Electronic Supplementary Information

Cp*Co(III)-Catalyzed *ortho*-Amidation of Azobenzenes with Dioxazolones

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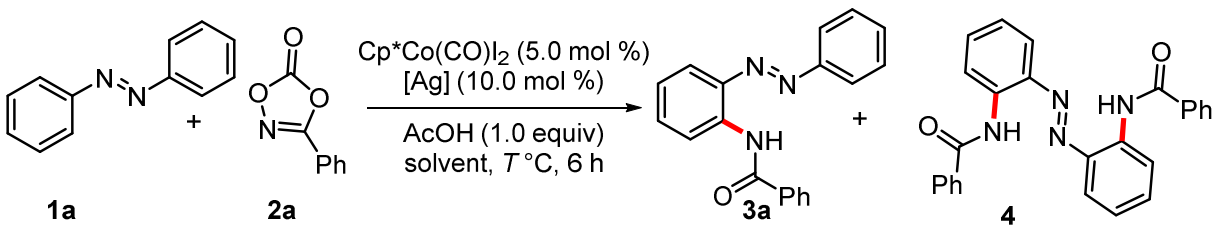
1. General remark

All reactions were carried out in an oven dried pressure tube. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Column chromatography was performed through silica gel (100–200 mesh) using a proper solvent system. ^{1}H NMR and ^{13}C NMR were recorded on a bruker 500 MHz spectrometer using $CDCl_3$ as solvent. NMR data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). Chemical shift for ^{1}H NMR spectra were reported with respect to the residual signal of TMS at 0.0 ppm present in $CDCl_3$. Chemical shifts for ^{13}C NMR spectra were mentioned in ppm with respect to the center of a triplet at 77.0 ppm of chloroform-d. High resolution mass spectra (HRMS) were recorded in TOF, ESI (+Ve) method. $Cp^*Co(CO)I_2$[1] and $[Cp^*Co(CH_3CN)_3](AgSbF_6)_2$[2] were prepared according to reported methods. Other solvents and reagents were obtained from commercial sources and used without further purification.

2. Table S1. Optimization of reaction conditions



entry	[Ag] salt	additive	solvent	Temp (*T*)	yield (%)[b]	
					3a	**4**
1	$AgSbF_6$	--	TFE	110	<5	0
2	$AgSbF_6$	AcOH	TFE	110	85 (82)[c]	5
3	$AgSbF_6$	PivOH	TFE	110	80	6
4	$AgSbF_6$	$PhCO_2H$	TFE	110	65	5
5[d]	$AgSbF_6$	AcOH	TFE	110	60	trace
6	AgOAc	AcOH	TFE	110	<10	0

7	$AgBF_4$	AcOH	TFE	110	65	4
8	AgOTf	AcOH	TFE	110	20	0
9	--	AcOH	TFE	110	<5	0
10[e]	$AgSbF_6$	AcOH	TFE	110	<5	0
11[f]	$AgSbF_6$	AcOH	TFE	80	25	0
12	$AgSbF_6$	AcOH	Toluene	110	<5	0
13	$AgSbF_6$	AcOH	EtOH	110	<5	0
14	$AgSbF_6$	AcOH	DCE	110	15	0
15[g]	--	AcOH	TFE	110	70	6
16[c,h]	$AgSbF_6$	AcOH	TFE	110	75	<10
17[c,i]	$AgSbF_6$	AcOH	TFE	110	68	18

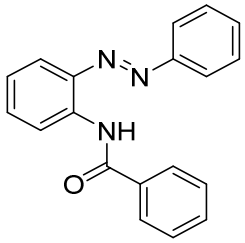
[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), Cp*Co(CO)I_2 (5.0 mol %), Ag-salt (10.0 mol %) and additive (1.0 equiv) in solvent (1 mL) at 110 °C for 6 h. [b]^{1}H NMR yield (CH_2Br_2 as internal standard). [c]Isolated yield in parentheses. [d]0.5 Equiv of AcOH was used. [e]Reaction without Co-catalyst. [f]Reaction at 80 °C. [g][Cp*Co($CH_3CN)_3$]($SbF_6)_2$ was used as catalyst. [h]1.0 equivalent of **2a** was used. [i]1.5 equivalent of **2a** was used.

3. General procedure for Co-catalyzed C–H amidation of azobenzene

To an oven-dried pressure tube azobenzene (**1**, 0.1 mmol), dioxazolone (**2**, 0.11 mmol), [CoCp*(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol) and 2,2,2-TFE (1.0 mL) were added and the reaction mixture was stirred at 110 °C for 6 h. Next the reaction mixture was cooled to room temperature and filtered through a celite pad followed by washing of the celite pad with EtOAc (10 mL x 3). The combined solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the desired monoamidated product.

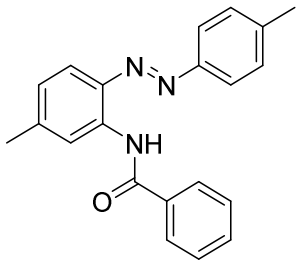
3. Characterization data of all compounds

(E)-N-[2-(Phenyldiazenyl)phenyl]benzamide (3a)



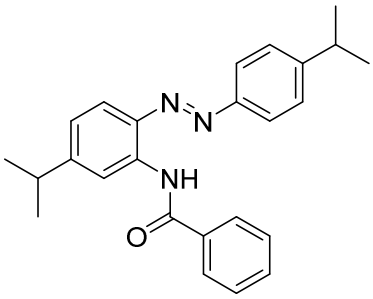
Orange solid (24.7 mg, 82%); mp: 124-129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.25 (m, 1H), 7.47 - 7.55 (m, 6H), 7.57 - 7.6 (m, 1H), 7.86 - 7.88 (m, 2H), 7.94 - 8.0 (m, 3H), 8.9 (dd, J = 8.3, 0.8 Hz, 1H), 11.47 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 122.4, 123.5, 124.7, 127.2, 128.8, 129.3, 131.4, 132.0, 133.0, 135.0, 135.2, 138.8, 152.2, 165.8 ppm. HRMS (ESI+): calcd. for $C_{19}H_{16}N_3O$ $[M+H]^+$: 302.1293, found: 302.1296.

(*E*)-*N*-[5-Methyl-2-(p-tolyldiazenyl)phenyl]benzamide (3b)



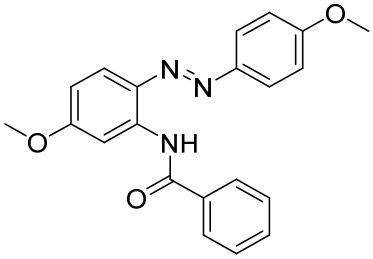
Orange solid (29.0 mg, 88%); mp: 137-139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.48 (s, 3H), 7.05 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.52 - 7.62 (m, 3H), 7.77 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.97 - 8.00 (m, 2H), 8.74 (s, 1H), 11.66 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 22.2, 120.4, 122.2, 124.6, 125.3, 127.3, 128.8, 130.0, 132.0, 134.5, 135.4, 137.1, 141.7, 143.8, 150.3, 166.0 ppm. HRMS (ESI+): calcd. for $C_{21}H_{20}N_3O$ $[M+H]^+$: 330.4110, found: 330.1602.

(*E*)-*N*-(5-Isopropyl-2-((4-isopropylphenyl)diazenyl)phenyl)benzamide (3c)



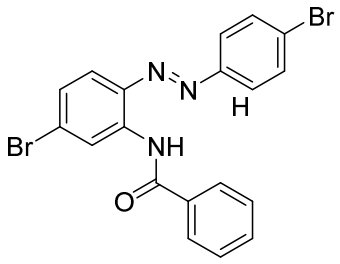
Orange solid (32.8 mg, 85%); mp: 70-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (d, J = 7.0 Hz, 6H), 1.34 (d, J = 6.9 Hz, 6H), 2.95 - 3.07 (m, 2H), 7.12 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 7.5 Hz, 2H), 7.51 - 7.61 (m, 3H), 7.79 - 7.82 (m, 2H), 7.89 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 2H), 8.83 (s, 1H), 11.72 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 23.8, 34.1, 34.7, 118.1, 121.8, 122.3, 125.7, 127.2, 127.3, 128.8, 131.9, 134.7, 135.4, 137.4, 150.6, 152.5, 154.5, 166.0 ppm. HRMS (ESI+): calcd. for $C_{25}H_{28}N_3O$ $[M+H]^+$: 386.2232, found: 386.2235.

(*E*)-*N*-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)benzamide (3d)



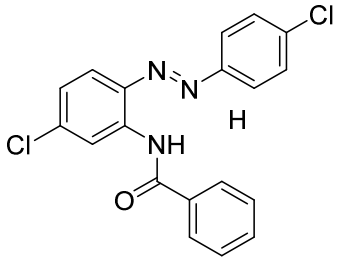
Orange solid (30.0 mg, 83%); mp: 127-129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.93 (s, 3H), 6.76 (dd, J = 8.9, 2.7 Hz, 1H), 6.99 (d, J = 9.0 Hz, 2H), 7.51 - 7.62 (m, 3H), 7.79 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 7.5 Hz, 2H), 8.54 (d, J=2.6 Hz, 1H), 12.02 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 55.7, 103.5, 110.8, 114.4, 123.6, 127.3, 128.0, 128.8, 132.0, 133.5, 135.3, 136.0, 146.5, 161.6, 162.7, 166.2 ppm. HRMS (ESI+): calcd. for $C_{21}H_{20}N_3O_3$ $[M+H]^+$: 362.1505, found: 362.1507.

(*E*)-*N*-(5-Bromo-2-((4-bromophenyl)diazenyl)phenyl)benzamide (3e)



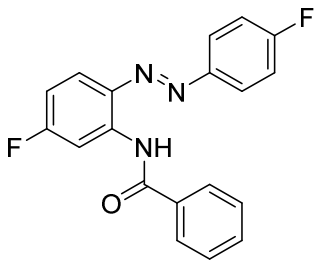
Orange solid (33.0 mg, 72%); mp: 204-206 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.6, 2.1 Hz, 1H), 7.53 - 7.58 (m, 2H), 7.60 - 7.65 (m, 1H), 7.66 - 7.70 (m, 2H), 7.73 - 7.76 (m, 2H), 7.81 (d, J = 8.5 Hz, 1H), 7.93 - 7.96 (m, 2H), 9.16 (d, J = 2.0 Hz, 1H), 11.39 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.2, 123.8, 124.4, 125.9, 126.2, 126.9, 127.2, 128.1, 129.0, 132.4, 132.7, 134.8, 135.8, 137.6, 150.9, 165.9 ppm. HRMS (ESI+): calcd. for $C_{19}H_{14}Br_2N_3O$ $[M+H]^+$: 457.9504, found: 457.9506.

(*E*)-*N*-(5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)benzamide (3f)



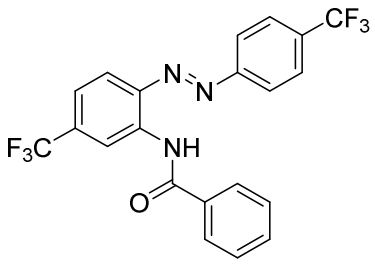
Orange solid (29.0 mg, 78%); mp: 183-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.6, 2.2 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.54 - 7.58 (m, 2H), 7.60 - 7.64 (m, 1H), 7.88 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.5 Hz, 1H), 7.93 - 7.96 (m, 2H), 8.98 (d, J = 2.1 Hz, 1H), 11.42 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 123.6, 123.9, 125.9, 127.2, 129.0, 129.7, 132.4, 134.8, 135.8, 137.2, 137.6, 139.4, 150.4, 165.9 ppm. HRMS (ESI+): calcd. for $C_{19}H_{14}Cl_2N_3O$ $[M+H]^+$: 370.0514, found: 370.0512.

(*E*)-*N*-(5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)benzamide (3g)



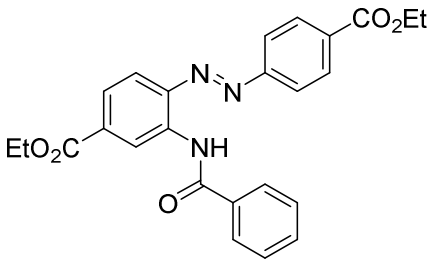
Orange solid (25.4 mg, 75%); mp: 158-161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89–6.98 (m, 1H), 7.18 - 7.25 (m, 2H), 7.53 - 7.59 (m, 2H), 7.59 - 7.65 (m, 1H), 7.82 - 7.89 (m, 2H), 7.91 - 8.00 (m, 3H), 8.69 (dd, *J* = 11.3, 1.8 Hz, 1H), 11.65 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.3 (d, *J* = 29.1 Hz), 110.8 (d, *J* = 23.6 Hz), 116.4 (d, *J* = 22.7 Hz), 124.2 (d, *J* = 9.1 Hz), 127.2, 127.6 (d, *J* = 10.0 Hz), 128.4, 134.9, 135.5 (d, *J* = 2.7 Hz), 136.4 (d, *J* = 13.6 Hz), 148.5 (d, *J* = 2.7 Hz), 164.4 (d, *J* = 253.0 Hz), 165.1 (d, *J* = 253.0 Hz), 166.0 ppm. HRMS (ESI+): calcd. for $C_{19}H_{14}F_2N_3O$ $[M+H]^+$: 338.1105, found: 338.1107.

(*E*)-*N*-(5-(Trifluoromethyl)-2-((4-(trifluoromethyl)phenyl)diazenyl)phenyl)benzamide (3h)



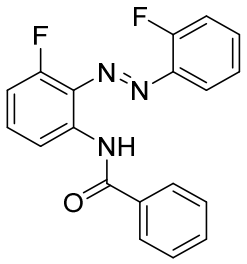
Orange solid (27.6 mg, 63%); mp: 182-185 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 - 7.52 (m, 1H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.61 - 7.67 (m, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.92 - 8.02 (m, 4H), 8.03 - 8.09 (m, 1H), 9.17 - 9.44 (m, 1H), 11.17 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.8 (q, *J* = 3.6 Hz), 120.2 (q, *J* = 3.6 Hz), 122.9, 124.1, 126.7 (q, *J* = 3.6 Hz), 127.1, 129.1, 132.6, 133.3 (q, *J* = 3.6 Hz), 134.6, 134.8 (q, *J* = 3.6 Hz), 135.9, 153.8, 165.9 ppm. HRMS (ESI+): calcd. for $C_{21}H_{14}F_6N_3O$ $[M+H]^+$: 438.1041, found: 438.1040.

Ethyl (*E*)-3-benzamido-4-((4-(ethoxycarbonyl)phenyl)diazenyl)benzoate (3i)



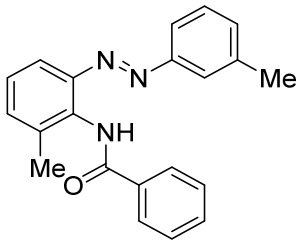
Orange solid (30.8 mg, 69%); mp: 180-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (t, J = 7.2 Hz, 3H), 1.45 (t, J = 7.2 Hz, 3H), 4.43 (q, J = 7.2 Hz, 2H), 4.45 (q, J = 7.2 Hz, 2H), 7.54 - 7.59 (m, 2H), 7.61 - 7.65 (m, 1H), 7.90 - 8.03 (m, 6H), 8.24 (d, J = 8.5 Hz, 2H), 9.53 (d, J = 1.5 Hz, 1H), 11.14 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.31, 14.32, 61.5, 61.6, 121.7, 122.5, 123.3, 124.7, 127.1, 129.0, 130.8, 132.4, 133.1, 134.5, 134.8, 135.5, 141.0, 154.6, 165.69, 165.71 165.73 ppm. HRMS (ESI+): calcd. for $C_{25}H_{24}N_3O_5$ $[M+H]^+$: 446.1716, found: 446.1718.

(*E*)-*N*-(3-fluoro-2-((2-fluorophenyl)diazenyl)phenyl)benzamide (3j)



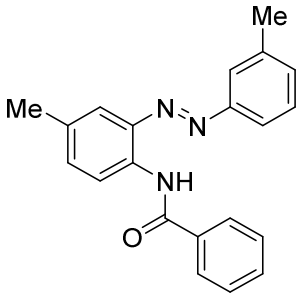
Orange solid (19.6 mg, 58%); mp: 161-164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (dd, J = 9.7, 8.8 Hz, 1H), 7.23 - 7.31 (m, 2H), 7.46 - 7.56 (m, 4H), 7.57 - 7.62 (m, 1H), 7.86 (m, 1H), 8.03 (d, J = 7.2 Hz, 2H), 8.78 (dd, J = 8.6, 0.8 Hz, 1H), 12.61 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.6 (d, J = 20.0 Hz), 116.1 (d, J = 4.5 Hz), 117.0 (d, J = 19.1 Hz), 117.7, 124.8 (d, J = 3.6 Hz), 127.9 (d, J = 3.6 Hz), 128.2 (d, J = 6.3 Hz), 128.7, 132.2, 132.8, 133.1 (d, J = 8.2 Hz), 134.5, 134.7 (d, J = 10.9 Hz), 140.4 (d, J = 6.3 Hz), 159.8 (d, J = 257.4 Hz), 162.0 (d, J = 258.8 Hz), 167.4 ppm. HRMS (ESI+): calcd. for $C_{19}H_{14}F_2N_3O$ $[M+H]^+$: 338.1105, found: 338.1108.

(*E*)-*N*-(2-Methyl-6-(m-tolyldiazenyl)phenyl)benzamide (3k-i)



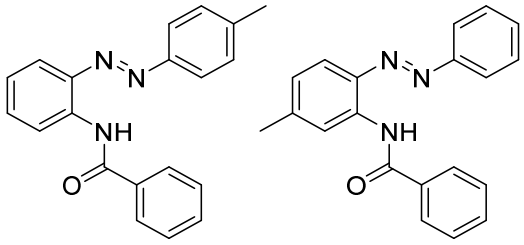
Orange solid (9.3 mg, 28%); mp: 78-80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.47 (s, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.52 - 7.57 (m, 2H), 7.58 - 7.63 (m, 1H), 7.66 - 7.73 (m, 3H), 7.80 (s, 1H), 7.96 - 8.00 (m, 2H), 9.17 (s, 1H), 11.49 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 22.4, 120.0, 122.7, 123.7, 126.3, 127.2, 128.8, 129.2, 129.9, 132.2, 132.4, 133.2, 135.0, 137.8, 139.3, 152.2, 165.7 ppm. HRMS (ESI+): calcd. for $C_{21}H_{20}N_3O$ $[M+H]^+$: 330.1606, found: 330.1607.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)benzamide (3k-ii)



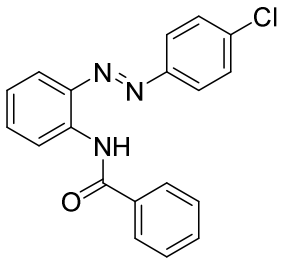
Orange solid (16.5 mg, 50%); mp: 86-88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.46 (s, 3H), 7.29 - 7.36 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.51 - 7.55 (m, 2H), 7.57 - 7.60 (m, 1H), 7.67 - 7.71 (m, 2H), 7.76 (s, 1H), 7.97 - 8.01 (m, 2H), 8.77 (d, J = 8.5 Hz, 1H), 11.38 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.4, 119.9, 120.1, 122.6, 124.3, 127.2, 128.8, 129.1, 131.9, 132.1, 132.8, 133.3, 133.7, 135.4, 138.8, 139.2, 152.3, 165.6 ppm. HRMS (ESI+): calcd. for $C_{21}H_{20}N_3O$ $[M+H]^+$: 330.1606, found: 330.1608.

(*E*)-*N*-[2-(*p*-Tolyldiazenyl)phenyl]benzamide & (*E*)-*N*-[5-methyl-2-(phenyldiazenyl)phenyl] benzamide (3i-i + 3l-ii)



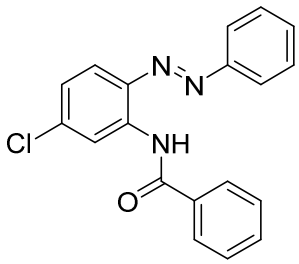
Orange solid (4:5 ratio, 27.0 mg, 85%); mp: 96-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 2.4H), 2.47 (s, 3H), 7.05 (dd, J = 8.2, 0.8 Hz, 1H), 7.21 - 7.25 (m, 0.8H), 7.32 (d, J = 8.1 Hz, 1.6H), 7.46 - 7.56 (m, 7.4H), 7.57 - 7.61 (m, 1.8H), 7.78 (d, J = 8.1 Hz, 1.6H), 7.83 - 7.87 (m, 3H), 7.93 (dd, J = 7.9, 1.4 Hz, 0.8H), 7.96 - 8.01 (m, 3.6H), 8.74 (d, J = 0.6 Hz, 1H), 8.88 (dd, J = 8.3, 1.1 Hz, 0.8H), 11.48 (br s, 0.8H), 11.66 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 22.2, 120.1, 120.4, 122.2, 122.4, 123.5, 124.4, 124.6, 125.7, 127.20, 127.22, 128.8, 129.3, 130.0, 131.0, 132.0, 132.6, 134.6, 134.9, 135.3, 137.1, 138.9, 142.1, 144.2, 150.3, 152.2, 165.8, 166.0 ppm. HRMS (ESI+): calcd. for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1450, found: 316.1454.

(*E*)-*N*-(2-((4-chlorophenyl)diazenyl)phenyl)benzamide (3m-i)



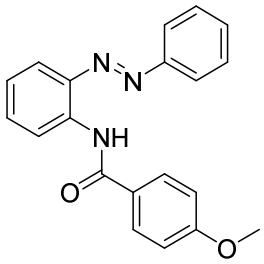
Orange solid (15.0 mg, 45%); mp: 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 - 7.29 (m, 1H), 7.50 - 7.58 (m, 5H), 7.59 - 7.63 (m, 1H), 7.81 - 7.86 (m, 2H), 7.92 - 8.00 (m, 3H), 8.79 - 8.98 (m, 1H), 11.35 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.3, 123.6, 123.7, 124.5, 127.2, 128.9, 129.7, 132.1, 133.4, 135.2, 135.3, 137.4, 138.9, 150.7, 165.9 ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_3O$ $[M+H]^+$: 336.0904, found: 306.0902.

