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Electronic Supplementary Information (ESI) for

Direct thioether metathesis enabled by in situ formed Pd nanocluster catalysts

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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. Liquid-state NMR spectra were recorded on JEOL JNM-ECA-500. ^{1}H and ^{13}C NMR spectra were measured at 500.16 and 125.77 Hz respectively. ^{1}H and ^{13}C NMR chemical shifts were referenced to tetramethylsilane (TMS) signal (0 ppm). ^{31}P NMR spectra were measured at 202.47 Hz. ^{19}F NMR spectra were measured at 470.62 Hz using CF_3COOH as an external reference (δ = –77.0 ppm). DLS characterization was conducted on Malvern Zetasizer NanoZS at the backscatter mode. Scanning transmission electron microscopy (STEM) observations were performed on a JEOL JEM-ARM200F. UV-Vis spectra were measured on JASCO V-570s and JASCO V-770 spectrometers with 1 cm quartz cells. 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.

XAS Measurements and EXAFS Fitting

X-ray absorption spectroscopy (XAS) was carried out at the BL14B2 beamline of SPring-8 (Proposal No. 2022B1656) and the BL11S2 beamline of Aichi Synchrotron Radiation Research Center (Proposal No. 202206105). Pd K-edge X-ray absorption fine structure (XAFS) measurements were conducted in transmission and fluorescence mode using a Si (311) crystal monochromator. Each sample was sealed into high purity polypropylene vials in an Ar-filled glovebox. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using Athena and Artemis software (Demeter, ver. 0.9.025; Bruce Ravel). The data reduction procedure for EXAFS consisted briefly of the following steps: pre-edge subtraction, background determination, normalization, and spectra averaging. The edge position is defined to be the first inflection point on the leading absorption peak. The energy was calibrated using Pd foil for the Pd K-edge XAS. The background in the EXAFS region was approximated using a cubic spline routine and optimized according to the criteria described by Cook and Sayers.[S1] Then, the spectra were normalized by the edge-step at 50 eV after the absorption edge. The k^3-weighted EXAFS functions were Fourier transformed, filtered, and fitted in R-space in the range of 3–12 Å^{-1} for Pd. Fourier filtering was used to isolate the contributions of specific shells and to eliminate low frequency background and high frequency noise. Fourier filtering was done by choosing a window in the Fourier transform spectrum and calculating the inverse Fourier Transform of the selected R-range.

Wavelet Transformation

The wavelet transform (WT) correlates the backscattering amplitudes of individual paths, in *k*-space, with their interatomic distances in *R*-space.[S2] Morlet wavelets of constant shape were used to generate continuous WT plots using Graph-R software.[S3,S4] The continuous WT of an EXAFS signal, $\chi(k)$, produces a new function $f(a,b)$, where a and b dilate and displace the wavelet (Y) along the *k*-axis respectively, eqn (1).[S5,S6]

$$f(a,b) = \int \chi(k)\Psi(ak + b)\mathrm{d}k \qquad (1)$$

The function $f(a,b)$ is plotted on (k, $R + a$) axes, where ($R + a$) is the interatomic distance without phase correction. The displacement b determines the position of the maximum in *k*-space, while the frequency-dependent value of ($R + a$) is determined by the wavelet dilation a. The mother wavelet Y has a fixed number of oscillations that, when shifted, dilated, and amplified, can be made to fit a region of the EXAFS signal. The Morlet wavelet parameters k and s define the shape of the mother wavelet. The k parameter represents the number of oscillations, while s is the half-width of the wavelet envelope.[S3] An individual EXAFS scattering path can be modeled by one wavelet with a single dilation coefficient, because the frequency of its EXAFS signal is constant. The WT maximum depends on the backscattering amplitude and is observed at the position in k-space where the wavelet amplitude is highest. For example, the WT of a k^3-weighted Pd–O path (R = 2.0 Å, σ^2 = 0.0030 Å^2) using a Morlet wavelet (k = 3, s = 1) generates a maximum at 5.6 Å^{-1}, Fig. S4. The WT resolution can be optimized in either *R*-space or *k*-space by the choice of adjustable parameters (k, s). Greater resolution in *k*-space is obtained with smaller wavelets, at the expense of resolution in *R*-space.[S2] Resolution is optimized in *k*-space when the product (ks) is ca. twice the pathlength, in Å, of the R-space region of focus.[S3] In this work, WT was performed over the regions 1.0–3.0 Å using the wavelet parameters (k = 3, σ = 1).

A Typical Procedure for Thioether Metathesis

In an Ar-filled glovebox, $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), **1a** (0.5 mmol), **1b** (0.1 mmol), 1,3,5-trimethoxybenzene (0.1 mmol, internal standard), xylene (1 mL), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL). The mixture was stirred at 50 °C for 5 min followed by 140 °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. As for isolation of the products, 1,3,5-trimethoxybenzene was not added. After the reaction, the catalyst was concentrated by evaporation, and then subjected to silica-gel column chromatography, giving the pure product. The products were identified by GC-MS, and NMR (^{1}H, ^{13}C, and ^{19}F). Some products, including **1ab–1ae**, **1bh**, **1ka**, **1la**, **1am**, and **1bn**, were difficult to be

isolated by silica-gel column chromatography, and thus, the NMR spectra of these products were shown as the mixture with the substrates after subjecting to silica-gel column chromatography.

As for time course plots, we prepared the same reaction solution in seven test tubes. Then, the mixture was stirred at 50 °C for 5 min followed by being stirred at 140 °C for 0, 10, 20, 60, 120, 240, and 480 min respectively. The reaction solutions were collected and stored in an Ar-filled glove box, and then they were subjected to GC, UV-Vis, and XAFS analysis.

Hot-filtration

To verify whether the observed catalysis was homogeneous or not, a hot-filtration test by cannula filtration was conducted. The procedure was as follows: $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), **1a** (0.5 mmol), **1b** (0.1 mmol), 1,3,5-trimethoxybenzene (0.1 mmol, internal standard), xylene (1 mL), and a Teflon-coated magnetic stir bar were placed in a Schlenk flask in an Ar atmosphere. The mixture was stirred at 50 °C for 5 min followed by 140 °C. 90 min after starting the reaction, the reaction solution was quickly filtered off using Omnipore^{TM} hydrophilic PTFE membrane filter (pore size: 0.2 μm, Merck Millipore) via cannula filtration to another Schlenk flask under an Ar atmosphere. Then, the filtrate was continually stirred at 140 °C.

Synthesis of Pd/RGO

To directly observe the Pd species in the reaction solutions, we supported them on reduced graphene oxide (RGO) by the equilibrium adsorption method. The procedure was as follows: $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), **1a** (0.5 mmol), **1b** (0.1 mmol), 1,3,5-trimethoxybenzene (0.1 mmol, internal standard), xylene (1 mL), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL). The mixture was stirred at 50 °C for 5 min followed by 140 °C for 1.5 h, then the mixture was cooled down to room temperature. RGO (50 mg) and xylene (2 mL) were added to the reaction solution and stirred for 4.5 h. The stirring time to support Pd species on RGO was determined from the results of UV-Vis spectra of the filtrate after removal of RGO suggesting that the adsorption equilibrium was almost achieved after being stirred for ~2 h (Fig. S8). After filtration of the reaction solution, Pd species supported on RGO (Pd/RGO) were washed with xylene (10 mL) followed by drying *in vacuo* for 30 min.

Thioether Metathesis in the Filtrate after Supporting Pd Species on RGO

In an Ar-filled glovebox, $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), **1a** (0.5 mmol), **1b** (0.1 mmol), 1,3,5-trimethoxybenzene (0.1 mmol, internal standard), xylene (1 mL), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL). The mixture was stirred at 50 °C for 5 min followed by being stirred at 140 °C for 1.5 h. After the mixture was cooled down to room temperature, RGO (50 mg) was added to the reaction solution followed by stirring for 2 h at

room temperature. Then, RGO was filtered off, and the filtrate was stirred at 140 °C for additional 22.5 h. GC analysis was conducted after stirring at 140 °C for 1.5 h and after stirring at 140 °C for the additional 22.5 h. As a control experiment, we prepared a reaction solution where the same procedure was performed without RGO.

Synthesis of Pd-PVP

Polyvinylpyrrolidone (PVP)-coated Pd nanoparticles (Pd-PVP) were synthesized referring to a previous report.[S7] $Pd(acac)_2$ (50 mg), PVP (160 mg), KBr (103 mg), *N*-methylpyrrolidone (NMP) (12 mL), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~40 mL) in an air. The resulting mixture was then heated at 140 °C for 2 h and was cooled to room temperature. The black precipitates were washed with ethanol (10 mL × 3) to afford Pd-PVP.

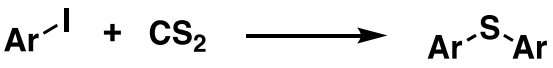
Synthesis of Thioethers

Condition A

Step 1 (thioester synthesis): Acyl chlorides (6.3 mmol) and thiols (6.0 mmol) were dissolved in dehydrated dichloromethane (10 mL) in an Ar atmosphere. The solution was stirred at 0 °C for a few minutes. Triethylamine (12.0 mmol) was added to the solution dropwise followed by stirring at room temperature overnight. After the reaction, aqueous HCl solution (10 mL) was added and the organic layer was washed with brine (10 mL × 3) and deionized water (10 mL × 1) to afford analytically pure thioesters. The products were purified by silica-gel column chromatography if necessary.[S8]

Step 2 (thioester decarbonylation): Thioesters, a hydroxyapatite-supported Pd nanoparticle catalyst (Pd/HAP, Pd: 8 mol%), dehydrated xylene (2 mL), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL) in an Ar atmosphere. The mixture was stirred at 160 °C for 24 h. After 24 h, Pd/HAP was removed by simple filtration. The crude thioethers were purified by silica-gel column chromatography using hexane and ethyl acetate as eluents, giving the pure products.[S9] **1b–1f**, **1h–1n** were synthesized under the Condition A.

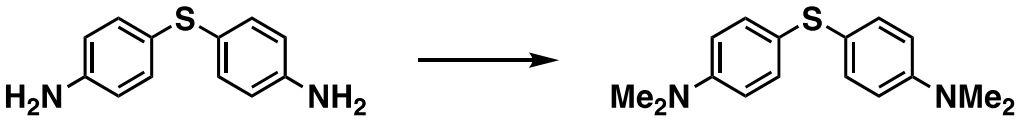
Condition B



Aryl iodides (1 mmol), CuI (10 mol%), and a Teflon-coated magnetic stir bar were placed in a Pyrex glass reactor (volume: ~20 mL). In an Ar-filled glovebox, DBU (2 mmol) and dehydrated toluene (1.5 mL) were added. Then, CS_2 (1 mmol) was added dropwise and heated at 100 °C for 12 h.

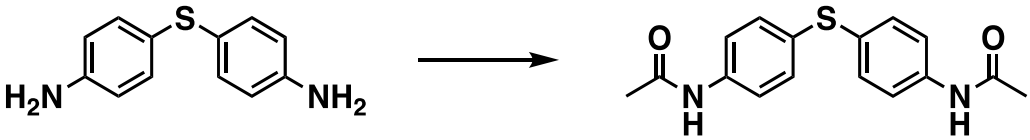
After the reaction, ethyl acetate (5 mL) and deionized water (5 mL) were added, and the aqueous layer was extracted with brine (5 mL × 3). The crude thioethers were purified by silica-gel column chromatography using hexane and ethyl acetate as eluents, giving the pure products.[S10] **1r**, **1u**, and **1v** were synthesized under the Condition B.

Condition C



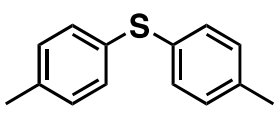
For the synthesis of bis[4-(*N*,*N*-dimethylamino)phenyl] sulfide (**1s**), *N*-methylation of bis(4-aminophenyl)sulfide (**1p**) was conducted. Bis(4-aminophenyl)sulfide and K_2CO_3 (10 eq.) were dissolved in acetone in an Ar atmosphere, then iodomethane (4.5 eq.) was added. The resulting mixture was heated under reflux conditions overnight. After the reaction, deionized water (30 mL) was added, and the products were extracted with ethyl acetate (10 mL × 3). The crude thioethers were purified by silica-gel column chromatography using hexane and ethyl acetate as eluents, giving the pure products.[S11]

Condition D

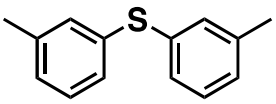


For the synthesis of *N*,*N*′-(thiodi-4,1-phenylene)bis acetamide (**1t**), *N*-amidation of bis(4-aminophenyl)sulfide (**1p**) was conducted. Bis(4-aminophenyl)sulfide was dissolved in dehydrated DCM (20 mL) at room temperature. Acetic anhydride (2.4 eq.) was added dropwise to afford precipitates immediately. After the reaction for 12 h, the precipitates were washed with ethyl acetate to afford analytically pure product.[S12]

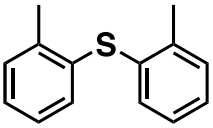
<u>Spectral Data of Thioether Substrates</u>



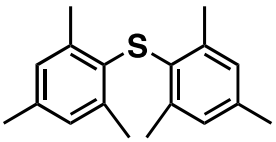
***p*-tolylsulfide** (CAS No. 6620-94-0, **1b**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21–7.23 (m, 4H), 7.08–7.09 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0, 132.8, 131.2, 130.0, 21.2. MS (EI): *m/z* (%): 215 (17), 214 (100) [M^+], 213 (16), 199 (38), 198 (16), 184 (23), 181 (13), 105 (17), 91 (27), 65 (14).[S13]



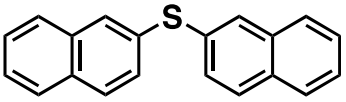
***m*-tolylsulfide** (CAS No. 3111-77-1, **1c**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.19 (m, 4H), 7.11–7.13 (m, 2H), 7.03–7.05 (m, 2H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1, 135.7, 131.7, 129.1, 128.2, 128.0, 21.4. MS (EI): *m/z* (%): 215 (16), 214 (100) [M^+], 213 (12), 199 (48), 198 (20), 197 (12), 184 (41), 165 (13), 105 (22), 91 (17), 77 (11), 65 (26), 63 (10).[S13]



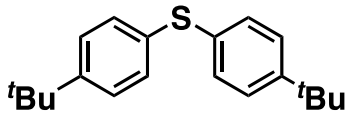
***o*-tolylsulfide** (CAS No. 4537-05-7, **1d**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–7.24 (m, 2H), 7.14–7.18 (m, 2H), 7.04–7.10 (m, 4H), 2.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9, 134.3, 131.1, 130.4, 127.1, 126.7, 20.4. MS (EI): *m/z* (%): 215 (16), 214 (100) [M^+], 199 (22), 197 (13), 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).[S13]



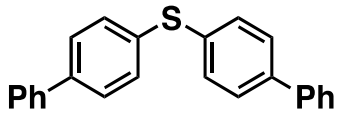
mesitylsulfide (CAS No. 5324-71-0, **1e**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (s, 4H), 2.22 (s, 6H), 2.18 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.3, 136.5, 131.0, 129.3, 21.6, 20.8. MS (EI): *m/z* (%): 271 (12), 270 (63) [M^+], 151 (14), 150 (100), 149 (26), 135 (18), 119 (15), 105 (15), 91 (21), 77 (11).[S10]



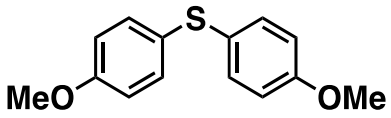
2-napthylsulfide (CAS No. 613-81-0, **1f**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (m, 2H), 7.71–7.81 (m, 6H), 7.42–7.49 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.0, 133.2, 132.5, 129.9, 129.0, 128.8, 127.9, 127.6, 126.8, 126.4. MS (EI): *m/z* (%): 287 (23), 286 (100) [M^+], 285 (54), 284 (28), 253 (20), 252 (27), 143 (10), 142 (14), 126 (14), 115 (12).[S13]



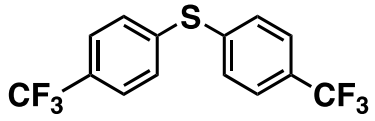
1,1′-thiobis[4-(1,1-dimethylethyl)benzene (CAS No. 52908-55-1, **1h**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.33 (m, 4H), 7.26–7.28 (m, 4H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 135.1, 133.3, 128.8, 37.1, 33.9. MS (EI): *m/z* (%): 299 (10), 298 (45) [M^+], 284 (21), 283 (100), 134 (12), 106 (22).



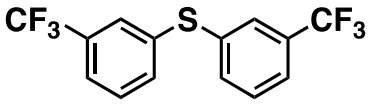
4-([1,1′-biphenyl]-4-ylthio)-1,1′-biphenyl (CAS No. 64554-57-0, **1i**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.59 (m, 8H), 7.42–7.46 (m, 8H), 7.34–7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.3, 140.1, 134.8, 131.4, 128.9, 127.9, 127.5, 127.0. MS (EI): *m/z* (%): 340 (8), 339 (26), 338 (100) [M^+], 337 (9), 321 (5), 306 (7), 261 (8), 260 (5), 184 (8), 169 (6), 152 (15), 115 (5).[S10]



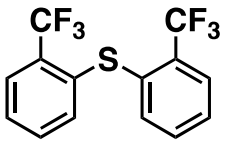
4,4'-dimethoxydiphenyl sulfide (CAS No. 3393-77-9, **1j**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.28 (m, 4H), 6.81–6.84 (m, 4H), 3.77 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 132.8, 127.5, 114.9, 55.4. MS (EI): *m/z* (%): 247 (17), 246 (100) [M^+], 231 (47), 215 (10), 214 (12), 203 (12), 199 (10), 188 (10), 171 (12), 115 (10).[S13]



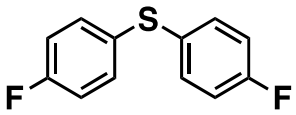
bis[(4-trifluoromethyl)phenyl]sulfide (CAS No. 90141-51-8, **1k**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.59 (m, 4H), 7.43–7.45 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.7, 131.2, 129.8 (q, J = 32.3 Hz), 126.4 (q, J = 3.6 Hz), 124.0 (q, J = 270.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −61.9. MS (EI): *m/z* (%): 323 (16), 322 (100) [M^+], 303 (13), 301 (17), 253 (13), 252 (11), 233 (27), 184 (13).[S13]



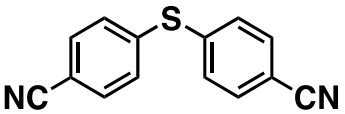
bis[(3-trifluoromethyl)phenyl]sulfide (CAS No. 1580-30-9, **1l**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (m, 2H), 7.53–7.54 (m, 2H), 7.48–7.50 (m, 2H), 7.43–7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 134.4, 132.1 (q, J = 33.4 Hz), 130.0, 127.8 (q, J = 3.6 Hz), 124.5 (q, J = 3.5 Hz), 123.7 (q, J = 270.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −62.1. MS (EI): *m/z* (%): 323 (15), 322 (100) [M^+], 303 (12), 301 (15), 233 (32), 184 (12).[S14]



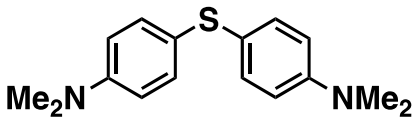
bis[(2-trifluoromethyl)phenyl]sulfide (CAS No. 1632046-24-2, **1m**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.74 (m, 2H), 7.35–7.43 (m, 4H), 7.22–7.24 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.8, 134.7, 132.5, 131.1 (q, J = 29.8 Hz), 127.5, 127.0 (q, J = 4.8 Hz), 123.6 (q, J = 273.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −60.5. MS (EI): *m/z* (%): 323 (14), 322 (100) [M^+], 301 (18), 283 (11), 234 (11), 233 (75), 184 (15), 95 (10).



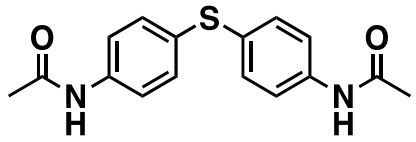
bis(4-fluorophenyl)sulfide (CAS No. 405-31-2, **1n**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.32 (m, 4H), 6.98–7.03 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.2 (d, J = 246.8 Hz), 133.0 (d, J = 7.1 Hz), 131.1 (d, J = 3.6 Hz), 116.4 (d, J = 22.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −113.6. MS (EI): *m/z* (%): 323 (16), 322 (100) [M^+], 303 (13), 301 (17), 253 (13), 252 (11), 233 (27), 184 (13). MS (EI): *m/z* (%): 224 (5), 223 (16), 222 (100) [M^+], 221 (49), 220 (20), 202 (18), 201 (15), 83 (23), 75 (14).[S13]



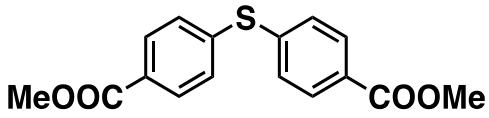
4,4′-thiobis[benzonitrile] (CAS No. 46836-99-1, **1r**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.63 (m, 4H), 7.41–7.43 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 133.0, 131.2, 118.2, 111.4. MS (EI): *m/z* (%): 237 (18), 236 (100) [M^+], 235 (46), 209 (15), 208 (18), 75 (12).[S15]



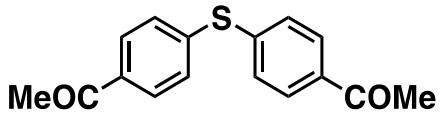
4,4′-thiobis[*N*,*N*-dimethylbenzenamine] (CAS No. 13604-44-9, **1s**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–7.25 (m, 4H), 6.63–6.66 (m, 4H), 2.92 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.6, 132.6, 123.0, 113.1, 40.5. MS (EI): *m/z* (%): 273 (19), 272 (100) [M^+], 241 (19), 240 (88), 225 (18), 224 (13), 152 (19), 136 (17), 120 (15), 119 (11).[S16]



***N*,*N*′-(thiodi-4,1-phenylene)bis[acetamide]** (CAS No. 7355-56-8, **1t**). ^{1}H NMR (500 MHz, DMSO): δ 10.11 (s, 2H), 7.56–7.59 (m, 4H), 7.22–7.25 (m, 4H), 2.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 138.7, 131.4, 128.6, 119.9, 24.0. MS (EI): *m/z* (%): 301 (21), 300 (100) [M^+], 259 (10), 258 (52), 217 (21), 216 (71), 215 (15), 184 (22), 183 (11), 124 (17).

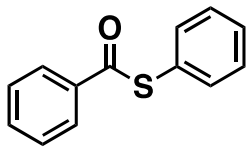


1,1′-dimethyl 4,4′-thiobis[benzoate] (CAS No. 14387-31-6, **1u**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96–8.00 (m, 4H), 7.37–7.40 (m, 4H), 3.92 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 140.8, 130.5, 130.4, 129.1, 52.3. MS (EI): *m/z* (%): 303 (18), 302 (100) [M^+], 272 (17), 271 (93), 184 (40), 120 (19), 92 (15).[S10]

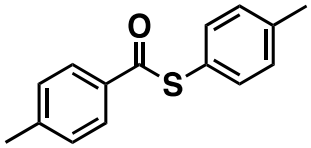


1,1′-(thiodi-4,1-phenylene)bis[ethanone] (CAS No. 2615-09-0, **1v**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.91 (m, 4H), 7.39–7.42 (m, 4H), 2.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 141.0, 135.9, 130.6, 129.2, 26.6. MS (EI): *m/z* (%): 271 (11), 270 (59) [M^+], 256 (17), 255 (100), 185 (13), 184 (18), 120 (11).[S15]

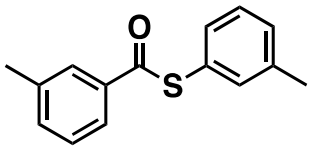
Spectral Data of Synthesized Thioester Substrates



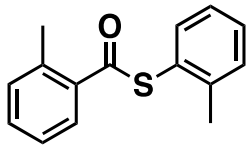
***S*-phenyl benzenecarbothioate** (CAS No. 884-09-3, **2a**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–8.05 (m, 2H), 7.60–7.63 (m, 1H), 7.45–7.54 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.2, 136.7, 135.1, 133.7, 129.5, 129.3, 128.8, 127.5, 127.4. MS (EI): *m/z* (%): 214 (2) [M^+], 109 (5), 106 (8), 105 (100), 78 (4), 77 (51), 65 (5), 51 (16), 50 (4), 39 (4).[S9]



***S*-(4-methylphenyl) 4-methylbenzenecarbothioate** (CAS No. 39248-95-8, **2b**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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).[S9]

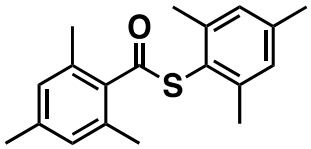


***S*-(3-methylphenyl) 3-methylbenzenecarbothioate** (CAS No. 98098-61-4, **2c**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.85 (m, 2H), 7.39–7.41 (m, 1H), 7.32–7.37 (m, 4H), 7.23–7.25 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.8, 139.4, 138.9, 137.0, 135.9, 134.7, 132.4, 130.7, 129.4, 128.9, 128.2, 127.4, 125.0, 21.6, 21.6. MS (EI): *m/z* (%): 242 (3) [M^+], 120 (9), 119 (100), 92 (3), 91 (39), 89 (3), 65 (14).[S9]

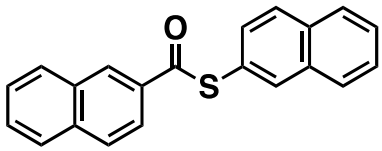


***S*-(2-methylphenyl) 2-methylbenzenecarbothioate** (CAS No. 101093-42-9, **2d**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96–7.98 (m, 1H), 7.49–7.51 (m, 1H), 7.41–7.44 (m, 1H), 7.36–7.38 (m, 2H), 7.26–7.33 (m, 3H), 2.49 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0, 142.5, 137.4, 137.1, 136.4,

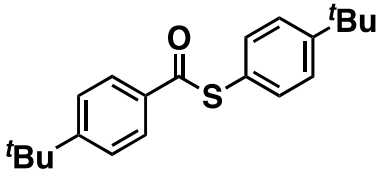
132.0, 131.8, 130.9, 130.3, 128.7, 127.7, 126.8, 125.9, 20.9, 20.8. MS (EI): *m/z* (%): 242 (0.7) [M^+], 120 (9), 119 (100), 92 (3), 91 (40), 89 (3), 77 (3), 65 (13).[S9]



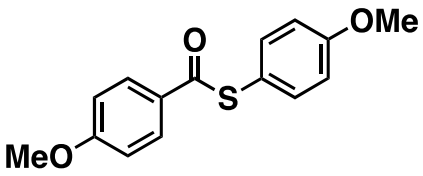
***S*-(2,4,6-trimethylphenyl) 2,4,6-trimethylbenzenecarbothioate** (CAS No. 81787-26-0, **2e**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–7.04 (m, 2H), 6.87–6.88 (m, 2H), 2.45 (s, 6H), 2.42 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.4, 142.7, 140.1, 139.4, 137.6, 134.0, 129.4, 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).[S9]



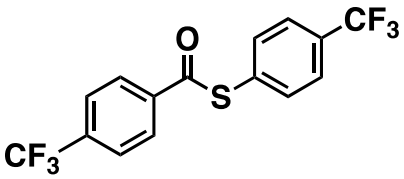
***S*-2-naphthalenyl 2-naphthalenecarbothioate** (CAS No. 98098-62-5, **2f**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65–8.66 (m, 1H), 8.09–8.11 (m, 1H), 8.05–8.07 (m, 1H), 8.01–8.03 (m, 1H), 7.86–7.95 (m, 5H), 7.52–7.66 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.3, 135.9, 135.0, 134.0, 133.7, 133.5, 132.5, 131.5, 129.7, 129.1, 128.9, 128.7, 128.0, 127.9, 127.9, 127.2, 127.0, 126.6, 124.8, 123.3. MS (EI): *m/z* (%): 314 (8) [M^+], 156 (12), 155 (100), 128 (7), 127 (61), 126 (7), 115 (11), 77 (6).[S9]



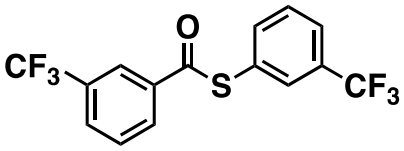
***S*-[4-(1,1-dimethylethyl)phenyl] 4-(1,1-dimethylethyl)benzenecarbothioate** (**2h**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95–2.99 (m, 2H), 7.41–7.51 (m, 6H), 1.35 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.1, 157.4, 152.6, 134.7, 134.1, 127.4, 126.4, 125.7, 124.0, 35.2, 34.8, 31.2, 31.1. MS (EI): *m/z* (%): 326 (2) [M^+], 162 (11), 161 (100), 146 (8), 118 (8), 91 (6).



