Supporting Information

Dicationic Copper(I) Complexes Bearing ENE (E = S, Se) Pincer Ligands; Catalytic Applications in Regioselective Cyclization of 1,6-diynes

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Materials and Methods

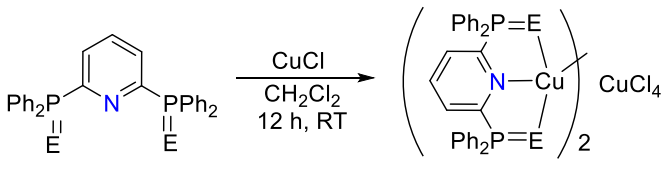
All the reagents were purchased from commercially available sources (Loba Chemie, Spectrochem and Sigma-Aldrich, TCI, and Avra). Pyridine bridging sulfide and selenides (BPPP)E_2 (E = S, Se) were prepared according to the reported procedures.[1] Internal terminal alkyne, 1-Phenyl-4-oxahepta-1,6-diyne, and its substituted derivatives were prepared according to the reported synthetic protocols.[2] Some starting materials were prepared by following reported procedures. Dichloromethane 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 dry N_2. All catalytic reactions were carried out in a Borosil-sealed tube in N_2 atmosphere. Using distilled petroleum ether 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 "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, DMSO-d_6, ^1H; 2.50, 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 single crystal X-ray analysis was performed using a Rigaku Smart Lab X-ray diffractometer.

Synthetic procedures and spectral data of ligands and corresponding copper complexes

Synthesis of 2a/2b

The pincer ligands (BPPP)E_2 (E = S (**2a**), Se (**2b**)) were prepared according to the previously reported procedure and used for the next step of reactions.[1]

Synthetic scheme for the preparation of 4a and 4b



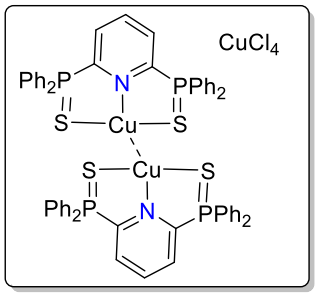
2a; E = S
2b; E = Se

4a; E = S (45%)
4b; E = Se (40%)

Scheme S1. Reactions of (BPPP)E_2 with copper(I) chloride.

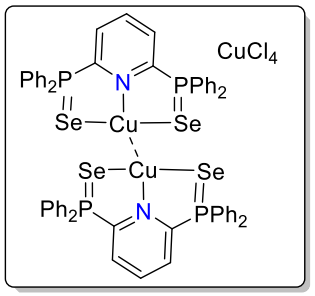
Synthesis of [(2a)Cu]$_2$CuCl$_4$ (4a)

A 25 mL Schlenk tube was charged with pyridine-2,6-diylbis(diphenylphosphine sulfide) (**2a**) (30 mg, 0.059 mmol) and cuprous chloride (5.8 mg, 0.059 mmol). Freshly distilled dry dichloromethane (10 mL) was added, and the reaction mixture was allowed to stir for 12 h at room temperature. During this period, the clear orange solution was observed. All the volatiles were removed under reduced pressure and washed the residue with *n*-hexane (3 x 5 mL), which afforded **4a** as a mustard color solid. Yield; 37 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.16 (br, 1H), 7.58 (br, 8H), and 7.45 (br, 14H) ppm. Analytical data for $C_{58}H_{46}Cl_4Cu_3N_2P_4S_4$ (1355.5930 g/mol): Calcd (%): C, 51.39; H, 3.42; N, 2.07; and S, 9.46; Found: C, 52.43; H, 3.467; N, 2.09; and S, 9.813. HRMS (ESI, positive mode, CH_3CN, *m/z*): 574.0027 $[M]^+$ calcd for $C_{29}H_{23}NS_2P_2Cu$; 574.0043.



Synthesis of [(2b)Cu]$_2$CuCl$_4$ (4b)

A 25 mL Schlenk tube was charged with (**2b**) pyridine-2,6-diylbis (diphenylphosphine selenide) (30 mg, 0.05 mmol) and cuprous chloride (4.9 mg, 0.05 mmol). To this, dry dichloromethane (10 mL) was added and the reaction mixture was allowed to stir for 12 h at room temperature. During this period, a deep orange color solution was observed. After 12 h of stirring at RT, all the volatiles and solvents were removed under reduced pressure and washed with *n*-hexane (3 x 5 mL), which afforded a rusk color solid. Yield; 31 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.23 (br, 1H), 7.65 (br, 9H), and 7.51 (br, 13H) ppm. $C_{58}H_{46}Cl_4Cu_3N_2P_4Se_4$ (1543.2402 g/mol): Calcd (%): C, 45.14; H, 3.00; and N, 1.82; Found: C, 45.05; H, 3.228; and N, 1.61. HRMS (ESI, positive ion mode, CH_3CN, *m/z*): 669.8942 (calcd for $C_{29}H_{23}NSe_2P_2Cu$; 669.8936).



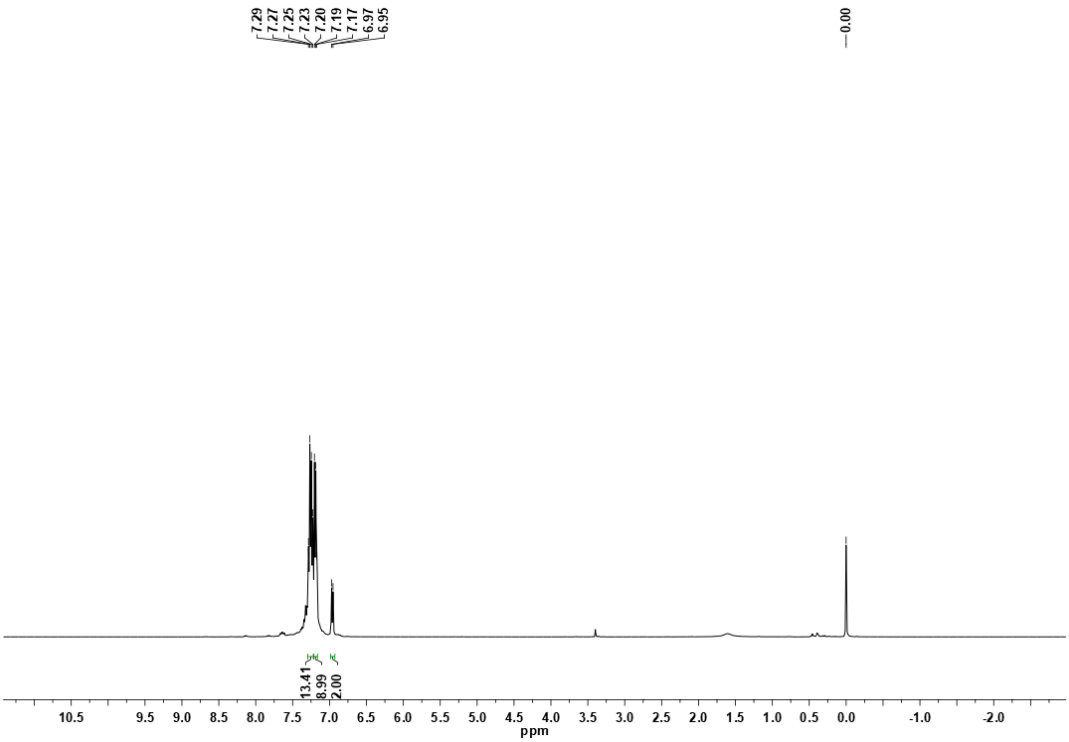


Figure S1. ^{1}H NMR spectrum of 1,6-bis(diphenylphosphino)pyridine **1** measured in $CDCl_3$.

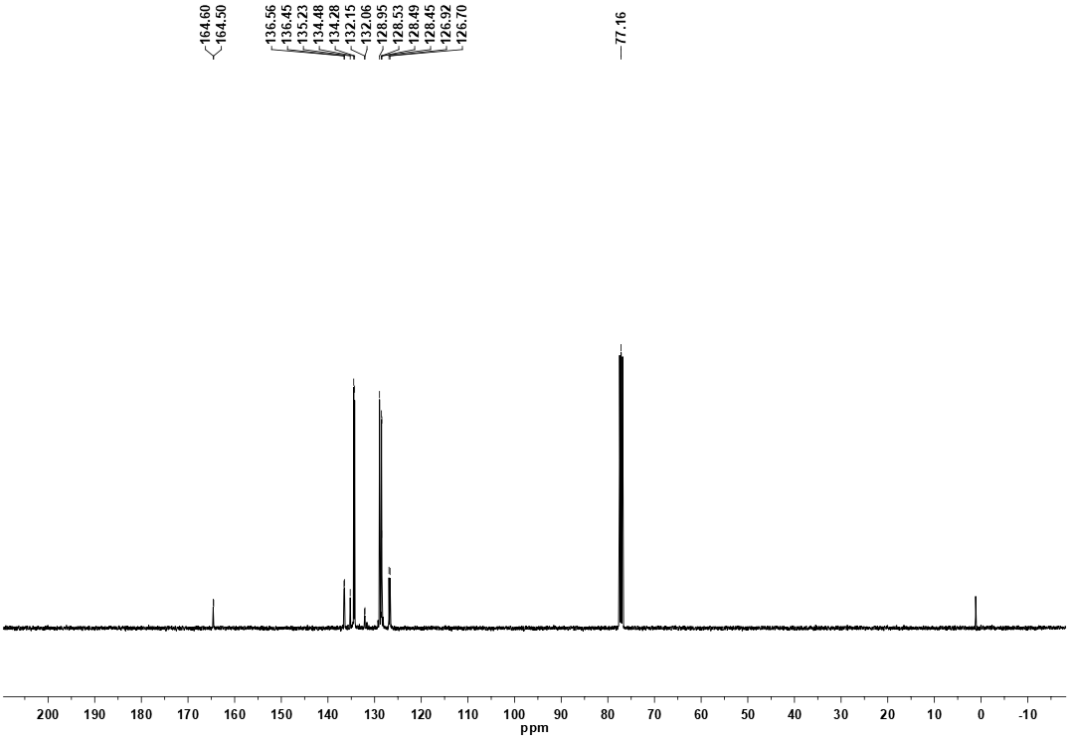


Figure S2. ^{13}C NMR spectrum of 1,6-bis(diphenylphosphino)pyridine (BPPP) **1** measured in $CDCl_3$.

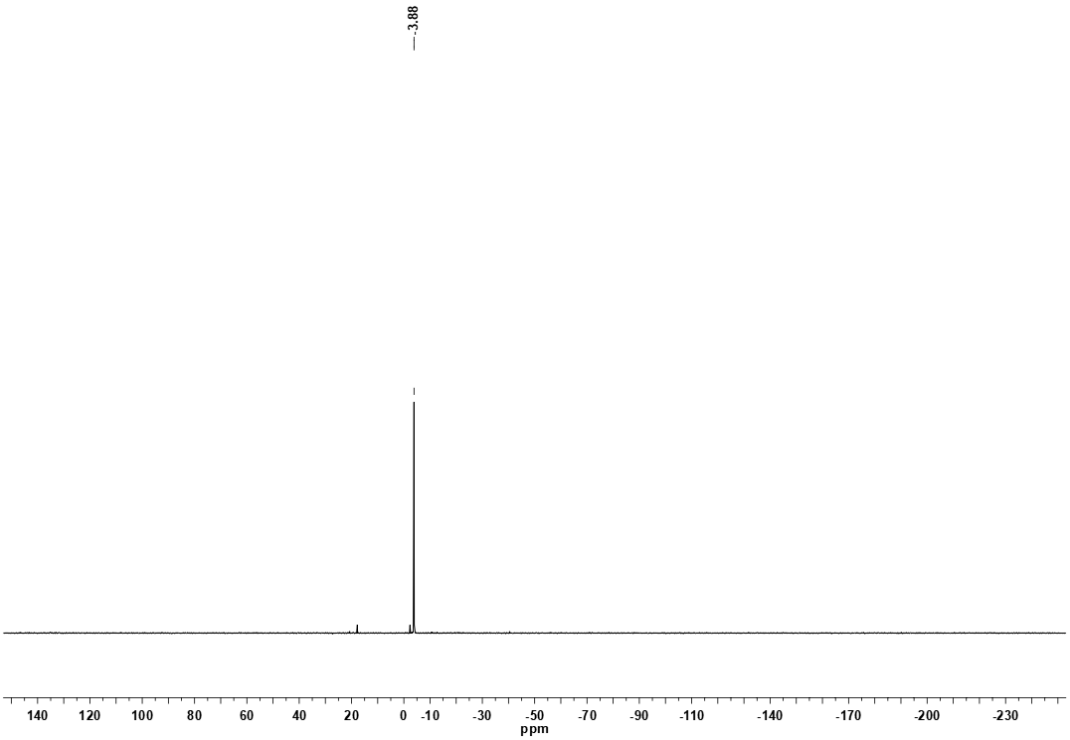


Figure S3. ^{31}P NMR spectrum of 1,6-bis(diphenylphosphino)pyridine (BPPP) **1** measured in $CDCl_3$.

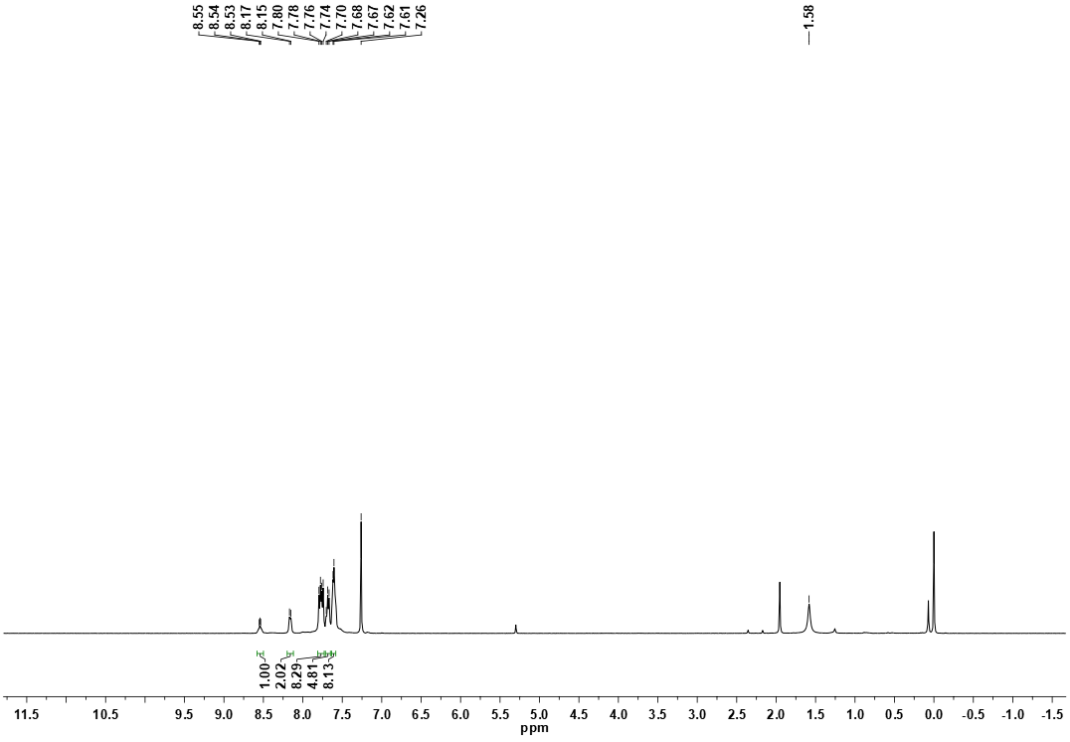


Figure S4. ^{1}H NMR spectrum of complex **3a** measured in $CDCl_3$.

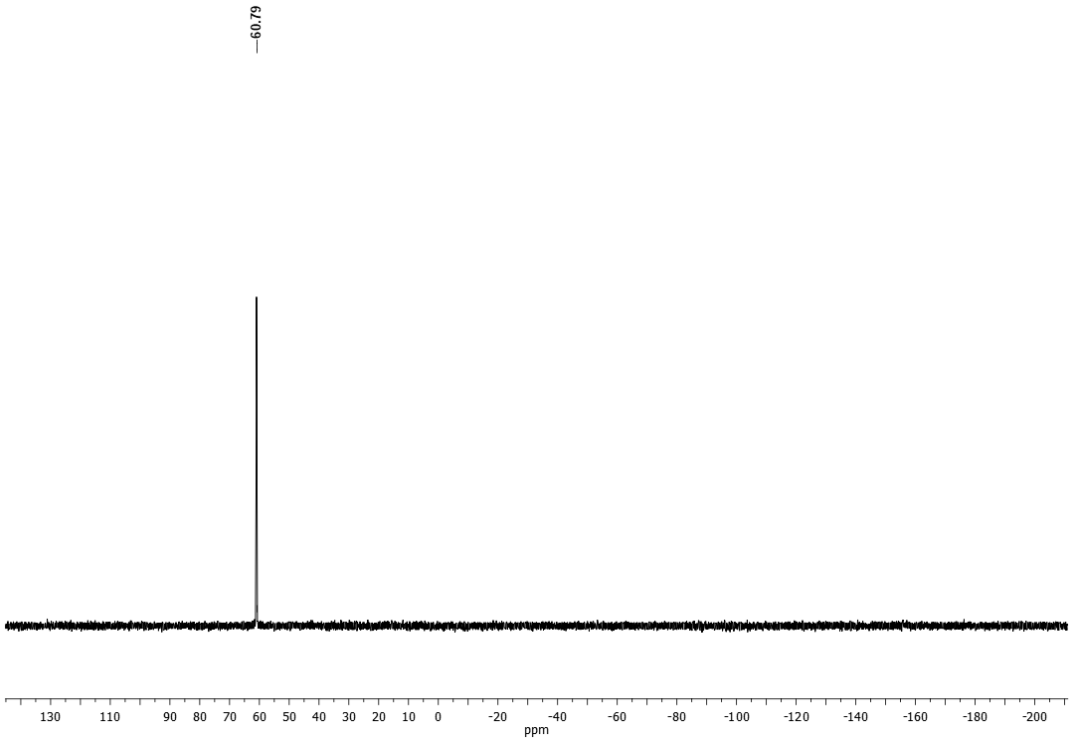


Figure S5. ^{31}P NMR spectrum of complex **3a** measured in $CDCl_3$.

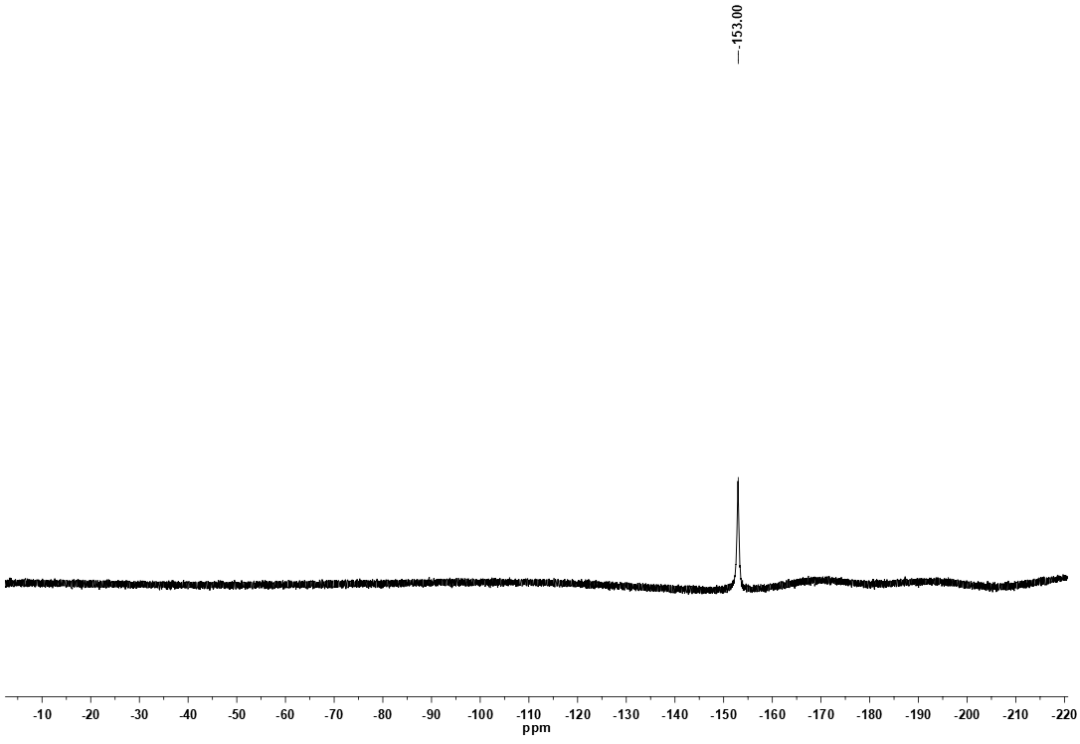


Figure S6. ^{19}F NMR spectrum of complex **3a** measured in $CDCl_3$.

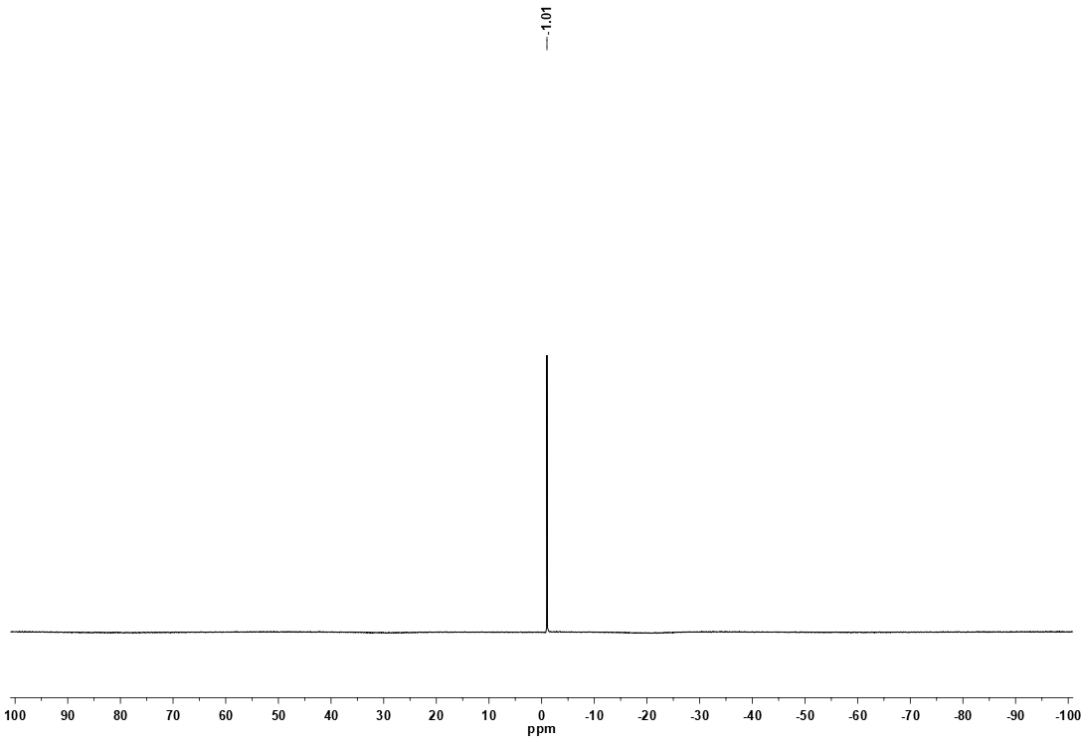


Figure S7. ^{11}B NMR spectrum of complex **3a** measured in $CDCl_3$.

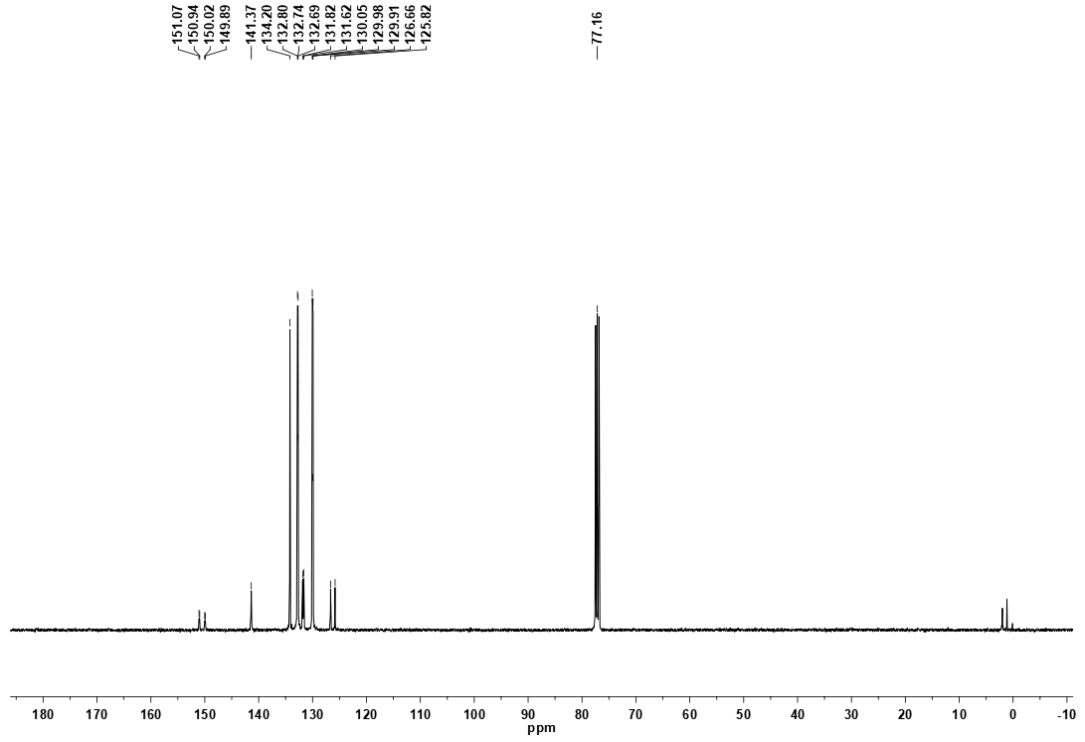


Figure S8. ^{13}C NMR spectrum of complex **3a** measured in $CDCl_3$.

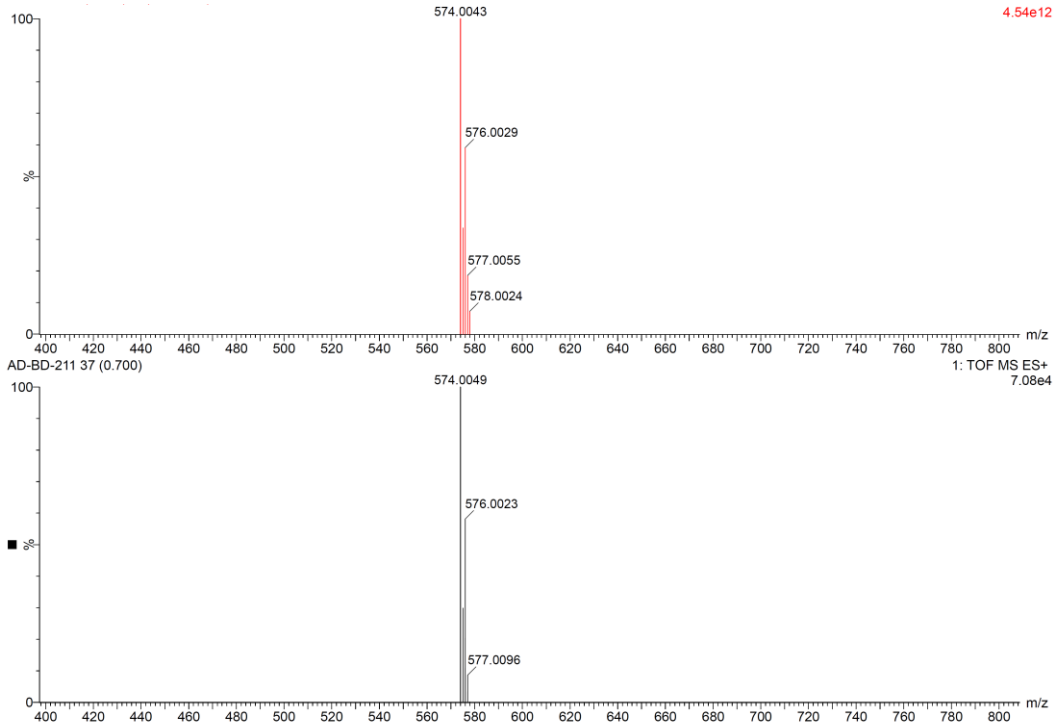


Figure S9. ESI-HRMS spectrum of complex **3a** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

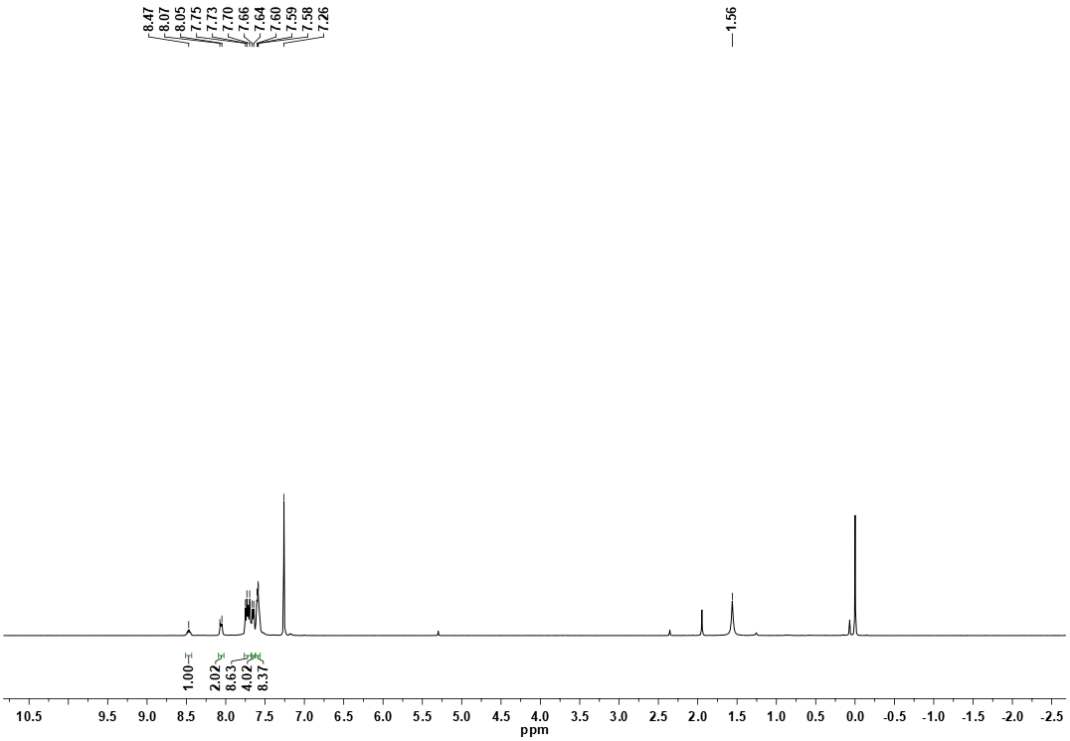


Figure S10. ^{1}H NMR spectrum of cationic copper complex **3b** measured in $CDCl_3$.

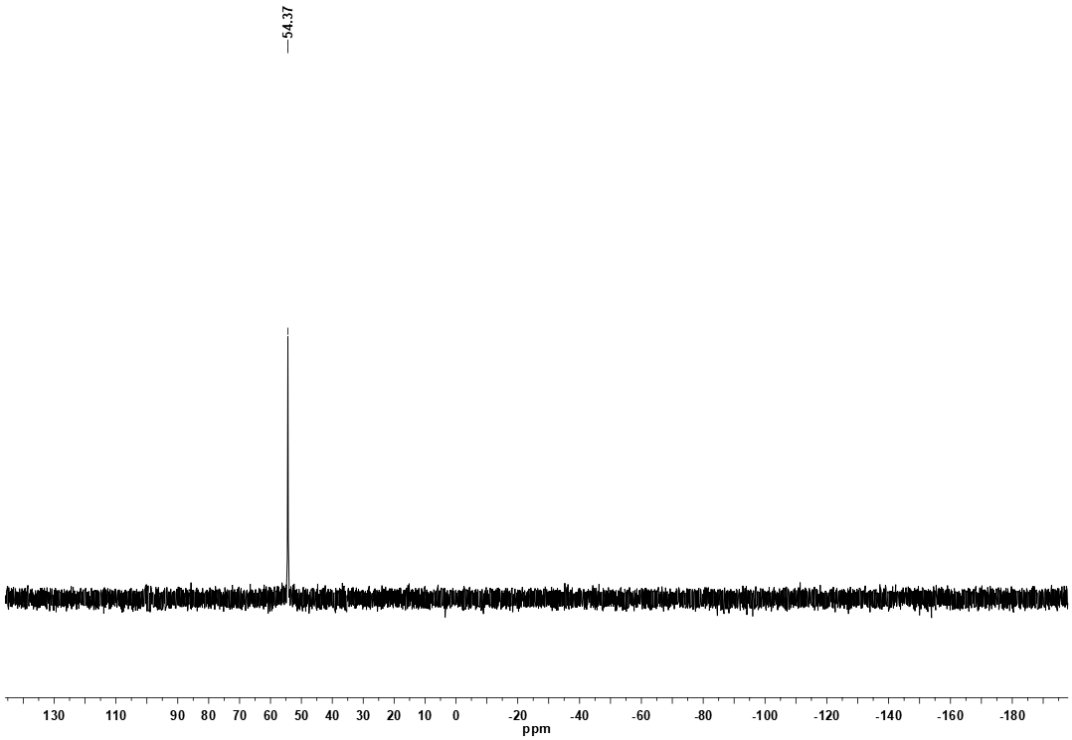


Figure S11. ^{31}P NMR spectrum of cationic copper complex **3b** measured in $CDCl_3$.

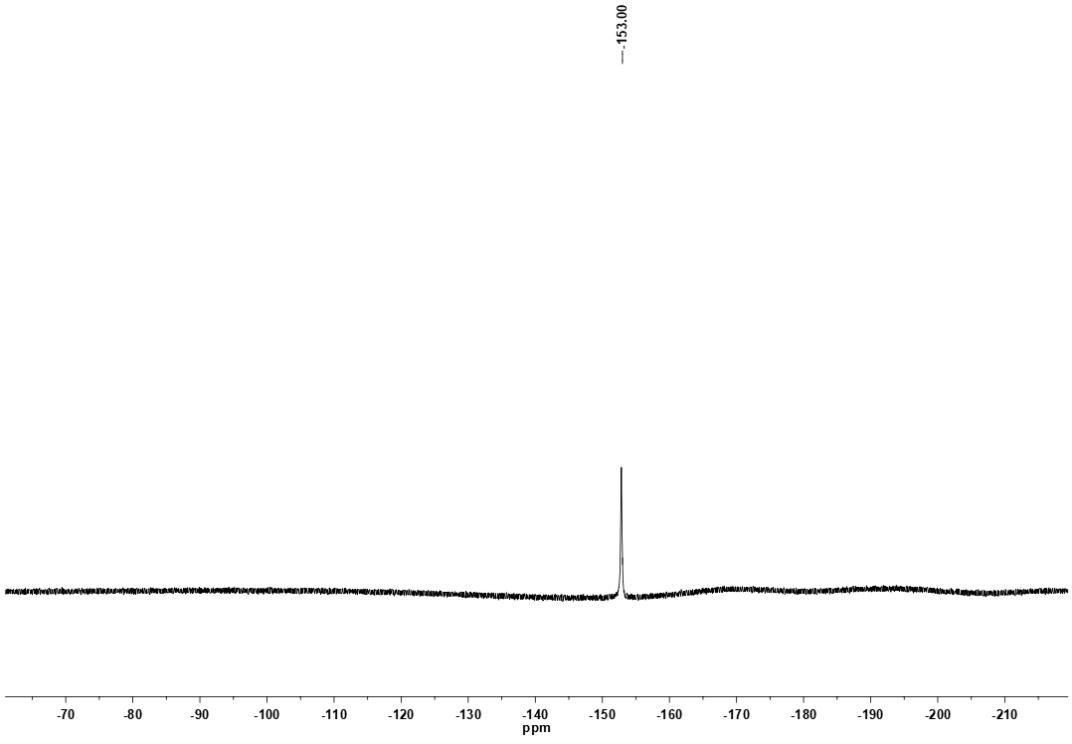


Figure S12. ^{19}F NMR spectrum of cationic copper complex **3b** measured in $CDCl_3$.

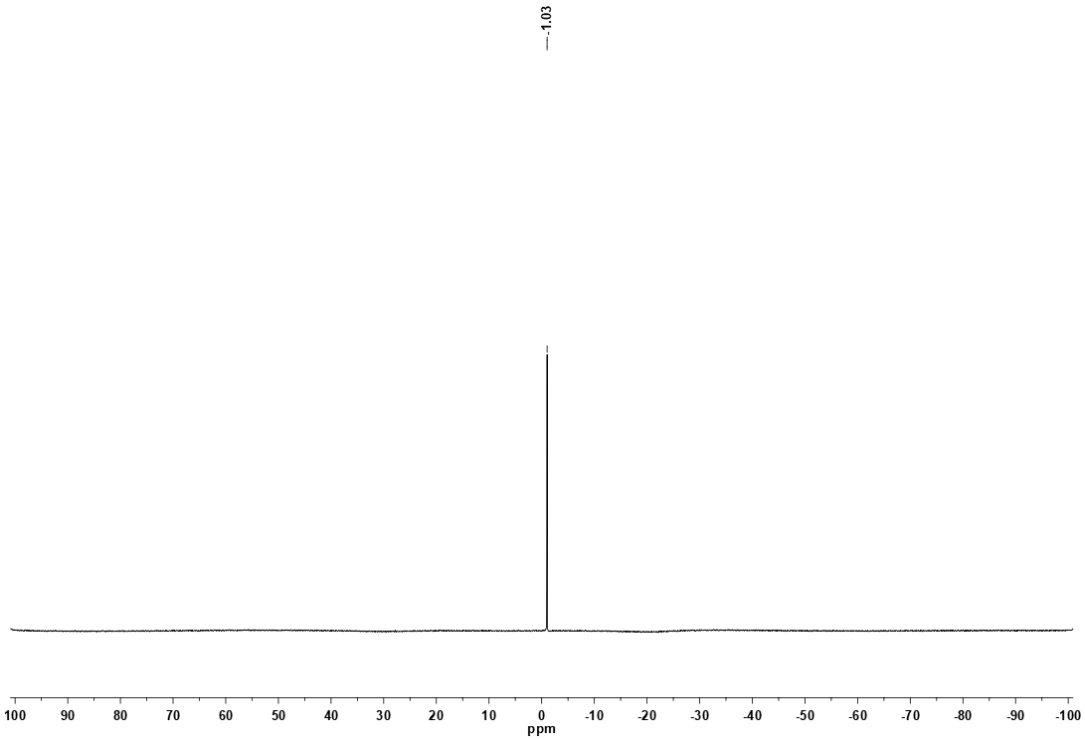


Figure S13. ^{11}B NMR spectrum of cationic copper complex **3b** measured in $CDCl_3$.

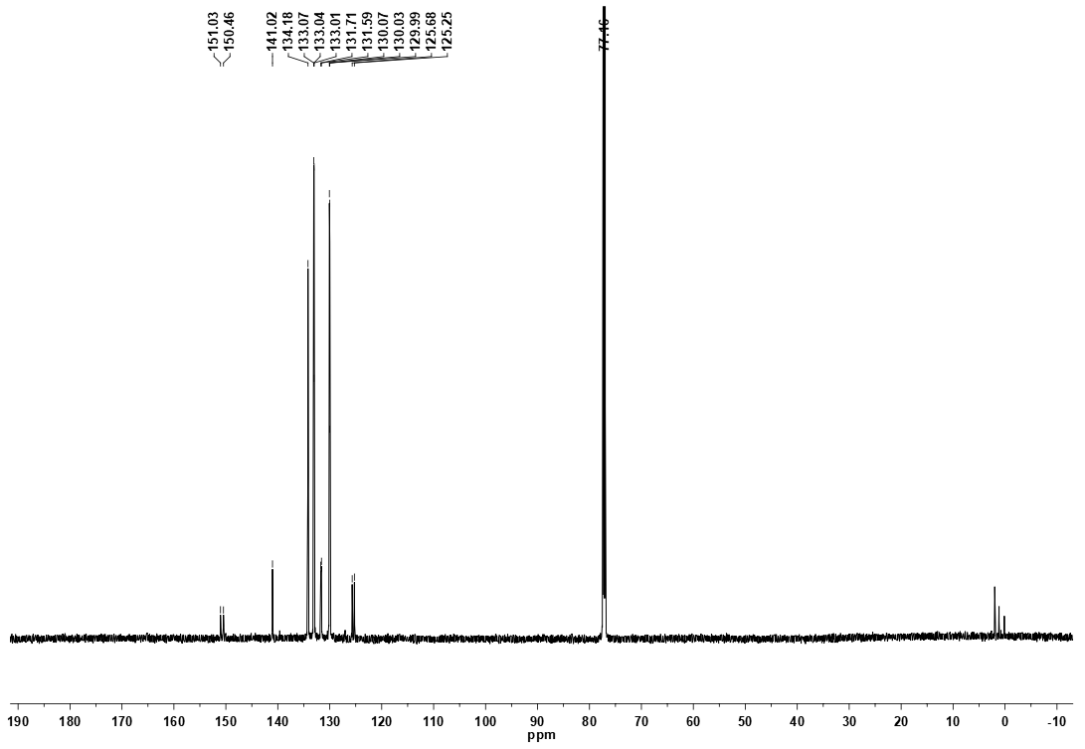


Figure S14. ^{13}C NMR spectrum of cationic copper complex **3b** measured in $CDCl_3$.

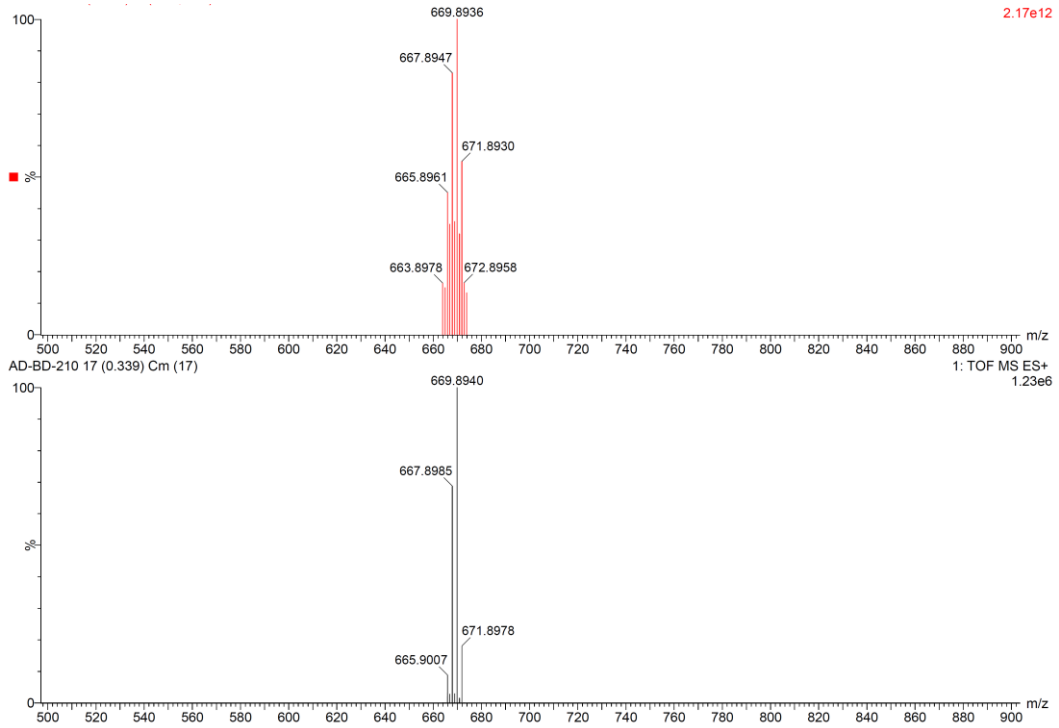


Figure S15. ESI-HRMS spectrum of cationic copper complex **3b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

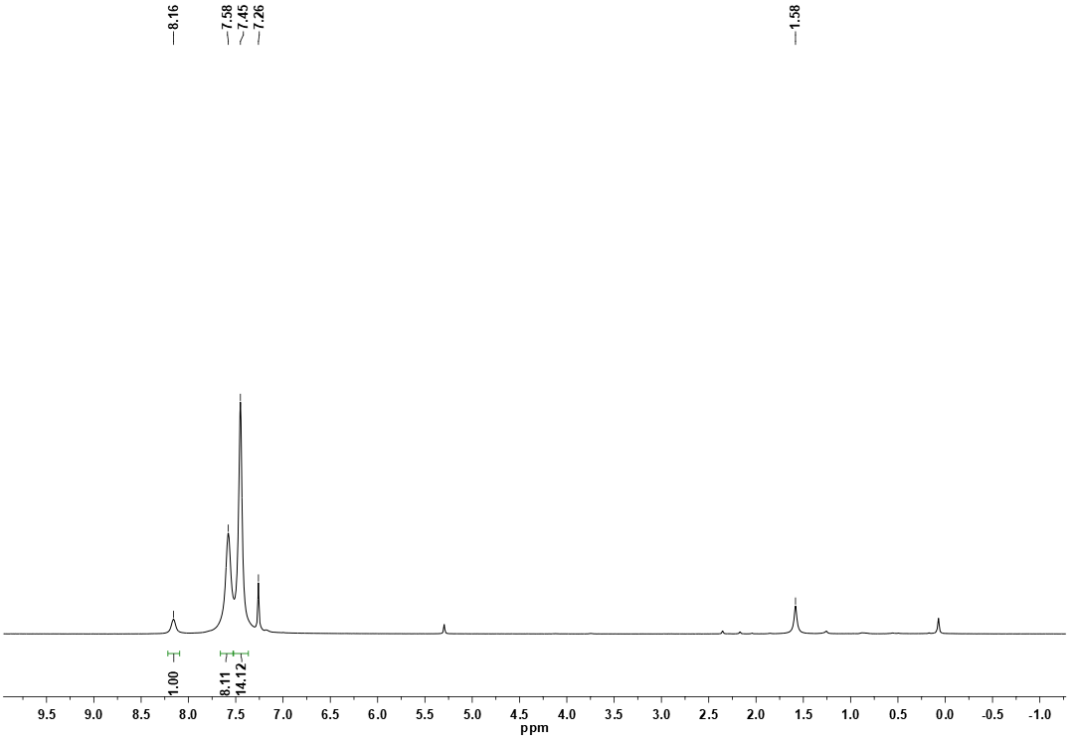


Figure S16. ^{1}H NMR spectrum of **4a** measured in $CDCl_3$.

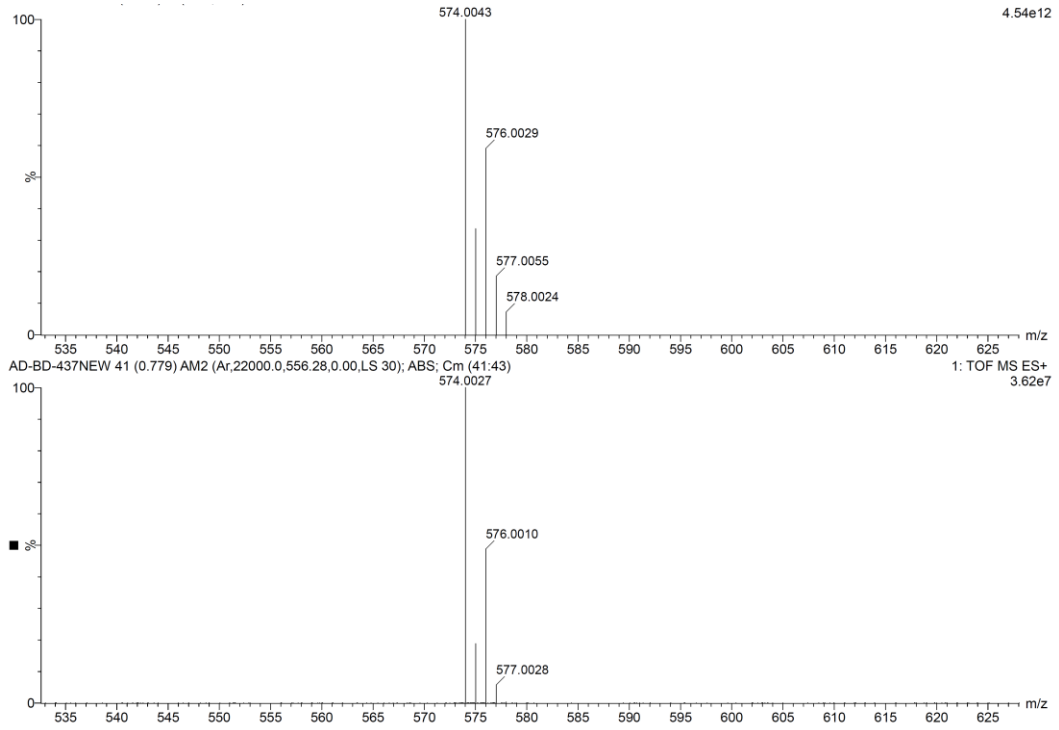


Figure S17. ESI-HRMS spectrum of **4a** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

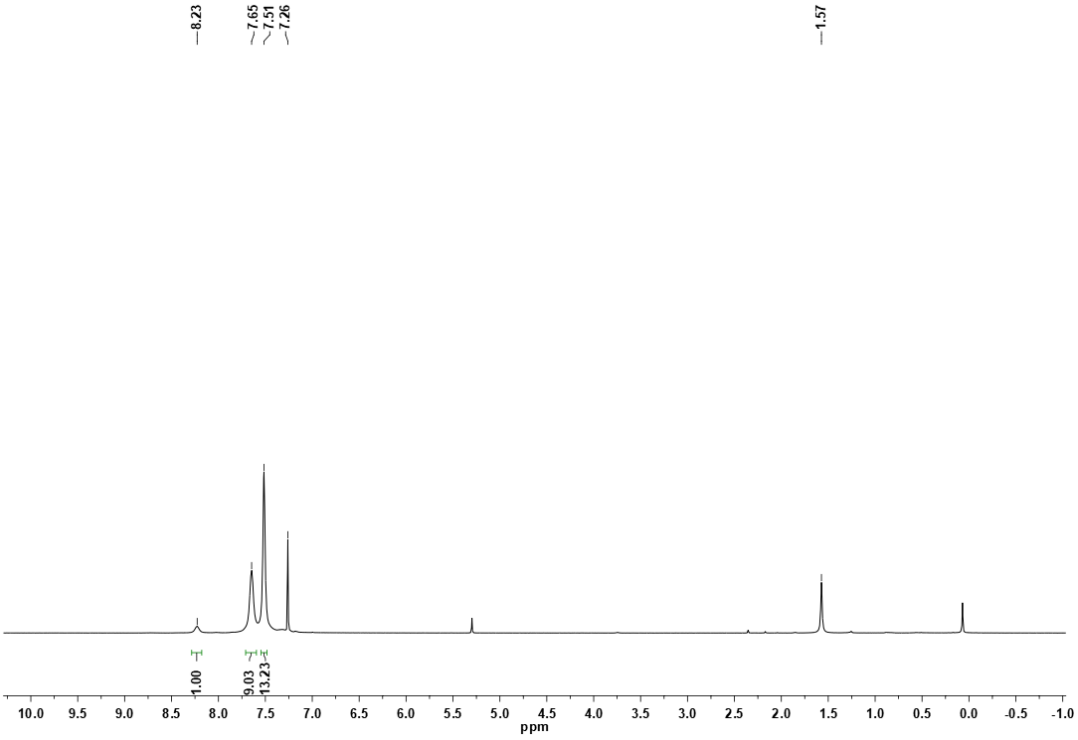


Figure S18. ^{1}H NMR spectrum of **4b** measured in $CDCl_3$.

