

*Electronic Supplementary Information (ESI) for*

**Heterogeneously catalyzed decarbonylation of thioesters by supported Ni, Pd, or Rh  
nanoparticle catalysts**

Takehiro Matsuyama,<sup>a</sup> Takafumi Yatabe<sup>\*ab</sup>, and Kazuya Yamaguchi<sup>\*a</sup>

<sup>a</sup>Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1  
Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

<sup>b</sup>Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and  
Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

\*e-mail: kyama@appchem.t.u-tokyo.ac.jp, yatabe@appchem.t.u-tokyo.ac.jp

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## **Experimental Methods and Spectral Data of Synthesized Substrates**

### **Instrumental and Reagents**

Gas chromatography (GC) analyses were conducted on Shimadzu GC-2014 equipped with a flame ionization detector (FID) and an InertCap-5 (60 m) using Shimadzu C-R8A Chromatopac Data Processor for area calculations. GC mass spectrometry (GC-MS) spectra were performed by Shimadzu GCMS-QP2020 equipped with an InertCap-5 MS/NP capillary column (30 m) at an ionization voltage of 70 eV. For the gas phase analysis, GC analyses were conducted on Shimadzu GC-2010 Plus equipped with barrier discharge ionization detector (BID) and a SHINCARBON-ST. Liquid-state nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-500.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured at 500.16 and 125.77 Hz respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were referenced to tetramethylsilane (TMS) signal ( $\delta = 0$  ppm).  $^{19}\text{F}$  NMR spectra were measured at 470.62 Hz using  $\text{CF}_3\text{COOH}$  as an external reference ( $\delta = -77.0$  ppm). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were conducted by Shimadzu ICPS-8100. Transmission electron microscope (TEM) observations were conducted by JEM-2010F. BET surface areas were measured on micromeritics ASAP 2010 and calculated from the  $\text{N}_2$  adsorption isotherm with the BET equation. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) was performed using FT/IR-6700 spectrometer (JASCO).  $\text{CeO}_2$  (BET:  $50 \text{ m}^2\text{g}^{-1}$ , Cat. No. 544841-25G, Aldrich),  $\text{Al}_2\text{O}_3$  (BET:  $204 \text{ m}^2\text{g}^{-1}$ , Cat. No. JRC-ALO-9, Nippon Light Metal Company, Ltd.),  $\text{TiO}_2$  (BET:  $316 \text{ m}^2\text{g}^{-1}$ , Cat. No. JRC-TIO-17, NIPPON AEROSIL CO., LTD.), and hydroxyapatite (HAP, BET:  $11 \text{ m}^2\text{g}^{-1}$ , Cat. No. 011-14882, FUJIFILM Wako Pure Chemical) were acquired from commercial sources. Column chromatography on silica gel was performed by using Biotage Isolera. Solvents and substrates were obtained from Tokyo Chemical Industry, Aldrich, Kanto Chemical, or FUJIFILM Wako Pure Chemical (reagent grade), and purified prior to being used, if necessary.

### **Preparation of Supported Catalysts**

$\text{Ni(OH)}_2/\text{CeO}_2$  was prepared as follows: The aqueous solution (60 mL) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (118.8 mg, 8.3 mM) containing  $\text{CeO}_2$  (2.0 g) was vigorously stirred at room temperature. After 15 min, the pH of the solution was adjusted to 10.0 by addition of an aqueous solution of NaOH (1.0 M), and the resulting slurry was stirred for 24 h. The solid was then filtered off, washed with a large amount of water (3 L), and dried to afford 2.0 g of  $\text{Ni(OH)}_2/\text{CeO}_2$  as a pale yellow powder.  $\text{Ni(OH)}_2/\text{CeO}_2$  was stored in an Ar-filled glove-box after being heated at  $150 \text{ }^\circ\text{C}$  for 15 min *in vacuo*.

$\text{Ni/CeO}_2$  was prepared based on our previous report<sup>S1</sup> with some modifications:  $\text{Ni(OH)}_2/\text{CeO}_2$  (1.0 g) was added to the THF solution (12 mL, 0.25 M) of sodium naphthalenide and stirred vigorously at room temperature for 90 minutes. The solid was then filtered off, washed with methanol (20 mL) and diethyl ether (20 mL), and dried under an Ar atmosphere to afford 1.0 g of  $\text{Ni/CeO}_2$  as black powder (Ni content: 1.38 wt%). Various supported nickel catalysts, such as  $\text{Ni/HAP}$

(Ni content: 1.39 wt%), Ni/TiO<sub>2</sub> (Ni content: 0.85 wt%), Ni/Al<sub>2</sub>O<sub>3</sub> (Ni content: 1.25 wt%) were prepared in the same manner.

Pd/HAP was prepared based on our previous report<sup>S2</sup> as follows: The aqueous solution (60 mL) of PdCl<sub>2</sub> (88.7 mg, 8.3 mM) and KCl (149.1 mg, 33.3 mM) containing HAP (2.0 g) was vigorously stirred at room temperature. After 15 min, the pH of the solution was adjusted to 10.0 by addition of an aqueous solution of NaOH (1.0 M), and the resulting slurry was stirred for 24 h. The solid was then filtered off, washed with a large amount of water (3 L), and dried to afford 2.0 g of Pd(OH)<sub>x</sub>/HAP as a brown powder. Pd(OH)<sub>x</sub>/HAP (2.0 g) was then dispersed in water (60 mL) and was vigorously stirred at room temperature. After a few minutes, NaBH<sub>4</sub> (240 mg) was added to the resulting mixture was stirred for 2 h. The solid was then filtered off, washed with a large amount of water (2 L), and dried to afford 2.0 g of Pd/HAP as a black powder (Pd content: 2.48 wt%).

Rh/HAP was prepared as follows: The aqueous solution (30 mL) of RhCl<sub>3</sub>·3H<sub>2</sub>O (132 mg, 16.7 mM) containing HAP (2.0 g) was vigorously stirred at room temperature. After 15 min, the pH of the solution was adjusted to 13.2 by addition of an aqueous solution of NaOH (1.0 M), and the resulting slurry was stirred for 24 h. The solid was then filtered off, washed with a large amount of water (3 L), and dried to afford 2.0 g of Rh(OH)<sub>x</sub>/HAP as a pale yellow powder. Rh(OH)<sub>x</sub>/HAP (2.0 g) was then dispersed in water (60 mL) and was vigorously stirred at room temperature. After a few minutes, NaBH<sub>4</sub> (240 mg) was added to the resulting mixture and stirred for 2 h. The solid was then filtered off, washed with a large amount of water (2 L), and dried to afford 2.0 g of Rh/HAP as a pale gray powder (Rh content: 1.43 wt%). Ru/HAP was prepared as described above using RuCl<sub>3</sub>·*n*H<sub>2</sub>O instead of RhCl<sub>3</sub>·3H<sub>2</sub>O.

### **A Typical Procedure for Decarbonylation of Thioesters**

In an Ar-filled glovebox, Ni/CeO<sub>2</sub> (5 mol%, 40 mg) or Pd/HAP (10 mol%, 80 mg), thioesters (0.2 mmol), 1,3,5-trimethoxybenzene (0.1 mmol, internal standard), xylene (2.0 mL), and Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL). The mixture was stirred at 160 °C for 24 h, then the mixture was cooled down to room temperature. Conversions and product yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were identified by GC-MS and NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F).

### **Large Scale Synthesis of 2k**

In an Ar-filled glovebox, Ni/CeO<sub>2</sub> (5 mol%, 800 mg), **1k** (4 mmol, 1.40 g), xylene (25 mL), and a Teflon-coated magnetic stir bar were placed in a 100 mL Schlenk flask. The mixture was stirred at 140 °C for 4.5 h with an Ar balloon. After the reaction, the catalyst was removed by simple filtration and the filtrate was concentrated by evaporation, and then subjected to silica-gel column chromatography using hexane as an eluent, giving the pure product.

## Leaching Test

### Leaching test using Ni/CeO<sub>2</sub>

A magnetic stir bar, 1,3,5-trimethoxybenzene (0.1 mmol), *S*-phenyl benzenecarbothioate (**1g**, 0.2 mmol), Ni/CeO<sub>2</sub> (80 mg, 10 mol%), and mesitylene (2 mL) were added to a Pyrex glass reactor, and the reaction was carried out at 140 °C in an Ar-filled glovebox. 20 min after the start of the reaction, half of the reaction solution was filtered by hot filtration using a disposable syringe with a hydrophilic PTFE membrane filter into another test tube that had been previously heated to 140 °C with a magnetic stir bar, and the reaction was continued without the catalyst at 140 °C.

A magnetic stir bar, 1,3,5-trimethoxybenzene (0.1 mmol), **1g** (0.2 mmol), Ni/CeO<sub>2</sub> (80 mg, 10 mol%), and xylene (2 mL) were added to a Pyrex glass reactor, and the reaction was carried out at 140 °C in an Ar-filled glovebox, and the solution 2 h after the start of the reaction was filtered using a disposable syringe with a hydrophilic PTFE membrane filter. The solvent xylene was removed using a rotary evaporator before aqua regia (0.5 mL) was added, and the amount of Ni species leached into the reaction solution was measured by ICP-AES. The measurement wavelength was 231.604 nm.

### Leaching test using Pd/HAP

A magnetic stir bar, 1,3,5-trimethoxybenzene (0.1 mmol), **1g** (0.2 mmol), Pd/HAP (80 mg, 10 mol%), and xylene (2 mL) were added to a Pyrex glass reactor, and the reaction was carried out at 140 °C. 6 min after the start of the reaction, the reaction solution was filtered by hot filtration using a disposable syringe with a hydrophilic PTFE membrane filter into another test tube that had been previously heated to 140 °C with a magnetic stir bar, and the reaction was continued without the catalyst at 140 °C.

The reaction was prepared as described above, and the solution 2 h after the start of the reaction was filtered using a disposable syringe with a hydrophilic PTFE membrane filter. The solvent xylene was removed using a rotary evaporator before aqua regia (0.5 mL) was added, and the amount of Pd species leached into the reaction solution was measured by ICP-AES. The measurement wavelength was 340.458 nm.

### Leaching test using Rh/HAP

A magnetic stir bar, 1,3,5-trimethoxybenzene (0.1 mmol), **1ek** (0.2 mmol), Rh/HAP (160 mg, 20 mol%), and mesitylene (2 mL) were added to a Pyrex glass reactor, and the reaction was carried out at 165 °C. 90 min after starting the reaction, the reaction solution was quickly filtered off using a hydrophilic PTFE membrane filter via cannula filtration to another Schlenk flask under an Ar atmosphere. Then, the filtrate was continually stirred at 165 °C.

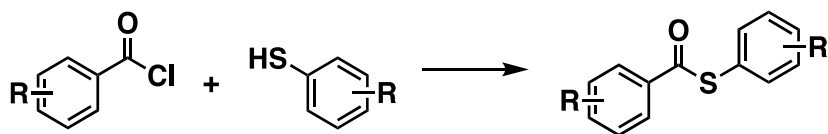
The reaction was prepared as described above, and the solution 12 h after the start of the reaction was filtered using a disposable syringe with a hydrophilic PTFE membrane filter. The solvent xylene

was removed using a rotary evaporator before aqua regia (0.5 mL) was added, and the amount of Rh species leached into the reaction solution was measured by ICP-AES. The measurement wavelength was 339.682 nm.

### **Reuse Test**

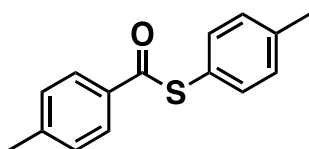
A magnetic stir bar, 1,3,5-trimethoxybenzene (0.1 mmol), **1k** (0.2 mmol), Pd/HAP (80 mg, 10 mol%), and xylene (2 mL) were added to a Pyrex glass reactor, and the reaction was carried out at 140 °C for 24 h. After the reaction, the catalyst was retrieved in the air by filtration through washing with 50 mL of Et<sub>2</sub>O followed by drying *in vacuo*. The used Pd/HAP was calcinated at 300 °C for 3 h under an air atmosphere. The calcinated Pd/HAP was then dispersed in water and reduced with NaBH<sub>4</sub> (120 mg per 1 g of Pd/HAP) in the open air. The resulting slurry was then stirred vigorously at room temperature for 2 h. The solid was then filtered off, washed with a large amount of water (2 L), and dried to afford Pd/HAP as a black powder.

### Synthesis of Thioesters

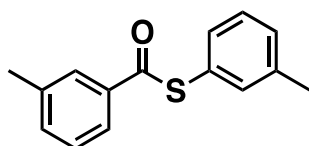


Benzoyl chloride (6.3 mmol), thiols (6.0 mmol) were dissolved in degassed  $\text{CH}_2\text{Cl}_2$  (12 mL) under an Ar atmosphere. The solution was stirred at room  $0^\circ\text{C}$  for a few minutes. Then,  $\text{Et}_3\text{N}$  (2 equivalent to thiols) were added dropwise and the resulting solution was stirred overnight at room temperature. After the reaction, 35wt%  $\text{HCl}/\text{H}_2\text{O}$  ( $v/v = 5\%$ , 10 mL) was added, and the aqueous layer was washed with brine (15 mL  $\times$  3). After removing the solvents, thioesters were obtained, and the purity was investigated by GC, GC-MS, and NMR. The products were purified by silica-gel column chromatography if necessary.<sup>S3</sup>

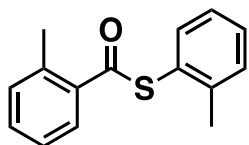
### Spectral Data of Thioesters



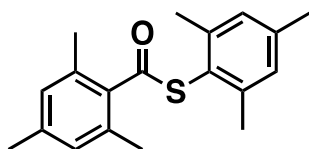
**S-(4-methylphenyl) 4-methylbenzenecarbothioate** (CAS No. 39248-95-8, **1a**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91–7.93 (m, 2H), 7.34–7.40 (m, 2H), 7.25–7.28 (m, 4H), 2.43 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.2, 144.5, 139.7, 135.1, 134.2, 130.1, 129.4, 127.5, 124.0, 21.7, 21.4. MS (EI):  $m/z$  (%): 242 (3) [ $M^+$ ], 120 (9), 119 (100), 91 (39), 65 (10), 39 (3).<sup>S4</sup>



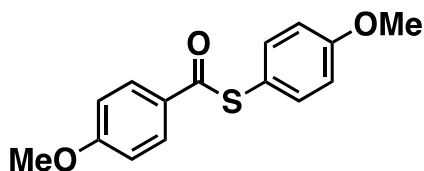
**S-(3-methylphenyl) 3-methylbenzenecarbothioate** (CAS No. 98098-61-4, **1b**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81–7.85 (m, 2H), 7.39–7.41 (m, 1H), 7.32–7.37 (m, 4H), 7.23–7.25 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 139.4, 138.9, 137.0, 135.9, 134.7, 132.4, 130.7, 129.4, 128.9, 128.2, 127.4, 125.0, 21.6. MS (EI):  $m/z$  (%): 242 (3) [ $M^+$ ], 120 (9), 119 (100), 92 (3), 91 (39), 89 (3), 65 (14).<sup>S4</sup>



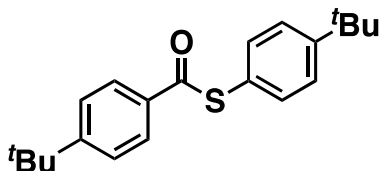
**S-(2-methylphenyl) 2-methylbenzenecarbothioate** (CAS No. 101093-42-9, **1c**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96–7.98 (m, 1H), 7.49–7.51 (m, 1H), 7.41–7.44 (m, 1H), 7.36–7.38 (m, 2H), 7.26–7.33 (m, 3H), 2.49 (s, 3H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.0, 142.5, 137.4, 137.1, 136.4, 132.0, 131.8, 130.9, 130.3, 128.7, 127.7, 126.8, 125.9, 20.9, 20.8. MS (EI):  $m/z$  (%): 242 (0.7) [ $M^+$ ], 120 (9), 119 (100), 92 (3), 91 (40), 89 (3), 77 (3), 65 (13).<sup>S4</sup>



**S-(2,4,6-trimethylphenyl) 2,4,6-trimethylbenzenecarbothioate** (CAS No. 81787-26-0, **1d**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.03–7.04 (m, 2H), 6.87–6.88 (m, 2H), 2.45 (s, 6H), 2.42 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.4, 142.7, 140.1, 139.4, 137.6, 134.0, 129.4, 128.5, 123.4, 21.9, 21.2, 21.1, 19.3. MS (EI):  $m/z$  (%): 298 (0.04) [ $M^+$ ], 148 (10), 147 (100), 119 (24), 117 (4), 115 (3), 91 (9), 77 (3).

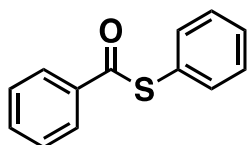


**S-(4-methoxyphenyl) 4-methoxybenzenecarbothioate** (CAS No. 98098-60-3, **1e**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99–8.00 (m, 2H), 7.40–7.41 (m, 2H), 6.93–6.98 (m, 4H), 3.86 (s, 3H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.6, 164.1, 160.8, 136.9, 129.8, 129.6, 118.3, 115.0, 114.0, 55.7, 55.5. MS (EI):  $m/z$  (%): 274 (3) [ $M^+$ ], 139 (3), 136 (9), 135 (100), 107 (11), 92 (10), 77 (17), 64 (5).<sup>S4</sup>

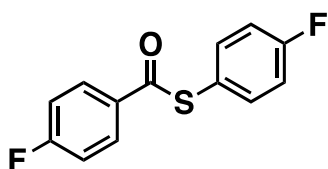


**S-(4-methylphenyl) 4-(1,1-dimethylethyl)benzenecarbothioate** (CAS No. 2346642-72-4, **1f**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95–7.99 (m, 2H), 7.41–7.51 (m, 6H), 1.35 (s, 9H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.1, 157.4, 152.6, 134.7, 134.1, 127.4, 126.4, 125.7, 124.0, 35.2, 34.8,

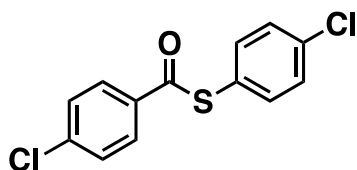
31.2, 31.1. MS (EI):  $m/z$  (%): 274 (6), 273 (19), 272 (100) [ $M^+$ ], 271 (6), 257 (7), 256 (6), 242 (5), 241 (17), 240 (80), 239 (8), 225 (16), 224 (11), 223 (5), 212 (5), 152 (8), 136 (15), 135 (8), 127 (5), 120 (12), 119 (8).<sup>S5</sup>



**S-phenyl benzenecarbothioate** (CAS No. 884-09-3, **1g**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02–8.05 (m, 2H), 7.60–7.63 (m, 1H), 7.45–7.54 (m, 7H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.2, 136.7, 135.1, 133.7, 129.5, 129.3, 128.8, 127.5, 127.4. MS (EI):  $m/z$  (%): 214 (2) [ $M^+$ ], 109 (5), 106 (8), 105 (100), 78 (4), 77 (51), 65 (5), 51 (16), 50 (4), 39 (4).<sup>S4</sup>

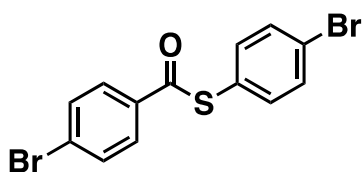


**S-(4-fluorophenyl) 4-fluorobenzenecarbothioate** (CAS No. 100045-97-4, **1h**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03–8.07 (m, 2H), 7.46–7.50 (m, 2H), 7.14–7.19 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.7, 166.2 (d,  $J = 254.0$  Hz), 163.7 (d,  $J = 249.1$  Hz), 137.2 (d,  $J = 8.4$  Hz), 132.7 (d,  $J = 2.4$  Hz), 130.1 (d,  $J = 9.5$  Hz), 122.3 (d,  $J = 2.5$  Hz), 116.6 (d,  $J = 21.5$  Hz), 116.0 (d,  $J = 22.6$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ): -103.0, -110.0. MS (EI):  $m/z$  (%): 250 (2) [ $M^+$ ], 127 (4), 124 (7), 123 (100), 96 (3), 95 (40), 83 (8), 75 (13), 69 (3), 57 (3).<sup>S4</sup>

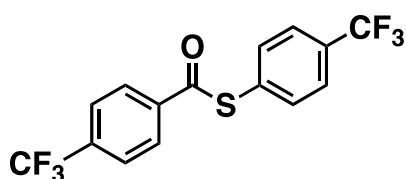


**S-(4-chlorophenyl) 4-chlorobenzenecarbothioate** (CAS No. 6310-31-2, **1i**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93–7.96 (m, 2H), 7.45–7.48 (m, 2H), 7.43 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.9, 140.7, 136.6, 136.5, 135.0, 129.9, 129.5, 129.2, 125.7. MS (EI):  $m/z$  (%): 286 (0.3), 285 (0.2), 284 (1), 283 (0.3) [ $M^+$ ], 282 (2), 141 (32), 140 (8), 139 (100), 113 (10), 111 (31), 108 (6), 76 (4), 75 (15), 50 (4).<sup>S4</sup>

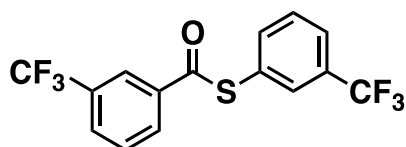




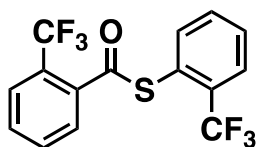
**S-(4-bromophenyl) 4-bromobenzenecarbothioate** (CAS No. 100045-96-3, **1j**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86–7.88 (m, 2H), 7.63–7.65 (m, 2H), 7.59–7.60 (m, 2H), 7.35–7.37 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.6, 136.5, 135.1, 132.6, 132.2, 129.0, 128.9, 126.0, 124.5. MS (EI):  $m/z$  (%): 372 (2) [ $M^+$ ], 186 (7), 185 (91), 184 (9), 183 (100), 157 (21), 155 (21), 108 (20), 76 (21), 75 (18), 74 (5), 50 (14).<sup>S6</sup>



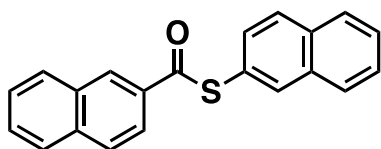
**S-[4-(trifluoromethyl)phenyl] 4-(trifluoromethyl)benzenecarbothioate** (**1k**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12–8.14 (m, 2H), 7.78–7.79 (m, 2H), 7.73–7.74 (m, 2H), 7.65–7.67 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.2, 139.0, 135.2, 131.9 (q,  $J = 32.3$  Hz), 131.3, 130.8 (q,  $J = 47.6$  Hz), 137.9, 126.2 (q,  $J = 3.1$  Hz), 126.0 (q,  $J = 3.6$  Hz), 123.8 (q,  $J = 270.6$  Hz), 123.4 (q,  $J = 270.6$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.2, -62.4. MS (EI):  $m/z$  (%): 350 (1) [ $M^+$ ], 174 (8), 173 (100), 145 (45), 125 (5), 95 (7).



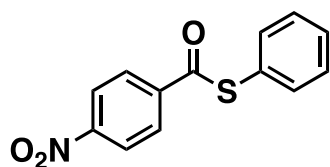
**S-[3-(trifluoromethyl)phenyl] 3-(trifluoromethyl)benzenecarbothioate** (**1l**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.25–8.28 (m, 1H), 8.19–8.21 (m, 1H), 7.88–7.90 (m, 1H), 7.80 (m, 1H), 7.70–7.74 (m, 2H), 7.59–7.67 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.1, 138.4, 136.9, 131.9 (q,  $J = 32.3$  Hz), 131.7 (q,  $J = 32.3$  Hz), 131.5 (q,  $J = 3.6$  Hz), 130.7, 130.4 (q,  $J = 3.6$  Hz), 129.8, 129.7, 128.0, 126.7 (q,  $J = 3.6$  Hz), 124.5 (q,  $J = 3.6$  Hz), 123.6 (q,  $J = 270.8$  Hz), 123.5 (q,  $J = 270.8$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.0, -62.1. MS (EI):  $m/z$  (%): 350 (1) [ $M^+$ ], 331 (7), 174 (8), 173 (100), 145 (44), 125 (5), 95 (8), 75 (5).



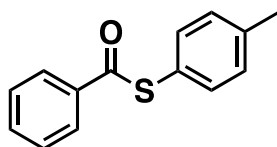
**S-[2-(trifluoromethyl)phenyl] 2-(trifluoromethyl)benzenecarbothioate (1m)**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83–7.87 (m, 2H), 7.78–7.79 (m, 1H), 7.59–7.71 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.6, 139.2, 136.9, 133.3 (q,  $J = 29.9$  Hz), 132.6, 131.9, 131.6, 130.4, 128.7, 127.6 (q,  $J = 32.1$  Hz), 127.3 (q,  $J = 4.8$  Hz), 127.1 (q,  $J = 4.8$  Hz), 125.7, 123.2 (q,  $J = 271.9$  Hz), 123.1 (q,  $J = 271.9$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -57.9, -59.6. MS (EI):  $m/z$  (%): 350 (0.1) [ $M^+$ ], 177 (3), 174 (9), 173 (100), 146 (3), 145 (36), 125 (4), 95 (8), 75 (4).



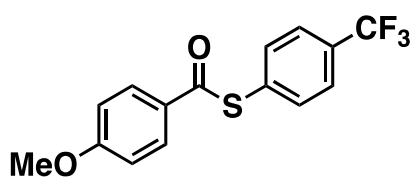
**S-2-naphthalenyl 2-naphthalenecarbothioate** (CAS No. 98098-62-5, **1n**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65–8.66 (m, 1H), 8.09–8.11 (m, 1H), 8.05–8.07 (m, 1H), 8.01–8.03 (m, 1H), 7.86–7.95 (m, 5H), 7.52–7.66 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.3, 135.9, 135.0, 133.7, 133.5, 131.5, 129.7, 129.1, 128.9, 128.7, 128.0, 127.9, 127.9, 127.2, 127.0, 126.6, 123.3. MS (EI):  $m/z$  (%): 314 (8) [ $M^+$ ], 156 (12), 155 (100), 128 (7), 127 (61), 126 (7), 115 (11), 77 (6).