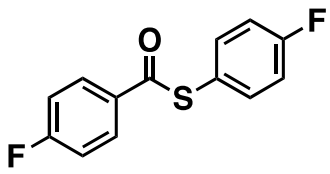
***S*-(4-methoxyphenyl) 4-methoxybenzenecarbothioate** (CAS No. 98098-60-3, **2j**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99–8.00 (m, 2H), 7.40–7.41 (m, 2H), 6.93–6.98 (m, 4H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.6, 164.1, 160.8, 136.9, 129.8, 129.6, 118.3, 115.0, 114.0, 55.7, 55.5. MS (EI): *m/z* (%): 274 (3) [M^+], 139 (3), 136 (9), 135 (100), 107 (11), 92 (10), 77 (17), 64 (5).[S9]



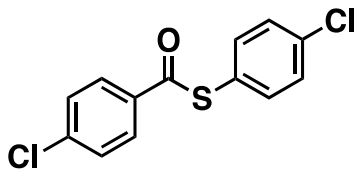
***S*-[4-(trifluoromethyl)phenyl] 4-(trifluoromethyl)benzenecarbothioate** (**2k**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12–8.14 (m, 2H), 7.78–7.79 (m, 2H), 7.73–7.74 (m, 2H), 7.65–7.67 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.2, 139.0, 135.2, 131.9 (q, J = 32.3 Hz), 131.3, 130.8 (q, J = 47.6 Hz), 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}F NMR (470 MHz, $CDCl_3$): −62.2, −62.4. MS (EI): *m/z* (%): 350 (1) [M^+], 174 (8), 173 (100), 145 (45), 125 (5), 95 (7).[S9]



***S*-[3-(trifluoromethyl)phenyl] 3-(trifluoromethyl)benzenecarbothioate** (**2l**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 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}C NMR (125 MHz, $CDCl_3$): δ 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}F NMR (470 MHz, $CDCl_3$): −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).[S9]

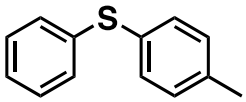


***S*-(4-fluorophenyl) 4-fluorobenzenecarbothioate** (CAS No. 100045-97-4, **2n**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–8.07 (m, 2H), 7.46–7.50 (m, 2H), 7.14–7.19 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.7, 166.2 (d, J = 254.0 Hz), 163.7 (d, J = 249.1 Hz), 137.2 (d, J = 8.4 Hz), 132.7 (d, J = 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}F NMR (470 MHz, $CDCl_3$): −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).[S9]

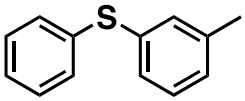


***S*-(4-chlorophenyl) 4-chlorobenzenecarbothioate** (CAS No. 6310-31-2, **2o**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93–7.96 (m, 2H), 7.45–7.48 (m, 2H), 7.43 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.9, 140.7, 136.6, 136.5, 135.0, 129.9, 129.5, 129.2, 125.7. MS (EI): *m/z* (%): 286 (0.3), 285 (0.2), 284 (1), 283 (0.3), 282 (2) [M^+], 141 (32), 140 (8), 139 (100), 113 (10), 111 (31), 108 (6), 76 (4), 75 (15), 50 (4).[S9]

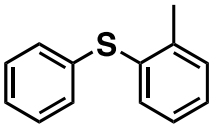
Spectral Data of Products



phenyl *p*-tolyl sulfide (CAS No. 3699-01-2, **1ab**): 82% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.3 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (calculated by calibration curve). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5, 137.1, 132.2, 131.3, 130.0, 129.7, 129.0, 126.3, 21.1. MS (EI): *m/z* (%): 202 (5), 201 (16), 200 (100) [M^+], 199 (26), 186 (7), 185 (42), 184 (33), 167 (14), 165 (9), 152 (9), 121 (5), 99 (13), 92 (5), 91 (30), 89 (5), 77 (12), 65 (17), 63 (6), 51 (12), 45 (6), 39 (9).[S17]

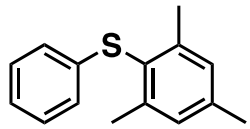


phenyl *m*-tolyl sulfide (CAS No. 13865-48-0, **1ac**): 78% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.2 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (estimated to be equal to that of **1ab**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 136.1, 135.2, 131.8, 130.7, 129.1, 129.0, 128.3, 128.0, 126.8, 21.2. MS (EI): *m/z* (%): 202 (5), 201 (16), 200 (100) [M^+],199 (23), 186 (7), 185 (44), 184 (40), 167 (6), 165 (7), 152 (7), 99 (11), 91 (9), 77 (8), 65 (14), 63 (5), 51 (9).[S17]

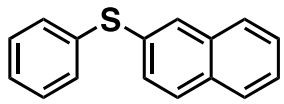


phenyl *o*-tolyl sulfide (CAS No. 13963-35-4, **1ad**): 74% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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 (estimated to be equal to that of **1ab**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 136.1, 133.7, 133.0, 130.6, 129.6, 129.1, 127.9, 126.7, 126.3, 20.6. MS (EI): *m/z* (%): 202 (6), 201 (15), 200 (100) [M^+], 199 (12), 197

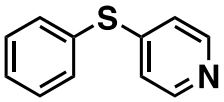
(5), 185 (22), 184 (17), 167 (10), 166 (5), 165 (13), 152 (7), 123 (6), 122 (38), 121 (26), 99 (13), 91 (27), 89 (9), 78 (8), 77 (10), 65 (18), 63 (6), 51 (12).[S18]



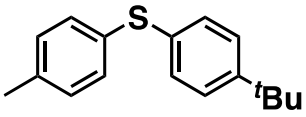
1,3,5-trimethyl-2-(phenylthio)benzene (CAS No. 33667-80-0, **1ae**): 63% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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), 2.43 (estimated by **1ab** and the effective carbon number concept). ^{13}C NMR (125 MHz, $CDCl_3$): 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 (18), 228 (100) [M^+], 213 (9), 198 (9), 195 (9), 180 (12), 179 (7), 178 (5), 165 (8), 151 (7), 150 (46), 149 (15), 135 (9), 119 (14), 117 (7), 115 (11), 106 (5), 105 (9), 104 (5), 103 (6), 99 (5), 91 (28), 78 (5), 77 (13), 65 (8), 51 (7), 45 (5), 41 (5), 39 (6).[S19]



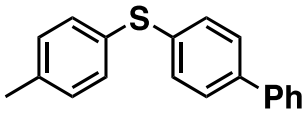
2-(phenylthio)naphthalene (CAS No. 7570-96-9, **1af**): 75% GC yield (53% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 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), 2.58 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.84 (m, 1H), 7.70–7.80 (m, 3H), 7.43–7.48 (m, 2H), 7.36–7.41 (m, 3H), 7.27–7.32 (m, 2H), 7.23–7.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.8, 133.8, 133.0, 132.3, 130.9, 129.9, 129.2, 128.8, 128.7, 127.7, 127.4, 127.1, 126.6, 126.2. MS (EI): *m/z* (%): 252 (6), 251 (20), 250 (100) [M^+], 249 (19), 236 (8), 235 (39), 234 (38), 217 (8), 215 (8), 202 (13), 127 (5), 126 (5), 125 (5), 124 (10), 117 (8), 115 (12), 91 (6), 77 (5).[S20]



4-(phenylthio)pyridine (CAS No. 33399-48-3, **1ag**): 66% GC yield (74% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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), 1.65 (calculated by calibration curve). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33–8.34 (m, 2H), 7.54–7.56 (m, 2H), 7.44–7.46 (m, 3H), 6.93–6.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3, 149.4, 135.2, 129.9, 129.7, 129.4, 120.8. MS (EI): *m/z* (%): 189 (5), 188 (16), 187 (100) [M^+], 186 (71), 160 (7), 154 (7), 115 (15), 110 (5), 109 (6), 92 (5), 78 (8), 77 (9), 65 (7), 51 (33), 50 (6), 39 (7).[S21]

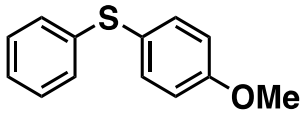


1-(1,1-dimethylethyl)-4-[(4-methylphenyl)thio]benzene (CAS No. 875713-05-6, **1bh**): 70% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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 1,3,5-trimethoxybenzene, internal standard), 2.77 (estimated by **1ab** and the effective carbon number concept). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 136.8, 132.7, 131.6, 131.0, 130.2, 129.9, 126.1, 34.5, 31.3, 21.1. MS (EI): *m/z* (%): 257 (10), 256 (52) [M^+], 243 (6), 242 (18), 241 (100), 213 (7), 123 (21), 120 (5), 118 (6), 117 (10), 115 (6), 106 (9), 91 (7), 79 (5).[S22]

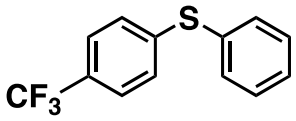


4-[(4-methylphenyl)thio]-1,1′-biphenyl (CAS No. 1361950-30-2, **1bi**): 63% GC yield (65% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 17.0 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 3.10 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500

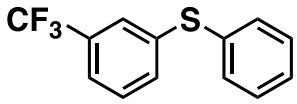
MHz, $CDCl_3$): δ 7.53–7.55 (m, 2H), 7.47–7.49 (m, 2H), 7.39–7.42 (m, 2H), 7.30–7.35 (m, 5H), 7.14–7.15 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4, 139.3, 137.7, 136.3, 132.4, 131.2, 130.1, 130.0, 128.8, 127.7, 127.3, 126.9, 21.1. MS (EI): *m/z* (%): 278 (7), 277 (22), 276 (100) [M^+], 275 (14), 261 (19), 260 (16), 244 (5), 243 (5), 228 (6), 184 (8), 152 (12), 115 (5), 91 (9), 65 (5).[S23]



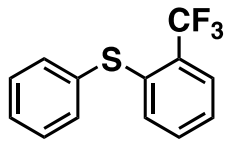
1-methoxy-4-(phenylthio)benzene (CAS No. 5633-57-8, **1aj**): 69% GC yield (74% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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), 1.94 (estimated by **1ab** and the effective carbon number concept). ^1H NMR (500 MHz, $CDCl_3$): δ 7.39−7.42 (m, 2H), 7.20−7.24 (m, 2H), 7.11−7.17 (m, 3H), 6.87−6.90 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 138.6, 135.3, 128.9, 128.2, 125.7, 124.3, 115.0, 55.3. MS (EI): *m/z* (%): 218 (6), 217 (15), 216 (100) [M^+], 215 (19), 202 (8), 201 (55), 200 (5), 185 (7), 184 (7), 173 (8), 172 (5), 171 (9), 139 (5), 129 (15), 128 (6), 77 (10), 63 (5), 51 (10), 45 (21).[S23]



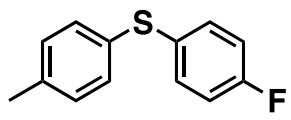
1-(phenylthio)-4-(trifluoromethyl)benzene (CAS No. 53451-90-4, **1ka**): 74% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 9.4 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (estimated by **1ab** and the effective carbon number concept). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9, 133.5, 132.5, 129.7, 128.7, 128.3, 128.1 (q, J = 33.5 Hz), 125.8 (q, J = 3.6 Hz), 124.1 (q, J = 270.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −61.7. MS (EI): *m/z* (%): 256 (6), 255 (16), 254 (100) [M^+], 253 (16), 235 (7), 233 (25), 186 (6), 185 (32), 184 (26), 109 (5), 77 (13), 69 (5), 65 (5), 51 (12).[S18]



1-(phenylthio)-3-(trifluoromethyl)benzene (CAS No. 2715-07-3, **1la**): 72% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 10 °C·min^{-1} (20 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 13.8 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (estimated by **1ab** and the effective carbon number concept). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.5, 133.5, 132.7, 132.5, 131.5 (q, J = 32.1 Hz), 129.6, 129.5, 128.2, 126.2 (q, J = 3.6 Hz), 123.8 (q, J = 270.8 Hz), 123.2 (q, J = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −62.0. MS (EI): *m/z* (%): 256 (6), 255 (16), 254 (100) [M^+], 253 (13), 235 (7), 234 (6), 233 (28), 186 (6), 185 (34), 184 (28), 152 (5), 109 (6), 77 (17), 67 (6), 65 (8), 51 (20), 50 (6).[S18]

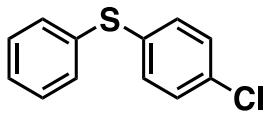


1-(phenylthio)-2-(trifluoromethyl)benzene (CAS No. 61405-41-2, **1am**): 69% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.3 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.10 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.59 (m, 4H), 7.43–7.45 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.7, 133.8, 133.0, 132.4, 132.0, 129.5, 128.2, 126.7 (q, J = 6.0 Hz), 126.2, 123.8 (q, J = 271.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): −59.9. MS (EI): *m/z* (%): 256 (6), 255 (15), 254 (100) [M^+], 253 (6), 234 (5), 233 (30), 215 (7), 186 (6), 185 (41), 184 (29), 109 (10), 108 (5), 77 (14), 69 (7), 65 (10), 51 (18), 50 (5).[S18]

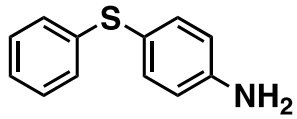


1-fluoro-4-[(4-methylphenyl)thio]benzene (CAS No. 42917-47-5, **1bn**): 64% GC yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (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

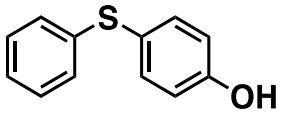
standard), 2.10 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.31 (m, 2H), 7.21–7.24 (m, 2H), 7.10–7.13 (m, 2H), 6.96–7.01 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0 (d, J = 245.6 Hz), 137.3, 132.8 (d, J = 8.4 Hz), 132.2, 131.5 (d, J = 3.6 Hz), 131.2, 130.0, 116.2 (d, J = 21.4 Hz), 21.1; ^{19}F NMR (470 MHz, $CDCl_3$): −114.2. MS (EI): *m/z* (%): 220 (6), 219 (16), 218 (100) [M^+], 217 (22), 204 (5), 203 (32), 202 (26), 185 (16), 183 (10), 108 (10), 98 (6), 91 (24), 83 (5), 65 (11).[S18]



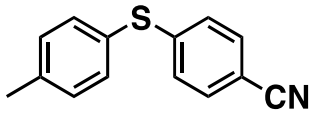
1-chloro-4-(phenylthio)benzene (CAS No. 13343-26-5, **1ao**): 45% GC yield (16% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 10.8 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.94 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.35 (m, 4H), 7.22–7.29 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.1, 134.7, 133.0, 132.0, 131.3, 129.34, 129.32, 127.4. MS (EI): *m/z* (%): 223 (5), 222 (34), 221 (16), 220 (100) [M^+], 219 (10), 186 (12), 185 (63), 184 (65), 183 (6), 152 (13), 139 (6), 109 (6), 108 (11), 92 (22), 79 (9), 77 (13), 75 (9), 69 (7), 65 (8), 63 (5), 51 (21), 50 (7), 39 (5).[S23]



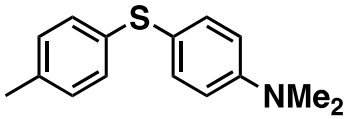
4-(phenylthio)benzenamine (CAS No. 1135-14-4, **1ap**): 62% GC yield (53% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 12.1 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.85 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.32 (m, 2H), 7.18–7.21 (m, 2H), 7.07–7.13 (m, 3H), 6.64–6.67 (m, 2H), 3.78 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 139.7, 136.1, 128.8, 127.3, 125.2, 120.4, 115.8. MS (EI): *m/z* (%): 203 (5), 202 (16), 201 (100) [M^+], 200 (52), 199 (8), 184 (6), 169 (19), 168 (5), 167 (5), 124 (16), 99 (5), 80 (18), 65 (8), 51 (7), 39 (6).[S24]



4-(phenylthio)phenol (CAS No. 5633-55-6, **1aq**): 50% GC yield (51% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 11.7 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.56 (calculated by calibration curve). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.37 (m, 2H), 7.21–7.25 (m, 2H), 7.12–7.18 (m, 3H), 6.80–6.84 (m, 2H), 4.58 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 138.4, 135.5, 128.9, 128.3, 125.9, 124.6, 116.5. MS (EI): *m/z* (%): 204 (5), 203 (15), 202 (100) [M^+], 201 (36), 185 (9), 184 (6), 183 (17), 173 (8), 171 (6), 170 (8), 169 (7), 141 (13), 139 (5), 129 (5), 125 (5), 115 (7), 97 (6), 92 (5), 81 (5), 77 (8), 69 (5), 65 (7), 63 (5), 53 (6), 51 (12), 45 (9), 39 (10).[S24]

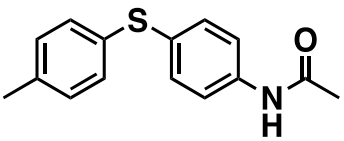


4-[(4-methylphenyl)thio]benzonitrile (CAS No. 104128-50-9, **1br**): 71% GC yield (61% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 12.7 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.17 (calculated by calibration curve). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.46 (m, 2H), 7.40–7.42 (m, 2H), 7.23–7.26 (m, 2H), 7.10–7.13 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 139.9, 134.9, 132.3, 130.8, 126.8, 126.7, 118.9, 108.3, 21.3. MS (EI): *m/z* (%): 227 (6), 226 (17), 225 (100) [M^+], 224 (22), 211 (5), 210 (31), 209 (17), 192 (22), 190 (6), 111 (10), 91 (36), 89 (6), 77 (7), 65 (18), 63 (7), 51 (6).[S25]

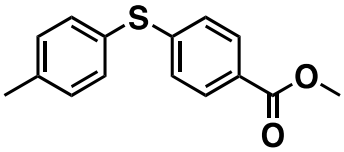


***N*,*N*-dimethyl-4-[(4-methylphenyl)thio]benzenamine** (CAS No. 2849-63-2, **1bs**): 48% GC yield (37% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 13.6 min; relative sensitivity for quantification (vs 1,3,5-

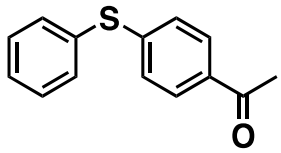
trimethoxybenzene, internal standard), 2.39 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.37 (m, 2H), 7.00–7.06 (m, 4H), 6.67–6.70 (m, 2H), 2.97 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 136.3, 135.6, 135.2, 129.7, 127.9, 118.8, 113.1, 40.5, 21.0. MS (EI): *m/z* (%): 245 (6), 244 (18), 243 (100) [M^+], 242 (14), 228 (8), 227 (10), 226 (6), 212 (13), 211 (38), 210 (33), 195 (9), 184 (10), 152 (11), 136 (5), 121 (6), 120 (7), 105 (5), 91 (5), 77 (5), 65 (5).[S26]



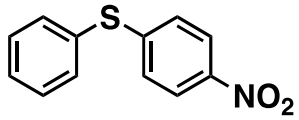
***N*-[4-[(4-methylphenyl)thio]phenyl]acetamide** (CAS No. 339096-10-5, **1bt**): 44% isolated yield (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 16.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.54 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (brs, 1H), 7.41–7.44 (m, 2H), 7.25–7.27 (m, 2H), 7.20–7.22 (m, 2H), 7.08–7.10 (m, 2H), 2.32 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 137.1, 136.9, 132.3, 131.7, 131.4, 131.1, 130.0, 120.6, 24.6, 21.1. MS (EI): *m/z* (%): 259 (6), 258 (18), 257 (100) [M^+], 217 (5), 216 (16), 215 (78), 214 (27), 200 (23), 199 (10), 184 (5), 183 (18), 182 (8), 124 (7), 91 (6), 65 (8).[S24]



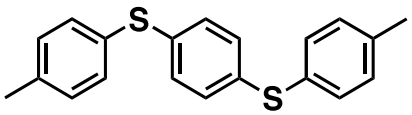
methyl 4-[(4-methylphenyl)thio]benzoate (CAS No. 1818399-49-3, **1bu**): 75% GC yield (68% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 13.3 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 2.27 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.88 (m, 2H), 7.38–7.41 (m, 2H), 7.20–7.22 (m, 2H), 7.13–7.15 (m, 2H), 3.87 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 145.4, 139.2, 134.4, 130.5, 130.0, 128.2, 127.0, 126.7, 52.0, 21.3. MS (EI): *m/z* (%): 260 (6), 259 (18), 258 (100) [M^+], 228 (10), 227 (63), 225 (5), 199 (19), 198 (7), 197 (8), 185 (6), 184 (42), 165 (5), 113 (5), 91 (9), 77 (5), 65 (5).[S27]



1-[4-(phenylthio)phenyl]ethanone (CAS No. 10169-55-8, **1av**): 65% GC yield (71% isolated yield) (Fig. 2a) (The isolated yield was shown after the subtraction of the amounts of residual solvents calculated from ^{1}H NMR). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 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), 2.10 (calculated by calibration curve). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.83 (m, 2H), 7.47–7.50 (m, 2H), 7.36–7.42 (m, 3H), 7.20–7.22 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 144.9, 134.5, 133.9, 132.1, 129.7, 128.9, 128.8, 127.5, 26.5. MS (EI): *m/z* (%): 229 (12), 228 (72) [M^+], 215 (6), 214 (15), 213 (100), 185 (16), 184 (58), 152 (11), 139 (5), 115 (5), 109 (6), 106 (6), 77 (6), 67 (5), 65 (8), 51 (9), 50 (5).[S22]



4-nitrophenyl phenyl sulfide (CAS No. 1952-97-6, **1aw**): 91% GC yield (71% isolated yield) (Fig. 2a). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 10 min, injection temp., 280 °C detection temp., 280 °C; retention time, 12.6 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 1.95 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–8.07 (m, 2H), 7.52–7.56 (m, 2H), 7.45–7.48 (m, 3H), 7.16–7.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.5, 145.3, 134.7, 130.4, 130.0, 129.7, 126.7, 124.0. MS (EI): *m/z* (%): 233 (5), 232 (14), 231 (100) [M^+], 202 (6), 201 (37), 200 (8), 186 (5), 185 (21), 184 (81), 183 (7), 152 (17), 139 (10), 129 (6), 115 (9), 109 (9), 92 (8), 77 (10), 69 (10), 65 (14), 63 (8), 51 (14), 50 (8).[S22]



1,4-bis[(4-methylphenyl)thio]benzene (CAS No. 55709-45-0, **1bab**): 55% GC yield (44% isolated yield). GC conditions and analysis: InertCap5 capillary column, 0.25 mm × 60 m, GL Science Inc.; carrier gas (N_2) flow rate, 1.7 mL·min^{-1}; initial column temp., 80 °C final column temp., 280 °C, progress rate, 20 °C·min^{-1} (10 min), 280 °C for 20 min, injection temp., 280 °C detection temp., 280 °C; retention time, 22.4 min; relative sensitivity for quantification (vs 1,3,5-trimethoxybenzene, internal standard), 3.20 (estimated by **1ab** and the effective carbon number concept). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.29 (m, 4H), 7.11–7.15 (m, 8H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 135.4, 132.3, 130.9, 130.2, 130.2, 21.1. MS (EI): *m/z* (%): 324 (11), 323 (22), 322 (100) [M^+], 200 (12), 199 (80), 198 (9), 197 (13), 184 (23), 166 (7), 165 (8), 91 (7), 65 (8).[S28]

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Supplementary Figures

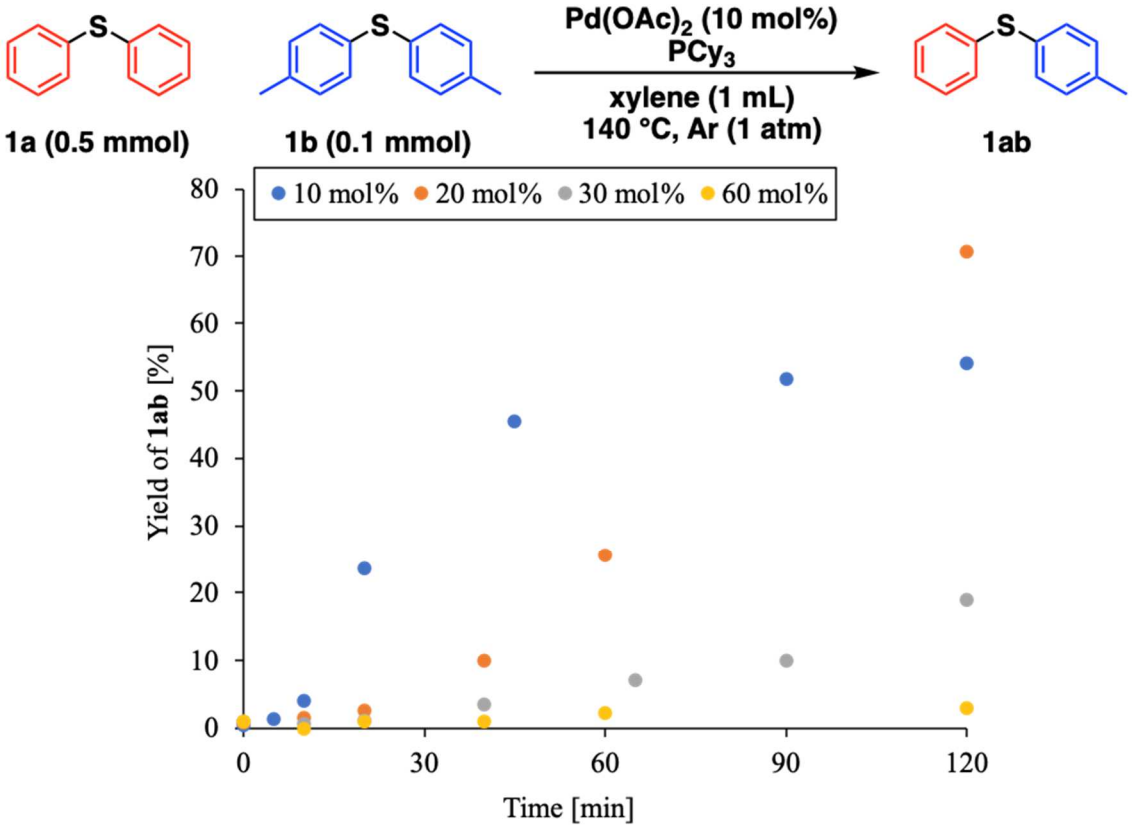


Fig. S1. Reaction profiles of C–S/C–S cross-metathesis of diaryl thioethers in the presence of different amounts of PCy_3. Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3, xylene (1 mL), Ar (1 atm) in a test tube.

