Supporting information for

Iron-catalyzed tetrasubstituted alkenes formation from alkynes and sodium sulfinates

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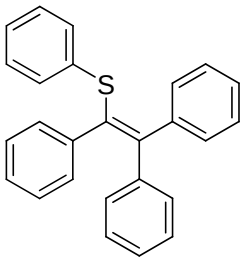
General information:

All experiments were carried out under an atmosphere of argon. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, HRMS and X-RD. The structure of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Aromatic sulfinic acid sodium salts **1a**, **1b**, **1f** and **1j** were purchased from Alfa Aesar, others were prepared according to the literature procedures. Solvents were used as received without further purification. Alkynes **1a** were purchased from Alfa Aesar, others were prepared according to the literature procedures.

General procedure: 1,1,2-triphenylethene (3a)

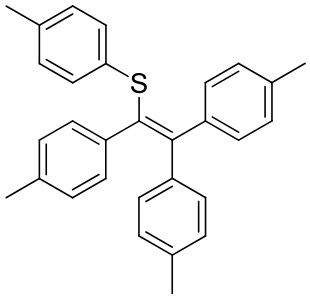
A 10 mL reaction vessel was charged with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol), diphenylethyne (**2a**, 35.6 mg, 0.2 mmol), $FeSO_4 \cdot 7H_2O$ (0.6 mg, 0.002 mmol), and 1,8-naphthalenediamine (0.9 mg, 0.004 mmol). The sealed reaction vessel was purged with argon three times and trifluoroacetic acid (0.2 mmol), methanesulfonic acid (0.2 mmol) and a mixture of 1,4-dioxane (0.3 mL) and H_2O (0.1 mL) were added by syringe. The resulting solution was heated to 120 ^{o}C for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 98:2) to give **3a** in 78% yield (56.8 mg) as light yellow solid, mp 147-148.5 ^{o}C.

Phenyl(1,2,2-triphenylvinyl)sulfane (3a, CAS: 69719-58-0) [1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39-7.29 (m, 7H), 7.19-6.98 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.2, 143.7, 142.5, 139.3, 135.7, 134.2, 131.1, 130.7, 129.8, 129.6, 128.4, 128.1, 127.6, 127.5, 127.2, 127.0, 126.6, 125.8; MS (EI) *m/z* (%) 77, 178, 239, 255, 364 (100).

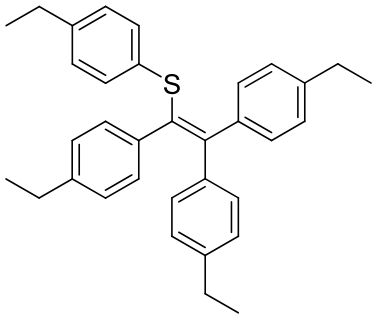
***p*-Tolyl(1,2,2-tris-tolylvinyl)sulfane (3b)**



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 142.4 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 60.5 mg, 72% yield of **3b** as light yellow solid, mp 181-182.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.23-7.18 (m, 4H), 7.11-7.04 (m, 4H), 6.91-6.81 (m, 8H), 2.34 (s, 3H), 2.22-2.17 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.9, 141.5, 140.0, 136.7, 136.4, 136.1, 135.3, 133.1, 132.7, 130.9, 130.7, 129.5, 129.2, 128.8, 128.3, 128.3, 125.2, 21.3, 21.1, 20.9; MS (EI) *m/z* (%) 189, 252, 282, 297 (100), 420; HRMS calcd. for: $C_{30}H_{29}S$ $[M+H]^+$: 421.19845, found 421.19833.

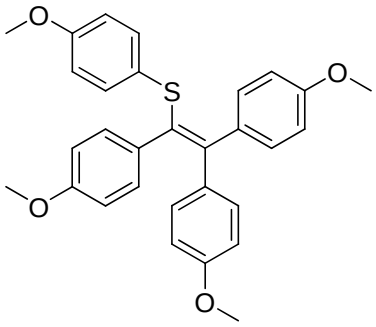
(4-Ethylphenyl)(1,2,2-tris(4-ethylphenyl)vinyl)sulfane (3c)



The reaction was conducted with sodium 4-ethylbenzenesulfinate (**1c**, 153.6 mg, 0.8 mmol) and 1,2-bis(4-ethylphenyl)ethyne (**2c**, 46.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 47.7 mg, 50% yield of **3c** as light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.24-7.19 (m, 4H), 7.12-7.05 (m, 4H), 6.92-6.83 (m, 8H), 2.64 (q, J = 8.0 Hz, 2H), 2.55-2.45 (m, 6H), 1.24 (t, J = 8.0 Hz, 3H), 1.16-1.08 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.6, 142.9, 142.7, 142.3, 141.7, 141.6, 140.3, 137.1, 133.5, 133.1, 131.0, 130.7, 129.8, 129.6, 127.9, 127.4, 127.0, 126.9, 28.6, 28.4, 28.3, 15.3, 15.2, 15.1; HRMS calcd. for: $C_{34}H_{37}S$ $[M+H]^+$: 477.26105, found 477.26110.

(4-Methoxyphenyl)(1,2,2-tris(4-methoxyphenyl)vinyl)sulfane (3d)

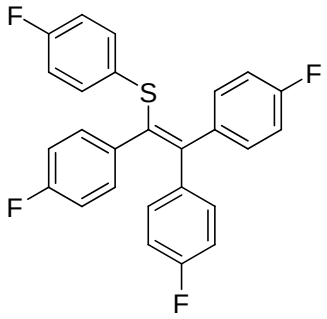


The reaction was conducted with sodium 4-methoxybenzenesulfinate (**1d**, 155.2 mg, 0.8 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (**2d**, 47.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 9:1) to provide 46.5 mg, 48% yield of **3d** as light yellow solid, mp 149-150 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.28 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.87-6.84 (m, 4H), 6.66-6.55 (m, 6H), 3.81-3.69 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.7, 158.3, 158.2, 158.0, 143.3, 136.8, 135.6, 133.1, 132.2, 132.2, 132.0, 131.9, 131.0,

126.8, 114.2, 113.5, 113.1, 113.1, 55.19, 55.17, 55.05, 55.03; HRMS calcd. for: $C_{30}H_{28}O_4S$ [M]: 484.17028, found 484.16989.

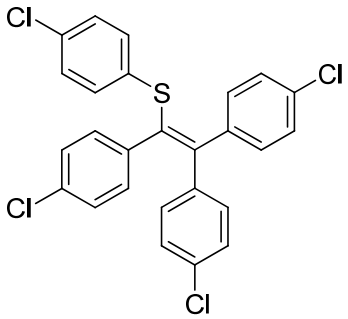
(4-Fluorophenyl)(1,2,2-tris(4-fluorophenyl)vinyl)sulfane (3e)



The reaction was conducted with sodium 4-fluorobenzenesulfinate (**1e**, 145.6 mg, 0.8 mmol) and 1,2-bis(4-fluorophenyl)ethyne (**2e**, 42.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 61.1 mg, 70% yield of **3e** as light yellow solid, mp 118.5-119.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34-7.30 (m, 2H), 7.21-7.17 (m, 2H), 7.13-7.10 (m, 2H), 7.05-7.01 (m, 2H), 6.90-6.87 (m, 2H), 6.83-6.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.1 (d, J = 240.0 Hz), 161.8 (d, J = 240.0 Hz), 161.7 (d, J = 240.0 Hz), 161.6 (d, J = 240.0 Hz),142.8, 139.0 (d, J = 3.3 Hz), 138.0 (d, J = 3.3 Hz), 134.7 (d, J = 3.6 Hz), 134.6, 132.6 (d, J = 8.1 Hz), 132.2 (d, J = 8.0 Hz), 131.4 (d, J = 7.9 Hz), 129.8 (d, J = 3.4 Hz), 115.8 (d, J = 21.9 Hz), 115.3 (d, J = 21.4 Hz), 114.9 (d, J = 21.5 Hz); MS (EI) *m/z* (%) 214, 268, 288, 309 (100), 436. HRMS calcd. for: $C_{26}H_{16}F_4S$ [M]: 436.0914, found 436.0909.

(4-Chlorophenyl)(1,2,2-tris(4-chlorophenyl)vinyl)sulfane (3f)

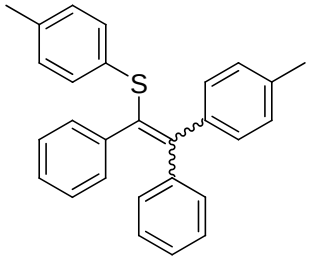


The reaction was conducted with sodium 4-chlorobenzenesulfinate (**1f**, 158.4 mg, 0.8 mmol) and 1,2-bis(4-chlorophenyl)ethyne (**2f**, 49.4 mg, 0.2 mmol). The crude mixture was purified by flash

column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 60.3 mg, 60% yield of **3f** as yellow solid, mp 168.5-169.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31-7.29 (m, 2.5H), 7.24-7.04 (m, 11.5H), 6.86-6.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.3, 141.3, 140.0, 137.0, 134.1, 133.7, 133.5, 133.3, 133.3, 132.6, 132.1, 131.9, 131.1, 130.9, 128.9, 128.6, 128.3; HRMS calcd. for: $C_{26}H_{16}Cl_4S$ [M]: 501.96918, found 501.96884.

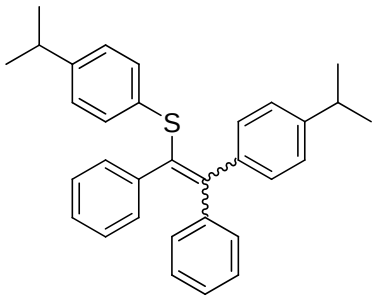
(1,2-Diphenyl-2-p-tolylvinyl)(p-tolyl)sulfane (3g+4g)



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 142.4 mg, 0.8 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 58.1 mg, 74% yield of **3g+4g** as light yellow solid. The ratio of **3g**/**4g** is 1.2:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38-7.26 (m, 5.65H), 7.07-6.84 (m, 12.36H), 2.35 (s, 1.35H = 0.45×3H), 2.21-2.19 (m, 4.65H); MS (EI) *m/z* (%) 91, 191, 253, 269, 392 (100); HRMS calcd. for: $C_{28}H_{25}S$ $[M+H]^+$: 393.16716, found 393.16703.

(4-Isopropylphenyl)(2-(4-isopropylphenyl)-1,2-diphenylvinyl)sulfane (3h+4h)

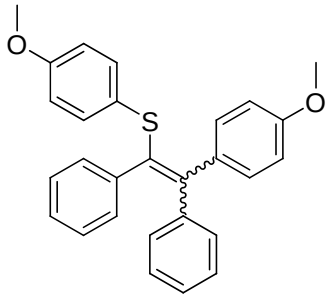


The reaction was conducted with sodium 4-isopropylbenzenesulfinate (**1g**, 164.8 mg, 0.8 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 44.9 mg, 50% yield

of **3h+4h** as light yellow solid. The ratio of **3h**/**4h** is 1.2:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37-7.28 (m, 4.77H), 7.25-7.24 (m, 1H), 7.14-6.84 (m, 12.22H), 2.92-2.85 (m, 0.46H = 0.23×2H), 2.79-2.71 (m, 1.54H = 0.77×2H), 1.25 (d, J = 8.0 Hz, 2.76H = 0.23×12H), 1.15-1.12 (m, 9.24H = 0.77×12 H); HRMS calcd. for: $C_{32}H_{33}S$ $[M+H]^+$: 449.22975, found 449.22949.

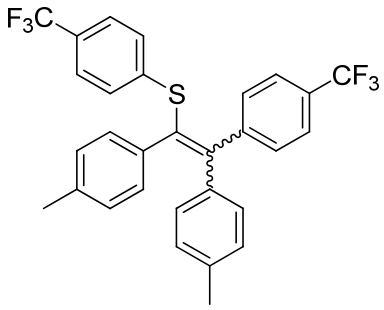
(4-Methoxyphenyl)(2-(4-methoxyphenyl)-1,2-diphenylvinyl)sulfane (3i+4i)



The reaction was conducted with sodium 4-methoxybenzenesulfinate (**1d**, 155.2 mg, 0.8 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 56.9 mg, 67% yield of **3i+4i** as light yellow solid. The ratio of **3i**/**4i** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40-7.28 (m, 3.94H), 7.25-7.20 (m, 1.4H), 7.11-6.84 (m, 9.68H), 6.64-6.55 (m, 3H), 3.81 (m, 1.5H = 0.25×6H), 3.68 (m, 4.5H = 0.75×6H); HRMS calcd. for: $C_{28}H_{25}O_2S$ $[M+H]^+$: 425.15698, found 425.15652.

(1,2-Dip-tolyl-2-(4-(trifluoromethyl)phenyl)vinyl)(4-(trifluoromethyl)phenyl)sulfane (3j+4j)

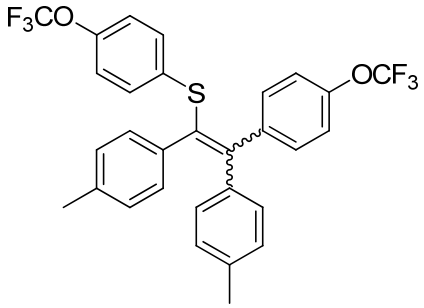


The reaction was conducted with sodium 4-(trifluoromethyl)benzenesulfinate (**1h**, 185.6 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 65.5 mg,

62% yield of **3j+4j** as light yellow solid. The ratio of **3j**/**4j** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53-7.51 (m, 1H), 7.40-7.31 (m, 4H), 7.24-7.07 (m, 7H), 6.92-6.82 (m, 4H), 2.35 (s, 1.5H = 0.25×6H), 2.25-2.21 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 189, 252, 336, 351 (100), 528; HRMS calcd. for: $C_{30}H_{22}F_6S$ [M]: 528.13409, found 528.13403.

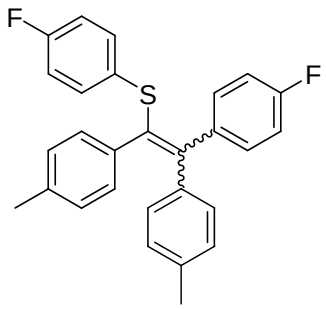
(1,2-Dip-tolyl-2-(4-(trifluoromethoxy)phenyl)vinyl)(4-(trifluoromethoxy)phenyl)sulfane (3k+4k)



The reaction was conducted with sodium 4-(trifluoromethoxy)benzenesulfinate (**1i**, 198.4 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 78.5 mg, 70% yield of **3k+4k** as light yellow oil. The ratio of **3k**/**4k** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.28 (m, 1H), 7.21-7.08 (m, 7H), 6.98-6.81 (m, 8H), 2.35 (s, 1.5H = 0.25×6H), 2.23-2.20 (m, 4.5H = 0.75×6H); HRMS calcd. for: $C_{30}H_{22}F_6O_2S$ [M]: 560.12392, found 560.12403.

(4-Fluorophenyl)(2-(4-fluorophenyl)-1,2-dip-tolylvinyl)sulfane (3l+4l)

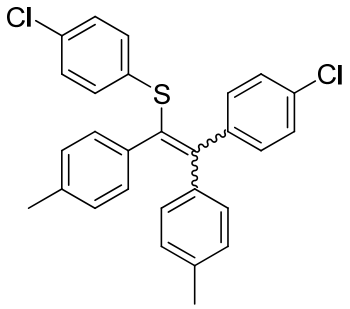


The reaction was conducted with sodium 4-fluorobenzenesulfinate (**1e**, 145.6 mg, 0.8 mmol) and

1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 58.3 mg, 68% yield of **3l+4l** as light yellow solid. The ratio of **3l**/**4l** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31-7.27 (m, 1H), 7.24-7.09 (m, 6H), 7.00-6.71 (m, 9H), 2.35 (s, 1.5H = 0.25×6H), 2.22-2.18 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 209, 270, 286, 301 (100), 428. HRMS calcd. for: $C_{28}H_{22}F_2S$ [M]: 428.14048, found 428.14017.