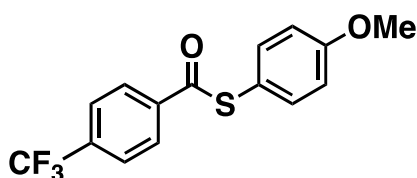
**S-phenyl 4-nitrobenzenecarbothioate** (CAS No. 3128-43-6, **1og**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33–8.36 (m, 2H), 8.17–8.20 (m, 2H), 7.48–7.54 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.9, 150.7, 141.3, 134.9, 130.1, 129.5, 128.5, 126.2, 124.0. MS (EI):  $m/z$  (%): 259 (8) [ $M^+$ ], 151 (8), 150 (100), 120 (25), 110 (4), 109 (8), 105 (3), 104 (35), 92 (20), 77 (4), 76 (26), 75 (7), 74 (3), 69 (3), 65 (9), 64 (3), 51 (4), 50 (10).<sup>S4</sup>



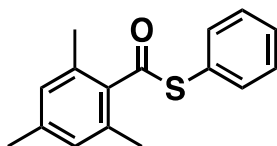
**S-(4-methylphenyl) benzenecarbothioate** (CAS No. 10371-42-3, **1ga**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01–8.04 (m, 2H), 7.58–7.63 (m, 1H), 7.46–7.50 (m, 2H), 7.38–7.41 (m, 2H), 7.26–7.28 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.6, 139.8, 136.7, 135.0, 133.6, 130.1, 128.7, 127.5, 123.8, 21.4. MS (EI):  $m/z$  (%): 228 (5) [ $M^+$ ], 106 (8), 105 (100), 78 (3), 77 (38), 51 (9).<sup>S3</sup>



**S-[4-(trifluoromethyl)phenyl] 4-methoxybenzenecarbothioate** (CAS No. 1450900-51-2, **1ke**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00–8.02 (m, 2H), 7.63–7.70 (m, 4H), 6.96–6.99 (m, 2H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.3, 164.3, 135.3, 132.5, 131.3 (q,  $J = 32.3$  Hz), 129.9, 129.0, 125.9 (q,  $J = 3.6$  Hz), 123.9 (q,  $J = 270.6$  Hz), 114.1, 55.6;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.0. MS (EI):  $m/z$  (%): 312 (0.04) [ $M^+$ ], 136 (9), 135 (100), 108 (3), 107 (15), 92 (13), 77 (22), 64 (8), 63 (5).<sup>S7</sup>

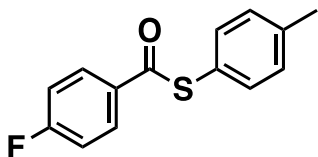


**S-(4-methoxyphenyl) 4-(trifluoromethyl)benzenecarbothioate** (CAS No. 144406-23-5, **1ek**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11–8.13 (m, 2H), 7.73–7.76 (m, 2H), 7.49–7.43 (m, 2H), 6.99–7.02 (m, 2H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.3, 161.1, 139.5, 136.6, 134.8 (q,  $J = 32.3$  Hz), 127.8, 125.8 (q,  $J = 3.6$  Hz), 124.6 (q,  $J = 270.8$  Hz), 117.1, 115.1, 55.4;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.3. MS (EI):  $m/z$  (%): 313 (3), 312 (17) [ $M^+$ ], 174 (9), 173 (100), 146 (3), 145 (38), 139 (6), 125 (3), 96 (4), 95 (8), 75 (3).<sup>S8</sup>

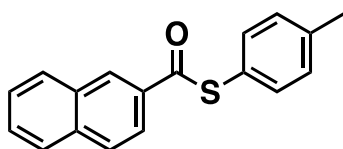


**S-phenyl 2,4,6-trimethylbenzenecarbothioate** (CAS No. 50404-53-0, **1dg**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52–7.55 (m, 2H), 7.43–7.48 (m, 3H), 6.86–6.88 (m, 2H), 2.39 (s, 6H), 2.30 (s, 3H);  $^{13}\text{C}$

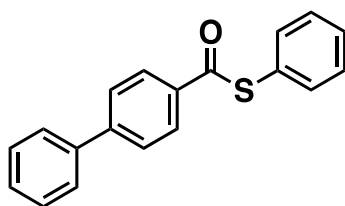
NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  196.0, 139.6, 137.2, 134.4, 133.7, 129.5, 129.3, 128.4, 128.1, 21.2, 19.1.  
MS (EI):  $m/z$  (%): 256 (0.02) [ $M^+$ ], 148 (11), 147 (100), 119 (36), 117 (6), 91 (16), 77 (7), 65 (5).<sup>S9</sup>



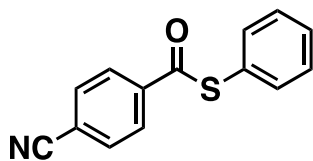
**S-(4-methylphenyl) 4-fluorobenzenecarbothioate** (CAS No. 90172-74-0, **1ha**) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.03–8.07 (m, 2H), 7.36–7.40 (m, 2H), 7.25–7.29 (m, 2H), 7.13–7.18 (m, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  189.1, 166.0 (d,  $J = 254.0$  Hz), 139.9, 135.0, 133.0 (d,  $J = 2.5$  Hz), 130.2, 130.0 (d,  $J = 9.6$  Hz), 123.5, 115.9 (d,  $J = 22.6$  Hz), 21.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): –103.6.  
MS (EI):  $m/z$  (%): 246 (7) [ $M^+$ ], 124 (8), 123 (100), 95 (33), 75 (8).<sup>S5</sup>



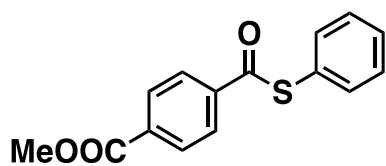
**S-(4-methylphenyl) 2-naphthalenecarbothioate** (CAS No. 2190510-55-3, **1na**) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.60–8.62 (m, 1H), 7.98–8.04 (m, 2H), 7.88–7.93 (m, 2H), 7.56–7.64 (m, 2H), 7.42–7.45 (m, 2H), 7.27–7.32 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  190.5, 139.8, 135.9, 135.1, 134.0, 132.5, 130.1, 129.6, 128.9, 128.6, 128.6, 127.8, 127.0, 123.9, 123.3, 21.4. MS (EI):  $m/z$  (%): 278 (4) [ $M^+$ ], 156 (12), 155 (100), 128 (6), 127 (56), 126 (8), 77 (8).<sup>S5</sup>



**S-phenyl [1,1'-biphenyl]-4-carbothioate** (CAS No. 1111250-50-0, **1pg**) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.09–8.12 (m, 2H), 7.70–7.73 (m, 2H), 7.63–7.66 (m, 2H), 7.53–7.56 (m, 2H), 7.45–7.50 (m, 5H), 7.40–7.44 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  189.7, 146.4, 139.7, 135.3, 135.1, 129.5, 129.3, 129.1, 129.0, 128.4, 128.1, 127.4, 127.3. MS (EI):  $m/z$  (%): 290 (1) [ $M^+$ ], 182 (13), 181 (100), 153 (20), 152 (32), 151 (7).<sup>S10</sup>

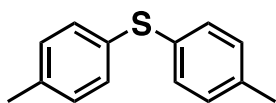


**S-phenyl 4-cyanobenzenecarbothioate** (CAS No. 97839-42-4, **1qg**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10–8.13 (m, 2H), 7.78–7.82 (m, 2H), 7.47–7.53 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.1, 139.8, 135.0, 132.6, 130.0, 129.5, 127.9, 126.2, 117.8, 116.9. MS (EI):  $m/z$  (%): 239 (7) [ $M^+$ ], 131 (9), 130 (100), 109 (6), 102 (39), 75 (8), 65 (6), 51 (7).<sup>S4</sup>

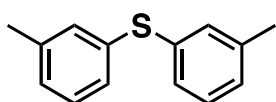


**methyl 4-[(phenylthio)carbonyl]benzoate** (CAS No. 106727-85-9, **1rg**)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13–8.18 (m, 2H), 8.06–8.09 (m, 2H), 7.46–7.55 (m, 5H), 3.97 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.7, 166.1, 140.0, 135.0, 134.4, 130.0, 129.8, 129.4, 127.4, 126.8, 52.5. MS (EI):  $m/z$  (%): 272 (2) [ $M^+$ ], 164 (10), 163 (100), 135 (19), 120 (7), 109 (5), 104 (7), 103 (12), 77 (7), 76 (9), 75 (6), 50 (5).<sup>S4</sup>

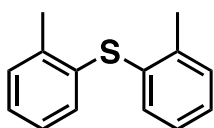
## Spectral Data of Products



**di-*p*-tolyl sulfide** (CAS No. 6620-94-0, **2a**) 94% (Ni/CeO<sub>2</sub>), 93% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 11.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (calculated by calibration curve). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.21–7.23 (m, 4H), 7.08–7.09 (m, 4H), 2.31 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 137.0, 132.8, 131.2, 130.0, 21.2. MS (EI): *m/z* (%): 215 (17), 214 (100) [*M*<sup>+</sup>], 213 (16), 199 (38), 198 (16), 184 (23), 181 (13), 105 (17), 91 (27), 65 (14).<sup>S11</sup>

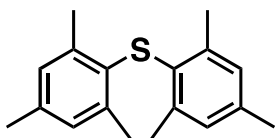


**di-*m*-tolyl sulfide** (CAS No. 3111-77-1, **2b**) 90% (Ni/CeO<sub>2</sub>), 94% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.7 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (the same as that of **2a**). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.16–7.19 (m, 4H), 7.11–7.13 (m, 2H), 7.03–7.05 (m, 2H), 2.30 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 139.1, 135.7, 131.7, 129.1, 128.2, 128.0, 21.4. MS (EI): *m/z* (%): 215 (16), 214 (100) [*M*<sup>+</sup>], 213 (12), 199 (48), 198 (20), 197 (12), 184 (41), 165 (13), 105 (22), 91 (17), 77 (11), 65 (26), 63 (10).<sup>S11</sup>

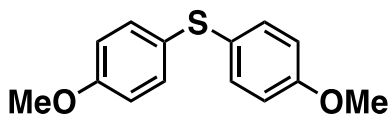


**di-*o*-tolyl sulfide** (CAS No. 4537-05-7, **2c**) 94% (Ni/CeO<sub>2</sub>), 88% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (estimated by the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.22–7.24 (m,

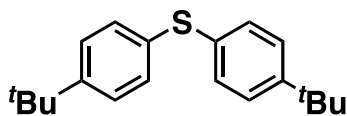
2H), 7.14–7.18 (m, 2H), 7.04–7.10 (m, 4H), 2.38 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.9, 134.3, 131.1, 130.4, 127.1, 126.7, 20.4. MS (EI):  $m/z$  (%): 215 (16), 214 (100) [ $M^+$ ], 199 (22), 197 (13), 184 (15), 166 (10), 165 (15), 123 (19), 122 (97), 121 (65), 105 (27), 92 (11), 91 (47), 89 (16), 78 (19), 77 (22), 65 (35), 63 (14), 51 (10).<sup>S11</sup>



**di-mesityl sulfide** (CAS No. 5324-71-0, **2d**) 31% (Ni/CeO<sub>2</sub>), 88% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7 mL $\cdot$ min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C $\cdot$ min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 20.1 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.94 (estimated by the effective carbon number concept).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.82 (s, 4H), 2.23 (s, 6H), 2.19 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.3, 136.5, 131.1, 129.3, 21.6, 20.8. MS (EI):  $m/z$  (%): 271 (12), 270 (63) [ $M^+$ ], 151 (14), 150 (100), 149 (26), 135 (18), 119 (15), 105 (15), 91 (21), 77 (11).<sup>S12</sup>

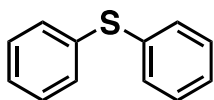


**bis(4-methoxyphenyl) sulfide** (CAS No. 3393-77-9, **2e**) 92% (Ni/CeO<sub>2</sub>), 94% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7 mL $\cdot$ min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C $\cdot$ min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 13.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.94 (estimated by the effective carbon number concept).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26–7.29 (m, 4H), 6.82–6.85 (m, 4H), 3.79 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.0, 132.7, 127.4, 114.8, 55.4. MS (EI):  $m/z$  (%): 247 (17), 246 (100) [ $M^+$ ], 231 (47), 215 (10), 214 (12), 203 (12), 199 (10), 188 (10), 171 (12), 115 (10).<sup>S11</sup>

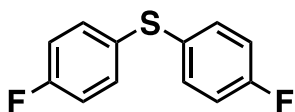


**1,1'-thiobis[4-(1,1-dimethylethyl)benzene]** (CAS No. 52908-55-1, **2f**).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31–7.33 (m, 4H), 7.26–7.28 (m, 4H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 135.1,

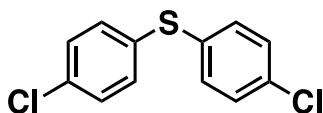
133.3, 128.8, 37.1, 33.9. MS (EI):  $m/z$  (%): 299 (10), 298 (45) [ $M^+$ ], 284 (21), 283 (100), 134 (12), 106 (22).



**di-phenyl sulfide** (CAS No. 139-66-2, **2g**) 89% (Ni/CeO<sub>2</sub>), 91% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 9.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.94 (estimated by the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.33–7.35 (m, 4H), 7.28–7.32 (m, 4H), 7.22–7.26 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 135.8, 131.0, 129.2, 127.0. MS (EI):  $m/z$  (%): 187 (16), 186 (100) [ $M^+$ ], 185 (79), 184 (35), 152 (10), 92 (13), 77 (10), 51 (14).<sup>S11</sup>



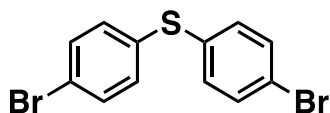
**bis(4-fluorophenyl)sulfide** (CAS No. 405-31-2, **2h**) 56% (Ni/CeO<sub>2</sub>), 78% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 14.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.94 (estimated by the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.28–7.32 (m, 4H), 6.98–7.03 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 162.2 (d,  $J$  = 246.8 Hz), 133.0 (d,  $J$  = 7.1 Hz), 131.1 (d,  $J$  = 3.6 Hz), 116.4 (d,  $J$  = 22.8 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): -133.6. MS (EI):  $m/z$  (%): 223 (15), 222 (100) [ $M^+$ ], 221 (50), 220 (21), 202 (17), 201 (14), 83 (22), 75 (13).<sup>S11</sup>



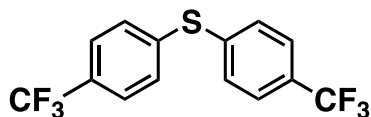
**bis(4-chlorophenyl)sulfide** (CAS No. 5181-10-2, **2i**) 87% (Ni/CeO<sub>2</sub>), 76% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention



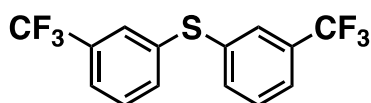
time, 12.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.89 (estimated by the effective carbon number concept).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24–7.30 (m, 8H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.9, 133.5, 132.3, 129.5. MS (EI):  $m/z$  (%): 258 (13), 256 (66), 255 (15) [ $M^+$ ], 254 (100), 221 (11), 220 (10), 219 (28), 218 (19), 185 (13), 184 (90), 183 (12), 109 (23), 108 (23), 91 (17), 75 (18).<sup>S12</sup>



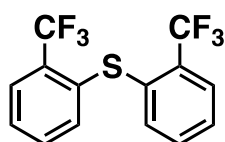
**bis(4-bromophenyl)sulfide** (CAS No. 3393-78-0, **2j**) 8% (Ni/CeO<sub>2</sub>), 40% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7  $\text{mL}\cdot\text{min}^{-1}$ ; initial column temp., 80  $^\circ\text{C}$  final column temp., 280  $^\circ\text{C}$ , progress rate, 10  $^\circ\text{C}\cdot\text{min}^{-1}$  (20 min), 280  $^\circ\text{C}$  for 10 min, injection temp., 280  $^\circ\text{C}$  detection temp., 280  $^\circ\text{C}$ ; retention time, 21.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.89 (estimated by the effective carbon number concept). MS (EI):  $m/z$  (%): 346 (59), 345 (15), 344 (100) [ $M^+$ ], 342 (49), 265 (38), 263 (39), 185 (10), 184 (68), 152 (10), 139 (11), 108 (34), 92 (36), 76 (11), 75 (12), 50 (12).<sup>S12</sup>



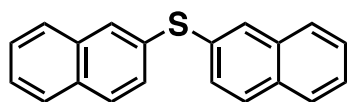
**bis[(4-trifluoromethyl)phenyl]sulfide** (CAS No. 90141-51-8, **2k**) 87% (Ni/CeO<sub>2</sub>), 93% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7  $\text{mL}\cdot\text{min}^{-1}$ ; initial column temp., 80  $^\circ\text{C}$  final column temp., 280  $^\circ\text{C}$ , progress rate, 20  $^\circ\text{C}\cdot\text{min}^{-1}$  (10 min), 280  $^\circ\text{C}$  for 10 min, injection temp., 280  $^\circ\text{C}$  detection temp., 280  $^\circ\text{C}$ ; retention time, 9.1 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (estimated by the effective carbon number concept).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57–7.59 (m, 4H), 7.43–7.45 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.5, 131.0, 129.7 (q,  $J = 32.3$  Hz), 126.3 (q,  $J = 3.6$  Hz), 123.9 (q,  $J = 270.6$  Hz);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -61.9. MS (EI):  $m/z$  (%): 323 (16), 322 (100) [ $M^+$ ], 303 (13), 301 (17), 253 (13), 252 (11), 233 (27), 184 (13).<sup>S11</sup>



**bis[(3-trifluoromethyl)phenyl]sulfide** (CAS No. 1580-30-9, **2l**) 87% (Ni/CeO<sub>2</sub>), 88% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 13.1 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (estimated by the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.62 (m, 2H), 7.53–7.55 (m, 2H), 7.44–7.50 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 136.2, 134.2, 131.9 (q, *J* = 33.4 Hz), 129.9, 127.8 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 3.5 Hz), 123.6 (q, *J* = 270.6 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): -62.1. MS (EI): *m/z* (%): 323 (15), 322 (100) [*M*<sup>+</sup>], 303 (12), 301 (15), 233 (32), 184 (12).<sup>S13</sup>

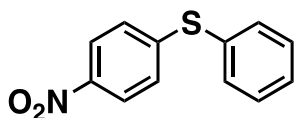


**bis[(2-trifluoromethyl)phenyl]sulfide** (CAS No. 1632046-24-2, **2m**) 85% (Ni/CeO<sub>2</sub>), 86% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 14.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (estimated by the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.73–7.75 (m, 2H), 7.36–7.43 (m, 4H), 7.22–7.24 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 134.8, 134.7, 132.4, 131.1 (q, *J* = 29.8 Hz), 127.5, 127.0 (q, *J* = 4.8 Hz), 123.6 (q, *J* = 273.1 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): -60.5. MS (EI): *m/z* (%): 323 (14), 322 (100) [*M*<sup>+</sup>], 301 (18), 283 (11), 234 (11), 233 (75), 184 (15), 95 (10).

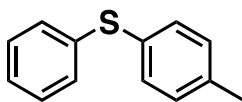


**di-2-naphthyl sulfide** (CAS No. 613-81-0, **2n**) 91% (Ni/CeO<sub>2</sub>), 73% (Pd/HAP) GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 20 min, injection temp., 280 °C detection temp., 280 °C; retention time, 30.9 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard),

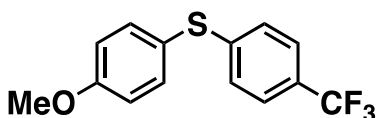
3.22 (estimated by the effective carbon number concept).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (m, 2H), 7.71–7.81 (m, 6H), 7.42–7.49 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.8, 133.1, 132.3, 129.8, 128.9, 128.7, 127.8, 127.4, 126.6, 126.2. MS (EI):  $m/z$  (%): 287 (23), 286 (100) [ $M^+$ ], 285 (54), 284 (28), 253 (20), 252 (27), 143 (10), 142 (14), 126 (14), 115 (12).<sup>S11</sup>



**4-nitrophenyl phenyl sulfide** (CAS No. 952-97-6, **2og**) 63% GC yield (Pd/HAP). GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7  $\text{mL}\cdot\text{min}^{-1}$ ; initial column temp., 80  $^\circ\text{C}$  final column temp., 280  $^\circ\text{C}$ , progress rate, 20  $^\circ\text{C}\cdot\text{min}^{-1}$  (10 min), 280  $^\circ\text{C}$  for 10 min, injection temp., 280  $^\circ\text{C}$  detection temp., 280  $^\circ\text{C}$ ; retention time, 12.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.77 (calculated by calibration curve).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05–8.08 (m, 2H), 7.53–7.56 (m, 2H), 7.45–7.47 (m, 3H), 7.17–7.19 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.5, 145.4, 134.8, 130.5, 130.0, 129.7, 126.7, 124.0. MS (EI):  $m/z$  (%): 233 (6), 232 (14), 231 (100) [ $M^+$ ], 201 (21), 186 (5), 185 (18), 184 (66), 183 (5), 152 (14), 139 (7), 115 (7), 109 (6), 92 (6), 77 (6), 69 (6), 65 (8), 51 (9), 50 (5).<sup>S14</sup>

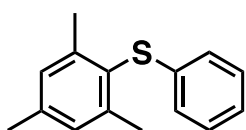


**phenyl *p*-tolyl sulfide** (CAS No. 3699-01-2, **2ga**) 79% GC yield (Rh/HAP). GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7  $\text{mL}\cdot\text{min}^{-1}$ ; initial column temp., 80  $^\circ\text{C}$  final column temp., 280  $^\circ\text{C}$ , progress rate, 20  $^\circ\text{C}\cdot\text{min}^{-1}$  (10 min), 280  $^\circ\text{C}$  for 10 min, injection temp., 280  $^\circ\text{C}$  detection temp., 280  $^\circ\text{C}$ ; retention time, 10.3 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (calculated by calibration curve). MS (EI):  $m/z$  (%): 202 (5), 201 (16), 200 (100) [ $M^+$ ], 199 (25), 186 (6), 185 (38), 184 (33), 167 (13), 165 (8), 152 (7), 99 (13), 91 (25), 77 (10), 65 (13), 63 (5), 51 (11), 45 (6), 39 (8).<sup>S15</sup>

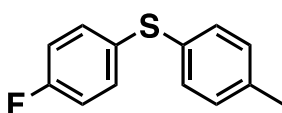


**4-methoxyphenyl[4-(trifluoromethyl)phenyl]sulfane** (CAS No. 53451-91-5, **2ek**, **2ke**) **2ek** 80% GC yield (74% isolated yield), **2ke** 77% GC yield (75% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $\text{N}_2$ ) flow rate, 1.7  $\text{mL}\cdot\text{min}^{-1}$ ; initial column temp., 80  $^\circ\text{C}$  final column temp., 280  $^\circ\text{C}$ , progress rate, 20  $^\circ\text{C}\cdot\text{min}^{-1}$  (10 min), 280  $^\circ\text{C}$

for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.9 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (calculated by calibration curve). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.41–7.48 (m, 4H), 7.11–7.15 (m, 2H), 6.93–6.98 (m, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.6, 144.9, 136.7, 127.2 (q, *J* = 32.3 Hz), 126.4, 125.6 (q, *J* = 2.4 Hz), 124.2 (q, *J* = 269.4 Hz), 121.7, 115.4, 55.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): –62.3. MS (EI): *m/z* (%): 286 (6), 285 (15), 284 (100) [*M*<sup>+</sup>], 283 (6), 270 (8), 269 (51), 265 (5), 241 (7), 221 (5), 215 (7), 172 (14), 171 (14), 95 (5), 63 (5), 45 (9).<sup>S15</sup>

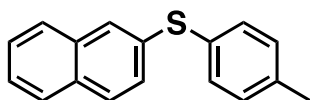


**1,3,5-trimethyl-2-(phenylthio)benzene** (CAS No. 33667-80-0, **2dg**) 18% GC yield (11% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 19.5 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.60 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.14–7.18 (m, 2H), 7.03–7.06 (m, 1H), 7.00–7.02 (m, 2H), 6.90–6.93 (m, 2H), 2.38 (s, 6H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 143.7, 139.3, 138.4, 129.3, 128.8, 127.0, 125.5, 124.5, 21.7, 21.1. MS (EI): *m/z* (%): 230 (6), 229 (17), 228(100) [*M*<sup>+</sup>], 213 (8), 198 (9), 195 (9), 180 (11), 179 (6), 165 (7), 151 (6), 150 (40), 149 (13), 135 (7), 119 (13), 117 (6), 115 (9), 105 (7), 103 (5), 91 (21), 77 (10), 65 (5), 51 (5).<sup>S16</sup>



**fluoro-4-[(4-methylphenyl)thio]benzene** (CAS No. 42917-47-5, **2ha**) 75% GC yield. GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.1 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.27–7.32 (m, 2H), 7.21–7.24 (m, 2H), 7.10–7.13 (m, 2H), 6.95–7.01 (m, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 162.0 (d, *J* = 244.4 Hz), 137.3, 132.8 (d, *J* = 8.4 Hz), 132.2, 131.5 (d, *J* = 4.8 Hz), 131.2, 130.0, 21.1; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): –114.3. MS (EI): *m/z* (%): 220 (6), 219

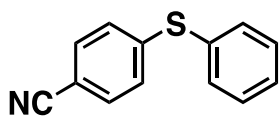
(16), 218 (100) [ $M^+$ ], 217 (23), 204 (5), 203 (32), 202 (26), 185 (16), 183 (10), 108 (10), 98 (5), 91 (24), 83 (6), 65 (11), 63 (5).<sup>S17</sup>



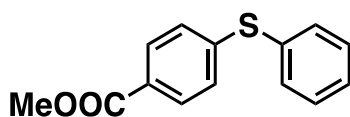
**2-[(4-methylphenyl)thio]naphthalene** (CAS No. 52258-16-9, **2na**) 82% GC yield (51% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $N_2$ ) flow rate, 1.7 mL $\cdot$ min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C $\cdot$ min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 14.5 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.91 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.67–7.79 (m, 4H), 7.40–7.47 (m, 2H), 7.31–7.37 (m, 3H), 7.12–7.16 (m, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):  $\delta$  137.6, 134.3, 133.8, 132.1, 132.0, 131.4, 130.1, 128.7, 128.4, 127.9, 127.7, 127.3, 126.5, 125.9, 21.1. MS (EI):  $m/z$  (%): 252 (6), 251 (19), 250 (100) [ $M^+$ ], 249 (19), 236 (8), 235 (39), 234 (39), 217 (9), 215 (7), 202 (14), 127 (5), 126 (5), 125 (5), 124 (11), 117 (9), 115 (13), 91 (6), 77 (6), 65 (5).<sup>S17</sup>



**4-(phenylthio)-1,1'-biphenyl** (CAS No. 59090-57-2, **2pg**) 76% GC yield (68% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm  $\times$  60 m, GL Science Inc.; carrier gas ( $N_2$ ) flow rate, 1.7 mL $\cdot$ min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C $\cdot$ min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 15.5 min; relative sensitivity for quantification (vs biphenyl, internal standard), 1.55 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.55–7.59 (m, 2H), 7.51–7.54 (m, 2H), 7.37–7.46 (m, 6H), 7.30–7.36 (m, 3H), 7.24–7.28 (m, 1H); <sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):  $\delta$  140.3, 140.0, 135.7, 134.9, 131.3, 131.2, 129.3, 128.8, 127.9, 127.5, 127.2, 127.0. MS (EI):  $m/z$  (%): 264 (6), 263 (22), 262 (100) [ $M^+$ ], 261 (30), 260 (7), 245 (5), 229 (5), 228 (10), 185 (11), 184 (13), 152 (14), 115 (5), 77 (5), 51 (5).<sup>S15</sup>