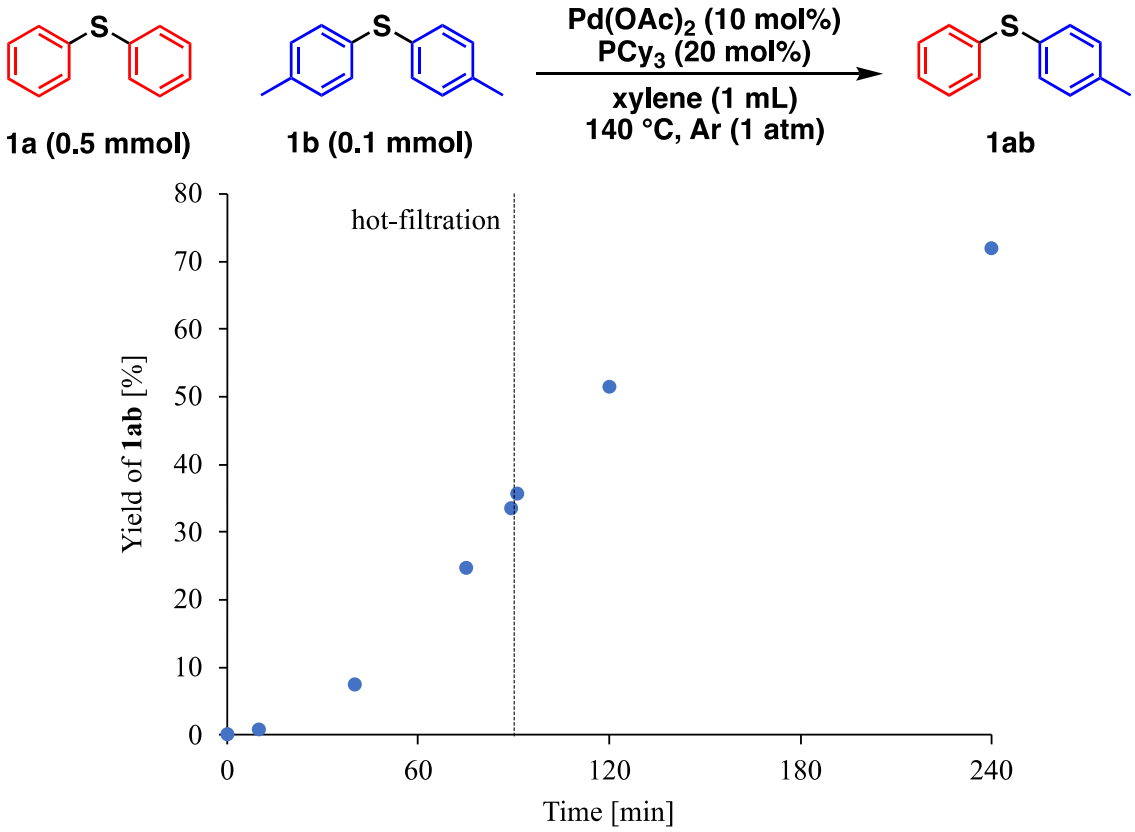


Fig. S2. Effect of hot-filtration on the metathesis between **1a** and **1b**. Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), xylene (1 mL), Ar (1 atm) in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

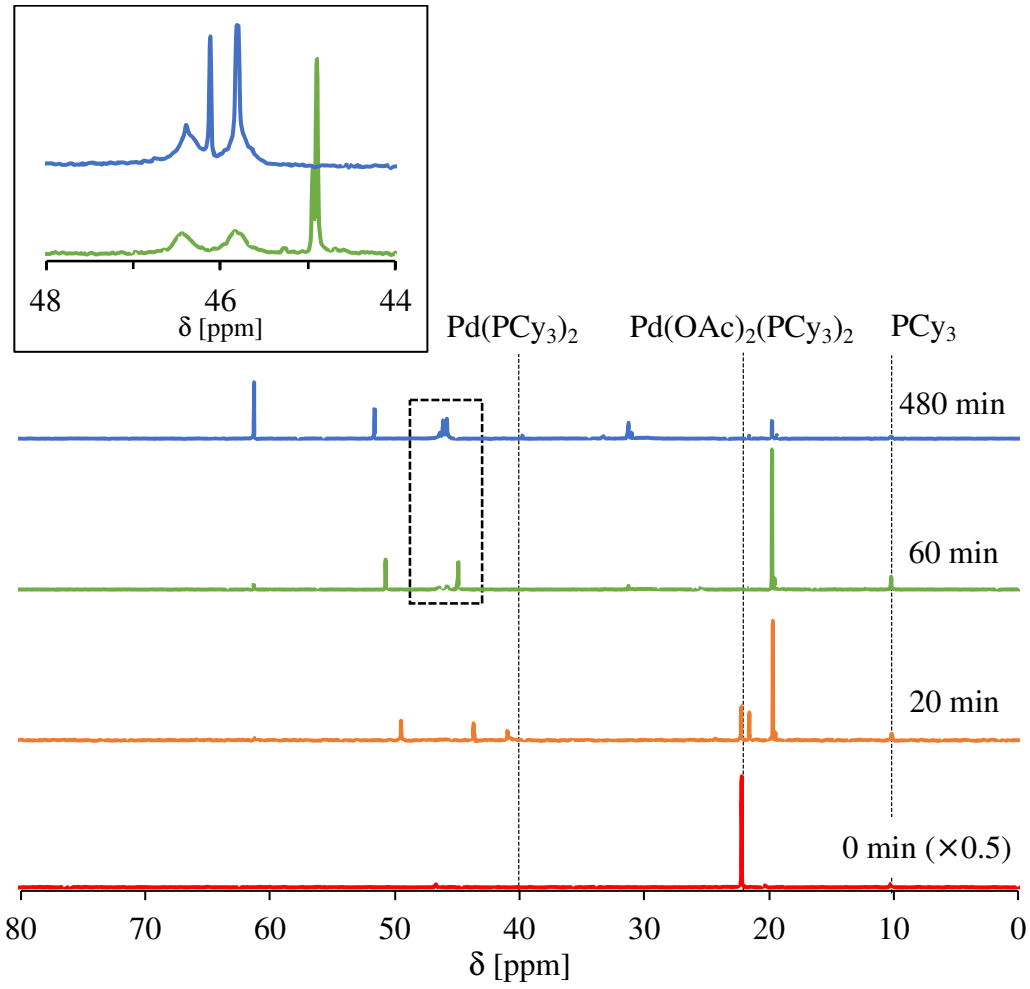


Fig. S3. ^{31}P NMR spectra of the reaction solutions. Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), xylene (1 mL), Ar (1 atm) in a test tube.

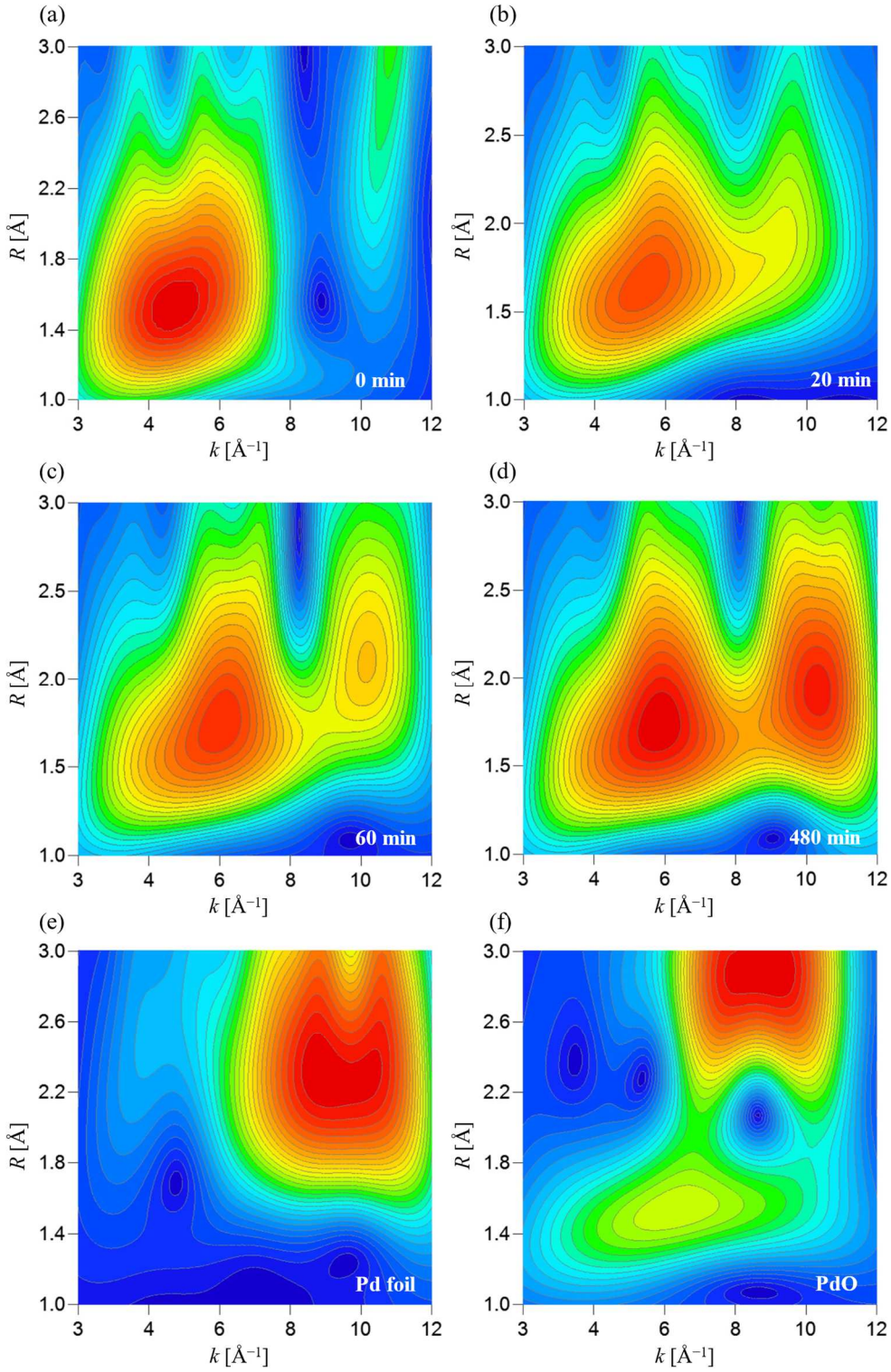


Fig. S4. The wavelet transformed Pd K-edge EXAFS oscillations of reaction solutions (a) 0 min, (b) 20 min, (c) 60 min, and (d) 480 min after starting the reaction, and those of (e) Pd foil and (f) PdO are also shown.

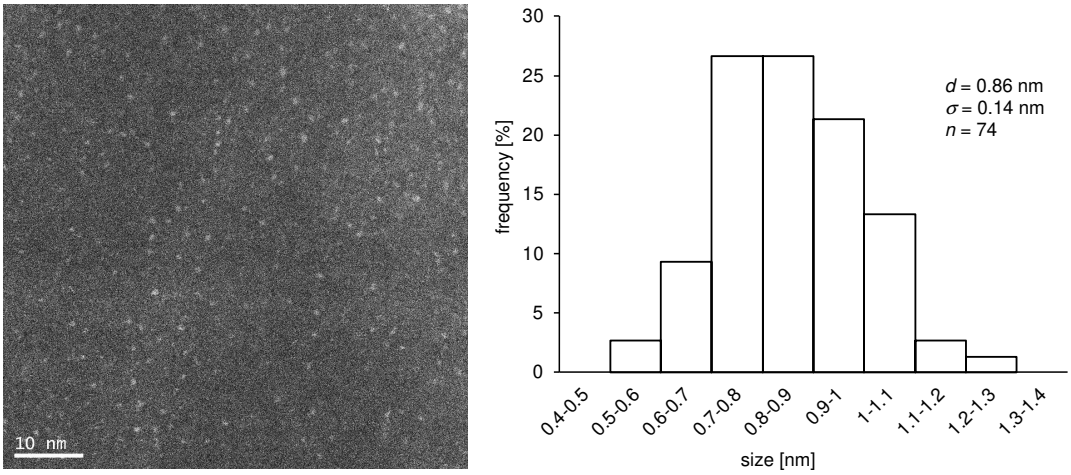


Fig. S5. HAADF-STEM image of Pd nanoclusters on Pd/RGO and size distribution of Pd nanoclusters.

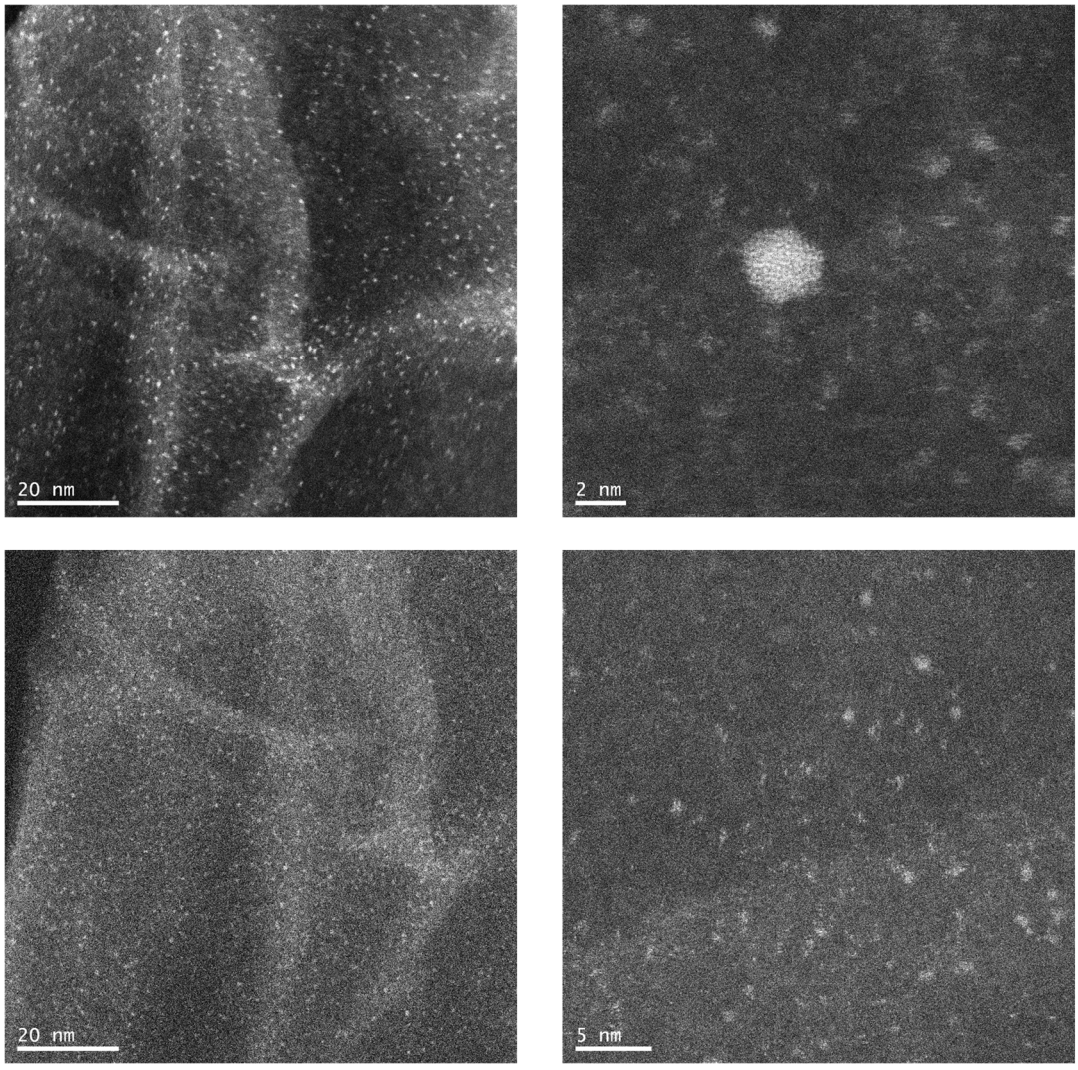


Fig. S6. HAADF-STEM images of Pd/RGO.

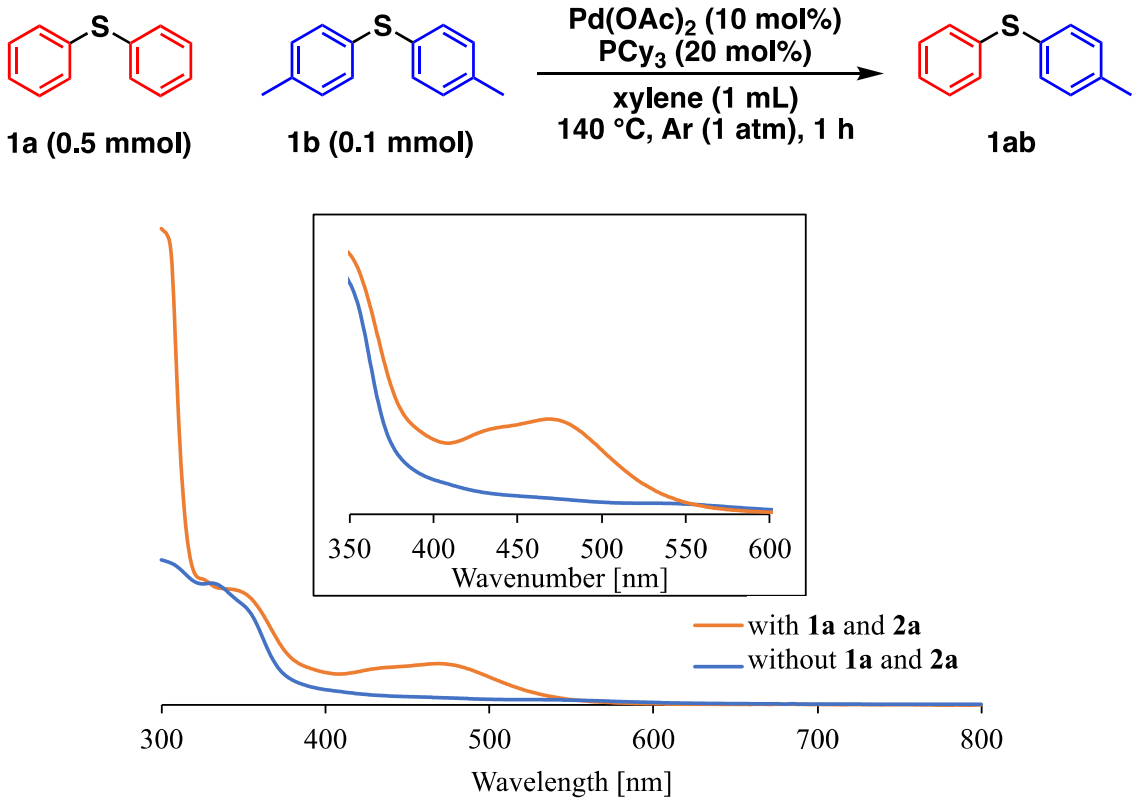


Fig. S7. UV-Vis spectra of the reaction solutions in the presence or absence of **1a** and **1b**. Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), xylene (1 mL), Ar (1 atm), 1 h in a test tube.

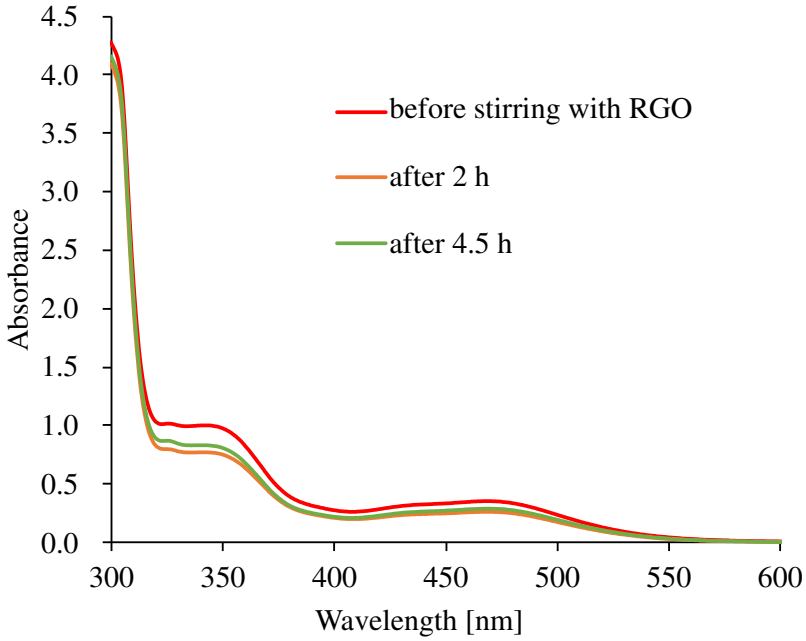


Fig. S8. UV-Vis spectra of the reaction solutions (filtrates) before and after stirring with RGO at room temperature for 2 h and 4.5 h. Reaction conditions: (before stirring with RGO) **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), xylene (1 mL), Ar (1 atm), 140°C, 1.5 h.

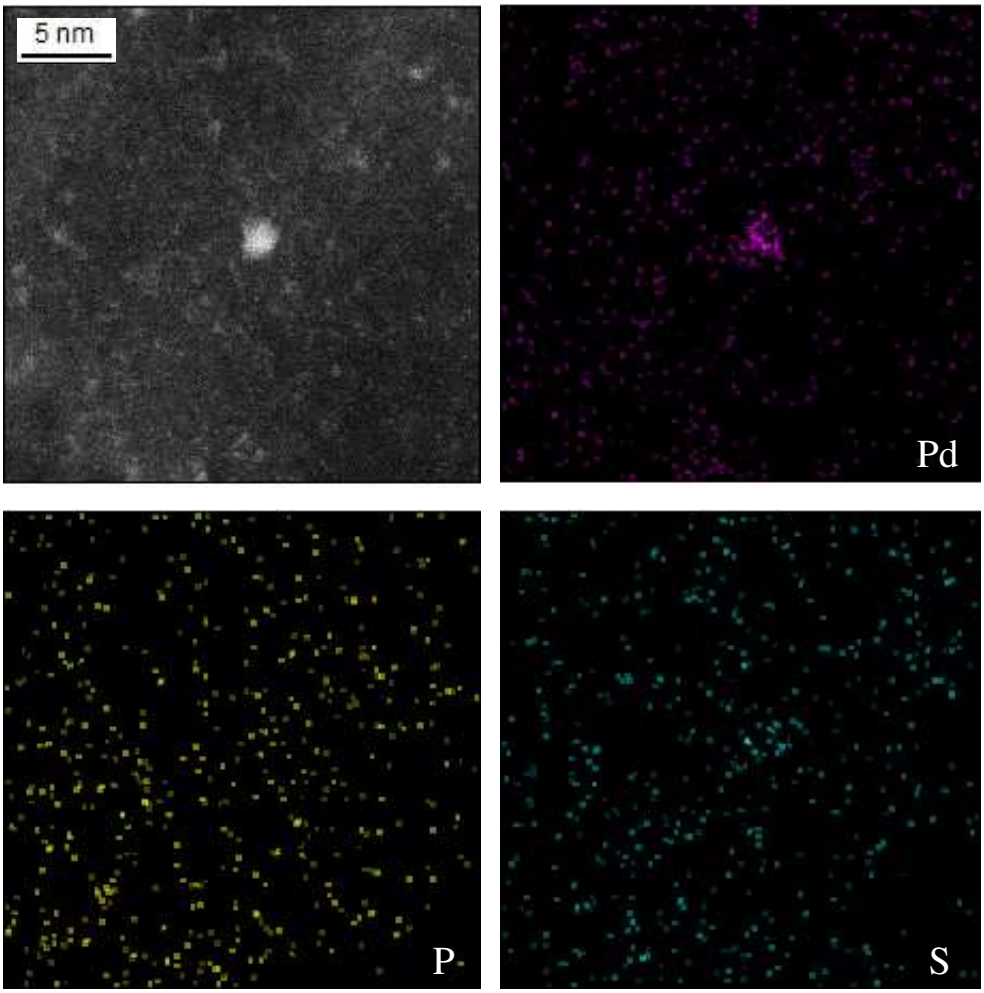
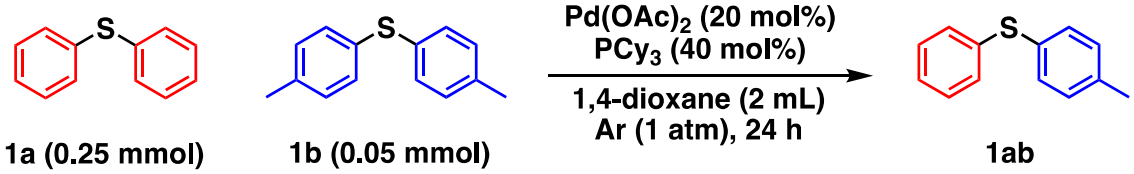


Fig. S9. HAADF-STEM images and STEM-EDS mappings of Pd/RGO showing the distribution of Pd in magenta, P in yellow, and S in cyan.

