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A double ouroboros-shaped noncovalent molecular dimer

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Contents

Experimental section.

Experimental Section

Materials and Methods

2-(4-Thiazolyl)benzimidazole, 1,3,5-tris(bromomethyl)benzene, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene were purchased from Sigma-Aldrich; KOH from Avra and dimethylformamide (DMF) from Finar and used as received. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and 1,3,5-tri(bromomethyl)-2,4-dimethylbenzene was prepared from previously reported methods.[10] ^{1}H NMR spectra were recorded on Bruker Avance III 400 and 500 MHz instruments. The mass spectra were obtained on a Bruker maXis mass spectrometer. Single crystal X-ray data of **TMe**, **TEt** and **TXy** were collected on a Rigaku Oxford Diffractometer (λ(Mo Kα) = 0.71073Å). The molecular structures were solved by direct methods using SHELXS-97 (Sheldrick 2008) and refined using the SHELXL-2018/3 program (within the WinGX program package). Non-H atoms were refined anisotropically.[1] The lattice solvent molecules in compound **TEt** could not be modelled and hence their contributions to intensities were excluded using SQUEEZE option in PLATON program.[2] The structure contains solvent accessible voids. A solvent mask was calculated and 119 electrons were found in a volume of 358 V(A^3) in 1 void per unit cell. This is consistent with the presence of 1[$CHCl_3$] per asymmetric unit which accounts for 119 electrons per unit cell. For compound **TEt**, one of the thiazole unit was found to be disordered over two positions. The disordered thiazole unit in **TEt** has been successfully modelled with the help of the instructions found in PART 1 (S1, N9, C28-C30) and PART 2 (S1A, N9A, C28-C30A). After refining as a free variable, the site-of-occupancy is almost 0.43 and 0.57, respectively. The disordered unit was modelled using restraints like SADI and SIMU.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)2,4,6-trimethylbenzene (TMe)

A mixture of 2-(4-thiazolyl)benzimidazole (302.66 mg, 1.50 mmol) and KOH (112.51 mg, 2.0 mmol) was stirred in DMF (10 mL) at room temperature for 3 h. 1,3,5-Tri(bromomethyl)2,4,6-trimethylbenzene (200 mg, 0.50 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Yellow crystals of **TMe** were obtained from chloroform: acetone at room temperature after few days. Yield: 80% (475 mg, 0.62 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ(ppm) 9.36 (d, 3H, J = 2 Hz, H^f), 8.53 (d, 3H, J = 2 Hz, H^e), 7.62 (d, 3H, J = 8.0 Hz, H^d), 7.14 (t, 3H, J = 7.5 Hz, H^c), 6.61 (t, 3H, J = 7.5 Hz, H^b), 6.34 (d, 3H, J = 8.0 Hz, H^a), 6.20 (s, 6H, –CH_2–), 2.18 (s, 9H, –CH_3). ^{13}C NMR (500 MHz,

DMSO-d_6): δ(ppm) 162.93, 155.74, 147.43, 142.99, 138.33, 135.40, 132.34, 123.21, 119.61, 111.72, 46.20, 36.29, 31.28. 17.21. HRMS (*m/z*): [**TMe** + H]$^+$ calc. for $C_{42}H_{34}N_9S_3$, 760.2099; found: 760.2099. Decomposition temperature: 360 °C.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)2,4,6-triethylbenzene (TEt)

A mixture of 2-(4-thiazolyl)benzimidazole (136.8 mg, 0.68 mmol) and KOH (50.8 mg, 0.90 mmol) was stirred in DMF (10 mL) at room temperature for 3h. 1,3,5-Tri(bromomethyl)2,4,6-triethylbenzene (100 mg, 0.22 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Colourless crystals of **TEt** were obtained from chloroform: acetone at room temperature after few days. Yield: 93.3% (194.7 mg, 0.24 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ(ppm) 9.39 (d, 3H, J = 1.5 Hz, H^f), 8.55 (d, 3H, J = 2.0 Hz, H^e), 7.64 (d, 3H, J = 8.0 Hz, H^d), 7.14 -7.10 (m, 3H, H^c), 6.37 (s, 6H, H^{a,b}), 6.16 (s, 6H, –CH_2–), 2.81 (d, 6H, J = 7.0 Hz, –CH_2(ethyl)), 0.67 (s, 9H, –CH_3). ^{13}C NMR (500 MHz, DMSO-d_6): δ(ppm) 162.46, 155.44, 147.23, 145.50, 143.02, 135.34, 131.22, 123.61, 122.57, 121.84, 119.43, 112.24, 44.71, 35.93, 30.93, 23.15, 15.02. HRMS (*m/z*): [**TEt** + H]$^+$ calc. for $C_{45}H_{40}N_9S_3$, 802.2569; found: 802.2570. Decomposition temperature: 390 °C.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)2,4-dimethylbenzene (TXy)

A mixture of 2-(4-thiazolyl)benzimidazole (156.84 mg, 0.78 mmol) and KOH (56.11 mg, 1.04 mmol) was stirred in DMF (10 mL) at room temperature for 3 h. 1,3,5-Tri(bromomethyl)-2,4 -dimethylbenzene (100 mg, 0.26 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Colourless crystals of **TXy** were obtained from chloroform: acetone at room temperature after few days. ^{1}H NMR (500 MHz, DMSO-d_6): Major isomer: δ(ppm) 8.99 (d, 2H, J = 2.1 Hz, H^f), 8.93 (d, 1H, J = 2.1 Hz, H$^{f'}$), 7.97 (d, 2H, J = 2Hz, H^e), 7.93 (d, 2H, J = 2Hz, H$^{e'}$), 7.62 (t, 3H, J = 8.7 Hz, H$^{d,d'}$), 7.19–7.16 (m, 3H, H$^{c,c'}$), 6.99-6.96 (m, 7H, H$^{a,\,a',b,b',g}$), 5.76 -5.75 (s, 6H, –CH_2–), 2,19 (s, 6H, –CH_3). ^{13}C NMR (500 MHz, DMSO-d_6): δ(ppm) 146.66, 142.56, 135.41, 133.57, 122.25, 119.33, 110.62, 45.53, 18.22, 14.92. HRMS (*m/z*): [**TXy** + H]$^+$ calc. for $C_{45}H_{40}N_9S_3$, 746.1943; found: 746.1947. Decomposition temperature: 370 °C.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)benzene (TH)

A mixture of 2-(4-thiazolyl)benzimidazole (169.17 mg, 0.84 mmol) and KOH (62.88 mg, 1.12 mmol) was stirred in DMF (10 mL) at room temperature for 3 h. 1,3,5-Tri(bromomethyl)benzene (100 mg, 0.28 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Yield: 91.4% (220 mg, 0.30 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ(ppm) 8.88 (d, 3H, J = 2 Hz, H^{f}), 8.21 (d, 3H, J = 2.5 Hz, H^{e}), 7.65 (d, 3H, J = 8.0 Hz, H^{d}), 7.27 (d, 3H, J = 8.0 Hz, H^{a}), 7.23 (t, 3H, J = 7.5 Hz, H^{c}), 7.13 (t, 3H, J = 7.5 Hz, H^{b}), 6.88 (s, 3H, H^{g}), 5.77 (s, 6H, –CH_2–). HRMS (m/z): ^{13}C NMR (500 MHz, DMSO-d_6): δ(ppm) 155.38, 147.02, 146.63, 142.96, 138.52, 135.87, 125.69, 122.94, 119.57, 111.29. [**TH** + H]$^{+}$ calc. for $C_{39}H_{28}N_9S_3$, 718.1630; found: 718.1630. Decomposition temperature: 410 °C

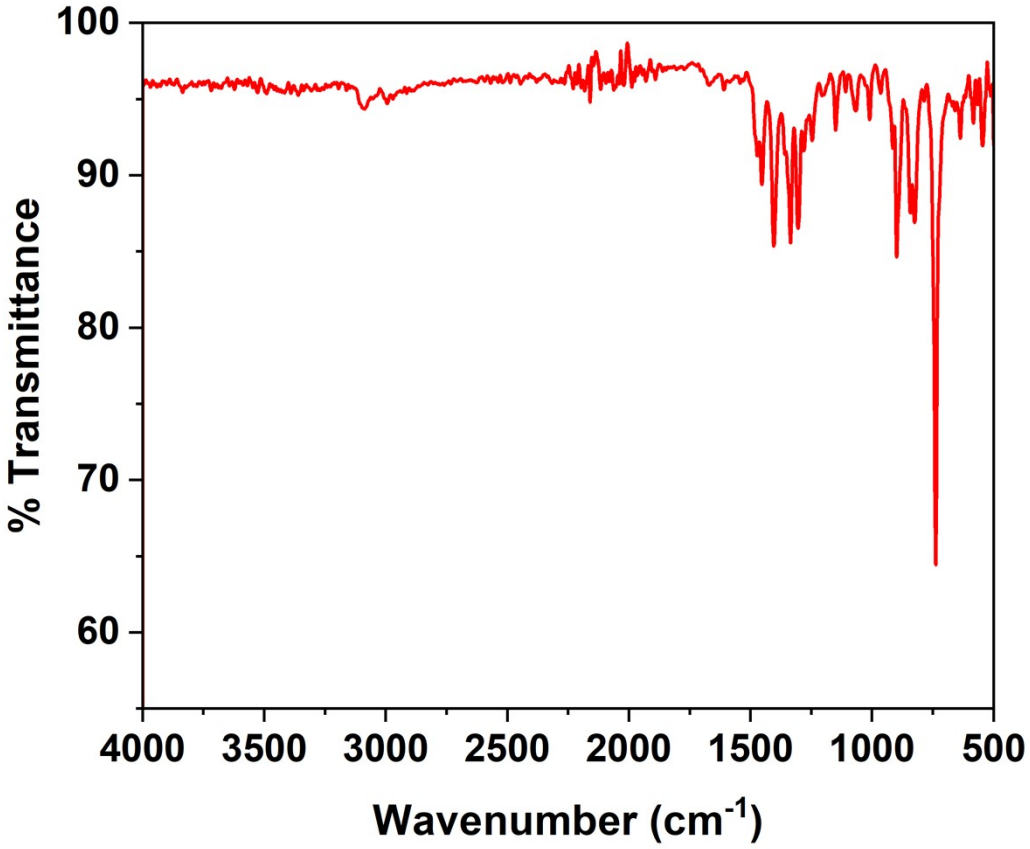

Figure S1. ATR-IR spectrum of **TMe**.

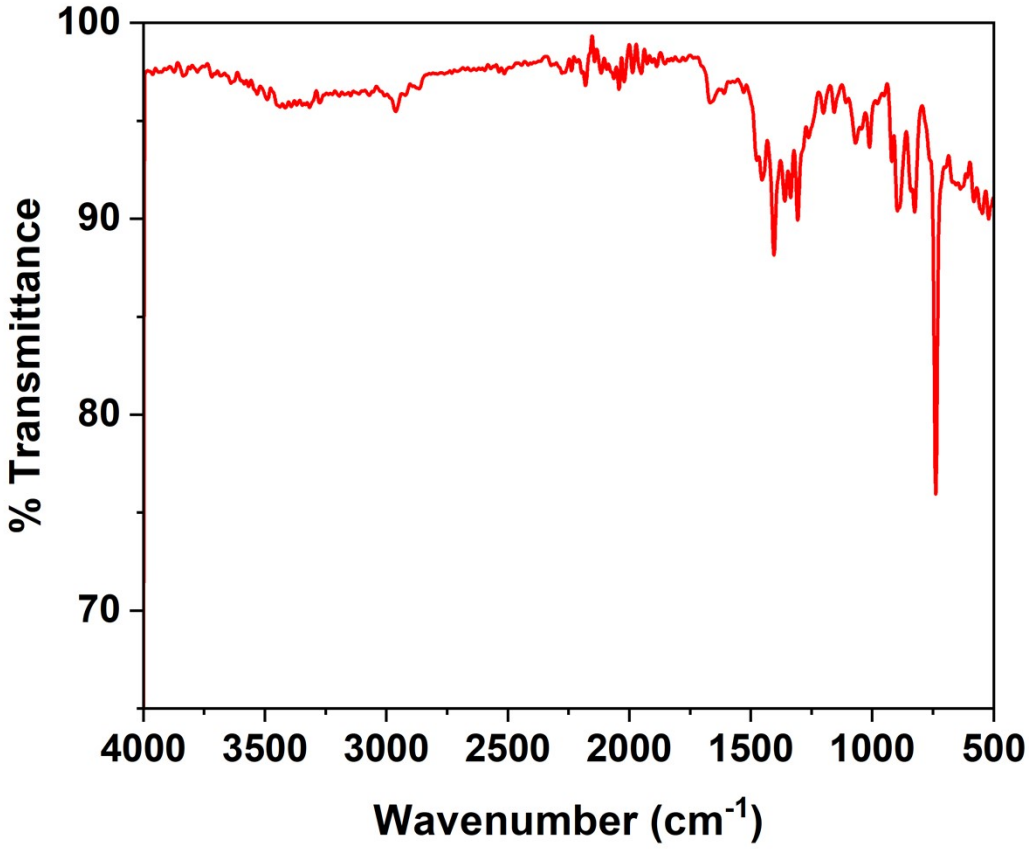

Figure S2. ATR-IR spectrum of **TEt**.

