Supporting Information

New Cationic Coinage Metal Complexes Featuring Silyl Group Functionalized Phosphine; Syntheses, Structures and Catalytic Studies in Alkyne-Azide Cycloaddition Reactions

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Materials and Methods

All the reagents were purchased from commercially available sources (Loba Chemie, Spectrochem and Sigma-Aldrich, TCI, and Avra). The silylated phosphine **1** was prepared by a slightly modified synthetic procedure reported previously[1]. Dichloromethane (DCM) was dried using a distillation setup over calcium hydride in an Argon/Nitrogen atmosphere. Tetrahydrofuran (THF) and *n*-hexane were dried using a distillation setup over sodium metal and benzophenone in an atmosphere of nitrogen and argon. Tensil Schlenk tubes and Schlenk flasks were used for the synthesis of the ligands and corresponding metal complexes in an atmosphere of N_2 and Ar. All catalytic reactions were carried out in a borosil-sealed tube in a N_2 atmosphere. Spectrochem chemical company's 100-200 mesh silica gel was used for column chromatography. Using distilled hexane and ethyl acetate, gradient elution was carried out. TLC plates were detected at 254 nm using UV light. A 400 and 700 MHz FT-NMR called the "Bruker AVANCE NEO Ascend 400 and 700" was used to measure the NMR spectra. Chemical shifts (δ) are expressed in ppm referenced to tetramethylsilane (TMS), using the residual solvent as an internal standard ($CDCl_3$, ^1H; 7.26 ppm, and ^{13}C; 77.16 ppm and DMSO-d_6, ^1H; 2.5 ppm, and ^{13}C; 39.52 ppm). Hertz units are used to express coupling constants. Individual peaks are reported as multiplicities (integration and coupling constants are given in Hz), where s = singlet, d = doublet, t = triplet, q = quartet, and dd = doublet of doublet, br = broad respectively. On the "Xevo G2-XS QT of Quadrupole Time of Flight Mass Spectrometer Waters," ESI-MS/HR-MS spectra were measured. "Elementar, UNICUBE" was used to perform measurements for elemental analysis. The XRD analysis carried out using Rigaku Smart Lab X-ray diffractometer.

Spectral data of ligand and its metal complexes (1-6)

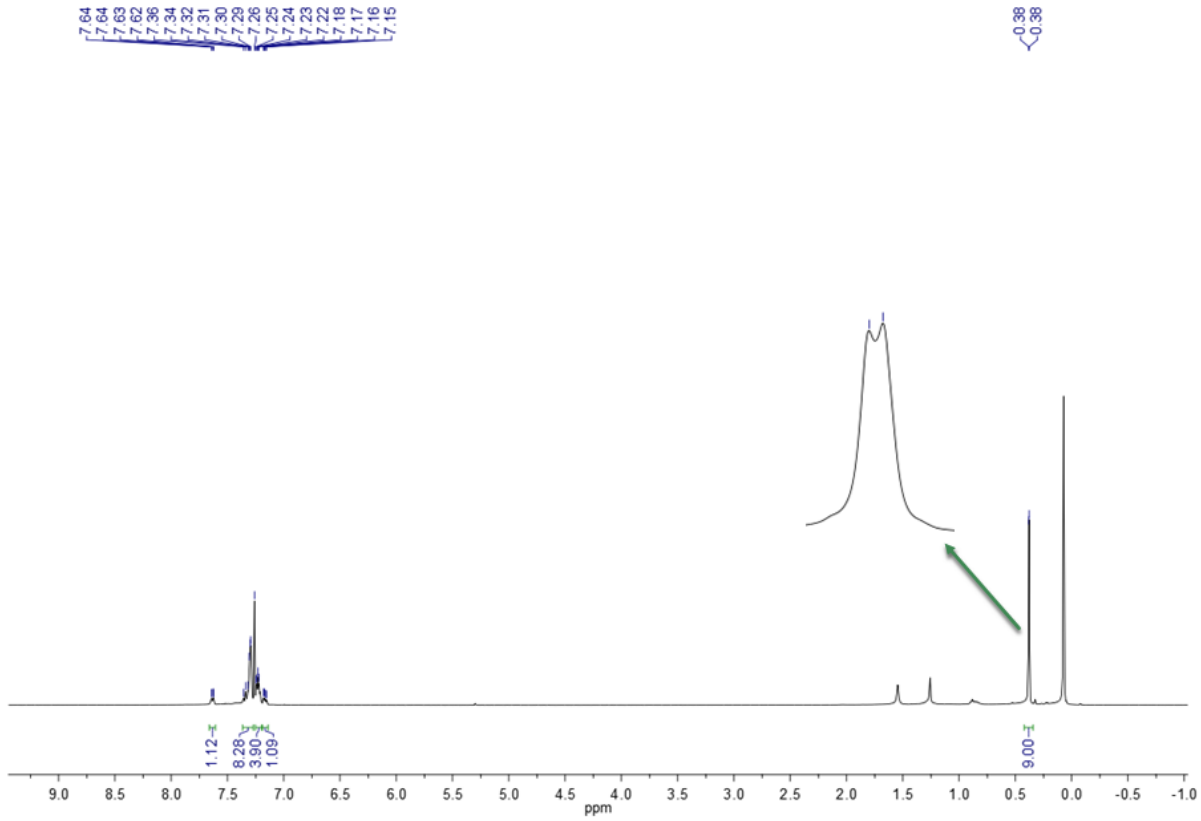


Figure S1. ^{1}H NMR spectrum of silylated phosphine **1** measured in $CDCl_3$.[1]

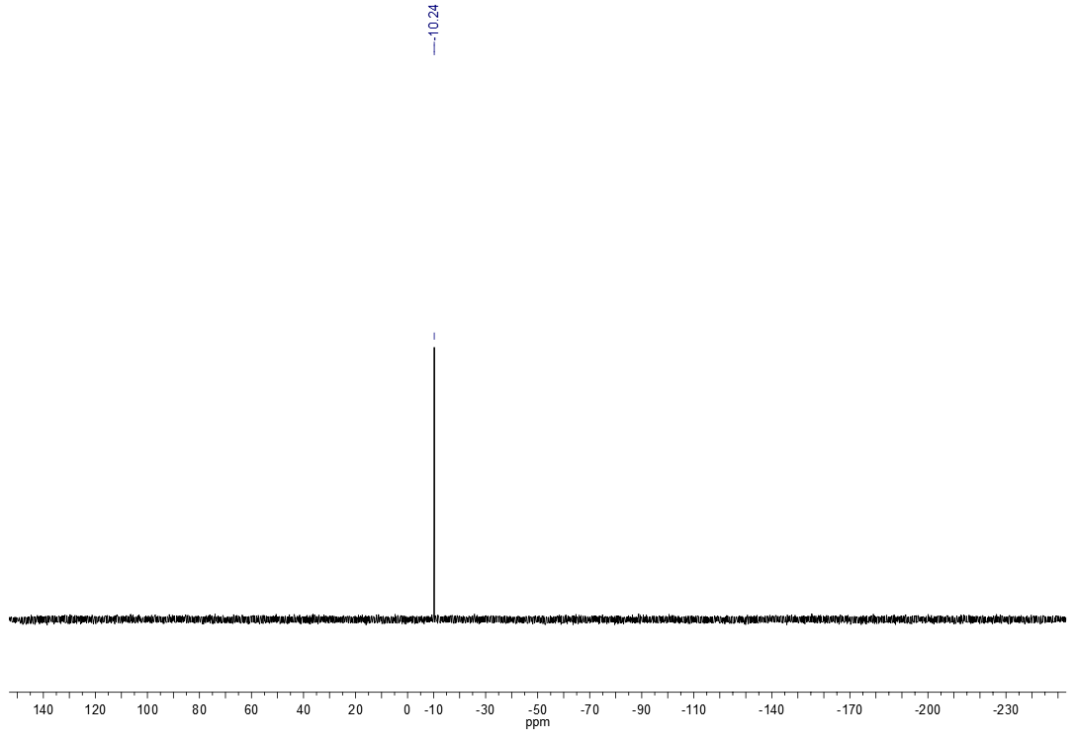


Figure S2. ^{31}P NMR spectrum of silylated phosphine **1** measured in $CDCl_3$.[1]

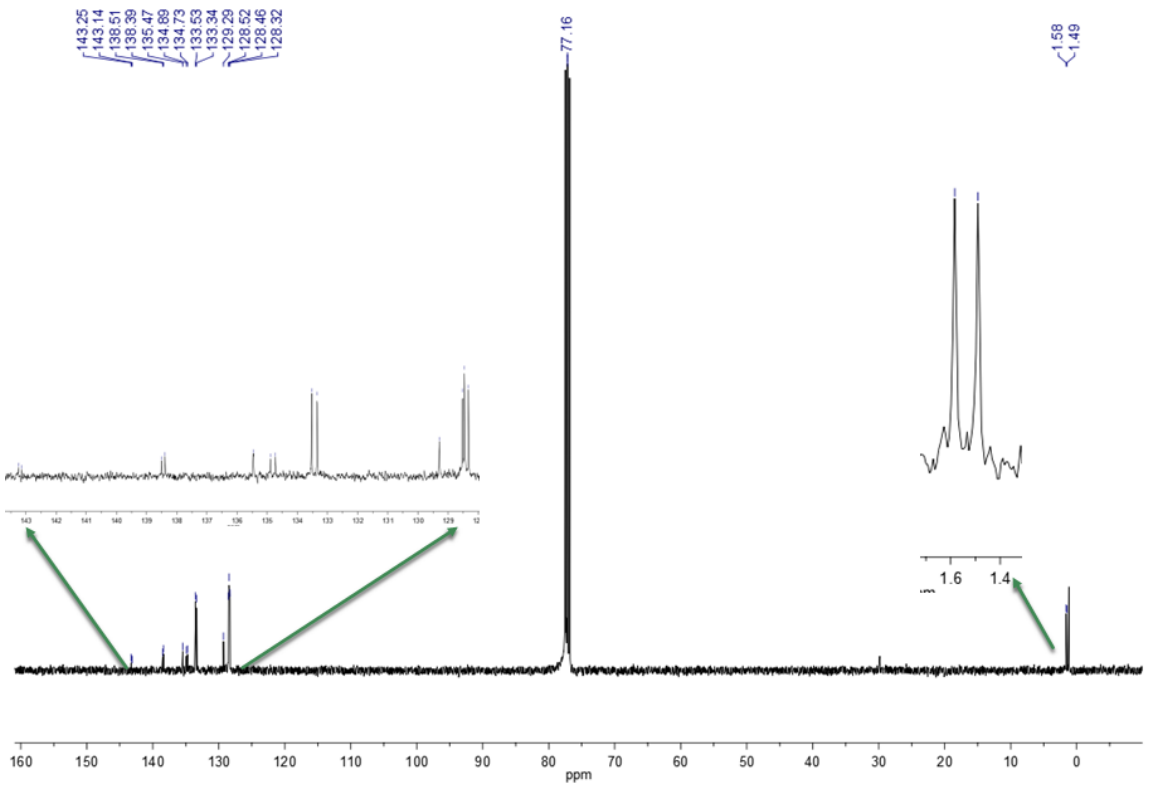


Figure S3. ^{13}C NMR spectrum of silylated phosphine **1** measured in $CDCl_3$.

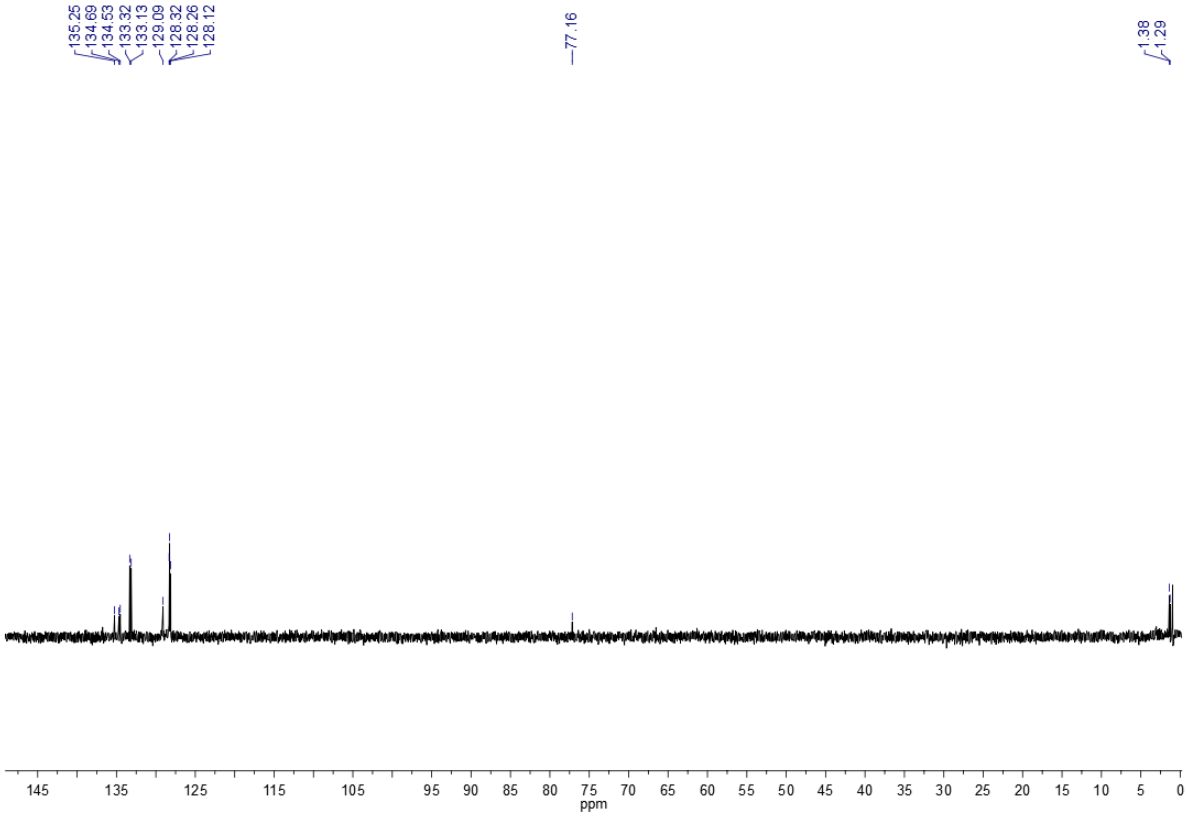


Figure S4. DEPT-135{^{13}C} NMR spectrum of silylated phosphine **1** measured in $CDCl_3$.

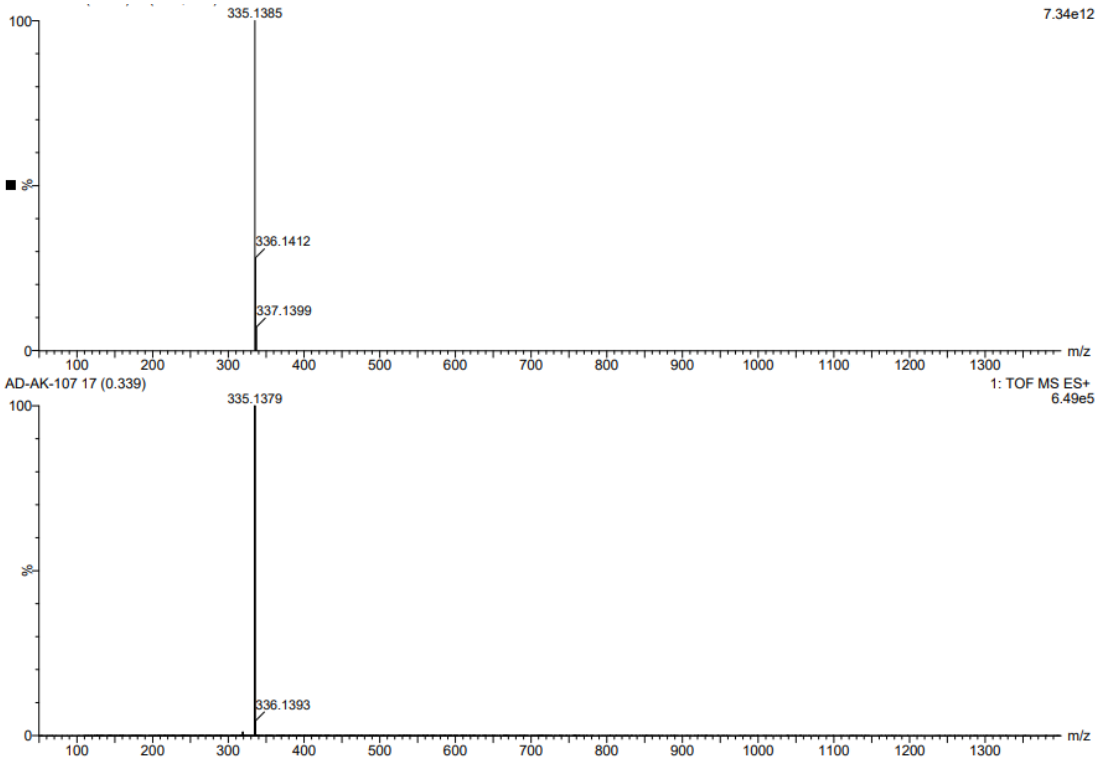


Figure S5. ESI-HRMS spectrum of silylated phosphine **1** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

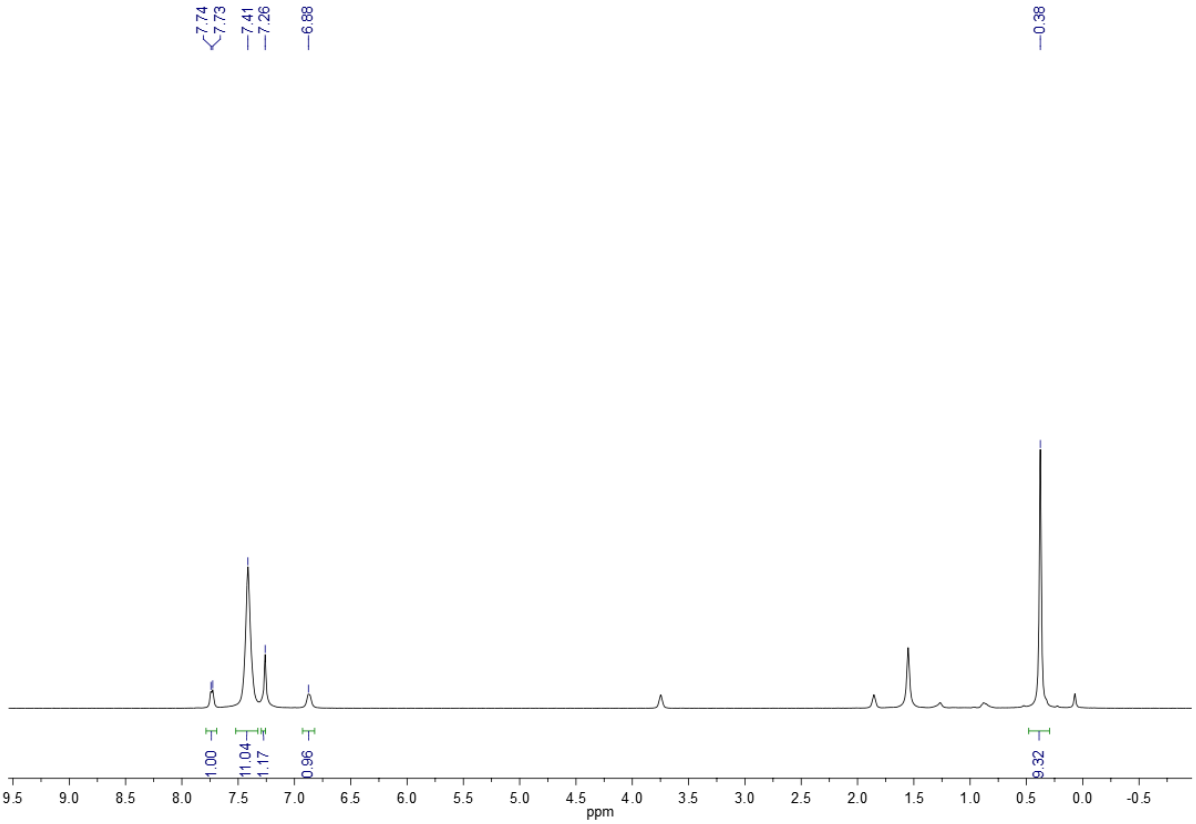


Figure S6. ^{1}H NMR spectrum of compound **2** measured in $CDCl_3$.

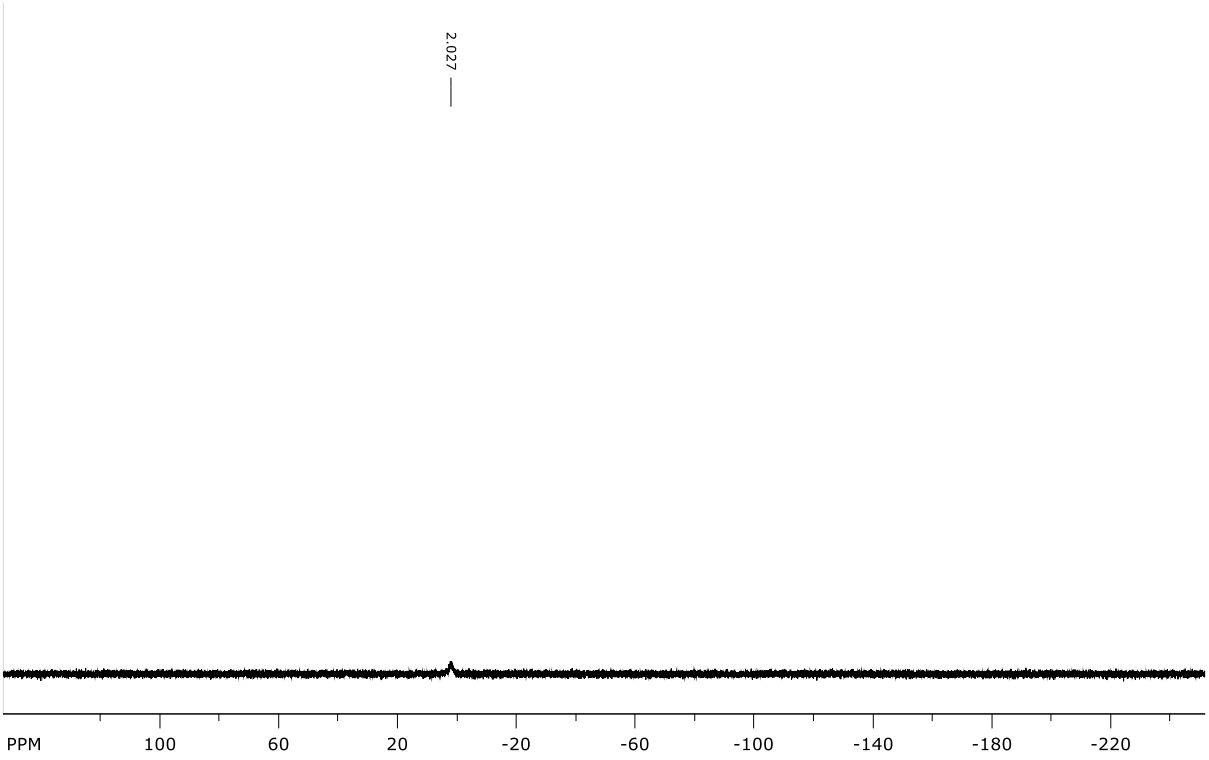


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** measured in $CDCl_3$.

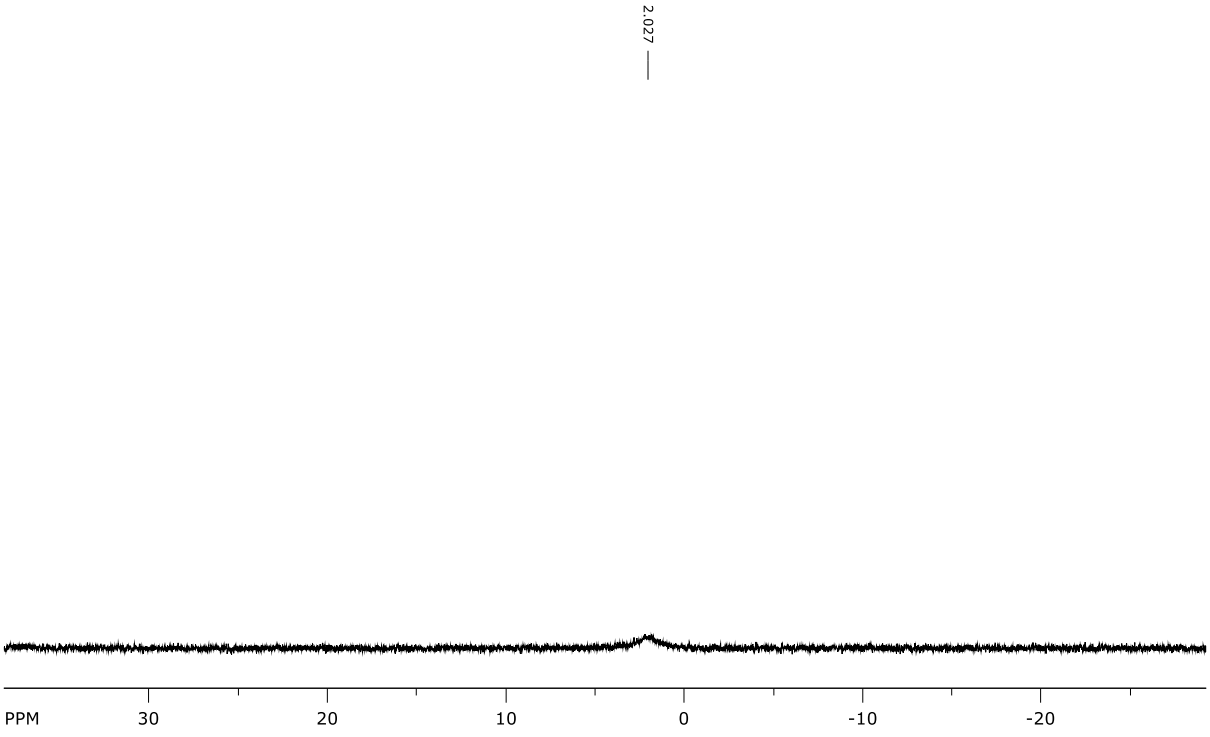


Figure S8. ^{31}P NMR spectrum (expanded version) of compound **2** measured in $CDCl_3$.

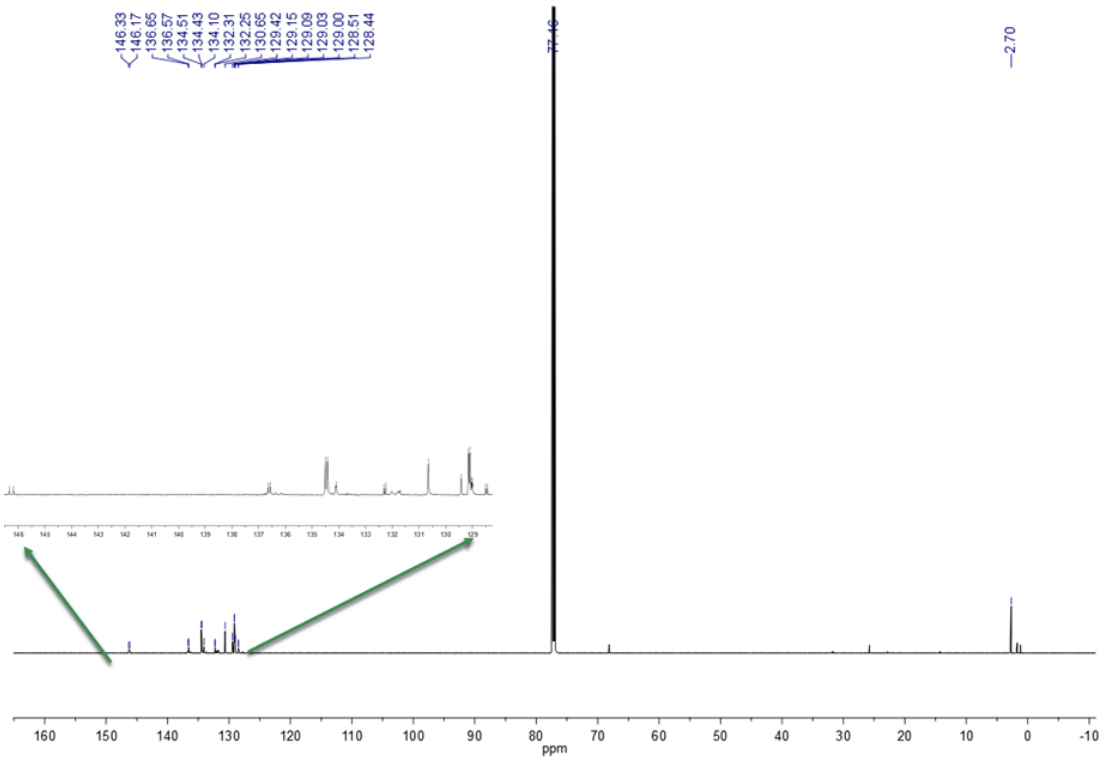


Figure S9. ^{13}C NMR spectrum of compound **2** measured in $CDCl_3$.

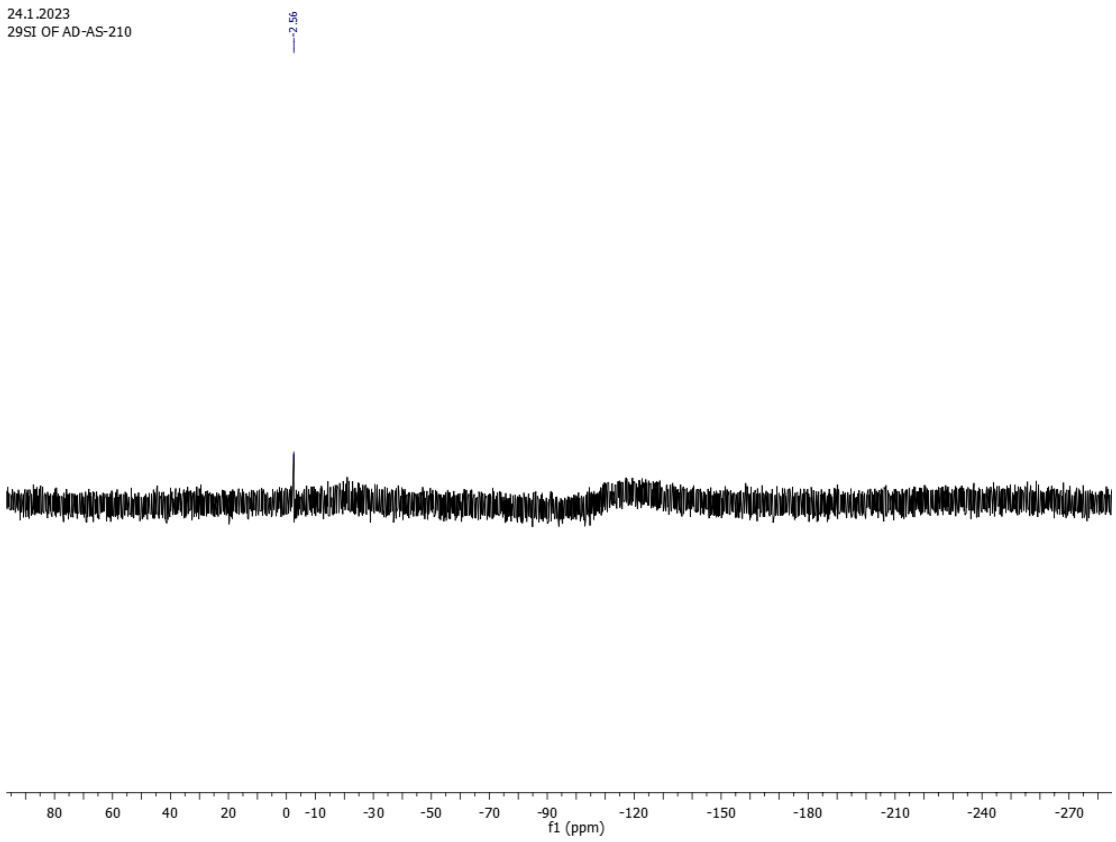


Figure S10. ^{29}Si NMR spectrum of compound **2** measured in $CDCl_3$.

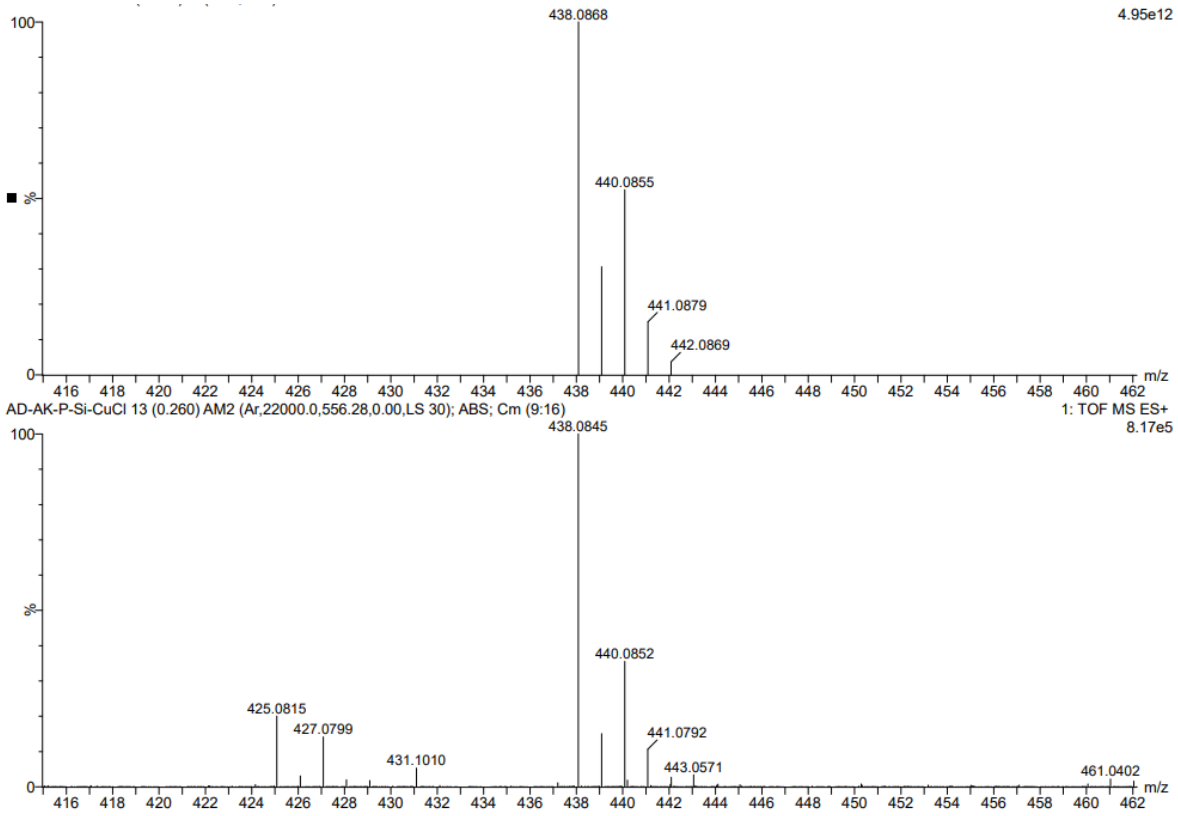


Figure S11. ESI-HRMS spectrum of compound **2** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

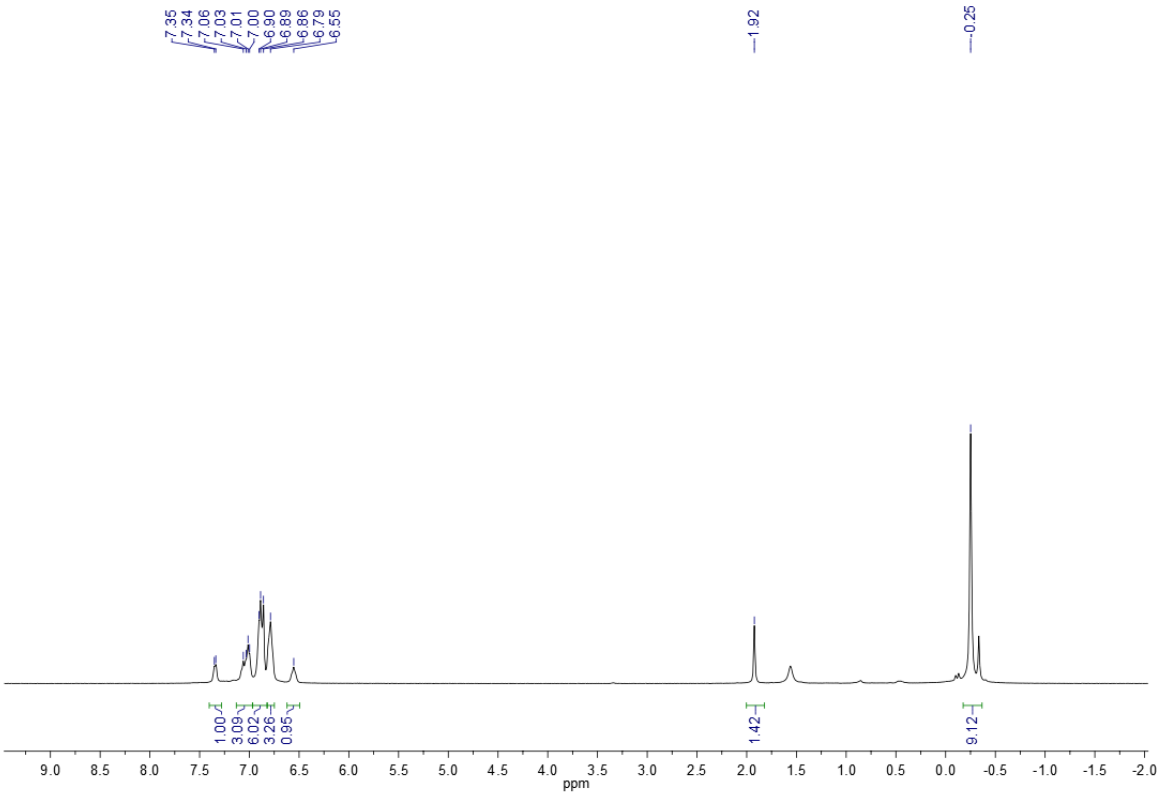


Figure S12. ^{1}H MR spectrum of compound **3** measured in $CDCl_3$.

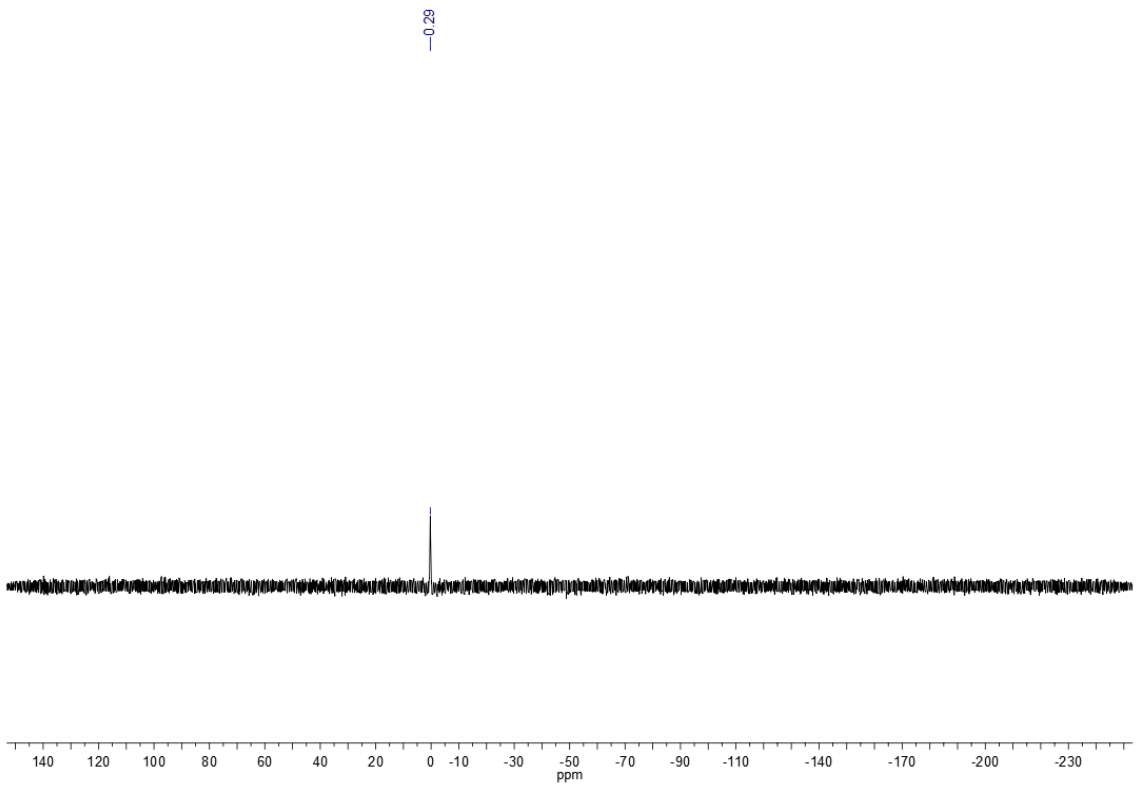


Figure S13. ^{31}P NMR spectrum of compound **3** measured in $CDCl_3$.

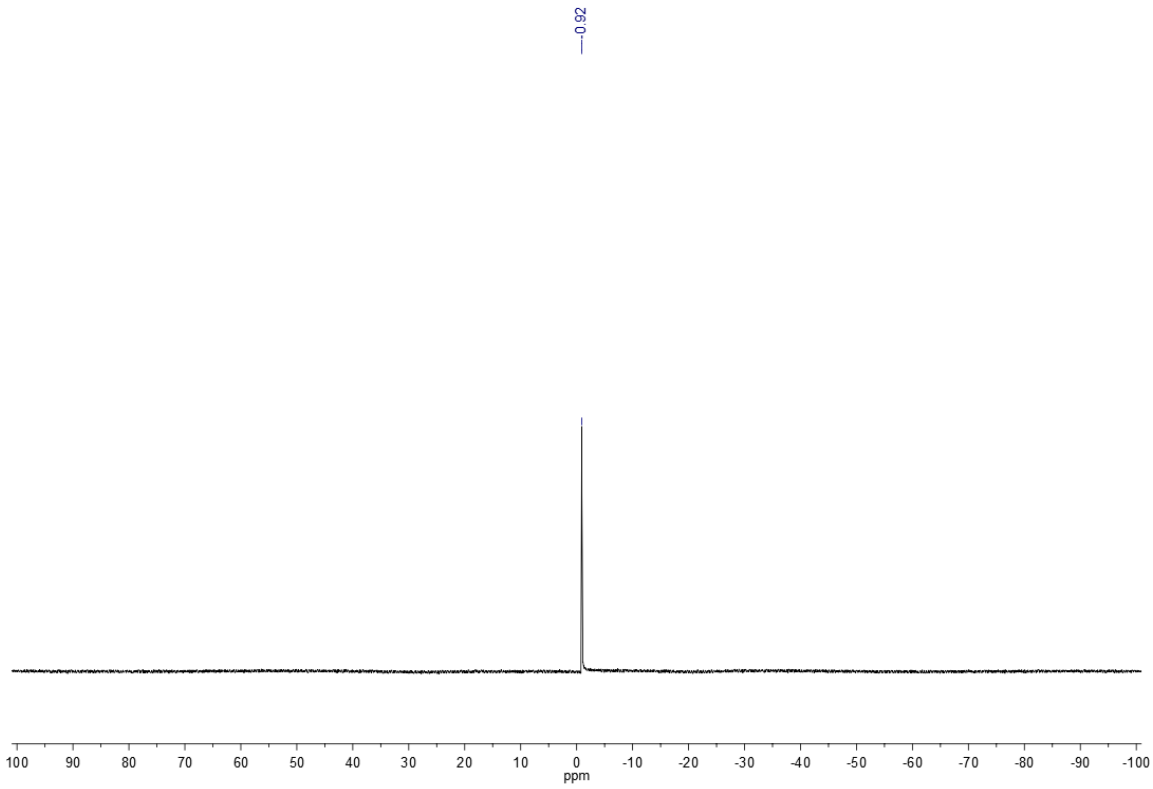


Figure S14. ^{11}B NMR spectrum of compound **3** measured in $CDCl_3$.

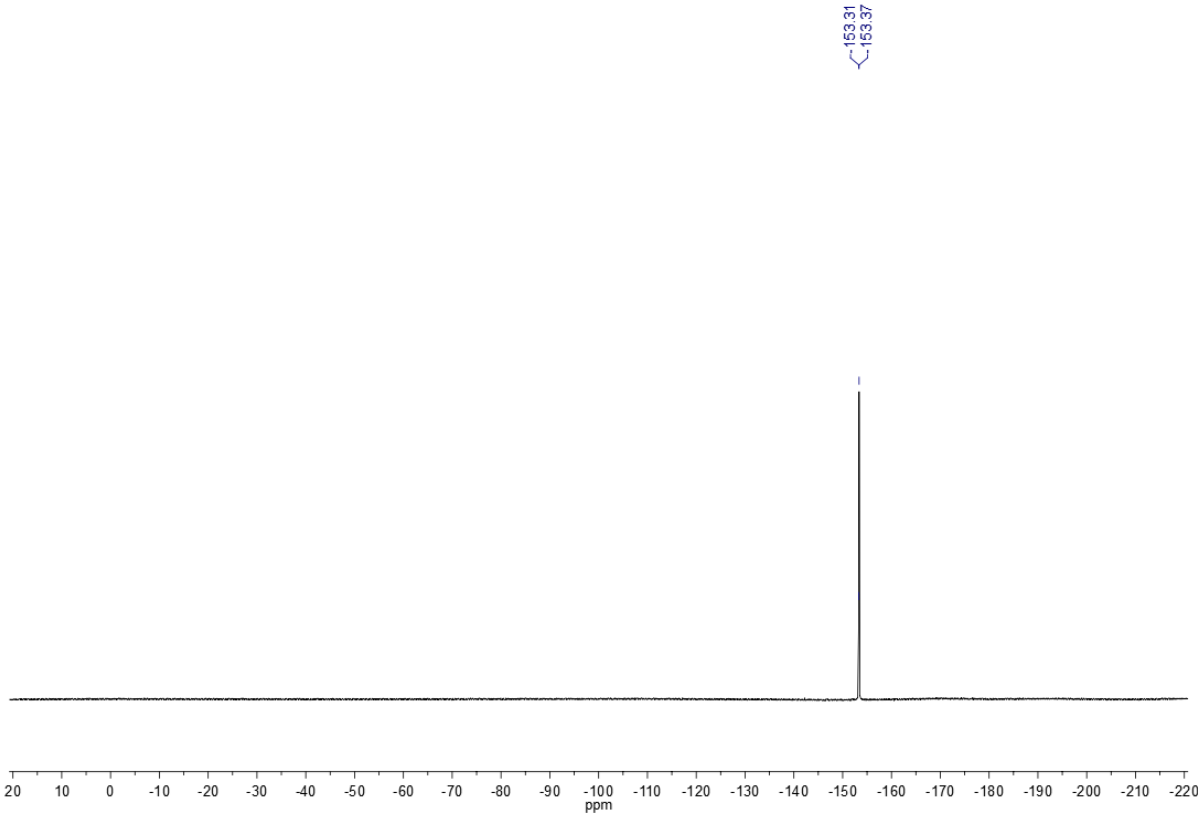


Figure S15. ^{19}F NMR spectrum of compound **3** measured in $CDCl_3$.

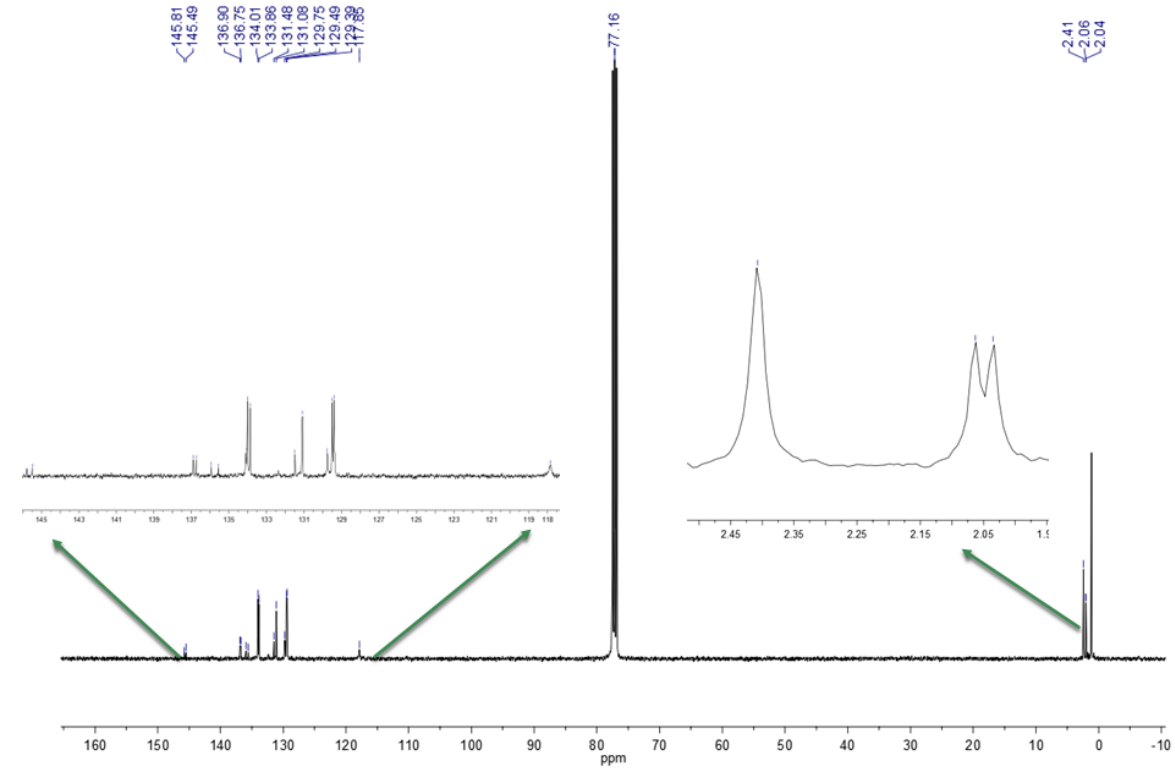


Figure S16. ^{13}C NMR spectrum of compound **3** measured in $CDCl_3$.

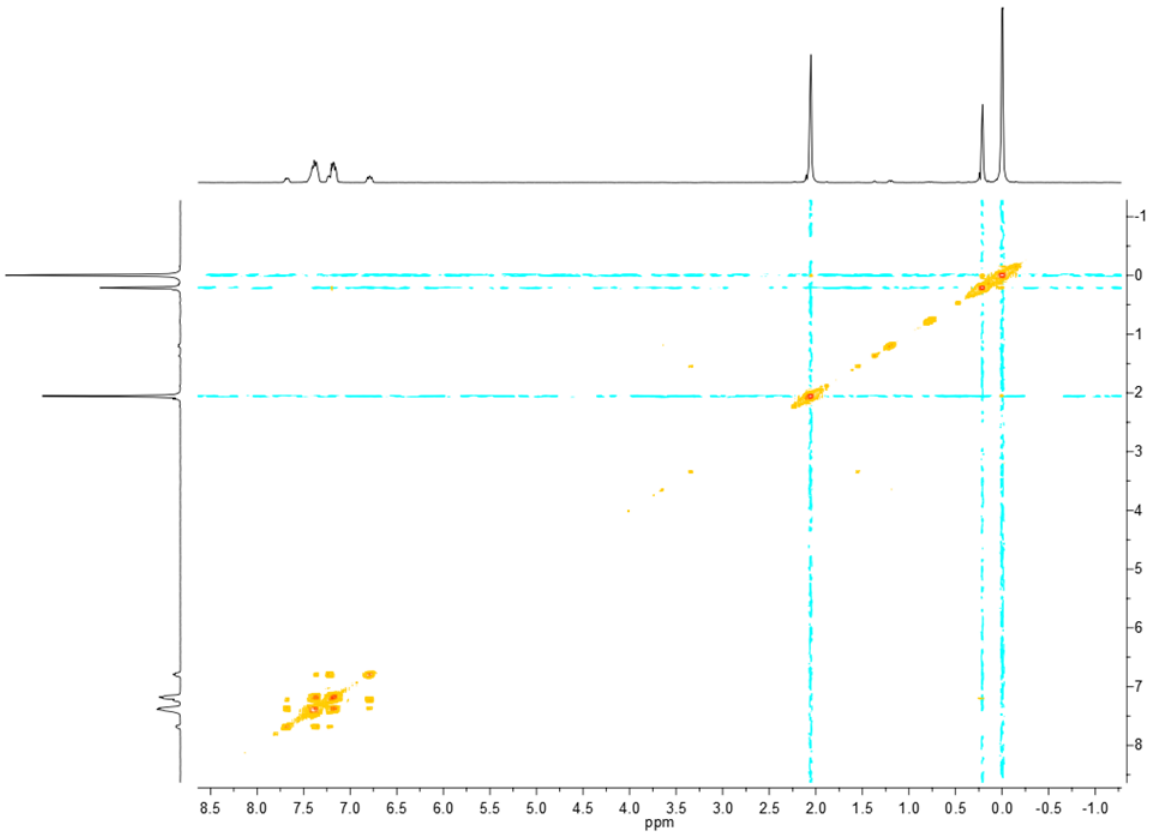


Figure S17. ^{1}H-^{1}H COSY NMR spectrum of compound **3** measured in $CDCl_3$.

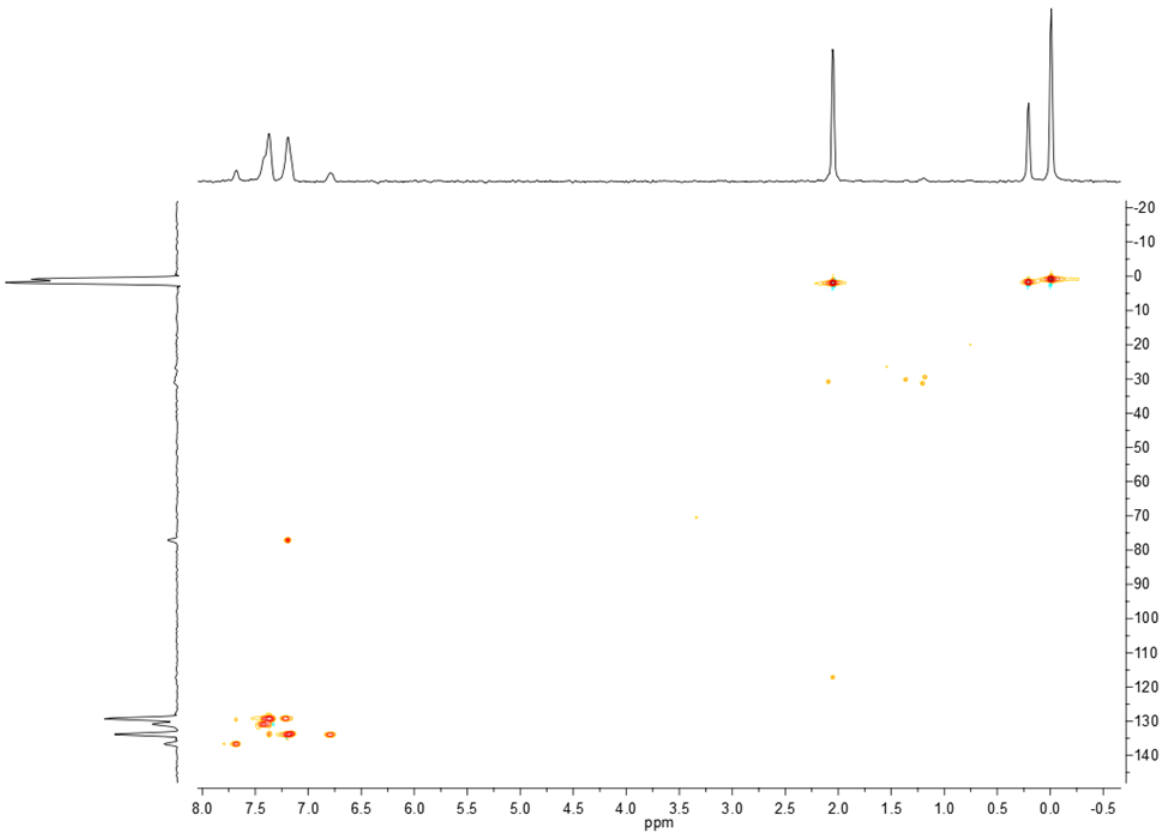


Figure S18. The HSQC spectrum of [(**1**)$_2$Cu(CH$_3$CN)]BF$_4$ (**3**) measured in $CDCl_3$.

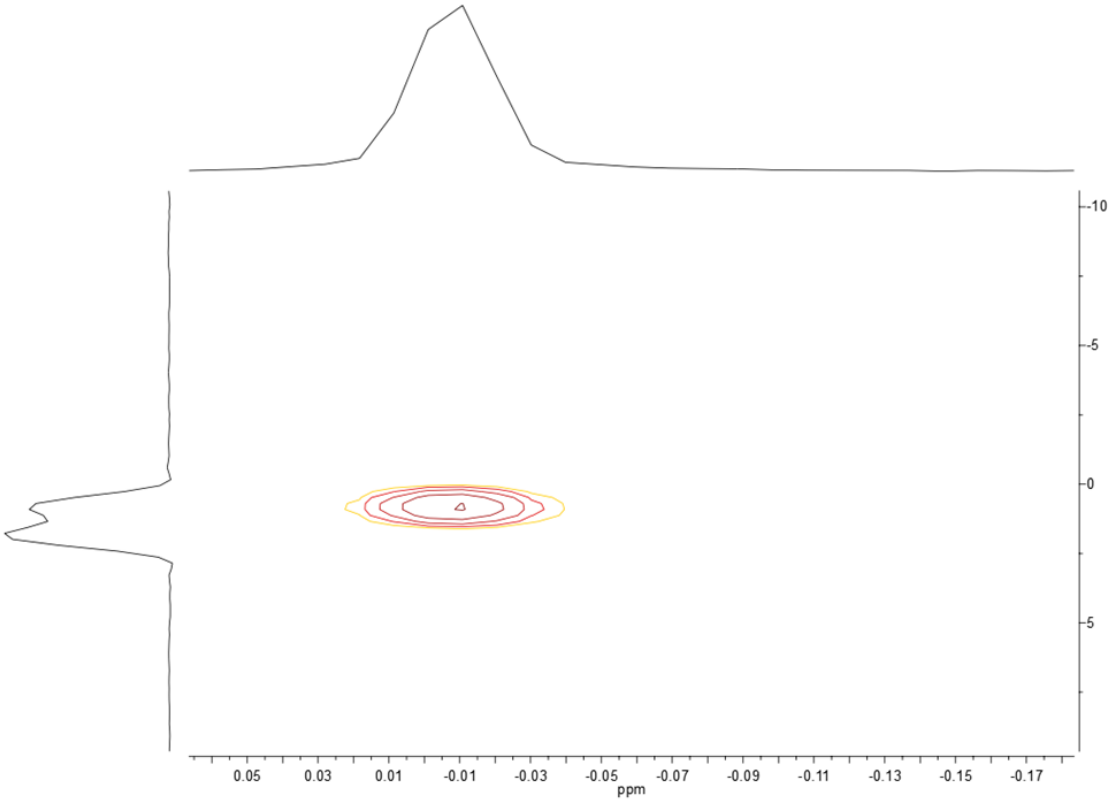


Figure S19. The HSQC spectrum of [(**1**)$_2$Cu(CH$_3$CN)]BF$_4$ (**3**); shows the correlation of SiMe$_3$ groups in the ligand part of the complex.

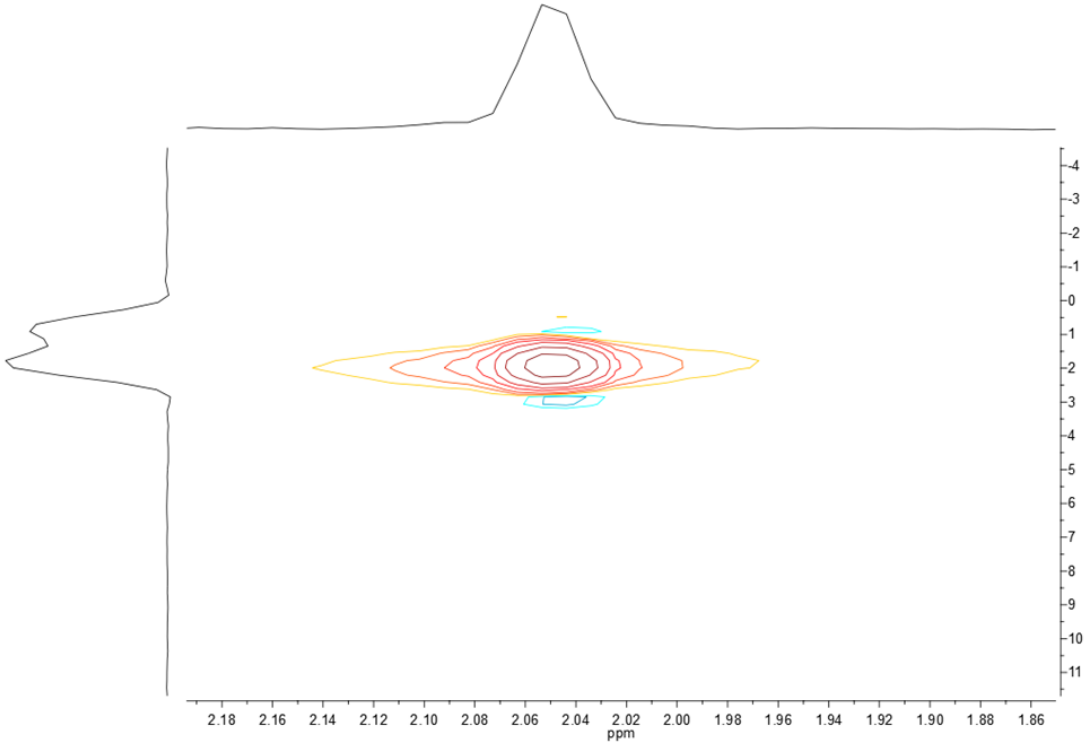


Figure S20. The HSQC spectrum of [(**1**)$_2$Cu(CH$_3$CN)]BF$_4$ (**3**); shows the correlation of the CH$_3$ group of CH$_3$CN in the ligand part of the complex.

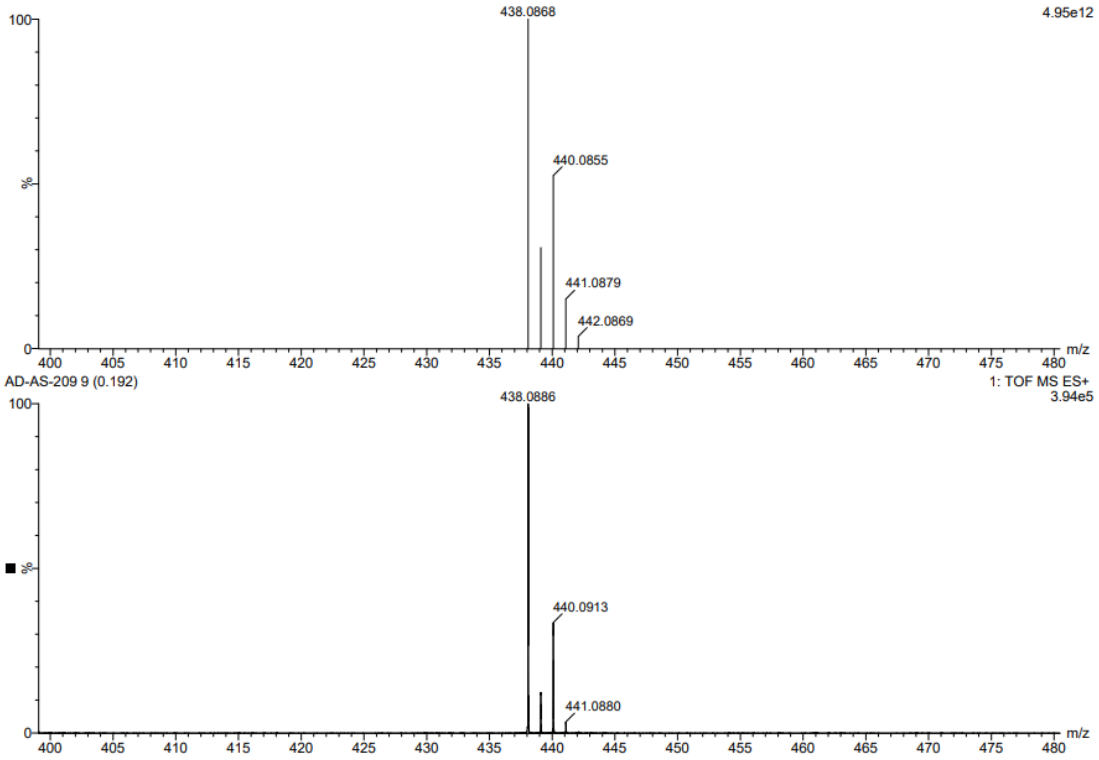


Figure S21. ESI-HRMS spectrum of compound **3** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

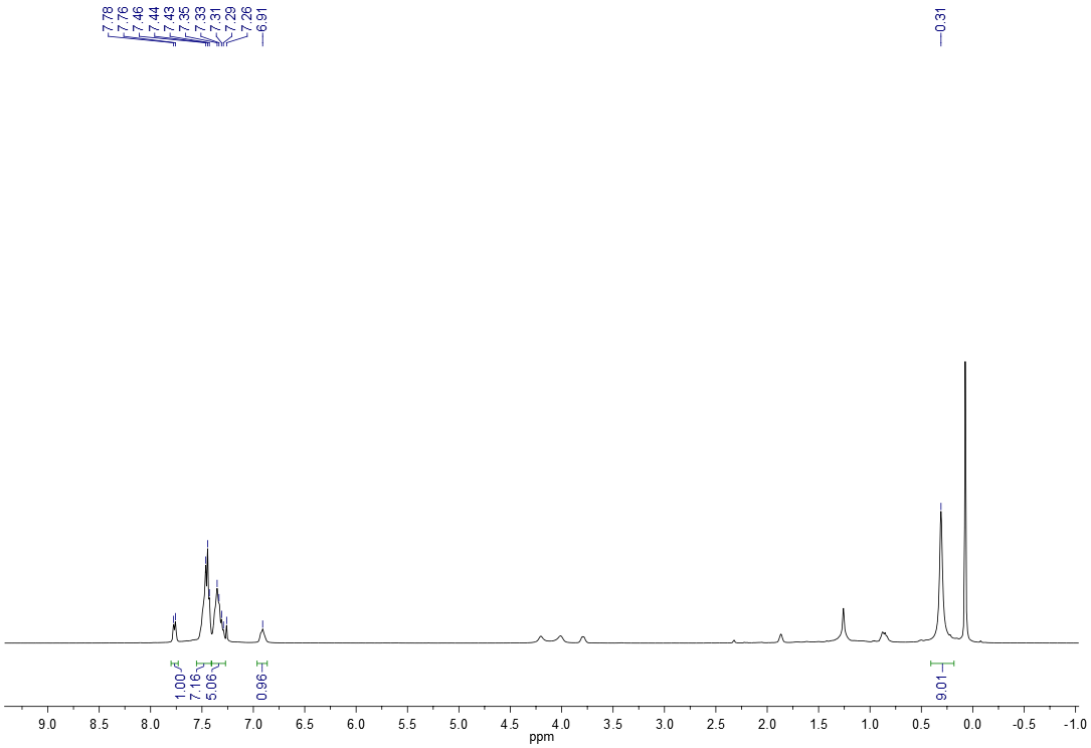


Figure S22. ^{1}H NMR spectrum of compound **4a** measured in $CDCl_3$.

