

## Supplementary material

### Efficient two-step access to azafluorenones and related compounds

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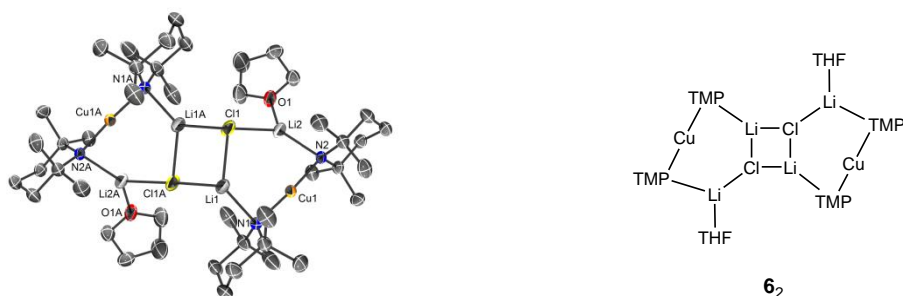
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### Synthetic and analytical data for lithiocuprate 1:

<sup>n</sup>BuLi (2.5 mL, 1.6 M in hexanes, 4 mmol) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (0.68 mL, 4 mmol) in dry toluene (4 mL) and dry THF (0.32 mL, 4 mmol) under N<sub>2</sub> at -78°C. The resulting solution of lithium 2,2,6,6-tetramethylpiperidide was allowed to reach room temperature. It was then added to a suspension of copper(I) chloride (198 mg, 2 mmol) in dry toluene (3 mL) under N<sub>2</sub> at -78°C. The mixture was allowed to reach room temperature whereupon it was filtered. The solvent was removed to ½ volume giving a pale orange solution from which **1** deposited after storage at -20°C for 12 h. Yield 195 mg (21% wrt CuCl); mp 173-175 °C; elemental analysis calcd (%) for C<sub>44</sub>H<sub>88</sub>Cu<sub>2</sub>Li<sub>4</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>: C 56.77, H 9.53, N 6.02, Cl 7.62; found: C 56.34, H 9.69, N 6.03, Cl 7.92; <sup>1</sup>H NMR (500 MHz, 298K, C<sub>6</sub>D<sub>6</sub>): δ 3.71 (br, m, 4H; THF), 2.09 (br, m, 2H; TMP-3,5), 1.84 (s, 6H; TMP-Me), 1.71-1.68 (m, 18H; TMP-Me), 1.50 (br, m, 6H; TMP-3,5), 1.43 (br, m, 4H; THF), 1.18 ppm (m, 4H; TMP-4); <sup>13</sup>C NMR (125 MHz, 298K, C<sub>6</sub>D<sub>6</sub>, *G* = lower-order or Gilman-type cuprate TMP<sub>2</sub>CuLi [**1**], *L* = higher-order or Lipshutz-type cuprate **1**): δ 68.7 (THF), 54.6 (TMP-2, *G*), 54.0 (TMP-2, *L*), 52.1 (TMP-2, *L*), 42.6 (TMP-3,5 *G*), 42.4 (TMP-3,5 *L*), 41.1 (TMP-3,5 *L*), 40.6 (TMP-Me, *G*), 39.0 (TMP-Me *L*), 38.6 (TMP-Me, *L*), 35.0 (TMP-Me, *G*), 34.6 (TMP-Me, *L*), 32.0 (TMP-Me, *L*), 25.3 (THF), 20.6 (TMP-4, *L*), 19.8 (TMP-4, *L*), 19.7 ppm (TMP-4, *G*); <sup>7</sup>Li NMR spectroscopy (194 MHz, 298K, C<sub>6</sub>D<sub>6</sub>, *G* = TMP<sub>2</sub>CuLi, *L* = **1**): δ 1.9 (s, 6Li, *L*), 1.3 ppm (s, Li, *G*); <sup>1</sup>H NMR (500 MHz, 298K, d<sub>8</sub>-THF): 3.65 (br, m, 4H; THF), 1.81 (br, m, 4H; THF), 1.68 (br, m, 4H; TMP-4), 1.38, 1.09 (s, 24H, TMP-Me), 1.33 ppm (br, m, 8H, TMP-3,5); <sup>13</sup>C NMR (125 MHz, 298K, d<sub>8</sub>-THF, *G* = TMP<sub>2</sub>CuLi, *L* = **1**): δ 68.2 (THF), 54.2 (TMP-2 *L*), 50.0 (TMP-2 *G*), 41.9 (TMP-3,5 *L*), 38.6 (TMP-3,5 *G*), 37.3 (br, m, TMP-Me, *L*), 32.2, 32.1 (TMP-Me *G*), 26.4 (THF), 20.5 (TMP-4 *L*), 19.3 ppm (TMP-4, *G*); <sup>7</sup>Li NMR spectroscopy (194 MHz, 298K, d<sub>8</sub>-THF): δ 0.7 ppm (s); <sup>1</sup>H NMR (500 MHz, 273K, d<sub>8</sub>-THF): δ 3.65 (br, m, 4H; THF), 1.81 (br, m, 4H; THF), 1.67 (br, m, 4H; TMP-4), 1.34, 1.08 (s, 24H, TMP-Me), 1.31 ppm (br, m, 8H, TMP-3,5); <sup>13</sup>C NMR (125 MHz, 273K, d<sub>8</sub>-THF, *G* = TMP<sub>2</sub>CuLi, *L* = **1**): δ 65.1 (THF), 51.3 (TMP-2 *L*), 47.1 (TMP-2 *G*), 39.1 (TMP-3,5 *L*), 35.7 (TMP-3,5 *G*), 34.8 (br, m, TMP-Me, *L*), 29.4, 29.3 (TMP-Me *G*), 23.0 (THF), 18.0 (TMP-4 *L*), 17.5 ppm (TMP-4, *G*); <sup>7</sup>Li NMR spectroscopy (194 MHz, 273K, d<sub>8</sub>-THF): δ 0.2 ppm (s). Single crystal data were collected using the 'oil drop technique' [2] to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Structures were solved using direct methods [3], with refinement, based on *F*<sup>2</sup>, by full-matrix least squares [4]. The sample was studied with graphite monochromatized MoK<sub>α</sub> radiation (λ = 0.71070 Å). X-ray diffraction data