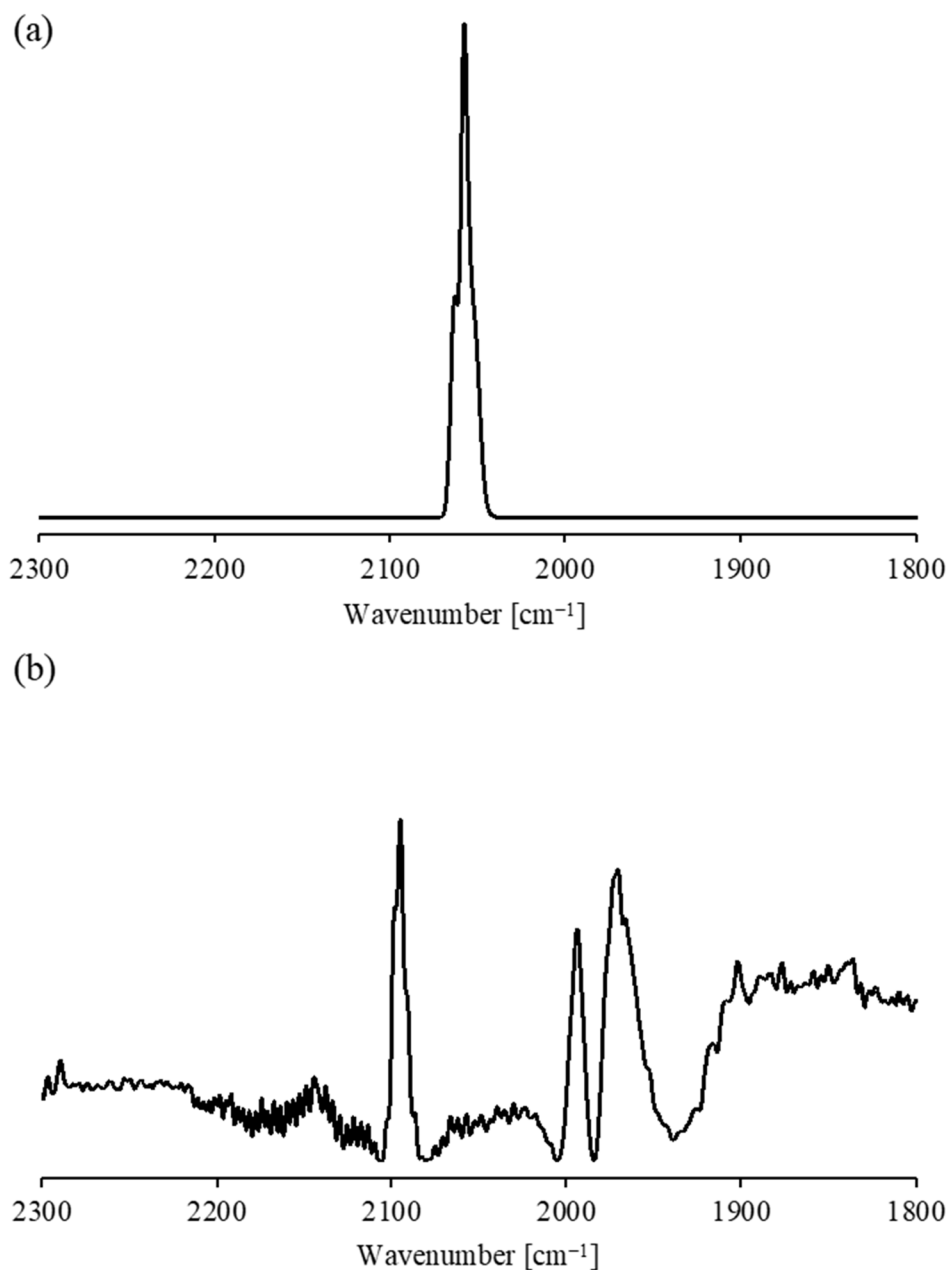


**4-(phenylthio)benzotrile** (CAS No. 51238-46-1, **2qg**) 41% GC yield (35% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min<sup>-1</sup> (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 18.2 min; relative sensitivity for quantification (vs biphenyl, internal standard), 1.08 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.50–7.54 (m, 2H), 7.46–7.49 (m, 2H), 7.42–7.45 (m, 3H), 7.15–7.18 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 145.8, 134.6, 132.5, 131.0, 130.0, 129.5, 127.4, 118.9, 108.8. MS (EI): *m/z* (%): 213 (5), 212 (18), 211 (100) [*M*<sup>+</sup>], 210 (68), 209 (14), 184 (8), 183 (11), 109 (5), 92 (11), 77 (15), 69 (5), 65 (7), 51 (21), 50 (5).<sup>S18</sup>

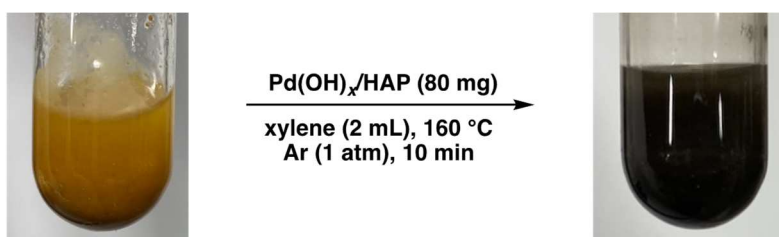


**methyl 4-(phenylthio)benzoate** (CAS No. 40730-41-4, **2rg**) 89% GC yield (42% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N<sub>2</sub>) flow rate, 1.7 mL·min<sup>-1</sup>; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min<sup>-1</sup> (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 12.4 min; relative sensitivity for quantification (vs biphenyl, internal standard), 1.05 (calculated by calibration curve and the effective carbon number concept). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.88–7.91 (m, 2H), 7.46–7.50 (m, 2H), 7.37–7.41 (m, 3H), 7.19–7.22 (m, 2H), 3.89 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.7, 144.4, 133.7, 132.4, 130.1, 129.6, 128.7, 127.6, 127.5, 52.1. MS (EI): *m/z* (%): 246 (6), 245 (16), 244 (100) [*M*<sup>+</sup>], 215 (5), 214 (13), 213 (85), 186 (5), 185 (20), 184 (50), 152 (9), 109 (5), 106 (8), 92 (7), 65 (5), 51 (6).<sup>S19</sup>

## Supplementary Figures

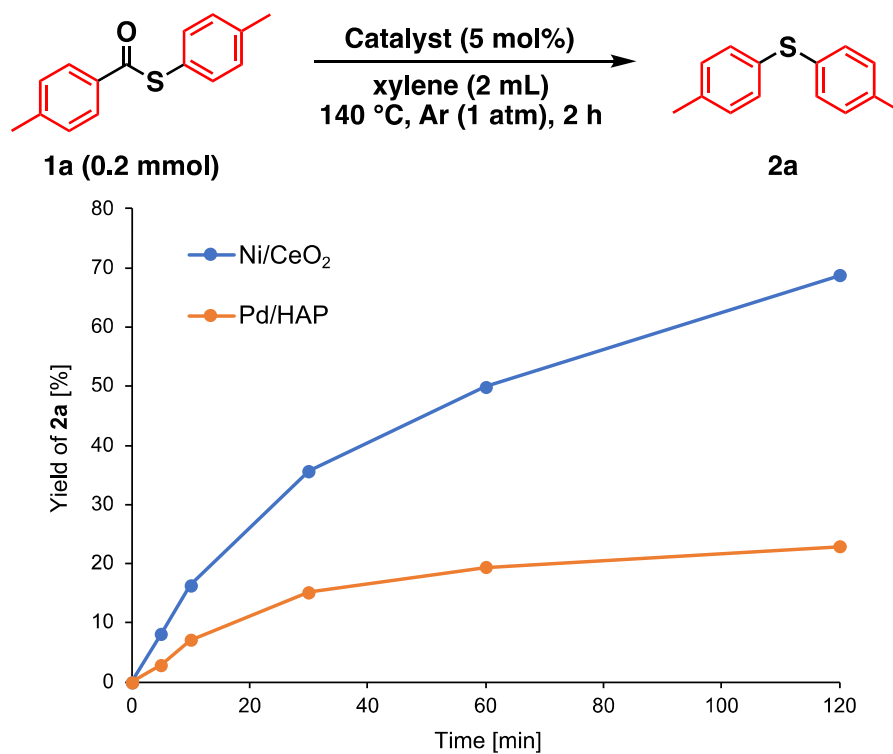


**Fig. S1** DRIFT spectra of CO adsorbed on (a) Ni/CeO<sub>2</sub> and (b) Pd/HAP at room temperature under the controlled CO atmosphere (16 Torr). These spectra are shown after Kubelka–Munk transform. The backgrounds measured in vacuo were subtracted. (a) The peak around 2050 cm<sup>-1</sup> can be attributed to CO species adsorbed on Ni(0) species.<sup>S20</sup> (b) The peaks around 2100, 1950–2000 cm<sup>-1</sup> were assigned to linear, and bridged CO species on Pd(0) species, respectively.<sup>S21</sup>

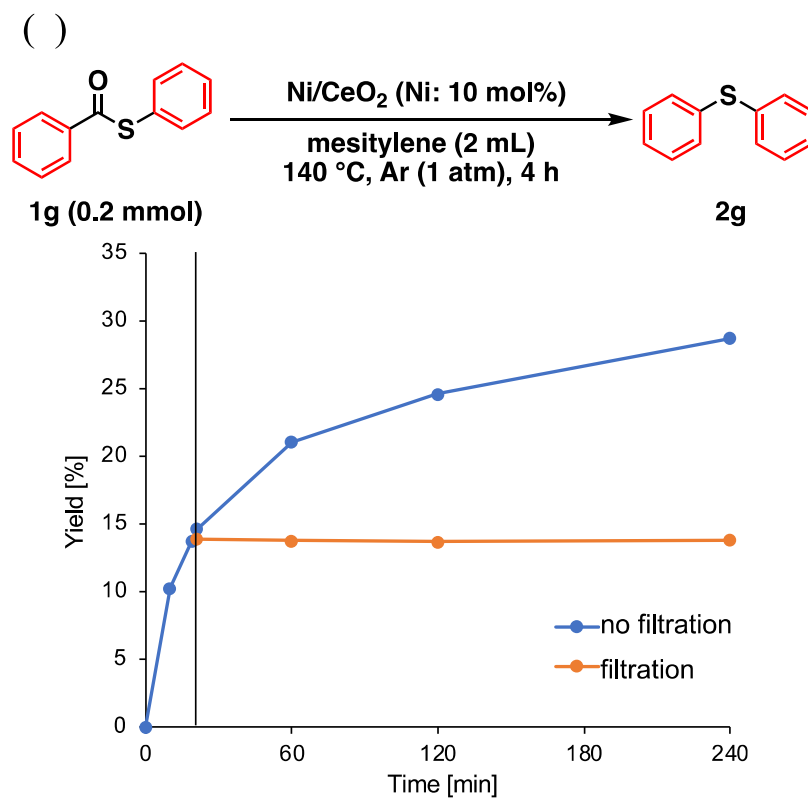


**Fig. S2** The color of  $\text{Pd(OH)}_2/\text{HAP}$  before and after heating in xylene. The conditions were indicated in the figure. The color change from brown to black suggested the reduction of Pd(II) species in  $\text{Pd(OH)}_2/\text{HAP}$  to afford Pd(0) species.

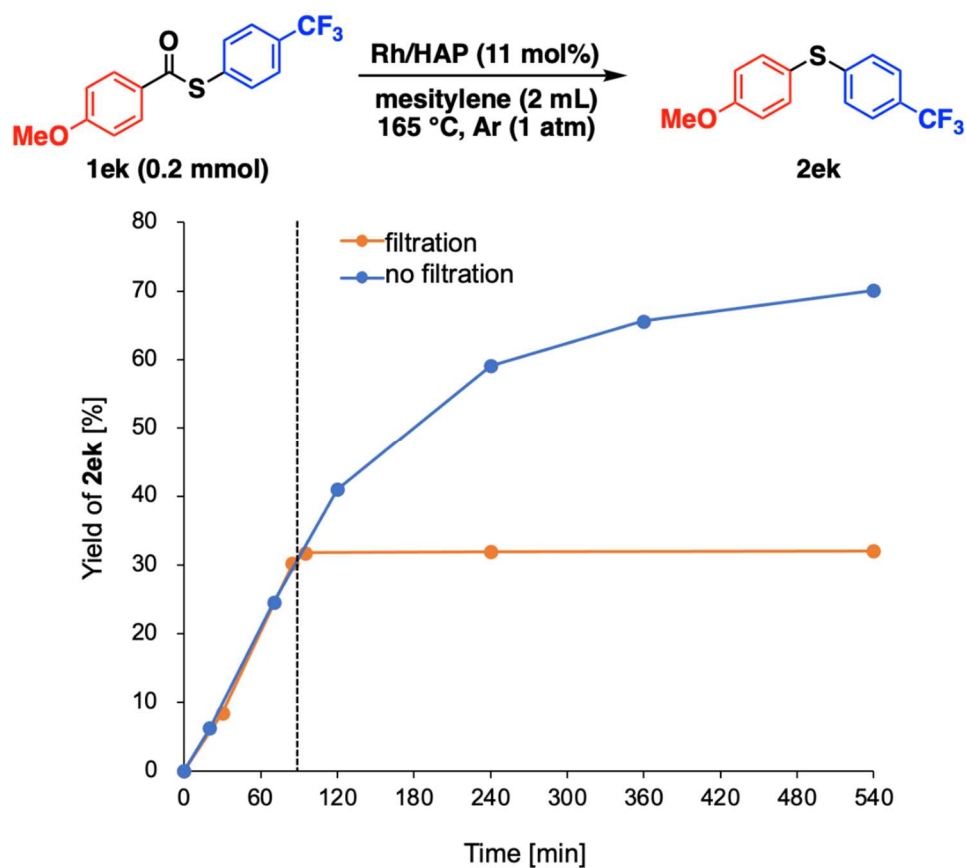




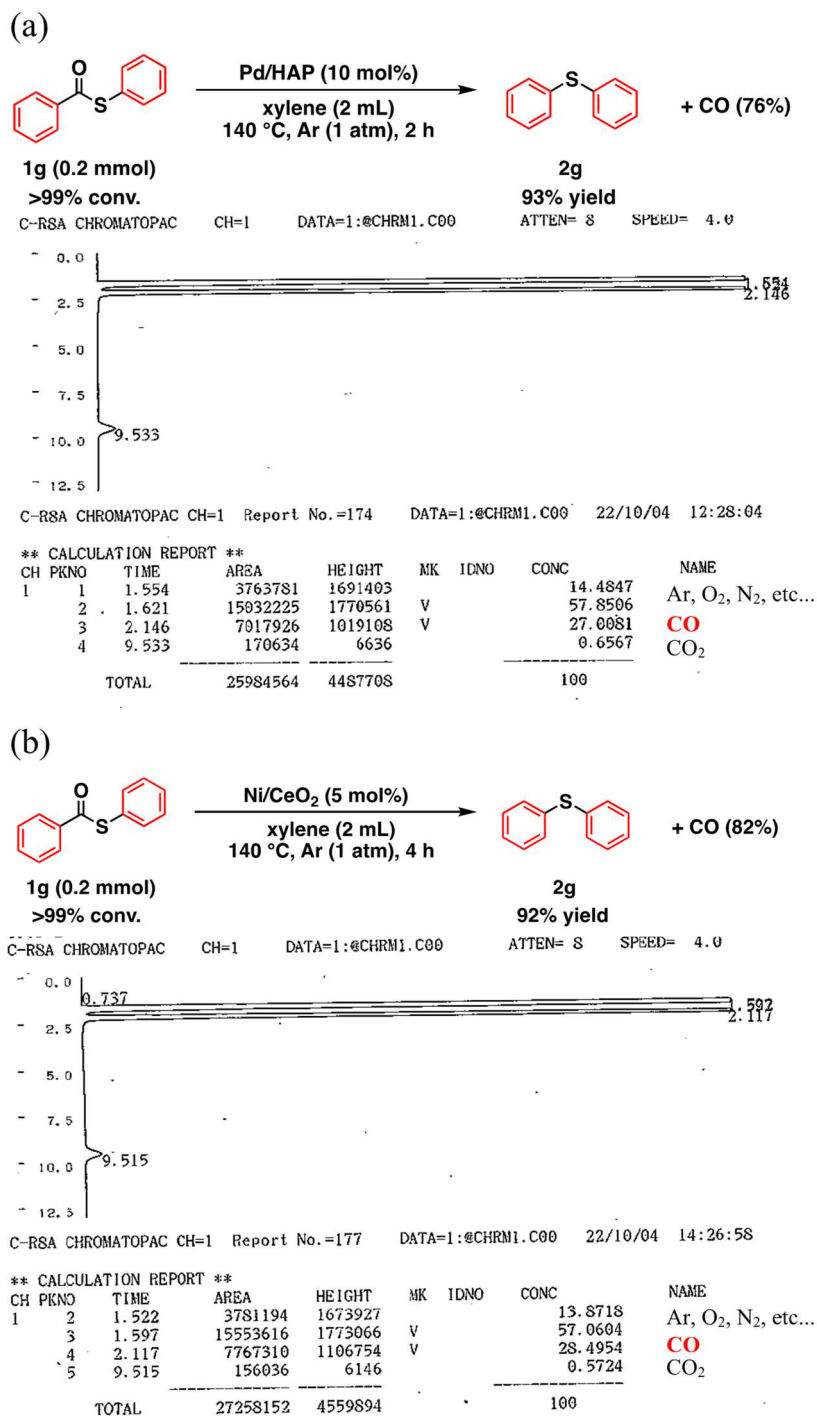
**Fig. S3** Reaction profiles for decarbonylation of **1a** in the presence of Pd/HAP or Ni/CeO<sub>2</sub>. Reaction conditions: **1a** (0.2 mmol), Pd/HAP (Pd: 5 mol%) or Ni/CeO<sub>2</sub> (Ni: 5 mol%), xylene (2 mL), Ar (1 atm), 140 °C. Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.



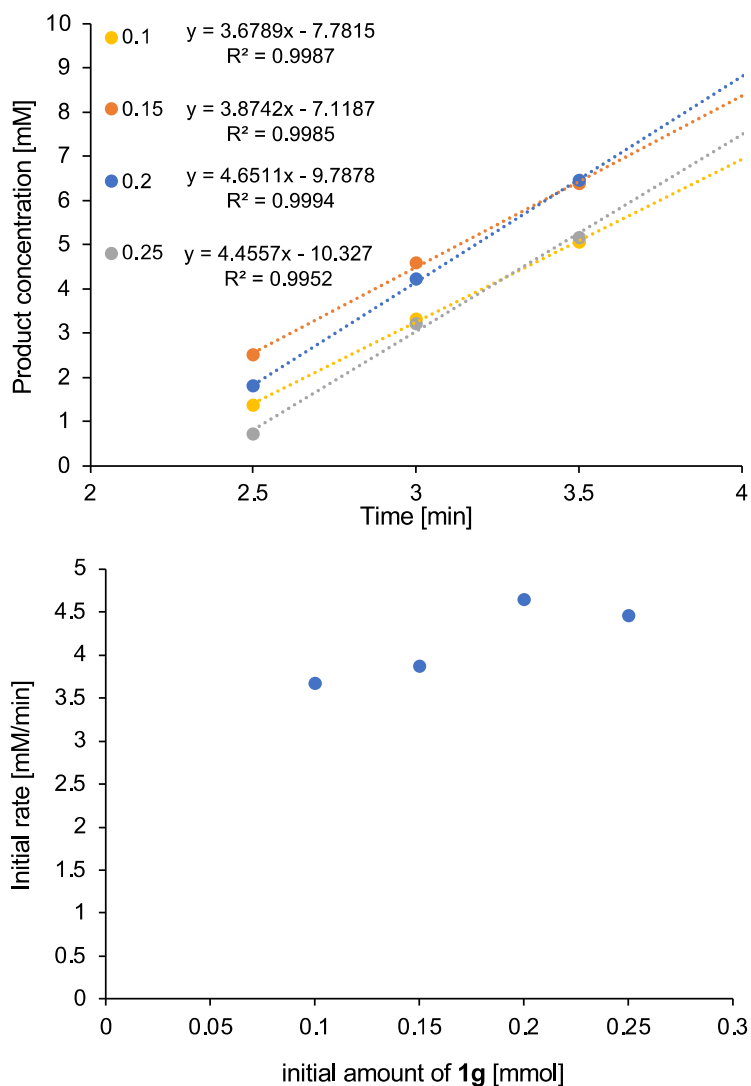
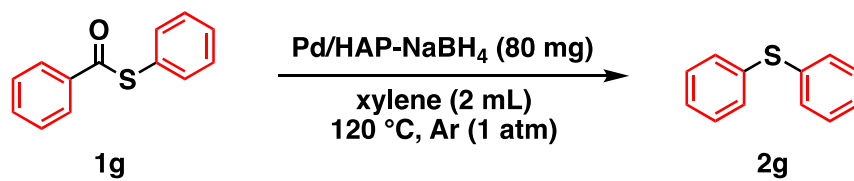
**Fig. S4** Effect of removal of  $\text{Ni/CeO}_2$  on the decarbonylation of **1g**. Reaction conditions: **1g** (0.2 mmol),  $\text{Ni/CeO}_2$  (Ni: 10 mol%), mesitylene (2 mL), Ar (1 atm), 140 °C. Yields of **2g** were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.



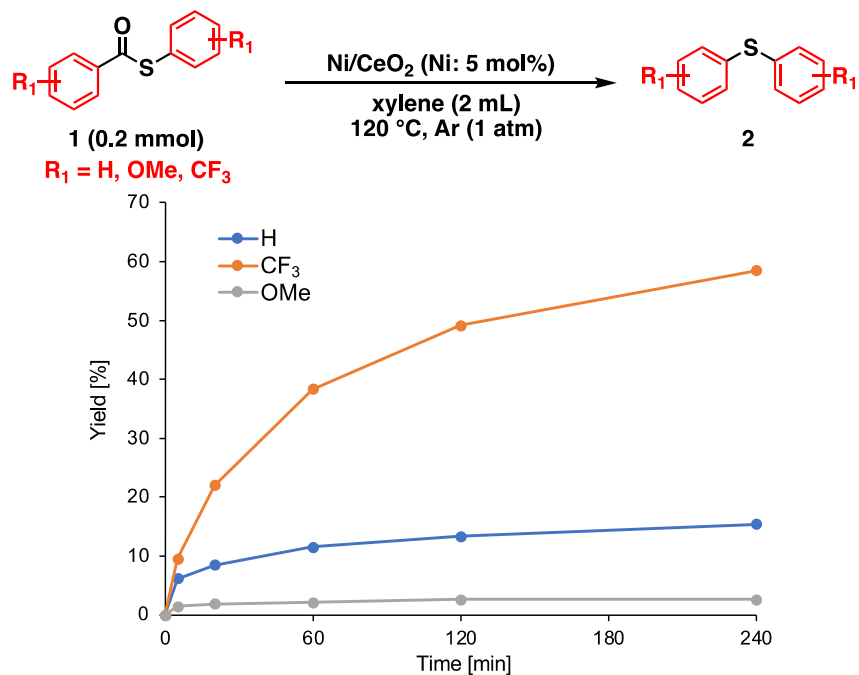
**Fig. S5** Effect of removal of Rh/HAP on the decarbonylation of **1ek**. Reaction conditions: **1ek** (0.2 mmol), Rh/HAP (Rh: 11 mol%), mesitylene (2 mL), Ar (1 atm), 165 °C. Yields of **2ek** were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.



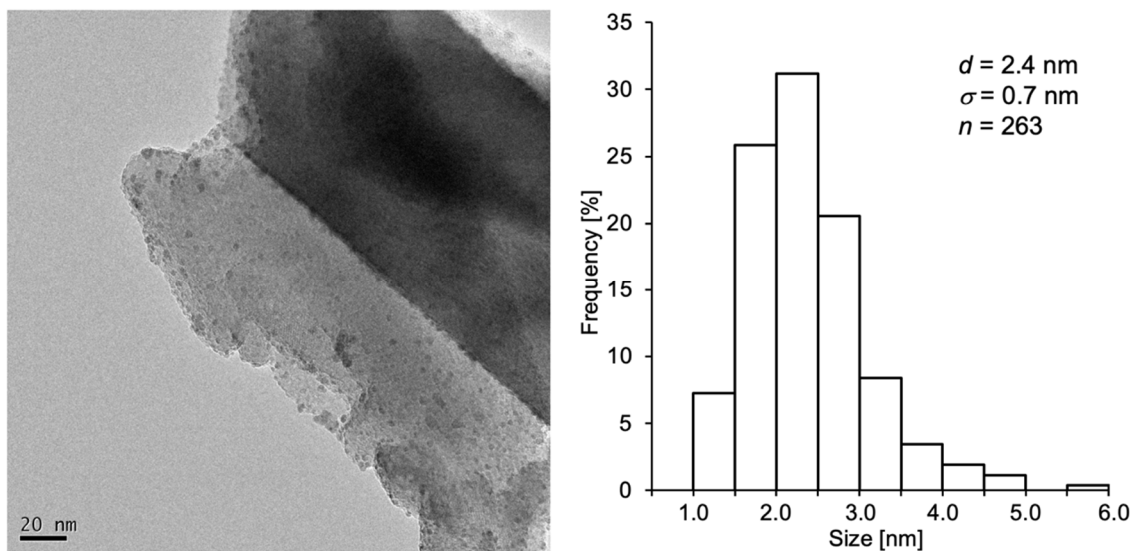
**Fig. S6** GC-BID chart of the gas phase after decarbonylation of **1g** in the presence of (a) Pd/HAP and (b) Ni/CeO<sub>2</sub>. Reaction conditions are shown in the figure. **2g** yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. CO yields were determined by the absolute calibration curve method.



**Fig. S7** The initial rate measurements of **1g** with different initial amounts of **1g**. Reaction conditions: **1g**, Pd/HAP (80 mg), xylene (2 mL), Ar (1 atm), 120 °C. Concentrations of **2g** were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.



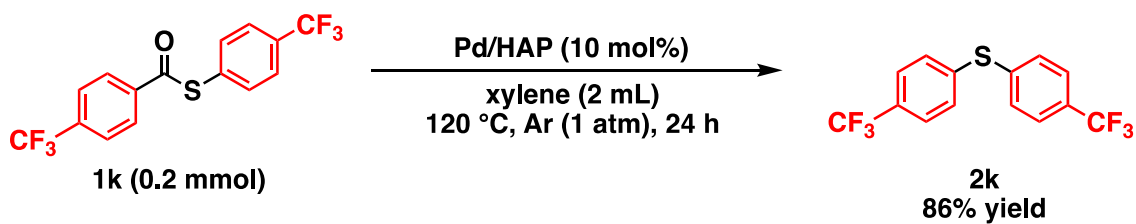
**Fig. S8** Reaction profiles of Ni/CeO<sub>2</sub>-catalyzed decarbonylation of non-substituted (**1g**) or 4,4'-substituted thioesters (**1e**, **1k**) independently. Reaction conditions are shown in the figure.



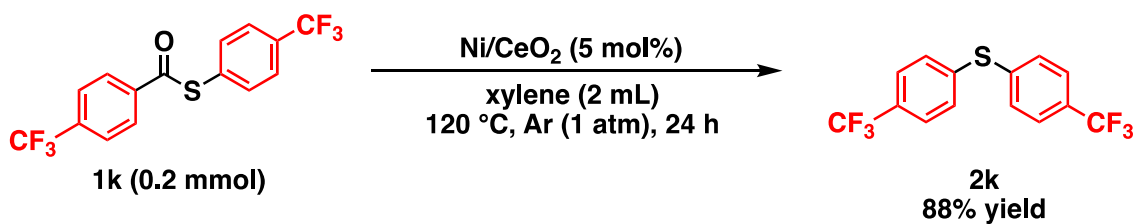
**Fig. S9** TEM image of Rh/HAP and Rh nanoparticle distribution of Rh/HAP.

## Supplementary Schemes

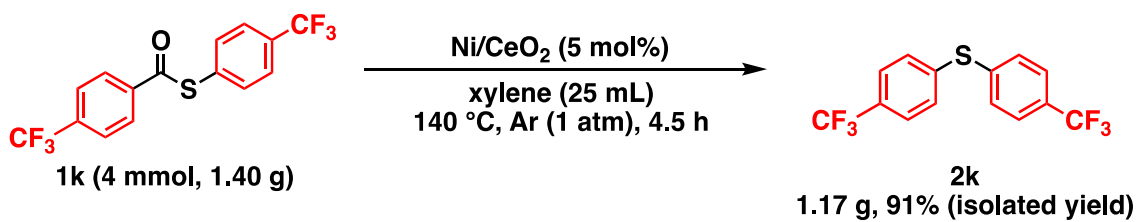
(a)



(b)



**Scheme S1** (a) Pd/HAP and (b) Ni/CeO<sub>2</sub>-catalyzed decarbonylation of **1k** at 120 °C. Reaction conditions are indicated in the scheme. GC yields are shown.



