SUPPORTING INFORMATION

PALLADIUM- AND NORBORNENE- CATALYZED SYNTHESIS OF HIGHLY FUNCTIONALIZED THIOPHENES: THE REMARKABLE EFFECT OF ELECTRON-POOR OLEFINS AS LIGAND

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Contents

General remarks

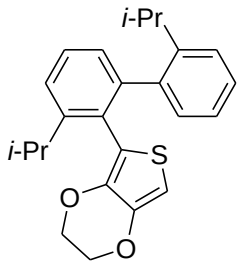
Most reagents were obtained from commercial sources and used as received. 2-*i*-Propyliodobenzene was prepared starting from the corresponding aniline derivative by diazotization procedure.[1] DMF was dried and stored over 4 Å molecular sieves under nitrogen. Reactions were carried out under nitrogen using standard Schlenk technique. Gas chromatography analyses were performed with a Carlo Erba HRGC 5300 instrument using a 30 m SE-30 capillary column. Flash column chromatography was performed on Merck Kieselgel 60 and thin-layer chromatography on Merck $60F_{254}$ plates. Melting points were determined with an Electrothermal apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 293 K, in $CDCl_3$ on Bruker AC-300 and AVANCE 300 spectrometers at 300.1 and 75.4 MHz respectively. ^{1}H and ^{13}C chemical shifts are reported relative to TMS and were determined by reference to residual ^{1}H and ^{13}C solvent resonances. The reported assignments are based on decoupling, COSY, NOESY, C–H HSQC, HMBC correlation experiments. GCMS spectra (EI, 70eV) were performed on a Hewlett Packard HP 6890 GC system equipped with a SE-52 capillary column and a HP5973 Mass Selective Detector mass analyzer. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

General procedure for the reaction of an ortho-substituted aryl iodide, an aryl bromide and 3,4-ethylenedioxythiophene

The *ortho*-substituted aryl iodide (0.36 mmol), the desired aryl bromide (0.36 mmol), 3,4-ethylenedioxythiophene (127 mg, 0.9 mmol), norbornene (34 mg, 0.36 mmol), $Pd(OAc)_2$ (4 mg, 0.018 mmol), methyl cinnamate (233 mg, 1.44 mmol) and K_2CO_3 (0.11 g, 0.8 mmol) in DMF (8 mL) were stirred in a Schlenk-type flask under nitrogen with a magnetic bar at 105 ˚C for 24–96 h. At the end of the reaction the mixture was allowed to cool to room temperature, diluted with EtOAc (30 mL), washed three times with brine (3 × 30 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude mixture was analyzed by GC and ^{1}H NMR spectroscopy. The products were isolated by flash column chromatography on silica gel using a mixture of hexane-EtOAc as eluent.

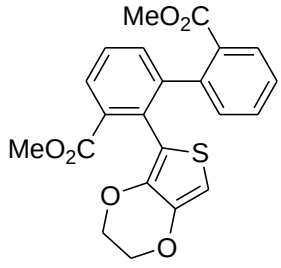
Product characterizations

2-(3,2'-Di-*i*-propyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**3a**)



Compound **3a** was previously characterized[2] as follows: the crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 95:5) to give the title compound as a pale yellow solid. M.p. (hexane): 130–131.5 ºC. A 4:3 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 7.47–7.40 (4H, m, (A, B)), 7.32–7.12 (9H, m, (4H for A, 5H for B)), 7.05 (1H, ddd, *J* = 7.8, 6.6, 1.9 Hz, A), 6.24, 6.18 (2H, 2 s, (B, A)), 4.20–3.96 (8H, m, (4H for A, 4H for B)), 3.11, 3.09 (2H, 2 hept, *J* = 6.9 Hz, (A, B)), 2.90, 2.86 (2H, 2 hept, *J* = 6.9 Hz, (B, A)), 1.37 (3H, d, *J* = 6.9 Hz, B), 1.30, 1.29 (6H, 2 d, *J* = 6.9 Hz, A), 1.22 (3H, d, *J* = 6.9 Hz, A), 1.21 (3H, d, *J* = 6.9 Hz, B), 1.20 (3H, d, *J* = 6.9 Hz, A), 1.12, 1.09 (6H, 2 d, *J* = 6.9 Hz, B). ^{13}C NMR: δ 150.2, 149.7, 146.7, 146.1, 143.7, 143.4, 140.5, 140.3, 140.21, 140.19, 138.1, 137.7, 130.7, 129.6, 129.2, 129.1, 128.1, 128.0, 127.6, 127.4, 127.23, 127.19, 124.6, 124.5, 124.2, 124.1, 124.0, 123.9, 114.6, 99.0, 98.0, 64.4, 64.22, 64.18, 30.6, 30.4, 29.8, 29.4, 25.6, 25.3, 24.8, 24.3, 24.1, 23.5, 23.0, 22.9. MS: M^{+} 378 (100), *m/z* 335 (53), 287 (20), 261 (15), 221 (18), 202 (24), 189 (17), 178 (12), 165 (15). Anal. Calcd. for $C_{24}H_{26}O_2S$: C, 76.15; H, 6.92; O, 8.45; S, 8.47. Found: C, 76.07; H, 6.94.

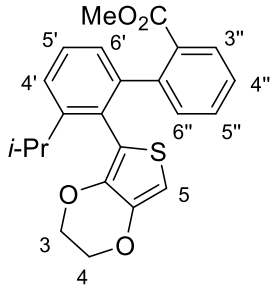
2-(3,2'-Dicarbomethoxy-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**4a**)



Compound **4a** was previously characterized[2] as follows: the crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 7:3) to give the title compound as a pale yellow solid. M.p. (hexane): 88–89 ºC. ^{1}H NMR: δ 7.86–7.81 (2H, m), 7.48–7.39 (3H, m), 7.32 (1H, td, *J* = 7.6, 1.5 Hz), 7.21 (1H, br d, *J* = 7.5 Hz), 6.17 (1H, s), 4.08–3.75 (4H, m), 3.72 (3H, s), 3.59 (3H, s). ^{13}C NMR: δ 168.2, 167.1, 144.5, 141.6, 140.2, 138.0, 133.1, 132.3, 131.3, 130.8, 130.0,

129.8, 129.7, 128.7, 127.5, 127.2, 113.6, 99.5, 64.2, 52.0, 51.6. MS: M^+ 410 (100), *m/z* 351 (29), 59 (10). Anal. Calcd. for $C_{22}H_{18}O_6S$: C, 64.38; H, 4.42; O, 23.39; S, 7.81. Found: C, 64.27; H, 4.46.

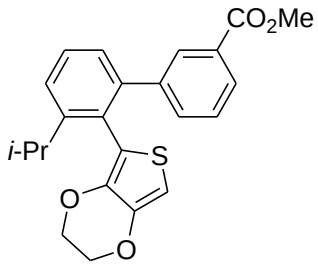
2'-(2''-Carbomethoxy-3'-*i*-propyl-1',1''-biphenyl-2'-yl)-3,4-ethylenedioxythiophene (**1a**)



The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (92 mg, 65% yield) as a pale yellow oil.

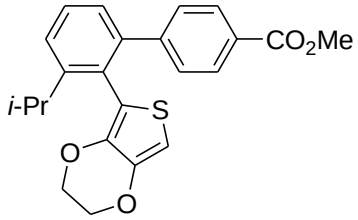
A 2:1 mixture of stereoisomers indicated as A and B. ^{1}H NMR: δ 7.86–7.82 (2H, m, H3"), 7.45–7.34 (6H, m, H6", H4', H5"), 7.32–7.25 (2H, m, H4"), 7.24–7.17 (2H, m, H5'), 7.09–7.02 (2H, m, H6'), 6.15 (1H, s, H5A), 6.14 (1H, s, H5B), 4.14–3.76 (8H, m, 2H3 and 2H4 (4H for A, 4H for B)), 3.62 (3H, s, CO_2CH_3 A), 3.54 (3H, s, CO_2CH_3 B), 3.06 (2H, hept, *J* = 6.8 Hz), 1.26 (3H, d, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.24, 1.23 (6H, 2 d, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.18 (3H, d, *J* = 6.8 Hz, $CH(CH_3)_2$). ^{13}C NMR: δ 167.7 (CO B), 167.5 (CO A), 149.5 (C3' A), 149.3 (C3'B), 144.1 (C2" A), 143.9 (C2" B), 143.1 (C1"A), 142.9 (C1" B), 140.5 (C2a B), 140.3 (C2a A), 138.2 (C4a B), 137.9 (C4a A), 131.4 (C4" B), 130.9 (C4"A), 130.6 (C5"B), 130.3 (C5"A), 130.1(C1'* B), 129.73 (C1'* A), 129.69 (C3" B), 129.4 (C3" A), 128.7 (C2'*B) , 128.2 (C6" A), 127.9 (C2'* A), 127.7 (C6" B), 126.7 (C5'A), 126.63 (C6' B), 126.58 ((C5'B), 125.9 (C6'A), 124.1 (C4'A), 124.0 (C4'B), 114.5 (C2 A), 114.1 (C2 B), 98.9 (C5 B), 98.4 (C5 A), 64.3 (C3, C4 B), 64.1 (C3, C4 A), 51.5 (CO_2CH_3 A), 51.3 (CO_2CH_3 B), 30.35 ($CH(CH_3)_2$ A) , 30.33 ($CH(CH_3)_2$ B), 24.5, 24.3, 23.9 ($CH(CH_3)_2$ A and B; 2C overlapping in 23.9 ppm signal). MS: M^+ 394 (100), *m/z* 335 (24), 317 (18), 259 (16), 202 (19), 189 (18), 59 (6). Anal. Calcd. for $C_{23}H_{22}O_4S$: C, 70.03; H, 5.62; O, 16.22; S, 8.13. Found: C, 69.91; H, 5.67.