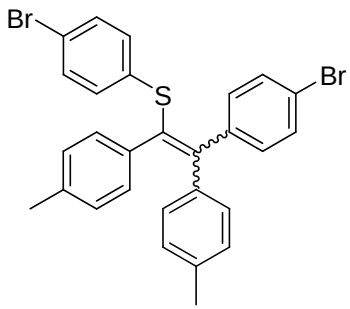
(4-Chlorophenyl)(2-(4-chlorophenyl)-1,2-dip-tolylvinyl)sulfane (3m+4m)



The reaction was conducted with sodium 4-chlorobenzenesulfinate (**1f**, 158.4 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 64.6 mg, 70% yield of **3m+4m** as light yellow solid. The ratio of **3m**/**4m** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.25-7.01 (m, 11H), 6.89-6.80 (m, 5H), 2.35 (s, 1.5H = 0.25×6H), 2.23-2.20 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 189, 252, 282, 317 (100), 460; HRMS calcd. for: $C_{28}H_{22}Cl_2S$ [M]: 460.08138, found 460.08134.

(4-Bromophenyl)(2-(4-bromophenyl)-1,2-dip-tolylvinyl)sulfane (3n+4n)

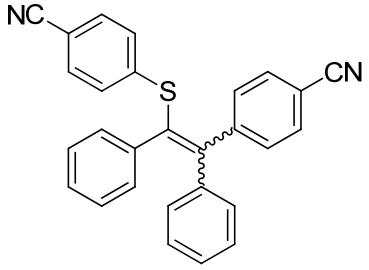


The reaction was conducted with sodium 4-bromobenzenesulfinate (**1j**, 194.4 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 79.3 mg, 72% yield of **3n+4n** as light yellow solid. The ratio of **3n**/**4n** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.42-7.40 (m, 1H), 7.22-7.11 (m, 8H), 7.01-6.99 (m, 2H), 6.89-6.80 (m, 5H), 2.35 (s, 1.5H = 0.25×6H), 2.23-2.21 (m, 4.5H = 0.75×6H); HRMS calcd. for: $C_{28}H_{22}Br_2S$ [M]: 549.97830, found 549.97816.

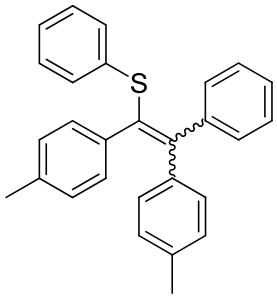
4-((2-(4-Cyanophenyl)-1,2-diphenylvinyl)thio)benzonitrile (3o+4o)



The reaction was conducted with sodium 4-cyanobenzenesulfinate (**1k**, 151.2 mg, 0.8 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 53.9 mg, 65% yield of **3o+4o** as light yellow oil. The ratio of **3o**/**4o** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61-7.27 (m, 10.4H), 7.22-6.92 (m, 7.65H); MS (EI) *m/z* (%) 77, 178, 252, 280 (100), 414.

Phenyl(2-phenyl-1,2-dip-tolylvinyl)sulfane (3p+4p)

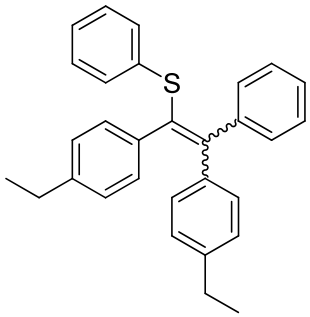


The reaction was conducted with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol) and 1,2-dip-tolylethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 55.7 mg, 71% yield of **3p+4p** as light yellow solid. The ratio of **3p**/**4p** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.26 (m, 2.5H), 7.22-6.98 (m, 11.5H), 6.86-6.80 (m,

4H), 2.33 (s, 1.5H = 0.25×6H), 2.22-2.15 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 91, 191, 253, 269, 392 (100); HRMS calcd. for: $C_{28}H_{25}S$ $[M+H]^+$: 393.16715, found 393.16687.

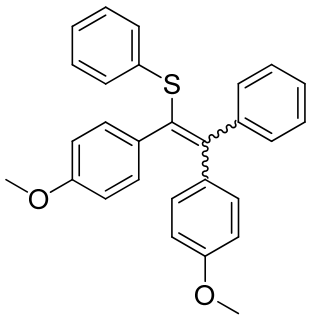
(1,2-Bis(4-ethylphenyl)-2-phenylvinyl)(phenyl)sulfane (3q+4q)



The reaction was conducted with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol) and 1,2-bis(4-ethylphenyl)ethyne (**2c**, 46.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 61.4 mg, 73% yield of **3q+4q** as light yellow solid. The ratio of **3q**/**4q** is 1:1.1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.27 (m, 2.7H), 7.23-6.99 (m, 11.41H), 6.87-6.82 (m, 3.9H), 2.64 (q, J = 8.0 Hz, 1.04H = 0.26×4H), 2.55-2.44 (m, 2.96H = 0.74×4H), 1.24 (t, J = 7.6 Hz, 1.56H = 0.26×6H), 1.16-1.07 (m, 4.44H = 0.74×6H); MS (EI) *m/z* (%) 253, 267, 282, 311, 420 (100); HRMS calcd. for: $C_{30}H_{29}S$ $[M+H]^+$: 421.19845, found 421.19769.

(1,2-Bis(4-methoxyphenyl)-2-phenylvinyl)(phenyl)sulfane (3r+4r)

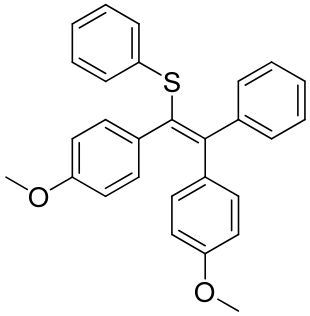


The reaction was conducted with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (**2d**, 47.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 57.7 mg, 68% yield of **3r+4r** as light yellow solid. The ratio of **3r**/**4r** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.27 (m, 3.01H), 7.24-6.81 (m, 12H), 6.62-6.53 (m, 3H),

3.79 (s, 1.5H = 0.25×6H), 3.72-3.67 (m, 4.5H = 0.75×6H).

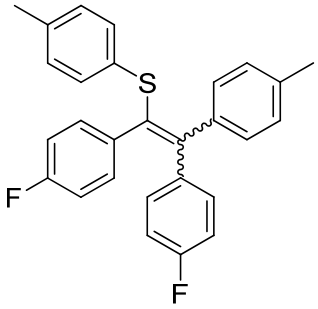
(*E*)-(1,2-Bis(4-methoxyphenyl)-2-phenylvinyl)(phenyl)sulfane (3r)



The reaction was conducted with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (**2d**, 47.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 28.9 mg, 34% yield of **3r** as light yellow solid, mp 151-152.5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.27 (m, 6H), 7.12-6.98 (m, 6H), 6.90-6.88 (m, 2H), 6.62-6.57 (m, 4H), 3.71 (s, J = 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.4, 158.2, 145.4, 144.4, 136.4, 135.2, 132.3, 132.1 131.9, 130.9, 129.6, 129.2, 128.4, 128.0, 127.7, 127.1, 125.5, 113.2, 55.09, 55.06; HRMS calcd. for: $C_{28}H_{25}O_2S$ $[M+H]^+$: 425.15698, found 425.15652.

(1,2-Bis(4-fluorophenyl)-2-p-tolylvinyl)(p-tolyl)sulfane (3s+4s)

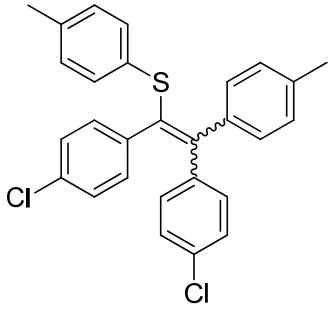


The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 142.4 mg, 0.8 mmol) and 1,2-bis(4-fluorophenyl)ethyne (**2e**, 42.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 61.7 mg, 72% yield of **3s+4s** as light yellow solid. The ratio of **3s**/**4s** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.27 (m, 1.97H), 7.23-6.69 (m, 14.03H), 2.35 (s, 1.5H = 0.25×6H), 2.23-2.21 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 91, 207, 290, 305, 428 (100). HRMS

calcd. for: $C_{28}H_{23}F_2S$ $[M+H]^+$: 429.14830, found 429.14813.

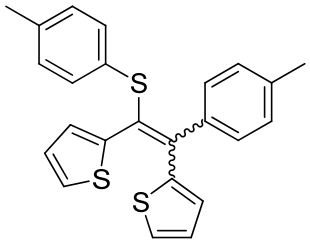
(1,2-Bis(4-chlorophenyl)-2-p-tolylvinyl)(p-tolyl)sulfane (3t+4t)



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 142.4 mg, 0.8 mmol) and 1,2-bis(4-chlorophenyl)ethyne (**2f**, 49.4 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 98:2) to provide 72.0 mg, 78% yield of **3t+4t** as light yellow solid. The ratio of **3t**/**4t** is 1:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.27 (m, 2.07H), 7.24-6.79 (m, 13.92H), 2.35 (s, 1.5H = 0.25×6H), 2.24-2.22 (m, 4.5H = 0.75×6H); MS (EI) *m/z* (%) 77, 207, 252 (100), 323, 432. HRMS calcd. for: $C_{28}H_{23}Cl_2S$ $[M+H]^+$: 461.08920, found 461.08909.

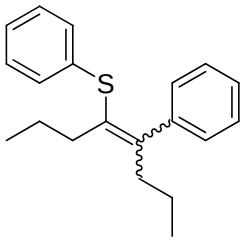
2,2'-(1-P-tolyl-2-(p-tolylthio)ethene-1,2-diyl)dithiophene (3u+4u)



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 142.4 mg, 0.8 mmol) and 1,2-di(thiophen-2-yl)ethyne (**2g**, 38.1 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to provide 41.3 mg, 51% yield of **3u+4u** as light yellow oil. The ratio of **3u**/**4u** is 1:1.5.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32-7.27 (m, 1.56H), 7.21-7.08 (m, 6.08H), 7.02-6.88 (m, 3.9H), 6.79-6.76 (m, 1.47H), 6.63-6.57 (m, 1H), 2.39 (s, 1.8H = 0.6×3H), 2.36 (s, 1.2H = 0.4×3H), 2.25-2.23 (m, 3H); MS (EI) *m/z* (%) 221, 248, 266, 281 (100), 404. HRMS calcd. for: $C_{24}H_{21}S_3$ $[M+H]^+$: 405.07999, found 405.07980.

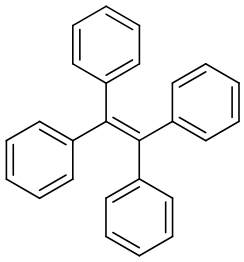
Phenyl(5-phenyloct-4-en-4-yl)sulfane (3v+4v)



The reaction was conducted with sodium benzenesulfinate (**1a**, 160 mg, 0.8 mmol) and oct-4-yne (**2h**, 29.3 μL, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 11.9 mg, 20% yield of **3v+4v** as light yellow oil. The ratio of **3v**/**4v** is 1.2:1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51-7.49 (m, 0.61H), 7.37-7.26 (m, 4.95H), 7.24-7.12 (m, 4.48H), 2.72 (t, J = 7.6 Hz, 1.1H = 0.275×4H), 2.51 (t, J = 7.6 Hz, 0.9H = 0.225×4H), 2.32 (t, J = 7.6 Hz, 0.9H = 0.225×4H), 1.98 (t, J = 7.4 Hz, 1.1H = 0.275×4H), 1.64-1.58 (m, 0.62H), 1.47-1.30 (m, 3.4H), 0.94-0.84 (m, 4.61H), 0.65 (t, J = 7.2 Hz, 1.41H); MS (EI) *m/z* (%) 91, 115, 129, 267, 296 (100).

1,1,2,2-Tetraphenylethene

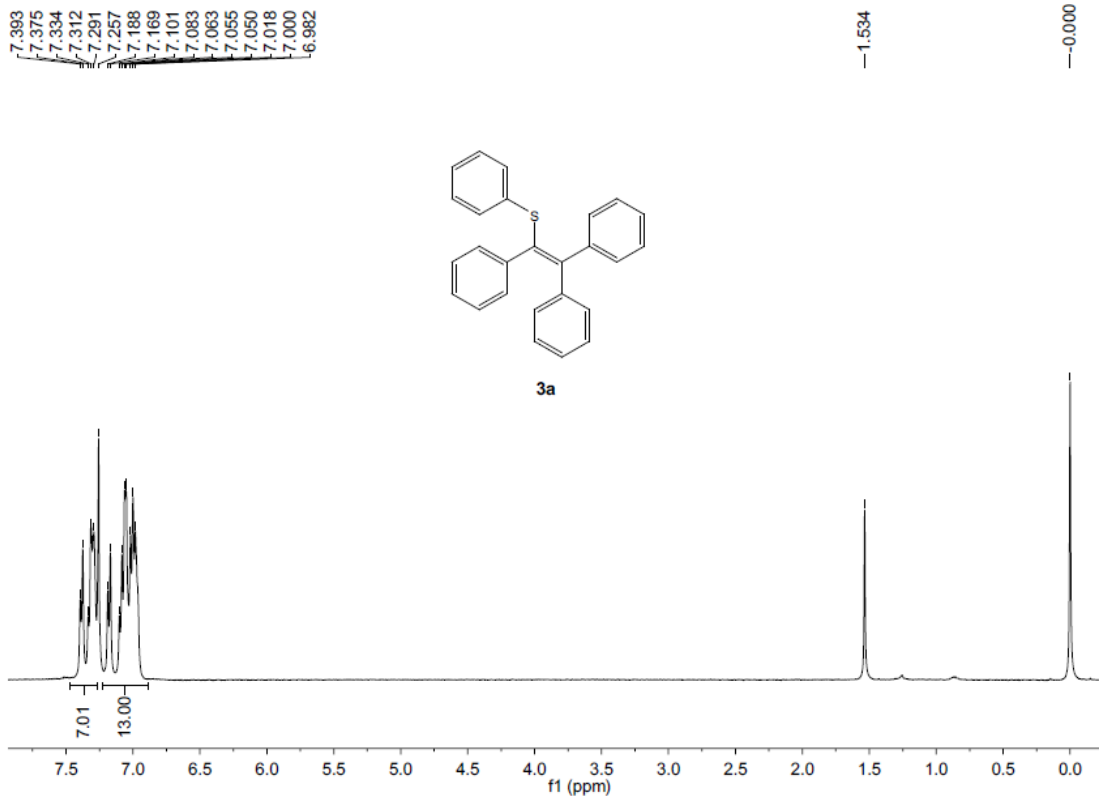


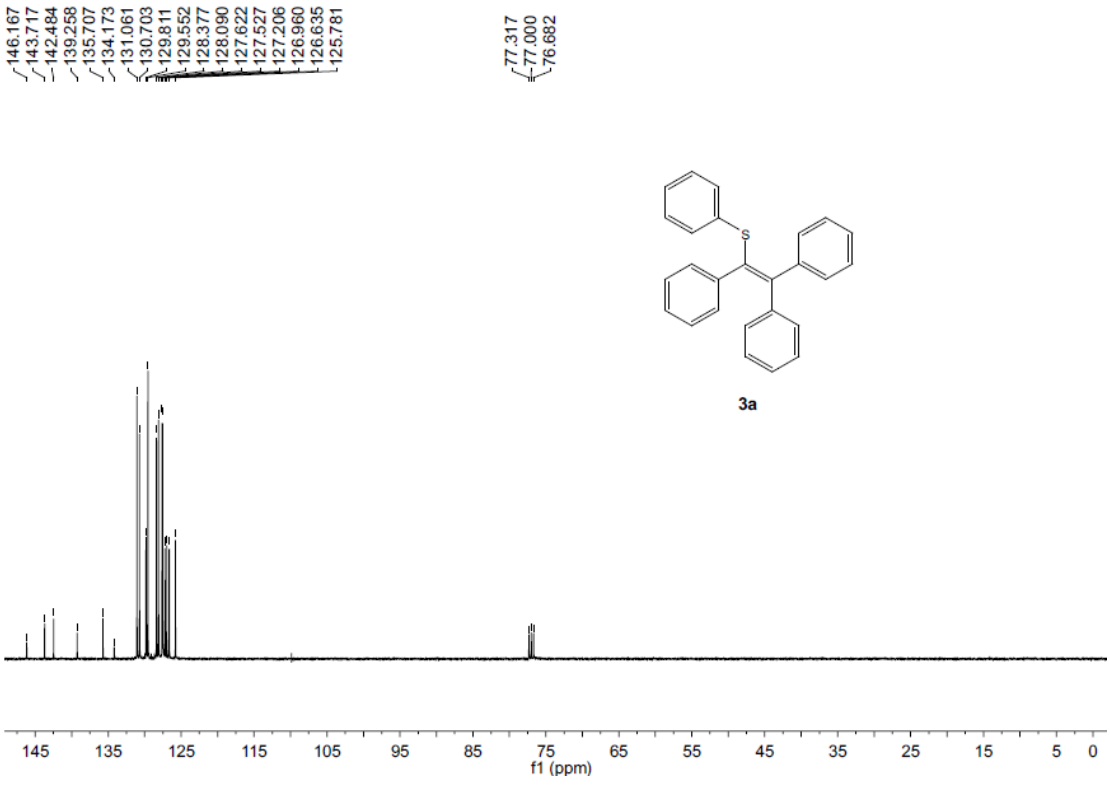
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.09-7.02 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 143.7, 141.1, 131.3, 127.6, 126.4; MS (EI) *m/z* (%) 77, 151, 239, 253, 332 (100).

