

Electronic Supplementary Information

Localized Surface Plasmon Resonance assisted photoredox catalysis of newly fabricated Copper-Nanorods: A decarboxylative approach towards carbon-hydrogen bond formation under visible light

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1. Materials and methods

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. Petroleum ether used in our experiments was in the boiling range of 60-80 °C. Column chromatography was performed on silica gel (100-200 mesh, 0.075-0.150 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV-254 fluorescent indicator. ¹H-NMR and ¹³C-NMR spectra were recorded at ambient temperature using 300 MHz & 400 MHz spectrometers (300 MHz for ¹H and 75 & 100 MHz for ¹³C). Chemical shift (δ) is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), brs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (IR Spectrophotometer) in thin film (KBr) or neat. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadrupole mass spectrophotometer (Qtof ESI-MS). For HPLC analysis, achiralpak IB column (1B00CE-LF003) was used.

The crystal structure of copper nanorods were determined using a X-ray diffractometer (Rigaku Miniflex600) with Cu K α radiation (0.154 nm). Transmission electron microscopy (TEM) images, HRTEM images were taken using an Ultra-high resolution field emission gun transmission electron microscope (UHR-FEG TEM, JEM-2100F, Jeol, Japan) operating at 200 kV. For the TEM observations, the sample dissolved in hexane was drop cast on a carbon coated aluminium grid. Valence state analysis was carried out by using an X-ray photoelectron spectroscopic (XPS, Omicron, model: 1712-62-11) method. XPS measurement was done using an Al-K α radiation source under 15 kV voltage and 5 mA current. For XPS measurement the hexane solution of the NCs was also drop cast over glass slide (2mm \times 2mm) till a naked eye visible thin layer was formed. The room temperature optical absorbance of the samples was recorded by a UH4150 Spectrophotometer (Hitachi High tech).

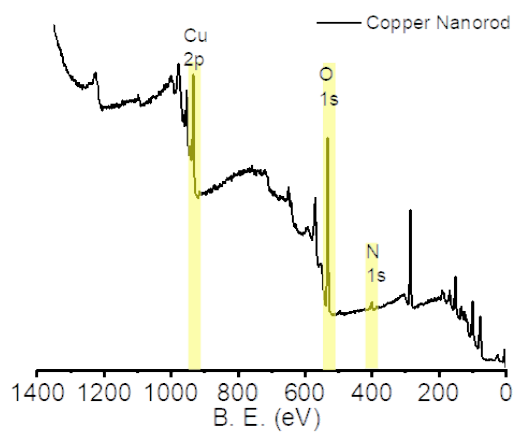
2. Synthetic procedure of Cu-NRs

150 mg Cu(I)Cl was dispersed in 5 ml degassed oleylamine in 25 ml round bottom flask. The solution was heated to 100 °C under continuous vacuum for 30 min to remove traces of water and oxygen. Then the reaction vessel purged with dry nitrogen gas and heated to 200 °C. The reaction was continued at this temperature for 1 h in nitrogen atmosphere. After completion of the reaction, the solution was naturally cooled to room temperature and the product was washed with cyclohexane. The washing process through centrifugation was repeated for 3-4 times before drying and storing.

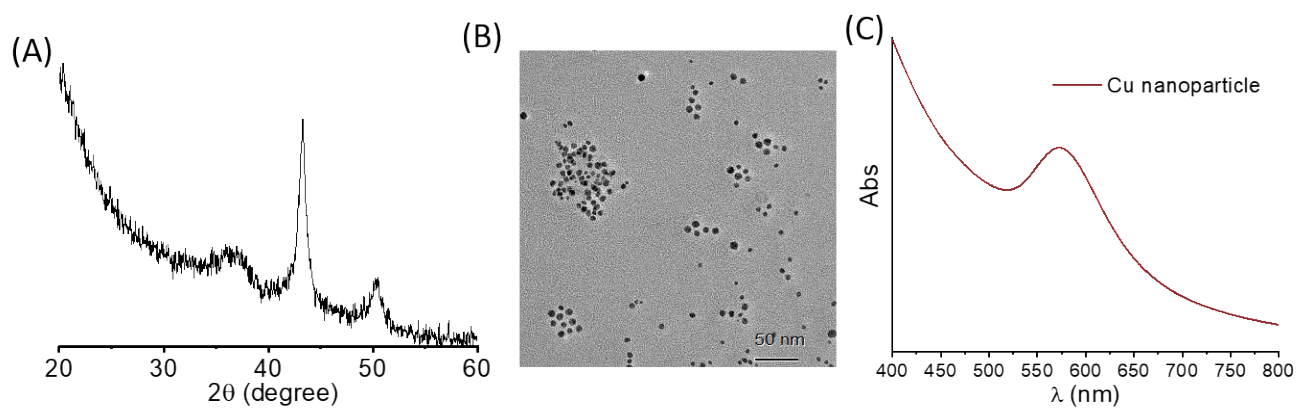
Synthesis of Cu nanoparticles:

50 mg of anhydrous CuCl₂ was first dissolved in a mixture solvent of 5 ml octadecene and 5 ml oleylamine in a 25 ml round bottom flask. The solution was heated to 100 °C under continuous vacuum for 30 min to remove traces of water and oxygen. Then the reaction vessel purged with dry nitrogen gas and heated to 180 °C. The reaction was continued at this temperature for 1 h in nitrogen atmosphere. The product was collected after naturally cooling the reaction solution. The product was washed with cyclohexane via centrifugation process.

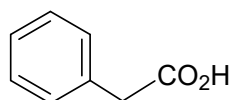
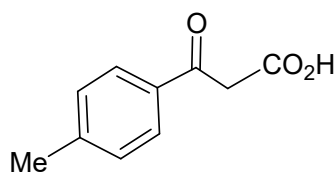
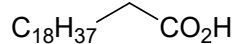
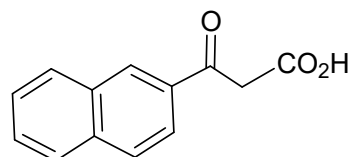
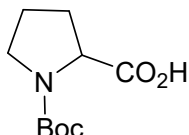
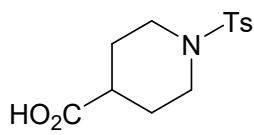
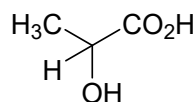
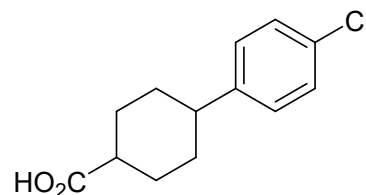
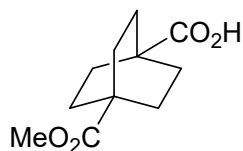
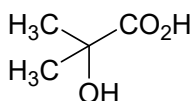
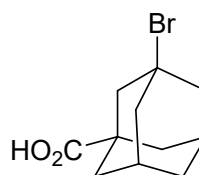
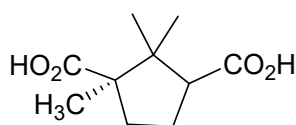
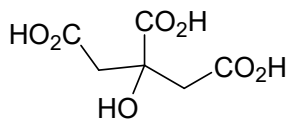
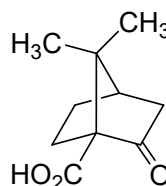
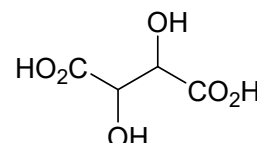
3. XPS data of Cu-NRs



4. XRD, TEM and LSPR absorbance of Cu-nanoparticles.



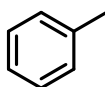
5. Starting materials used (1a-o)

Primary Substrates:**1a:** phenyl acetic acid**1b:** 3-oxo-3-(p-tolyl)propanoic acid**1c:** nonadecyl carboxylic acid**1d:** 3-(naphthalen-2-yl)-3-oxopropanoic acid**Secondary Substrates:****1e:** *tert*-butoxycarbonyl proline**1f:** 1-tosylpiperidine-4-carboxylic acid**1g:** 2-hydroxypropanoic acid**1h:** 4-(4-chlorophenyl)cyclohexane-1-carboxylic acid**Tertiary Substrates:****1i:** 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid**1j:** 2-hydroxy-2-methylpropanoic acid**1k:** 3-bromoadamantane-1-carboxylic acid**some naturally occurring organic acids****1l:** (+) Camphoric acid**1m:** Citric acid**1n:** (+) Ketopinic acid**1o:** Tartaric acid**6. General procedure for the Cu-NRs catalysed direct decarboxylation towards alkane analogues (2a-n)**

A solution containing 1.0 mmol of carboxylic acids (**1**) was taken in 5.0 mL of dry acetonitrile in a 10 mL RB capped with a septum, and Cs_2CO_3 (0.5 equivalents) was subsequently added, depending on the carboxylic acid group (s) present in the substrate and a balloon of N_2 dipped with a needle. A suspension of Cu-NRs (5 mol%) in 1 mL of acetonitrile was injected into reaction mixture under stirring conditions at room temperature (~ 30 to 35°C) in a nitrogen atmosphere and under the illumination of a 10W Red LED. The reaction progress was monitored using thin-layer chromatography (TLC), and after 8 hours, a single spot was observed, indicating completion of the reaction. The reaction mixture was then filtered, and all the products (**2a-n**) were isolated through HPLC technique using an achiralpak IB column (1B00CE-LF003) with mobile phase: hex/ea 98:2 at temperature: 25°C , flow rate: 0.9 ml/min and pressure: 26 kgf.

7. Characterization data of the synthesized compounds (2a-n)

7.1. Toluene (2a)



Yield: 78% (45 mg, 0.79 mmol).

Characteristic: Colorless liquid.

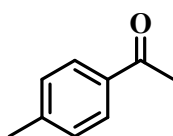
¹H-NMR (300 MHz, CDCl₃): δ 7.46-7.41 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 3H), 2.53 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 138.0, 129.2, 128.4, 125.5, 21.6.

FT-IR (neat, cm⁻¹): 3099, 3068, 3032, 2925, 1615, 1506, 1465, 1086, 1035.

HRMS (ESI-TOF) *m/z* Calcd. for C₇H₉ [M]⁺: 92.0626, found 92.0623.

7.2. 1-(p-tolyl)ethan-1-one (2b)



Yield: 80% (45 mg, 0.80 mmol).

Characteristic: Colorless liquid.

¹H-NMR (300 MHz, CDCl₃): δ 7.83 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 6.3 Hz, 2H), 2.54 (d, *J* = 2.4 Hz, 3H), 2.38 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6.

FT-IR (neat, cm⁻¹): 3064, 3015, 2972, 1680, 1605, 1590, 1482.

HRMS (ESI-TOF) *m/z* Calcd. for C₉H₁₁O [M+H]⁺: 135.0810, found 135.0812.

7.3. Nonadecane (2c)



Yield: 70% (188 mg, 0.70 mmol).

Characteristic: Colorless liquid.

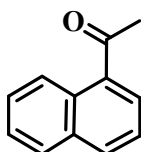
¹H-NMR (300 MHz, CDCl₃): δ 1.33-1.26 (m, 34H), 0.90-0.86 (m, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 32.0, 29.8, 29.7, 29.4, 22.7, 14.1.

FT-IR (neat, cm⁻¹): 2956, 2920, 2852, 1466, 1378.

HRMS (ESI-TOF) *m/z* Calcd. for C₁₉H₄₀Na [M+Na]⁺: 291.3028, found 291.3027.

7.4. 1-(naphthalen-1-yl)ethan-1-one (2d)¹



Yield: 75% (127.5 mg, 0.75 mmol).

Characteristic: Colorless oil.

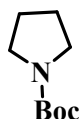
¹H-NMR (300 MHz, CDCl₃): δ 8.83 (d, *J* = 8.4 Hz, 1H), 7.98-7.85 (m, 3H), 7.65-7.42 (m, 3H), 2.73 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃): δ 201.8, 135.3, 134.0, 133.1, 130.2, 128.8, 128.5, 128.1, 126.5, 126.1, 124.4, 30.0.

FT-IR (neat, cm⁻¹): 3040, 3002, 2960, 1645, 1605, 1578, 1452.

HRMS (ESI-TOF) *m/z* Calcd. for C₁₂H₁₁O [M+H]⁺: 171.0810, found 171.0814.

7.5. *tert*-butyl pyrrolidine-1-carboxylate (2e)



Yield: 82% (140 mg, 0.82 mmol).

Characteristic: Colorless oil.

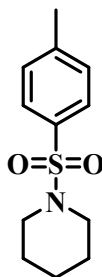
¹H-NMR (300 MHz, CDCl₃): δ 3.28 (t, *J* = 7.2 Hz, 4H), 1.82-1.79 (m, 4H), 1.43 (s, 9H).

¹³C-NMR (75 MHz, CDCl₃): δ 154.7, 45.9, 45.6, 28.5, 25.7, 25.0.

FT-IR (neat, cm⁻¹): 2978, 2939, 2879, 1696.

HRMS (ESI-TOF) *m/z* Calcd. for C₉H₁₈NO₂ [M+H]⁺: 172.1338, found 172.1335.

7.6. 1-Tosylpiperidine (2f)²



Yield: 80% (191.2 mg, 0.80 mmol).

Characteristic: Brown crystalline solid.

Melting range: 144-145 °C.

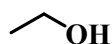
¹H-NMR (300 MHz, CDCl₃): δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 5.4 Hz, 4H), 2.43 (s, 3H), 1.66-1.59 (m, 4H), 1.40 (t, *J* = 6.0 Hz, 2H).

¹³C-NMR (100 MHz, CDCl₃): δ 143.4, 133.1, 129.6, 127.7, 46.9, 25.2, 23.5, 21.5.

FT-IR (KBr, cm⁻¹): 3136, 1459, 1418, 1340, 1312, 1207.

HRMS (ESI-TOF) *m/z* Calcd. for C₁₂H₁₇NO₂S [M]⁺: 239.0980, found 239.0978.

7.7. Ethanol (2g)



Yield: 68% (28 mg, 0.68 mmol).

Characteristic: Colorless liquid.

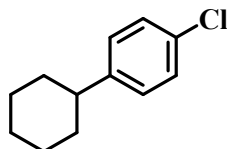
¹H-NMR (300 MHz, CDCl₃): δ 3.70-3.62 (m, 2H), 3.41 (d, *J* = 4.2 Hz, 1H), 1.20 (t, *J* = 6.9 Hz, 3H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 58.0, 18.1.

FT-IR (neat, cm^{-1}): 3323, 2959, 2942, 1368, 1300, 1163, 1132.

HRMS (ESI-TOF) m/z Calcd. for $\text{C}_2\text{H}_6\text{O}$ $[\text{M}]^+$: 46.0419, found 46.0421.

7.8. 1-Chloro-4-cyclohexylbenzene (2h)



Yield: 78% (152 mg, 0.78 mmol).

Characteristic: Colorless oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.26 (q, $J = 1.8$ Hz, 2H), 7.16-7.13 (m, 2H), 2.50-2.42 (m, 1H), 2.00-1.72 (m, 5H), 1.40-1.17 (m, 5H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 146.5, 130.9, 128.3, 128.1, 44.0, 34.4, 26.8, 26.1.

FT-IR (neat, cm^{-1}): 3054, 2922, 2850, 1492, 1448.

HRMS (ESI-TOF) m/z Calcd. for $\text{C}_{12}\text{H}_{15}\text{Cl}$ $[\text{M}]^+$: 194.0862, found 194.0861.

7.9. Methyl bicyclo[2.2.2]octane-1-carboxylate (2i)



Yield: 70% (118 mg, 0.70 mmol).

Characteristic: Colorless oil.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.61 (s, 3H), 1.75-1.68 (m, 6H), 1.62-1.52 (m, 7H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 178.6, 51.5, 38.3, 28.0, 25.8, 23.5.

FT-IR (neat, cm^{-1}): 2950, 2915, 2869, 1731, 1249.

HRMS (ESI-TOF) m/z Calcd. for $\text{C}_{10}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 191.1048, found 191.1044.

7.10. Propan-2-ol (2j)



Yield: 75% (45 mg, 0.75 mmol).

Characteristic: Colorless liquid.

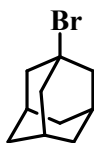
$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 3.85-3.72 (m, 2H), 1.03-1.01 (m, 6H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 63.6, 24.9.

FT-IR (neat, cm^{-1}): 3333, 2969, 2932, 2883, 1466, 1378, 1308, 1160, 1128.

HRMS (ESI-TOF) m/z Calcd. for $\text{C}_3\text{H}_8\text{NaO}$ $[\text{M}+\text{Na}]^+$: 83.0473, found 83.0472.

7.11. 1-Bromoadamantane (2k)



Yield: 65% (140 mg, 0.65 mmol).

Characteristic: White solid.

¹H-NMR (300 MHz, CDCl₃): δ 2.37 (d, J = 2.1 Hz, 6H), 2.12-2.07 (m, 3H), 1.73 (t, J = 3.0 Hz, 6H).

¹³C-NMR (75 MHz, CDCl₃): δ 49.4, 37.5, 35.6, 32.8.

FT-IR (KBr, cm⁻¹): 2915, 1440, 1360.

HRMS (ESI-TOF) m/z Calcd. for C₁₀H₁₅Br [M]⁺: 214.0357, found 214.0355 (One of the major peaks).

7.12. (S)-1,1,2-trimethylcyclopentane (2l)



Yield: 70% (78 mg, 0.70 mmol).

Characteristic: Colorless liquid.

¹H-NMR (300 MHz, CDCl₃): δ 1.60-1.23 (m, 7H), 0.96 (s, 3H), 0.82 (d, J = 7.2 Hz, 3H), 0.72 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ 49.2, 40.8, 33.6, 26.8, 25.2, 20.3, 16.4.

FT-IR (neat, cm⁻¹): 2975, 2875.

HRMS (ESI-TOF) m/z Calcd. for C₈H₁₇ [M+H]⁺: 113.1330, found 113.1331.

7.13. (1R,4R)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (2m)



Yield: 74% (102 mg, 0.74 mmol).