2-(3'-Carbomethoxy-3-*i*-propyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1b**)



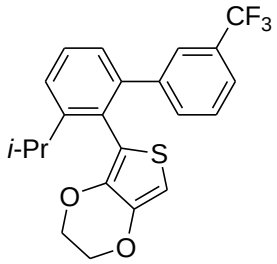
The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (83 mg, 59% yield) as a pale yellow oil. ^{1}H NMR: δ 7.97 (1H, t, *J* = 2.0 Hz), 7.88 (1H, dt, *J* = 7.7, 1.6 Hz), 7.47–7.37 (3H, m), 7.30 (1H, t, *J* = 7.9 Hz), 7.22 (1H, d, *J* = 6.1, 2.6 Hz), 6.21 (1H, s), 4.18–3.79, 3.88 (4H, m + 3H, s), 3.15 (1H, hept, *J* = 6.9 Hz), 1.24, 1.23 (6H, two partly overlapping d, *J* = 6.9 Hz). ^{13}C NMR: δ 167.0, 150.3, 143.2, 142.4, 140.8, 138.9, 133.2, 130.3, 129.2, 129.0, 128.4, 127.5, 127.4, 127.0, 124.9, 114.2, 98.8, 64.4, 64.3, 51.9, 30.5, 24.4, 24.0. MS: M^{+} 394 (100), *m/z* 349 (18), 295 (23), 221 (20), 202 (37), 189 (40), 165 (19), 59 (30). Anal. Calcd. for $C_{23}H_{22}O_4S$: C, 70.03; H, 5.62; O, 16.22; S, 8.13. Found: C, 70.12; H, 5.69.

2-(4'-Carbomethoxy-3-*i*-propyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1c**)



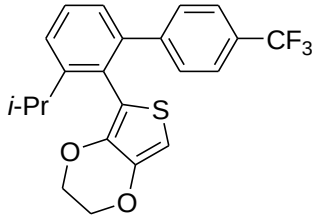
The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (0.110 g, 78% yield) as a pale yellow oil. ^{1}H NMR: δ 7.93–7.87 (2H, m), 7.48–7.39 (2H, m), 7.33–7.25 (2H, m), 7.24–7.17 (1H, m), 6.23 (1H, s), 4.13–3.90 (3H, m), 3.89 (3H, s), 3.65 (1H, ddd, *J* = 11.4, 6.9, 1.8 Hz), 3.18 (1H, hept, *J* = 6.9 Hz), 1.23 (6H, t, *J* = 7.1 Hz). ^{13}C NMR: δ 167.1, 150.2, 147.2, 143.1, 140.8, 138.7, 128.9, 128.6, 128.2, 127.9, 127.0, 125.2, 114.1, 98.8, 64.4, 64.2, 51.9, 30.4, 24.5, 24.0. MS: M^{+} 394 (100), *m/z* 349 (23), 334 (18), 295 (34), 260 (19), 221 (36), 202 (69), 189 (79), 178 (22), 165 (39), 59 (68). Anal. Calcd. for $C_{23}H_{22}O_4S$: C, 70.03; H, 5.62; O, 16.22; S, 8.13. Found: C, 69.87; H, 5.56.

2-(3-*i*-Propyl-3'-trifluoromethyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1d**)



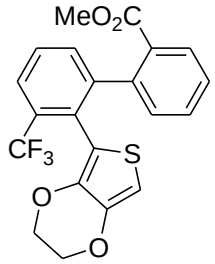
The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (107 mg, 74% yield) as a pale yellow oil. ^{1}H NMR: δ 7.60–7.57 (1H, m), 7.53–7.34 (5H, m), 7.28–7.13 (1H, m), 6.27 (1H, s), 4.19–4.05 (2H, m), 4.01–3.92 (1H, m), 3.81–3.72 (1H, m), 3.22 (1H, hept, J = 6.8 Hz), 1.28, 1.26 (6H, two partly overlapping d, J = 6.8 Hz). ^{13}C NMR: δ 150.4, 143.0, 142.8, 140.9, 138.8, 132.1, 129.0, 127.9 (q, CCF$_3$, J = 31.2 Hz), 127.7, 126.9, 126.0 (q, $J_{C,F}$ = 4.0 Hz), 125.2, 124.3 (q, CF$_3$, $J_{C,F}$ = 273.0 Hz), 123.0 (q, $J_{C,F}$ = 4.0 Hz), 114.0, 98.9, 64.3, 64.2, 30.5, 24.4, 24.0. MS: M$^+$ 404 (100), *m/z* 359 (28), 344 (21), 305 (35), 259 (26), 233 (29), 202 (24), 189 (25), 69 (8). Anal. Calcd. for $C_{22}H_{19}F_3O_2S$: C, 65.33; H, 4.74; F, 14.09; O, 7.91; S, 7.93. Found: C, 65.25; H, 4.69.

2-(3-*i*-Propyl-4'-trifluoromethyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1e**)



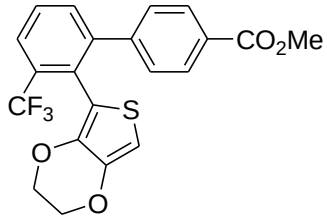
The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (93 mg, 64% yield) as a colourless oil. ^{1}H NMR: δ 7.54–7.43 (4H, m), 7.37–7.31 (2H, m), 7.24–7.18 (1H, m), 6.28 (1H, s), 4.15–3.98 (2H, m), 3.92 (1H, ddd, J = 11.3, 5.2, 1.8 Hz), 3.67 (1H, ddd, J = 11.4, 6.5, 1.8 Hz), 3.21 (1H, hept, J = 6.9 Hz), 1.27, 1.24 (6H, two partly overlapping d, J = 6.9 Hz). ^{13}C NMR: δ 150.3, 146.0, 142.8, 140.9, 138.7, 129.2 (2C), 129.0, 127.2 (q, CCF$_3$, J = 30.9 Hz), 127.1, 125.3, 124.3 (q, CF$_3$, $J_{C,F}$ = 268.9 Hz), 124.1 (q, 2C, $J_{C,F}$ = 3.4 Hz), 114.0, 98.9, 64.4, 64.2, 30.4, 24.5, 24.0. MS: M$^+$ 404 (100), *m/z* 359 (33), 344 (22), 305 (32), 259 (27), 233 (26), 202 (23), 189 (22), 69 (10). Anal. Calcd. for $C_{22}H_{19}F_3O_2S$: C, 65.33; H, 4.74; F, 14.09; O, 7.91; S, 7.93. Found: C, 65.21; H, 4.78.

2-(2'-Carbomethoxy-3-trifluoromethyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1f**)



The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (101 mg, 67% yield) as a white solid. M.p. (hexane): 113–114 ºC. A 2:1 mixture of stereoisomers indicated as A and B. ^{1}H NMR: δ 7.96–7.87 (2H, m, 1H (A), 1H (B)), 7.83–7.73 (2H, m, 1H (A), 1H (B)), 7.59–7.28 (8H, m, 4H (A), 4H (B)), 7.24 (1H, dd, *J* = 7.5, 1.5 Hz, A), 7.12 (1H, dd, *J* = 7.5, 1.5 Hz, B), 6.17 (2H, s, 1H (A), 1H (B)), 4.13–3.81 (8H, m, 4H (A), 4H (B)), 3.66 (3H, s, A), 3.58 (3H, s, B). ^{13}C NMR: δ 167.2, 167.1, 146.9, 146.5, 141.5, 141.0, 140.2, 139.9, 139.2, 139.0, 133.1, 132.1, 131.5, 131.3, 131.0, 130.9, 130.7, 130.1, 130.0 (q, *C*CF_3, *J* = 31.1 Hz), 129.9, 129.7, 129.4, 128.2, 127.6, 127.5, 125.2, 125.1 (q, $J_{C,F}$ = 5.4 Hz), 123.9 (q, 2CF_3, $J_{C,F}$ = 272.3 Hz), 111.2, 111.0, 99.9, 99.7, 64.42, 64.39, 64.2, 51.9, 51.7. MS: M^+ 420 (100), *m/z* 361 (40), 289 (18), 264 (17), 233 (19), 232 (18), 182 (13), 59 (8). Anal. Calcd. for $C_{21}H_{15}F_3O_4S$: C, 60.00; H, 3.60; F, 13.56; O, 15.22; S, 7.63. Found: C, 59.89; H, 3.65.