Supplementary Tables

Table S1. Effect of reaction temperatures[a]

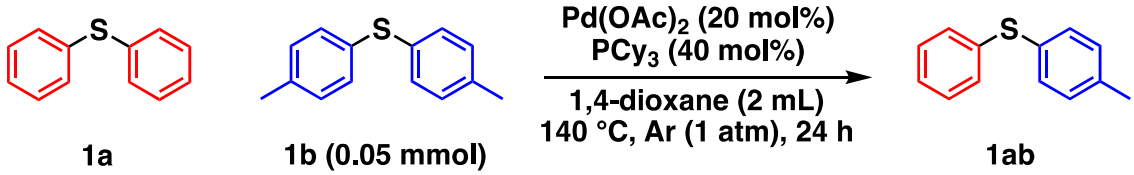


1a (0.25 mmol) **1b (0.05 mmol)** **1ab**

entry	temperature (°C)	conv. (%)		yield (%)
		1a	**1b**	**1ab**
1	120	18	81	76
2	140	17	88	82
3	160	19	78	71

[a]Reaction conditions: **1a** (0.25 mmol), **1b** (0.05 mmol), $Pd(OAc)_2$ (20 mol%), PCy_3 (40 mol%), dioxane (2 mL), 24 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Effect of ratios of **1a** and **1b**[a]

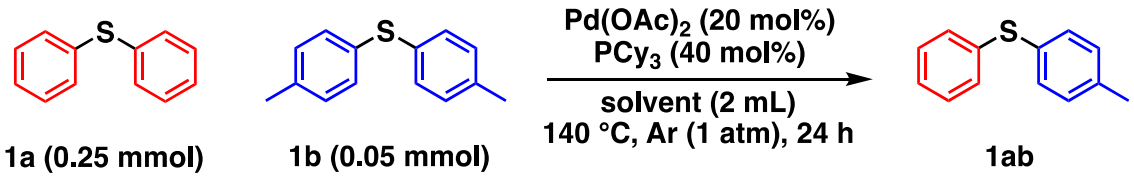


1a **1b (0.05 mmol)** **1ab**

entry	**1a** amount (mmol)	conv. (%)		yield (%)
		1a	**1b**	**1ab**
1	0.07	58	58	49
2	0.15	35	77	69
3	0.25	17	88	82
4	0.40	2	54	51

[a]Reaction conditions: **1a**, **1b** (0.05 mmol), $Pd(OAc)_2$ (20 mol%), PCy_3 (40 mol%), dioxane (2 mL), 140 °C, 24 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Effect of solvents[a]

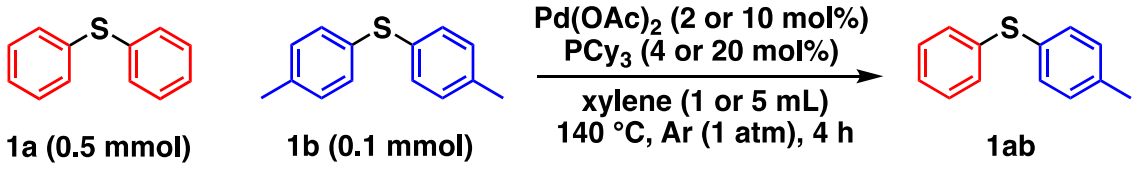


1a (0.25 mmol) **1b (0.05 mmol)** **1ab**

entry	solvent	conv. (%)		yield (%)
		1a	**1b**	**1ab**
1	1,4-dioxane	17	88	82
2	MCH	20	81	74
3	xylene	19	82	73
4	DMA	12	52	40

[a]Reaction conditions: **1a** (0.25 mmol), **1b** (0.05 mmol), $Pd(OAc)_2$ (20 mol%), PCy_3 (40 mol%), solvent (2 mL), 140 °C 24 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S4. Effect of Pd catalyst amount and concentration.[a]

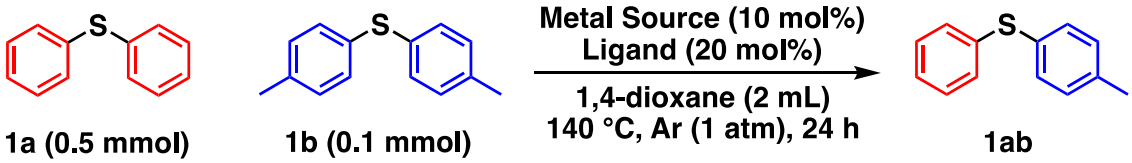


1a (0.5 mmol) **1b (0.1 mmol)** **1ab**

entry	catalyst (mol%)	solvent (mL)	conv. (%)		yield (%)	TOF (h^{-1})
			1a	**1b**	**1ab**	
1	10	1	17	84	82	2.1
2	10	5	15	59	52	1.3
3	2	1	10	18	9	1.1

[a]Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (2 or 10 mol%), PCy_3 (2 equivalent to $Pd(OAc)_2$), xylene (1 or 5 mL), 140 °C, 4 h in test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. TOF: turnover frequency based on Pd, calculated via dividing the turnover numbers by the reaction times.

Table S5. Effect of active metal species[a]

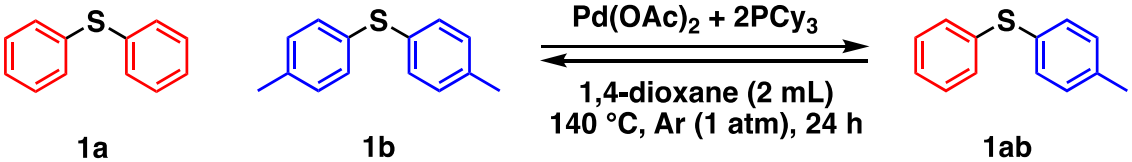


1a (0.5 mmol) **1b (0.1 mmol)** **1ab**

entry	metal source	ligand	conv. (%)		yield (%)
			1a	**1b**	**1ab**
1	$Pd(OAc)_2$	PCy_3	24	85	77
2	$Ni(cod)_2$	PCy_3	4	10	1
3	$Ni(cod)_2$	IPr	4	8	<1
4	$[Rh(cod)Cl]_2$	PCy_3	<1	<1	<1
5	$[Rh(cod)Cl]_2$	IPr	<1	<1	<1

[a]Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), metal source (10 mol%), ligand (20 mol%), 1,4-dioxane (2 mL), Ar (1 atm), 140 °C, 24 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S6. Forward and reverse reactions of the metathesis of **1a**, **1b**, and **1ab**[a]

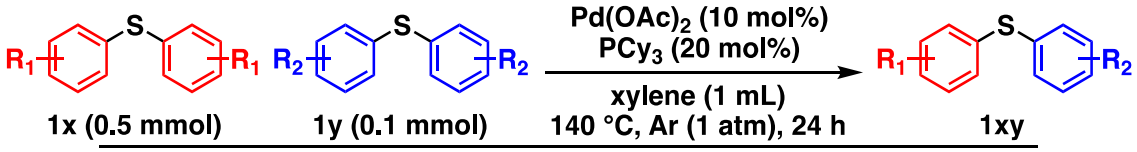


1a **1b** **1ab**

entry			amount (mmol)		
			1a	**1b**	**1ab**
1	forward	initial	0.1	0.1	0
		after 24 h	0.048	0.047	0.099 (50% yield)
2	reverse	initial	0	0	0.2
		after 24 h	0.044	0.043	0.091
3	forward	initial	0.5	0.1	0
		after 24 h	0.38	0.015	0.16 (77% yield)

[a]Reaction conditions: **1a** and **1b** or **1ab**, $Pd(OAc)_2$ (0.01 mmol), PCy_3 (0.02 mmol), 1,4-dioxane (2 mL), 140 °C 24 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S7. The amounts of thioethers after the transformations demonstrated in Fig. 2a.[a]

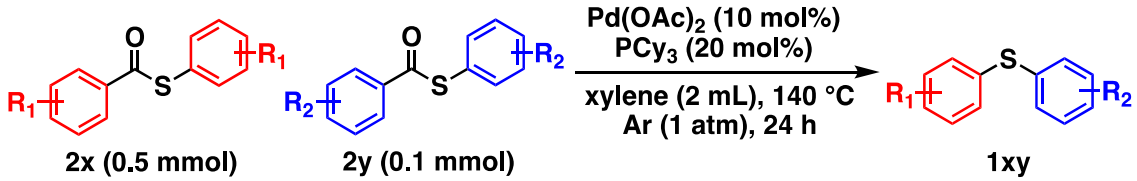


1x (0.5 mmol) 1y (0.1 mmol) 1xy

entry	product (**1xy**)	amount (mmol)		
		1x	**1y**	**1xy**
1	**1ab**	0.36	0.015	0.16
2	**1ac**	0.40	0.013	0.15
3	**1ad**	0.36	0.013	0.14
4	**1ae**	0.40	0.021	0.13
5	**1af**	0.38	0.010	0.14
6	**1ag**	0.37	0.004	0.15
7	**1bh**	0.38	0.013	0.14
8	**1bi**	0.42	0.007	0.14
9	**1aj**	0.36	0.012	0.14
10	**1ka**	0.36	0.017	0.15
11	**1la**	0.39	0.018	0.14
12	**1am**	0.38	0.006	0.15
13	**1bn**	0.42	0.013	0.16
14	**1ao**	0.38	0.010	0.094
15	**1ap**	0.37	0.013	0.13
16	**1aq**	0.40	trace	0.10
17	**1br**	0.41	trace	0.14
18	**1bs**	0.45	0.029	0.093
19	**1bu**	0.42	0.004	0.16
20	**1av**	0.38	0.006	0.13
21	**1aw**	0.45	trace	0.18

[a]Respective reaction conditions are shown in Fig. 2a. The amounts of thioethers were determined by GC analysis.

Table S8. The amounts of thioethers after the transformations demonstrated in Fig. 2e.[a]

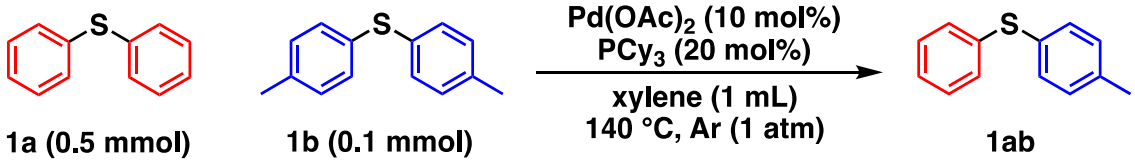


2x (0.5 mmol) **2y (0.1 mmol)** **1xy**

entry	product (**1xy**)	amount (mmol)		
		1x	**1y**	**1xy**
1	**1ab**	0.40	0.015	0.16
2	**1ac**	0.38	0.013	0.15
3	**1ad**	0.37	0.018	0.18
4	**1ae**	0.38	0.005	0.18
5	**1af**	0.38	0.010	0.16
6	**1bh**	0.39	0.016	0.16
7	**1aj**	0.41	0.017	0.15
8	**1ak**	0.40	0.009	0.17
9	**1al**	0.40	0.010	0.16
10	**1bn**	0.39	0.015	0.17
11	**1ao**	0.37	0.010	0.14

[a]Respective reaction conditions are shown in Fig. 2e. The amounts of compounds were determined by GC analysis. All of the thioesters were decarbonylated to thioethers after the reactions.

Table S9. Catalytic performances of the supernatant after supporting a part of Pd species on RGO.[a]

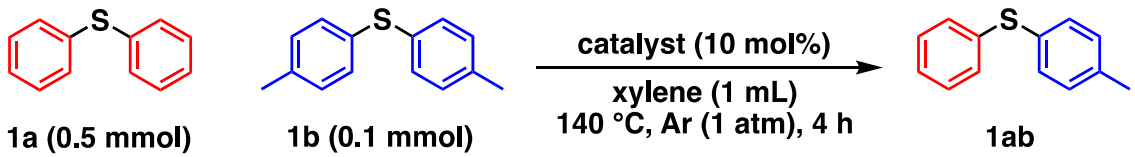


1a (0.5 mmol) **1b (0.1 mmol)** **1ab**

entry	time (h)	conv. (%)		yield (%)
		1a	**1b**	**1ab**
1	1.5	15	42	34
	24	16	81	81

[a]Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%), xylene (1 mL), Ar (1 atm), 140 °C in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. RGO (50 mg) was added to the reaction solution 1.5 h after the reaction started, and RGO was removed after being stirred at room temperature for 2 h. The metathesis reaction at 140 °C was carried out without RGO.

Table S10. Effect of Pd nanoparticle catalysts[a]

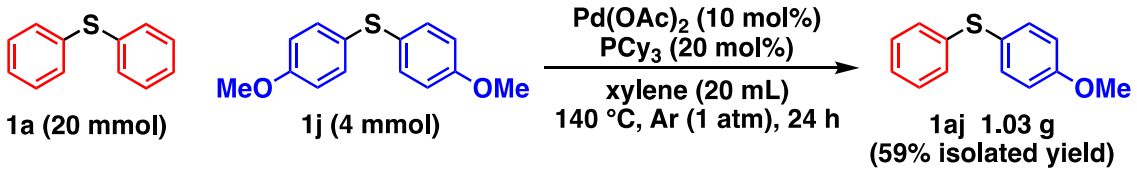


1a (0.5 mmol) **1b (0.1 mmol)** **1ab**

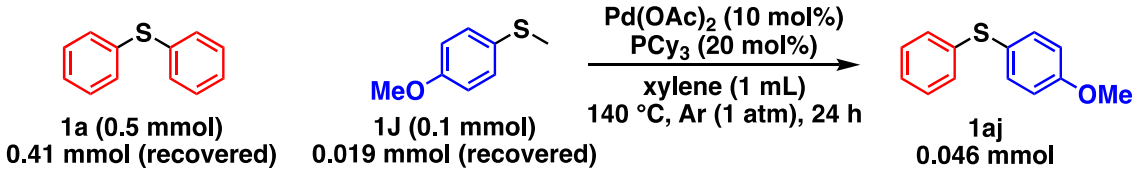
entry	catalyst	conv. (%)		yield (%)
		1a	**1b**	**1ab**
1	$Pd(OAc)_2 + PCy_3$	17	84	82
2	Pd/HAP	3	27	22
3[b]	Pd-PVP	<1	2	<1

[a]Reaction conditions: **1a** (0.5 mmol), **1b** (0.1 mmol), catalyst (Pd: 10 mol%), PCy_3 (0 or 20 mol%), xylene, 140 °C 4 h in a test tube. Conversions and yields were determined by GC analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]24 h.

Supplementary Schemes

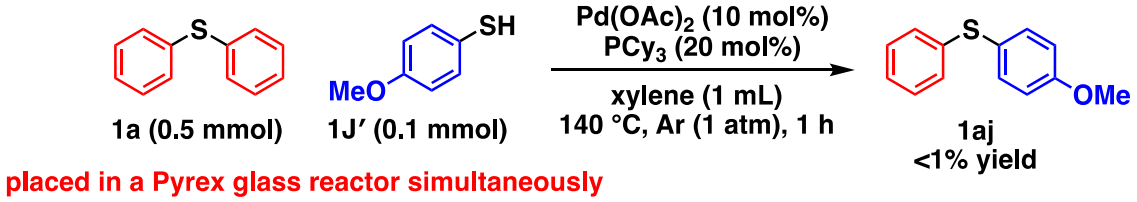


Scheme S1. Gram-scale synthesis of **1aj**. The reaction conditions were indicated in the scheme.

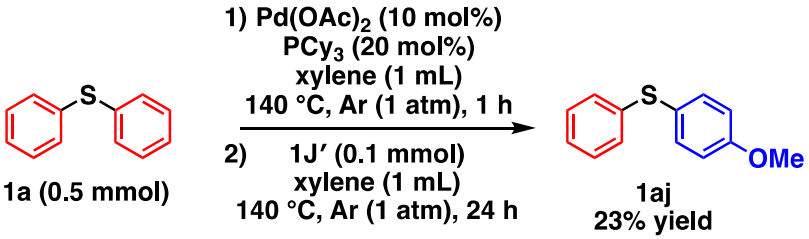


Scheme S2. The amounts of thioethers after the transformation demonstrated in Fig. 2c. Reaction conditions were indicated in the scheme.

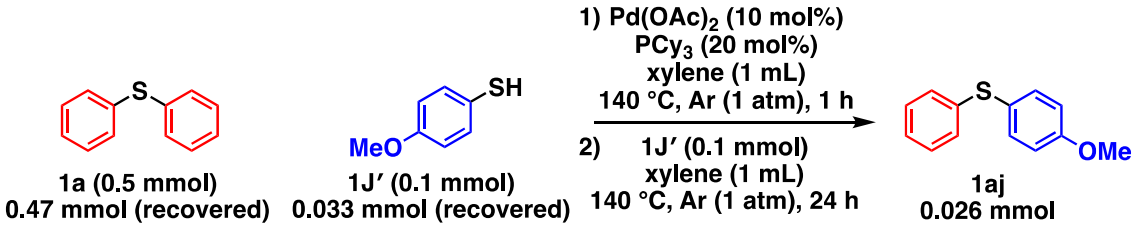
(a)



(b)



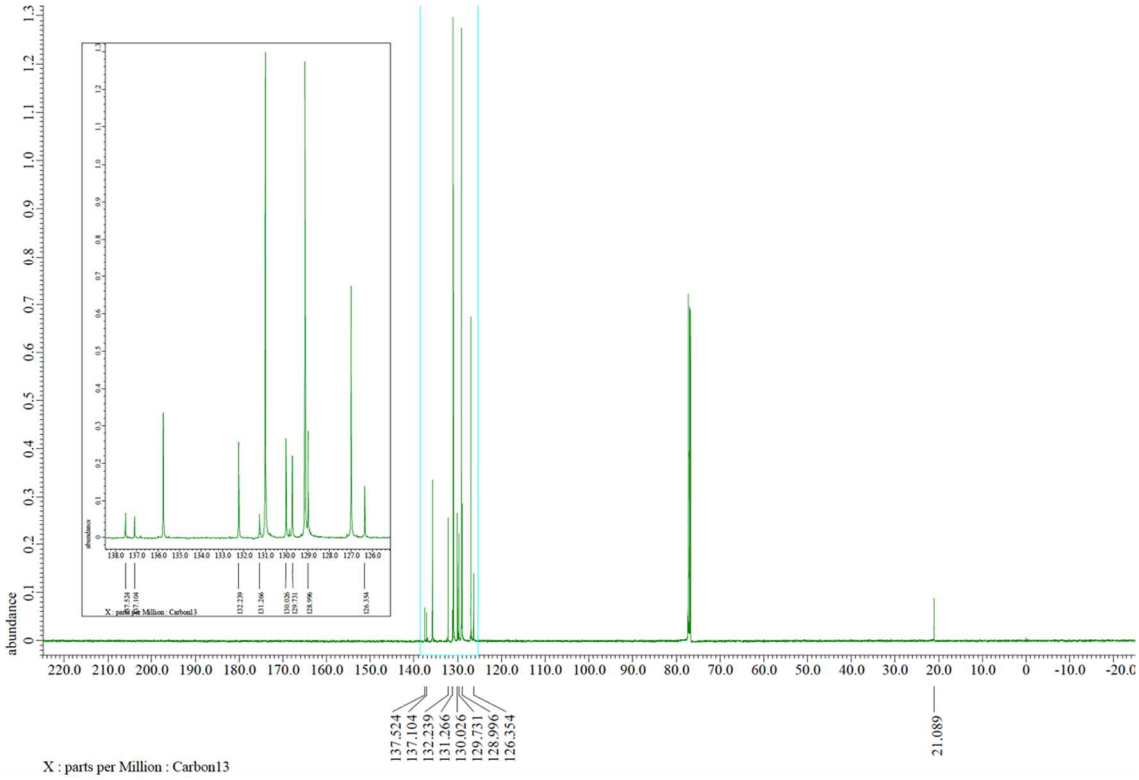
Scheme S3. C–S/S–H metathesis between **1a** and **1J′**. (a) **1a** and **1J′** were added in a Pyrex glass reactor simultaneously. (b) **1J′** was added after Pd nanocluster formation. The reaction conditions were indicated in the scheme.



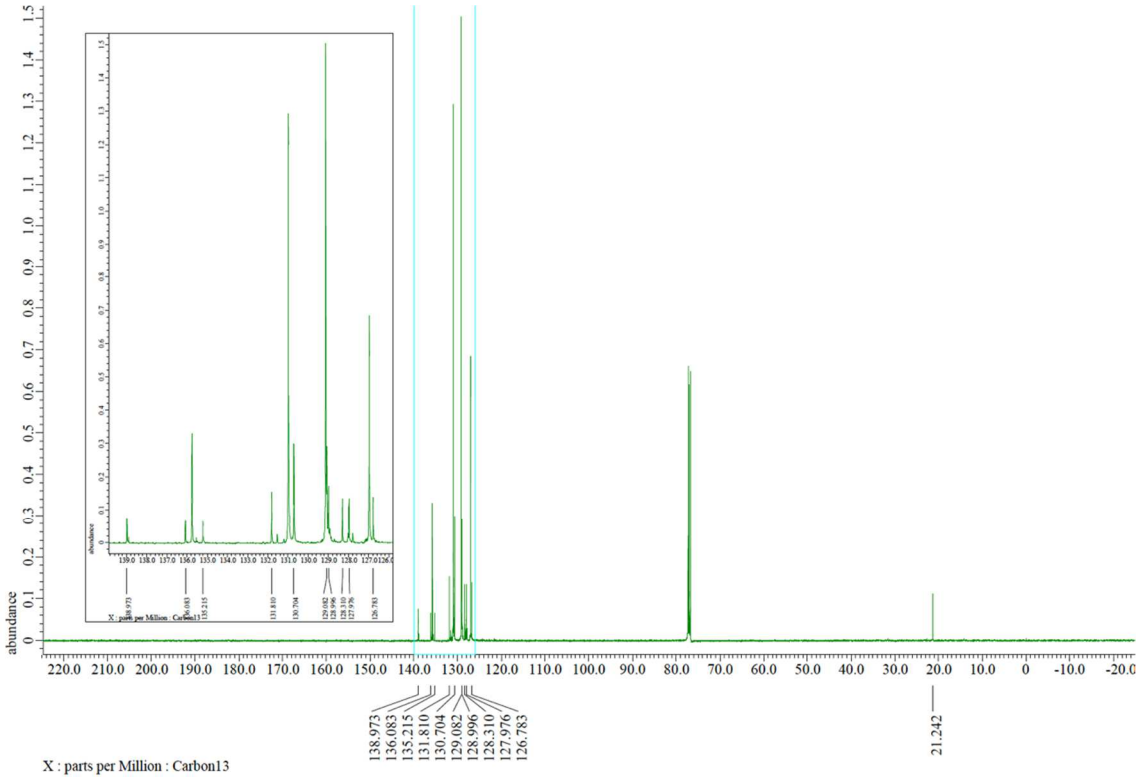
Scheme S4. The amounts of compounds after the transformation demonstrated in Fig. 2d. Reaction conditions were indicated in the scheme.