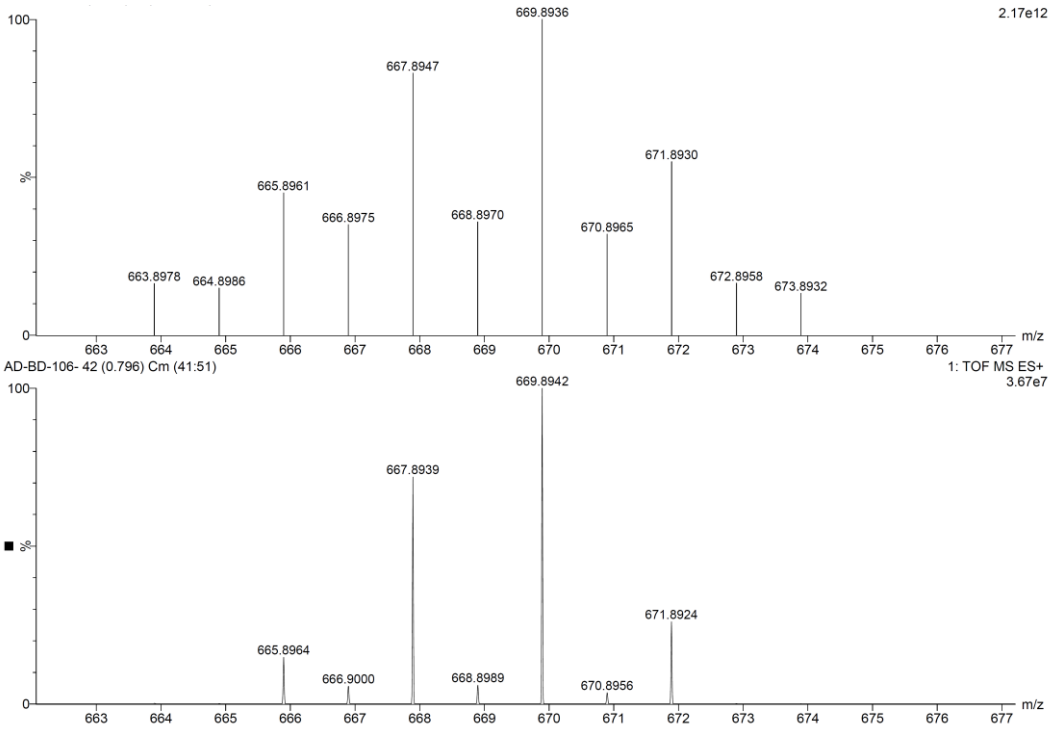


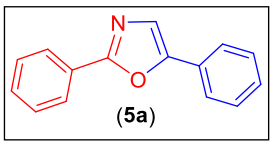
Figure S19. HRMS spectrum of **4b** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

General experimental procedures for the synthesis of substituted oxazoles and triazoles

In a 50 mL seal tube charged with a magnetic bar was added azide (1 equiv.), alkyne (1.2 equiv.), and pre-catalyst **3a** (10 mol%) under nitrogen atmosphere. Then, the reaction mixture was allowed to stir for 12 h at 60 °C. After cooling to room temperature, the crude reaction mixture was purified by silica gel column chromatography (10% EtOAc/hexane mixture) to afford the corresponding substituted oxazoles.

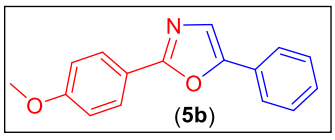
Preparation of oxazole (5a)[3]

5a was prepared according to the general procedure mentioned above. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (10.8 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.14-8.09 (m, 2H), 7.74 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.52-7.42 (m, 6H), and 7.38-7.31 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 161.3, 151.5, 130.5, 129.1, 128.9, 128.6, 128.2, 127.6, 126.4, 124.4, and 123.6 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{11}NO$ $[M+H]^+$: 222.0919; found: 222.0915.



Preparation of oxazole (5b)[3]

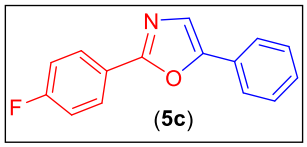
5b was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (12.5 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.07 – 8.02 (m, 2H), 7.71 (dd, *J* = 5.2, 3.3 Hz, 2H),



7.47 – 7.39 (m, 3H), 7.35 – 7.30 (m, 1H), 7.03 – 6.98 (m, 2H), and 3.88 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 161.5, 161.4, 150.9, 129.1, 128.4, 128.1, 124.2, 123.4, 120.5, 114.4, and 55.6 (OCH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 252.1024; found: 252.1052.

Preparation of oxazole (5c)[4]

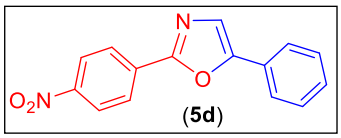
5c was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (9.2 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$); δ = 8.14 – 8.07 (m, 2H), 7.75 – 7.68 (m, 2H), 7.45 (dd, *J* = 10.9, 5.2 Hz, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), and 7.21 – 7.14 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 164.9, 163.5, 151.5, 129.1, 128.7, 128.6, 128.5, 128.1, 124.3, 123.9, 123.6, 116.3, and 116.1 ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –109.4 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}NOF$ $[M+H]^+$: 240.0825; found: 240.0850.



(**5c**)

Preparation of oxazole (5d)[3]

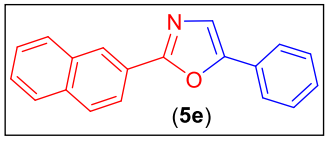
5d was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (7.1 mg, 51%). ^1H NMR (400 MHz, $CDCl_3$); δ = 8.38–8.33 (m, 2H), 8.30–8.24 (m, 2H), 7.78–7.73 (m, 2H), 7.54 (s, 1H), 7.48 (dd, *J* = 8.2, 6.8 Hz, 2H), and 7.43 – 7.36 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 159.1, 152.9, 148.7, 133.6, 132.9, 129.3, 129.3, 127.5, 127.0, 124.6, and 124.4 ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}N_2O_3$ $[M+H]^+$: 267.0770; found: 267.0786.



(**5d**)

Preparation of oxazole (5e)[5]

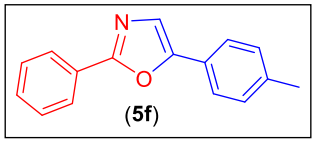
5e was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (8.5 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$); δ = 8.61 (s, 1H), 8.20 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 11.3, 5.8 Hz, 2H), 7.88 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.58 – 7.53 (m, 2H), 7.51 – 7.45 (m, 3H), and 7.37 (t, *J* = 7.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 161.5, 151.6, 134.3, 133.2, 129.1, 128.9, 128.8, 128.7, 128.2, 128.0, 127.4, 126.9, 126.3, 124.9, 124.4, 123.8, and 123.4 ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}N_2O_3$ $[M+H]^+$: 272.1075; found: 272.1089.



(**5e**)

Preparation of oxazole (5f)[3]

5f was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (10.7 mg, 67%). ^1H NMR (400

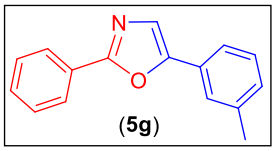


(**5f**)

MHz, $CDCl_3$); δ = 8.11 (dt, *J* = 4.1, 2.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.40 (s, 1H), 7.26 (s, 2H), and 2.40 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 160.9, 151.6, 138.7, 130.4, 129.8, 128.9, 127.7, 126.4, 125.5, 124.3, 122.9, and 21.5 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1075; found: 236.1089.

Preparation of oxazole (5g)[6]

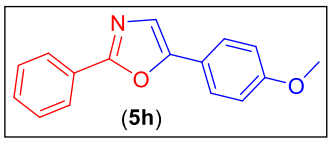
5g was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (8.9 mg, 56%). ^1H NMR (400 MHz, $CDCl_3$); δ = 8.12 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.57 – 7.45 (m, 5H), 7.44 (d, *J* = 4.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), and 2.43 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 161.2, 151.6, 138.8, 130.4, 129.4, 129.0, 128.9, 128.1, 127.7, 126.4, 124.9, 123.5, 121.5, and 21.6 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1075; found: 236.1089.



(**5g**)

Preparation of oxazole (5h)[4,6]

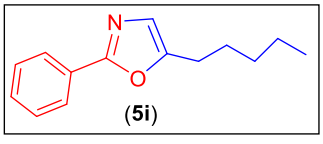
5h was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (12 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$); δ = 8.09 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.51 –7.43 (m, 3H), 7.33 (s, 1H), 7.01 – 6.95 (m, 2H), and 3.86 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 160.7, 159.9, 151.5, 130.3, 128.9, 127.7, 126.3, 125.9, 122.1, 121.1, 114.6, and 55.53 (OCH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NO_2$ $[M+H]^+$: 252.1024; found: 252.1070.



(**5h**)

Preparation of oxazole (5i)

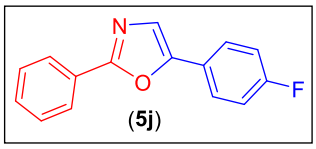
5i was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (8.9 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$); δ = 7.99 (ddd, *J* = 8.8, 5.0, 2.0 Hz, 2H), 7.48 – 7.37 (m, 3H), 6.84 (s, 1H), 2.75 – 2.66 (m, 2H), 1.76 – 1.65 (m, 2H), 1.42 – 1.32 (m, 4H), and 0.96 – 0.88 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 160.7, 153.4, 129.9, 128.8, 128.0, 126.1, 123.7, 31.4 (alkyl chain), 27.5 (alkyl chain), 25.8 (alkyl chain), 22.9 (alkyl chain), and 14.1 (alkyl chain) ppm. HRMS (ESI) *m/z* calcd for $C_{14}H_{17}NO$ $[M+H]^+$: 216.1388; found: 216.1384.



(**5i**)

Preparation of oxazole (5j)[6]

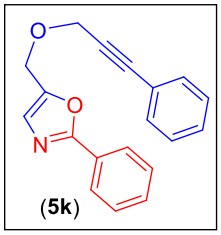
5j was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (9.3 mg, 70%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.12 – 8.08 (m, 2H), 7.71 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.51–7.46 (m, 3H), 7.39 (s, 1H), and 7.15 (t, *J* = 8.6 Hz, 2H) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 163.6, 162.1, 161.3, 150.6, 130.6, 129.0, 127.5, 126.4, 126.3, 126.2, 123.3, 116.3, and 116.2 ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –112.2 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}FNO$ $[M+H]^+$: 240.0825; found: 240.0837.



(**5j**)

Preparation of oxazole (5k)

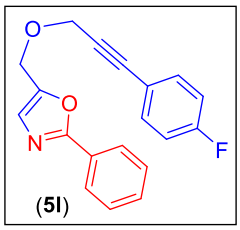
5k was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (12.8 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.08 – 8.02 (m, 2H), 7.49 – 7.42 (m, 5H), 7.35 – 7.29 (m, 3H), 7.21 (s, 1H, NCH), 4.75 (s, 2H, CH_2O), and 4.46 (s, 2H, OCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 162.5, 148.1, 131.9, 130.7, 128.9, 128.8, 128.5, 128.3, 127.5, 126.6, 122.5, 87.3 (*C*≡C-), 84.3 (C≡*C*-), 61.1 (*C*H_2O), and 58.1 (O*C*H_2) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_2$ $[M+H]^+$: 290.1181; found: 290.1193. IR (ATR mode, solid sample, ν(cm^{-1})): 3057 (w), 2920 (w), 2851 (w), 2229 (w), 1718 (m), 1670 (m), 1543 (m), 1484 (m), 1443 (m), 1354 (m), 1255 (m), 1071 (s), 919 (w), 844 (w), 757 (s), and 699 (s).



(**5k**)

Preparation of oxazole (5l)

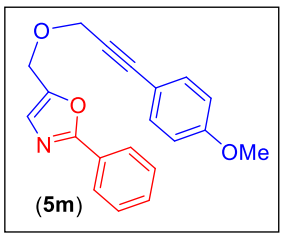
5l was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (15.7 mg, 74%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.05 (d, *J* = 3.4 Hz, 2H), 7.48 – 7.40 (m, 5H), 7.21 (s, 1H, NCH), 7.03 – 6.97 (m, 2H), 4.73 (s, 2H, CH_2O), and 4.44 (s, 2H, OCH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 163.5 (C-F), 162.7, 162.1, 148.0, 133.9, 133.9, 130.7, 128.9, 128.3, 127.4, 126.6, 115.8, 115.7, 86.2 (*C*≡C), 84.1 (C≡*C*), 61.2 (*C*H_2O), and 58.0 (O*C*H_2) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –110.3 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{14}NO_2F$ $[M+H]^+$: 308.1087; found: 308.1103. IR (ATR mode, solid sample, ν(cm^{-1})): 3060 (w), 2921 (w), 2853 (w), 2224 (w), 1898 (m), 1667 (m), 1599 (s), 1500 (m), 1355 (s), 1226 (s), 1072 (s), 835 (s), 706 (s), and 537 (w).



(**5l**)

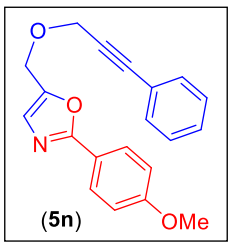
Preparation of oxazole (5m)

5m was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (14.6 mg, 67%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.08–8.03 (m, 2H), 7.45 (d, *J* = 3.2 Hz, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.21 (s, 1H, NCH), 6.84 (d, *J* = 8.5 Hz, 2H), 4.74 (s, 2H, CH_2O), 4.44 (s, 2H, OCH_2), and 3.81 (s, 3H, OCH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 162.6, 160.0, 148.2, 133.5, 130.6, 128.9, 128.2, 127.5, 126.6, 114.6, 114.1, 87.3 (*C*≡C-), 82.9 (C≡*C*-), 61.1 (*C*H_2O), 58.2 (O*C*H_2), and 55.4 (O*C*H_3) ppm. HRMS (ESI) *m/z* calcd for $C_{20}H_{17}NO_3$ [M+H] $^{+}$: 320.1287; found: 320.1304. IR (ATR mode, solid sample, ν(cm^{-1})): 2843 (w), 2214 (w), 1675 (m), 1602 (s), 1506 (s), 1447 (m), 1354 (m), 1289 (s), 1246 (m), 1171 (m), 1069 (s), 1027 (s), 833 (s), 710 (s), and 536 (w).



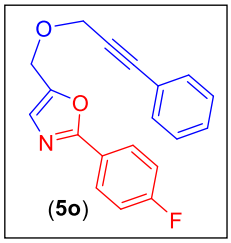
Preparation of oxazole (5n)

5n was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (10.4 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.92 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.26 (s, 2H), 7.19 (s, 1H), 7.10 (s, 1H, NCH), 6.89 (d, *J* = 7.9 Hz, 2H), 4.66 (s, 2H, CH_2O), 4.38 (s, 2H, OCH_2), and 3.79 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 162.8 (Ar*C*-OMe), 161.6 (N*C*O), 147.4, 131.9, 128.8, 128.5, 128.3, 128.2, 122.5, 120.3, 114.3, 87.2 (*C*≡C), 84.4 (C≡*C*), 61.1 (*C*H_2O), 57.9 (O*C*H_2), and 55.5 (O*C*H_3) ppm. HRMS (ESI) *m/z* calcd for $C_{20}H_{17}NO_3$ [M+H]$^{+}$: 320.1287; found: 320.1278. IR (ATR mode, solid sample, ν(cm^{-1})): 2917 (w), 2844 (w), 2227 (w), 1609 (s), 1491 (s), 1354 (m), 1302 (m), 1251 (s), 1174 (m), 1070 (s), 1027 (m), 839 (s), 754 (s), and 604 (w).



Preparation of oxazole (5o)

5o was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (15.8 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.01 – 7.94 (m, 2H), 7.39 (d, *J* = 6.6 Hz, 2H), 7.25 (s, 2H), 7.19 (s, 1H), 7.12 (s, 1H, NCH), 7.07 (t, *J* = 8.1 Hz, 2H), 4.67 (s, 2H, CH_2O), and 4.39 (s, 2H, OCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 165.6, 163.1, 161.9, 148.1, 131.9, 128.8, 128.7, 128.5, 128.3, 116.2, 115.9, 87.3 (*C*≡C), 84.3 (C≡*C*), 61.1 (*C*H_2O), and 58.1 (O*C*H_2) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –109.21 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{14}NO_2F$ [M+H]$^{+}$: 308.1087; found: 308.1079. IR (ATR mode, solid sample, ν(cm^{-1})): 2922



(w), 2219 (w), 1720 (m), 1604 (m), 1490 (s), 1355 (m), 1231 (s), 1072 (s), 843 (s), 751 (s), and 597 (w).

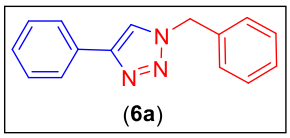
General experimental procedure for triazole derivatives synthesis

In a 50 mL seal tube charged with a magnetic bar was added benzyl azide (1 equiv.), alkyne (1.2 equiv.), and pre-catalyst **3a** (2 mol%) under the nitrogen atmosphere. Then, the reaction mixture was allowed to stir for 4 h at room temperature. Then the crude reaction mixture was purified by silica gel column chromatography (30% EtOAc/hexane mixture) to afford the corresponding triazole derivatives.

Spectroscopic Data of Substituted Triazoles

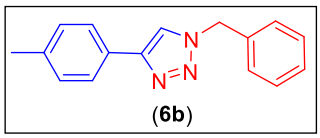
Preparation of triazole (6a)[7]

6a was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (15.2 mg, 86%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.81–7.78 (m, 2H), 7.66 (s, 1H, NCH), 7.38 (tdd, *J* = 8.0, 6.5, 2.3 Hz, 5H), 7.33–7.30 (m, 3H), and 5.58 (s, 2H, CH_2Ph) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 148.4, 134.8, 130.7, 129.3, 128.9, 128.3, 128.2, 125.9, 119.6, and 54.4 (CH_2) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_3$ $[M+H]^+$: 236.1186; found: 236.1197.


(6a)

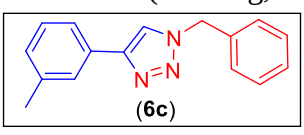
Preparation of triazole (6b)[8]

6b was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (16.82 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) ; δ = 7.69 (d, *J* = 8.1 Hz, 2H), 7.61 (s, 1H, NCH), 7.38 (dd, *J* = 5.5, 3.5 Hz, 3H), 7.33–7.29 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.57 (s, 2H, CH_2Ph), and 2.36 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 148.5, 138.2, 134.9, 129.6, 129.3, 128.9, 128.2, 127.9, 125.8, 119.3, 54.4 (CH_2), and 21.4 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_3$ $[M+H]^+$: 250.1344; found: 250.1337.


(6b)

Preparation of triazole (6c)[9]

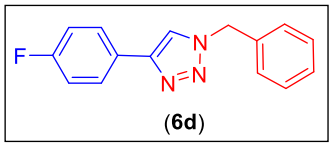
6c was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (13.5 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.65 (d, *J* = 5.4 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.30 (dd, *J* = 10.2, 4.9 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 5.58 (s, 2H, CH_2Ph), and 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 148.4, 138.5, 134.7, 130.4, 129.2, 128.9, 128.8, 128.7, 128.1, 126.4,


(6c)

122.8, 119.4, 54.2 (CH_2), and 21.4 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_3$ $[M+H]^+$: 250.1344; found: 250.1358.

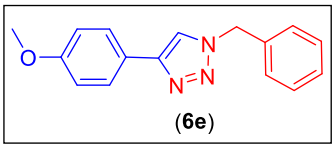
Preparation of triazole (6d)[8]

6d was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (14.43 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.79 -7.74 (m, 2H), 7.61 (s, 1H, NCH), 7.42 – 7.36 (m, 3H), 7.34 – 7.29 (m, 2H), 7.12–7.05 (m, 2H), and 5.57 (s, 2H, CH_2Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 164.1 (C-F), 161.6, 147.5, 134.7, 129.3, 128.2, 127.6, 127.5, 119.4, 116.0, 115.8, and 54.4 (CH_2) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –113.5 (m) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FN_3$ $[M+H]^+$: 254.1093; found: 254.1105.


(6d)

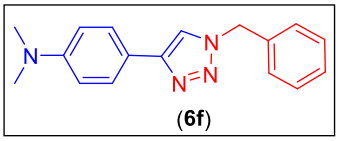
Preparation of triazole (6e)[8]

6e was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (12.50 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.75-7.69 (m, 2H), 7.57 (s, 1H, NCH), 7.40 – 7.35 (m, 3H), 7.33-7.28 (m, 2H), 6.95-6.91 (m, 2H), 5.57 (s, 2H, CH_2Ph), and 3.83 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 159.8, 148.2, 134.9, 129.3, 128.9, 128.2, 127.2, 123.4, 118.7, 114.4, 55.5 (CH_2), and 54.4 (OCH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}ON_3$ $[M+H]^+$: 266.1293; found: 266.1299.


(6e)

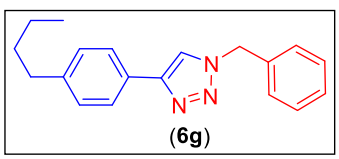
Preparation of triazole (6f)[10]

6f was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (12.30 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.68–7.64 (m, 2H), 7.52 (s, 1H, NCH), 7.37 (td, *J* = 5.5, 3.6 Hz, 3H), 7.32 – 7.28 (m, 2H), 6.76 – 6.72 (m, 2H), 5.55 (s, 2H, CH_2Ph), and 2.97 (s, 6H, CH_3NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 150.6, 148.9, 135.1, 129.2, 128.8, 128.2, 126.8, 118.9, 118.2, 112.6, 54.3 (H_2), and 40.6 (CH_3NCH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}N_4$ $[M+H]^+$: 279.1610; found: 279.1620.


(6f)

Preparation of triazole (6g)[7]

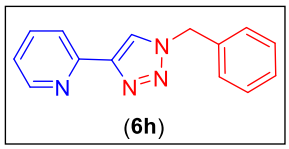
6g was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (15.50 mg, 71%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.70 (d, *J* = 8.1 Hz, 2H), 7.62 (s, 1H, NCH), 7.41–


(6g)

7.34 (m, 3H), 7.30 (d, J = 6.7 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.57 (s, 2H, CH_2Ph), 2.64 – 2.59 (m, 2H, CH_2), 1.64 – 1.57 (m, 2H, CH_2), 1.39 – 1.31 (m, 2H, CH_2), and 0.92 (t, J = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 148.5, 143.2, 134.9, 129.3, 129.0, 128.9, 128.2, 128.1, 125.8, 119.3, 54.4 (CH_2Ph), 35.6 (CH_2), 33.7 (CH_2), 22.5 (CH_2), and 14.1 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}N_3$ $[M+H]^+$: 292.1814; found: 292.1808.

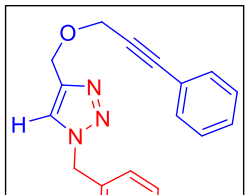
Preparation of triazole (6h)

6h was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded a white solid (12.40 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.55 – 8.51 (m, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H, NCH), 7.77 (td, J = 7.8, 1.8 Hz, 1H), 7.40 – 7.31 (m, 5H), 7.21 (ddd, J = 7.5, Hz, 1H), and 5.58 (s, 2H, CH_2Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 150.4, 149.5, 148.9, 137.1, 134.5, 129.3, 129.0, 128.5, 123.0, 122.1, 120.4, and 54.4 (CH_2) ppm. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_4$ $[M+H]^+$: 237.1140; found: 237.1149.



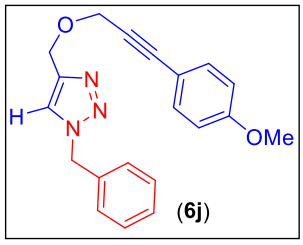
Preparation of triazole (6i)

6i was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (16.70 mg, 77%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.49 (s, 1H, NC*H*), 7.43 (d, J = 6.6 Hz, 2H), 7.36 (t, J = 6.8 Hz, 3H), 7.31 (q, J = 6.8 Hz, 3H), 7.26 (s, 2H), 5.52 (s, 2H, CH_2Ph), 4.77 (s, 2H, OCH_2), and 4.44 (s, 2H, CH_2O) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 145.3, 134.6, 131.9, 129.3, 128.9, 128.7, 128.4, 128.3, 127.7, 122.6, 86.9 (*C*≡C), 84.7 (C≡*C*), 63.4 (CH_2O), 58.6 (OCH_2), and 54.4 (CH_2Ph) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{18}N_3O[M+H]^+$: 304.1450; found: 304.1428. IR (ATR mode, solid sample, ν(cm^{-1})): 3139 (w), 3059 (w), 2925 (w), 2855 (w), 2217 (m), 1705 (s), 1491 (m), 1447 (m), 1352 (m), 1280 (m), 1171 (m), 1072 (m), 809 (s), 715 (s), and 579 (w).



Preparation of triazole (6j)

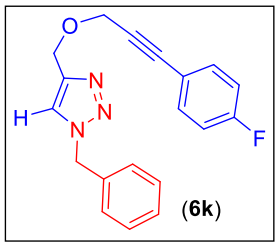
6j was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (15.34 mg, 64%). ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.49 (s, 1H, NC*H*), 7.39 – 7.34 (m, 5H), 7.26 (s, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.52 (s, 2H, CH_2Ph), 4.76 (s, 2H, OCH_2), 4.42 (s, 2H, CH_2O), and 3.80 (s, 3H, OCH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 159.9, 145.3, 134.6, 133.5, 129.3, 128.9, 128.3, 122.7, 114.7, 114.1, 86.8 (*C*≡C), 83.3 (C≡*C*), 63.3



(CH_2O), 58.7 (OCH_2), 55.4 (CH_2Ph), and 54.4 (OCH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}N_3O_2[M+H]^+$: 334.1555; found: 334.1567. IR (ATR mode, solid sample, ν(cm^{-1})): 2920 (m), 2213 (w), 1713 (w), 1603 (m), 1507 (s), 1455 (m), 1253 (m), 1168 (m), 1032 (m), 830 (m), and 731 (s).

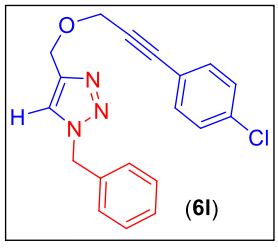
Preparation of triazole (6k)

6k was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded white solid (14.30 mg, 62%). ^1H NMR (700 MHz, $CDCl_3$); δ = 7.49 (s, 1H, NCH), 7.41 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.26 (s, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.52 (s, 2H, CH_2Ph), 4.76 (s, 2H, OCH_2), and 4.41 (s, 2H, CH_2O) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 163.2, 162.1, 145.2, 134.6, 133.9, 133.9, 129.3, 128.9, 128.3, 122.7, 118.7, 115.8, 115.7, 85.8 (*C*≡C), 84.5 (C≡*C*), 63.4 (CH_2O), 58.5 (OCH_2), and 54.4 (CH_2Ph) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –110.5 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_3OF[M+H]^+$: 322.1356; found: 322.1345. IR (ATR mode, solid sample, ν(cm^{-1})): 2923 (w), 2237 (w), 1727 (m), 1598 (s), 1502 (m), 1456 (m), 1356 (m), 1223 (s), 1079 (s), 833 (s), and 729 (s).



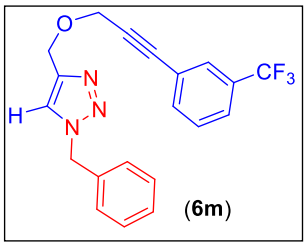
Preparation of triazole (6l)

6l was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded off white solid (28 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$); δ = 7.42 (s, 1H, NCH), 7.31-7.25 (m, 5H), 7.22-7.16 (m, 4H), 5.43 (s, 2H, CH_2Ph), 4.68 (s, 2H, OCH_2), and 4.34 (s, 2H, CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 144.0, 133.7, 133.5, 132.1, 128.2, 127.9, 127.7, 127.3, 121.7, 120.0, 84.7 (*C*≡C), 84.7 (C≡*C*), 62.4 (CH_2O), 57.4 (OCH_2), and 53.3 (CH_2Ph) ppm. DEPT-135 {^{13}C} NMR (100 MHz, $CDCl_3$); δ = 132.0, 128.1, 127.8, 127.6, 127.1, 121.6, 62.3 (CH_2O), 57.3 (OCH_2), 53.2 (CH_2Ph) ppm. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_3OCl$ $[M+H]^+$: 338.1060; found: 338.0999. IR (ATR mode, solid sample, ν(cm^{-1})): 2242(w), 1487 (m), 1355 (m), 1258 (m), 1222 (m), 1080 (s), 1017 (m), 908 (s), 826 (s), 726 (s), 647 (w), and 526 (w).



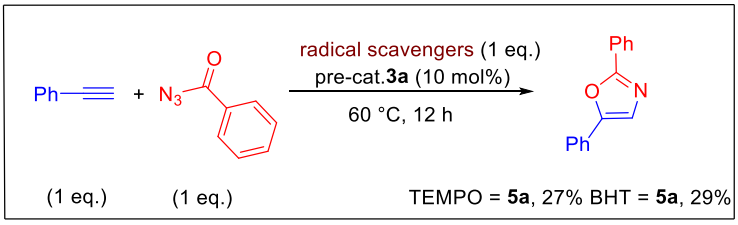
Preparation of triazole (6m)

6m was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (30% EtOAc/hexane mixture) which afforded off white solid (40 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.60 (s, 1H, NCH), 7.53 – 7.46 (m, 2H), 7.42 (s, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.18 (dd, *J* = 7.6, 2.6 Hz, 3H), 5.43 (s, 2H, CH_2Ph), 4.68 (s, 2H, OCH_2), and 4.35 (s, 2H, CH_2O) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –63.0 (s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 135.0, 134.6, 131.2, 130.9, 129.3, 128.9, 128.8, 128.8, 128.7, 128.7, 128.3, 125.3, 125.2, 123.6 (CF_3), 86.5(*C*≡C), 85.3, 63.5 (C≡*C*), 58.4 (*C*H_2O), and 54.4 (O*C*H_2) ppm. HRMS (ESI) *m/z* calcd for $C_{20}H_{16}N_3F_3O$ $[M+H]^+$: 372.1324; found: 372.1270. IR (ATR mode, solid sample, ν(cm^{-1})): 2249 (w), 1331 (m), 1130 (m), 1079 (m), 904 (s), 803 (m), 727 (s), and 650 (m).



Mechanistic studies

(a) Radical process experiment



An oven-dried Schlenk tube was charged with benzoyl azide (1 equiv, 0.082 mmol), phenylacetylene (1 equiv, 0.082 mmol), pre-cat.**3a** (0.10 equiv, 0.008 mmol), radical scavengers (BHT and TEMPO) (1.0 equiv, 0.082 mmol) in solvent-free condition. The reaction mixtures were allowed to stir at 60 °C on the preheated aluminum block for 12 h. After 12 h, the reaction mixtures were diluted with ethyl acetate and passed through a short celite pad. Then, the solvent was evaporated under reduced pressure, and the residue was submitted for ^{1}H NMR using the internal standard trimethoxy benzene to determine the yield of product **5a**. An experiment involving a radical process was carried out to determine the nature of the intermediate. We saw reasonable reactivity in the presence of 1 equiv of a radical scavenger like TEMPO and BHT, producing 29% and 27% of the intended product **5a**, respectively, indicating that the reaction was proceeding through an ionic pathway or a nonradical pathway. (Under optimal reaction conditions, the presence of radical scavengers such TEMPO and BHT did not succeed in preventing the synthesis of the product, indicating a nonradical pathway for the reaction.)

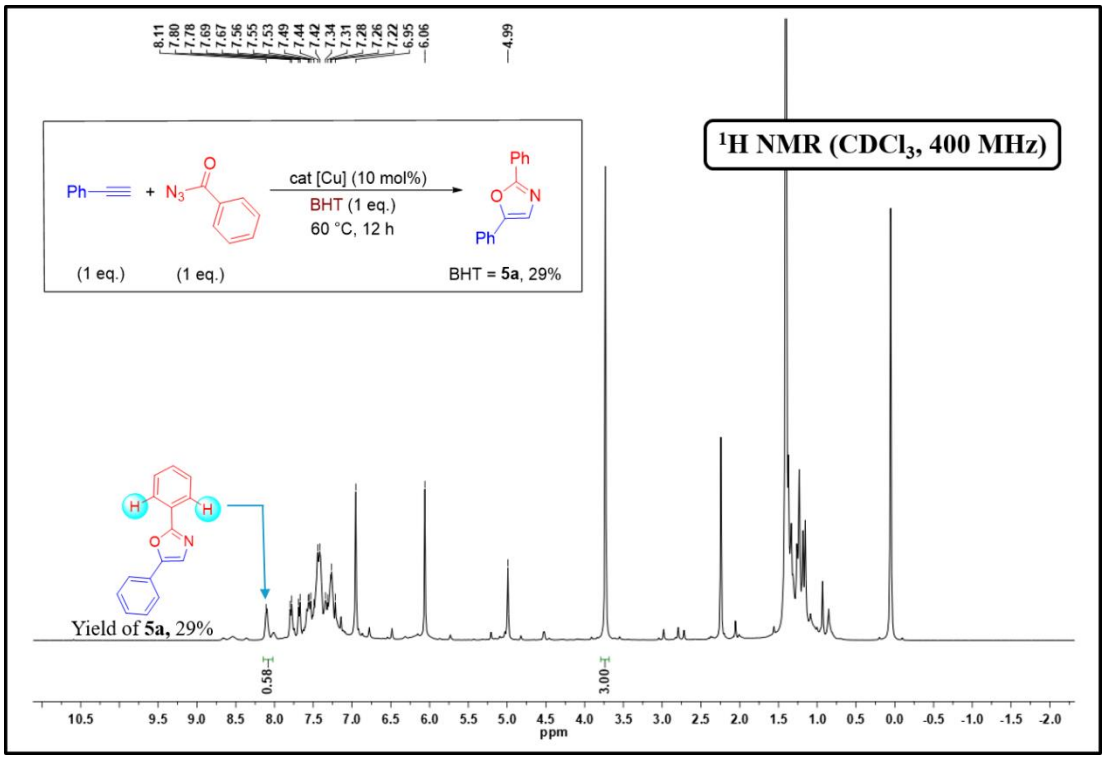


Figure S20. ^{1}H NMR spectrum of radical scavenger (BHT) experiment measured in $CDCl_3$.

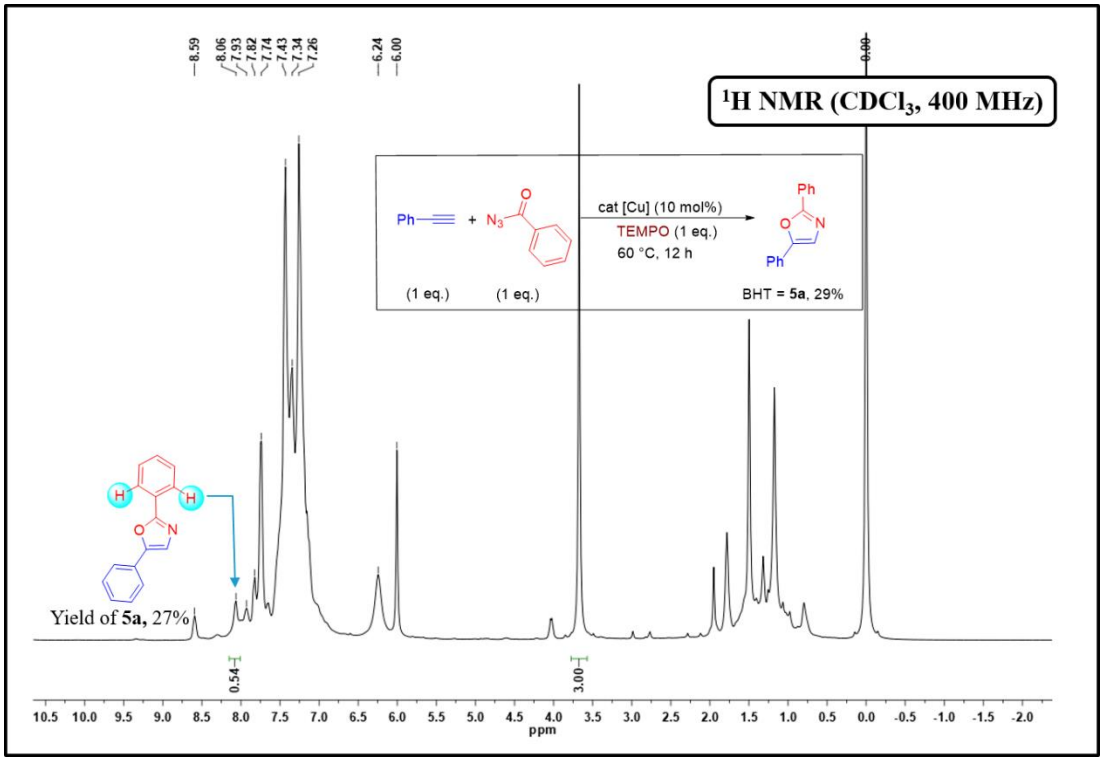
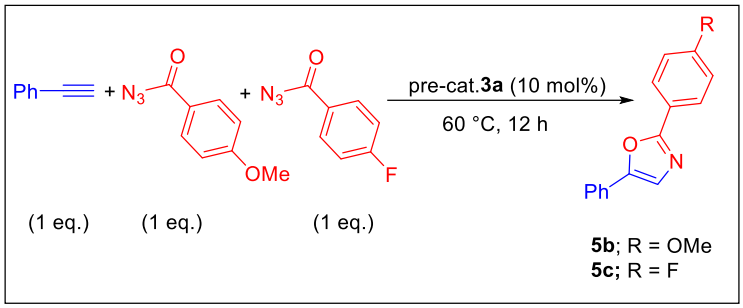


Figure S21. ^{1}H NMR spectrum of radical scavenger (TEMPO) experiment measured in $CDCl_3$.

(b) Competition studies with substrates



To a pre-dried sealed tube under N_2, the mixture of 4-methoxy benzoyl azide (1 equiv., 0.0605 mmol), 4-fluoro benzoyl azide (1 equiv., 0.0605 mmol), phenylacetylene (1 equiv., 0.0605 mmol), and pre-cat.**3a** (10 mol %) were added to a pre-dried sealed tube under N_2 and the reaction mixture was allowed to stir at 60 ℃ on the preheated aluminum block for the 12 h. After 12 h (completion of the reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with ethyl acetate, and passed through a short celite pad, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using (10%, EtOAc/hexane) mixture on silica gel to afford **5b** and **5c** as pure products with 1.2 (40% yield):1 (33% yield) ratio yield. ^{1}H NMR (400 MHz, $CDCl_3$) of **5b**; δ = 8.05 (d, *J* = 9.0 Hz, 2H), 7.72 (s, 2H), 7.43 (dd, *J* = 14.6, 6.7 Hz, 3H), 7.36 – 7.30 (m, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), and 3.88 (s, 3H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$) of **5c**; δ = 8.11 (dd, *J* = 9.0, 5.3 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.35 (t, *J* = 6.8 Hz, 1H), and 7.18 (t, *J* = 8.7 Hz, 2H) ppm.

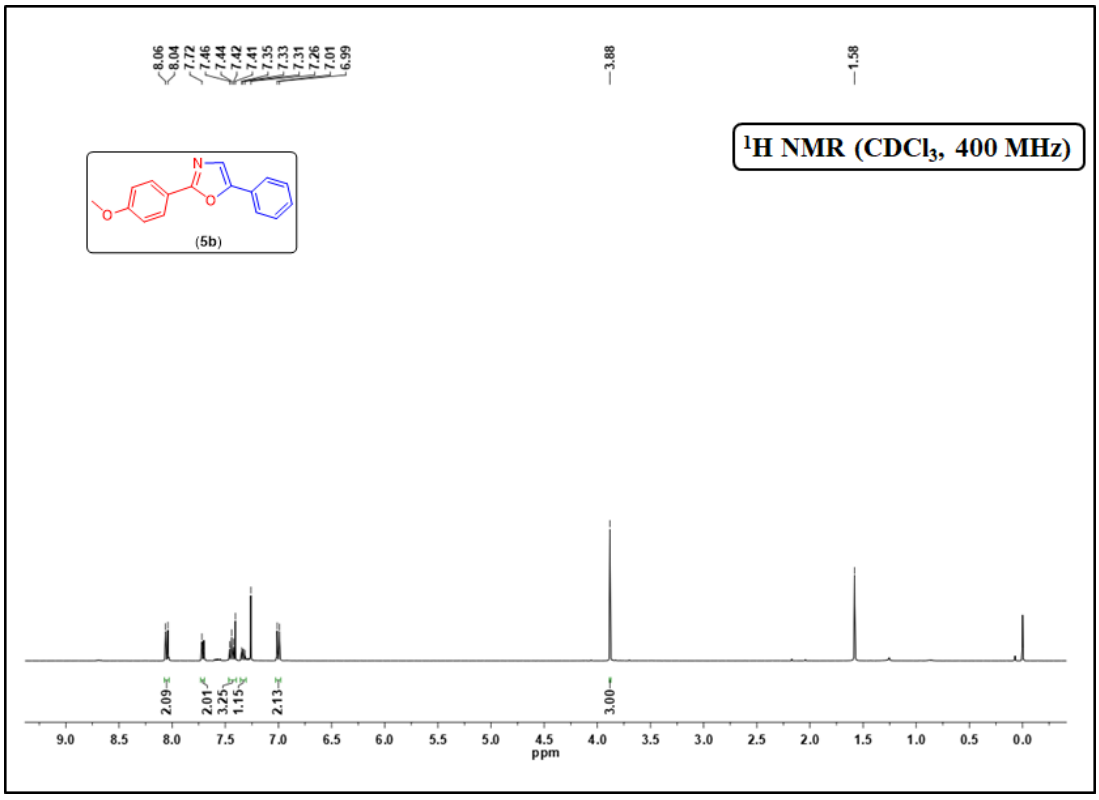


Figure S22. ^{1}H NMR spectrum of **5b** isolated from competition reaction measured in $CDCl_3$.

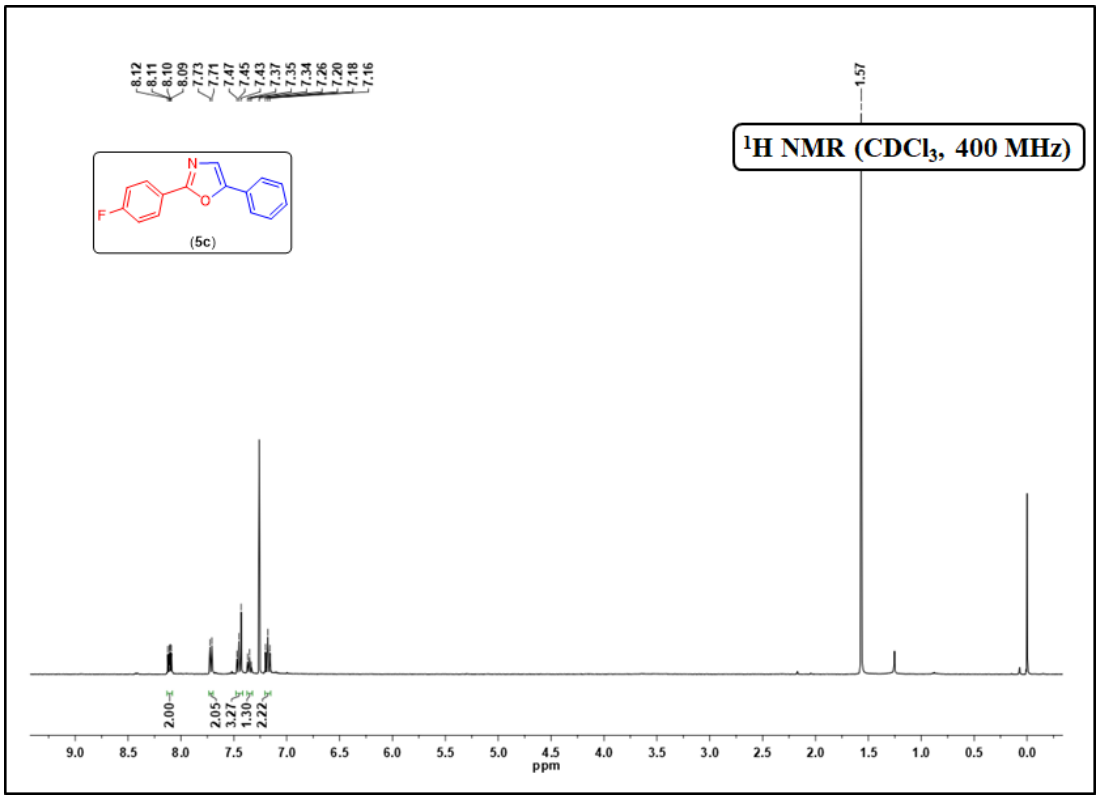
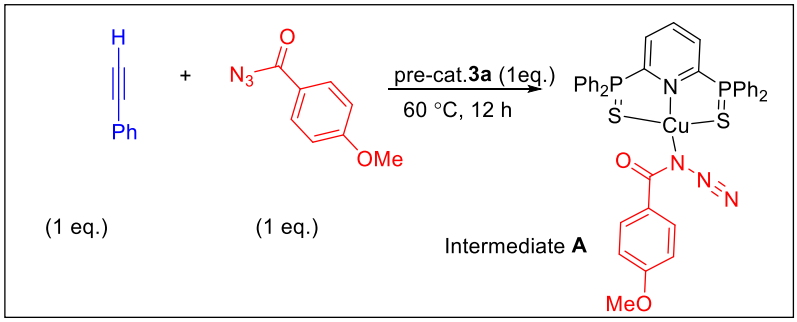


Figure S23. ^{1}H NMR spectrum of **5c** isolated from competition reaction measured in $CDCl_3$.

(c) Detection of intermediate for oxazole



ESI mass m/z calcd for $C_{37}H_{30}CuN_4O_2P_2S_2$ [M+K]: 790.0219; found: 790.0199

To a pre-dried Schlenk tube under N_2, the mixture of phenylacetylene (1 equiv., 0.028 mmol), 4-methoxy benzoyl azide (1 equiv., 0.028 mmol), and pre-cat.**3a** (1 equiv., 0.028 mmol) were added. Then, the reaction mixture was allowed to stir at 60 °C on the preheated aluminum block for 12 h. This reaction mixture was analyzed at various intervals by using mass spectroscopy.

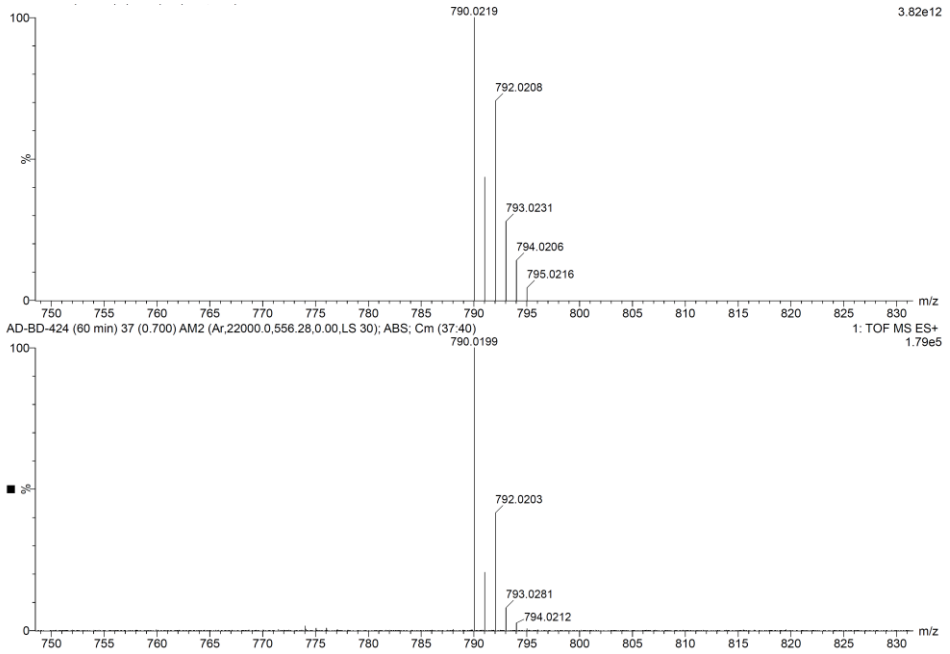


Figure S24. HRMS spectrum of intermediate **A** measured in acetonitrile, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern). Intermediate **A**: (ESI) m/z calcd for $C_{37}H_{30}CuN_4O_2P_2S_2$ [M+K]: 790.0219; found: 790.0199.

GC analysis for Nitrogen gas detection released from oxazole synthesis

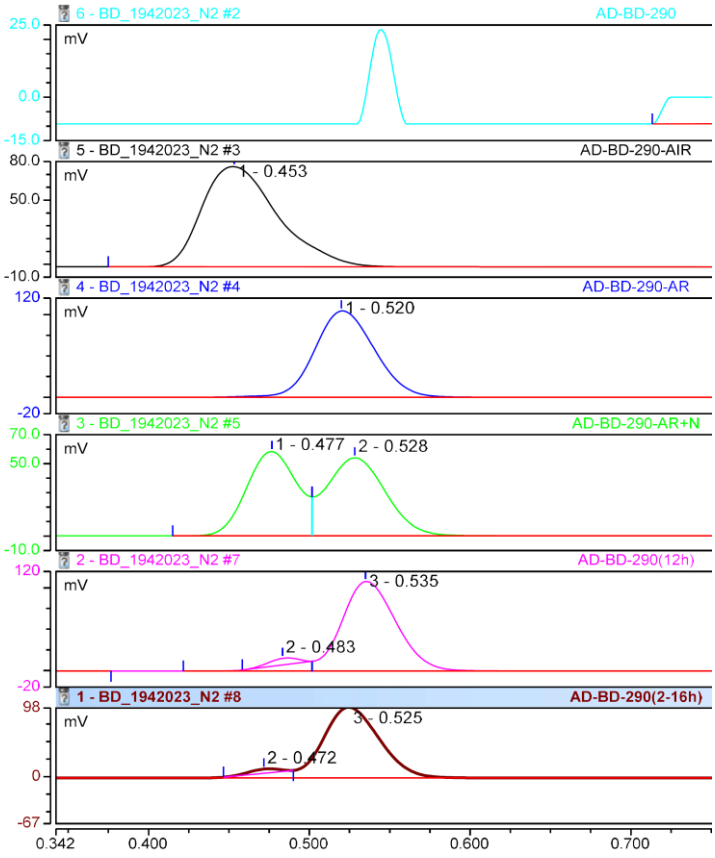
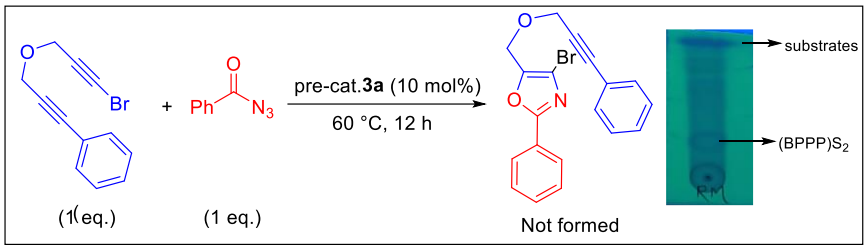


Figure S25. GC-TCD analysis for N_2 of 500 µL of (a) injection of gas from the reaction mixture after 2 h stirring, (b) gas injection from air atmosphere, (c) pure argon gas, (d) 1:1 mixture of N_2 and

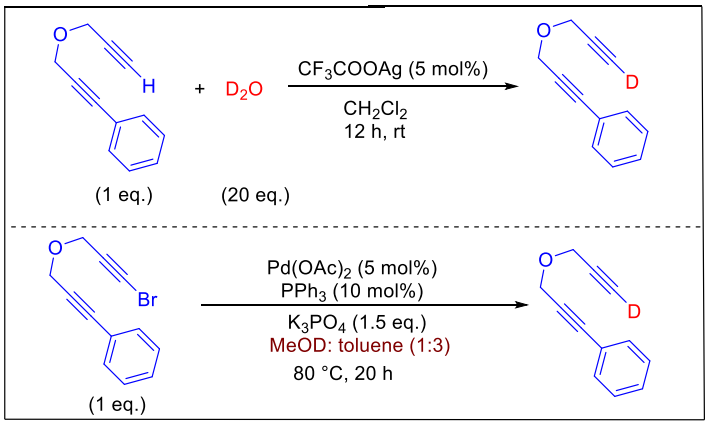
argon, (e) evolved gas by the injection of the reaction mixture (2nd batch reaction) after 12 h stirring, and (f) injection of gas from the first batch reaction mixture after 16 h stirring at 60 °C in time (min) vs response (mV).