2-(4'-Carbomethoxy-3-trifluoromethyl-1,1'-biphenyl-2-yl)-3,4-ethylenedioxythiophene (**1g**)

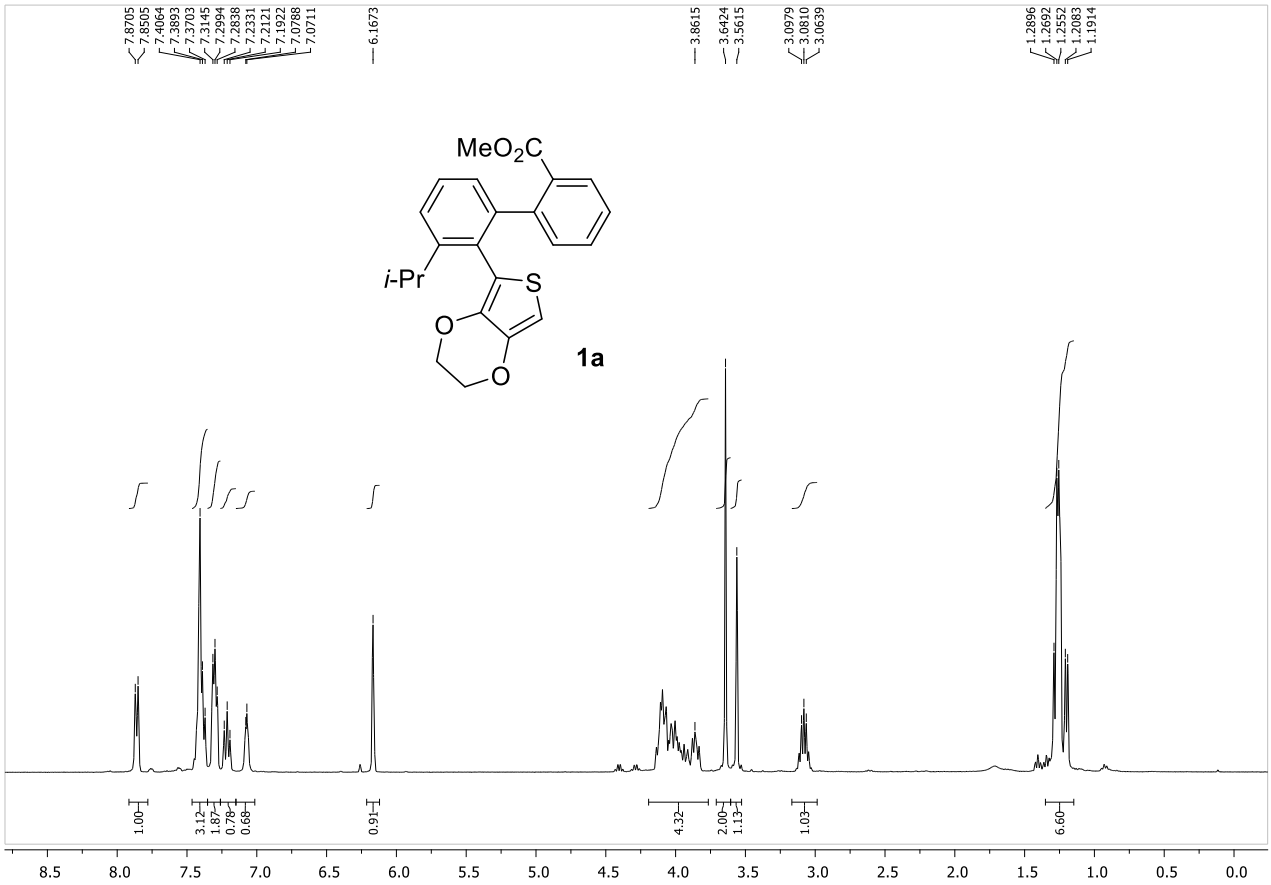


The crude product was purified by flash chromatography on silica gel (hexane:ethylacetate = 8:2) to give the title compound (94 mg, 62% yield) as a white solid. M.p. (hexane): 131–132 ºC. ^{1}H NMR: δ 7.96–7.89 (2H, m), 7.84–7.75 (1H, m), 7.62–7.53 (2H, m), 7.32–7.23 (2H, m), 6.28 (1H, s), 4.15–3.92 (3H, m), 3.91 (3H, s), 3.73–3.66 (1H, m). ^{13}C NMR: δ 166.9, 145.5, 145.2, 140.3, 139.6, 133.0, 131.7 (q, *C*CF_3, *J* = 30.9 Hz), 130.7 (q, $J_{C,F}$ = 5.2 Hz), 128.84 (2C), 128.80 (2C), 128.76, 128.7, 125.9 (q, $J_{C,F}$ = 5.3 Hz), 123.7 (q, CF_3, $J_{C,F}$ = 258.7 Hz), 110.8, 100.1, 64.34, 64.30, 52.1. MS: M^+ 420 (100), *m/z* 355 (20), 232 (14), 59 (7). Anal. Calcd. for $C_{21}H_{15}F_3O_4S$: C, 60.00; H, 3.60; F, 13.56; O, 15.22; S, 7.63. Found: C, 60.15; H, 3.57.

References

(1) M. S. Lesslie and U. J. H. Mayer, *J. Chem. Soc.*, 1961, 611–618.

