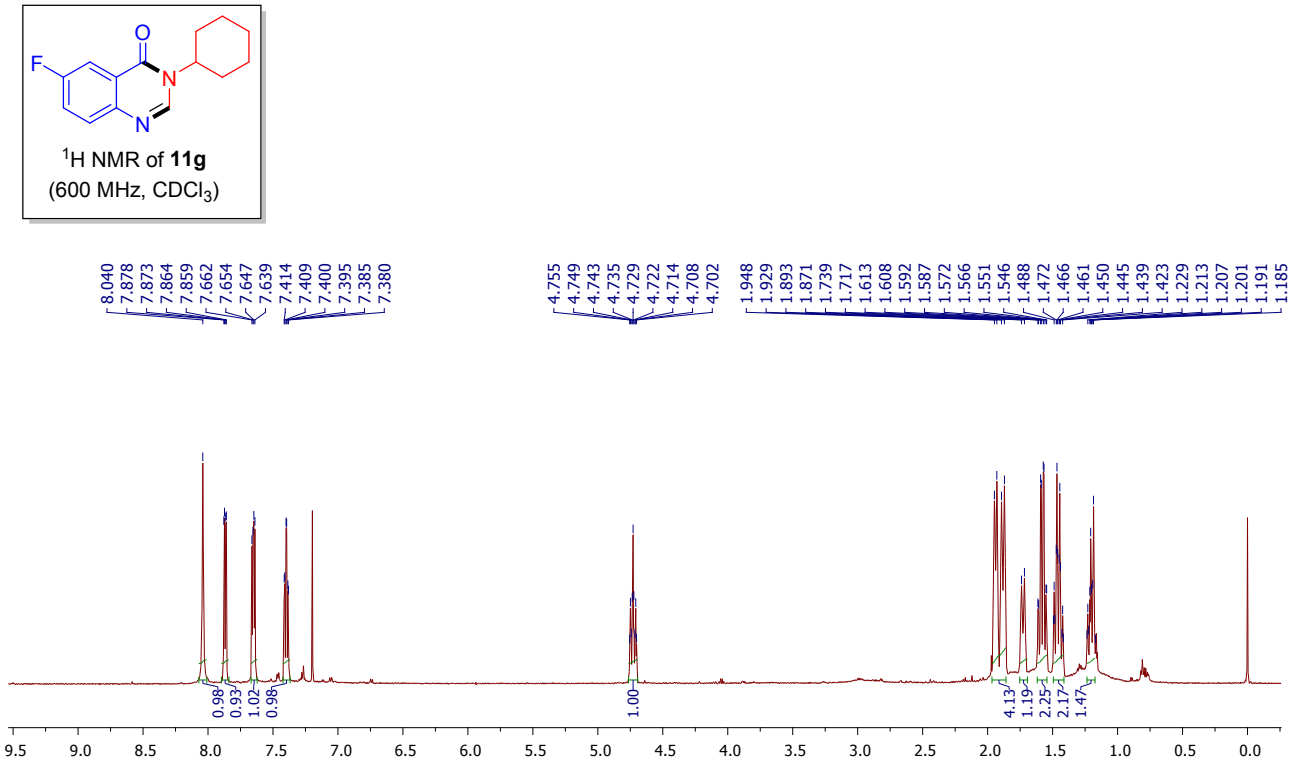
^{1}H NMR of **11f**
(600 MHz, $CDCl_3$)