(*E*)-*N*-(5-chloro-2-(phenyldiazenyl)phenyl)benzamide (3m-ii)



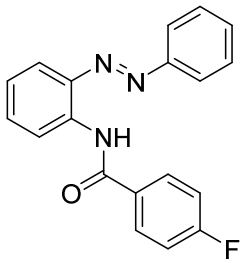
Orange solid (12.1 mg, 34%); mp: 145-148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.5, 2.3 Hz, 1H), 7.46 - 7.58 (m, 5H), 7.59 - 7.64 (m, 1H), 7.87 (dd, J = 8.0, 1.6 Hz, 2H), 7.90 (d, J = 8.5 Hz, 1H), 7.95 - 7.99 (m, 2H), 8.99 (d, J = 2.3 Hz, 1H), 11.57 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.1, 122.4, 123.8, 126.2, 127.2, 128.9, 129.4, 131.6, 132.3, 134.8, 135.6, 137.2, 139.0, 152.0, 165.9 ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_3O$ $[M+H]^+$: 336.0904, found: 336.0903.

(*E*)-4-Methoxy-N-(2-(phenyldiazenyl)phenyl)benzamide (5a)



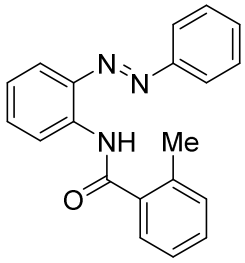
Orange solid (23.3 mg, 70%); mp: 135-136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 3H), 7.00 - 7.05 (m, 2H), 7.20 - 7.26 (m, 1H), 7.49 - 7.59 (m, 4H), 7.87 - 7.92 (m, 2H), 7.94 - 7.98 (m, 3H), 8.88 (dd, J = 8.4, 1.1 Hz, 1H), 11.43 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 114.0, 120.2, 122.4, 123.3, 124.8, 127.5, 129.1, 129.4, 131.3, 133.0, 135.3, 138.9, 152.3, 162.6, 165.5 ppm. HRMS (ESI+): calcd. for $C_{20}H_{18}N_3O_2$ $[M+H]^+$: 332.1399, found: 332.1395.

(*E*)-4-Fluoro-N-(2-(phenyldiazenyl)phenyl)benzamide (5b)



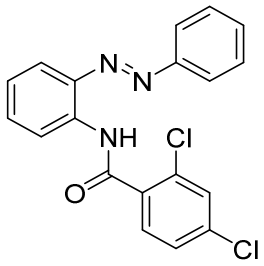
Orange solid (28.2 mg, 88%); mp: 124-125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 - 7.26 (m, 3H), 7.47 - 7.56 (m, 4H), 7.85 (d, J = 7.2 Hz, 2H), 7.93 - 8.01 (m, 3H), 8.85 (d, J=8.4 Hz, 1H), 11.48 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.9 (d, J = 21.8 Hz), 120.2, 122.3, 123.6, 125.2, 129.4, 129.6 (d, J = 9.1 Hz), 131.4, 133.0, 134.7, 138.8, 152.1, 164.8, 165.0 (d, J = 253.4 Hz) ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}FN_3O$ $[M+H]^+$: 320.1199, found: 320.1197.

(*E*)-2-Methyl-N-(2-(phenyldiazenyl)phenyl)benzamide (5c)



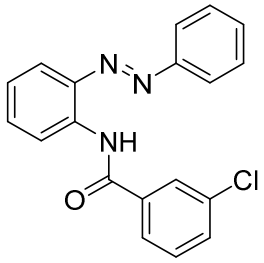
Orange solid (24.3 mg, 77%); mp: 126-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (s, 3H), 7.20 - 7.26 (m, 1H), 7.28 - 7.34 (m, 2H), 7.38 - 7.43 (m, 1H), 7.45 - 7.50 (m, 3H), 7.51 - 7.55 (m, 1H), 7.62 (dd, J = 8.0, 1.1 Hz, 1H), 7.74 - 7.79 (m, 2H), 7.93 (dd, J = 8.1, 1.5 Hz, 1H), 8.89 (d, J = 8.2 Hz, 1H), 10.86 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 120.1, 122.5, 123.2, 123.6, 126.0, 126.9, 129.2, 130.6, 131.3, 131.6, 132.9, 135.5, 136.3, 137.1, 138.8, 152.0, 168.1 ppm. HRMS (ESI+): calcd. for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1450, found: 316.1455.

(*E*)-2,4-dichloro-N-(2-(phenyldiazenyl)phenyl)benzamide (5d)



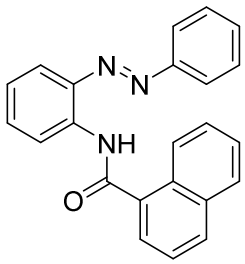
Orange solid (26.7 mg, 72%); mp: 136-138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.28 (m, 1H), 7.38 - 7.42 (m, 1H), 7.47 - 7.59 (m, 5H), 7.79 - 7.85 (m, 3H), 7.91 (dd, *J*=8.1, 1.4 Hz, 1H), 8.86 (d, *J* = 8.2 Hz, 1H), 10.80 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 120.4, 122.8, 124.2, 127.8, 129.3, 130.4, 131.5, 131.7, 131.8, 133.0, 133.7, 135.8, 137.4, 139.4, 152.2, 163.4 ppm. HRMS (ESI+): calcd. for $C_{19}H_{14}Cl_2N_3O$ $[M+H]^+$:370.0514, found: 370.0515.

(*E*)-3-Chloro-N-(2-(phenyldiazenyl)phenyl)benzamide (5e)



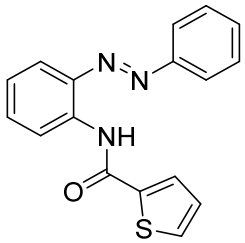
Orange solid (27.6 mg, 82%); mp: 97-100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.28 (m, 1H), 7.44 - 7.57 (m, 6H), 7.85 - 7.91 (m, 3H), 7.95 - 7.99 (m, 2H), 8.85 (d, *J*=8.4 Hz, 1H), 11.67 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 122.4, 123.8, 125.5, 126.0, 127.3, 129.4, 130.2, 131.5, 132.0, 133.0, 134.3, 135.0, 137.0, 138.7, 152.0, 164.4 ppm. HRMS (ESI+): calcd. for $C_{19}H_{15}ClN_3O$ $[M+H]^+$: 336.0904, found: 336.0905.

(*E*)-N-[2-(phenyldiazenyl)phenyl]-1-naphthamide (5f)



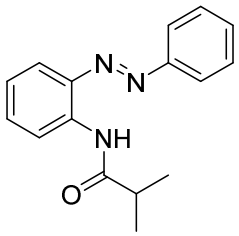
Orange solid (23.8 mg, 68%); mp: 153-156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 - 7.30 (m, 1H), 7.48 - 7.65 (m, 6H), 7.91 - 8.03 (m, 6H), 8.05 - 8.09 (m, 1H), 8.51 (s, 1H), 8.96 (d, J = 8.2 Hz, 1H), 11.81 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.3, 122.5, 123.6, 123.7, 125.4, 127.0, 127.8, 127.9, 128.0, 128.8, 129.0, 129.4, 131.5, 132.5, 132.7, 133.1, 135.0, 135.0, 138.9, 152.2, 166.0 ppm. HRMS (ESI+): calcd. for $C_{23}H_{18}N_3O$ $[M+H]^+$: 352.1450, found: 352.1452.

(*E*)-N-[2-(Phenyldiazenyl)phenyl]thiophene-2-carboxamide (5g)



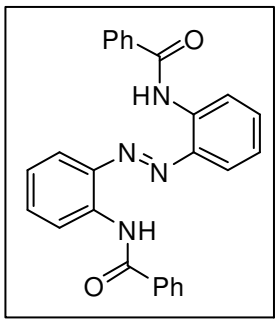
Orange solid (25.8 mg, 84%); mp: 120-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 - 7.20 (m, 1H), 7.20 - 7.25 (m, 1H), 7.47 - 7.54 (m, 2H), 7.54 - 7.60 (m, 3H), 7.73 (d, J = 3.8 Hz, 1H), 7.91 - 7.96 (m, 3H), 8.80 (d, J = 8.4 Hz, 1H), 11.21 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 122.5, 123.6, 123.9, 128.0, 128.9, 129.4, 131.0, 131.4, 133.0, 135.0, 138.7, 139.8, 152.3, 160.1 ppm. HRMS (ESI+): calcd. for $C_{17}H_{14}N_3OS$ $[M+H]^+$: 308.0858, found: 308.0856.

(E)-N-(2-(Phenyldiazenyl)phenyl)isobutyramide (5h)



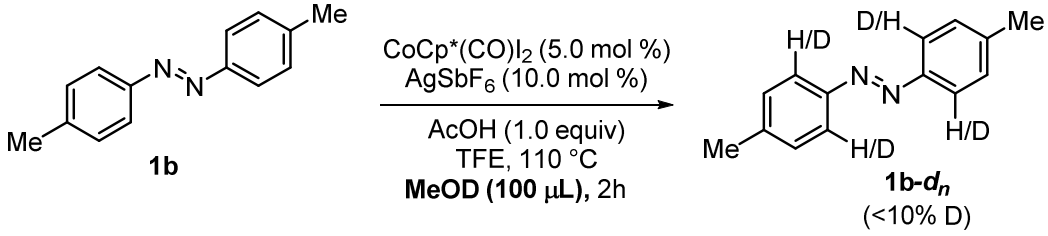
Orange solid (18.0 mg, 67%); mp: 136-137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (d, J = 7.0 Hz, 6H), 2.65 (spt, J = 6.9 Hz, 1H), 7.15 - 7.20 (m, 1H), 7.45 - 7.50 (m, 1H), 7.50 - 7.58 (m, 3H), 7.84 - 7.90 (m, 3H), 8.73 (dd, J = 8.4, 0.9 Hz, 1H), 10.31 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 37.4, 120.2, 121.7, 122.5, 123.2, 129.3, 131.3, 133.0, 135.9, 138.8, 152.4, 175.6 ppm. HRMS (ESI+): calcd. for $C_{16}H_{18}N_3O$ $[M+H]^+$: 268.1450, found: 268.1454.

(*E*)-*N*, *N*'-[diazene-1,2-diylbis(2,1-phenylene)]dibenzamide (4): To an oven-dried sealed tube (*E*)-1-phenyl-2-(phenyl)diazene (**1a**, 18.8 mg, 0.1 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (49.0 mg, 0.3 mmol), [CoCp*(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol) and 2,2,2-TFE (1.0 mL) were added. Then the reaction was stirred at 110 °C for 6 h. Next the reaction mixture was cooled to room temperature and filtered through a celite pad followed by washing of the celite pad with EtOAc (10 mL x 3). The combined solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the mixture of diamidated product **4** (21.4mg, 51%) and monoamidated product (12.0 mg, 39%) respectively. Orange solid; mp: 240-242 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 - 7.59 (m, 6H), 7.60 - 7.64 (m, 4H), 7.82 (dd, J = 8.2, 1.4 Hz, 2H), 8.00 (dd, J = 8.2, 1.1 Hz, 4H), 8.67 (d, J = 8.5 Hz, 2H), 11.76 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.6, 114.6, 121.8, 127.3, 128.9, 129.8, 131.6, 132.2, 135.3, 136.0, 136.2, 166.0 ppm. HRMS (ESI+): calcd. for $C_{26}H_{21}N_4O_2$ $[M+H]^+$: 421.1665, found: 421.1667

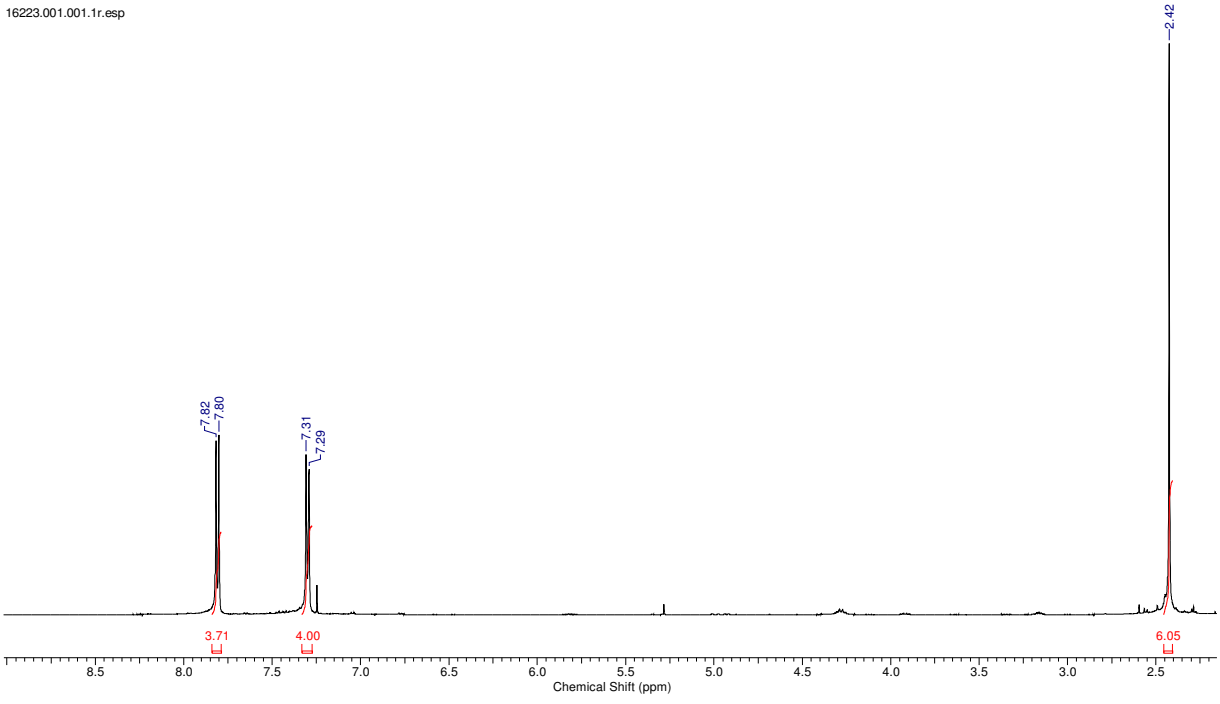


4. Experimental Procedures of the Mechanistic Studies

4.1. Deuterium Exchange Study in absence of Diazo compound



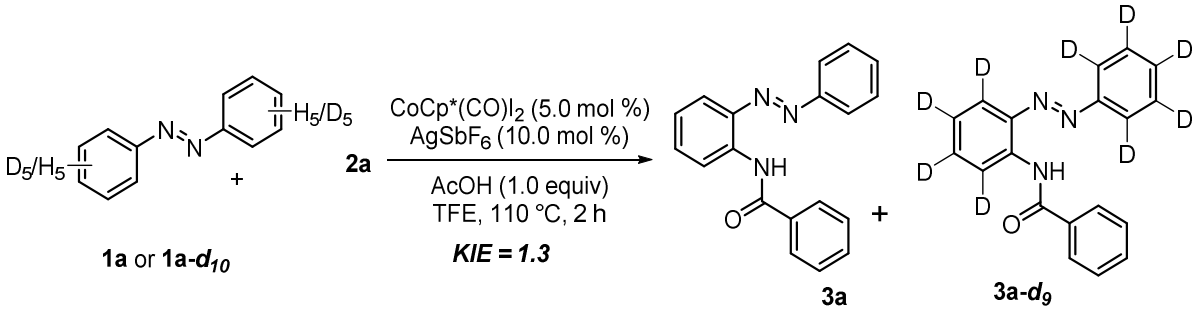
To a pressure tube diazobenzene **1b** (19.7 mg, 0.1 mmol) was added along with [Cp*Co(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol), 2,2,2-TFE (1.0 mL) and MeOD (100 μL) under atmosphric conditions. The reaction mixture was stirred at 110 °C for 2 h. Next, the reaction mixture was cooled and filtered through a pad of celite and then the celite pad was washed with CH_2Cl_2 (5 mL x 3). Solvents were removed under reduced pressure and the compound was analyzed by ^{1}H NMR analysis which shows negligible (<10%) deuterium scrambling.



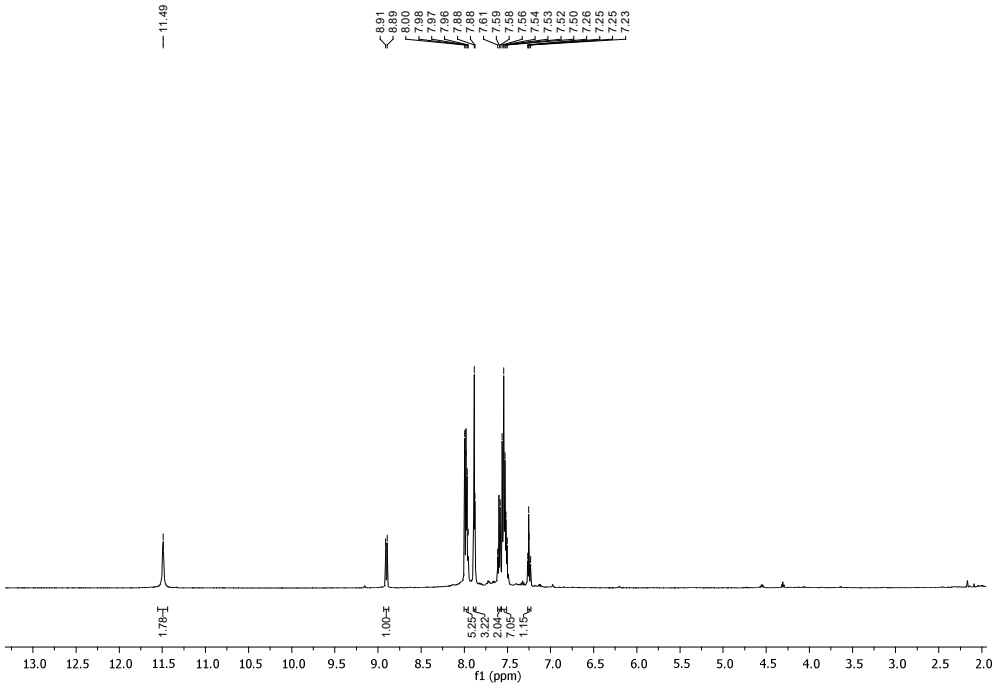
^{1}H NMR spectra of **1a-*d*$_n$** in $CDCl_3$

4.2. Study of Kinetic Isotop Effect

4.2.1. Parallel experiments

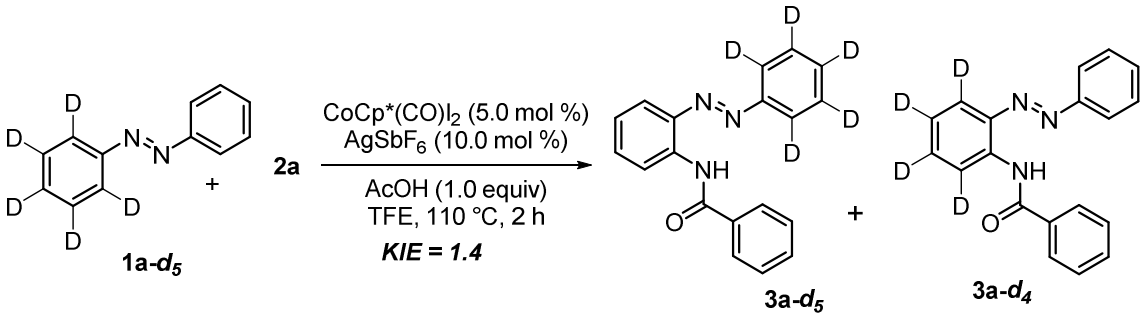


(E)-1,2-diphenyldiazene (**1a**, 18.3 mg, 0.1 mmol) or *(E)*-1,2-diphenyldiazene-d_{10} (**1a-*d*$_{10}$**, 19.3 mg, 0.1 mmol) were added into two different pressur tube, along with dioxazolone **2a** (16.4 mg, 0.1 mmol), [Cp*Co(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol) and 2,2,2-TFE (0.75 mL) under atmospheric conditions. Each of the reaction mixture was stirred at 110 °C for 2 h. After cooling to room temperature, both the reaction mixture were combined and filtered through a pad of celite and the celite pad was washed with EtOAc (5 mL x 3). The solvent was removed under reduced pressure and the residue was purify by column chromatography (EtOAc/Hexane) to afford the mixture of **3a** and **3a-*d*$_9$**. From the ^{1}H NMR analysis the KIE was measure to be 1.3.

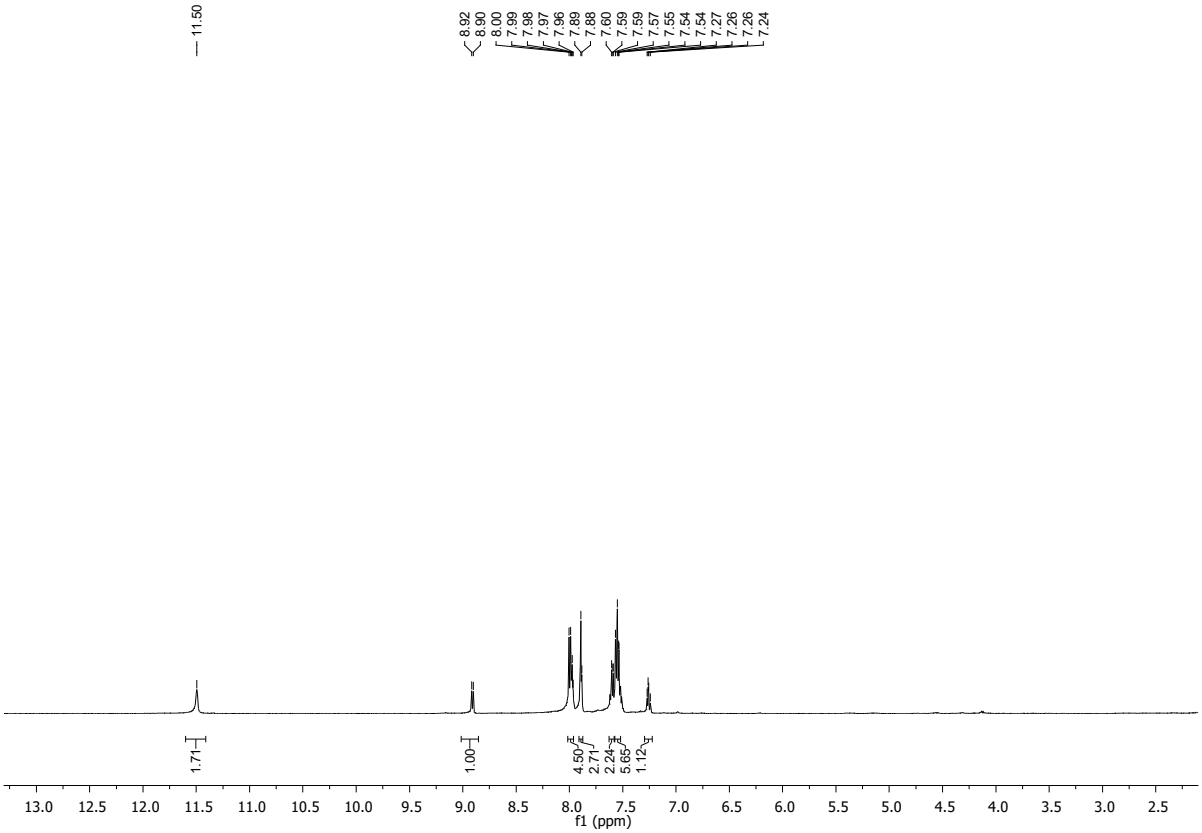


^{1}H NMR spectra of **3a** and **3a-*d*$_9$** in $CDCl_3$

4.2.2. Intramolecular Competitive experiments

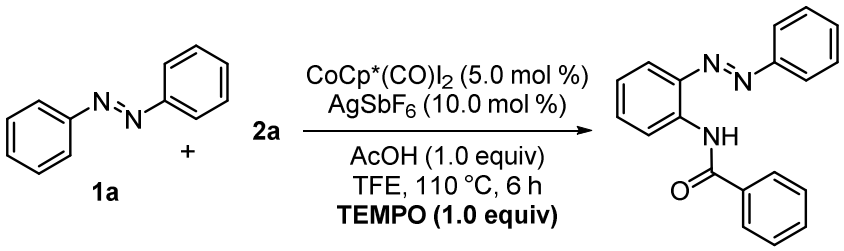


To an oven-dried sealed tube (E)-1-phenyl-2-(phenyl-d5)diazene (**1a-*d*$_5$**) (18.8 mg, 0.1 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (16.3 mg, 0.1 mmol), [CoCp*(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol) and 2,2,2-TFE (1.0 mL) were added. Then the reaction was stirred at 110 °C for 2 h. Next the reaction mixture was cooled to room temperature and filtered through a celite pad followed by washing of the celite pad with EtOAc (10 mL x 3). The combined solvent was removed under reduced pressure and the residue was purify by column chromatography (EtOAc/Hexane) to afford the mixture of **3a-*d*$_5$** and **3a-*d*$_4$**. From the ^{1}H NMR analysis the KIE was measure to be 1.4.