NMR Spectra

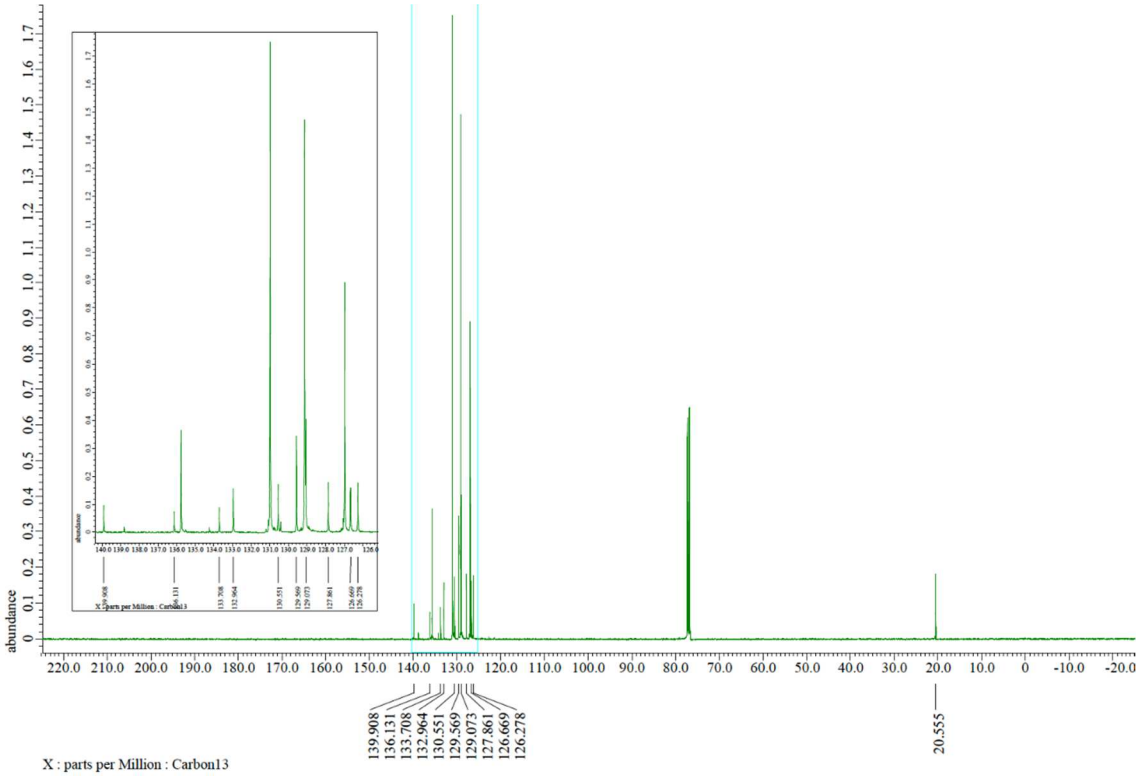
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ab**



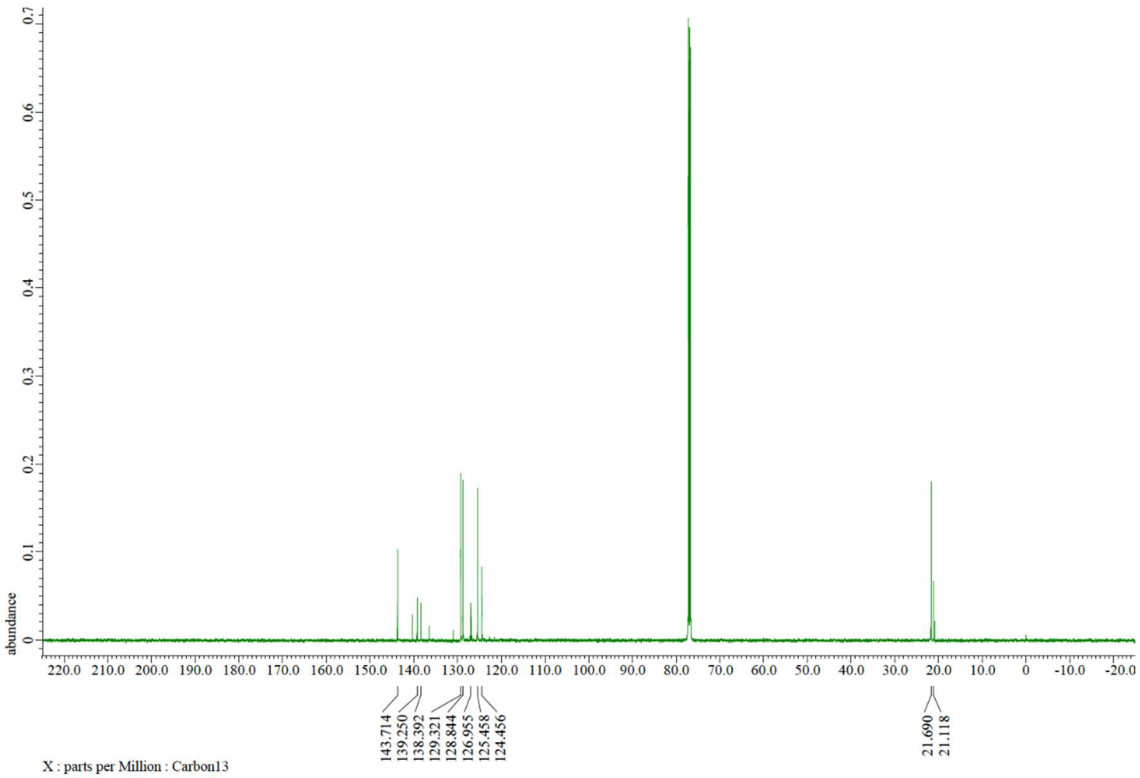
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ac**



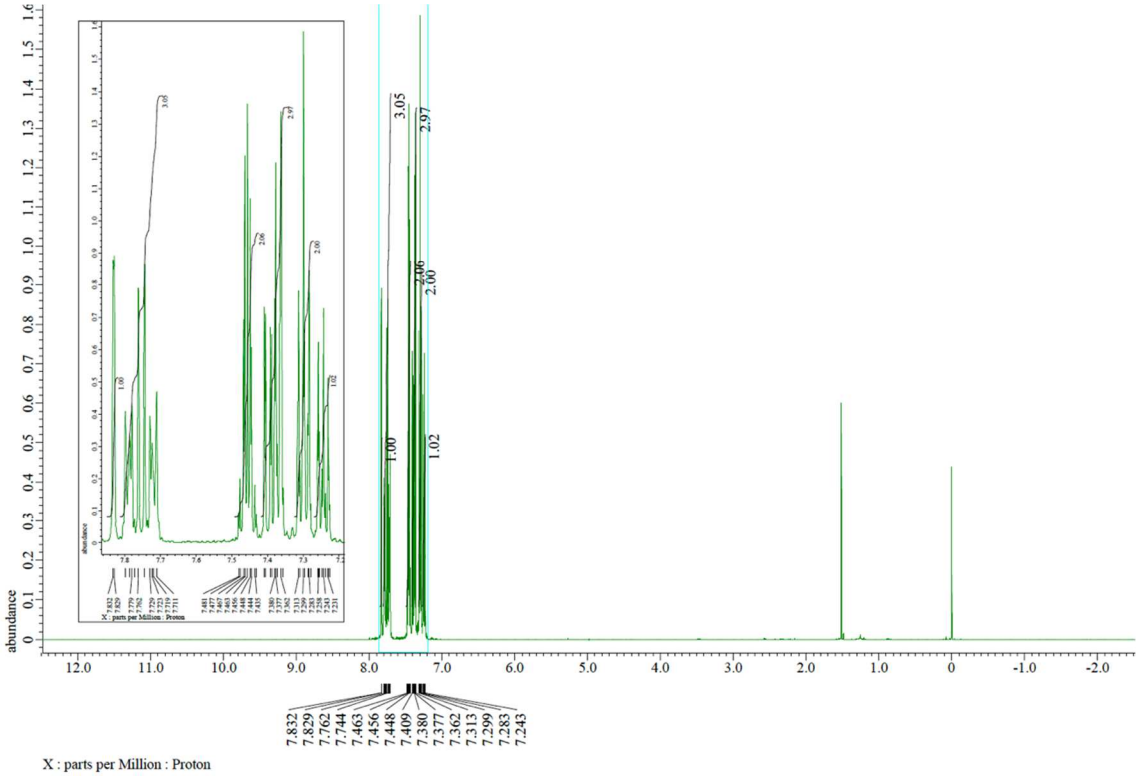
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ad**



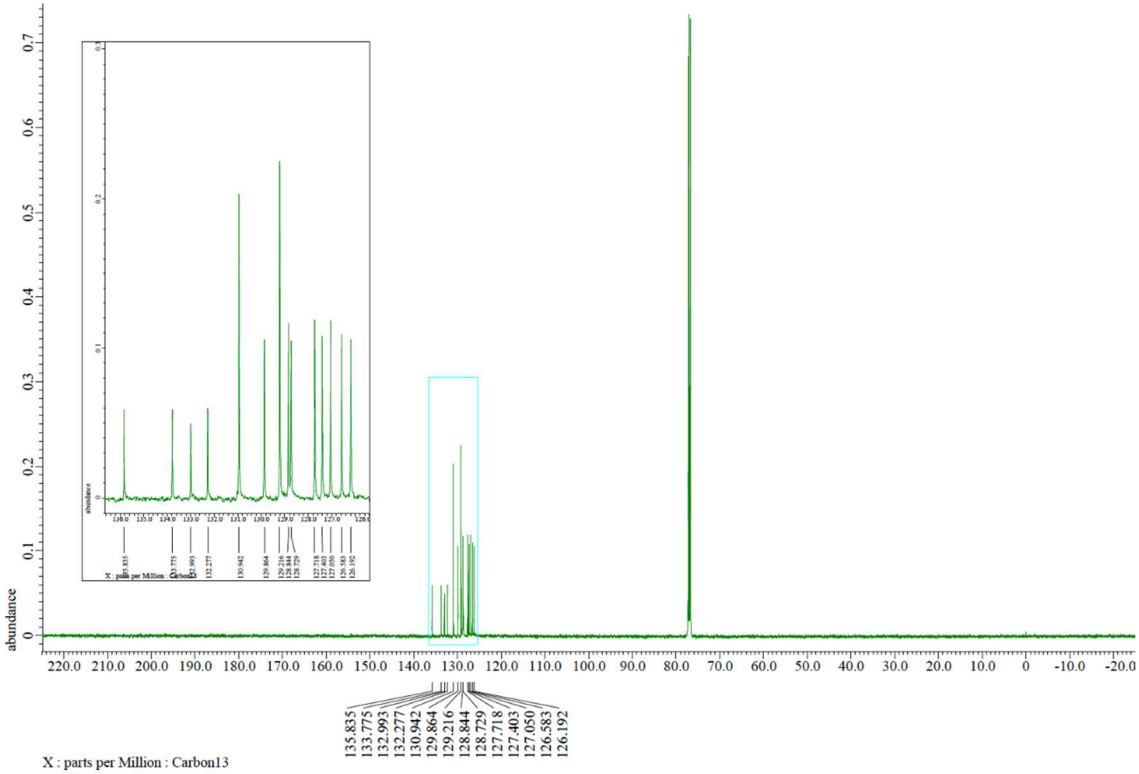
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ae**



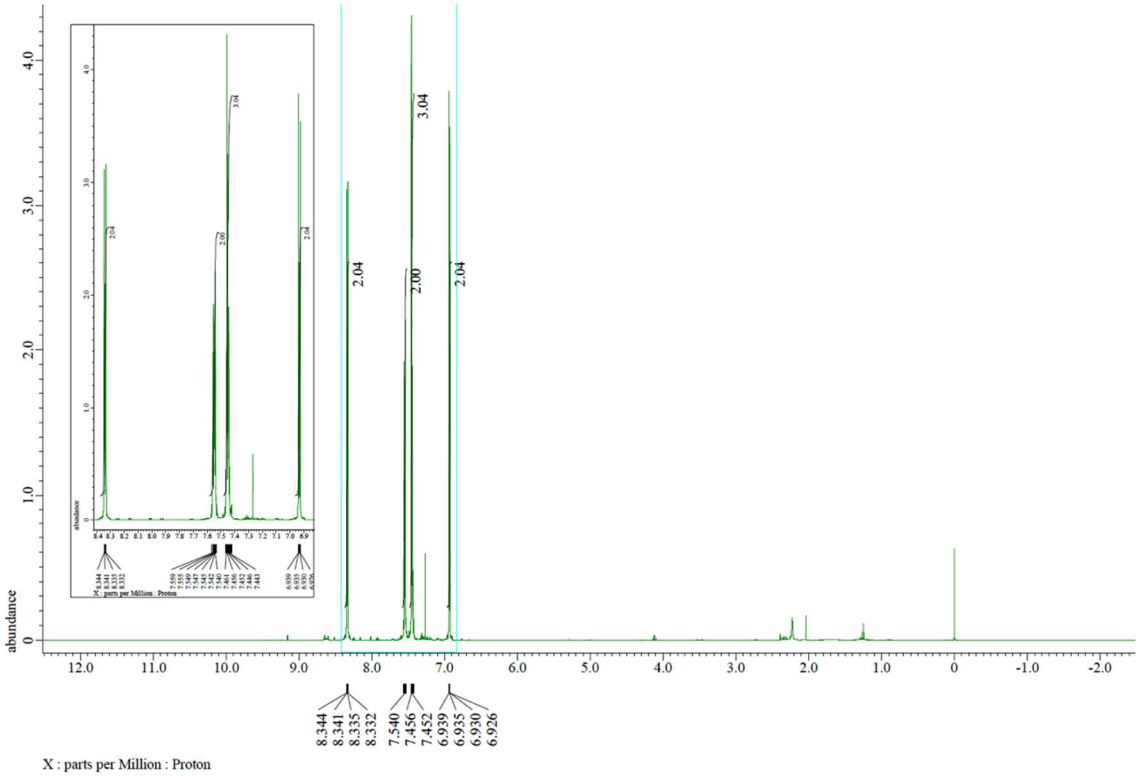
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1af**



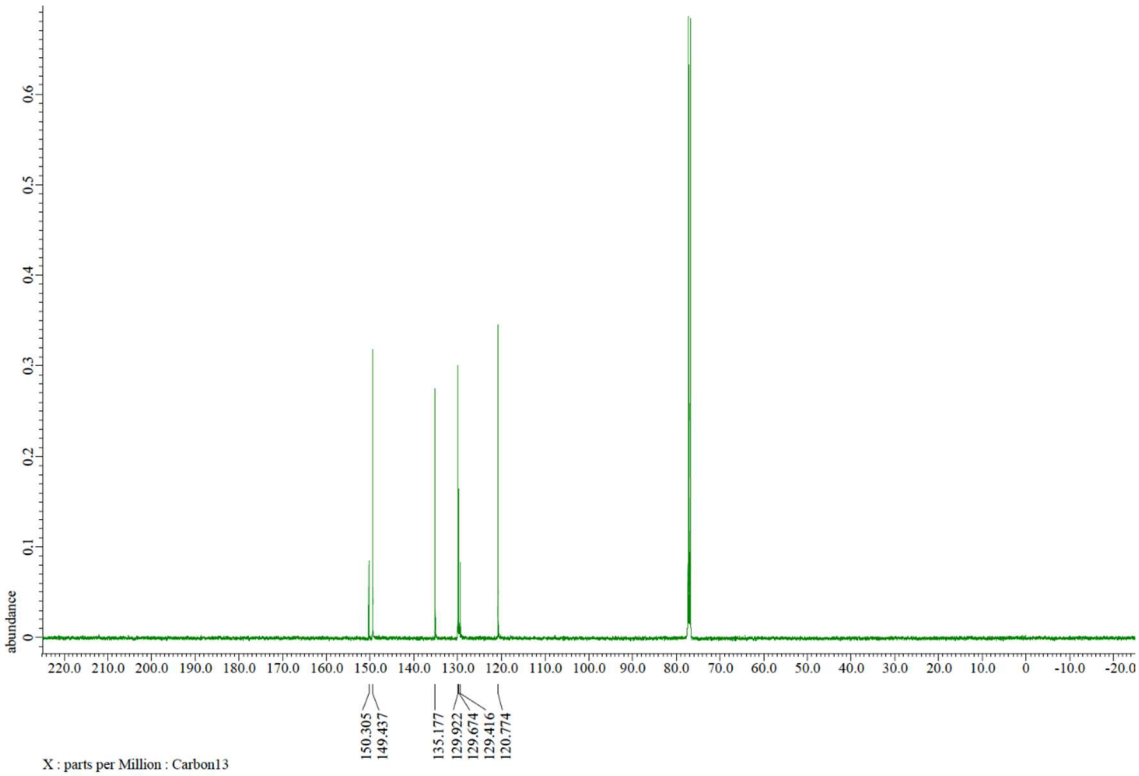
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1af**



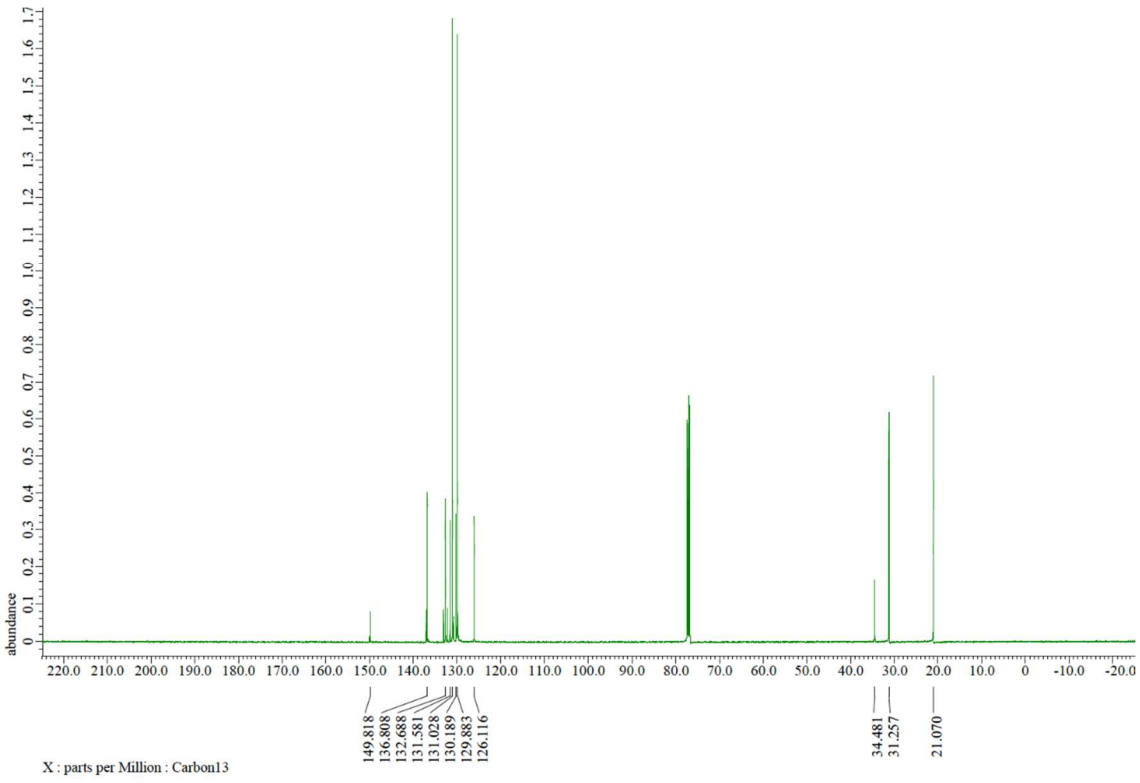
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1ag**



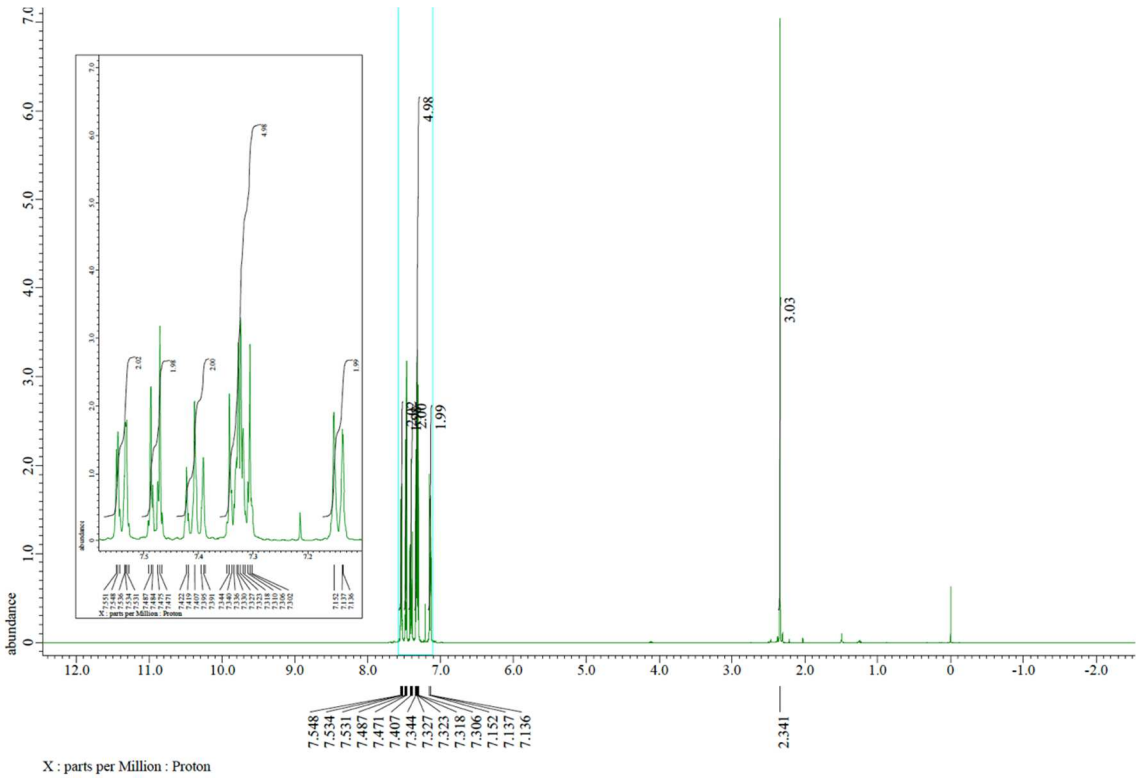
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ag**



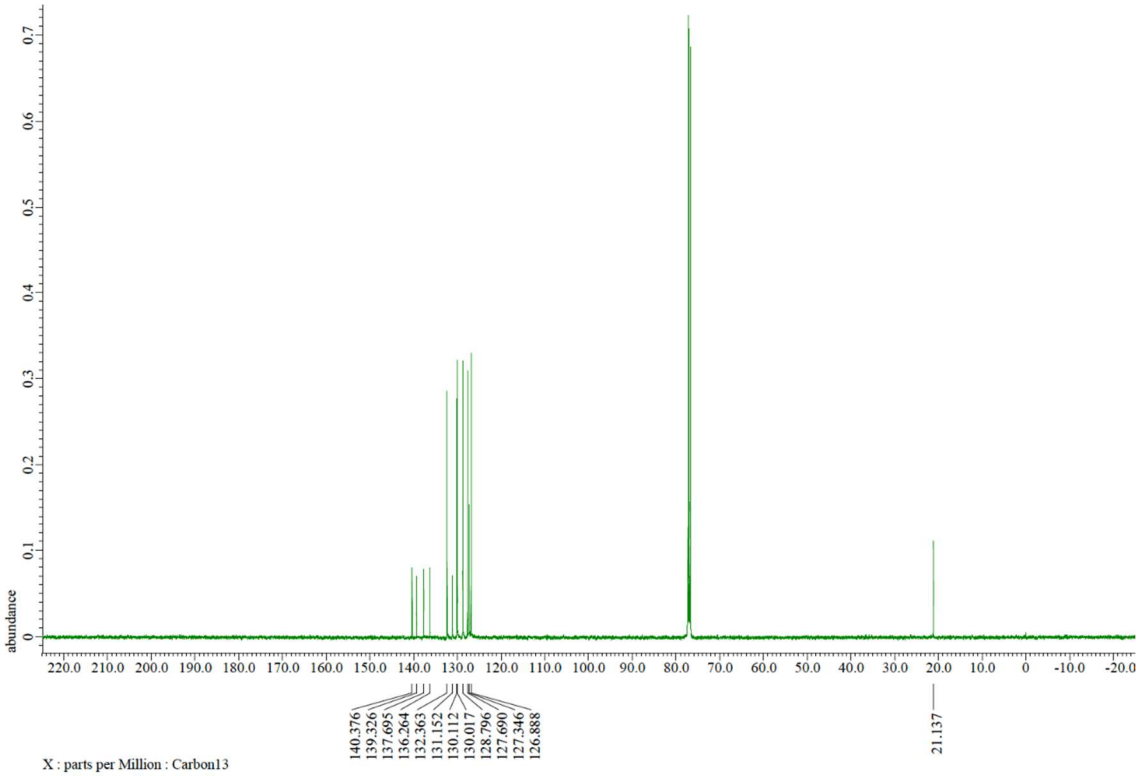
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bh**



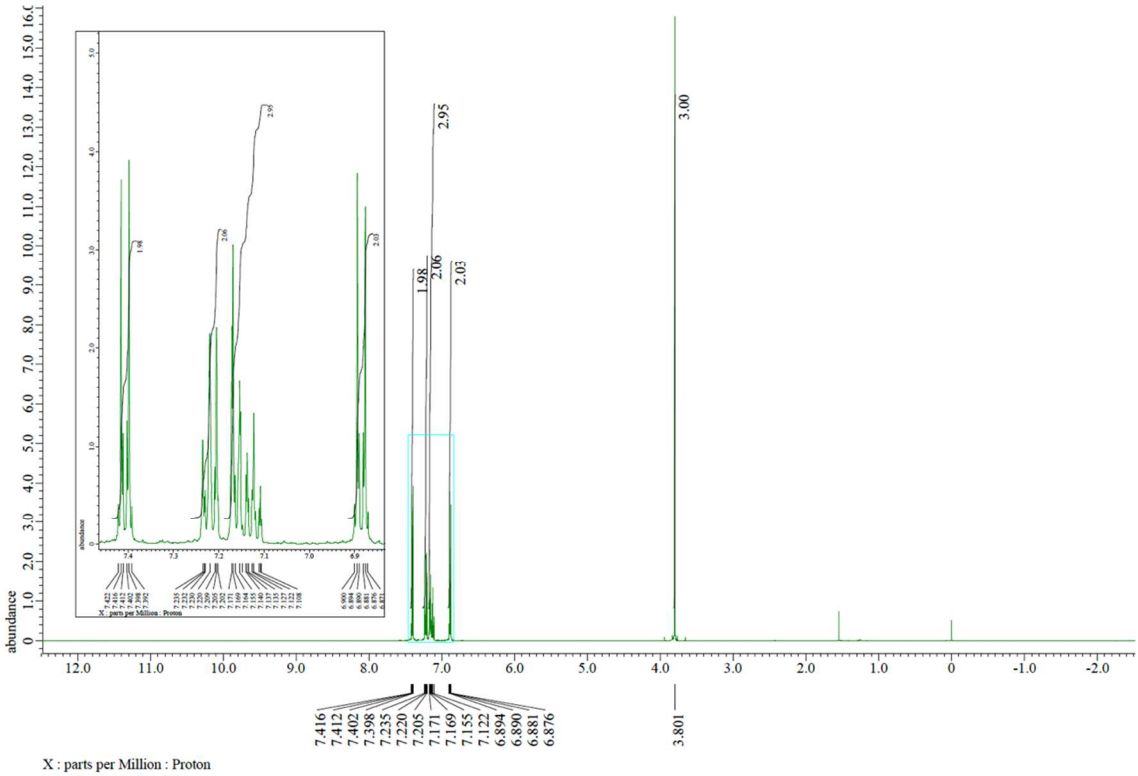
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bi**



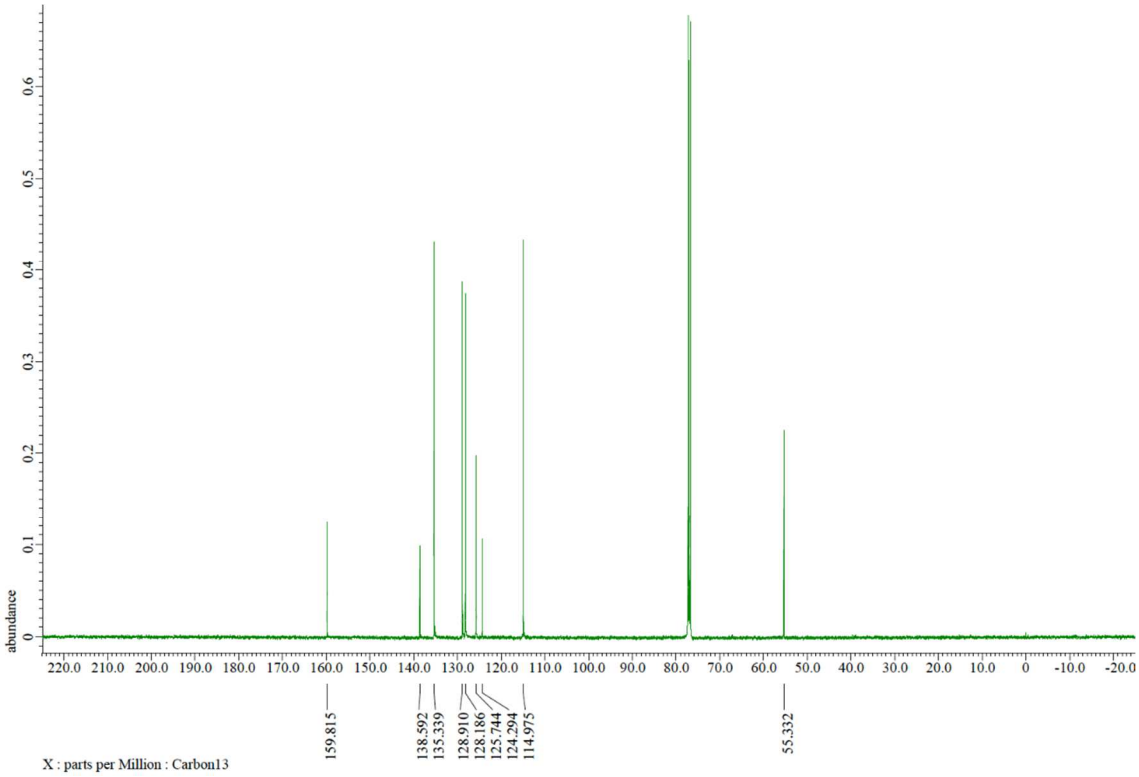
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bi**