were collected at  $T = 180$  K. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F2 with 6110 unique intensities and 269 parameters converged at  $\omega R(F2) = 0.1450$  ( $R(F) = 0.0569$ ) for 4478 observed reflections with  $I > 2\sigma(I)$ . For **1<sub>2</sub>**:  $C_{44}H_{88}Cu_2Li_4N_4O_2Cl_2$ ;  $M = 930.92$ ; monoclinic; space group  $P21/c$ ,  $a = 14.3830(3)$  Å,  $b = 8.1954(2)$  Å,  $c = 22.1569(5)$  Å,  $\beta = 97.2250(10)^\circ$ ;  $V = 2590.99(10)$  Å<sup>3</sup>,  $Z = 2$ ;  $d = 1.193$  g.cm<sup>-3</sup>;  $\mu = 0.959$  mm<sup>-1</sup>. CCDC 884940 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

ORTEP figure

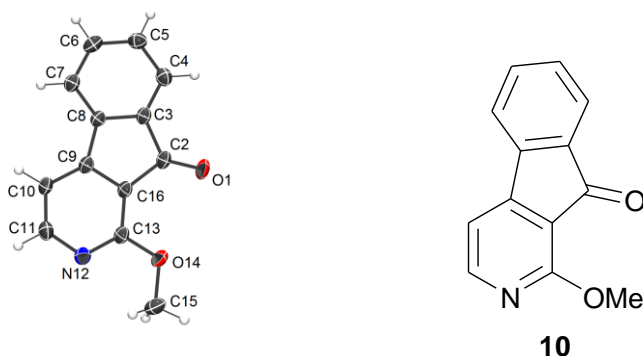


- [1] S. Komagawa, S. Usui, J. Haywood, P. J. Harford, A. E. H. Wheatley, Y. Matsumoto, K. Hirano, R. Takita, M. Uchiyama, *Angew. Chem. Int. Ed.* 51 (2012) 12081.
- [2] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* 26 (1993) 615.
- [3] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467.
- [4] G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

### X-ray diffraction analysis of compound 10

The sample was studied with graphite monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). X-ray diffraction data were collected at  $T = 150(2) \text{ K}$  using APEXII Bruker-AXS diffractometer. The structure was solved by direct methods using the SIR97 program [5], and then refined with full-matrix least-square methods based on  $F^2$  (SHELX-97) [6] with the aid of the WINGX program [7]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on  $F^2$  with 2202 unique intensities and 146 parameters converged at  $\omega R(F2) = 0.1169$  ( $R(F) = 0.0522$ ) for 1296 observed reflections with  $I > 2\sigma(I)$ .

### ORTEP figure



### Crystal data

**10**:  $\text{C}_{13}\text{H}_9\text{NO}_2$ ;  $M = 211.21$ ; monoclinic; space group  $P2_1/a$ ,  $a = 13.779(3) \text{ \AA}$ ,  $b = 4.9068(11) \text{ \AA}$ ,  $c = 14.519(4) \text{ \AA}$ ,  $\beta = 94.354(10)^\circ$ ,  $V = 978.8(4) \text{ \AA}^3$ ,  $Z = 4$ ;  $d = 1.43 \text{ g.cm}^{-3}$ ;  $\mu = 0.098 \text{ mm}^{-1}$ .

CCDC 885440 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[5] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.

