Supporting Information

Continuous Flow Electrochemical Reactor using Readily Available Metal Wires and Carbon Fibers: Environmentally Benign Halogenations Of Alkenes, Alkynes And Aromatics

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1. General

^{1}H NMR (400 MHz, 600 MHz),^{13}C NMR (100 MHz, 150 MHz), and ^{19}F NMR (376 MHz, 564 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR, and δ 77.0 ppm for ^{13}C NMR). Alternatively, ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Coupling constants (*J*) are reported in Hertz (Hz). TLC was developed on silica gel 60 F254 glass plates. The products were purified using a commercial flash chromatography system or a regular glass column. GC analyses were performed using a Shimadzu GC-2010 ultra gas chromatography-mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler. All reactions were carried out under an ambient atmosphere without protection. Commercial reagents and solvents were obtained from commercial providers and used without further purification. Electrolysis experiments were performed using an IKA ElectraSyn 2.0 purchased from an IKA China agent or a DC power supply (Henghui PLD-7505). A Vapourtec Easy-Scholar setup was used for the flow experiments.

2. Preparation of electrochemical flow reactors

2.1 Preparation of platinum wire-based electrochemical flow reactor.

Materials (Figure S1). Platinum wires (0.5 mm diameter) as electrodes, the Teflon tubing (2 x 3.175 mm, 20 cm) as the flow channel, a porous polytetrafluoroethylene (PTFE) tube (0.5 x 1.5 mm) as a spacer, PTFE three-way adapters (T-type) for flow of liquids and electronic connection of electrodes (platinum wires), the heat-shrinkable tubes (0.5 mm, 1 mm, 1.5 mm) and inverted cone press rings and threaded adapters as the sealing means.

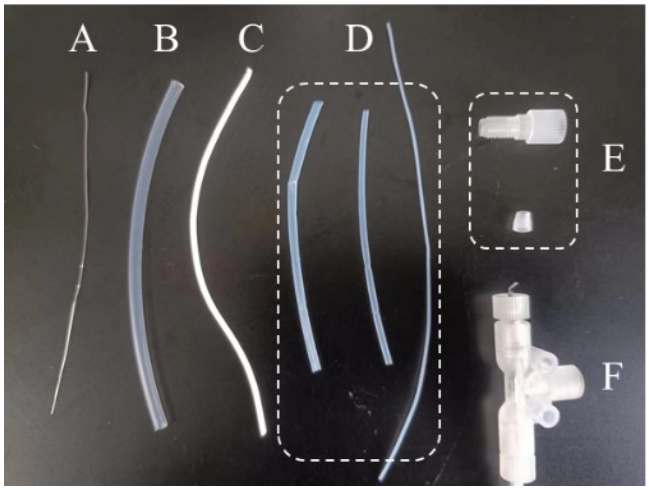


Figure S1. Materials required.

Preparation.

Step 1) One platinum wire (**A**) was inserted into the porous PTFE tube (**C**) (**Figure S2**).

Step 2) One unwrapped platinum and one porous PTFE tube-wrapped platinum wire were inserted into the Teflon tube (**B**).

Step 3) One end of the electrode passes through the three-way adapter (**F**), and three heat-shrinkable tubes (**D**) were used in conjunction with inverted cone press rings and threaded adapters (**E**) to ensure

tightness. The same goes for the electrode encased in a PTFE tube.

Step 4) The Teflon tube was connected to the other side of the three-way adapter (**F**) (sealed using inverted cone press rings and threaded adapters), which gave the final setup (**Figure S3**).

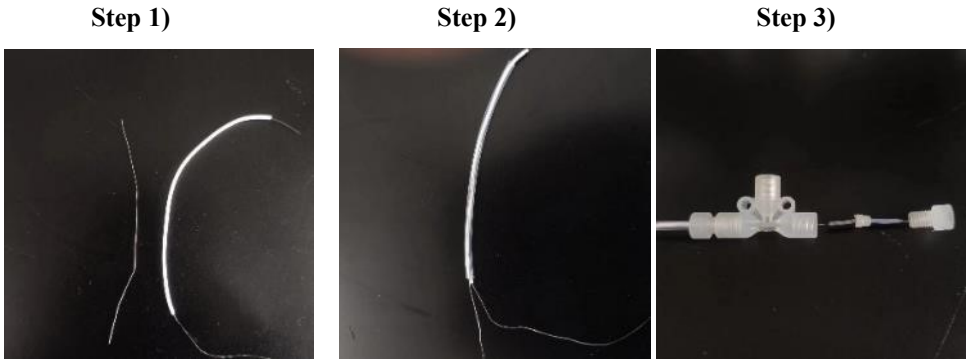


Figure S2. Preparation steps of the metal wires reactor

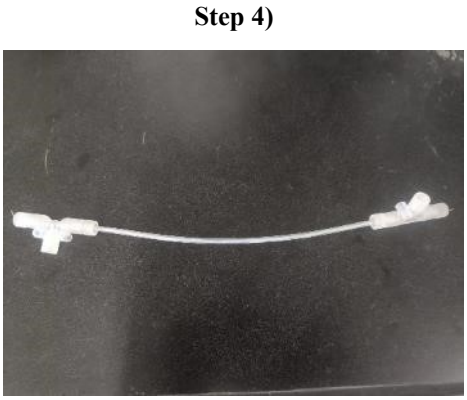


Figure S3. Final flow reactor setup.

2.2 Preparation of carbon fibers-based electrochemical flow reactor.

Materials (Figure S4). Carbon fibers (1 mm, containing 6,000 filaments with a diameter of 7 μm) as electrodes, the Teflon tubing (4 x 6 mm, 100 cm) as the flow channel, a PTFE tube (2 x 3 mm) as a spacer, PP plastic three-way adapters (T-type) for flow of liquids and electronic connection of electrodes (platinum wires), photosensitive adhesive and another Teflon tubing (2 x 3.175 mm, 4 cm) as the sealing method.

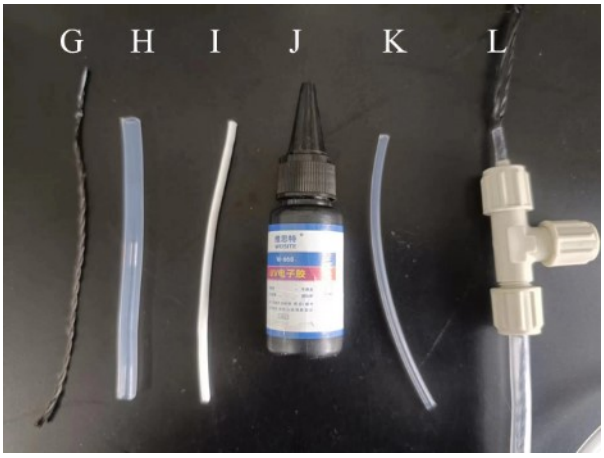


Figure S4. Materials required.

Preparation.

Step 1) Four carbon fiber wires (**G**) were divided into two groups as electrodes; one group was inserted into the porous PTFE tube (**I**) (**Figure S5**).

Step 2) One unwrapped group and the PTFE tube-wrapped carbon fibers were inserted into the Teflon tube (**H**).

Step 3) One end of the electrode passes through the three-way adapter (**L**); the exposed end is passed through another Teflon tube (**K**) and injected with photosensitive adhesive (**J**) for light solidification to ensure sealing. The same goes for the electrode encased in a PTFE tube.

Step 4) The Teflon tube was connected to the other side of the three-way adapter **(L**) (the tiny gap between the sealing pipeline and the three-way adapter was also sealed with photosensitive adhesive), which gave the final setup (**Figure S6**).

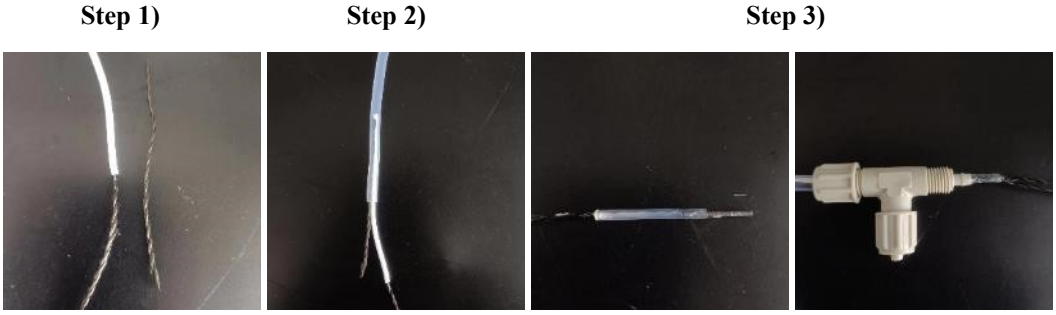


Figure S5. Preparation steps of the carbon wires reactor

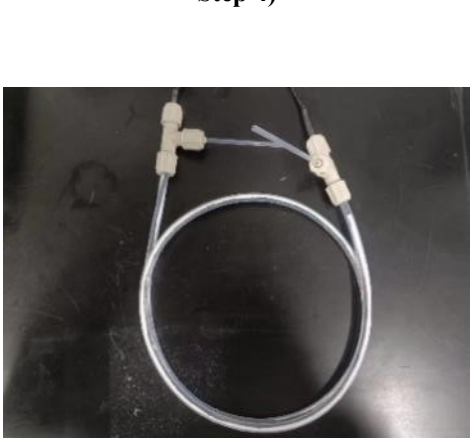


Figure S6. Finished flow reactor setup.

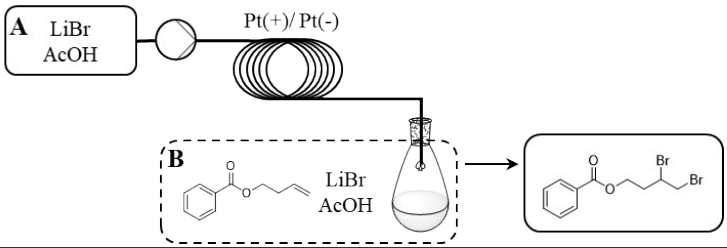
3. Synthesis of alkene starting materials

All the ynamide precursors used in the present study were prepared following a known procedure.

The following paragraphs list the characterization data for the new compounds (**1k-1m**[1]**, 1o-1x** and **2z-2ab**[2]**, 2ac-2ae**[3]).

4. Optimization of halogenation conditions

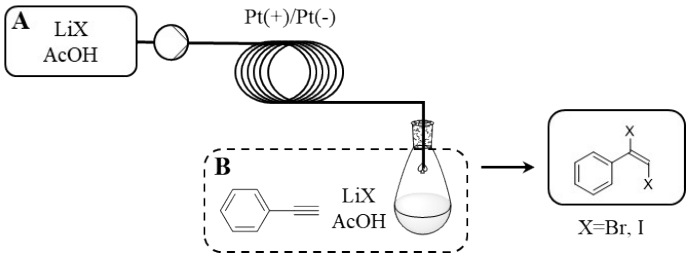
Table S1. Optimization for Dibromination of Alkenes[a]



Entry	A-LiBr	B-LiBr	Electricity	Flow rate	yield[b]
1	4 mmol	-	16 mA	200 µL/min	76%
2	5 mmol	-	3 V	200 µL/min	70%
3	1 mmol	-	10 V	100 µL/min	70%
4	1 mmol	-	8 V	100 µL/min	71%
5	2 mmol	-	8 V	100 µL/min	71%
6	1 mmol	0.4 mmol	8 V	100 µL/min	89%
7	1 mmol	0.8 mmol	8 V	100 µL/min	90%
8	**1 mmol**	**0.4 mmol**	**6 V**	**100 µL/min**	**97%**
9	1 mmol	0.4 mmol	4 V	100 µL/min	80%
10	1 mmol	0.4 mmol	10 V	100 µL/min	90%
11	1 mmol	0.4 mmol	8 V	200 µL/min	90%
12	1 mmol	0.4 mmol	8 V	300 µL/min	71%
13	1 mmol	0.4 mmol	8 V	400 µL/min	65%

[a] Reaction conditions: Undivided cell, Solution A: LiBr (0.5 M), AcOH; Solution B: But-3-en-1-yl benzoate (0.2 mmol/ 0.25M), LiBr, AcOH (0.8 ml); Pt (+)/Pt (-), rt.; [b] Isolated yield.

Table S2. Optimization for bromination and iodination of alkynes

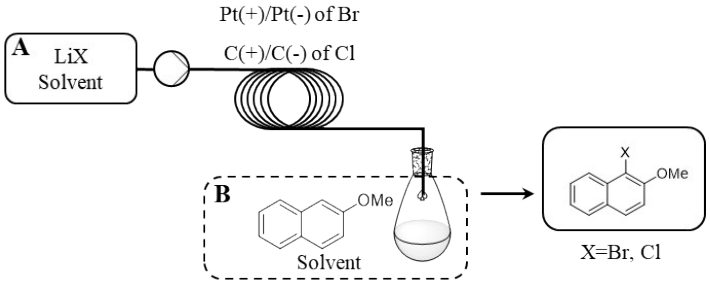


Entry	A-LiX	Electricity	Flow	Yield[b]	LiX
1	4 mmol	30 mA	300 µL/min	78%[d]	LiBr
2	3.5 mmol	30 mA	300 µL/min	67% [d]	LiBr
3	3 mmol	30 mA	300 µL/min	58% [d]	LiBr
4	5 mmol	30 mA	300 µL/min	48% [d]	LiBr
5	2 mmol	8 V	100 µL/min	69% [d]	LiBr

6	**1 mmol**	**8 V**	**100 μL/min**	**90%** [d]	**LiBr**
1	1 mmol	8 V	100 μL/min	61%	LiI
2	2 mmol	8 V	100 μL/min	71%	LiI
3	**1 mmol**	**16 V**	**100 μL/min**	**77%**	**LiI**
4	1 mmol	20 V	100 μL/min	71%	LiI
5	1 mmol	24V	100 μL/min	71%	LiI

[c] Reaction conditions: Undivided cell, Solution A: LiX (0.5 M), AcOH; Solution B: Phenylacetylene (0.2 mmol/ 0.25M), LiX (0.4 mmol), AcOH (0.8 ml); Pt (+)/Pt (-), rt.; [d] Products are cis-trans isomeric mixtures of dibromination; [b] Isolated yield.

Table S3. Optimization for Chlorination and Bromination of Aromatic ring[e]



Entry	A-LiBr	Solvent	Electricity	Flow	Yield[b]	LiX
1	2 mmol	AcOH	8 V	100 μL/min	30%	LiCl
2	2 mmol	AcOH	16 V	200 μL/min	67%	LiCl
3	2 mmol	MeCN/ AcOH (9:1)	8 V	200 μL/min	10%	LiCl
4	2 mmol	AcOH/ $CHCl_3$ (1:1)	8 V	200 μL/min	NR.	LiCl
5[f]	2 mmol	AcOH	8 V	200 μL/min	50%	LiCl
6	2 mmol	AcOH	8 V	200 μL/min	79%	LiCl
7	1 mmol	AcOH	8 V	200 μL/min	45%	LiCl
8	2.5 mmol	AcOH	8 V	200 μL/min	96%	LiCl
9[g]	2 mmol	AcOH	8 V	200 μL/min	41%	LiCl
10	**3 mmol**	**AcOH**	**8 V**	**200 μL/min**	**98%**	**LiCl**
11	4 mmol	AcOH	16 mA	300 μL/min	80%	LiBr
12	2 mmol	AcOH	16 mA	100 μL/min	98%	LiBr
13	1 mmol	AcOH	16 mA	100 μL/min	98%	LiBr
14	**1mmol**	**AcOH**	**8 V**	**100 μL/min**	**100%**	**LiBr**

[e] Reaction conditions: Undivided cell, Solution A: LiX (0.5 M), Solvent; Solution B: 2-Methoxynaphthalene (0.2 mmol/ 0.25M), Solvent (0.8 ml); rt, C (+)/C (-), rt.; [f] Extre DMSO (20% mmol) add to B; [g] Solution B reacted at 45℃; [b] Isolated yield.

5. General pocedure for the halogenations

Continuous Flow Electrochemical Halogenation Experiments.

For continuous flow electrochemical experiments, a general procedure is shown in **Figure S7** and the detailed experimental setup is shown in **Figure S8**.

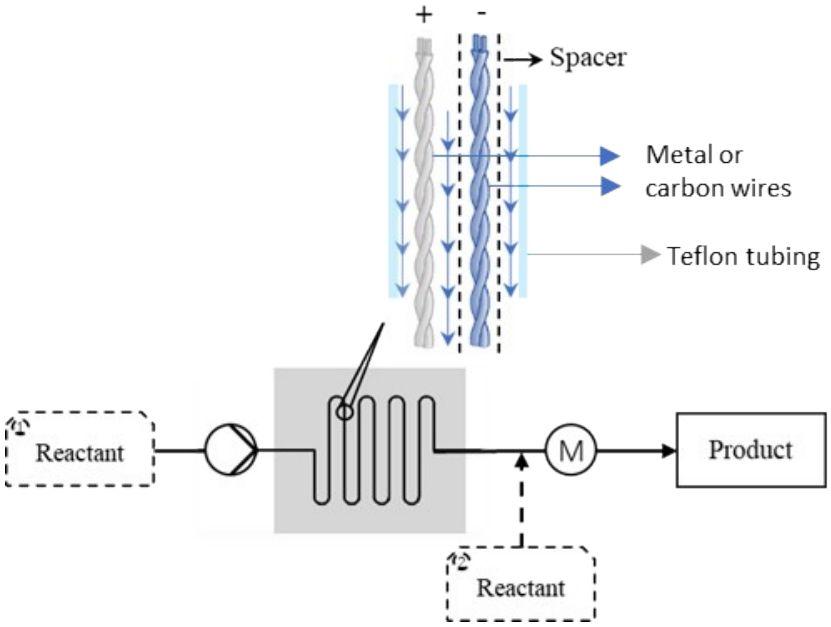


Figure S7. General setup

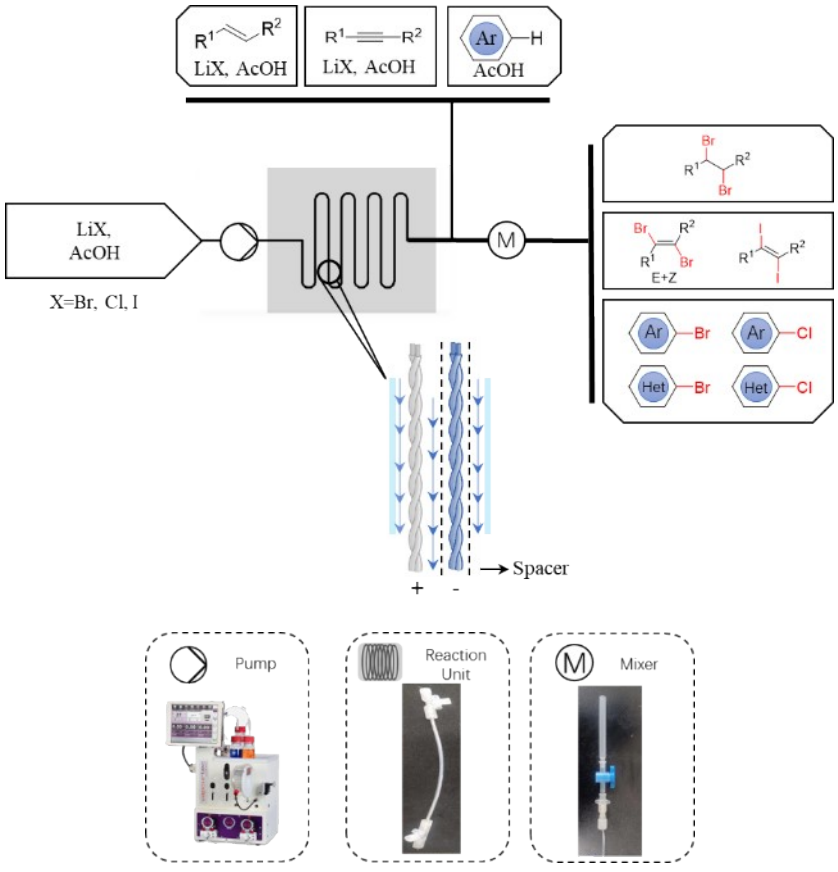
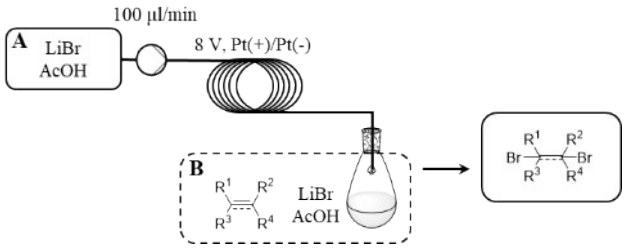


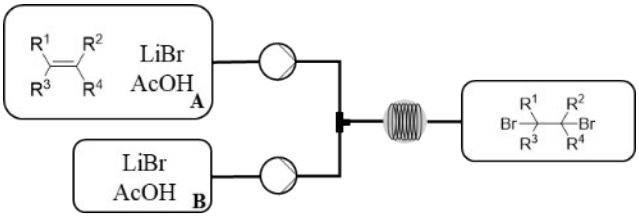
Figure S8. Description of the 2-feed continuous flow reactor

Small-scale flow electrochemical reaction for debromination



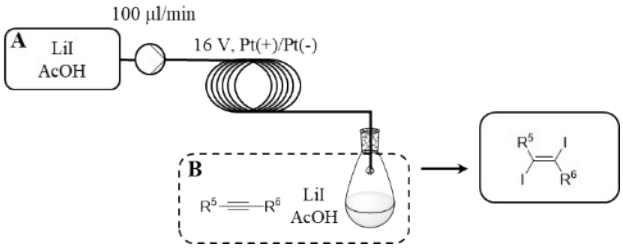
Solution A: The solution of lithium bromide (1 mmol, 0.5 M) dissolved in AcOH (2 ml) at a flow rate of 100 µl/min into the platinum electrodes reactor at a constant voltage of 8 V. **Solution B**: The solution of alkene or alkyne (0.2 mmol, 0.25 M), lithium bromide (0.4 mmol) dissolved in AcOH (0.8 ml). The solution from Solution A passed through the reactor and driped into the flask of Solution B. After Solution A's solution ran out, the product in the flask was collected. The slightly modified conditions were given in each case. Upon completion, the reaction mixture was diluted with EtOAc and washed with water and a saturated Na_2CO_3 solution. The organic layer was dried over Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate).

Small-scale flow electrochemical reaction for debromination (premixed mode)



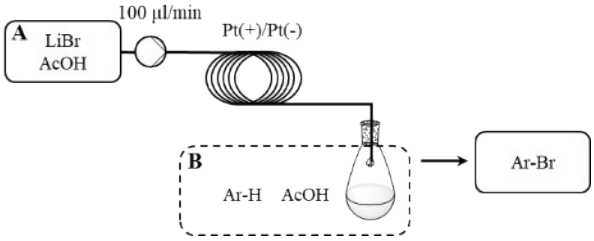
Solution A: The solution of alkene or alkyne (0.2 mmol, 0.25 M) and lithium bromide (0.4 mmol) dissolved in AcOH (0.8 ml) at a flow rate of 100 µl/min. **Solution B**: The solution of lithium bromide (1 mmol, 0.5 M) dissolved in AcOH (2 mL) at a flow rate of 100 µl/min. Solution B first fills into the platinum electrodes reactor at a constant voltage of 6 V. Then, Solution A flows through the device and reacts. After the solution ran out, the product in the flask was collected. The slightly modified conditions were given in each case. Upon completion, the reaction mixture was diluted with EtOAc and washed with water and a saturated Na_2CO_3 solution. The organic layer was dried over Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate).

Small-scale flow electrochemical reaction for diiodination



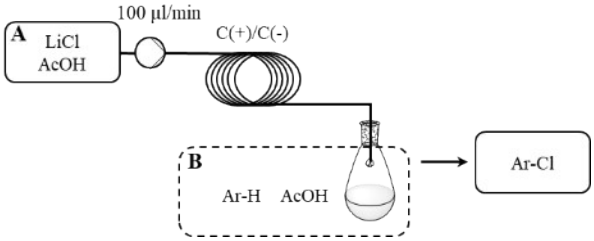
Solution A: The solution of lithium iodide (1 mmol, 0.5 M) dissolved in AcOH (2 ml) at a flow rate of 100 µl/min into the platinum electrodes reactor at a constant voltage of 16 V. **Solution B**: The solution of alkyne (0.2 mmol, 0.25 M), lithium bromide (0.4 mmol) dissolved in AcOH (0.8 ml). The solution from Solution A passed through the reactor and driped into the flask containing Solution B. After Solution A's solution ran out, the product in the flask was collected. The slightly modified conditions were given in each case. Upon completion, the reaction mixture was diluted with EtOAc and washed with water and a saturated Na_2CO_3 solution. The organic layer was dried over Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate).

Small-scale flow electrochemical reaction for bromination



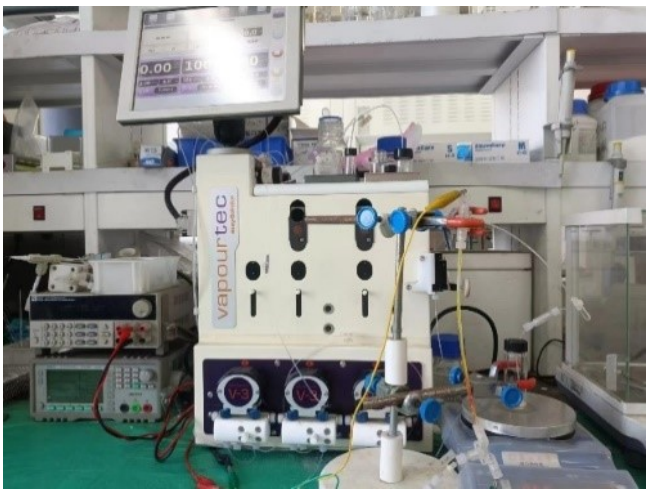
Solution A: The solution of lithium bromide (1 mmol, 0.5 M) dissolved in AcOH (2 ml) at a flow rate of 100 µl/min into the platinum electrodes reactor at a constant voltage of 8 V. **Solution B**: The solution of arene (0.2 mmol, 0.25 M) dissolved in AcOH (0.8 mL). The solution from Solution A passed through the reactor and driped into the flask containing Solution B. After Solution A's solution ran out, the product in the flask was collected. The slightly modified conditions were given in each case. Upon completion, the reaction mixture was diluted with EtOAc and washed with water and a saturated Na_2CO_3 solution. The organic layer was dried over Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/ethyl acetate).

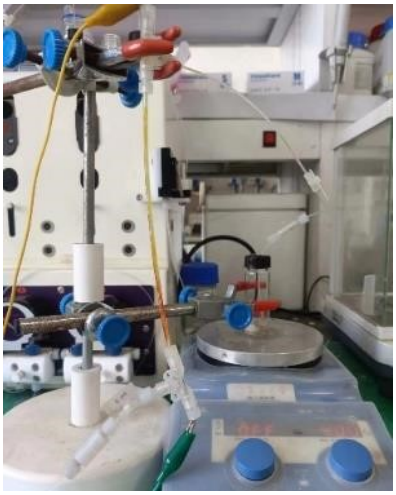
Small-scale flow electrochemical reaction for chlorination



Solution A: The solution of lithium chloride (3 mmol, 0.5 M) dissolved in AcOH (6 ml) at a flow rate of 200 µl/min into the carbon fiber electrodes reactor at a constant voltage of 8 V. **Solution B**: The

solution of arene (0.2 mmol, 0.25 M) dissolved in AcOH (0.8 mL). The solution from Solution A passed through the reactor and driped into the flask of Solution B. After Solution A's solution ran out, the product in the flask was collected. The slightly modified conditions were given in each case. Upon completion, the reaction mixture was diluted with EtOAc and washed with water and a saturated Na_2CO_3 solution. The organic layer was dried over Na_2SO_4 and concentrated to dryness. The residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate).

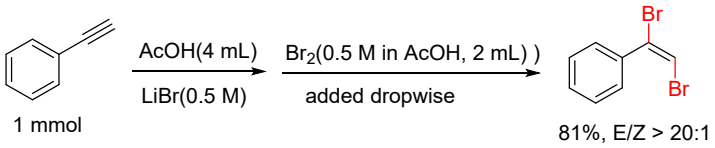




6. Investigation on the Z/E selectivity of the debrominations

The Z/E selectivity of the debromination was low (Table 2, 3a-3c), we suspected that Br_2 was not the only electrophilic bromination reagent generated in the flow reactor; a higher valence of bromination agent was possibly generated (see SI for the detained investigation).Thanks for the very helpful comments. We have done more work to find out what is happening.

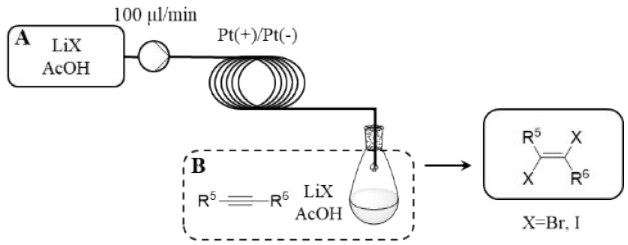
First, we tested the selectivity of using Br_2 directly, adding Br_2 slowly to the alkyne solution, and we obtained a good ratio of E-product.



1 mmol

81%, E/Z > 20:1

Since the above condition is very similar to our electrochemical conditions, we suspected that Br_2 was not the only electrophilic bromination reagent generated in the flow reactor; a higher valence of bromination agent was possibly generated. To test this hypothesis, we run the following reaction at different voltages,



Solution A: LiBr (1 mmol)，AcOH (2 mL)；flow rate 100 µL/min

Solution B: Phenylacethlene (0.2 mmol)，LiBr (0.4 mmol)，AcOH (0.8 mL)

volatage	4 V	8 V	16 V
E/Z	7:1	1.4:1	0.14:1

We also tested higher voltage (20 v and 25v), but too much bubble was generated, and the temperature of the flow reactor increased significantly (around 50 °C). We can conclude that higher voltage leads to the formation of more Z-isomers. This result seems to confirm the formation of a higher valence bromination reagent.

7. Investigation of current efficiency

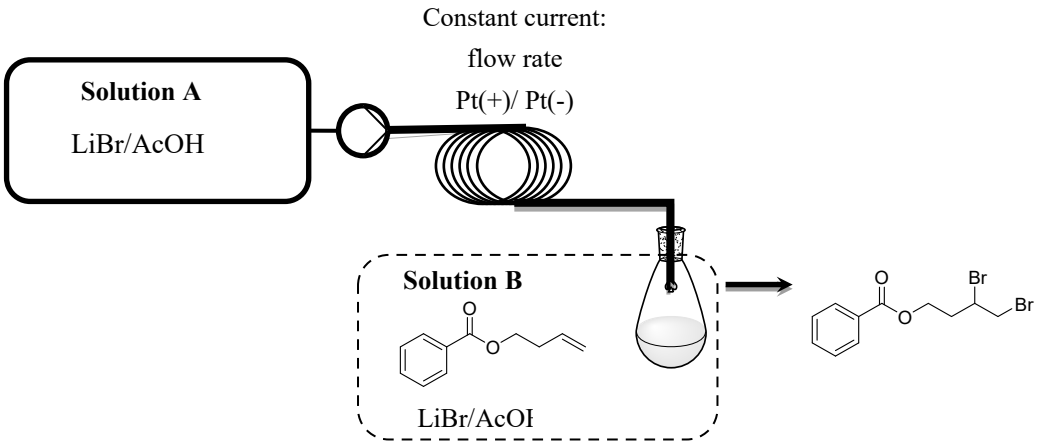
The debromination of akene is highly efficient with a quantitative yield, so we use the isolation dibromo product to measure the Br_2 formation and calculate the current efficiency. In order to make all the Br2 generated react with alkene, we use an excess amount of akene in the reaction.

Calculation of Current Efficiency (CE):

$CE = M/M_{theo}$

$M_{theo} = (I*T)/(F*N)$

M is the actual amount of product produced (M), M_{theo} is the theoretical amount of product substance produced. I is the current in Amperes, T is the time in seconds, N is the oxidation state (2 in our case, because it needs 2 electrons to generate a Br_2 molecular), F is the Faraday constant (96485 C/mol, the charge of one mole of electrons).



Conditions 1 (slow flow rate)：

Solution A (1 mmol LiBr, 2 mL AcOH), Solution B（0.5 mmol alkene starting material, LiBr (1 mmol), AcOH (2 mL). Solution A flow rate: 100 μl/min, constant current 25 mA (volate is around 7.3-8.4 v), time 30 min, isolated dibromo product (47 mg, 0.14 mmol).

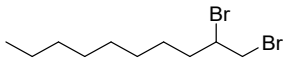
M_{theo} = (I*T)/(F*N) = (0.025A*30*60 sec) /(96485*2) = 0.00023 mol = 0.23 mmol
M = M/M_{theo} = 0.14/0.23 = 61%
F = It/ZNF = (0.025A*0.5h)/(2*0.0002mol*26.8Ah) = 1.2 F/mol.

Conditions 2 (faster flow rate, shorter flow time)：
Solution A (1 mmol LiBr, 2 mL AcOH), Solution B (0.2 mmol alkene starting material, LiBr 0.4 mmol, AcOH 0.8 mL). Solution A flow rate: 500 μl/min, constant current 30 mA (volate is around 7.3-8.4 v), time 7 min, isolated dibromo product (19.8 mg, 0.059 mmol).
M_{theo} = (I*T)/(F*N) = (0.030A*60*7 sec) /(96485*2) = 0.000065 mmol = 0.065 mmol
M = M/M_{theo} = 0.059/0.065 = 91%
In general, the current efficiency is relatively high. At a faster flow, the current efficiency is even higher, possibly because the Br_2 generated has less chance of being reduced by the cathode.

Measurement of reaction time:
1) Start passing solution A to the flow reactor; at this time, the electricity is off, and there is no solution or only pure solvent (AcOH) in the flow reactor.
2) When solution A arrives at the entrance of the flow reactor, turn on the electricity and start the counting of time. The flow of the solution is easy to see because the tubing is transparent.
3) When all solution A (e.g., 2 mL) was used, let a small amount of air enter the pump, and then add some fresh solvent (AcOH) to continue the flow.
4) When all solution A passes through the flow reactor, turn off the electricity and stop the counting of time. The color of the solution and the air bubble introduced in step 3 could help us determine the ending.

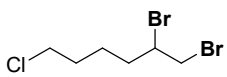
8. The characterization data of compounds

1,2-Dibromodecane **(2a)**[4]



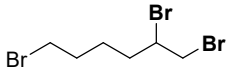
Colorless oil, 71% yield. 1H NMR (400 MHz, Chloroform-d) δ 4.20 – 4.14 (m, 1H), 3.85 (dd, J = 10.2, 4.5 Hz, 1H), 3.63 (t, J = 10.0 Hz, 1H), 2.18 – 2.09 (m, 1H), 1.83 – 1.73 (m, 1H), 1.61 – 1.52 (m, 1H), 1.45 – 1.36 (m, 1H), 1.28 (s, 9H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 53.3, 36.5, 36.2, 32.0, 29.5, 29.3, 29.0, 26.9, 22.8, 14.3.

1,2-Dibromo-6-chlorohexane **(2b)**



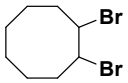
Colorless oil, 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.20 – 4.14 (m, 1H), 3.87 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.63 (t, *J* = 10.1 Hz, 1H), 3.57 (t, *J* = 6.5 Hz, 2H), 2.23 – 2.16 (m, 1H), 1.88 – 1.70 (m, 4H), 1.65 – 1.54 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 52.5, 44.7, 36.2, 35.4, 31.9, 24.4. HRMS (FI^{+}): Calcd. for $C_6H_{11}Br_2Cl$ [M]$^{+}$: *m/z* 275.8911, found: 275.8910.

1,2,6-Tribromohexane **(2c)**[5]



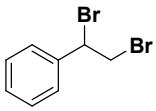
Colorless oil, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.20 – 4.13 (m, 1H), 3.87 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.63 (t, *J* = 10.1 Hz, 1H), 3.44 (t, *J* = 6.7 Hz, 2H), 2.23 – 2.15 (m, 1H), 1.97 – 1.70 (m, 4H), 1.63 – 1.55 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 52.4, 36.2, 33.3, 32.0, 25.7.

1,2-Dibromocyclooctane **(2d)**[6]



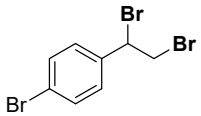
Colorless oil, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.61 – 4.56 (m, 2H), 2.45 – 2.38 (m, 2H), 2.14 – 2.05 (m, 2H), 1.90 – 1.81 (m, 2H), 1.74 – 1.66 (m, 2H), 1.65 – 1.54 (m, 2H), 1.51 – 1.42 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 61.8, 33.4, 26.1, 25.5.

(1,2-Dibromoethyl)denzene **(2e)**[7]



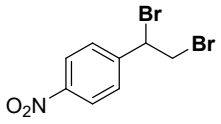
White solid, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 5H), 5.14 (dd, *J* = 10.6, 5.5 Hz, 1H), 4.07 (dd, *J* = 10.3, 5.5 Hz, 1H), 4.02 (t, *J* = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.7, 129.3, 129.0, 127.8, 51.0, 35.2.

1-Bromo-4-(1,2-bibromoethyl)benzene **(2f)**[7]



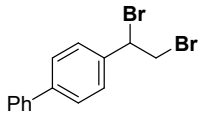
Yellow solid, 76% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 – 7.50 (m, 2H), 7.29 – 7.26 (m, 2H), 5.08 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.05 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.98 – 3.94 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 137.8, 132.2, 129.4, 123.3, 49.7, 34.7.

1-(1,2-Dibromoethyl)-4-nitrobenzene **(2g)**



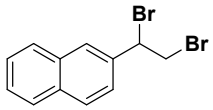
Yellow solid, 76% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 5.18 (dd, *J* = 11.3, 5.0 Hz, 1H), 4.10 (dd, *J* = 10.4, 5.0 Hz, 1H), 3.99 (t, *J* = 10.8Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.2, 145.6, 128.9, 124.2, 47.9, 34.0. HRMS (EI$^+$): Calcd. for $C_8H_7O_2NBr_2$ [M]$^+$: *m/z* 306.8838, found: 306.8836.

4-(1,2-Dibromoethyl)-1,1'-biphenyl **(2h)**[7]



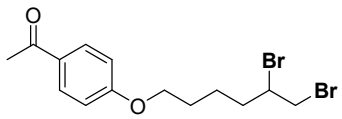
White solid, 66% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.57 (m, 4H), 7.44 (dd, *J* = 14.0, 8.0 Hz, 4H), 7.37 – 7.33 (m, 1H), 5.19 (dd, *J* = 10.4, 5.7 Hz, 1H), 4.12 – 4.03 (m, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.2, 140.3, 137.6, 129.0, 128.2, 127.8, 127.7, 127.3, 50.8, 35.0.

2-(1,2-Dibromoethyl)naphthalene **(2i)**[7]



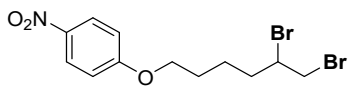
White solid, 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 4H), 7.52 – 7.49 (m, 3H), 5.32 (dd, *J* = 9.4, 6.7 Hz, 1H), 4.16 – 4.13 (m, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.8, 133.6, 133.0, 129.2, 128.3, 127.9, 127.6, 127.0, 126.8, 124.5, 51.5, 34.9.

