Supporting Information for

Telescoped continuous flow generation of a library of highly substituted 3-thio-1,2,4-triazoles

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1. GENERAL PROCEDURE FOR THE BATCH SYNTHESIS OF HYDRAZIDES 1b-d

The respective ester (3 mmol), and hydrazine monohydrate (882 µL, 18 mmol) were refluxed in ethanol/methanol overnight. The reaction was diluted in 20 mL of water, and extracted with EtOAc (6 x 20 mL). The organic phase was evaporated under reduced pressure to give the desired products.

4-nitrobenzohydrazide (1b). Quantitative. Compound description: light yellow solid. **^{1}H NMR (400 MHz, DMSO-d6):** δ 10.17 (s, 1 H), 8.30 (d, *J* = 8.7 Hz, 2 H), 8.06 (d, *J* = 8.7 Hz, 2 H); **^{13}C NMR (101 MHz, DMSO-d6):** δ 164.3 (C_0), 149.4 (C_0), 139.5 (C_0), 128.9 (CH), 124.0 (CH). This data was consistent with published data [C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao and S. K. Prasad, *J. Org. Chem.*, 2009, **74**, 3168–3171].

Picolinohydrazide (1c). Quantitative. Compound description: white solid. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 8.54 – 8.37 (m, 1 H), 8.08 (d, *J* = 7.8 Hz, 1 H), 7.75 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.34 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1 H); **^{13}C NMR (63 MHz, $CDCl_3$):** δ 164.6 (C_0), 149.1 (C_0), 148.3 (CH), 137.2 (CH), 126.3 (CH), 122.2 (CH). This data was consistent with published data [J. Xie, X. Zhu, M. Huang, F. Meng, W. Chen and Y. Wan, *European J. Org. Chem.*, 2010, 3219–3223].

3,5-dimethoxybenzohydrazide (1d). Quantitative. Compound description: white solid solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 (s, 1 H), 6.86 (d, *J* = 2.2 Hz, 2 H), 6.59 (t, *J* = 2.2 Hz, 1 H), 3.82 (s, 6 H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.6 (C_0), 161.0 (C_0), 134.8 (C_0), 104.8 (CH), 103.9 (CH), 55.6 (CH_3).

7. ^{1}H and ^{13}C NMR spectra of compounds

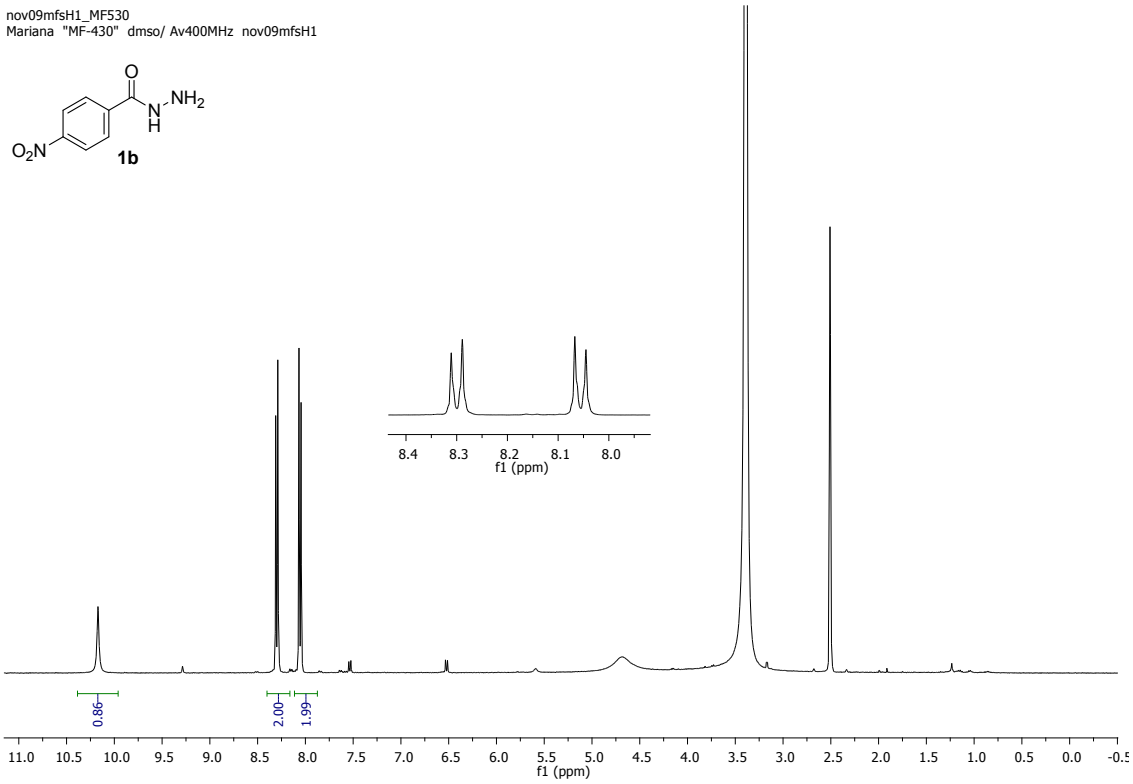

Figure S1. ^{1}H NMR spectrum (DMSO-d6, 400 MHz) of compound **1b**.

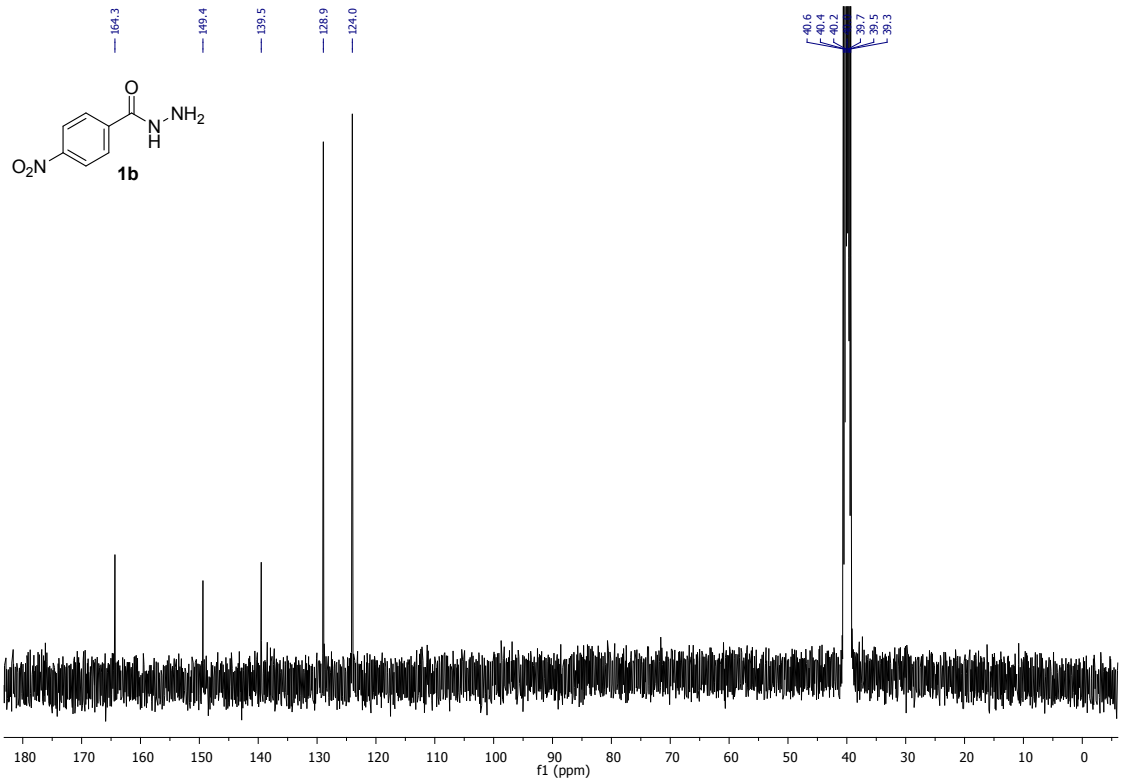

Figure S2. ^{13}C NMR spectrum (DMSO-d6, 101 MHz) of compound **1b**.

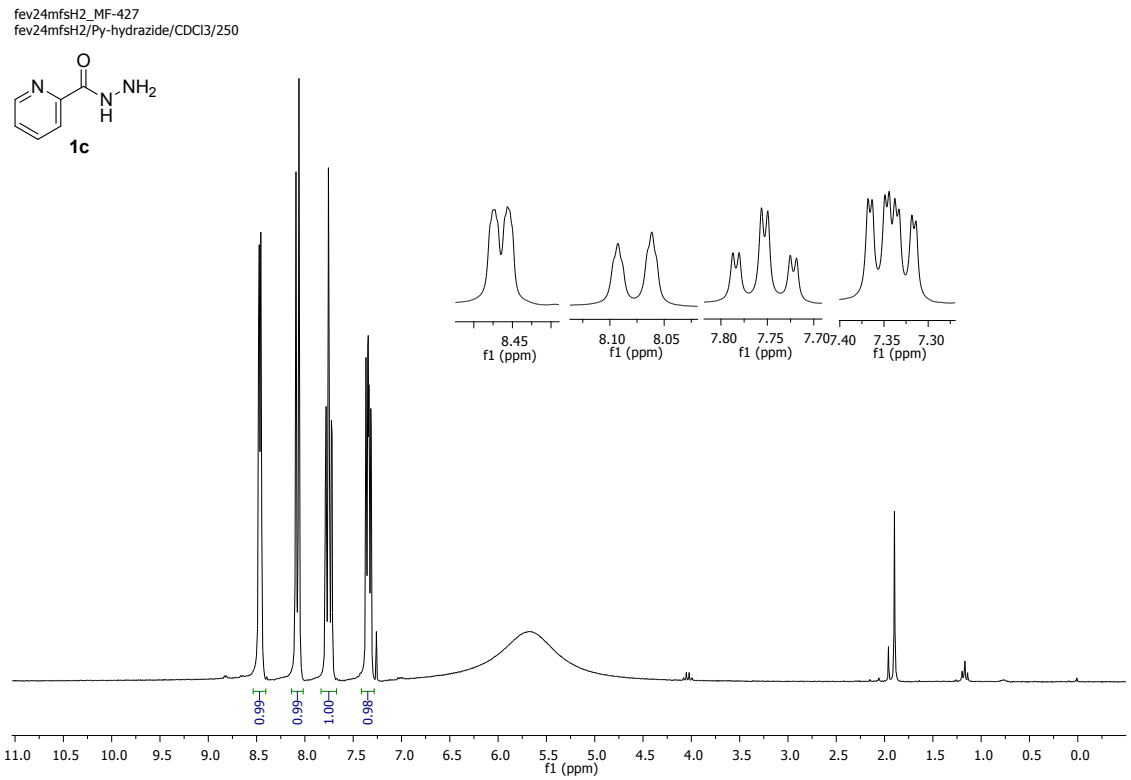

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of compound **1c**.

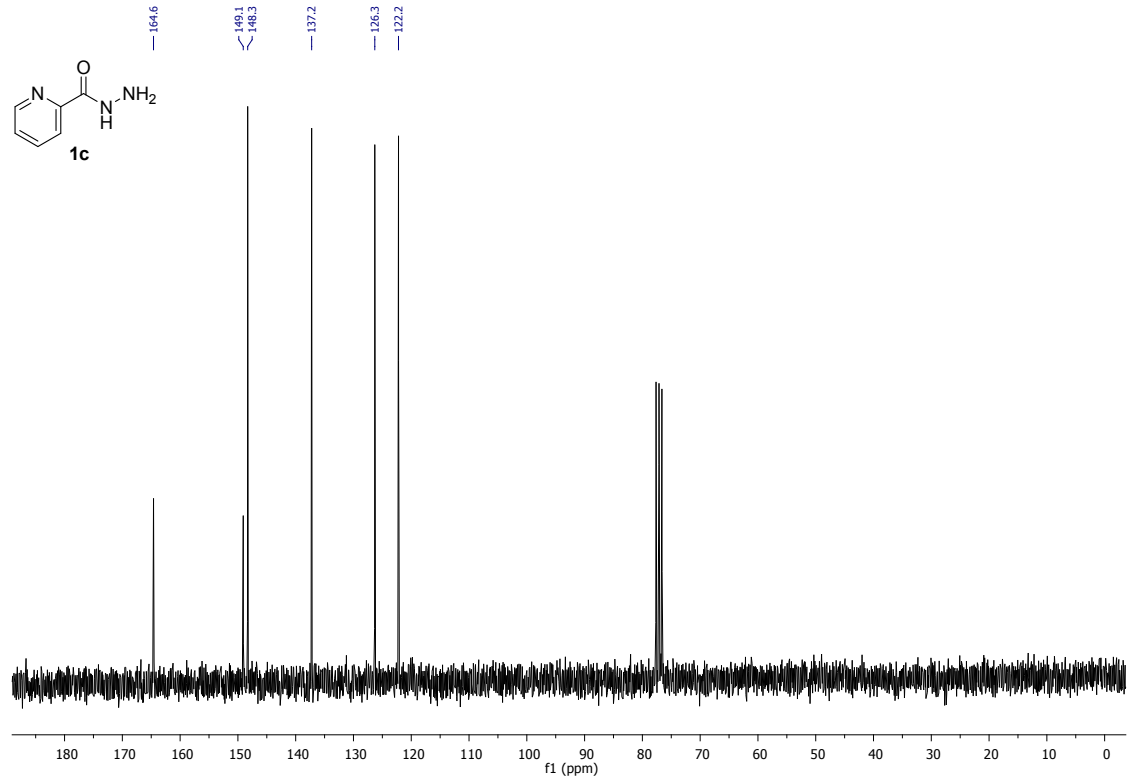

Figure S4. ^{13}C NMR spectrum (DMSO-d6, 63 MHz) of compound **1c**.

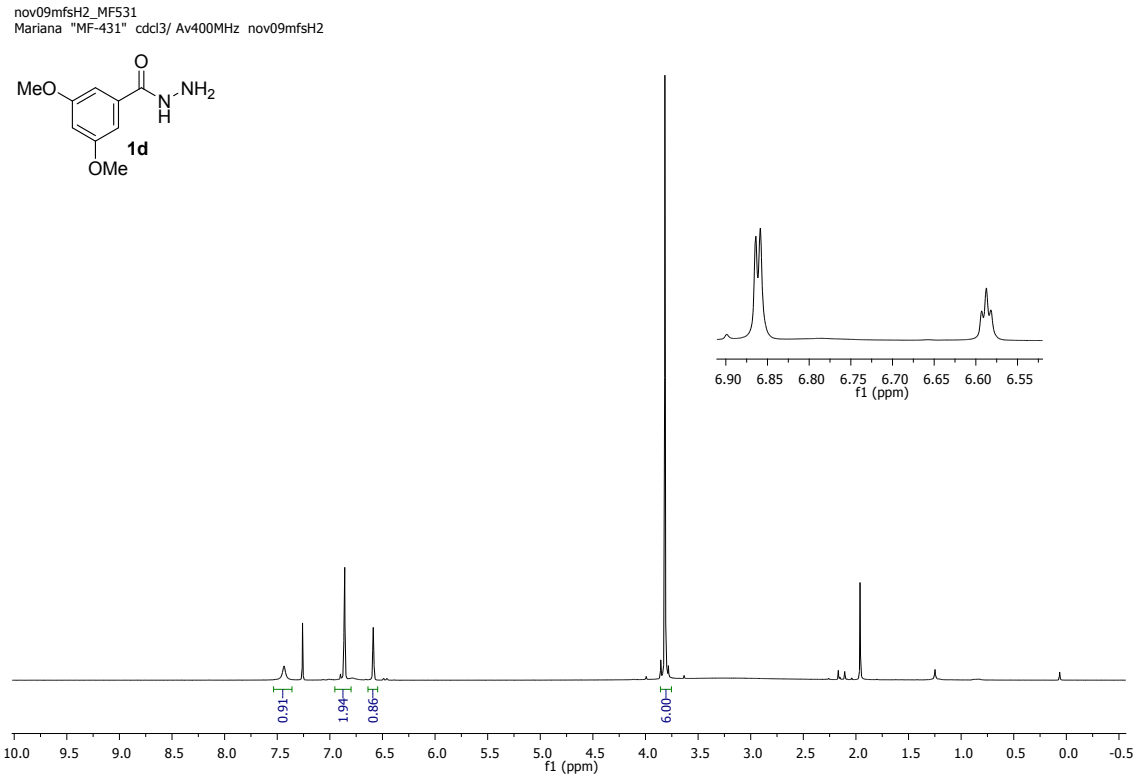

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **1d**.