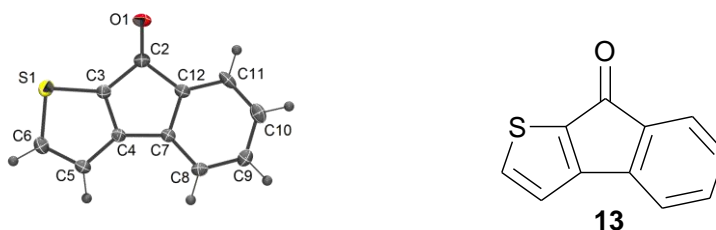
[6] G. M. Sheldrick, *Acta Crystallogr., Sect. A* A64 (2008) 112.

[7] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.

### X-ray diffraction analysis of compound 13:

The sample was studied with graphite monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). X-ray diffraction data were collected at  $T = 150(2) \text{ K}$  using APEXII Bruker-AXS diffractometer. The structure was solved by direct methods using the SIR97 program [5], and then refined with full-matrix least-square methods based on  $F^2$  (SHELX-97) [6] with the aid of the WINGX [7] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on  $F^2$  with 1669 unique intensities and 118 parameters converged at  $\omega R(F_2) = 0.0887$  ( $R(F) = 0.0361$ ) for 1507 observed reflections with  $I > 2\sigma(I)$ .

#### ORTEP figure



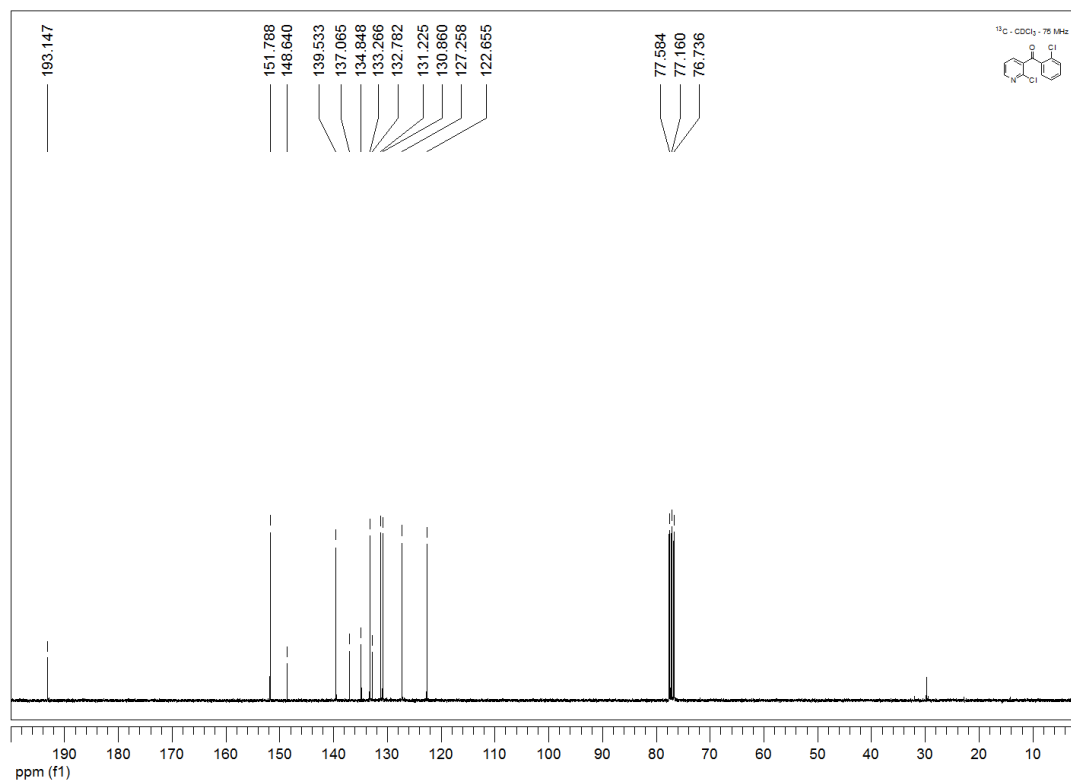
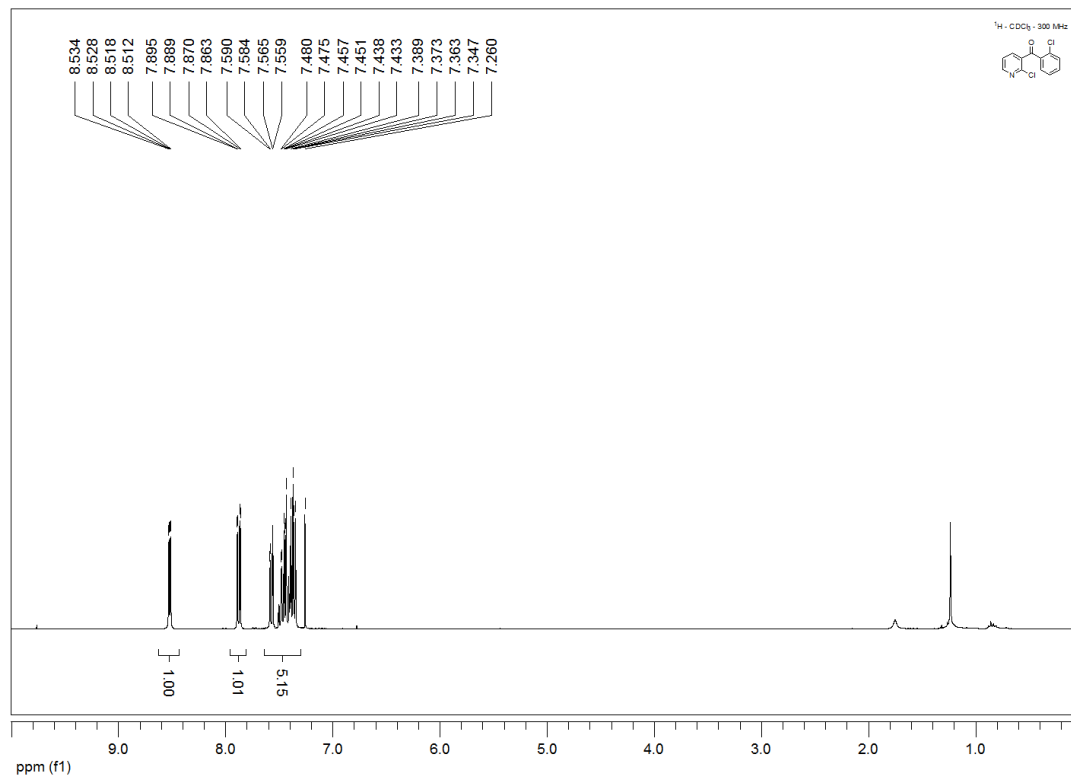
#### Crystal data

