SUPPORTING INFORMATION

Reversed-Polarity Synthesis of Diaryl Ketones through Palladium-Catalyzed Direct Arylation of 2-Aryl-1,3-dithianes

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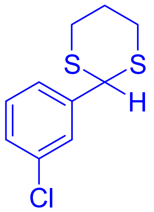
1. General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. Anhydrous THF was purchased from Sigma-Aldrich and used as solvent without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI America or Matrix Scientific, and solvents were purchased from Fisher Scientific. TLC was performed with Merck TLC Silicagel60 F_{254} plates and detection was under UV light at 254 nm. Silica gel (230–400 mesh, Silicycle) was used for flash chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte.

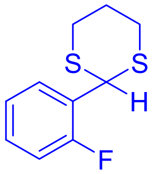
2. Preparation and Characterization of 2-aryl-1,3-dithianes.

Dithianes **4**, **6** and **14** were prepared according to the literature procedure.[1] Dithianes **5**, **7**, **8** and **15** were prepared according to modified literature procedure;[1] General Procedure A.

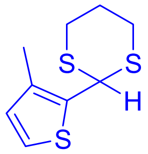
2.1. General Procedure A: An oven-dried 10 mL reaction vial equipped with a stirring bar was charged with a benzaldehyde derivative (8.4 mmol, 1.0 equiv.) and $Cu(BF_4)_2.xH_2O$ (0.169 mmol, 2.0 mol %). To the neat stirred aldehyde, 1,3-propanedithiol (10 mmol, 1.0 mL) was added and the vial was closed with a rubber septa. The vial was placed into the preheated (60 ^{o}C) oil bath and the reaction mixture stirred at this temperature for 1 h. After cooling to room temperature, the reaction mixture was diluted with in 20 mL CH_2Cl_2 and washed with water (2 × 10 mL). The organic phase was dried over $MgSO_4$, filtrated and the solvent was removed in a rotatory evaporator. The solid white residue was recrystallized from hexanes to give 2,2-diaryl-1,3-dithianes.



2-(3-Chlorophenyl)-1,3-dithiane (**5**): The reaction was performed following General Procedure A with 3-chlorobenzaldehyde (8.4 mmol, 0.95 mL), $Cu(BF_4)_2.xH_2O$ (0.169 mmol, 40 mg) and 1,3-propanedithiol (10 mmol, 1.0 mL). The solid white residue was recrystallized from hexanes to give 2-(3-chlorophenyl)-1,3-dithiane (**5**, 1.38 g, 71% yield). The NMR spectral data match with the previously published data.[2]

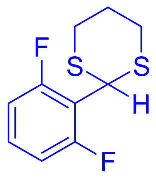


2-(2-Fluorophenyl)-1,3-dithiane (**7**): The reaction was performed following General Procedure A with 2-fluorobenzaldehyde (8.4 mmol, 0.87 mL), $Cu(BF_4)_2.xH_2O$ (0.169 mmol, 40 mg) and 1,3-propanedithiol (10 mmol, 1.0 mL). The solid white residue was recrystallized from hexanes to give 2-(2-fluorophenyl)-1,3-dithiane (**7**, 1.48 g, 82% yield). The NMR spectral data match with the previously published data.[3]



2-(3-Methylthiophen-2-yl)-1,3-dithiane (**8**): The reaction was performed following General Procedure A with 3-methyl-2-thiophenecarboxyaldehyde (8.4 mmol, 0.90 mL), $Cu(BF_4)_2.xH_2O$ (0.169 mmol, 40 mg) and 1,3-propanedithiol (10 mmol, 1.0 mL). The brown residue was recrystallized from hexanes to give 2-(3-methylthiophen-2-yl)-1,3-dithiane (**8**, 1.18 g, 65% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, J = 5.0 Hz, 1H), 6.77 (d, J = 5.0 Hz, 1H), 5.49 (s, 1H), 3.11−3.05 (m, 2H), 2.94−2.89 (m, 2H), 2.28 (s, 3H), 2.20−2.14 (m, 1H), 2.01−1.92 (m, 1H) ppm; $^{13}C\ \{^1H\}$ NMR (125 MHz,

$CDCl_3$): δ 135.12, 134.61, 129.64, 124.16, 43.78, 32.32, 24.73, 13.87 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_9H_{13}S_3$ 217.0179, found 217.0175 (− 1.8 ppm).

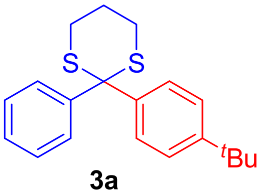


2-(2,6-Difluorophenyl)-1,3-dithiane (**15**): The reaction was performed following General Procedure A with 2,6-difluorobenzaldehyde (8.4 mmol, 0.91 mL), $Cu(BF_4)_2.xH_2O$ (0.169 mmol, 40 mg) and 1,3-propanedithiol (10 mmol, 1.0 mL). The solid white residue was recrystallized from hexanes to give 2-(2,6-difluorophenyl)-1,3-dithiane (**15**, 1.34 g, 69% yield). The NMR spectral data match with the previously published data.[4]

3. Preparation and Characterization for Pd-Catalyzed Arylation of 2-Aryl-1,3-dithianes

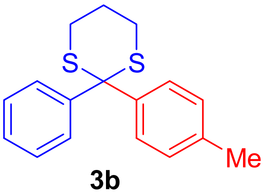
3.1. General Procedure B: An oven-dried 10 mL reaction vial equipped with a stirring bar was charged with 2-aryl-1,3-dithiane (0.2 mmol, 1.0 equiv.) and aryl bromide -if it was solid- (0.4 mmol, 2.0 equiv.) and the vial was brought into a glovebox. The reaction vial was charged with base [$LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$] (0.4 mmol, 2.0 equiv.), 1.4 mL THF, 0.4 mL THF solution (0.025 M) of NiXantphos and 0.2 mL THF solution of (0.025 M) $[PdCl(allyl)]_2$, respectively. The vial was sealed with a rubber septa, wrapped with a strip of Parafilm, and taken out of the glovebox. The sealed vial was charged with aryl bromide -if it was liquid- (0.4 mmol, 2.0 equiv.) by a syringe. The resulting solution was stirred for the given time at the stated temperature. The reaction mixture was quenched with 0.1 mL of water and filtered through a small pad of Celite. The pad was then rinsed additional CH_2Cl_2. The combined organic solution was mixed with 0.5 g of deactivated silica gel and the solvent was removed in a rotatory evaporator. The remaining solid residue was loaded onto a deactivated silica gel column and purified by flash chromatography. The silica gel was deactivated by flushing with 5% triethylamine/hexanes solution (3 times) followed by 20:1 hexanes/ethyl acetate solution (3 times) to remove excess triethylamine.

3.1.1. Substrate scope of the aryl bromide with 2-phenyl-1,3-dithiane.



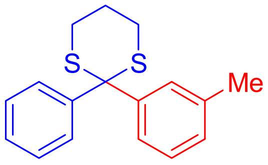
3a

2-(4-*tert*-butylphenyl)-2-phenyl-1,3-dithiane (**3a**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), and 1-bromo-4-*tert*-butylbenzene (**2a**, 0.4 mmol, 69 μL) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure and the procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3a** (59 mg, 90%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37−7.31 (m, 4H), 7.29−7.26 (m, 1H), 2.79 (t, *J* = 6.0 Hz, 4H), 2.03−1.98 (m, 2H), 1.30 (s, 9H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 150.46, 142.45, 139.74, 129.52, 128.72, 128.39, 127.40, 125.27, 62.57, 34.45, 31.28, 29.41, 24.54 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{20}H_{25}S_2$ 329.1398, found 329.1397 (− 0.3 ppm).



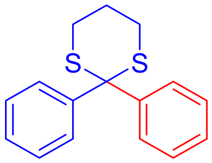
3b

2-phenyl-2-*p*-tolyl-1,3-dithiane (**3b**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 4-bromotoluene (**2b**, 0.4 mmol, 50 μL) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3b** (50 mg, 88%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.24−7.27 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 2.78 (t, *J* = 5.5 Hz, 4H), 2.34 (s, 3H), 2.02−1.97 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 142.71, 139.65, 137.32, 129.34, 129.20, 129.12, 128.37, 127.47, 62.62, 29.42, 24.53, 20.98 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{17}H_{19}S_2$ 287.0928, found 287.0927 (−0.3 ppm).



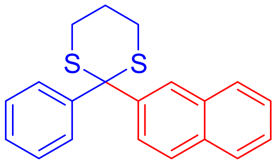
3c

2-phenyl-2-*m*-tolyl-1,3-dithiane (**3c**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 3-bromotoluene (**2c**, 0.4 mmol, 49 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3c** (51 mg, 89%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.5 Hz, 2H), 7.55 (s, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 2.78 (t, J = 6.0 Hz, 4H), 2.34 (s, 3H), 2.02−1.97 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 142.56, 142.51, 138.01, 129.75, 129.34, 128.34, 128.21,127.45, 126.35, 62.71, 29.38, 24.49, 21.57 ppm (one aromatic signal was not observed or co-incident); HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{17}H_{19}S_2$ 287.0928, found 287.0936 (2.8 ppm).



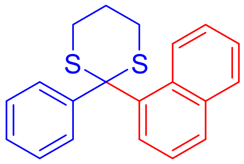
3d

2,2-diphenyl-1,3-dithiane (**3d**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), bromobenzene (**2d**, 0.4 mmol, 42 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed the following general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3a** (48 mg, 89%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 7.7 Hz, 4H), 7.36−7.32 (m, 4H), 7.28−7.25 (m, 2H), 2.80−2.78 (m, 4H), 2.03−1.99 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 142.52, 129.26, 128.34, 127.49, 62.72, 29.32, 24.43 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{16}H_{17}S_2$ 273.0772, found 273.0777 (1.8 ppm).



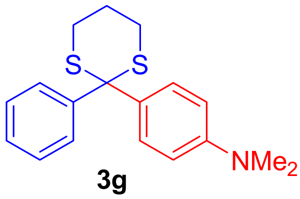
3e

2-(naphthalen-2-yl)-2-phenyl-1,3-dithiane (**3e**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg) and 2-bromonaphthalene (**2e**, 0.4 mmol, 83 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3e** (54 mg, 84%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.89−7.80 (m, 4H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.50−7.46 (m, 2H), 7.34−7.31 (m, 2H), 7.28−7.26 (m, 1H), 2.88−2.78 (m, 4H), 2.07−2.00 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.72, 139.63, 133.08, 132.55, 129.17, 128.89, 128.47, 128.40, 128.16, 127.70, 127.37, 127.22, 126.44, 126.13, 62.73, 29.38, 24.47 ppm; HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{20}H_{18}S_2$ 322.0850, found 322.0834 (− 5.0 ppm).



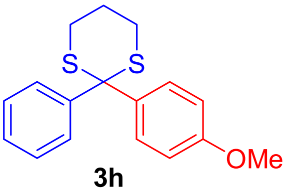
3f

2-(naphthalen-1-yl)-2-phenyl-1,3-dithiane (**3f**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg),1-bromonaphthalene (**2f**, 0.4 mmol, 56 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3f** (56 mg, 87%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.84−7.81 (m, 2H), 7.67−7.65 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.38−7.35 (m, 1H), 7.32−7.29 (m, 2H), 7.27−7.20 (m, 2H), 2.98−2.92 (m, 2H), 2.84−2.80 (m, 2H), 2.12−2.03 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.82, 136.99, 135.31, 130.46, 129.68, 129.36, 128.67, 128.60, 128.48, 128.17, 127.61, 125.12, 124.07, 61.59, 29.67, 24.49 ppm; HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{20}H_{18}S_2$ 322.0850, found 322.0865 (4.7 ppm).



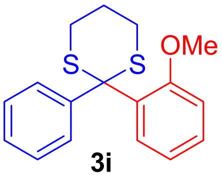
3g

2-(4-*N,N*-dimethylaminophenyl)-2-phenyl-1,3-dithiane (**3g**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 4-bromo-*N,N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3g** (54 mg, 86%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.27−7.24 (m, 1H), 6.66 (d, *J* = 9.0 Hz, 2H), 2.95 (s, 6H), 2.82−2.74 (m, 4H), 2.00−1.96 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.61, 143.02, 130.07, 129.95, 129.46, 128.26, 127.26, 111.89, 62.62, 43.34, 29.53, 24.61 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{18}H_{22}NS_2$ 316.1194, found 316.1193 (−0.3 ppm).

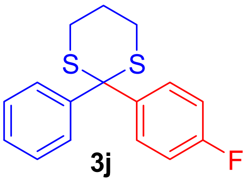


3h

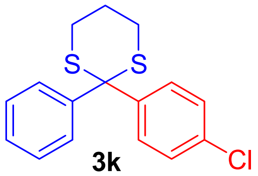
2-(4-methoxyphenyl)-2-phenyl-1,3-dithiane (**3h**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 4-bromoanisole (**2h**, 0.4 mmol, 50 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on deactivated silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3h** (48 mg, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.36−7.32 (m, 2H), 7.28−7.25 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 2.79−2.77 (m, 4H), 2.02−1.97 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.80, 142.68, 134.62, 130.55, 129.33, 128.36, 127.47, 113.59, 62.35, 55.23, 29.44, 24.48 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{17}H_{19}OS_2$ 303.0877, found 303.0872 (−1.6 ppm).


3i

2-(2-methoxyphenyl)-2-phenyl-1,3-dithiane (**3i**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 2-bromoanisole (**2i**, 0.4 mmol, 50 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C. After cooling, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3i** (39 mg, 65%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.30 (dt, *J* = 1.5, 8.0 Hz, 1H), 7.27–7.24 (m, 2H), 7.20–7.17 (m, 1H), 7.04 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.86 (dd, *J* = 1.2, 8.0 Hz, 1H), 3.42 (s, 3H), 2.96–2.91 (m, 2H), 2.86–2.81 (m, 2H), 2.08–1.97 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 157.57, 144.44, 132.03, 130.39, 129.13, 127.72, 127.33, 126.81, 119.97, 113.96, 59.13, 55.72, 29.31, 24.43 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{17}H_{19}OS_2$ 303.0877, found 303.0886 (3.0 ppm).

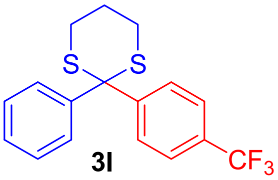

3j

2-(4-fluorophenyl)-2-phenyl-1,3-dithiane (**3j**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg) and 1-bromo-4-fluorobenzene (**2j**, 0.4 mmol, 44 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed the following general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3j** (56 mg, 96%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.67–7.64 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.29–7.26 (m, 1H), 7.01 (t, *J* = 9.0 Hz, 2H), 2.79–2.77 (m, 4H), 2.03–1.99 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 161.97 (d, *J* = 248 Hz), 142.32, 138.46, 131.21 (d, *J* = 8.0 Hz), 129.25, 128.48, 127.68, 115.12 (d, *J* = 21 Hz), 62.12, 29.29, 24.37 ppm; HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{16}H_{15}FS_2$ 290.0599, found 290.0598 (– 0.3 ppm).



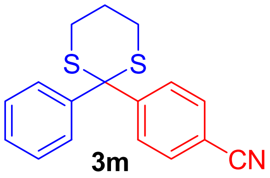
3k

2-(4-chlorophenyl)-2-phenyl-1,3-dithiane (**3k**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3k** (51 mg, 83%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.67−7.64 (m, 4H), 7.36−7.23 (m, 5H), 2.79−2.76 (m, 4H), 2.03−1.98 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 142.17, 141.20, 133.46, 130.89, 129.12, 128.49, 127.75, 62.13, 29.34, 24.32 ppm (one aromatic signal was not observed or co-incident); HRMS [TOF MS CI+]: m/z [M]$^+$ calcd. for $C_{16}H_{15}ClS_2$ 306.0304, found 306.0299 (−1.6 ppm).



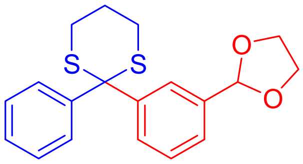
3l

2-(4-(trifluoromethyl)phenyl)-2-phenyl-1,3-dithiane (**3l**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 4-bromobenzotrifluoride (**2l**, 0.4 mmol, 56 μL) and LiN(SiMe$_3$)$_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3l** (51 mg, 75%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.37−7.34 (m, 2H), 7.28−7.25 (m, 1H), 2.83−2.73 (m, 4H), 2.04−2.00 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 146.73, 141.89, 129.88, 129.64 (q, J = 33 Hz), 129.10, 128.59, 127.91, 125.40 (q, J = 3.7 Hz), 121.87 (q, J = 272 Hz), 62.20, 29.30, 24.25 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{17}H_{16}F_3S_2$ 341.0646, found 341.0658 (3.5 ppm).



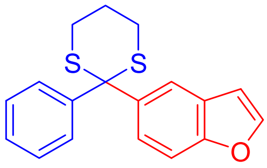
3m

4-(2-phenyl-1,3-dithian-2-yl)benzonitrile (**3m**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg) and 4-bromobenzonitrile (**2m**, 0.4 mmol, 73 mg) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3m** (40 mg, 67%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.65−7.62 (m, 4H), 7.38−7.35 (m, 2H), 7.31−7.28 (m, 1H), 2.83−2.72 (m, 4H), 2.05−2.02 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 148.19, 141.43, 132.18, 130.21, 129.04, 128.68, 128.05, 118.56, 111.40, 62.16, 29.25, 24.12 ppm; HRMS [TOF MS CI+]: m/z [M]$^+$ calcd. for $C_{17}H_{15}NS_2$ 297.0646, found 297.0640 (−2.0 ppm).



3n

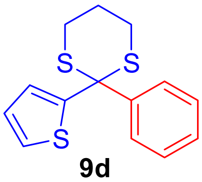
4-(2-phenyl-1,3-dithian-2-yl)benzonitrile (**3n**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 2-(3-bromophenyl)-1,3-dioxolane (**2n**, 0.4 mmol, 60 µL) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3n** (46 mg, 67%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.90 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.43−7.36 (m, 2H), 7.33−7.30 (m, 2H), 7.26−7.24 (m, 1H), 5.79 (s, 1H), 4.15−4.08 (m, 2H), 4.05−3.99 (m, 2H), 2.79−2.77 (m, 4H), 2.02−1.98 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 142.61, 142.49, 138.18, 130.45, 129.15, 128.60, 128.37, 127.96, 127.62, 125.60, 103.75, 63.31, 62.65, 29.38, 24.39 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{19}H_{21}O_2S_2$ 345.0983, found 345.0989 (1.7 ppm).



3o

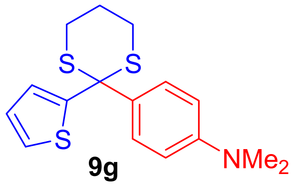
5-(2-phenyl-1,3-dithian-2-yl)benzofuran (**3o**): The reaction was performed following General Procedure B with **1** (0.2 mmol, 39.3 mg), 5-bromobenzofuran (**2o**, 0.4 mmol, 79 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C temperature. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **3o** (49 mg, 78%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.75 (d, J = 7.7 Hz, 2H), 7.72 (dd, J = 2.0, 9.0 Hz, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.30−7.27 (m, 1H), 6.74−6.73 (m, 1H), 2.83−2.81 (m, 4H), 2.05−2.00 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.16, 145.54, 142.83, 137.37, 129.44, 128.42, 127.53, 127.39, 125.89, 122.31, 111.10, 106.97, 62.91, 29.56, 24.51 ppm; HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{18}H_{16}OS_2$ 312.0643, found 312.0657 (4.5 ppm).

3.1.2. Substrate scope of 2-aryl-1,3-dithiane and aryl bromide



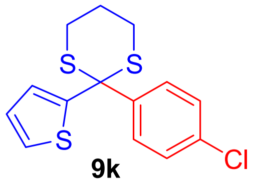
9d

2-phenyl-2-(thiophen-2-yl)-1,3-dithiane (**9d**): The reaction was performed following General Procedure B with **4** (0.2 mmol, 40.4 mg), bromobenzene (**2d**, 0.4 mmol, 42 μL) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **9d** (47 mg, 85%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 5.0 Hz, 1H), 7.32−7.29 (m, 2H), 7.27−7.25 (m, 2H), 7.03 (dd, J =3.5, 5.0 Hz, 1H), 3.06−3.00 (m, 2H), 2.82−2.78 (m, 2H), 2.10−1.98 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.01, 143.31, 129.44, 128.28, 128.16, 128.13, 127.37, 127.03, 58.43, 29.85, 24.25 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{14}H_{15}S_3$ 279.0336, found 279.0339 (1.1 ppm).



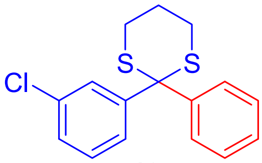
9g

2-(4-*N*,*N*-dimethylaminophenyl)-2-(thiophen-2-yl)-1,3-dithiane (**9g**): The reaction was performed following General Procedure B with **4** (0.2 mmol, 40.4 mg, 4-bromo-*N*,*N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and LiN(SiMe$_3$)$_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **9g** (53 mg, 83%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.26−7.25 (m, 1H), 7.03−7.00 (m, 1H), 6.63 (d, *J* =9.0 Hz, 2H), 3.06−2.97 (m, 2H), 2.93 (s, 6H), 2.81−2.76 (m, 2H), 2.07−1.95 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 150.06, 149.81, 130.81, 129.22, 128.96, 127.05, 126.92, 111.73, 58.09, 40.33, 30.05, 24.35 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{16}H_{20}NS_3$ 322.0758, found 322.0755 (−0.9 ppm).



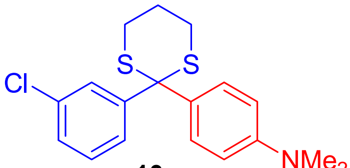
9k

2-(4-chlorophenyl)-2-(thiophen-2-yl)-1,3-dithiane (**9k**): The reaction was performed following General Procedure B with **4** (0.2 mmol, 40.4 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and LiN(SiMe$_3$)$_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **9k** (56 mg, 90%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.28−7.23 (m, 3H), 7.03 (dd, *J* =4.0, 5.0 Hz, 1H), 3.05−2.99 (m, 2H), 2.82−2.77 (m, 2H), 2.10−1.97 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 148.51, 141.94, 133.99, 129.71, 129.51, 128.40, 127.59, 127.14, 57.82, 29.83, 24.11 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{14}H_{14}S_3Cl$ 312.9946, found 312.9952 (1.9 ppm).



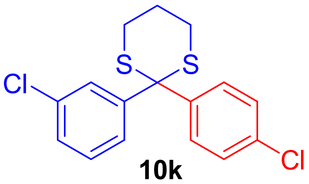
10d

2-(3-chlorophenyl)-2-phenyl-1,3-dithiane (**10d**): The reaction was performed following General Procedure B with **5** (0.2 mmol, 46 mg), bromobenzene (**2d**, 0.4 mmol, 42 µL) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). The reaction was stirred for 1 h at 60 °C temperature. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **10d** (55 mg, 89%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.65−7.60 (m, 3H), 7.34−7.33 (m, 2H), 7.29−7.24 (m, 3H), 2.79−2.77 (m, 4H), 2.03−1.98 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 144.74, 142.06, 134.45, 129.60, 129.05, 128.50, 127.82, 127.75, 127.69, 62.10, 29.33, 24.28 ppm (one aromatic signal was not observed or co-incident); HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{16}H_{15}S_2Cl$ 306.0334, found 306.0292 (−3.9 ppm).

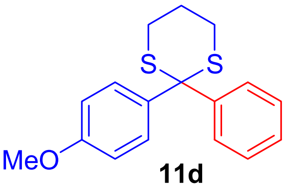


10g

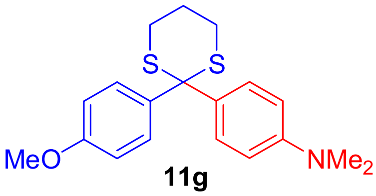
2-(3-chlorophenyl)-2-(4-*N,N*-dimethylaminophenyl)-1,3-dithiane (**10g**): The reaction was performed following General Procedure B with **5** (0.2 mmol, 46 mg), 4-bromo-*N,N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). The reaction was stirred for 1 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **10g** (60 mg, 86%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.29−7.23 (m, 2H), 6.65 (d, J =8.8 Hz, 2H), 2.95 (s, 6H), 2.81−2.72 (m, 4H), 2.00−1.96 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.73, 145.27, 134.30, 129.84, 129.70, 129.47, 127.83, 127.46, 111.90, 61.95, 40.29, 29.50, 24.40 ppm (one aromatic signal was not observed or co-incident); HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{18}H_{21}NS_2Cl$ 350.0804, found 350.0801 (−0.9 ppm).


10k

2-(3-chlorophenyl)-2-(4-chlorophenyl)-1,3-dithiane (10k): The reaction was performed following General Procedure B with **5** (0.2 mmol, 46 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **10k** (52 mg, 76%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.61−7.56 (m, 3H), 7.33−7.27 (m, 4H), 2.78−2.76 (m, 4H), 2.04−1.99 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 144.37, 140.70, 134.60, 133.82, 130.69, 129.73, 129.46, 128.67, 128.02, 127.54, 61.52, 29.34, 24.16 ppm; HRMS [TOF MS CI+]: m/z $[M]^+$ calcd. for $C_{16}H_{14}S_2Cl_2$ 339.9914, found 339.9916 (0.6 ppm).

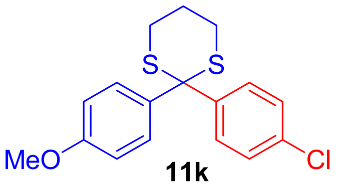

11d

2-(4-methoxyphenyl)-2-phenyl-1,3-dithiane (11d): The reaction was performed following General Procedure B with **6** (0.2 mmol, 45 mg), bromobenzene (**2d**, 0.4 mmol, 42 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **11d** (47 mg, 77%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.36−7.32 (m, 2H), 7.28−7.25 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 2.79−2.77 (m, 4H), 2.02−1.97 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 158.80, 142.68, 134.62, 130.55, 129.33, 128.36, 127.47, 113.59, 62.35, 55.23, 29.44, 24.48 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{17}H_{19}OS_2$ 303.0877, found 303.0872 (−1.6 ppm).



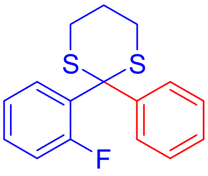
11g

2-(4-*N,N*-dimethylaminophenyl)-2-(4-methoxyphenyl)-1,3-dithiane (11g): The reaction was performed following General Procedure B with **6** (0.2 mmol, 45 mg), 4-bromo-*N,N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **11g** (60 mg, 87%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.64 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* =9.0 Hz, 2H), 6.68 (d, *J* =9.0 Hz, 2H), 3.81 (s, 3H), 2.96 (s, 6H), 2.82−2.74 (m, 4H), 2.01−1.96 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 158.64, 149.52, 135.13, 130.67, 130.10, 113.46, 111.91, 62.20, 55.21, 40.37, 29.57, 24.62 ppm (one aromatic signal was not observed or co-incident); HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{19}H_{24}NOS_2$ 346.1299, found 346.1303 (1.2 ppm).



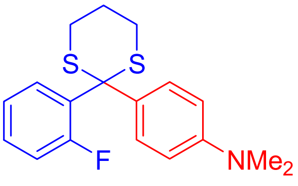
11k

2-(4-chlorophenyl)-2-(4-methoxyphenyl)-2-phenyl-1,3-dithiane (11k): The reaction was performed following General Procedure B with **6** (0.2 mmol, 45 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **11k** (41 mg, 61%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.67 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* =9.0 Hz, 2H), 6.86 (d, *J* =9.0 Hz, 2H), 3.80 (s, 3H), 2.80−2.72 (m, 4H), 2.01−1.97 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 158.96, 141.35, 134.42, 133.38, 130.94, 130.41, 128.47, 113.69, 61.73, 55.25, 29.43, 24.34 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{17}H_{18}OS_2Cl$ 337.0488, found 337.0471 (− 5.0 ppm).



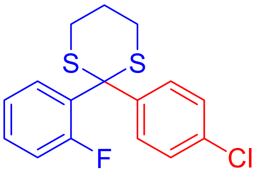
12d

2-(2-fluorophenyl)-2-phenyl-1,3-dithiane (**12d**): The reaction was performed following General Procedure B with **7** (0.2 mmol, 43 mg), bromobenzene (**2d**, 0.4 mmol, 42 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **12d** (53 mg, 92%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (td, J = 2.0, 8.0 Hz, 1H), 7.60−7.58 (m, 2H), 7.33−7.28 (m, 3H), 7.26−7.23 (m, 1H), 7.19 (td, J = 1.0, 8.0 Hz, 1H), 7.01−6.97 (m, 1H), 2.94−2.88 (m, 2H), 2.85−2.80 (m, 2H), 2.09−1.96 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.44 (d, J = 253 Hz) 142.48, 131.50 (d, J = 1.8 Hz), 130.45 (d, J = 8.3 Hz), 129.76 (d, J = 8.3 Hz), 128.23, 127.83, 127.70, 123.29 (d, J = 4.4 Hz), 117.20 (d, J = 23 Hz), 57.95 (d, J = 3.6 Hz), 29.43, 24.23 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{16}H_{16}S_2F$ 291.0677, found 291.0680 (1.0 ppm).



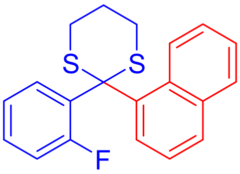
12g

2-(4-*N*,*N*-dimethylaminophenyl)-2-(2-fluorophenyl)-1,3-dithiane (**12g**): The reaction was performed following General Procedure B with **7** (0.2 mmol, 43 mg), 4-bromo-*N*,*N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **12g** (55 mg, 83%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (td, J = 2.0, 8.0 Hz, 1H), 7.41 (d, J = 9.0 Hz, 2H), 7.32−7.28 (m, 1H), 7.17 (td, J = 1.0, 8.0 Hz, 1H), 7.03−6.99 (m, 1H), 6.63 (d, J = 9.0 Hz, 2H), 2.93 (s, 6H), 2.92−2.86 (m, 2H), 2.83−2.78 (m, 2H), 2.07−1.95 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.58 (d, J = 253 Hz) 149.73, 131.87 (d, J = 1.9 Hz), 130.66 (d, J = 8.2 Hz), 129.47 (d, J = 8.3 Hz), 129.48, 128.68, 123.16 (d, J = 3.7 Hz), 117.15 (d, J = 23 Hz), 111.79, 57.83 (d, *J* = 3.6 Hz), 40.28, 29.73, 24.38 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{18}H_{21}NS_2F$ 334.1099, found 334.1087 (−3.6 ppm).



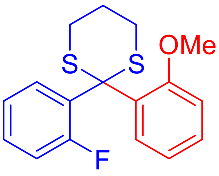
12k

2-(4-chlorophenyl)-2-(2-fluorophenyl)-1,3-dithiane (**12k**): The reaction was performed following General Procedure B with **7** (0.2 mmol, 39.3 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **12k** (51 mg, 78%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (td, *J* = 2.0, 8.0 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.35−7.30 (m, 1H), 7.28−7.25 (m, 2H), 7.20 (td, *J* = 1.0, 8.0 Hz, 1H), 7.02−6.98 (m, 1H), 2.93−2.87 (m, 2H), 2.84−2.80 (m, 2H), 2.09−1.96 (m, 2H) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.34 (d, *J* = 253 Hz) 141.16, 133.50, 131.28 (d, *J* = 2.0 Hz), 130.06 (d, *J* = 8.7 Hz), 130.02 (d, *J* = 8.3 Hz), 129.45, 128.37, 123.45 (d, *J* = 3.7 Hz), 117.25 (d, *J* = 22 Hz), 57.37 (d, *J* = 3.7 Hz), 29.39, 24.09 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{16}H_{15}FS_2Cl$ 325.0288, found 325.0289 (0.3 ppm).



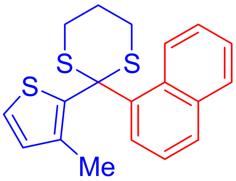
12f

2-(2-fluorophenyl)-2-(naphthalen-1-yl)-1,3-dithiane (**12f**): The reaction was performed following General Procedure B with **7** (0.2 mmol, 43 mg), 1-bromonaphthalene (**2f**, 0.4 mmol, 56 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **12f** (63 mg, 93%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 7.4 Hz, 1H), 8.24−8.21 (m, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.80 (dd, *J* = 4.0, 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.27−7.23 (m, 2H), 7.19−7.15 (m, 1H), 6.85−6.80 (m, 1H), 3.01−2.92 (m, 4H), 2.15−2.04 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 160.12 (d, *J* = 252 Hz), 137.52 (d, *J* = 1.9 Hz), 135.03, 131.79 (d, *J* = 9.0 Hz), 130.03, 129.68, 129.61, 129.13, 128.91, 127.15 (d, *J* = 2.7 Hz), 126.66, 125.02, 124.54, 124.42, 123.80 (d, *J* = 3.7 Hz), 117.13 (d, *J* = 23.0 Hz), 58.29, 29.04, 24.28 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{20}H_{18}FS_2$ 341.0834, found 341.0828 (− 1.8 ppm).



12i

2-(2-fluorophenyl)-2-(2-methoxyphenyl)-1,3-dithiane (12i): The reaction was performed following General Procedure B with **7** (0.2 mmol, 43 mg), 2-bromoanisole (**2i**, 0.4 mmol, 50 µL) and NaN(SiMe$_3$)$_2$ (0.4 mmol, 73 mg). The reaction was stirred for 1 h at 60 °C. After cooling to rt, the workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **12i** (40 mg, 63%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.11 (dd, *J* = 1.6, 7.9 Hz, 1H), 8.06 (td, *J* = 1.6, 7.9 Hz, 1H), 7.29−7.26 (m, 1H), 7.23−7.14 (m, 2H), 7.07−7.03 (m, 1H), 6.90−6.85 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.37 (s, 3H), 2.97−2.88 (m, 4H), 2.06−2.01 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 159.74 (d, *J* = 251 Hz), 156.98, 132.06, 131.87, 130.20 (d, *J* = 1.7 Hz), 128.97, 128.67 (d, *J* = 2.7 Hz), 128.47 (d, *J* = 8.3 Hz), 122.86 (d, *J* = 3.7 Hz), 120.40, 116.31 (d, *J* = 23 Hz), 113.44, 56.20, 55.72, 28.47, 24.13 ppm; HRMS [TOF MS ES+]: m/z [M + H]$^+$ calcd. for $C_{17}H_8OFS_2$ 321.0783, found 321.0782 (− 0.3 ppm).

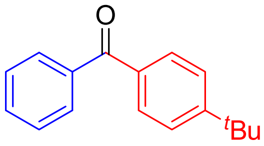


13f

2-(3-methylthiophen-2-yl)-2-(naphthalen-1-yl)-1,3-dithiane (13f): The reaction was performed following General Procedure B with **8** (0.2 mmol, 43 mg), 1-bromonaphthalene (**2f**, 0.4 mmol, 56 µL) and LiN(SiMe$_3$)$_2$ (0.4 mmol, 67 mg). The reaction was stirred for 2 h at room temperature. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **13f** (55 mg, 81%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.9 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40−7.37 (m, 1H), 7.31−7.28 (m, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 6.66 (d, *J* = 5.0 Hz, 1H), 2.99−2.97 (m, 4H), 2.15−2.10 (m, 2H), 1.54 (s, 3H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.72, 137.07, 135.73, 135.12, 132.50, 130.46, 129.61, 128.73, 128.39, 127.38, 125.36, 124.56, 124.18, 123.51, 57.61, 29.30, 24.27, 15.44 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{19}H_{19}S_3$ 343.0649, found 343.0637 (− 3.5 ppm).

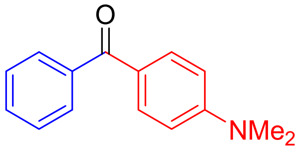
4. Preparation and Characterization for One-pot Umpolung Synthesis of Diaryl Ketones

4.1. General Procedure C: An oven-dried 10 mL reaction vial equipped with a stirring bar was charged with 2-aryl-1,3-dithiane (0.2 mmol, 1.0 equiv.) and aryl bromide -if it was solid- (0.4 mmol, 2.0 equiv.) and then the vial was brought into a glovebox. The reaction vial was charged with base [$LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$] (0.4 mmol, 2.0 equiv.), 1.4 mL THF, 0.4 mL THF solution (0.025 M) of NiXantphos and 0.2 mL THF solution of (0.025 M) $[PdCl(allyl)]_2$, respectively. The vial was sealed with a rubber septum wrapped with a strip of Parafilm and removed from the glovebox. The sealed vial was charged with aryl bromide -if it was liquid- (0.4 mmol, 2.0 equiv.) by syringe. After having stirred the mixture for the given time at the stated temperature, the vial was cooled to rt (if the reaction was carried out 60 ^{o}C) and, opened to air and 0.5 mL H_2O, I_2 (1.2 mmol, 0.3 g), and $CaCO_3$ (1.6 mmol, 0.16 g) were added (**Method A**) [or 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**); or 0.5 mL H_2O and Selectfluor^{TM} (0.79 mmol, 0.28 g) (**Method C**)]. The resulting mixture stirred at rt for 1 h. The reaction mixture was taken up in 10 mL CH_2Cl_2 and washed with water (2 × 5 mL). The aqueous phase was extracted with 10 mL CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$), filtrated and mixed with 0.5 g of silica gel. The solvent was then removed in a rotatory evaporator. The remaining solid residue was loaded onto a silica gel column and purified by flash chromatography.



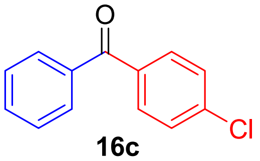
16a

4-*tert*-butylbenzophenone (**16a**) The reaction was performed following General Procedure C with **1** (0.2 mmol, 39.3 mg), 1-bromo-4-*tert*-butylbenzene (**2a**, 0.4 mmol, 69 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 2 h at room temperature, 0.5 mL H_2O, I_2 (1.2 mmol, 0.3 g), and $CaCO_3$ (1.6 mmol, 0.16 g) were added (**Method A**) [0.5 mL H_2O, NBS (1.0 mmol, 0.18 g) (**Method B**); 0.5 mL H_2O, Selectfluor^{TM} (0.79 mmol, 0.28 g) (**Method C**)]. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **16a** (40 mg, 84%, Method A; 36 mg, 75%, Method B; 43 mg, 91% Method C) as a white solid. The NMR spectral data match with the previously published data.[5]



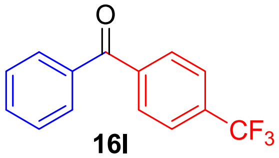
16g

4-*N*,*N*-dimethylaminobenzophenone (**16g**) The reaction was performed following General Procedure C with **1** (0.2 mmol, 39.3 mg), 4-bromo-*N*, *N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 2 h at room temperature, 0.5 mL H_2O, I_2 (1.2 mmol, 0.3 g), and $CaCO_3$ (1.6 mmol, 0.16 g) were added (**Method A**). The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **16g** (30 mg, 66%) as a white solid. The NMR spectral data match with the previously published data.[6]



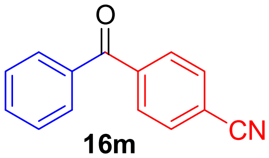
16c

4-chlorobenzophenone (**16c**) An oven-dried 100 mL reaction vial equipped with a stirring bar was charged with **1** (6.0 mmol, 1.18 g) and 1-bromo-4-chlorobenzene (**2c**, 12.0 mmol, 2.3 g) and then the vial was brought into a glovebox. The reaction vial was then charged with base $NaN(SiMe_3)_2$ (12 mmol, 2.2 g), NiXantphos (5.0 mol %, 55 mg), $[PdCl(allyl)]_2$ (2.5 mol %, 165 mg) and 60 mL dry THF, respectively. The vial was sealed with a rubber septum, wrapped with a strip of Parafilm, and removed from the glovebox. After the mixture was stirred at room temperature for 3 h, the vial was opened to air and 20 mL H_2O and Selectfluor^{TM} (22.2 mmol, 7.86 g) (**Method C**) were added. The resulting mixture stirred at rt for 3.5 h. The reaction mixture was then extracted with 150 mL CH_2Cl_2 and washed with water (2 × 25 mL). The aqueous phase was extracted with 100 mL CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$), filtrated and mixed with 2.0 g of silica gel. The solvent was removed in a rotatory evaporator. The remaining solid residue was loaded onto a silica gel column and purified by flash chromatography using 20:1 hexanes/ethyl acetate as eluent to yield the product **16c** (0.89 g, 69%) as a white solid. The NMR spectral data match with the previously published data.[7]



16l

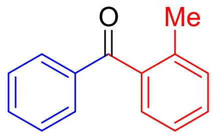
4-trifluoromethylbenzophenone (**16l**) The reaction was performed following General Procedure C with **1** (0.2 mmol, 39.3 mg), 4-bromobenzotrifluoride (**2l**, 0.4 mmol, 56 µL) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). After the reaction was stirred for 2 h at room temperature, the vial was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture was stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **16l** (44 mg, 87%) as a white solid. The NMR spectral data match with the previously published data.[8]



16m

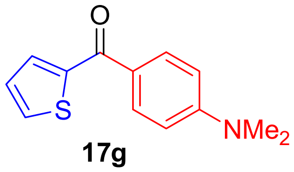
4-cyanobenzophenone (**16m**) The reaction was performed following General Procedure C with **1** (0.2 mmol, 39.3 mg), 4-bromobenzonitrile (**2m**, 0.4 mmol, 73 mg) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 2 h at room temperature the vial was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**); [or 0.5 mL H_2O and Selectfluor^{TM}

(0.79 mmol, 0.28 g) (**Method C**)] were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **16m** (21 mg, 50%, Method B and C) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.80−7.78 (m, 4H), 7.66−7.63 (m, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), ppm; ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 195.00, 141.20, 136.29, 133.30, 133.14, 130.20, 130.03, 128.60, 117.98, 115.63 ppm; HRMS [TOF MS CI+]: m/z [M]$^+$ calcd. for $C_{14}H_{19}NO$ 207.0684, found 207.0676 (−3.4 ppm).



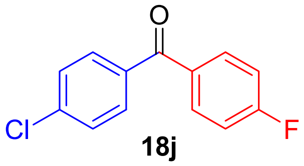
16p

2-methylbenzophenone (**16p**) The reaction was performed following General Procedure C with **1** (0.2 mmol, 39.3 mg), 2-bromotoluene (**2p**, 0.4 mmol, 48 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 1 h at 60 °C the reaction mixture was allowed to cool to rt, opened to air, and 0.5 mL H_2O and Selectfluor^{TM} (0.79 mmol, 0.28 g) were added (**Method C**). The resulting mixture stirred at rt for 1 h. The workup was performed following general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **16p** (29 mg, 73%) as a white solid. The NMR spectral data match with the previously published data.[5]



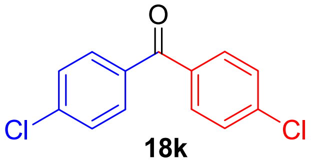
17g

4-*N*,*N*-(dimethylamino)phenyl-2-thienylmethanone (**17g**): The reaction was performed following General Procedure C with **4** (0.2 mmol, 40.4 mg), 4-bromo-*N*,*N*-dimethylaniline (**2g**, 0.4 mmol, 80 mg) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). After the reaction was stirred for 2 h at room temperature it was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **17g** (26 mg, 57%) as a white solid. . ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 9.0 Hz, 2H), 7.64−7.62 (m, 2H), 7.13 (t, J = 4.3 Hz, 1H), 6.70 (d, J = 9.0 Hz, 2H), 3.07 (s, 6H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 186.16, 153.23, 144.44, 132.90, 132.17, 131.83, 127.43, 125.24, 110.68, 40.03 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{13}H_{14}NOS$ 232.0796, found 232.0791 (−2.2 ppm).



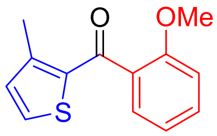
18j

4-chloro-4'-fluorobenzophenone (**18j**) The reaction was performed following General Procedure C with **14** (0.2 mmol, 46 mg), 1-bromo-4-fluorobenzene (**2j**, 0.4 mmol, 44 µL) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). After the reaction was stirred for 2 h at room temperature it was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **18j** (45 mg, 95%) as a white solid. The NMR spectral data match with the previously published data.[7]

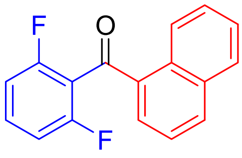


18k

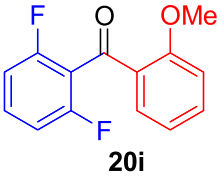
4-4'-dichlorobenzophenone (**18k**) The reaction was performed following General Procedure C with **14** (0.2 mmol, 46 mg), 1-bromo-4-chlorobenzene (**2k**, 0.4 mmol, 77 mg) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). After the reaction was stirred for 2 h at room temperature it was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **18k** (47 mg, 93%) as a white solid. The NMR spectral data match with the previously published data.[7]


19i

2-methoxyphenyl-(3-methylthiophen-2-yl)methanone (**19i**) The reaction was performed following General Procedure C with **8** (0.2 mmol, 43 mg), 2-bromoanisole (**2i**, 0.4 mmol, 50 µL) and $LiN(SiMe_3)_2$ (0.4 mmol, 67 mg). After the reaction was stirred for 2 h at room temperature it was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **19i** (35 mg, 75%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 5.0 Hz, 1H), 7.41−7.34 (m, 3H), 7.11−7.09 (m, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 3.85 (s, 3H), 2.50 (s, 3H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.29, 159.42, 145.96, 141.17, 134.76, 132.12, 130.91, 129.20, 121.65, 118.48, 113.46, 55.39, 16.71 ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{13}H_{13}O_2S$ 233.0636, found 233.0630 (−2.1 ppm).