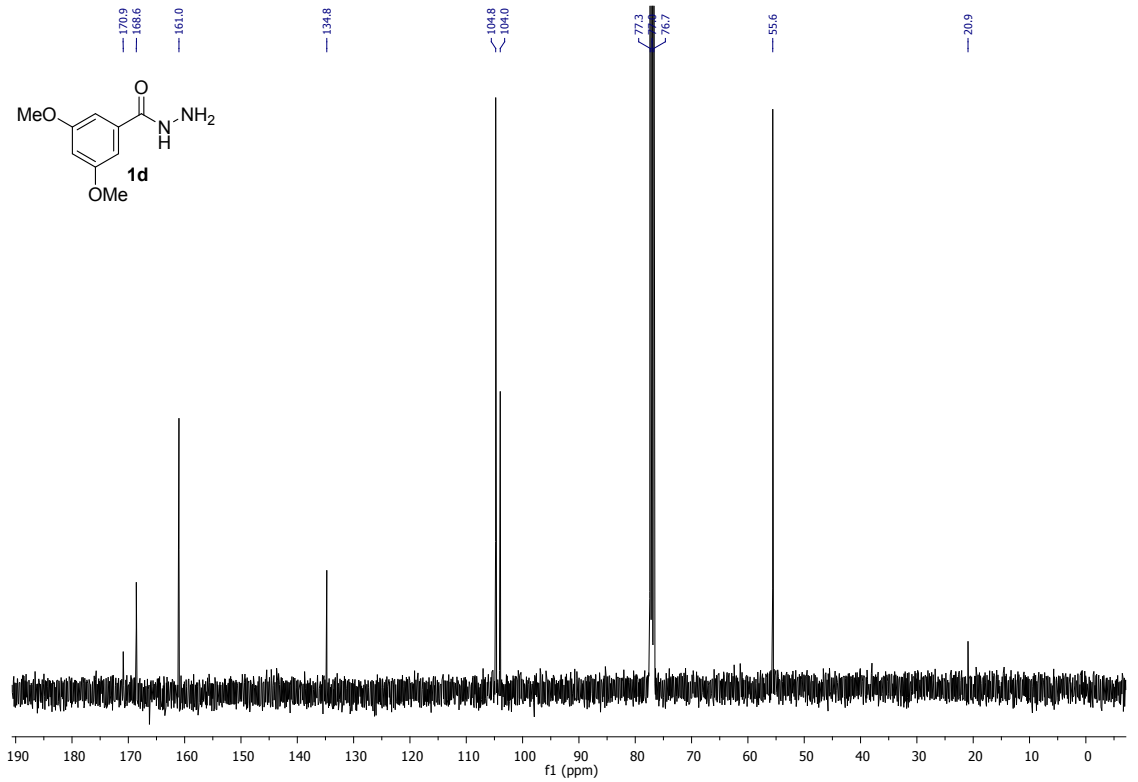

Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **1d**.

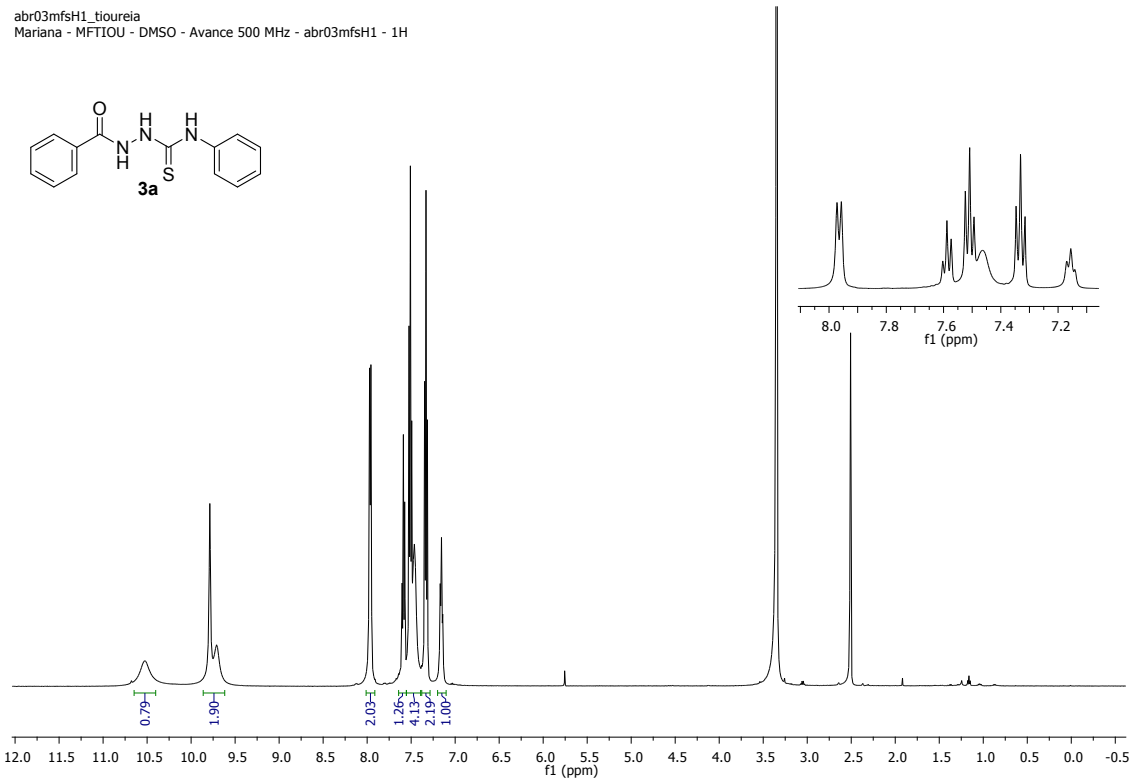

Figure S7. ^{1}H NMR spectrum (DMSO-d6, 500 MHz) of compound **3a**.

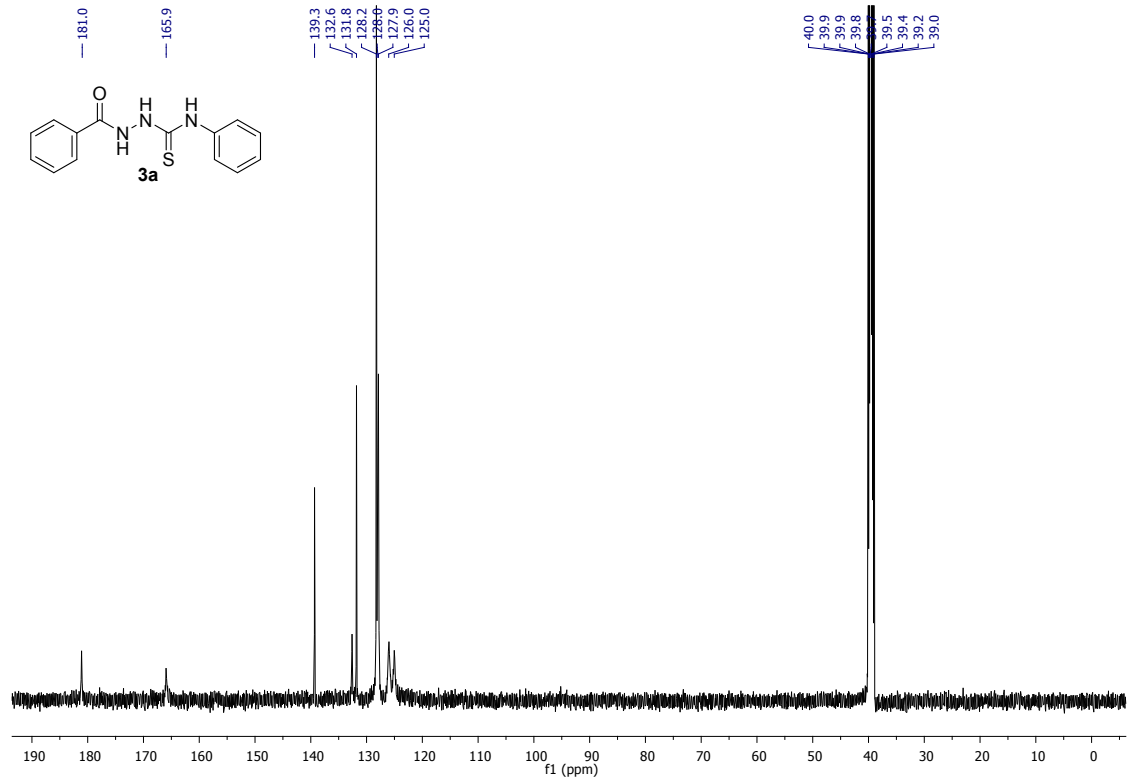

Figure S8. ^{13}C NMR spectrum (DMSO-d6, 126 MHz) of compound **3a**.

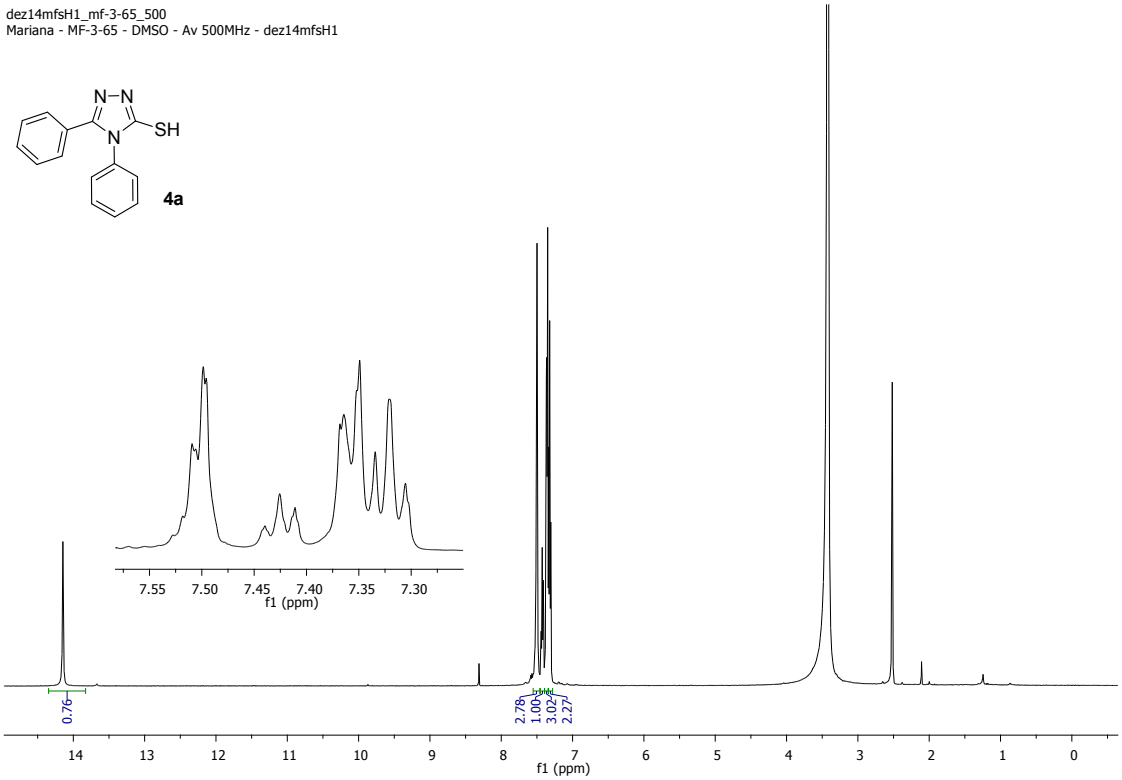

Figure S9. ^{1}H NMR spectrum (DMSO-d6, 500 MHz) of compound **4a**.

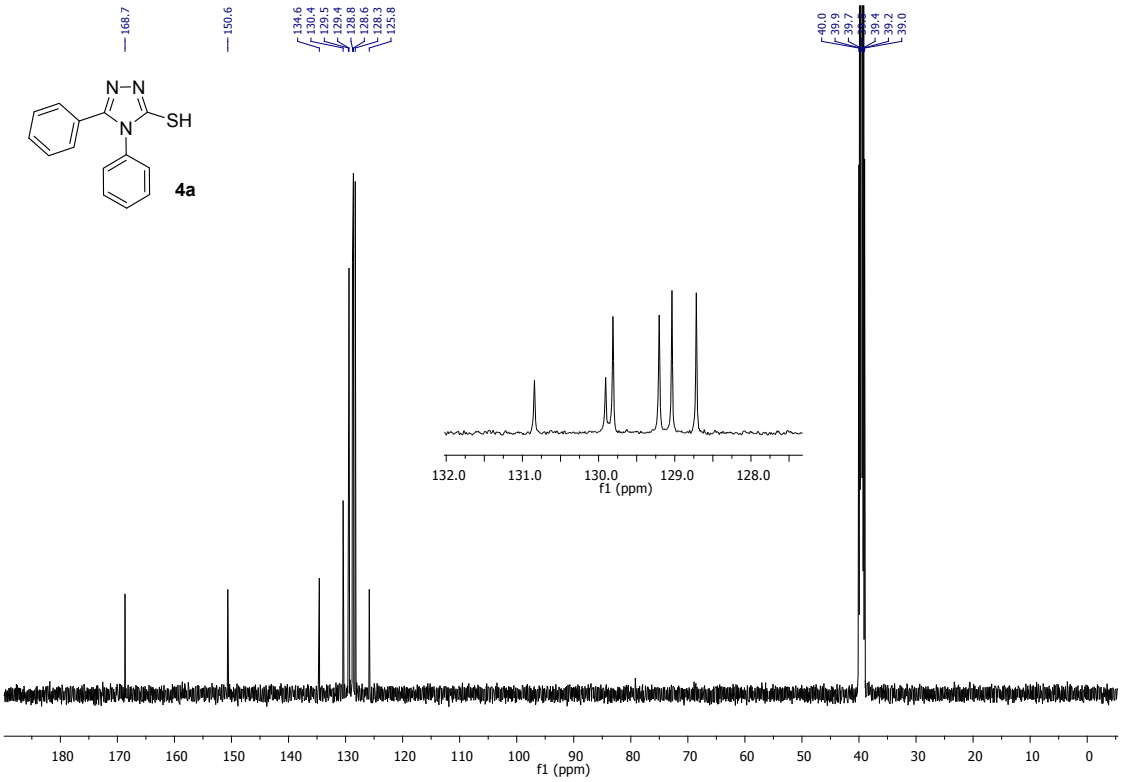

Figure S10. ^{13}C NMR spectrum (DMSO-d6, 126 MHz) of compound **4a**.

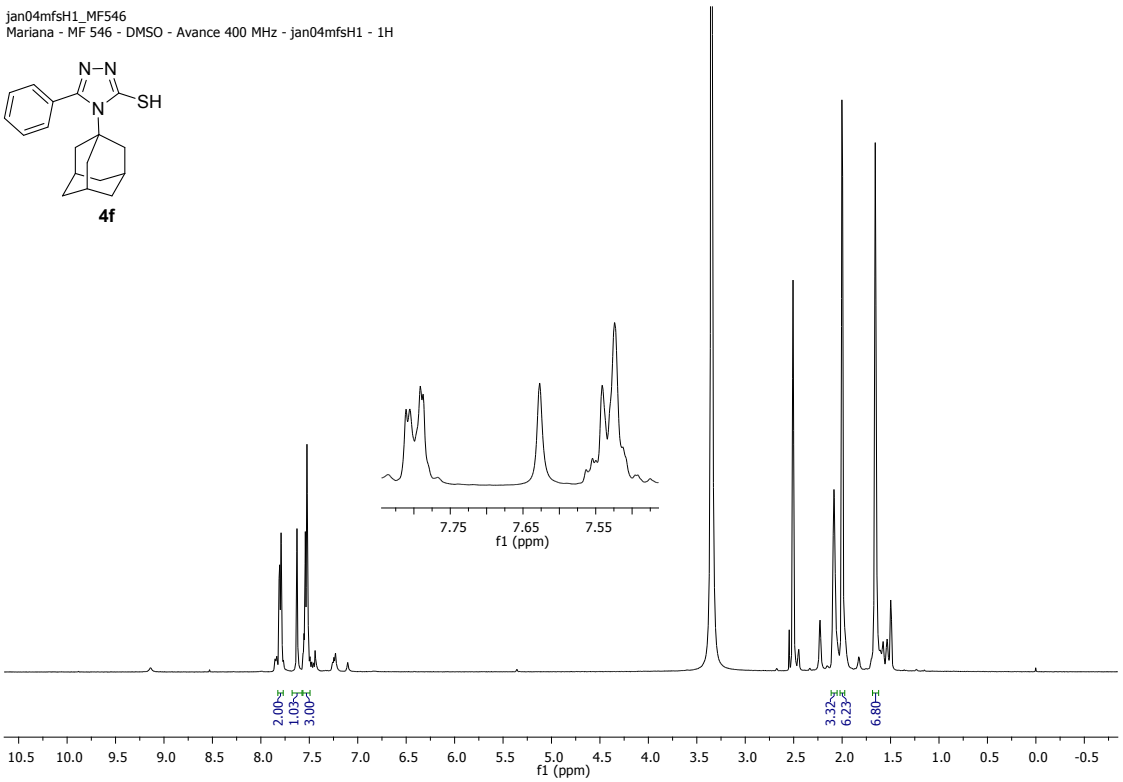

Figure S11. ^{1}H NMR spectrum (DMSO-d6, 400 MHz) of compound **4f**.