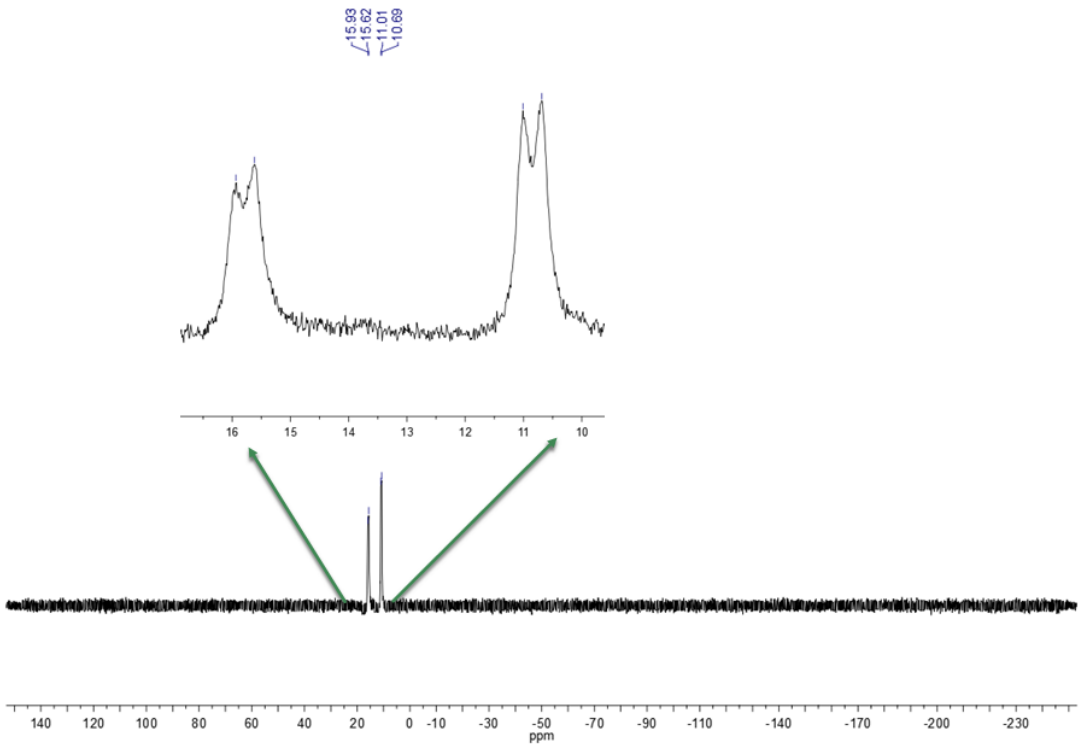


Figure S23. ^{31}P NMR spectrum of compound **4a** measured in $CDCl_3$.

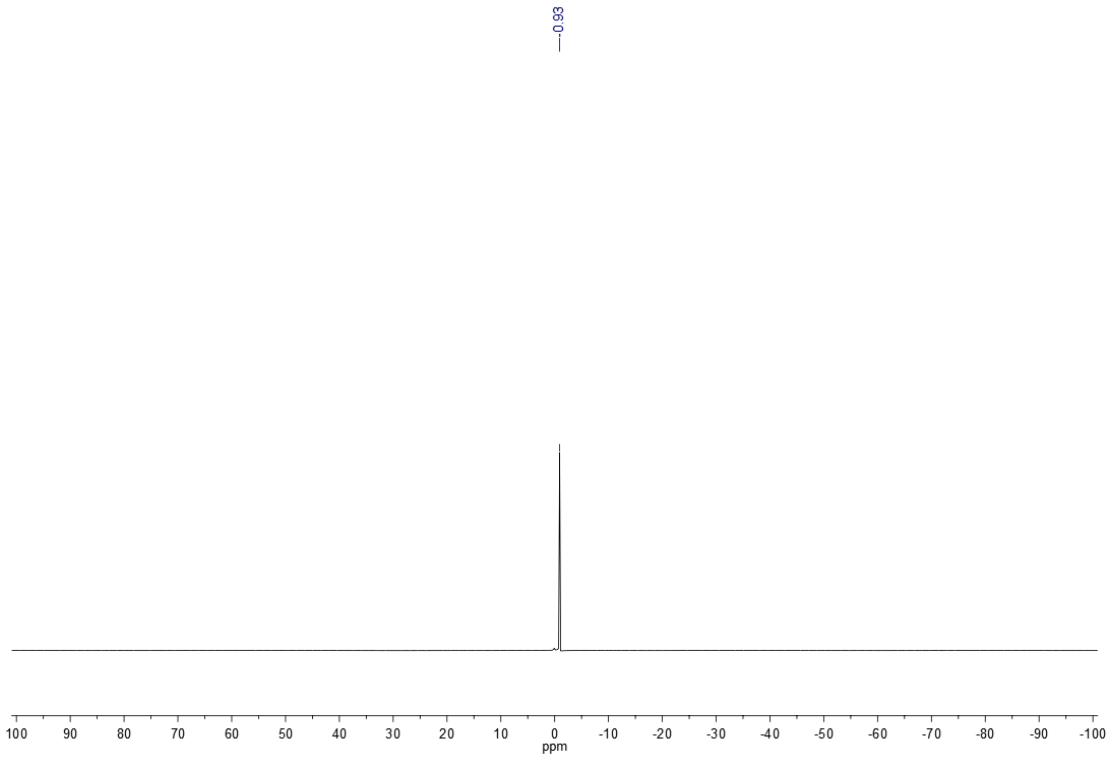


Figure S24. ^{11}B NMR spectrum of compound **4a** measured in $CDCl_3$.

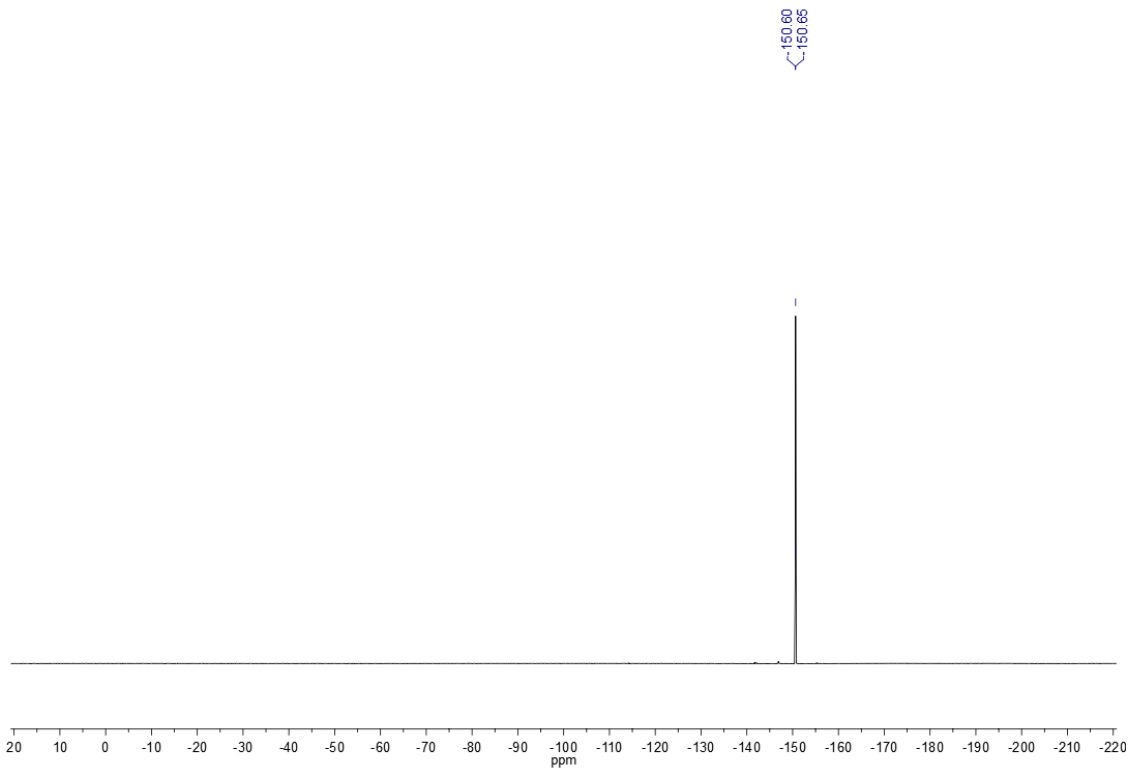


Figure S25. ^{19}F NMR spectrum of compound **4a** measured in $CDCl_3$.

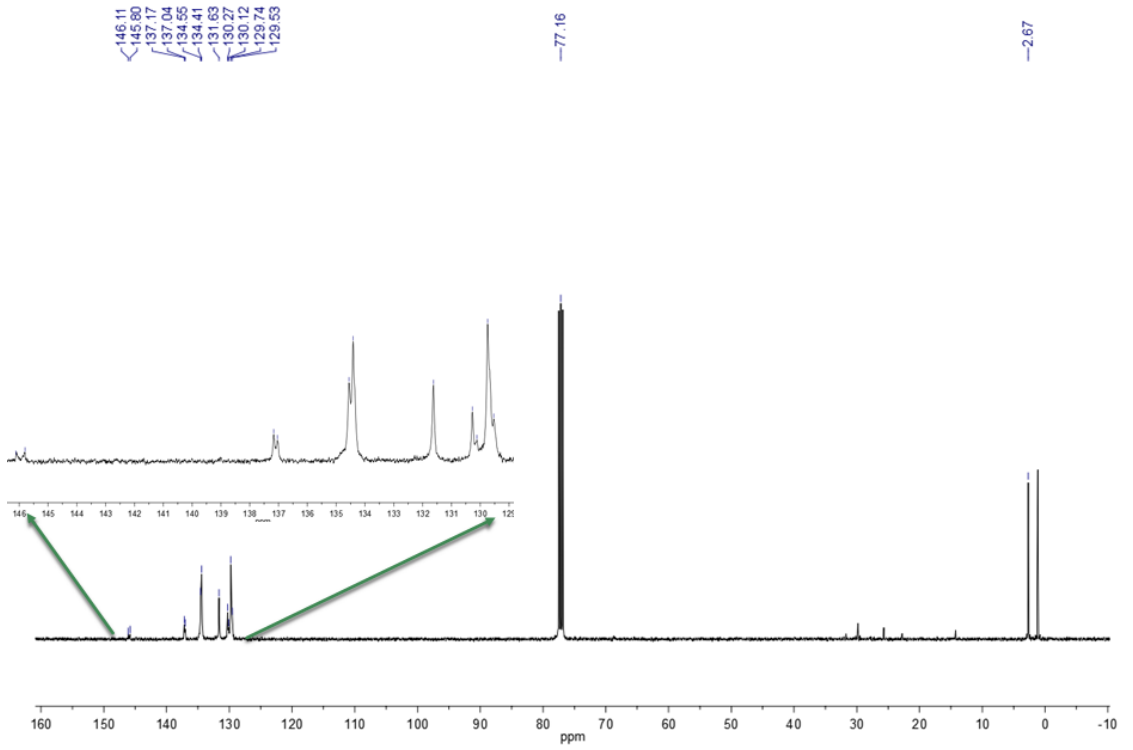


Figure S26. ^{13}C NMR spectrum of compound **4a** measured in $CDCl_3$.

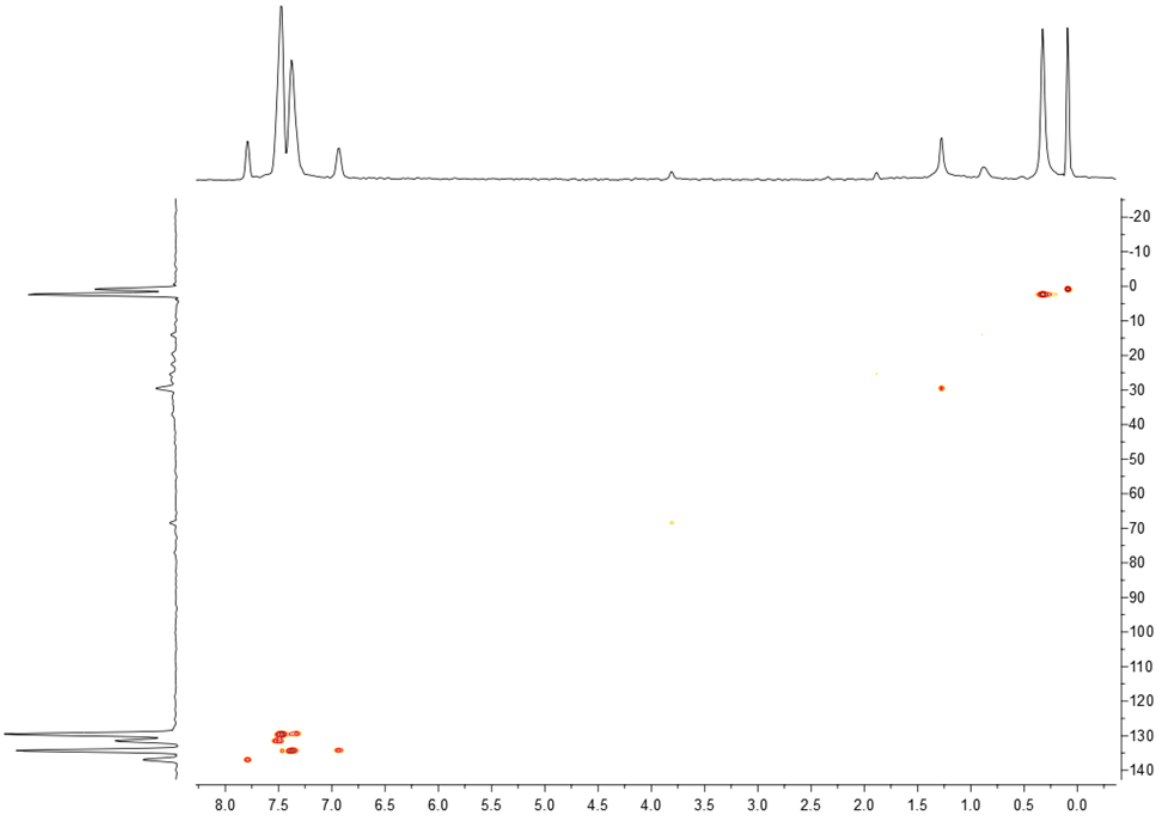


Figure S27. The HSQC spectrum of **4a** measured in $CDCl_3$.

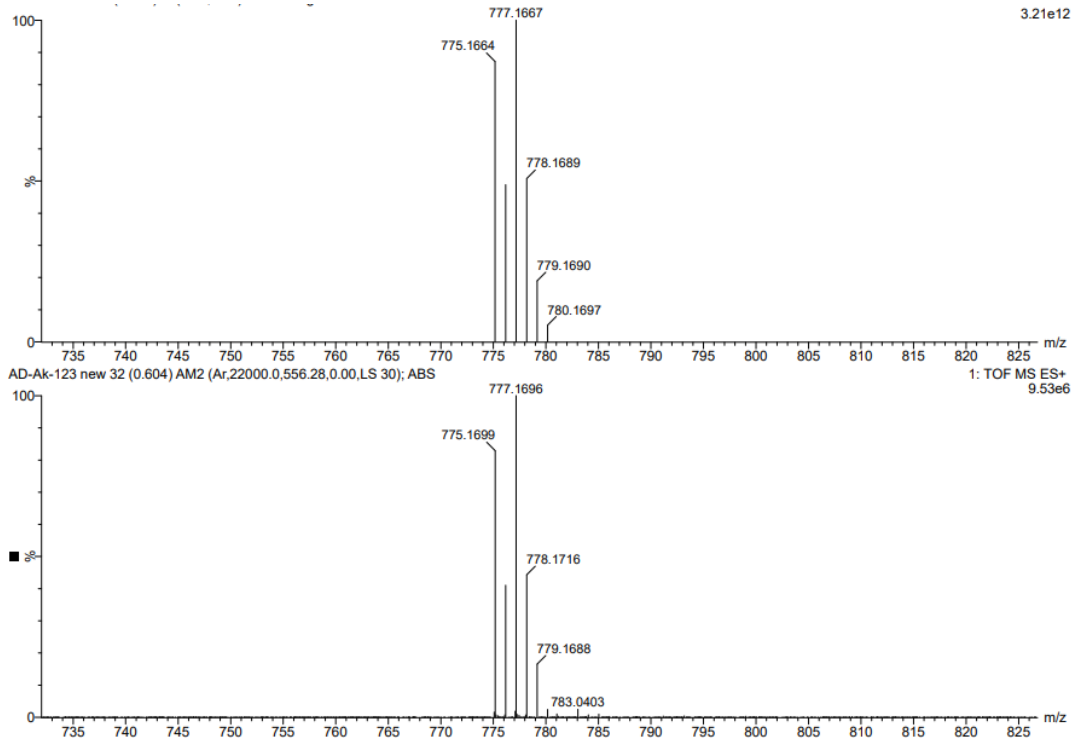


Figure S28. ESI-HRMS spectrum of compound **4a** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

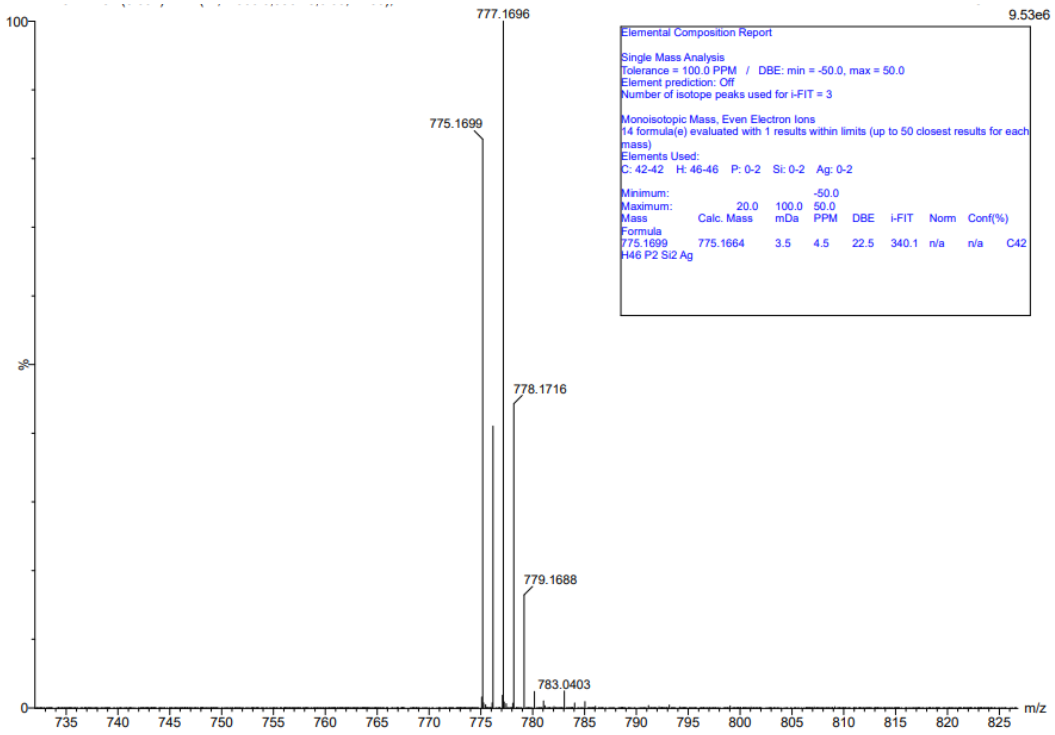


Figure S29. ESI-HRMS report of compound **4a** measured in acetonitrile.

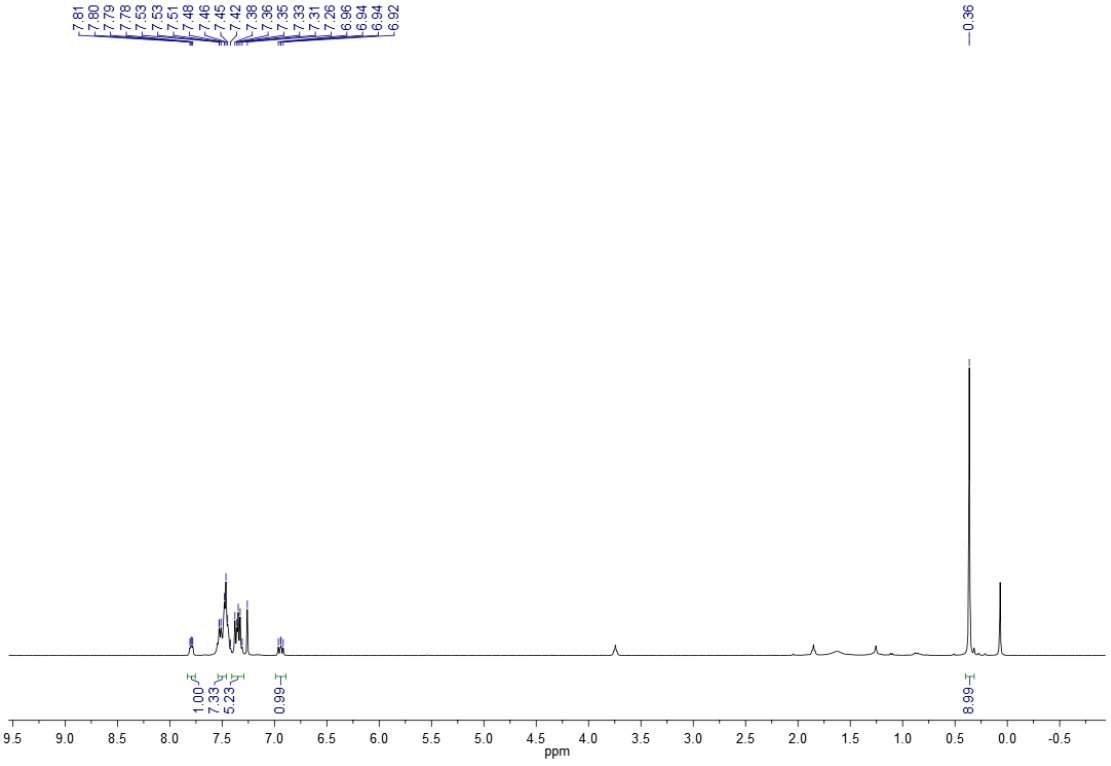


Figure S30. ^{1}H NMR spectrum of compound **4b** measured in $CDCl_3$.

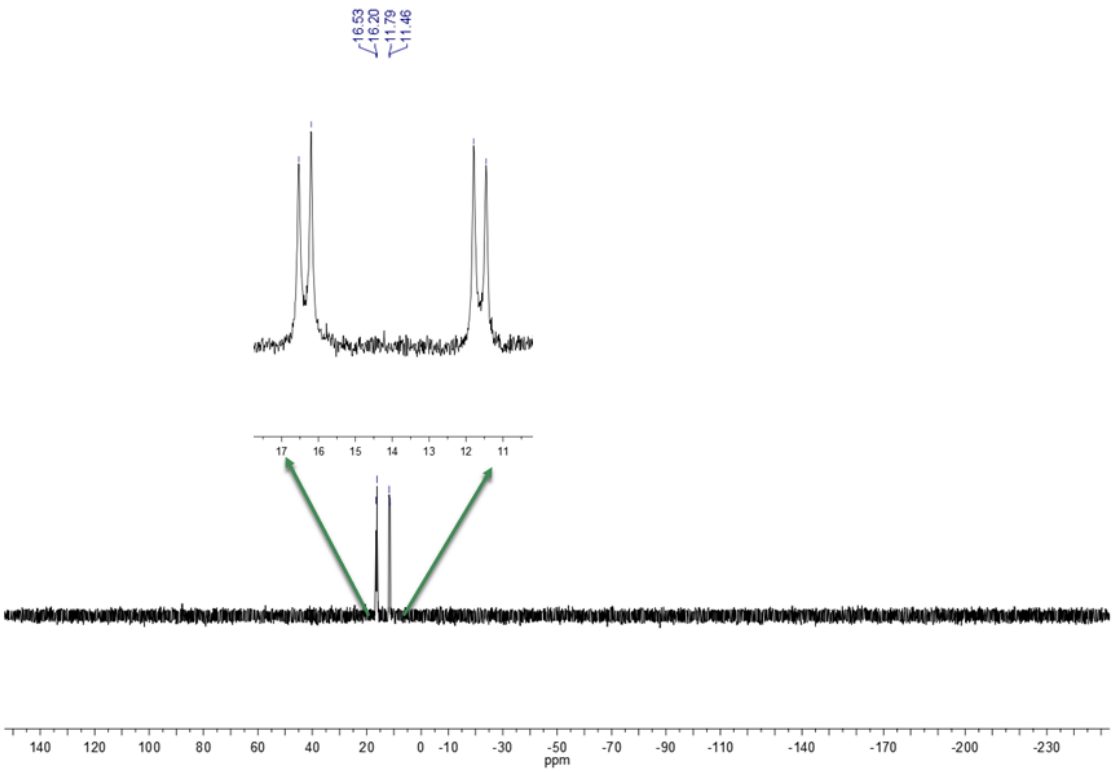


Figure S31. ^{31}P NMR spectrum of compound **4b** measured in $CDCl_3$.

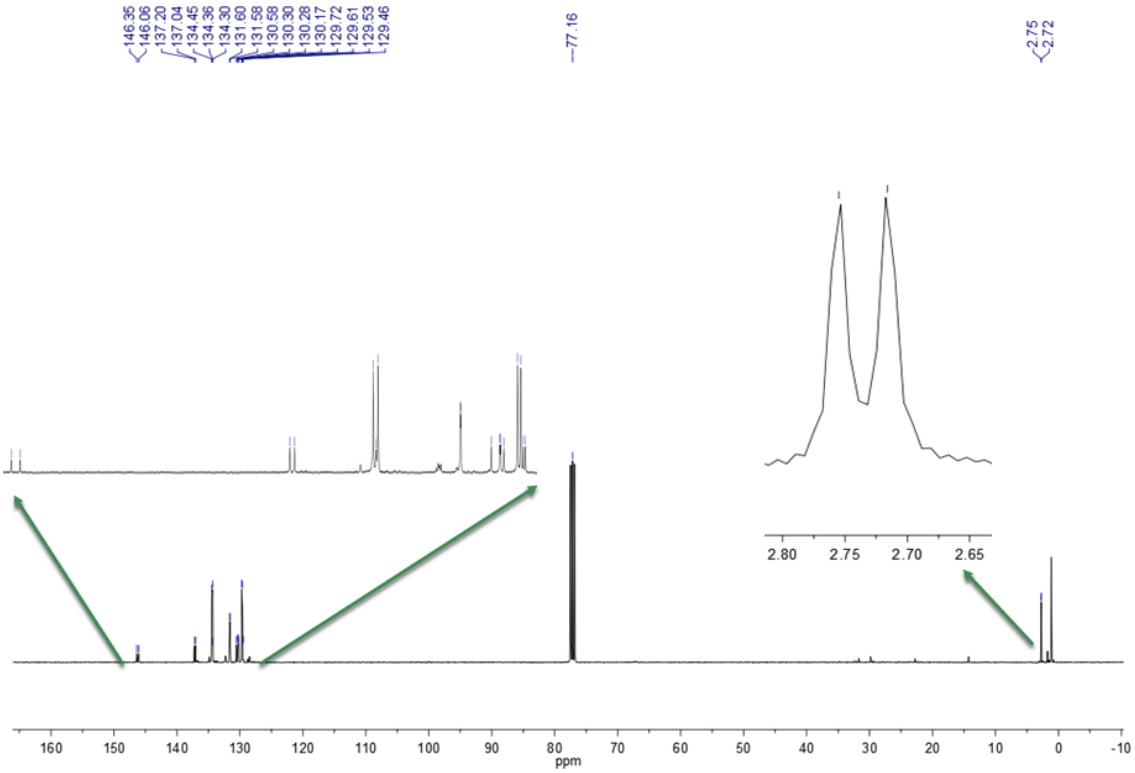


Figure S32. ^{13}C NMR spectrum of compound **4b** measured in $CDCl_3$.

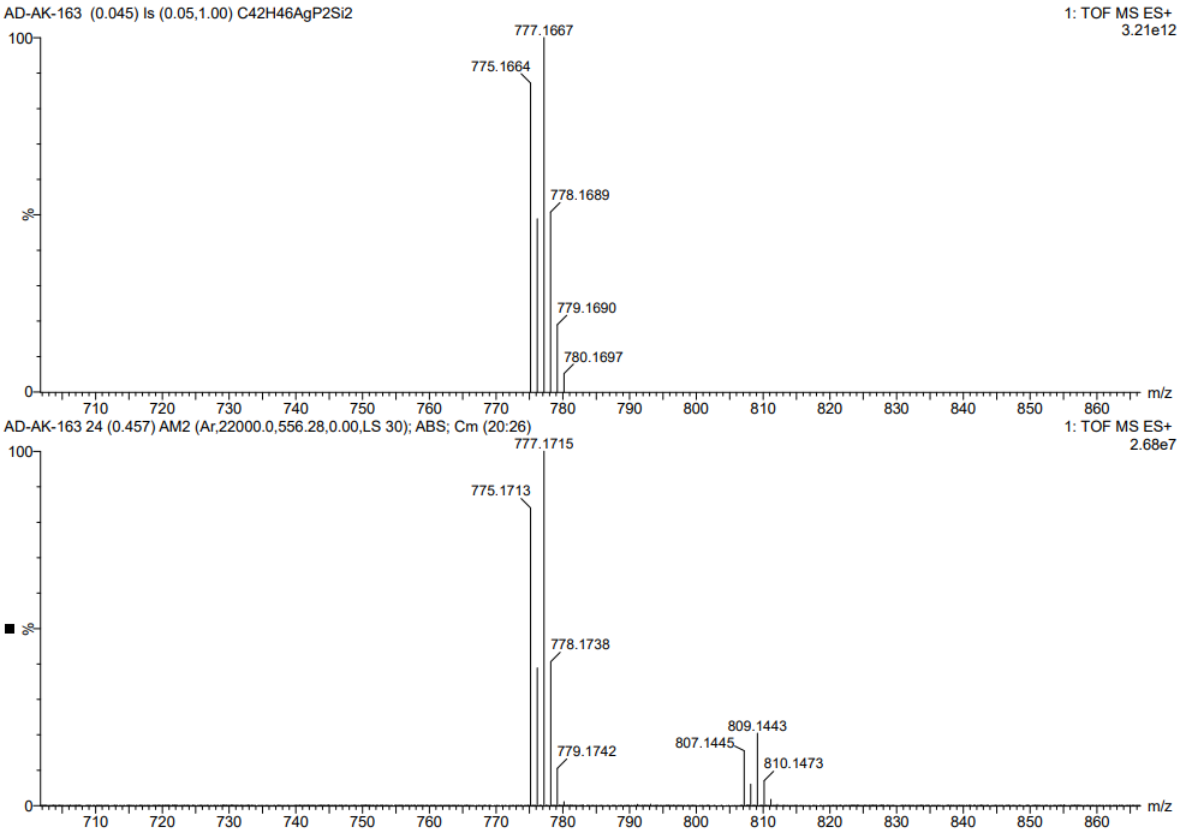


Figure S33. ESI-HRMS spectrum of compound **4b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

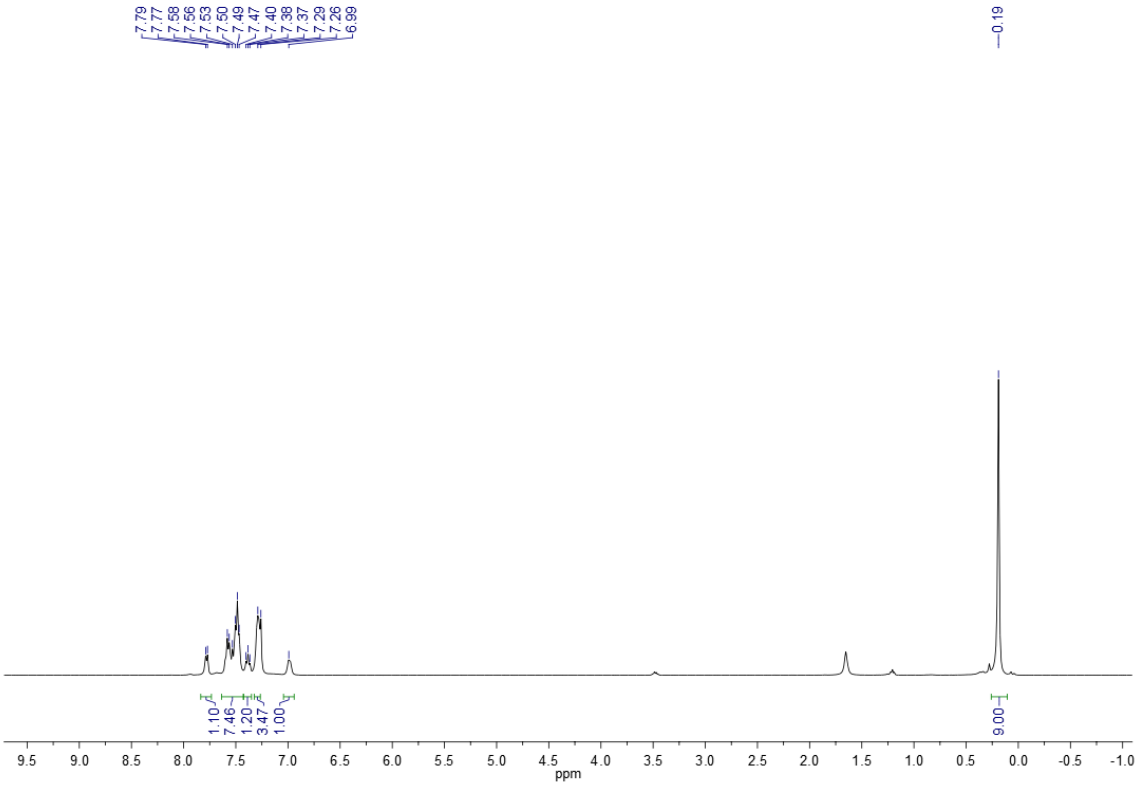


Figure S34. ^{1}H NMR spectrum of compound **4c** measured in $CDCl_3$.

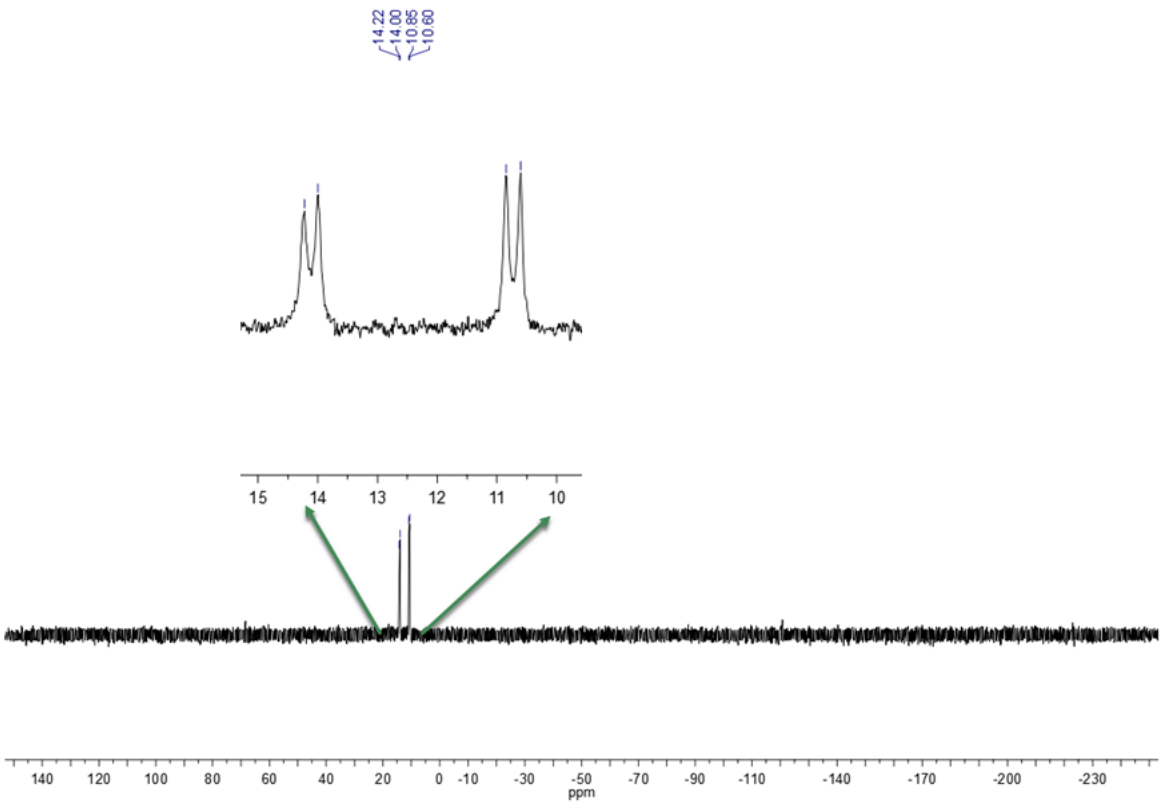


Figure S35. ^{31}P NMR spectrum of compound **4c** measured in $CDCl_3$.

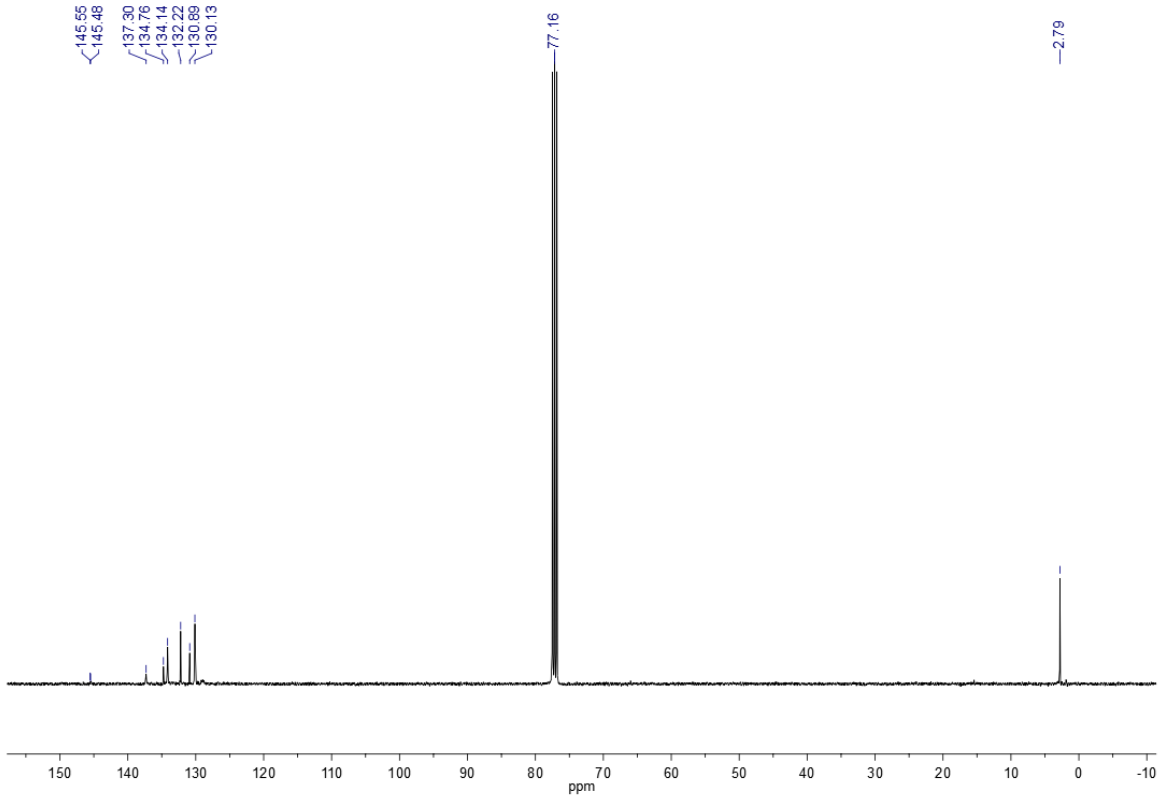


Figure S36. ^{13}C NMR spectrum of compound **4c** measured in $CDCl_3$

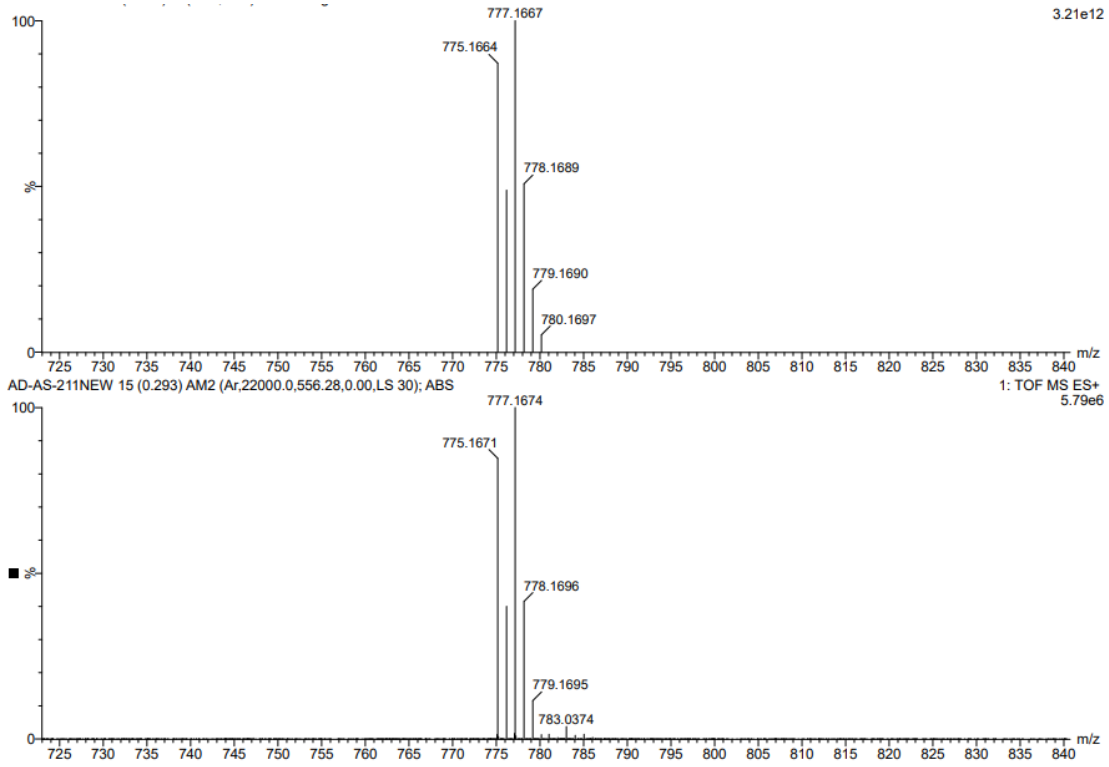


Figure S37. ESI-HRMS spectrum of compound **4c** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

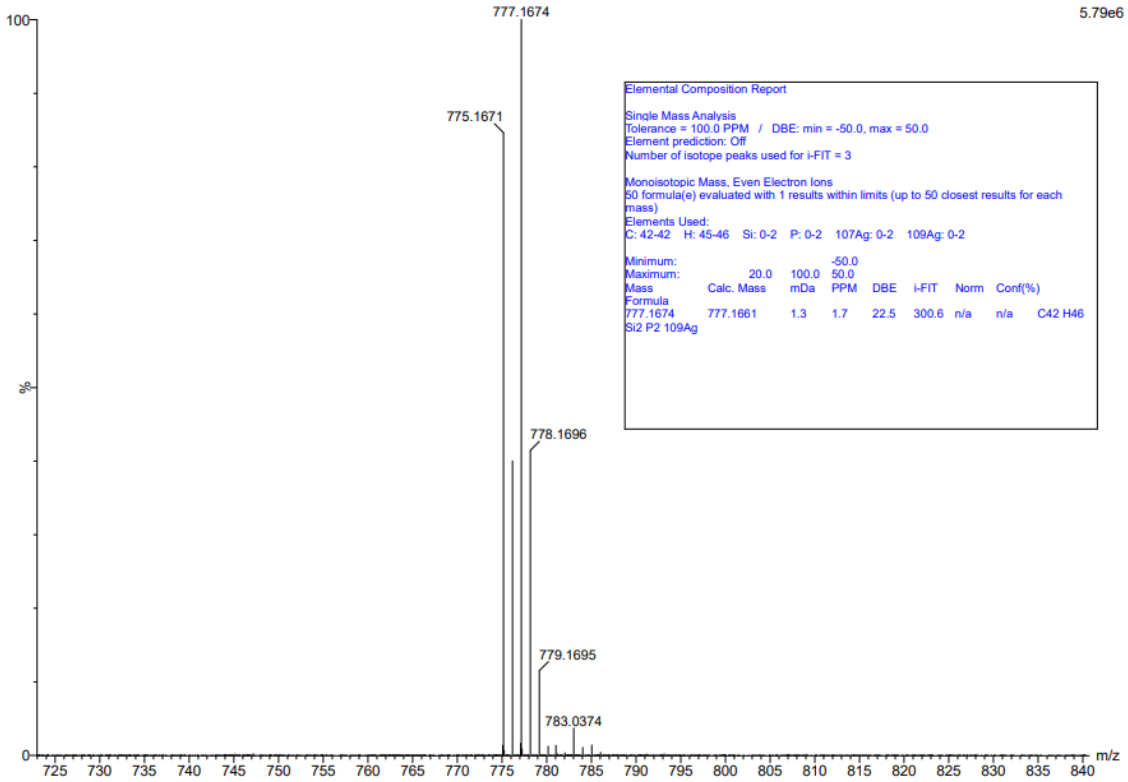


Figure S38. ESI-HRMS report of compound **4c** measured in acetonitrile.

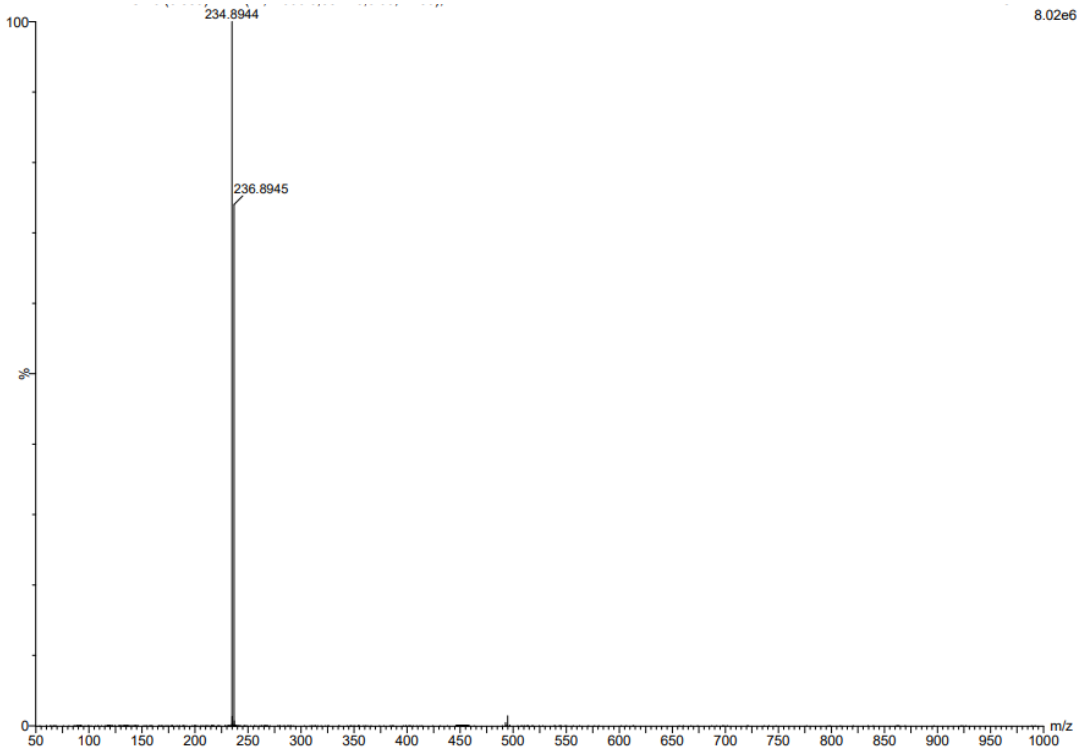


Figure S39. ESI-HRMS report of the negative region of compound **4c** showing the presence of SbF_6 counter anion measured in acetonitrile.

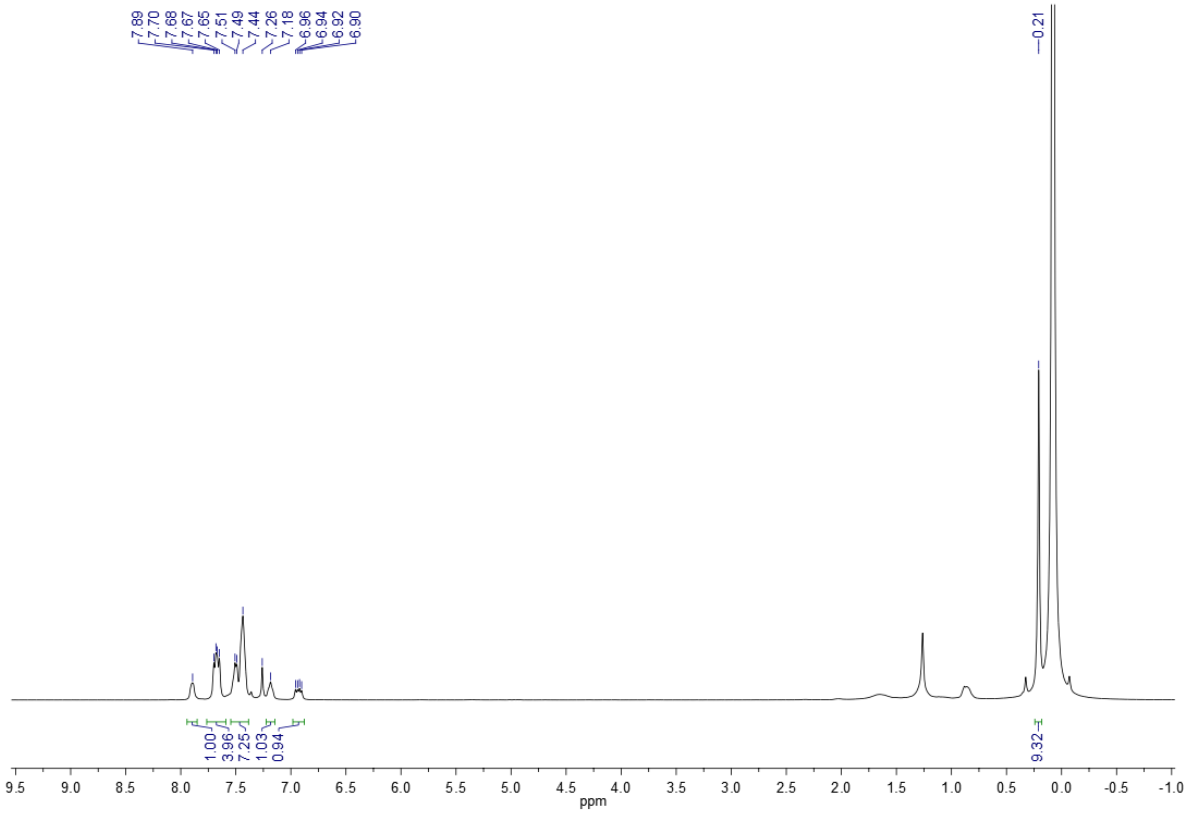


Figure S40. ^{1}H NMR spectrum of compound **5a** measured in $CDCl_3$.

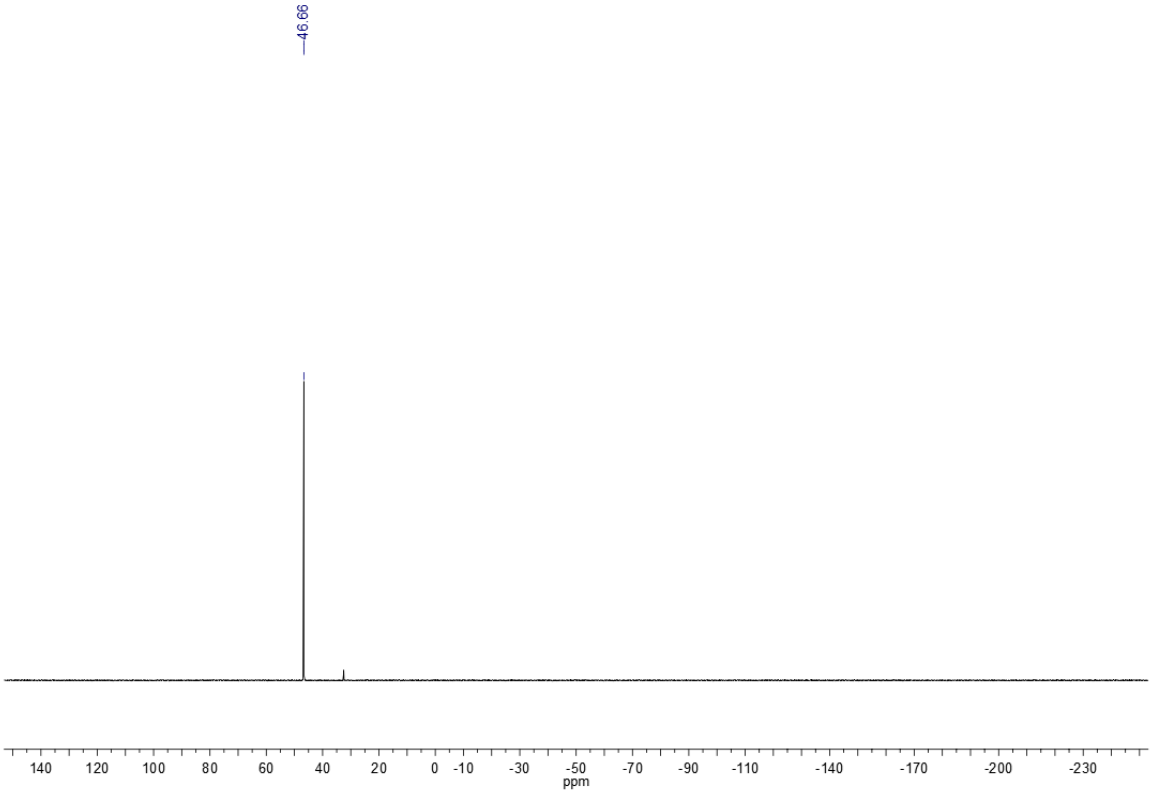


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5a** measured in $CDCl_3$.

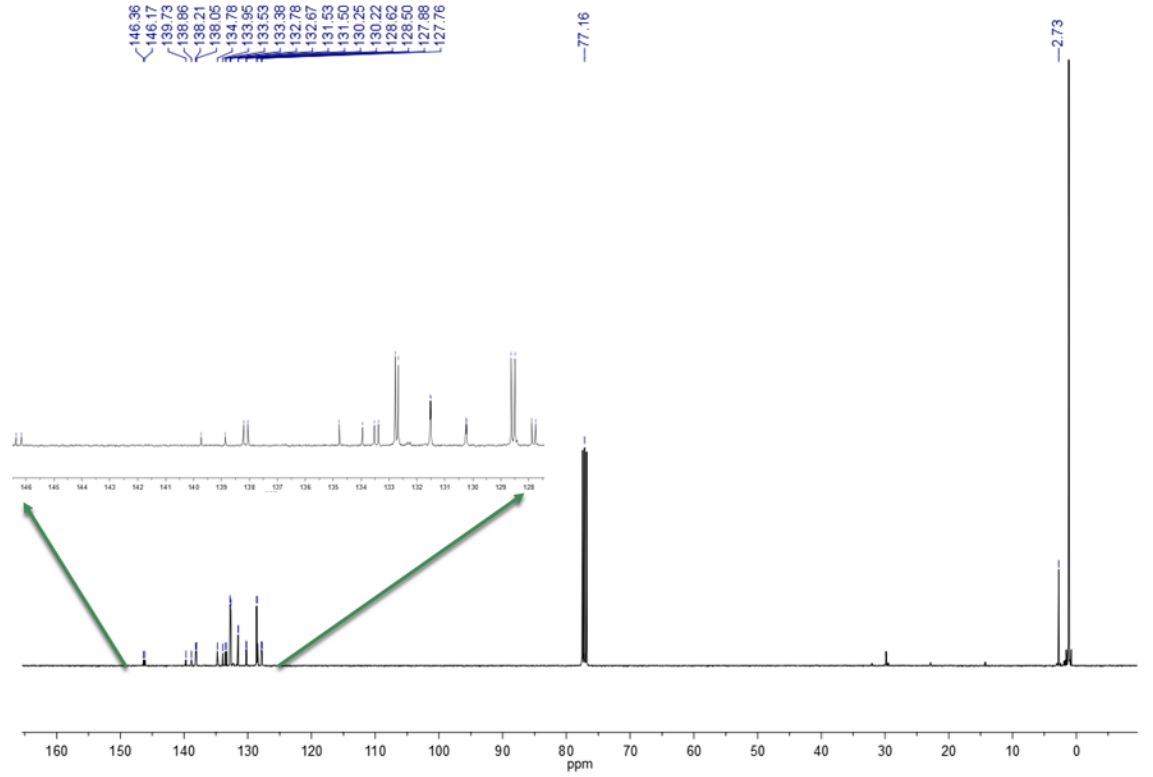


Figure S42. ^{13}C NMR spectrum of compound **5a** measured in $CDCl_3$.

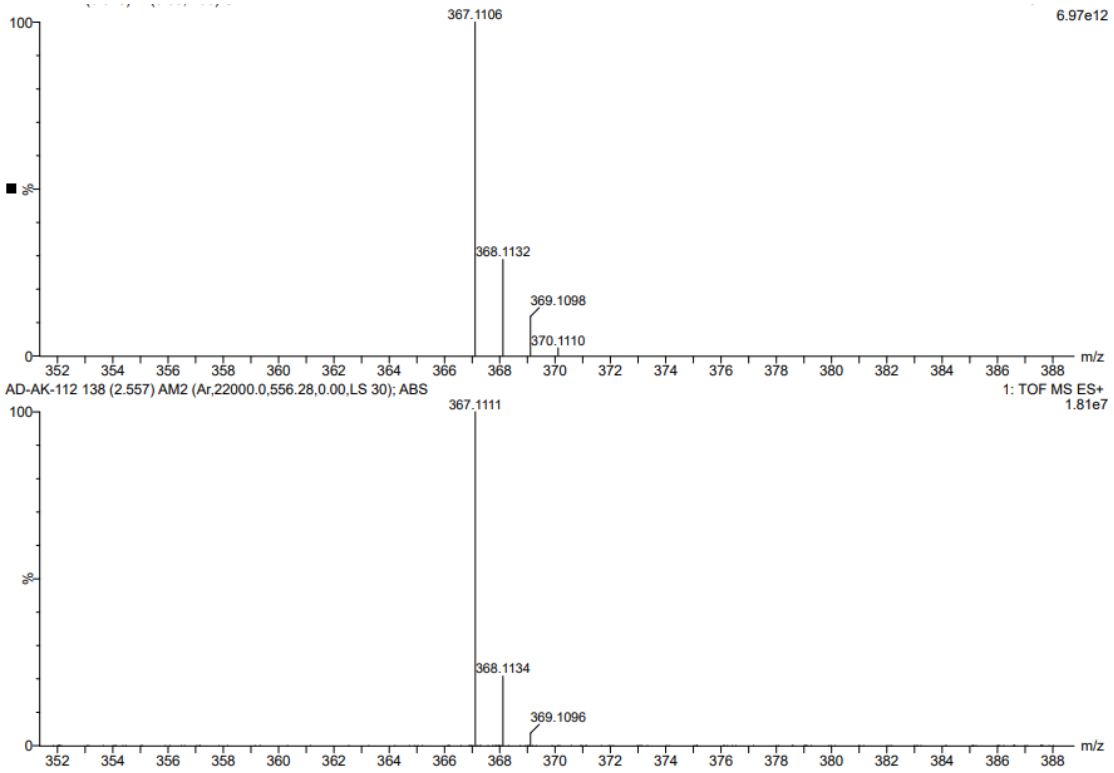


Figure S43. ESI-HRMS spectrum of compound **5a** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

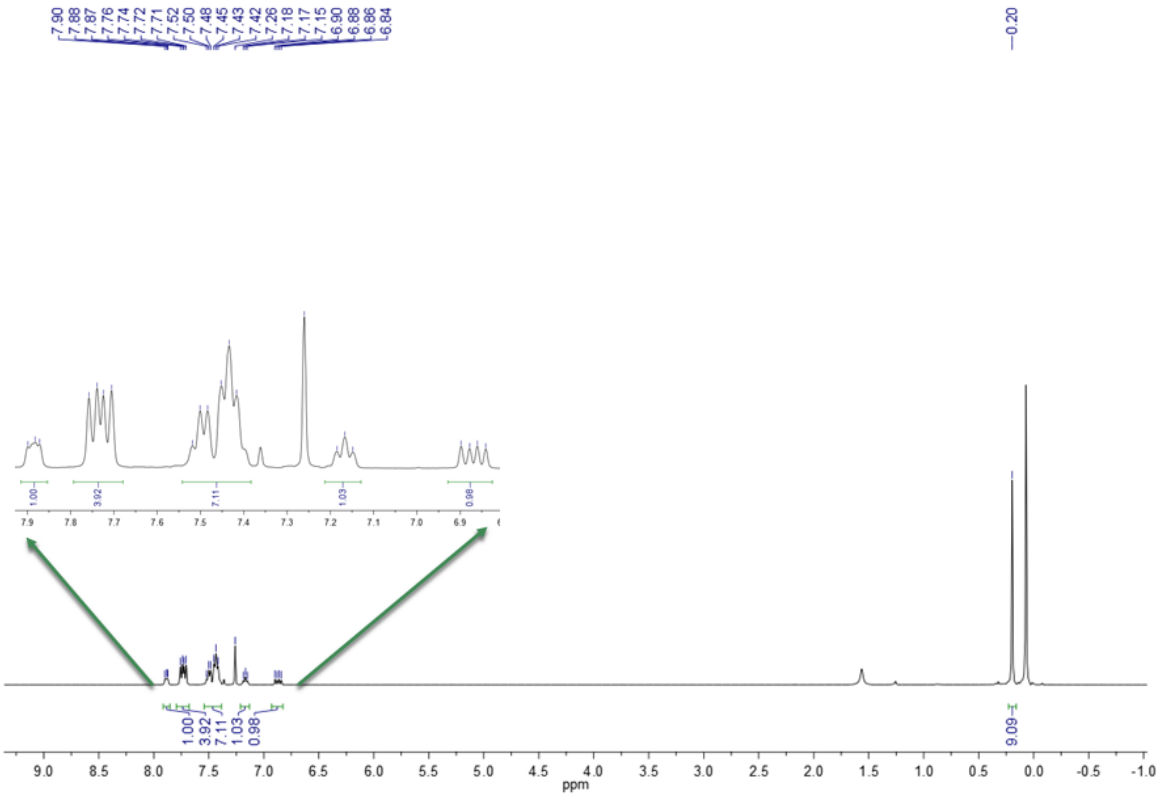


Figure S44. ^{1}H NMR spectrum of compound **5b** measured in $CDCl_3$.

