Palladium Nanoparticles for the Synthesis of Phenanthridinones and Benzo[*c*]chromenes via C-H Activation Reaction

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1. General Procedures and Equipment

1.1 General Methods

Purification of desired compounds was carried out by column chromatography on silica gel or by High Performance Liquid Chromatograpy (HPLC) preparative. Gas chromatographic (GC) analysis was performed with a flame-ionization detector, on 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. Gas chromatography-mass spectroscopy (GC-MS) analysis were performed employing an electronic impact (EI) ionization method and a 30 m x 0.32 mm x 0.25 μm column with a 5% phenylpolysiloxane phase. ^{1}H NMR and ^{13}C NMR {1H} spectra were recorded on 400 MHz in spectrometer with $CDCl_3$, acetone-d_6 or DMSO-d_6 as solvents with TMS as internal standard. Coupling constants are given in Hz and chemical shifts are reported in δ values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. All unknown products were further characterized by high resolution mass spectrometry (HRMS). HRMS analyses were carried out using a time-of-flight mass spectrometry (TOF-MS) instrument with an electrospray ionization (ESI) source.

1.2 Materials

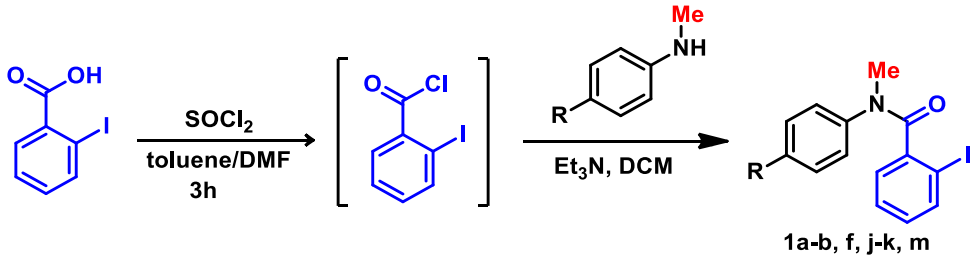
Aniline, *N*-methylaniline, 4-methoxyaniline, 4-methylaniline, 4-*tert*-butylaniline, 1-naphtylamine, 2-chloroaniline, 2-chloro-5-methoxyaniline, 4-(trifluoromethoxy)aniline, 4-fluoroaniline, 4-nitroaniline, 4-bromoaniline, 2-iodoaniline, formaldehyde, 2-iodobenzoic acid, 2-bromobenzoic acid, benzoic acid, triethylamine, methyl iodide, $NaBH_4$, KO^tBu, K_2CO_3, H_2PdCl_4, sodium citrate, polyvinylpyrrolidone (PVP), 4-nitroacetophenone, phenol, 4-(*tert*-butyl)phenol, 2-bromobenzyl bromide, 2-iodobenzyliodide, *p*-cresol, 4-fluorophenol, 4-chlorophenol, 4-nitrophenol, 4-(trifluoromethoxy)phenol, 2,4-di-*tert*-butylphenol, 2-isopropyl-5-methylphenol, 4-hydroxybenzonitrile, 18-crown-6, 2-bromo-4-methylaniline, iodobenzene, NaO^tBu, bis[(2-diphenylphosphino)phenyl] ether (DPEphos), $Pd(OAc)_2$, KOAc and anhydrous Na_2SO_4 were purchased from commercial suppliers and used without further purification. Acetone, DCM, EtOAc and $SOCl_2$, were previously distilled. DMSO and toluene were distilled and dried under molecular sieves (3 Å). DMA, DMF, THF, EtOH, MeOH and MeCN HPLC were previously filtered. All solvents were analytical grade. The silica used in column chromatography corresponds to silica gel 60 (0.063−0.200 mm).

1.3 Typical Procedures for the Synthesis of Compounds 1, 6 and 9

1.3.1. Methylation of Anilines: Employing previously described conditions,[1] Na (10 mmol) was slowly added to MeOH (5 mL). Once the evolution of hydrogen had ceased, the corresponding aniline (1 equiv, 2 mmol) was added following by formaldehyde (1.4 equiv, 2.8 mmol). The mixture was stirred at r. t. for 5 h and then $NaBH_4$ (1 equiv, 2 mmol) was added. The resulting solution was finally heated under reflux during 24-48 h. The reaction mixture was then cooled to room temperature and water was added and the layers separated. The residue was then extracted with EtOAc (3 x 30 mL). The organic layer was washed with water (3 x 20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the reaction crude which was analyzed by TLC, GC and isolated with column chromatography over silica gel.

1.3.2. Synthesis of 2-iodo-*N*-methyl-*N*-phenylbenzamide (1a-1n)

Method A:



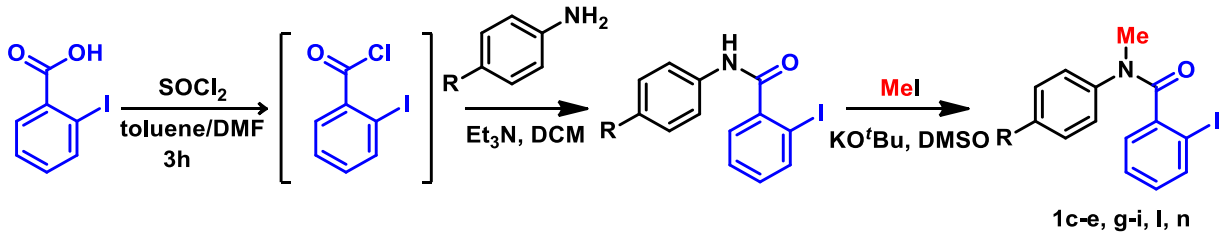
A round-bottomed flask was charged with 2-iodobenzoic acid (1 equiv, 2 mmol) in toluene (5 mL) and cooled to 0°C in an ice bath. To this solution, DMF (0.1 equiv) was added, followed by the dropwise addition of $SOCl_2$ (1.5 equivs). After stirring at 0°C for five minutes, the reaction mixture was placed on an oil bath while maintaining the temperature at 80°C and stirred for another 3 hours at the same temperature.

Upon completion of the reaction, the mixture was cooled and used directly for a nucleophilic acyl substitution reaction, without further purification.

Previously synthesized *N*-methylaniline (1 equiv, 2 mmol, see Section 1.3.1) and triethylamine (3 equivs, 6 mmol) in 10 mL of DCM were added to a round-bottomed flask and cooled to 0°C in an ice bath. After 5 minutes of stirring, the toluene solution of acid chloride (1.0 equiv) was added dropwise to the reaction mixture and allowed to warm to room temperature overnight.

After that, water was added and the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to yield the crude reaction product.

Method B:



A round-bottomed flask was charged with 2-iodobenzoic acid (1 equiv, 2 mmol) in toluene (5 mL) and cooled to 0°C in an ice bath. To this solution, DMF (0.1 equiv) was added, followed by the dropwise addition of $SOCl_2$ (1.5 equivs). After stirring at 0°C for five minutes, the reaction mixture was placed on an oil bath while maintaining the temperature at 80°C and stirred for another 3 h at the same temperature.

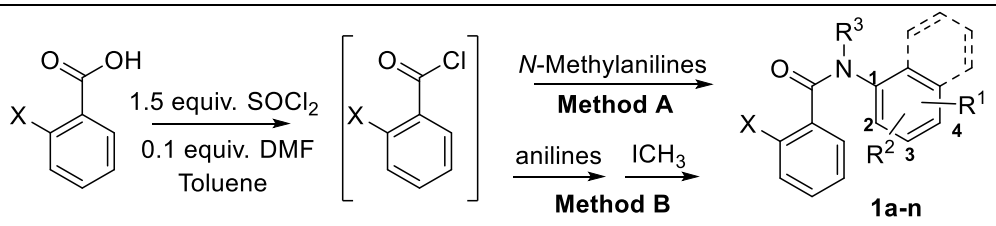
Upon completion of the reaction, the mixture was cooled and used directly for a nucleophilic acyl substitution reaction, without further purification.

Aniline (1 equiv, 2 mmol), triethylamine (3 equiv, 6 mmol), and 10 mL of DCM were added to a round-bottomed flask and cooled to 0°C in an ice bath. After 5 min of stirring, the toluene solution of acid chloride (1.0 equiv) was added dropwise to the reaction mixture and allowed to warm to room temperature.

After that, water was added and the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to yield the crude reaction product. The amide derivative was purified by column chromatography on silica gel eluting with hexane/EtOAc and used without characterization in the methylation reaction to obtain the corresponding *N*-methyl-*N*-phenylbenzamides.

Methylation of Synthetized *N*-phenylbenzamide. The reaction was carried out in a round-bottom flask equipped with a magnetic stirred bar. KO^tBu was added (1.1 equiv) to a solution of previously synthetized *N*-phenylbenzamide (1 equiv) in DMSO (2 mL) and then iodomethane (3 equiv) was slowly added. The resulting mixture was stirred at rt overnight. Water was added, the crude was extracted with EtOAc (3 x 30 mL) and the layers were separated. The organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4 and concentered under reduced pressure to leave the crude products. The reaction was analyzed with TLC, GC and isolated with column chromatography over silica gel.

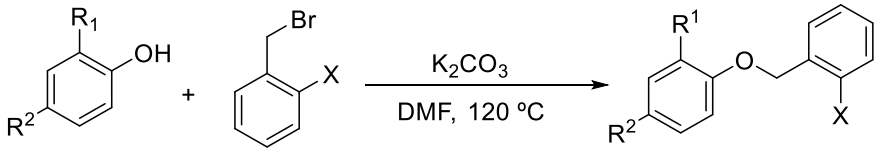
Table S1. Preparation of 2-halo-*N*-methyl-*N*-phenylbenzamides



Entry	X	R^1	R^2	R^3	Method	1, yield (%)[a]
1	I	H	H	Me	A	**1a**, 86
2	Br	H	H	Me	A	**1b**, 68
3	I	H	H	H	B	**1c**, 75
4	H	2-I	H	H	B	**1d**, 53
5	I	4-OMe	H	Me	B	**1e**, 85
6	I	4-Me	H	Me	A	**1f**, 32
7	I	4-^{t}Bu	H	Me	B	**1g**, 73
8	I	1-naphthyl amine		Me	B	**1h**, 89
9	I	2-Cl	H	Me	B	**1i**, 53
10	I	2-Cl	5-OMe	Me	A	**1j**, 78
11	I	4-OCF_3	H	Me	A	**1k**, 44
12	I	4-F	H	Me	B	**1l**, 60
13	I	4-NO_2	H	Me	A	**1m**, 77
14	I	4-Br	H	Me	B	**1n**, 36

[a] Isolated yields.

1.3.3. Synthesis of aryl-2-halobenzyl ethers (6a-k)

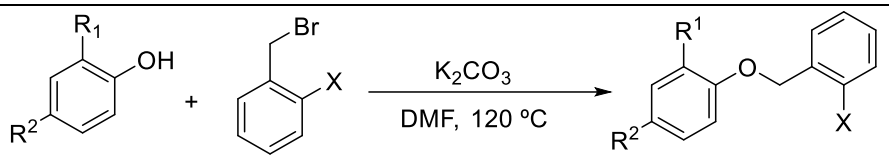


6a-k

To a solution of the corresponding phenol (1 equiv, 2 mmol) with K_2CO_3 (1 equiv, 2 mmol, 276 mg) in DMF (7.2 mL), 18-crown-6 (1 equiv, 2 mmol, 426 µL) and the required 2-halobenzyl bromide (1 equiv, 2 mmol) were added. The mixture was stirred followed by heating to 120 °C for 17 h. The reaction mixture was then cooled to room temperature and water was added and the layers separated. The organic layer was washed with water (3 x 20 mL), dried over Na_2SO_4 and

concentrated under reduced pressure to afford the reaction crude which was analyzed by TLC, GC and isolated with column chromatography over silica gel.

Table S2. Preparation of Compounds 6a-k from the corresponding phenols and 2-halobenzyl bromide. [a]

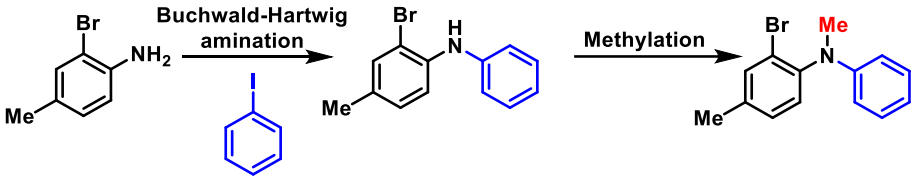


6a-k

Entry	R^1	R^2	X	**6**, yield (%)[b]
1	H	H	Br	**6a**, 53
2	H	H	I	**6b**, 37
3	H	^{t}Bu	Br	**6c**, 48
4	H	Me	Br	**6d**, 53
5	H	F	Br	**6e**, 32
6	H	Cl	Br	**6f,** 33
7	H	NO_2	Br	**6g**, 52
8	H	CF_3	Br	**6h**, 77
9	^{t}Bu	^{t}Bu	Br	**6i**, 58
10	^{i}Prop	Me	I	**6j**, 46
11	H	CN	Br	**6k**, 94

Conditions: [a] Phenol (1 equiv) in DMF with K_2CO_3 (1 equiv) and 18-crown-6 (1 equiv) is treated with benzyl halide (1 equiv) at 120 °C for 24 h. [b] Isolated yields.

1.3.4. Synthesis of 2-bromophenyl-*N*-methylanilines 9:



Buchwald–Hartwig amination:[2] An oven-dried Schlenk tube was charged with 2-bromo-4-methylaniline (1.2 equiv, 2.4 mmol), $Pd(OAc)_2$ (0.010 mmol), and DPEphos (0.015 mmol), then evacuated and filled with nitrogen. Iodobenzene (1 equiv, 2 mmol) was added to the flask via syringe, followed by toluene (4 mL). The resulting mixture was stirred for 5 min at room temperature, affording a clear yellow solution. The flask was opened, solid NaO^{t}Bu (1.4 equiv, 2.8 mmol) was added in one portion, and the solution turned a deep red. The reaction tube was purged for 3 min with nitrogen, and the mixture was heated with stirring to 100 °C until the iodobenzene was consumed as judged by GC analysis. The mixture was then cooled to room temperature and taken up in methylene chloride. The resulting solution was dried over anhydrous

sodium sulfate, filtered, and concentrated. The amide derivative was purified by column chromatography on silica gel eluting with hexane/EtOAc and used without characterization.

Methylation of Synthetized 2-bromo-4-methyl-*N*-phenylaniline. The reaction was carried out in a round-bottom flask equipped with a magnetic stirred bar. KO^{t}Bu was added (1.1 equiv) to a solution of previously synthetized 2-bromo-4-methyl-*N*-phenylaniline (1 equiv) in DMSO (2 mL) and then iodomethane (3 equiv) was slowly added. The resulting mixture was stirred at rt overnight. Water was added, the crude was extracted with EtOAc (3 x 30 mL) and the layers were separated. The organic layers extracted were combined, washed with water, dried with anhydrous Na_2SO_4 and concentered under reduced pressure to leave the crude products. The reaction was analyzed with TLC, GC and isolated with column chromatography over silica gel.

1.4. Synthesis of the Pd nanoparticle suspension (Pd-PVP NPs)

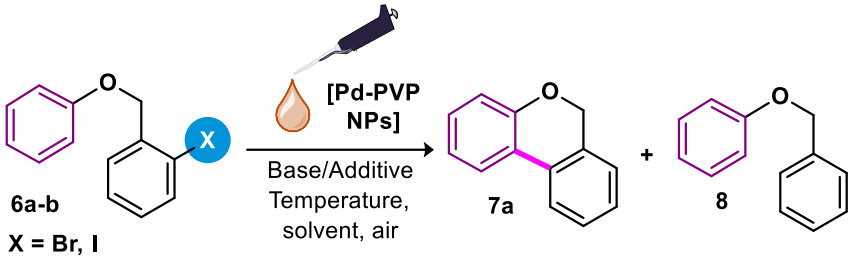
The Pd-PVP NPs synthesis was performed following the procedure previously described.[3] Into a 10 mL scintillation vial equipped with a magnetic stirrer, 44.0 mg PVP (2% w/v), 11.0 mg of sodium citrate (molar ratio Pd^{2+}: citrate = 1:10) and 2 mL of a feedstock aqueous solution of H_2PdCl_4 (2 mM) were placed. Then, the vial was sealed and high purity nitrogen was bubbled for 5 min to saturate the solution. The reaction mixture was irradiated under vigorous magnetic stirring for 1 hour in a photochemical reactor equipped with a 3 W Blue LED (462 nm). The color of the mixture changed to the characteristic dark brown of Pd NPs. Finally, the vial was opened to the air, and the Pd–PVP NPs dispersion was stored in a Falcon tube to be used as a catalyst without further purification. The Pd NPs were characterized by transmission electron microscopy (TEM) using a JEM-JEOL 1120 microscope operating at 80 kV, available at the Research Institute IPAVE-INTA-CIAP in Córdoba, Argentina.

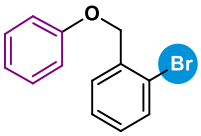
1.5. Intramolecular arylation reactions catalyzed by Pd-PVP NPs

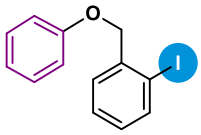
General procedure to obtain Phenanthridinones (2a-2n): In a 10 mL screw-cap reaction tube were added *N*-methyl-*N*-phenyl-2-iodobenzamide **1a** (0.2 mmol), K_2CO_3 (3 equiv.), DMA (2 mL), 1 mL of Pd-PVP NPs solution 2 mM (1 mol%), and 1 mL of water. The reaction mixture was heated to 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and water (5 mL) and ethyl acetate (5 mL) were added. It was extracted with ethyl acetate (3 x 10 mL) and the organic layer was washed with water (3 x 10 mL). Finally, the organic phase was dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the reaction crude which was analyzed by TLC, GC and ^{1}H NMR.

General procedure to obtain Benzo[*c*]chromenes (7a-7k): In a 10 mL screw-cap reaction tube were added 2-bromobenzyl phenyl ether **6a** (0.2 mmol), K_2CO_3 (3 equiv.), DMA (2 mL), and 2 mL of Pd-PVP NPs solution 5 mM (5 mol%). The reaction mixture was heated to 100 °C for 48 h. Then, the reaction mixture was cooled to room temperature and water (5 mL) and ethyl acetate (5 mL) were added. It was extracted with ethyl acetate (3 x 10 mL) and the organic layer was washed with water (3 x 10 mL). Finally, the organic phase was dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the reaction crude which was analyzed by TLC, GC and ^{1}H NMR.

Table S3. **Optimization of reaction conditions to obtain benzo[*c*]chromenes 7a**.[a]



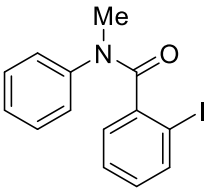
Entry	Substrate	Catalyst (mol %)	Solvent (1:1)	Additive/base	Temp. (°C)	Time (h)	7a (%)[b]	8a (%)[b]
1		--	H_2O:DMA	K_2CO_3	100	48	--	--
2		5	H_2O:DMA	K_2CO_3	100	48	62	7
3		2	H_2O:DMA	PivOH/K_2CO_3	140	72	22	8
4		2	H_2O:DMSO	PivOH/K_2CO_3	140	72	6	7
5		2	DMA	PivOH/K_2CO_3	140	72	7	10
6		2	H_2O:DMA	PivOH/K_2CO_3	140	48	32	34
7		2	H_2O:DMA	PivOH/K_2CO_3	140	24	29	19
8		2	H_2O:DMA	PivOH/K_2CO_3	140	48	56	28
9		2	H_2O:DMA	PivOH/K_2CO_3	110	48	26	15
10		2	H_2O:DMA	KOAc	140	48	18	16
11		5	H_2O:DMA	K_2CO_3	140	48	52	30

12		5	H_2O:DMA	PivOH/K_2CO_3	140	43	15	22

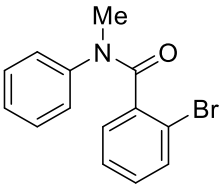
[a] Reactions were carried out under air atmosphere using **6a-b** (1 equiv, 0.2 mmol), base (3 eq.), 0.3 equiv additive (when was added) and solvent (4 mL), heating in an oil bath for the time indicated. [b] Yields were quantified by ^{1}H NMR using 4-nitroacetophenone as standard.

General procedure to obtain carbazole (10): In a 10 mL screw-cap reaction tube were added 2-bromophenyl-*N*-methylaniline **9** (0.1 mmol), K_2CO_3 (3 equiv.), DMA (2 mL), and 1 mL of Pd-PVP NPs solution 5 mM (5 mol%). The reaction mixture was heated to 120 °C for 72 h. Then, the reaction mixture was cooled to room temperature and water (5 mL) and ethyl acetate (5 mL) were added. It was extracted with ethyl acetate (3 x 10 mL) and the organic layer was washed with water (3 x 10 mL). Finally, the organic phase was dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the reaction crude which was analyzed by TLC, GC and ^{1}H NMR.

2. Characterization data of 2-halo-*N*-methyl-*N*-phenylbenzamides (1a-n), aryl-2-halobenzyl ethers (6a-k) and *N*-methyl aryl amine (9)

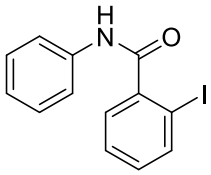


2-Iodo-*N*-methyl-*N*-phenylbenzamide (1a).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5→70:30). A mixture of rotamers (5:1) as a brown solid was obtained in 86% yield (579.9 mg, 1.72 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.10 (m, 6H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.2 Hz, 1 H), 3.52 (s, 3H); minor isomer: δ 7.88 (m, 1 H), 7.48 – 7.30 (m, 8H), 3.20 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer δ 170.1, 143.3, 142.4, 139.1, 129.7, 128.9, 128.5, 127.2, 127.1, 127.0, 93.6, 37.2. **GC/MS (EI)** *m/z* 337 (M^+, 34), 231 (100), 210 (47), 203 (22), 105 (20), 104 (23), 77 (59), 76 (76).

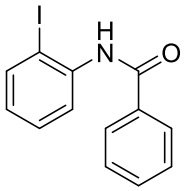


2-Bromo-*N*-methyl-*N*-phenylbenzamide (1b).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (100:0→80:20). A mixture of rotamers (6:1) as a brown oil was obtained in 68% yield (205 mg, 1.09 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ 7.38 – 6.99 (m, 9H), 3.51 (s, 3H); minor isomer: δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.38 – 6.99 (m, 8H), 3.20 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer δ 168.7, 143.1, 138.4, 132.5, 129.7, 129.0, 128.8, 127.1, 126.8, 126.6, 119.7, 37.1. **GC/MS (EI)** *m/z* 291 (M^+ + 2,

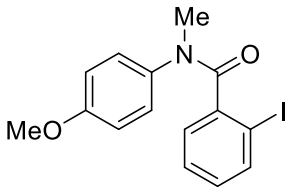
21), 289 (M^+, 22), 210 (36), 185 (95), 183 (100), 157 (31), 155 (33), 105 (16), 104 (26), 78 (14), 77 (83), 76 (55), 75 (45), 51 (35), 50 (30).



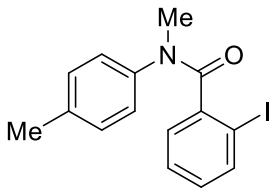
2-Iodo-*N*-phenylbenzamide (1c).[5] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (80:20) as a light-yellow solid was obtained in 75% yield (184 mg, 0.57 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.52 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.20 – 7.11 (m, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 167.2, 142.1, 140.0, 137.5, 131.5, 129.1, 128.5, 128.4, 124.9, 120.1, 92.3. **GC/MS (EI)** *m/z* 323 (M^+, 45), 231 (92), 203 (22), 196 (25), 105 (21), 77 (49), 76 (100), 75 (13), 65 (21), 51 (27), 50 (37).



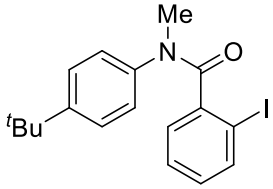
***N*-(2-Iodophenyl)benzamide (1d).**[6] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (80:20) as a light-yellow solid was obtained in 53 % yield (171.2 mg, 0.53 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.30 (s br, 1H), 8.02 – 7.90 (m, 2H), 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.57 – 7.51 (m, 2H), 7.48 – 7.36 (m, 1H), 6.89 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 165.3, 138.8, 138.3, 134.5, 132.2, 129.4, 129.0, 127.2, 126.0, 121.7, 90.2. **GC/MS (EI)** *m/z* 323 (M^+, 2), 196 (35), 106 (7), 105 (92), 91 (12), 77 (100), 76 (6), 65 (7), 64 (12), 63 (10), 51 (33), 50 (10).



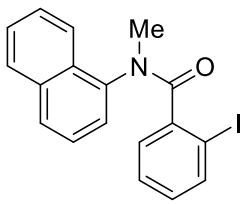
2-Iodo-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (1e).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (100:0→50:50). A mixture of rotamers (6:1) as a light-yellow oil was obtained in 85% yield (312.1 g, 0.85 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer: δ 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.15 – 7.09 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.84 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.71 – 6.67 (m, 2H), 3.71 (s, 3H), 3.47 (s, 3H); minor isomer: δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.15 – 7.14 (m, 1H), 6.97 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 3.15 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 170.4, 158.3, 142.7, 139.1, 136.2, 129.5, 128.4, 128.2, 127.3, 114.1, 93.5, 55.3, 37.6. **GC/MS (EI)** *m/z* 368 (M^+ +1, 12), 367 (M^+, 71), 244 (33), 240 (11), 231 (100), 203 (19), 136 (14), 120 (23), 92 (13), 77 (23), 76 (52), 65 (11), 50 (18).



2-Iodo-*N*-methyl-*N*-(*p*-tolyl)benzamide (1f).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→60:40). A orange oil was obtained in 32% yield (99 mg, 0.28 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer: δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.07 – 7.03 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.85 (td, *J* = 7.7, 1.8 Hz, 1H), 3.48 (s, 3H), 2.23 (s, 3 H); minor isomer δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 3H), 7.27 – 7.25 (m, 1H), 7.14 – 7.10 (m, 1H), 3.17 (s, 3H), 2.38 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 170.4, 142.8, 140.9, 139.2, 137.1, 129.8, 129.7, 128.7, 127.4, 126.9, 93.8, 37.6, 21.1. **GC/MS (EI)** *m/z* 351 (M^+, 53), 231 (100), 224 (38), 203 (24), 119 (14), 118 (15), 91 (54), 77 (35), 76 (84), 75 (10), 65 (30), 51 (17), 50 (28).

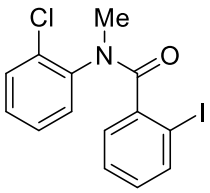


***N*-(4-(*tert*-Butyl)phenyl)-2-iodo-*N*-methylbenzamide (1g).** Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (80:20→60:40). A mixture of rotamers (3.5:1) as a light-yellow oil was obtained in 73% yield (353 mg, 0.97 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer: δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 – 7.07 (m, 3H), 7.02 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.84 (td, *J* = 7.6, 1.7 Hz, 1H), 3.49 (s, 3H), 1.21 (s, 9H); minor isomer: δ 7.86 (d, *J* = 8.0, 1H), 7.48 – 7.36 (m, 7H), 3.18 (s, 3H), 1.34 (s, 9H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 170.3, 150.1, 142.4, 140.5, 139.1, 129.6, 128.5, 127.2, 126.4, 125.8, 93.7, 37.4, 34.4, 31.1. **GC/MS (EI)** *m/z* 394 (M^+ +1, 13), 393 (M^+, 60), 378 (18), 250 (10), 244 (37), 231 (100), 210 (50), 203 (24), 146 (16), 105 (10), 91 (17), 77 (28), 76 (54), 57 (26), 50 (12). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{21}INO$ 394.0662, found 394.0668.

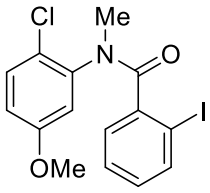


2-Iodo-*N*-methyl-*N*-(naphthalen-1-yl)benzamide (1h). Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→70:30). A mixture of rotamers (5.5:1) as a brown solid was obtained with an overall yield of 89% (45.8 mg, 0.12 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer: δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.56 – 7.51 (m, 2H), 7.29 – 7.25 (m, 1H), 6.84 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.77 (td, *J* = 7.5, 1.3 Hz, 1H), 6.71 (td, *J* = 7.6, 1.8 Hz, 1H), 3.58 (s, 3H); minor isomer: δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.59 – 7.51 (m, 5H), 7.29 – 7.21 (m, 1H); 7.20 – 7.14 (m, 1H), 3.27 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 171.0, 142.1, 139.7, 139.2, 134.4, 129.7, 128.7, 128.6, 127.3, 126.9, 126.5, 126.5, 125.8, 125.5,

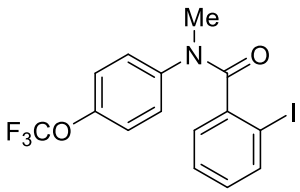
125.1, 122.8, 93.9, 37.5. **CG/MS (EI)** *m/z* 387 (M^+, 42), 245 (12), 244 (78), 231 (100), 203 (26), 154 (18), 128 (23), 127 (26), 77 (24), 76 (70), 75 (12), 50 (20). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}INO$ 388.0193, found 388.0198.



***N*-(2-Chlorophenyl)-2-iodo-*N*-methylbenzamide (1i).** Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→70:30). A mixture of rotamers (4.1:1) as a yellow oil was obtained in 74% yield (268.5 mg, 0.72 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.35 – 7.32 (m, 1H), 7.18 – 7.02 (m, 4H), 6.84 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H), 3.42 (s, 3H); minor isomer: δ 7.88 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.48 – 7.30 (m, 4H), 7.17 – 7.05 (m, 1H), 3.12 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 170.1, 141.9, 140.9, 139.2, 132.3, 130.3, 130.1, 130.0, 129.4, 127.8, 127.4, 126.6, 93.8, 36.0. **CG/MS (EI)** *m/z* 371 (M^+, 1), 337 (16), 336 (99), 230 (61), 203 (19), 111 (7), 104 (9), 78 (6), 77 (49), 76 (100), 75 (25), 74 (9), 63 (10), 51 (20), 50 (38). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{14}H_{12}ClINO$ 371.9647, found 371.9652.

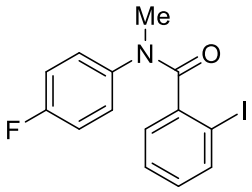


***N*-(2-Chloro-5-methoxyphenyl)-2-iodo-N-methylbenzamide (1j).** Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→60:40). A mixture of rotamers (5: 1) as a brown oil was obtained in 78% yield (312 mg, 0.78 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ 7.70 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 (d, *J* = 3.0 Hz, 1H), 6.87 (td, *J* = 7.6, 1.8 Hz, 1H), 6.66 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.69 (s, 3H), 3.41 (s, 3H); minor isomer: δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.45 (td, *J* = 7.4, 0.9 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.14 – 7.10 (m, 1H), 7.04 – 7.03 (m, 1H), 6.87 – 6.86 (m, 1H), 3.96 (s, 3H), 3.83 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer: δ 170.1, 158.7, 142.1, 141.3, 139.1, 130.6, 130.4, 130.2, 127.6, 126.7, 116.4, 114.4, 93.8, 55.8, 35.9. **GC/MS (EI)** *m/z* 401 (M^+, 1), 367 (18), 366 (100), 238 (6), 231 (27), 203 (12), 77 (18), 76 (55), 75 (8), 63 (10), 51 (9), 50 (18). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{15}H_{14}ClINO_2$ 401.9752, found 401.9757.

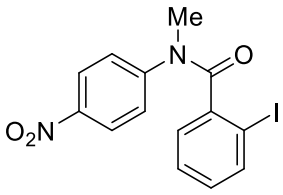


2-Iodo-*N*-methyl-*N*-(4-(trifluoromethoxy)phenyl)benzamide (1k). Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→60:40). A brown oil was obtained in 44% yield (185 mg, 0.44 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 3H), 6.92 – 6.86 (m, 1H), 3.51 (s, 3H); minor isomer: δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.43

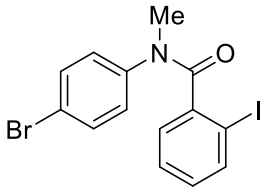
(m, 3H), 7.41 – 7.28 (m, 3H), 7.23 – 7.10 (m, 1H), 3.19 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer δ 170.1, 147.6, 142.1, 141.8, 139.3, 130.0, 128.5, 127.5, 121.3, 120.3 (q, *J*= 259.8 Hz), 93.5, 37.4. **GC/MS (EI)** *m/z* 421 (M^+, 45), 231 (100), 203 (20), 95 (13), 77 (26), 76 (85), 75 (15), 50 (27). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{15}H_{12}F_3INO_2$ 421.9859, found 421.9865.



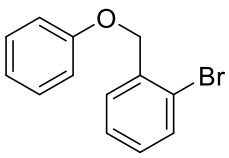
***N*-(4-Fluorophenyl)-2-iodo-*N*-methylbenzamide (1l).**[7] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (100:0→60:40). A brown oil was obtained in 60% yield (355 mg, 1.2 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.19 – 7.13 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz,1H), 6.90 – 6.85 (m, 3H), 3.48 (s, 3H); minor isomer: δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.44 (m, *J* = 6.6 Hz, 3H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 3H), 3.96 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) major isomer δ: 170.2, 161.2 (d, *J* = 248.5 Hz), 142.3, 139.3, 139.2, 129.9, 128.9 (d, *J* = 10.1 Hz), 128.5, 127.4, 115.9 (d, *J* = 23.2 Hz), 93.5, 37.5. **GC/MS (EI)** *m/z* 355 (M^+, 48), 231 (100), 228 (14), 203 (20), 123 (12), 122 (15), 95 (23), 77 (22), 76 (89), 75 (28), 50 (29).



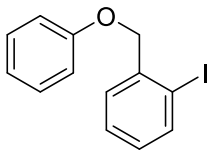
2-Iodo-*N*-methyl-*N*-(4-nitrophenyl)benzamide (1m).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (70:30→60:40). A yellow solid was obtained in 77 % yield (295 mg, 0.77 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.13 (m, 4H), 7.02 (s, 1H), 3.49 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 170.2, 148.7, 145.7, 141.8, 139.6, 131.9, 130.8, 128.2, 126.8, 124.5, 93.0, 37.8. **CG/MS (EI)** *m/z* 382 (M^+, 17), 231 (100), 203 (23), 77 (17), 76 (69), 50 (21).



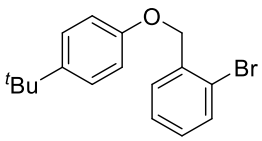
***N*-(4-Bromophenyl)-2-iodo-*N*-methylbenzamide (1n).** Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (90:10→70:30). A brown oil was obtained in 36% yield (150 mg, 0.36 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) major isomer δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 3H), 6.90 (t, *J* = 7.7 Hz, 1H), 3.48 (s, 3H); minor isomer: δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.47 – 7.44 (m, 1H), 7.39 – 7.37 (m, 3H), 7.18 – 7.14 (m, 1H), 3.17 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 170.0, 142.3, 142.1, 139.3, 132.1, 130.0, 128.6, 128.5, 127.5, 120.7, 93.5, 37.3. **CG/MS (EI)** *m/z* 416 (M^+ +2, 21), 414 (M+, 22), 232 (8), 231 (100), 209 (15), 203 (20), 105 (10), 104 (12), 77 (25), 76 (86), 75 (17), 74 (6), 63 (11), 51 (13), 50 (32). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{14}H_{12}BrINO$ 415.9141, found 415.9147.



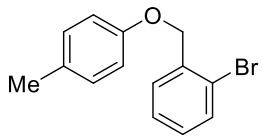
2-Bromobenzyl phenyl ether (6a).[8] Titled compound was obtained according to Section 1.3.2 and purified by column chromatography on silica gel eluting with hexane/EtOAc (90:10). White solid was isolated in 53% yield (282 mg, 1.07 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 10.3, 7.9, 1.4 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 – 6.92 (m, 3H), 5.14 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 158.6, 136.5, 132.7, 129.7, 129.3, 129.0, 127.7, 122.4, 121.3, 115.0, 69.5. **GC/MS (EI)** *m/z* 264 (M^+ +2, 12), 262 (M^+, 11), 183 (19), 171 (75), 169 (82), 92 (11), 91 (13), 90 (100), 89 (80), 77 (15), 65 (20), 64 (14), 63 (35), 51 (24).



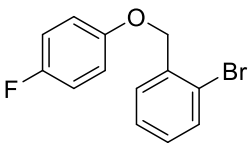
2-Iodobenzyl phenyl ether (6b).[8] Titled compound was obtained according to Section 1.3.2 and purified by column chromatography on silica gel eluting with pentane. White solid was isolated in 37% yield (226.8 mg, 0.74 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (ddd, *J* = 6.4, 0.8 Hz, 1H), 7.36 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.02 (td, *J* = 7.7, 1.7 Hz, 1H), 7.00 – 6.97 (m, 3H), 5.05 (s, 2H). **^{13}C NMR {1H}** (126 MHz, $CDCl_3$) δ 158.6, 139.4, 139.3, 129.7, 129.6, 128.8, 128.5, 121.4, 115.1, 97.3, 74.0. **GC/MS (EI)** *m/z* 310 (M^+, 15), 217 (96), 207 (12), 183 (22), 91 (14), 90 (100), 89 (50), 65 (12), 63 (21), 51 (13).



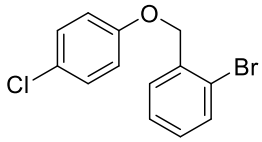
2-Bromobenzyl 4-*tert*-butylphenyl ether (6c).[9] Titled compound was obtained according to Section 1.3.2 and purified by vacuum distillation using Kügelrohr apparatus. Brown oil was isolated in 48% yield (317 mg, 1.0 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H). 7.36 – 7.29 (m, 3H), 7.18 (ddd, *J* = 8.5, 4.9, 1.4 Hz, 1H), 6.95 – 6.89 (m, 2H), 5.11 (s, 2H), 1.30 (s, 9H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 156.4, 144.0, 136.8, 132.7, 129.3, 129.1, 127.7, 126.5, 122.4, 114.5, 69.6, 34.3, 31.7. **GC/MS EI** *m/z* 171 (M^+ +2, 76), 169 (M^+, 78), 90 (100), 89 (77), 64 (16), 63 (33), 51 (14).



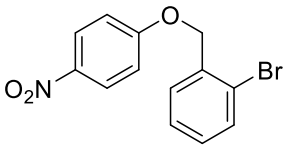
2-Bromobenzyl 4-methylphenyl ether (6d).[8] Titled compound was obtained according to Section 1.3.2 and was purified by vacuum distillation using Kügelrohr apparatus. Yellow oil was isolated in 53% yield (223 mg, 1.05 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (ddd, *J* = 7.7, 4.7, 0.9 Hz, 2H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.09 (dd, *J* = 8.7, 0.6 Hz, 2H), 6.91 – 6.86 (m, 2H), 5.10 (s, 2H), 2.29 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 156.5, 136.7, 132.7, 130.6, 130.1, 129.3, 129.0, 127.7, 122.4, 114.9, 69.7, 20.6. **GC/MS (EI)** *m/z* 278 (M^+ +2, 19), 276 (M^+, 14), 197 (14), 171 (93), 169 (97), 91 (13), 90 (100), 89 (75), 77 (28), 65 (12), 63 (26), 51 (19).



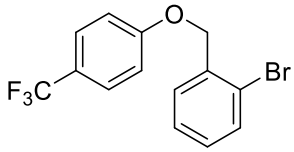
2-Bromobenzyl 4-fluorophenyl ether (6e).[8] Titled compound was obtained according to Section 1.3.2 and was purified by vacuum distillation using Kügelrohr apparatus. Yellow oil was isolated in 32% yield (178 mg, 0.63 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 (ddd, *J* = 7.9, 7.5, 1.7 Hz, 1H), 7.02 – 6.89 (m, 4H), 5.09 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 157.6 (d, *J* = 240 Hz), 154.7 (d, *J* = 2 Hz), 136.3, 132.8, 129.5, 129.0, 127.7, 122.5, 116.2 (d, *J* = 1 Hz), 116.0 (d, *J* = 13 Hz), 70.2. **GC/MS (EI)** *m/z* 282 (M^+ +2, 11), 280 (M^+, 11), 171 (78), 169 (76), 90 (100), 89 (85), 83 (16), 75 (12), 64 (12), 63 (35), 51 (14).



2-Bromobenzyl 4-chlorophenyl ether (6f).[10] Titled compound was was obtained according to Section 1.3.2 and purified by vacuum distillation using Kügelrohr apparatus. An oil was obtained in 33% yield (173.4 mg, 0.58 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.09 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 157.2, 136.0, 132.8, 129.6, 129.5, 129.0, 127.7, 126.2, 122.5, 116.3, 69.8. **GC/MS (EI)** *m/z* 298 (M^+ +2, 13), 296 (M^+, 11), 171 (92), 169 (99), 90 (100), 89 (78), 75 (13), 64 (12), 63 (36), 51 (12).

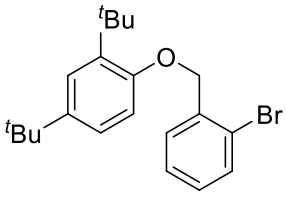


2-Bromobenzyl 4-nitrophenyl ether (6g).[10] Titled compound was obtained according to Section 1.3.2 and purified by vacuum distillation using Kügelrohr apparatus. An oil was obtained in 52% yield (318.3 mg, 1.04 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 – 8.17 (m, 2H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.09 – 7.01 (m, 2H), 5.23 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 163.5, 142.0, 134.9, 133.1, 130.0, 129.1, 127.9, 126.1, 122.7, 115.0, 70.2. **GC/MS EI** *m/z* 171 (90), 169 (100), 90 (37), 89 (29), 63 (19).

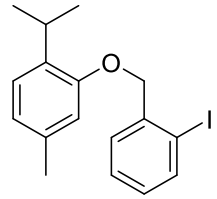


2-Bromobenzyl 4-(trifluoromethyl)phenyl ether (6h).[10] Titled compound was obtained according to Section 1.3.2 and purified by vacuum distillation using Kügelrohr apparatus. Yellow-light solid was obtained in 77% yield (507.0 mg, 1.54 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.54 – 7.48 (m, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.20 (td, *J* = 7.7, 1.7 Hz, 1H), 7.07 – 7.02 (m, 2H), 5.17 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 161.0, 135.6, 132.9, 129.7, 129.0, 128.8, 127.1 (q, *J*=3.7 Hz), 125.0 (q, *J*=271.7 Hz),

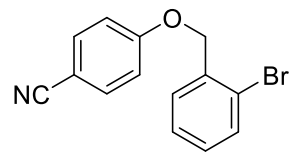
123.5 (q, *J*=31.9), 122.5, 115.0, 69.7. **GC/MS (EI)** *m/z* 330 (M^+, 10), 171 (94), 169 (100), 90 (53), 89 (47), 63 (27), 50 (7).



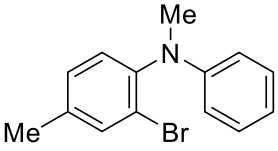
2-Bromobenzyl 2,4-di-*tert*-butylphenyl ether (6i).[11] Titled compound was obtained according to Section 1.3.2 and purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0 → 98:2). An oil was isolated in 58% yield (438.5 mg, 1.17 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 2H), 7.46 – 7.28 (m, 2H), 7.25 – 7.14 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 5.16 (s, 2H), 1.44 (s, 9H), 1.31 (s, 9H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 155.0, 143.1, 137.5, 137.0, 132.5, 128.9, 128.7, 127.5, 124.0, 123.4, 122.0, 112.1, 69.9, 35.1, 34.3, 31.6, 29.9. **GC/MS (EI)** *m/z* 376 (M^++2, 21), 374 (M^+, 23), 361 (14), 359 (15), 171 (59), 169 (61), 149 (9), 91 (12), 90 (19), 89 (14), 57 (100).



2-((2-Iodobenzyl)oxy)1-isopropyl-4-methylbenzene (6j).[12] Titled compound was obtained according to Section 1.3.2 and purified by column chromatography on silica gel eluting with hexane/EtOAc (80:20 → 98:2). White solid was isolated in 46% yield (0.91 mmol, 333.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (ddd, *J* = 7.7, 1.8, 0.8 Hz, 1H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.03 (td, *J* = 7.7, 1.7 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.72 (dd, *J* = 1.6, 1H), 5.01 (s, 2H), 3.40 (m,1H), 2.33 (s, 3H), 1.24 (d, *J* = 6.8, 6H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 155.5, 139.9, 139.3, 136.6, 134.5, 129.4, 128.5, 128.5, 126.2, 121.9, 112.9, 97.1, 74.2, 26.8, 23.0, 21.5. **GC/MS (EI)** *m/z* 366 (M^+, 73), 217 (100), 197 (20), 148 (12), 91 (17), 90 (46), 89 (20).

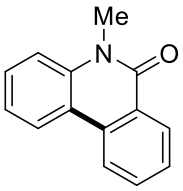


4-((2-Bromobenzyl)oxy)benzonitrile (6k).[10] Titled compound compound was obtained according to Section 1.3.2 and was purified by vacuum distillation using Kügelrohr apparatus. White solid was isolated in 94% yield (543.6 mg, 1.88 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 3H), 7.51 – 7.45 (m, 1H), 7.35 (td, *J* = 7.6, 1.1 Hz, 1H), 7.22 (td, *J* = 7.9, 1.7 Hz, 1H), 7.09 – 6.99 (m, 2H), 5.18 (s, 2H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 161.6, 135.0, 134.1, 132.8, 129.7, 128.9, 127.7, 122.4, 119.0, 115.6, 104.5, 69.2. **GC/MS EI** *m/z* 289 (M^+ +2, 7), 287 (M^+, 8), 171 (85), 169 (100), 90 (54), 89 (41), 64 (15), 63 (23), 51 (8).

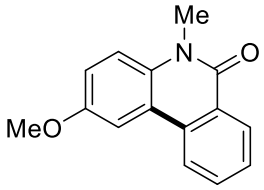


2-Bromo-*N*,4-dimethyl-*N*-phenylaniline (9).[13] Title compound was obtained according to Section 1.3.4 and purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (97:3 → 90:10. Colorless oil was isolated in 57 % yield (311.6 mg, 1.15 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 0.5 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.13 (d, *J* = 1.1 Hz, 2H), 6.77 – 6.70 (m, 1H), 6.56 – 6.54 (m, 2H), 3.20 (s, 3H), 2.35 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 148.7, 144.1, 138.0, 134.4, 130.1, 129.7, 128.9, 124.0, 117.4, 113.1, 38.9, 20.7. **GC-MS (EI)** *m/z* 277 (M^+ +2, 42), 275 (M^+, 55), 196 (34), 194 (22), 181 (100), 180 (31), 98 (16), 97 (39), 90 (16), 77 (10).

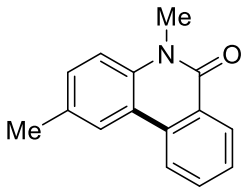
3. Characterization data of 5-methylphenanthridin-6(5H)-ones (2a-2n), benzo[c]chromenes (6a-6k) and carbazole (10)



5-Methylphenanthridin-6(5*H*)-one (2a).[4] Titled compound was purified by column chromatography on silica gel eluting with hexane/ EtOAc (100:0→70:30). A white solid was obtained in 88% yield (37.6 mg, 0.18 mmol) from **1a**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.28 (dd, *J* = 7.9, 3.7 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 161.8, 138.2, 133.7, 132.5, 129.7, 129.1, 128.1, 125.8, 123.4, 122.6, 121.8, 119.5, 115.2, 30.1. **GC-MS (EI)** *m/z* 210 (M^+ +1, 15), 209 (M^+, 100), 208 (21), 181 (15), 180 (28), 179 (10), 178 (31), 152 (27), 151 (13), 105 (11), 90 (17), 89 (12), 77 (16), 76 (26), 75 (10), 63 (16).

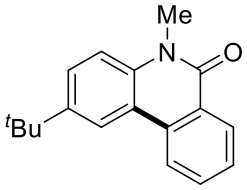


2-Methoxy-5-methylphenanthridin-6(5*H*)-one (2e).[4] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0→70:30). Brown solid was isolated in 85% yield (40.7 mg, 0.17 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 9.1 Hz, 1H), 7.15 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.94 (s, 3H), 3.81 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 161.4, 155.3, 133.4, 132.4, 129.2, 128.3, 126.1, 121.8, 116.7, 116.4, 107.4, 55.9, 30.2. **GC-MS (EI)** *m/z* 240 (M^+ +1, 17), 239 (M^+, 97), 225 (17), 224 (100), 196 (25), 178 (16), 167 (17), 153 (14), 152 (11), 139 (15), 127 (15), 126 (11), 120 (11), 101 (12), 77 (10), 76 (10), 75 (13), 63 (10).

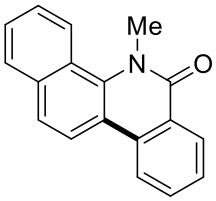


2,5-Dimethylphenanthridin-6(5*H*)-one (2f).[4] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5→60:40). Yellow solid was isolated in 50% yield (22.3 mg, 0.10 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.04, 1H)

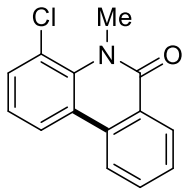
8.06 (s, 1H), 7.76 – 7.72 (m, 1H), 7.58 – 7.55 (1H, m), 7.36 – 7.29 (m, 2H), 3.79 (s, 3H), 2.49 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 161.5, 135.9, 133.5, 132.2, 131.9, 130.5, 128.9, 127.8, 125.7, 123.3, 121.5, 119.1, 114.9, 29.9, 20.9. **GC-MS (EI)** *m/z* 224 (M^+ +1, 16), 223 (M^+, 100), 222 (32), 194 (15), 192 (16), 165 (17), 152 (16), 97 (12), 84 (15), 82 (11), 77 (11), 76 (12).



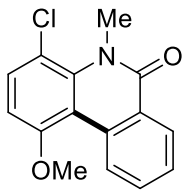
2-(*tert*-Butyl)-5-methylphenanthridin-6(5*H*)-one (2g).[14] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0→80:20). Yellow oil was isolated in 85% yield (45.1 mg, 0,17 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 7.6 Hz, 1H), 8.33 (dd, *J* = 10.5, 5.1 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 1.46 (s, 9H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 161.8, 145.4, 136.1, 134.0, 132.4, 129.2, 127.9, 127.3, 125.9, 121.6, 119.7, 115.0, 34.7, 31.6 (x3), 30.1. **GC-MS (EI)** *m/z* 265 (M^+, 35), 251 (20), 241 (19), 250 (100), 111 (13), 97 (17).



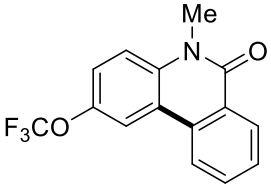
5-Methylbenzo[*c*]phenanthridin-6(5*H*)-one (2h).[15] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5→80:20). White solid was isolated in 50% (25.4 mg, 0.1 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 8.0, 1.5, 0.6 Hz, 1H), 8.38 – 8.32 (m, 1H), 8.30 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.79 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.77 – 7.68 (m, 1H), 7.61 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.58 – 7.47 (m, 2H), 4.06 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 164.6, 136.5, 134.9, 133.9, 132.6, 128.6, 128.5, 127.9, 126.5, 125.5, 125.4, 125.0, 124.7, 124.1, 122.0, 119.9, 117.2, 41.1. **GC-MS (EI)** *m/z* 260 (M^+ +1, 13), 259 (M^+, 75), 258 (100), 230 (12), 202 (13), 114 (14), 101 (17), 88 (12).



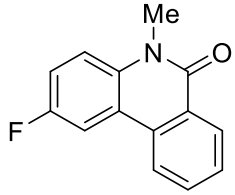
4-Chloro-5-methylphenanthridin-6(5*H*)-one (2i).[15] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5→70:30). White solid was isolated in 70% yield (34.1 mg, 0.14 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.63 – 7.56 (m, 1H), 7.53 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 163.8, 137.1, 133.2, 132.9, 132.8, 128.9, 128.7, 125.8, 123.5, 123.4, 122.3, 122.0, 122.0, 38.7. **GC-MS (EI)** *m/z* 245 (M^+ +2, 32), 244 (M^+ +1, 25), 243 (M^+, 100), 242 (27), 215 (14), 214 (25), 213 (14), 212 (13), 208 (32), 180 (11), 179 (13), 178 (35), 177 (16), 164 (13), 152 (32), 151 (35), 150 (14), 104 (10), 90 (15), 89 (39), 87 (11).



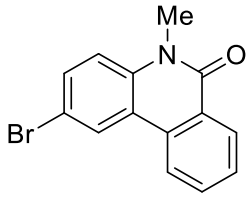
4-Chloro-1-methoxy-5-methylphenanthridin-6(5*H*)-one (2j).[15] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (95:5→85:15). White solid was isolated in 52% yield (28.4 mg, 0.104 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 8.5 Hz, 1H), 8.54 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.72 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 4.05 (s, 3H), 3.87 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 164.1, 157.5, 138.9, 132.9, 132.6, 131.9, 128.4, 128.0, 127.7, 125.8, 114.7, 113.8, 107.1, 56.3, 39.8. **GC-MS (EI)** *m/z* 275 (M^+ +2, 35), 274 (M^+ +1, 21), 273 (M^+,100), 272 (11), 258 (11), 244 (11), 243 (15), 238 (24), 208 (16), 195 (11), 167 (12), 166 (10), 152 (11), 139 (16), 83 (11), 75 (11), 69 (11), 63 (10).



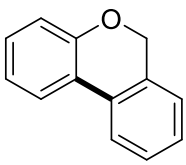
5-Methyl-2-(trifluoromethoxy)phenanthridin-6(5*H*)-one (2k).[15] Title compound was purified by column chromatography on silica gel eluting with hexane/dichloromethane (100:0→60:40). White solid was isolated in 81% yield (47.5 mg, 0.16 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.82 – 7.78 (m, 1H), 7.66 – 7.62 (m, 1H), 7.43 (s, 2H), 3.82 (s, 3H). **^{13}C NMR {1H}** (101 MHz, $CDCl_3$) δ 161.4, 144.4 (d, 1C, *J* = 2 Hz), 136.7, 132.7, 132.5, 129.1, 128.9, 125.9, 122.3, 121.9, 120.6 (q, *J* = 256, 1C), 120.5, 116, 115.9, 30.2. **GC-MS (EI)** *m/z* 294 (M^+ +1, 28), 293 (M^+, 86), 224 (100), 207 (14), 196 (19), 178 (32), 168 (20), 167 (24), 153 (14), 152 (11), 140 (20), 139 (28), 127 (17), 126 (13), 101 (12), 77 (13), 75 (17), 74 (10), 73 (13), 69 (53), 63 (16), 51 (11).



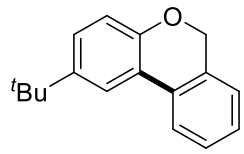
2-Fluoro-5-methylphenanthridin-6(5*H*)-one (2l).[15] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0→70:30). Yellow solid was isolated in 67% yield (30.4 mg, 0.13 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.6 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.95 (dd, *J* = 9.7, 2.8 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 3.82 (s, 3H). **^{13}C NMR {^{1}H}** (101 MHz, $CDCl_3$) δ 159.9, 157.5, 134.7, 132.8, 132.7, 129.3, 128.8, 124.1, 122.0, 120.9, 116.9 (*J* = 23 Hz), 116.7 (*J* = 8 Hz), 109.5 (*J* = 24 Hz), 30.4. **GC-MS (EI)** *m/z* 228 (M^+ +1, 16), 227 (M^+, 100), 226 (23), 199 (13), 198 (29), 197 (14), 196 (31), 170 (22), 114 (11), 99 (16), 89 (12), 85 (21), 76 (10), 75 (11).



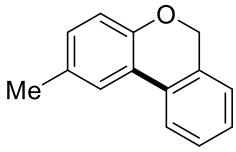
2-Bromo-5-methylphenanthridin-6(5*H*)-one (2n).[16] Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0→40:60). White solid was isolated in 24% yield (13.8 mg, 0.048 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.0, 0.9 Hz, 1H), 8.37 (d, *J* = 2.2 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.64 – 7.60 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR {1 H}** (101 MHz, $CDCl_3$) δ 161.3, 137.0, 132.6, 132.3, 132.2, 129.0, 128.7, 126.0, 125.8, 121.7, 121.1, 116.7, 115.7, 30.1. **GC-MS (EI)** *m/z* 290 (M^+ +2, 19), 289 (M^+ +1, 100), 288 (M^+, 28), 287 (100), 286 (19), 281 (17), 260 (13), 259 (10), 258 (24), 256 (17), 209 (10), 208 (20), 207 (44), 180 (23), 179 (25), 178 (22), 165 (15), 164 (17), 153 (14), 152 (39), 151 (28), 150 (13), 139 (14), 138 (12), 113 (12), 104 (29), 99 (10), 97 (11), 96 (15), 90 (42), 89 (29), 88 (14), 87 (19), 86 (11), 77 (37), 76 (48), 75 (39), 74 (15), 73 (37), 69 (12), 63 (26), 62 (12), 57 (12), 55 (11), 51 (16), 50 (12).



6*H*-Benzo[*c*]chromene (7a).[8] Titled compound was purified by HPLC preparative eluting with MeOH. Light yellow oil was isolated in 50% yield (18.3 mg, 0.1 mmol) from **6a**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.12 (s, 2H).**^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 131.4, 130.1, 129.4, 128.4, 128.0, 127.6, 124.6, 123.3, 122.9, 122.1, 122.0, 117.4, 68.5. **GC/MS EI** *m*/*z* 183 (M^+ +1, 7), 182 (M^+ 61), 181 (100), 152 (36), 151 (13), 91 (27), 77 (15), 76 (50), 75 (13), 64 (10), 63 (24), 51 (13).

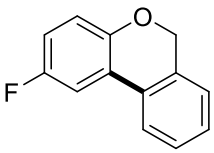


2-(*tert*-Butyl)-6*H*-benzo[*c*]chromene (7c).[8] Titled compound was purified by HPLC preparative eluting with MeOH. Light yellow oil was isolated in 42% yield (20.0 mg, 0.08 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 5.09 (s, 2H), 1.36 (s, 9H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 152.5, 144.8, 131.6, 130.5, 128.3, 127.4, 126.6, 124.6, 122.1, 121.8, 119.9, 116.8, 68.5, 41.0, 31.5 **GC/MS EI** *m*/*z* 239 (M^+ +1, 8), 238 (M^+, 42), 224 (20), 223 (100), 195 (26), 180 (15), 165 (24), 153 (12), 152 (14), 115 (10), 97 (37).

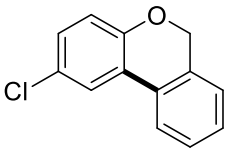


2-Methyl-6*H*-benzo[*c*]chromene (7d).[8] Titled compound was purified by HPLC preparative eluting with MeOH. Light yellow oil was isolated in 38% yield (14.9 mg, 0.076 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.3 Hz, 1H),

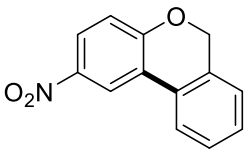
7.14 (d, *J* = 7.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.08 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 152.8, 131.8, 131.5, 130.4, 130.2, 128.5, 127.7, 124.8, 123.8, 122.8, 122.1, 117.2, 68.7, 21.1. **GC/MS EI** *m*/*z* 197 (M^+ +1, 11), 196 (M^+, 74), 195 (100), 165 (19), 153 (12), 152 (23), 97 (25), 82 (11), 63 (12).



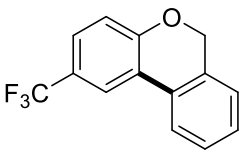
2-Fluoro-6*H*-benzo[*c*]chromene (7e).[8] Title compound was purified by column chromatography on silica gel eluting with hexane. Yellow oil was isolated in 44% yield (17.6 mg, 0.088 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.94 – 6.91 (m, 2H), 5.09 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6 (*J* = 240 Hz), 150.9, 131.7, 129.6 (*J* = 3 Hz), 128.7, 128.5, 124.9, 124.8 (*J* = 2 Hz), 122.4, 118.6 (*J* = 8 Hz), 115.9 (*J* = 23 Hz), 109.8 (*J* = 24 Hz), 68.7. **GC/MS EI** *m*/*z* 201 (M^+ +1, 8), 200 (M^+ 63), 211 (67), 199 (100), 171 (12), 170 (32), 85 (13), 76 (14).



2-Chloro-6*H*-benzo[*c*]chromene (7f).[12] Titled compound was purified by HPLC preparative eluting with MeOH. Yellow oil was isolated in 30% yield (13.0 mg, 0.06 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.20 – 7.13 (m, 2H), 6.92 (d, *J* = 8.6 Hz, 1H), 5.11 (s, 2H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 153.4, 131.4, 129.2 (x2), 128.8, 128.5, 127.3, 124.9, 124.5, 123.3, 122.3, 118.9, 68.7. **GC/MS EI** *m*/*z* 218 (M^+ +2, 22), 217 (M^+ +1, 38), 216 (M^+, 66), 215 (100), 181 (12), 153 (22), 152 (51), 151 (18), 90 (17), 76 (48), 75 (14), 63 (17).

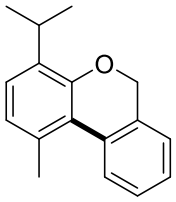


2-Nitro-6*H*-benzo[*c*]chromene (7g).[10] Title compound was purified by column chromatography on silica gel eluting with hexane/AcOEt (100:0→98:2). Light yellow solid was isolated in 14% yield (6.4 mg, 0.028 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.7 Hz, 1H), 8.12 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.38 (td, *J* = 7.4, 1.3 Hz, 1H), 7.23 – 7.13 (m, 1H), 7.05 (d, *J* = 8.9 Hz, 1H), 5.26 (s, 2H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 160.0, 142.9, 130.7, 129.3, 129.2, 128.1, 125.1, 124.9, 123.2, 122.6, 119.5, 118.2, 69.0. **GC/MS EI** *m*/*z* 228 (M^+ +1, 13), 227 (M^+, 100), 226 (96), 181 (11), 180 (37), 153 (16), 152 (53), 151 (20), 115 (11), 76 (19), 63 (12).

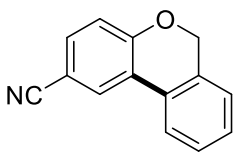


2-(Trifluoromethyl)-6*H*-benzo[*c*]chromene (7h).[10] Titled compound was purified by HPLC preparative eluting with MeOH. Brown oil was isolated in 51% yield (25.5 mg, 0.102 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* =

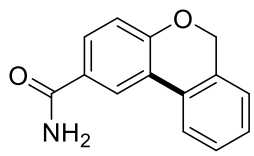
2.1 Hz, 1H), 7.72 (d, *J* = 7.8, 1H), 7.47 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.41 (t, *J* = 7.6, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 5.17 (s, 2H). **^{13}C NMR{1H}** (101 MHz, $CDCl_3$) δ 157.4, 131.2, 128.9, 128.7, 126.5 (q, *J* = 3.7 Hz), 126.2 (q, *J* = 272.7 Hz), 124.9, 124.4 (q, *J* = 32.0 Hz), 123.2, 122.4, 120.8 (q, *J* = 3.7 Hz), 118.0, 68.7. **GC/MS EI** *m/z* 250 (M^+, 58), 249 (100), 207 (12), 201 (14), 152 (23), 115 (12), 76 (11).



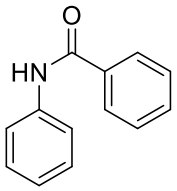
4-Isopropyl-1-methyl-6*H*-benzo[*c*]chromene (7j).[12] Titled compound was purified by HPLC preparative eluting with MeOH. White solid was isolated in 10% yield (0.02 mmol, 4.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.37 (td, *J* = 7.5, 1.8 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.93 (s, 2H), 3.32 (hept, *J* = 6.9 Hz, 1H), 2.65 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 7H).**^{13}C NMR{1H}** (101 MHz, $CDCl_3$) δ 153.8, 134.9, 134.2, 132.7, 131.4, 127.8, 126.8, 126.7, 125.5, 125.2, 124.8, 123.3, 69.1, 27.2, 22.9, 22.6. **GC/MS EI** *m/z* 239 (M^+ +1, 13), 238 (M^+, 62), 224 (17), 223 (100), 208 (20), 207 (10), 205 (12), 195 (32), 180 (11), 179 (14), 178 (19), 165 (35), 152 (13), 115 (12), 89 (17).



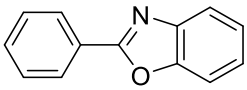
6*H*-Benzo[*c*]chromene-2-carbonitrile (7k).[5] Titled compound was purified by HPLC preparative eluting with MeOH. White solid was isolated in 10 % yield (4.1 mg, 0.02 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.46 – 7.34 (m, 2H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 4.8 Hz, 1H), 5.21 (s, 2H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 158.3, 133.2, 130.8, 129.1 (x2), 128.0, 127.7, 125.0, 123.8, 122.3, 119.2, 118.7, 105.7, 68.7. **GC/MS EI** *m/z* 208 (M^+ +1, 8), 207 (M^+, 60), 206 (100), 177 (13), 151 (21), 103 (10), 76 (17), 75 (11).



6*H*-Benzo[c]chromene-2-carboxamide (7k´). Title compound was purified by column chromatography on silica gel eluting with hexane/EtOAc (100:0→0:100) and recrystallized in acetone. White solid was isolated in 55% yield (24.8 mg, 0.11 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.2 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.46 – 7.37 (m, 1H), 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.67 (s br, 2H), 5.19 (s, 2H). **^{13}C NMR** {**1H**} (101 MHz, $CDCl_3$) δ 168.9, 158.0, 131.0, 129.2, 128.9, 128.5, 128.4, 127.2, 124.9, 123.6, 123.1, 122.4, 117.6, 68.8. **GC/MS EI** *m/z* 226 (M^+ +1, 15), 225 (M^+, 100), 224 (85), 209 (26), 181 (11), 153 (32), 152 (41), 151 (18), 104 (45), 90 (23), 77 (10), 76 (50), 75 (12), 63 (18). **HRMS (ESI-TOF$^+$)** *m/z*: $[M + H]^+$ calcd for $C_{14}H_{12}NO_2$ 226.0863, found 226.0868.

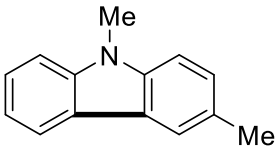


***N*-phenylbenzamide (4).[17] GC/MS EI** *m*/*z* 197 (17), 106 (8), 105 (100), 78 (7), 77 (94), 51 (30).



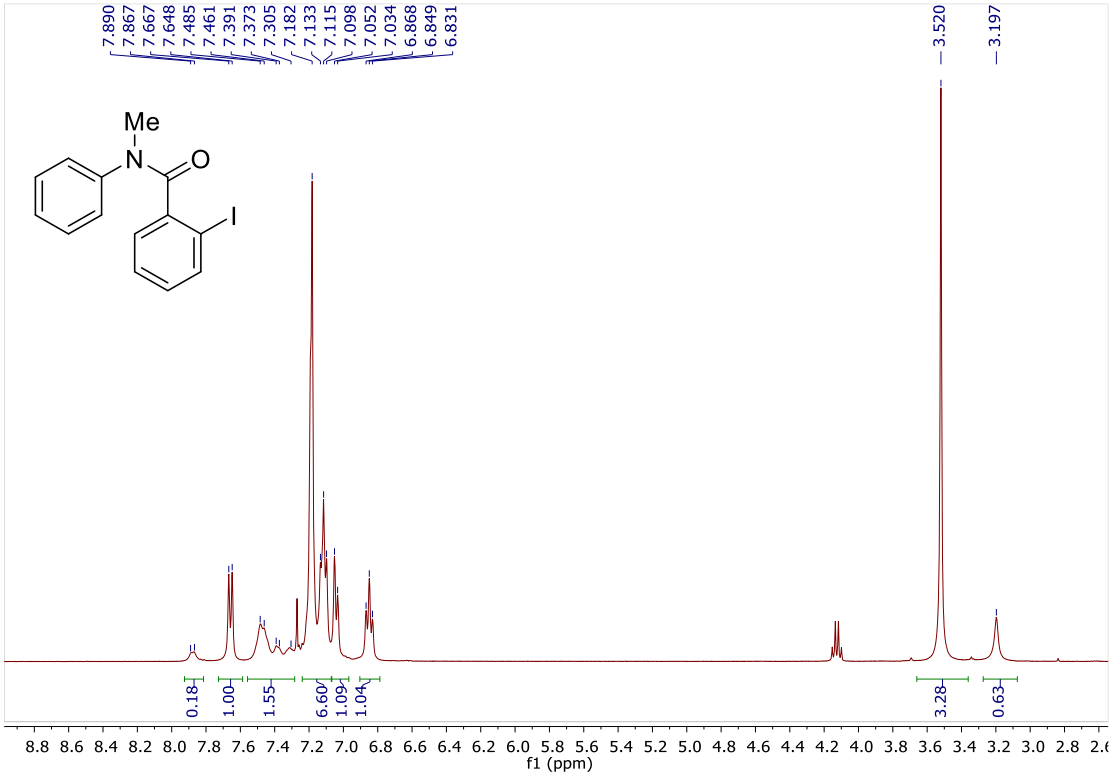
2-Phenylbenzo[*d*]oxazole (5).[18] GC/MS EI *m*/*z* 196 (M^+ +1, 12), 195 (M^+, 67), 167 (26), 103 (11), 92 (24), 84 (23), 77 (44), 76 (18), 64 (67), 63 (100), 62 (17), 51 (35), 50 (18).