20f

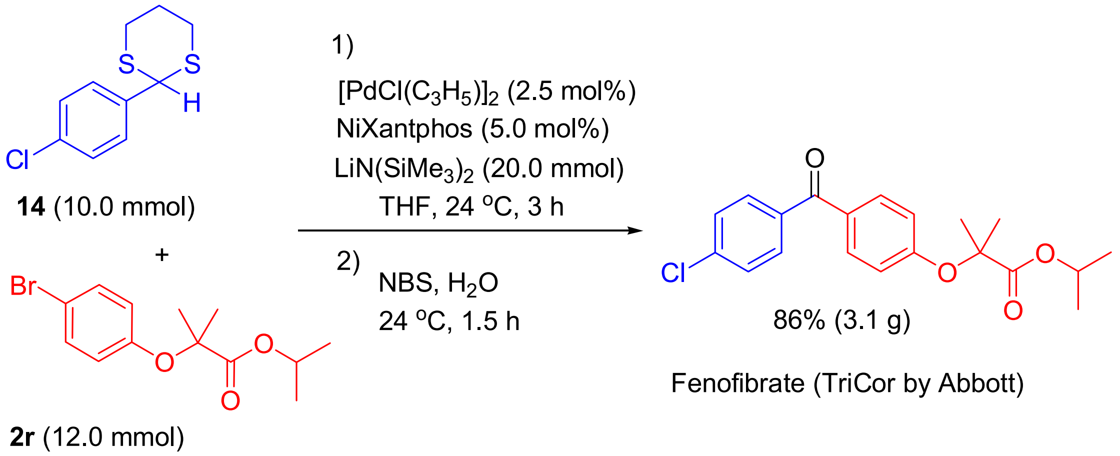
2,6-difluorophenyl(naphthalene-1-yl)methanone (**20f**) The reaction was performed following General Procedure C with **15** (0.2 mmol, 46 mg), 1-bromo-naphthalene (**2f**, 0.4 mmol, 56 µL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 2 h at room temperature it was opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) were added (**Method B**). The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **20f** (51 mg, 95%) as a white solid. . ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.09 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.71−7.68 (m, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.47−7.41 (m, 2H), 7.02−6.98 (m, 2H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.53, 159.90 (dd, *J* = 7.3, 252 Hz), 134.80, 133.91, 133.80, 132.76, 131.88 (t, *J* = 10.0 Hz), 130.60, 128.86, 128.53, 126.78, 125.82, 124.33, 118.86 (t, *J* = 21.1 Hz), 111.88 (dd, *J* = 4.6, 20.3 Hz) ppm; HRMS [TOF MS ES+]: m/z $[M + H]^+$ calcd. for $C_{17}H_{11}OF_2$ 269.0774, found 269.0776 (− 0.7 ppm).



20i

2,6-difluorophenyl-2'-methoxybenzophenone (**20i**) The reaction was performed following General Procedure C with **15** (0.2 mmol, 46 mg), 2-bromoanisole (**2i**, 0.4 mmol, 50 μL) and $NaN(SiMe_3)_2$ (0.4 mmol, 73 mg). After the reaction was stirred for 2 h at 60 °C it was cooled to rt, opened to air and 0.5 mL H_2O and NBS (1.0 mmol, 0.18 g) (**Method B**) were added. The resulting mixture stirred at rt for 1 h. The workup was performed following the general procedure. The crude material was purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **20i** (42 mg, 85%). The NMR spectral data match with the previously published data.[9]

5. Preparation and Characterization for 10.0 mmol Scale One-pot Umpolung Synthesis of Fenofibrate



An oven-dried 250 mL two-neck round-bottomed reaction flask equipped with a stirring bar and a glass stopcock adapter connected to a Schlenk line was charged with 2-(4-chlorophenyl)-1,3-dithiane (**14**, 10 mmol, 2.31 g), 2-(4-bromophenoxy)-2-methylpropanoate (**2r**, 12 mmol, 3.61 g), NiXantphos (5.0 mol %, 276 mg) and $[PdCl(allyl)]_2$ (2.5 mol %, 91 mg), respectively. The open neck was closed with a rubber septum and sealed with a strip of Parafilm. The flask was evacuated by vacuum and then refilled with nitrogen gas. This process was repeated 3 times and 80 mL dry THF was added through the septum by syringe. The resulting solution was stirred at room temperature for 3 min and a solution of $LiN(SiMe_3)_2$ (20 mmol, 20 mL of a 1.0 M of THF solution) was added by syringe under a nitrogen atmosphere. The flask was removed from the Schlenk line and the reaction mixture was stirred under a nitrogen atmosphere at room temperature. After complete consumption (3 hours) of 2-(4-chlorophenyl)-1,3-dithiane (**14**), 25 mL H_2O and NBS (45 mmol, 8.0 g) were added and the flask was closed with a rubber septum. The reaction mixture was stirred for 1.5 h at rt and added to a sepratory funnel with 250 mL CH_2Cl_2 and washed with water (2 × 50 mL). The aqueous phase was extracted with 250 mL CH_2Cl_2, and combined organic phases were dried ($MgSO_4$), filtrated and mixed with 5 g of silica gel. The solvent was removed in a rotatory evaporator. The remaining solid residue was loaded onto a silica gel column and purified by flash chromatography on silica gel using 20:1 hexanes/ethyl acetate as eluent to yield the product **fenofibrate** (3.1 g, 86%) as a white solid. The NMR spectral data match with the previously published data.[10]

6. References

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(**7**) Ushijima, S.; Dohi, S.; Moriyama, K.; Togo, H. *Tetrahedron* **2012**, *68*, 1436.

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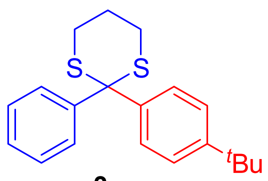
(**10**) Bjerglund, K. M.; Skrydstrup, T.; Molander, G. A. *Org. Lett*. **2014**, *16*, 1888.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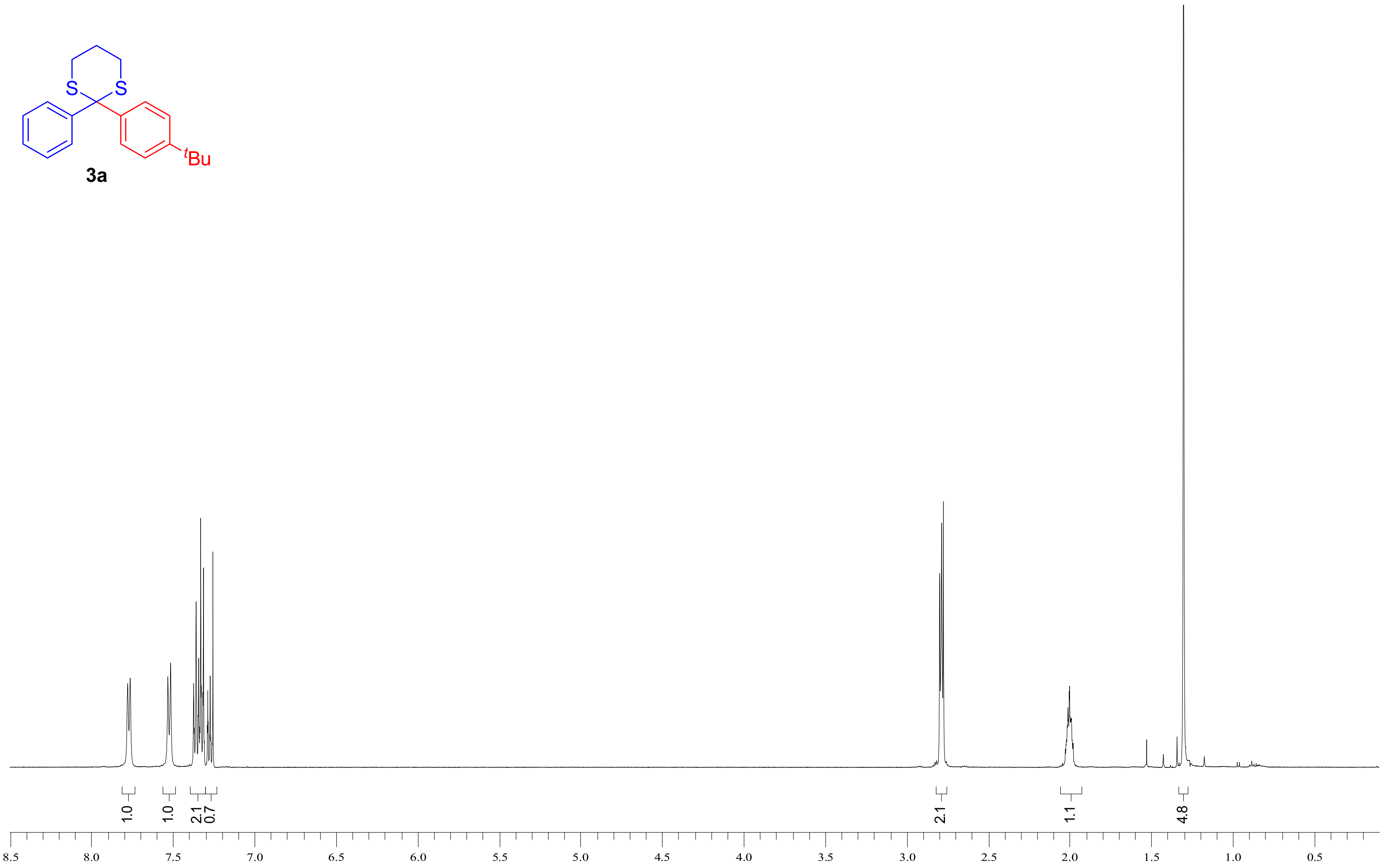
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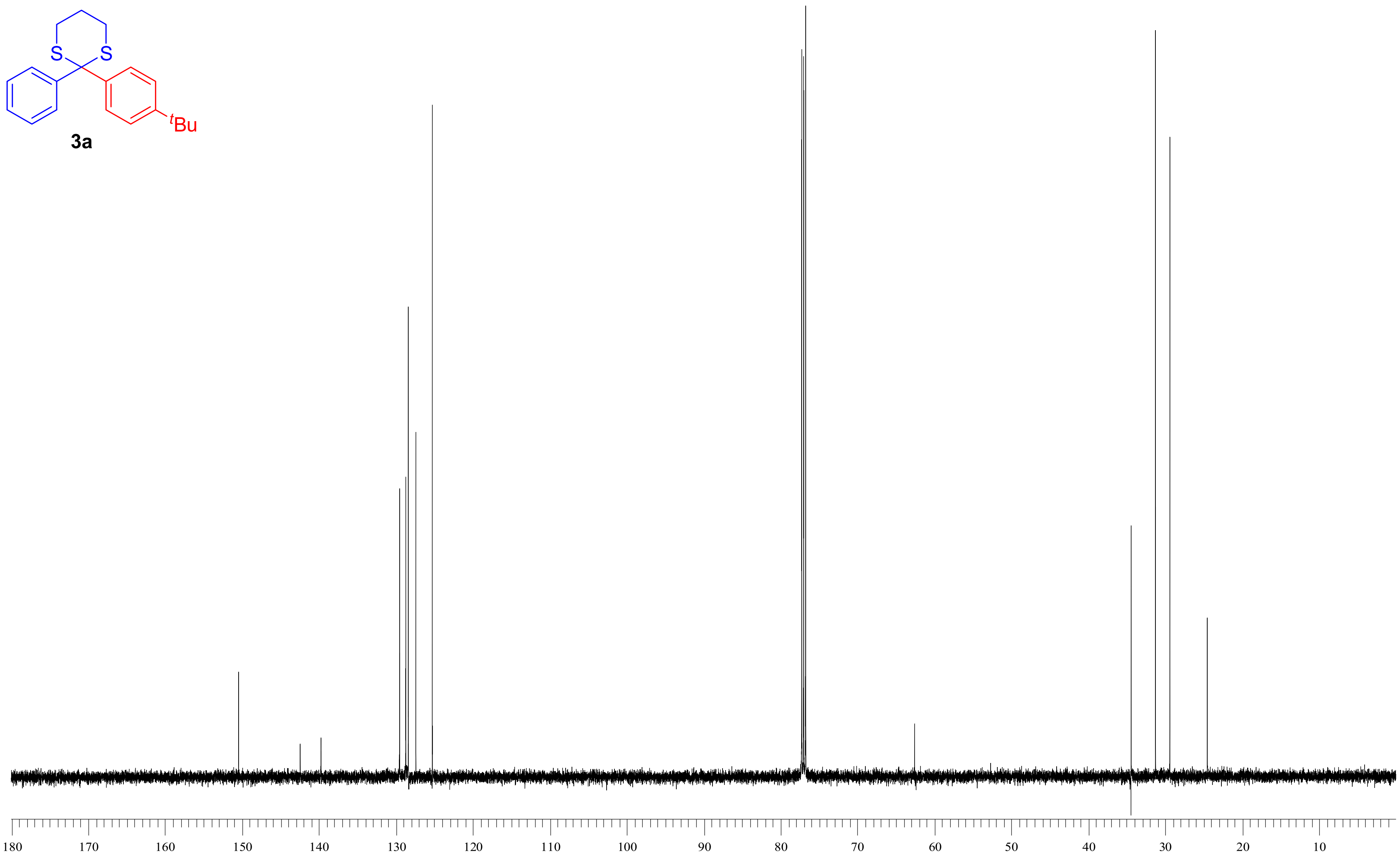
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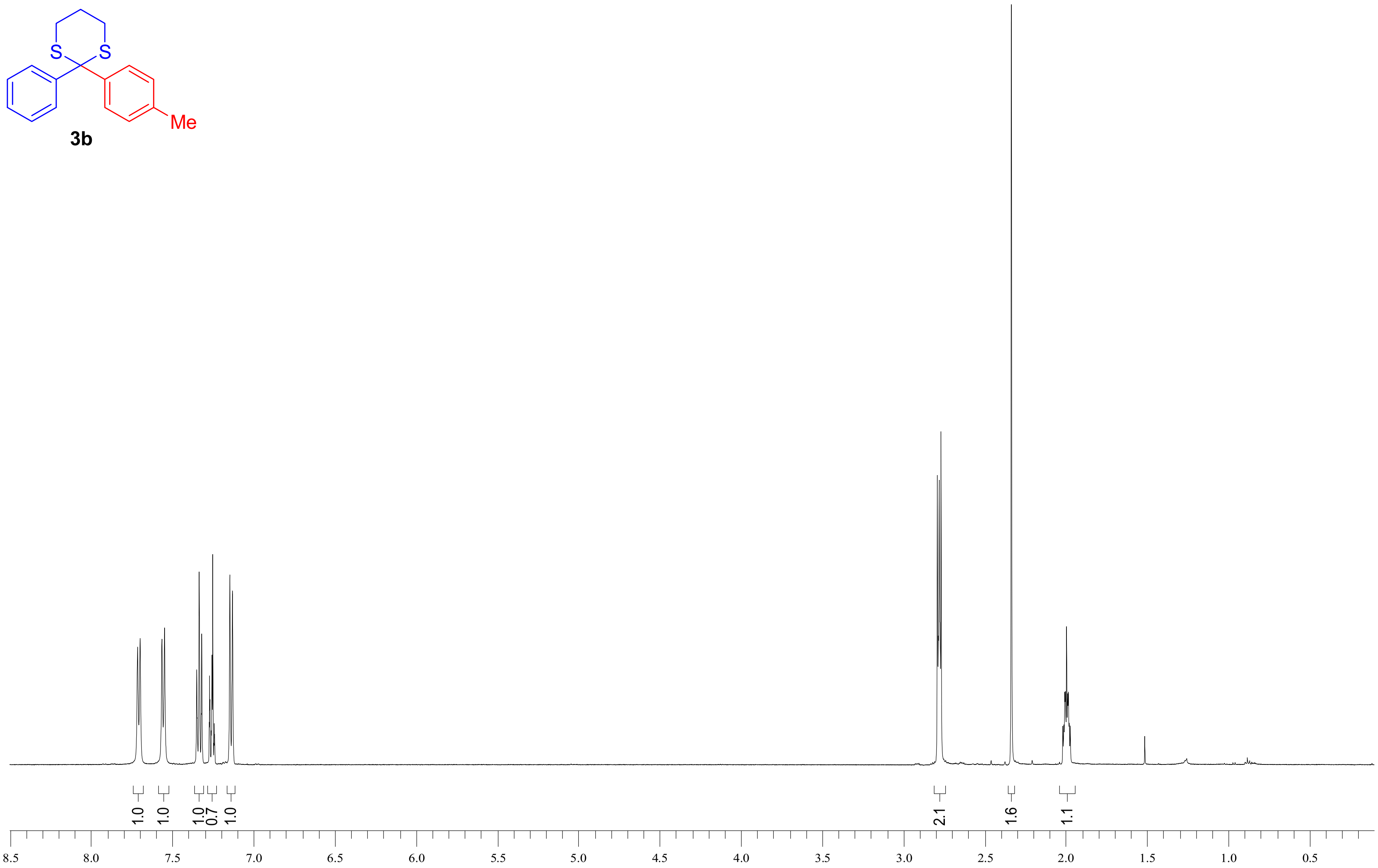

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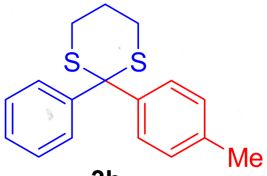

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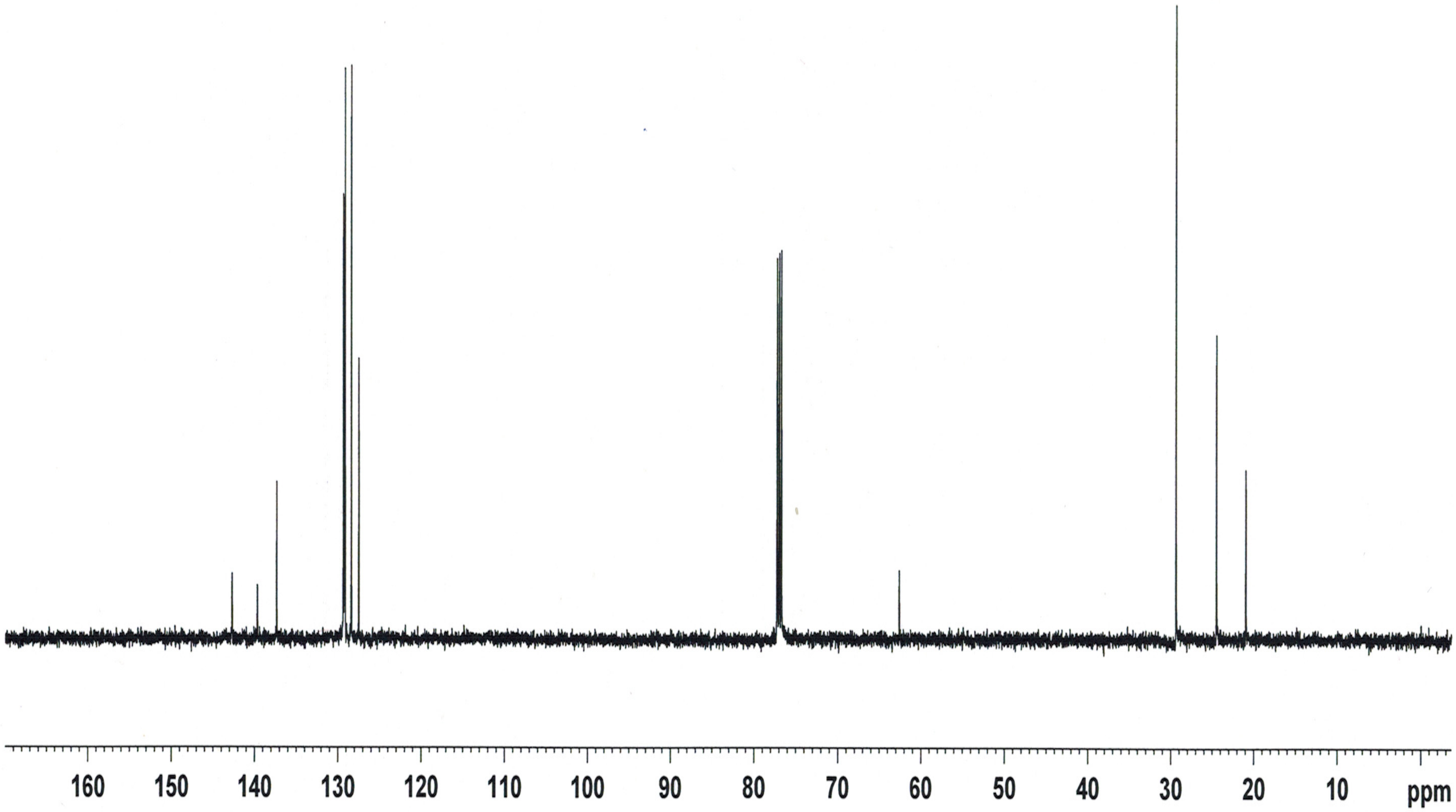

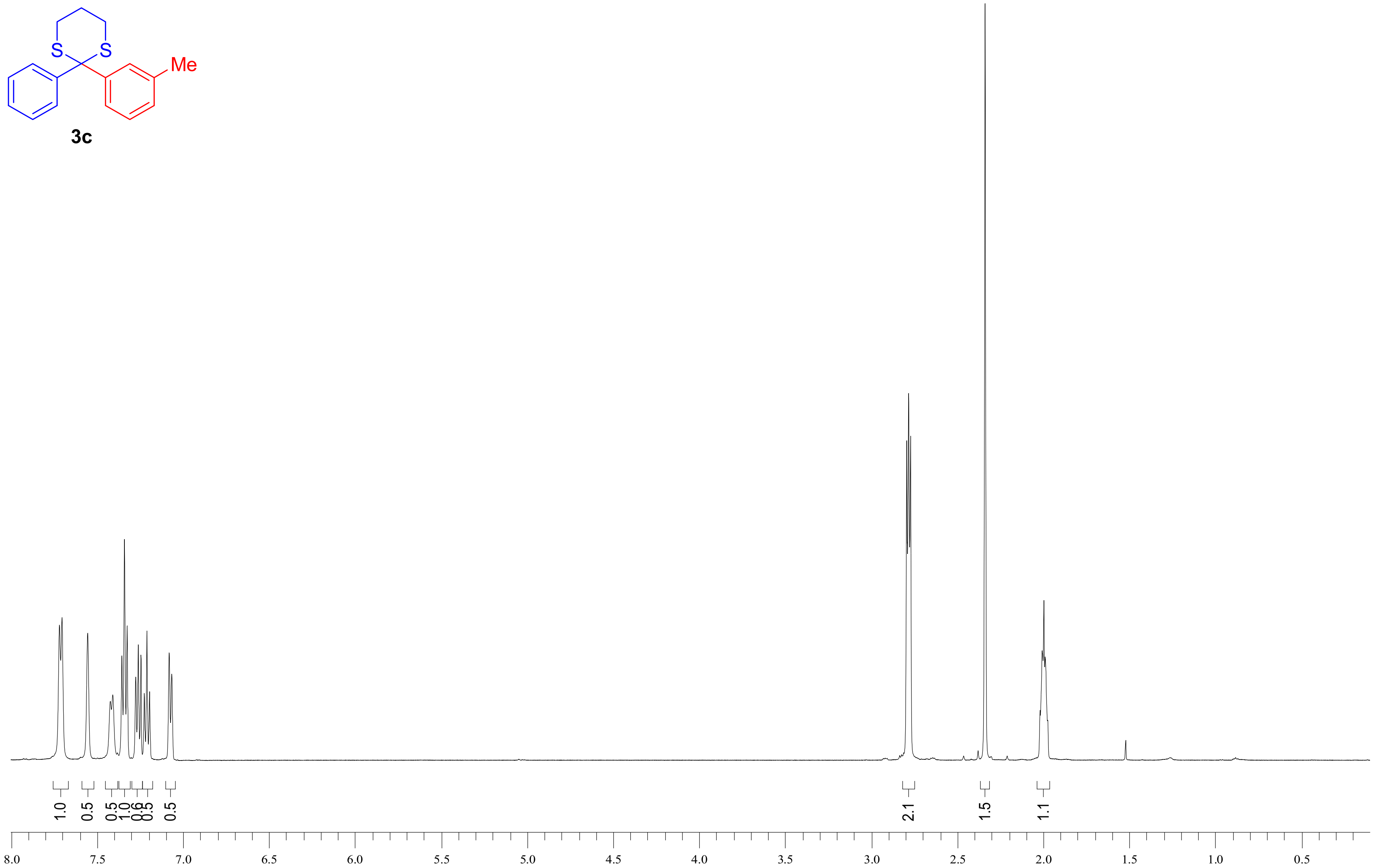

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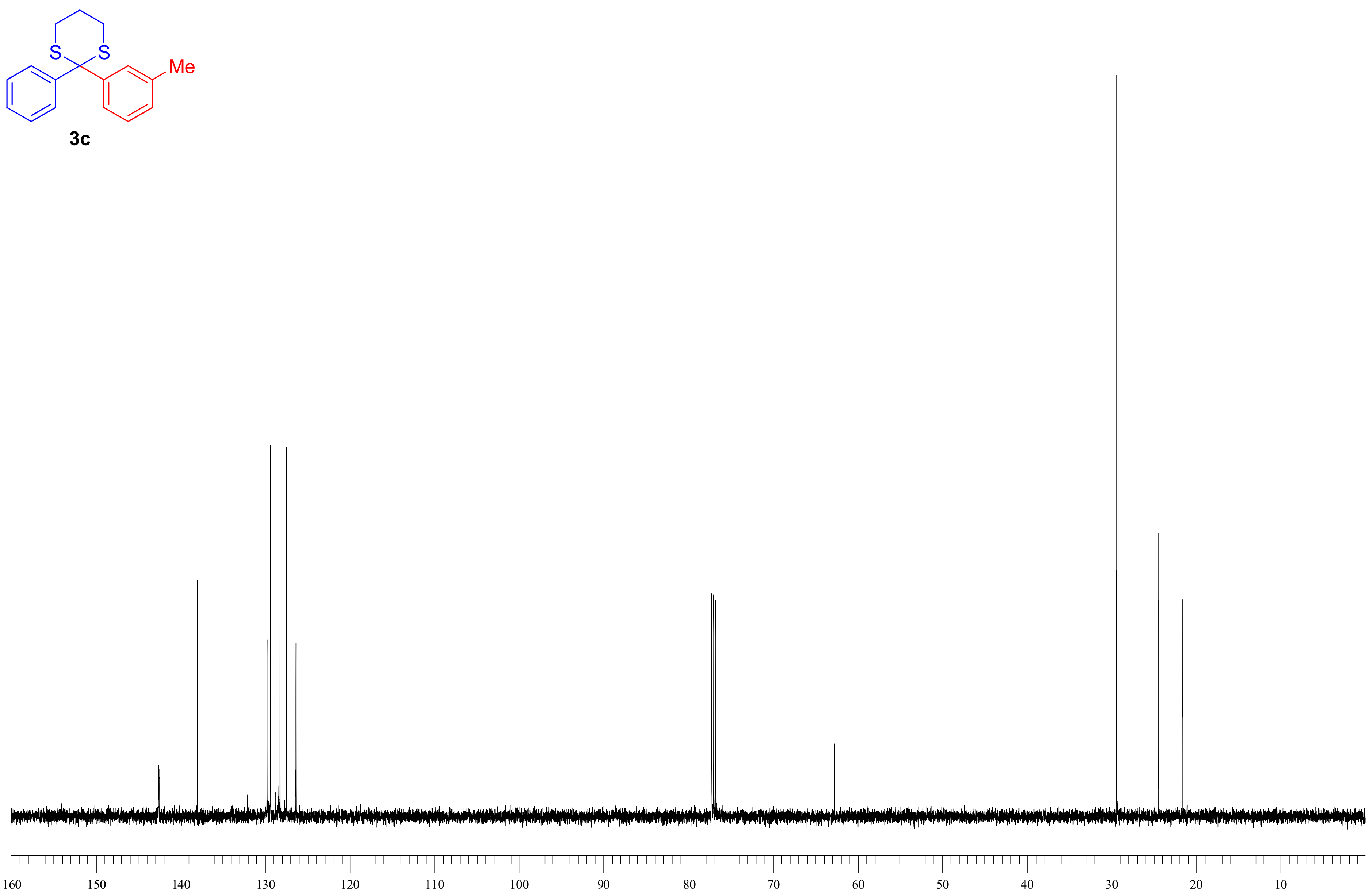

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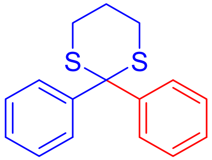

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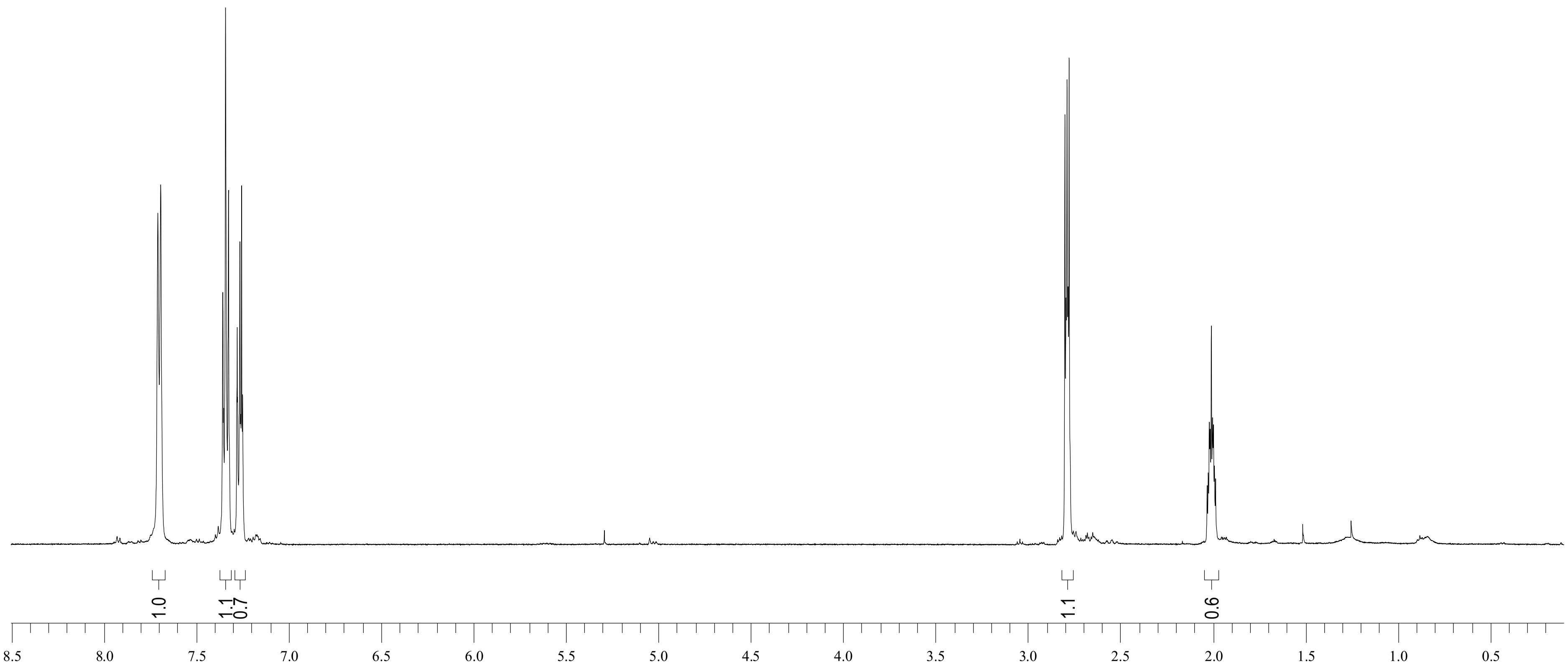

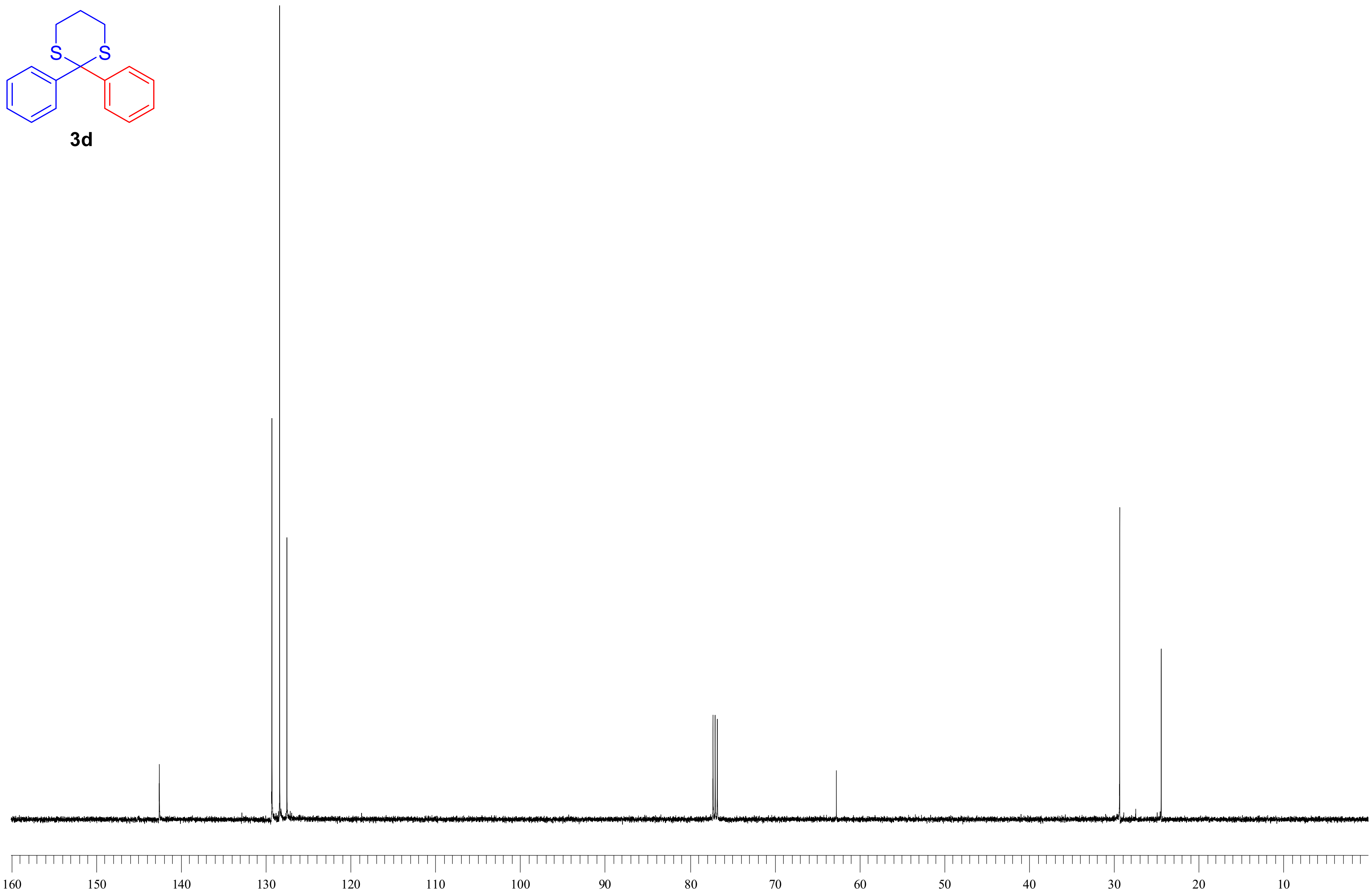
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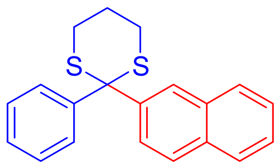
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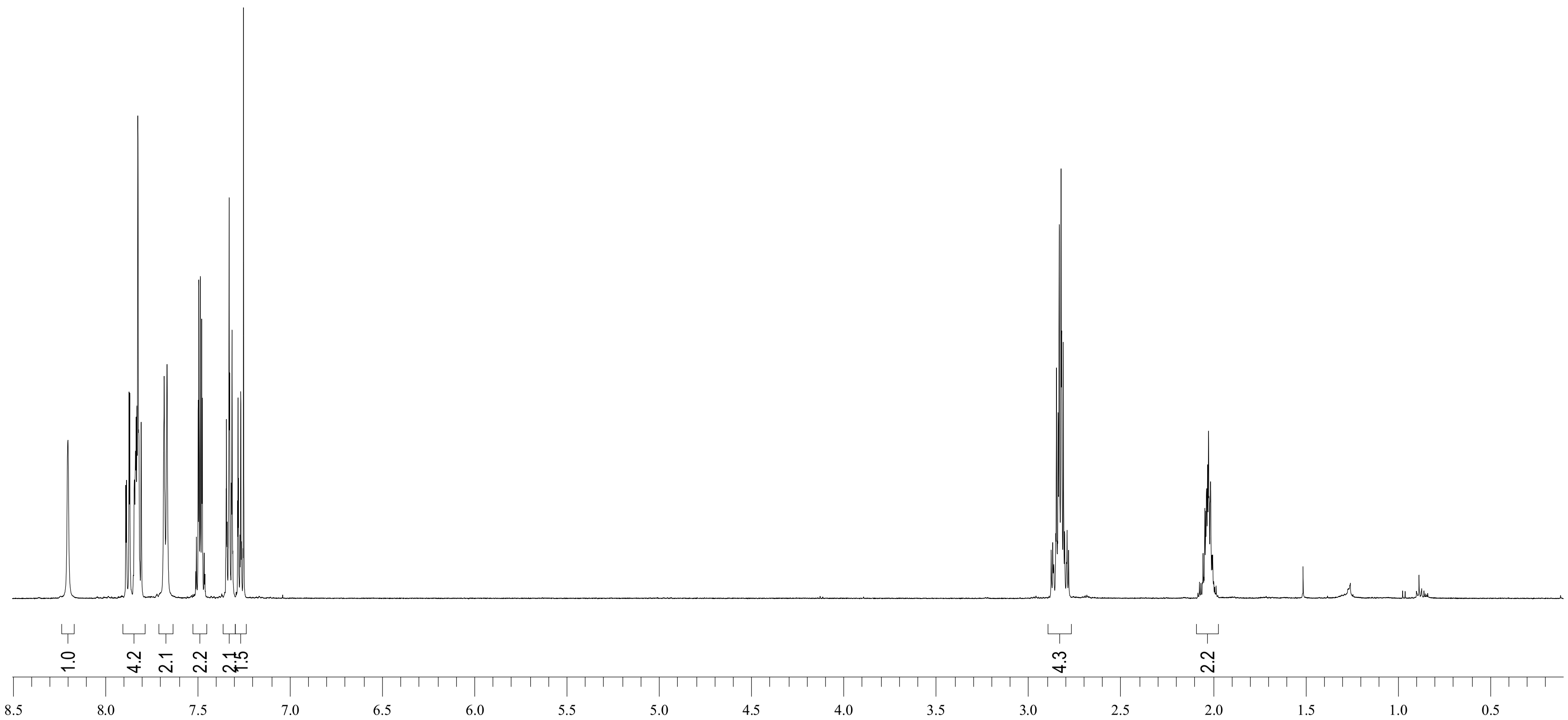
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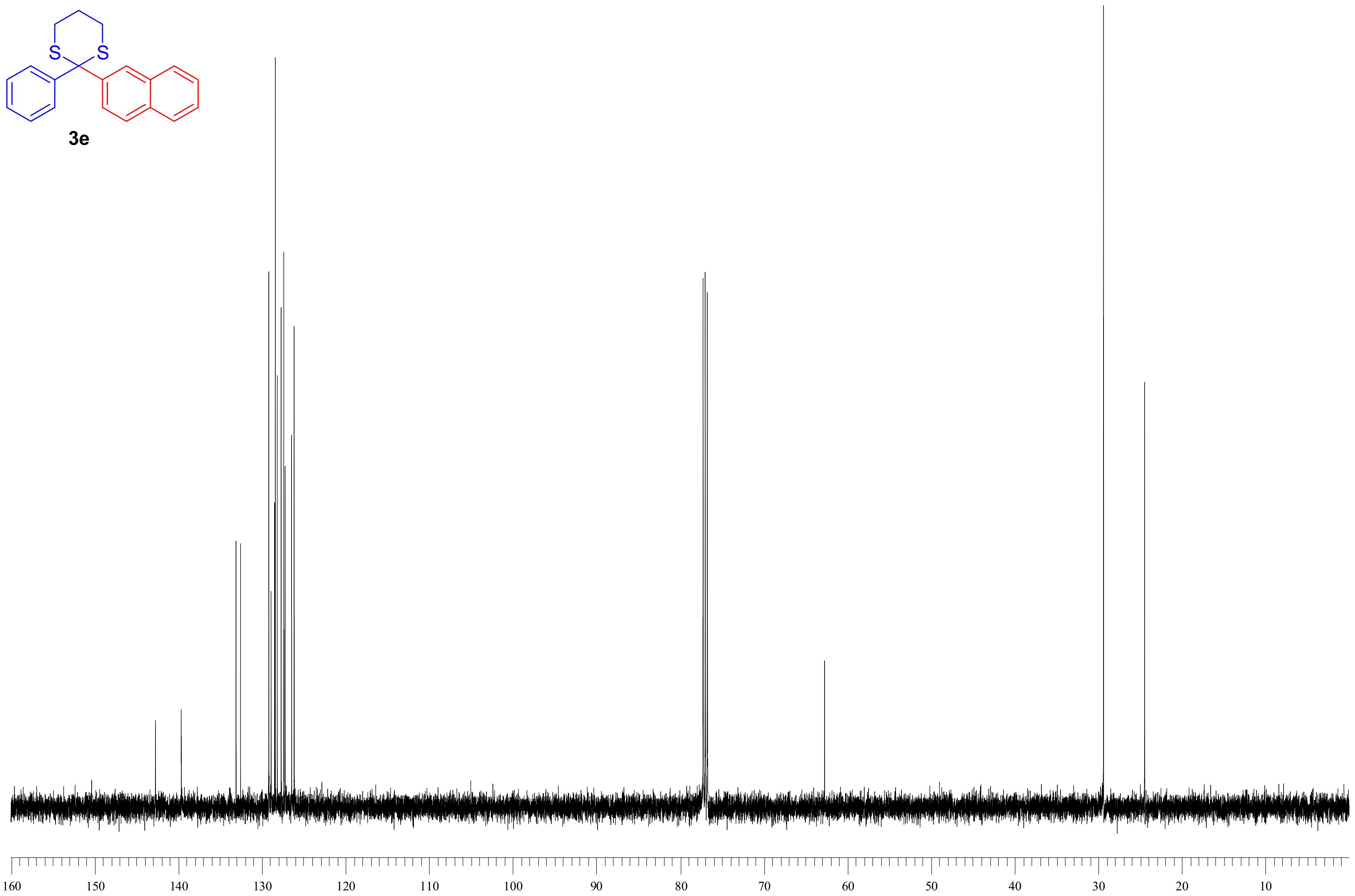

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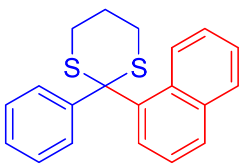