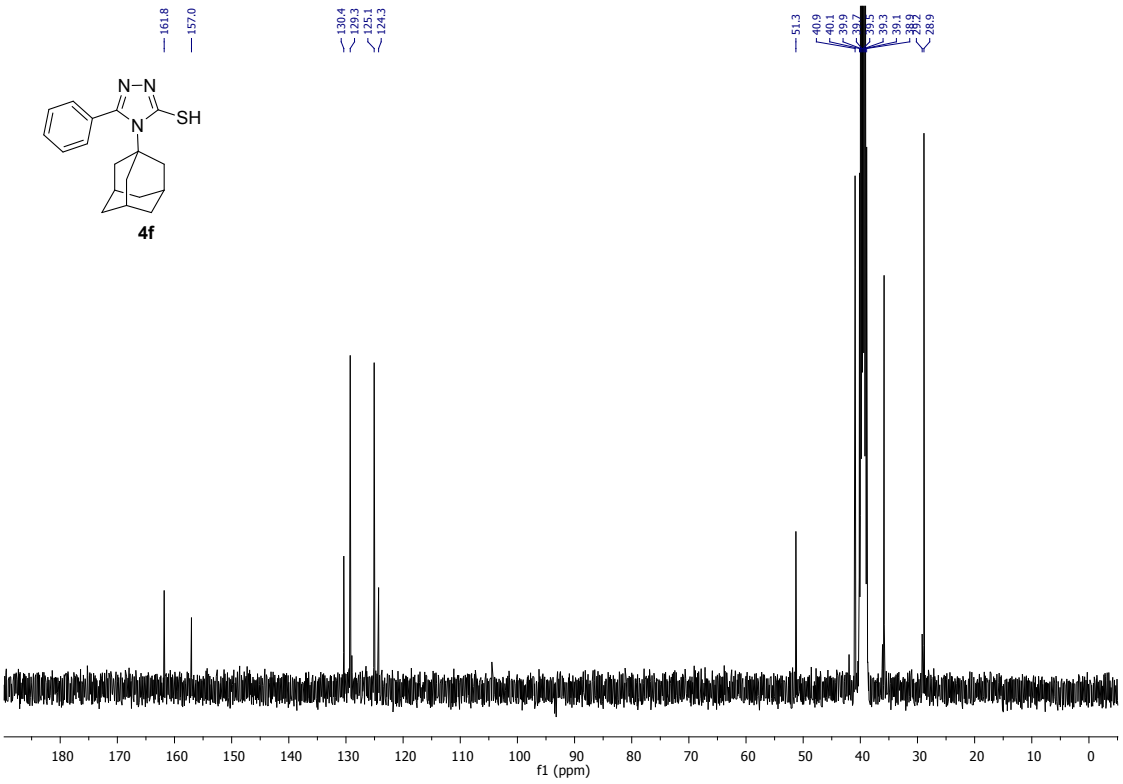

Figure S12. ^{13}C NMR spectrum (DMSO-d6, 101 MHz) of compound **4f**.

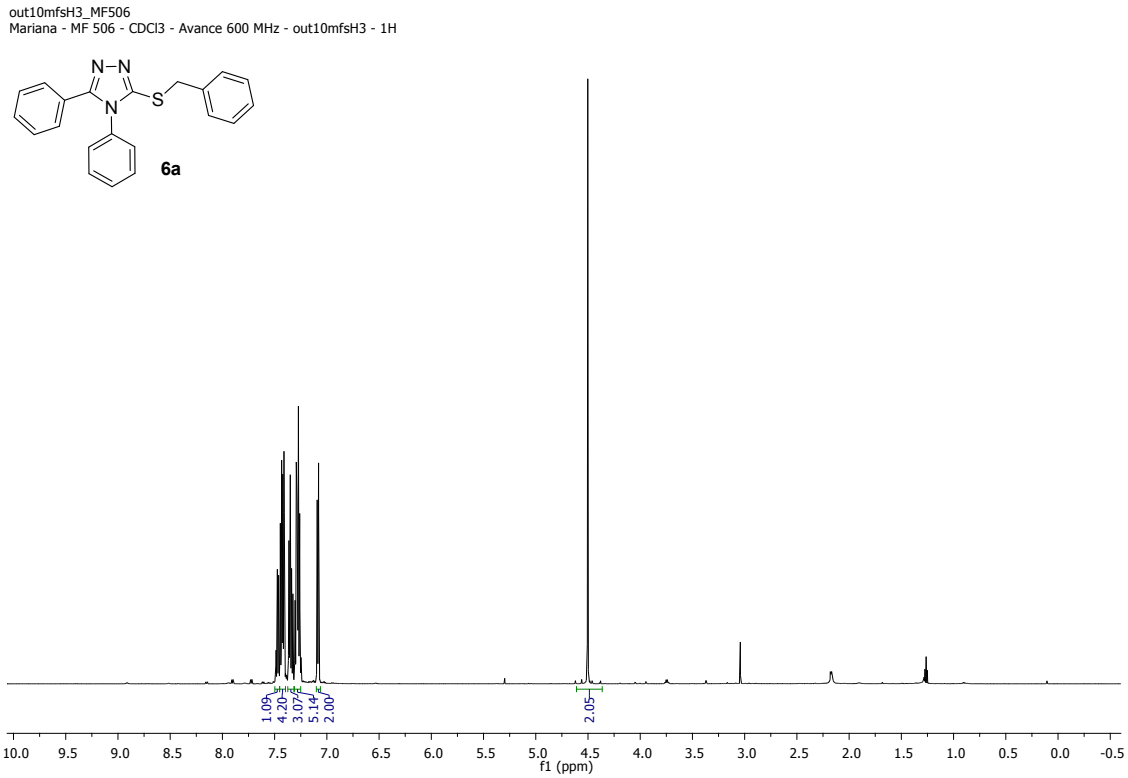

Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **6a**.

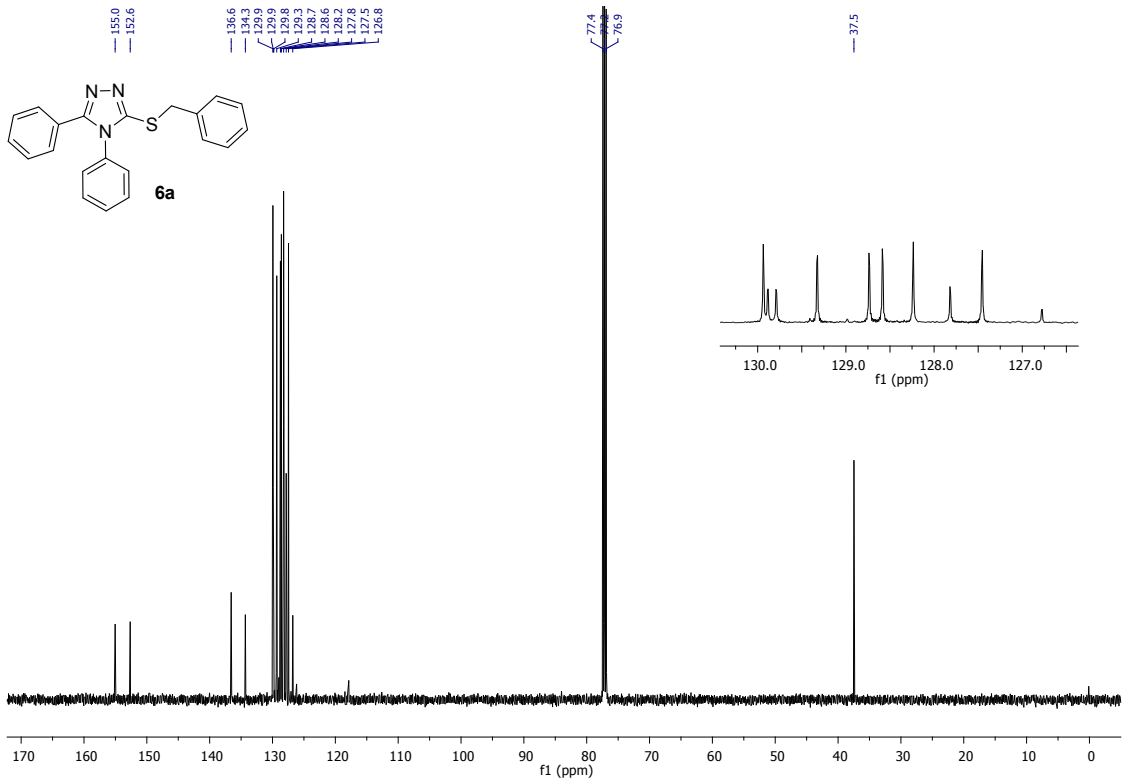

Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **6a**.

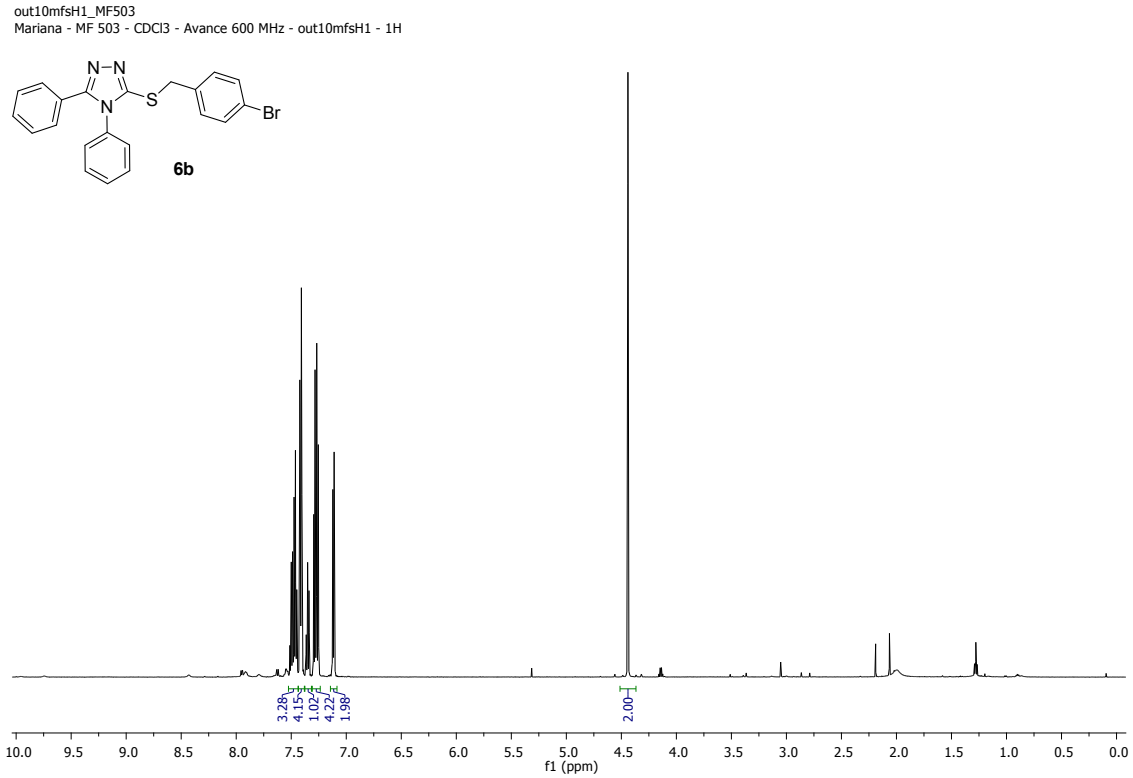

Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **6b**.

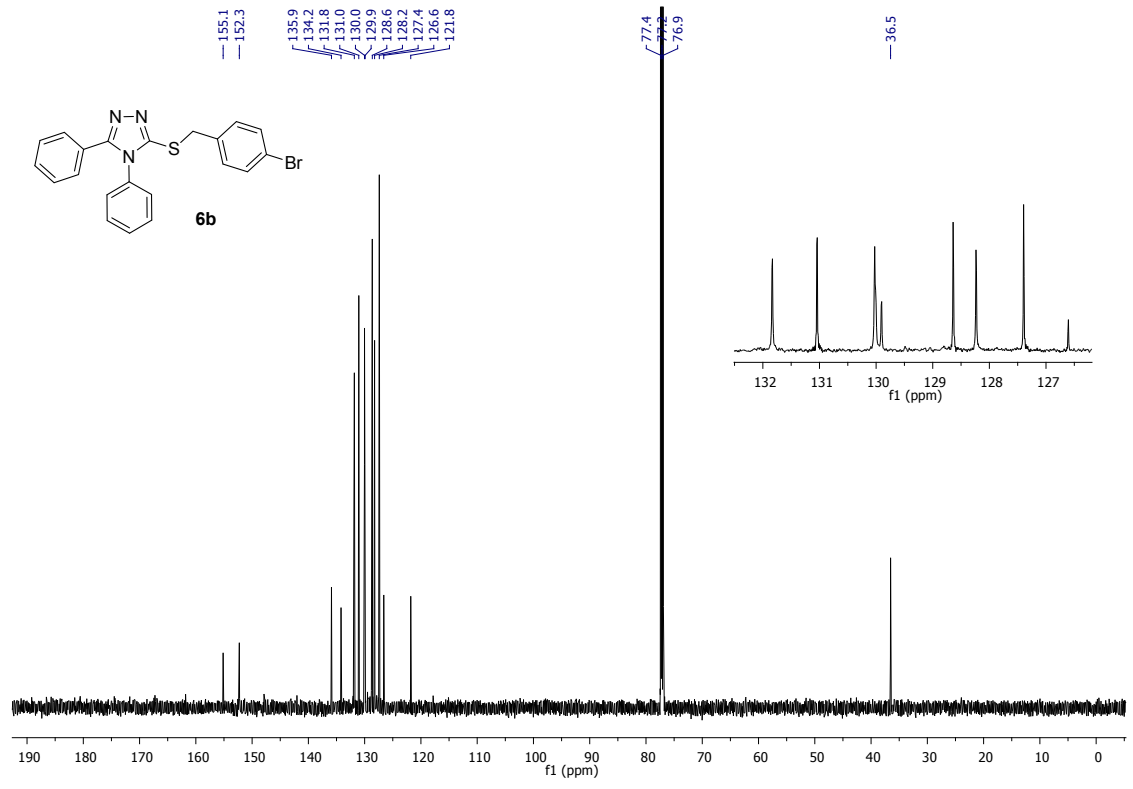

Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **6b**.

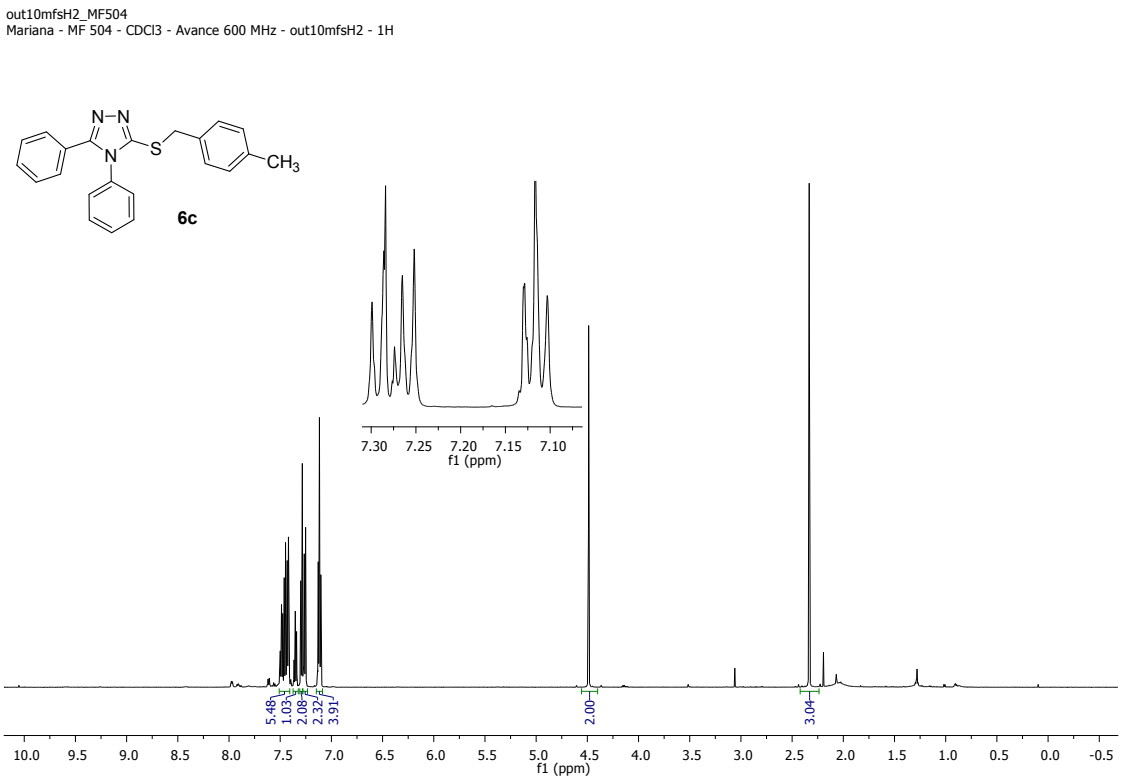

Figure S17 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **6c**.