(2) N. Della Ca', G. Maestri and Marta Catellani, *Chem. Eur. J.*, 2009, **15**, 7850.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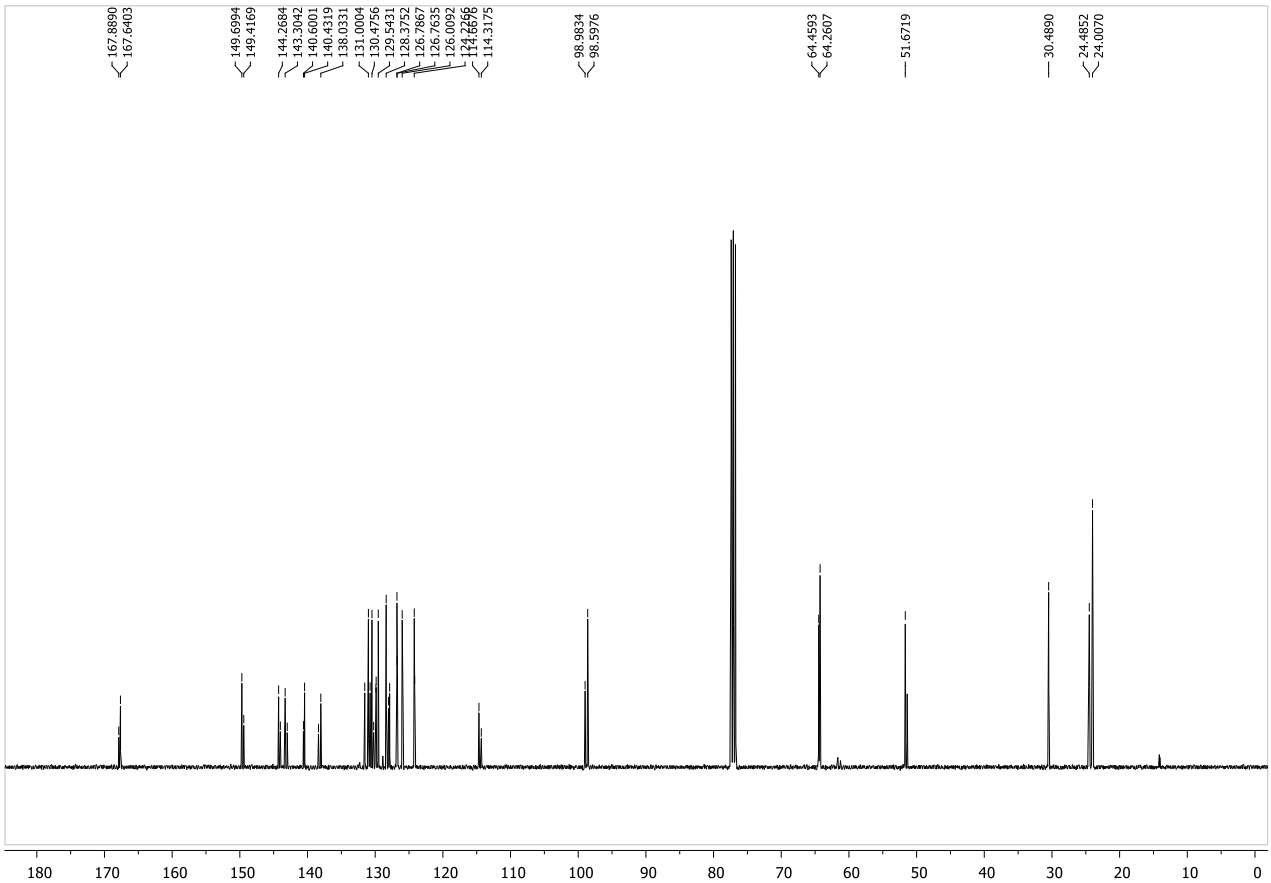
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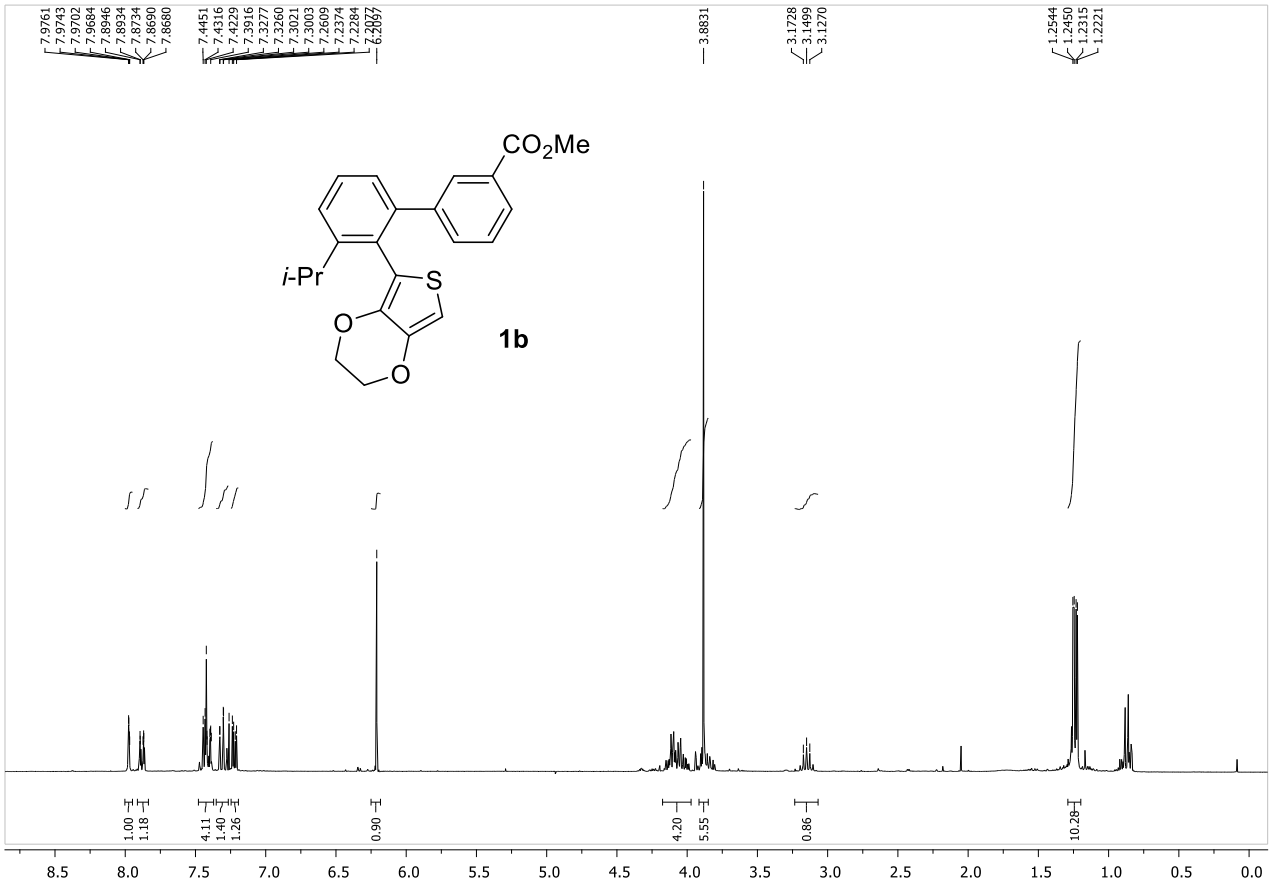