(d) Reaction with bromo-substituted alkyne



To a pre-dried Schlenk tube under N_2, the mixture of benzoyl azide (1 equiv., 0.0605 mmol), phenyl 3-((3-bromoprop-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzene (1 equiv., 0.0605 mmol), and pre-cat.**3a** (10 mol %) was added to a pre-dried sealed tube under N_2 and the reaction mixture was allowed to stir at 60 °C on preheated aluminum block for the 12 h. After 12 h (completion of reaction as monitored by TLC analysis), it was observed there was no product formation, which also indicating the reaction goes through a non-radical mechanism path way.

(e) H/D exchange studies



Reaction of (3-(prop-2-yn-1-yloxy)prop-1-yn-1-yl)benzene with D_2O

To a pre-dried Schlenk tube under N_2, the mixture of (3-(prop-2-yn-1-yloxy)prop-1-yn-1-yl)benzene (1 equiv.), D_2O (20 equiv), CF_3COOAg (5 mol%) and dry CH_2Cl_2 (1 mL) were added and sealed. The reaction mixture was stirred at room temperature for 12 h. After 12 h (completion of reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with ethyl acetate and passed through a short celite pad, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using EtOAc/hexane (2%) mixture on silica gel (100-200 mesh) to give the pure product as colorless liquid.

Deuteration of (3-((3-bromoprop-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzene

To a pre-dried Schlenk tube under N_2, $Pd(OAc)_2$ (5 mol%), triphenyl phophine (10 mol%) and K_3PO_4 (1.5 equiv.), (3-((3-bromoprop-2-yn-1-yl)oxy)prop-1-yn-1-yl)benzene (1 equiv.) in CD_3OD (0.25 mL) and toluene (2.0 mL) was stirred at 80 °C on preheated aluminum block for the 20 h (completion of reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with ethyl acetate/dichloromethane and passed through a short Celite pad, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using EtOAc/hexane (2%) mixture on silica gel (100-200 mesh) to give the pure product as colorless liquid. ^{1}H NMR (700 MHz, $CDCl_3$); δ = 7.48 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.37 – 7.32 (m, 3H), 4.52 (s, 2H, CH_2), and 4.35 (s, 2H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$); δ = 131.9, 128.7, 128.4, 122.6, 86.9 (C≡C), 84.2 (C≡C), 79.1 (C≡C), 75.1 (C≡C), 57.5 (*C*H_2O), and 56.6 (O*C*H_2) ppm.

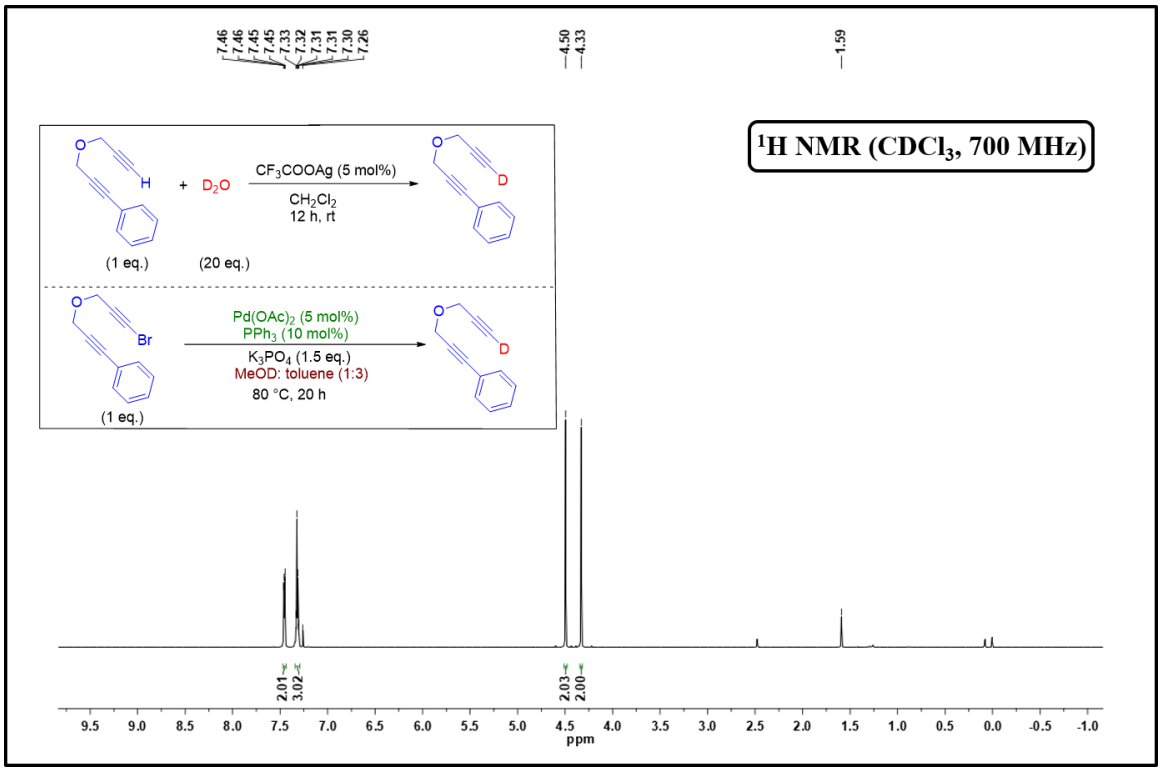


Figure S26. ^{1}H NMR spectrum of (3-((prop-2-yn-1-yl-3-d)oxy)prop-1-yn-1-yl)benzene measured in $CDCl_3$.

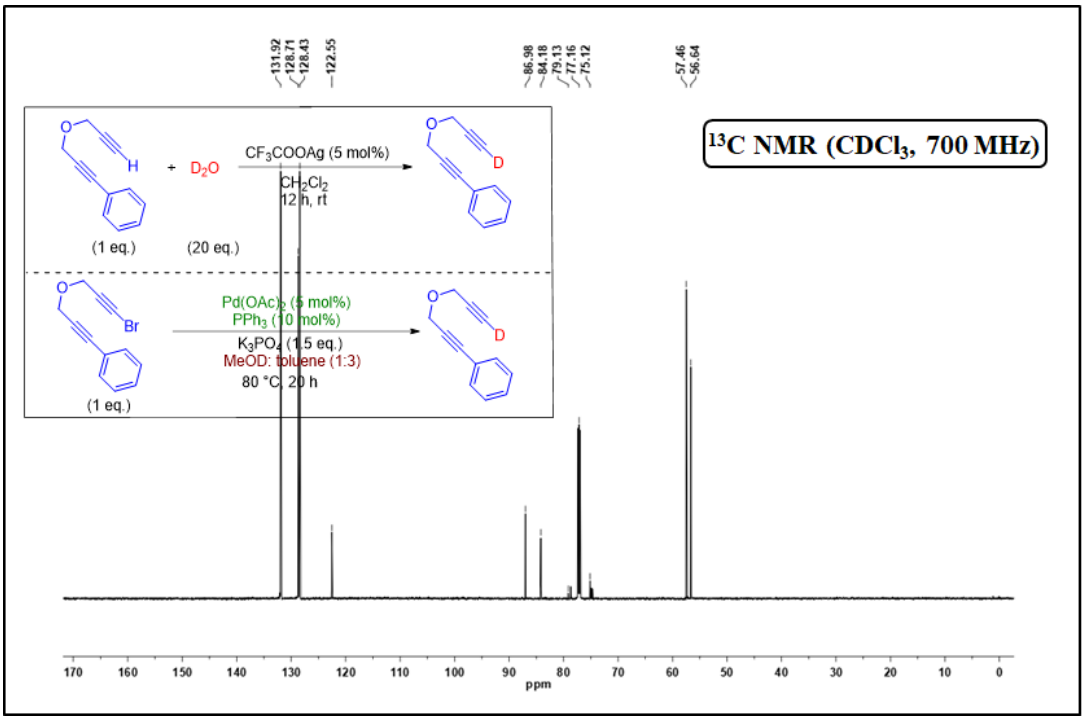


Figure S27. ^{13}C NMR spectrum of (3-((prop-2-yn-1-yl-3-d)oxy)prop-1-yn-1-yl)benzene measured in $CDCl_3$.

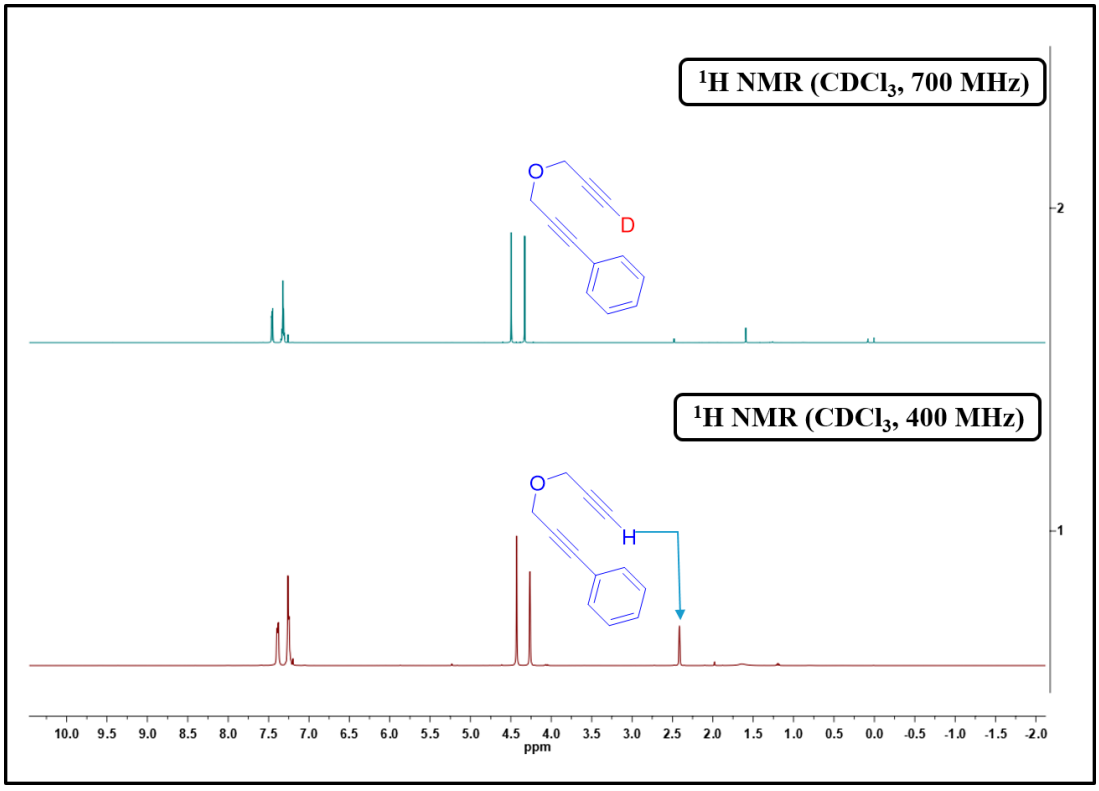
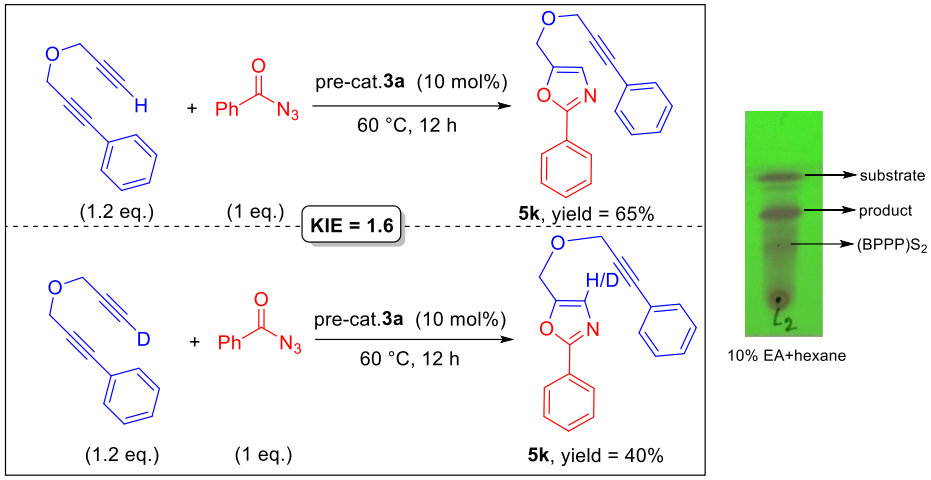


Figure S28. Stacked ^{1}H NMR spectra of deuterated and non-deuterated alkynes measured in $CDCl_3$.[2]

Kinetic isotope study (for oxazoles synthesis)



In a 50 mL sealed tube charged with magnetic bar was added azide (0.1 mmol), alkyne (0.12 mmol) and pre-cat.**3a** (10 mol%) under nitrogen atmosphere. Then, the reaction mixture was allowed to stir for 12 h at 60 °C. After cooling to room temperature, the crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (using 10% EtOAc/hexane mixture) to afford the corresponding oxazole **5k** as orange solid (8.0 mg, 40% yield). The value of KIE was calculated based on yield of the product (P_H/P_D) **5k**, which is 1.6 in case of oxazole. ^{1}H NMR (700 MHz, $CDCl_3$); δ = 8.11 – 8.05 (m, 2H), 7.50 – 7.46 (m, 5H), 7.37 – 7.32 (m, 3H), 7.24 (s, 1H), 4.77 (s, 2H), and 4.48 (s, 2H) ppm.

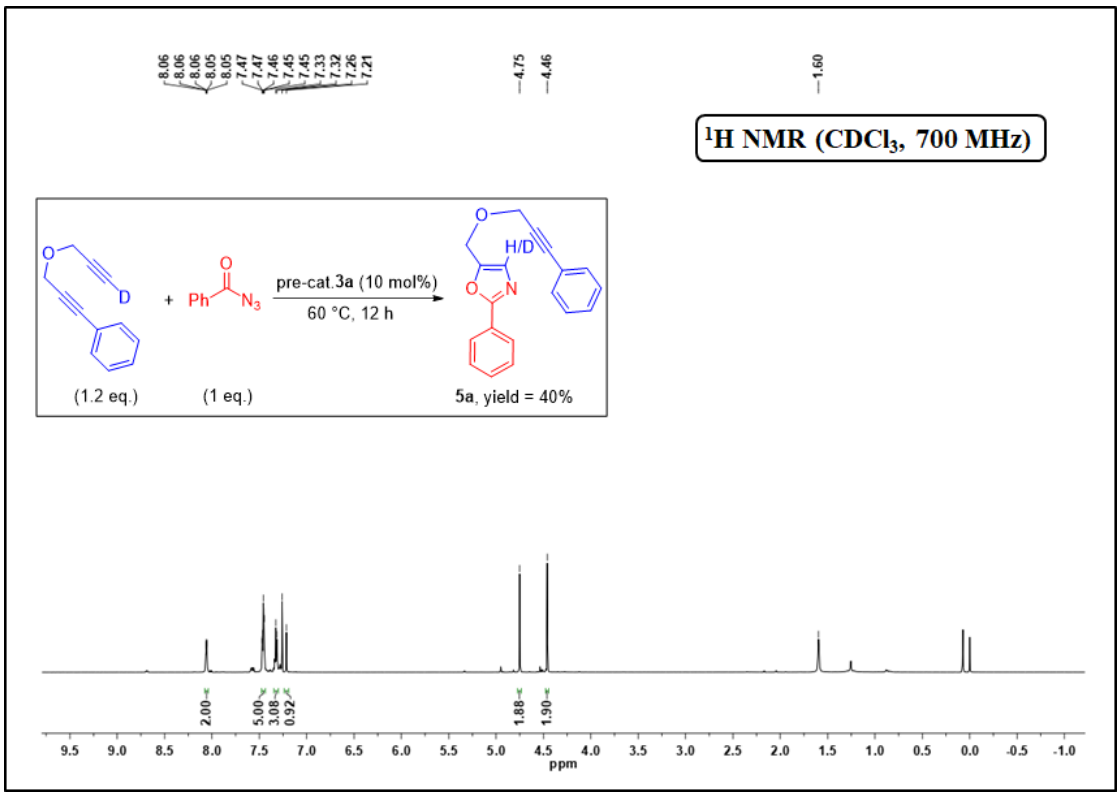
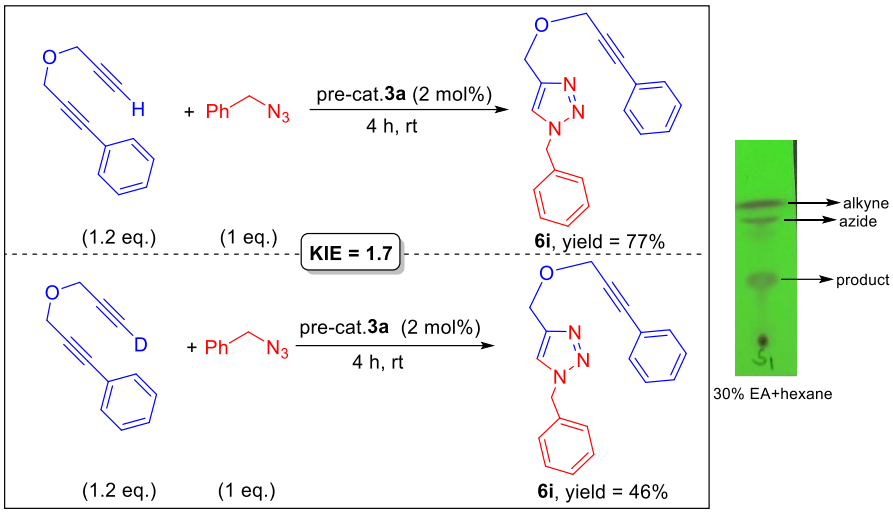


Figure S29. ^{1}H NMR spectrum of **5k** measured in $CDCl_3$.

(f) Kinetic isotope study (for triazole synthesis)



In a 50 mL sealed tube charged with magnetic bar was added benzyl azide (0.064 mmol), alkyne (0.076 mmol) and pre-cat.**3a** (2 mol%) under nitrogen atmosphere. Then, the reaction mixture was allowed to stir for 4 h at room temperature. Then the crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (using 30% EtOAc/hexane mixture) to afford the corresponding triazole **6i** as white solid. The value of KIE was calculated based on yield of the product (P_H/P_D) **6i**, which is 1.7 in case of triazole. Yield: 9.0 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.50 (s, 1H), 7.45 – 7.41 (m, 2H), 7.38 – 7.34 (m, 3H), 7.33 – 7.29 (m, 3H), 7.28 (d, *J* = 2.9 Hz, 2H), 5.52 (s, 2H), 4.78 (s, 2H), and 4.44 (s, 2H) ppm.

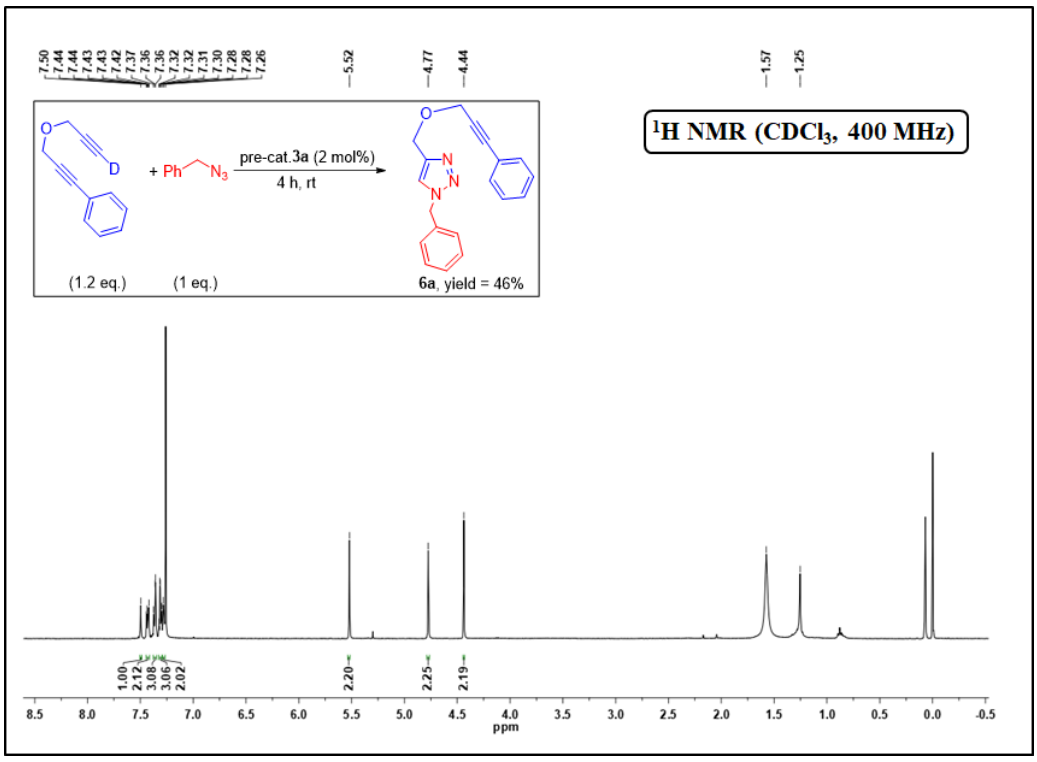
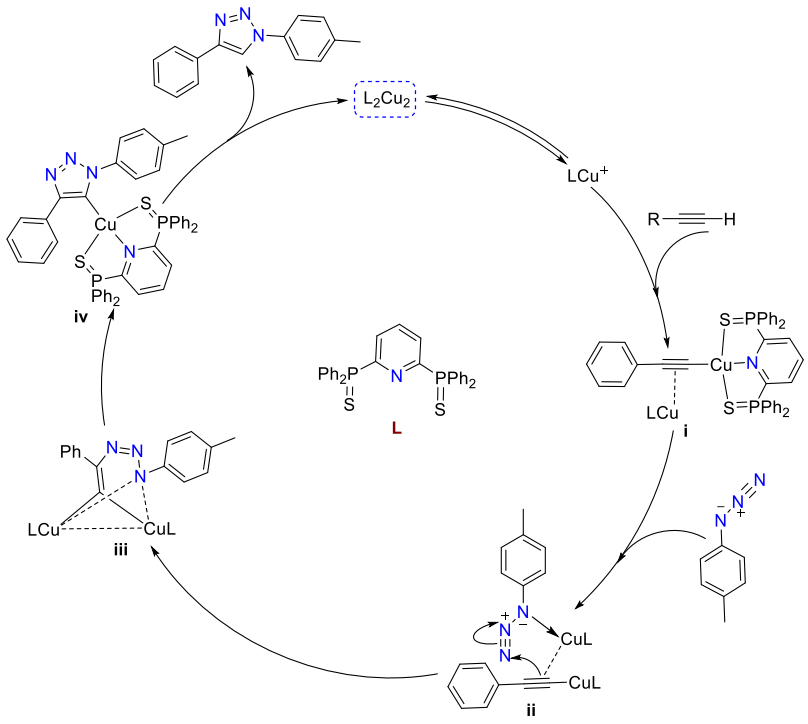


Figure S30. ^{1}H NMR spectrum of **6i** measured in $CDCl_3$.

Scheme S2. Proposed mechanism for the formation of triazoles catalyzed by pre-cat.**3a**



Characterization details of substituted oxazoles and triazoles synthesized in this study

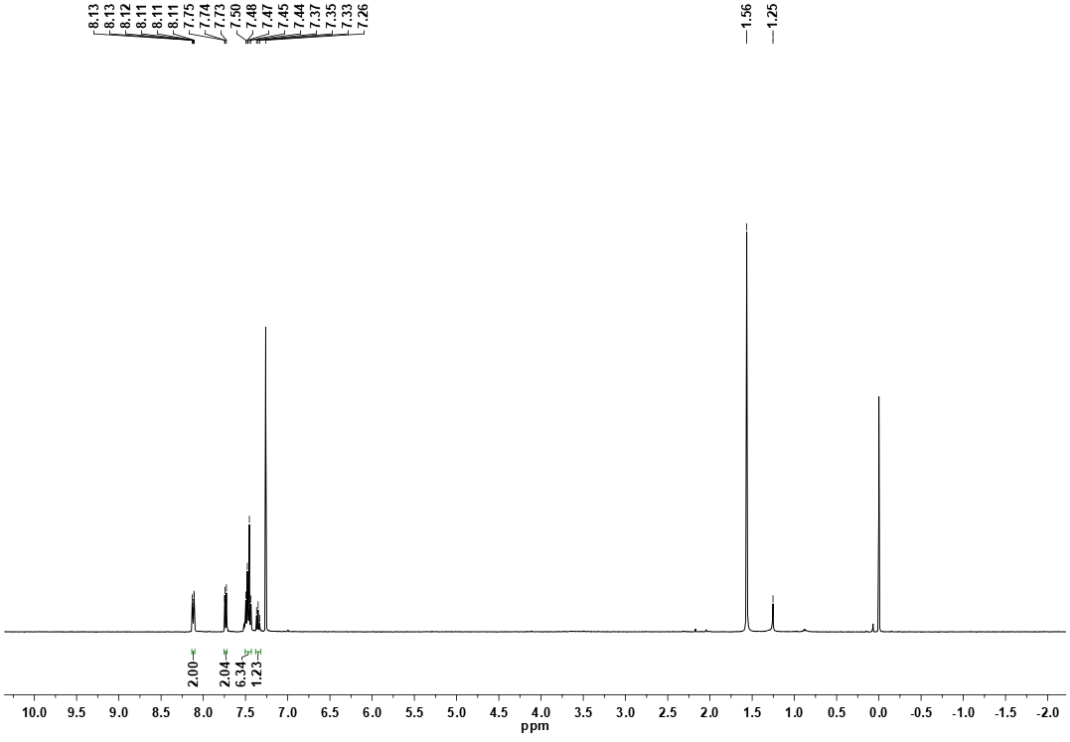


Figure S31. ^{1}H NMR spectrum of oxazole **5a** measured in $CDCl_3$.

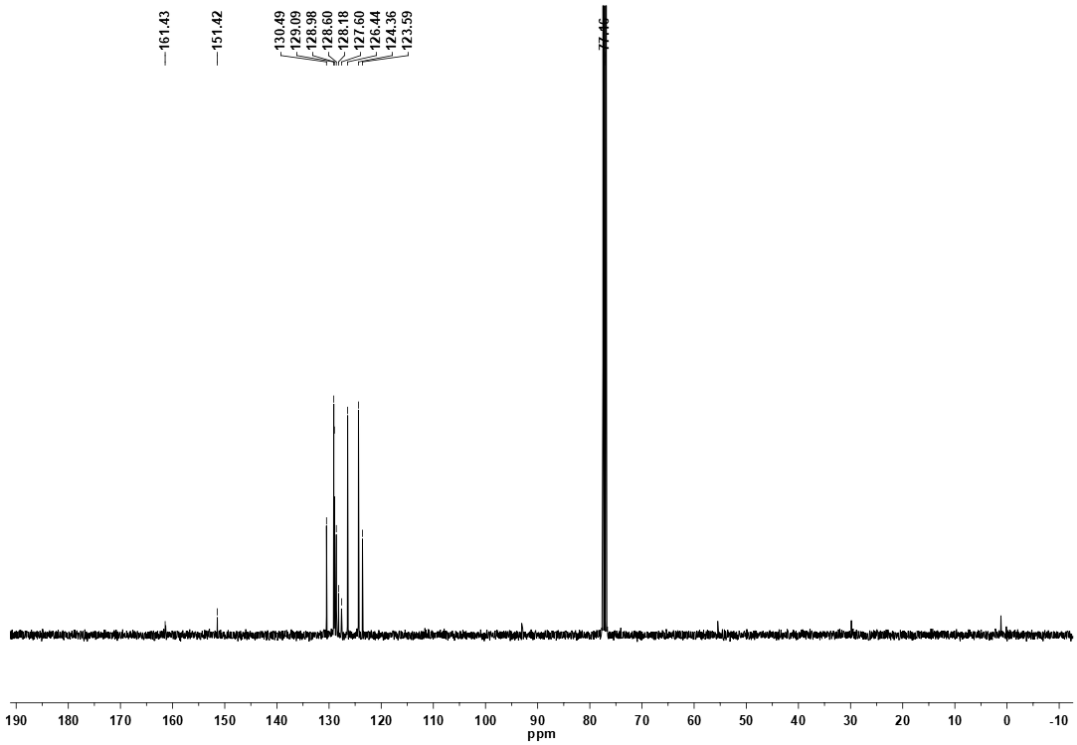


Figure S32. ^{13}C NMR spectrum of oxazole **5a** measured in $CDCl_3$.

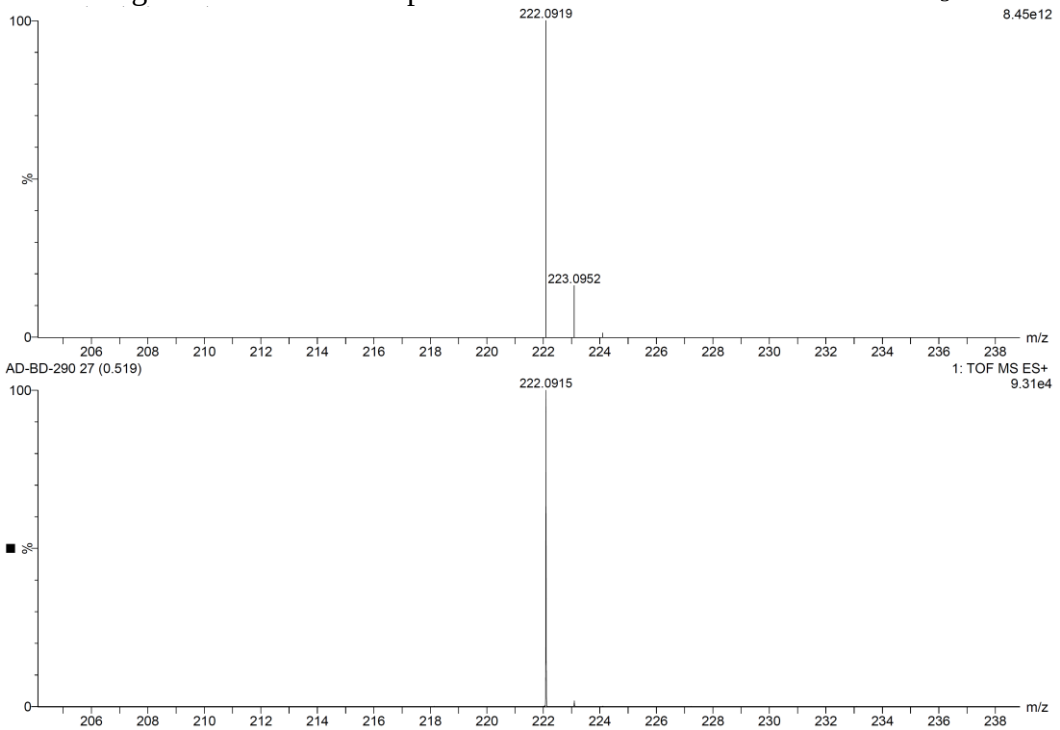


Figure S33. HRMS spectrum of oxazole **5a** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

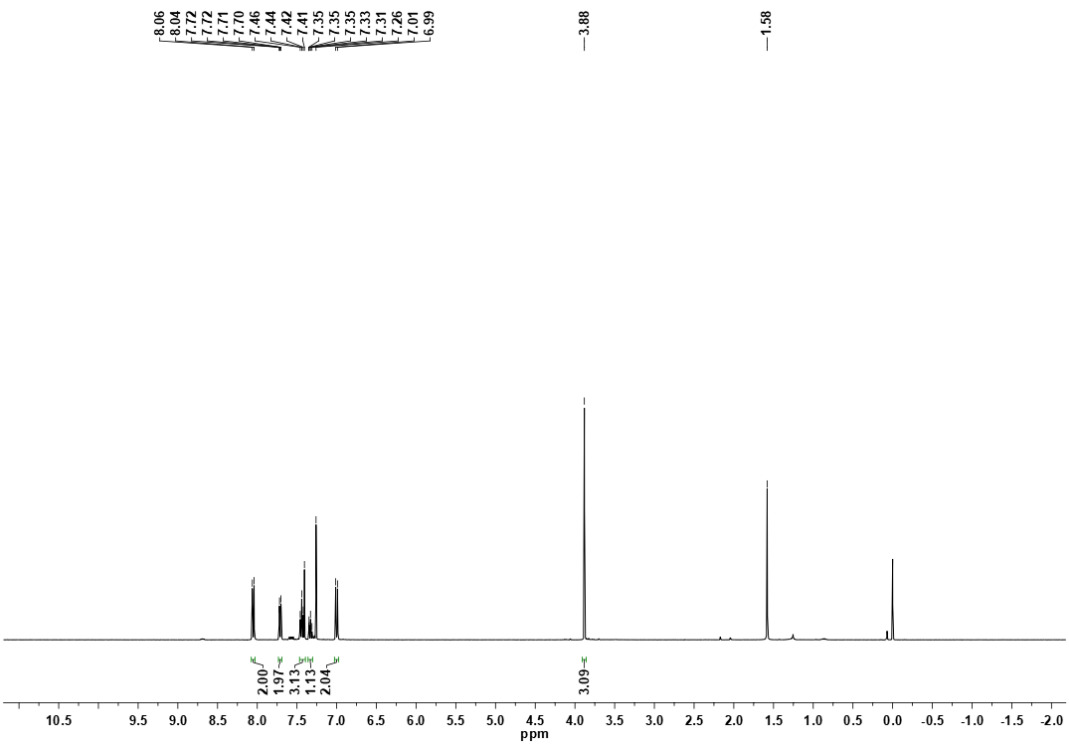


Figure S34. ^{1}H NMR spectrum of oxazole **5b** measured in $CDCl_3$.

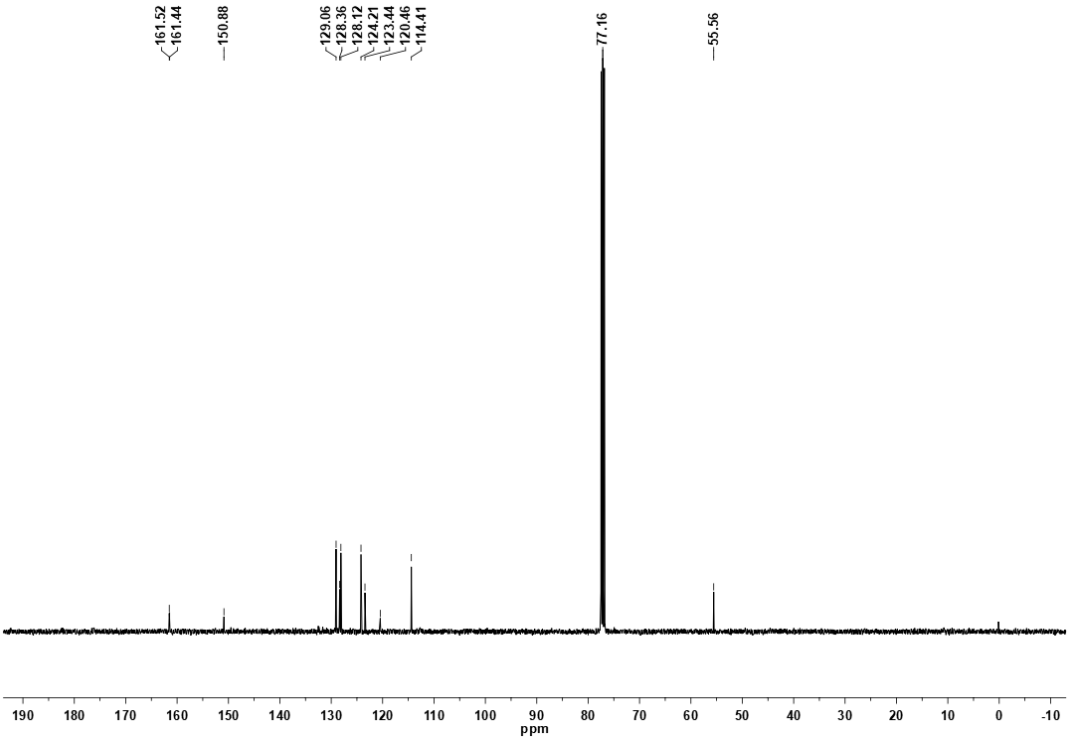


Figure S35. ^{13}C NMR spectrum of oxazole **5b** measured in $CDCl_3$.

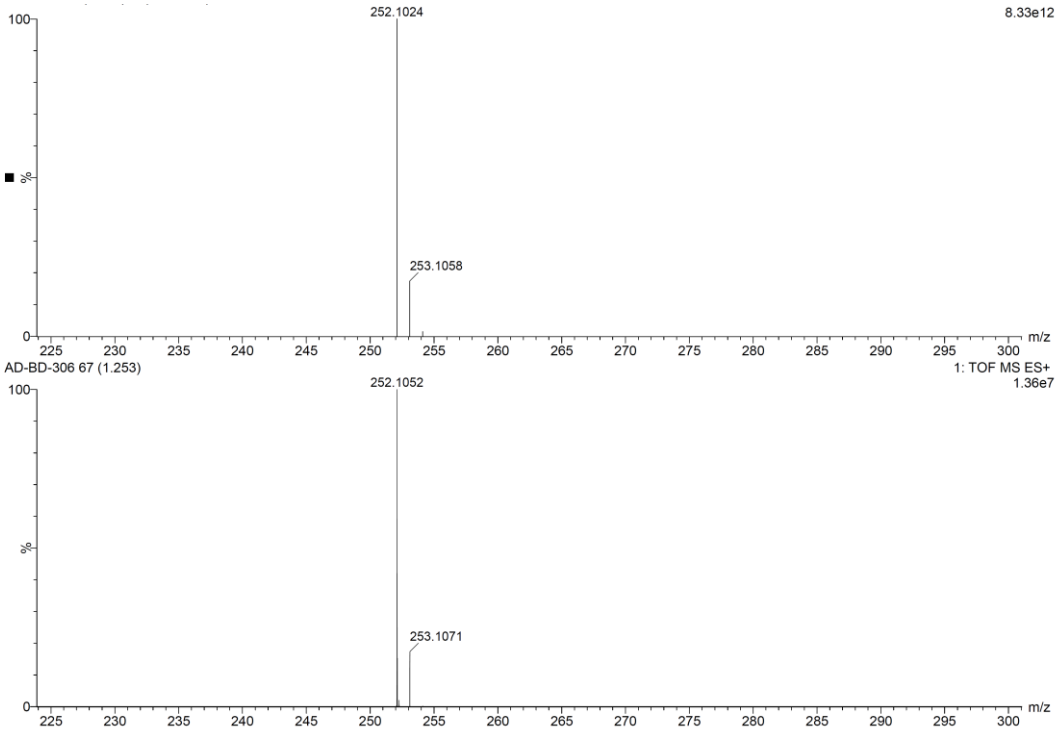


Figure S36. HRMS spectrum of oxazole **5b** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

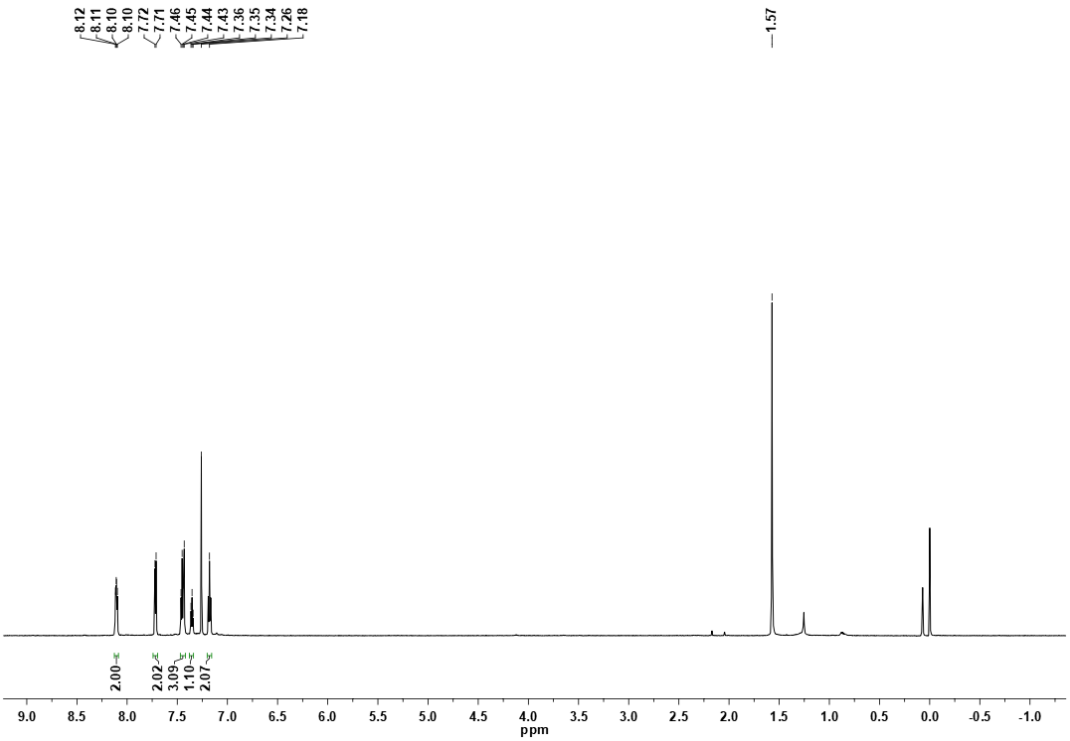


Figure S37. ^{1}H NMR spectrum of oxazole **5c** measured in $CDCl_3$.

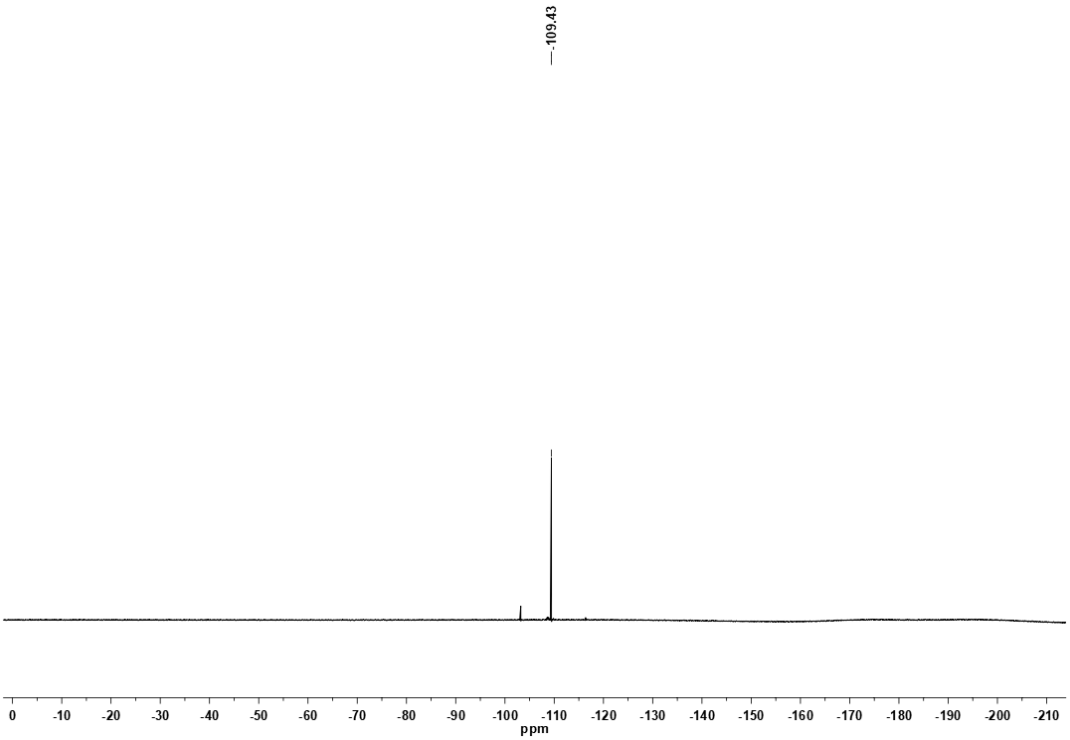


Figure S38. ^{19}F NMR spectrum of oxazole **5c** measured in $CDCl_3$.

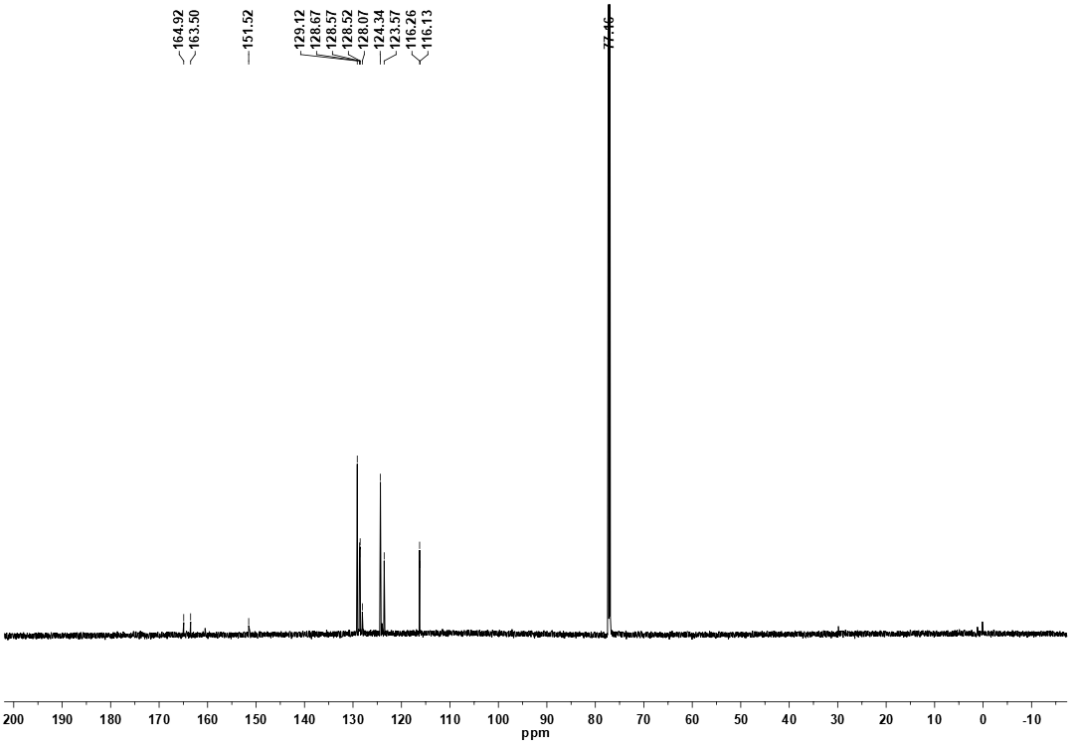


Figure S39. ^{13}C NMR spectrum of oxazole **5c** measured in $CDCl_3$.

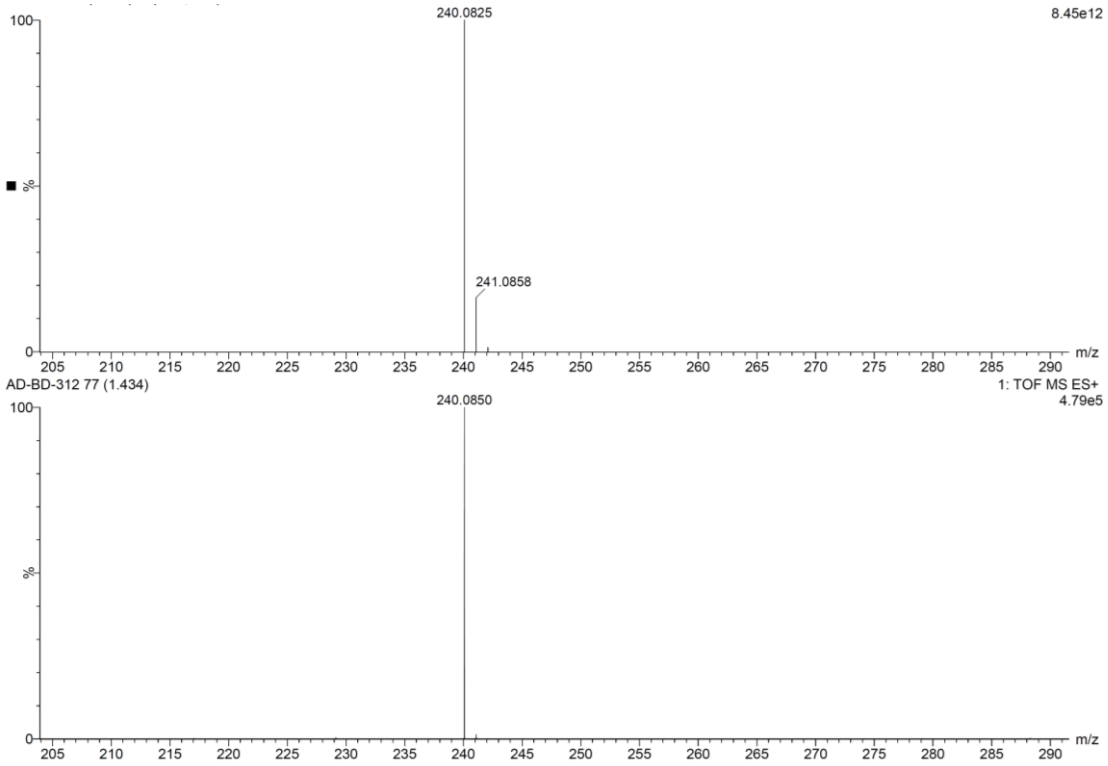


Figure S40. HRMS spectrum of oxazole **5c** measured in methanol, (*top*; theoretical isotopic pattern, bottom; calculated isotopic pattern).