^{1}H NMR spectra of **3a-*d*$_5$** and **3a-*d*$_4$** in $CDCl_3$

4.3. Amidation in presence of radical scavenger



3a (55%)

To an oven-dried shield tube azobenzene (**1**, 0.1 mmol), dioxazolone (**2**, 0.11 mmol), [CoCp*(CO)I_2] (2.4 mg, 5.0 mol %), $AgSbF_6$ (3.4 mg, 10.0 mol %), AcOH (6.0 mg, 0.1 mmol), TEMPO (1.0 equiv) and 2,2,2-TFE (1.0 mL) were added and the reaction mixture was stirred at 110 °C for 6 h. Next the reaction mixture was cooled to room temperature and filtered through a celite pad followed by washing of the celite pad with EtOAc (10 mL x 3). The combined solvent was removed under reduced pressure and the residue was purify by column chromatography to afford the desired monoamidated product in 55% yield.

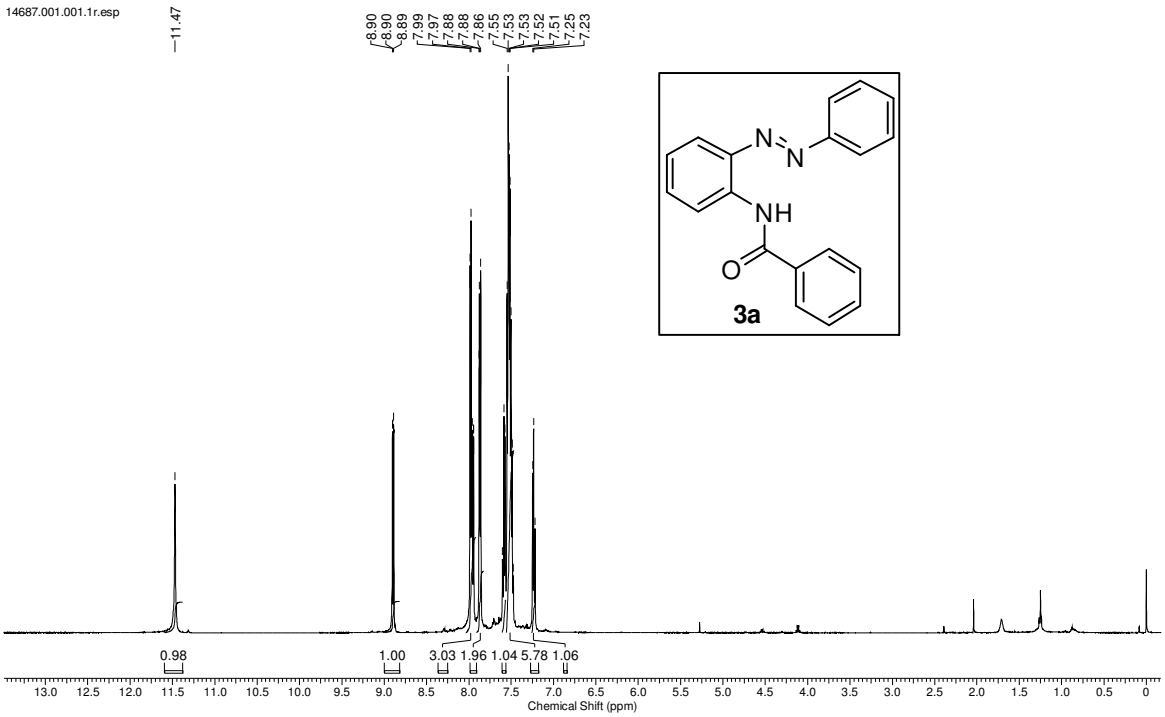
5. References

1. B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal.*, 2014, **356**, 1491.

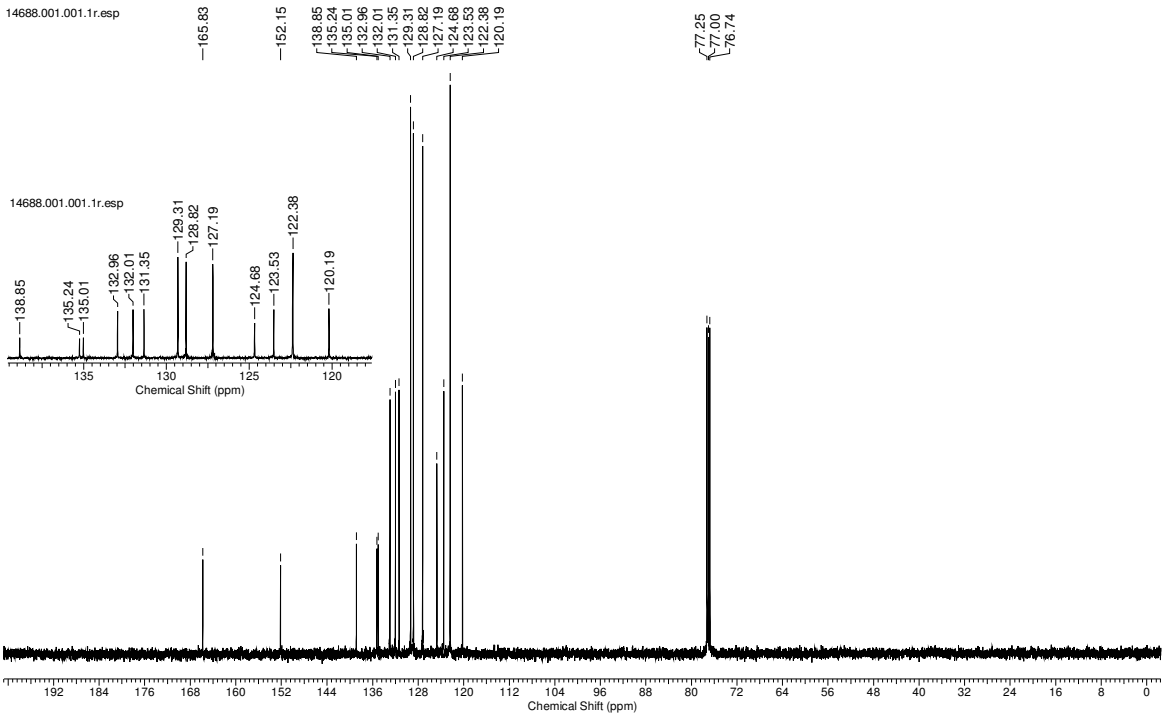
2. D.-G. Yu, T. Gensch, F. d. Azambuja, S. Vásquez-Céspedes, and F. Glorius, *J. Am. Chem. Soc.* 2014, **136**, 17722.

^{1}H and ^{13}C spectra of all products

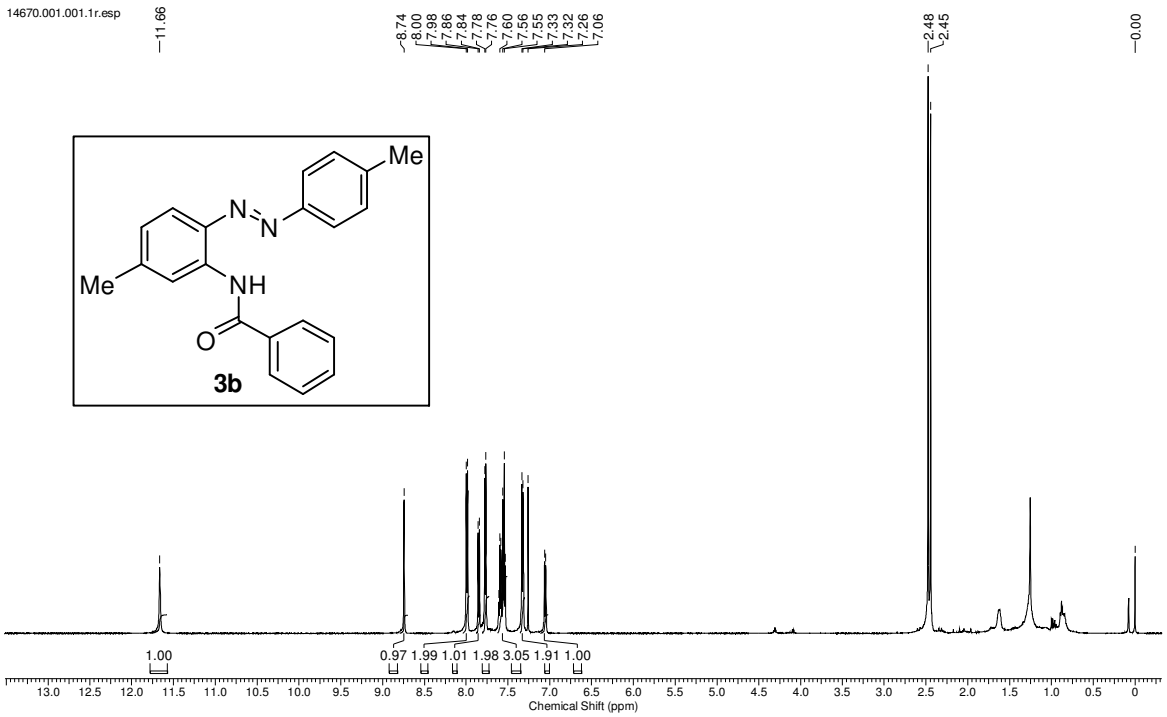
^{1}H NMR of Compound **3a** in $CDCl_3$



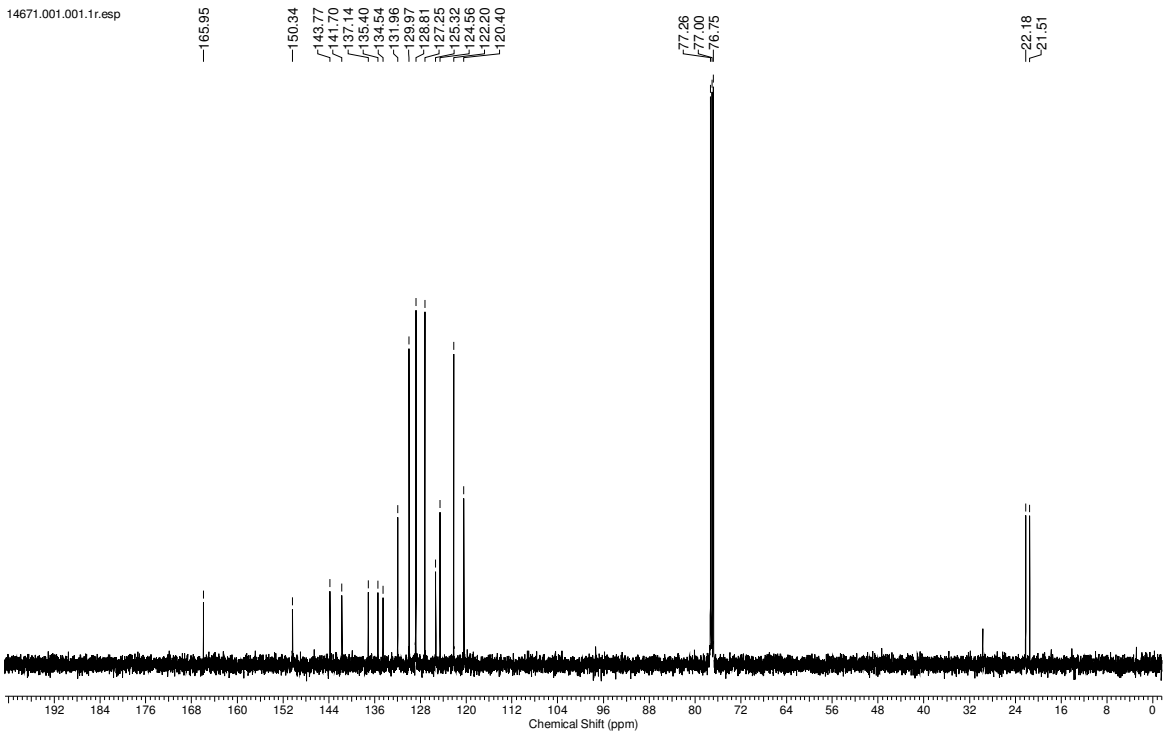
^{13}C NMR of Compound **3a** in $CDCl_3$



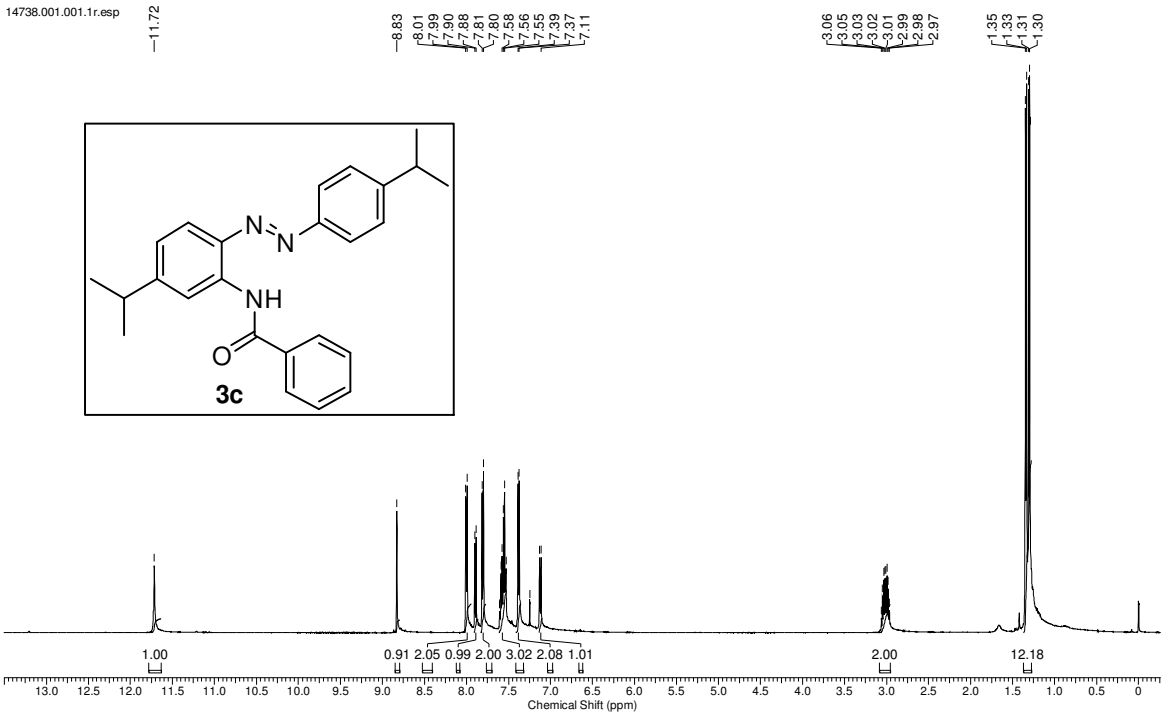
^{1}H NMR of Compound **3b** in $CDCl_3$



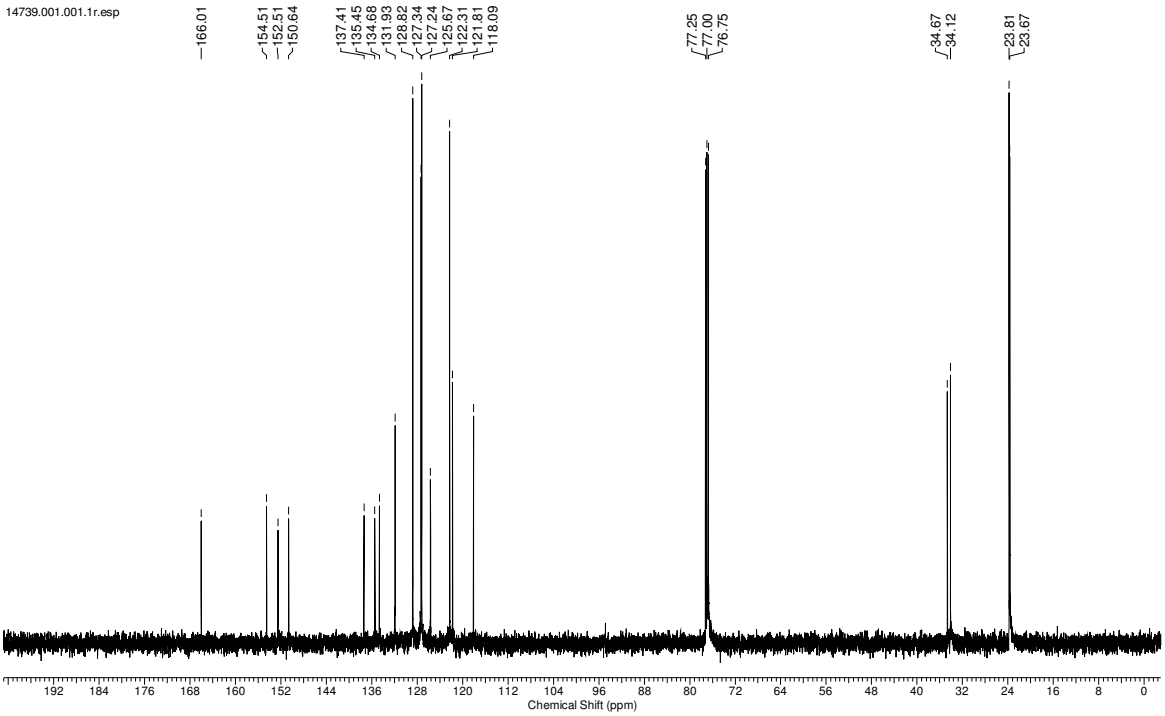
^{13}C NMR of Compound **3b** in $CDCl_3$



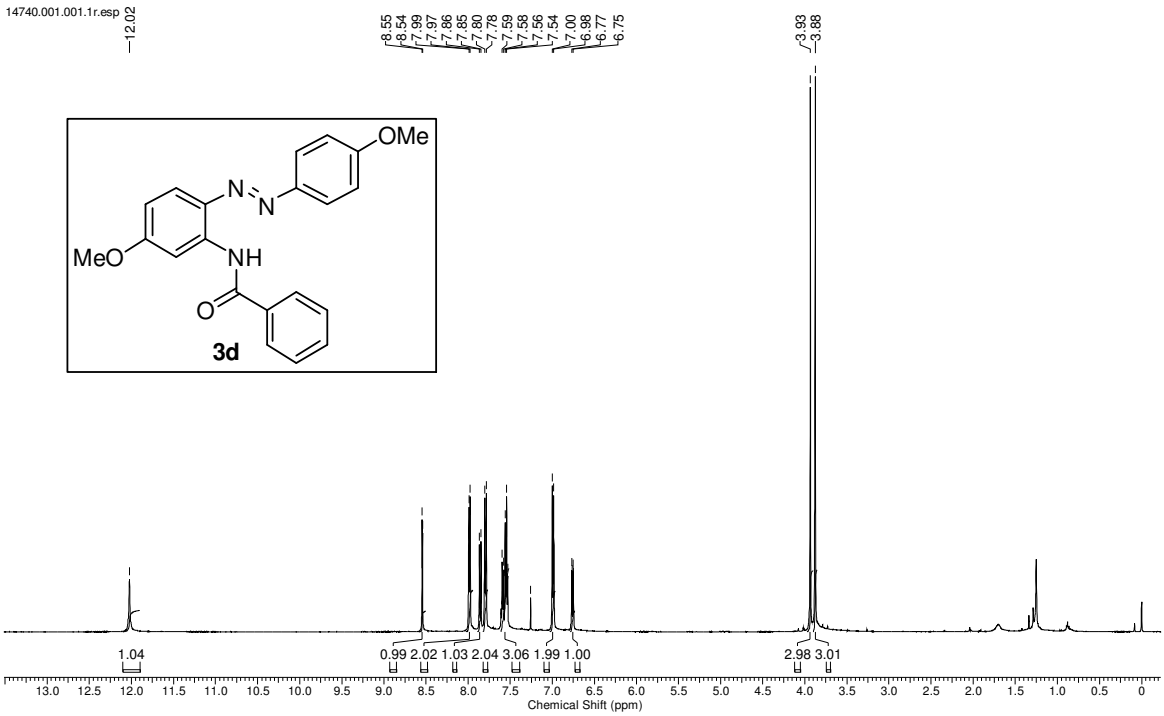
^{1}H NMR of Compound **3c** in $CDCl_3$