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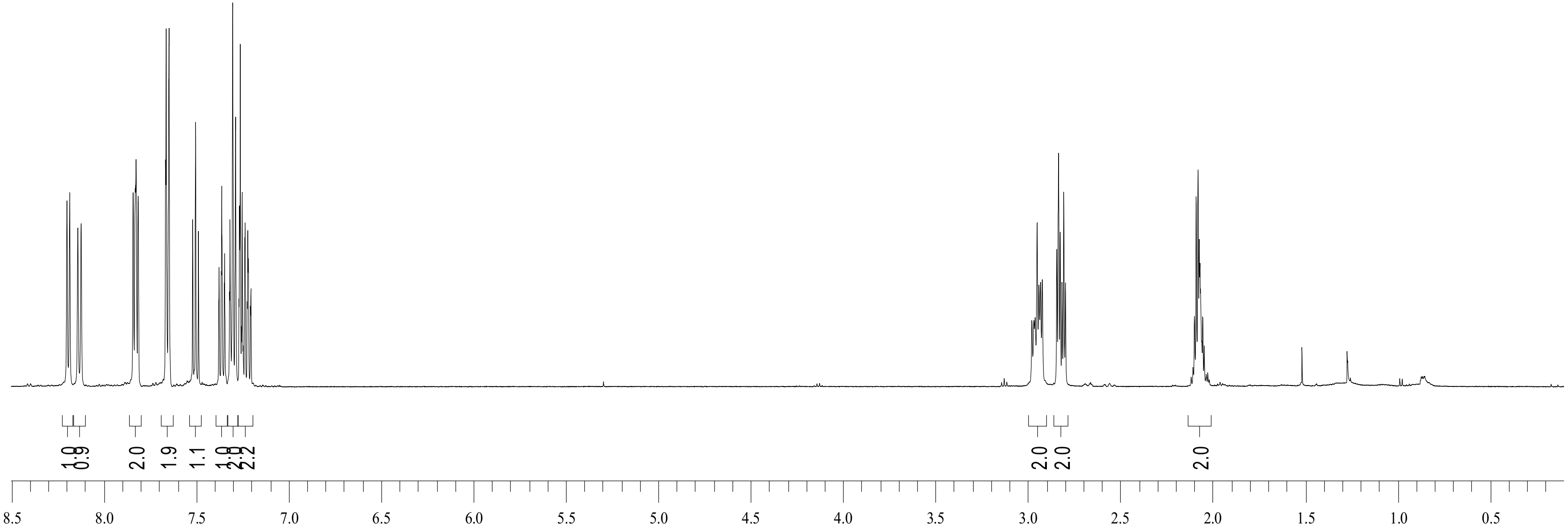
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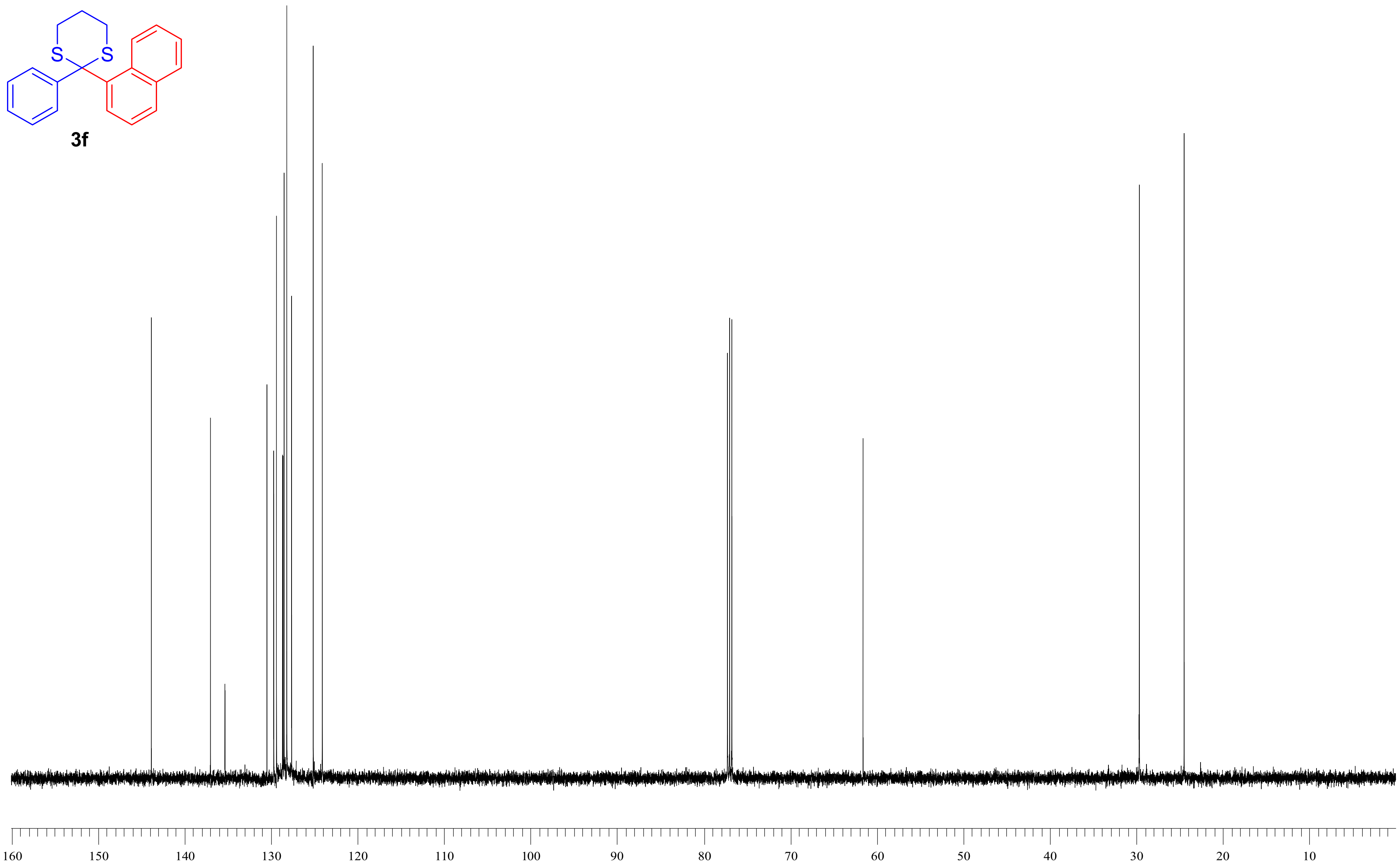
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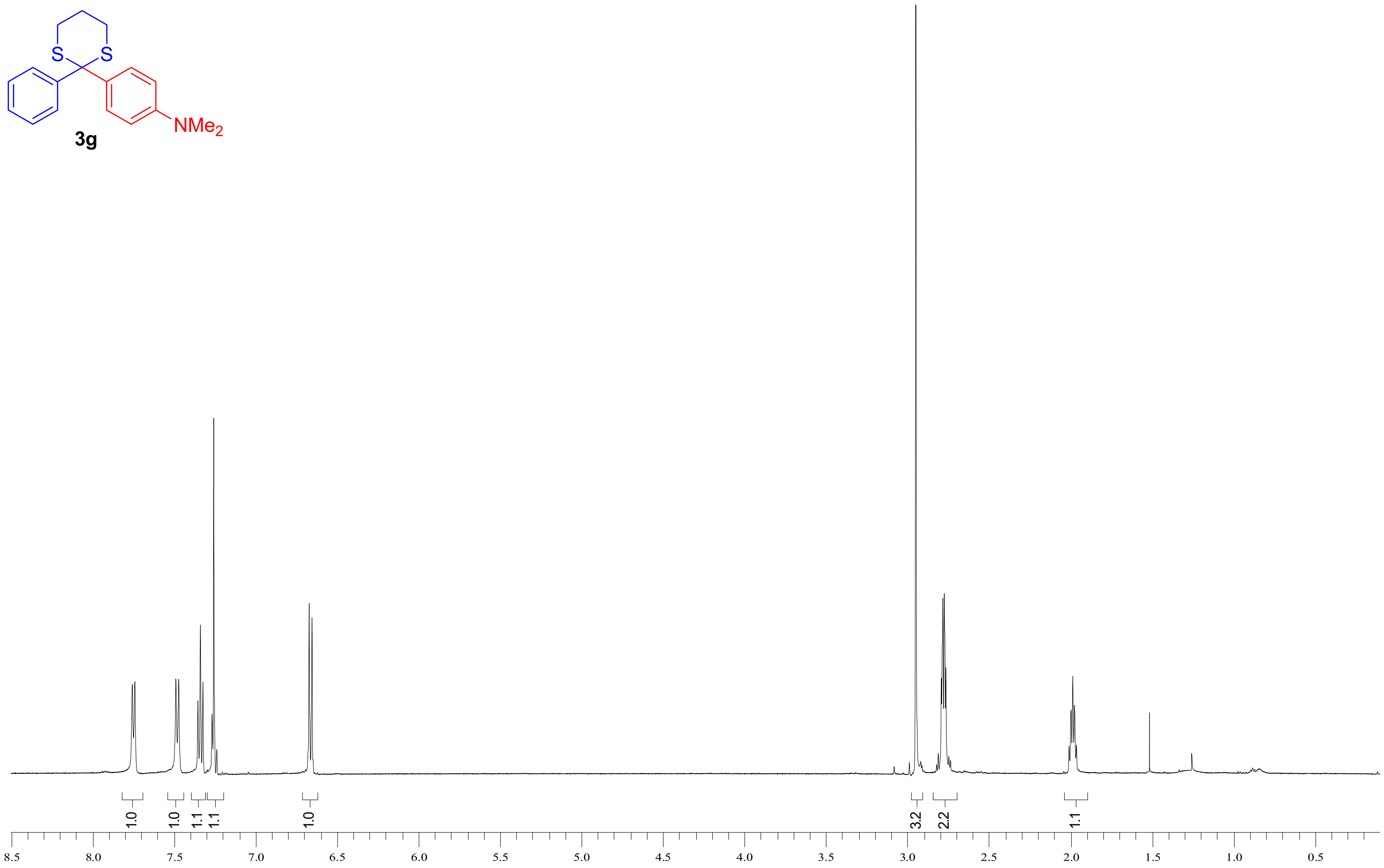
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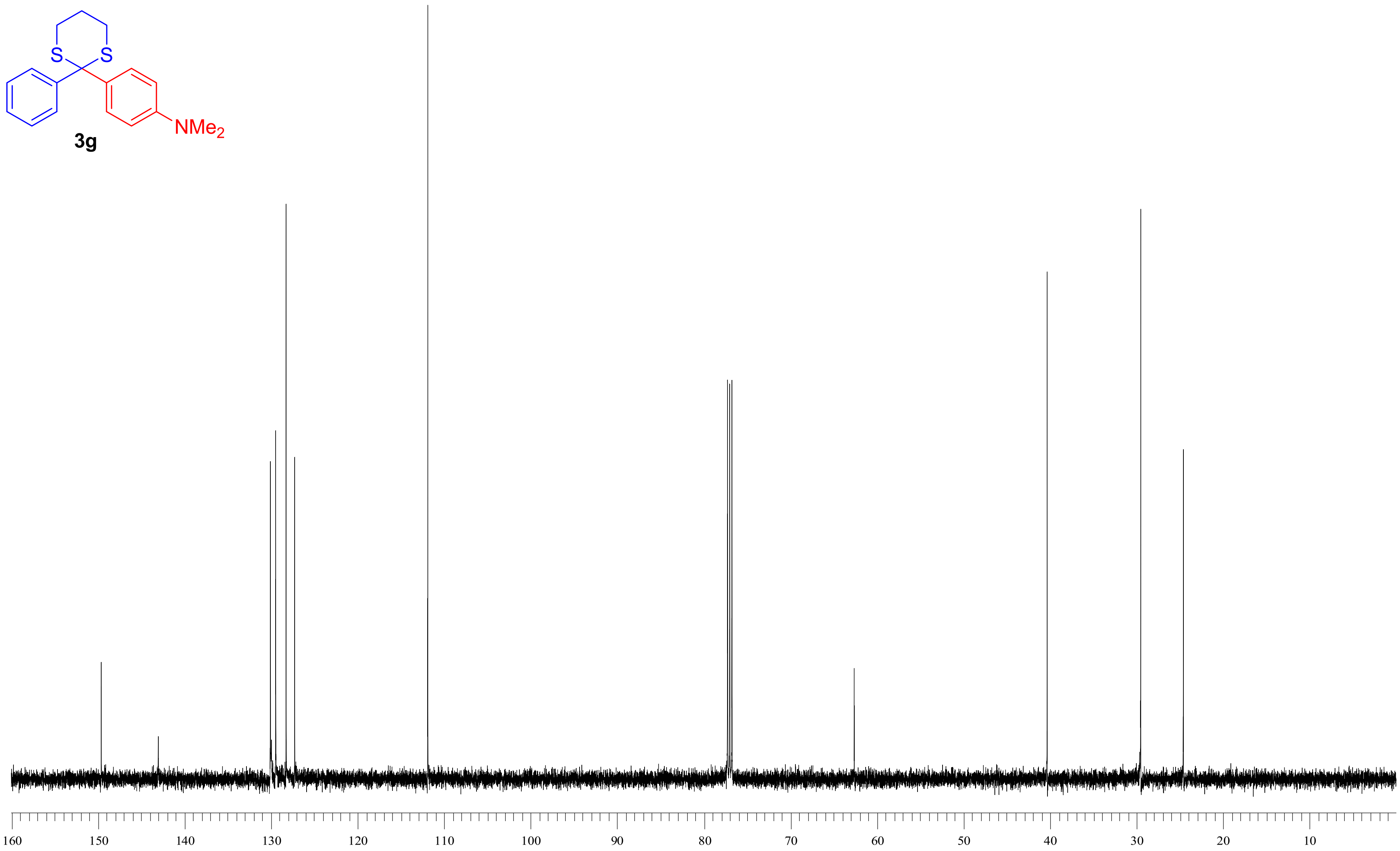

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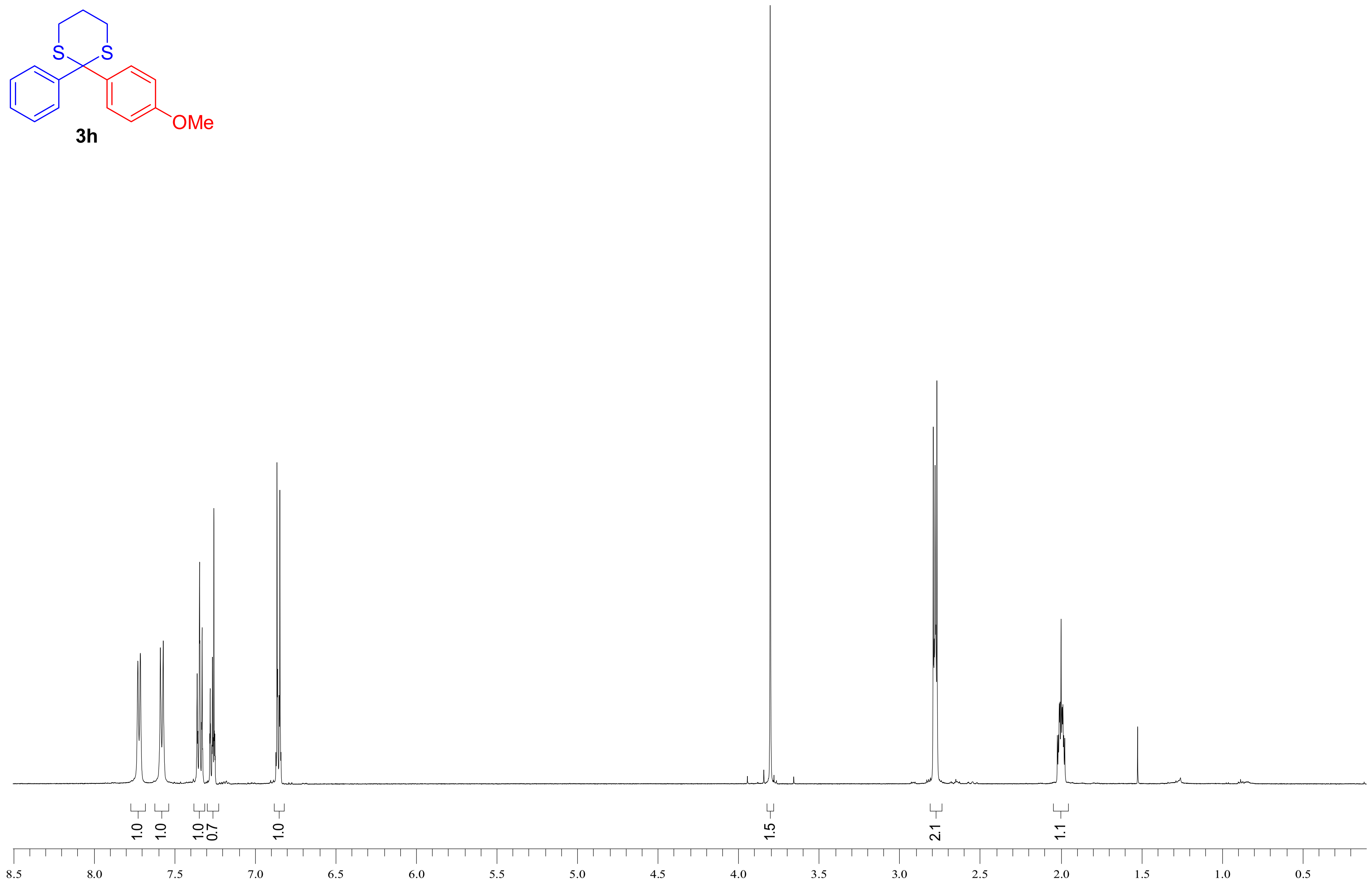

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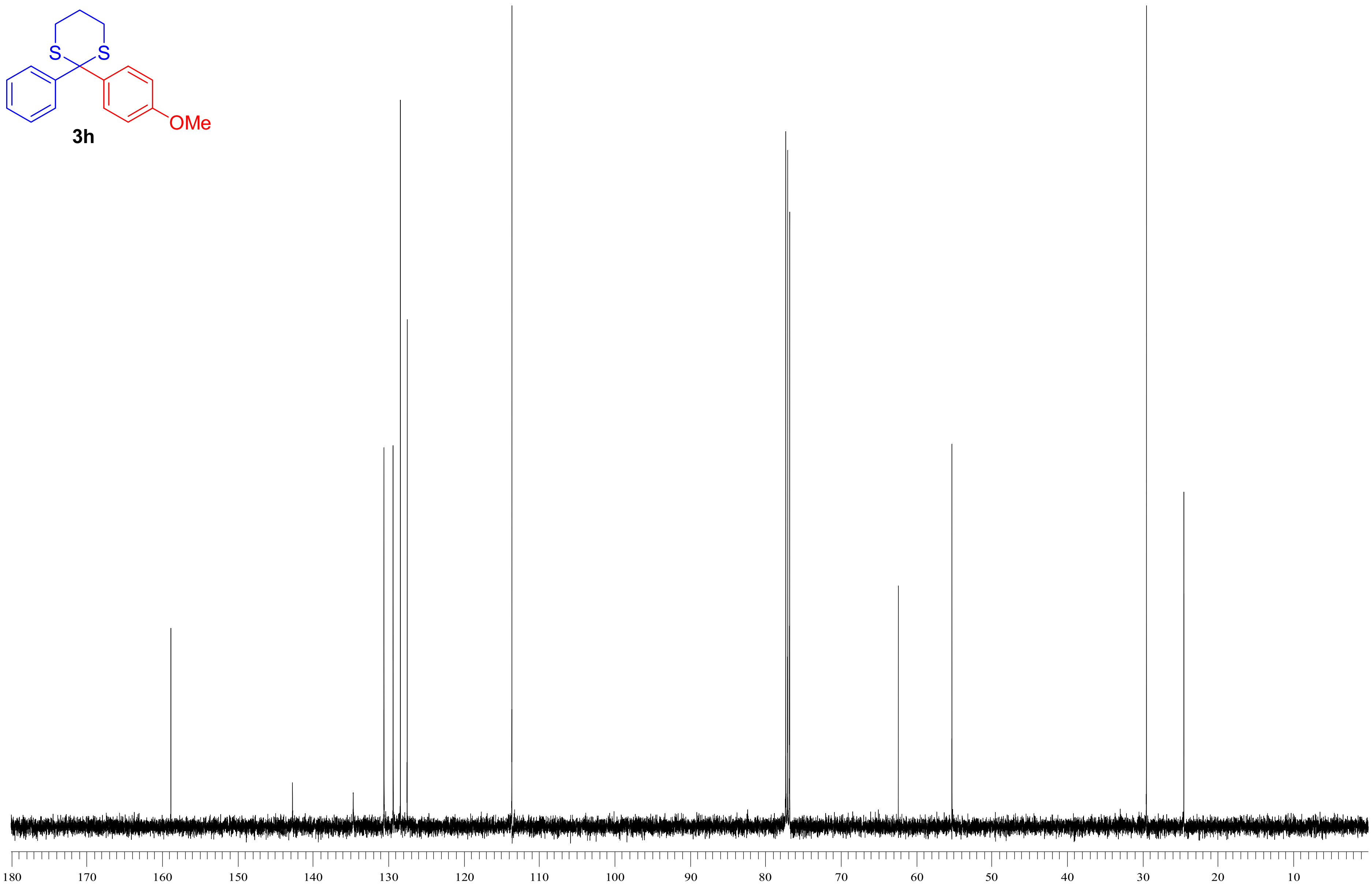
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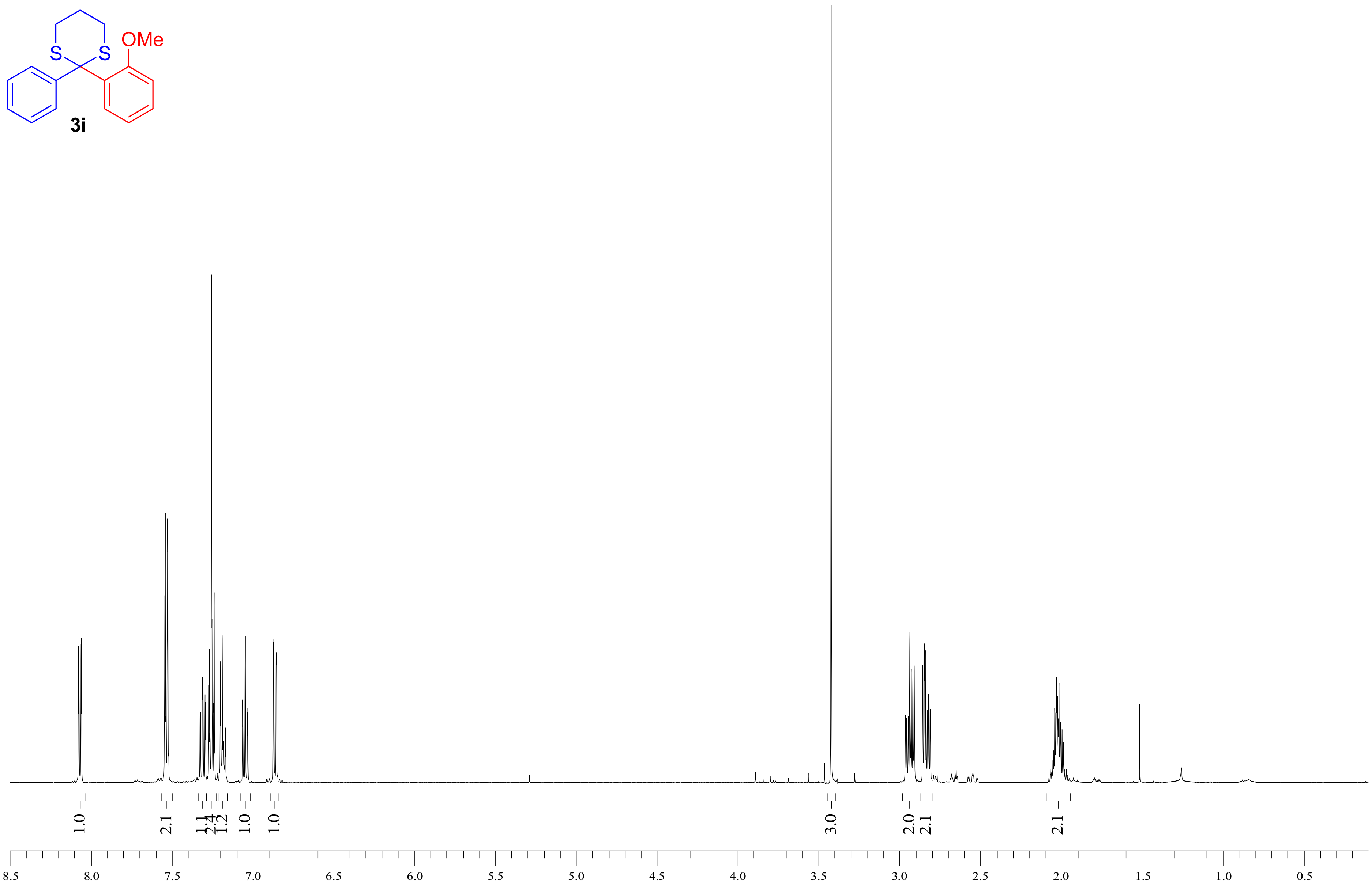
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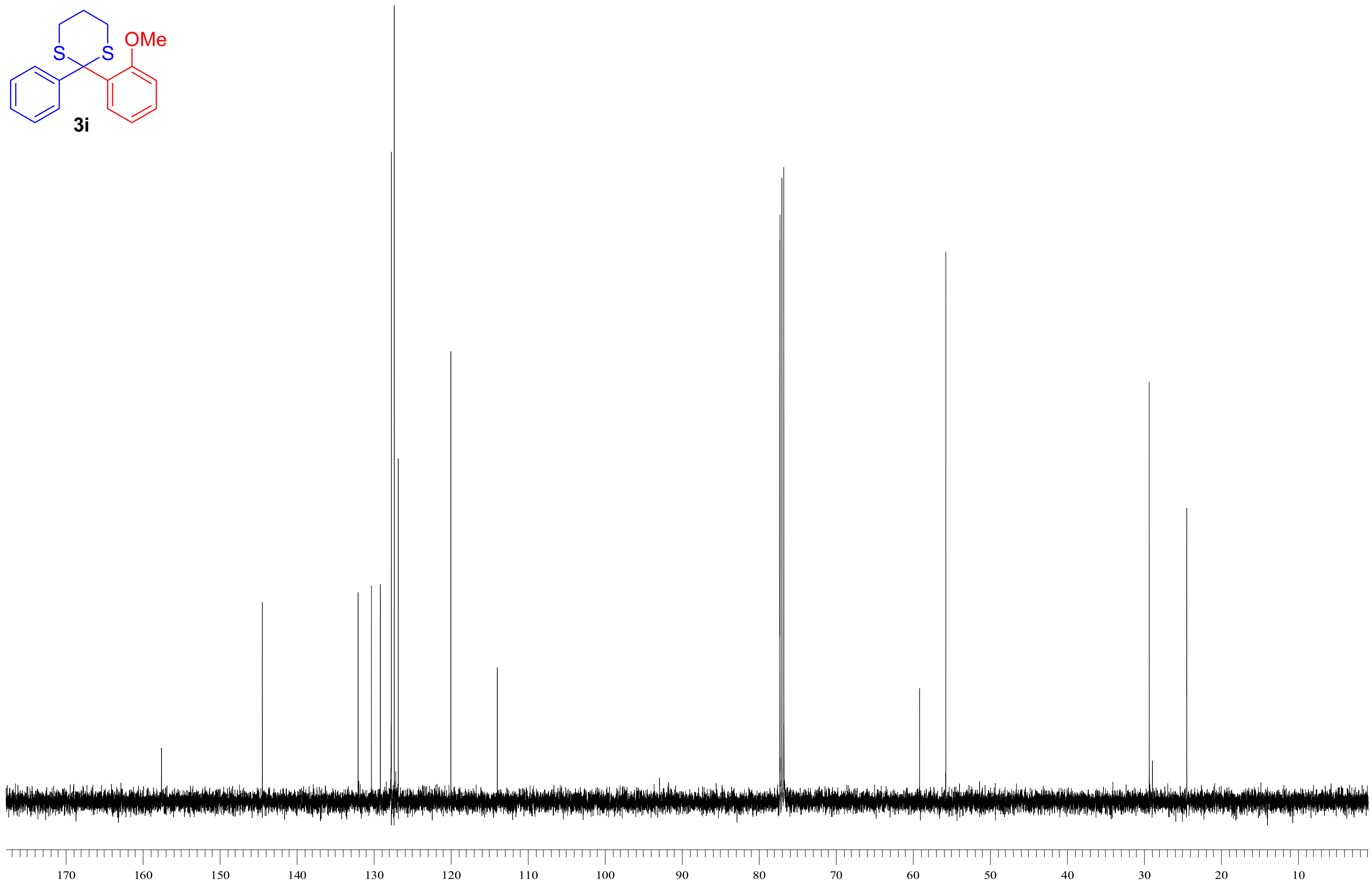

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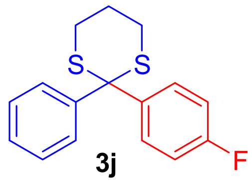

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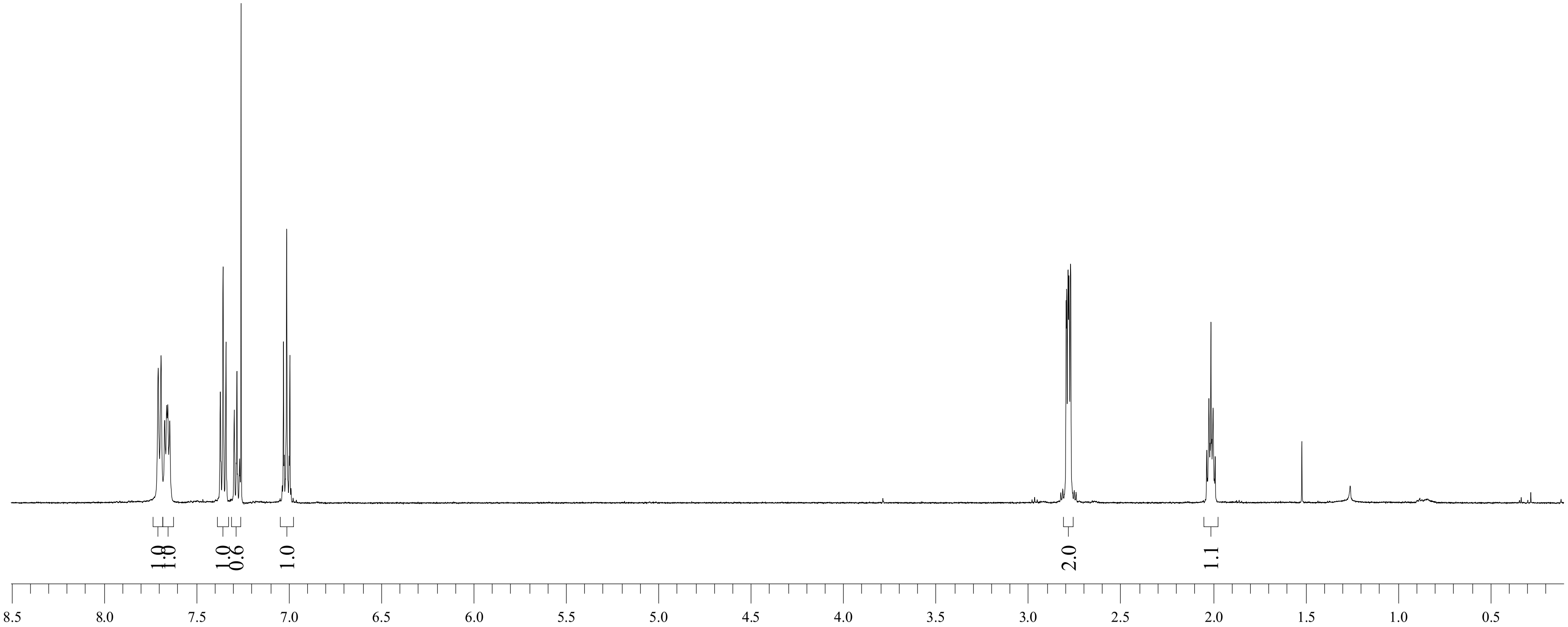

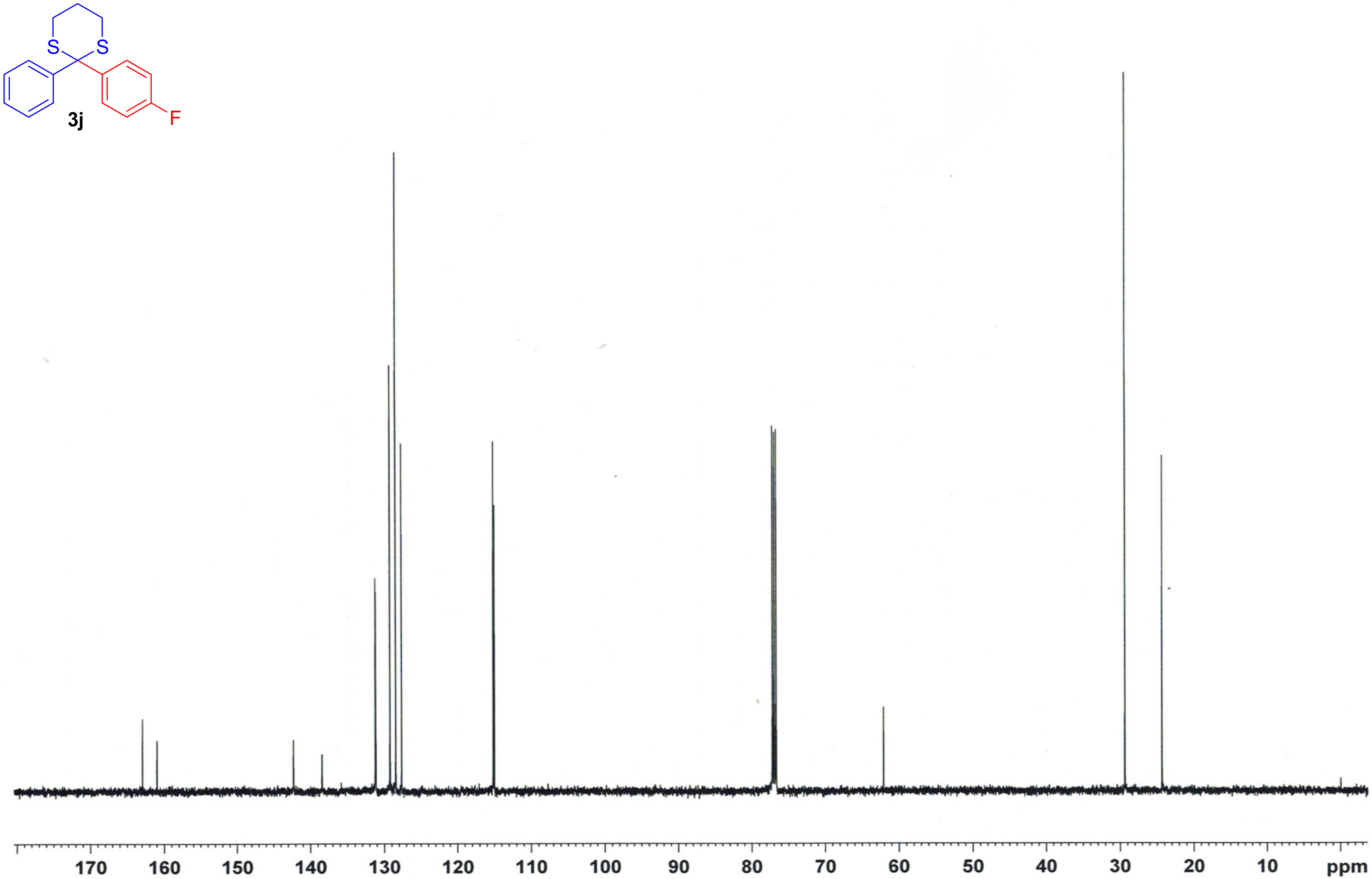

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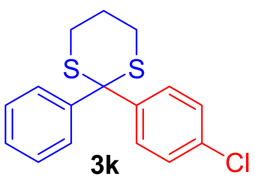

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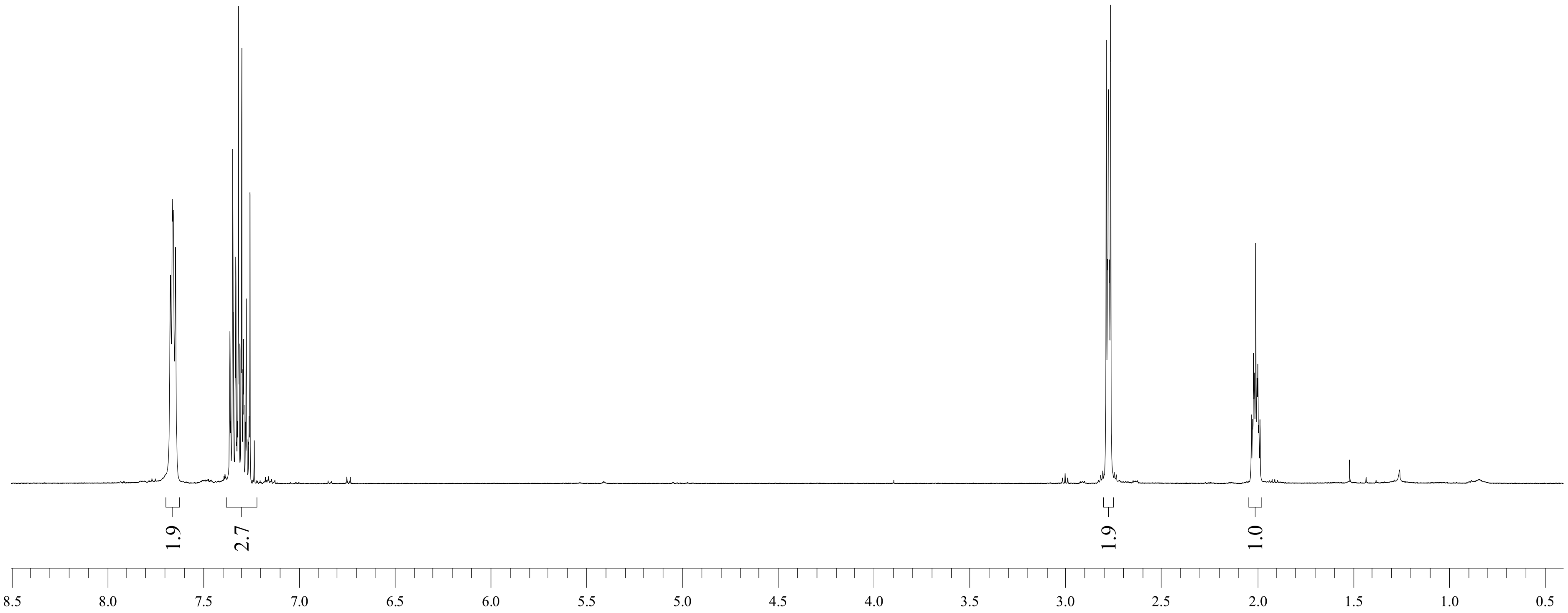

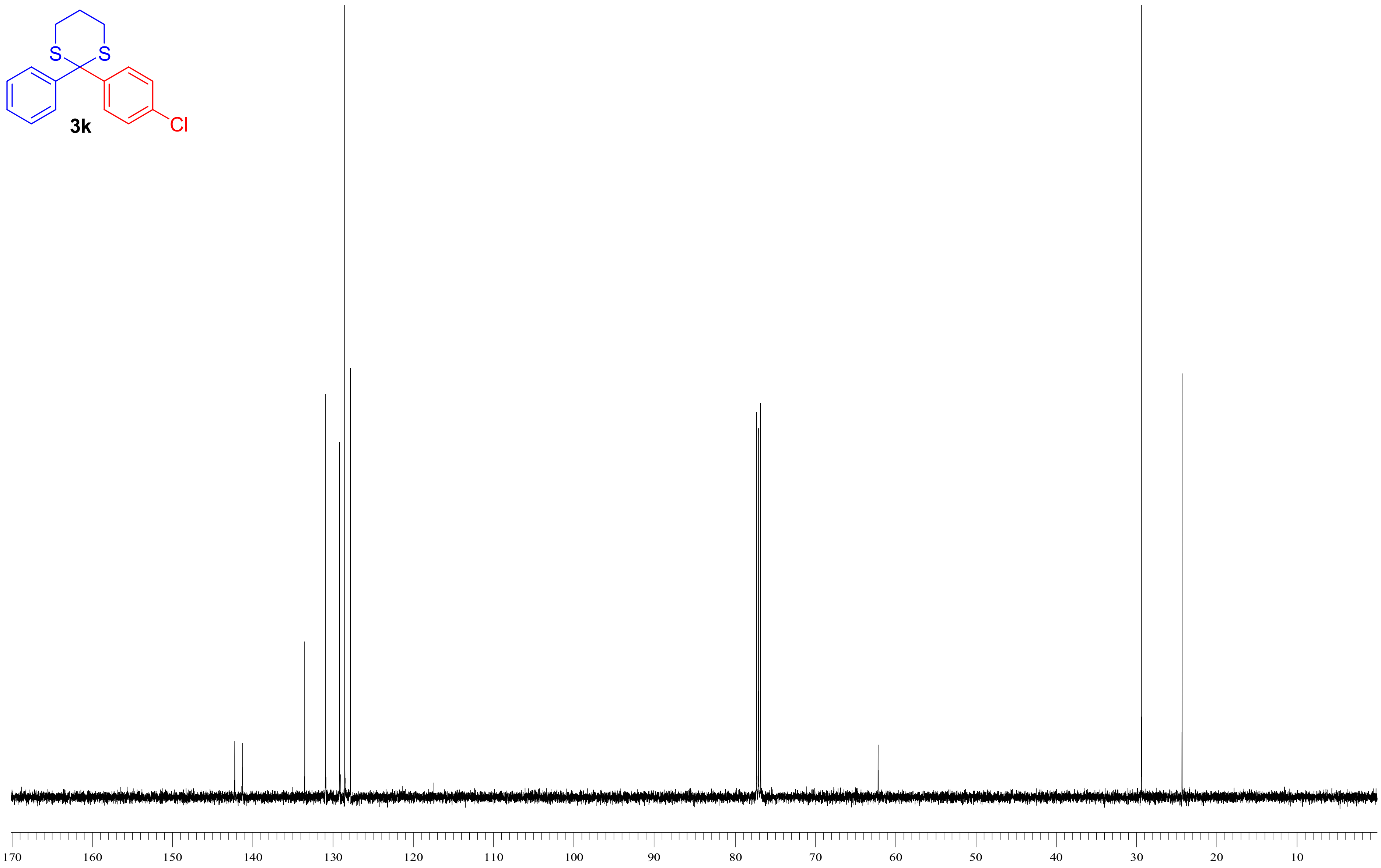

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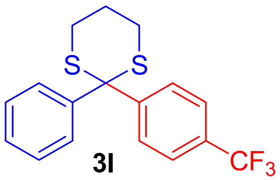

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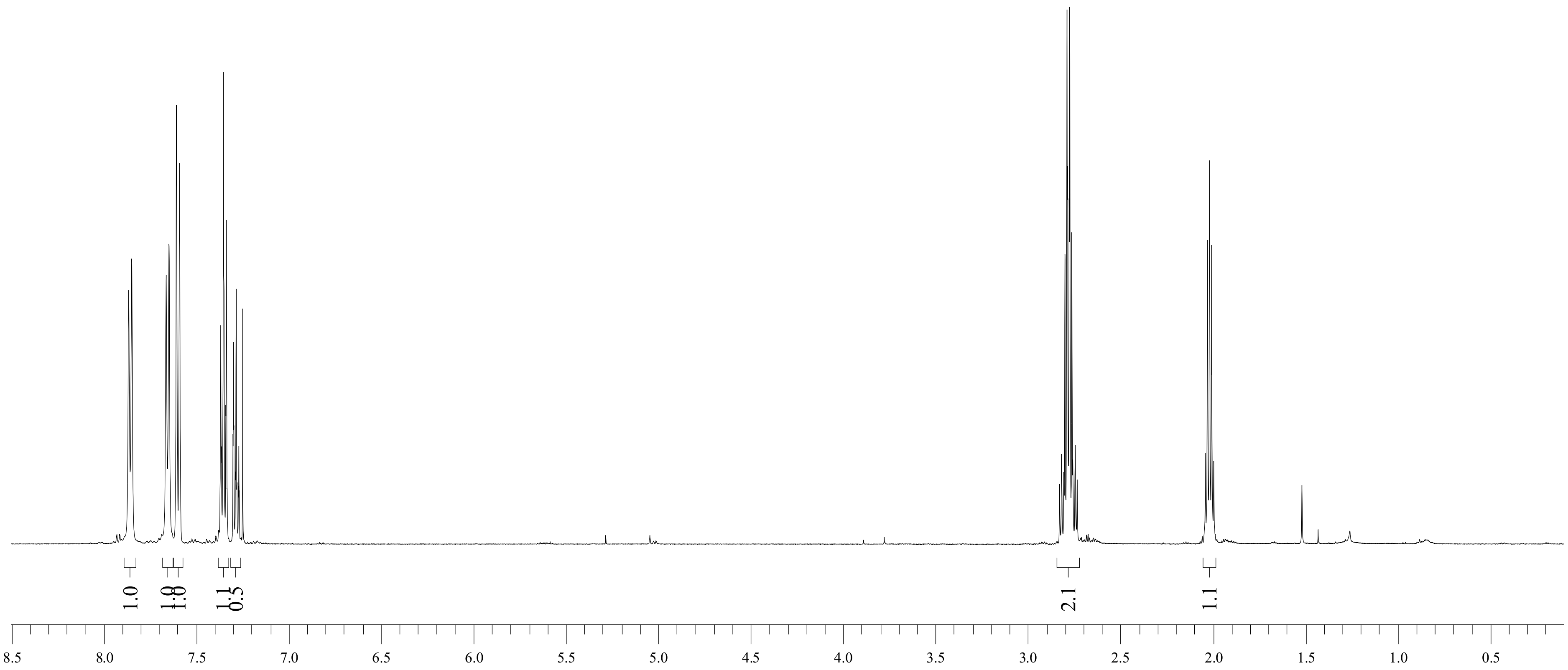