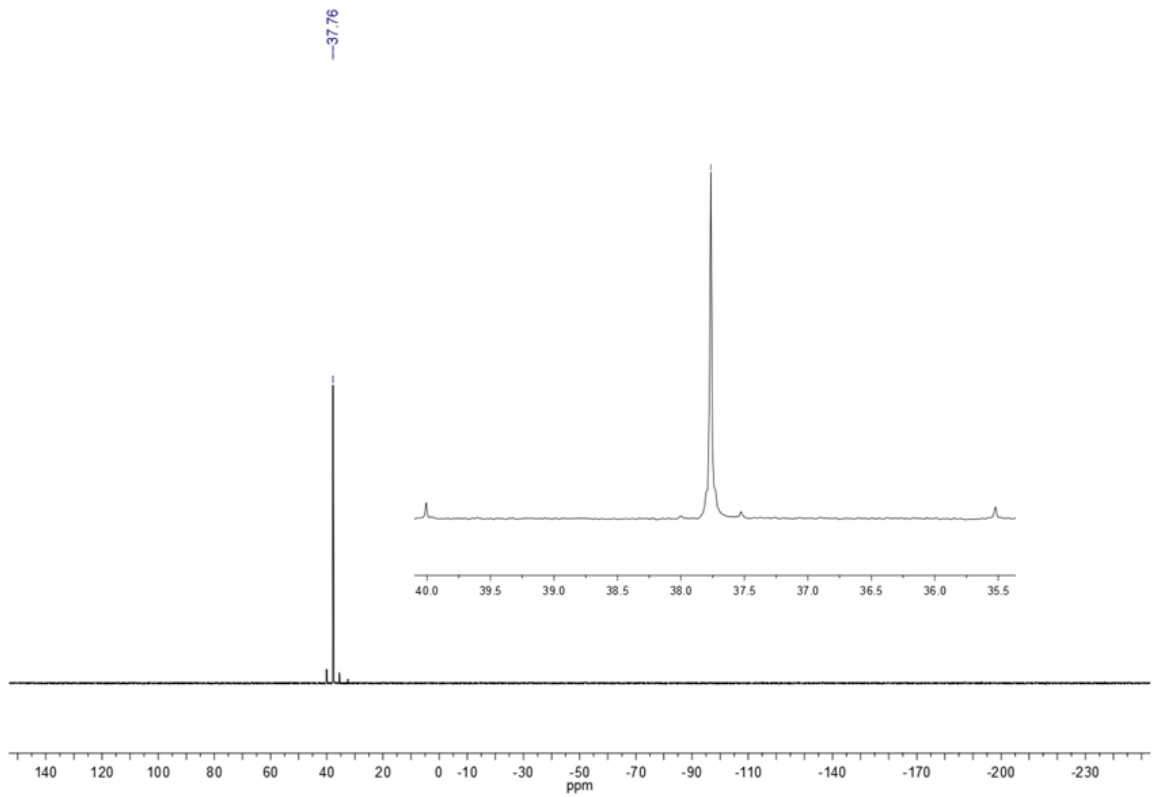


Figure S45. ^{31}P NMR spectrum of compound **5b** measured in $CDCl_3$.

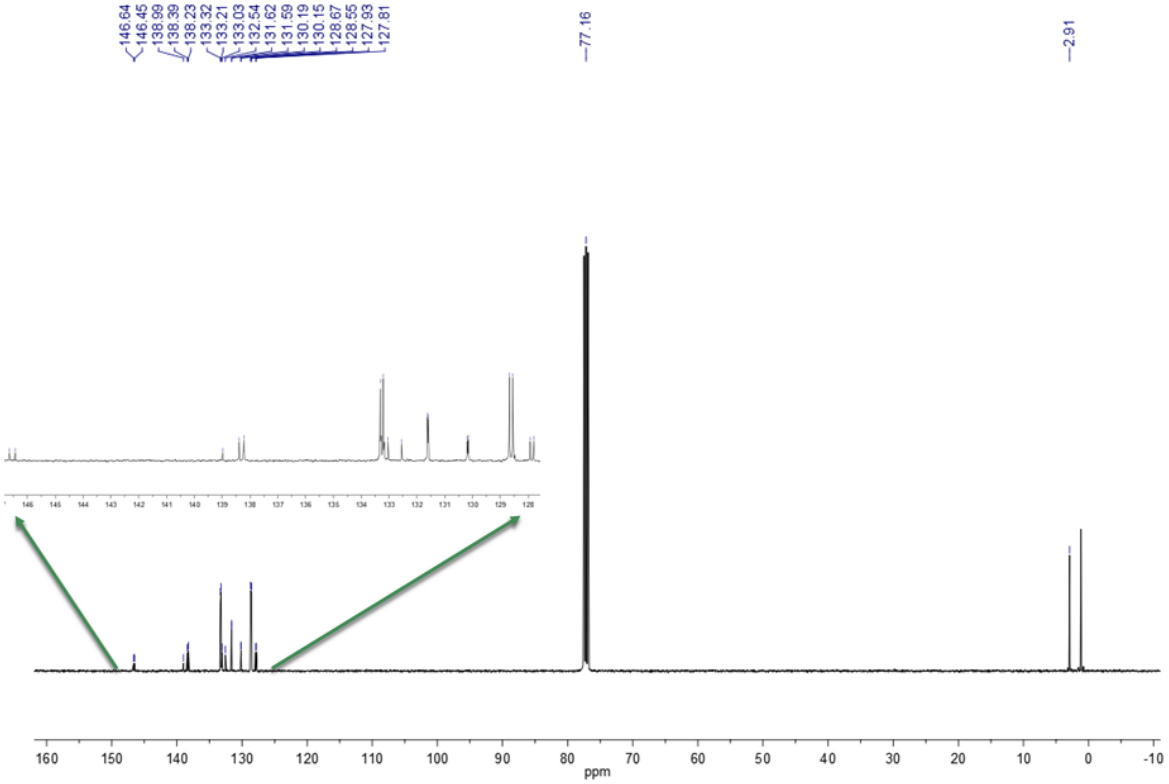


Figure S46. ^{13}C NMR spectrum of compound **5b** measured in $CDCl_3$.

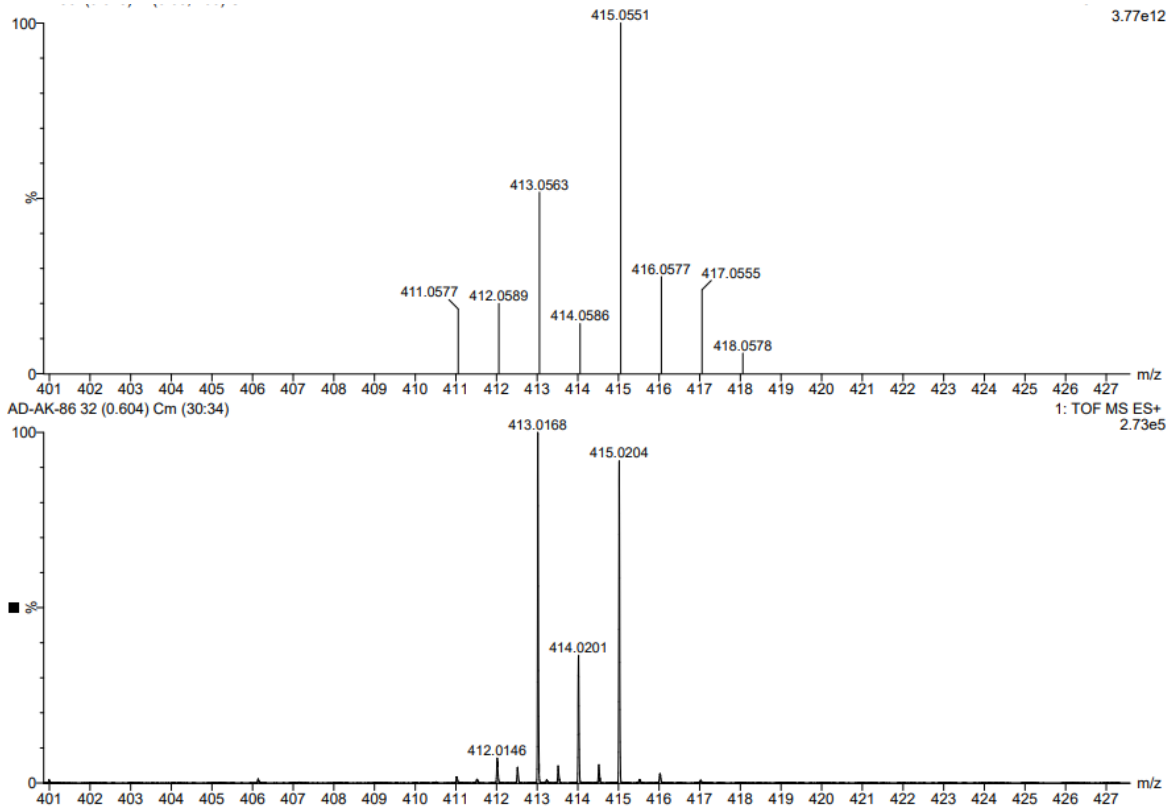


Figure S47. ESI-HRMS spectrum of compound **5b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

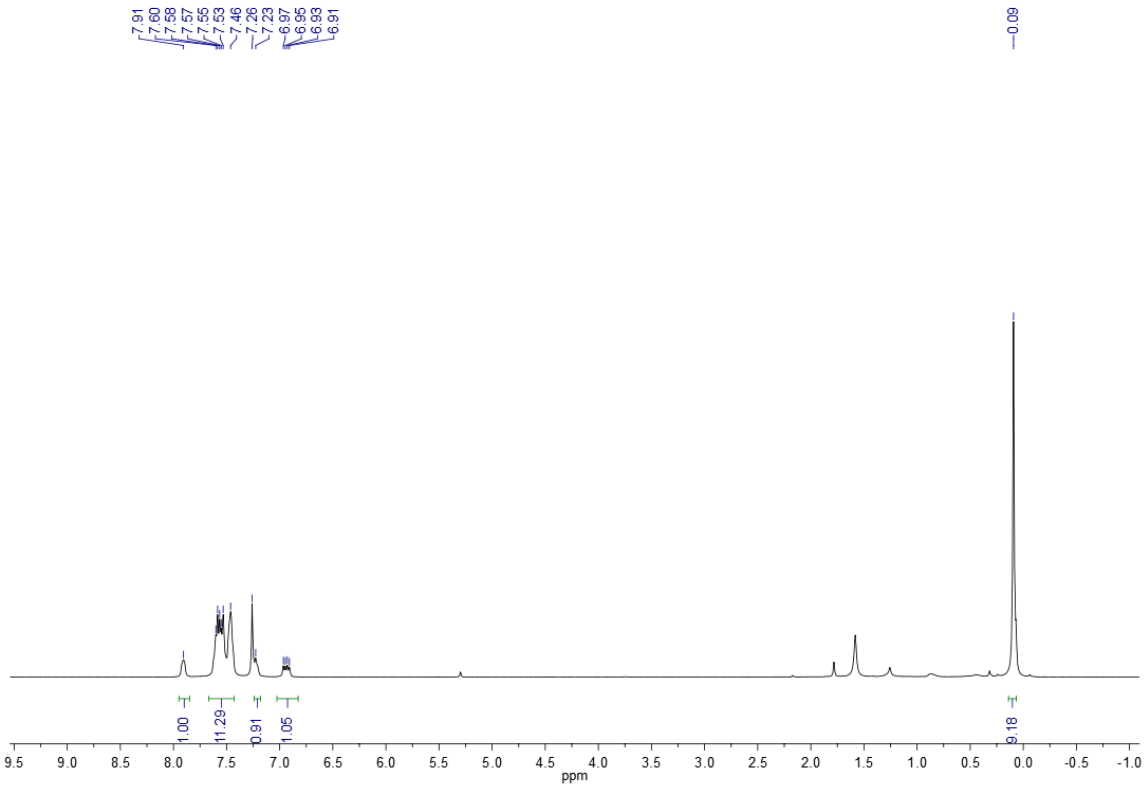


Figure S48. ^{1}H NMR spectrum of compound **6a** measured in $CDCl_3$.

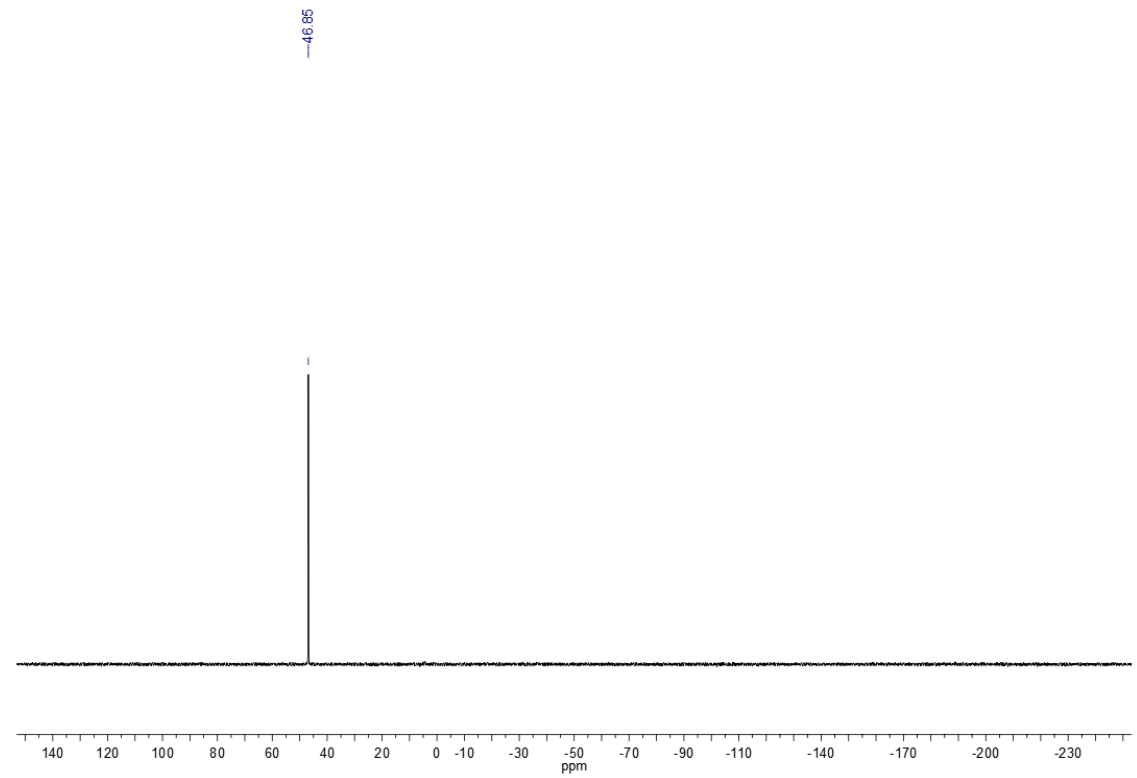


Figure S49. ^{31}P NMR spectrum of compound **6a** measured in $CDCl_3$.

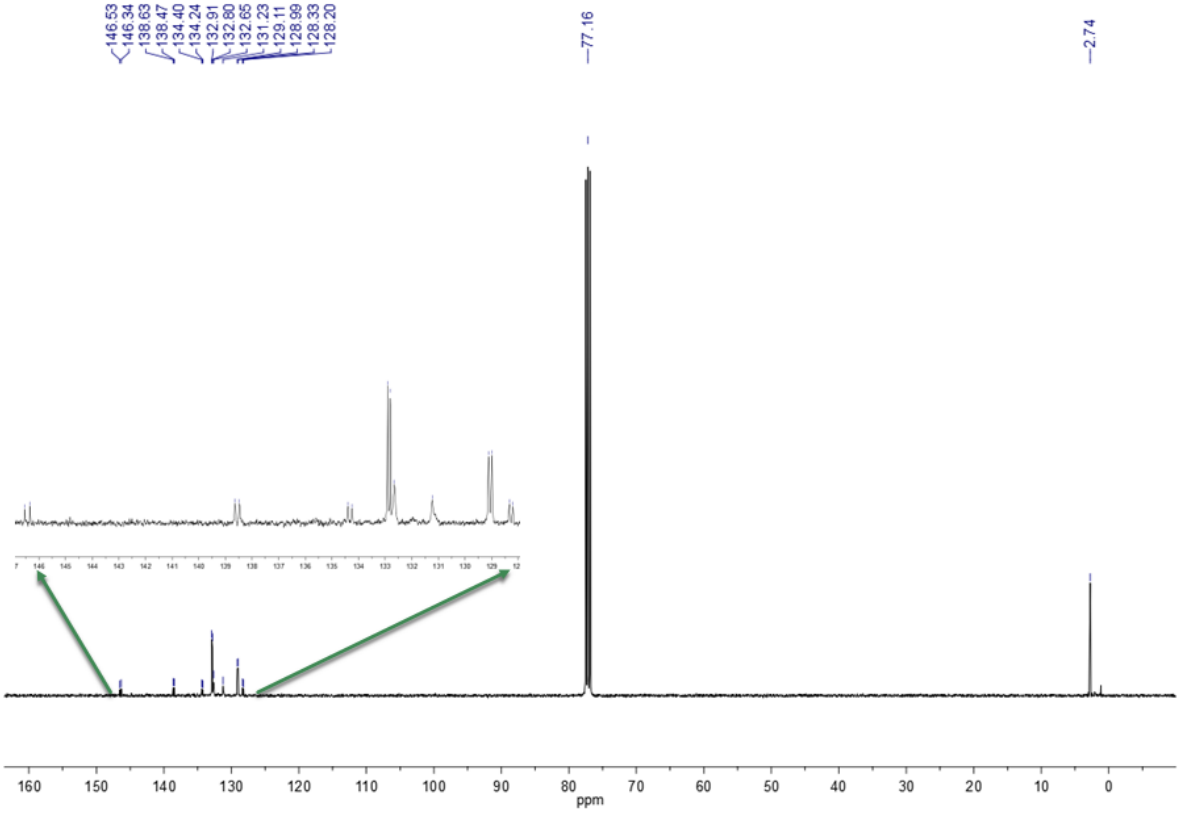


Figure S50. ^{13}C NMR spectrum of compound **6a** measured in $CDCl_3$.

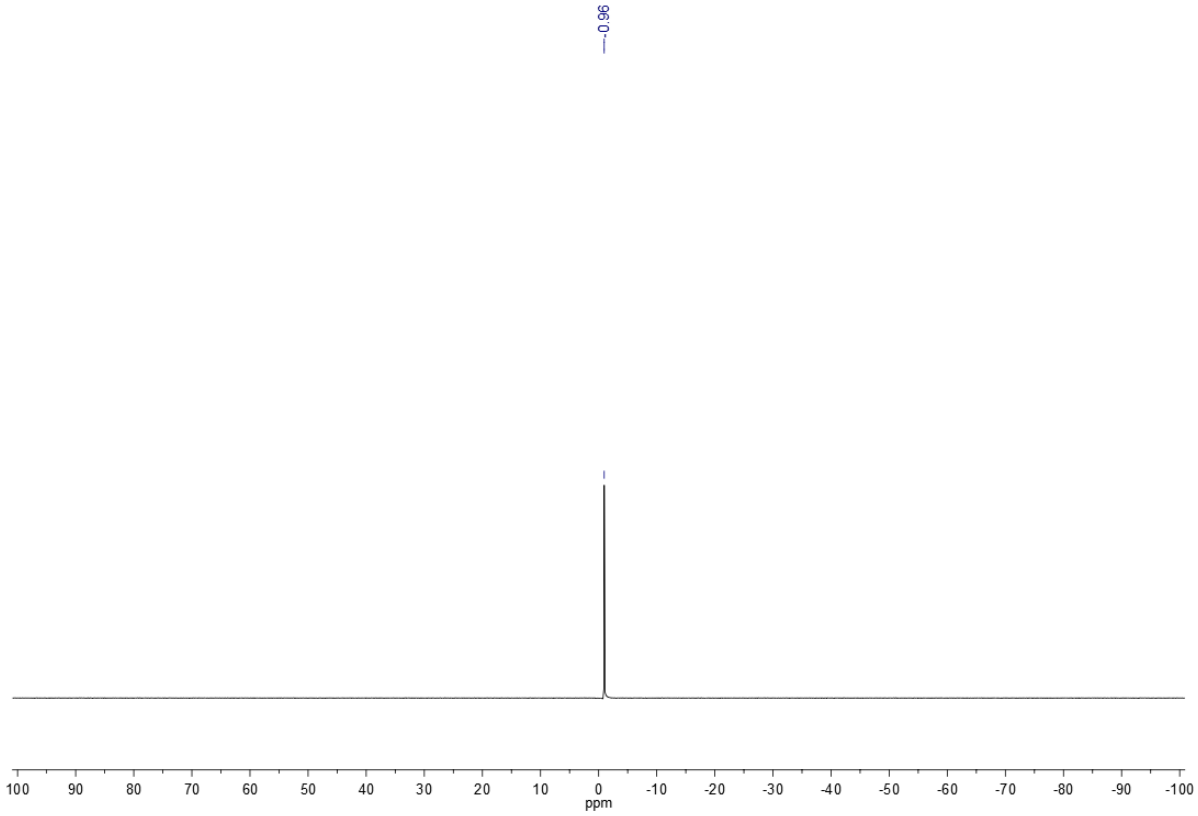


Figure S51. ^{11}B NMR spectrum of compound **6a** measured in $CDCl_3$.

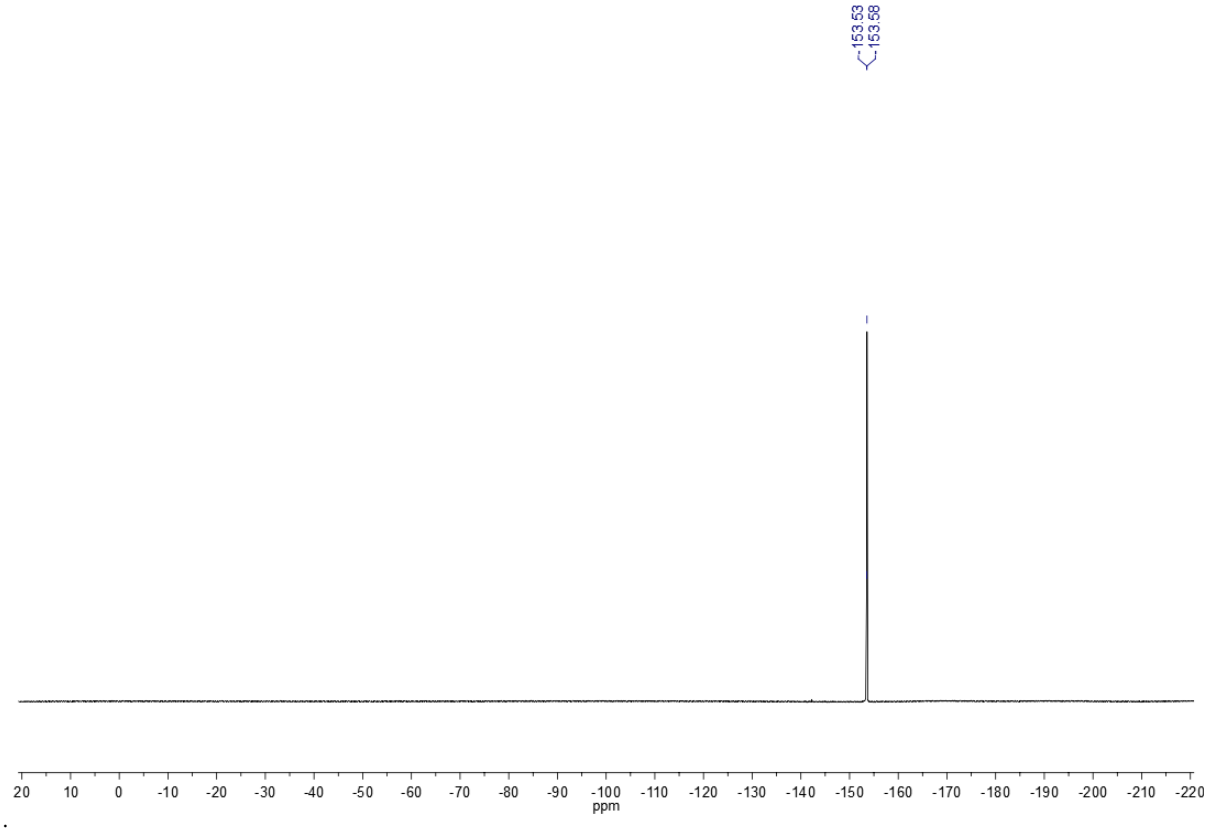


Figure S52. ^{19}F NMR spectrum of compound **6a** measured in $CDCl_3$.

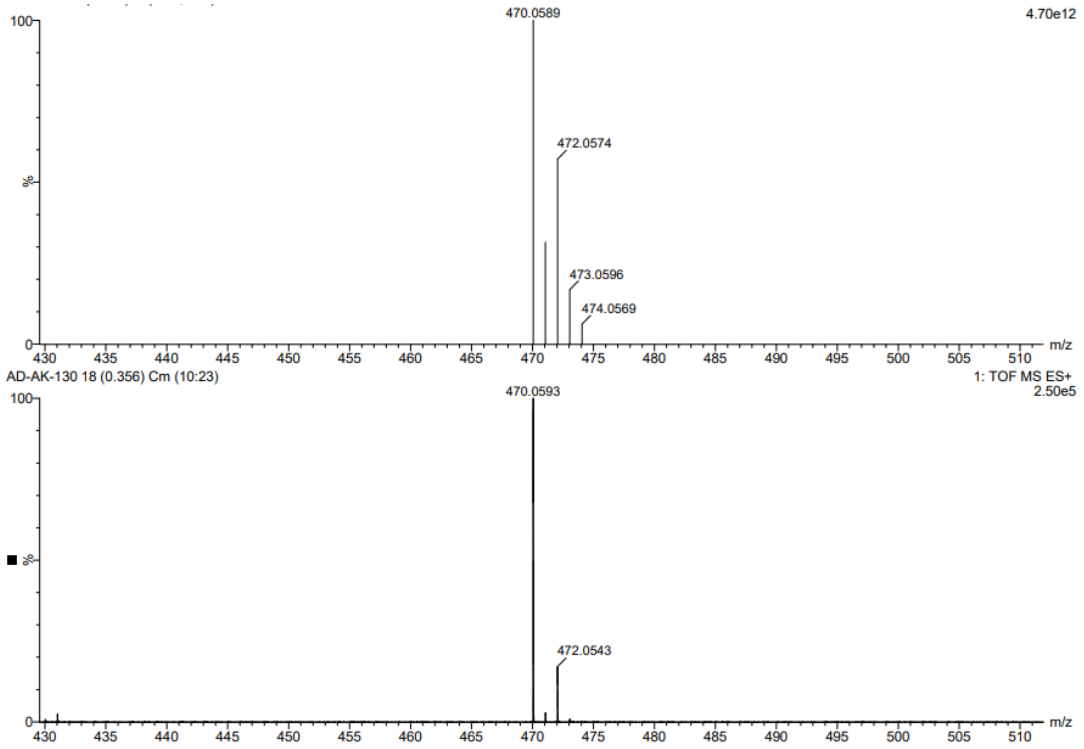


Figure S53. ESI-HRMS spectrum of compound **6a** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

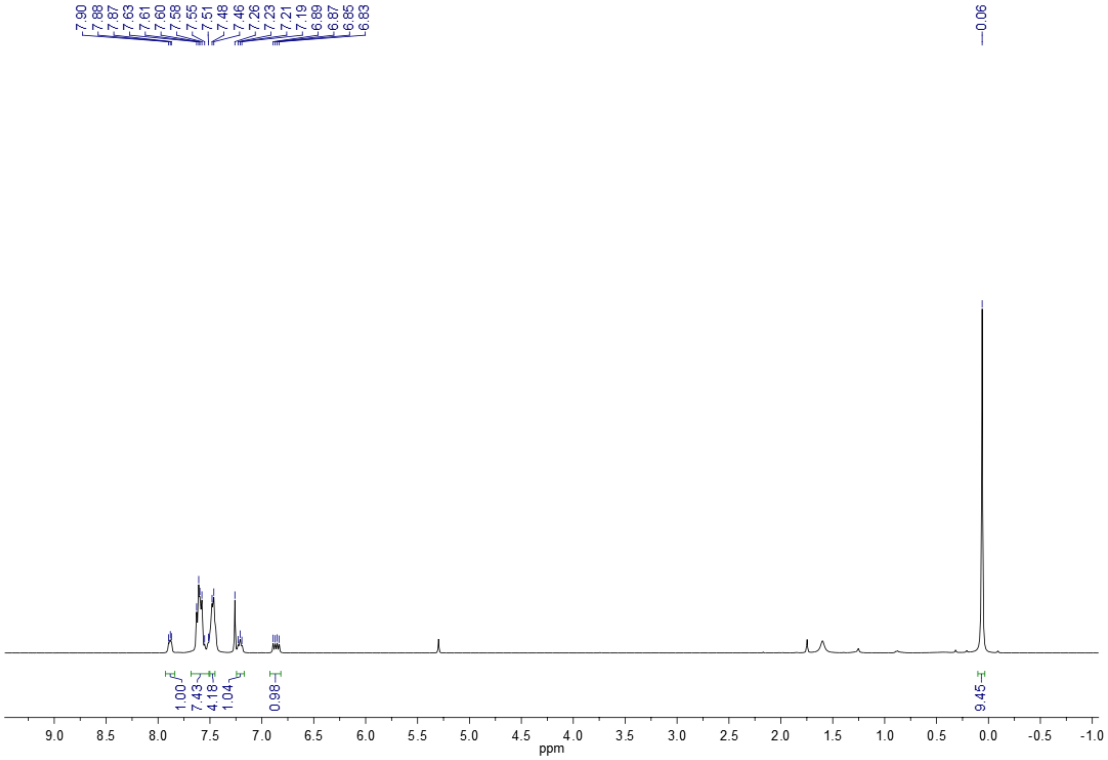


Figure S54. ^{1}H NMR spectrum of compound **6b** measured in $CDCl_3$.

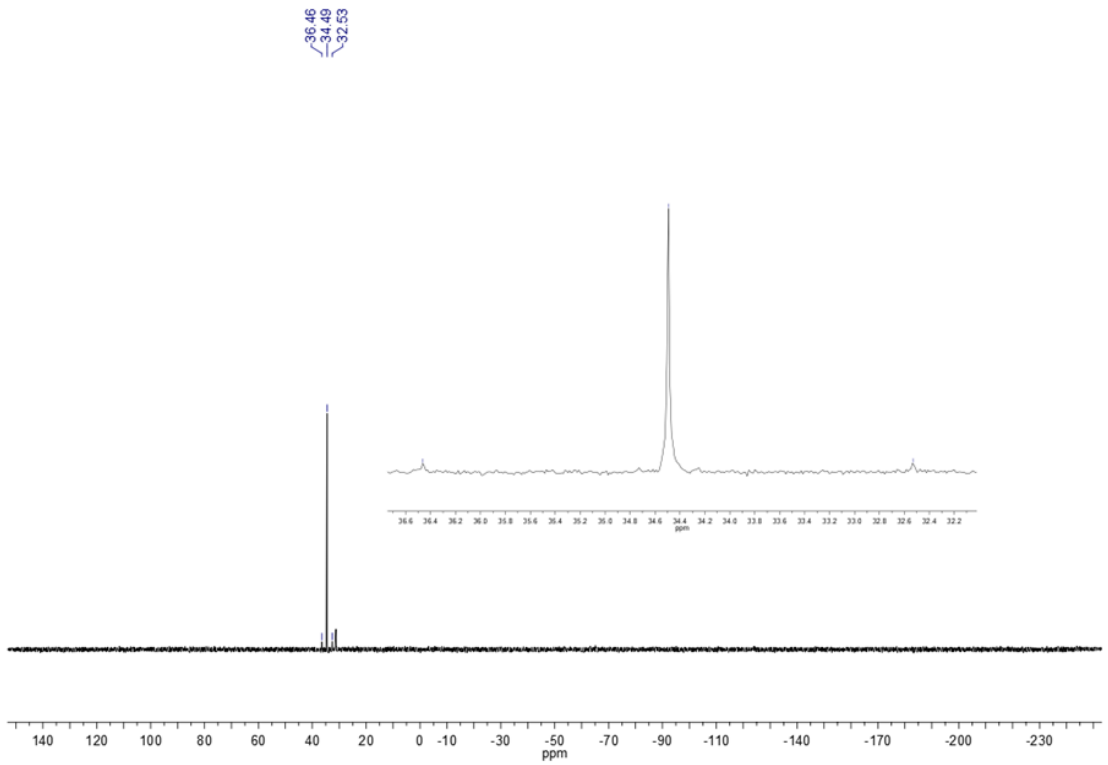


Figure S55. ^{31}P NMR spectrum of compound **6b** measured in $CDCl_3$.

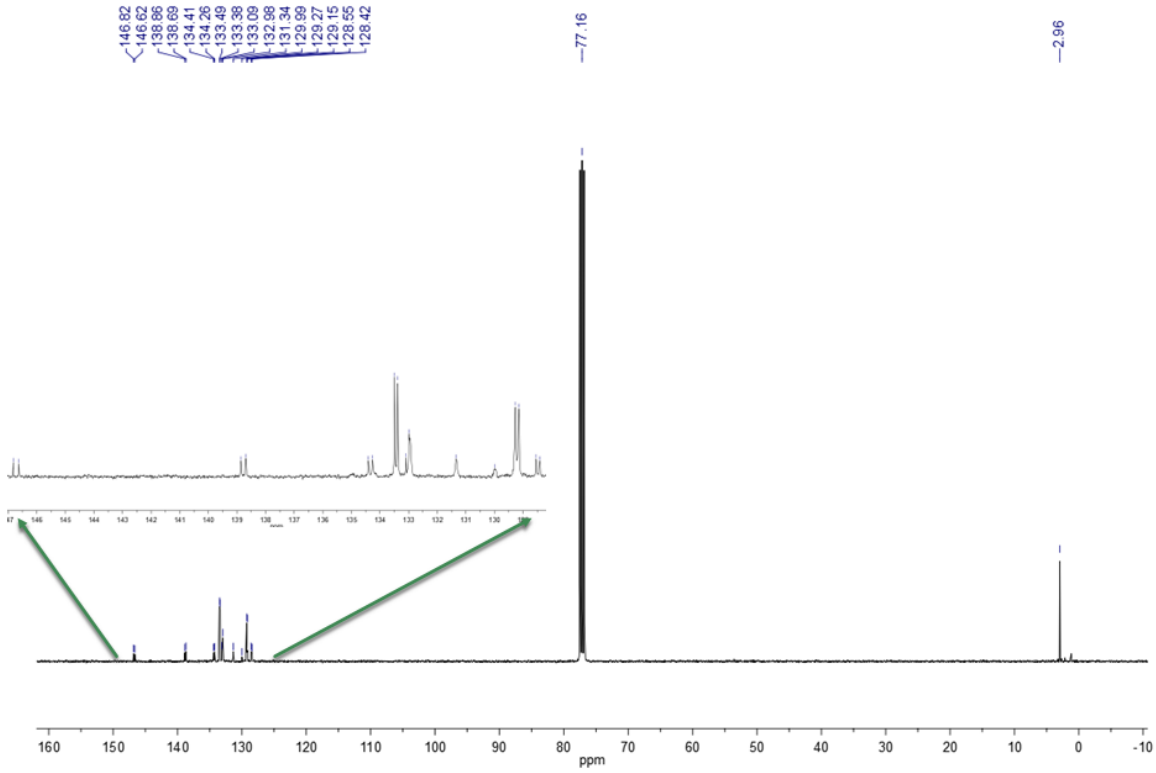


Figure S56. ^{13}C NMR spectrum of compound **6b** measured in $CDCl_3$.

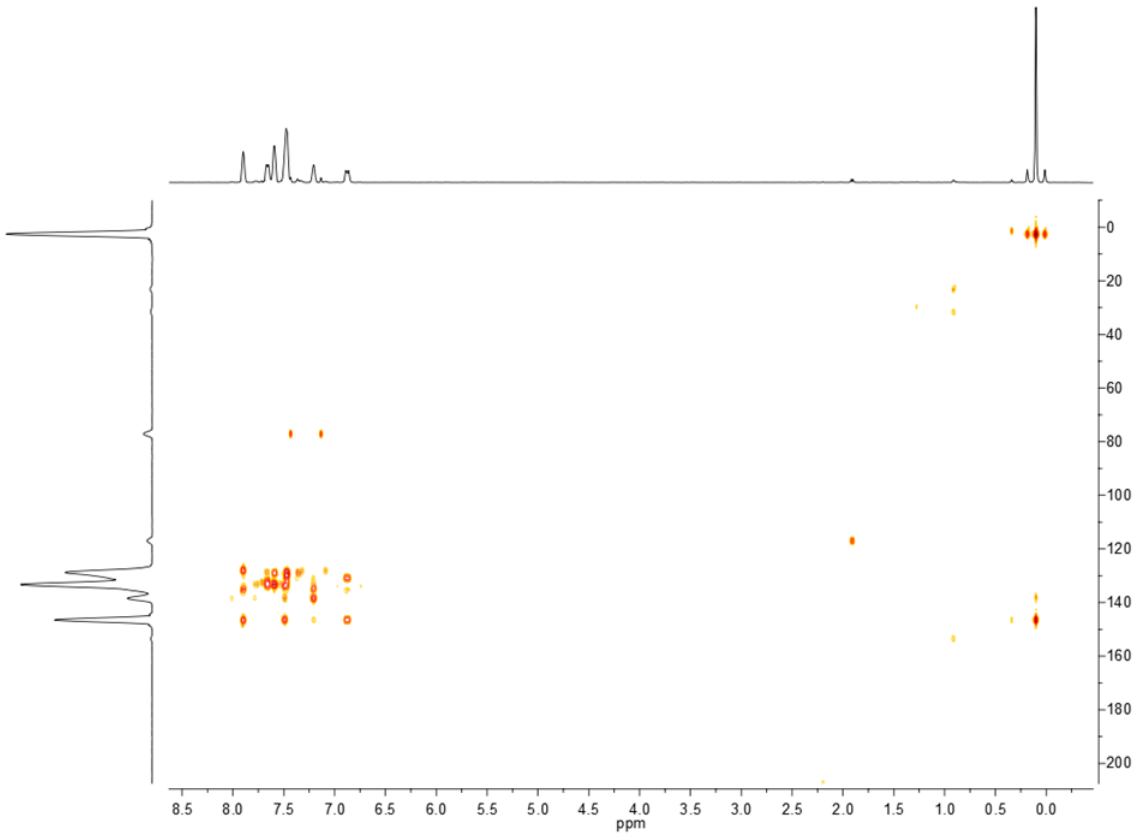


Figure S57. The HSQC spectrum of [(**5b**)$_3$Cu]BF$_4$ (**6b**) measured in CDCl$_3$.

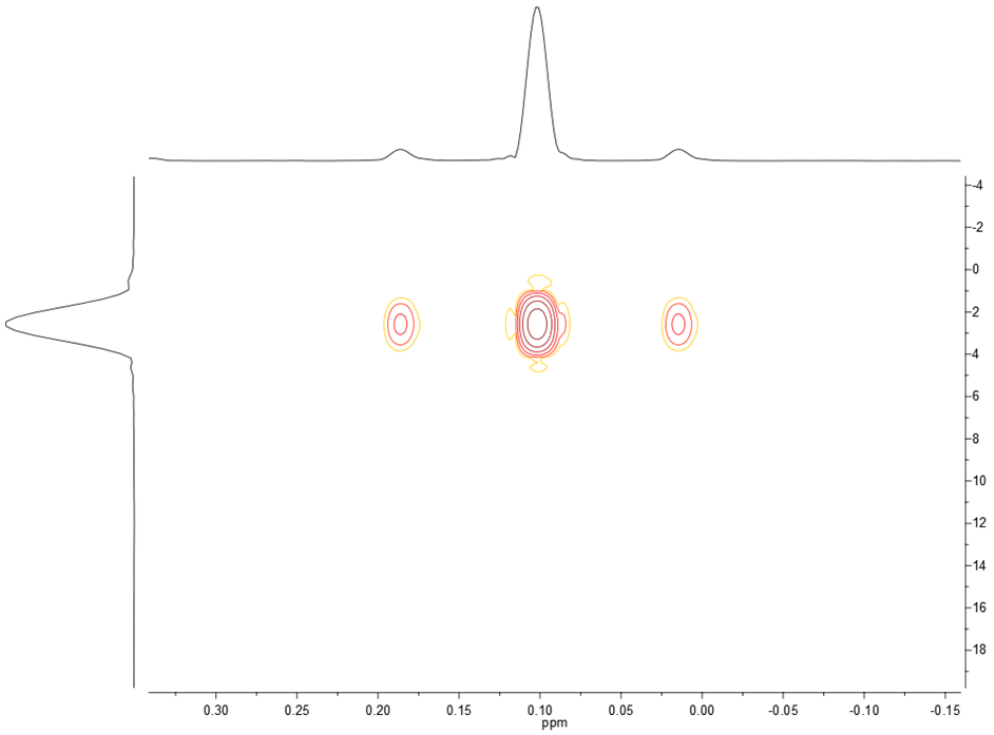


Figure S58. The HSQC (expanded region) spectrum of [(**5b**)$_3$Cu]BF$_4$ (**6b**); shows the correlation of SiMe$_3$ groups in the ligand part of the complex.

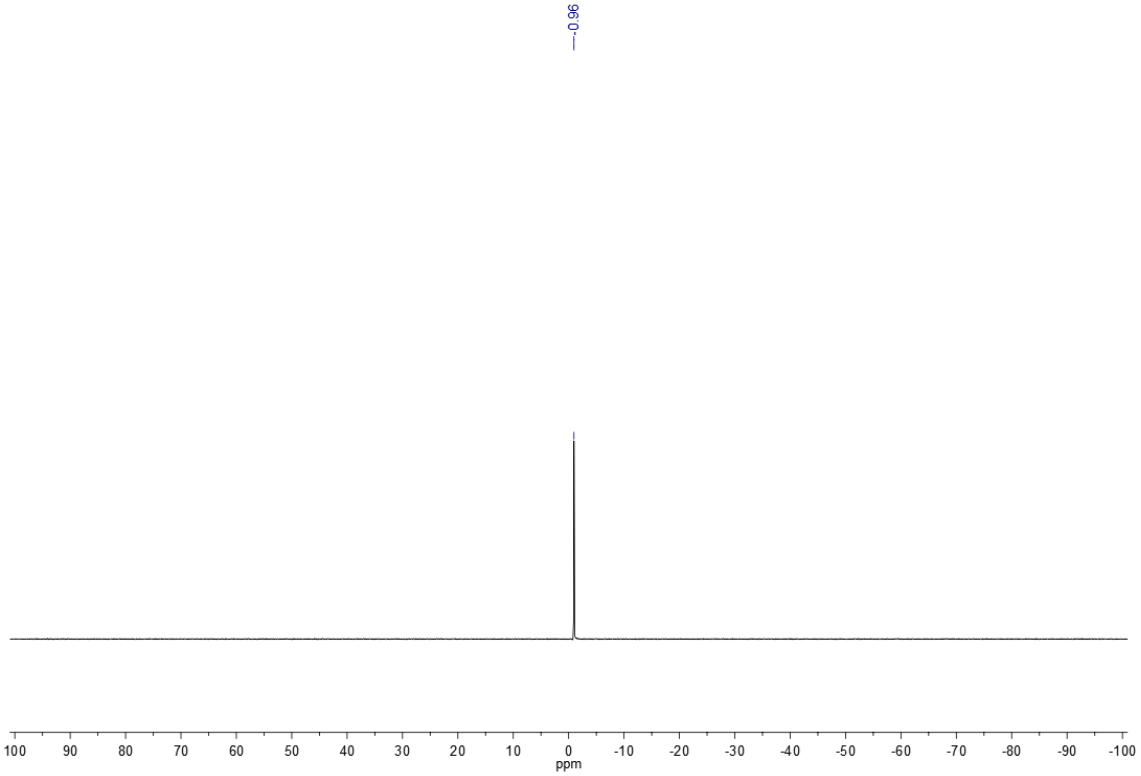


Figure S59. ^{11}B NMR spectrum of compound **6b** measured in $CDCl_3$.

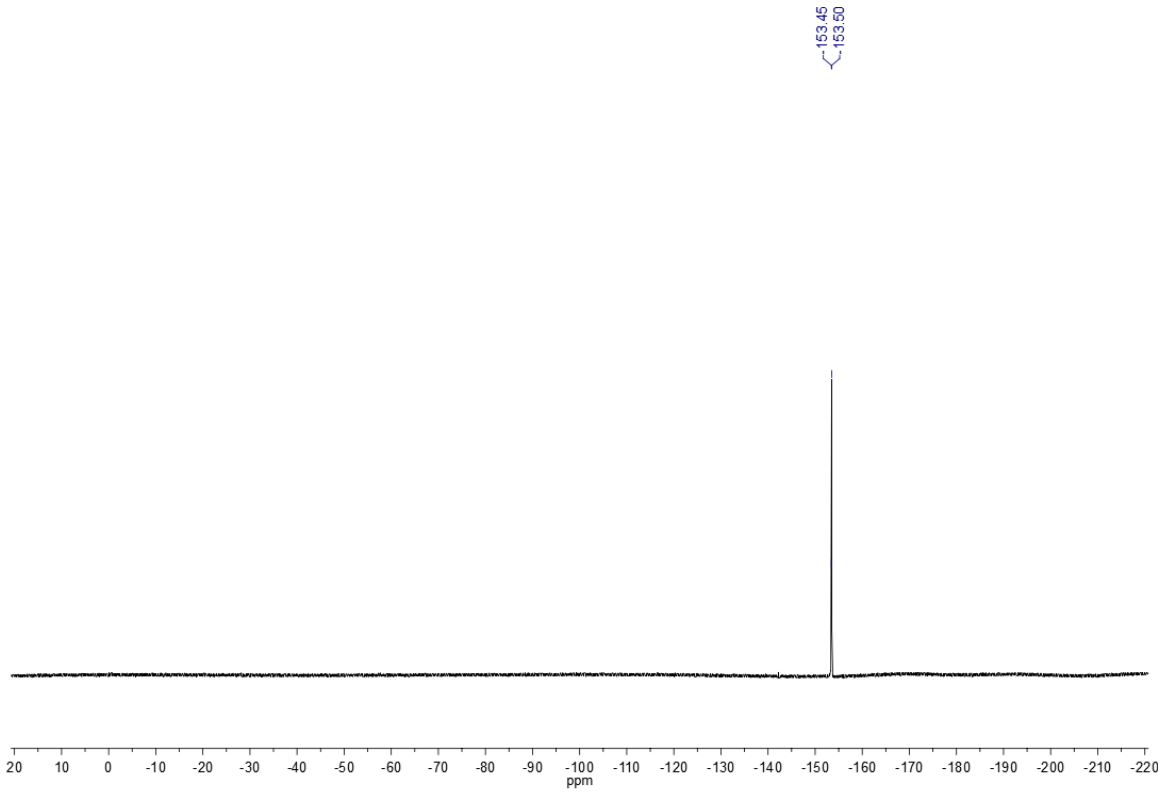


Figure S60. ^{19}F NMR spectrum of compound **6b** measured in $CDCl_3$.

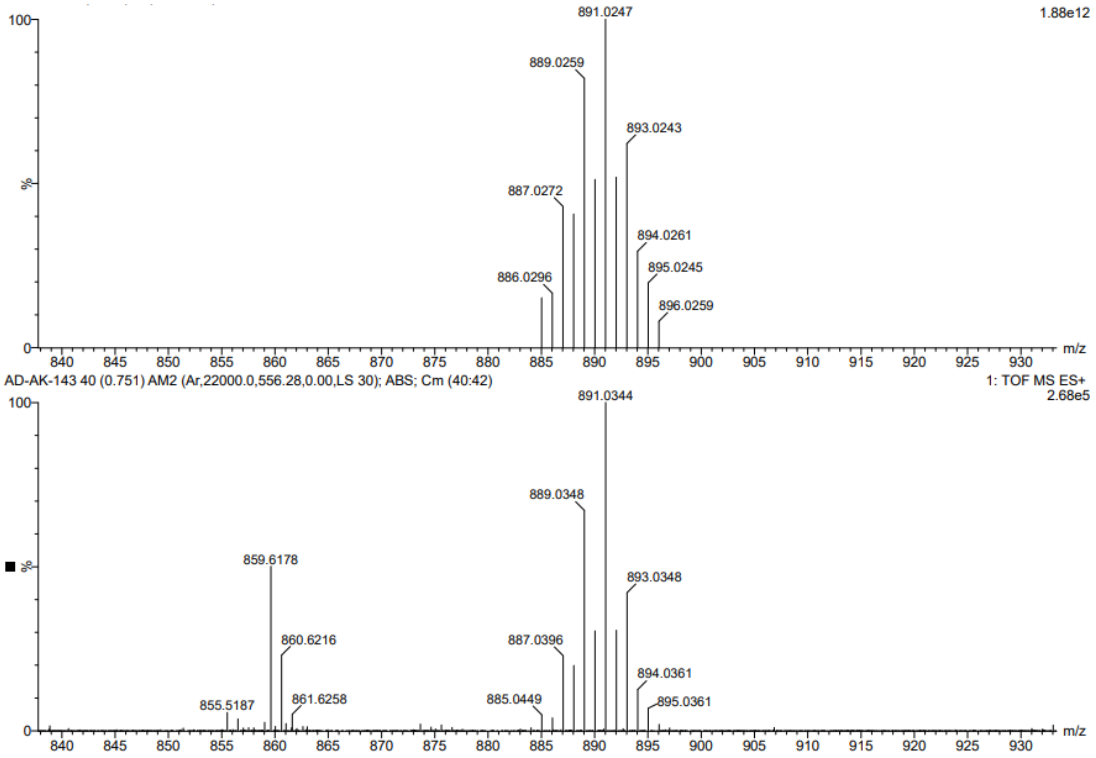
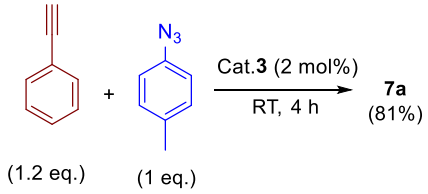
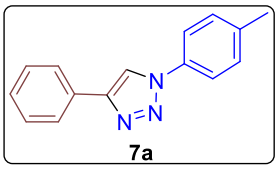


Figure S61. ESI-HRMS spectrum of compound **6b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

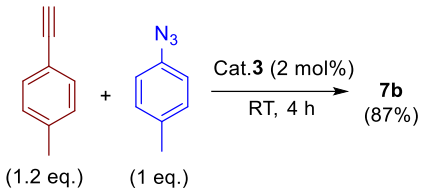
Preparation of triazole (7a)[2]



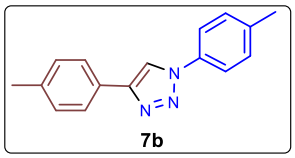
7a was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (28.6 mg, 81%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.16 (s, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.32 (m, 3H), and 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 148., 139.1, 134.9, 130.4, 129.1, 128.5, 125.98, 120.6, 117.8, and 21.3 (CH_3) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{15}H_{14}N_3$: 236.1188; found 236.1129.



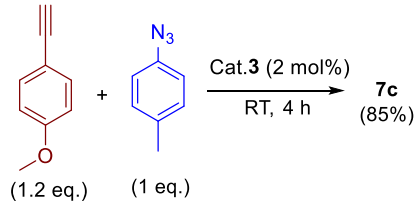
Preparation of triazole (7b)[3]



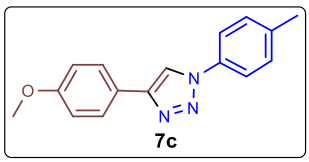
7b was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (65 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.11 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 2.44 (s, 3H, CH_3-tolyl azide), and 2.40 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 148.5, 138.9, 138.4, 135.0, 130.4, 129.7, 127.7, 125.9, 120.6, 117.4, 21.5 (*C*H_3), and 21.3 (*C*H_3) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{16}H_{16}N_3$: 250.1344; found 250.1307.



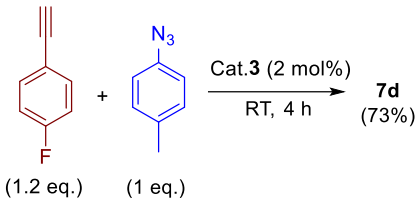
Preparation of triazole (7c)[4]



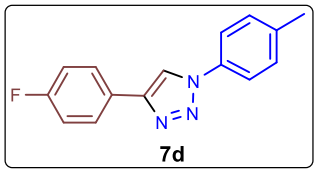
7c was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (67.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.15 (s, 1H), 7.85 (s, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.00 (d, *J* = 5.5 Hz, 2H), 3.86 (s, 3H, OCH_3), and 2.43 (s, 3H, CH_3-tolyl) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 159.9, 138.9, 135.1, 130.4, 127.3, 123.2, 120.6, 114.5, 55.5 (O*C*H_3), and 21.3 (*C*H_3-tolyl) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{16}H_{16}N_3O$: 266.1293; found 266.1263.



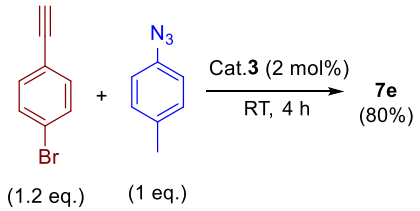
Preparation of triazole (7d)[5]



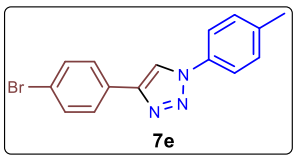
7d was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (55 mg, 73%). 1H NMR (400 MHz, $CDCl_3$); δ = 8.22 (s, 1H), 7.90 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), and 2.44 (s, 3H, CH_3-tolyl) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = -113.2 (s). ^{13}C NMR (101 MHz, CDCl3); δ = 164.2, 161.7, 139.2, 130.5, 127.7 (d, *J* = 8.1 Hz), 120.7, 116.2, 115.9, and 21.3 (CH_3-tolyl) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{15}H_{13}N_3F$: 254.1093; found 254.1084.



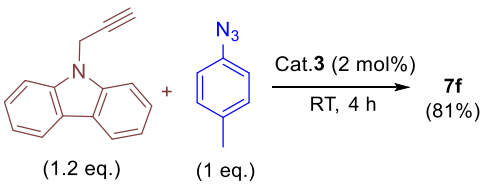
Preparation of triazole (7e)[6]



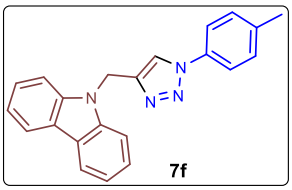
7e was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (75 mg, 80%). ^1H NMR (700 MHz, $CDCl_3$); δ = 8.12 (s, 1H), 7.88 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 2.44 (s, 3H, CH_3-tolyl) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 163.6, 162.2, 147.5, 139.2, 134.8, 130.4, 127.7, 127.7, 126.7, 126.7, 120.6, 117.6, 116.1, 116.0, and 21.3 (CH_3-tolyl) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{15}H_{13}N_3Br$: 314.0293; found 314.0299.



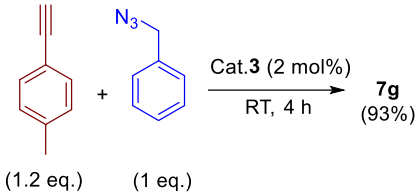
Preparation of triazole (7f)[7]



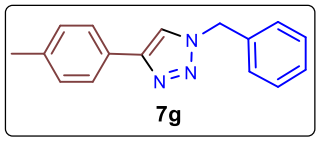
7f was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (82.2 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.12 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.41 (m, 5H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.73 (s, 2H, NCH_2), and 2.35 (s, 3H, CH_3-tolyl) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 140.2, 139.1, 130.4, 126.2, 123.3, 120.7, 120.6, 119.7, 108.9 (NCH_2), and 21.2 (CH_3-tolyl) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{22}H_{19}N_4$: 339.1610; found 339.1556.



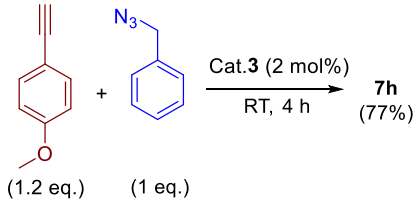
Preparation of triazole (7g)[8,9]



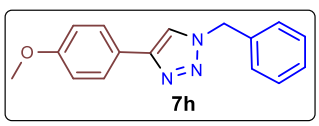
7g was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (69.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.70 (d, *J* = 6.5 Hz, 2H), 7.38 (m, 3H), 7.31 (d, *J* = 6.6 Hz, 2H), 7.21 (d, *J* = 6.6 Hz, 2H), 5.57 (s, 2H, NCH_2), and 2.36 (s, 3H, CH_3-tolyl) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 138.2, 134.8, 129.6, 129.3, 128.9, 128.2, 125.7, 54.4 (NCH_2), and 21.4 (CH_3-tolyl) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{16}H_{16}N_3$: 250.1344; found 250.1361.



Preparation of triazole (7h)[8,9]

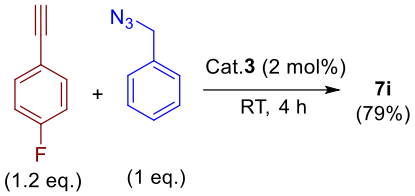


7h was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (61 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.74 (d, *J* = 6.8 Hz, 2H), 7.37 (t, 3H), 7.30 (d, *J* = 6.9 Hz, 2H), 6.93 (d, *J* = 6.9 Hz, 2H), 5.56 (s, 2H, NCH_2), 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 159.7, 134.9, 129.3, 128.9,

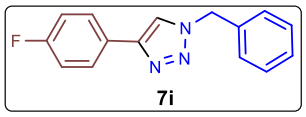


128.2, 127.1, 123.4, 114.3, 55.4 (N*C*H$_2$), and 54.4 (O*C*H$_3$) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{16}H_{16}N_3O$: 266.1293; found 266.1263.

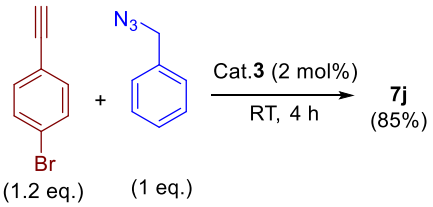
Preparation of triazole (7i)[8]



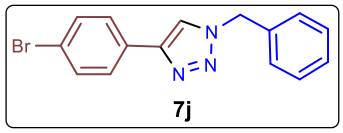
7i was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (60 mg, 79%). ^{1}H NMR (400 MHz, CDCl$_3$); δ = 7.81 (s, 2H), 7.39 (m, 3H), 7.31 (m, 2H), 7.09 (m, 2H), 5.57 (s, 2H, N*C*H$_2$) ppm. ^{19}F NMR (377 MHz, CDCl$_3$) δ -113.52 (s) ppm. ^{13}C NMR (176 MHz, CDCl$_3$); δ = 163.5, 162.0, 134.7, 129.3, 129.0, 128.2, 127.5 (d, *J* = 8.0 Hz), 116.0, 115.9, and 54.6 (N*C*H$_2$) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{15}H_{13}N_3F$: 254.1094; found 254.1116.



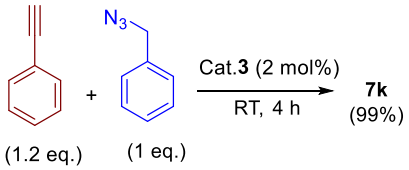
Preparation of (7j)[8]



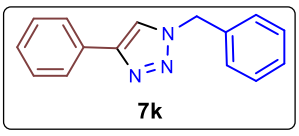
7j was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (80 mg, 85%). ^{1}H NMR (400 MHz, CDCl$_3$) ; δ = 7.68 (s, 1H), 7.66 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 3H), 7.31 (d, *J* = 6.5 Hz, 2H), 5.57 (s, 2H, N*C*H$_2$) ppm. ^{13}C NMR (176 MHz, CDCl$_3$); δ = 147.3, 134.5, 132.1, 129.4, 129.1, 128.3, 127.4, 122.3, 119.9, and 54.6 (N*C*H$_2$) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{15}H_{13}BrN_3$: 314.0293; found 314.0316.



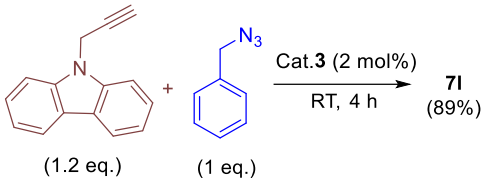
Preparation of (7k)[8]



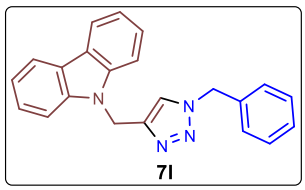
7k was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (70 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.82 (d, *J* = 5.1 Hz, 2H), 7.39 (m, 5H), 7.32 (m, 3H), and 5.58 (s, 2H, NCH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 134.8, 130.7, 129.3, 128.96, 128.3, 128.2, 125.8, and 54.5 (NCH_2) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{15}H_{14}N_3$: 236.1188; found 236.1263.



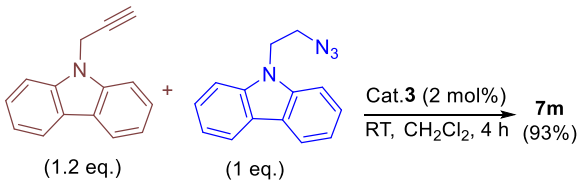
Preparation of (7l)[7]



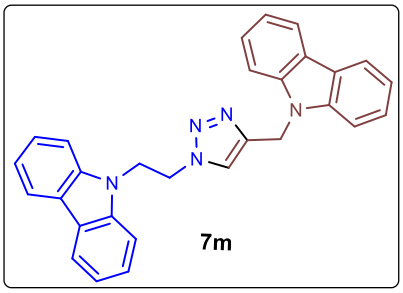
7l was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (90.35 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.45 (m, 4H), 7.26 (m, 6H), 7.13 (s, 2H), 5.61 (s, 2H, NCH_2-benzyl), 5.40 (s, 2H, NCH_2-carbazolyl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.18 (s), 134.39 (s), 129.16 (s), 128.86 (s), 128.05 (s), 126.09 (s), 123.22 (s), 120.53 (s), 119.56 (s), 108.96 (s), 54.91 (s, NCH_2-benzyl), 38.73 (s, NCH_2-carbazolyl). Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{22}H_{19}N_4$: 339.1610; found 339.1624.



Preparation of (7m)[10]

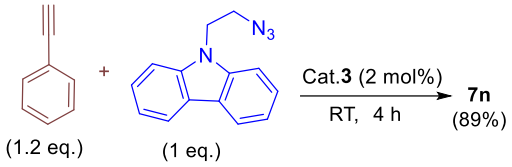


7m was prepared according to the general procedure in the CH_2Cl_2 solvent medium. The precipitate formed was filtered and washed with dichloromethane (3×5 mL) and *n*-hexane (2×3 mL) and dried in a high vacuum to afford an off-white solid. (52.15 mg, 93%). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 8.14 (d, *J* = 7.7 Hz, 2H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.85 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.05 (m, 8H),

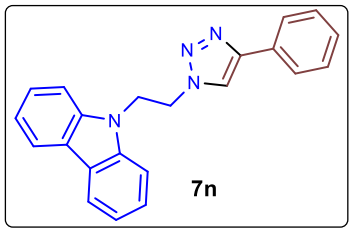


5.52 (s, 2H, NCH_2), 4.75 (d, *J* = 4.9 Hz, 2H, NCH_2CH_2N), and 4.70 (d, *J* = 4.9 Hz, 2H, NCH_2CH_2N) ppm. ^{13}C NMR (101 MHz, DMSO-d_6); δ = 143.3, 139.7 (d, *J* = 3.5 Hz), 125.7, 125.5, 123.4, 122.2, 122.1, 120.1 (d, *J* = 7.3 Hz), 118.9, 109.4, 108.7, 48.4 (NCH_2), 42.8 (NCH_2CH_2N), and 37.6 (NCH_2CH_2N) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{29}H_{24}N_5$: 442.2032; found 442.1999.

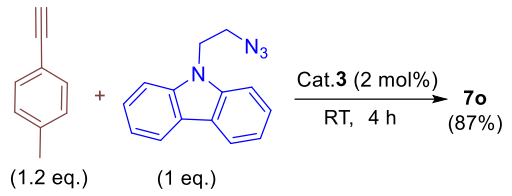
Preparation of (7n)[10]



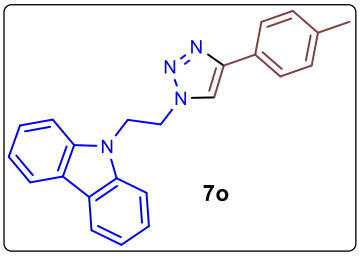
7n was prepared according to the general procedure. The crude reaction mixture was washed with EtOAc (3×5 mL) and with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (38.25 mg, 89%). ^1H NMR (400 MHz, DMSO-d_6); δ = 8.39 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.26 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 2H), 4.93 (t, *J* = 5.5 Hz, 2H, NCH_2CH_2N), and 4.86 (t, *J* = 5.6 Hz, 2H, NCH_2CH_2N) ppm. ^{13}C NMR (101 MHz, DMSO-d_6); δ = 150.6, 146.4, 139.8, 130.7, 128.8, 127.8, 125.7, 125.1, 122.2, 122.0, 120.2, 119.1, 108.9, 48.5 (NCH_2CH_2N), and 42.8(NCH_2CH_2N) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{22}H_{19}N_4$: 339.1610; found 339.1560.