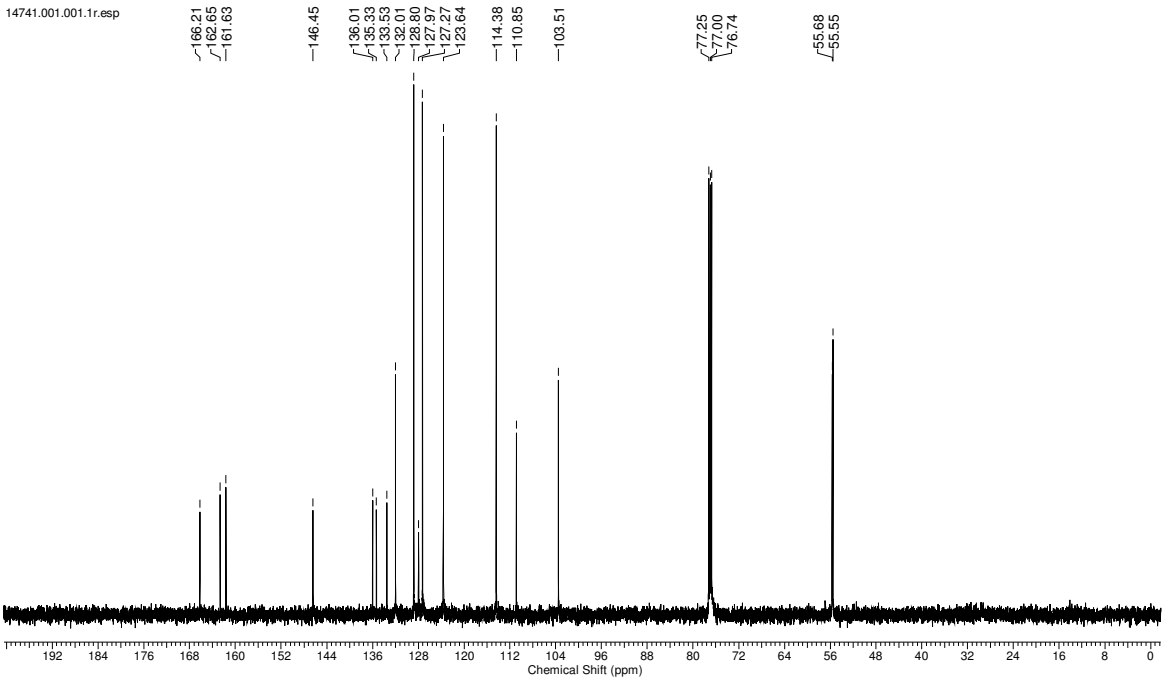
^{13}C NMR of Compound **3c** in $CDCl_3$



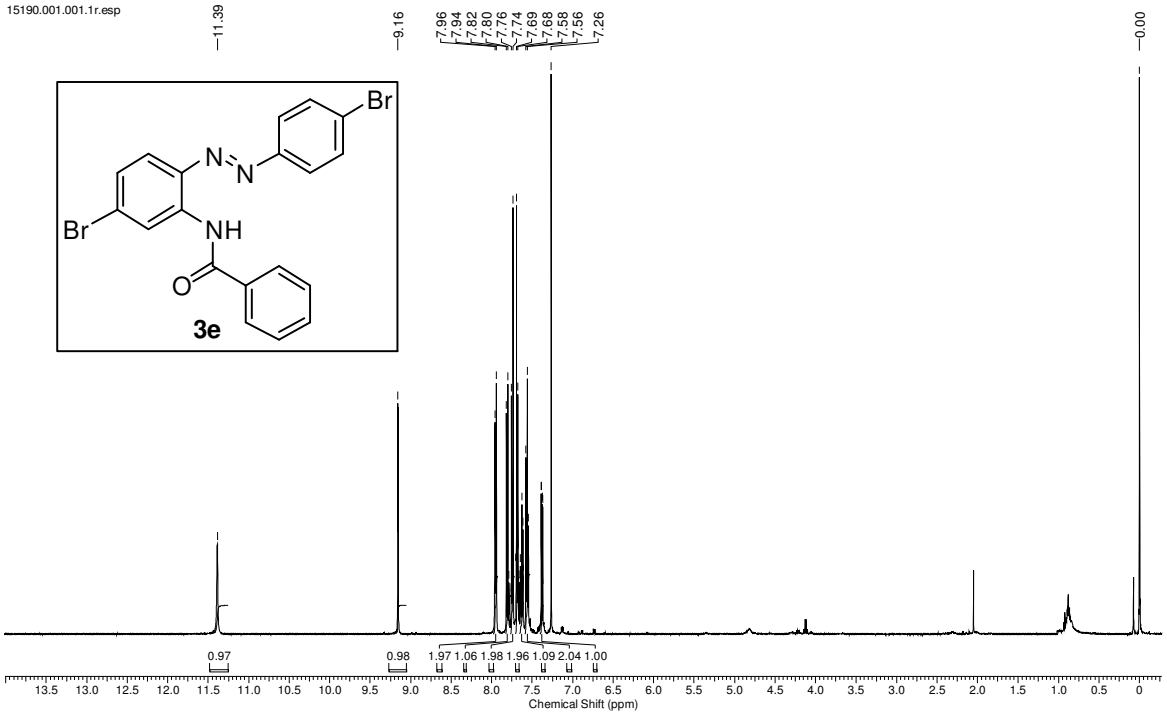
^{1}H NMR of Compound **3d** in $CDCl_3$



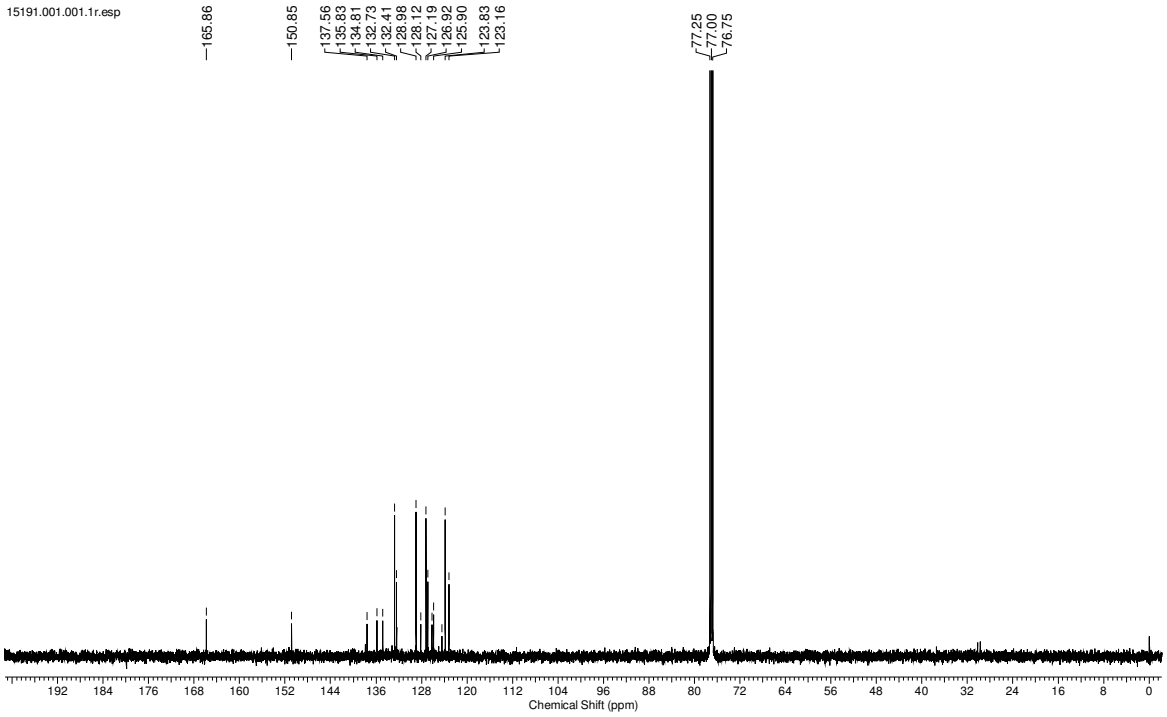
^{13}C NMR of Compound **3d** in $CDCl_3$



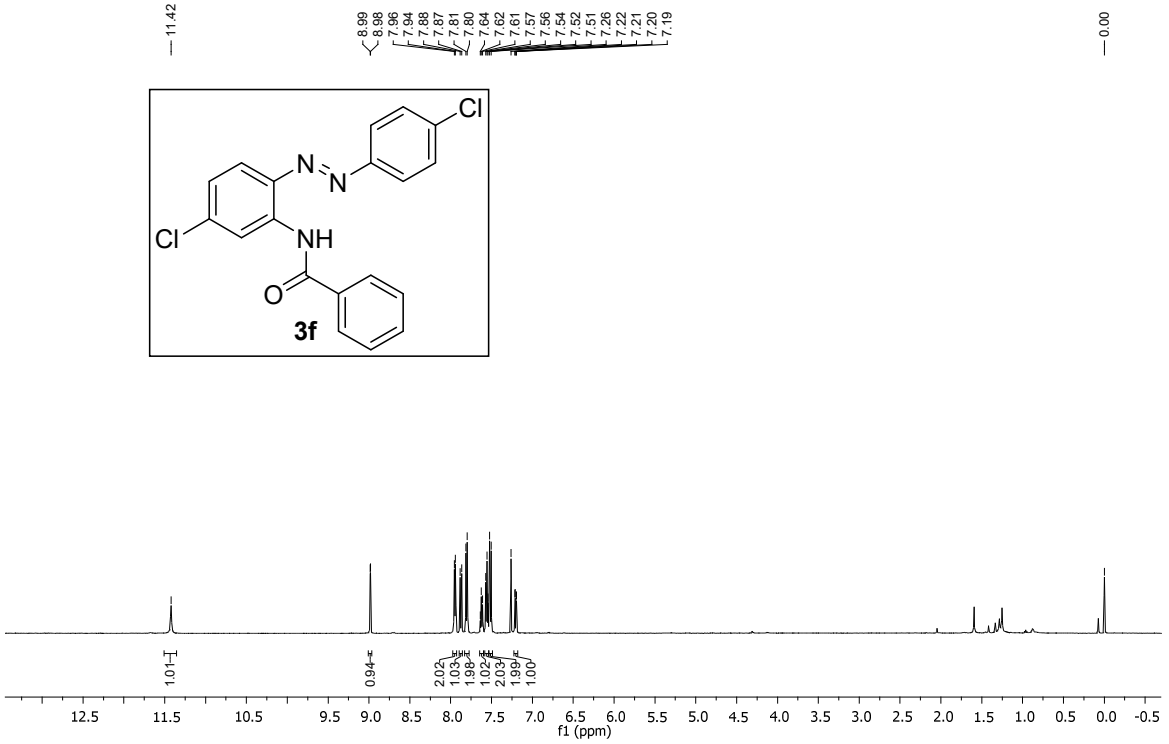
^{1}H NMR of Compound **3e** in $CDCl_3$



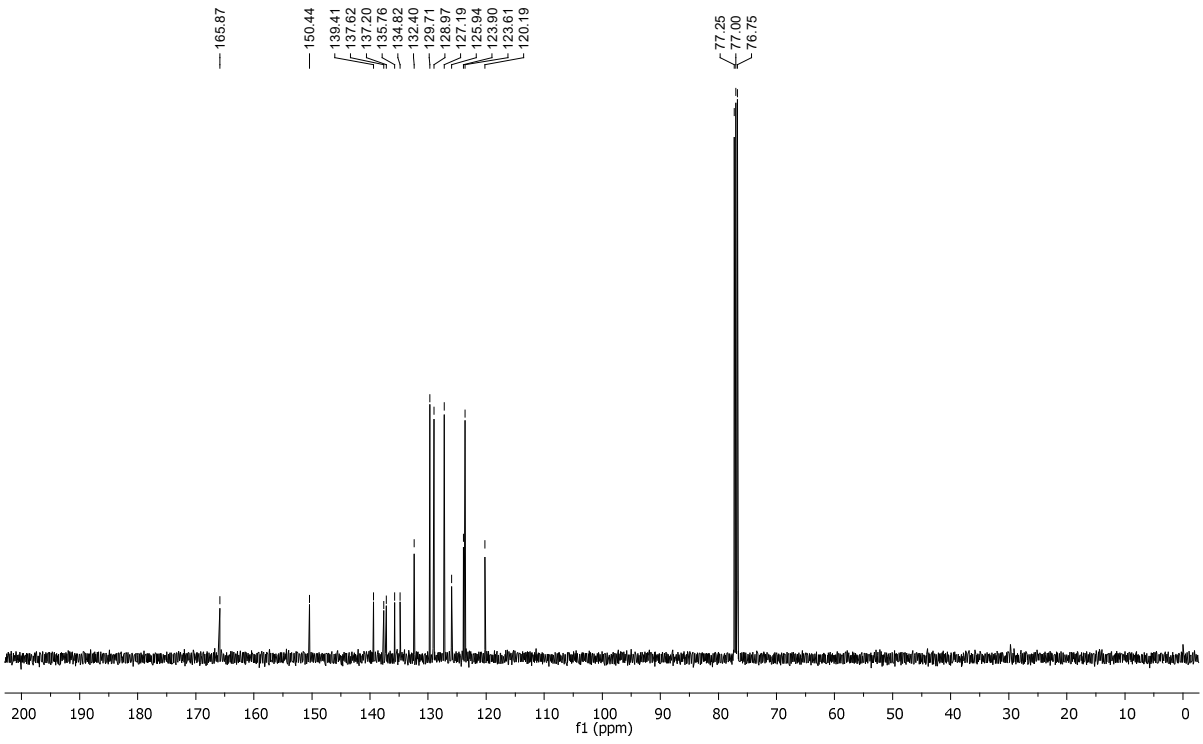
^{13}C NMR of Compound **3e** in $CDCl_3$



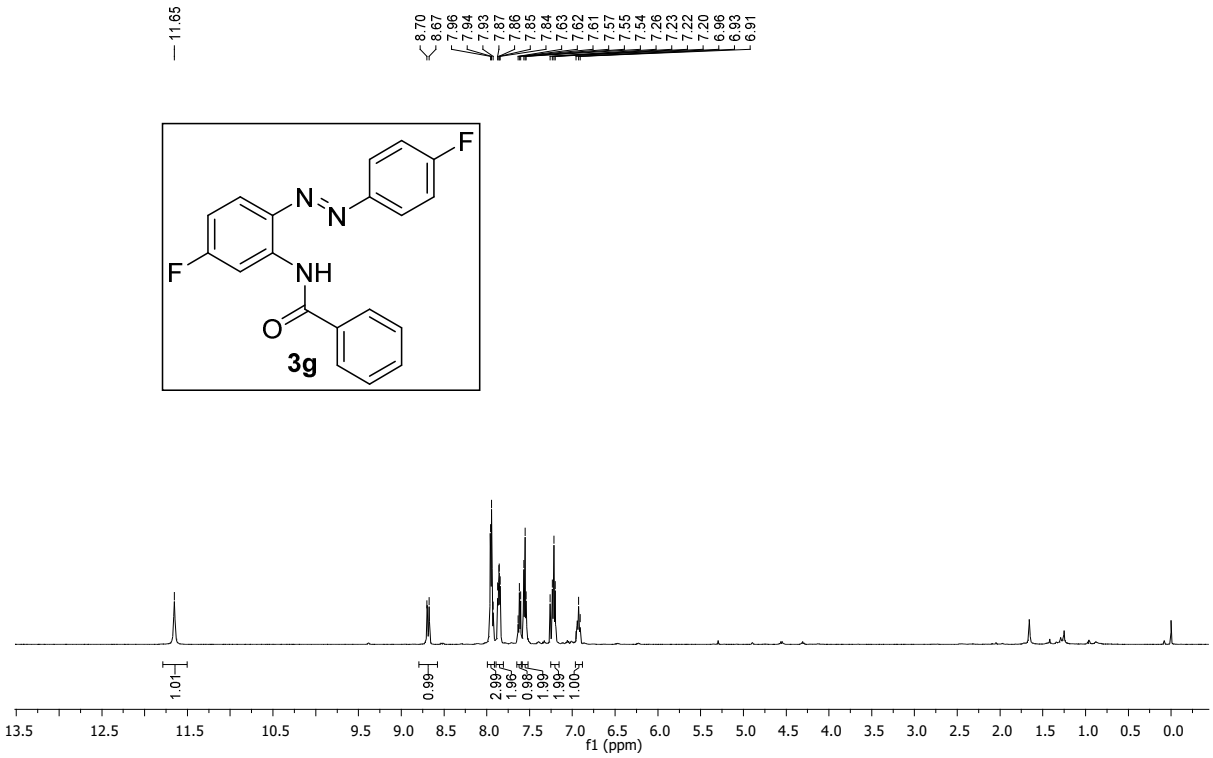
^{1}H NMR of Compound **3f** in $CDCl_3$



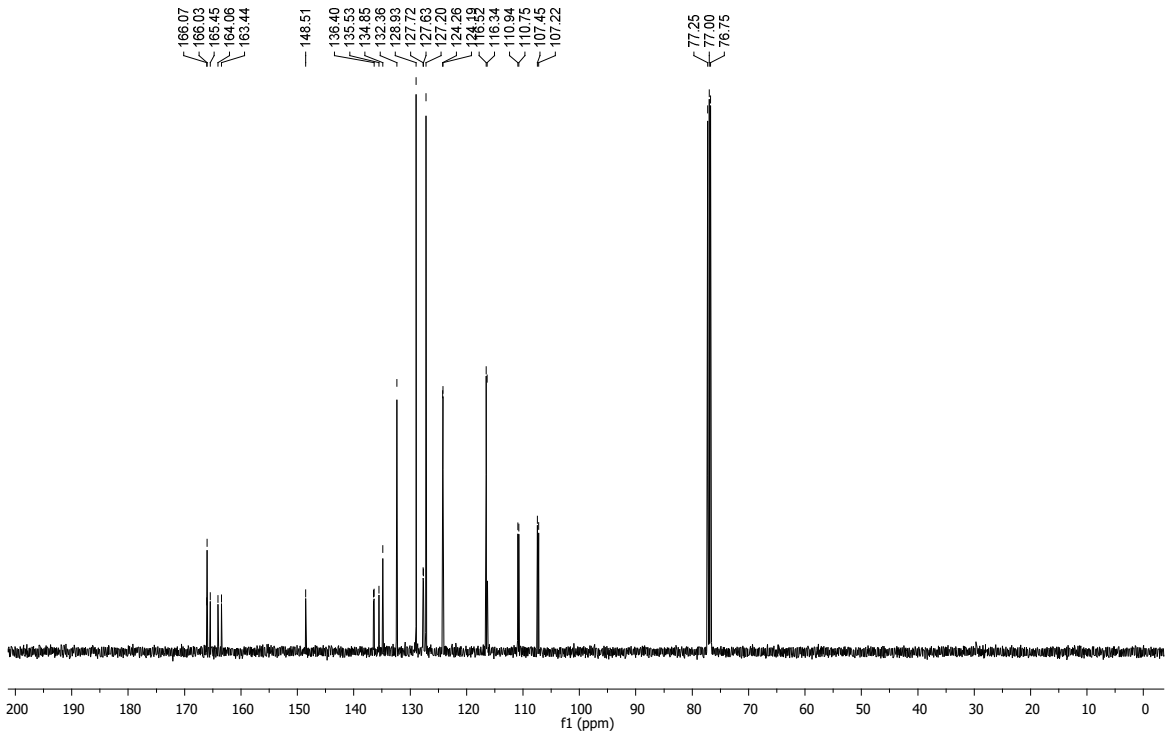
^{13}C NMR of Compound **3f** in $CDCl_3$



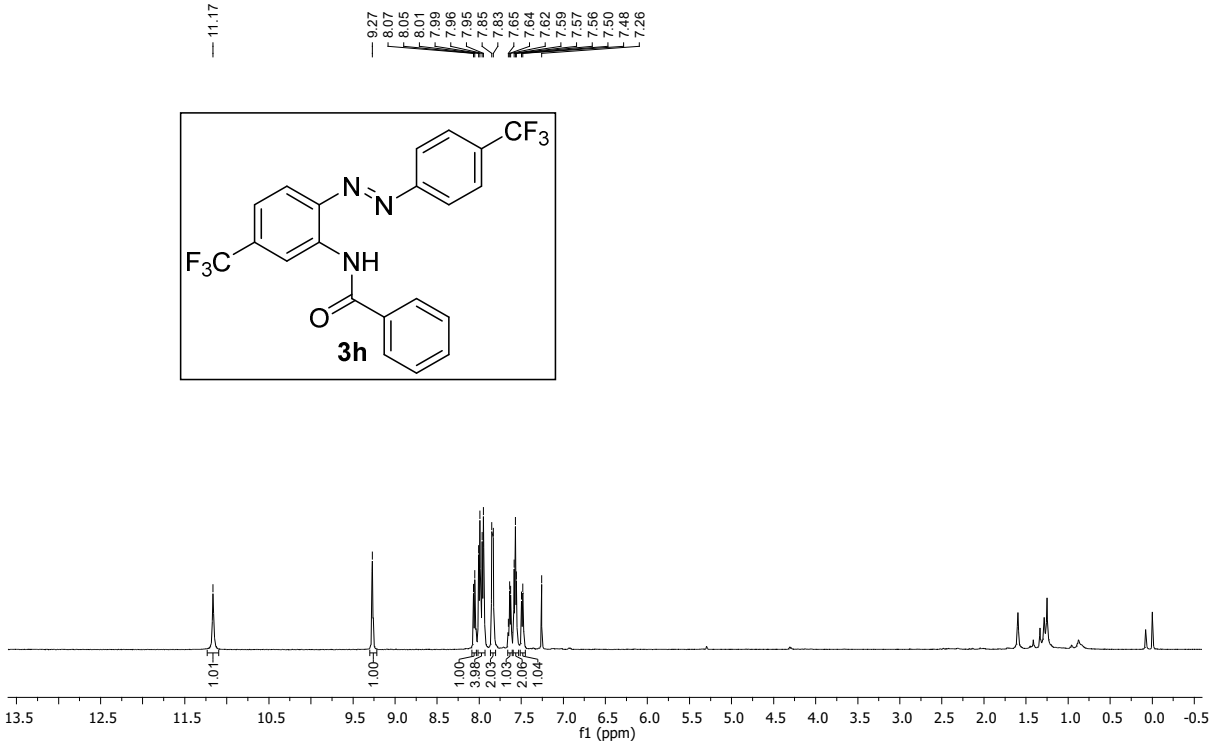
^{1}H NMR of Compound **3g** in $CDCl_3$