**13:**  $\text{C}_{11}\text{H}_6\text{OS}$ ;  $M = 186.22$ ; orthorhombic; space group  $P 2_1 n$ ,  $a = 3.8393(2) \text{ \AA}$ ,  $b = 13.4713(8) \text{ \AA}$ ,  $c = 15.9269(10) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ;  $V = 823.74(8) \text{ \AA}^3$ ,  $Z = 4$ ;  $d = 1.502 \text{ g.cm}^{-3}$ ;  $\mu = 0.337 \text{ mm}^{-1}$ .

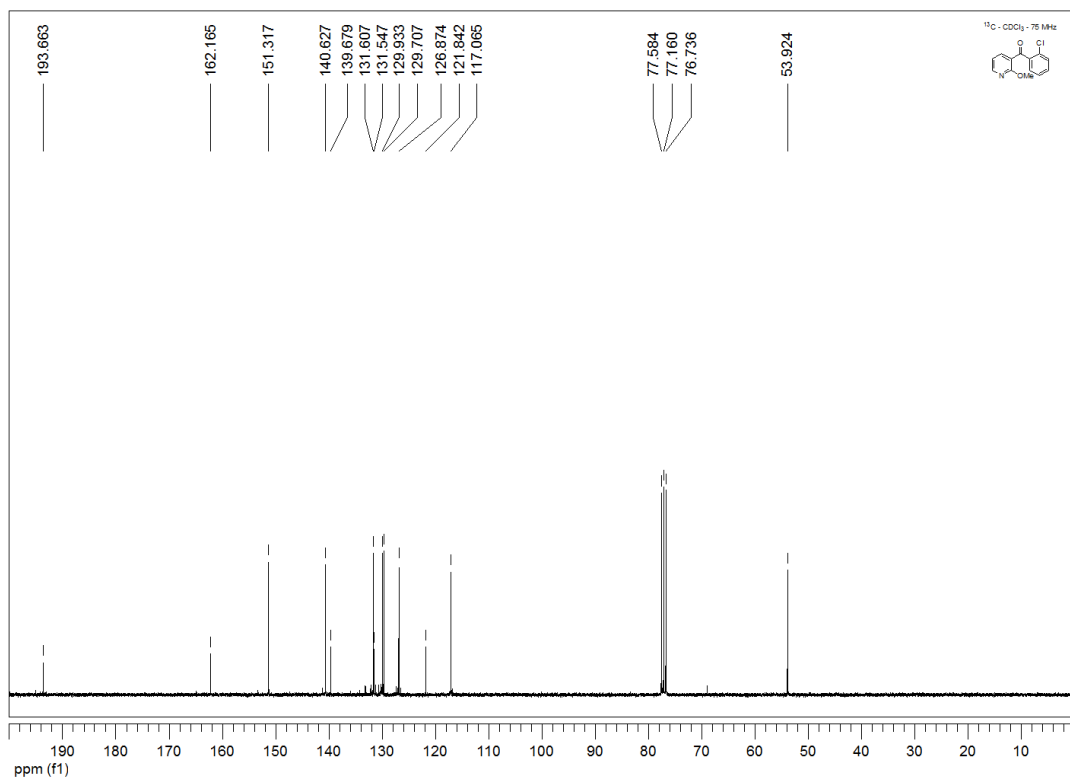
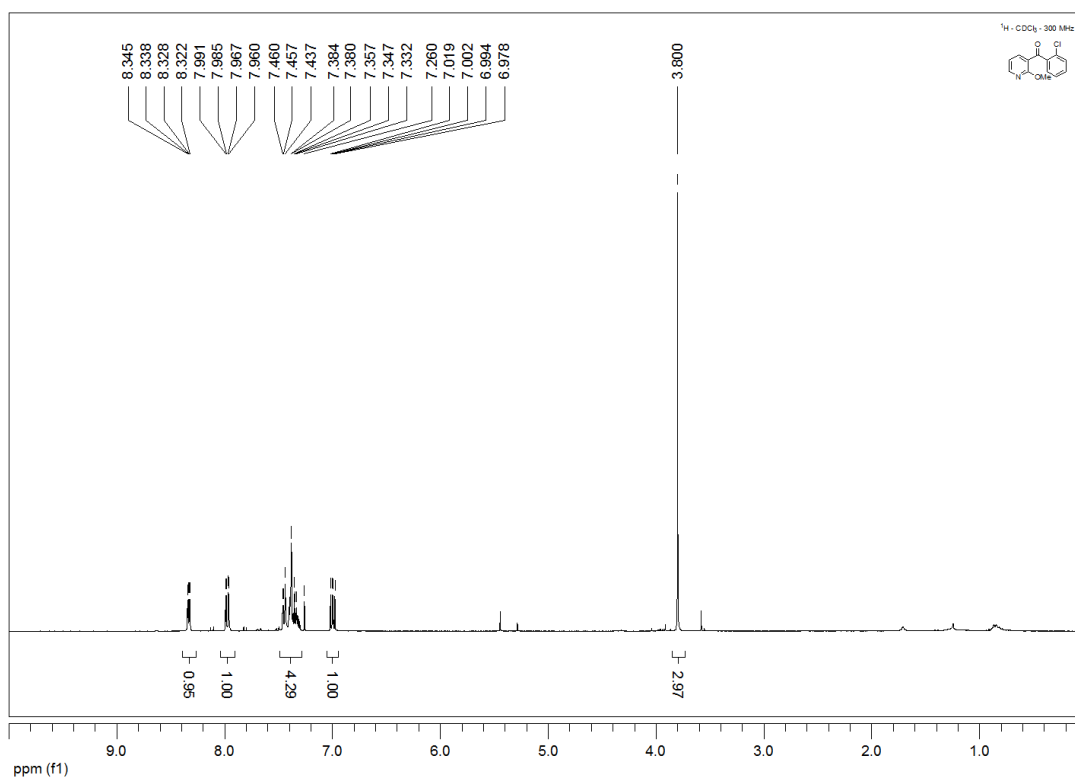
CCDC 885439 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

NMR spectra:

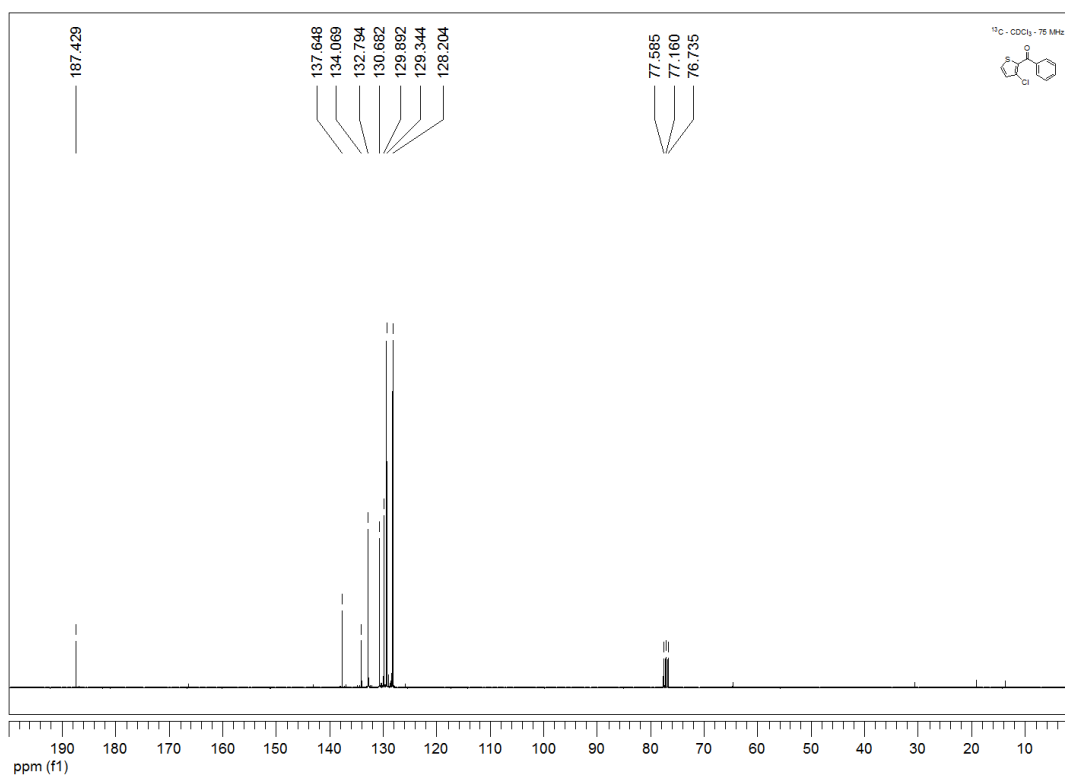
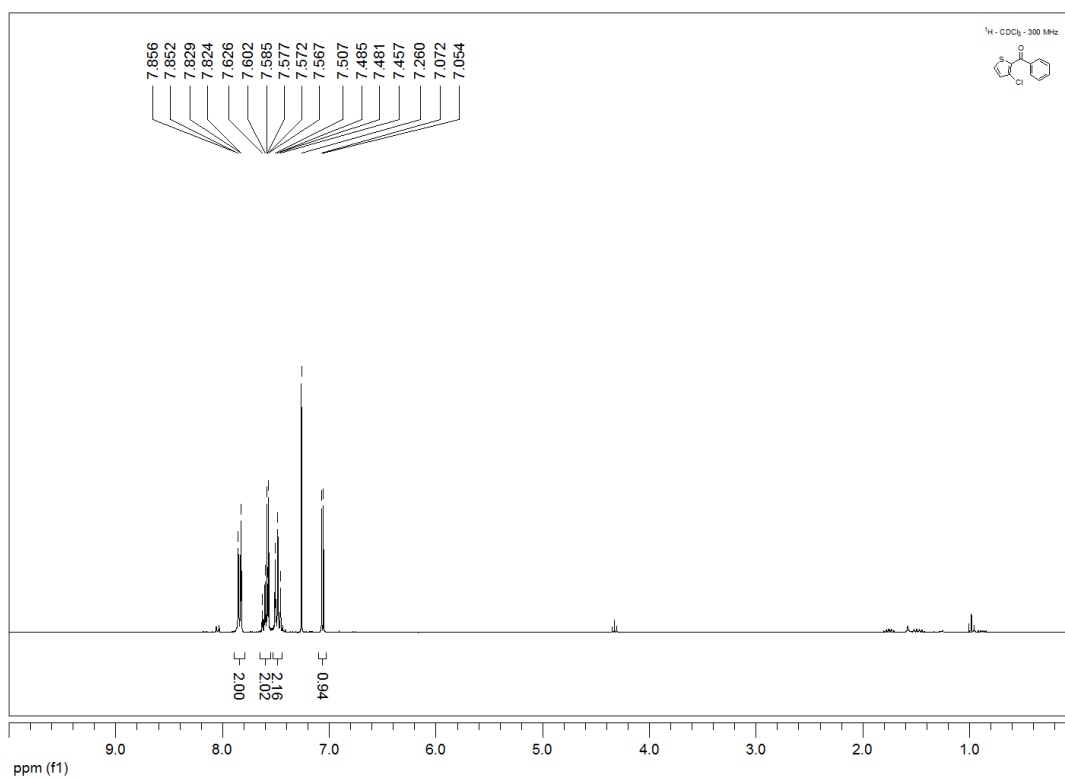
Compound 3c