**Scheme S2** Gram-scale synthesis of **2k** from **1k**. The reaction conditions were indicated in the scheme.

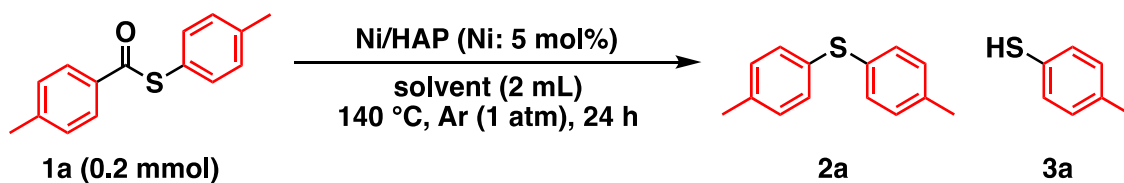
## Supplementary Tables

**Table S1** Comparison of this work with previously reported thioester decarbonylation.

| Entry    | Catalyst/Ligand   | Number of Substrates | Yields        | Ref.             |
|----------|---|----------------------|---------------|------------------|
| <b>1</b> | <b>Ni/CeO<sub>2</sub>, Pd/HAP, or Rh/HAP</b>  | <b>24 examples</b>   | <b>18–95%</b> | <b>This work</b> |
| 2        | RhCl(PPh <sub>3</sub> ) <sub>3</sub> (stoichiometric)<br>or Pd(PCy <sub>3</sub> ) <sub>2</sub>                    | 7 examples           | 43–>99%       | (6a)             |
| 3        | [Rh(cod)Cl] <sub>2</sub>  | 26 examples          | 70–98%        | (6b)             |
| 4        | Pd(PPh <sub>3</sub> ) <sub>4</sub>  | 10 examples          | 3–97%         | (6c)             |
| 5        | Pd[P( <i>o</i> -tol) <sub>3</sub> ] <sub>2</sub> + PAd <sub>2</sub> Bn<br>Ni(cod) <sub>2</sub> + PCy <sub>3</sub> | 23 examples          | 50–99%        | (6d)             |
| 6        | PdCl <sub>2</sub> + PPh <sub>3</sub>  | 26 examples          | 25–85%        | (6e)             |
| 7        | Pd(OAc) <sub>2</sub> + dppb   | 25 examples          | 66–88%        | (6f)             |
| 8        | [Pd(IPr)(μ-Cl)Cl] <sub>2</sub>  | 15 examples          | 35–85%        | (6g)             |
| 9        | NiCl <sub>2</sub> ·6H <sub>2</sub> O (stoichiometric)<br>PPh <sub>3</sub> (8 eq.)                                 | 11 examples          | 42–86%        | (6h)             |
| 10       | Ni(dppp)Cl <sub>2</sub>   | 24 examples          | 62–98%        | (6i)             |
| 11       | Ni(OAc) <sub>2</sub><br>P <sup><i>n</i></sup> Bu <sub>3</sub> or dppb   | 30 examples          | 20–95%        | (6j)             |
| 12       | Ni(cod) <sub>2</sub> + IPr <sup>Me</sup> ·HCl   | 13 examples          | 57–79%        | (6k)             |
| 13       | Ni(cod) <sub>2</sub> + dppf   | 28 examples          | 33–99%        | (6l)             |
| 14       | Ni(dppp)Cl <sub>2</sub> + dppp  | 28 examples          | 20–94%        | (6m)             |
| 15       | Ni(cod) <sub>2</sub> + dppp   | 41 examples          | 36–99%        | (6n)             |

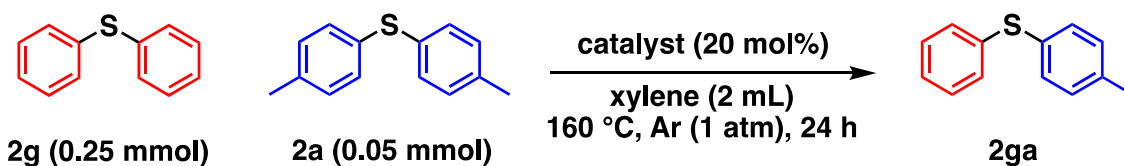
PPh<sub>3</sub> = triphenylphosphine, PCy<sub>3</sub> = tricyclohexylphosphine, cod = 1,5-cyclooctadiene, P(*o*-tol)<sub>3</sub> = tris(*o*-tolyl)phosphine, PAd<sub>2</sub>Bn = di(1-adamantyl)benzylphosphine, OAc = acetate, dppb = 1,4-bis(diphenylphosphino)butane, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, dppp = 1,3-bis(diphenylphosphino)propane, P<sup>*n*</sup>Bu<sub>3</sub> = tributylphosphine, IPr<sup>Me</sup> = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazol-2-ylidene, dppf = 1,1'-bis(diphenylphosphino)ferrocene.



**Table S2** Effect of solvents on the decarbonylation of **1a**.<sup>a</sup>

| Entry | Solvent     | Yield (%) |           |
|-------|-------------|-----------|-----------|
|       |             | <b>2a</b> | <b>3a</b> |
| 1     | xylene      | 86        | <1        |
| 2     | CPME        | 53        | <1        |
| 3     | MCH         | 25        | <1        |
| 4     | 1,4-dioxane | 25        | <1        |
| 5     | NMP         | 7         | <1        |

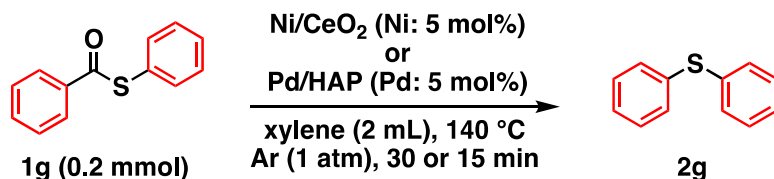
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), Ni/HAP (Ni: 5 mol%), solvent (2 mL), Ar (1 atm), 160 °C, 24 h. Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. CPME = cyclopentylmethylether. MCH = methylcyclohexane. NMP = *N*-methyl-2-pyrrolidone.

**Table S3** Effect of catalysts on the C–S bond metathesis of **2a** and **2g**.<sup>a</sup>

| Entry | Catalyst | Yield (%)  |
|-------|----------|------------|
|       |          | <b>2ga</b> |
| 1     | Ni/HAP   | 24         |
| 2     | Pd/HAP   | 21         |
| 3     | Rh/HAP   | 7          |

<sup>a</sup>Reaction conditions: **2g** (0.25 mmol), **2a** (0.05 mmol), catalyst (20 mol%), xylene (2 mL), 160 °C, 24 h. Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. The yield of **2ga** was calculated based on the two equivalents of **2a**.

**Table S4** The effect of addition of 1,3,5-trimethoxybenzene on Ni/CeO<sub>2</sub>- or Pd/HAP-catalyzed decarbonylation of **1g**.

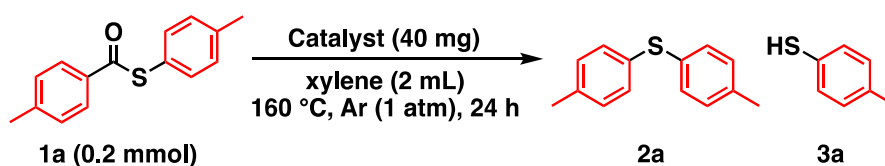


| Entry          | Time (min) | Catalyst            | Yield (%) |
|----------------|------------|---------------------|-----------|
|                |            |                     | <b>2g</b> |
| 1              | 30         | Ni/CeO <sub>2</sub> | 47        |
| 2 <sup>b</sup> | 30         | Ni/CeO <sub>2</sub> | 46        |
| 3              | 15         | Pd/HAP              | 36        |
| 4 <sup>b</sup> | 15         | Pd/HAP              | 35        |

<sup>a</sup>Reaction conditions: **1g** (0.2 mmol), catalyst (5 mol%), xylene (2 mL), 140 °C, 15 or 30 min, Ar (1 atm). Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

<sup>b</sup>1,3,5-trimethoxybenzene was added after the reaction.

**Table S5** The effect of the supports on the decarbonylation of **1a** without supported metal species.



| Entry | Catalyst                       | Yield (%) |           |
|-------|--------------------------------|-----------|-----------|
|       |                                | <b>2a</b> | <b>3a</b> |
| 1     | CeO <sub>2</sub>               | <1        | <1        |
| 2     | Al <sub>2</sub> O <sub>3</sub> | <1        | 4         |

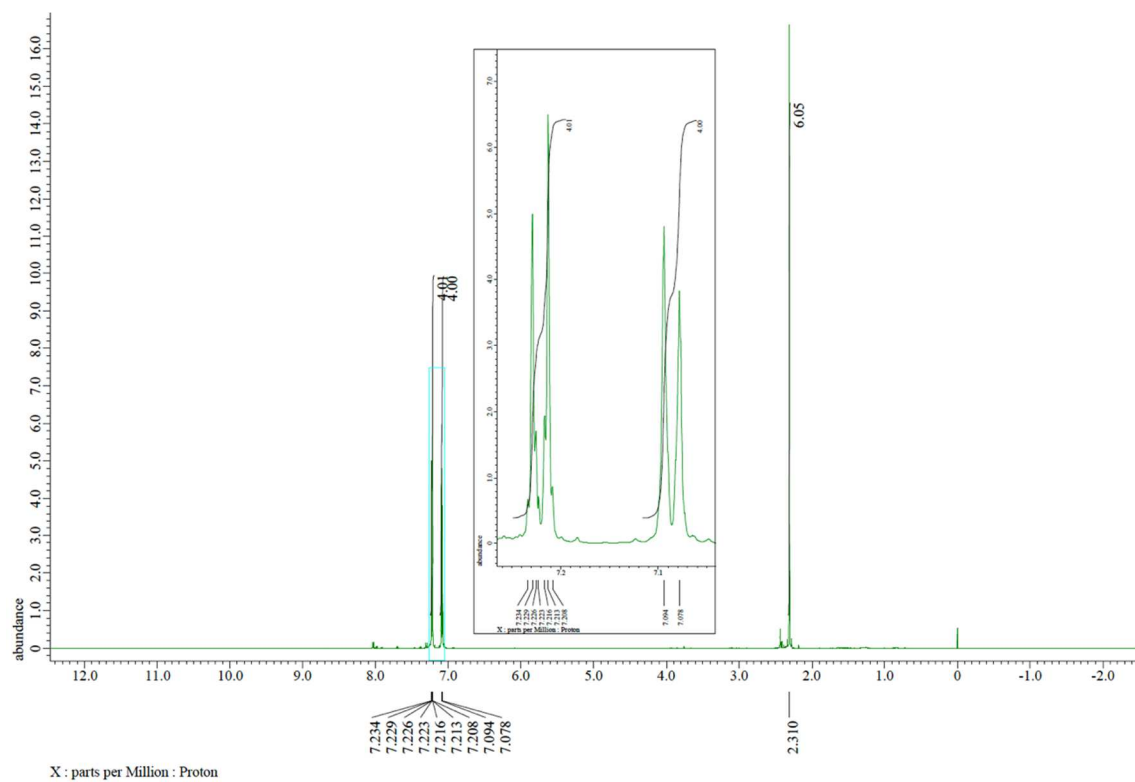
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), CeO<sub>2</sub> (40 mg) or Al<sub>2</sub>O<sub>3</sub> (40 mg), xylene (2 mL), Ar (1 atm), 160 °C, 24 h. Yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

### **Supplementary References**

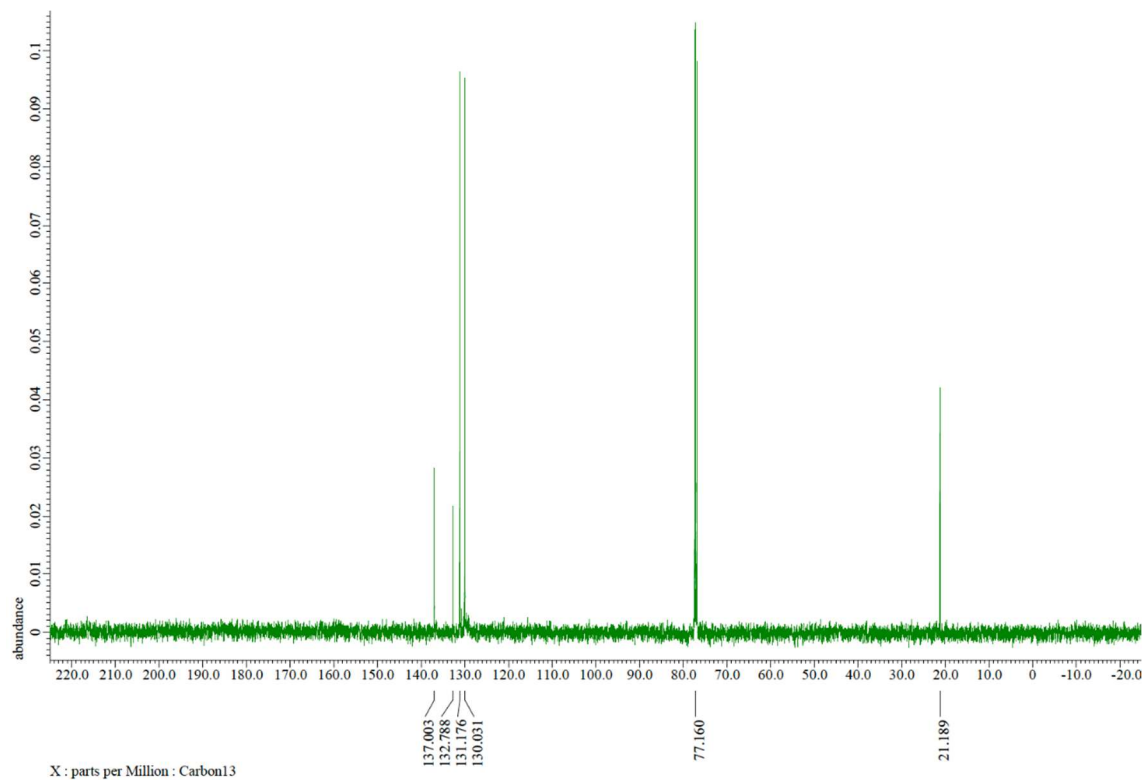
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## NMR Spectra

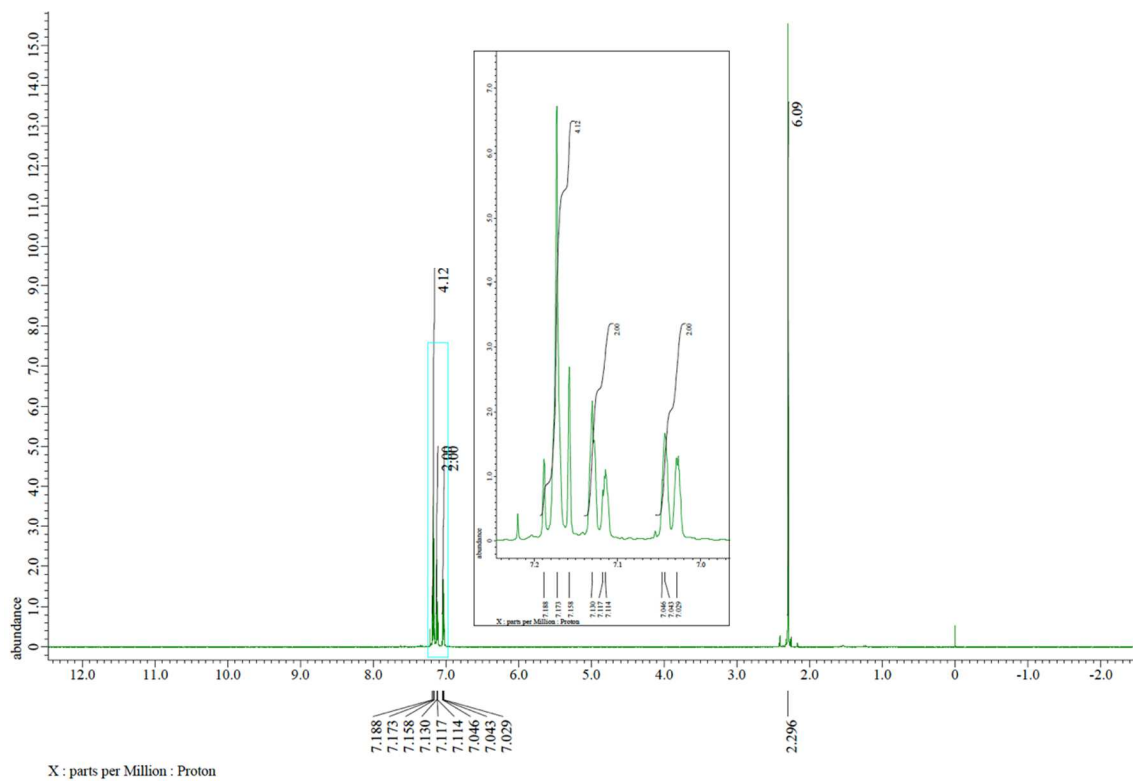
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2a**



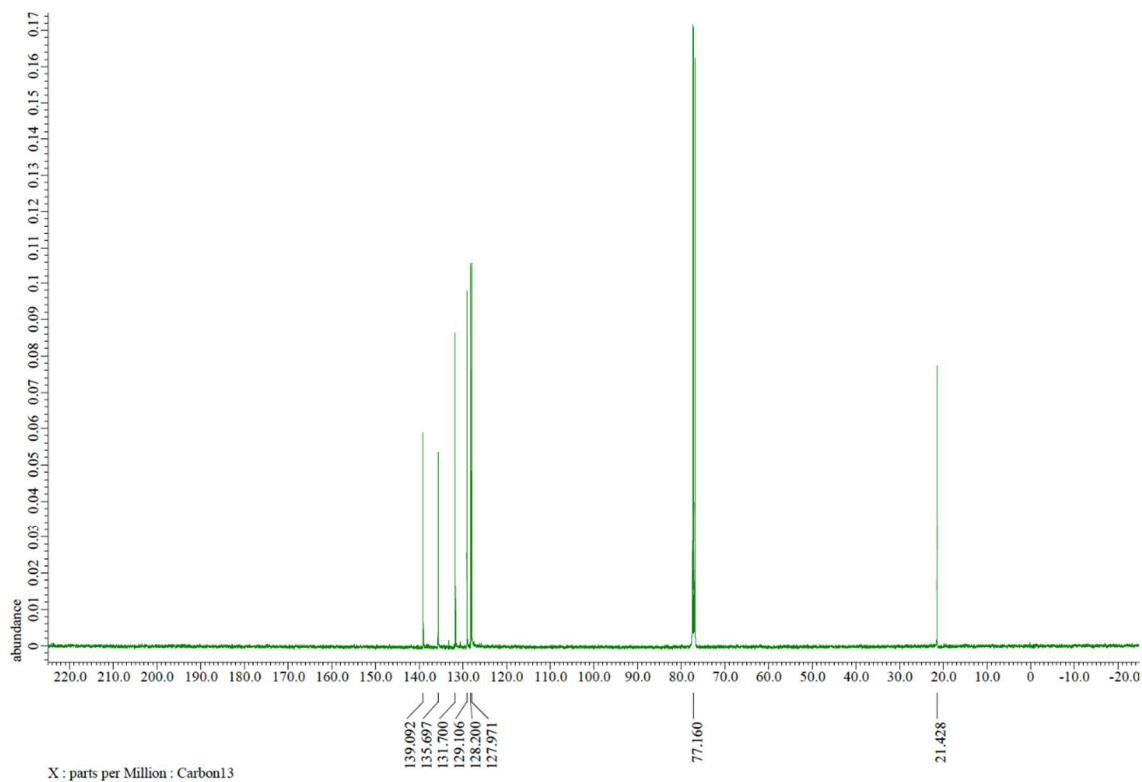
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2a**



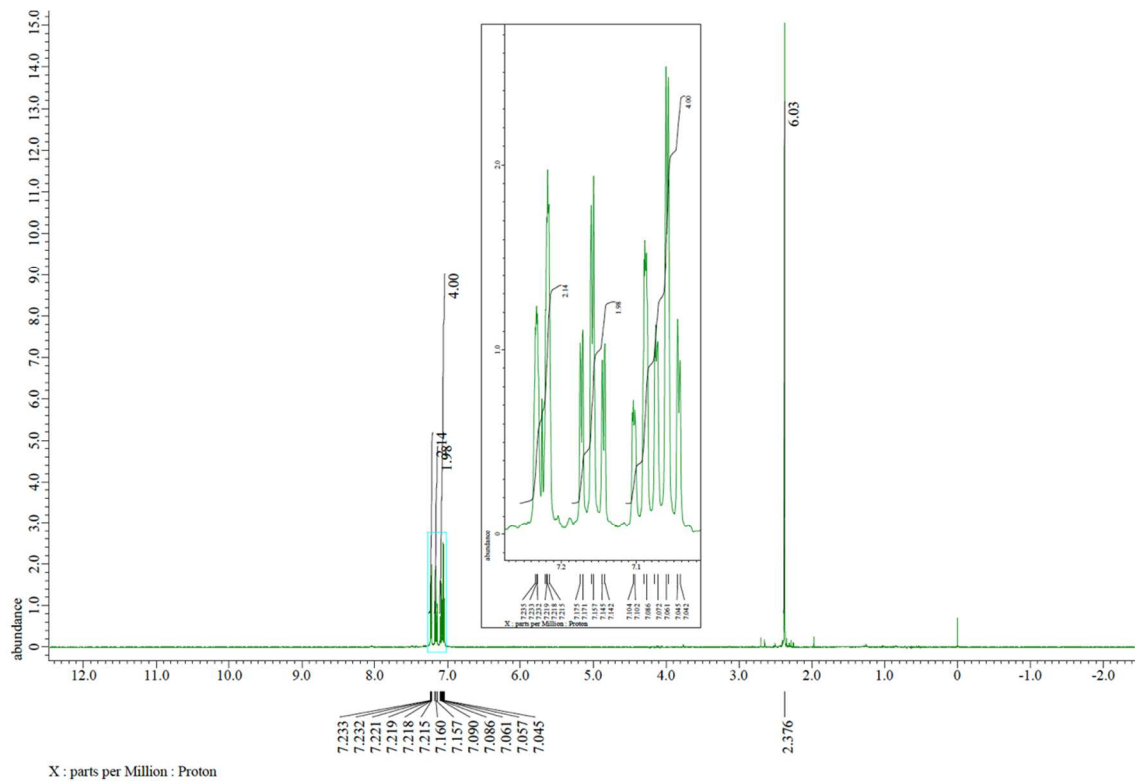
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2b**



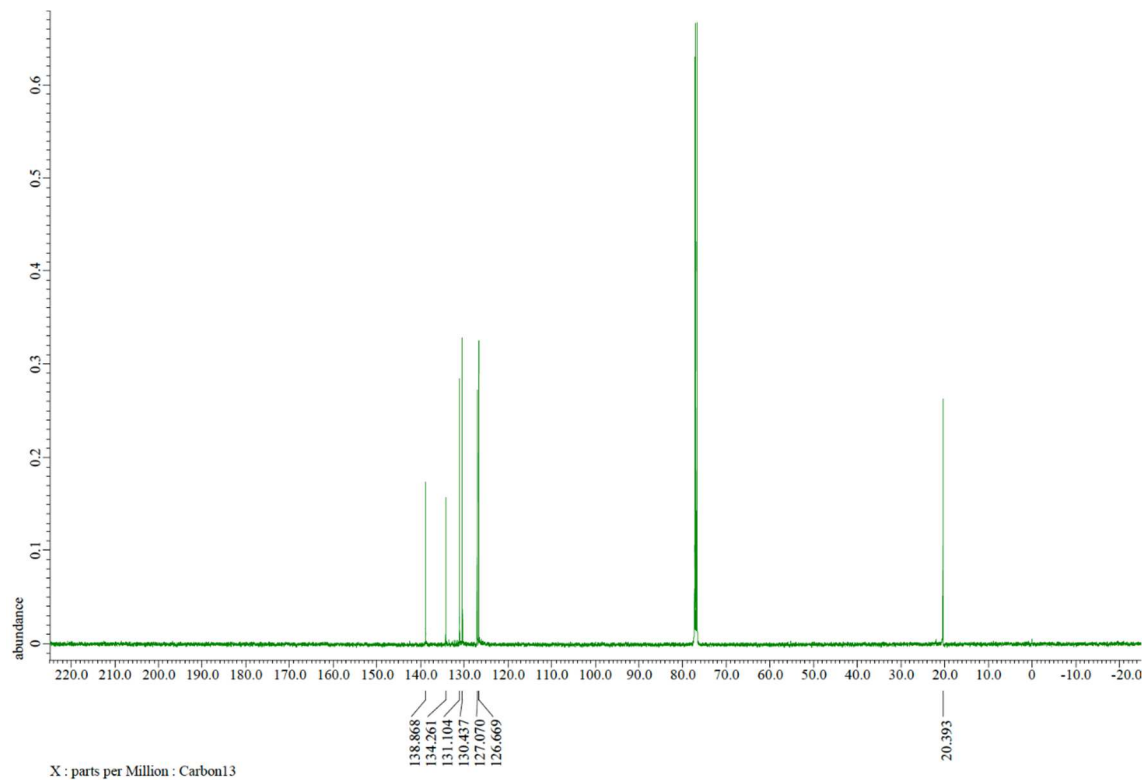
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2b**



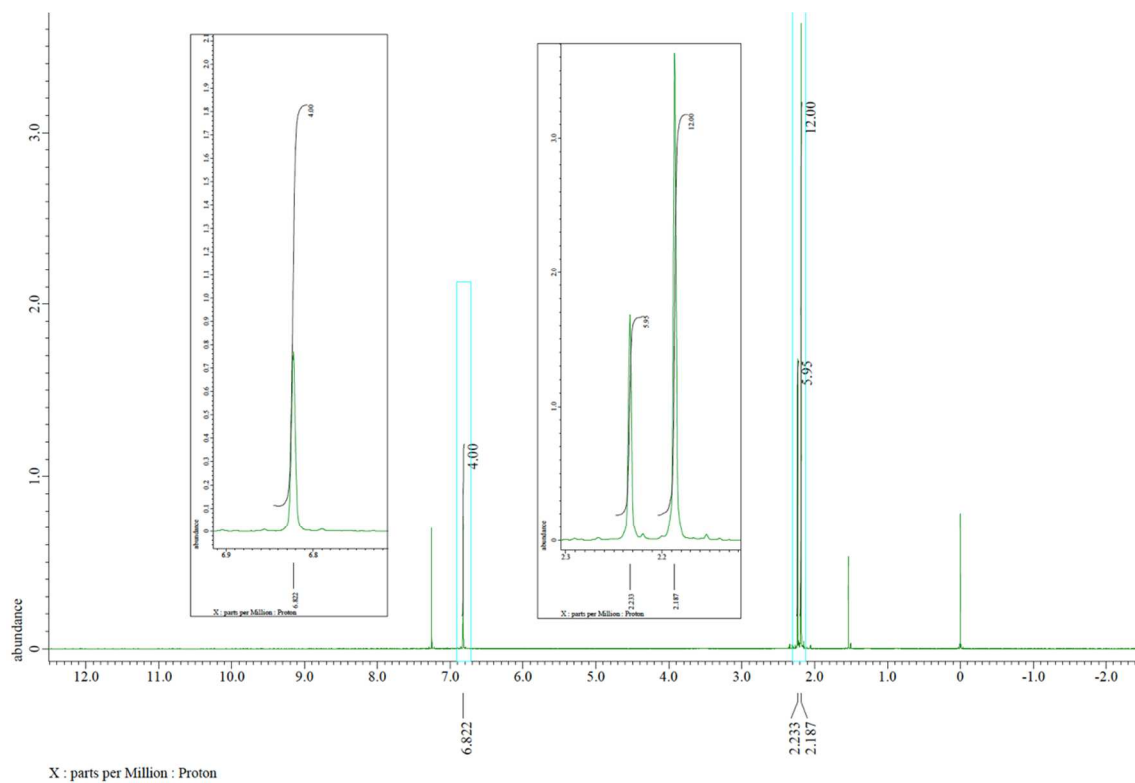
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2c**