Characteristic: White solid

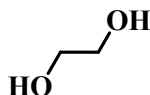
¹H-NMR (300 MHz, CDCl₃): δ 2.48-2.39 (m, 1H), 2.07-1.98 (m, 4H), 1.78 (d, J = 17.1 Hz, 1H), 1.53-1.38 (m, 2H), 1.04 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃): δ 218.6, 57.7, 46.0, 44.9, 43.5, 27.4, 22.8, 21.6, 20.2.

FT-IR (KBr, cm⁻¹): 2967, 2890, 1740.

HRMS (ESI-TOF) m/z Calcd. for C₉H₁₅O [M+H]⁺: 139.1123, found 139.1120.

7.14. Ethane-1,2-diol (2n)



Yield: 80% (49.6 mg, 0.80 mmol).

Characteristic: Colorless liquid.

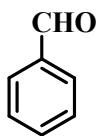
¹H-NMR (300 MHz, CDCl₃): δ 3.73 (s, 4H), 3.19 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃): δ 63.7, 63.3.

FT-IR (KBr, cm^{-1}): 3350, 2956, 2887, 2353, 1603, 1446, 1318, 1111.

HRMS (ESI-TOF) m/z Calcd. for $\text{C}_2\text{H}_6\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 85.0265, found 85.0268.

8. Control experiment data: Benzaldehyde (3a)



Characteristic: Colourless liquid.

^1H NMR (300 MHz, CDCl_3): δ 10.03 (s, 1H), 7.90-7.88 (m, 2H), 7.66-7.62 (m, 1H), 7.56-7.46 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3): δ 192.5, 136.4, 134.5, 129.7, 129.0.

FT-IR (neat, cm^{-1}): 2860, 2820, 1828, 1664.

HRMS (ESI-TOF) (m/z) Calcd. for $\text{C}_7\text{H}_7\text{O}$ $[\text{M}+\text{H}]^+$: 107.0497, found: 107.0499.

9. Comparative study of our protocol with similar literature reports:

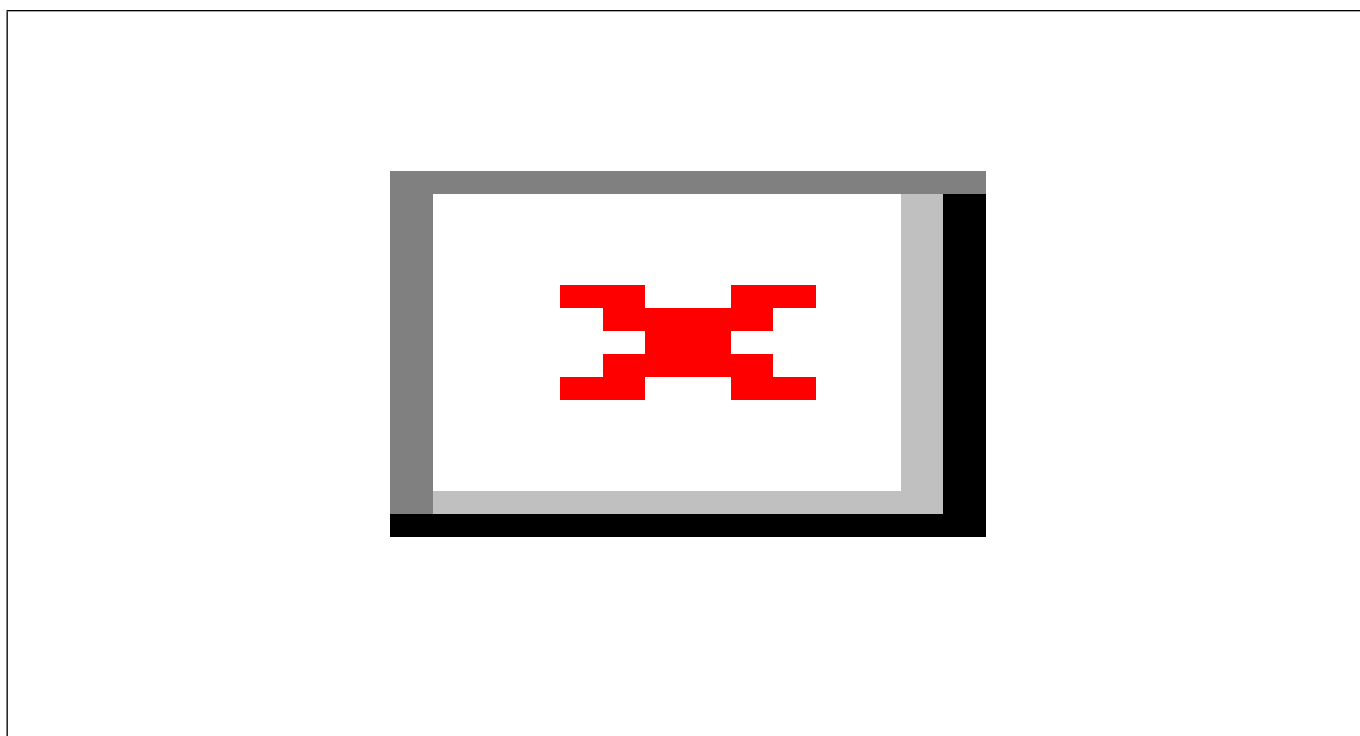
Common Product	% Yield in our protocol [LSPR of Cu-NRs]	Pervious Literature reports (% yield)	
		Lee <i>et al</i> (2022) ³ $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$	Baran <i>et al</i> (2017) ⁴ $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - \text{Ph}_3\text{SiH}/\text{Zn}]$
2c	70	35	-
2d	75	73	-
2e	82	<5	-
2f	80	65	71
2h	78	71	-
2i	70	87	49
2k	65	50	-
2m	74	58	-

10. Reference:

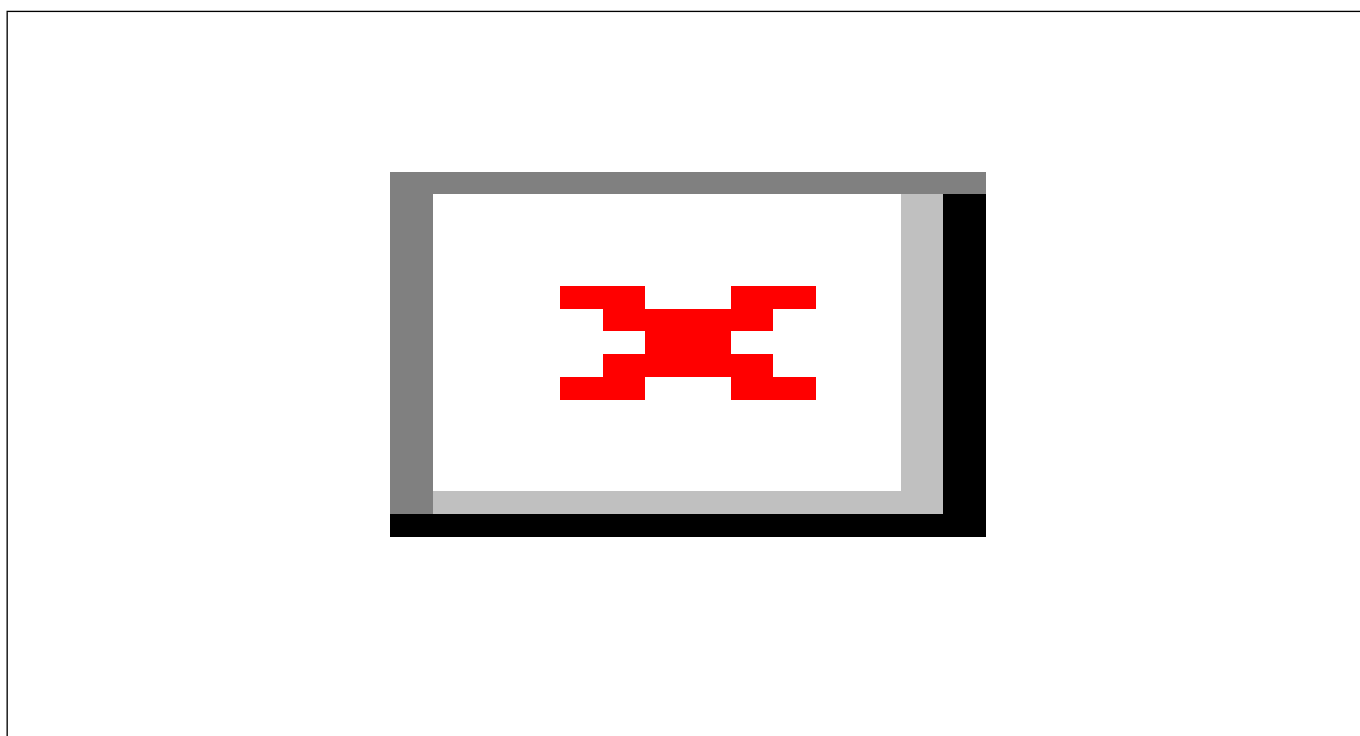
- (1) X. Wang, M. Liu, L. Xu, Q. Wang, J. Chen, J. Ding, H. Wu, *Org. Chem.*, 2013, **78** (11), 5273–5281.
- (2) A. Kamal, H. K. Singh, S. K. Maury, A. K. Kushwaha, V. Srivastava, S. Singh, *Asian J. Org. Chem.*, 2023, **12**, 1-6.
- (3) E. B. McLean, D. T. Mooney, D. J. Burns, A. –L. Lee, *Org. Lett.* 2022, **24**, 686–691.
- (4) T. Qin, L. R. Malins, J. T. Edwards, R. R. Merchant, A. J. E. Novak, J. Z. Zhong, R. B. Mills, M. Yan, C. Yuan, M. D. Eastgate, P. S. Baran, *Angew. Chem., Int. Ed.* 2017, **56**, 260–265.

11. Mass spectra of the of the synthesized compounds (2a-n)

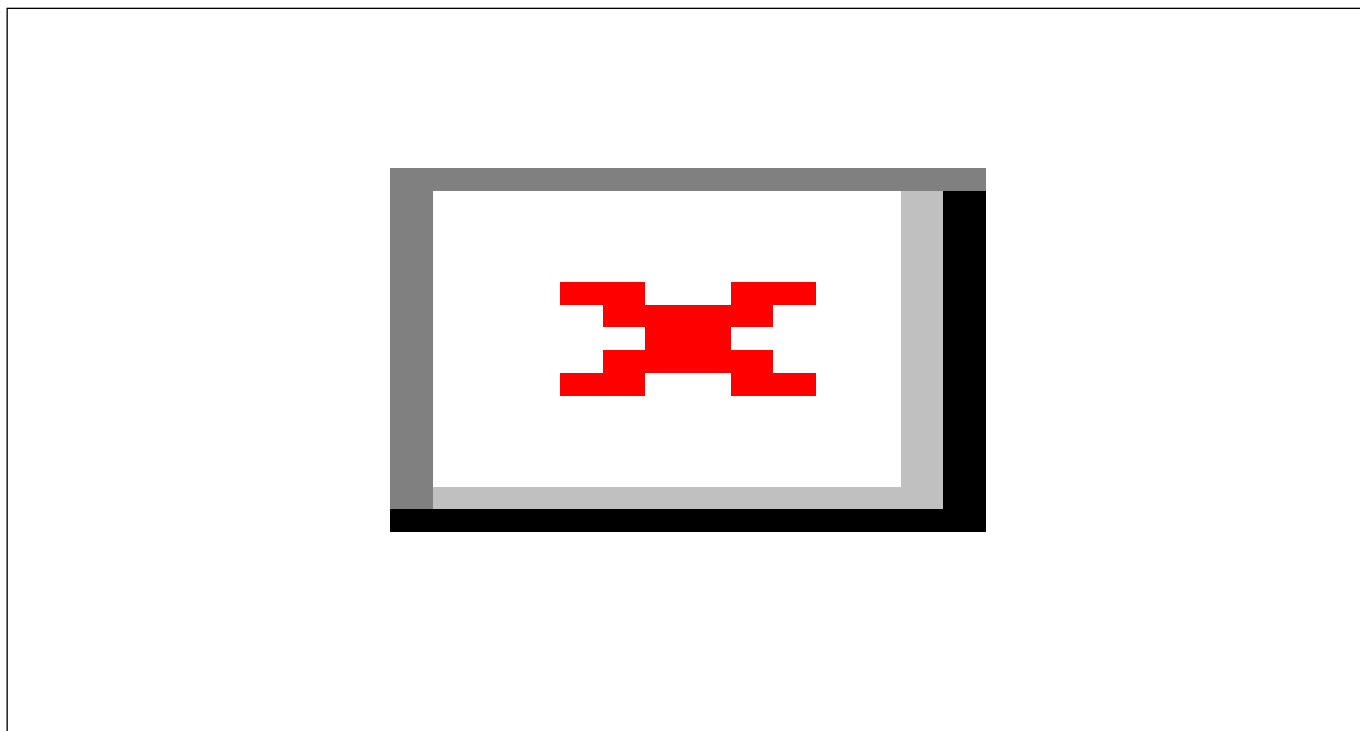
SI Figure 1: HRMS spectrum of 2a; Calcd. for C_7H_8 $[M]^+$: 92.0626, found 92.0623.



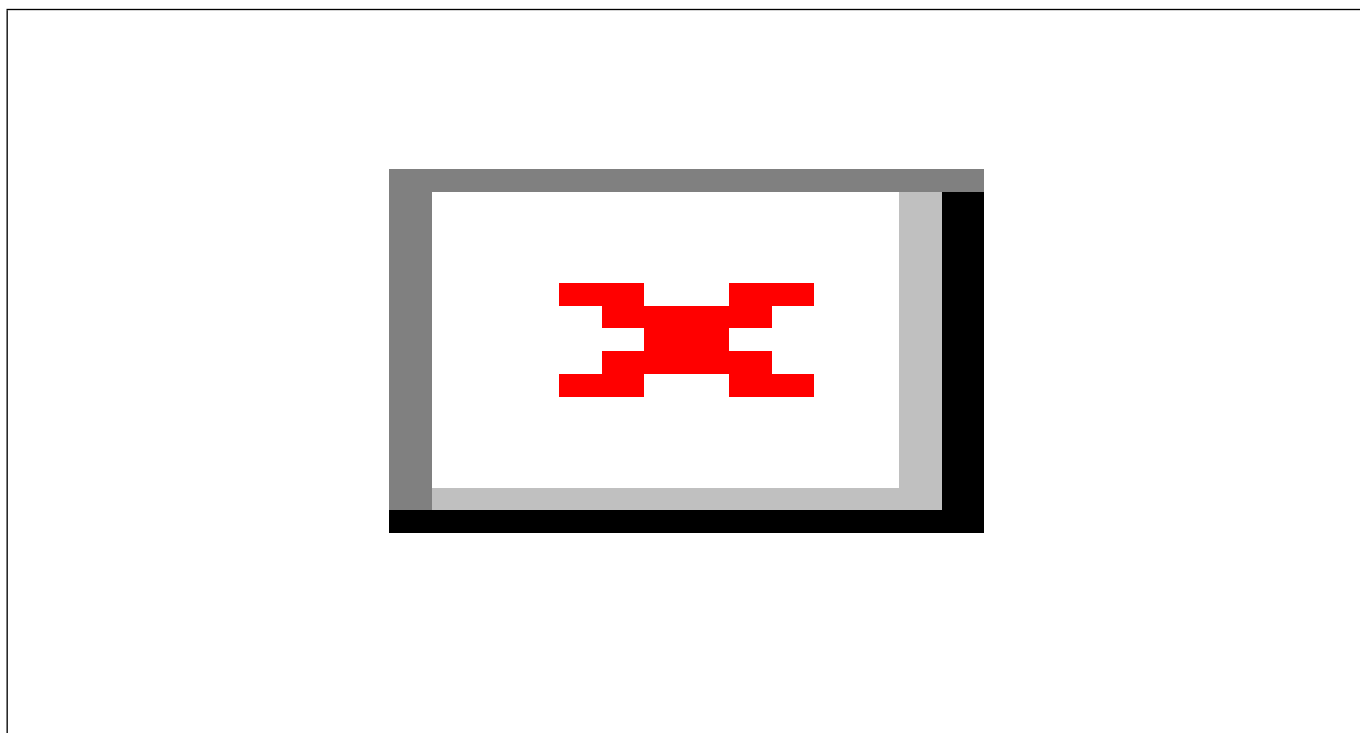
SI Figure 2: HRMS spectrum of 2b; Calcd. for $C_9H_{11}O$ $[M+H]^+$: 135.0810, found 135.0812.



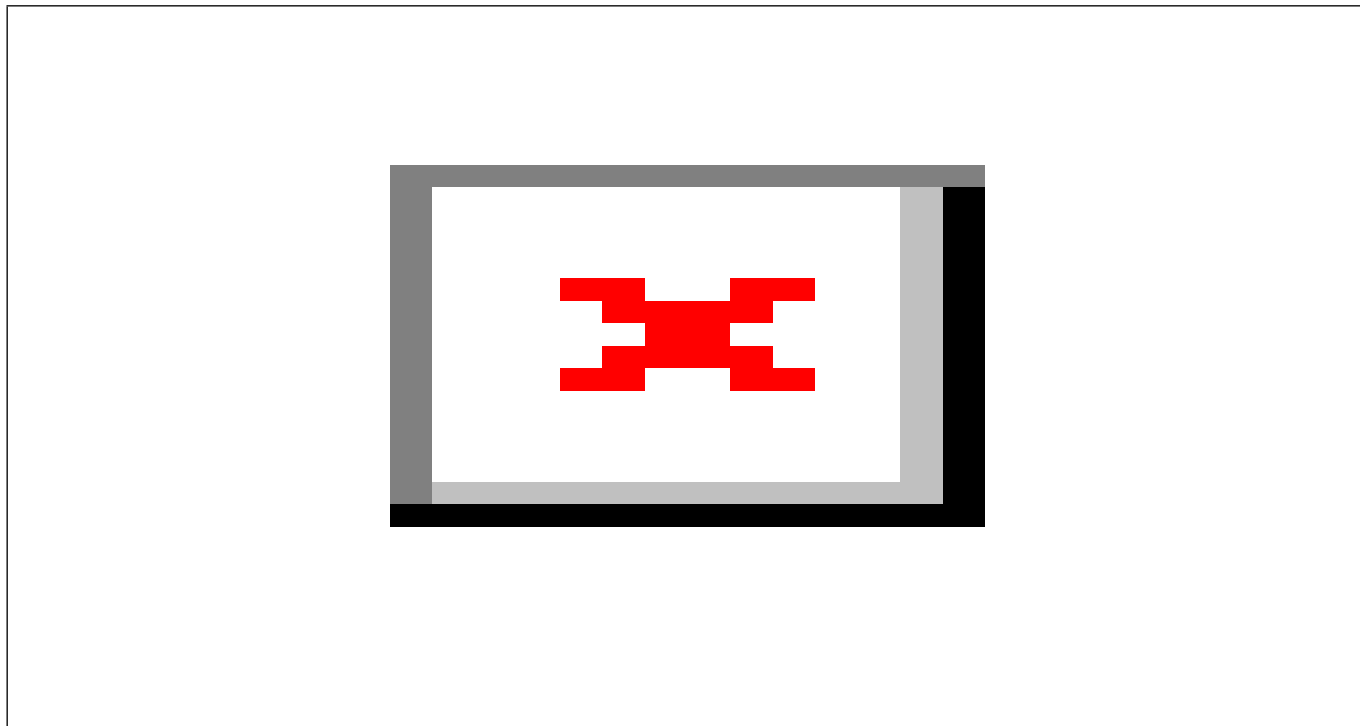
SI Figure 3: HRMS spectrum of 2c; Calcd. for $C_{19}H_{40}Na$ $[M+Na]^+$: 291.3028, found 291.3027.