# Compound 4

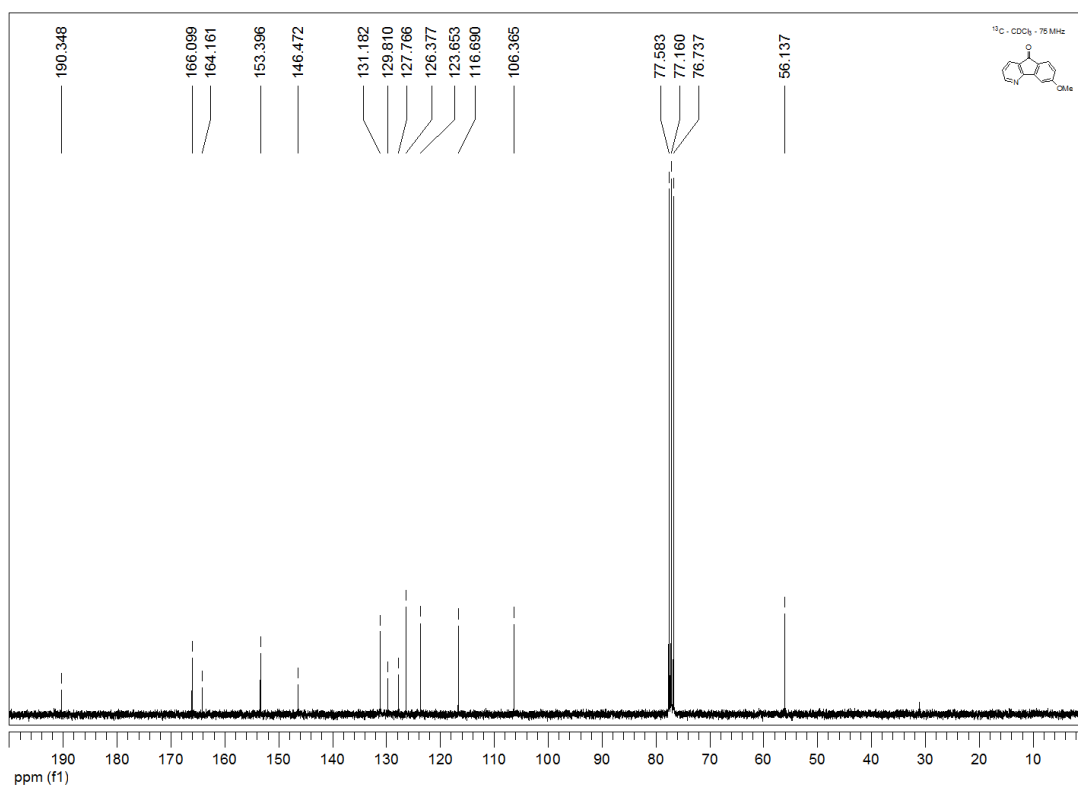
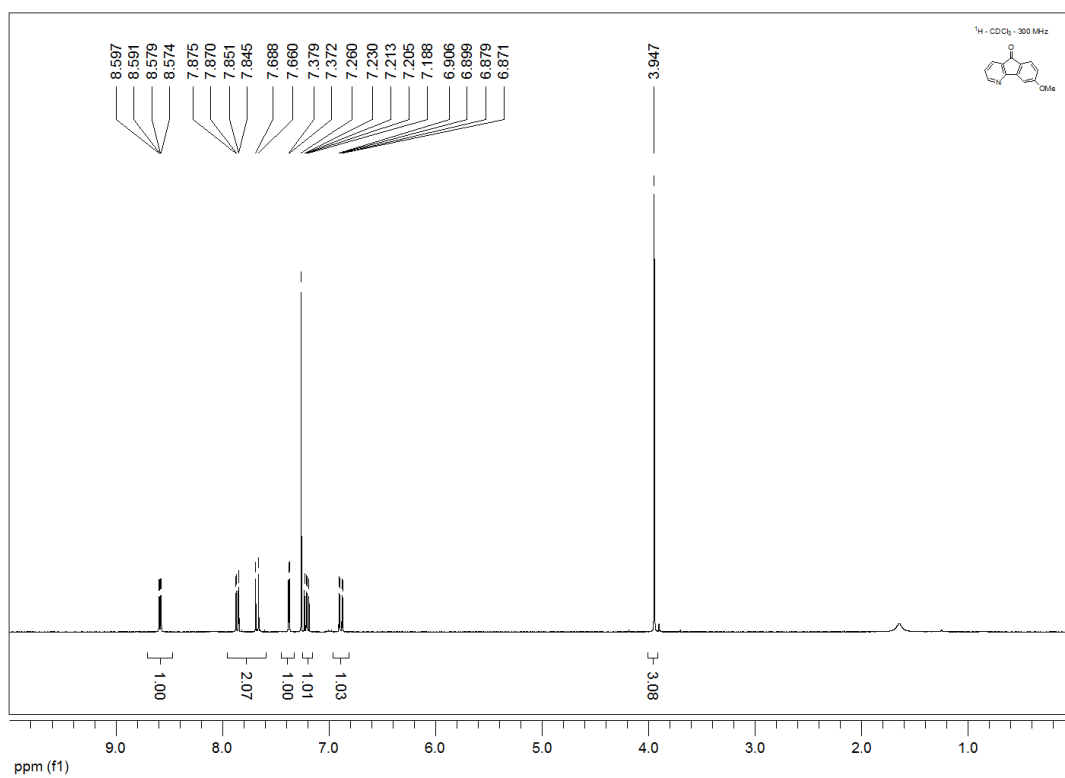