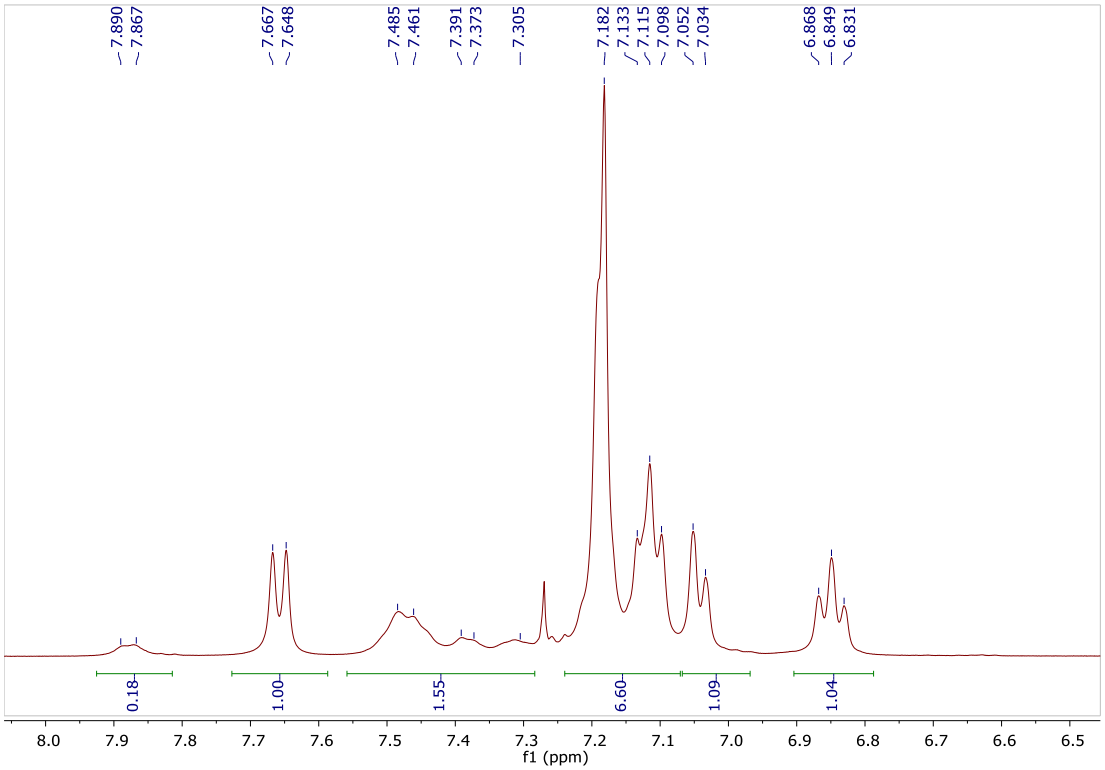
3,9-Dimethyl-9*H*-carbazole (10).[19] Title compound was purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (100:0→93:7). White solid was isolated in 55% yield (10.7 mg, 0.055 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.44 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.36 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.28 (t, *J* = 1.1 Hz, 2H), 7.25 – 7.14 (m, 1H), 3.80 (s, 3H), 2.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 139.3, 128.1, 126.9, 125.4, 122.9, 122.6, 120.2, 120.2, 118.5, 108.3, 108.1, 29.0, 21.4. **GC-MS (EI)** *m/z* 196 (M^+ +1, 12), 195 (M^+, 87), 194 (100), 179 (10), 97 (11), 96 (14).



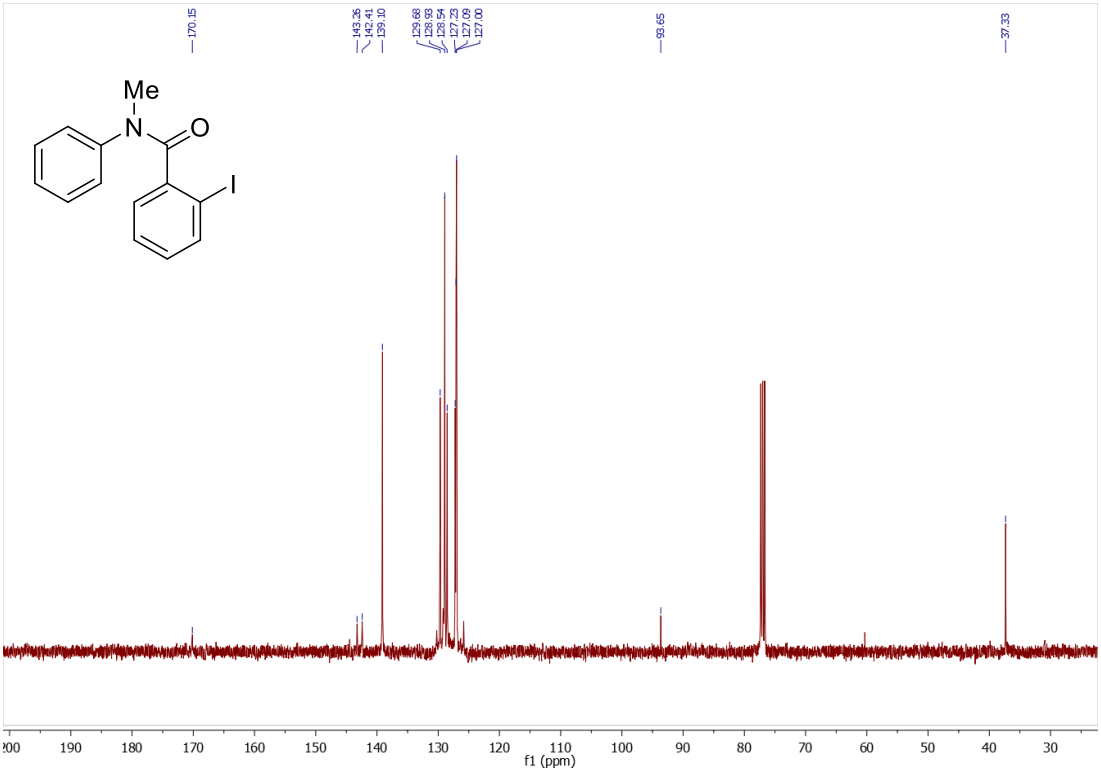
4. NMR spectra of compounds 1a-n, 6a-k and 9

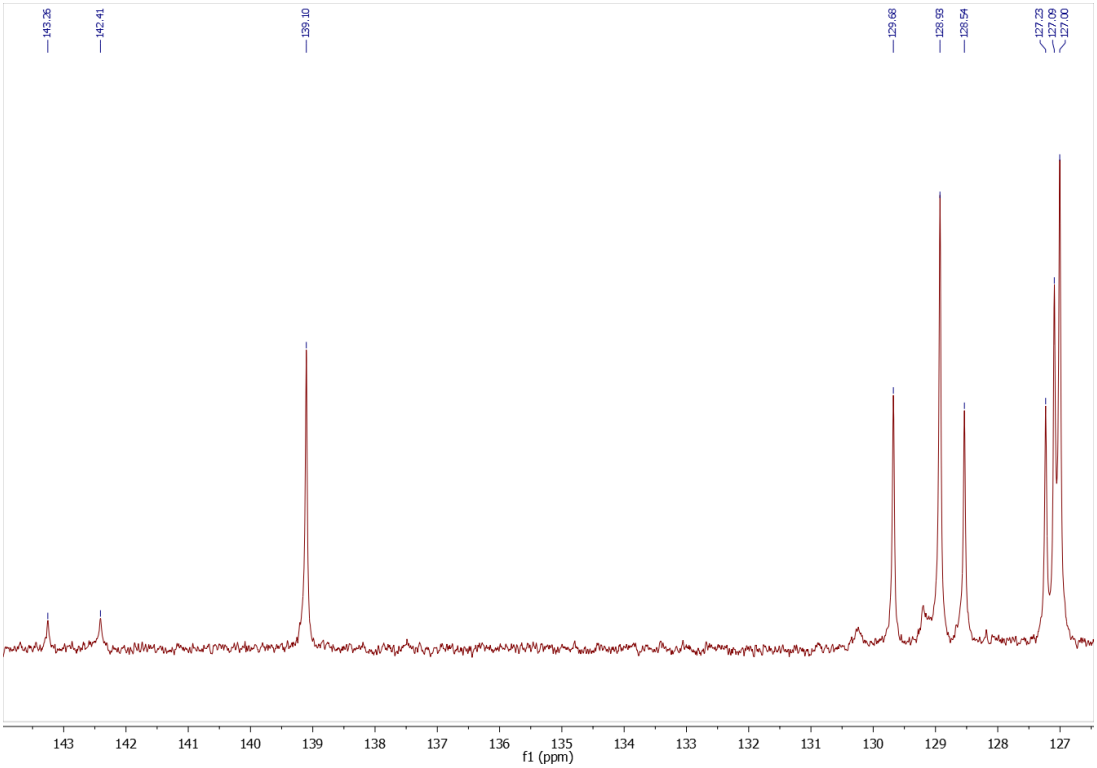
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-phenylbenzamide (1a)



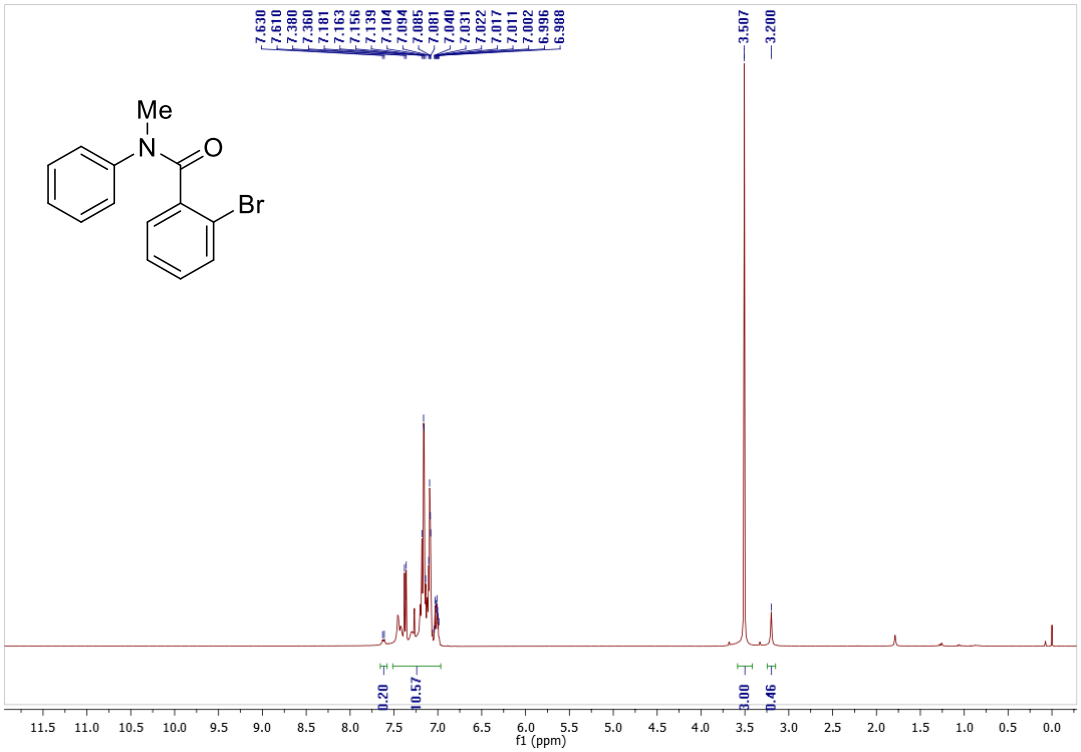


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-phenylbenzamide (1a)

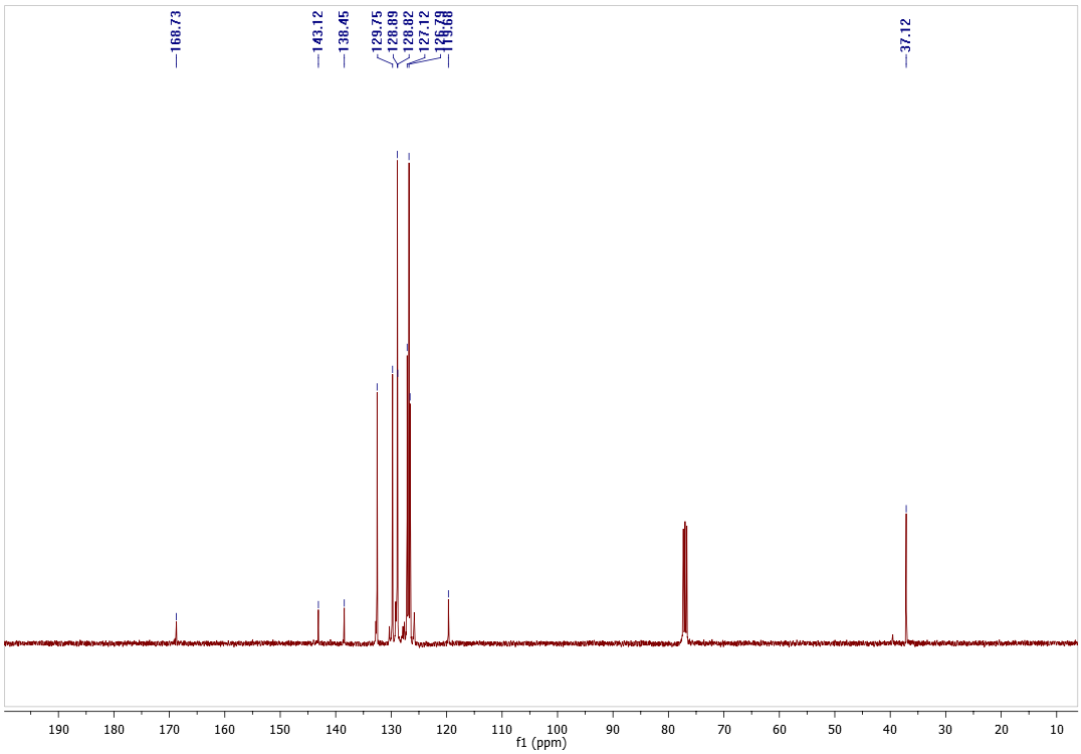




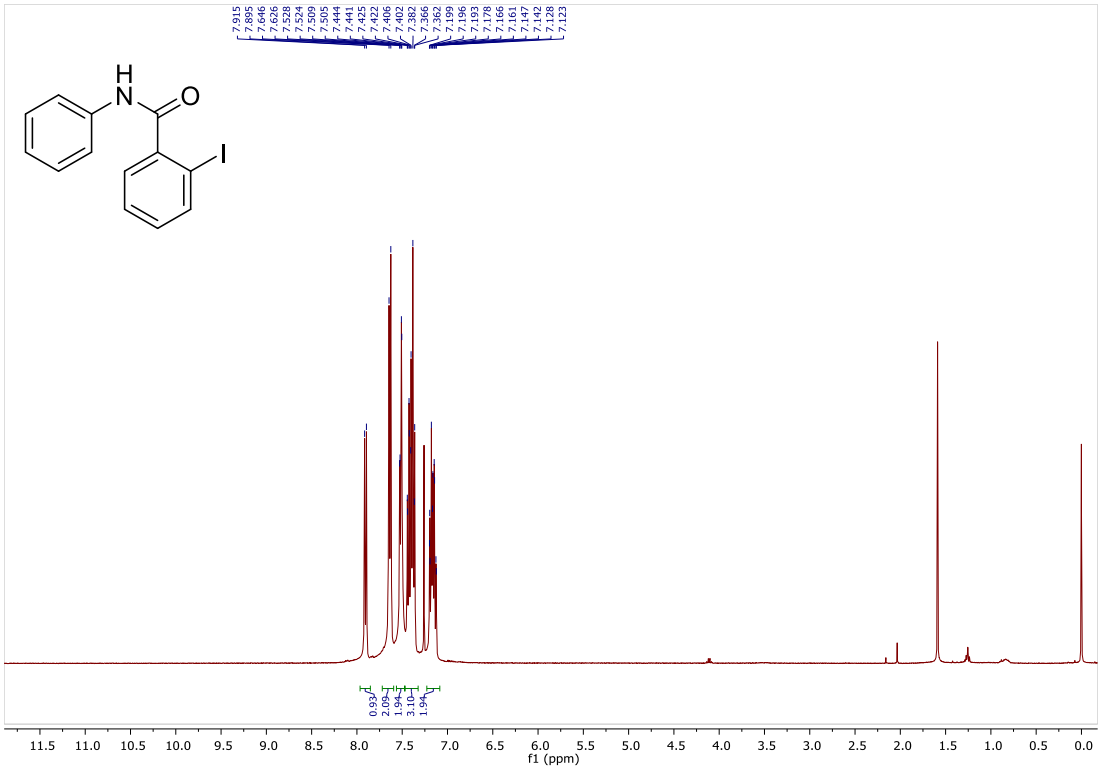
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromo-*N*-methyl-*N*-phenylbenzamide (1b).

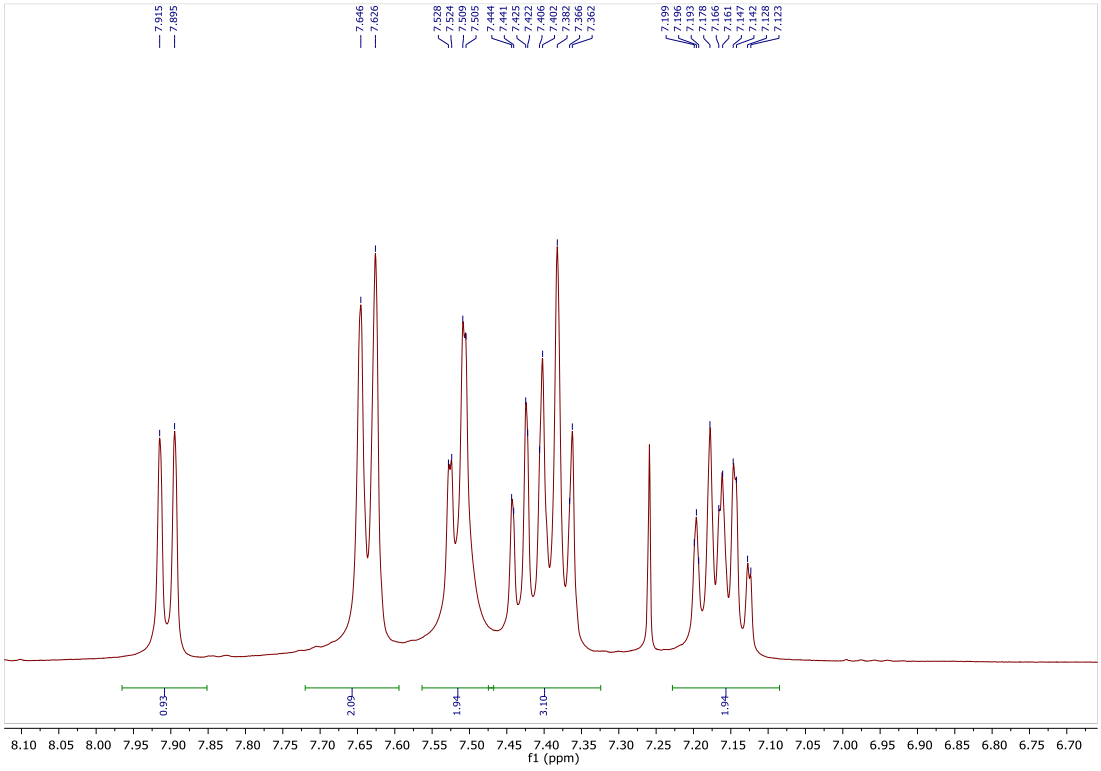


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Bromo-*N*-methyl-*N*-phenylbenzamide (1b).

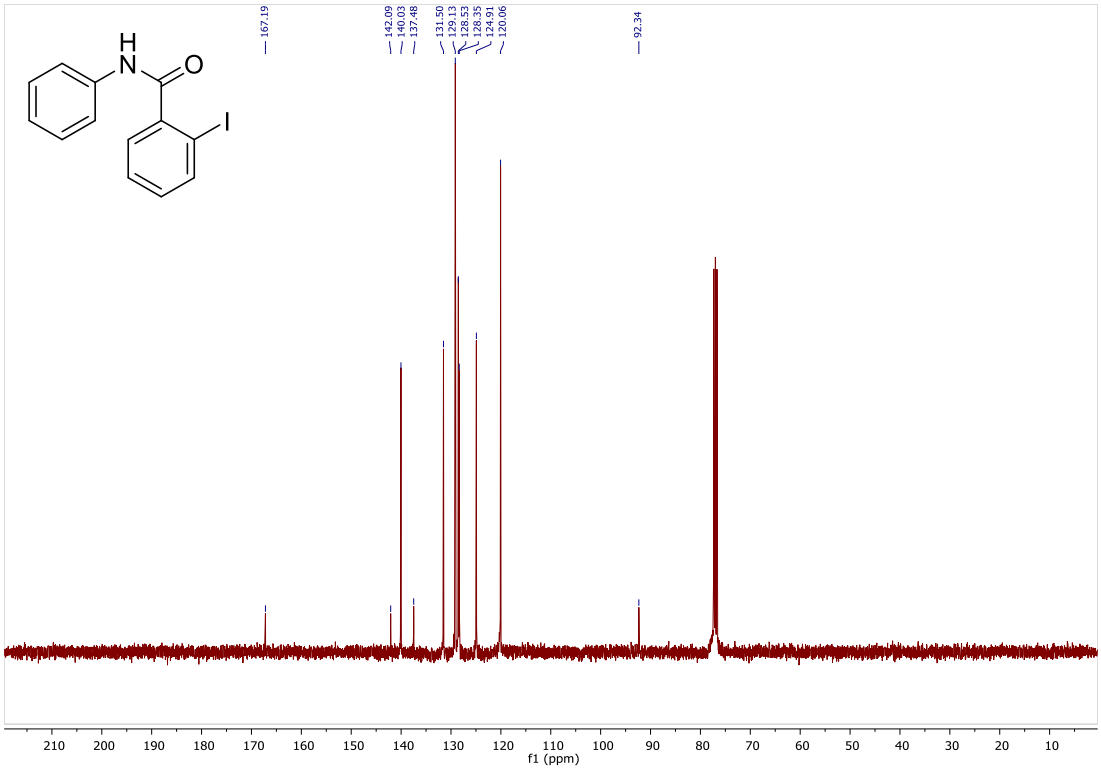


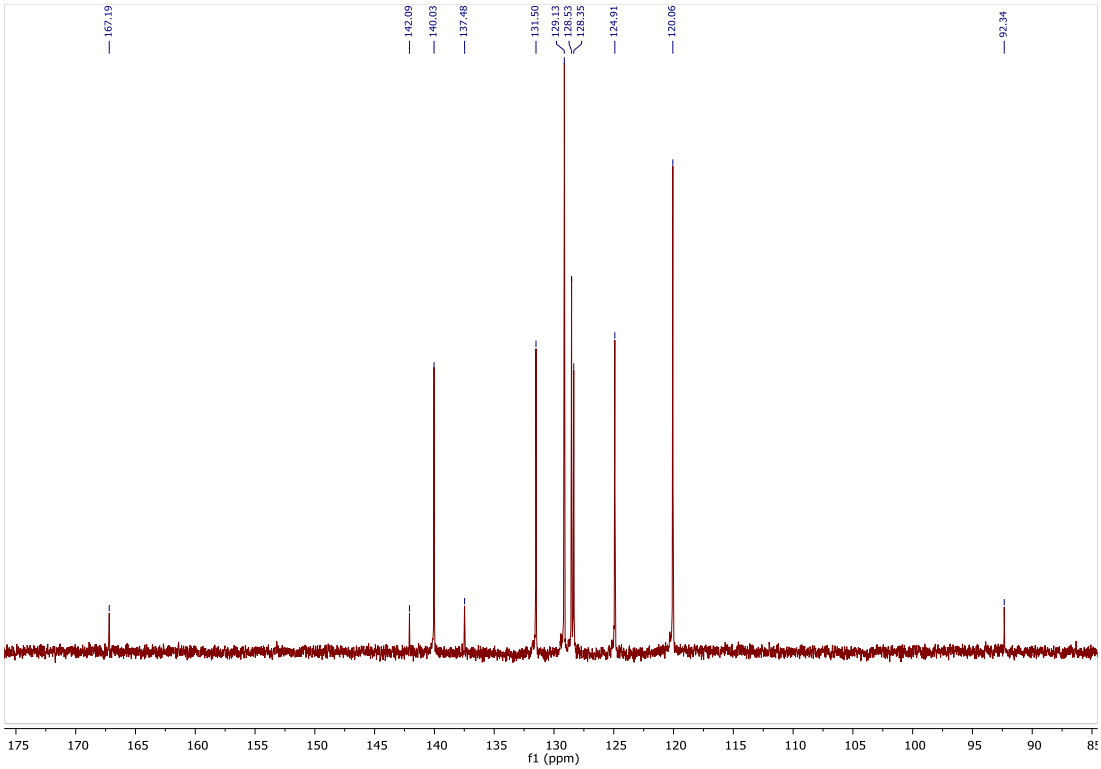
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-phenylbenzamide (1c).



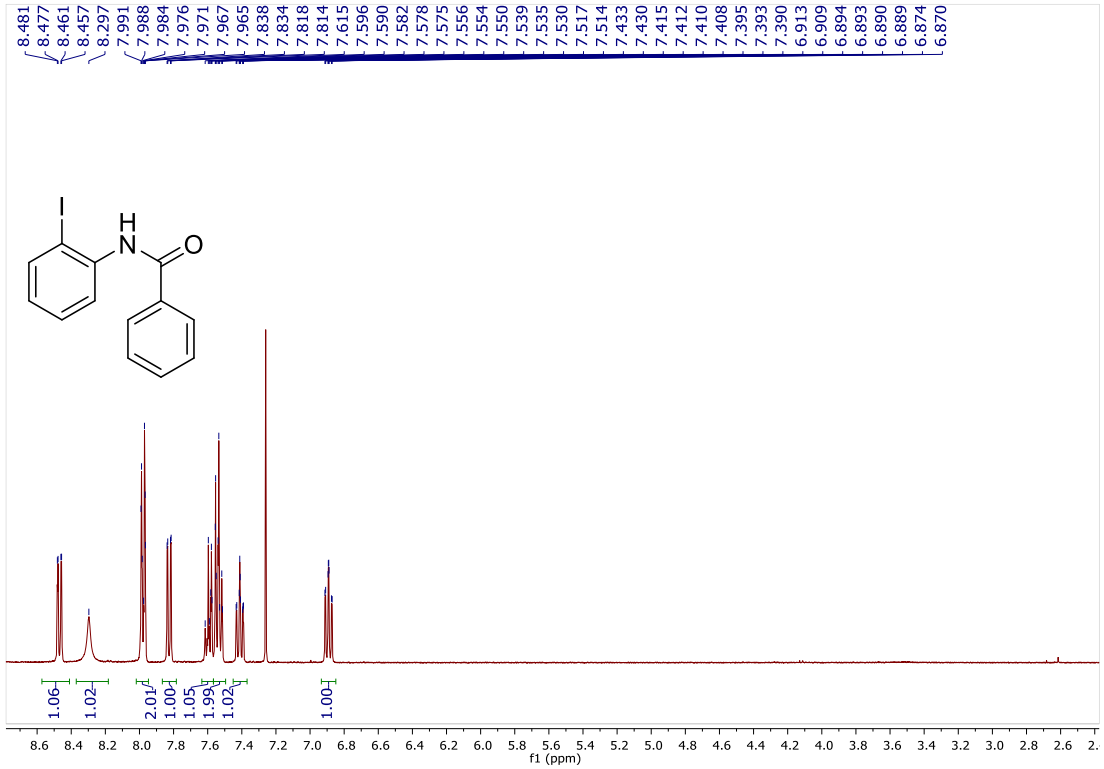


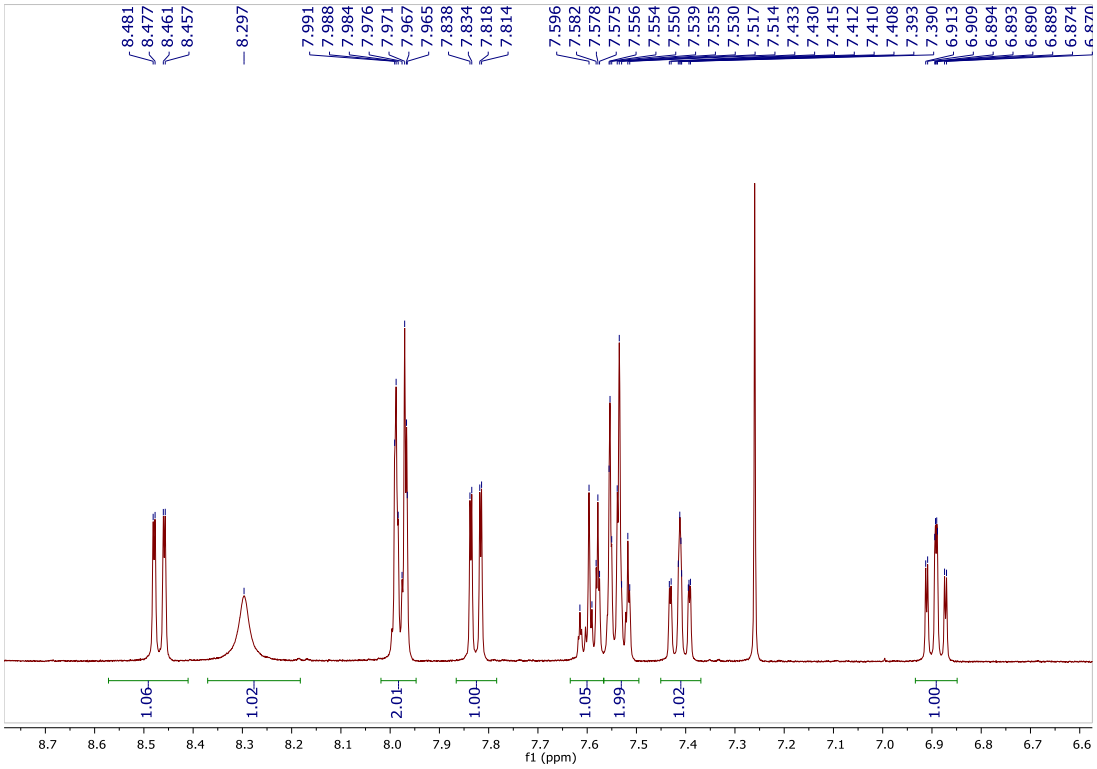
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-phenylbenzamide (1c).



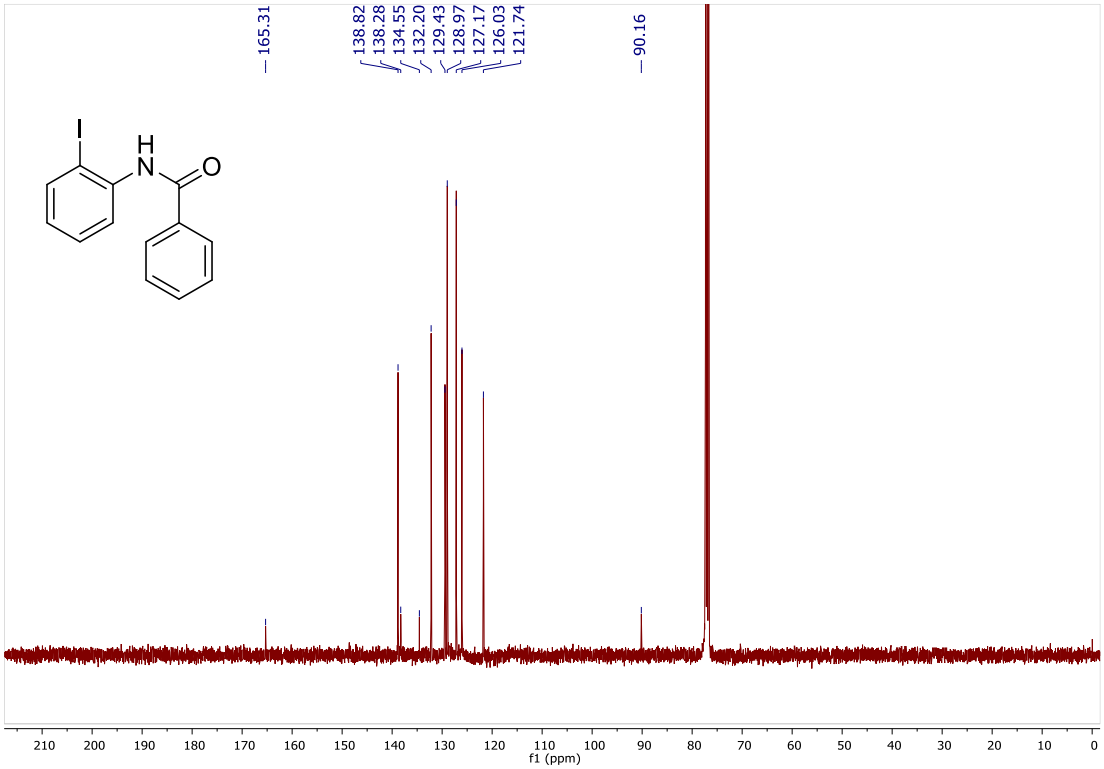


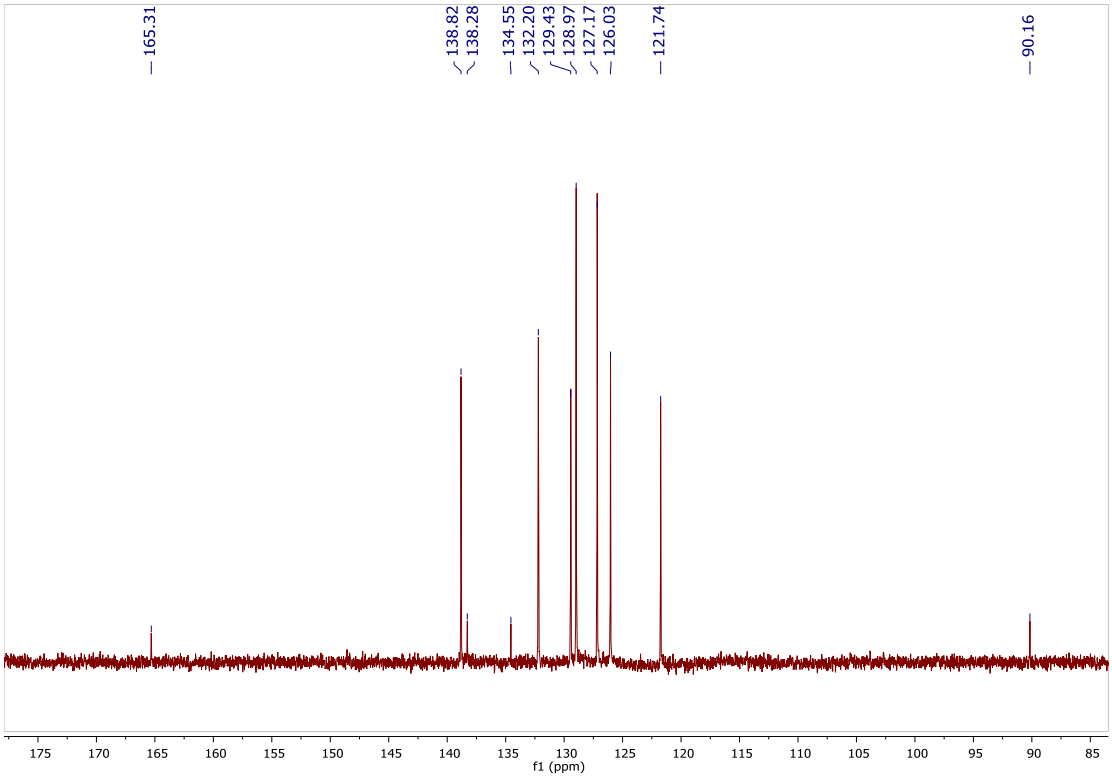
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(2-iodophenyl)benzamide (1d).



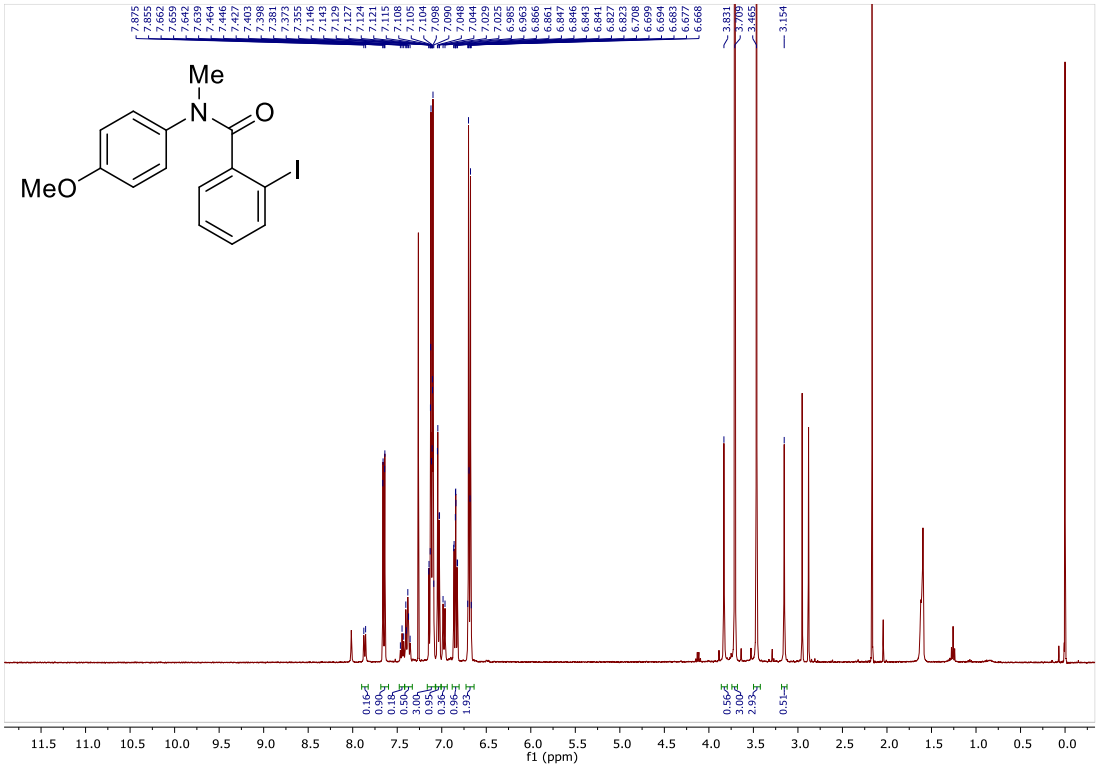


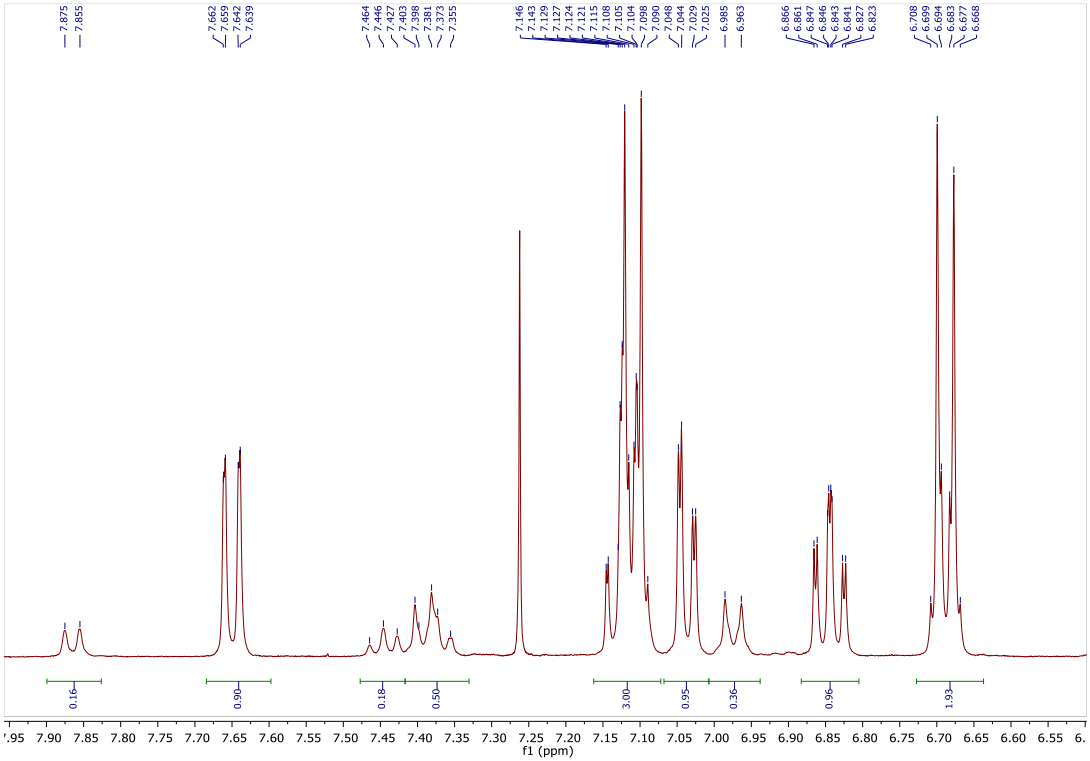
^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(2-iodophenyl)benzamide (1d).



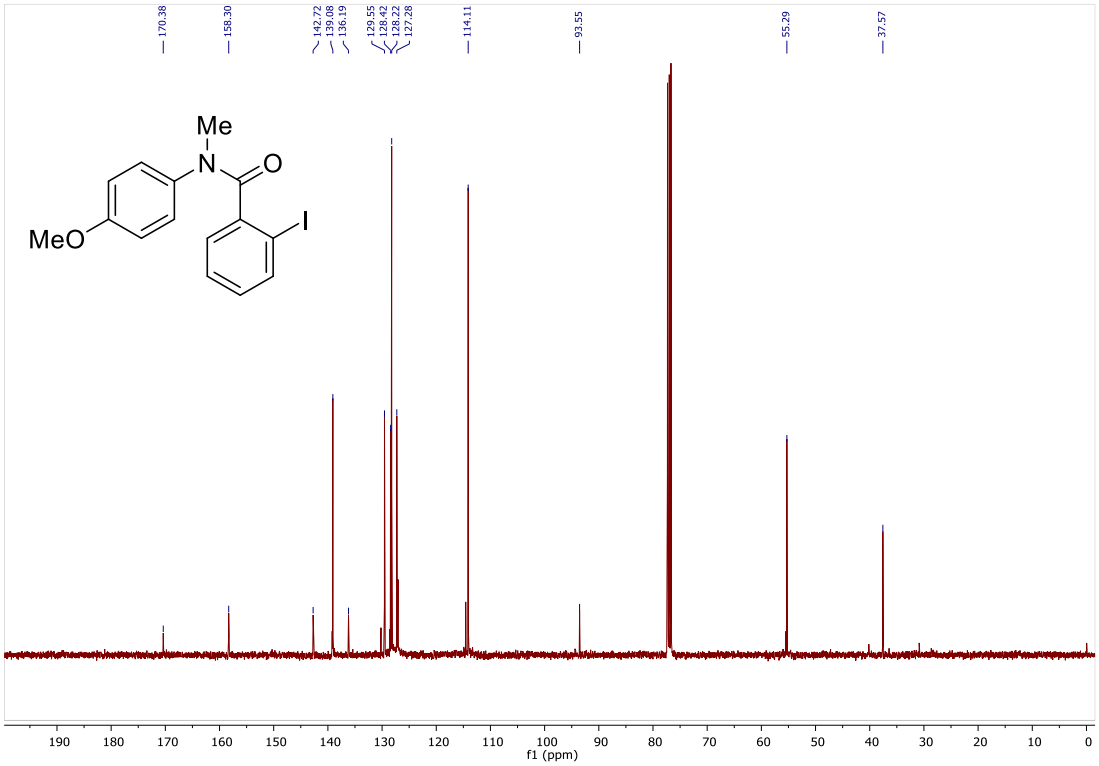


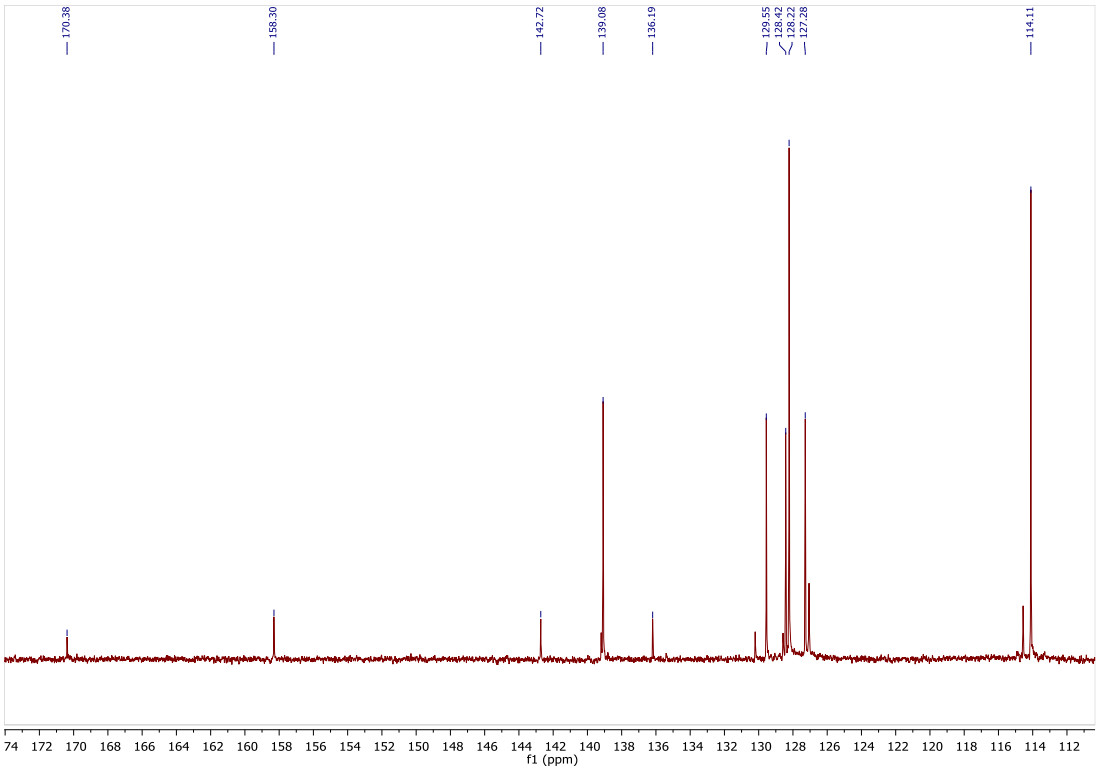
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (1e).



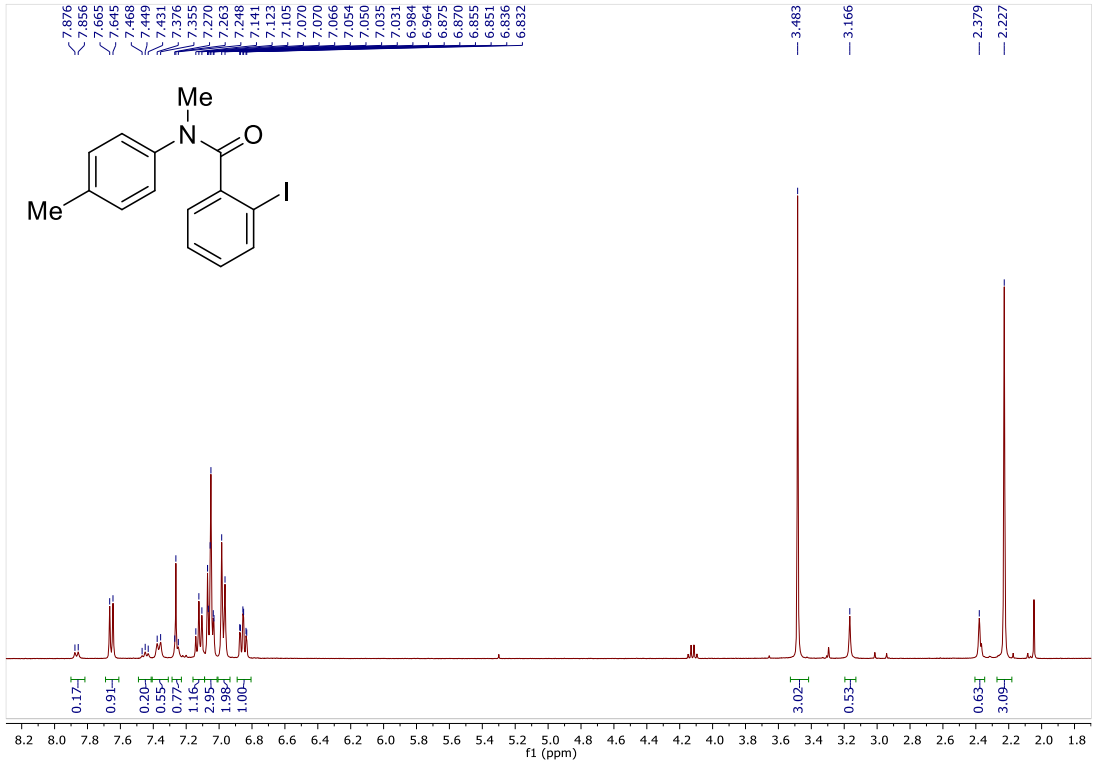


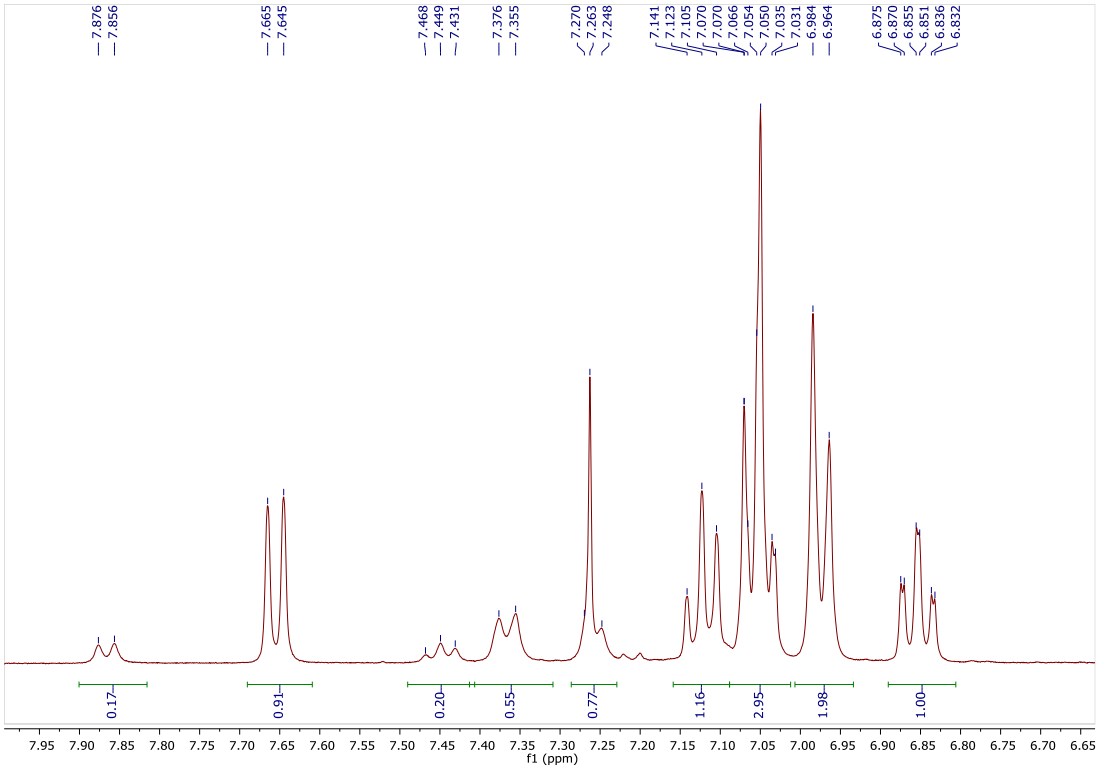
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (1e).



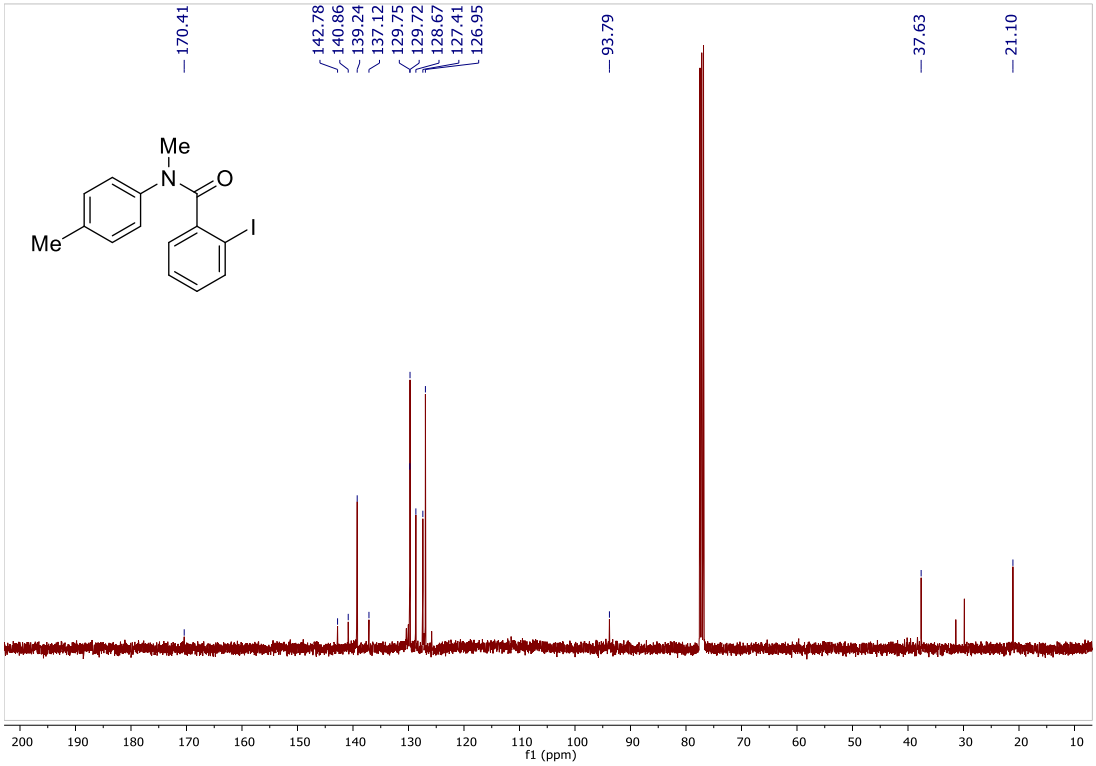


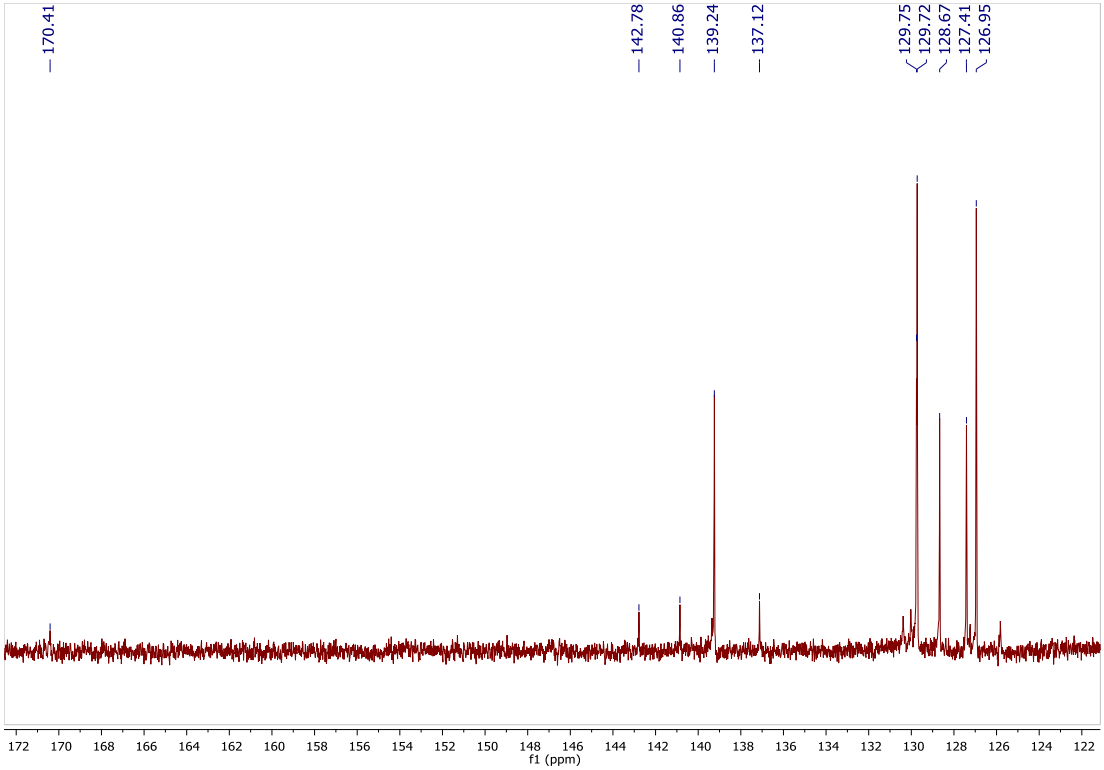
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(*p*-tolyl)benzamide (1f)



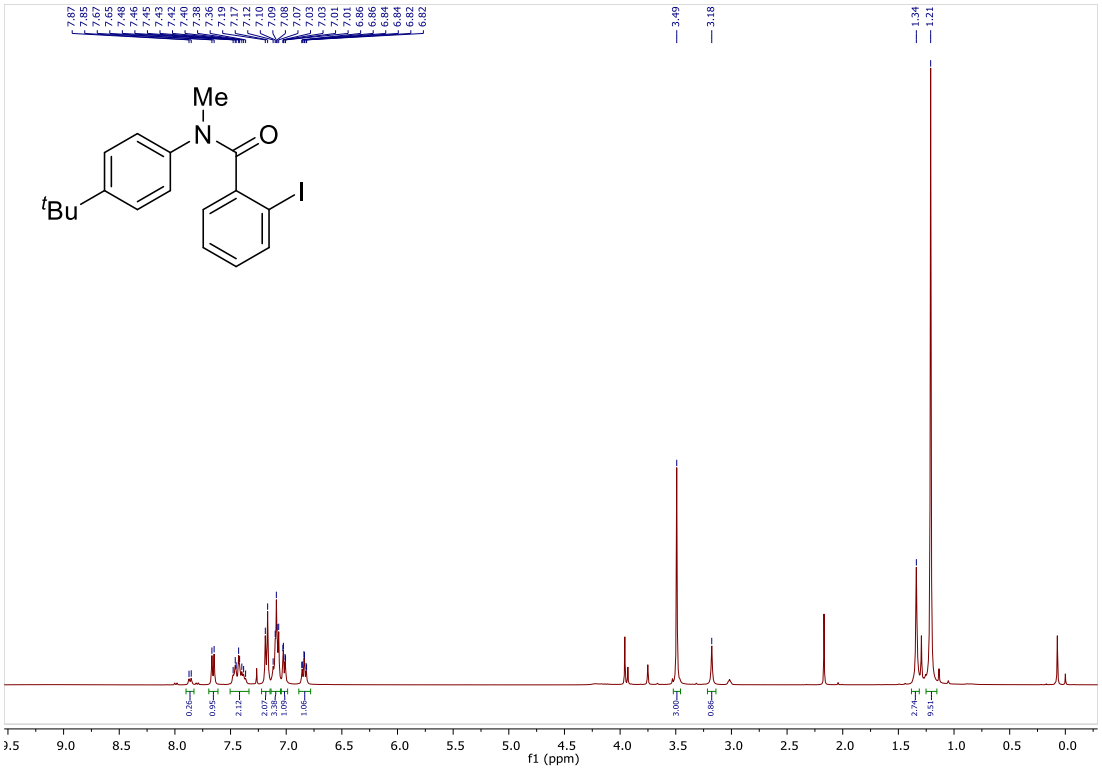


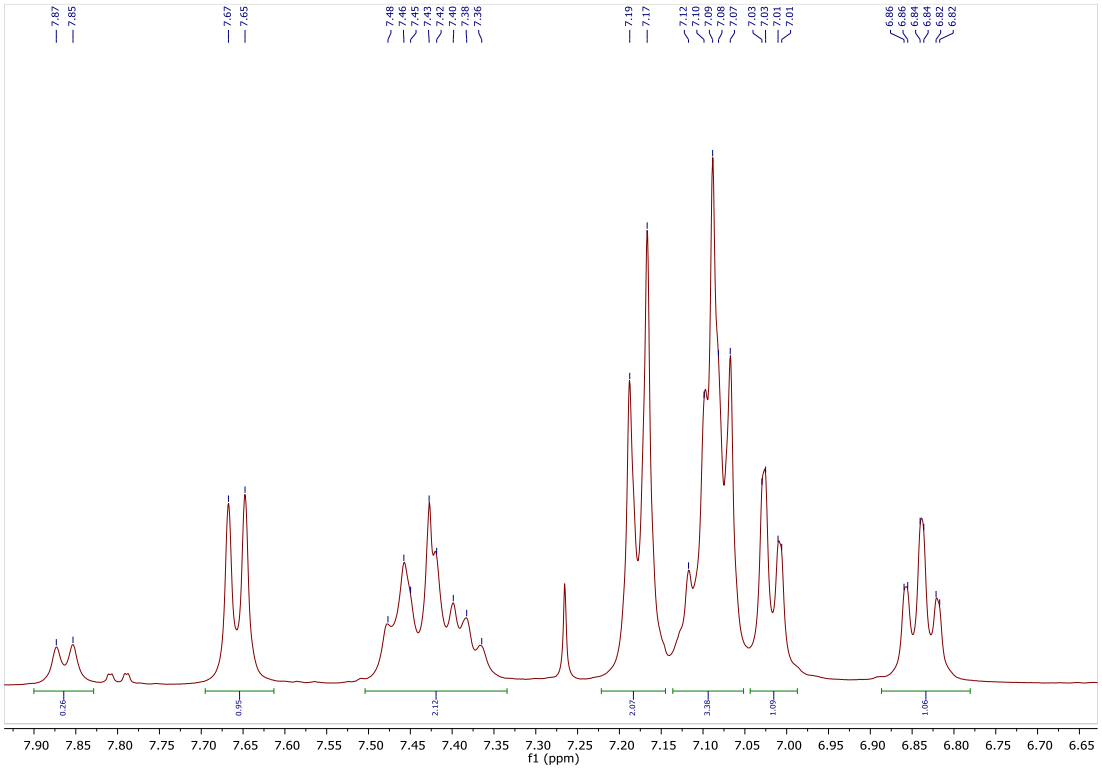
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(*p*-tolyl)benzamide (1f)



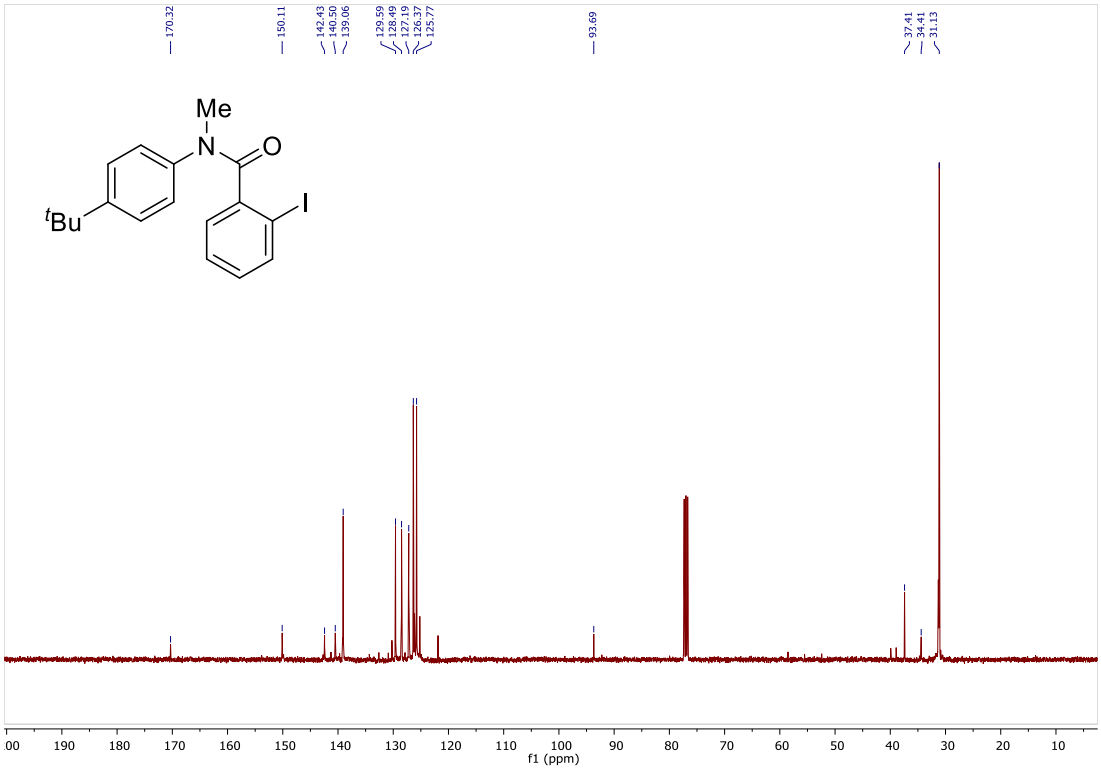


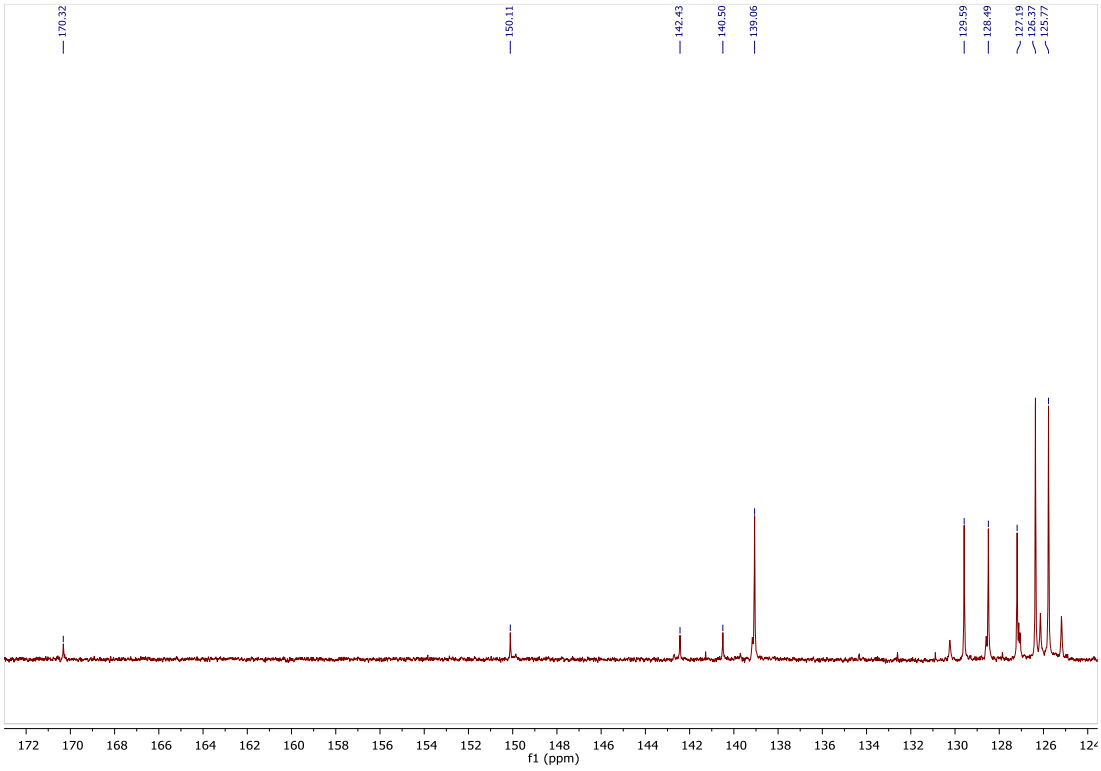
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(4-(*tert*-Butyl)phenyl)-2-iodo-*N*-methylbenzamide (1g).



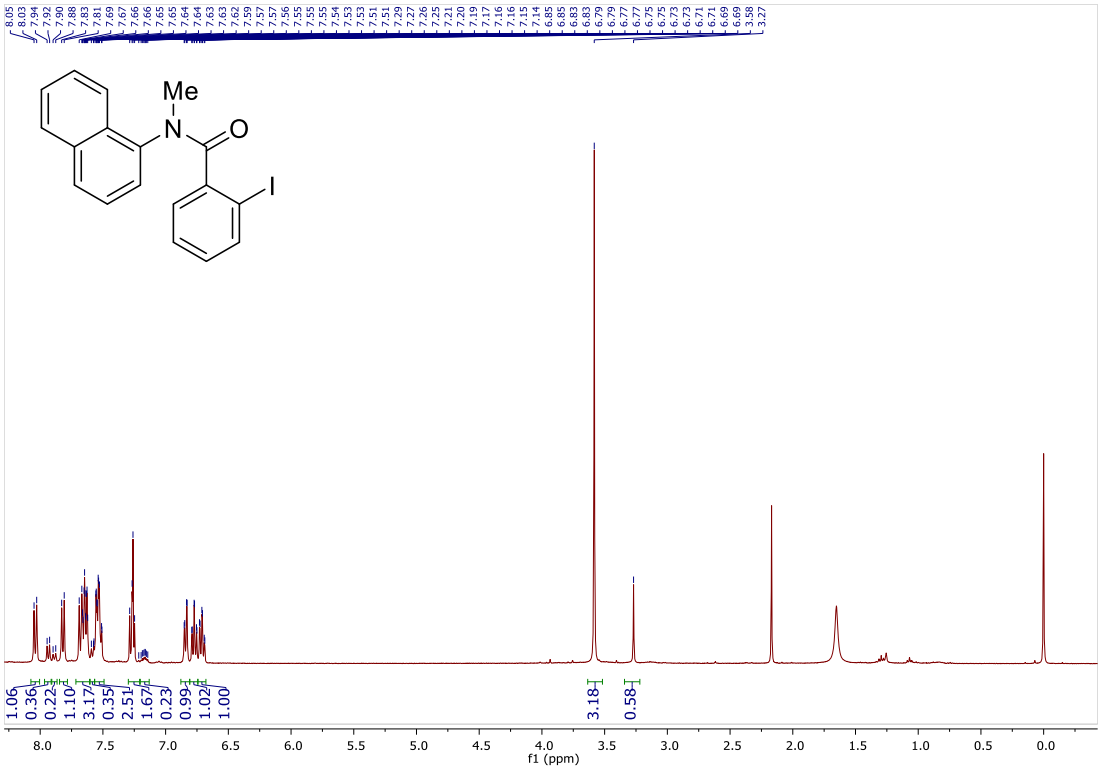


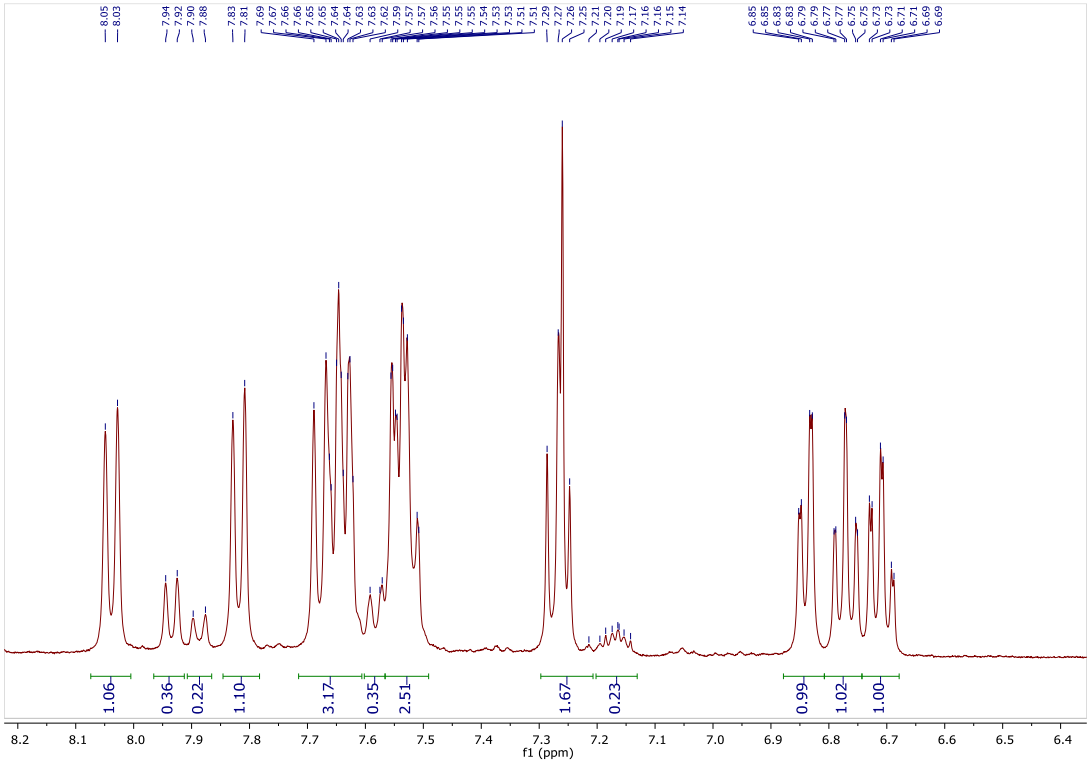
^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(4-(*tert*-Butyl)phenyl)-2-iodo-*N*-methylbenzamide (1g).