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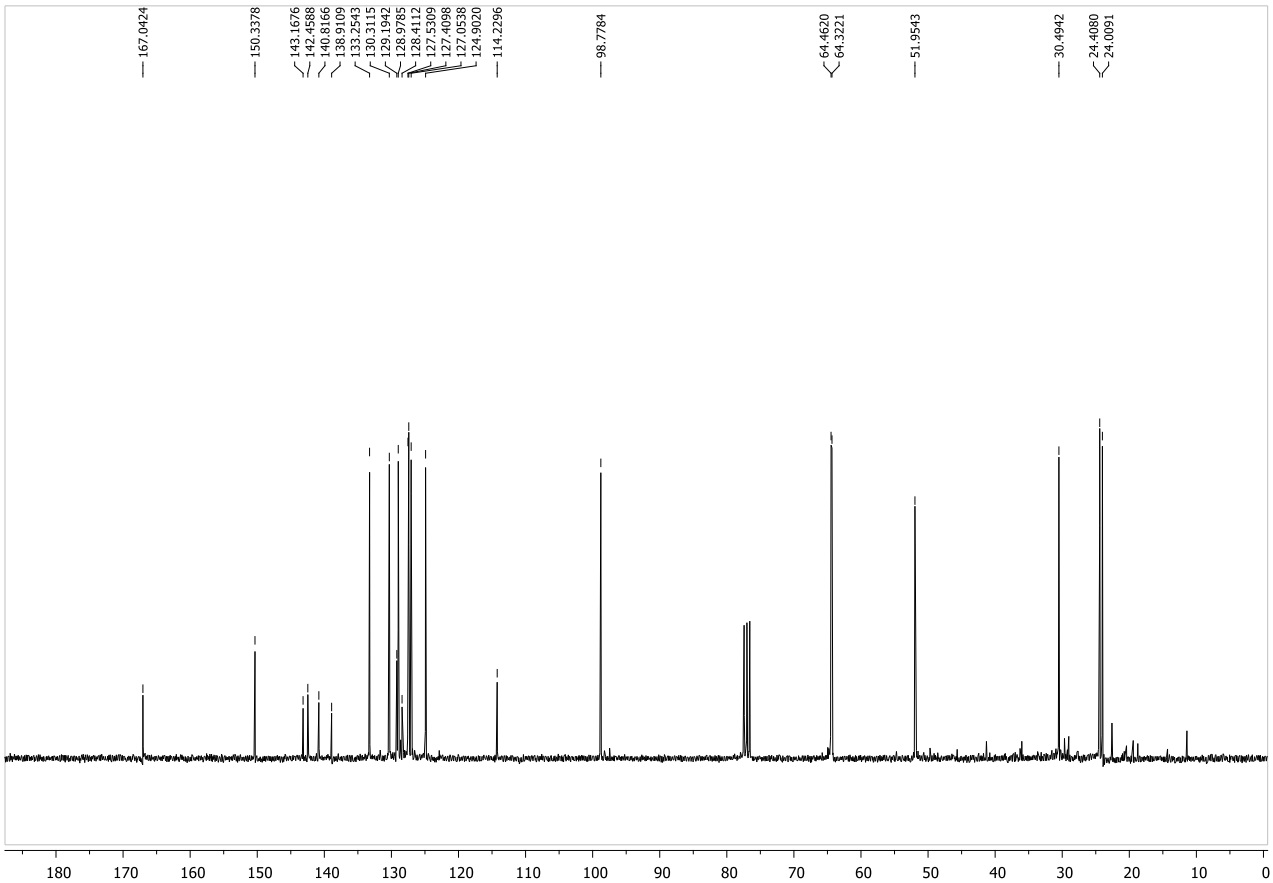
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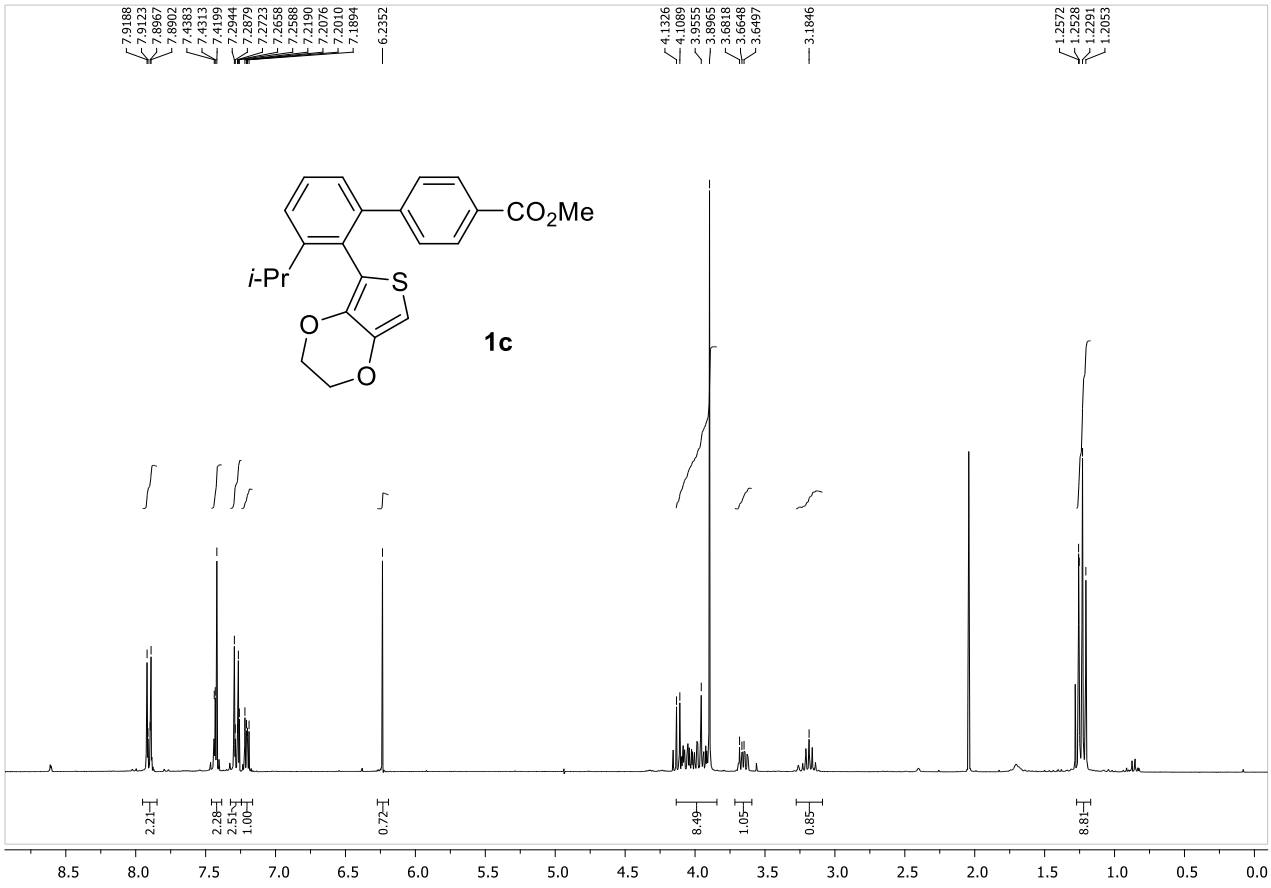
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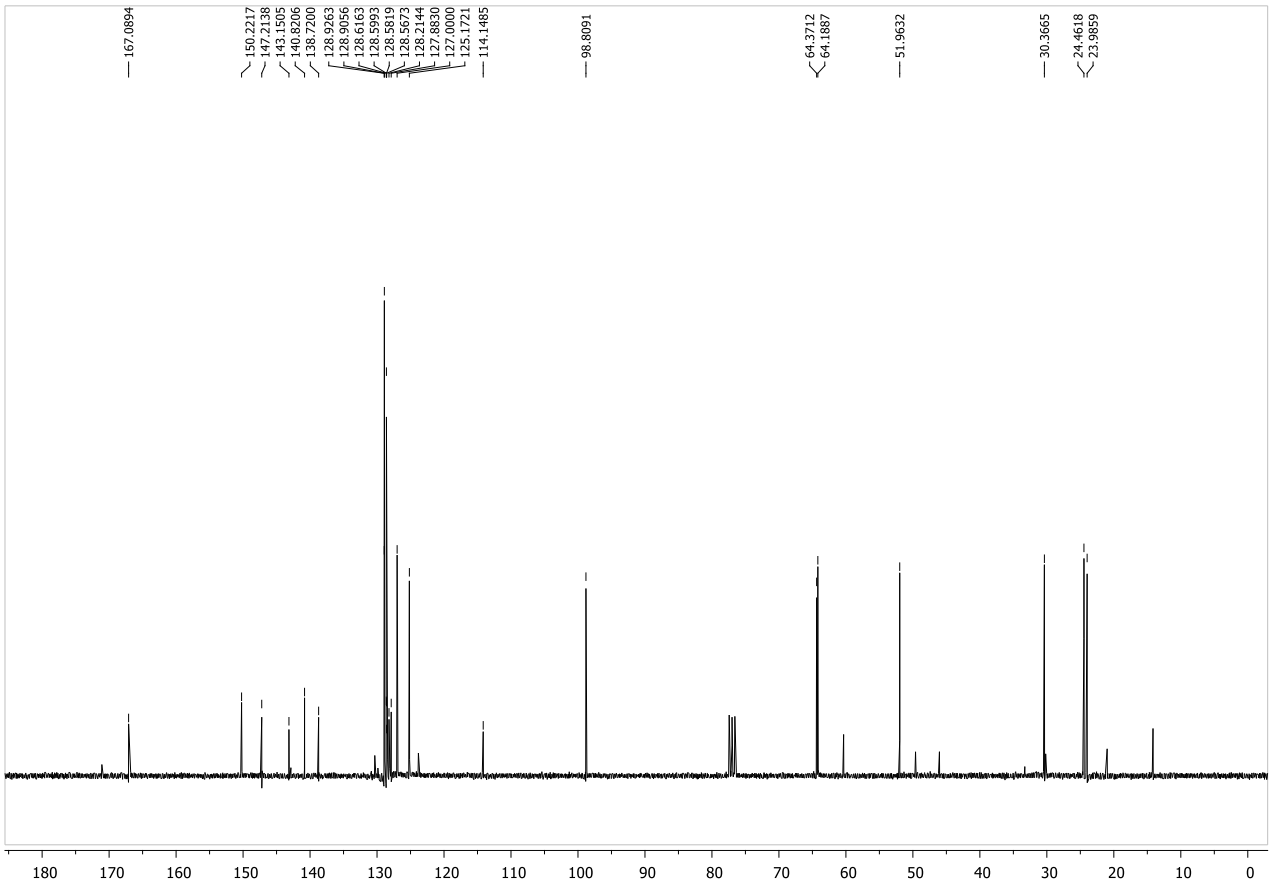