1-(4-((5,6-Dibromohexyl)oxy)phenyl)ethan-1-one **(2k)**



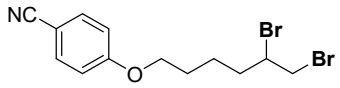
Colorless oil, 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.23 – 4.16 (m, 1H), 4.05 (t, *J* = 6.1 Hz, 2H), 3.87 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.55 (s, 3H), 2.29 – 2.20 (m, 1H), 1.92 – 1.75 (m, 4H), 1.67 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.8, 163.0, 130.7, 130.3, 114.2, 67.8, 52.6, 36.2, 35.8, 28.4, 26.5, 23.6. HRMS (DART$^+$): Calcd. for $C_{14}H_{19}O_2Br_2$ [M+H]$^+$: *m/z* 376.9746, found: 376.9744.

1-((5,6-Dibromohexyl)oxy)-4-nitrobenzene **(2l)**



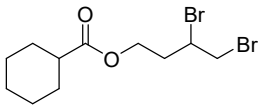
Brown oil, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.17 (m, 2H), 6.97 – 6.93 (m, 2H), 4.23 – 4.17 (m, 1H), 4.09 (t, *J* = 6.2 Hz, 2H), 3.88 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.65 (t, *J* = 10.1 Hz, 1H), 2.30 – 2.21 (m, 1H), 1.98 – 1.76 (m, 4H), 1.68 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 141.5, 126.0, 114.5, 68.5, 52.5, 36.2, 35.7, 28.3, 23.6. HRMS (EI^{+}): Calcd. for $C_{12}H_{15}O_3NBr_2$ $[M]^{+}$: *m/z* 378.9413, found: 378.9418.

4-((5,6-Dibromohexyl)oxy)benzonitrile **(2m)**



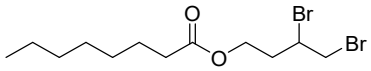
Colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.23 – 4.16 (m, 1H), 4.03 (t, *J* = 6.1 Hz, 2H), 3.87 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.64 (t, *J* = 10.1 Hz, 1H), 2.29 – 2.20 (m, 1H), 1.95 – 1.73 (m, 4H), 1.68 – 1.57 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3, 134.1, 119.4, 115.3, 104.0, 68.0, 52.6, 36.2, 35.7, 28.3, 23.6. HRMS (DART^{+}): Calcd. for $C_{13}H_{16}ONBr_2$ $[M+H]^{+}$: *m/z* 359.9593, found: 359.9592.

3,4-Dibromobutyl cyclohexanecarboxylate **(2n)**



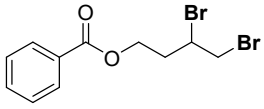
Yellow oil, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.37 – 4.32 (m, 1H), 4.30 – 4.18 (m, 2H), 3.89 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.66 (t, *J* = 10.1 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.35 – 2.28 (m, 1H), 2.08 – 1.99 (m, 1H), 1.93 – 1.88 (m, 2H), 1.79 – 1.73 (m, 2H), 1.67 – 1.62 (m, 1H), 1.50 – 1.40 (m, 2H), 1.34 – 1.17 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.9, 61.6, 48.8, 43.2, 36.3, 35.4, 29.1, 25.8, 25.5. HRMS (DART^{+}): Calcd. for $C_{11}H_{19}O_2Br_2$ $[M+H]^{+}$: *m/z* 340.9746, found: 340.9746.

3,4-Dibromobutyl octanoate **(2o)**



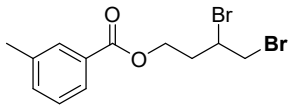
Colorless oil, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.38 – 4.32 (m, 1H), 4.30 – 4.19 (m, 2H), 3.89 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.66 (t, *J* = 10.0 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.09 – 2.01 (m, 1H), 1.67 – 1.59 (m, 2H), 1.34 – 1.26 (m, 8H), 0.90 – 0.87 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 61.7, 48.7, 36.2, 35.4, 34.4, 31.8, 29.2, 29.0, 25.1, 22.7, 14.2. HRMS (DART^{+}): Calcd. for $C_{12}H_{23}O_2Br_2$ $[M+H]^{+}$: *m/z* 357.0059, found: 357.0057.

3,4-Dibromobutyl benzoate **(2p)**



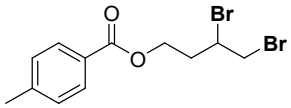
Yellow oil, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.62 – 4.57 (m, 1H), 4.51 – 4.45 (m, 1H), 4.39 – 4.33 (m, 1H), 3.92 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.24 – 2.15 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 133.2, 129.7, 128.5, 62.4, 48.7, 36.3, 35.4. HRMS (DART$^+$): Calcd. for $C_{11}H_{13}O_2Br_2$ [M+H]$^+$: *m/z* 334.9277, found: 334.9276.

3,4-Dibromobutyl 3-methylbenzoate **(2q)**



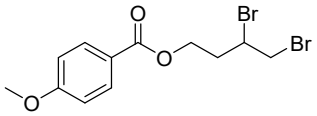
Colorless oil, 63% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 11.2 Hz, 2H), 7.39 – 7.31 (m, 2H), 4.61 – 4.56 (m, 1H), 4.50 – 4.44 (m, 1H), 4.39 – 4.32 (m, 1H), 3.92 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.41 (s, 3H), 2.24 – 2.16 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6, 138.3, 134.0, 130.3, 129.9, 128.4, 126.8, 62.4, 48.7, 36.3, 35.4, 21.4. HRMS (DART$^+$): Calcd. for $C_{12}H_{15}O_2Br_2$ [M+H]$^+$: *m/z* 348.9433, found: 348.9432.

3,4-Dibromobutyl 4-methylbenzoate **(2r)**



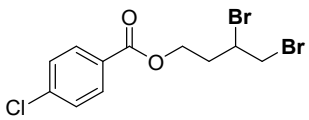
Yellow oil, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.60 – 4.54 (m, 1H), 4.49 – 4.42 (m, 1H), 4.38 – 4.32 (m, 1H), 3.92 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 2.73 – 2.65 (m, 1H), 2.41 (s, 3H), 2.23-2.14 (m, 1H). ^{13}C NMR (100z MHz, Chloroform-*d*) δ 166.5, 144.0z, 129.7, 129.3, 127.2, 62.3, 48.8, 36.3, 35.4, 21.8. HRMS (DART$^+$): Calcd. for $C_{12}H_{15}O_2Br_2$ [M+H]$^+$: *m/z* 348.9433, found: 348.9432.

3,4-Dibromobutyl 4-methoxybenzoate **(2s)**



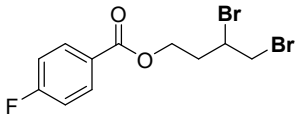
Yellow oil, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.58 – 4.53 (m, 1H), 4.47 – 4.41 (m, 1H), 4.38 – 4.32 (m, 1H), 3.91 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.85 (s, 3H), 3.70 (t, *J* = 10.0 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.23 – 2.14 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.0, 163.5, 131.7, 122.3, 113.7, 62.1, 55.5, 48.8, 35.4. HRMS (DART$^+$): Calcd. for $C_{12}H_{15}O_3Br_2$ [M+H]$^+$: *m/z* 364.9382, found: 364.9380.

3,4-Dibromobutyl 4-chlorobenzoate **(2t)**



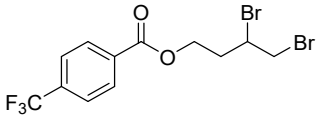
Colorless oil, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.97 (m, 2H), 7.44 – 7.41 (m, 2H), 4.62 – 4.56 (m, 1H), 4.51 – 4.45 (m, 1H), 4.37 – 4.30 (m, 1H), 3.92 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.70 (t, *J* = 10.1 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.25 – 2.16 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.5, 139.7, 131.1, 128.9, 128.4, 62.7, 48.5, 36.1, 35.3. HRMS (FI$^+$): Calcd. for $C_{11}H_{11}O_2Br_2Cl$ [M]$^+$: *m/z* 367.8809, found: 367.8806.

3,4-Dibromobutyl 4-fluorobenzoate **(2u)**



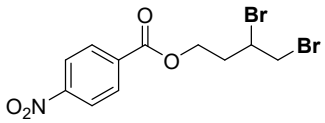
Colorless oil, 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.05 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 4.62 – 4.56 (m, 1H), 4.51 – 4.45 (m, 1H), 4.38 – 4.31 (m, 1H), 3.93 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.70 (t, *J* = 10.1 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.25 – 2.16 (m, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.2 - -105.3 (m, 1F). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.9 (d, *J* = 254.3 Hz), 165.3, 132.2 (d, *J* = 9.4 Hz), 126.1 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.0 Hz), 62.5, 48.5, 36.1, 35.2. HRMS (FI$^+$): Calcd. for $C_{11}H_{11}O_2Br_2F$ [M]$^+$: *m/z* 351.9104, found: 351.9103.

3,4-Dibromobutyl 4-(trifluoromethyl)benzoate **(2v)**



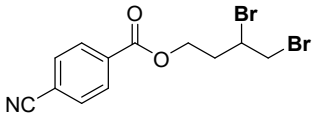
Colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 4.66 – 4.61 (m, 1H), 4.56 – 4.50 (m, 1H), 4.38 – 4.31 (m, 1H), 3.94 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.71 (t, *J* = 10.2 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.28 – 2.19 (m, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.2, 134.7 (q, *J* = 32.5 Hz), 133.2, 130.2, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 271.1 Hz), 63.1, 48.4, 36.0, 35.3. HRMS (FI$^+$): Calcd. for $C_{12}H_{11}O_2Br_2F_3$ [M]$^+$: *m/z* 401.9072, found: 401.9070.

3,4-Dibromobutyl 4-nitrobenzoate **(2w)**



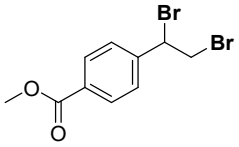
Yellow solid, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 9.0 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 4.69 – 4.63 (m, 1H), 4.59 – 4.53 (m, 1H), 4.38 – 4.32 (m, 1H), 3.95 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.72 (t, *J* = 10.2 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.30 – 2.21 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.5, 150.70, 135.3, 130.9, 123.7, 63.4, 48.2, 36.0, 35.1. HRMS (FI$^+$): Calcd. for $C_{11}H_{11}O_4NBr_2$ [M]$^+$: *m/z* 378.9049, found: 378.9054.

3,4-Dibromobutyl 4-cyanobenzoate **(2x)**



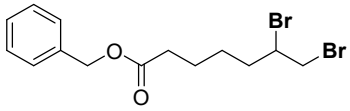
Colorless oil, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 4.67 – 4.61 (m, 1H), 4.57 – 4.51 (m, 1H), 4.37 – 4.30 (m, 1H), 3.94 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.71 (t, *J* = 10.2 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.28 – 2.19 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7, 133.7, 132.4, 130.2, 118.0, 116.7, 63.3, 48.3, 36.0, 35.2. HRMS (FI$^+$): Calcd. for $C_{12}H_{11}O_2NBr_2$ [M]$^+$: *m/z* 358.9150, found: 358.9148.

Methyl 4-(1,2-dibromoethyl)benzoate **(2y)**[8]



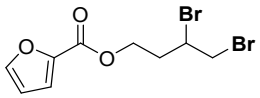
Yellow solid, 72% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.15 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.08 (dd, *J* = 10.3, 5.1 Hz, 1H), 4.01 (t, *J* = 10.7 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 166.5, 143.5, 130.9, 130.3, 127.9, 52.4, 49.4, 34.5.

Benzyl 6,7-dibromoheptanoate **(2z)**



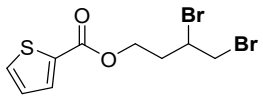
Colorless oil, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 4.17 – 4.10 (m, 1H), 3.82 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.59 (t, *J* = 10.0 Hz, 1H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.19 – 2.11 (m, 1H), 1.85 – 1.58 (m, 4H), 1.47 – 1.44 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 136.1, 128.7, 128.3, 66.3, 52.6, 36.3, 35.8, 34.1, 26.4, 24.2. HRMS (DART$^+$): Calcd. for $C_{14}H_{19}O_2Br_2$ [M+H]$^+$: *m/z* 376.9746, found: 376.9746.

3,4-Dibromobutyl furan-2-carboxylate **(2aa)**



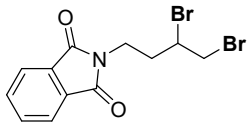
Yellow oil, 80% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.21 (d, *J* = 3.4 Hz, 1H), 6.53 – 6.52 (m, 1H), 4.59 -4.56 (m, 1H), 4.49 – 4.45 (m, 1H), 4.36 – 4.31 (m, 1H), 3.91 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 2.69 – 2.64 (m, 1H), 2.22 – 2.16 (m, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 158.5, 146.7, 144.4, 118.4, 112.0, 62.4, 48.5, 36.2, 35.3. HRMS (DART$^+$): Calcd. for $C_9H_{11}O_3Br_2$ [M+H]$^+$: *m/z* 324.9069, found: 324.9069.

3,4-Dibromobutyl thiophene-2-carboxylate **(2ab)**



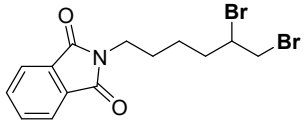
Yellow oil, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.59 – 4.54 (m, 1H), 4.49 – 4.43 (m, 1H), 4.37 – 4.30 (m, 1H), 3.92 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.71 (t, *J* = 10.0 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.24 – 2.15 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0, 133.8, 133.5, 132.8, 128.0, 62.6, 48.6, 36.2, 35.4. HRMS (DART^{+}): Calcd. for $C_9H_{11}O_2Br_2S$ $[M+H]^+$: *m/z* 340.8841, found: 340.8840.

2-(3,4-Dibromobutyl)isoindoline-1,3-dione **(2ac)**



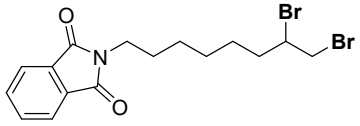
White solid, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.21 – 4.15 (m, 1H), 3.98 – 3.85 (m, 3H), 3.67 (t, *J* = 10.0 Hz, 1H), 2.76 – 2.59 (m, 1H), 2.23 – 2.13 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.3, 134.2, 132.0, 123.5, 49.0, 36.0, 35.1. HRMS (DART^{+}): Calcd. for $C_{12}H_{12}O_2NBr_2$ $[M+H]^+$: *m/z* 359.9229, found: 359.9227.

2-(5,6-Dibromohexyl)isoindoline-1,3-dione **(2ad)**



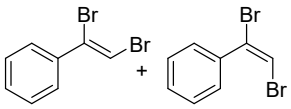
White solid, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 4.18 – 4.12 (m, 1H), 3.84 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.72 (t, *J* = 7.1 Hz, 2H), 3.62 (t, *J* = 10.0 Hz, 1H), 2.26 – 2.17 (m, 1H), 1.88 – 1.60 (m, 4H), 1.54 – 1.43 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 134.0, 132.2, 52.6, 37.76, 36.3, 35.6, 27.9, 24.3. HRMS (DART^{+}): Calcd. for $C_{14}H_{16}O_2NBr_2$ $[M+H]^+$: *m/z* 387.9542, found: 387.9541.

2-(7,8-Dibromooctyl)isoindoline-1,3-dione **(2ae)**



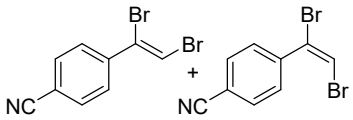
Colorless oil, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.19 – 4.12 (m, 1H), 3.83 (dd, *J* = 10.2, 4.5 Hz, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 3.62 (t, *J* = 10.0 Hz, 1H), 2.16 – 2.08 (m, 1H), 1.82 – 1.66 (m, 3H), 1.61 – 1.52 (m, 1H), 1.46- 1.36 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 133.9, 132.1, 123.1, 53.0, 37.9, 36.4, 35.9, 29.7, 28.5, 28.3, 26.6. HRMS (DART^{+}): Calcd. for $C_{16}H_{20}O_2NBr_2$ $[M+H]^+$: *m/z* 415.9855, found: 415.9853.

(*Z/E*)-(1,2-Dibromovinyl)benzene **(3a)**[9]



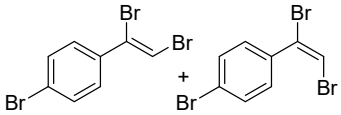
Yellow oil, 90% yield, *Z/E*=10:7. *Z* isomer: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 5H), 7.04 (s, 1H); *E* isomer: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 5H), 6.79 (s, 1H).

(*Z*+*E*)-4-(1,2-Dibromovinyl)benzonitrile **(3b)**[9]



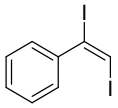
Yellow solid, 83% yield, *Z/E*=10:11. *Z* isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.65 (m, 4H), 7.24 (s, 1H); *E* isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.60 (m, 4H), 6.91 (s, 1H).

(*Z*+*E*)-1-Bromo-4-(1,2-dibromovinyl)benzene **(3c)**[10]



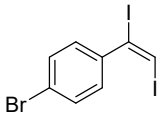
Yellow oil, 85% yield. *Z* isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.39 – 7.36 (m, 2H), 7.06 (s, 1H). *E* isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.46 (m, 2H), 7.36 – 7.34 (m, 2H), 6.81 (s, 1H)

(*E*)-(1,2-Diiodovinyl)benzene **(4a)**[11]



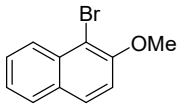
Yellow solid, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 5H), 7.25 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 143.2, 129.1, 128.6, 128.6, 96.3, 81.0.

(*E*)-1-Bromo-4-(1,2-diiodovinyl)benzene **(4b)**[11]



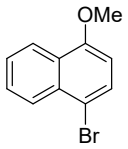
Yellow solid, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.28 (s, 1H), 7.25 – 7.21 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 142.1, 131.8, 130.3, 123.2, 94.7, 81.8.

1-Bromo-2-methoxynaphthalene **(5a)**[12]



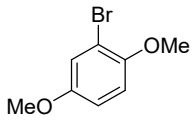
Yellow solid, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.56 – 7.52 (m, 1H), 7.39 – 7.35 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.8, 133.2, 129.9, 129.1, 128.1, 127.8, 126.2, 124.4, 113.7, 108.7, 57.1.

1-Bromo-4-methoxynaphthalene **(5b)**[13]



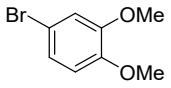
Yellow oil, 95% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.51 – 7.47 (m, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.3, 132.5, 129.6, 127.9, 127.0, 126.9, 126.0, 122.5, 113.3, 104.6, 55.8.

2-Bromo-1,4-dimethoxybenzene **(5c)**[12]



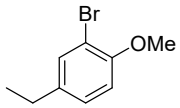
Yellow oil, 82% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 2.8 Hz, 1H), 6.84 – 6.80 (m, 2H), 3.84 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.1, 150.4, 119.1, 113.8, 113.0, 112.0, 57.0, 56.0.

4-Bromo-1,2-dimethoxybenzene **(5d)**[12]



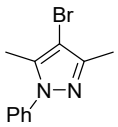
Yellow oil, 98% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.05 – 6.97 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 149.8, 148.4, 123.4, 114.8, 112.8, 112.5, 56.1, 56.1.

2-Bromo-4-ethyl-1-methoxybenzene **(5e)**[13]



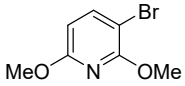
Yellow oil, 81% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 2.2 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 2.59 – 2.55 (m, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.0, 138.1, 132.7, 127.8, 112.0, 111.5, 56.4, 27.8, 15.8.

4-Bromo-3,5-dimethyl-1-phenyl-1H-pyrazole **(5f)**[14]



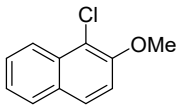
Brown oil, 100% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.35 (m, 5H), 2.30 (s, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 147.6, 139.9, 137.6, 129.2, 127.9, 124.7, 96.5, 12.5, 11.9.

3-Bromo-2,6-dimethoxypyridine **(5g)**[15]



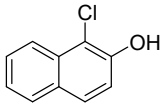
Yellow oil, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 1H), 3.99 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 162.2, 158.5, 143.7, 102.8, 95.5, 54.3, 53.9.

1-Chloro-2-methoxynaphthalene **(6a)**[16]



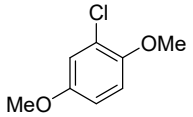
Yellow solid, 96% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.6 Hz, 1H), 7.73 (dd, *J* = 22.4, 8.6 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.22 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 152.6, 131.9, 129.6, 128.1, 128.1, 127.5, 124.4, 123.5, 116.8, 113.7, 57.0.

1-Chloronaphthalen-2-ol **(6b)**[16]



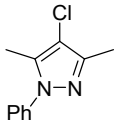
Brown solid, 80% yiele. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 5.92 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 149.4, 131.2, 129.6, 128.5, 128.3, 127.7, 124.3, 122.9, 117.3, 113.4.

2-Chloro-1,4-dimethoxybenzene **(6c)**[17]



Colorless oil, 65% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 3.0 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.77 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 153.9, 149.5, 123.1, 116.3, 113.3, 113.0, 56.9, 56.0

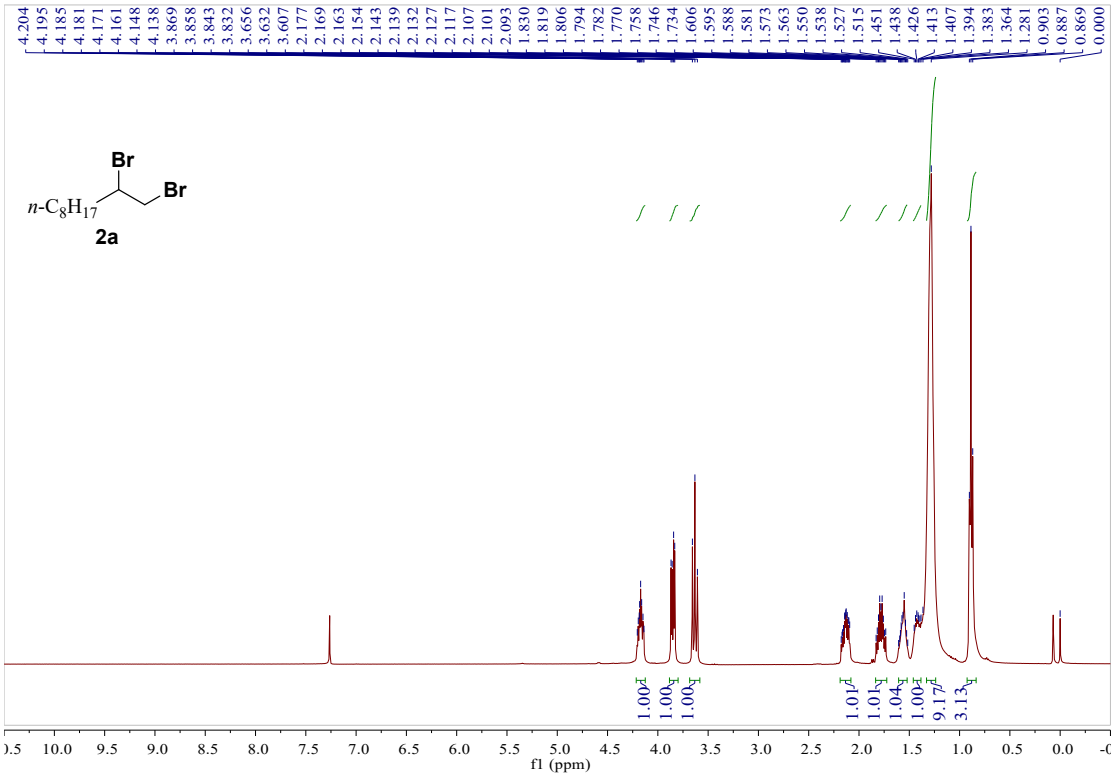
4-Chloro-3,5-dimethyl-1-phenyl-1H-pyrazole **(6d)**[14]



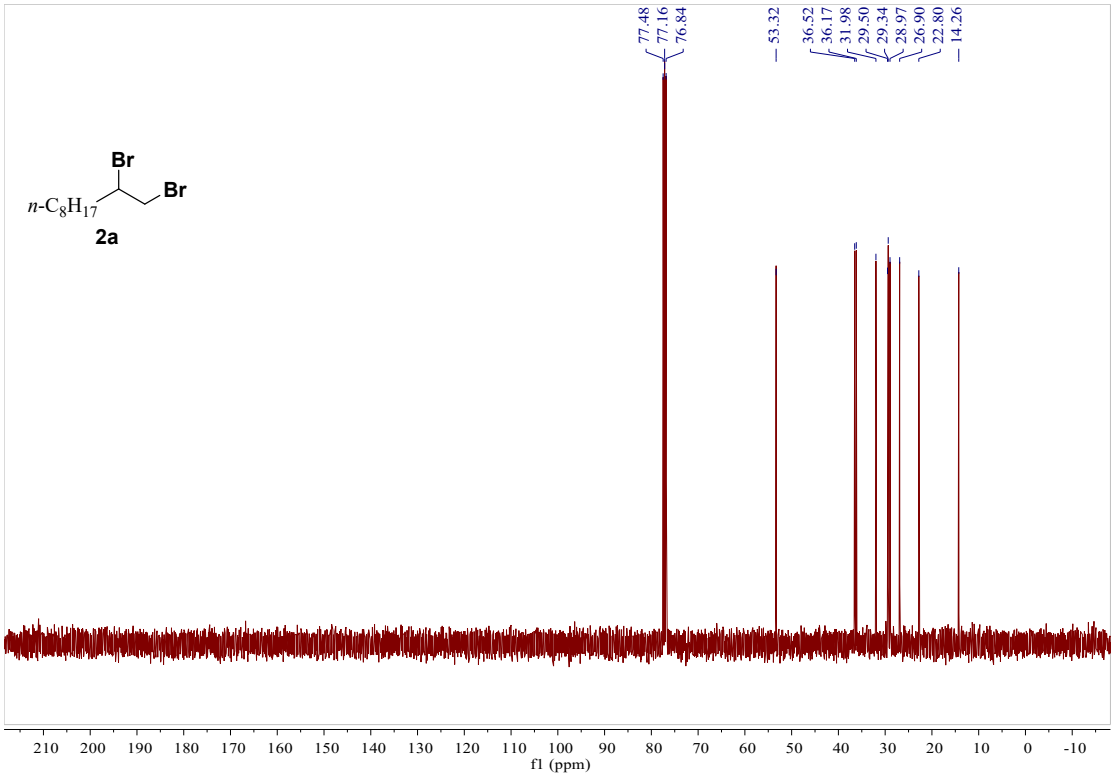
Yellow oil, 77% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.35 (m, 5H), 2.29 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 146.1, 139.8, 135.8, 129.3, 127.8, 124.6, 109.9, 11.5, 10.9.

9. Copies of NMR spectra

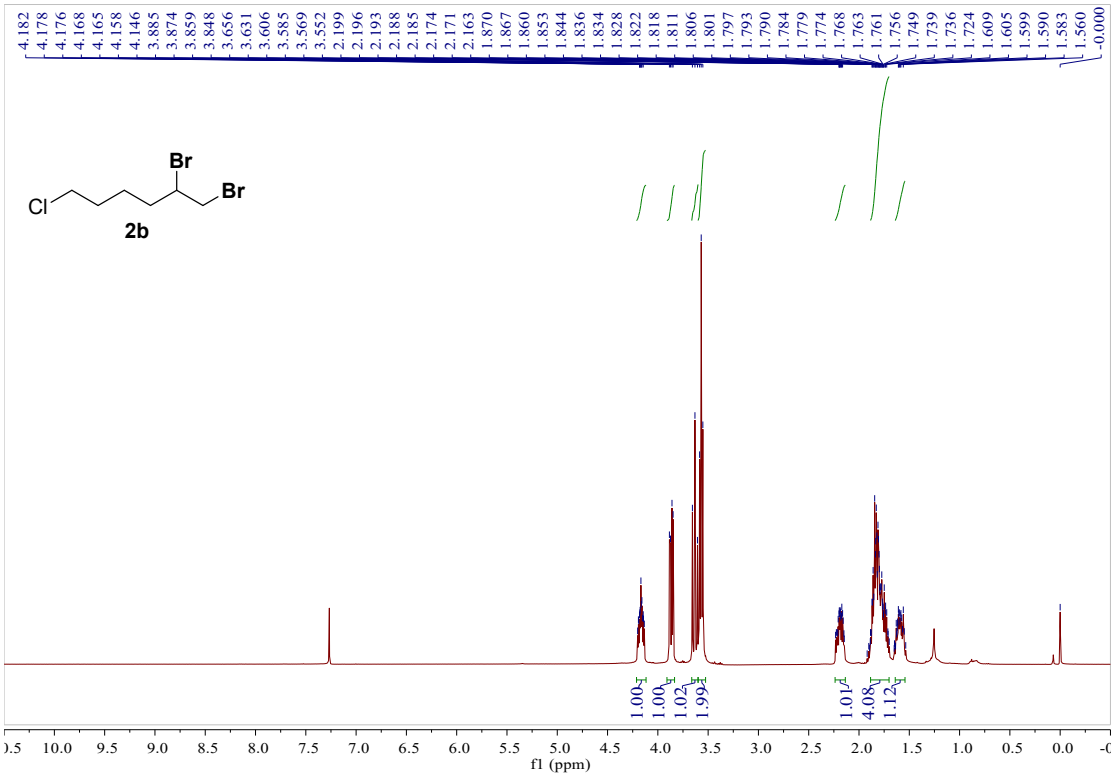
^{1}H NMR spectra for compound (2a)



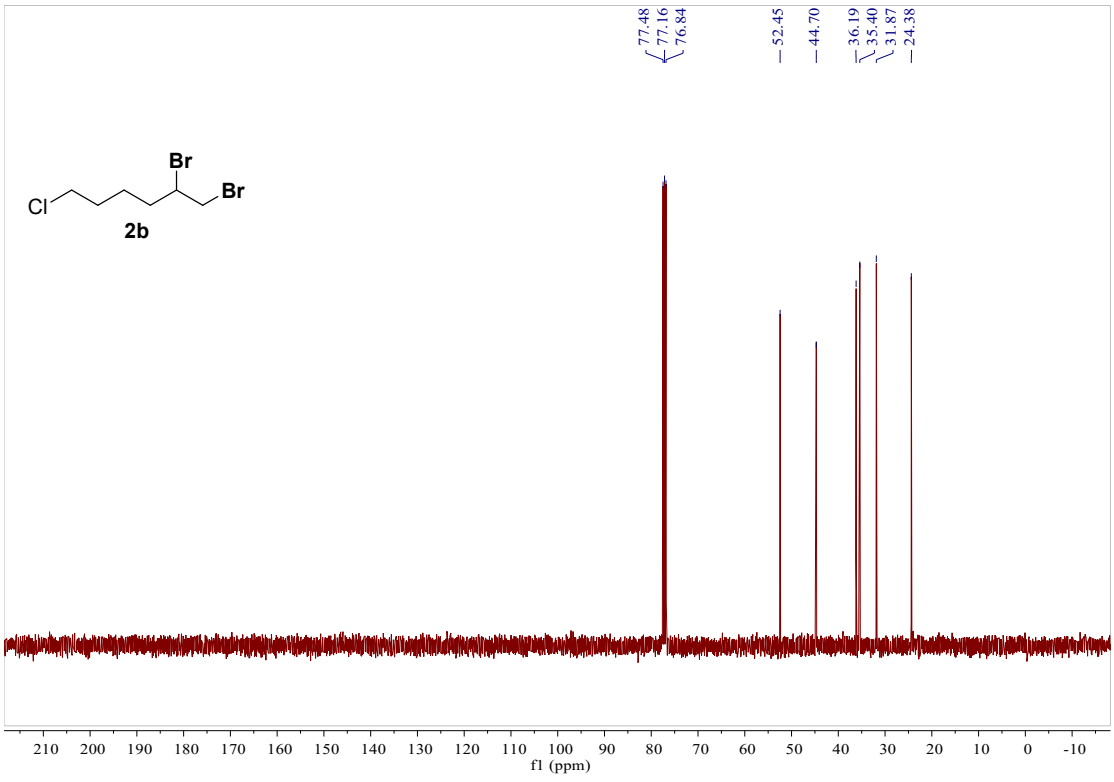
^{13}C NMR spectra for compound (2a)



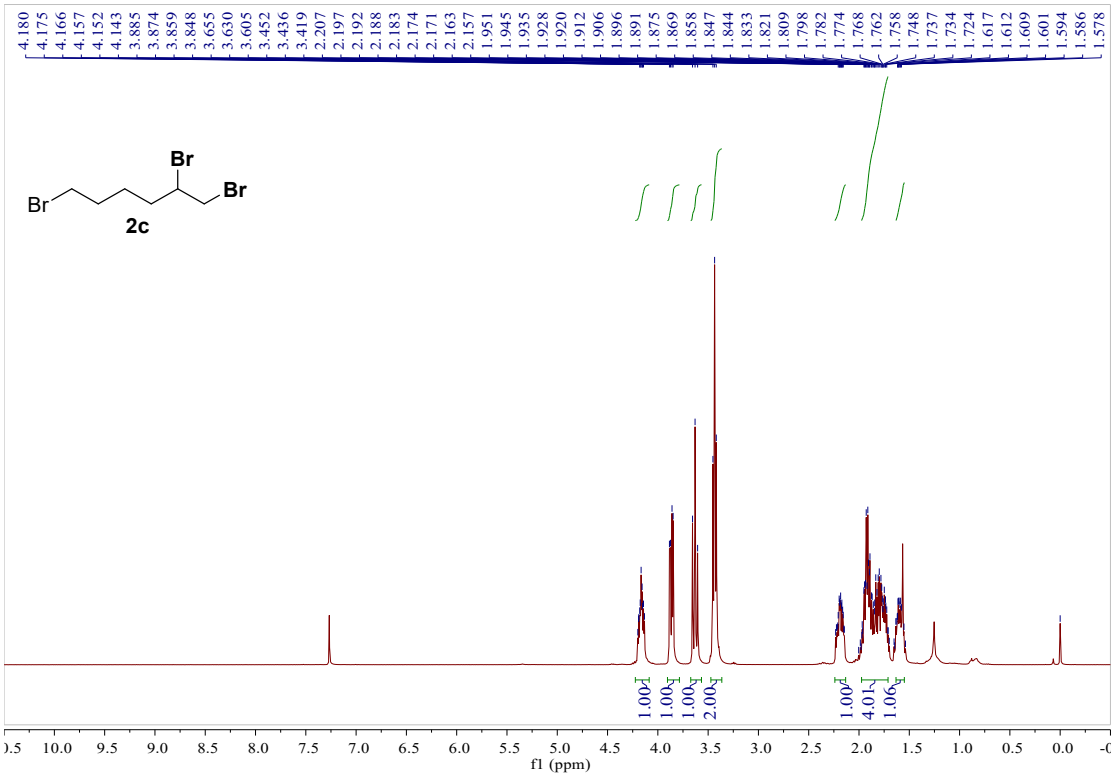
^{1}H NMR spectra for compound 2b



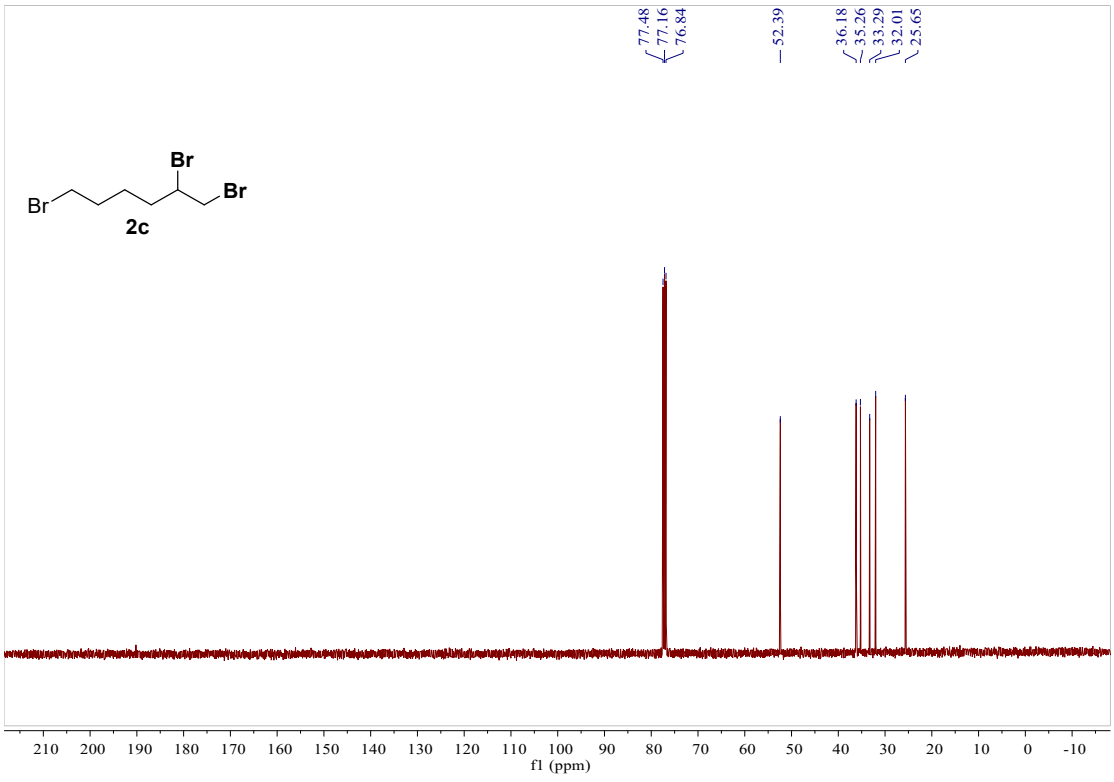
^{13}C NMR spectra for compound (2b)



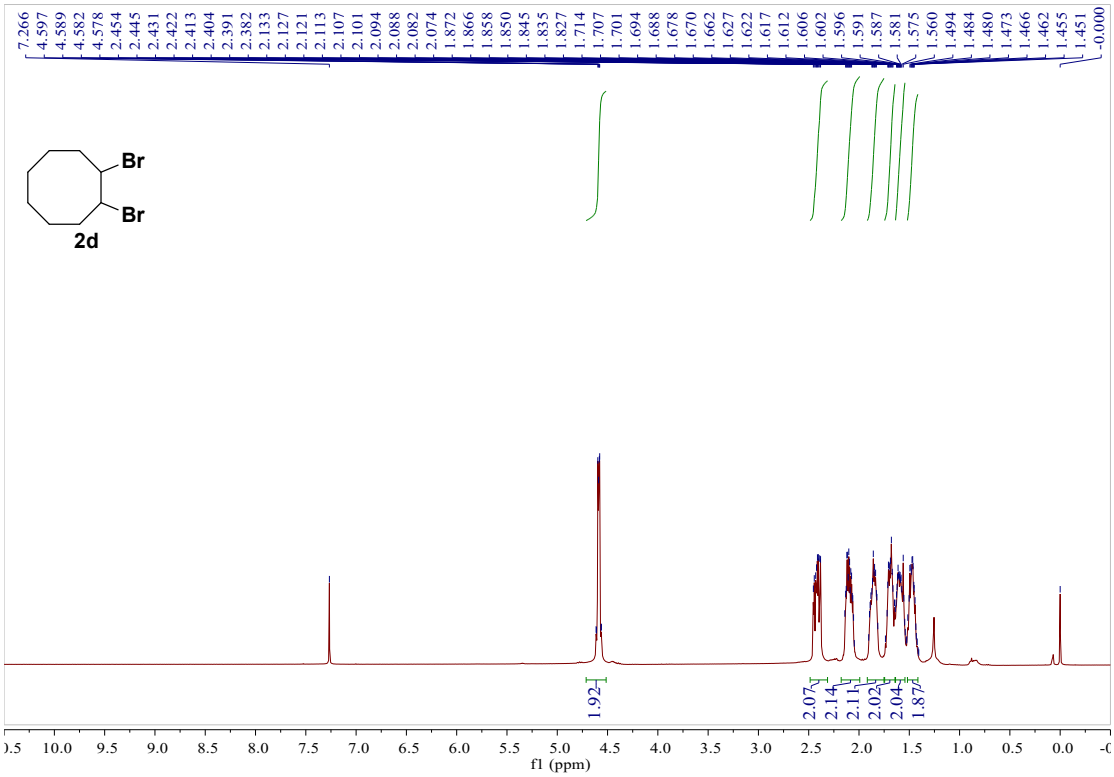
^{1}H NMR spectra for compound (2c)



