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Synthesis and optical properties of novel unsymmetrically substituted benzothiadiazole-based luminophores

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General information

All reactions were carried out under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. All reagents were used as purchased. 4,7-Dibromo-1,3,5-benzothiadiazole [M. E. Mohanty, C. Madhu, V. L. Reddy, M. Paramasivam, P. R. Bangal and V. J. Rao, *Phys. Chem. Chem. Phys.*, 2017**, 19**, 9118] and 4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole [S. Förtsch, A. Vogt and P. Bäuerle, *J. Phys. Org. Chem.*, 2017**, 30**, 3743] were prepared according to the published methods and characterized by NMR spectra. NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F ($CFCl_3$ as reference).). The chemical shifts are frequency referenced relative to the solvent residual peaks. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs.

Photophysical properties

Optical absorption spectra were recorded using a PC 2000 OceanOptics spectrophotometer (deuterium lamp). The PL spectra were recorded using a Varian Cary Eclipse spectrofluorimeter (Xe pulse lamp pulsed at 80 Hz, pulse width at half peak height ~ 2 μs, peak power equivalent to 75 kW). Quartz cuvettes 10x10 mm was used for both cases.

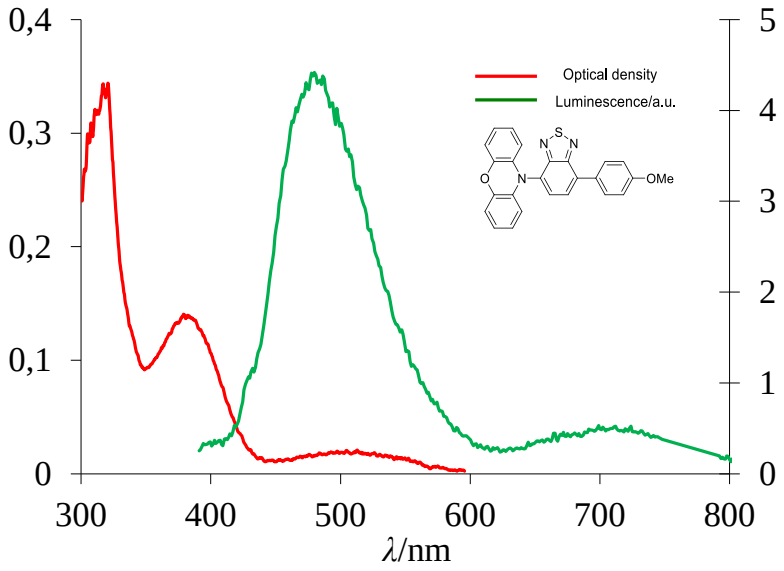


Figure S1 Absorption and PL spectra of **3a.** (λ^{abs}_{max} = 383 nm, λ^{PL}_{max} = 480 nm) in toluene (C=2·10^{-5} M).

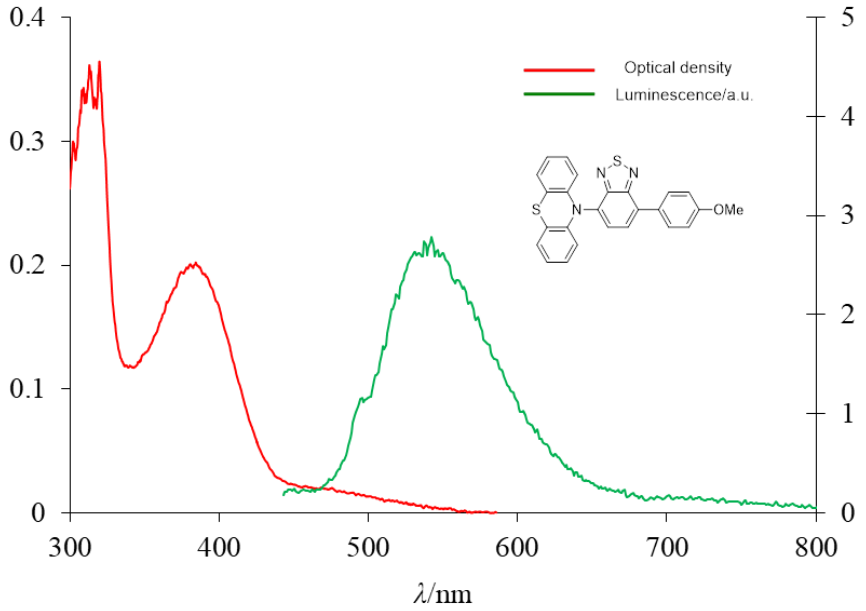


Figure S2 Absorption and PL spectra of **3b.** (λ^{abs}_{max} = 384 nm, λ^{PL}_{max} = 540 nm) in toluene (C=2·10^{-5} M).

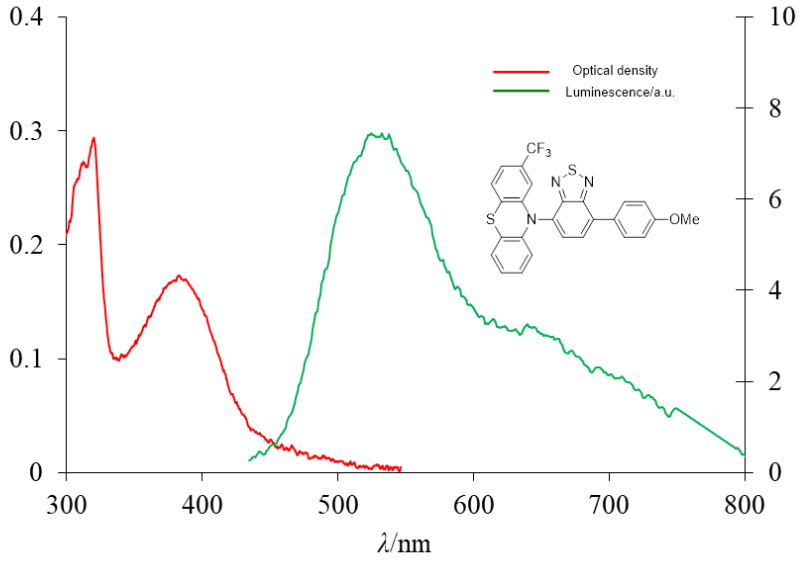


Figure S3 Absorption and PL spectra of **3c.** (λ^{abs}_{max} = 385 nm, λ^{PL}_{max} = 530 nm) in toluene (C=$2\cdot10^{-5}$ M).

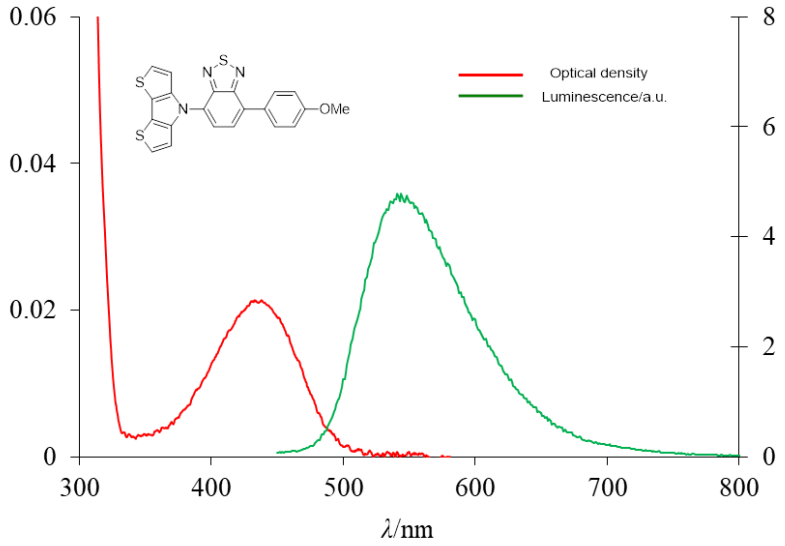


Figure S4 Absorption and PL spectra of **3d.** (λ^{abs}_{max} = 437 nm, λ^{PL}_{max} = 542 nm) in toluene (C=$0.2\cdot10^{-5}$ M).

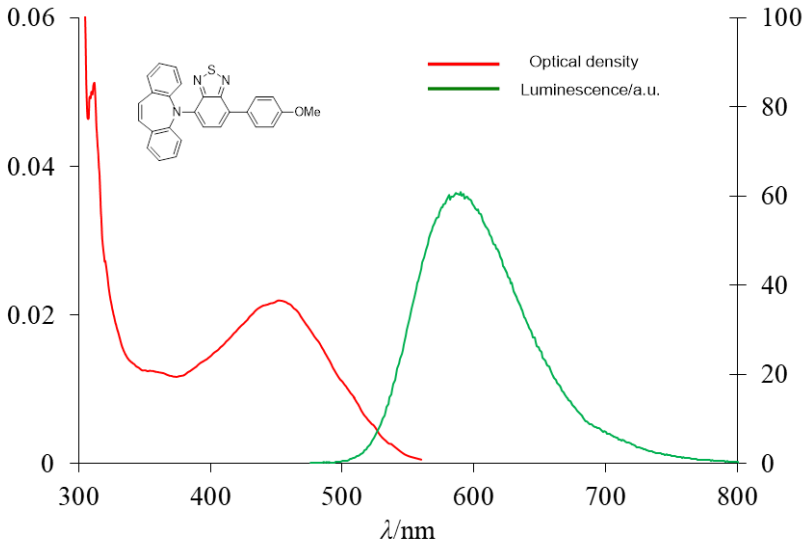


Figure S5 Absorption and PL spectra of **3e.** (λ^{abs}_{max} = 455 nm, λ^{PL}_{max} = 587 nm) in toluene (C=0.2·10^{-5} M).