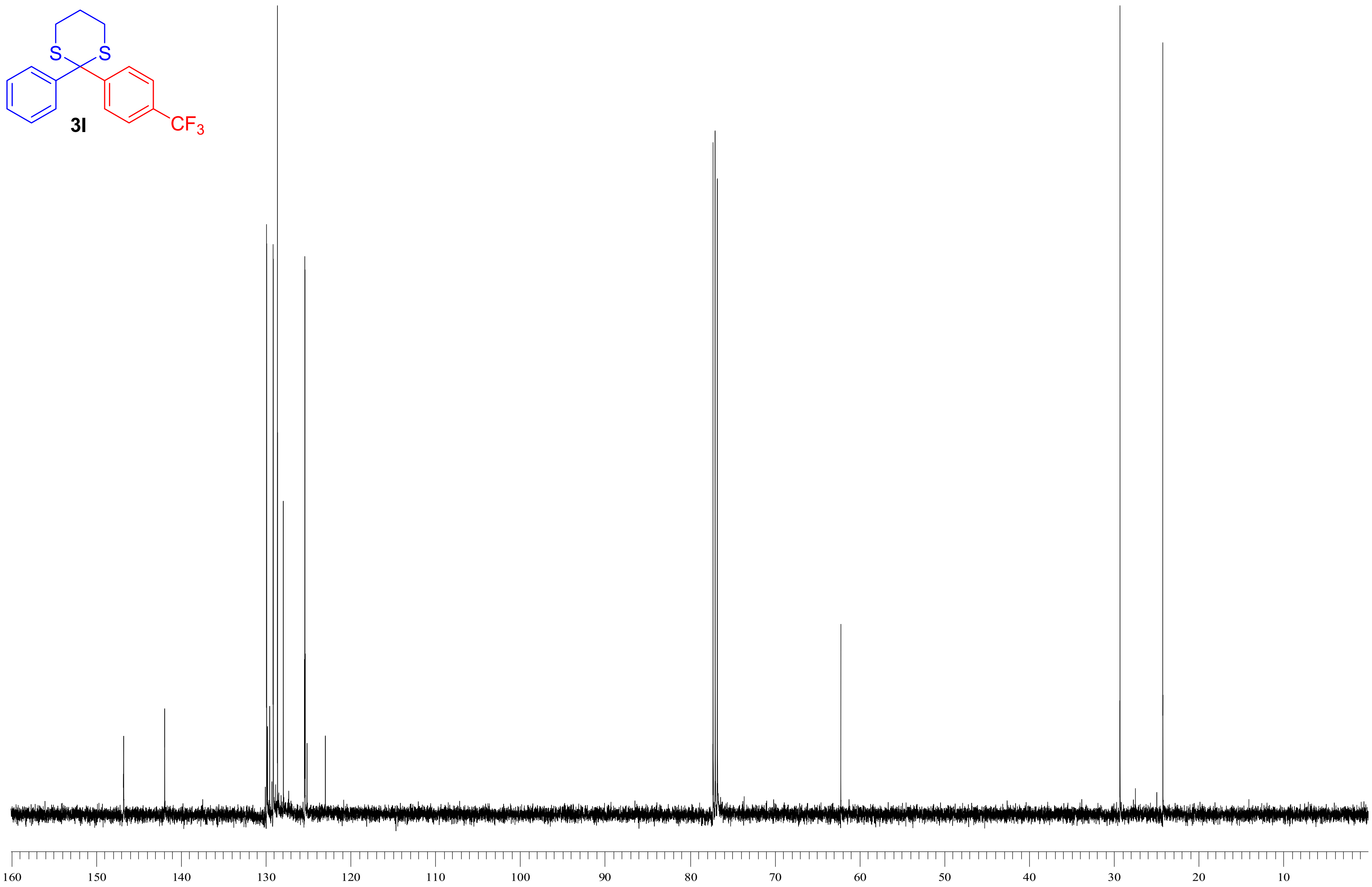
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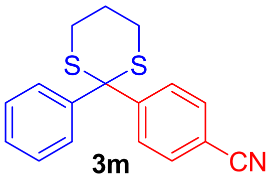
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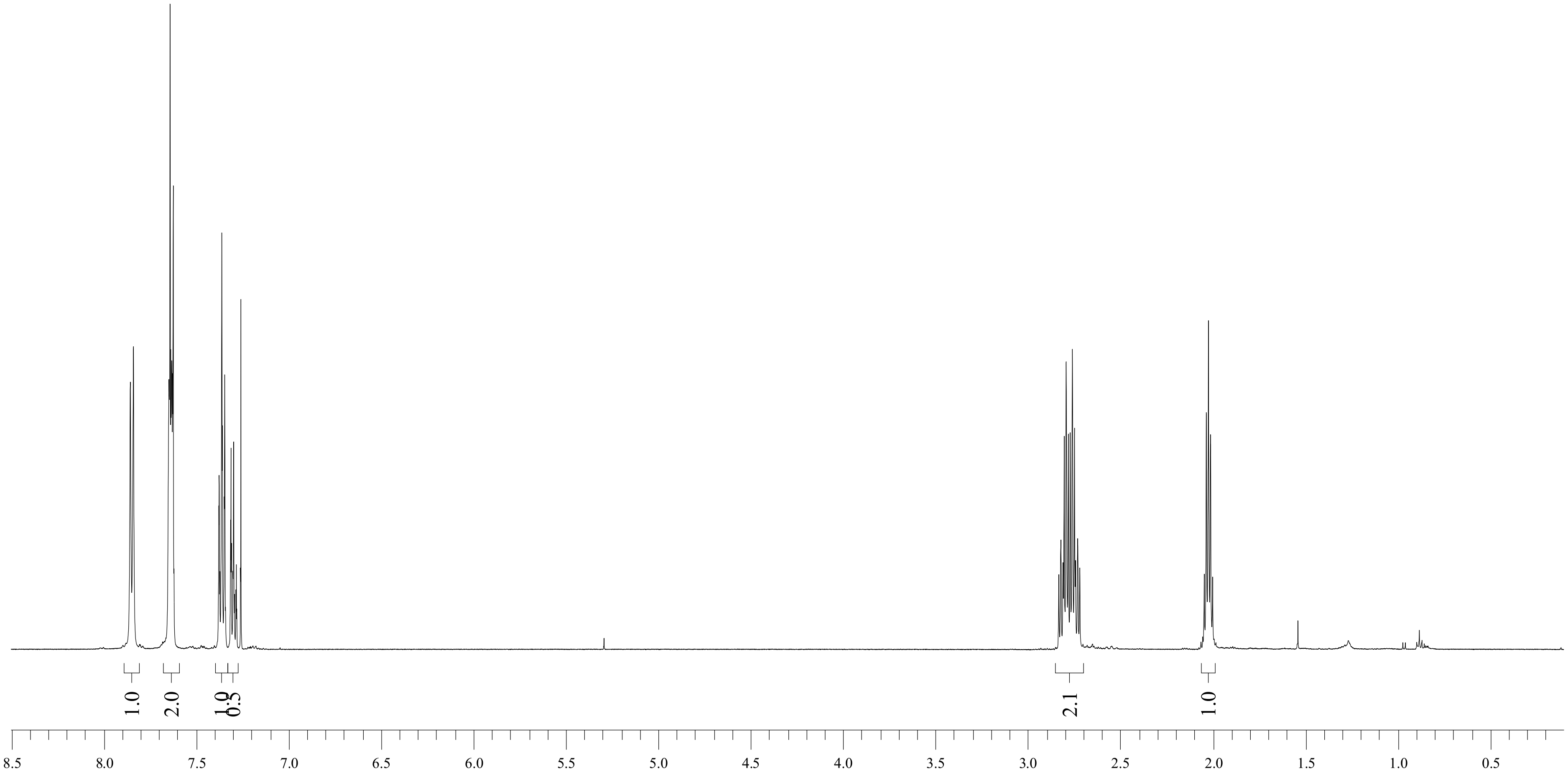
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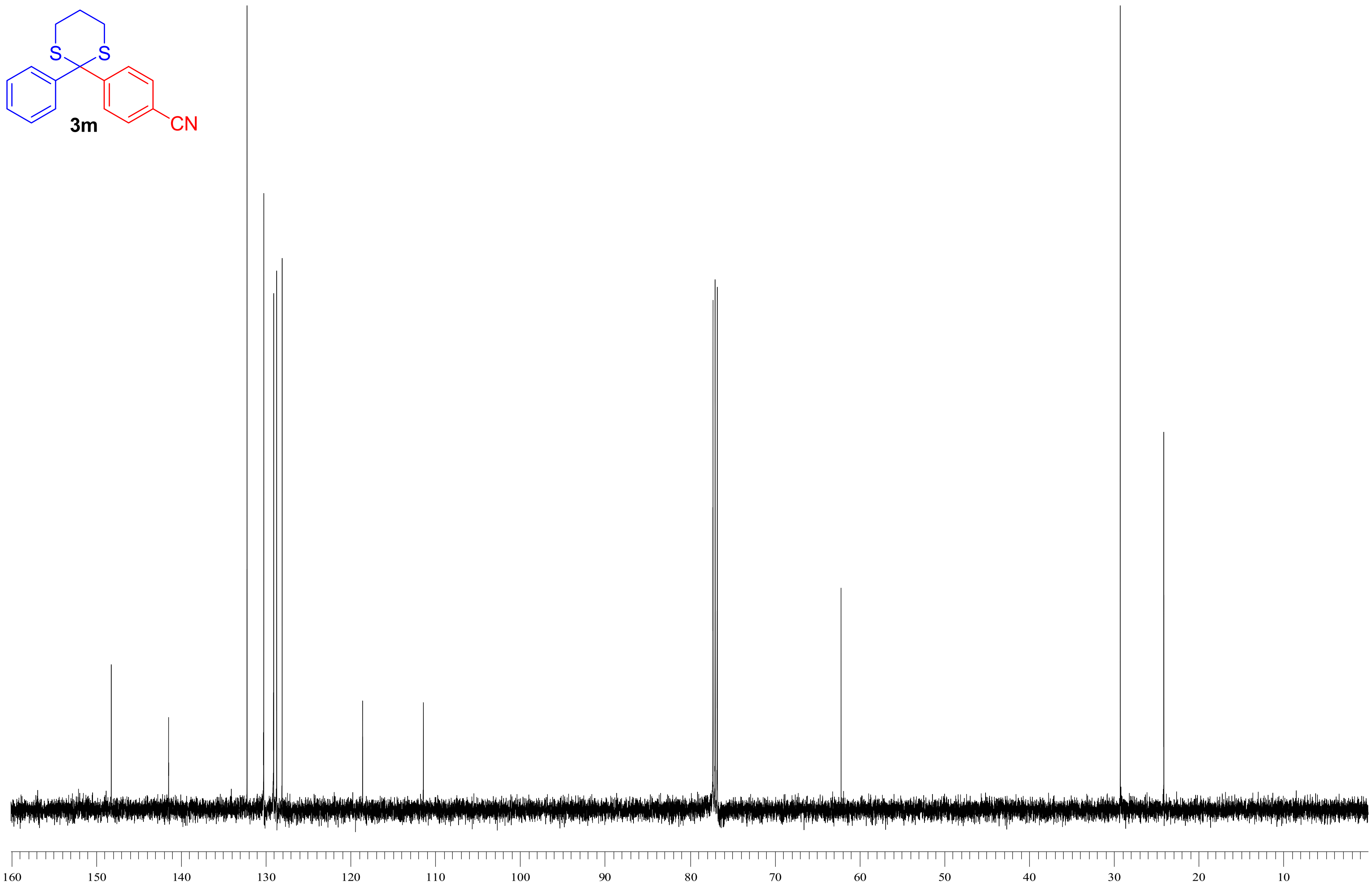

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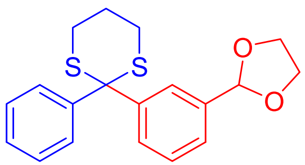
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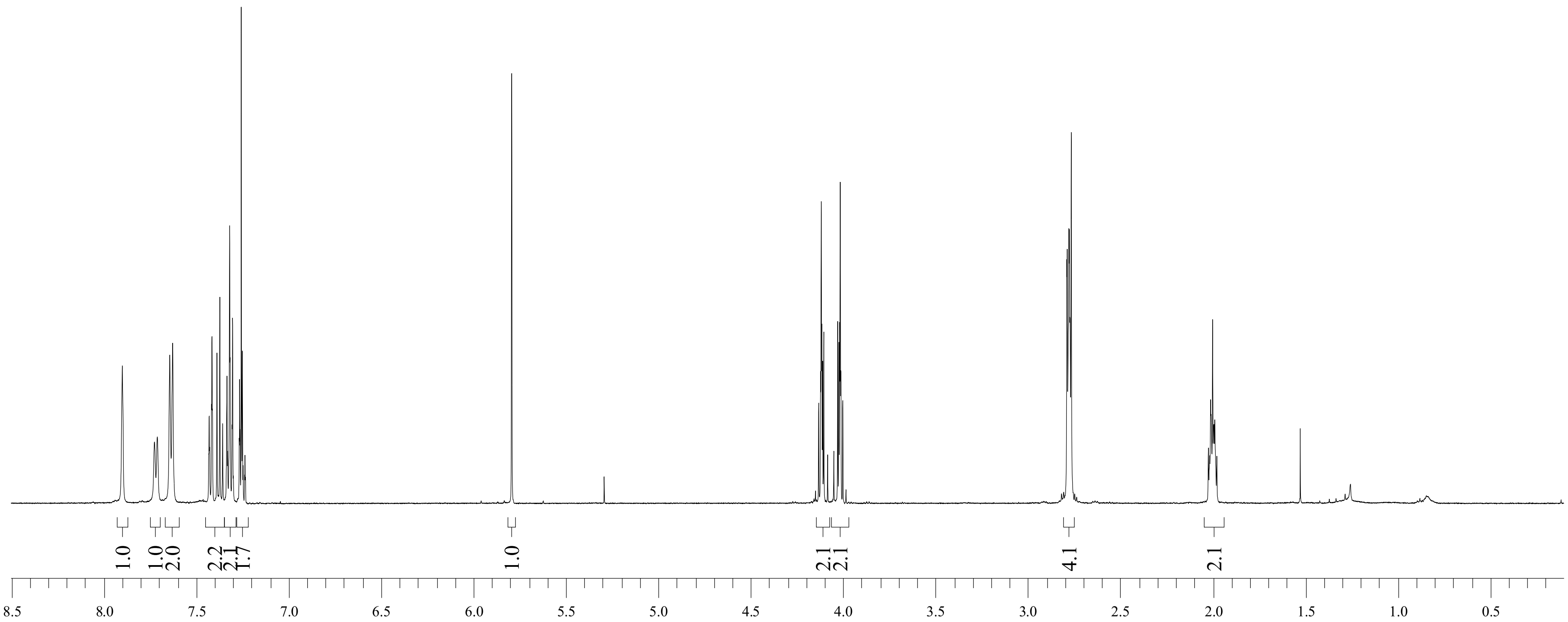
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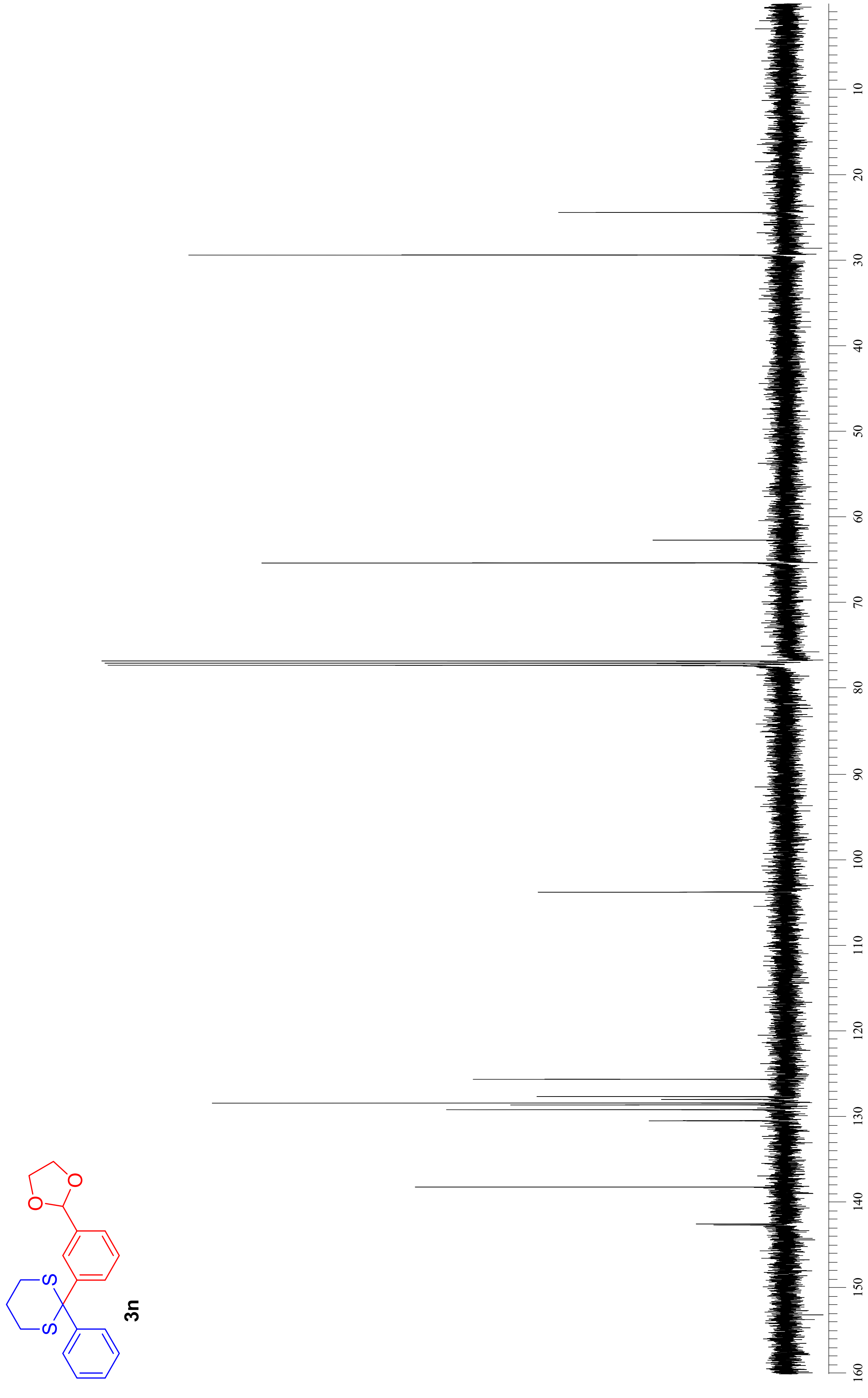
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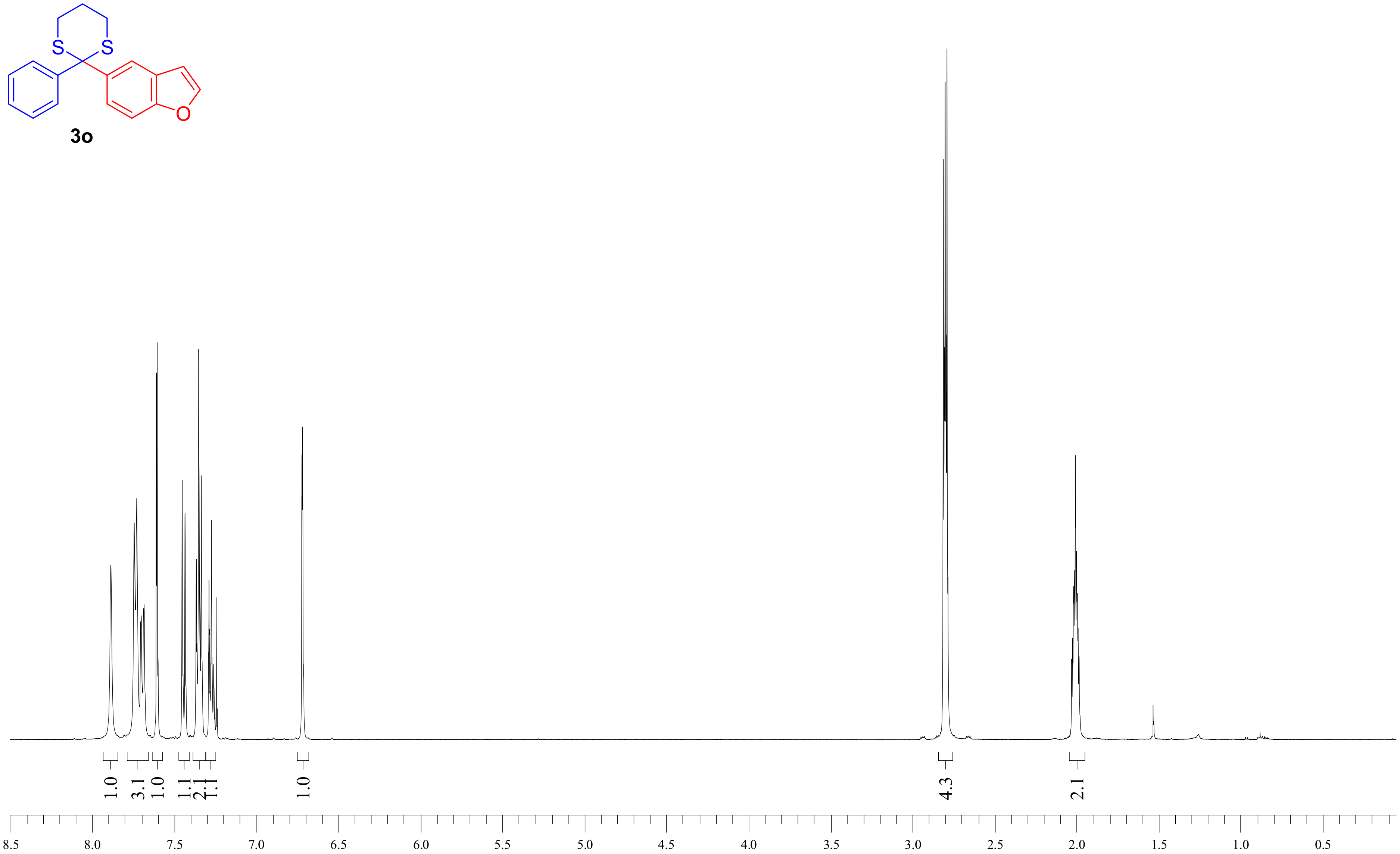
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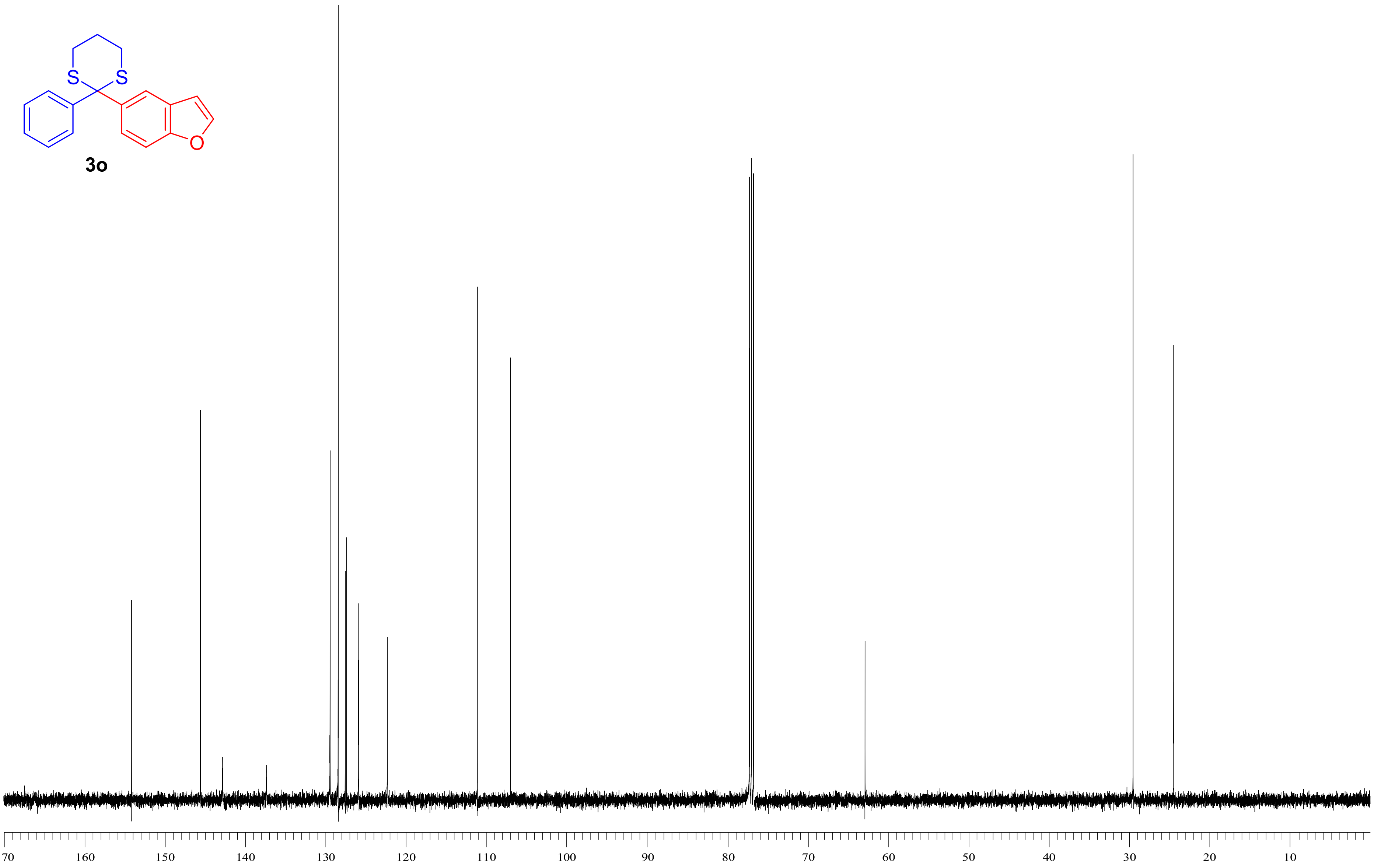
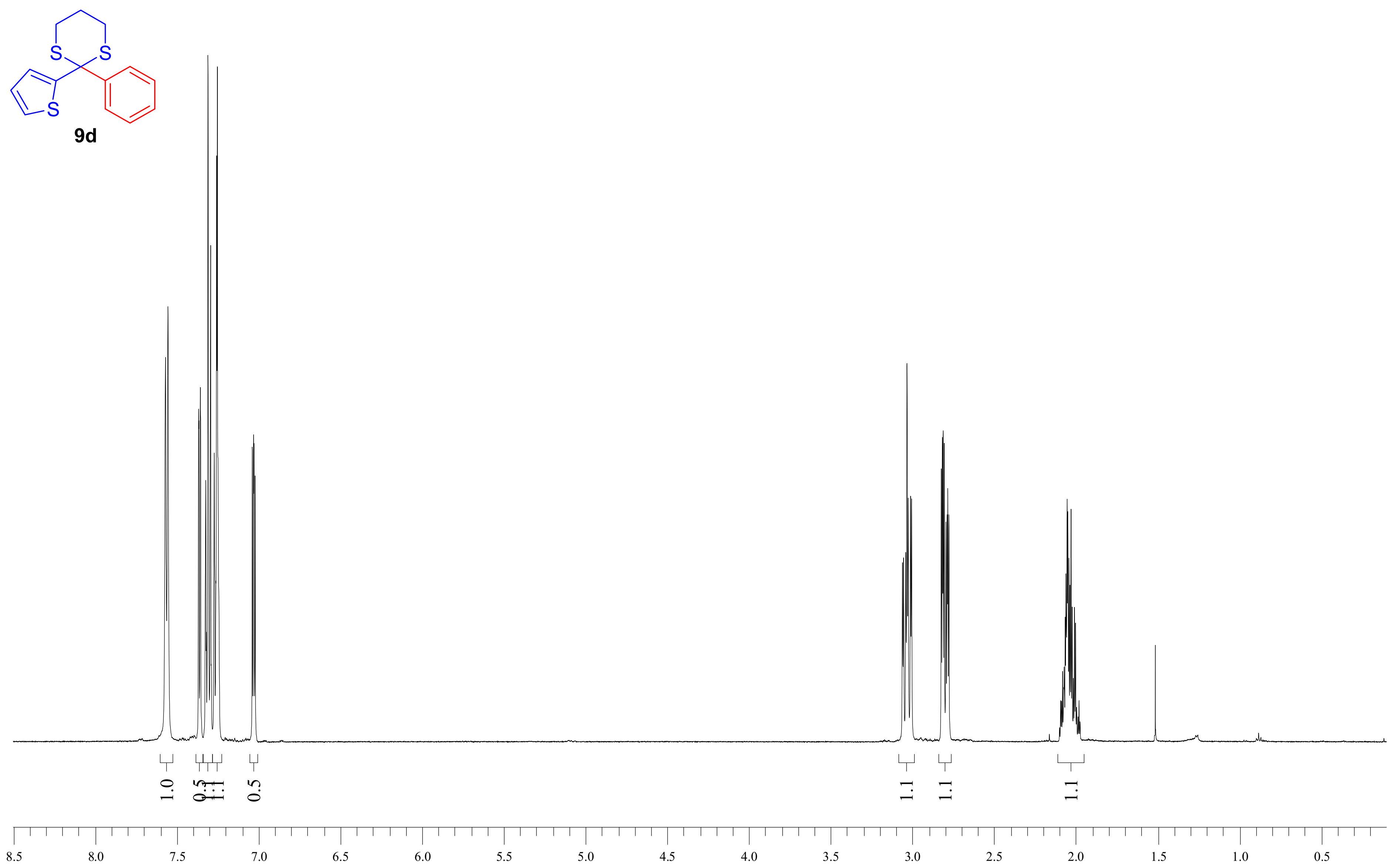
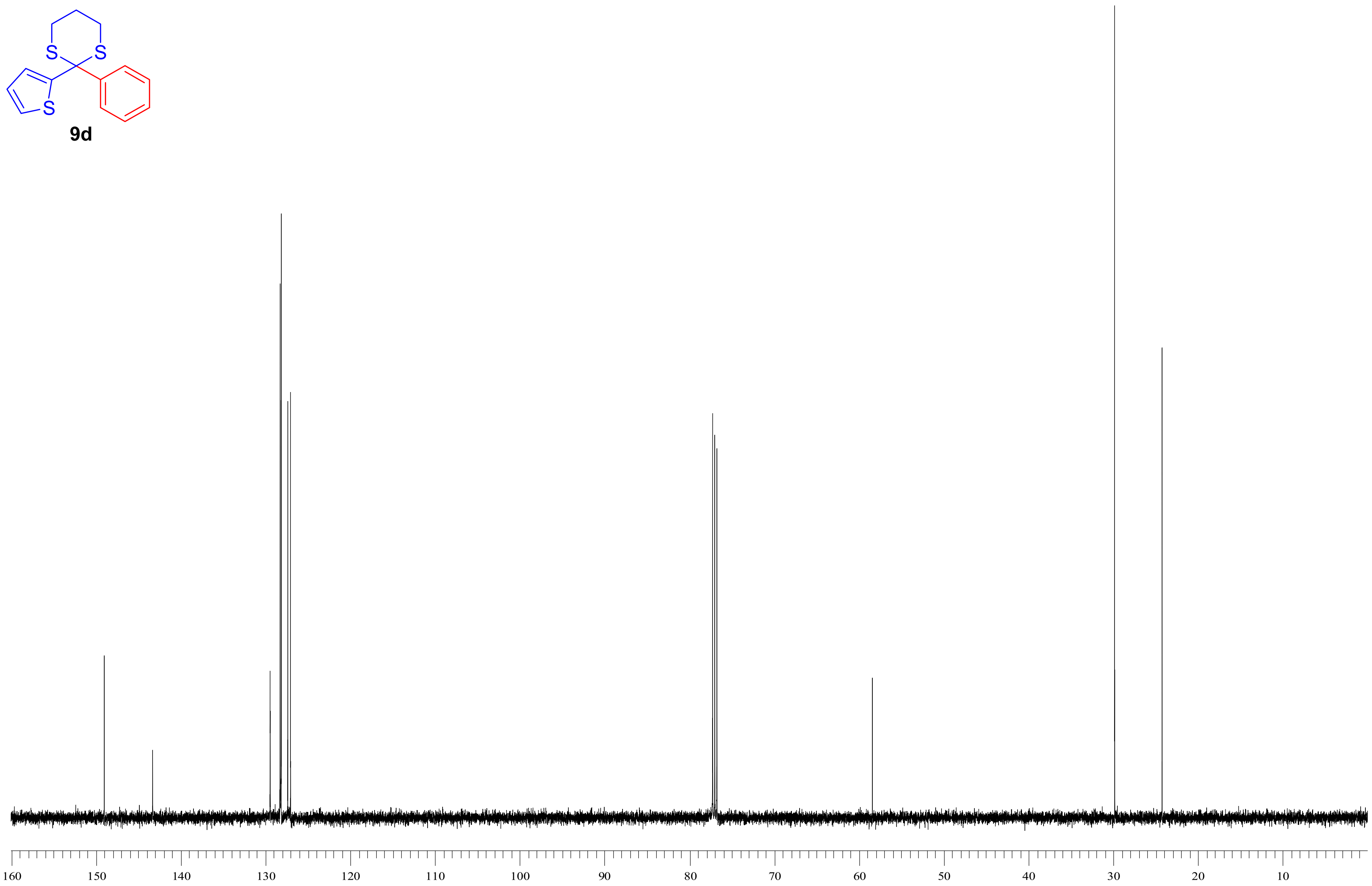
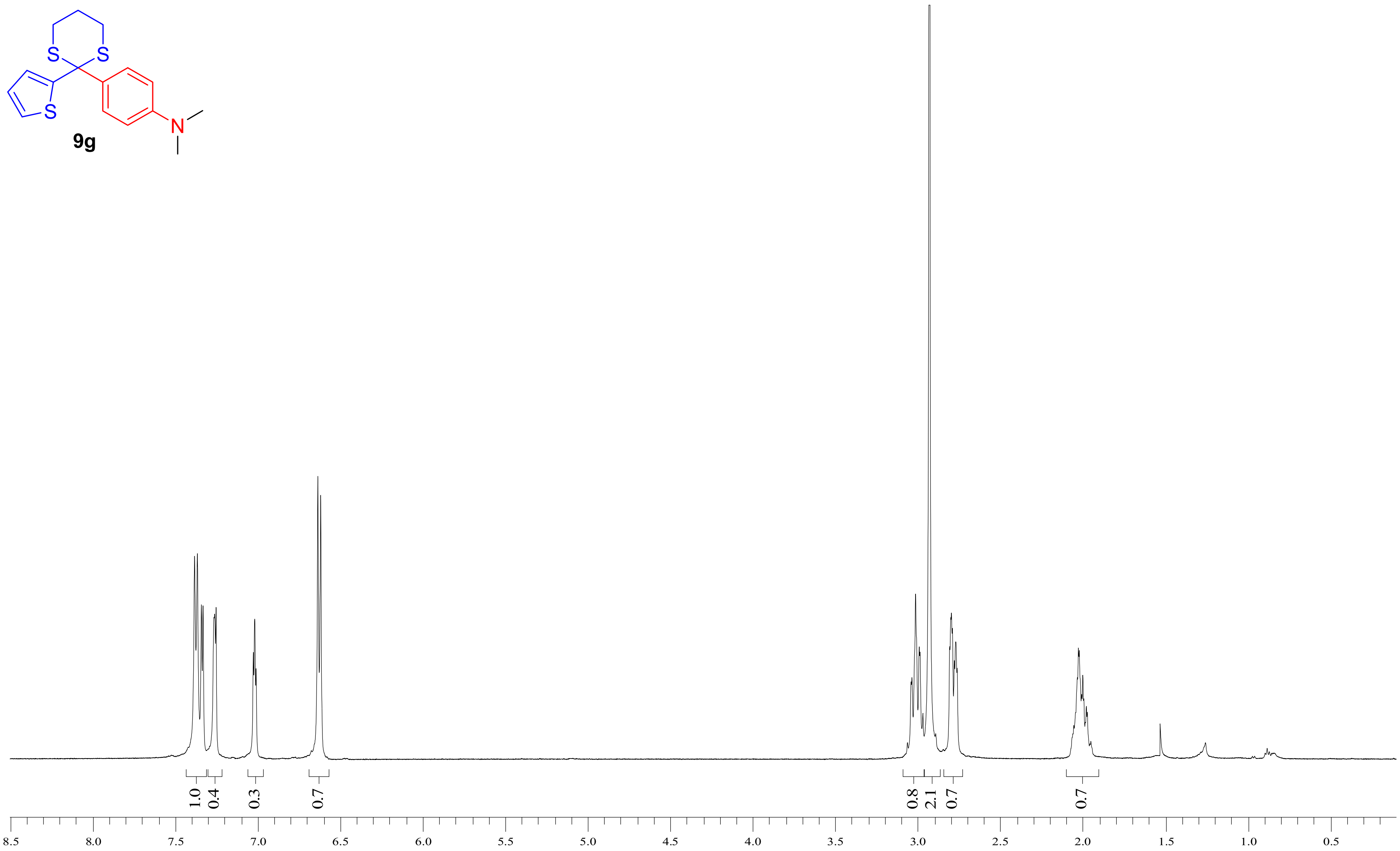


3o


9d
1.0
0.5
1.1
1.1
0.5
1.1
1.1
1.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

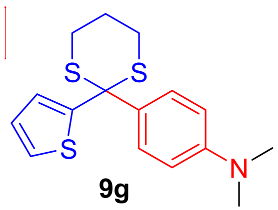


9d

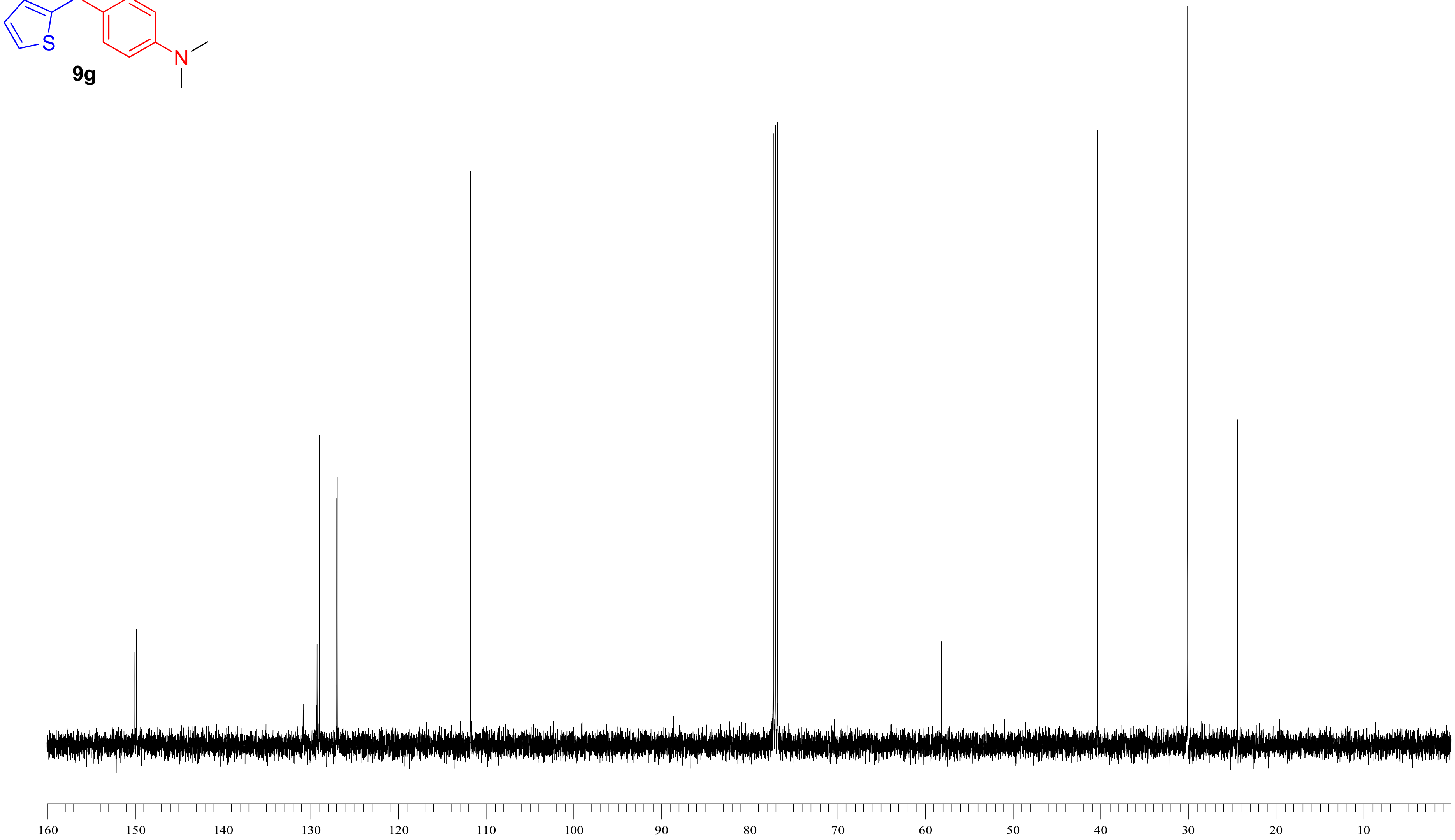


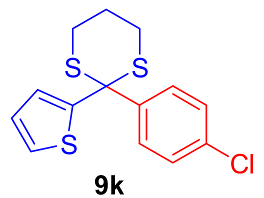
9g

1.0
0.4
0.3
0.7
0.8
2.1
0.7
0.7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