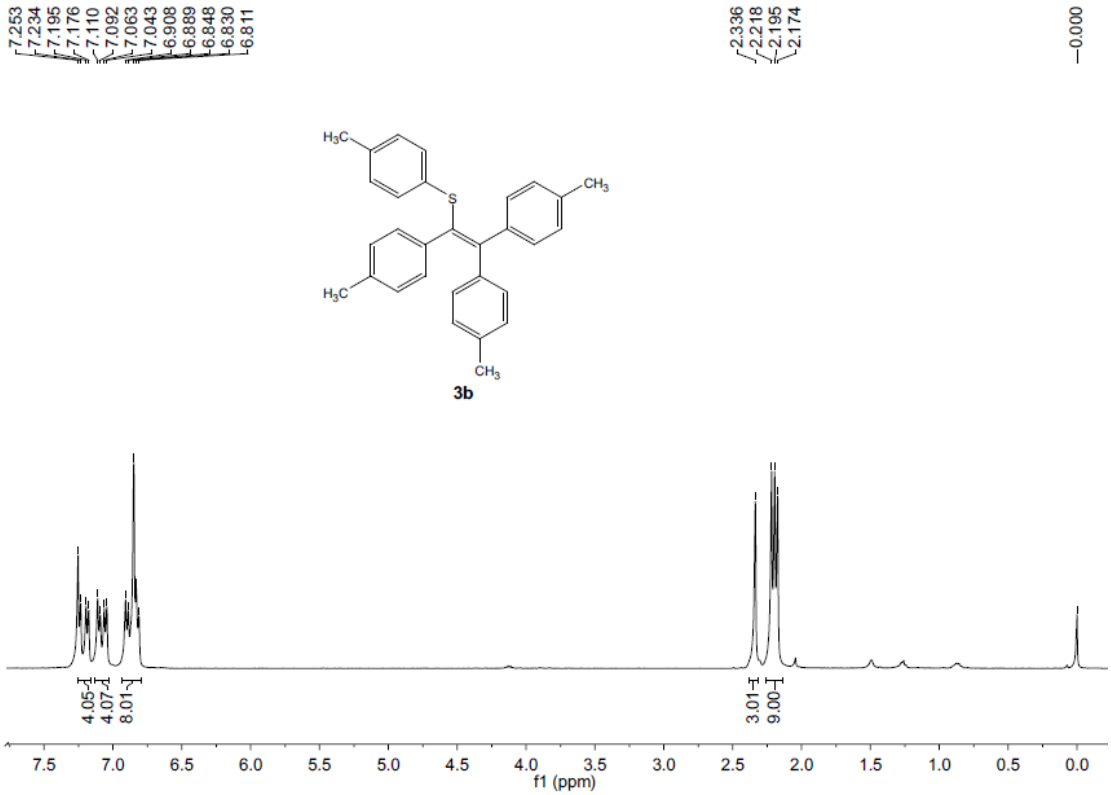
References

[1] A. Alfonso, G. Carlo, G. Patrizia, G. Alessandra, B.-Y. Michal, R. Zvi, Eur. J. Org. Chem. 2002, 13, 2136.