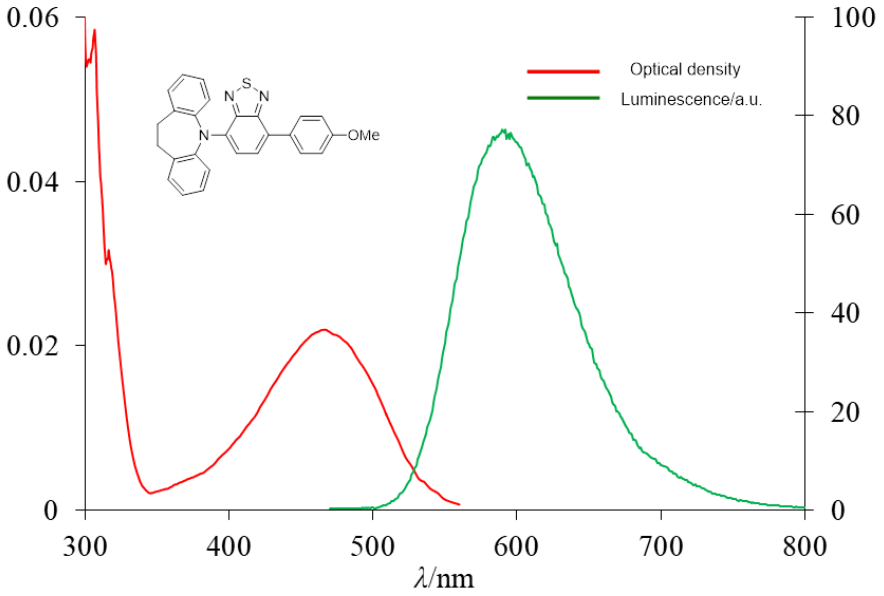


Figure S6 Absorption and PL spectra of **3f.** (λ^{abs}_{max} = 467 nm, λ^{PL}_{max} = 591 nm) in toluene (C=0.2·10^{-5} M).

DFT calculations

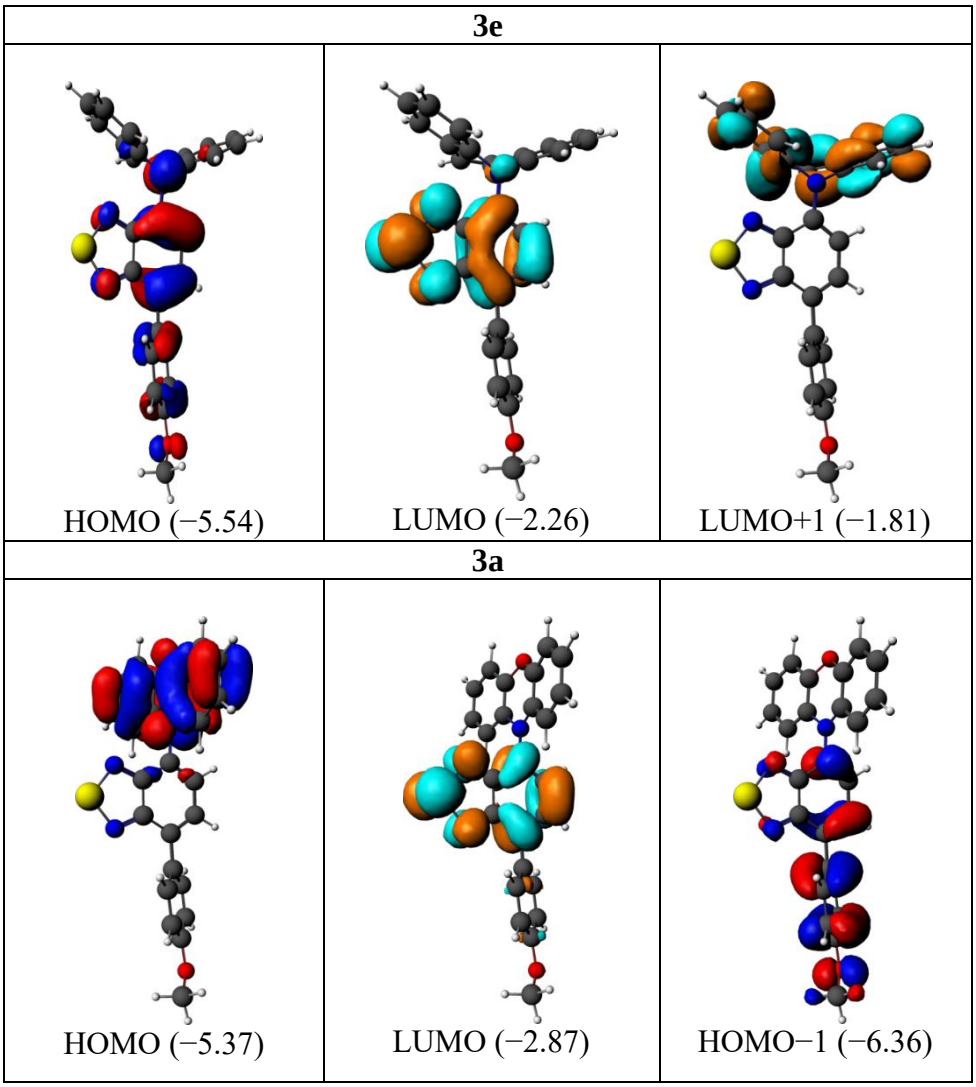
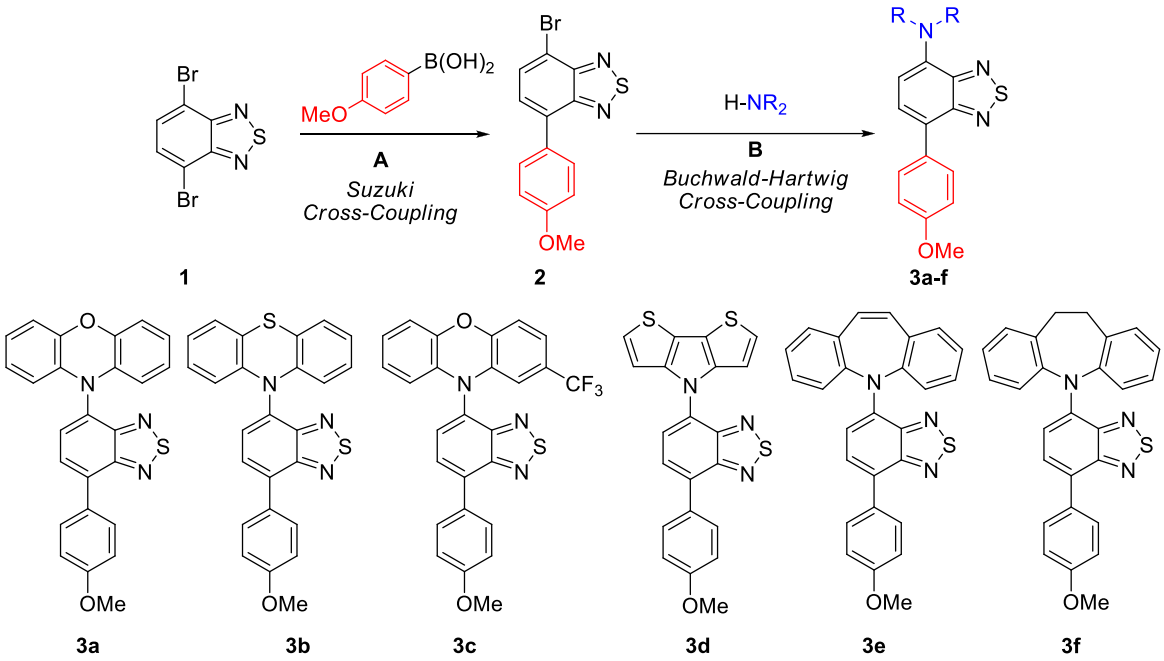


Figure S7 Frontier molecular orbitals of **3e** (top) and **3a** (bottom) at the B3LYP/DZP level. Energies of the orbitals are given in parentheses in eV.

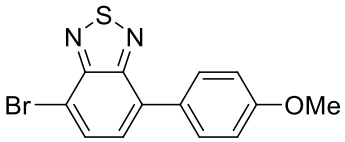
Synthetic procedure



General procedure A

A 25 ml round-bottomed flask, equipped with a magnetic stir bar and reflux condenser, was charged with 4,7-dibromo-2,1,3-benzothiadiazole (2.0 mmol, 588 mg), 4-methoxyphenylboronic acid (2.0 mmol, 304 mg), 1,4-dioxane-water mixture (3:1, 12 ml), $NaHCO_3$ (504 mg, 3.0 eq.) and $Pd(PPh_3)_2Cl_2$ (14 mg, 1 mol%). The resulting mixture was deaerated with argon and refluxed under argon for 24 h. On completion, the mixture was poured into water and extracted with dichloromethane (3 × 10 ml). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by chromatography (eluent – hexane: ethyl acetate 60:1) gave pure product **2** (327 mg, 51%) as yellow solid. Its NMR data are in agreement with previously reported [F. S. Mancilha, L. Barloy, F. S. Rodembusch, J. Dupont and M. Pfeffer, *Dalton Trans.*, 2011**, 40**, 10535].

*4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole (**2**)*

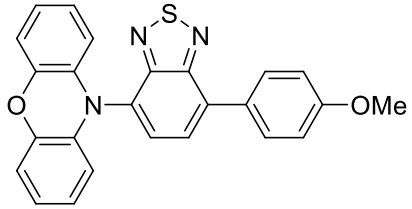


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2 , 153.3 , 133.7 , 132.4 , 130.5 , 129.1 , 127.5 , 114.3 , 112.3 , 55.5 .

General procedure B for the Buchwald – Hartwig synthesis of 3a-f

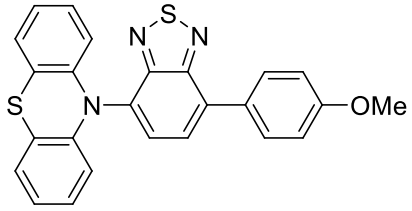
Under argon in a Schlenk tube with magnetic stirring bar, 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole (150 mg, 0.47 mmol), the corresponding amine (1.05 eq.), palladium acetate (5 mg, 5 mol%), RuPhos (22 mg, 10 mol%) and sodium *tert*-butoxide (68 mg, 1.5 eq.) were dissolved in dry 1,4-dioxane (4 ml). The solution was degassed by argon. Then, the reaction mixture was stirred at 100 °C (oil bath temperature) for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane (3 × 10 ml). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by chromatography (eluent – hexane: ethyl acetate 40:1) gave analytically pure products **3a-f**.