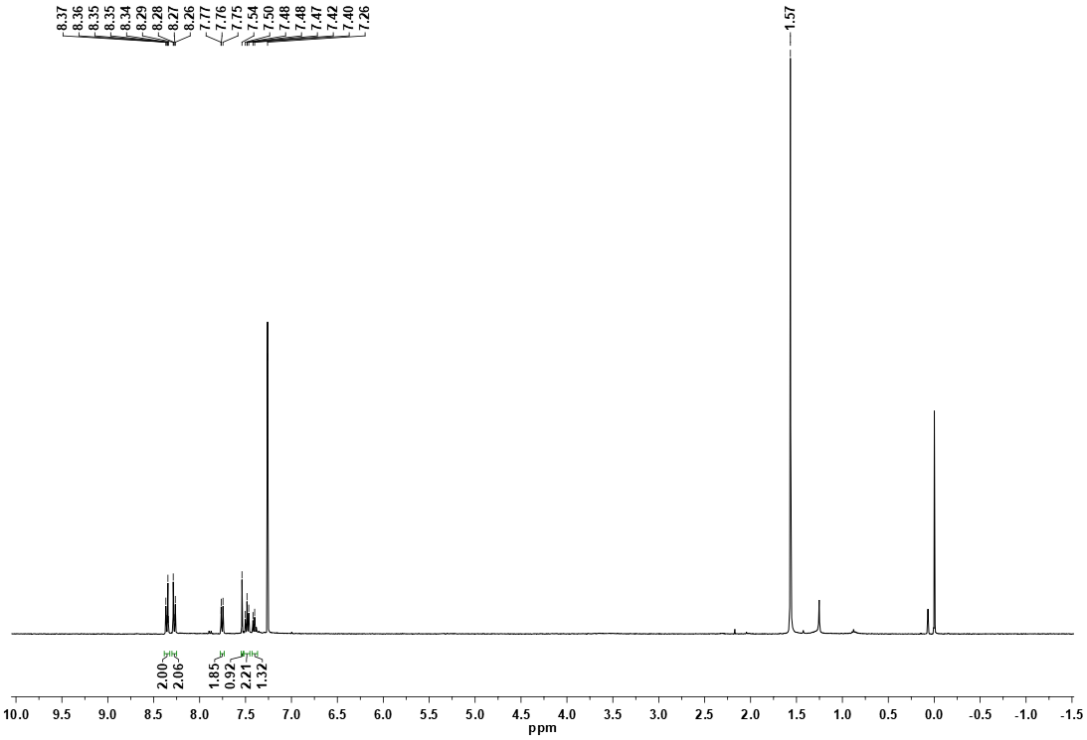


Figure S41. ^{1}H NMR spectrum of oxazole **5d** measured in $CDCl_3$.

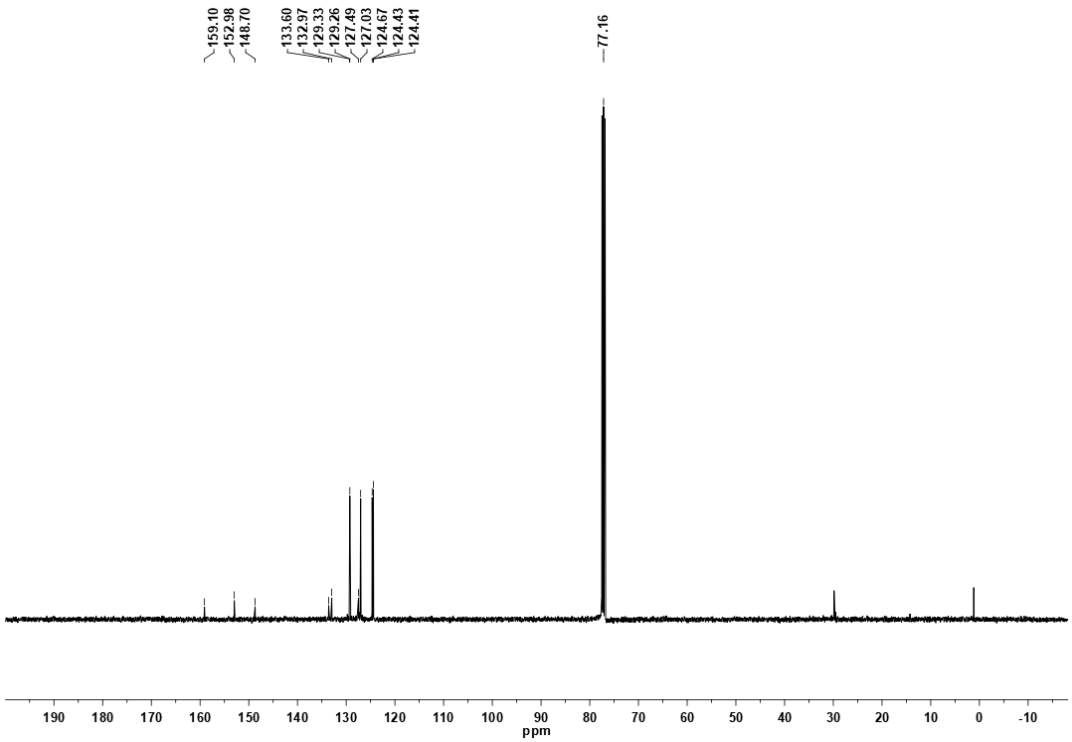


Figure S42. ^{13}C NMR spectrum of oxazole **5d** measured in $CDCl_3$.

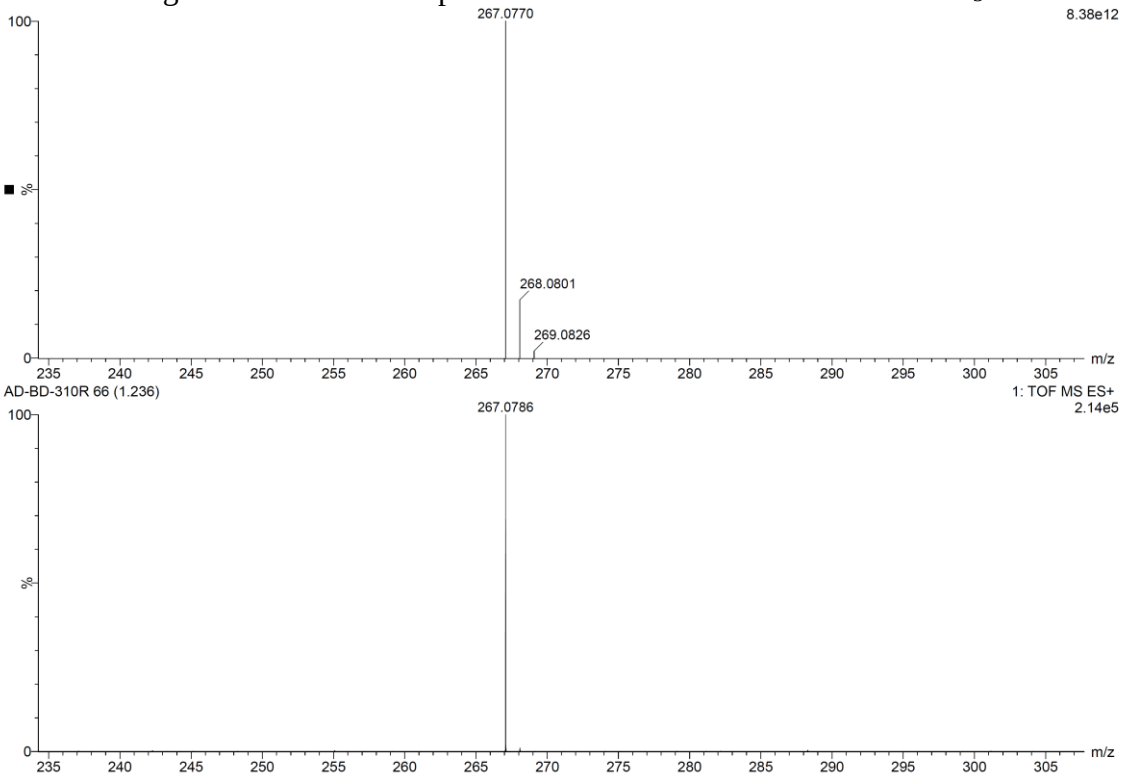


Figure S43. HRMS spectrum of oxazole **5d** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

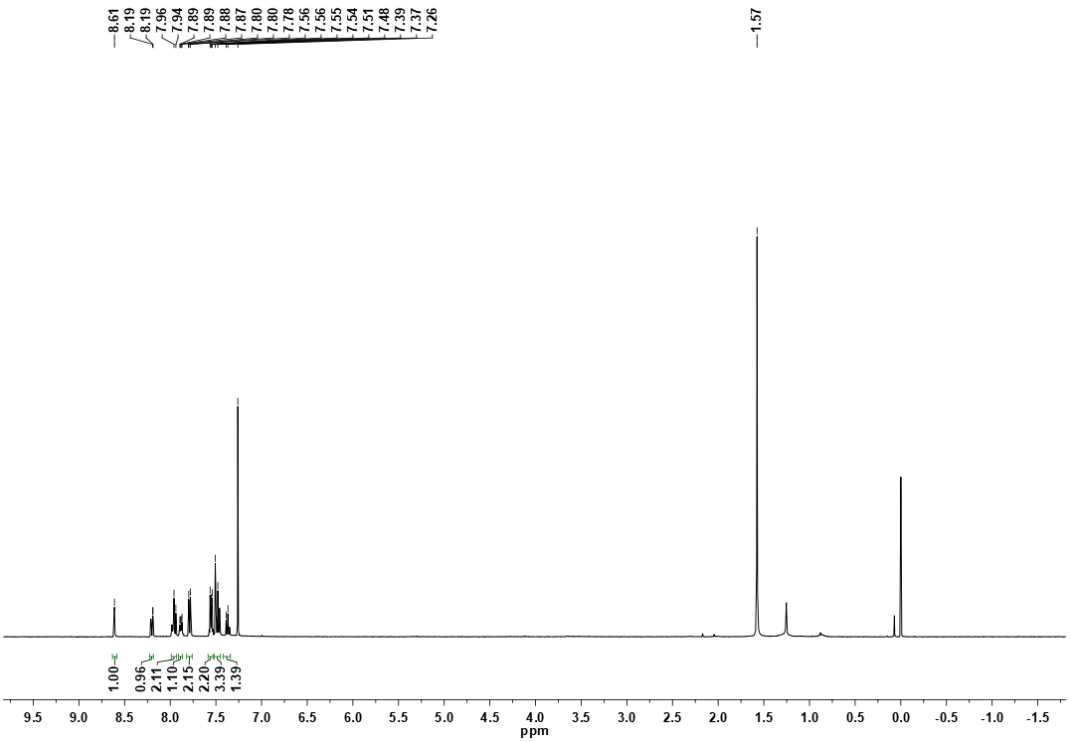


Figure S44. ^{1}H NMR spectrum of oxazole **5e** measured in $CDCl_3$.

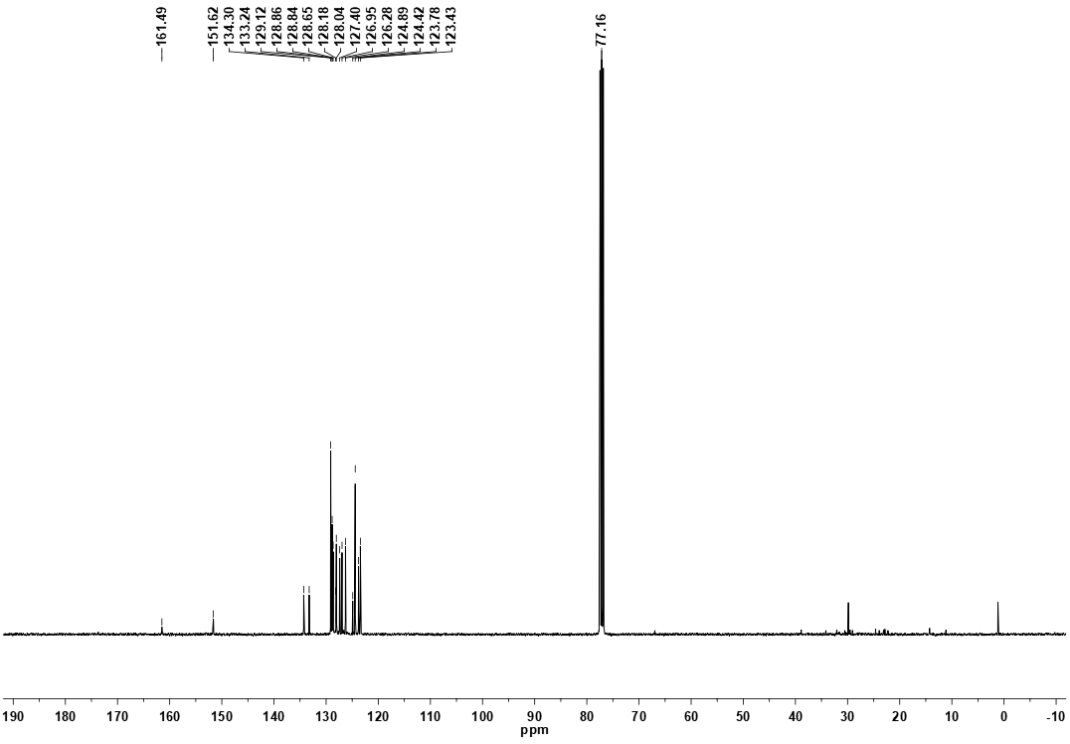


Figure S45. ^{13}C NMR spectrum of oxazole **5e** measured in $CDCl_3$.

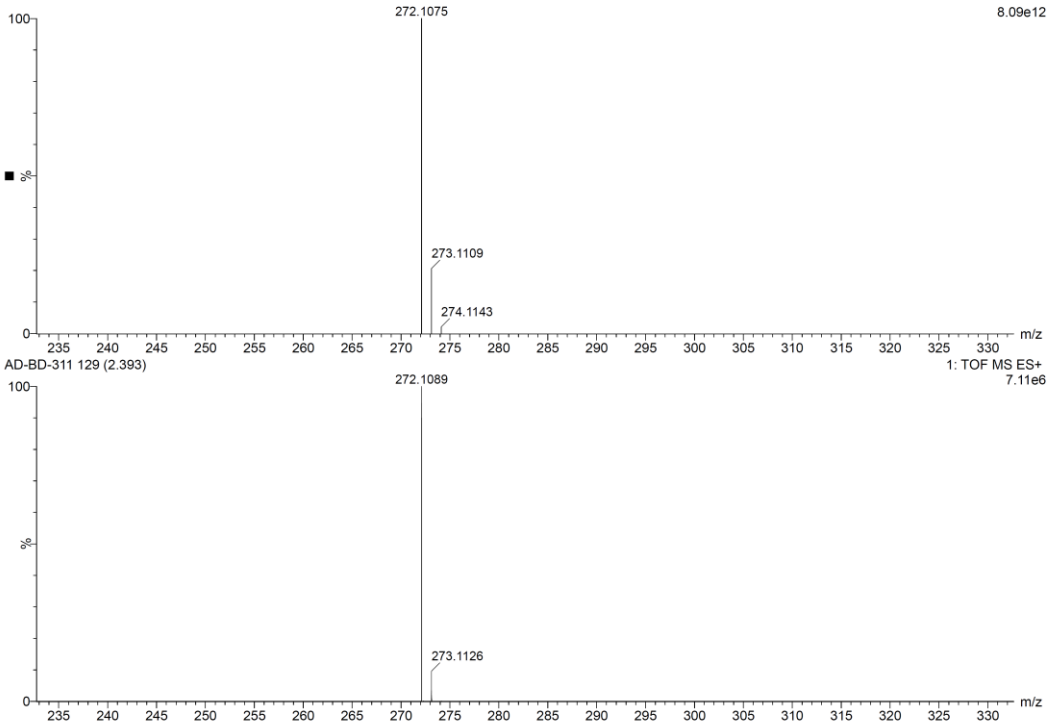


Figure S46. HRMS spectrum of oxazole **5e** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

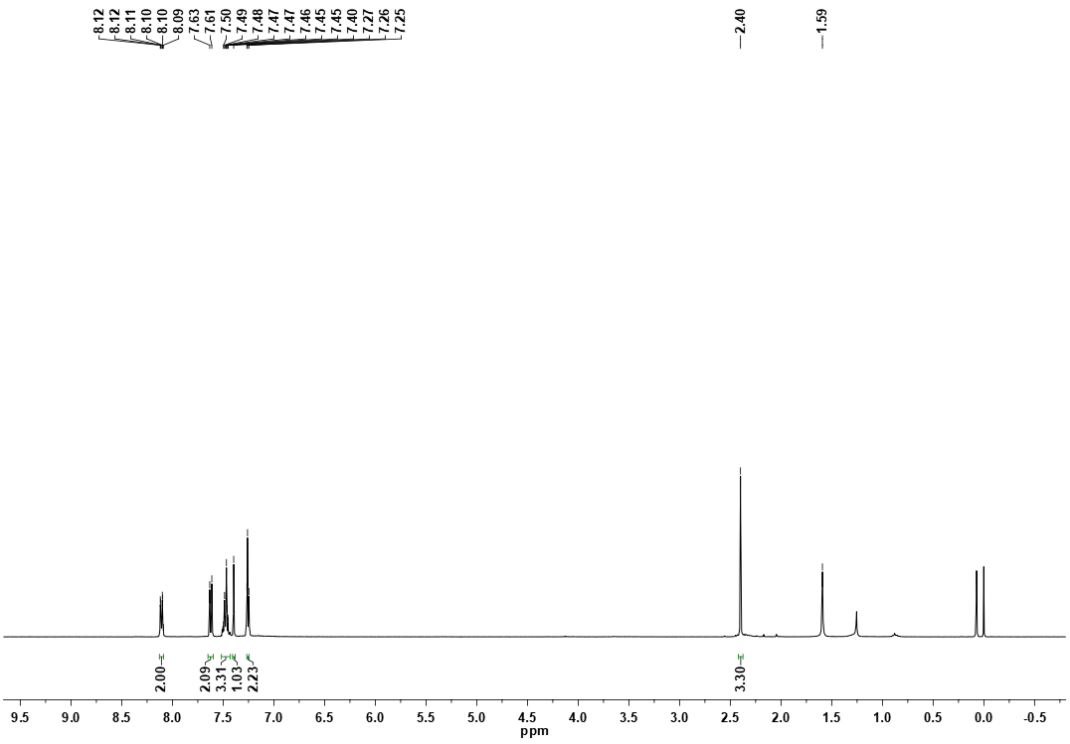


Figure S47. ^{1}H NMR spectrum of oxazole **5f** measured in $CDCl_3$.

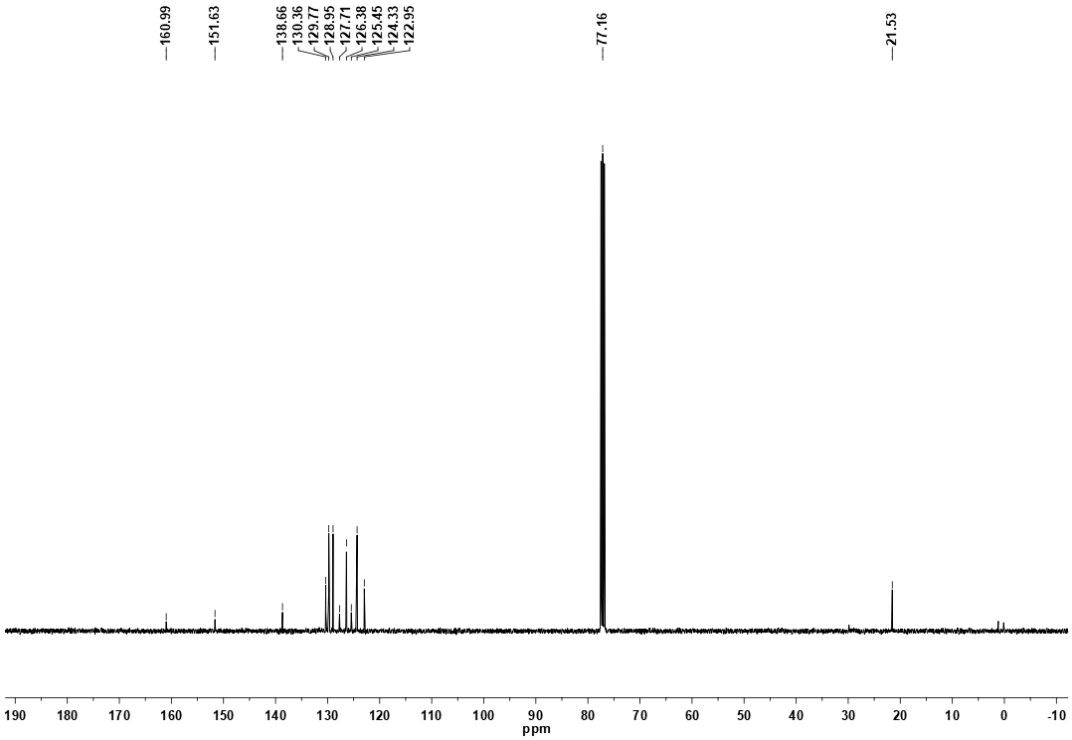


Figure S48. ^{13}C NMR spectrum of oxazole **5f** measured in $CDCl_3$.

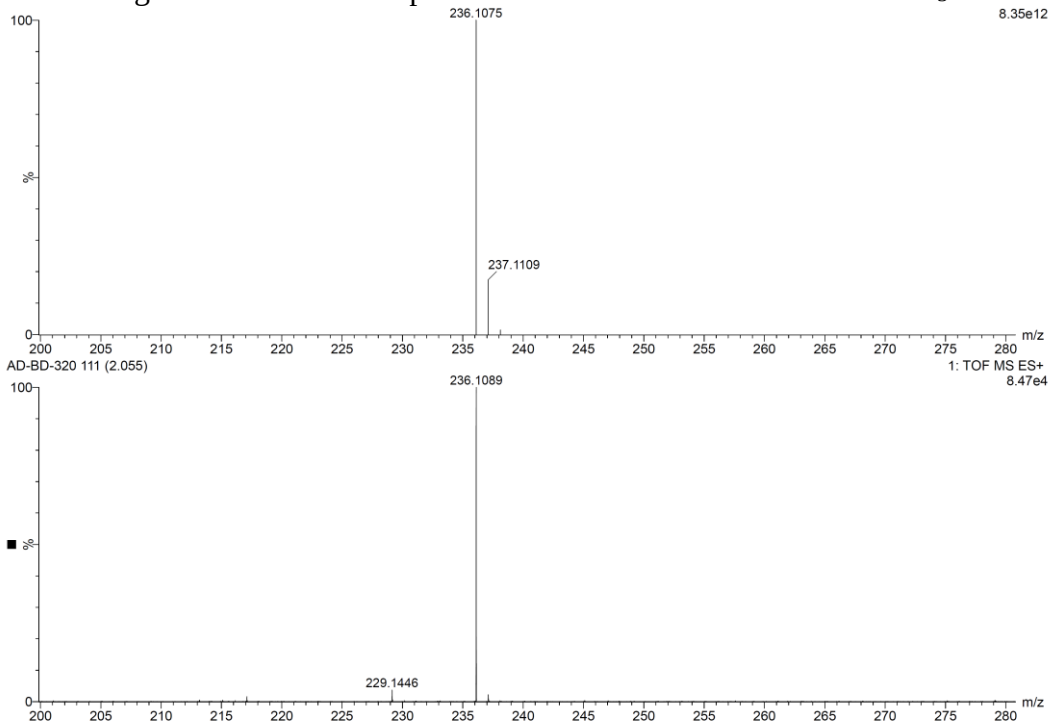


Figure S49. HRMS spectrum of oxazole **5f** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

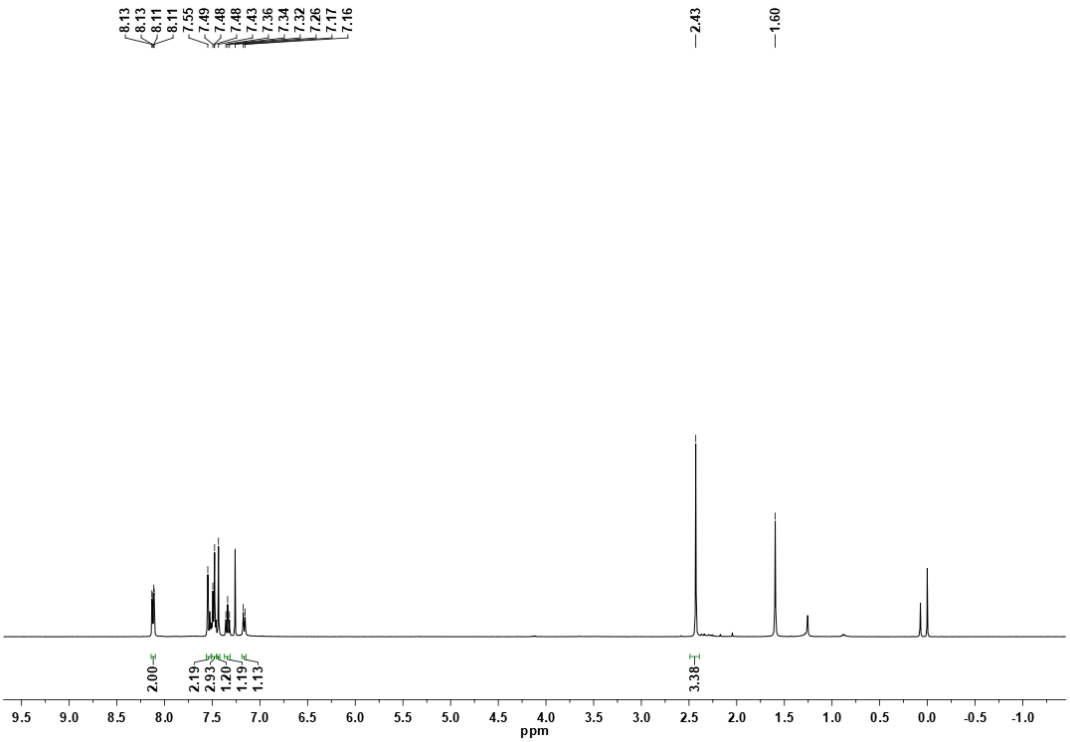


Figure S50. ^{1}H NMR spectrum of oxazole **5g** measured in $CDCl_3$.

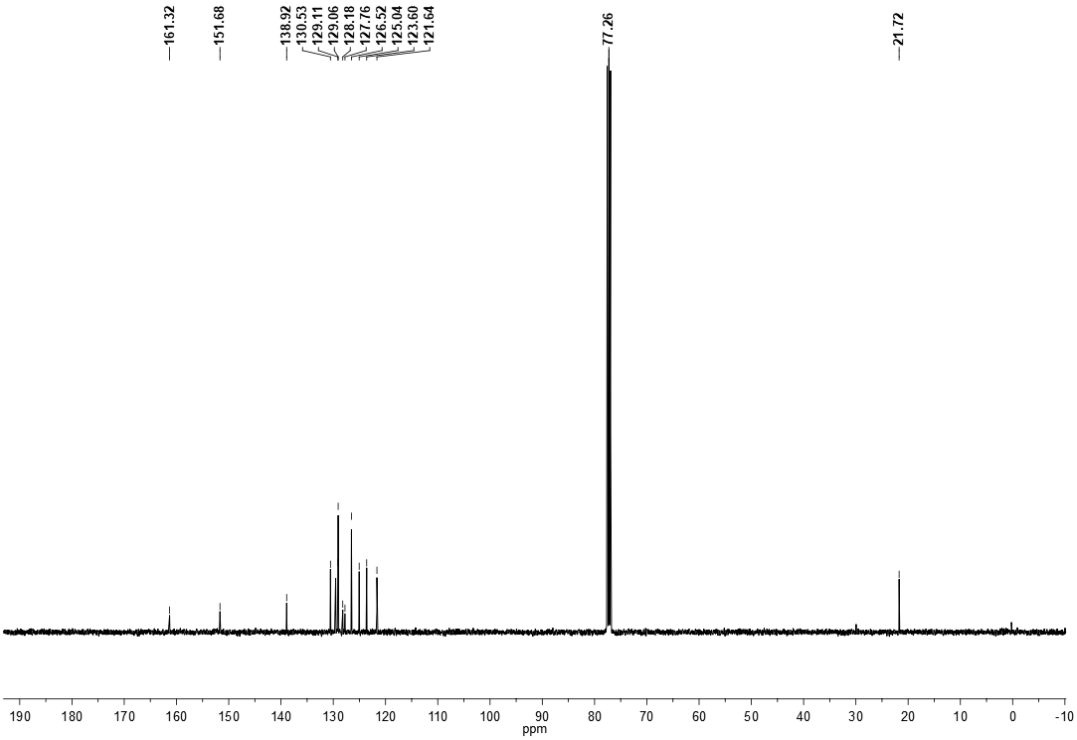


Figure S51. ^{13}C NMR spectrum of oxazole **5g** measured in $CDCl_3$.

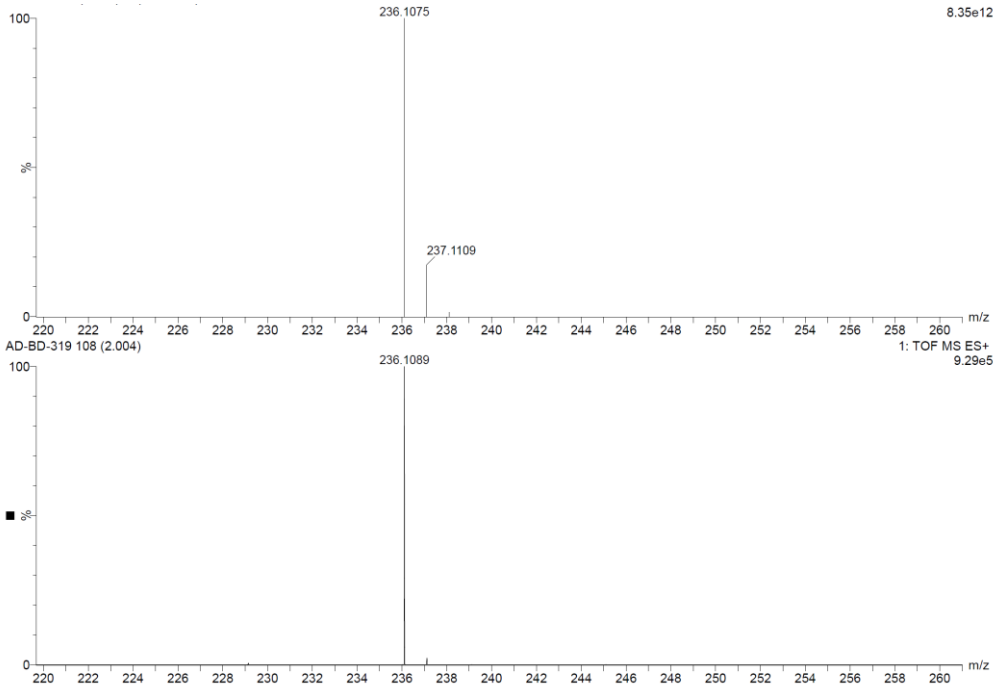


Figure S52. HRMS spectrum of oxazole **5g** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

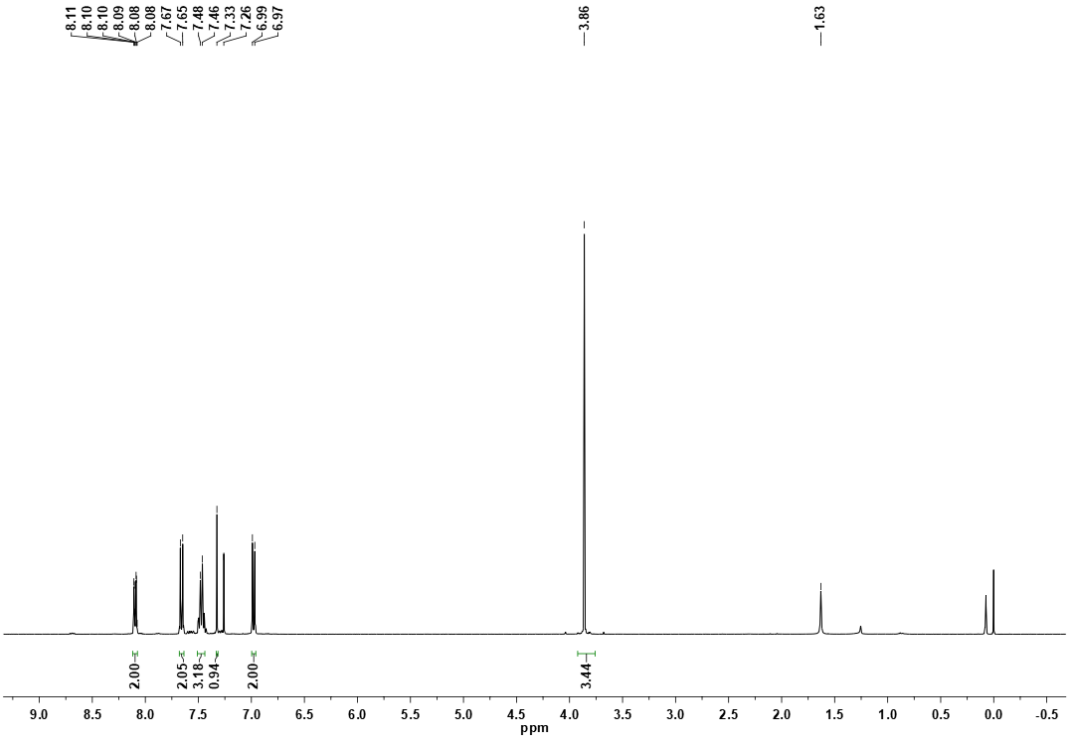


Figure S53. ^{1}H NMR spectrum of oxazole **5h** measured in $CDCl_3$.

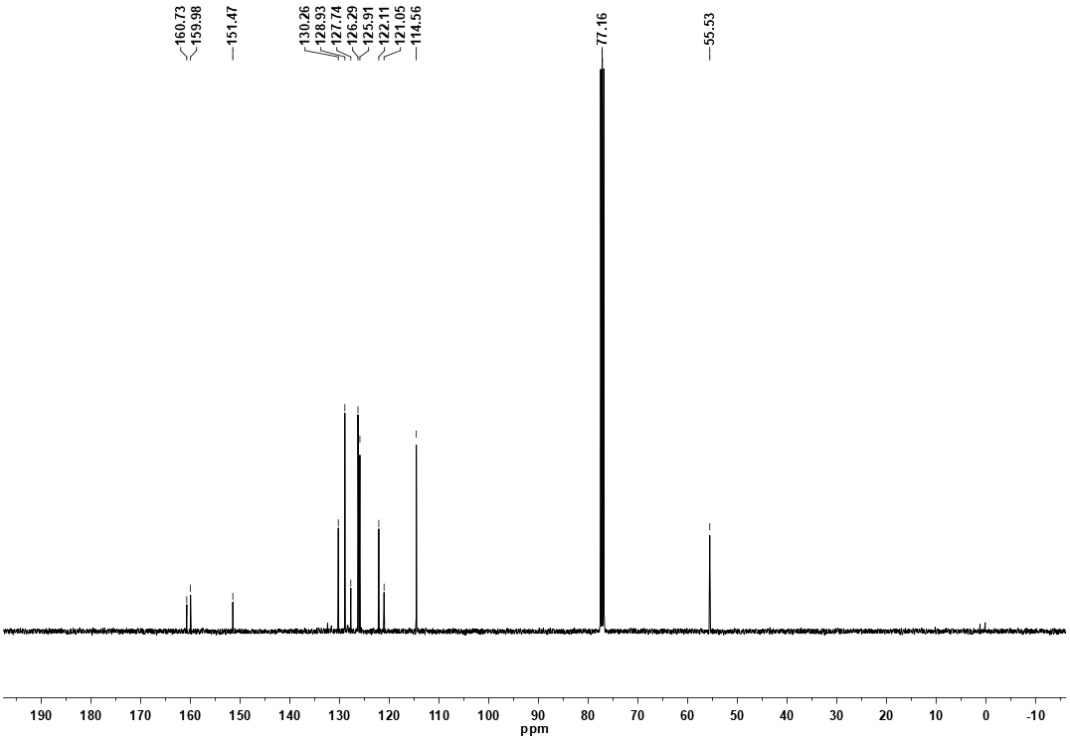


Figure S54. ^{13}C NMR spectrum of oxazole **5h** measured in $CDCl_3$.

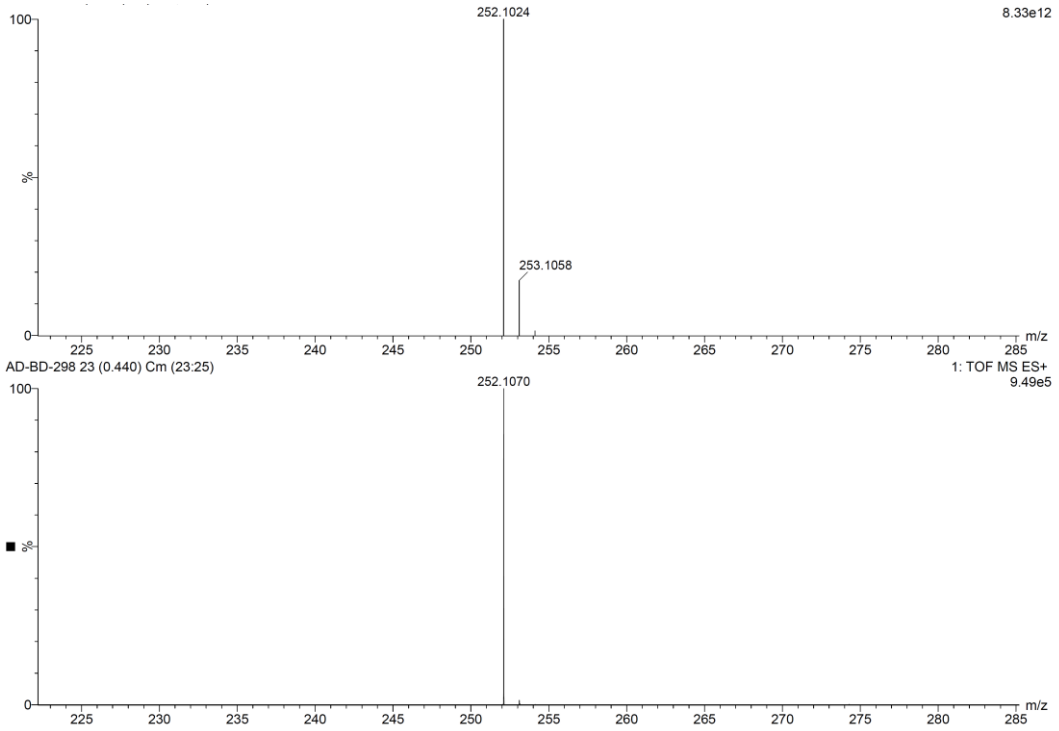


Figure S55. HRMS spectrum of oxazole **5h** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

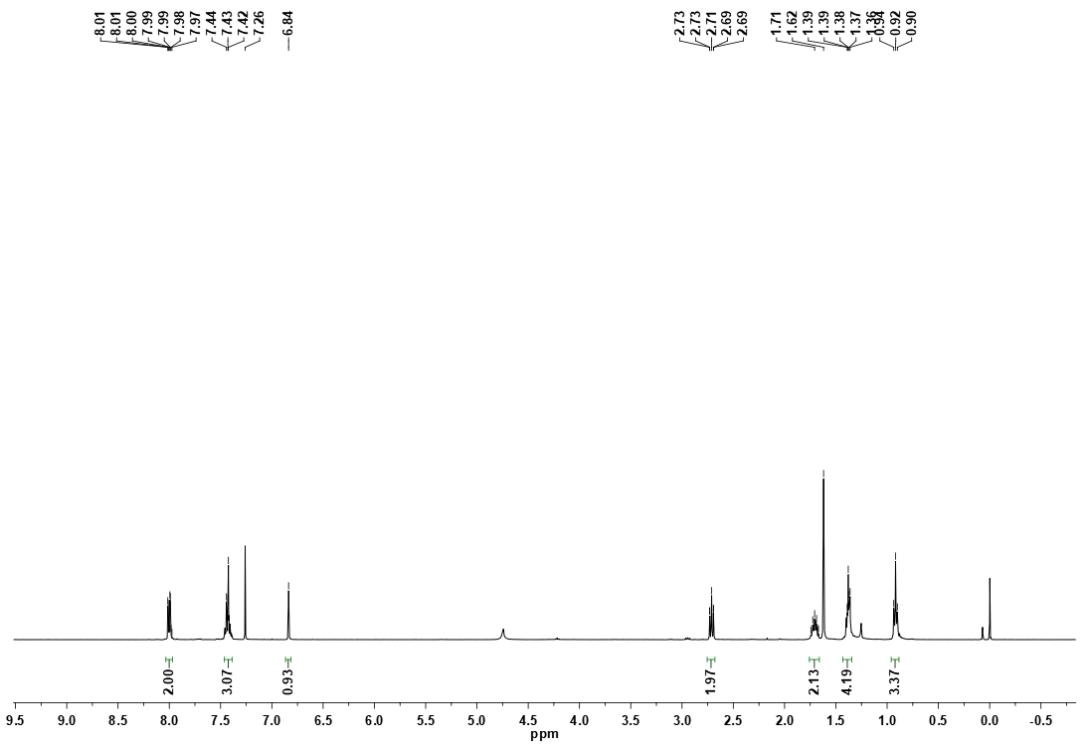


Figure S56. ^{1}H NMR spectrum of oxazole **5i** measured in $CDCl_3$.

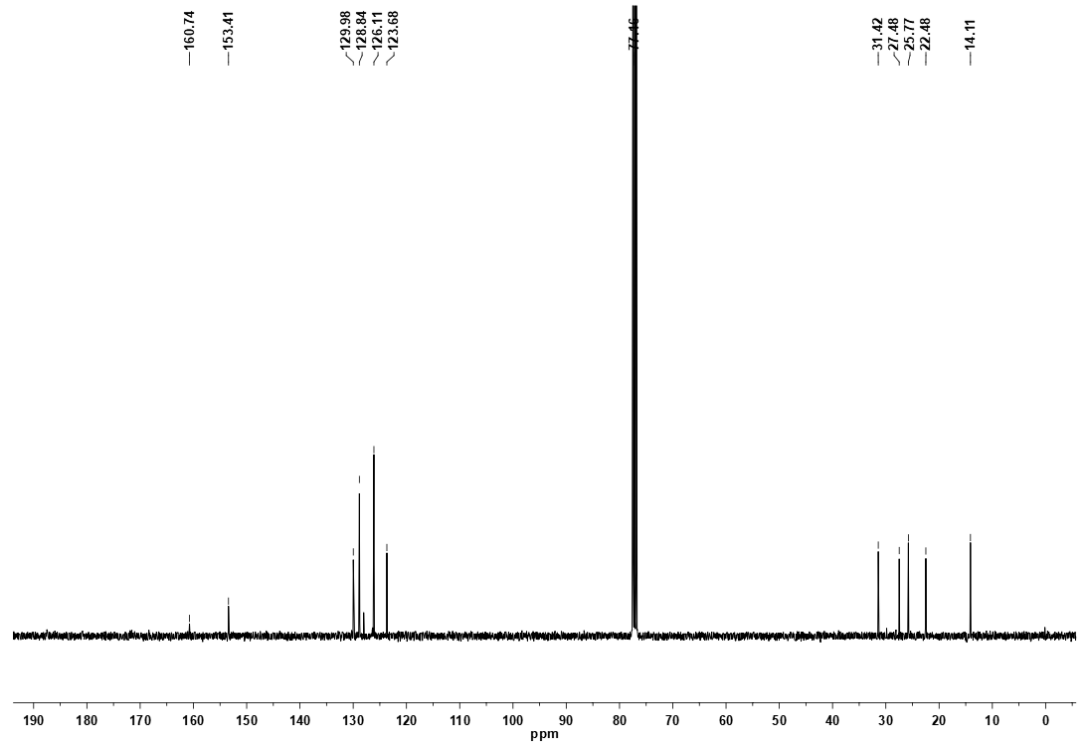


Figure S57. ^{13}C NMR spectrum of oxazole **5i** measured in $CDCl_3$.

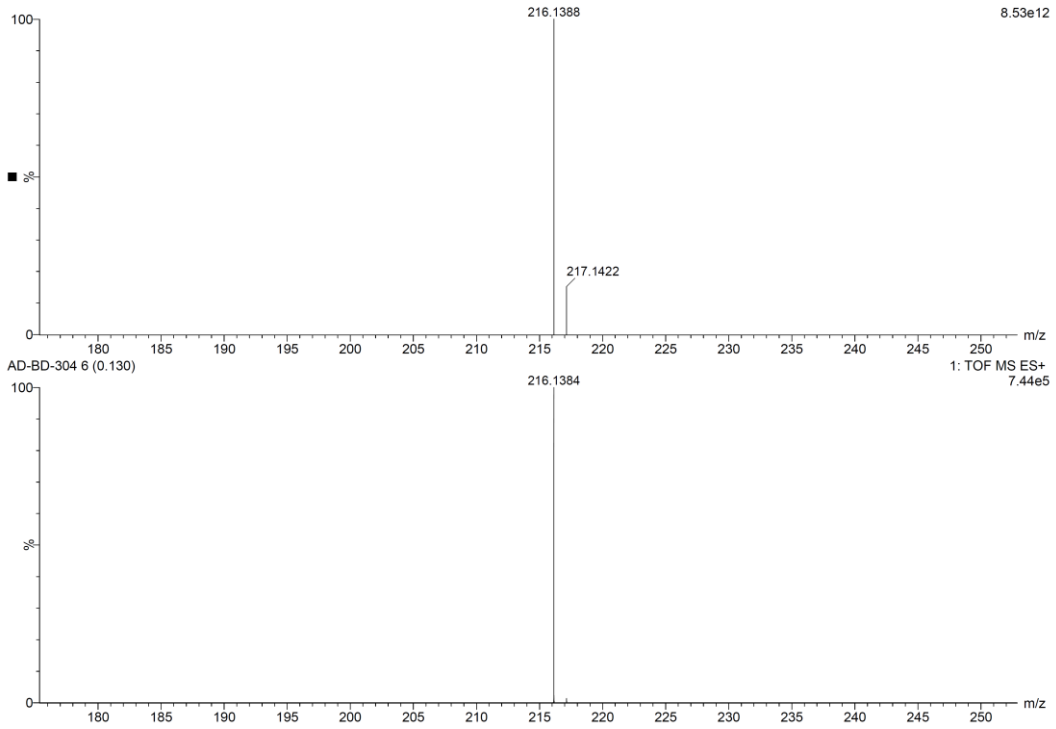


Figure S58. HRMS spectrum of oxazole **5i** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

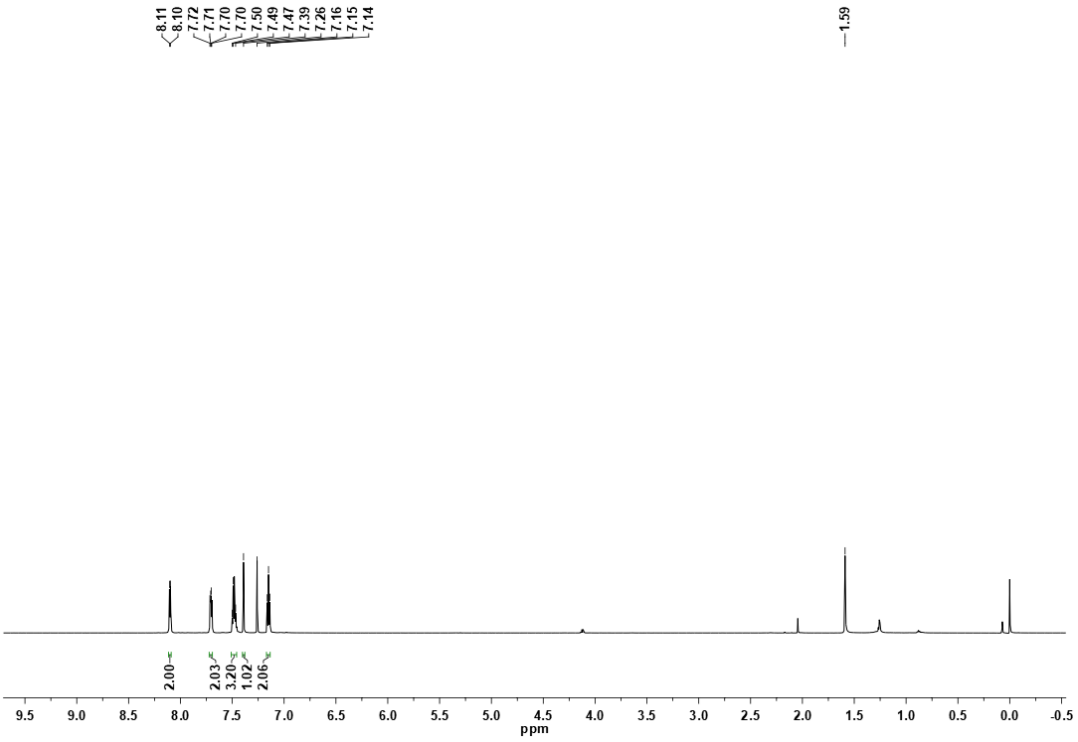


Figure S59. ^{1}H NMR spectrum of oxazole **5j** measured in $CDCl_3$.

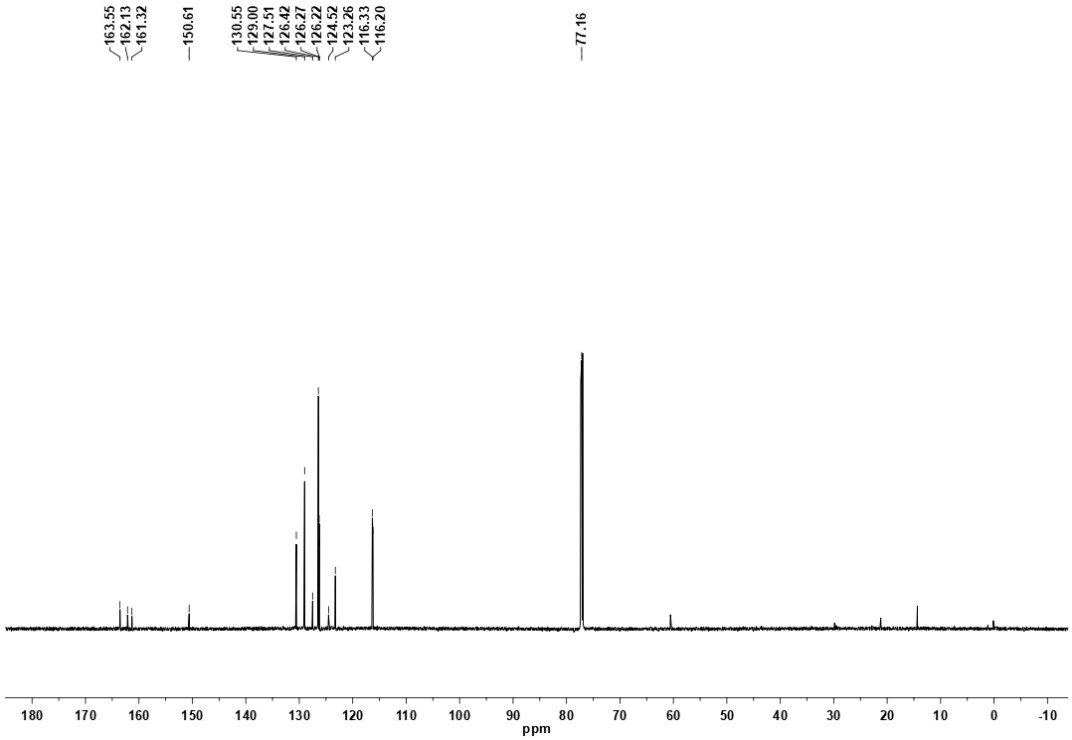


Figure S60. ^{13}C NMR spectrum of oxazole **5j** measured in $CDCl_3$.