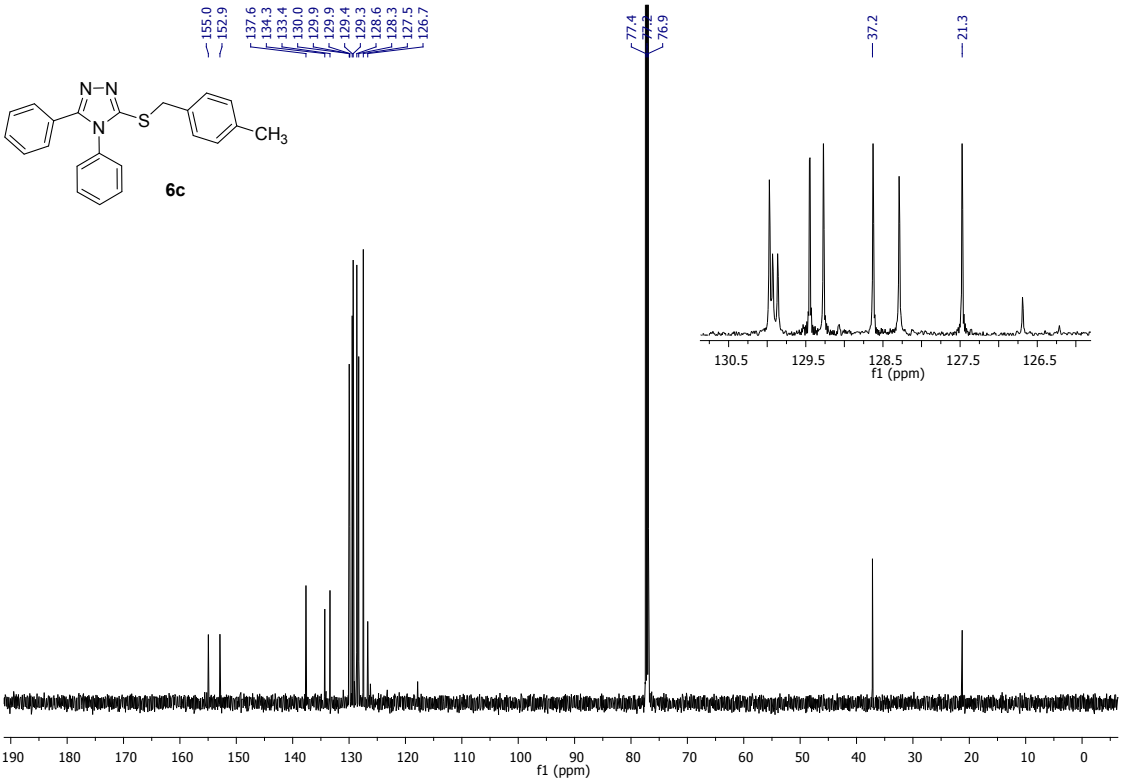

Figure S18 ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **6c**.

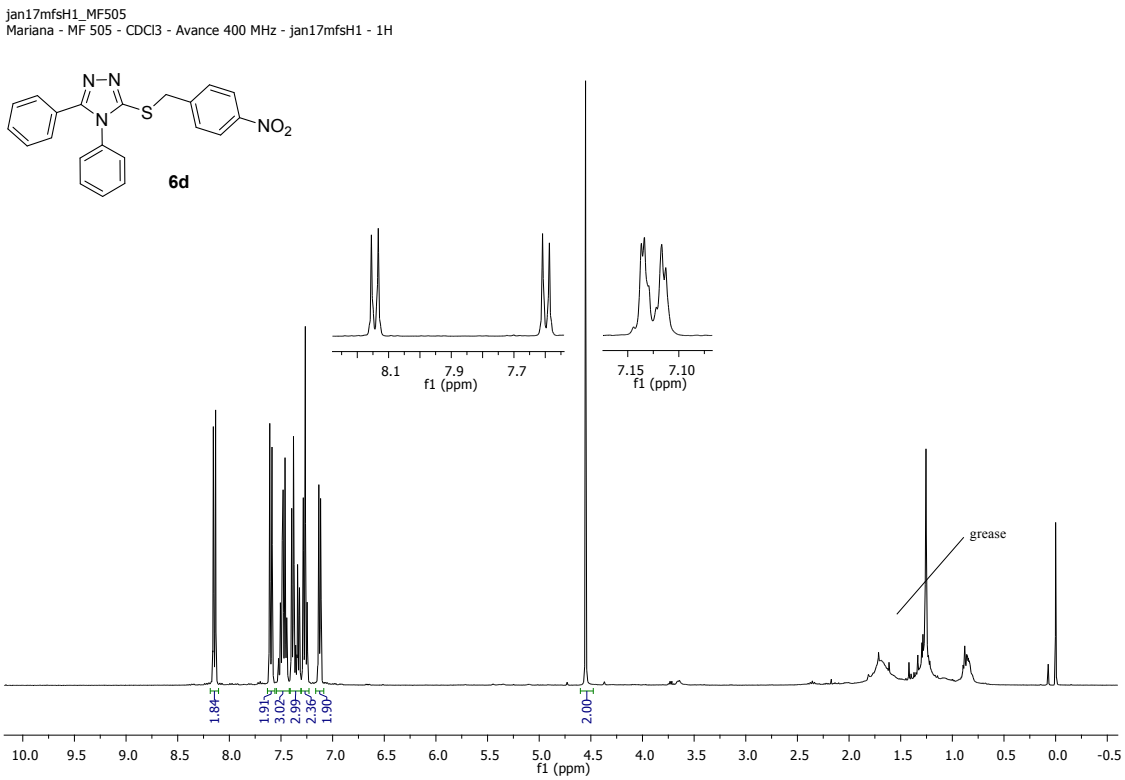

Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **6d**.

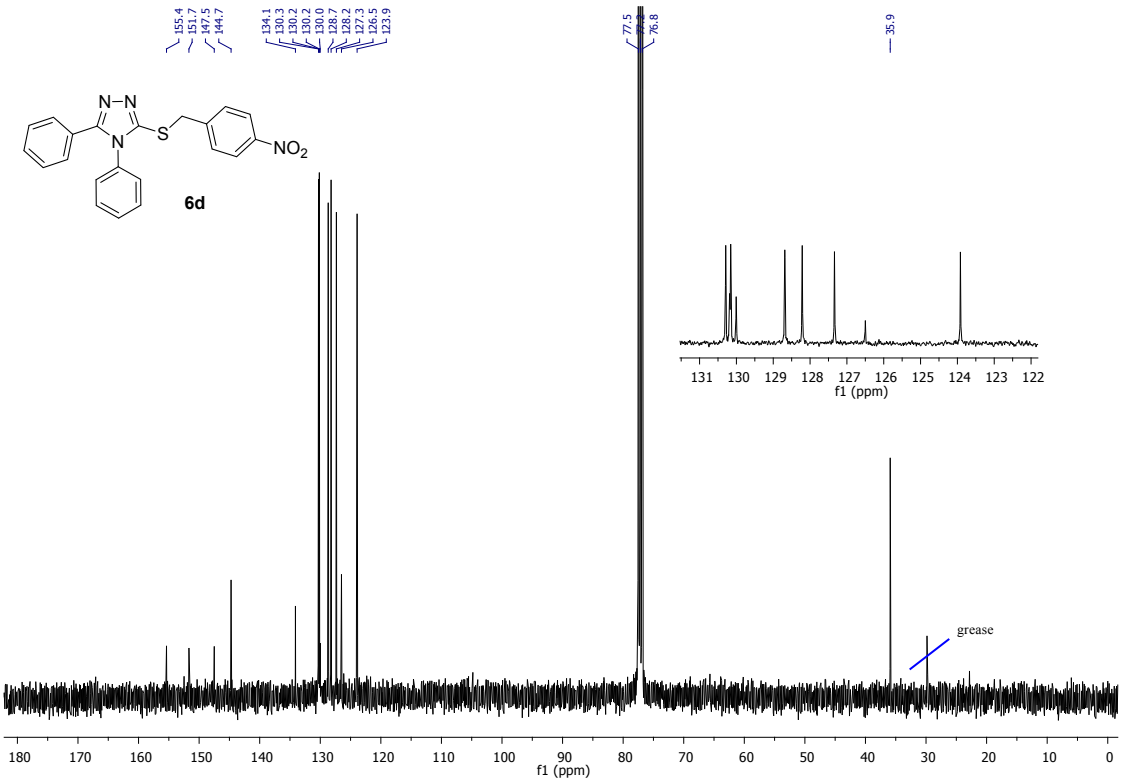

Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **6d**.

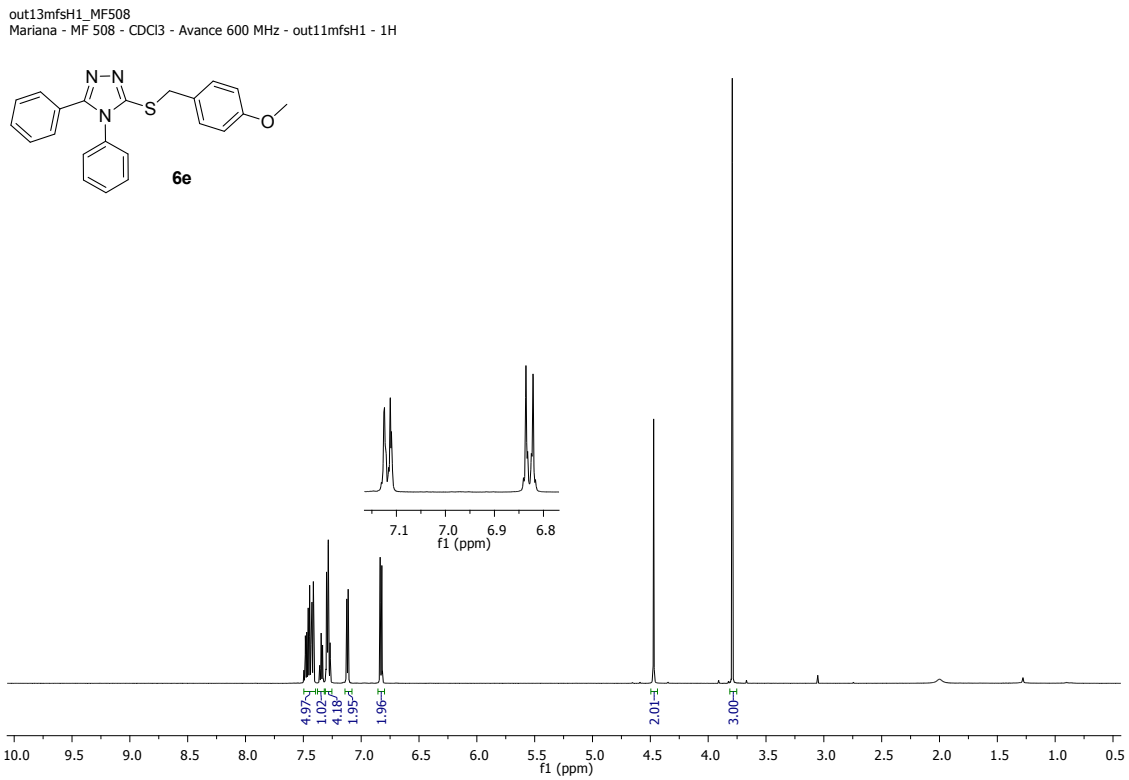

Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **6e**.

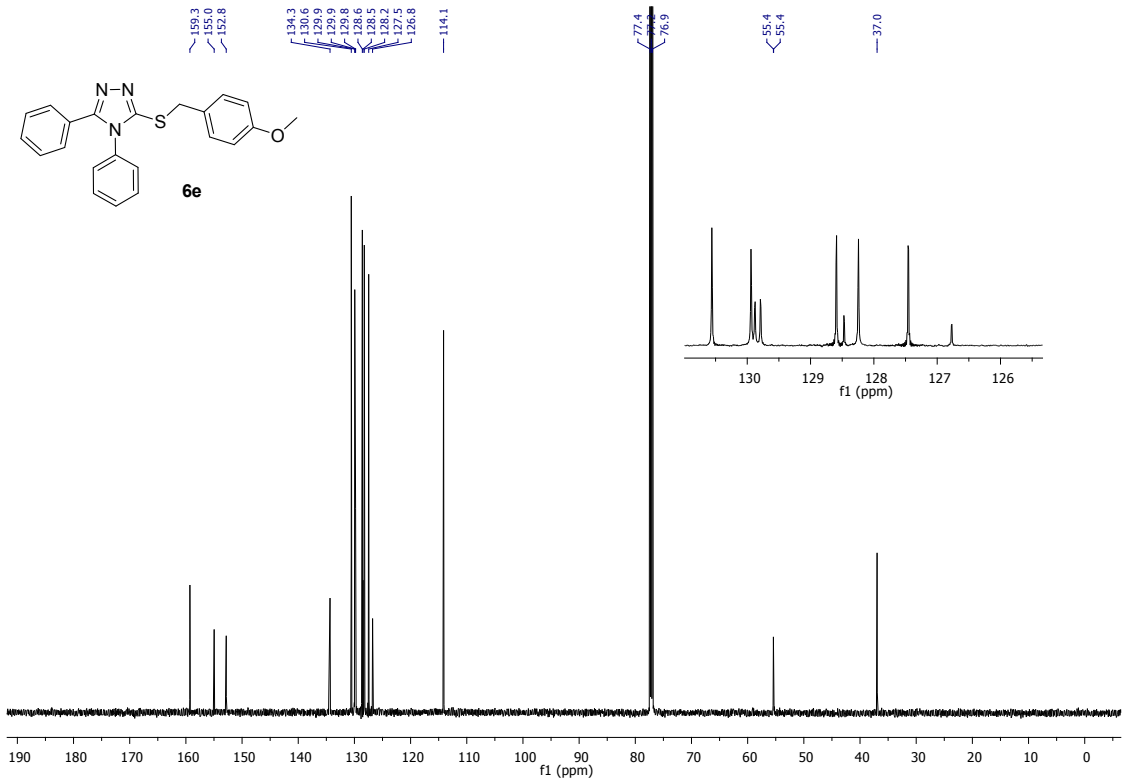

Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **6e**.

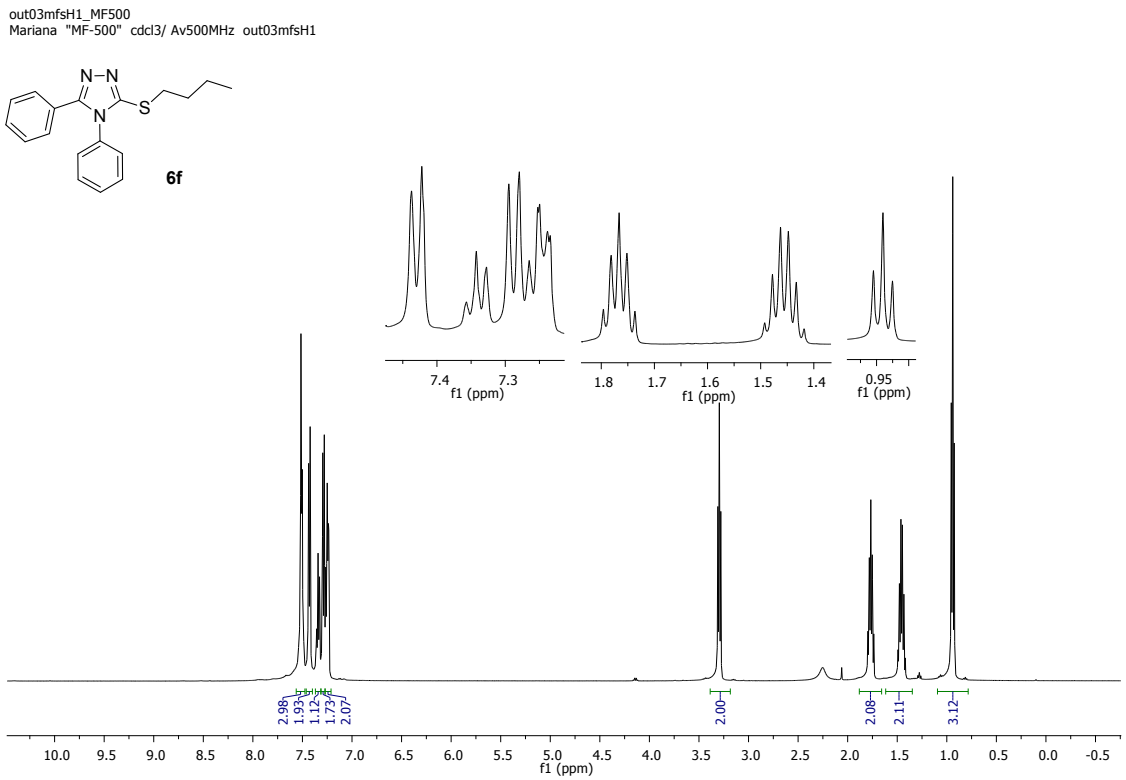

Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **6f**.