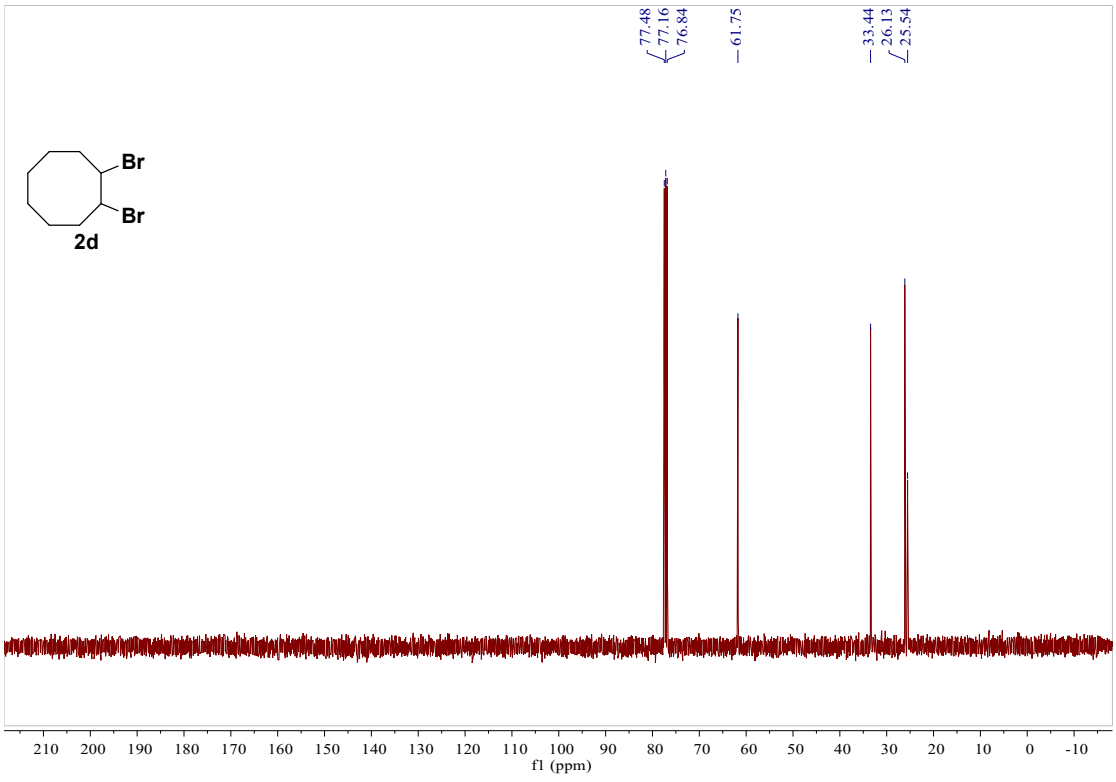
^{13}C NMR spectra for compound (2c)



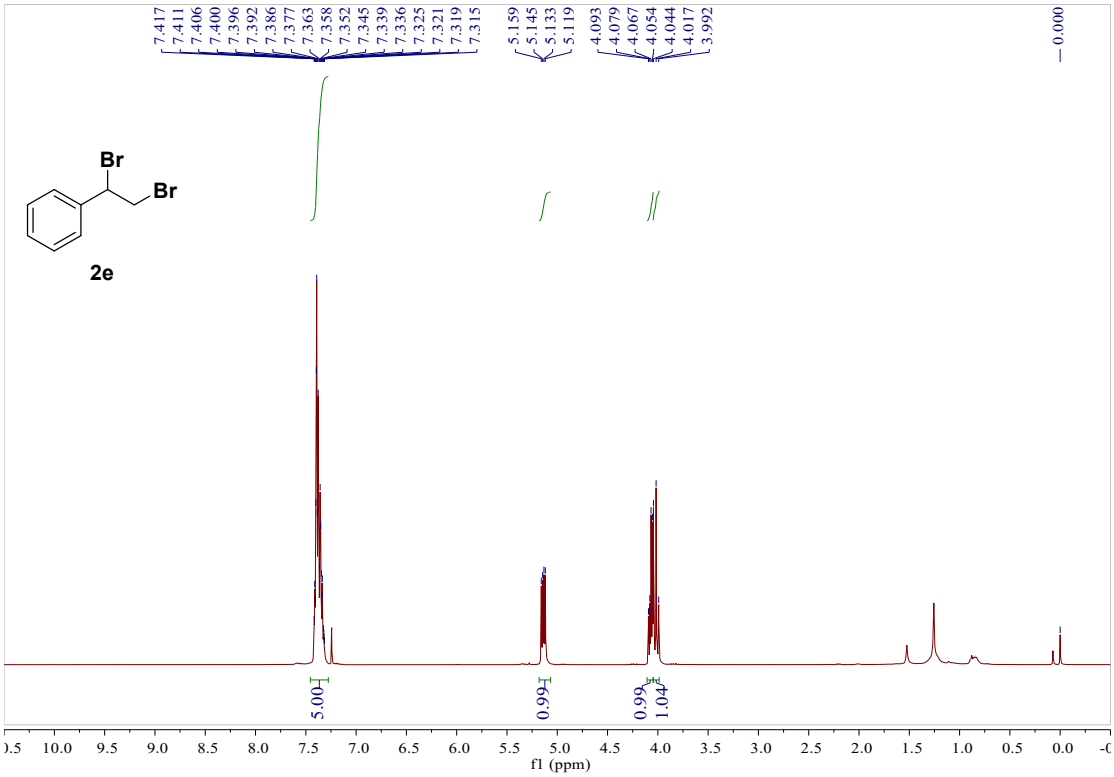
^{1}H NMR spectra for compound (2d)



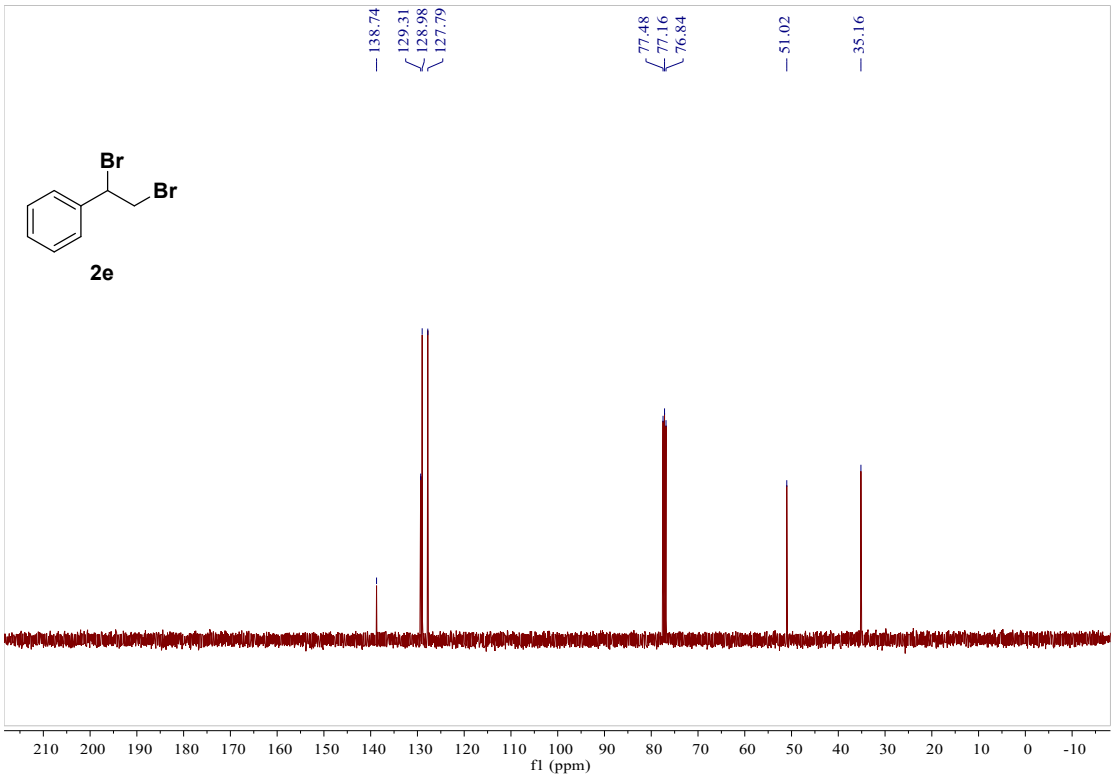
^{13}C NMR spectra for compound (2d)



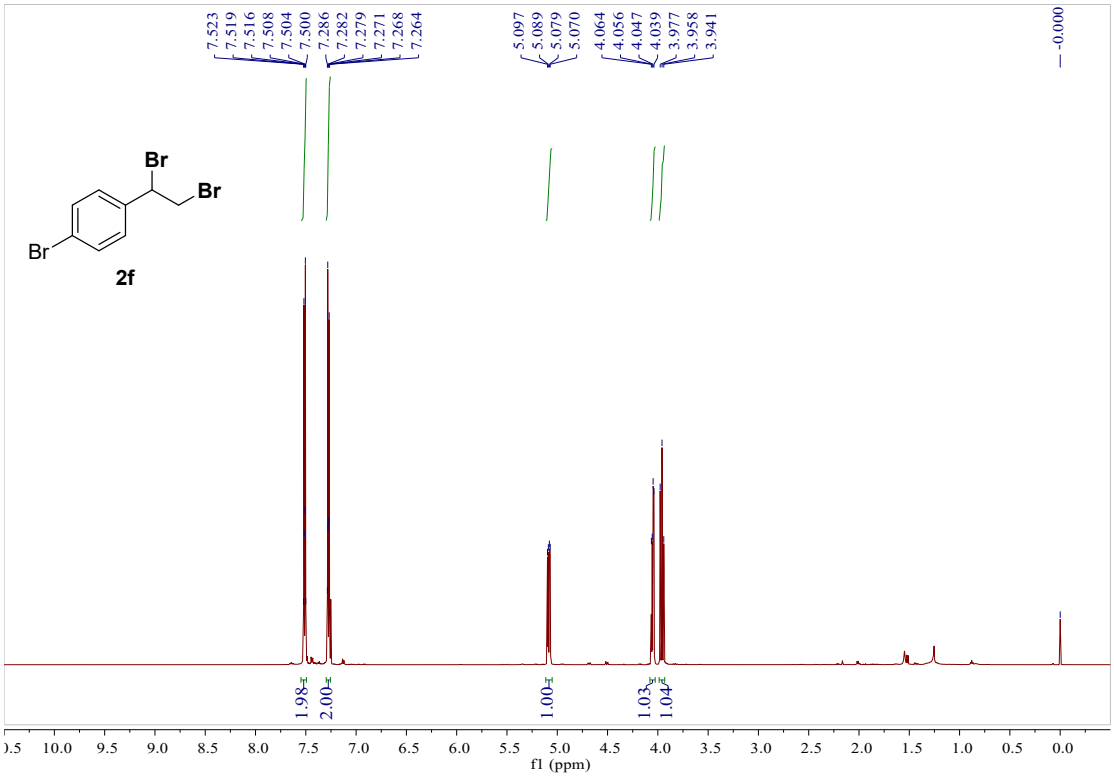
^{1}H NMR spectra for compound (2e)



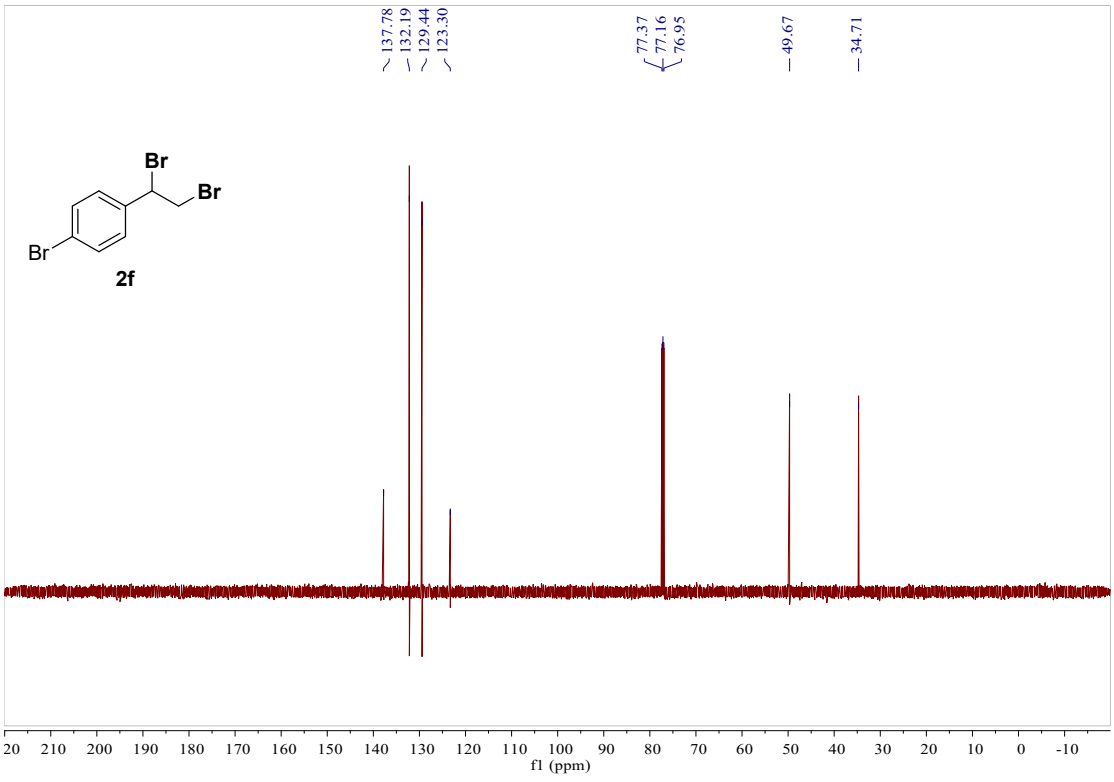
^{13}C NMR spectra for compound (2e)



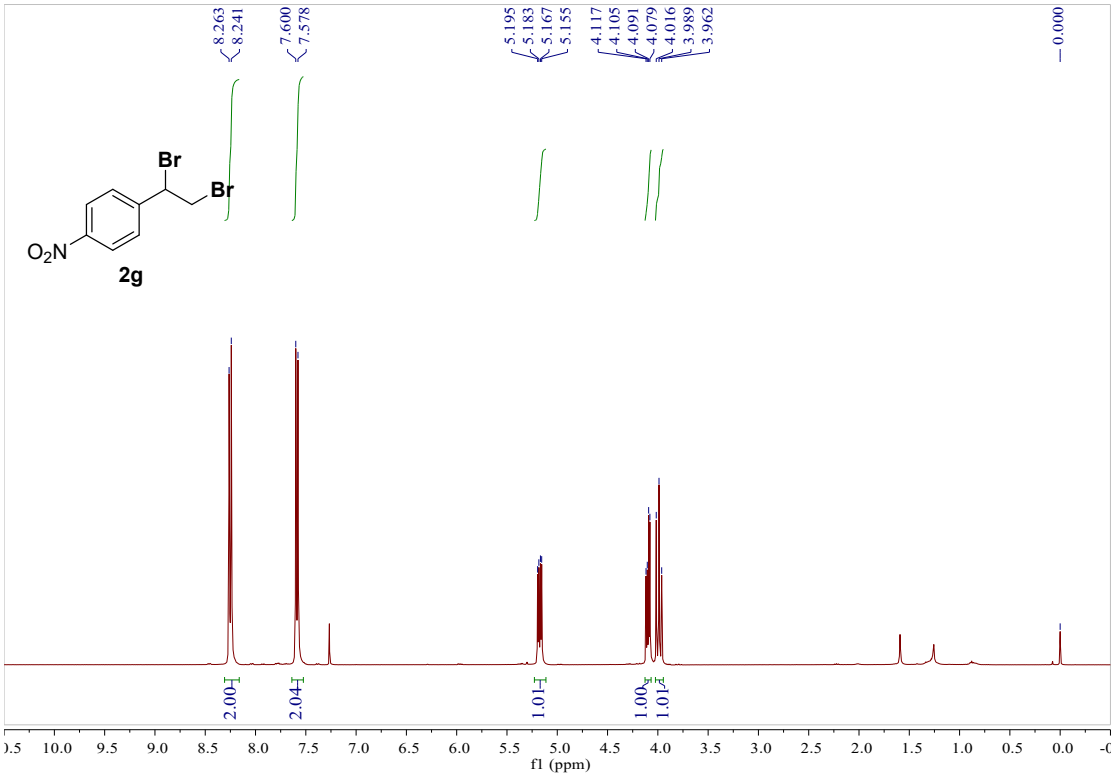
^{1}H NMR spectra for compound (2f)



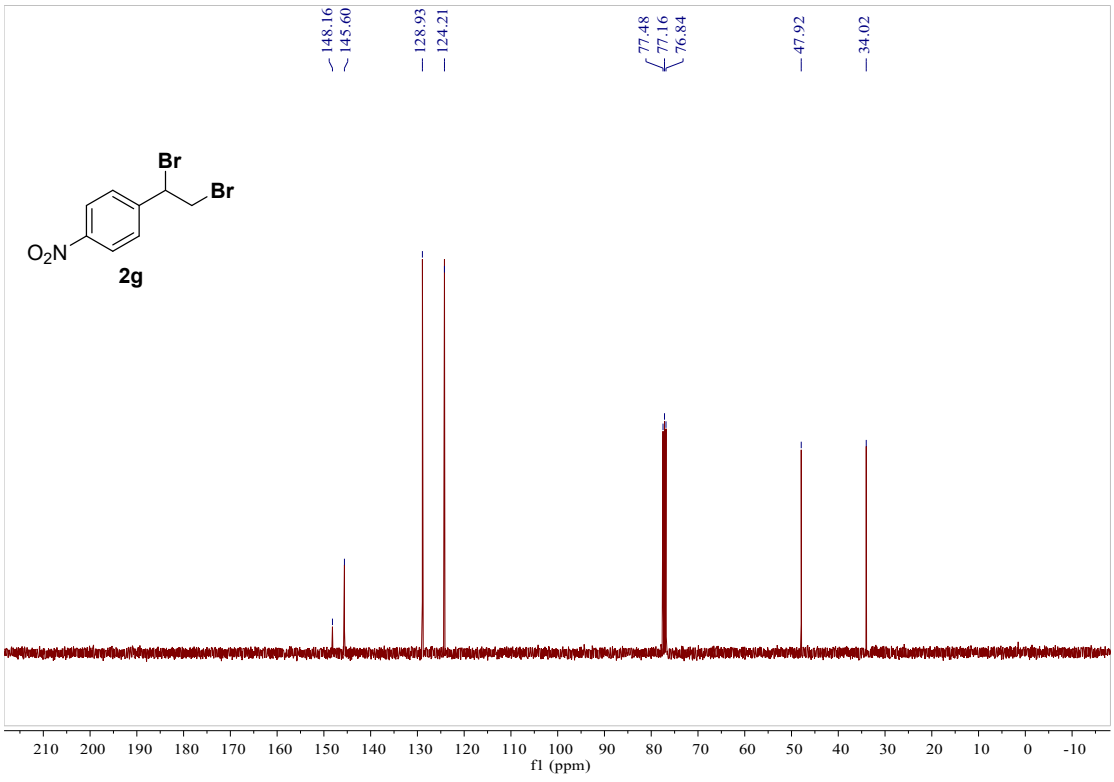
^{13}C NMR spectra for compound (2f)



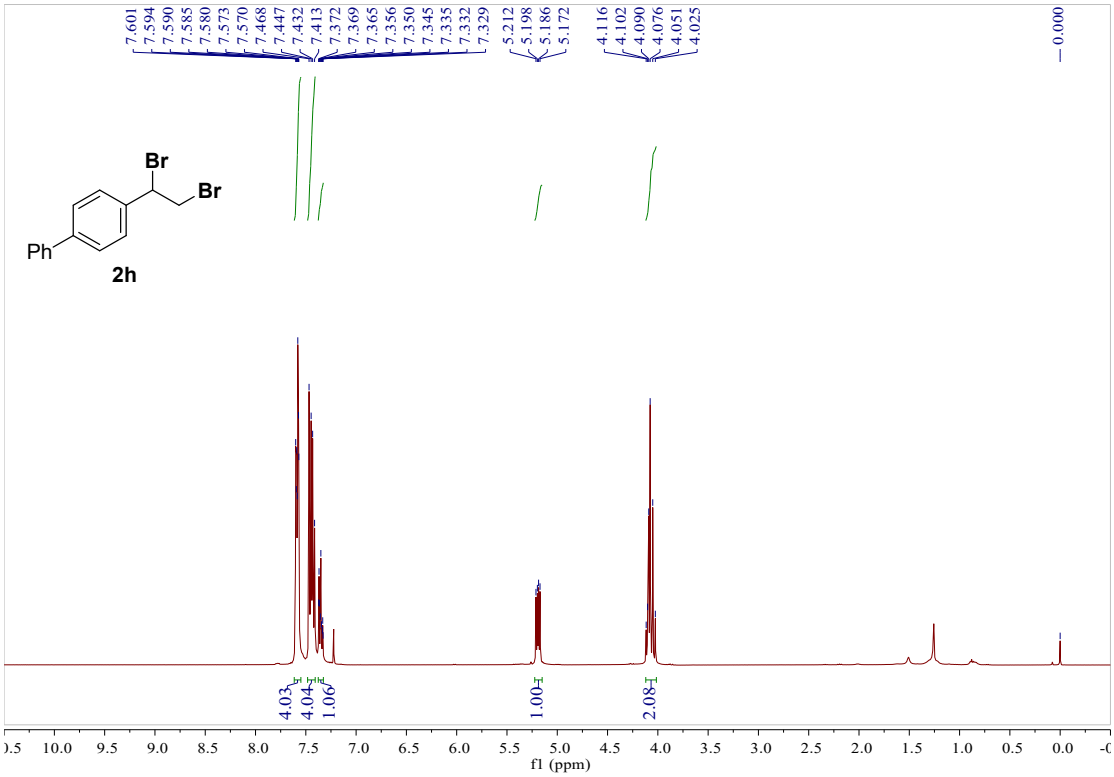
^{1}H NMR spectra for compound (2g)



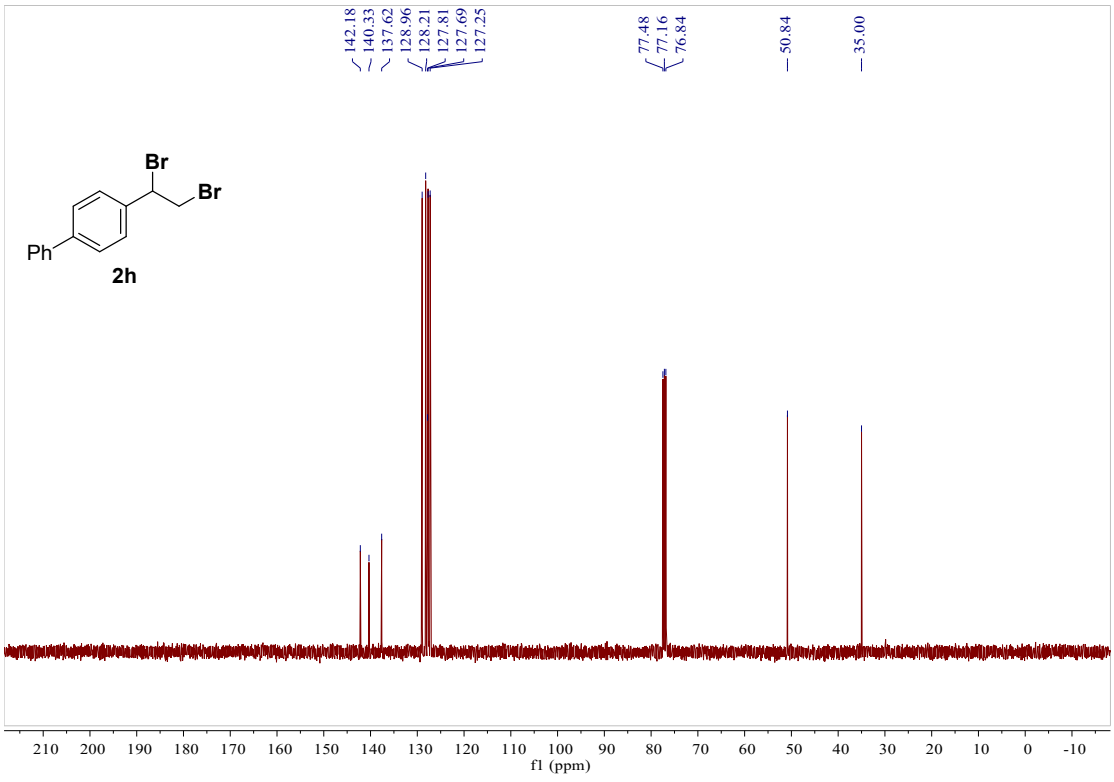
^{13}C NMR spectra for compound (2g)



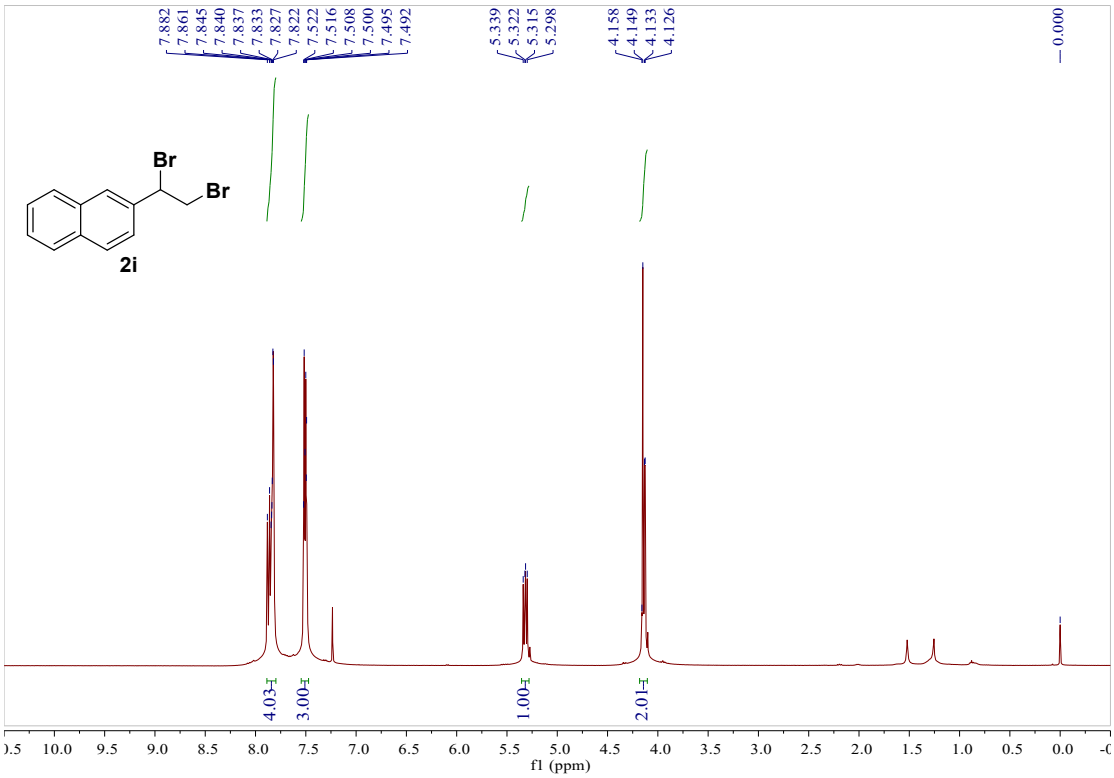
^{1}H NMR spectra for compound (2h)



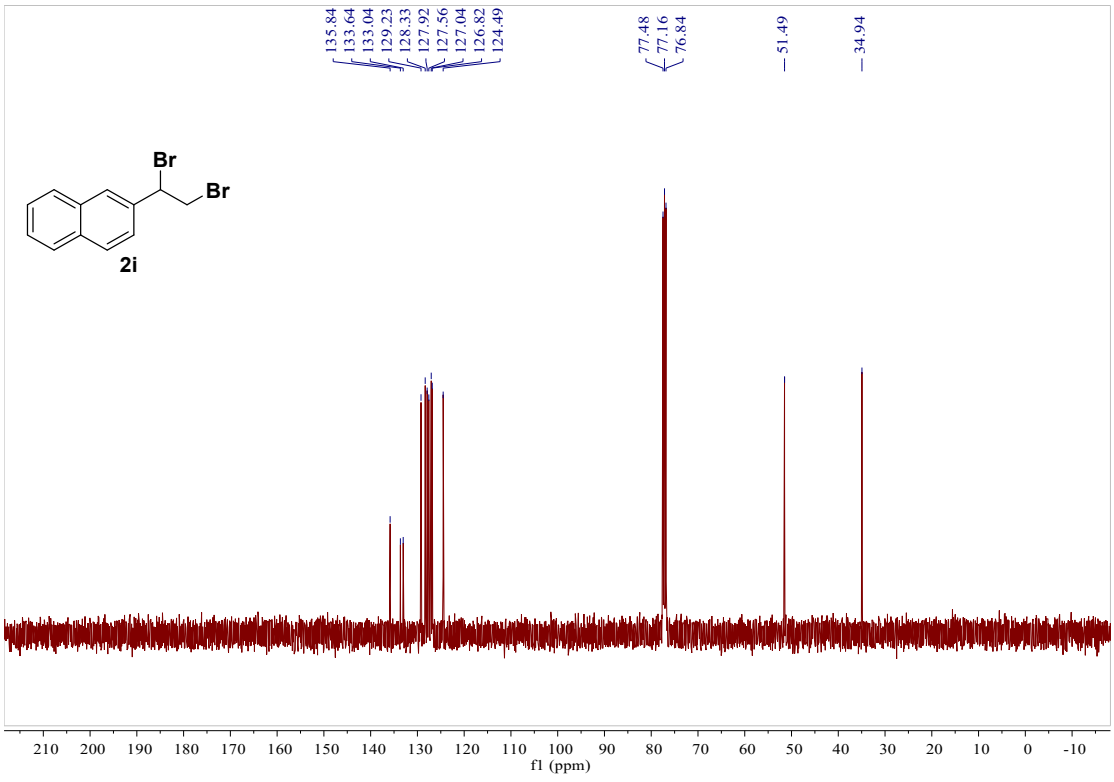
^{13}C NMR spectra for compound (2h)



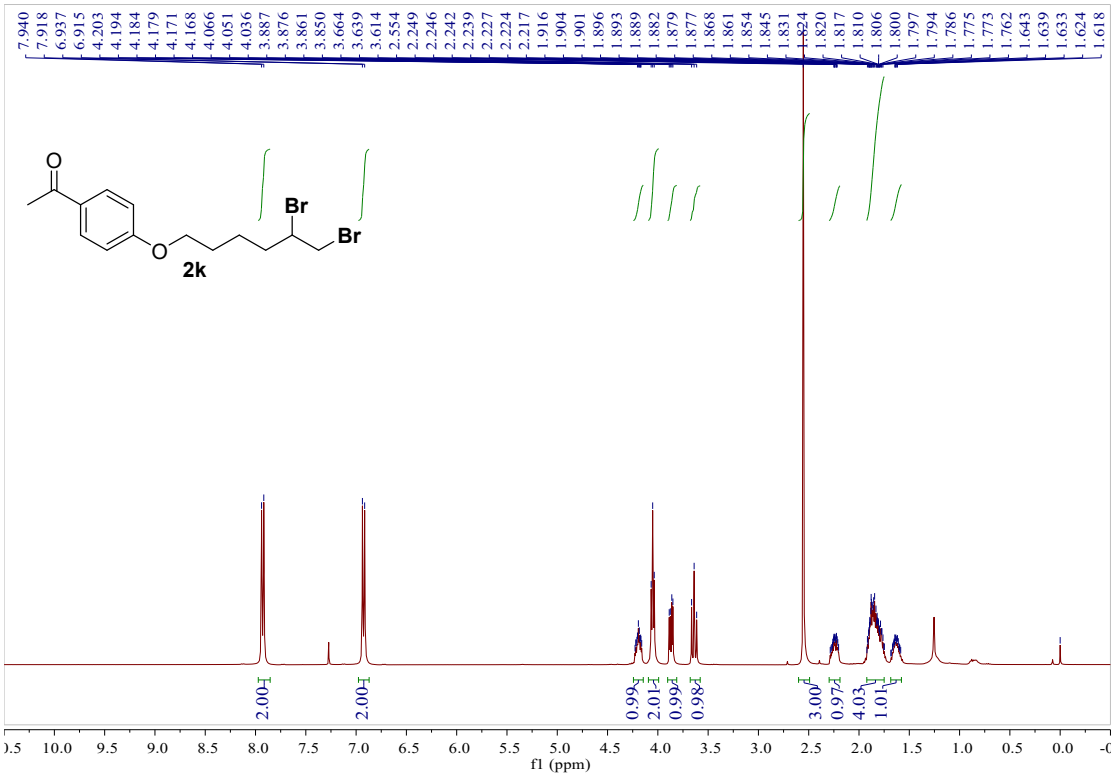
^{1}H NMR spectra for compound (2i)



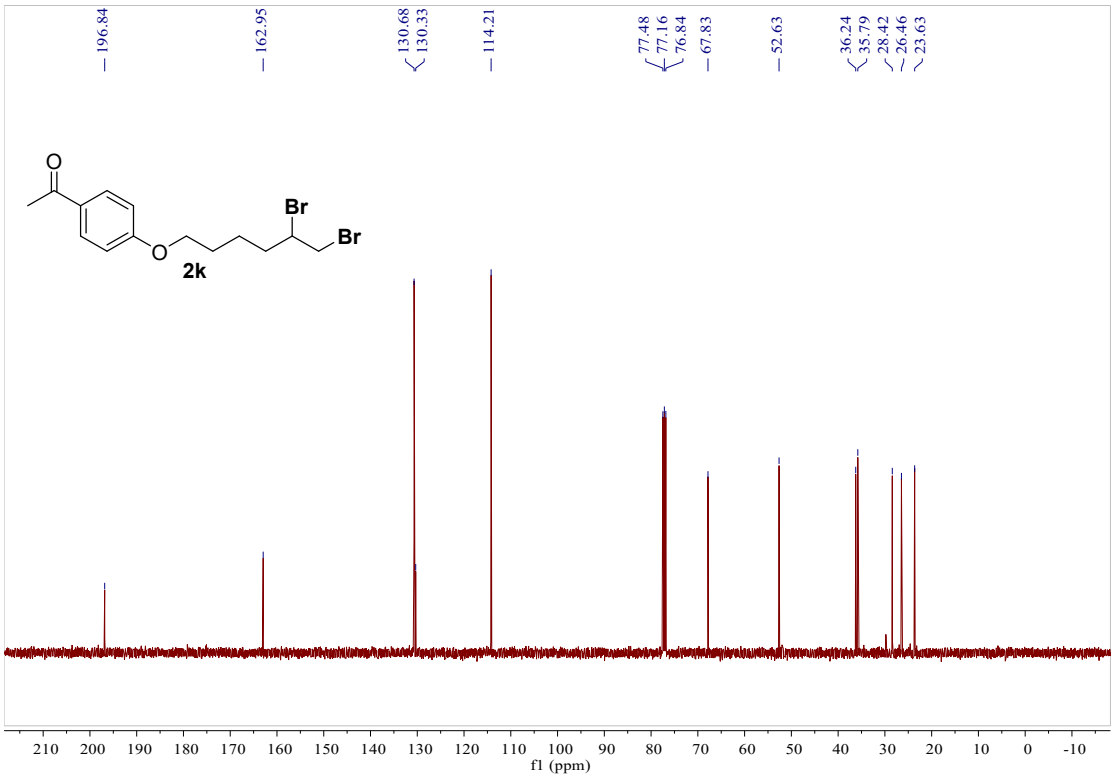
^{13}C NMR spectra for compound (2i)



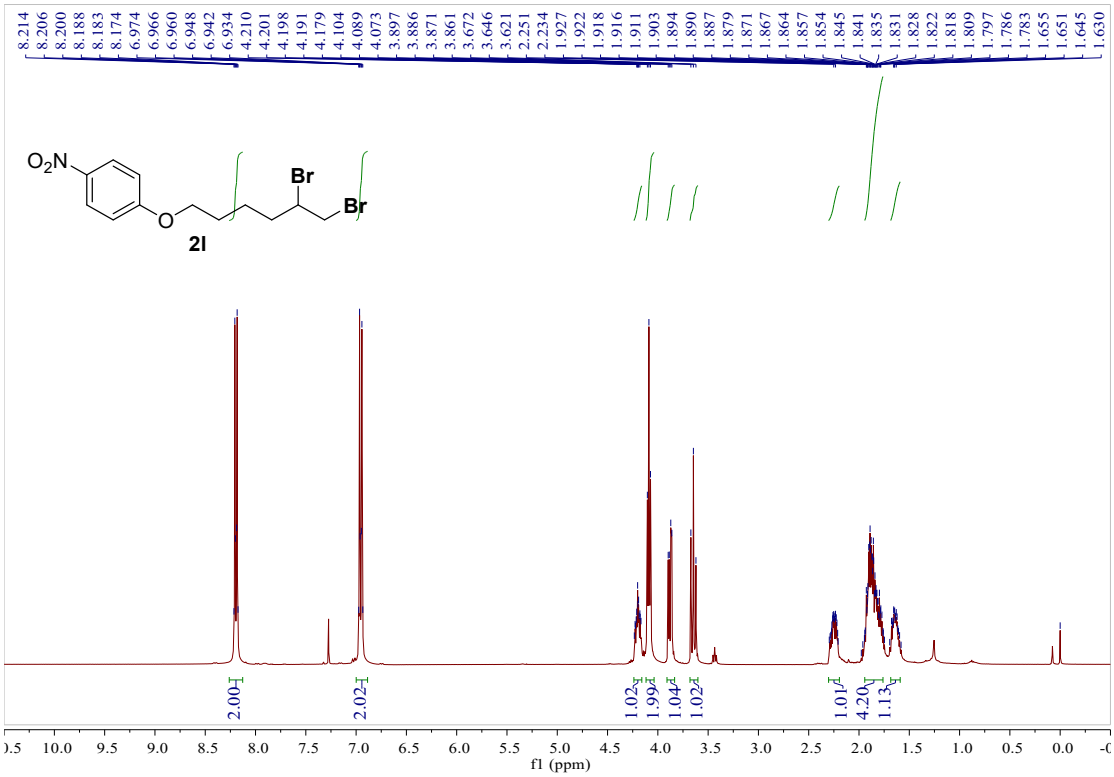
^{1}H NMR spectra for compound (2k)