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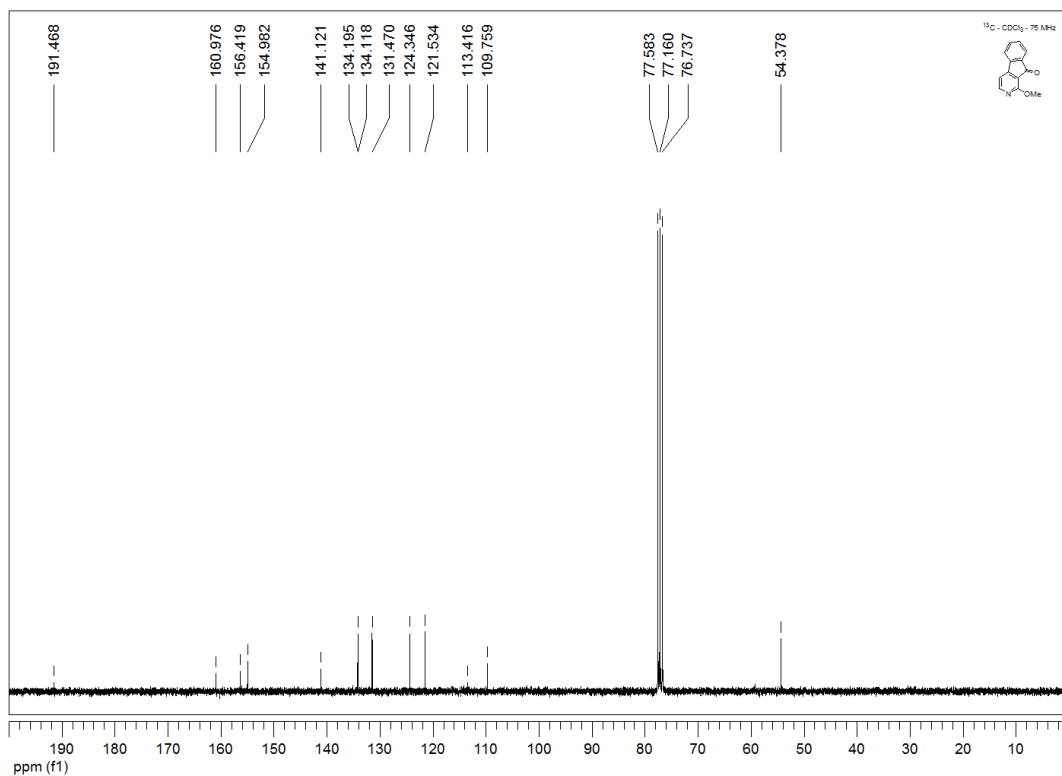
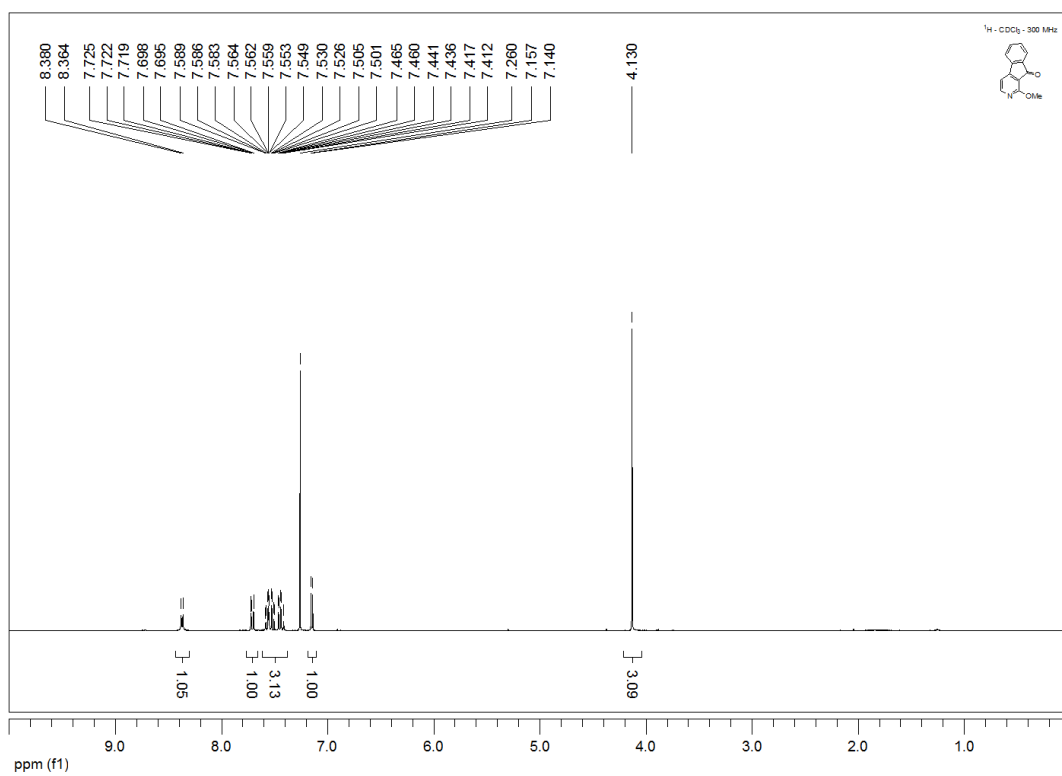




# Compound 9



# Compound 10



# Compound 13