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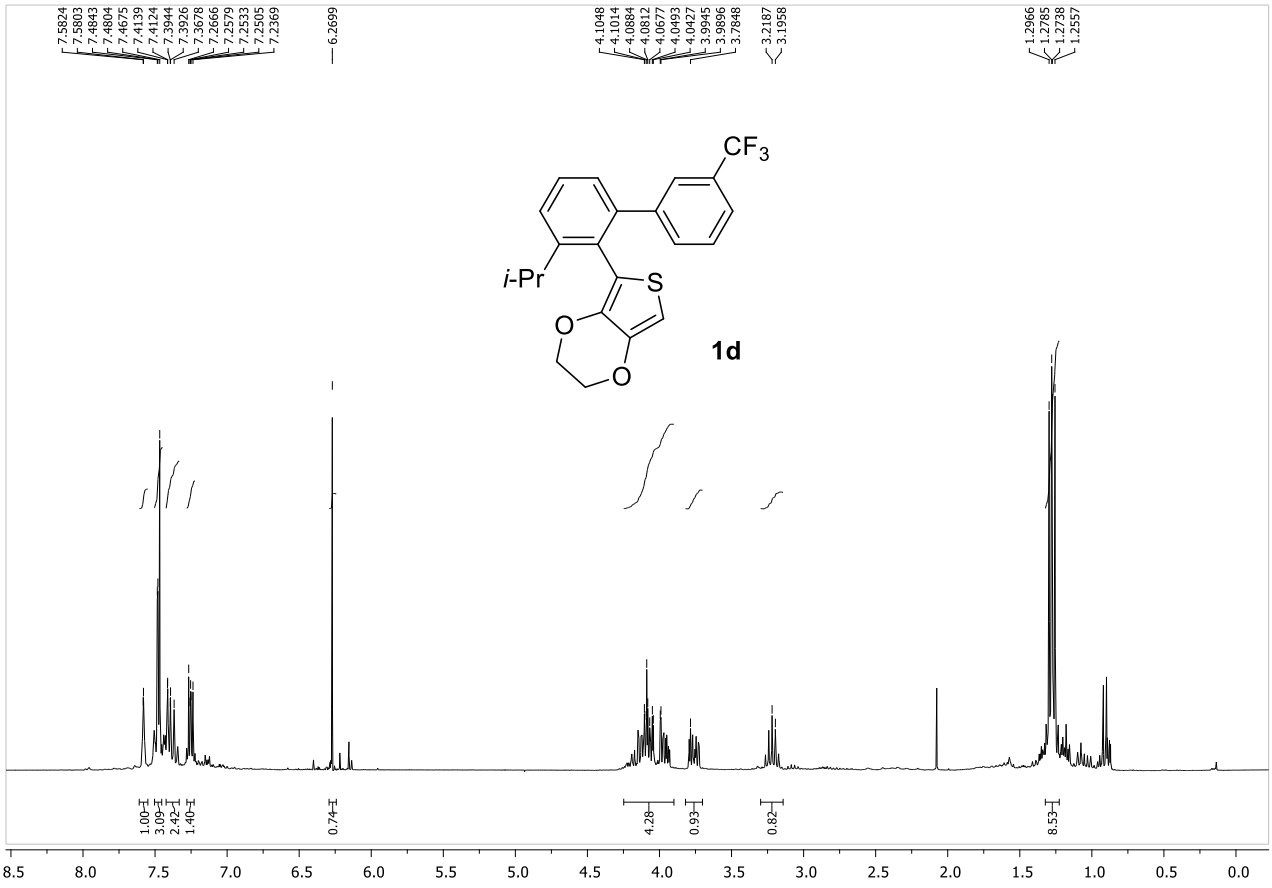
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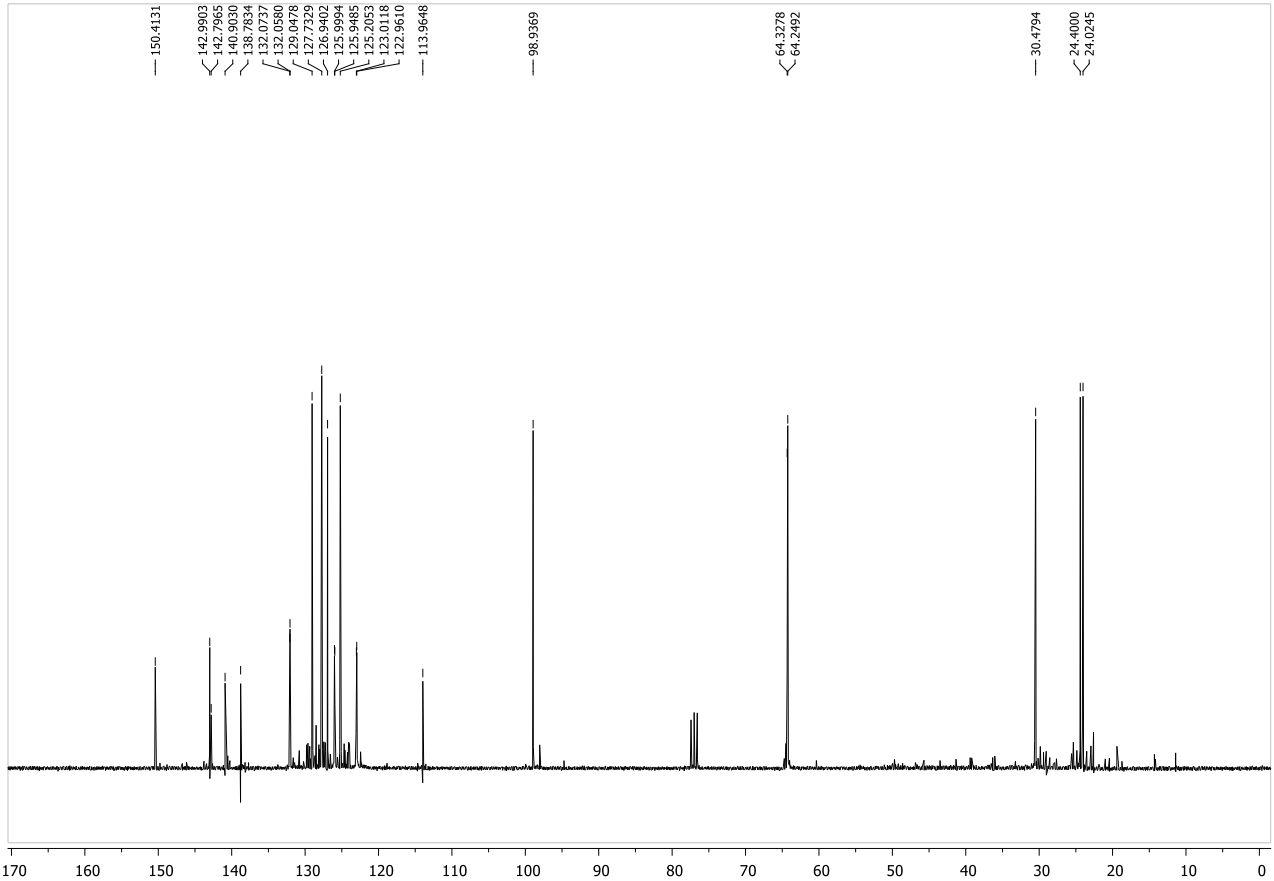
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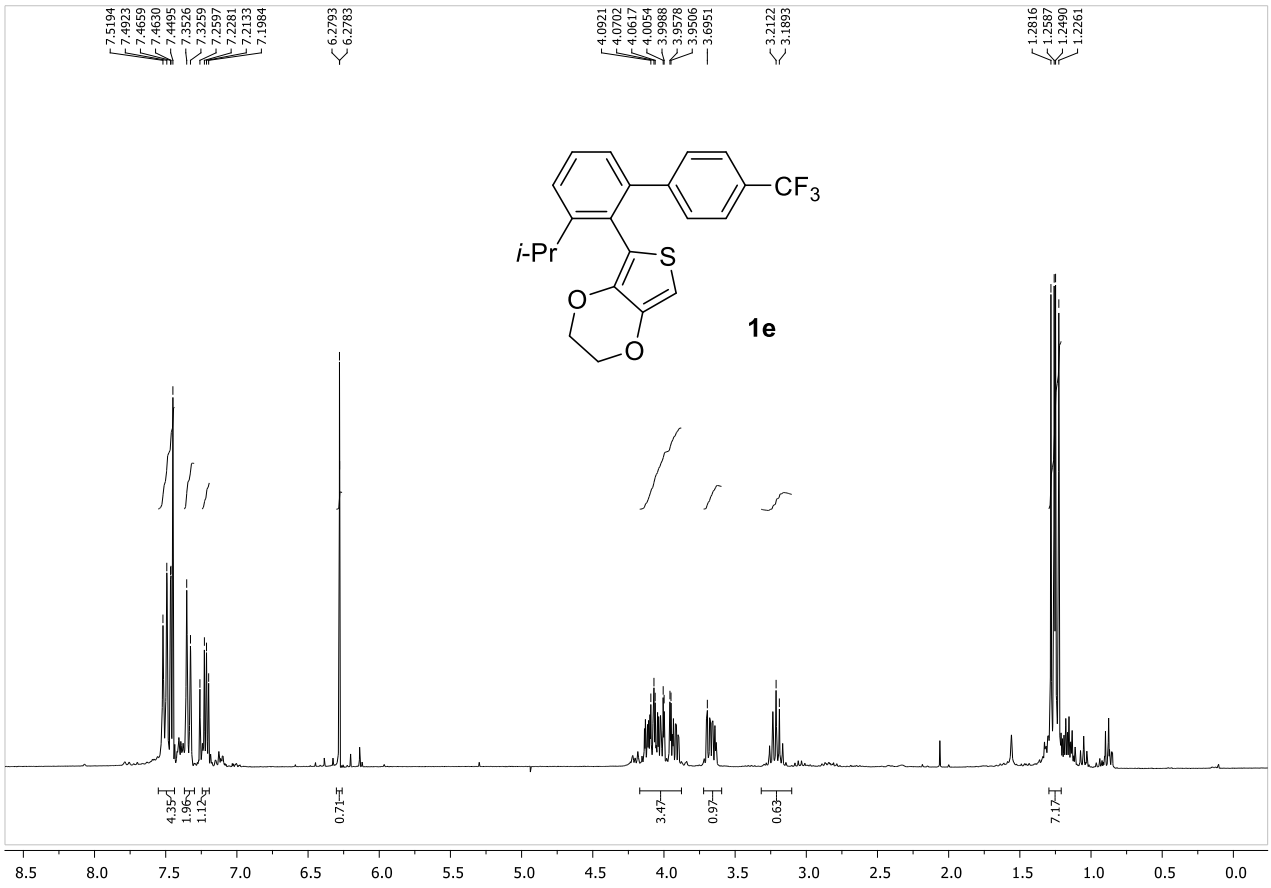