Preparation of (7o)

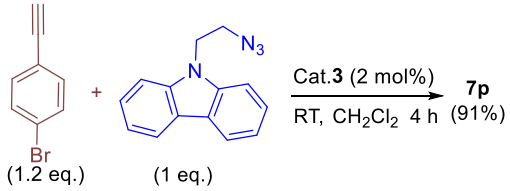


7o was prepared according to the general procedure. The crude reaction mixture was washed with EtOAc (3×5 mL) and with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (38.9 mg, 87%). ^1H NMR (400 MHz, DMSO-d_6); δ = 8.33 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.09 (m, 4H), 4.92 (t, *J* = 5.8 Hz, 2H, NCH_2CH_2N), 4.83 (t, *J* = 5.7 Hz, 2H, NCH_2CH_2N), and 2.29 (s, 3H, tolyl CH_3) ppm. ^{13}C NMR (101 MHz, DMSO-d_6); δ = 146.4, 139.8, 137.0, 129.3, 127.9, 125.6, 125.0, 122.2, 121.5, 120.2,

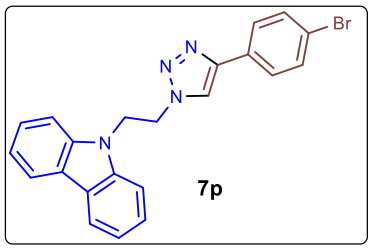


119.0, 108.8, 48.4 (NCH$_2$CH$_2$N), 42.7 (NCH$_2$CH$_2$N), and 20.7 (tolyl CH$_3$) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{23}H_{21}N_4$: 353.1766; found 353.1770.

Preparation of (7p)

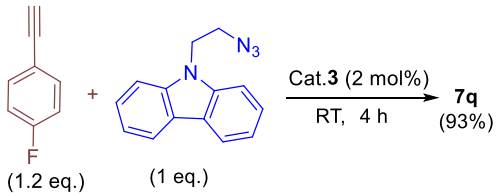


7p was prepared according to the general procedure in the CH_2Cl_2 solvent medium. The

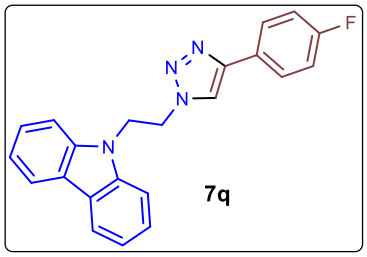


precipitate formed was filtered and washed with dichloromethane (3×5 mL) and *n*-hexane (2×3 mL) and dried in a high vacuum to afford an off-white solid. (48.2 mg, 91%). ^{1}H NMR (400 MHz, DMSO-d$_6$); δ = 8.43 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.60 (s, 4H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 2H), 4.92 (t, *J* = 5.6 Hz, 2H, NCH$_2$CH$_2$N), and 4.85 (t, *J* = 5.5 Hz, 2H, NCH$_2$CH$_2$N) ppm. ^{13}C NMR (101 MHz, DMSO-d$_6$); δ = 145.3, 139.8, 131.8, 129.9, 127.1, 125.7, 122.4, 122.2, 120.8, 120.2, 119.1, 108.8, 48.6 (NCH$_2$CH$_2$N), and 42.8 (NCH$_2$CH$_2$N) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{22}H_{18}BrN_4$: 417.0715; found 417.0735.

Preparation of (7q)

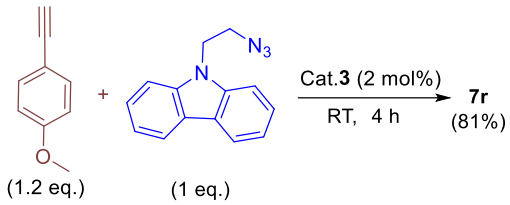


7q was prepared according to the general procedure. The crude reaction mixture was washed with EtOAc (3×5 mL) and with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (42.1 mg, 93%). ^{1}H NMR (400 MHz, DMSO-d$_6$); δ = 8.37 (s, 1H), 8.11 (d, *J* = 7.7

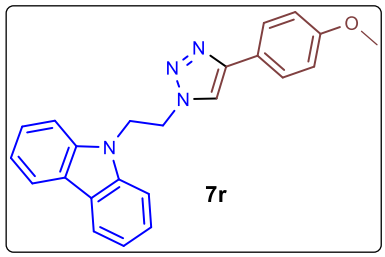


Hz, 2H), 7.68 (dd, *J* = 7.9, 5.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 8.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 4.92 (d, *J* = 5.2 Hz, 2H, NCH$_2$CH$_2$N), and 4.86 (d, *J* = 5.2 Hz, 2H, NCH$_2$CH$_2$N) ppm. ^{19}F NMR (377 MHz, DMSO-d$_6$); δ = -114.2 ppm. ^{13}C NMR (101 MHz, DMSO-d$_6$); δ = 162.9, 160.5, 145.5, 139.8, 127.1 (d, *J* = 8.0 Hz), 125.6, 122.2, 121.9, 120.2, 119.1, 115.7 (d, *J* = 21.7 Hz), 108.8, 48.5 (NCH$_2$CH$_2$N), and 42.8 (NCH$_2$CH$_2$N) ppm. Mass spectral data (HRMS, CH$_3$CN, *m/z*): [M+H] calcd for $C_{22}H_{18}FN4$: 357.1516; found 357.1535.

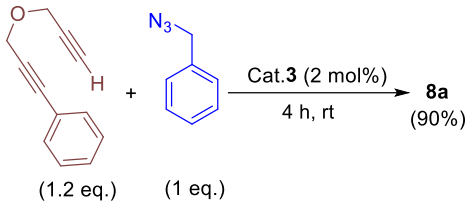
Preparation of triazole (7r)



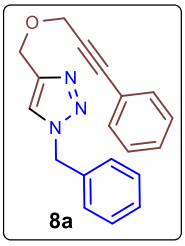
7r was prepared according to the general procedure. The crude reaction mixture was washed with EtOAc (3×5 mL) and with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (37.87 mg, 81%). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 8.28 (s, 1H), 8.12 (s, 2H), 7.56 (s, 2H), 7.40 (d, *J* = 32.2 Hz, 4H), 7.16 (s, 2H), 6.96 (s, 2H), 4.87 (d, *J* = 32.5 Hz, 4H, NCH_2CH_2N), 3.76 (s, 3H, OCH_3) ppm. ^{13}C NMR (101 MHz, DMSO-d_6); δ = 158.9, 139.8, 126.4, 125.6, 123.3, 122.2, 121.0, 120.2, 119.1, 114.2, 108.9, 55.1 (NCH_2CH_2N), 48.4 (NCH_2CH_2N), and 42.7 (OCH_3) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{23}H_{21}N_4O$: 369.1715; found 369.1771.



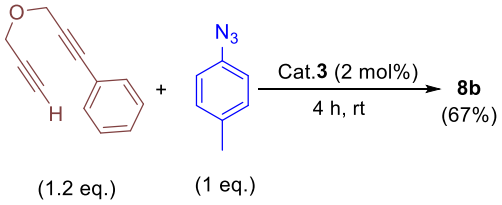
Preparation of triazole (8a)[11]



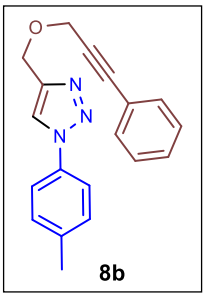
8a was prepared according to the general procedure. The crude reaction mixture was purified (using a 30% EtOAc/hexane mixture) which afforded a yellowish sticky semi-solid (40.9 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.55 (s, 1H), 7.37 – 7.31 (m, 2H), 7.27 (m, 3H), 7.24 – 7.20 (m, 3H), 7.19 – 7.14 (m, 2H), 5.42 (s, 2H, NCH_2), 4.67 (s, 2H, OCH_2), and 4.37 (s, 2H, OCH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 134.5, 131.9, 129.2, 128.9, 128.6, 128.4, 128.3, 122.5, 86.8 (*C*≡*C*), 84.7(*C*≡*C*), 63.3(NCH_2), 58.5 (OCH_2), and 54.5(OCH_2) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{19}H_{18}N_3O$: 304.1450; found 304.1400.



Preparation of triazole (8b)

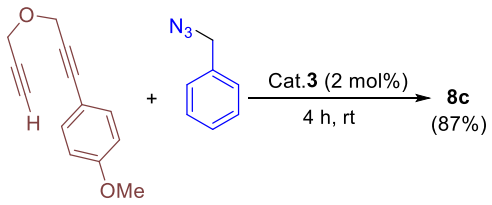


8b was prepared according to the general procedure. The crude reaction mixture was purified

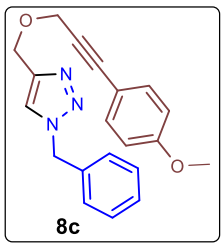


(using a 30% EtOAc/hexane mixture) which afforded a yellowish-orange semi-solid (30.4 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.99 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.34 – 7.28 (m, 5H), 4.89 (s, 2H, O*C*H$_2$), 4.51 (s, 2H, O*C*H$_2$), and 2.42 (s, 3H, tolyl-*C*H$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 145.4, 139.1, 134.9, 131.9, 130.4, 128.7, 128.5, 122.6, 121.1, 120.7, 86.98 (*C*≡*C*), 84.7 (*C*≡*C*), 63.4 (O*C*H$_2$), 58.7 (O*C*H$_2$), and 21.2 (tolyl-*C*H$_3$) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{19}H_{18}N_3O$: 304.1450; found 304.1471.

Preparation of triazole (8c)[11]

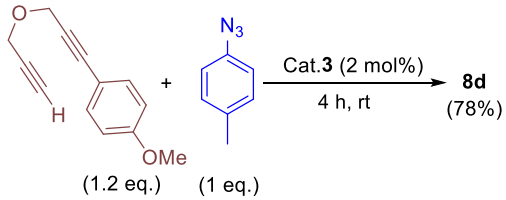


8c was prepared according to the general procedure. The crude reaction mixture was purified

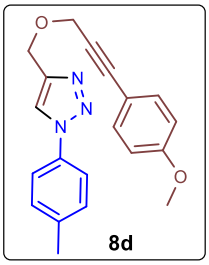


(using a 30% EtOAc/hexane mixture) which afforded a yellowish-orange semi-solid (43.5 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.32 – 7.22 (m, 6H), 7.19 – 7.11 (m, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.40 (s, 2H, N*C*H$_2$), 4.64 (s, 2H, O*C*H$_2$), 4.37 (s, 2H, O*C*H$_2$), and 3.69 (s, 3H, O*C*H$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 159.8, 134.5, 133.4, 129.1, 128.8, 128.3, 114.6, 113.96, 86.8 (*C*≡*C*), 83.4 (*C*≡*C*), 63.2 (O*C*H$_2$), 58.6 (O*C*H$_2$), and 55.3 (O*C*H$_3$) ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{20}H_{20}N_3O_2$: 334.1555; found 334.1253.

Preparation of triazole (8d)

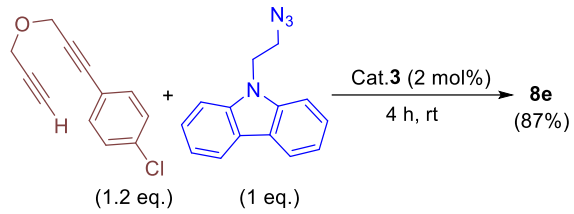


8d was prepared according to the general procedure. The crude reaction mixture was purified

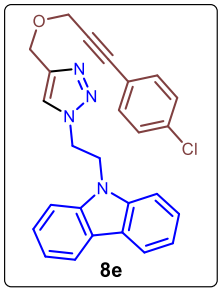


(using a 30% EtOAc/hexane mixture) which afforded a yellowish semi-solid (39 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.99 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.87 (s, 2H, OCH_2), 4.49 (s, 2H, OCH_2), 3.81 (s, 3H, OCH_3), and 2.42 (s, 3H, tolyl-CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 159.9, 145.5, 139.1, 133.5, 130.4, 120.7, 114.1, 86.9 (*C*≡*C*), 83.3 (*C*≡*C*), 63.3 (O*C*H_2), 58.8 (O*C*H_2), 55.4 (O*C*H_3), and 21.2 (tolyl-*C*H_3) ppm. Mass spectral data (HRMS, MeOH, *m/z*): [M+H] calcd for $C_{20}H_{20}N_3O_2$: 334.1555; found 334.1606.

Preparation of triazole (8e)

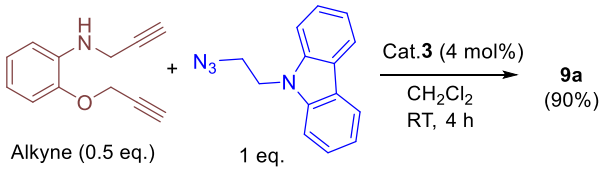


8e was prepared according to the general procedure. The crude reaction mixture was purified

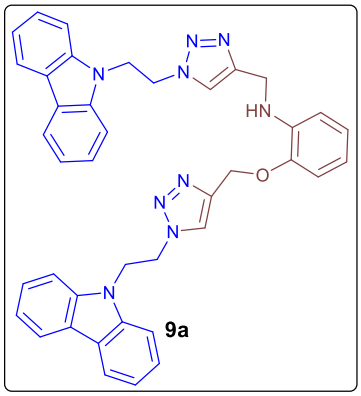


by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford pale-yellow solid (57 mg, 87%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.06 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.82 (s, 4H, NCH_2CH_2N), 4.48 (s, 2H, OCH_2), and 3.96 (s, 2H, OCH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 139.9, 134.7, 133.1, 128.8, 126.3, 123.1, 121.1, 120.7, 119.9, 107.9, 85.8 (*C*≡*C*), 85.5 (*C*≡*C*), 62.5 (NCH_2CH_2N), 57.5, 43.4, and 31.7 ppm. DEPT-135{^{13}C} NMR (176 MHz, $CDCl_3$); δ = 132.9, 128.6, 126.1, 120.5, 119.7, 107.8, 62.3, 57.3, and 43.2 ppm. Mass spectral data (HRMS, CH_3CN, *m/z*): [M+H] calcd for $C_{26}H_{22}ClN_4O$: 441.1482; found 441.1461. IR (ATR mode, cm^{-1}): 1599, 1485, 1451, 1330, 1222, 1073, 921, 823, 748, 718, and 524.

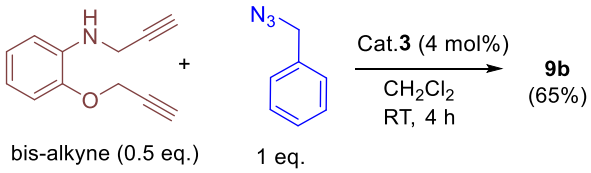
Preparation of bis-triazole (9a)



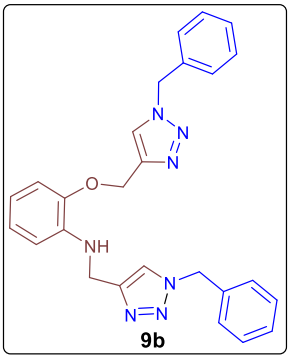
A 25 mL Schlenk tube was charged with carbazolyl azide (2 equiv), bis-terminal alkyne (1 equiv) and cat. **3** (4 mol%) under nitrogen atmosphere. To this solid mixture CH_2Cl_2 was added and stirred for 4h at RT. A white precipitate formed was filtered and washed with CH_2Cl_2 (2 × 3 mL), followed by *n*-hexane (2 × 3 mL). After washings it was then vacuum to afford a pale brown solid. Yield; 75 mg (90%). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 8.10 (d, *J* = 8.0 Hz, 5H), 7.77 (s, 1H), 7.34 (m, *J* = 18.5, 8H), 7.16 (m, 4H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.52 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 1H), 4.98 (s, 3H), 4.90-4.66 (m, 8H), and 4.19 (d, *J* = 4.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6); δ = 145.1, 143.1, 139.8, 137.6, 125.7, 125.61, 124.9, 122.2, 122.1, 121.5, 120.2, 120.16, 119.1, 119.0, 115.9, 111.3, 109.7, 108.8, 108.7, 61.5 (OCH_2), 48.4 (NCH_2CH_2), 48.4 (NCH_2CH_2), 42.9 (NCH_2CH_2), 42.8 (NCH_2CH_2), and 38.5 ($HNCH_2$-) ppm. HRMS (MeOH, *m/z*): 658.3066; calcd for $C_{40}H_{36}N_9O$; 658.3043 $[M+H]^+$. IR (ATR mode, solid sample, cm^{-1}): 3051, 1598, 1516, 1452, 1331, 1214, 1130, 1046, 1016, 847, 745, 666, 615, and 561.



Preparation of bis-triazole (9b)



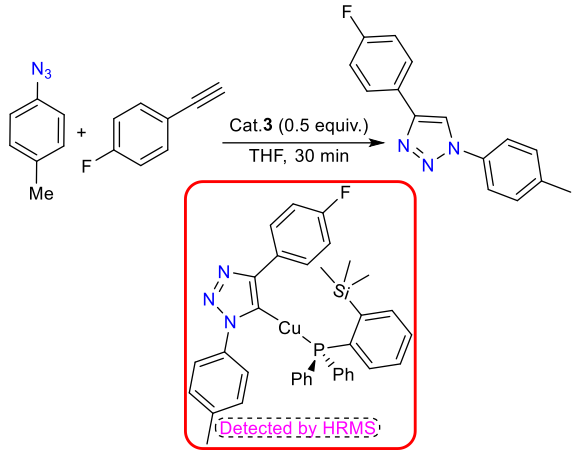
A Schlenk tube containing benzyl azide (2 equiv.), bis-terminal alkyne (1 equiv.), and cat. **3** (4 mol%) was added CH_2Cl_2 (1 mL) and stirred for 4h at RT. Then removed the solvent under reduced pressure, the obtained residue was purified by flash column (silica gel) chromatography by using ethyl acetate (15 mL). The solvent was removed from the resulting filtrate, followed by washing with *n*-hexane (4 mL), and drying under vacuum afforded **9b** as yellow oily substance. Yield; 44 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.53 (s, 1H), 7.33 (m, 9H, ArH), 7.24-7.20 (m, 3H, ArH), 6.94-6.81 (m, 2H, ArH), 6.64 (dd, *J* = 7.9 Hz, 2H, ArH), 5.51 (s, 2H, $BnCH_2$), 5.46 (s, 2H, $BnCH_2$), 5.18 (s, 2H, OCH_2), and 4.42 (s, 2H, $HNCH_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$); δ = 147.1, 145.8, 144.6, 138.1, 134.8, 134.6, 129.3, 128.8, 128.9, 128.8,



128.2, 128.1, 123.0, 122.3, 121.8, 117.3, 112.1, 110.96, 62.8 (OCH_2), 54.4 ($BnCH_2$), 54.3 ($BnCH_2$), and 39.9 ($HNCH_2$) ppm. HRMS (ESI, MeOH, *m/z*): 452.2208; calcd for $C_{26}H_{26}N_7O$: 452.2199 $[M+H]^+$. IR (ATR mode, cm^{-1}): 3052, 1600, 1511, 1449, 1334, 1262, 1208, 1122, 1048, 900, 847, 805, and 732.

Mechanistic studies

Scheme S1. Detection of copper(I) triazolide (A Click intermediate) by HRMS



To a pre-dried 25ml Schlenk tube under N_2, the mixture of 1-ethynyl-4-fluorobenzene (1 equiv., 0.083 mmol), 1-azido-4-methylbenzene (1.2 equiv., 0.0996 mmol), and Cat.**3** (0.5 equiv., 0.042 mmol) were added. Then, to this reaction mixture, 5 mL of anhydrous THF was added and the resulting reaction mixture was allowed to stir at RT for 30 min. This reaction mixture was analysed at various time intervals by using mass spectroscopy.

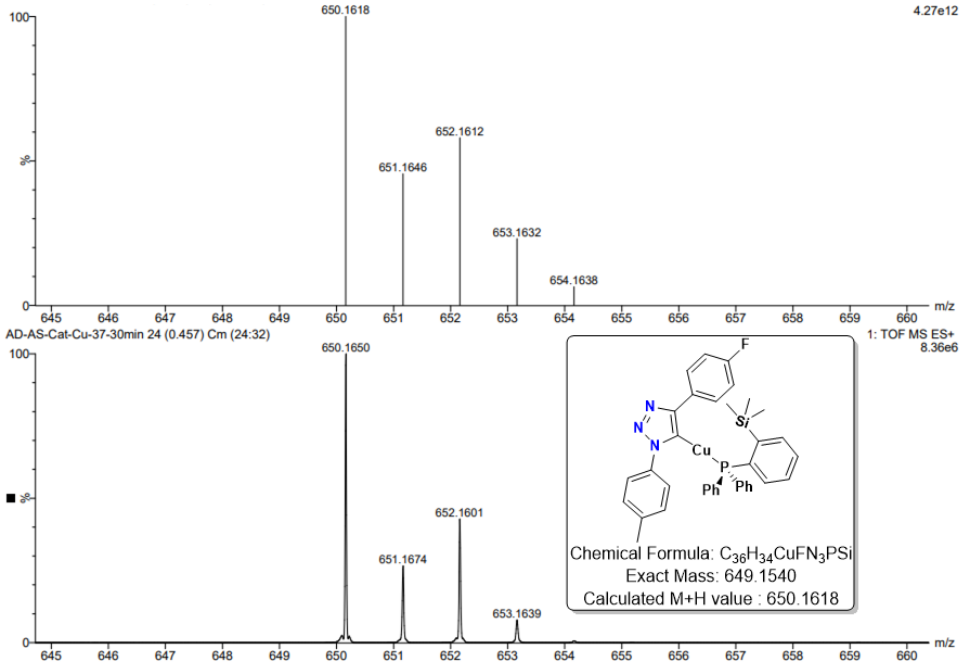
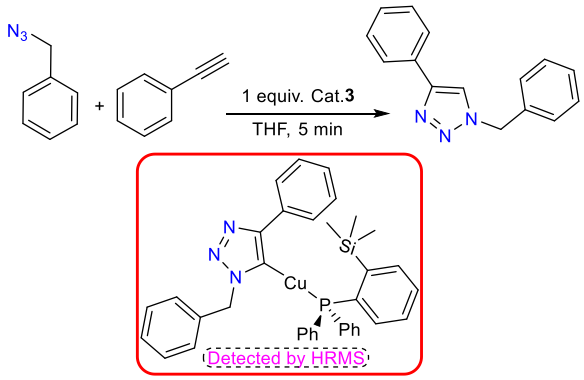


Figure S62. HRMS spectrum of intermediate **D** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern). Intermediate **D**: (ESI) m/z calcd for $C_{36}H_{35}CuFN_3PSi$ [M+H]: 650.1618; found: 650.1650.

Scheme S2. Detection of copper triazolide (A Click intermediate) by HRMS



To a pre-dried 25 mL Schlenk tube under N_2, the mixture of ethylbenzene (1 equiv., 0.016 mmol), benzyl azide (1 equiv., 0.016 mmol), and Cat.**3** (1 equiv., 0.016 mmol) were added. Then, to this reaction mixture, 5 mL of anhydrous THF was added and the resulting reaction mixture was allowed to stir at RT for 5 min. After 5min. the small amount of aliquot was taken under a nitrogen atmosphere and dissolved in anhydrous acetonitrile and submitted for mass analysis.

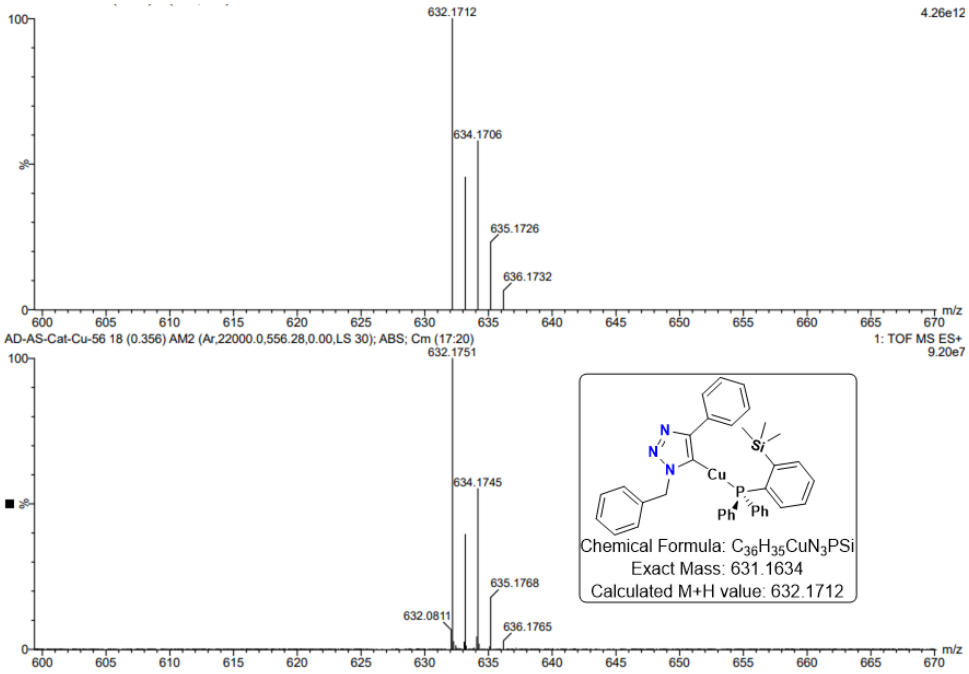
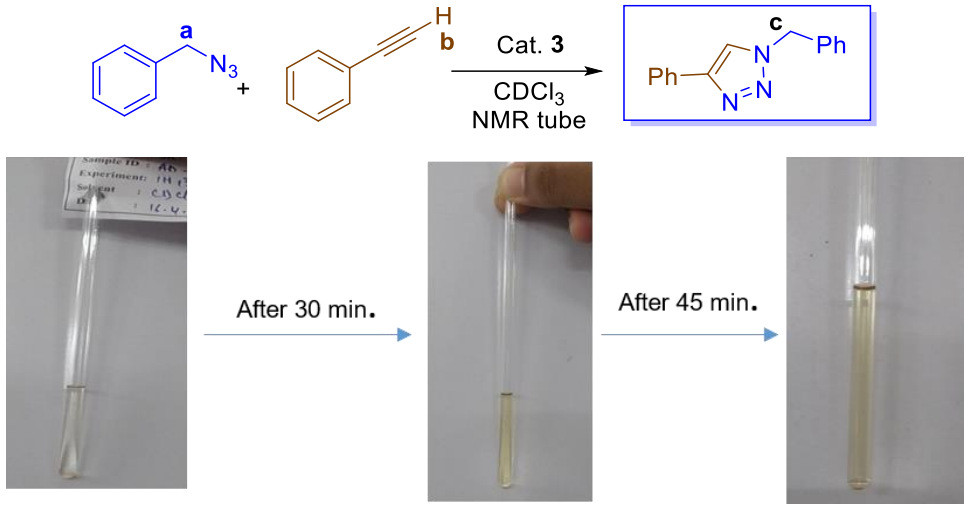


Figure S63. HRMS spectrum of intermediate measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern). Intermediate: (ESI) *m/z* calcd for $C_{36}H_{36}CuN_3PSi$ [M+H]: 632.1712; found: 632.1751.

Scheme S3. Reactivity of cat.3 towards triazole synthesis (NMR tube experiment)



Ethynylbenzene (1 equiv., 0.016 mmol), benzyl azide (1 equiv., 0.016 mmol), and Cat.**3** (1 equiv., 0.016 mmol) were combined and put in a pre-dried NMR tube under N_2. The proton NMR was then measured in intervals of 5 minutes, 15 minutes, 30 minutes, and 45 minutes after 0.6 mL of $CDCl_3$ was added to this. It was noted that ethynyl benzene and benzyl azide were completely converted to the appropriate triazole after 30 minutes.

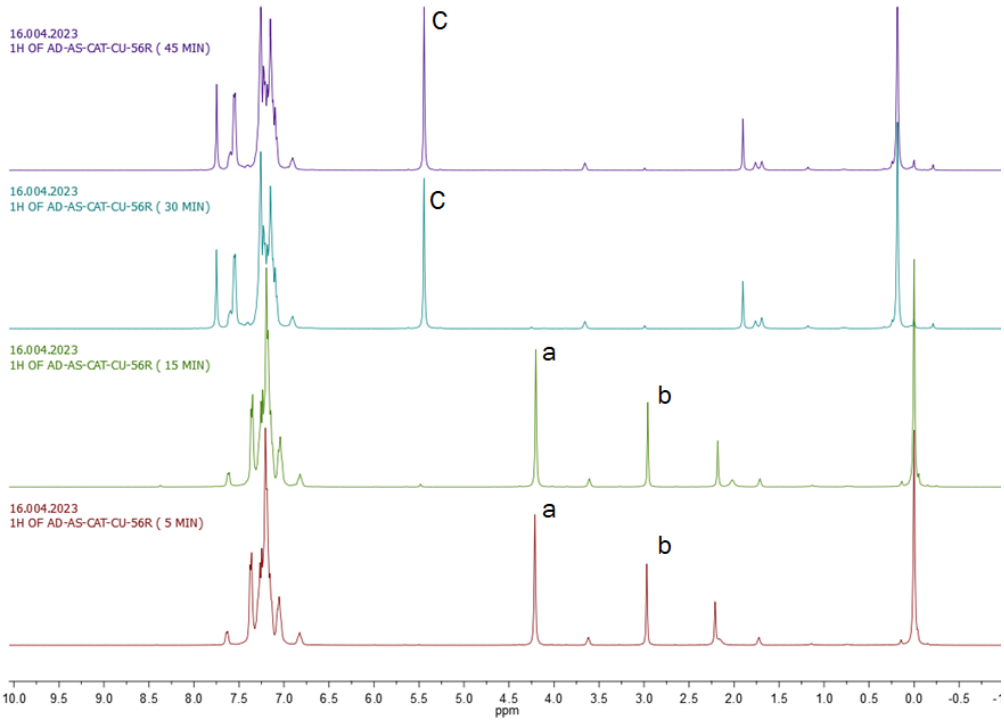
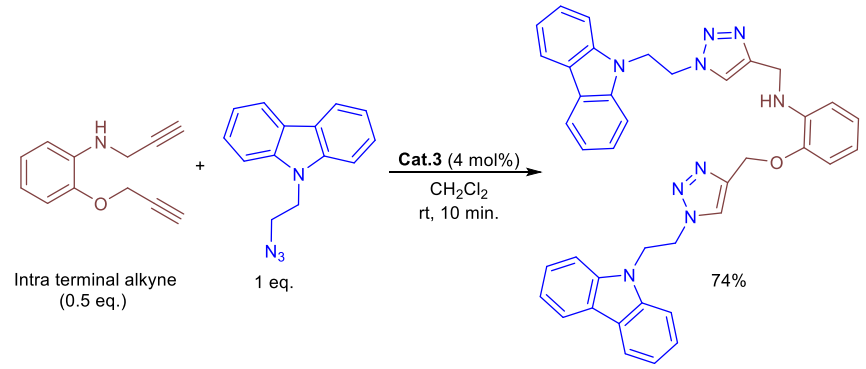
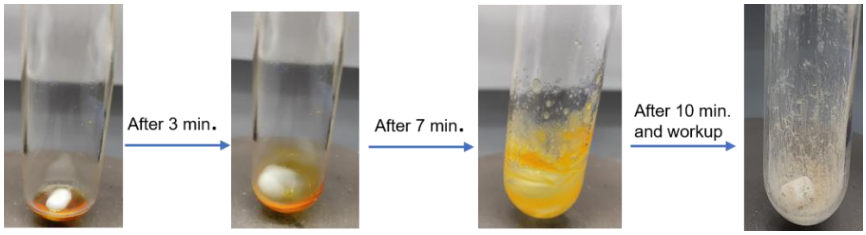


Figure S64. ^{1}H NMR spectrum of NMR tube experiment for the synthesis of **7k** measured in intervals of 5 minutes, 15 minutes, 30 minutes, and 45 minutes in $CDCl_3$.

Scheme S4. Synthesis of bis(triazoles) by copper(I) catalysis within 10 min





In a 50 mL Schlenk tube charged with a magnetic bar was added azide (0.254 mmol), bis terminal alkyne (0.127 mmol) and catalyst (4 mol%) under a nitrogen atmosphere. Then, 1 mL of dichloromethane was added to the reaction mixture and the reaction mixture was allowed to

stir for 10 min at RT. After 10 min, the precipitate formed was filtered and washed with dichloromethane (3×5 mL) and *n*-hexane (2×3 mL) and dried in a high vacuum to afford a pale brownish solid. (64 mg, 77%).

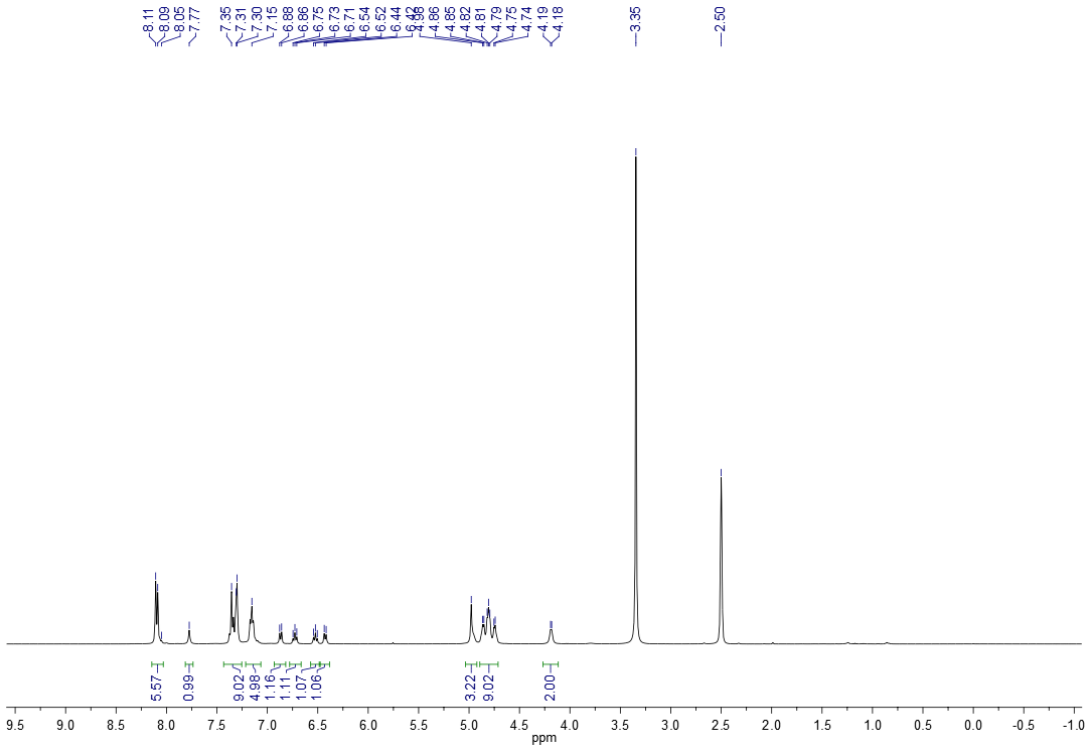


Figure S65. ^{1}H NMR spectrum of **9b** measured in DMSO-d_6 (10 min reaction)

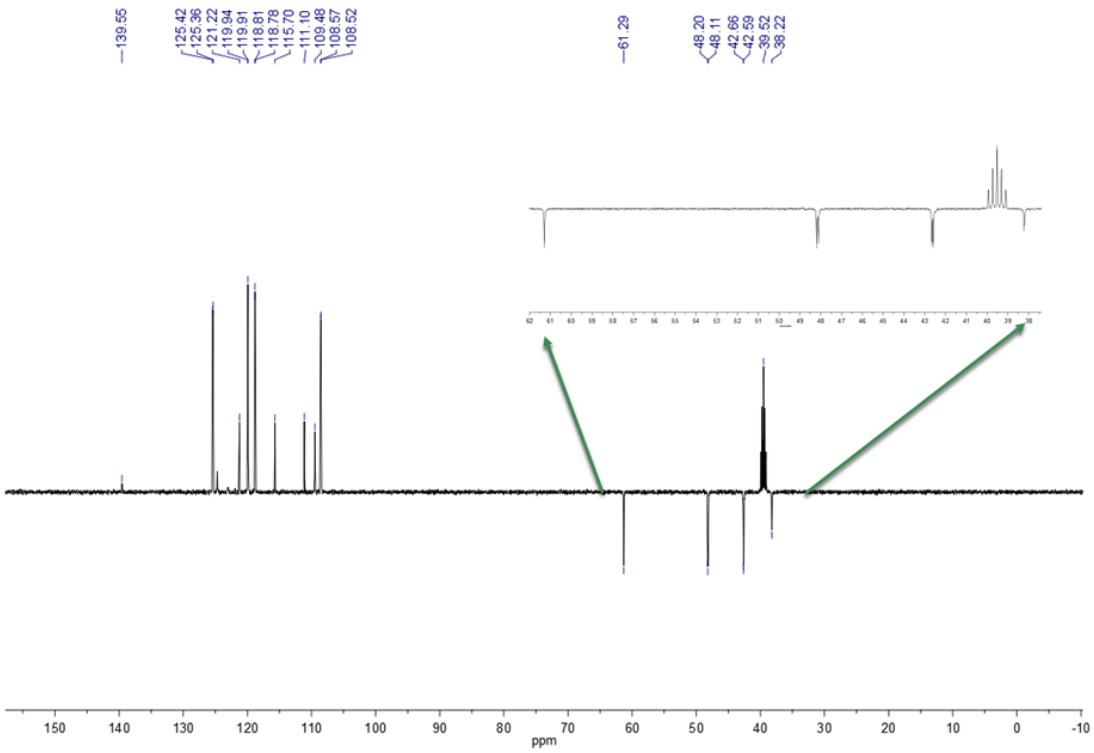
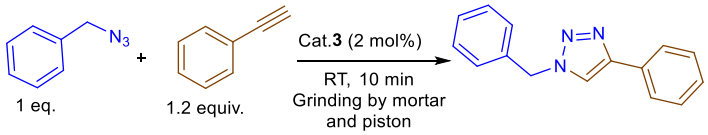


Figure S66. DEPT-135 (^{13}C) NMR spectrum of **9b** measured in DMSO-d_6 (10 min reaction)

Scheme S5. Synthesis and spectral data of triazole by the mechanical grinding method using Cat.3



Scheme S5**.** Preparation of **7k** from grinding method by using cat.**3**.

Alkyne (0.18 mmol), azide (0.15 mmol), and 2 mol% cat. **3** were placed into an oven-dried mortar and pestle. The reaction mixture was then mortared for 5 minutes. The product was isolated by passing the reaction mixture via flash column chromatography with ethyl acetate as the eluent. The solvent was then evaporated by rota vapour, yielding the respective triazole as a white solid with an 86% yield.

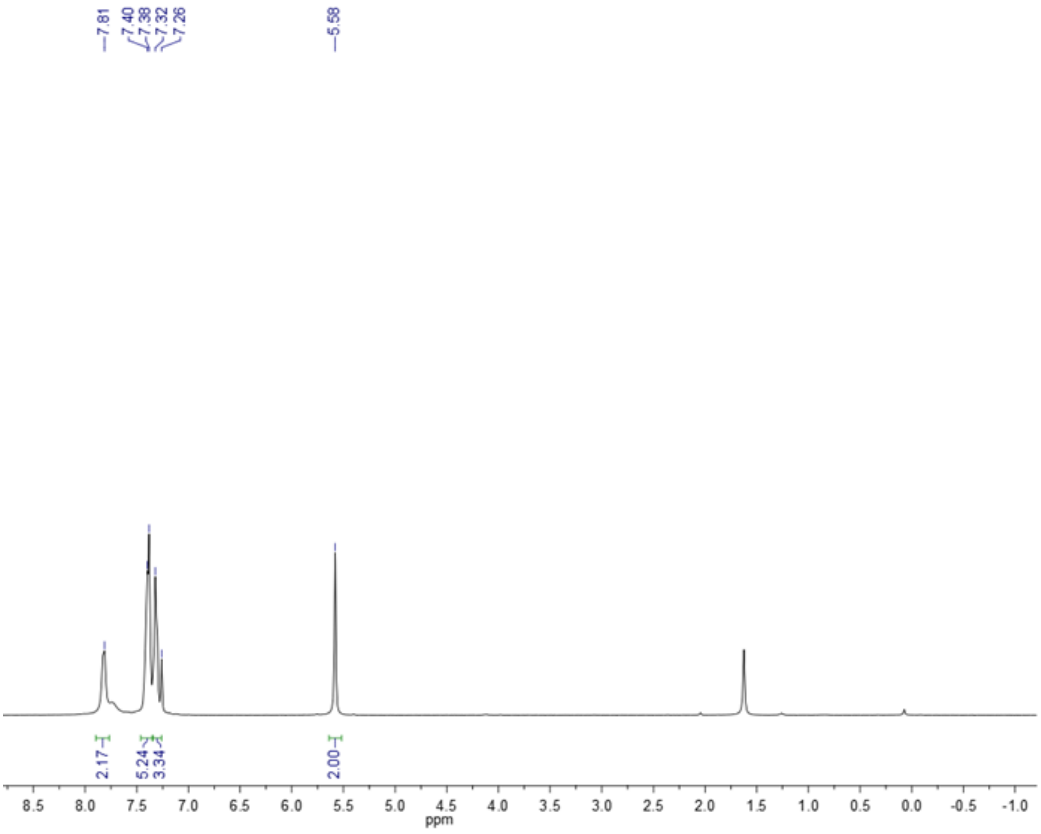


Figure S67. ^{1}H NMR spectrum of **7k** measured in $CDCl_3$ (5 min grinding method)

Spectral data of triazoles and bis-triazoles

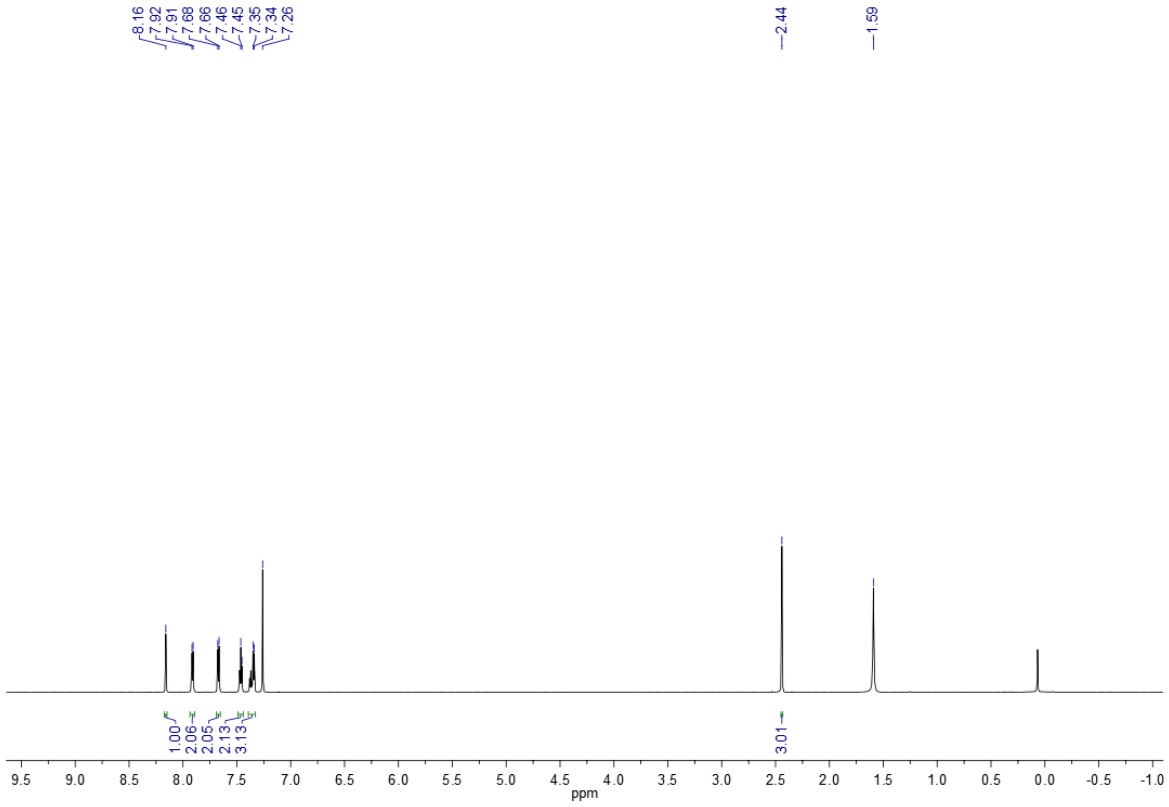


Figure S68. ^{1}H NMR spectrum of **7a** measured in $CDCl_3$.

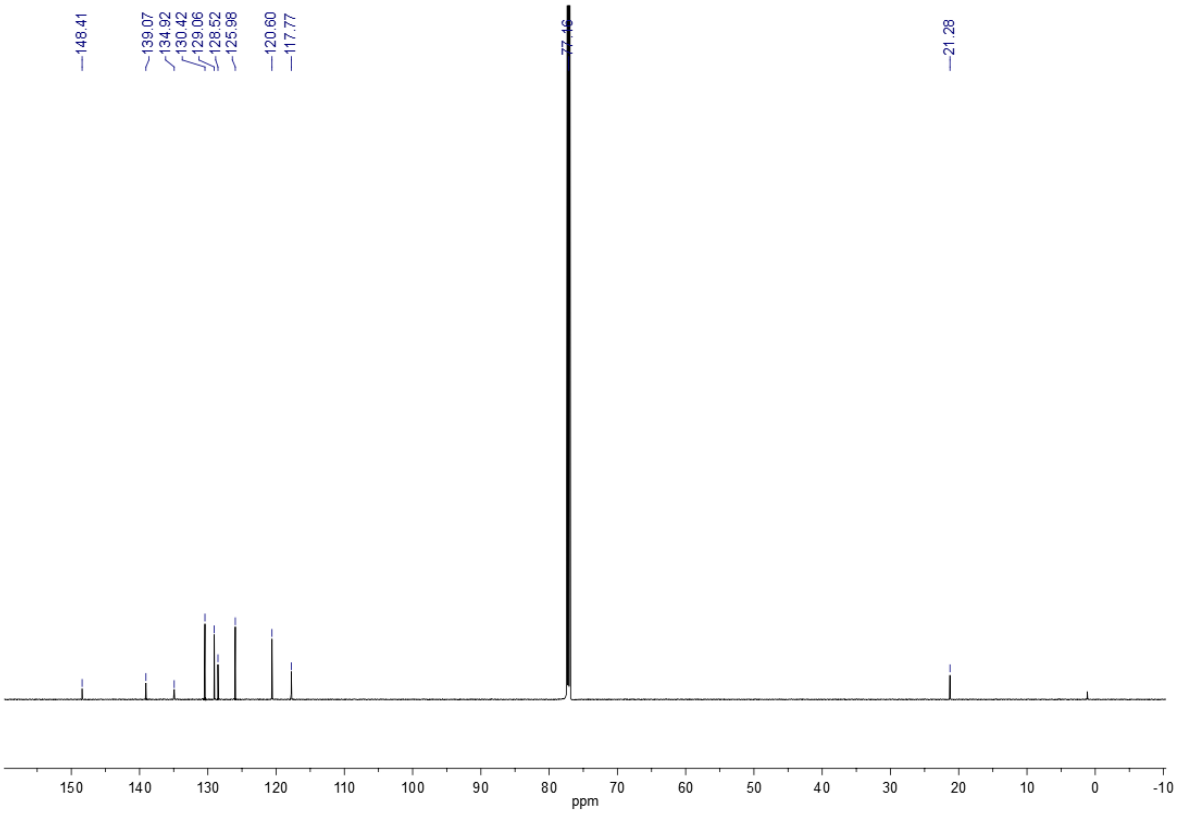


Figure S69. ^{13}C NMR spectrum of **7a** measured in $CDCl_3$.

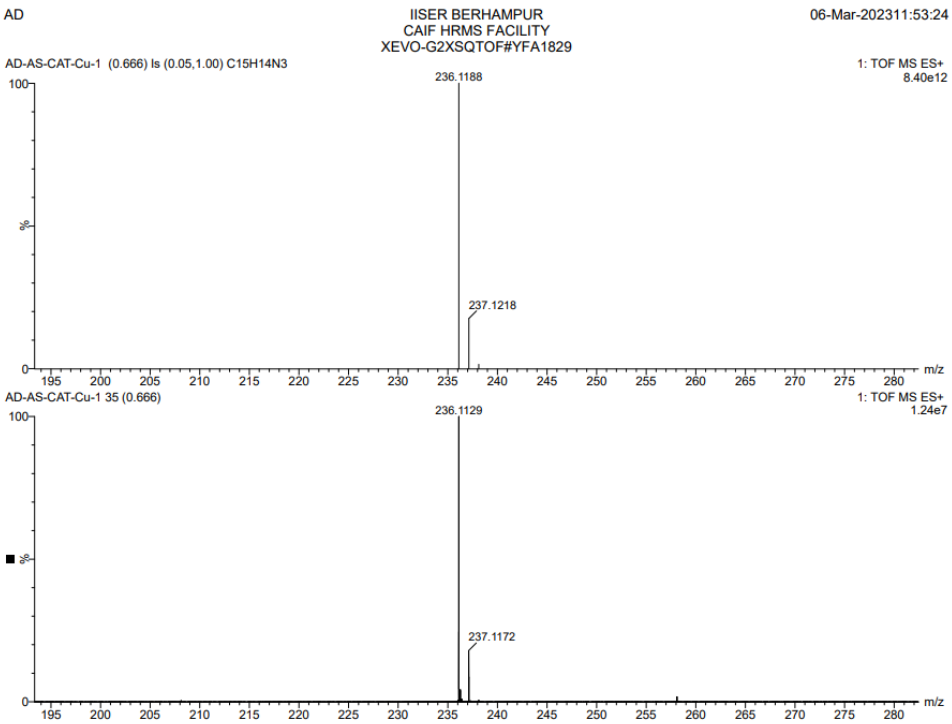


Figure S70. HRMS spectrum of **7a** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

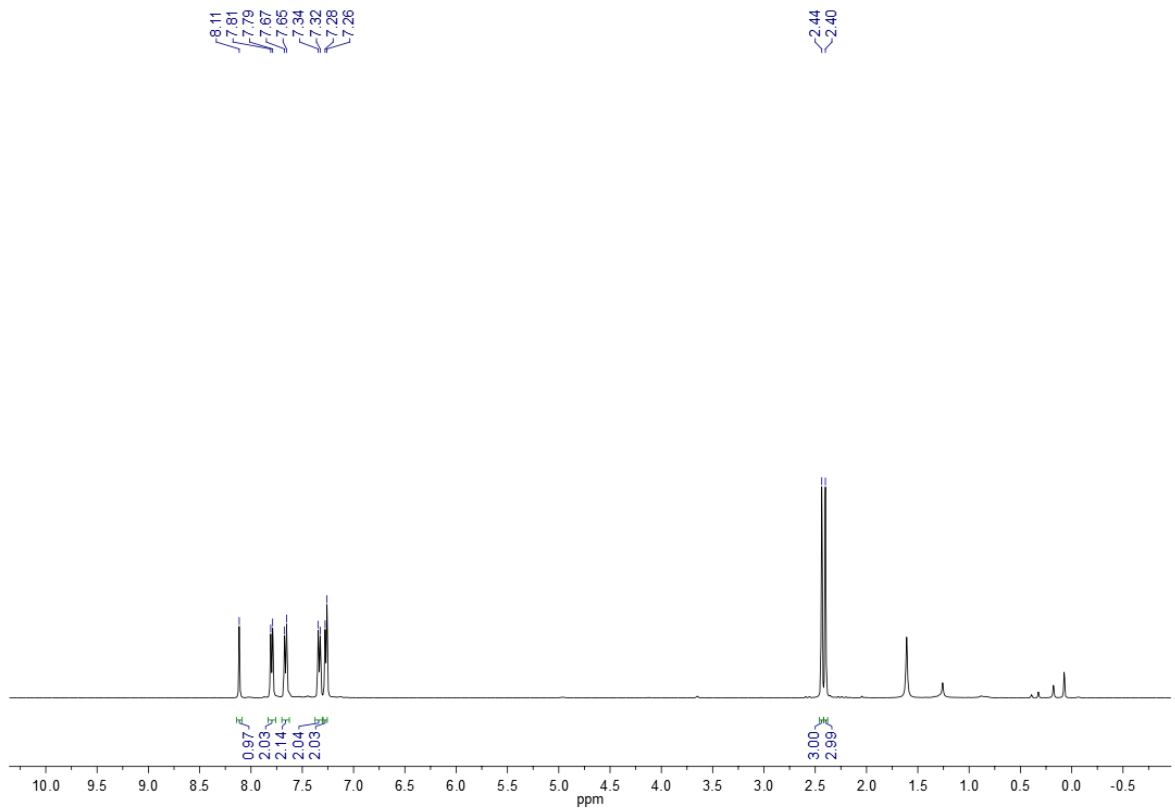


Figure S71. ^{1}H NMR spectrum of **7b** measured in $CDCl_3$.

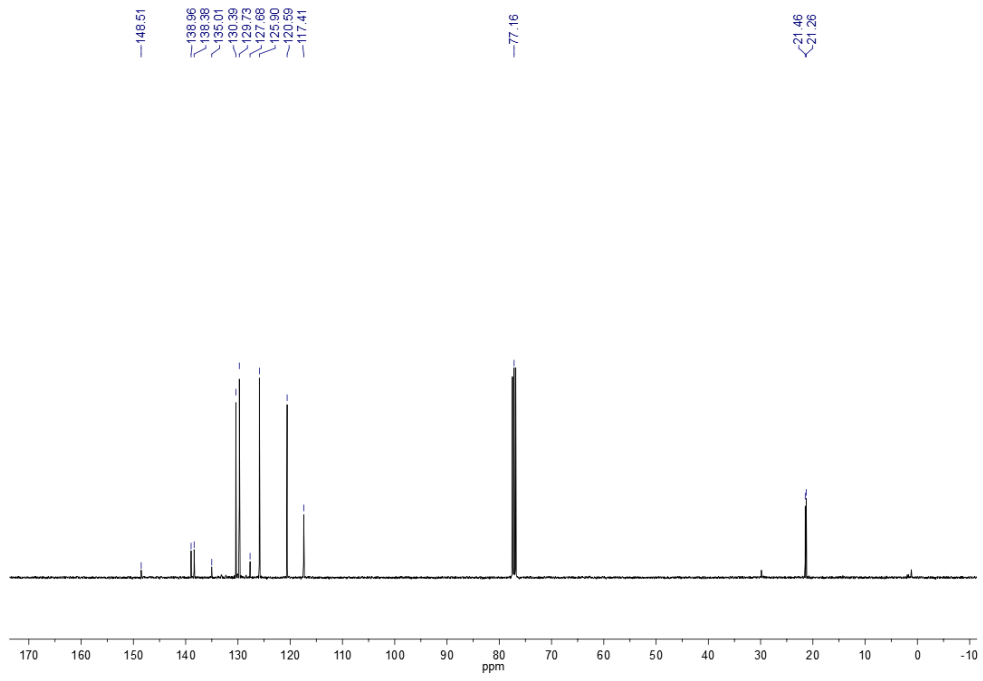


Figure S72. ^{13}C NMR spectrum of **7b** measured in $CDCl_3$.

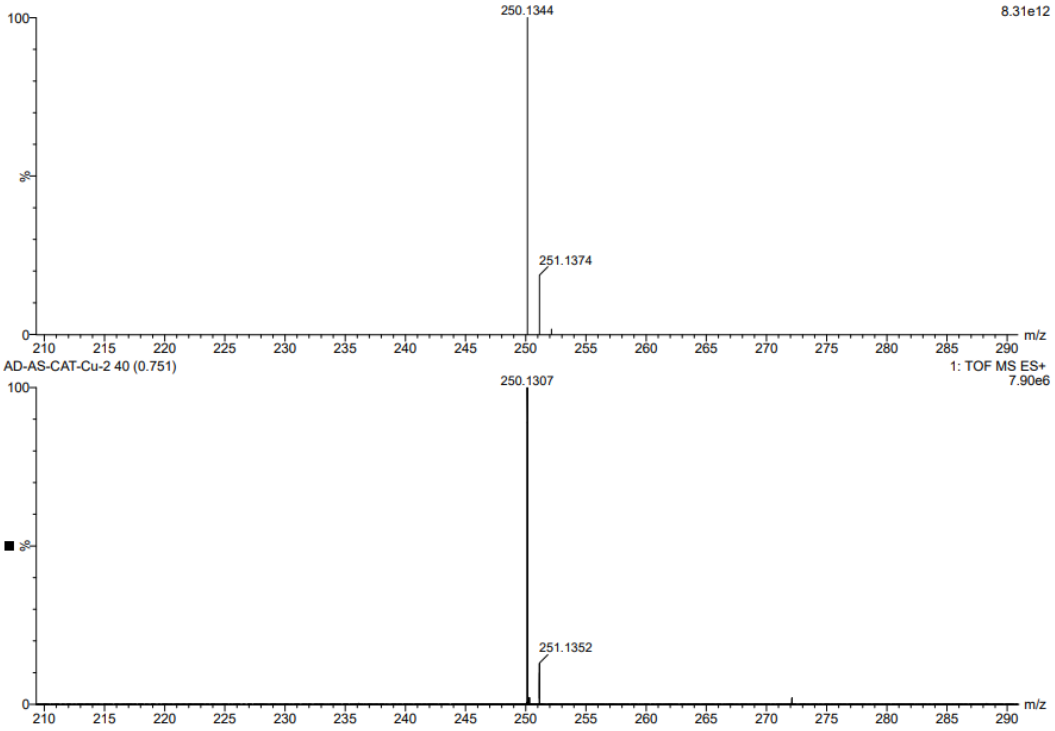


Figure S73. HRMS spectrum of **7b** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

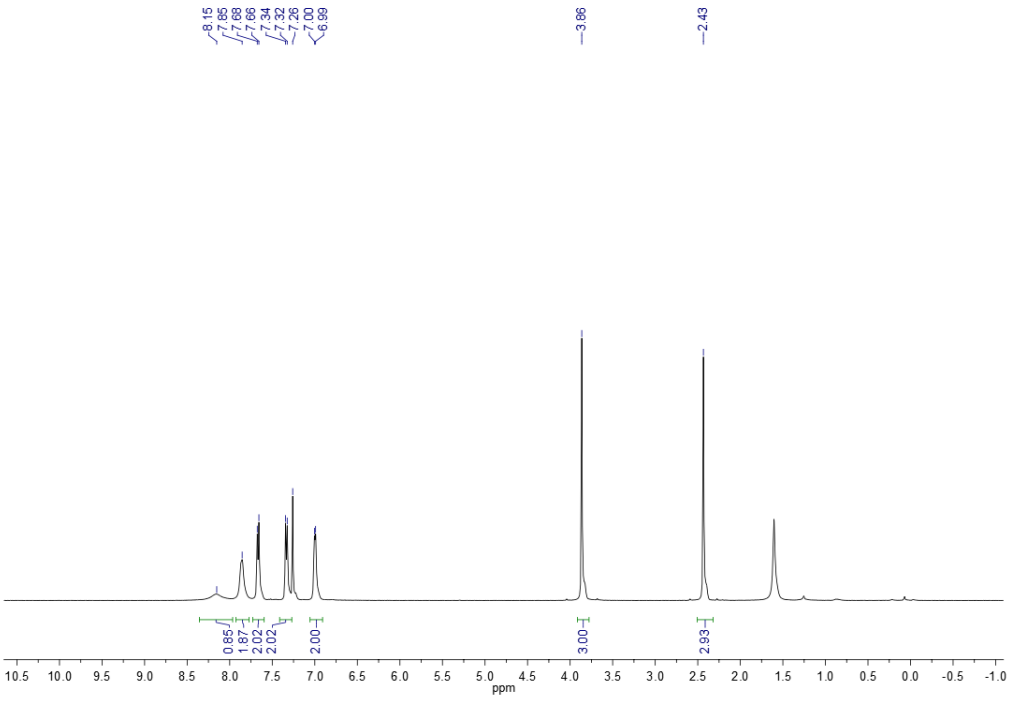


Figure S74. ^{1}H NMR spectrum of 7**c** measured in $CDCl_3$.

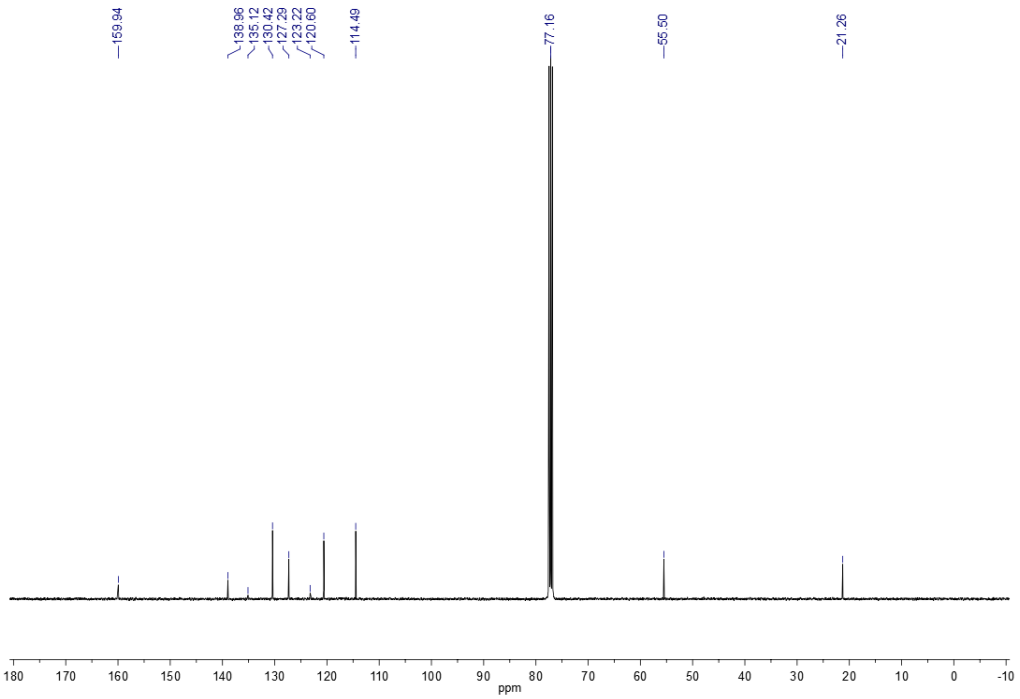


Figure S75. ^{13}C NMR spectrum of triazole **7c** measured in $CDCl_3$.

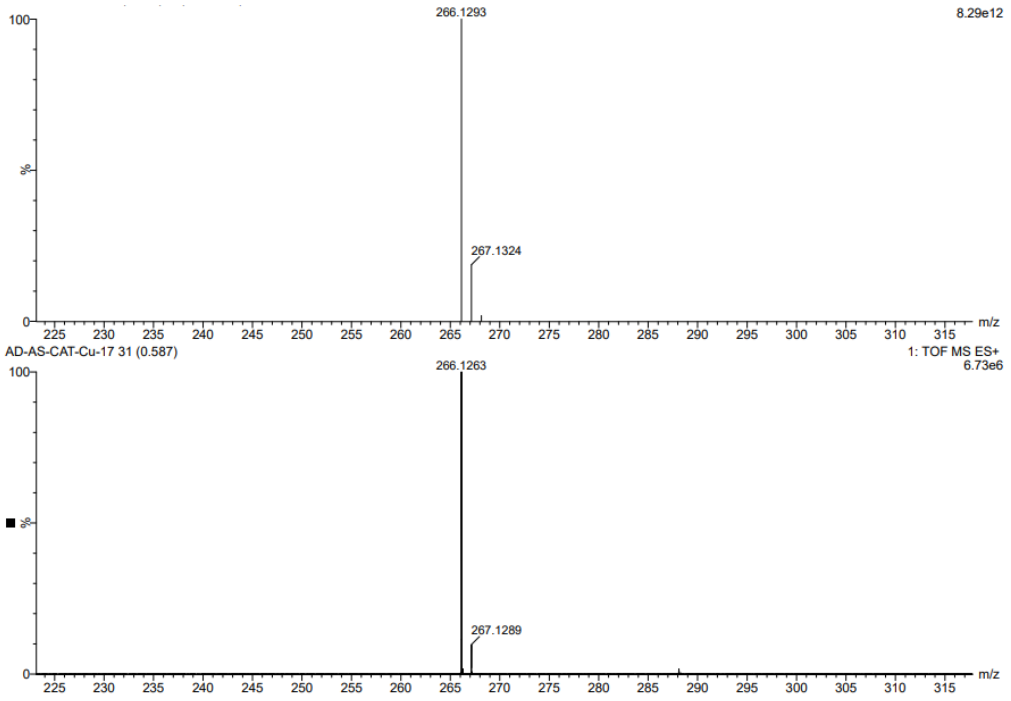


Figure S76. HRMS spectrum of **7c** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

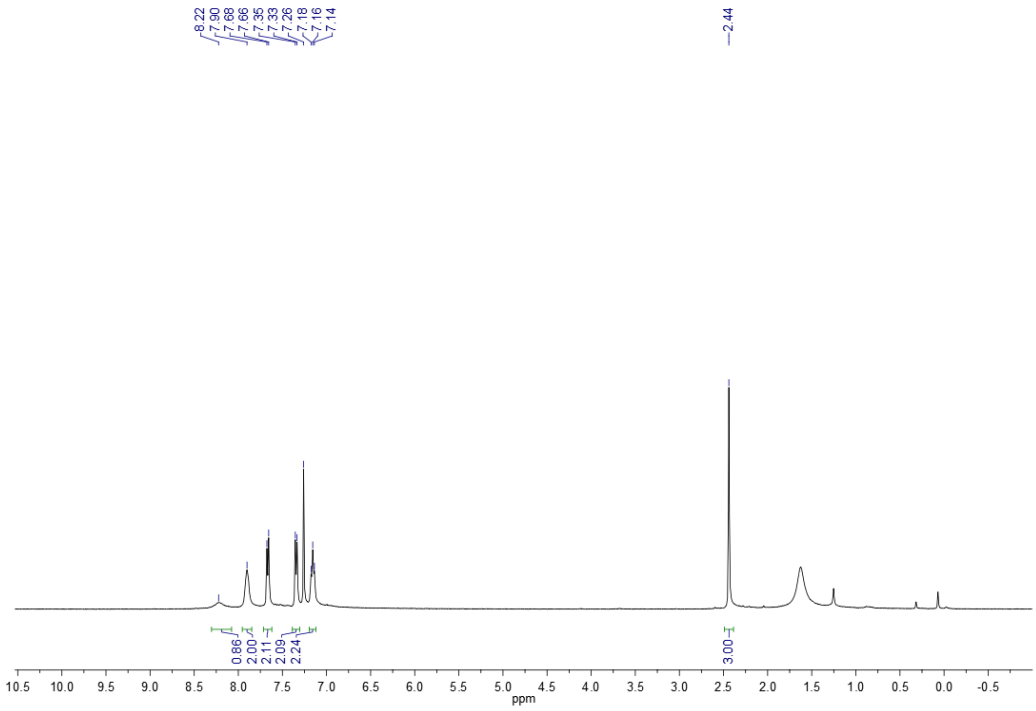


Figure S77. ^{1}H NMR spectrum of **7d** measured in $CDCl_3$.