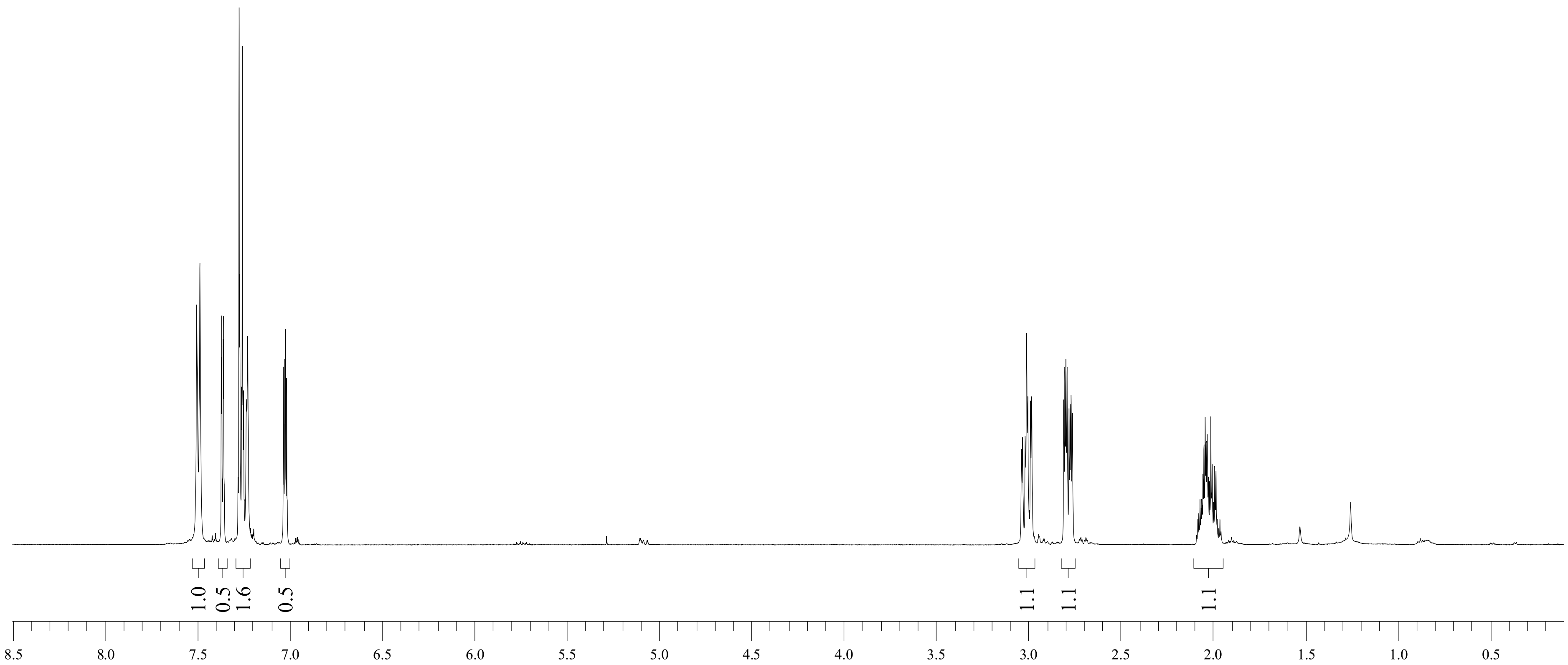


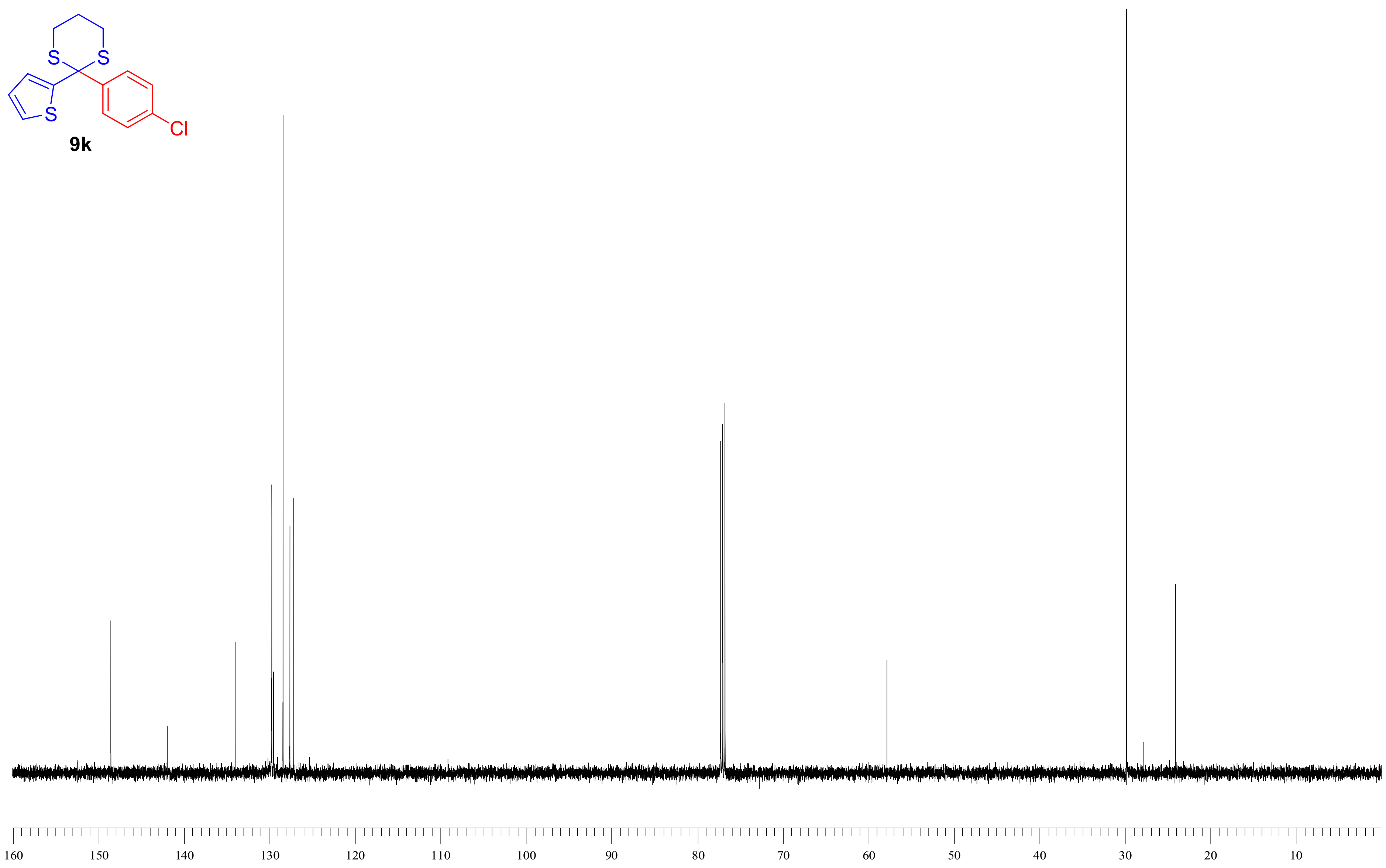
9g



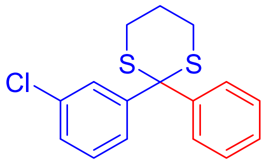


9k

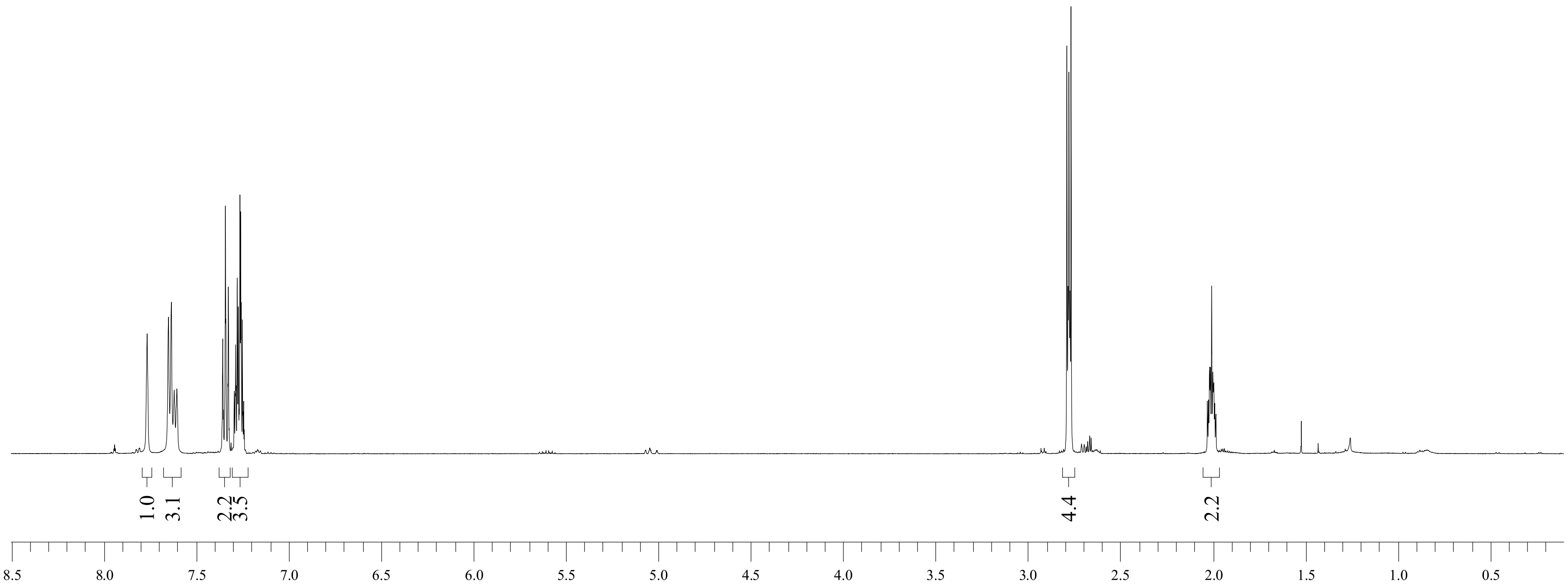


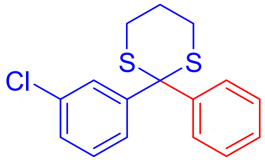


9k

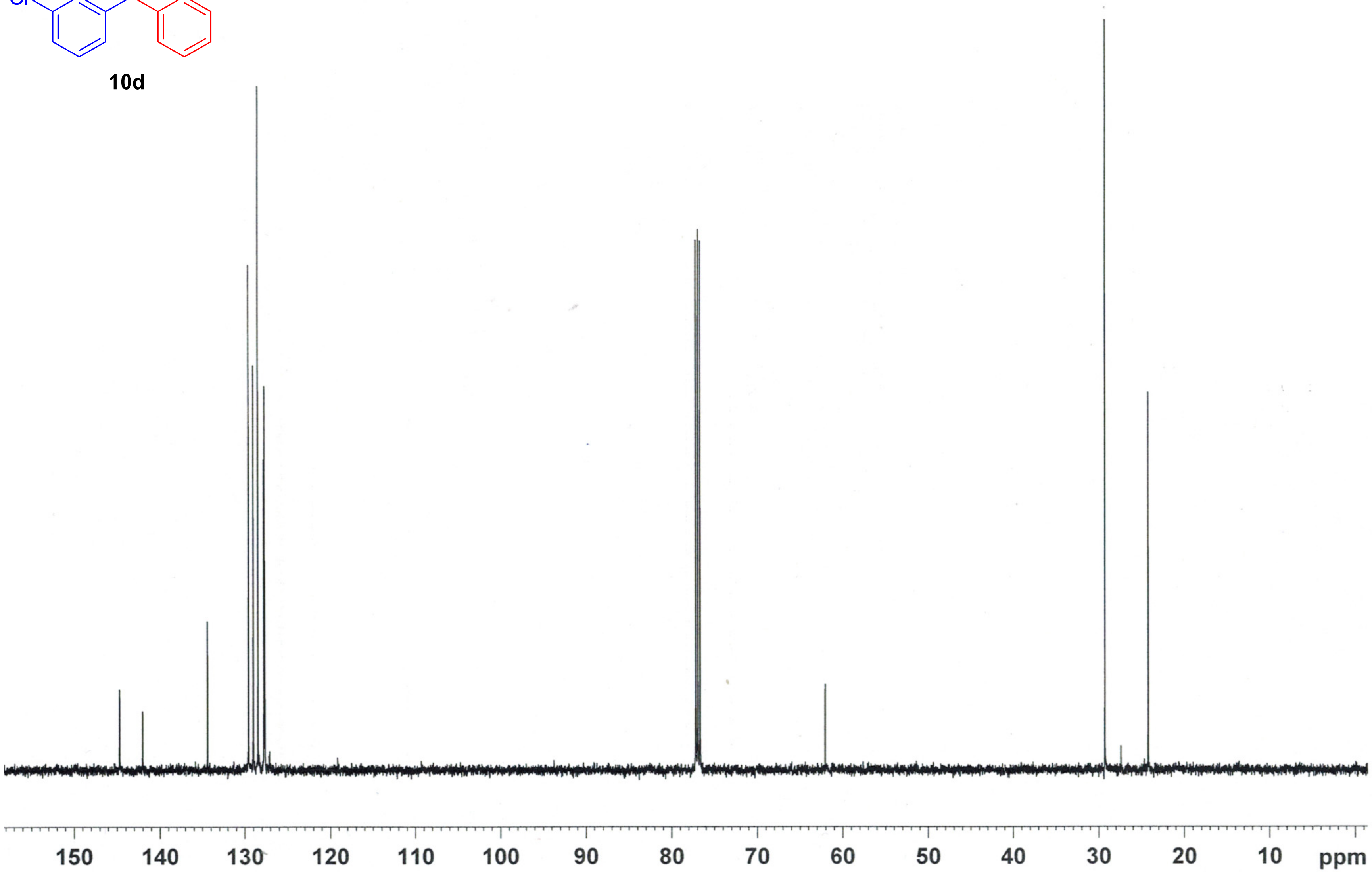


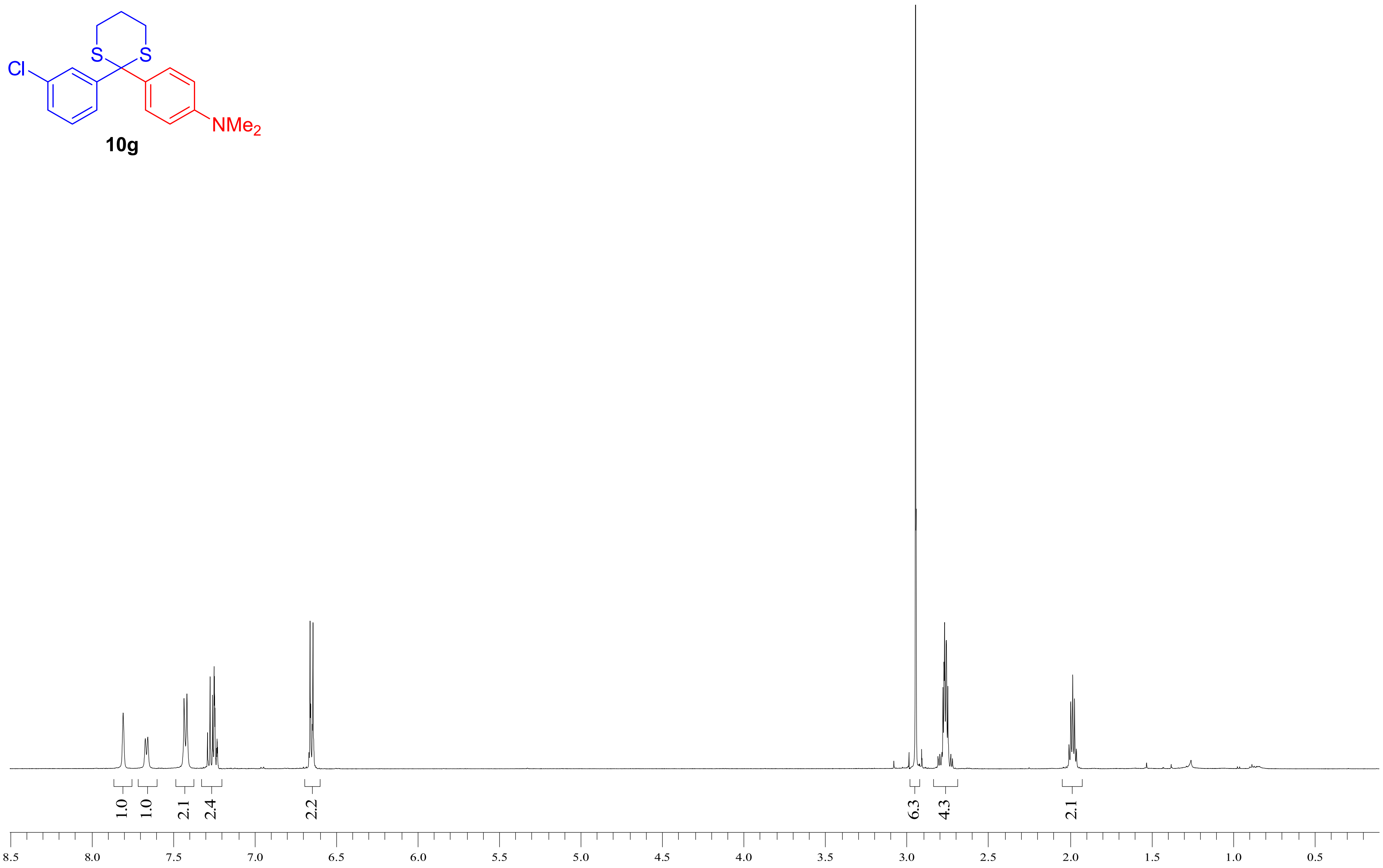
10d





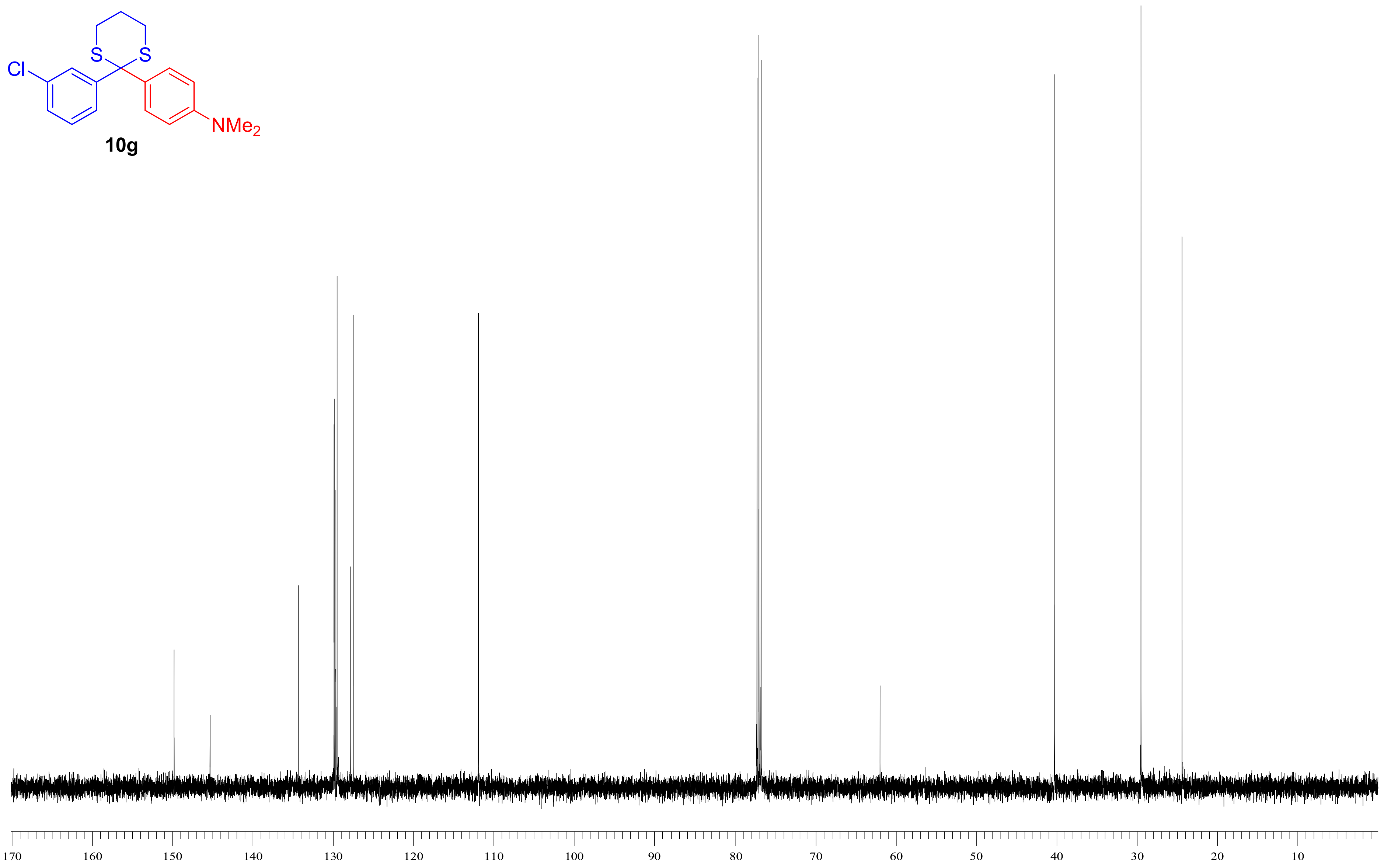
10d





10g

Cl
S
S
NMe$_2$
1.0
1.0
2.1
2.4
2.2
6.3
4.3
2.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


Cl
S
S
NMe$_2$
10g
170
160
150
140
130
120
110
100
90
80
70
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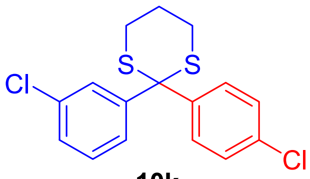
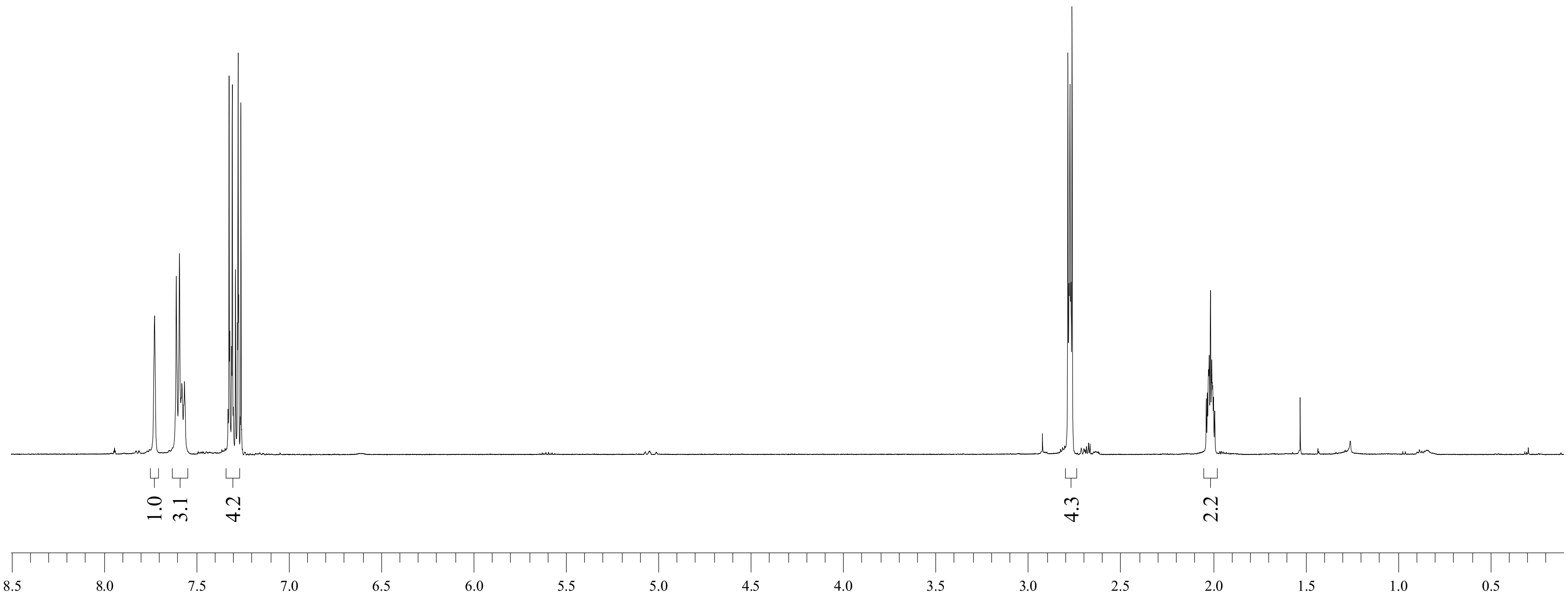
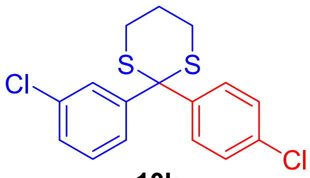
50
40
30
20
10

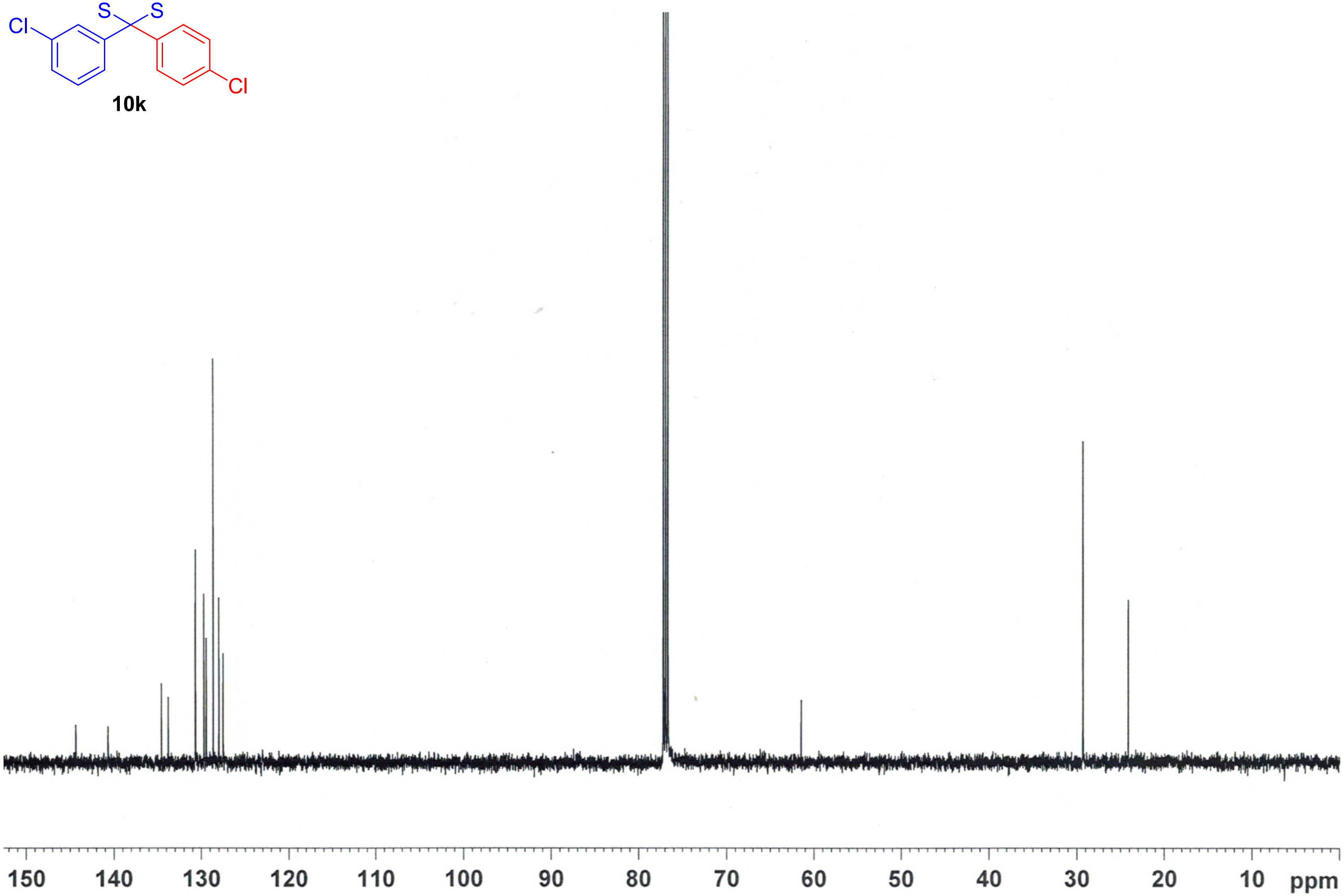

Cl
S
S
Cl

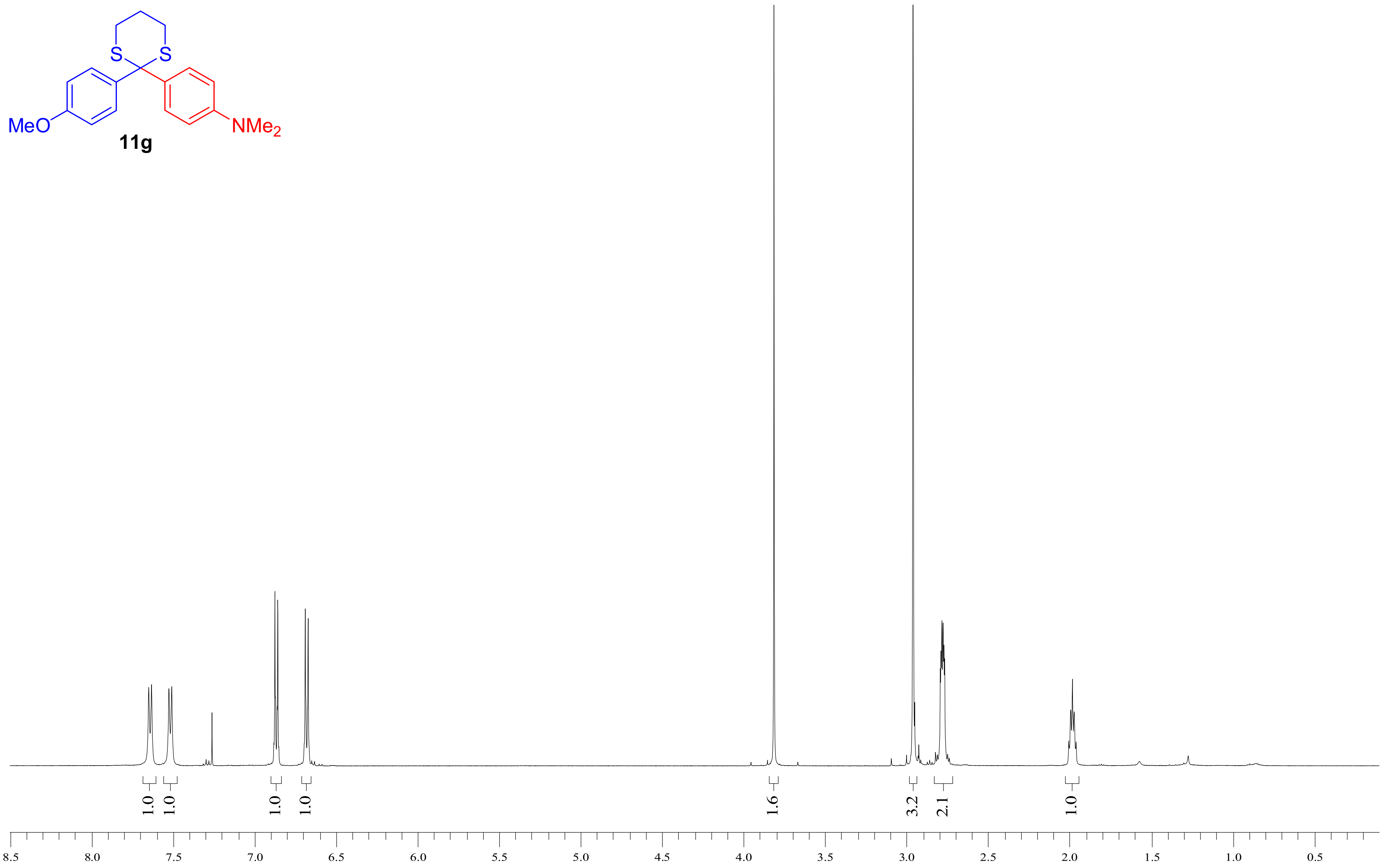
10k


1.0
3.1
4.2
4.3
2.2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



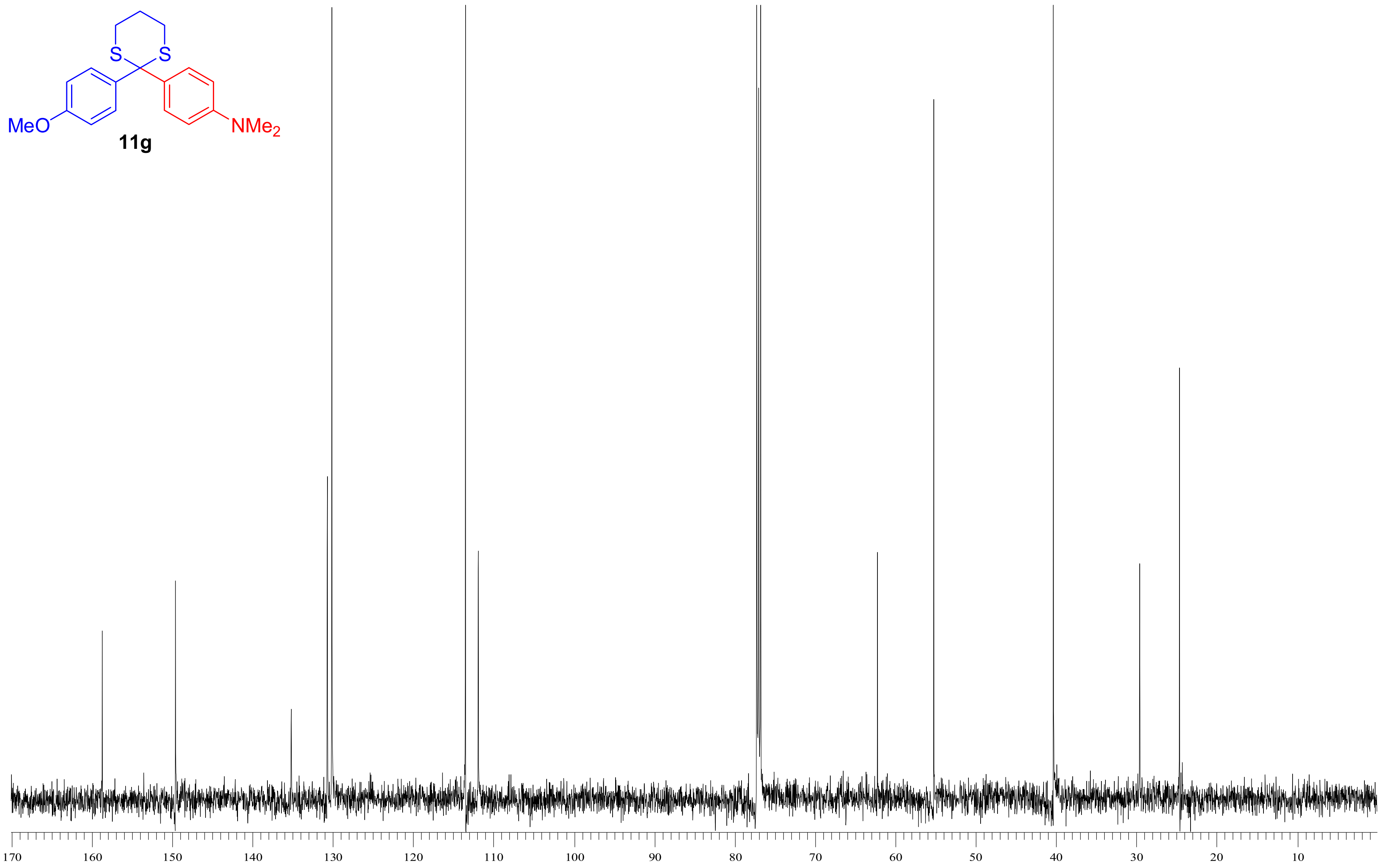
10k





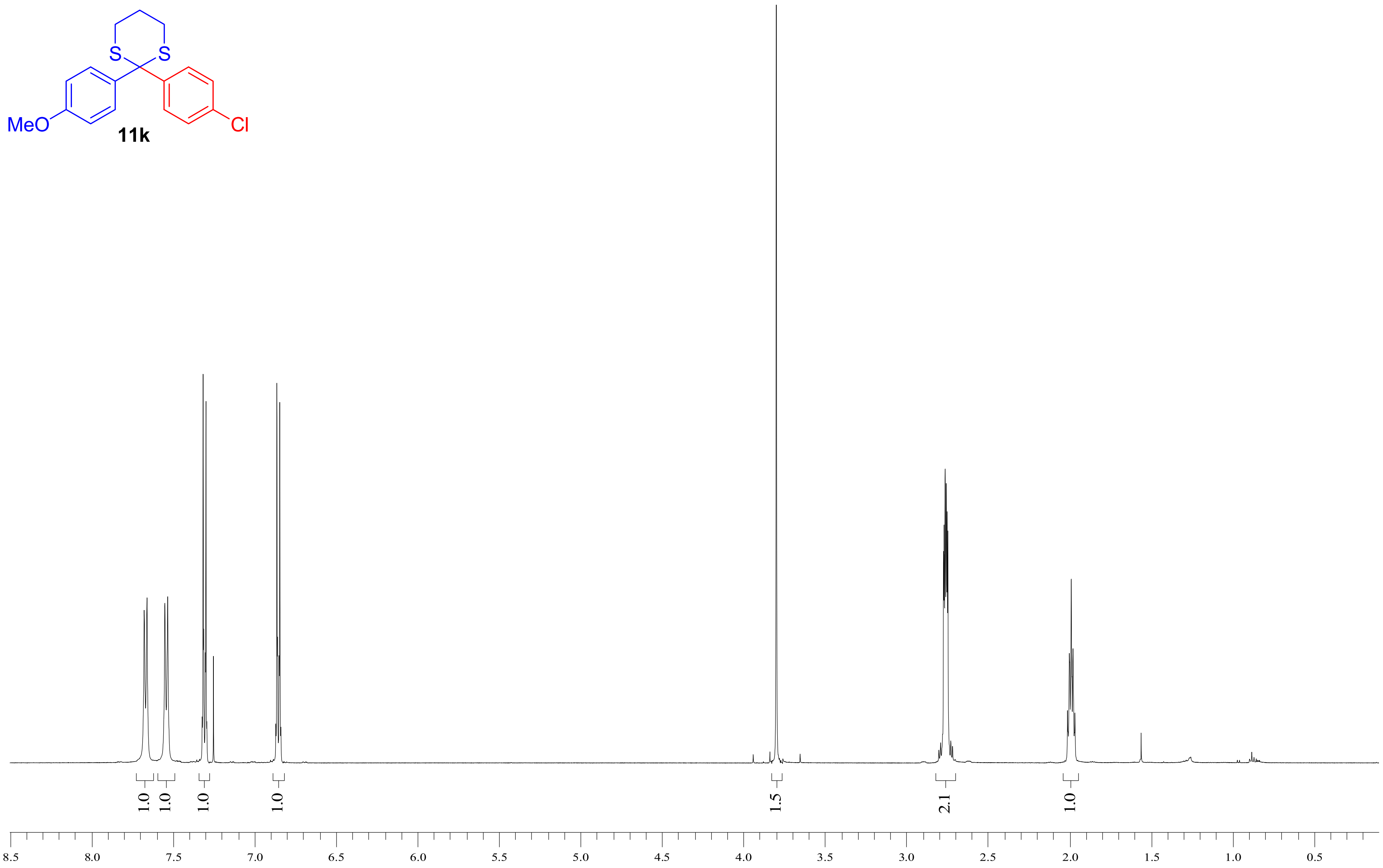
11g

MeO
S
S
NMe$_2$
1.0
1.0
1.0
1.0
1.6
3.2
2.1
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



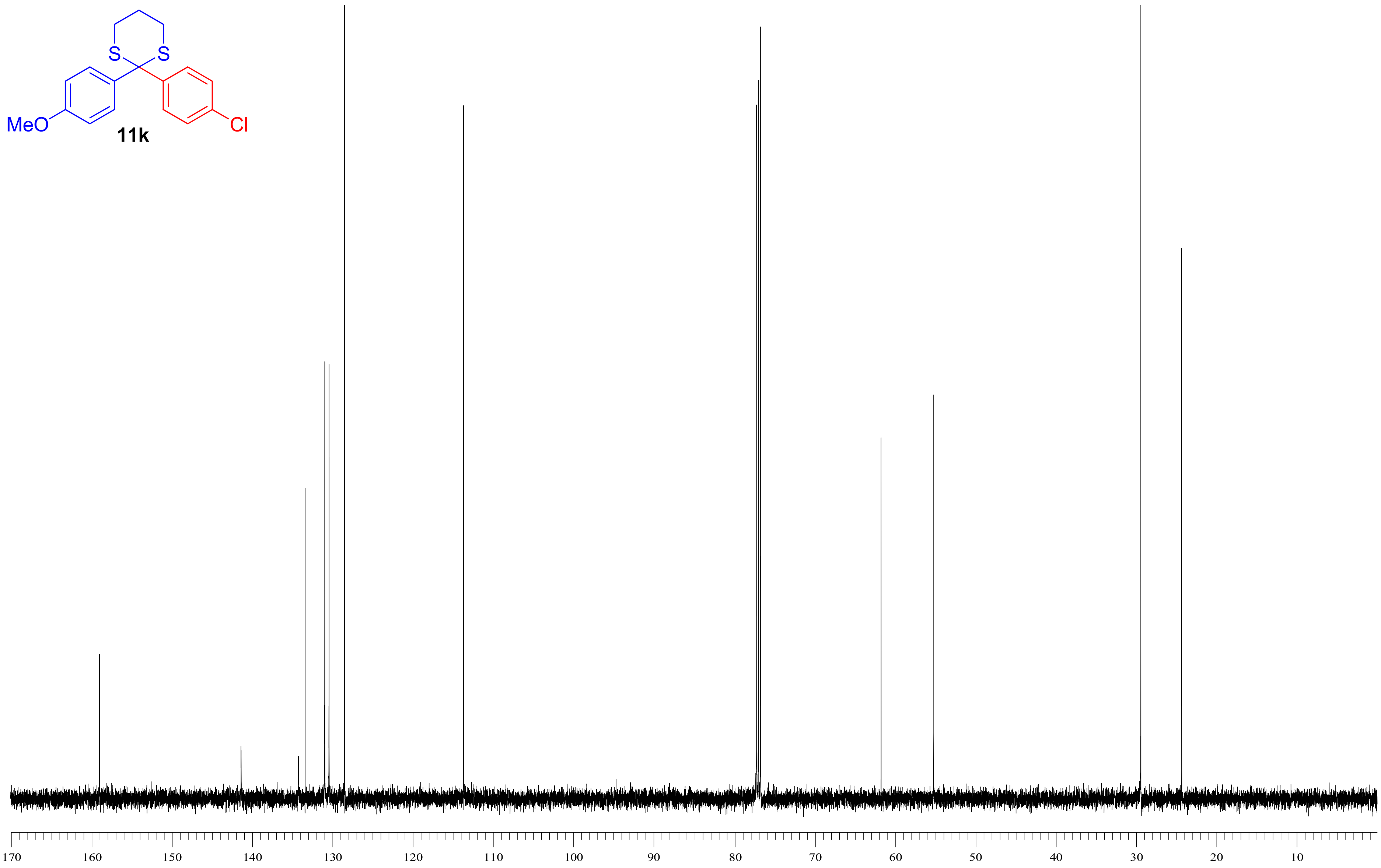
11g

MeO
S
S
NMe$_2$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

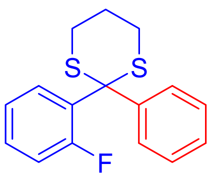


11k

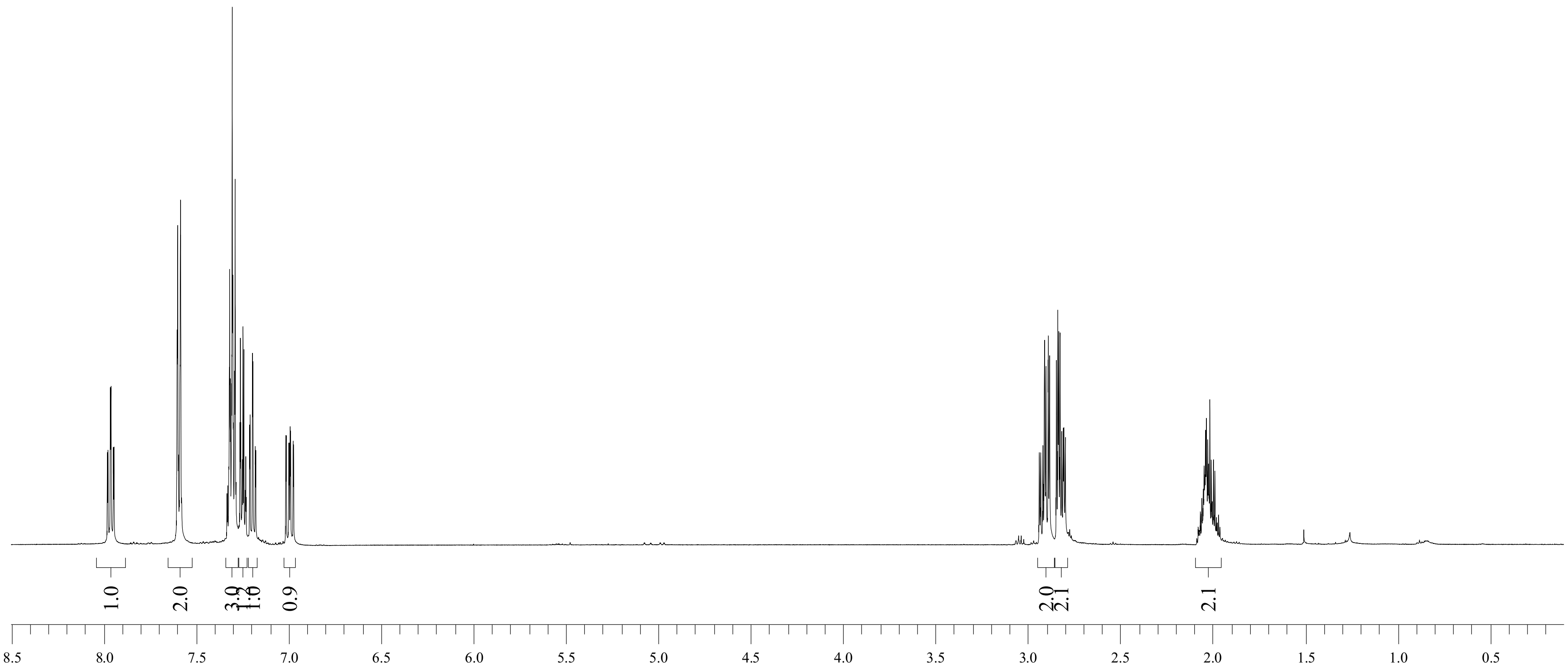
MeO
S
S
Cl
1.0
1.0
1.0
1.0
1.5
2.1
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