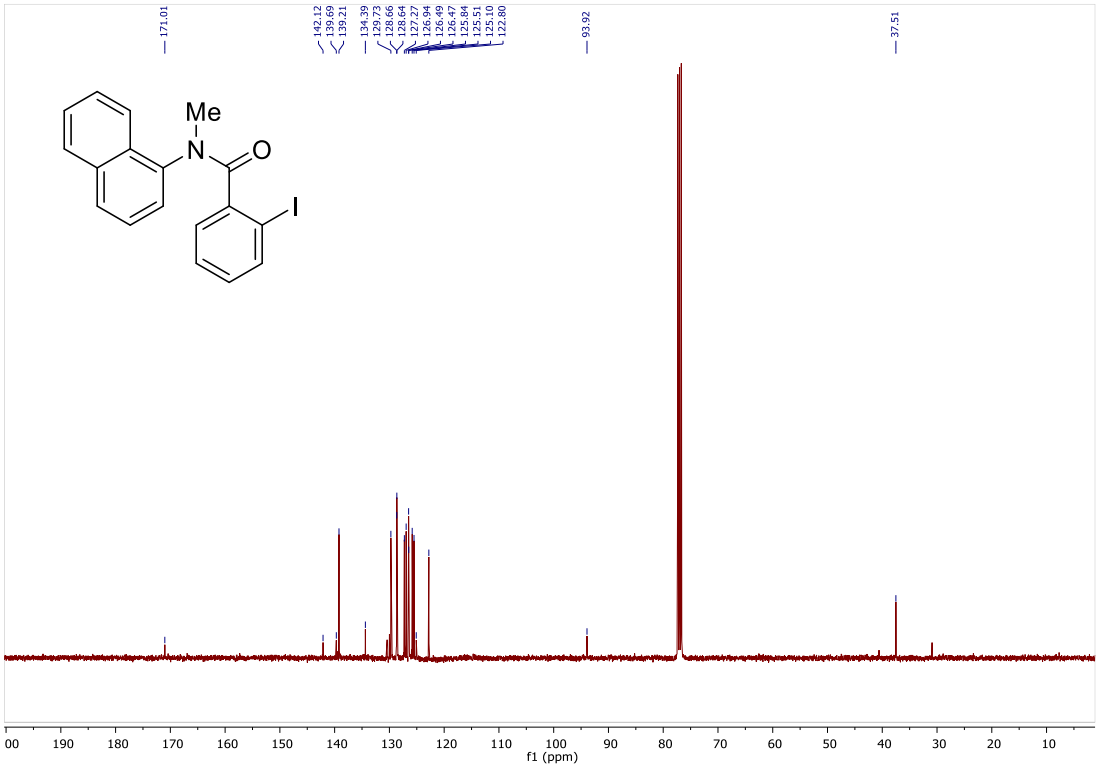


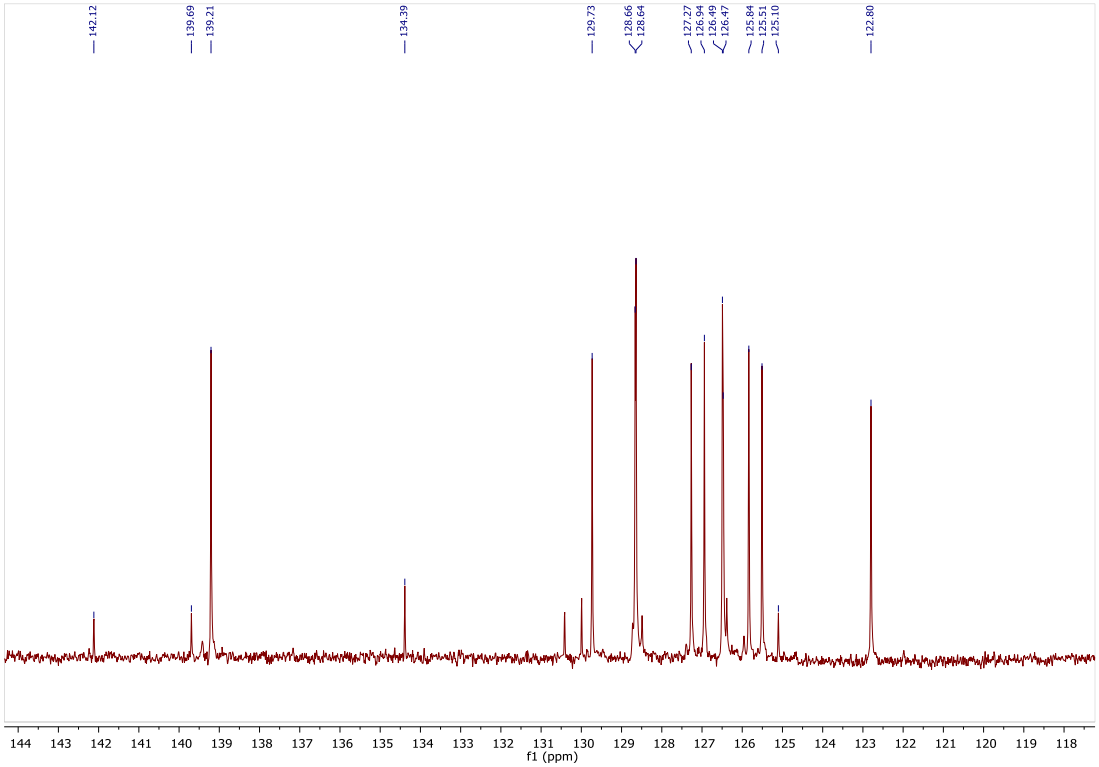
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(naphthalen-1-yl)benzamide (1h).



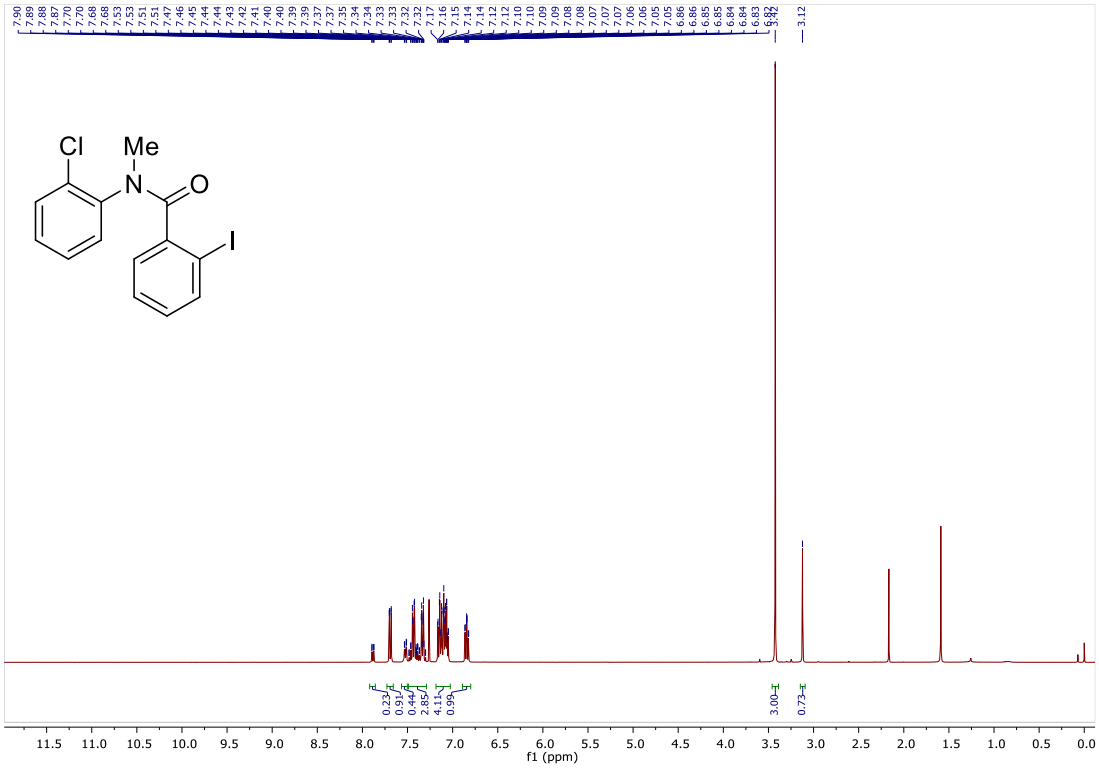


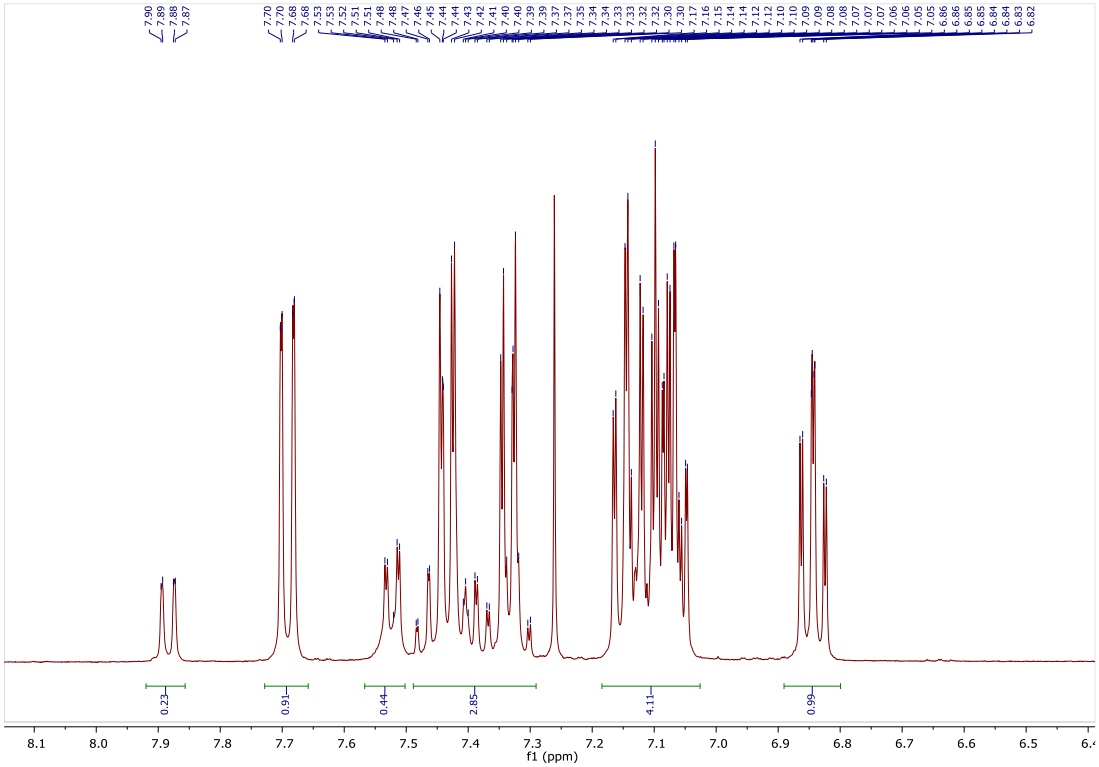
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(naphthalen-1-yl)benzamide (1h).



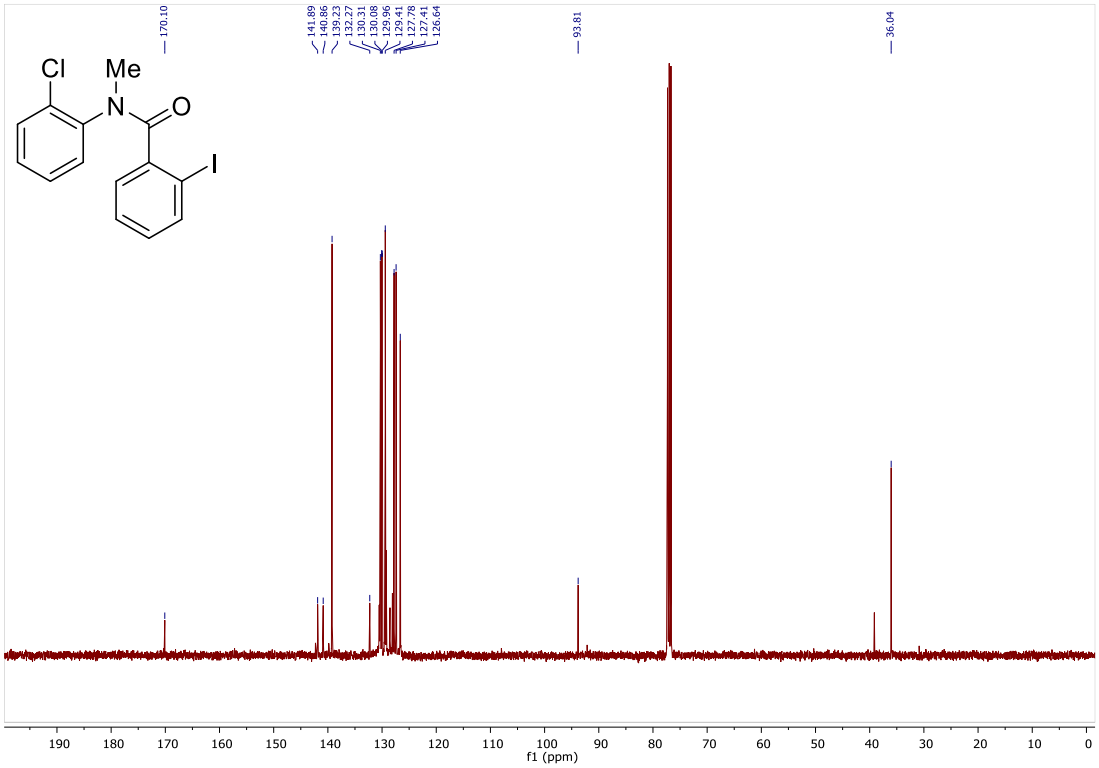


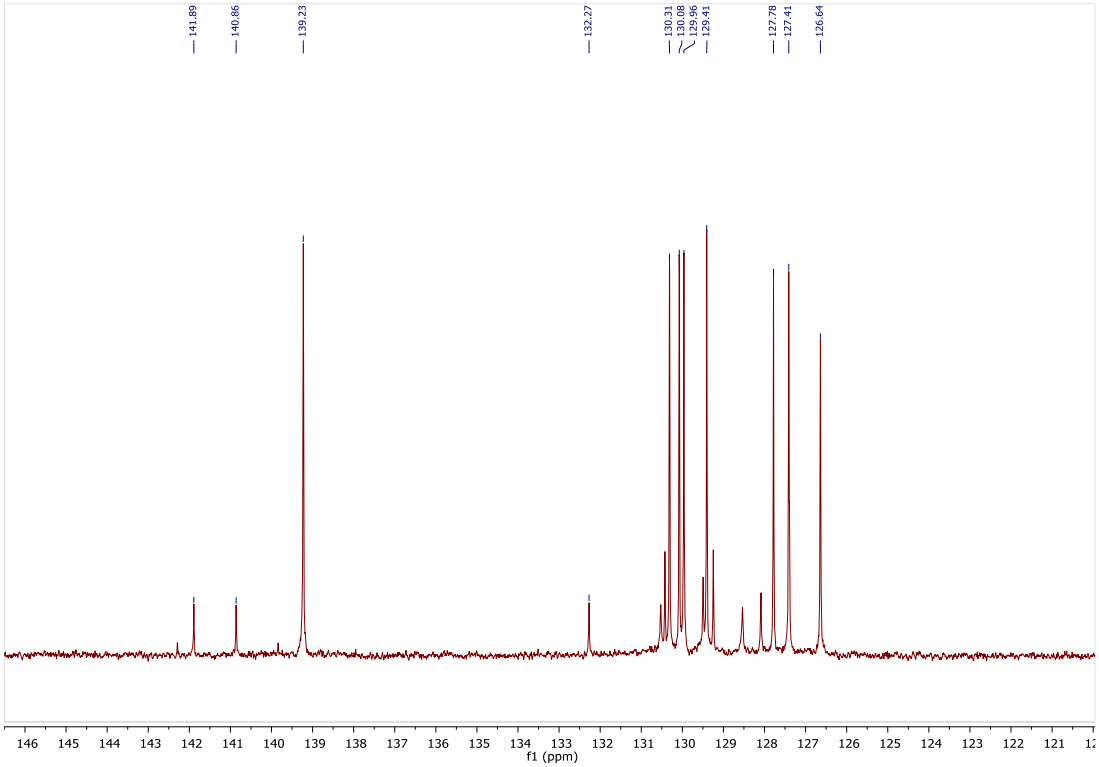
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(2-Chlorophenyl)-2-iodo-*N*-methylbenzamide (1i).



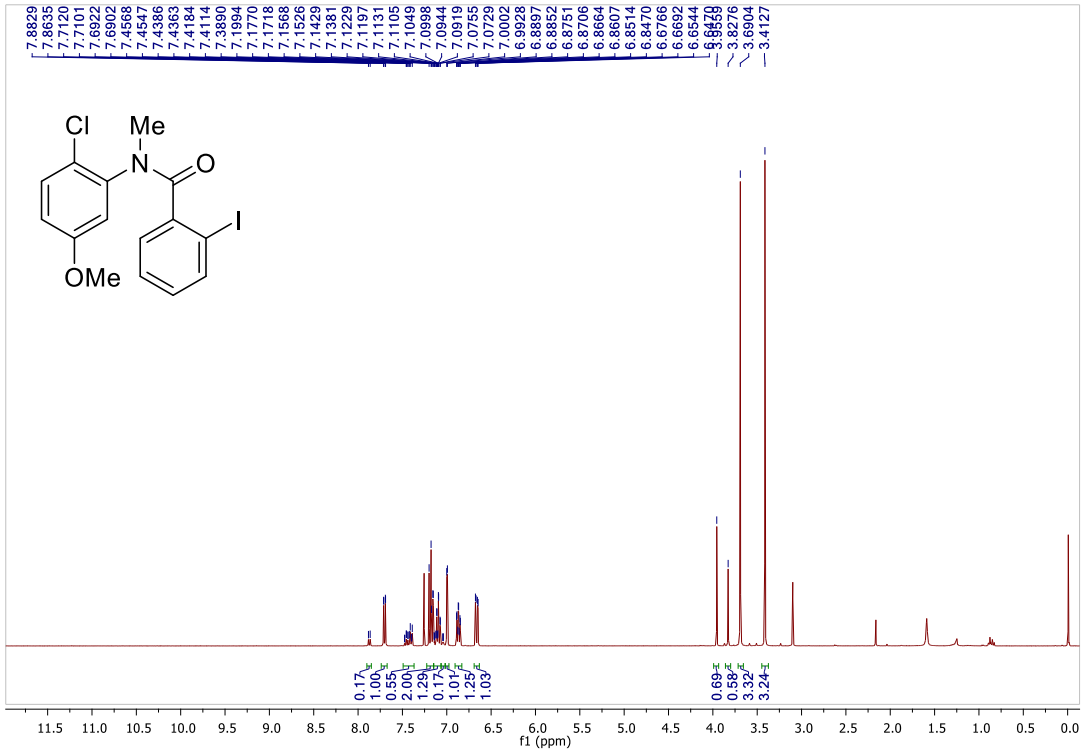


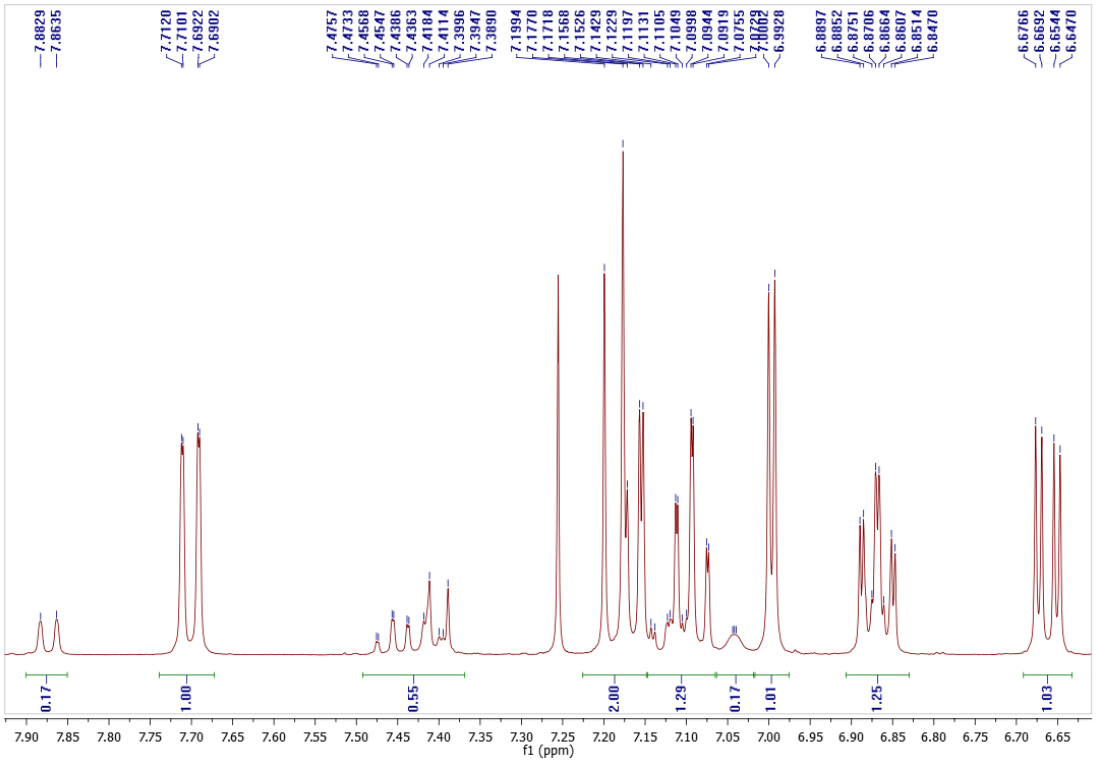
^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(2-Chlorophenyl)-2-iodo-*N*-methylbenzamide (1i).



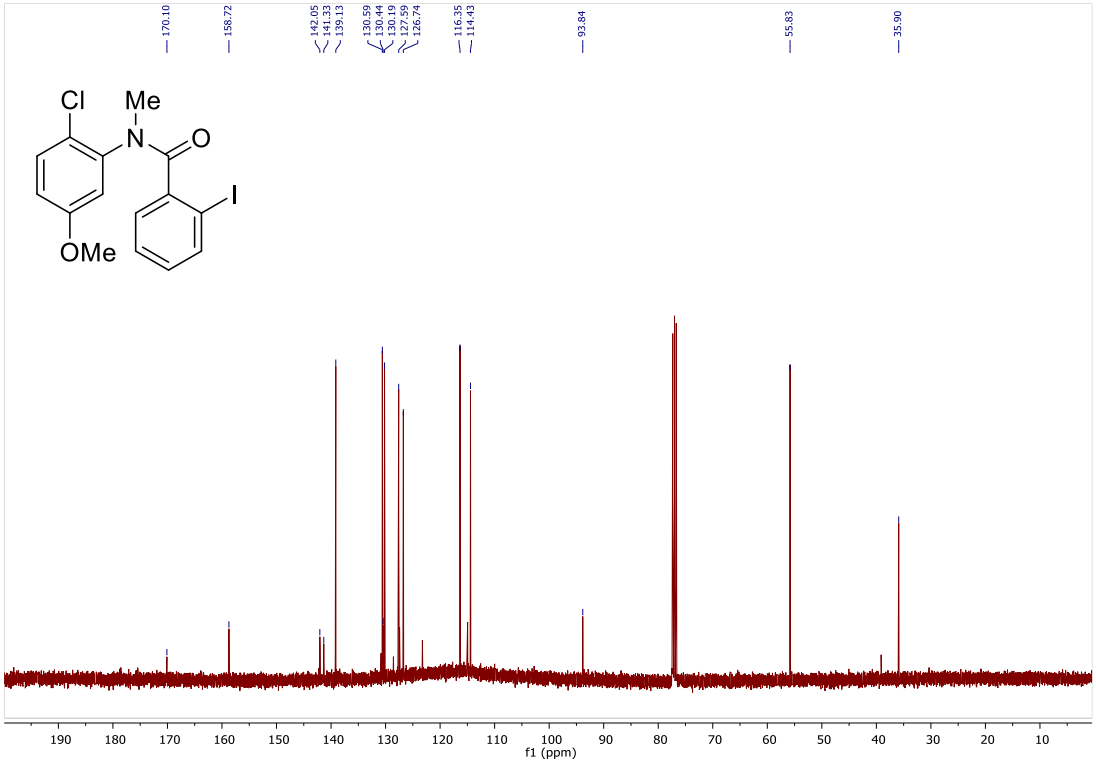


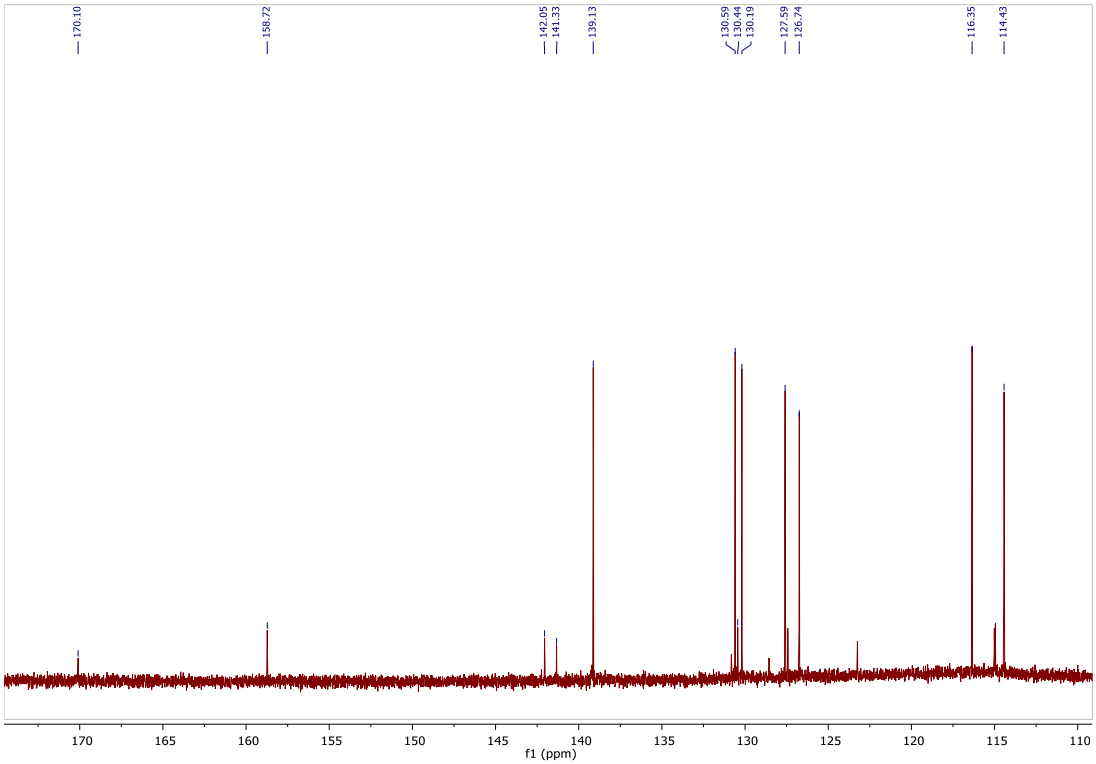
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(2-Chloro-5-methoxyphenyl)-2-iodo-*N*-methylbenzamide (1j)



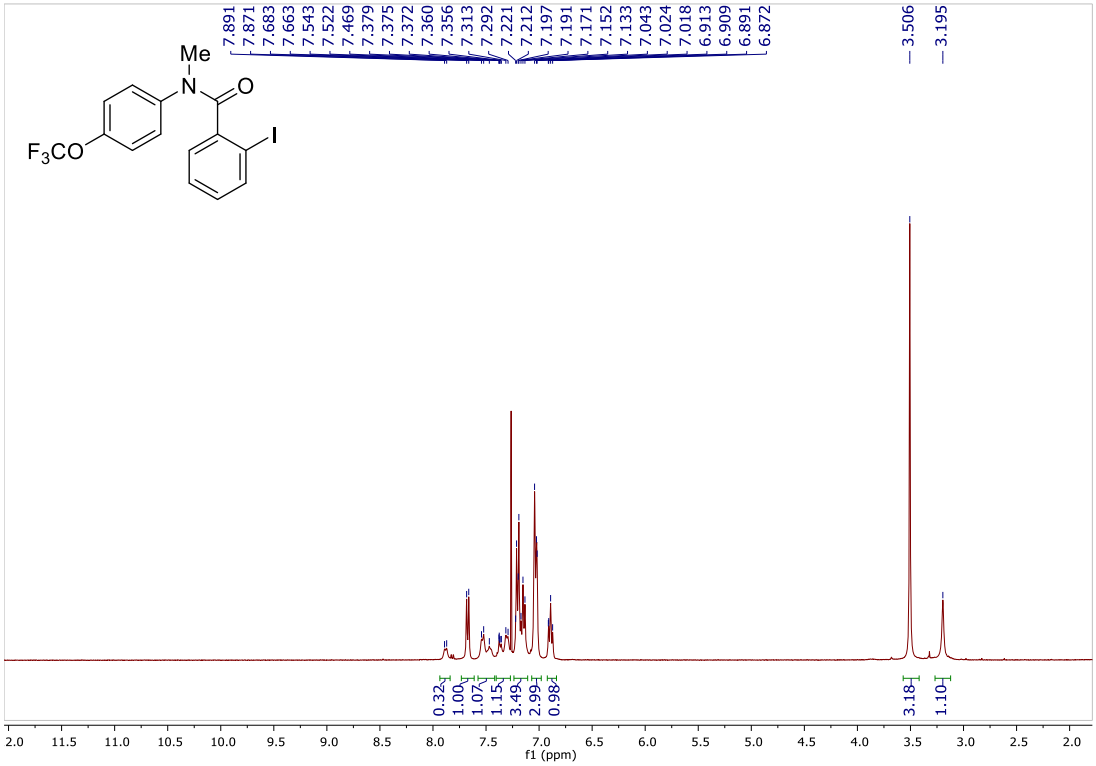


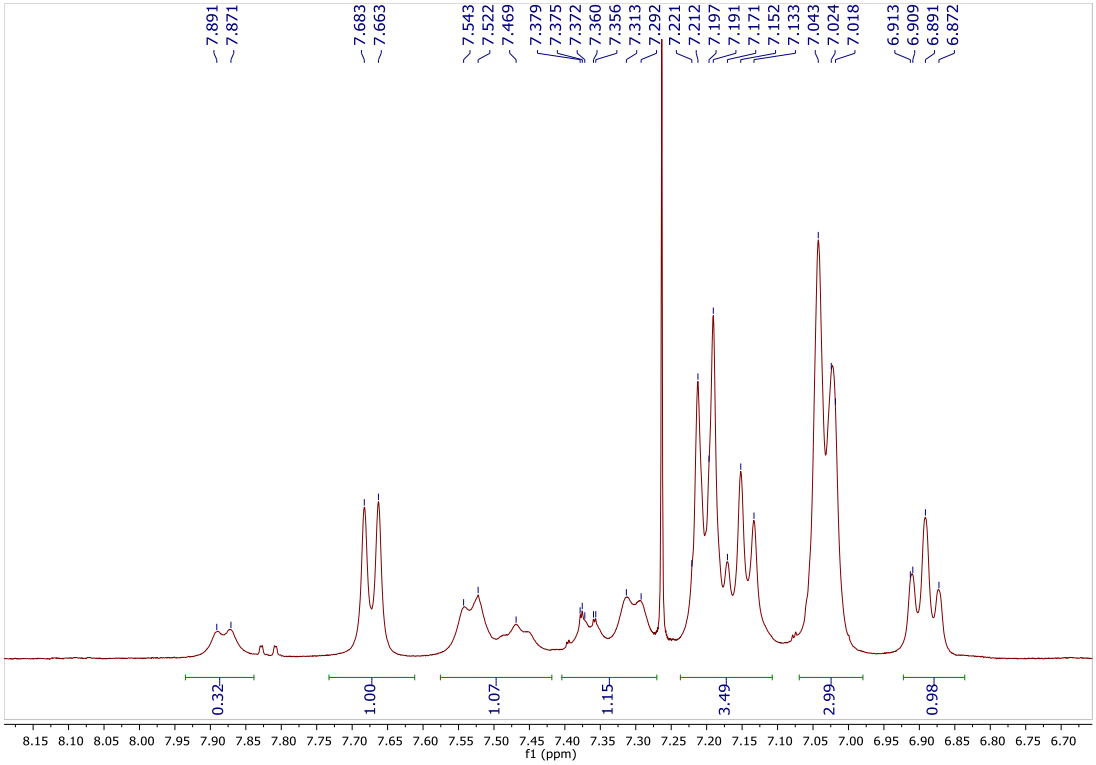
^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(2-Chloro-5-methoxyphenyl)-2-iodo-*N*-methyl benzamide (1j)



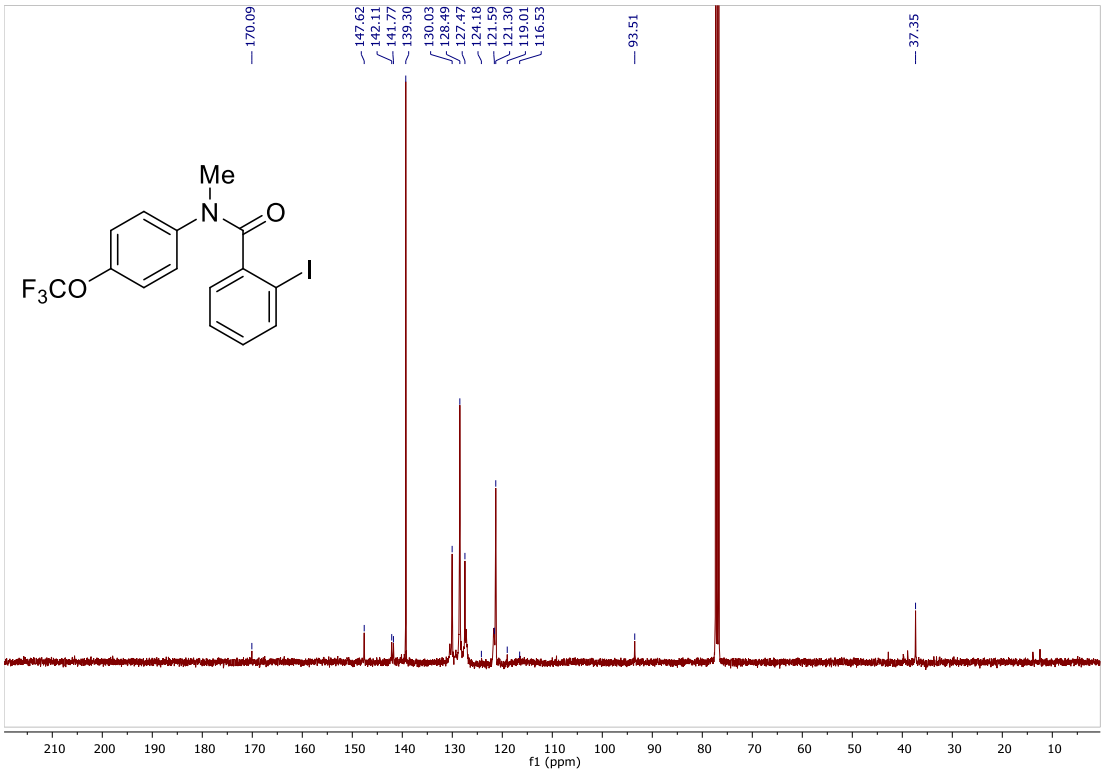


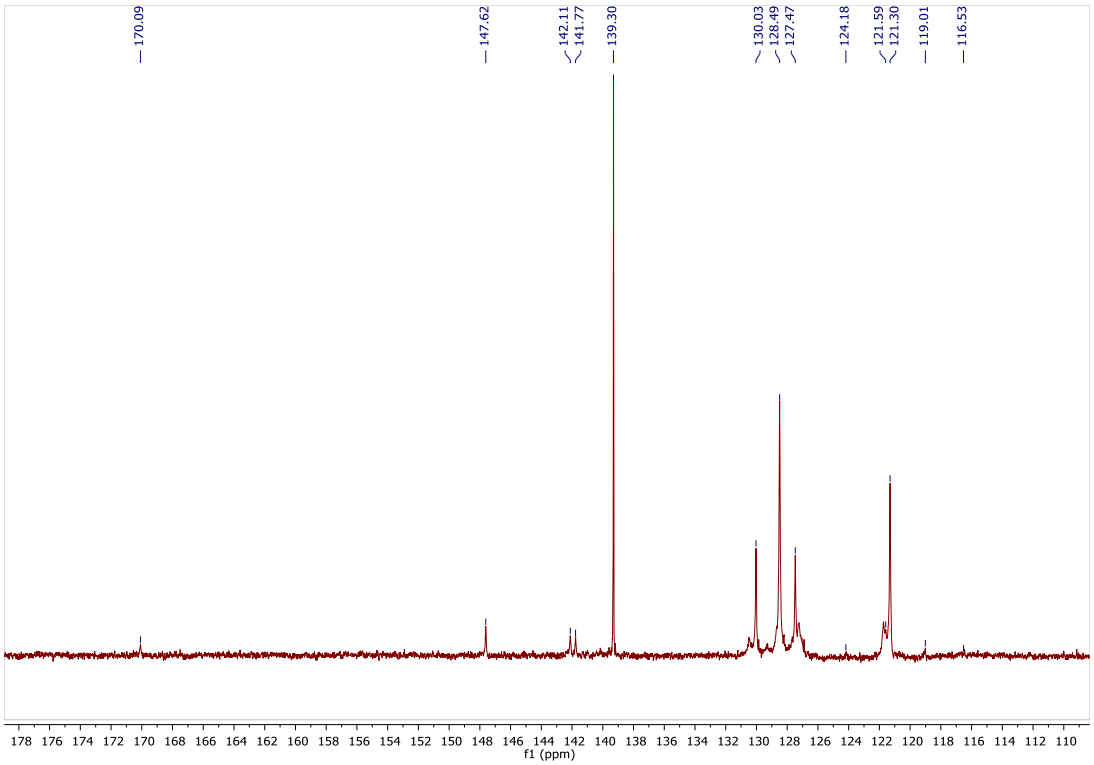
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(4-(trifluoromethoxy)phenyl)benzamide (1k).



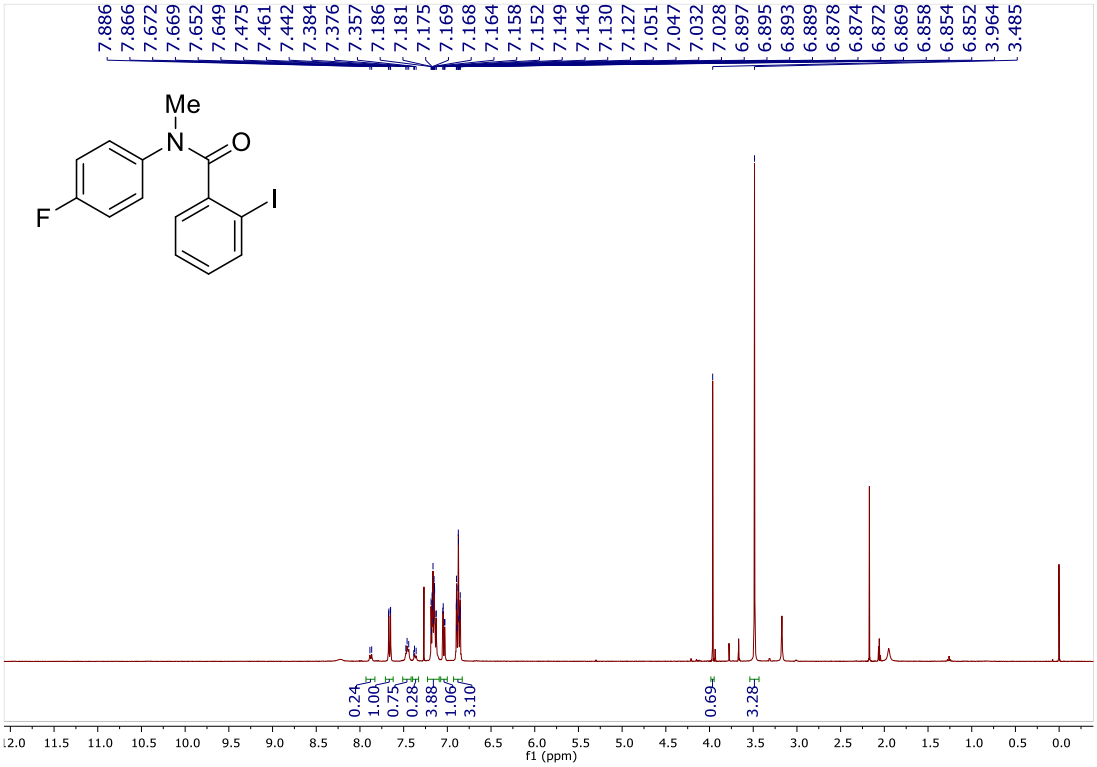


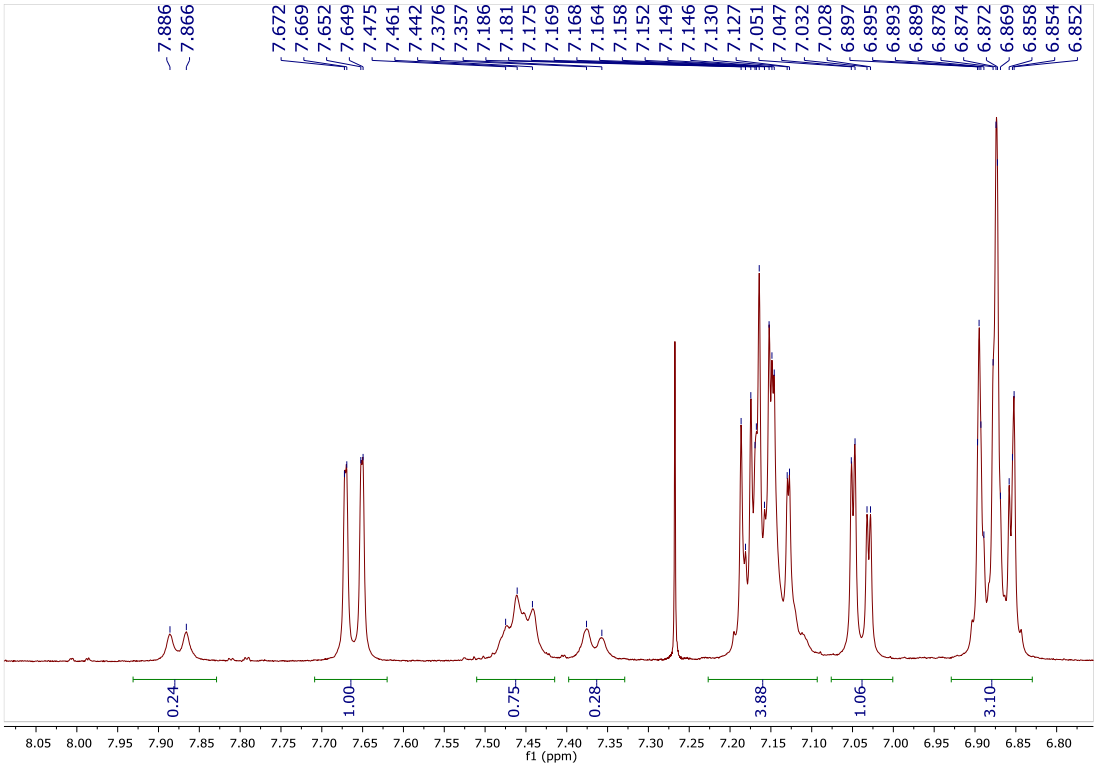
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(4-(trifluoromethoxy)phenyl)benzamide (1k).



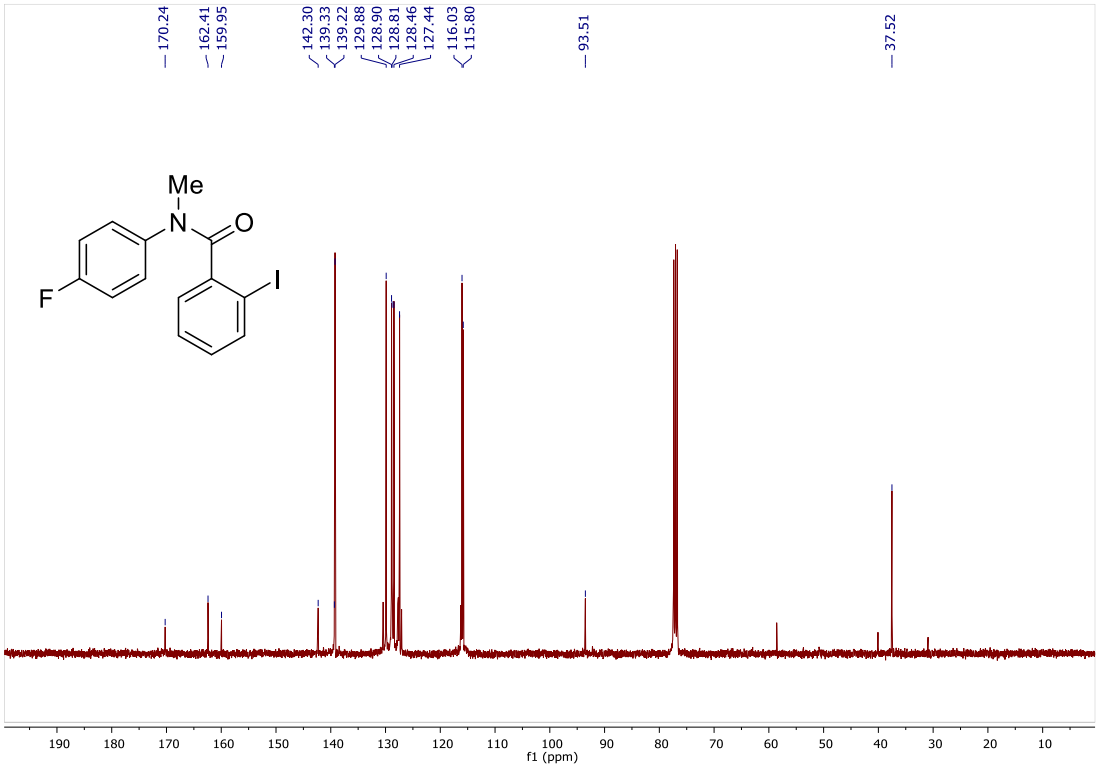


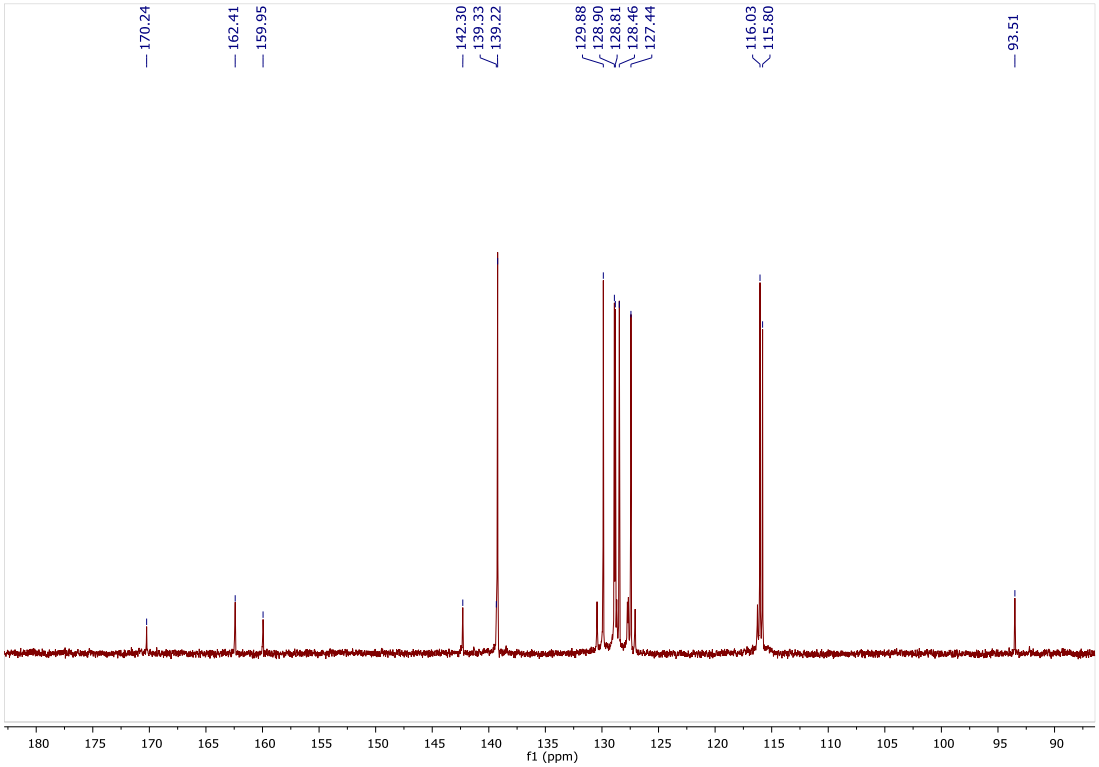
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(4-Fluorophenyl)-2-iodo-*N*-methylbenzamide (1l).



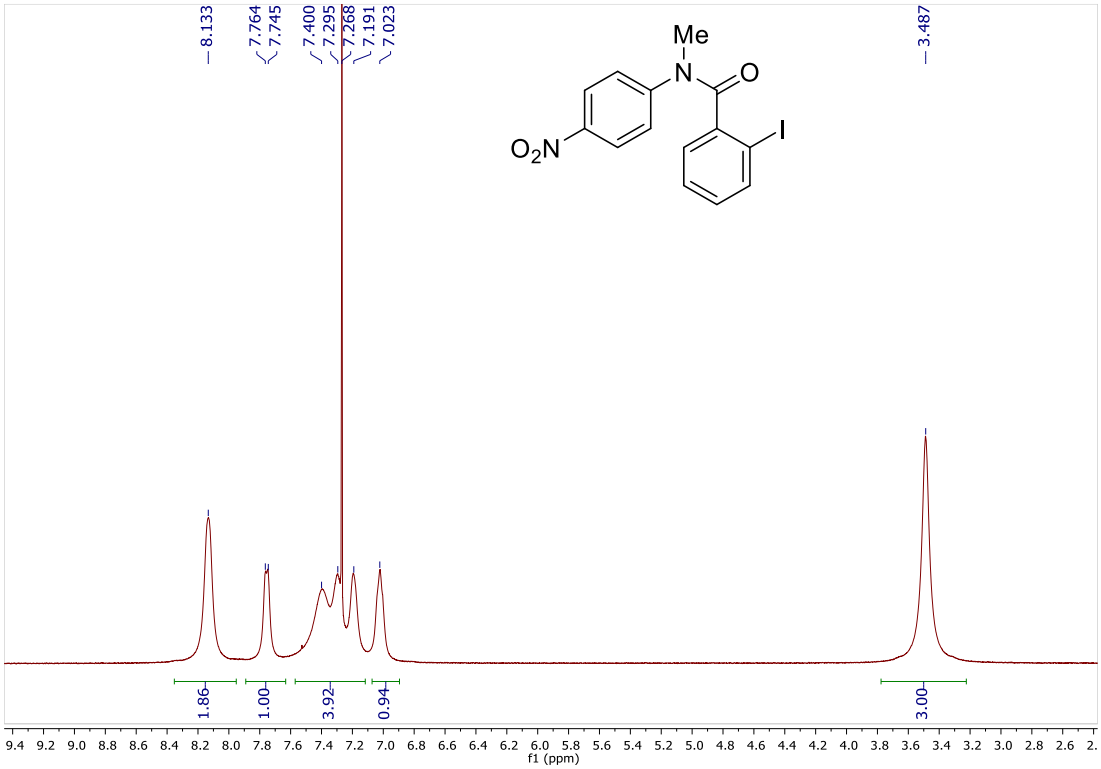


^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(4-Fluorophenyl)-2-iodo-*N*-methylbenzamide (1l).

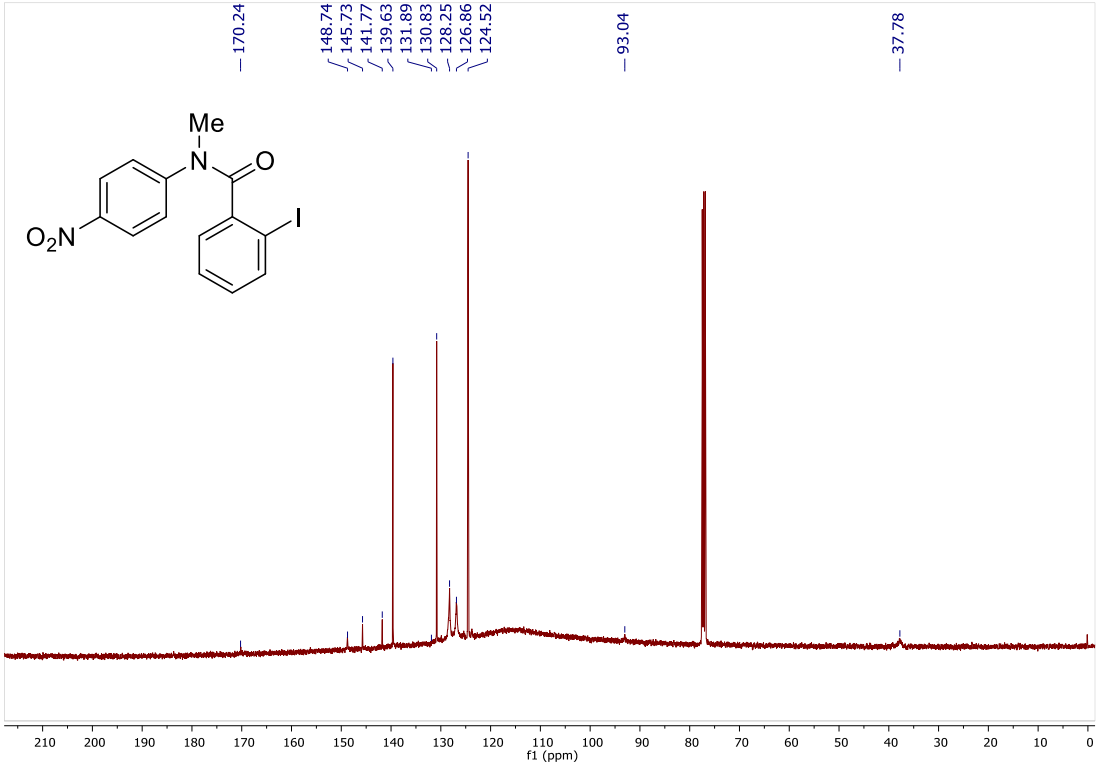




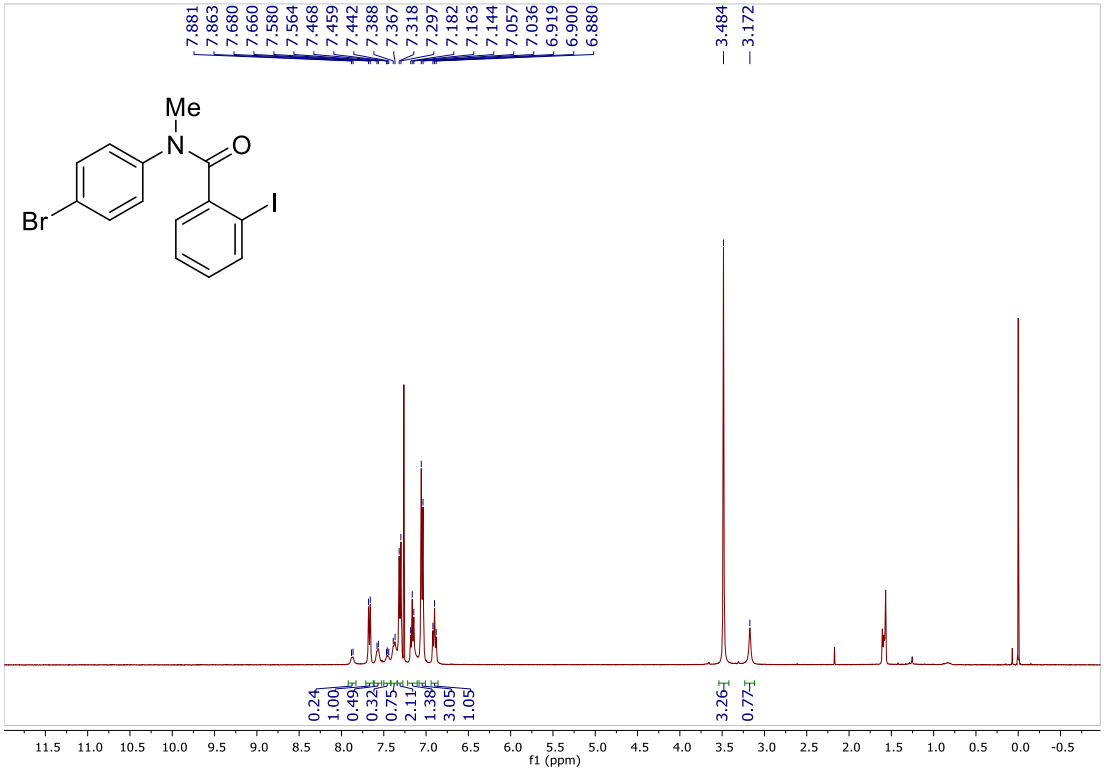
^{1}H NMR (400 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(4-nitrophenyl)benzamide (1m).

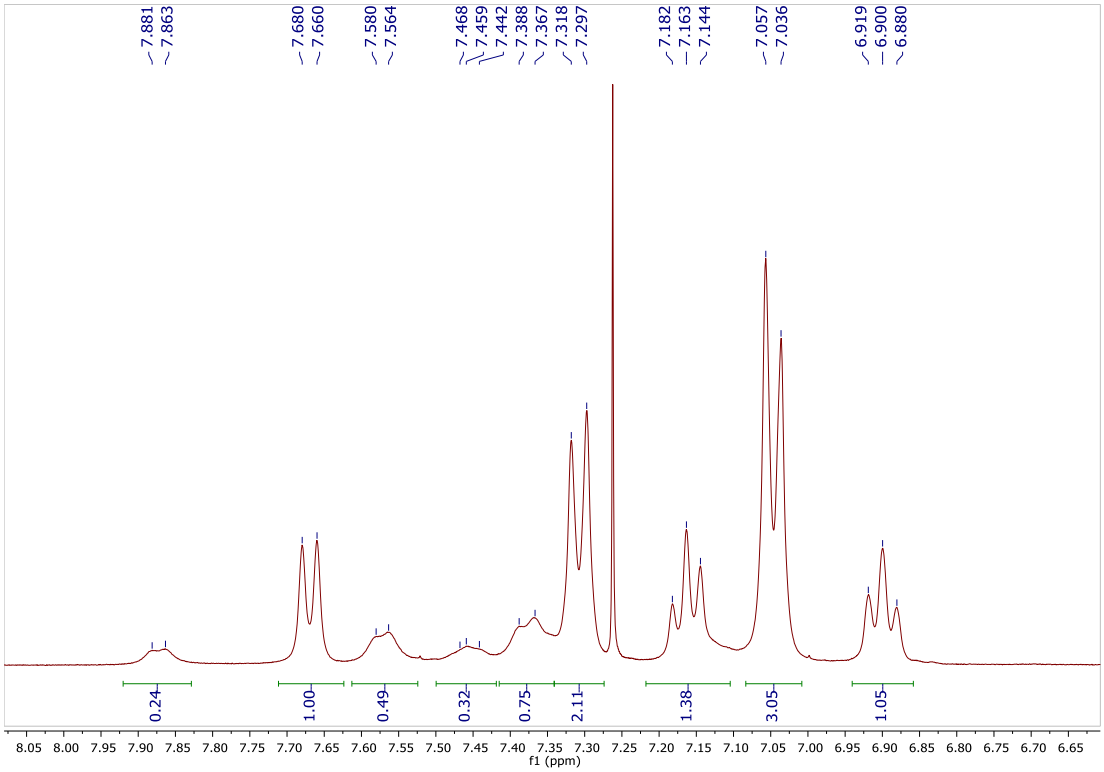


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Iodo-*N*-methyl-*N*-(4-nitrophenyl)benzamide (1m).

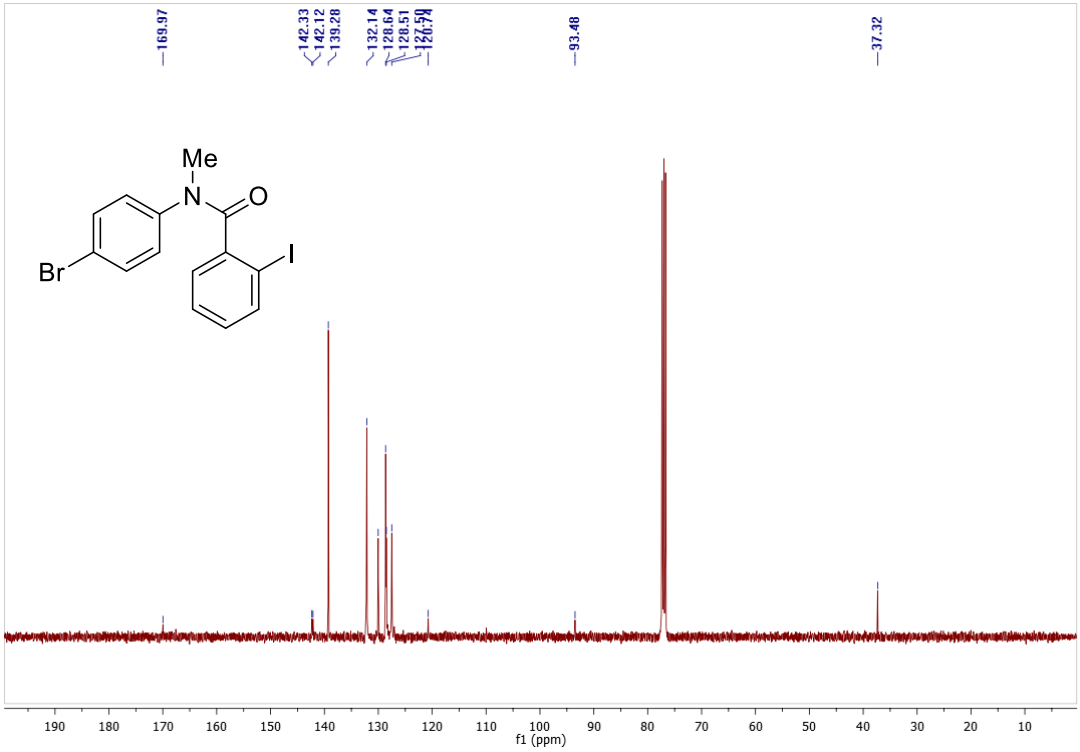


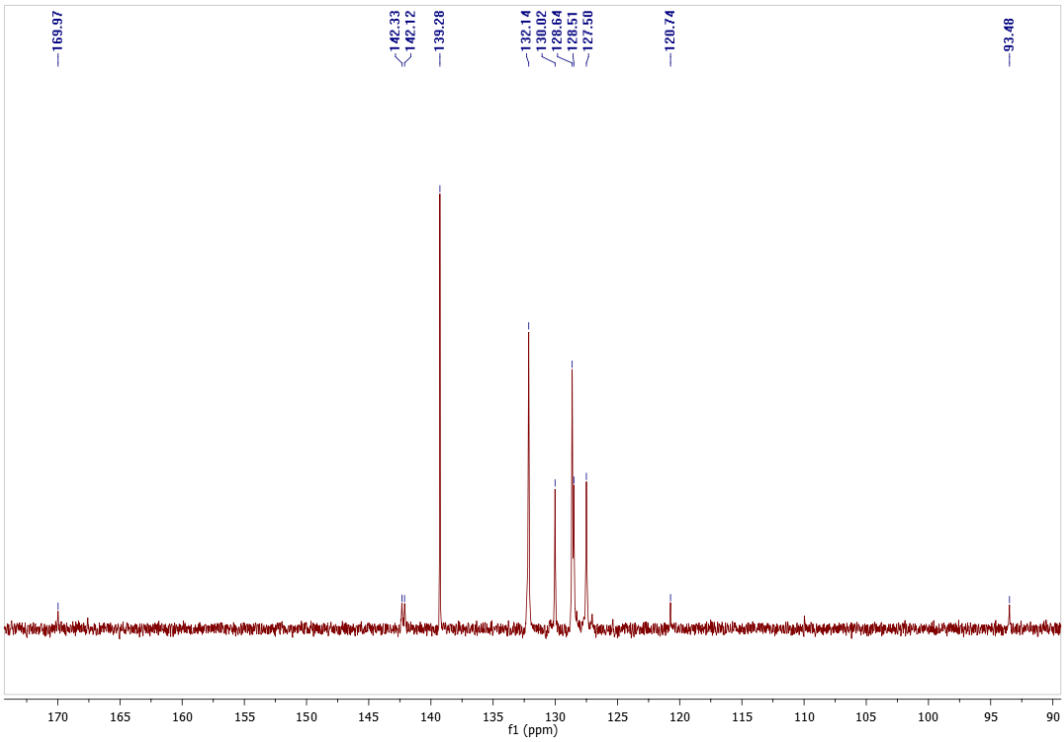
^{1}H NMR (400 MHz, $CDCl_3$). *N*-(4-Bromophenyl)-2-iodo-*N*-methylbenzamide (1n).