^{1}H and ^{13}C NMR spectra



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6.811
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2.218
2.195
2.174
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H3C
CH3
3b
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4.07
8.01
3.01
9.00
7.5
7.0
6.5
6.0
5.5
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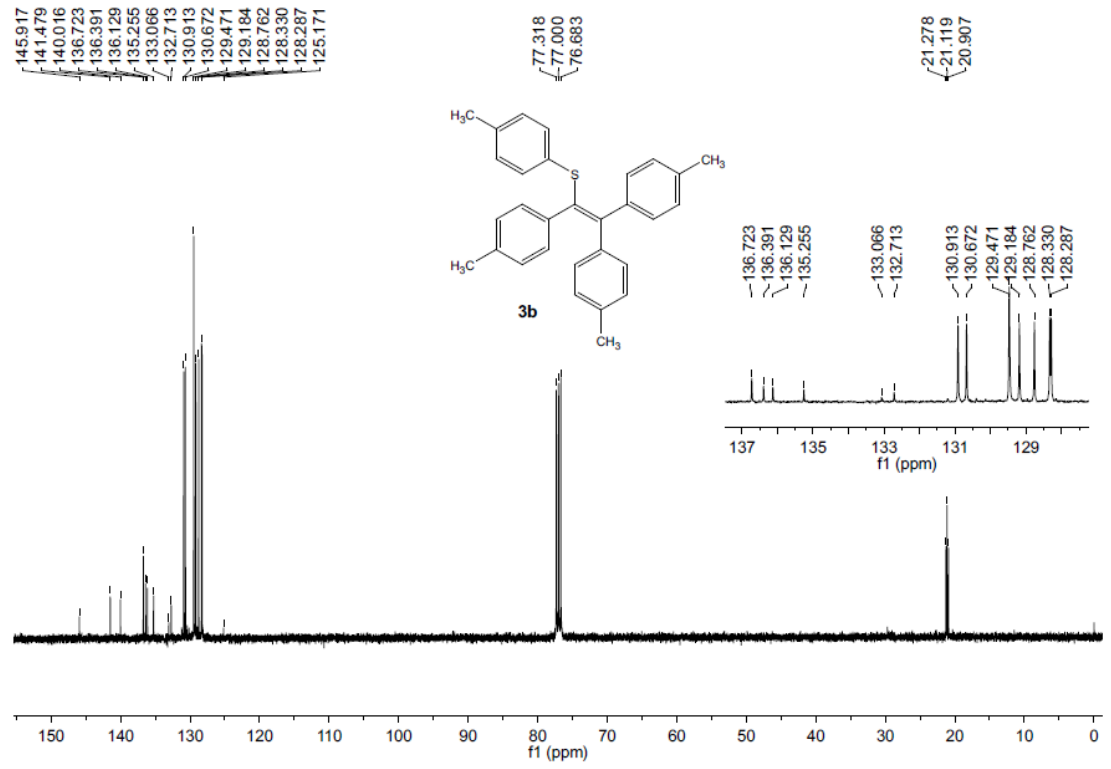
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S
CH3
H3C
CH3
3b
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136.391
136.129
135.255
133.066
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130.672
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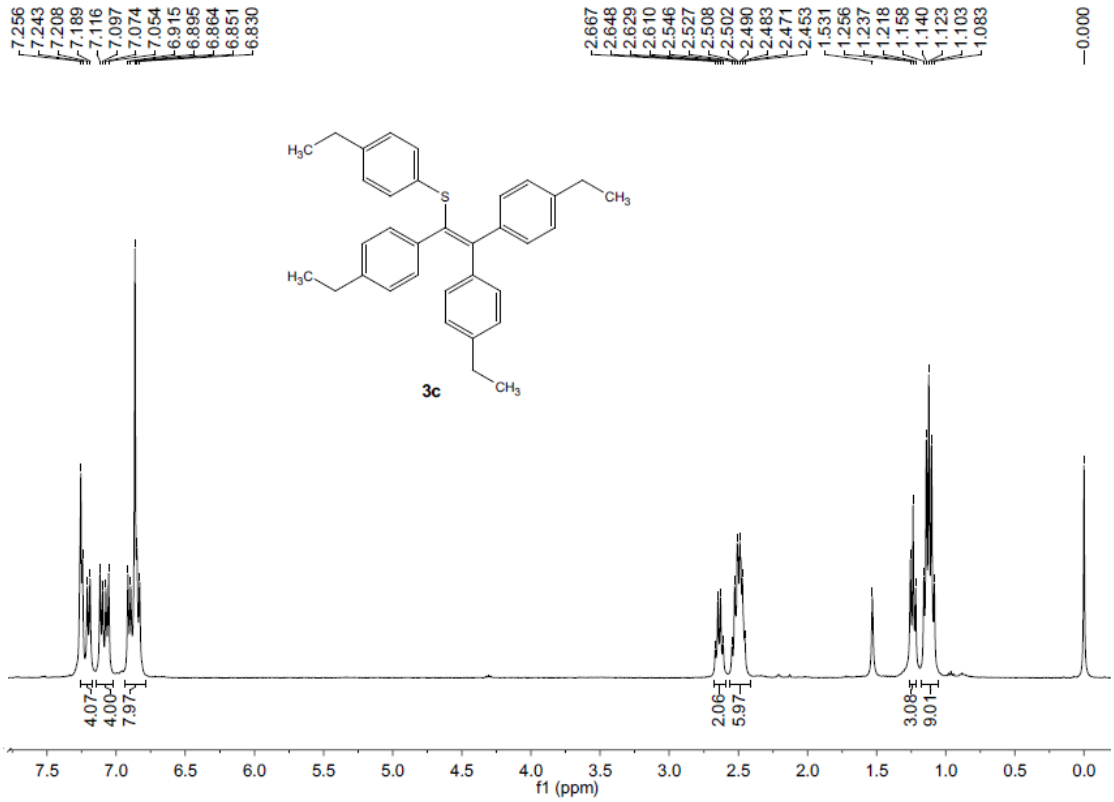
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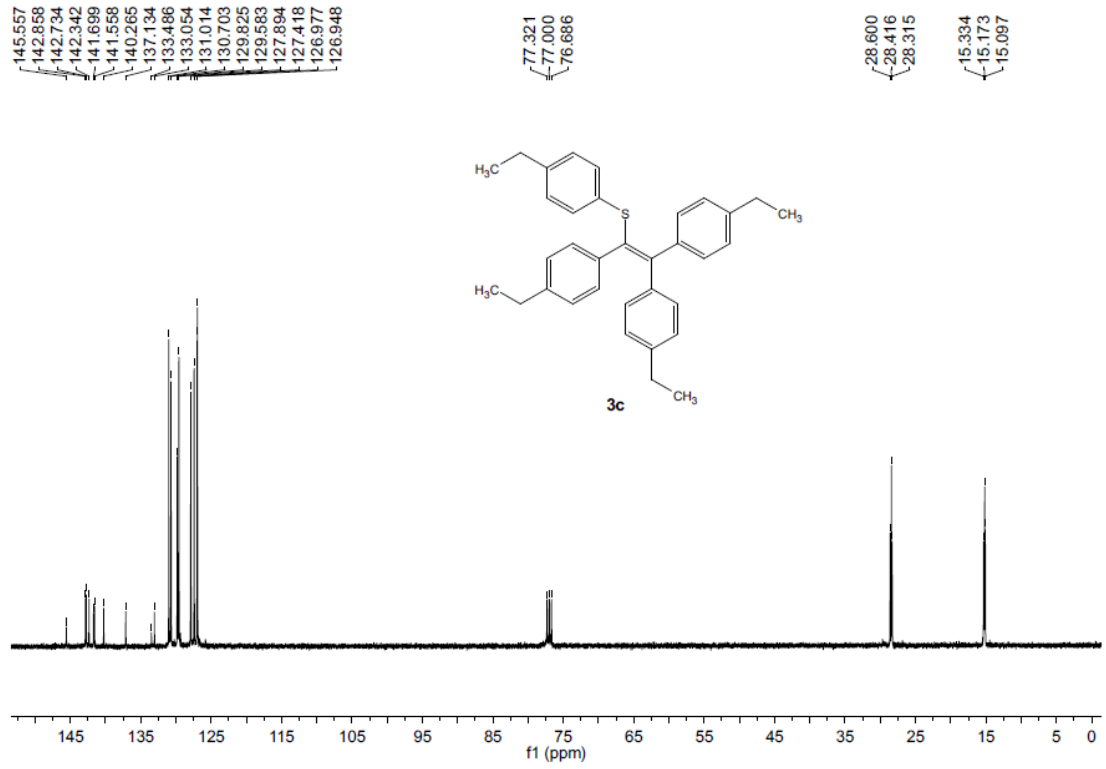
f1 (ppm)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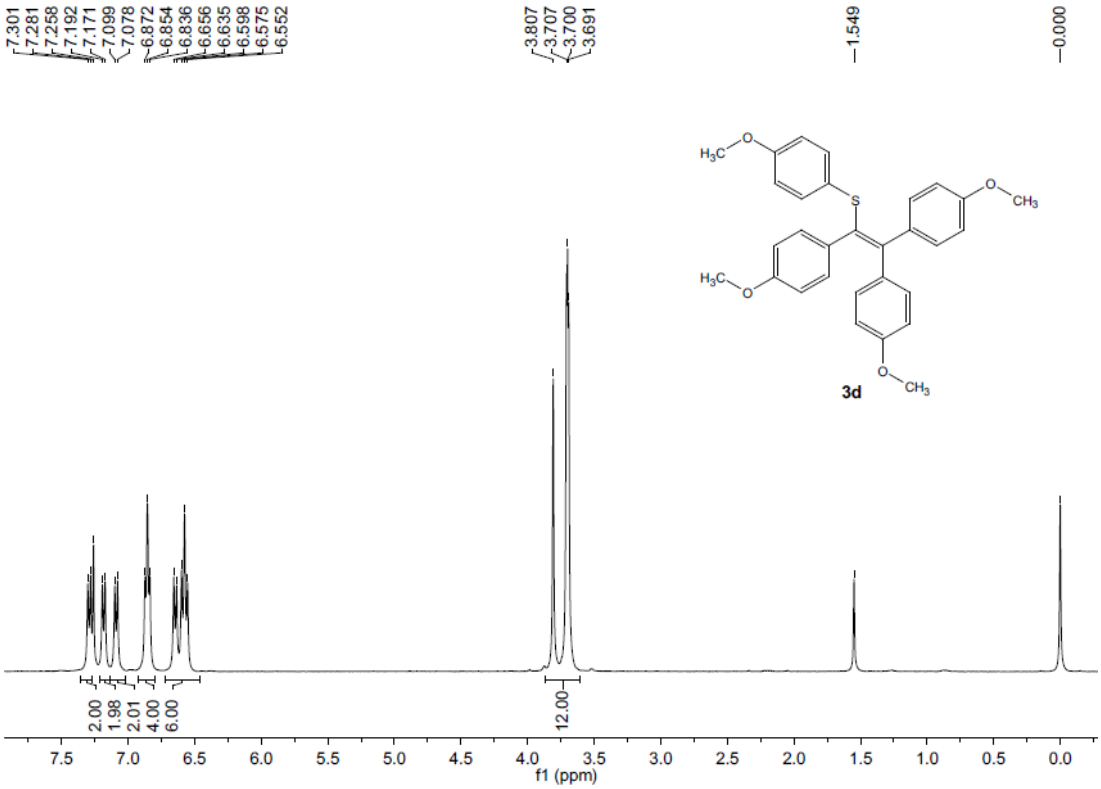
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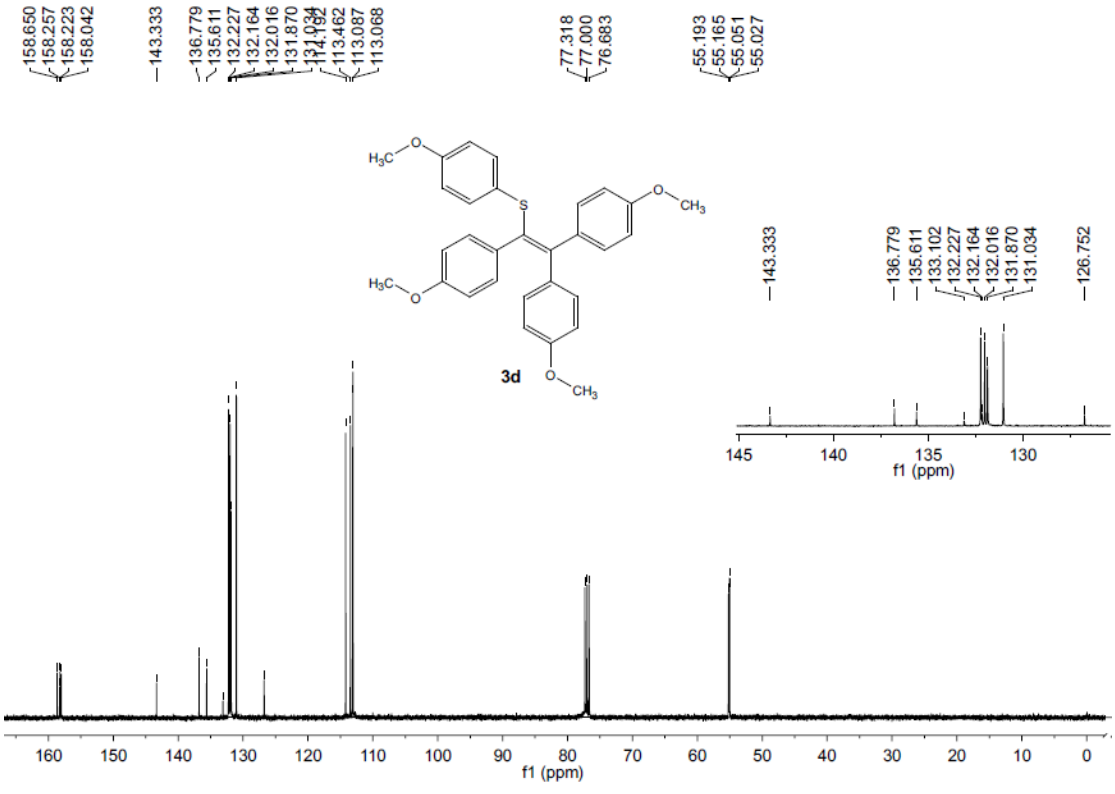
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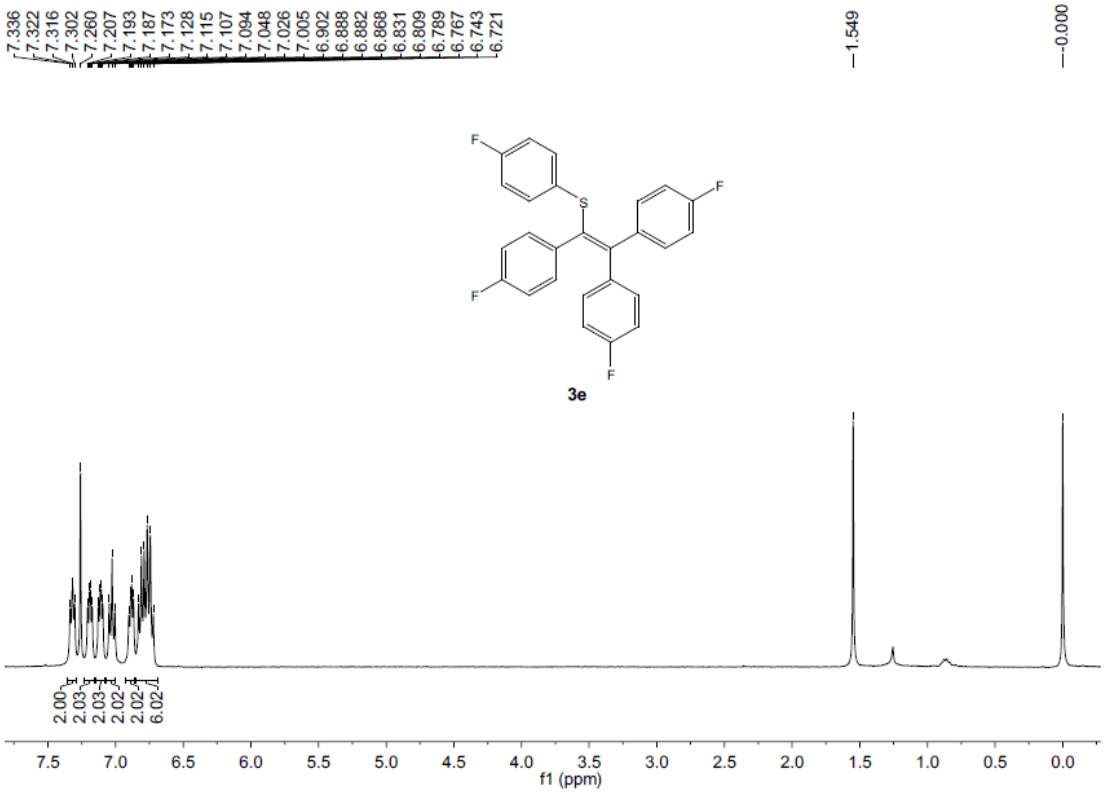
f1 (ppm)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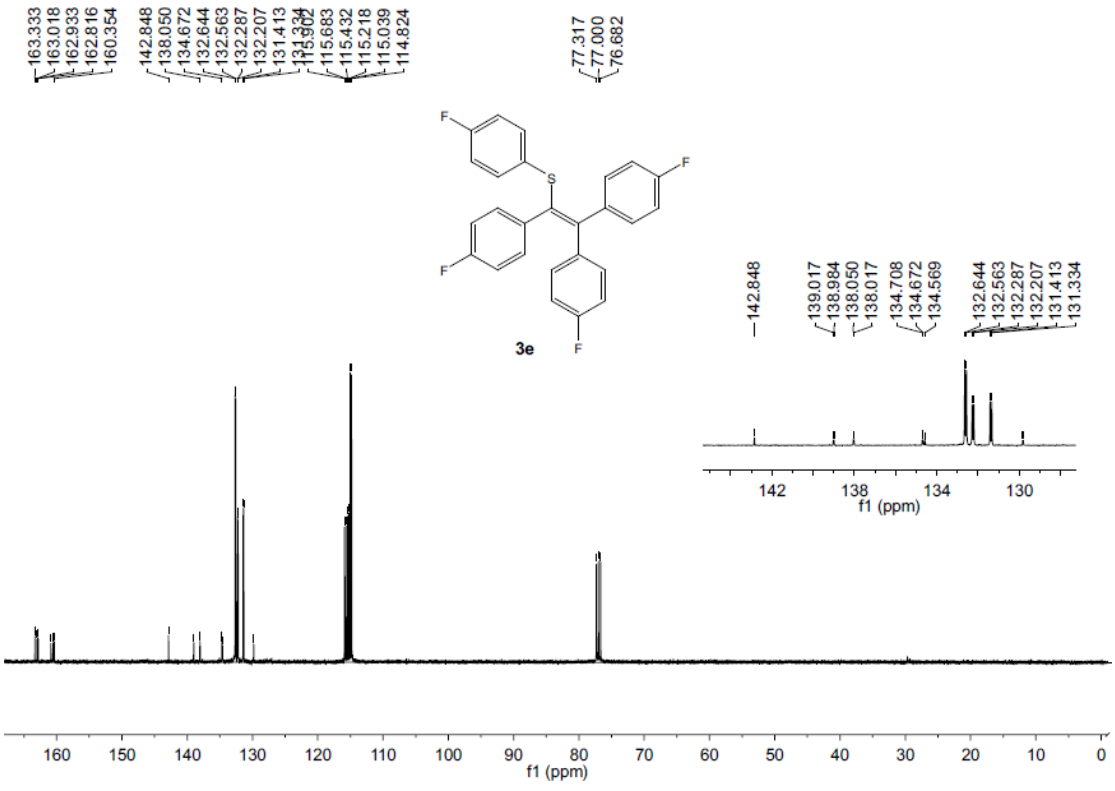
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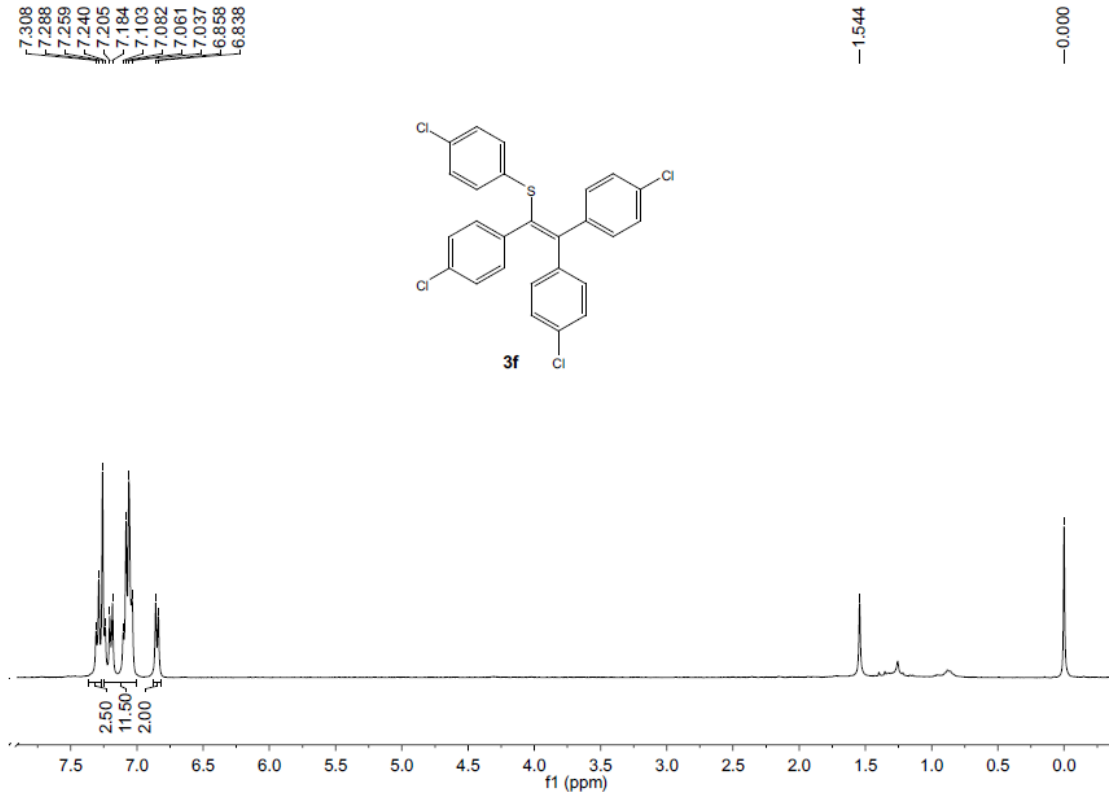
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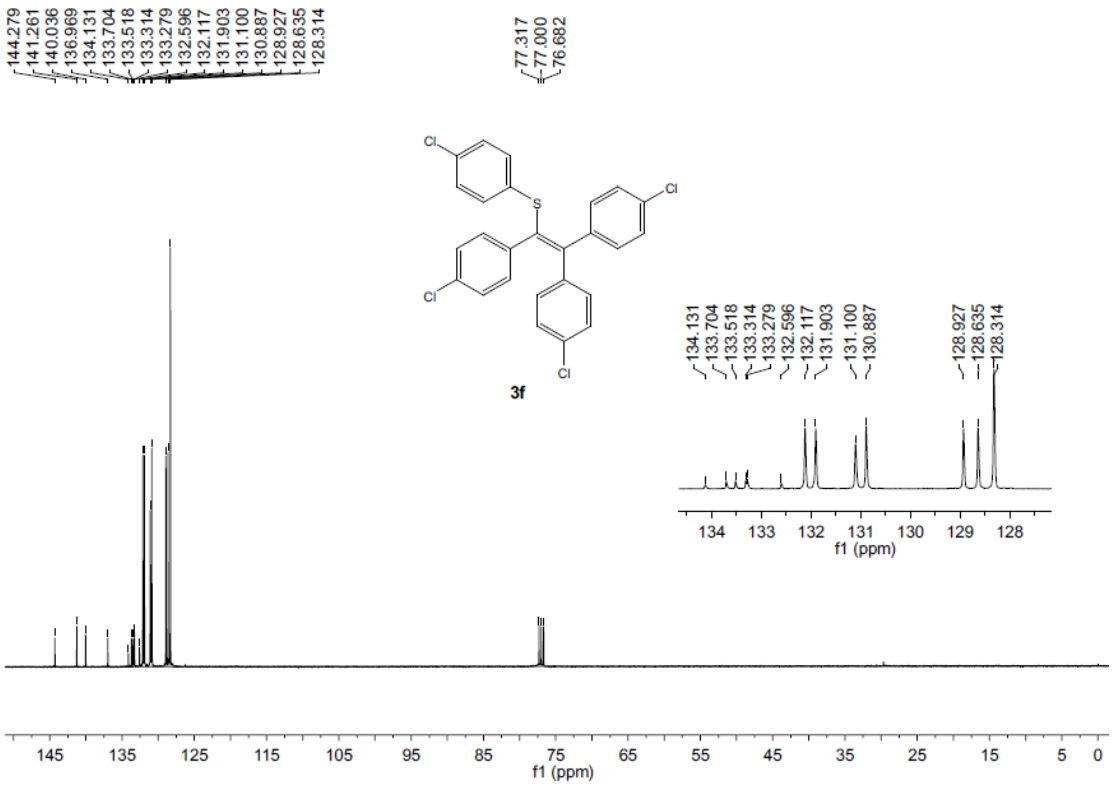
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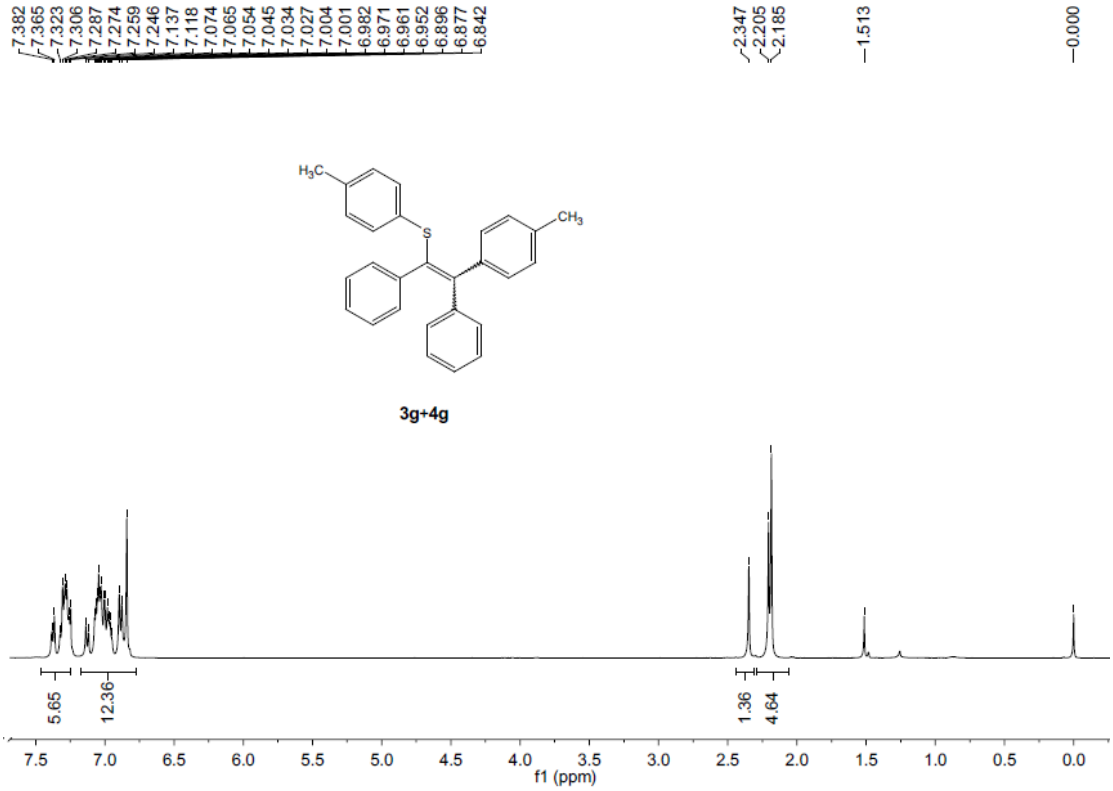
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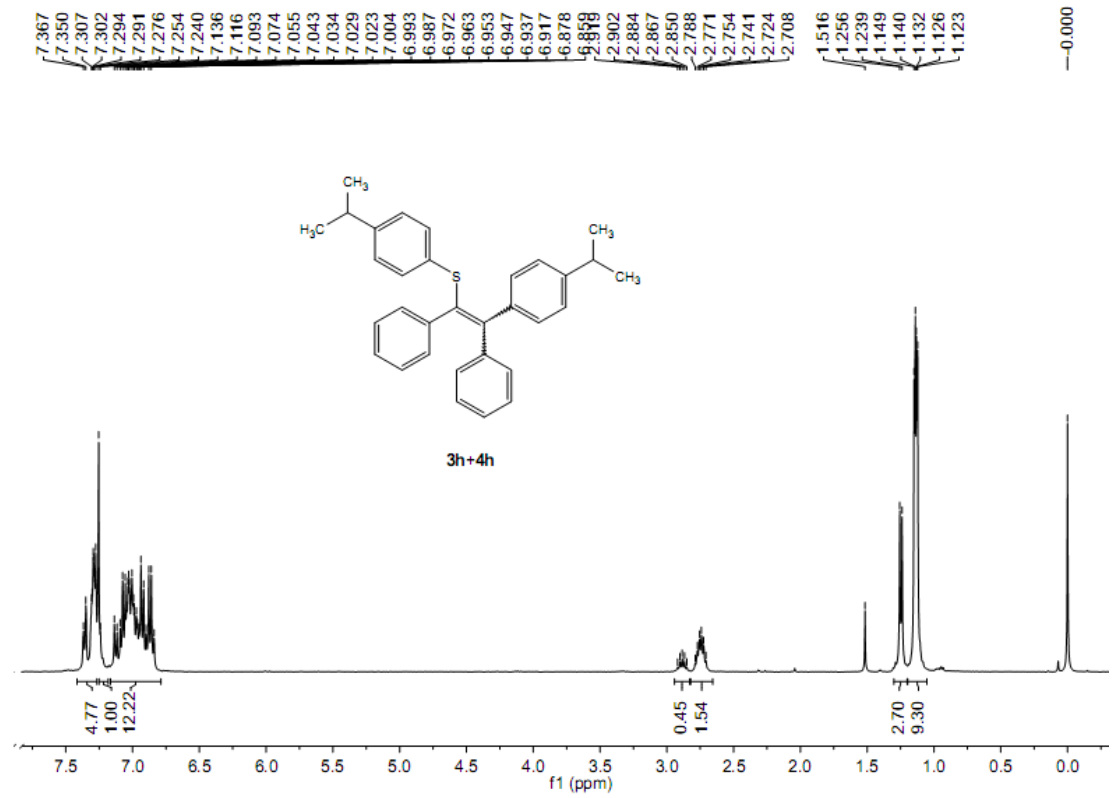
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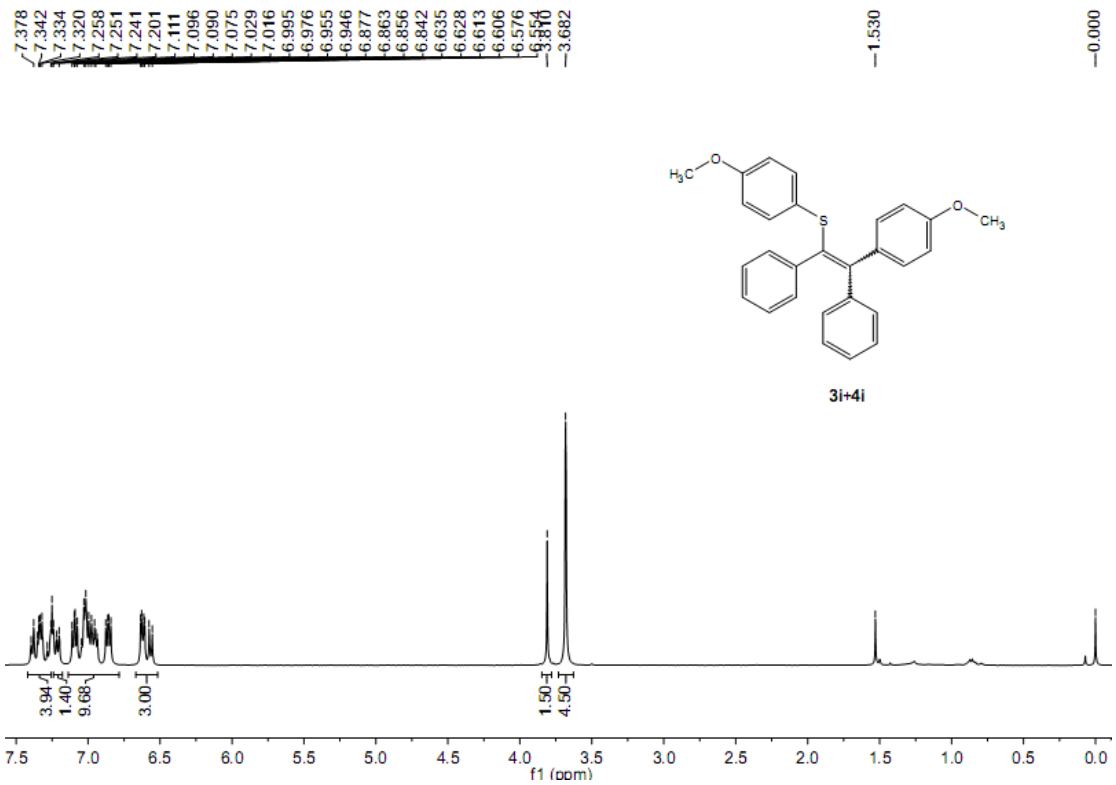
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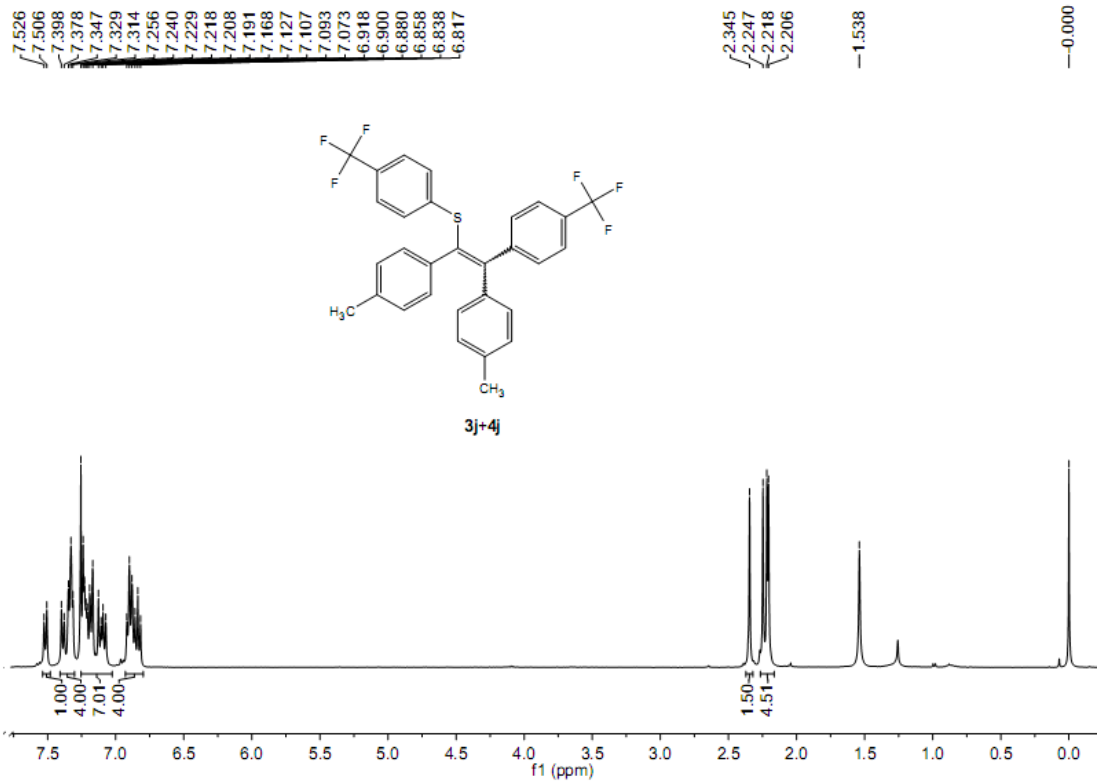