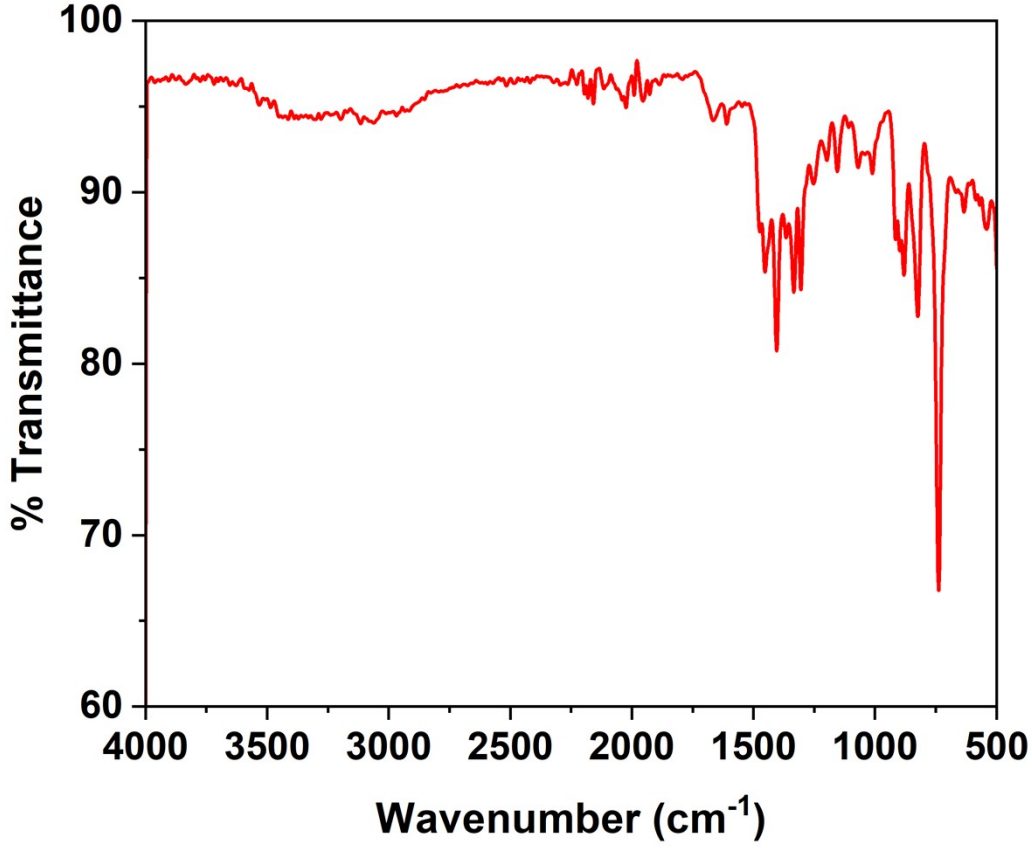

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Figure S3. ATR-IR spectrum of **TXy**.

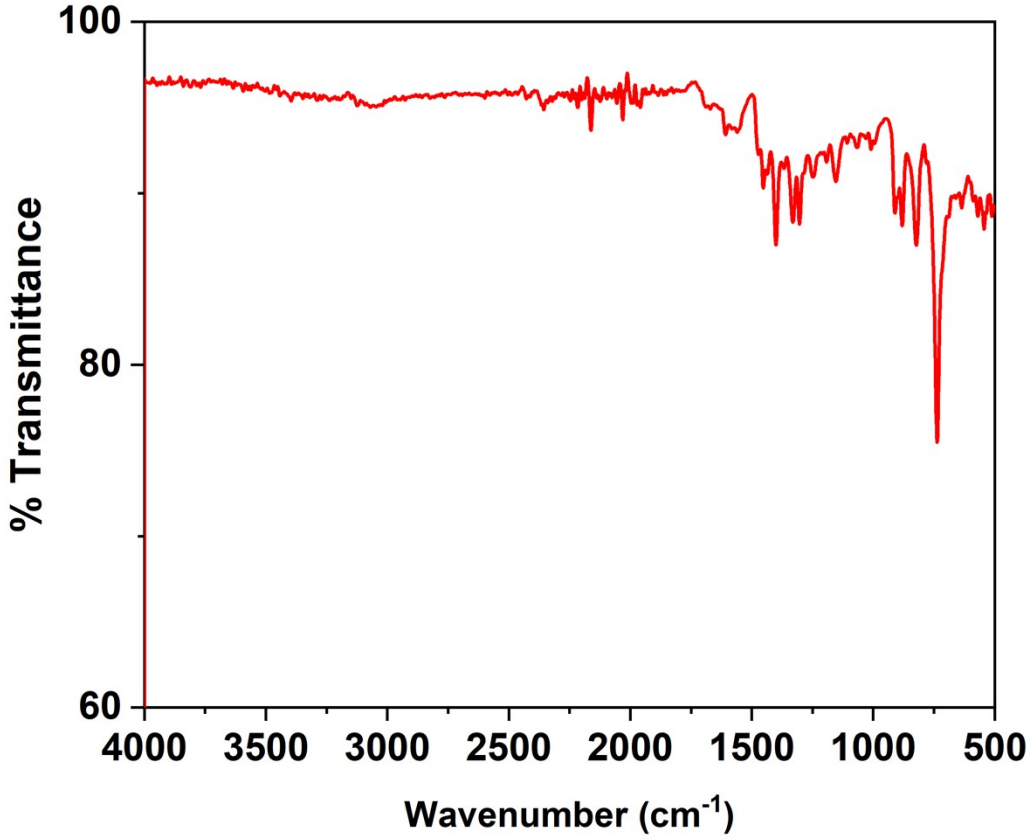


Figure S4. ATR-IR spectrum of **TH**.

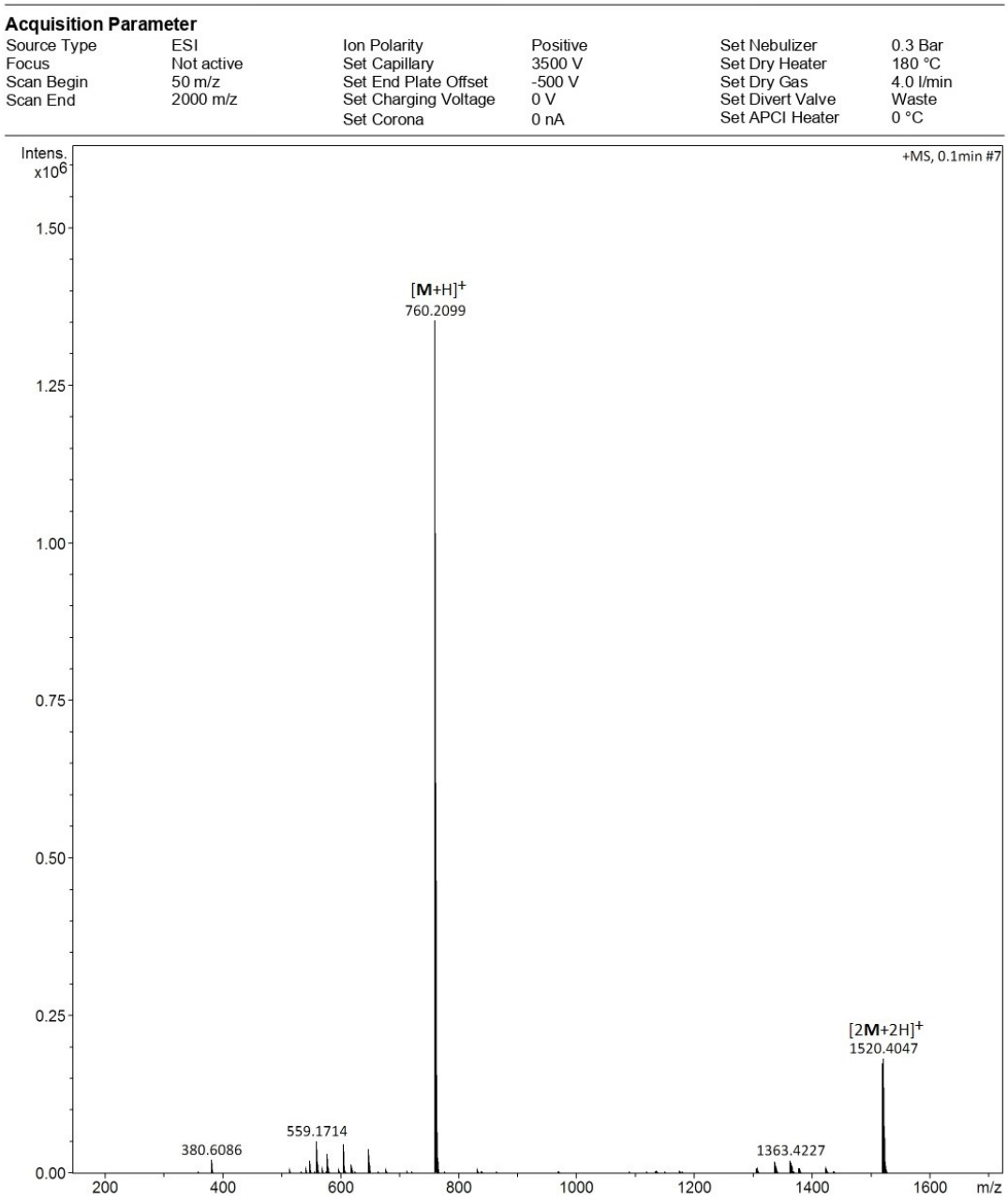
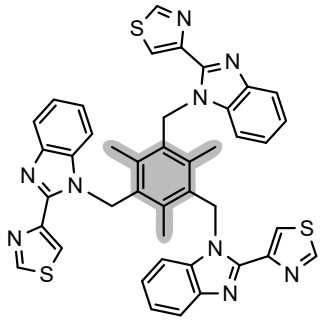


Figure S5. ESI-MS spectrum of **TMe** in positive ion mode.



TMe

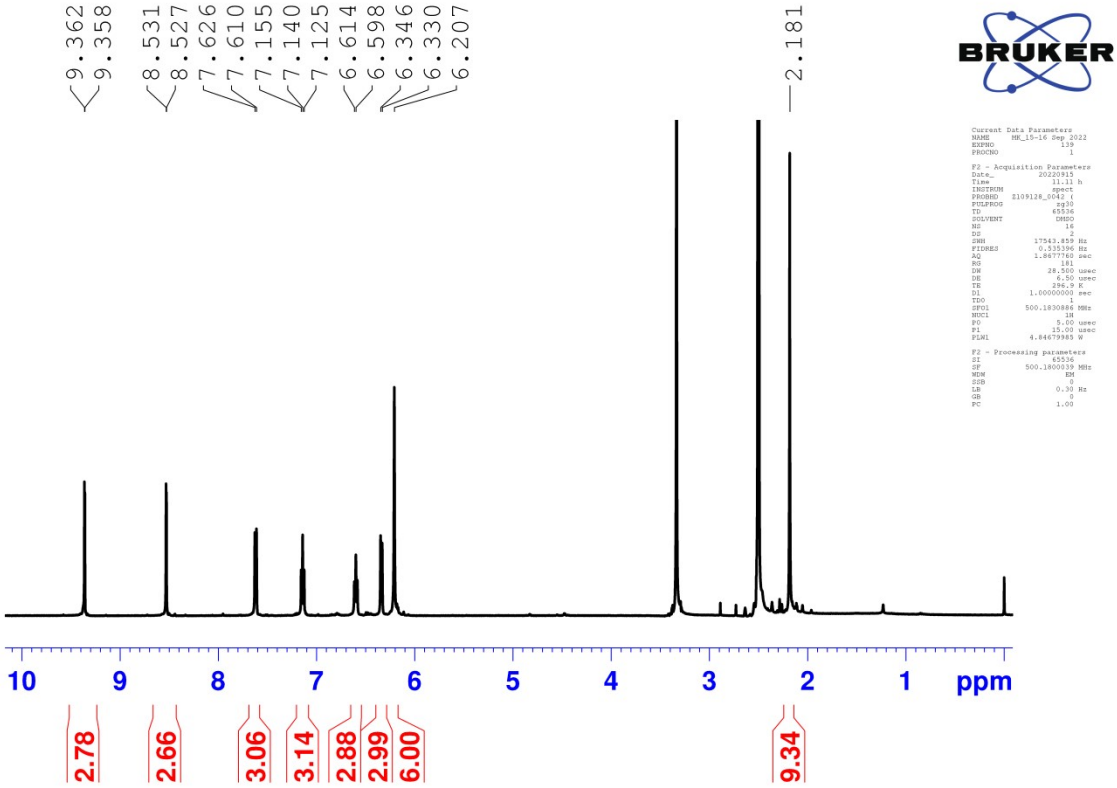


Figure S6. ^{1}H NMR spectrum of **TMe** in DMSO-d_6.