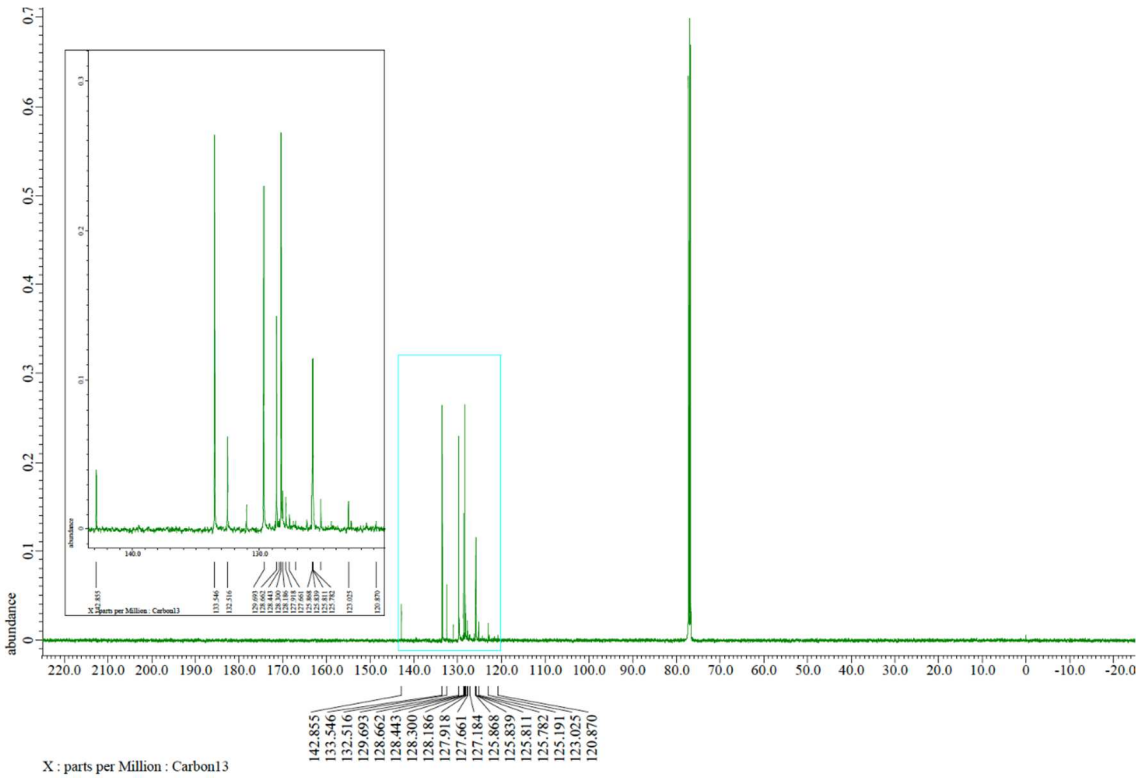
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1aj**



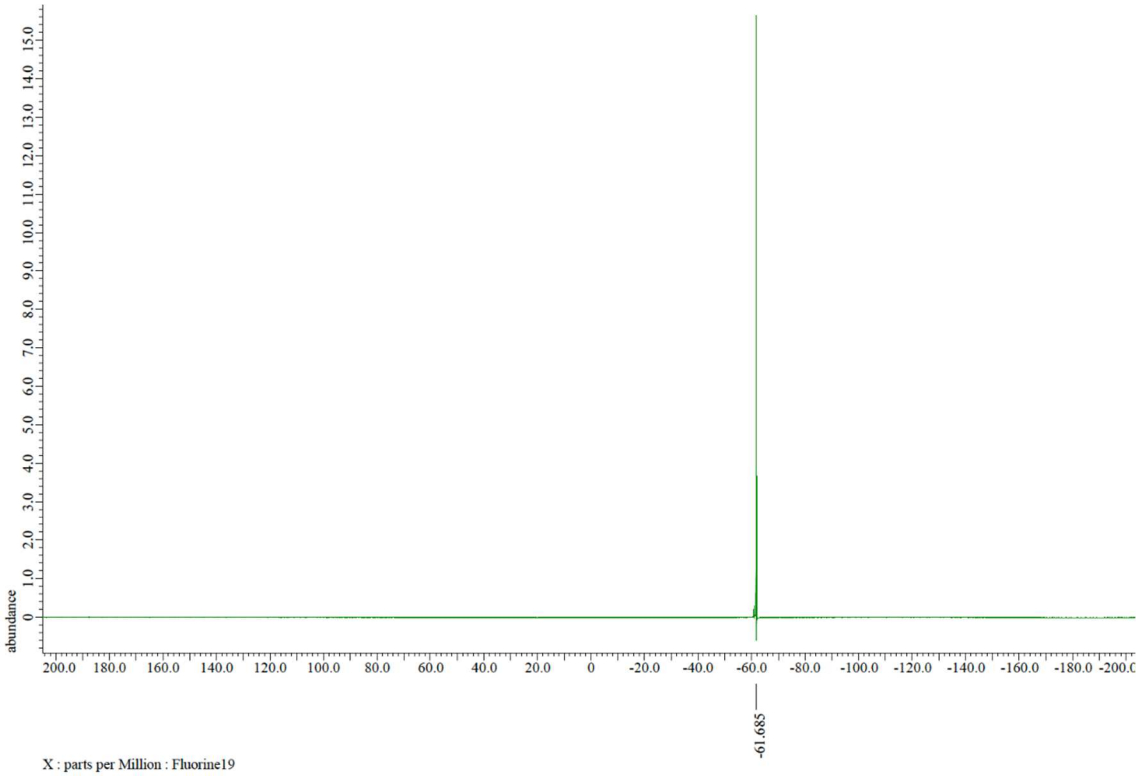
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1aj**



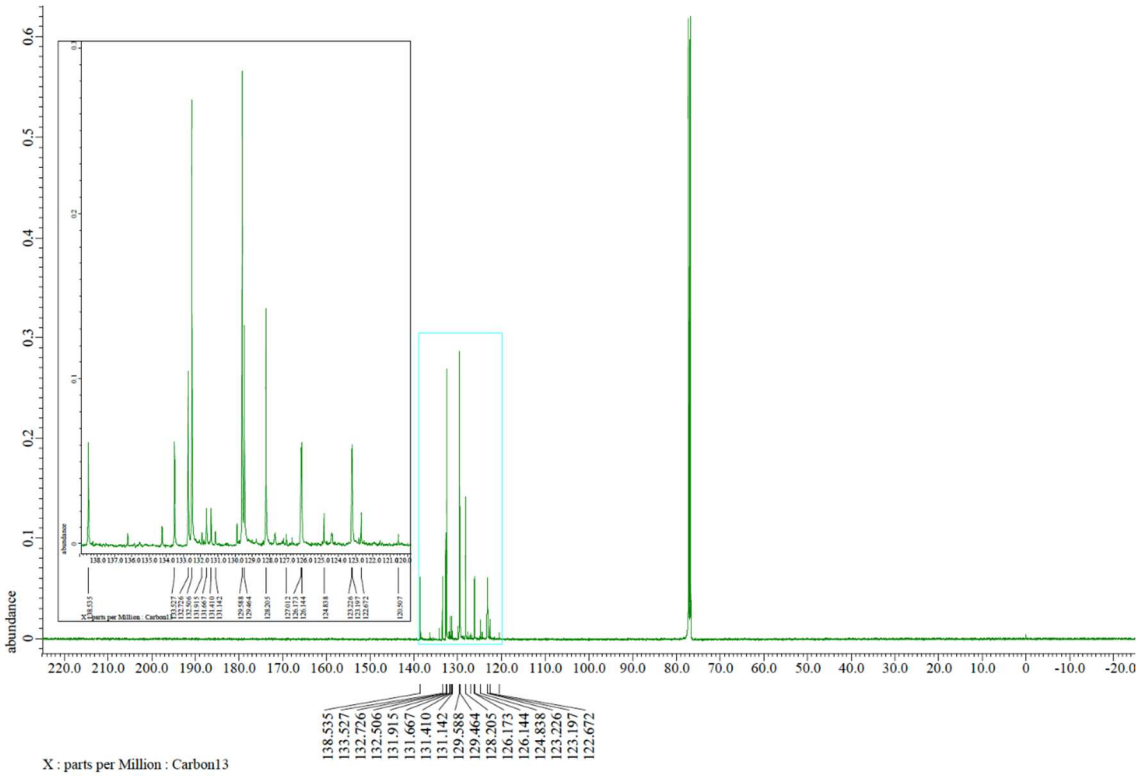
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ka**



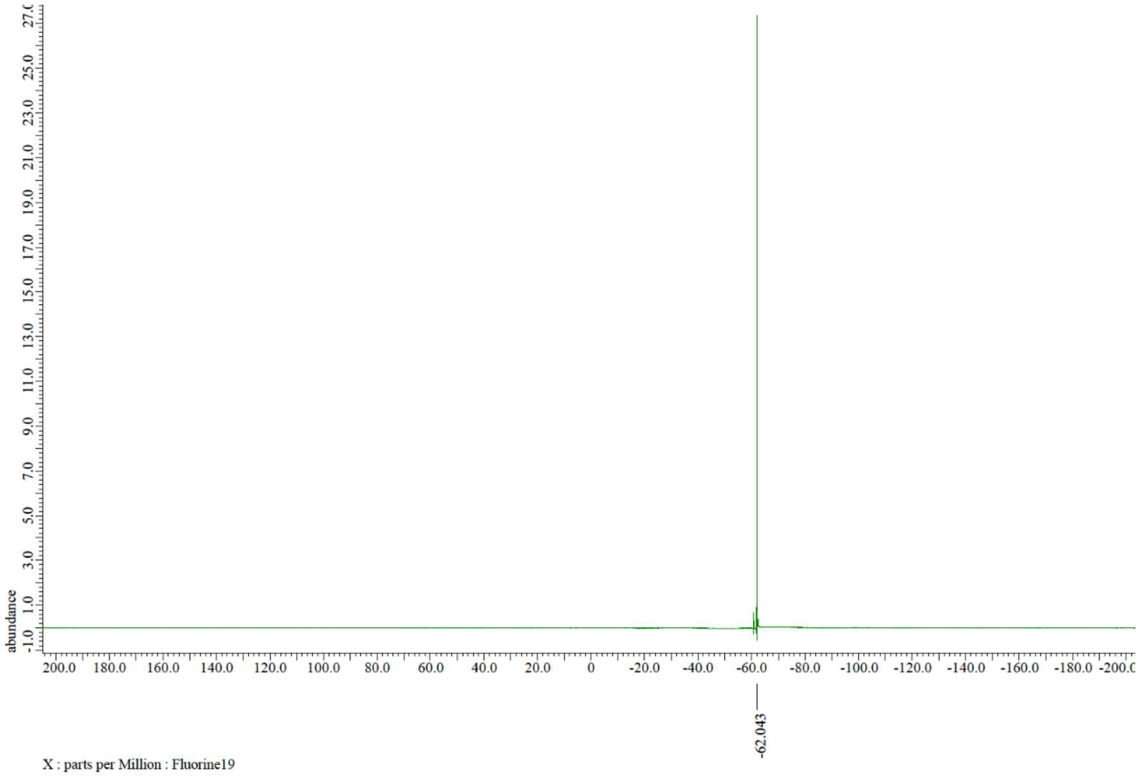
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **1ka**



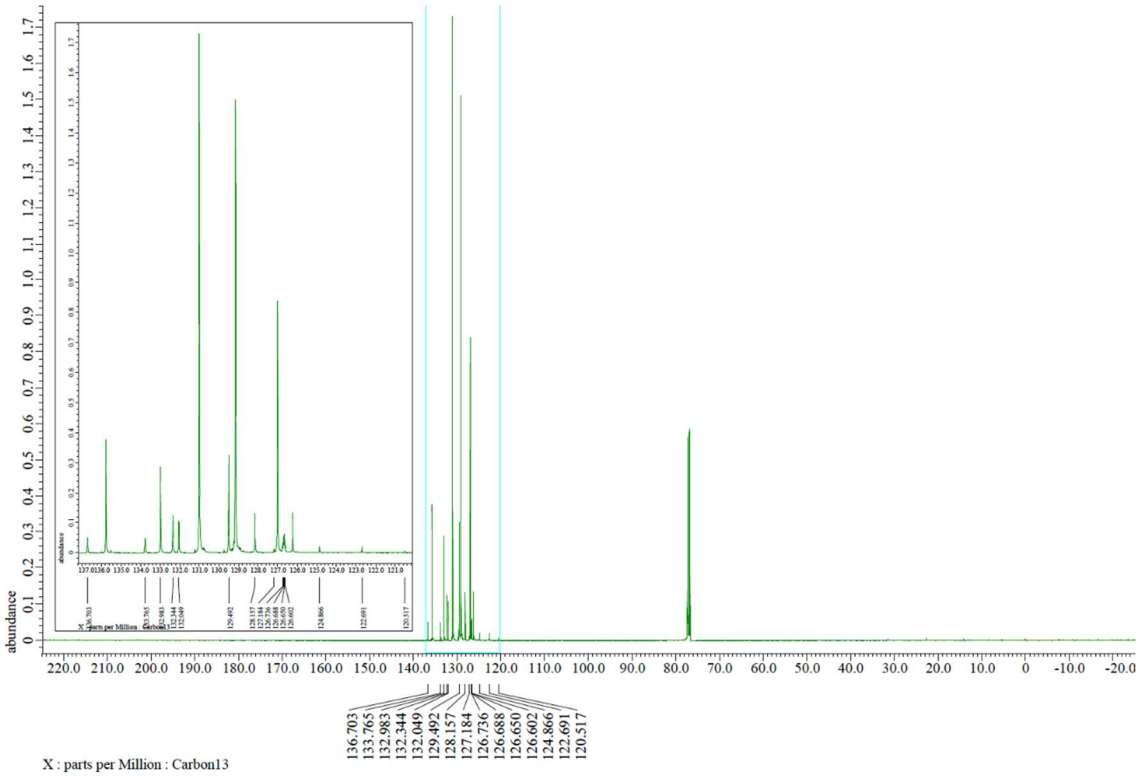
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1la**



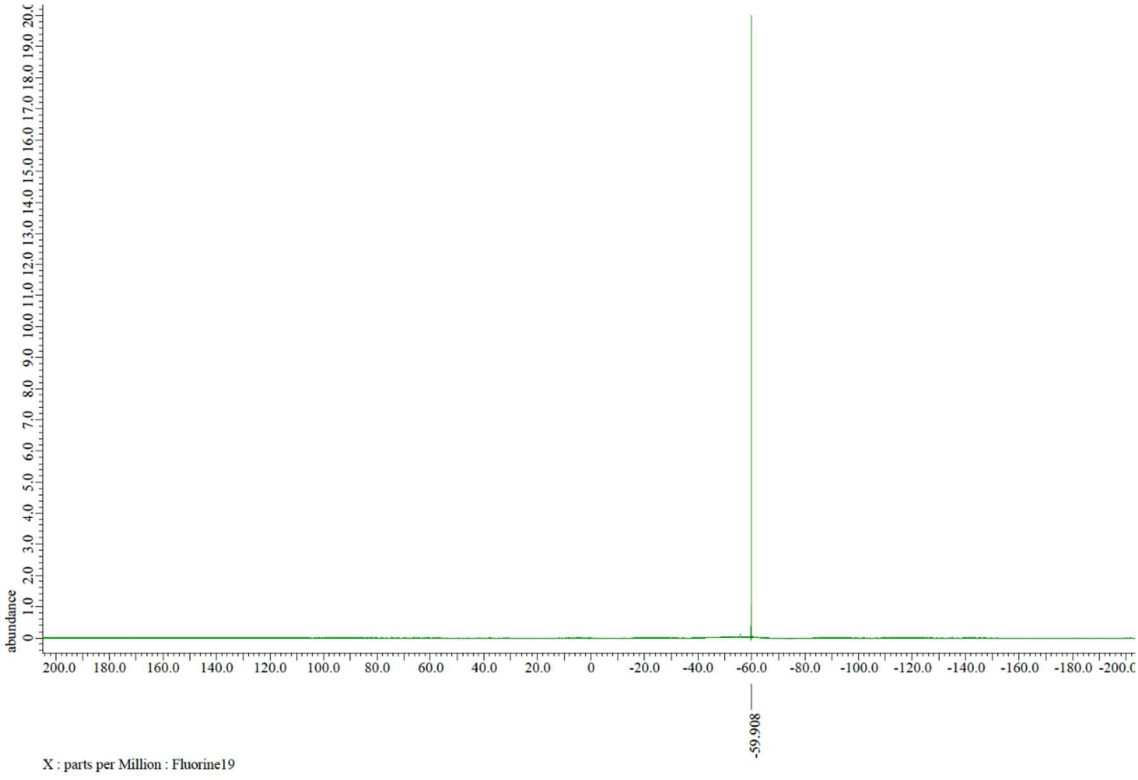
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **1la**



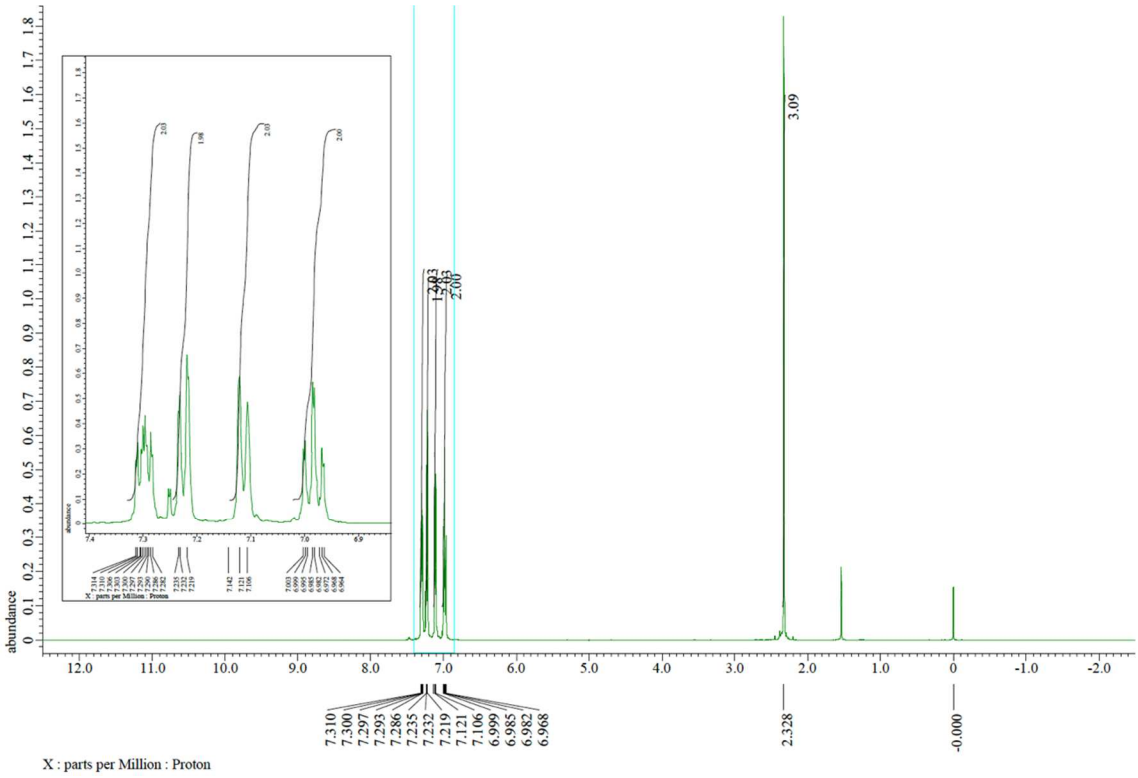
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1am**



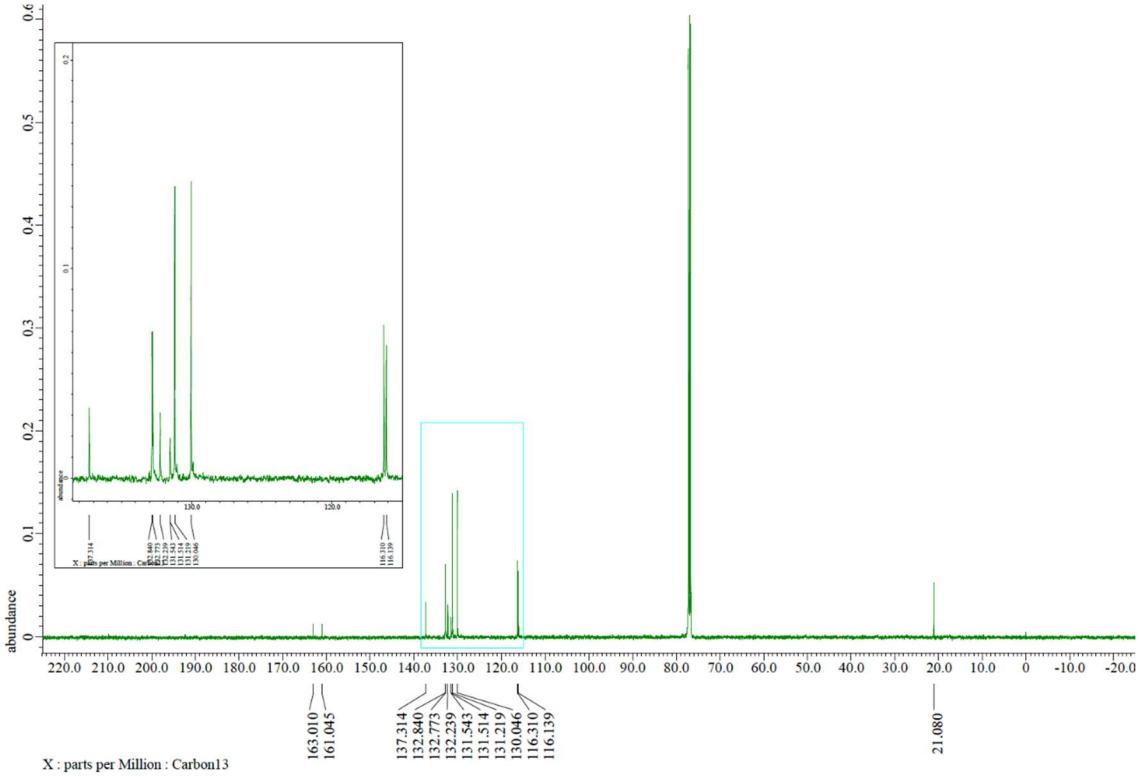
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **1am**



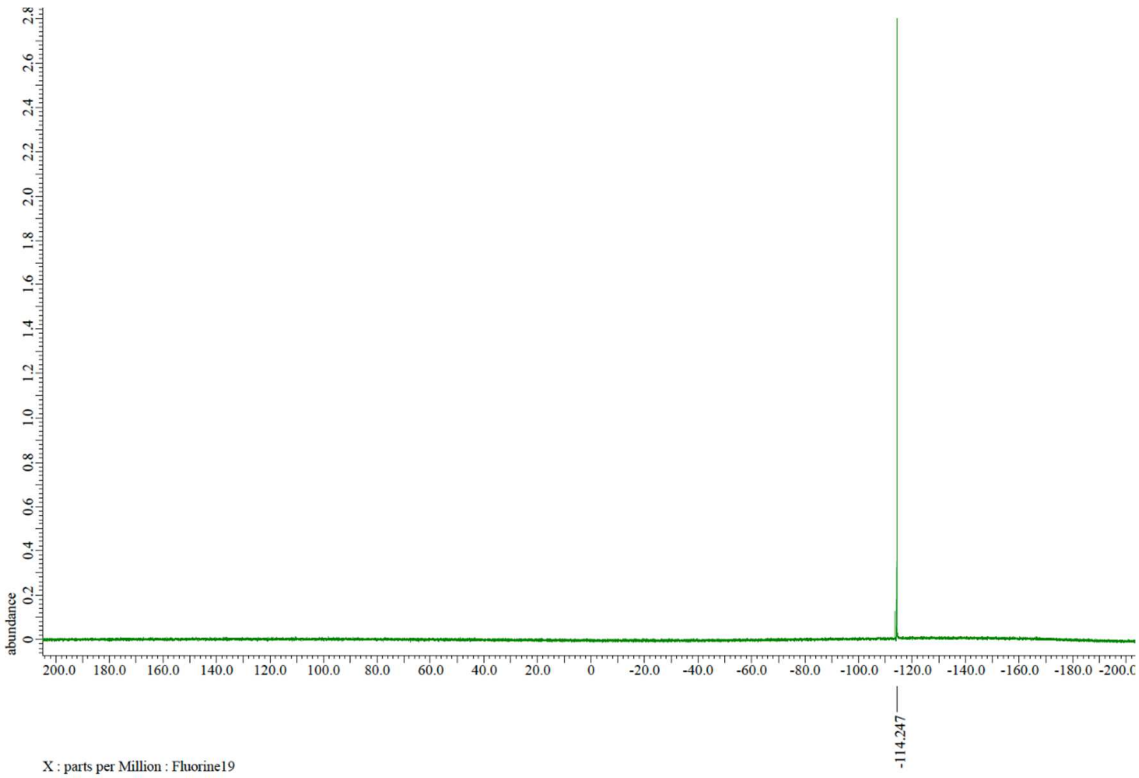
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bn**