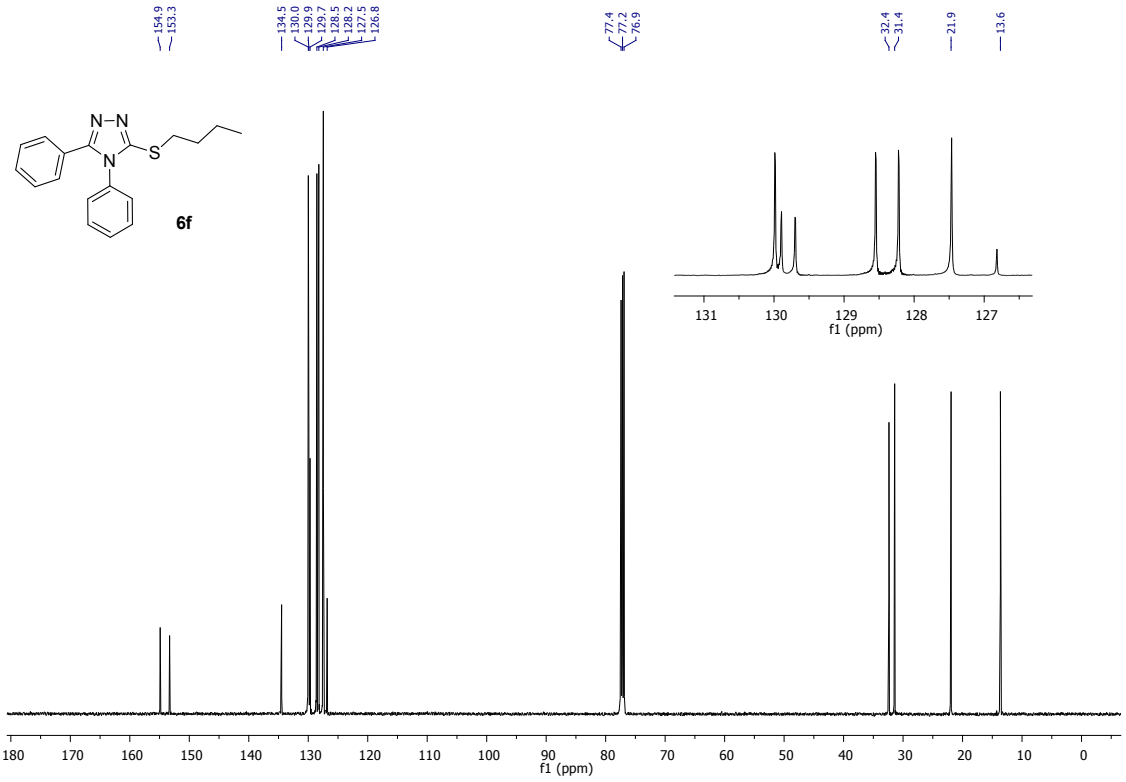

Figure S24. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **6f**.

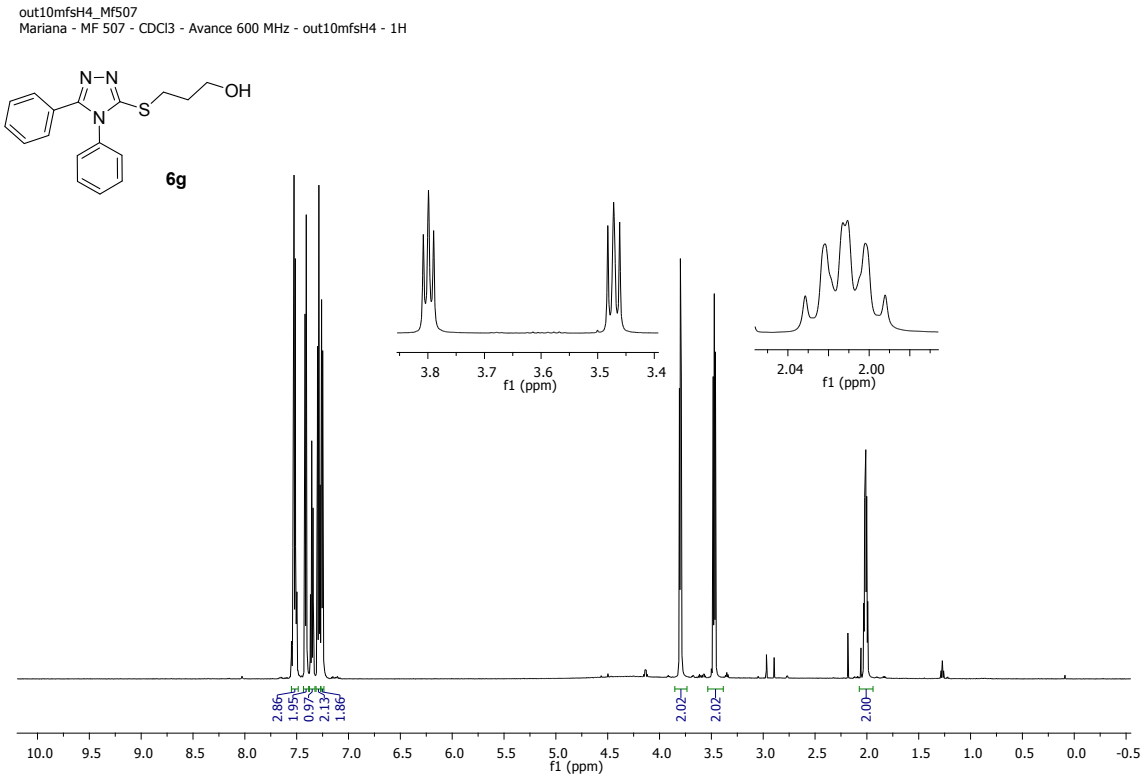

Figure S25. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **6g**.

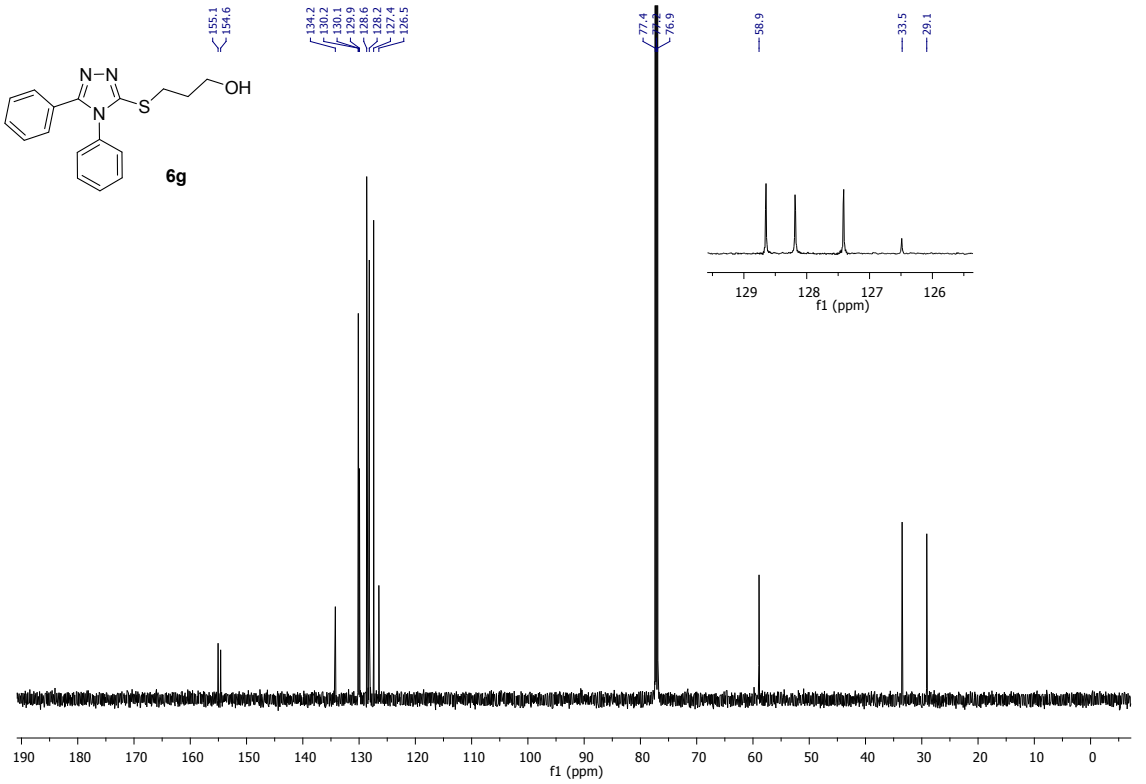

Figure S26. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **6g**.

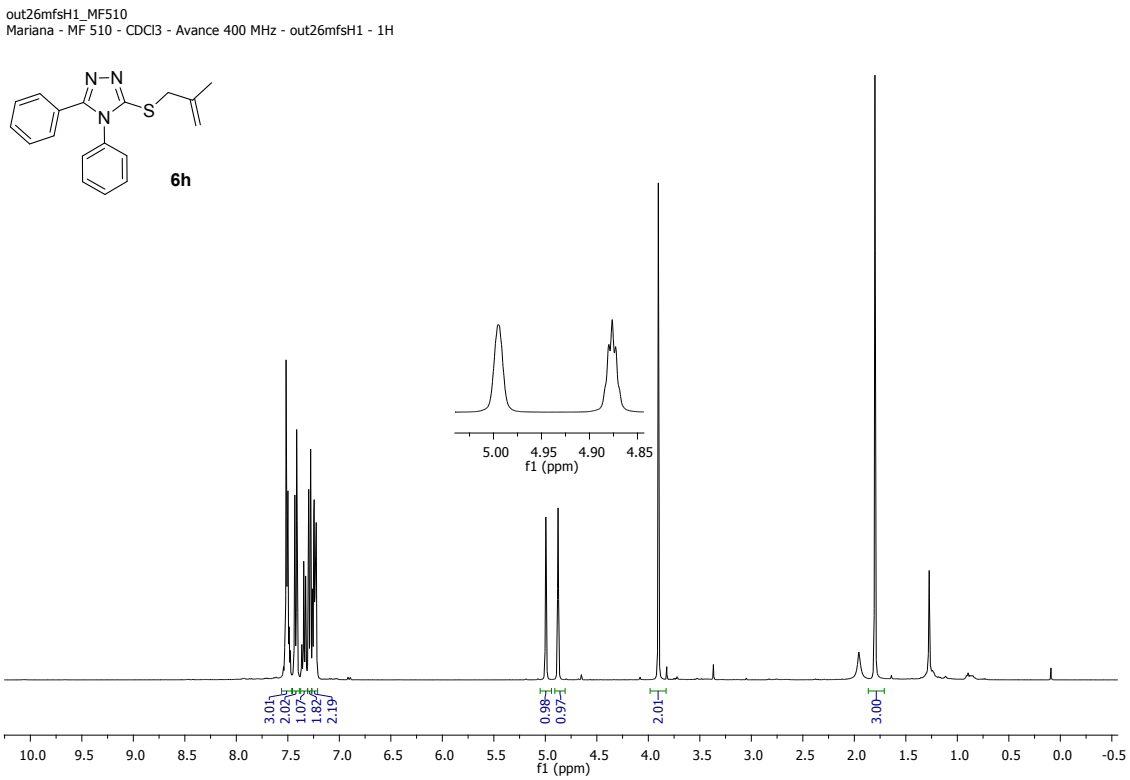

Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **6h**.

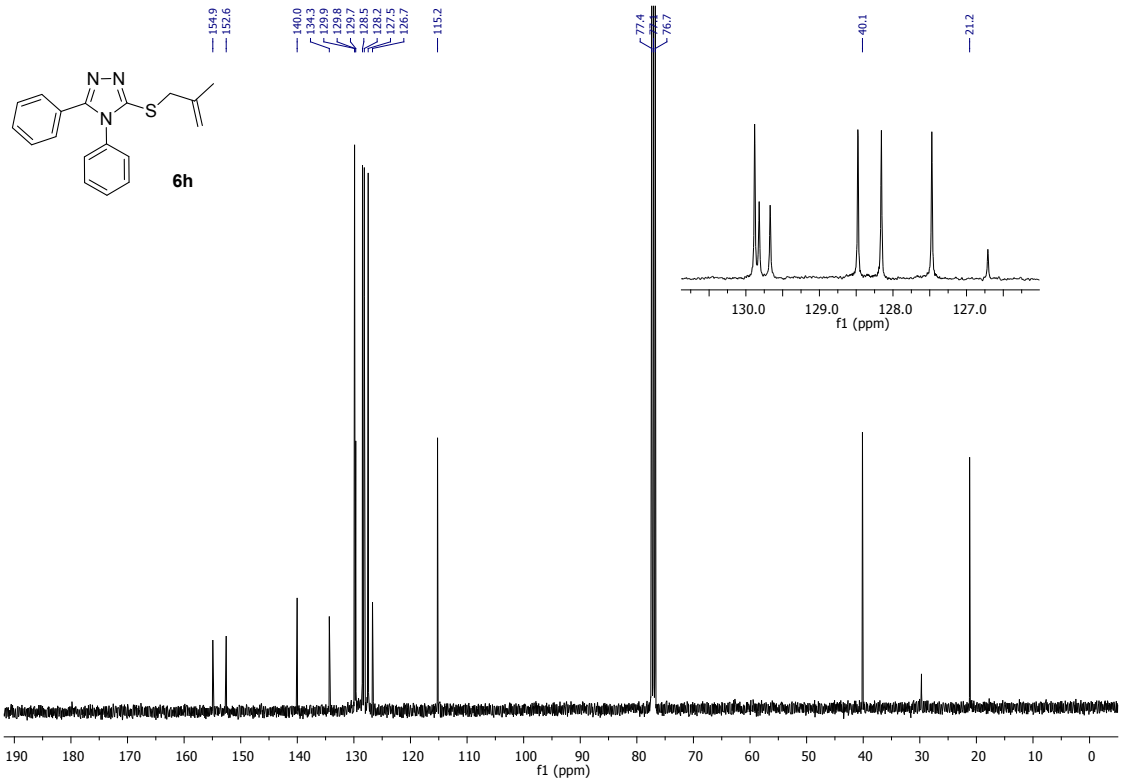

Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **6h**.