*10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-10H-phenoxazine (**3a**)*



Following general procedure B **3a** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 10*H*-phenoxazine as red solid (151 mg, 76%). M.p. 240-242 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.11 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.71 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 2H), 5.95 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 144.8 , 134.4 , 131.6 , 128.4 , 124.4 , 122.9 , 122.6 , 122.2 , 116.4 , 116.3 , 114.9 , 114.6 , 114.2 , 55.7 . HRMS (APPI): calcd for $C_{25}H_{17}N_3O_2S$ $[M]^+$: 423.1036; found: 423.1037.

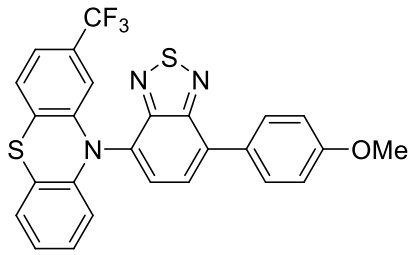
*10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl])-10H-phenothiazine (**3b**)*



Following general procedure B **3b** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 10*H*-phenothiazine as red solid (186 mg, 85%). M.p. 198-200 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.12 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.98 – 7.94 (m, 1H),

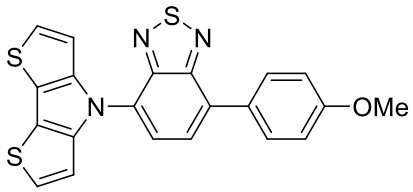
7.16 (d, *J* = 8.9 Hz, 2H), 7.08 (dd, *J* = 7.3, 1.7 Hz, 2H), 6.85 (td, *J* = 7.4, 1.5 Hz, 2H), 6.80 (td, *J* = 7.7, 1.8 Hz, 2H), 6.12 (dd, *J* = 8.1, 1.4 Hz, 2H), 3.92 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) δ 161.2 , 155.9 , 144.6 , 135.8 , 133.7 , 132.2 , 131.6 , 130.0 , 128.6 , 127.9 , 127.3 , 123.6 , 120.7 , 117.0 , 114.9 , 110.9 , 55.7 . HRMS (APPI): calcd for $C_{25}H_{17}N_3OS_2$ $[M]^+$: 439.0808; found: 439.0811.

*10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-2-trifluoromethyl-10H-phenothiazine (**3c**)*



Following general procedure B **3c** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 2-trifluoromethyl-10*H*-phenothiazine as orange solid (199 mg, 84%). M.p. 196-197 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.13 (d, *J* = 8.8 Hz, 2H), 8.10 – 8.04 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 3H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.9 Hz, 1H), 6.35 (s, 1H), 6.15 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) δ 161.4 , 156.0 , 154.1 , 145.1 , 143.8 , 136.2 , 134.0 , 131.7 , 131.2 , 129.9 , 129.6 (q, *J* = 32.2 Hz), 128.5 , 128.0 , 127.5 , 126.4 , 124.8 (q, *J* = 271.3 Hz), 124.4 , 120.2 (q, J = 3.7 Hz), 117.5 , 114.9 , 112.6 (q, J = 3.5 Hz), 55.7 . ^{19}F NMR (376 MHz, Acetone-d_6) δ -63.5 . HRMS (APPI): calcd for $C_{26}H_{16}F_3N_3OS_2$ $[M]^+$: 507.0681; found: 507.0686.

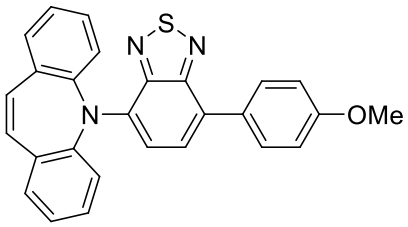
*4-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-4H-dithieno[3,2-b:2',3'-d]pyrrole (**3d**)*



Following general procedure B **3d** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole as yellow solid (98 mg, 50%). M.p. 222-223 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.19 (d, *J* = 5.3 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 160.1 , 154.8 , 150.5 , 144.8 , 132.6 , 130.6 , 130.4 , 129.5 , 127.1 ,

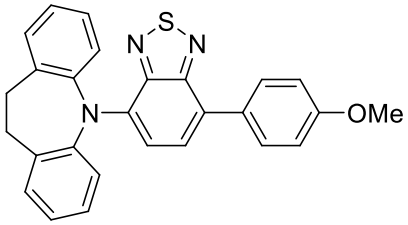
123.5 , 123.3 , 117.9 , 114.4 , 113.3 , 55.6 . HRMS (APPI): calcd for $C_{21}H_{13}N_3OS_3$ $[M]^+$: 419.0215; found: 419.0218.

*4-(5H-dibenzo[b,f]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole (**3e**)*



Following general procedure B **3e** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 5*H*-dibenzo[*b*,*f*]azepine as bright orange solid (168 mg, 82%). M.p. 199-201 °C. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.19 – 7.17 (m, 2H), 7.15 – 7.09 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.65 (s, 2H), 6.33 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 159.4 , 144.2 , 144.0 , 139.4 , 136.6 , 130.8 , 130.6 , 130.3 , 129.9 , 129.8 , 127.3 , 114.2 , 108.7 , 54.8 . HRMS (APPI): calcd for $C_{27}H_{19}N_3OS$ $[M]^+$: 433.1243; found: 433.1248.

*4-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole (**3f**)*



Following general procedure B **3f** was obtained from 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole and 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine as bright orange solid (160 mg, 78%). M.p. 198-199 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.33 – 7.23 (m, 6H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.10 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 160.1 , 156.1 , 149.3 , 146.1 , 140.4 , 138.6 , 131.4 , 130.7 , 130.2 , 129.4 , 128.1 , 127.7 , 124.6 , 119.0 , 114.6 , 112.1 , 55.7 , 31.6 . HRMS (APPI): calcd for $C_{27}H_{21}N_3OS$ $[M]^+$: 435.1400; found: 435.1404.

NMR spectra

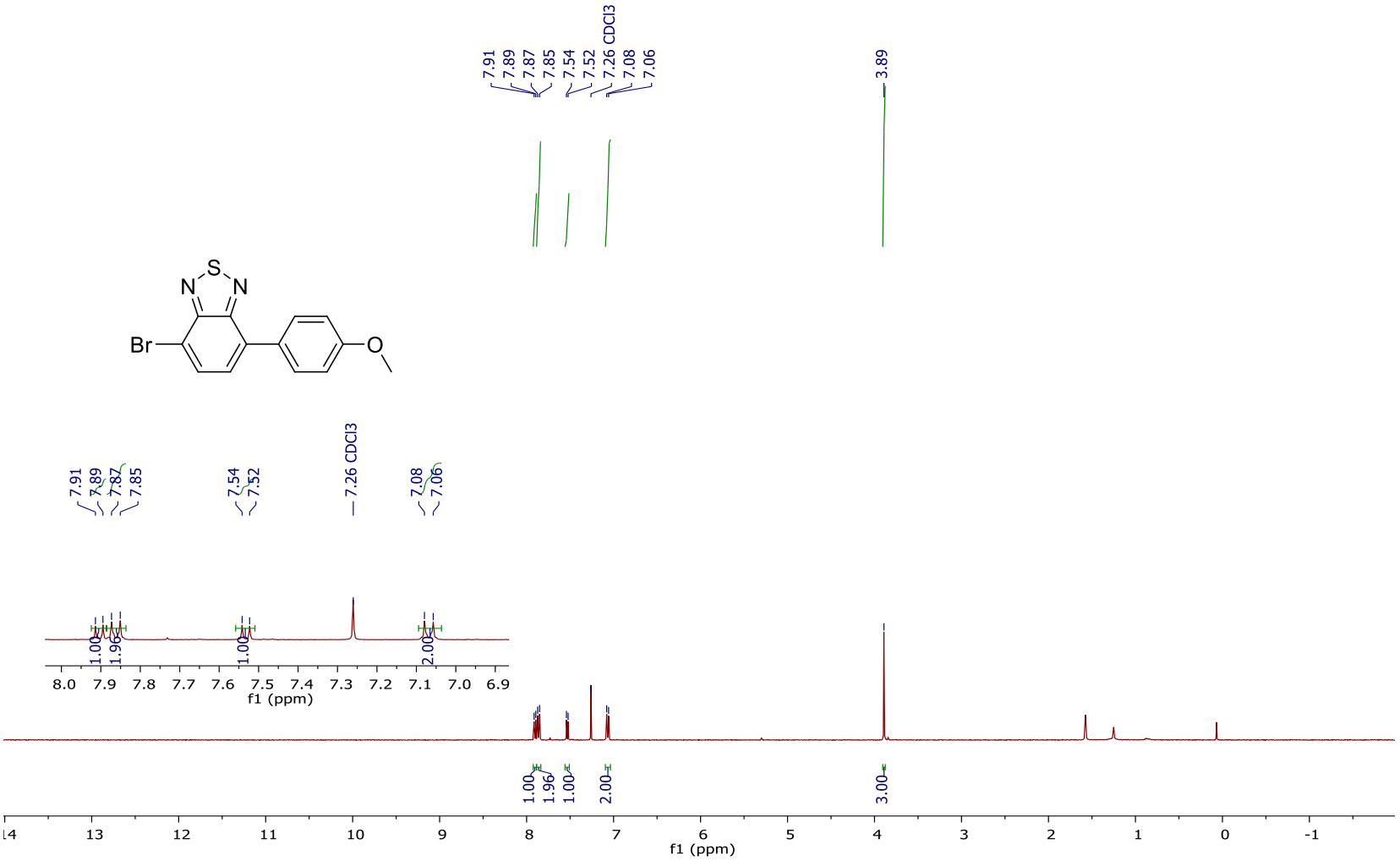


Figure S8. ^{1}H NMR (400 MHz, Chloroform-*d*) of 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole