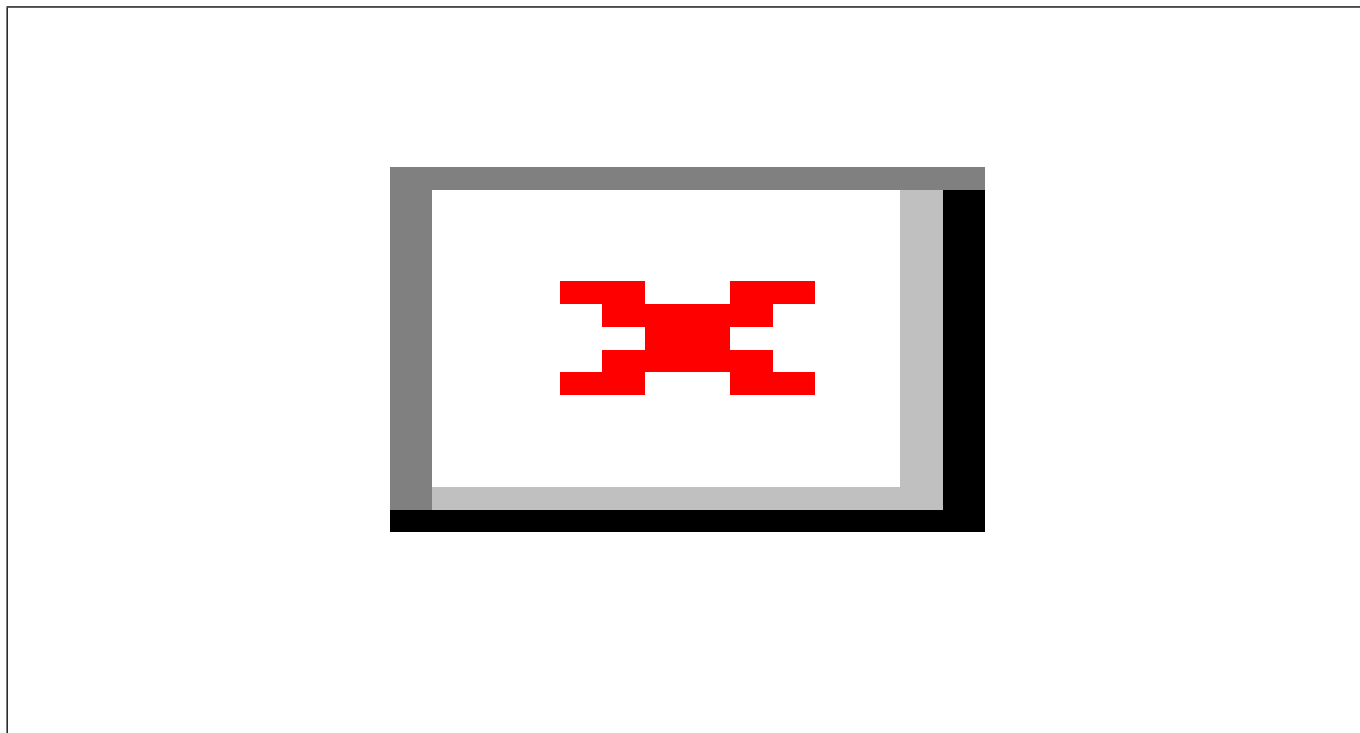
SI Figure 4: HRMS spectrum of 2d; Calcd. for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found 171.0814.



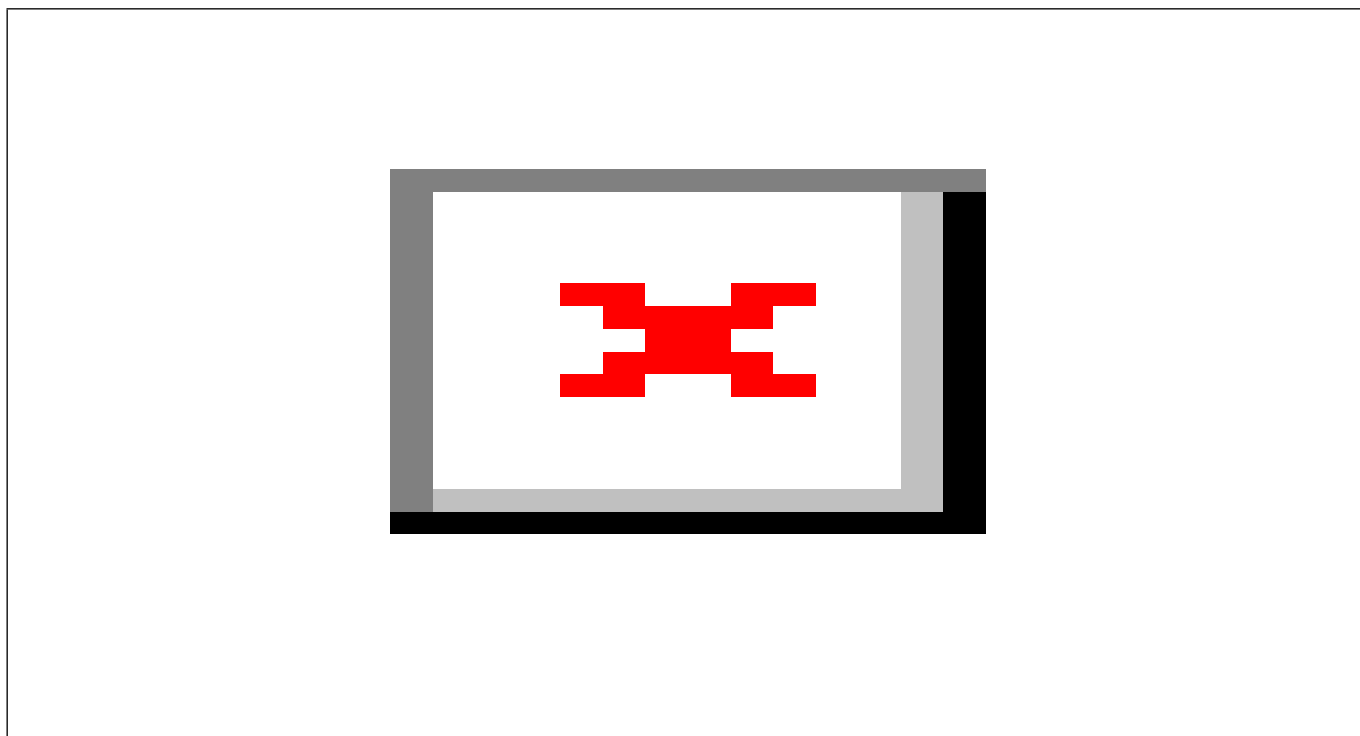
SI Figure 5: HRMS spectrum of 2e; Calcd. for $C_9H_{18}NO_2$ $[M+H]^+$: 172.1338, found 172.1335.



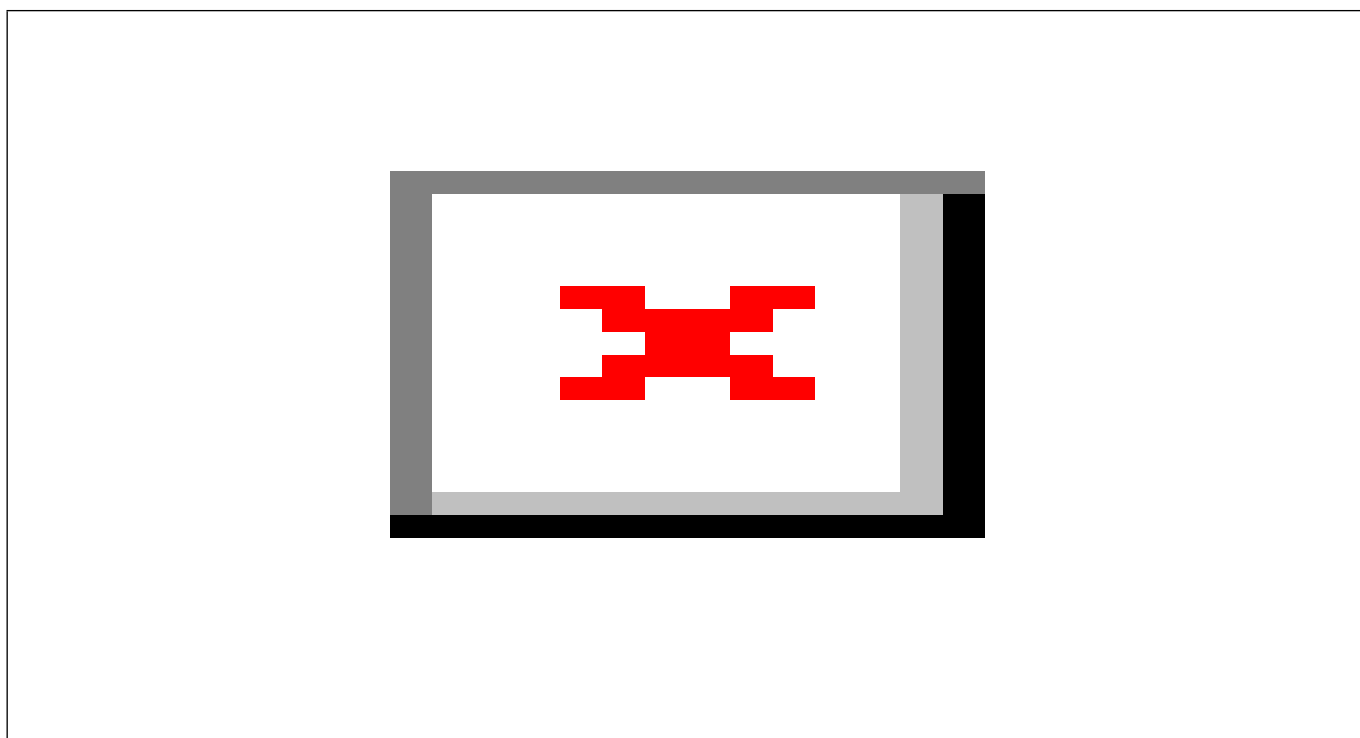
SI Figure 6: HRMS spectrum of 2f; Calcd. for $C_{12}H_{17}NO_2S$ $[M]^+$: 239.0980, found 239.0976.



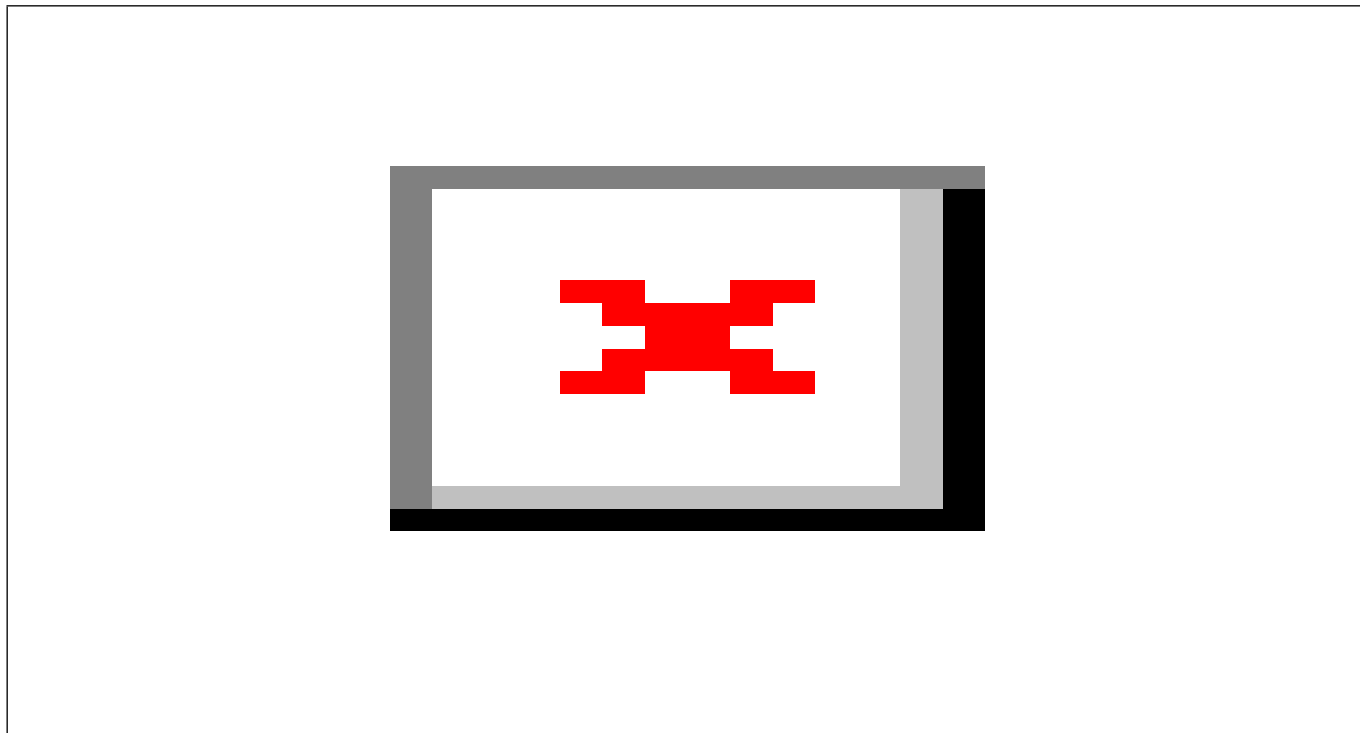
SI Figure 7: HRMS spectrum of 2g; Calcd. for $C_2H_6O [M]^+$: 46.0419, found 46.0421.



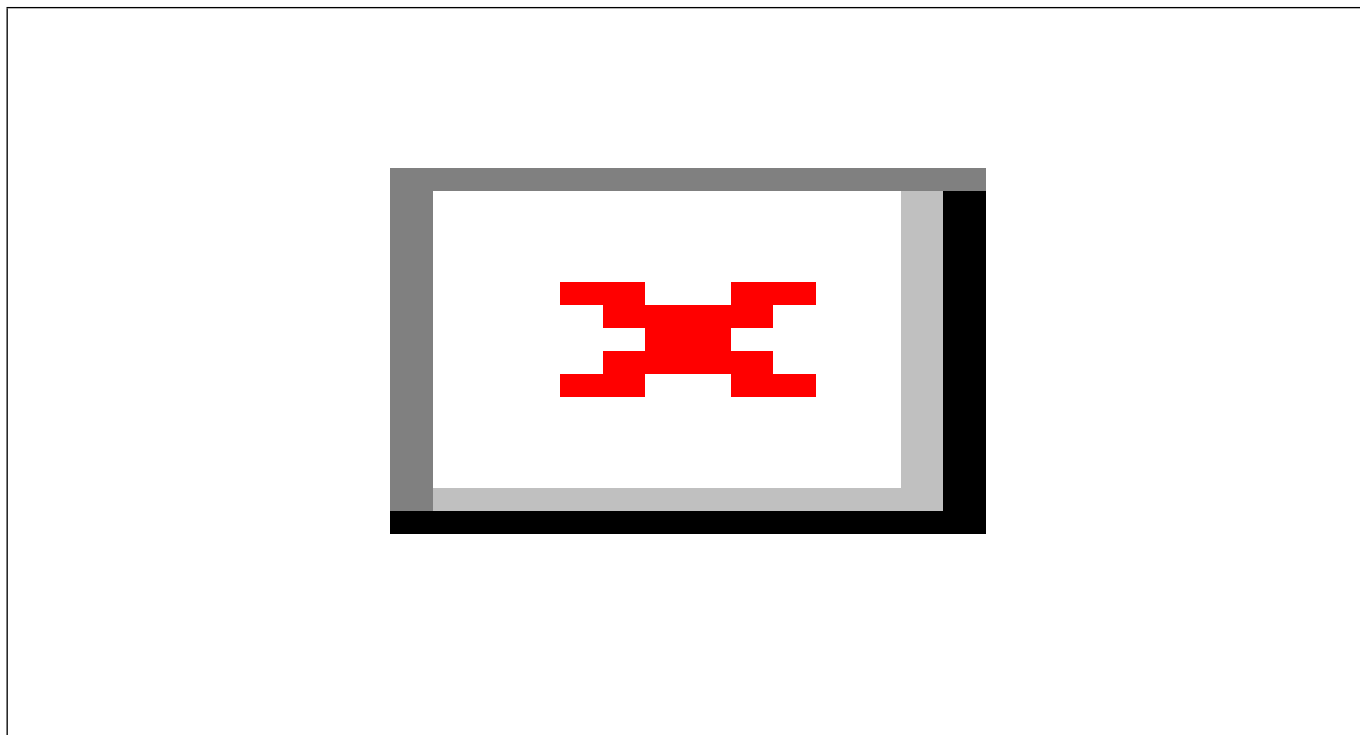
SI Figure 8: HRMS spectrum of 2h; Calcd. for $C_{12}H_{15}Cl [M]^+$: 194.0862, found 194.0861.