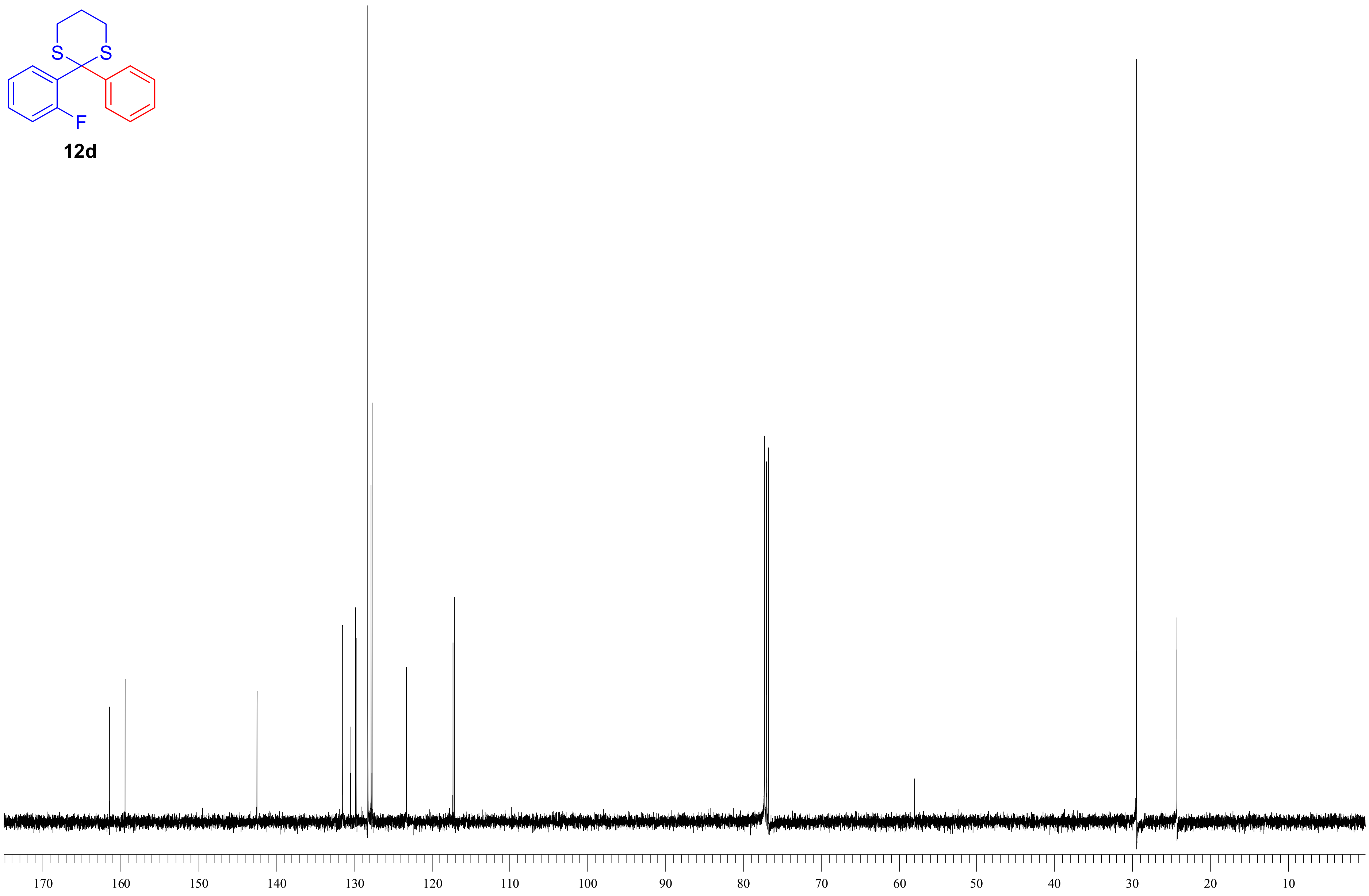


11k

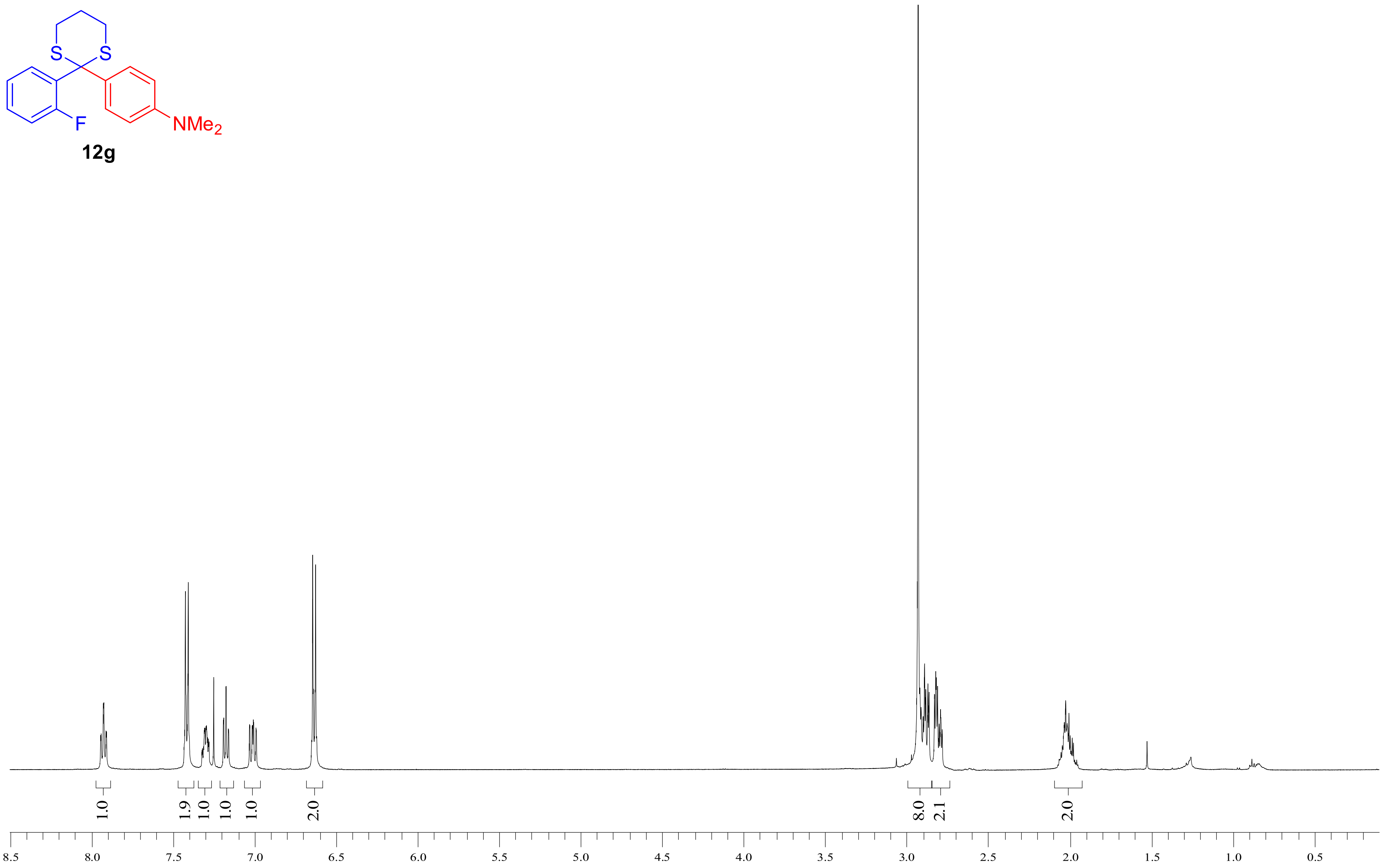


12d


1.0
2.0
3.0
1.2
1.0
0.9
2.0
2.1
2.1
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

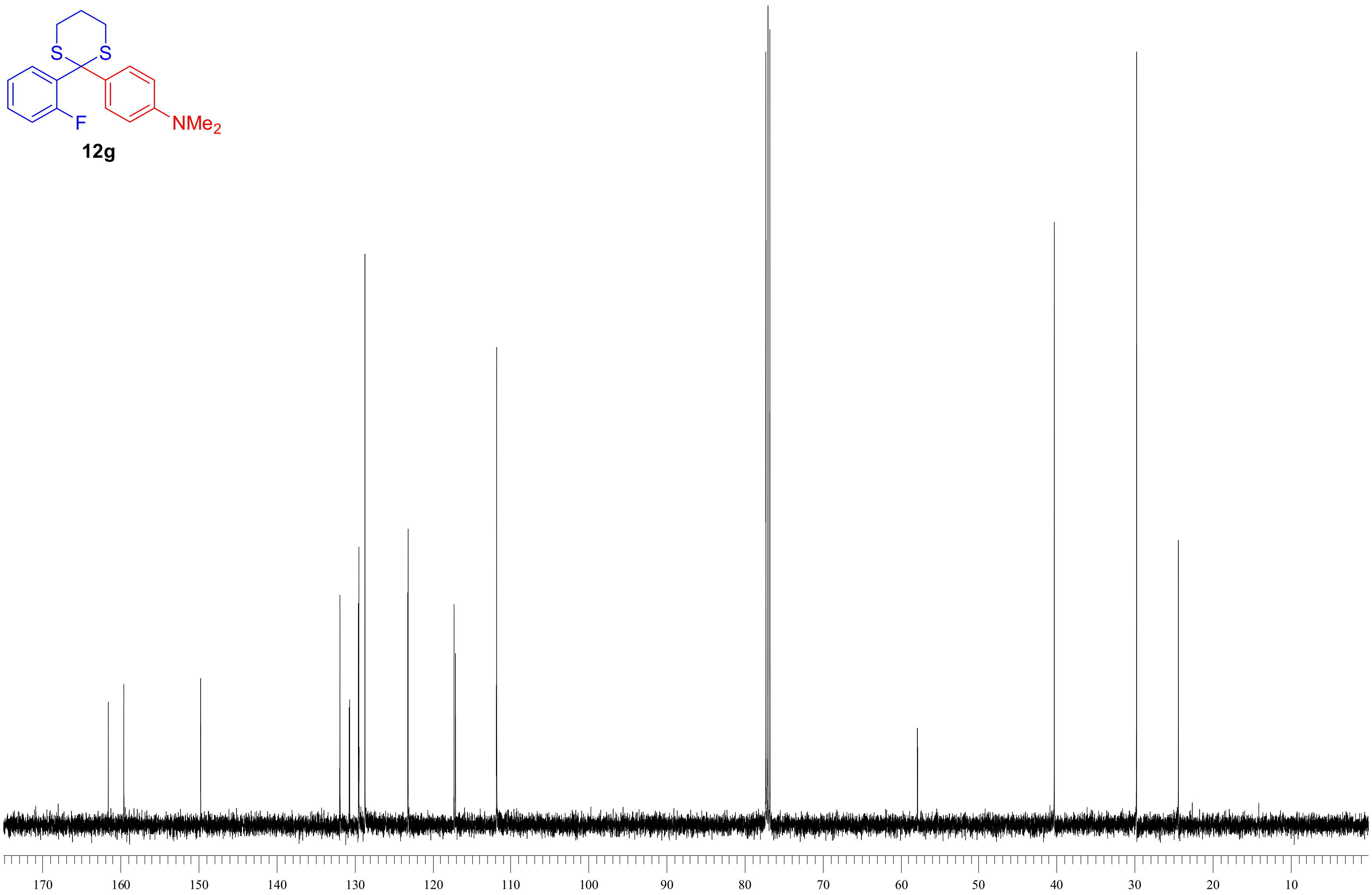


12d

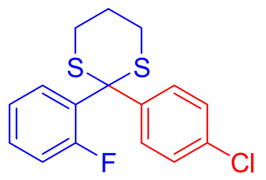


12g

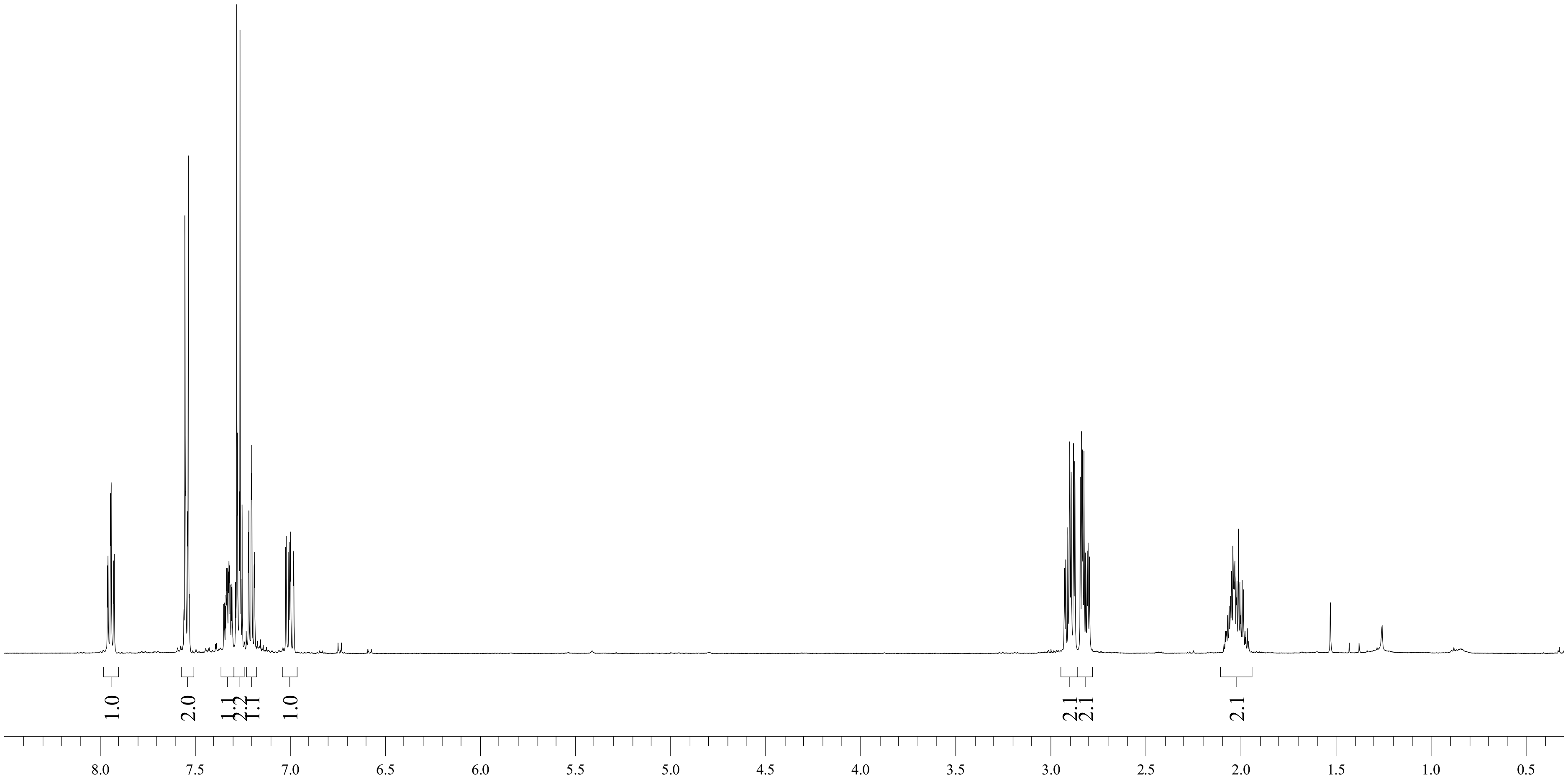
S
S
F
NMe$_2$
1.0
1.9
1.0
1.0
1.0
2.0
8.0
2.1
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



12g


S
S
F
Cl

12k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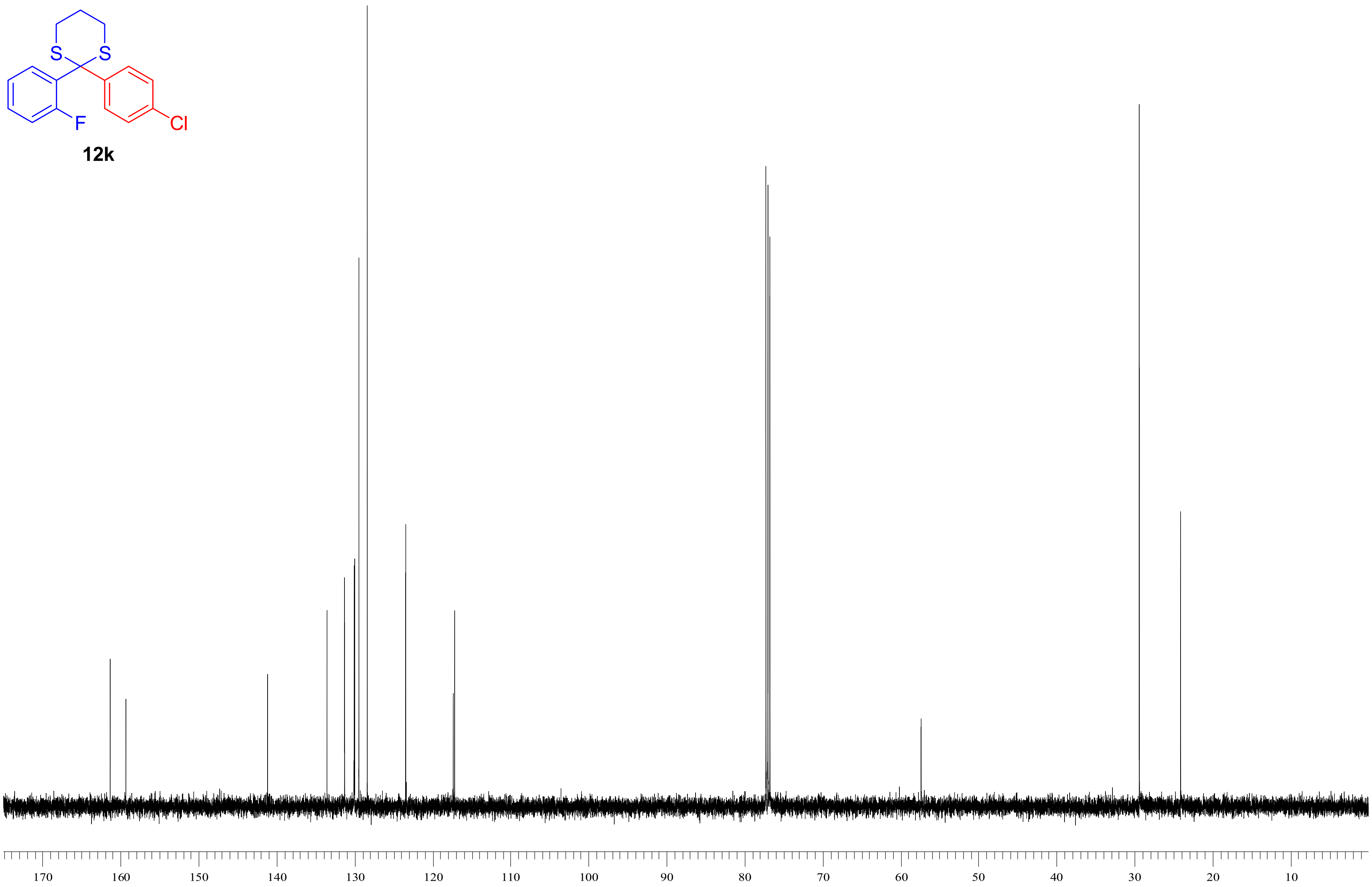
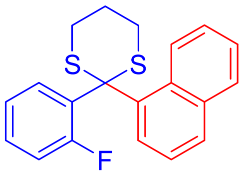
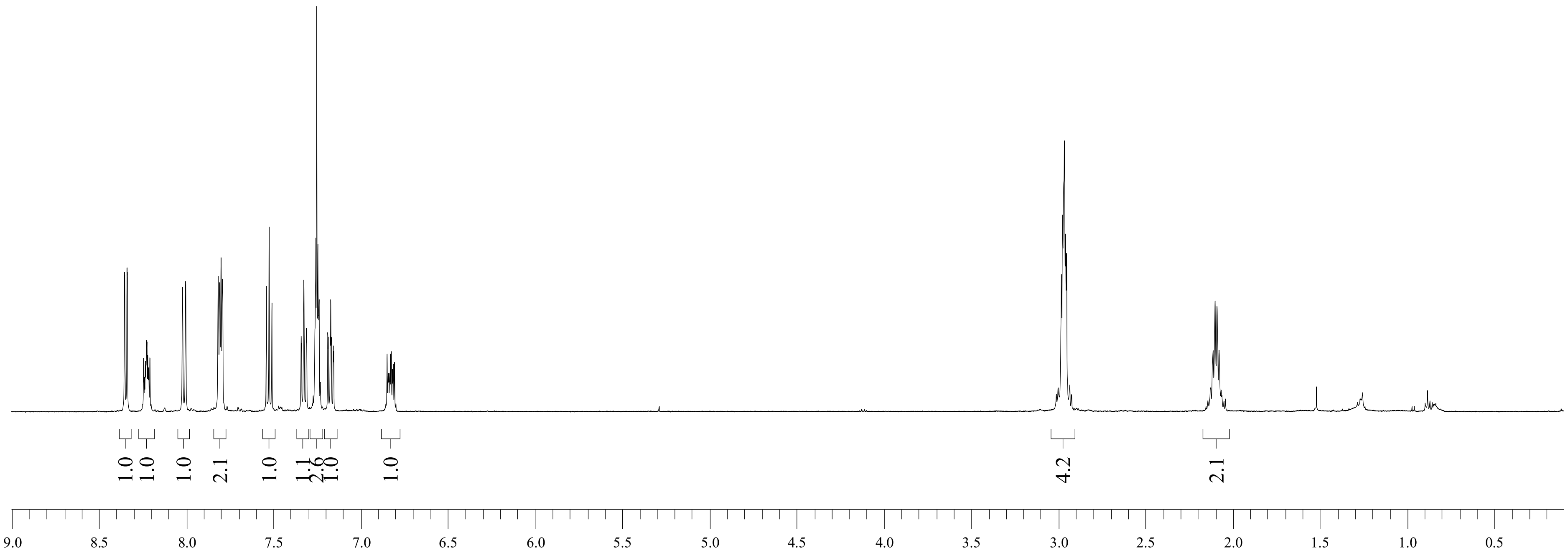
1.1
2.2
1.1
1.0
2.1
2.1
2.1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



12k


S
S
F

12f


1.0
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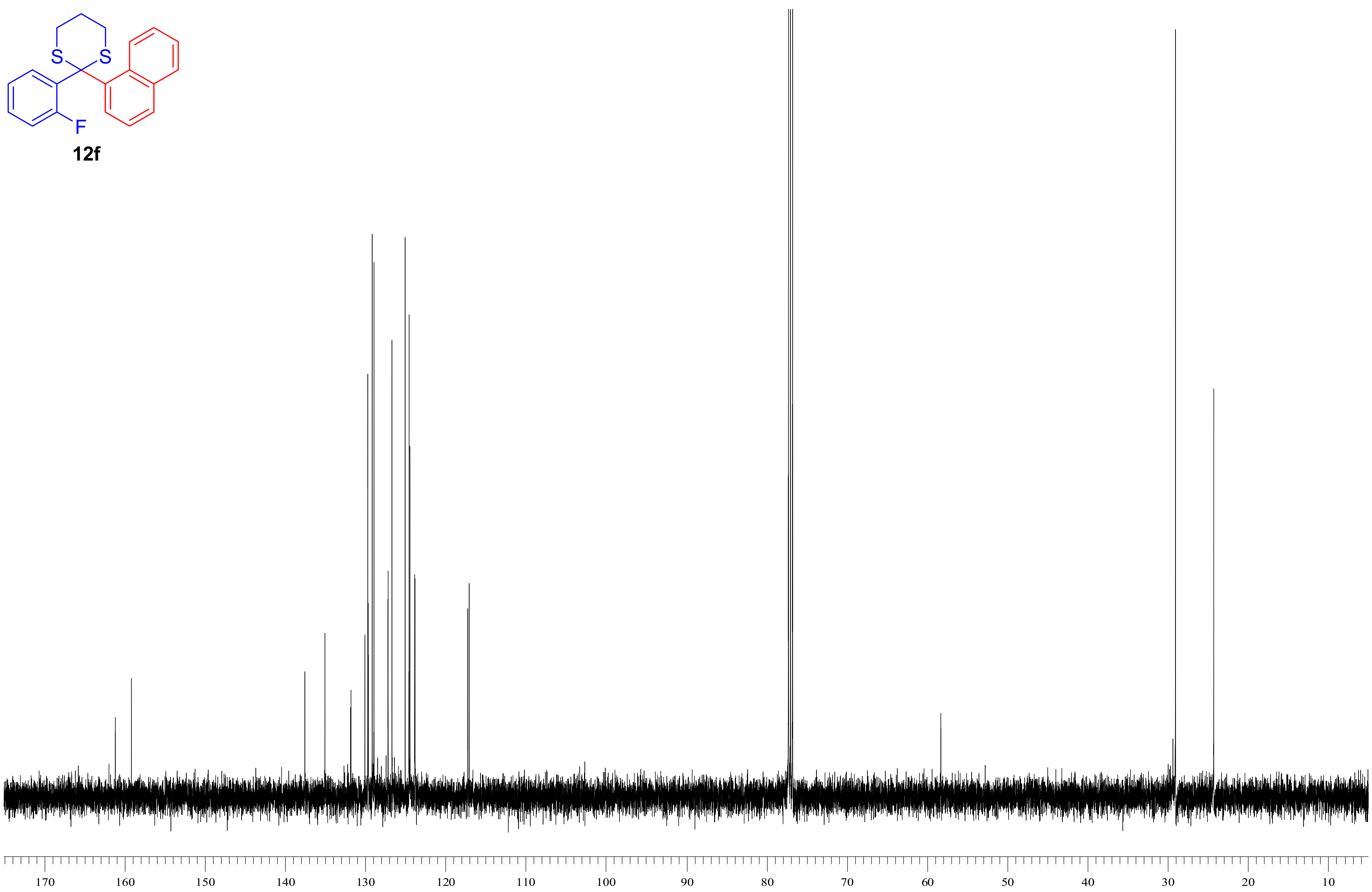
1.0
2.1
1.0
1.1
2.6
1.0
1.0
4.2
2.1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


12f
S
S
F
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160
150
140
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120
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100
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80
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40
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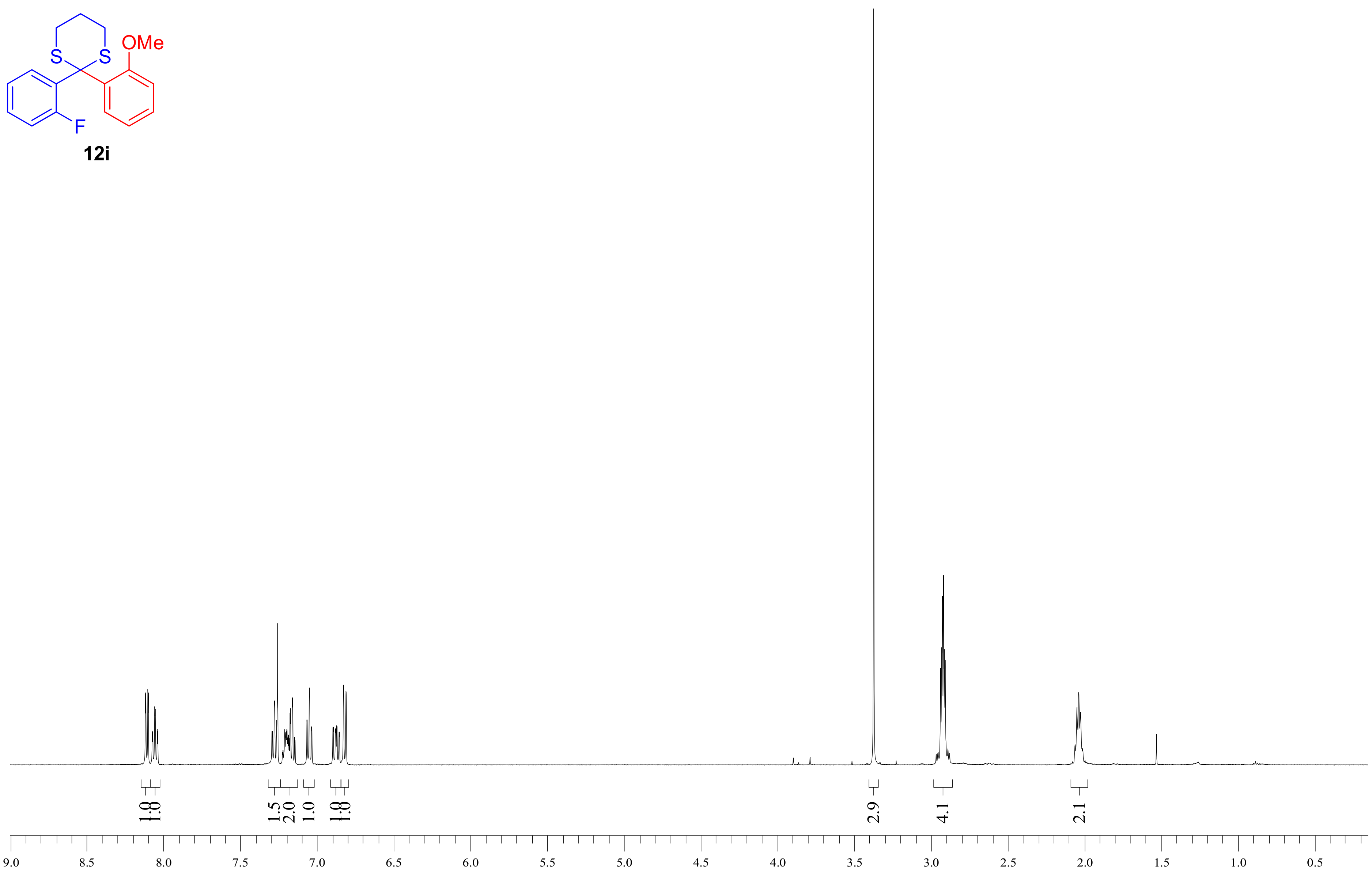
20
10



12i

S
S
OMe
F
1.0
1.0
1.5
2.0
1.0
1.0
1.0
2.9
4.1
2.1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
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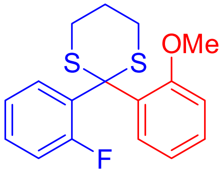
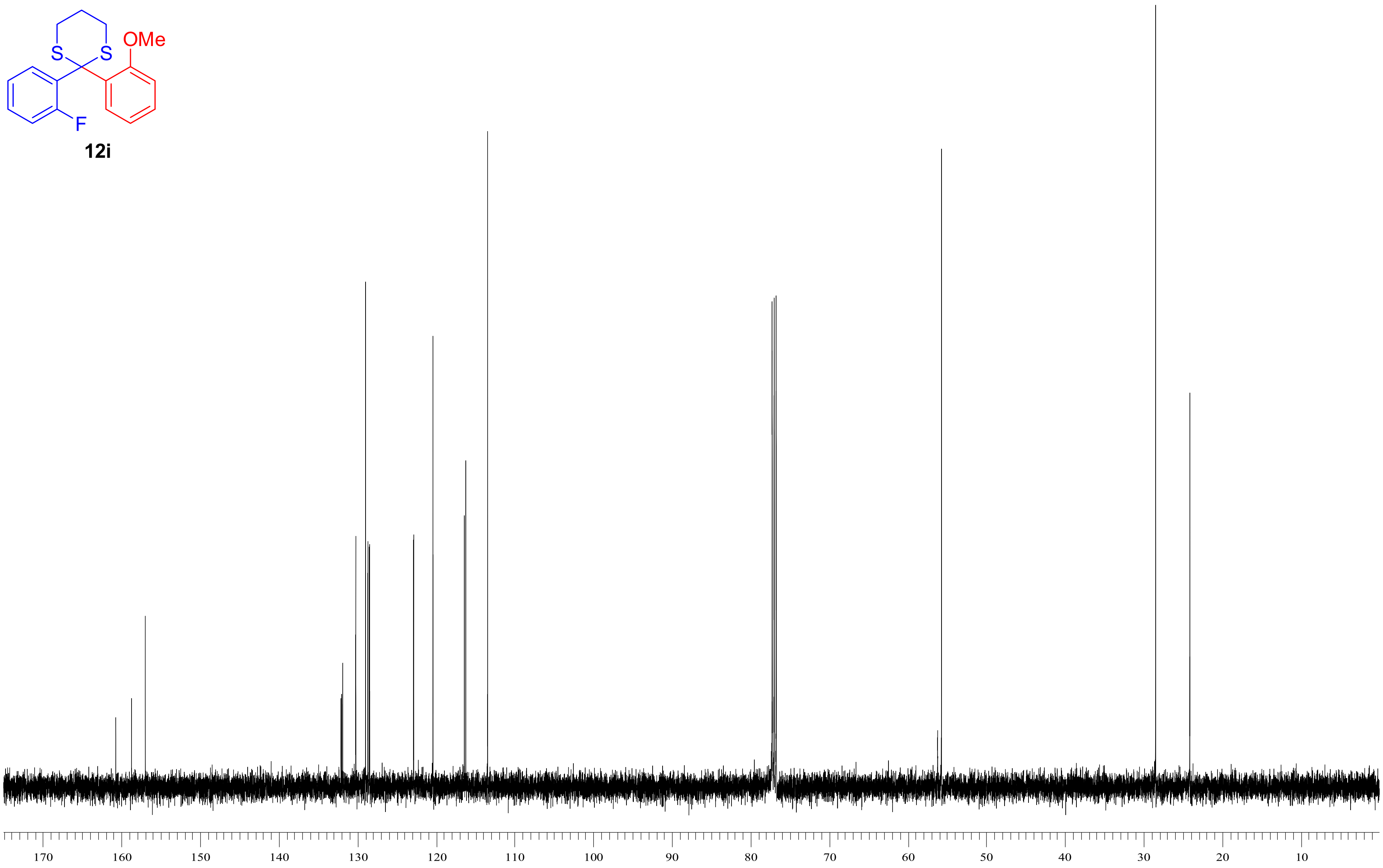
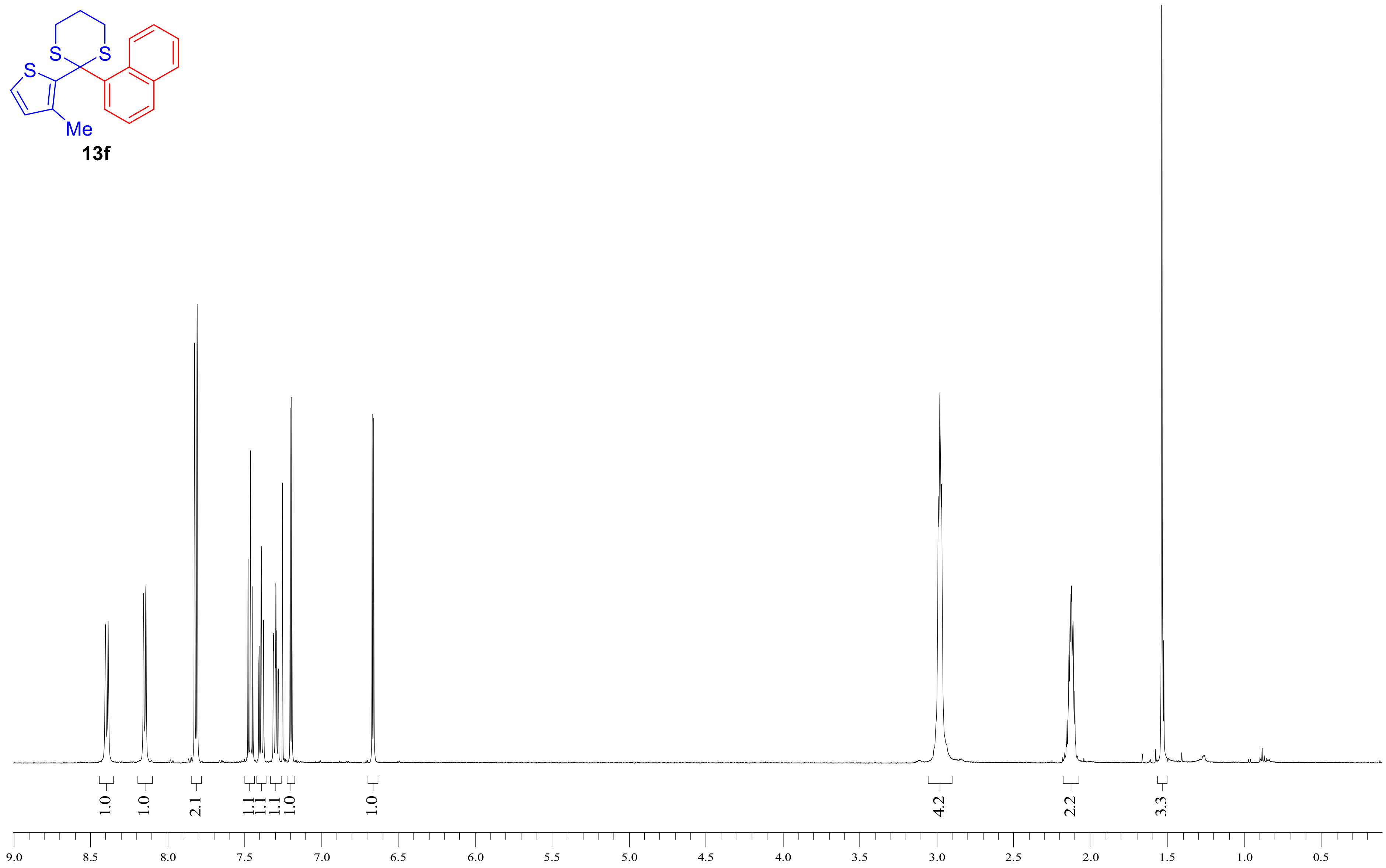
1.0
0.5



12i




S
S
S
Me
13f
1.0
1.0
2.1
1.1
1.1
1.1
1.0
1.0
4.2
2.2
3.3
9.0
8.5
8.0
7.5
7.0
6.5
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5.5
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4.5
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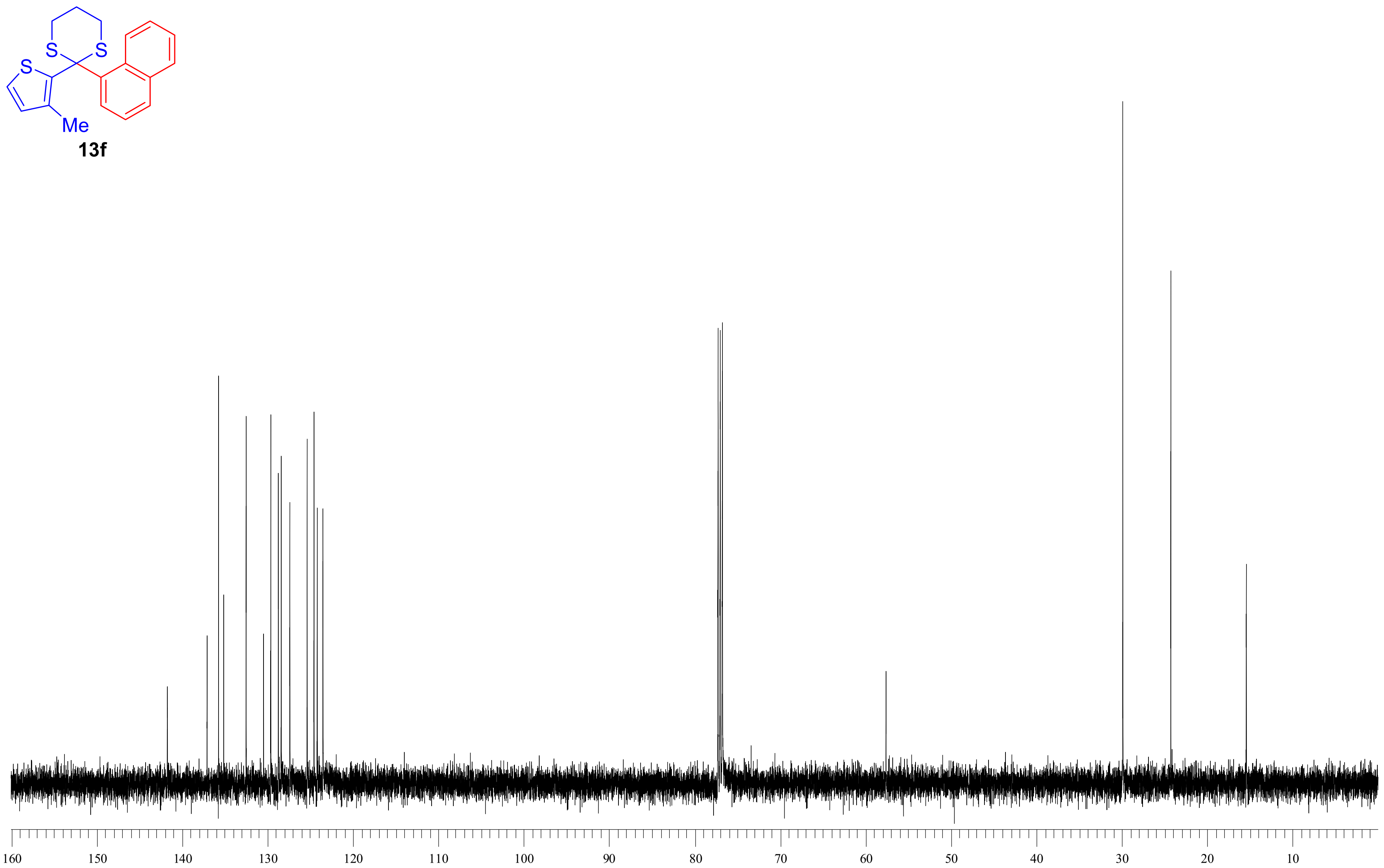
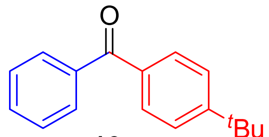
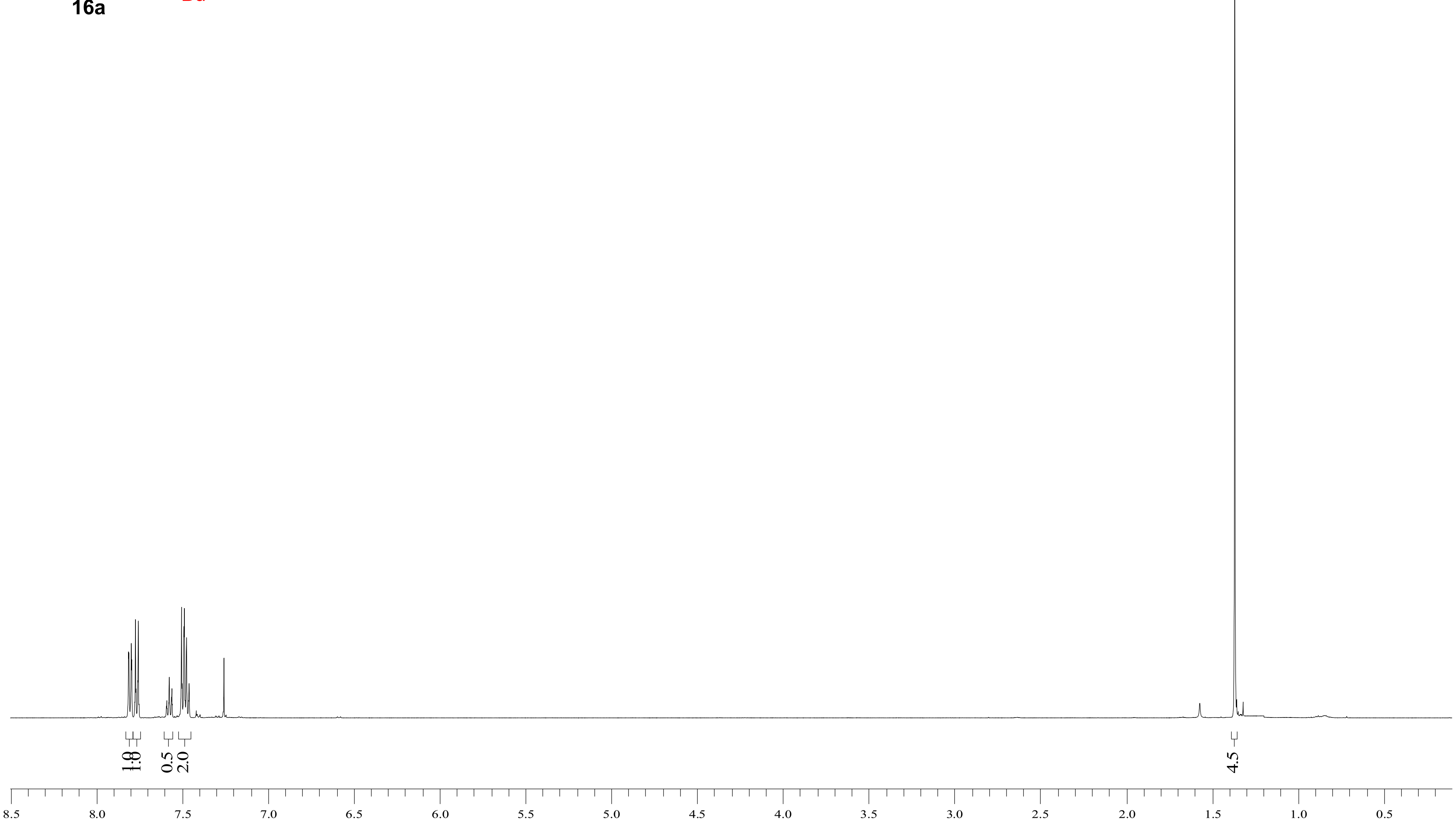
0.5