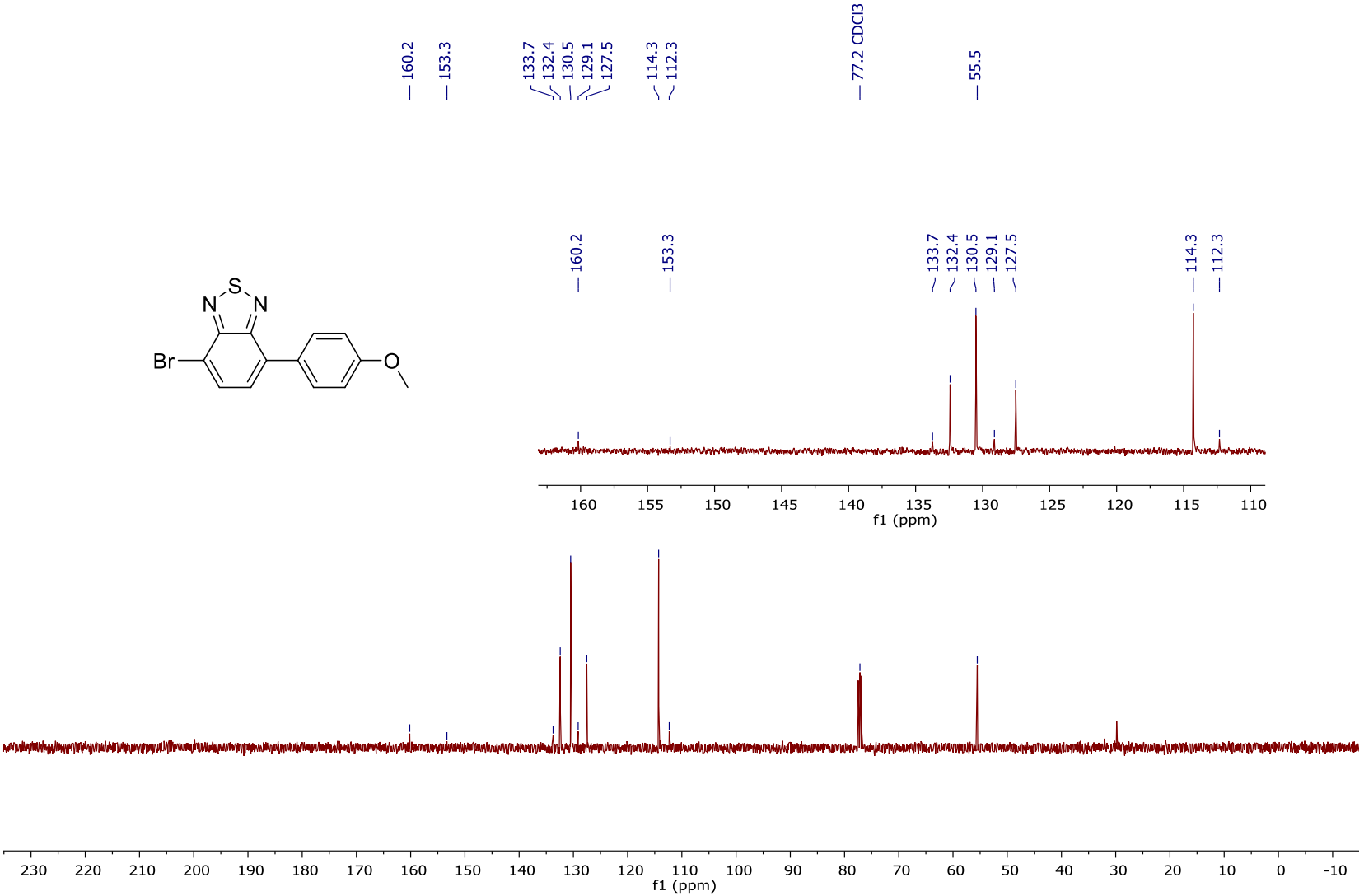


Figure S9. $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) of 4-bromo-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole

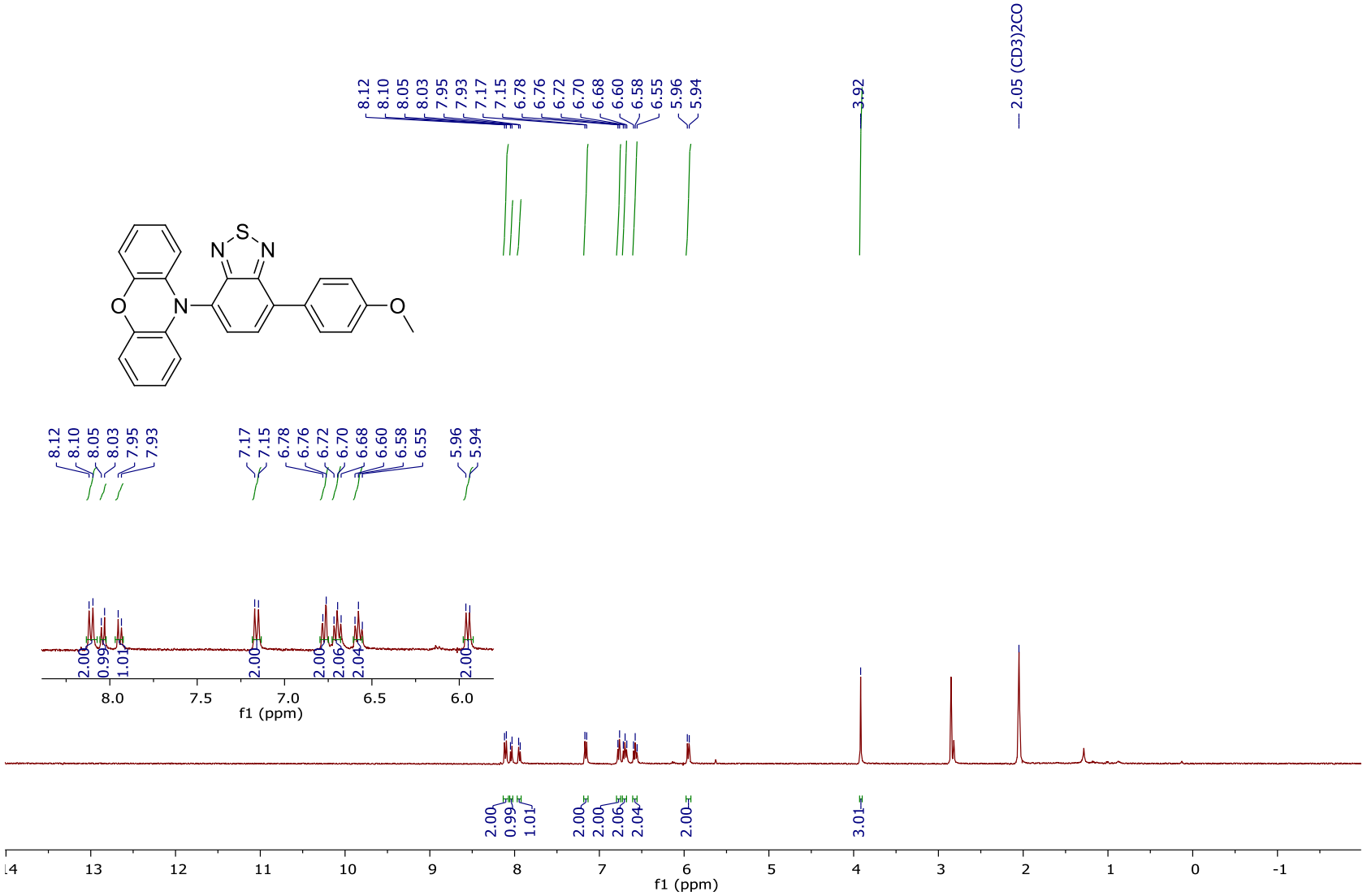


Figure S10. ^{1}H NMR (400 MHz, Acetone-d_6) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-10*H*-phenoxazine

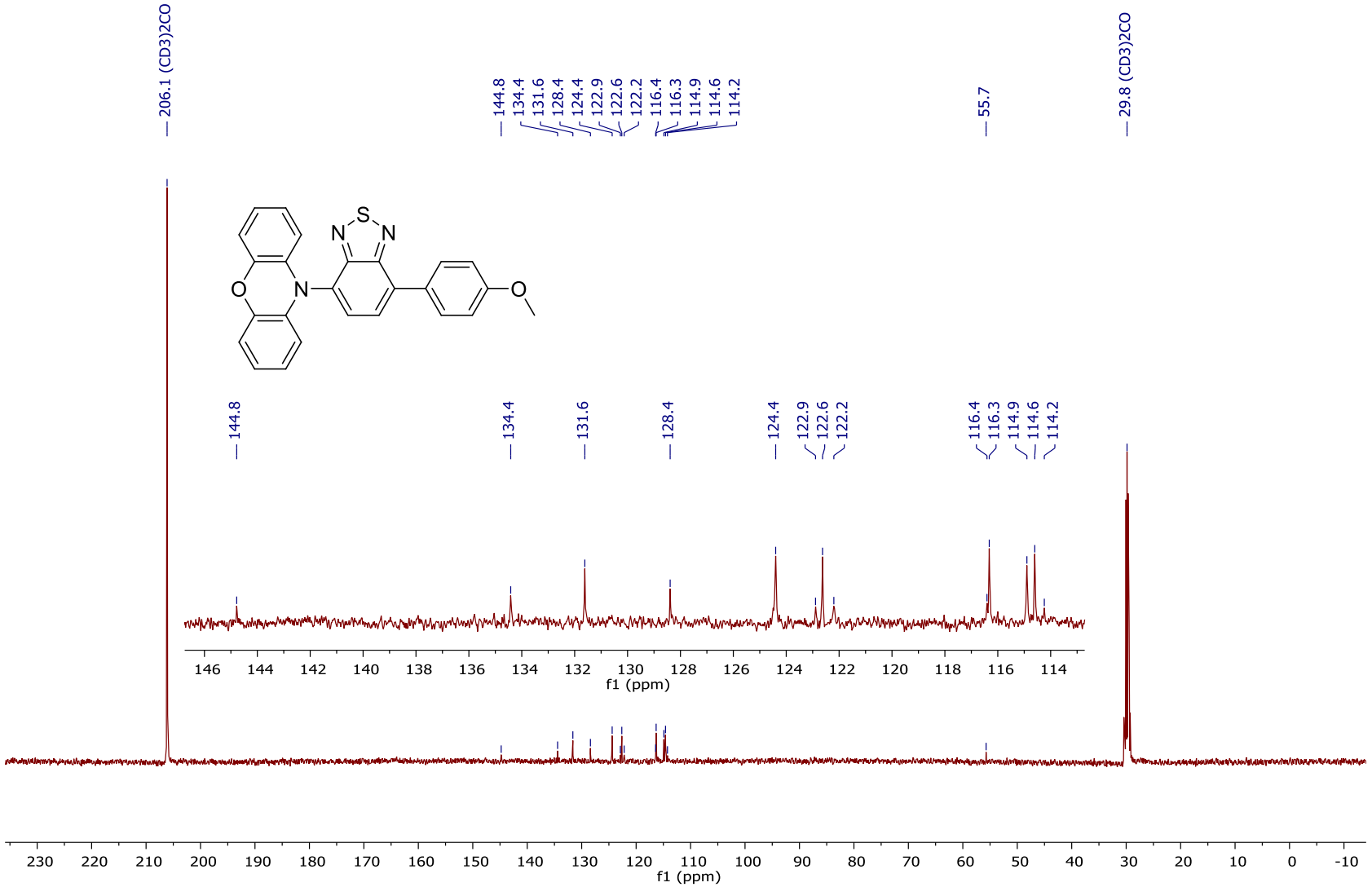


Figure S11. $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-10*H*-phenoxazine