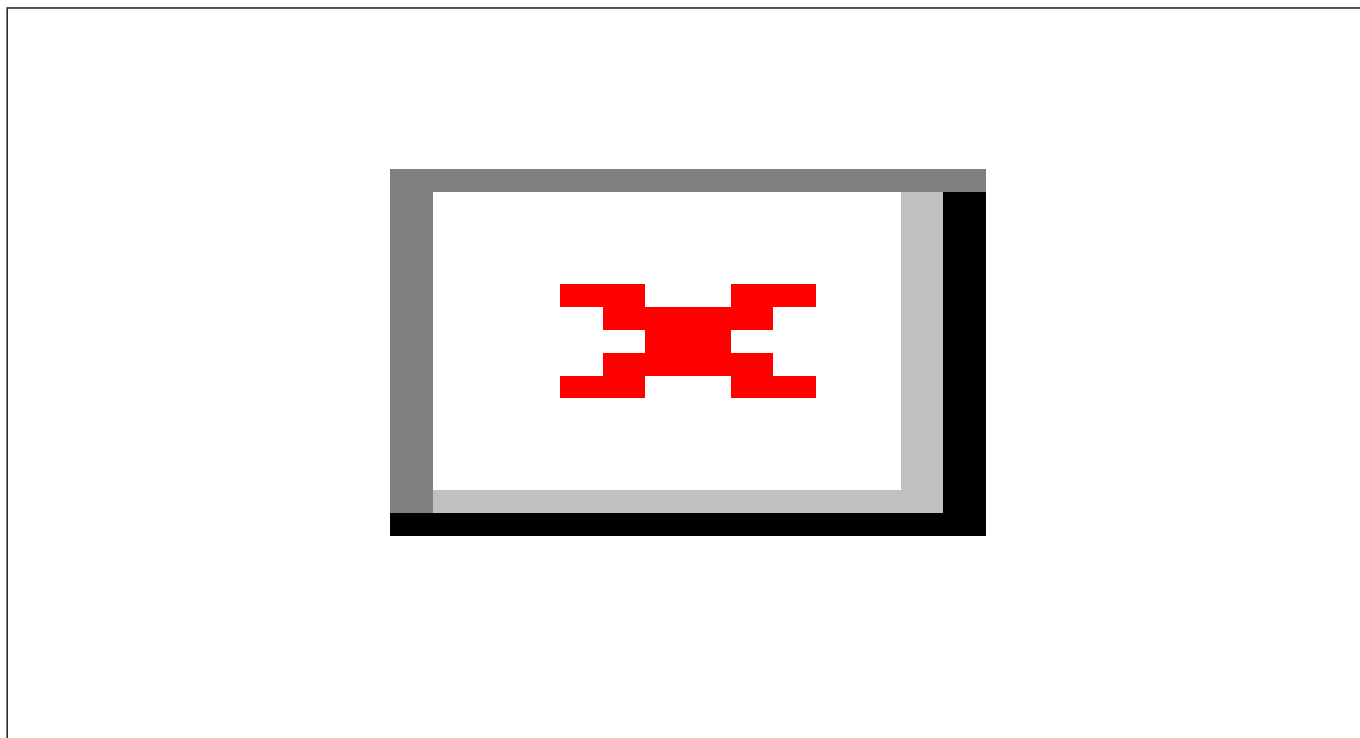
SI Figure 9: HRMS spectrum of 2i; Calcd. for $C_{10}H_{16}NaO_2$ $[M+Na]^+$: 191.1048, found 191.1044.



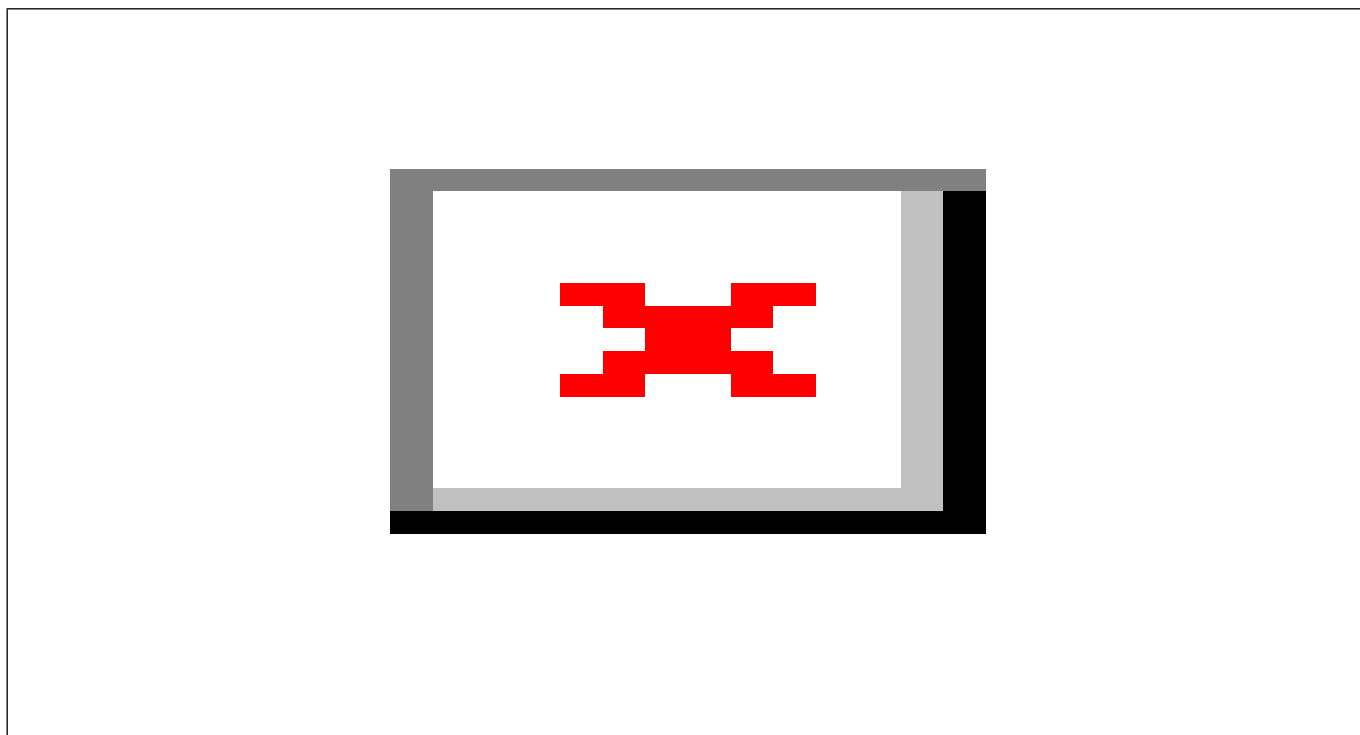
SI Figure 10: HRMS spectrum of 2j; Calcd. for C_3H_8NaO $[M+Na]^+$: 83.0473, found 83.0472.



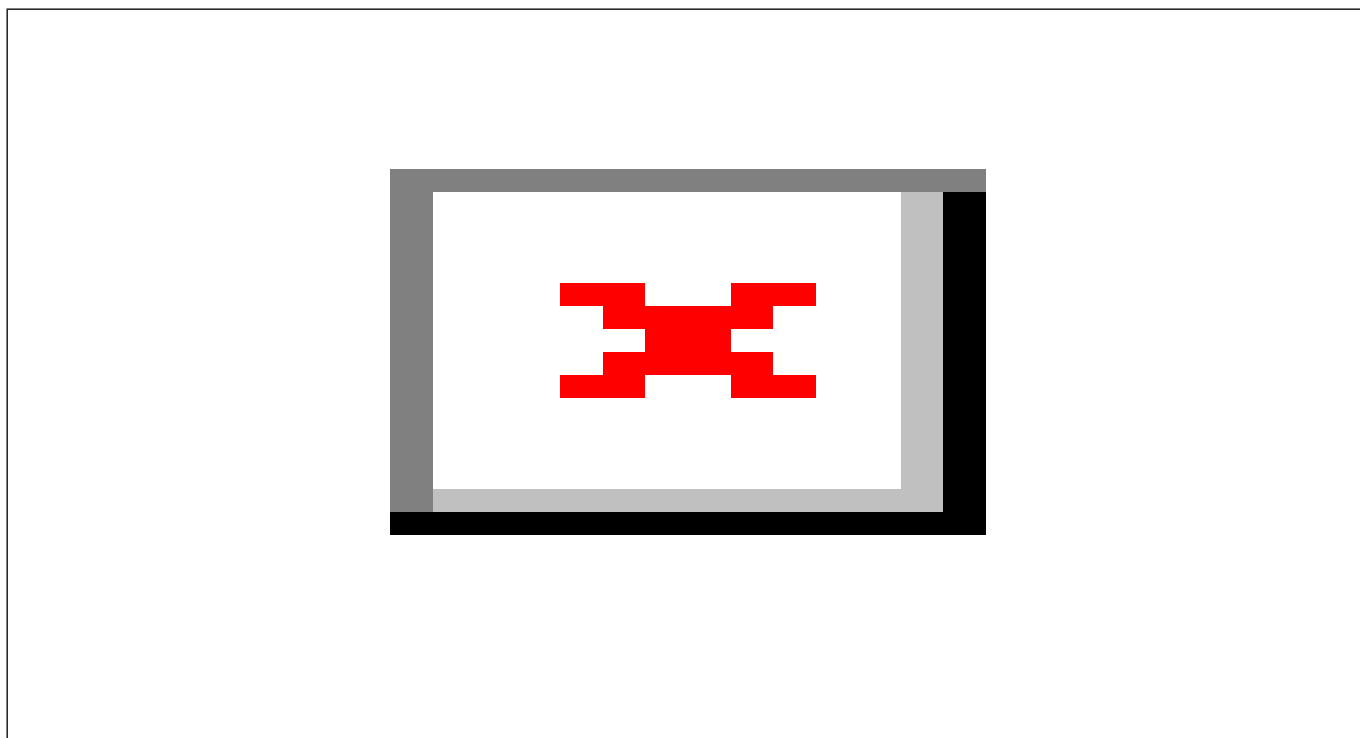
SI Figure 11: HRMS spectrum of 2k; Calcd. for $C_{10}H_{15}Br$ $[M]^+$: 214.0357, found 214.0355 $[M]^+$ and 216.0339 $[M+2]^+$.



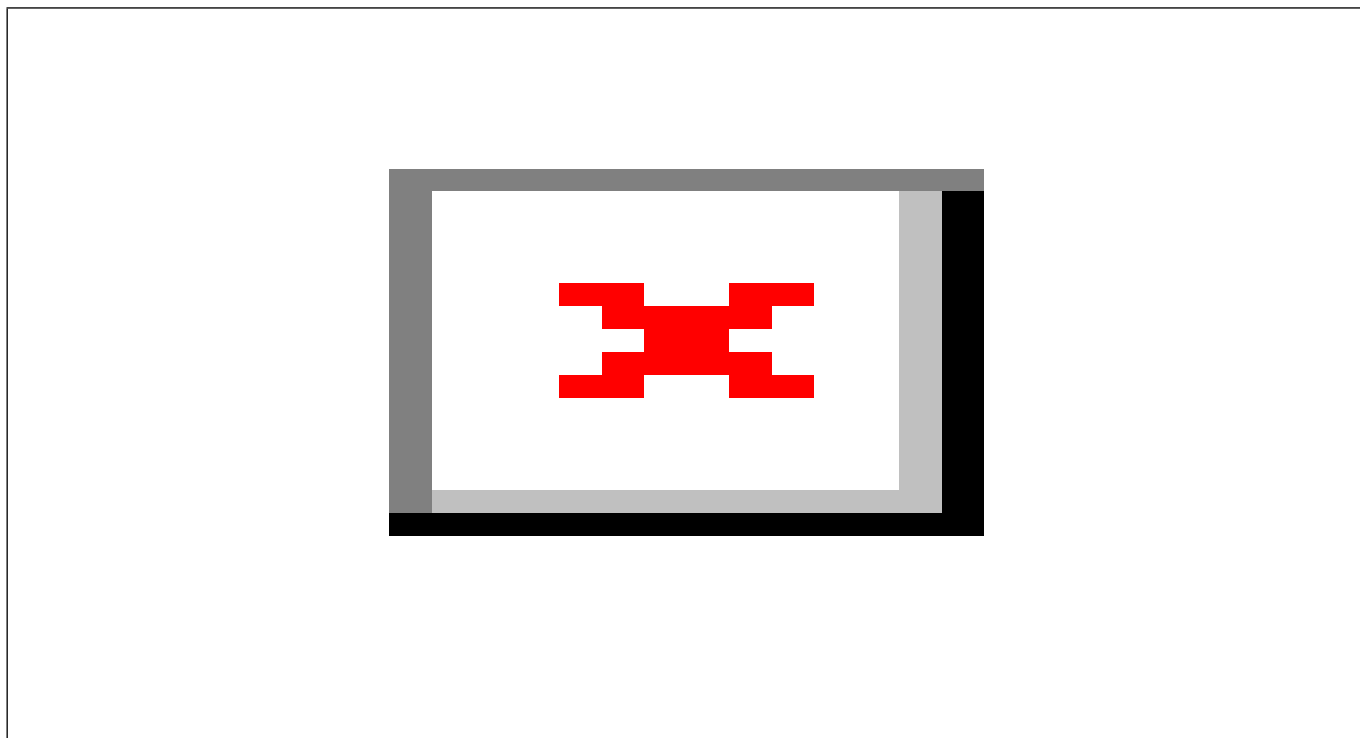
SI Figure 12: HRMS spectrum of 2l; Calcd. for C_8H_{17} $[M+H]^+$: 113.1330, found 113.1331.



SI Figure 13: HRMS spectrum of 2m; Calcd. for $C_9H_{15}O$ $[M+H]^+$: 139.1123, found 139.1120.

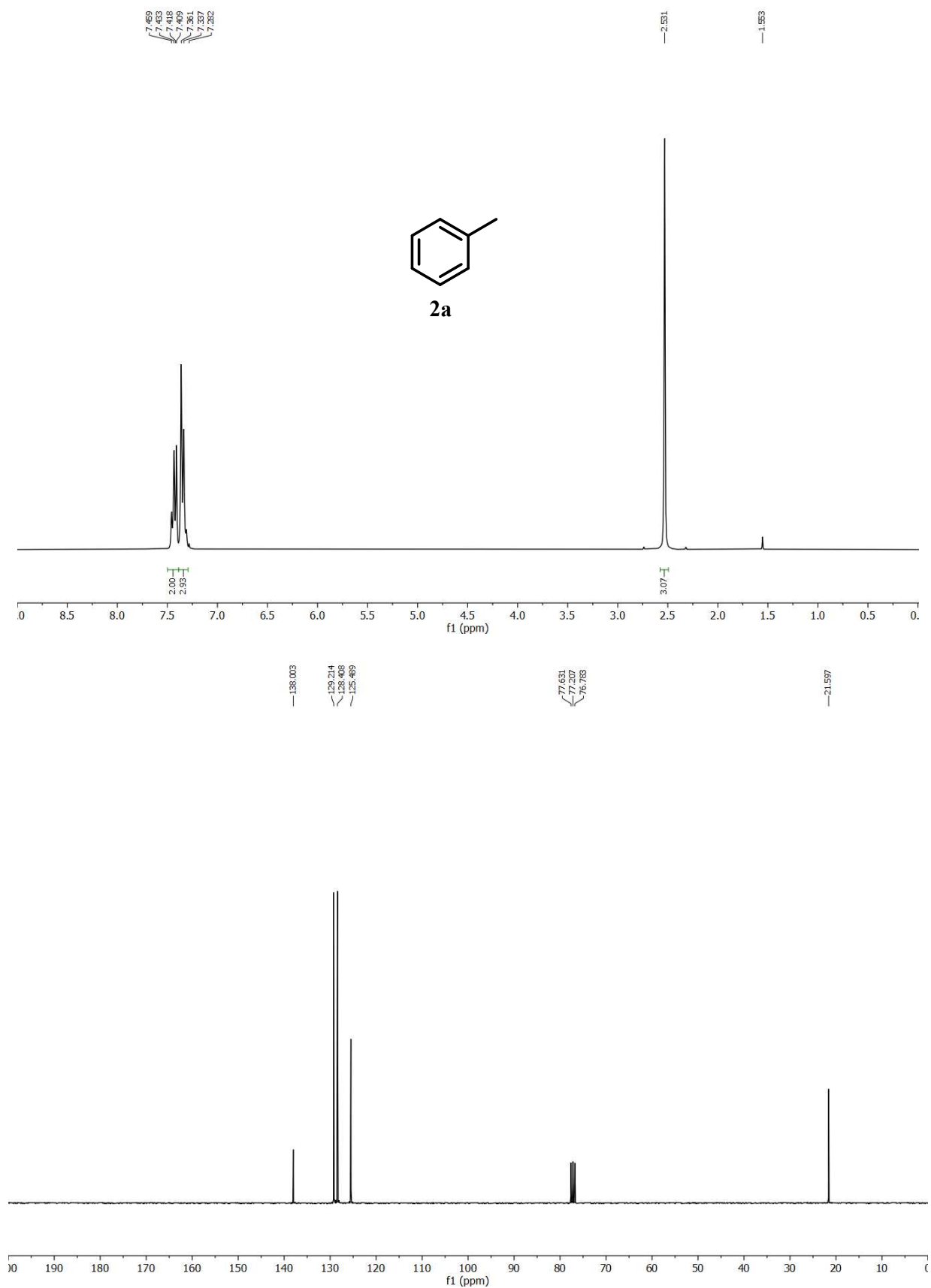


SI Figure 14: HRMS spectrum of 2n; Calcd. for $C_2H_6NaO_2$ $[M+Na]^+$: 85.0265, found 85.0268.