f1 (ppm)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7.191
7.168
7.127
7.107
7.093
7.073
6.918
6.900
6.880
6.858
6.838
6.817
2.345
2.247
2.218
2.206
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0.000
3j+4j
1.00
4.00
7.01
4.00
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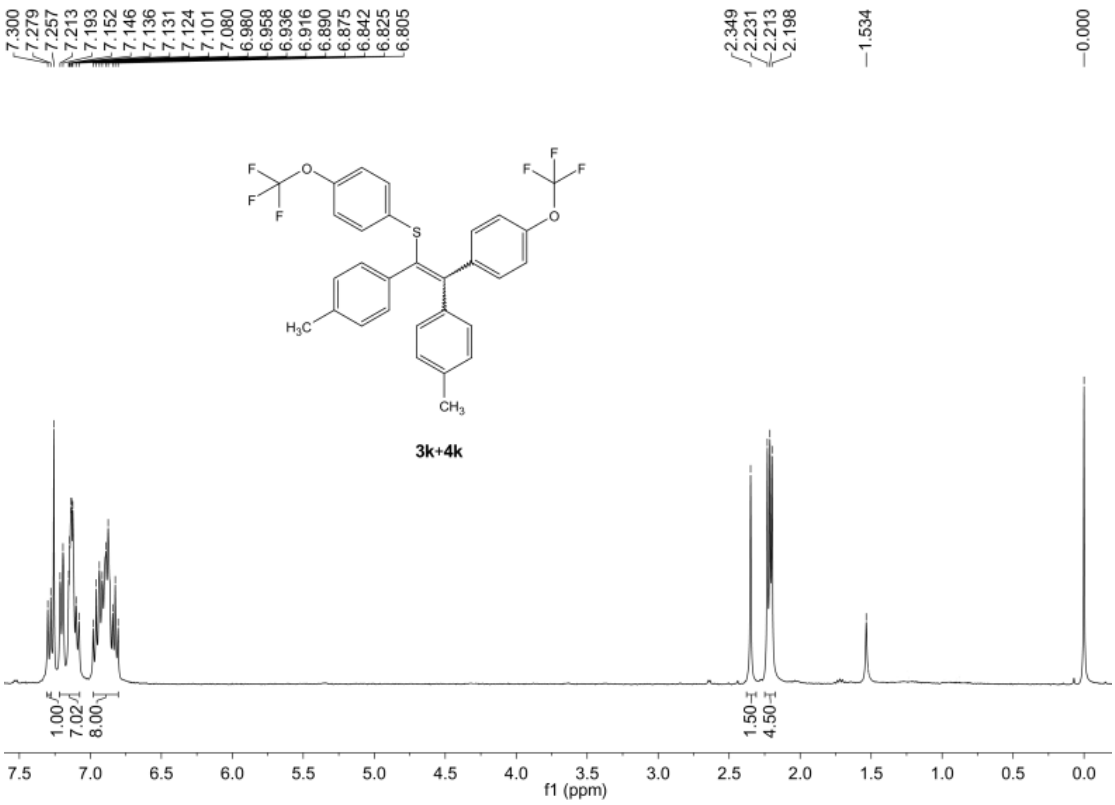
4.51
f1 (ppm)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7.124
7.101
7.080
6.980
6.958
6.936
6.916
6.890
6.875
6.842
6.825
6.805
2.349
2.231
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0.000
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1.00
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8.00
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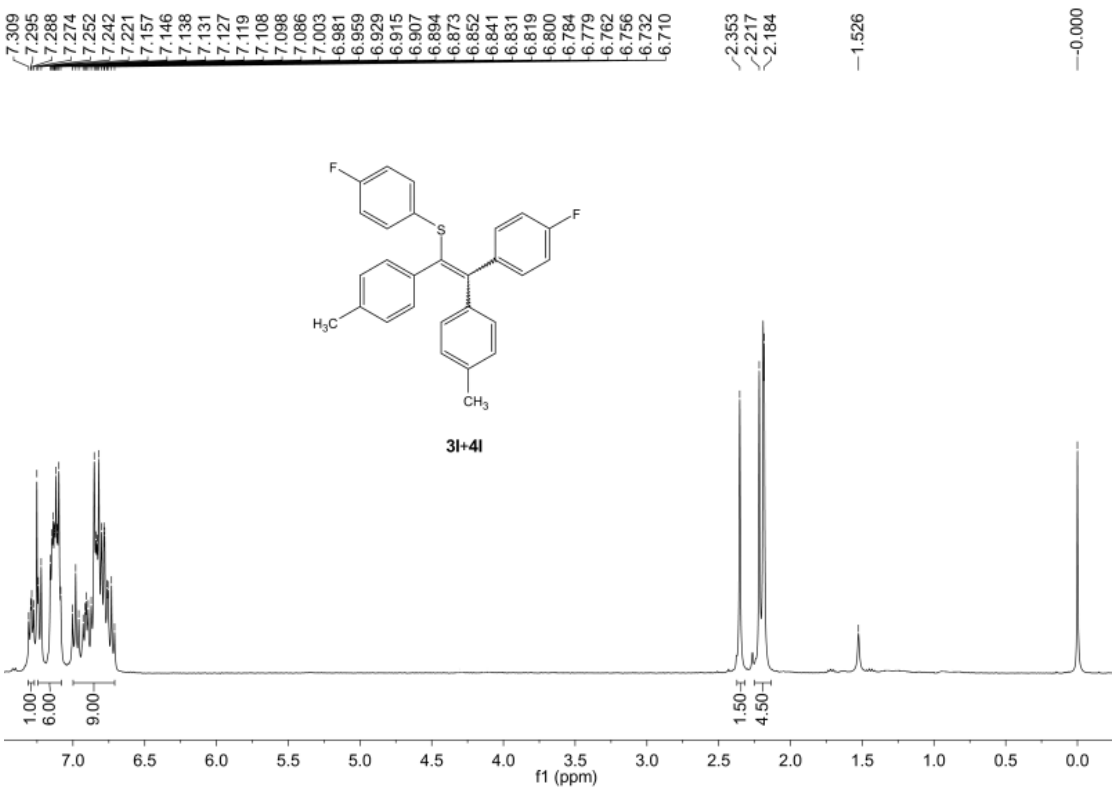
f1 (ppm)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7.138
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7.127
7.119
7.106
7.098
7.086
7.003
6.981
6.959
6.929
6.915
6.907
6.894
6.873
6.852
6.841
6.831
6.819
6.800
6.784
6.779
6.762
6.756
6.732
6.710
2.353
2.217
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0.000
3l+4l
1.00
6.00
9.00
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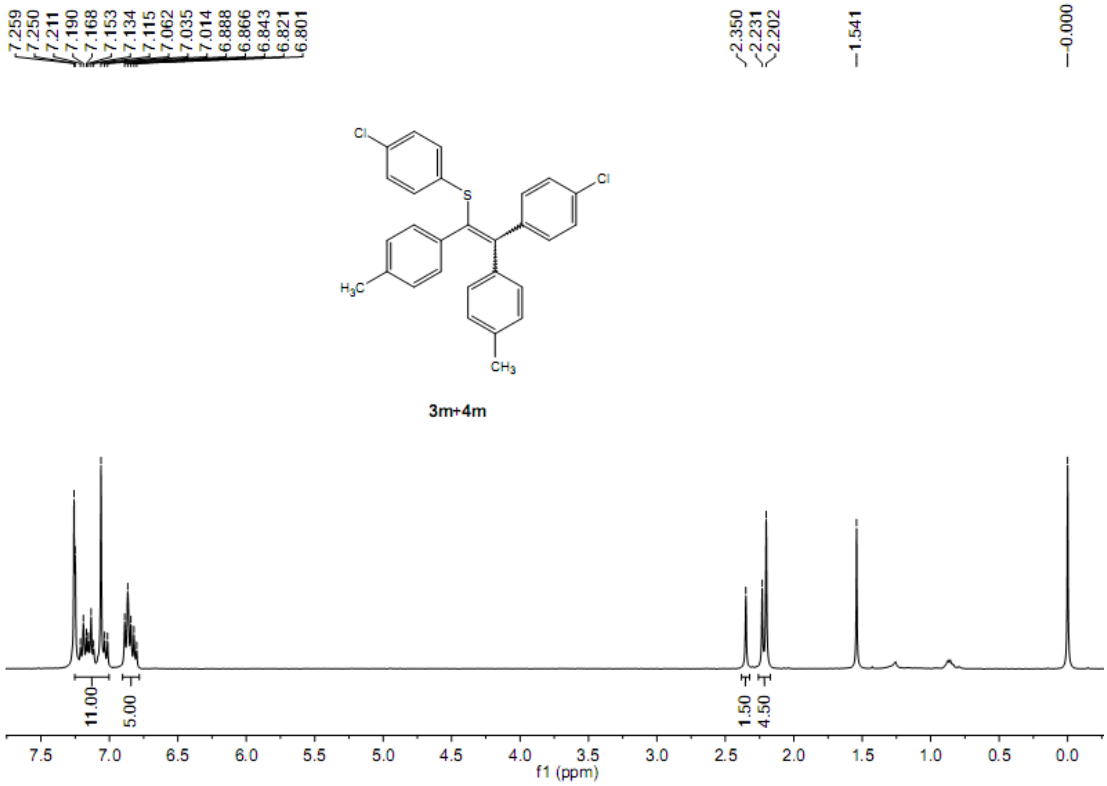
4.50
f1 (ppm)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7.115
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7.014
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6.866
6.843
6.821
6.801
2.350
2.231
2.202
1.541
0.000
Cl
S
Cl
H3C
CH3
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5.00
1.50
4.50
7.5
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6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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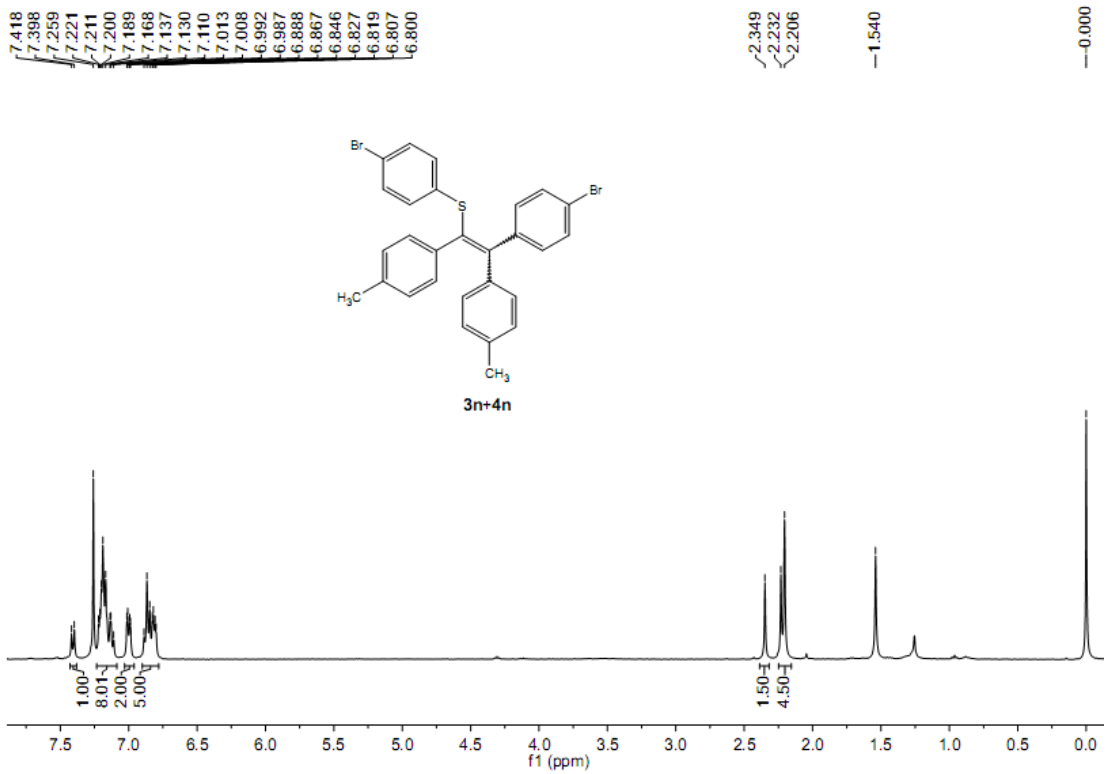
0.5
0.0
f1 (ppm)