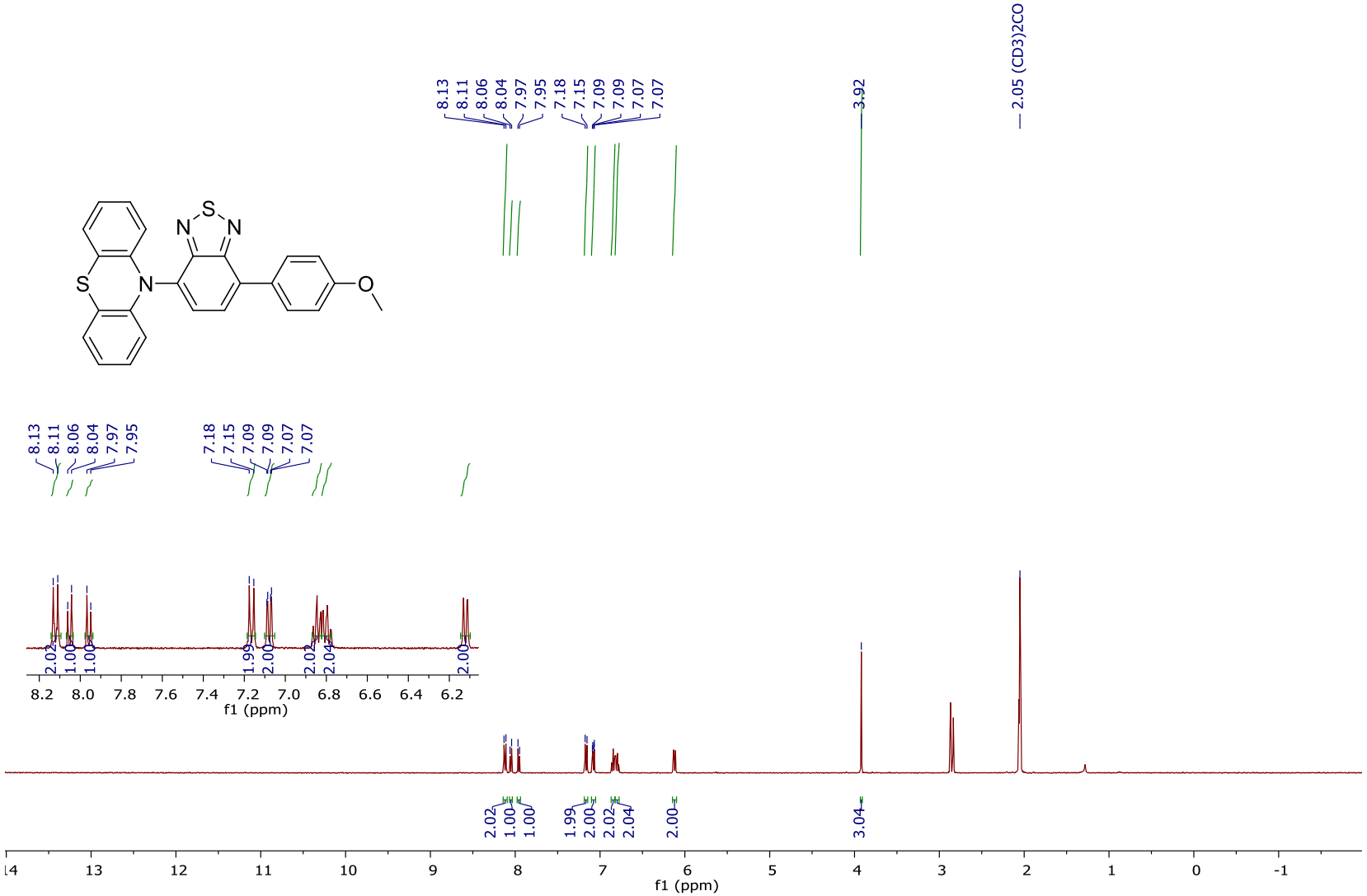


Figure S12. ^{1}H NMR (400 MHz, Acetone-*d*$_6$) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-10*H*-phenothiazine

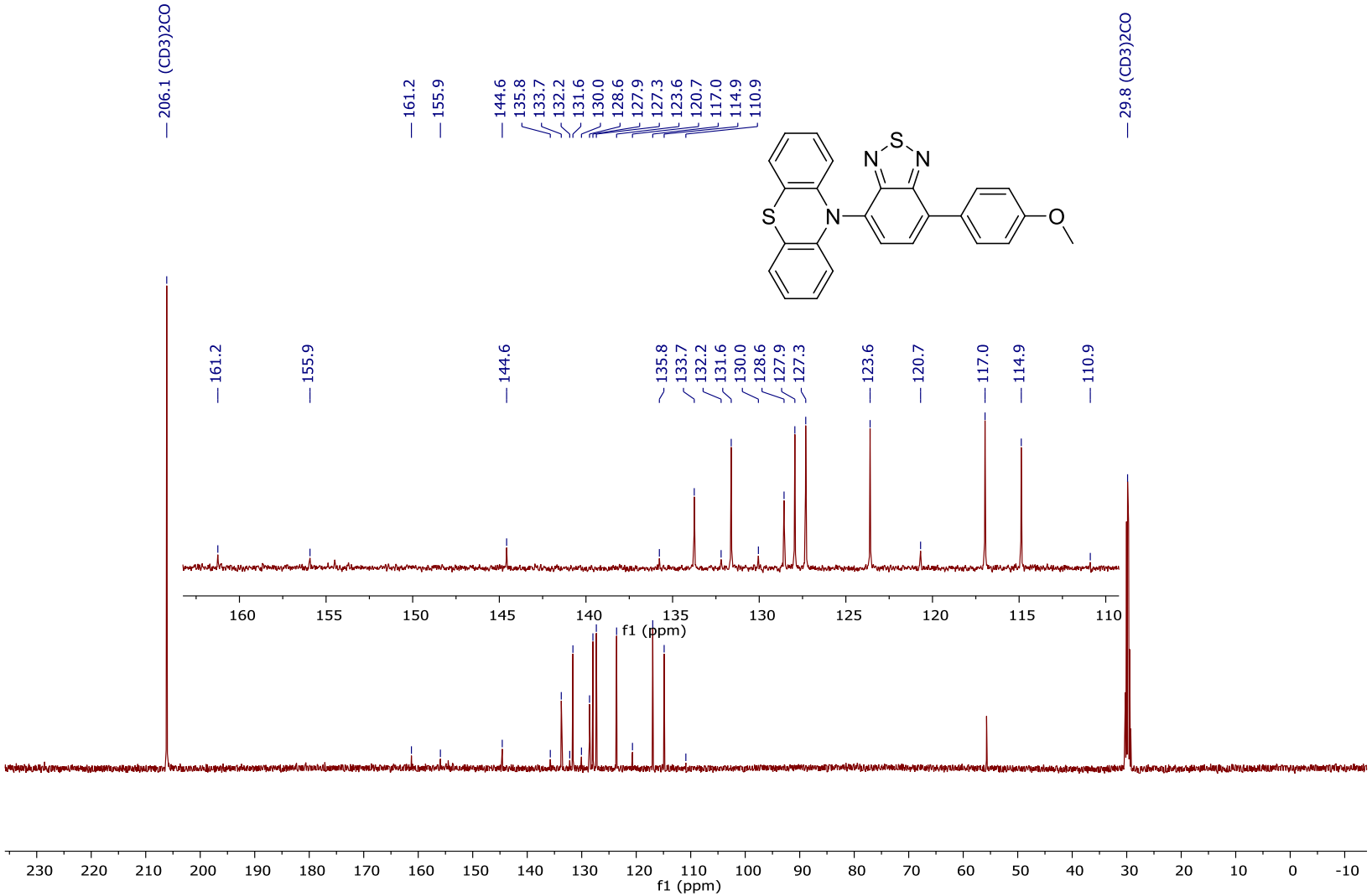


Figure S13. $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-*d*$_6$) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-10*H*-phenothiazine