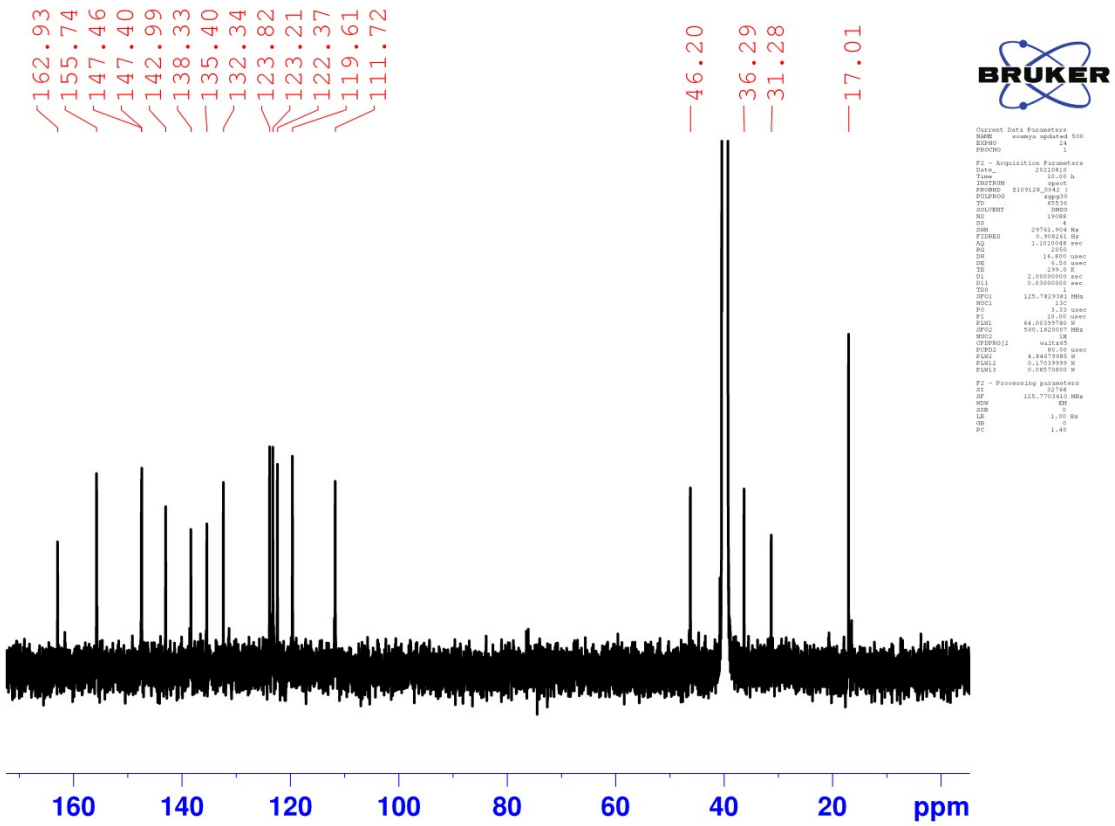


Figure S7. ^{13}C NMR spectrum of **TMe** in DMSO-d_6.

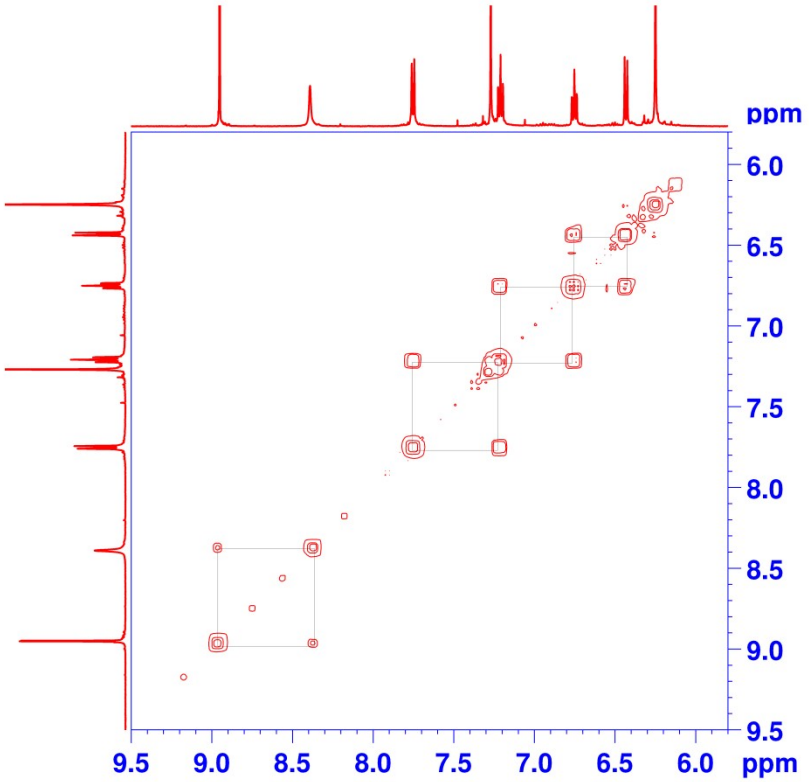


Figure S8. Partial ^{1}H-^{1}H COSY NMR spectrum of **TMe** in $CDCl_3$.

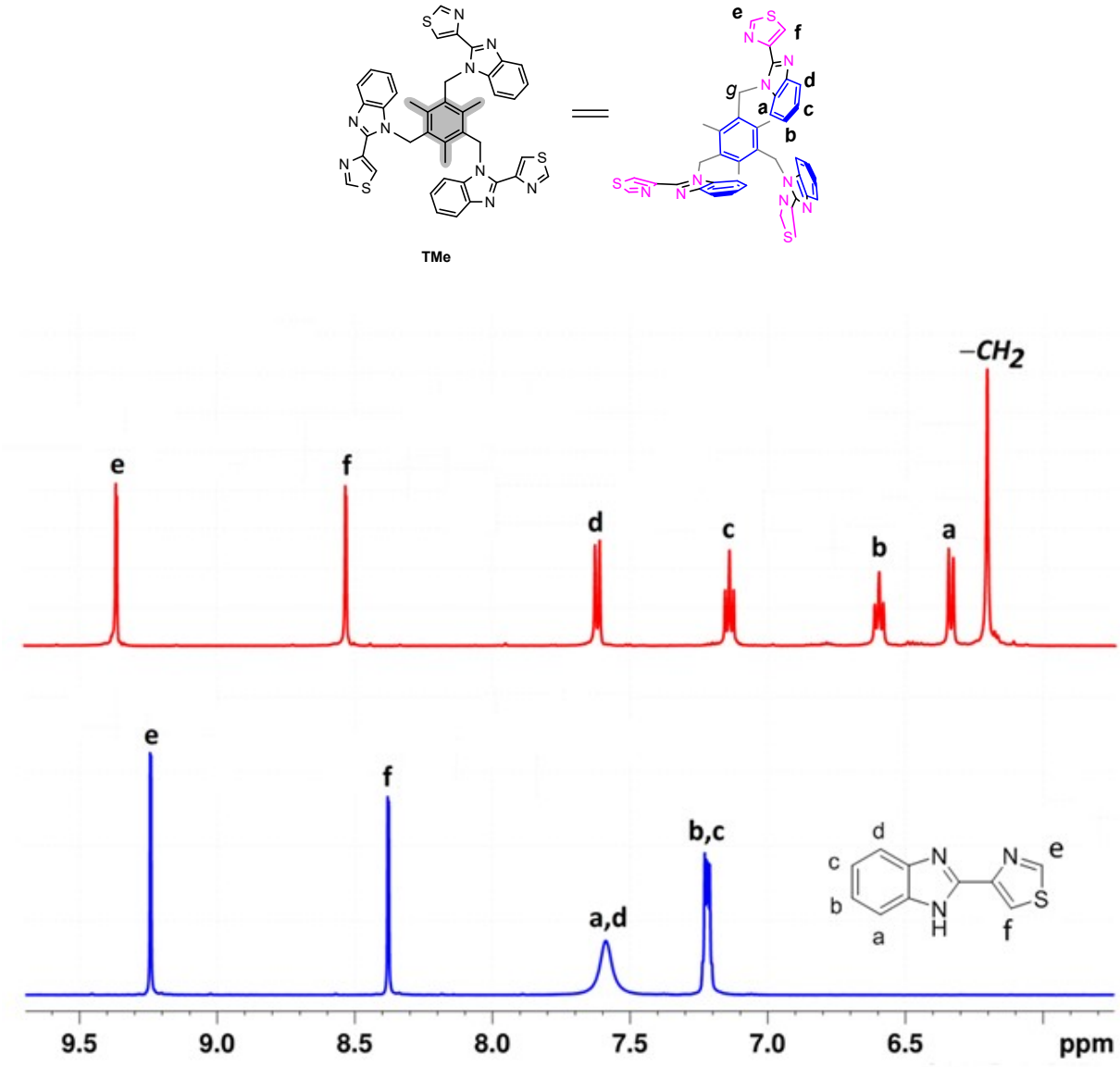
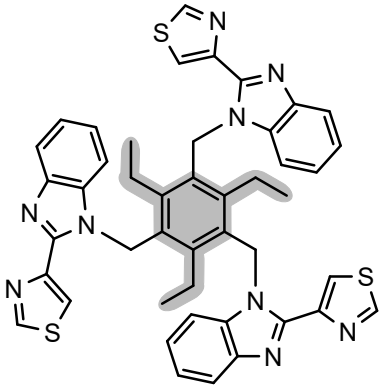


Figure S9. Partial ^{1}H NMR spectra of H-Tzbim and **TMe** (top) in DMSO-d_6.



TEt

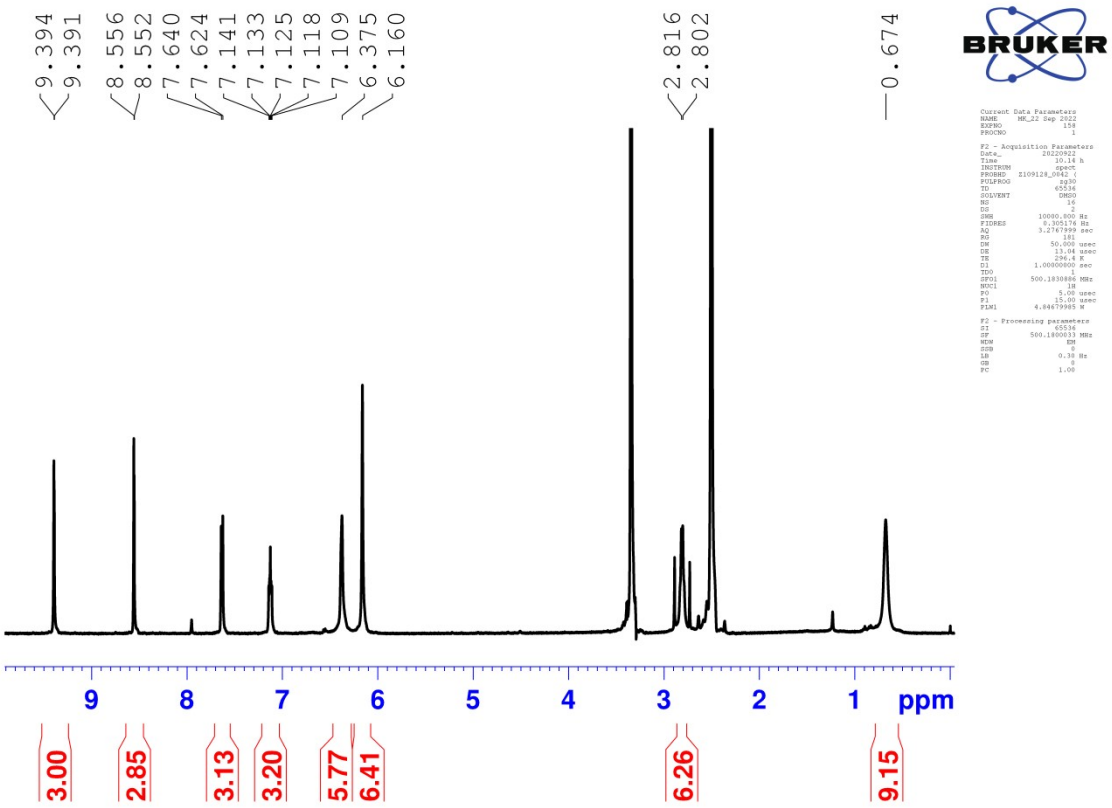


Figure S10. ^{1}H NMR spectrum of **TEt** in DMSO-d_6.