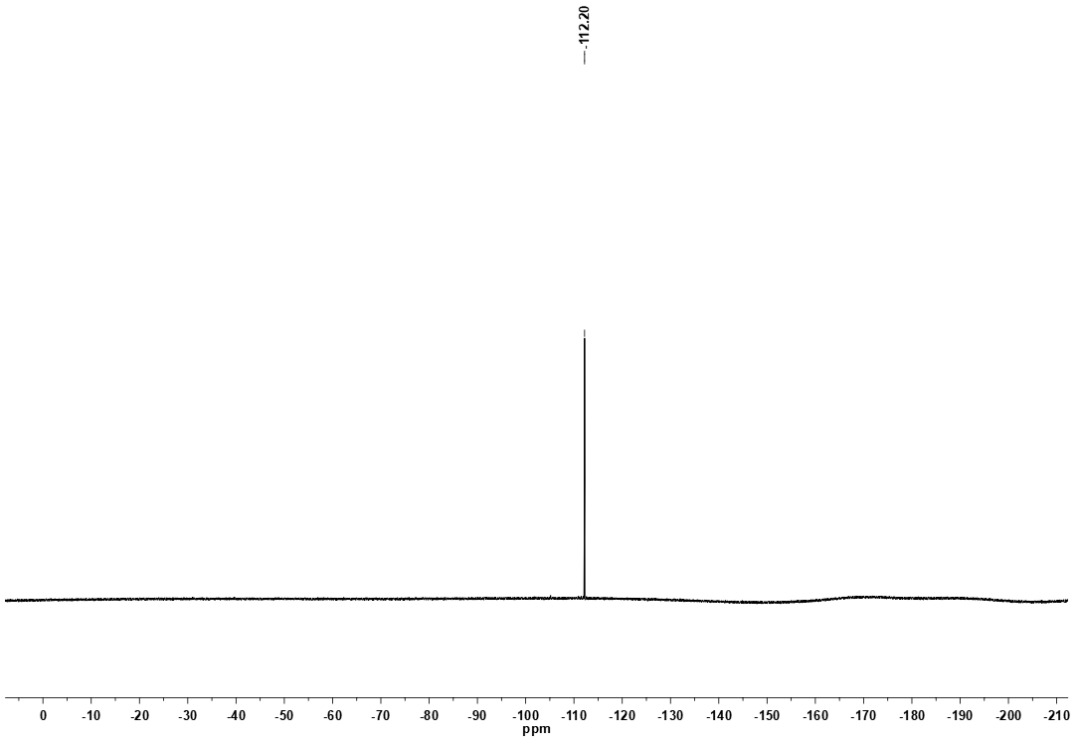


Figure S61. ^{19}F NMR spectrum of oxazole **5j** measured in $CDCl_3$.

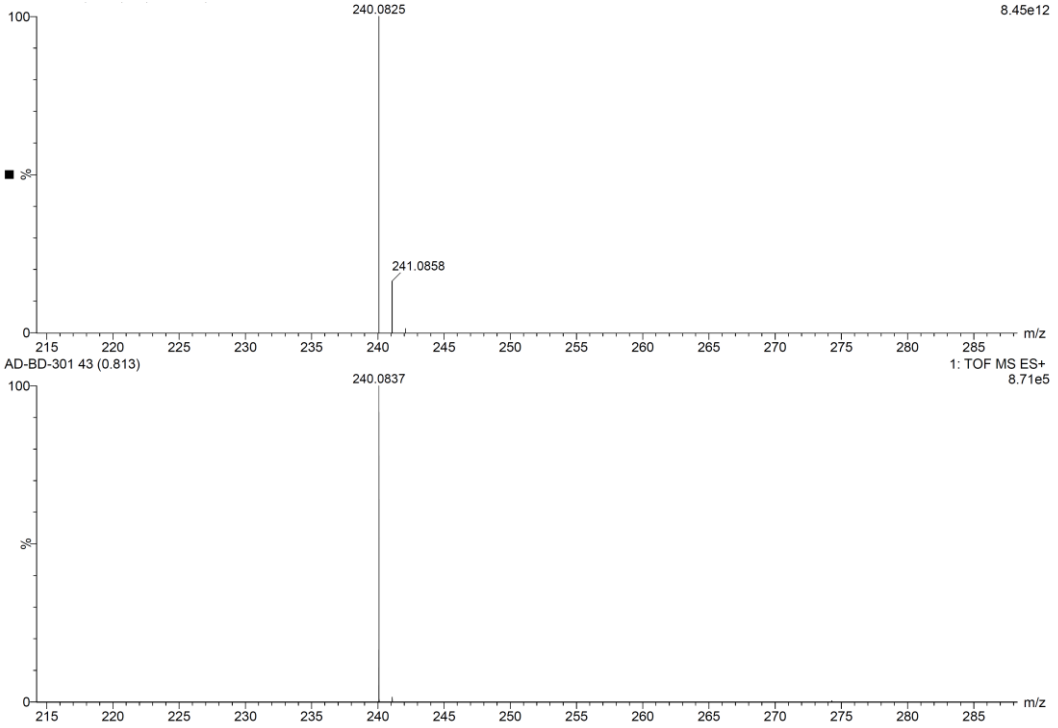


Figure S62. HRMS spectrum of oxazole **5j** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

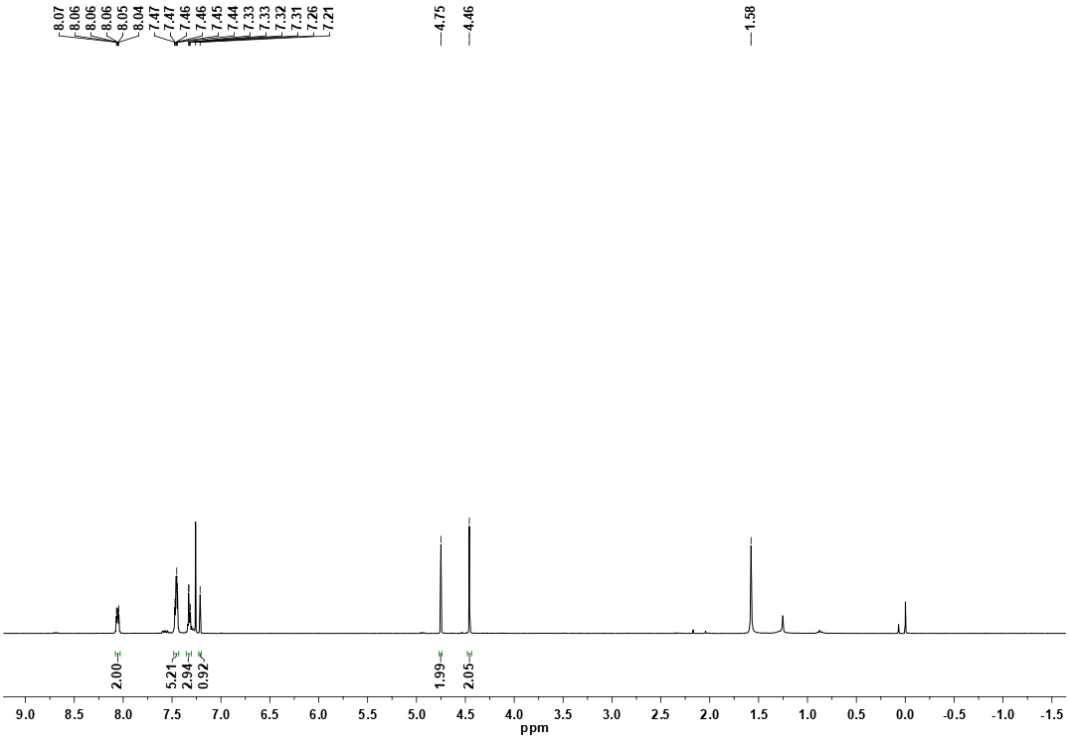


Figure S63. ^{1}H NMR spectrum of oxazole **5k** measured in $CDCl_3$.

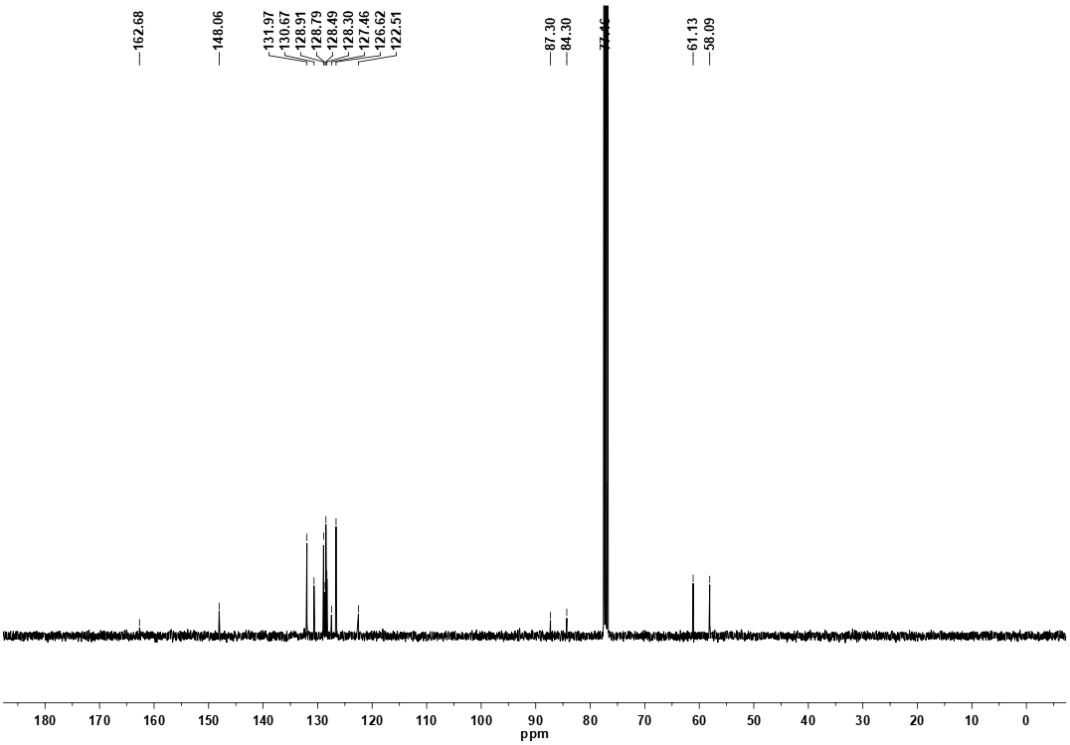


Figure S64. ^{13}C NMR spectrum of oxazole **5k** measured in $CDCl_3$.

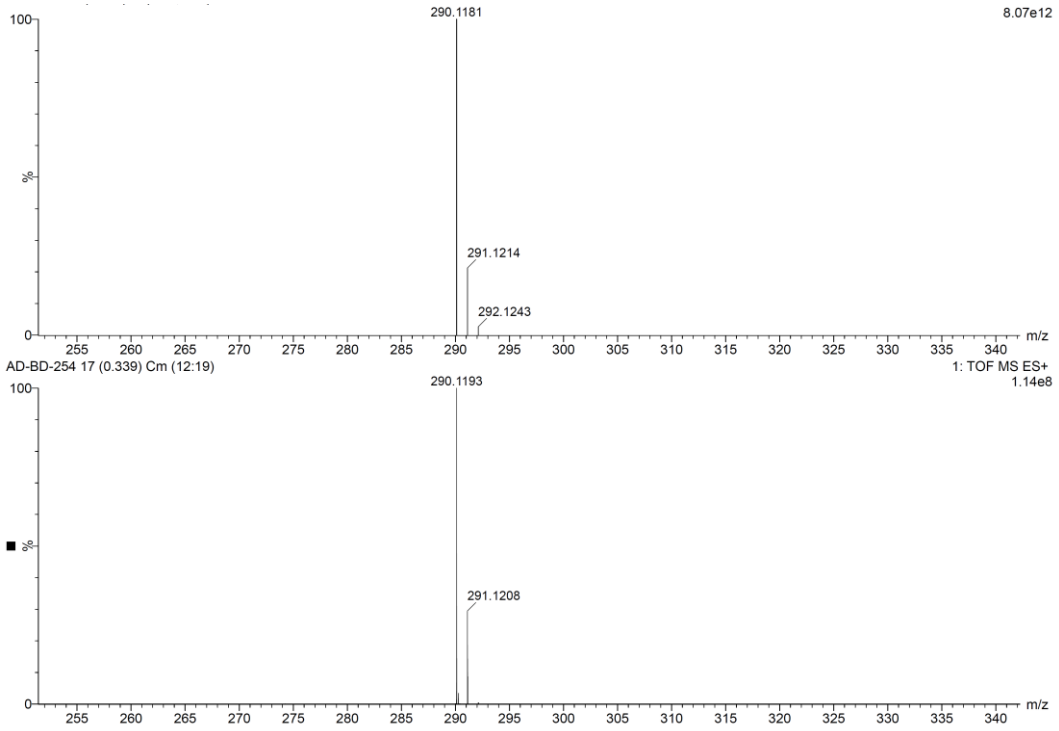


Figure S65. HRMS spectrum of oxazole **5k** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

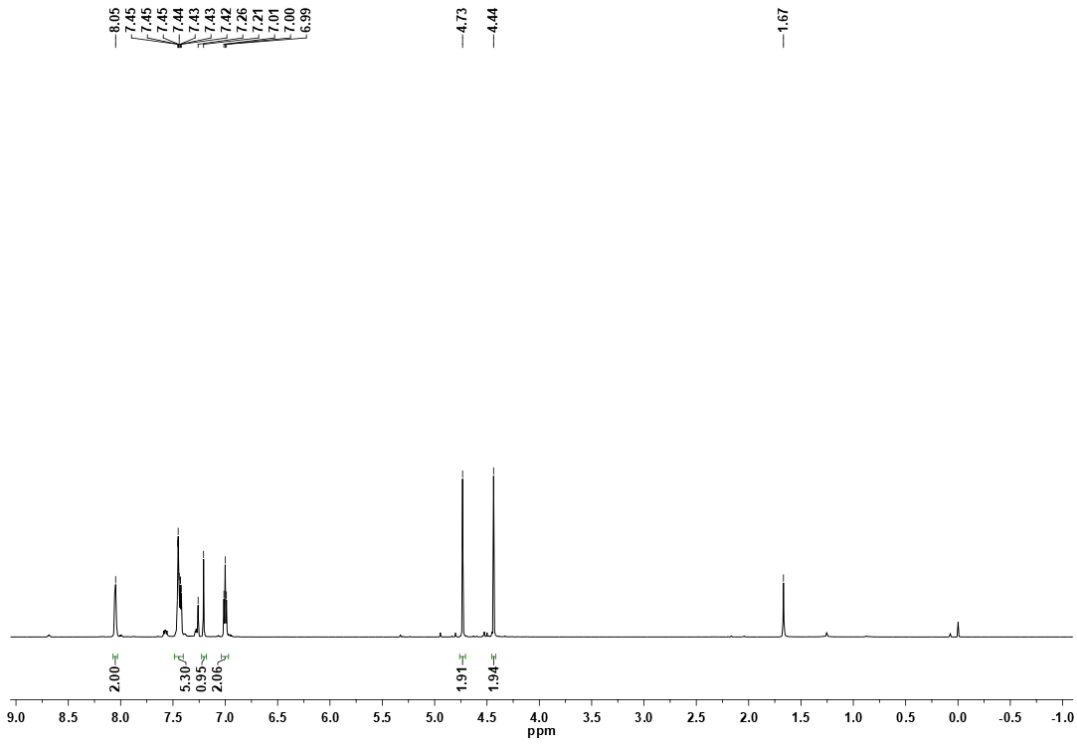


Figure S66. ^{1}H NMR spectrum of oxazole **5l** measured in $CDCl_3$.

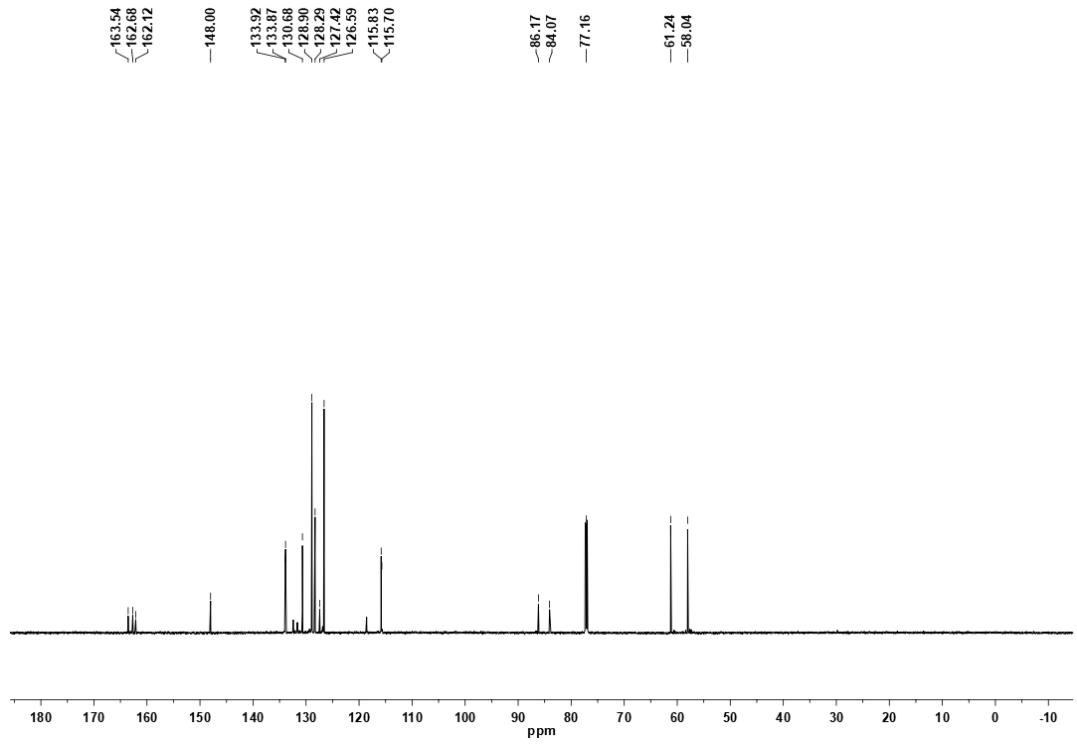


Figure S67. ^{13}C NMR spectrum of oxazole **5l** measured in $CDCl_3$.

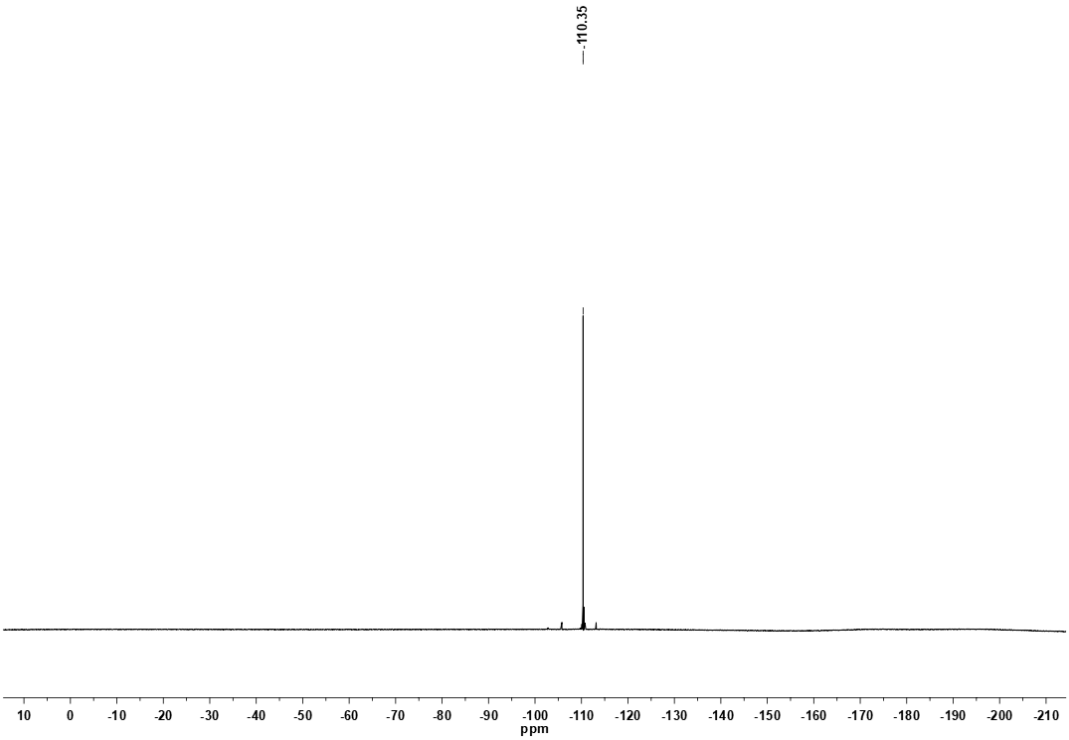


Figure S68. ^{19}F NMR spectrum of oxazole **5l** measured in $CDCl_3$.

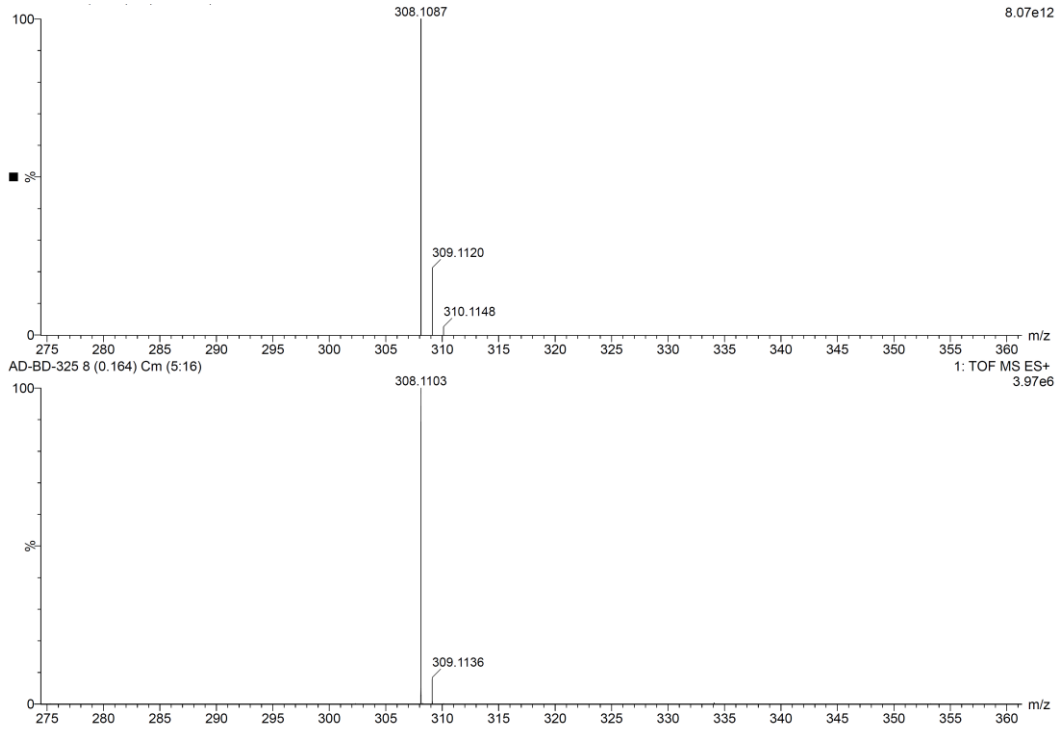


Figure S69. HRMS spectrum of oxazole **5l** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

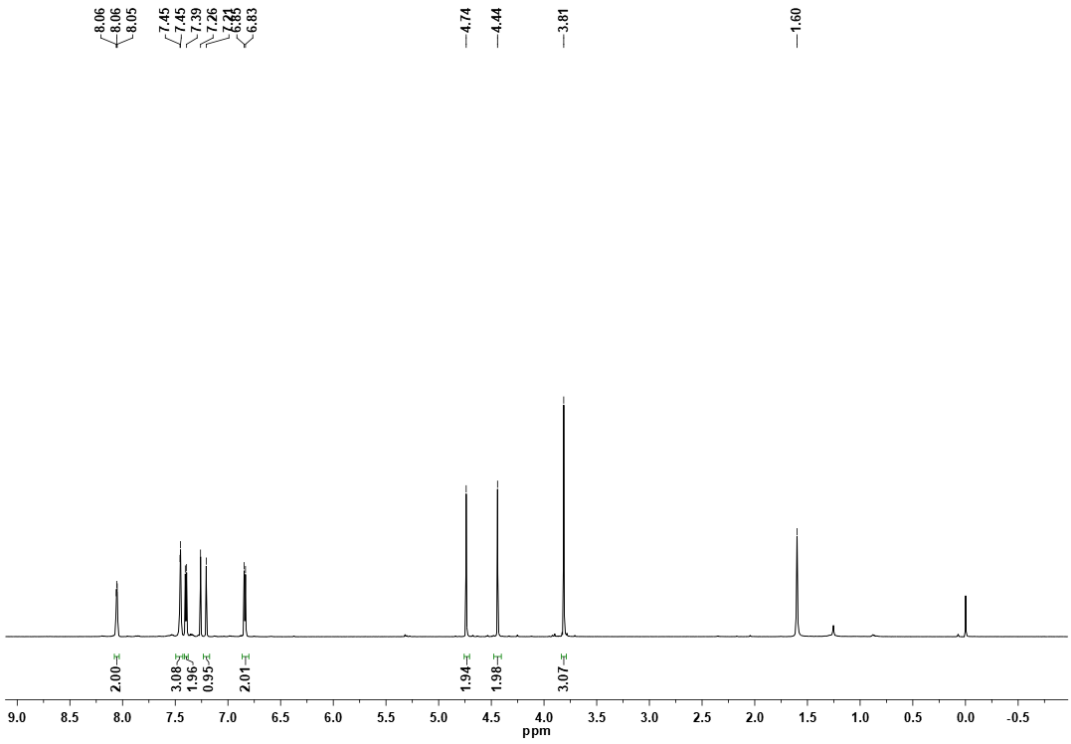


Figure S70. ^{1}H NMR spectrum of oxazole **5m** measured in $CDCl_3$.

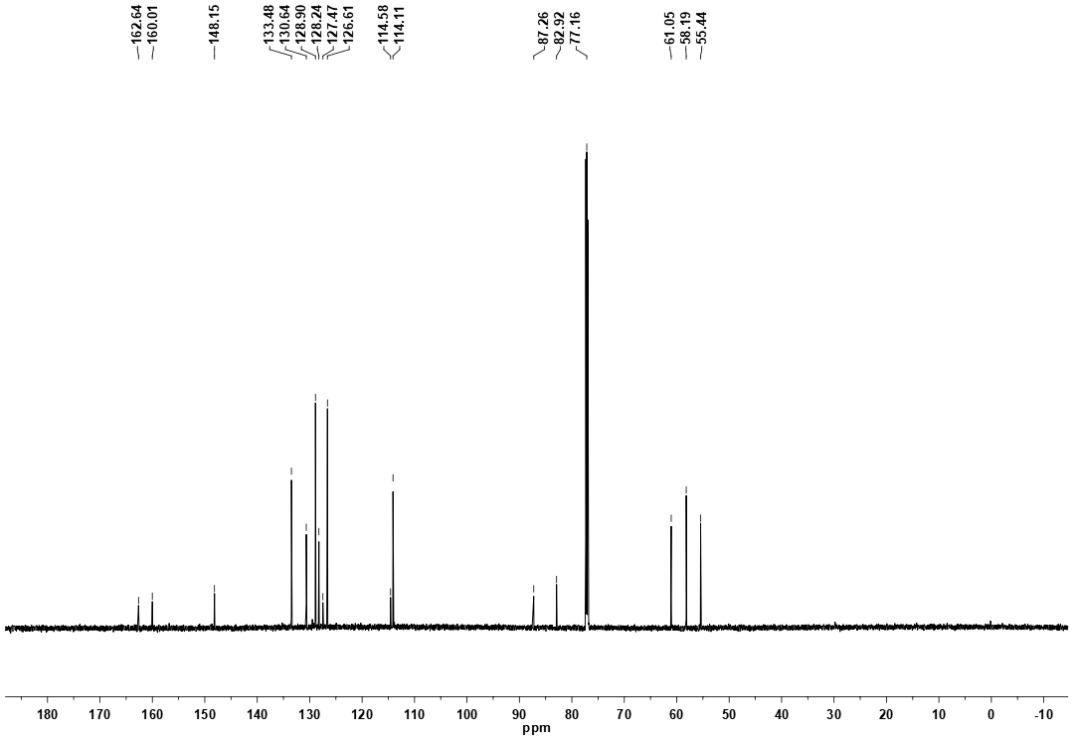


Figure S71. ^{13}C NMR spectrum of oxazole **5m** measured in $CDCl_3$.

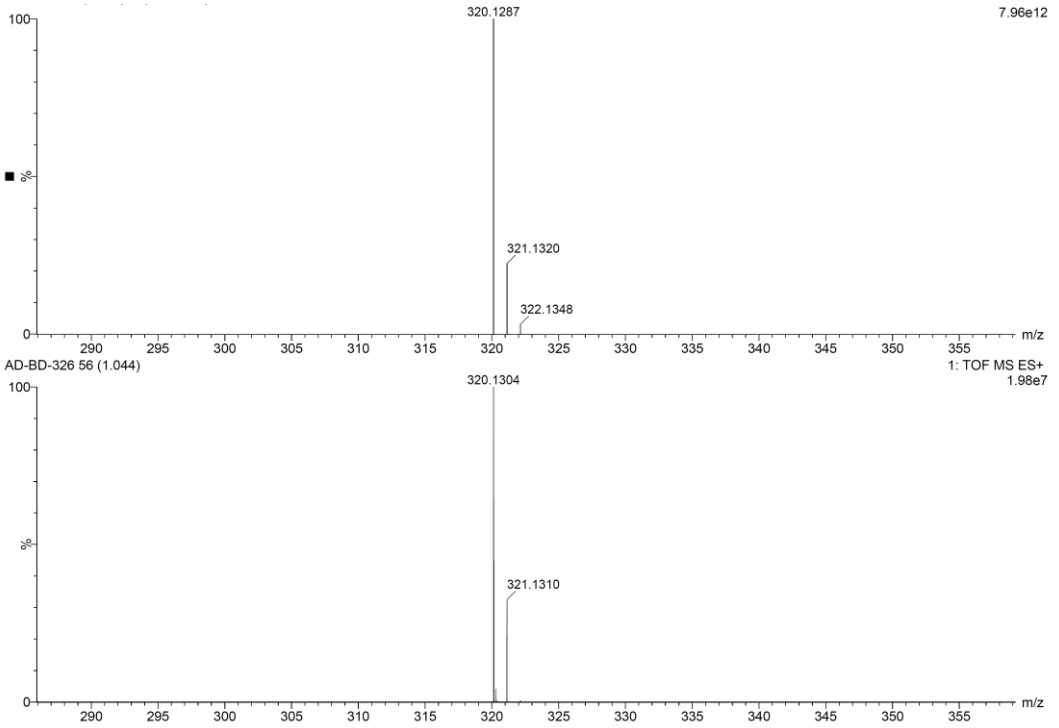


Figure S72. HRMS spectrum of oxazole **5m** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

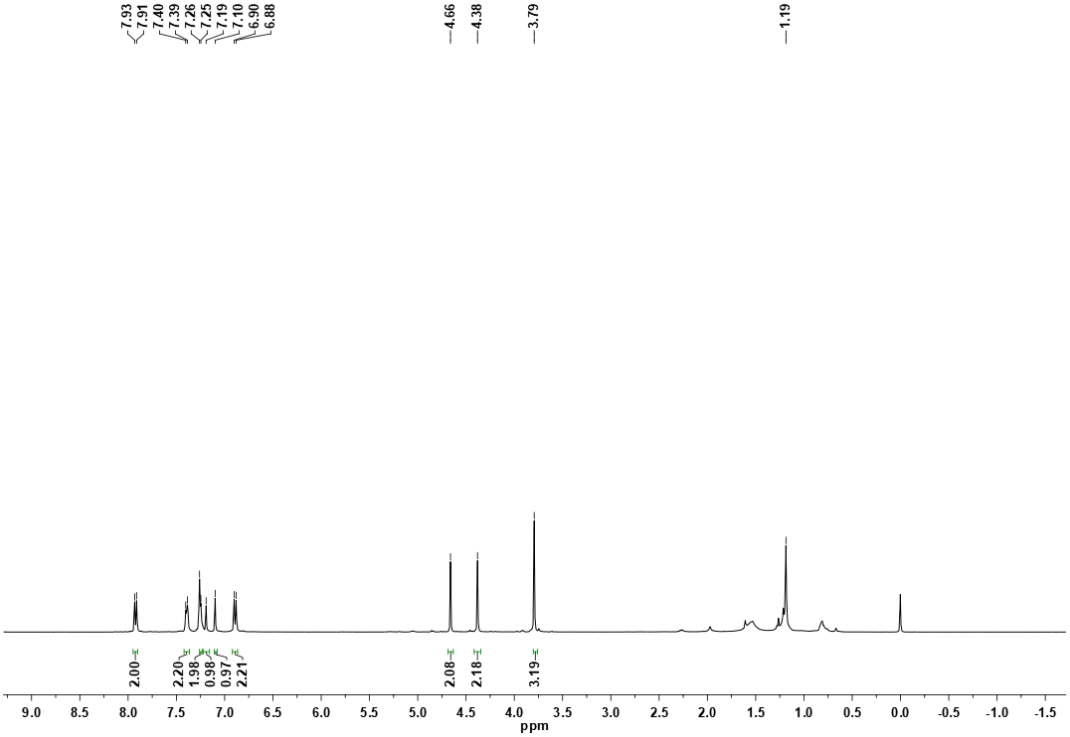


Figure S73. ^{1}H NMR spectrum of oxazole **5n** measured in $CDCl_3$.

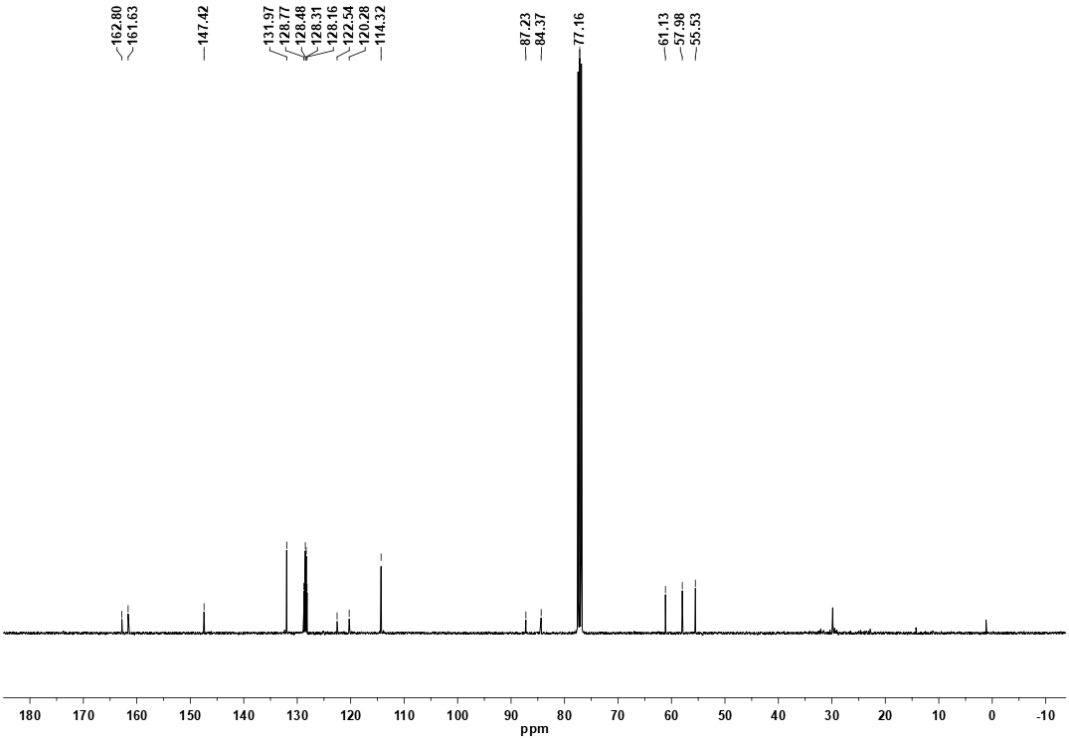


Figure S74. ^{13}C NMR spectrum of oxazole **5n** measured in $CDCl_3$.

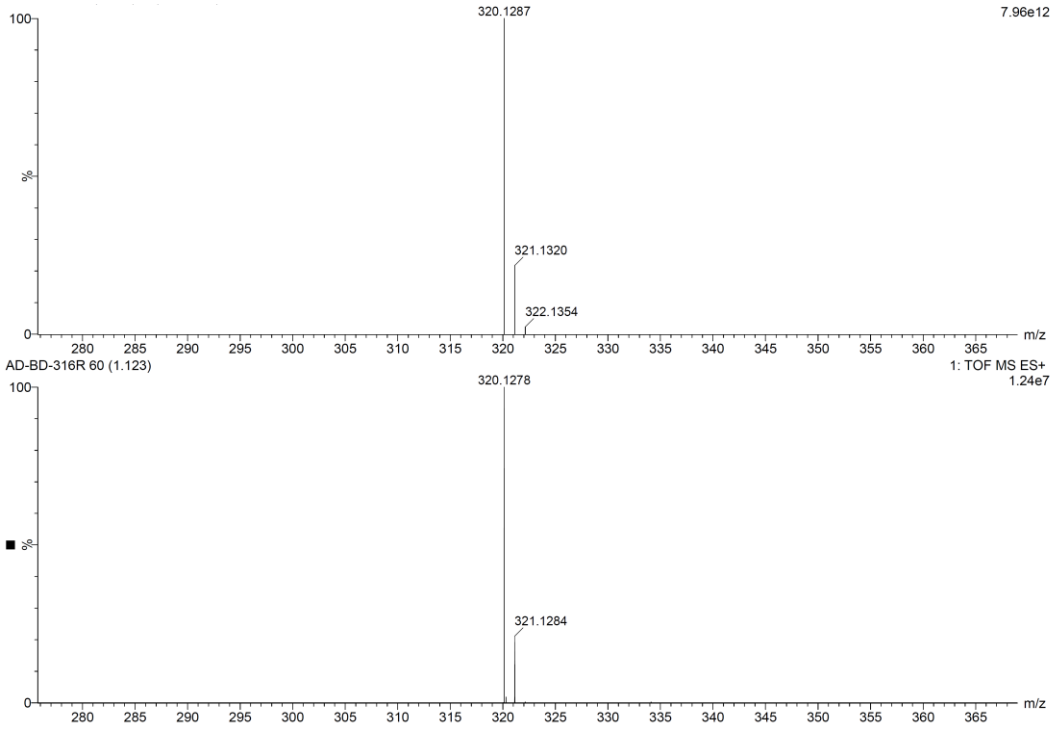


Figure S75. HRMS spectrum of oxazole **5n** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

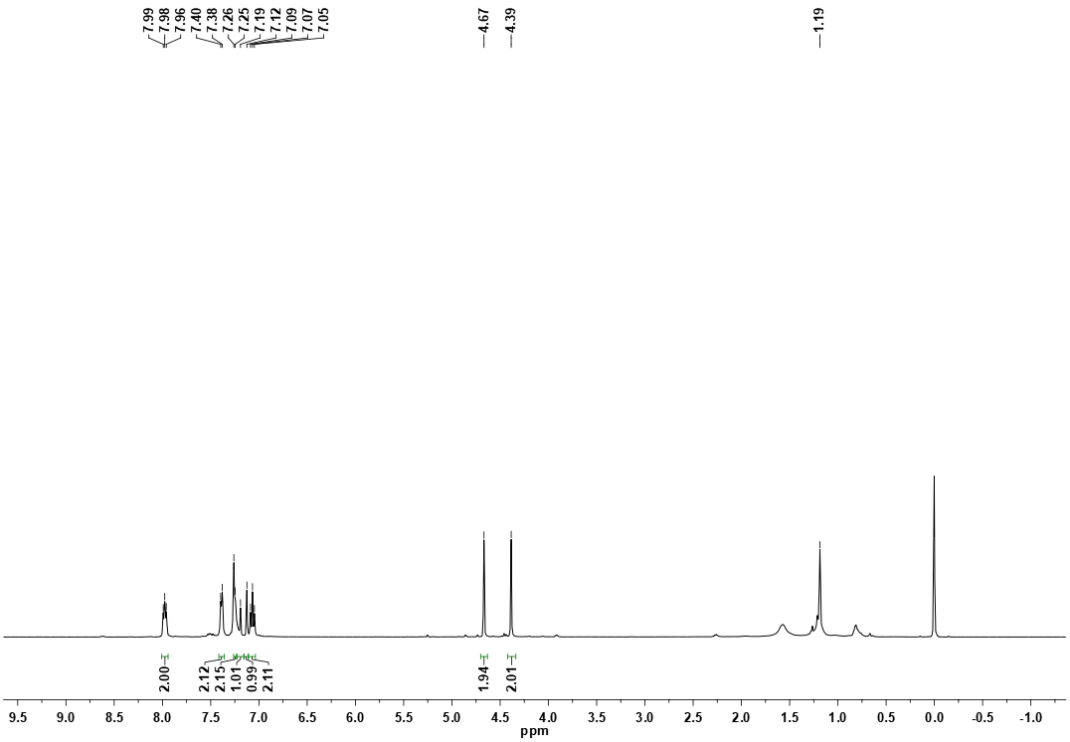


Figure S76. ^{1}H NMR spectrum of oxazole **5o** measured in $CDCl_3$.

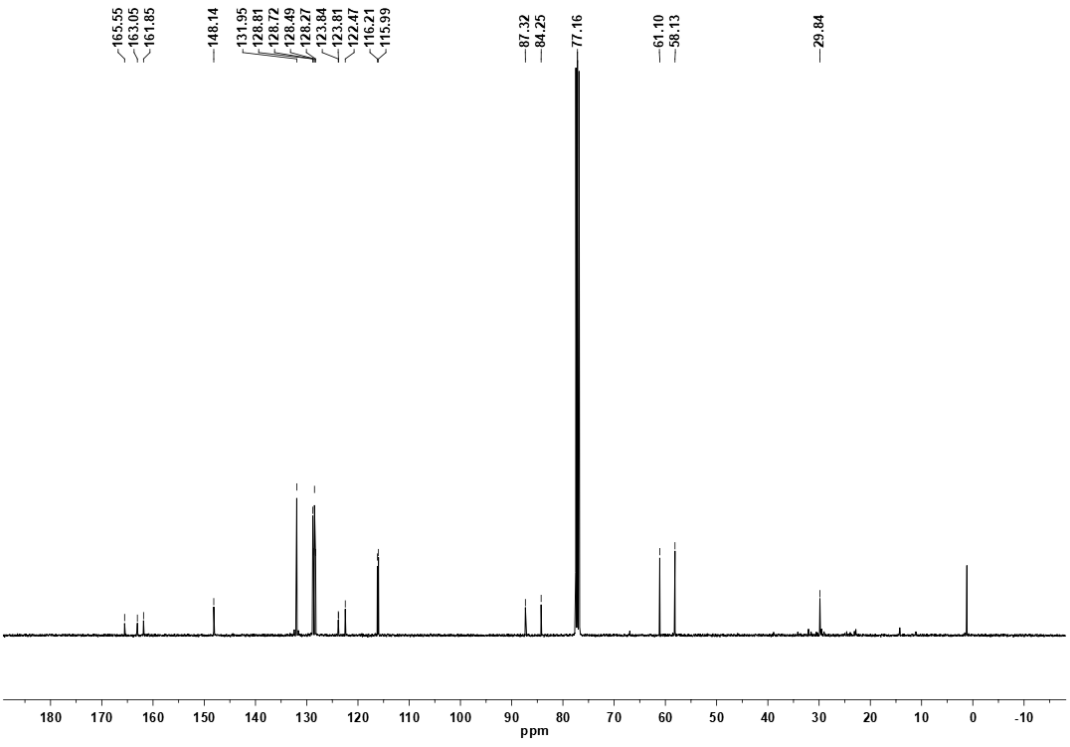


Figure S77. ^{13}C NMR spectrum of oxazole **5o** measured in $CDCl_3$.

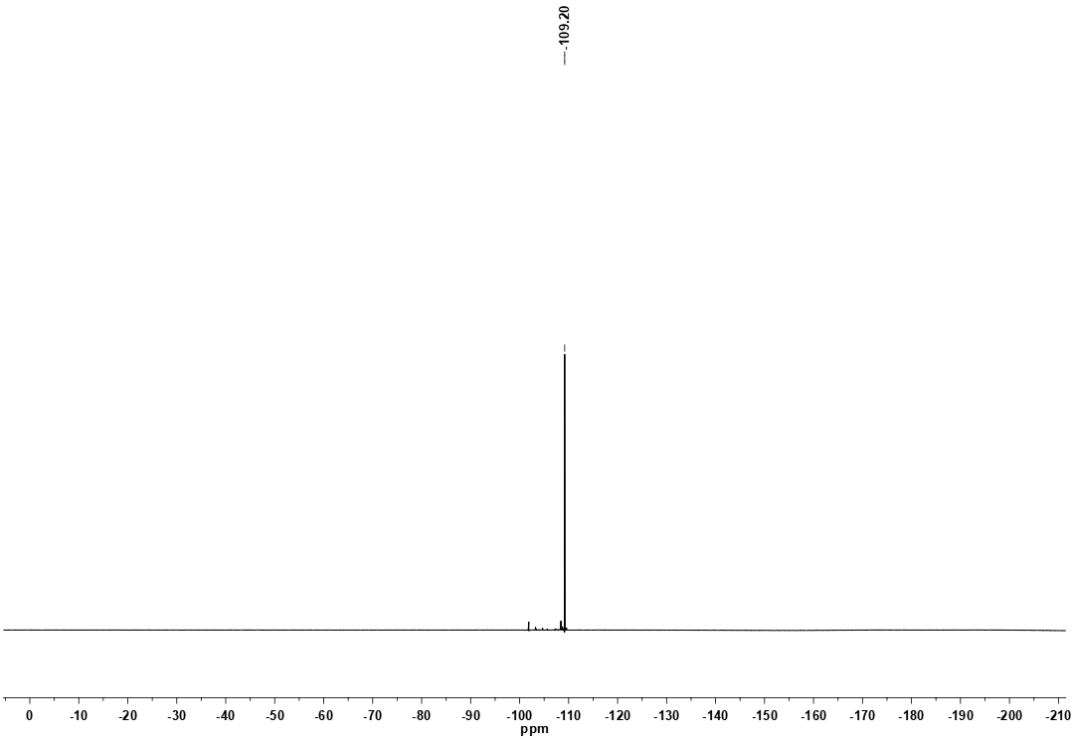


Figure S78. ^{19}F NMR spectrum of oxazole **5o** measured in $CDCl_3$.

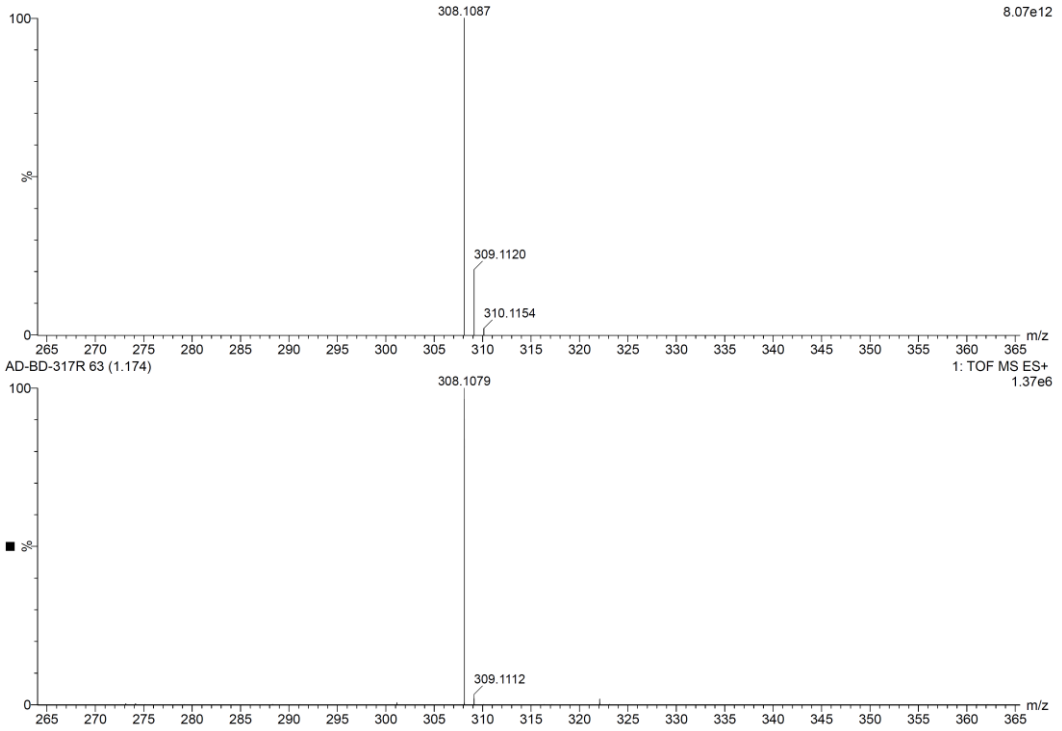


Figure S79. HRMS spectrum of oxazole **5o** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

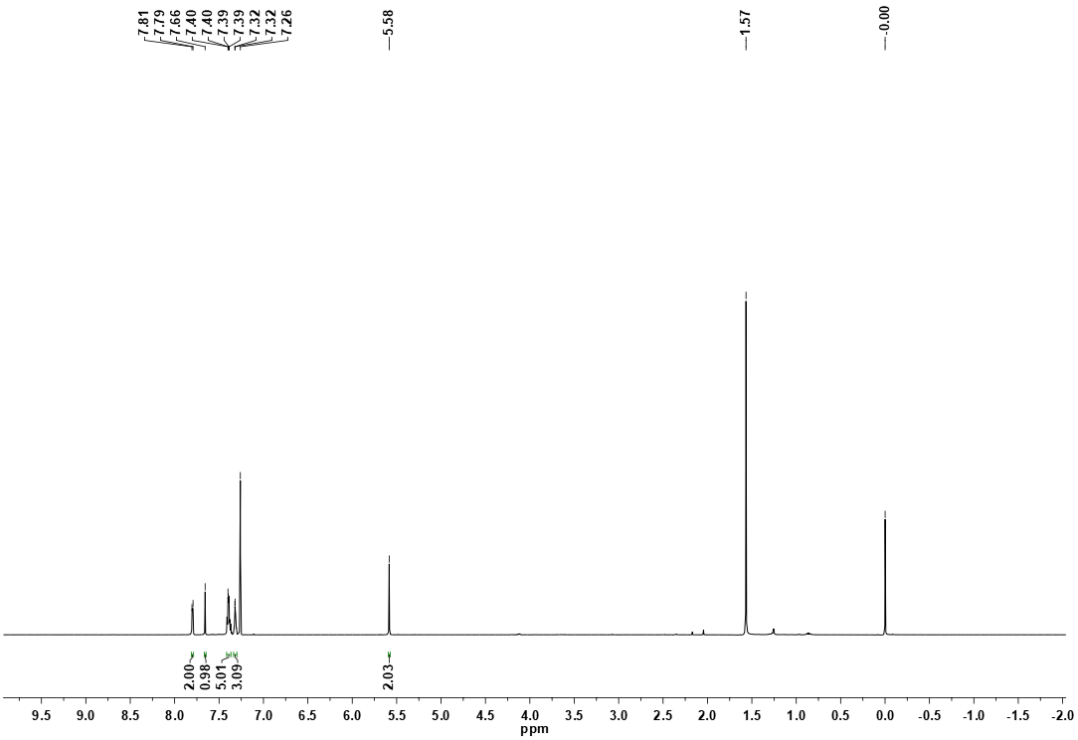


Figure S80. ^{1}H NMR spectrum of triazole **6a** measured in $CDCl_3$.