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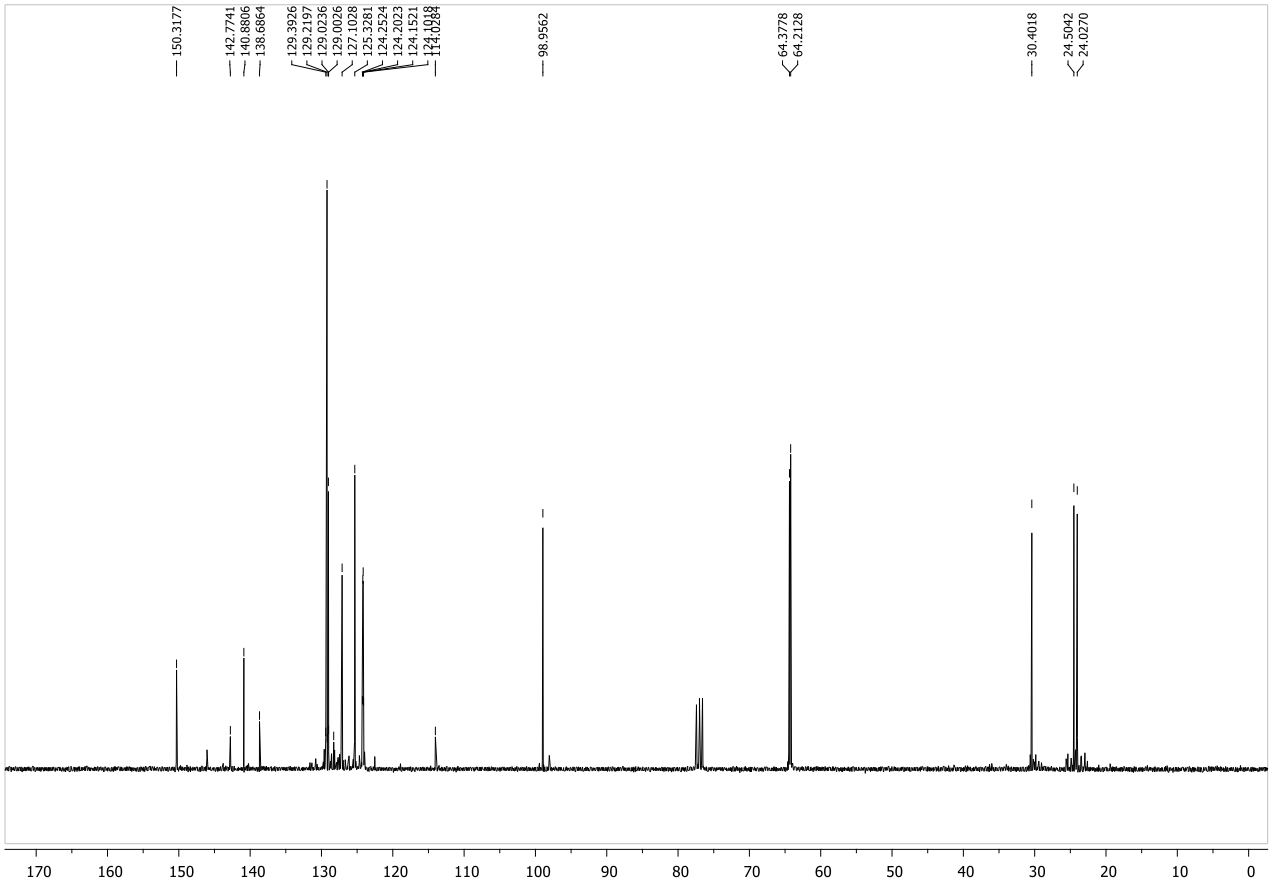
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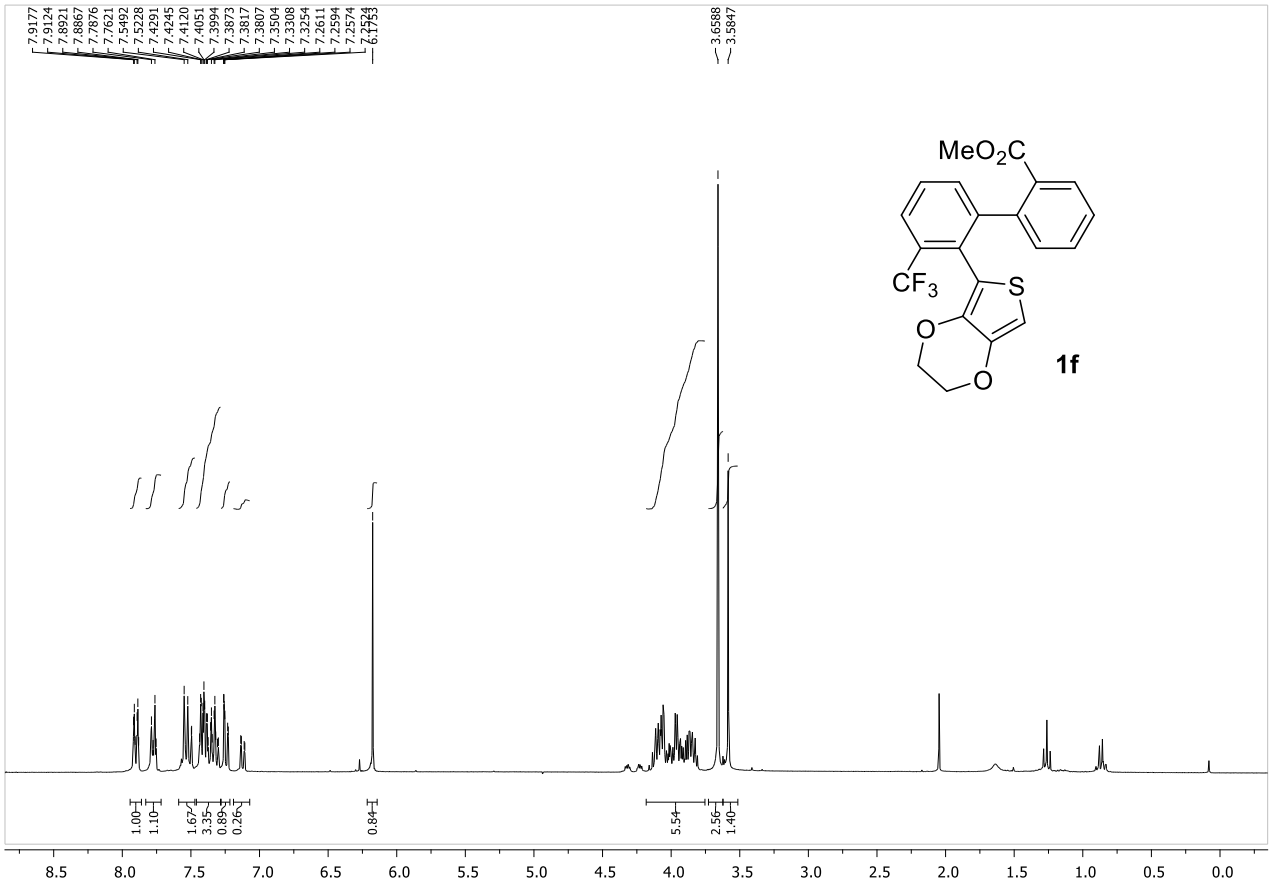
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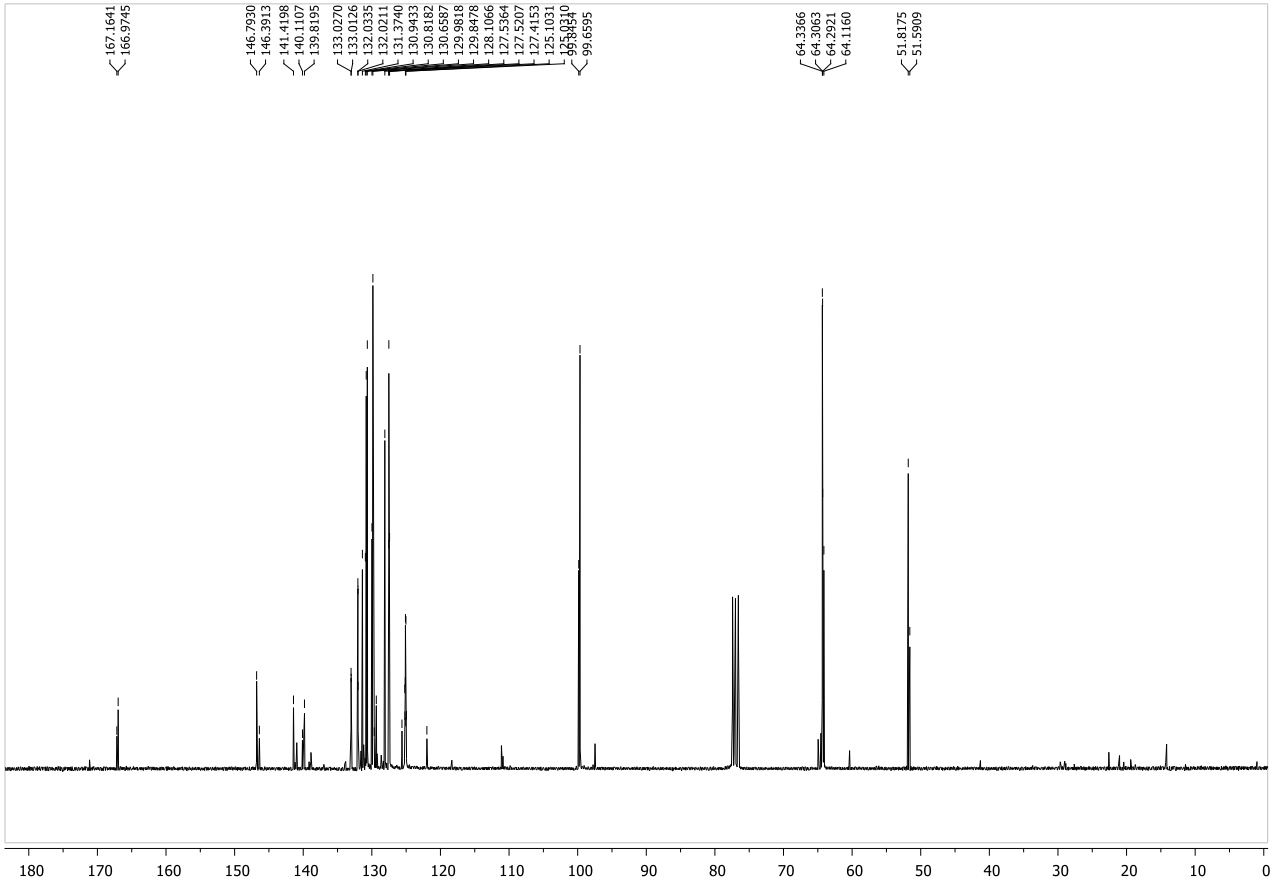