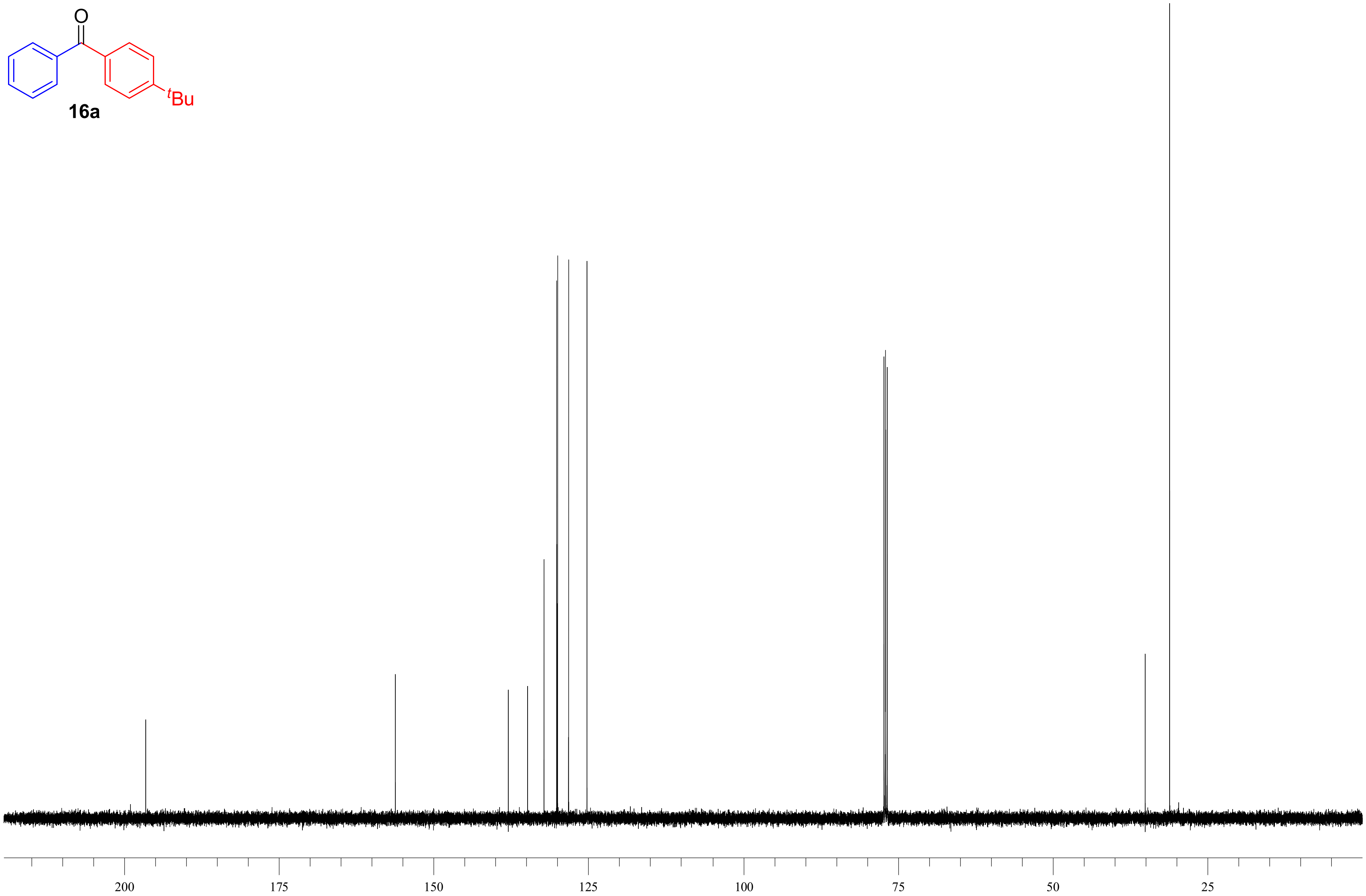


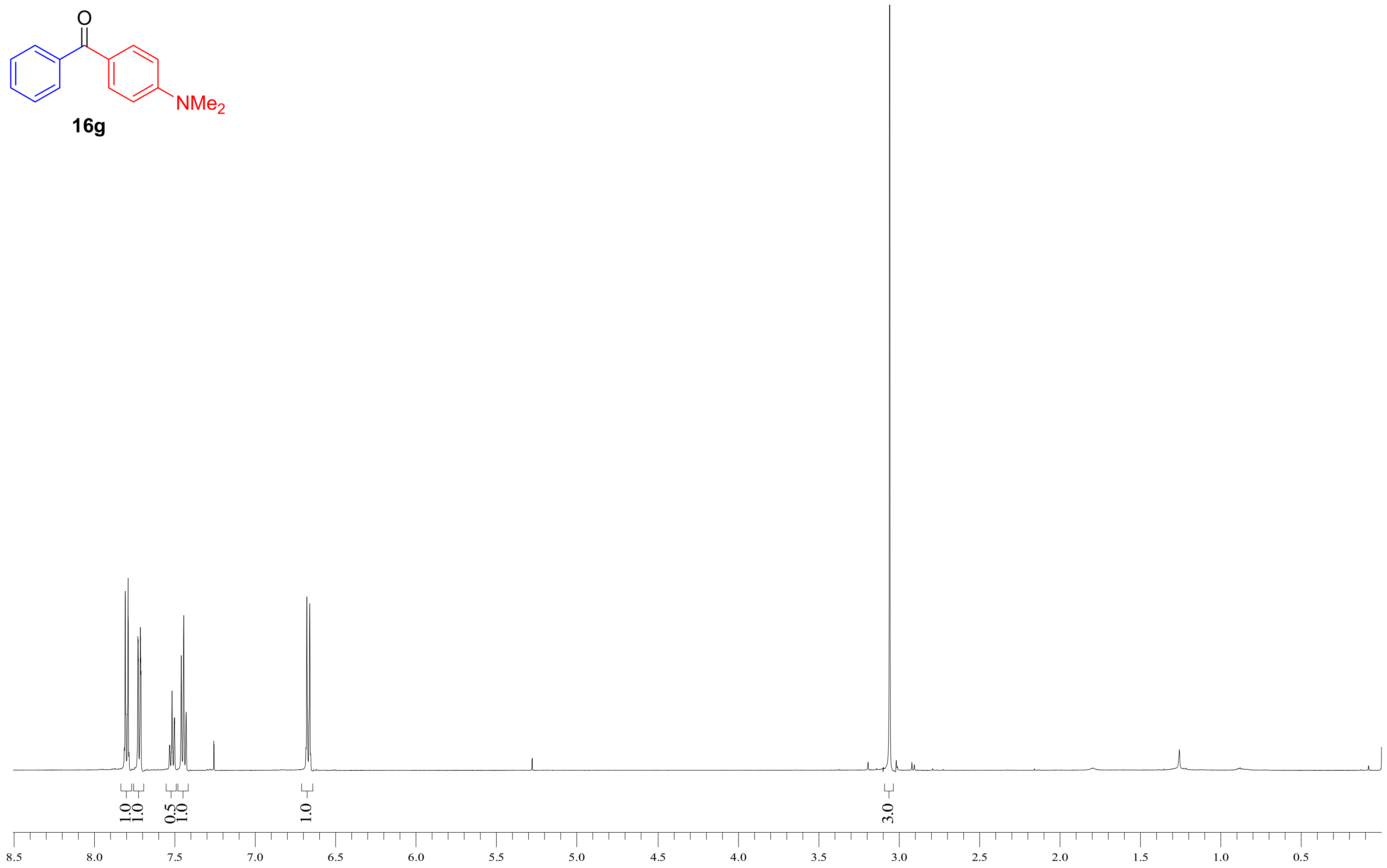
13f



16a




O
tBu
16a
200
175
150
125
100
75
50
25


NMe2
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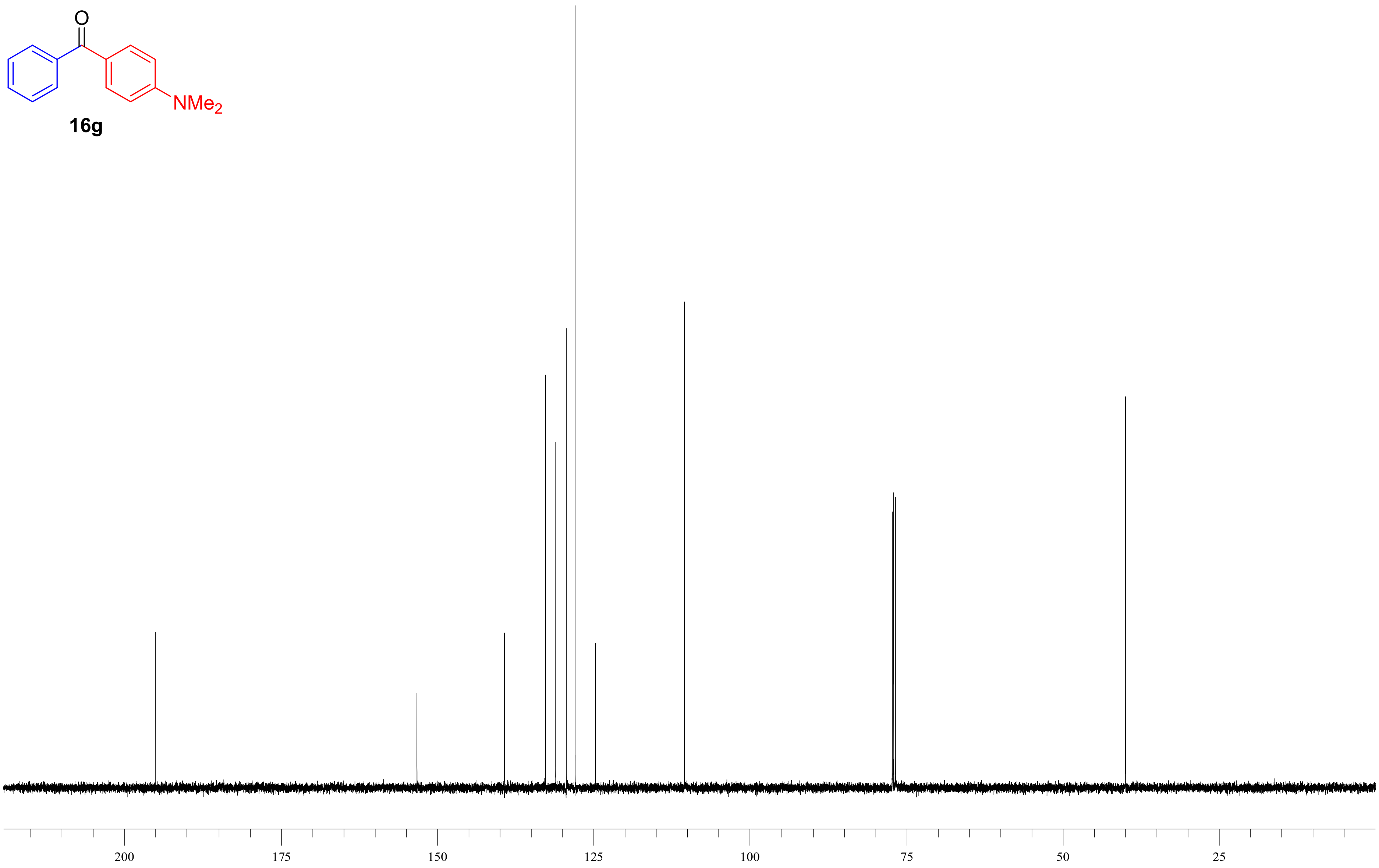
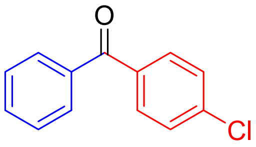
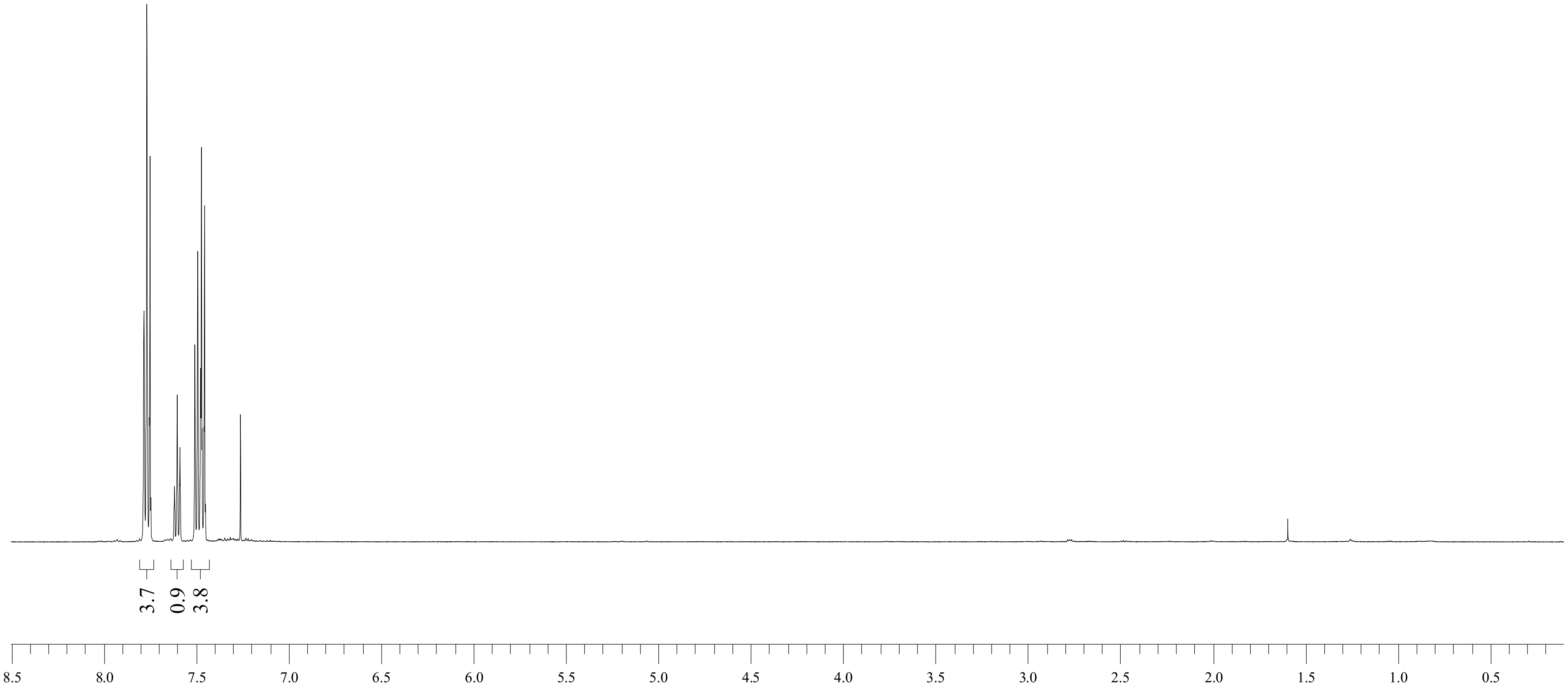
1.0
0.5
1.0
1.0
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

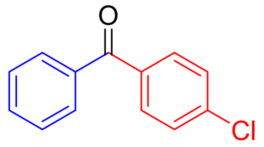
16g


O
NMe$_2$
16g
200
175
150
125
100
75
50
25

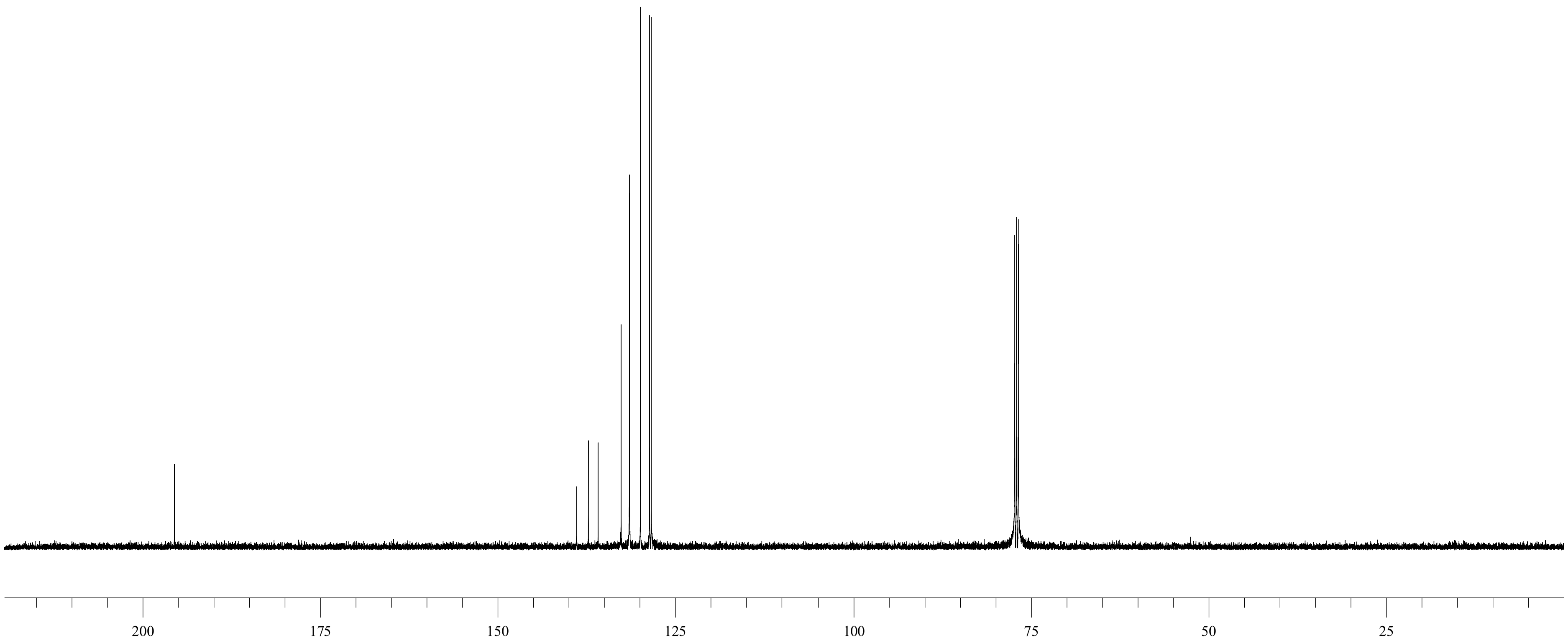


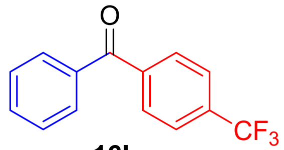
16k



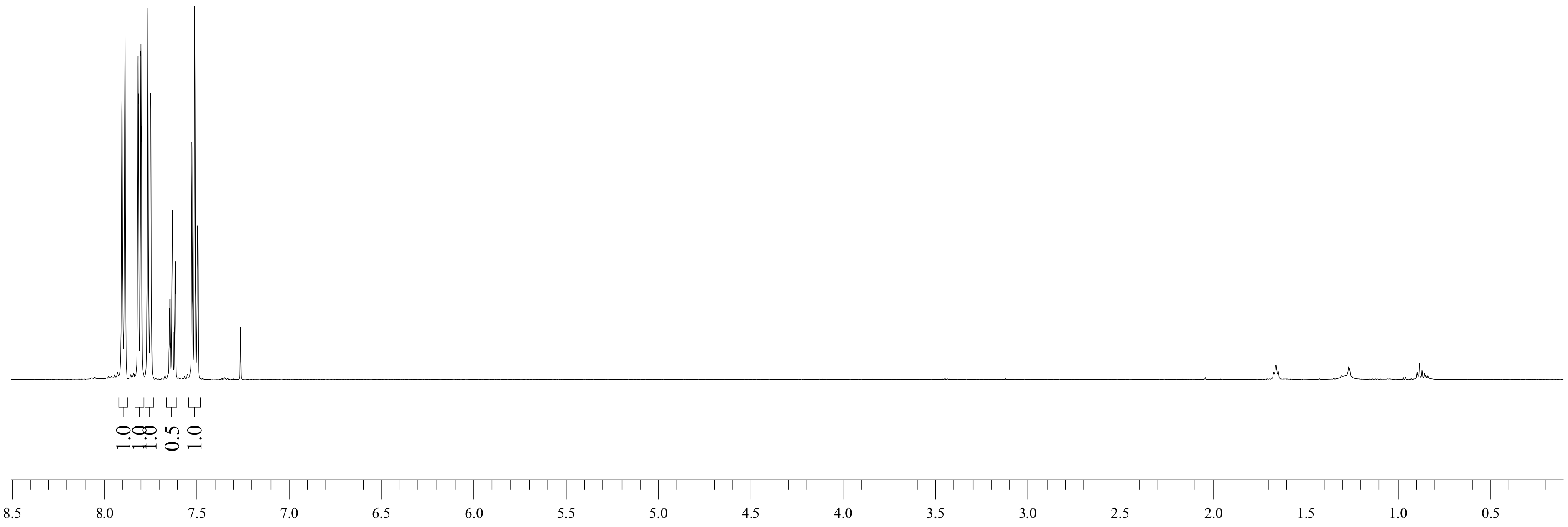


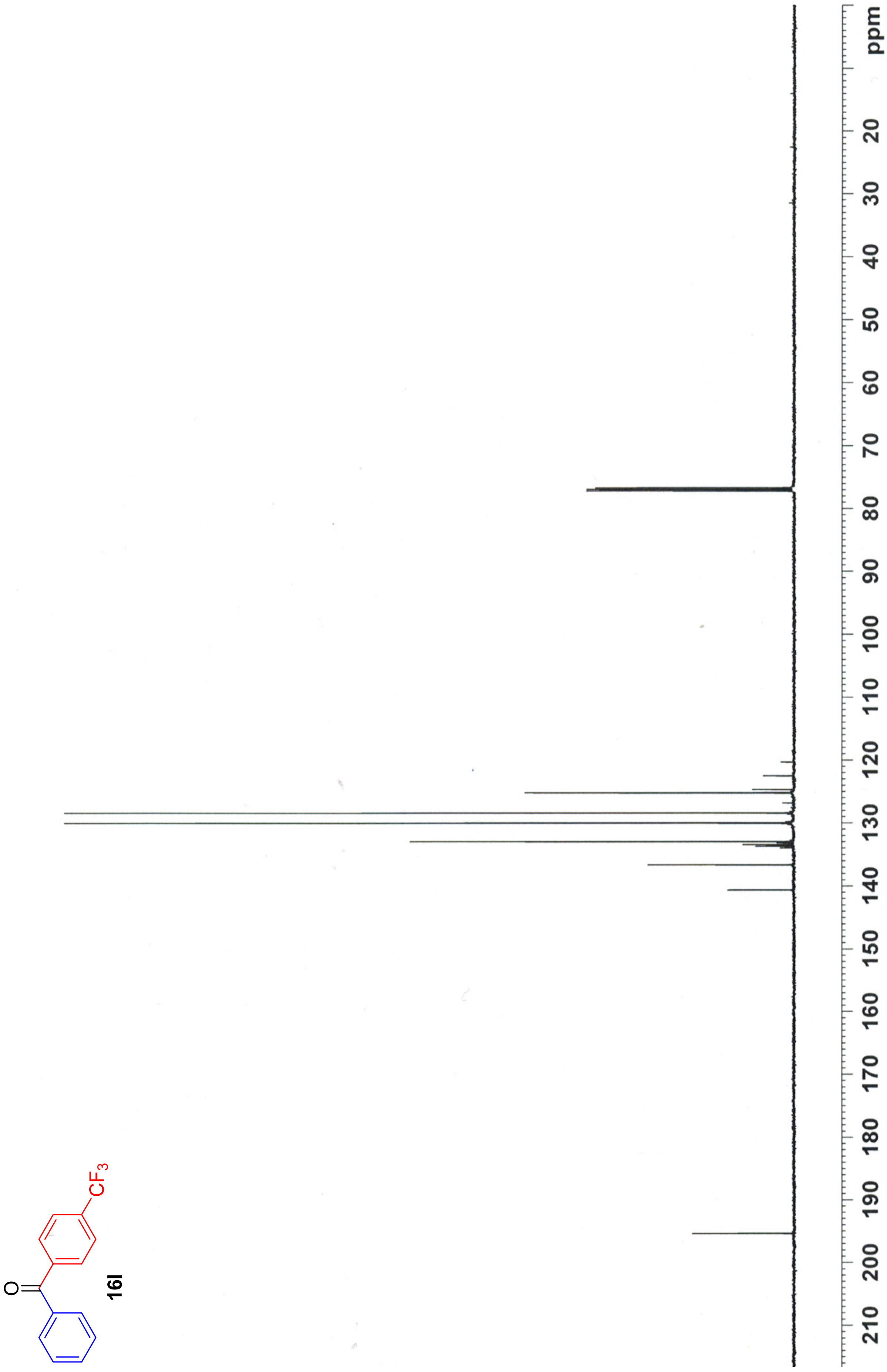
16k





16l




CF3
O
ppm
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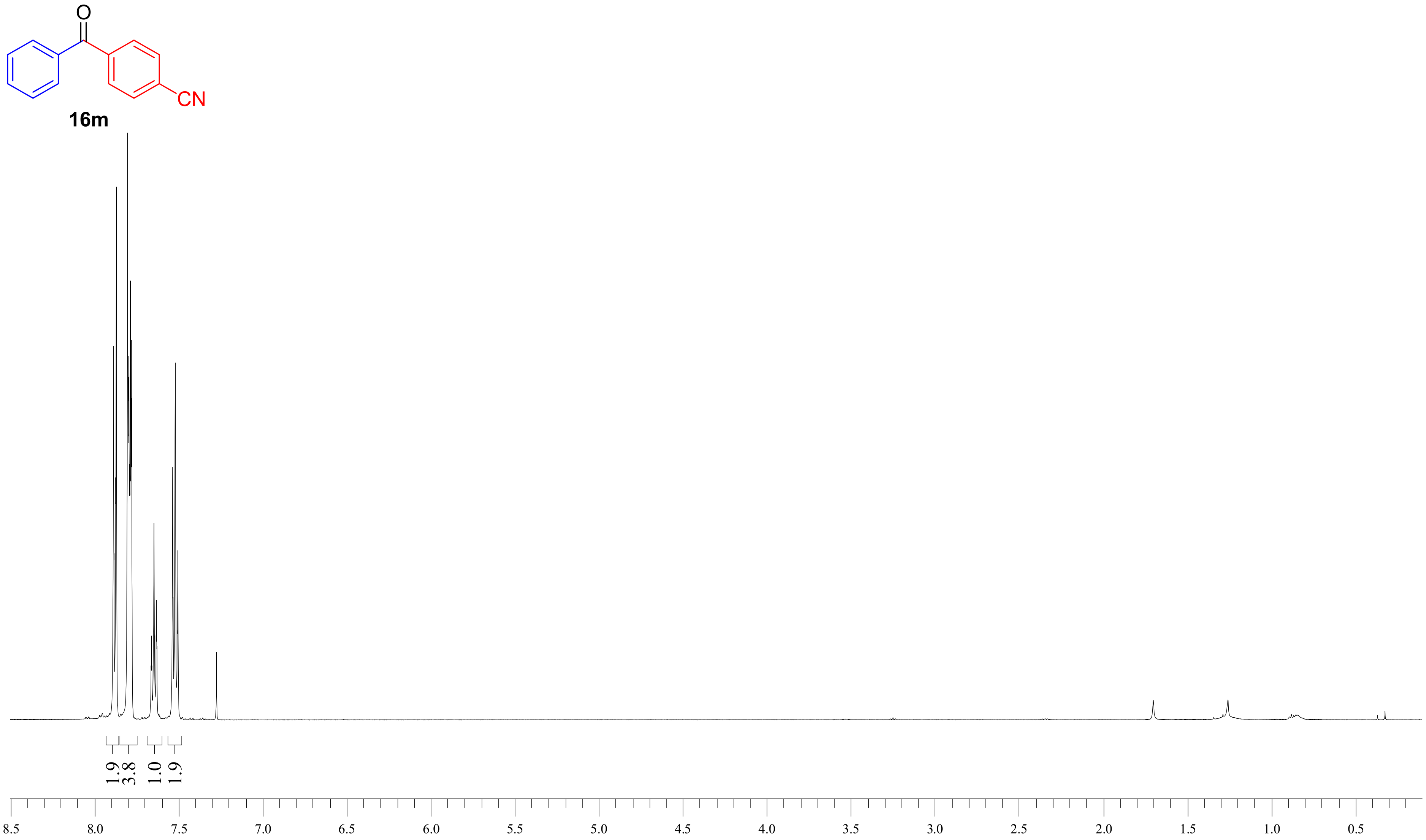
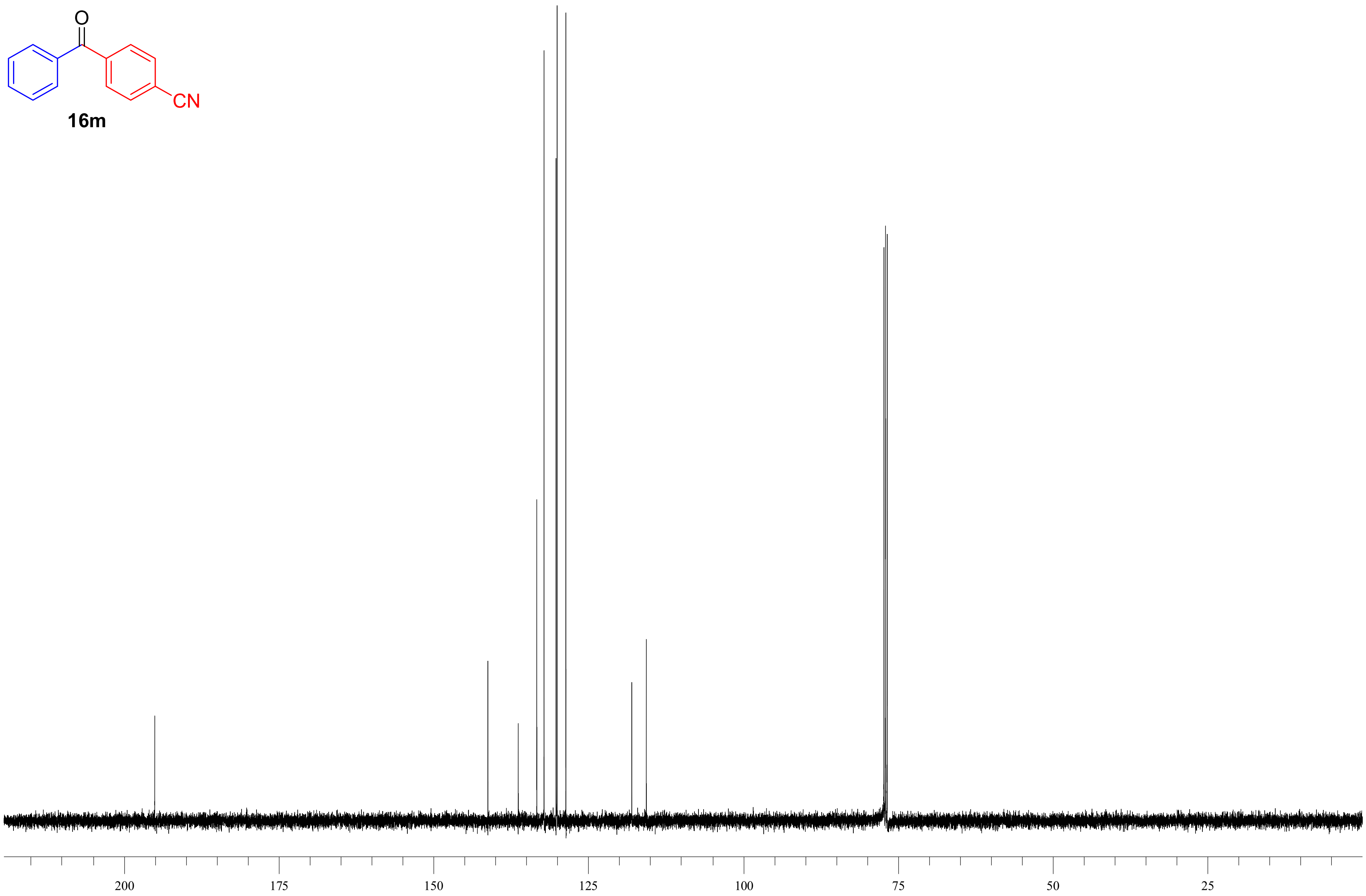
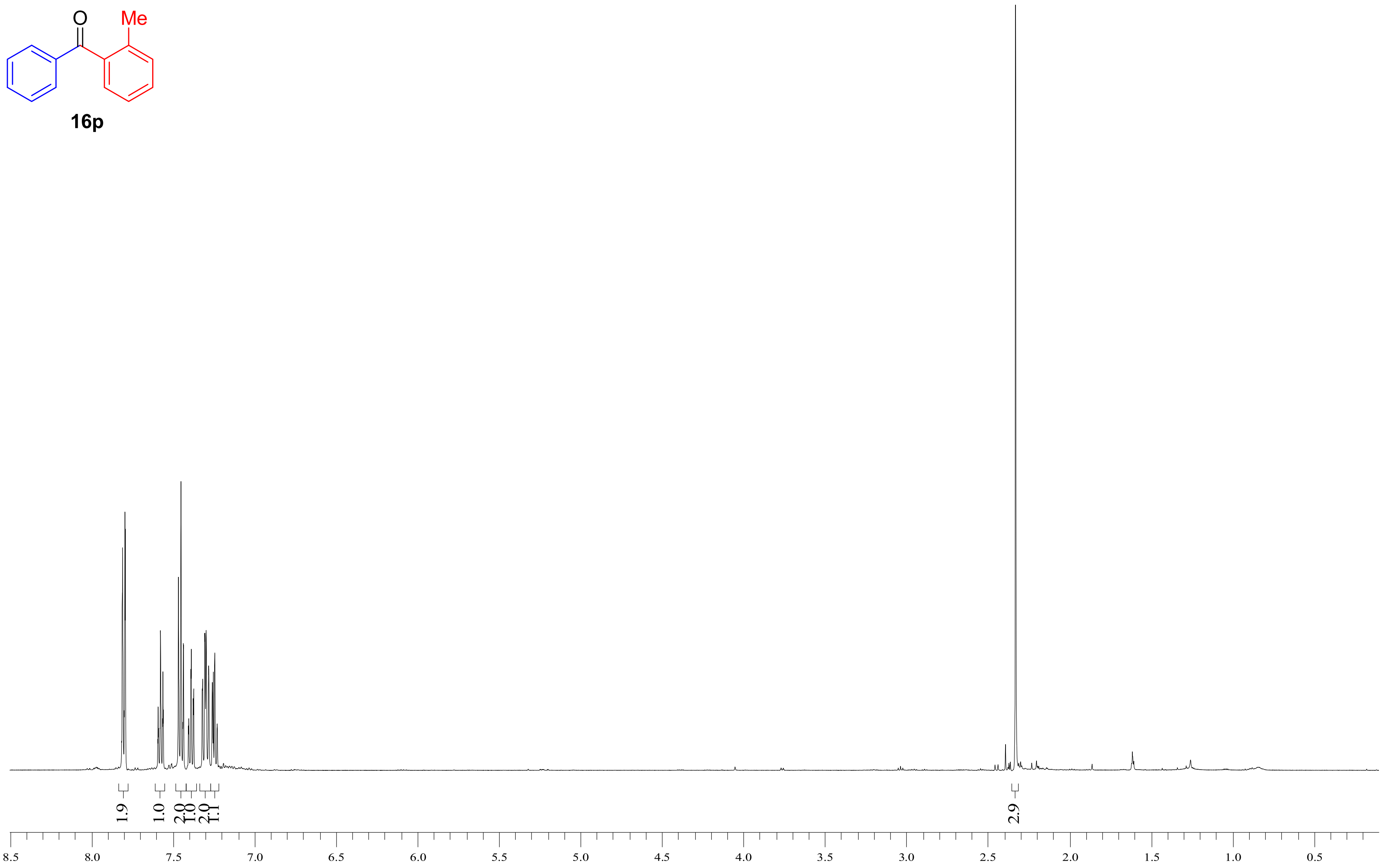
150
160
170
180
190
200
210

16l

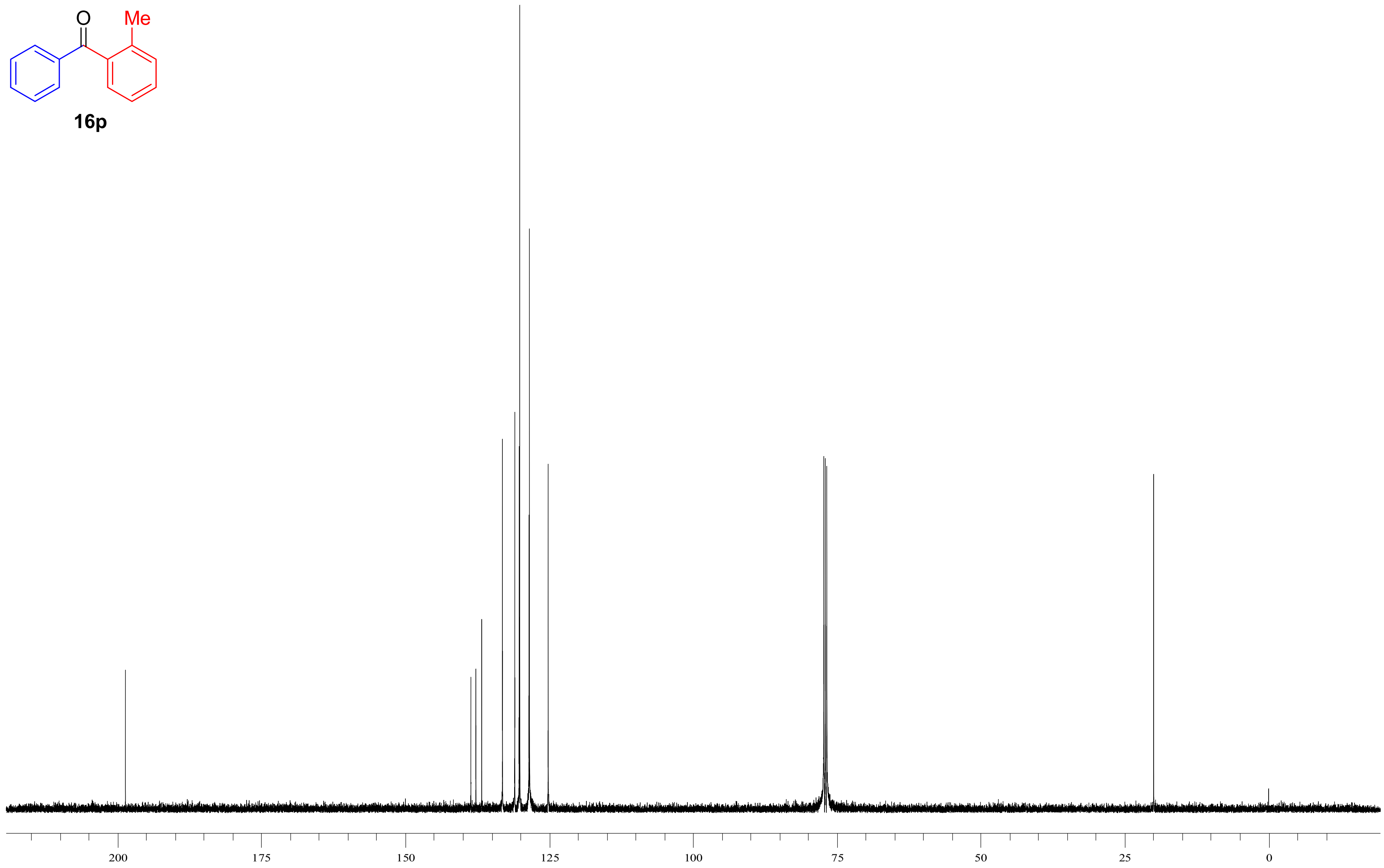

16m



16m


16p

O
Me
1.9
1.0
2.0
1.0
2.0
1.1
2.9
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


O
Me
16p
200
175
150
125
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75
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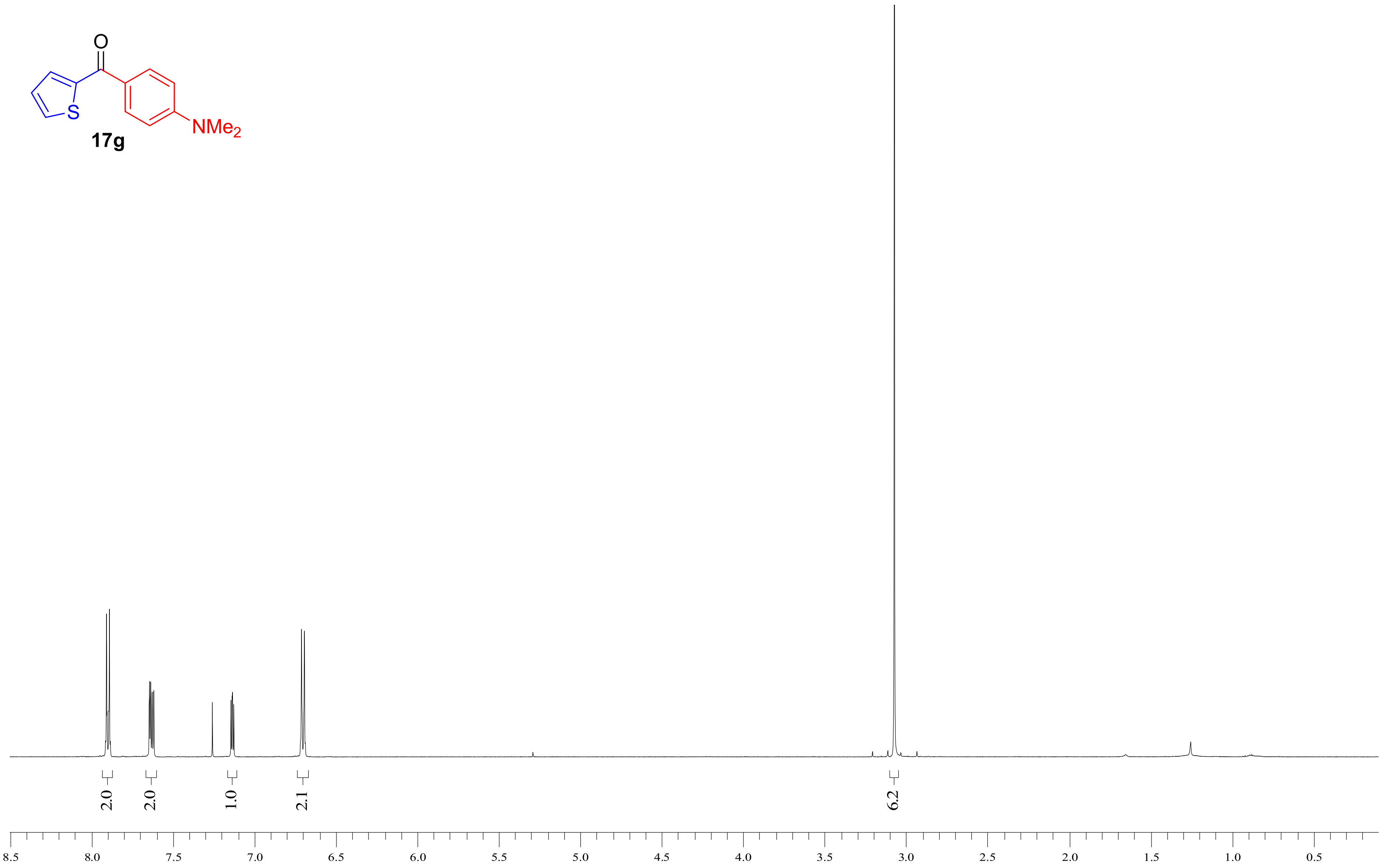

17g

NMe2
O
S
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6.2
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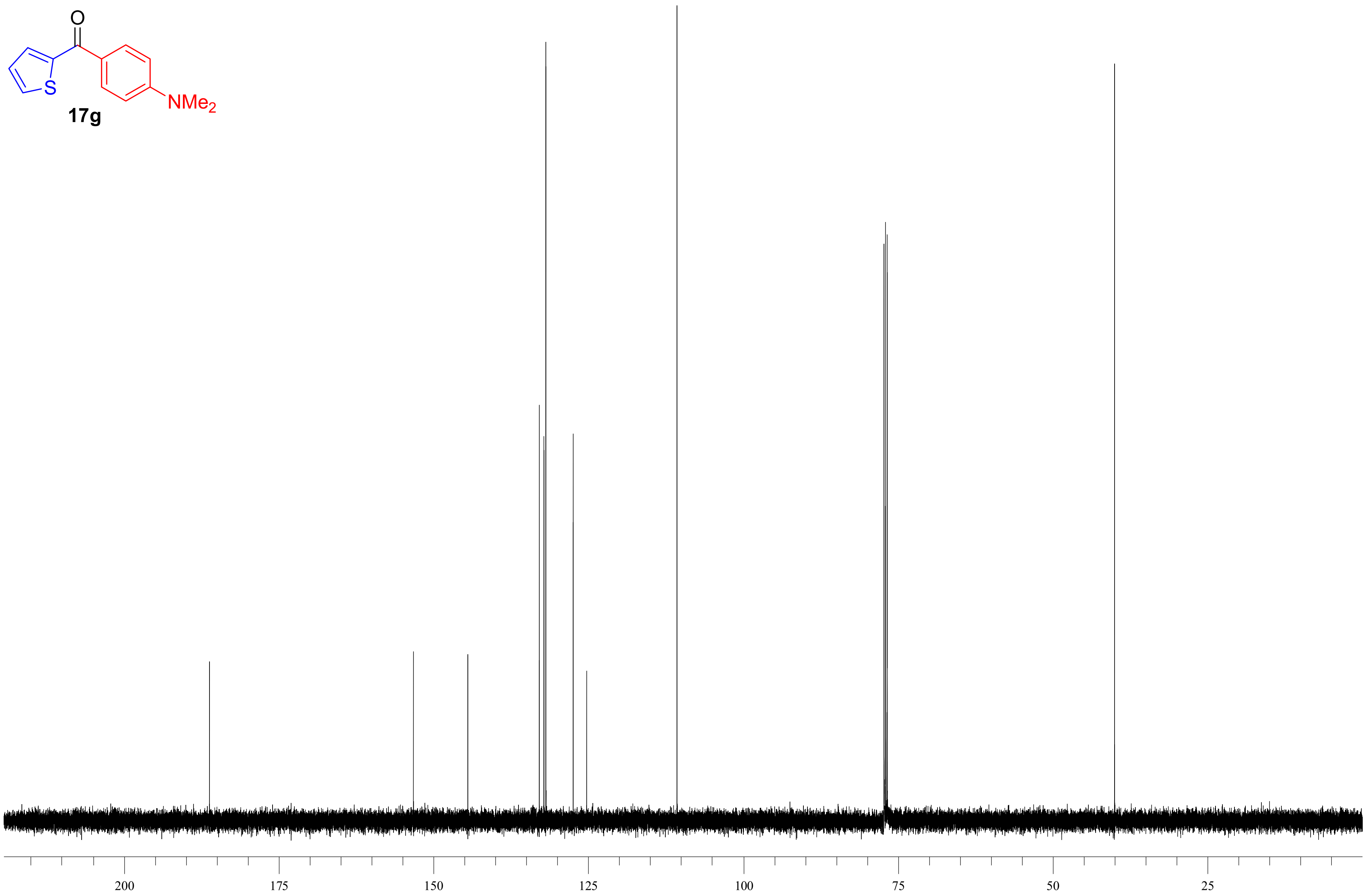
0.5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S
NMe$_2$
17g
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100
75
50
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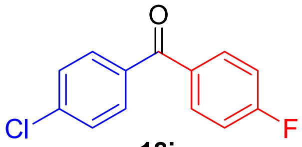