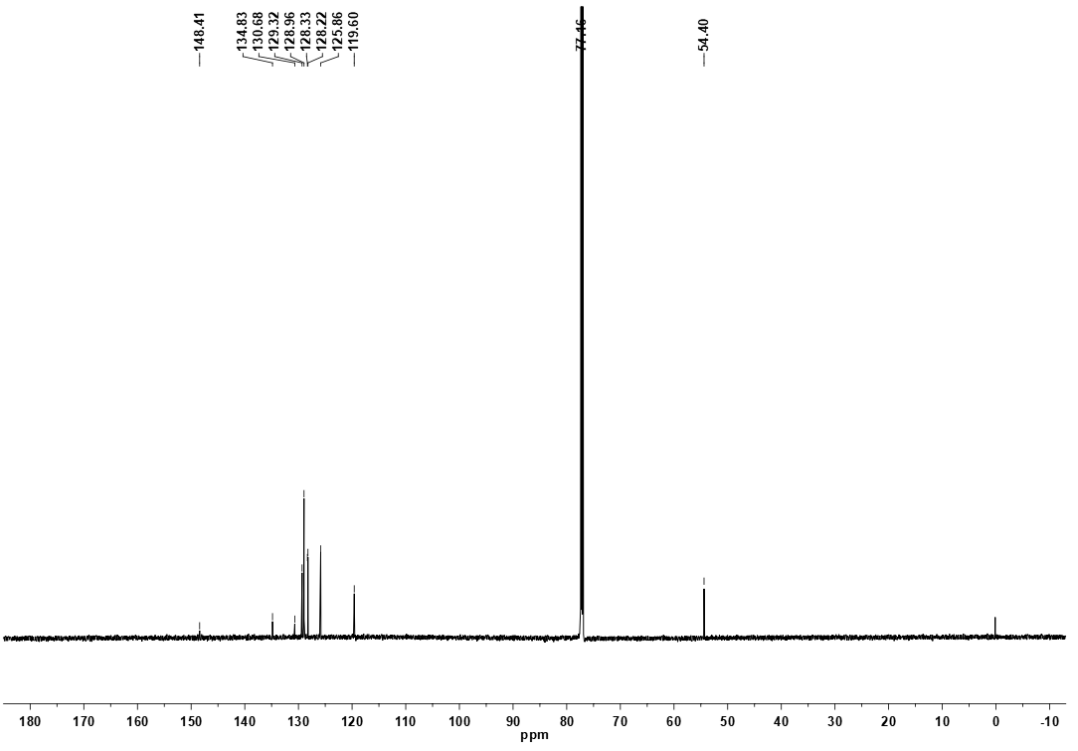


Figure S81. ^{13}C NMR spectrum of triazole **6a** measured in $CDCl_3$.

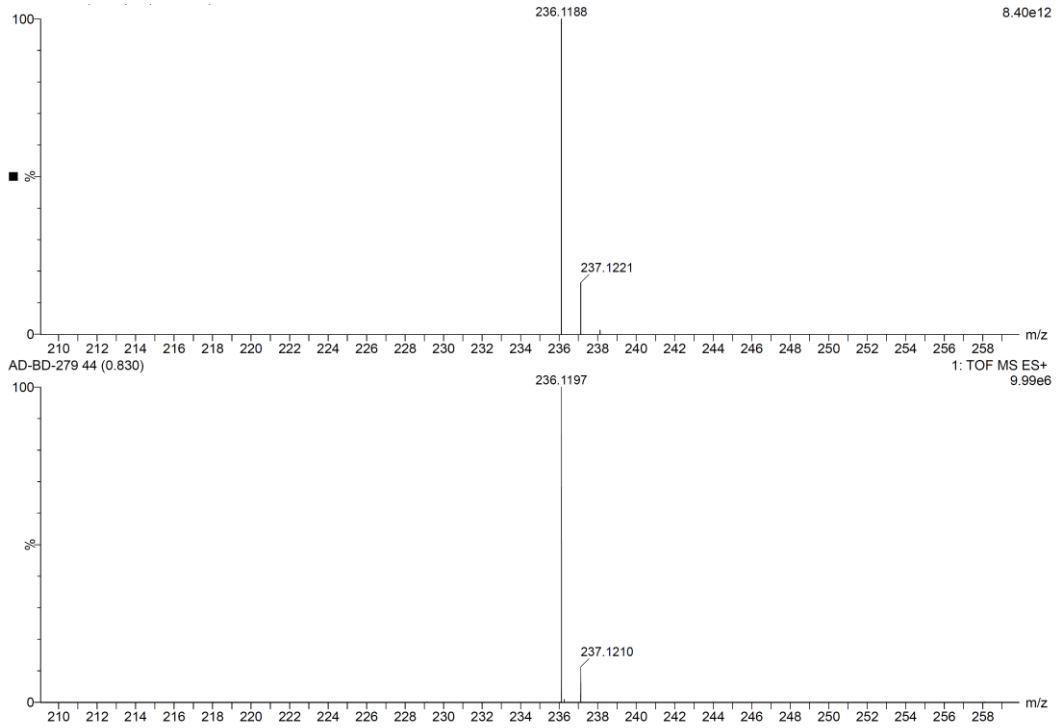


Figure S82. HRMS spectrum of triazole **6a** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

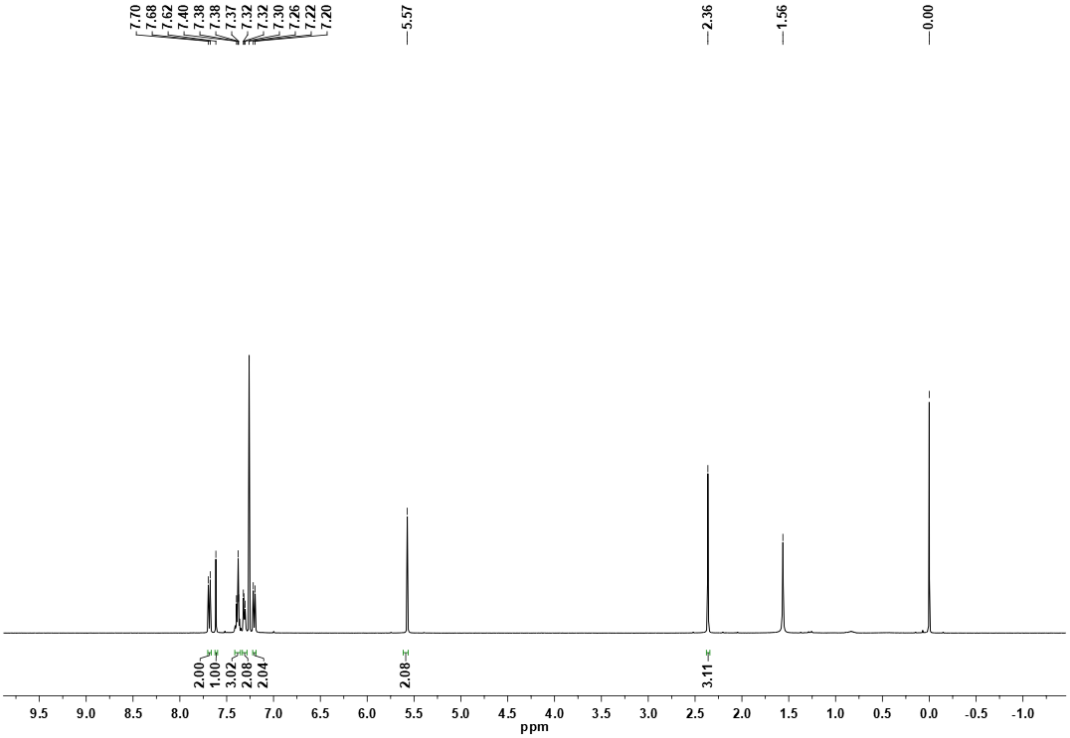


Figure S83. ^{1}H NMR spectrum of triazole **6b** measured in $CDCl_3$.

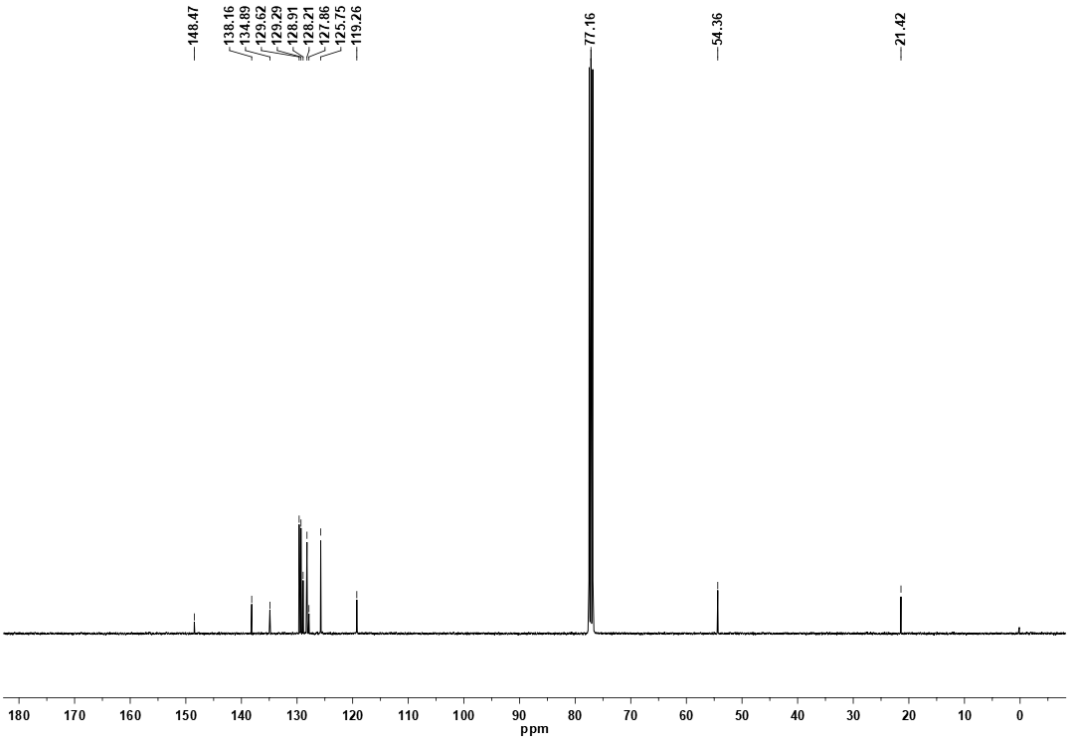


Figure S84. ^{13}C NMR spectrum of triazole **6b** measured in $CDCl_3$.

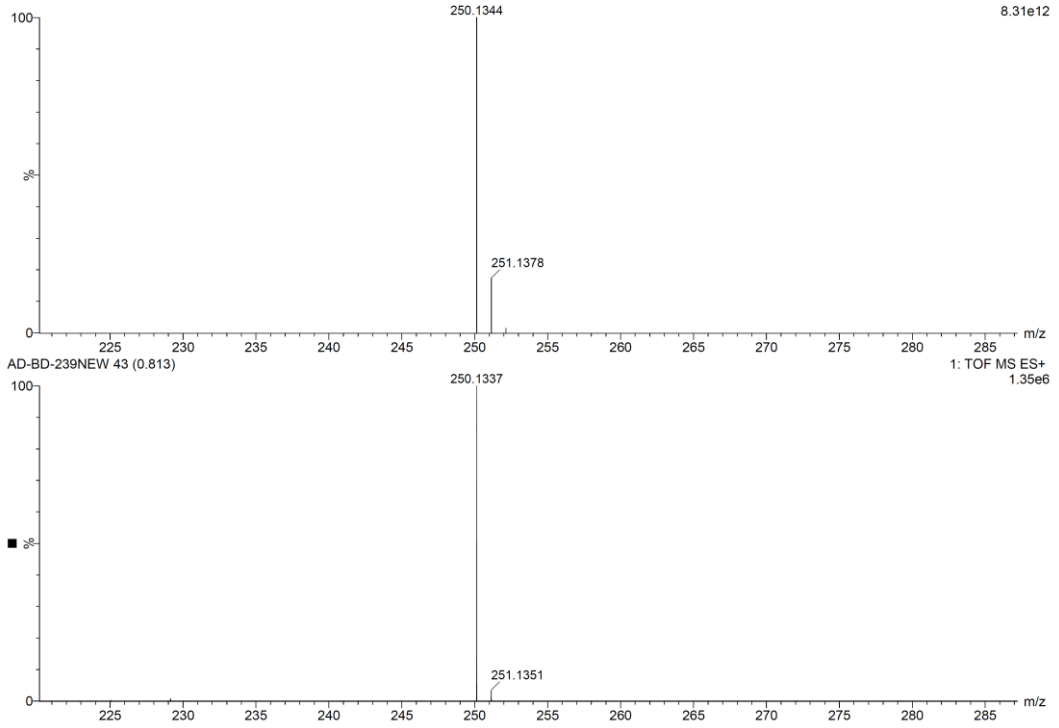


Figure S85. HRMS spectrum of triazole **6b** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

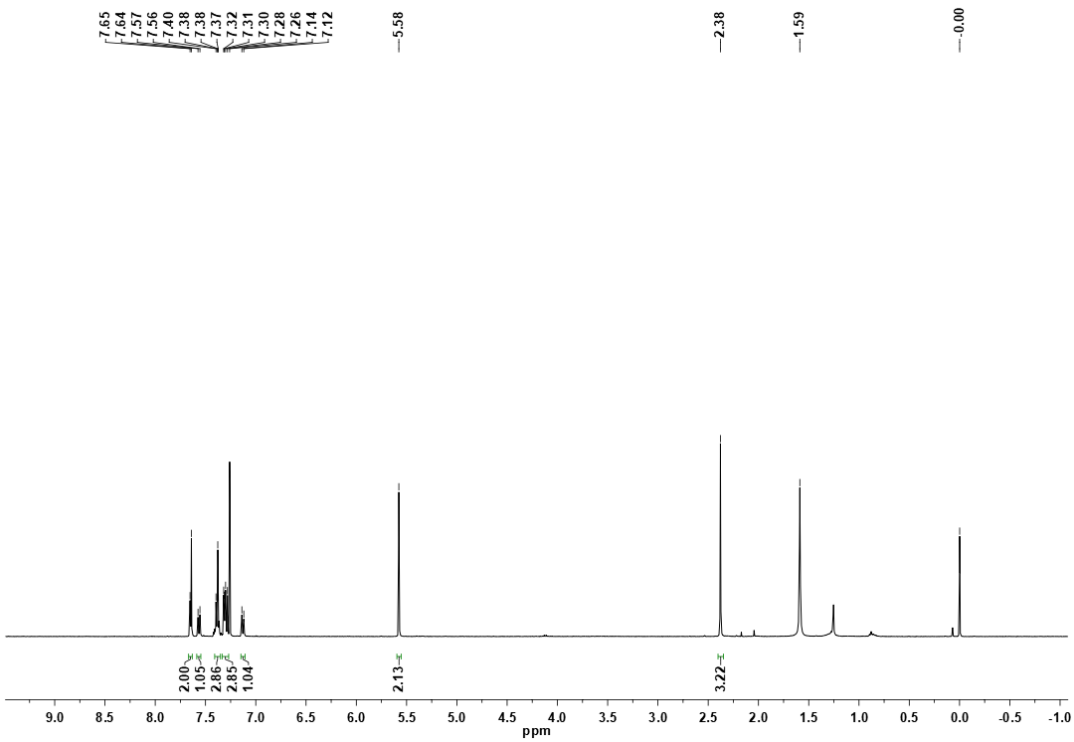


Figure S86. ^{1}H NMR spectrum of triazole **6c** measured in $CDCl_3$.

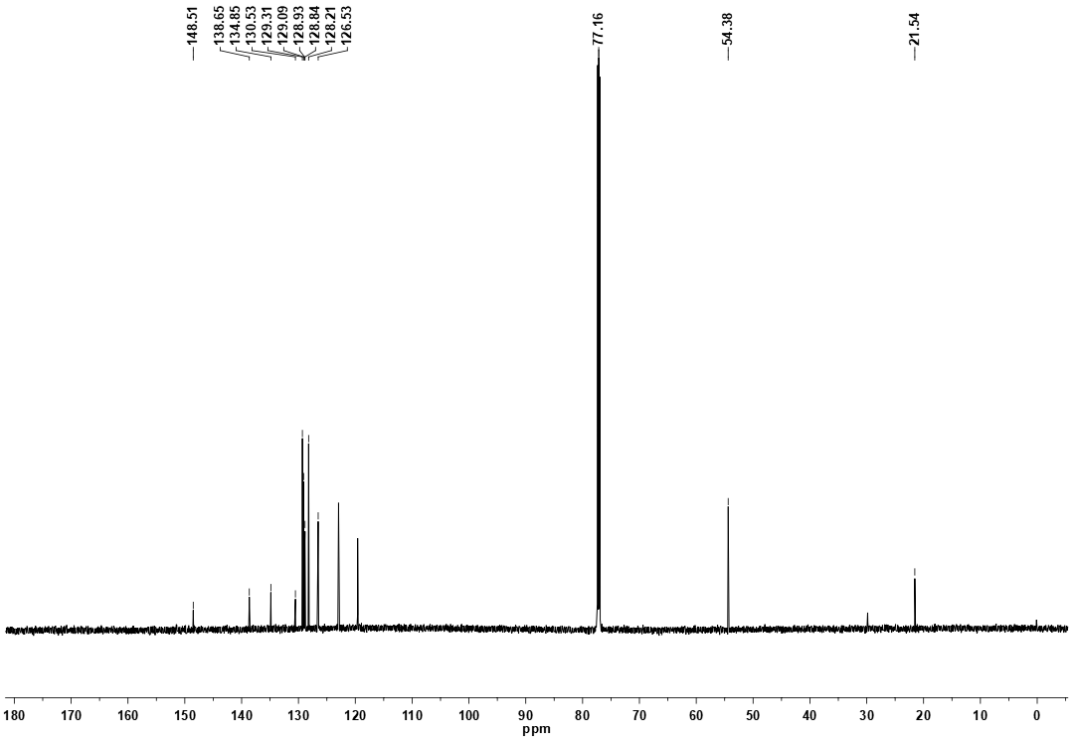


Figure S87. ^{13}C NMR spectrum of triazole **6c** measured in $CDCl_3$.

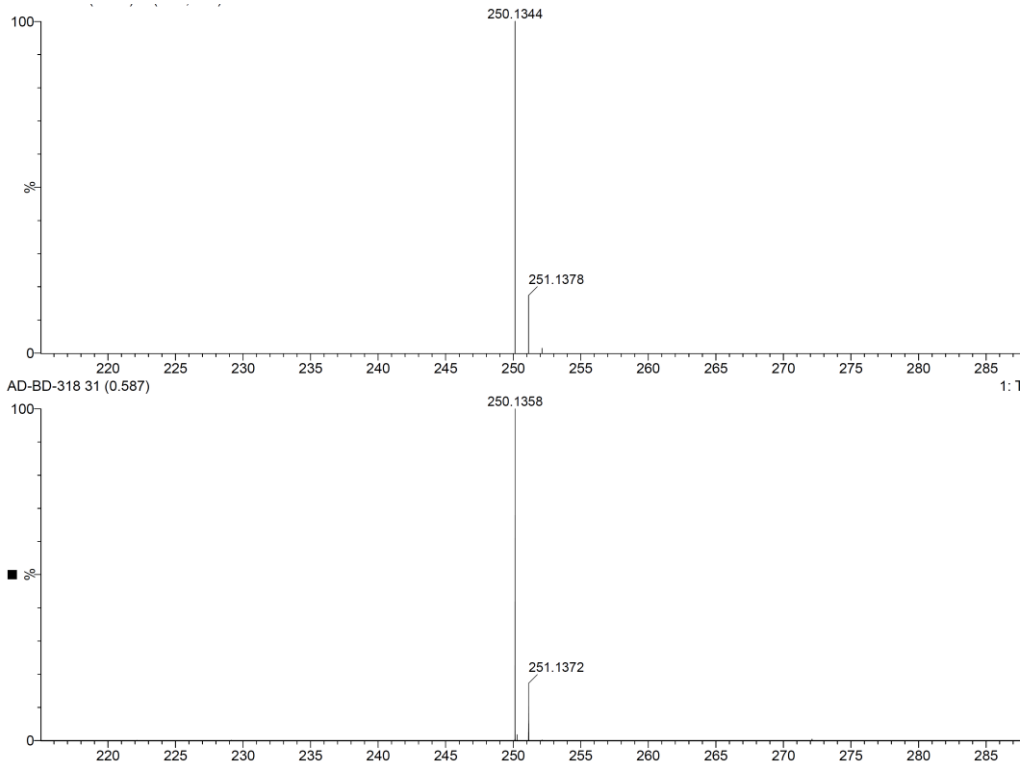


Figure S88. HRMS spectrum of triazole **6c** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

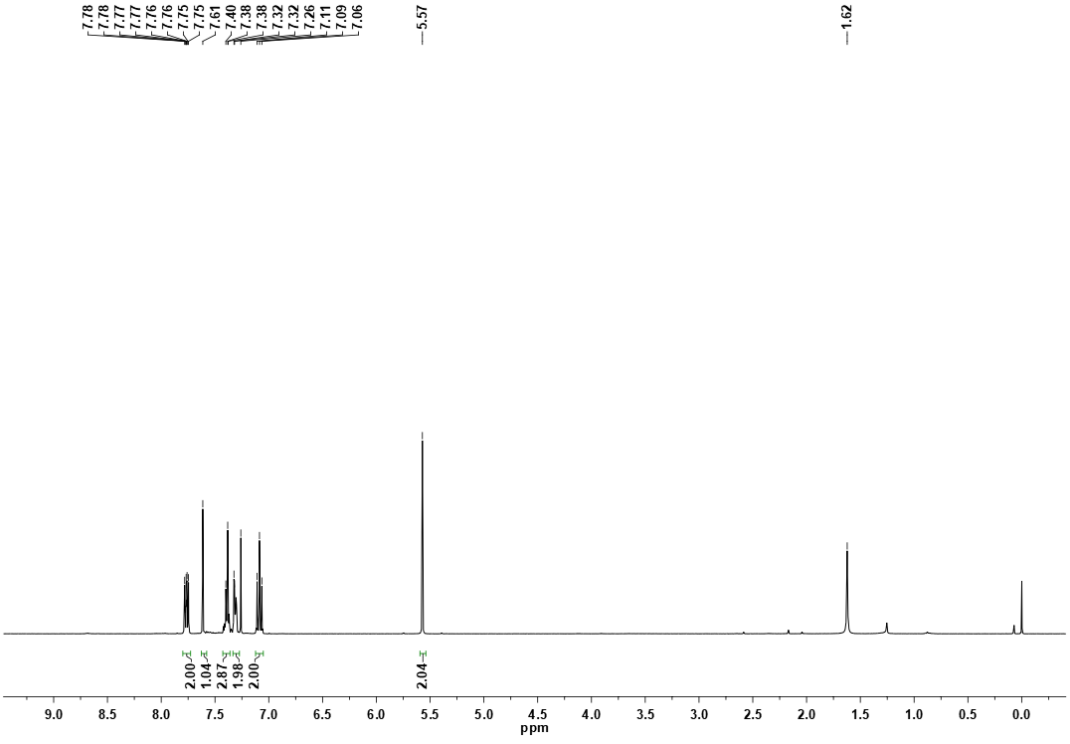


Figure S89. ^{1}H NMR spectrum of triazole **6d** measured in $CDCl_3$.

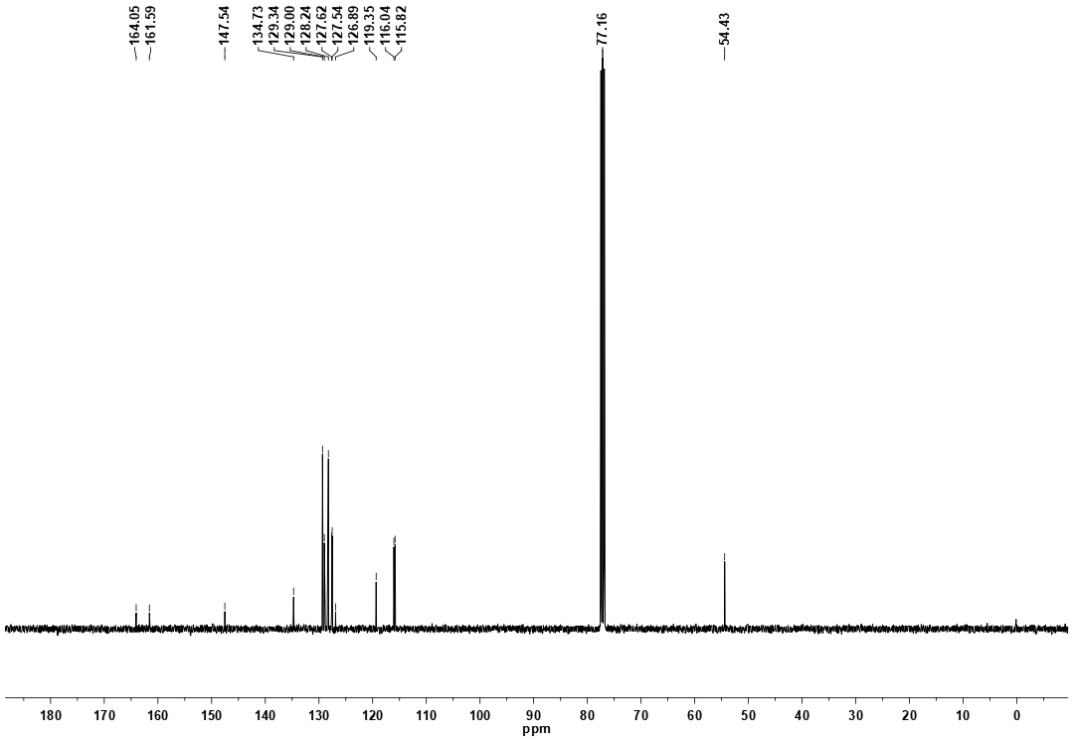


Figure S90. ^{13}C NMR spectrum of triazole **6d** measured in $CDCl_3$.

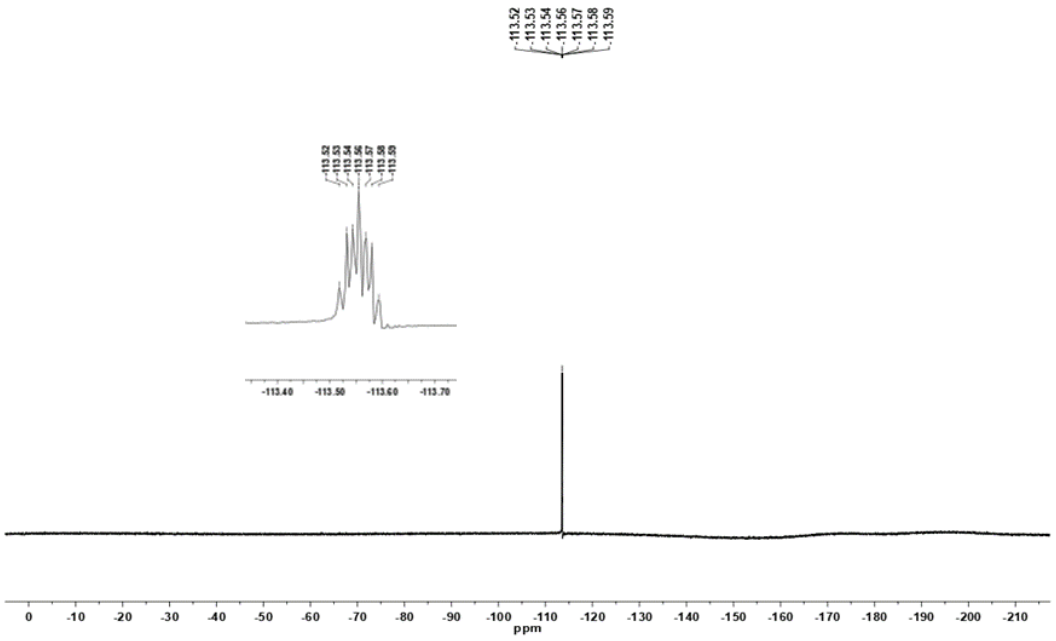


Figure S91. ^{19}F NMR spectrum of triazole **6d** measured in $CDCl_3$.

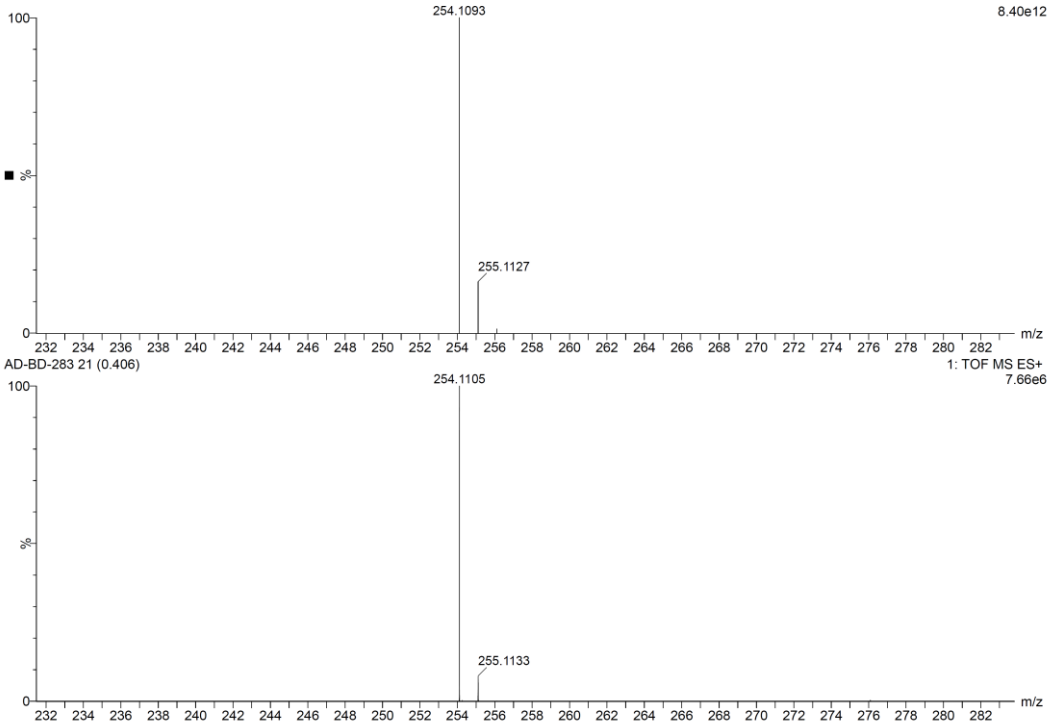


Figure S92. HRMS spectrum of triazole **6d** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

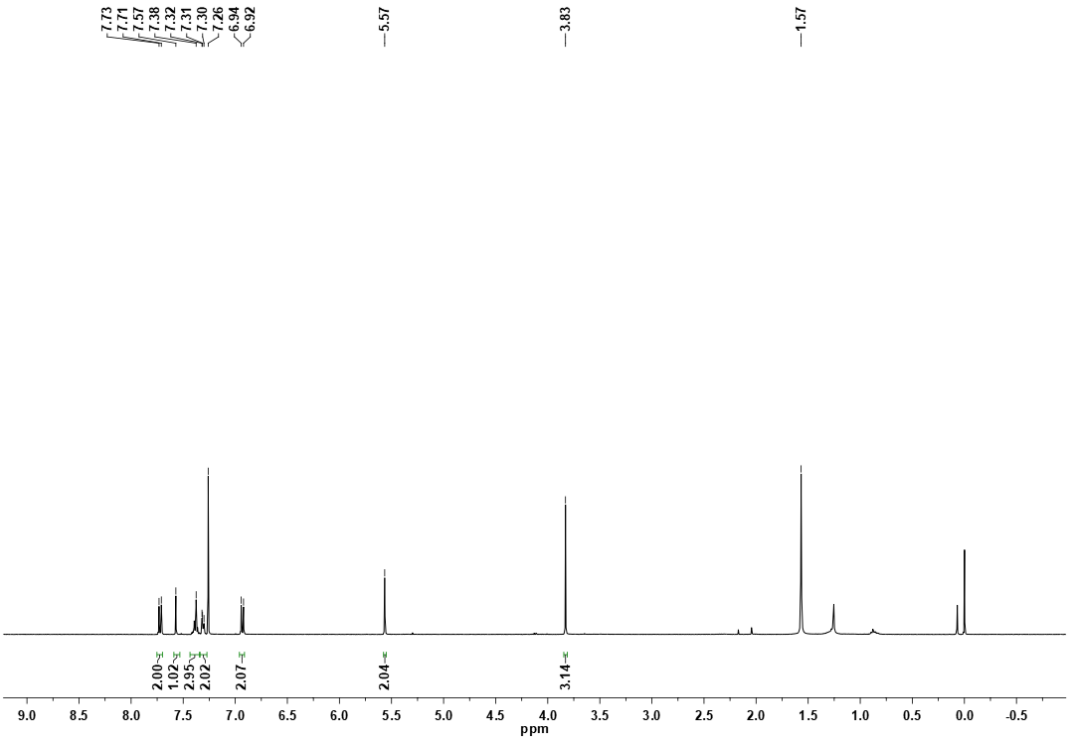


Figure S93. ^{1}H NMR spectrum of triazole **6e** measured in $CDCl_3$.

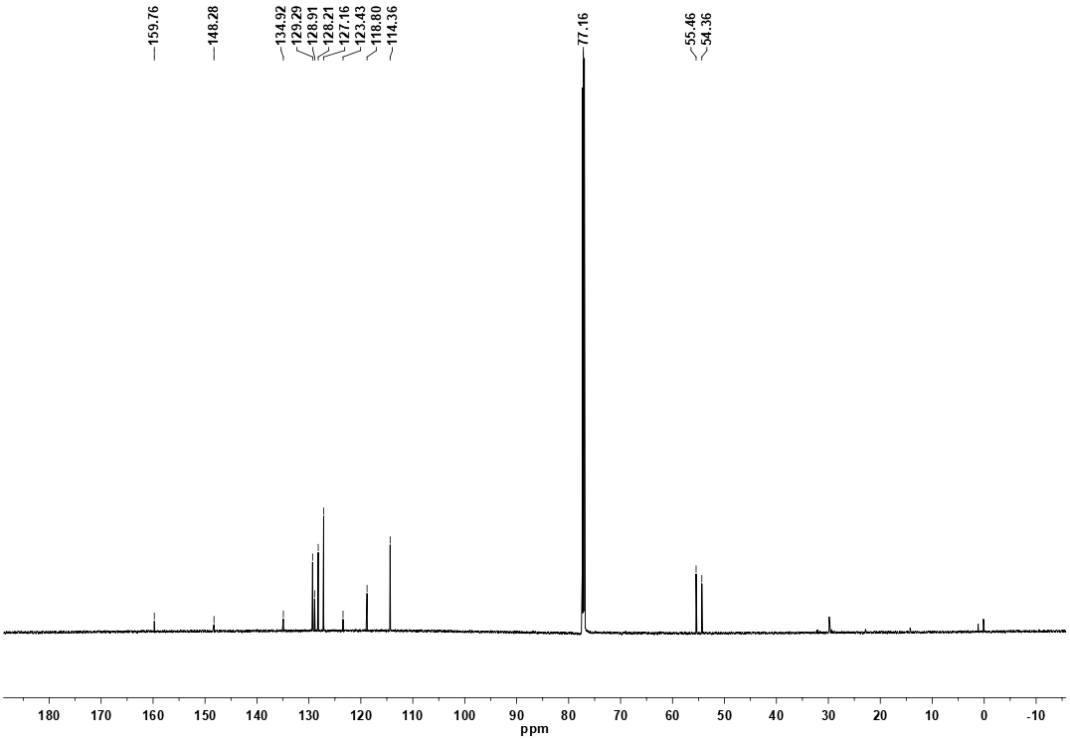


Figure S94. ^{13}C NMR spectrum of triazole **6e** measured in $CDCl_3$.

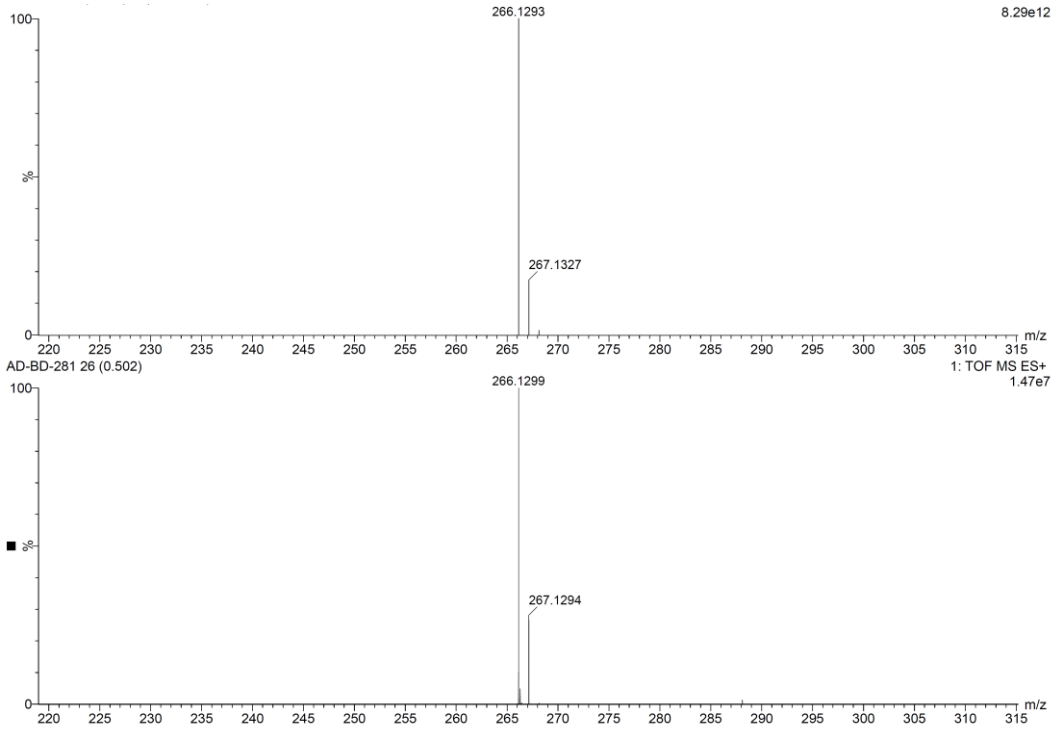


Figure S95. HRMS spectrum of triazole **6e** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

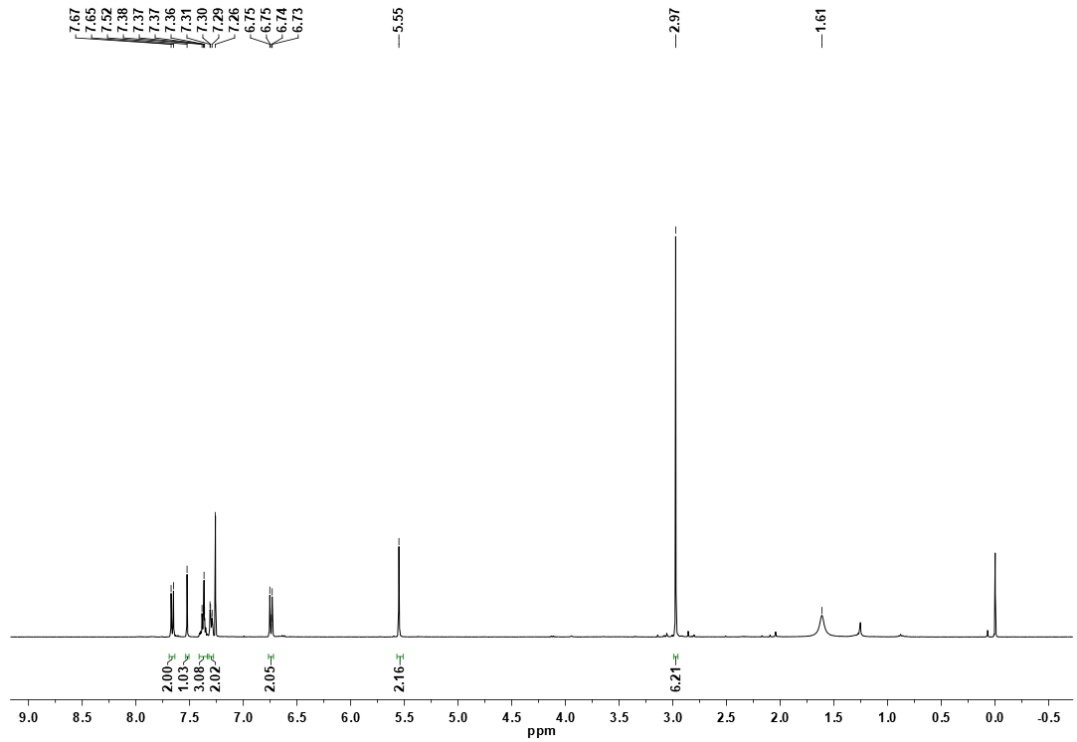


Figure S96. ^{1}H NMR spectrum of triazole **6f** measured in $CDCl_3$.

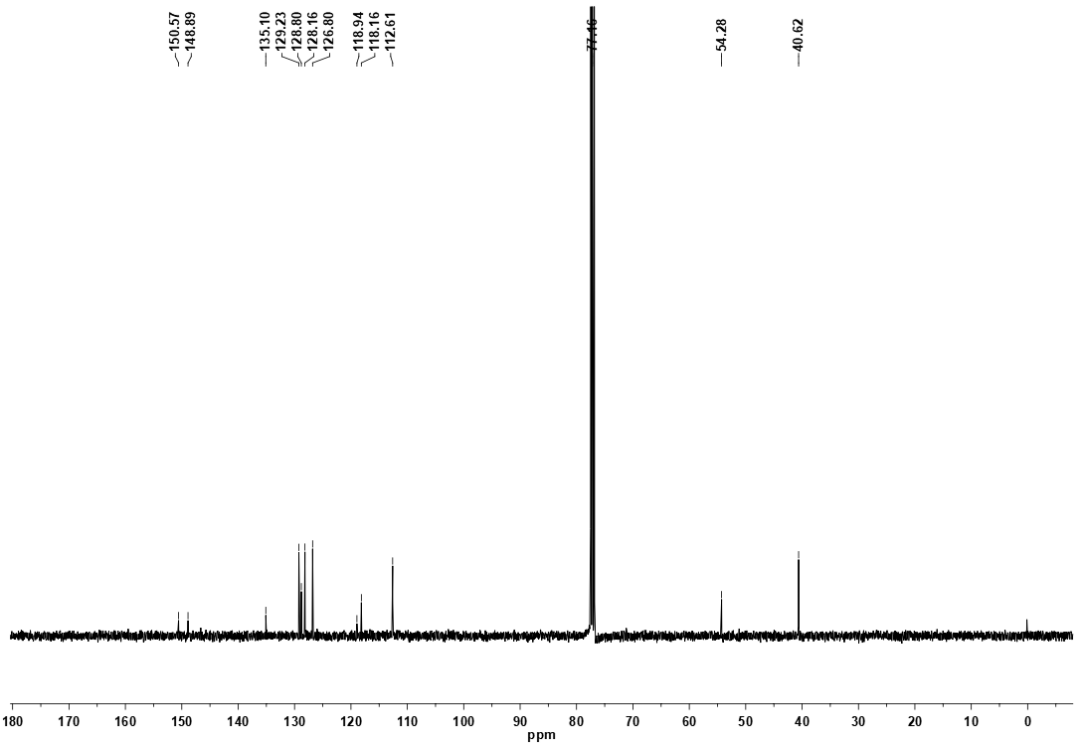


Figure S97. ^{13}C NMR spectrum of triazole **6f** measured in $CDCl_3$.

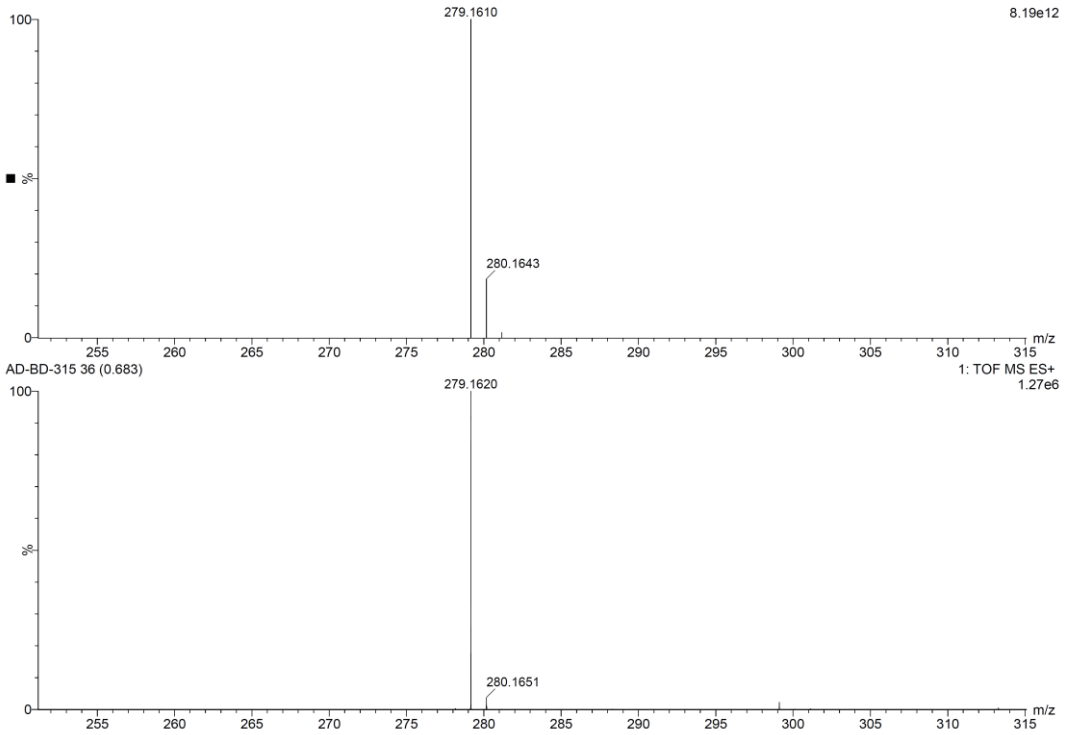


Figure S98. HRMS spectrum of triazole **6f** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

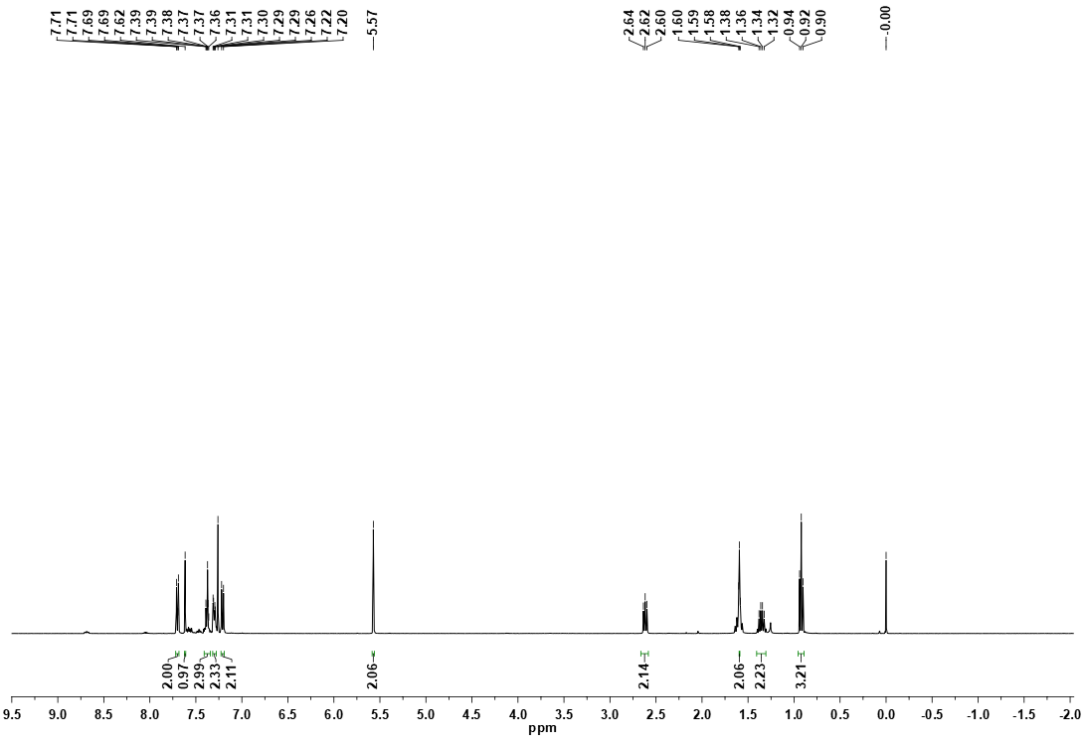


Figure S99. ^{1}H NMR spectrum of triazole **6g** measured in $CDCl_3$.