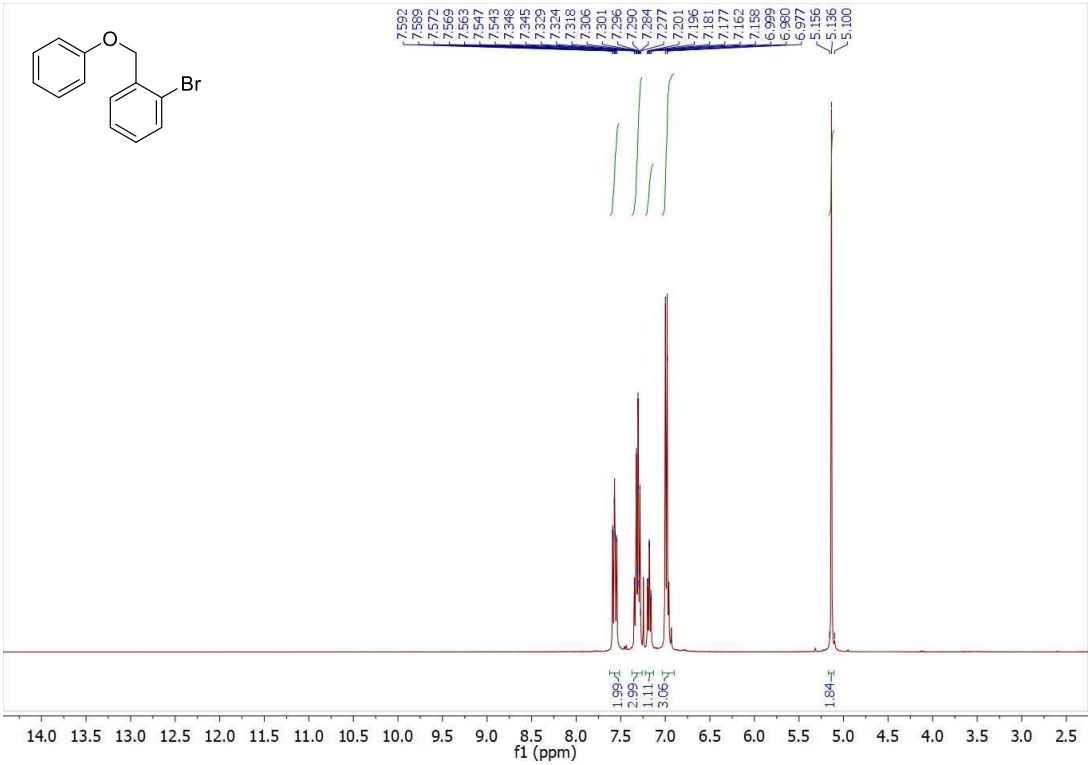


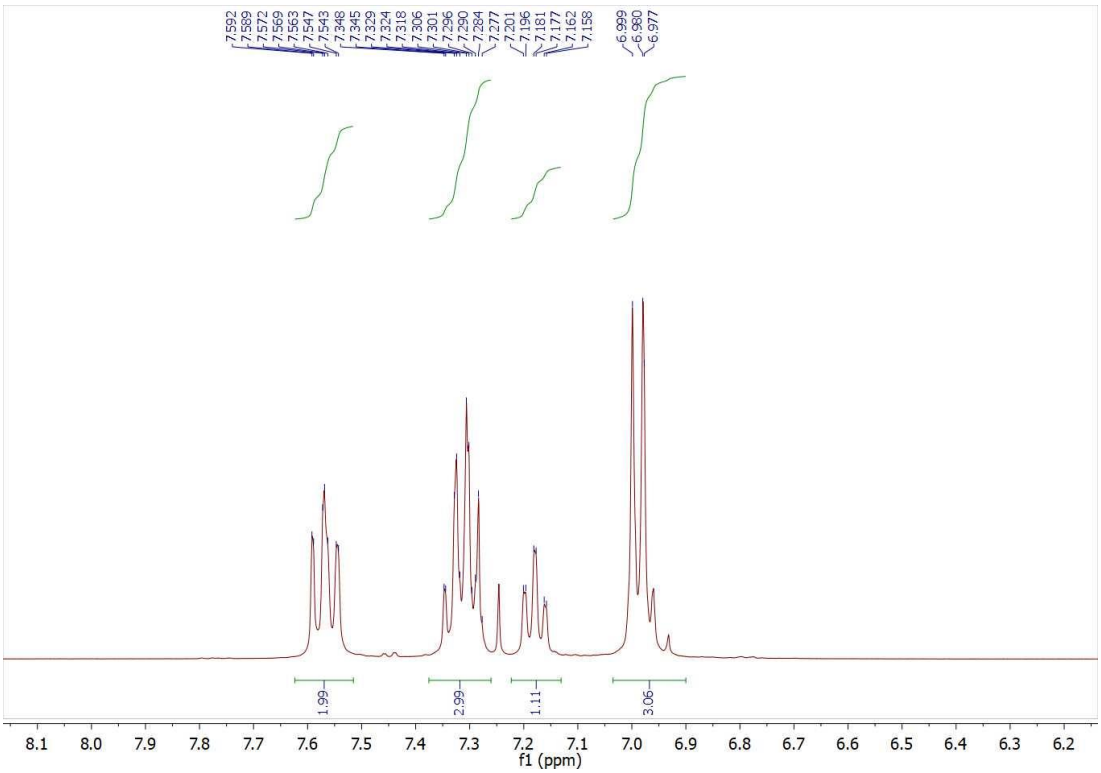
^{13}C NMR {1H} (101 MHz, $CDCl_3$). *N*-(4-Bromophenyl)-2-iodo-*N*-methylbenzamide (1n).



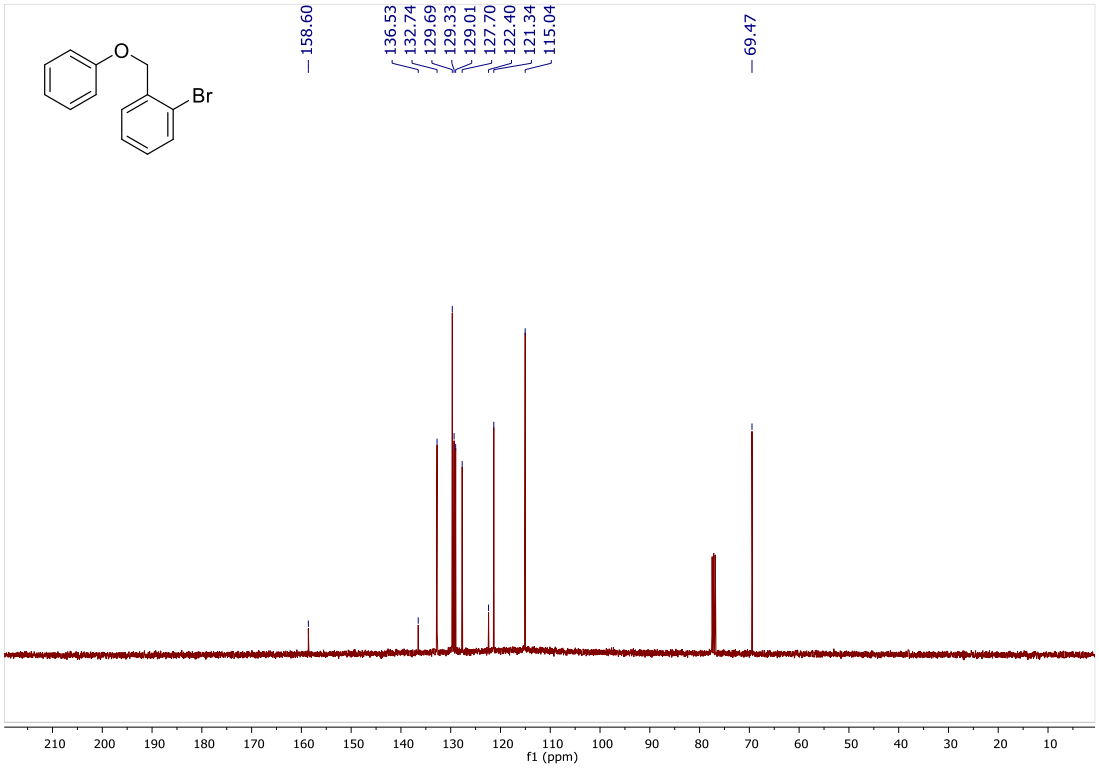


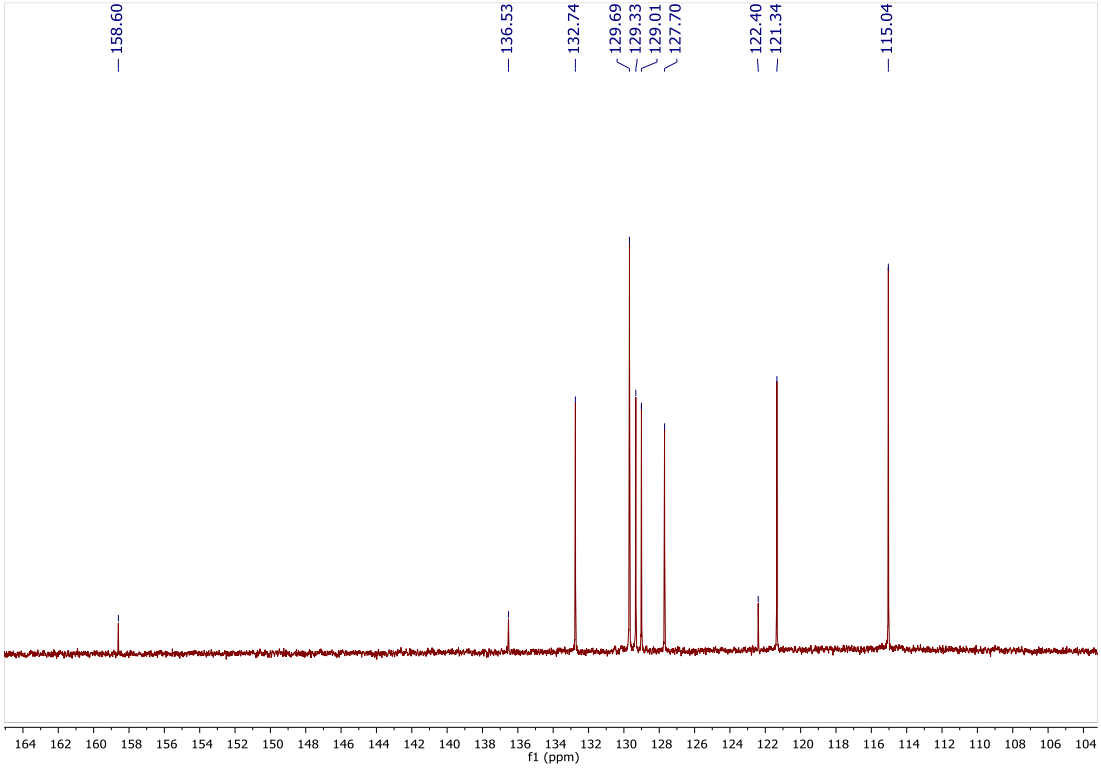
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl phenyl ether (6a)



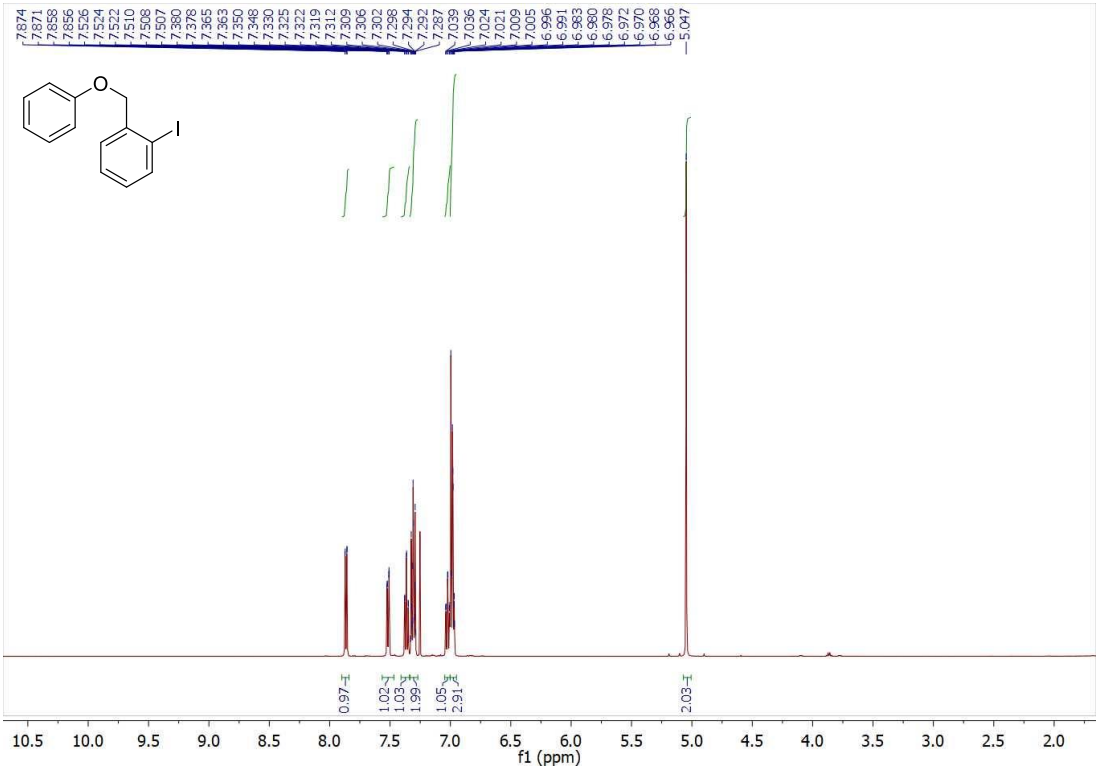


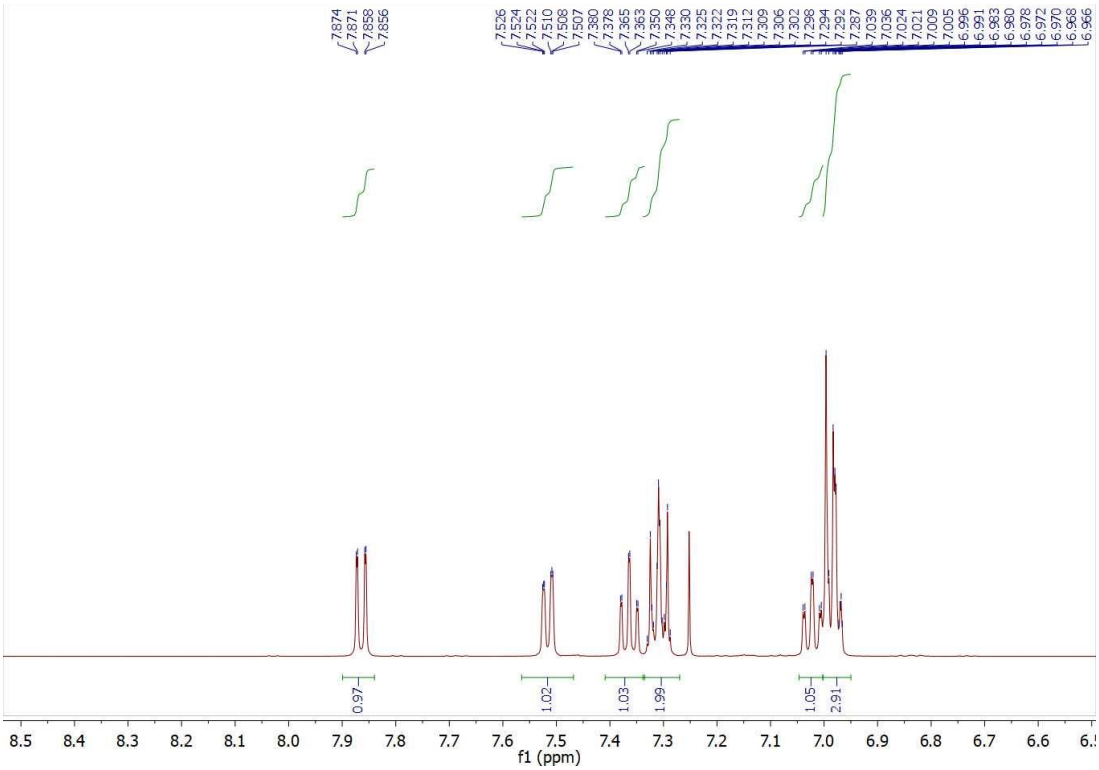
^{13}C NMR {1H} (126 MHz, $CDCl_3$). 2-Bromobenzyl phenyl ether (6a)



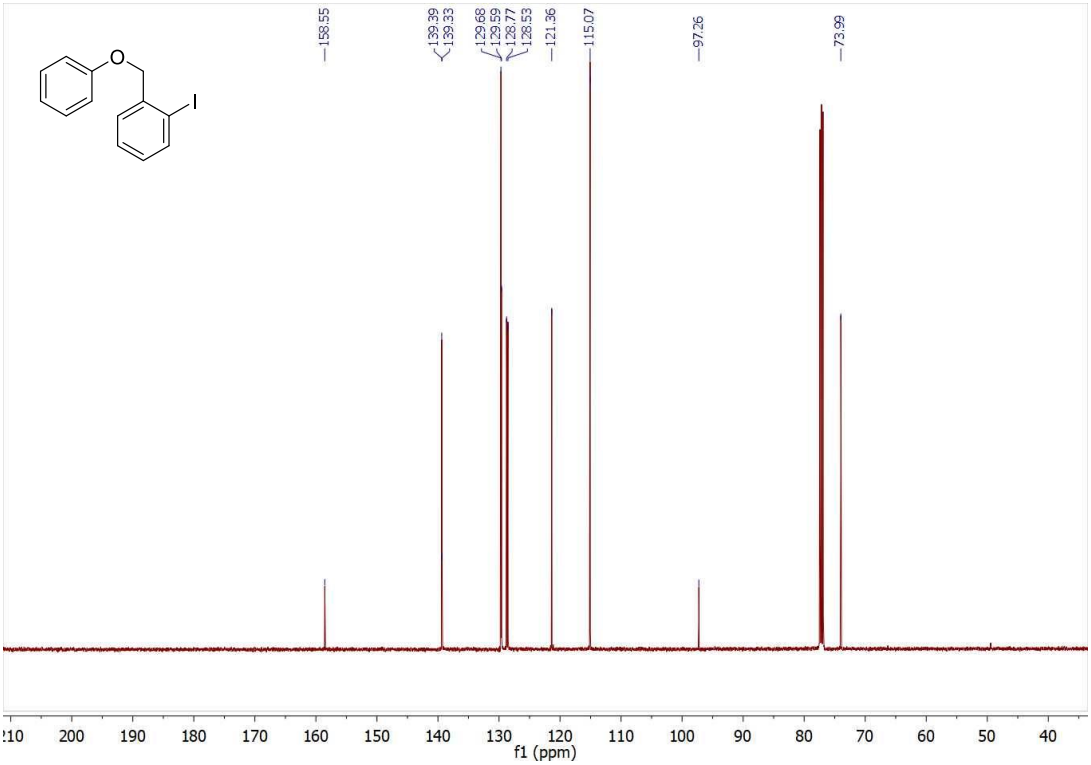


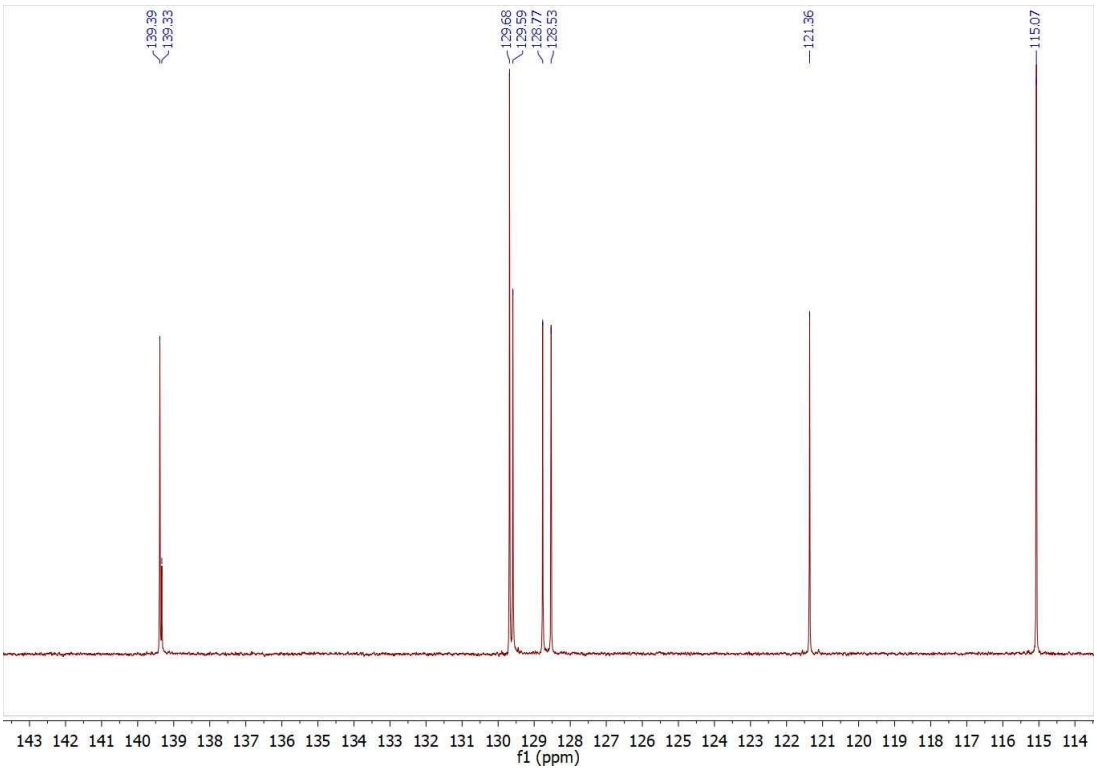
^{1}H NMR (500 MHz, $CDCl_3$). 2-Iodobenzyl phenyl ether (6b)



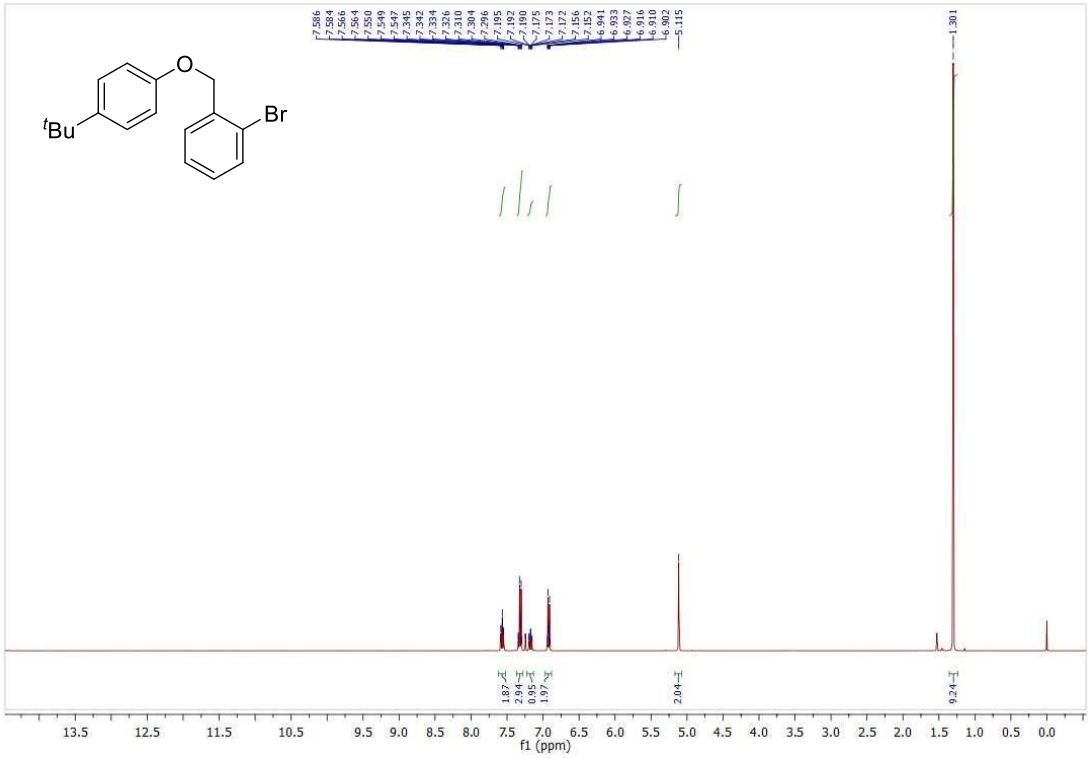


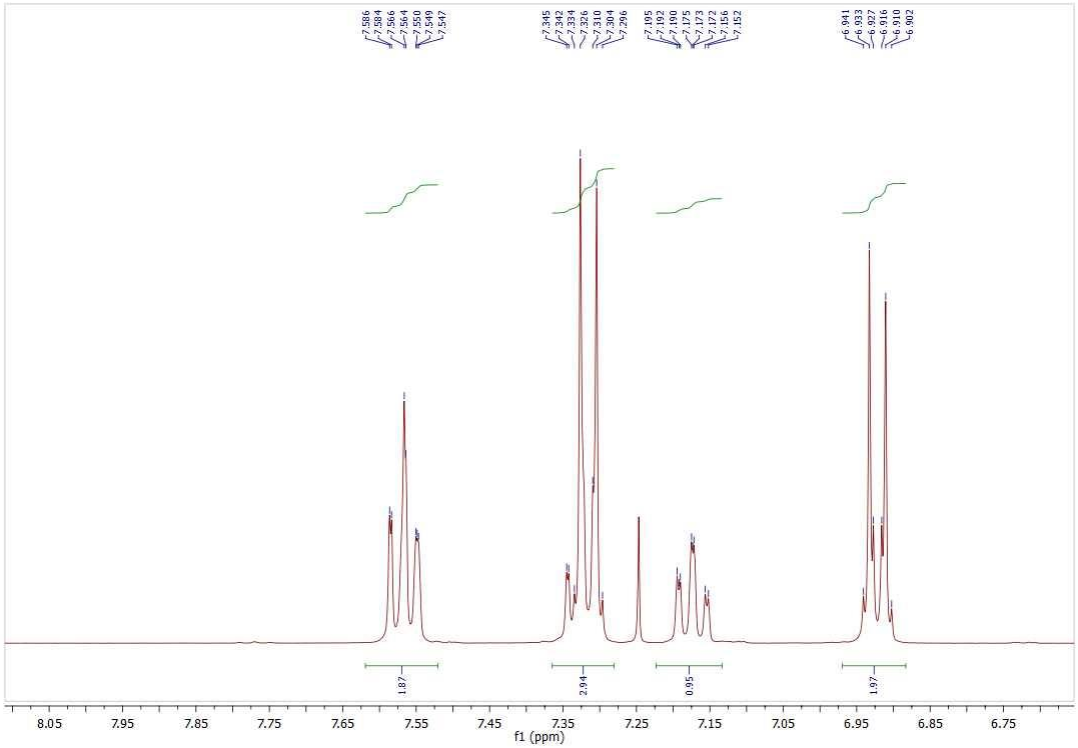
^{13}C NMR {1H} (126 MHz, $CDCl_3$). 2-Iodobenzyl phenyl ether (6b)



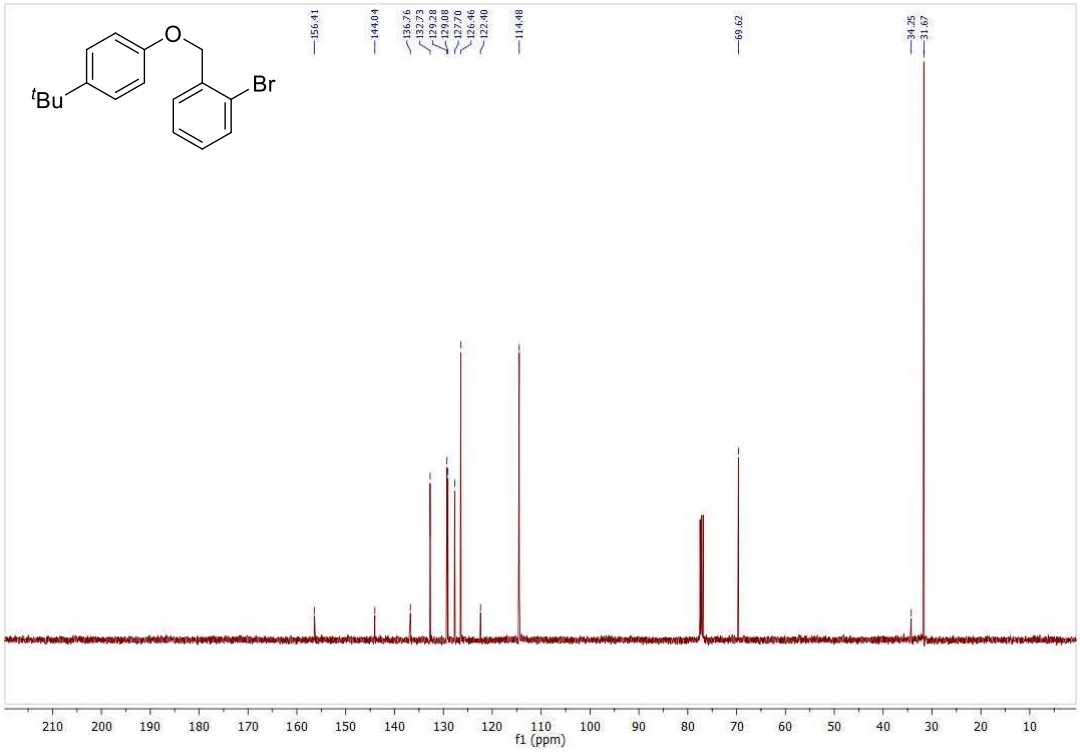


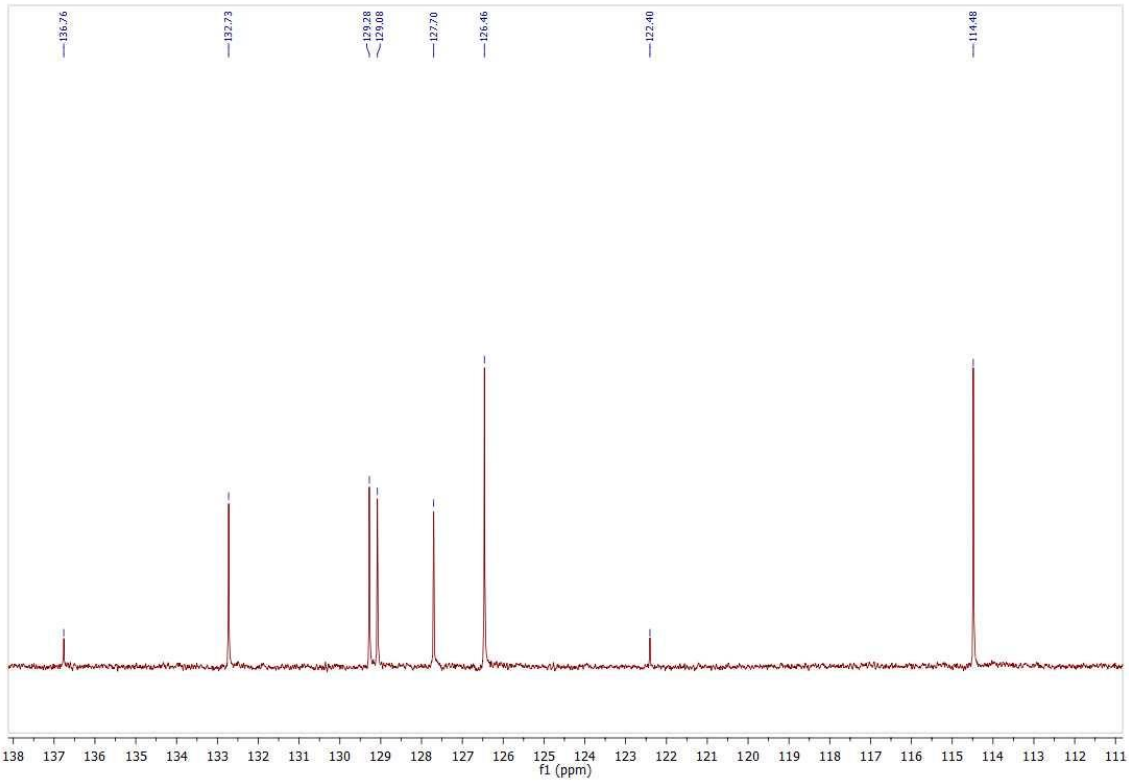
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-*tert*-butylphenyl ether (6c)



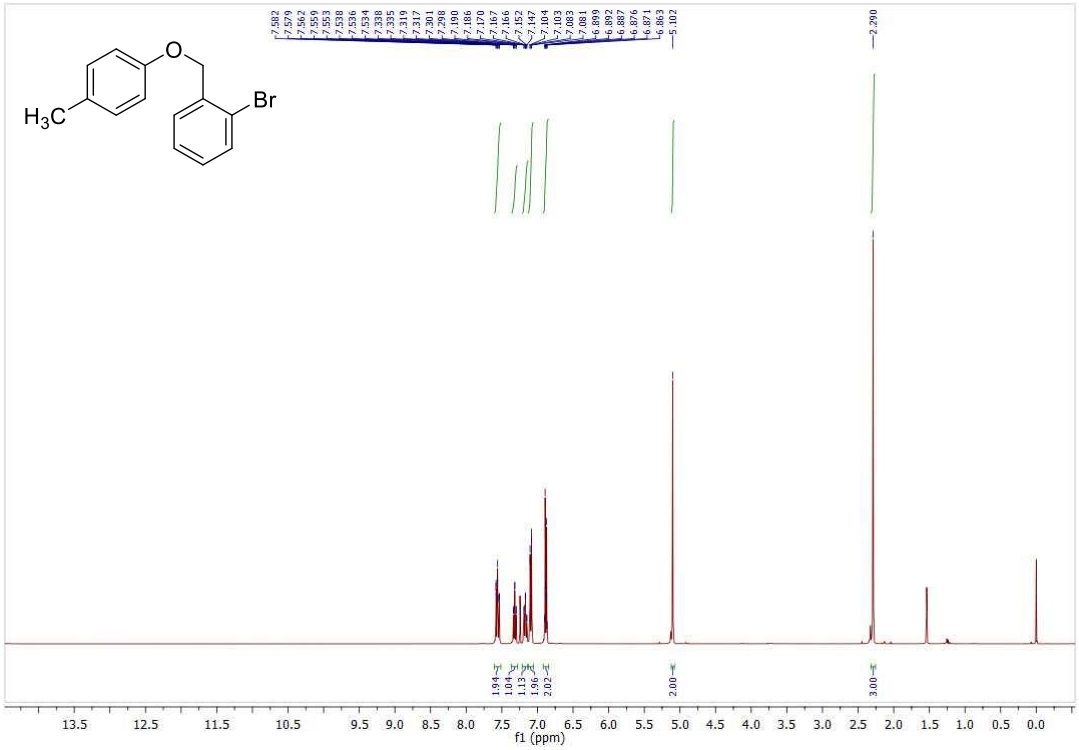


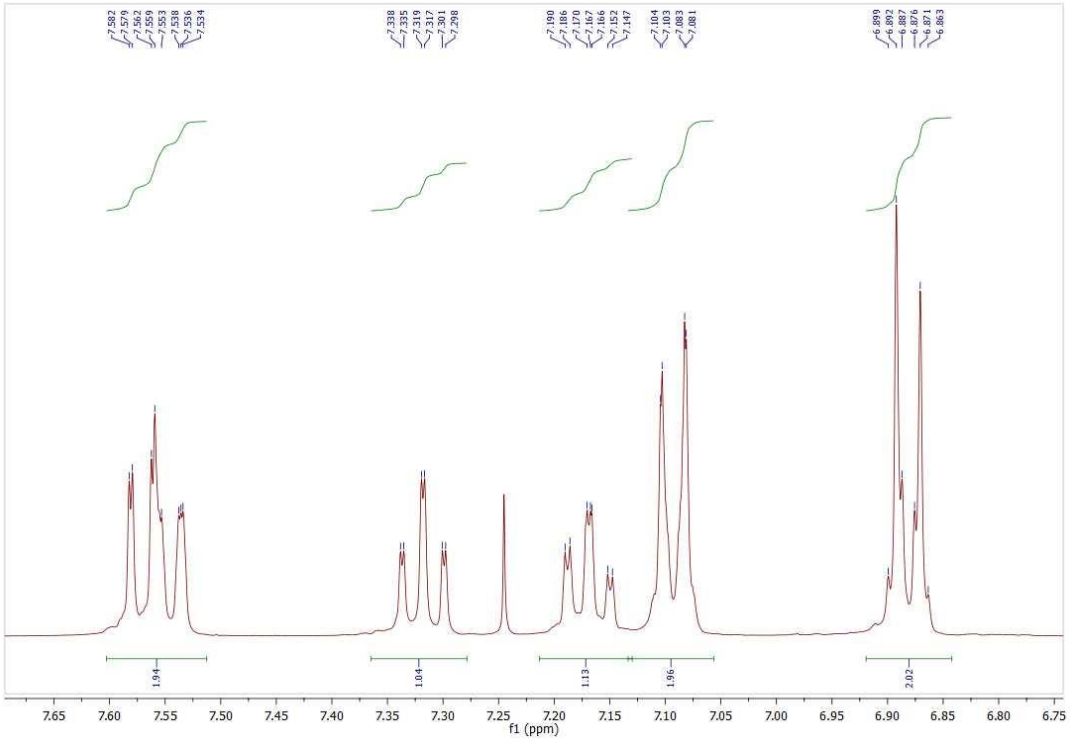
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-*tert*-butylphenyl ether (6c)



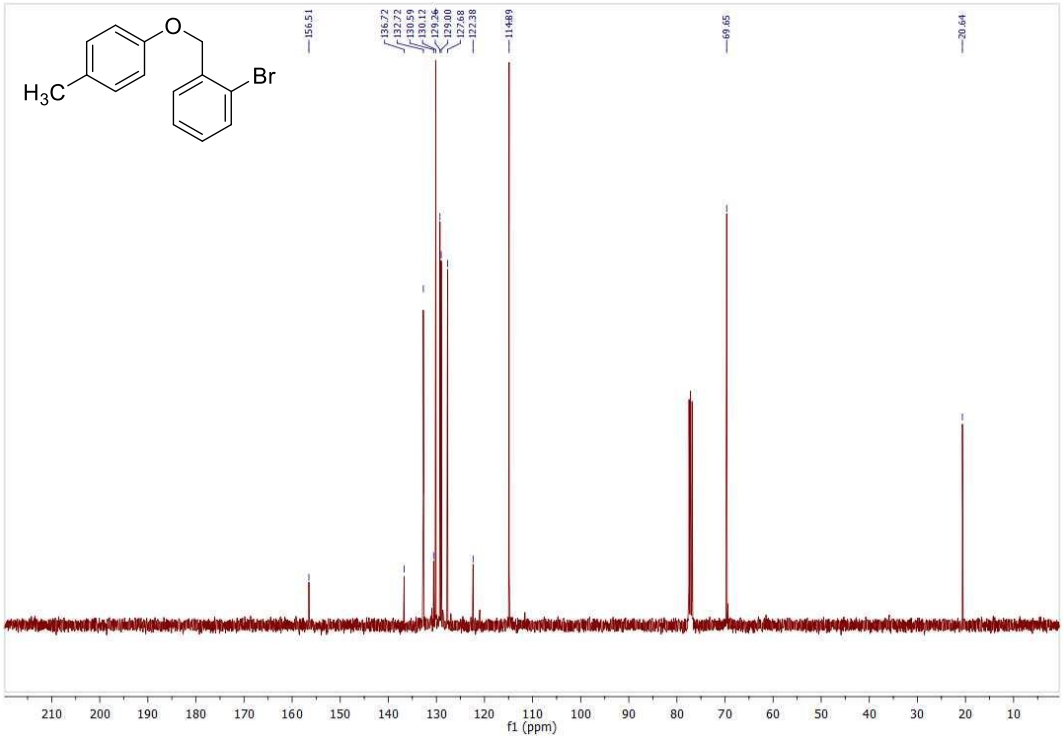


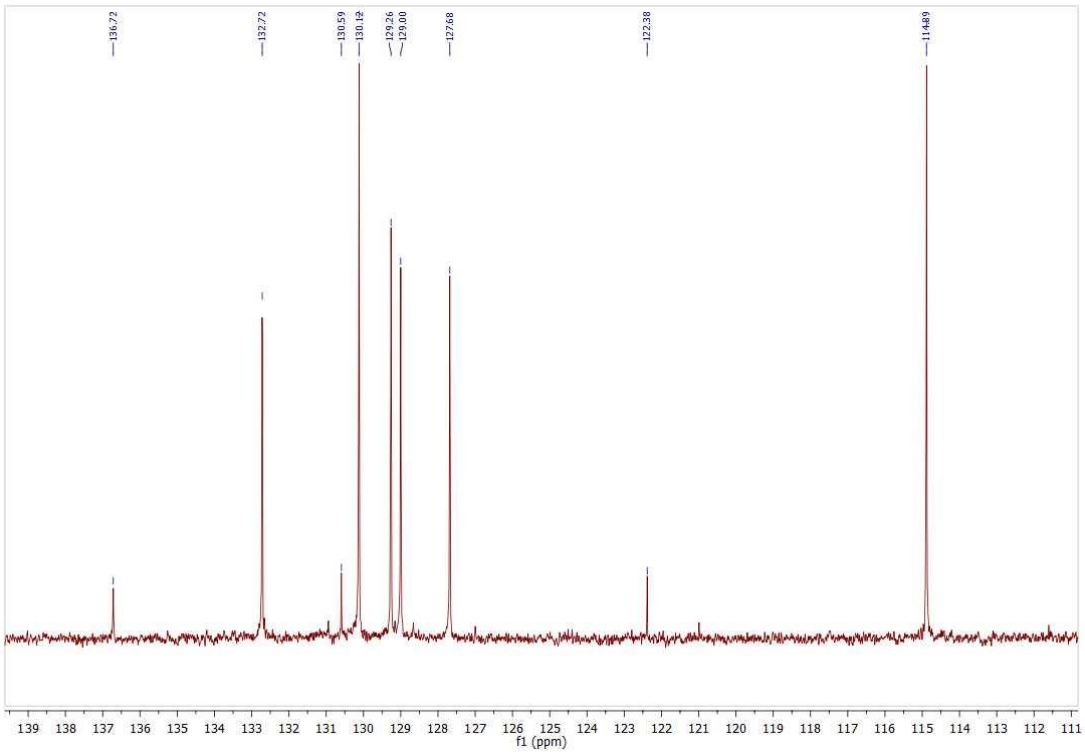
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-methylphenyl ether (6d).



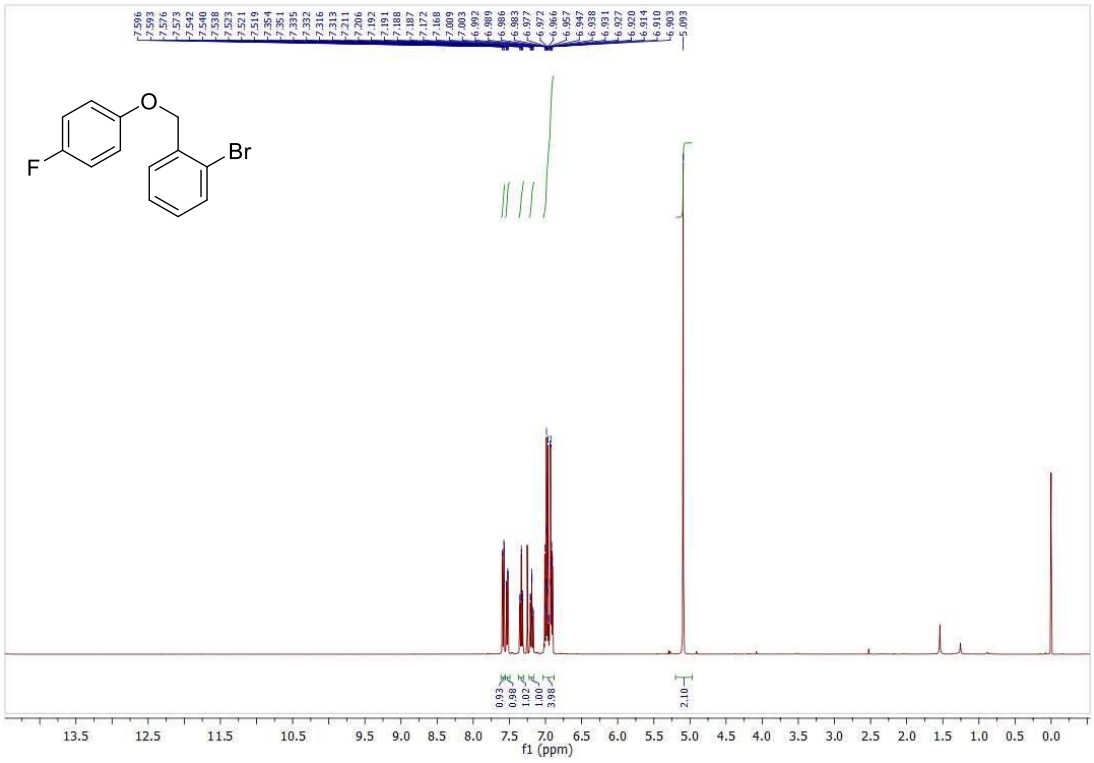


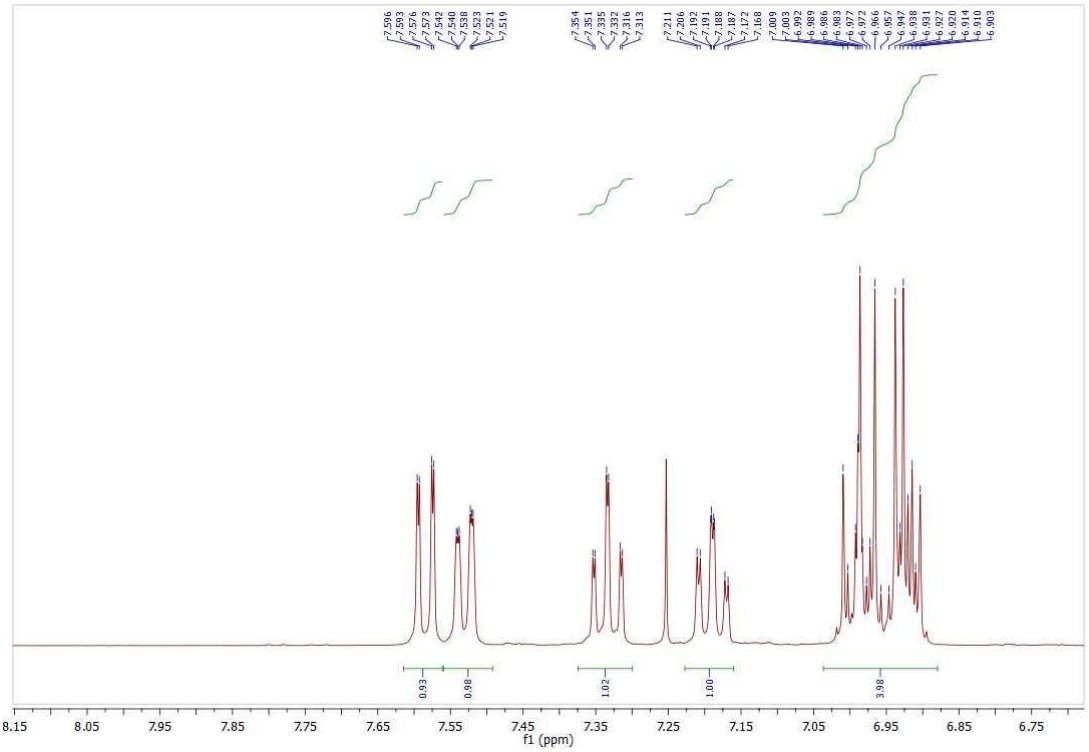
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-methylphenyl ether (6d).



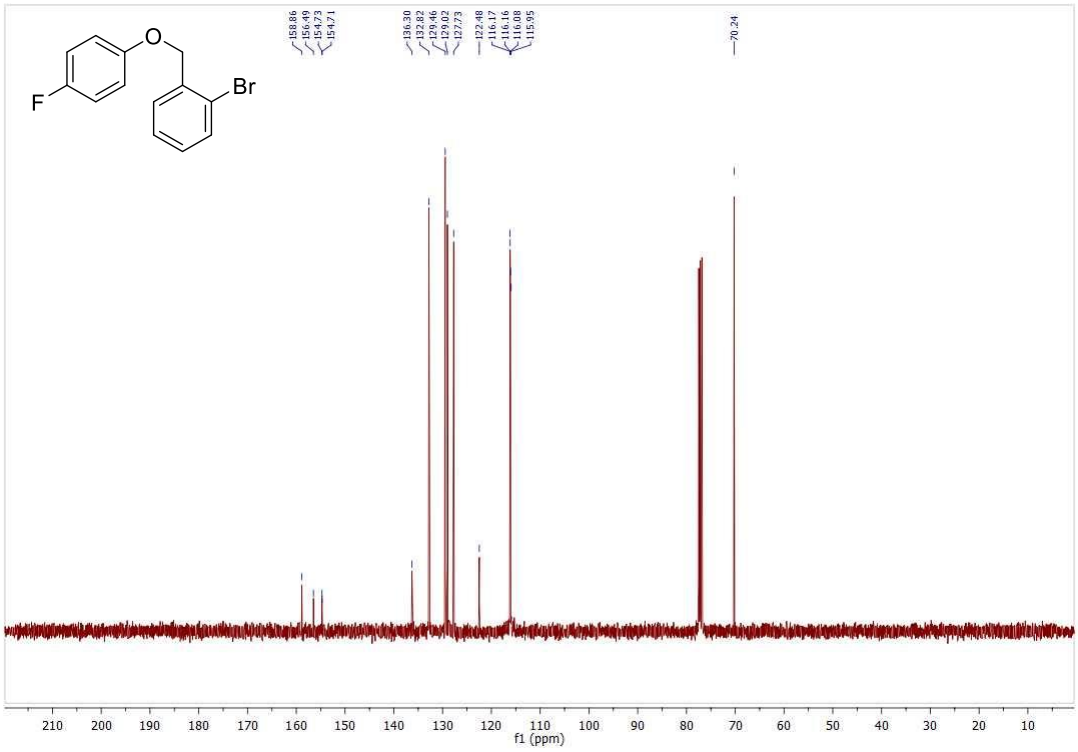


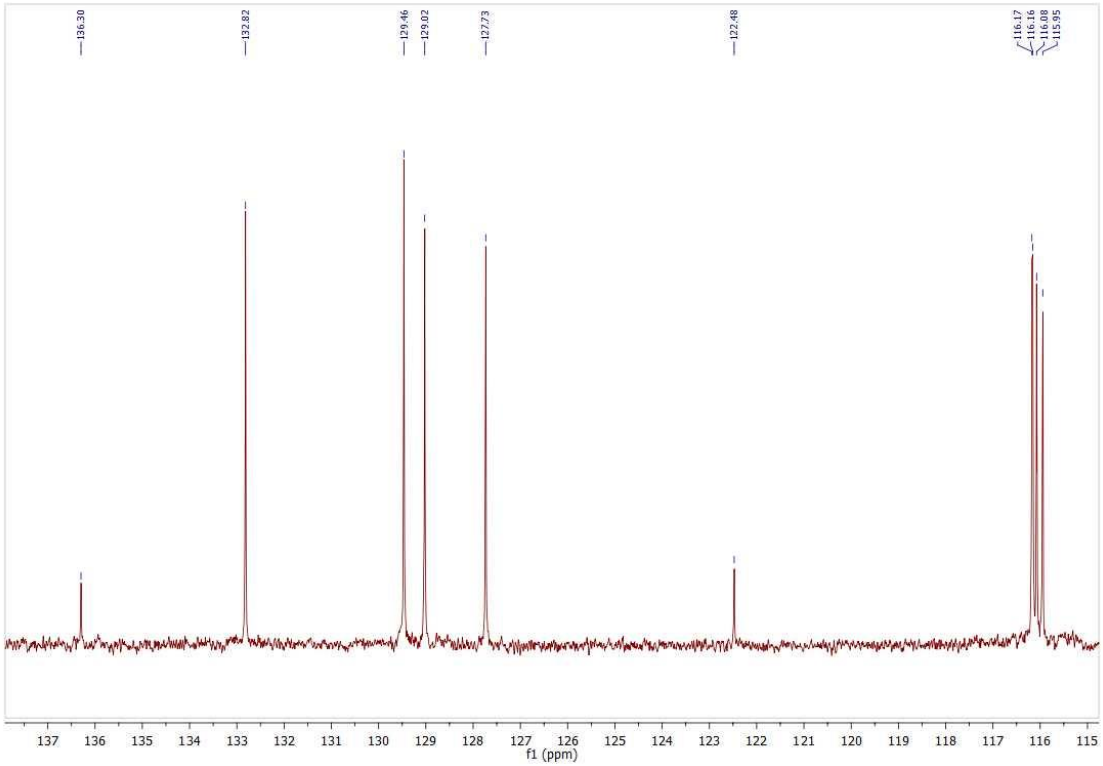
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-fluorophenyl ether (6e).



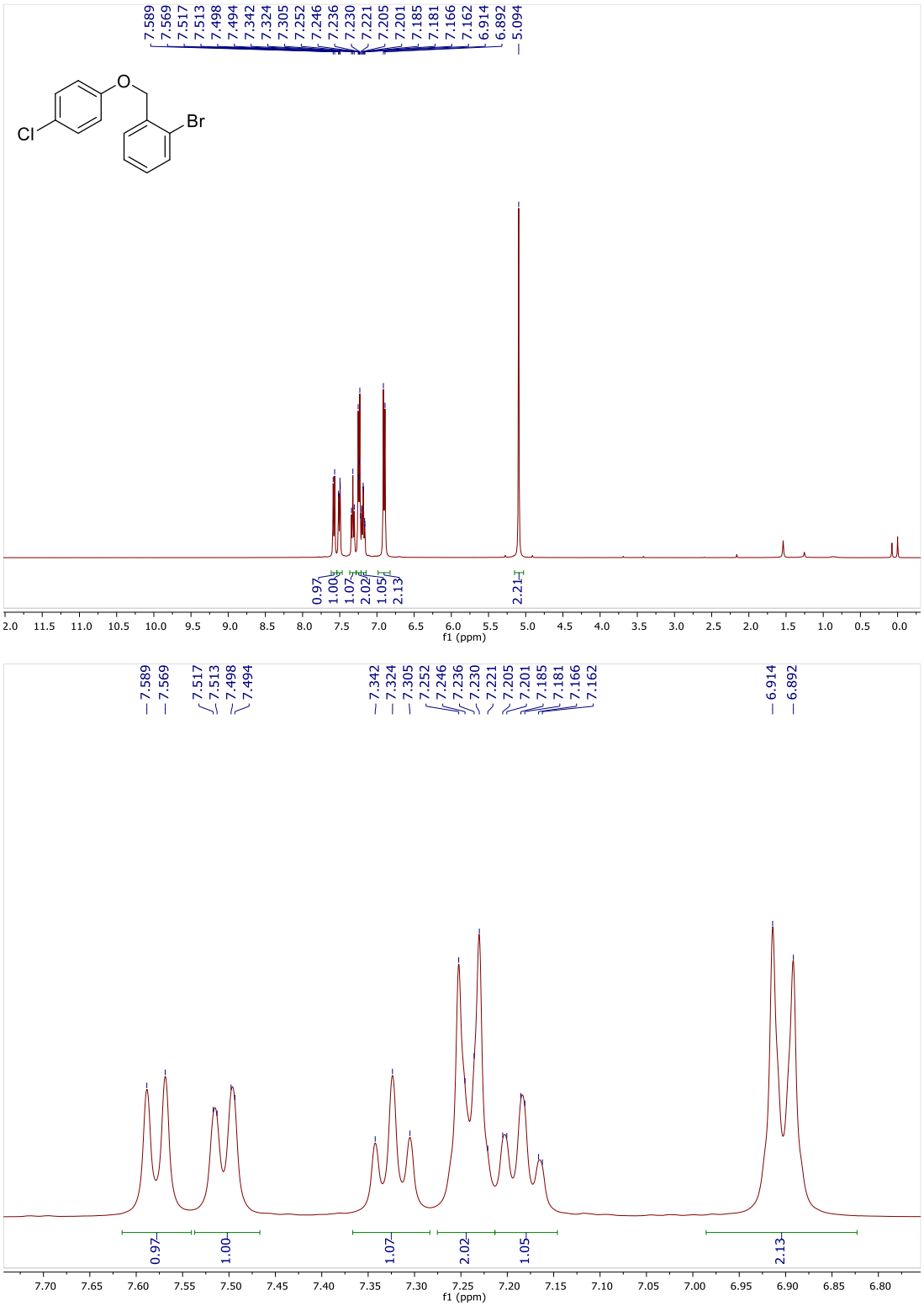


^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-fluorophenyl ether (6e).

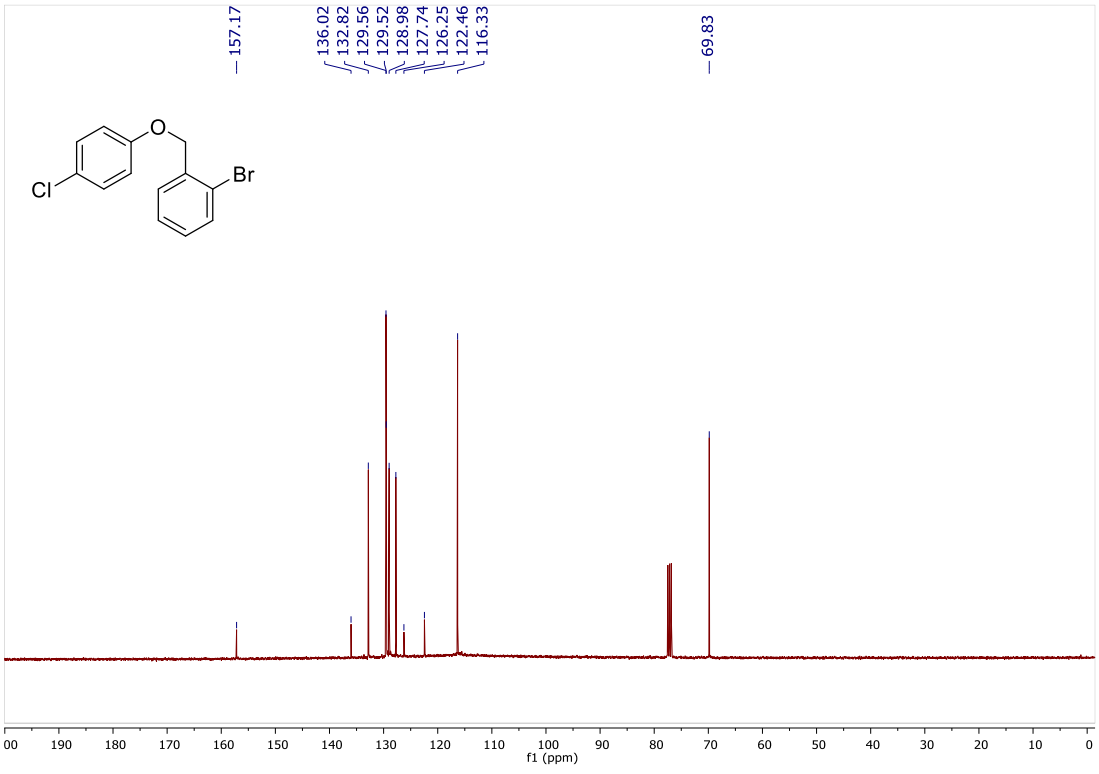


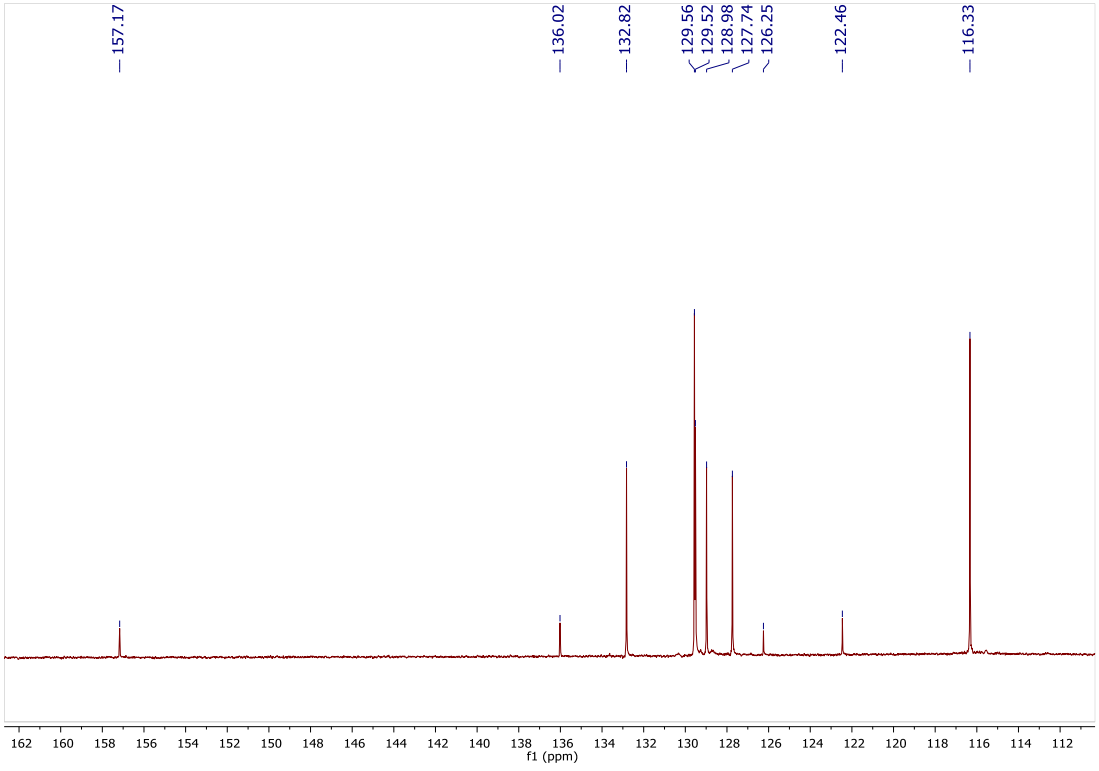


^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-chlorophenyl ether (6f)

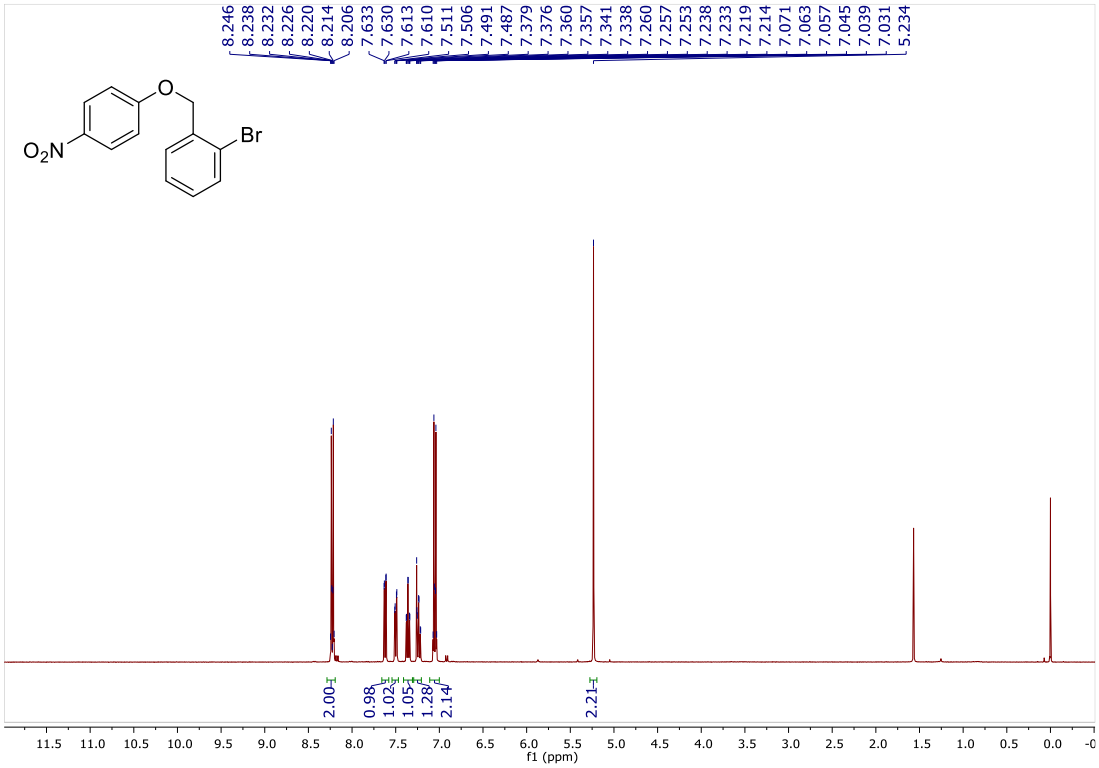


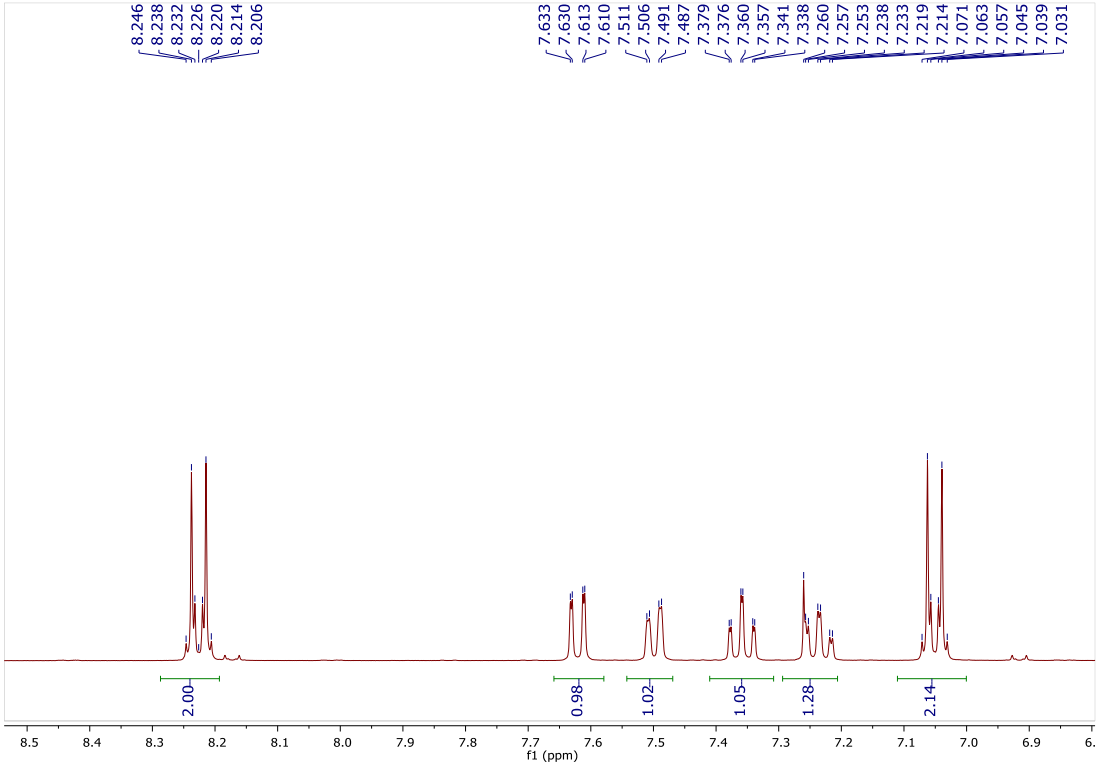
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-chlorophenyl ether (6f)



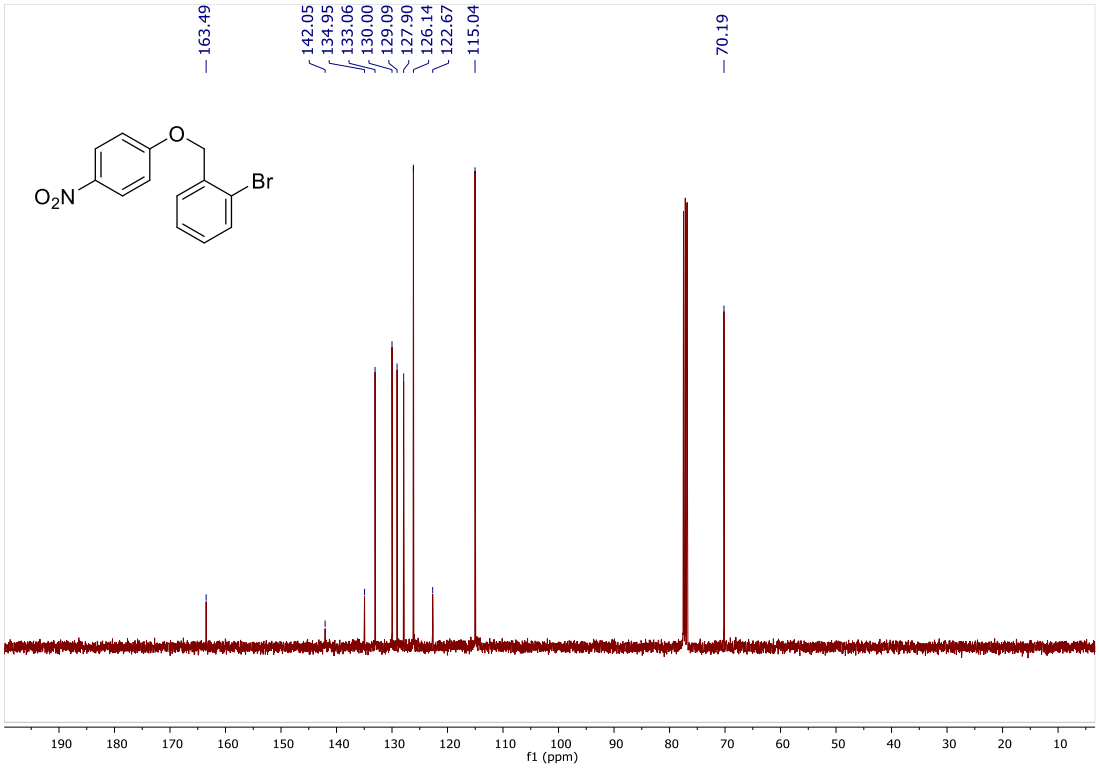


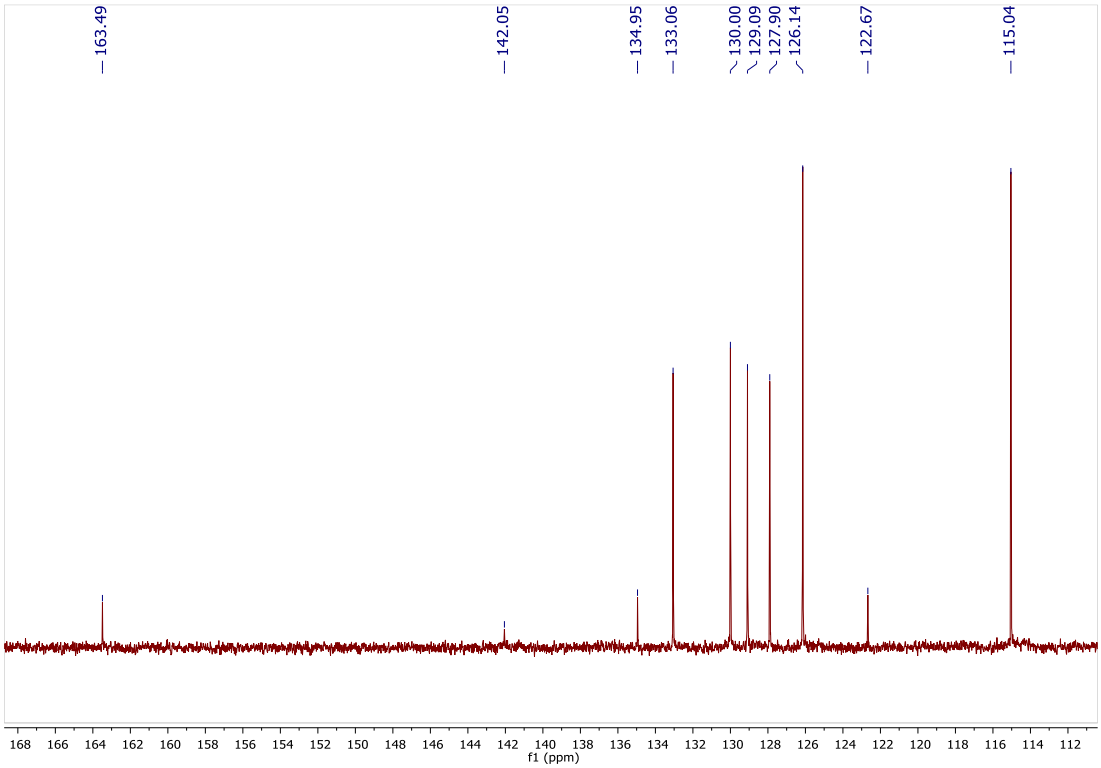
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-nitrophenyl ether (6g).