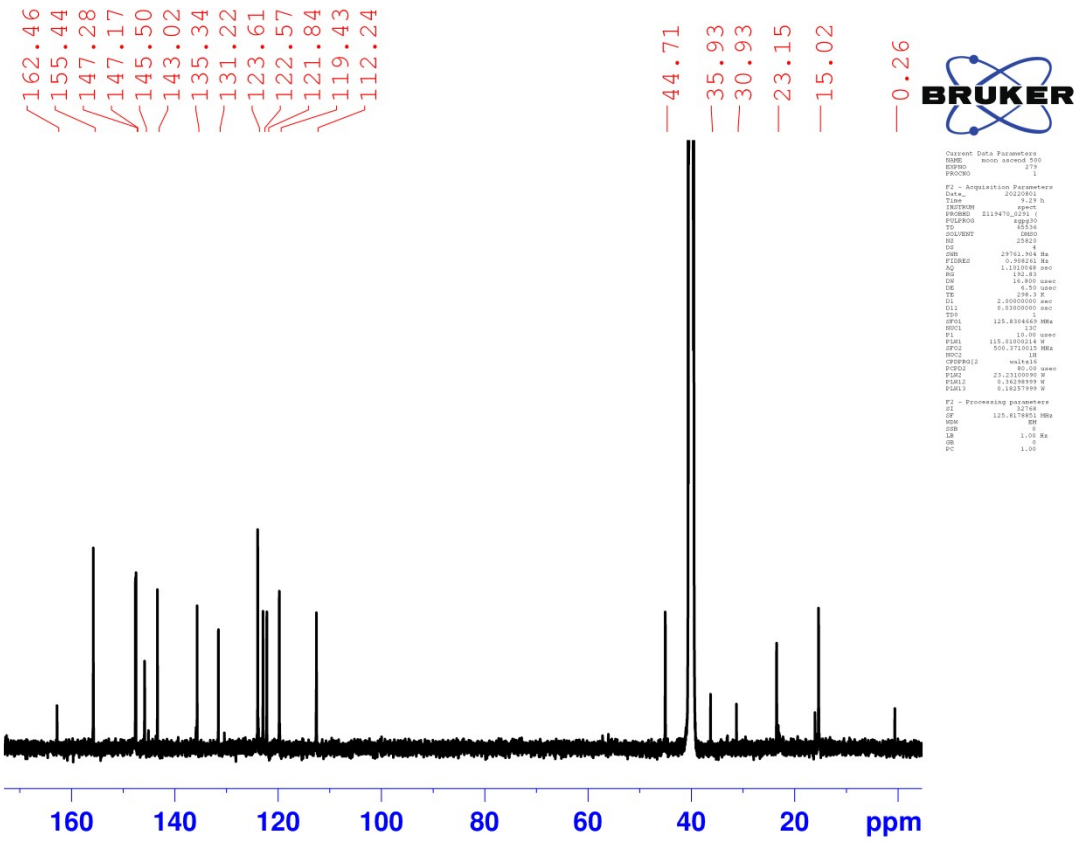


Figure S11. ^{13}C NMR spectrum of **TEt** in DMSO-d_6.

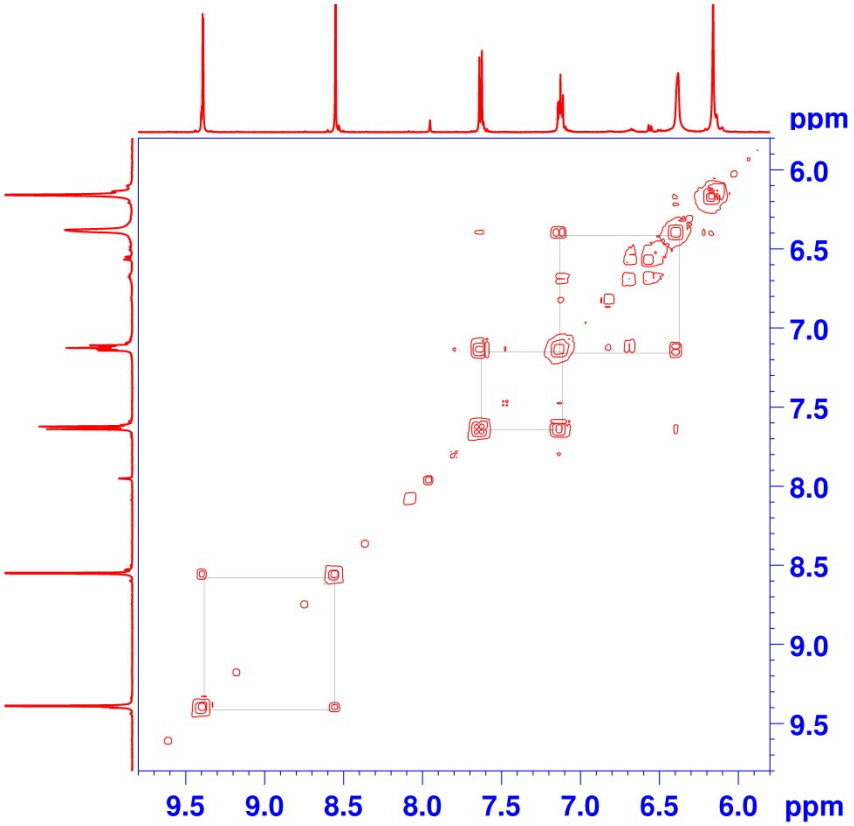


Figure S12. Partial ^{1}H–^{1}H COSY NMR spectrum of **TEt** in DMSO-d_6.

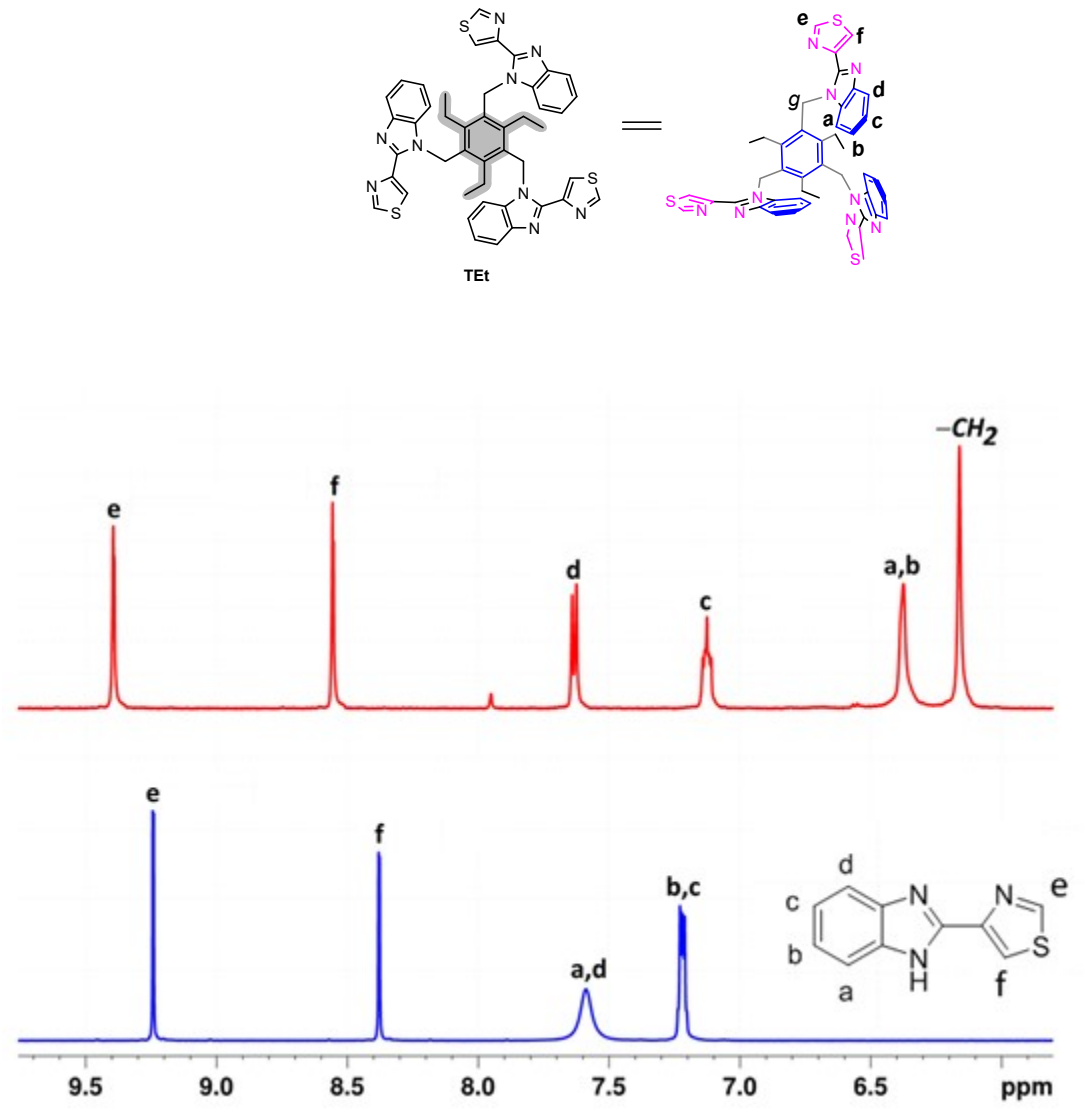


Figure S13. Partial ^{1}H NMR of spectra of H-Tzbim and **TEt** (top) in DMSO-d_6.

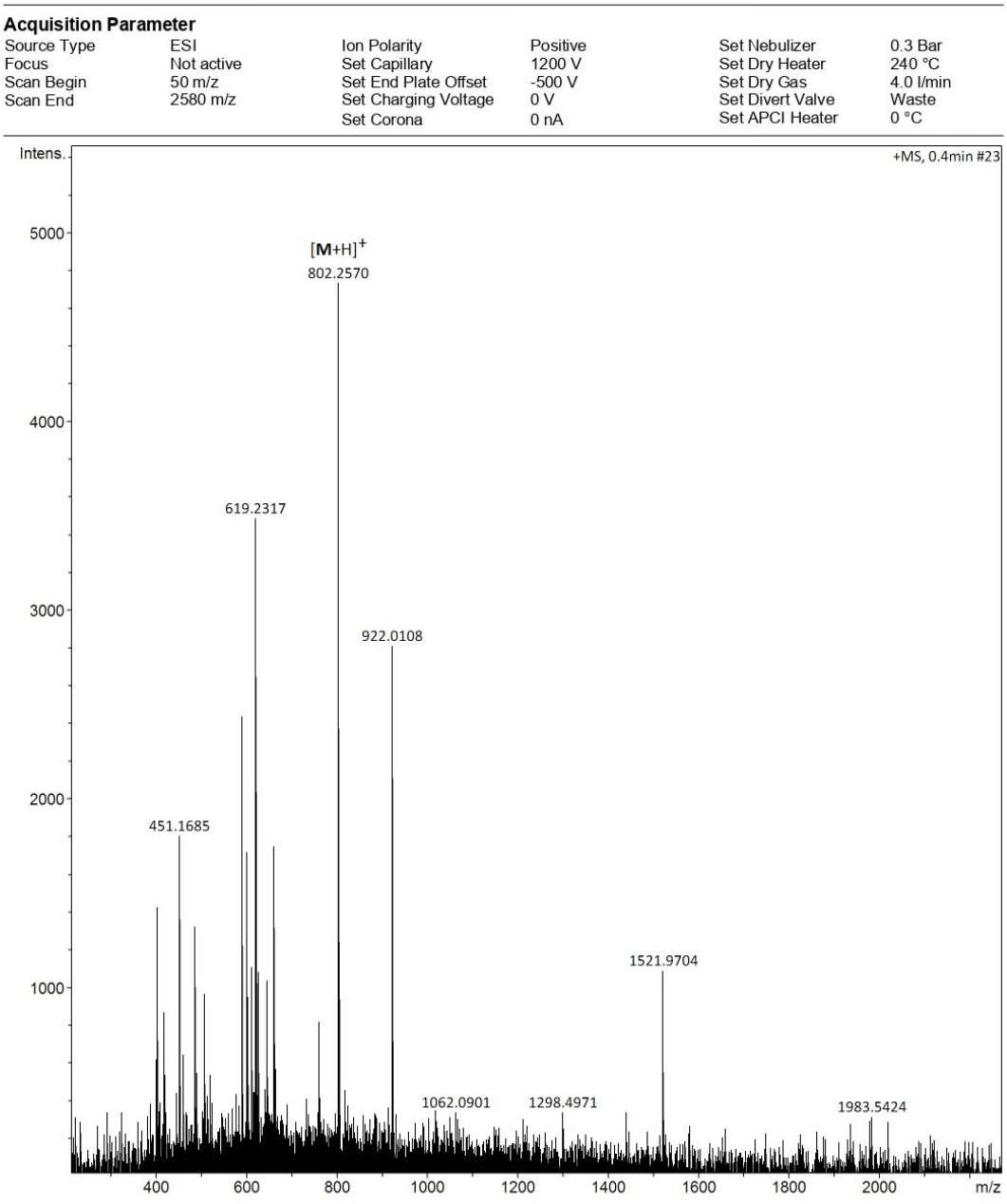
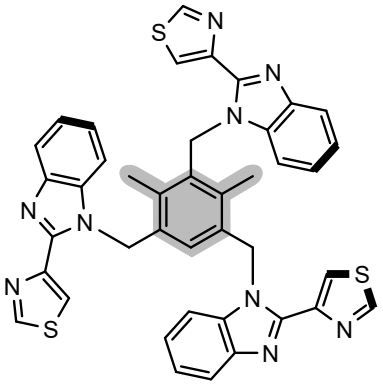


Figure S14. ESI-MS spectrum of **TEt** in positive ion mode.