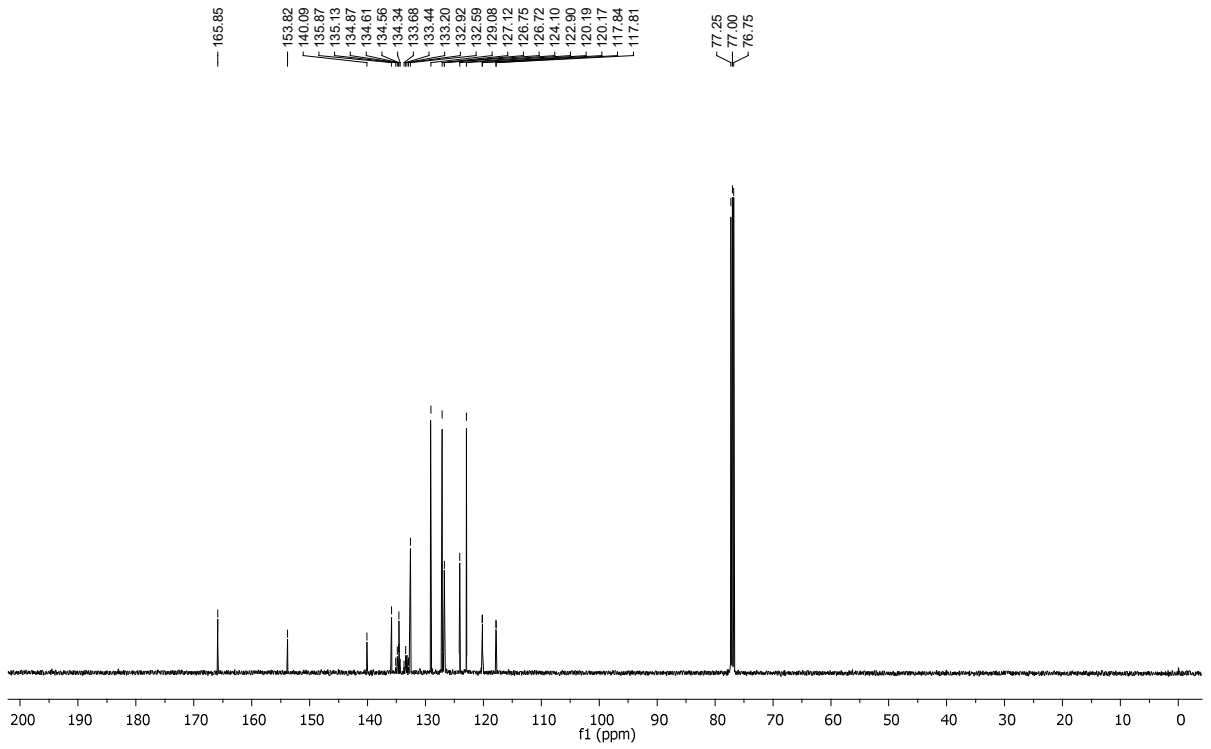
^{13}C NMR of Compound **3g** in $CDCl_3$



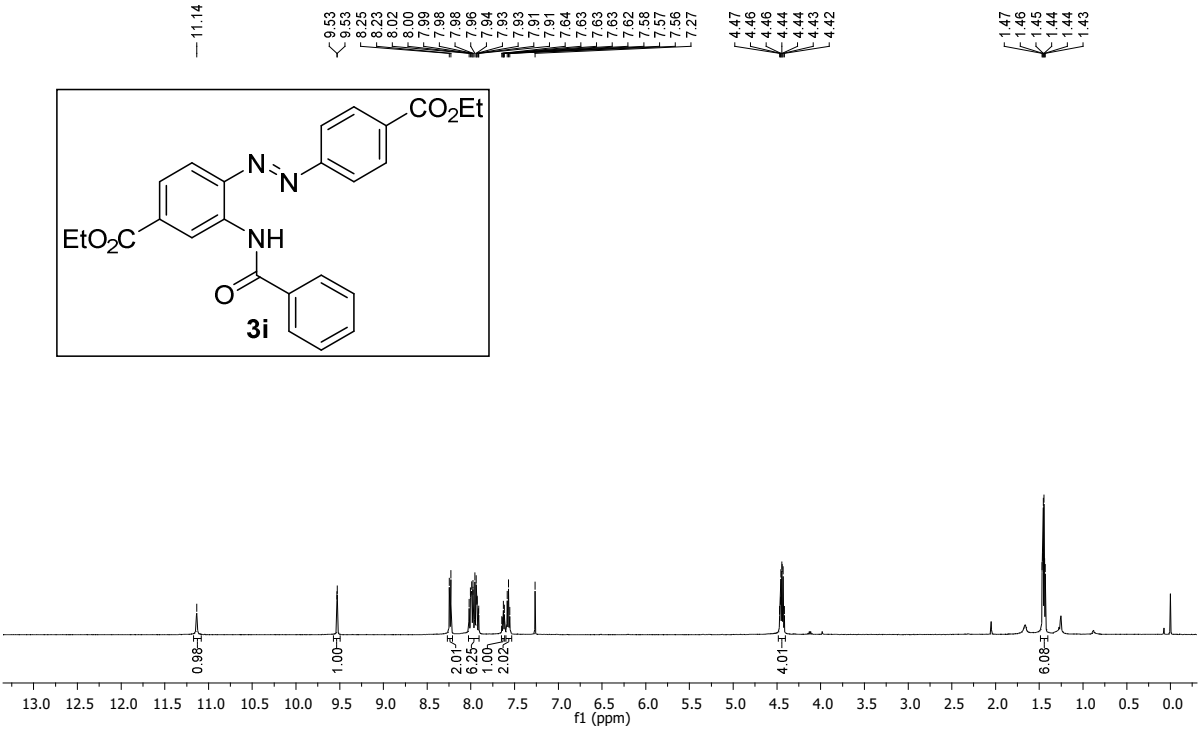
^{1}H NMR of Compound **3h** in $CDCl_3$



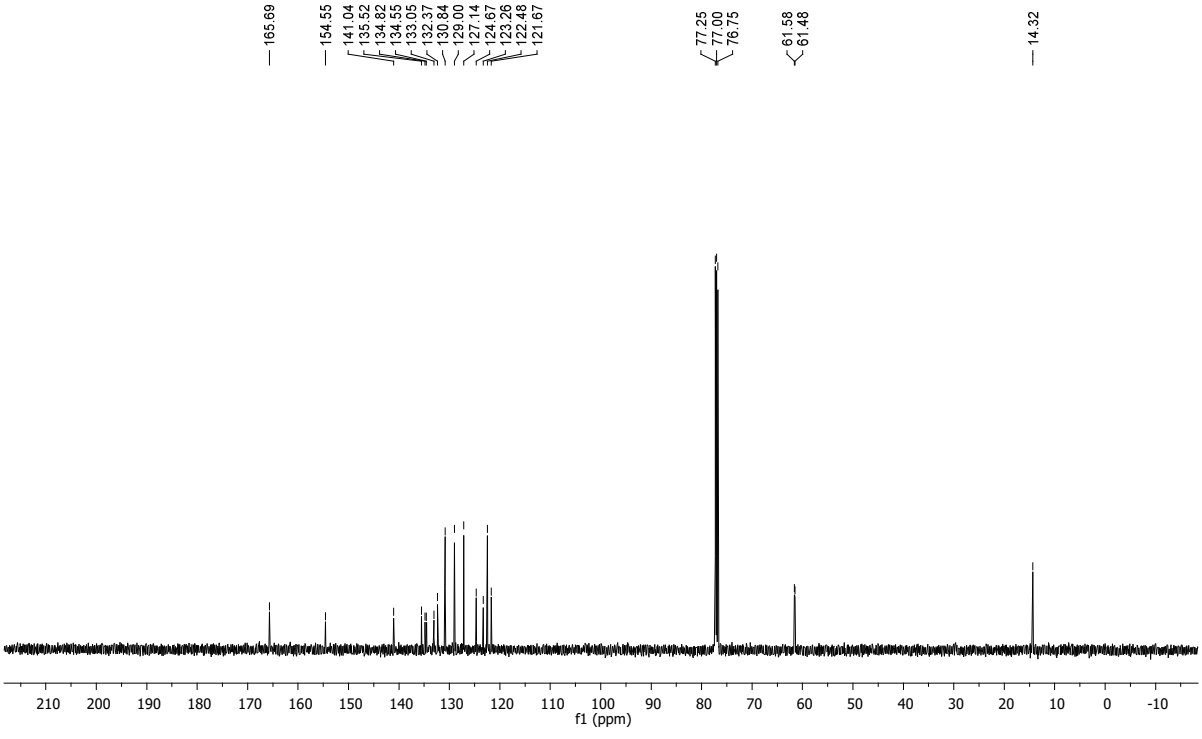
^{13}C NMR of Compound **3h** in $CDCl_3$



^{1}H NMR of Compound **3i** in $CDCl_3$



^{13}C NMR of Compound **3i** in $CDCl_3$



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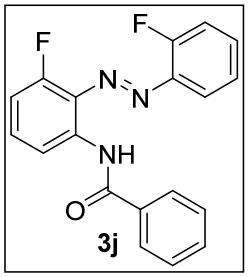
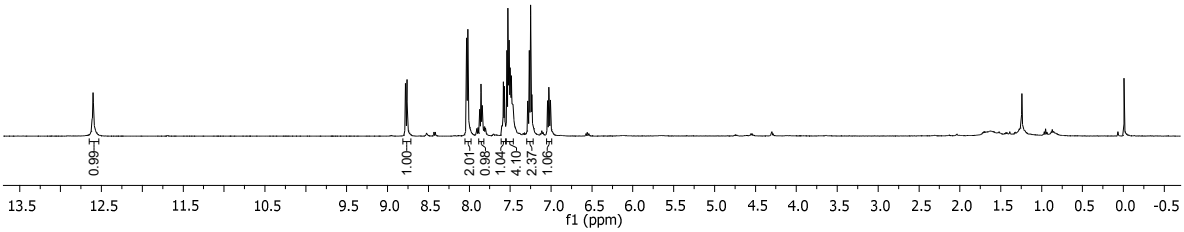
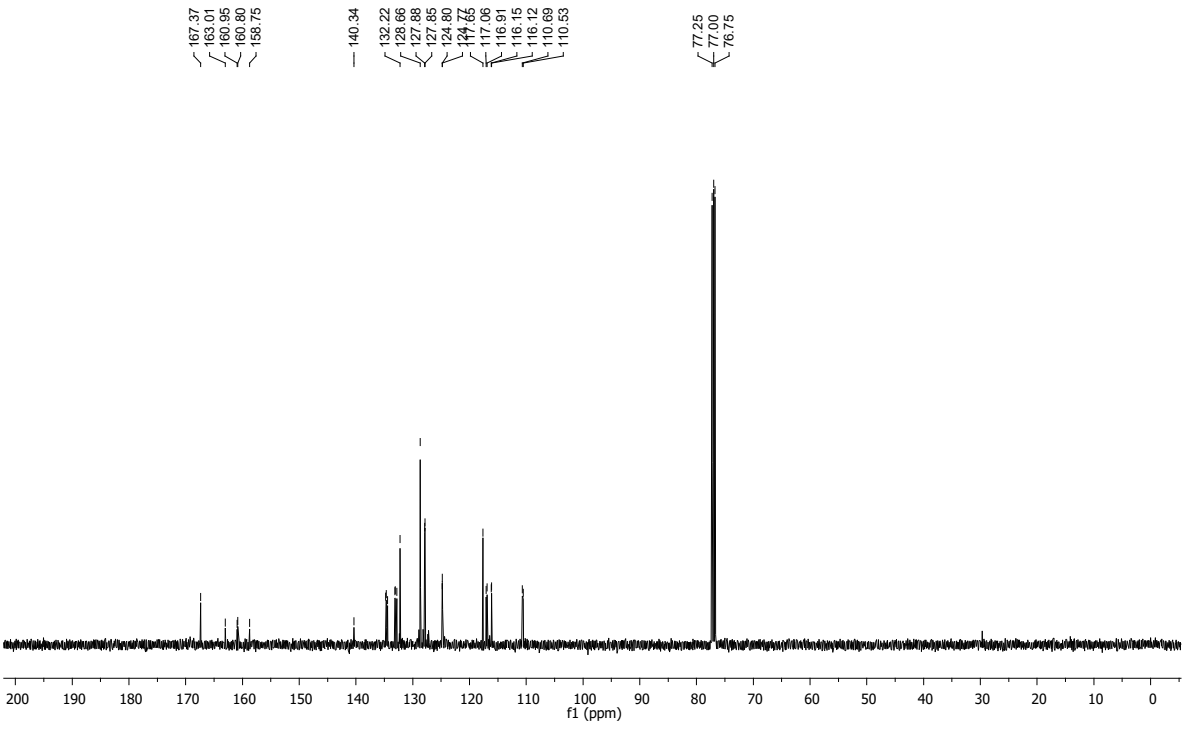
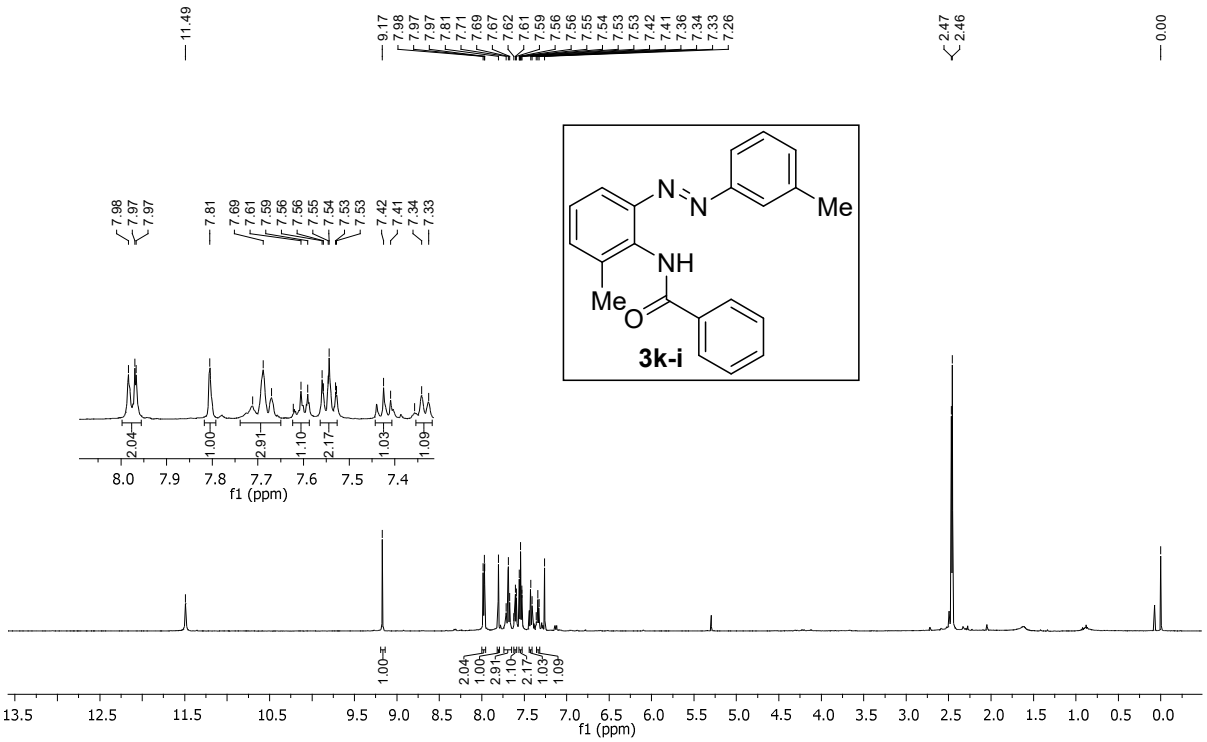




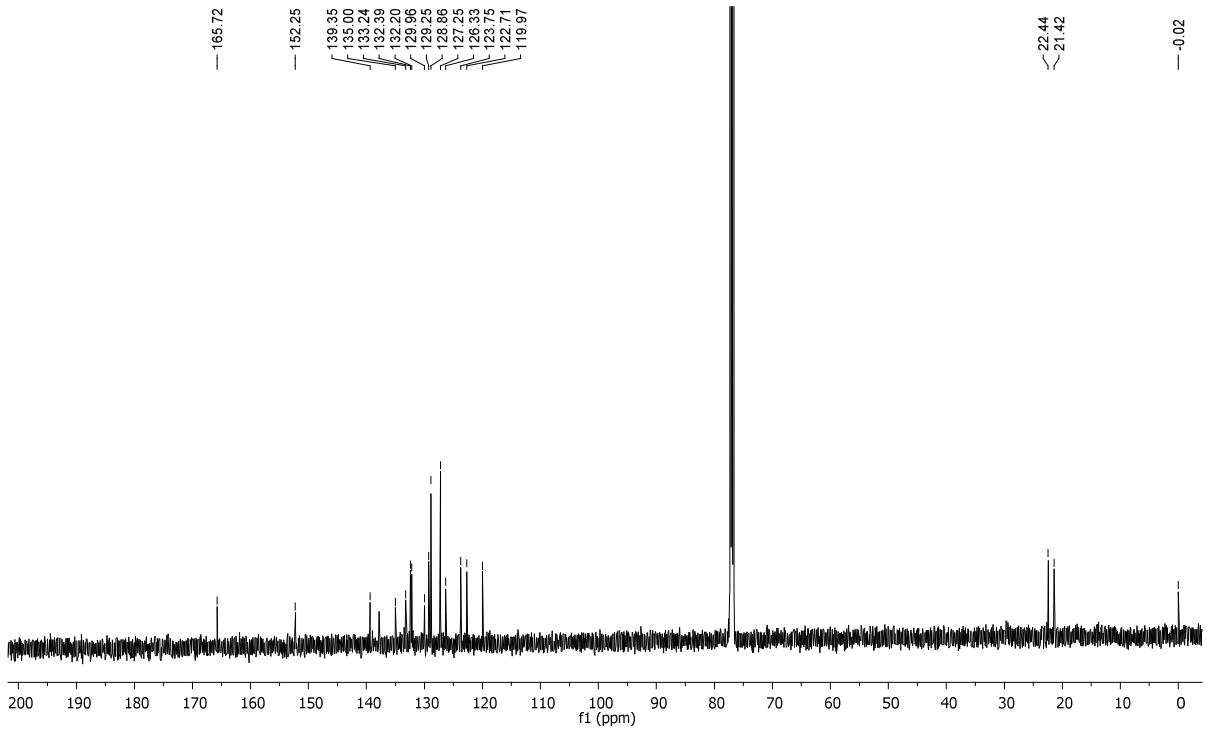
^{13}C NMR of Compound **3j** in $CDCl_3$



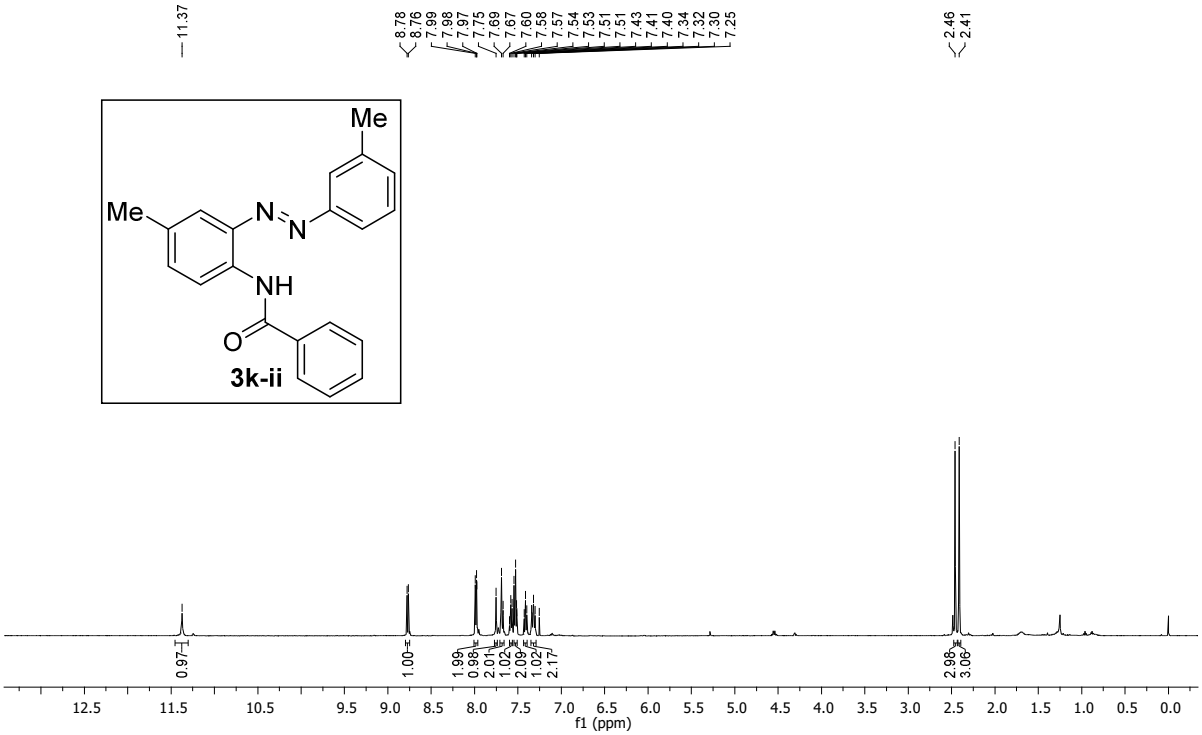
^{1}H NMR of Compound **3k-i** in $CDCl_3$