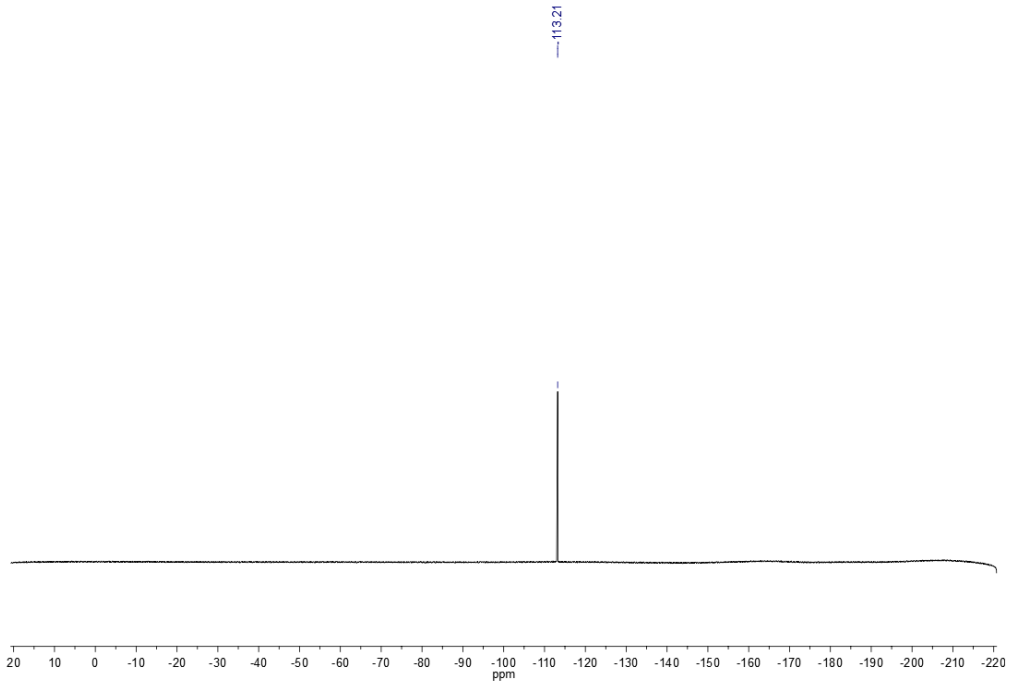


Figure S78. ^{19}F NMR spectrum of **7d** measured in $CDCl_3$.

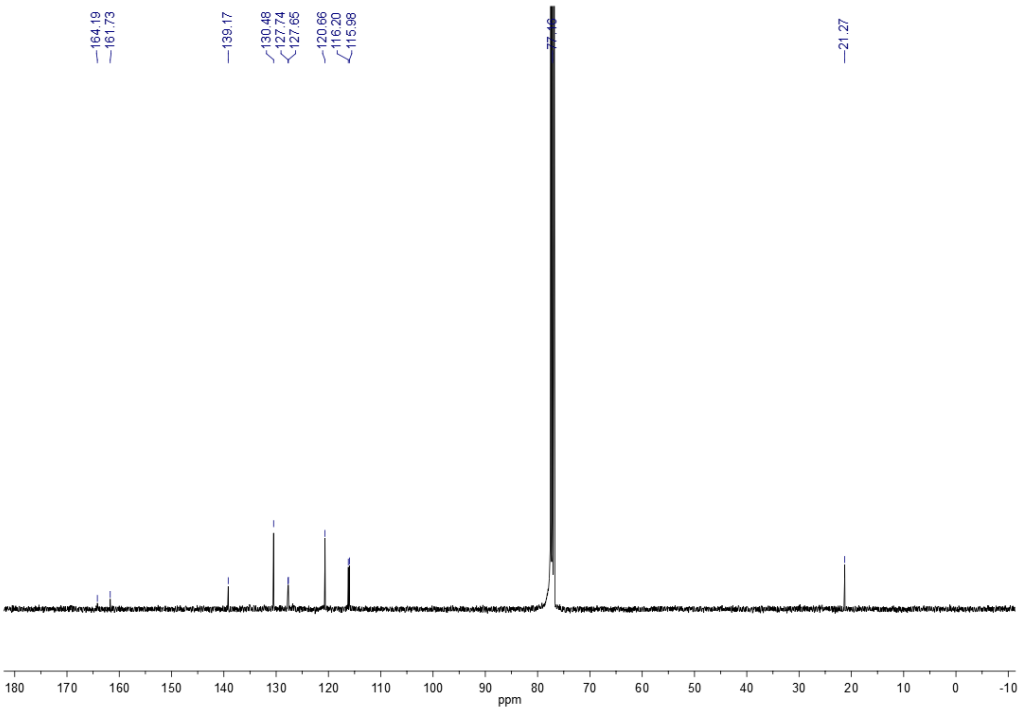


Figure S79. ^{13}C NMR spectrum of **7d** measured in $CDCl_3$.

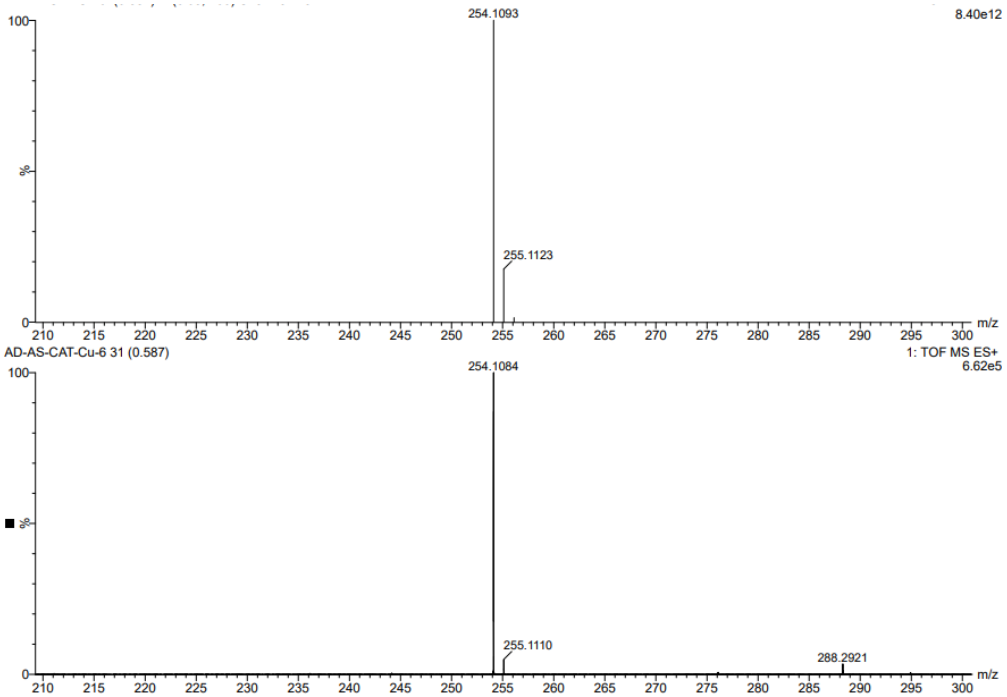


Figure S80. HRMS spectrum of **7d** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

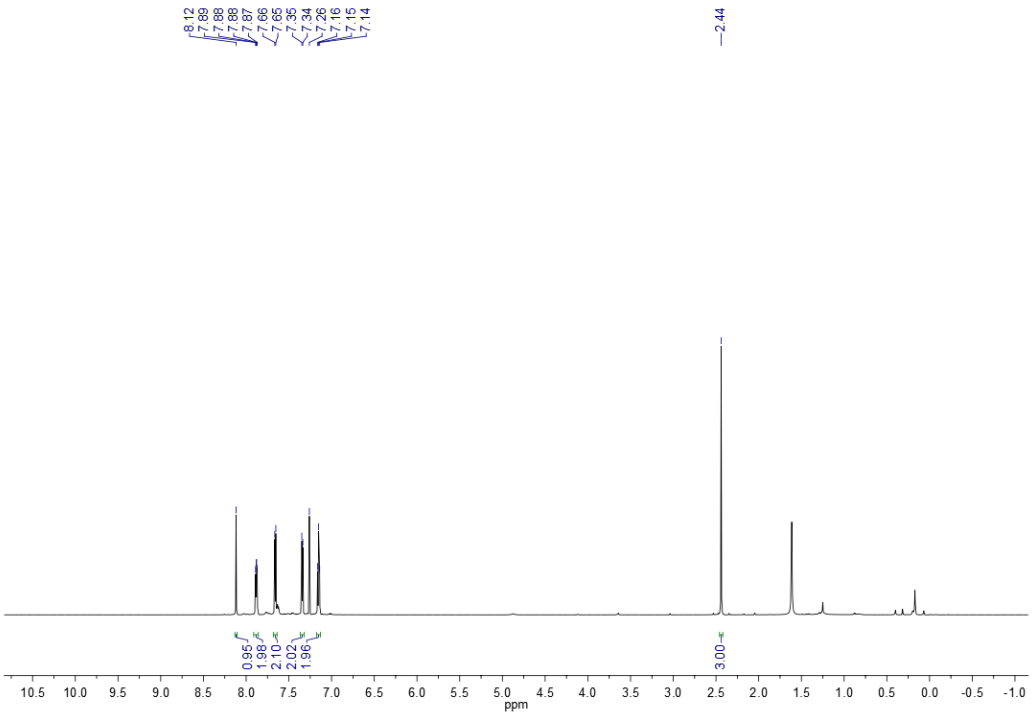


Figure S81. ^{1}H NMR spectrum of **7e** measured in $CDCl_3$.

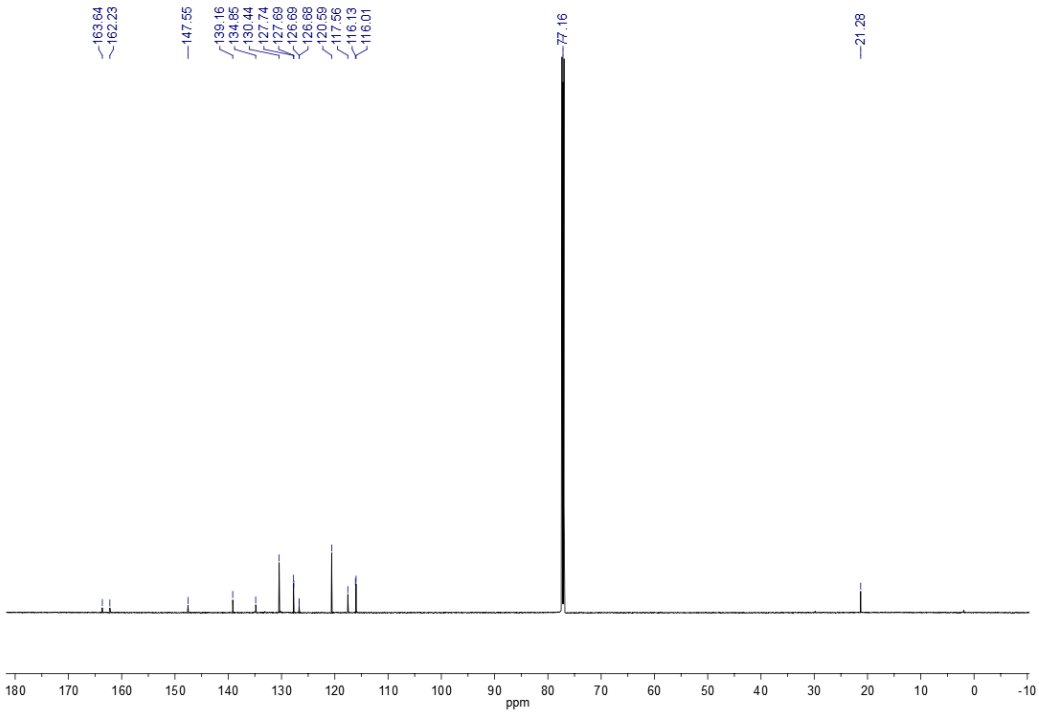


Figure S82. ^{13}C NMR spectrum of **7e** measured in $CDCl_3$.

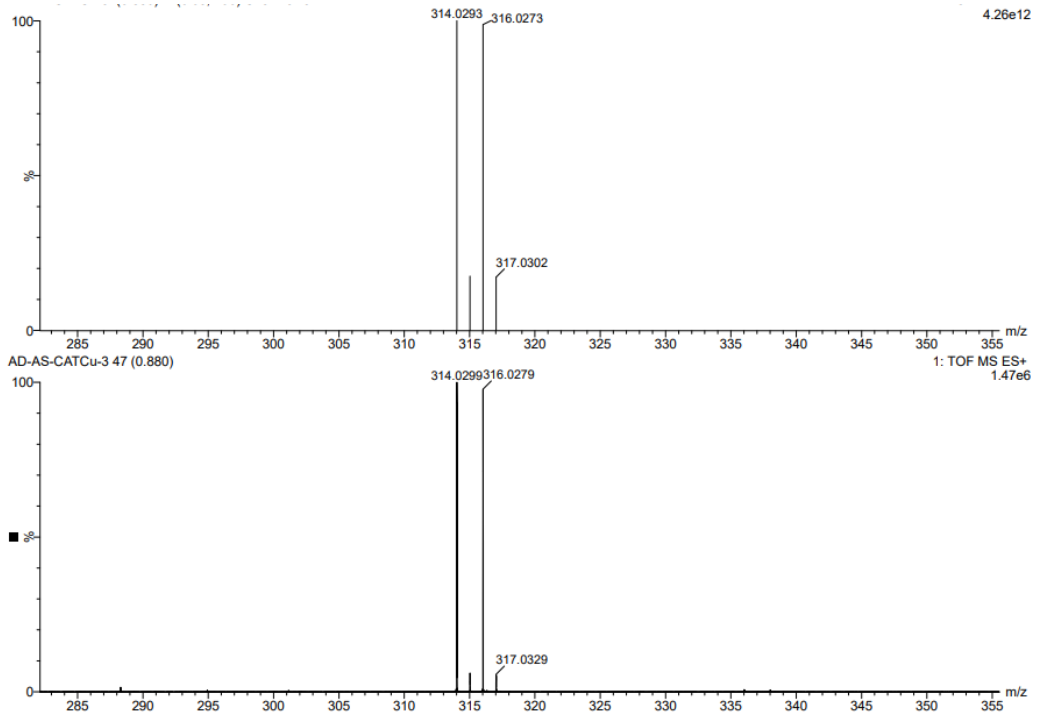


Figure S83. HRMS spectrum of **7e** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

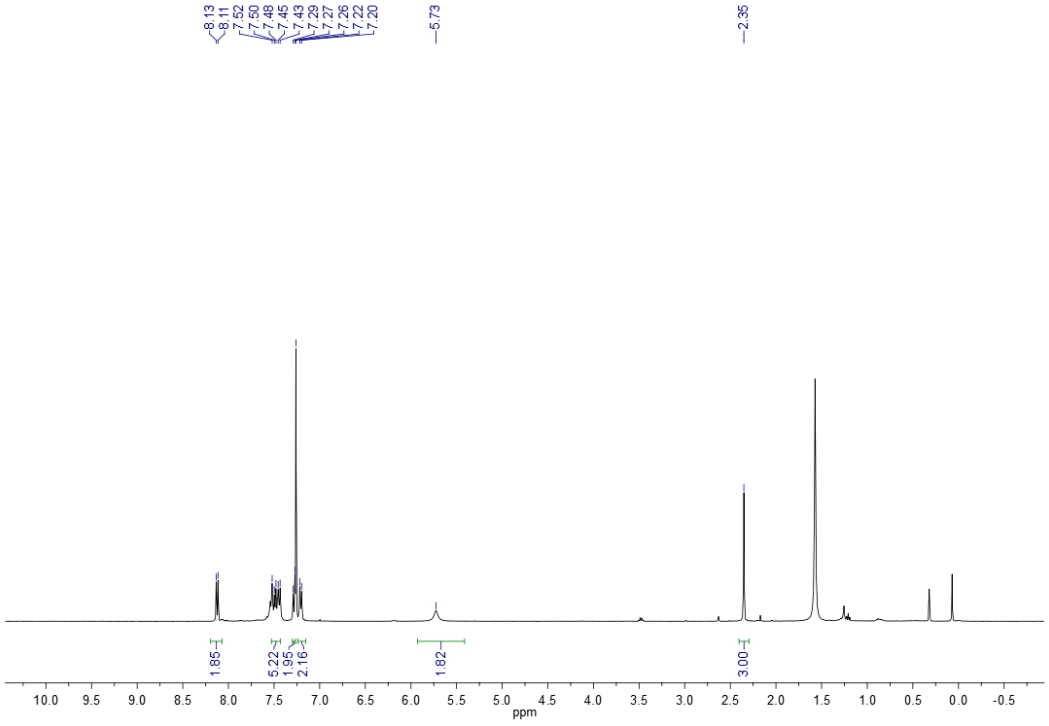


Figure S84. ^{1}H NMR spectrum of 7**f** measured in $CDCl_3$.

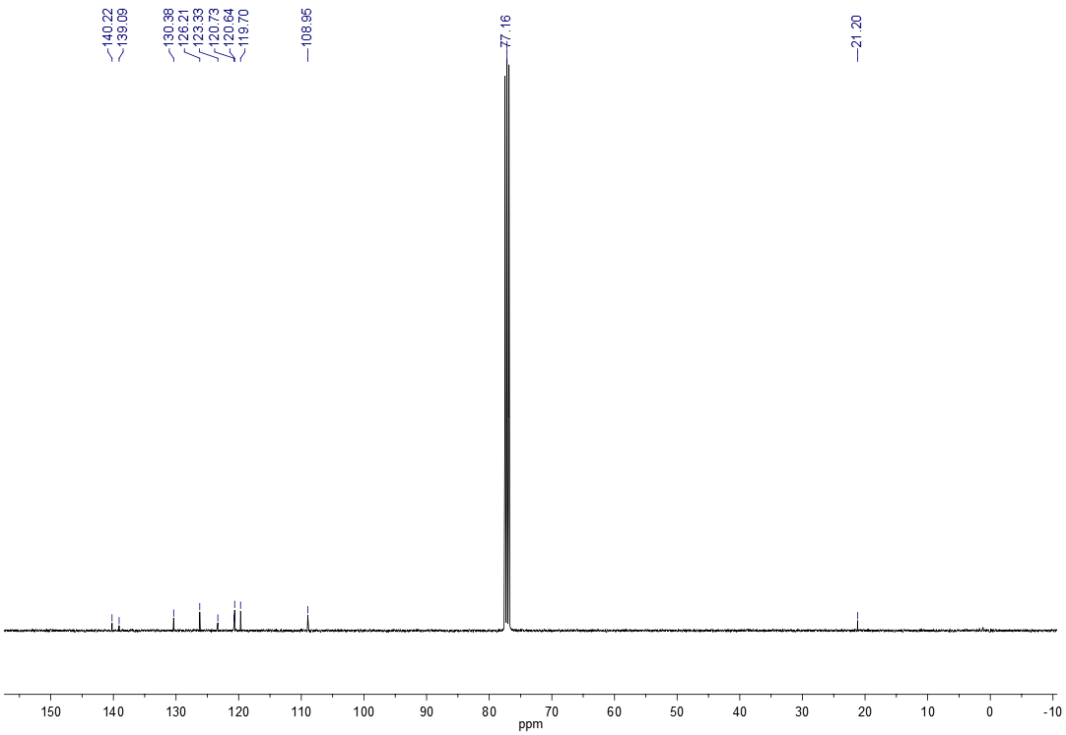


Figure S85. ^{13}C NMR spectrum of 7**f** measured in $CDCl_3$.

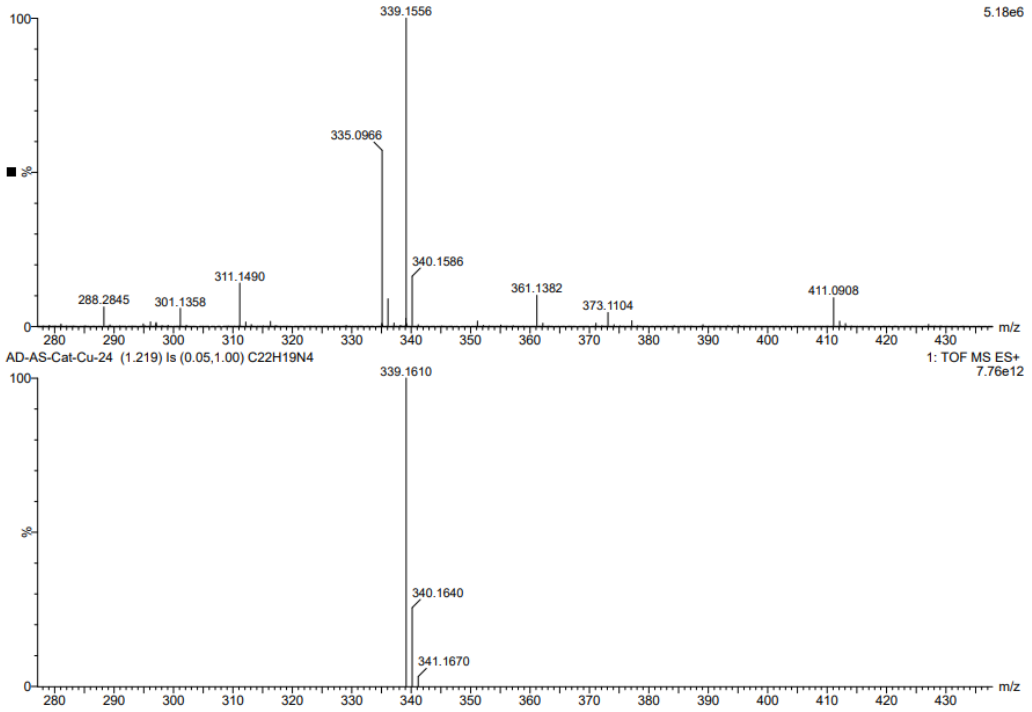


Figure S86. HRMS spectrum of **7f** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

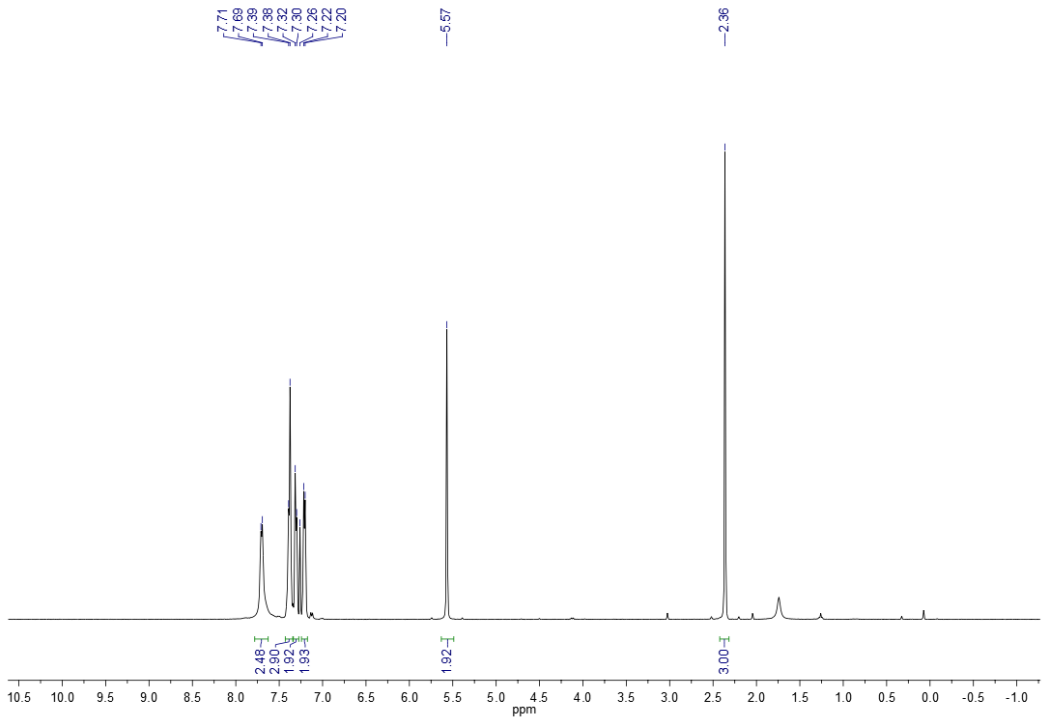


Figure S87. ^{1}H NMR spectrum of **7g** measured in $CDCl_3$.

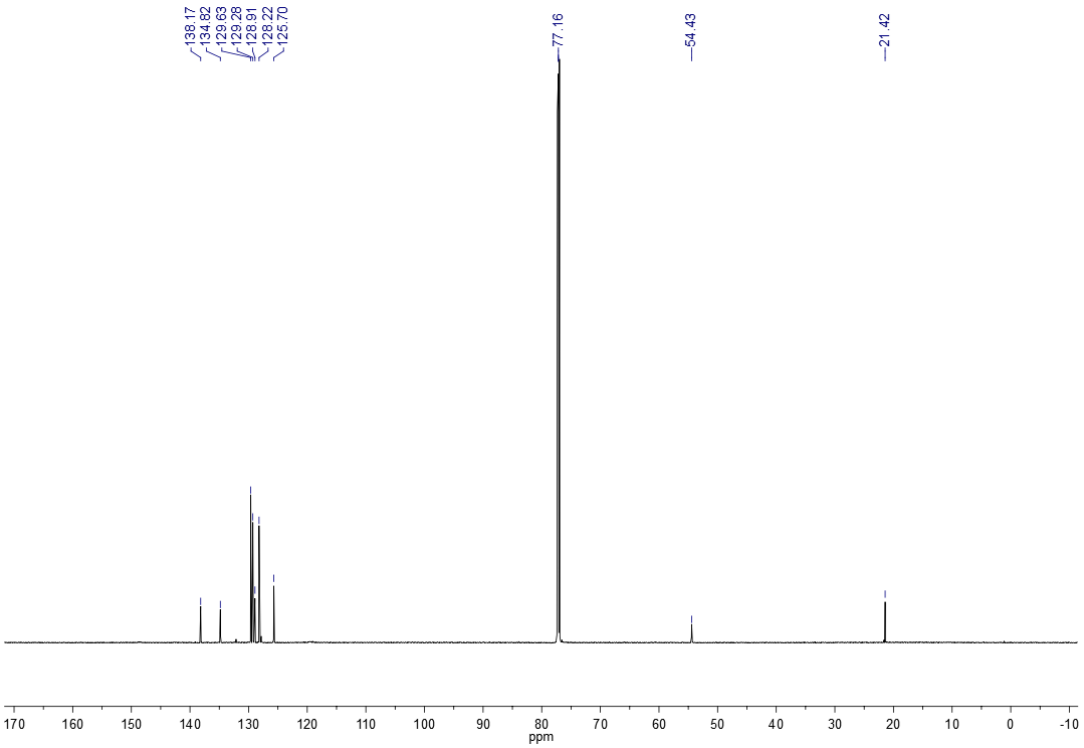


Figure S88. ^{13}C NMR spectrum of **7g** measured in $CDCl_3$.

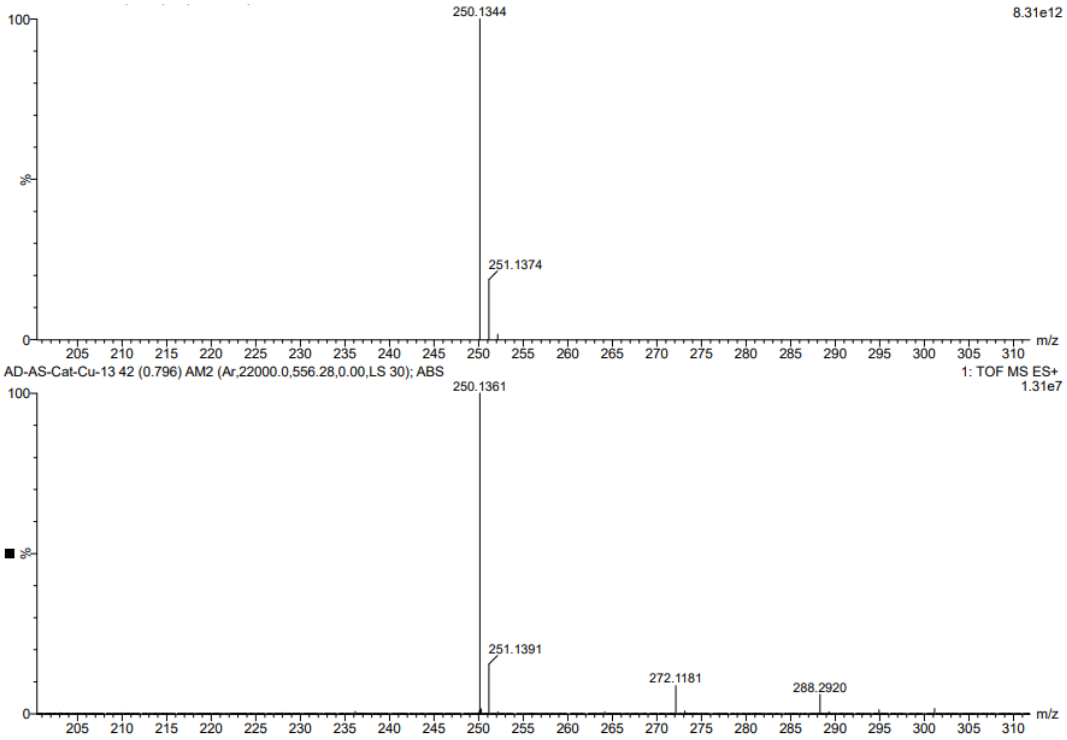


Figure S89. HRMS spectrum of **7g** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

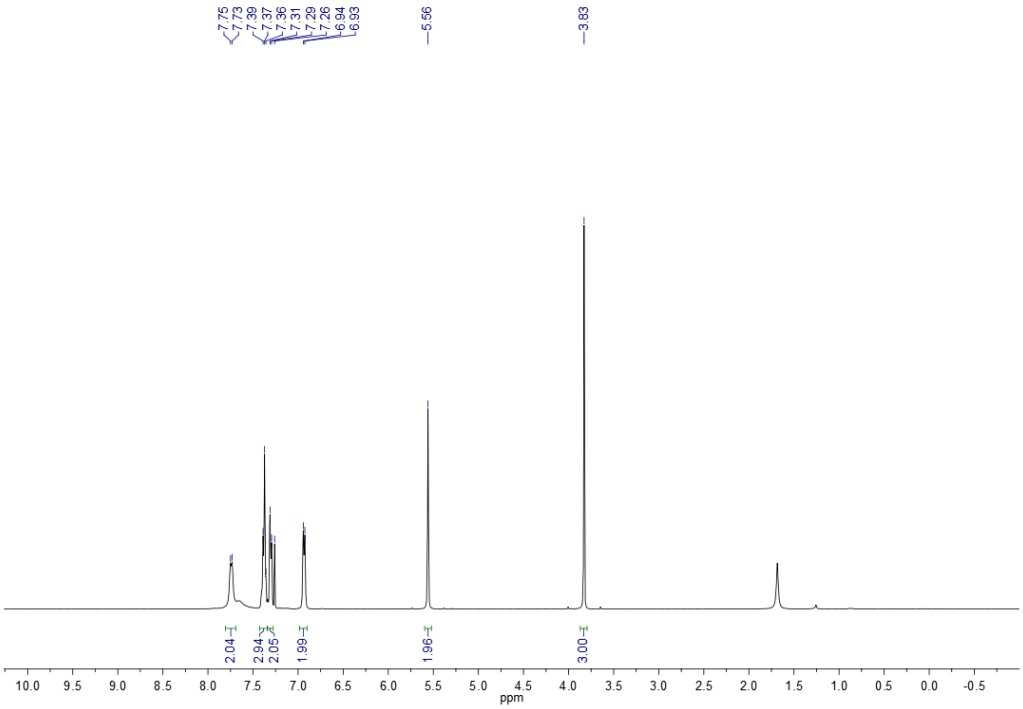


Figure S90. ^{1}H NMR spectrum of 7**h** measured in $CDCl_3$.

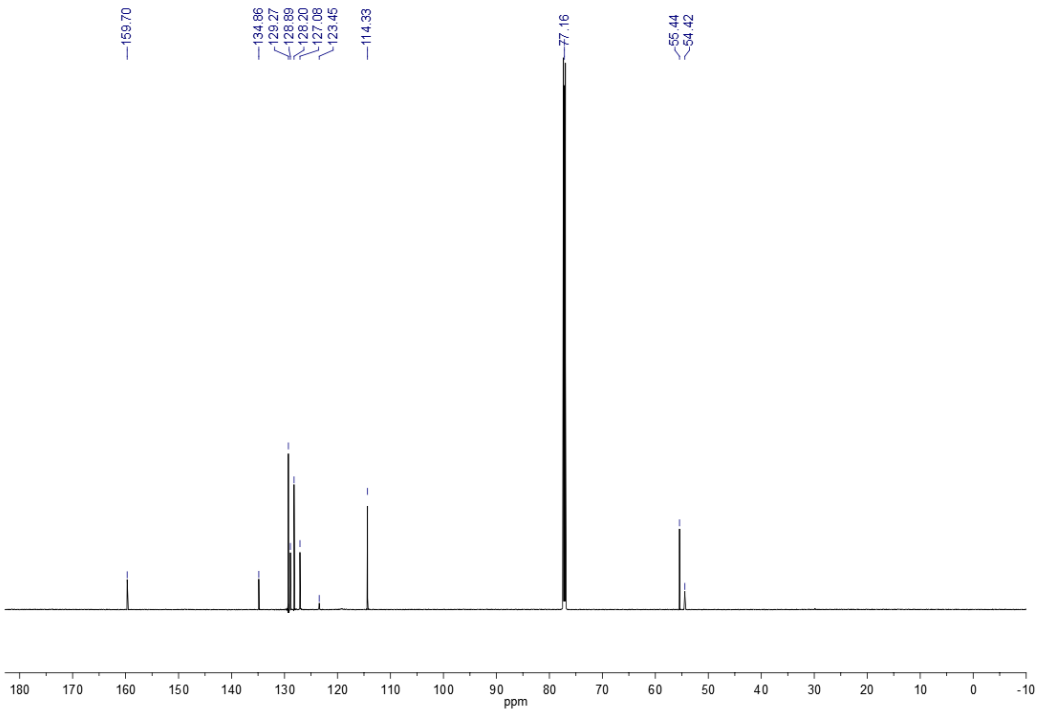


Figure S91. ^{13}C NMR spectrum of **7h** measured in $CDCl_3$.

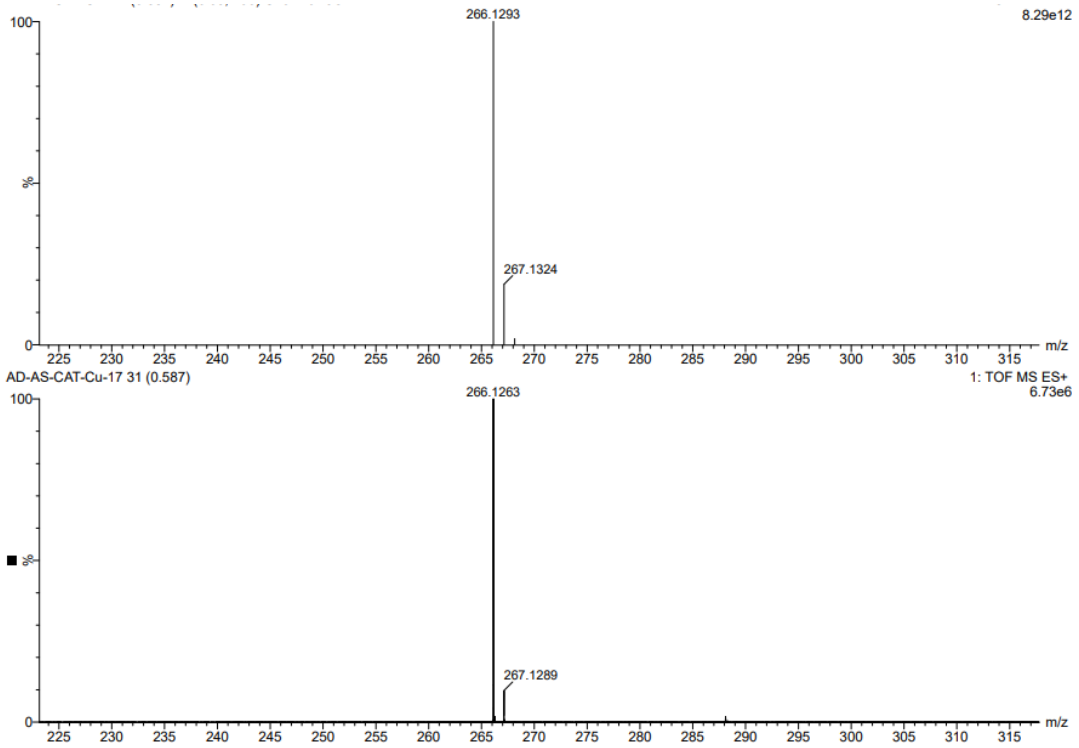


Figure S92. HRMS spectrum of **7h** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

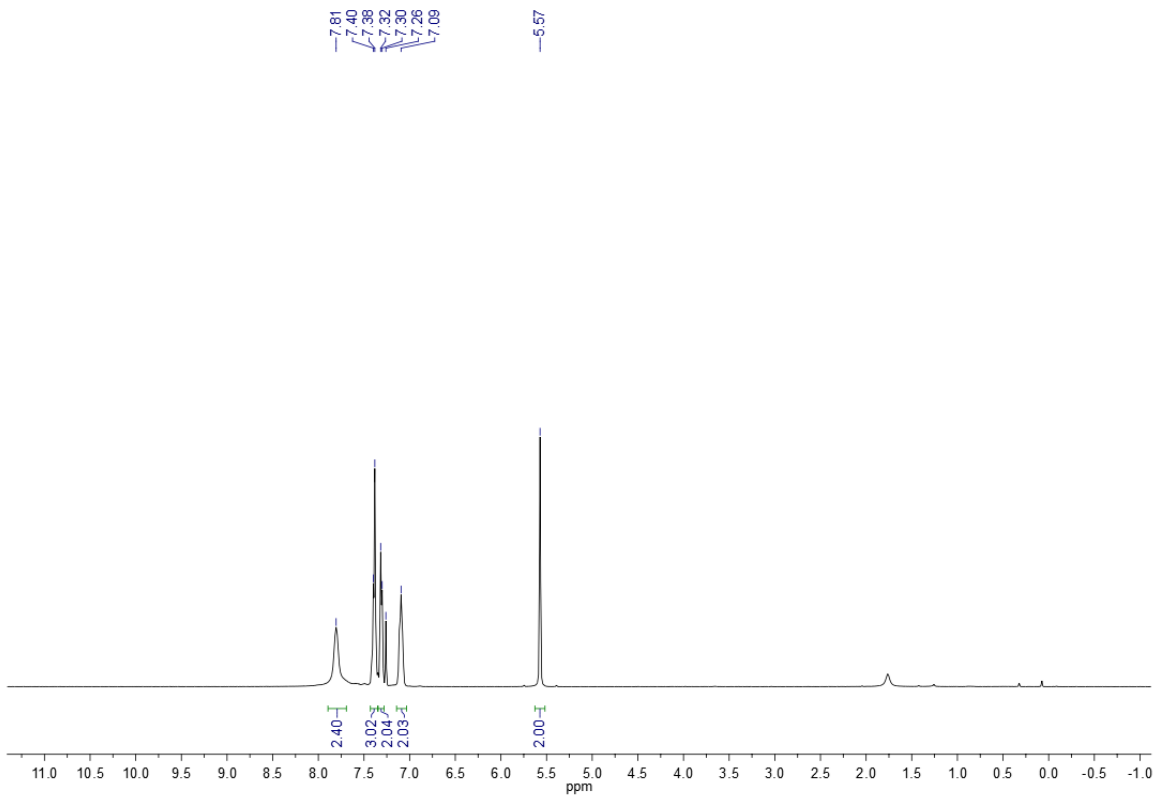


Figure S93. ^{1}H NMR spectrum of **7i** measured in $CDCl_3$.

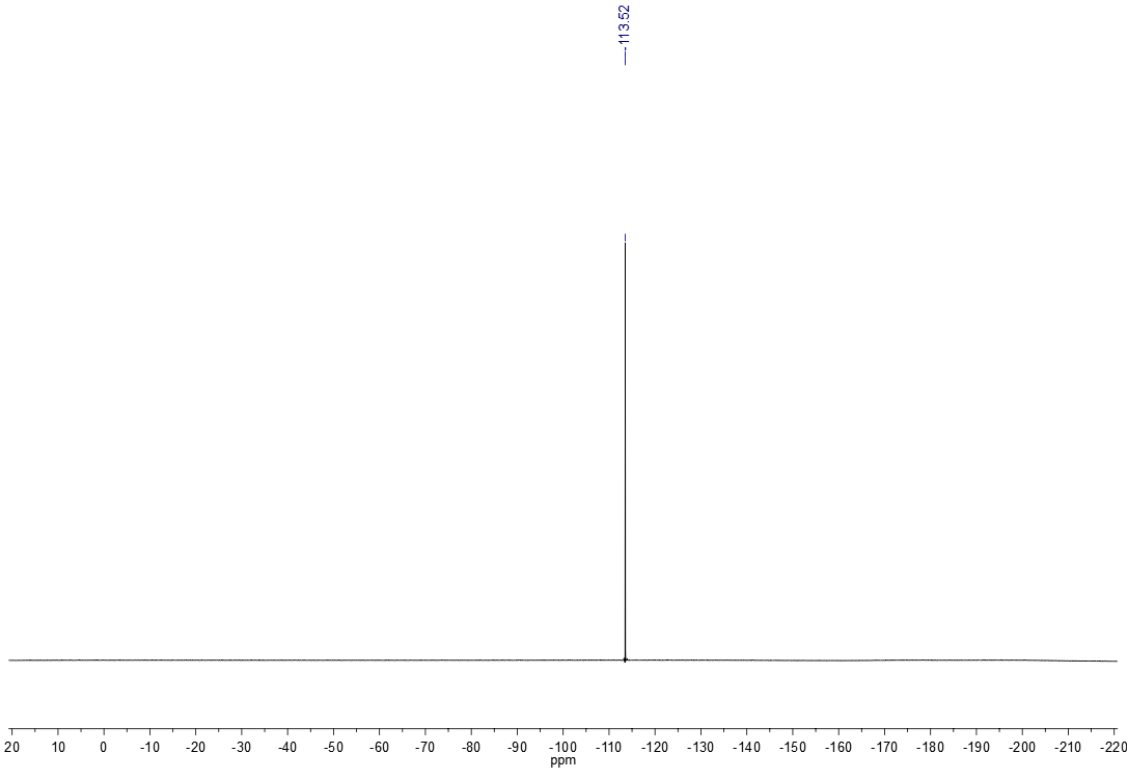


Figure S94. ^{19}F NMR spectrum of **7i** measured in $CDCl_3$.

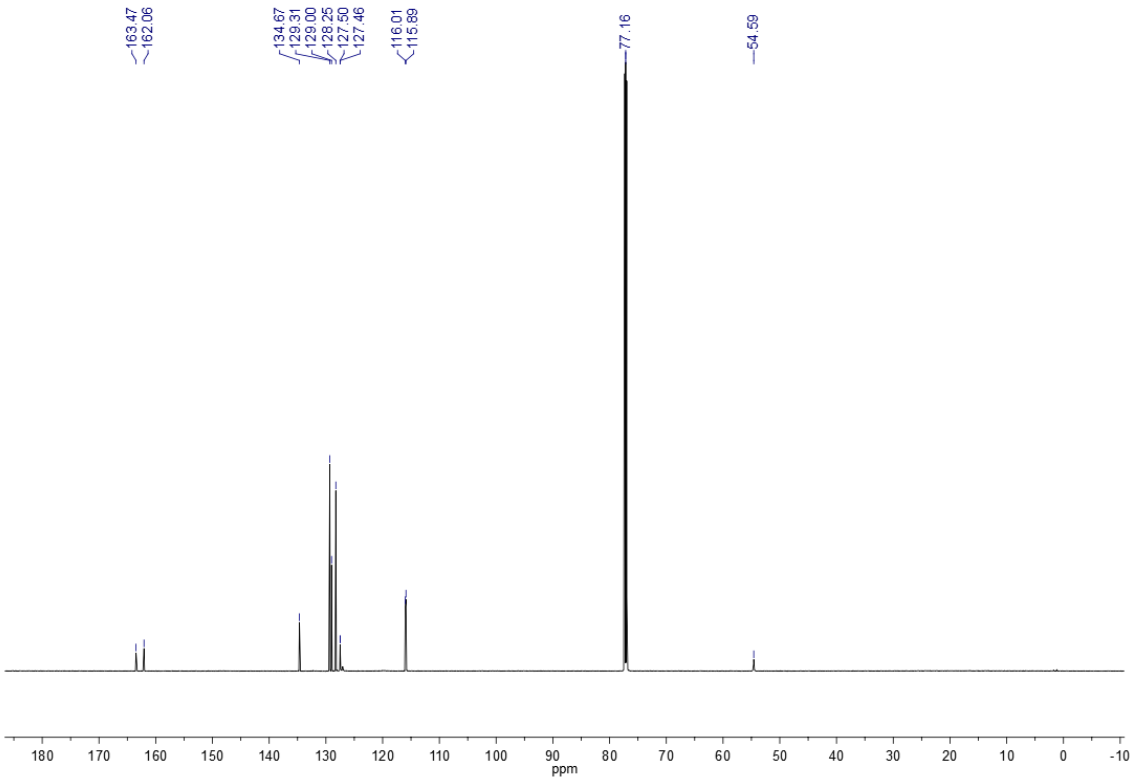


Figure S95. ^{13}C NMR spectrum of **7i** measured in $CDCl_3$.

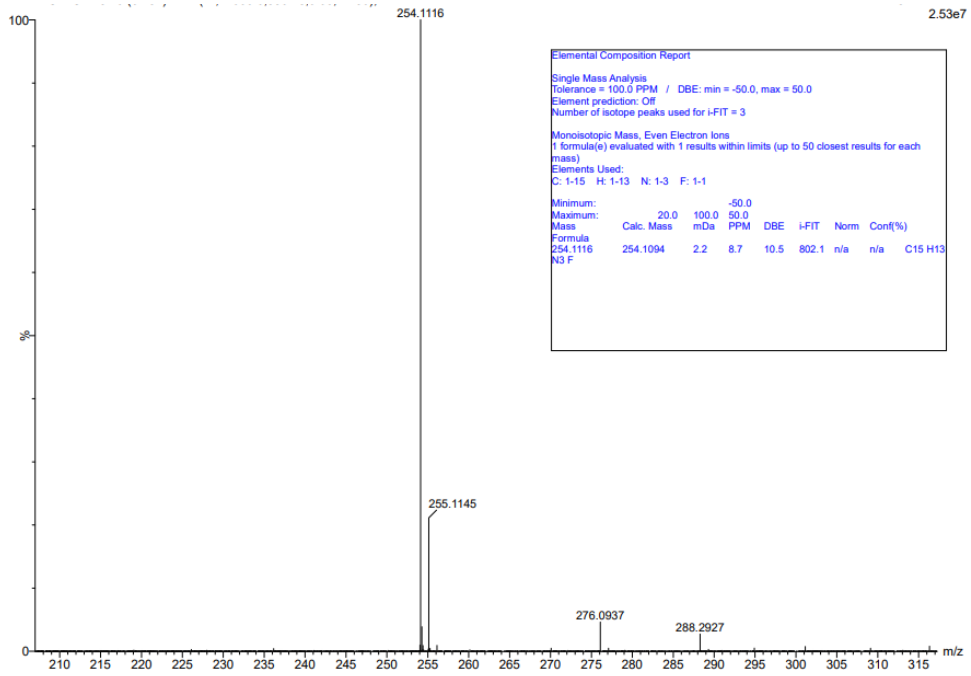


Figure S96. HRMS spectrum of **7i** measured in methanol.

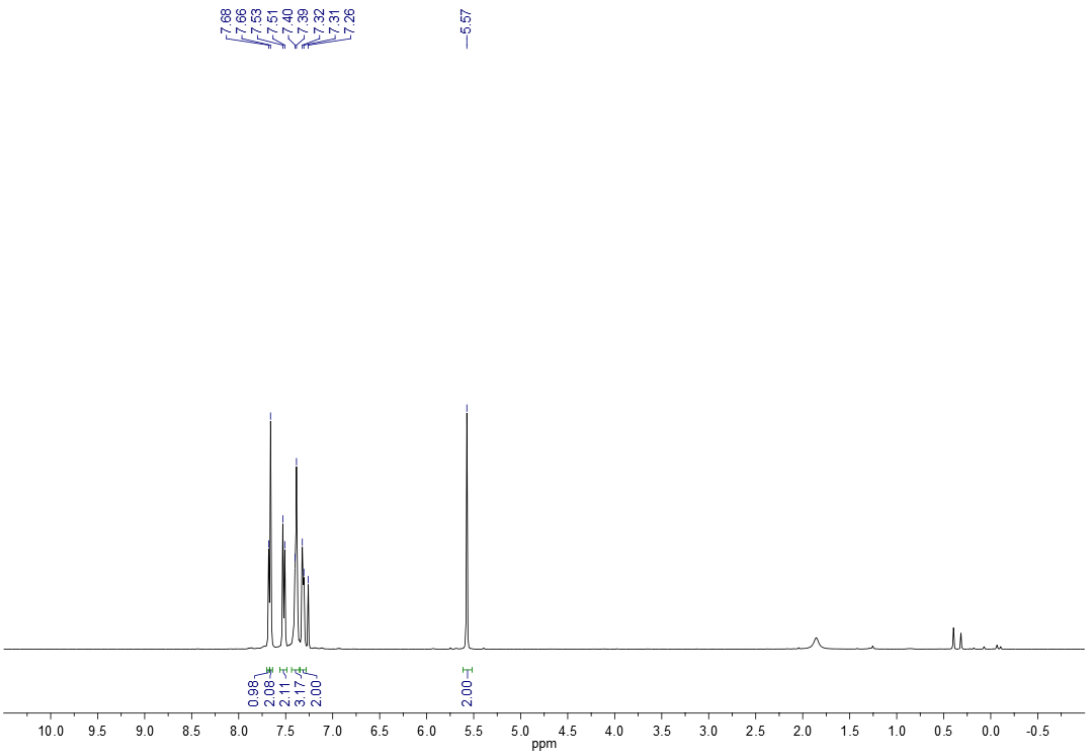


Figure S97. ^{1}H NMR spectrum of **7j** measured in $CDCl_3$.

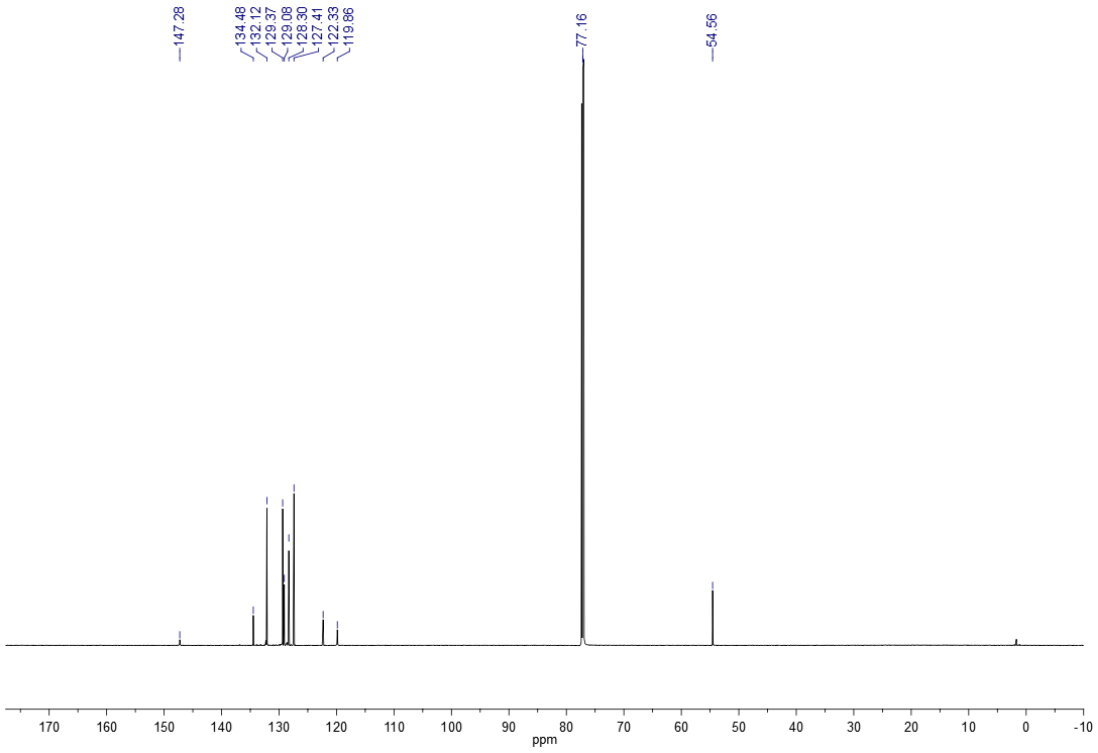


Figure S98. ^{13}C NMR spectrum of **7j** measured in $CDCl_3$.

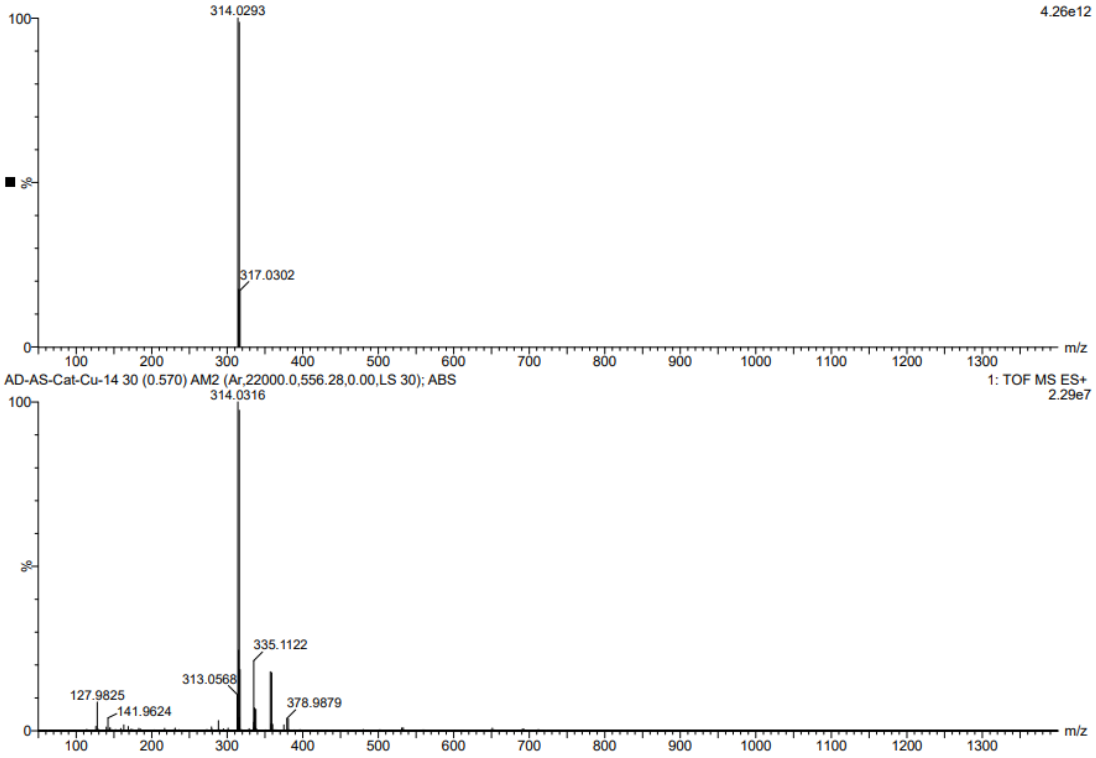


Figure S99. HRMS spectrum of **7j** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

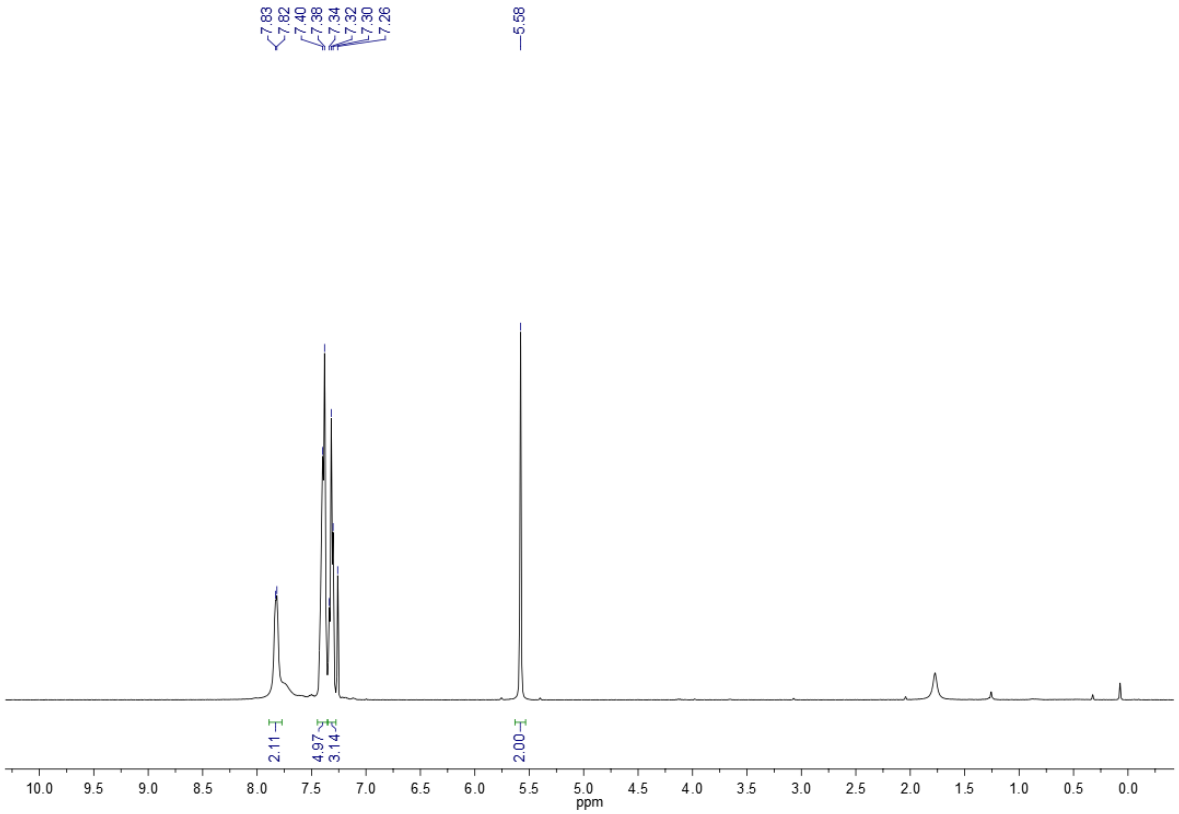


Figure S100. ^{1}H NMR spectrum of **7k** measured in $CDCl_3$.

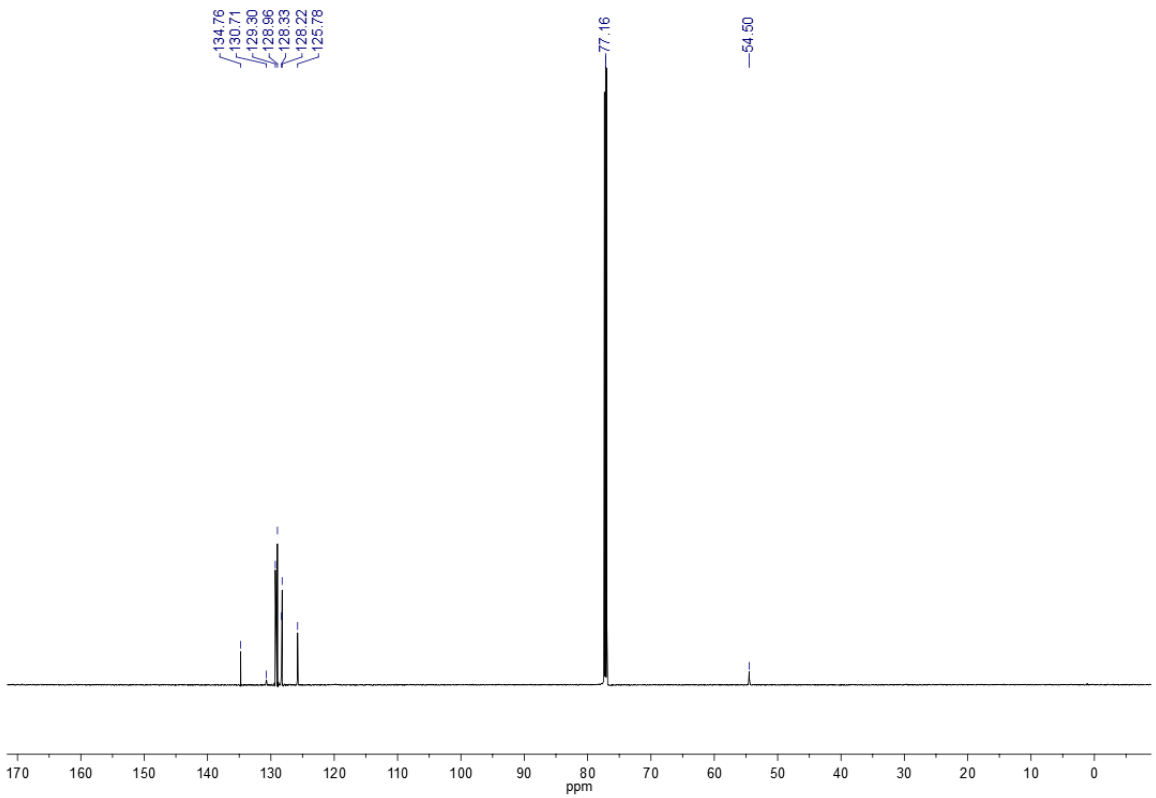


Figure S101. ^{13}C NMR spectrum of **7k** measured in $CDCl_3$.

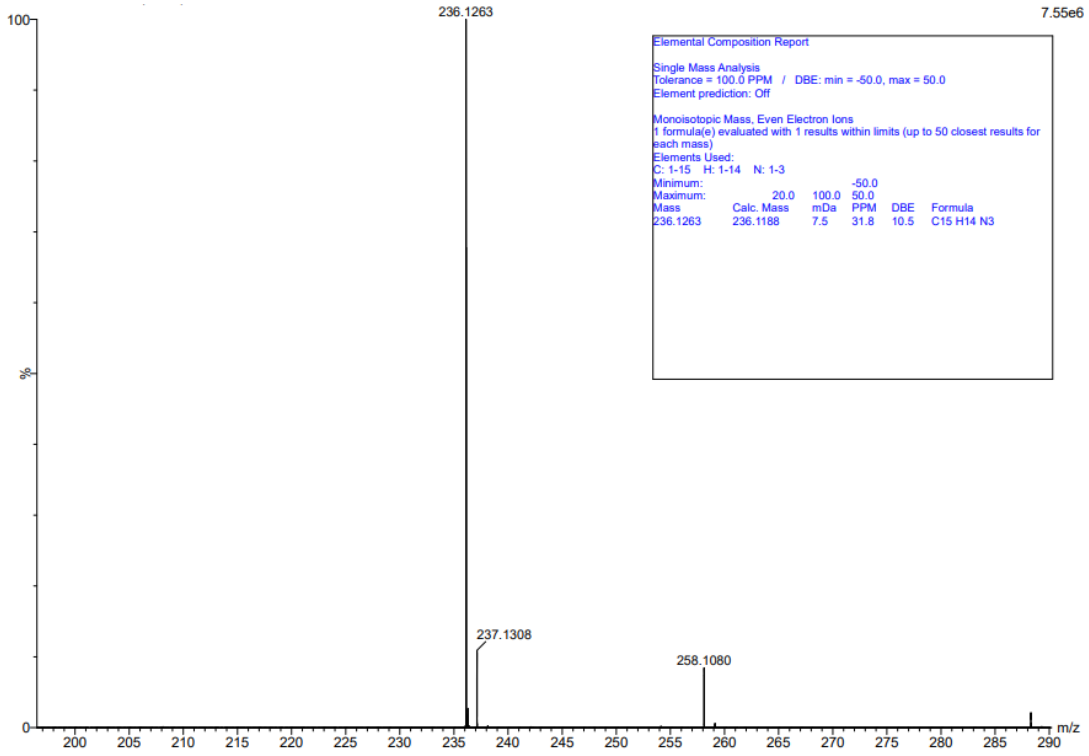


Figure S102. HRMS report of **7k** measured in methanol.