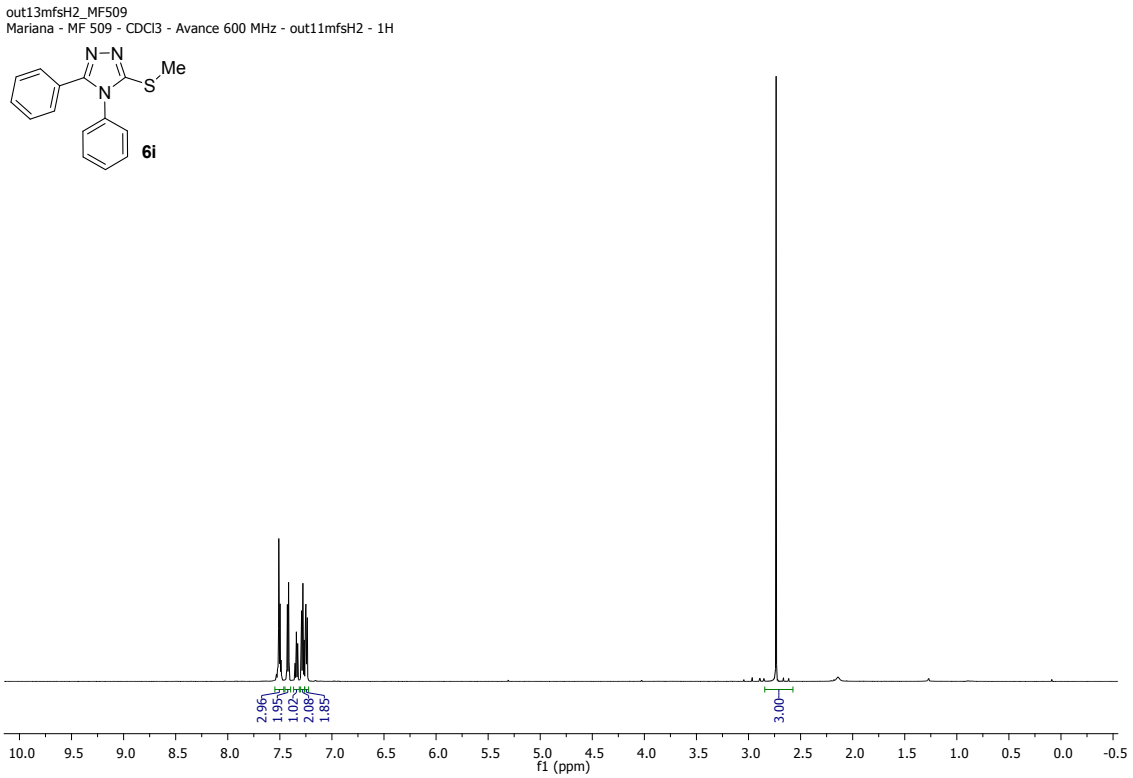

Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **6i**.

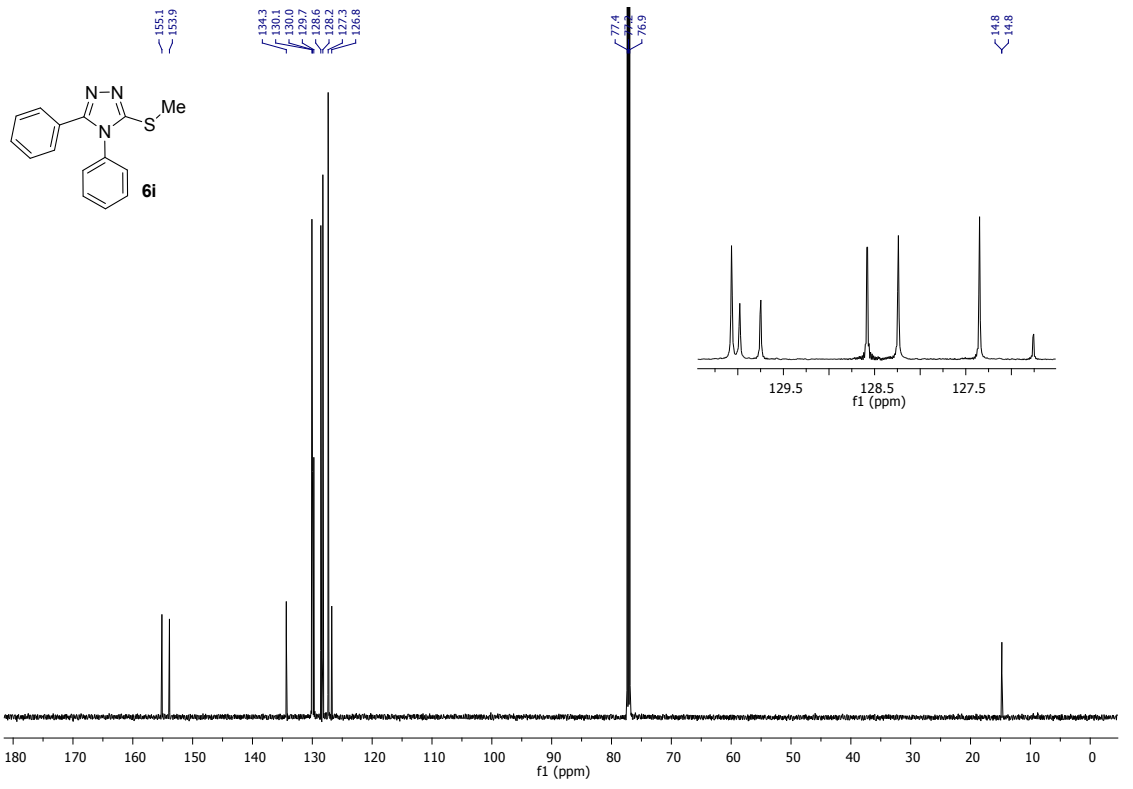

Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **6i**.

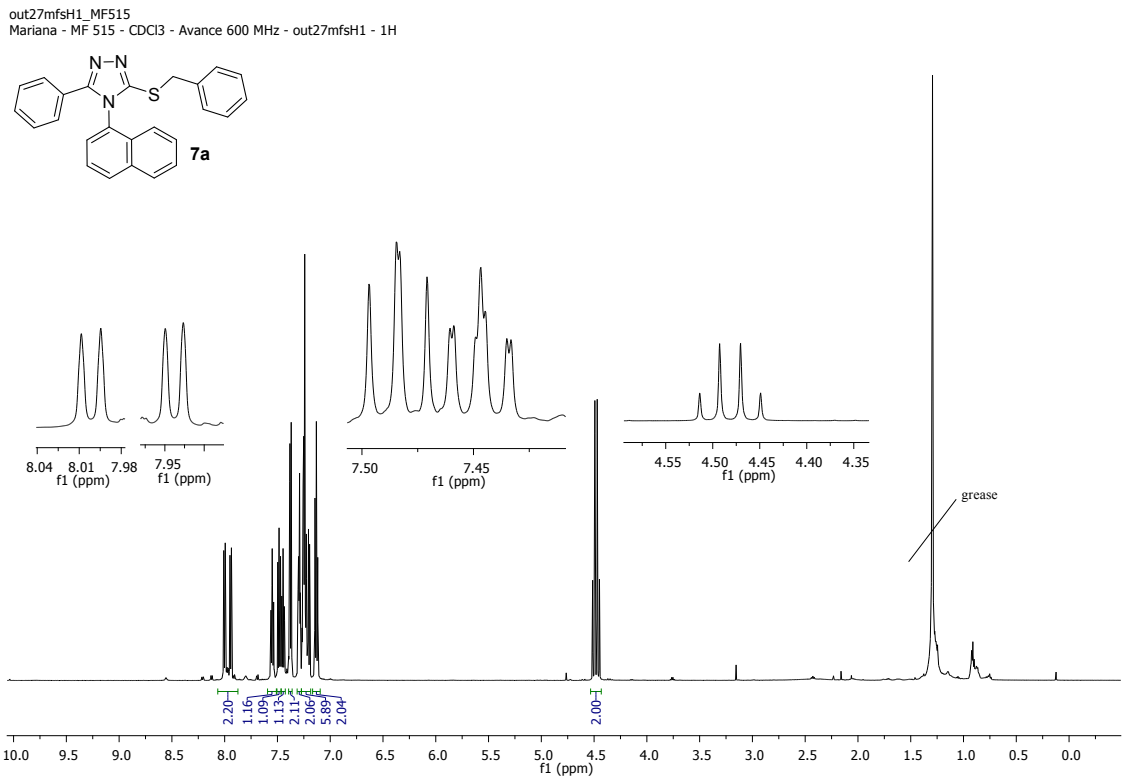

Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **7a**.

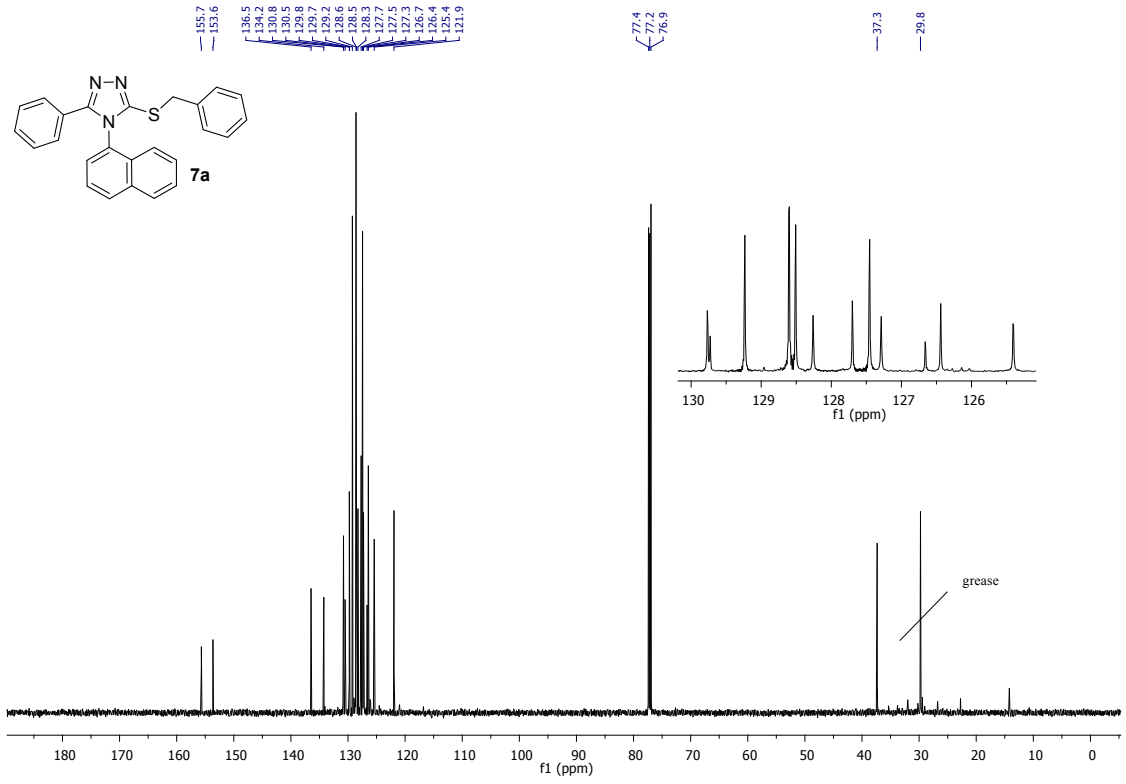

Figure S32. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **7a**.

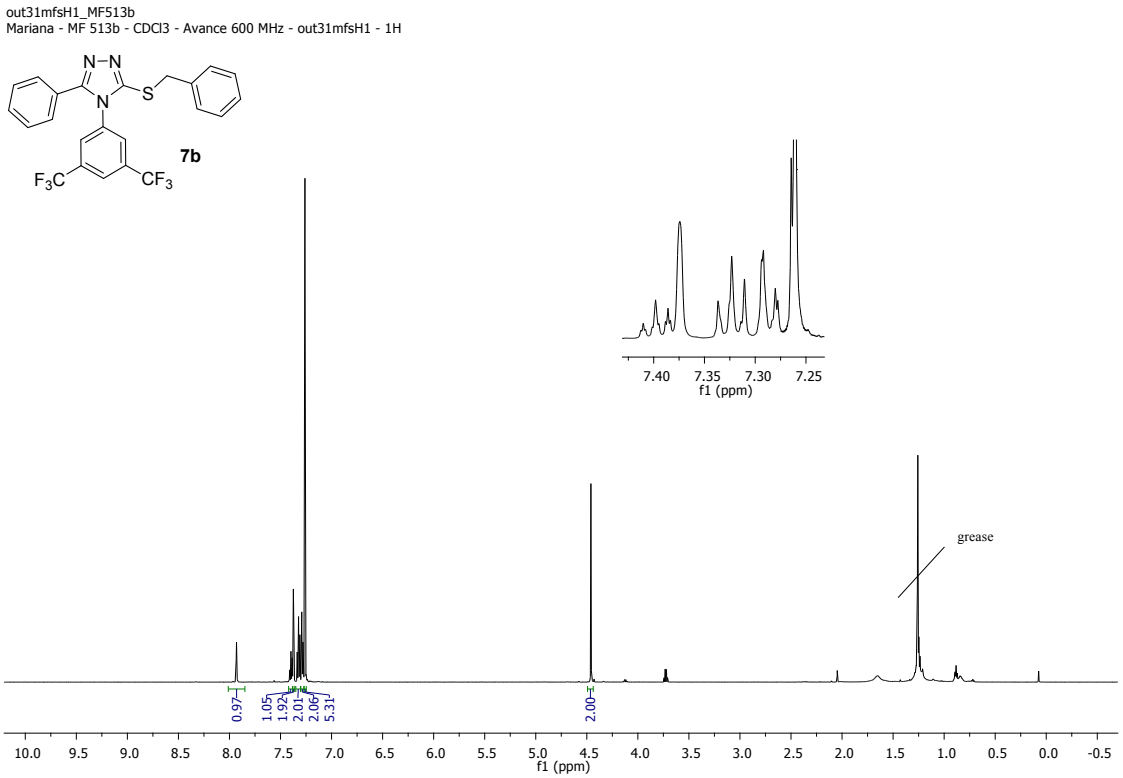

Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **7b**.

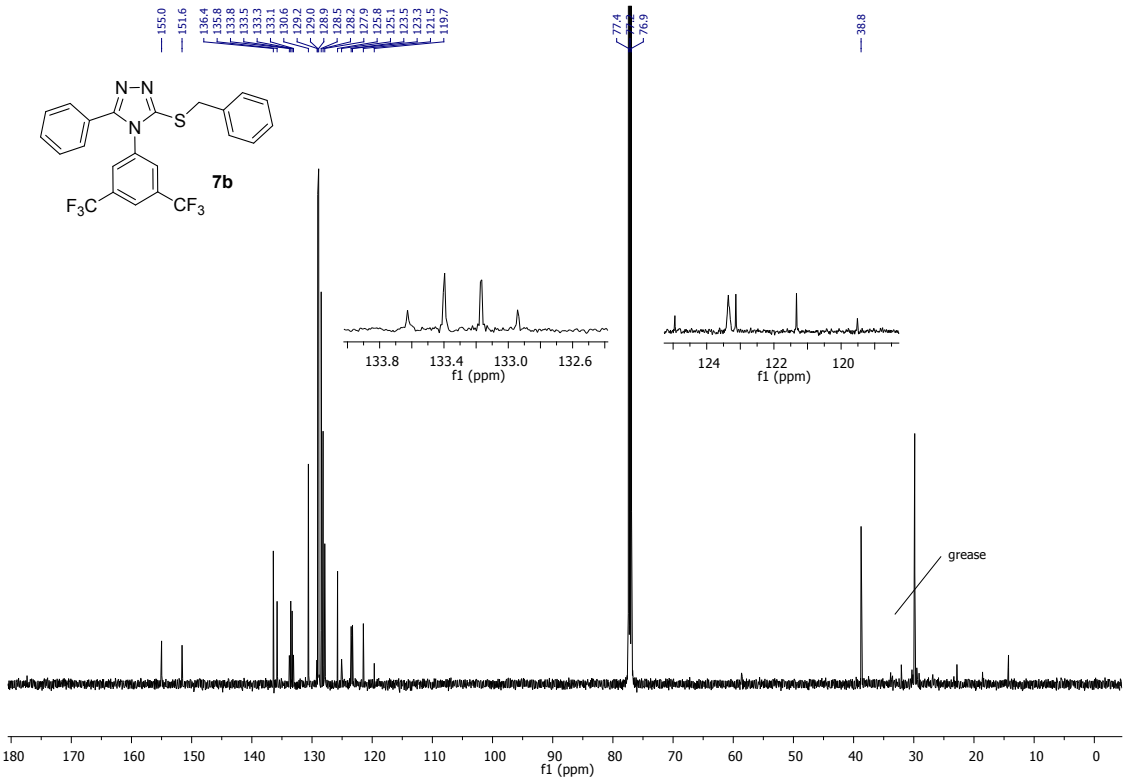

Figure S34. ^{13}C NMR spectrum ($CDCl_3$, 151 MHz) of compound **7b**.