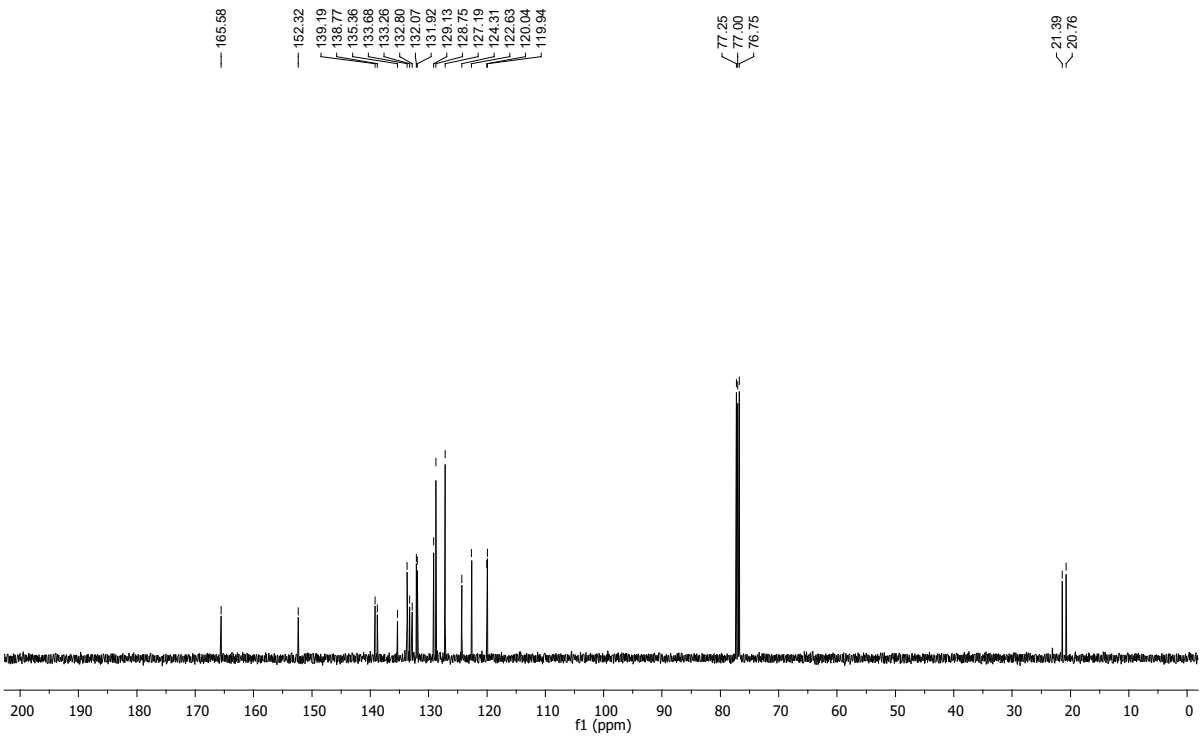
^{13}C NMR of Compound **3k-i** in $CDCl_3$



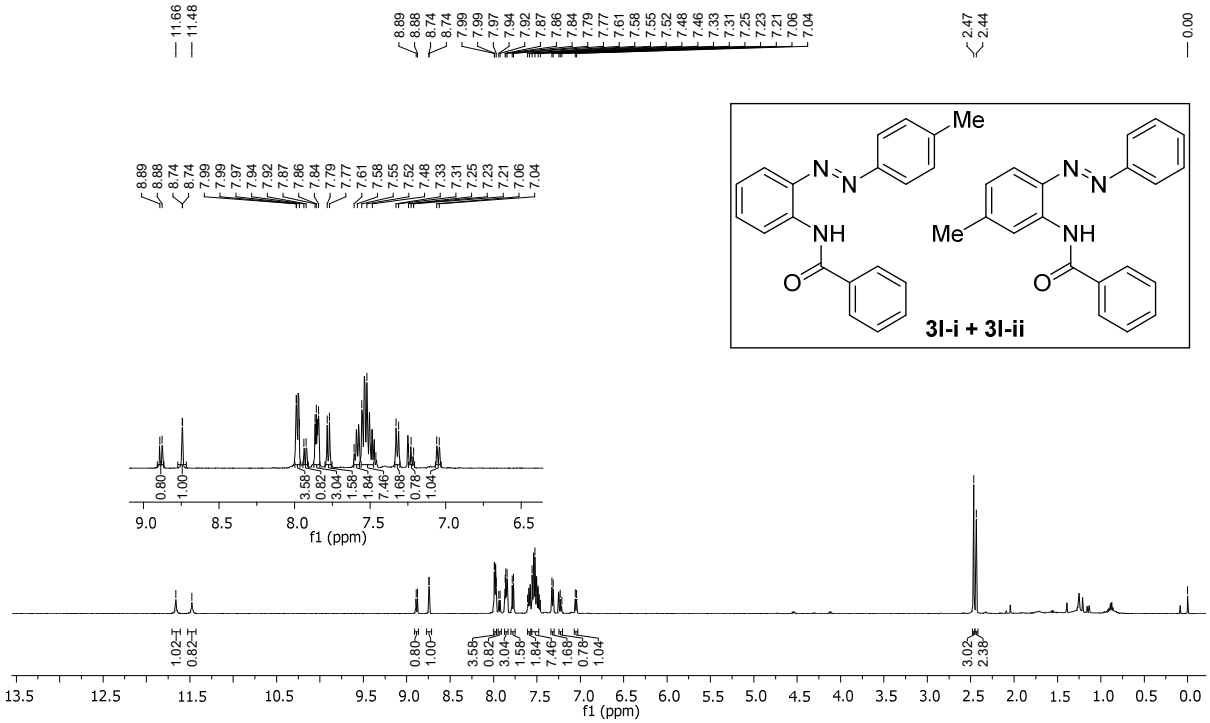
^{1}H NMR of Compound **3K-ii** in $CDCl_3$



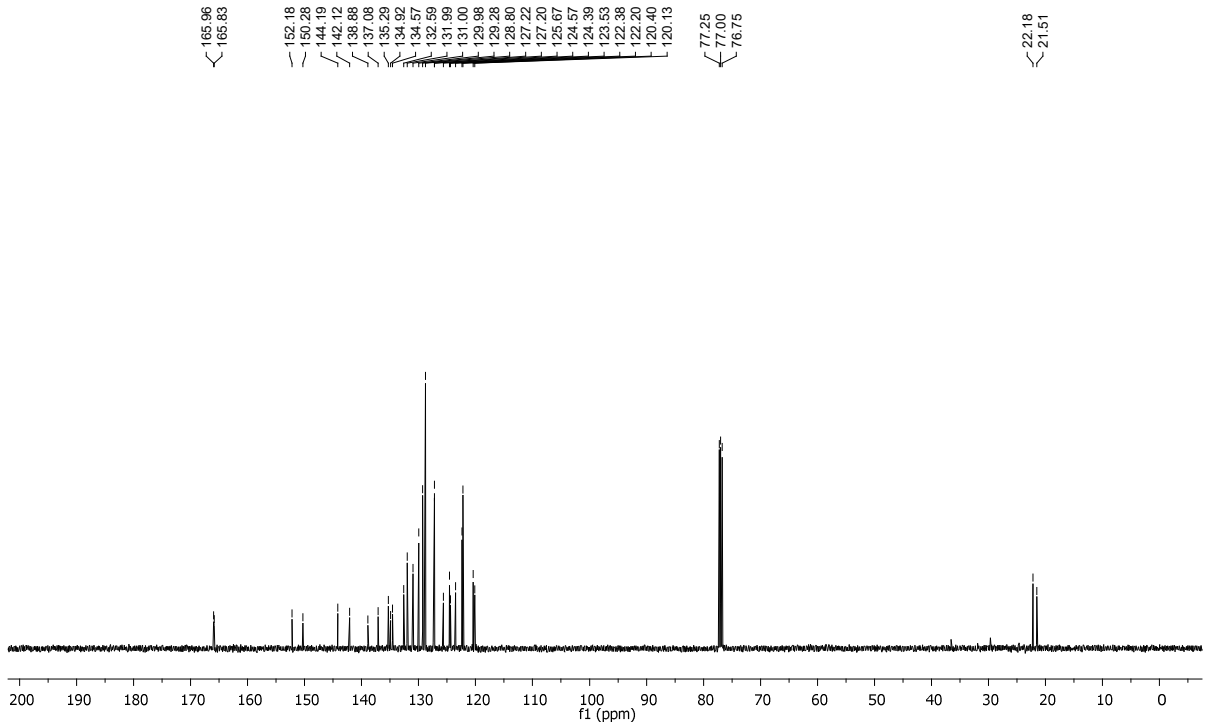
^{13}C NMR of Compound **3k-ii** in $CDCl_3$



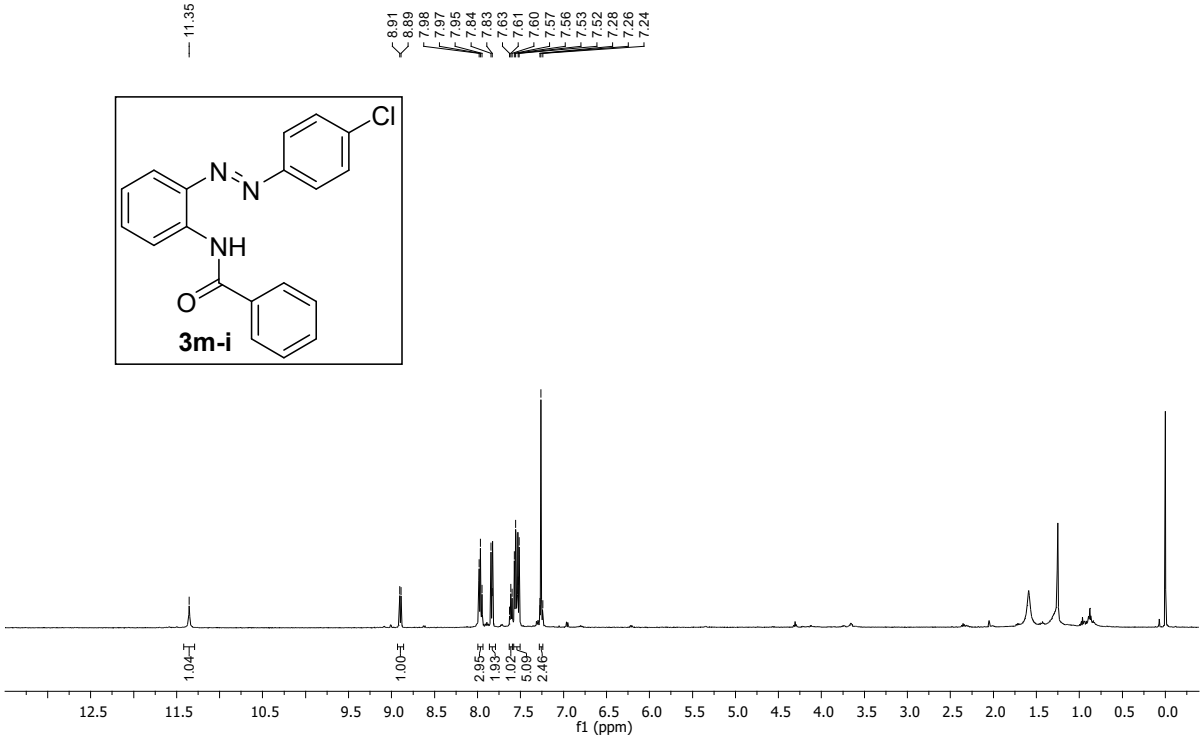
^{1}H NMR of Compound **3l-i + 3l-ii** in $CDCl_3$



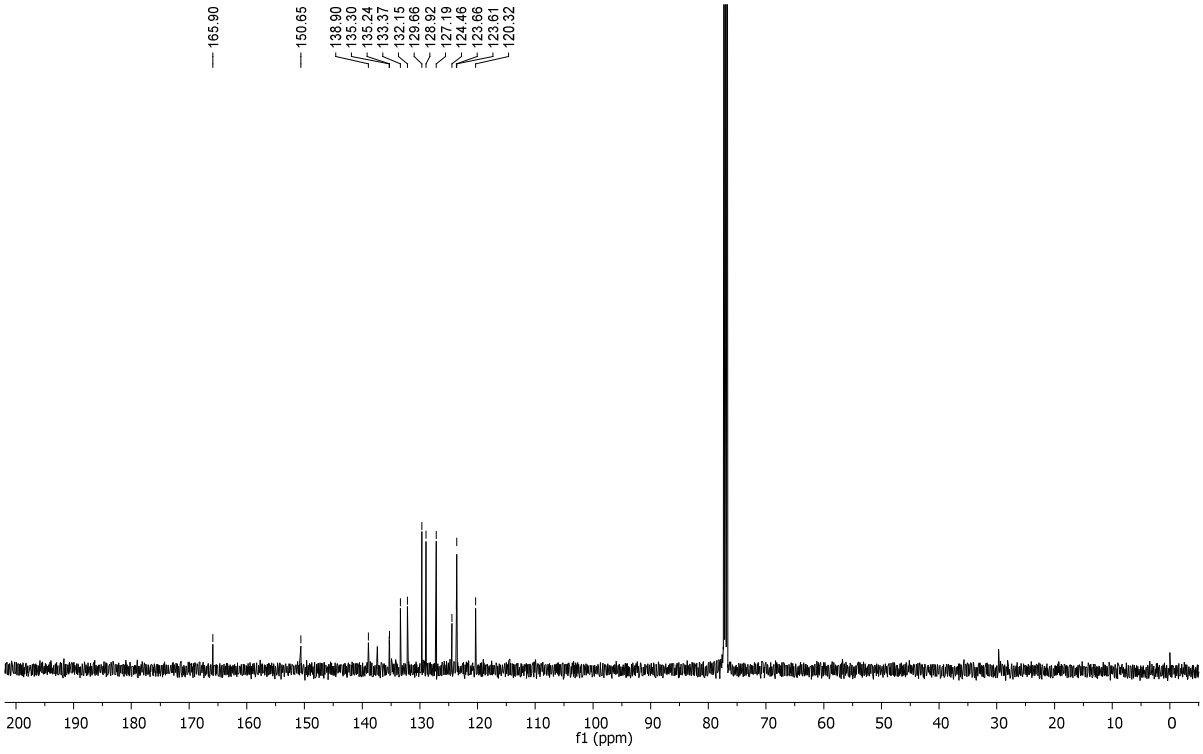
^{13}C NMR of Compound **3l-i + 3l-ii** in $CDCl_3$



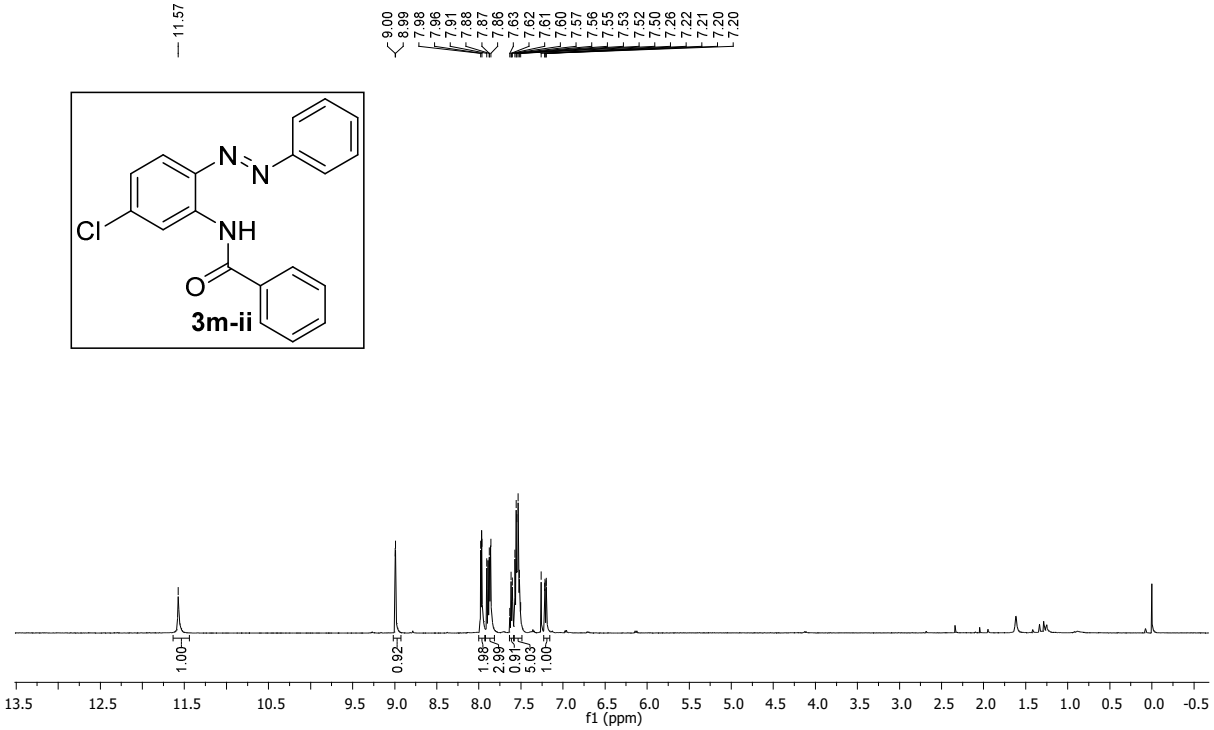
^{1}H NMR of Compound **3m-i** in $CDCl_3$



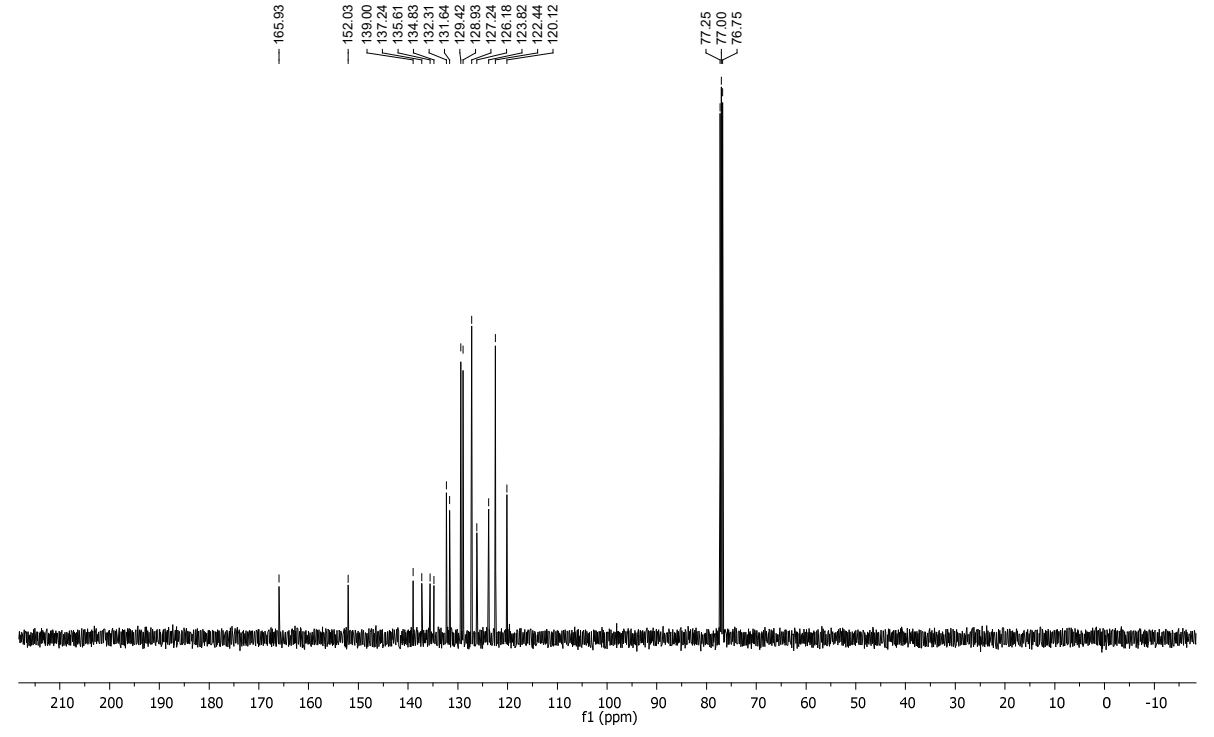
^{13}C NMR of Compound **3m-i** in $CDCl_3$



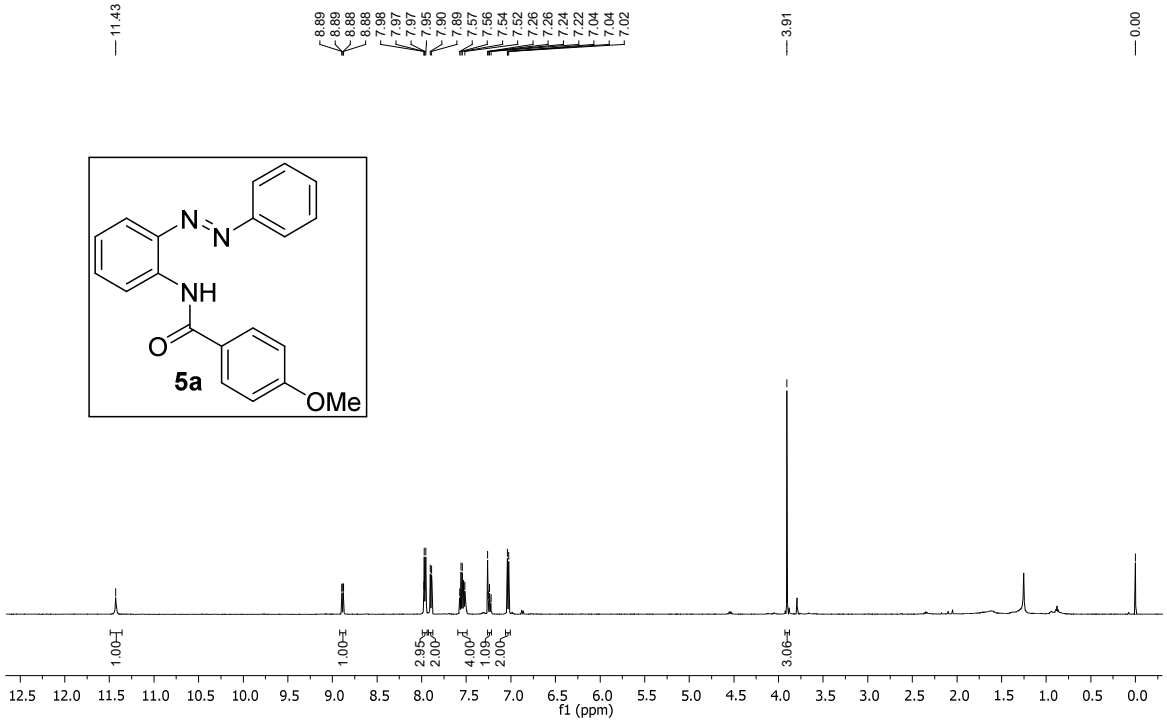
^{1}H NMR of Compound **3m-ii** in $CDCl_3$