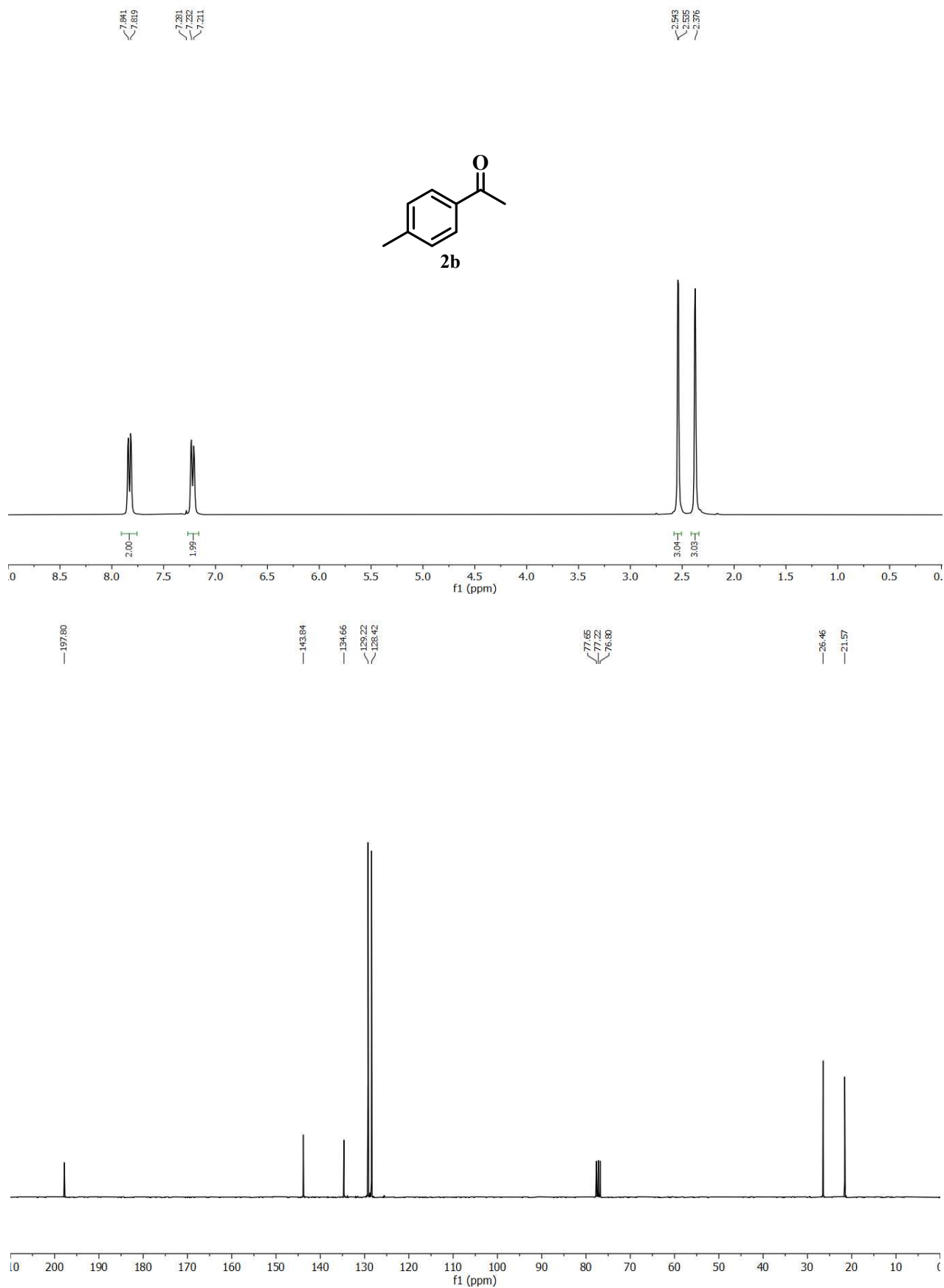


12. 1H and ^{13}C -NMR spectra of all the synthesized compounds (2a-n) & 3a

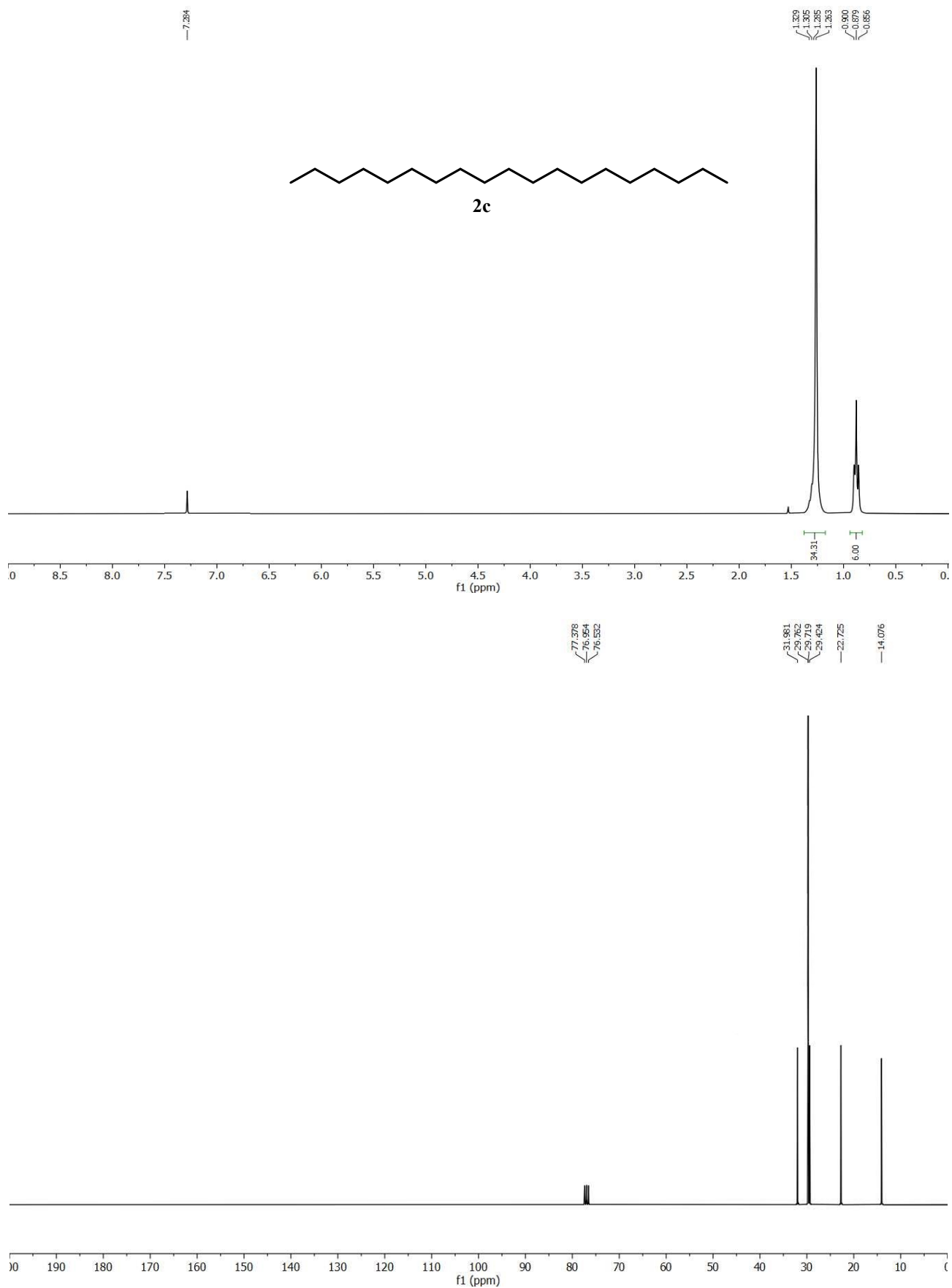
SI Figure 15: ^1H and ^{13}C -NMR spectra of compound **2a**



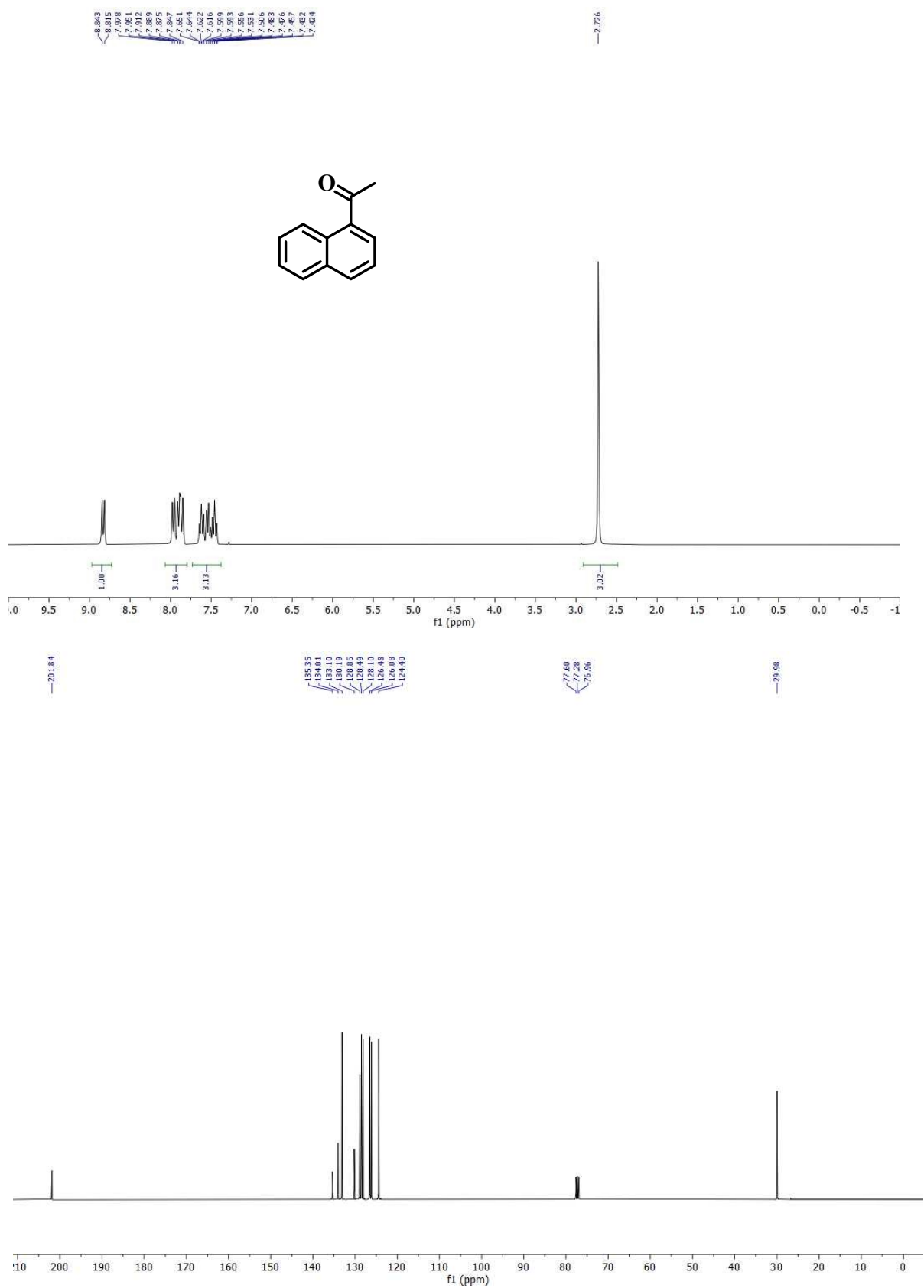
SI Figure 16: ^1H and ^{13}C -NMR spectra of compound **2b**



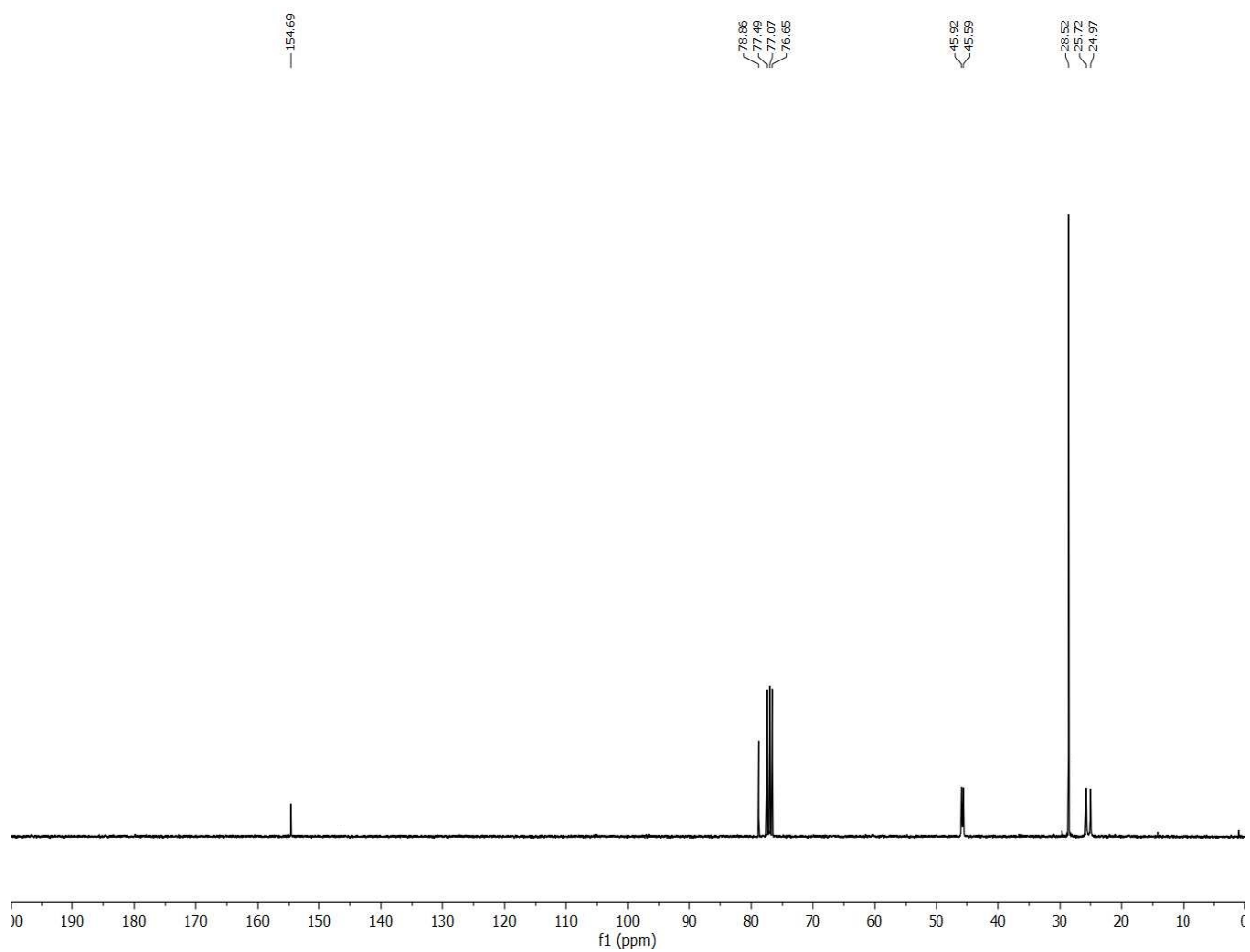
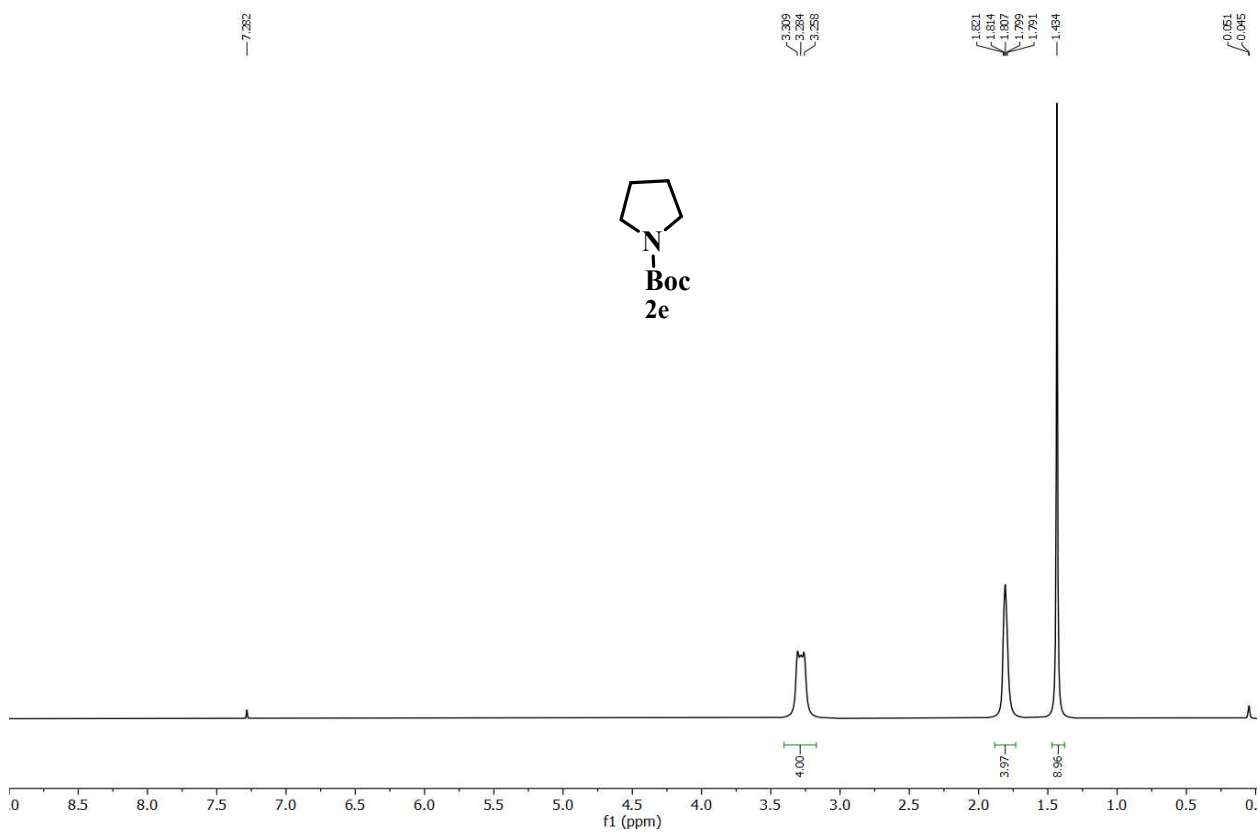
SI Figure 17: ¹H and ¹³C-NMR spectra of compound 2c