TXy

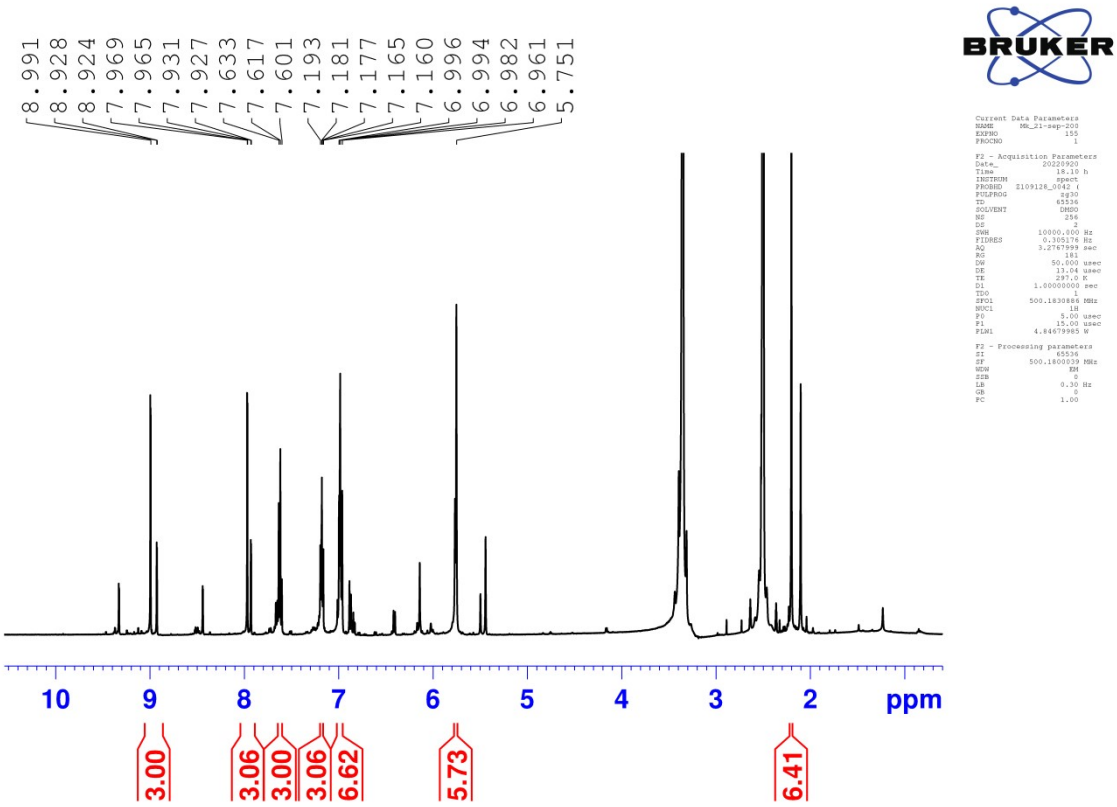


Figure S15. ^{1}H NMR spectrum of **TXy** in DMSO-d_6.

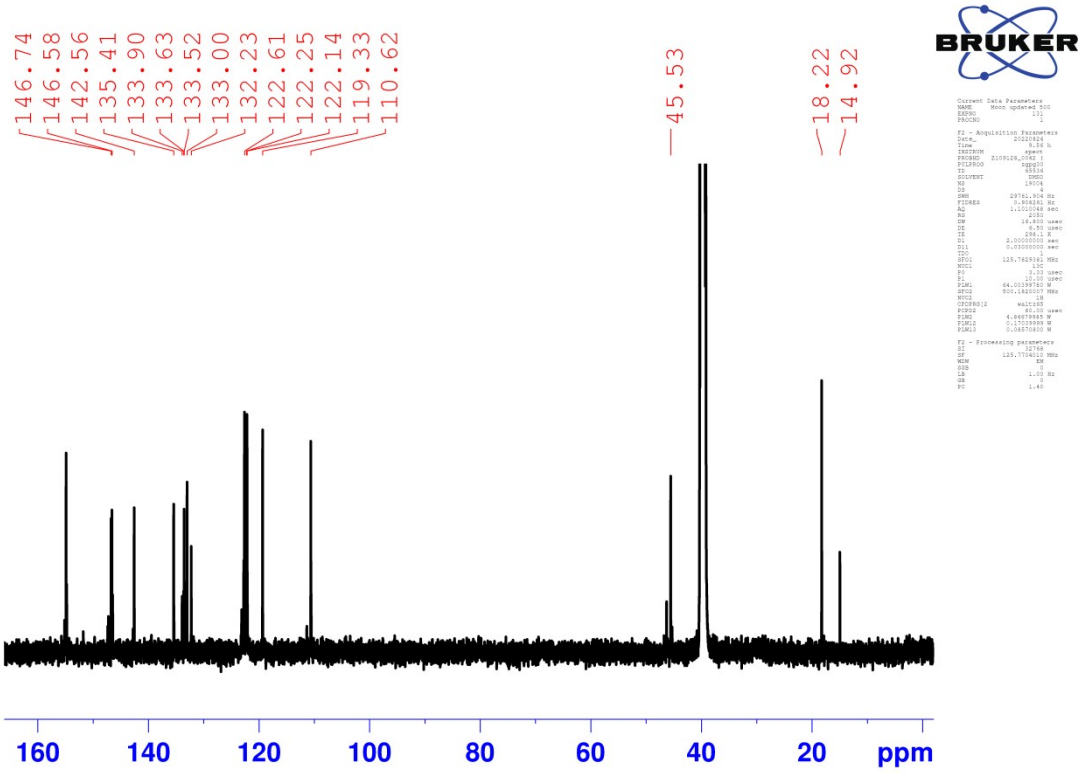


Figure S17. ^{13}C NMR spectrum of **TXy** in DMSO-d_6.

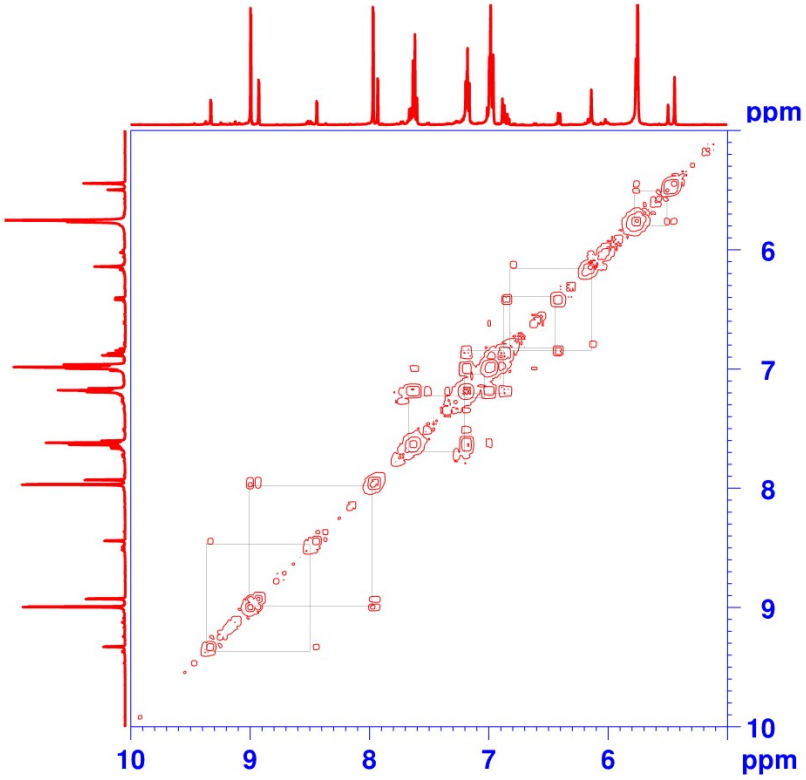


Figure S16. Partial ^{1}H-^{1}H COSY NMR spectrum of **TXy** in DMSO-d_6.

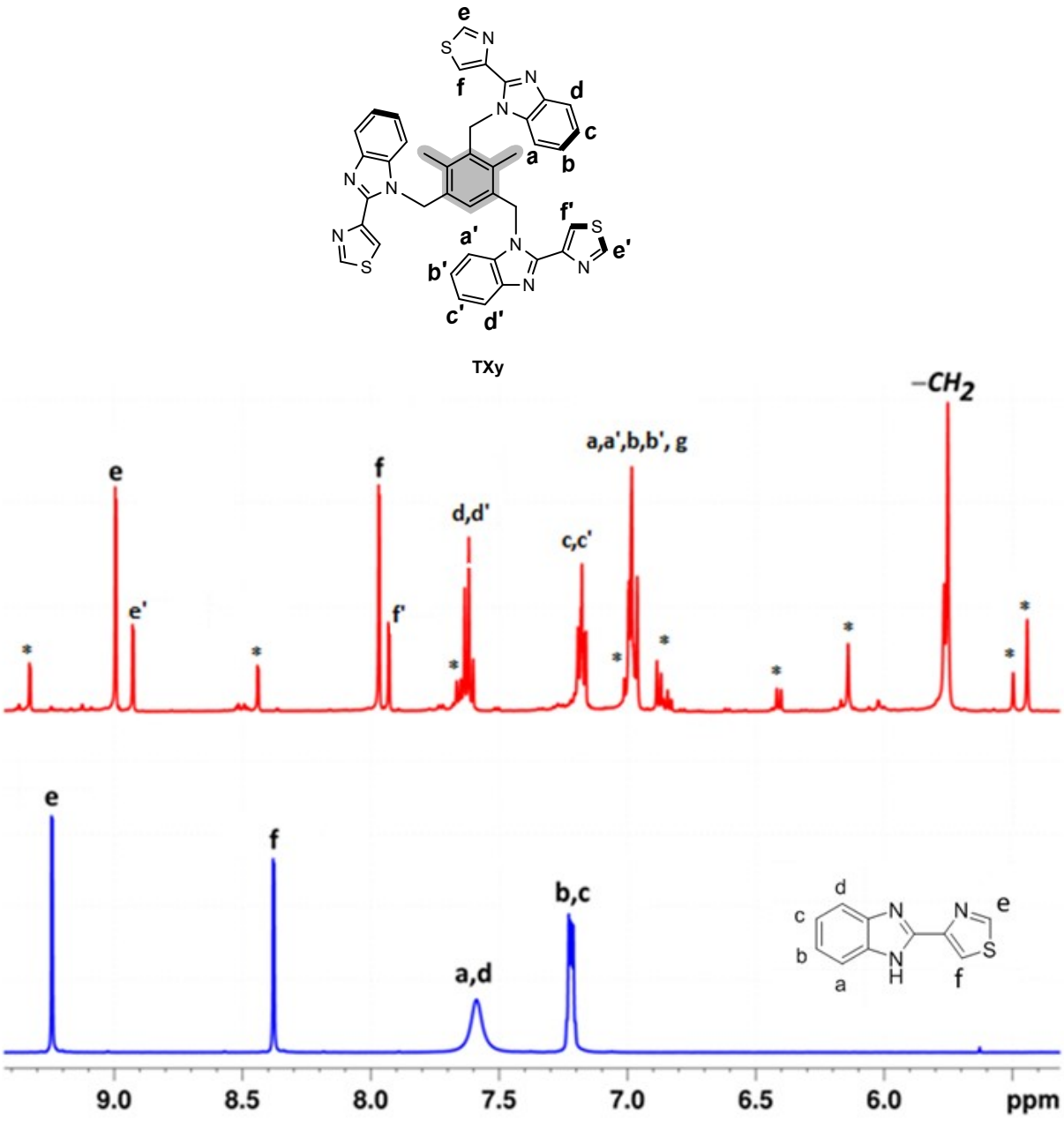


Figure S18. Partial ^{1}H NMR spectra of H-Tzbim and **TXy** in DMSO-d_6.