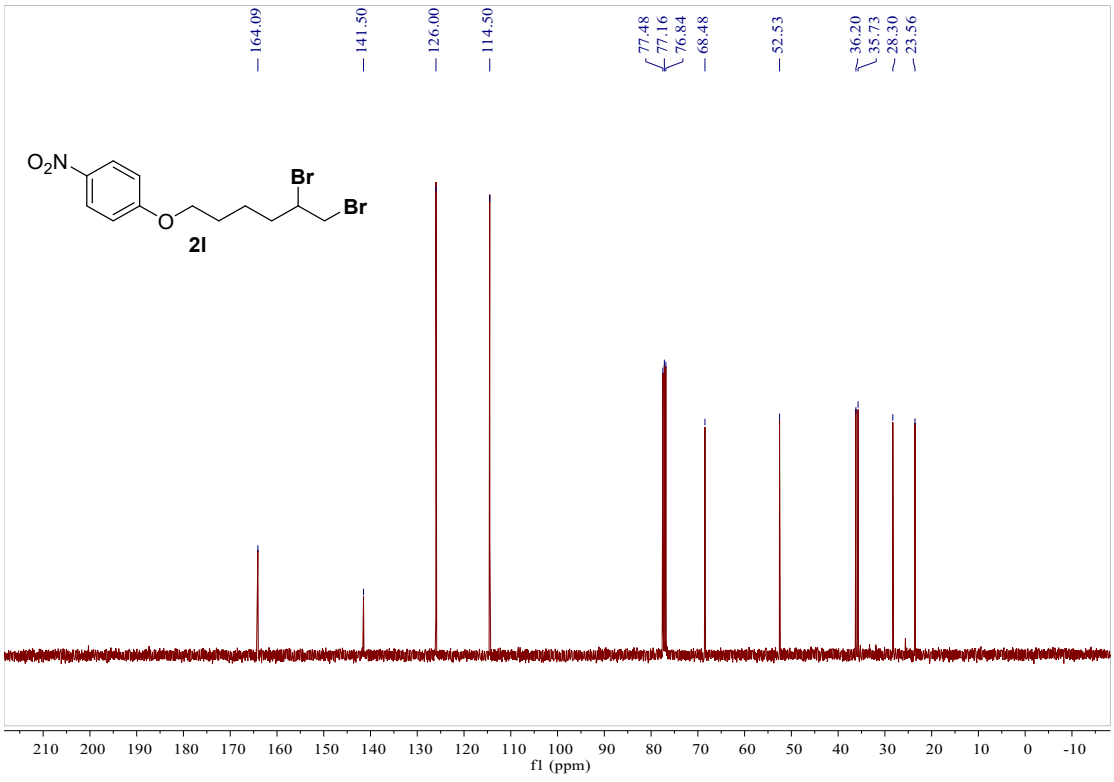
^{13}C NMR spectra for compound (2k)



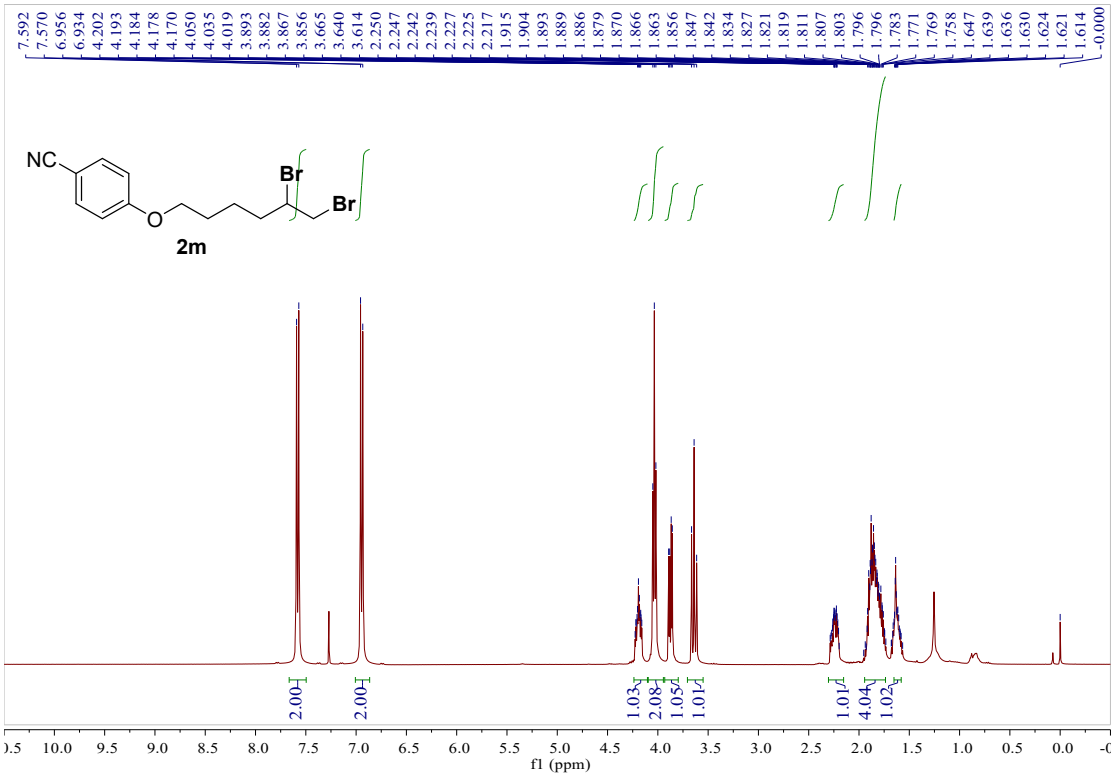
^{1}H NMR spectra for compound (2l)



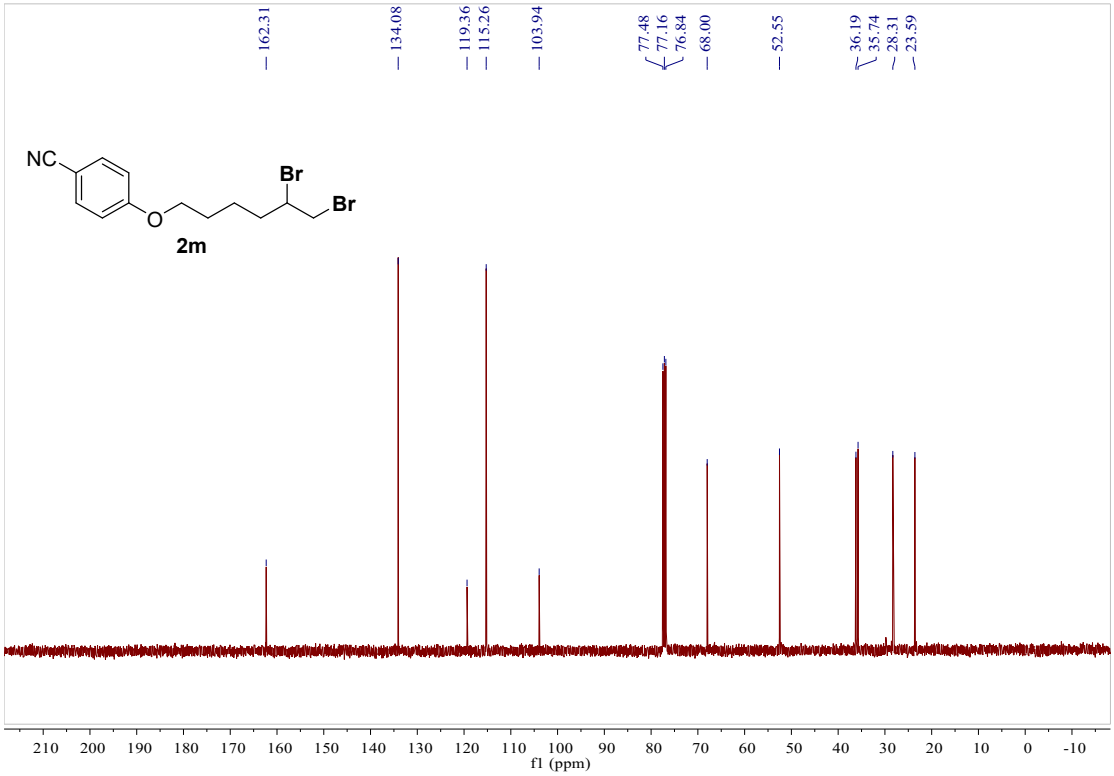
^{13}C NMR spectra for compound (2l)



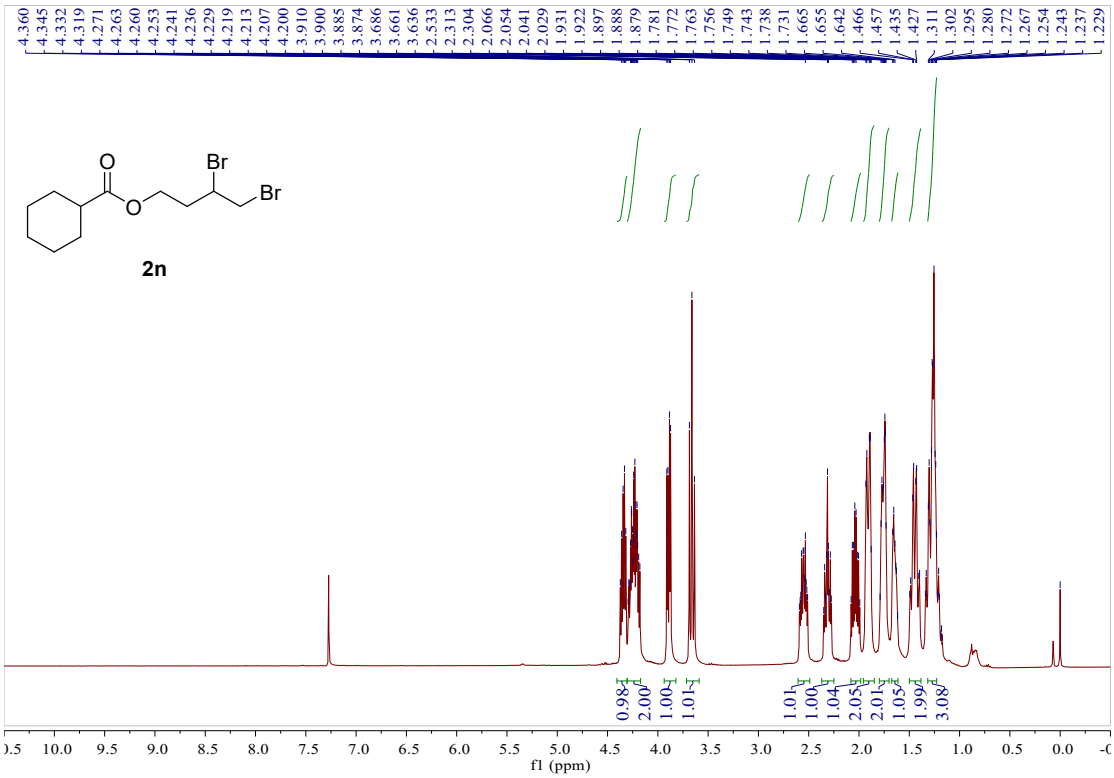
^{1}H NMR spectra for compound (2m)



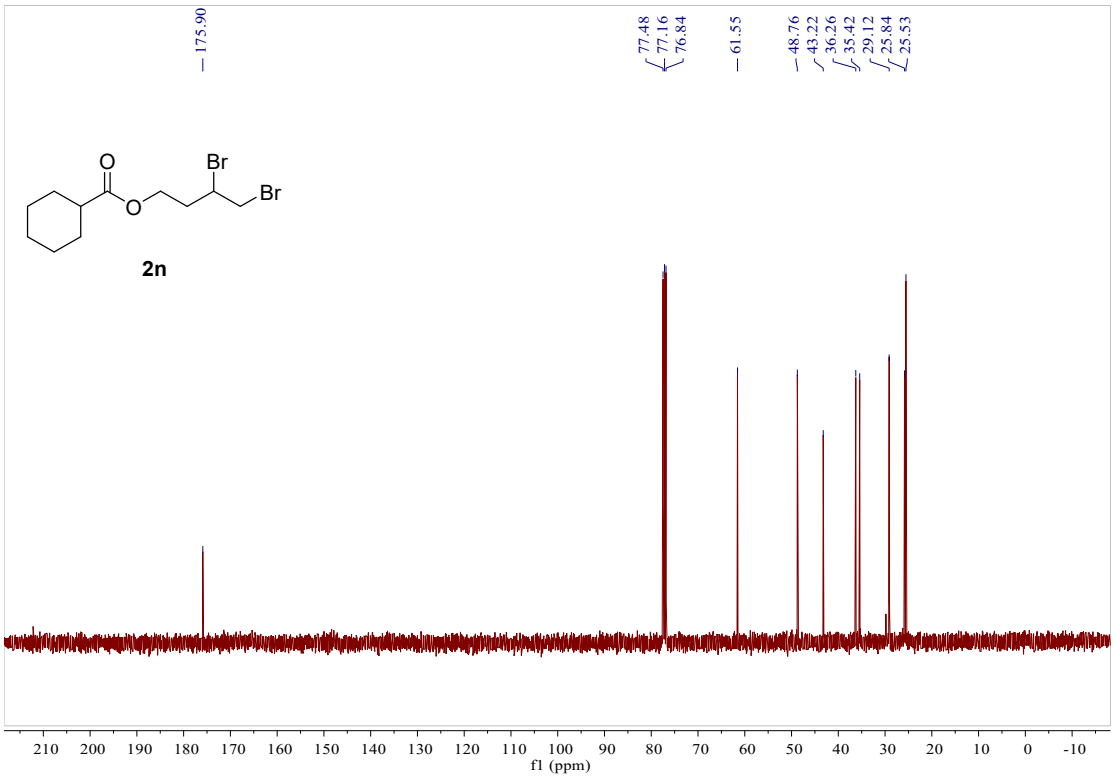
^{13}C NMR spectra for compound (2m)



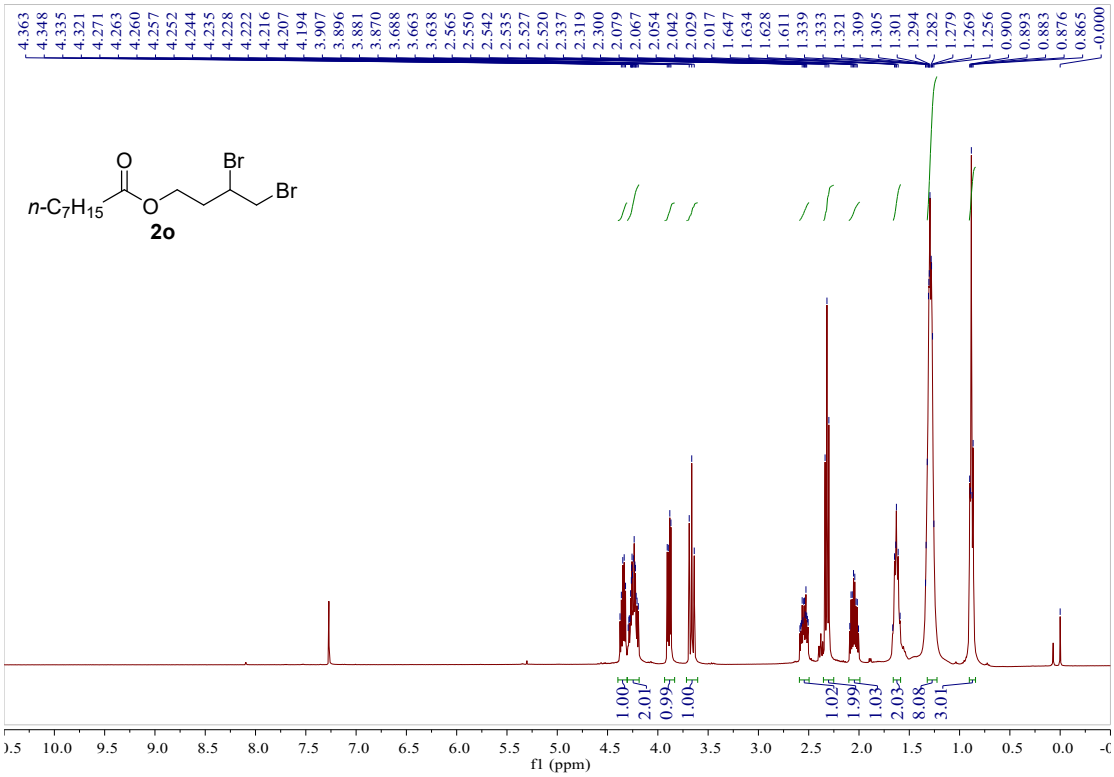
^{1}H NMR spectra for compound (2n)



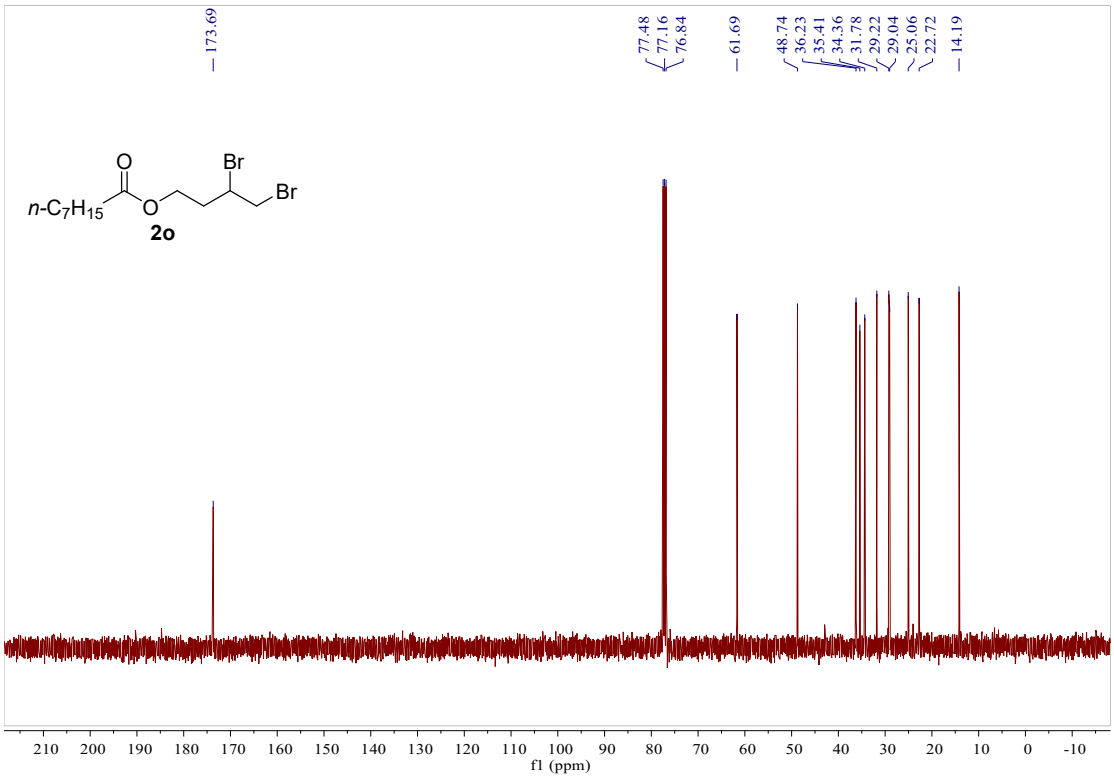
^{13}C NMR spectra for compound (2n)



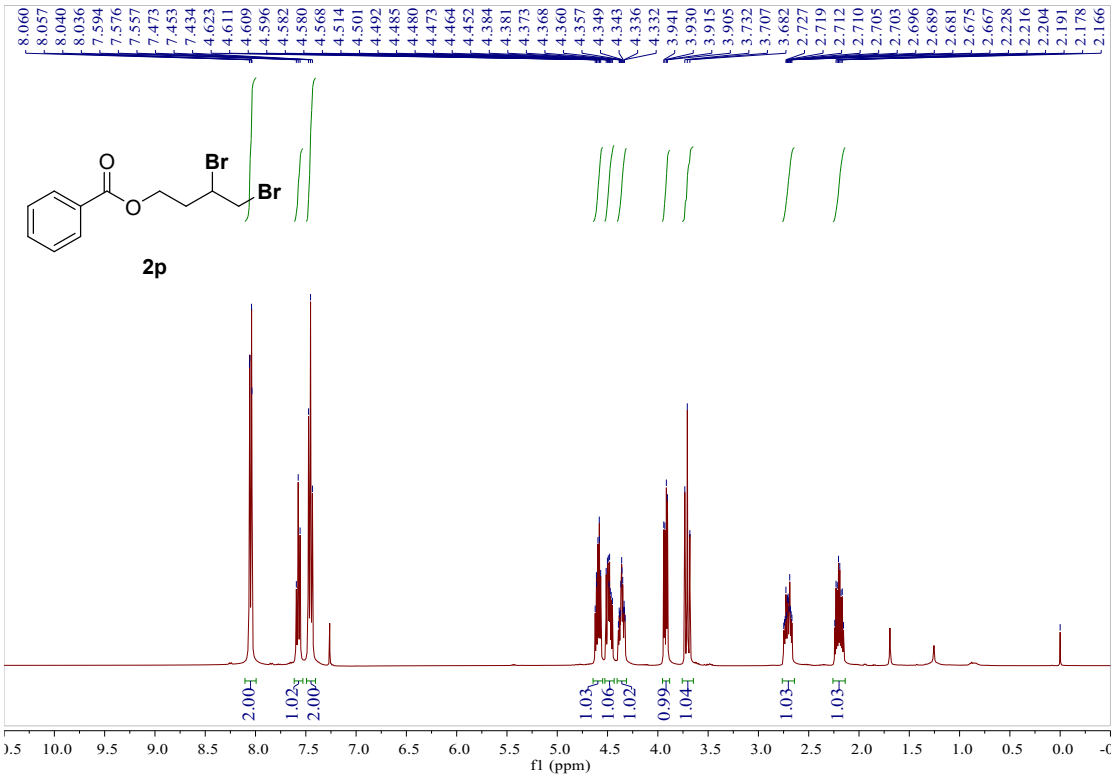
^{1}H NMR spectra for compound (2o)



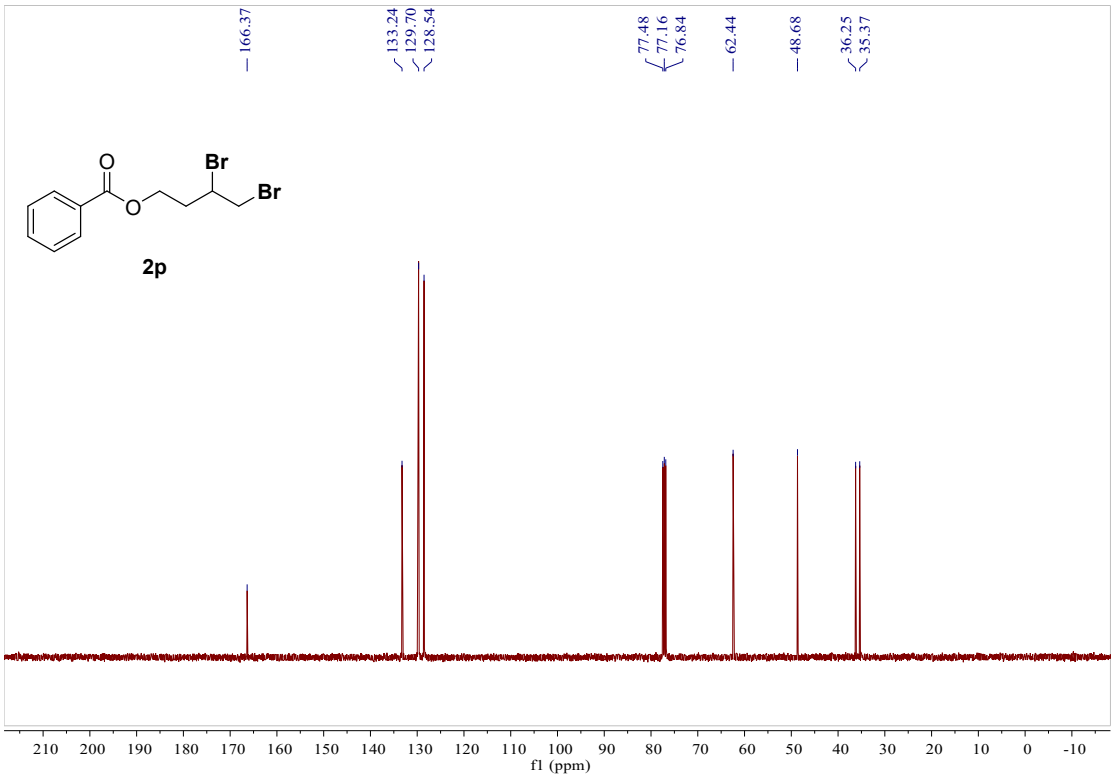
^{13}C NMR spectra for compound (2o)



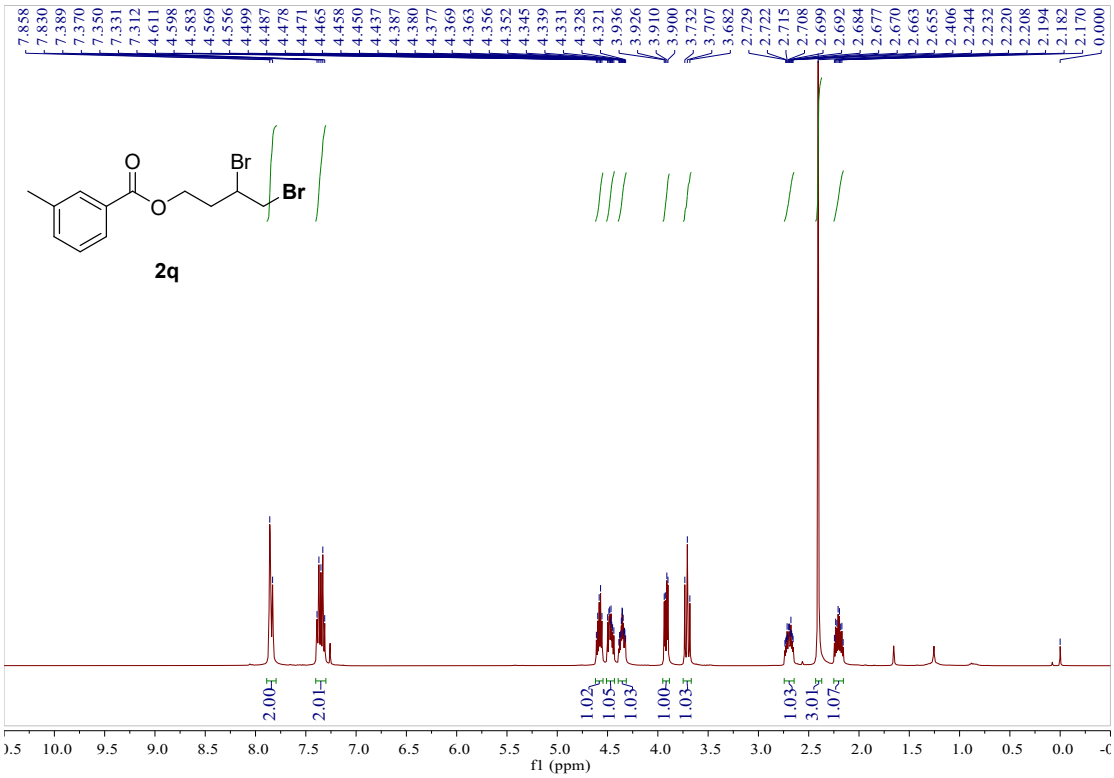
^{1}H NMR spectra for compound (2p)



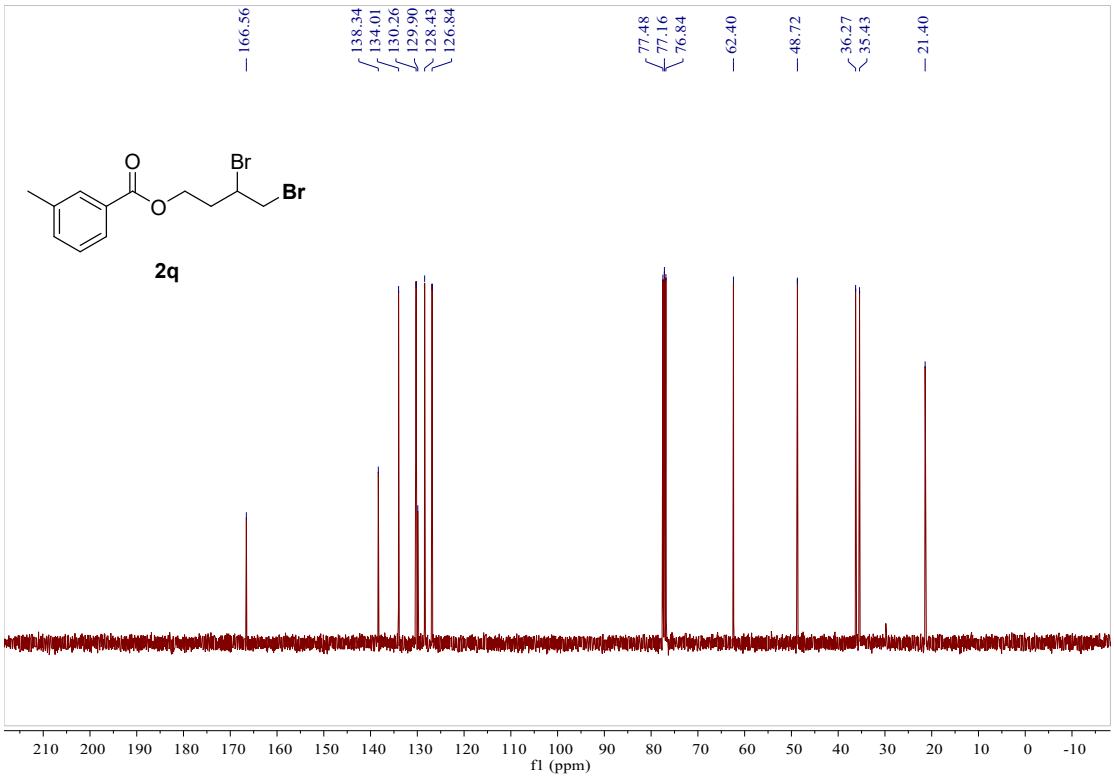
^{13}C NMR spectra for compound (2p)



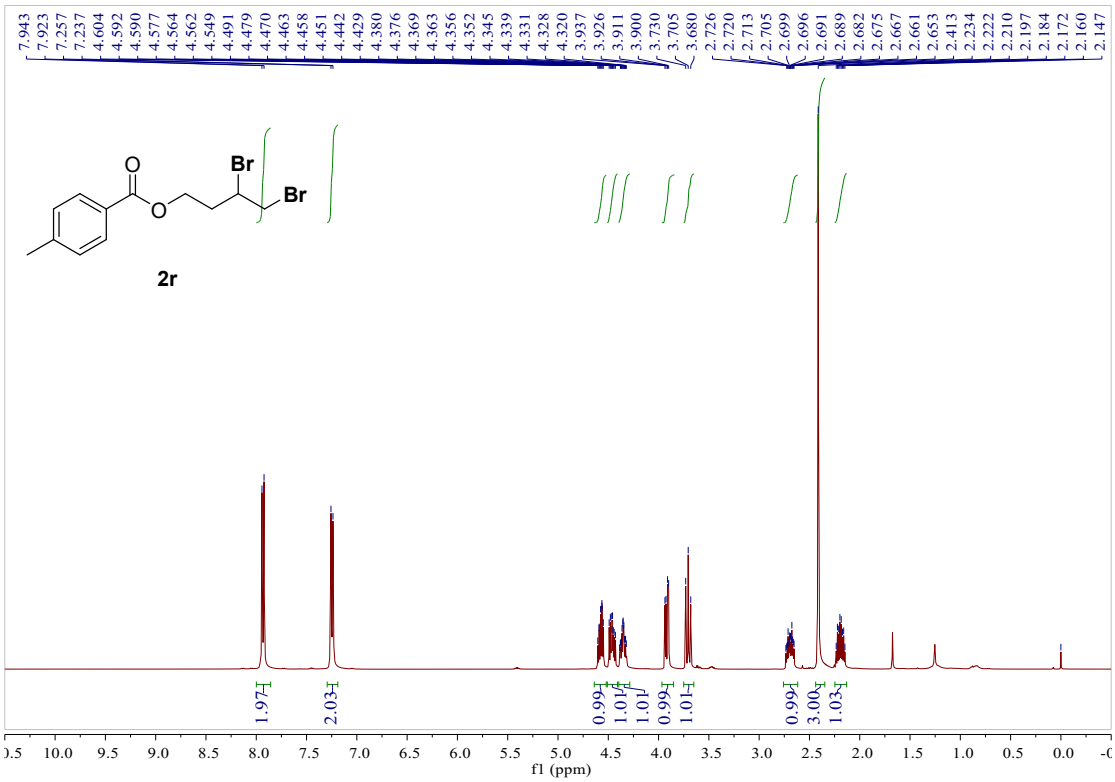
^{1}H NMR spectra for compound (2q)



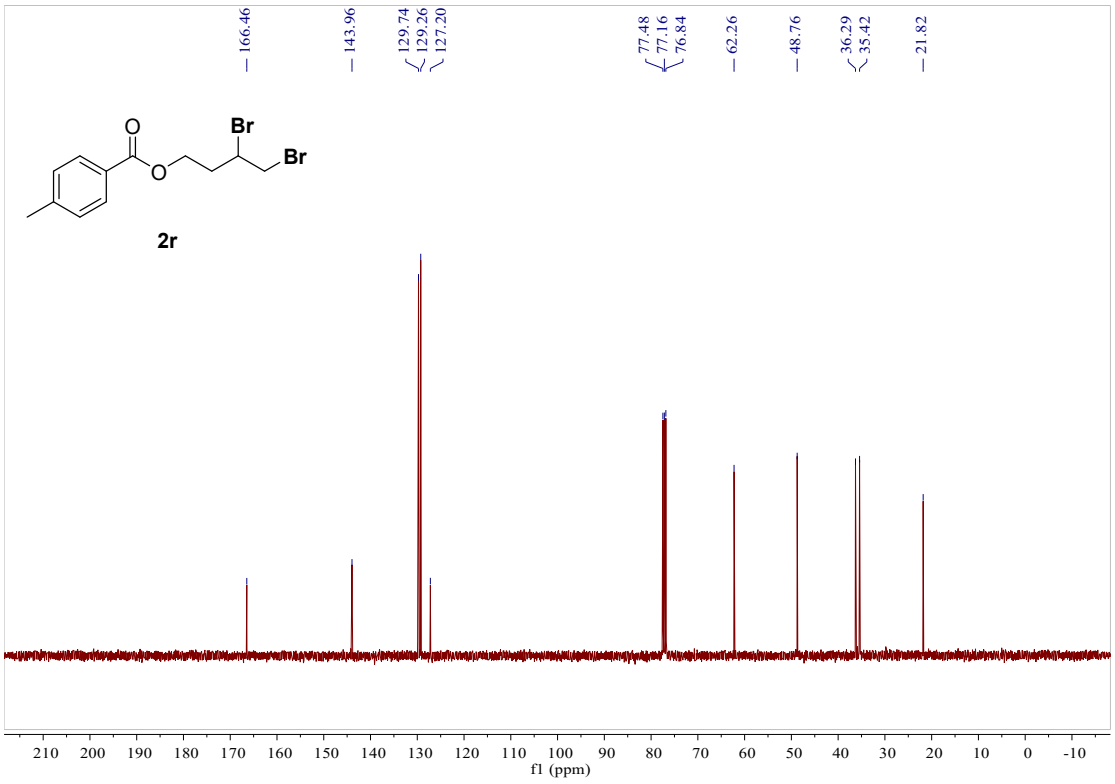
^{13}C NMR spectra for compound (2q)



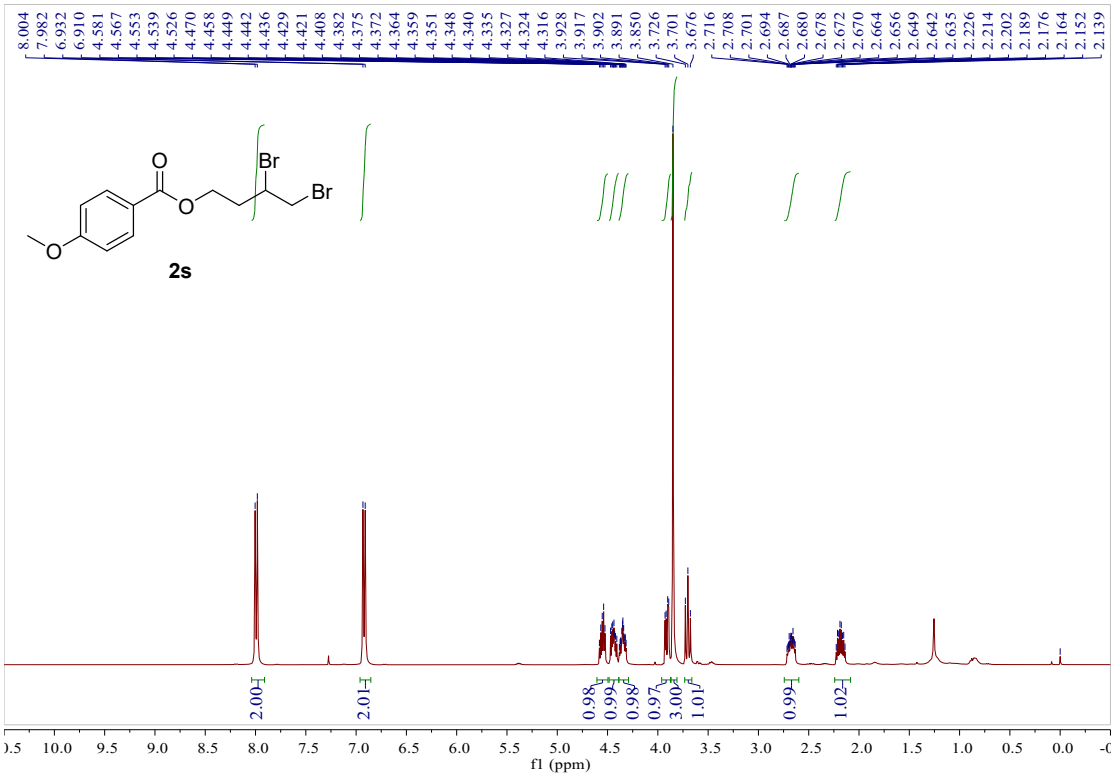
^{1}H NMR spectra for compound (2r)