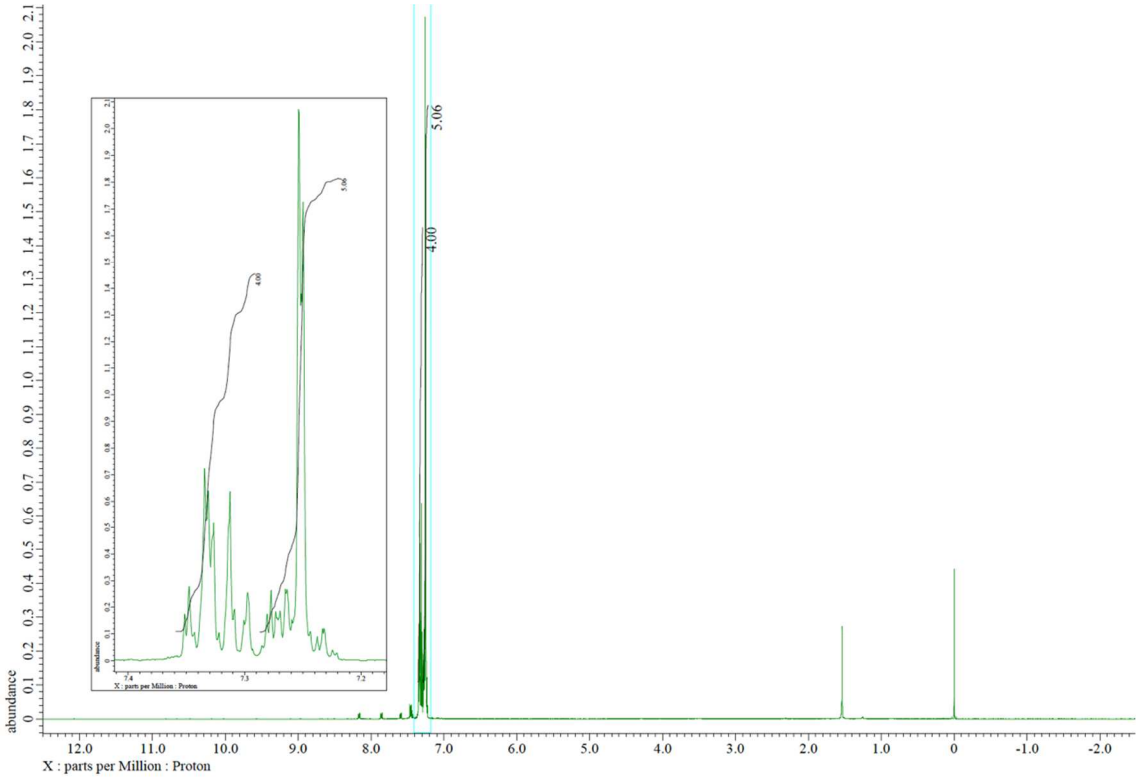
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bn**



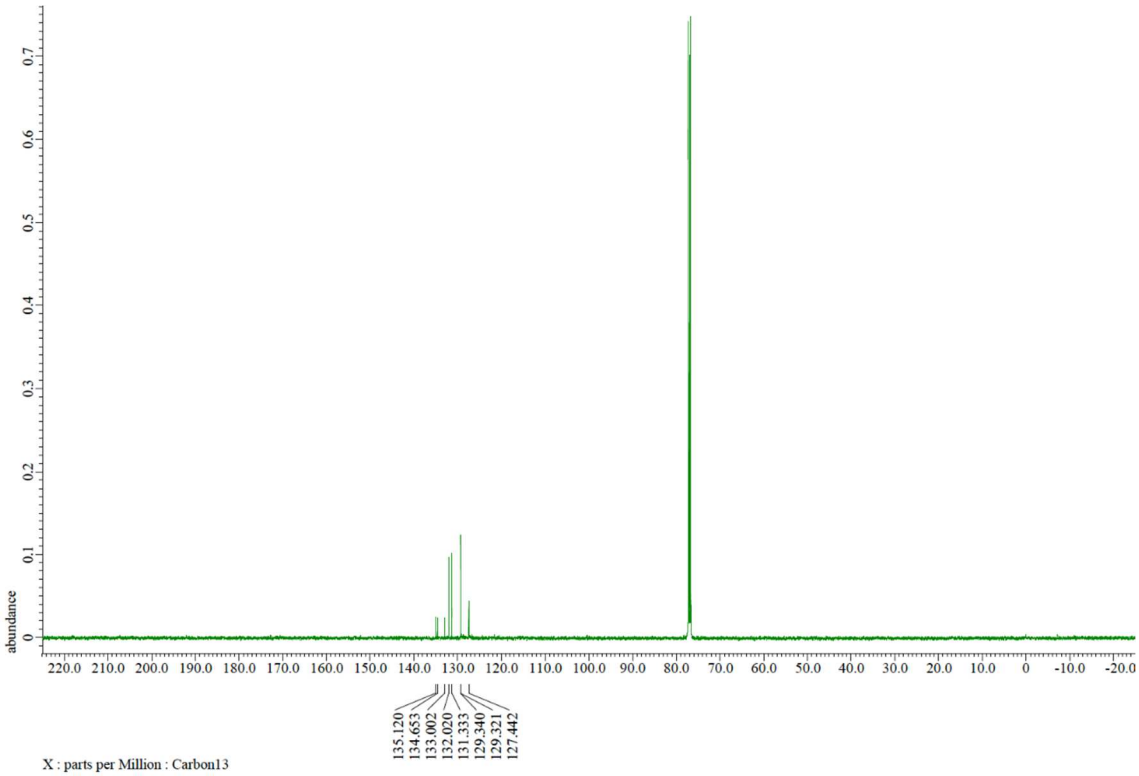
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **1bn**



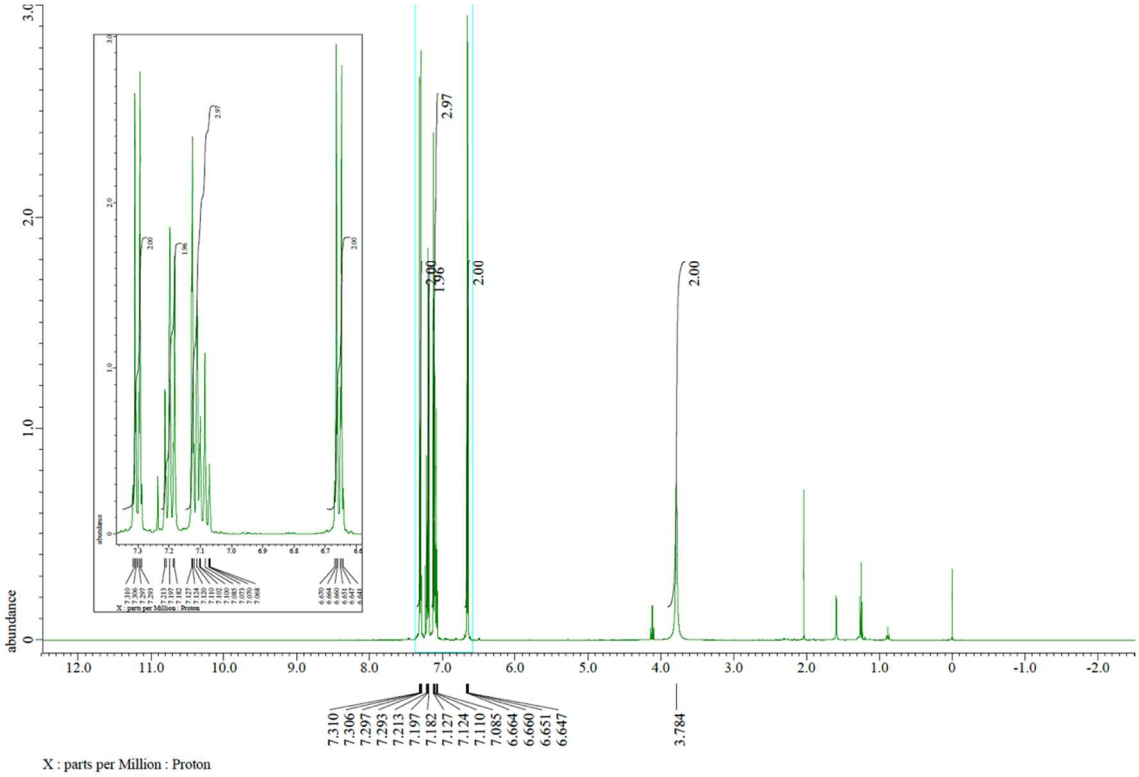
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1ao**



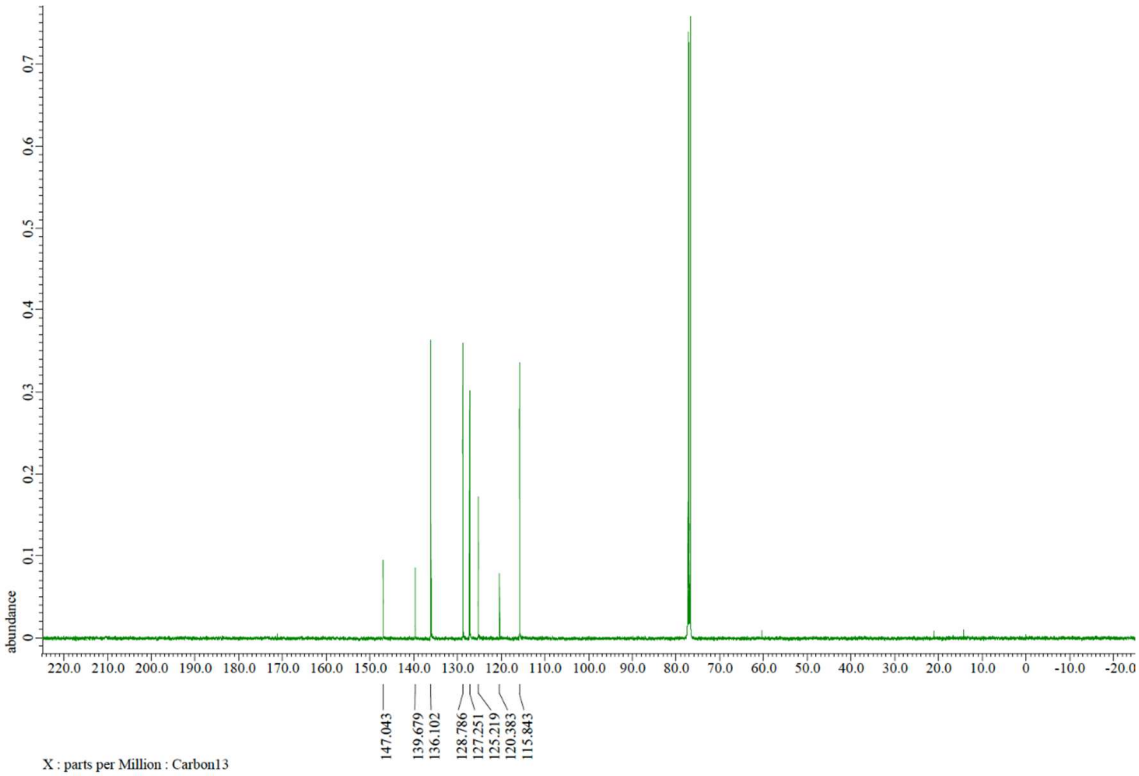
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ao**



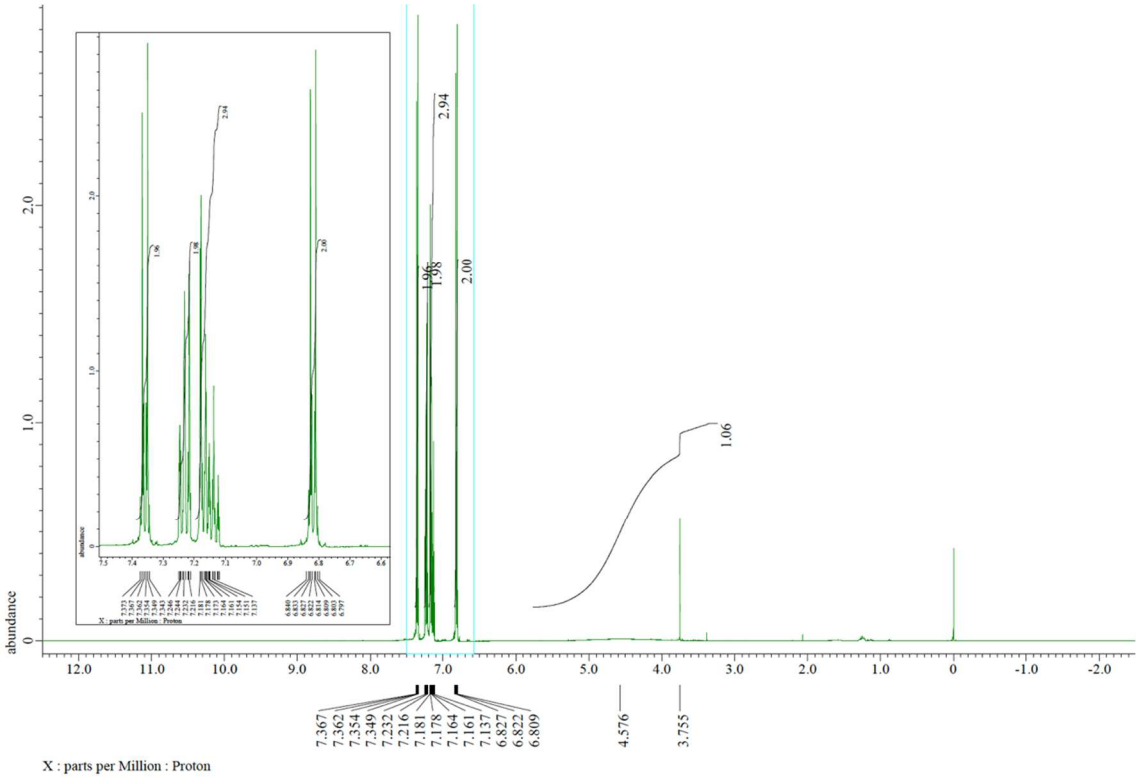
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1ap**



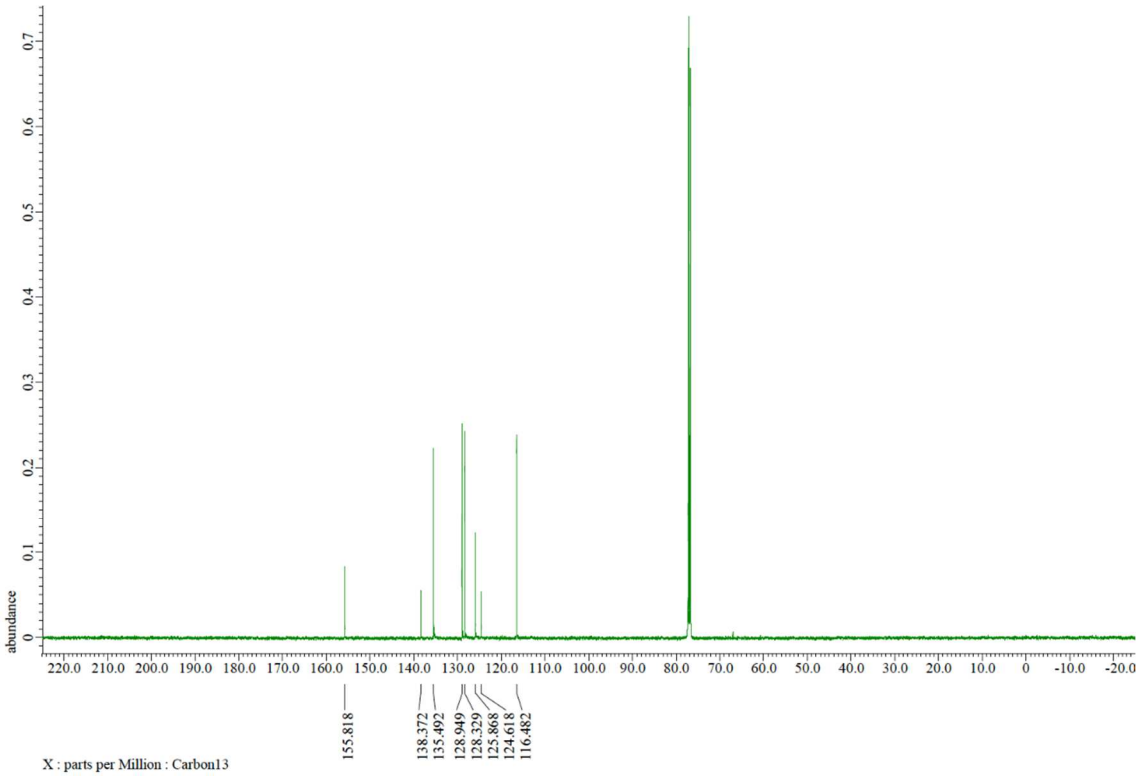
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1ap**



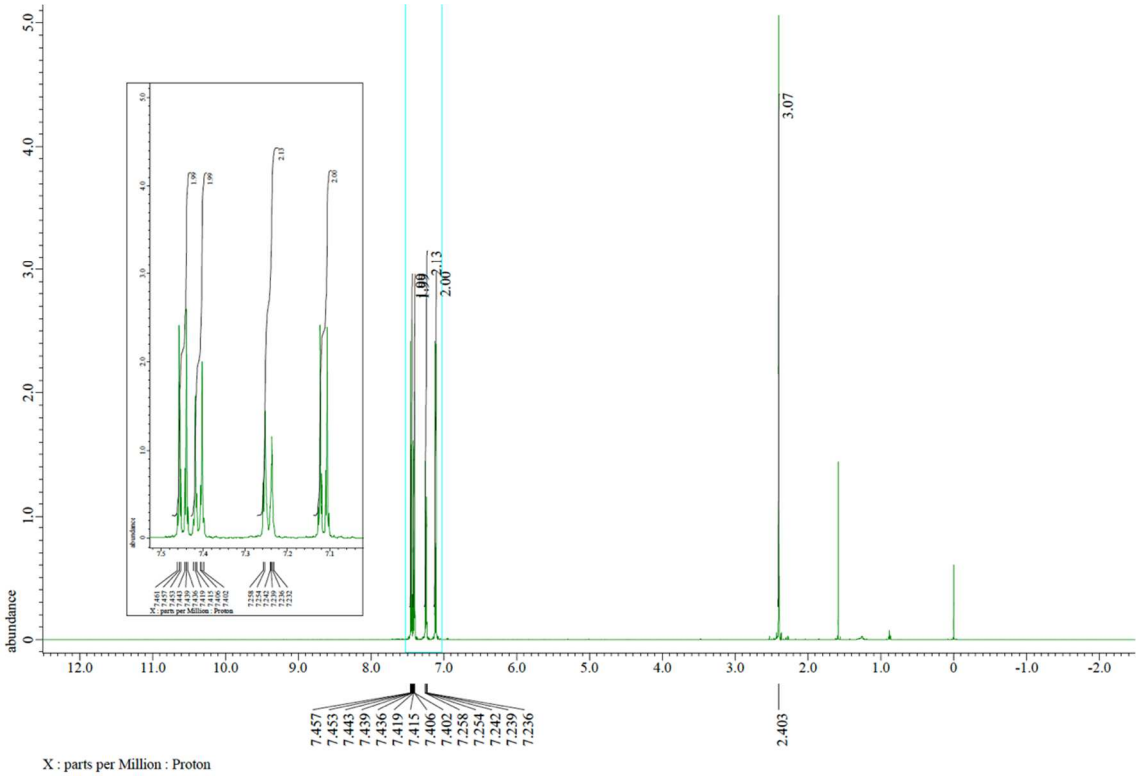
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1aq**



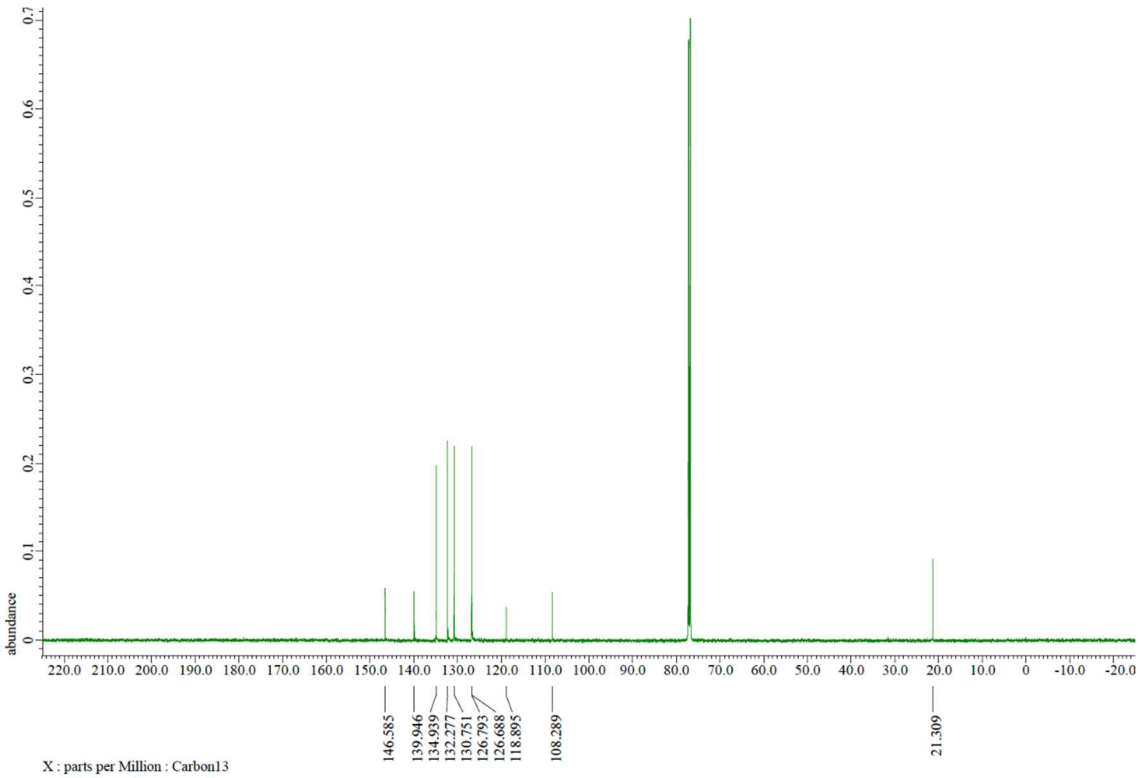
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1aq**



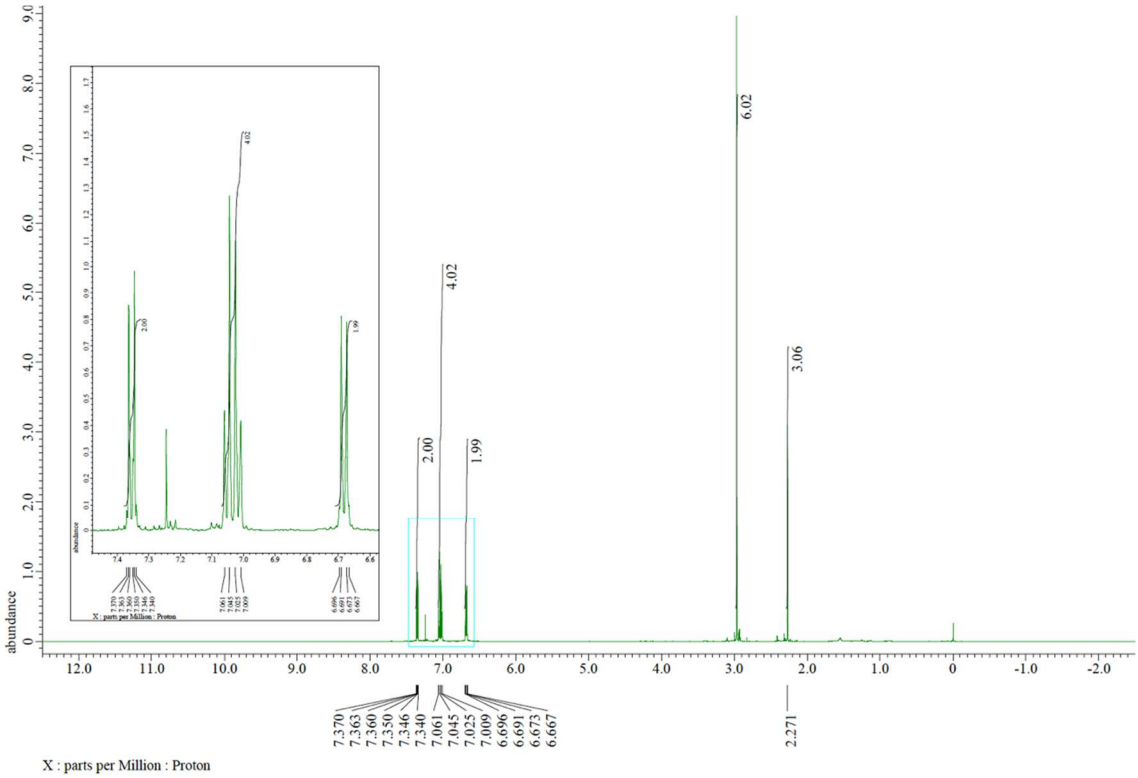
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1br**



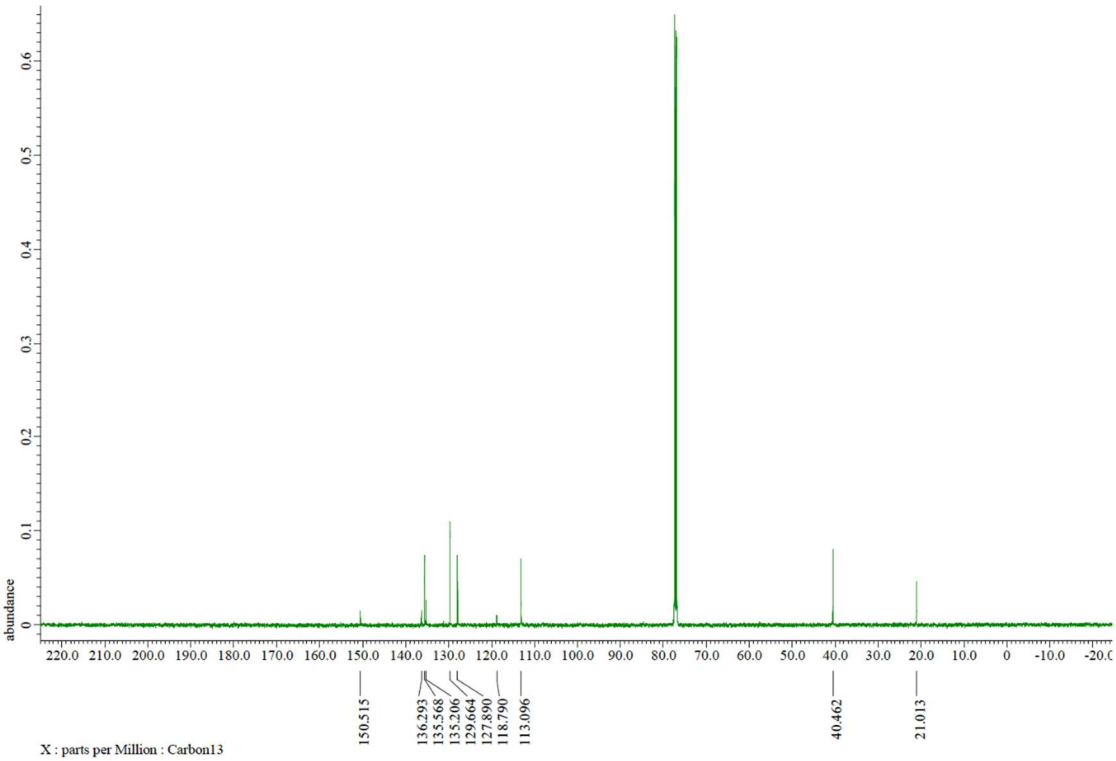
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1br**