3m+4m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7.130
7.110
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6.888
6.867
6.846
6.827
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S
Br
H3C
CH3
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5.00
1.50
4.50
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7.0
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6.0
5.5
5.0
4.5
4.0
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3.0
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2.0
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1.0
0.5
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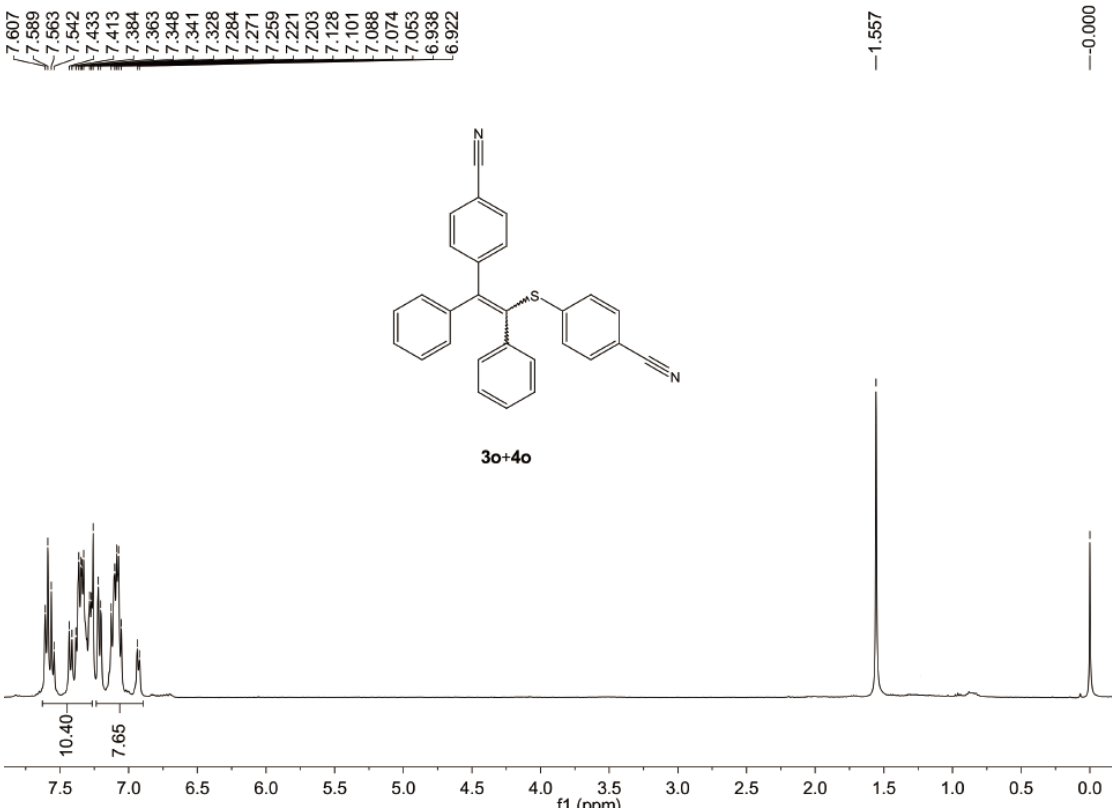
f1 (ppm)