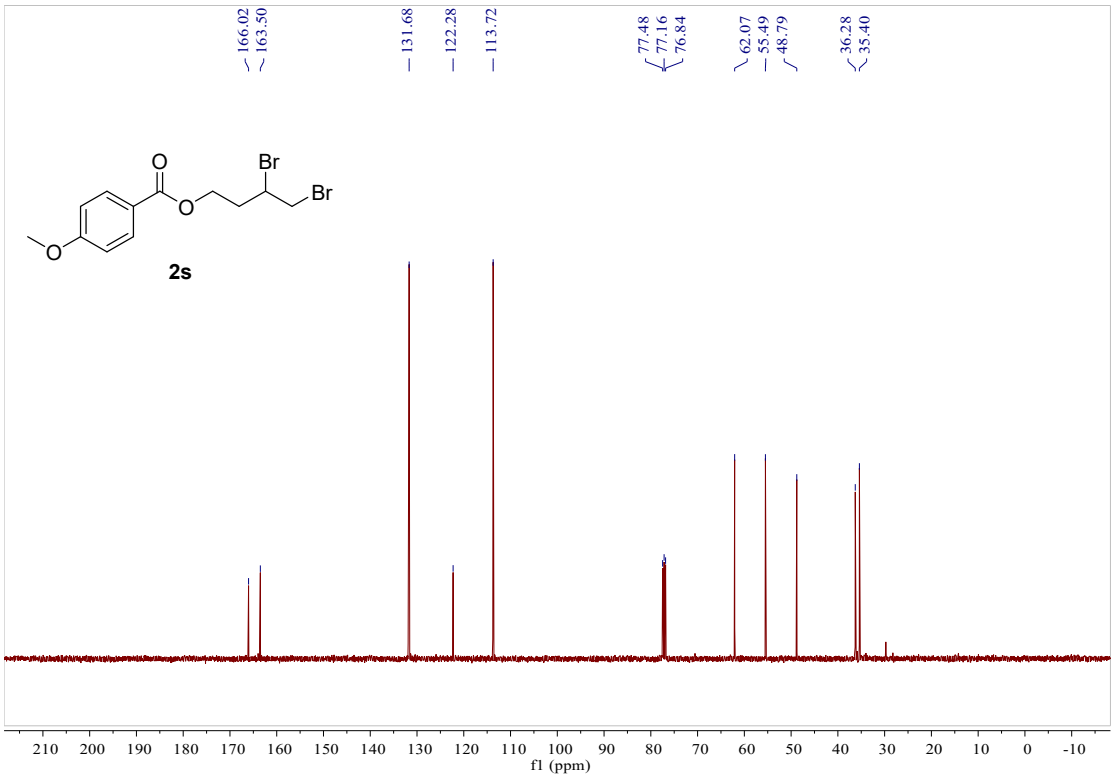
^{13}C NMR spectra for compound (2r)



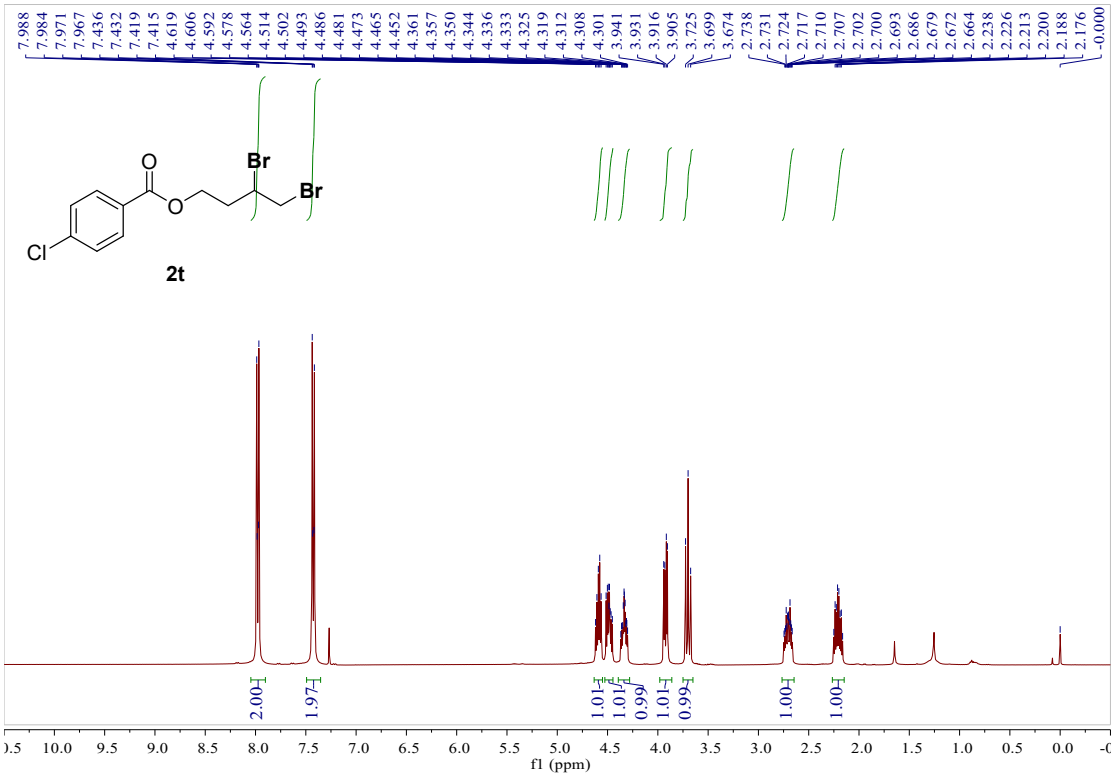
^{1}H NMR spectra for compound (2s)



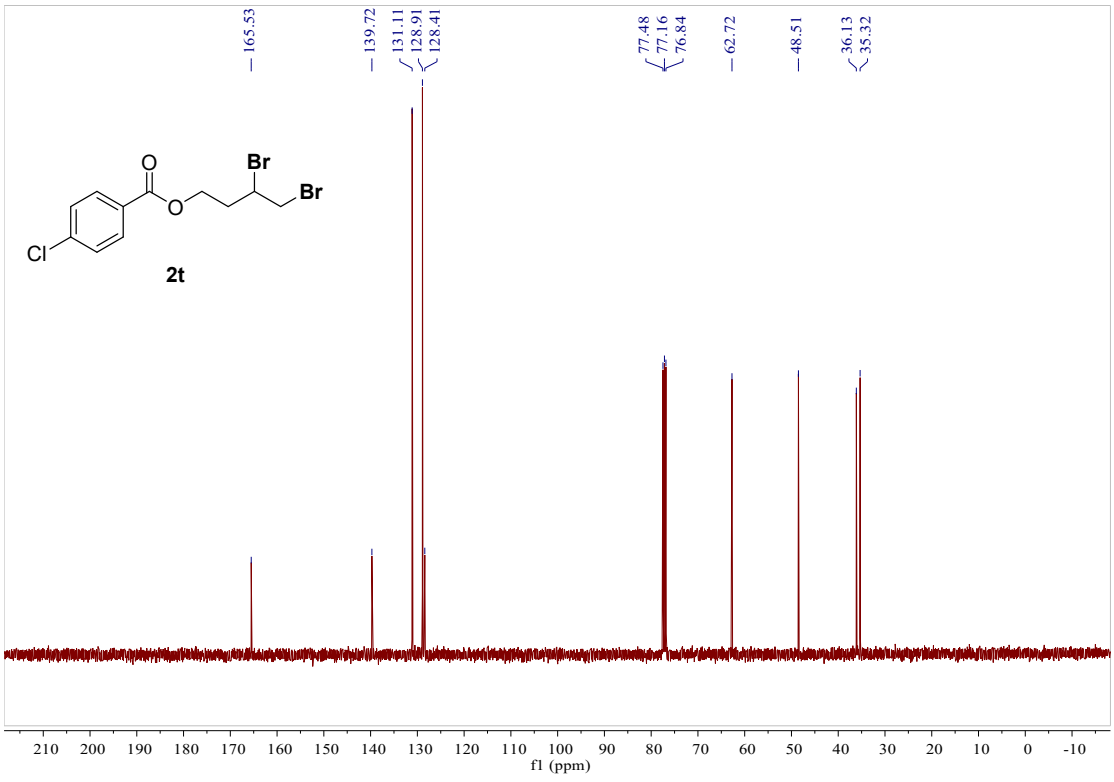
^{13}C NMR spectra for compound (2s)



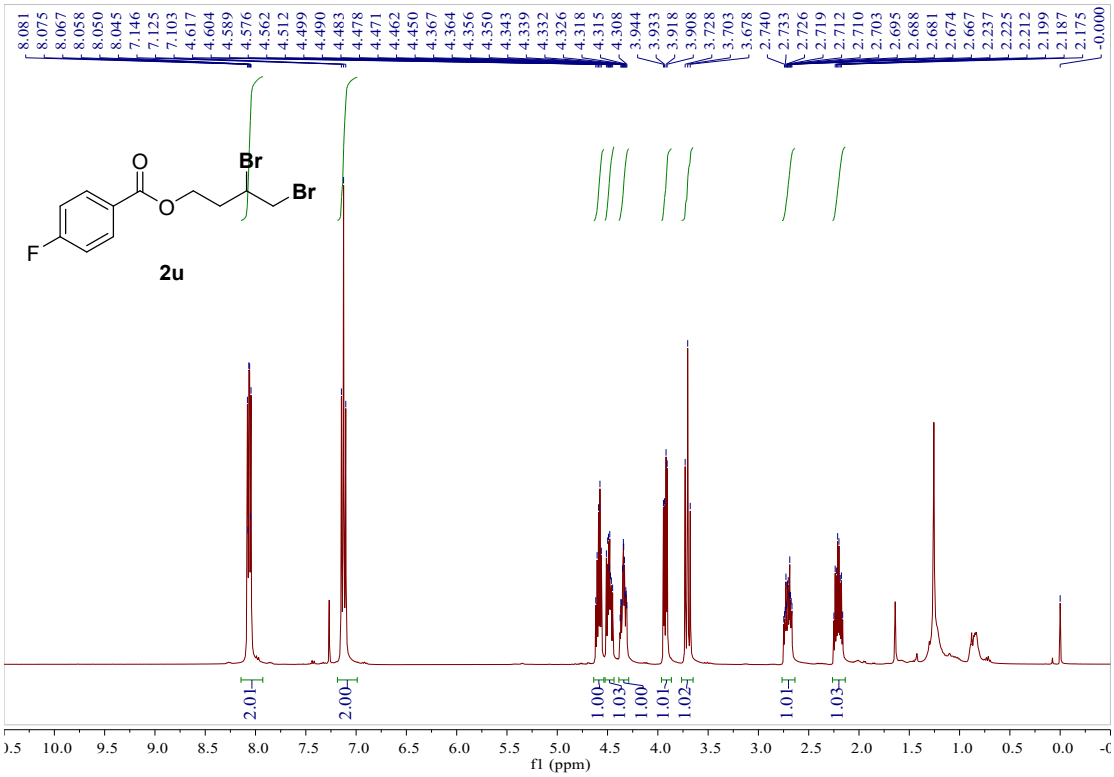
^{1}H NMR spectra for compound (2t)



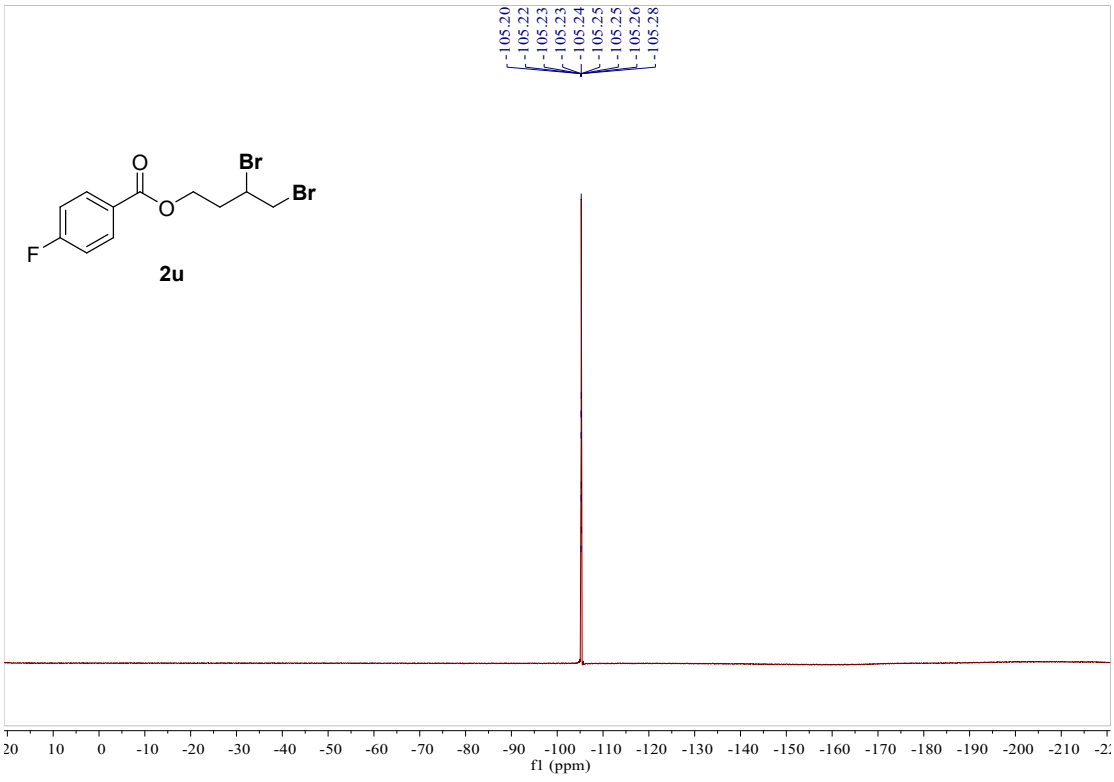
^{13}C NMR spectra for compound (2t)



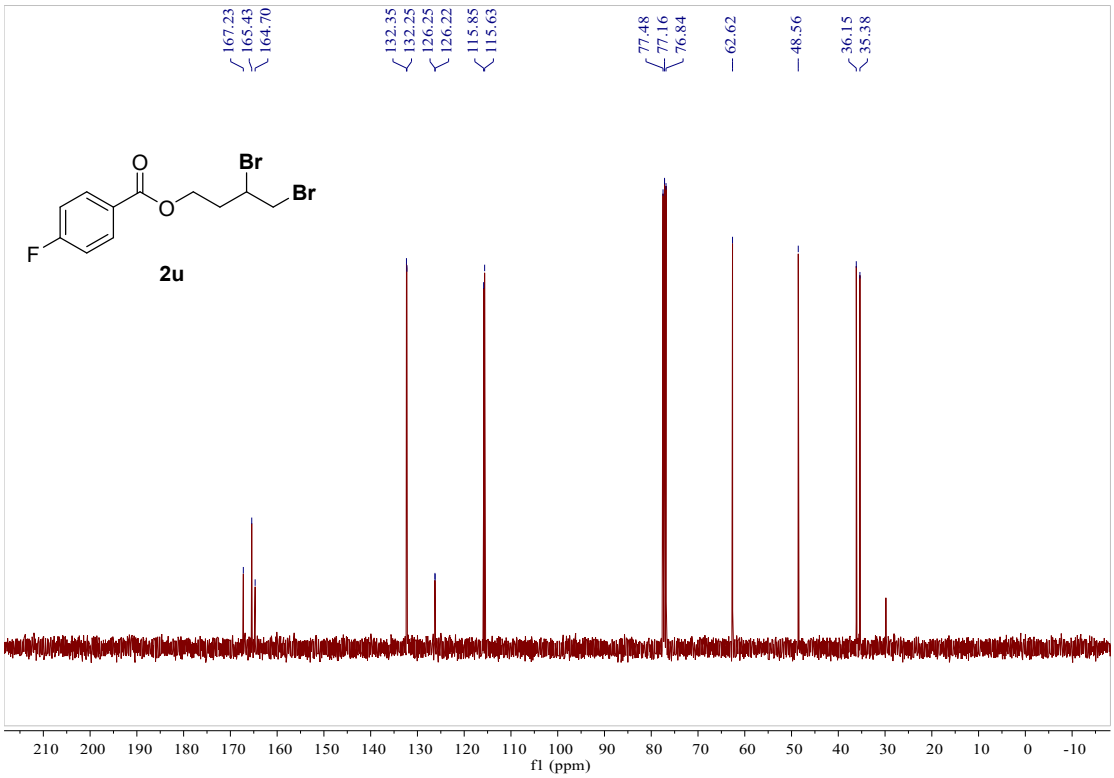
^{1}H NMR spectra for compound (2u)



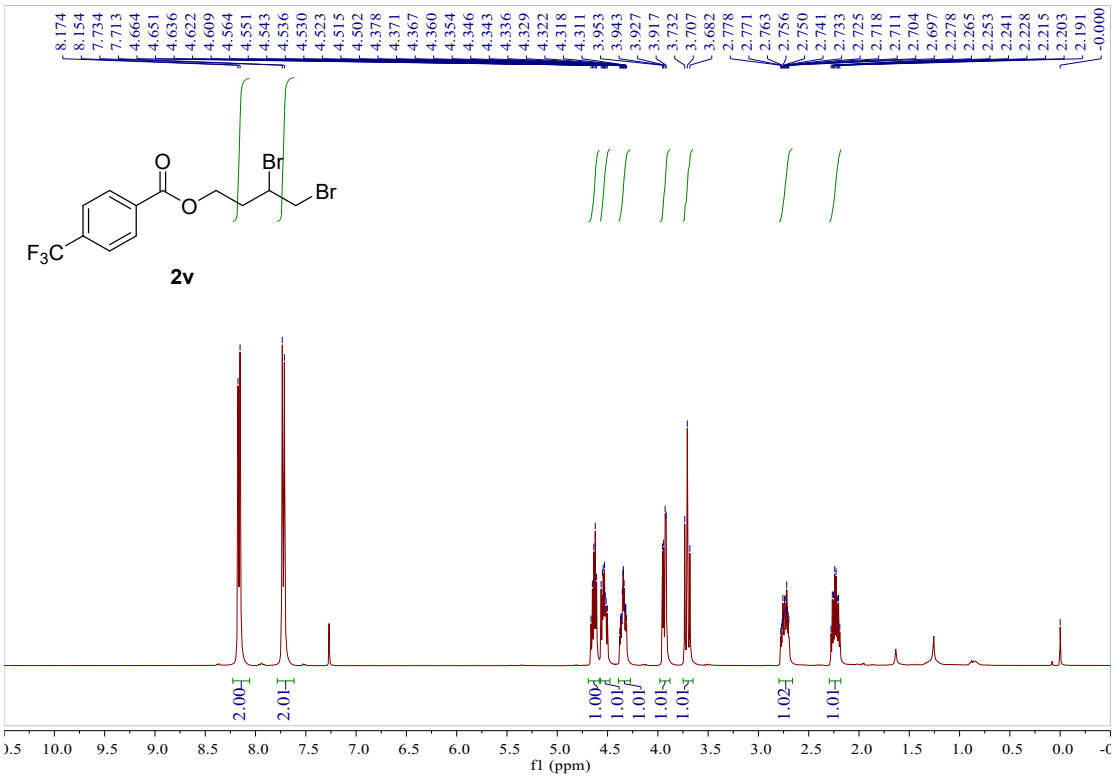
^{19}F NMR spectra for compound (2u)



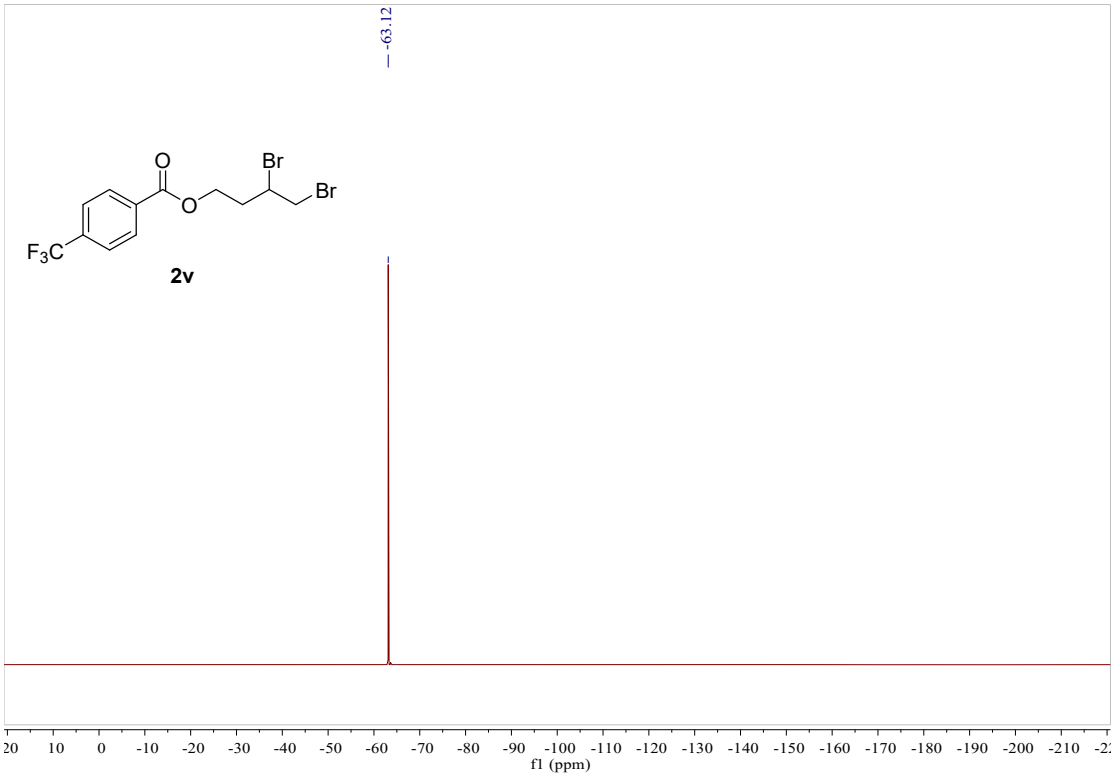
^{13}C NMR spectra for compound (2u)



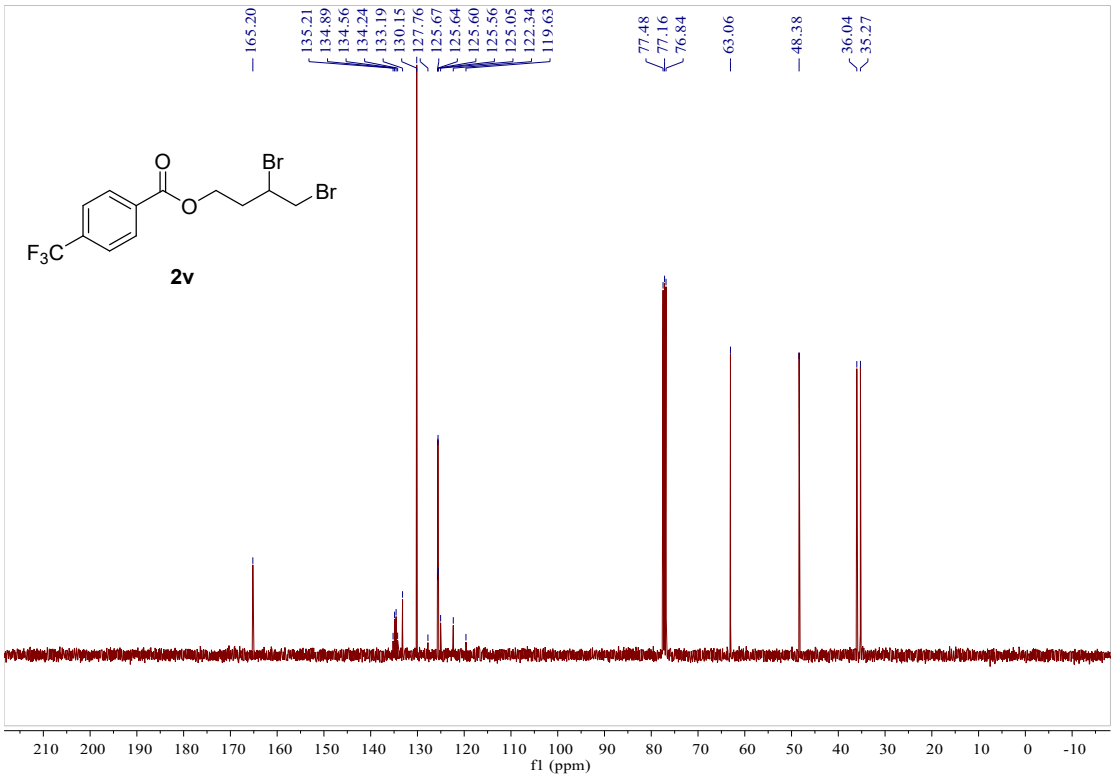
^{1}H NMR spectra for compound (2v)



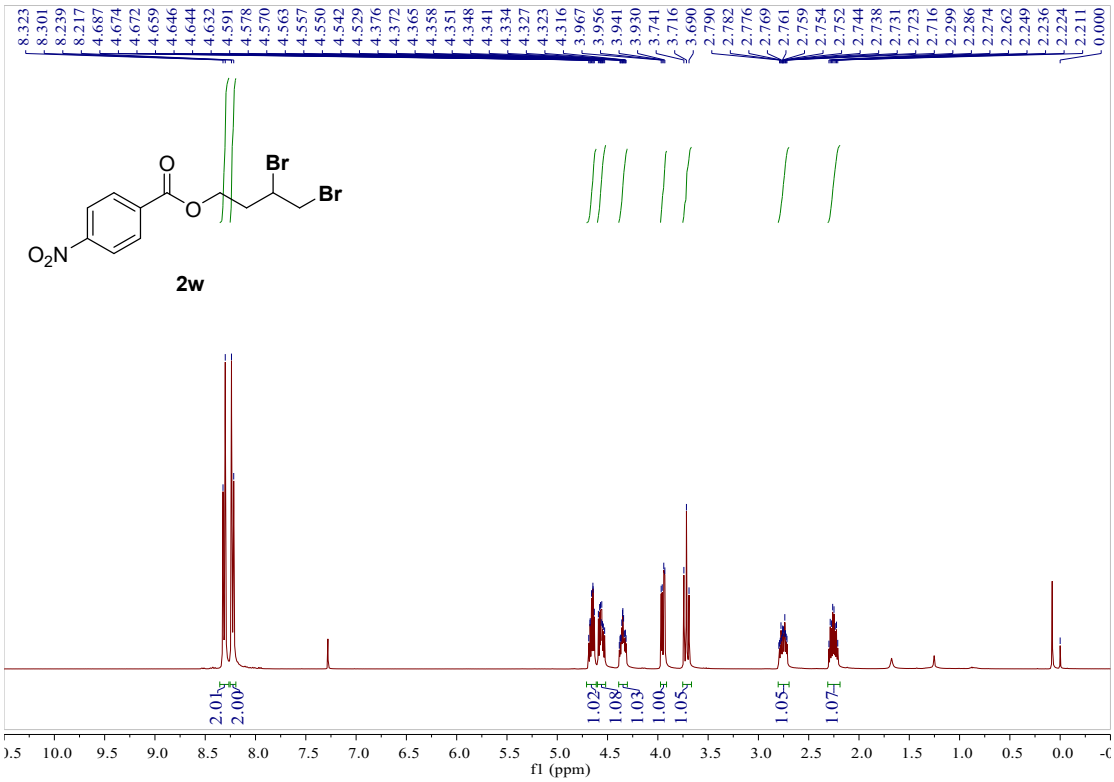
^{19}F NMR spectra for compound (2v)



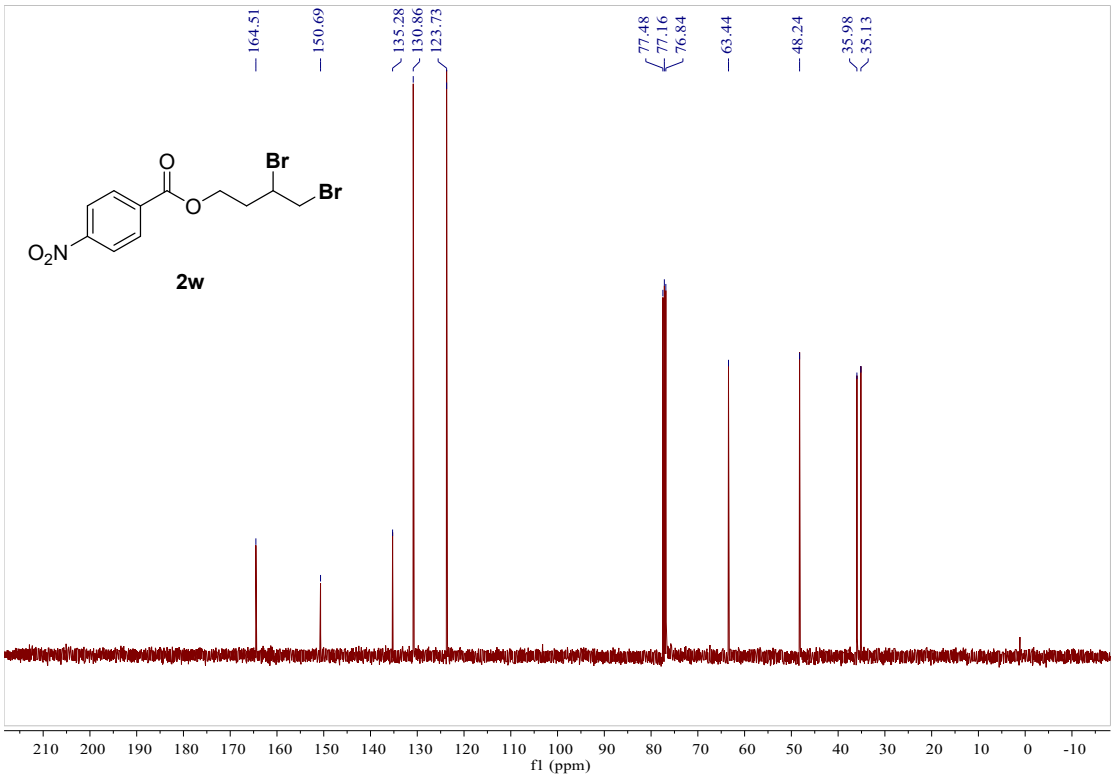
^{13}C NMR spectra for compound (2v)



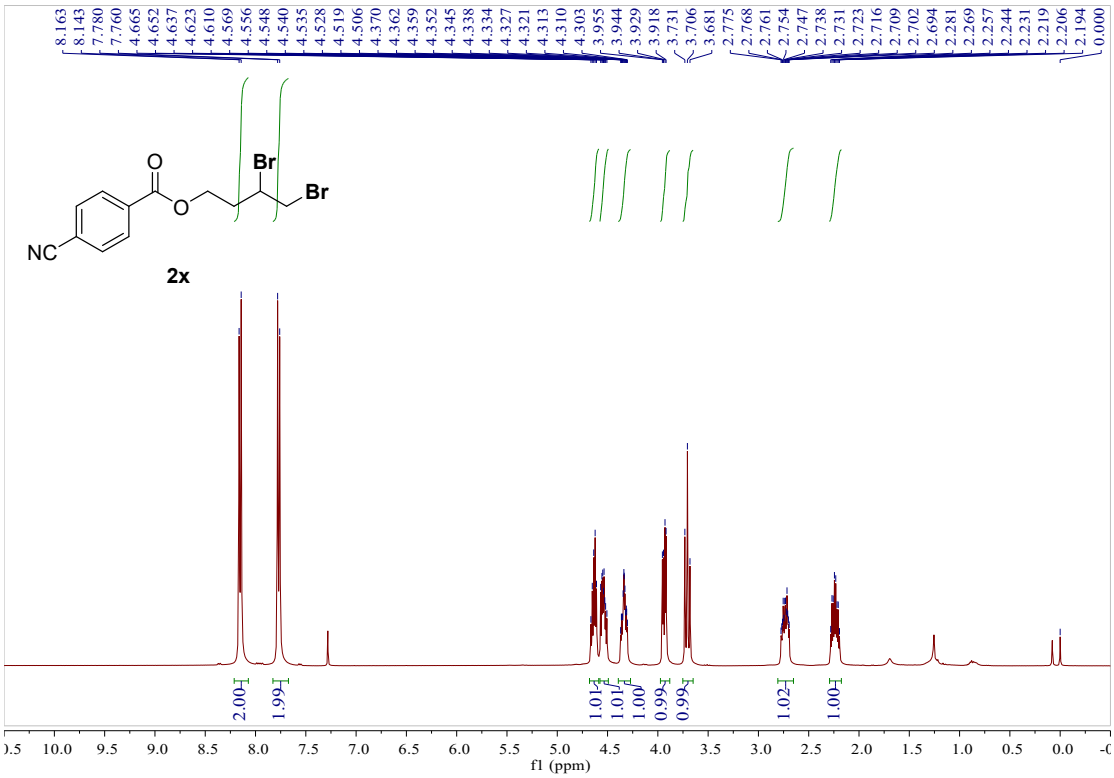
^{1}H NMR spectra for compound (2w)



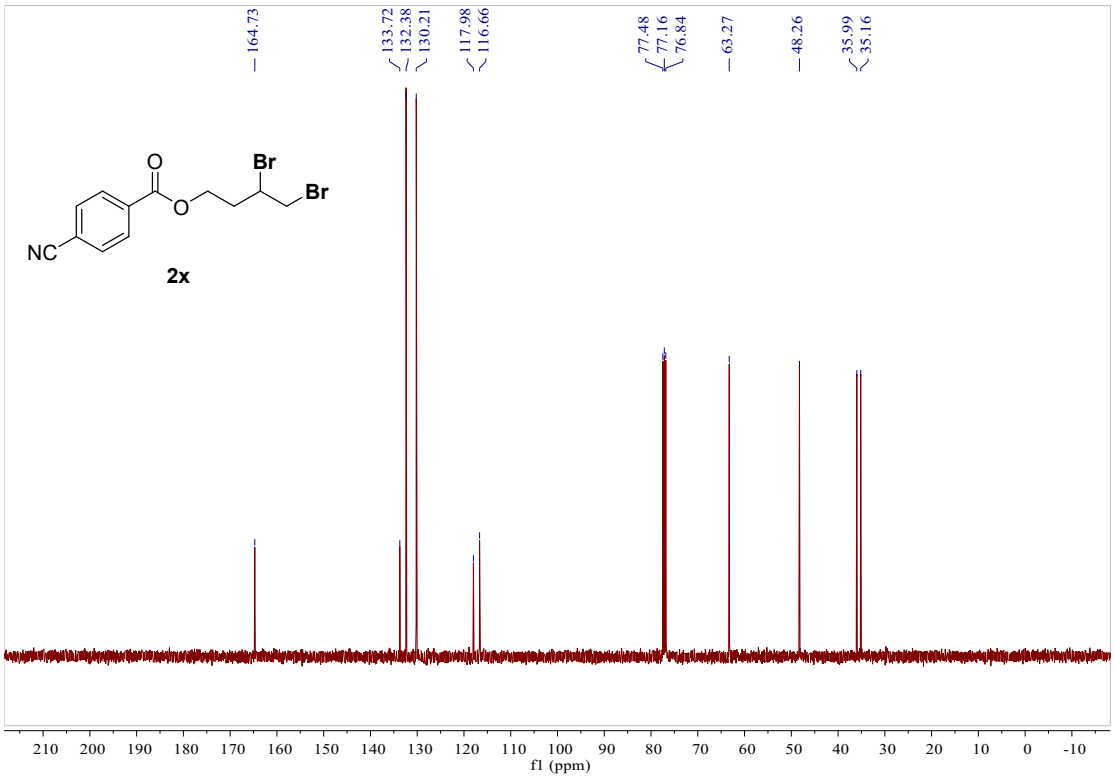
^{13}C NMR spectra for compound (2w)



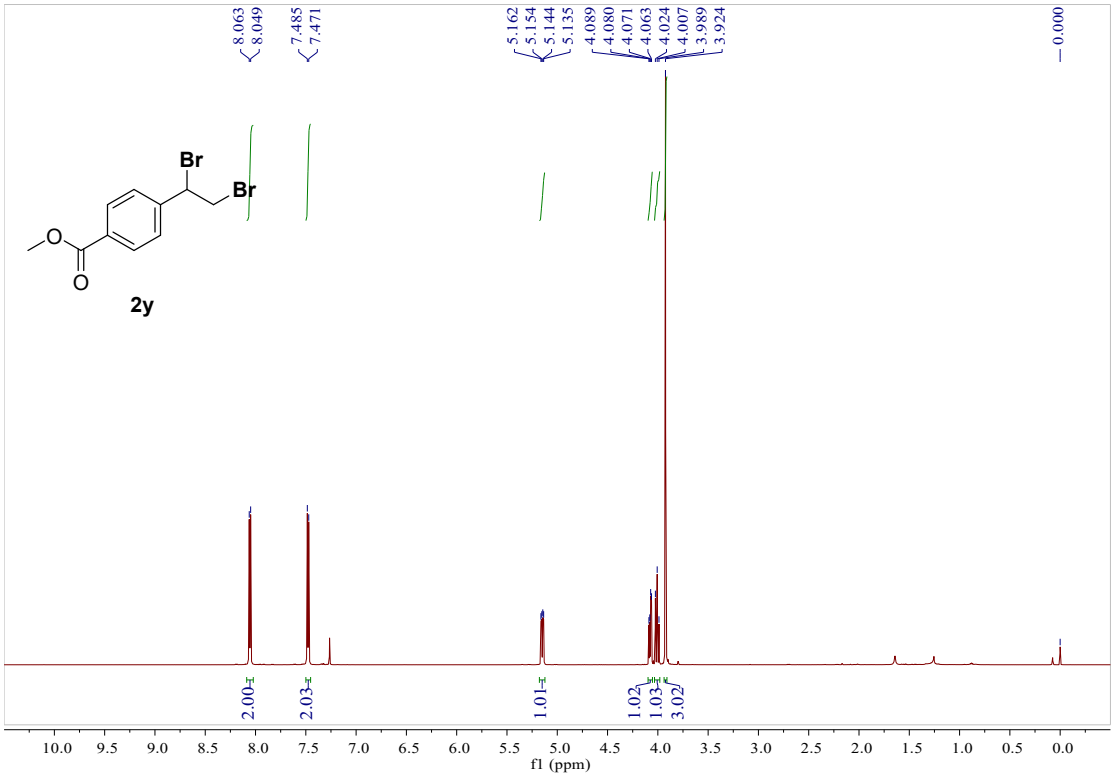
^{1}H NMR spectra for compound (2x)