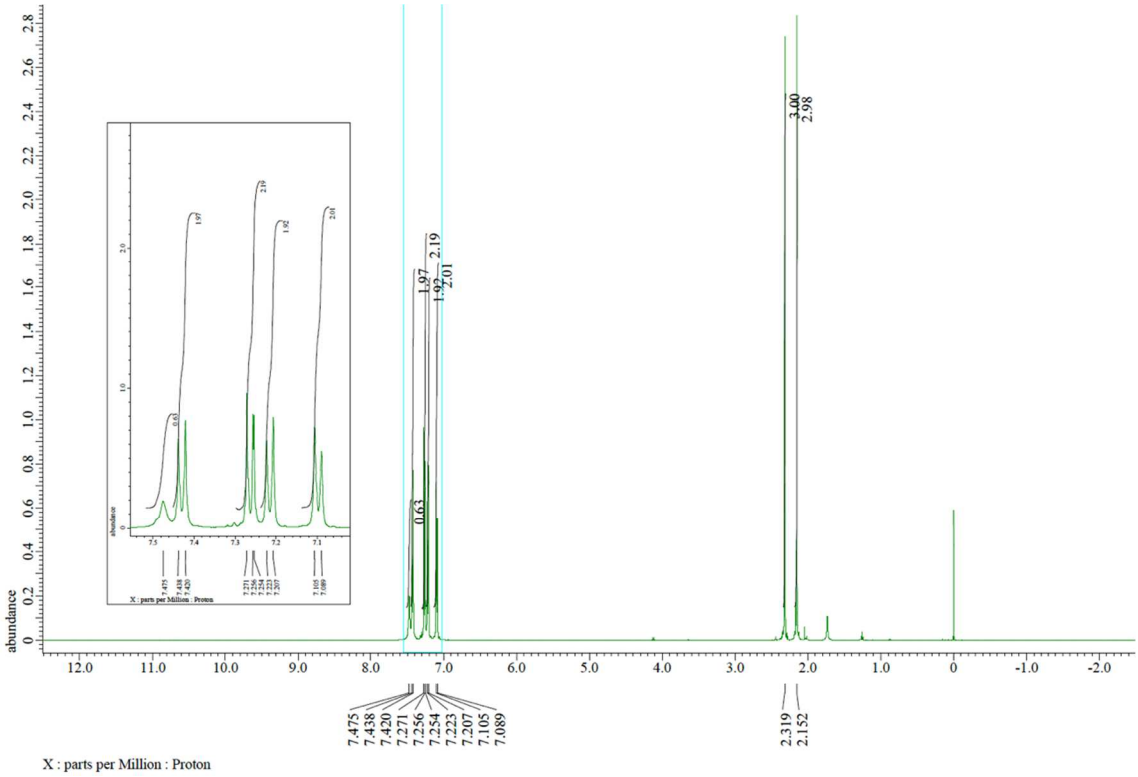
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bs**



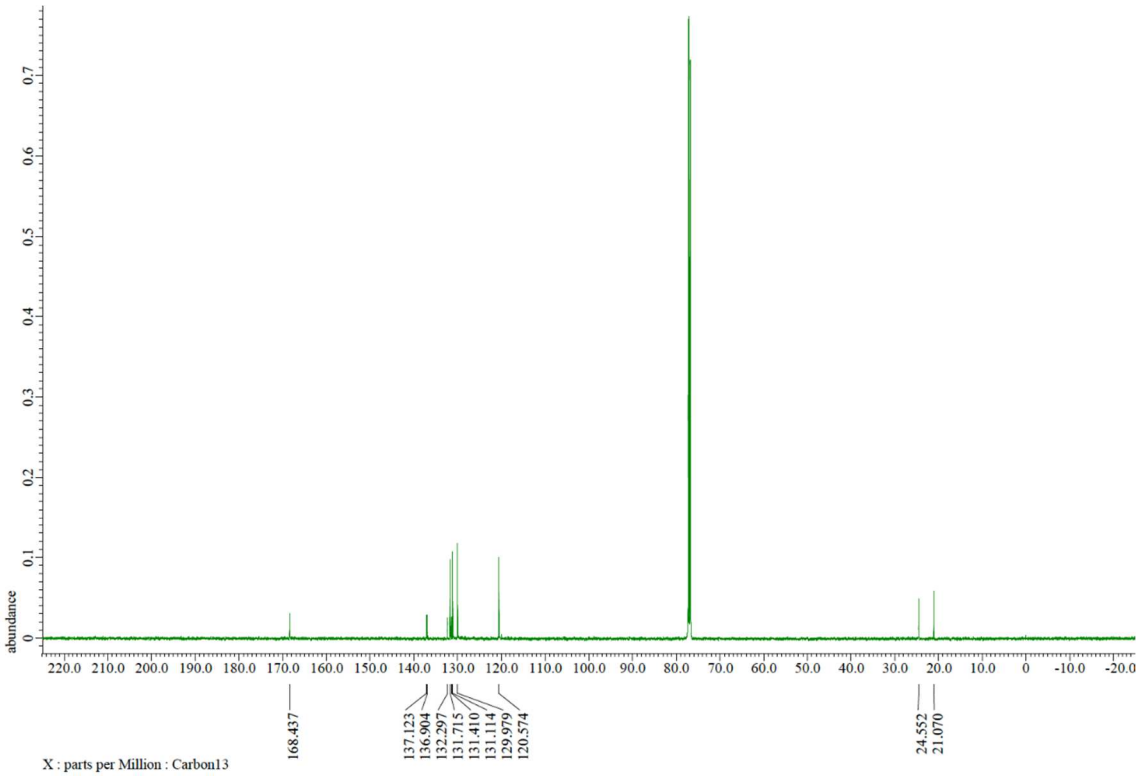
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bs**



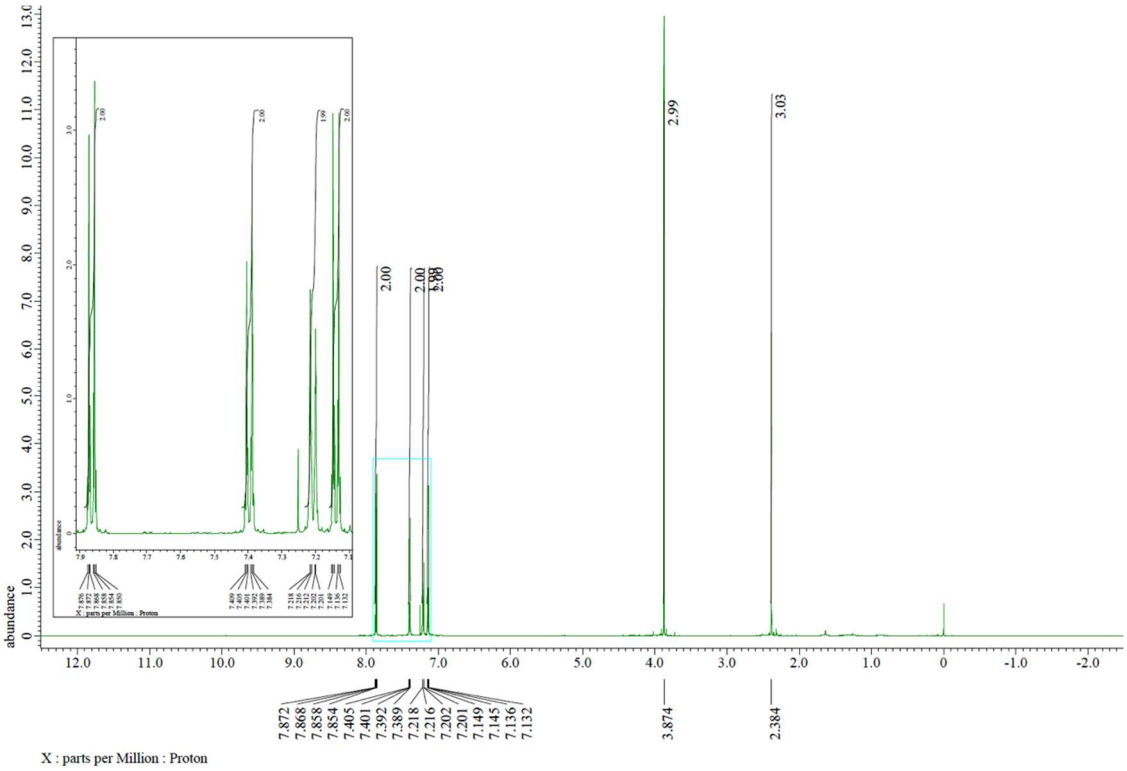
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bt**



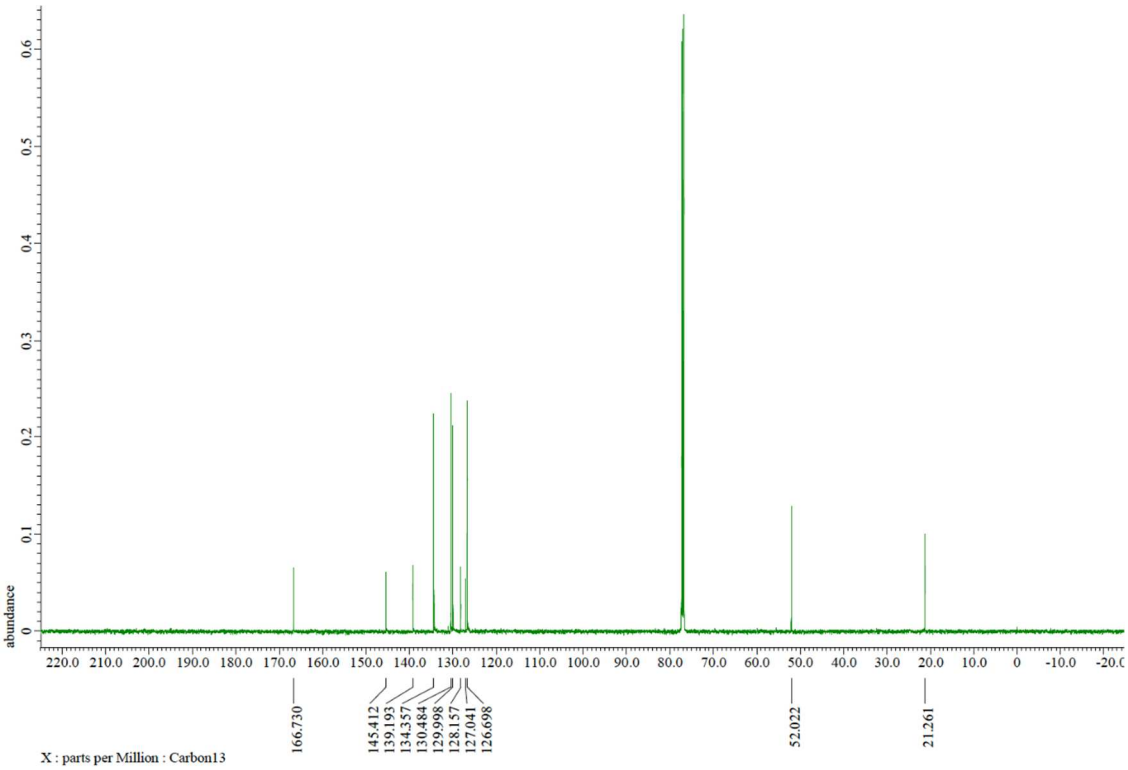
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bt**



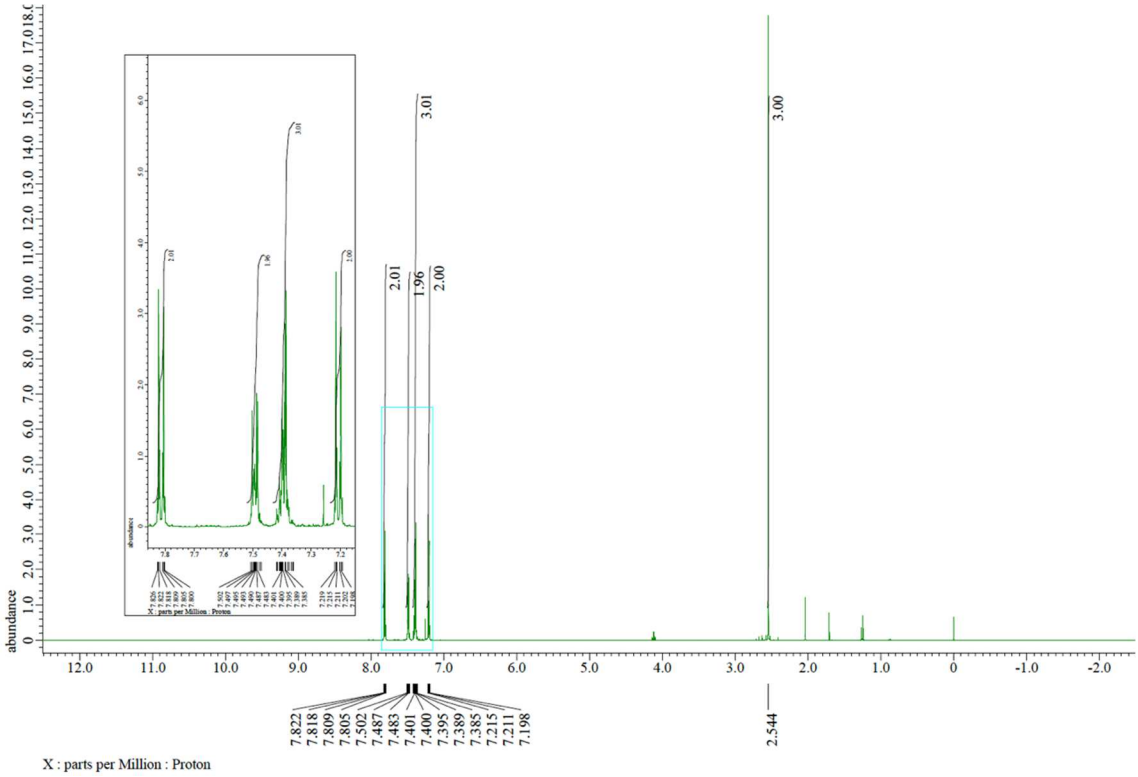
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bu**



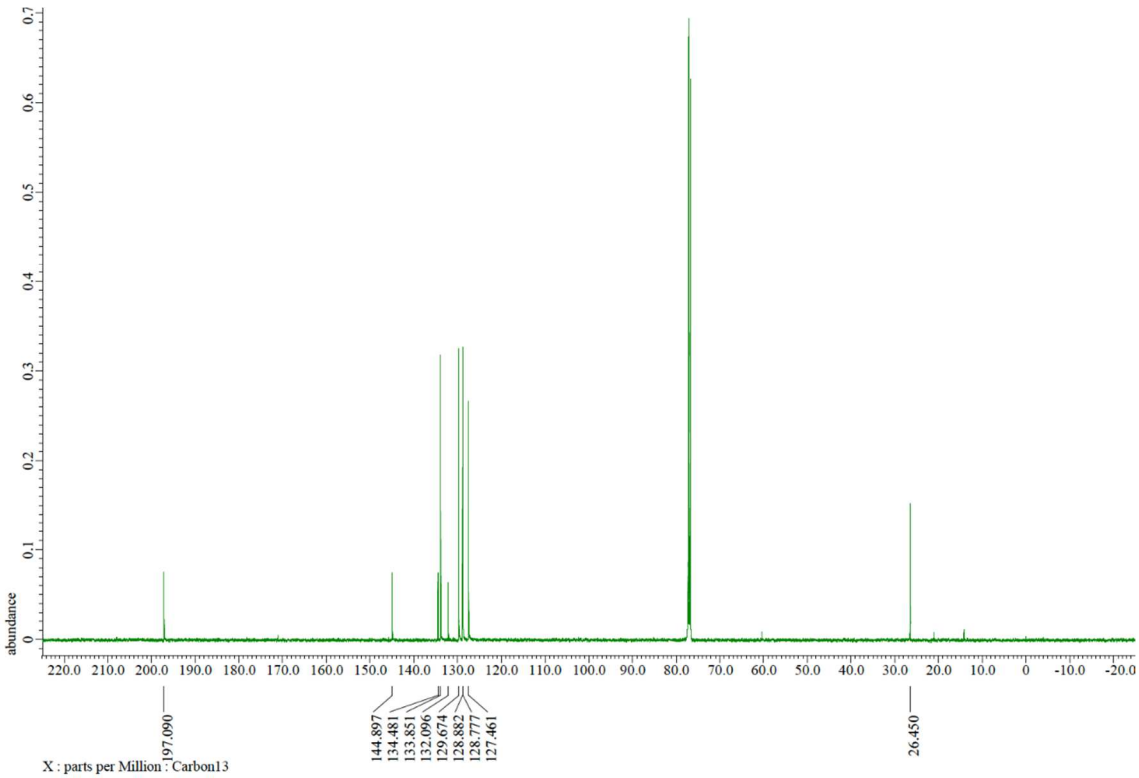
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bu**



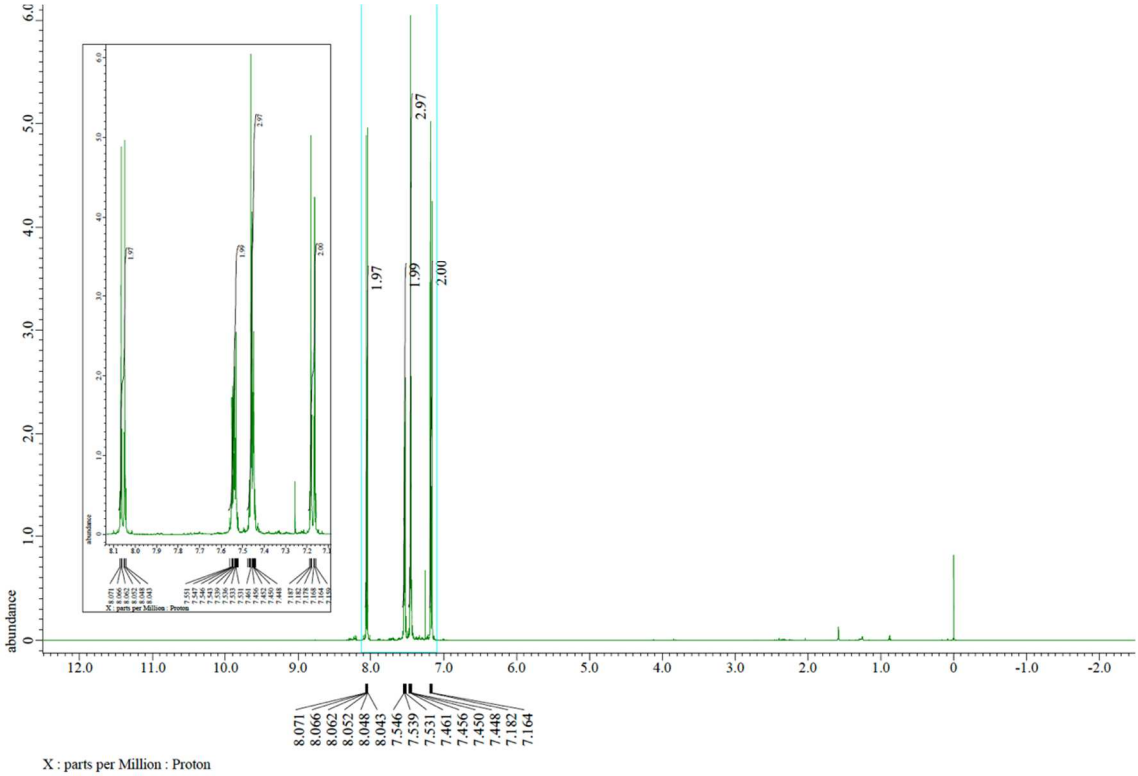
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1av**



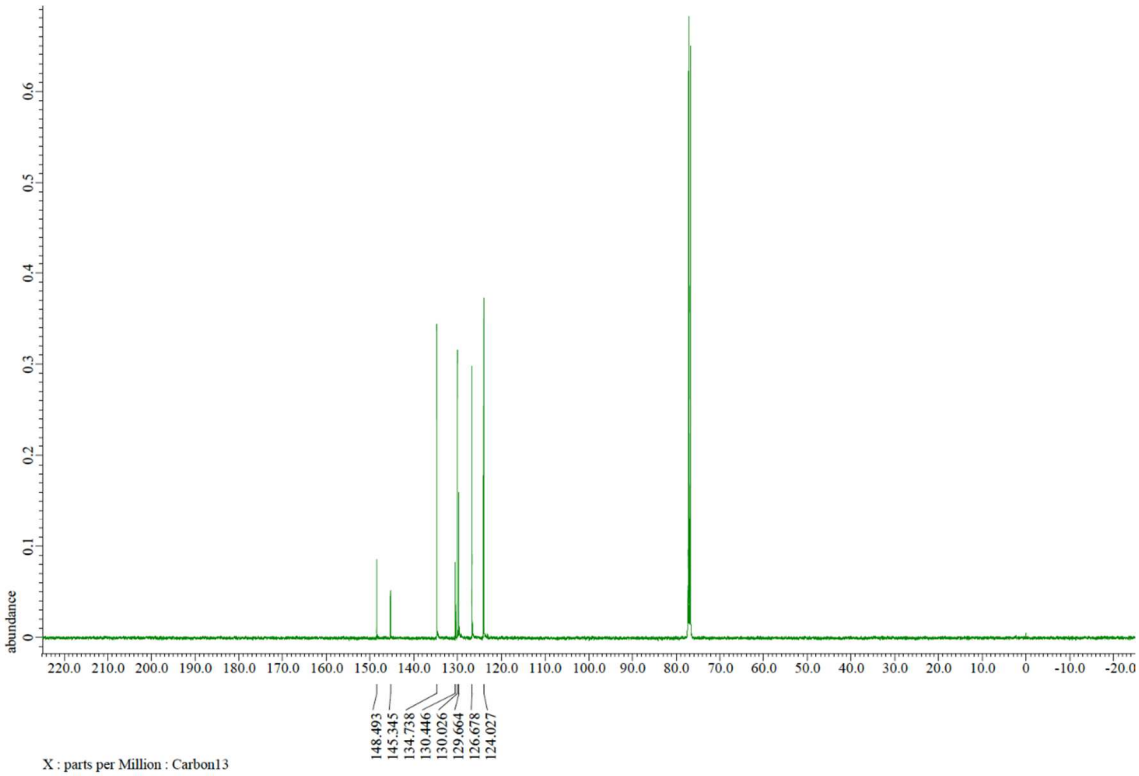
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1av**



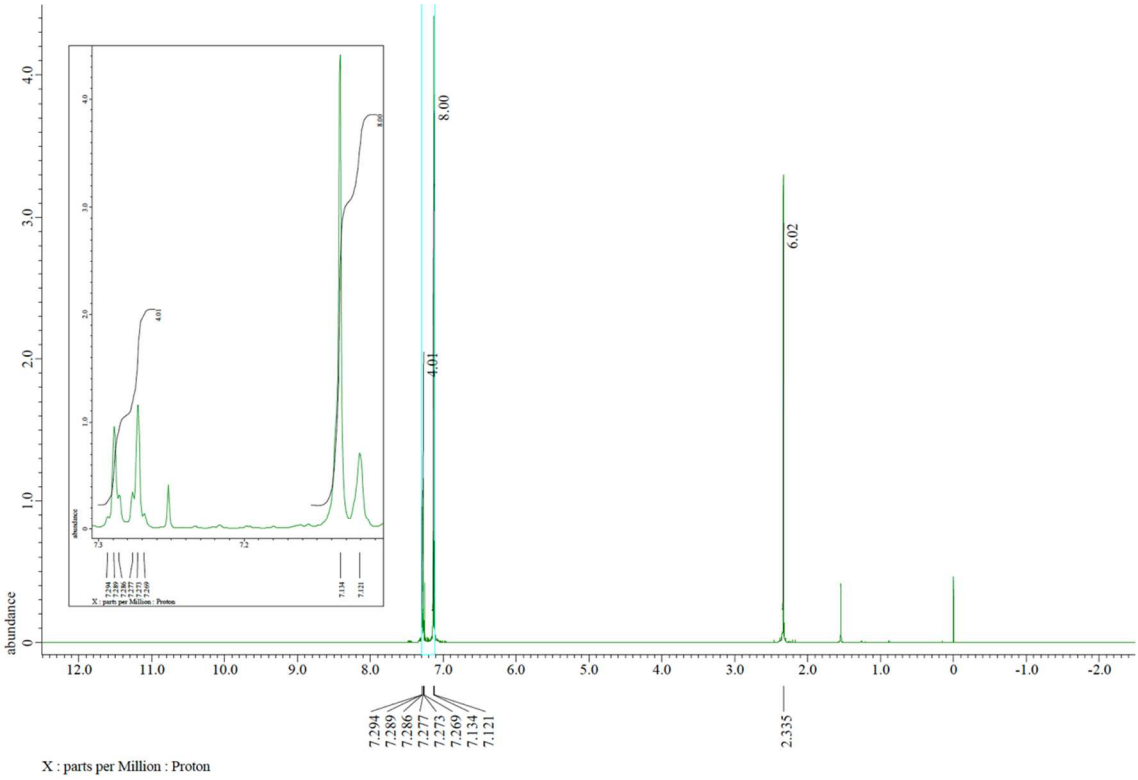
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1aw**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1aw**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1bab**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1bab**