3n+4n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7.341
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7.271
7.259
7.221
7.203
7.128
7.101
7.088
7.074
7.053
6.938
6.922
1.557
0.000
N
S
N
3o+4o
10.40
7.65
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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3.0
2.5
2.0
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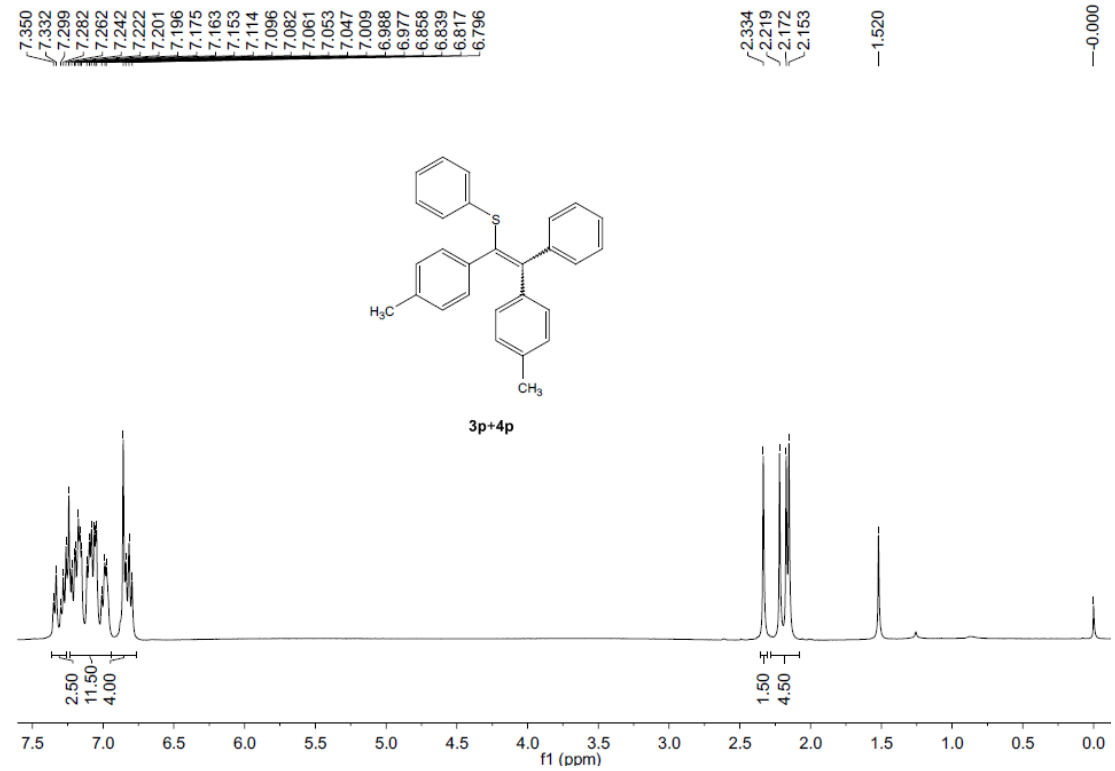
1.0
0.5
0.0
f1 (ppm)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7.242
7.222
7.201
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7.175
7.163
7.153
7.114
7.096
7.082
7.061
7.053
7.047
7.009
6.988
6.977
6.858
6.839
6.817
6.796
2.334
2.219
2.172
2.153
1.520
0.000
S
H3C
CH3
3p+4p
2.50
11.50
4.00
1.50
4.50
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
1.0
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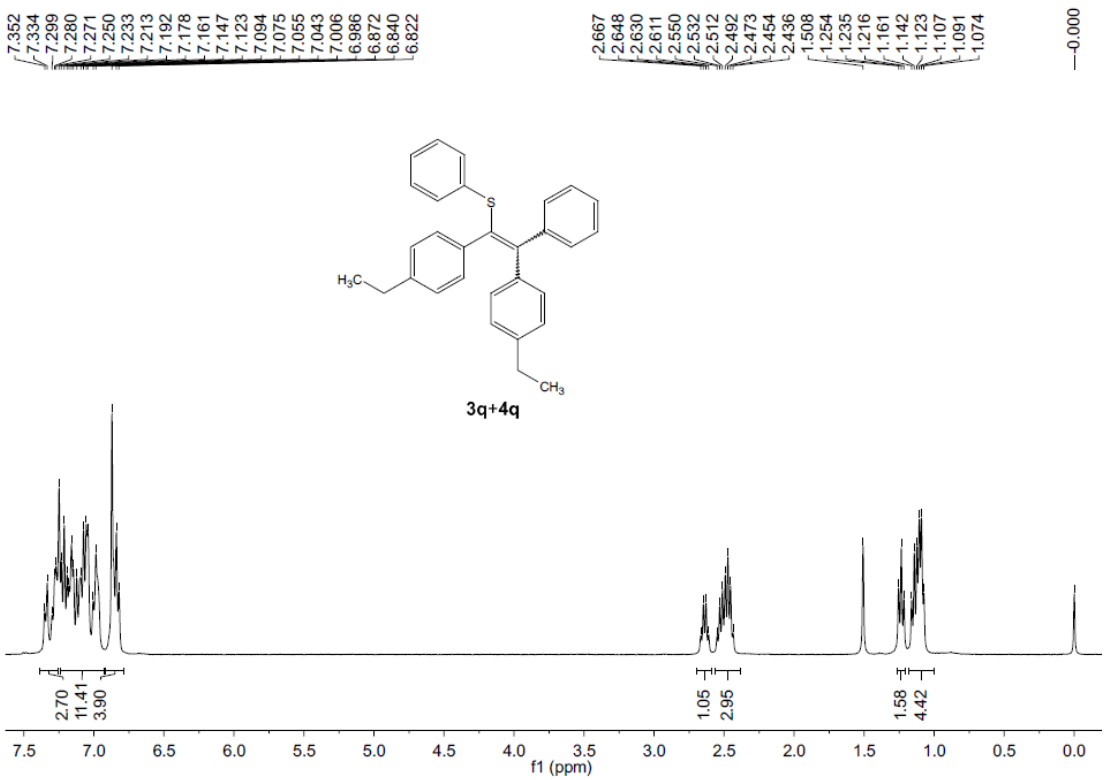
0.0
f1 (ppm)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7.233
7.213
7.192
7.178
7.161
7.147
7.123
7.094
7.075
7.055
7.043
7.006
6.986
6.872
6.840
6.822
2.667
2.648
2.630
2.611
2.550
2.532
2.512
2.492
2.473
2.454
2.436
1.508
1.254
1.235
1.216
1.161
1.142
1.123
1.107
1.091
1.074
0.000
S
H3C
CH3
3q+4q
2.70
11.41
3.90
1.05
2.95
1.58
4.42
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2.0
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1.0
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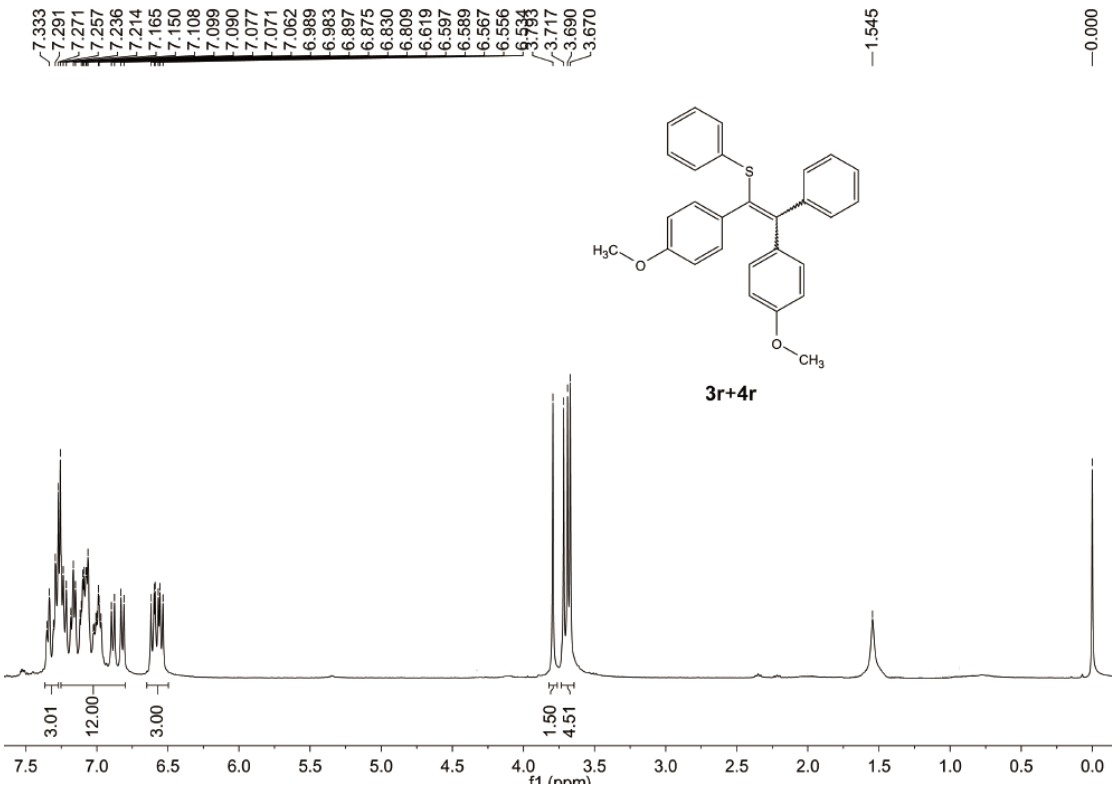
f1 (ppm)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7.062
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6.983
6.897
6.875
6.830
6.809
6.619
6.597
6.589
6.567
6.556
3.717
3.690
3.670
1.545
0.000
S
H3C
O
O
CH3
3r+4r
3.01
12.00
3.00
1.50
4.51
7.5
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6.5
6.0
5.5
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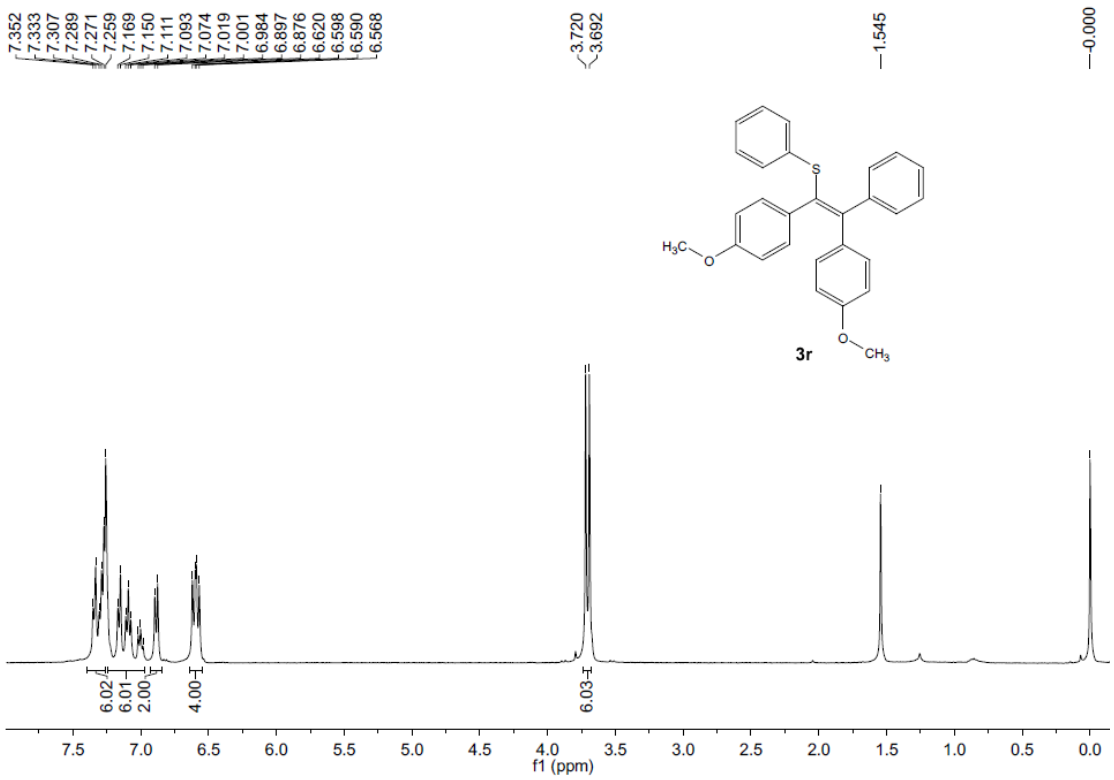
0.0
f1 (ppm)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7.074
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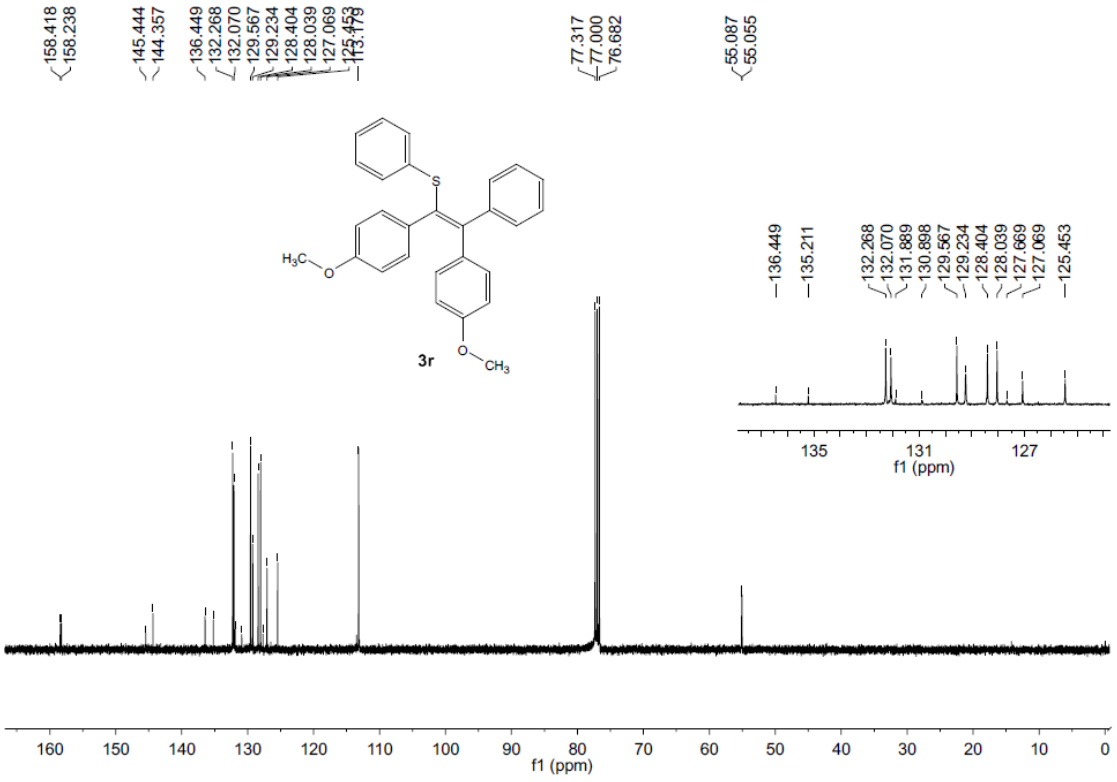
f1 (ppm)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77.000
76.682
55.087
55.055
3r
136.449
135.211
132.268
132.070
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130.898
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135
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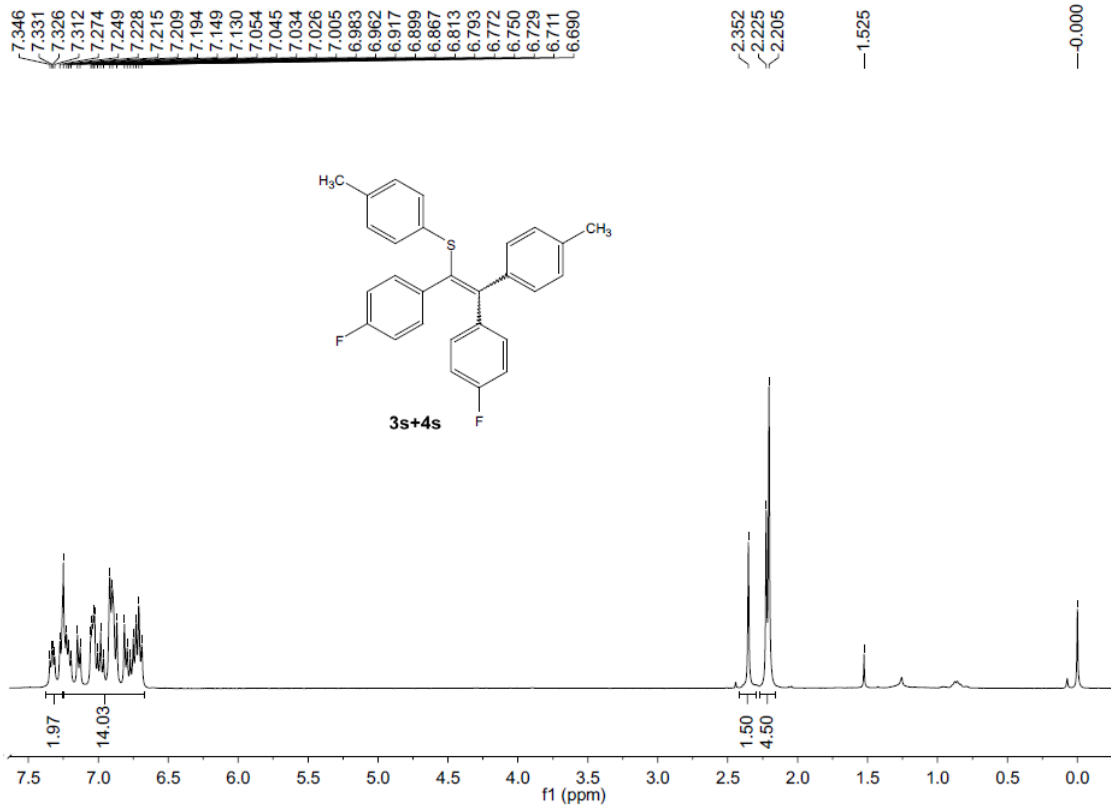
127
f1 (ppm)
f1 (ppm)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7.045
7.034
7.026
7.005
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6.962
6.917
6.899
6.867
6.813
6.793
6.772
6.750
6.729
6.711
6.690
2.352
2.225
2.205
1.525
0.000
H3C
CH3
S
F
F
3s+4s
1.97
14.03
1.50
4.50
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6.5
6.0
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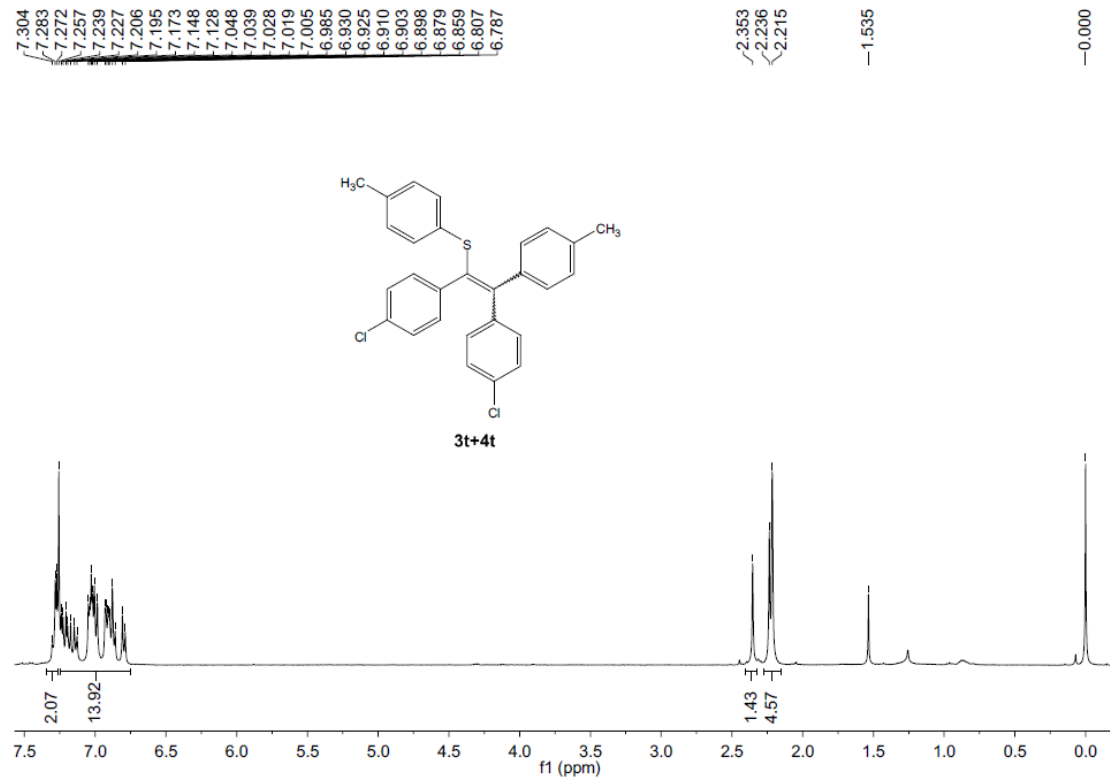
1.0
0.5
0.0
f1 (ppm)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7.272
7.257
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7.227
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7.195
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7.039
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7.019
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6.859
6.807
6.787
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2.215
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0.000
H3C
CH3
S
Cl
Cl
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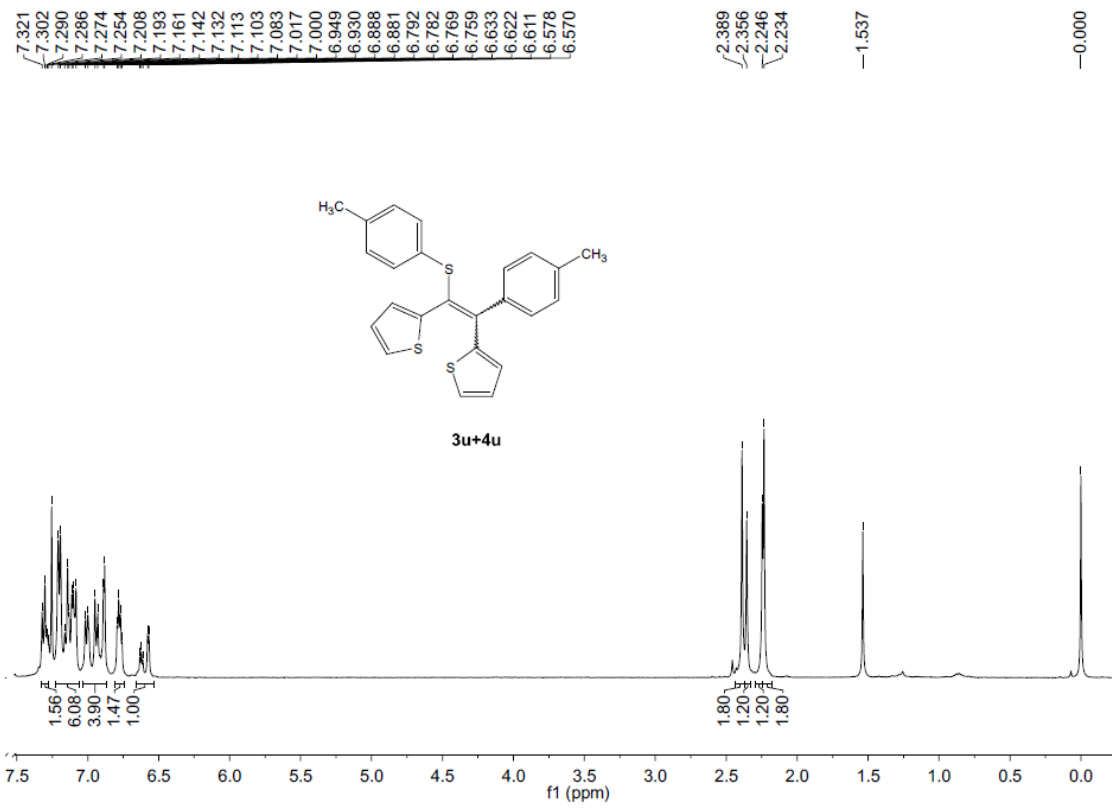
f1 (ppm)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6.792
6.782
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6.633
6.622
6.611
6.578
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2.246
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1.537
0.000
H3C
CH3
S
S
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3u+4u
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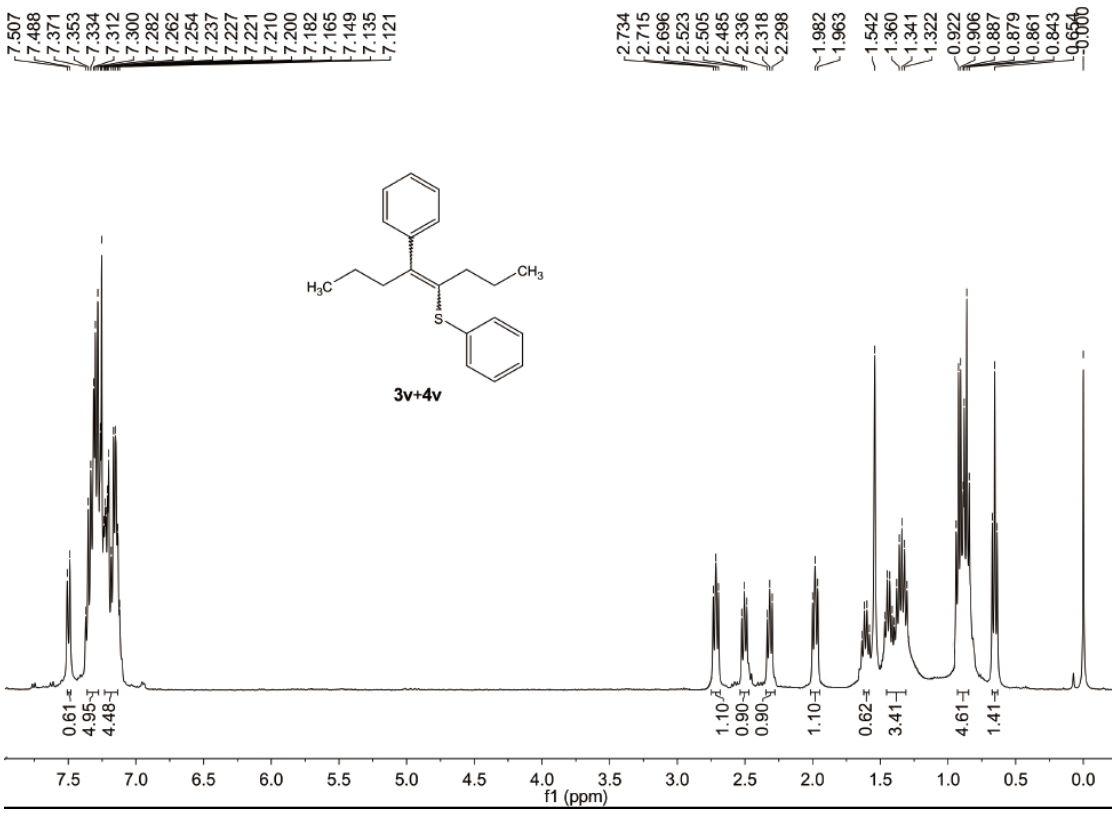
f1 (ppm)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7.210
7.200
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7.149
7.135
7.121
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2.696
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2.505
2.485
2.336
2.318
2.298
1.982
1.963
1.542
1.360
1.341
1.322
0.922
0.906
0.887
0.879
0.861
0.843
0.654
0.000
H3C
CH3
S
3v+4v
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4.95
4.48
1.10
0.90
0.90
1.10
0.62
3.41
4.61
1.41
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6.5
6.0
5.5
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4.5
4.0
3.5
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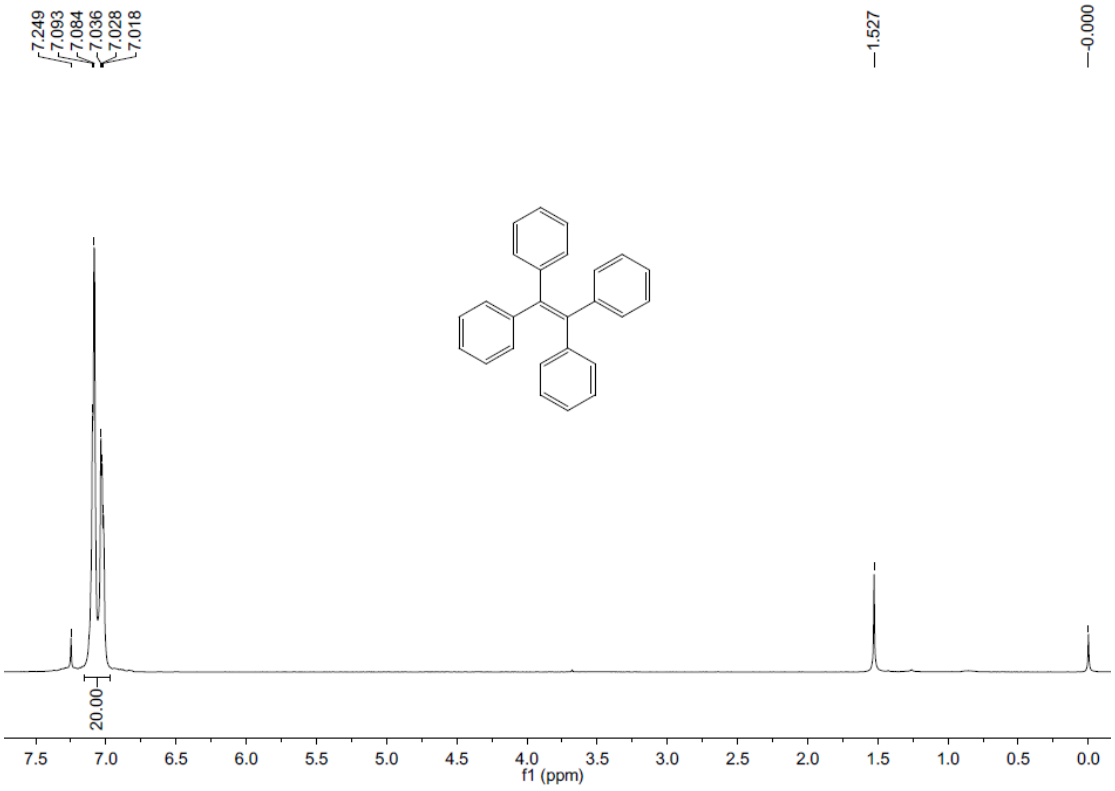
f1 (ppm)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6.0
5.5
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3.5
3.0
2.5
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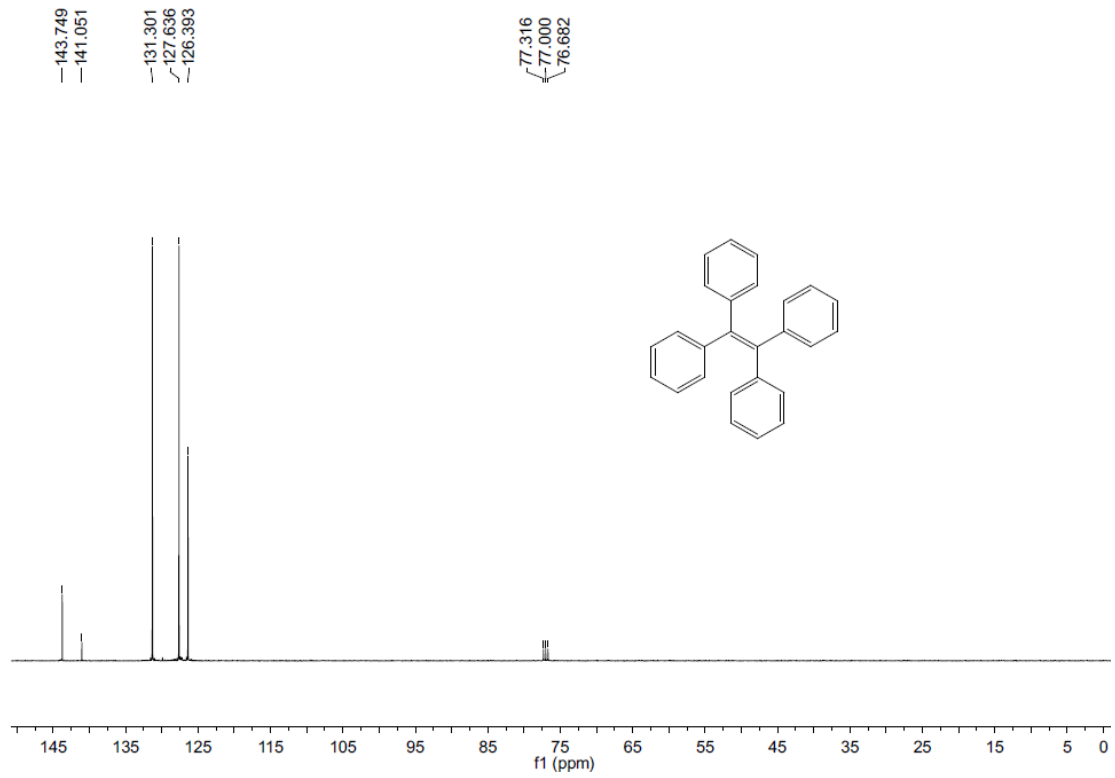
1.5
1.0
0.5
0.0
f1 (ppm)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145
135
125
115
105
95
85
75
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35
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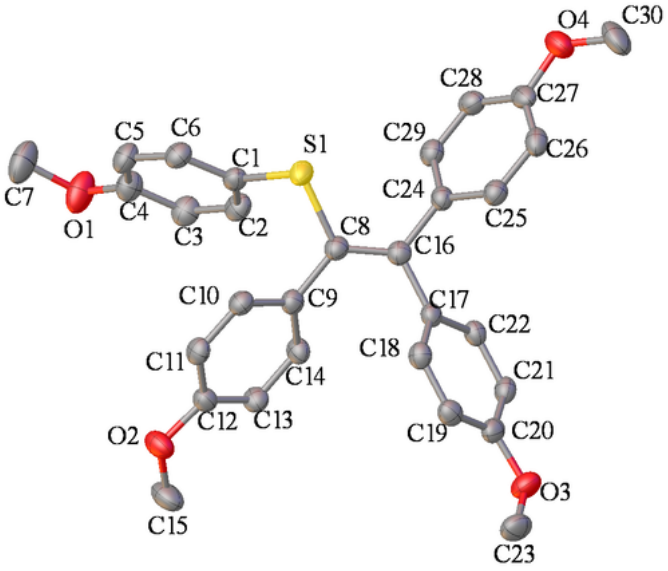
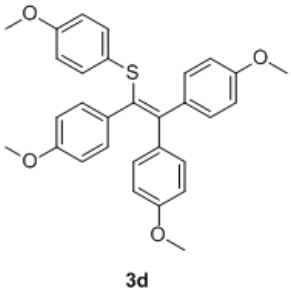
f1 (ppm)