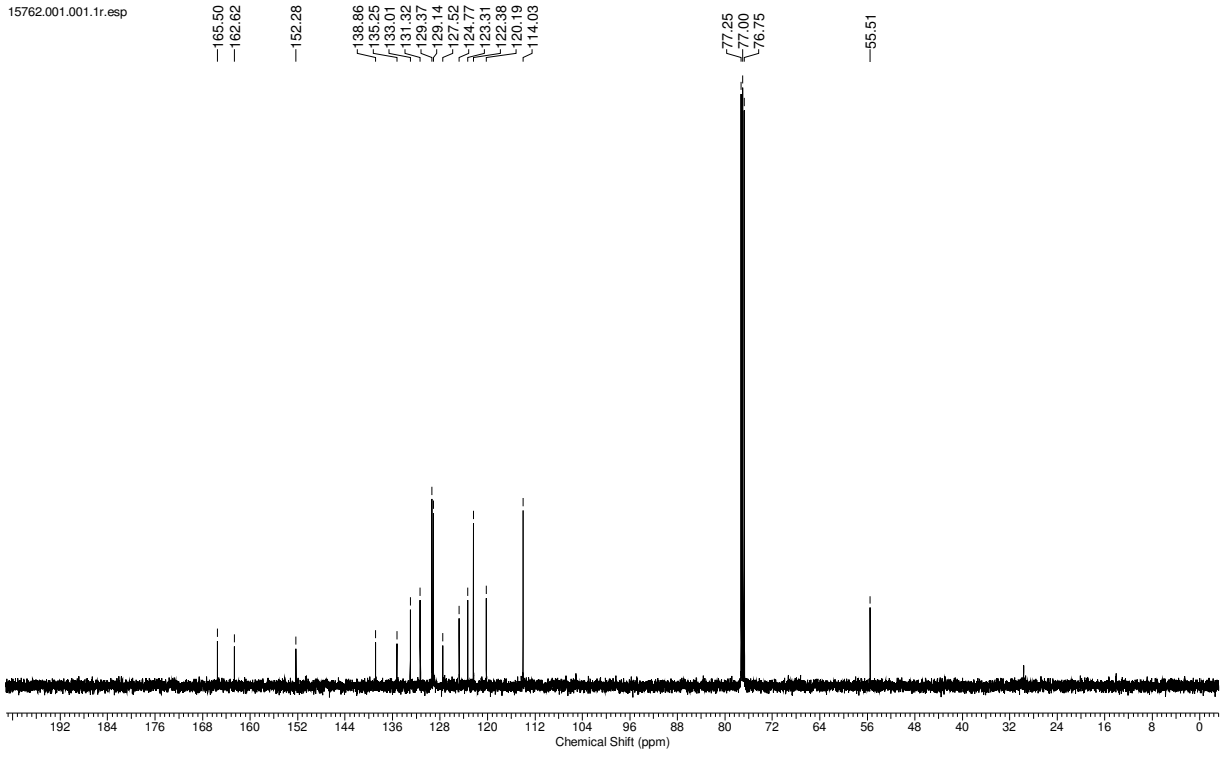
^{13}C NMR of Compound **3m-ii** in $CDCl_3$



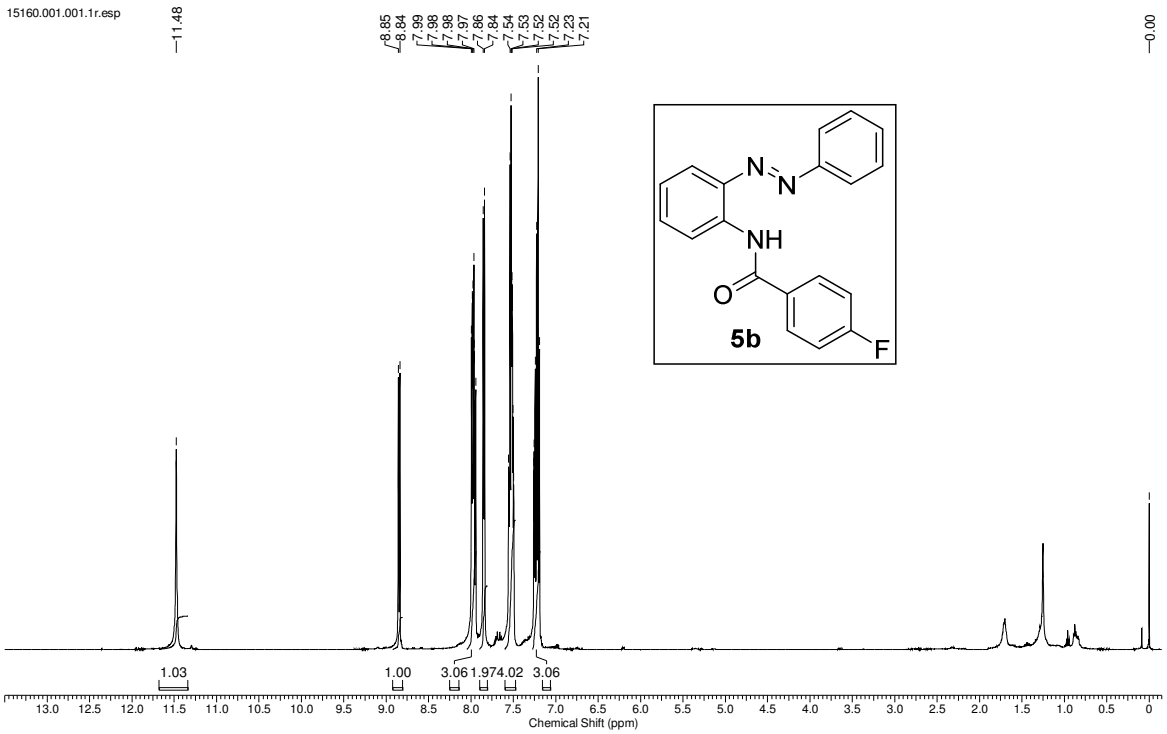
^{1}H NMR of Compound **5a** in $CDCl_3$



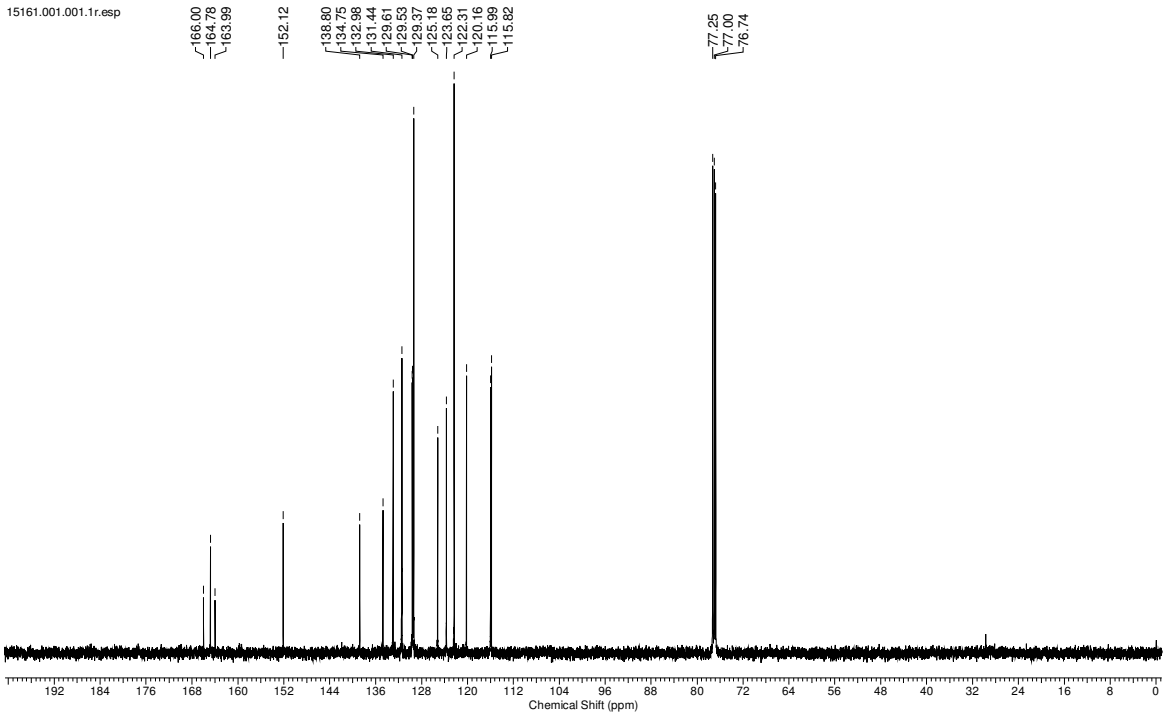
^{13}C NMR of Compound **5a** in $CDCl_3$



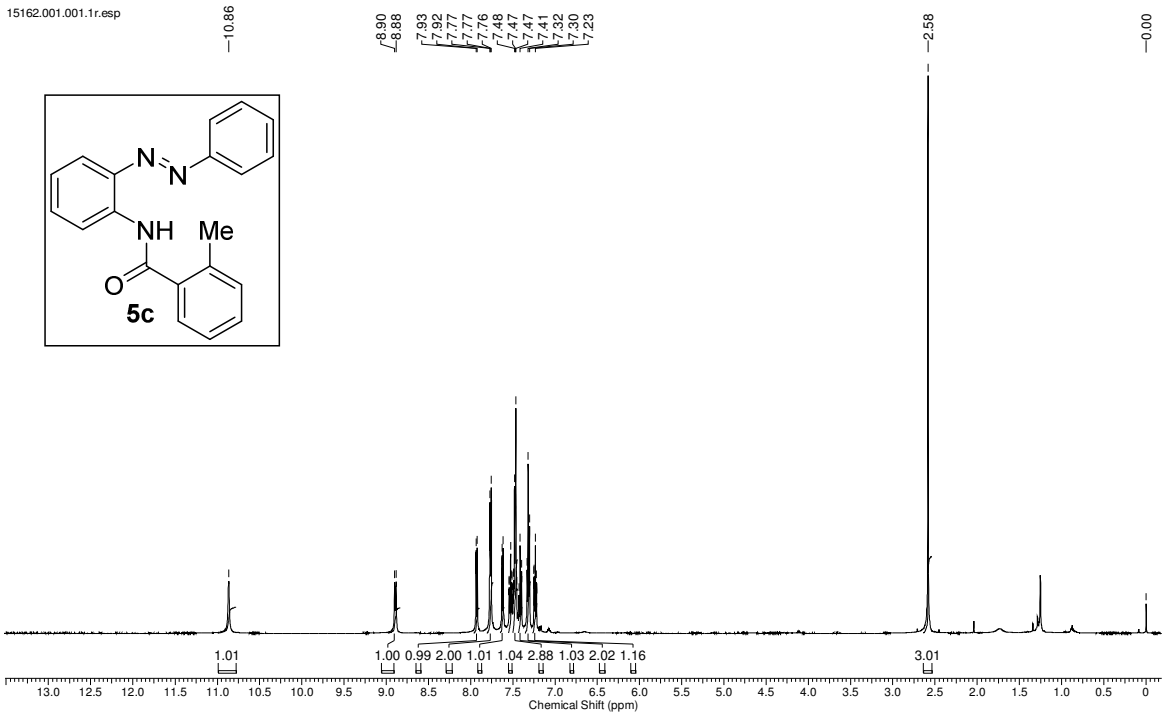
^{1}H NMR of Compound **5b** in $CDCl_3$



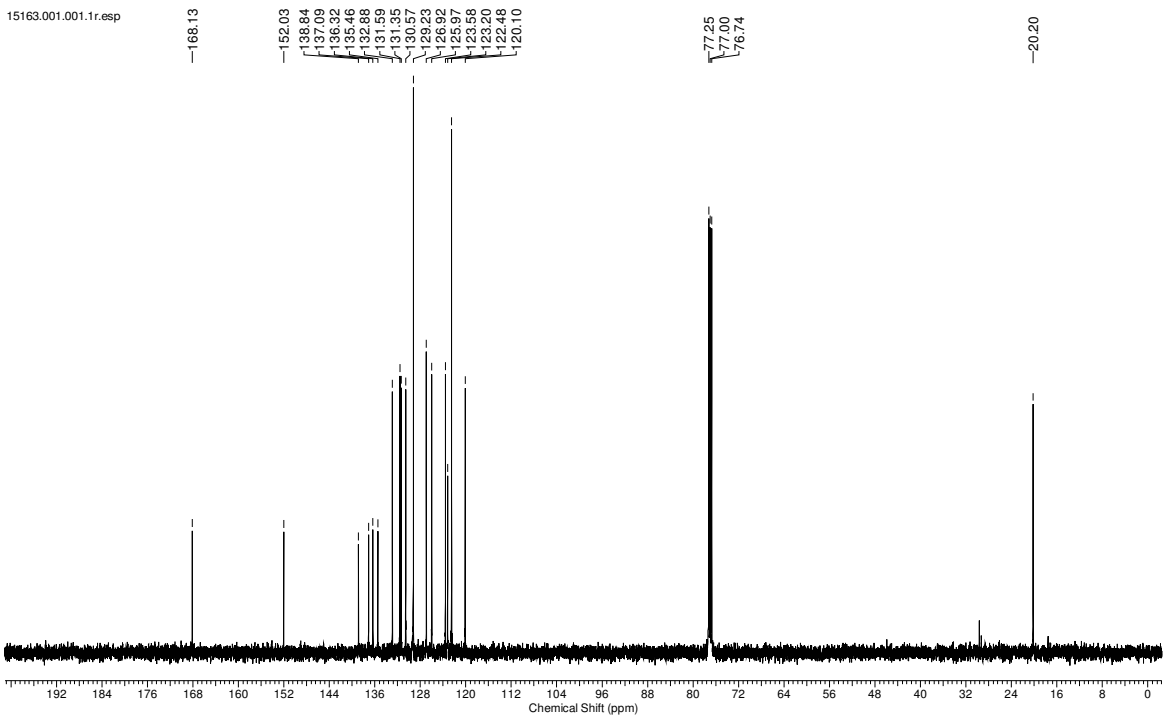
^{13}C NMR of Compound **5b** in $CDCl_3$



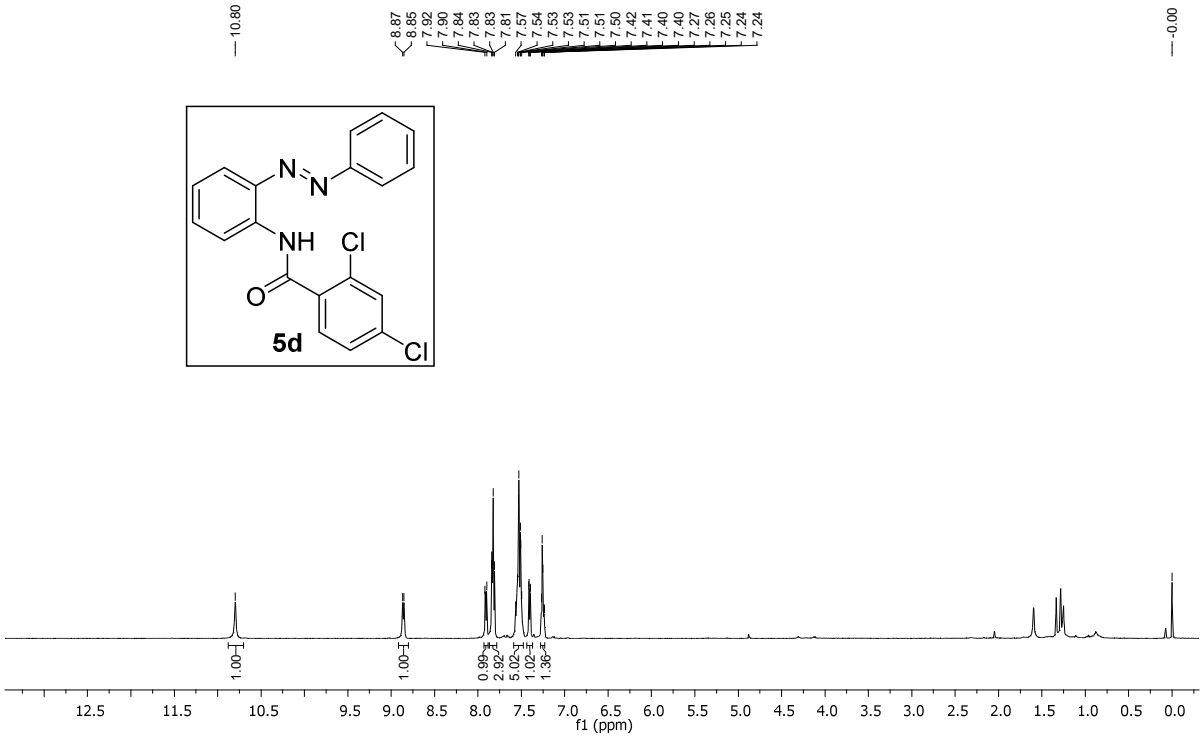
^{1}H NMR of Compound 5**c** in $CDCl_3$



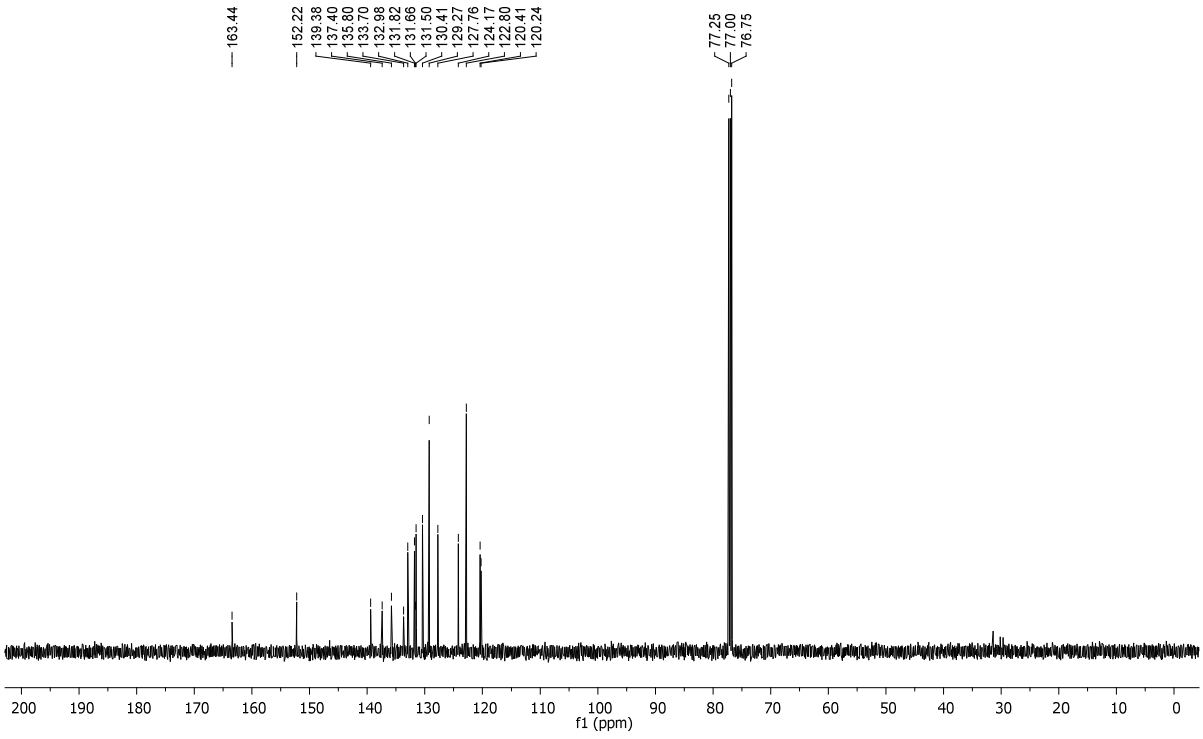
^{13}C NMR of Compound **5c** in $CDCl_3$



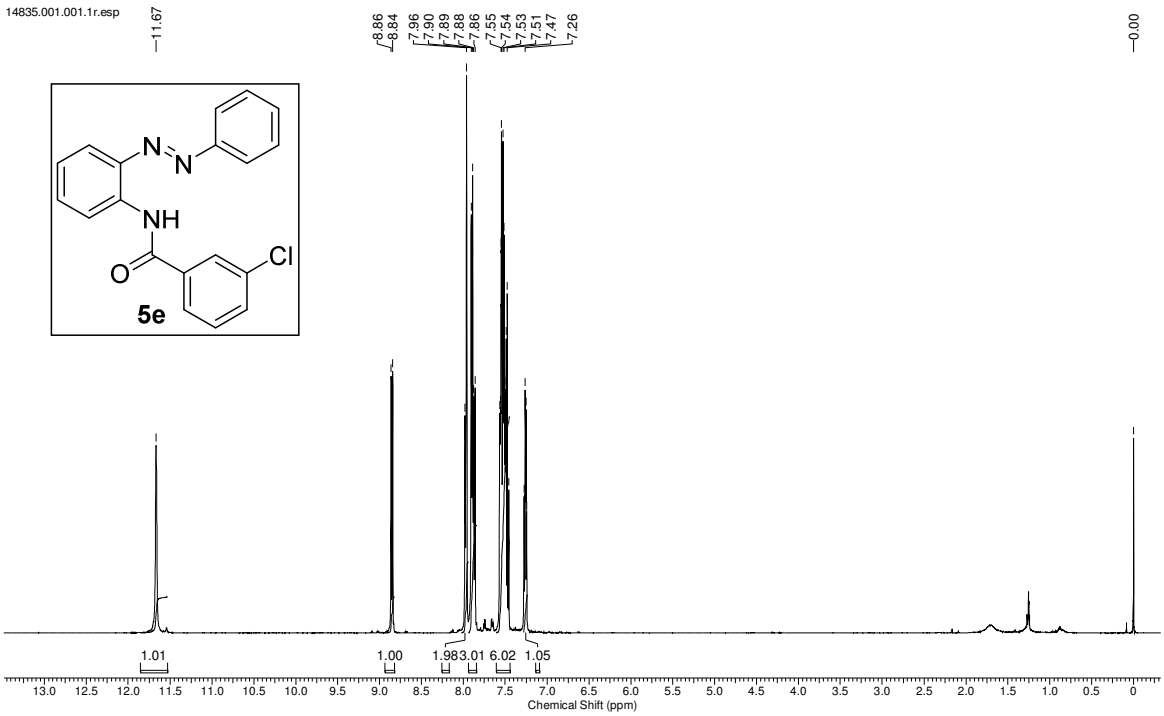
^{1}H NMR of Compound **5d** in $CDCl_3$