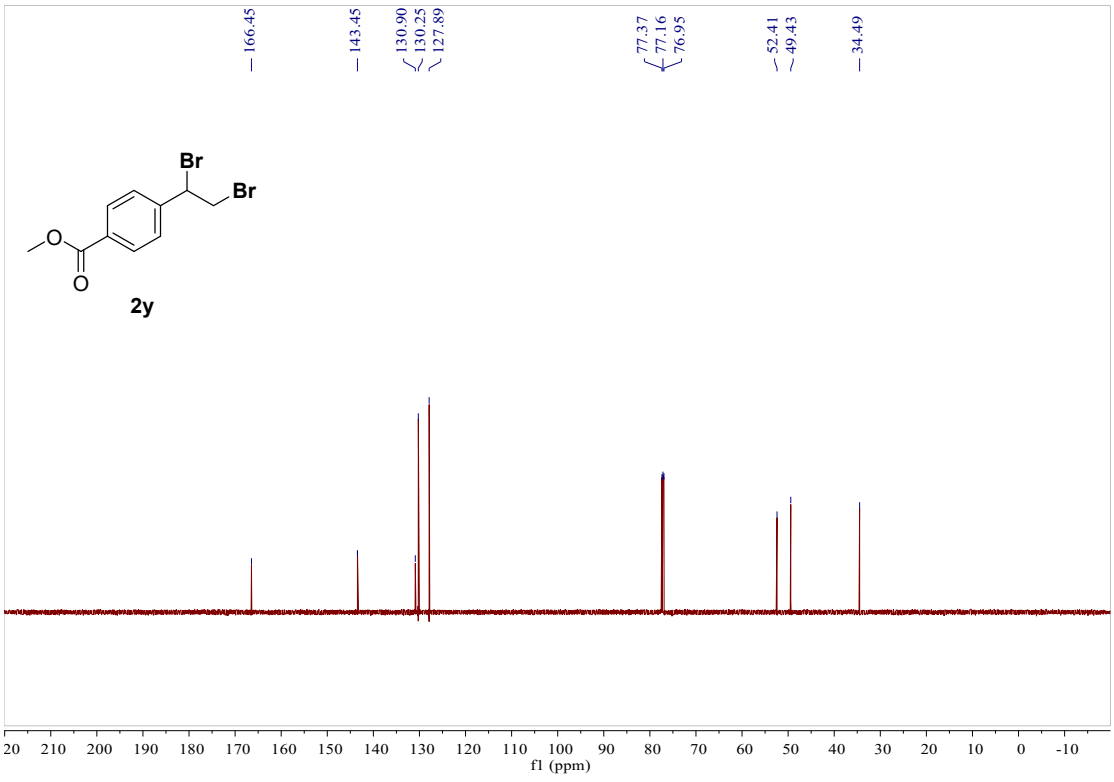
^{13}C NMR spectra for compound (2x)



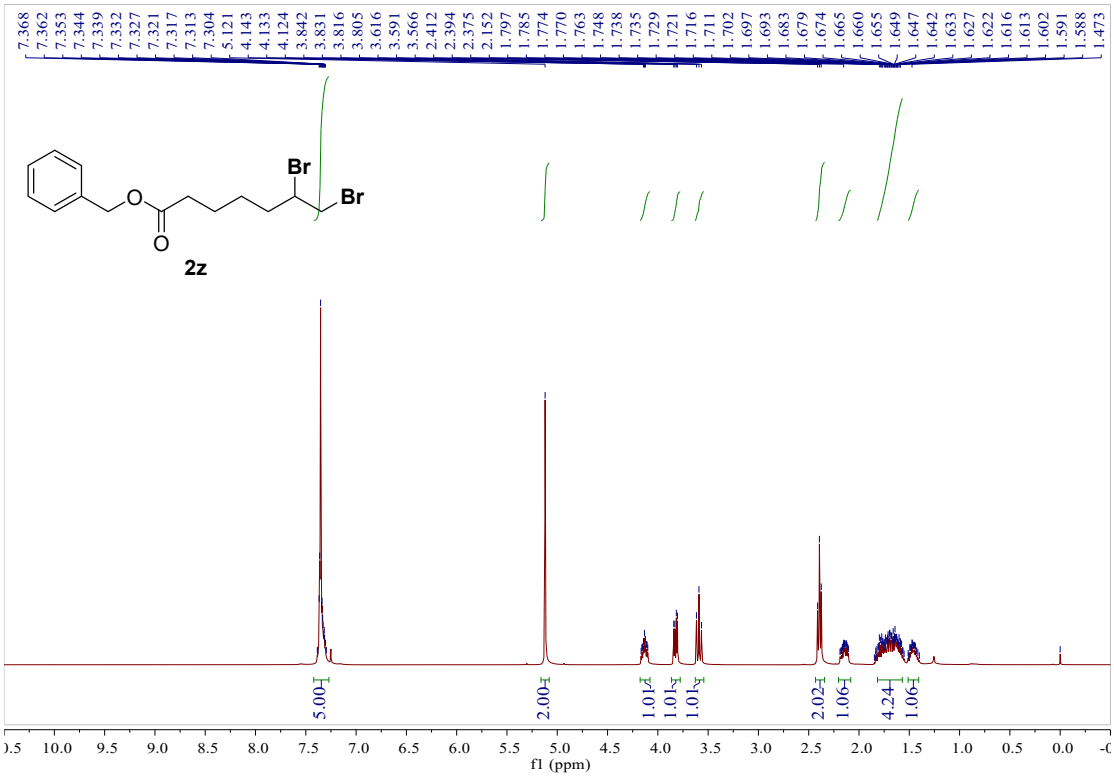
^{1}H NMR spectra for compound (2y)



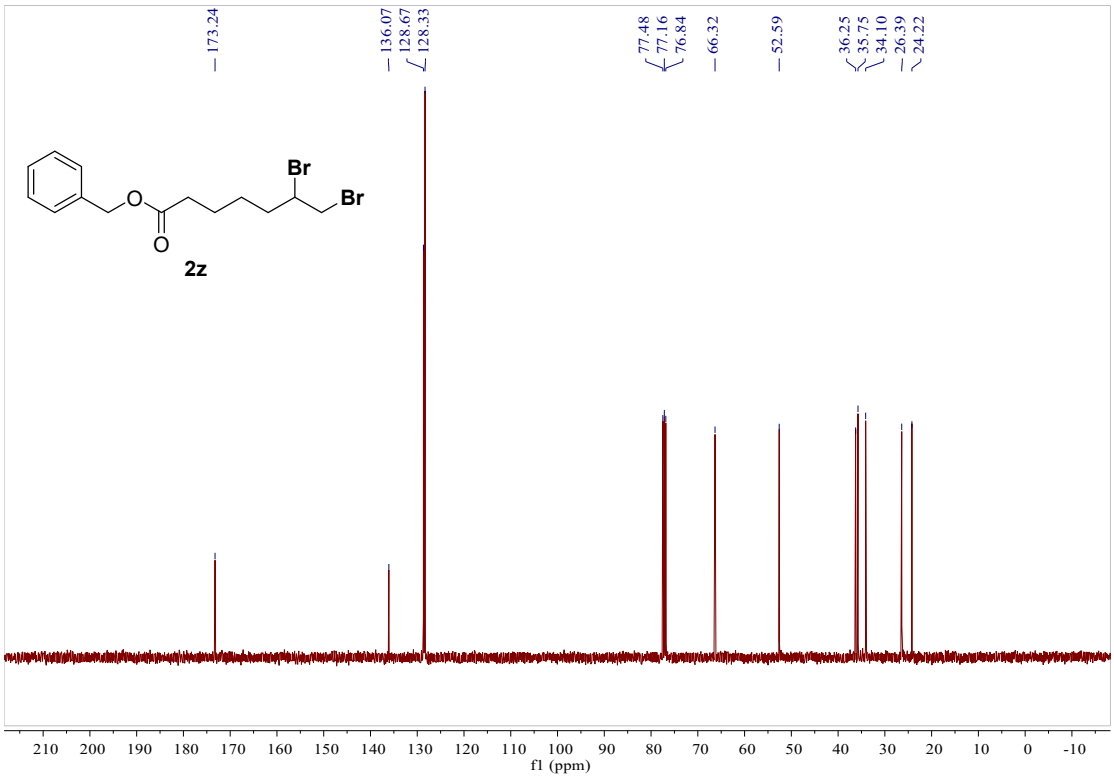
^{13}C NMR spectra for compound (2y)



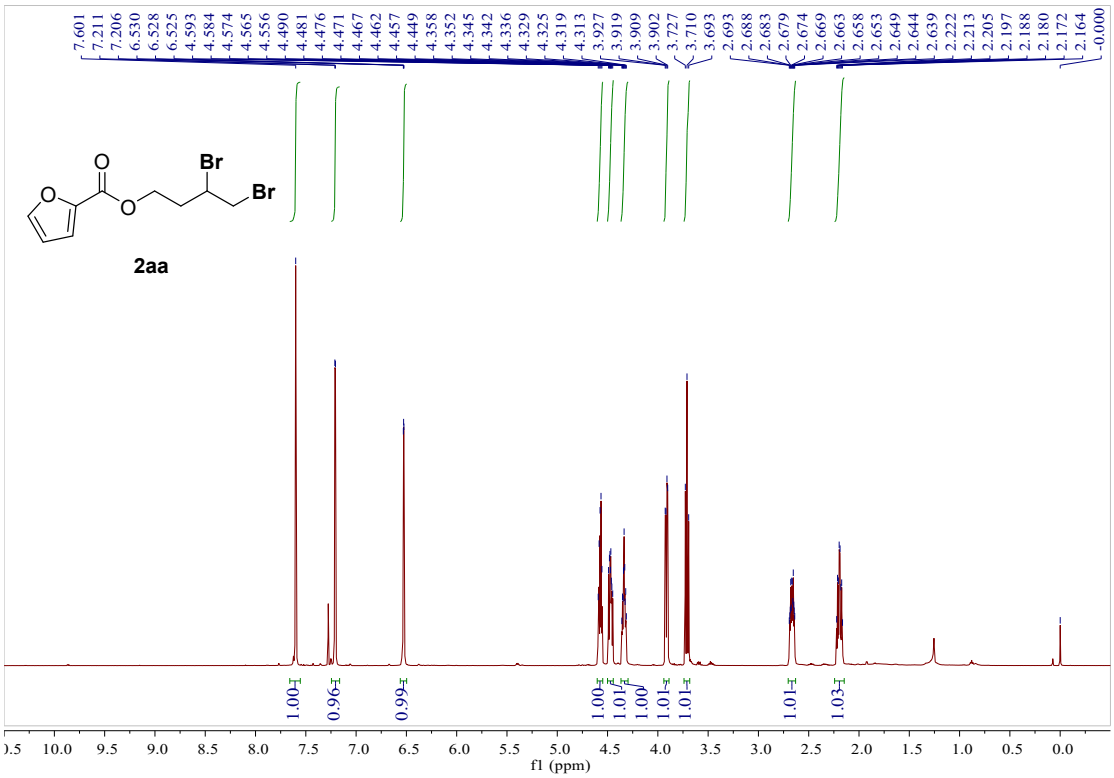
^{1}H NMR spectra for compound (2z)



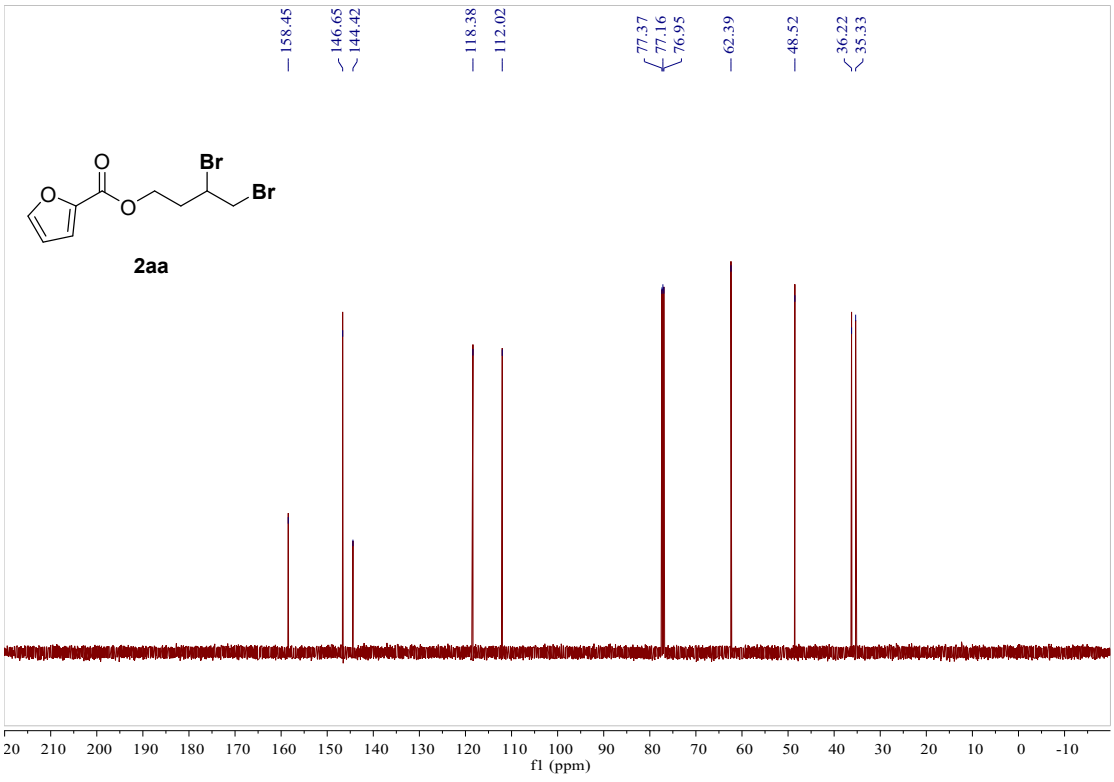
^{13}C NMR spectra for compound (2z)



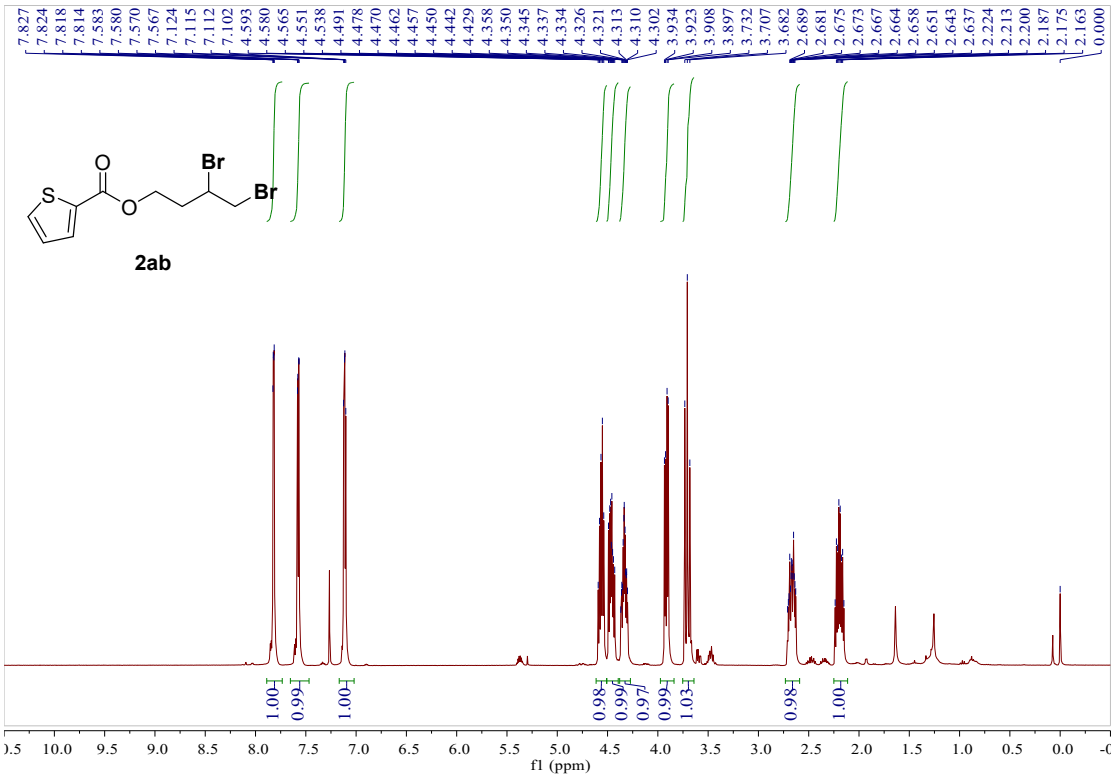
^{1}H NMR spectra for compound (2aa)



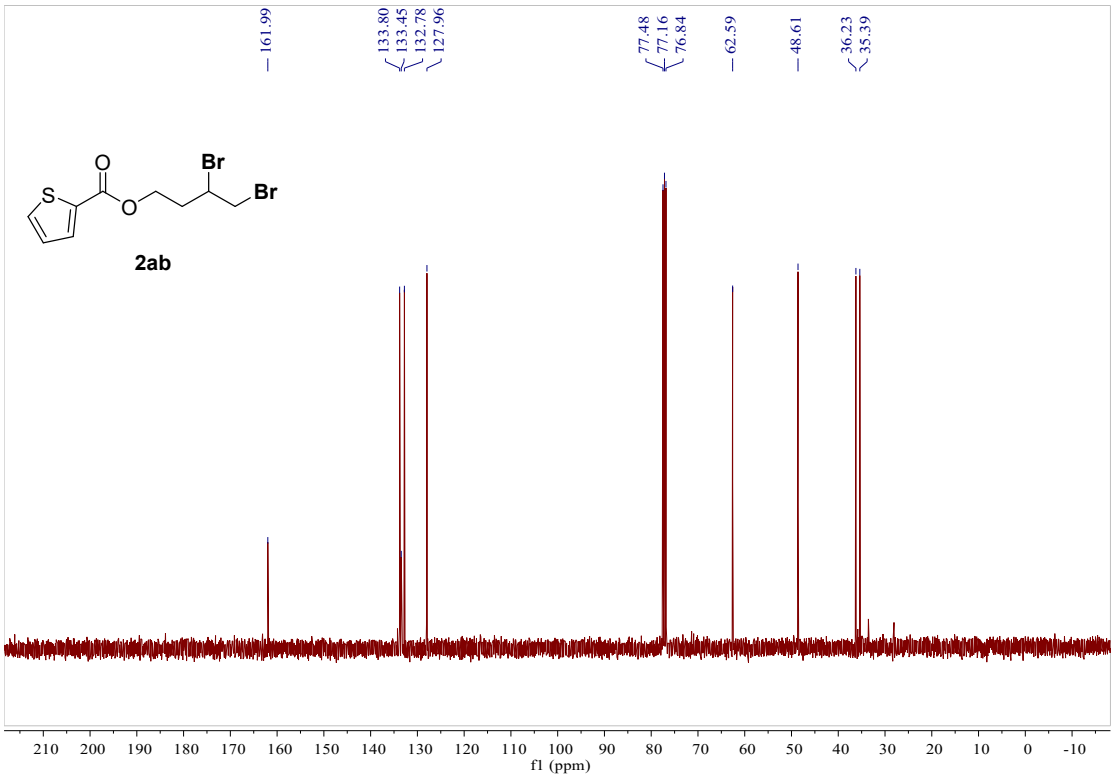
^{13}C NMR spectra for compound (2aa)



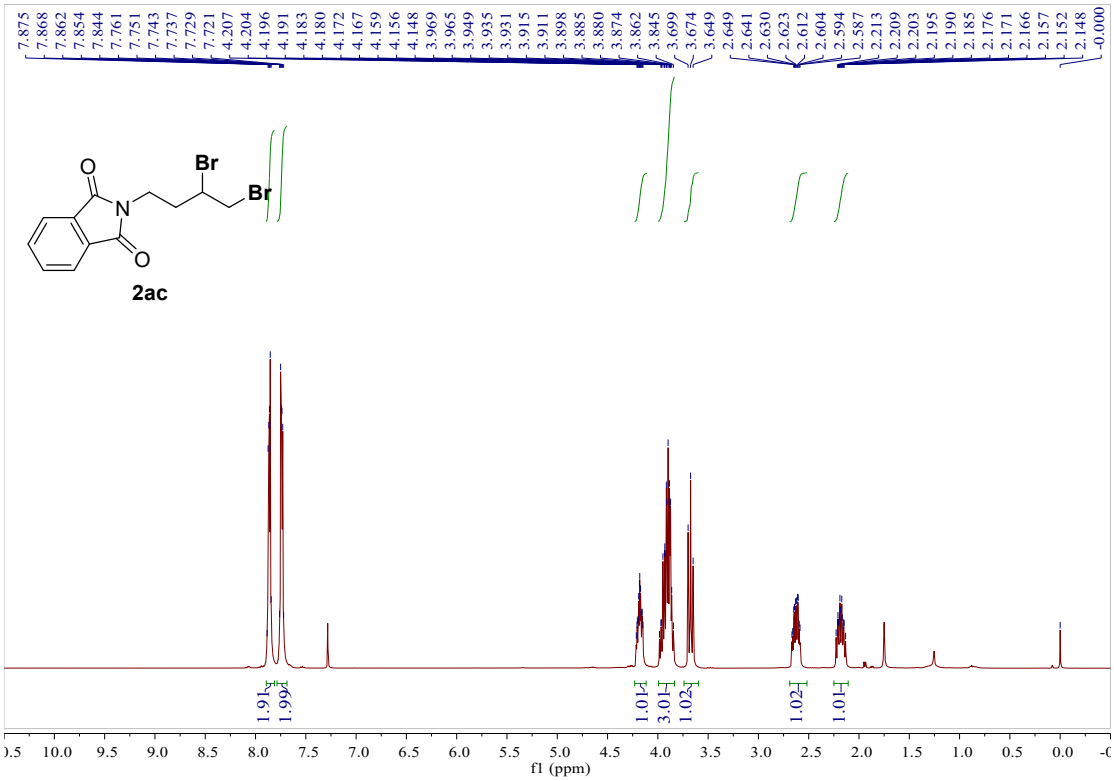
^{1}H NMR spectra for compound (2ab)



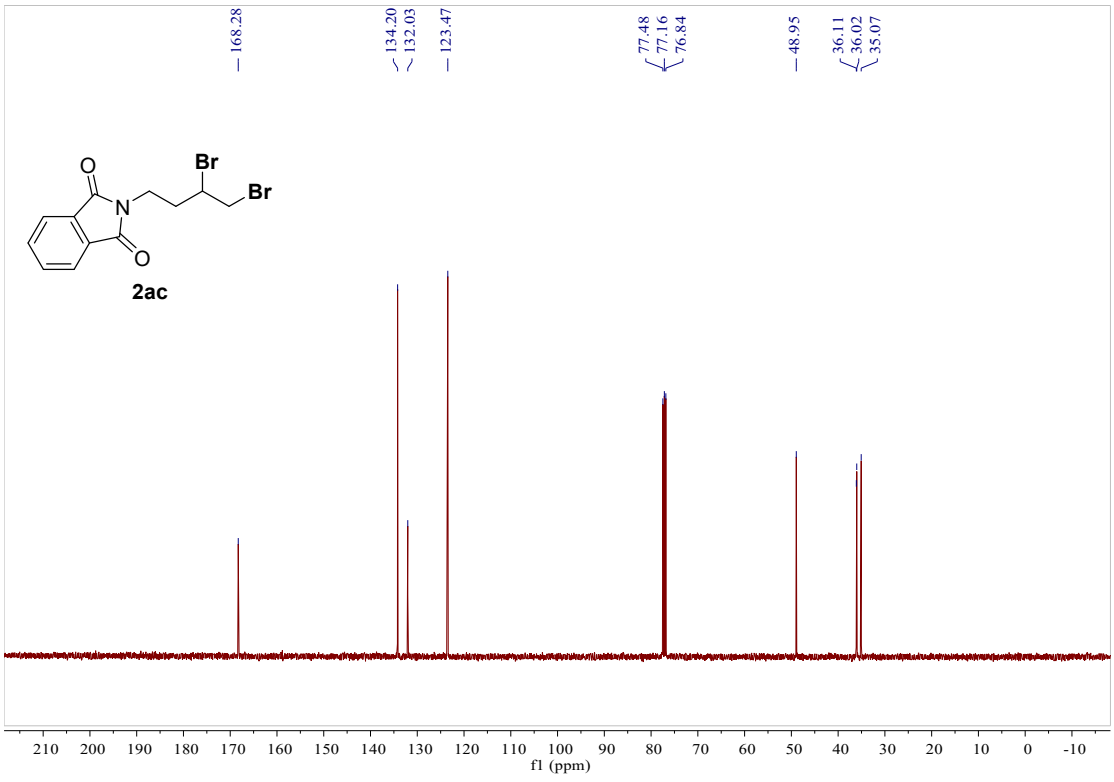
^{13}C NMR spectra for compound (2ab)



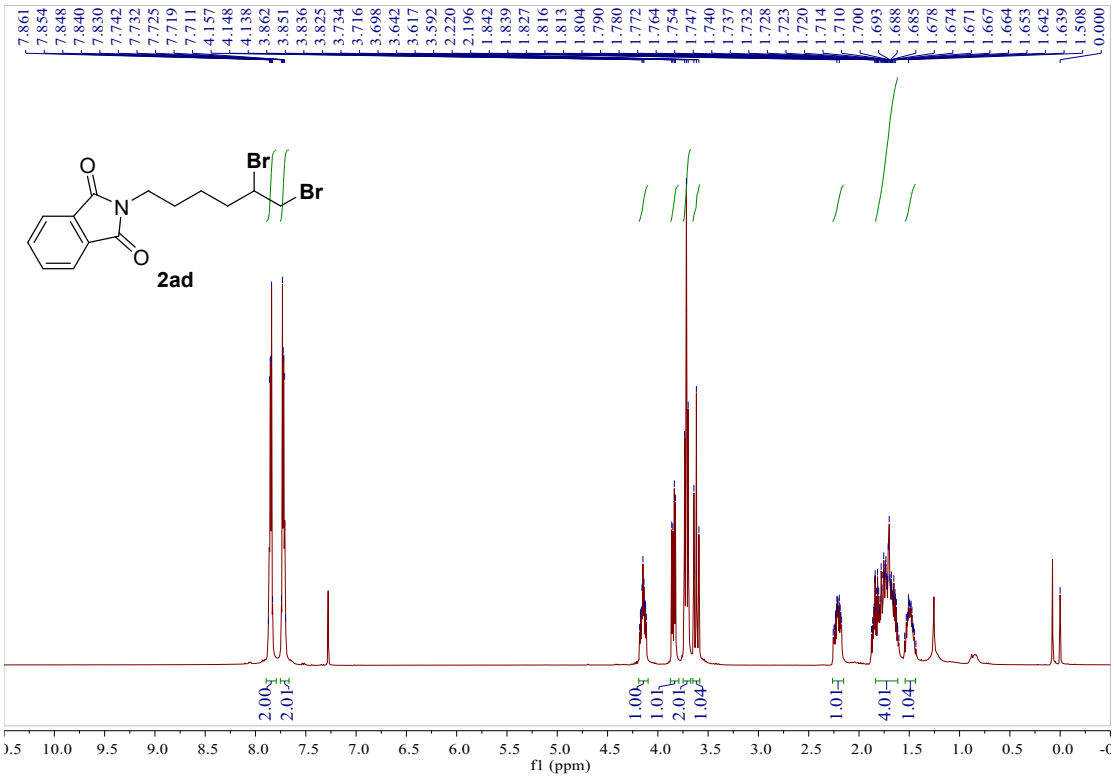
^{1}H NMR spectra for compound (2ac)



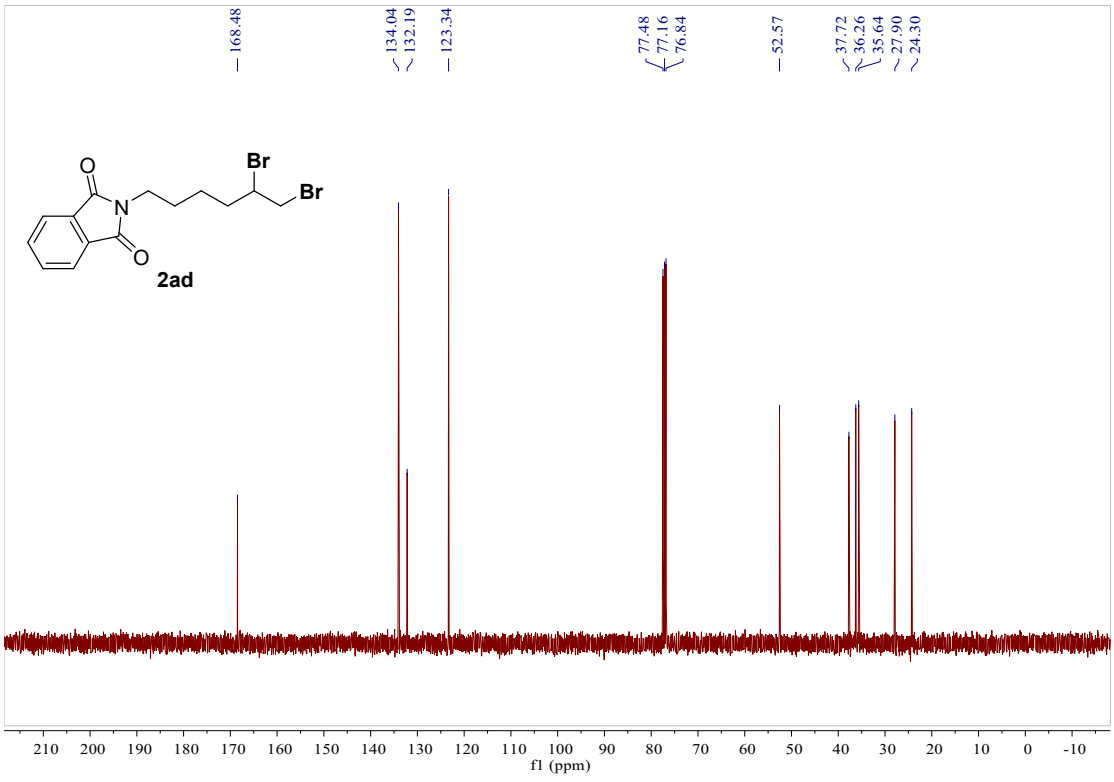
^{13}C NMR spectra for compound (2ac)



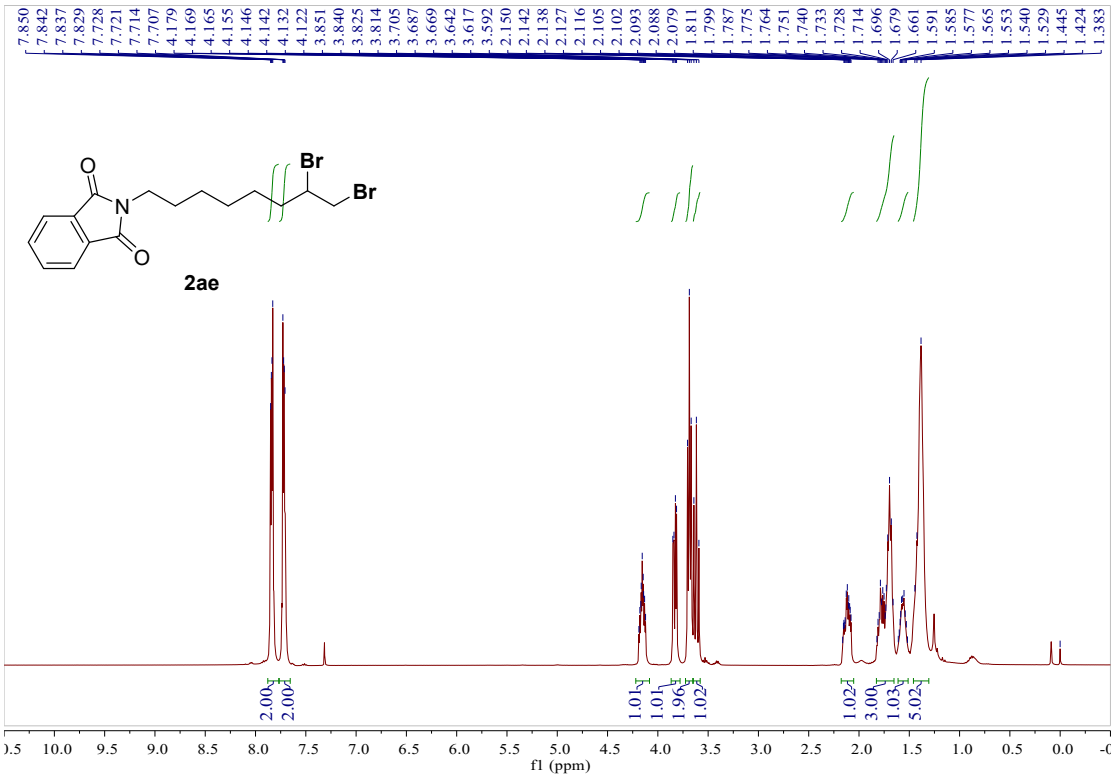
^{1}H NMR spectra for compound (2ad)



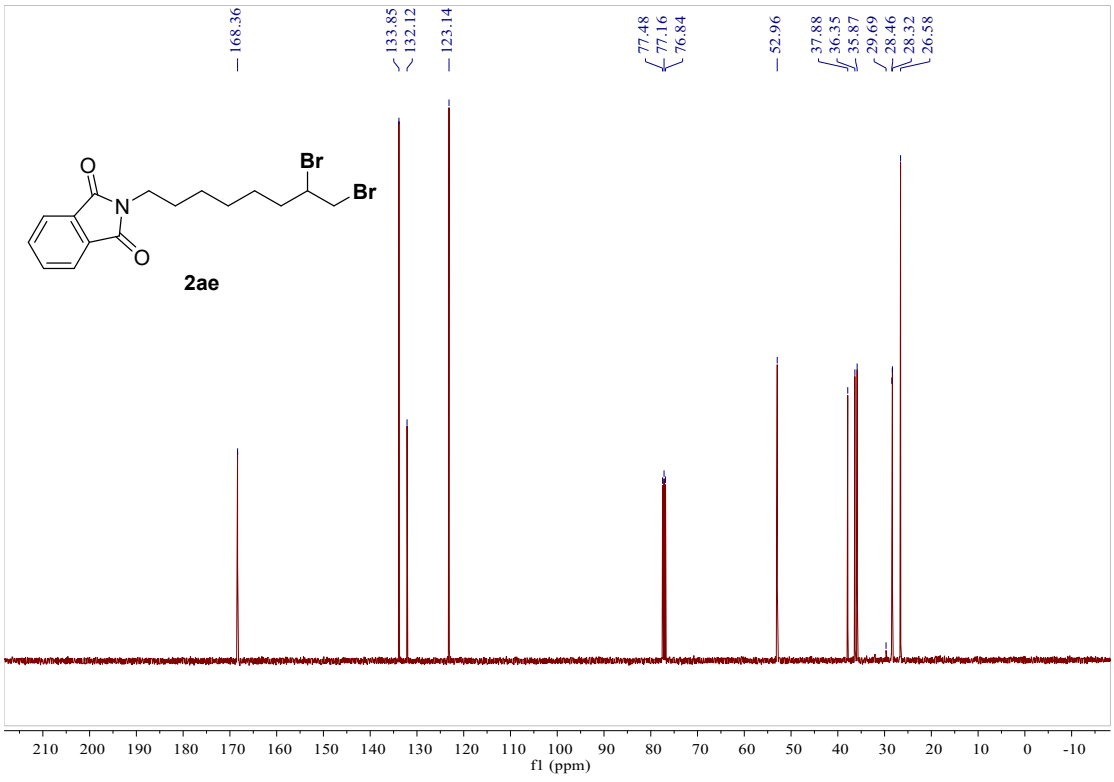
^{13}C NMR spectra for compound (2ad)



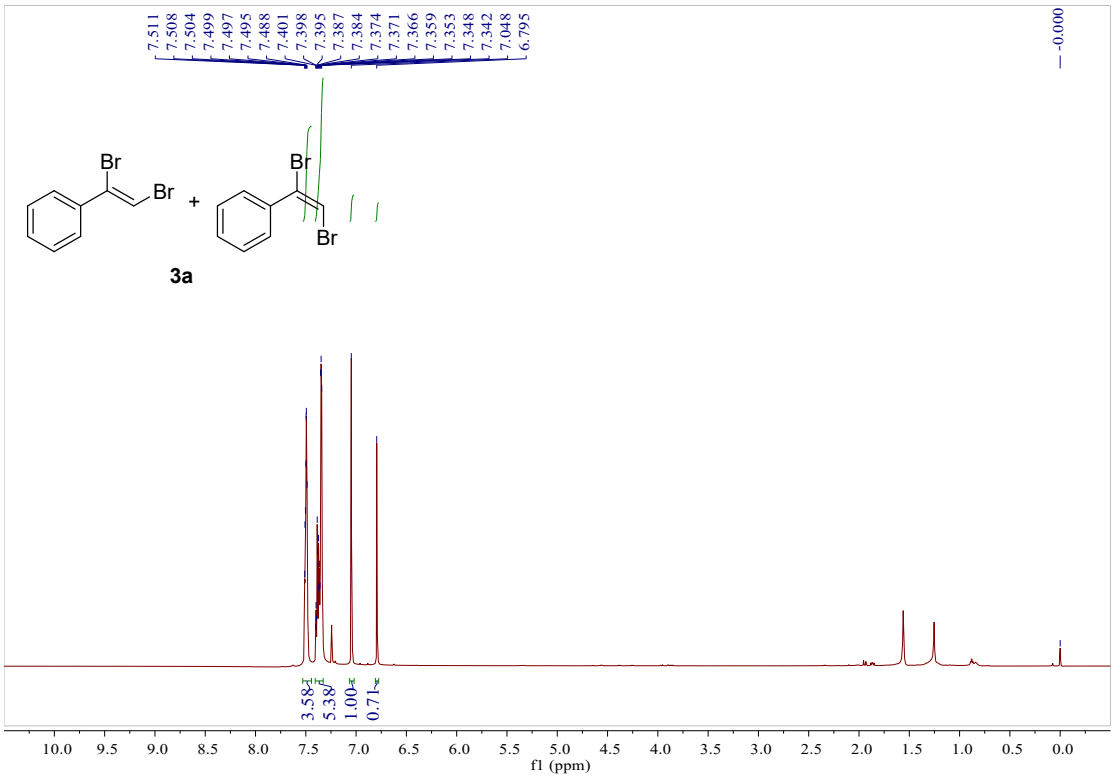
^{1}H NMR spectra for compound (2ae)



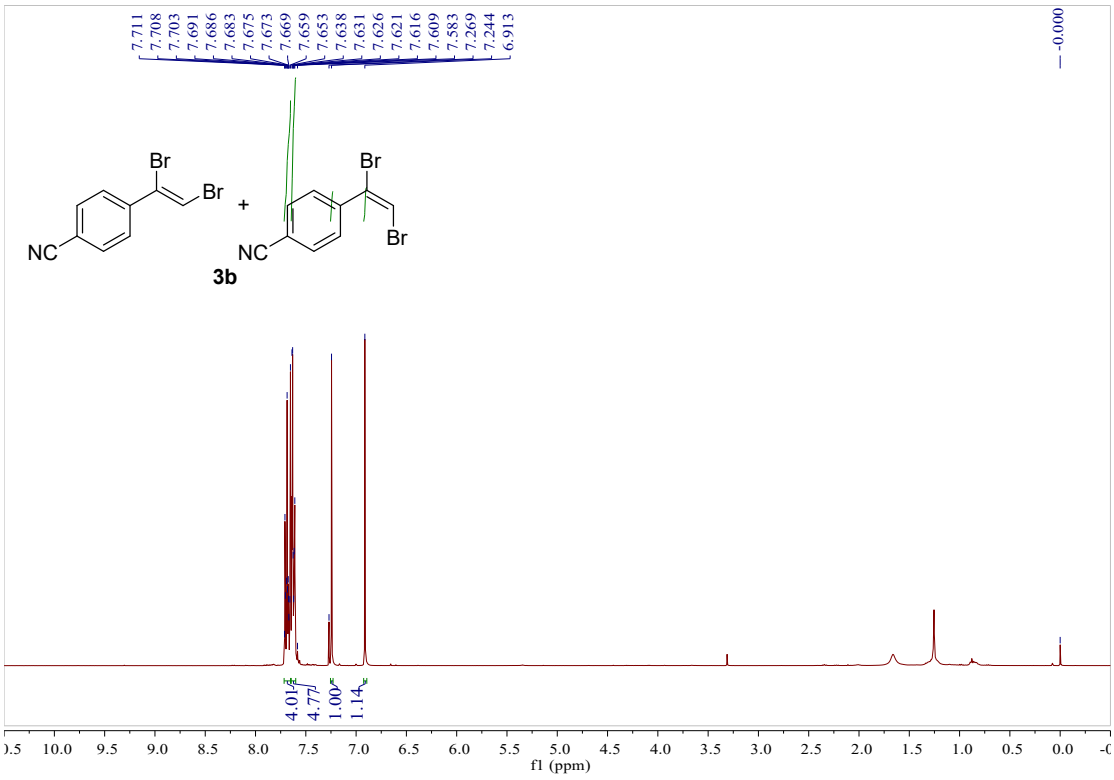
^{13}C NMR spectra for compound (2ae)