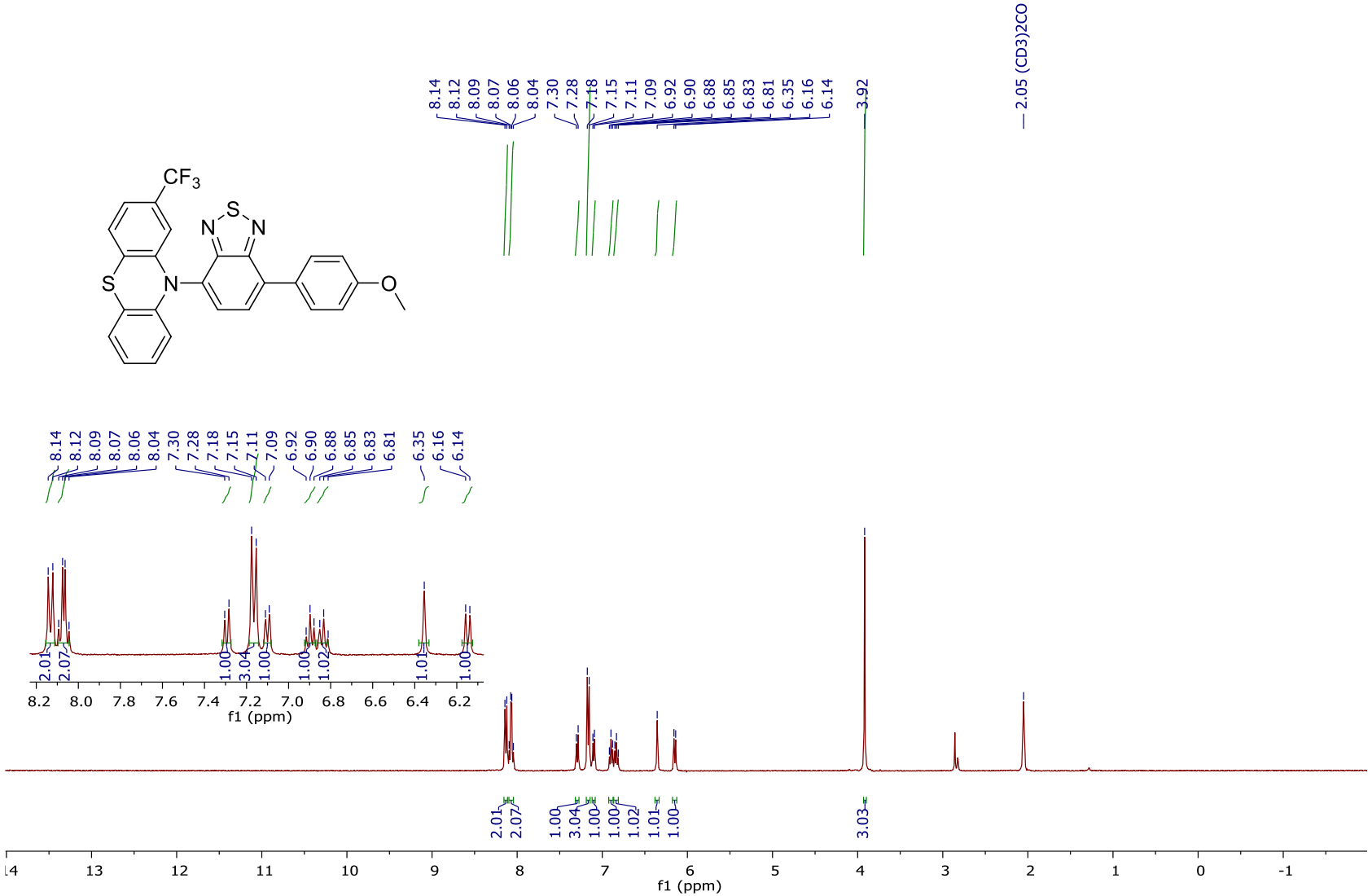


Figure S14. ^{1}H NMR (400 MHz, Acetone-d_6) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl)-2-trifluoromethyl-10*H*-phenothiazine

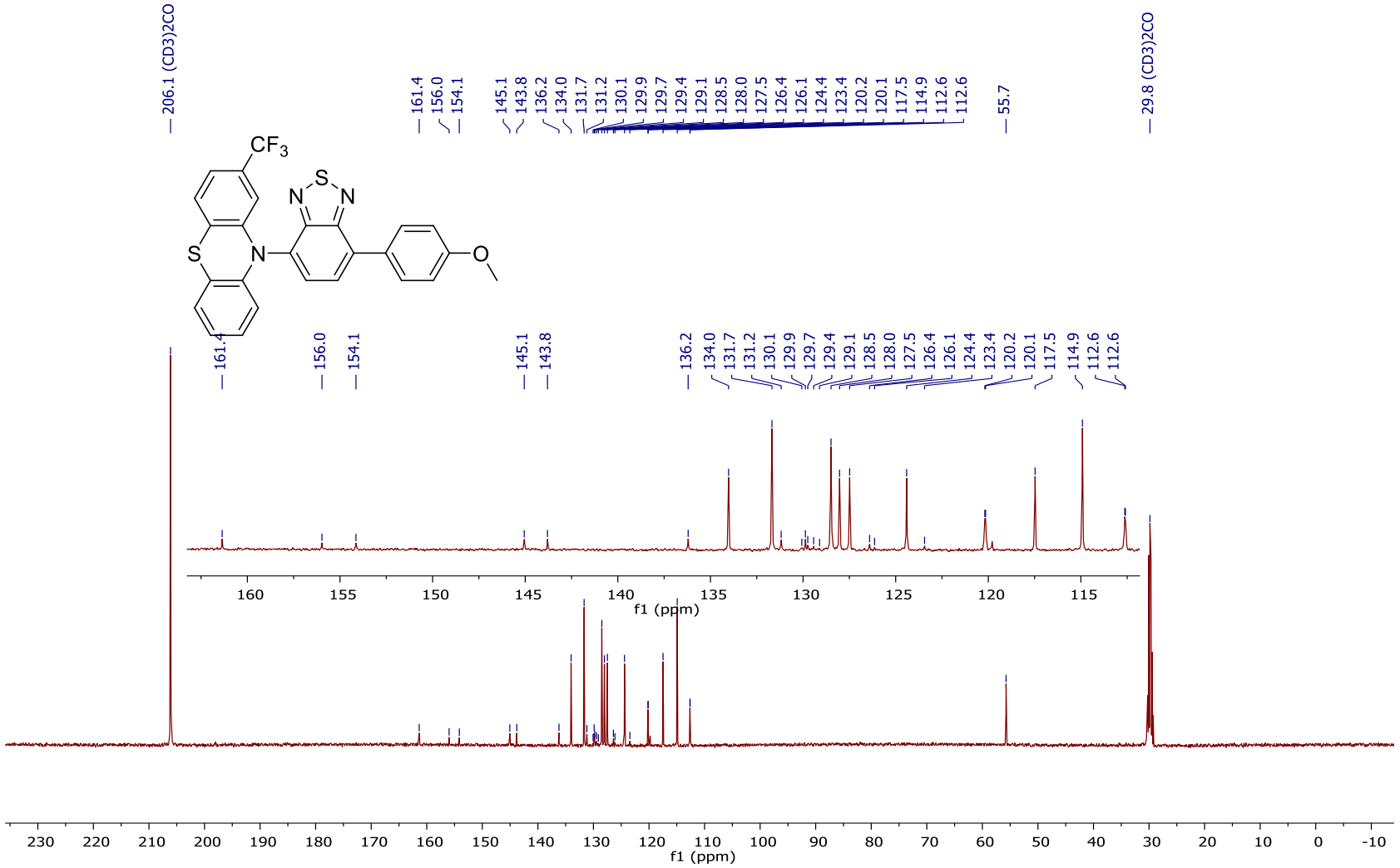


Figure S15. $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) of 10-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-2-trifluoromethyl-10*H*-phenothiazine

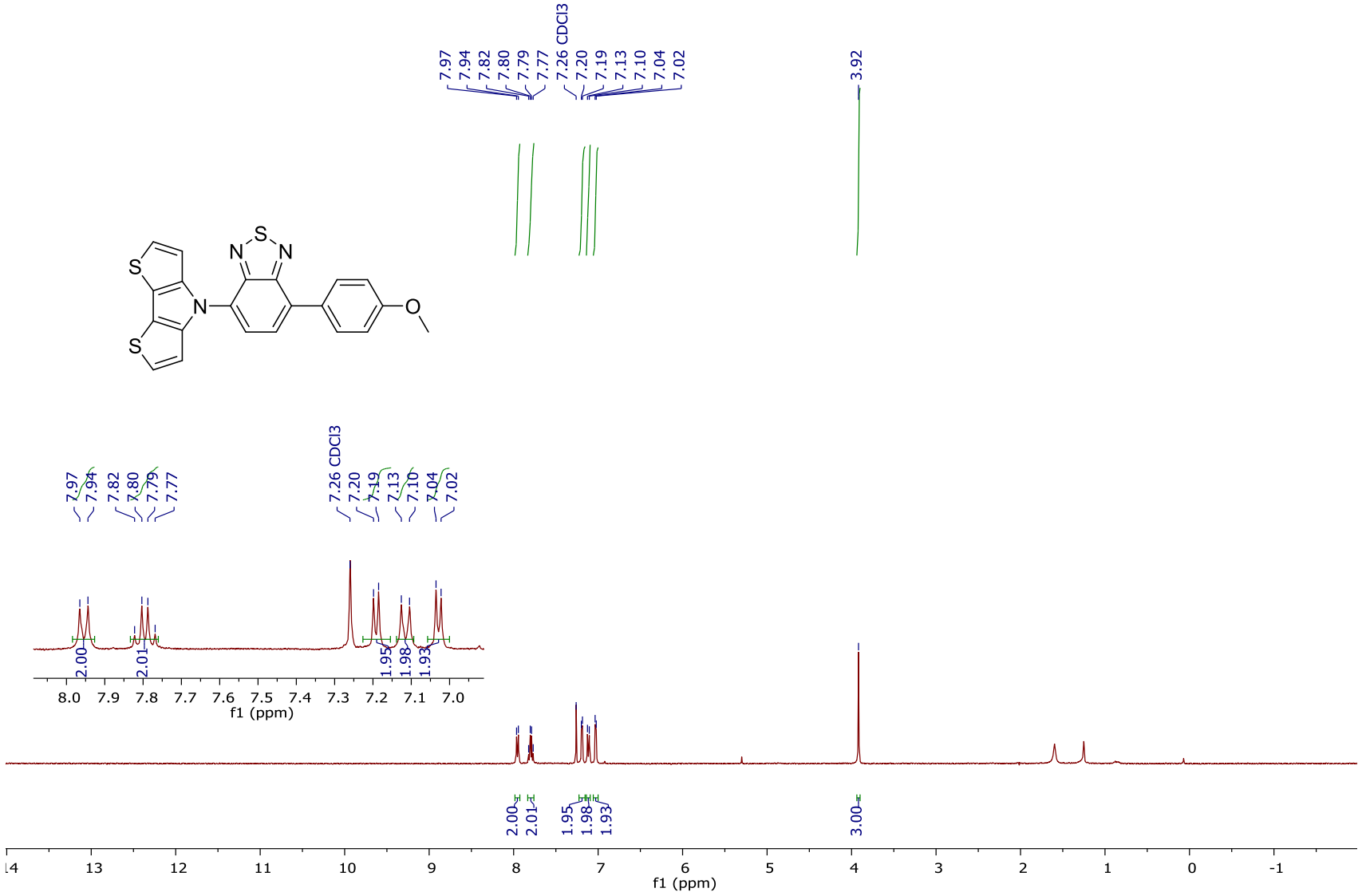


Figure S16. ^{1}H NMR (400 MHz, Chloroform-*d*) of 4-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole

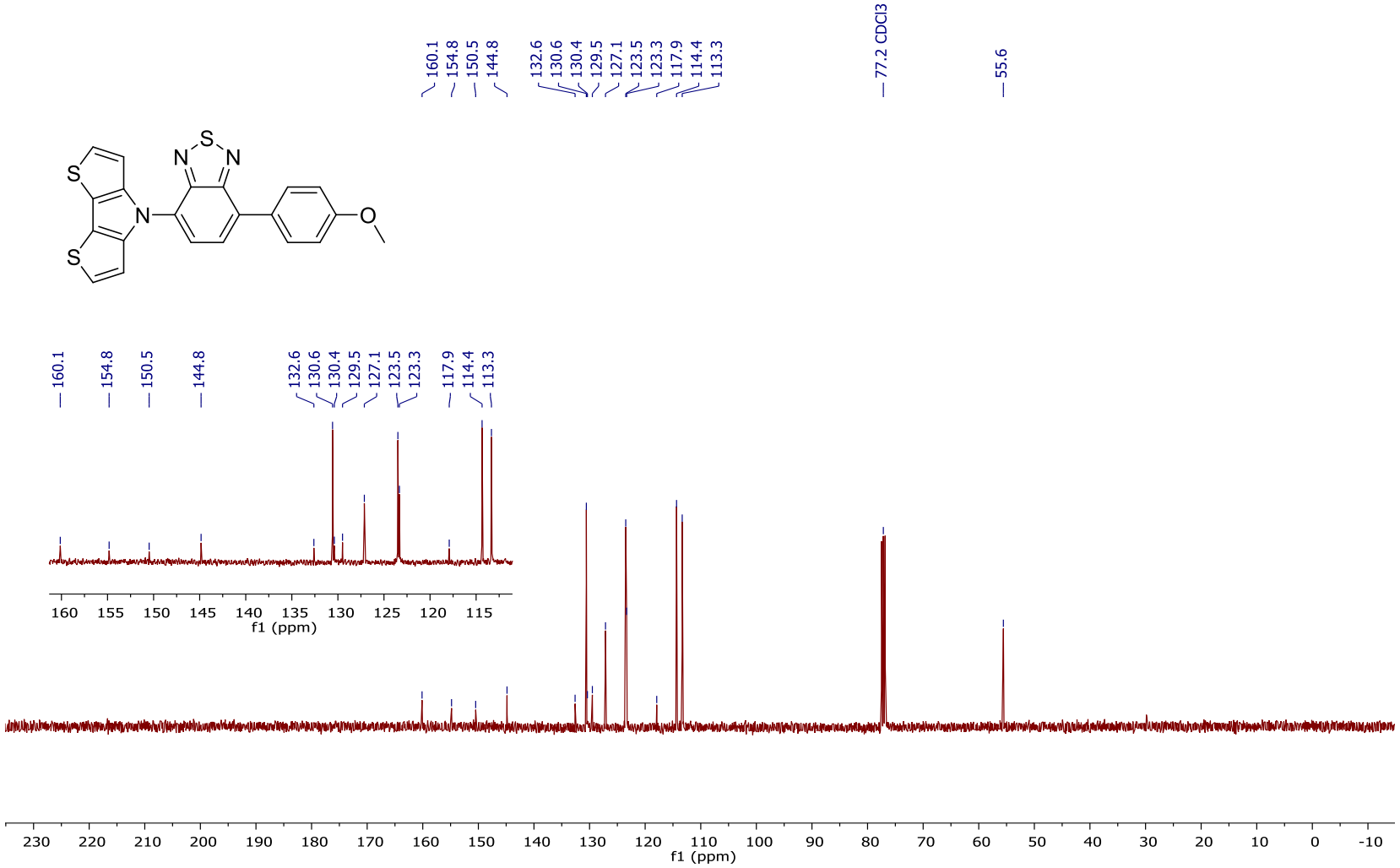


Figure S17. $^{13}C\{^{1}H\}$ **NMR (101 MHz, Chloroform-*d*) of 4-[7-(4-methoxyphenyl)-2,1,3-benzothiadiazol-4-yl]-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole**

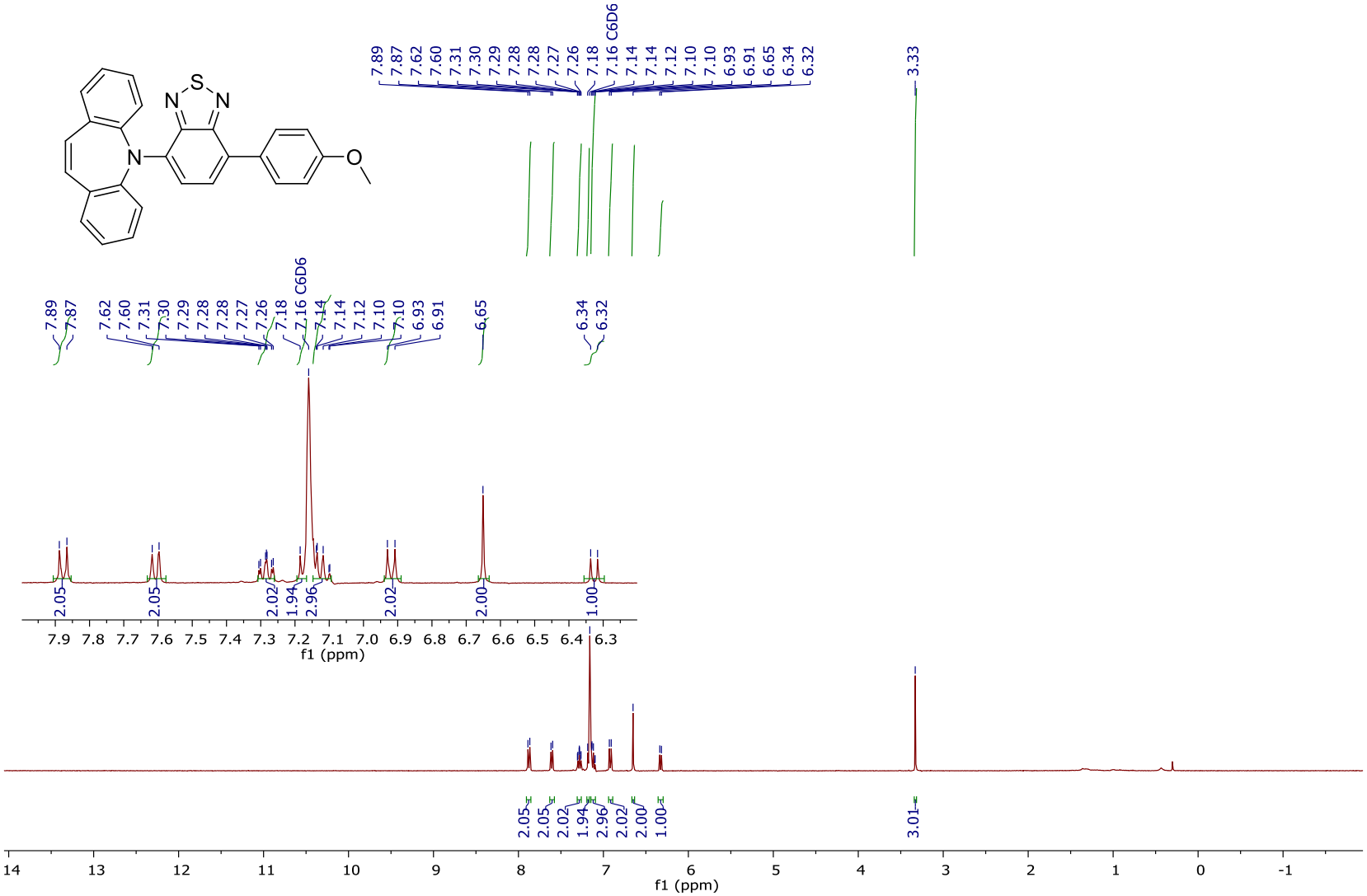


Figure S18. ^{1}H NMR (400 MHz, Benzene-d_6) of 4-(5*H*-dibenzo[*b*,*f*]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole

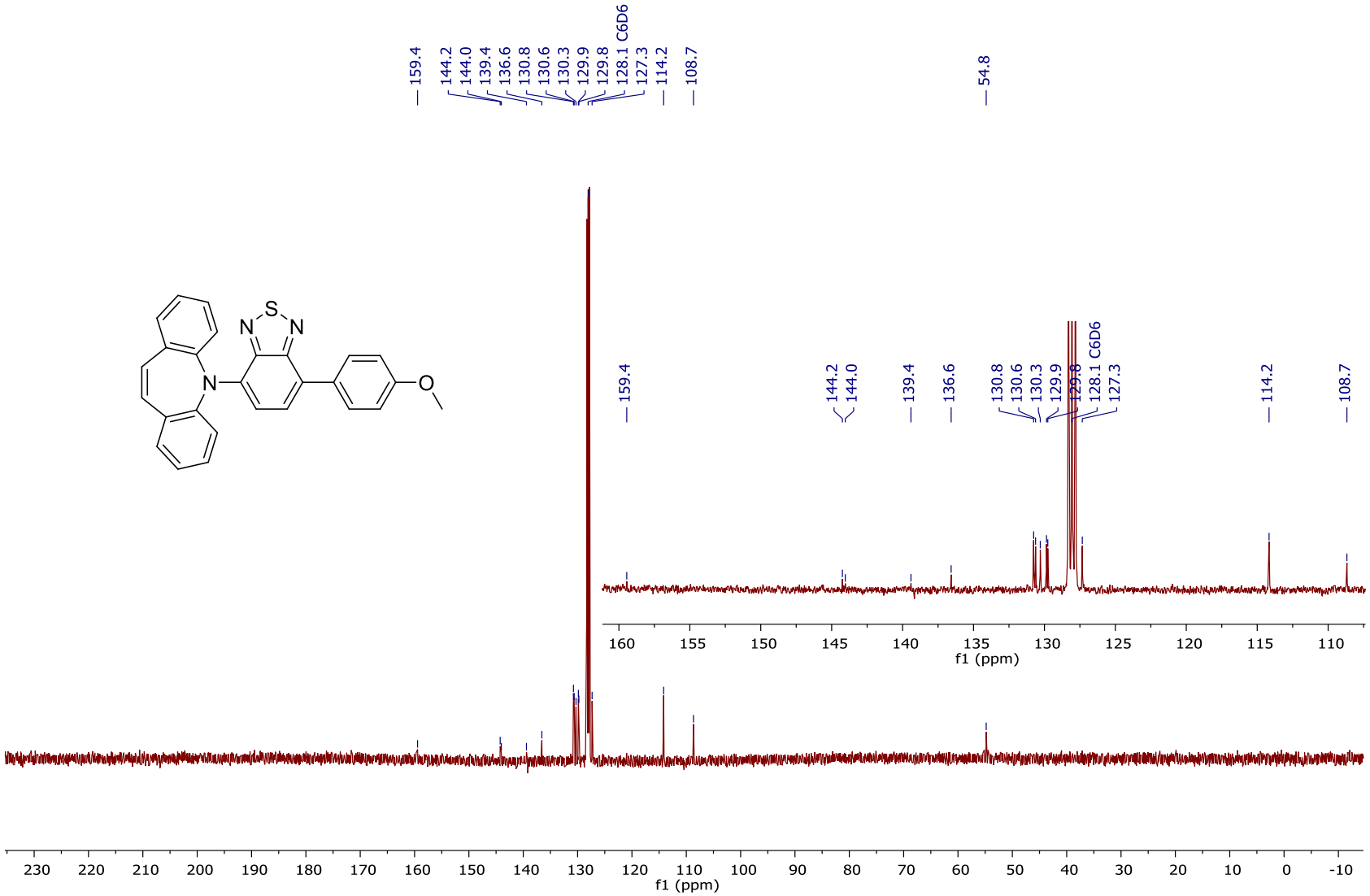


Figure S19. $^{13}C\{^{1}H\}$ NMR (101 MHz, Benzene-d_6) of 4-(5*H*-dibenzo[*b,f*]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole

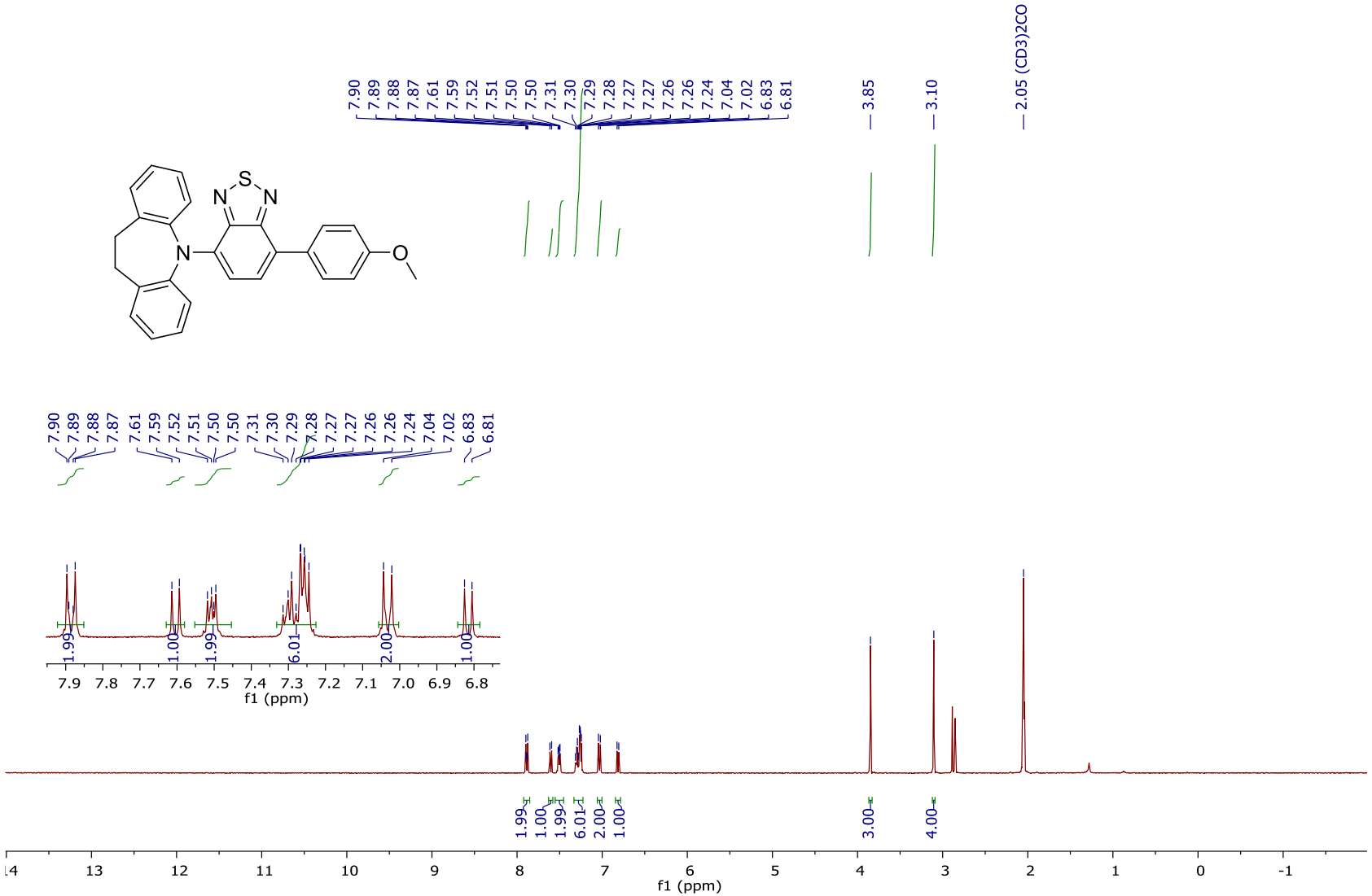


Figure S20. ^{1}H NMR (400 MHz, Acetone-d_6) of 4-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole

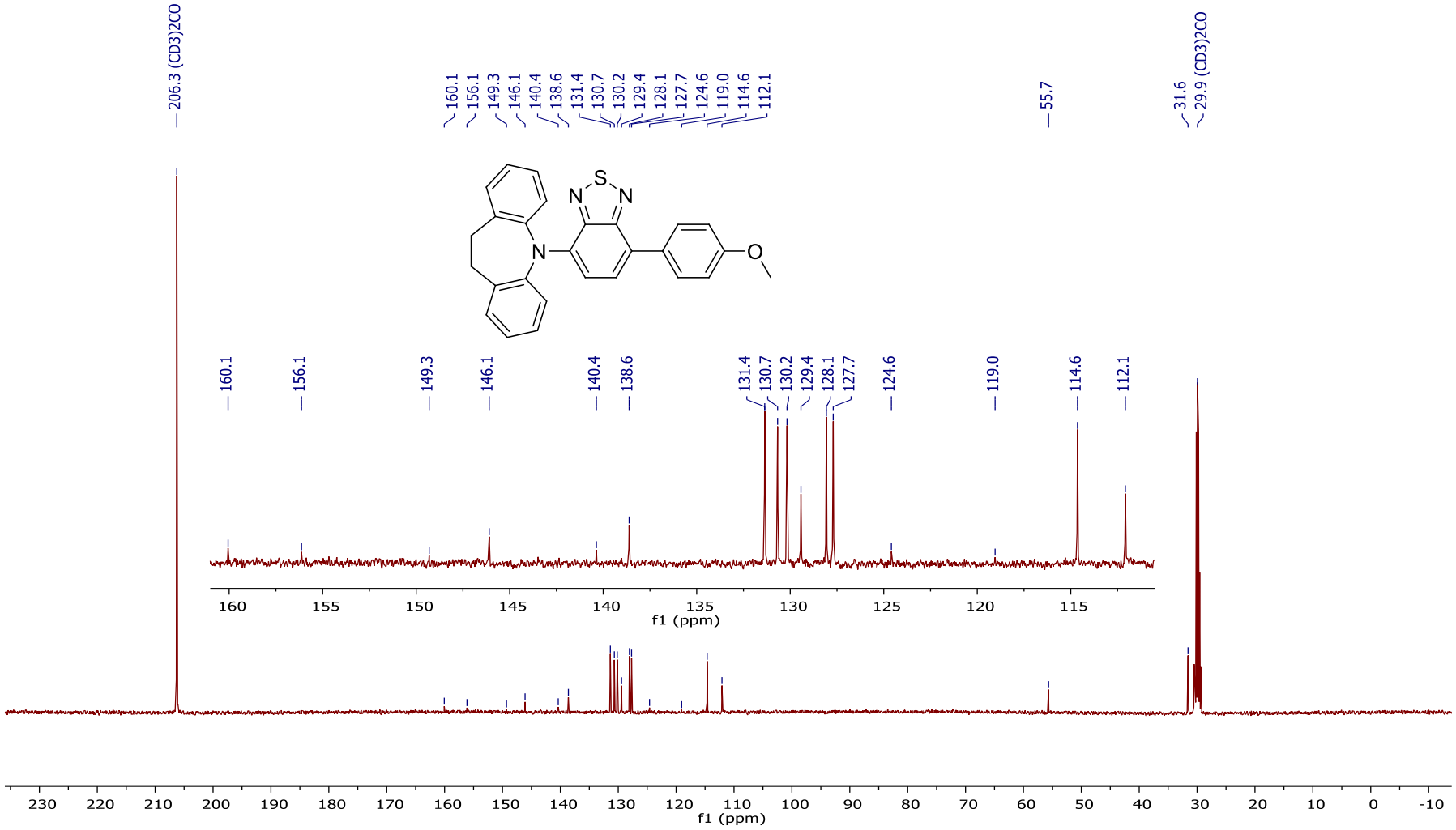


Figure S21. $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) of 4-(10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)-7-(4-methoxyphenyl)-2,1,3-benzothiadiazole