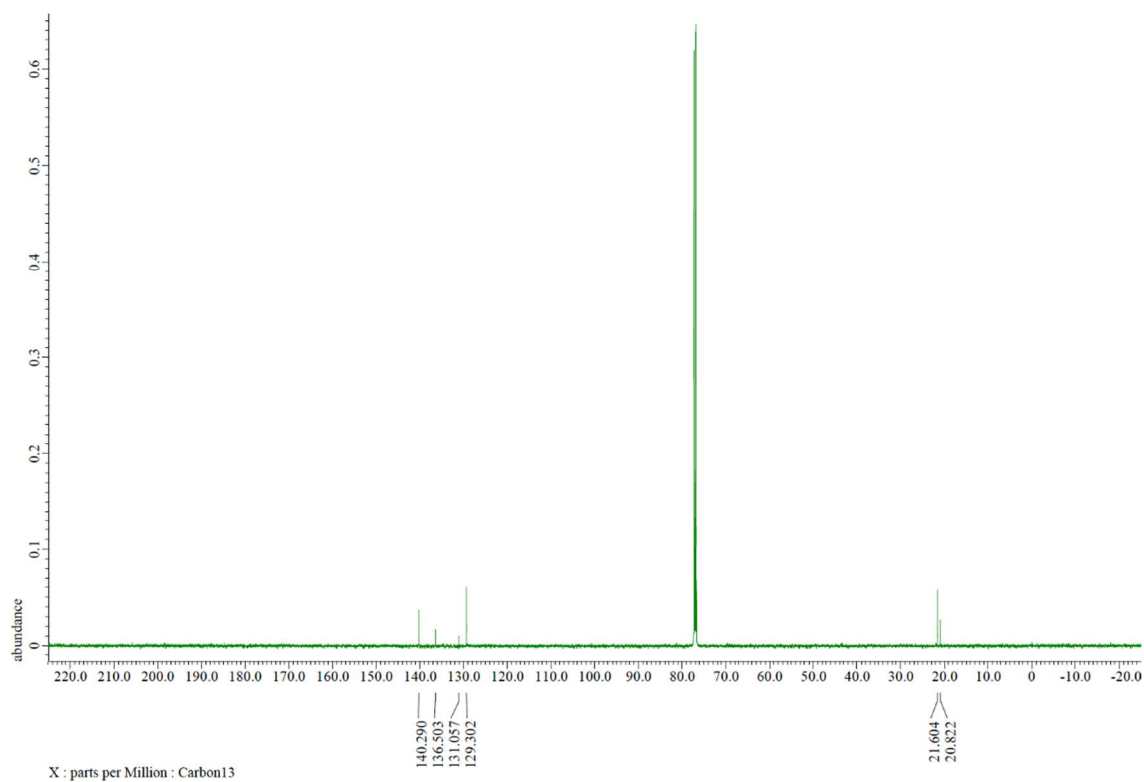
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2c**



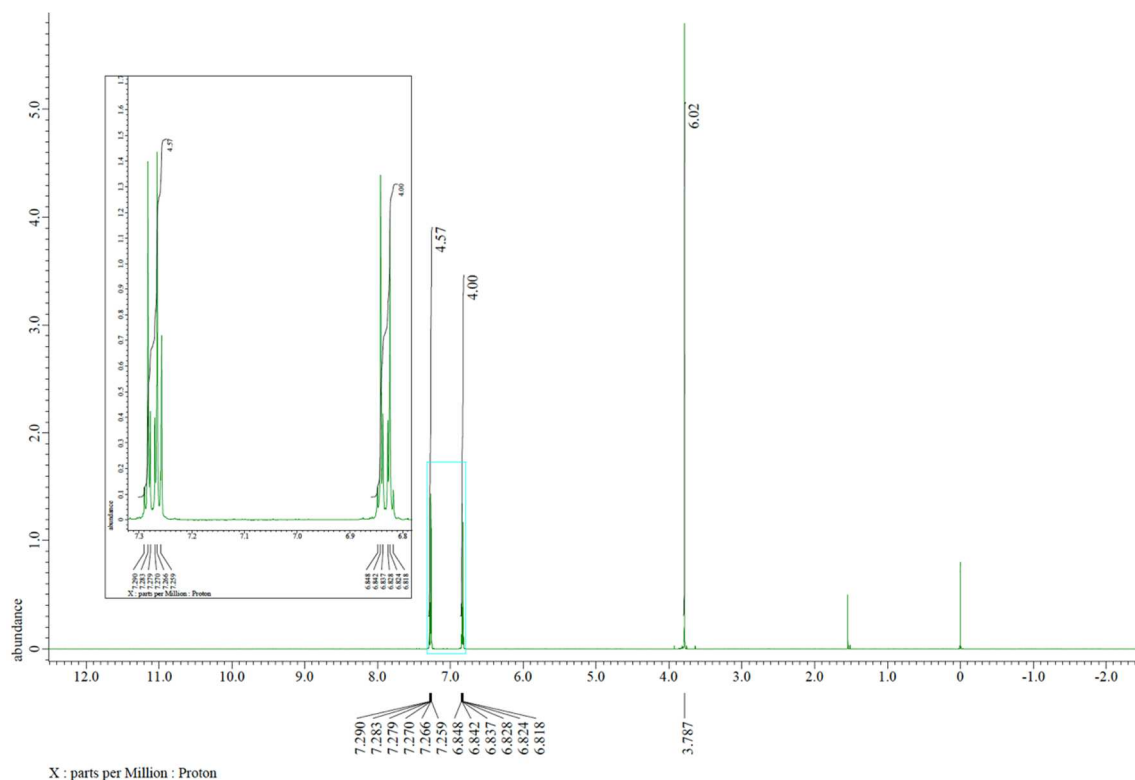
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2d**



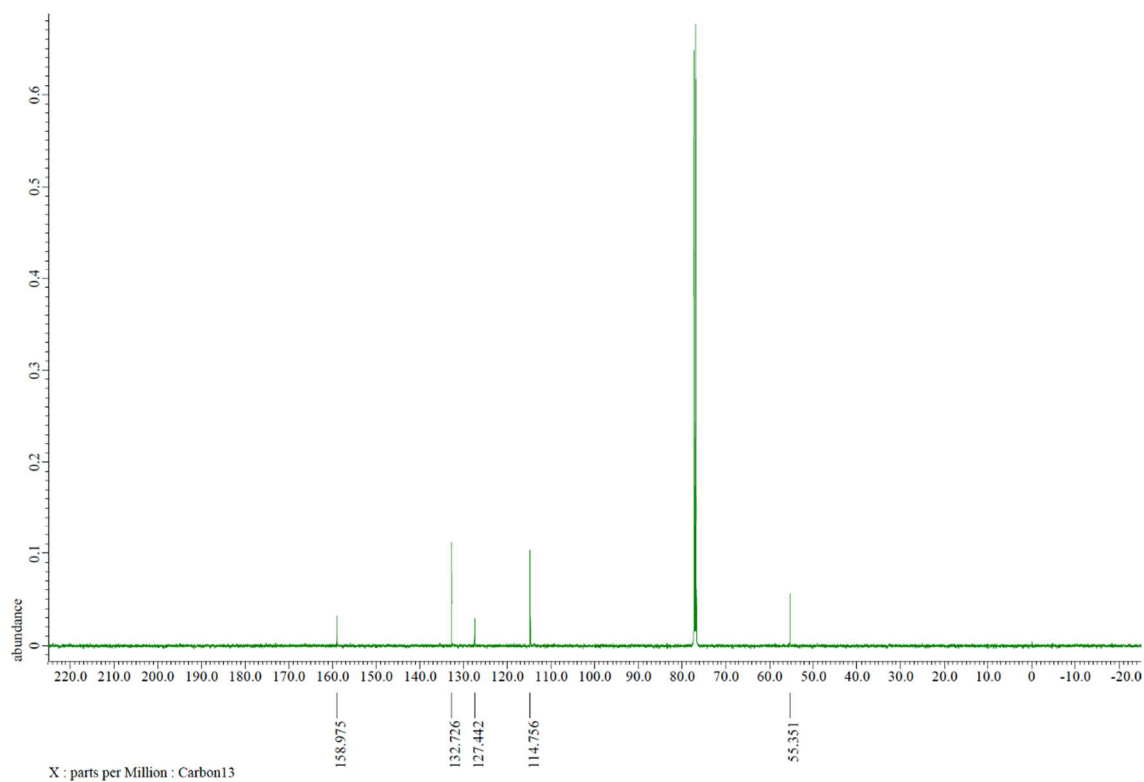
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2d**



$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2e**

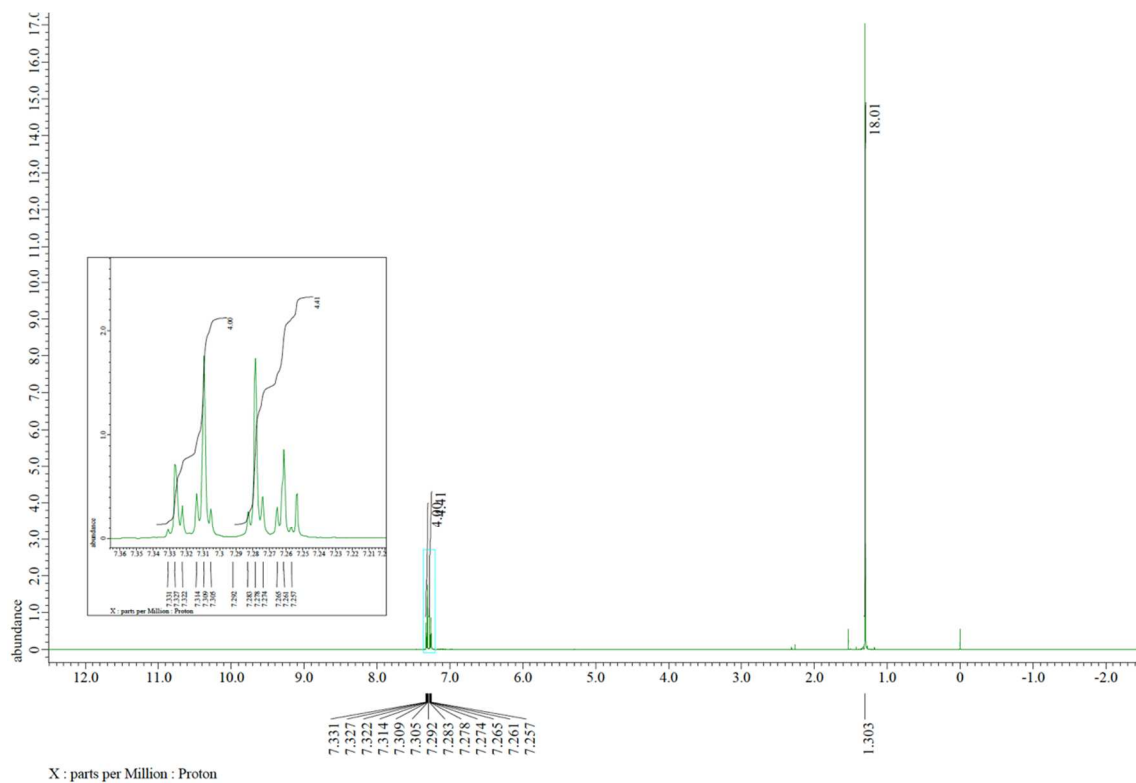


$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2e**

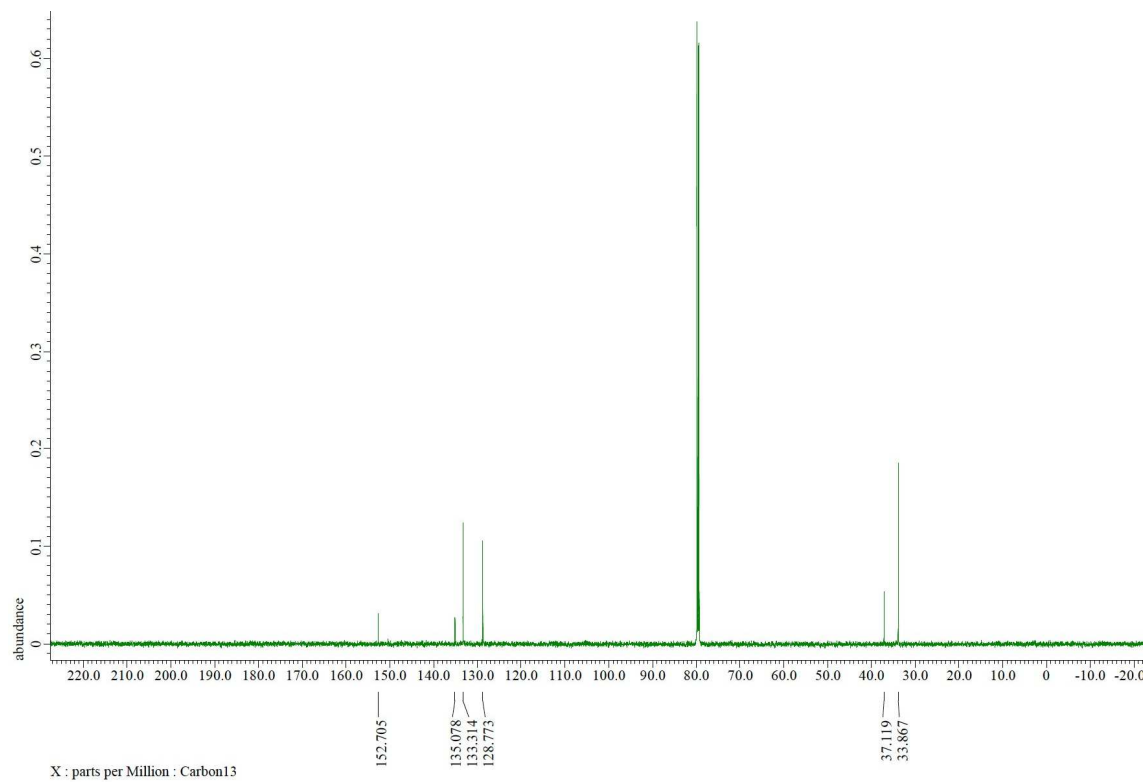




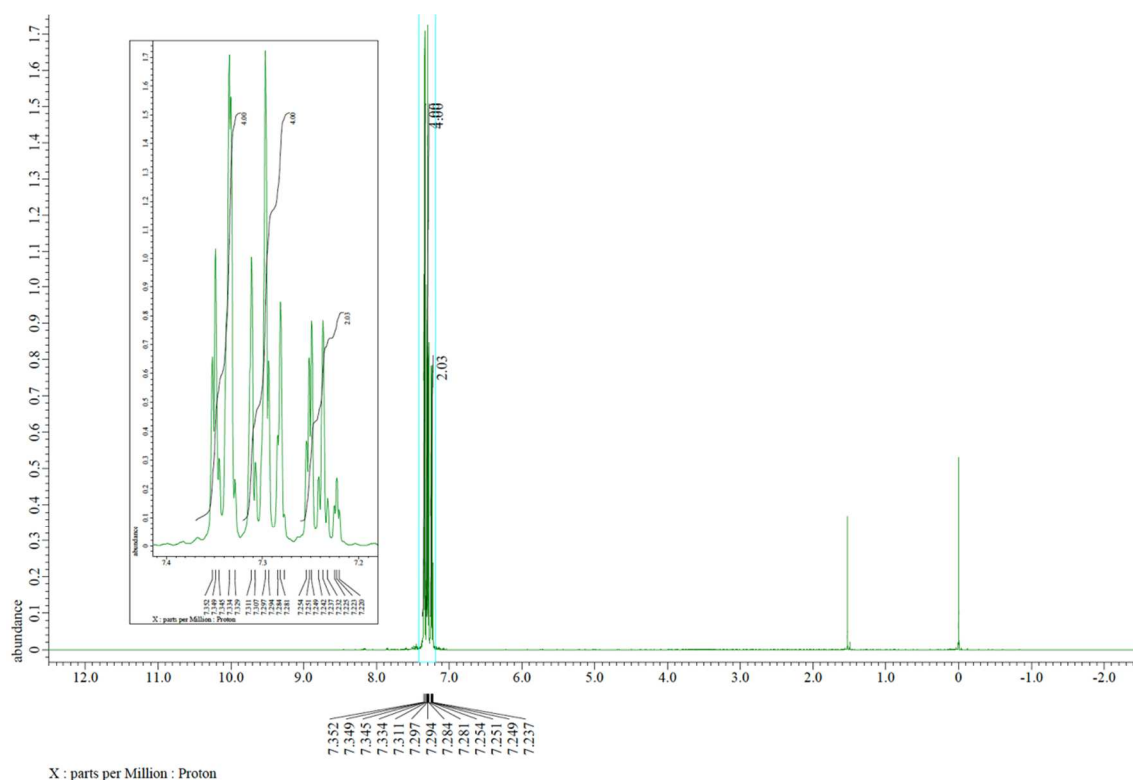
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2f**



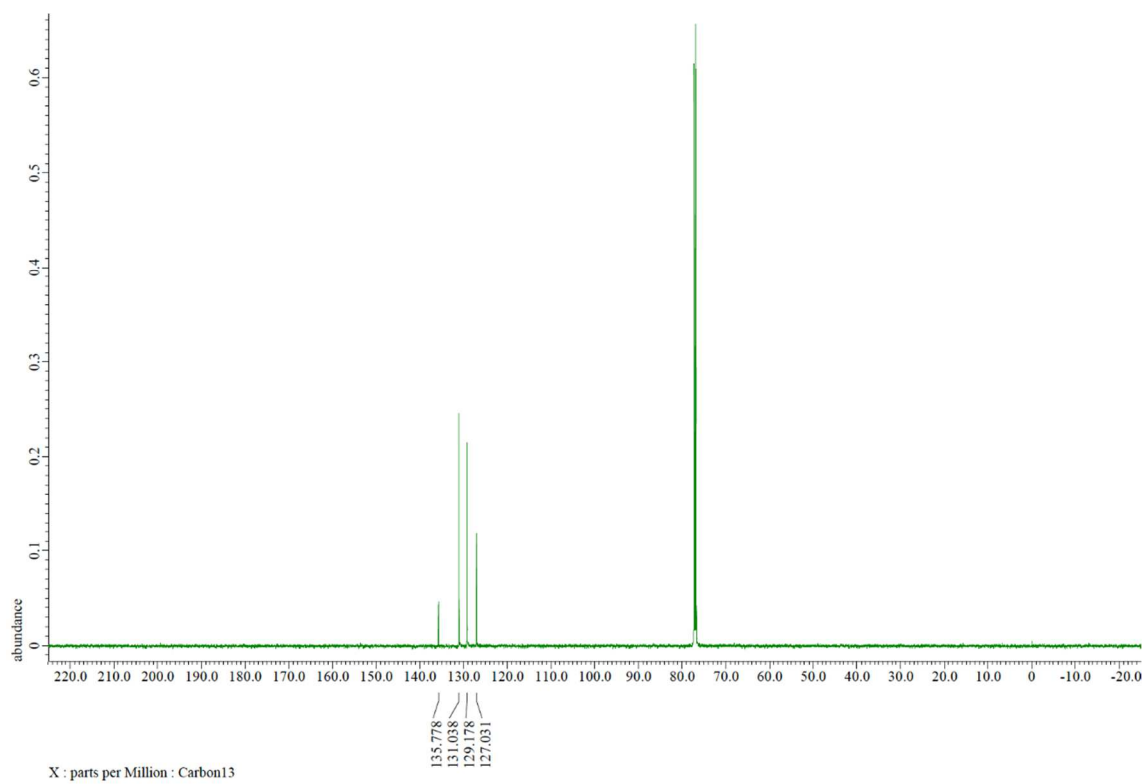
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2f**



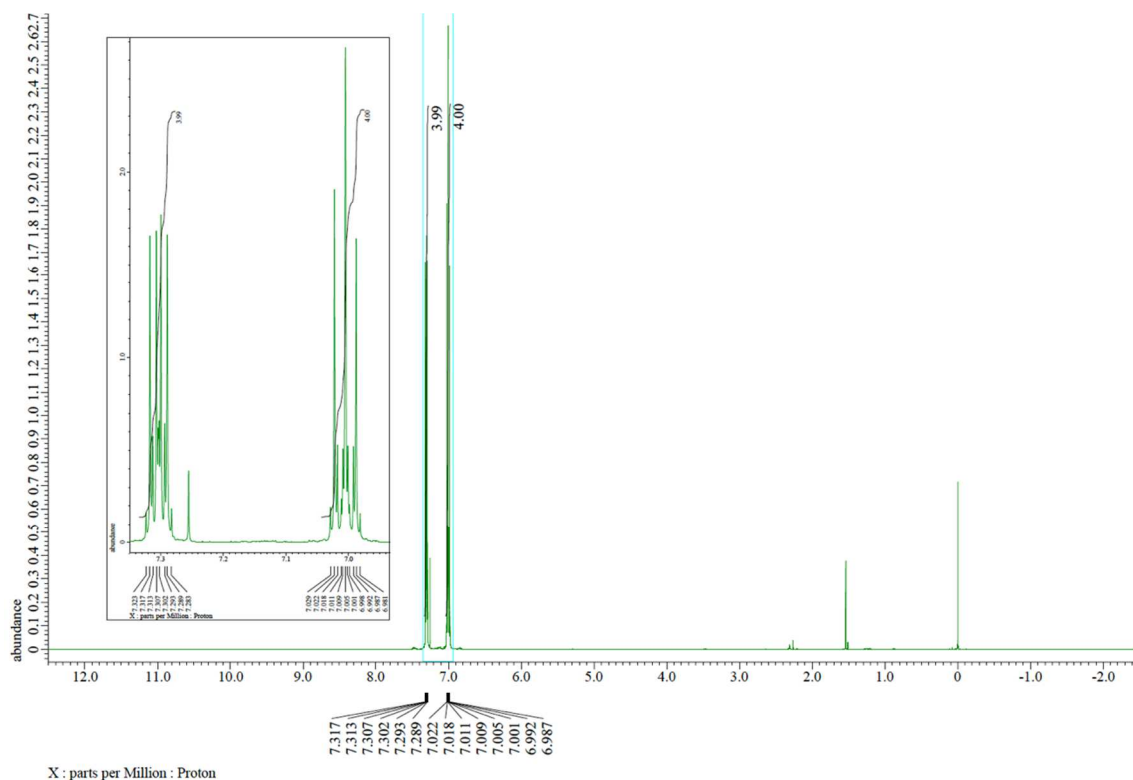
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2g**



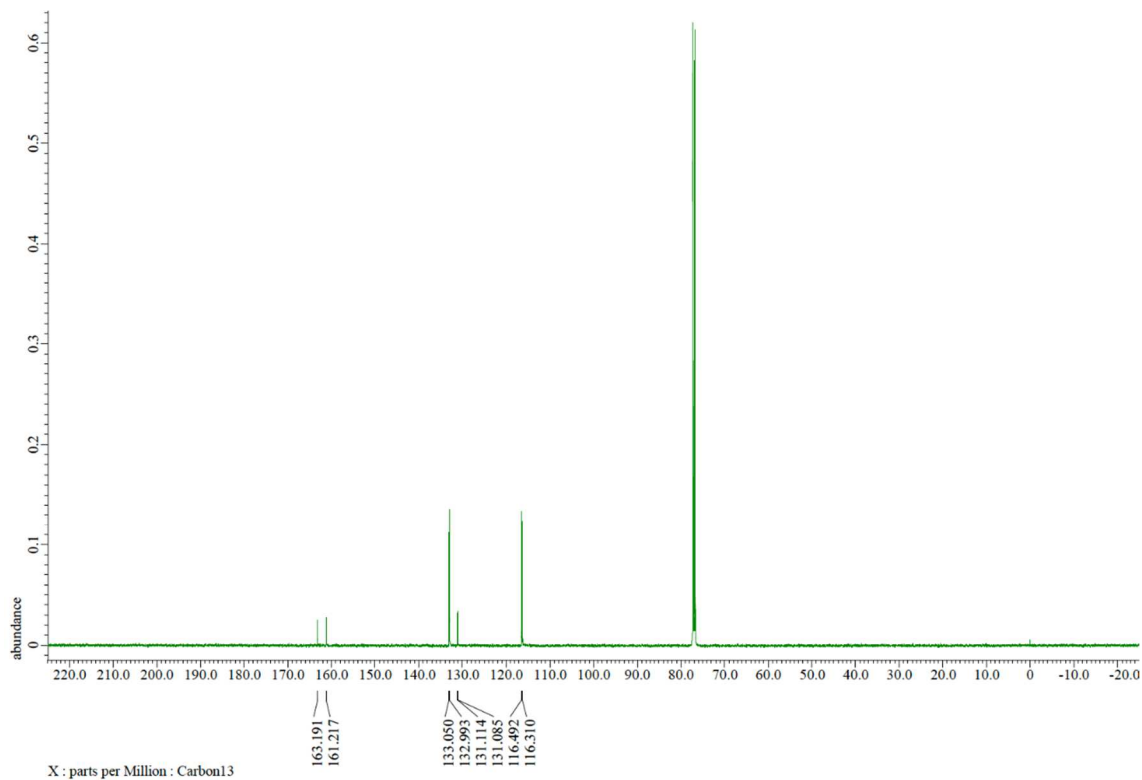
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2g**



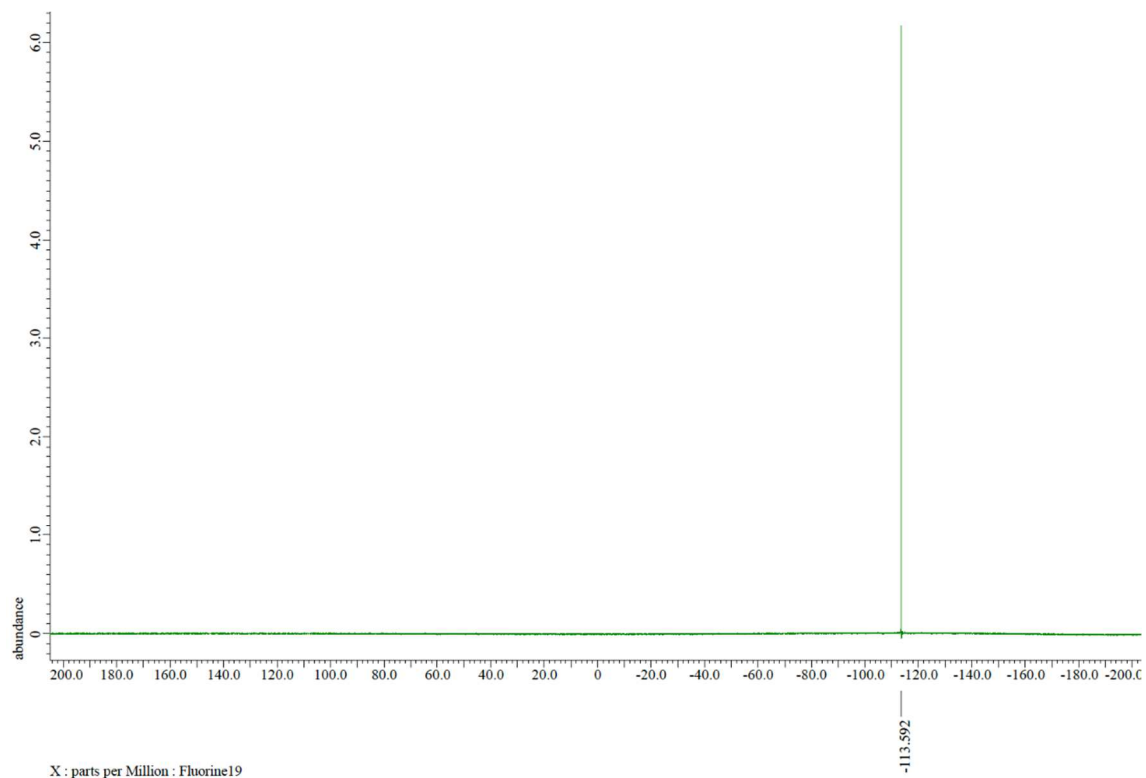
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2h**