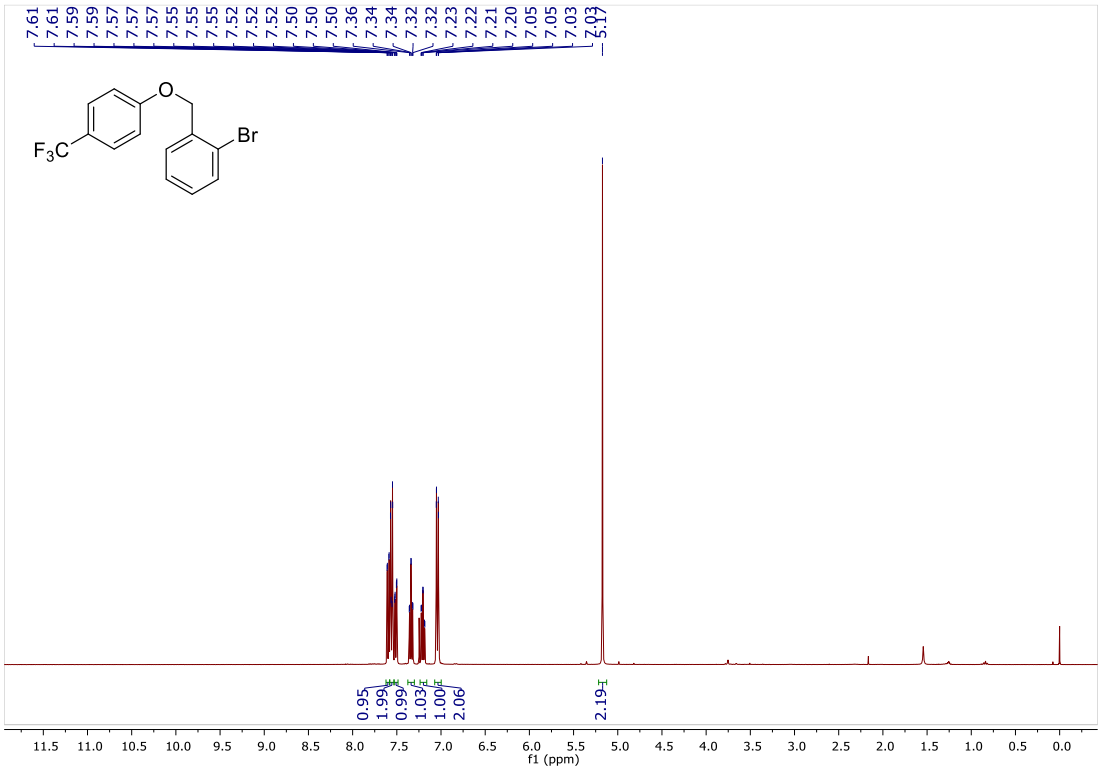


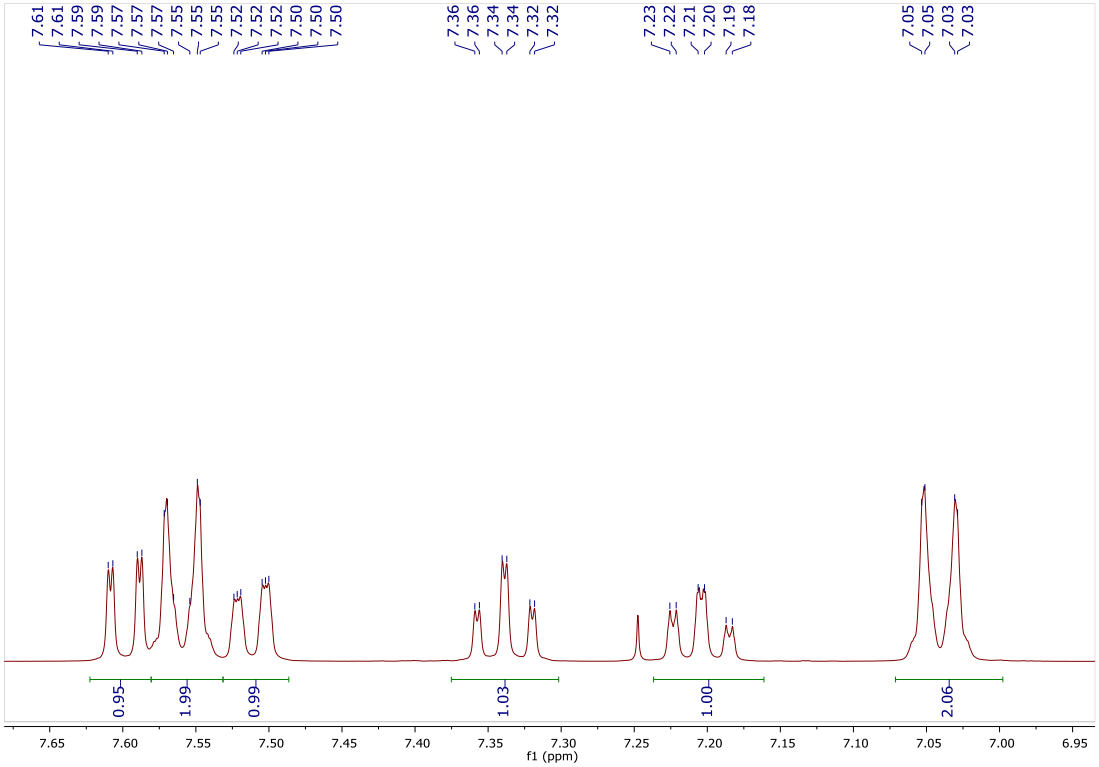
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-nitrophenyl ether (6g).



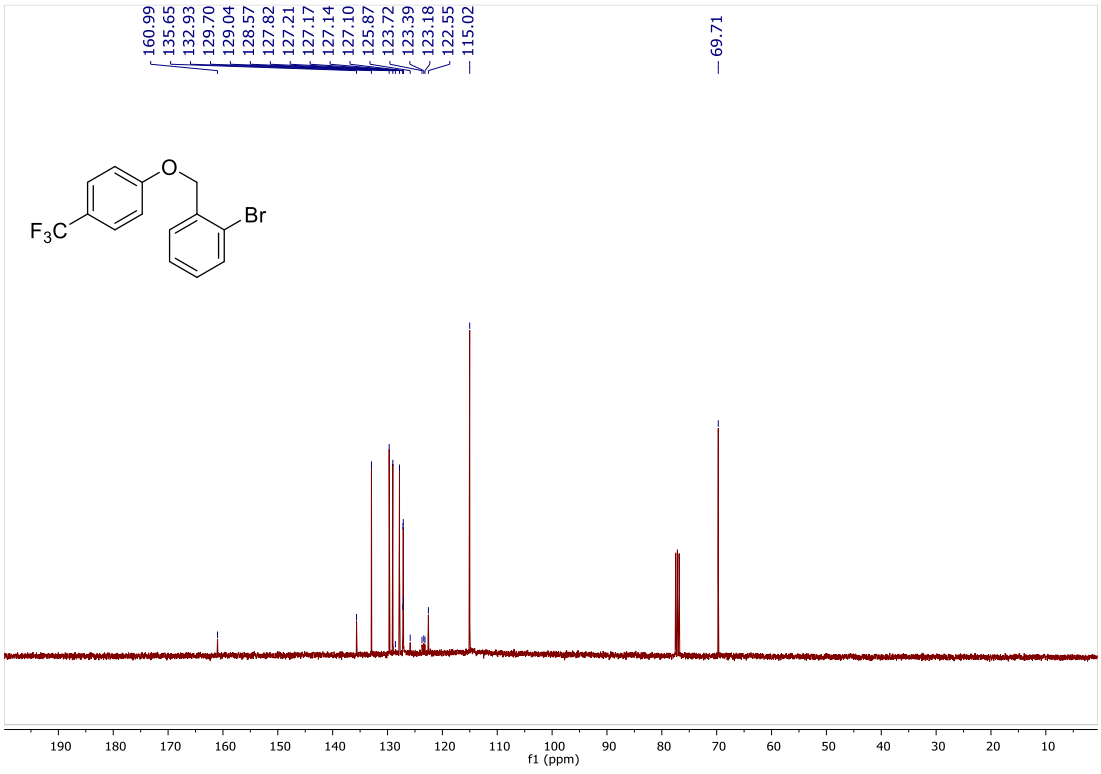


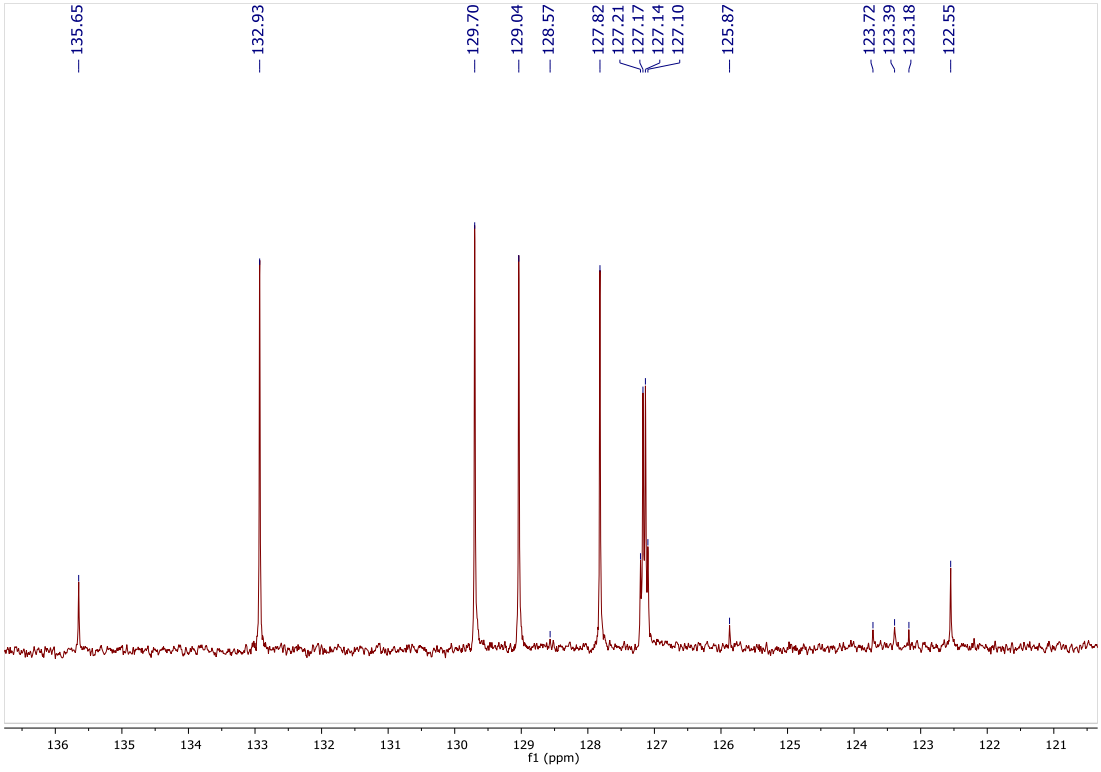
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 4-(trifluoromethyl)phenyl ether (6h)



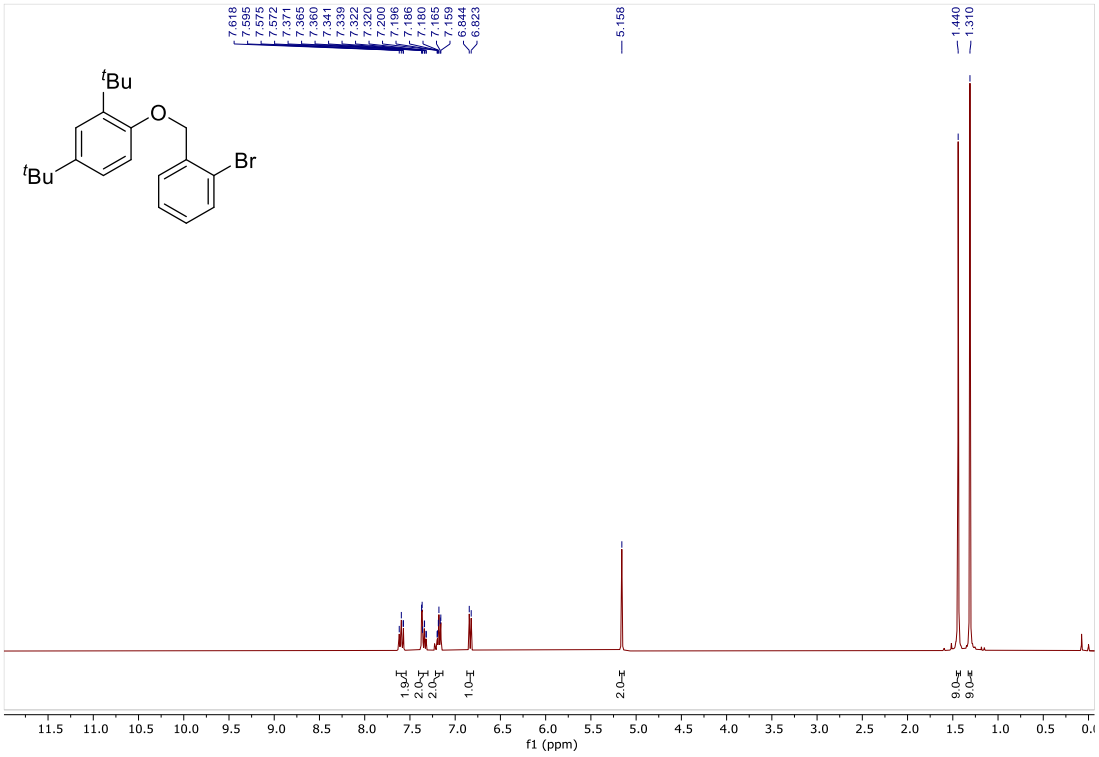


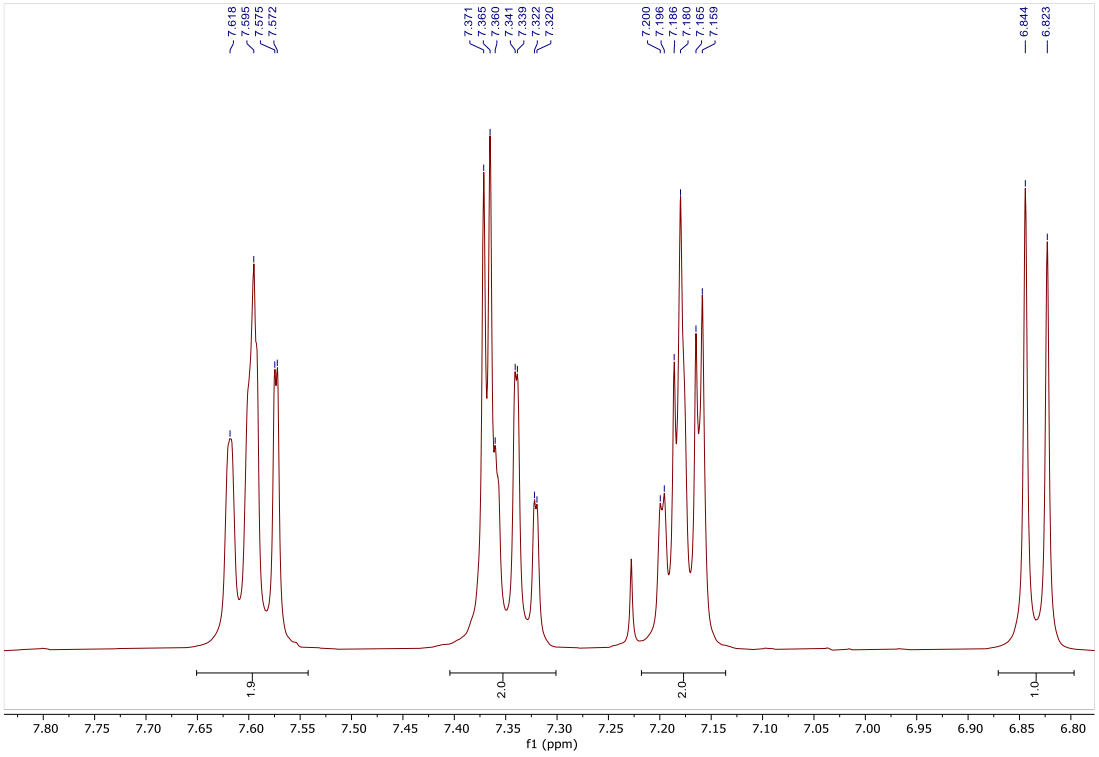
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 4-(trifluoromethyl)phenyl ether (6h)



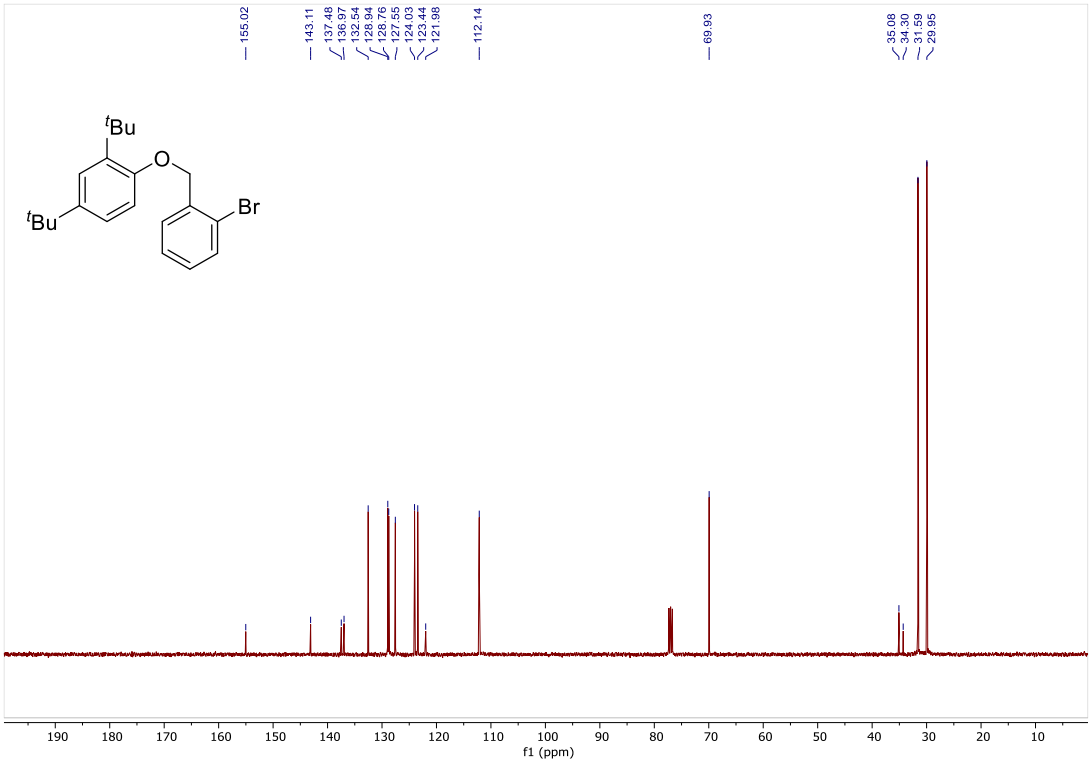


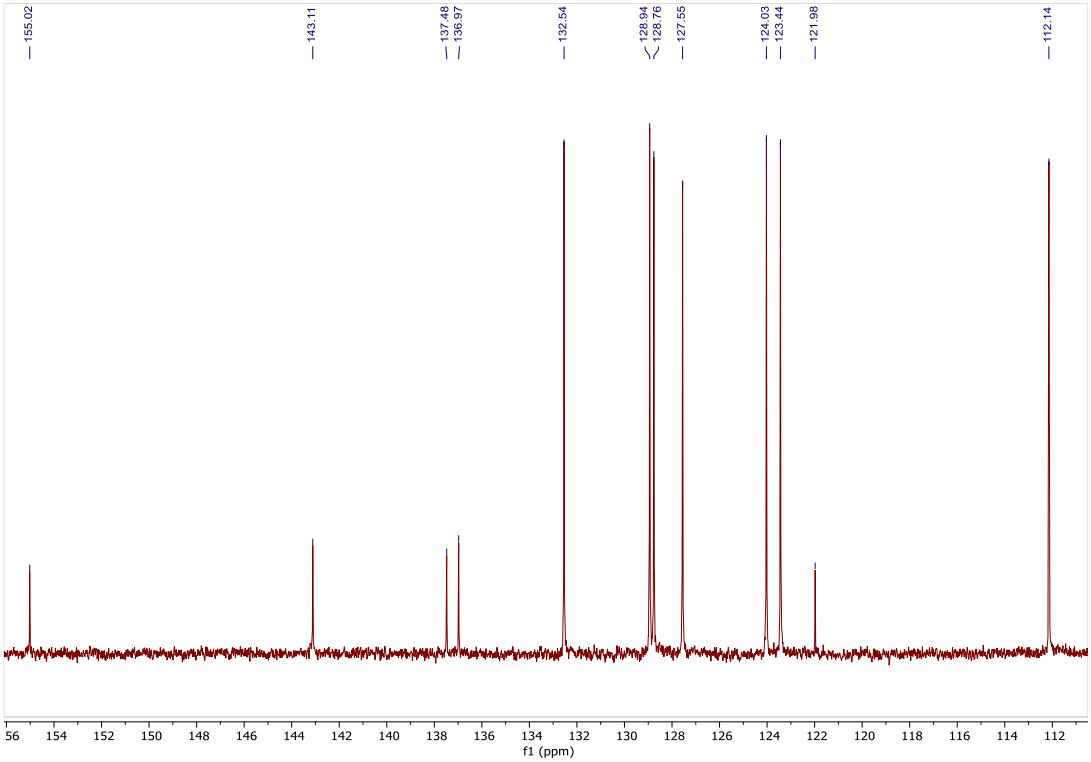
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromobenzyl 2,4-di-*tert*-butylphenyl ether (6i)



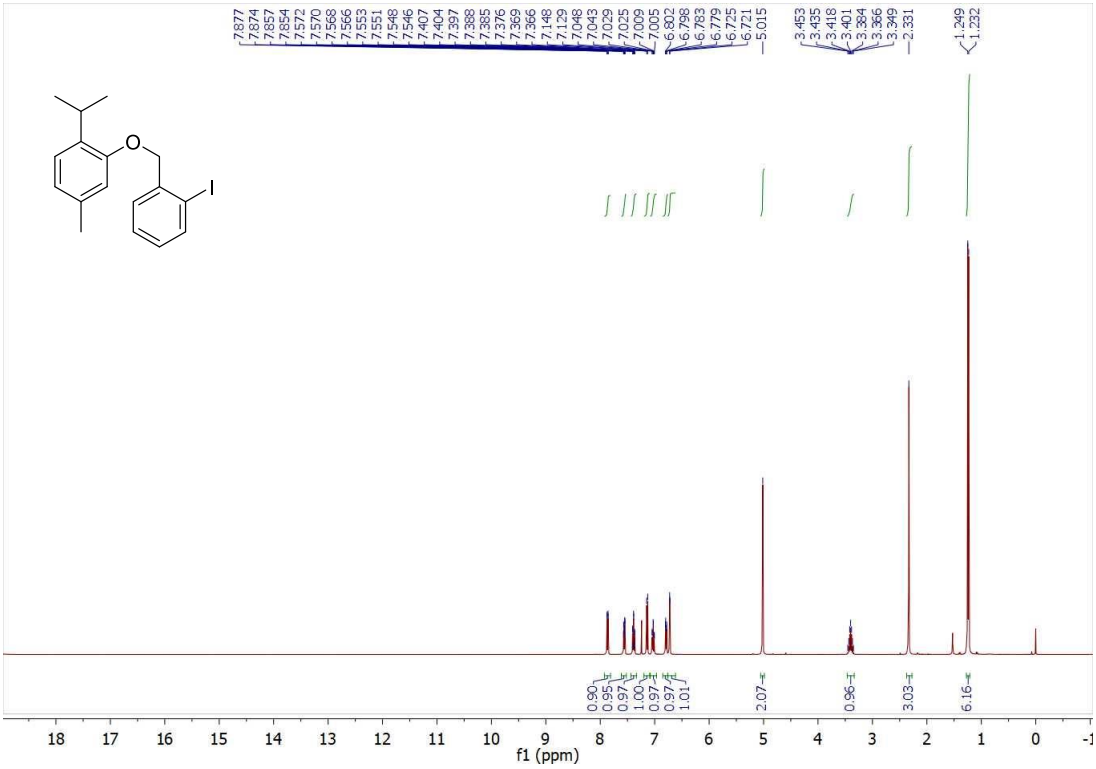


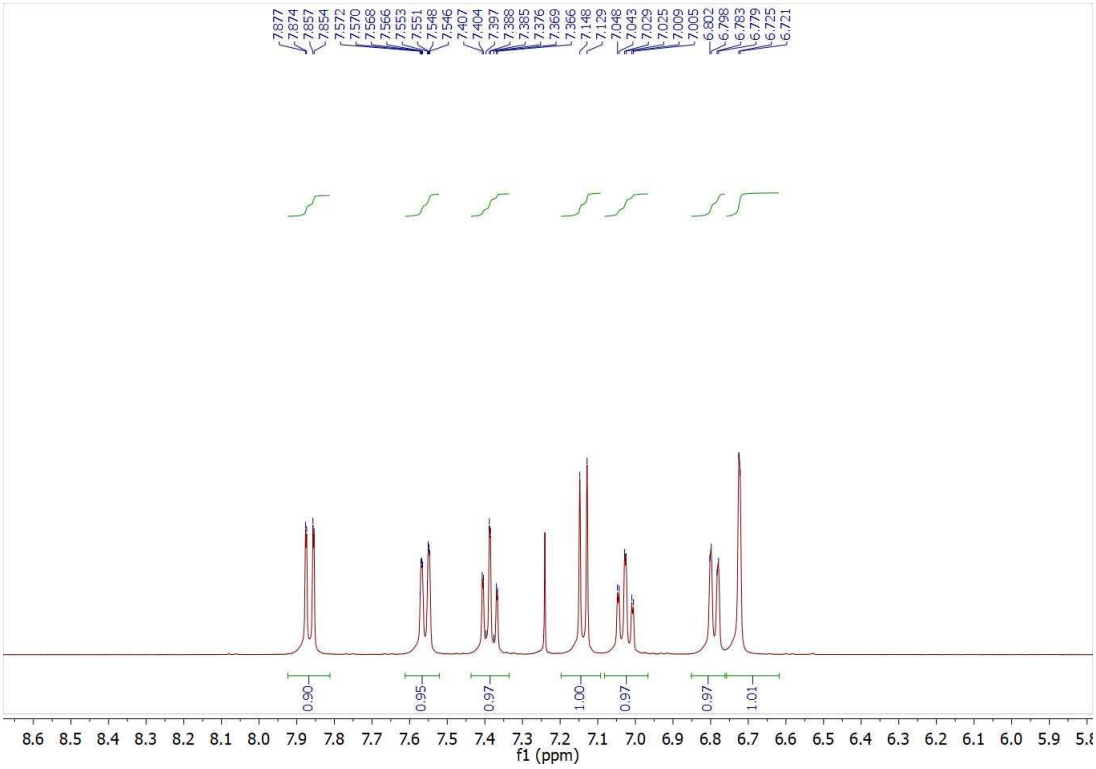
^{13}C NMR {1H} (100 MHz, $CDCl_3$). 2-Bromobenzyl 2,4-di-*tert*-butylphenyl ether (6i)



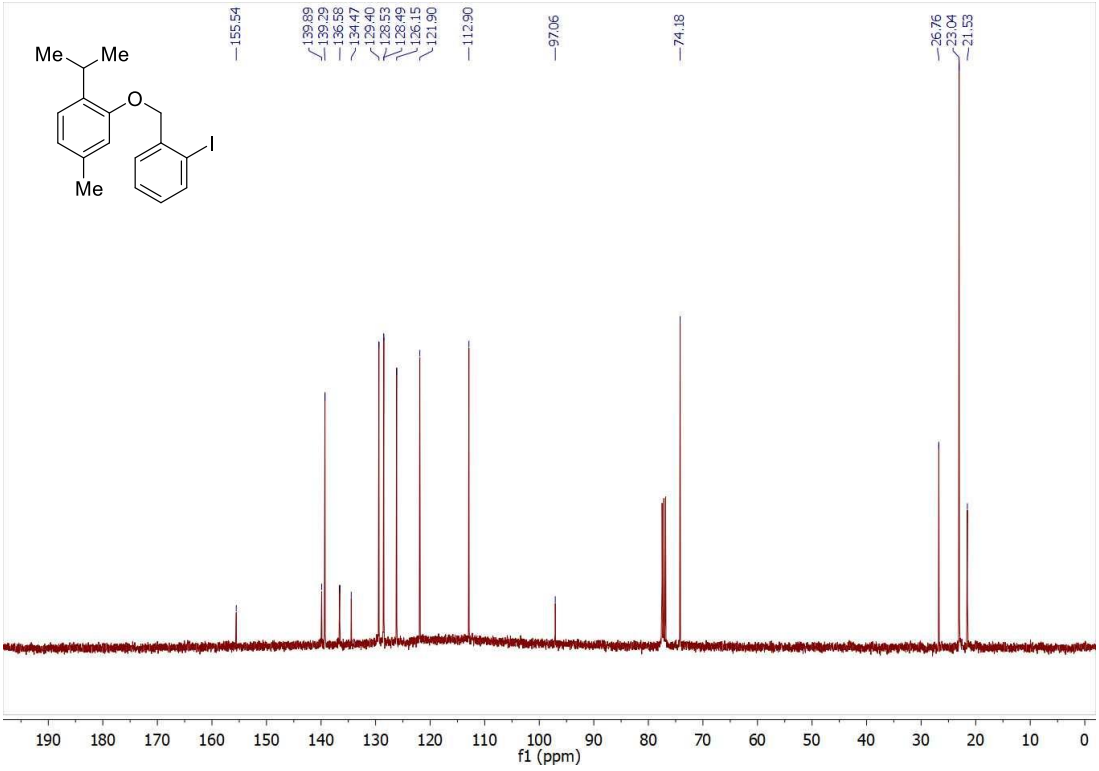


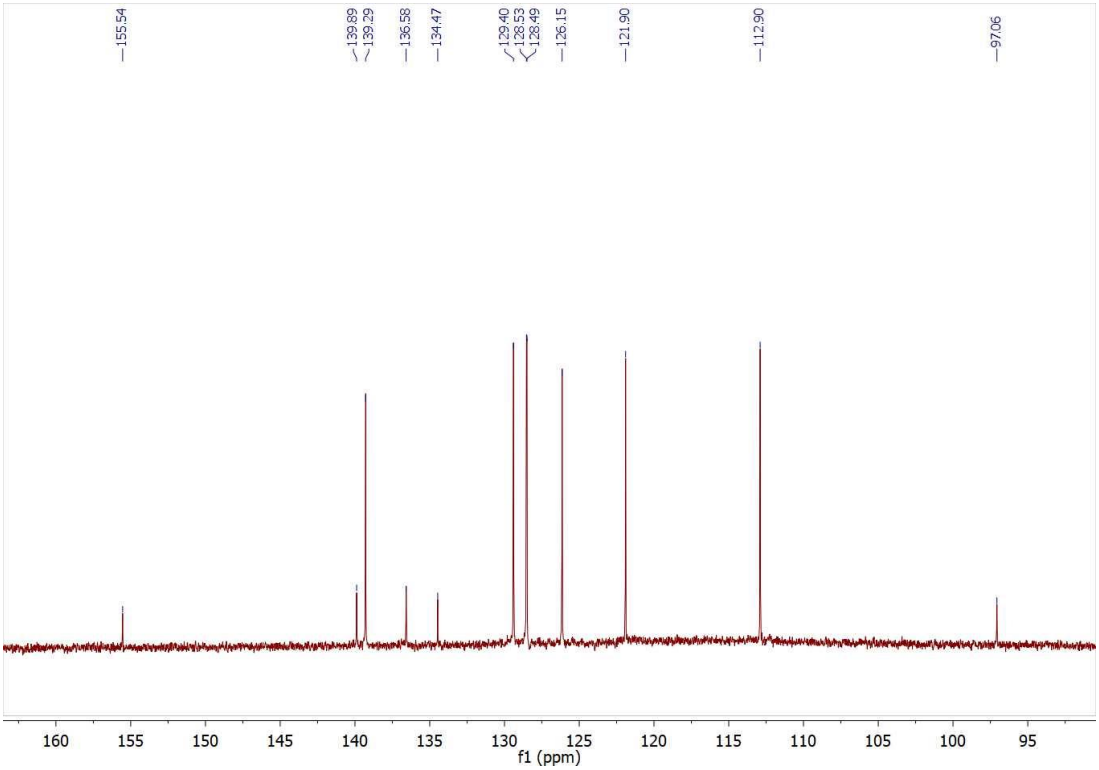
^{1}H-NMR (400 MHz, $CDCl_3$). 2-((2-Iodobenzyl)oxy)1-isopropyl-4-methylbenzene (6j).



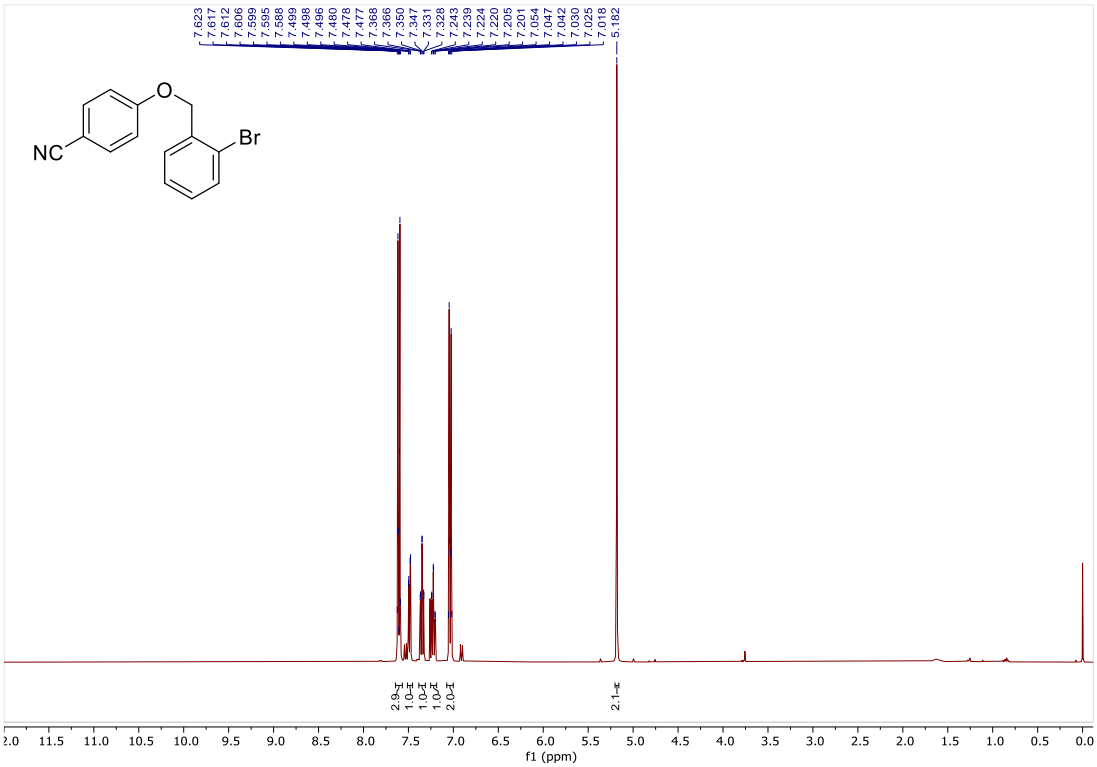


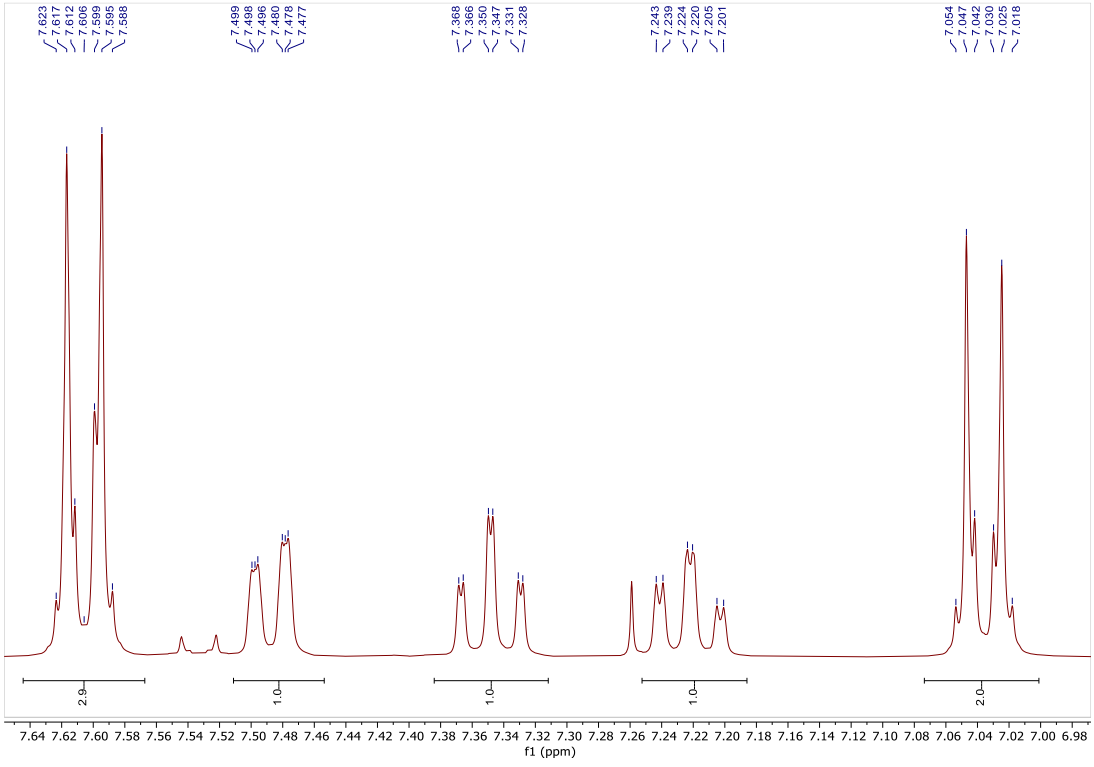
^{13}C NMR{1H} (101 MHz, $CDCl_3$). 2-((2-Iodobenzyl)oxy)1-isopropyl-4-methylbenzene (6j).



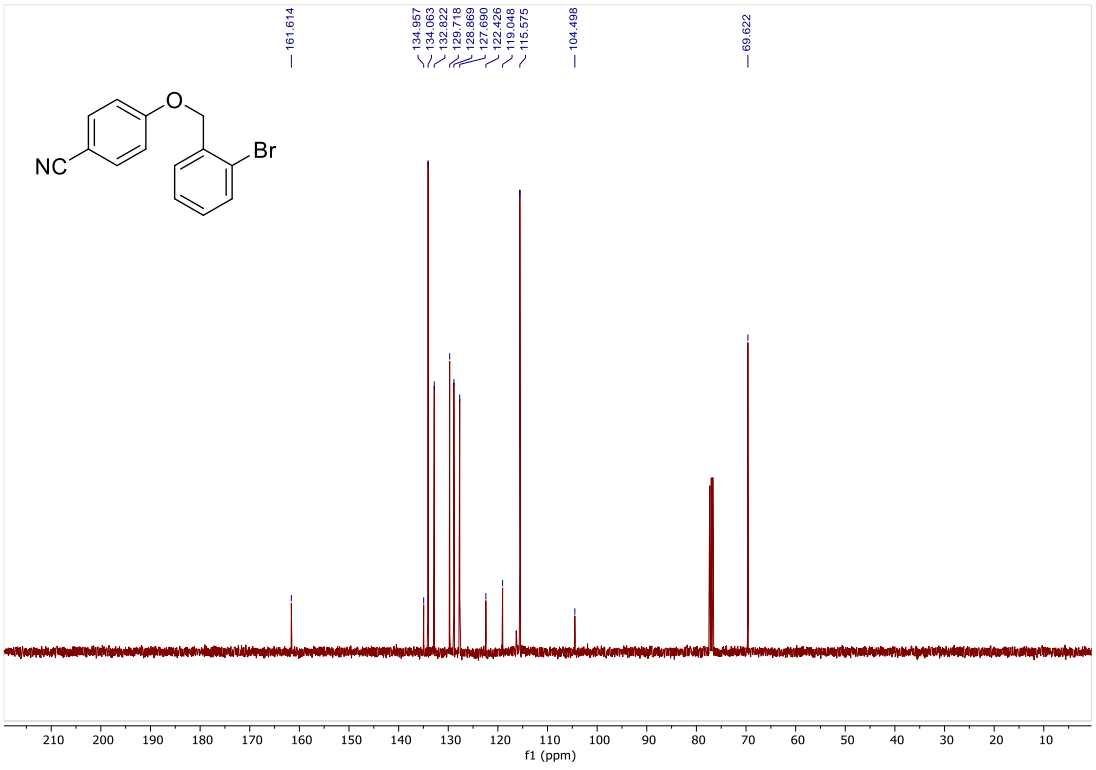


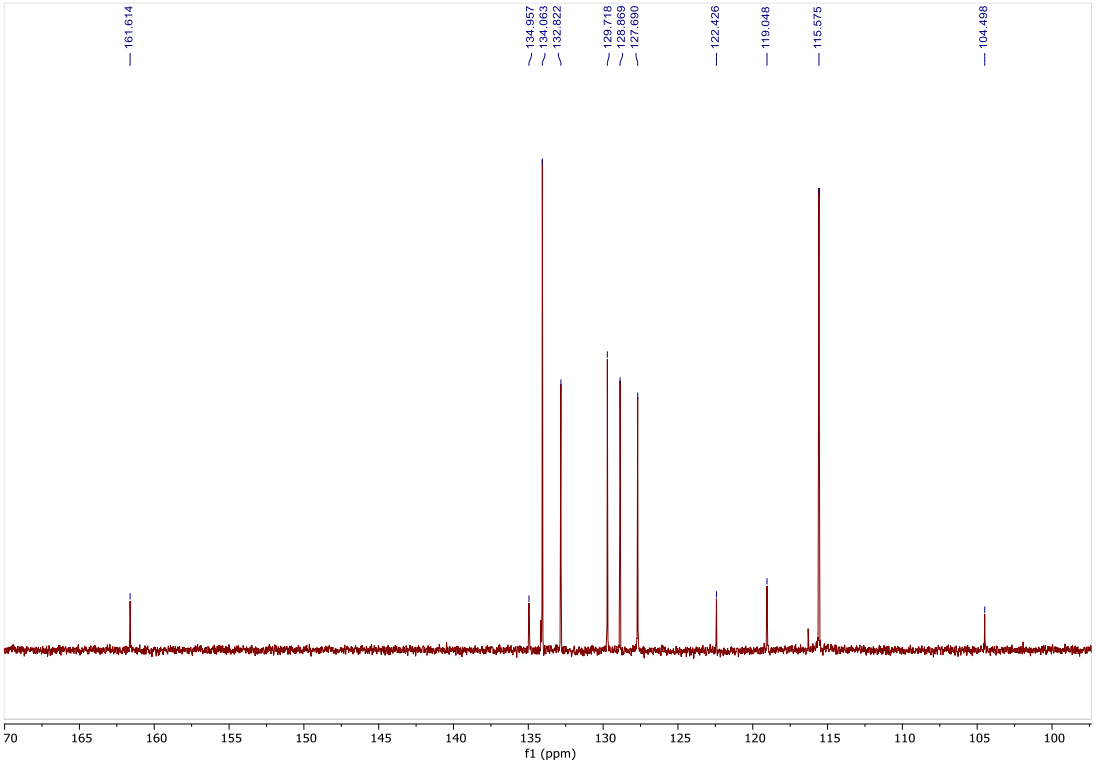
^{1}H NMR (400 MHz, $CDCl_3$). 4-((2-Bromobenzyl)oxy)benzonitrile (6k)



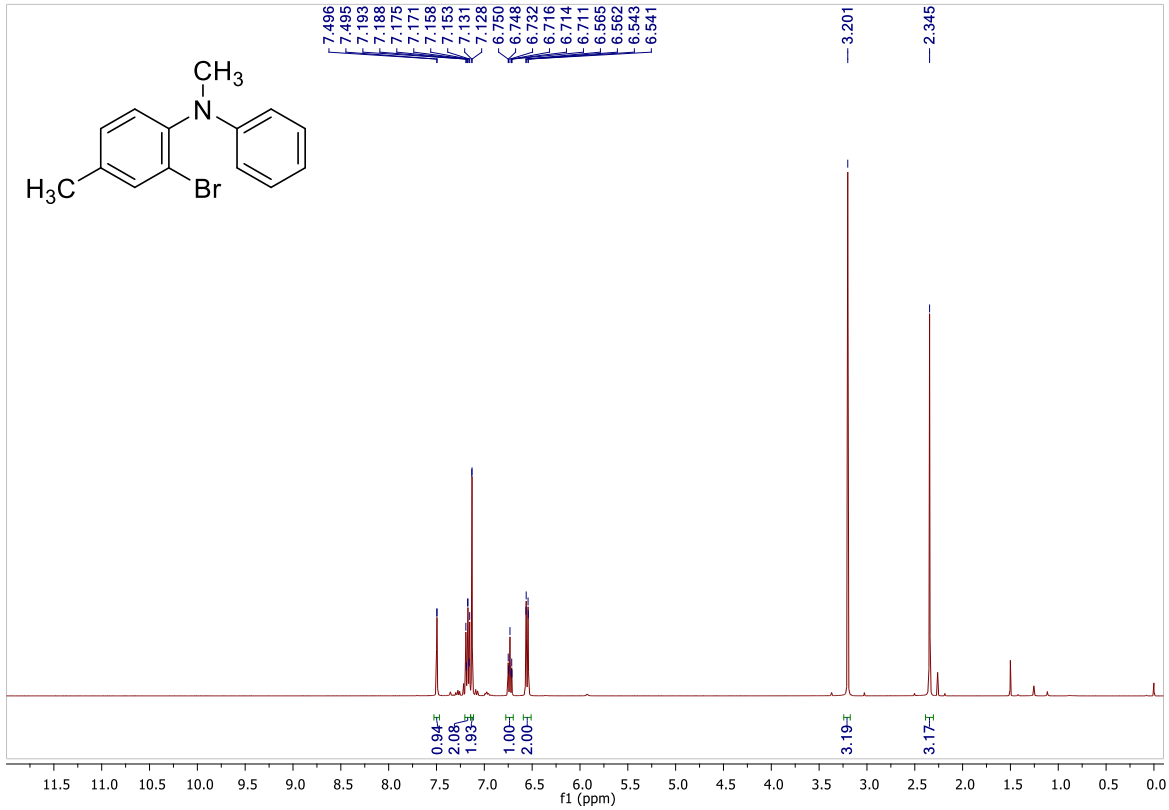


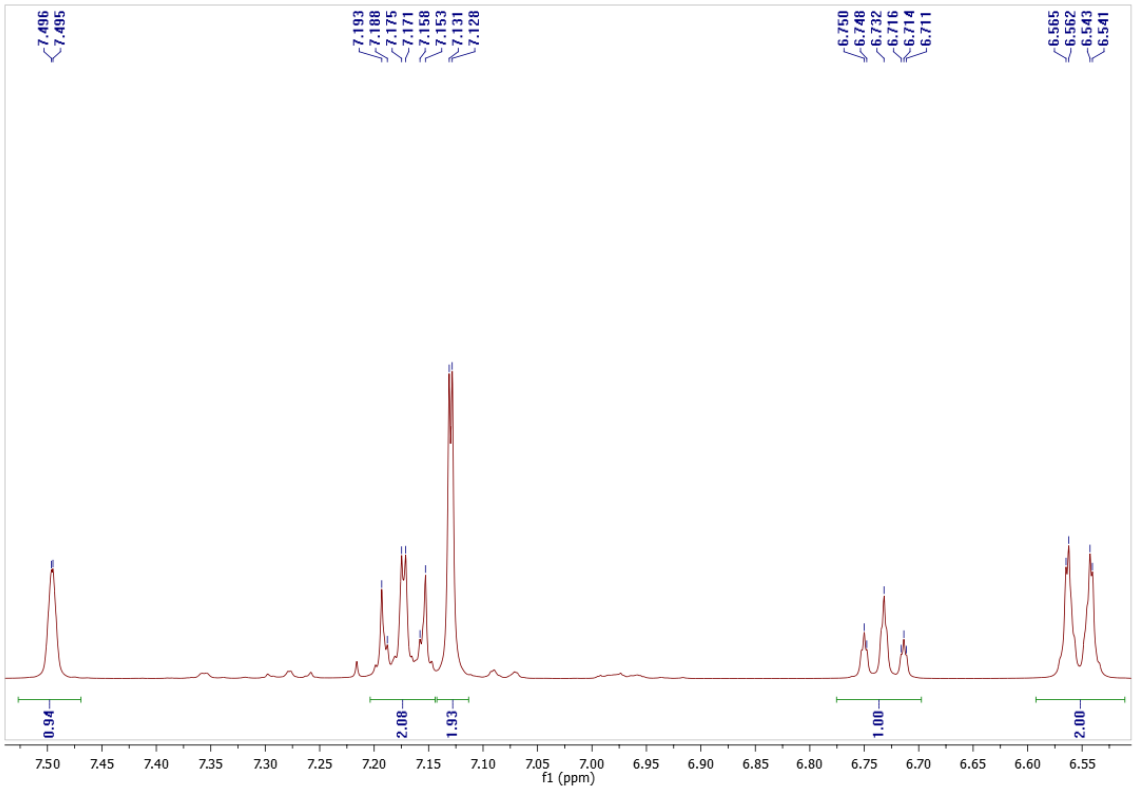
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 4-((2-Bromobenzyl)oxy)benzonitrile (6k)



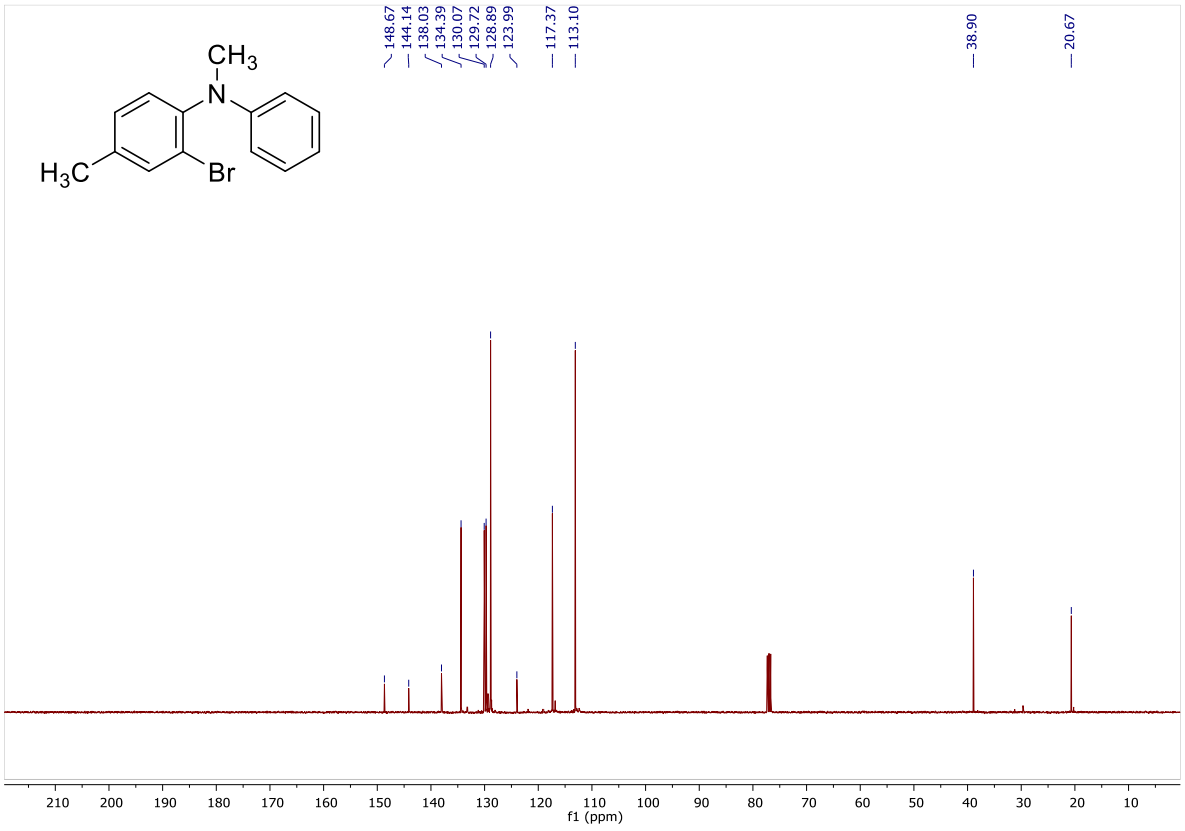


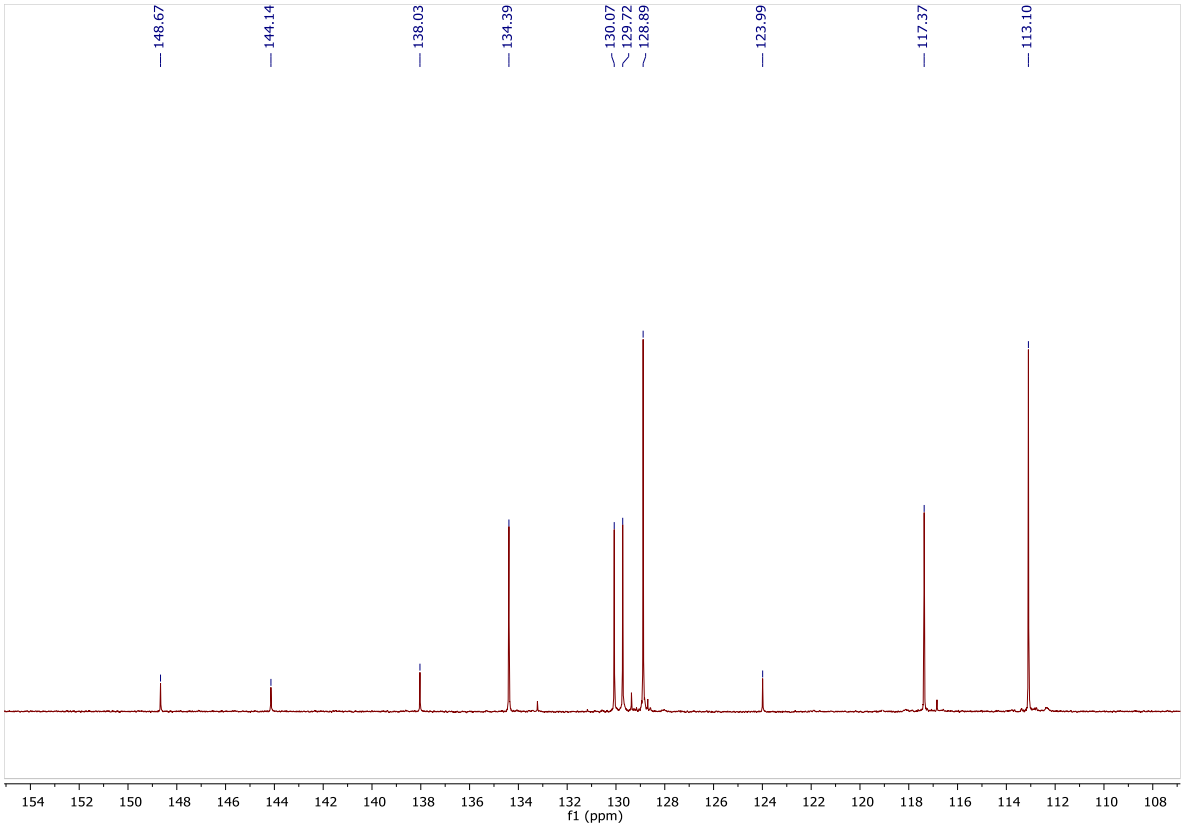
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromo-*N*,4-dimethyl-*N*-phenylaniline (9).





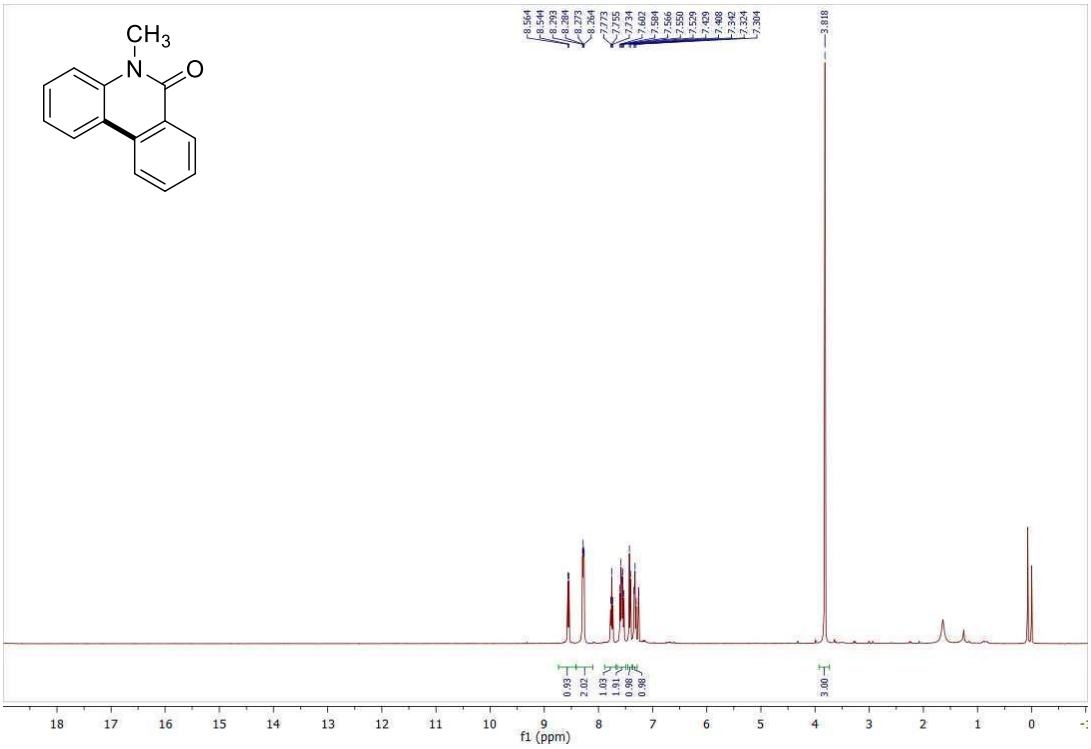
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Bromo-*N*,4-dimethyl-*N*-phenylaniline (9).

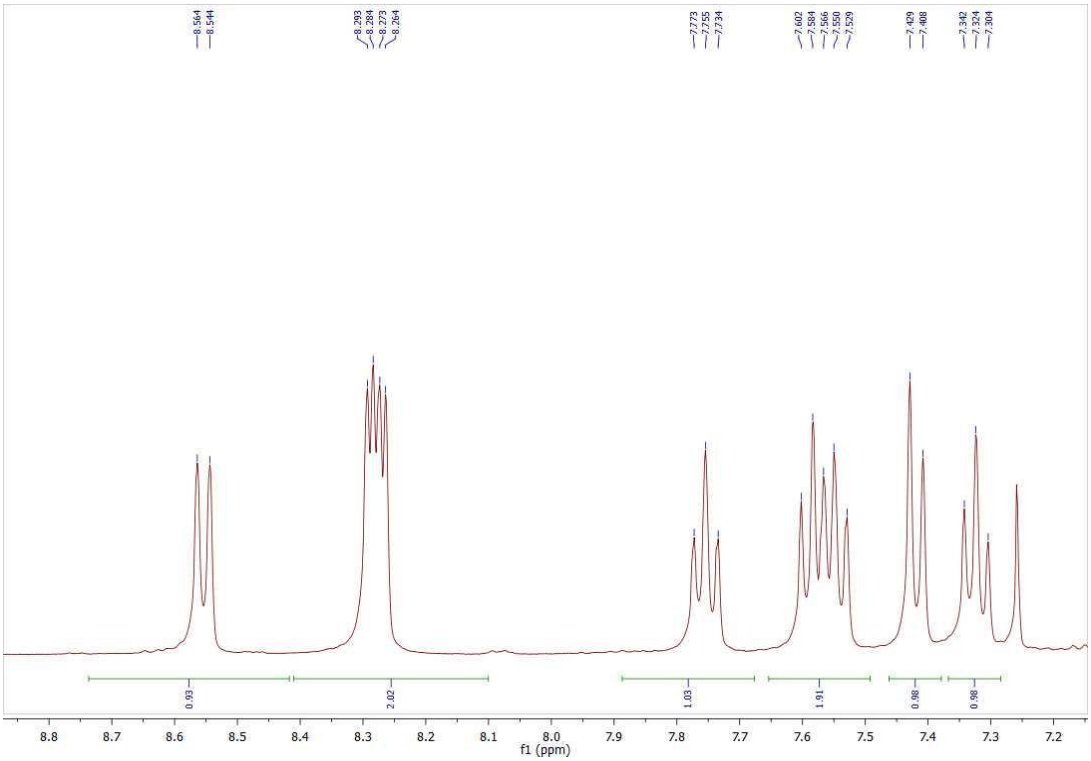




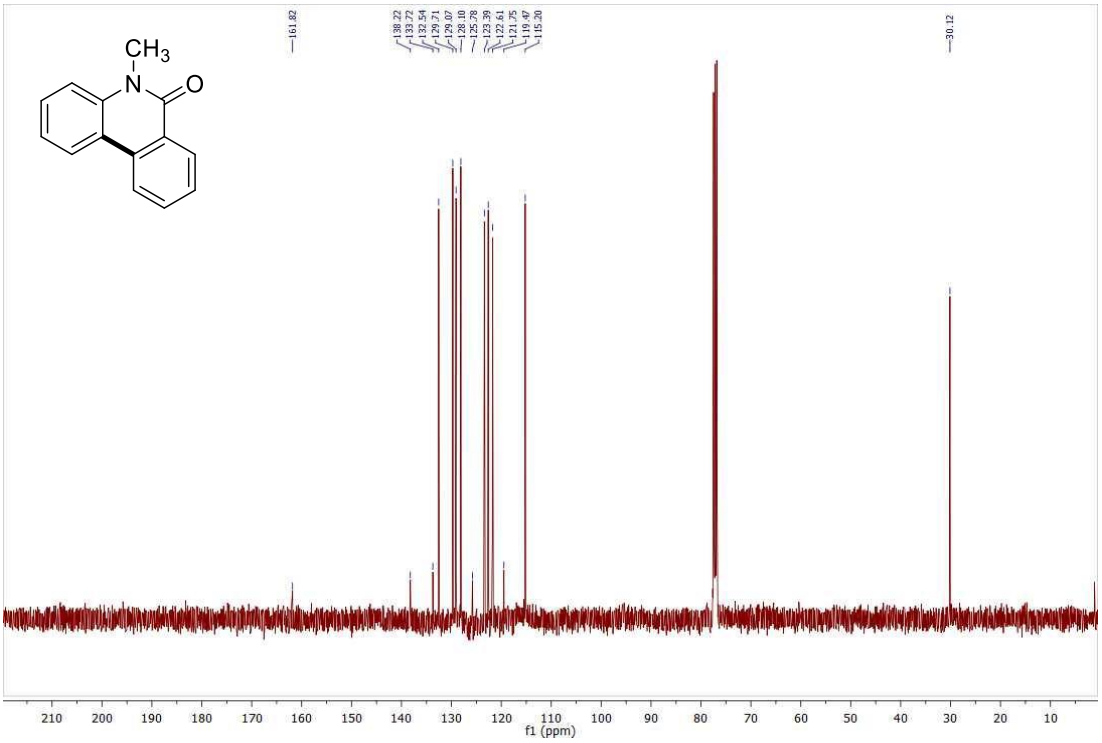
5. NMR spectra of compounds 2a-n, 7a-k and 10

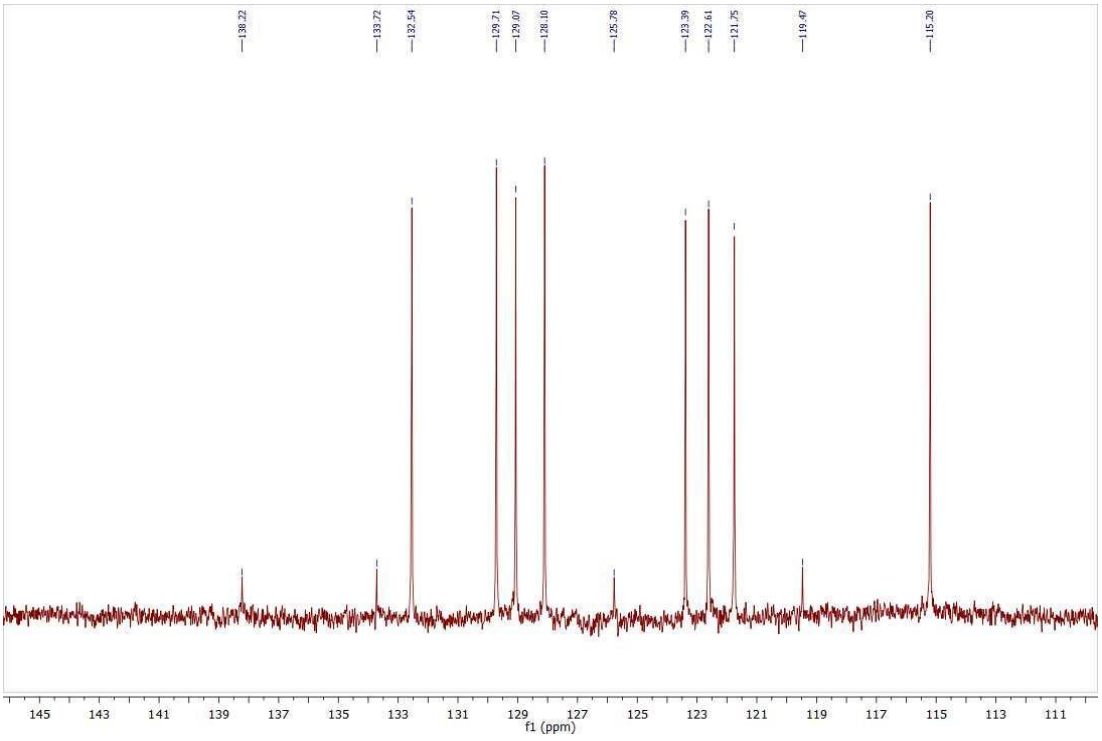
^{1}H NMR (400 MHz, $CDCl_3$). 5-Methyl-phenanthridin-6(5*H*)-one (2a).



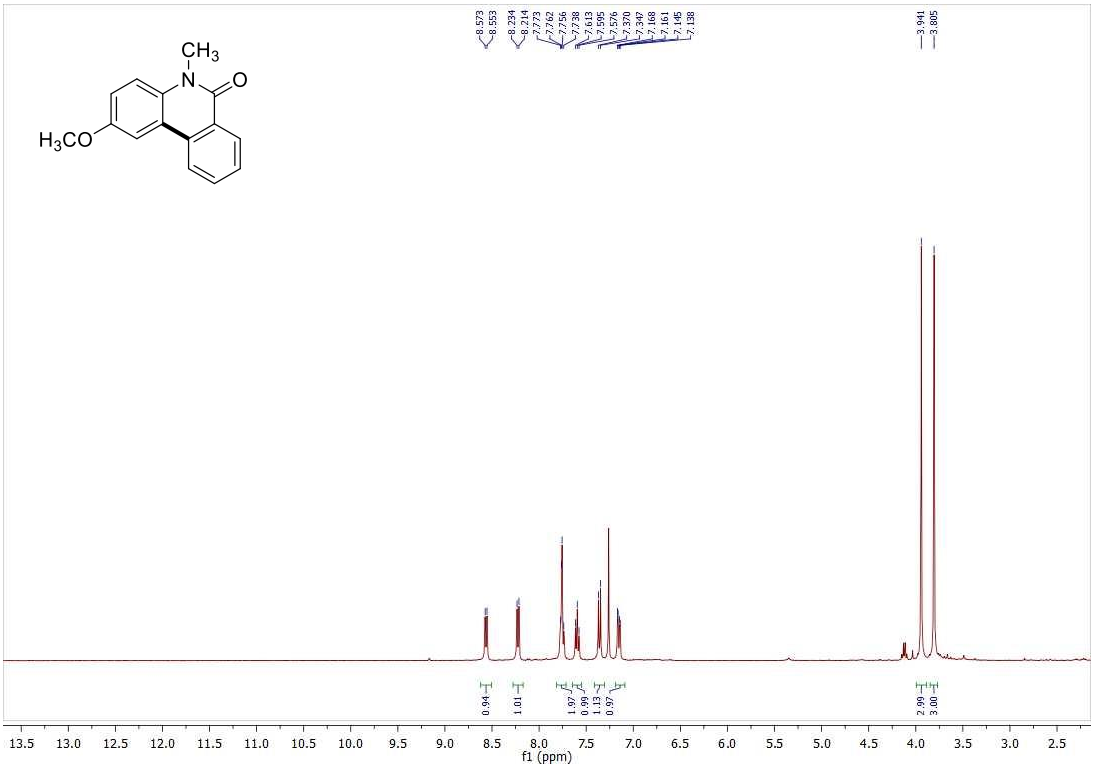


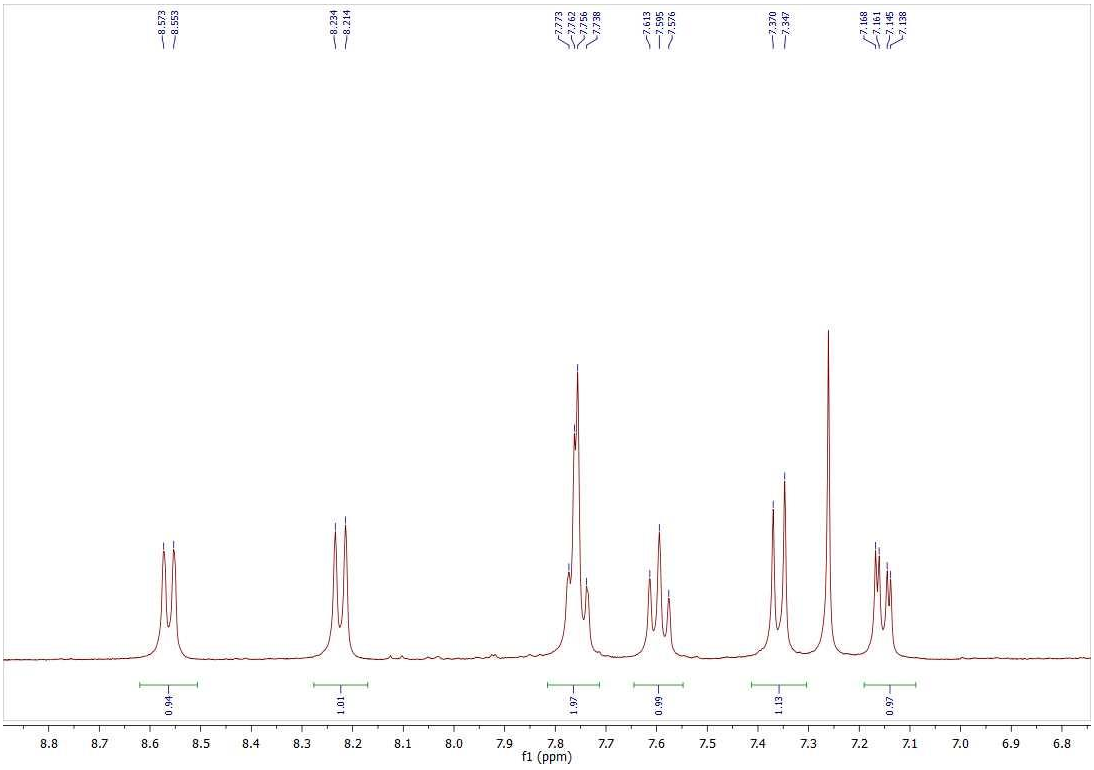
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 5-Methyl-phenanthridin-6(5*H*)-one (2a).