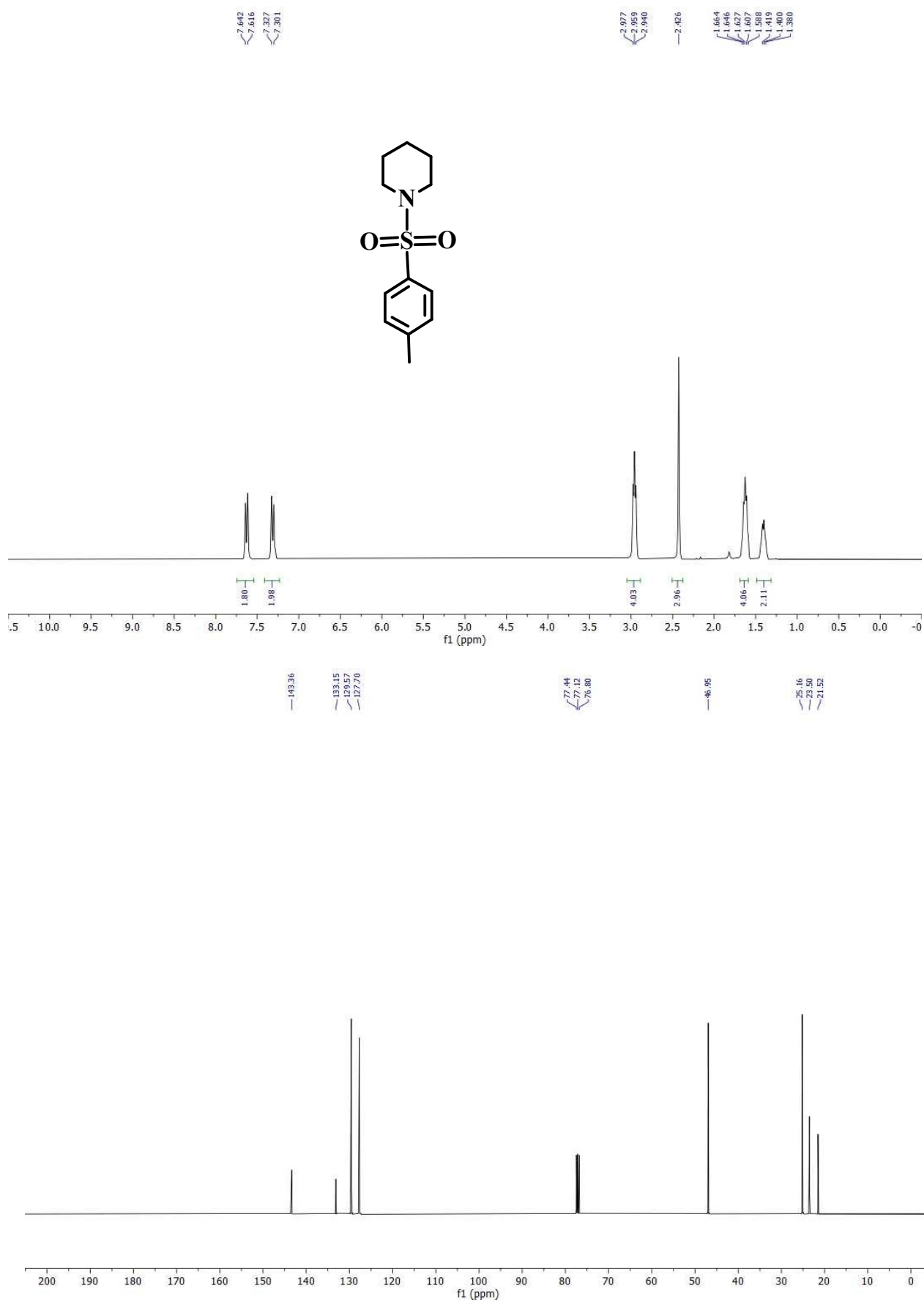
SI Figure 18: ¹H and ¹³C-NMR spectra of compound 2d



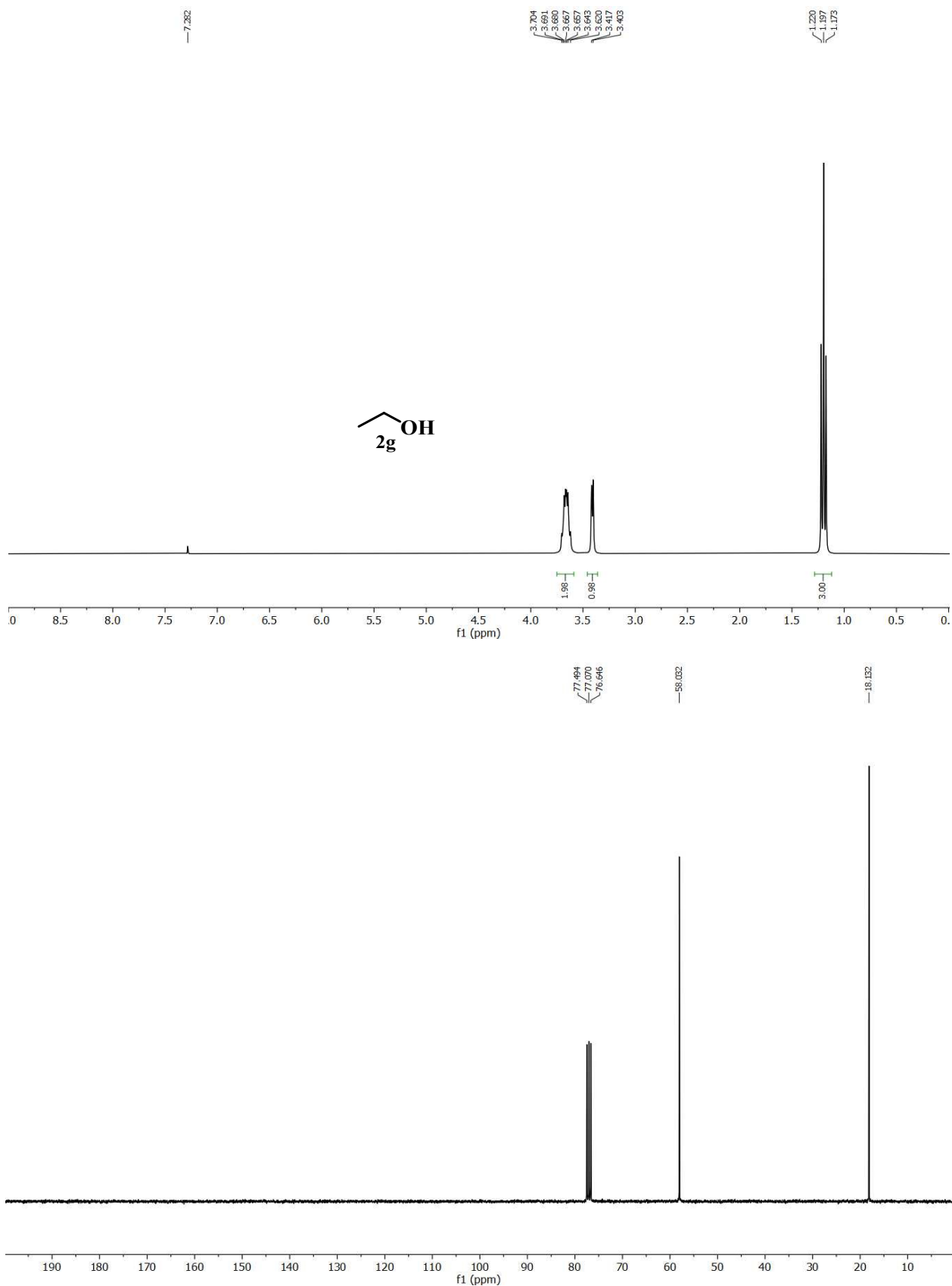
SI Figure 19: ¹H and ¹³C-NMR spectra of compound 2e



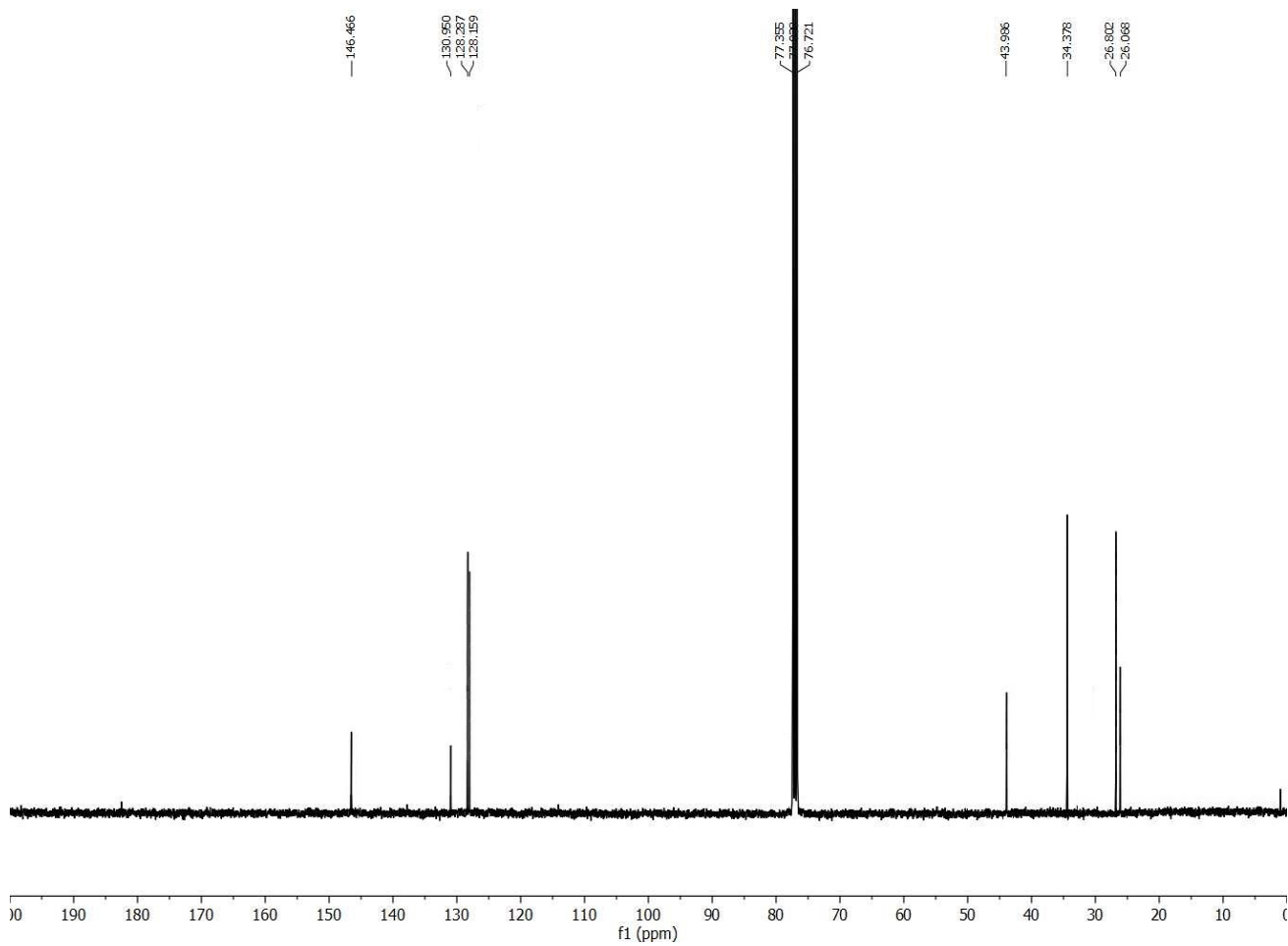
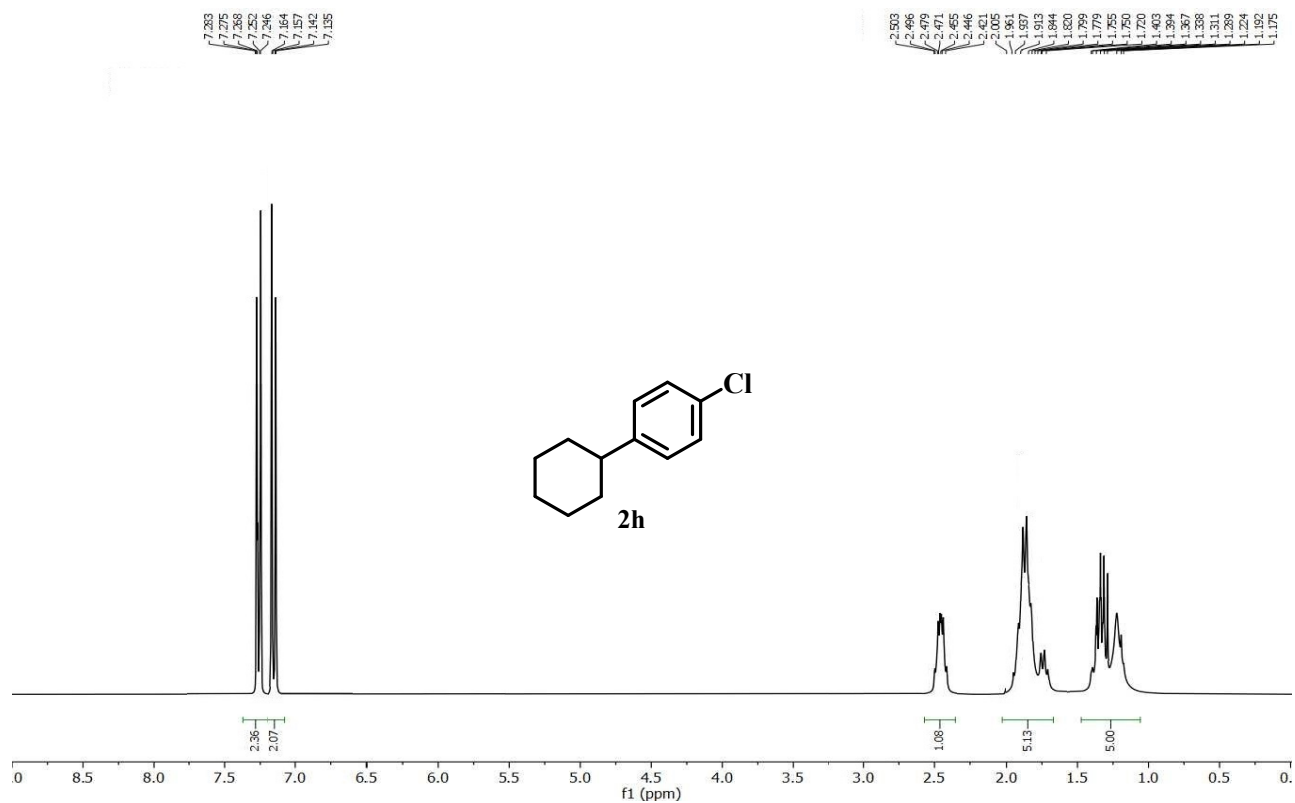
SI Figure 20: ¹H and ¹³C-NMR spectra of compound 2f