Acquisition Parameter

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Scan End	2500 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

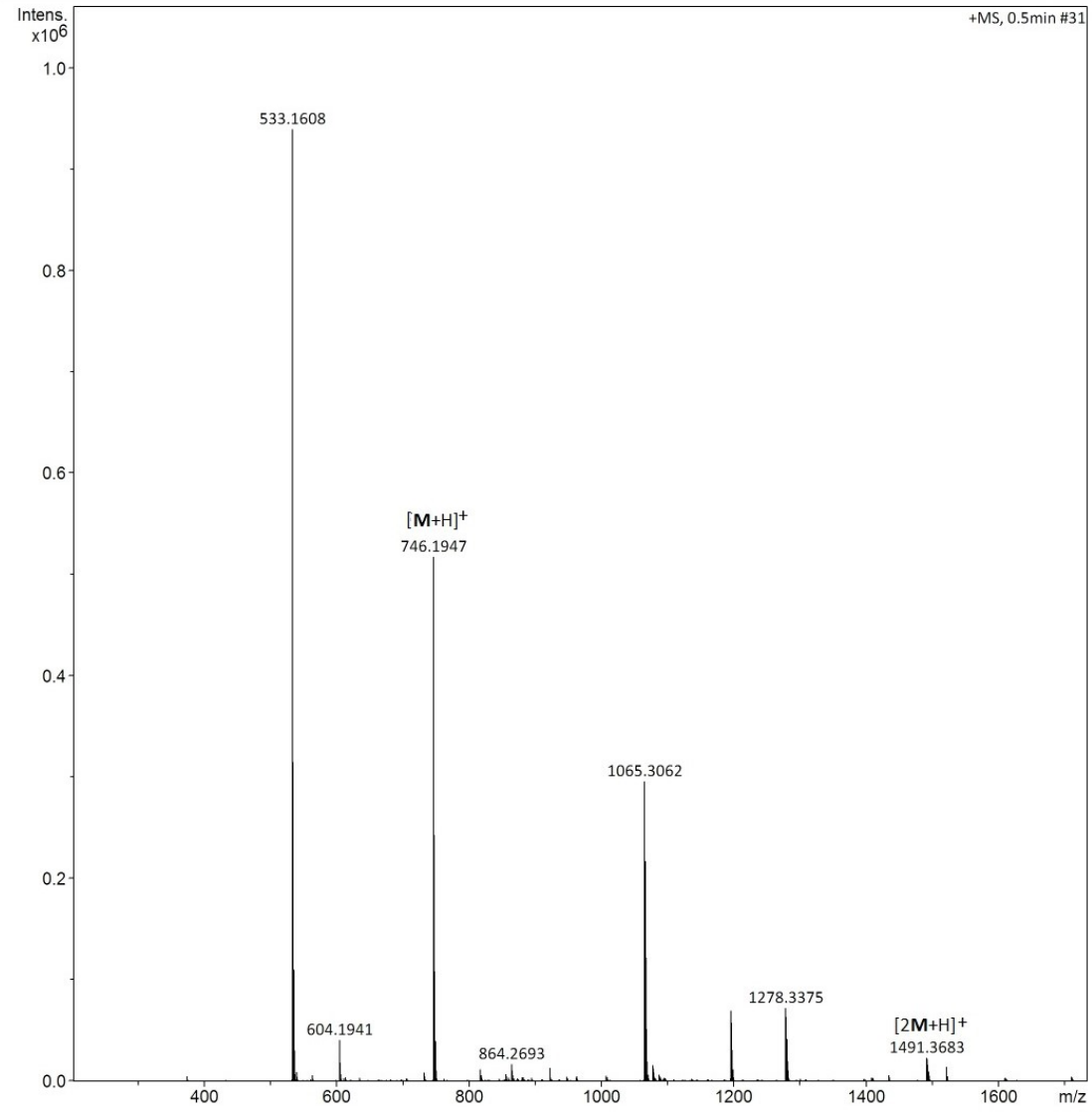
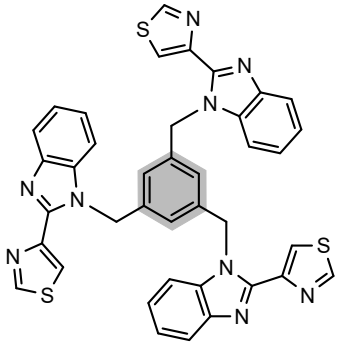


Figure S19. ESI-MS spectrum of **TXy** in positive ion mode.



TH

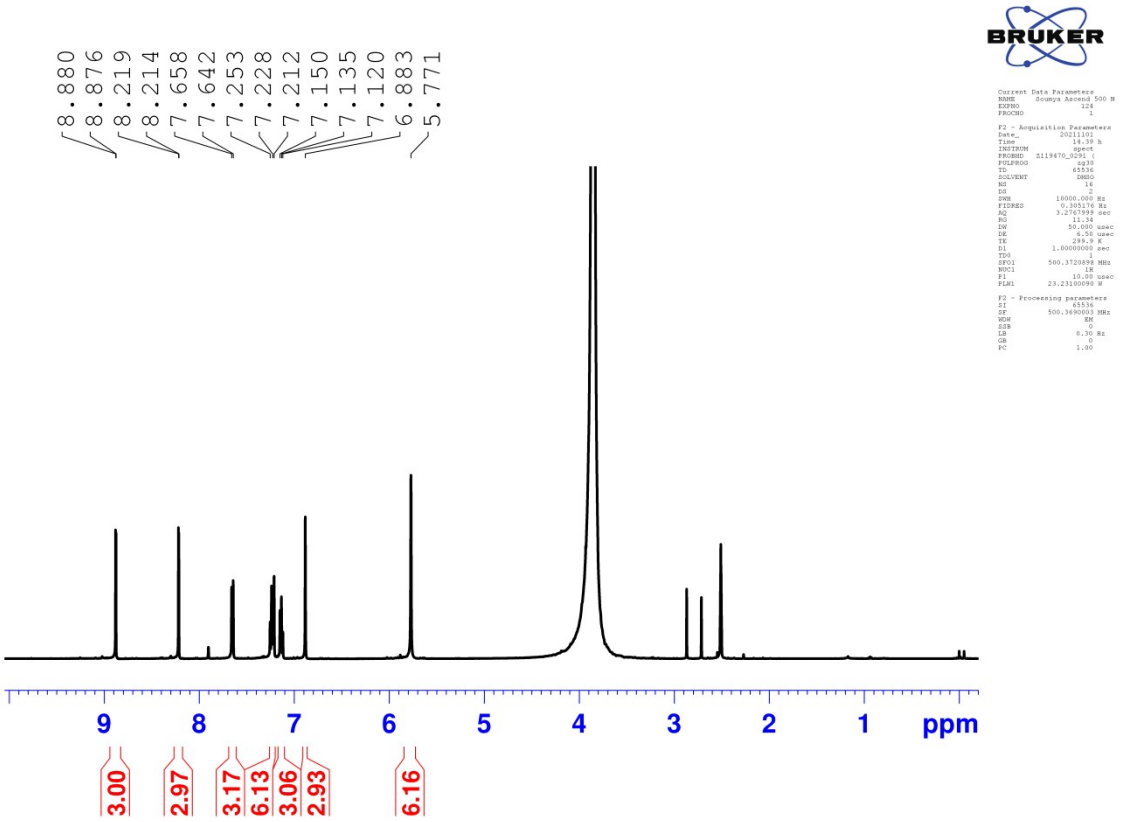


Figure S20. ^{1}H NMR spectrum of **TH** in DMSO-d_6.

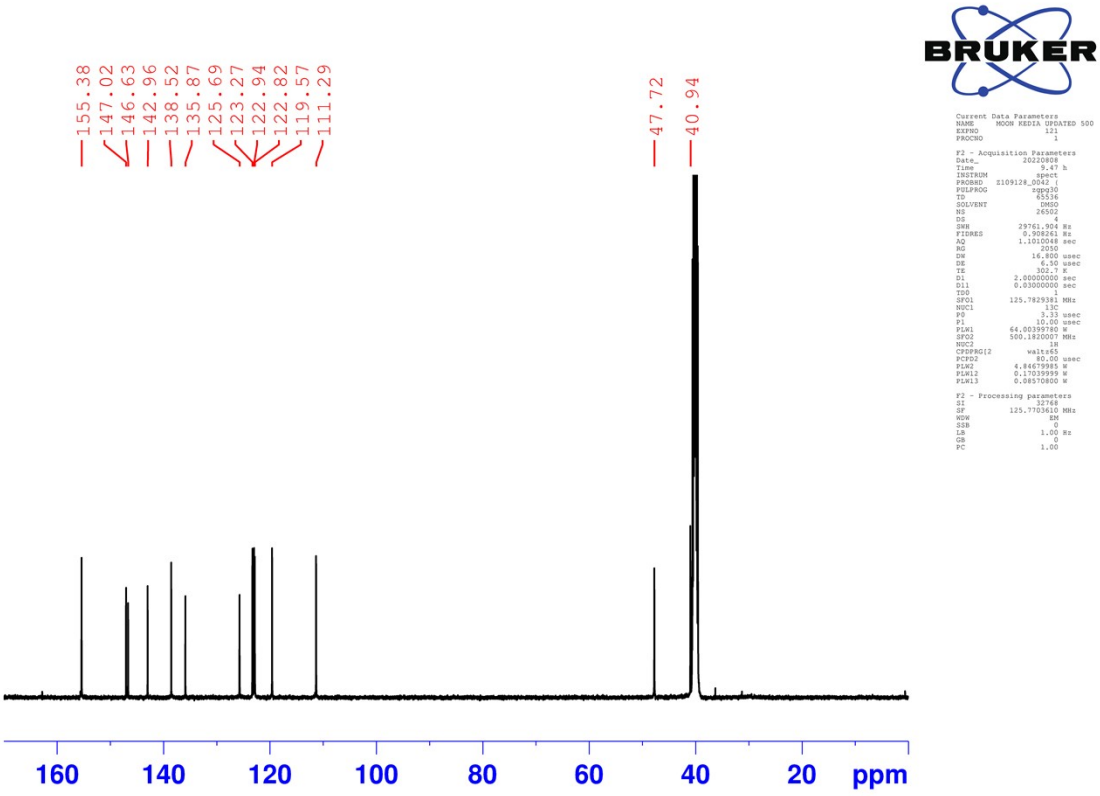


Figure S21. ^{13}C NMR spectrum of **TH** in DMSO-d_6.

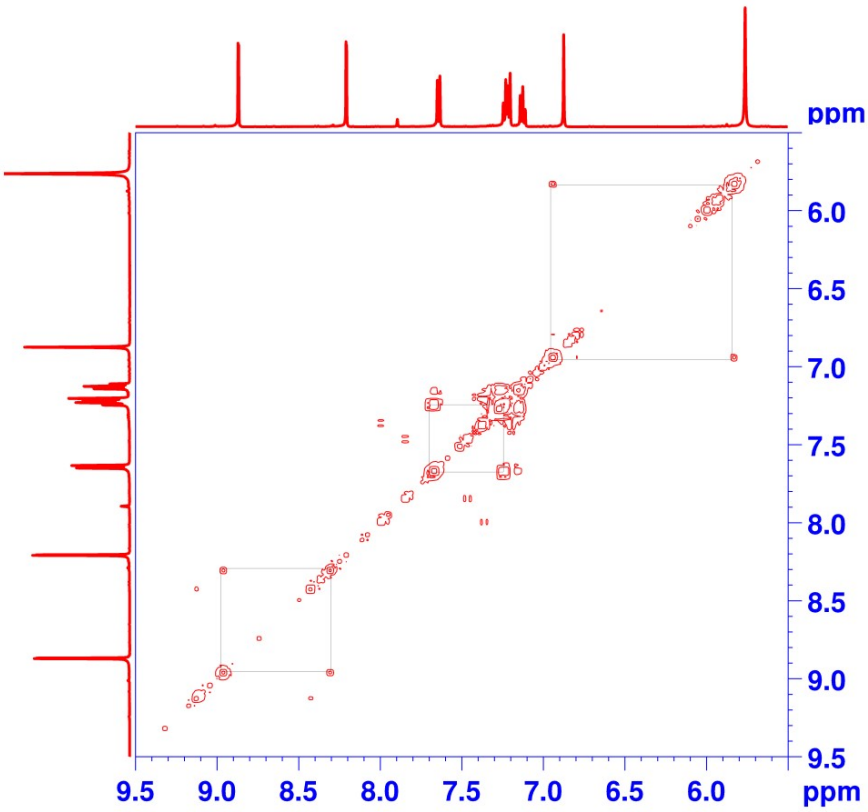


Figure S22. Partial ^{1}H-^{1}H COSY NMR spectrum of **TH** in DMSO-d_6.