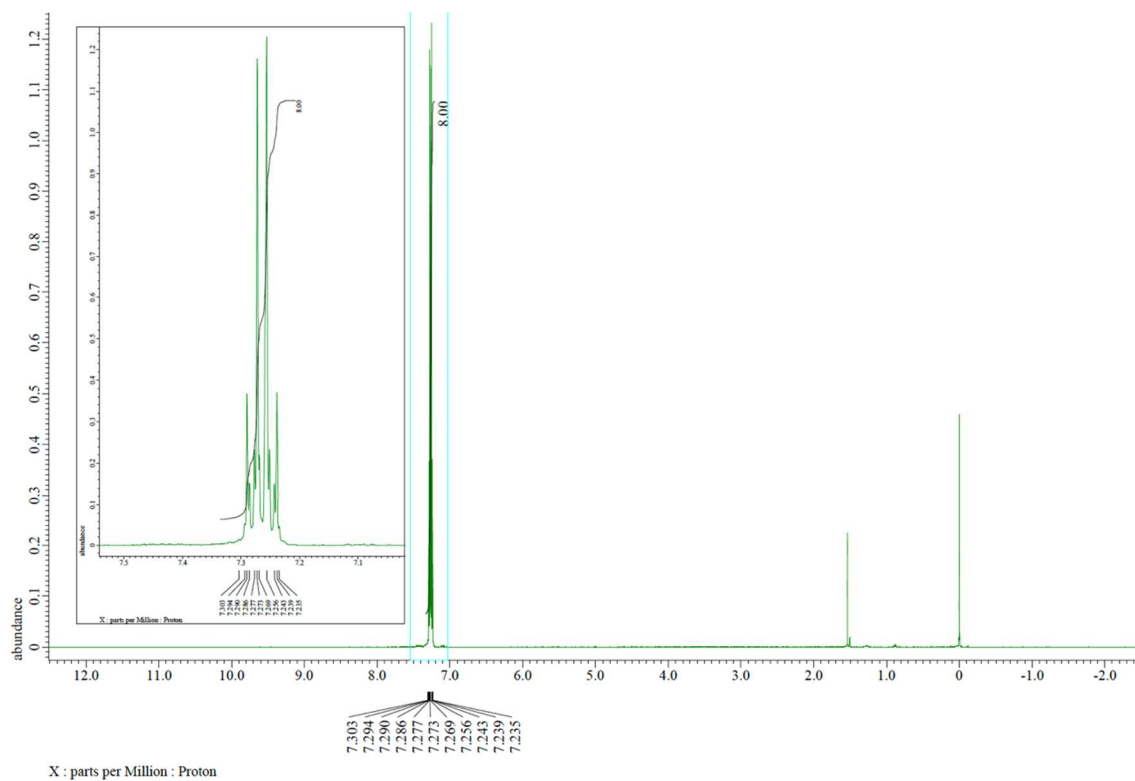
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2h**



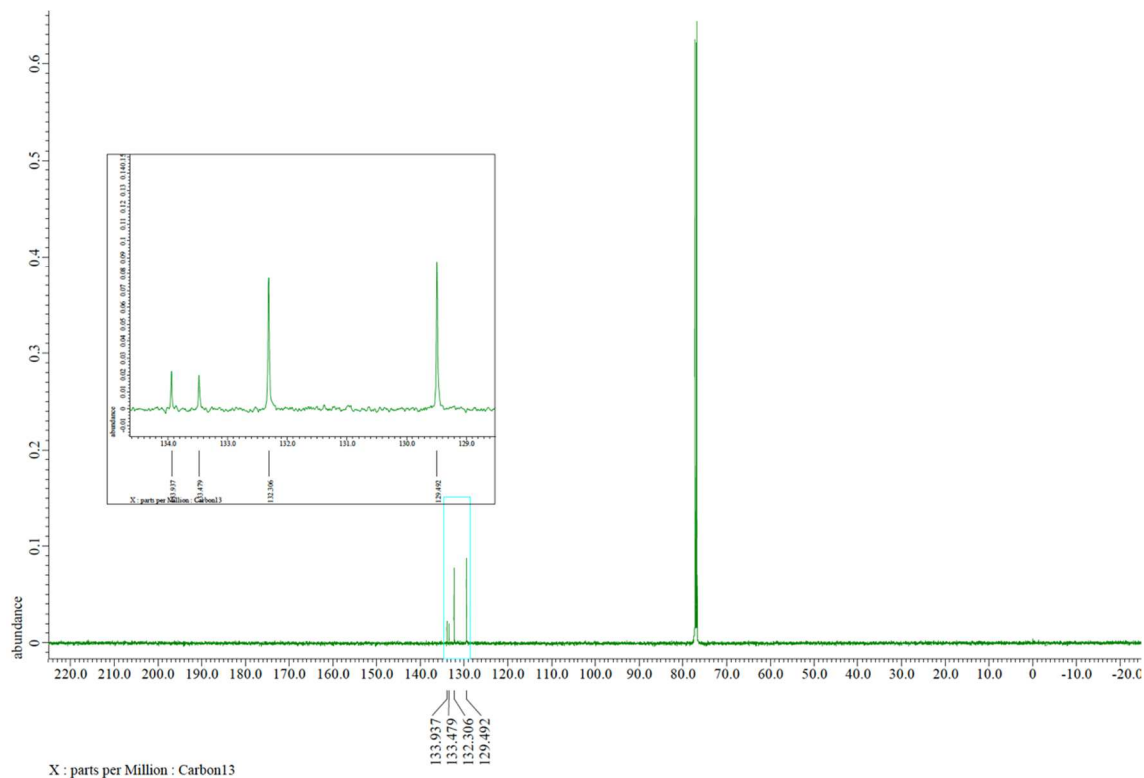
$^{19}\text{F}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2h**



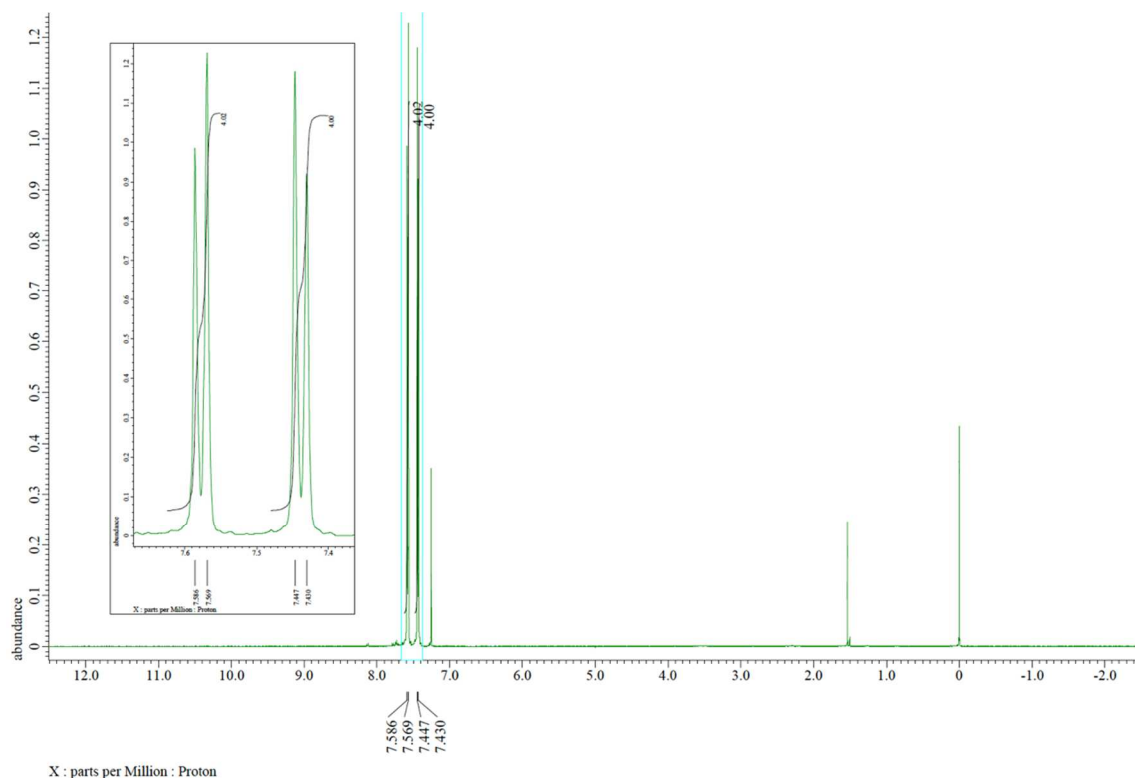
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2i**



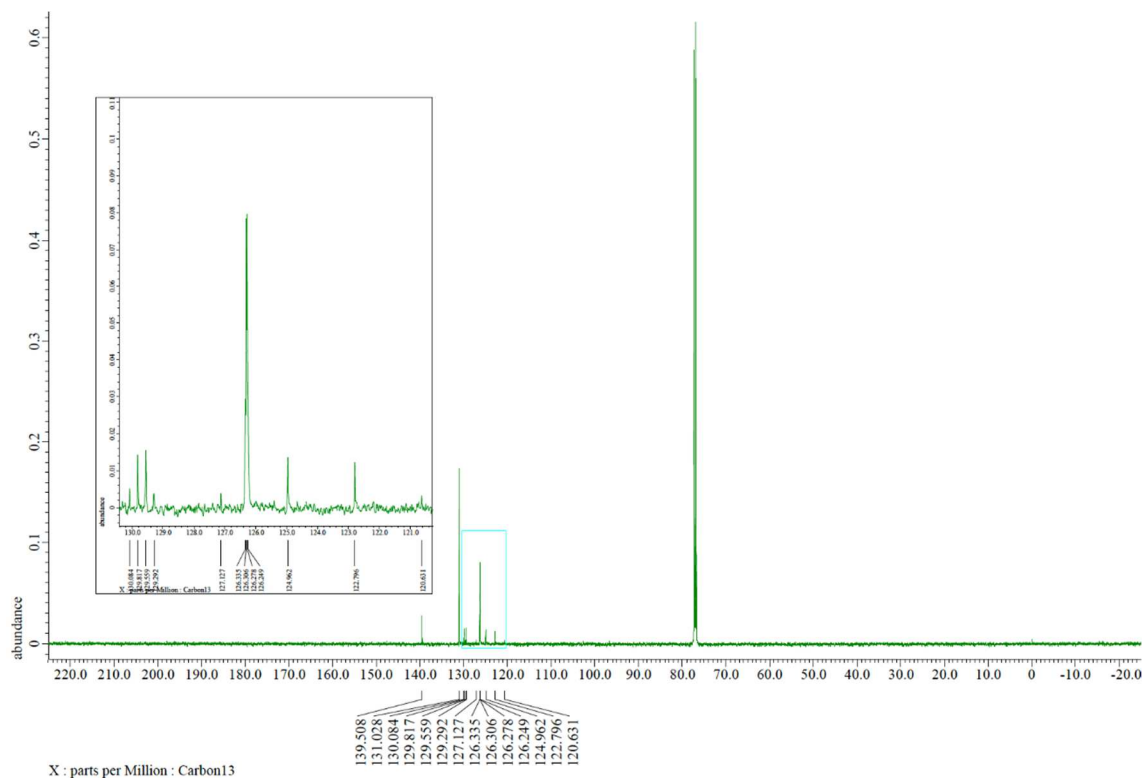
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2i**



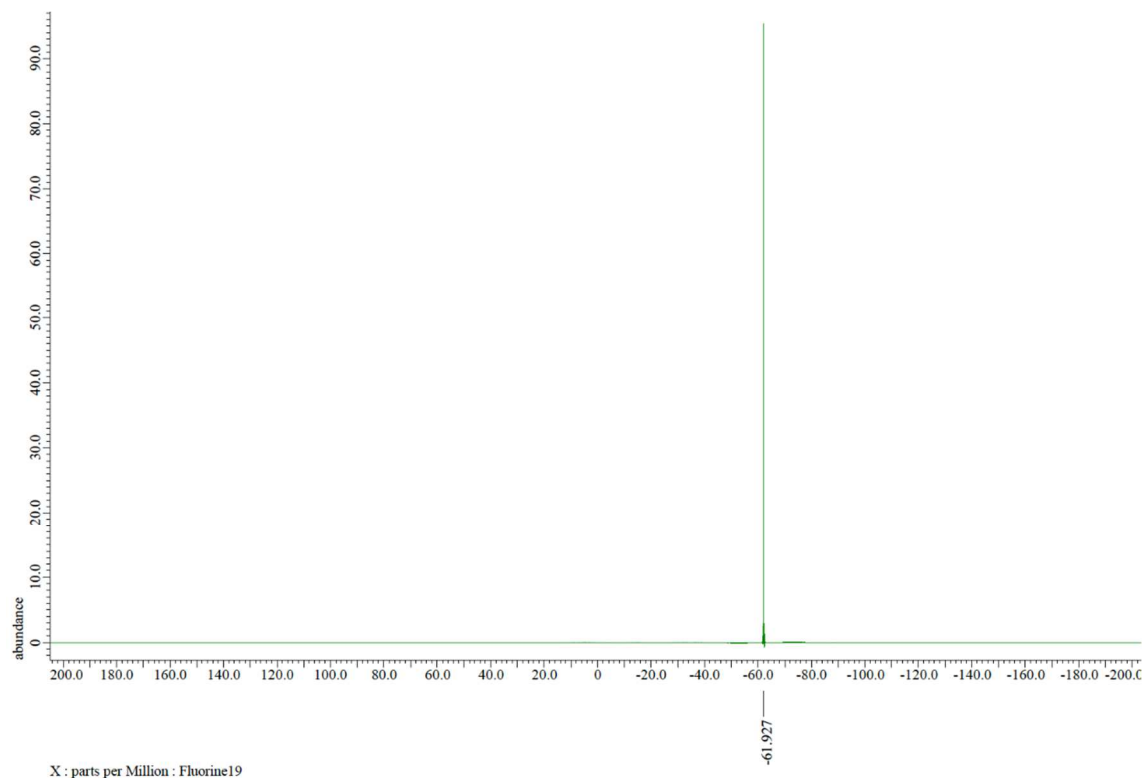
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2k**



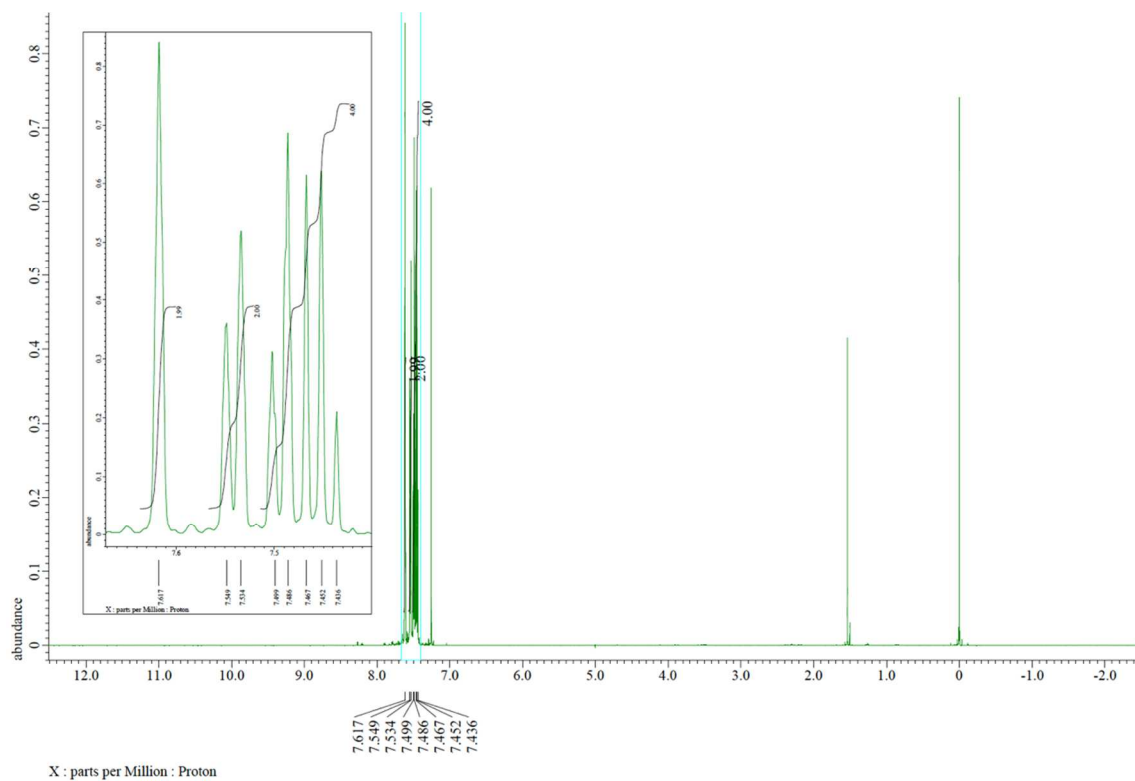
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2k**



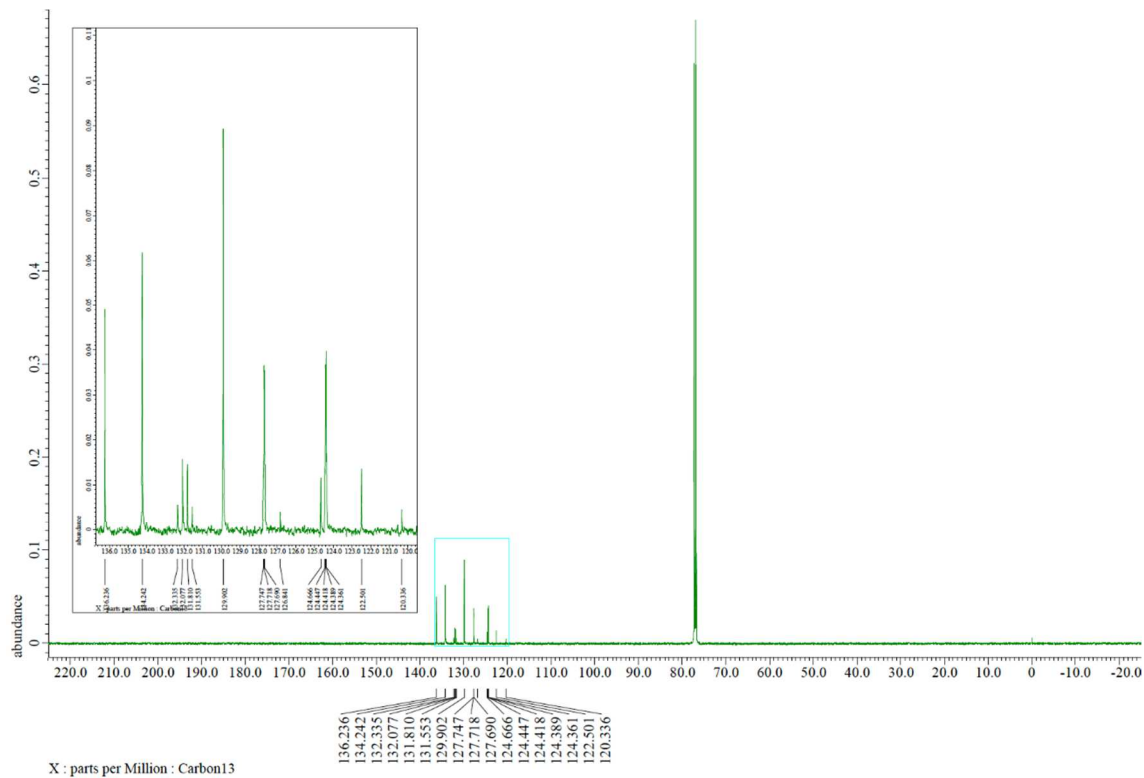
$^{19}\text{F}$  NMR spectrum (470 MHz,  $\text{CDCl}_3$ ) of **2k**



$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **21**

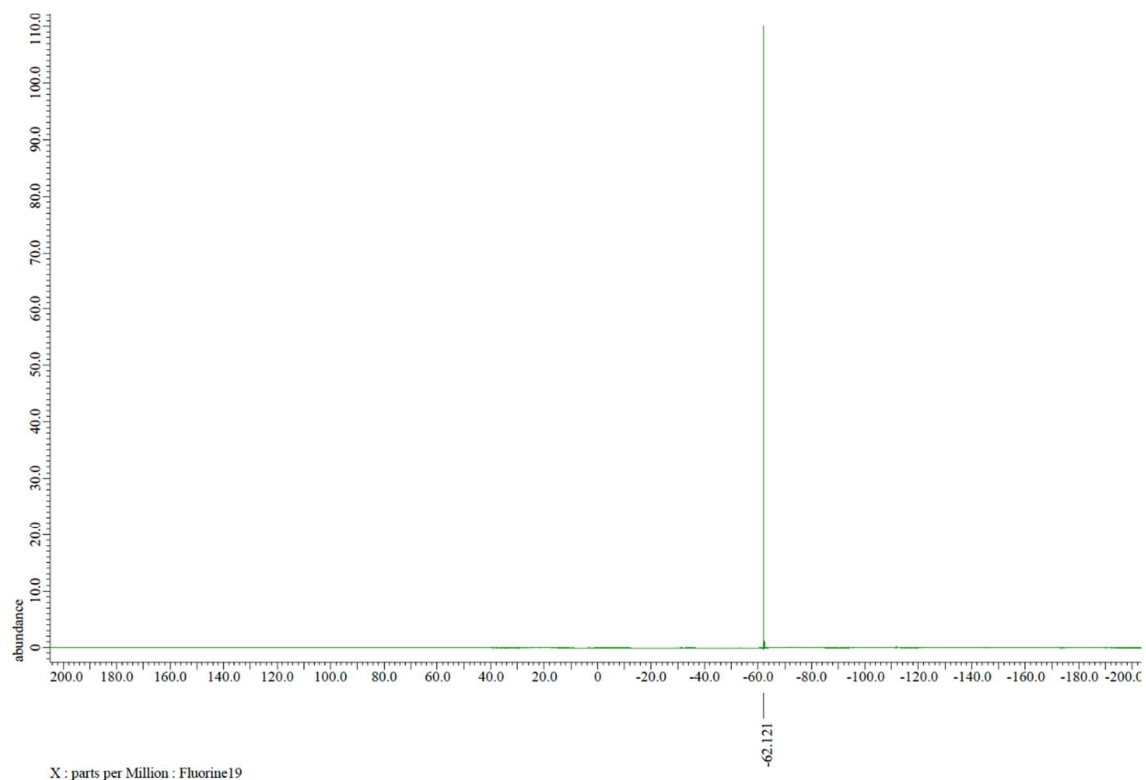


$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **21**

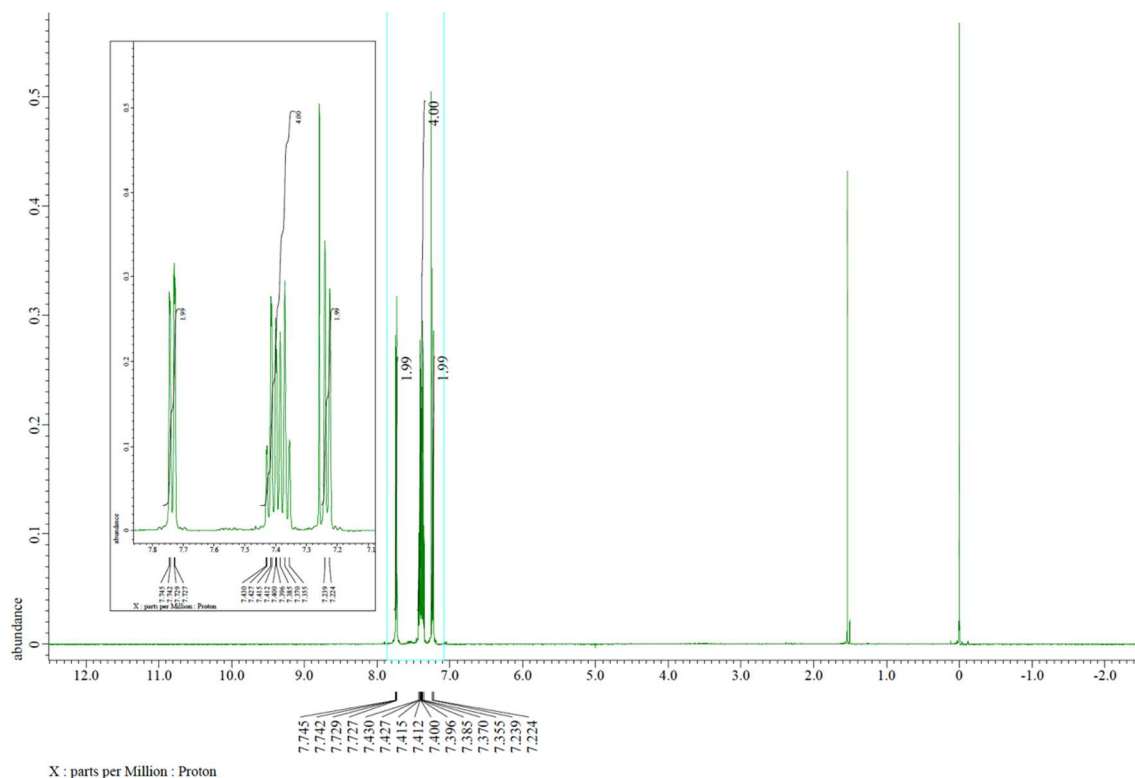




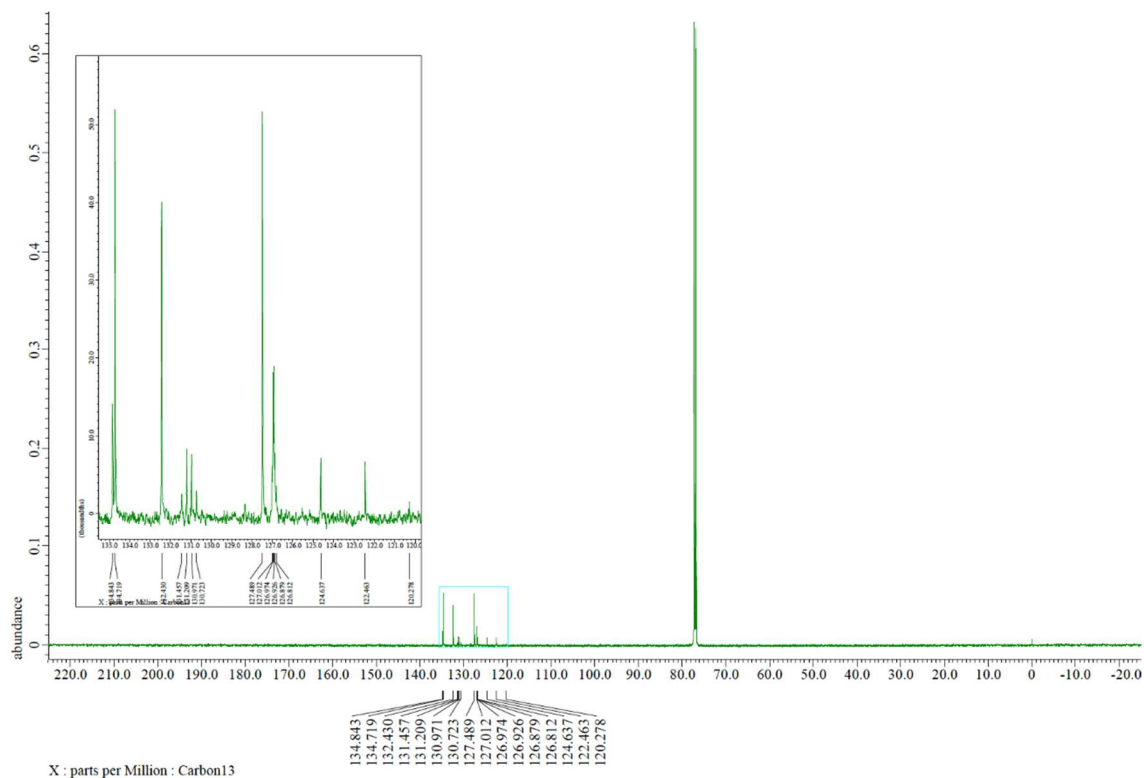
$^{19}\text{F}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2I**