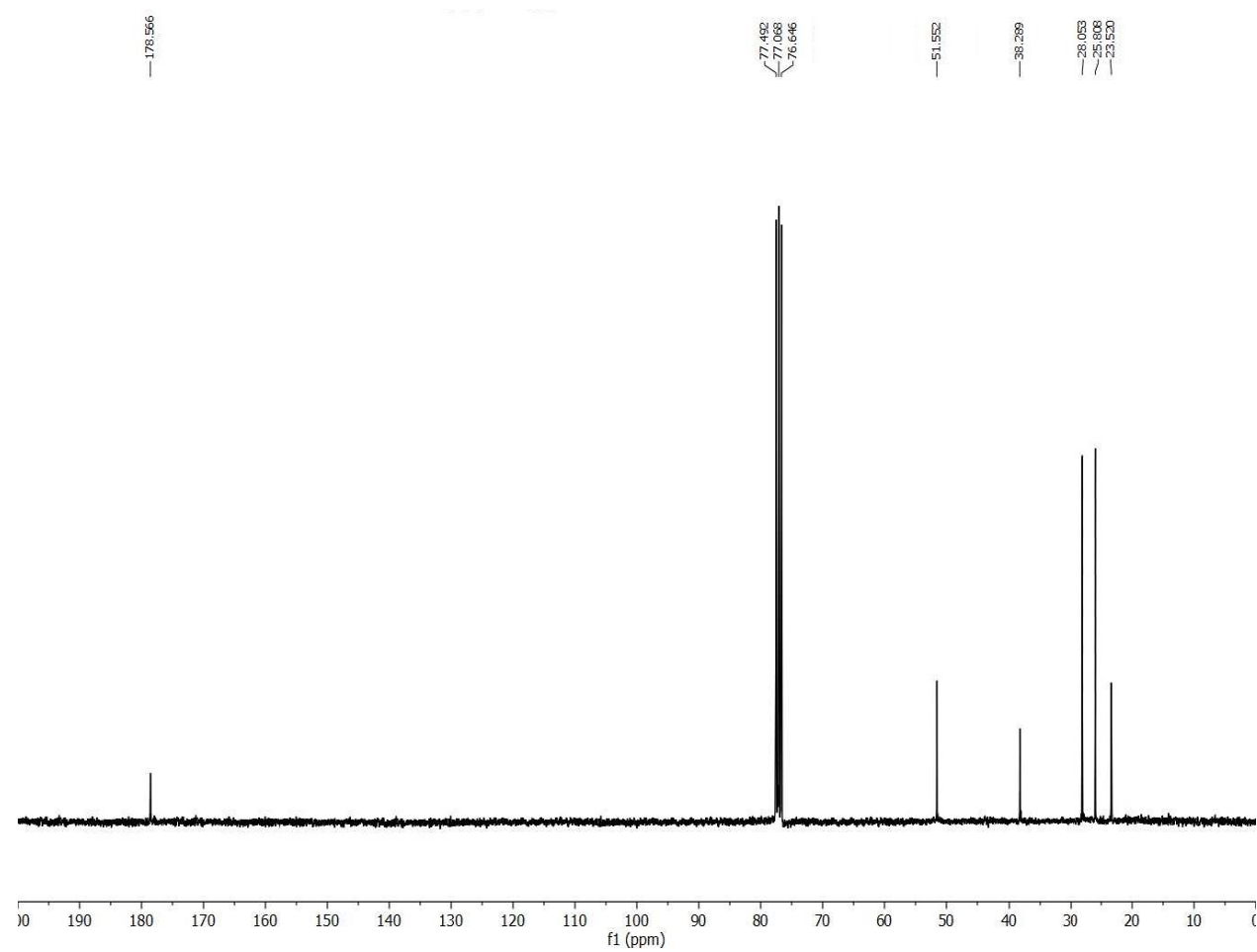
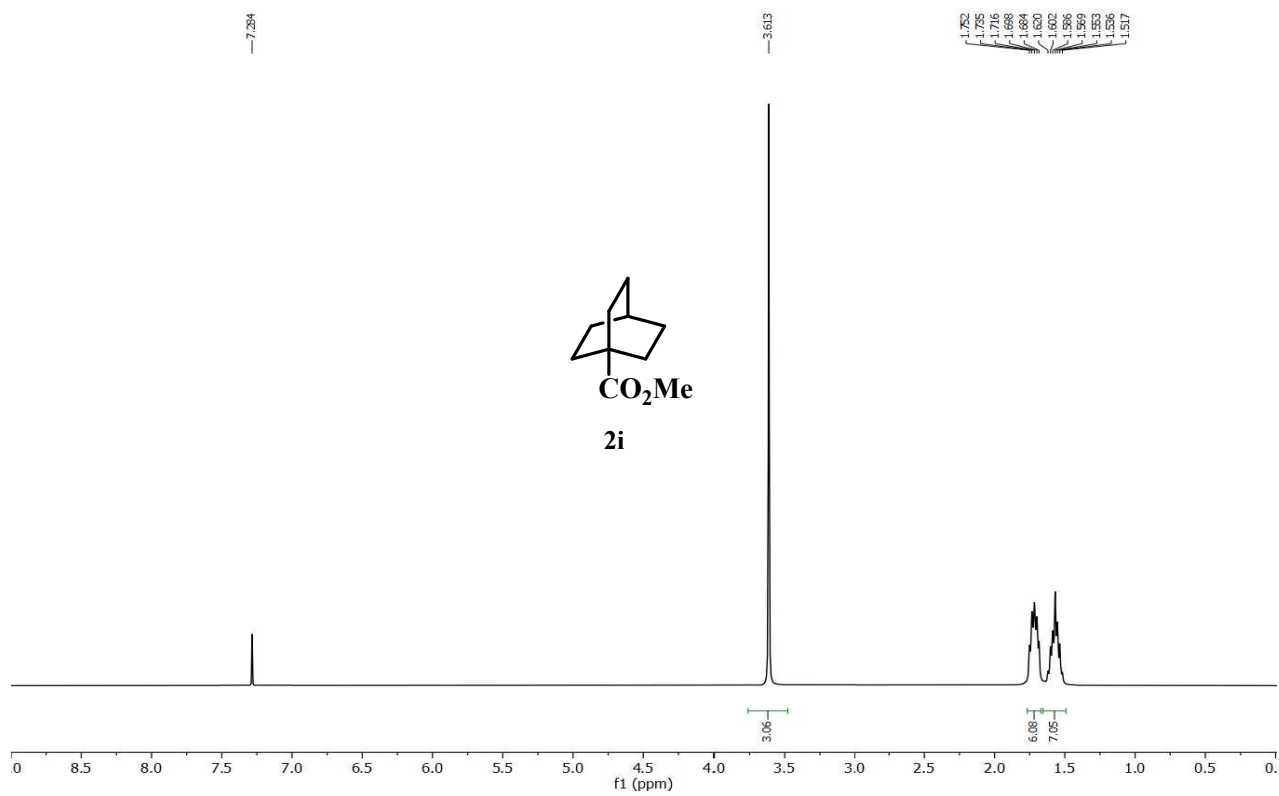
SI Figure 21: ¹H and ¹³C-NMR spectra of compound 2g



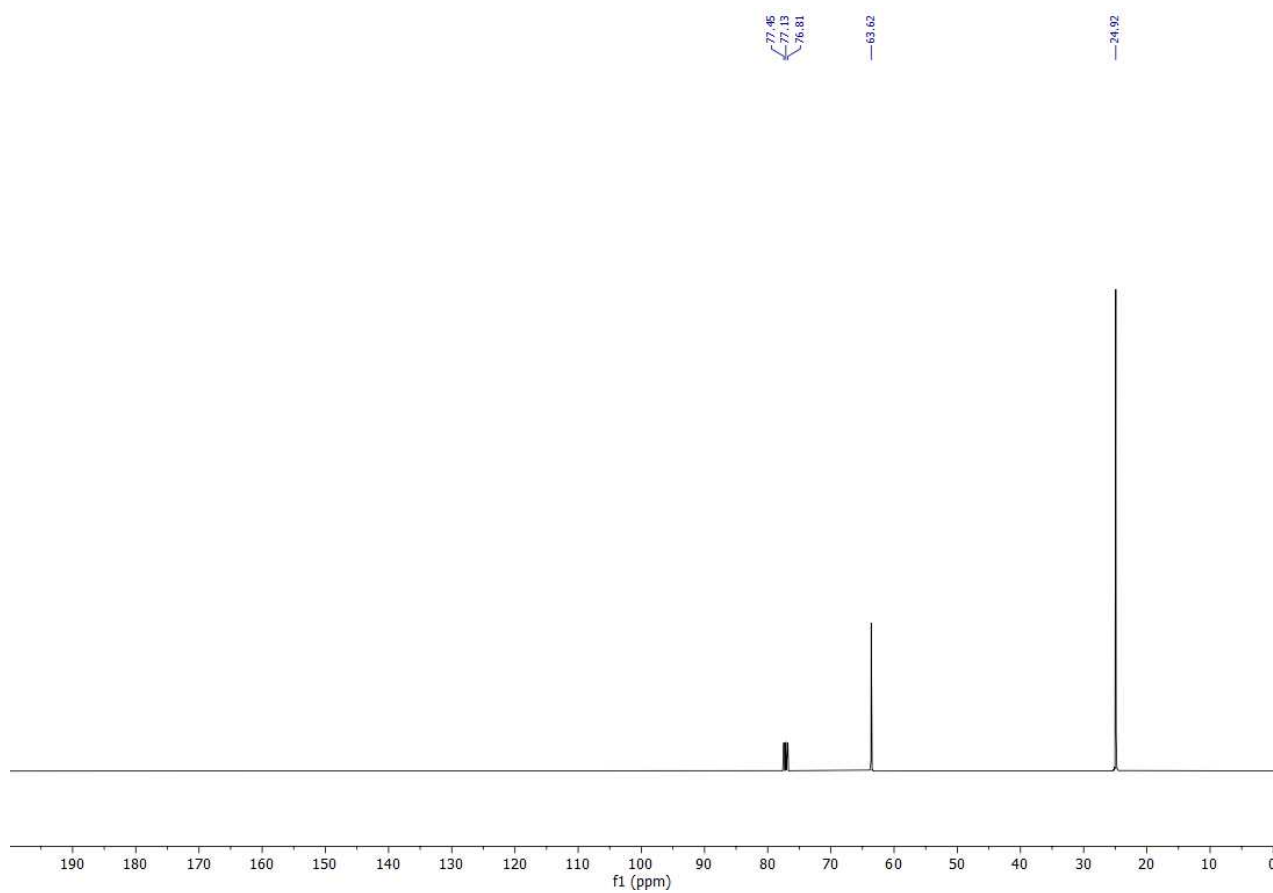
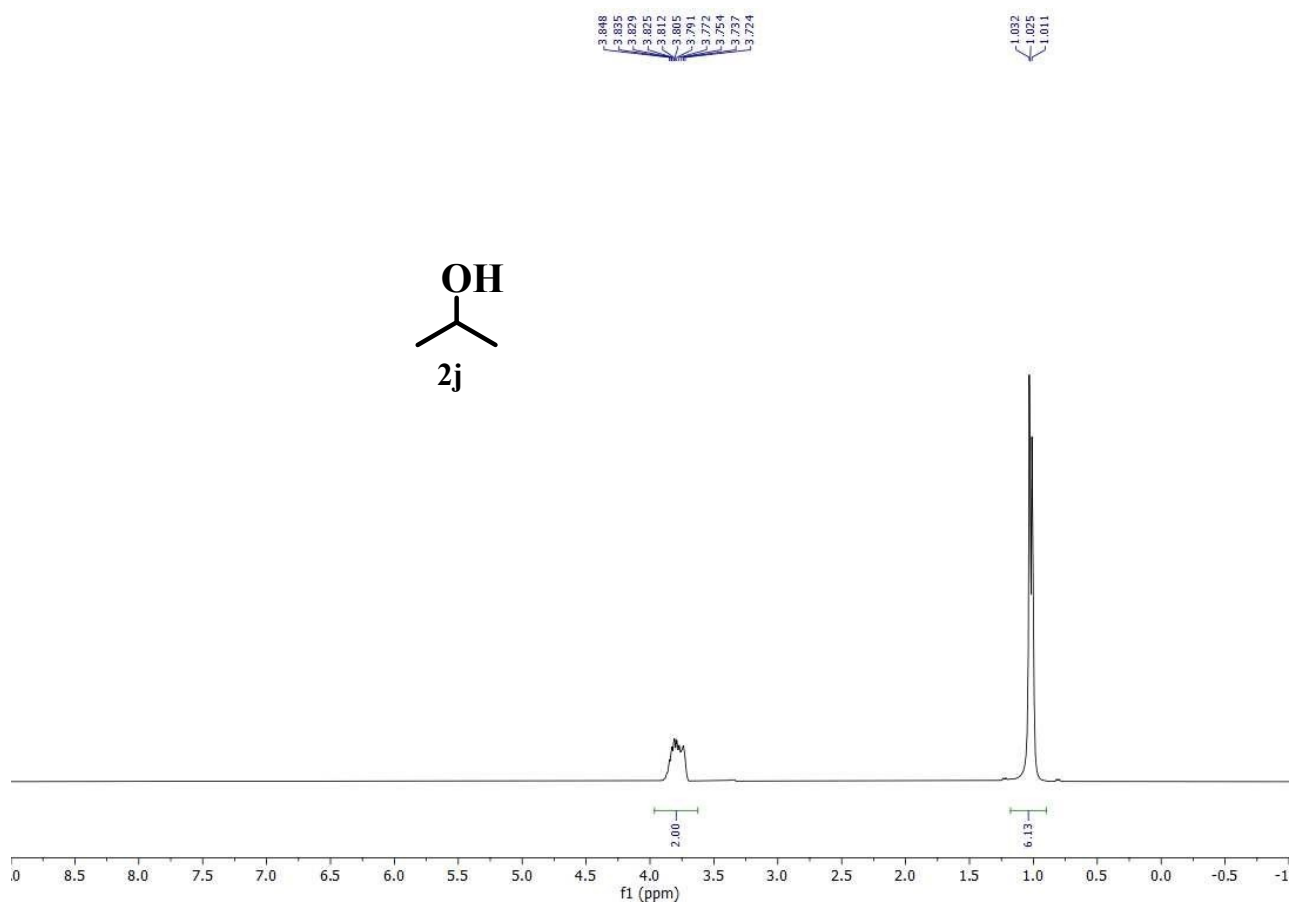
SI Figure 22: ¹H and ¹³C-NMR spectra of compound **2h**



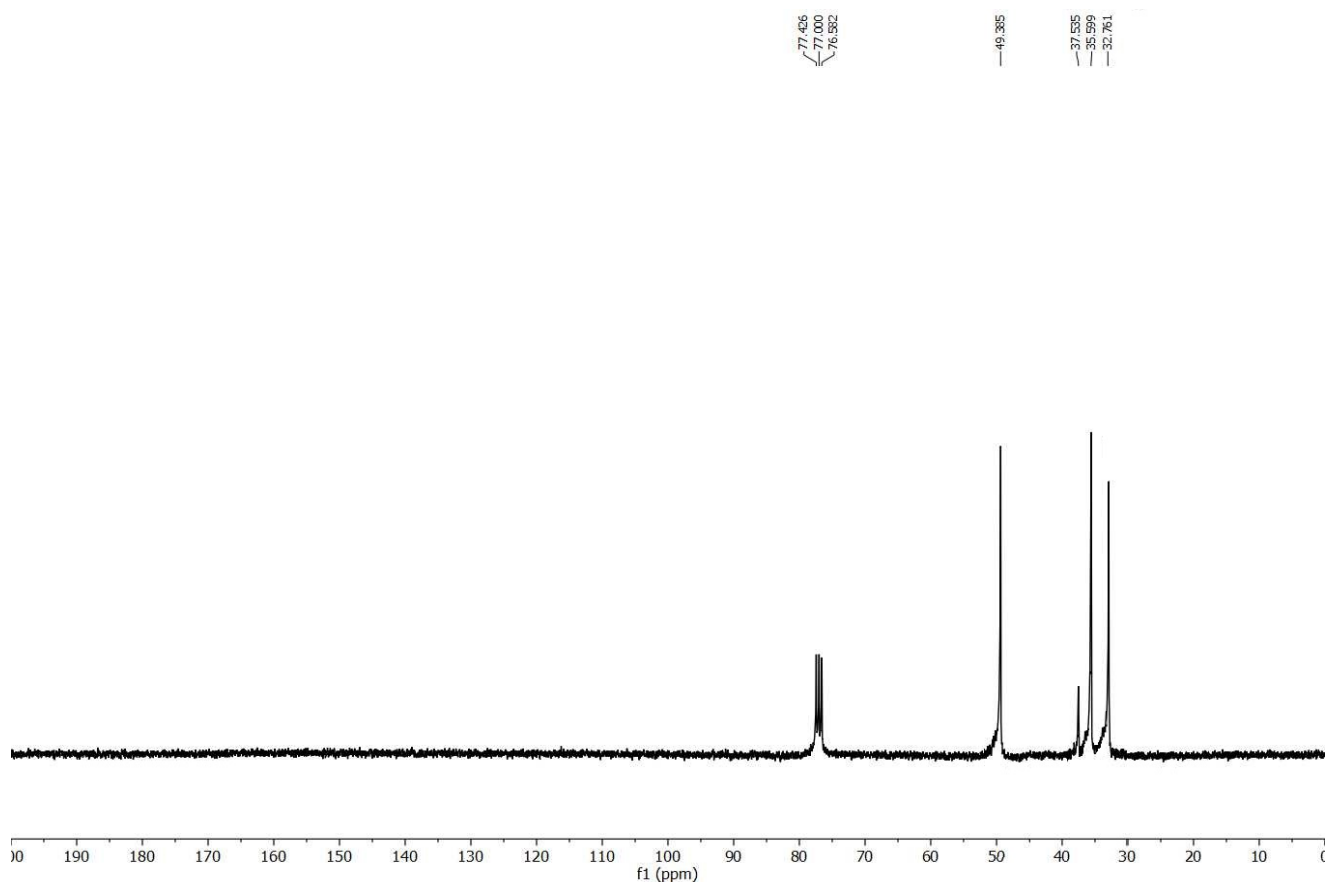
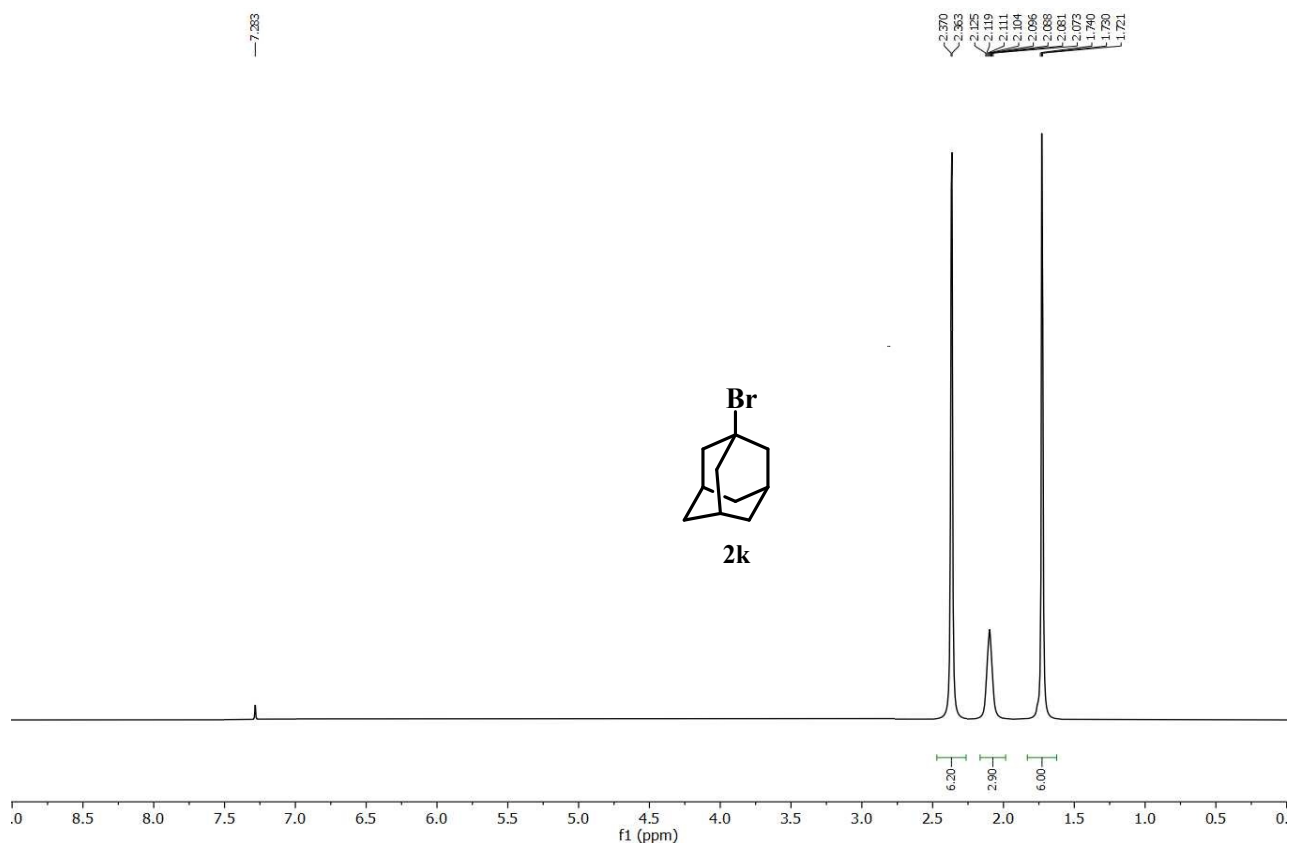
SI Figure 23: ¹H and ¹³C-NMR spectra of compound **2i**