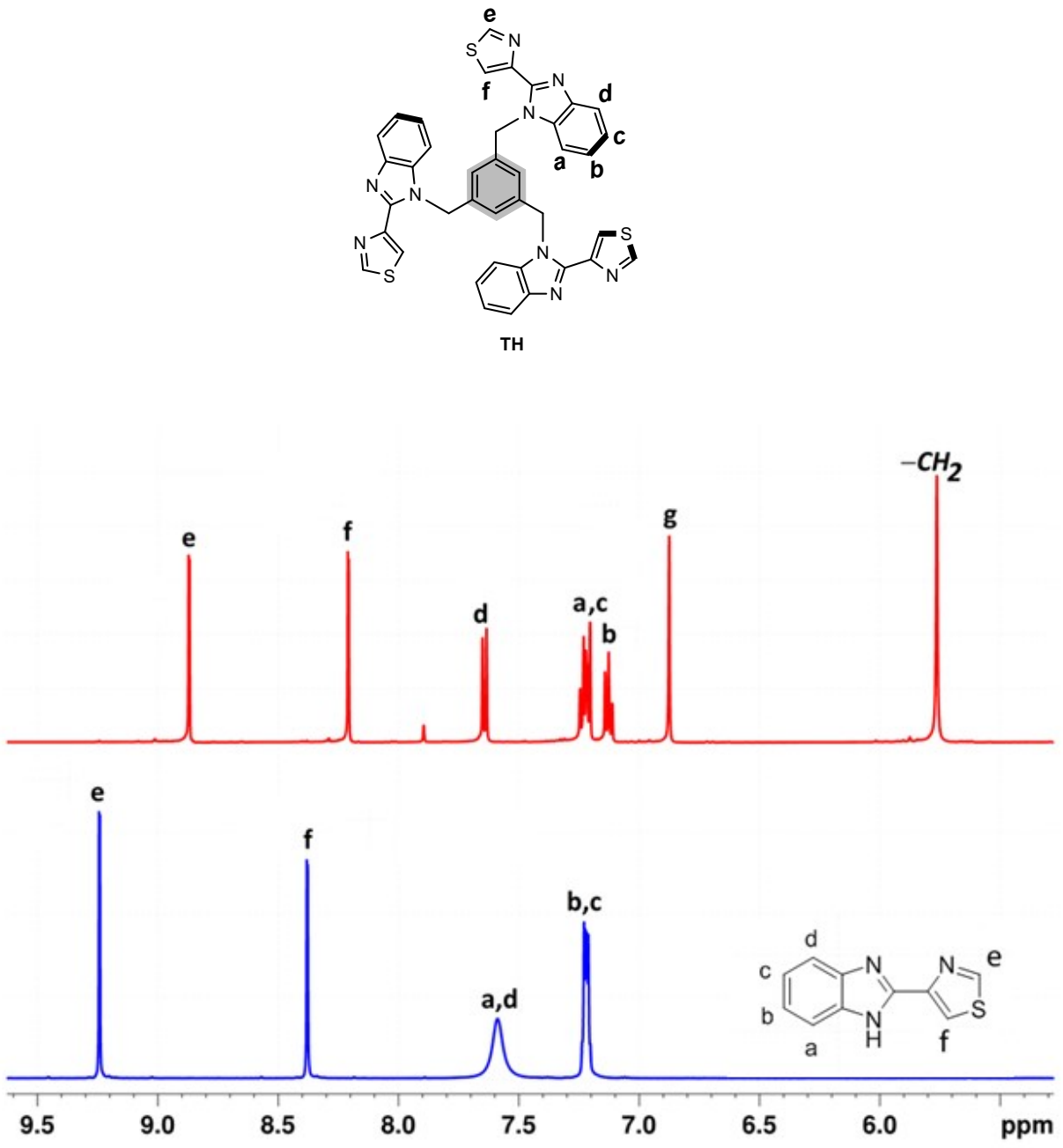


Figure S23. Partial ^{1}H NMR spectra of H-Tzbim and **TH** in DMSO-d_6.

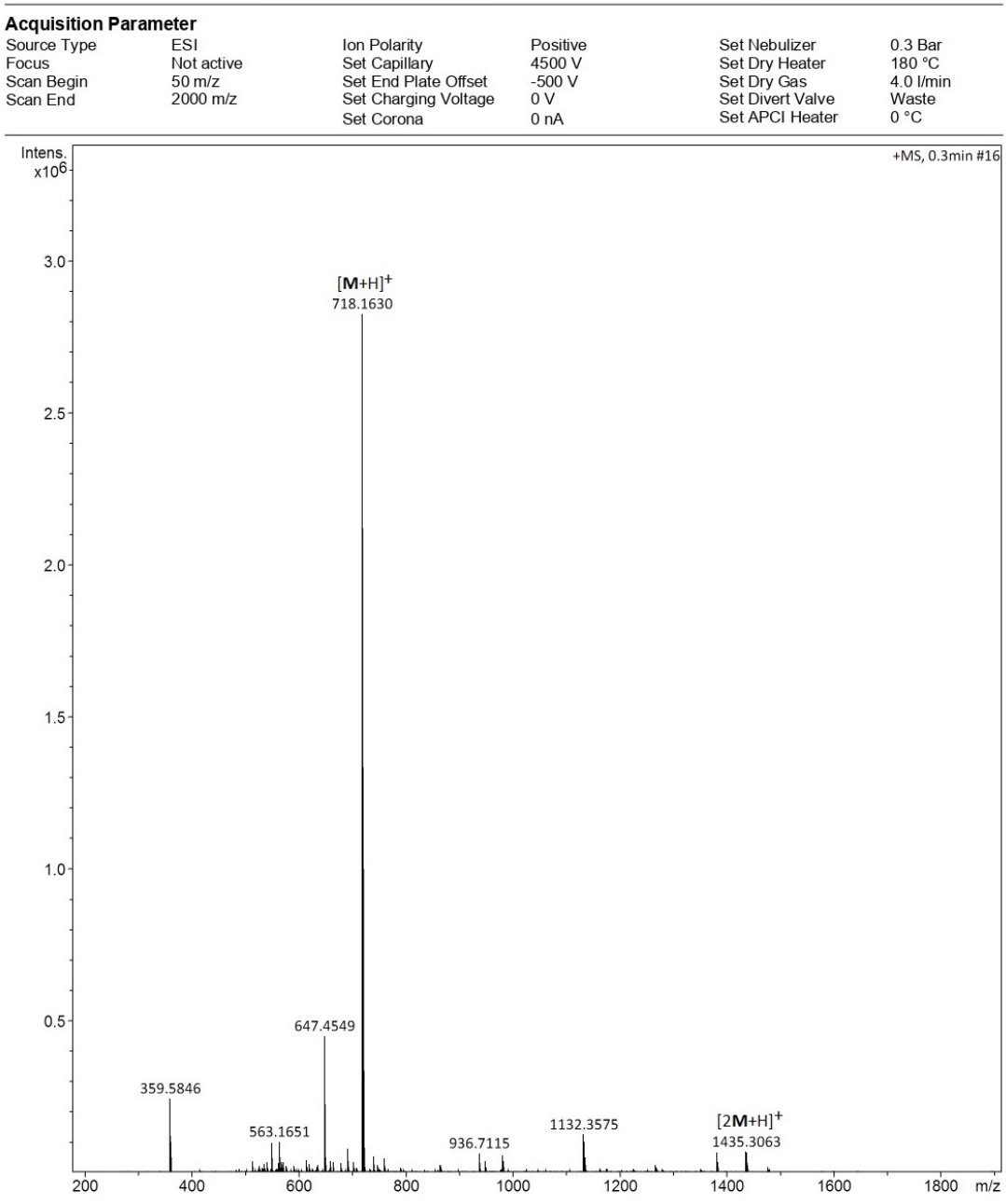


Figure S24. ESI-MS spectrum of **TH** in positive ion mode.

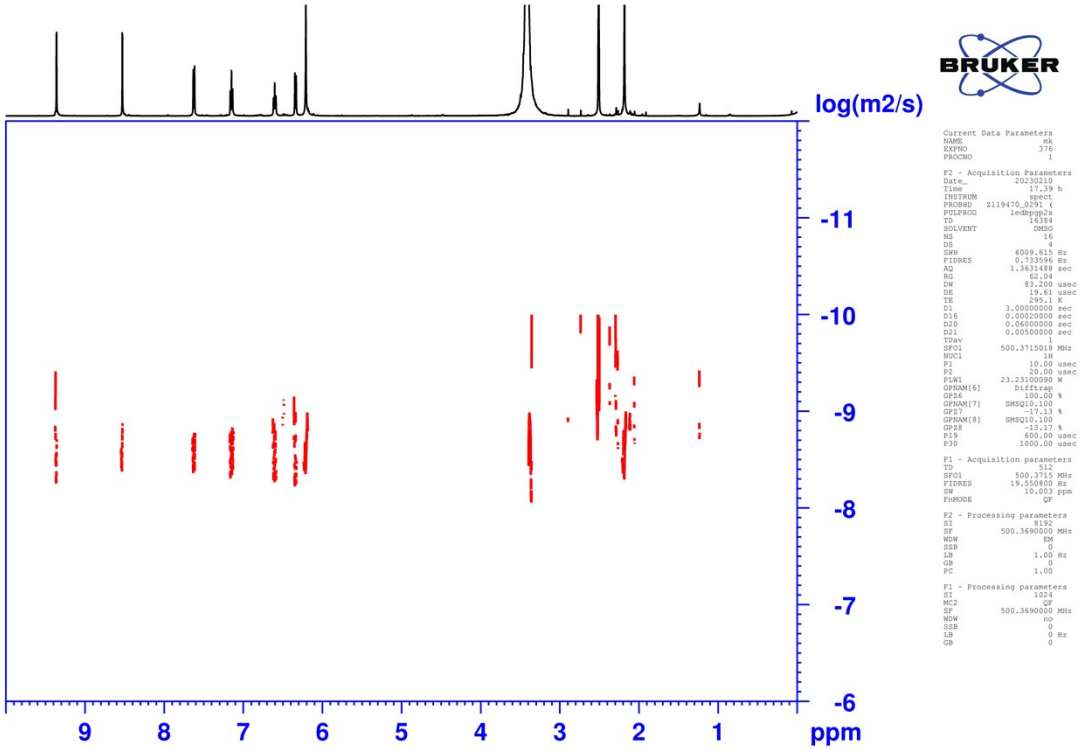


Figure S25. Partial ^{1}H-^{1}H DOSY NMR spectrum of **TMe** in DMSO-d_6.

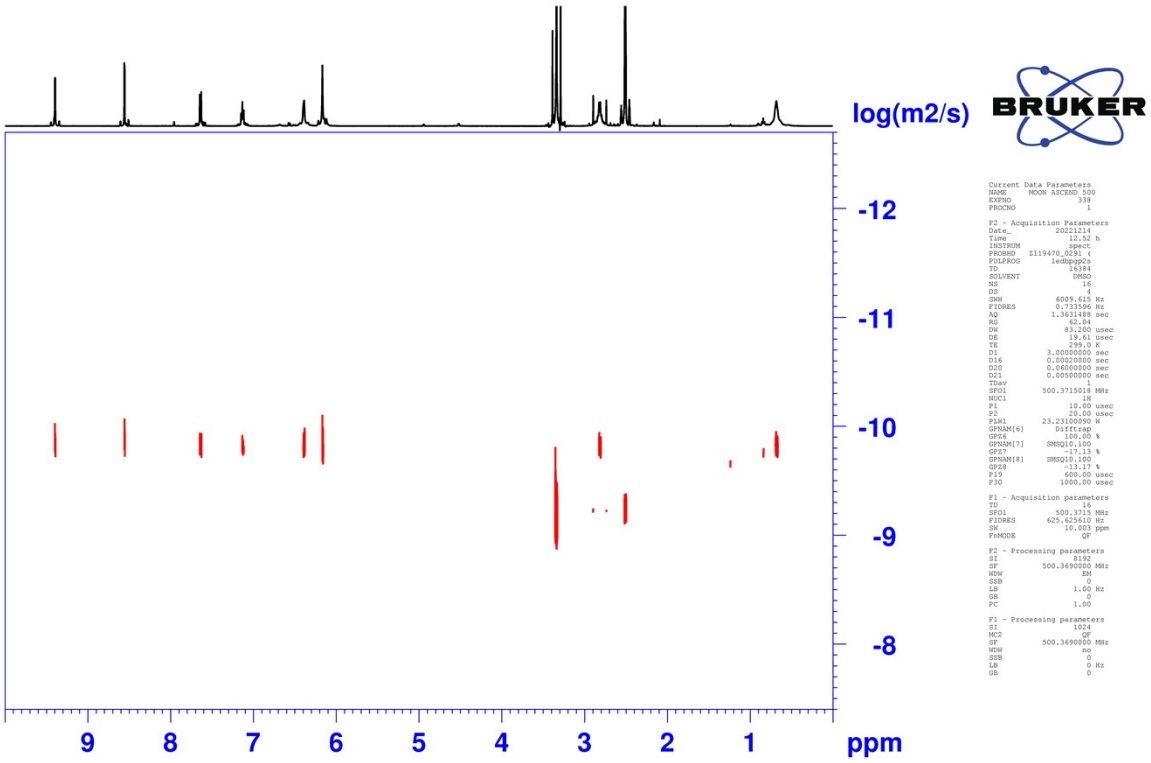


Figure S26. Partial ^{1}H-^{1}H DOSY NMR spectrum of **TEt** in DMSO-d_6.