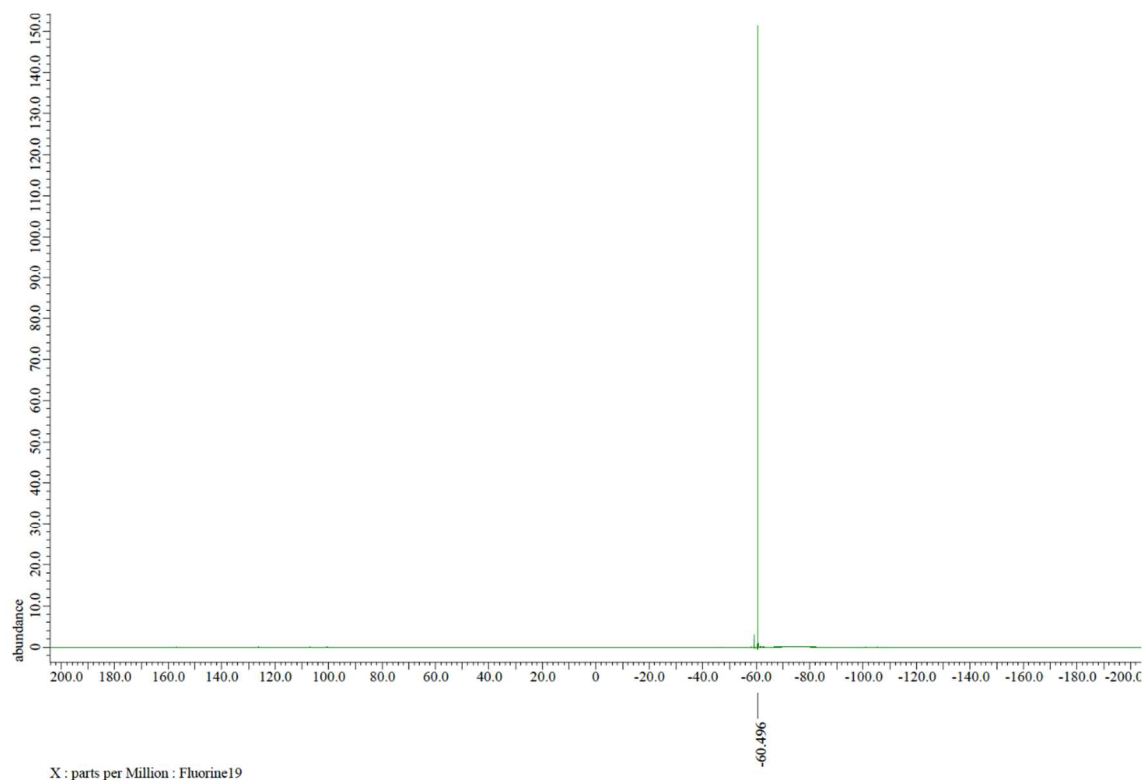
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2m**



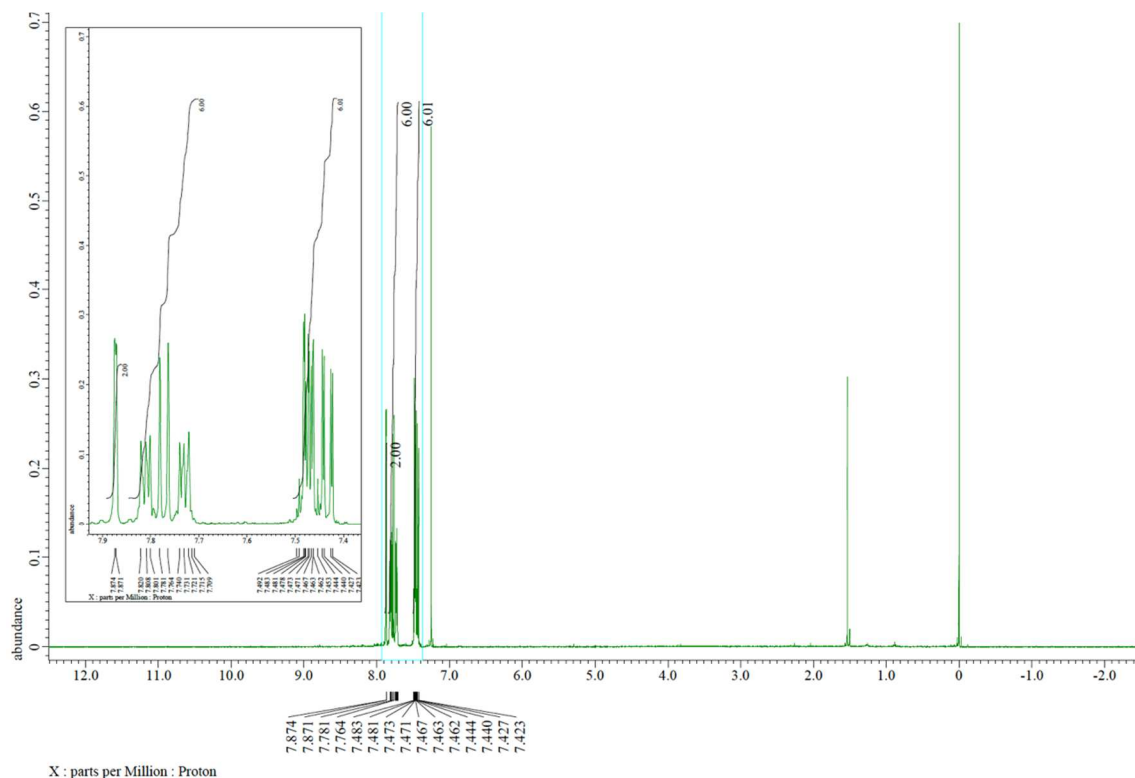
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2m**



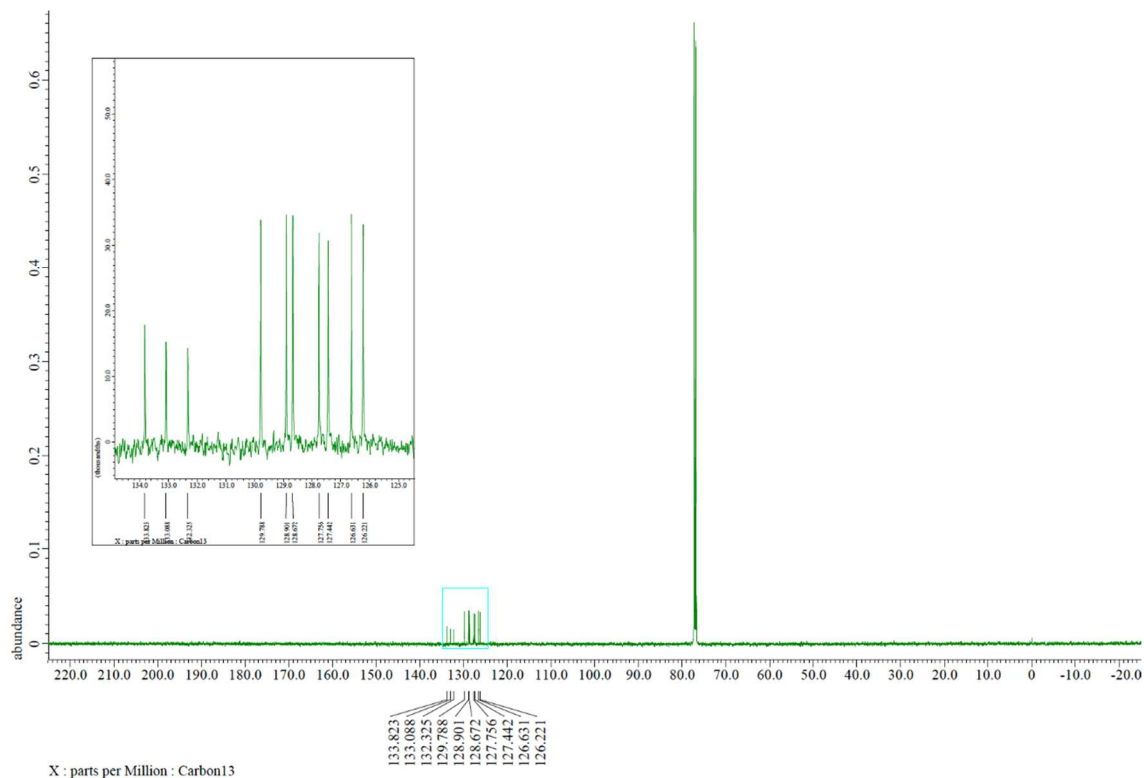
$^{19}\text{F}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2m**



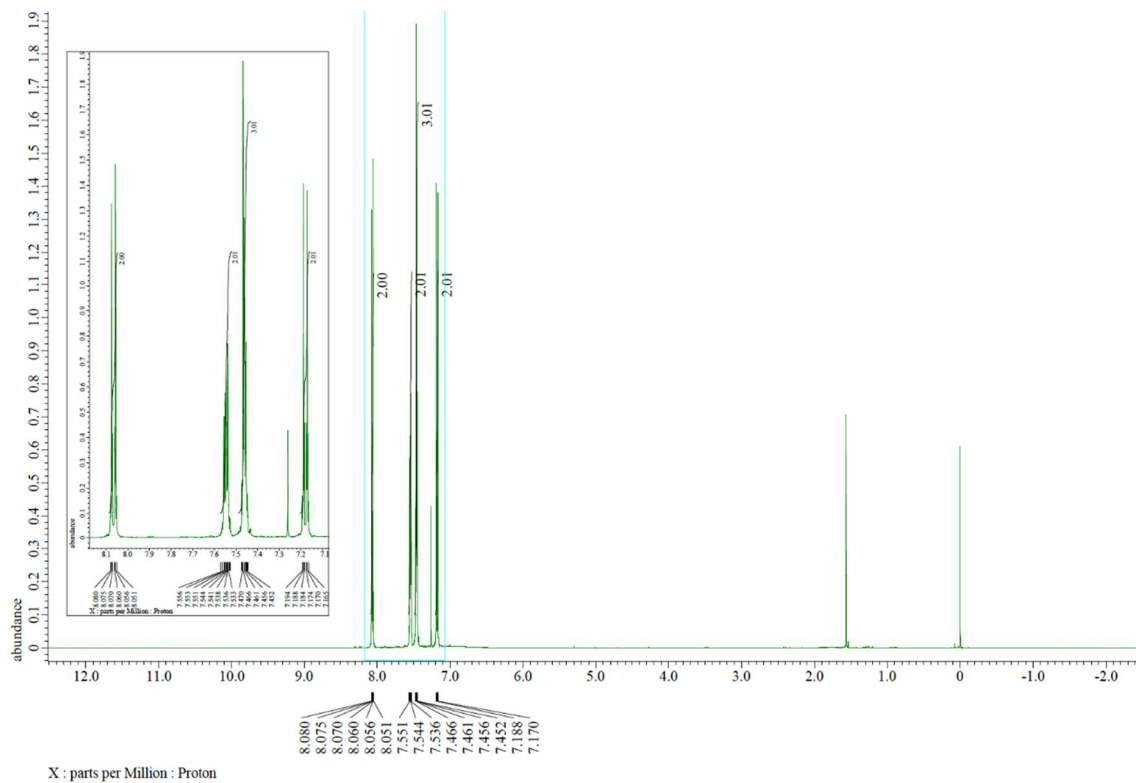
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2n**



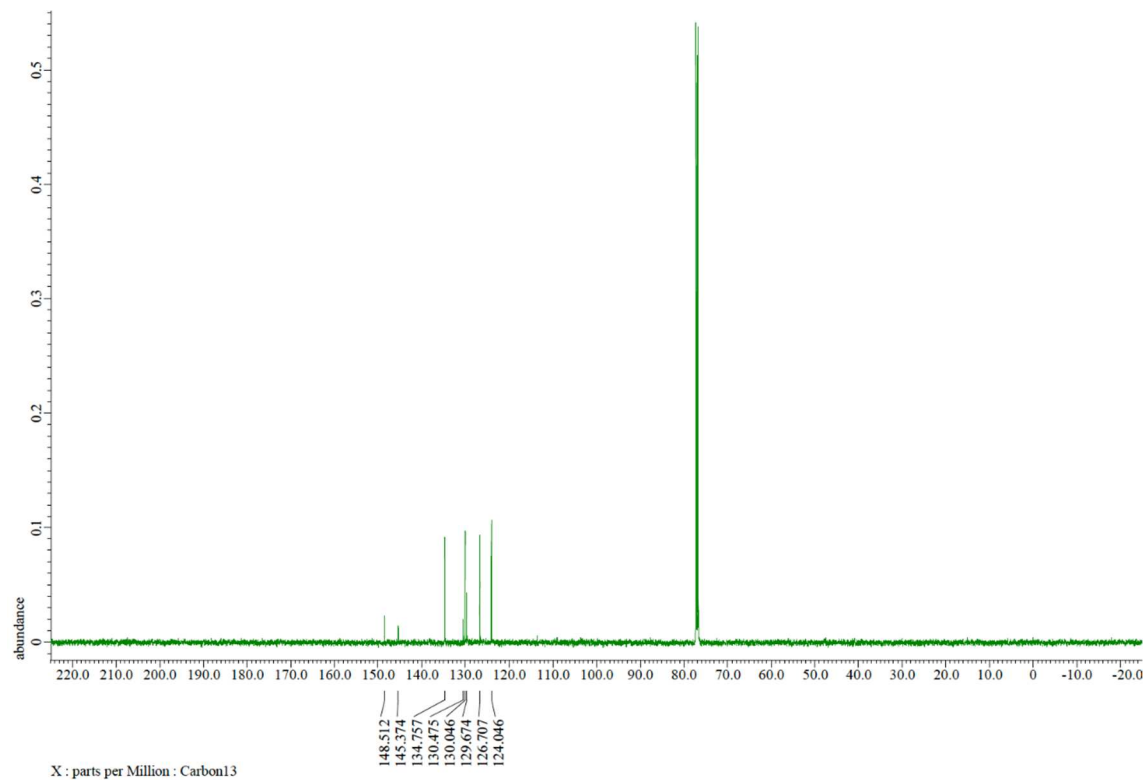
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2n**



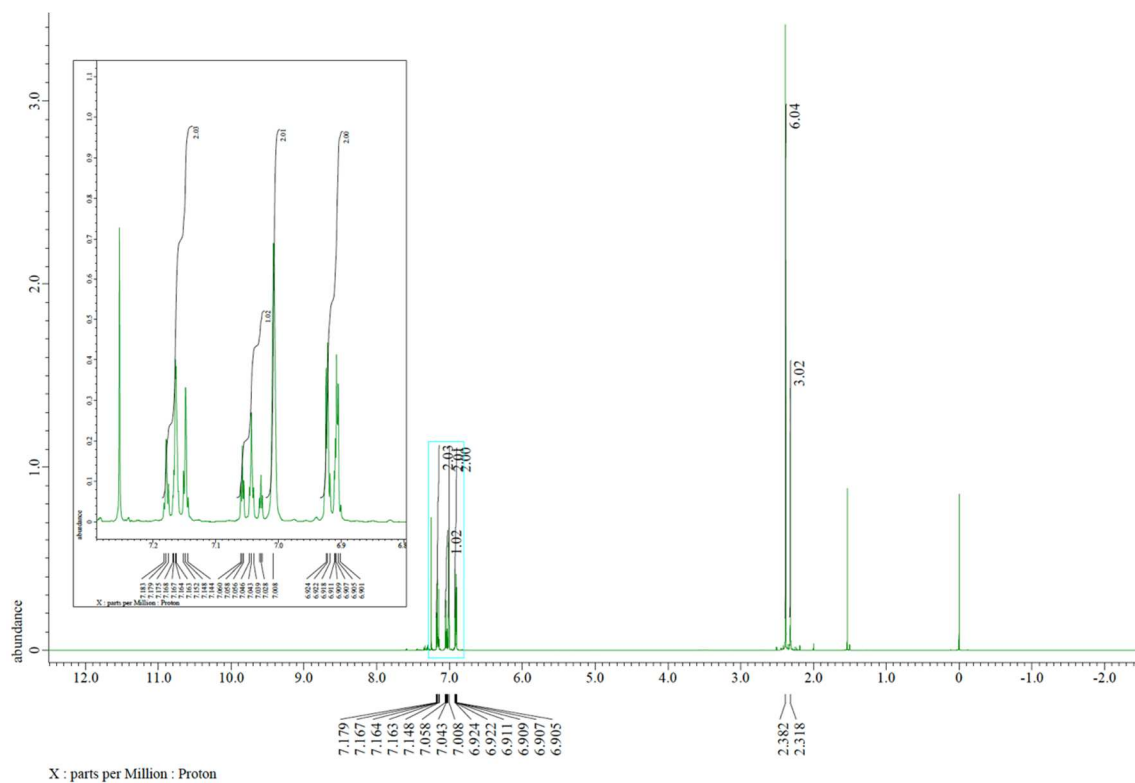
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2og**



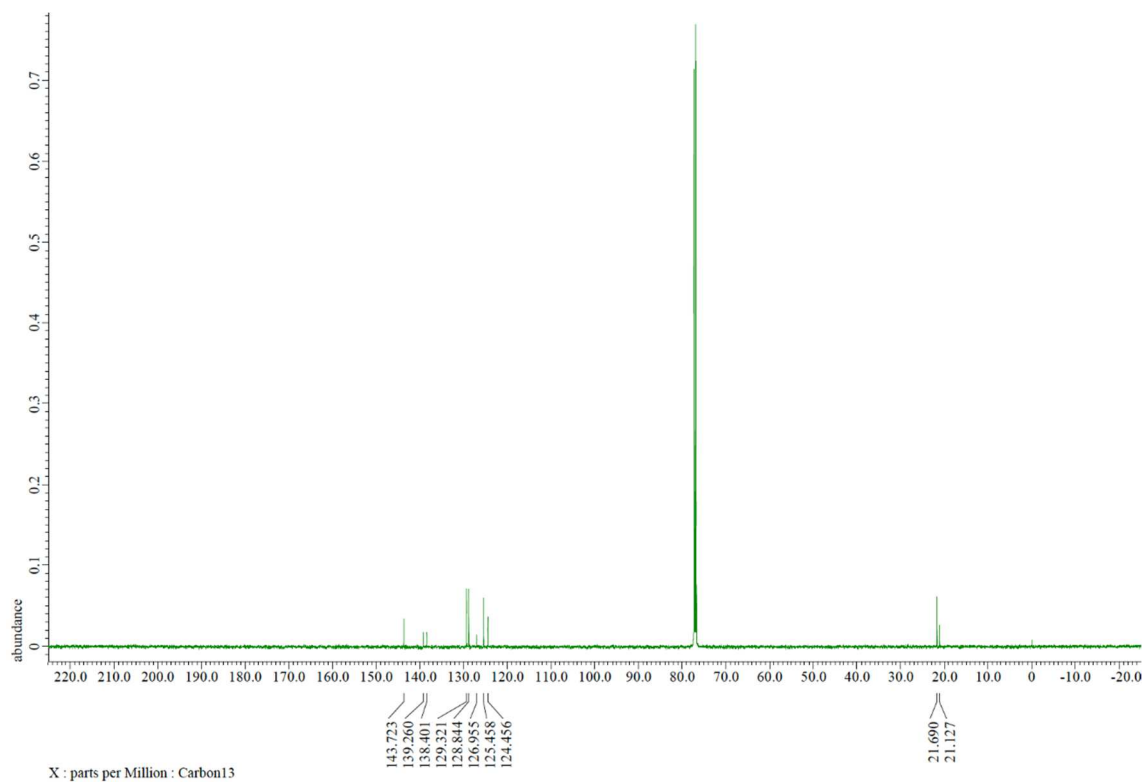
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2og**



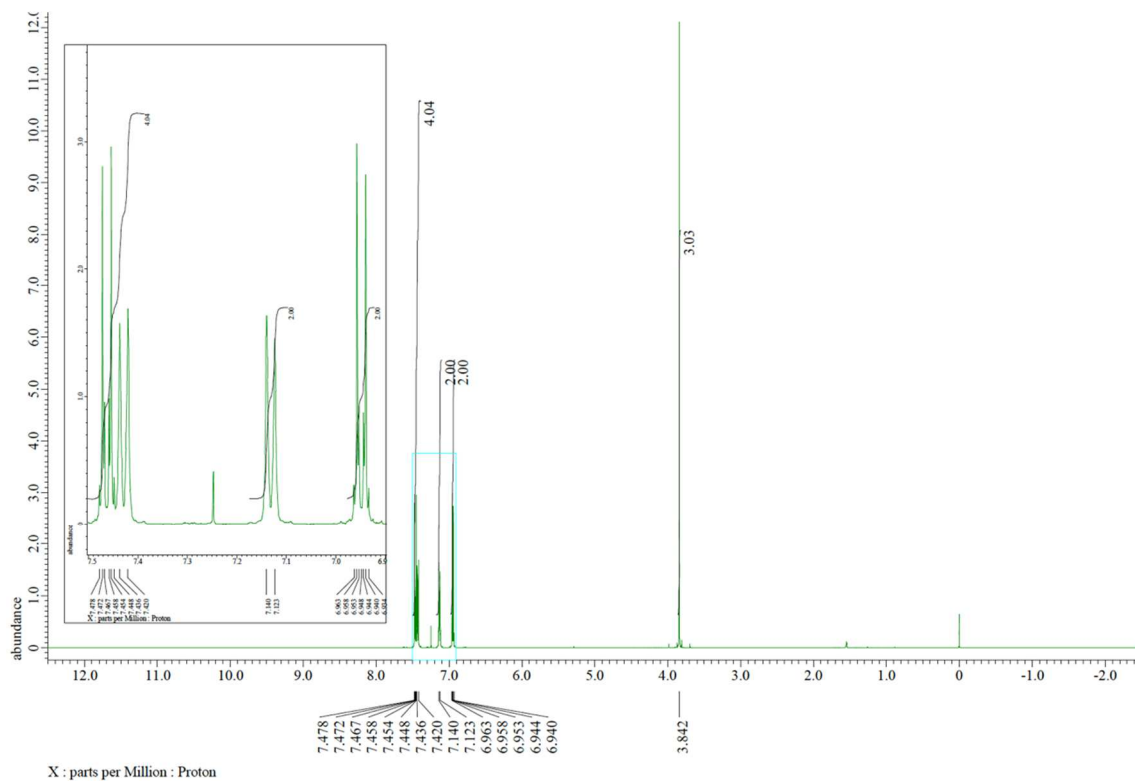
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2dg**



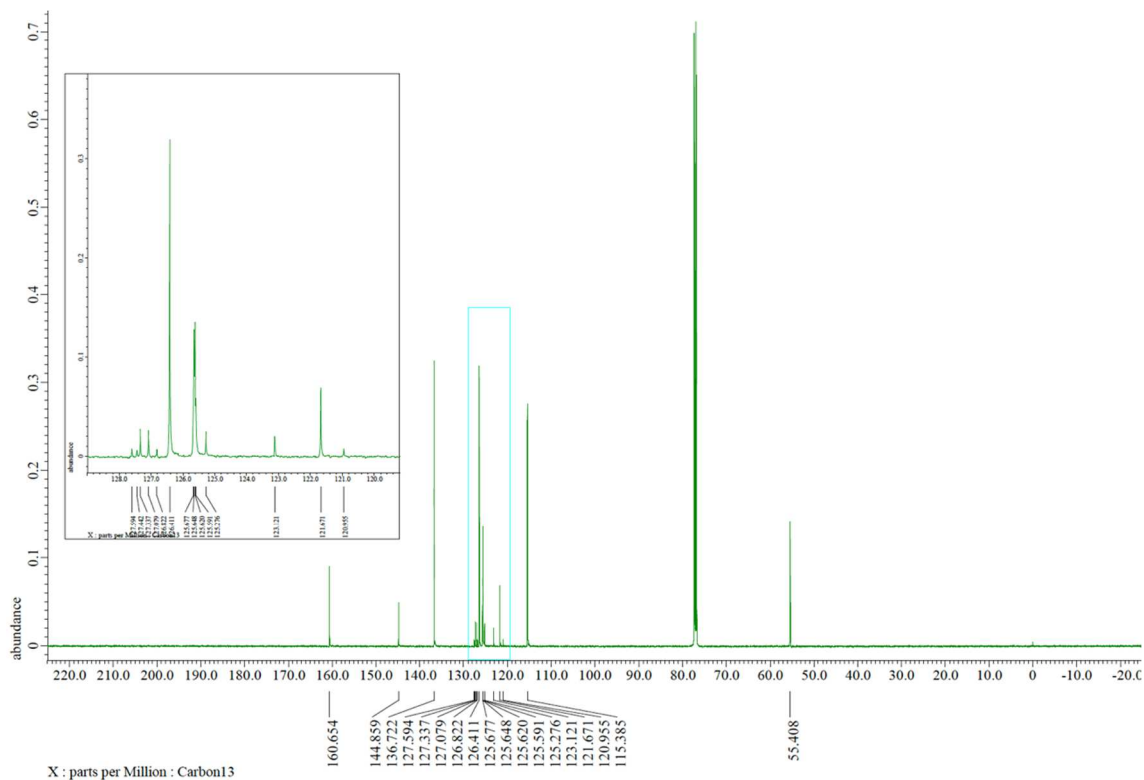
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2dg**



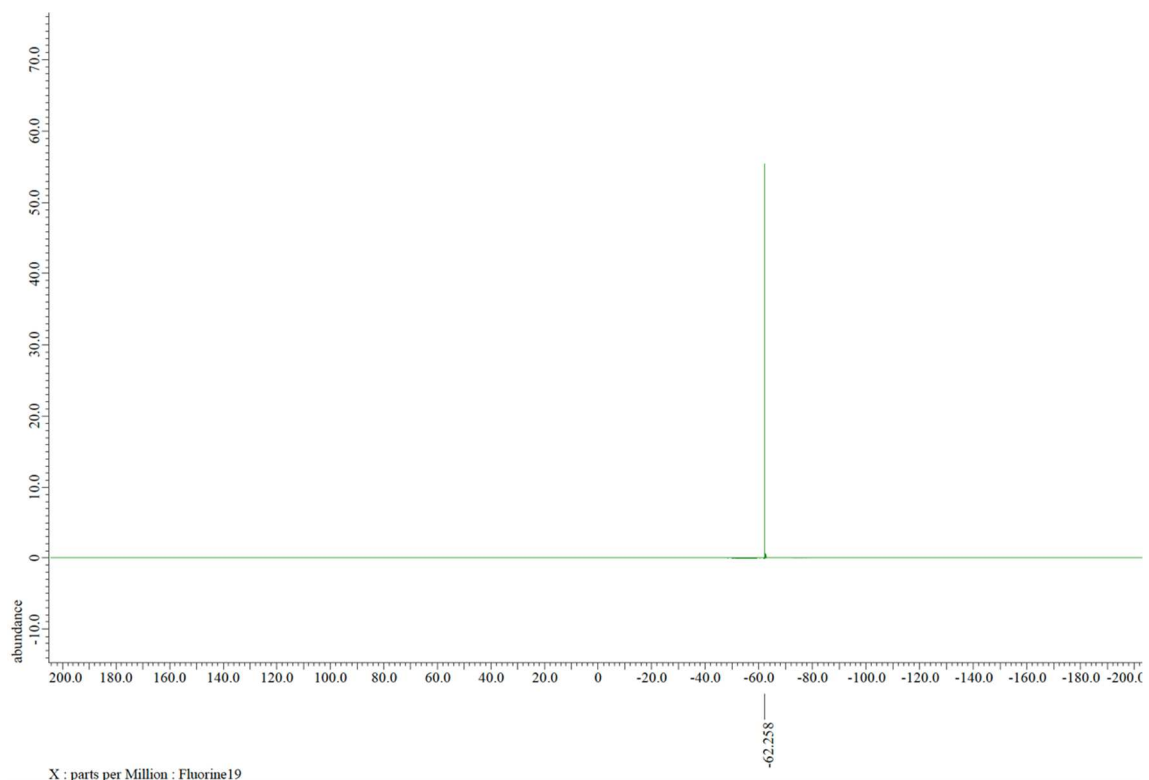
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2ek**