X-ray crystallographic structures of 3d and 3q

X-ray crystallographic structures of 3d



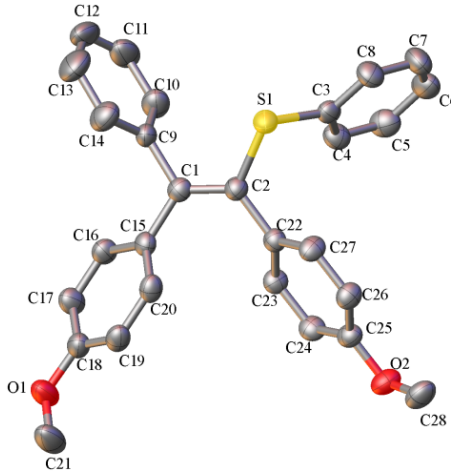


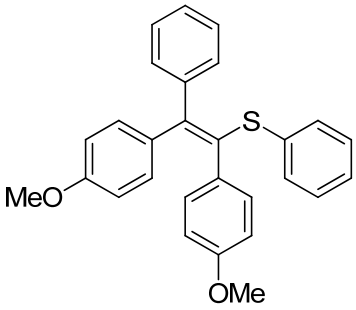
3d

Table 1. Crystal data and structure refinement for **3d**.

Identification code	**3d**
Empirical formula	$C_{30}H_{28}O_4S$
Formula weight	484.58
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.694(3) Å α = 90°. b = 9.672(3) Å β = 95.745(3)°. c = 27.021(8) Å γ = 90°.
Volume	2520.8(12) $Å^3$
Z, Calculated density	4, 1.277 Mg/m^3
Absorption coefficient	0.163 mm^{-1}
F(000)	1024
Crystal size	0.29 x 0.27 x 0.19 mm
Theta range for data collection	3.02 to 27.46°.
Limiting indices	-11<=h<=12, -12<=k<=12, -35<=l<=35
Reflections collected / unique	17290 / 5749 [R(int) = 0.0465]
Completeness to theta = 27.46	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6142
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5749 / 0 / 320
Goodness-of-fit on F^2	1.181
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1406
R indices (all data)	R1 = 0.0790, wR2 = 0.1459
Largest diff. peak and hole	0.376 and -0.315 e. $Å^3$

X-ray crystallographic structures of 3q





3q

Table 1. Crystal data and structure refinement for **3q**.

Identification code	**3q**	
Empirical formula	$C_{28}H_{24}O_2S$	
Formula weight	424.53	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 5.9048(14) Å	α= 90°.
	b = 20.852(5) Å	β= 94.460(4)°.
	c = 9.218(2) Å	γ = 90°.
Volume	1131.6(4) $Å^3$	
Z, Density (calculated)	2, 1.246 Mg/m^3	
Absorption coefficient	0.165 mm^{-1}	
F(000)	448	
Crystal size	0.22 x 0.15 x 0.1 mm^3	
Theta range for data collection	2.955 to 27.470°.	
Index ranges	-7<=h<=7, -26<=k<=26, -11<=l<=11	
Reflections collected	10003	
Independent reflections	4645 [R(int) = 0.0404]	
Completeness to theta = 26.000°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4645 / 1 / 282	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1023	
R indices (all data)	R1 = 0.0519, wR2 = 0.1055	
Absolute structure parameter	-0.02(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.253 and -0.200 $e.Å^{-3}$	