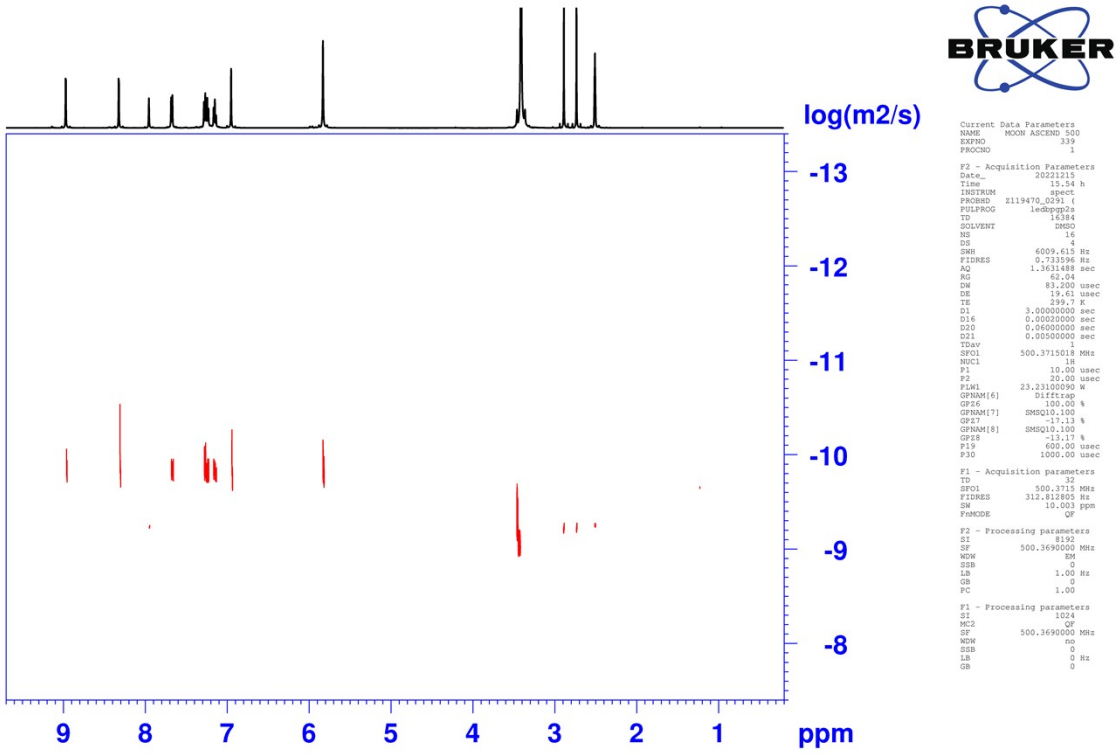


Figure S27. Partial ^{1}H-^{1}H DOSY NMR spectrum of **TXy** in DMSO-d_6.

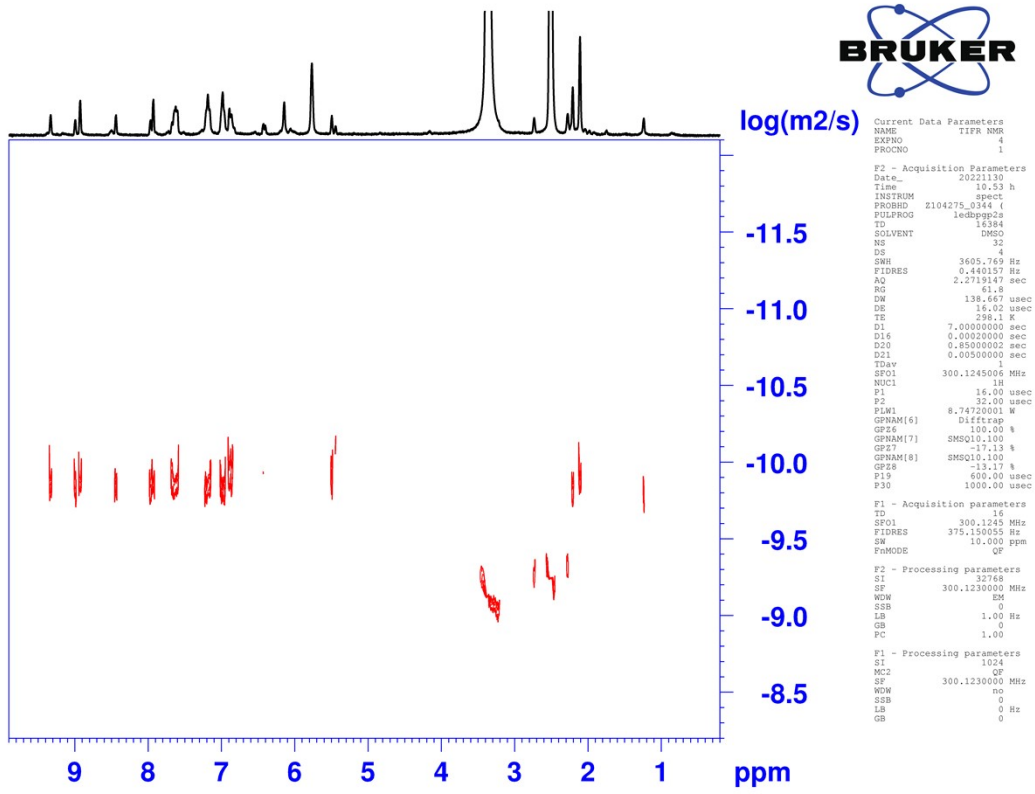


Figure S28. Partial ^{1}H-^{1}H DOSY NMR spectrum of **TH** in DMSO-d_6.

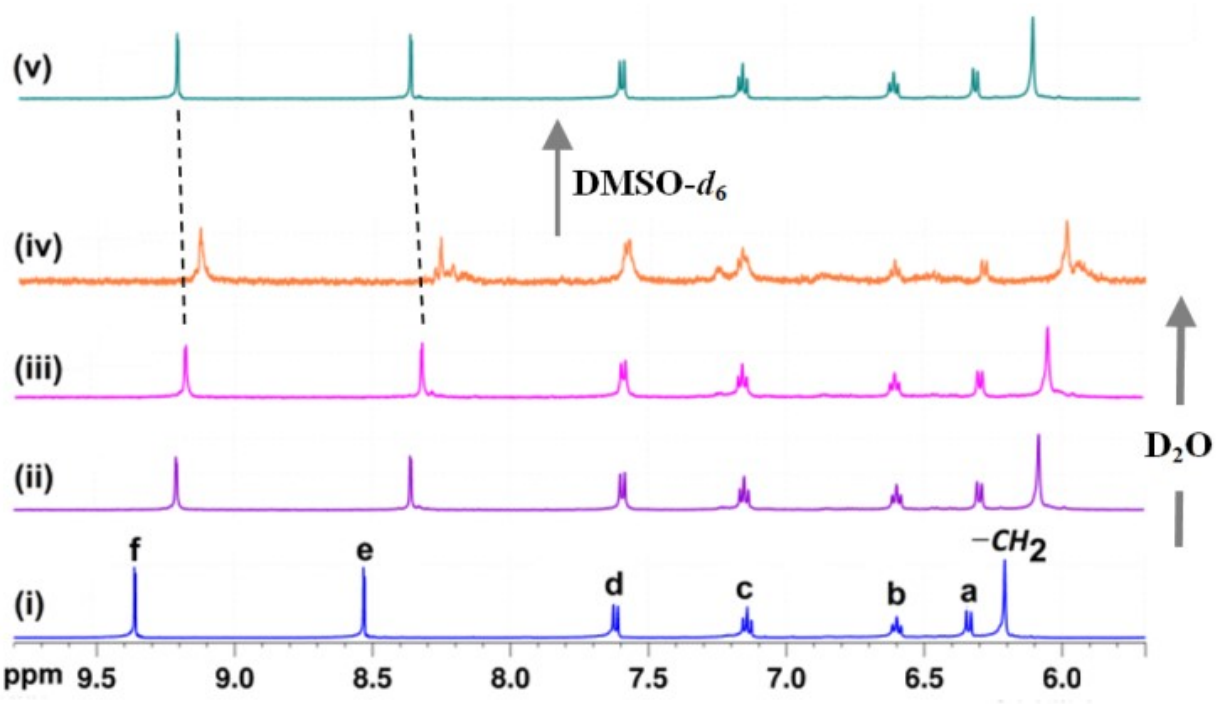


Figure S29. ^{1}H-NMR titration at 298 K of **TMe** in DMSO-d_6/D_2O mixture in the following vol/vol ratio (i) 100:0, (ii) 77:23, (iii) 71:29, (iv) 56:44 and (v) 71:29.

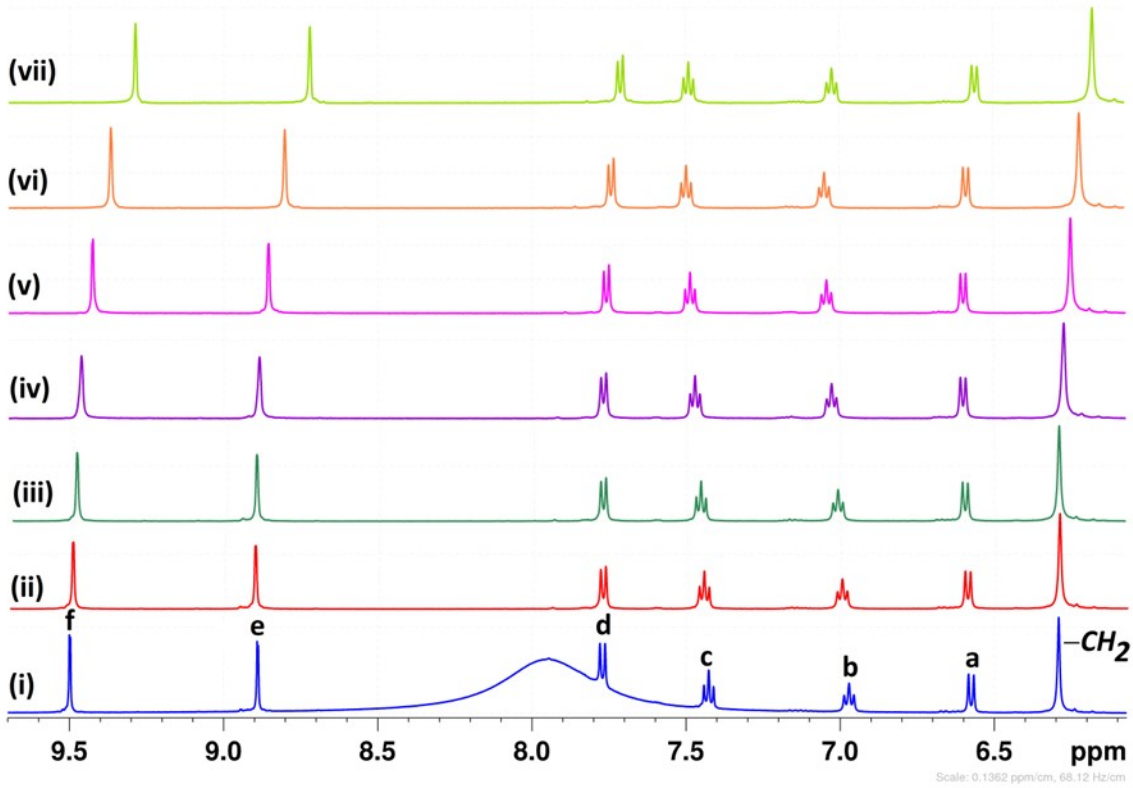


Figure S30. ^{1}H-NMR spectra of titration of **TMe** +CF_3COOH at 298 K in DMSO-d_6/ D_2O mixture in the following vol/vol ratio (i) 100:0 (ii) 98.5:1.5, (iii) 97:3,(iv) 92.5:7.5, (v) 72:28, (vi) 87.5:12.5 and (vii) 66:34.

References

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