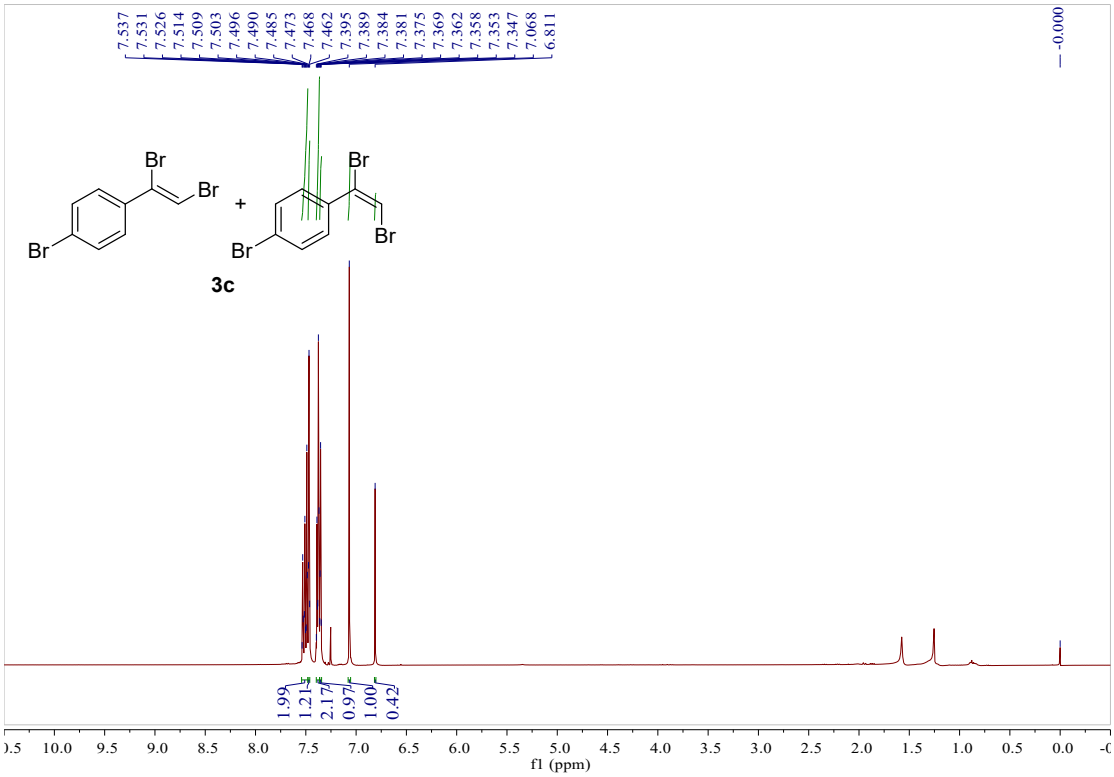
^{1}H NMR spectra for compound (3a)



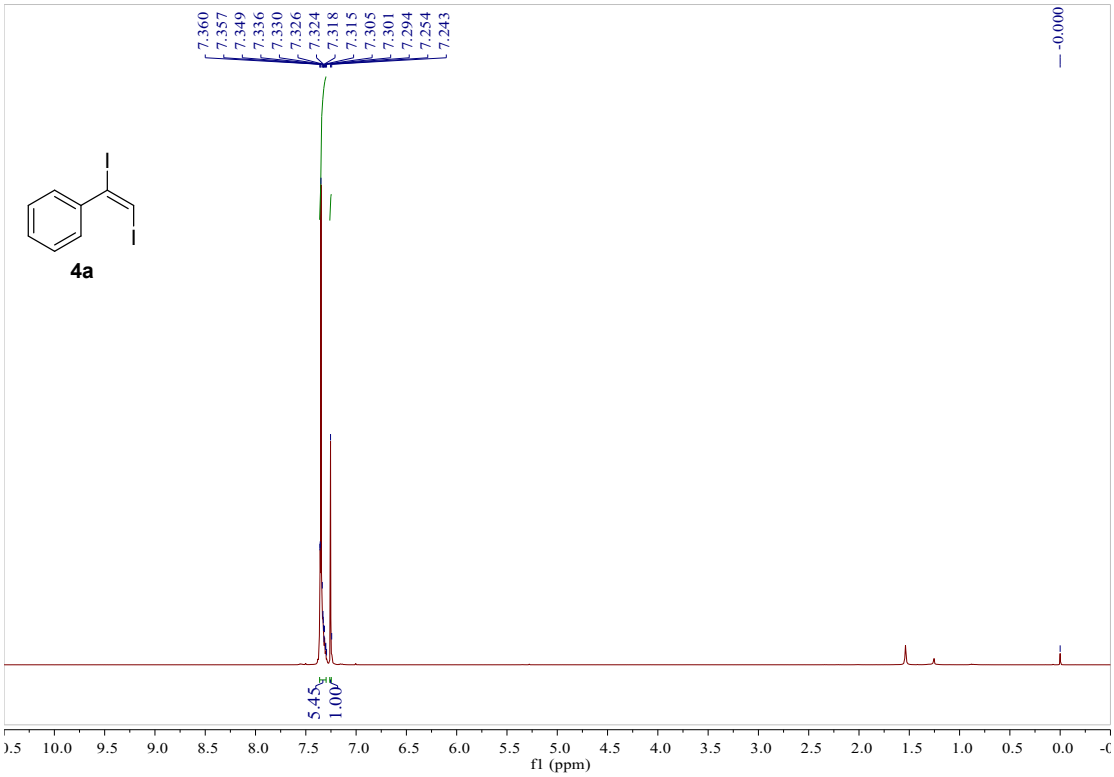
^{1}H NMR spectra for compound (3b)



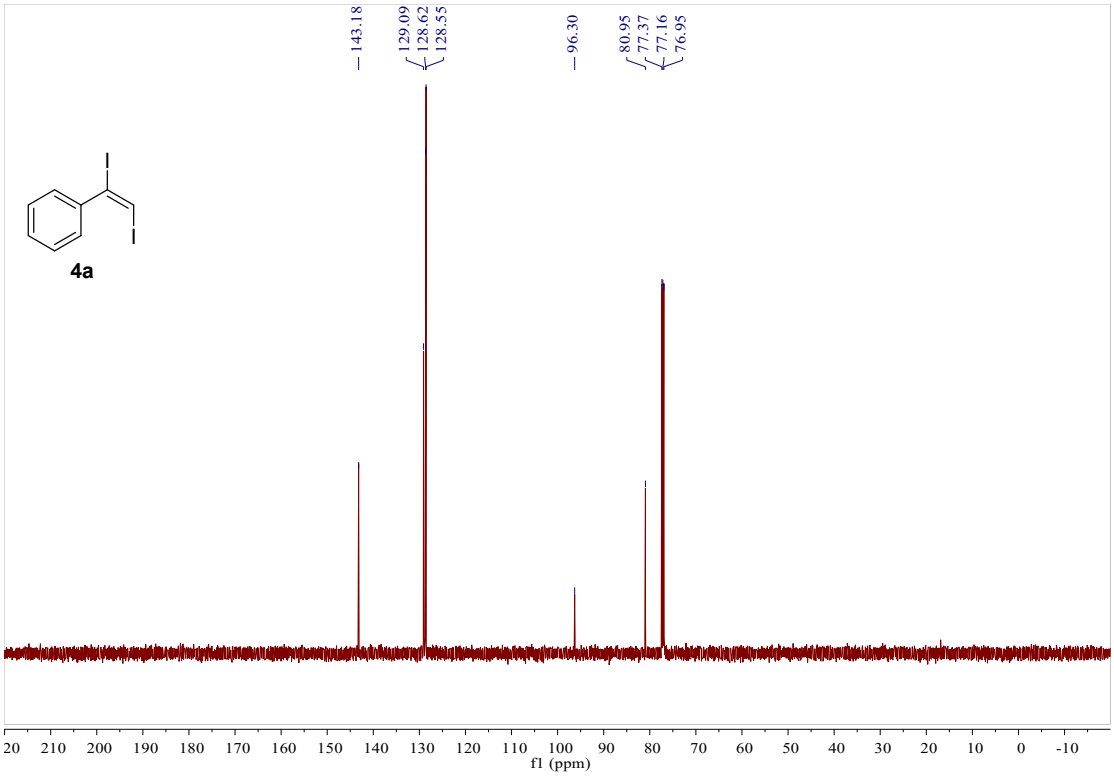
^{1}H NMR spectra for compound (3c)



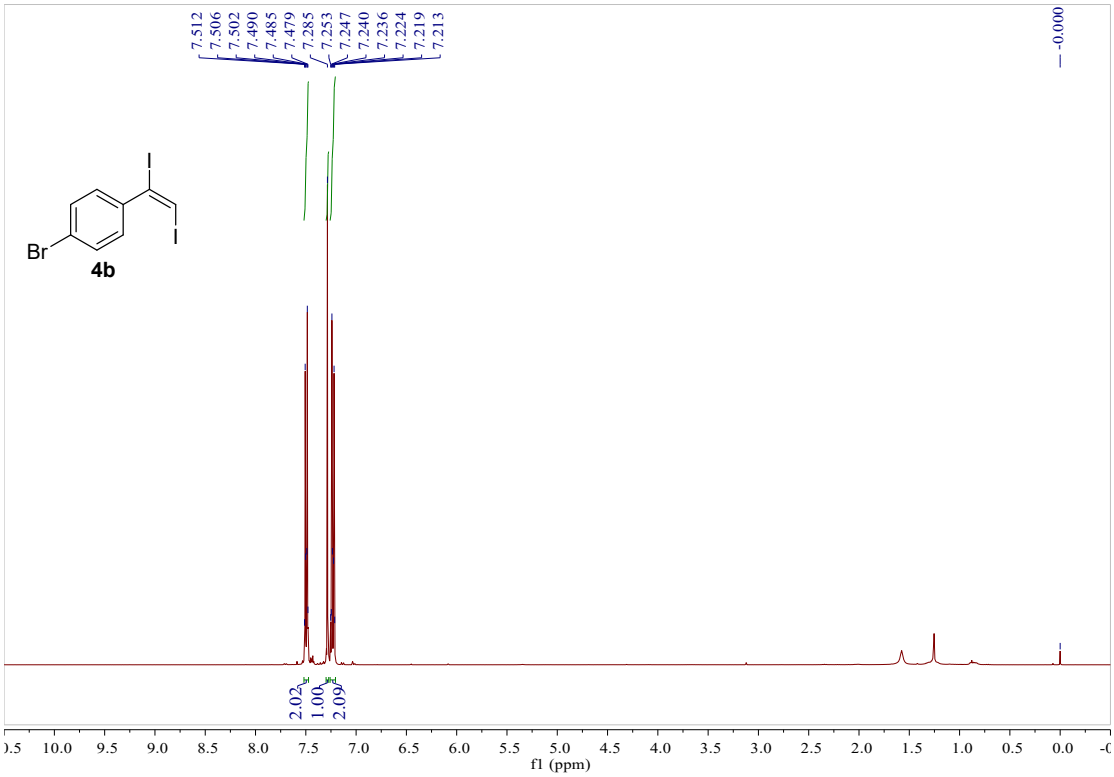
^{1}H NMR spectra for compound (4a)



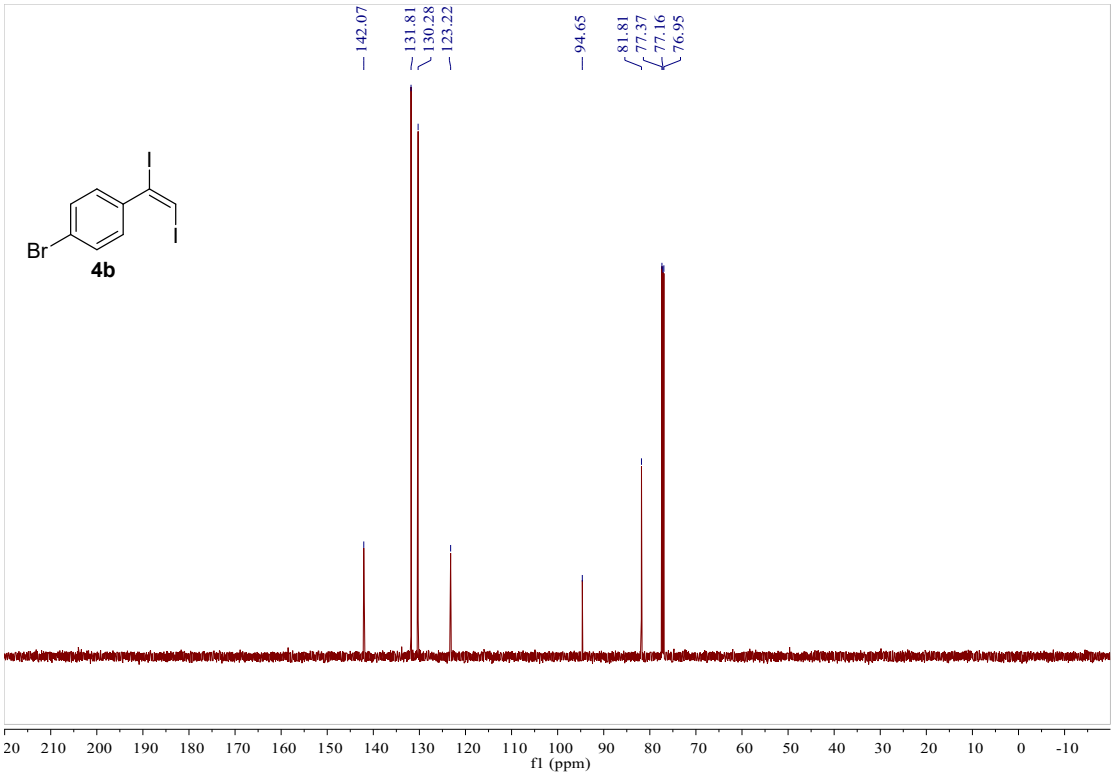
^{13}C NMR spectra for compound (4a)



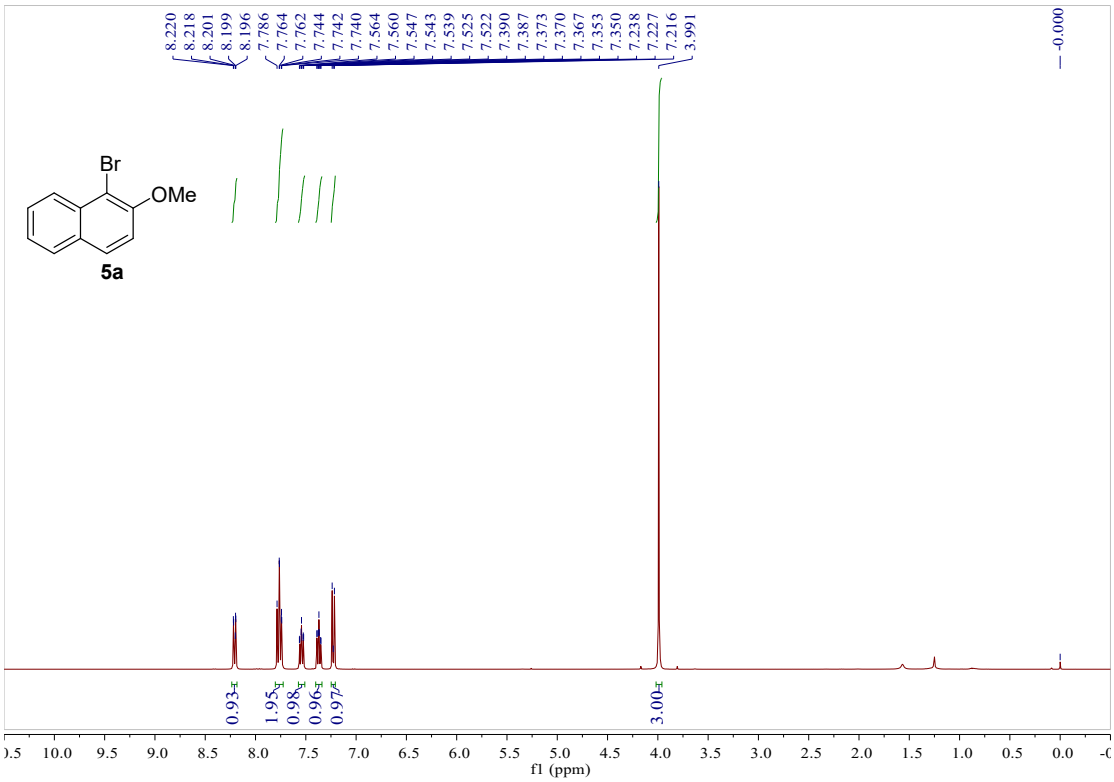
^{1}H NMR spectra for compound (4b)



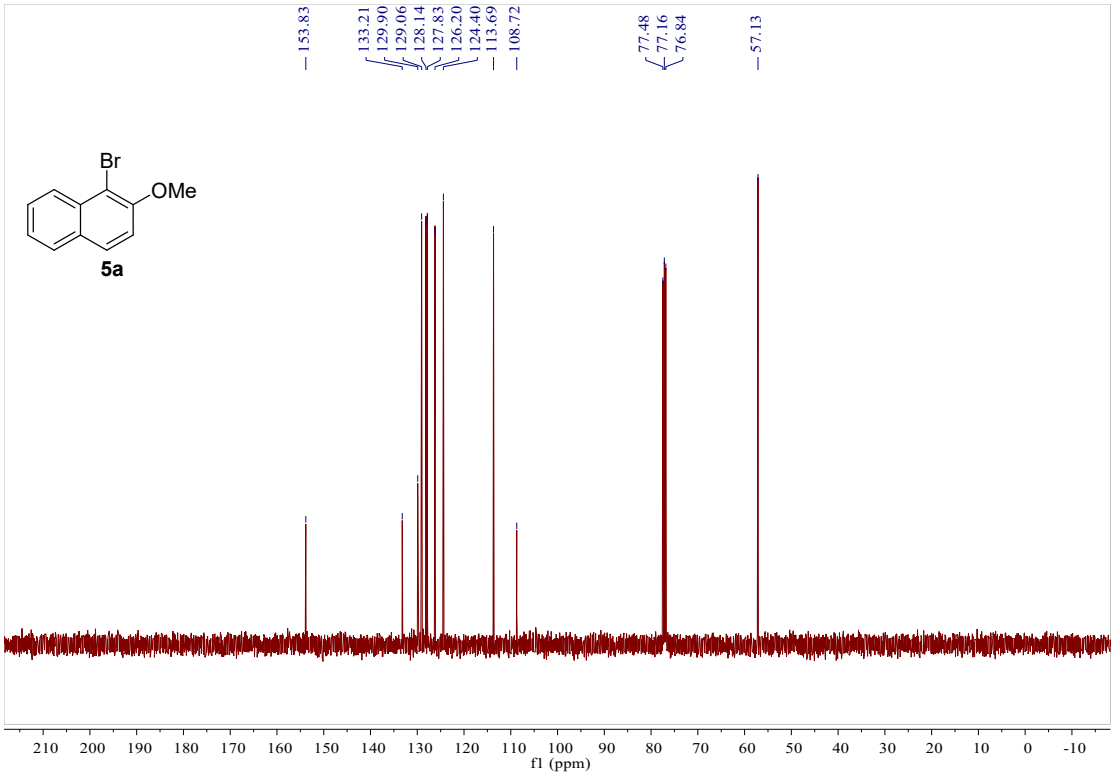
^{13}C NMR spectra for compound (4b)



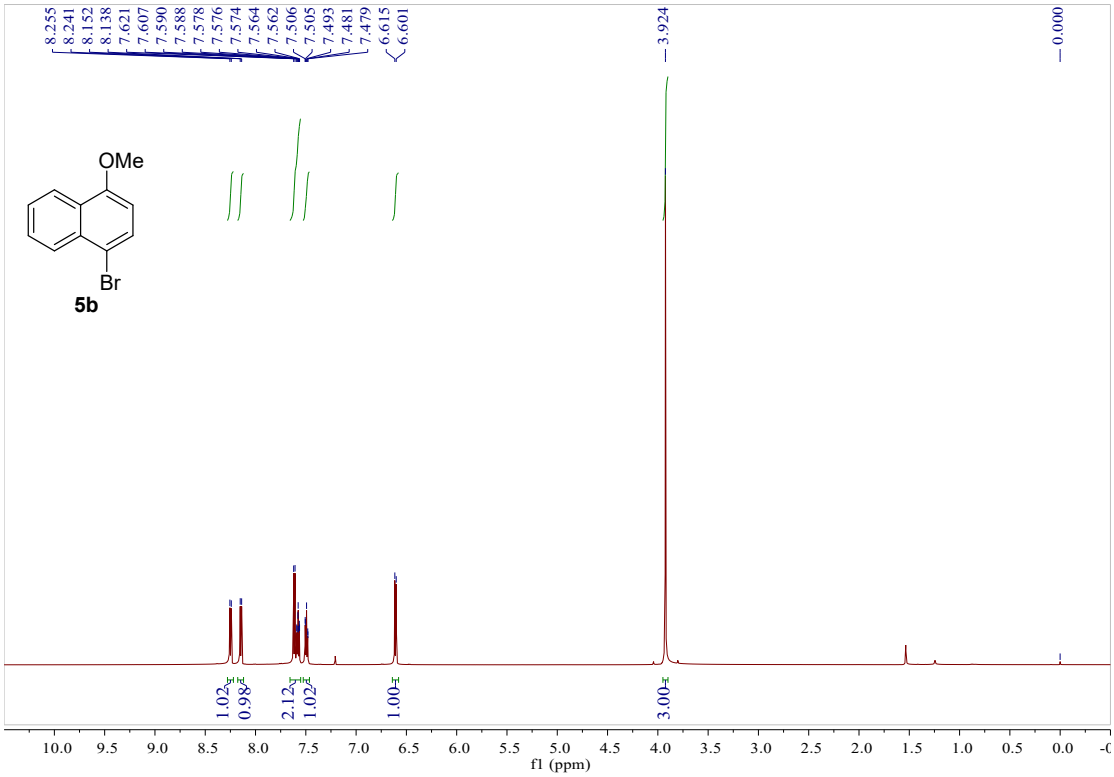
^{1}H NMR spectra for compound (5a)



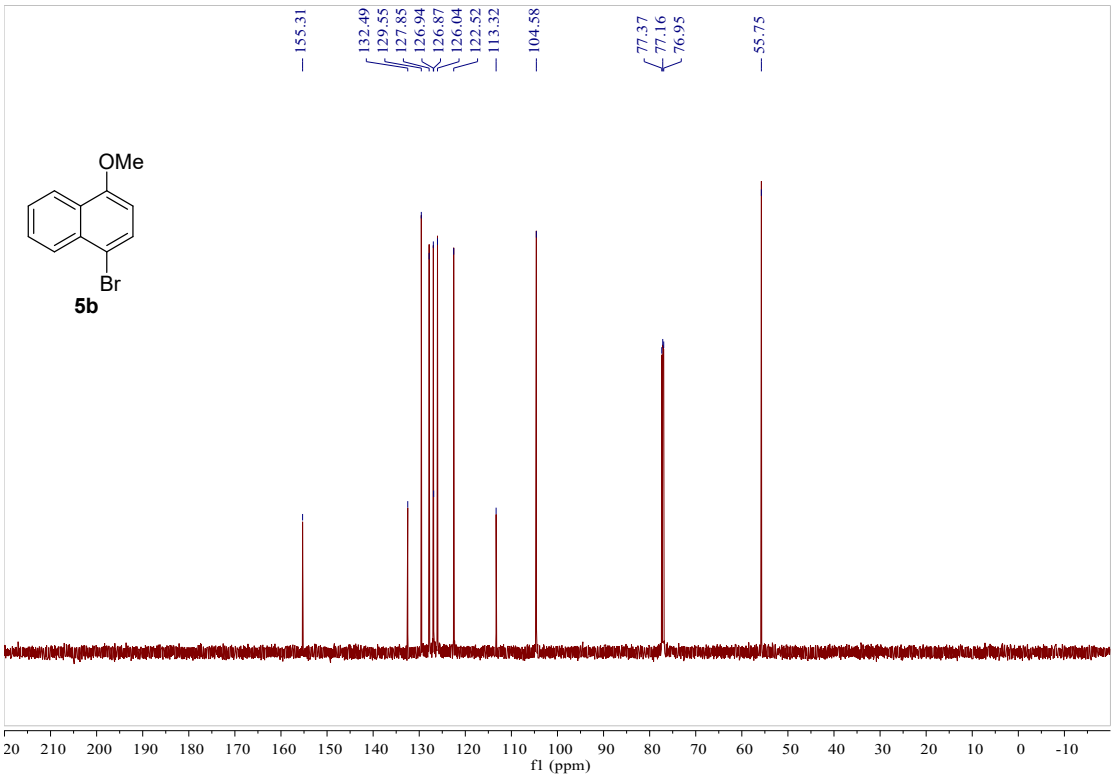
^{13}C NMRspectra for compound (5a)



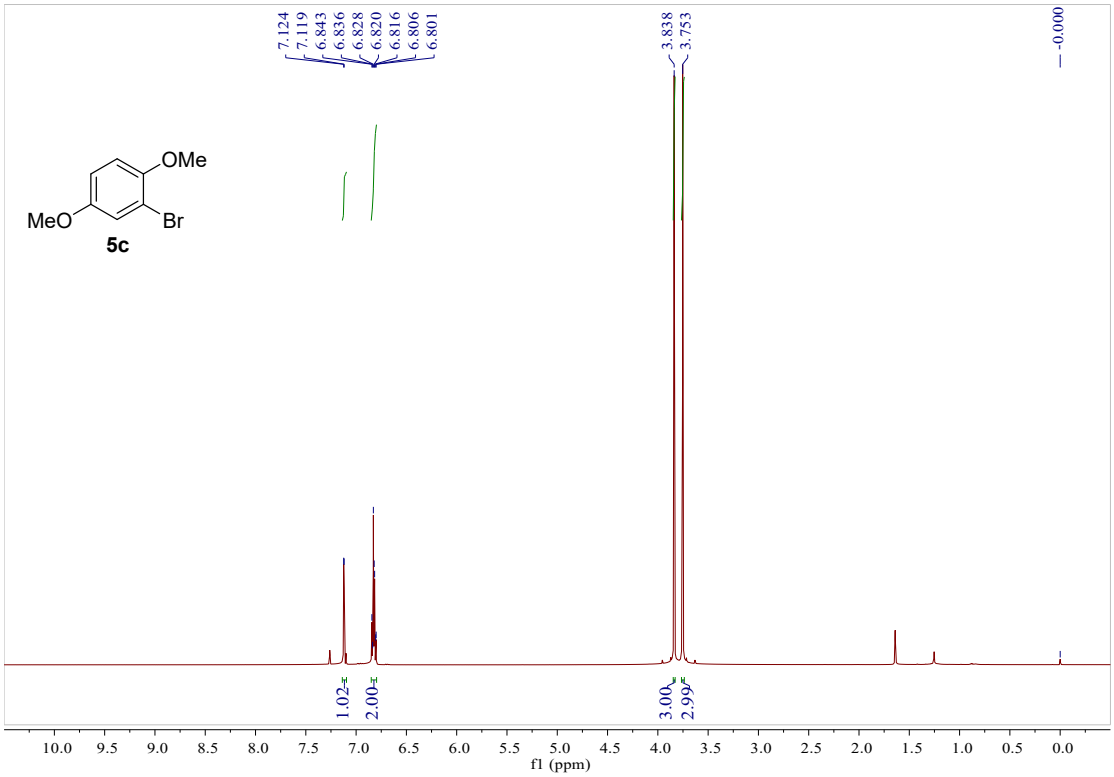
^{1}H NMR spectra for compound (5b)



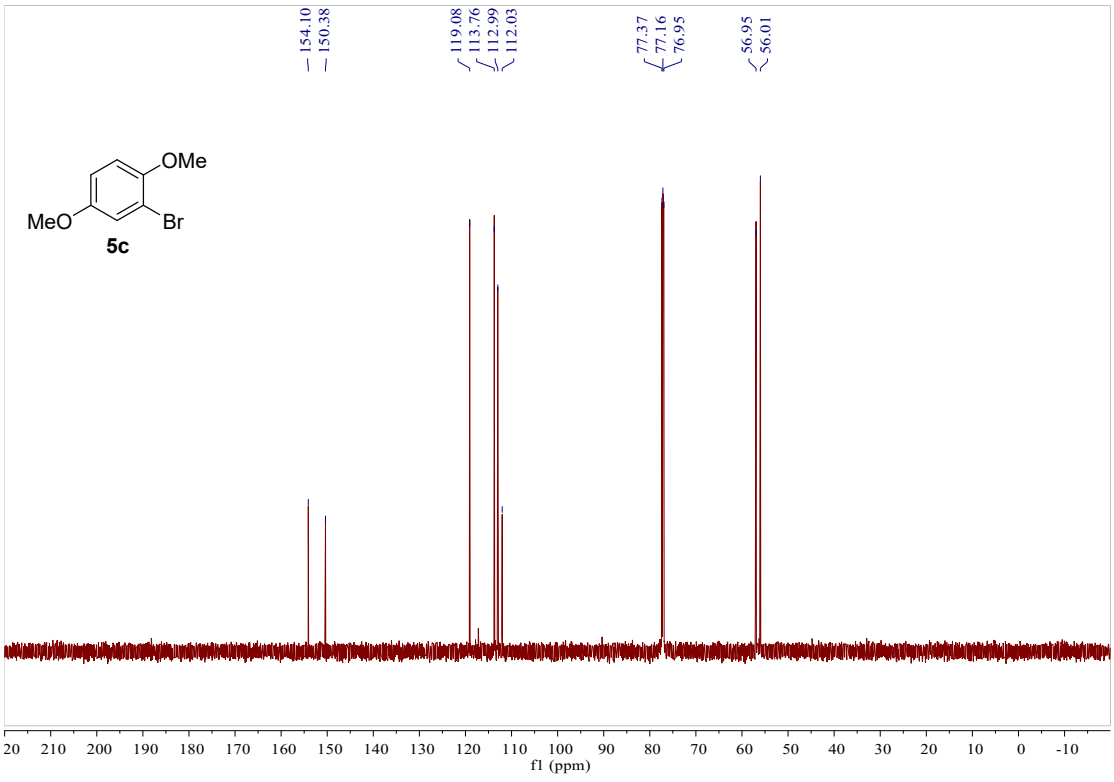
^{13}C NMR spectra for compound (5b)



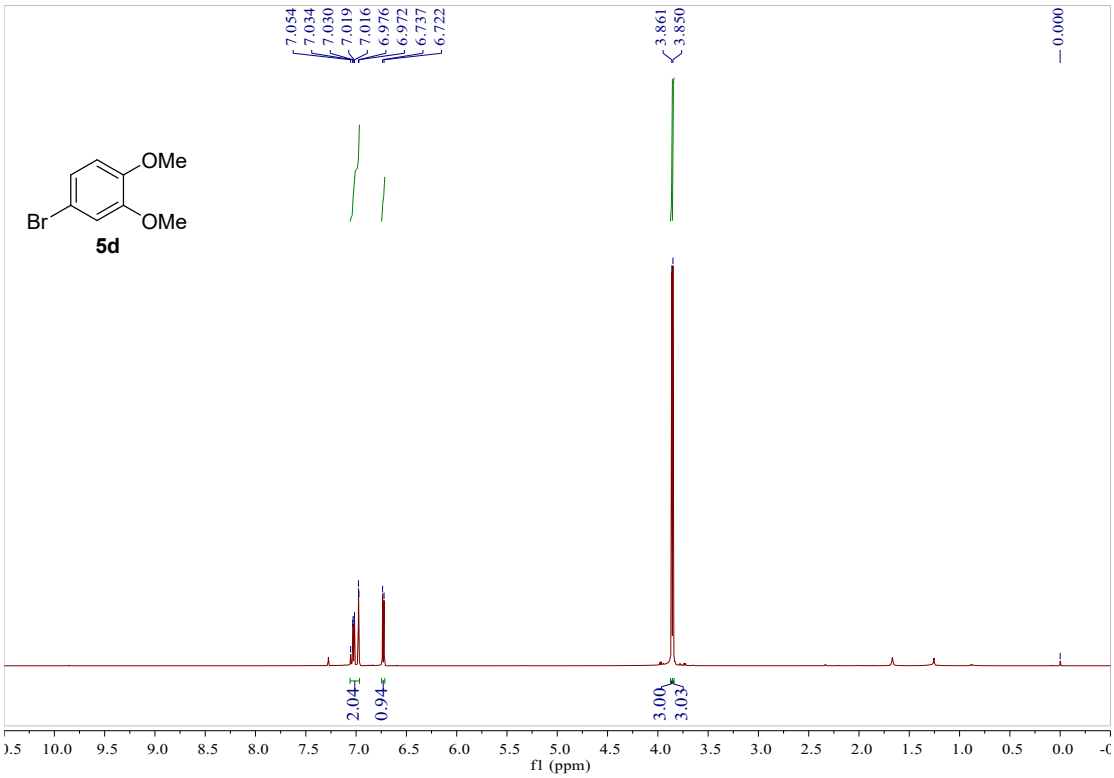
^{1}H NMR spectra for compound (5c)



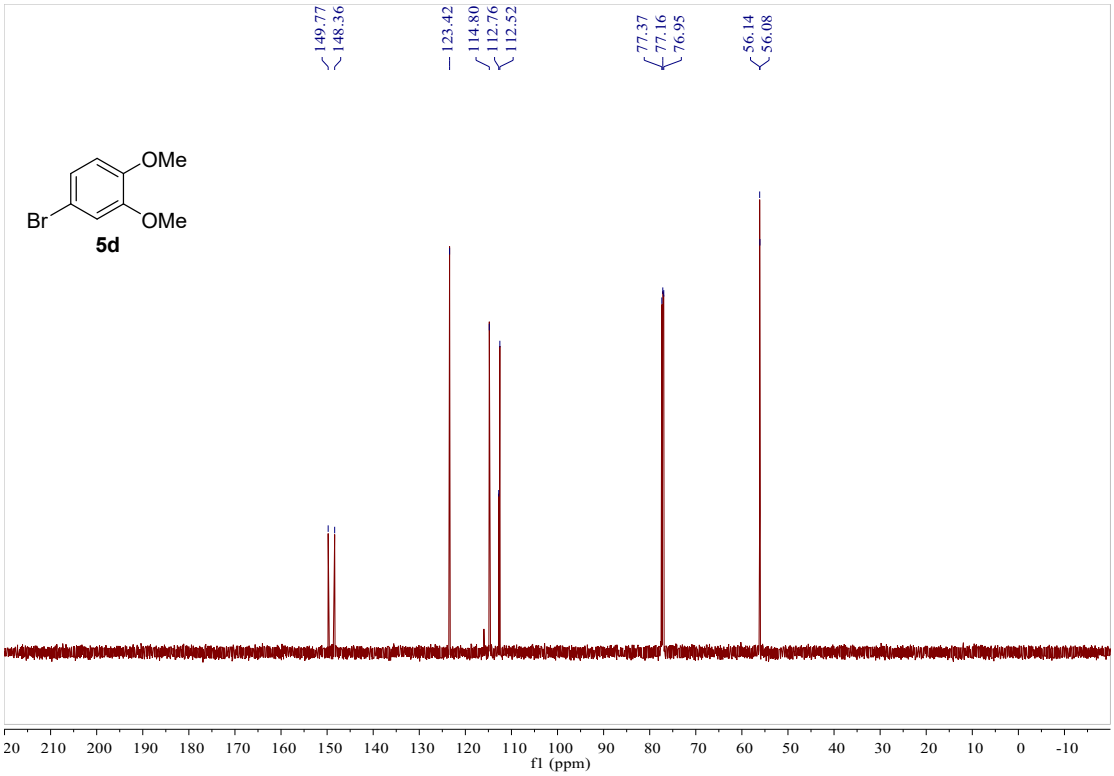
^{13}C NMR spectra for compound (5c)



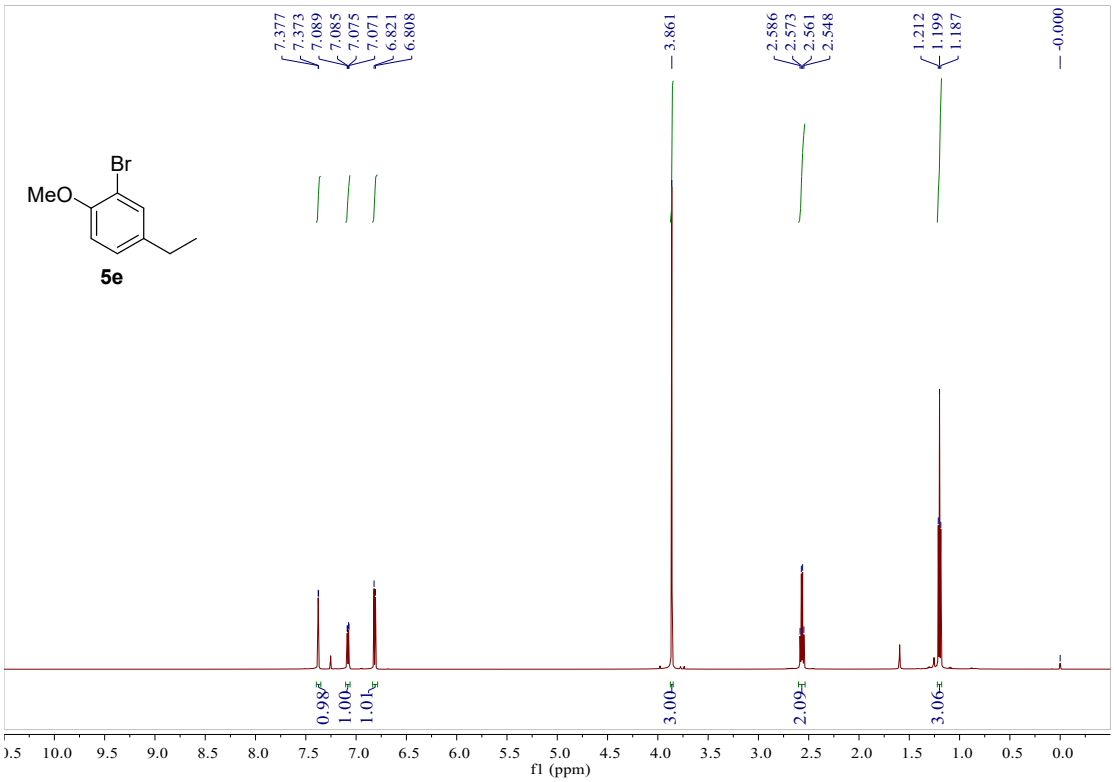
^{1}H NMR spectra for compound (5d)