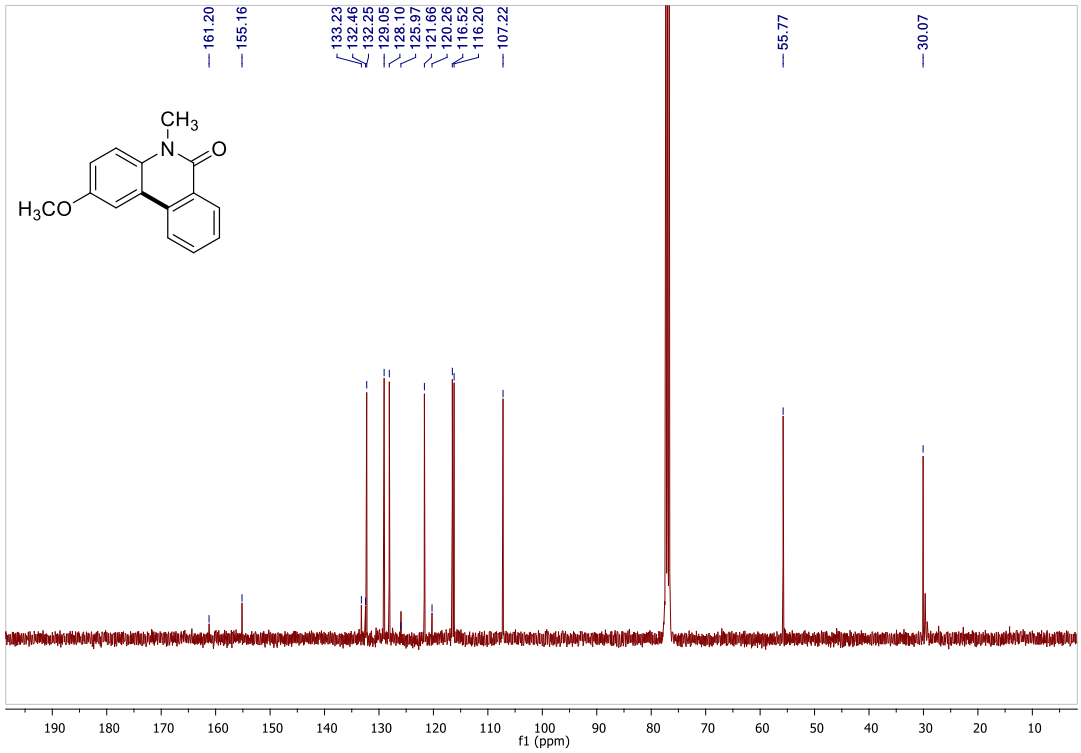


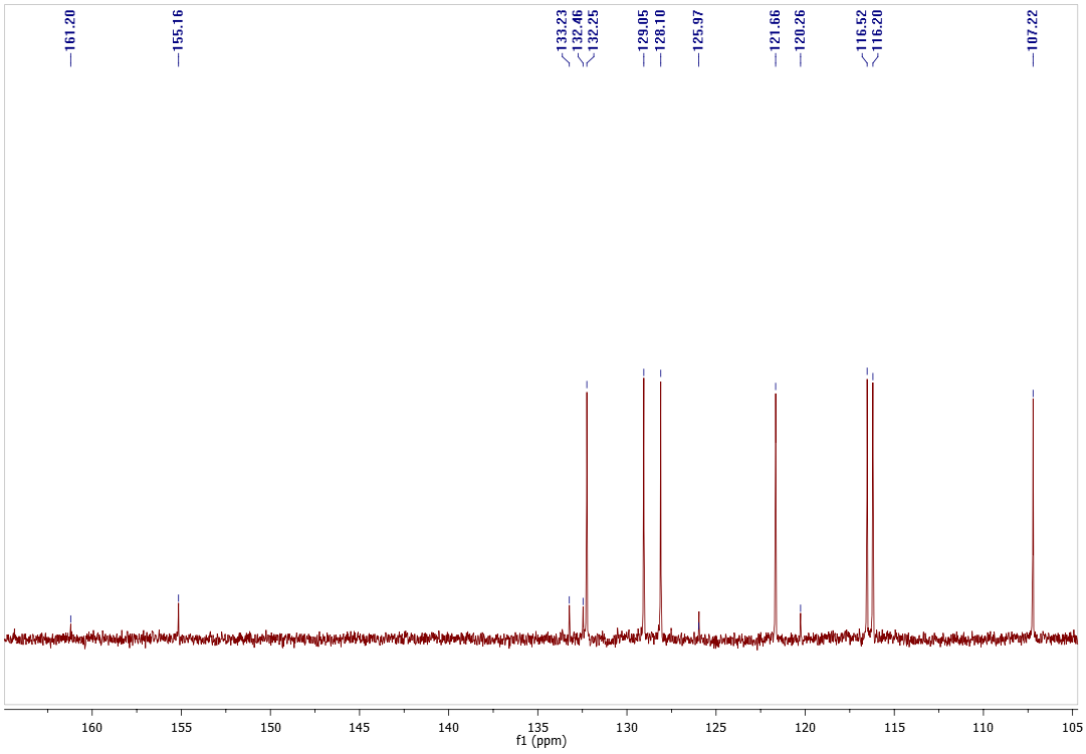
^{1}H NMR (400 MHz, $CDCl_3$). 2-Methoxy-5-methylphenanthridin-6(5*H*)-one (2e).



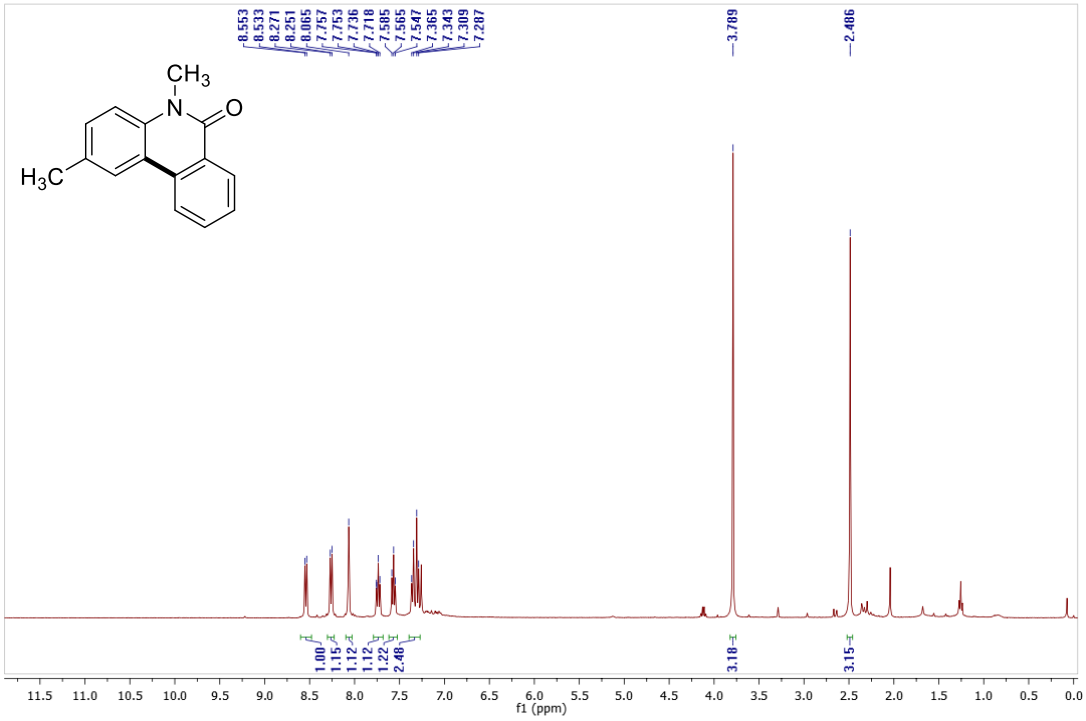


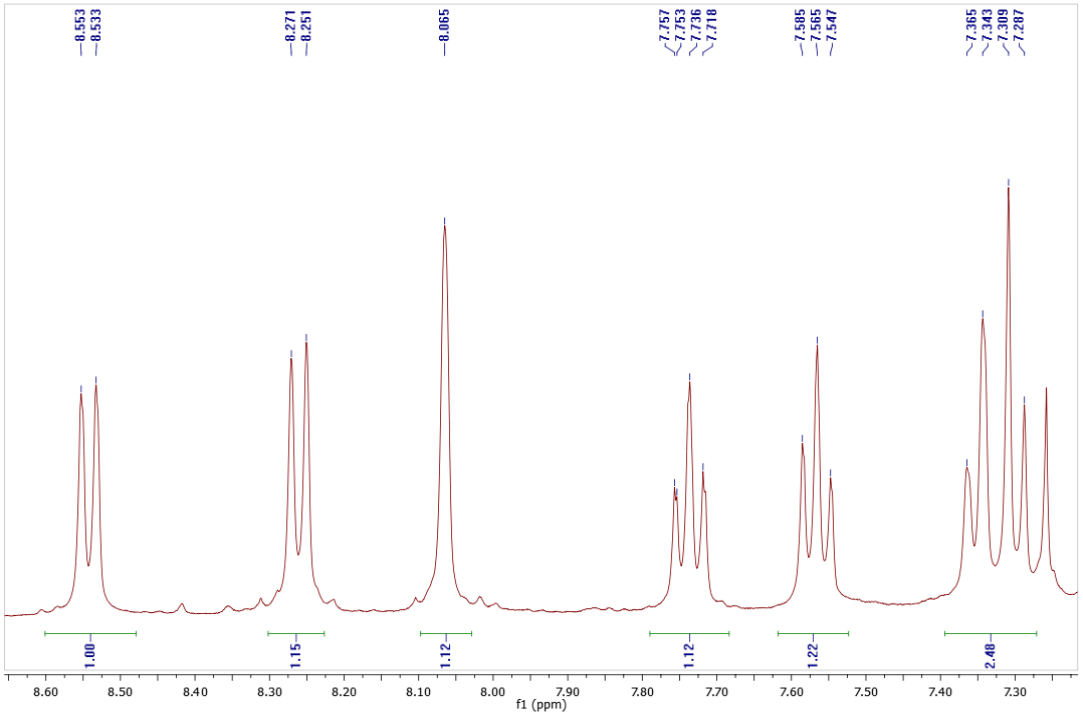
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Methoxy-5-methylphenanthridin-6(5*H*)-one (2e).



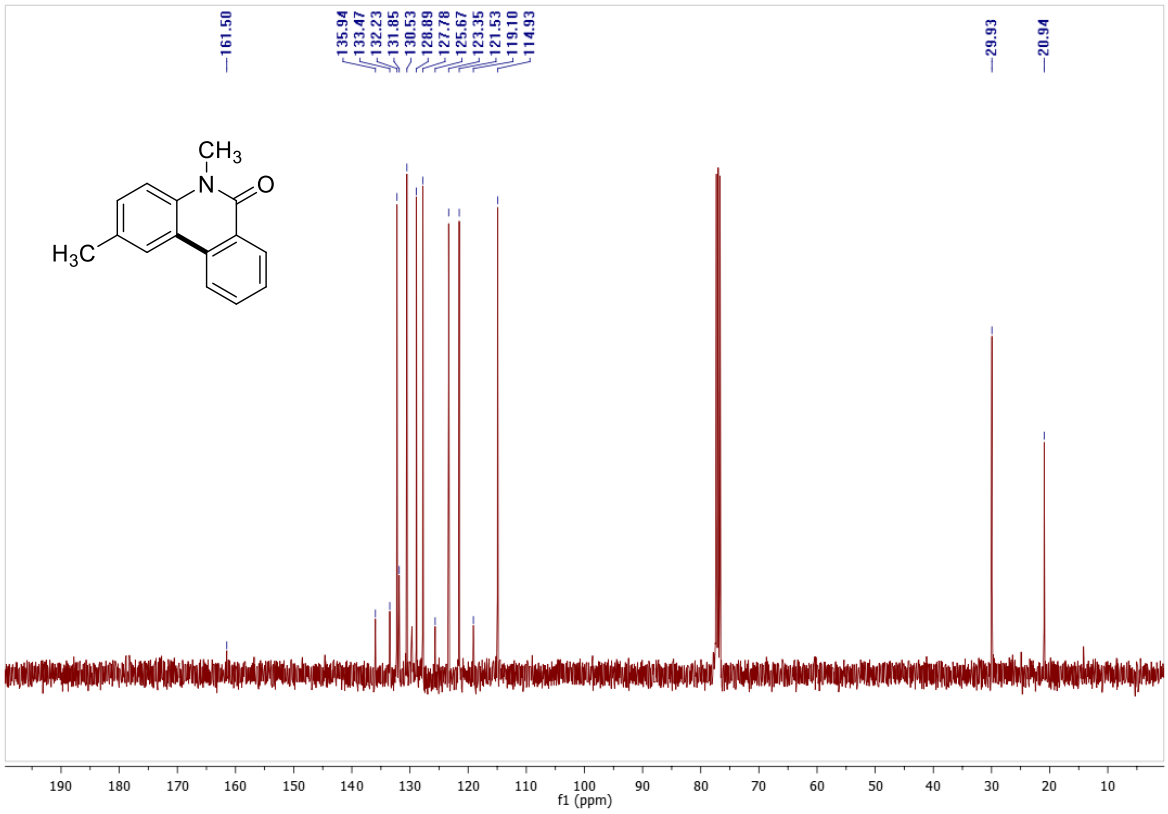


^{1}H NMR (400 MHz, $CDCl_3$). 2,5-Dimethylphenanthridin-6(5*H*)-one (2f).

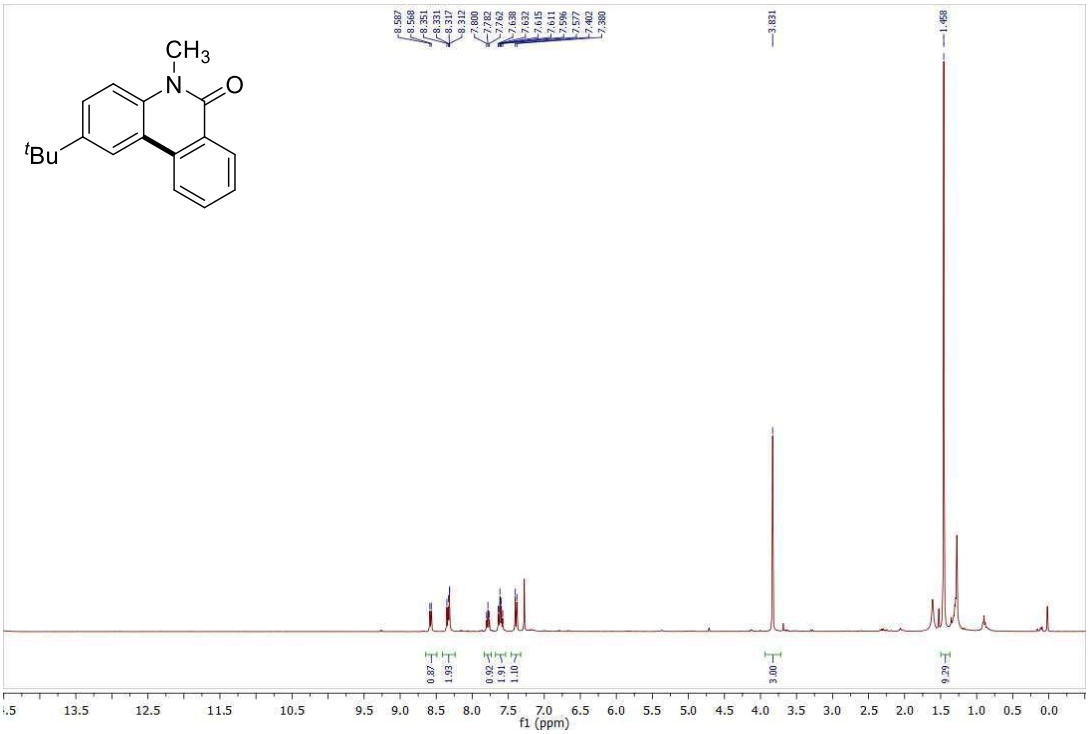


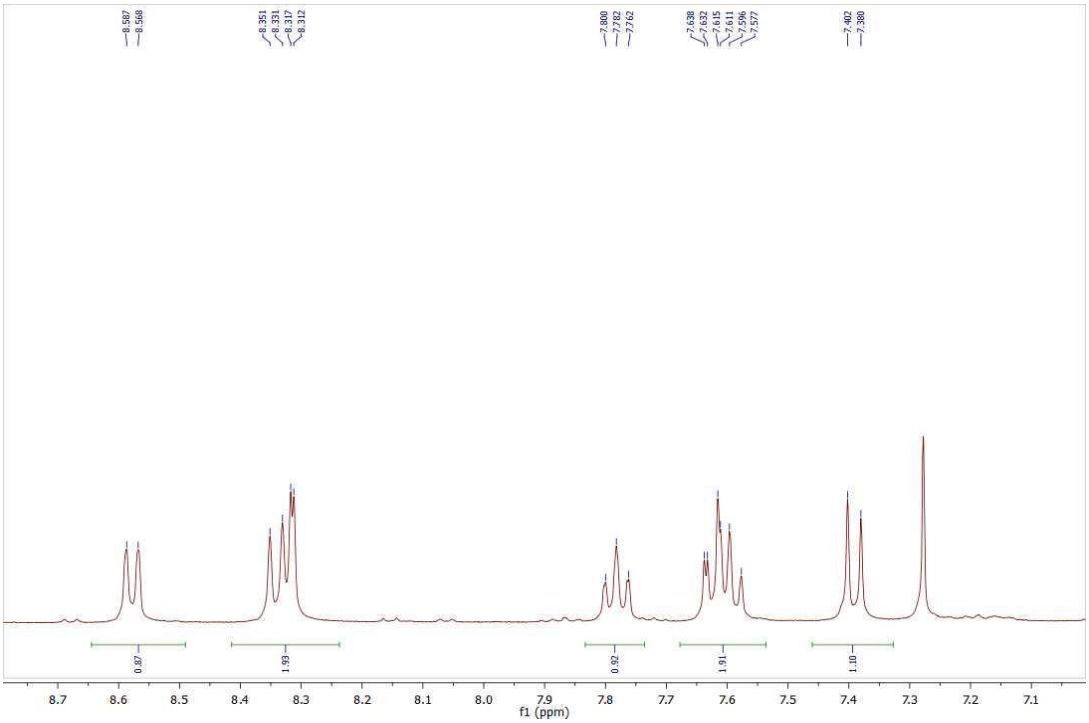


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2,5-Dimethylphenanthridin-6(5*H*)-one (2f).

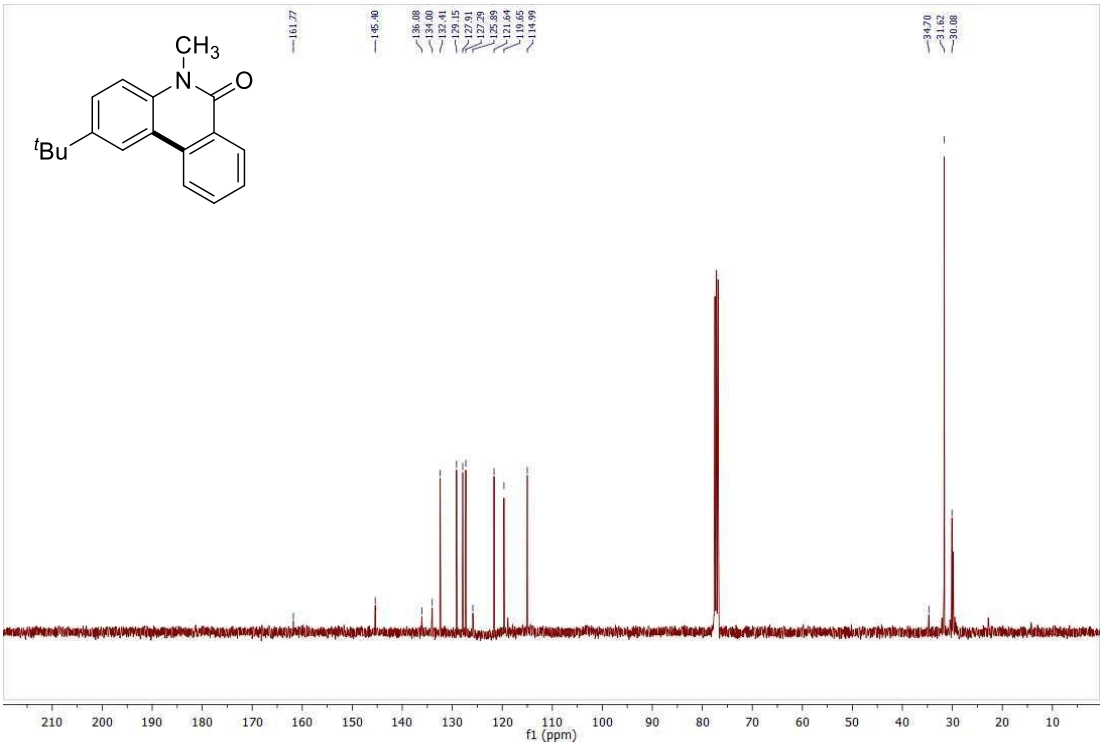


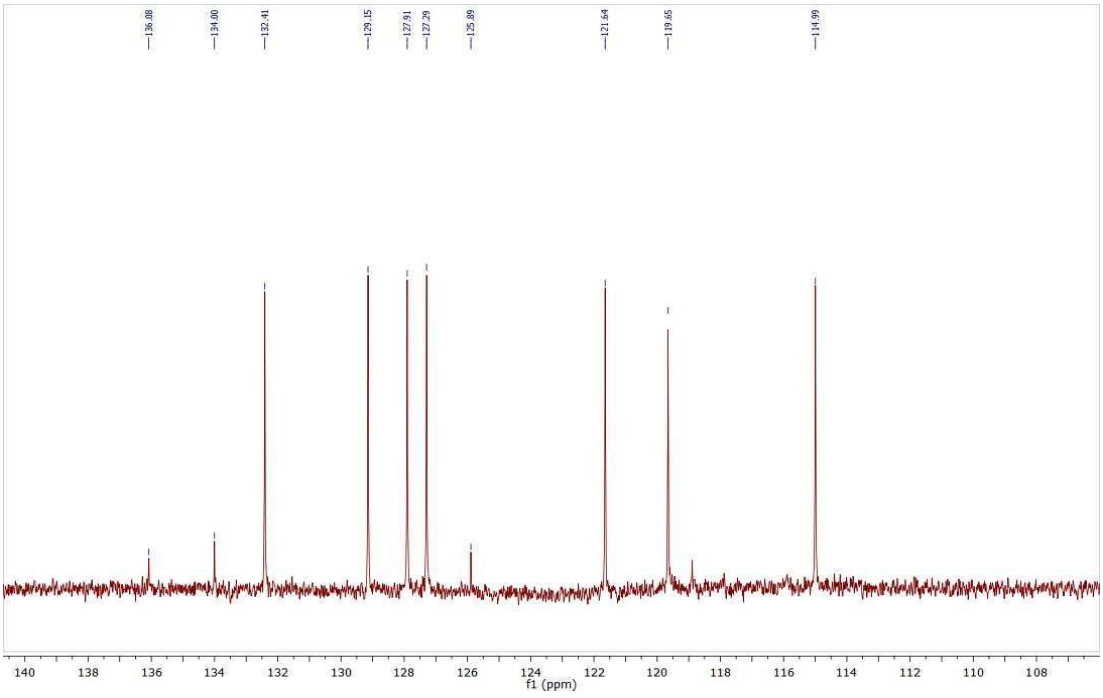
^{1}H NMR (400 MHz, $CDCl_3$). 2-(*tert*-Butyl)-5-methylphenanthridin-6(5*H*)-one (2g).



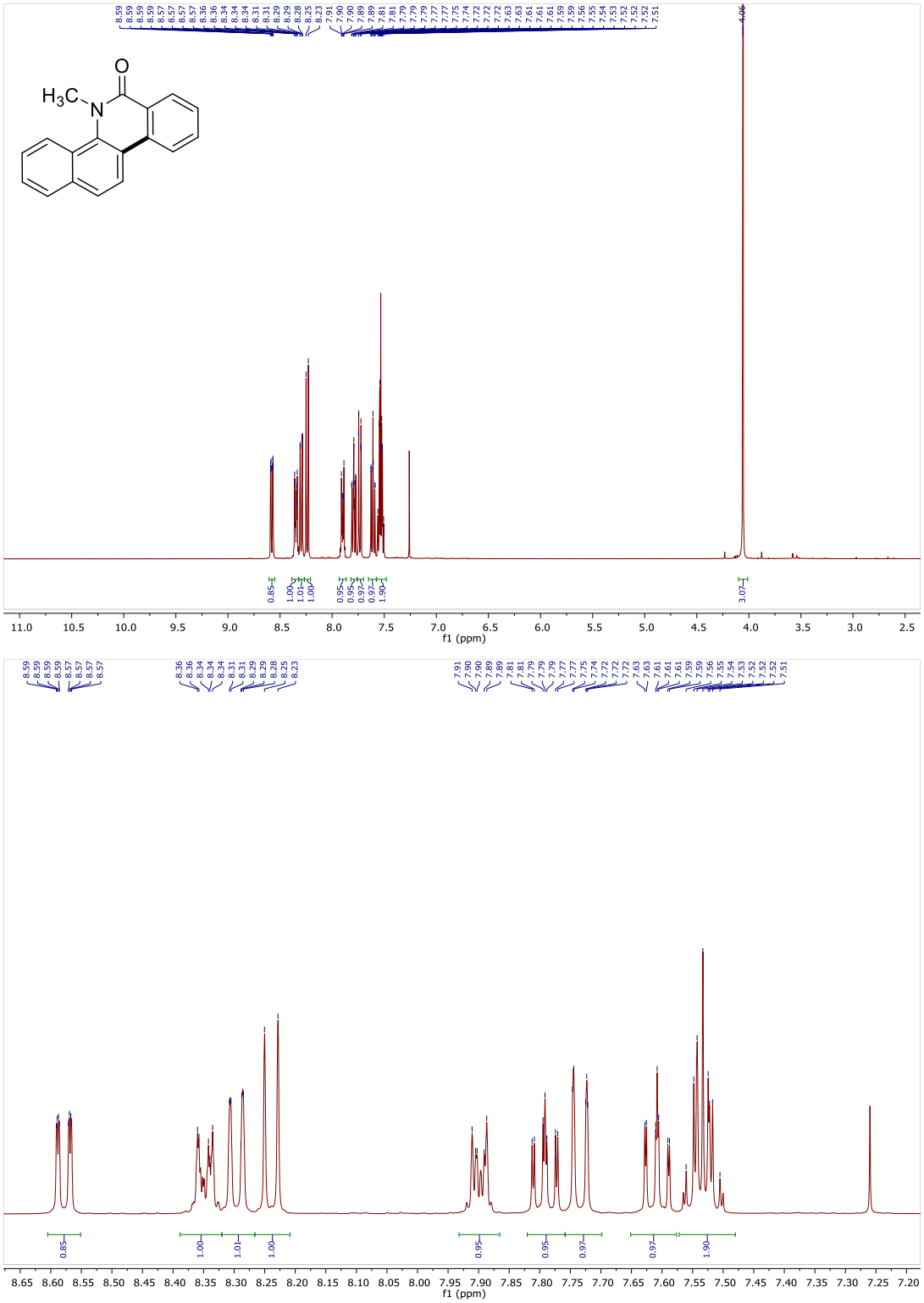


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-(*tert*-Butyl)-5-methylphenanthridin-6(5*H*)-one (2g).

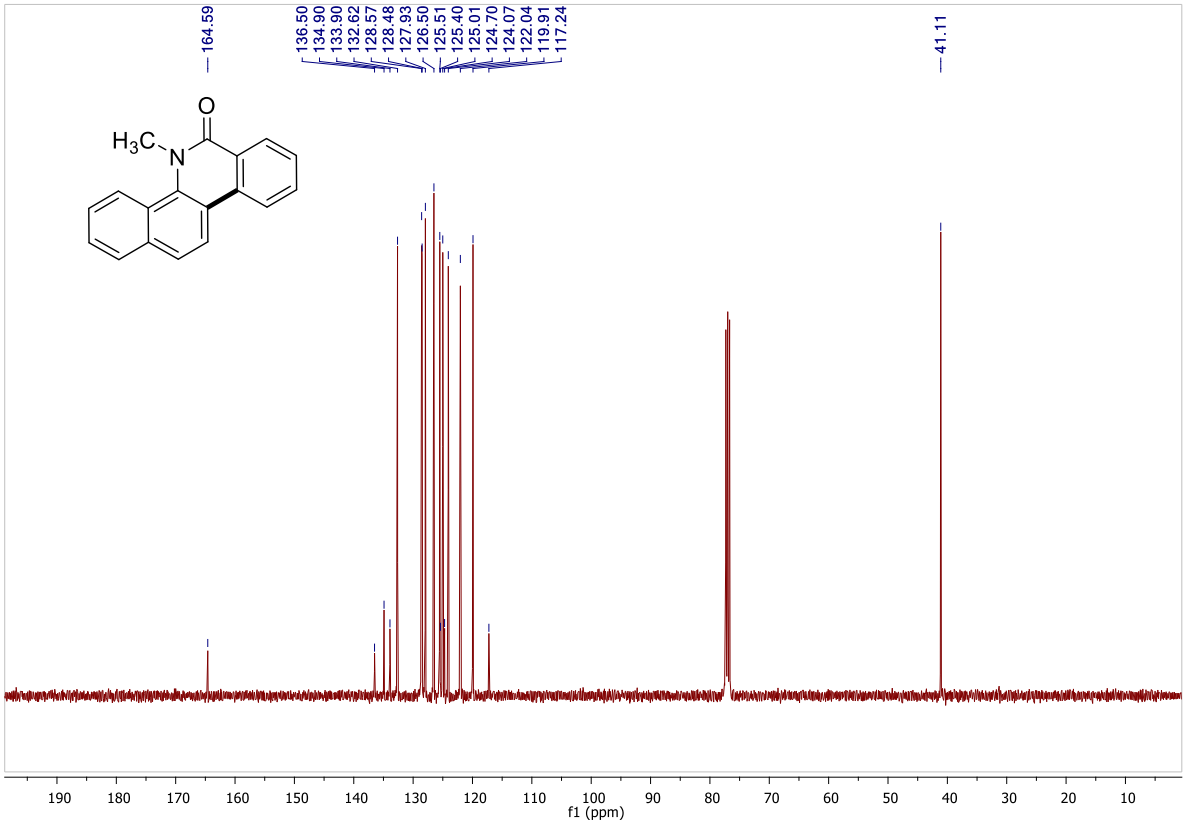


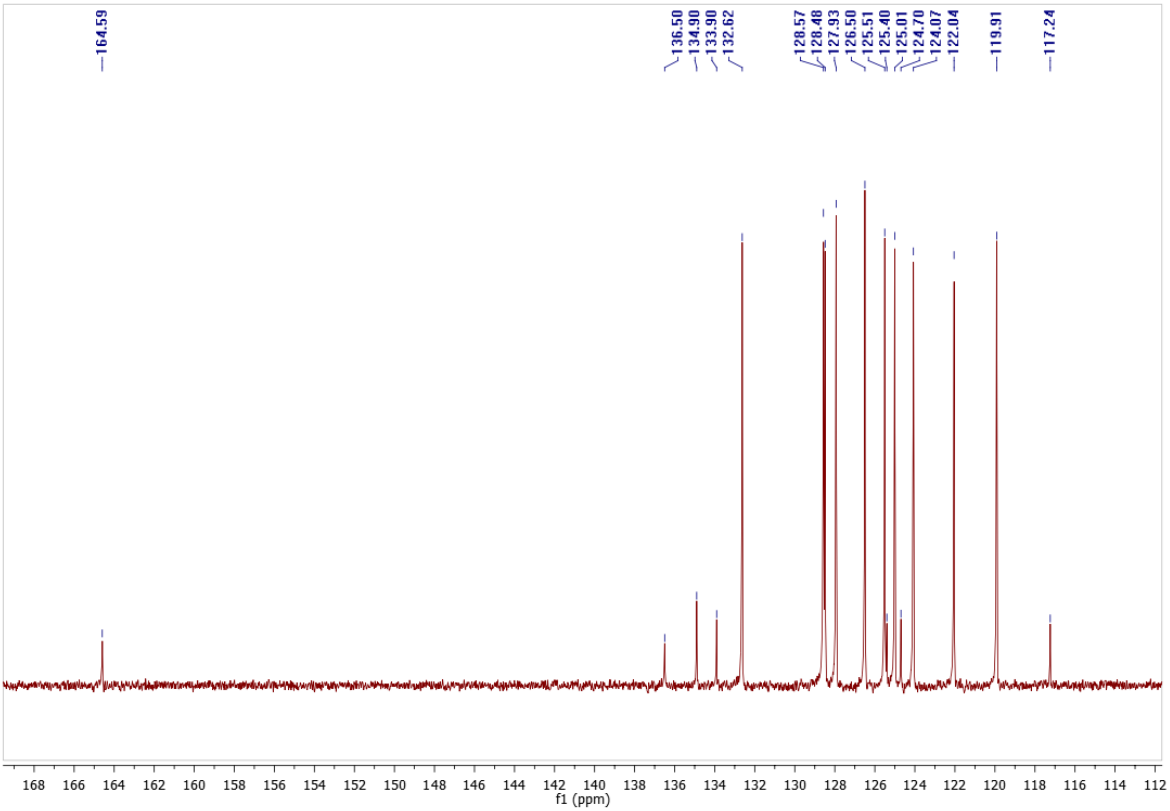


^{1}H NMR (400 MHz, $CDCl_3$). 5-Methylbenzo[*c*]phenanthridin-6(5*H*)-one (2h)

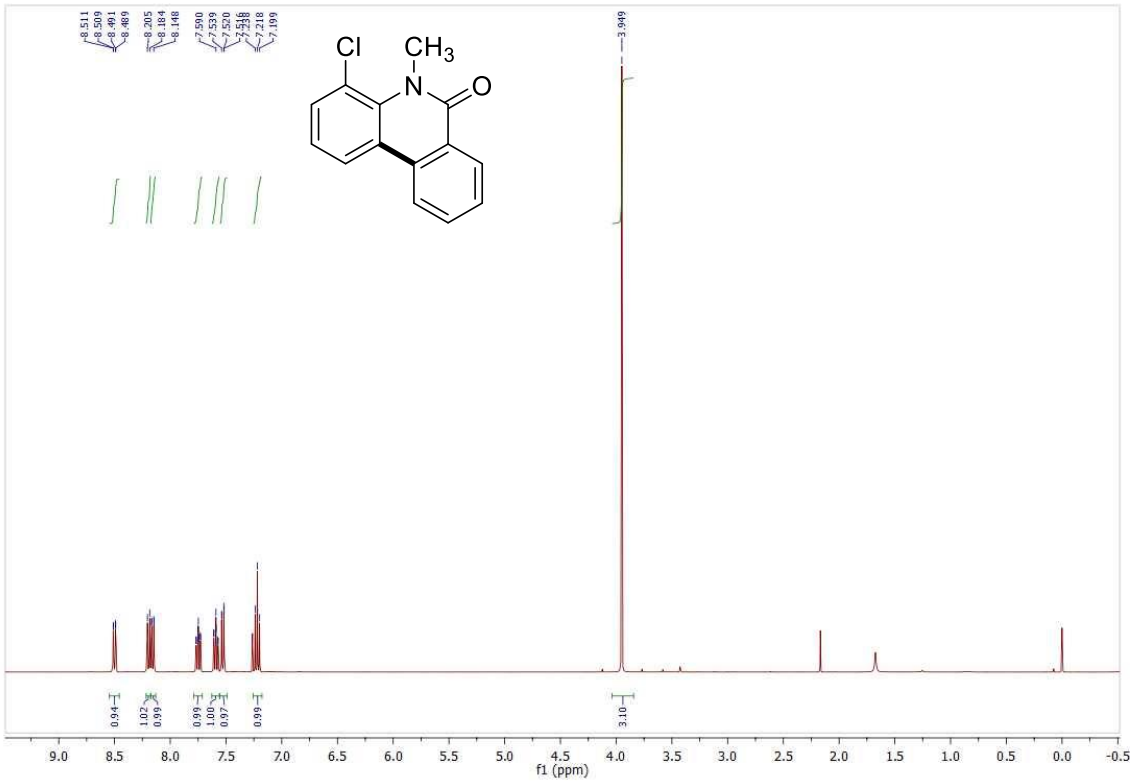


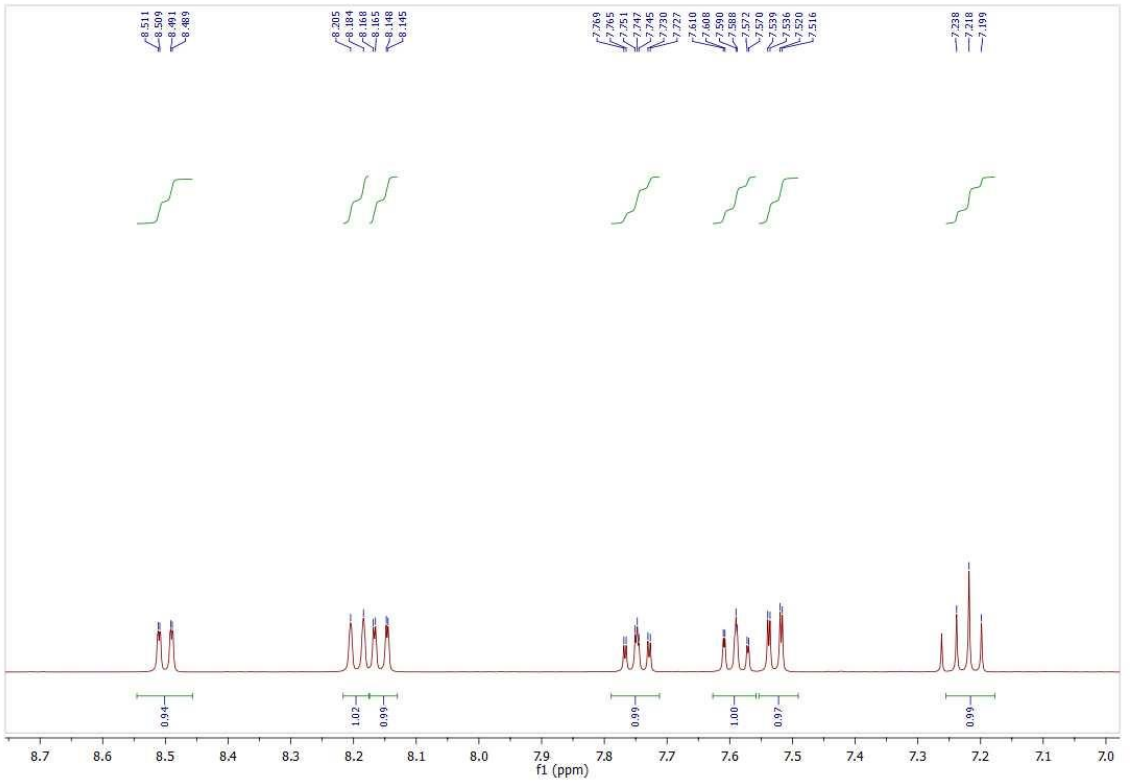
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 5-Methylbenzo[*c*]phenanthridin-6(5*H*)-one (2h)



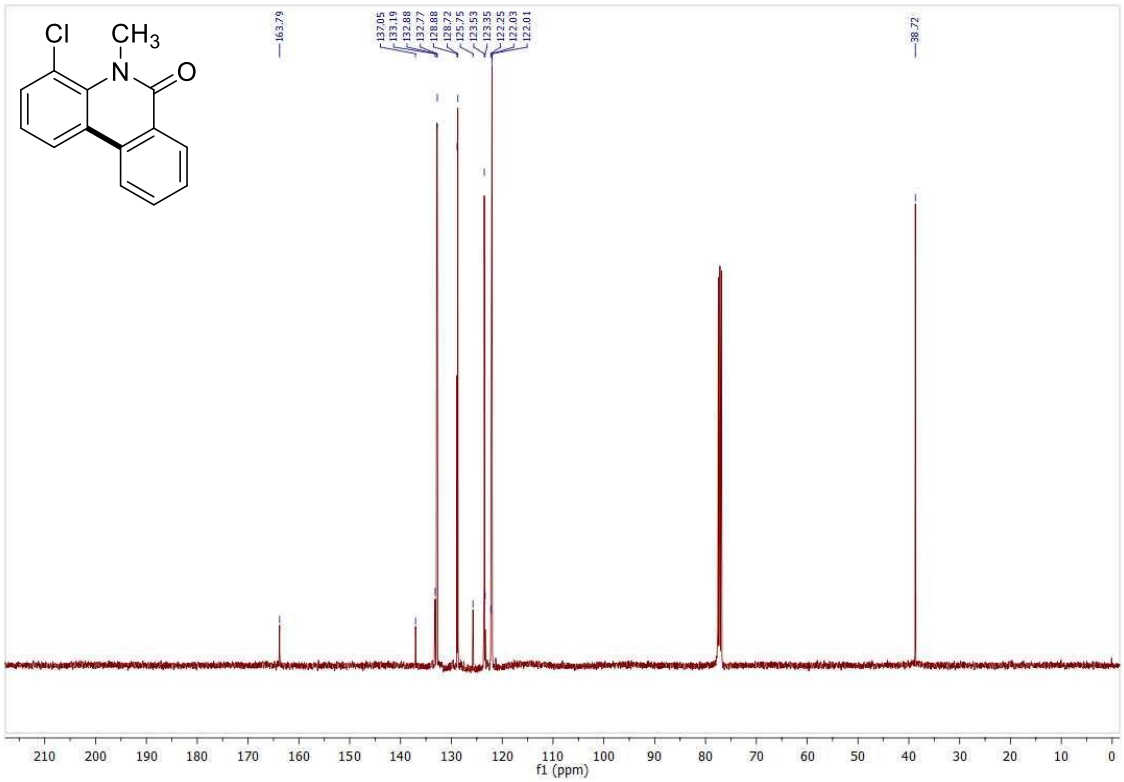


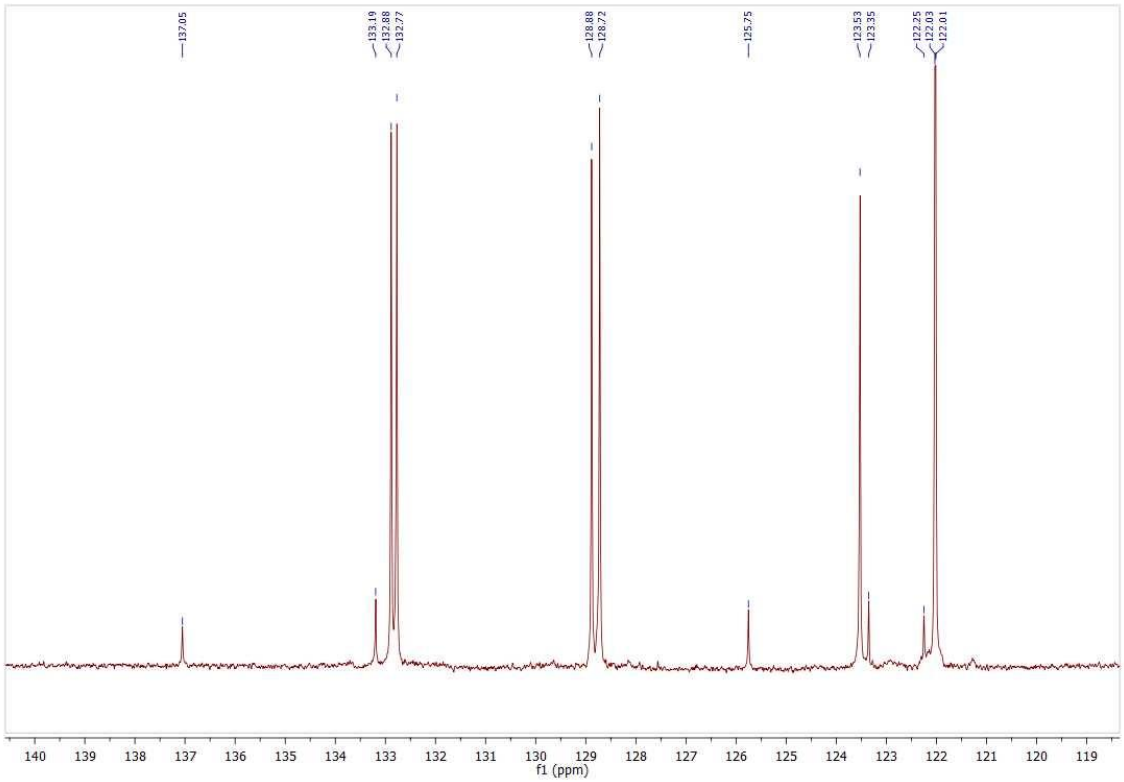
^{1}H NMR (400 MHz, $CDCl_3$). 4-Chloro-5-methylphenanthridin-6(5*H*)-one (2i).



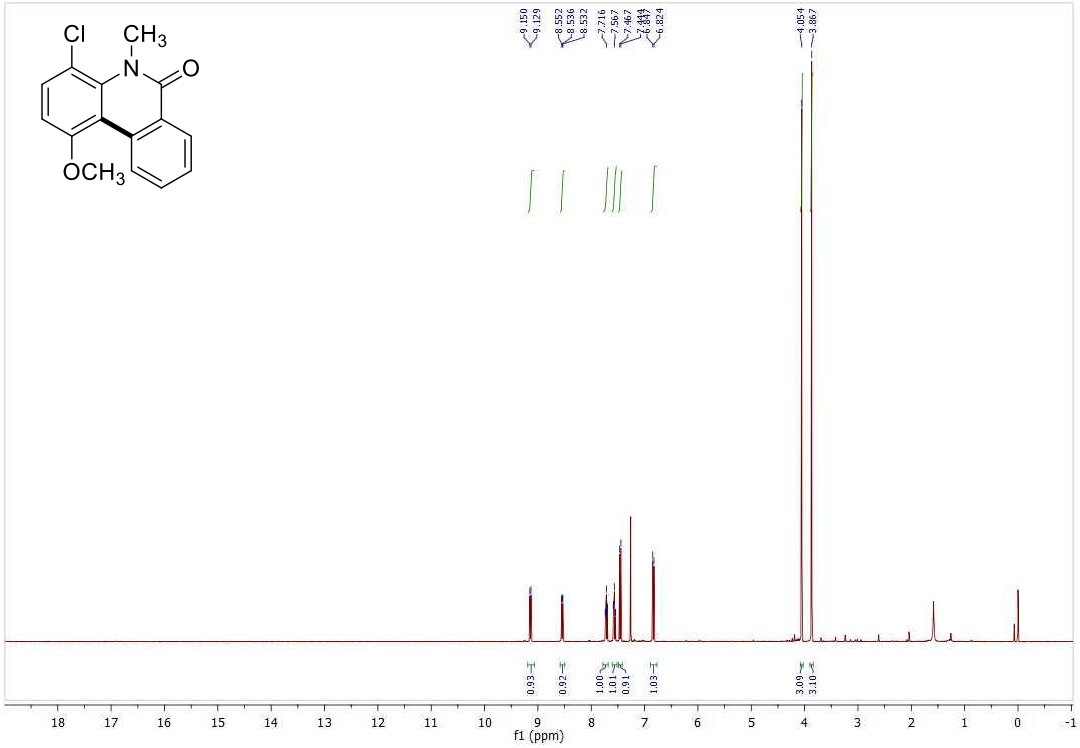


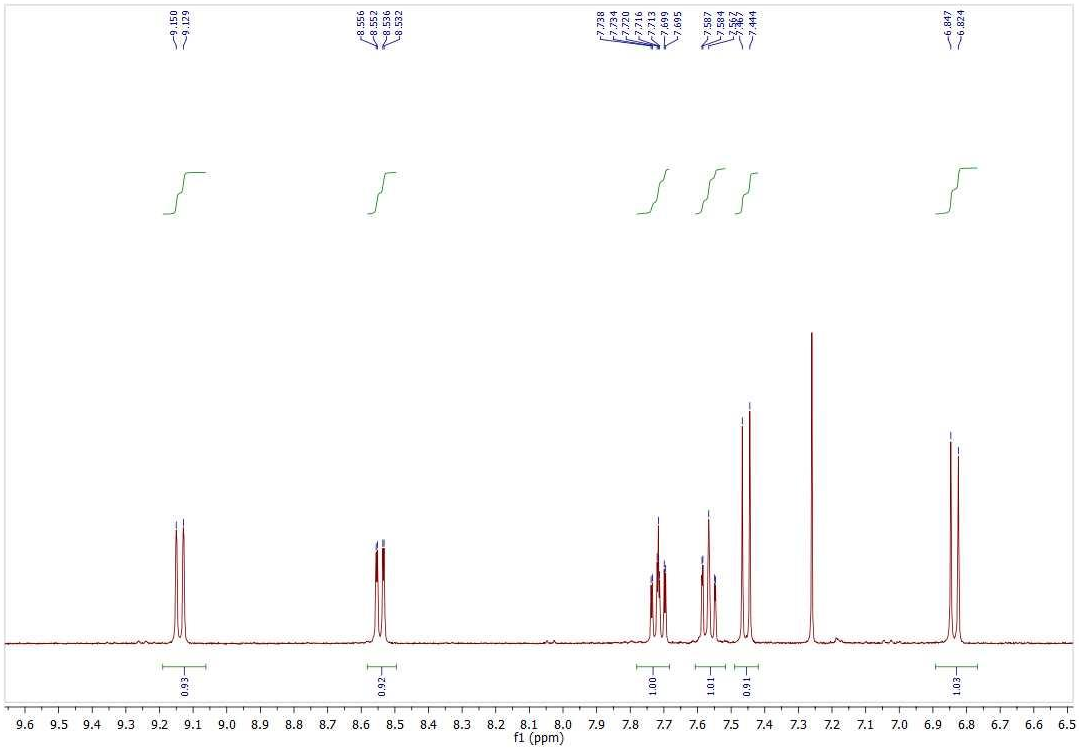
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 4-Chloro-5-methylphenanthridin-6(5*H*)-one (2i).



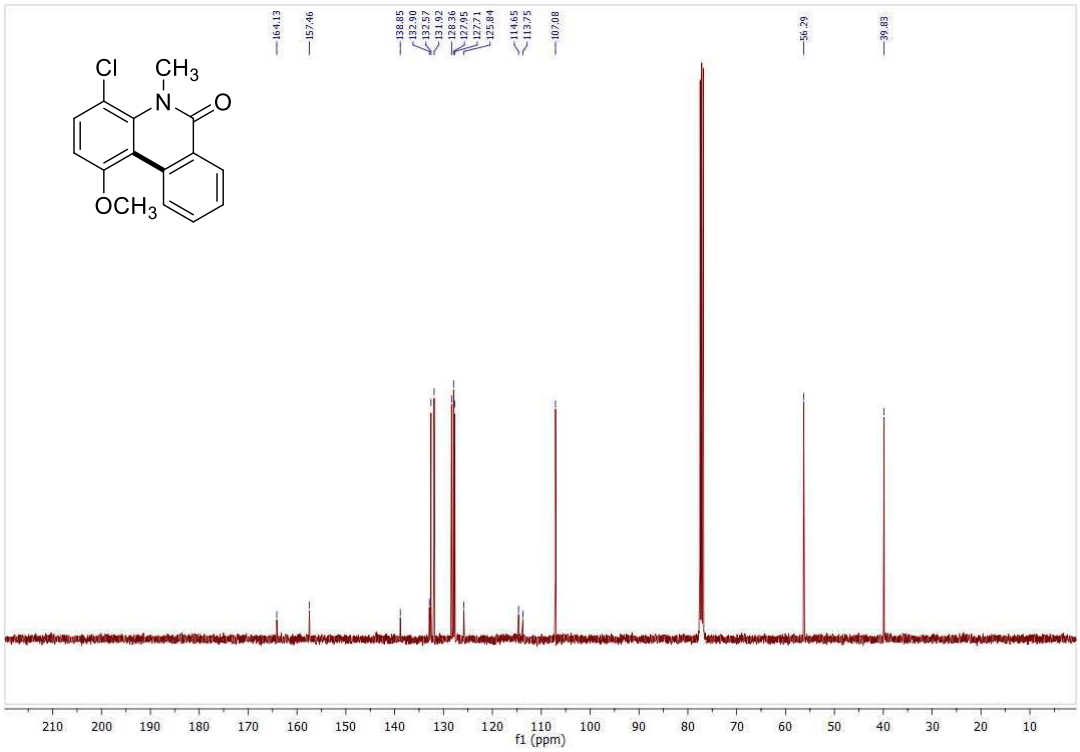


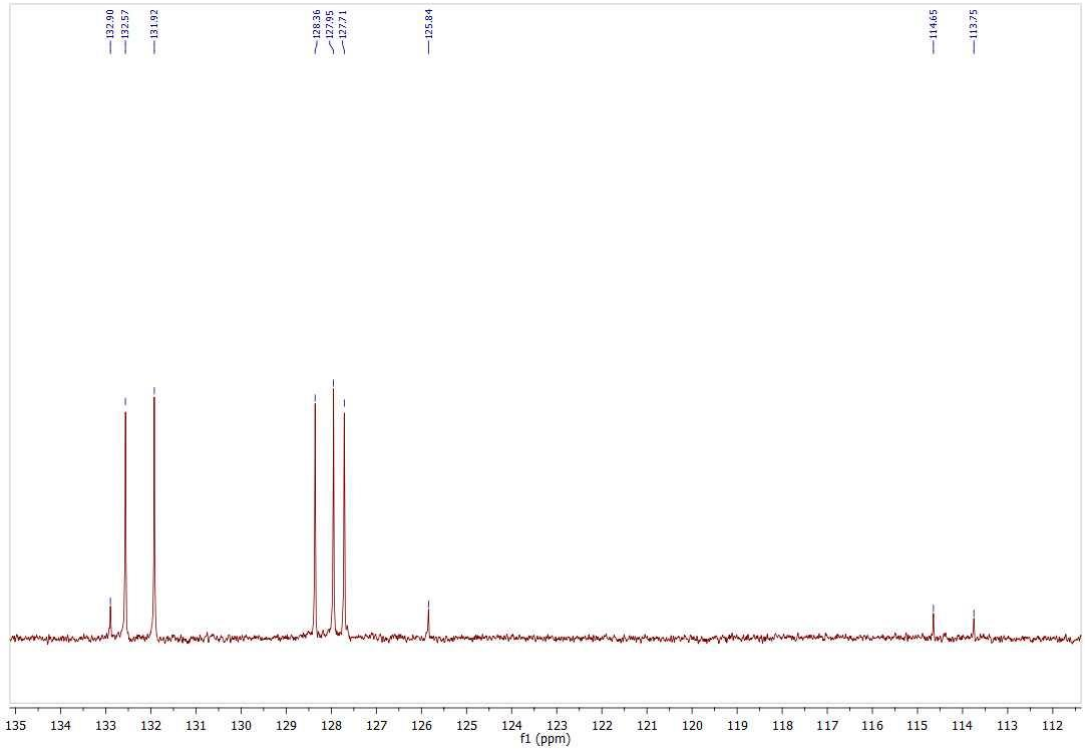
^{1}H NMR (400 MHz, $CDCl_3$). 4-Chloro-1-methoxy-5-methylphenanthridin-6(5*H*)-one (2j)



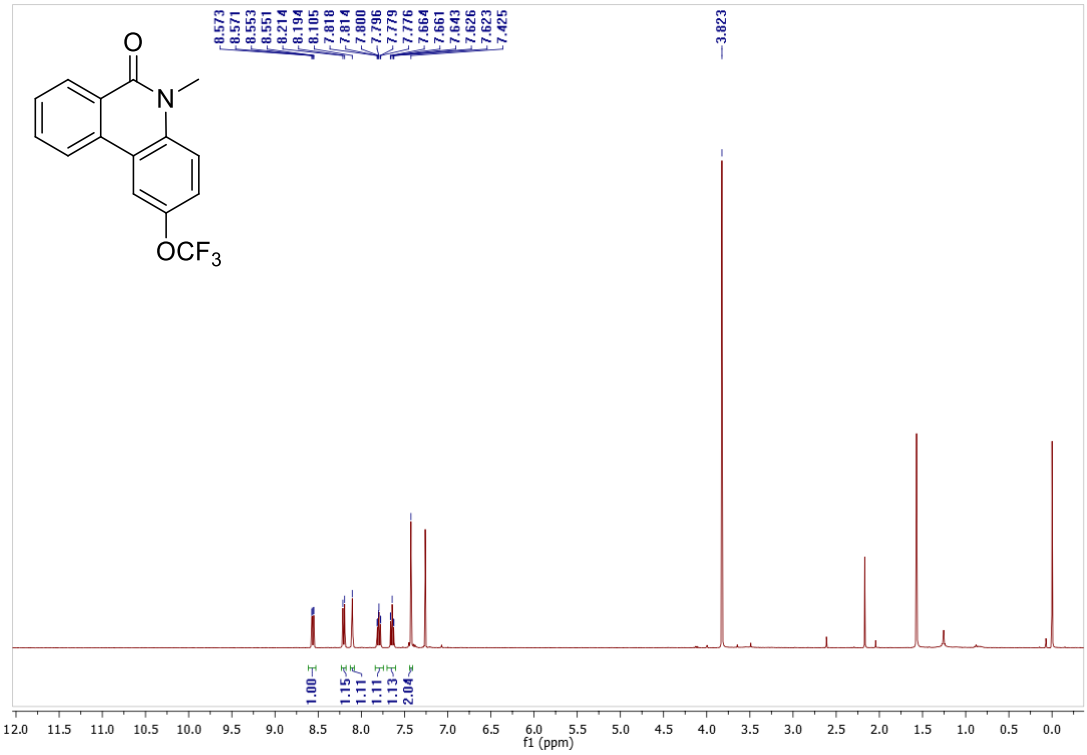


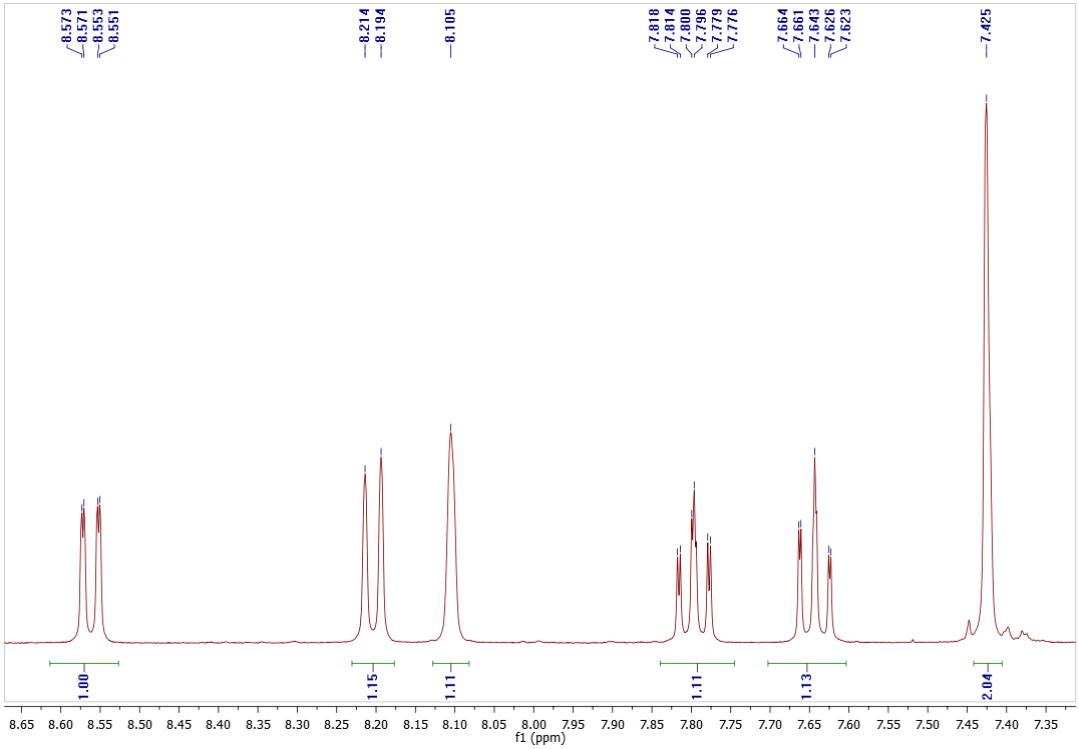
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 4-Chloro-1-methoxy-5-methylphenanthridin-6(5*H*)-one (2j)



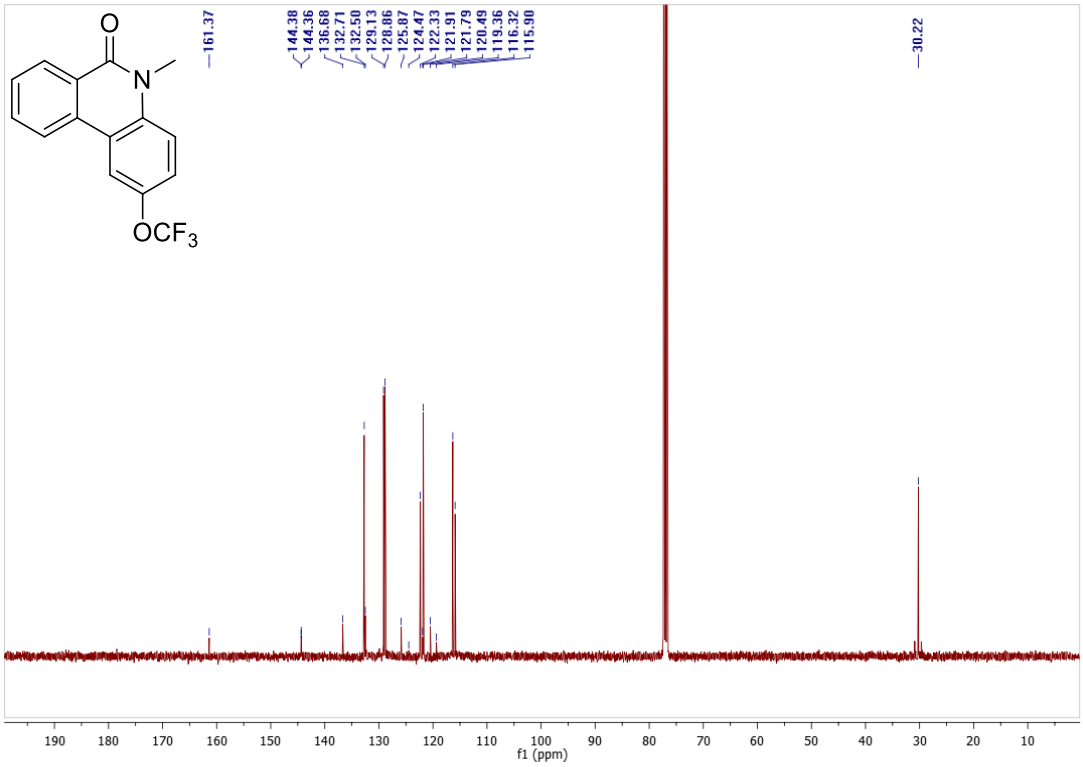


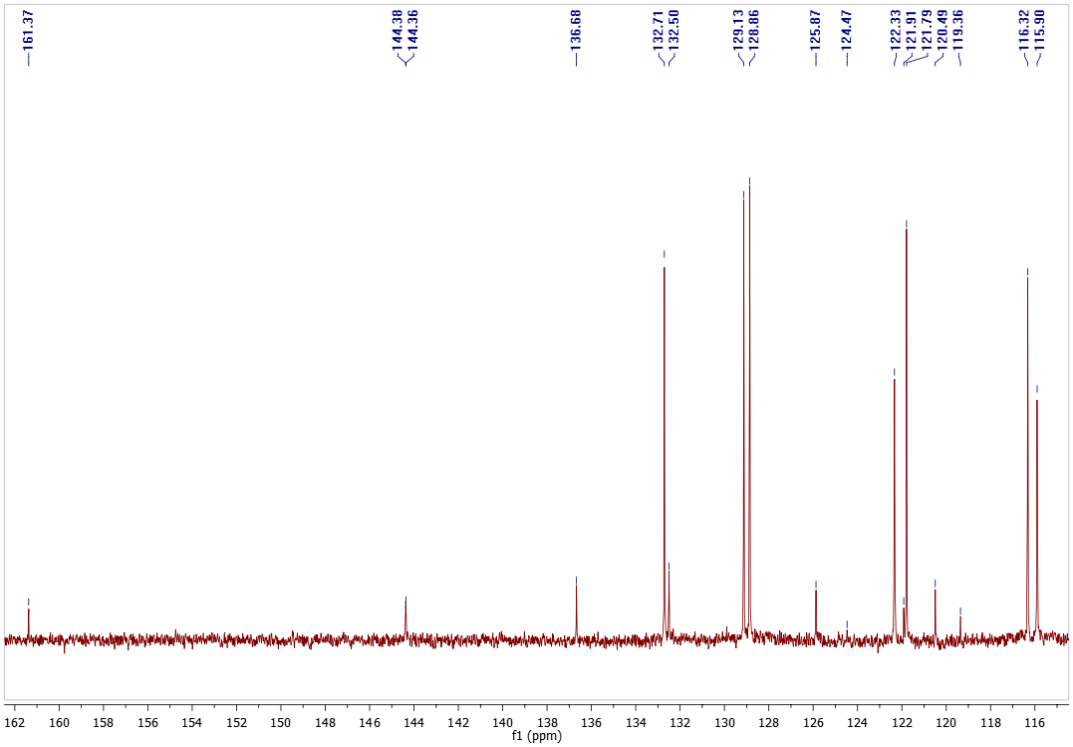
^{1}H NMR (400 MHz, $CDCl_3$). 5-Methyl-2-(trifluoromethoxy)phenanthridin-6(5*H*)-one (2k).