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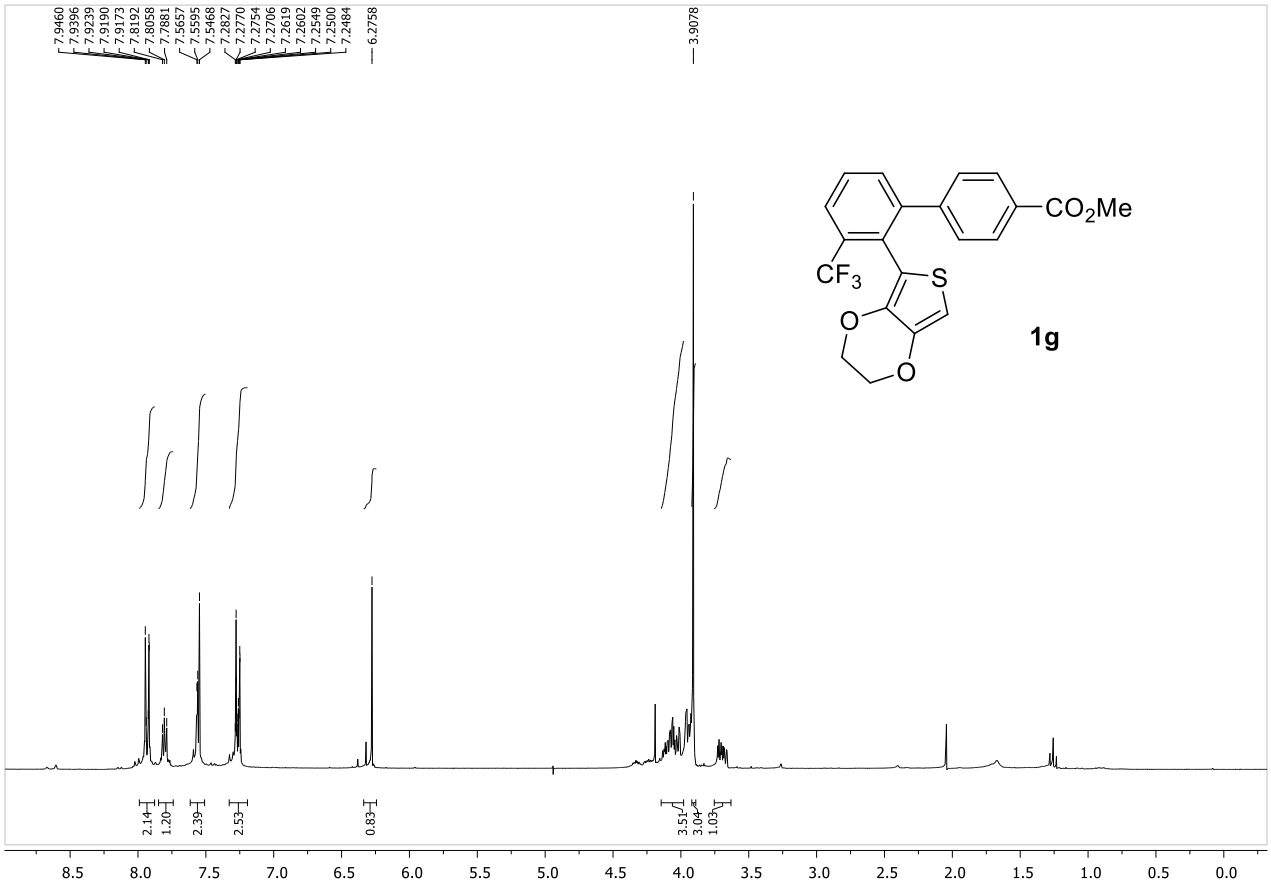
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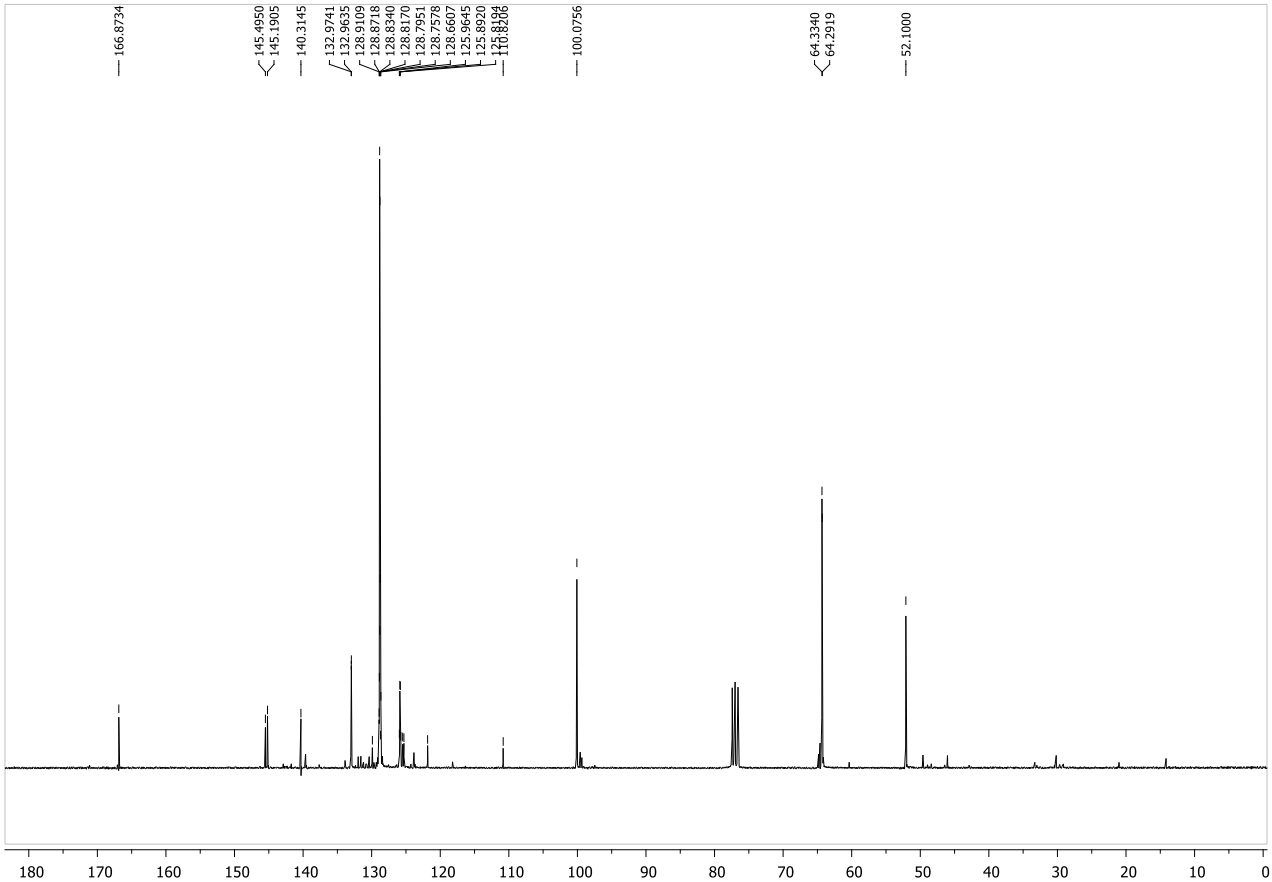
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