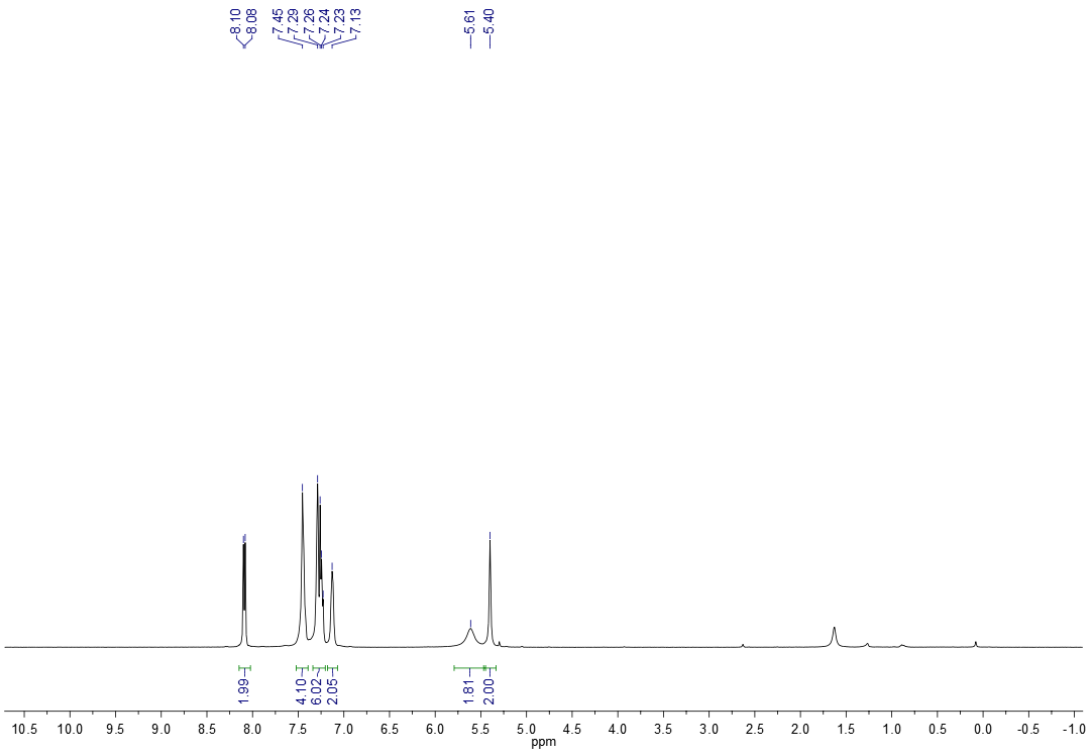


Figure S103. ^{1}H NMR spectrum of **7l** measured in $CDCl_3$.

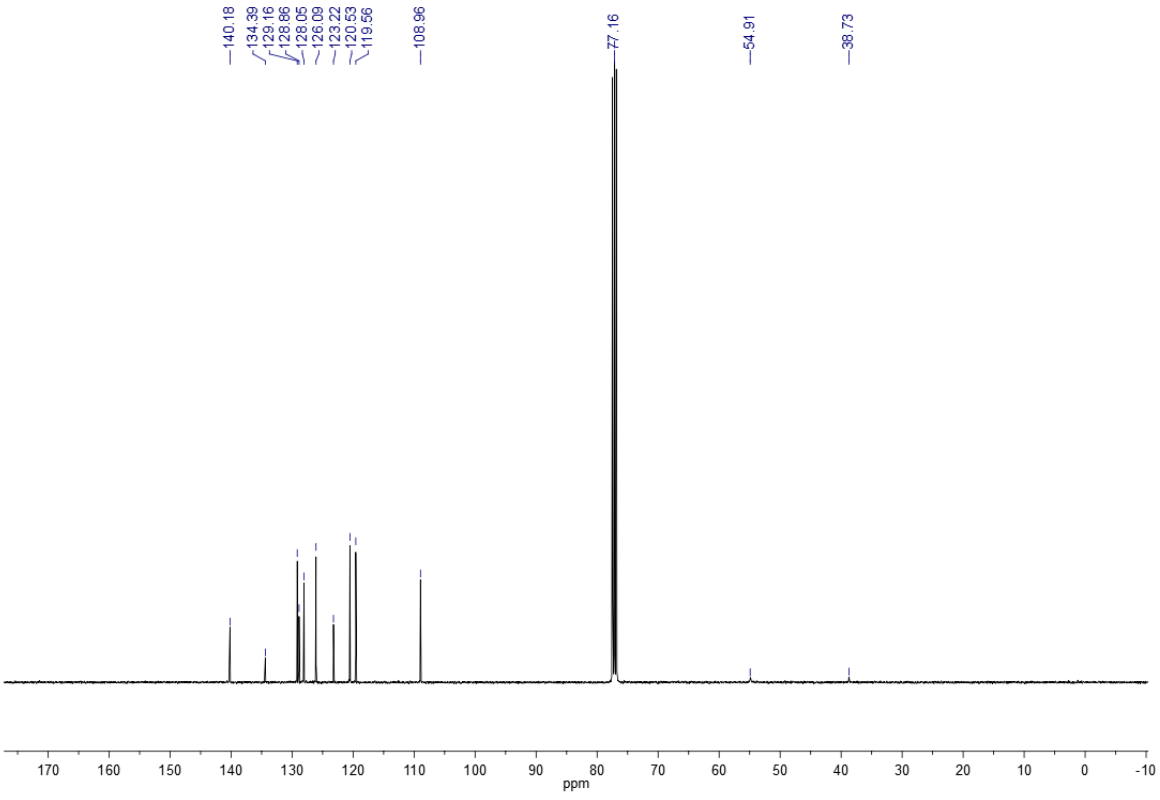


Figure S104. ^{13}C NMR spectrum of **7l** measured in $CDCl_3$.

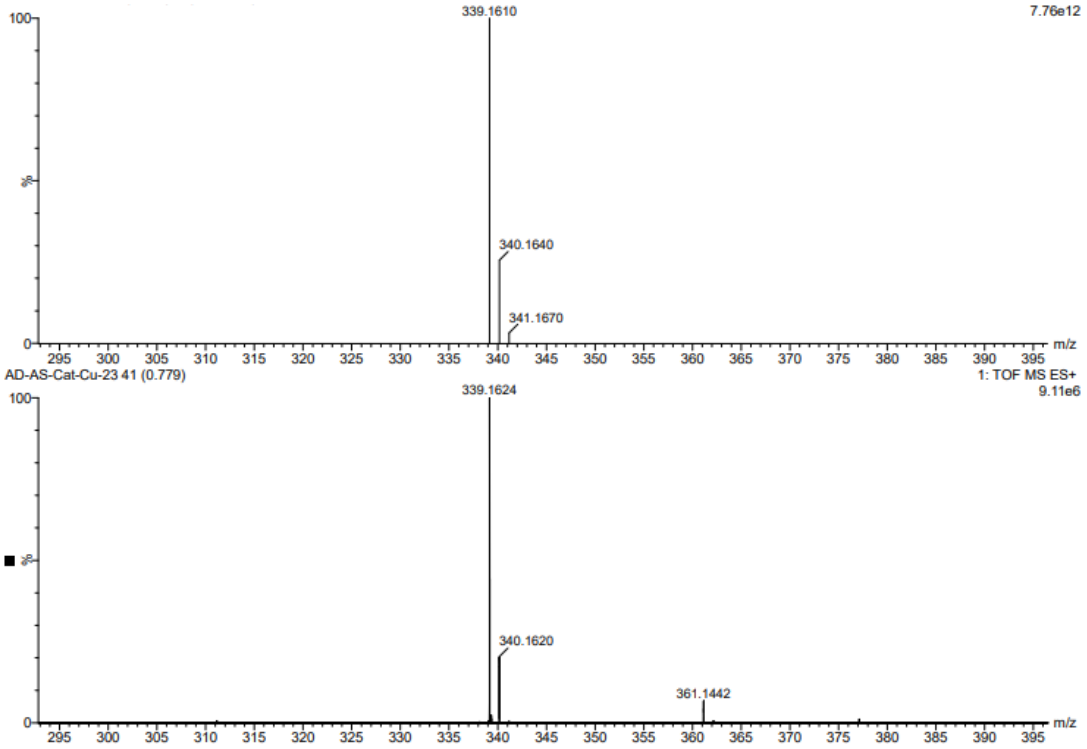


Figure S105. HRMS spectrum of **7l** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

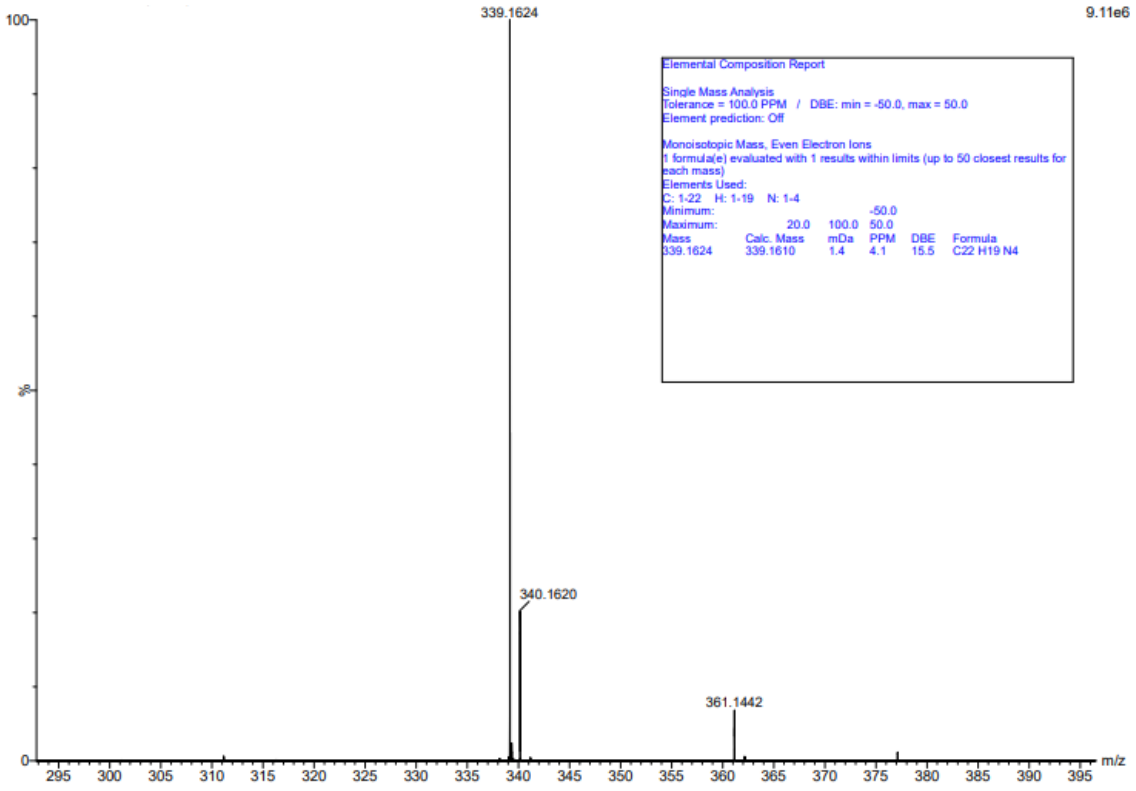


Figure S106. HRMS report of **7l** measured in methanol.

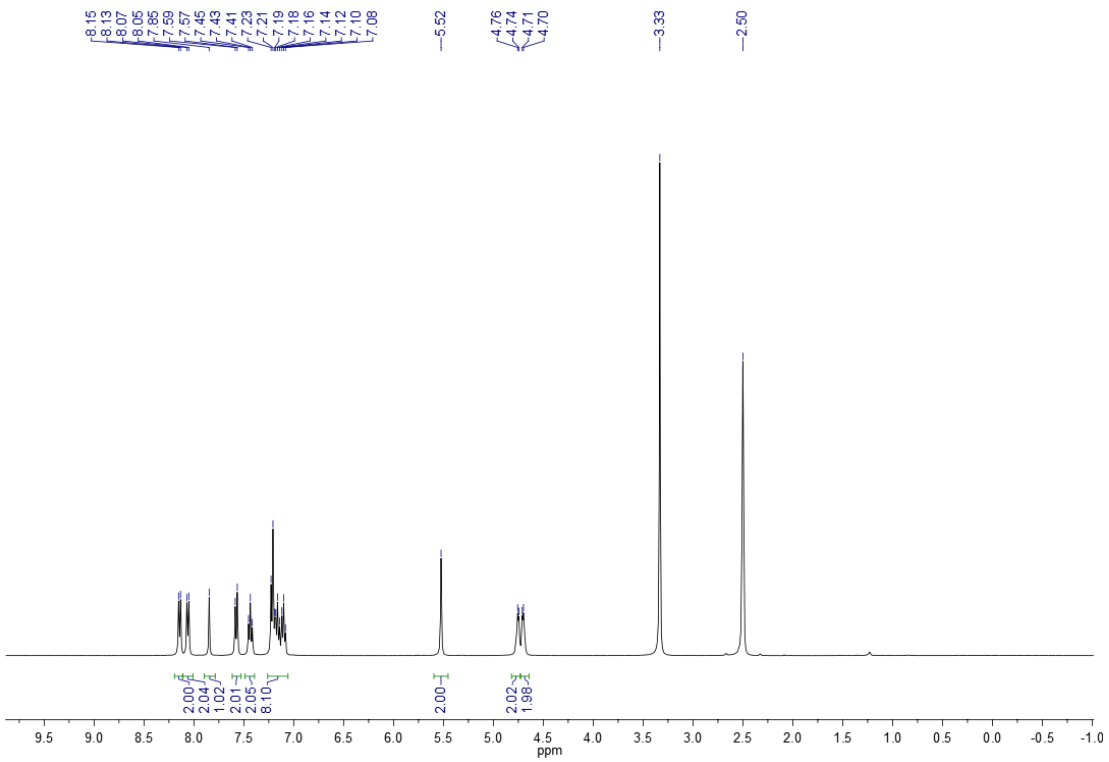


Figure S107. ^{1}H NMR spectrum of Synthesis of **7m** measured in DMSO-d_6.

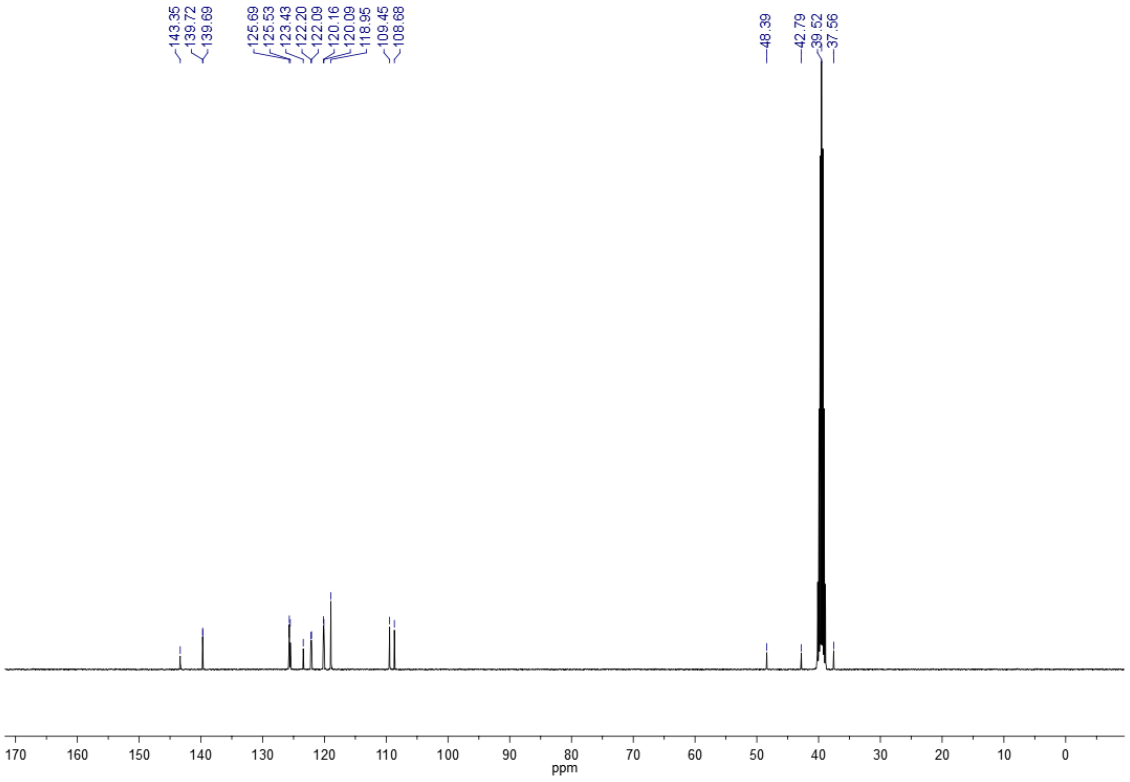


Figure S108. ^{13}C NMR spectrum of Synthesis of **7m** measured in DMSO-d_6.

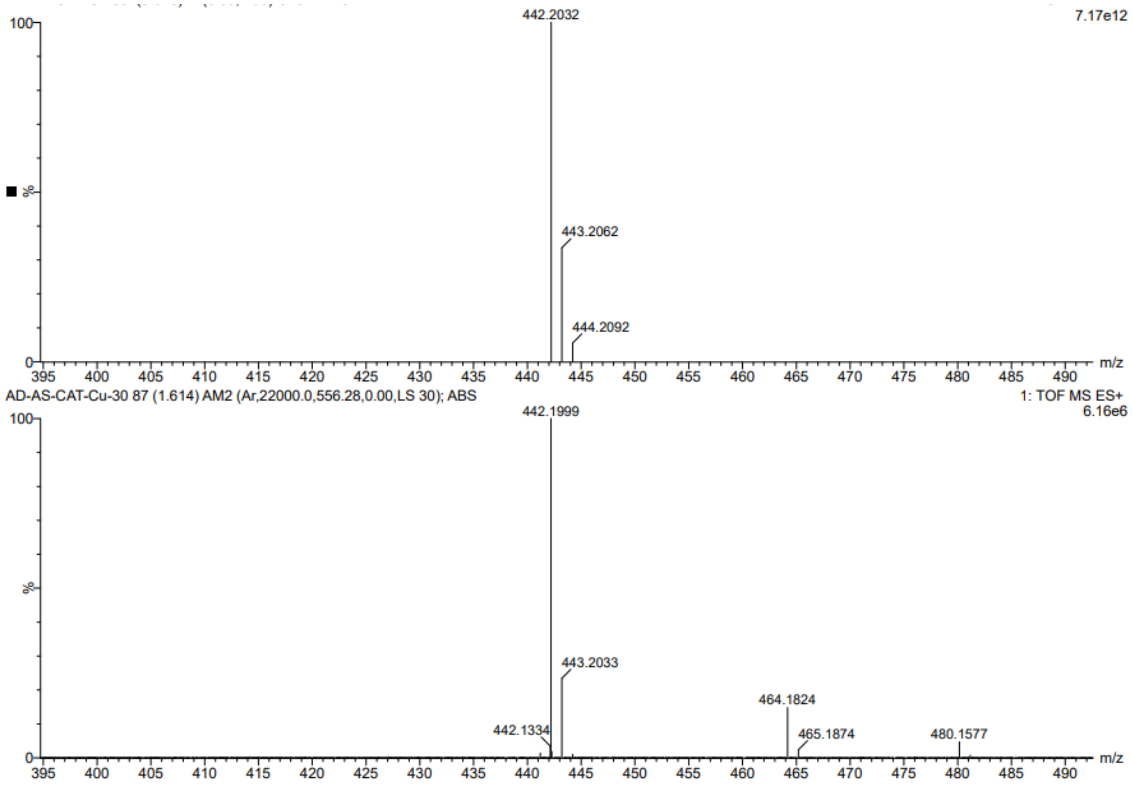


Figure S109. HRMS spectrum of Synthesis of **7m** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

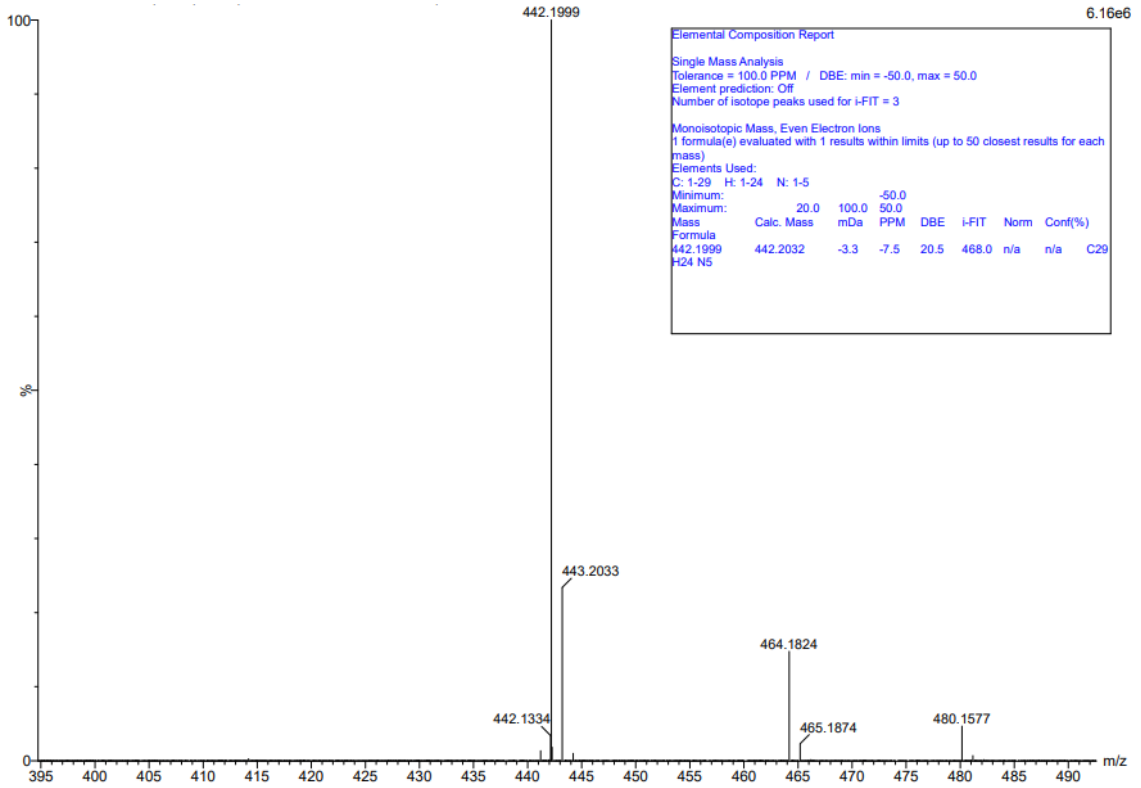


Figure S110. HRMS report of Synthesis of **7m** measured in methanol.

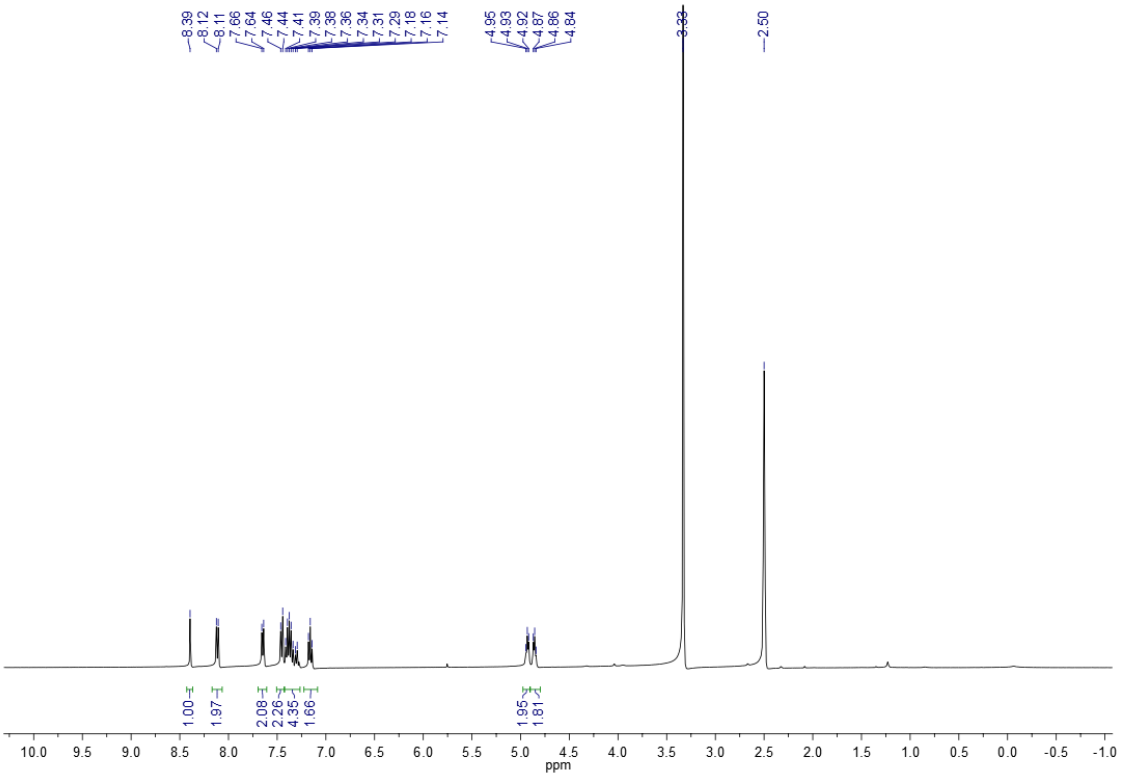


Figure S111. ^{1}H NMR spectrum of **7n** measured in DMSO-d_6.

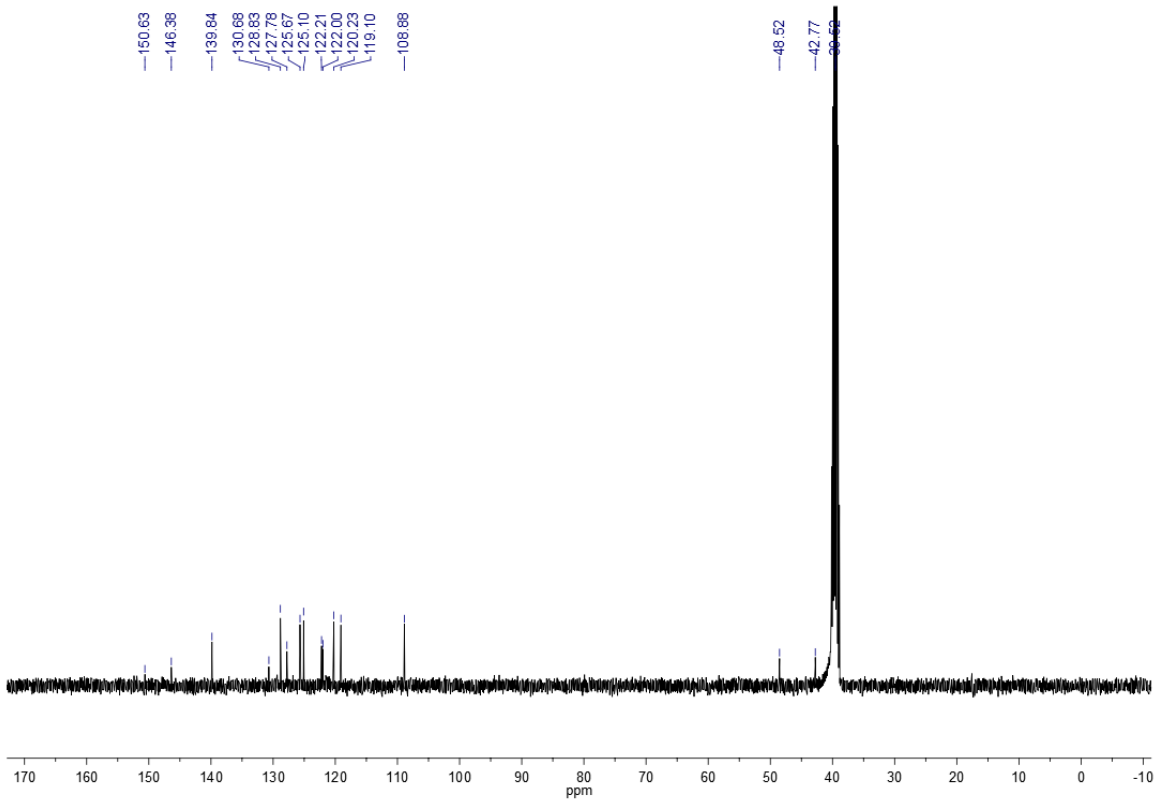


Figure S112. ^{13}C NMR spectrum of **7n** measured in DMSO-d_6.

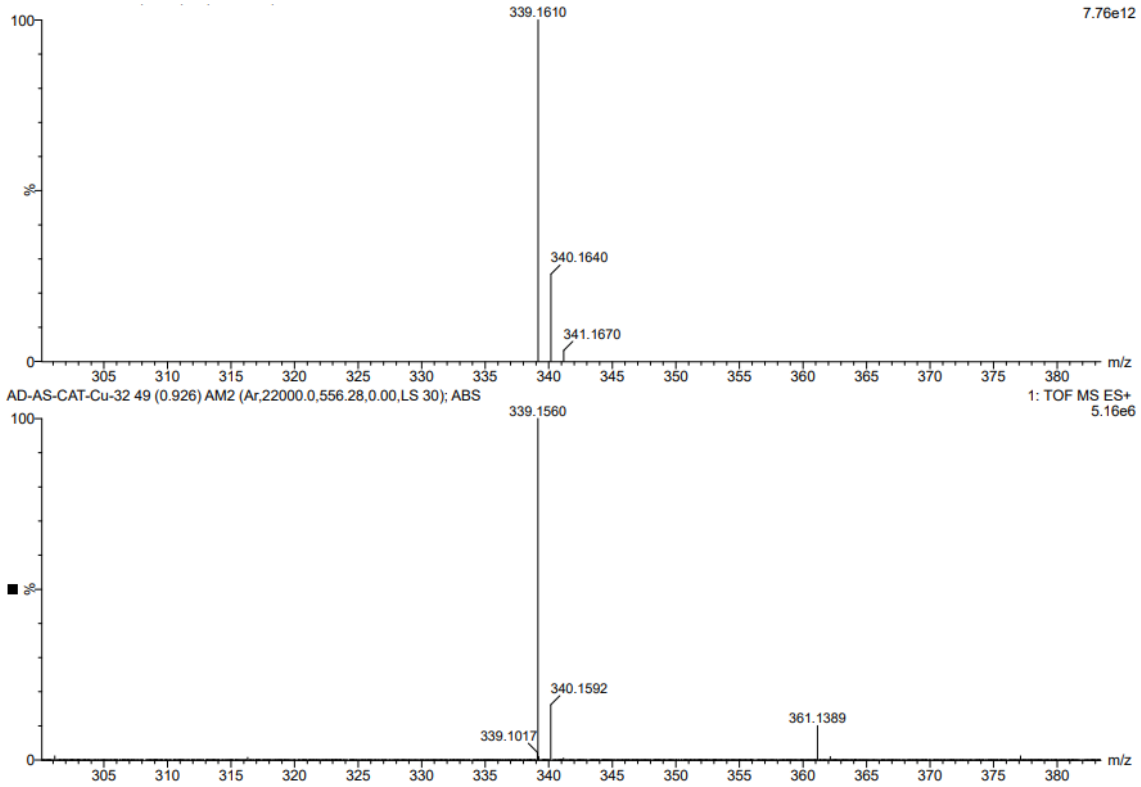


Figure S113. HRMS spectrum of **7n** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

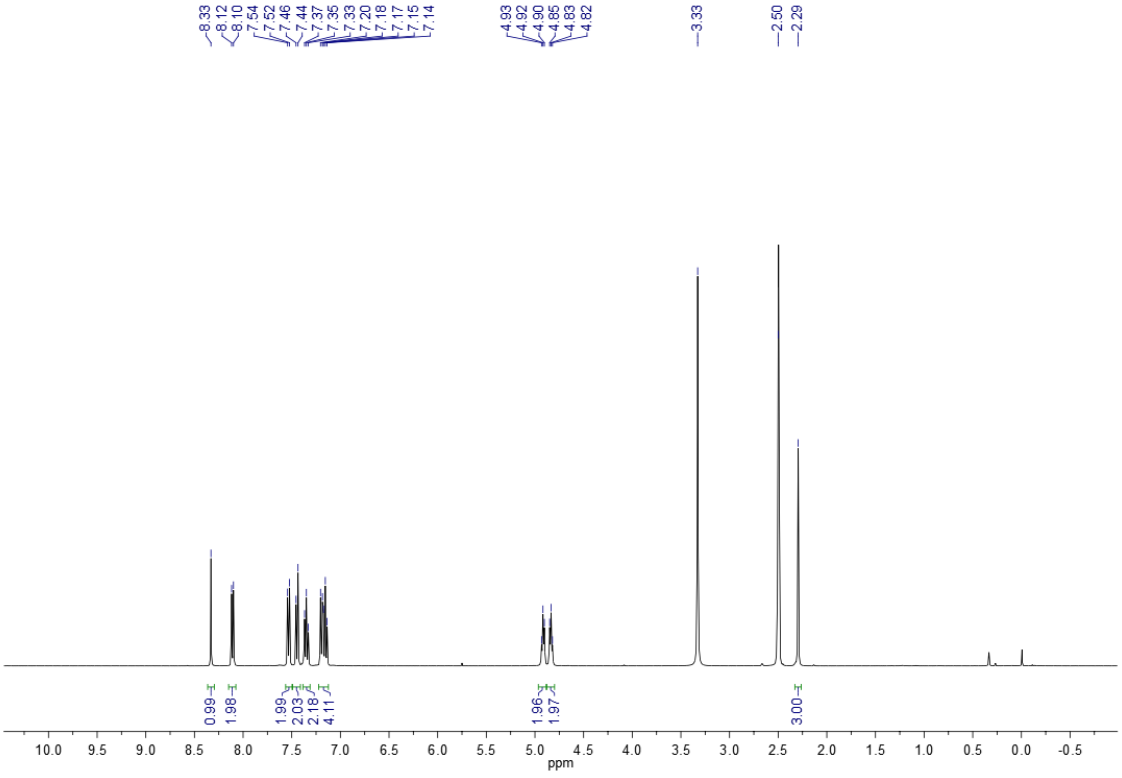


Figure S114. ^{1}H NMR spectrum of **7o** measured in DMSO-d_6.

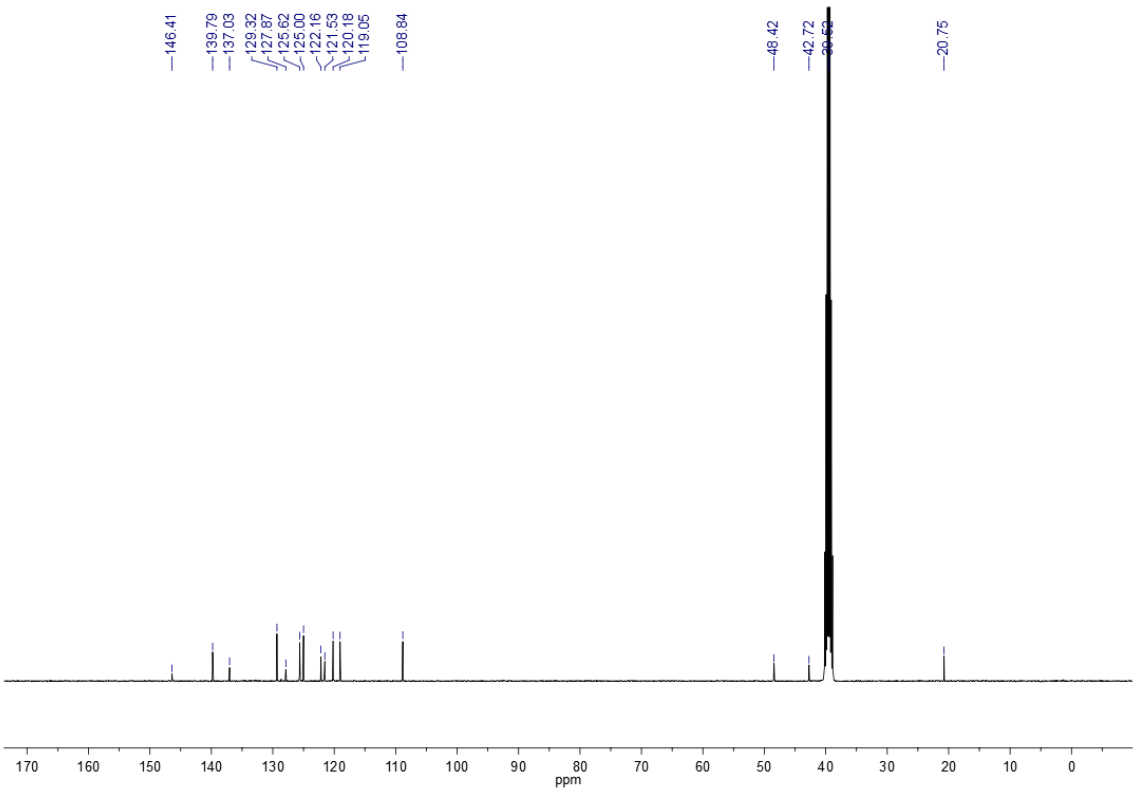


Figure S115. ^{13}C NMR spectrum of **7o** measured in DMSO-d_6.

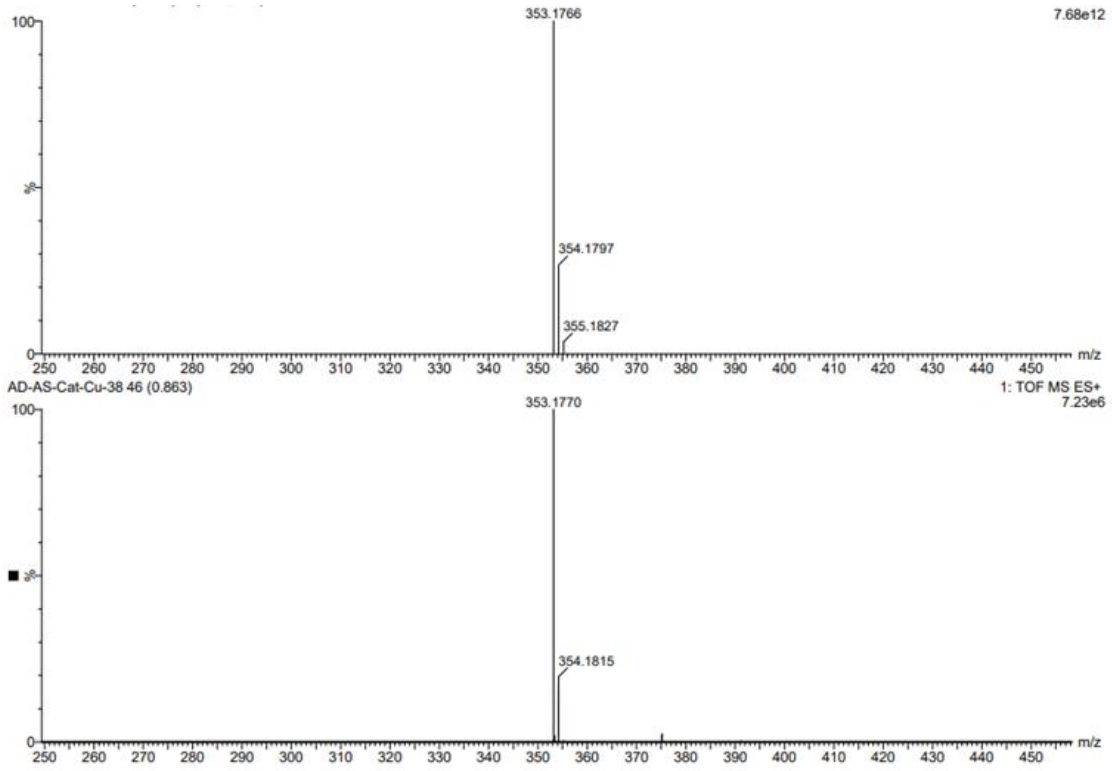


Figure S116. HRMS spectrum of **7o** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

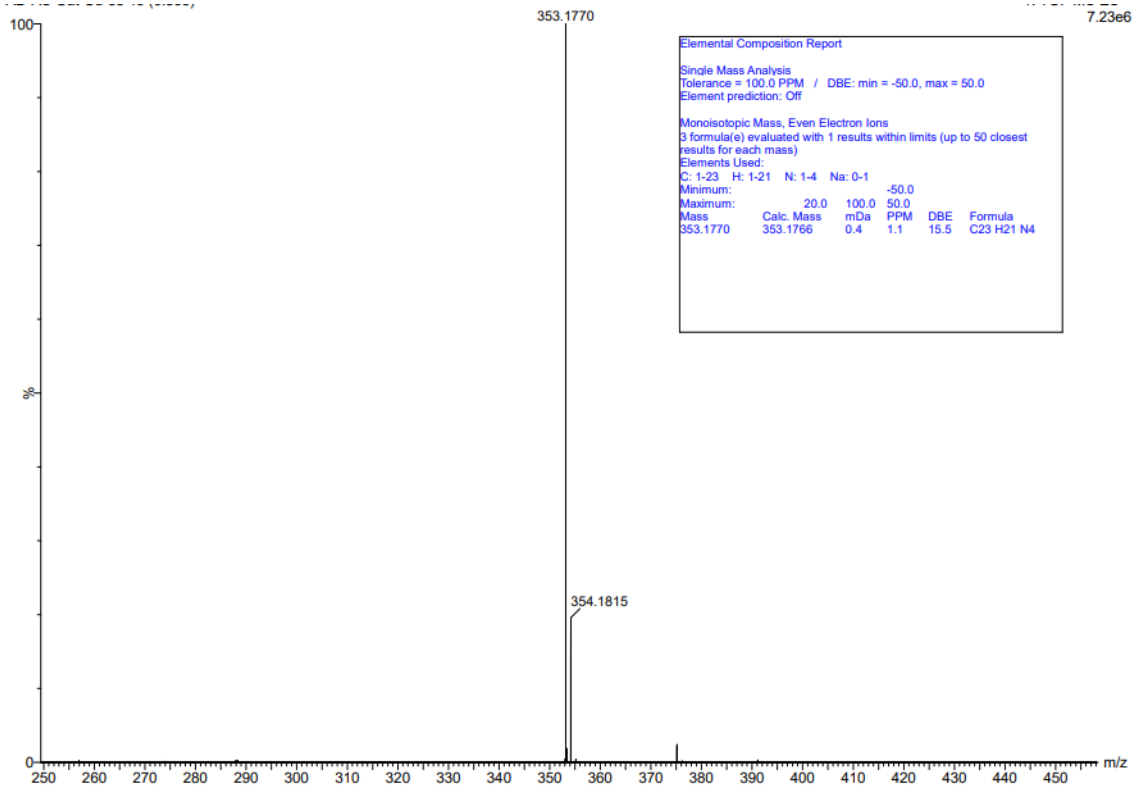


Figure S117. HRMS report of **7o** measured in methanol.

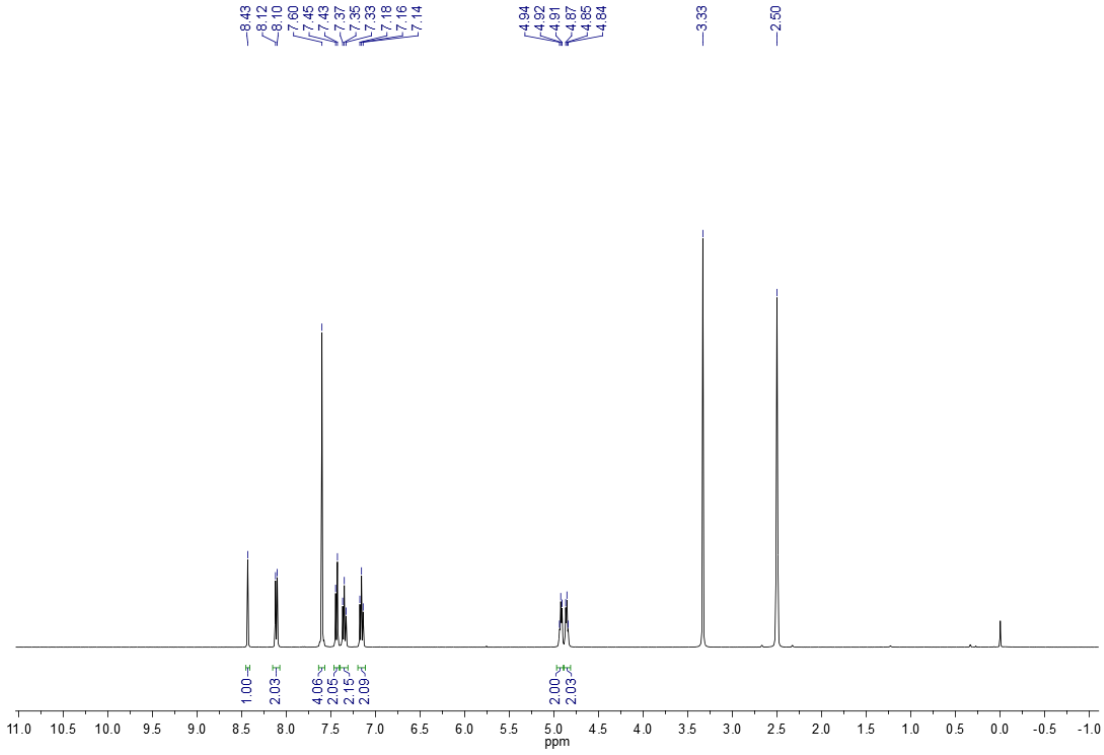


Figure S118. ^{1}H NMR spectrum of **7p** measured in DMSO-d_6.

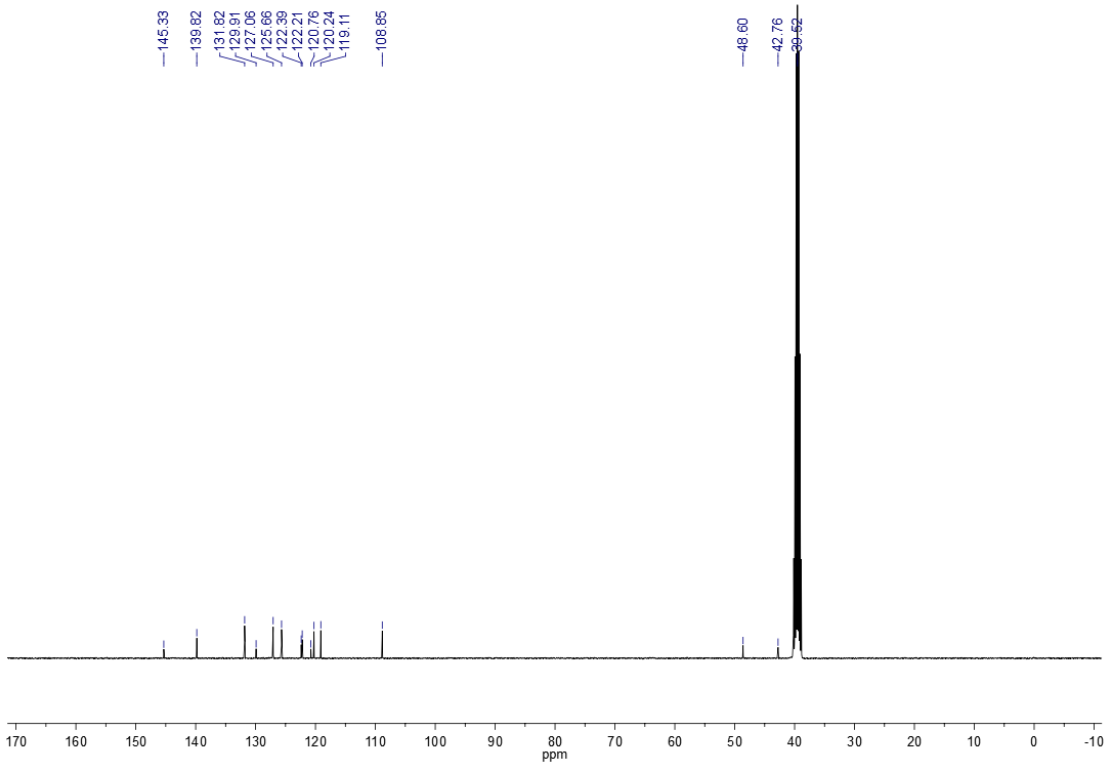


Figure S119. ^{13}C NMR spectrum of **7p** measured in DMSO-d_6.

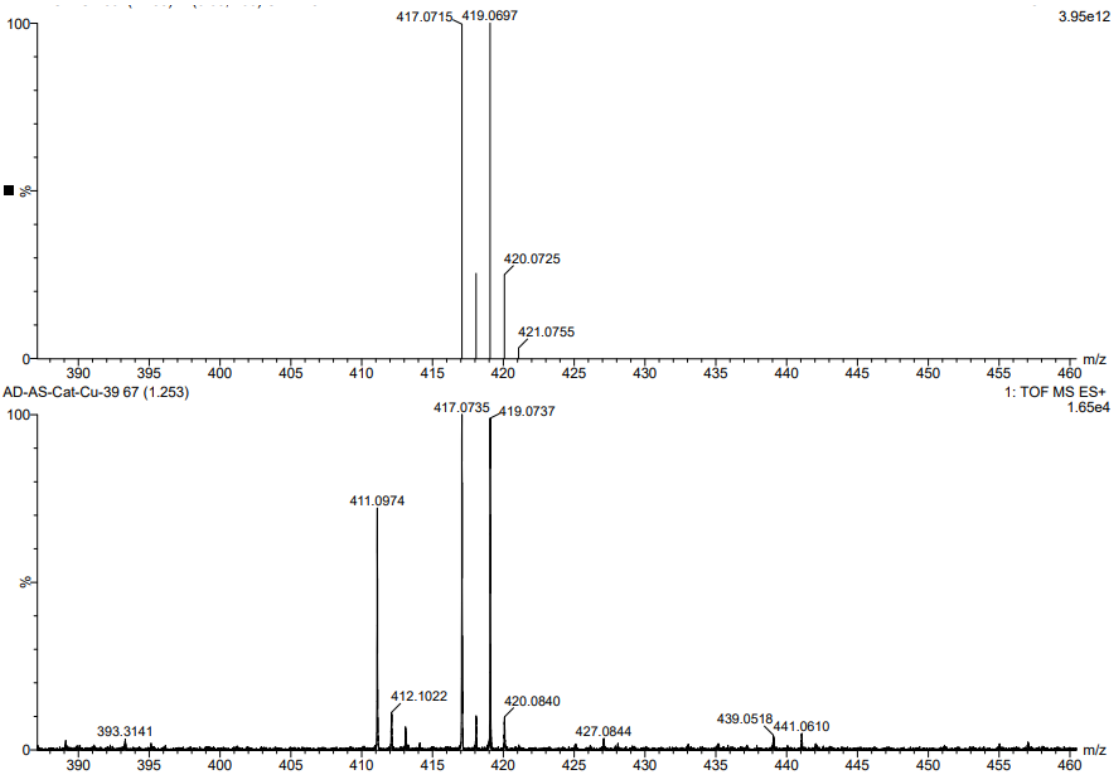


Figure S120. HRMS spectrum of **7p** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

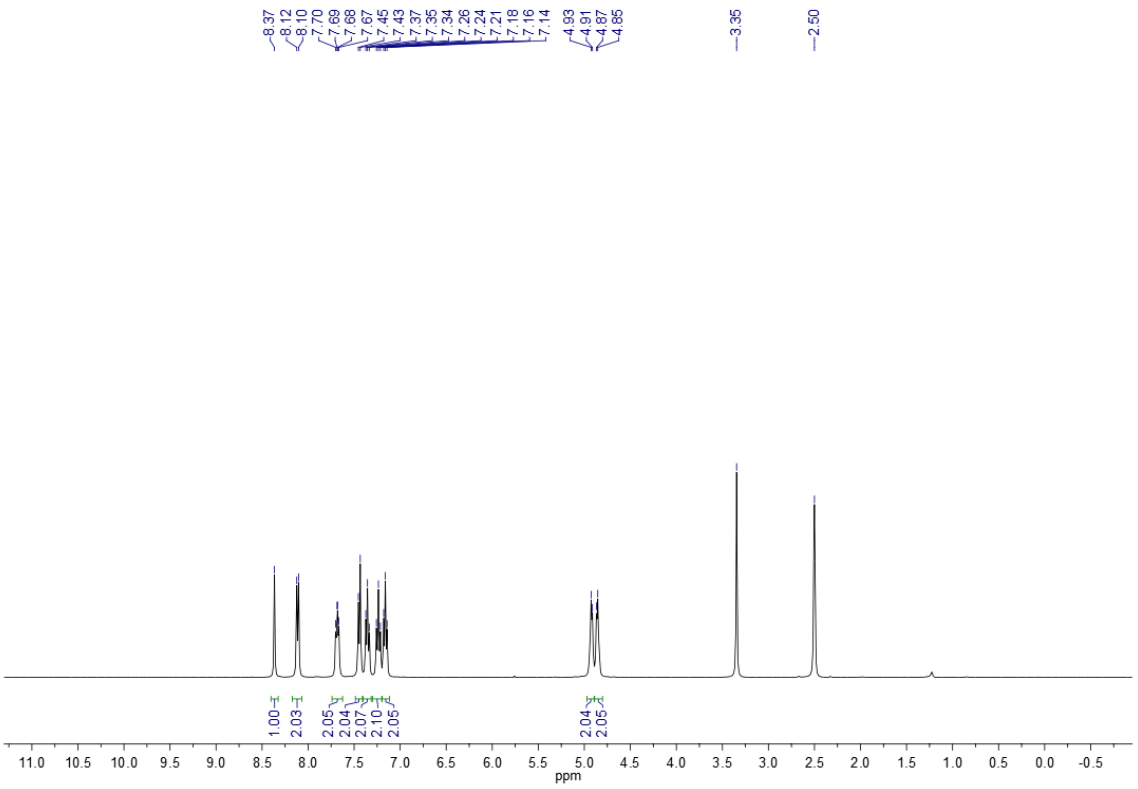


Figure S121. ^{1}H NMR spectrum of **7q** measured in DMSO-d_6.

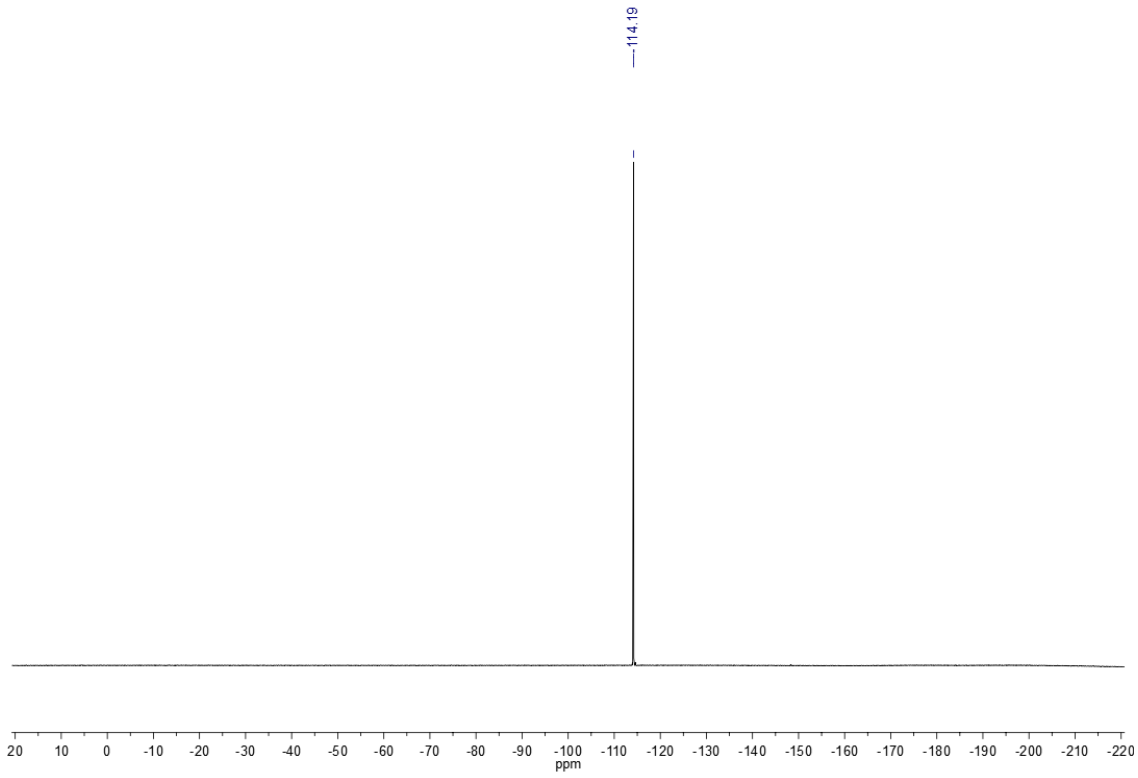


Figure S122. ^{19}F NMR spectrum of **7q** measured in DMSO-d_6.

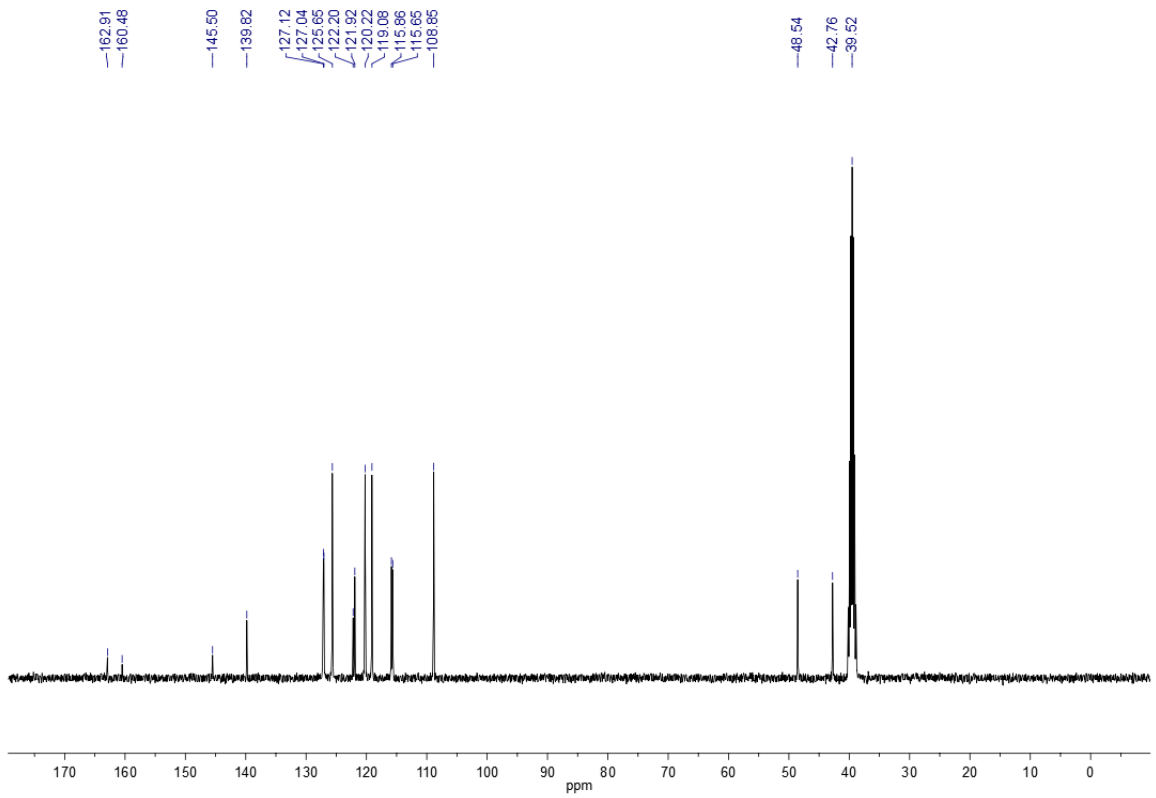


Figure S123. ^{13}C NMR spectrum of **7q** measured in DMSO-d_6.

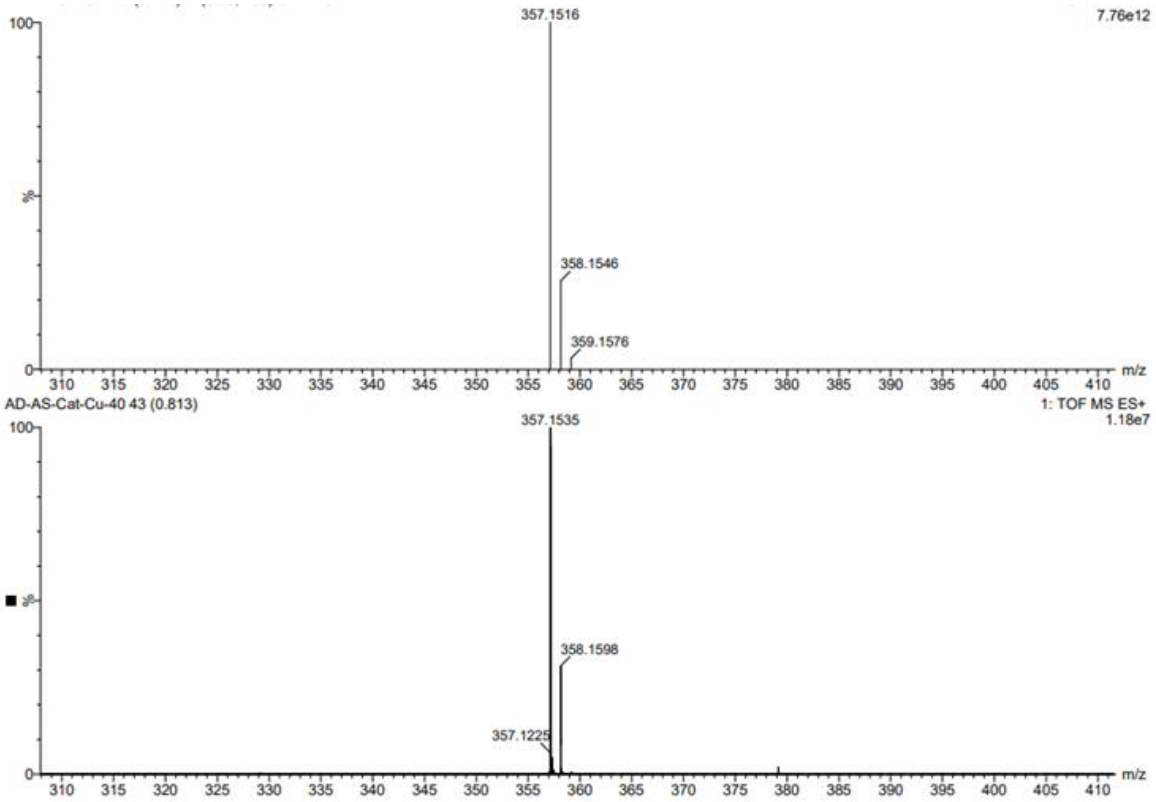


Figure S124. HRMS spectrum of **7q** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

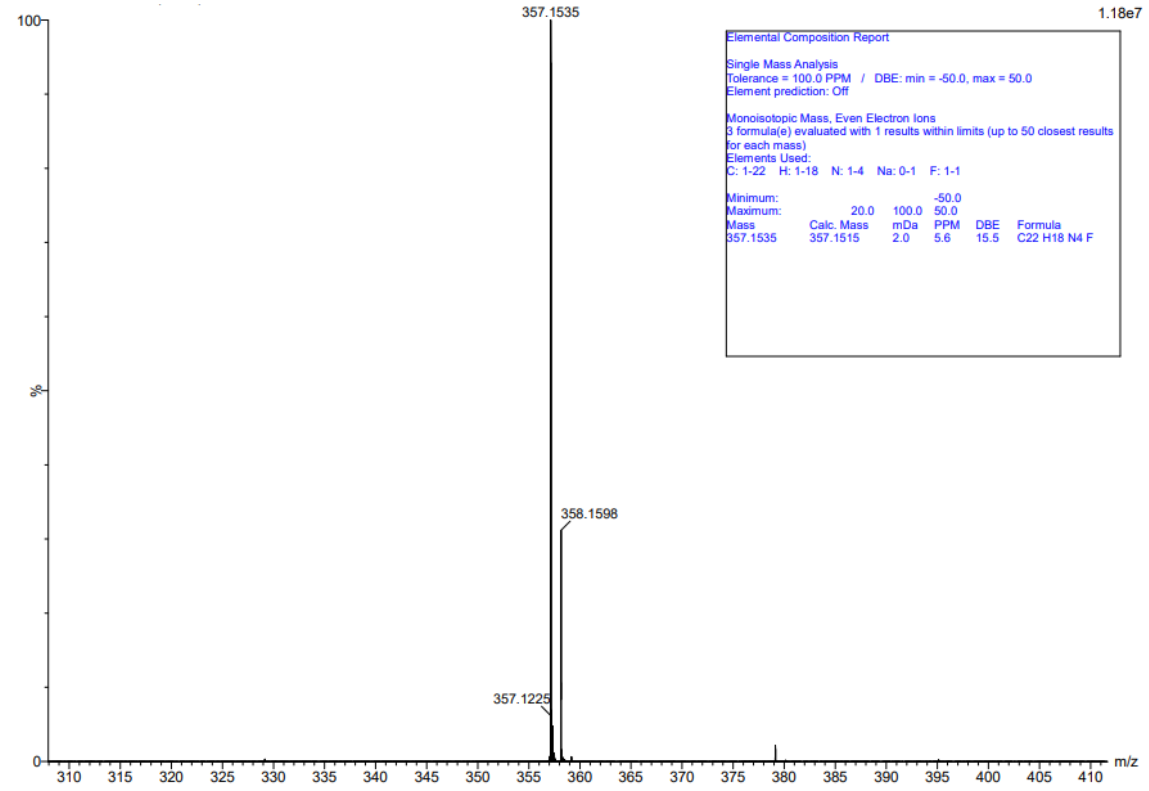


Figure S125. HRMS report of **7q** measured in methanol.