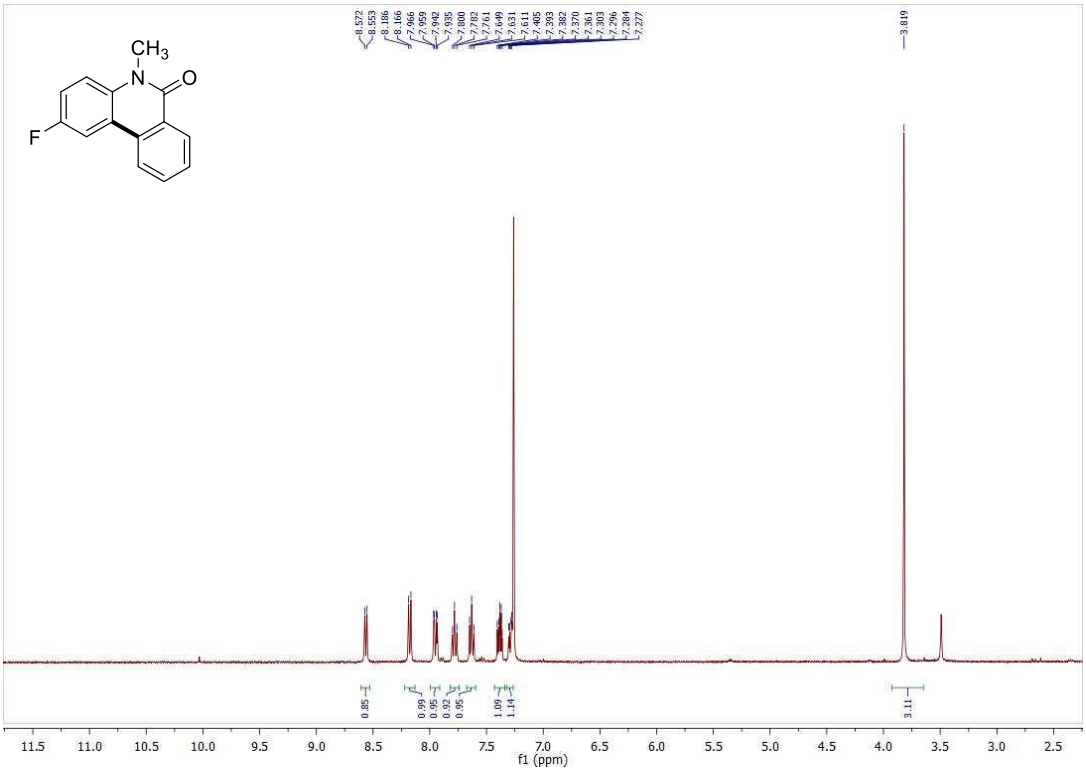


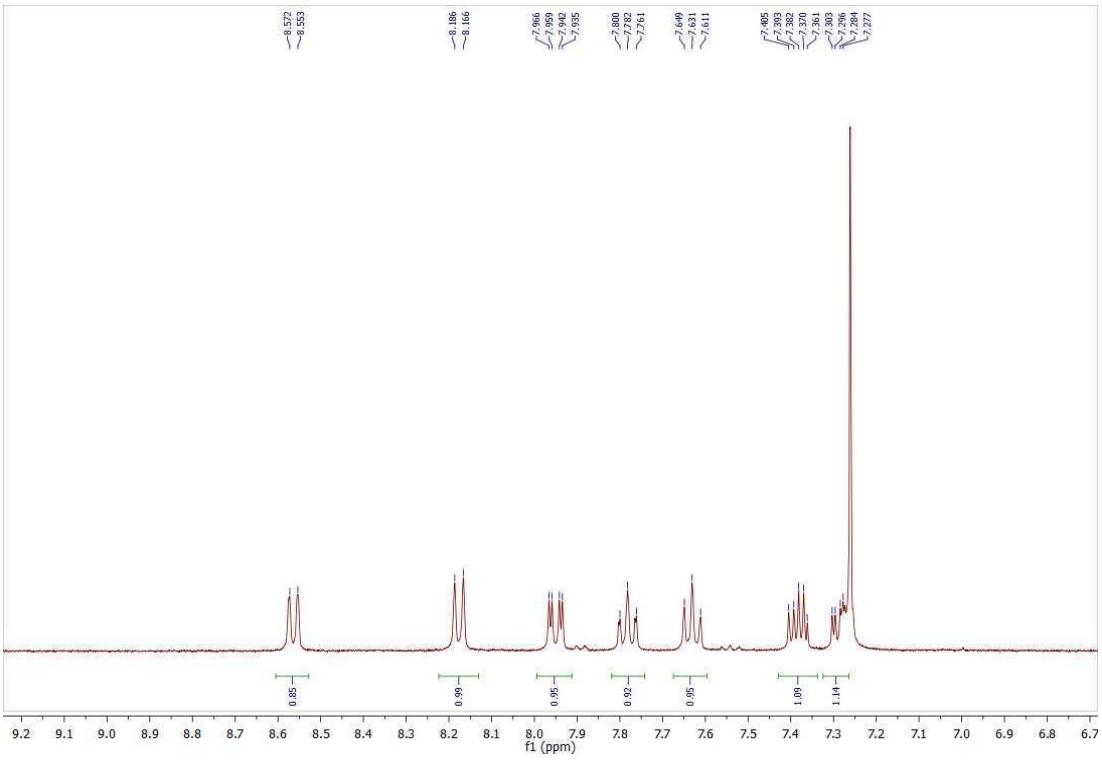
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 5-Methyl-2-(trifluoromethoxy)phenanthridin-6(5*H*)-one (2k).



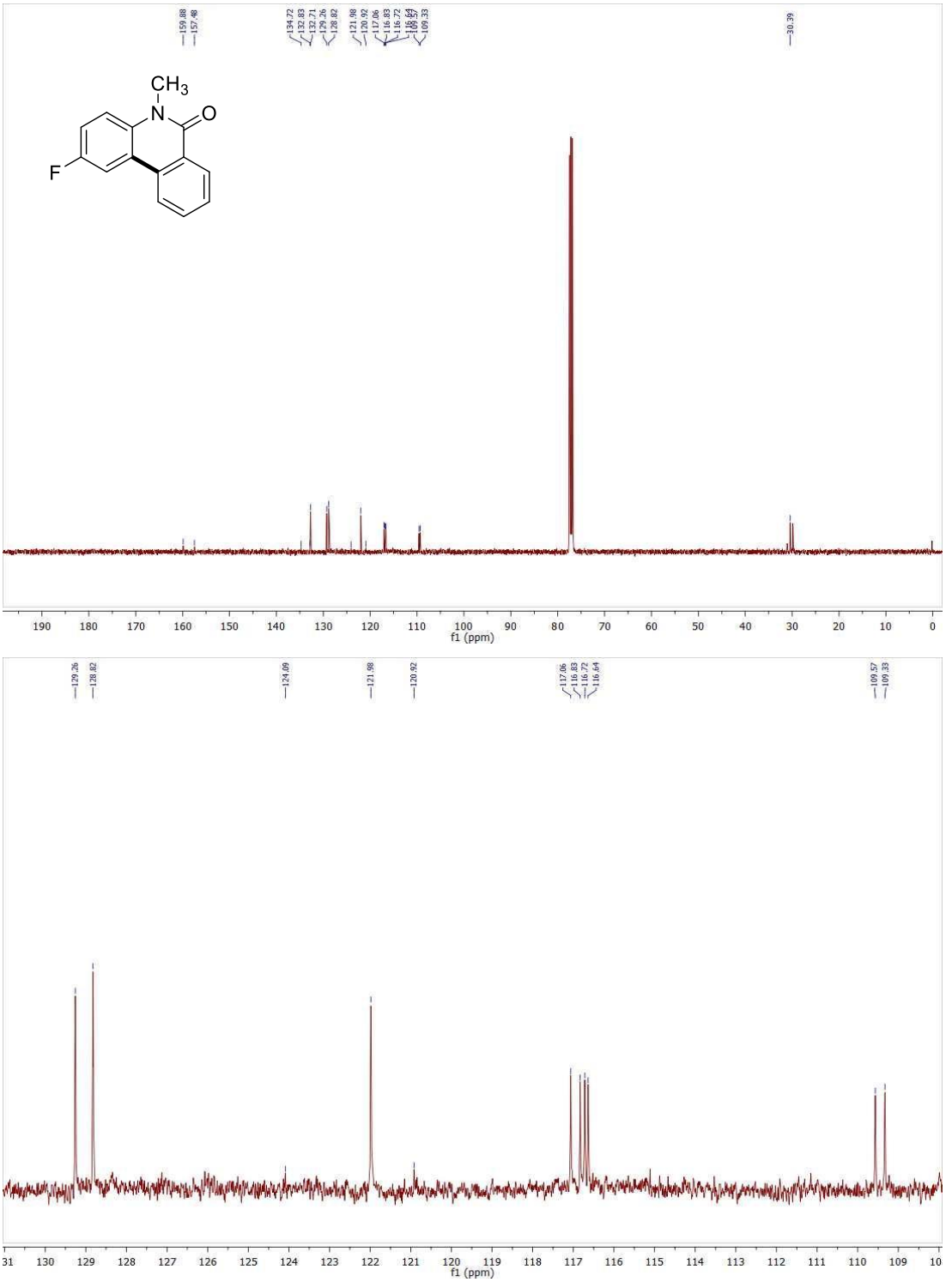


^{1}H NMR (400 MHz, $CDCl_3$). 2-Fluoro-5-methylphenanthridin-6(5*H*)-one (2l).

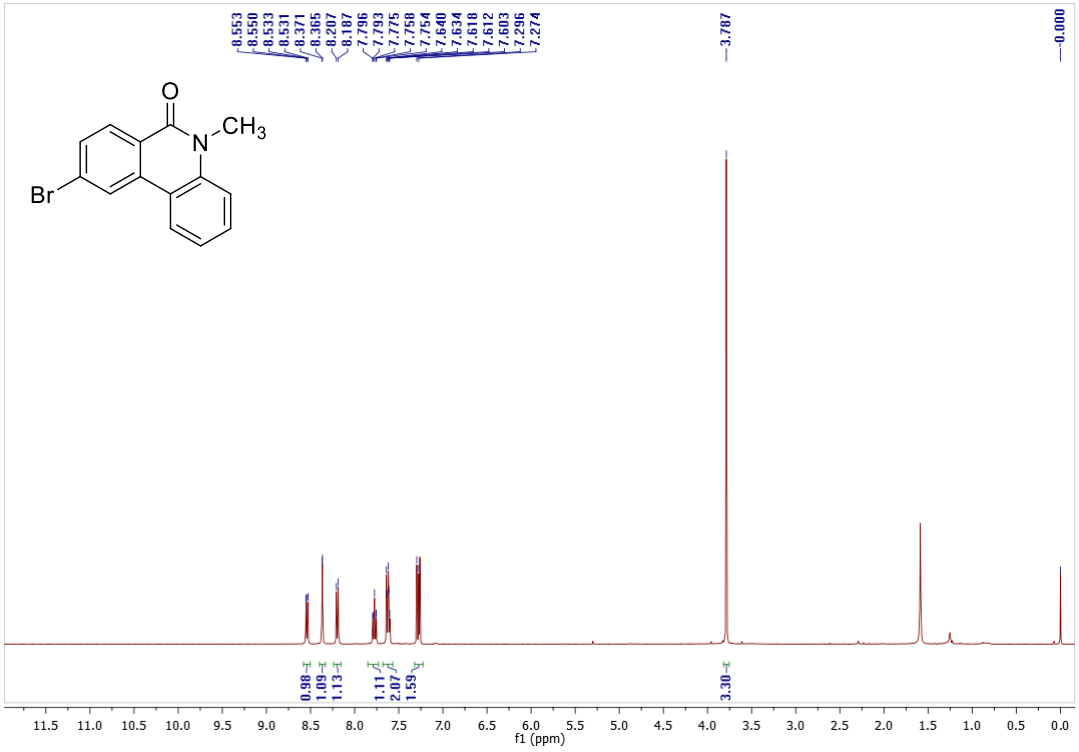


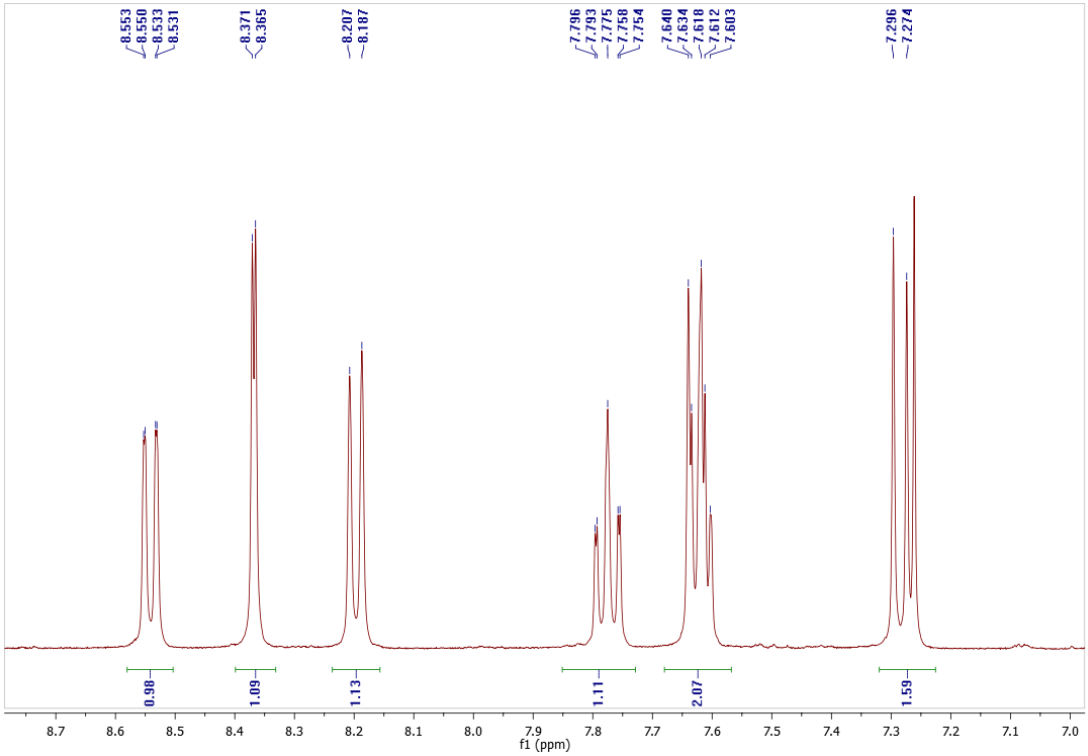


^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Fluoro-5-methylphenanthridin-6(5*H*)-one (2l).

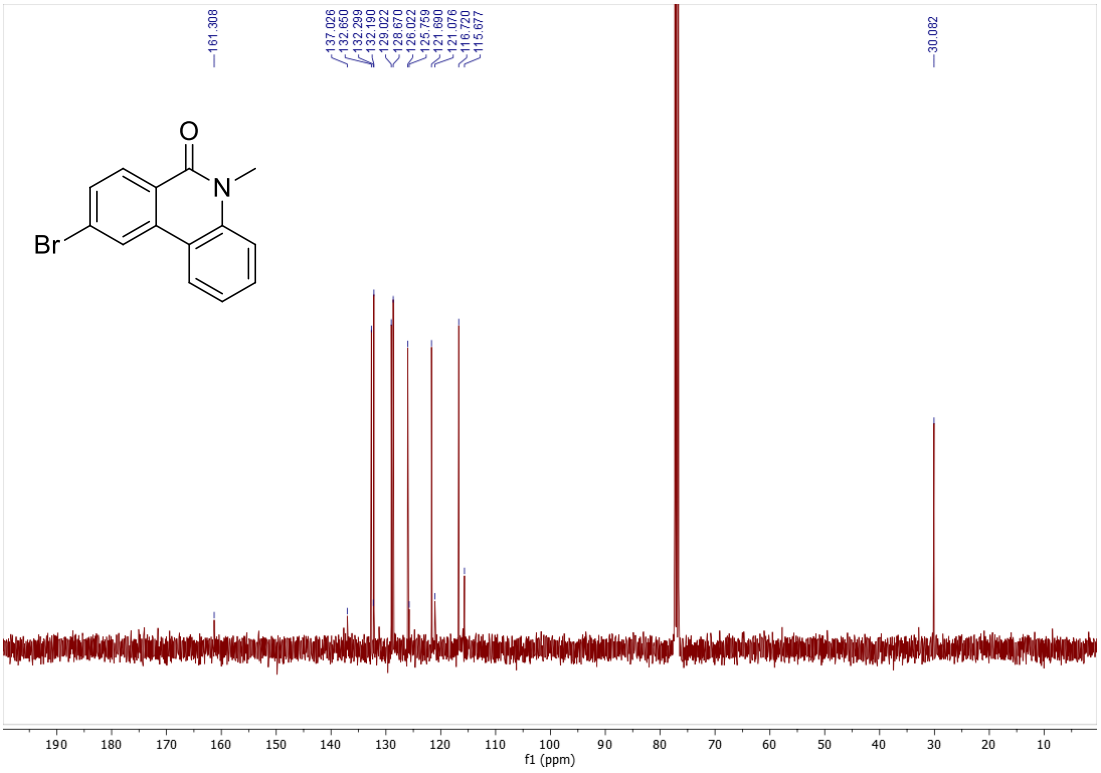


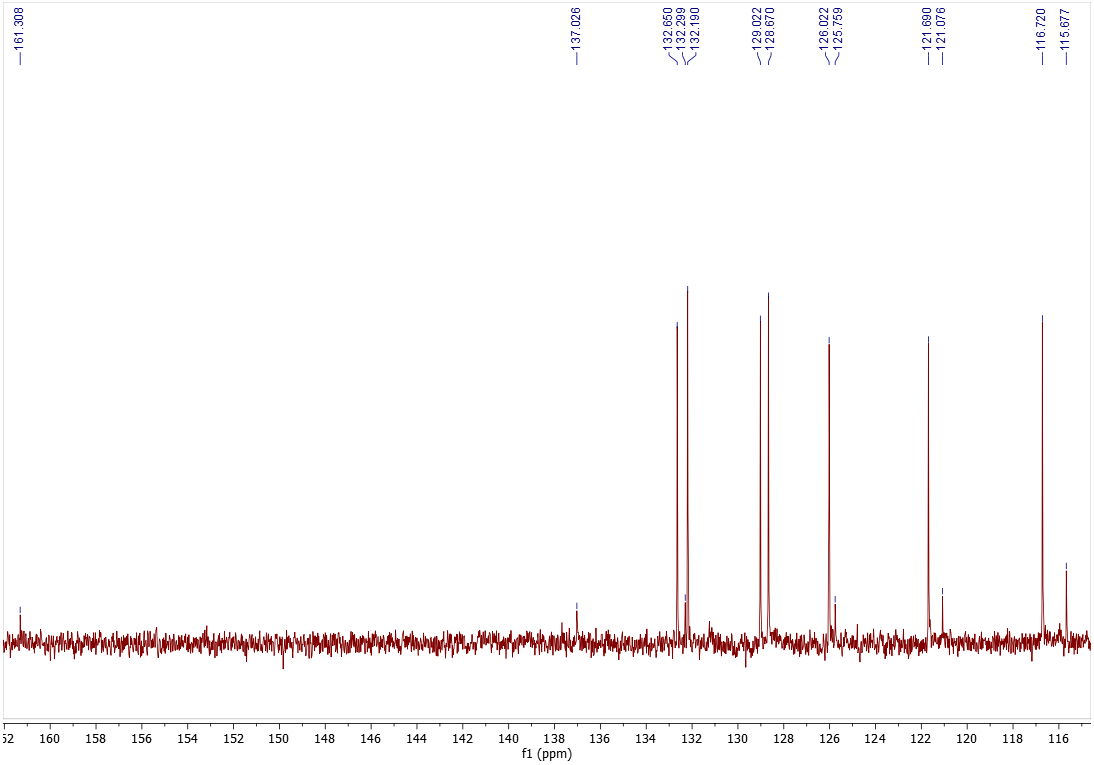
^{1}H NMR (400 MHz, $CDCl_3$). 2-Bromo-5-methylphenanthridin-6(5*H*)-one (2n)



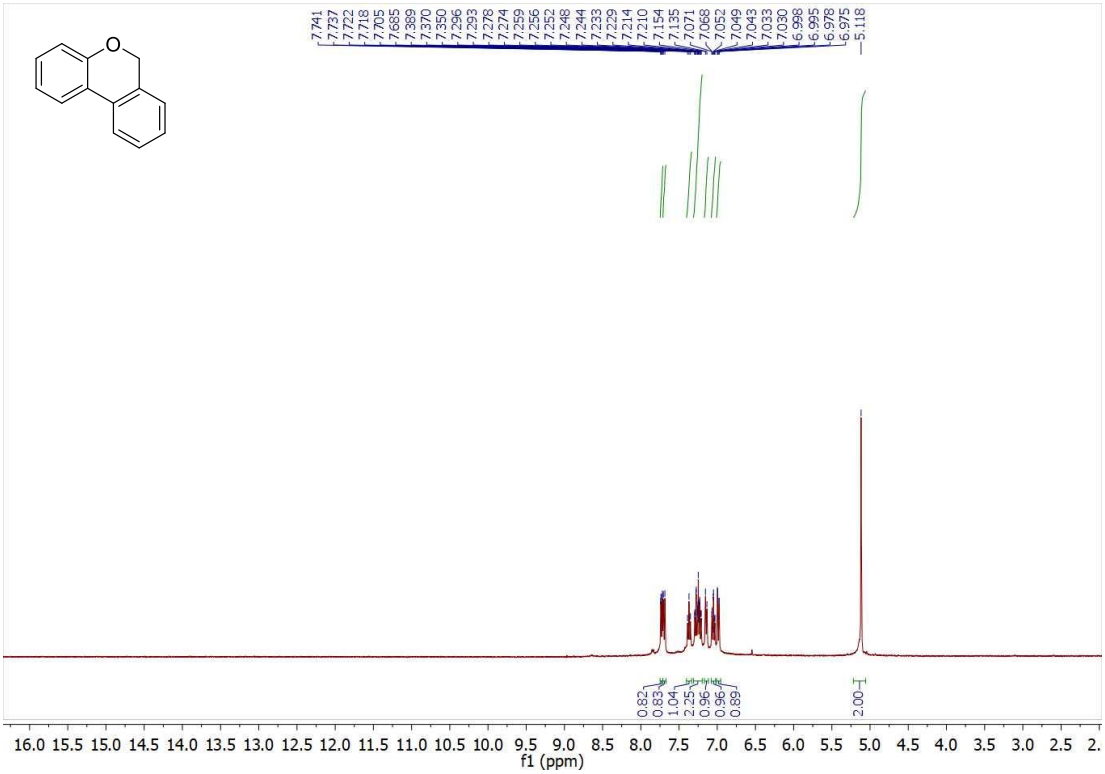


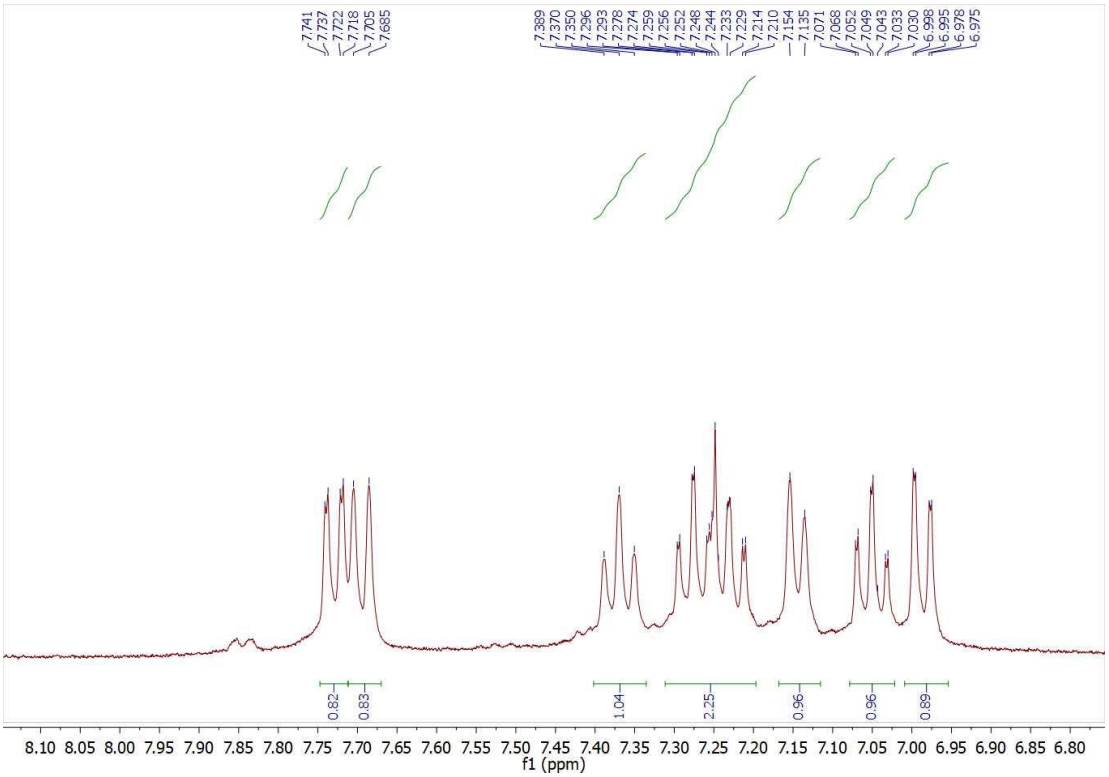
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Bromo-5-methylphenanthridin-6(5*H*)-one (2n)



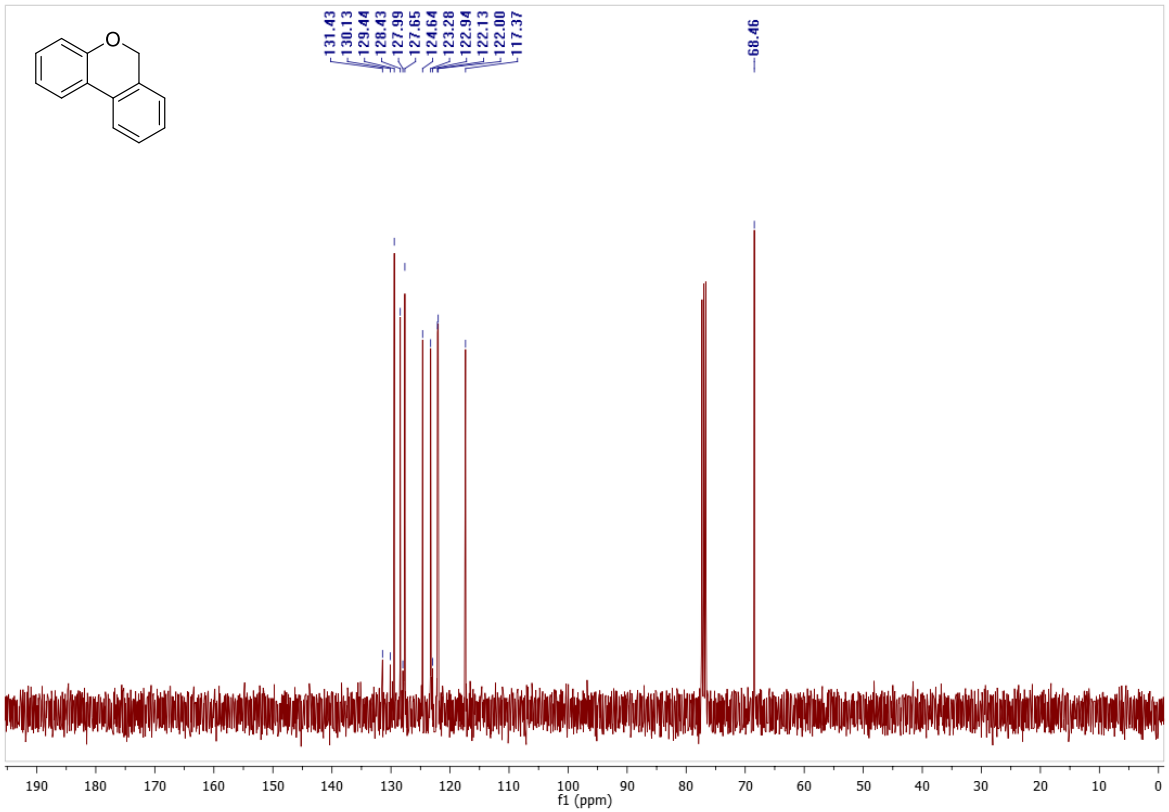


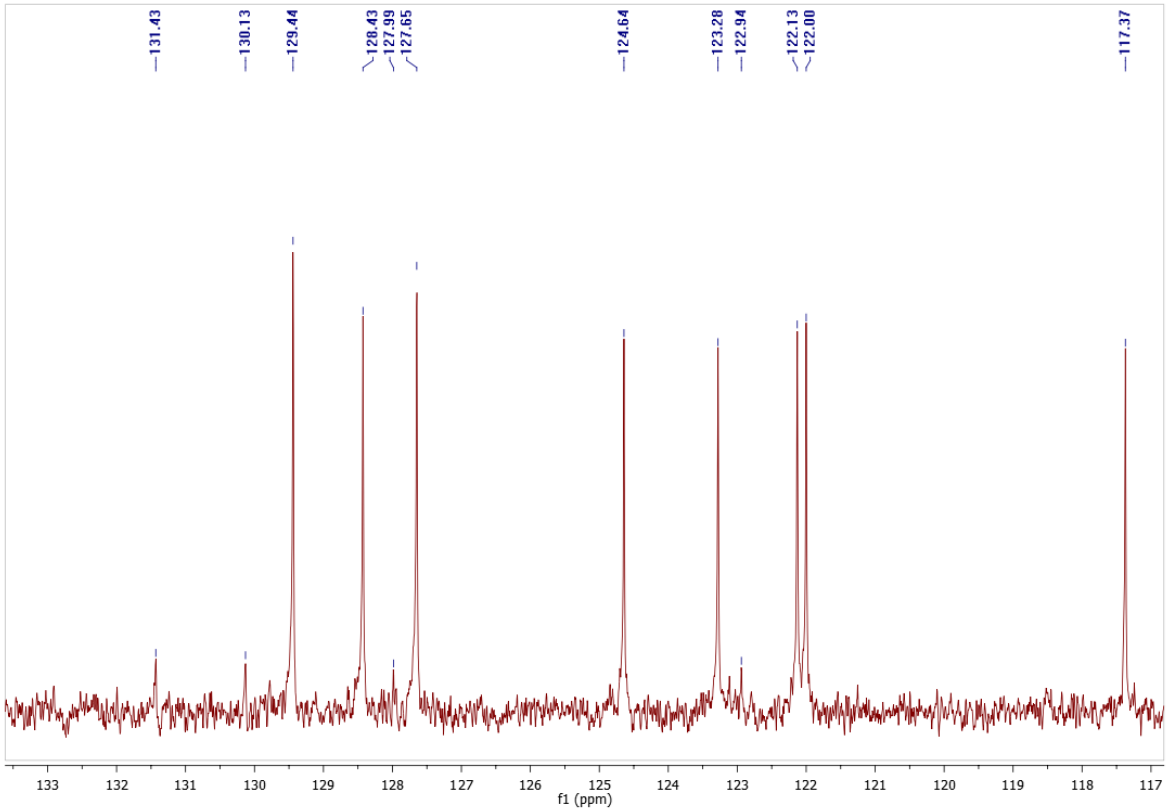
^{1}H NMR (400 MHz, $CDCl_3$). 6*H*-Benzo[*c*]chromene (7a).



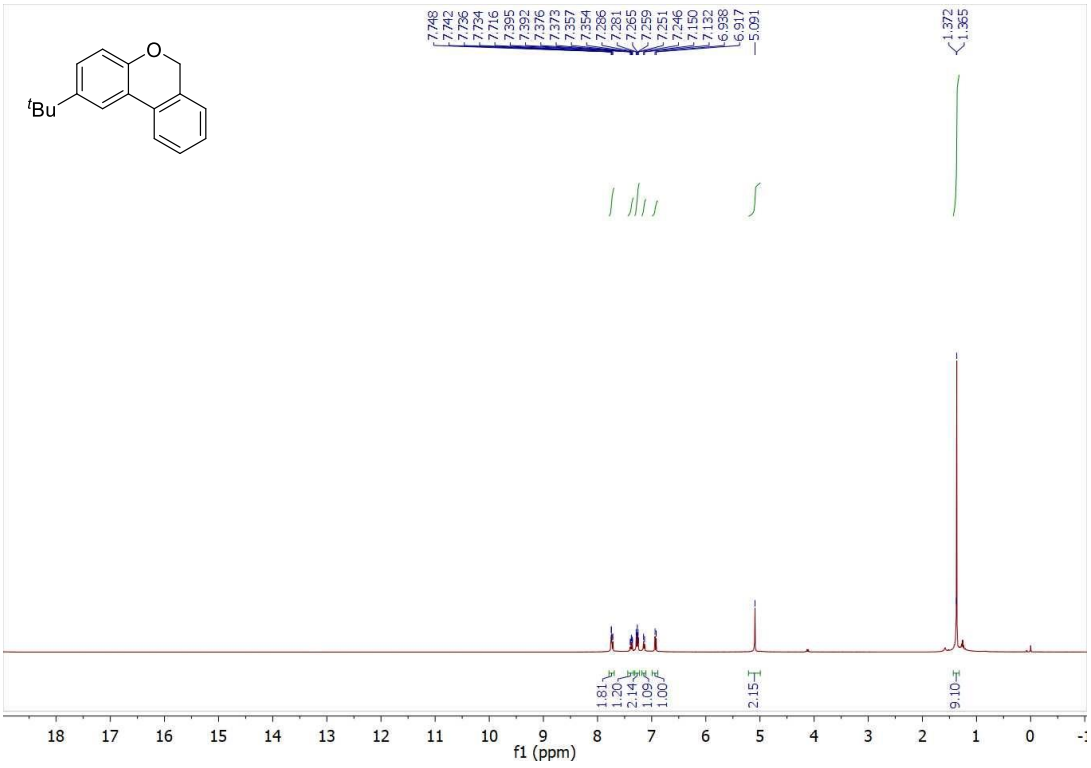


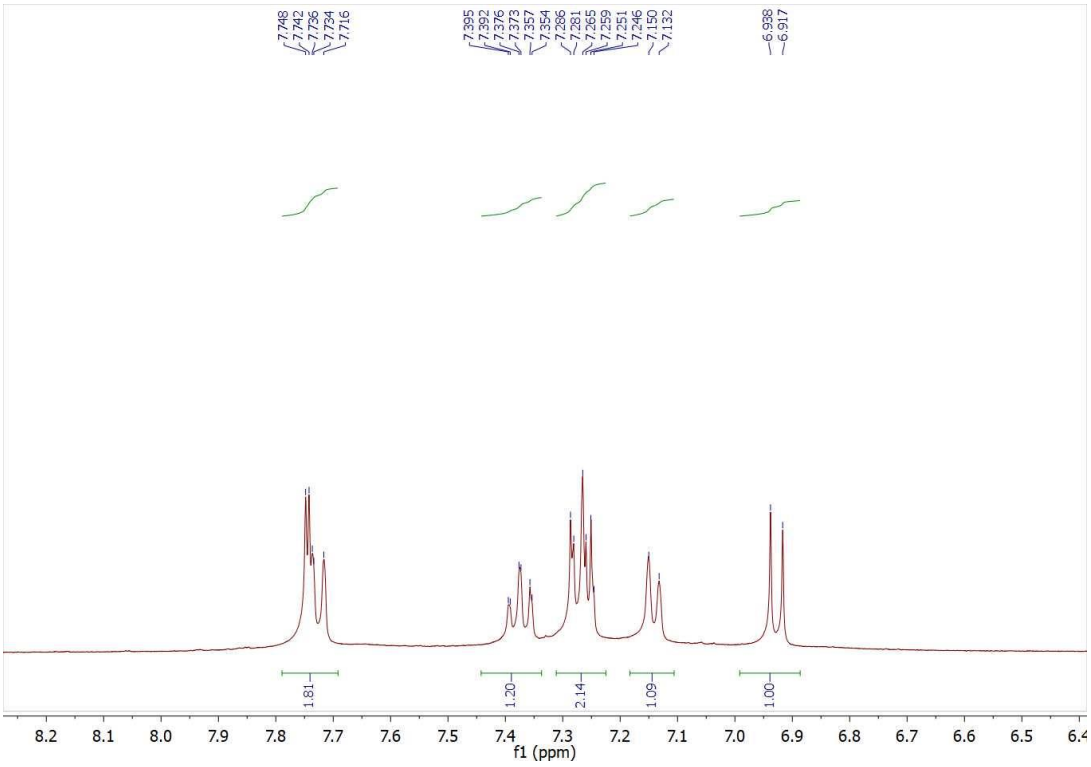
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 6*H*-Benzo[*c*]chromene (7a).



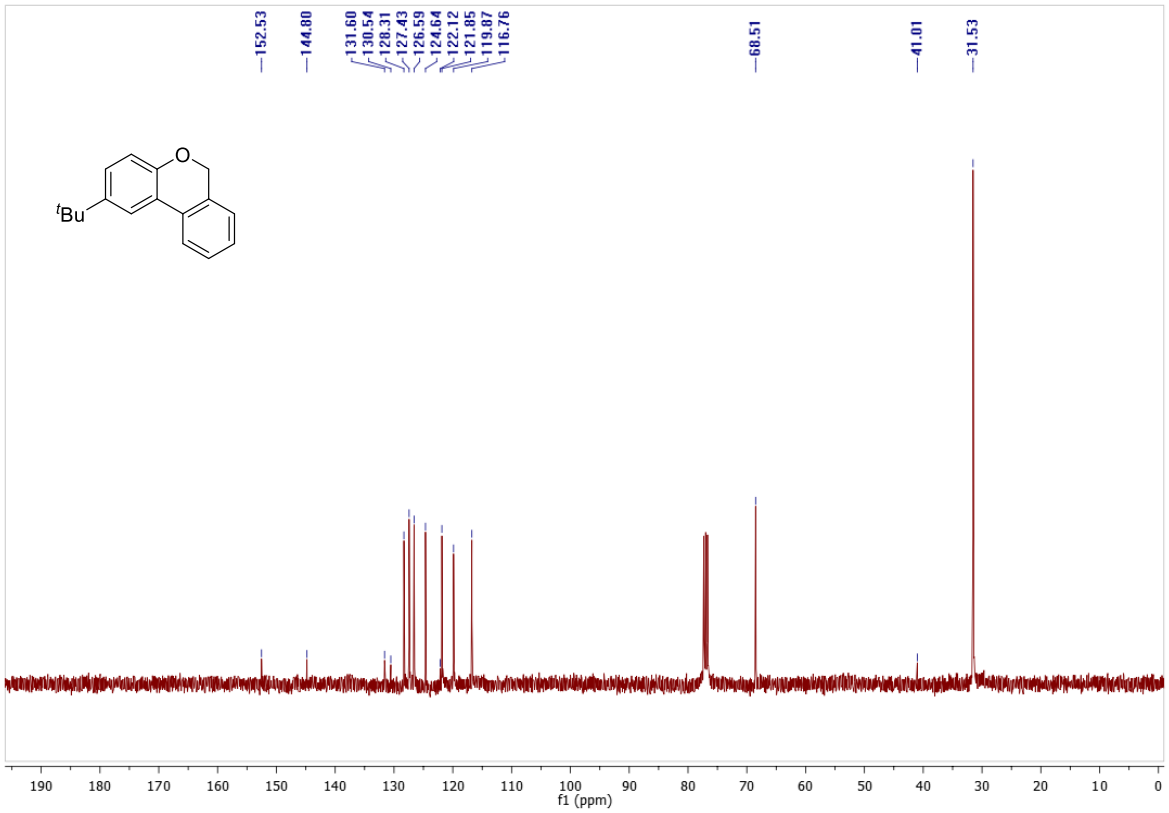


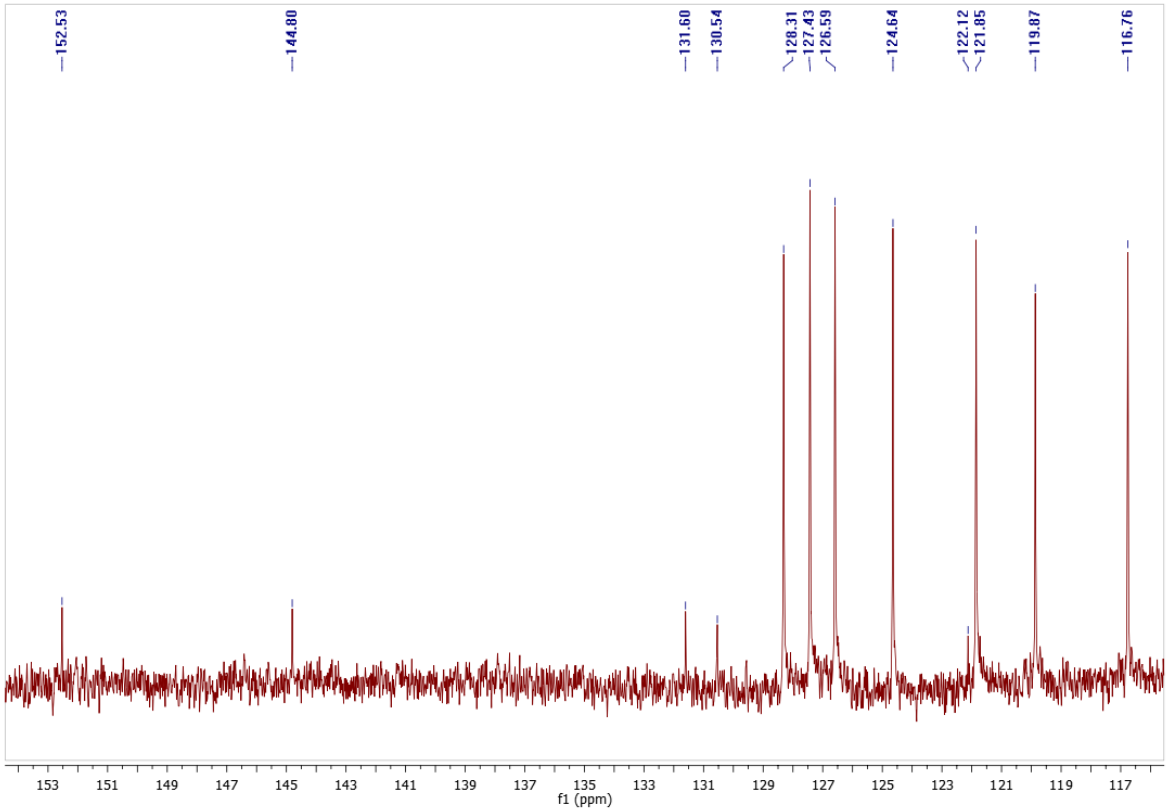
^{1}H NMR (400 MHz, $CDCl_3$). 2-(*tert*-Butyl)-6*H*-benzo[*c*]chromene (7c)



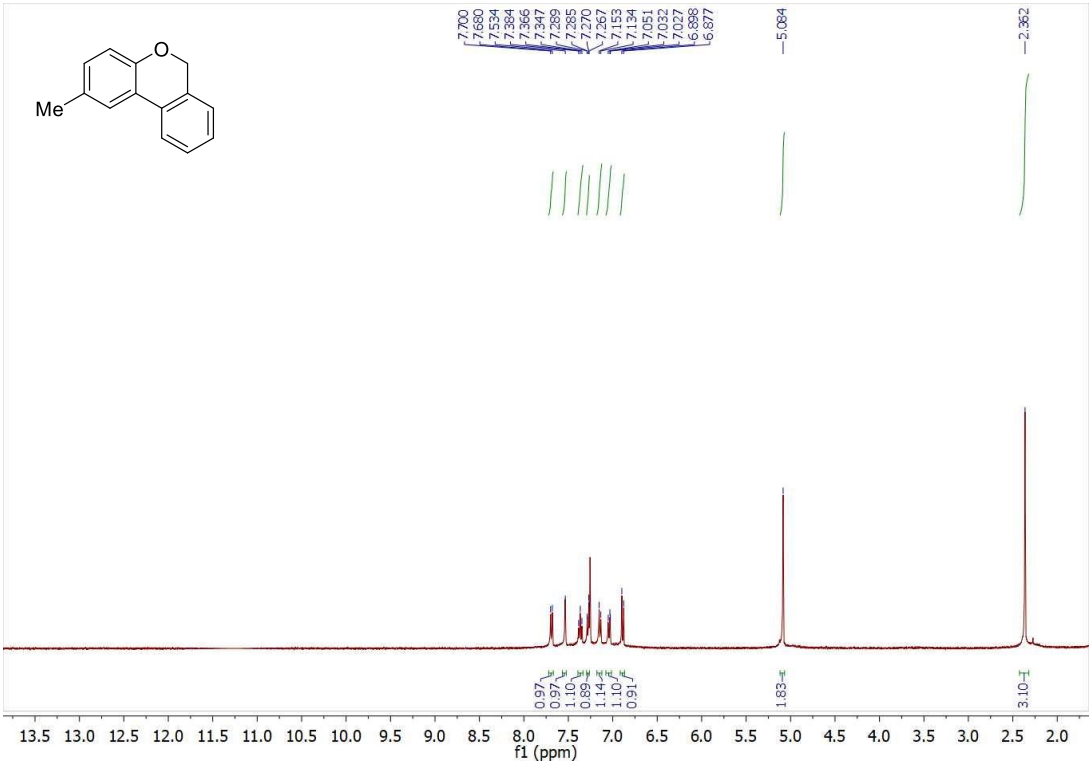


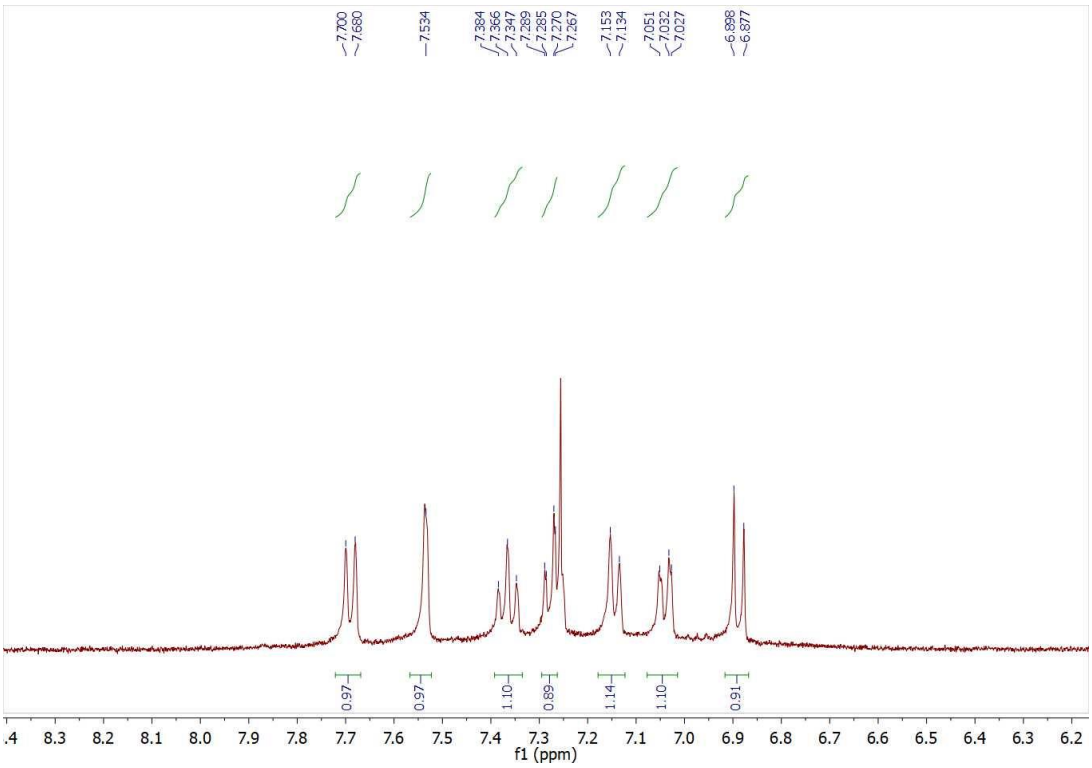
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-(*tert*-Butyl)-6*H*-benzo[*c*]chromene (7c)



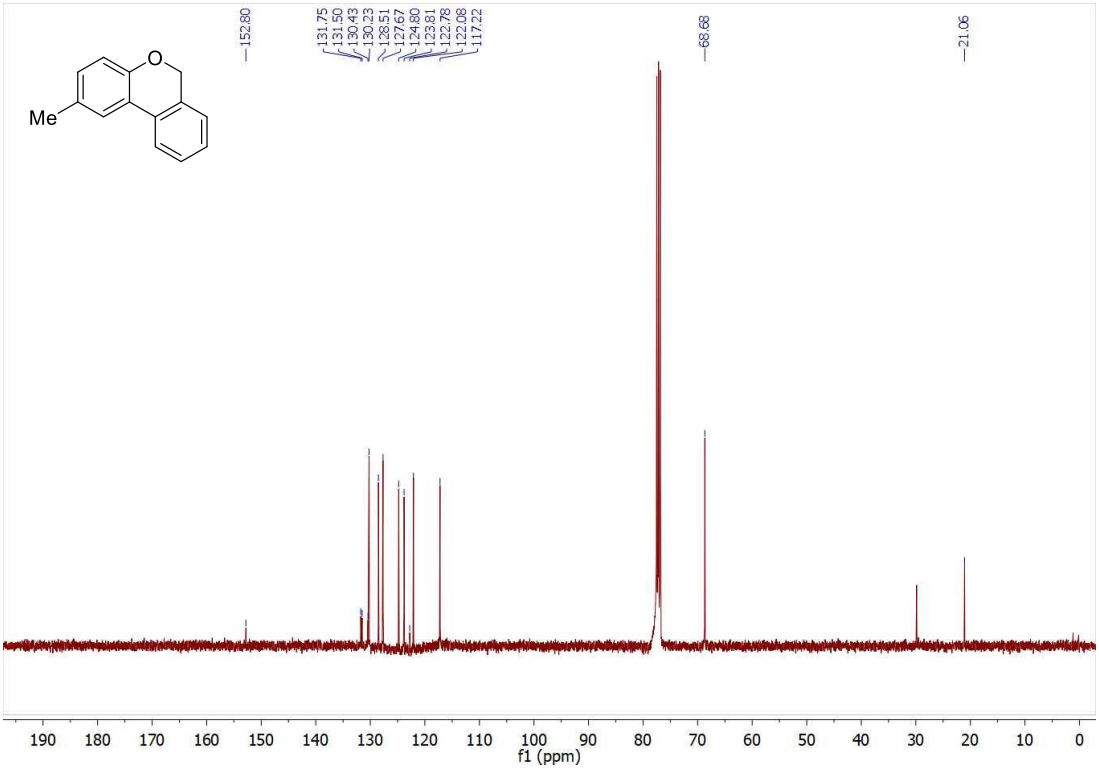


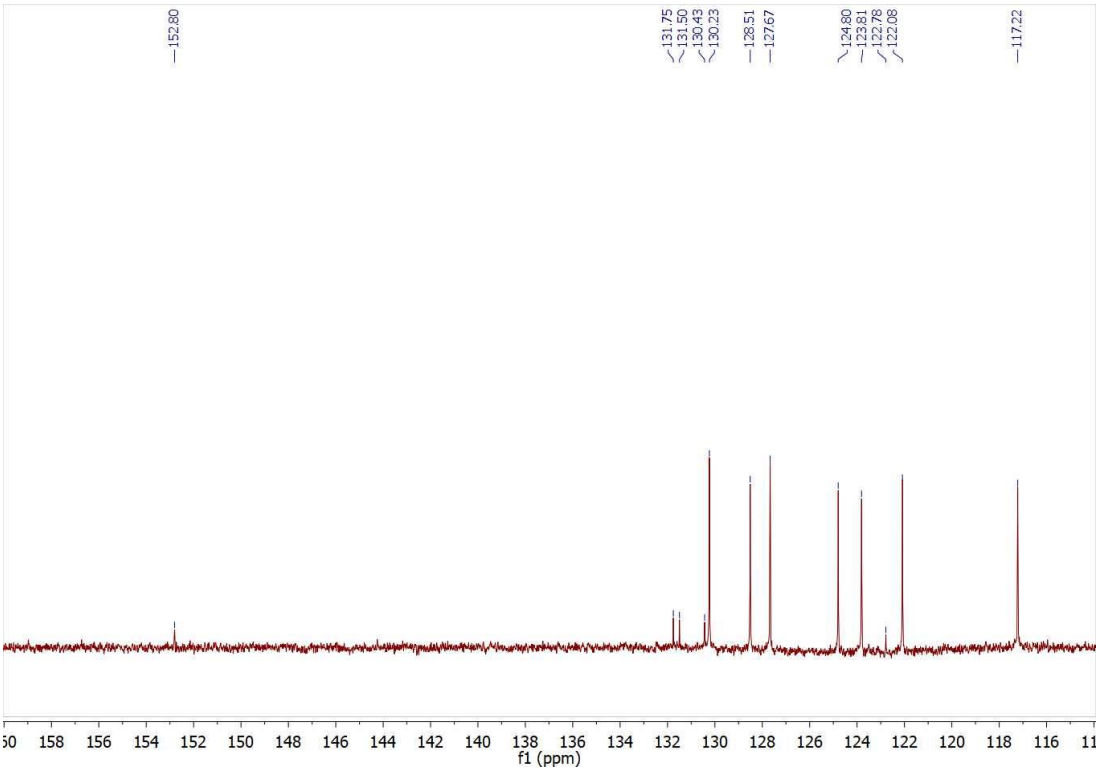
^{1}H NMR (400 MHz, $CDCl_3$). 2-Methyl-6*H*-benzo[*c*]chromene (7d)



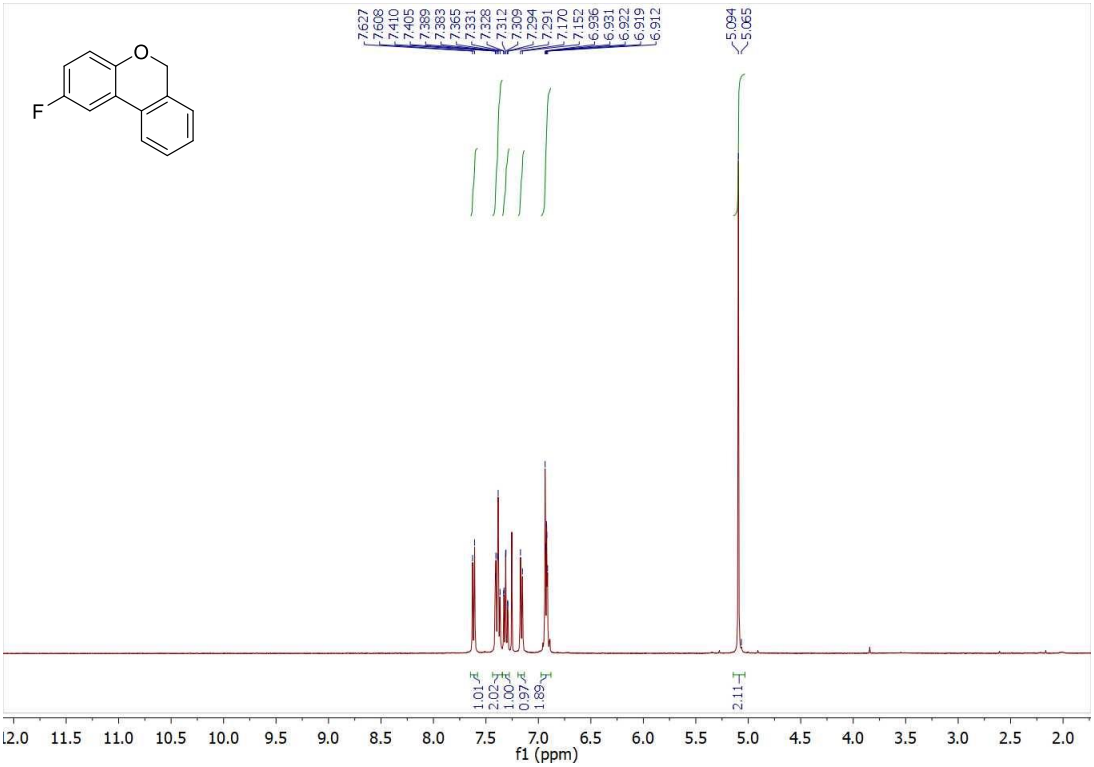


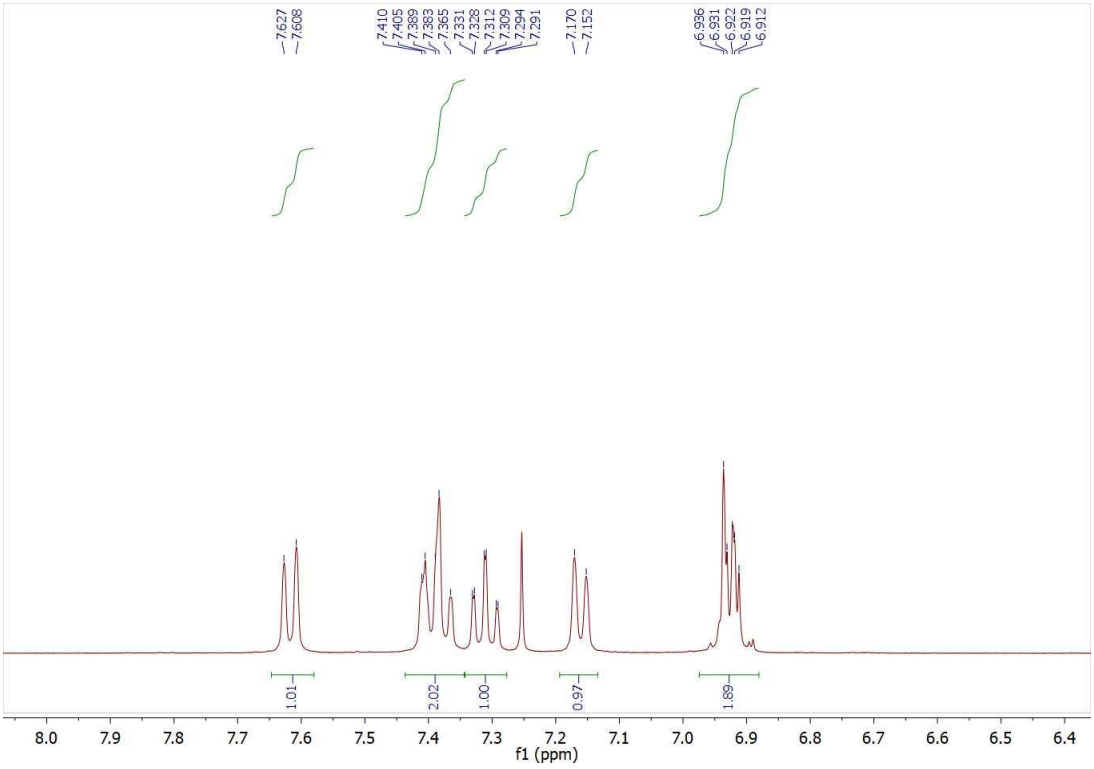
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Methyl-6*H*-benzo[*c*]chromene (7d)



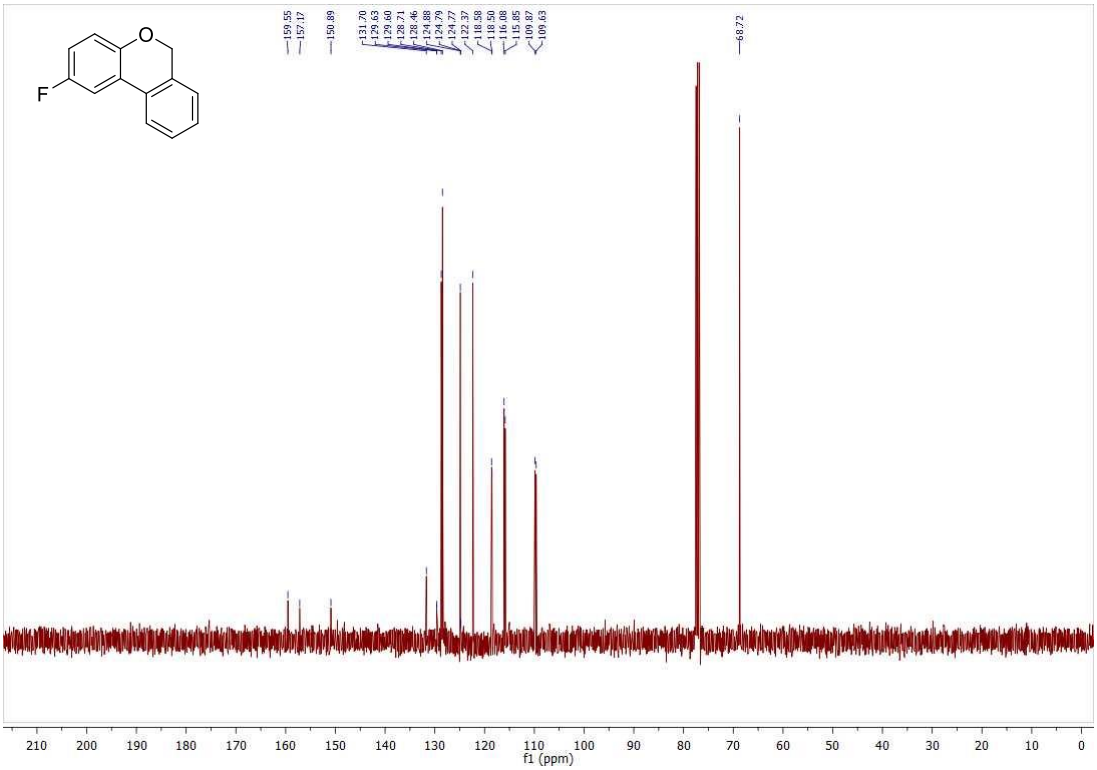


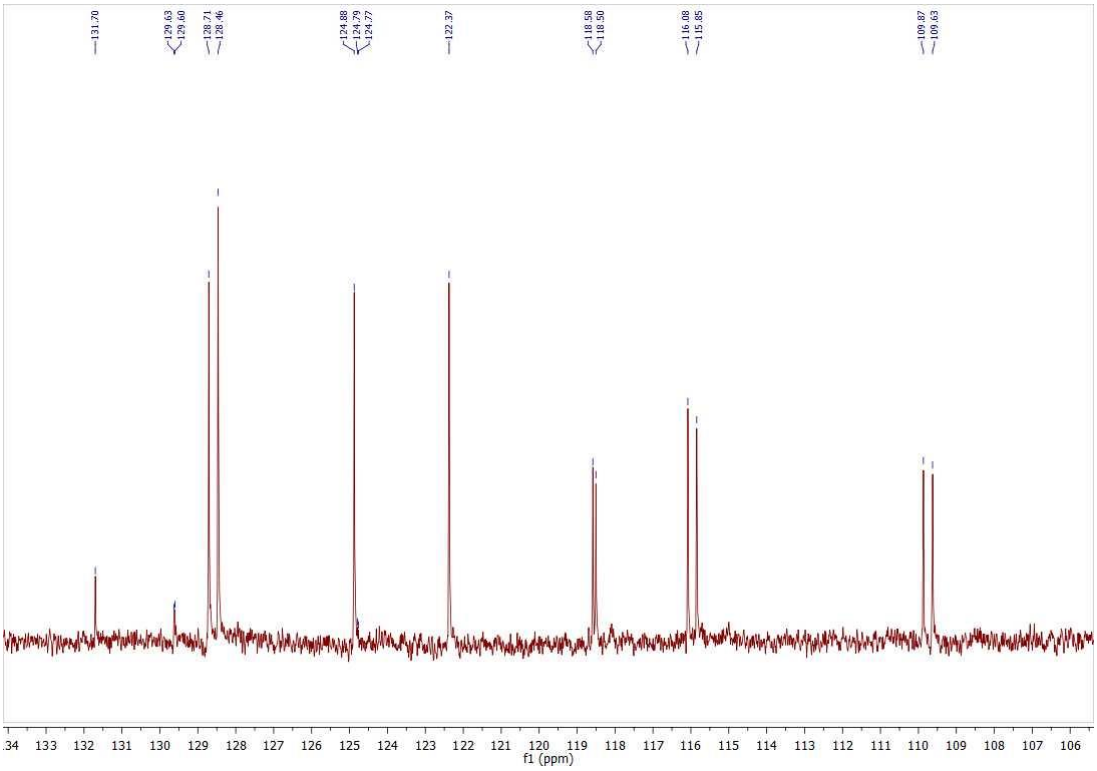
^{1}H NMR (400 MHz, $CDCl_3$). 2-Fluoro-6*H*-benzo[*c*]chromene (7e).



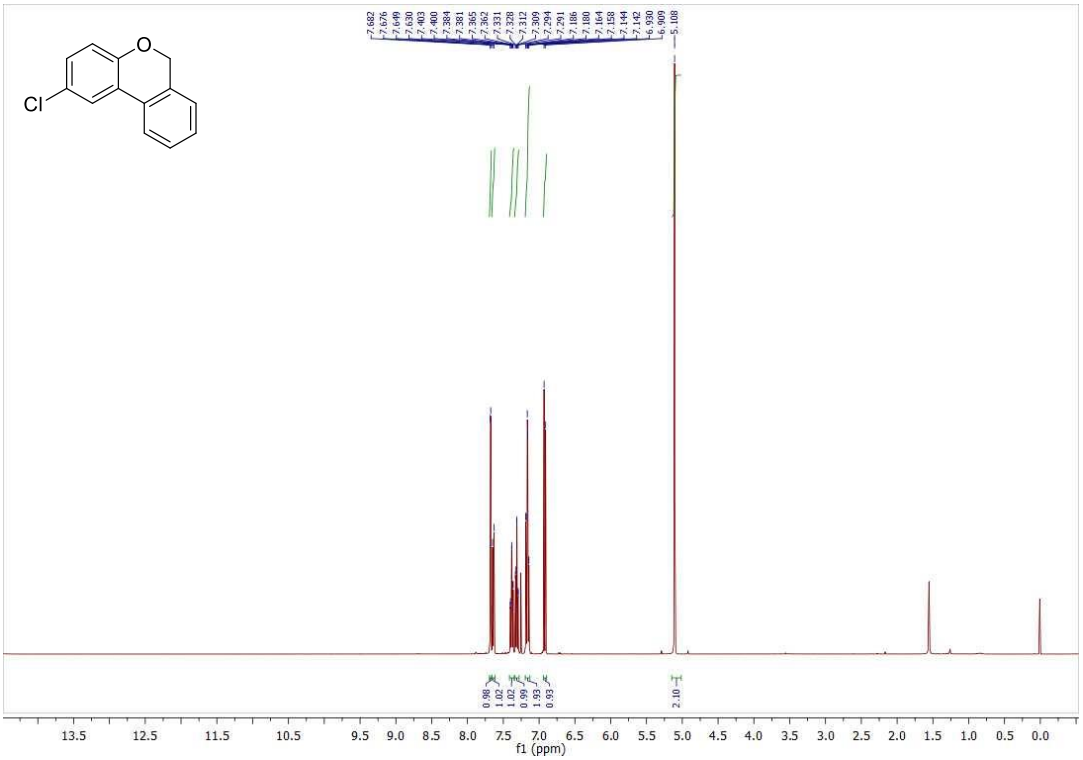


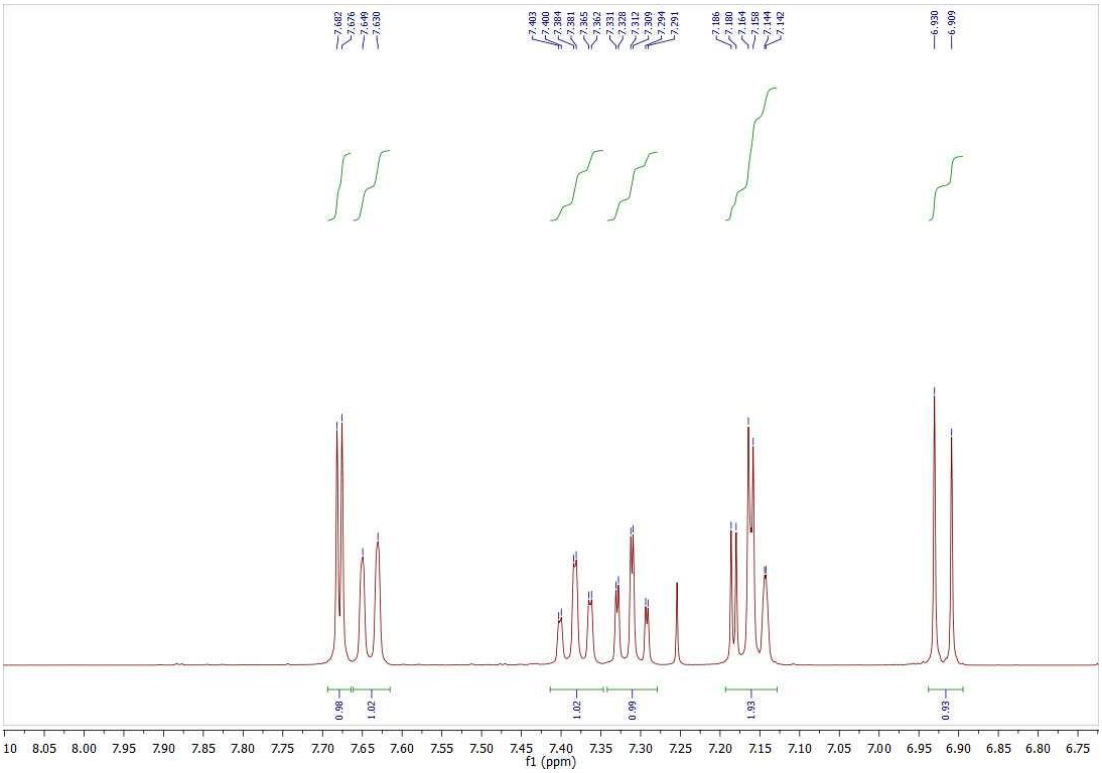
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Fluoro-6*H*-benzo[*c*]chromene (7e).



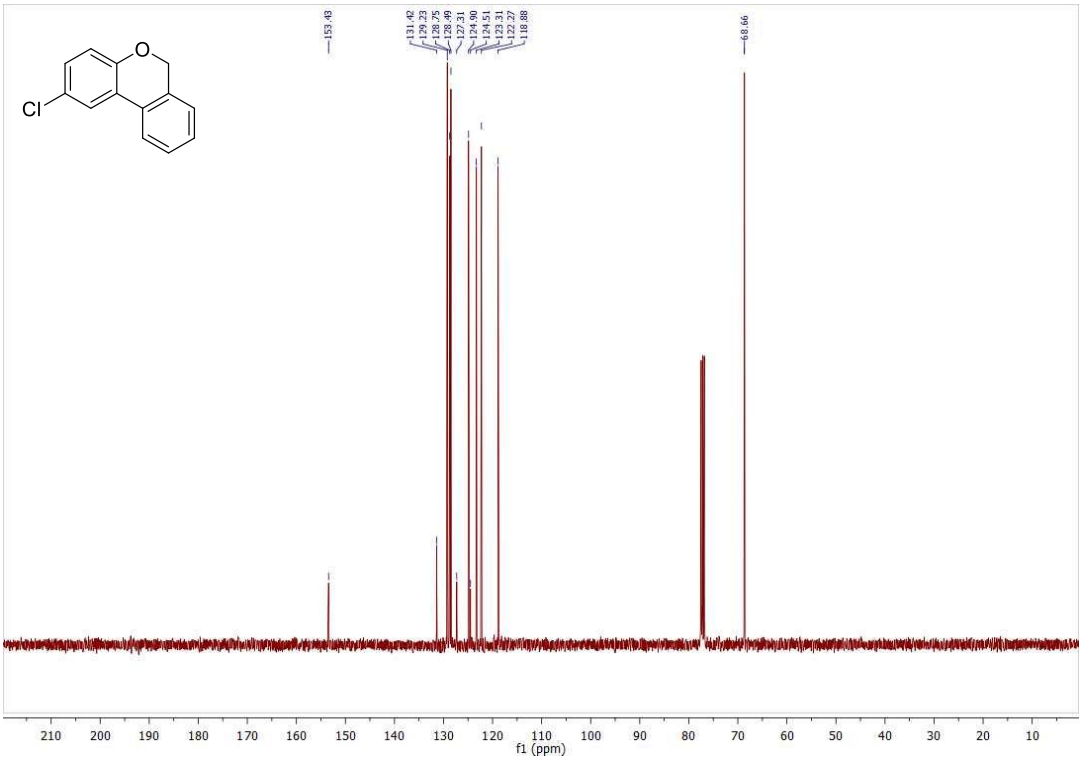


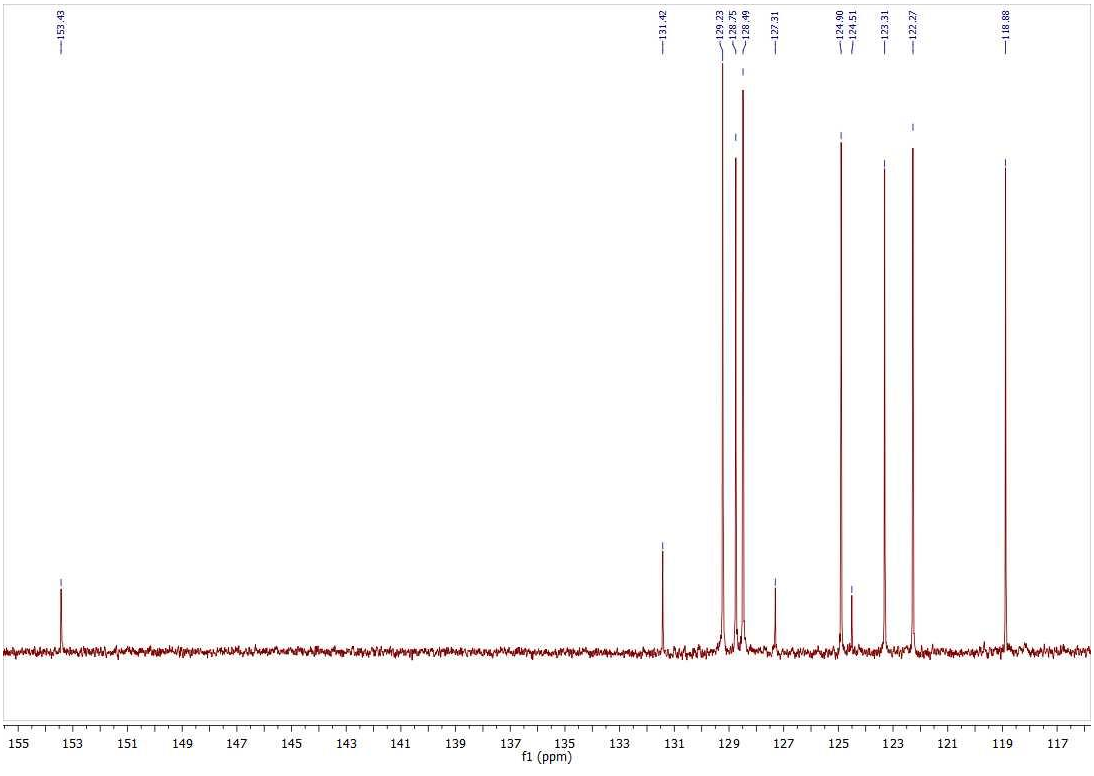
^{1}H NMR (400 MHz, $CDCl_3$). 2-Chloro-6*H*-benzo[*c*]chromene (7f).