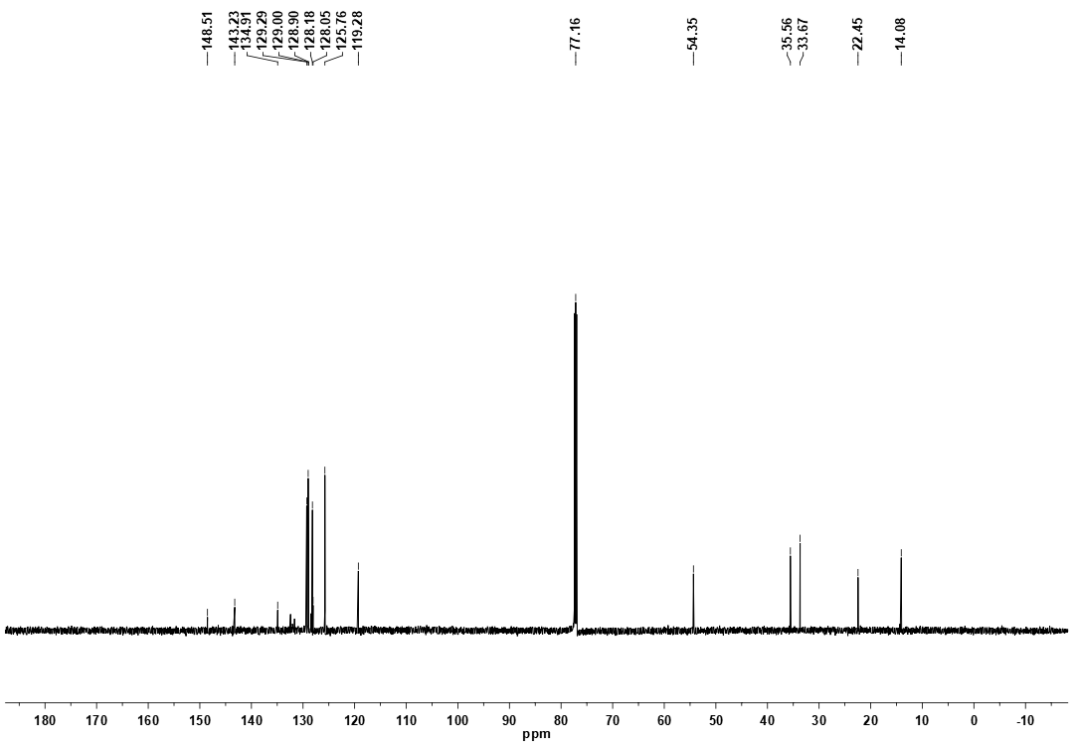


Figure S100. ^{13}C NMR spectrum of triazole **6g** measured in $CDCl_3$.

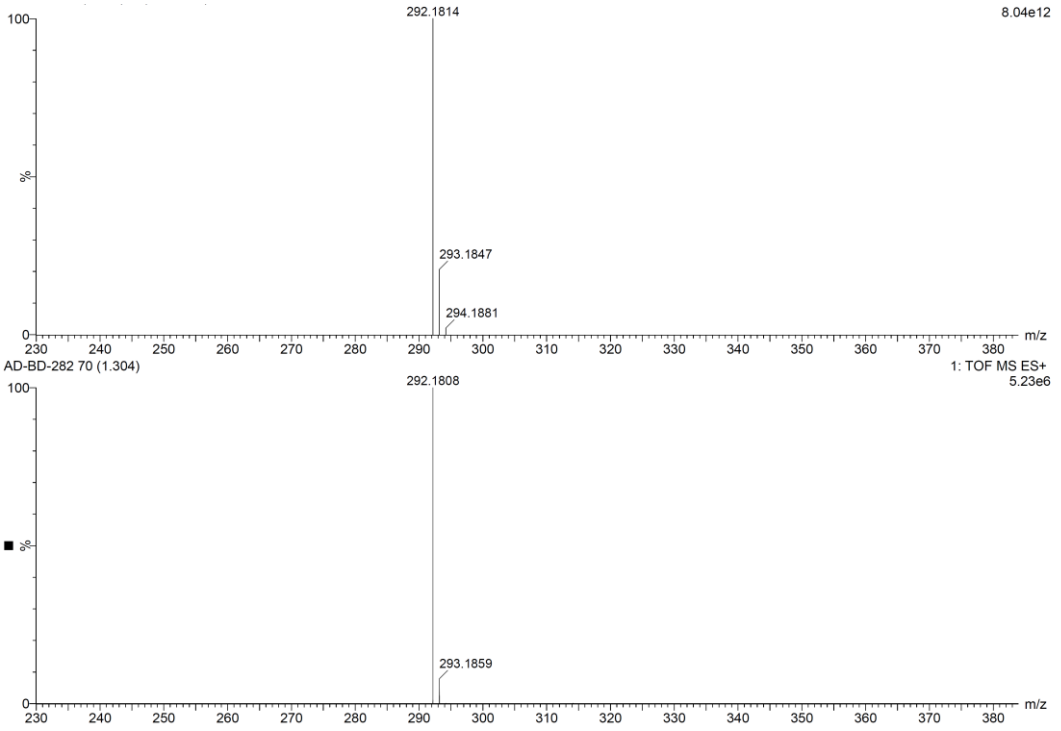


Figure S101. HRMS spectrum of triazole **6g** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

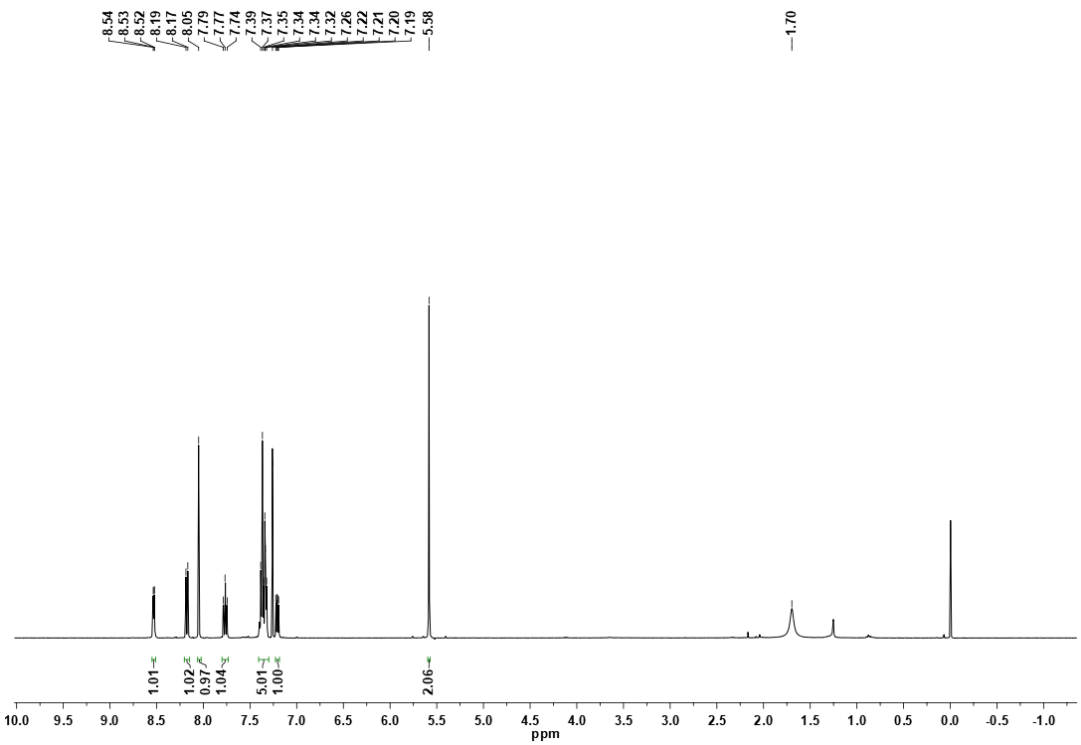


Figure S102. ^{1}H NMR spectrum of triazole **6h** measured in $CDCl_3$.

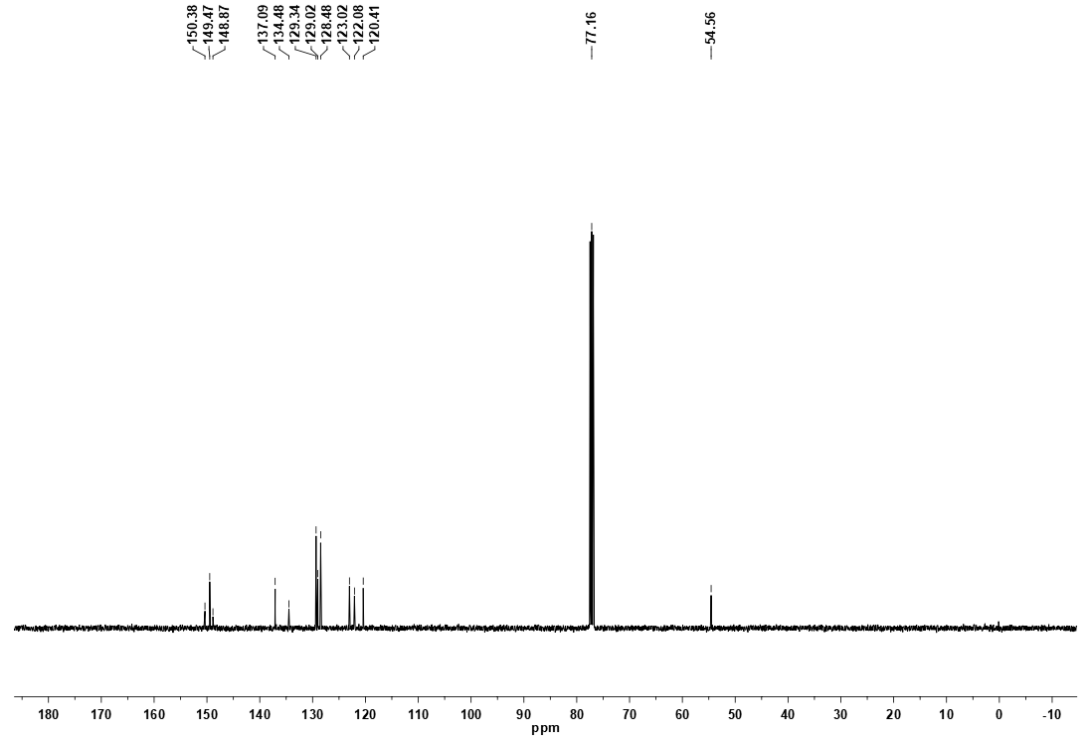


Figure S103. ^{13}C NMR spectrum of triazole **6h** measured in $CDCl_3$.

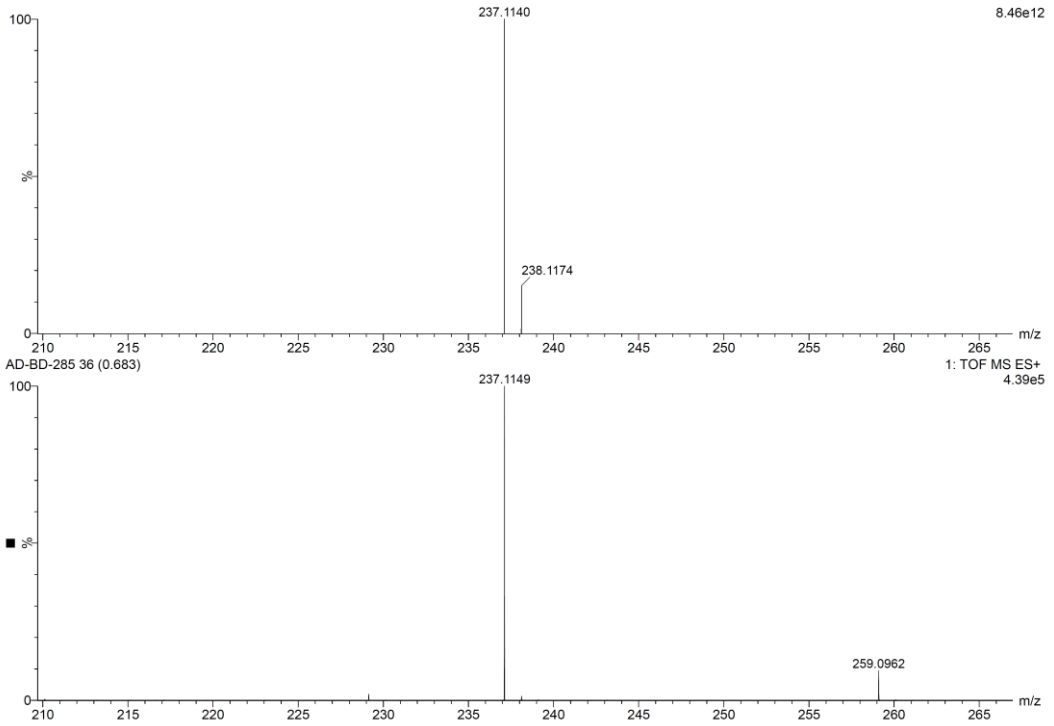


Figure S104. HRMS spectrum of triazole **6h** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

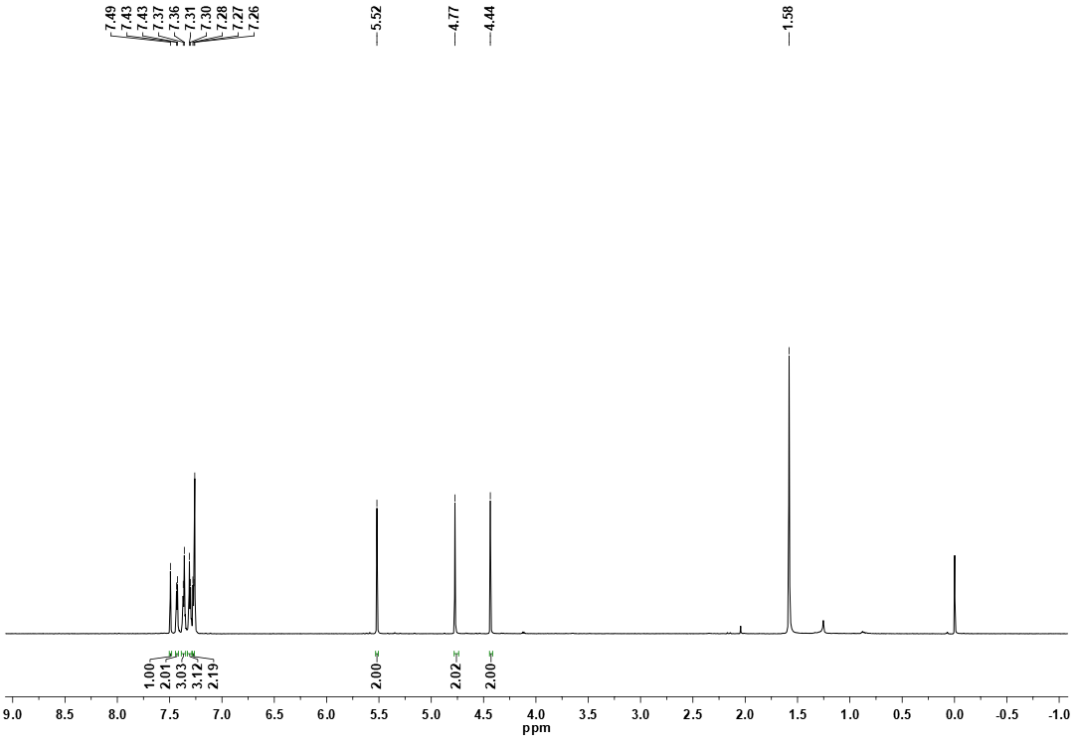


Figure S105. ^{1}H NMR spectrum of triazole **6i** measured in $CDCl_3$.

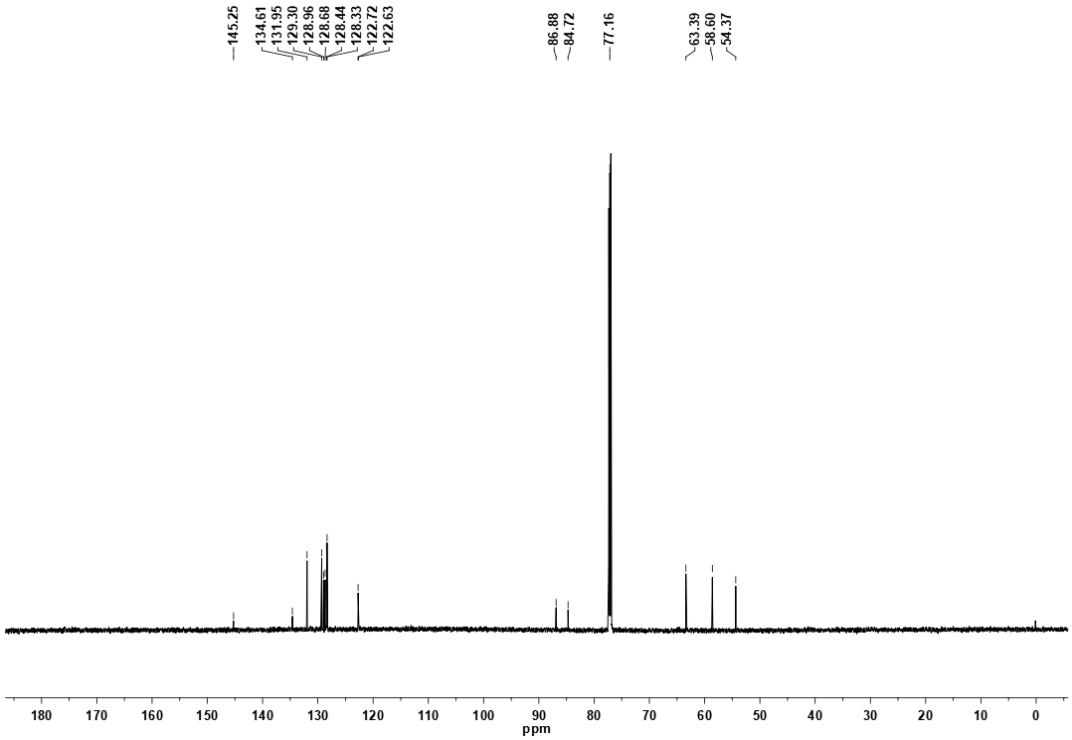


Figure S106. ^{13}C NMR spectrum of triazole **6i** measured in $CDCl_3$.

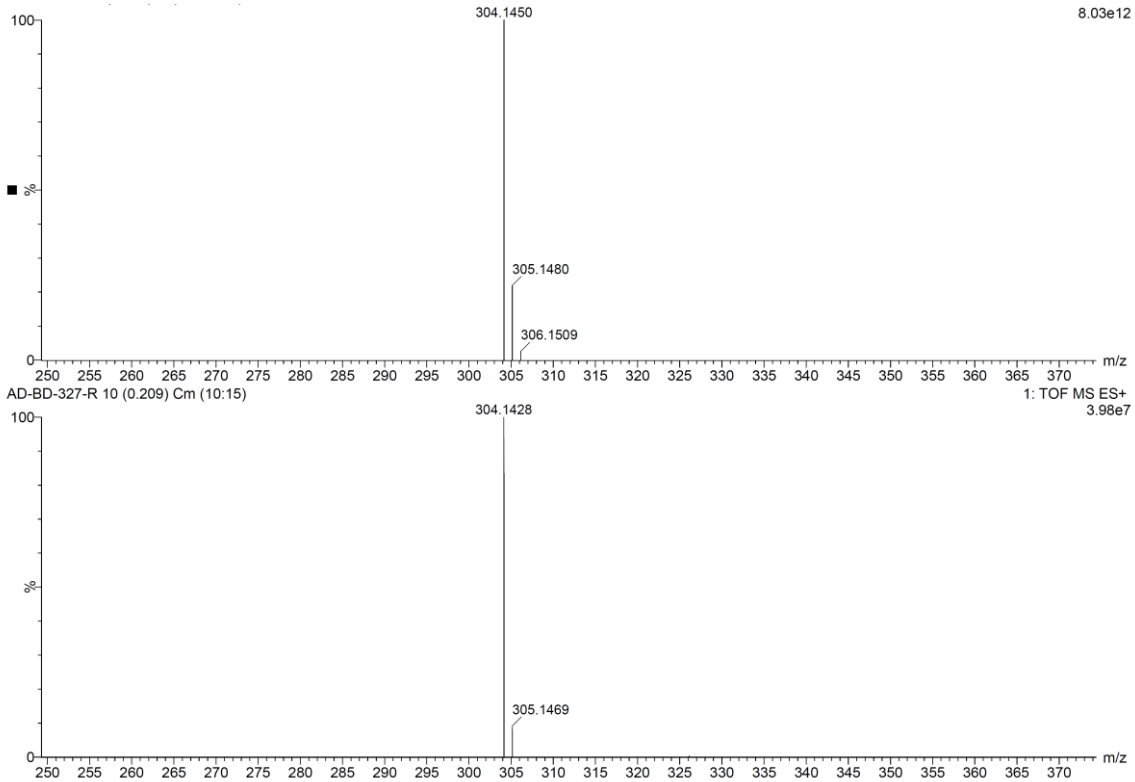


Figure S107. HRMS spectrum of triazole **6i** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

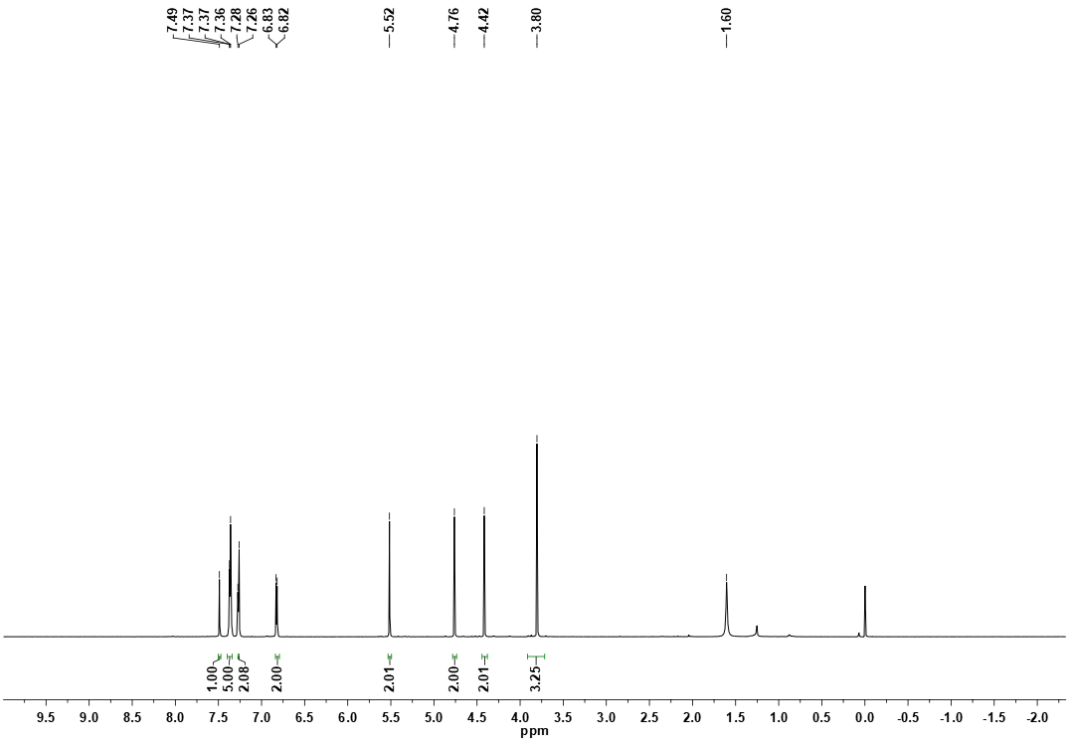


Figure S108. ^{1}H NMR spectrum of triazole **6j** measured in $CDCl_3$.

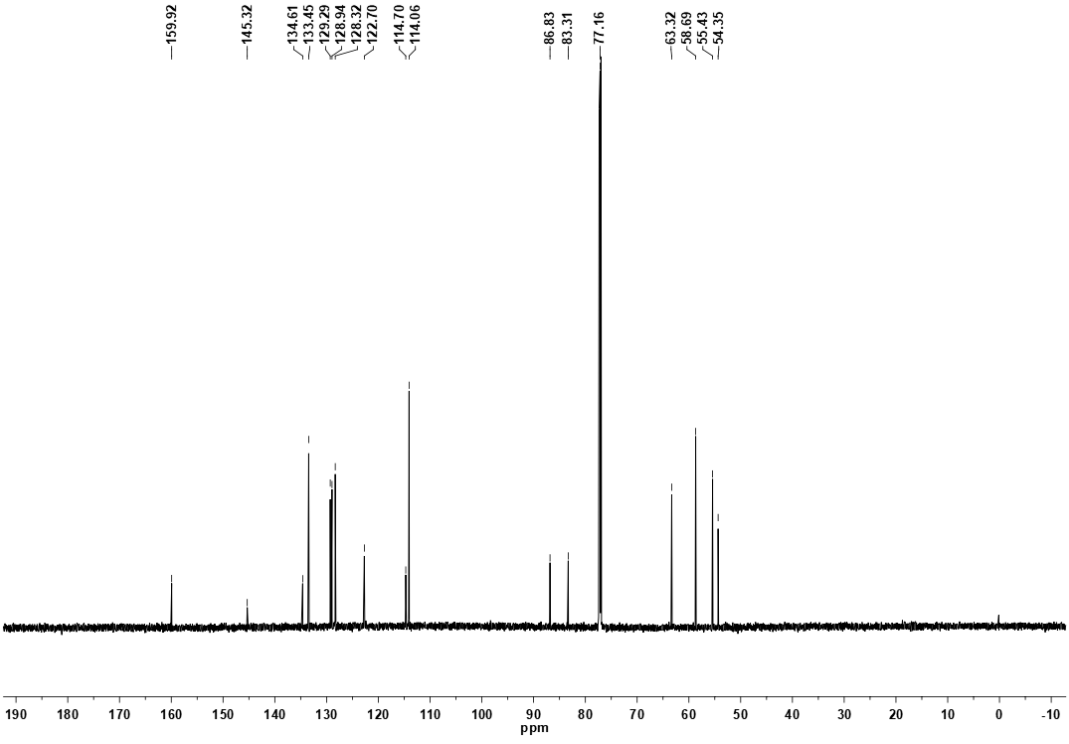


Figure S109. ^{13}C NMR spectrum of triazole **6j** measured in $CDCl_3$.

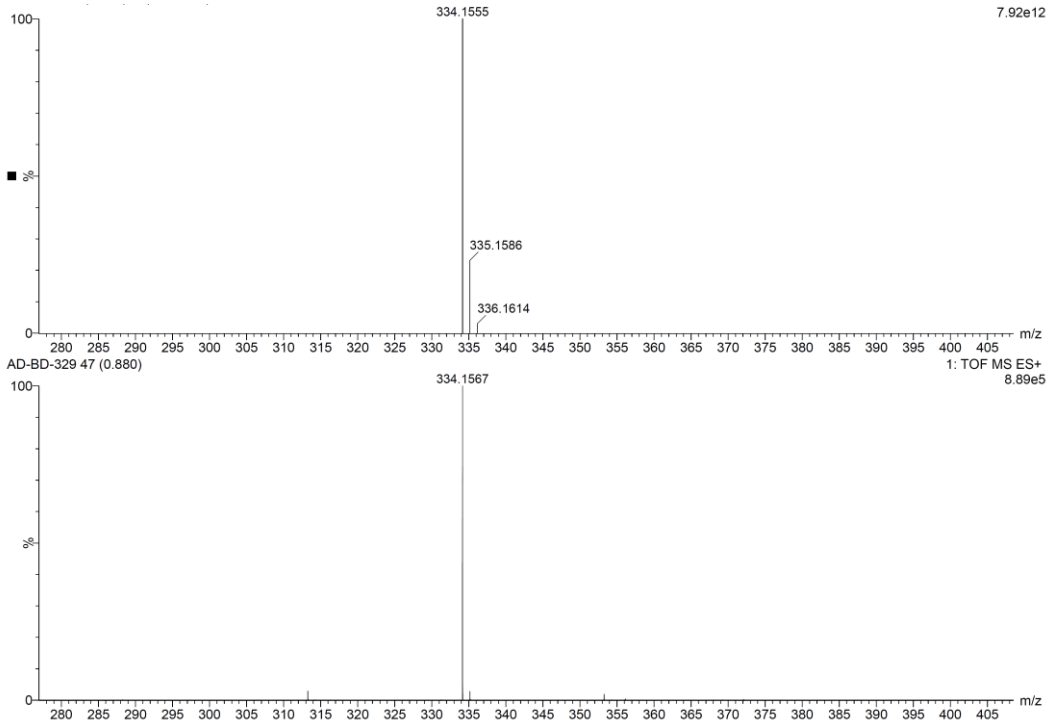


Figure S110. HRMS spectrum of triazole **6j** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

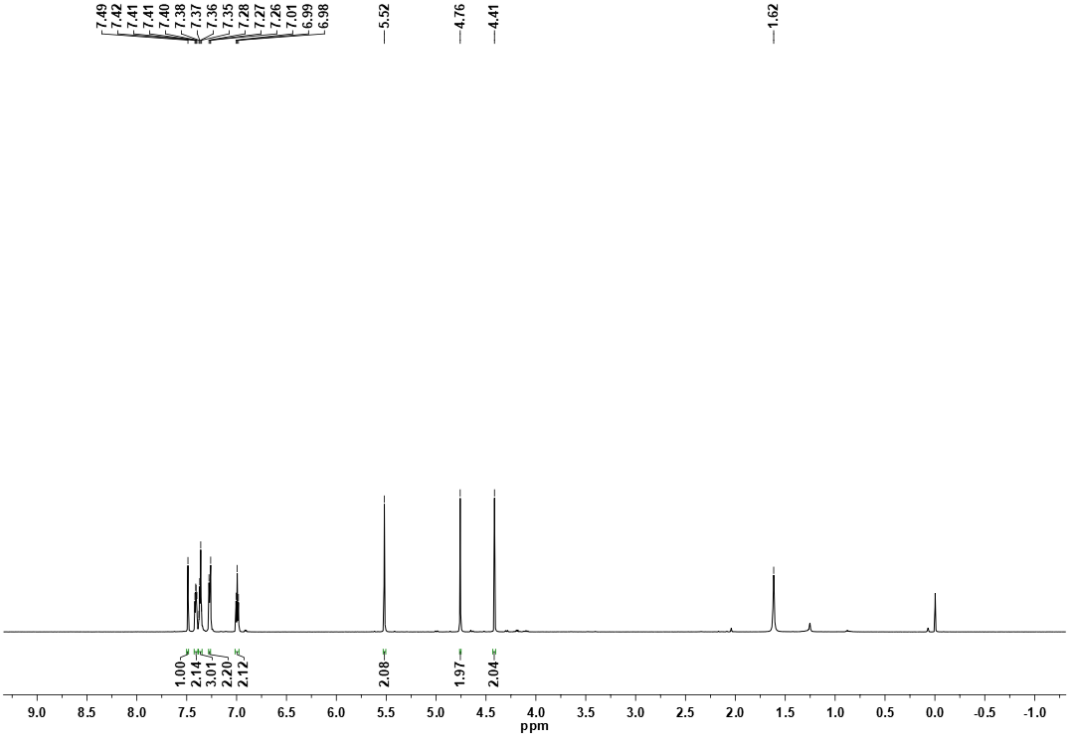


Figure S111. ^{1}H NMR spectrum of triazole **6k** measured in $CDCl_3$.

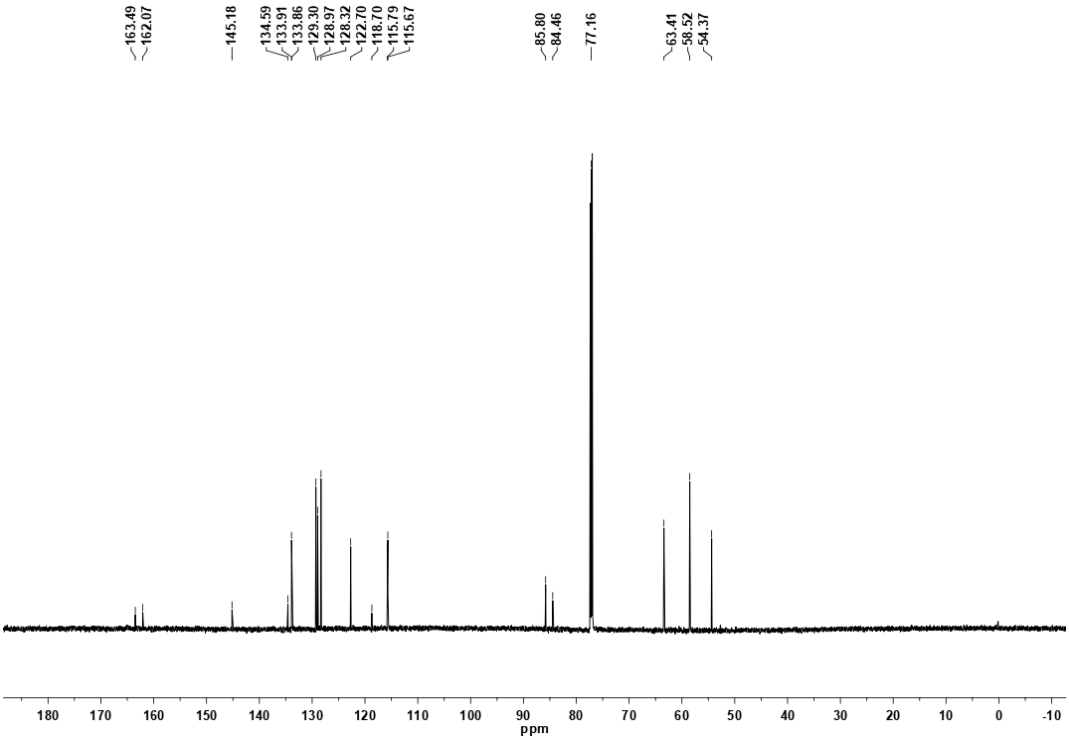


Figure S112. ^{13}C NMR spectrum of triazole **6k** measured in $CDCl_3$.

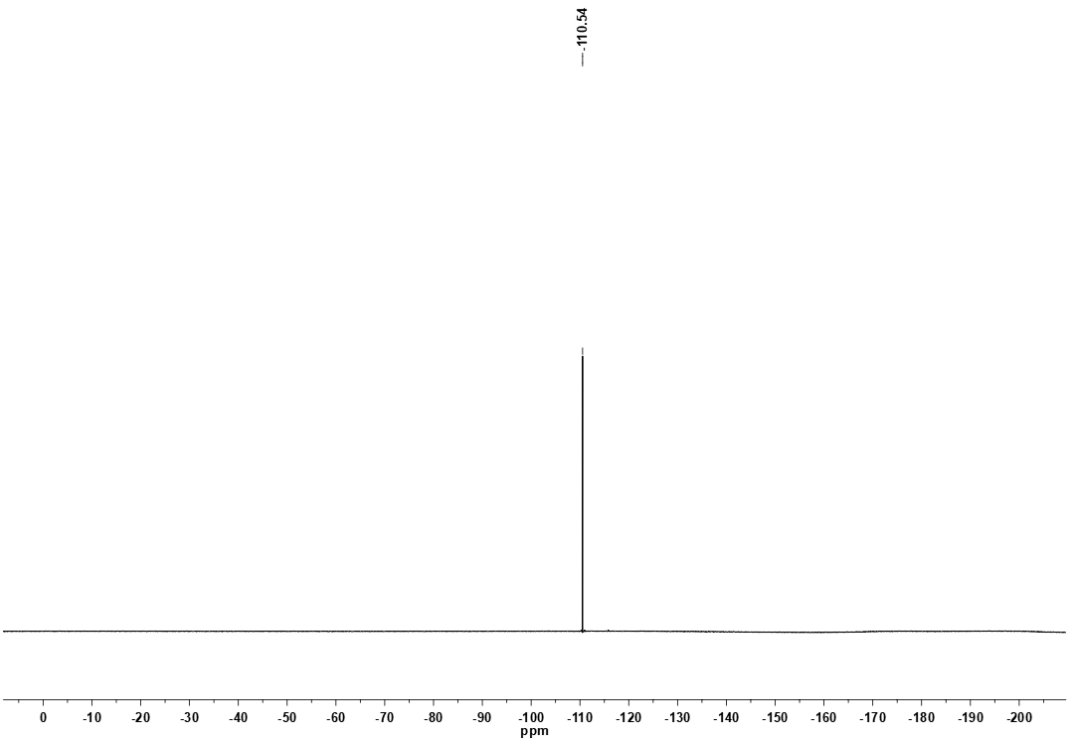


Figure S113. ^{19}F NMR spectrum of triazole **6k** measured in $CDCl_3$.

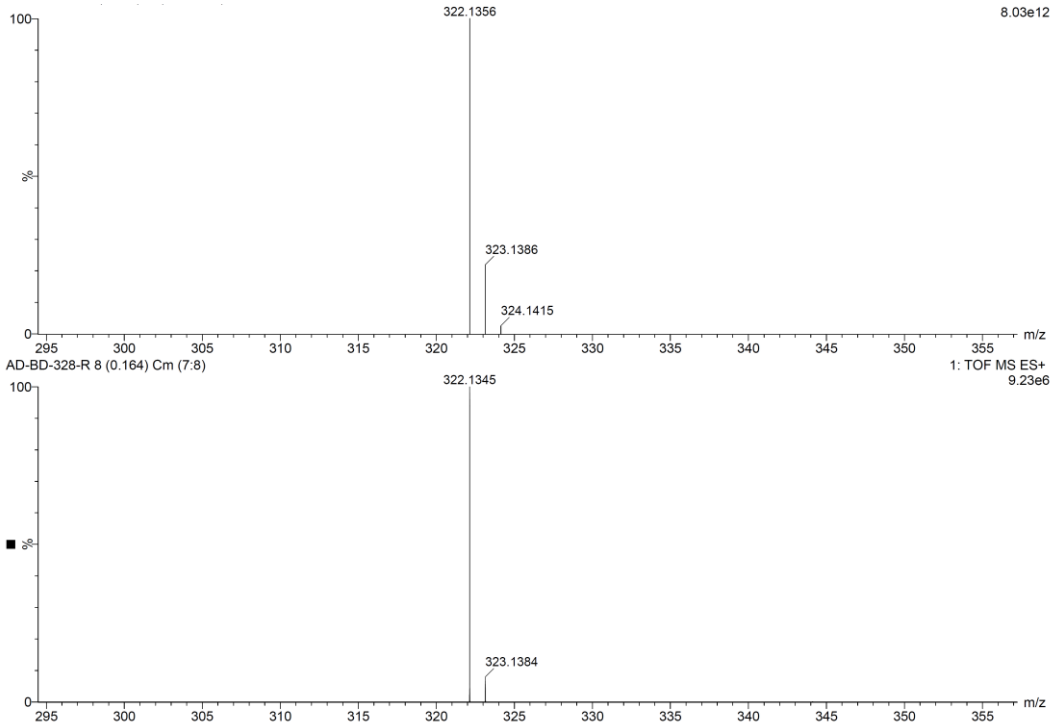


Figure S114. HRMS spectrum of triazole **6k** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

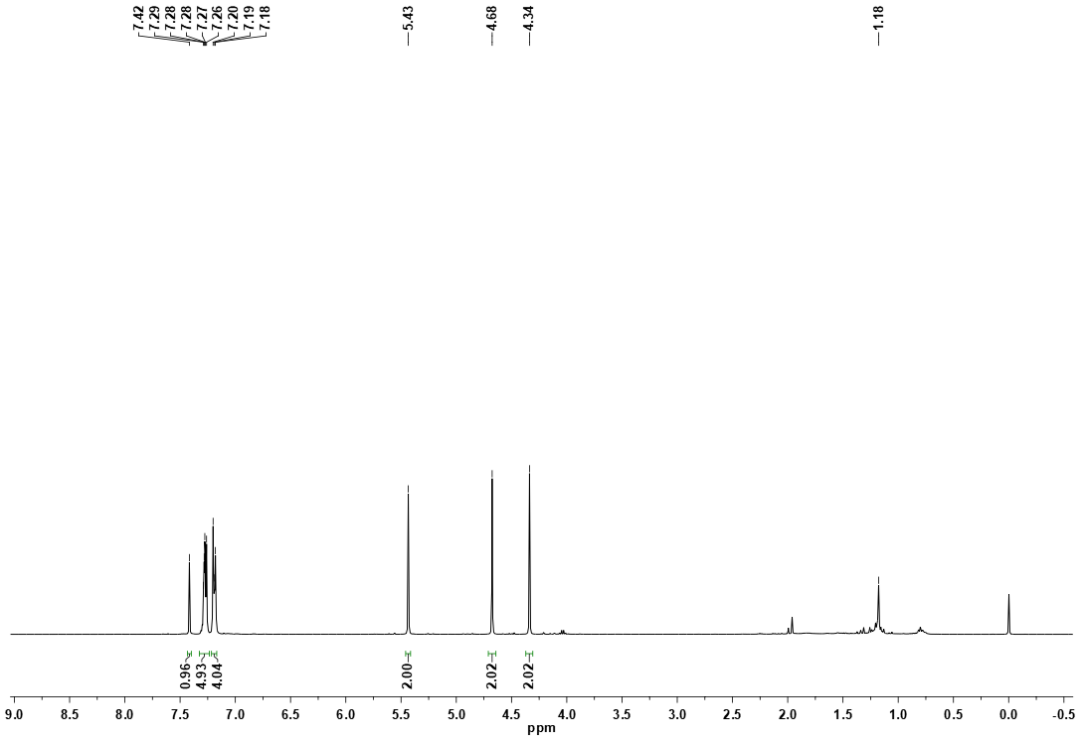


Figure S115. ^{1}H NMR spectrum of triazole **6l** measured in $CDCl_3$.

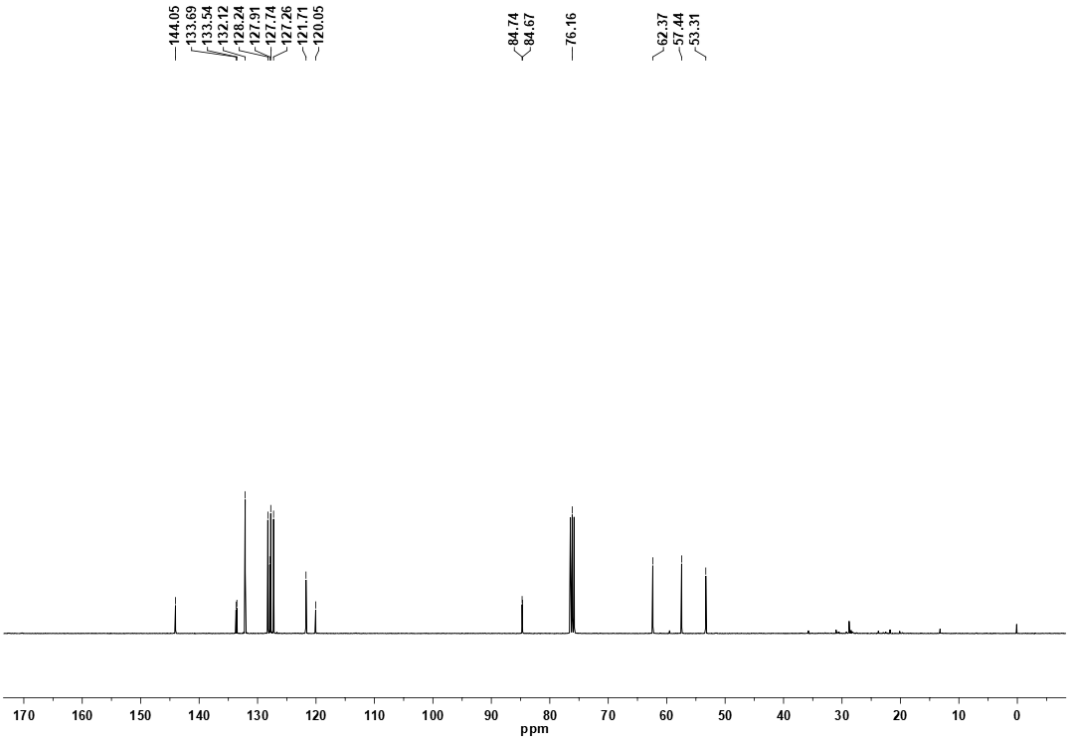


Figure S116. ^{13}C NMR spectrum of triazole **6l** measured in $CDCl_3$.

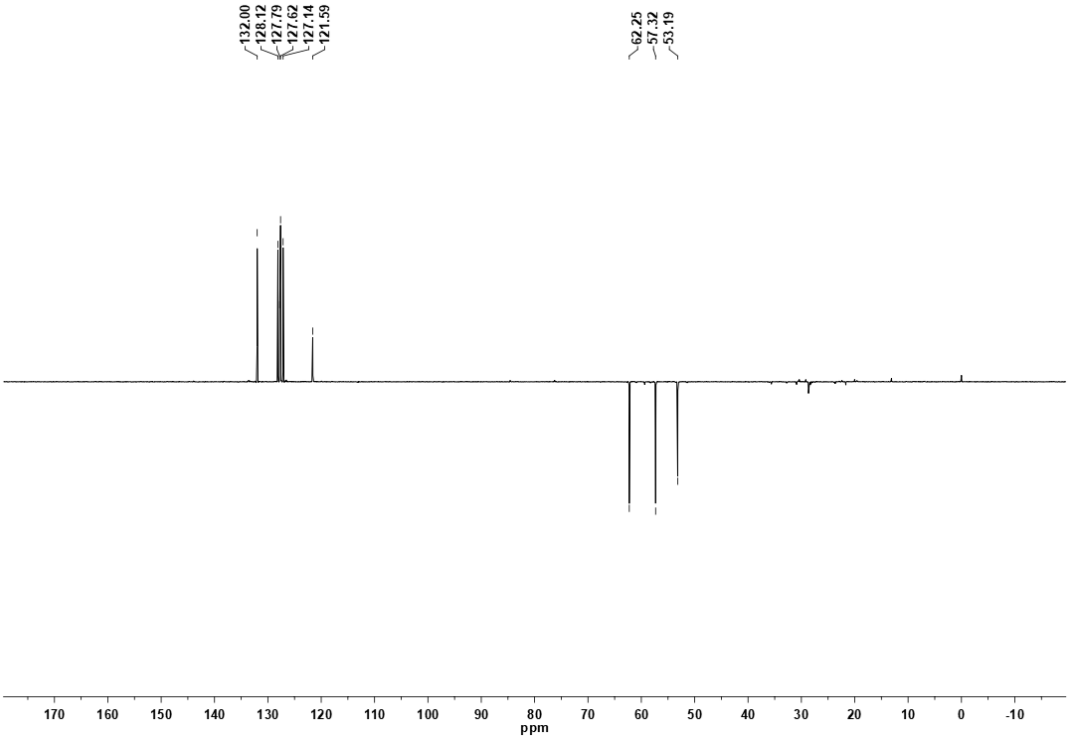


Figure S117. DEPT-135{^{13}C} NMR spectrum of triazole **6l** measured in $CDCl_3$.

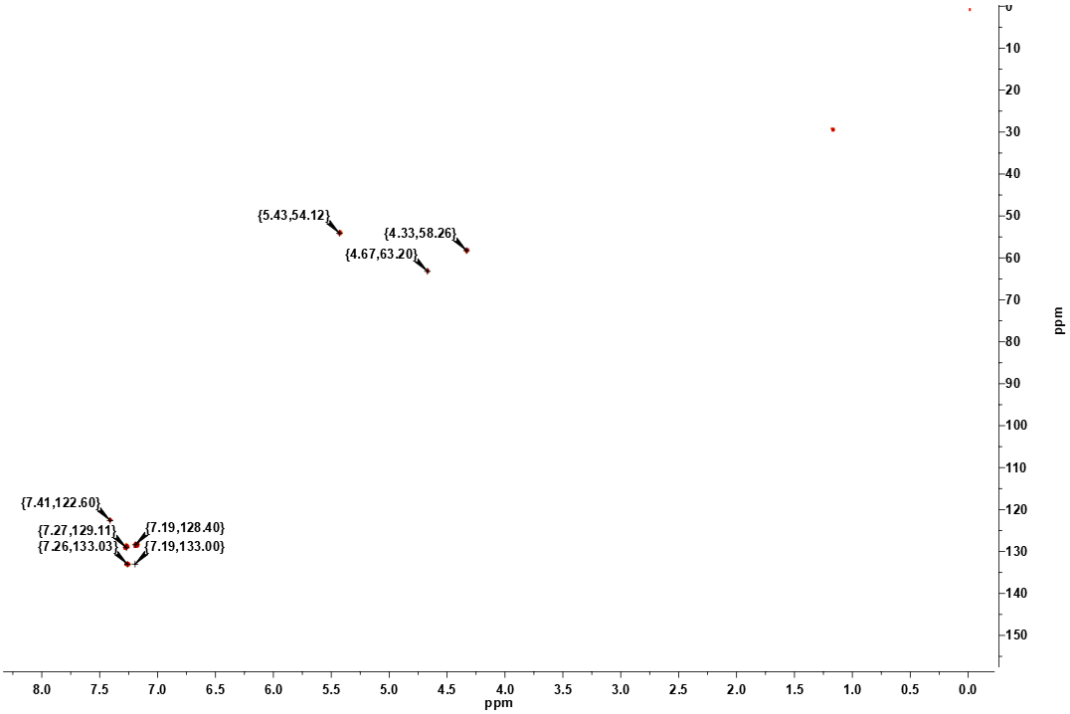


Figure S118. HSQC NMR spectrum of triazole **6l** measured in $CDCl_3$.