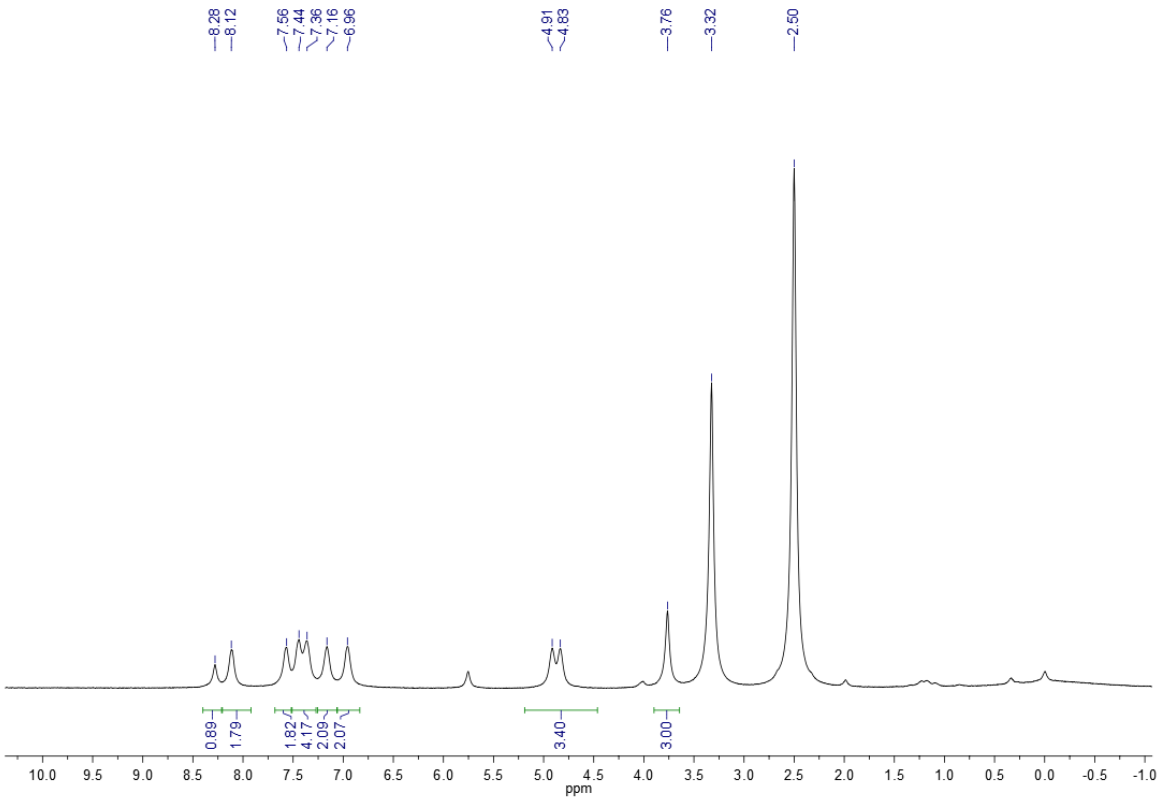


Figure S126. ^{1}H NMR spectrum of 7**r** measured in DMSO-d_6.

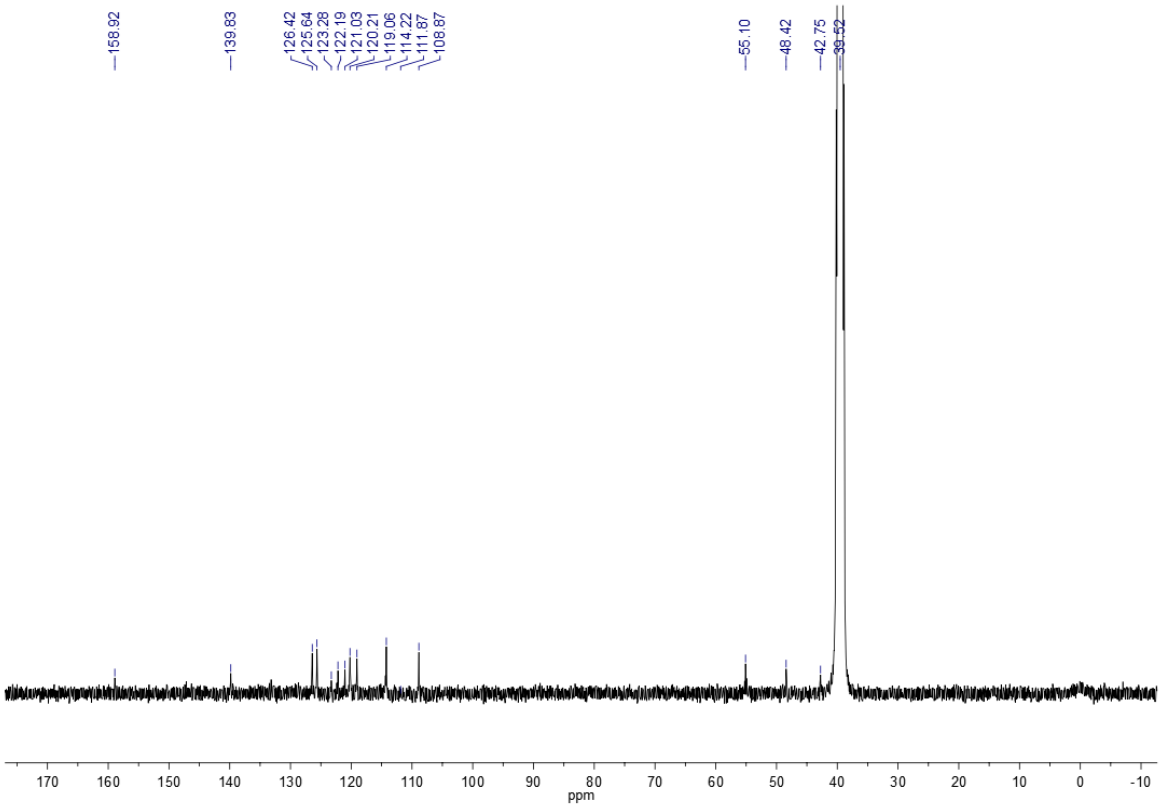


Figure S127. ^{13}C NMR spectrum of 7**r** measured in DMSO-d$_6$.

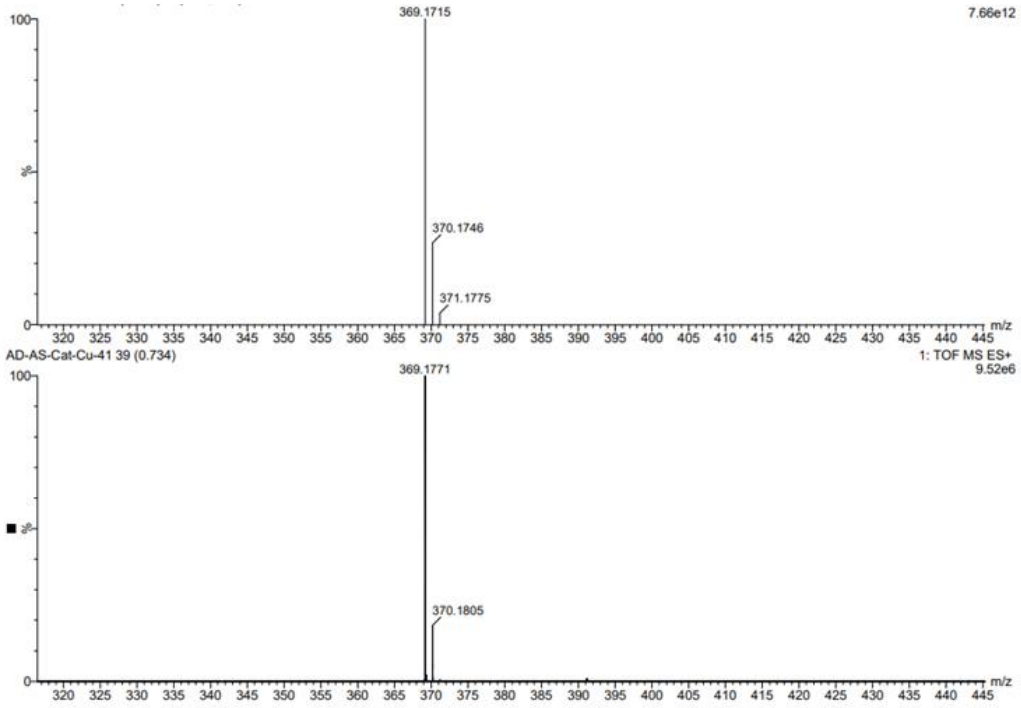


Figure S128. HRMS spectrum of **7r** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

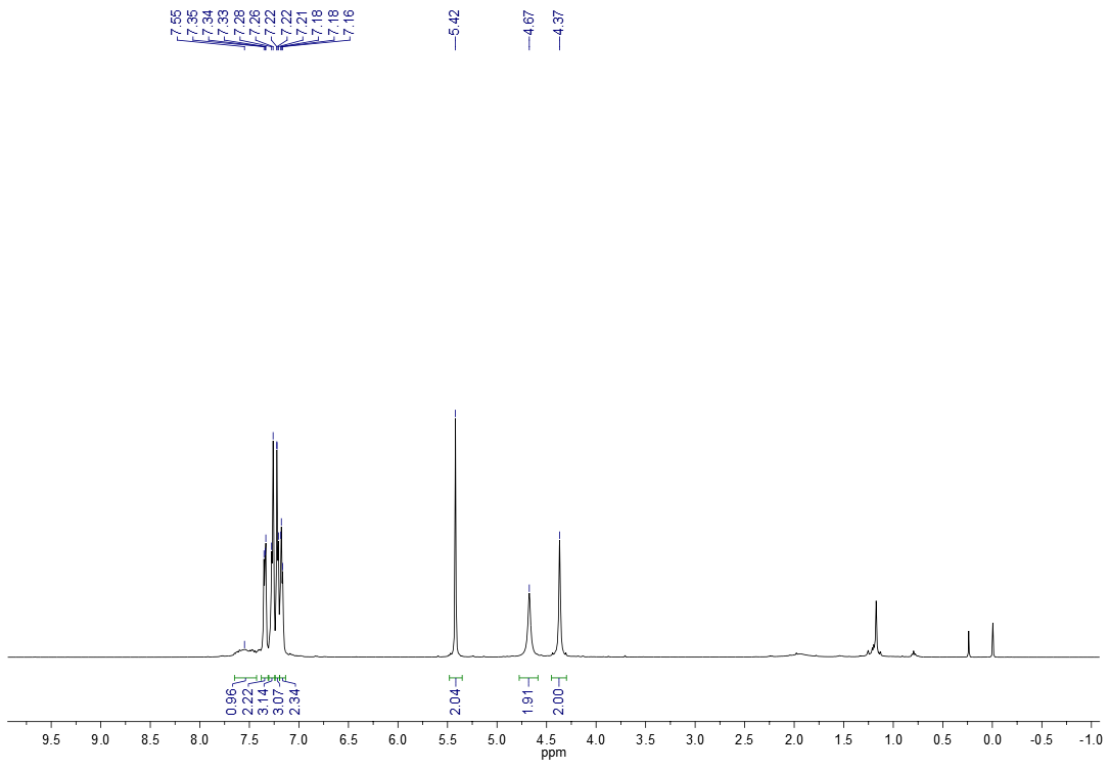


Figure S129. ^{1}H NMR spectrum of 8**a** measured in $CDCl_3$.

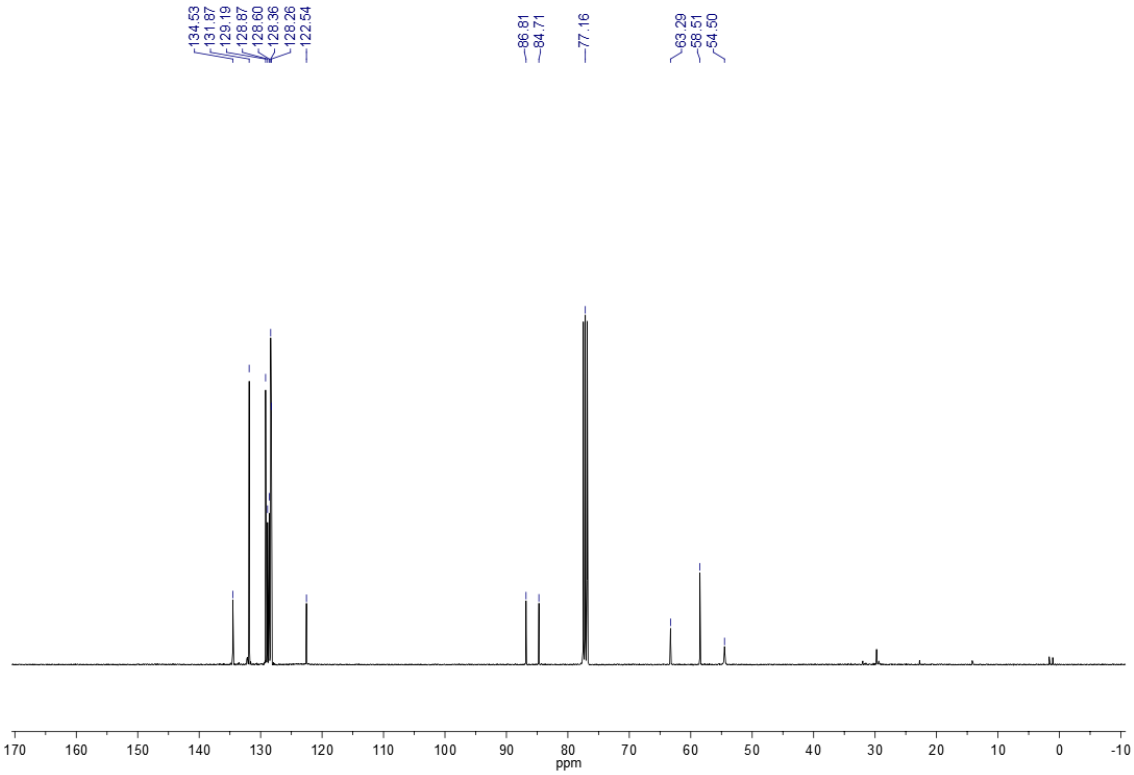


Figure S130. ^{13}C NMR spectrum of **8a** measured in $CDCl_3$.

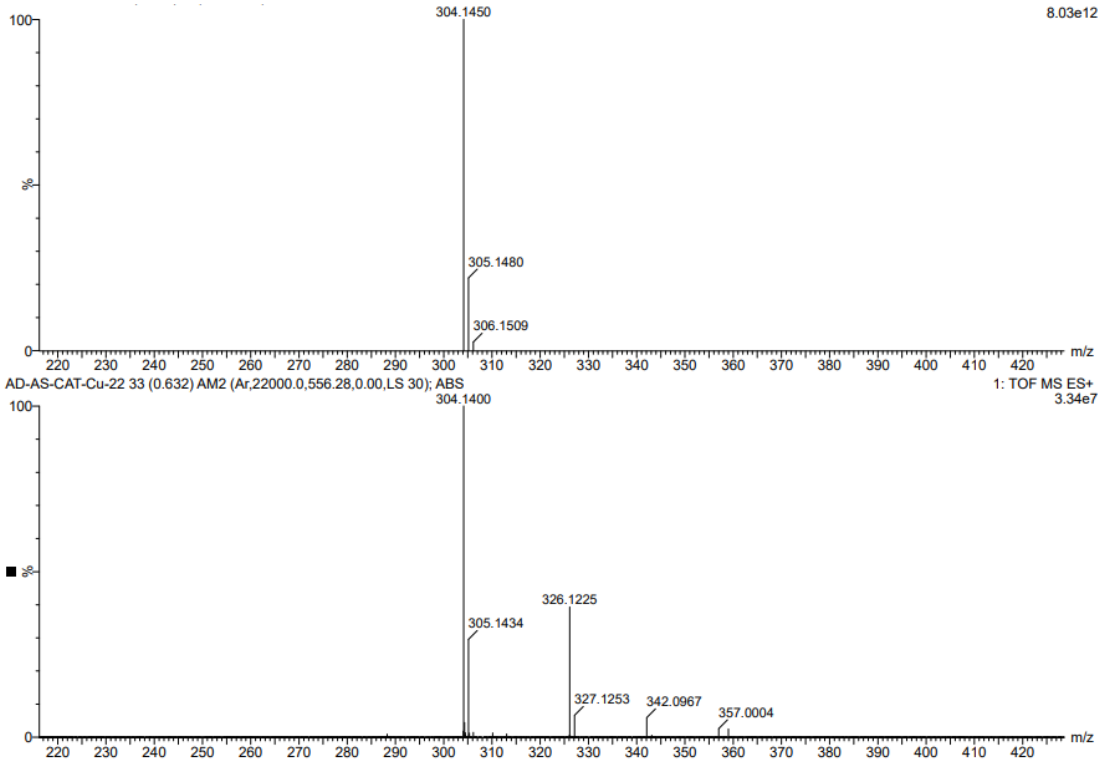


Figure S131. HRMS spectrum of **8a** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

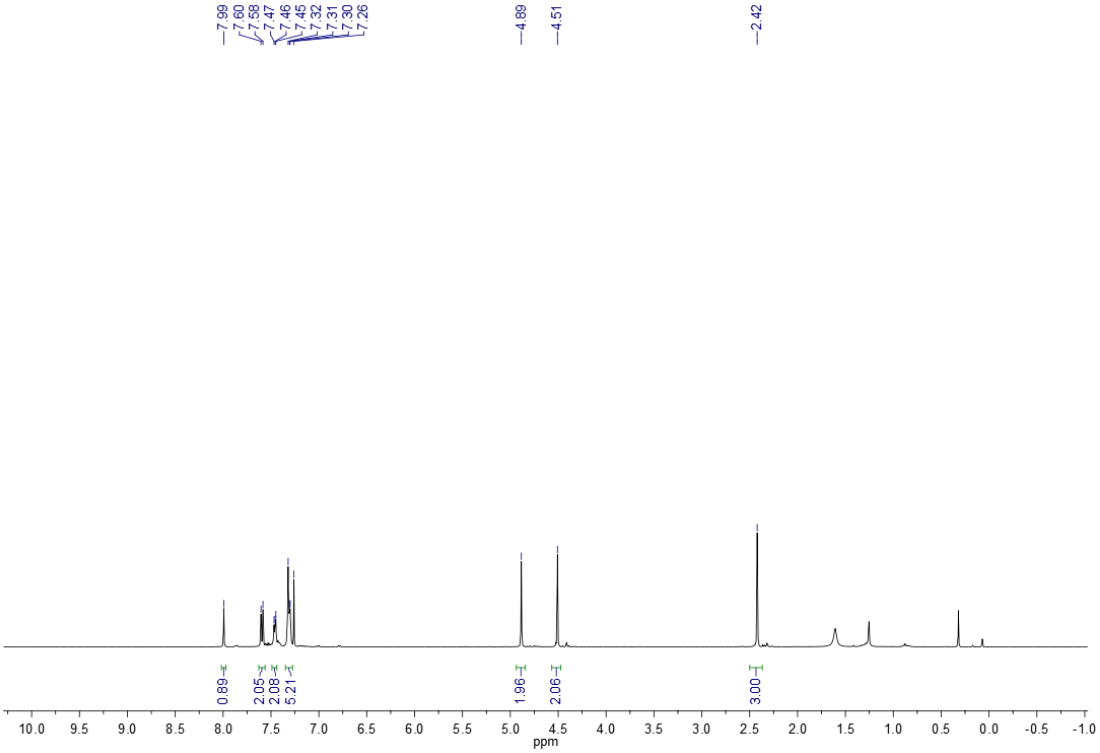


Figure S132. ^{1}H NMR spectrum of **8b** measured in $CDCl_3$.

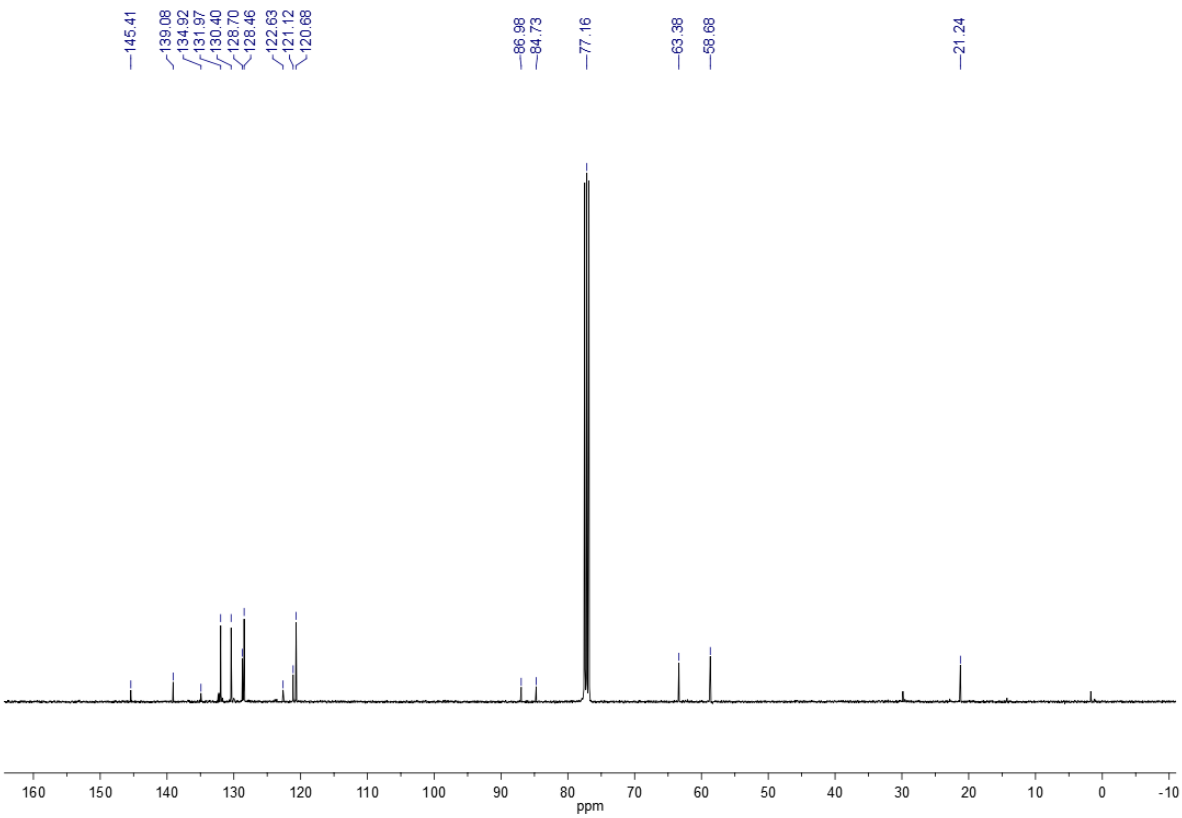


Figure S133. ^{13}C NMR spectrum of **8b** measured in $CDCl_3$.

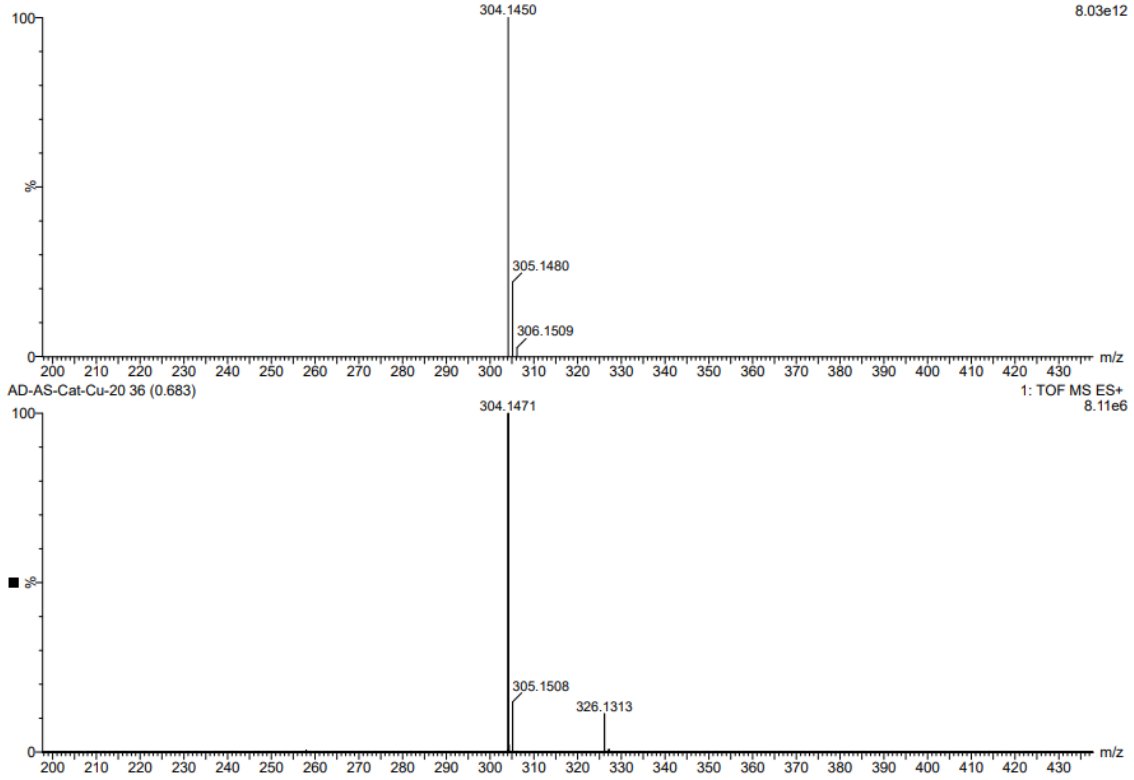


Figure S134. HRMS spectrum of **8b** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

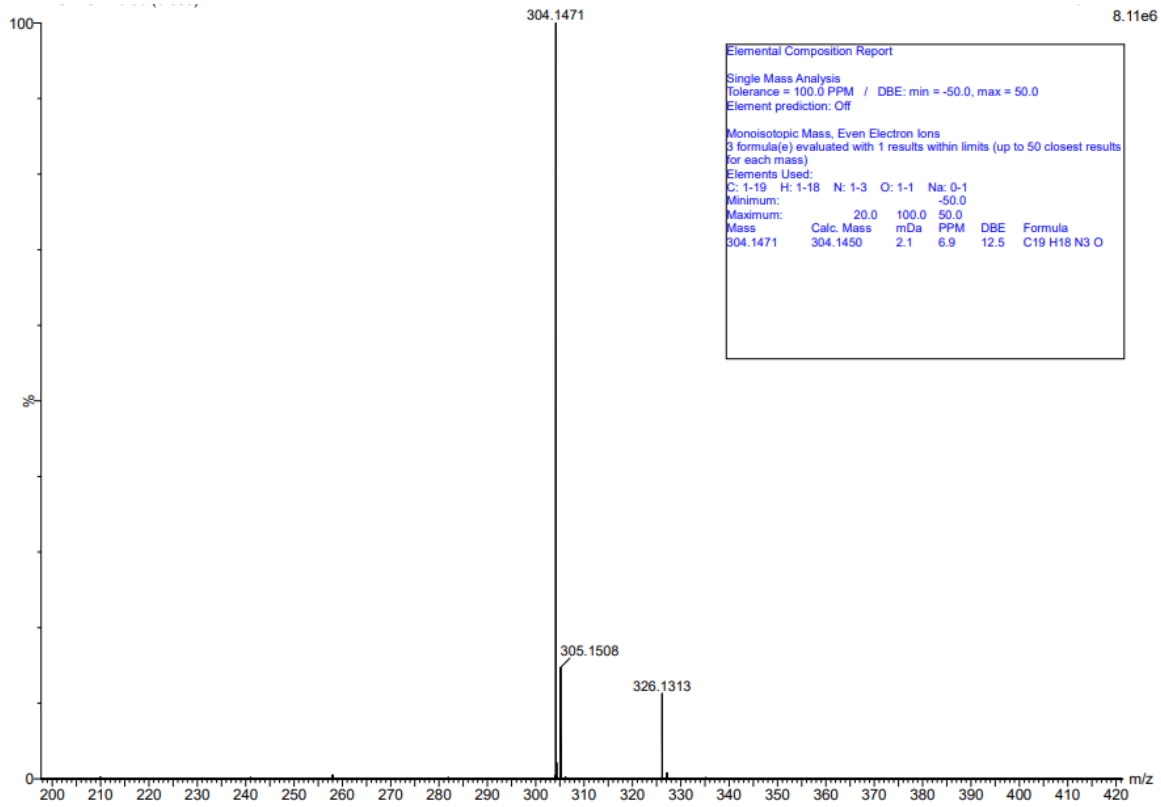


Figure S135. HRMS report of **8b** measured in methanol.

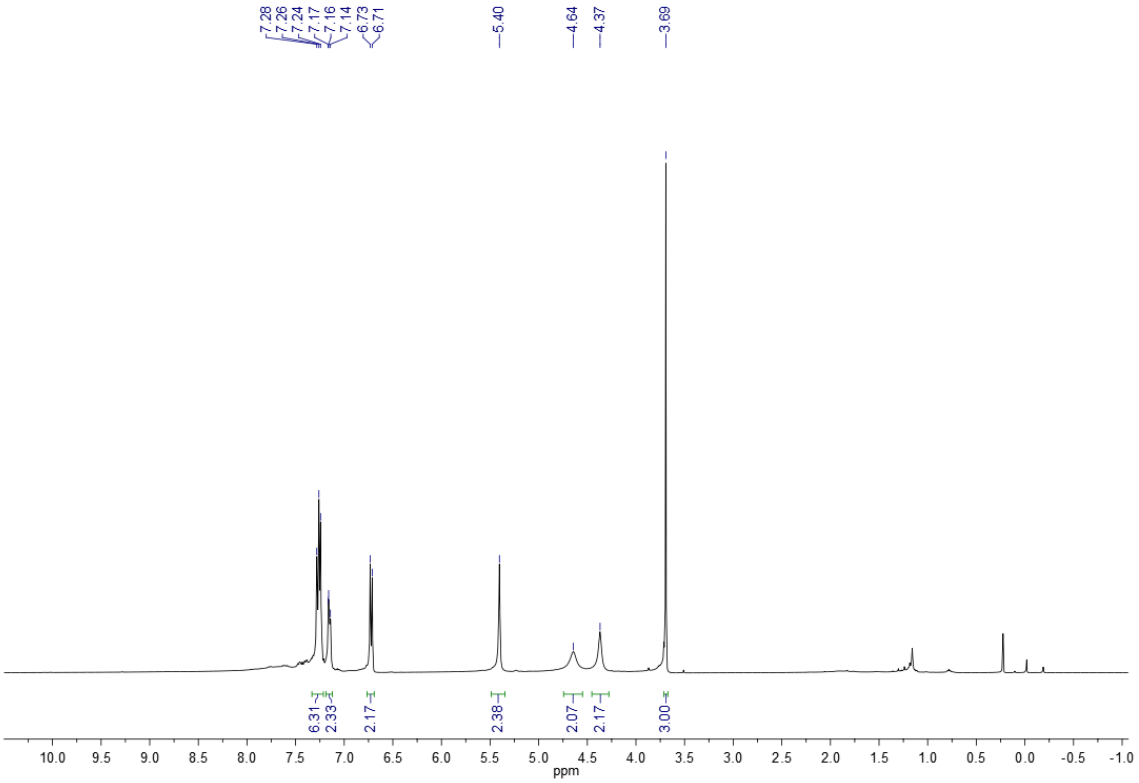


Figure S136. ^{1}H NMR spectrum of **8c** measured in $CDCl_3$.

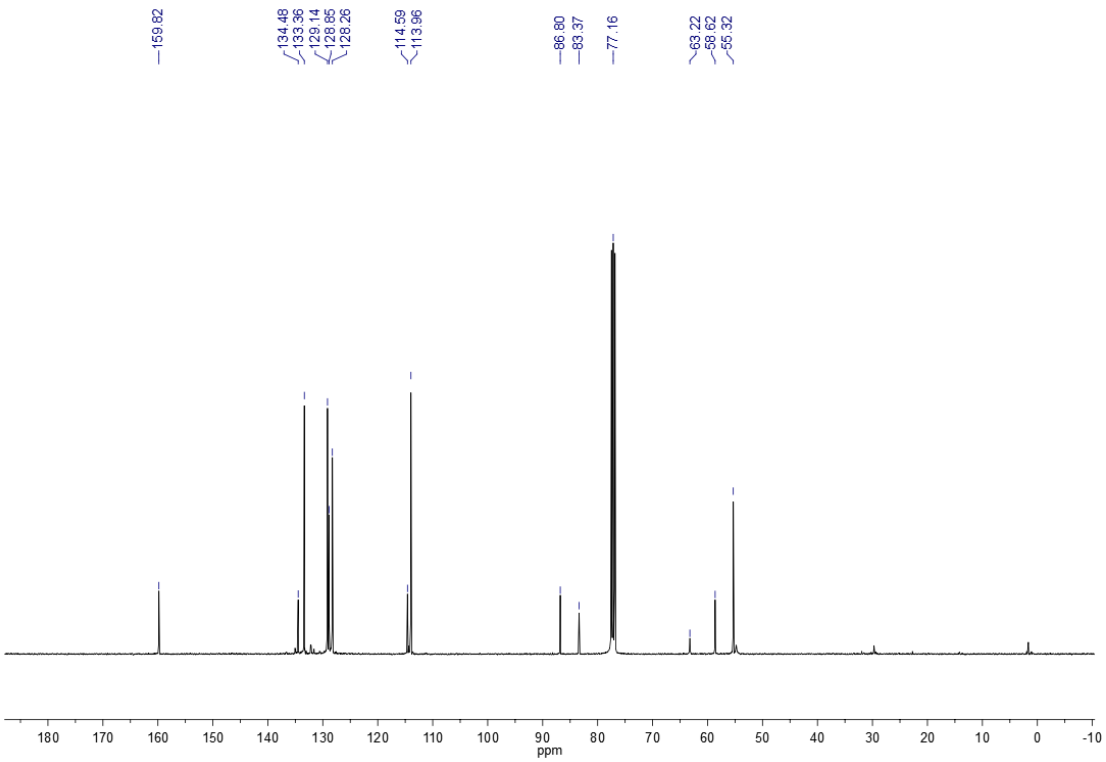


Figure S137. ^{13}C NMR spectrum of **8c** measured in $CDCl_3$.

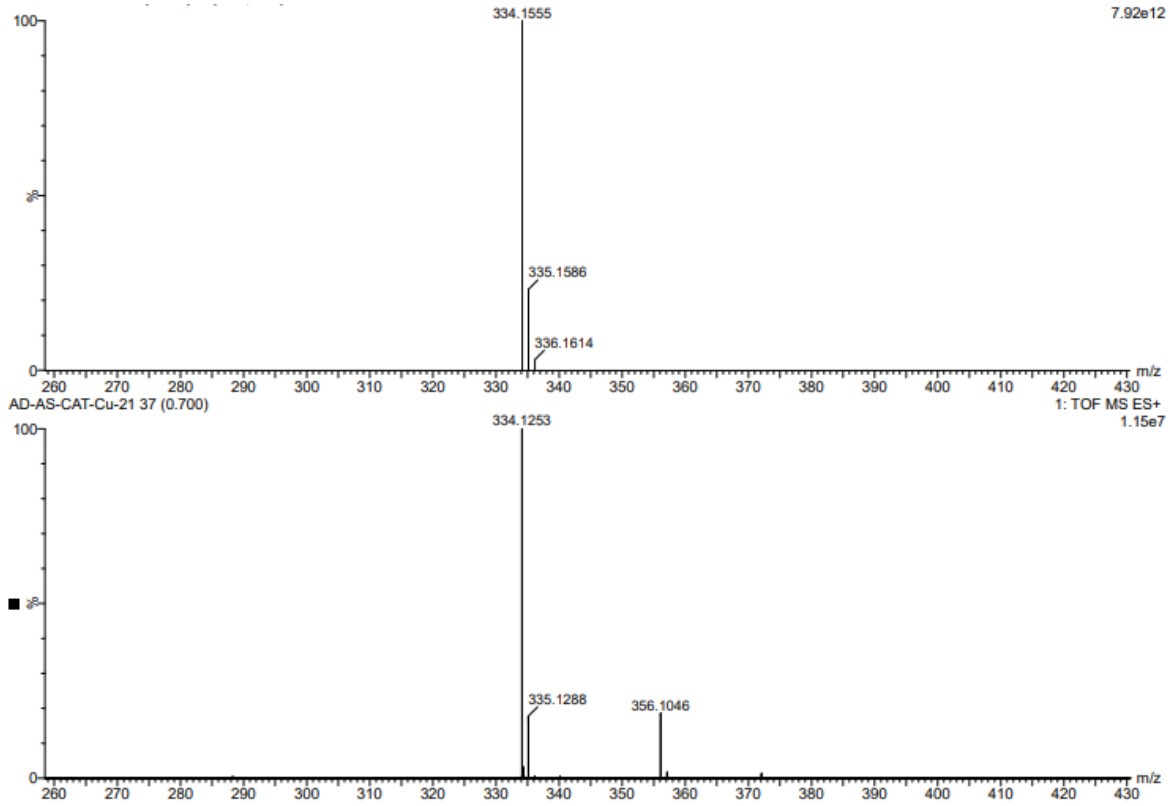


Figure S138. HRMS spectrum of **8c** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

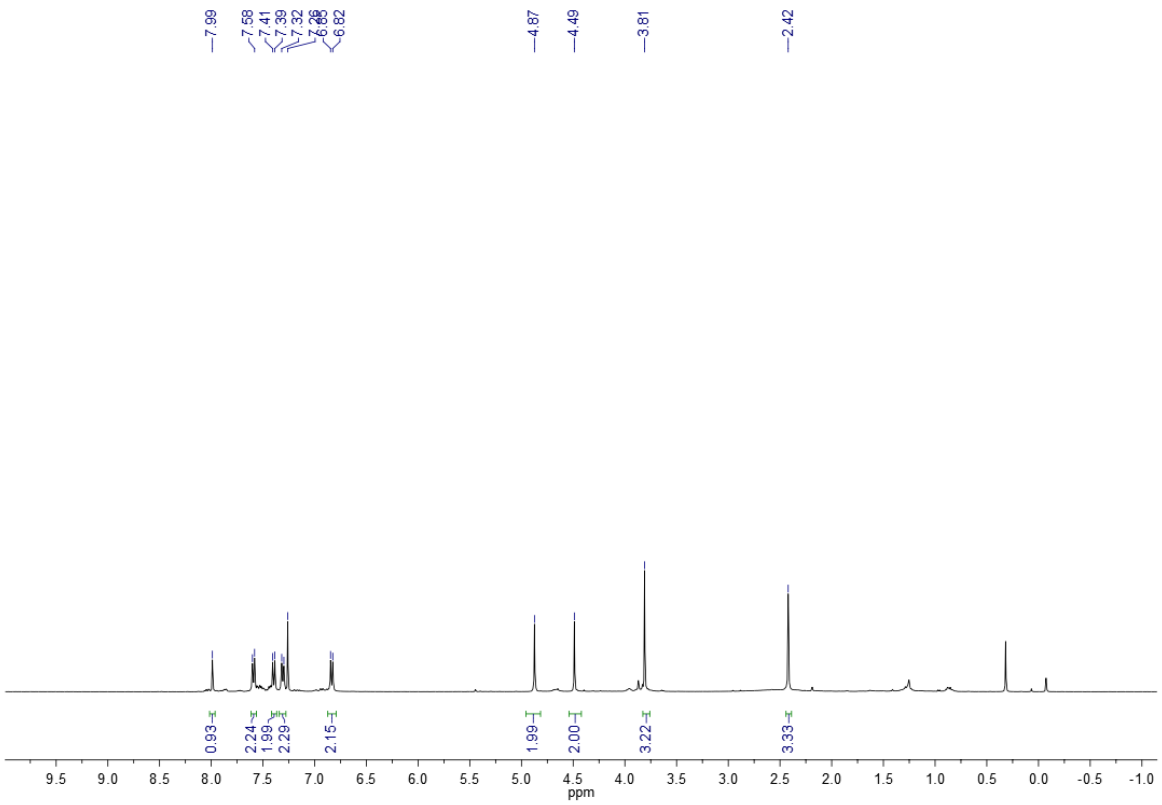


Figure S139. ^{1}H NMR spectrum of **8d** measured in $CDCl_3$.

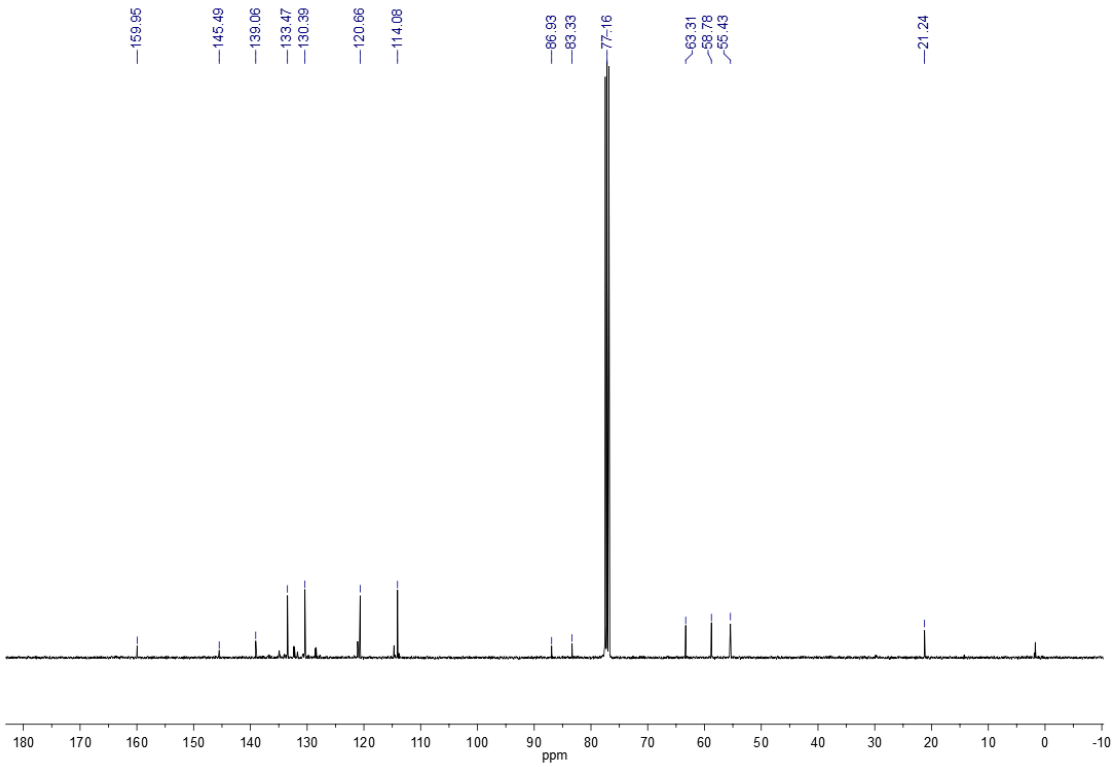


Figure S140. ^{13}C NMR spectrum of **8d** measured in $CDCl_3$.

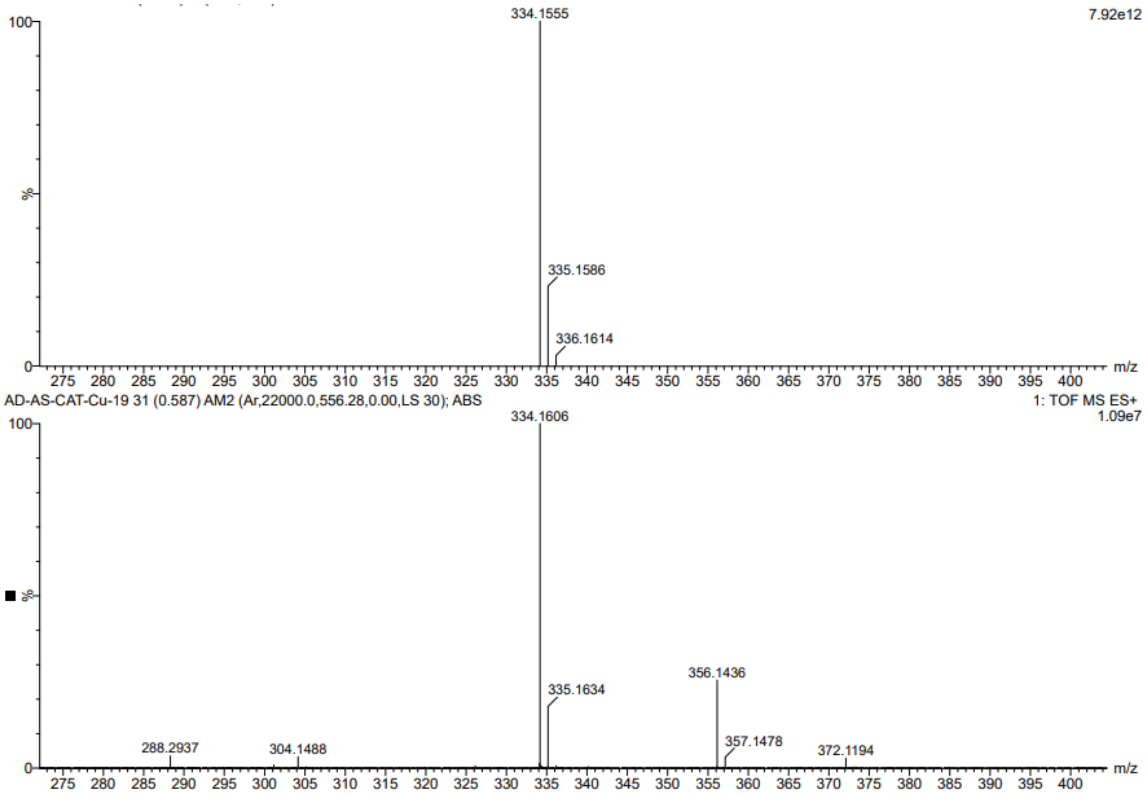


Figure S141. HRMS spectrum of **8d** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

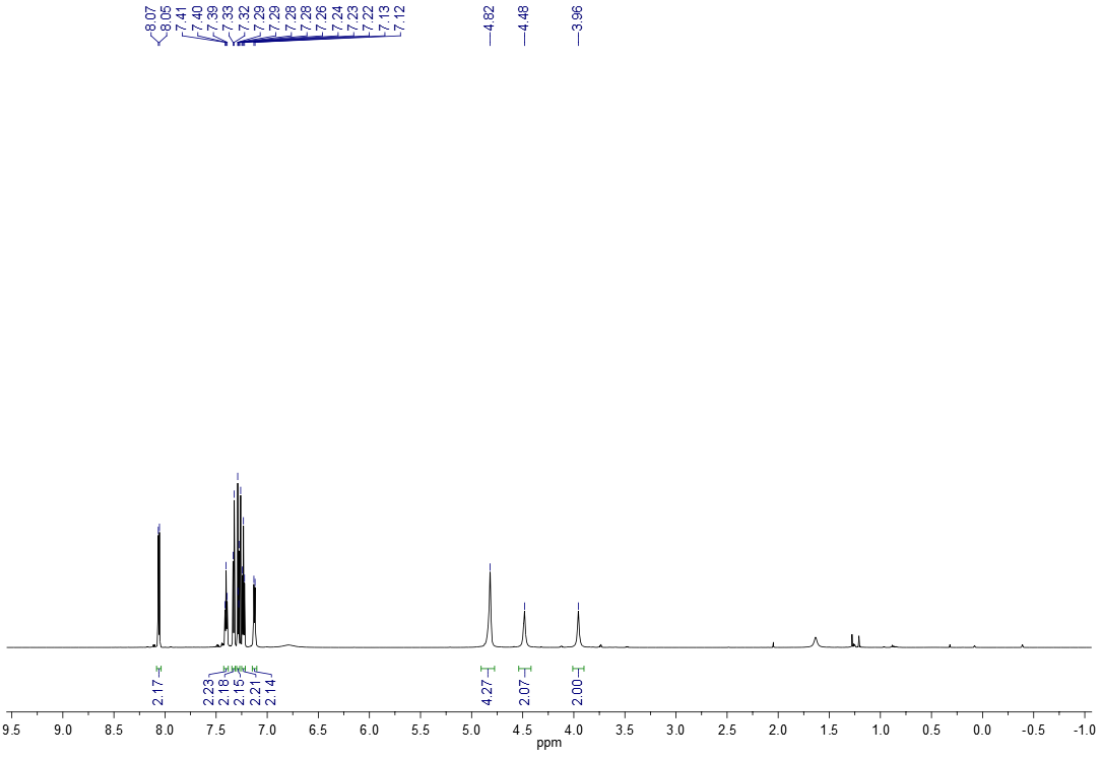


Figure S142. ^{1}H NMR spectrum of **8e** measured in $CDCl_3$.

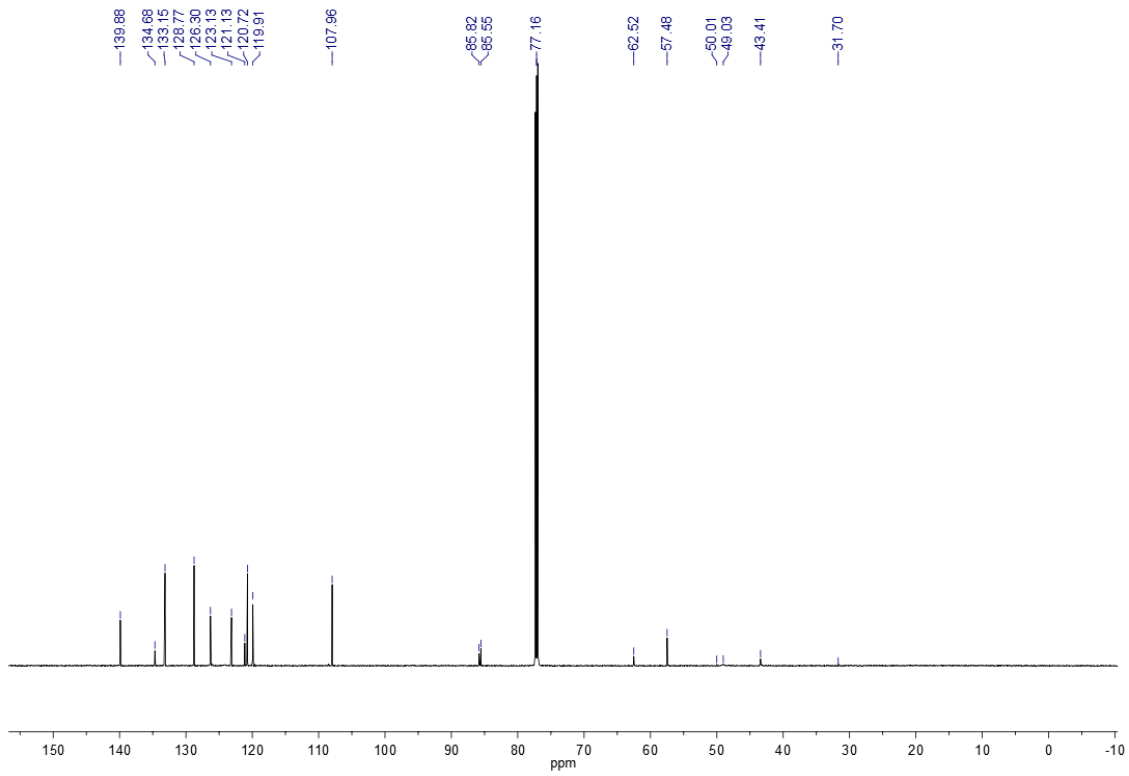


Figure S143. ^{13}C NMR spectrum of **8e** measured in $CDCl_3$.

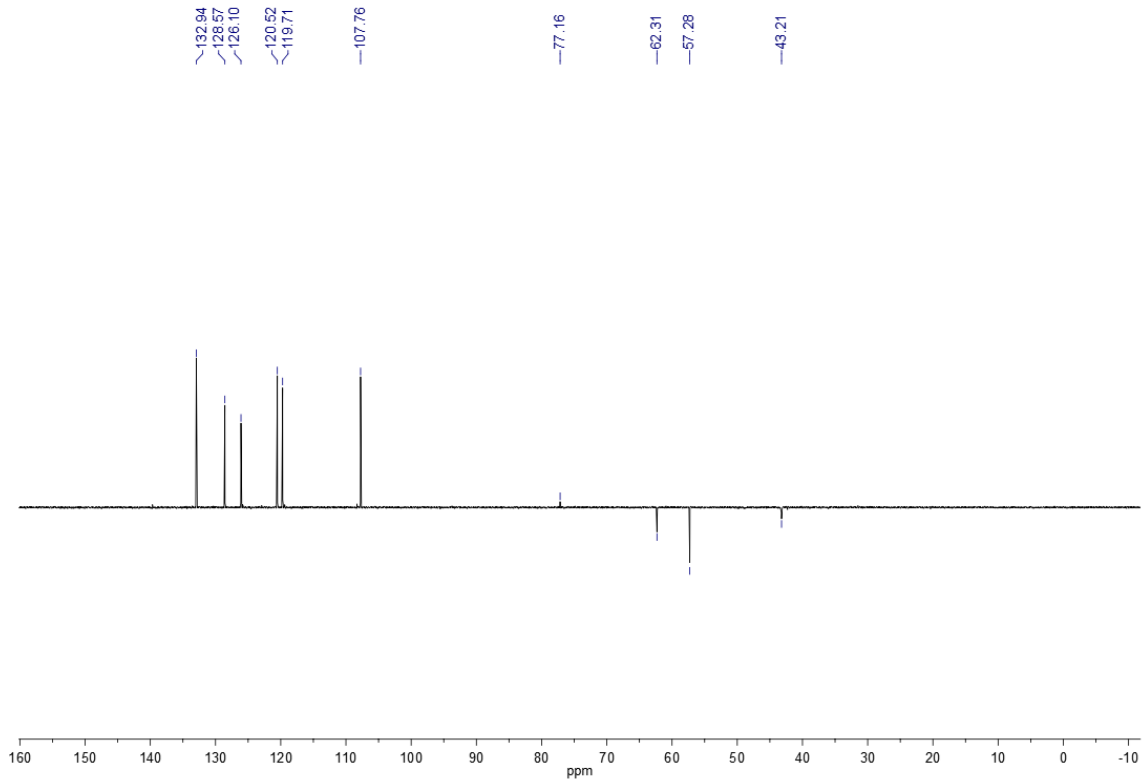


Figure S144. DEPT-135{^{13}C} NMR spectrum of **8e** measured in $CDCl_3$.

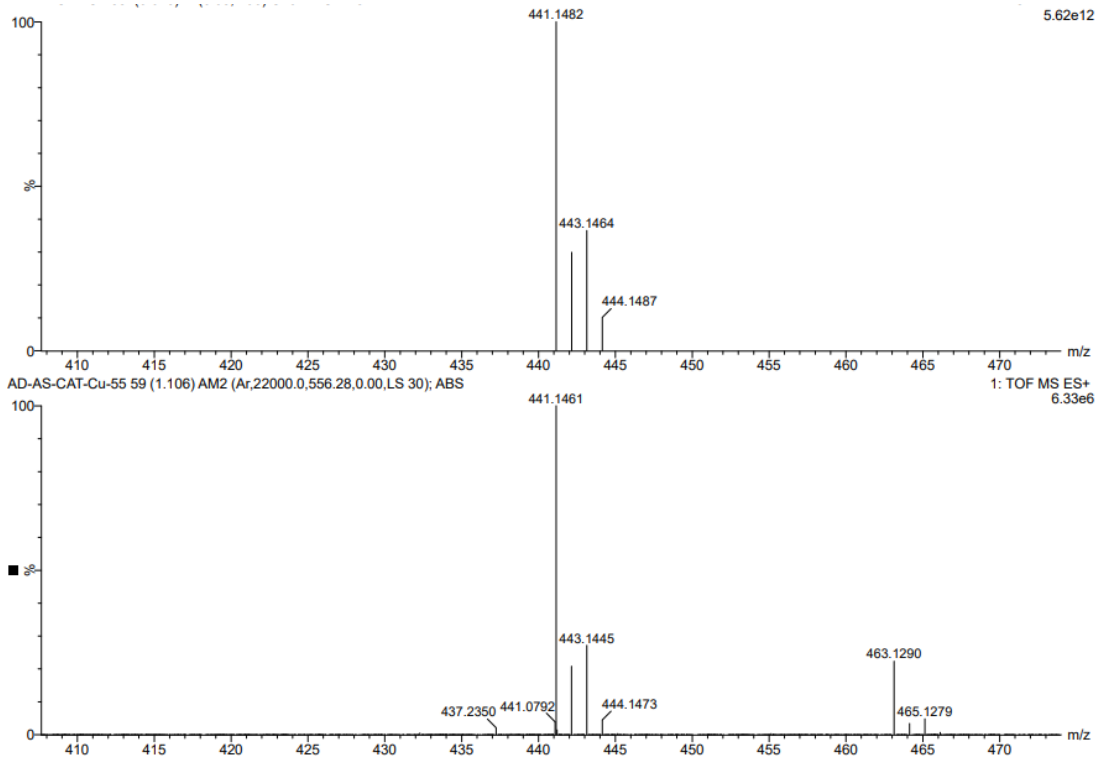


Figure S145. HRMS spectrum of **8e** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

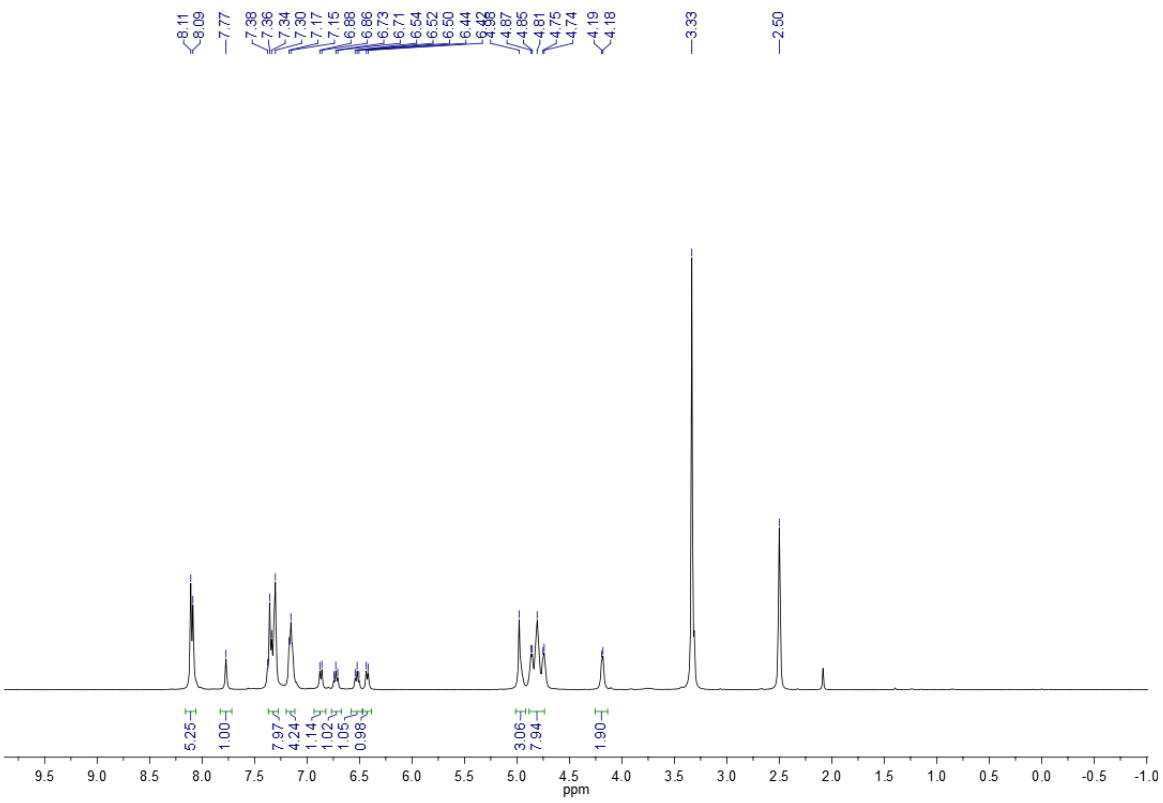


Figure S146. ^{1}H NMR spectrum of **9a** measured in DMSO-d_6.

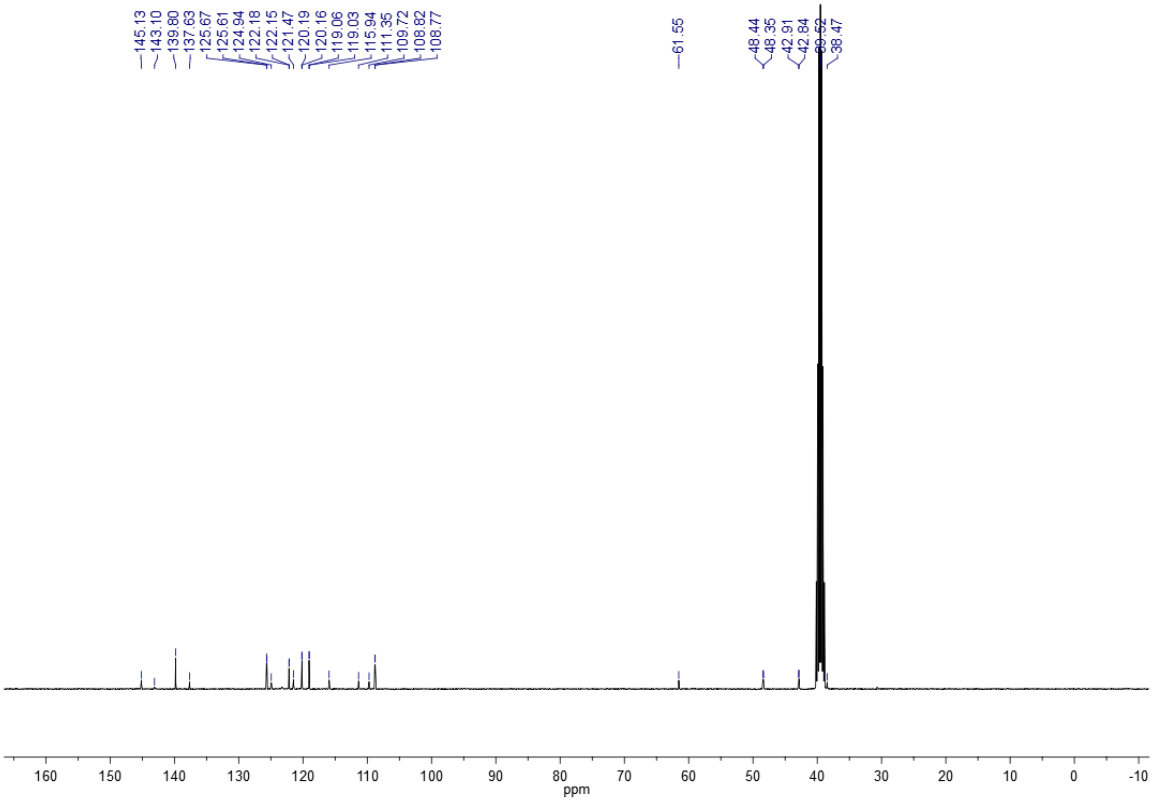


Figure S147. ^{13}C NMR spectrum of **9a** measured in DMSO-d_6.