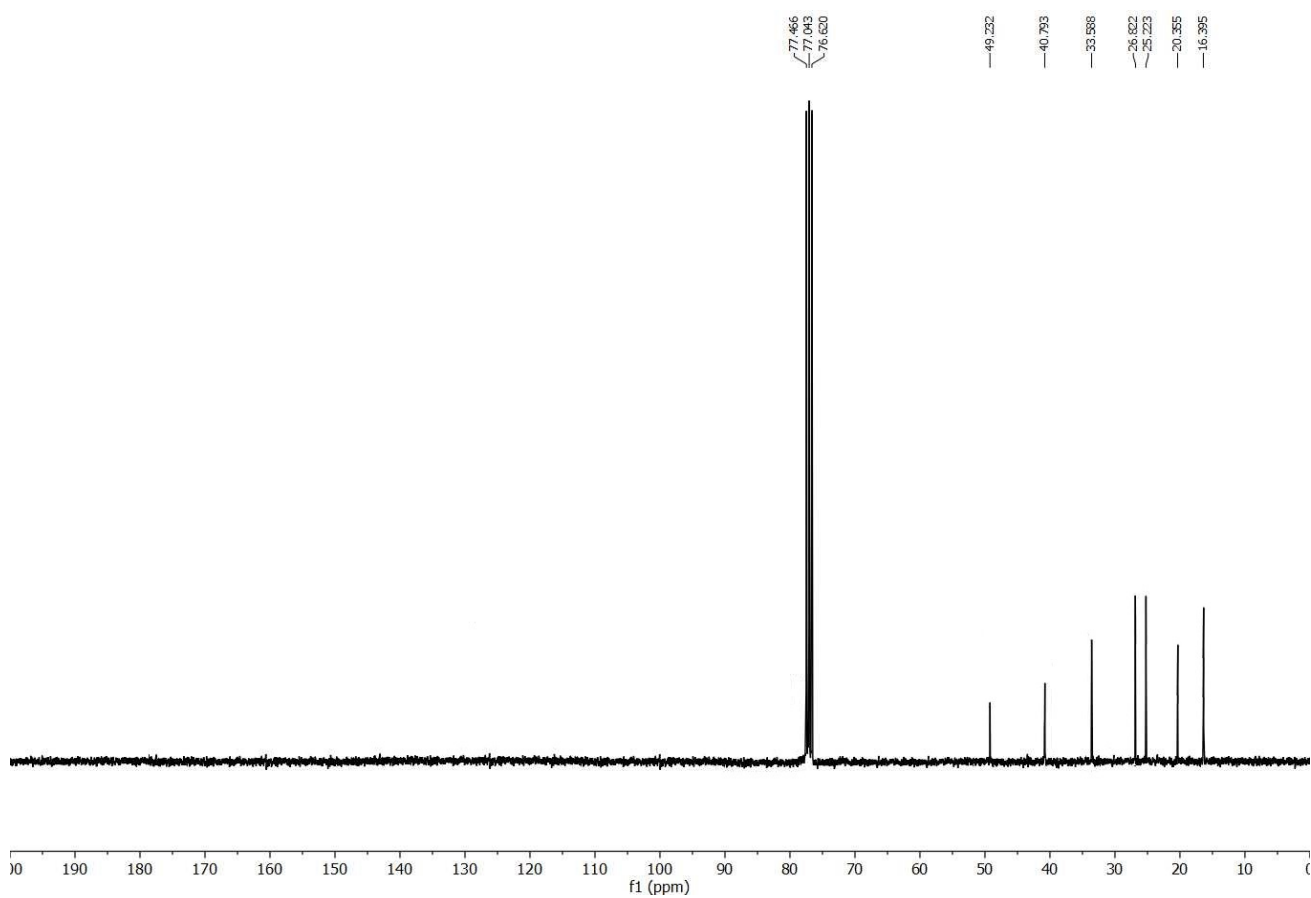
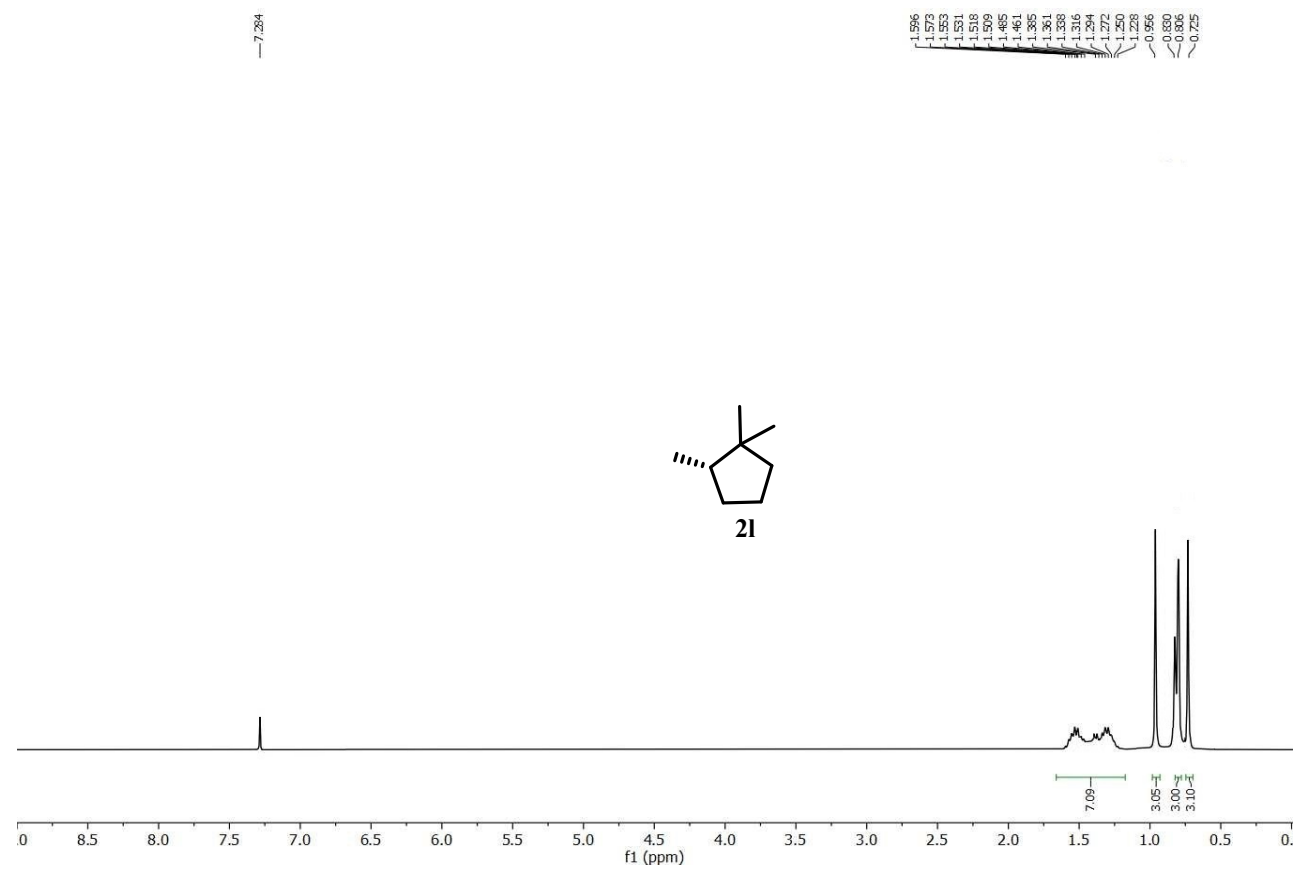
SI Figure 24: ¹H and ¹³C-NMR spectra of compound **2j**



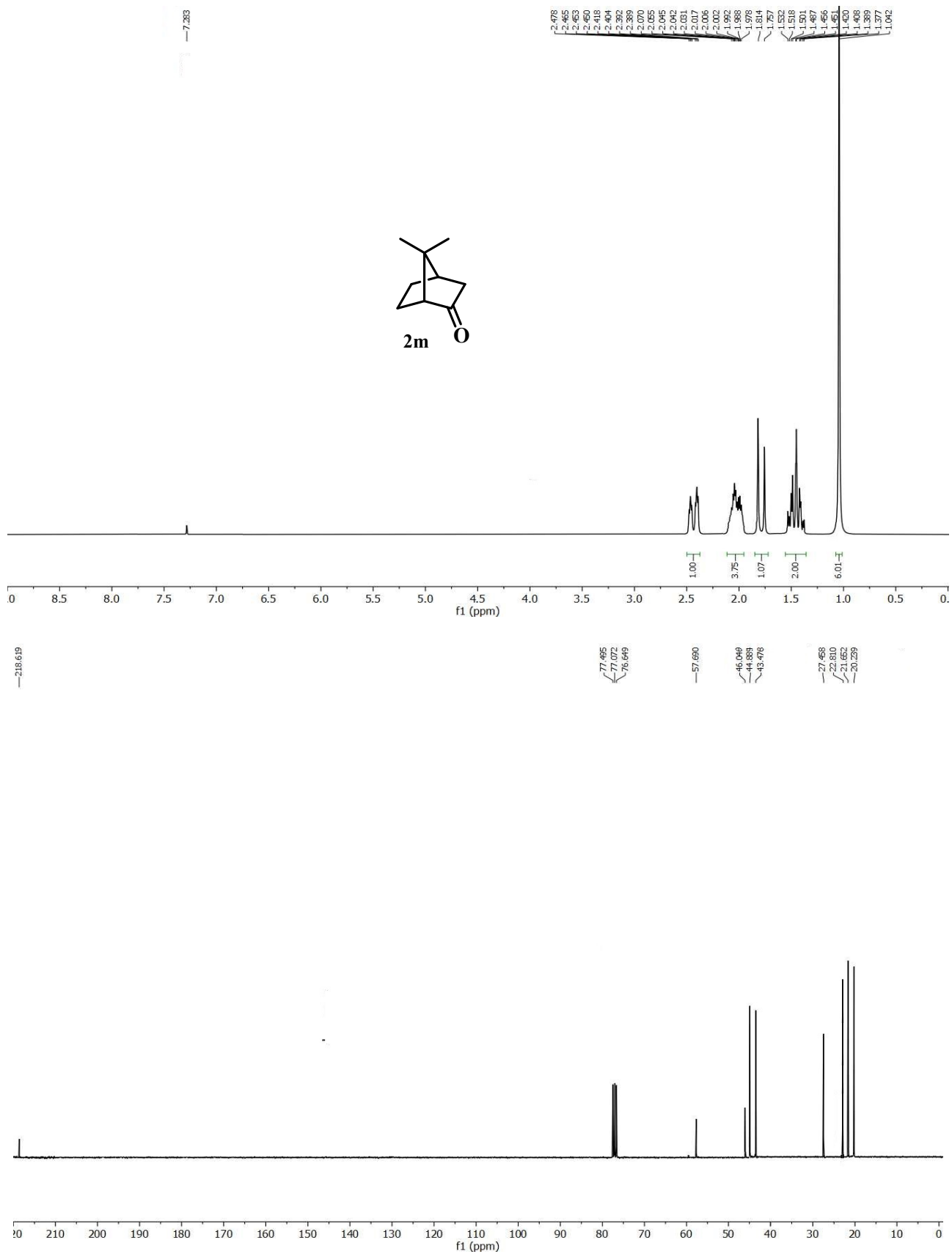
SI Figure 25: ^1H and ^{13}C -NMR spectra of compound **2k**



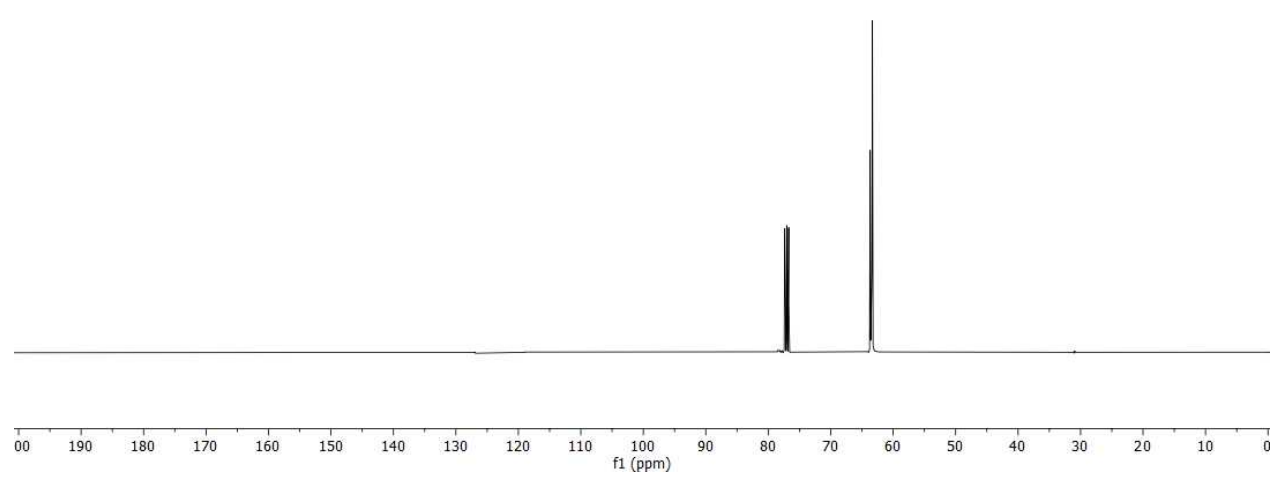
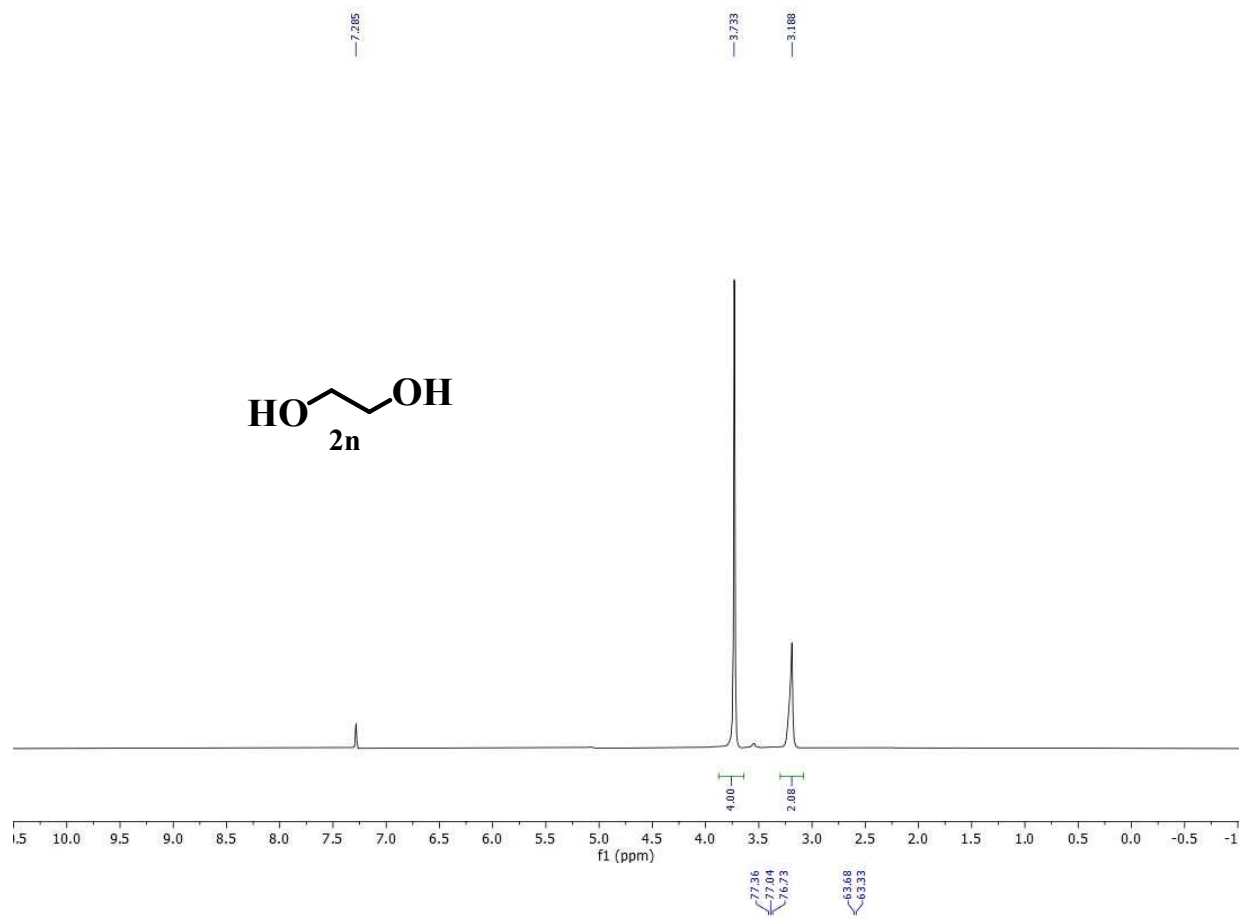
SI Figure 26: ^1H and ^{13}C -NMR spectra of compound **2k**



SI Figure 27: ^1H and ^{13}C -NMR spectra of compound **2m**



SI Figure 28: ¹H and ¹³C-NMR spectra of compound 2n



SI Figure 29: ¹H and ¹³C-NMR spectra of 3a