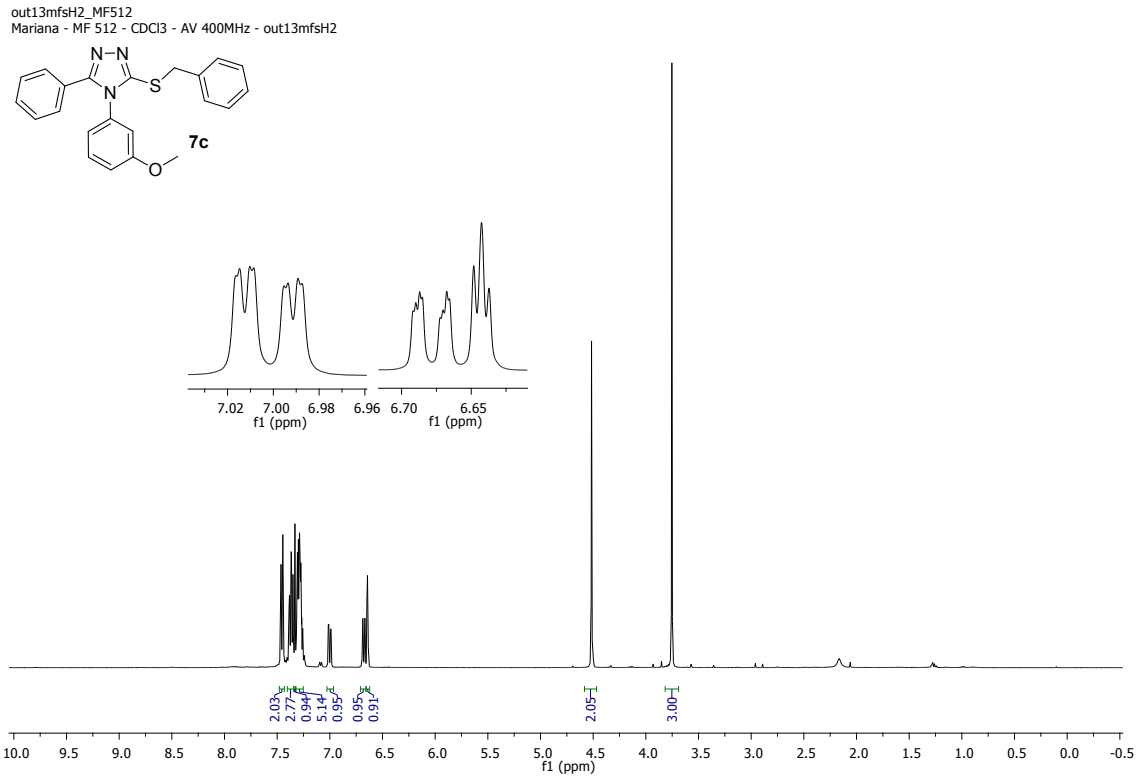

Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **7c**.

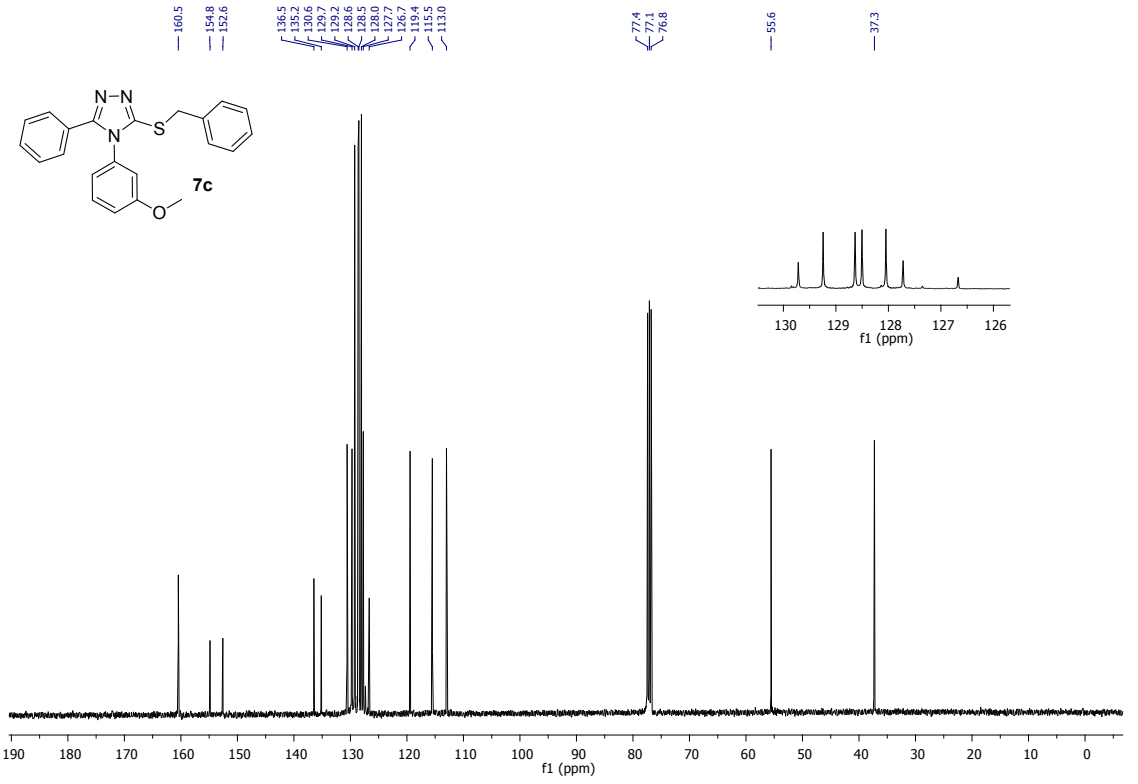

Figure S36. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **7c**.

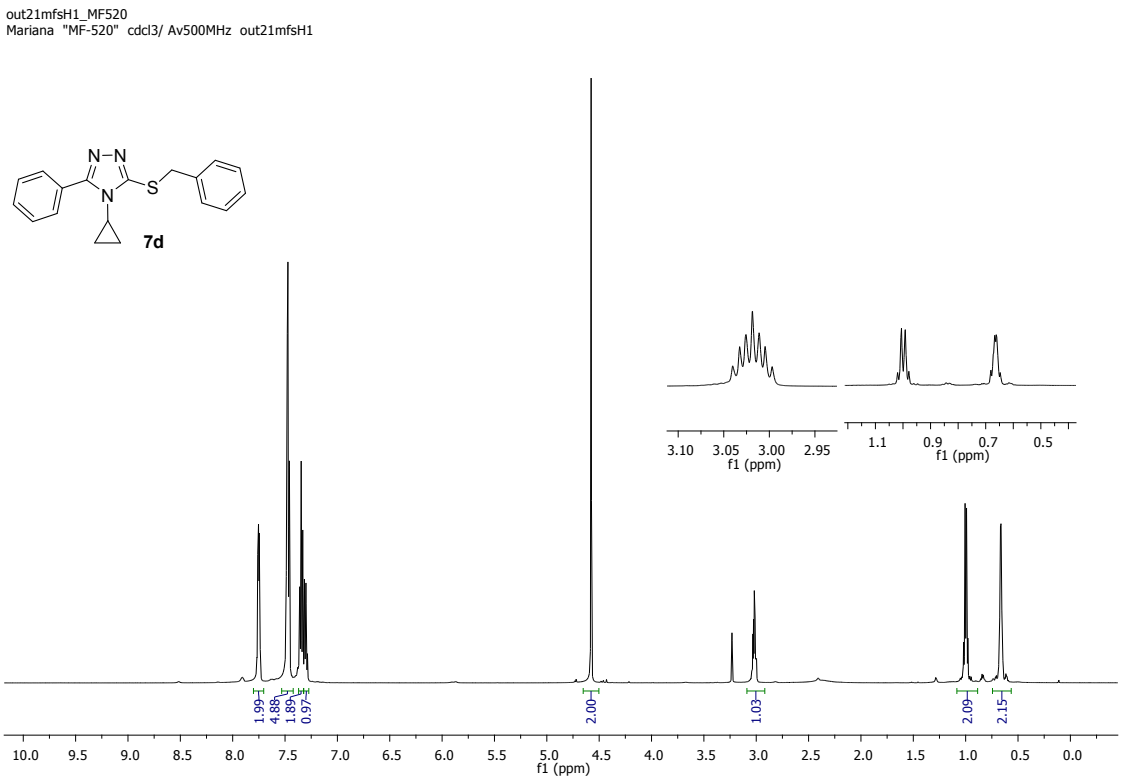

Figure S37. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **7d**.

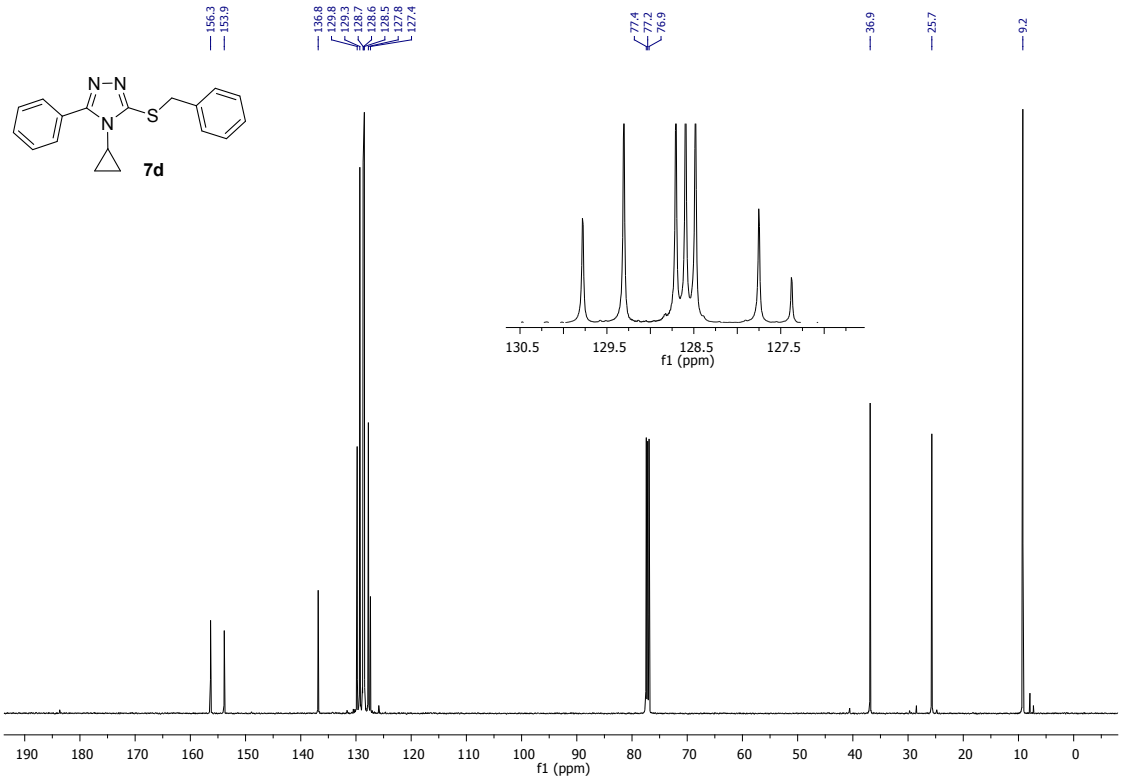

Figure S38. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **7d**.

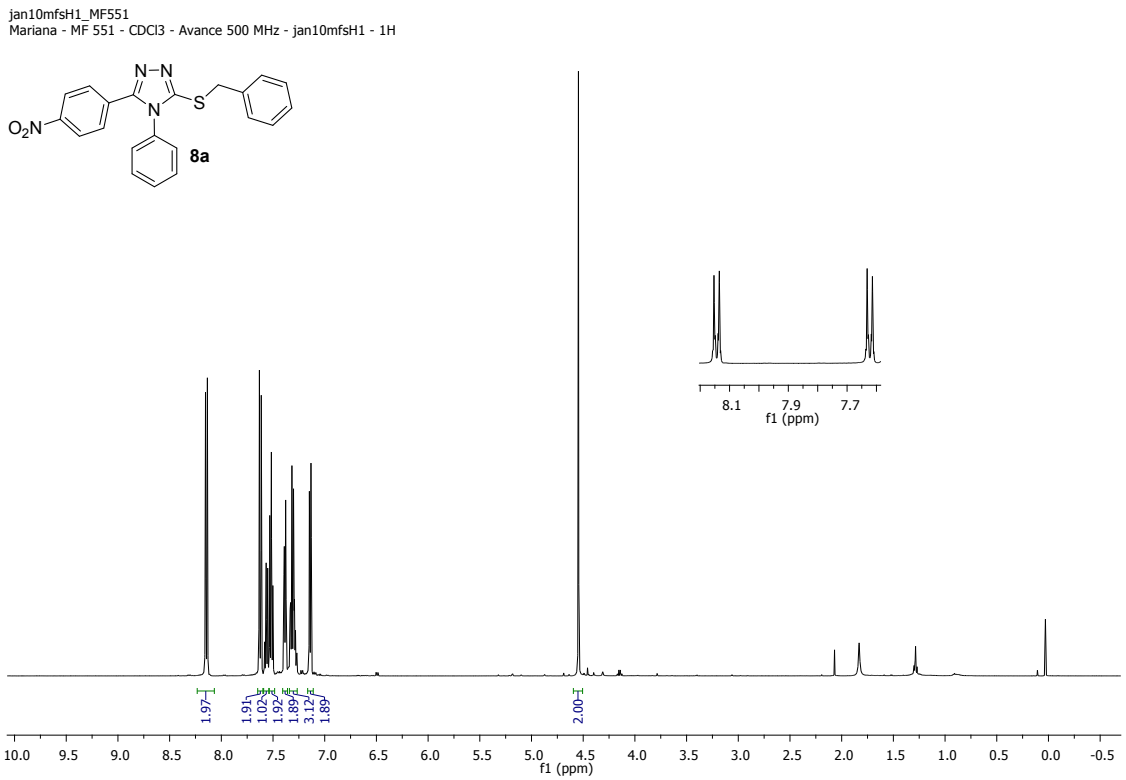

Figure S39. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **8a**.

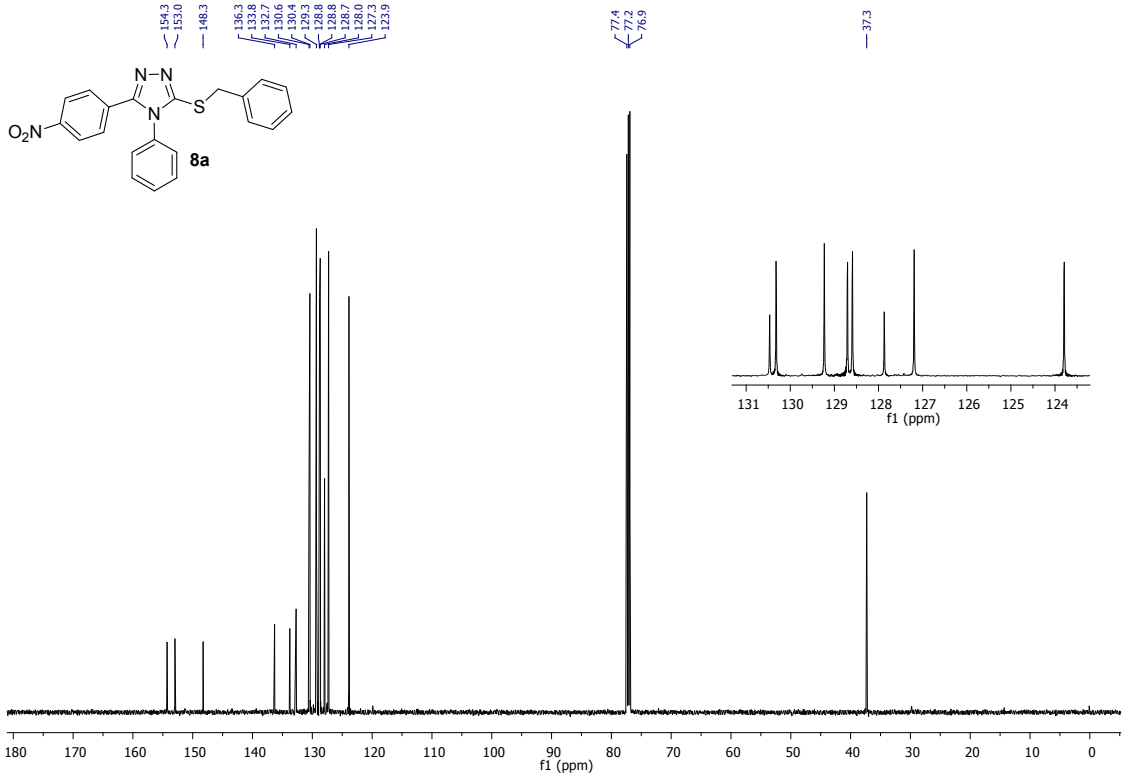

Figure S40. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **8a**.