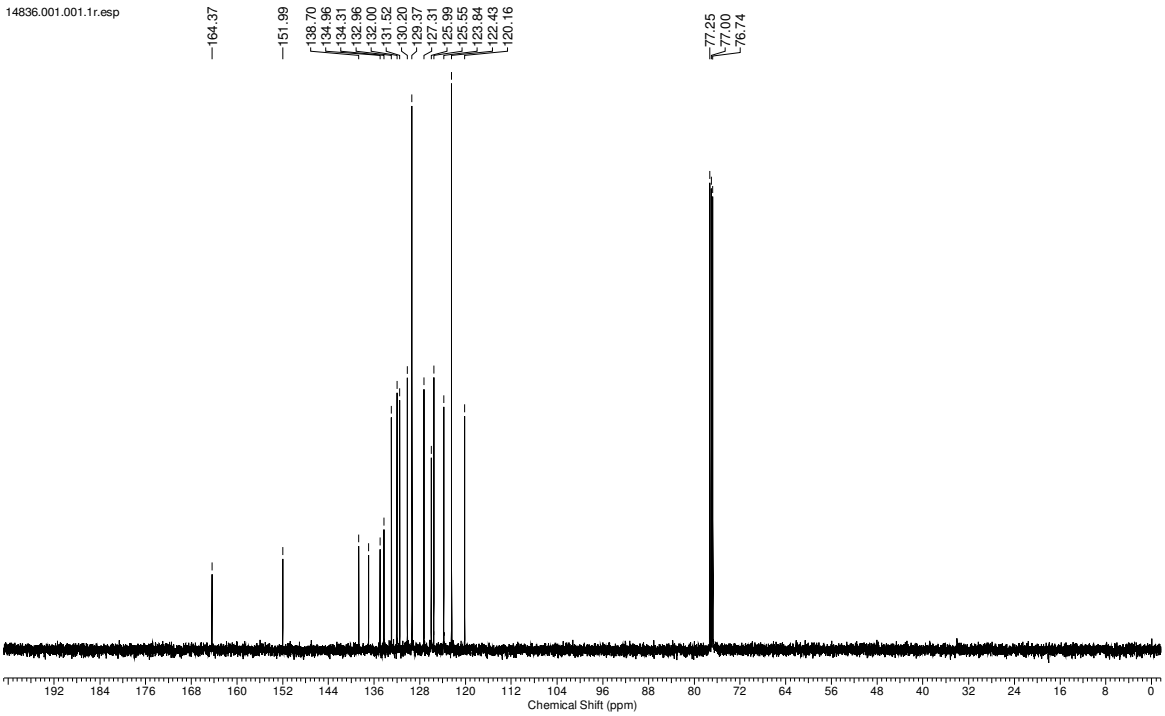
^{13}C NMR of Compound **5d** in $CDCl_3$



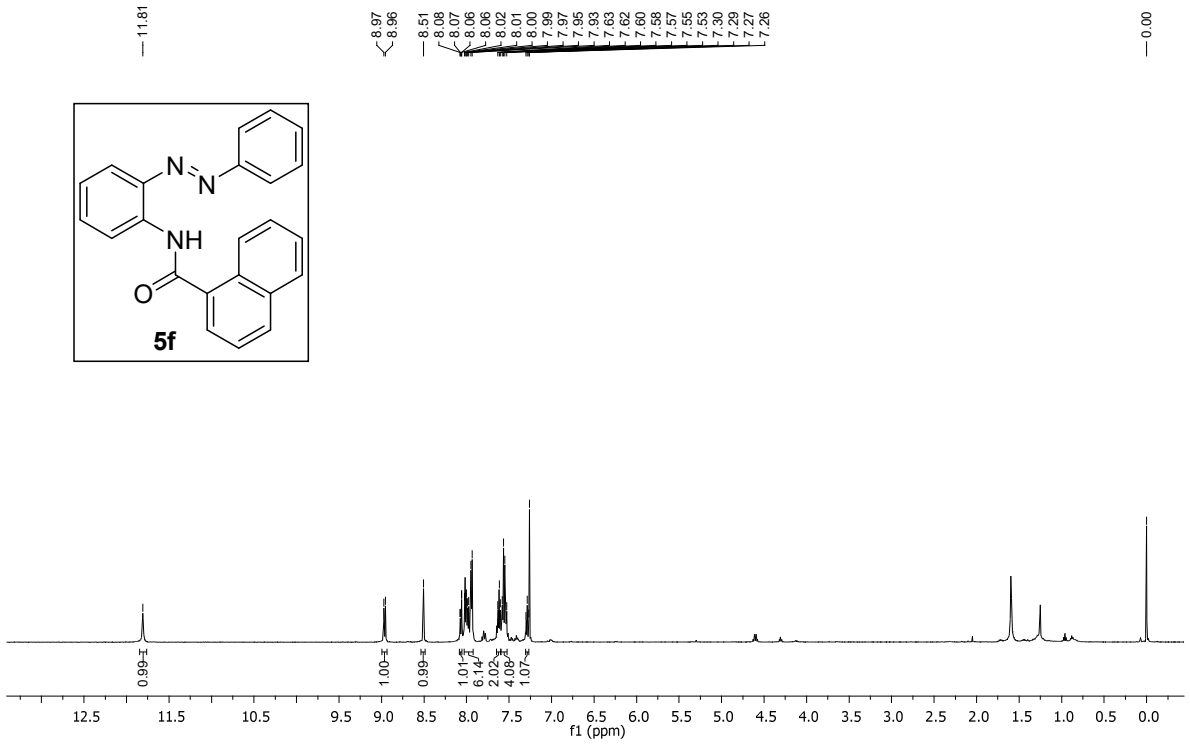
^{1}H NMR of Compound **5e** in $CDCl_3$



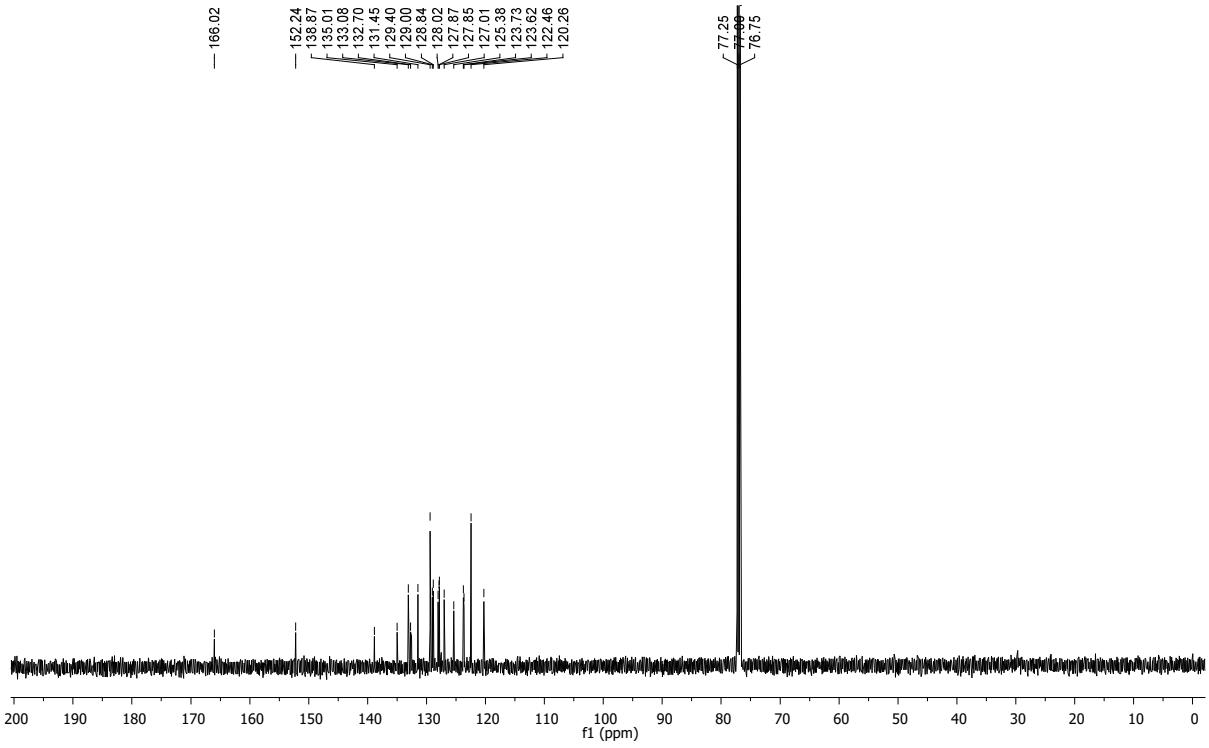
^{13}C NMR of Compound **5e** in $CDCl_3$



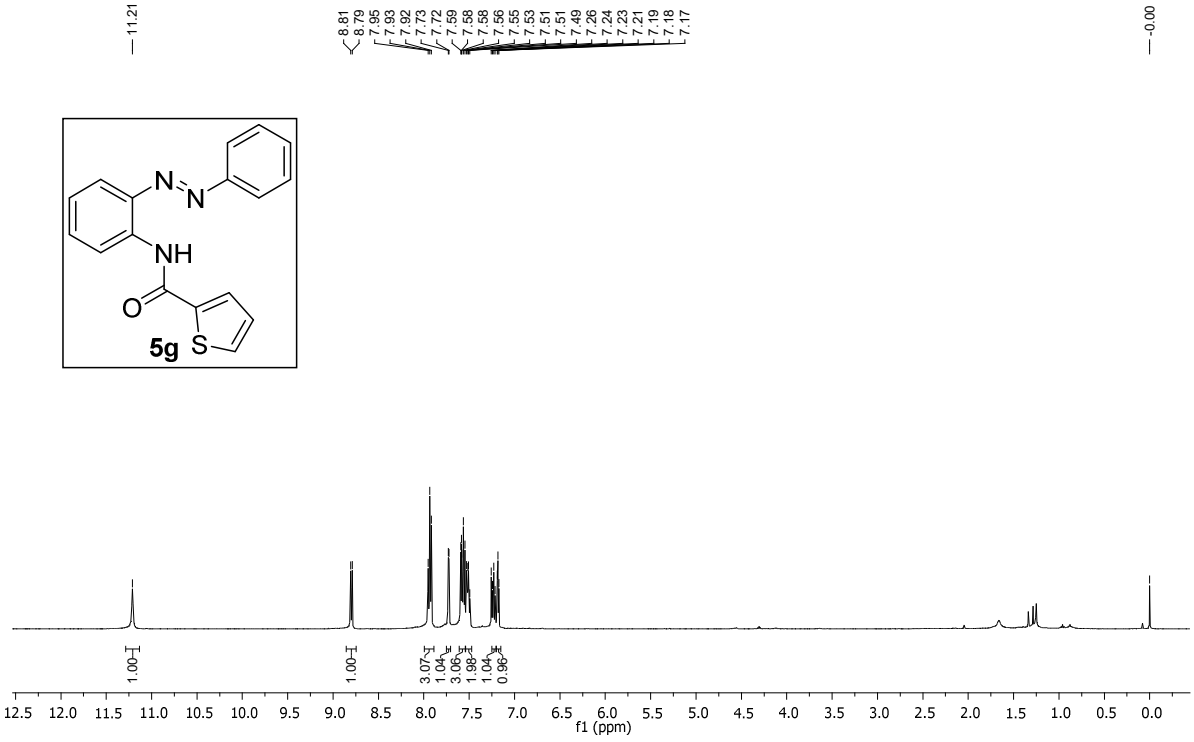
^{1}H NMR of Compound **5f** in $CDCl_3$



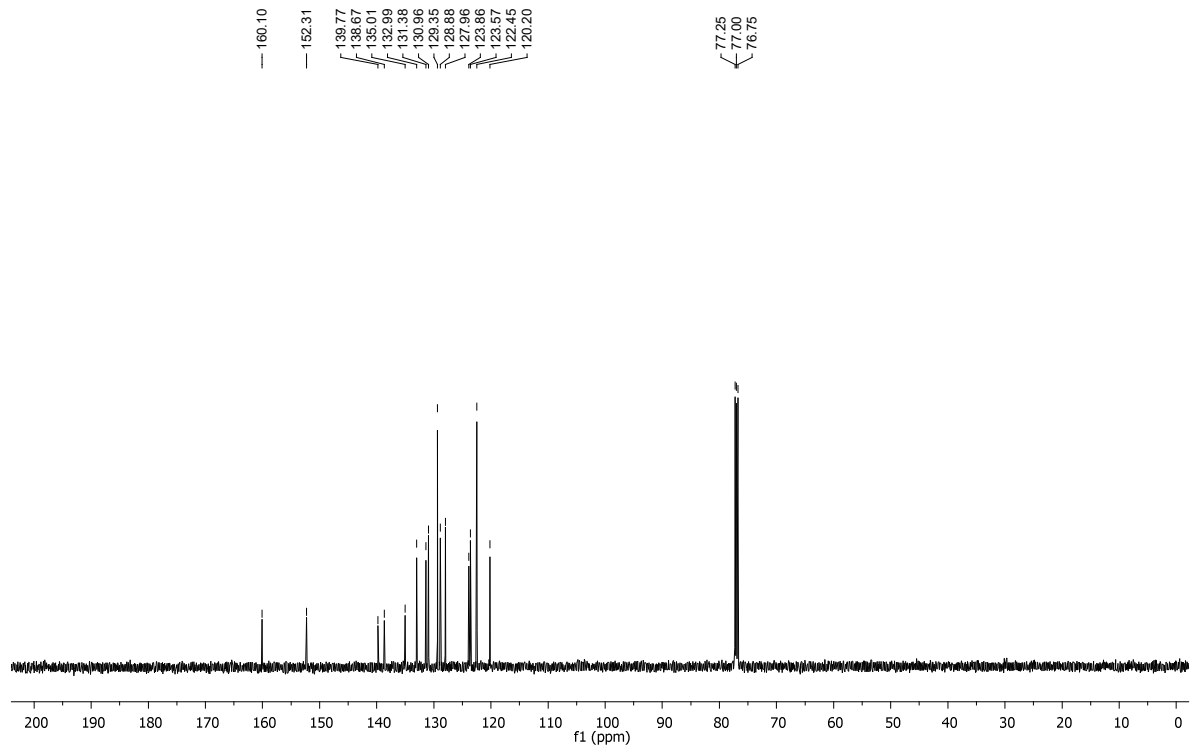
^{13}C NMR of Compound **5f** in $CDCl_3$



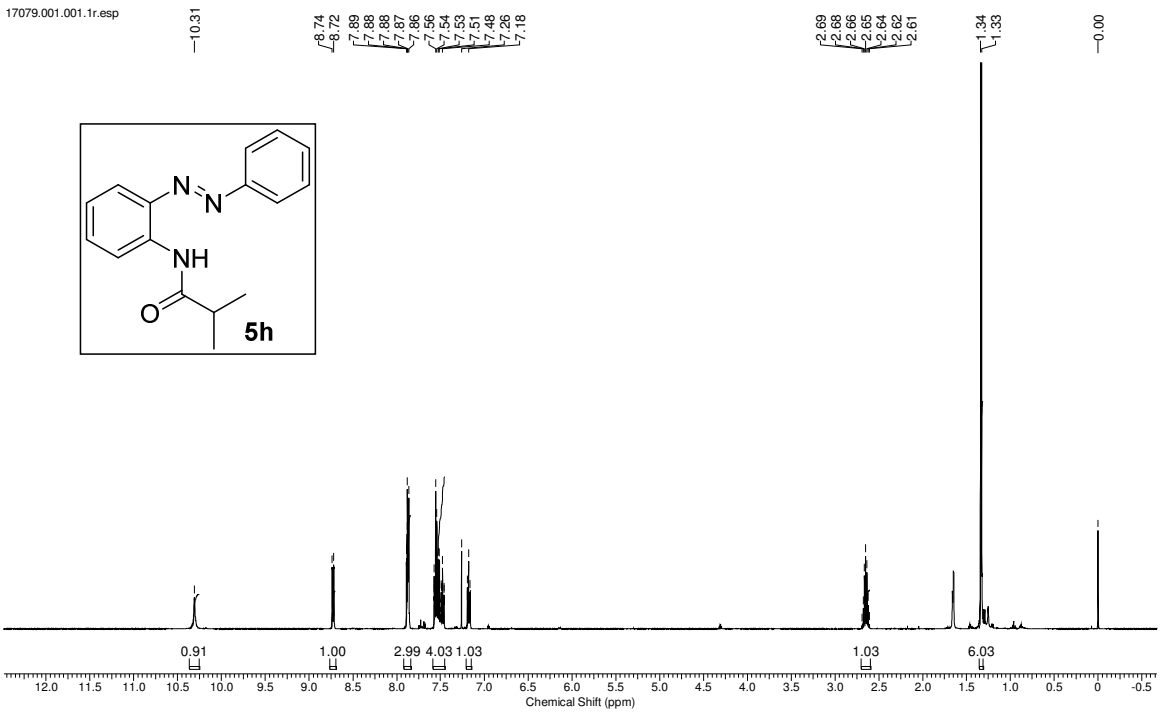
^{1}H NMR of Compound **5g** in $CDCl_3$



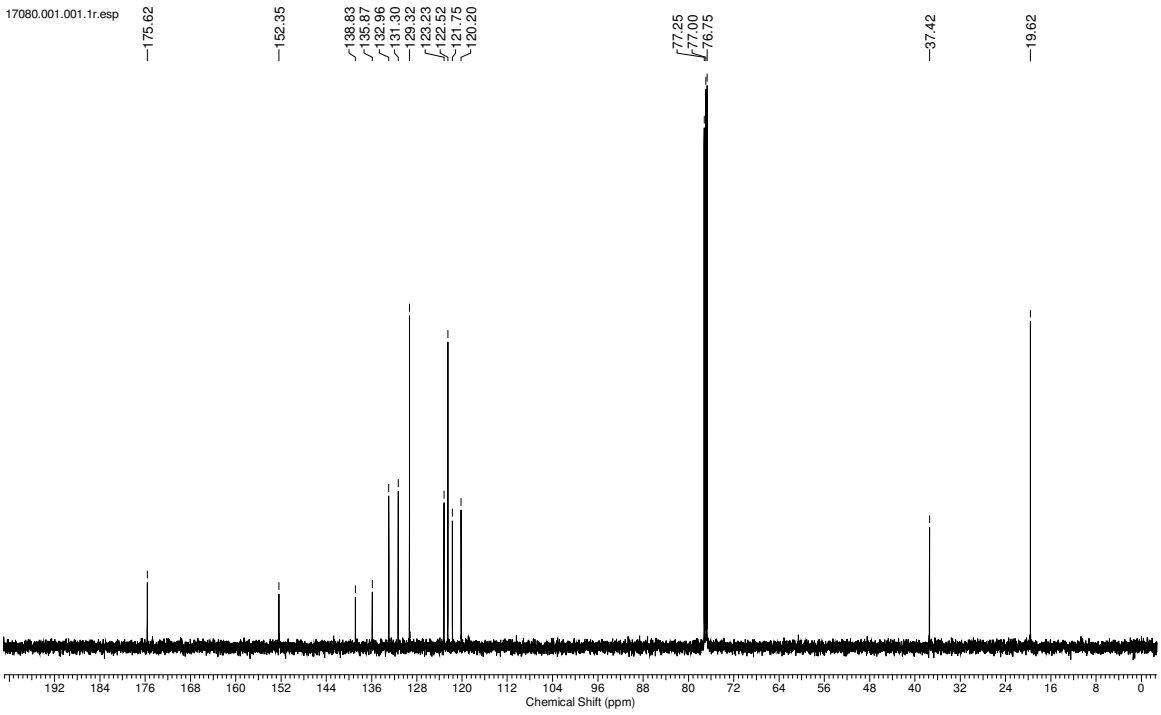
^{13}C NMR of Compound **5g** in $CDCl_3$



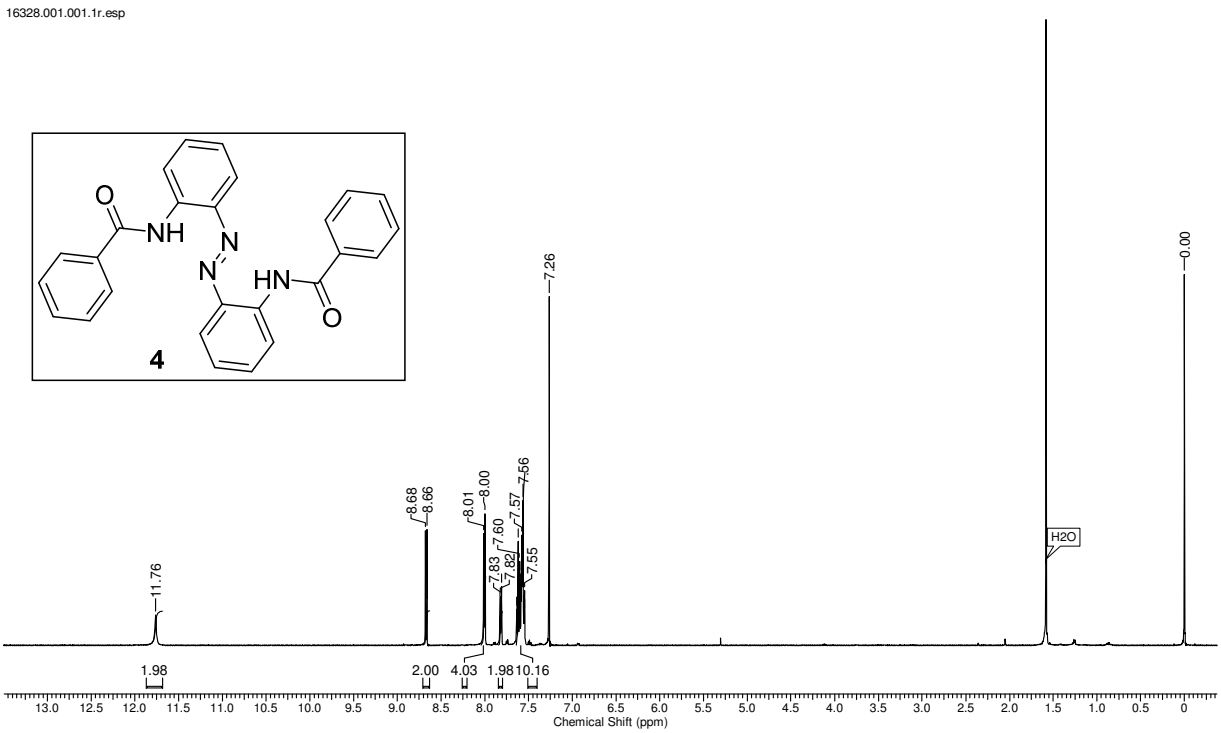
^{1}H NMR of Compound **5h** in $CDCl_3$



^{13}C NMR of Compound **5h** in $CDCl_3$



^{1}H NMR of Compound **4** in $CDCl_3$



^{13}C NMR of Compound **4** in $CDCl_3$