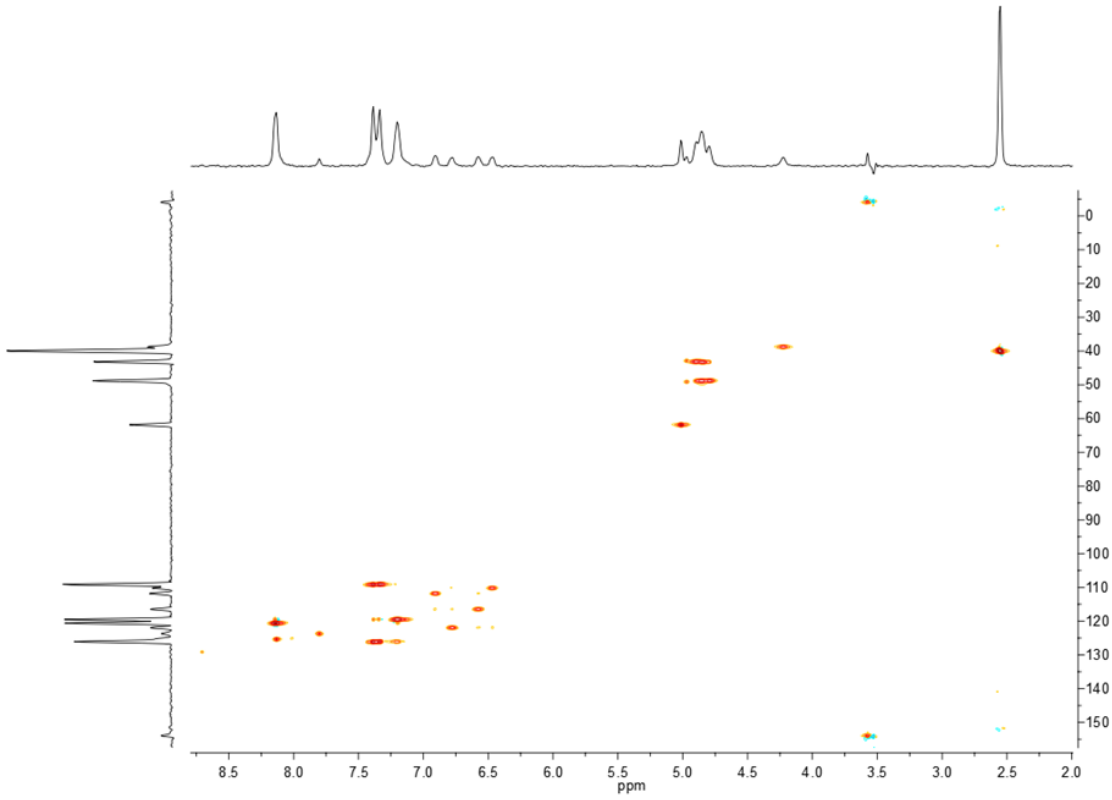


Figure S148. HSQC NMR spectrum of **9a** measured in DMSO-d_6.

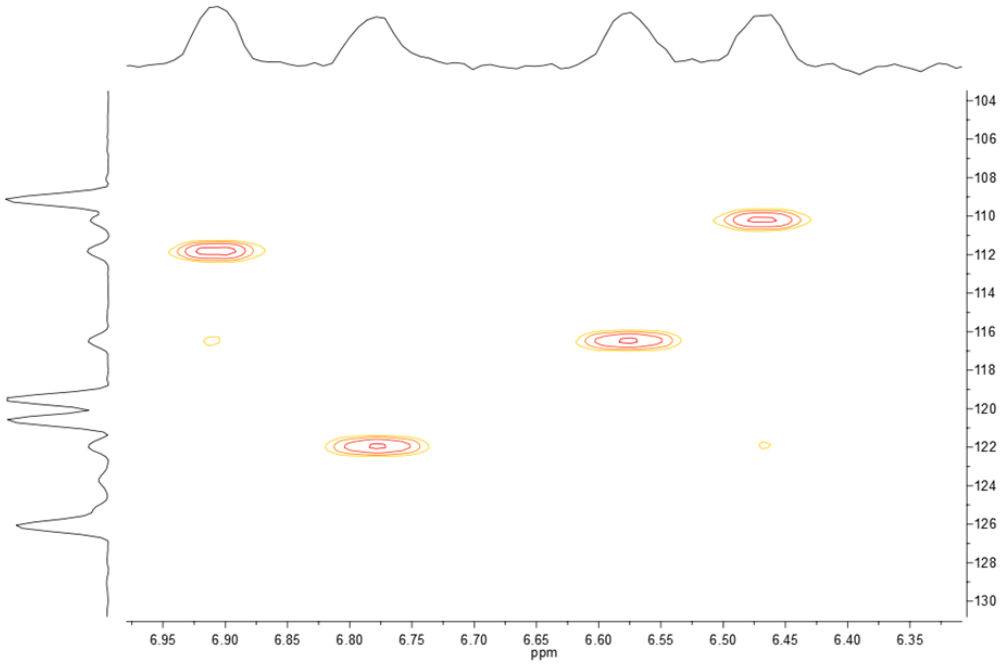


Figure S149. HSQC NMR spectrum expanded version of **9a** measured in DMSO-d_6.

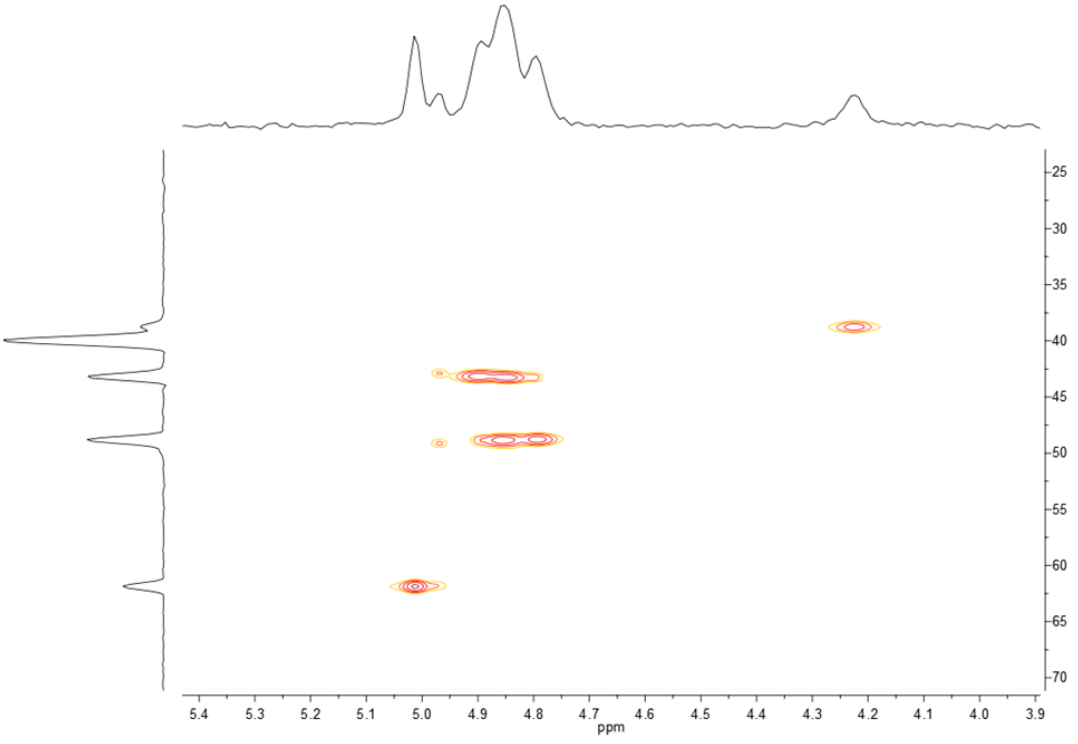


Figure S150. HSQC NMR spectrum expanded version of **9a** measured in DMSO-d_6.

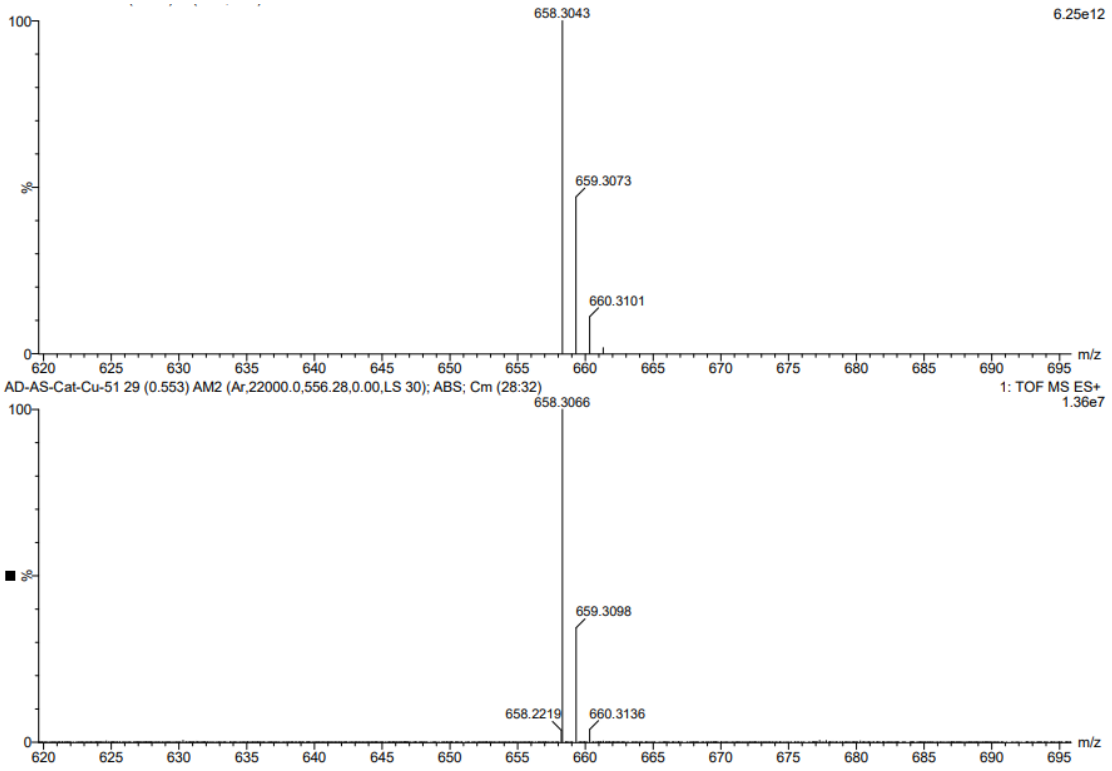


Figure S151. HRMS spectrum of **9a** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

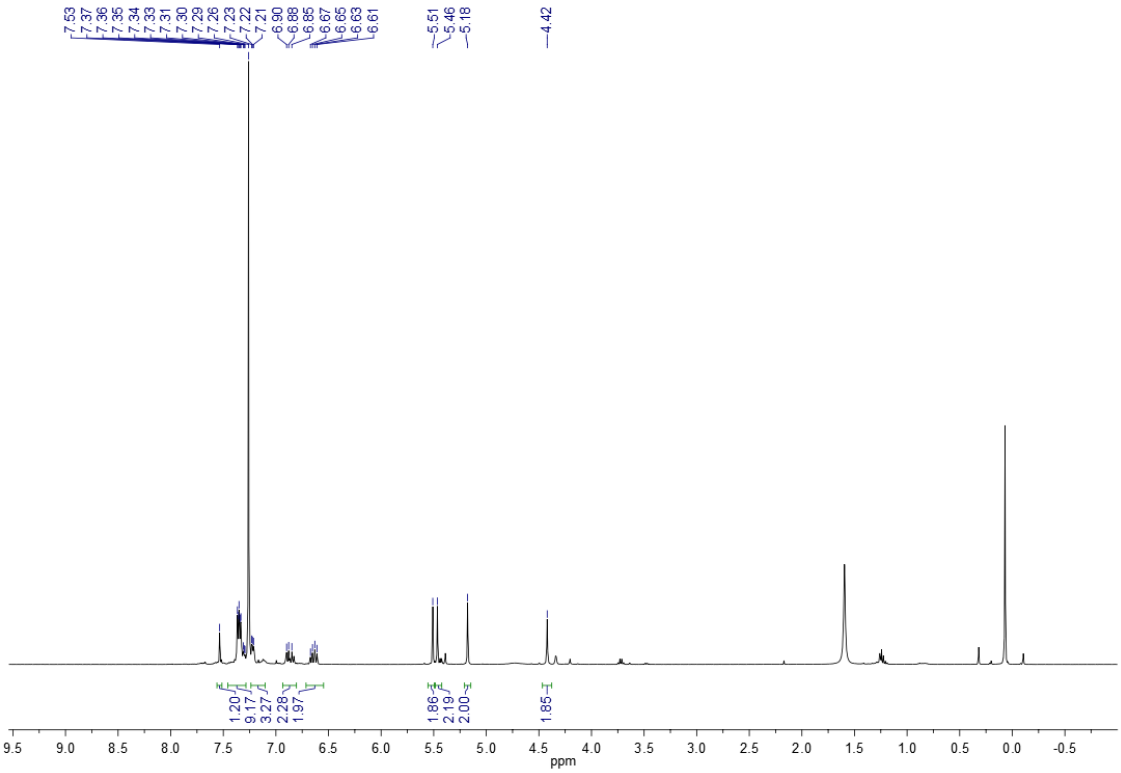


Figure S152. ^{1}H NMR spectrum of bis-triazole **9b** measured in $CDCl_3$.

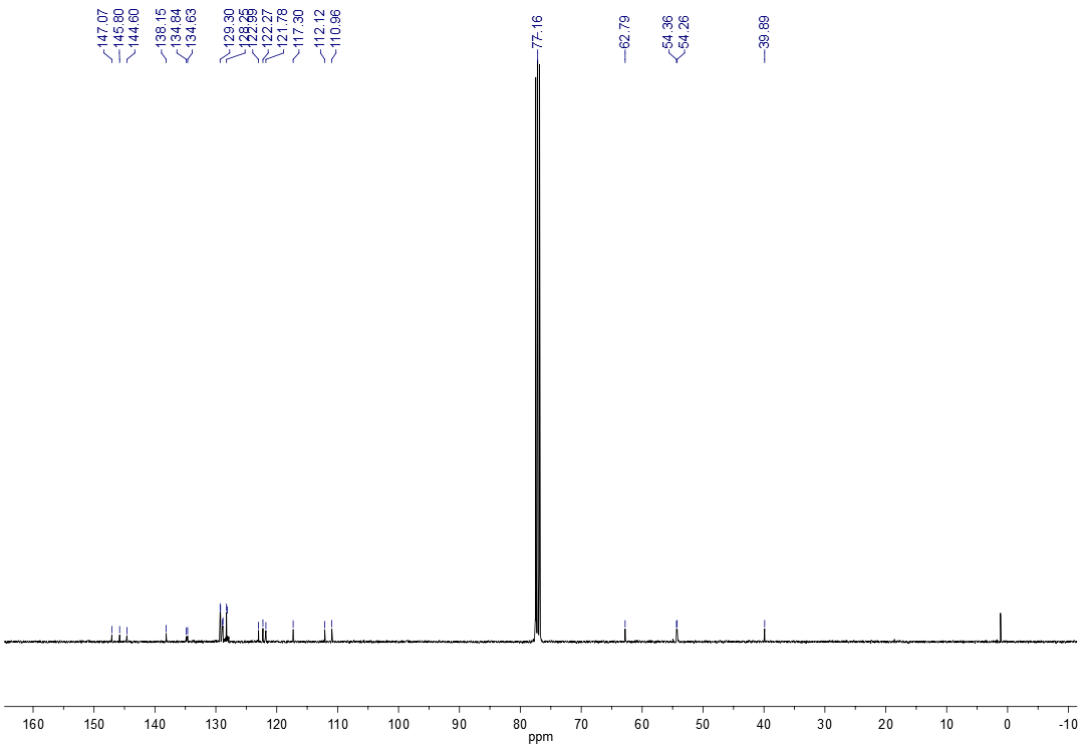


Figure S153. ^{13}C NMR spectrum of bis-triazole **9b** measured in $CDCl_3$.

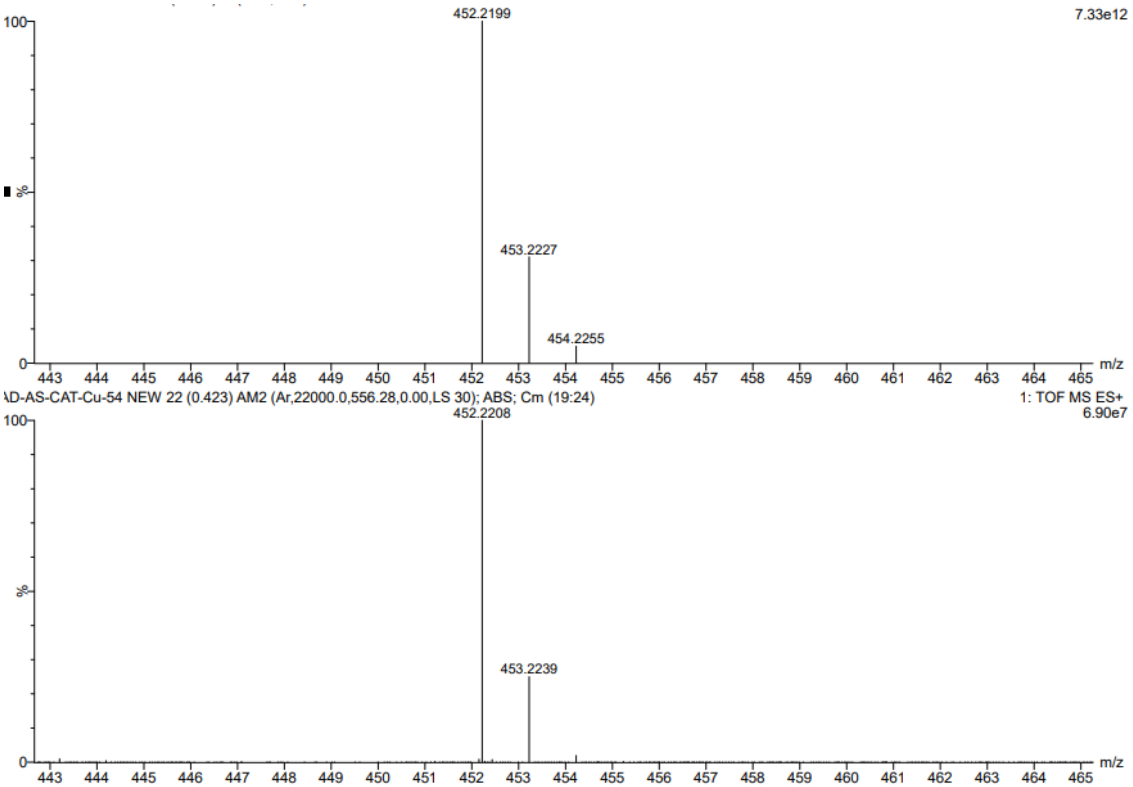
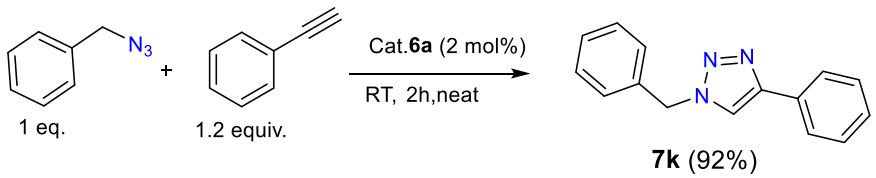


Figure S154. HRMS spectrum of bis-traizole **9b** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

Synthesis and spectral data of triazole 7K by using cat.6a



Scheme S6. Synthesis and spectral data of triazole **7K** by using cat.6a within 2 hours Alkyne (0.18 mmol), azide (0.15 mmol), and 2 mol% **cat. 6a** were placed into an oven-dried 10 mL Schlenk tube. The reaction mixture was then allowed to stir for 2h at RT. The product was isolated by passing the reaction mixture via flash column chromatography with ethyl acetate as the eluent. The solvent was then evaporated by rota vapour, yielding the respective triazole as a white solid in 92% yield.

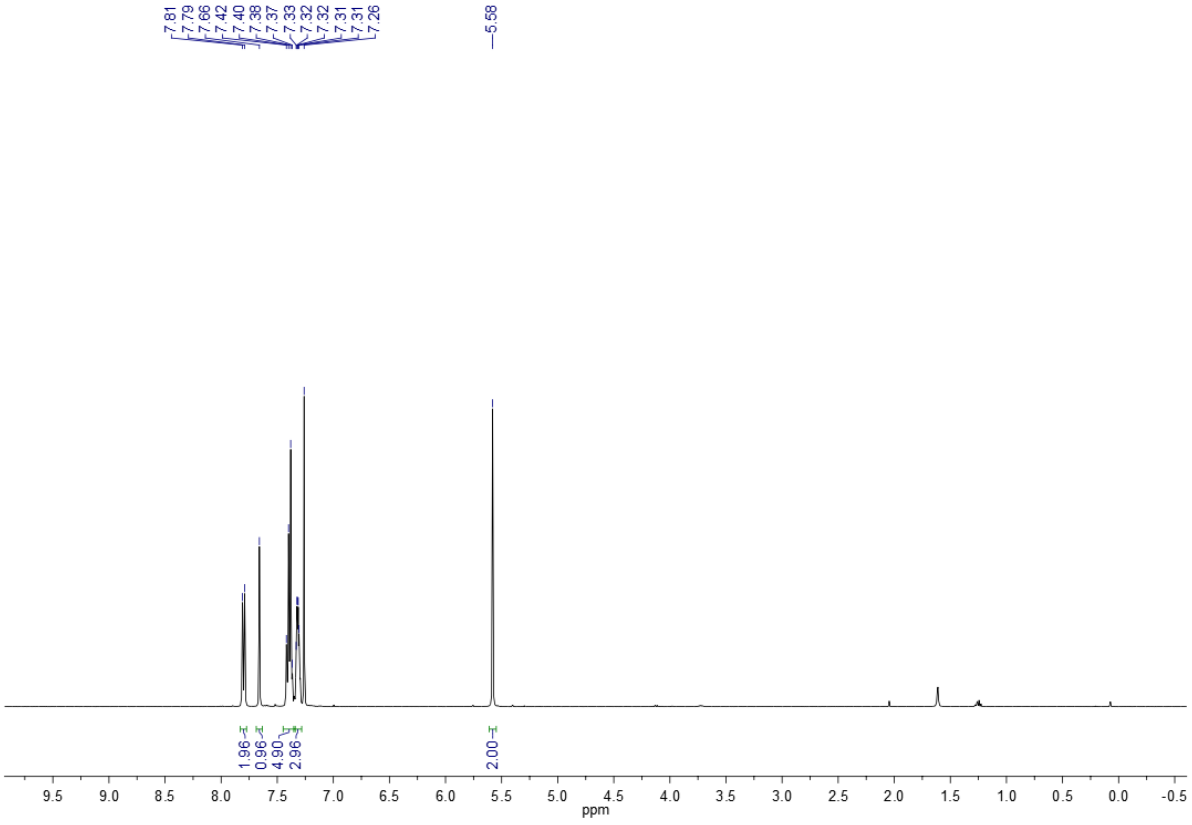
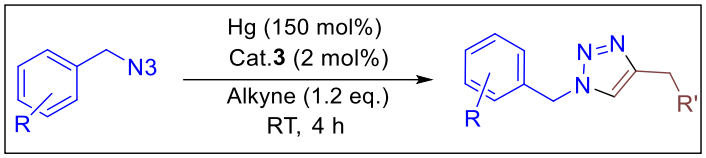


Figure S155. ^{1}H NMR spectrum of **7k** measured in $CDCl_3$.

Mercury drop test for homogeneity of the catalytic cycle

Under N_2 atmosphere, a 25 mL flame-dried Schlenk tube was charged with azide (1 equiv.), alkyne (1.2 equiv.), and catalyst **3** (2 mol%) sequentially followed by mercury (150 mol%) was added into the tube. The reaction mixture was then stirred for 4h at room temperature, and the crude mixture was purified by silica gel flash column chromatography using ethyl acetate as an eluent. The substances obtained were washed with *n*-hexane followed by drying under vacuum afforded the corresponding triazoles as clean products.

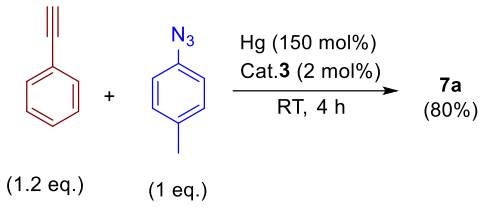


Scheme S7. Alkyne-Azide coupling in the presence of Hg metal and Cat.**3**

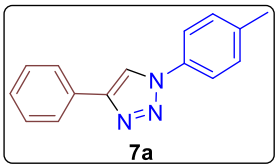
Results of Hg drop test			
Triazole	Yields obtained with only **Cat.3**	Yields obtained; in the presence of 2:150 mol% of **Cat.3**/Hg metal	Remarks (*all are isolated yields)
7a	81%	80%	Nearly negligible difference in yields
7d	73%	70%	Nearly negligible difference in yields
7i	79%	70%	No significant change in yields
7k	99%	90%	No significant change in yields

As shown in the above scheme; the following sections contain the experimental procedures for a series of reactions performed with their specific spectroscopic data, and obtained yields.

Preparation of triazole (7a)



7a was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (28.2 mg, 80%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.15 (s, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.33 (m, 3H), and 2.44 (s, 3H, CH_3) ppm.



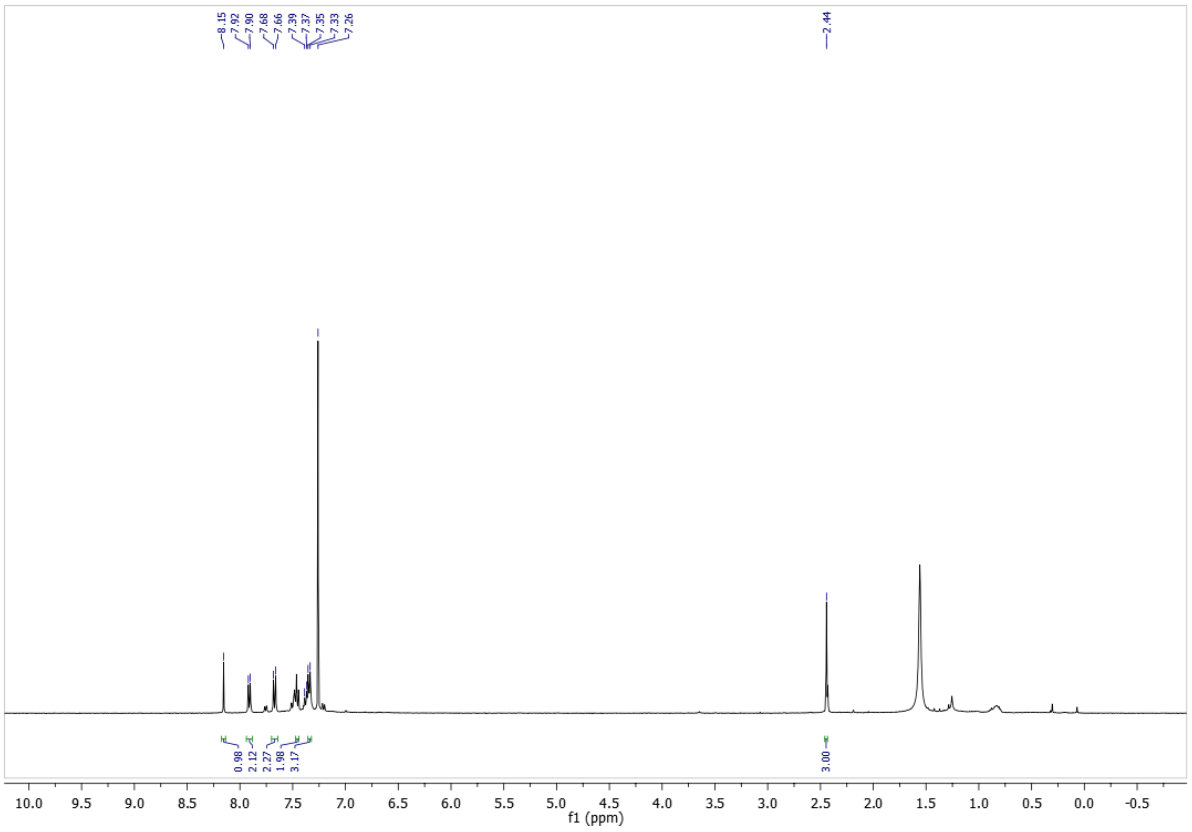
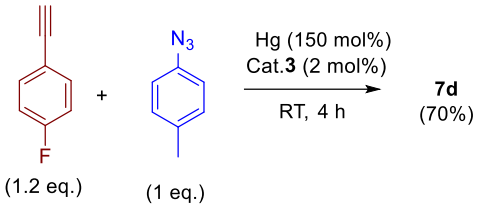
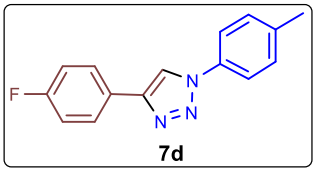


Figure S156. ^{1}H NMR spectrum of triazole **7a** measured in $CDCl_3$.

Preparation of triazole (7d)



7d was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (24.7 mg, 70%). 1H NMR (400 MHz, $CDCl_3$); δ = 8.11 (s, 1H), 7.88 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), and 2.44 (s, 3H, CH_3-tolyl) ppm.



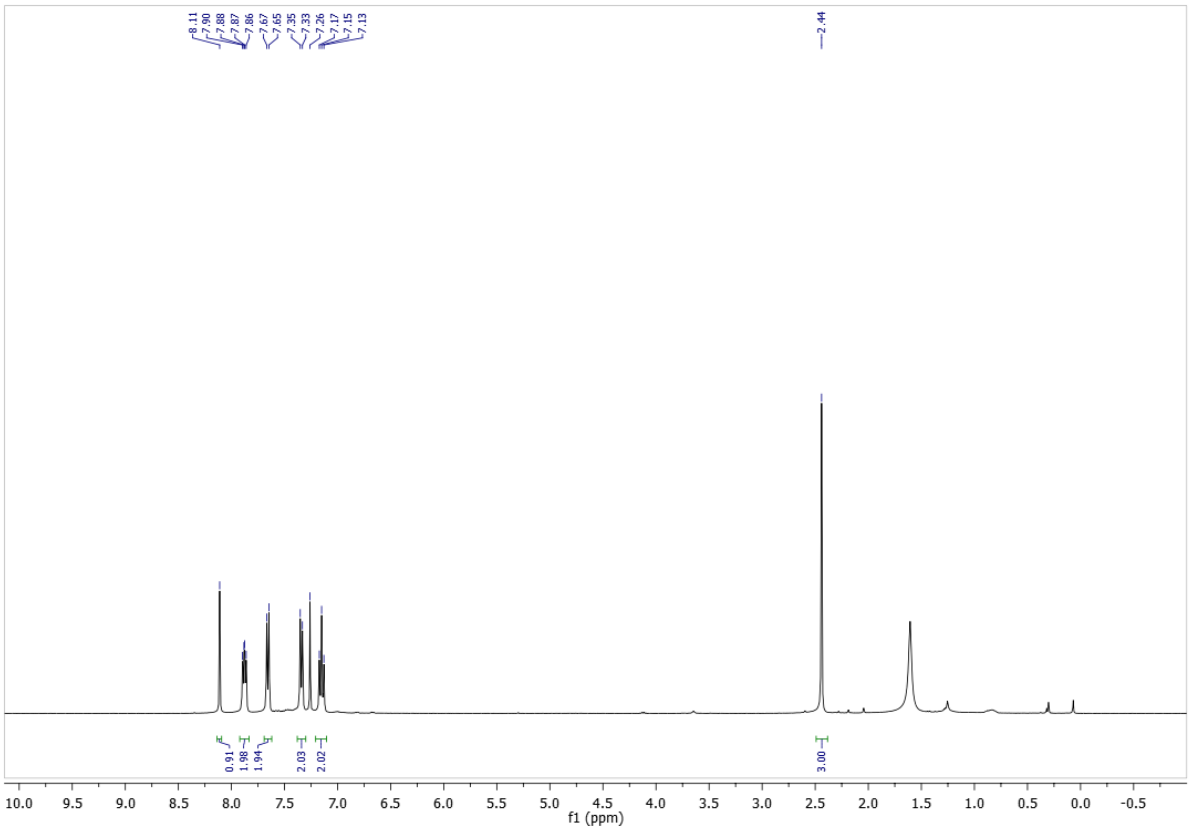
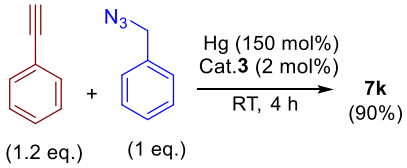
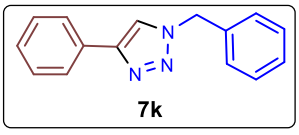


Figure S157. ^{1}H NMR spectrum of triazole **7d** measured in $CDCl_3$.

Preparation of triazole (7k)



7k was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (16.24 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.82 – 7.76 (m, 2H), 7.66 (s, 1H), 7.44 – 7.36 (m, 5H), 7.34 – 7.29 (m, 3H), 5.58 (s, 2H) ppm.



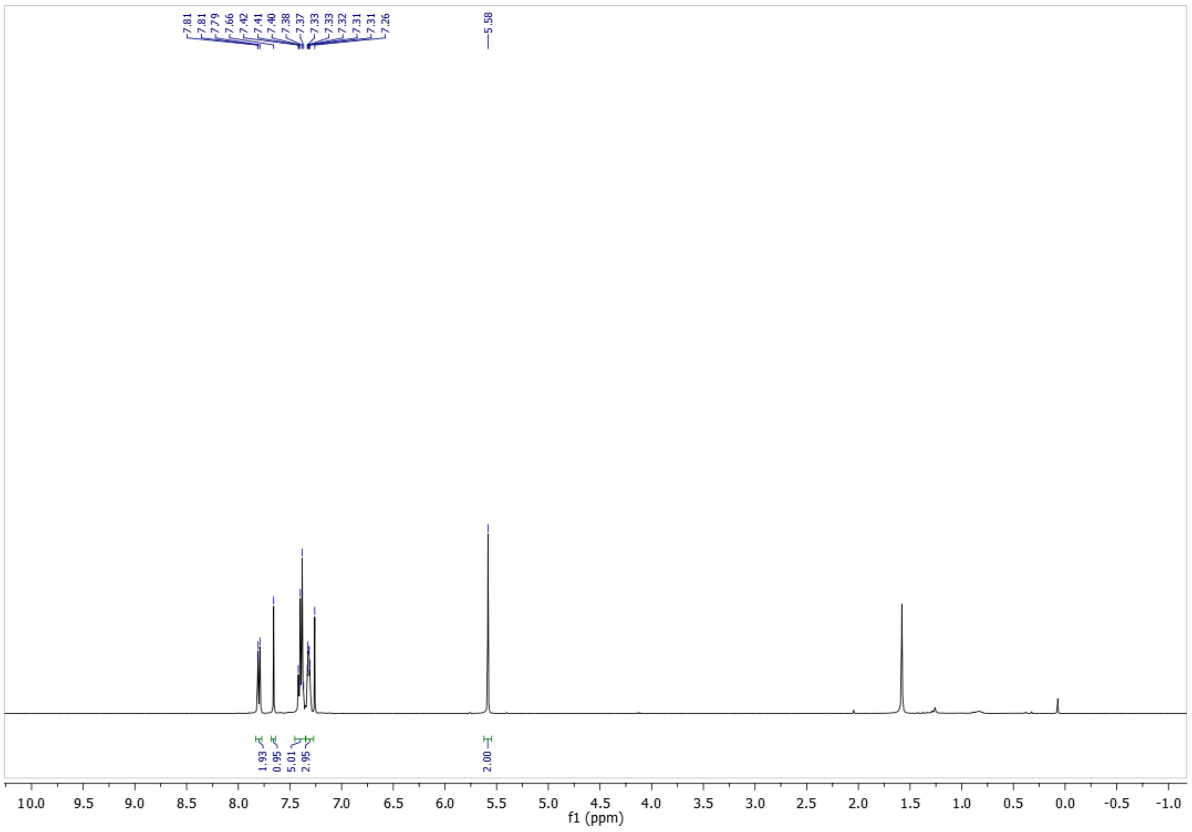
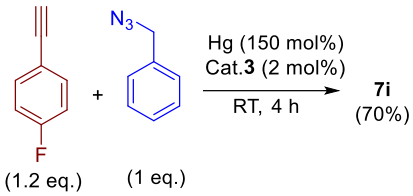
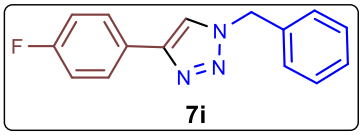


Figure S158. ^{1}H NMR spectrum of triazole **7k** measured in $CDCl_3$.

Preparation of triazole (7i)



7i was prepared according to the general procedure. The crude reaction mixture was purified by silica gel flash column chromatography (EtOAc) and washed with *n*-hexane (2×3 mL) and dried in a high vacuum to afford a white solid (12.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.77 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.62 (s, 1H), 7.44 – 7.36 (m, 3H), 7.34 – 7.28 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 5.57 (s, 2H) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.55 (s) ppm.



7i

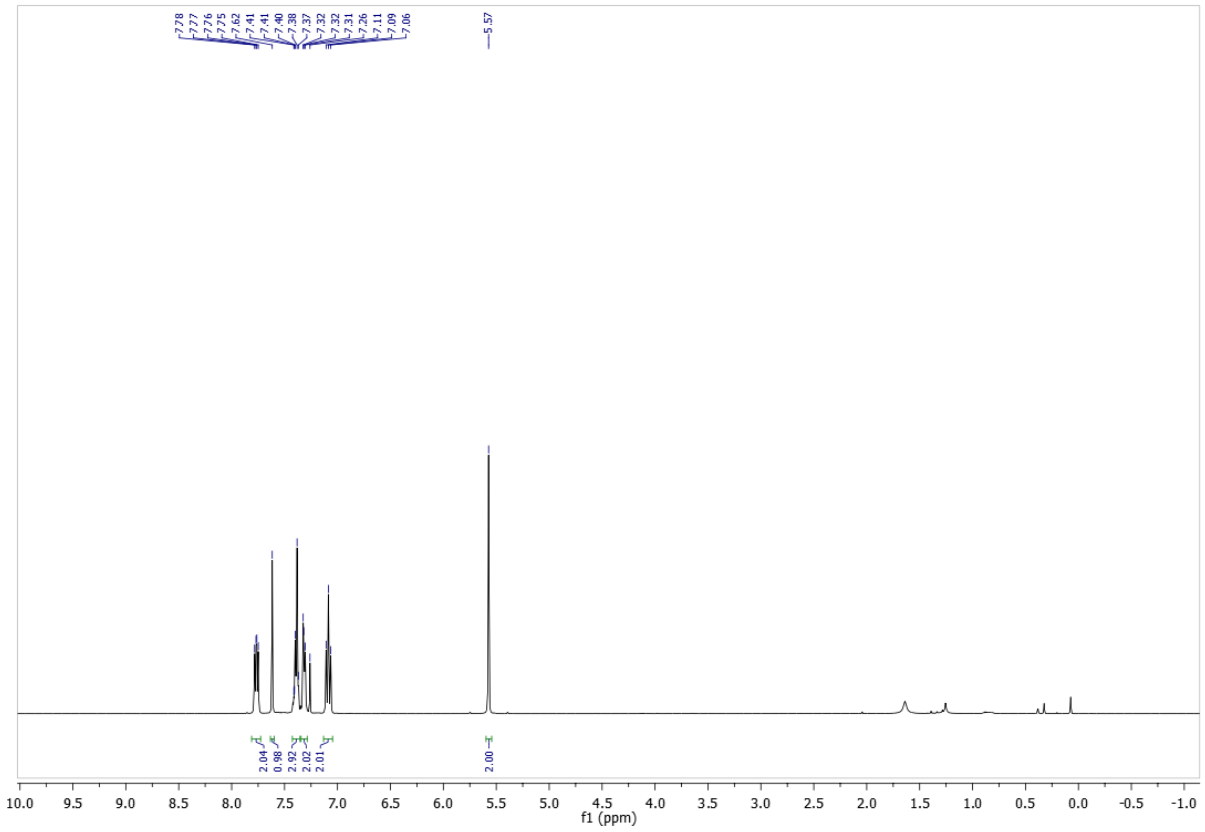


Figure S159. ^{1}H NMR spectrum of triazole **7i** measured in $CDCl_3$.

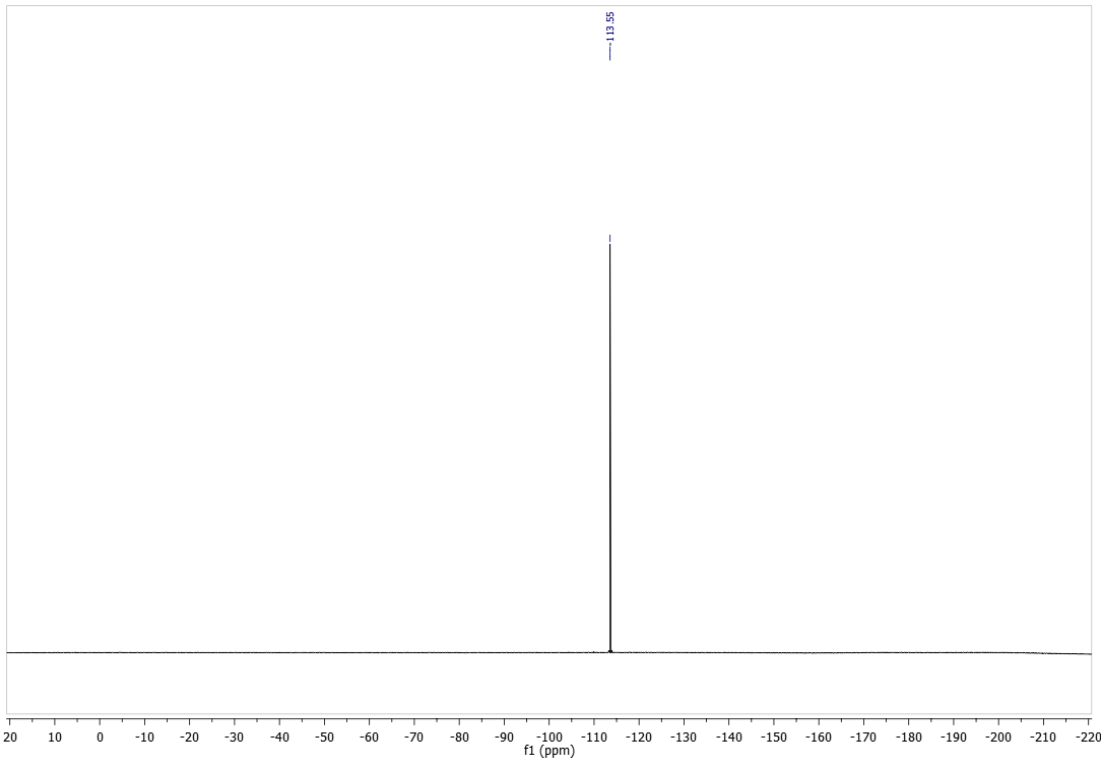


Figure S160. ^{19}F NMR spectrum of triazole **7i** measured in $CDCl_3$.

X-ray crystallographic information of complexes 1-4, 6a and 8e

X-ray crystallographic information of o-silylated phosphine **1**

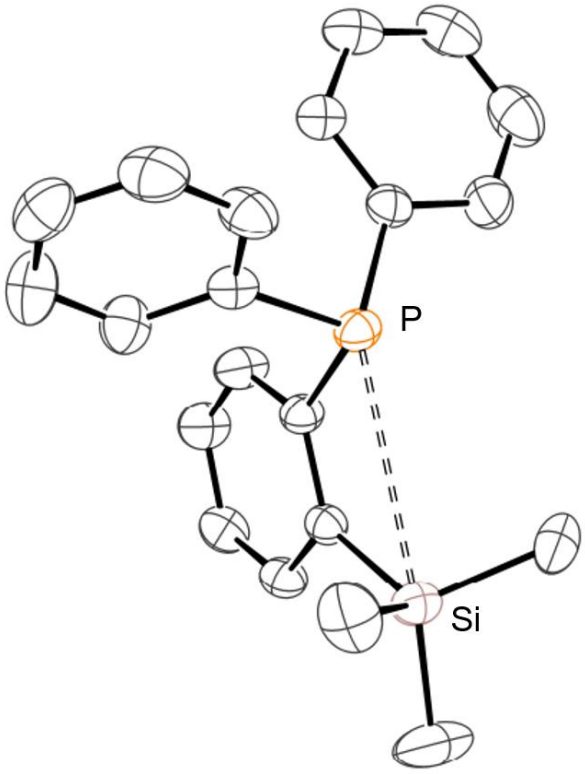


Figure S161. ORTEP view of **1** with 30% ellipsoid probability. Hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P–Si 3.403.

Table S1. Crystal data and structure refinement parameters of **1**

CCDC identification number	2264786
Empirical formula	$C_{21}H_{23}PSi$
Formula weight	334.45
Temperature/K	288(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.05060(10)
b/Å	24.7054(4)
c/Å	19.7244(3)
α/°	90
β/°	95.628(2)
γ/°	90
Volume/Å^3	3904.14(10)

Z	8
ρ_{calc}g/cm^3	1.138
μ/mm^{-1}	1.794
F(000)	1424.0
Crystal size/mm^3	0.32 × 0.28 × 0.26
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.156 to 155.874
Index ranges	-10 ≤ h ≤ 10, -31 ≤ k ≤ 30, -25 ≤ l ≤ 21
Reflections collected	31560
Independent reflections	8060 [R_{int} = 0.0366, R_{sigma} = 0.0299]
Data/restraints/parameters	8060/0/424
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0806, wR_2 = 0.2217
Final R indexes [all data]	R_1 = 0.0883, wR_2 = 0.2325
Largest diff. peak/hole / e Å^{-3}	1.72/-0.25

X-ray crystallographic information of phosphine **2**

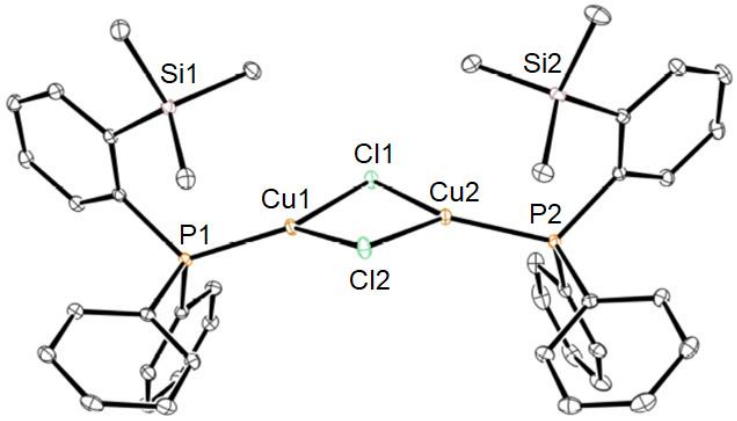


Figure S162. ORTEP view **2** with 30% ellipsoid probability. The hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–Cu1 2.1867 (4) P2–Cu2 2.1759 (4) Cu1–Cl1 2.3089 (4), Cu1–Cl2 2.3135 (5), Cu2–Cl2 2.2867 (4), Cu2–Cl1 2.3056 (4), P1–Si1 3.547, P2–Si2 3.531, Cu1–Cl1–Cu2 81.320 (15), Cu1–Cl2–Cu2 81.625 (15), Cl1–Cu1–Cl2 97.294 (16), Cl1–Cu2–Cl2 98.151 (16), P1–Cu1–Cl1 135.184 (18), P1–Cu1–Cl2 127.086 (18), P2–Cu2–Cl1 131.683 (18), and P2–Cu2–Cl2 128.684 (19)

Table S2. Crystal data and structure refinement parameters of complex **2**

CCDC identification number	2264791
Empirical formula	$C_{42}H_{46}Cl_2Cu_2P_2Si_2$
Formula weight	866.89
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.3025(2)
b/Å	16.1615(2)
c/Å	17.2690(3)
α/°	90
β/°	115.546(2)
γ/°	90
Volume/Å^3	4105.11(12)
Z	4
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	3.988
F(000)	1792.0
Crystal size/mm^3	0.3 × 0.24 × 0.21
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.882 to 156.11
Index ranges	$-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $-21 \leq l \leq 20$
Reflections collected	33570
Independent reflections	8580 [R_{int} = 0.0375, R_{sigma} = 0.0289]
Data/restraints/parameters	8580/0/457
Goodness-of-fit on F2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0808
Largest diff. peak/hole / e Å-3	0.41/-0.56

X-ray crystallographic information of complex **3**

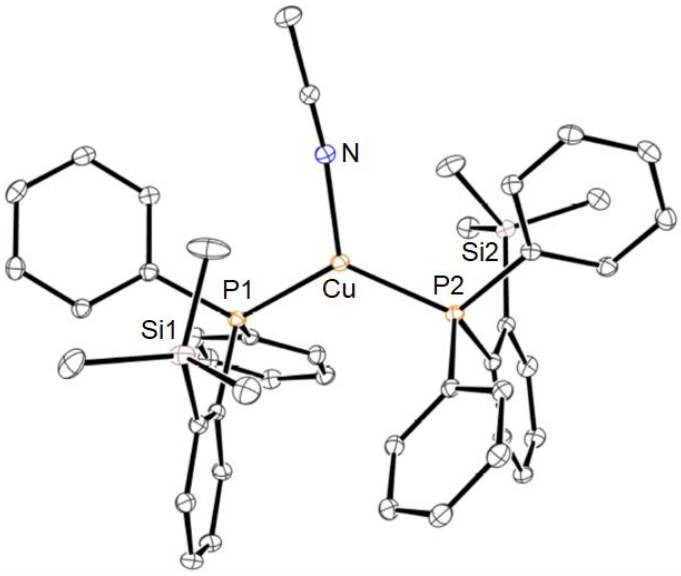


Figure S163. ORTEP view **3** with 30% ellipsoid probability. Anionic part and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–Cu 2.2694 (5), P2–Cu 2.2681 (5), Cu–N 1.9910 (17), P1–Si1 3.702, P2–Si2 3.686, P1–Cu–P2 127.66 (2), N–Cu–P1 118.26 (5), and N–Cu–P2 113.99 (5).

Table S3. Crystal data and structure refinement parameters of complex **3**

CCDC identification number	2264792
Empirical formula	$C_{44}H_{49}BCuF_4NP_2Si_2$
Formula weight	860.31
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.02920(10)
b/Å	13.37500(10)
c/Å	13.54990(10)
α/°	94.6820(10)
β/°	105.4300(10)
γ/°	106.4460(10)
Volume/Å3	2151.36(3)
Z	2
ρcalcg/cm3	1.328
μ/mm-1	2.358
F(000)	896.0
Crystal size/mm3	0.35 × 0.29 × 0.24

Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.868 to 159.03
Index ranges	-11 ≤ h ≤ 16, -17 ≤ k ≤ 16, -17 ≤ l ≤ 16
Reflections collected	36072
Independent reflections	9184 [Rint = 0.0258, Rsigma = 0.0176]
Data/restraints/parameters	9184/0/503
Goodness-of-fit on F2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0408, wR2 = 0.1033
Final R indexes [all data]	R1 = 0.0411, wR2 = 0.1035
Largest diff. peak/hole / e Å-3	1.70/-0.93

X-ray crystallographic information of complex **4a**

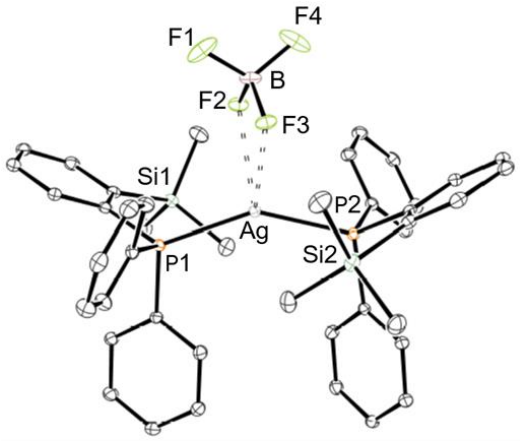


Figure S164. ORTEP view **4a** with 30% ellipsoid probability. Counter anions and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–Ag 2.4241 (5), P2–Ag 2.4223 (5), B1–F1 1.366 (3), B1–F2 1.404 (3) , B1–F3 1.409 (3) , B1–F4 1.368 (3) , Ag–F2 2.644 , Ag–F3 2.626, P1–Si1 3.689, P2–Si2 3.714, P1–Ag–P2 147.34 (2), and F3–Ag–F2 50.91.

Table S4. Crystal data and structure refinement parameters of complex **4a**

CCDC identification number	2264784
Empirical formula	$C_{42}H_{46}AgBF_4P_2Si_2$
Formula weight	863.59
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pccn

a/Å	24.2410(3)
b/Å	21.6058(3)
c/Å	15.7379(2)
α/°	90
β/°	90
γ/°	90
Volume/Å3	8242.67(19)
Z	8
ρcalcg/cm3	1.392
μ/mm-1	5.604
F(000)	3552.0
Crystal size/mm3	0.32 × 0.28 × 0.21
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.294 to 155.944
Index ranges	-30 ≤ h ≤ 23, -20 ≤ k ≤ 27, -15 ≤ l ≤ 19
Reflections collected	35651
Independent reflections	8544 [Rint = 0.0436, Rsigma = 0.0314]
Data/restraints/parameters	8544/0/476
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0358, wR2 = 0.0983
Final R indexes [all data]	R1 = 0.0384, wR2 = 0.1000
Largest diff. peak/hole / e Å-3	0.76/-1.32

X-ray crystallographic information of complex **4b**

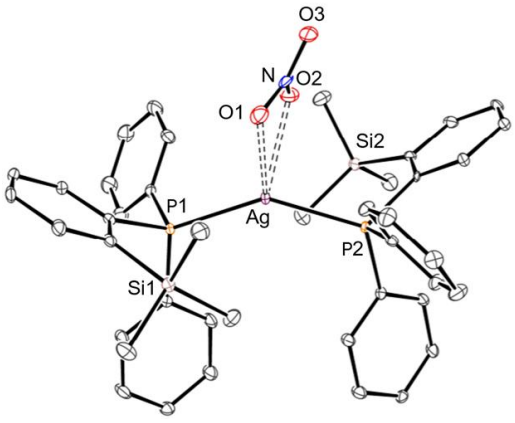


Figure S165. ORTEP view **4b** with 30% ellipsoid probability. Counter anions and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–Ag 2.4157 (8), P2–Ag 2.4457 (8), N–O1 1.251 (5), N–O2 1.267 (5) , N–O3 1.241 (4) , Ag–O1 2.576 (3),

Ag–O2 2.504 (3), P1–Si1 3.693, P2–Si2 3.718, P1–Ag1–P2 1473.85 (3), and O1–Ag–O2 50.47 (10).

Table S5. Crystal data and structure refinement parameters of complex **4b**

Empirical formula	$C_{42}H_{48}AgNO_4P_2Si_2$
CCDC number	2264789
Formula weight	856.80
Temperature/K	99.98
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.6194(3)
b/Å	22.2002(4)
c/Å	23.7789(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	8245.4(3)
Z	8
$\rho_{calc}g/cm^3$	1.380
μ/mm^{-1}	5.540
F(000)	3552.0
Crystal size/mm^3	0.33 × 0.28 × 0.26
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.436 to 158.134
Index ranges	$-17 \leq h \leq 19$, $-28 \leq k \leq 27$, $-30 \leq l \leq 28$
Reflections collected	35343
Independent reflections	8639 [R_{int} = 0.0570, R_{sigma} = 0.0316]
Data/restraints/parameters	8639/6/478
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1738
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1783
Largest diff. peak/hole / e $Å^{-3}$	0.94/-2.00

X-ray crystallographic information of complex **4c**

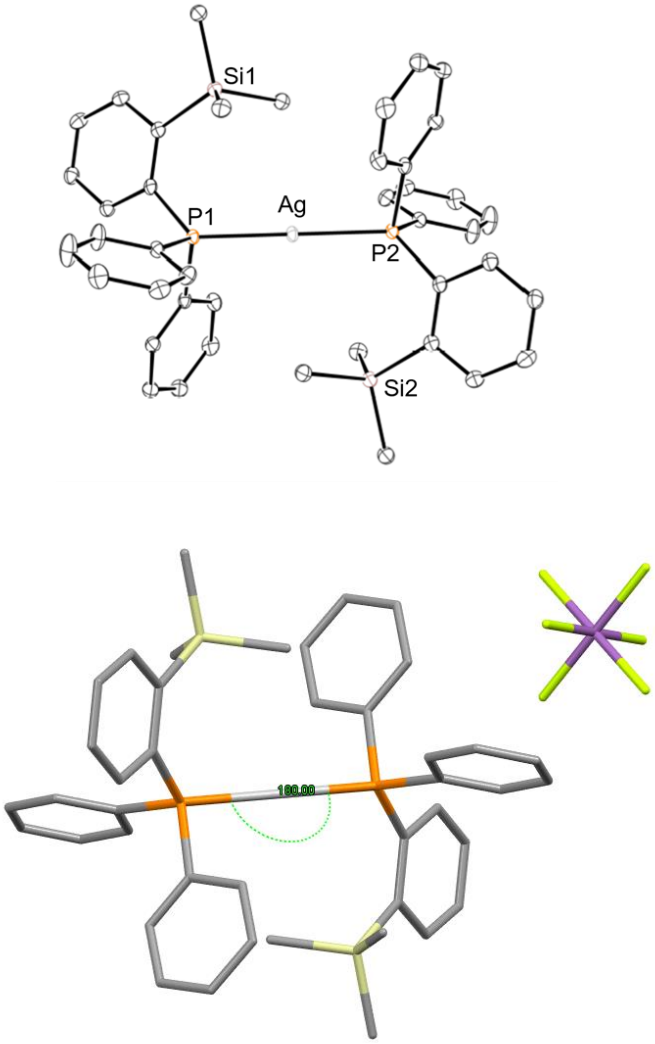


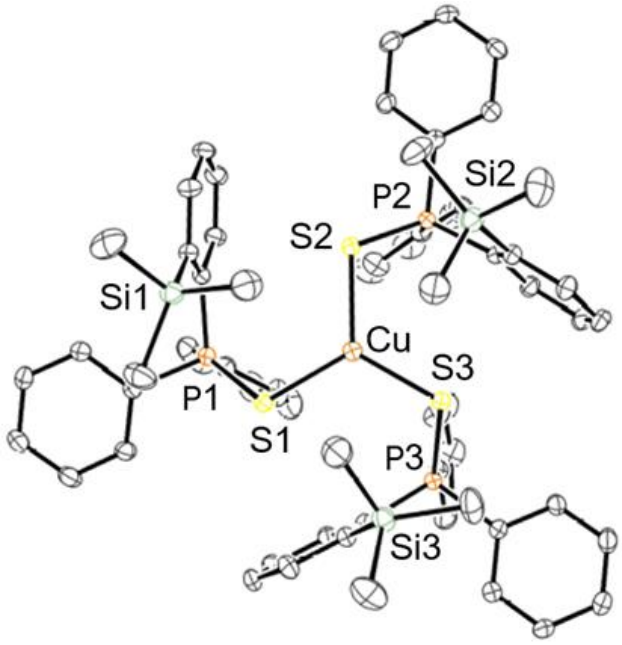
Figure S166. ORTEP view **4c** with 30% ellipsoid probability. Counter anions and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–Ag 2.3936 (6), P2–Ag 2.3936 (6), P1–Si1 3.594, P2–Si2 3.594 and P1–Ag–P2 180.0

Table S6. Crystal data and structure refinement parameters of complex **4c**

Empirical formula	$C_{42}H_{46}AgF_6P_2SbSi_2$
CCDC number	2264788
Formula weight	1012.53
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.2983(2)
b/Å	10.5547(3)

c/Å	12.5094(3)
α/°	98.729(2)
β/°	91.481(2)
γ/°	101.102(2)
Volume/Å^3	1060.98(5)
Z	1
ρ_{calc}g/cm^3	1.585
μ/mm^{-1}	10.480
F(000)	508.0
Crystal size/mm^3	0.33 × 0.29 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.16 to 155.648
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	16610
Independent reflections	4411 [R_{int} = 0.0815, R_{sigma} = 0.0544]
Data/restraints/parameters	4411/0/250
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1198
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1216
Largest diff. peak/hole / e Å^{-3}	1.38/-1.74

X-ray crystallographic information of **6a**



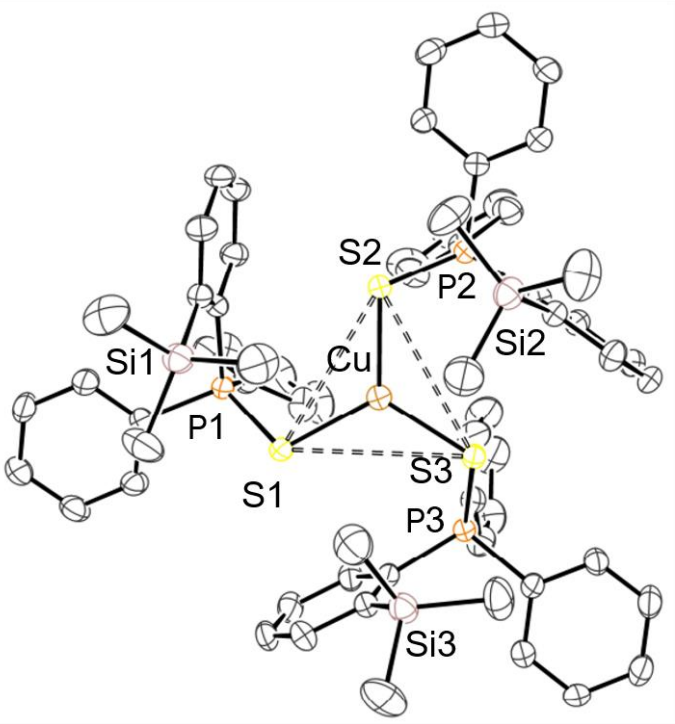


Figure S167. ORTEP view of **6a** with 30% ellipsoid probability. The counter anion and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. P1–S1 1.990, P2–S2 1.990, P3–S3 1.990, S1–Cu 2.254, S2–Cu 2.254, S3–Cu 2.254, P1–Si1 3.690, P2–Si2 3.690, P3–Si3 3.690, S1–Si1 3.752, S2–Si2 3.752, S3–Si3 3.752, P1–S1–Cu 106.92, P2–S2–Cu 106.92, P3–S3–Cu 106.92, S1–Cu–S2 119.42, S2–Cu–S3 119.42, and S3–Cu–S1 119.42 .

Table S7. Crystal data and structure refinement parameters of complex **6a**

Empirical formula	$C_{63}H_{69}BCuF_4P_3S_3Si_3$
CCDC number	2264785
Formula weight	1249.89
Temperature/K	297.1(3)
Crystal system	trigonal
Space group	P31c
a/Å	15.64330(10)
b/Å	15.64330(10)
c/Å	16.00190(10)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3391.24(5)

Z	2
ρ_{calc}g/cm^3	1.224
μ/mm^{-1}	2.870
F(000)	1304.0
Crystal size/mm^3	0.26 × 0.26 × 0.22
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.552 to 158.574
Index ranges	-19 ≤ h ≤ 19, -15 ≤ k ≤ 19, -18 ≤ l ≤ 20
Reflections collected	18846
Independent reflections	4234 [R_{int} = 0.0319, R_{sigma} = 0.0245]
Data/restraints/parameters	4234/1/238
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0757, wR_2 = 0.2092
Final R indexes [all data]	R_1 = 0.0760, wR_2 = 0.2097
Largest diff. peak/hole / e Å^{-3}	0.34/-1.33
Flack parameter	0.11(6)

X-ray crystallographic information of compound **8e**

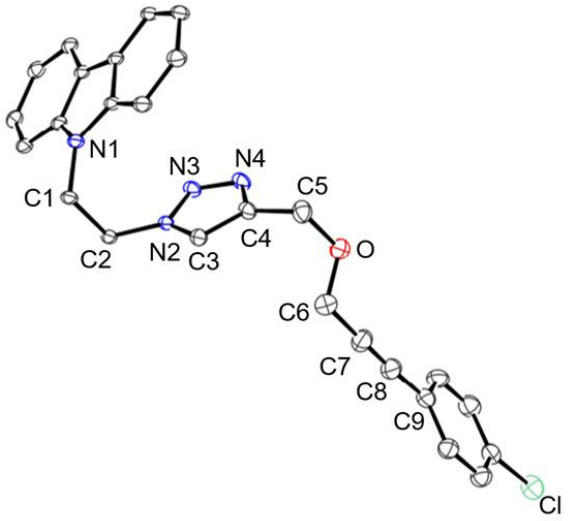


Figure S168. ORTEP view **8e** with 30% ellipsoid probability. Hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. N1–C1 1.448 (4), C1–C2 1.528 (4), C2–N2 1.457 (4), O–C5 1.429 (4), O–C6 1.417 (5), C6–C7 1.456 (6), C7–C8 1.189 (6), C8–C9 1.439 (6), C6–C7–C8 179.0 (6), C5–O–C6 110.4 (3) and N1–C1–C2 112.7 (2).

Table S8. Crystal data and structure refinement parameters of compound **8e**

CCDC number	2264790
Empirical formula	$C_{26}H_{21}ClN_4O$
Formula weight	440.92
Temperature/K	100.05
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7468(4)
b/Å	5.53310(10)
c/Å	33.9191(15)
α/°	90
β/°	99.623(4)
γ/°	90
Volume/Å^3	2173.59(13)
Z	4
ρ_{calc}g/cm^3	1.347
μ/mm^{-1}	1.764
F(000)	920.0
Crystal size/mm^3	0.26 × 0.2 × 0.17
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.634 to 156.914
Index ranges	$-14 \leq h \leq 14$, $-6 \leq k \leq 7$, $-42 \leq l \leq 42$
Reflections collected	33818
Independent reflections	4594 [R_{int} = 0.0837, R_{sigma} = 0.0442]
Data/restraints/parameters	4594/0/289
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0857, wR_2 = 0.2315
Final R indexes [all data]	R_1 = 0.0927, wR_2 = 0.2372
Largest diff. peak/hole / e Å^{-3}	0.95/-0.89

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