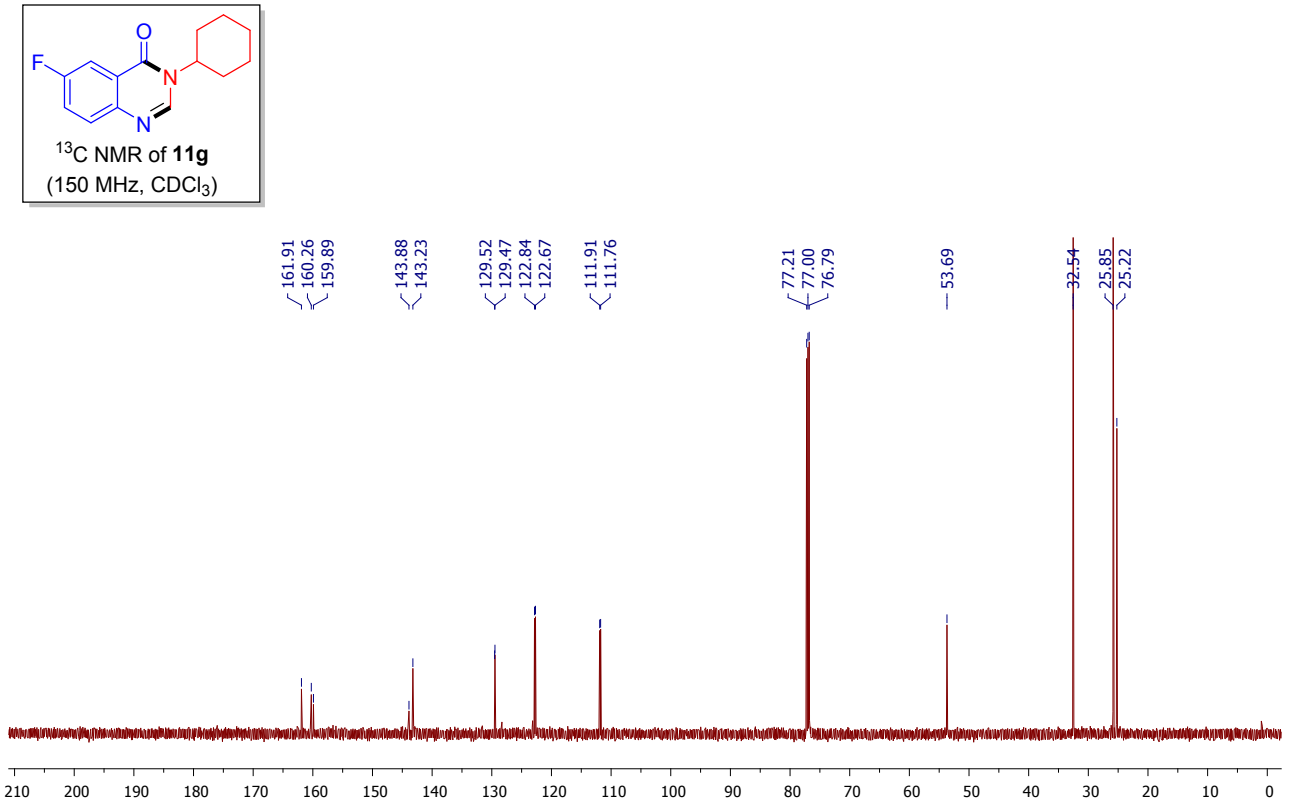




^{13}C NMR of **11f**
(150 MHz, $CDCl_3$)




F
O
N
N
^{1}H NMR of **11g**
(600 MHz, $CDCl_3$)
8.040 7.878 7.873 7.864 7.859 7.662 7.654 7.647 7.639 7.414 7.409 7.400 7.395 7.385 7.380
4.755 4.749 4.743 4.735 4.729 4.722 4.714 4.708 4.702
1.948 1.929 1.893 1.871 1.739 1.717 1.613 1.608 1.592 1.587 1.572 1.566 1.551 1.546 1.488 1.472 1.466 1.461 1.450 1.445 1.439 1.423 1.229 1.213 1.207 1.201 1.191 1.185
0.98 0.93 1.02 0.98 1.00 4.13 1.19 2.25 2.17 1.47
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


F
O
N
N
^{13}C NMR of **11g**
(150 MHz, $CDCl_3$)
161.91 160.26 159.89 143.88 143.23 129.52 129.47 122.84 122.67 111.91 111.76 77.21 77.00 76.79 53.69 32.54 25.85 25.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Experimental section for fluorescence sensing

Fluorescence sensing of Fe^{3+} ions

The fluorescent spectra of nine of the synthesized compounds (0.001 M) were measured in acetonitrile at room temperature, upon excitation wavelength at 360 nm. Then, 0.50 mL of compound **3n** (0.001 M) in acetonitrile was taken in a 4 mL quartz cuvette as a fluorescent probe and was titrated with 50 μM of various metal ions in acetonitrile for selectivity studies. Further, the fluorescent sensitivity of compound **3n** (0.001 M) was studied towards different concentrations of Fe^{3+} in acetonitrile. All the fluorescent (Hitachi-7000 F) measurements were carried out at room temperature at 360 nm (excitation wavelength).