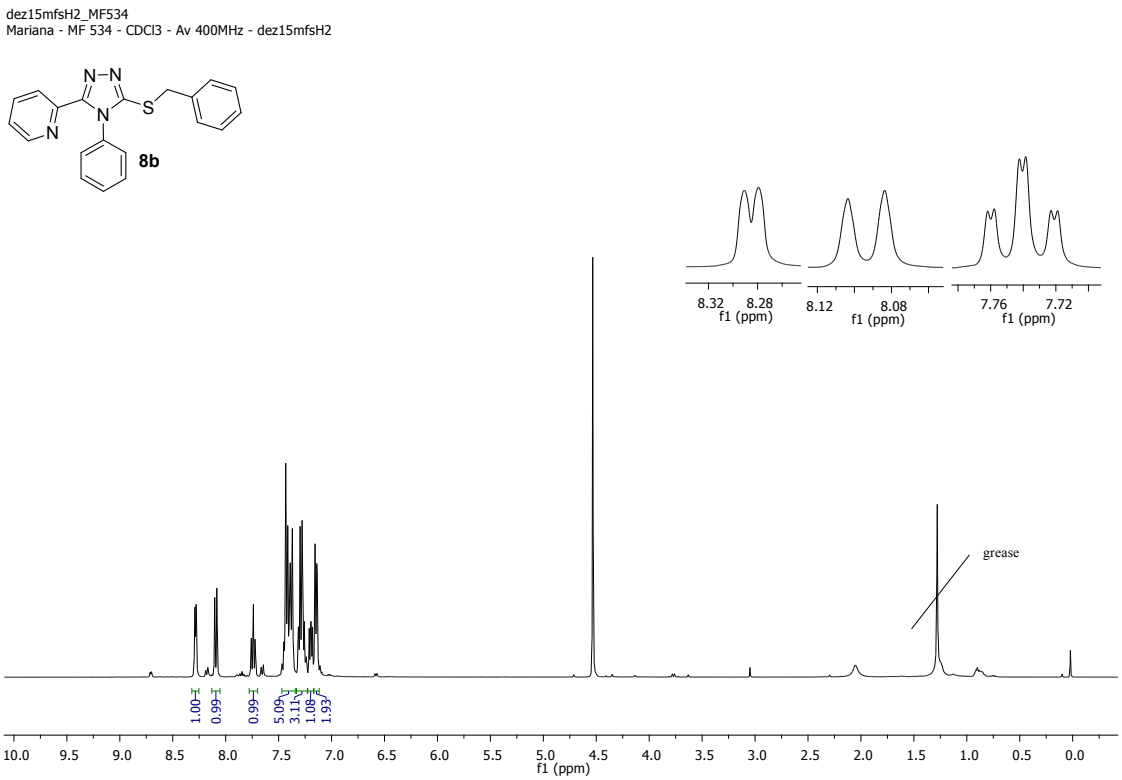

Figure S41. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8b**.

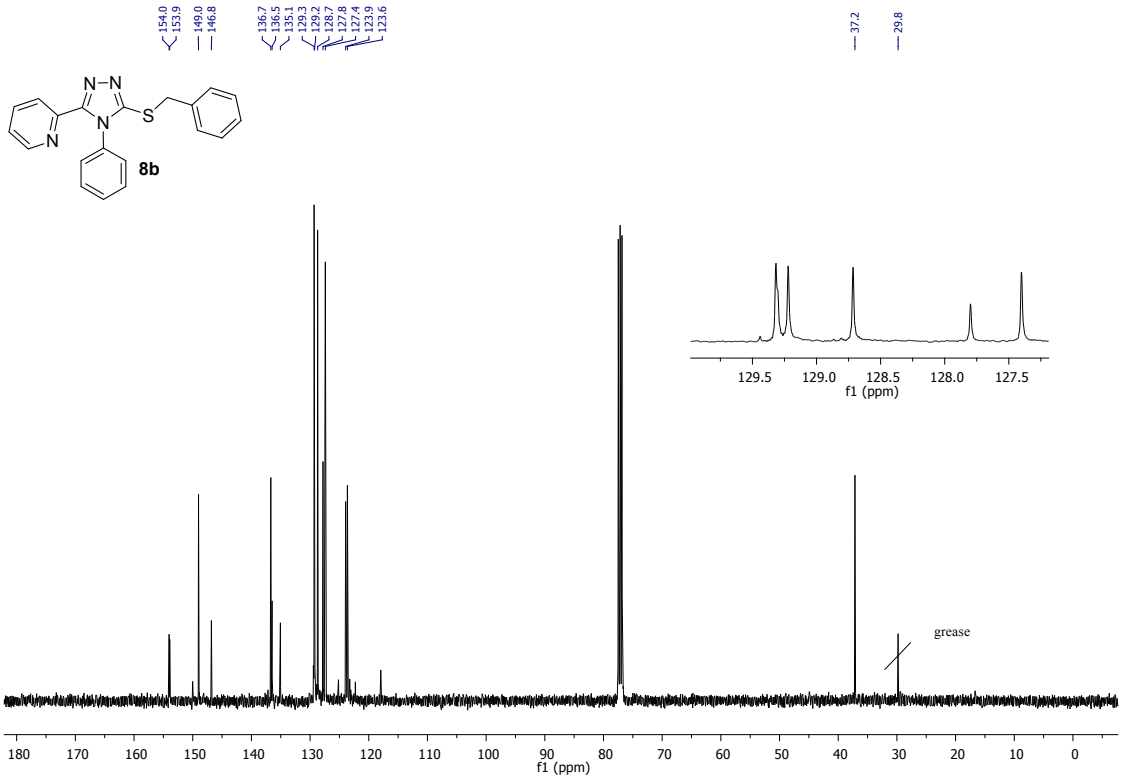

Figure S42. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **8b**.

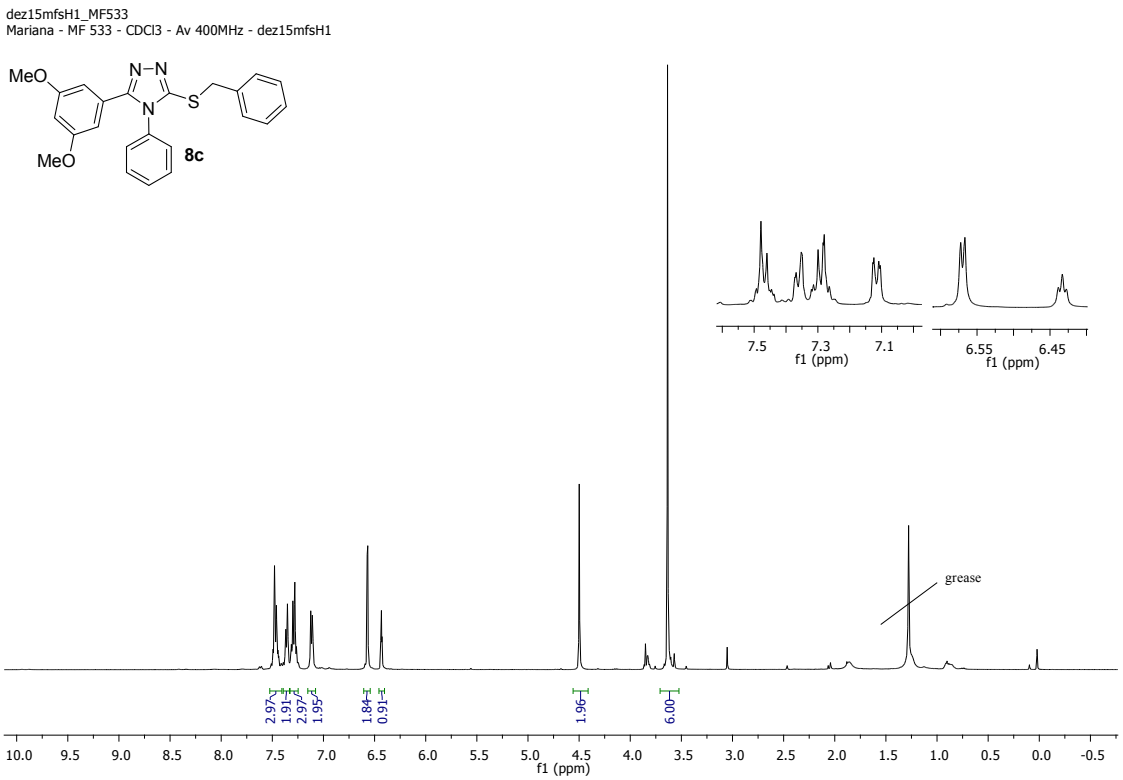

Figure S43. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8c**.

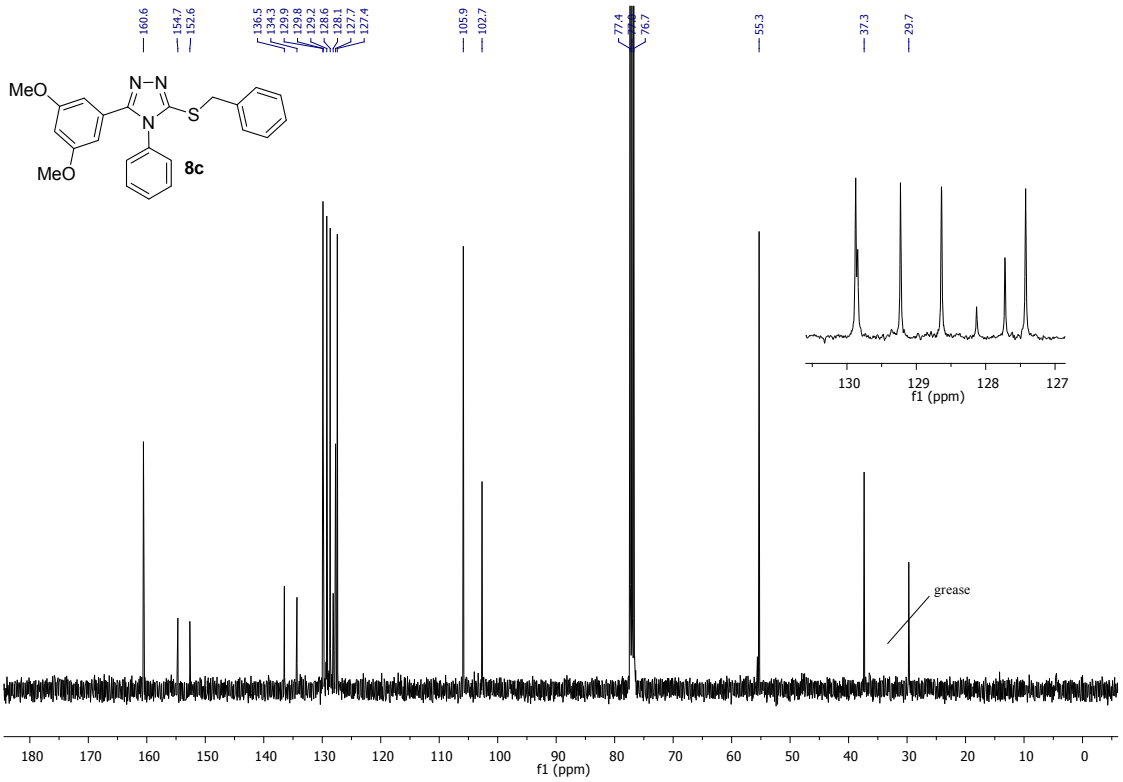

Figure S44. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **8c**.

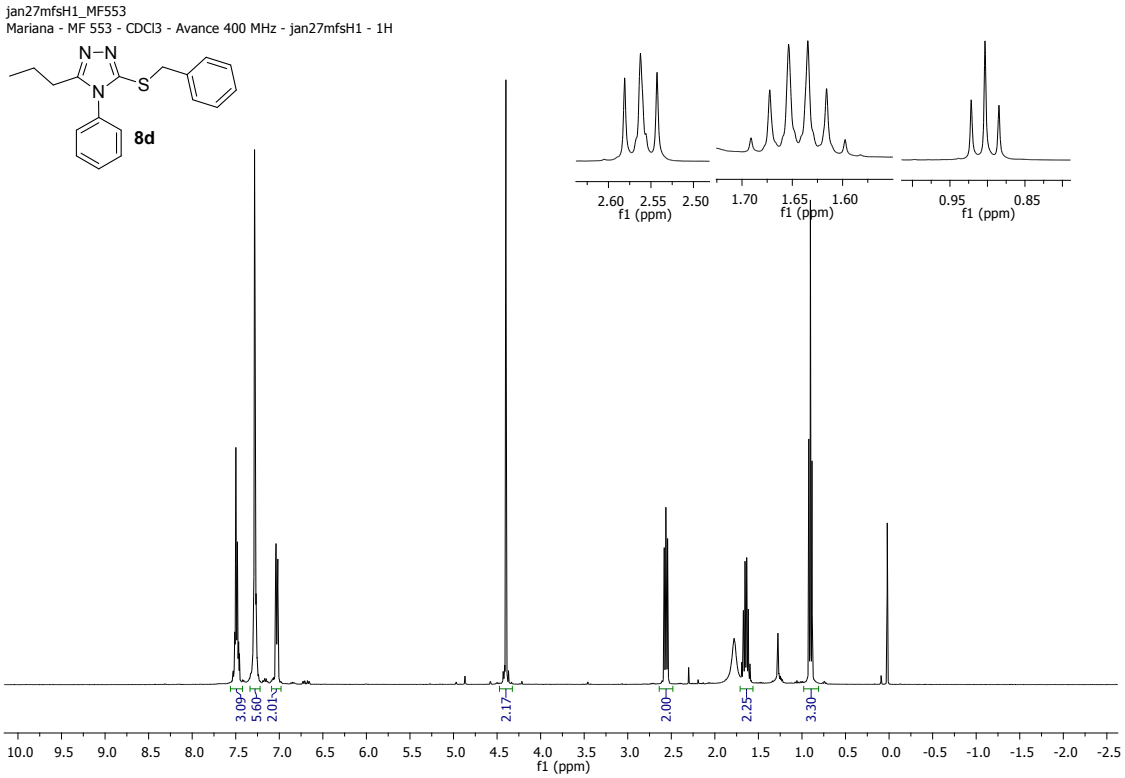

Figure S45. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8d**.

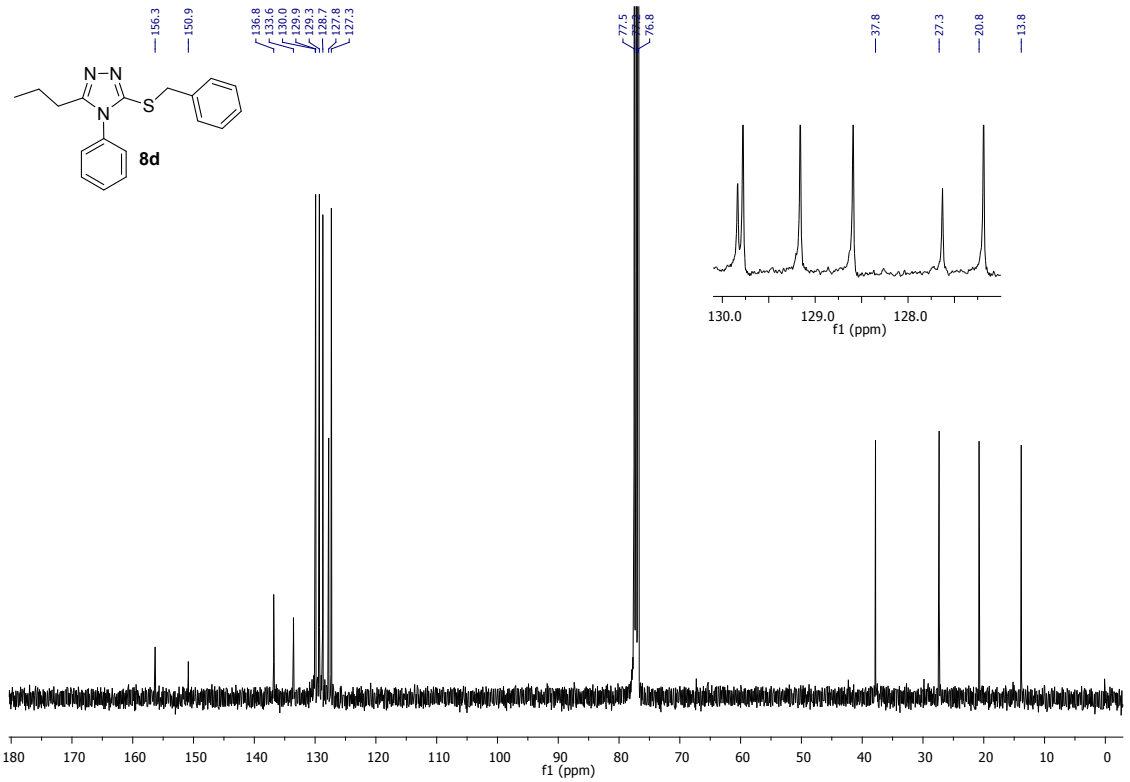

Figure S46. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **8d**.