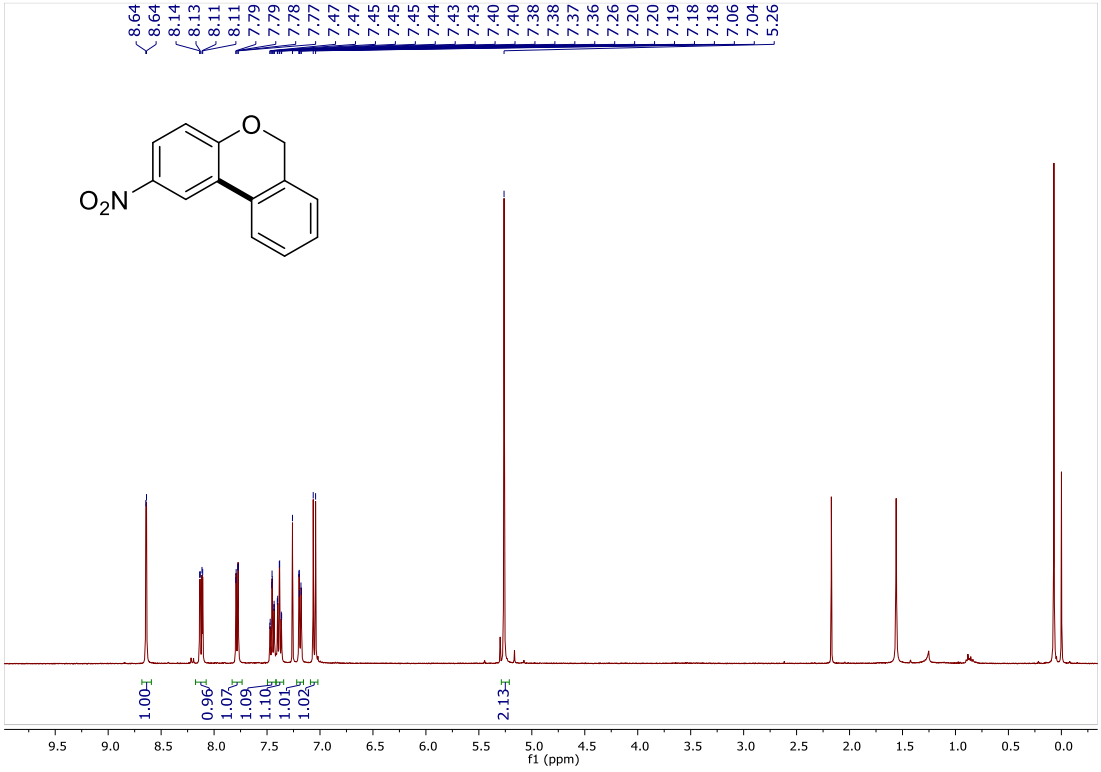


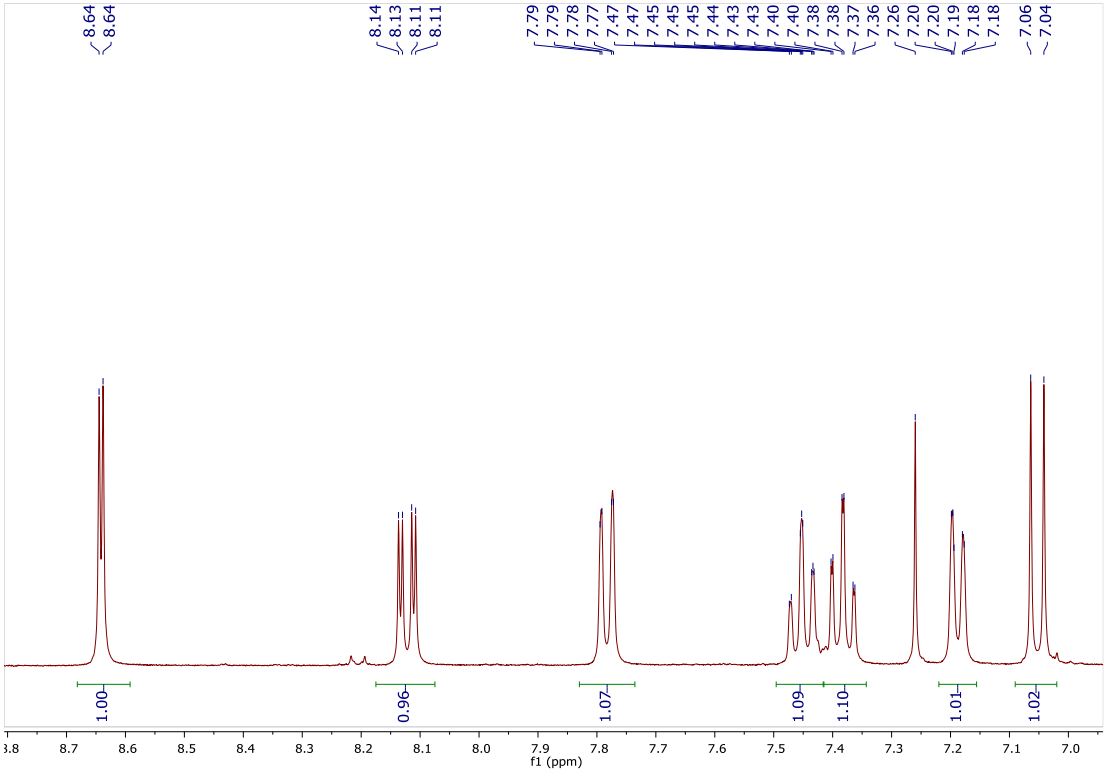
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Chloro-6*H*-benzo[*c*]chromene (7f).



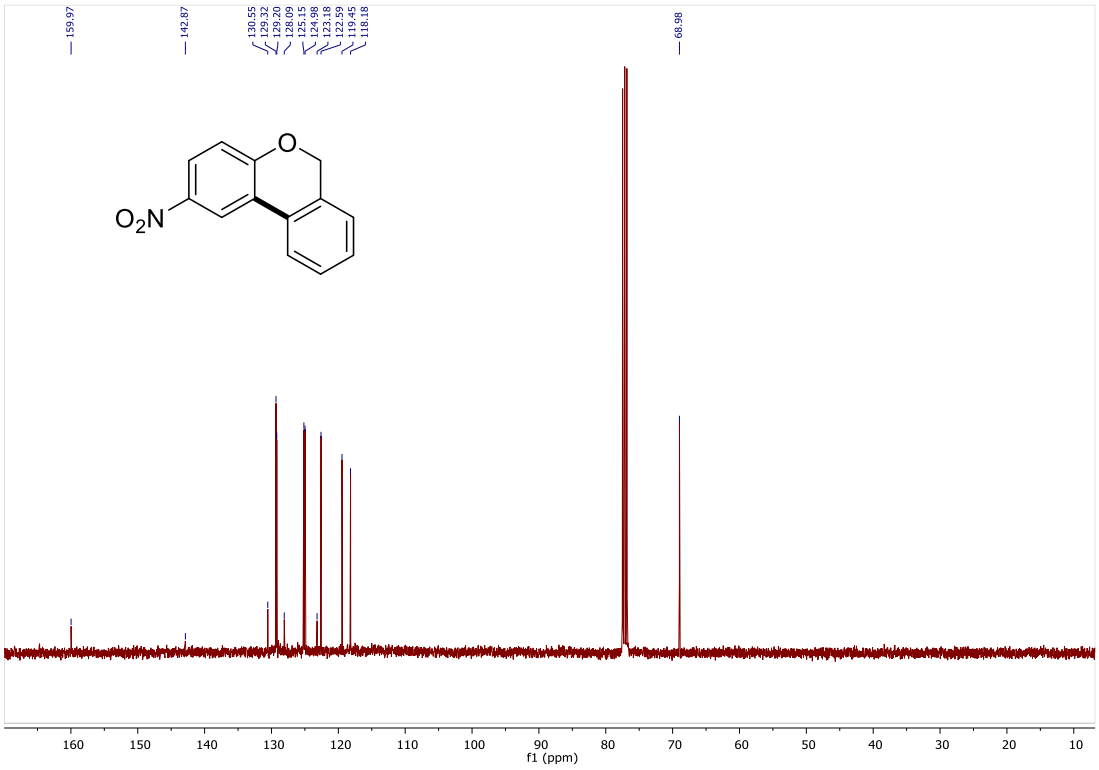


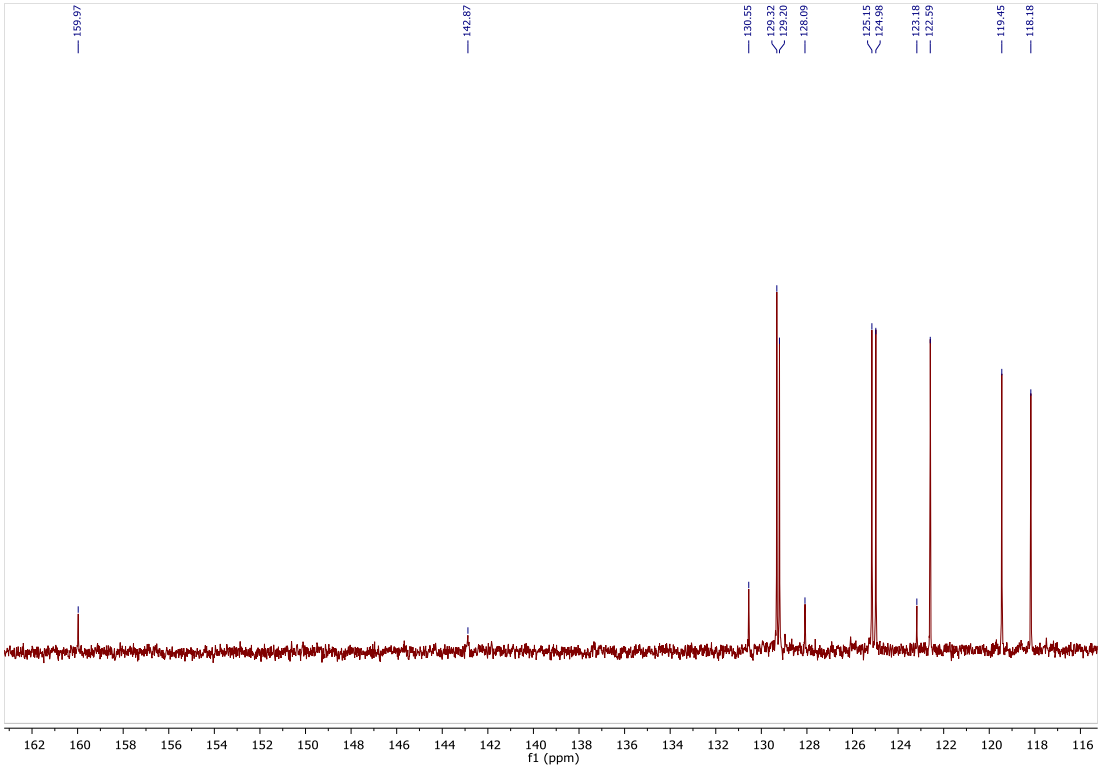
^{1}H NMR (400 MHz, $CDCl_3$). 2-Nitro-6*H*-benzo[*c*]chromene (7g).



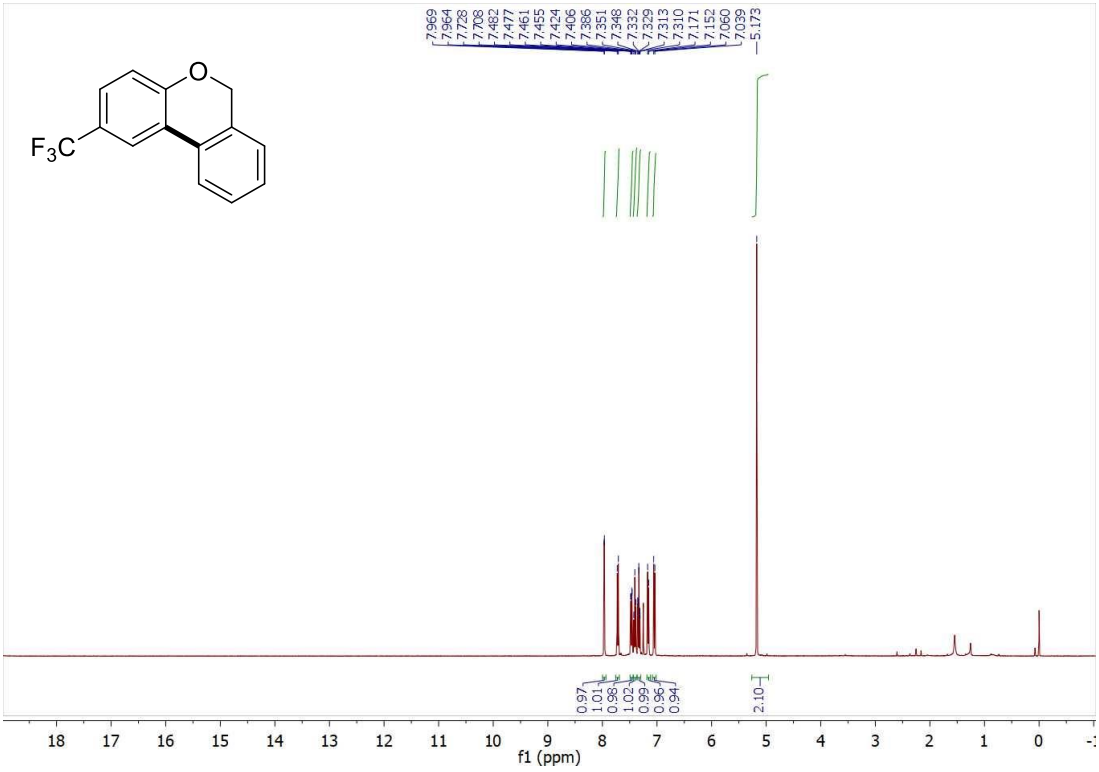


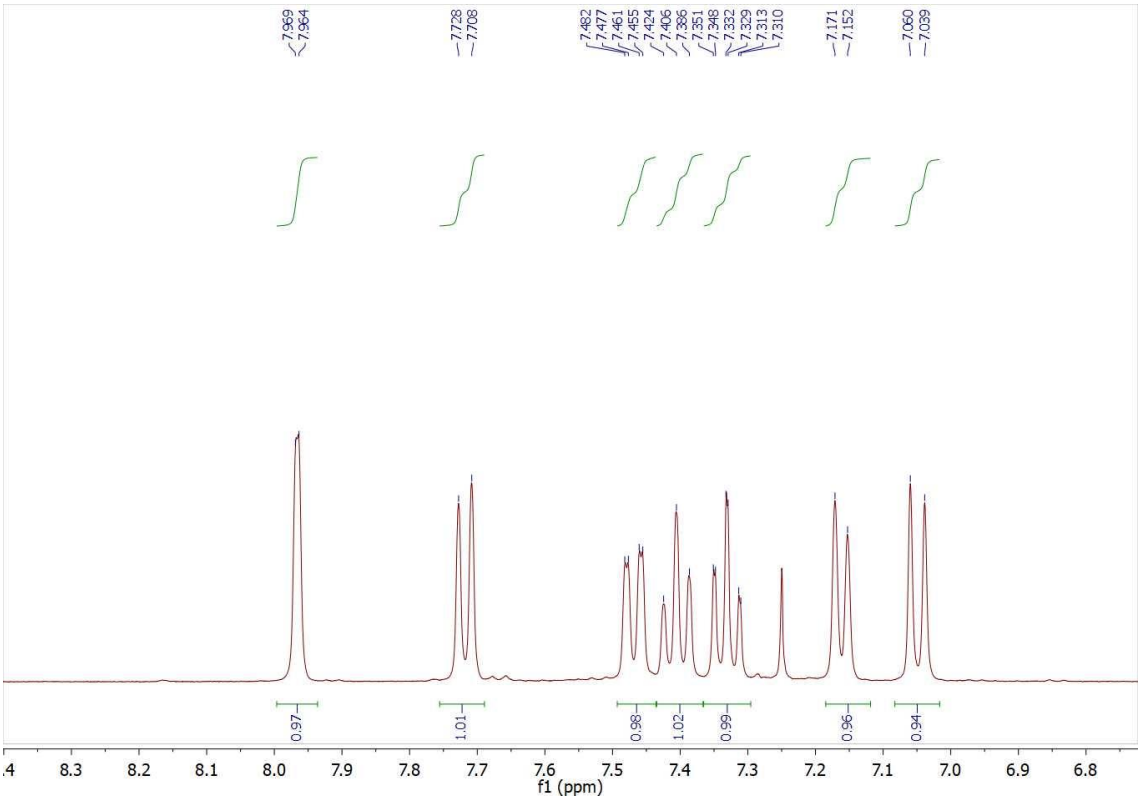
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-Nitro-6*H*-benzo[*c*]chromene (7g).



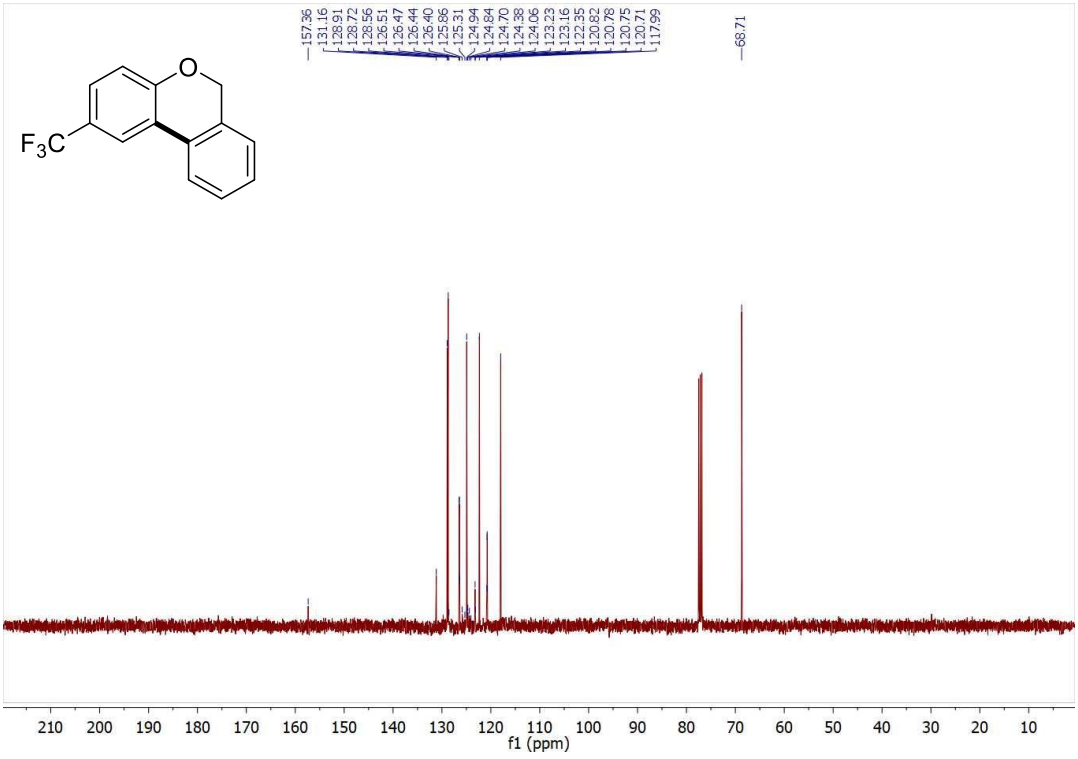


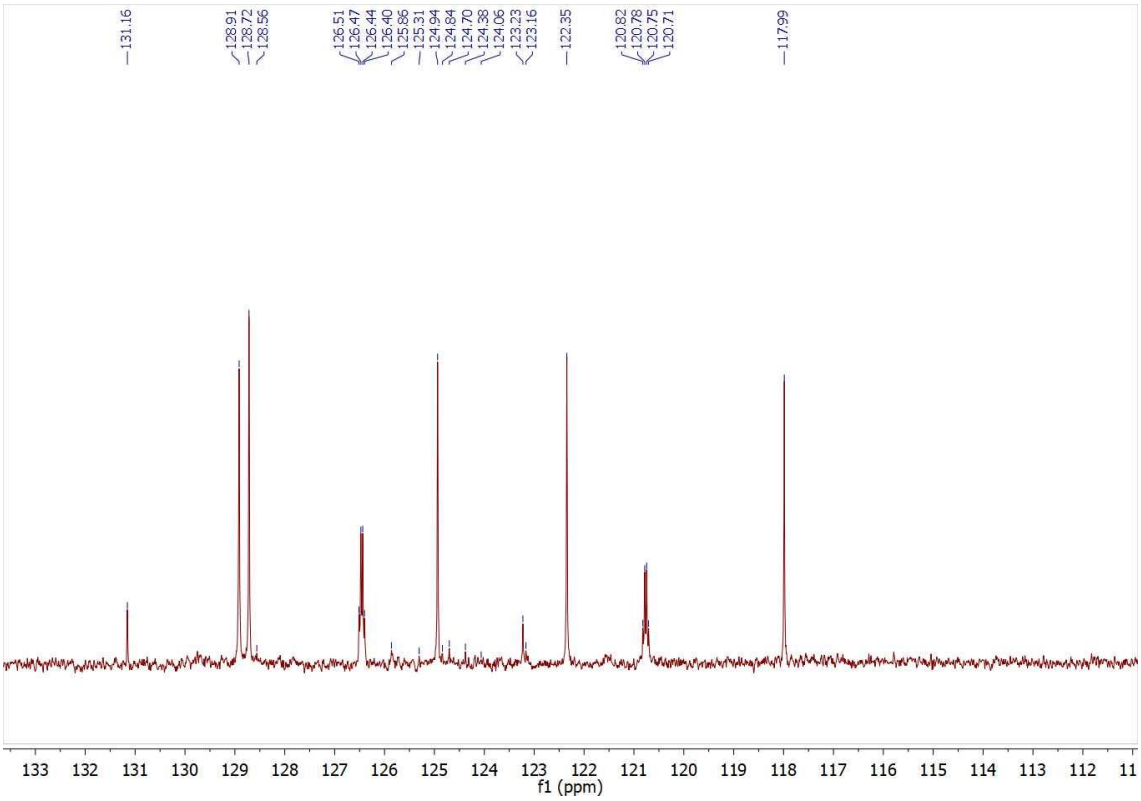
^{1}H NMR (400 MHz, $CDCl_3$). 2-(Trifluoromethyl)-6*H*-benzo[*c*]chromene (7h)



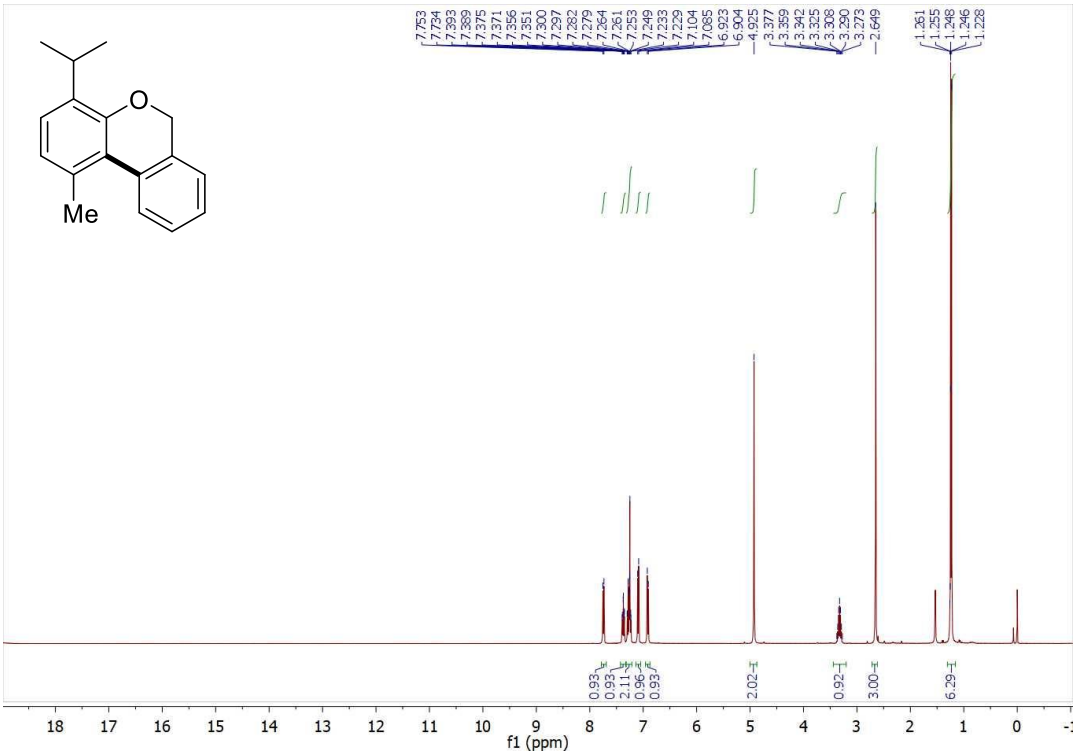


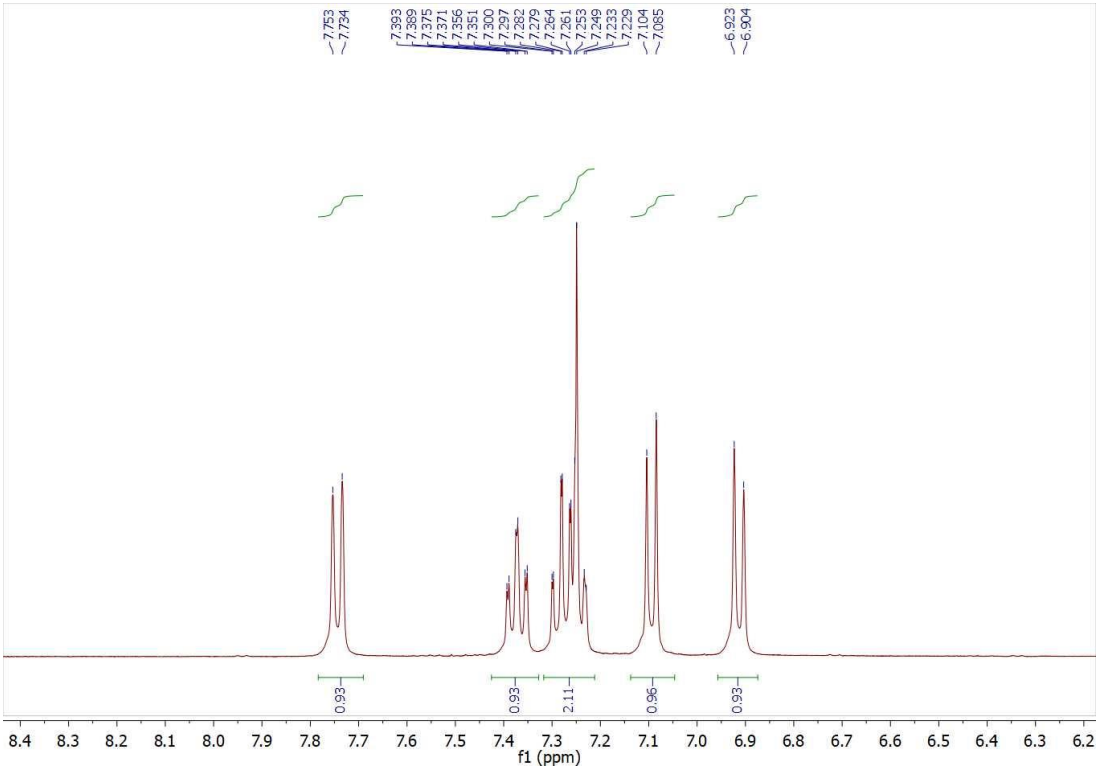
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 2-(Trifluoromethyl)-6*H*-benzo[*c*]chromene (7h)



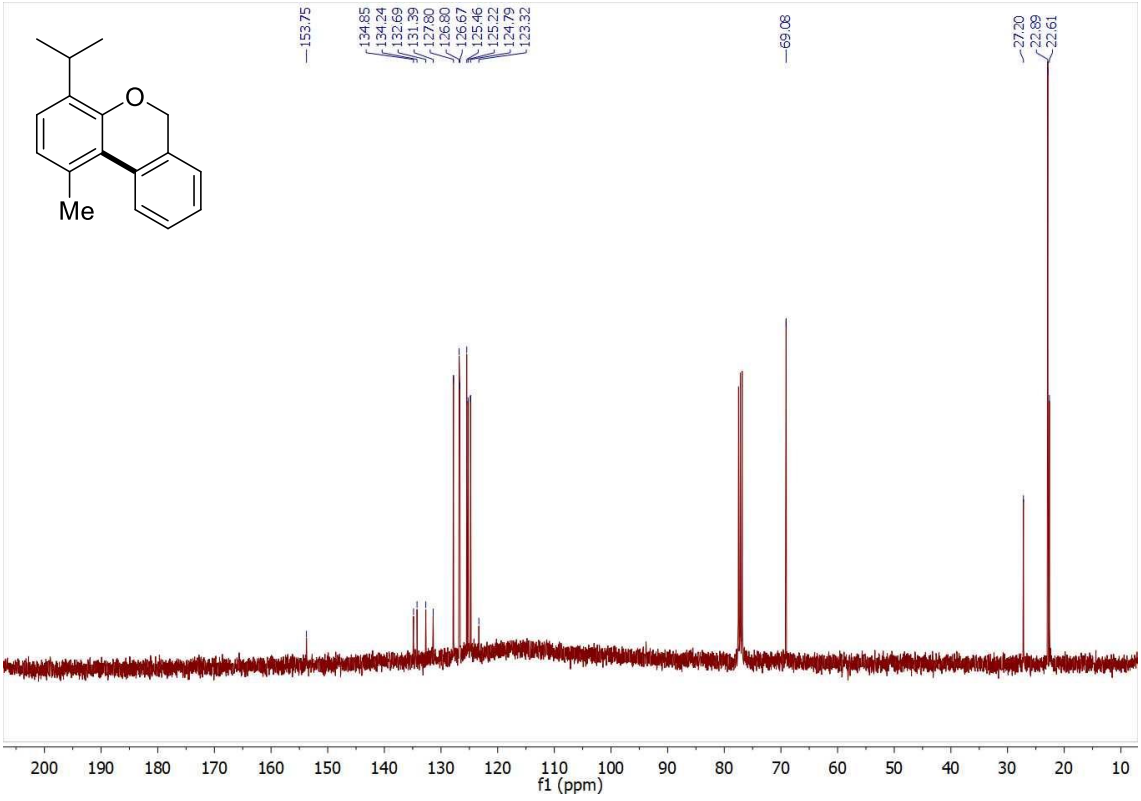


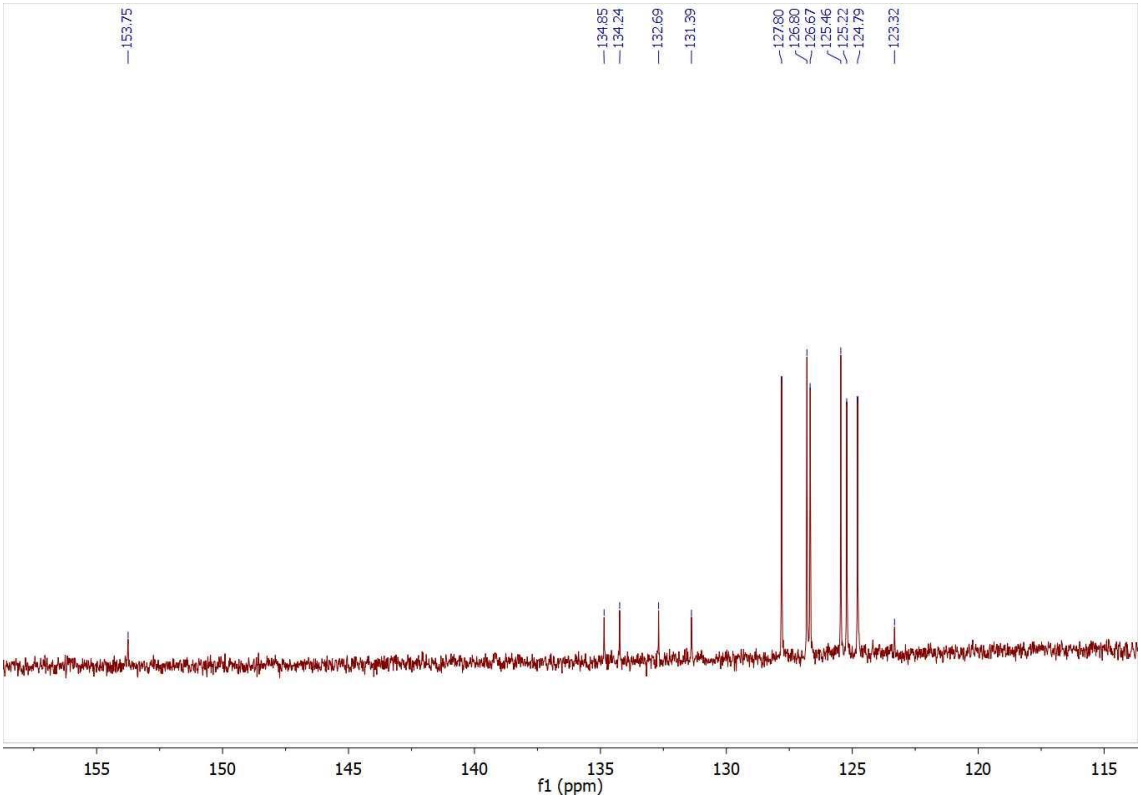
^{1}H-NMR (400 MHz, $CDCl_3$). 4-Isopropyl-1-methyl-6*H*-benzo[*c*]chromene (7j)



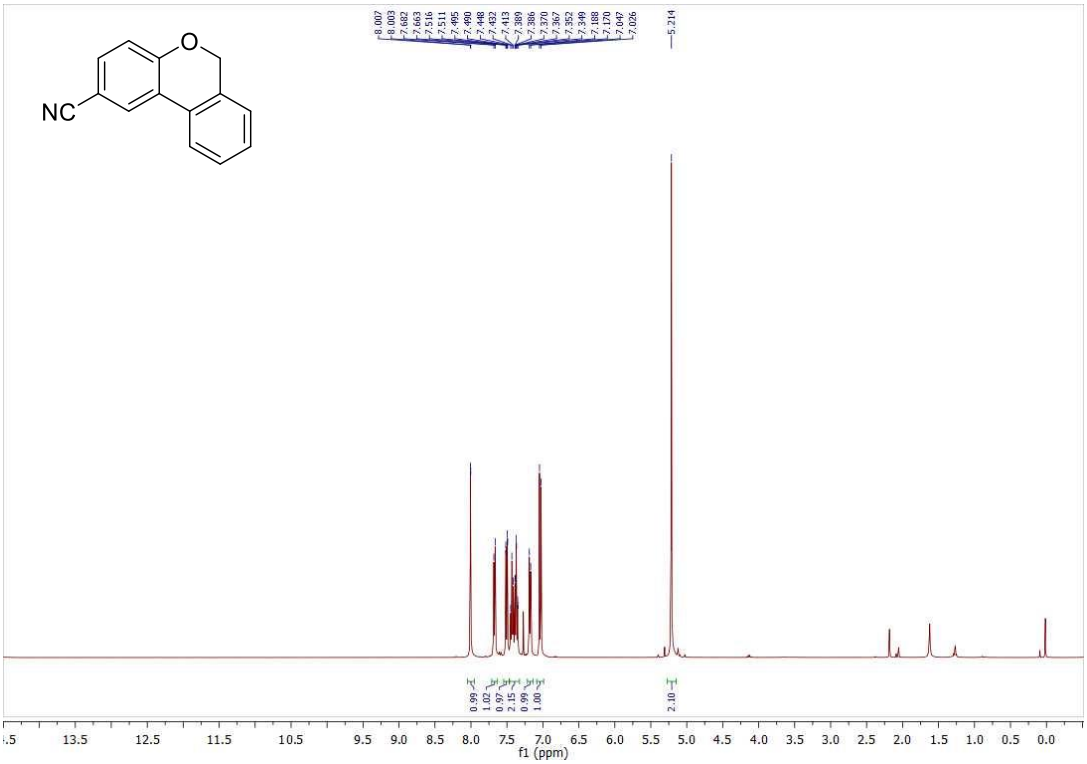


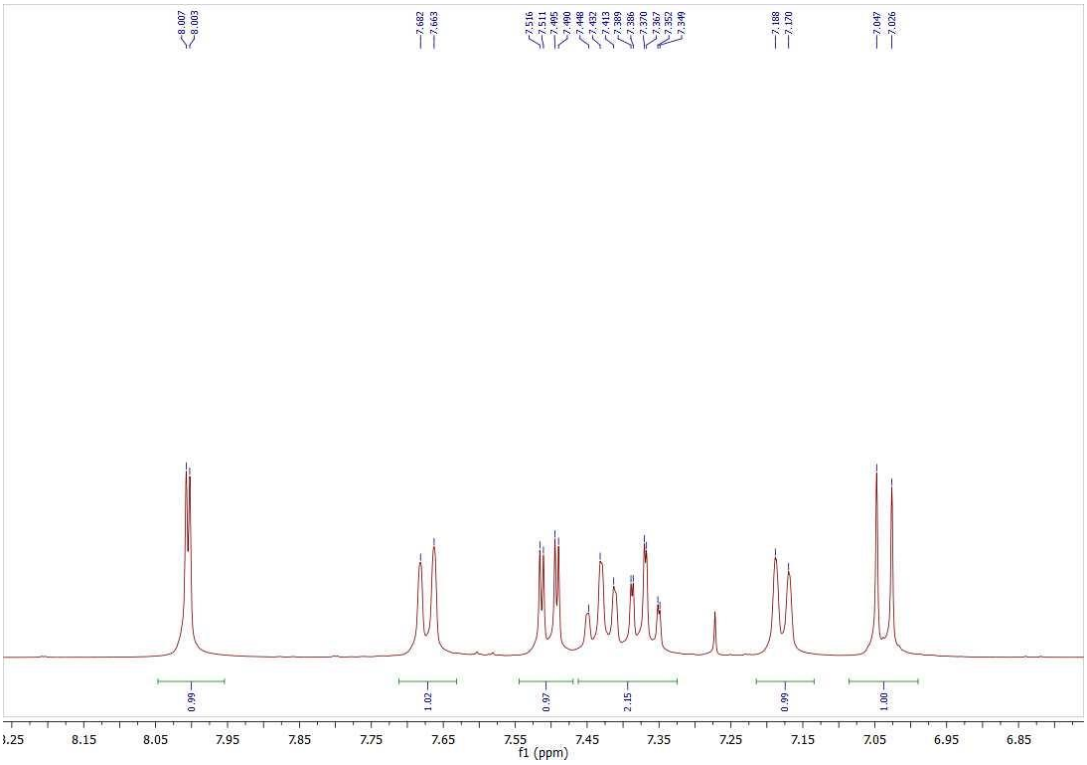
^{13}C NMR{1H} (101 MHz, $CDCl_3$). 4-Isopropyl-1-methyl-6*H*-benzo[*c*]chromene (7j)



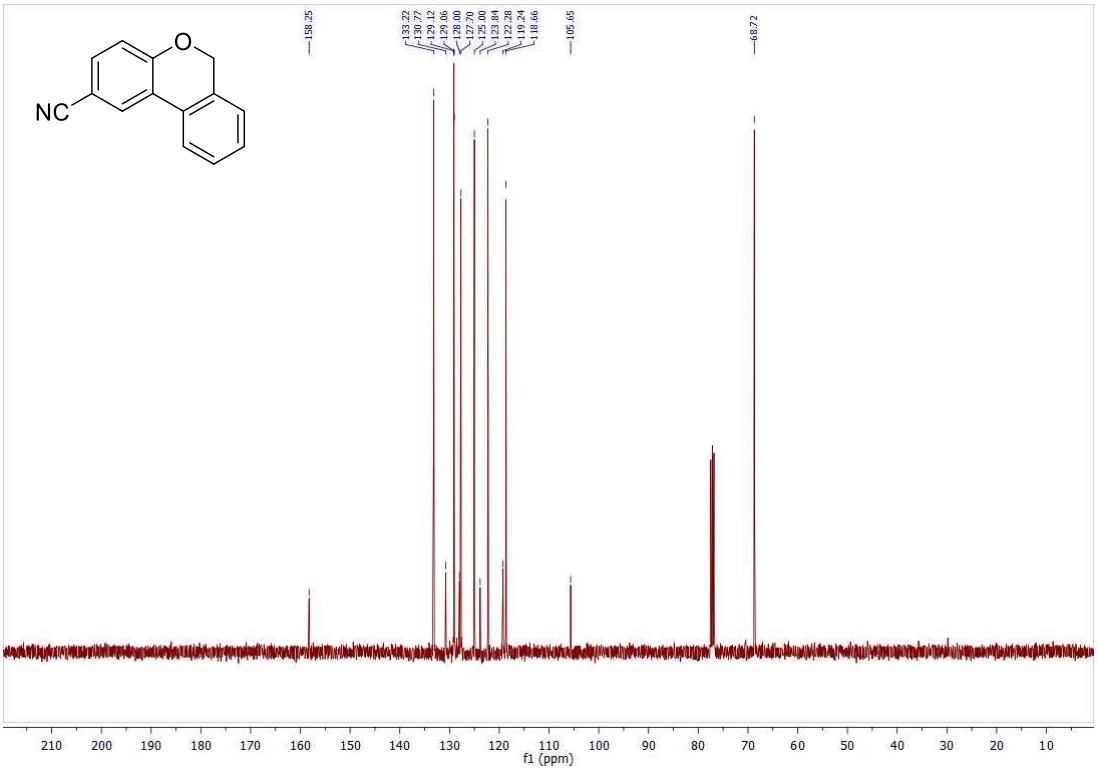


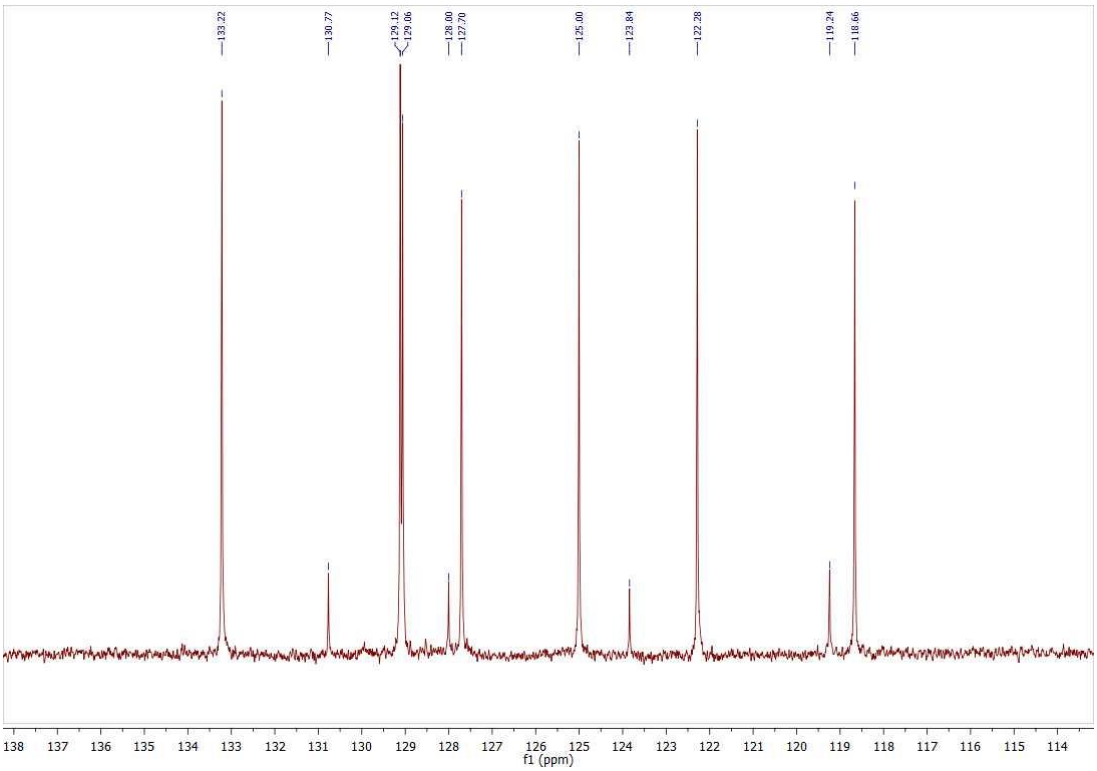
^{1}H NMR (400 MHz, $CDCl_3$). 6*H*-Benzo[*c*]chromene-2-carbonitrile (7k).



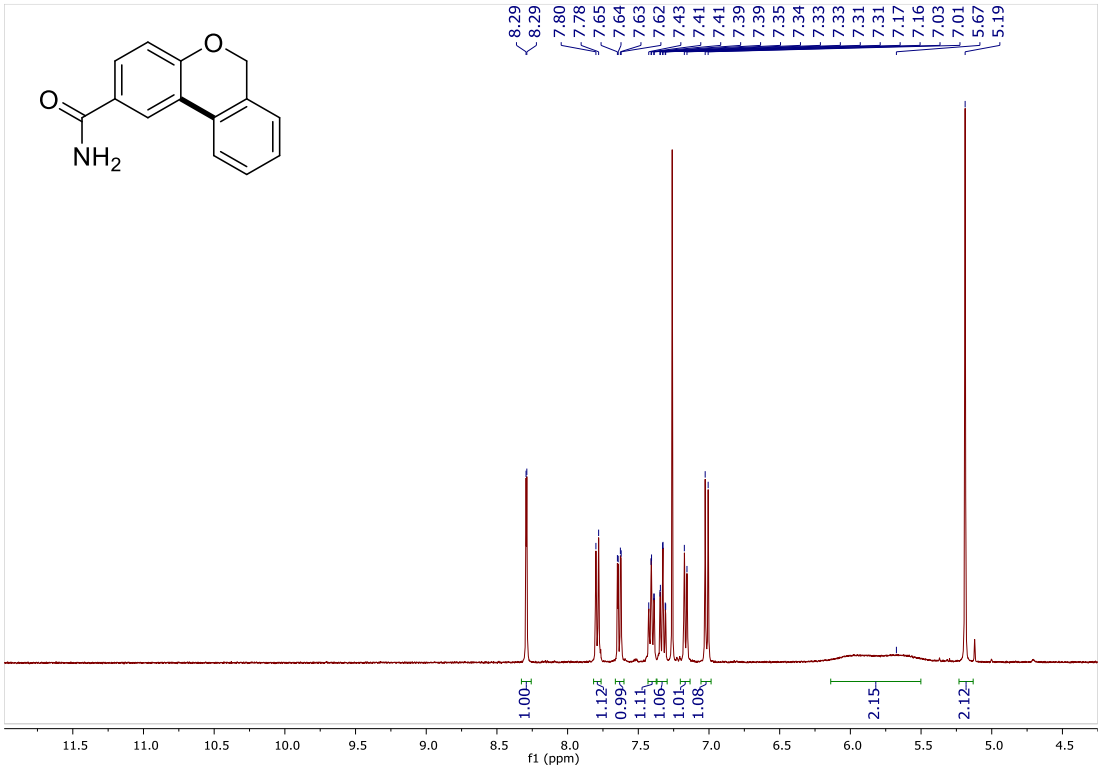


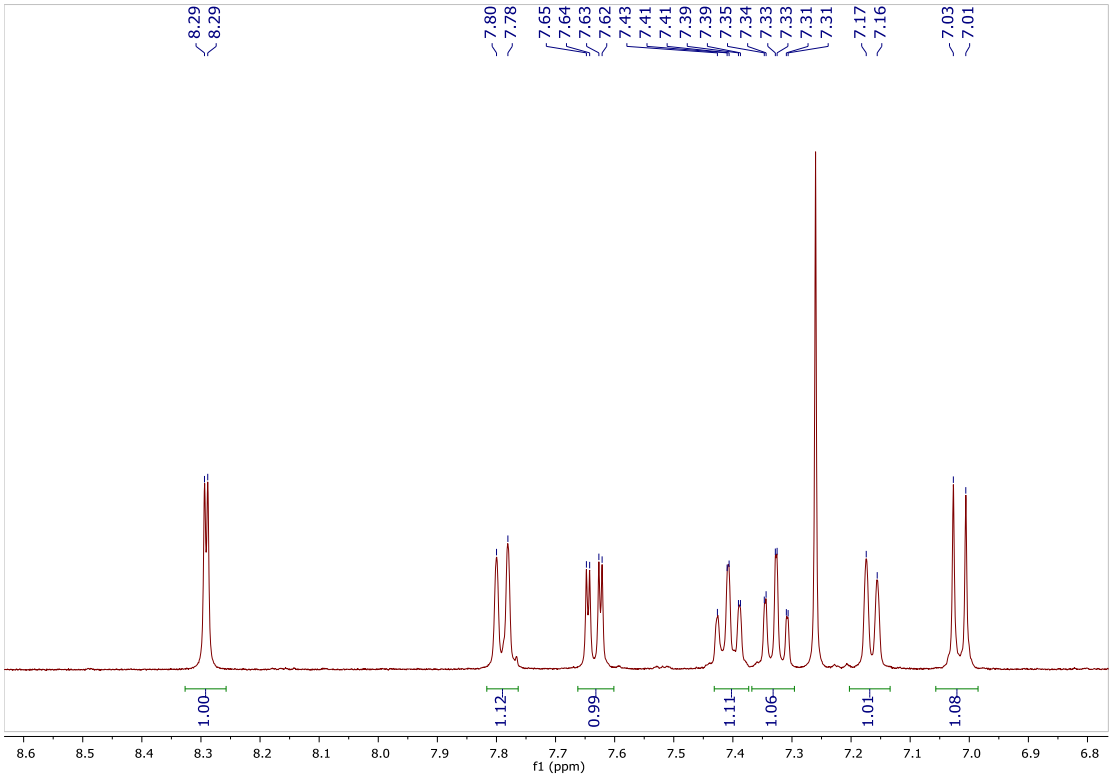
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 6*H*-Benzo[*c*]chromene-2-carbonitrile (7k).



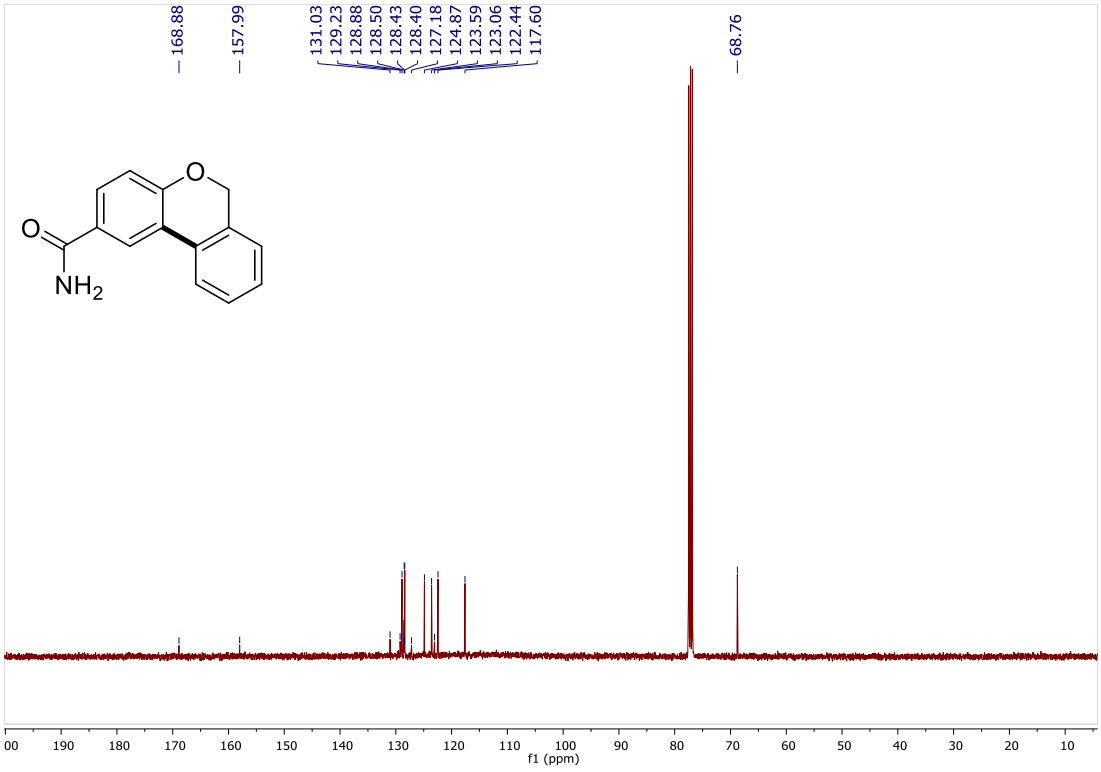


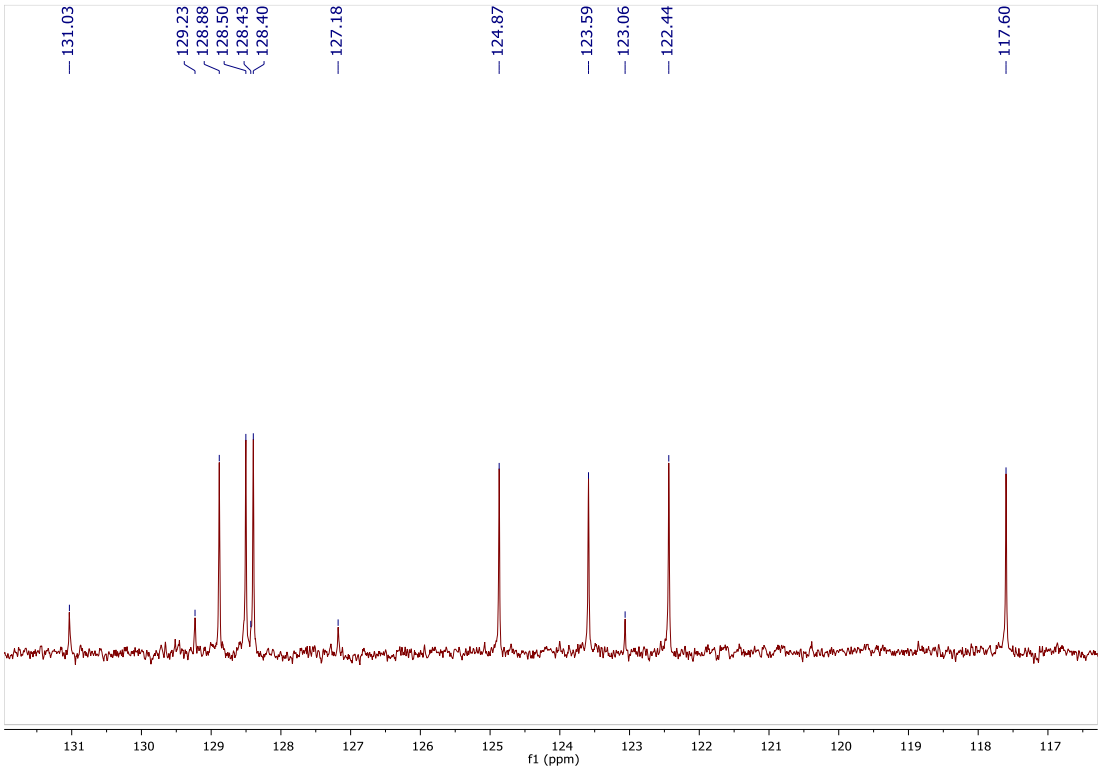
^{1}H NMR (400 MHz, $CDCl_3$). 6*H*-Benzo[*c*]chromene-2-carboxamide (7k´).



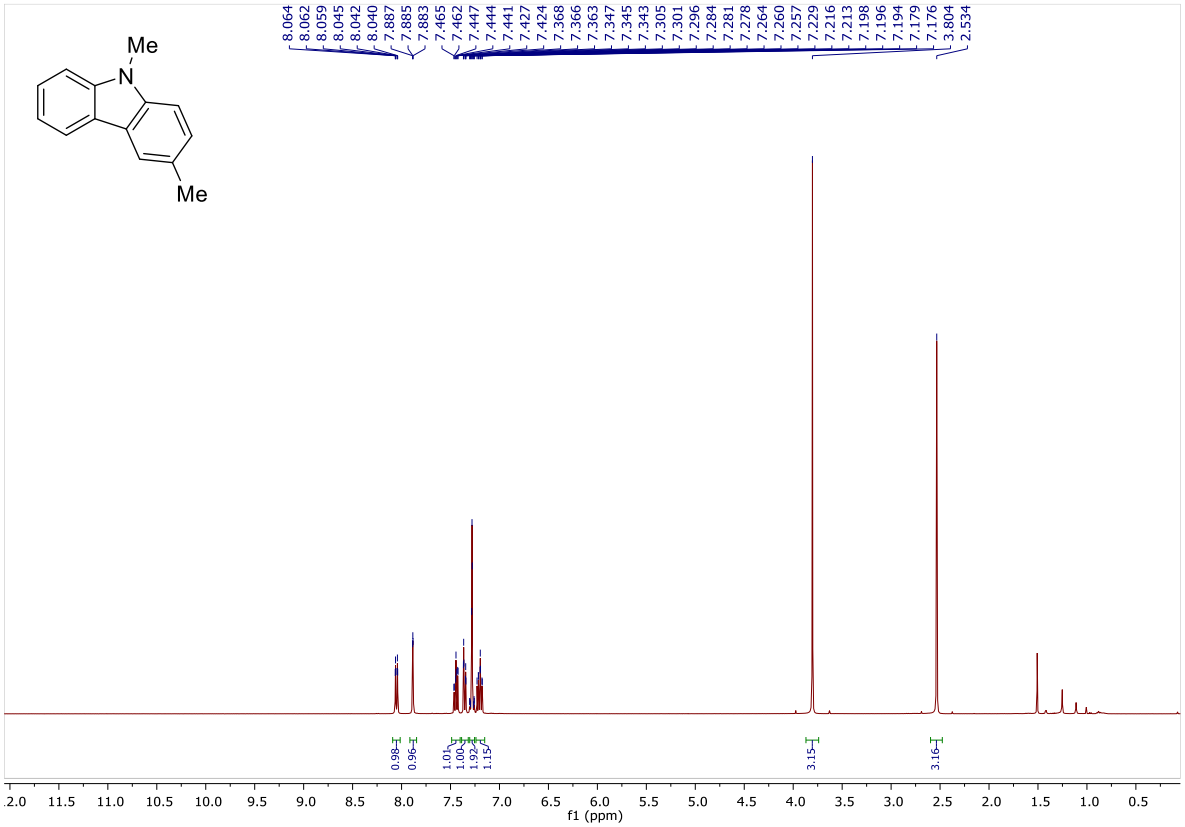


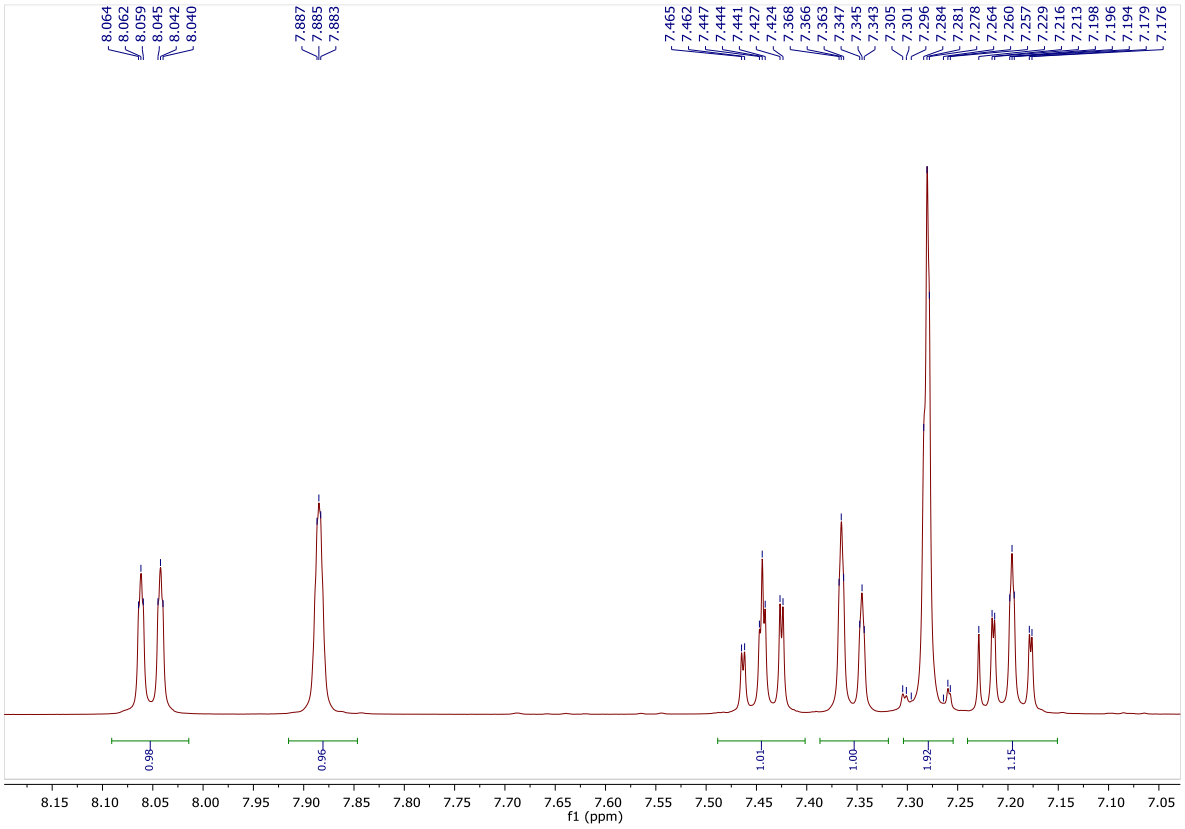
^{13}C NMR {1H} (101 MHz, $CDCl_3$). 6*H*-Benzo[c]chromene-2-carboxamide (7k´).



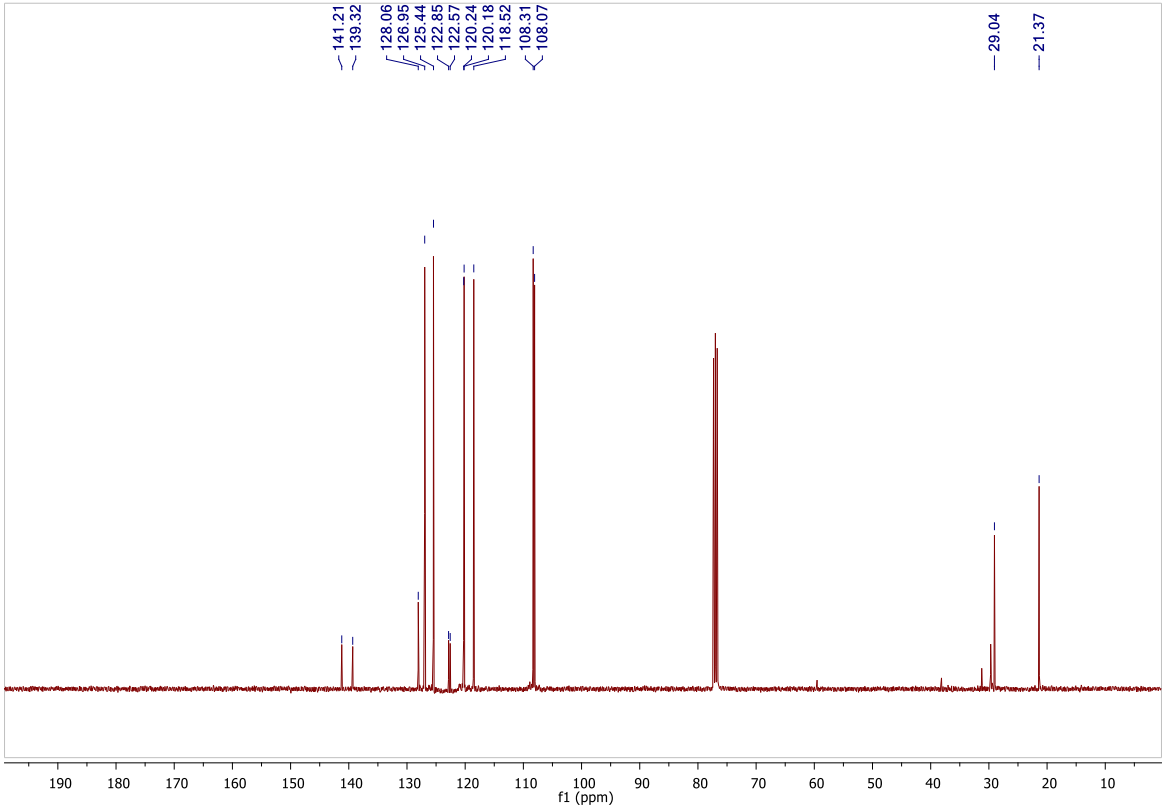


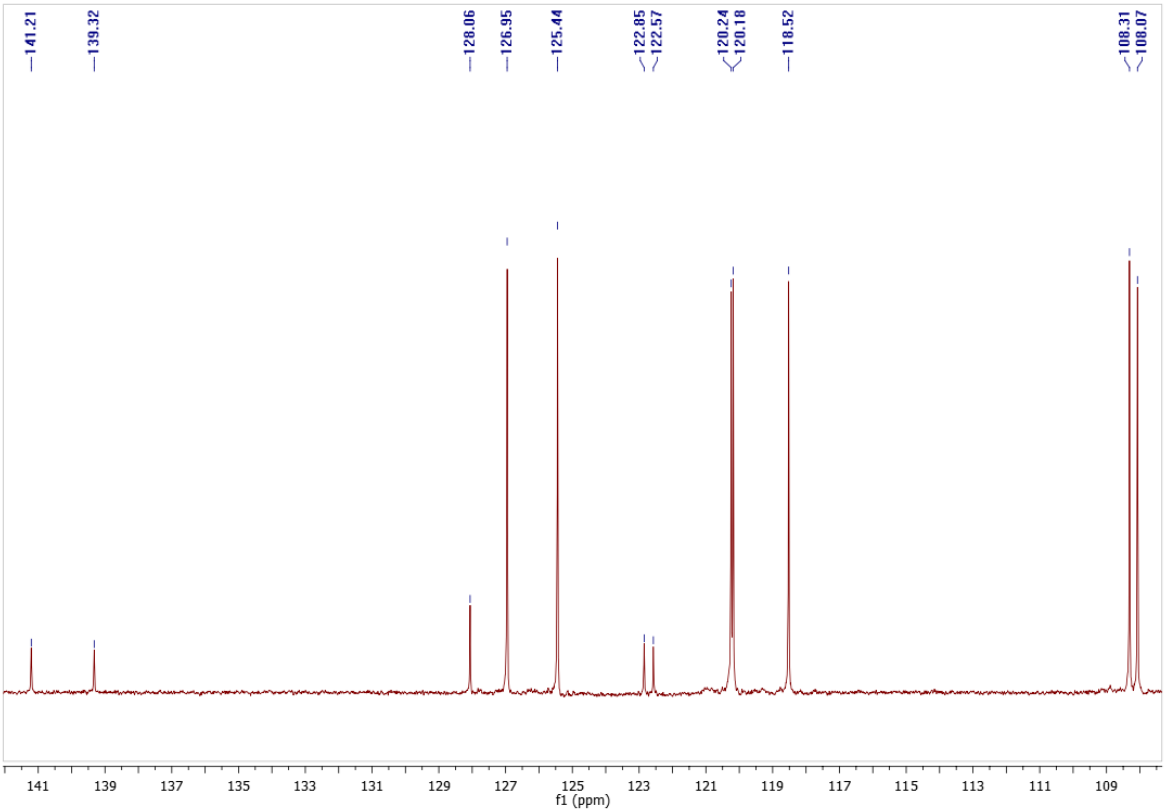
^{1}H NMR (400 MHz, $CDCl_3$). 3,9-Dimethyl-9*H*-carbazole (10)





^{13}C NMR {1H} (101 MHz, $CDCl_3$). 3,9-Dimethyl-9*H*-carbazole (10)





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