^{13}C NMR spectra for compound (5d)



^{1}H NMR spectra for compound (5e)



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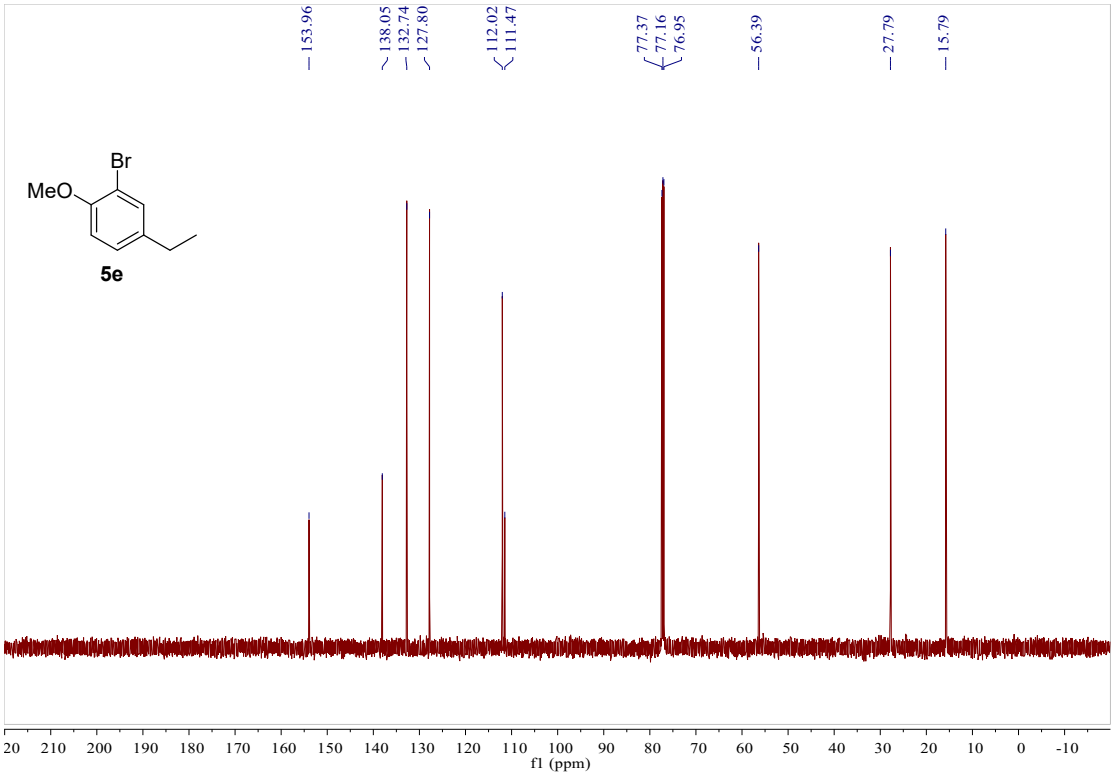
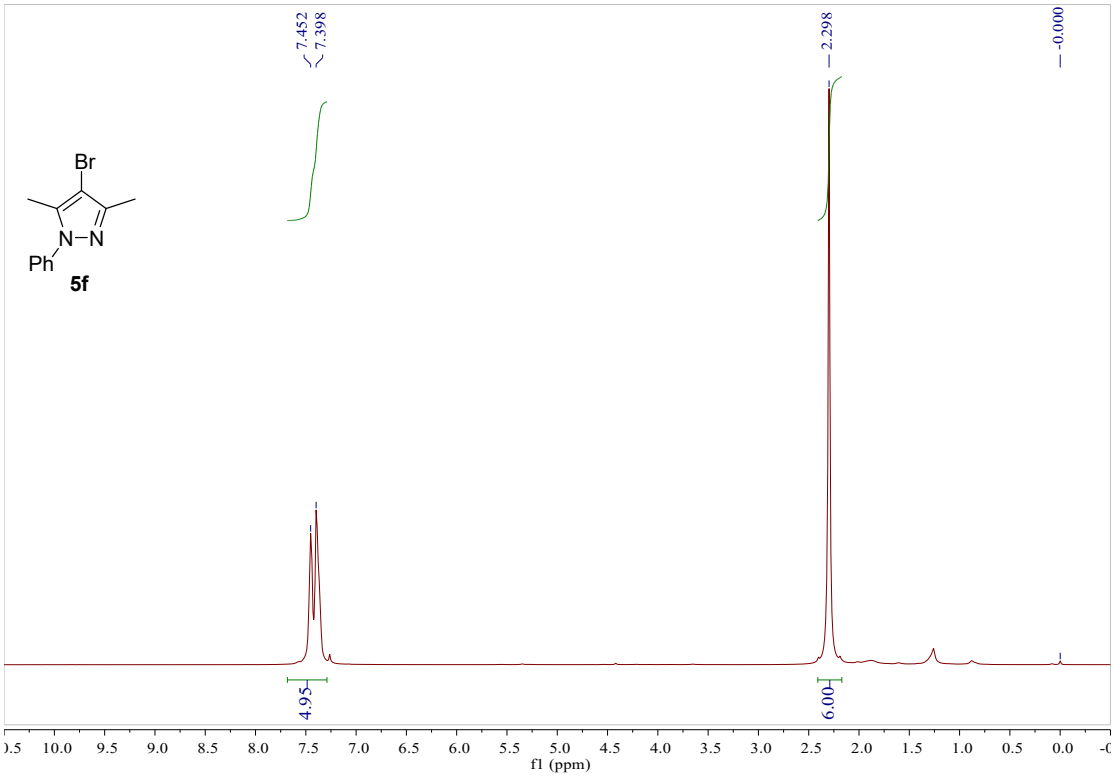
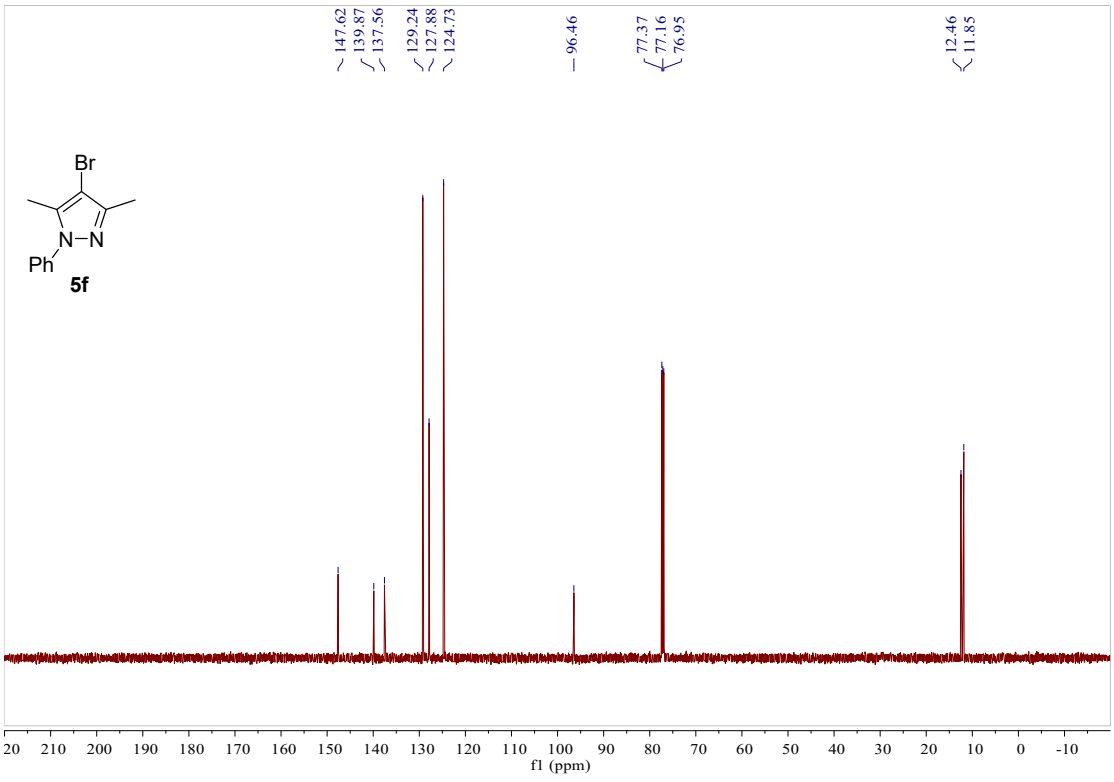


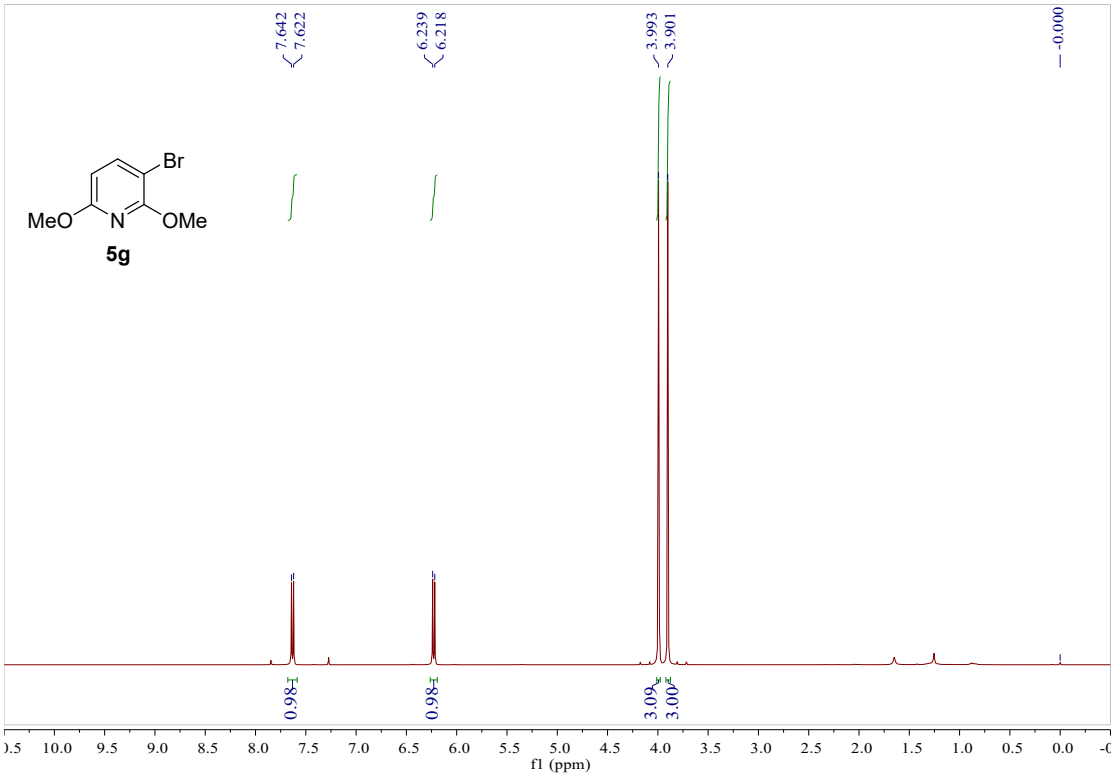
^{1}H NMR spectra for compound (5f)



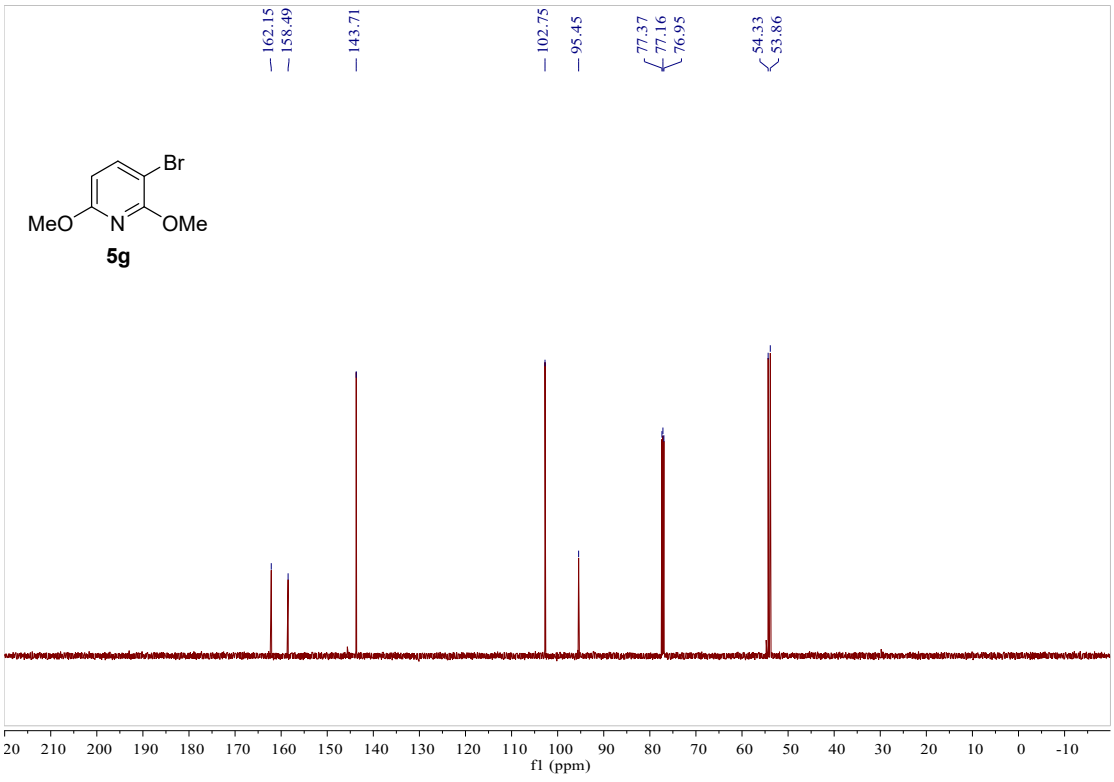
^{13}C NMR spectra for compound (5f)



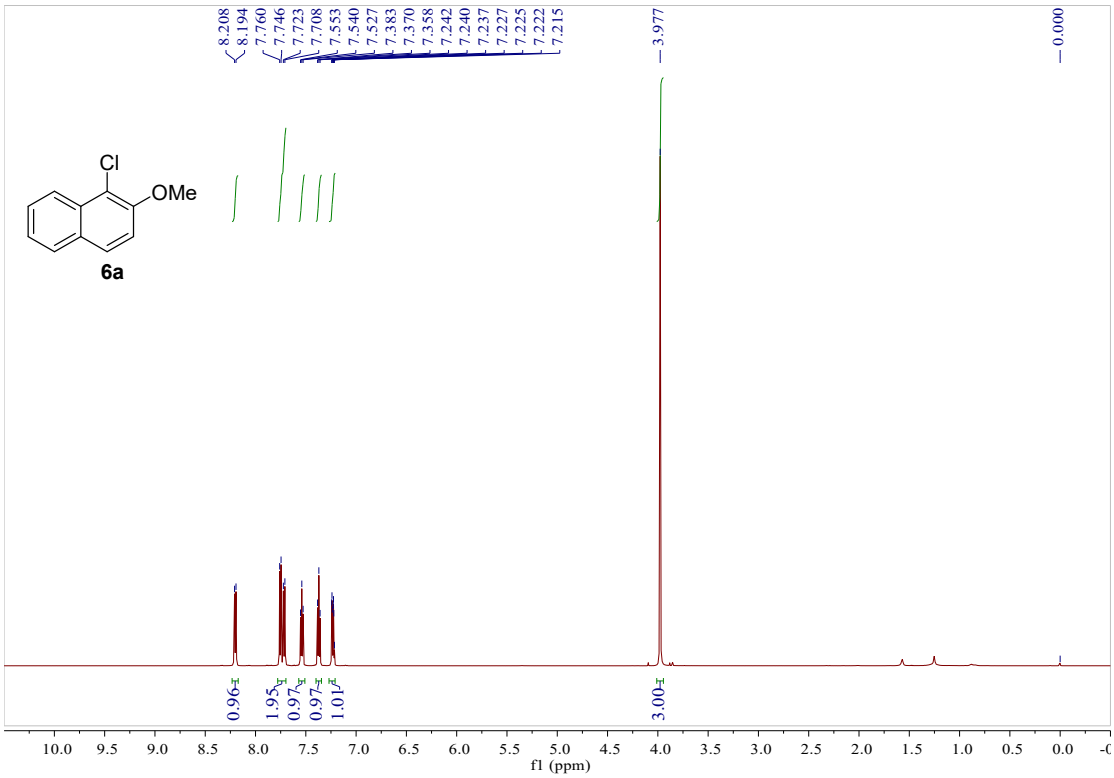
^{1}H NMR spectra for compound (5g)



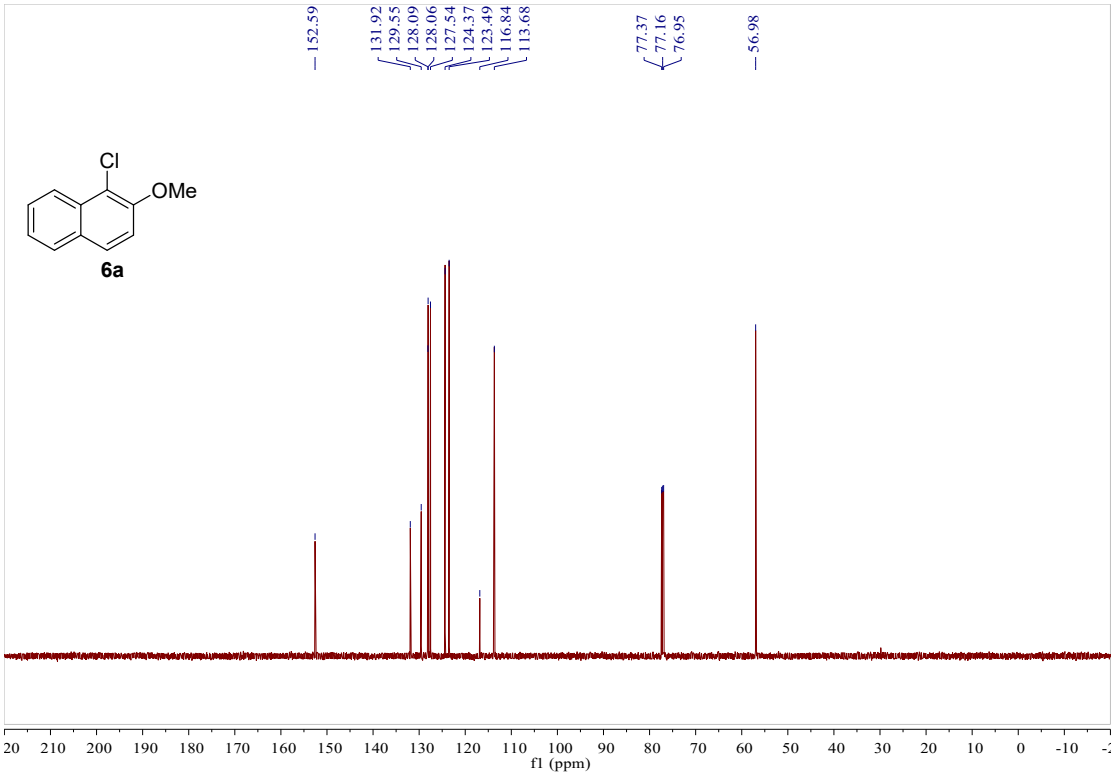
^{13}C NMR spectra for compound (5g)



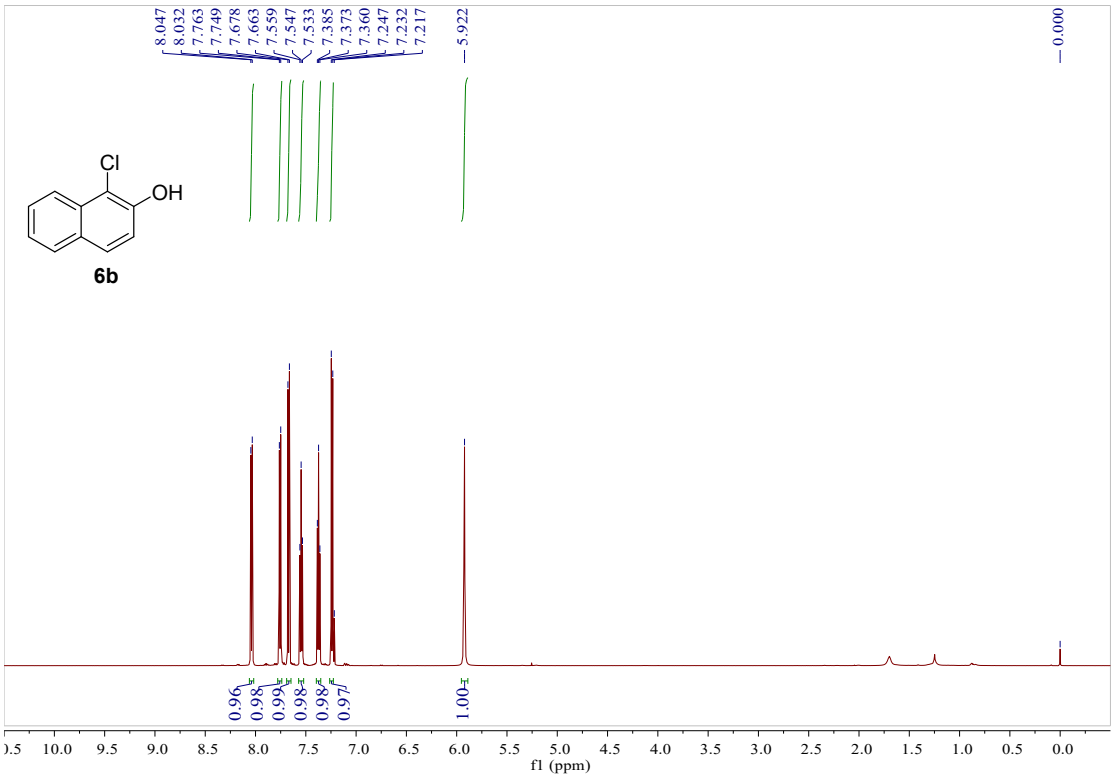
^{1}H NMR spectra for compound (6a)



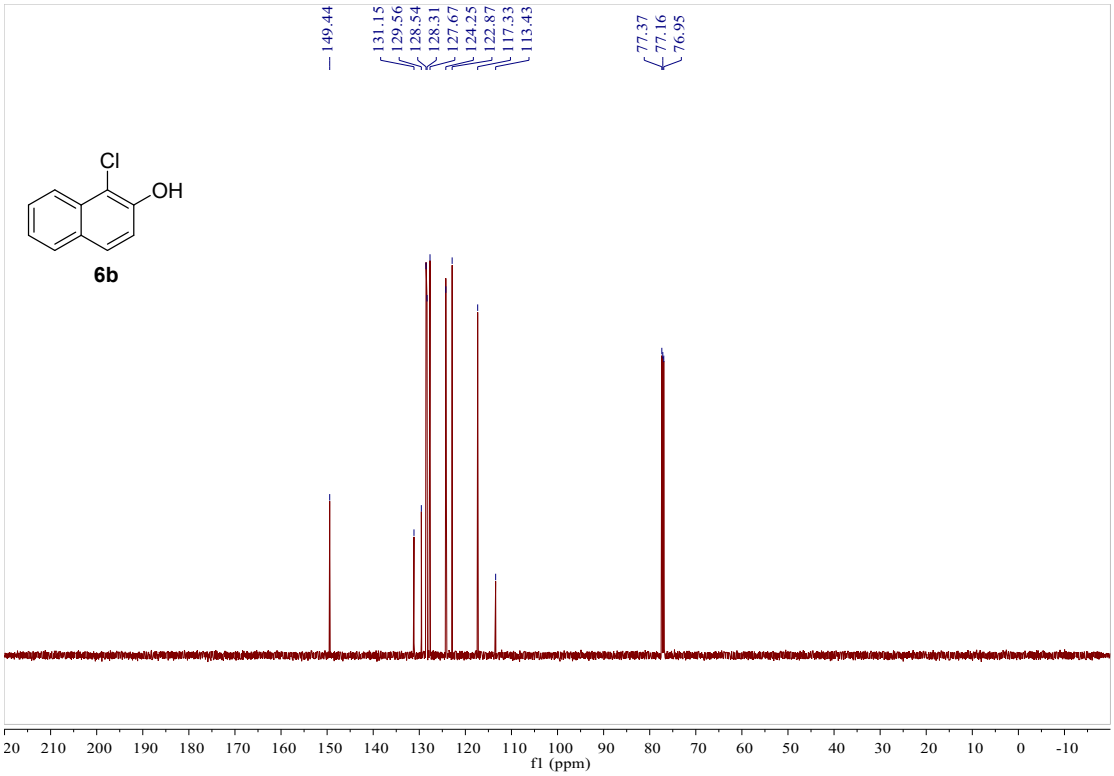
^{13}C NMR spectra for compound (6a)



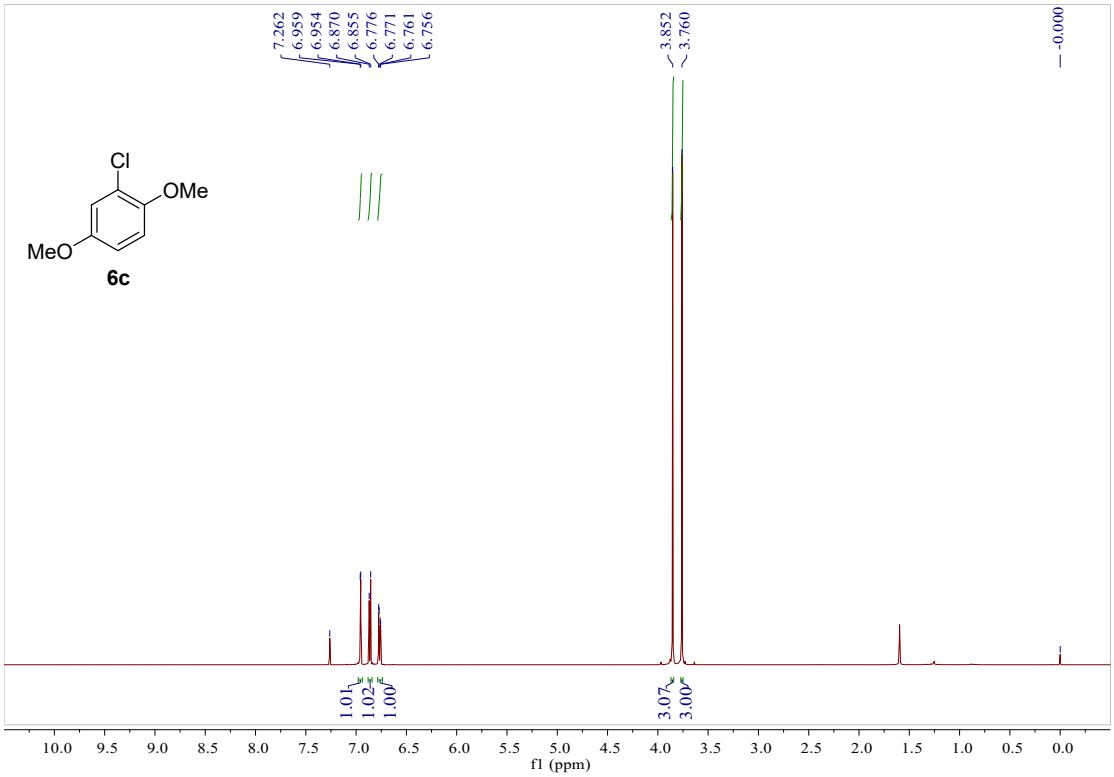
^{1}H NMR spectra for compound (6b)



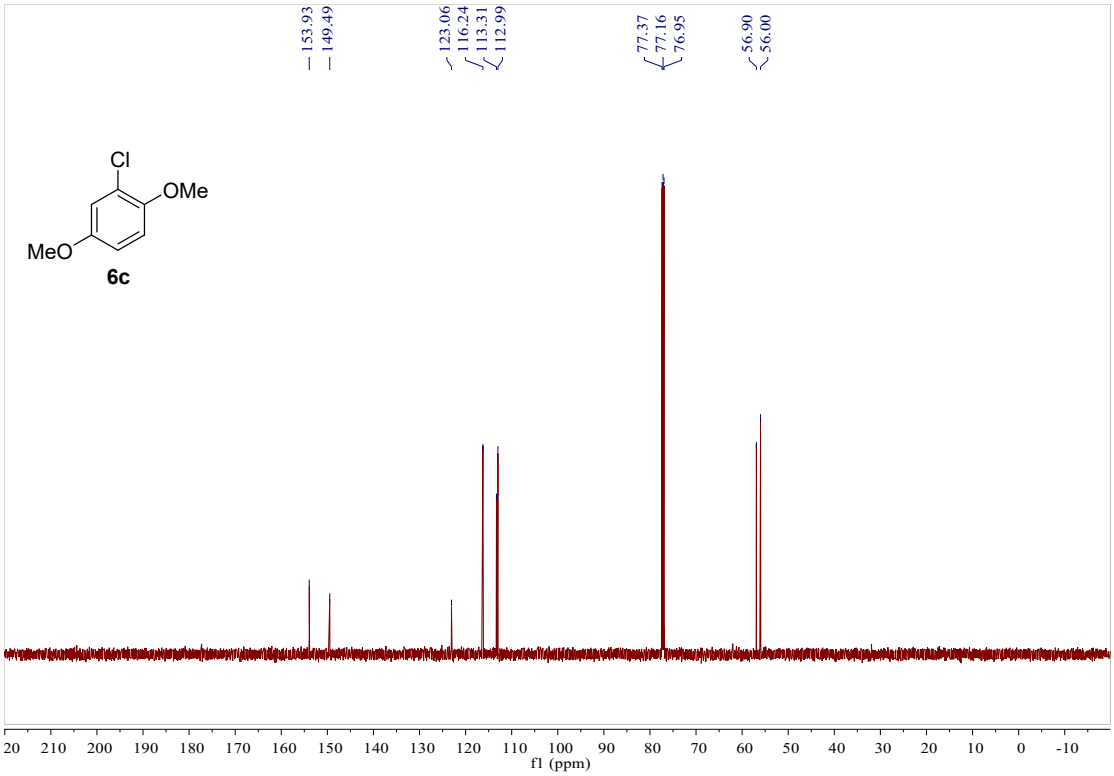
^{13}C NMR spectra for compound (6b)



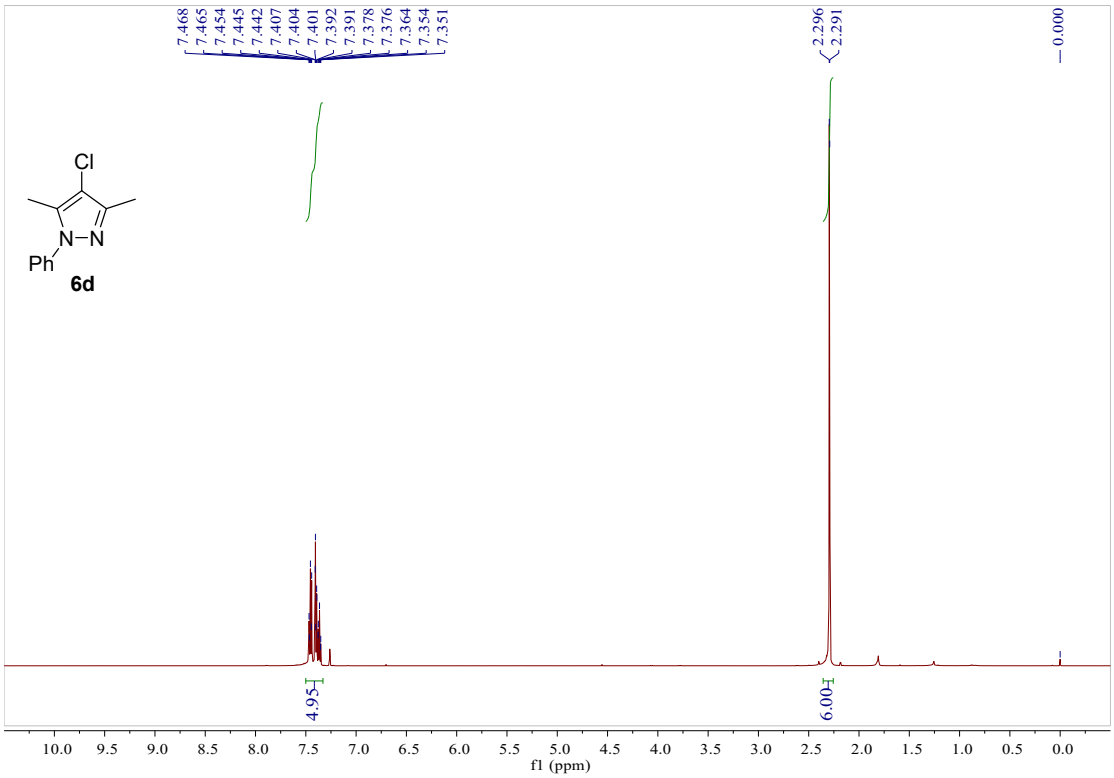
^{1}H NMR spectra for compound (6c)



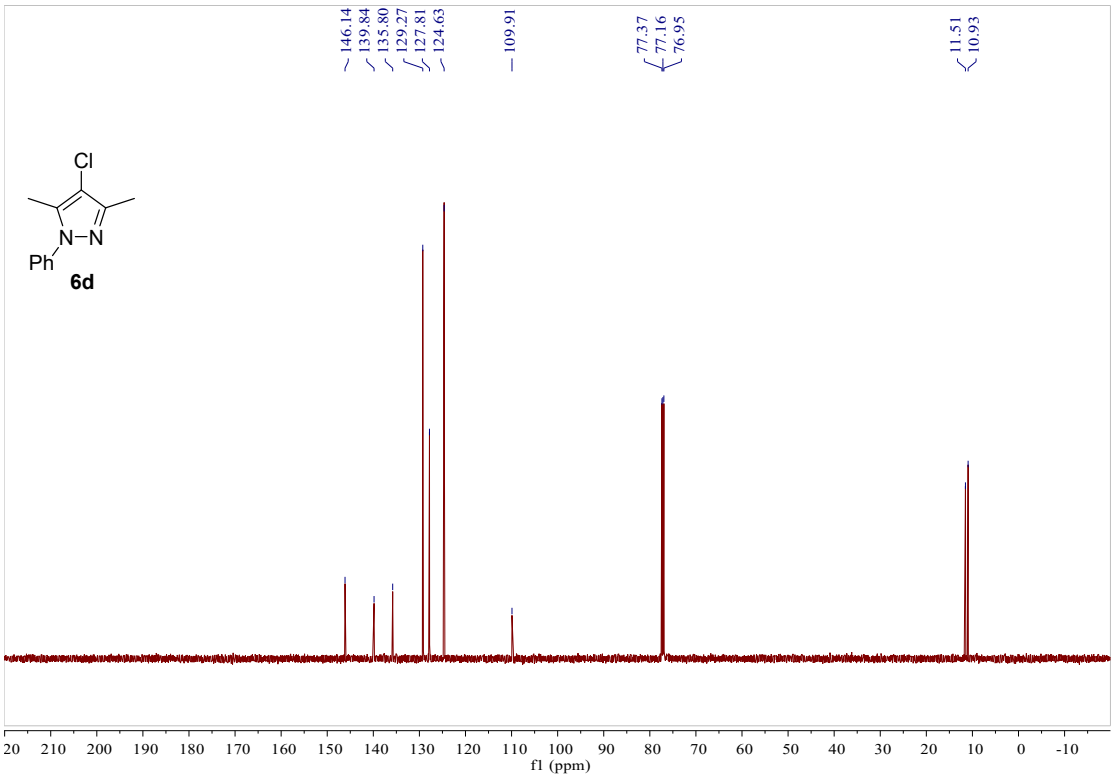
^{13}C NMR spectra for compound (6c)



^{1}H NMR spectra for compound (6d)



^{13}C NMR spectra for compound (6d)



10. References

1. T. Kitagawa, J. Nishino, T. Inomata, T. Ozawa, Y. Funahashi and H. Masuda, *Chem. Commun.*, 2016, **52**, 4780-4783.
2. X. Wang and Y. Wu, *Chem. Commun.*, 2018, **54**, 1877-1880.
3. B. H. Lipshutz, S. Ghorai and W. W. Y. Leong, *J. Org. Chem.*, 2009, **74**, 2854-2857.
4. Y. Yuan, A. Yao, Y. Zheng, M. Gao, Z. Zhou, J. Qiao, J. Hu, B. Ye, J. Zhao, H. Wen and A. Lei, *Iscience*, 2019, **12**, 293-+.
5. R. C. Lamb and P. W. Ayers, *J. Org. Chem*, 1962, **27**, 1441-1442.
6. B. Das, Y. Srinivas, C. Sudhakar, K. Damodar and R. Narender, *Synth. Commun.*, 2009, **39**, 220-227.
7. S. Song, X. Li, X. Sun, Y. Yuan and N. Jiao, *Green Chem.*, 2015, **17**, 3285-3289.
8. N. S. Y. Loy, S. Kim and C.-M. Park, *Org. Lett.*, 2015, **17**, 395-397.
9. K. Schuh and F. Glorius, *Synthesis-Stuttgart*, 2007, DOI: 10.1055/s-2007-983782, 2297-2306.
10. J. Xiang, R. Yuan, R. Wang, N. Yi, L. Lu, H. Zou and W. He, *J. Org. Chem.*, 2014, **79**, 11378-11382.
11. R. Banothu, S. Peraka, S. Kodumuri, D. Chevella, K. S. Gajula, V. Amrutham, D. R. Yennamaneni and N. Nama, *New J. Chem.*, 2018, **42**, 17879-17883.
12. K. Yubata and H. Matsubara, *Tetrahedron Lett.*, 2019, **60**, 1001-1004.
13. Y. Shi, Z. Ke and Y.-Y. Yeung, *Green Chem.*, 2018, **20**, 4448-4452.
14. H. A. Stefani, C. M. P. Pereira, R. B. Almeida, R. C. Braga, K. P. Guzen and R. Cella, *Tetrahedron Lett.*, 2005, **46**, 6833-6837.
15. I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti and B. Koenig, *Science*, 2019, **365**, 360-+.
16. P. D. Nahide, V. Ramadoss, K. A. Juarez-Ornelas, Y. Satkar, R. Ortiz-Alvarado, J. M. J. Cervera-Villanueva, A. J. Alonso-Castro, J. R. Zapata-Morales, M. A. Ramirez-Morales, A. J. Ruiz-Padilla, M. A. Deveze-Alvarez and C. R. Solorio-Alvarado, *Eur. J. Org. Chem.*, 2018, **2018**, 485-493.
17. A. Bose and P. Mal, *Tetrahedron Lett.*, 2014, **55**, 2154-2156.