$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2ek**

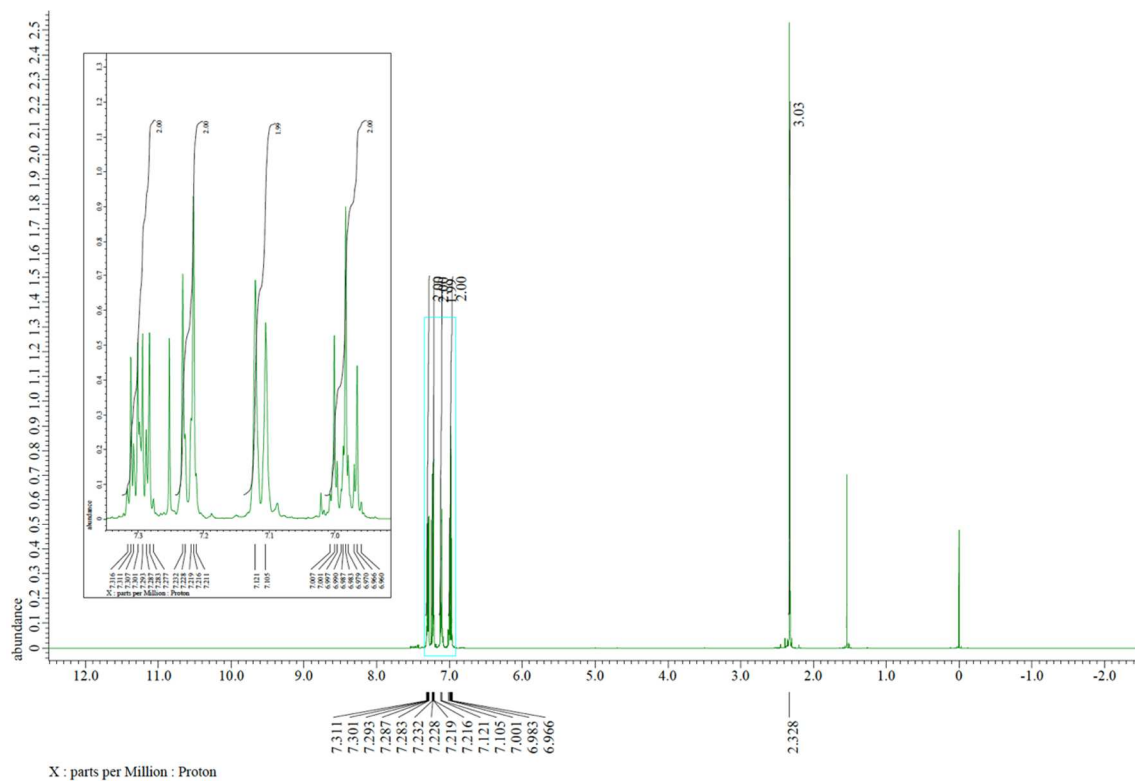


$^{19}\text{F}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2ek**

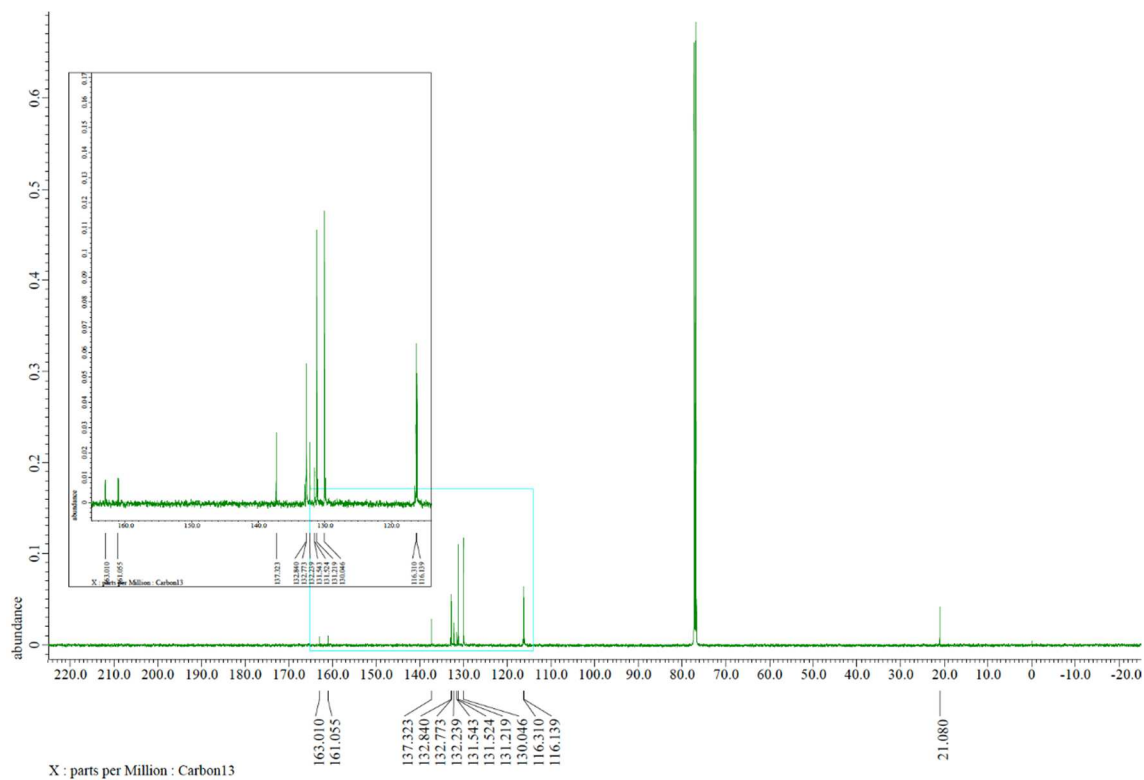




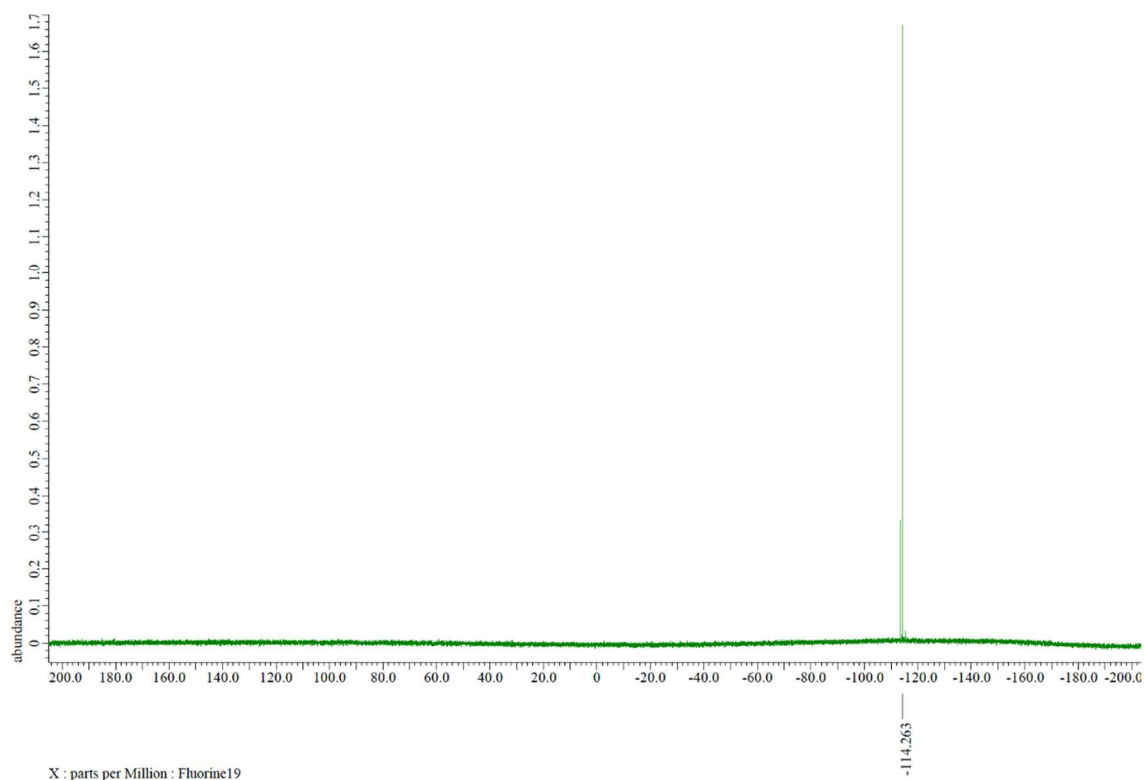
<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of **2ha**



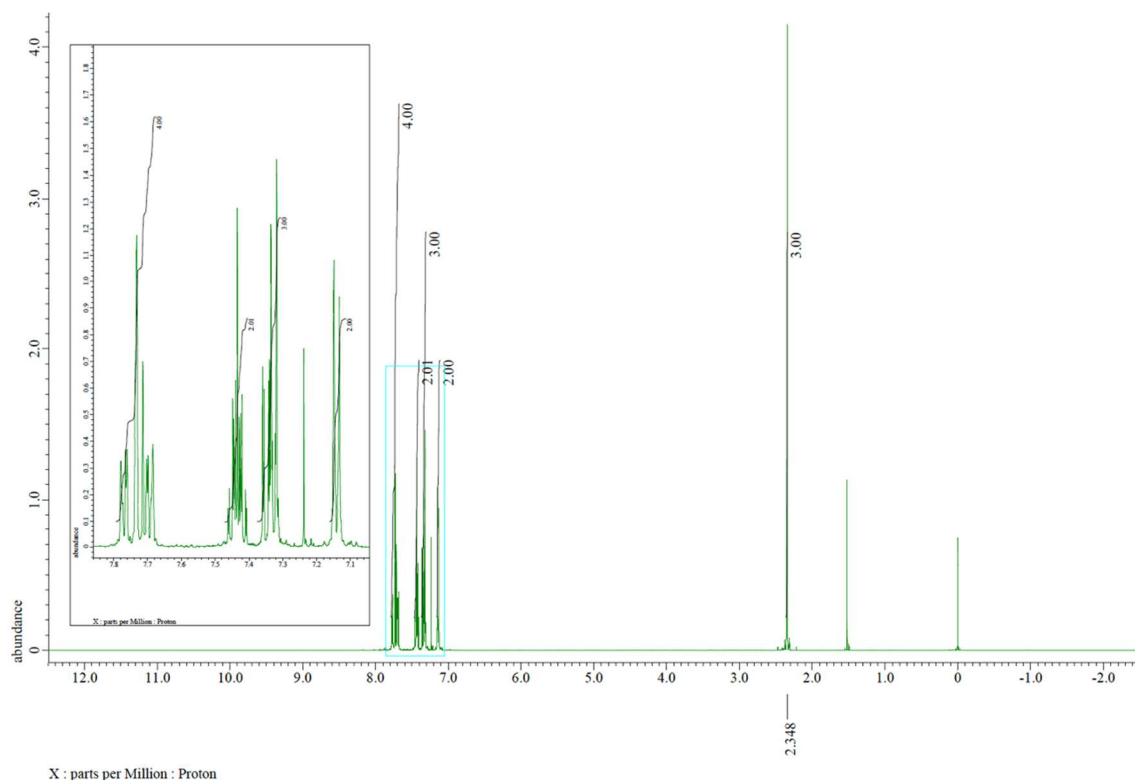
<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>) of **2ha**



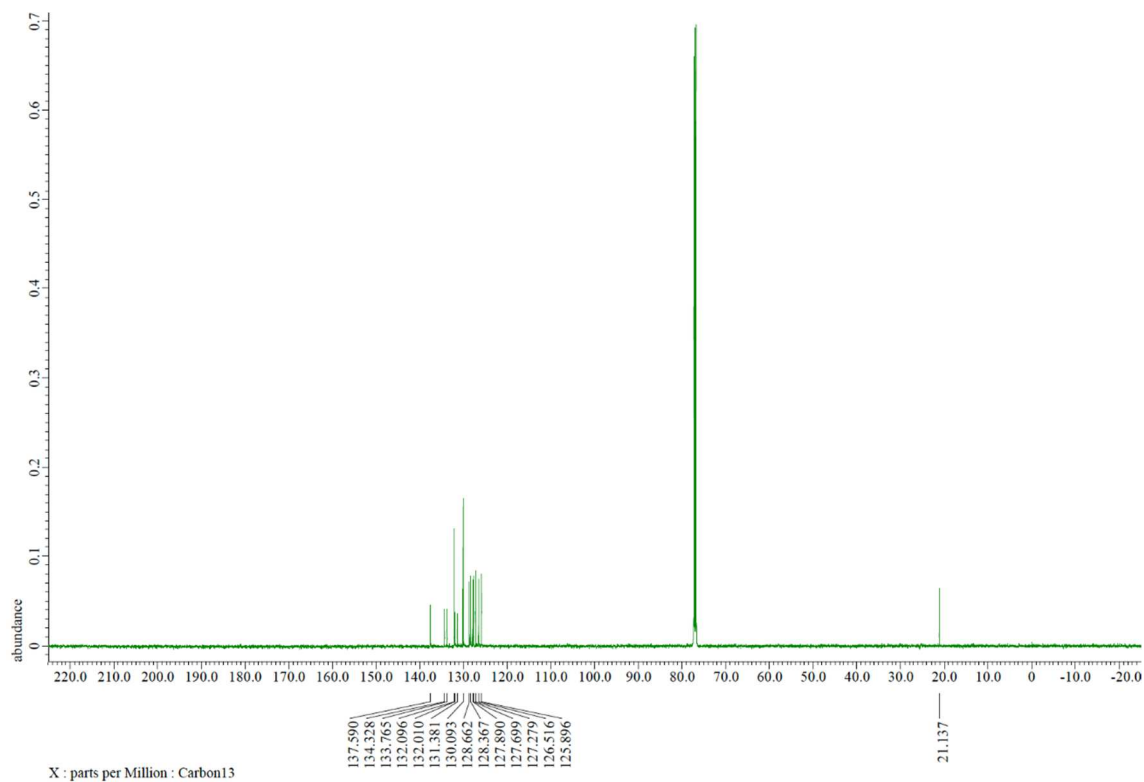
$^{19}\text{F}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2ha**



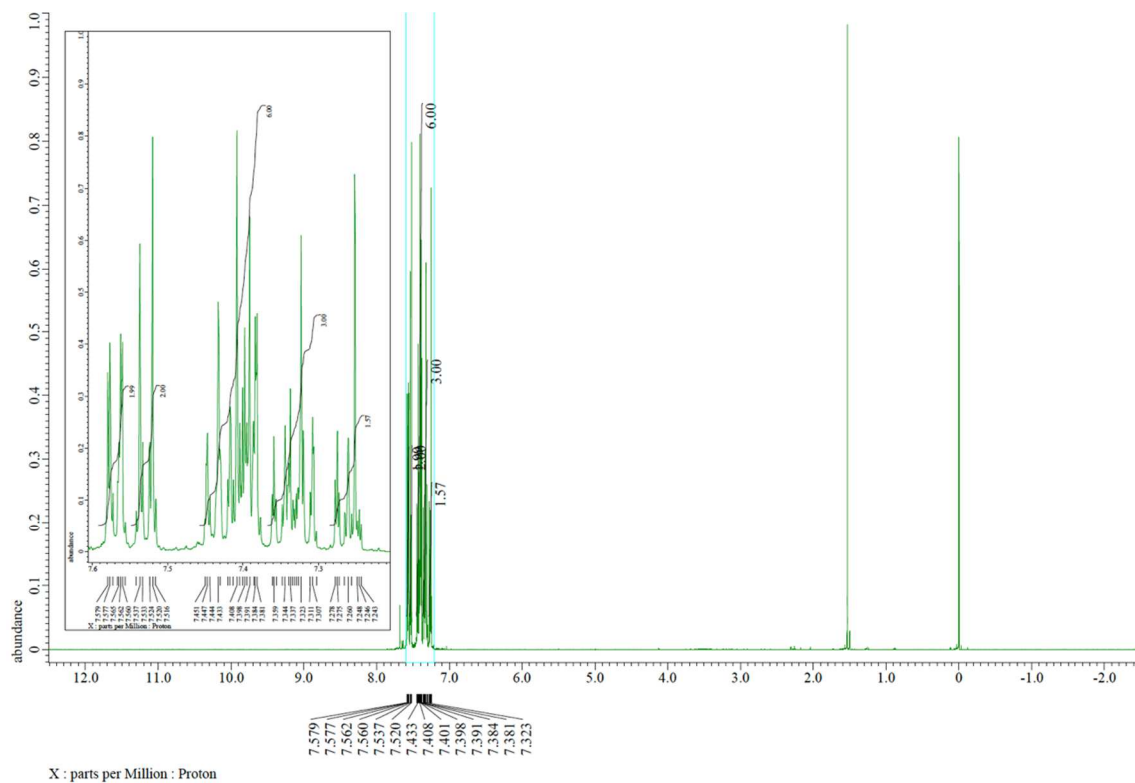
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2na**



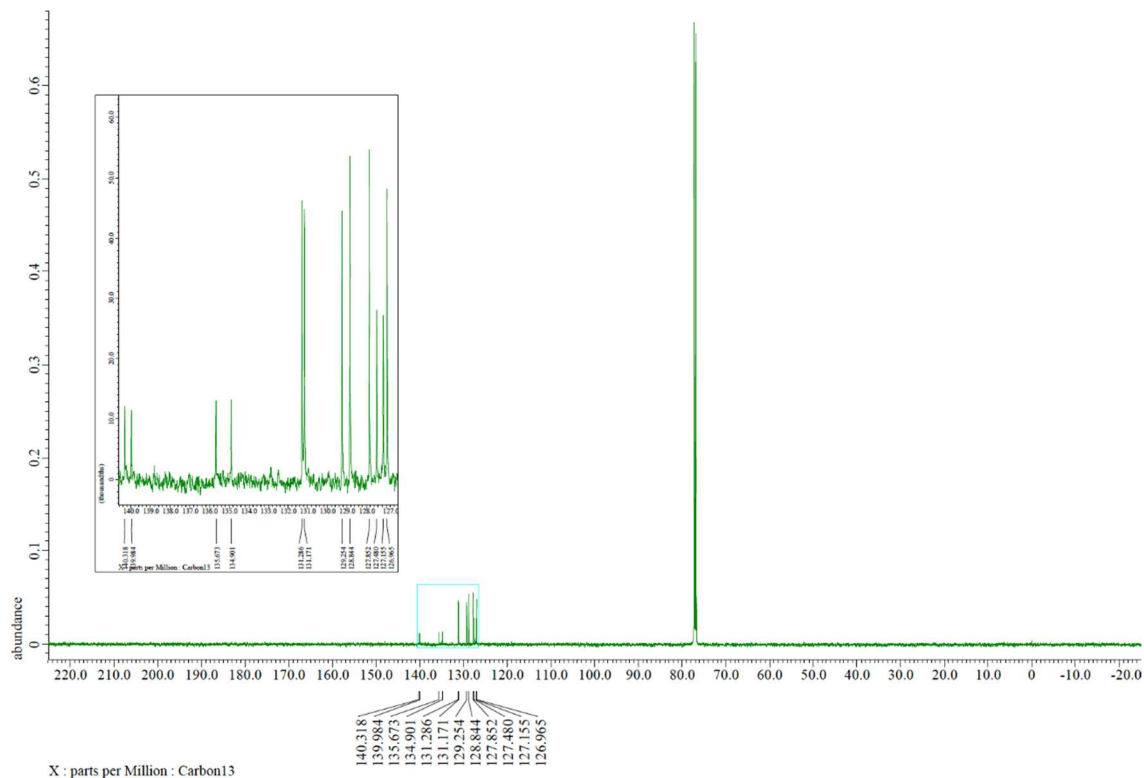
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2na**



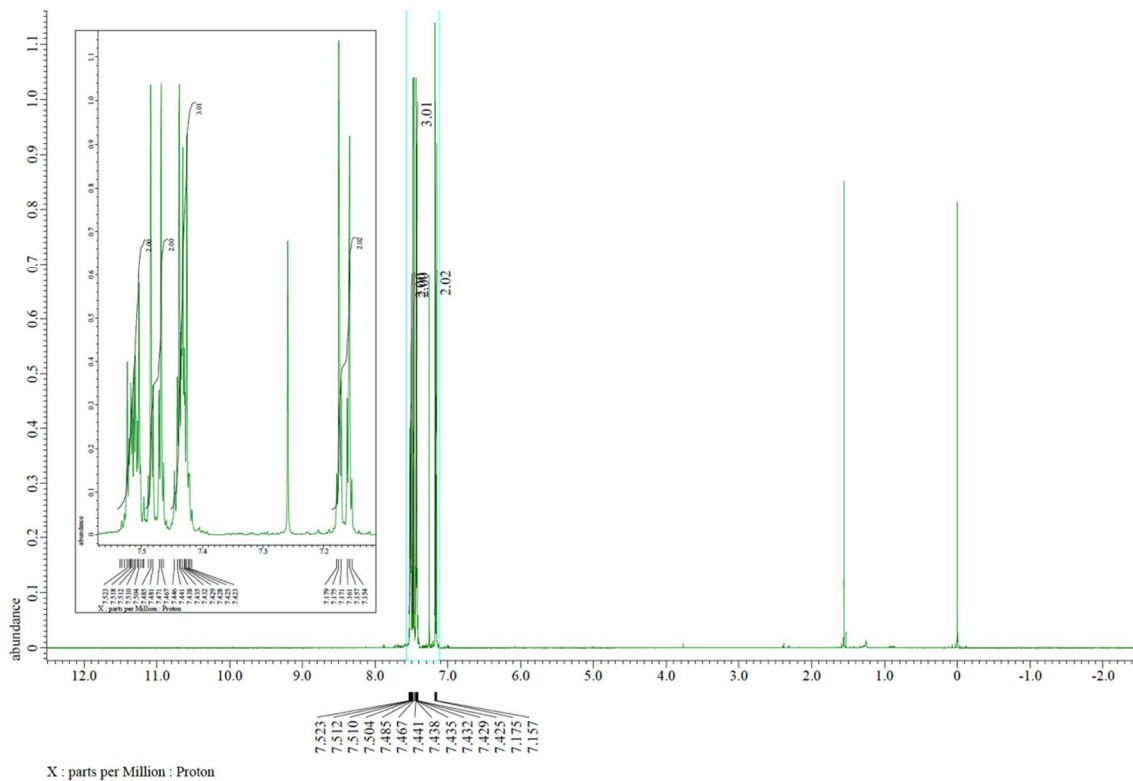
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2pg**



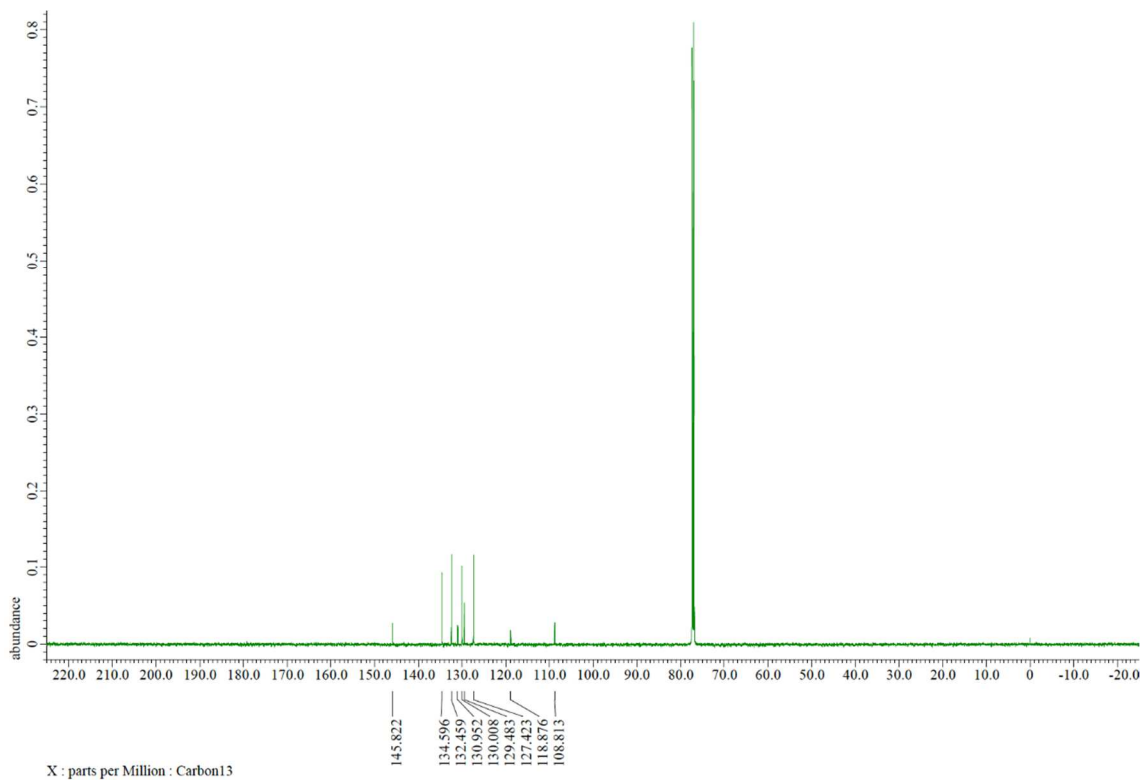
$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2pg**



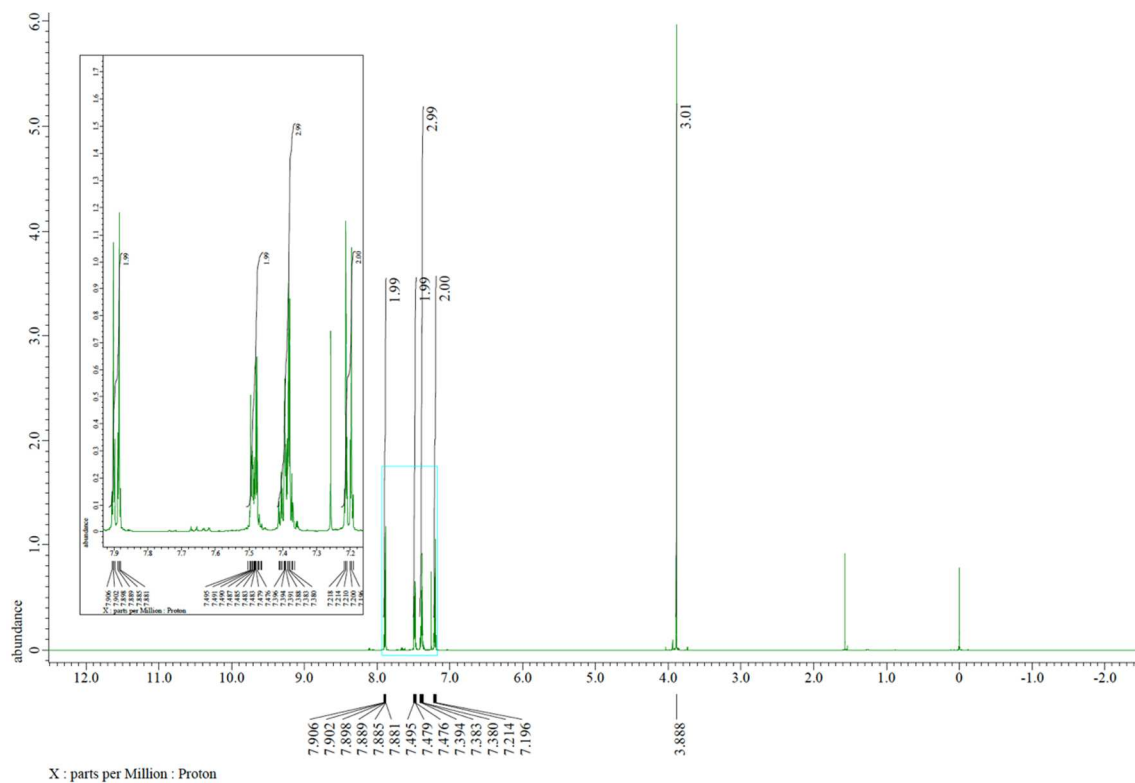
$^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **2qg**



$^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of **2qg**



<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of **2rg**



<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>) of **2rg**