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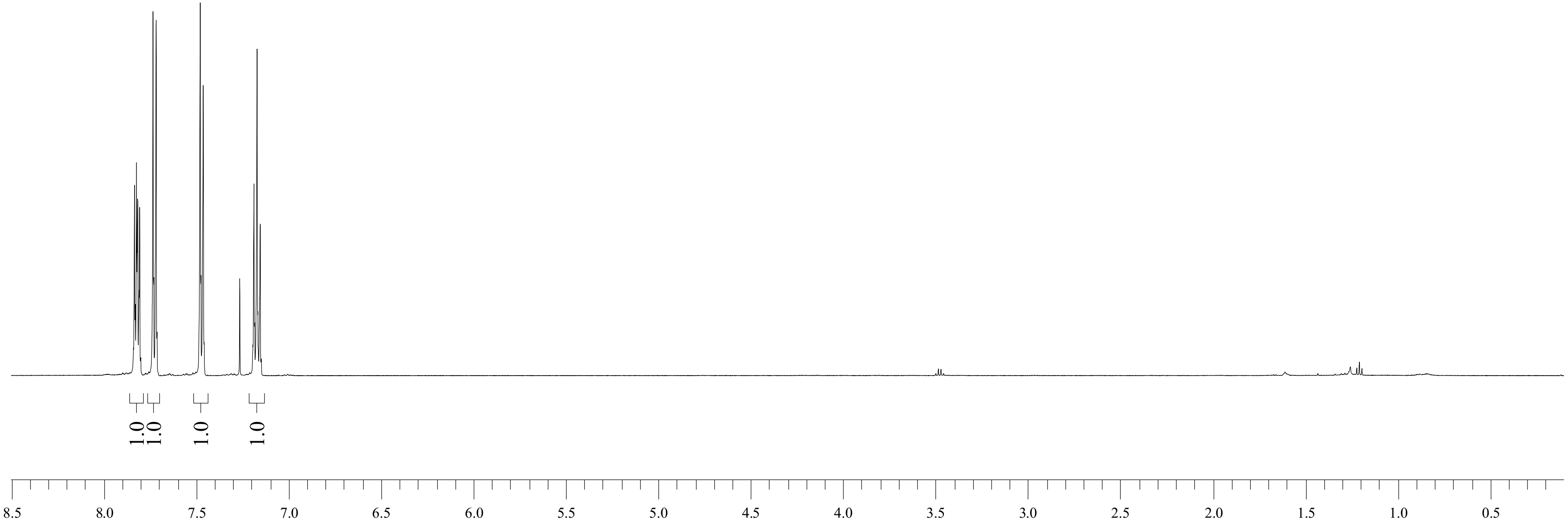

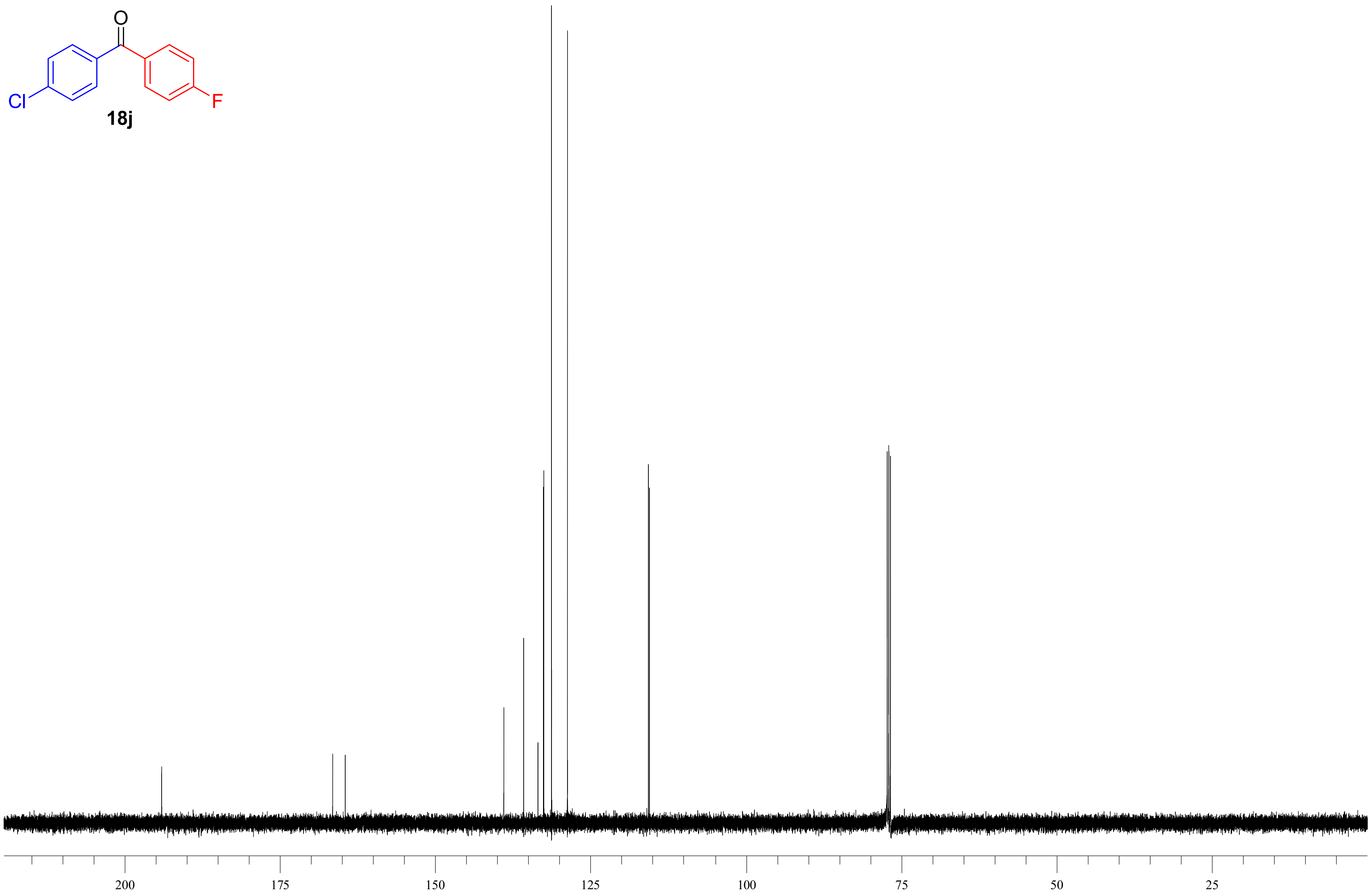

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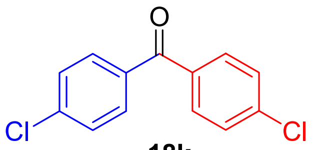

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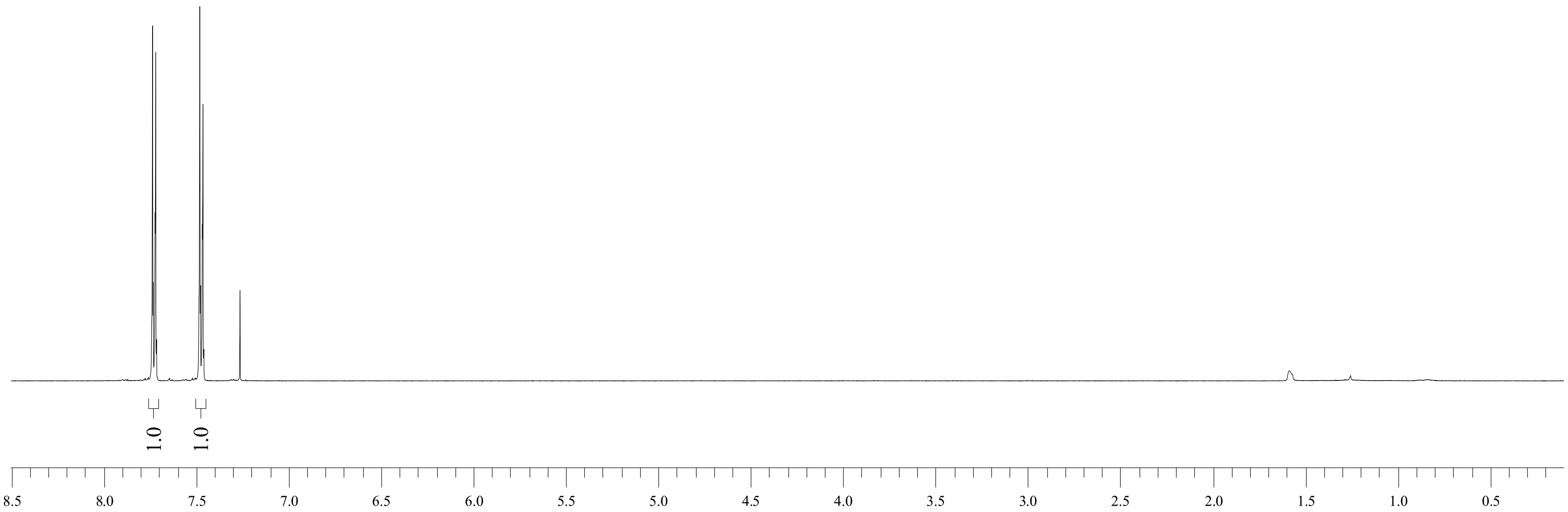

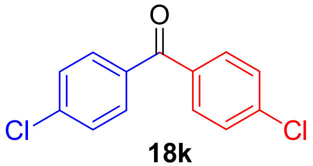

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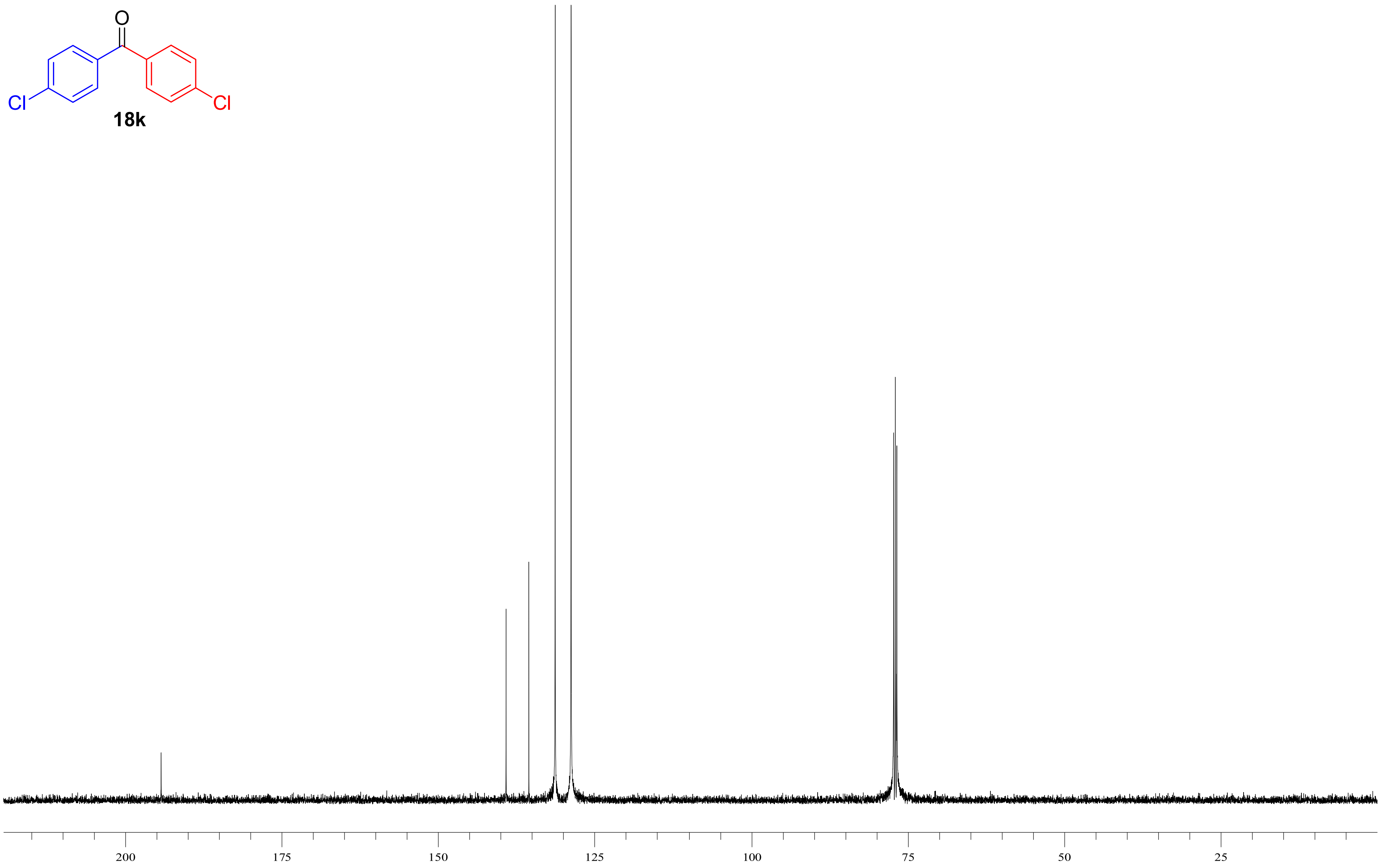
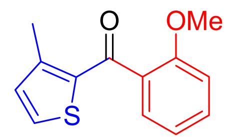
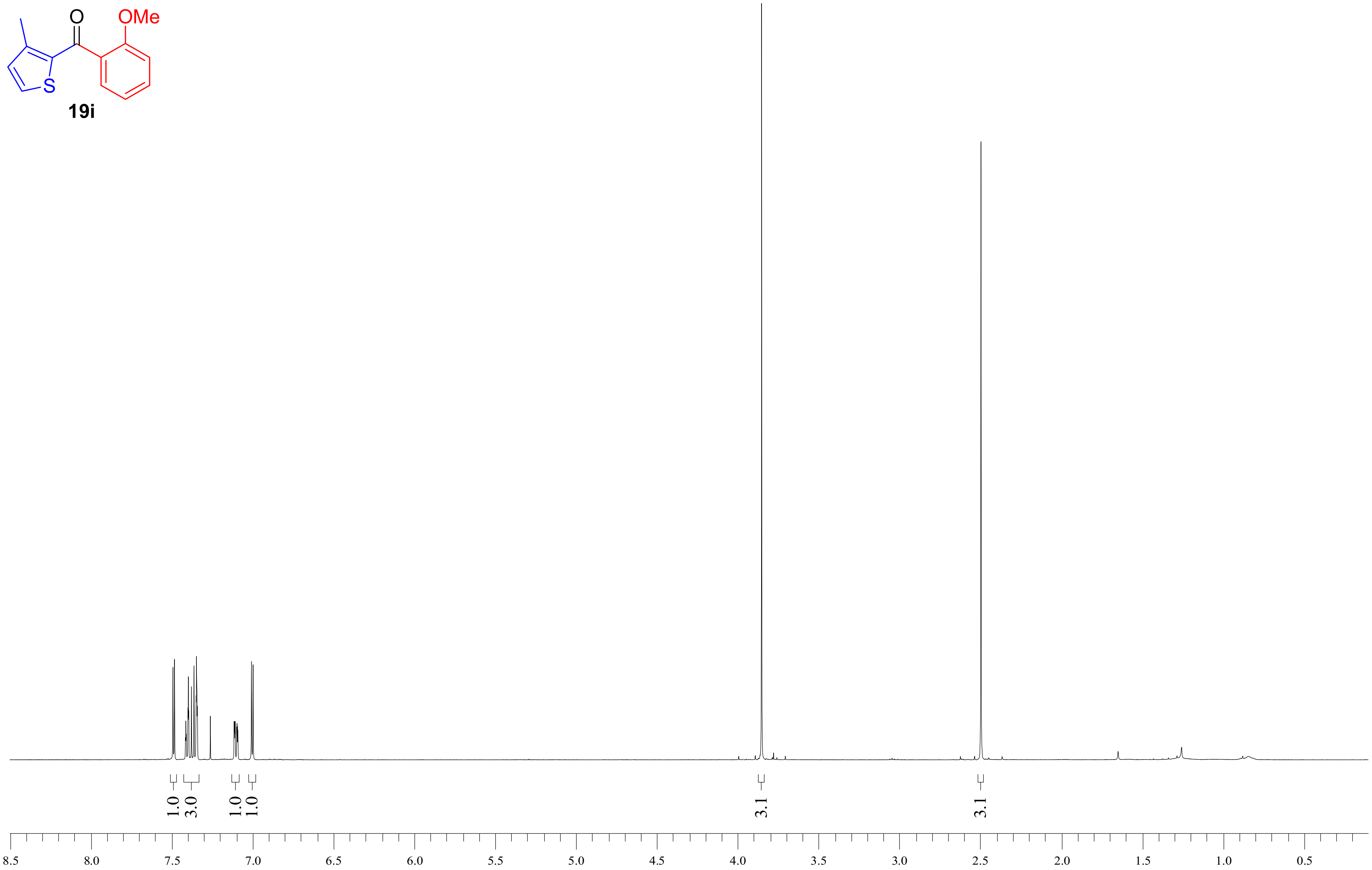



O
OMe
S

19i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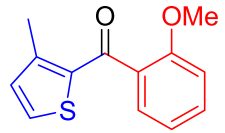
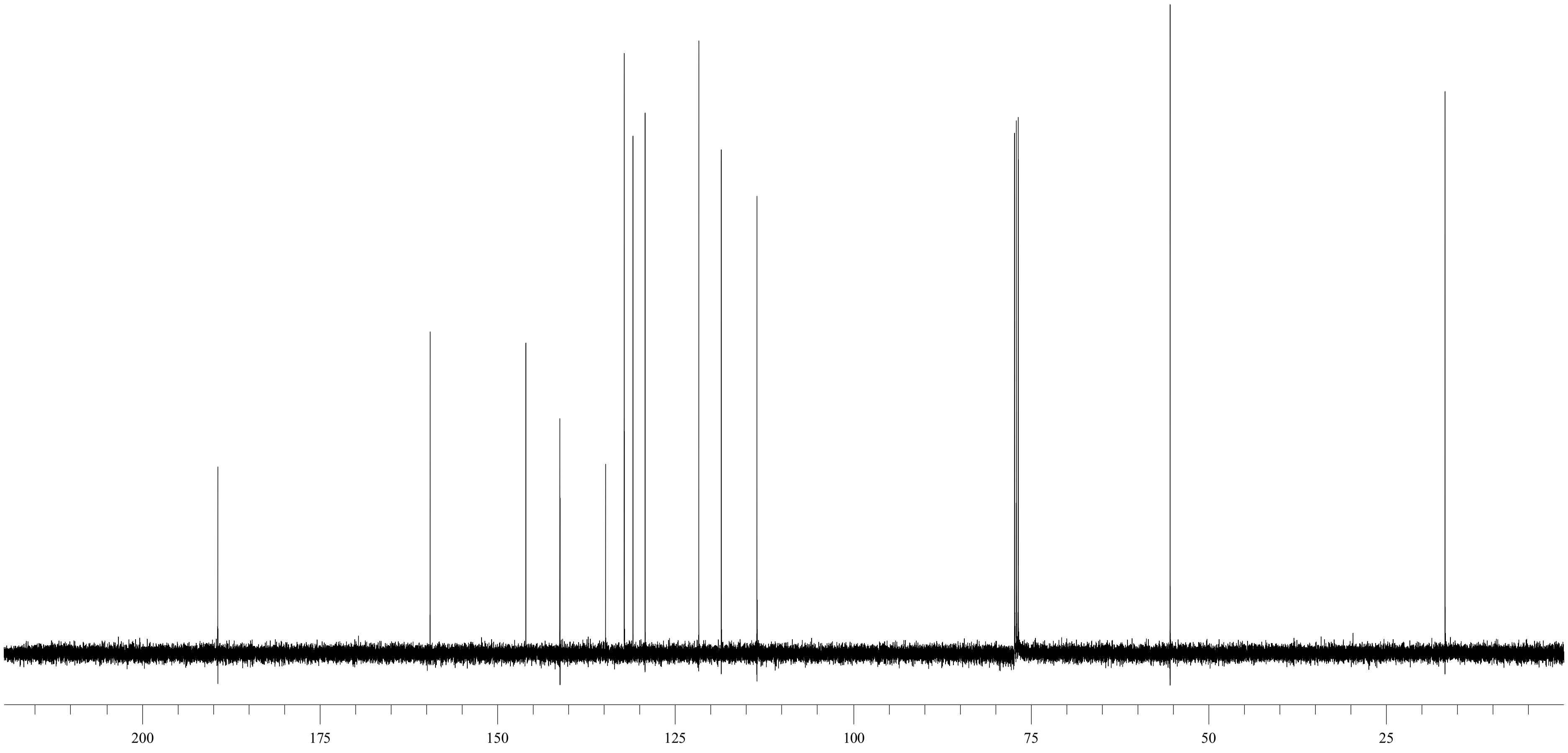
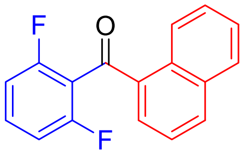
0.5



19i





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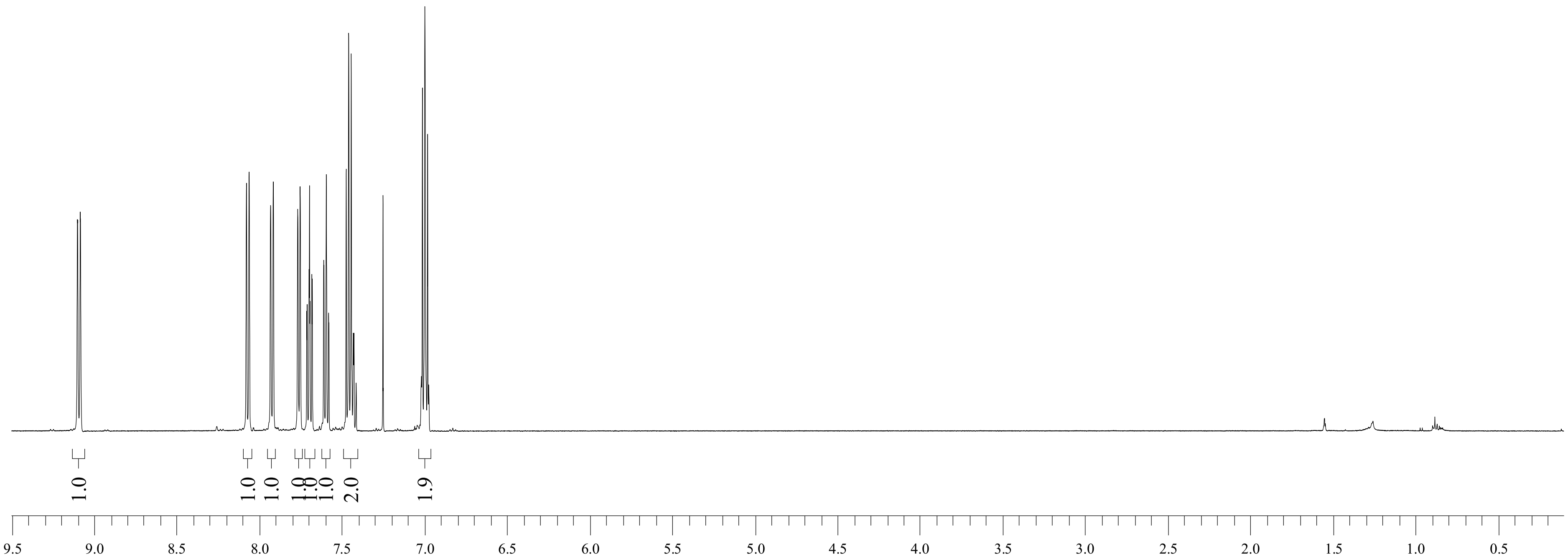
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6.5
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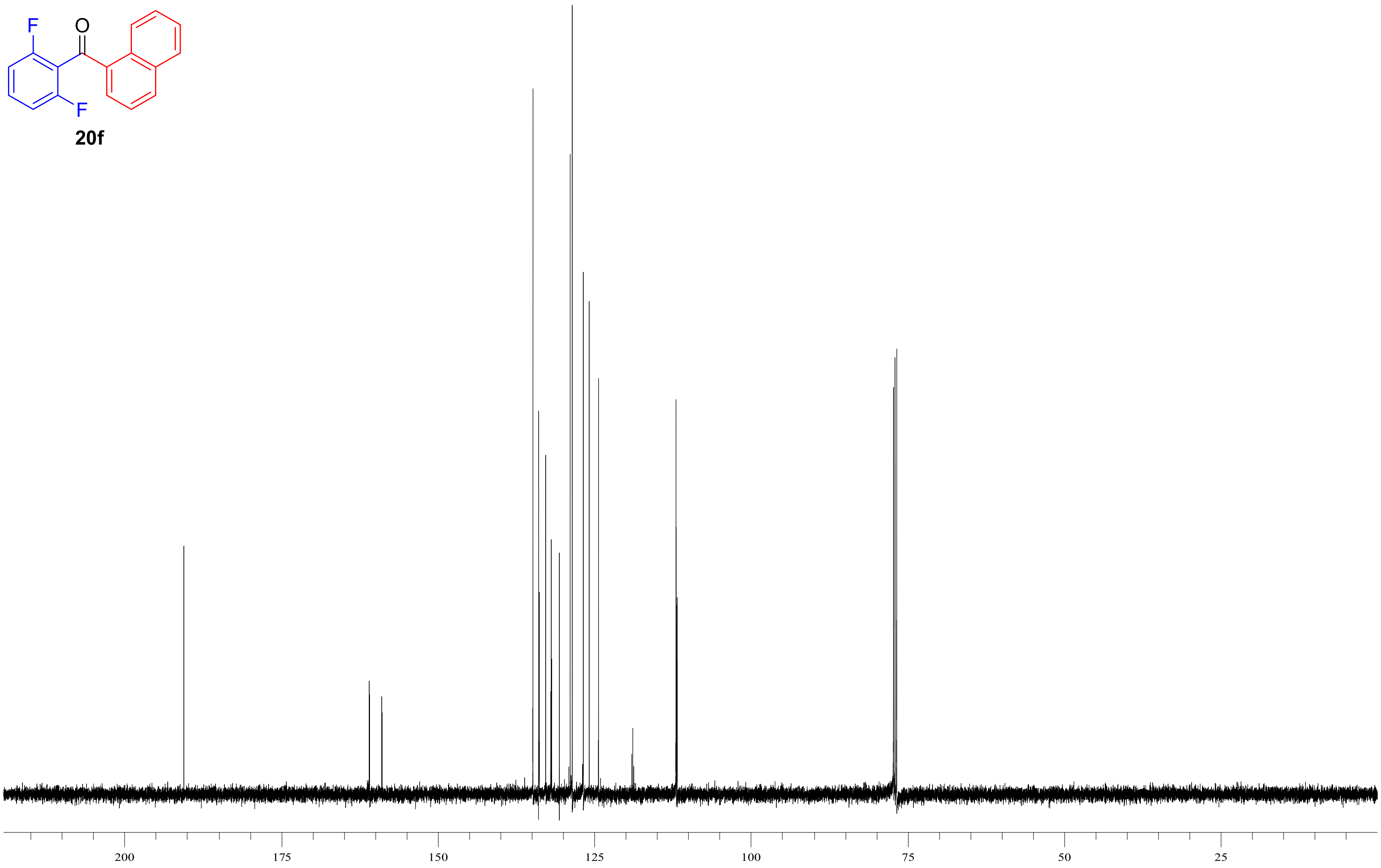
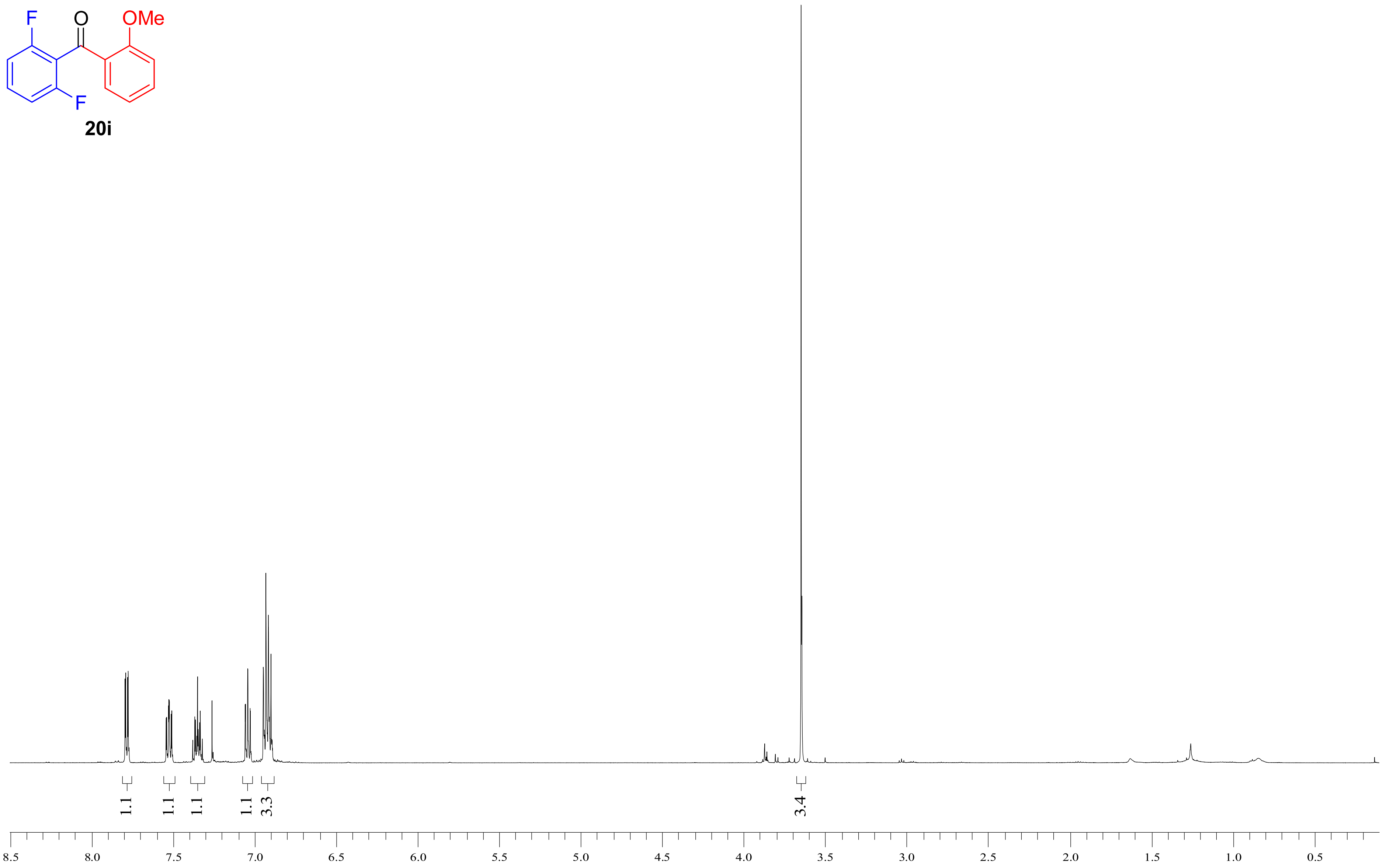
0.5



20f



20i

F
O
OMe
F
1.1
1.1
1.1
1.1
3.3
3.4
8.5
8.0
7.5
7.0
6.5
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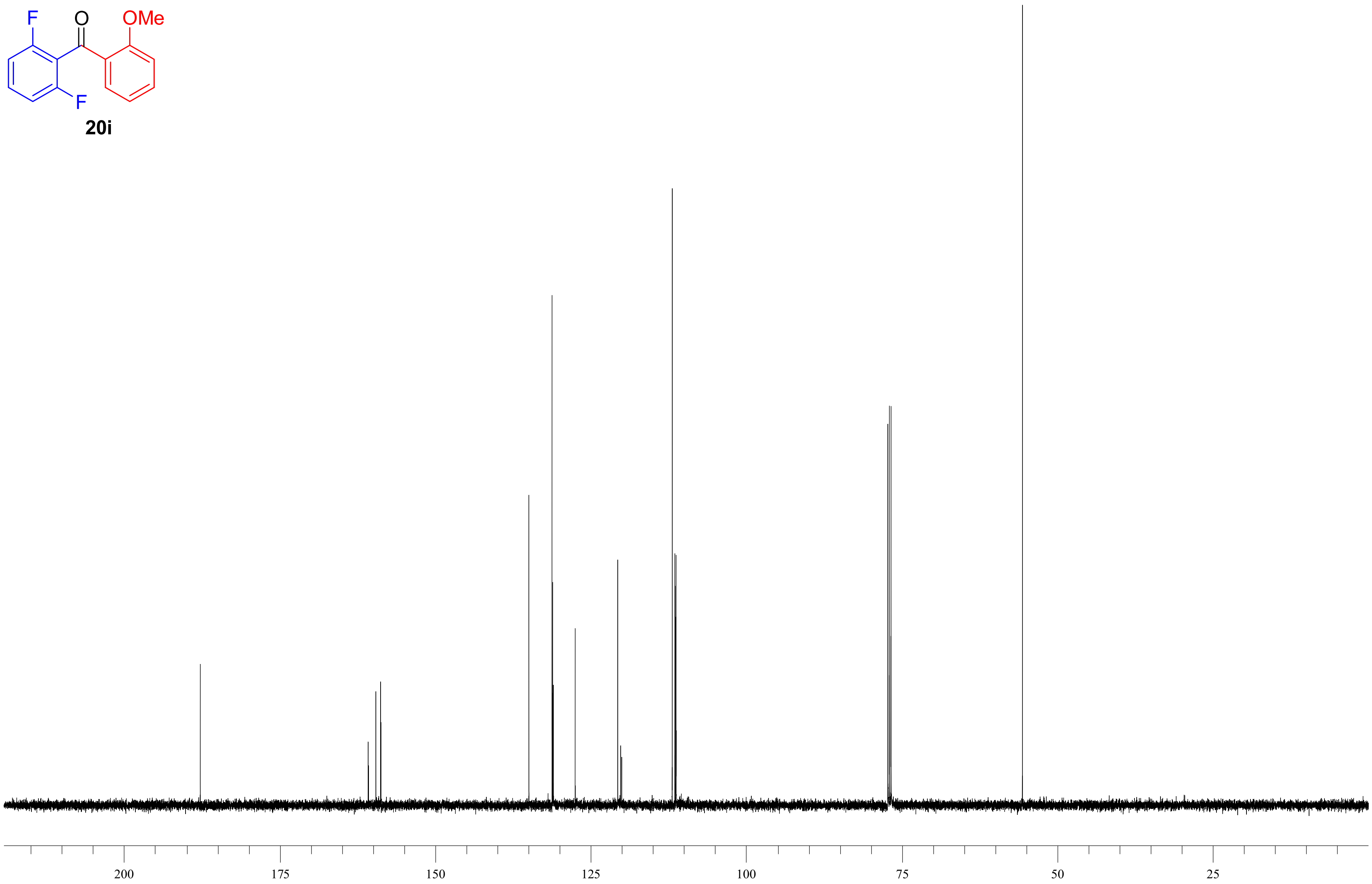

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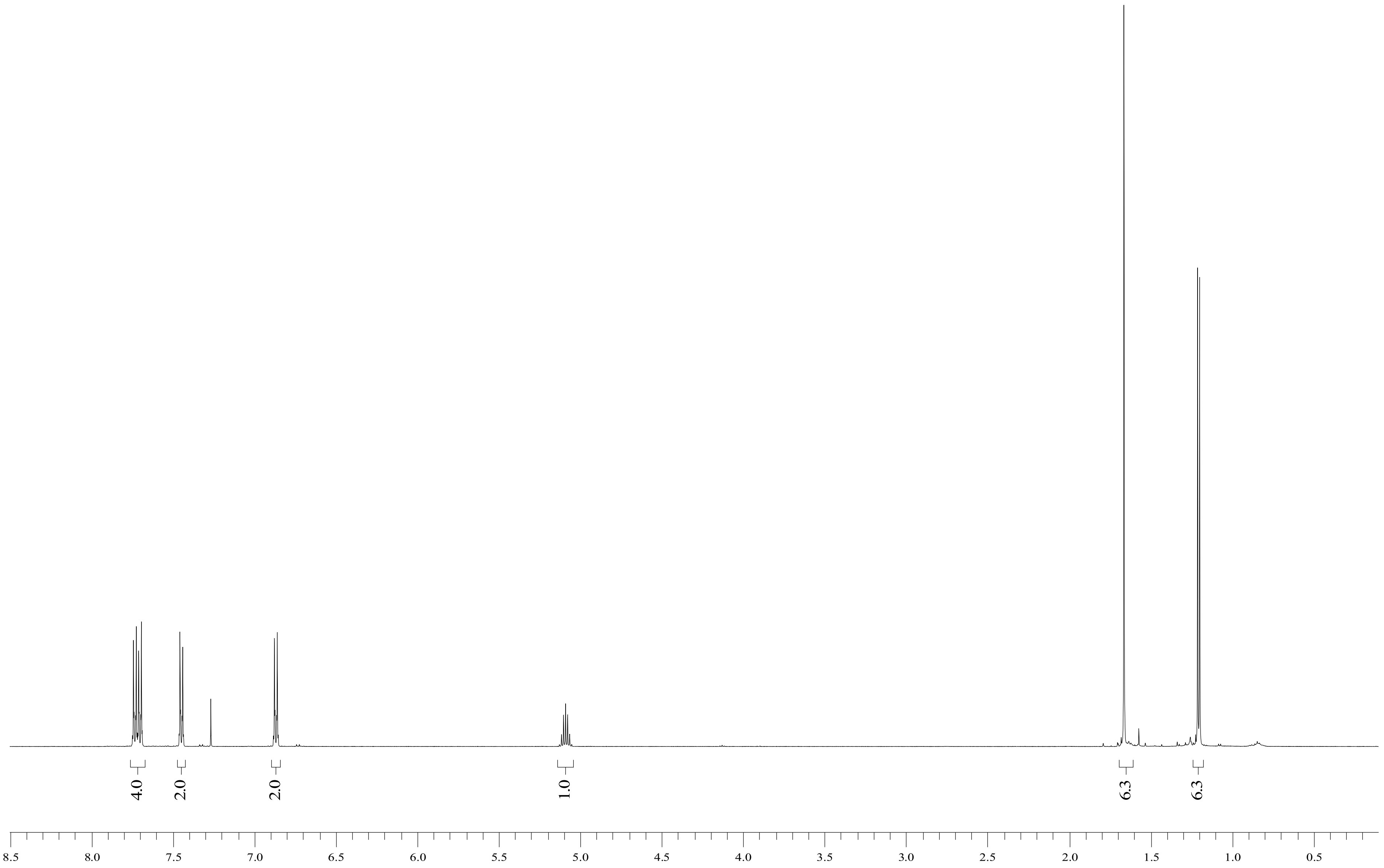
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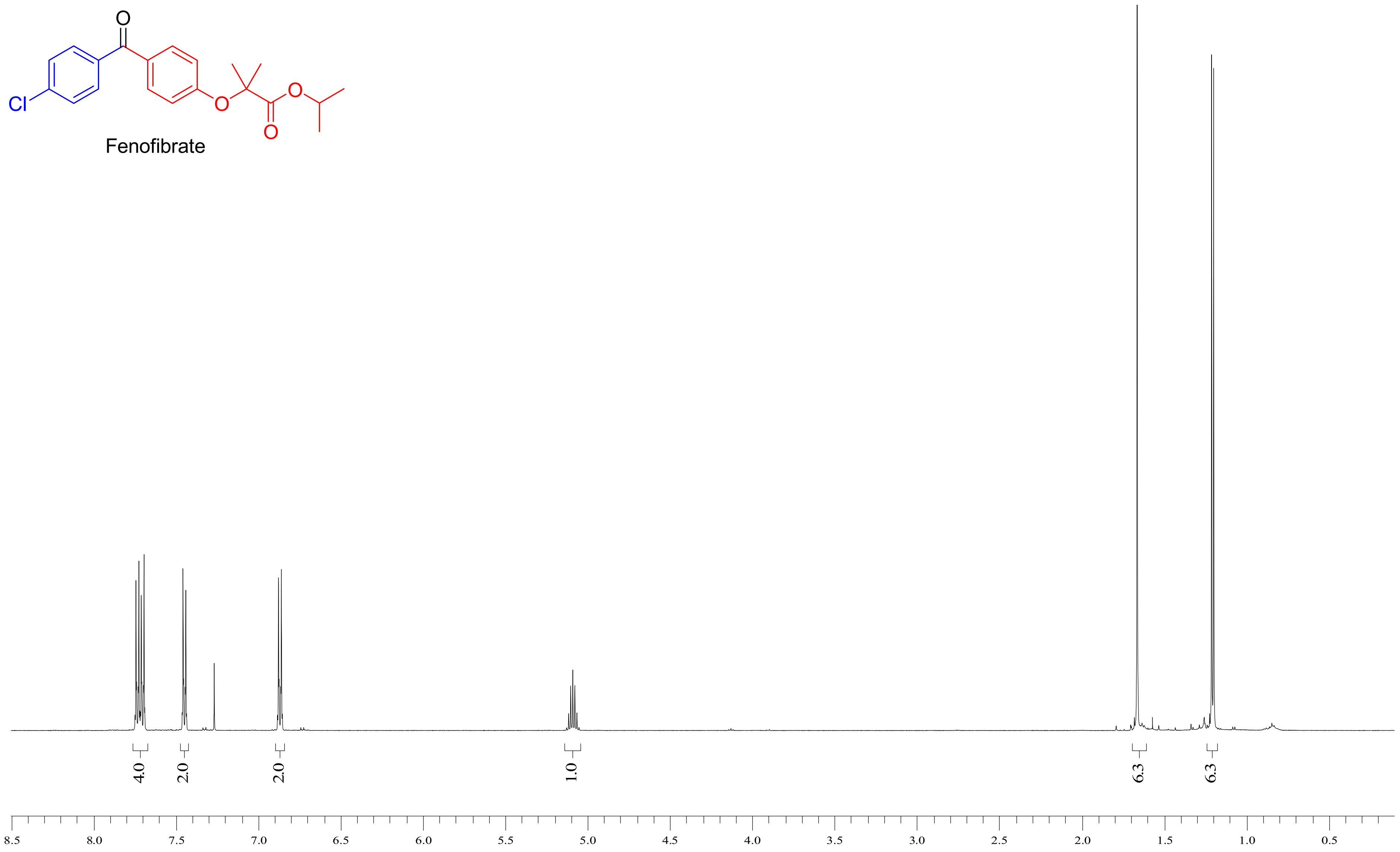
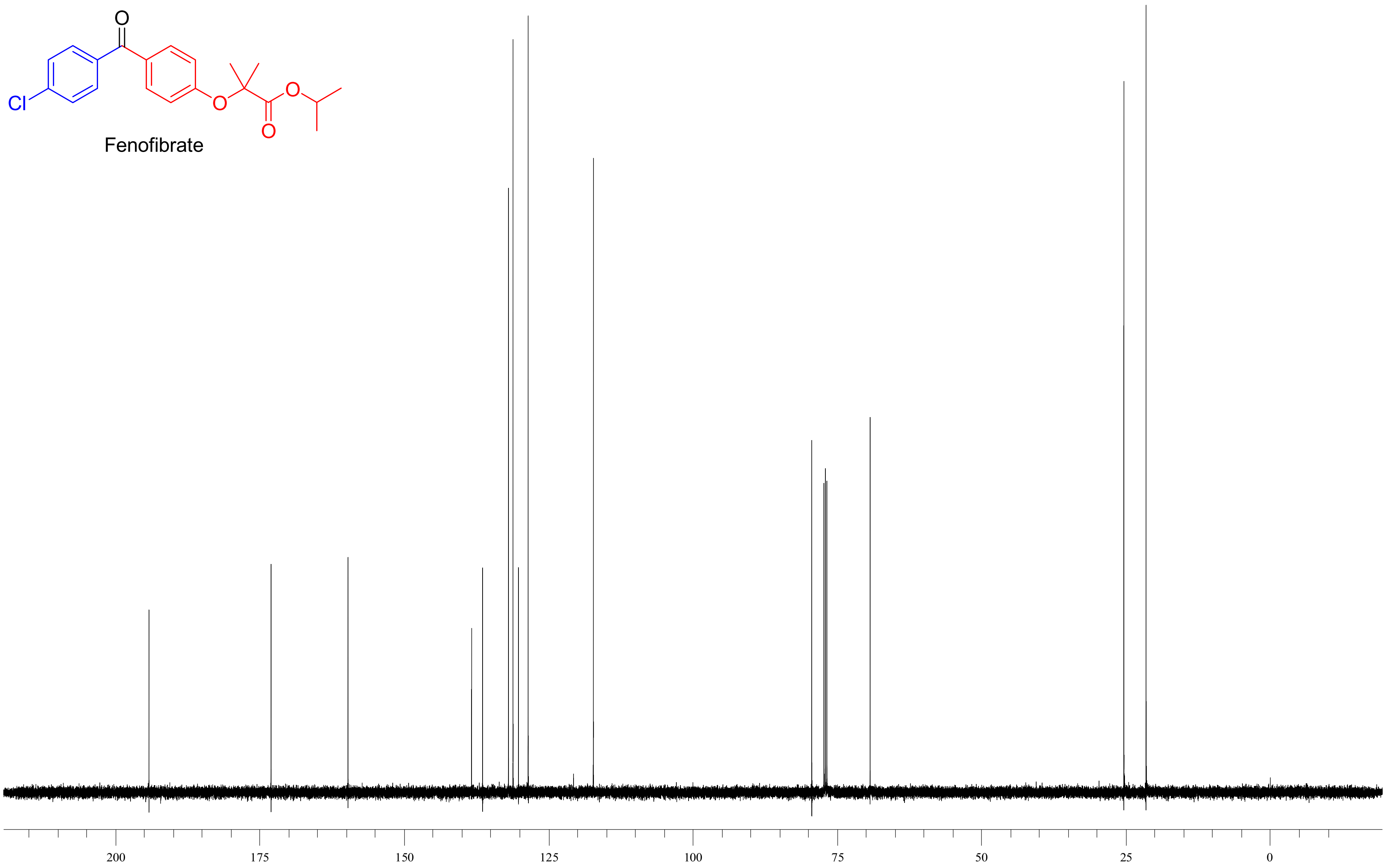


Fenofibrate


Fenofibrate