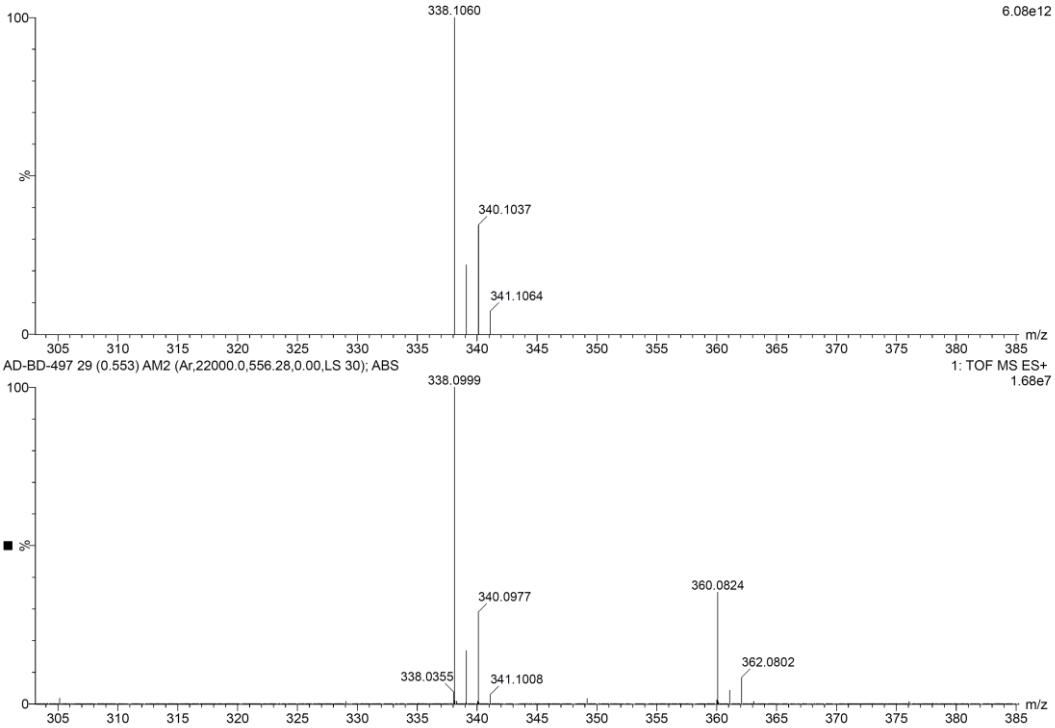


Figure S119. HRMS spectrum of triazole **6l** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

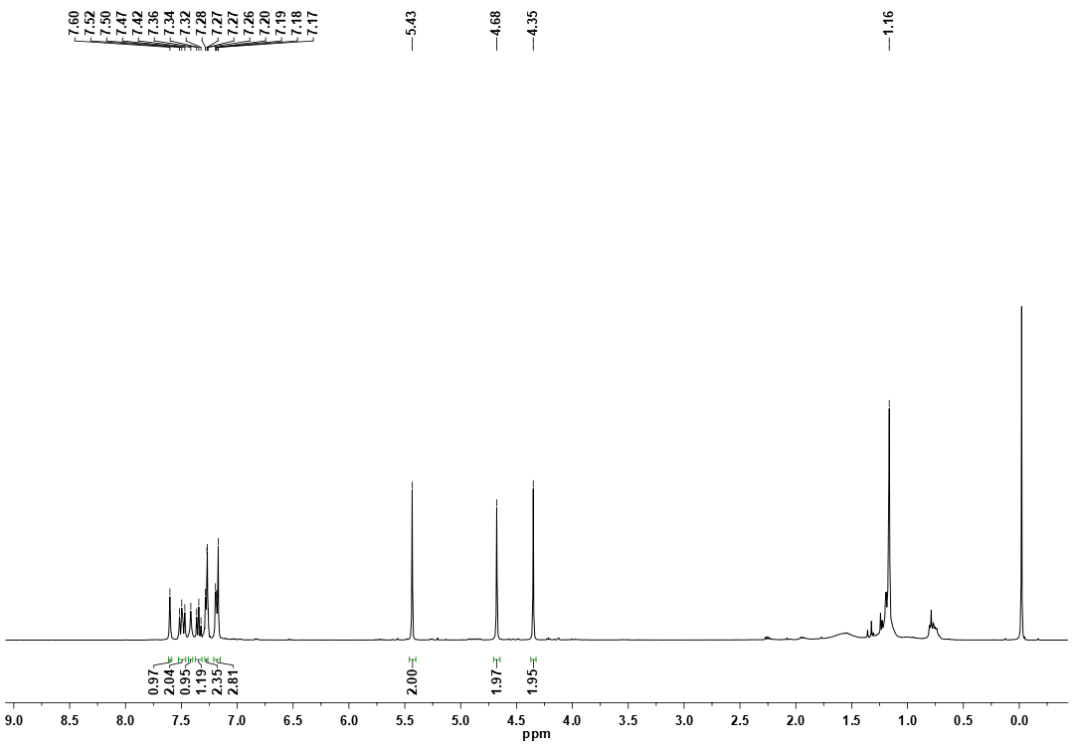


Figure S120. ^{1}H NMR spectrum of triazole **6m** measured in $CDCl_3$.

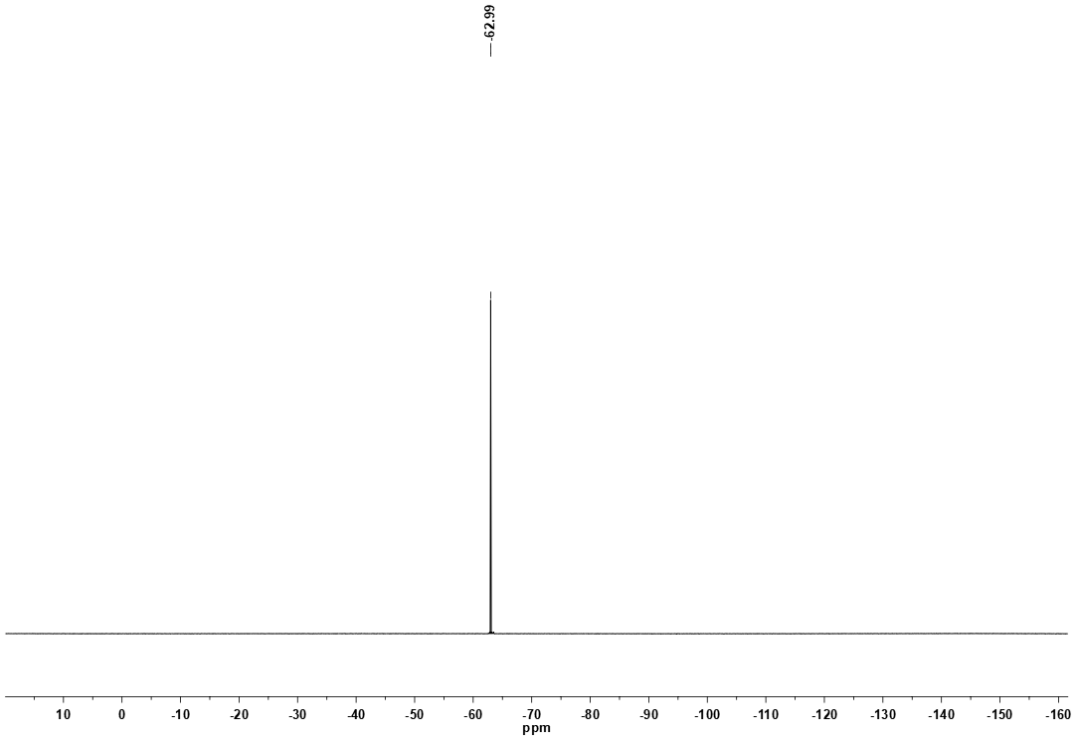


Figure S121. ^{19}F NMR spectrum of triazole **6m** measured in $CDCl_3$.

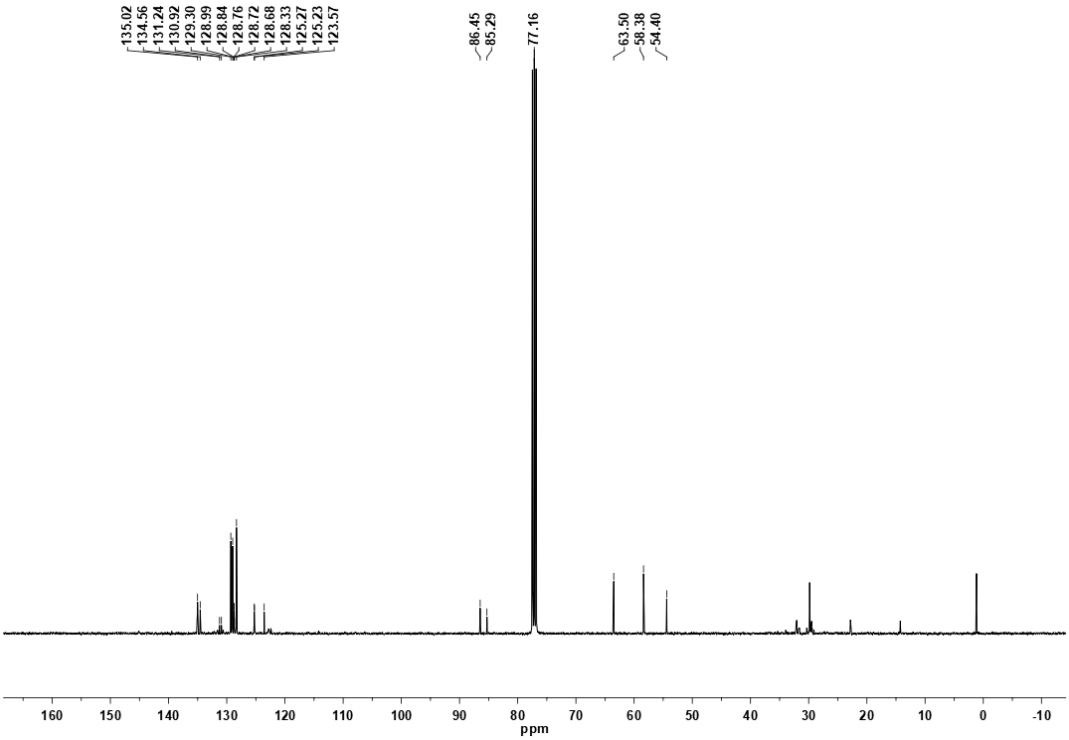


Figure S122. ^{13}C NMR spectrum of triazole **6m** measured in $CDCl_3$.

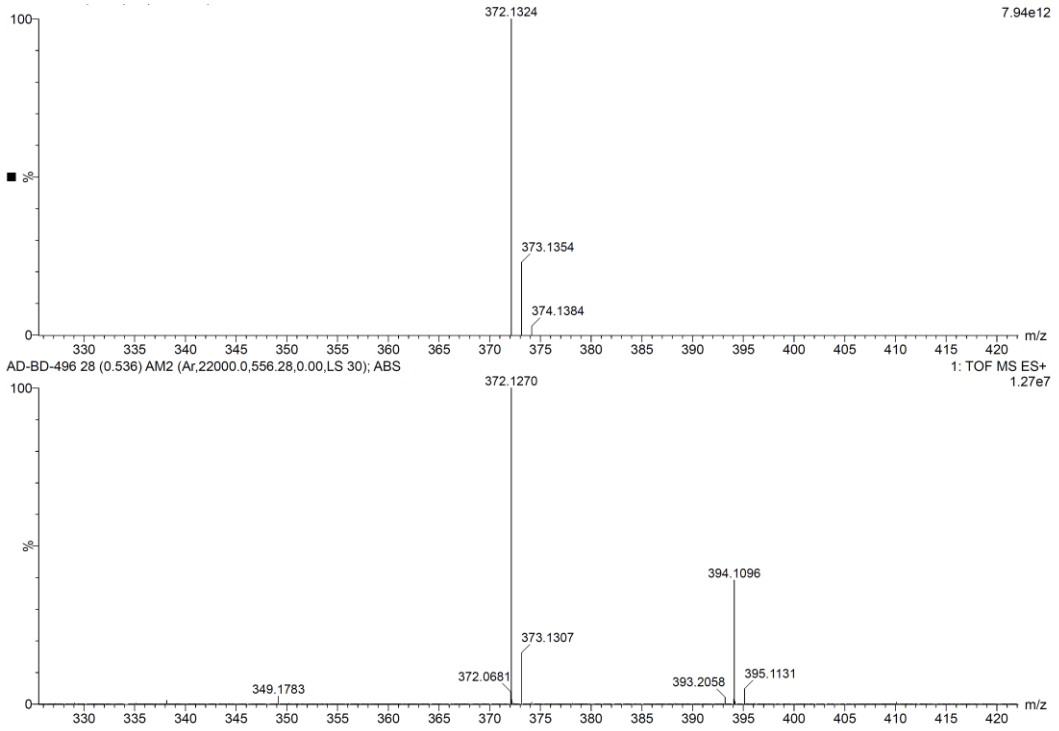


Figure S123. HRMS spectrum of triazole **6m** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

X-ray crystallographic information of complexes 3a/3b

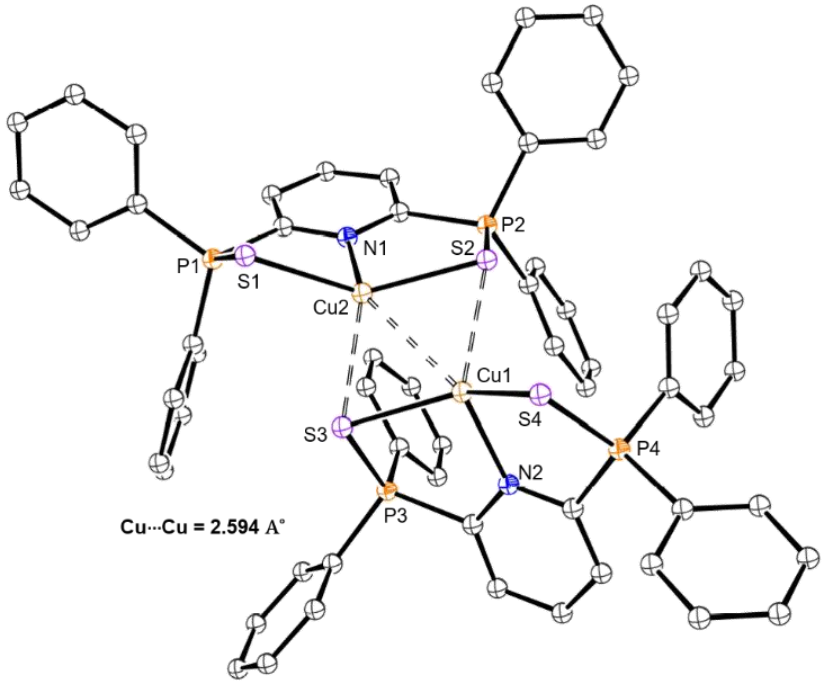


Figure S124. ORTEP view with 40% ellipsoid probability of the cationic part of the complex [(**2a**)Cu]$_2$[BF$_4$]$_2$ (**3a**). Anionic part and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. Cu1–Cu2 2.5941 (6), Cu1–S1 2.3286 (8), Cu1–S3 2.4146(9), Cu1–S4 2.3135 (8), Cu1–N1 2.069 (3), Cu2–S1 2.4731 (9), Cu2–S3 2.3358 (9), Cu2–S2 2.3034 (9), Cu2–N2 2.092 (3), S1–P2 2.0055 (11), S3–P3 2.0023 (12), S4–P1 1.9811 (11), P4-S2 1.9820 (13), S2–Cu2-S3 138.04 (4), and S4–Cu1–S1 136.39 (3).

Table S1. Crystal data and structure refinement parameters of complex (**3a**)

CCDC identification number	2257376
Empirical formula	$C_{59}H_{49.4}B_2Cl_{0.81}Cu_2F_8N_2O_{0.34}P_4S_4$
Formula weight	1373.28
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	26.6320(8)
b/Å	13.0574(4)
c/Å	17.0639(4)
α/°	90
β/°	95.917(2)
γ/°	90
Volume/Å^3	5902.3(3)
Z	4
ρ_{calc}g/cm^3	1.545
μ/mm^{-1}	1.075
F(000)	2791.0
Crystal size/mm^3	0.28 × 0.27 × 0.22

Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.73 to 61.138
Index ranges	-35 ≤ h ≤ 35, -17 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	63264
Independent reflections	14558 [R_{int} = 0.0585, R_{sigma} = 0.0540]
Data/restraints/parameters	14558/0/817
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0541, wR_2 = 0.1265
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1400
Largest diff. peak/hole / e $Å^{-3}$	1.20/-1.10

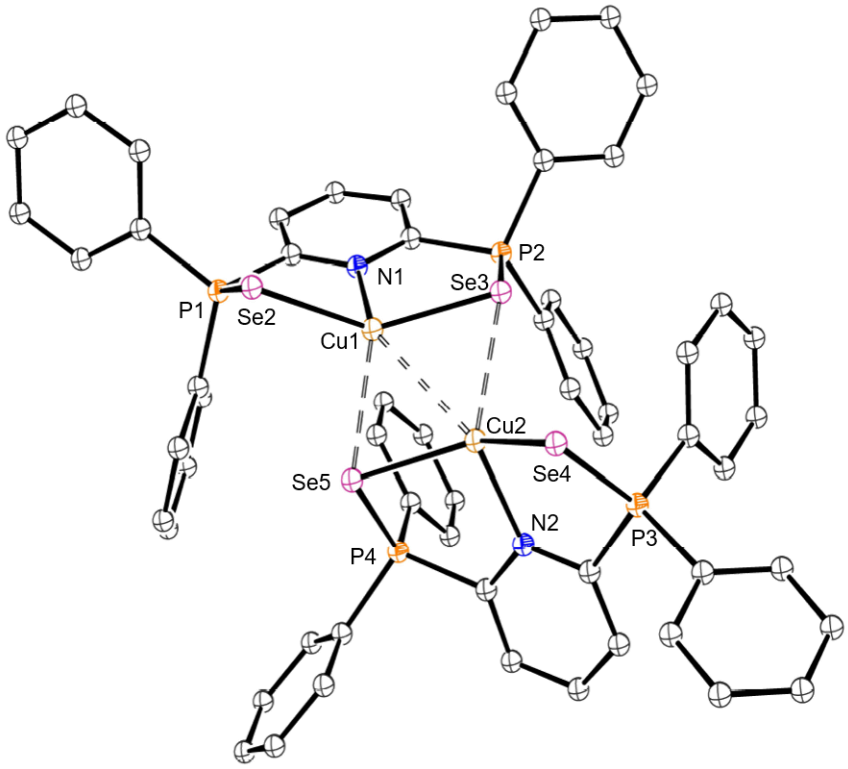


Figure S125**.** ORTEP view with 40% ellipsoid probability of the cationic part of the complex [(**2b**)Cu]$_2$[BF_4]$_2$ (**3b**). Anionic part and hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]. Cu1–Cu2 2.7291 (6), Cu1–Se3 2.4123 (6), Cu2–Se3 2.2.5407 (6), P2–S3 2.1634 (10), Cu1–N1 2.113 (3), Cu2–S4 2.4329 (6), Cu1–S5 2.5541 (6), Cu2–S5 2.4199 (6), Cu2–N2 2.094 (3), S4–P3 2.1396 (11), S5–P4 2.1581 (11), S2–P1 2.581 (11), Se2–Cu1-Se3 118.8 (3), and Se4–Cu2–Se5 137.49 (2).

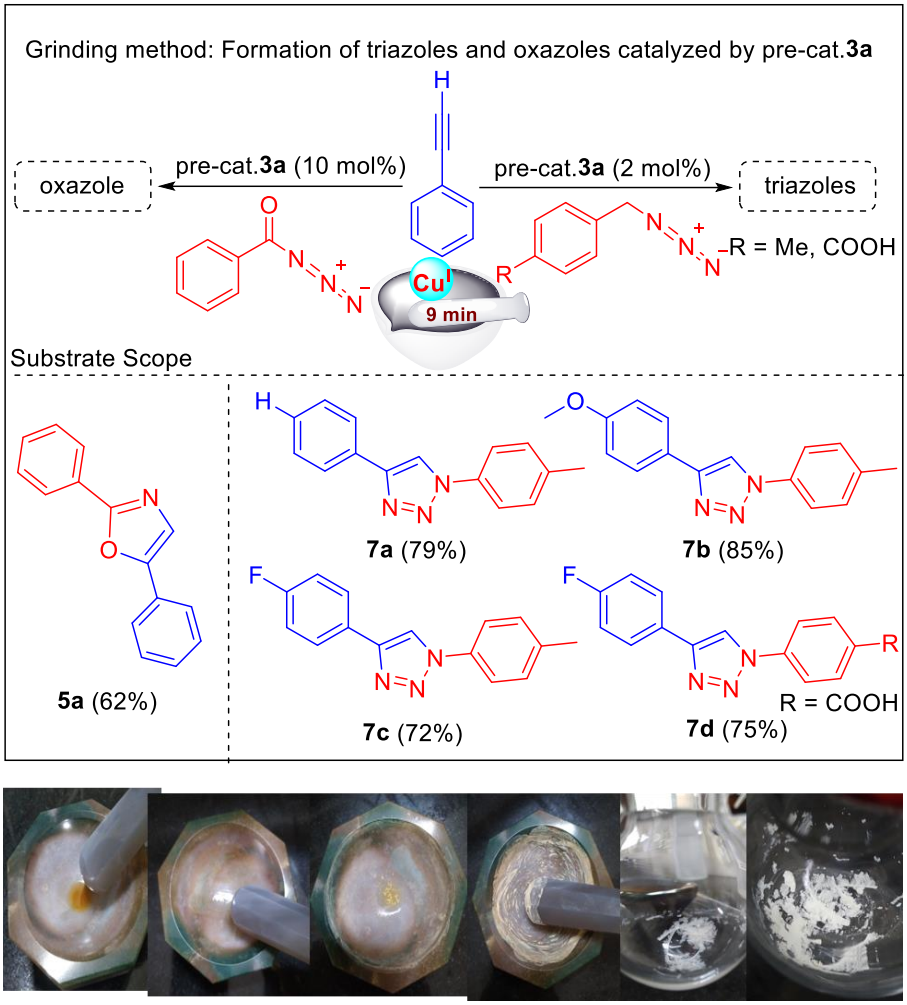
Table S2. Crystal data and structure refinement parameters of complex (**3b**)

CCDC identification code	**2257375**
Empirical formula	$C_{59}H_{47.33}B_2Cl_{1.98}Cu_2F_8N_2P_4Se_4$
Formula weight	1594.62
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1/n$

a/Å	14.4083(4)
b/Å	24.9105(8)
c/Å	17.3957(6)
α/°	90
β/°	100.231(3)
γ/°	90
Volume/$Å^3$	6144.4(3)
Z	4
$\rho_{calc}g/cm^3$	1.724
μ/mm^{-1}	3.314
F(000)	3139.0
Crystal size/mm^3	0.3 × 0.27 × 0.26
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.612 to 61.19
Index ranges	$-17 \leq h \leq 18$, $-31 \leq k \leq 34$, $-22 \leq l \leq 24$
Reflections collected	69099
Independent reflections	15100 [R_{int} = 0.0685, R_{sigma} = 0.0646]
Data/restraints/parameters	15100/0/796
Goodness-of-fit on F^2	1.006
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.1016
Largest diff. peak/hole / e $Å^{-3}$	1.48/-0.81

Synthesis and spectral data of triazole and oxazole derivatives by mechanical grinding method using pre-cat.3a

In addition to the above protocols, pre-cat.**3a** was also employed in the mechanical grinding method for the synthesis of triazoles and oxazoles starting from terminal alkynes and azides (Scheme S3).[11] By this method four triazoles (**7a-7d**) and one oxazole (**5a**) were achieved in 72-85% and 62% isolated yields respectively, and in contrast to the above protocol, it requires only short reaction times. Theorefore, it can be a sustainable copper(I) catalytic approach to achieve better yields and selectivity, especially in the case of oxazole derivative.[3,4] Furthermore, we have examined the same reaction under shaking technique by using Spinix. Two examples one each from oxazole and triazole were studied, and achieved the corresponding oxazole (**5a**) (Figure S141), and triazole derivatives (**6a**) (Figure S142) in 27% and 94% yields respectively.



Scheme S3**.** Preparation of **5** and **7** from mechanical grinding method by using pre-cat.**3a**

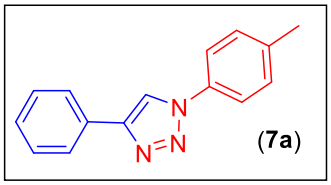
General methodology for the preparation of 7a-7d by grinding method

An oven-dried mortar and pestle was loaded with alkyne (1.2 equiv.) and azide (1 equiv.), and the reaction mixture was gently grounded for 1 min. To this mixture, 2 mol% and 10 mol% of pre-cat. **3a** were then added respectively for triazoles and oxazoles, and further mortared for 10 min. The products were isolated by subjecting the resulting substances through flash column chromatography, and typical column chromatography for triazoles and oxazoles respectively.

Spectroscopic data of substituted triazoles and oxazole synthesized through grinding method

Preparation of triazole (7a)[12]

7a was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (60-120 mesh) flash column chromatography (using ethyl acetate) which afforded white solid (42 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.08 (s, 1H, NCH), 7.84 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.19 (s, 1H), and 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 148.4, 139.1, 134.9, 130.5, 130.4, 129.1,



128.5,126.0, 120.6, 117.8, and 21.3 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_3$ $[M+H]^+$: 236.1188; found: 236.1209.

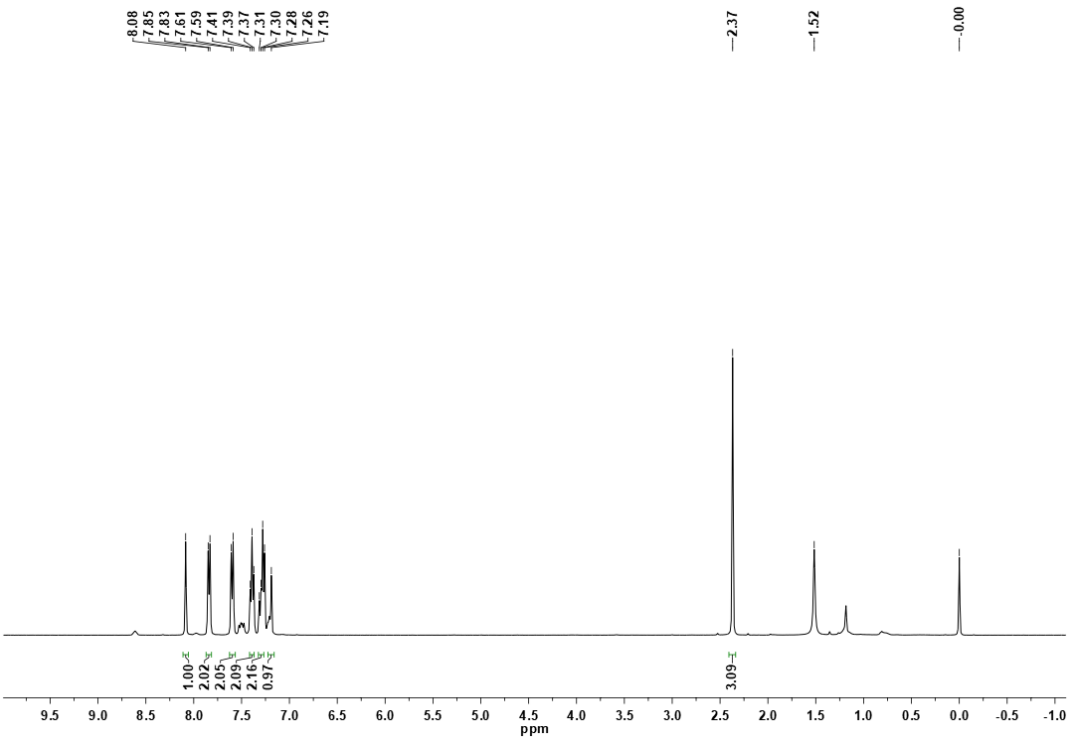


Figure S126. ^{1}H NMR spectrum of triazole **7a** measured in $CDCl_3$.

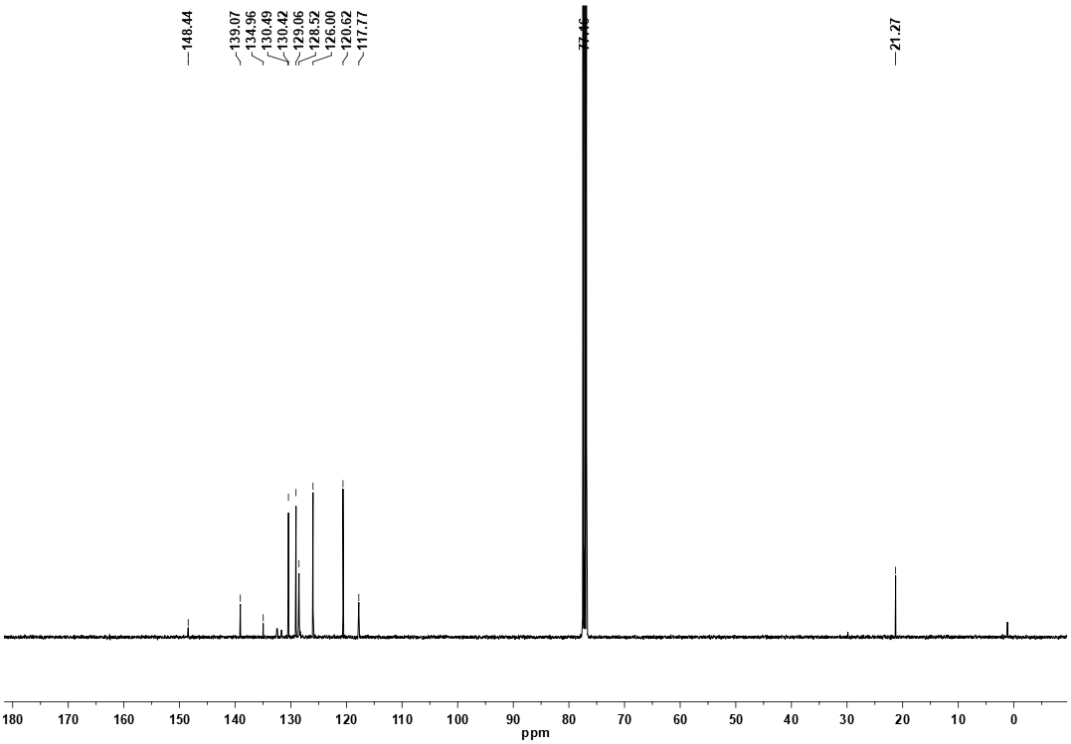


Figure S127. ^{13}C NMR spectrum of triazole **7a** measured in $CDCl_3$.

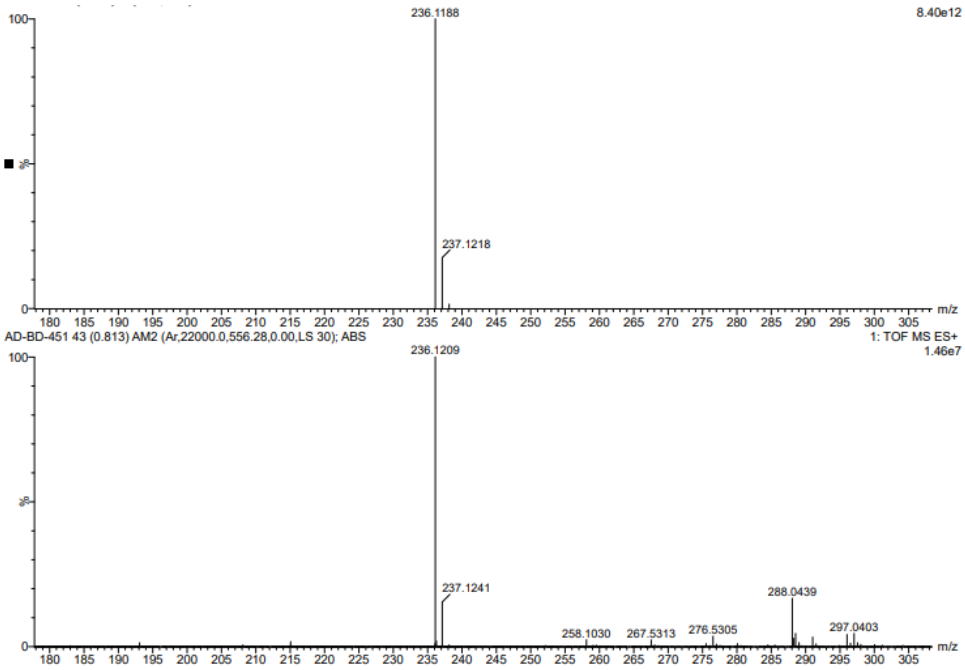
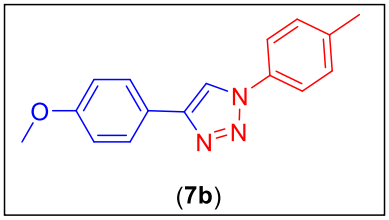


Figure S128. HRMS spectrum of triazole **7a** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of triazole (7b)[13]

7b was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (60-120 mesh) flash column chromatography (using ethyl acetate) which afforded white solid (50 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.07 (s, 1H, NCH), 7.83 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 3.86 (s, 3H, OCH_3), and 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 159.9, 148.4, 138.9, 135.2, 130.4, 127.3, 123.2, 120.6, 116.9, 114.5, 55.5 (OCH_3), and 21.3 (CH_3) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_3O$ $[M+H]^+$: 266.1293; found: 266.1312.



(**7b**)

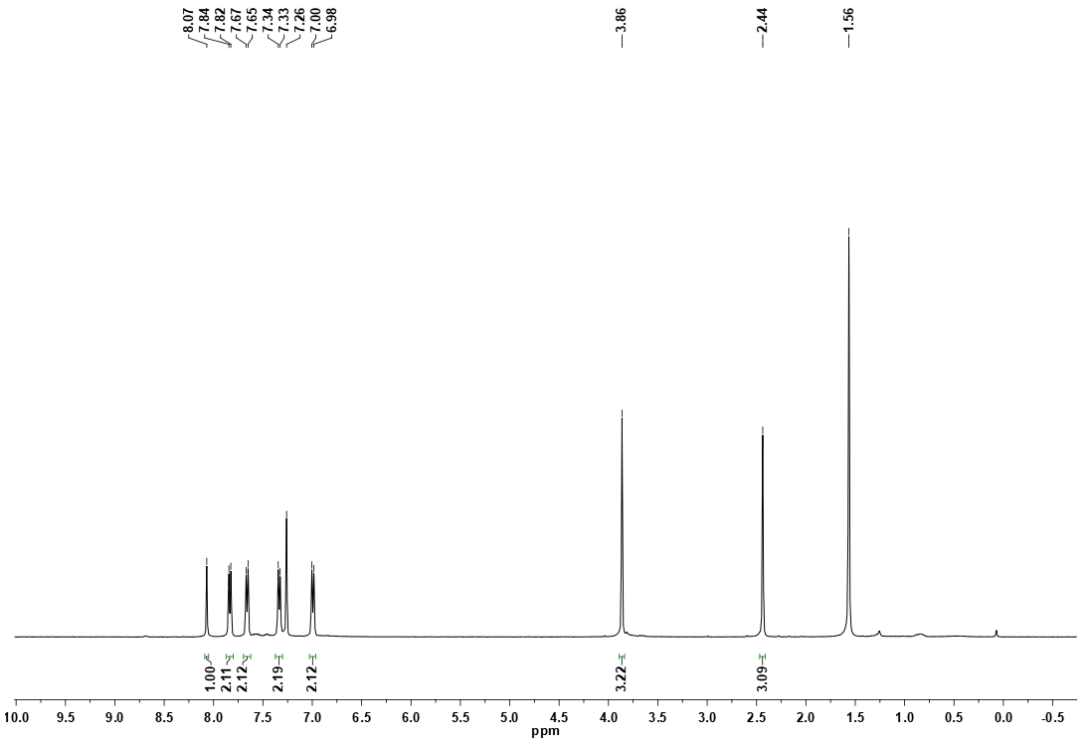


Figure S129. ^{1}H NMR spectrum of triazole **7b** measured in $CDCl_3$.

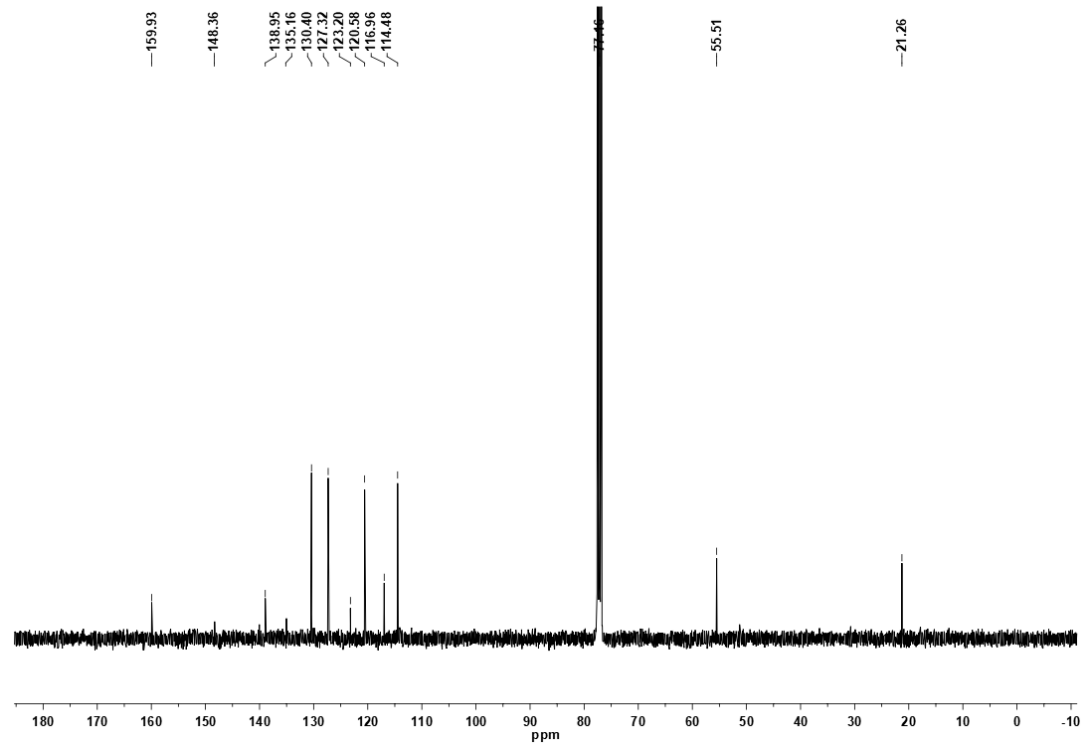


Figure S130. ^{13}C NMR spectrum of triazole **7b** measured in $CDCl_3$.

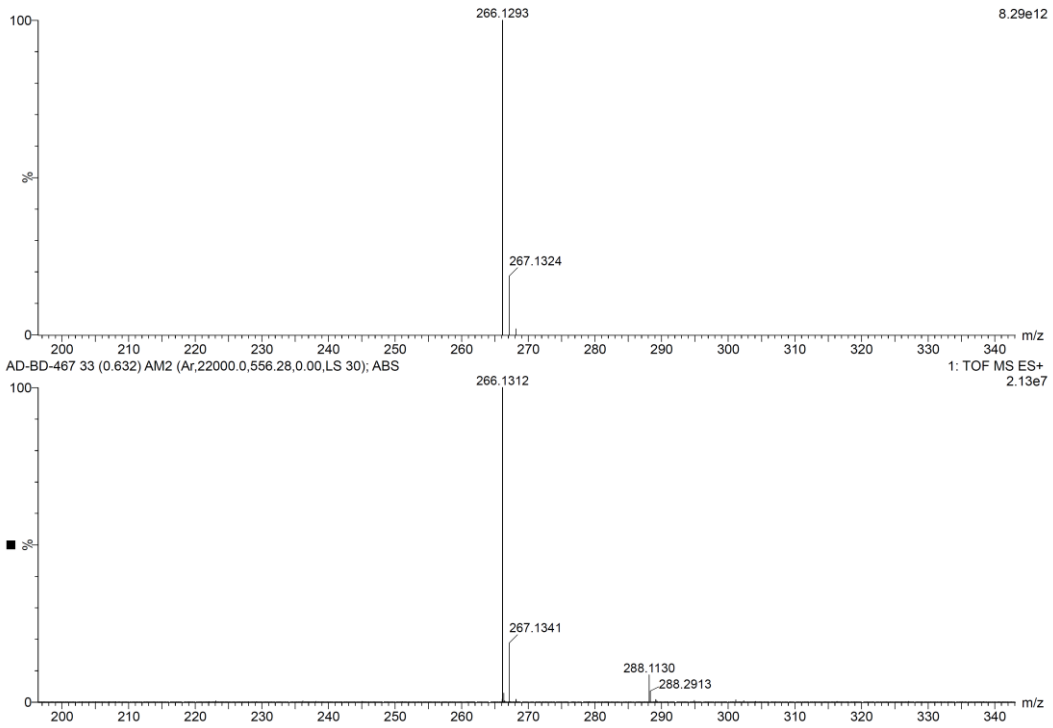
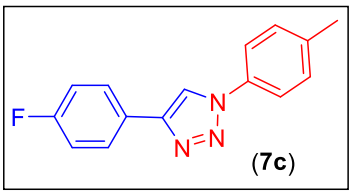


Figure S131. HRMS spectrum of triazole **7b** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of triazole (7c)[13]

7c was prepared according to the general procedure. The crude reaction mixture was purified by silica gel (60-120 mesh) flash column chromatography (using ethyl acetate) which afforded white solid (41 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.11 (s, 1H, NCH), 7.92 – 7.84 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), and 2.44 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$); δ = 164.2, 161.7, 147.6, 139.2, 134.9, 130.5, 127.8, 127.7, 126.6, 120.6, 117.6, 116.2, 115.9, and 21.3 (CH_3) ppm. ^{19}F NMR (377 MHz, $CDCl_3$); δ = –113.2 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}N_3F$ $[M+H]^+$: 254.1093; found: 254.1115.



(**7c**)

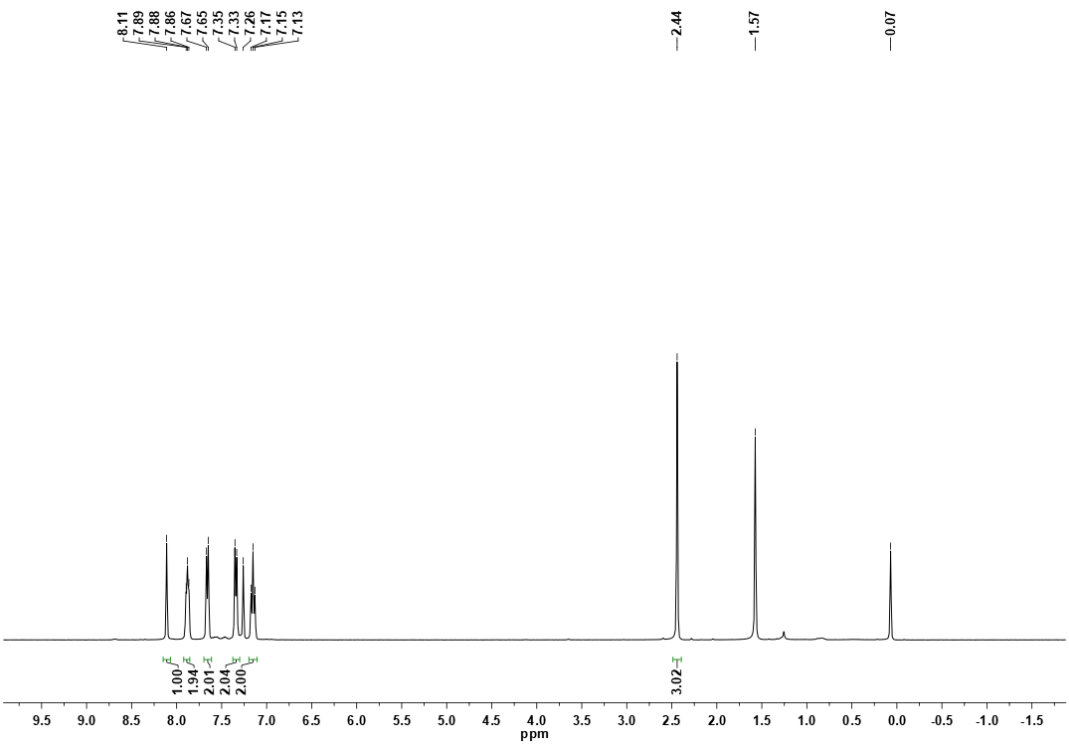


Figure S132. ^{1}H NMR spectrum of triazole **7c** measured in $CDCl_3$.

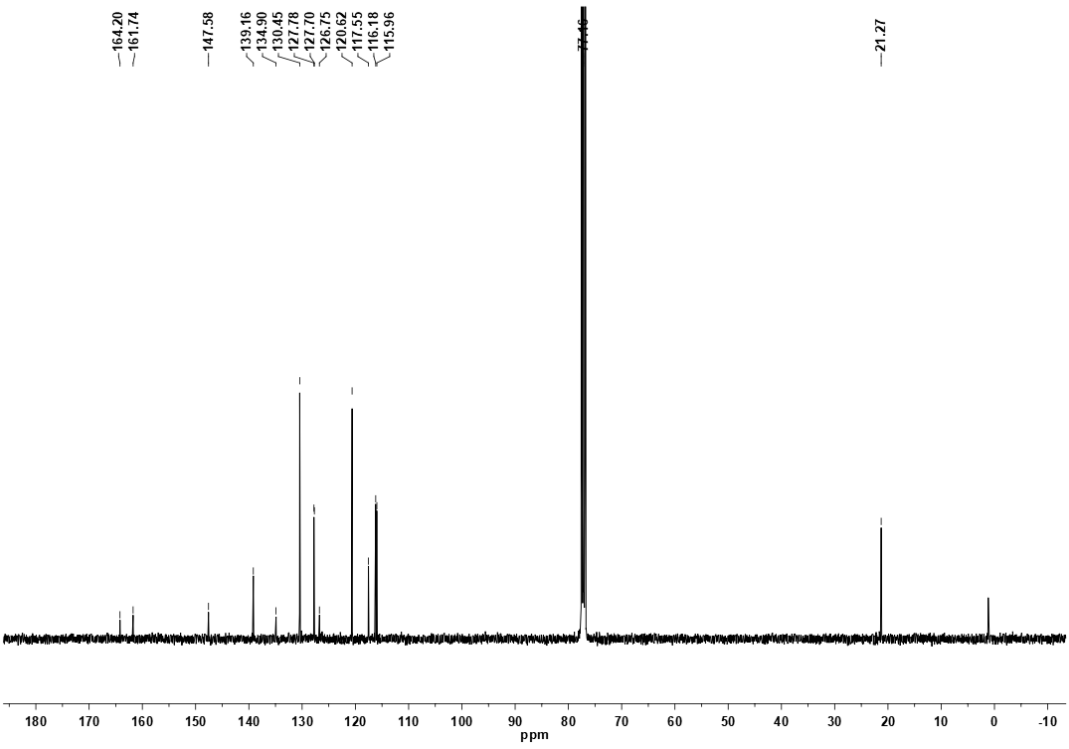


Figure S133. ^{13}C NMR spectrum of triazole **7c** measured in $CDCl_3$.

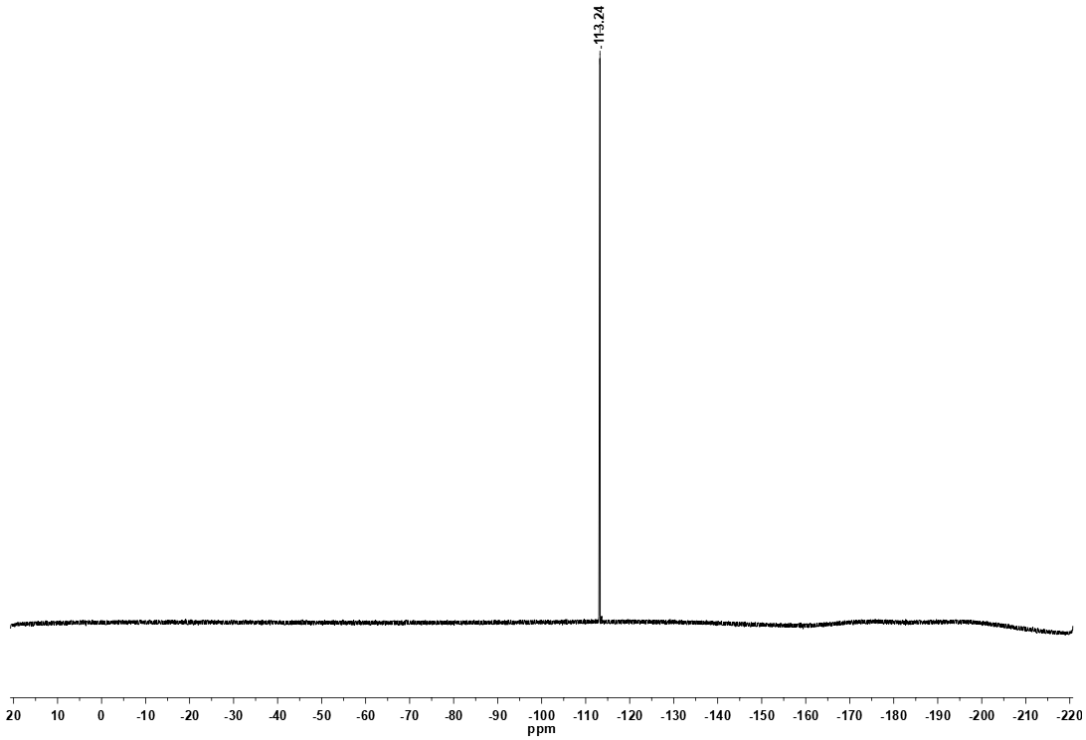


Figure S134. ^{19}F NMR spectrum of triazole **7c** measured in $CDCl_3$.

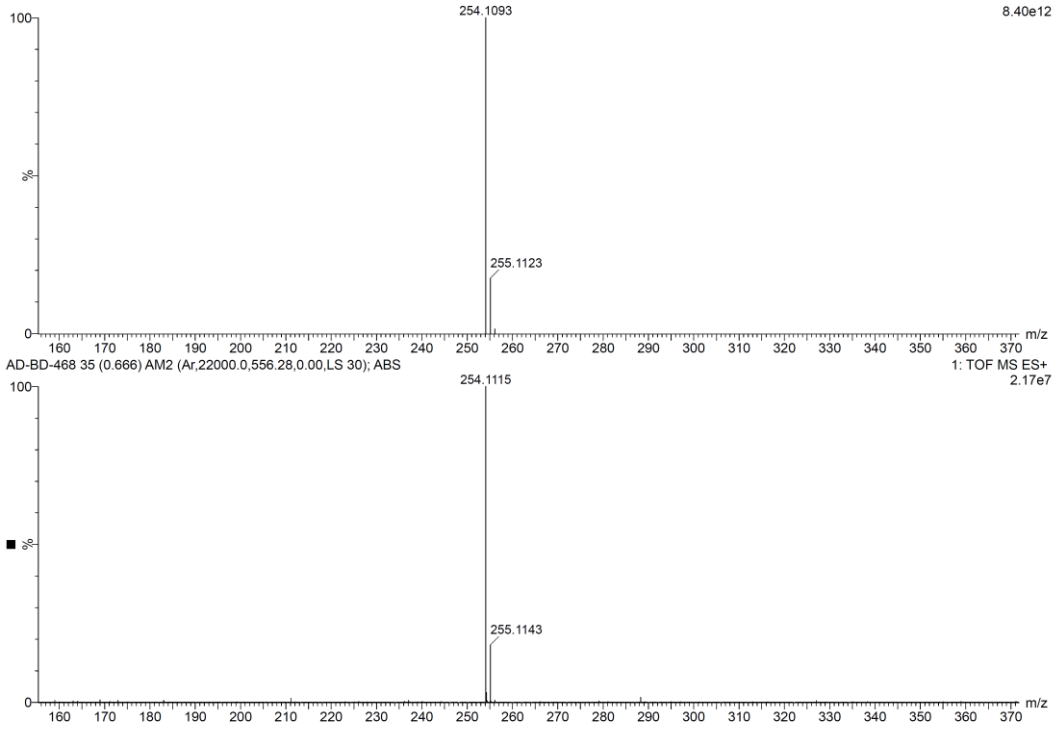
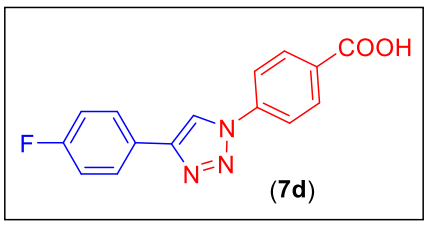


Figure S135. HRMS spectrum of triazole **7c** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of triazole 7d

7d was prepared according to the general procedure. The crude reaction mixture was purified by washing with ethyl acetate (5 mL × 3) which afforded creamy solid (39 mg, 75%). ^{1}H NMR (400 MHz, DMSO-d_6); δ = 13.24 (s, 1H, COOH), 9.41 (s, 1H, NC*H*), 8.15 (s, 4H), 8.08–7.92 (m, 3H), and 7.36 (t, *J* = 8.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6); δ = 162.8, 161.4, 146.7, 139.5, 127.5, 127.5, 126.6, 126.6, 119.7, 116.2, and 116.0 ppm. ^{19}F NMR (377 MHz, DMSO-d_6); δ = –113.3 (s) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}N_3FO_2$ $[M+H]^+$: 284.0835; found: 284.0809.



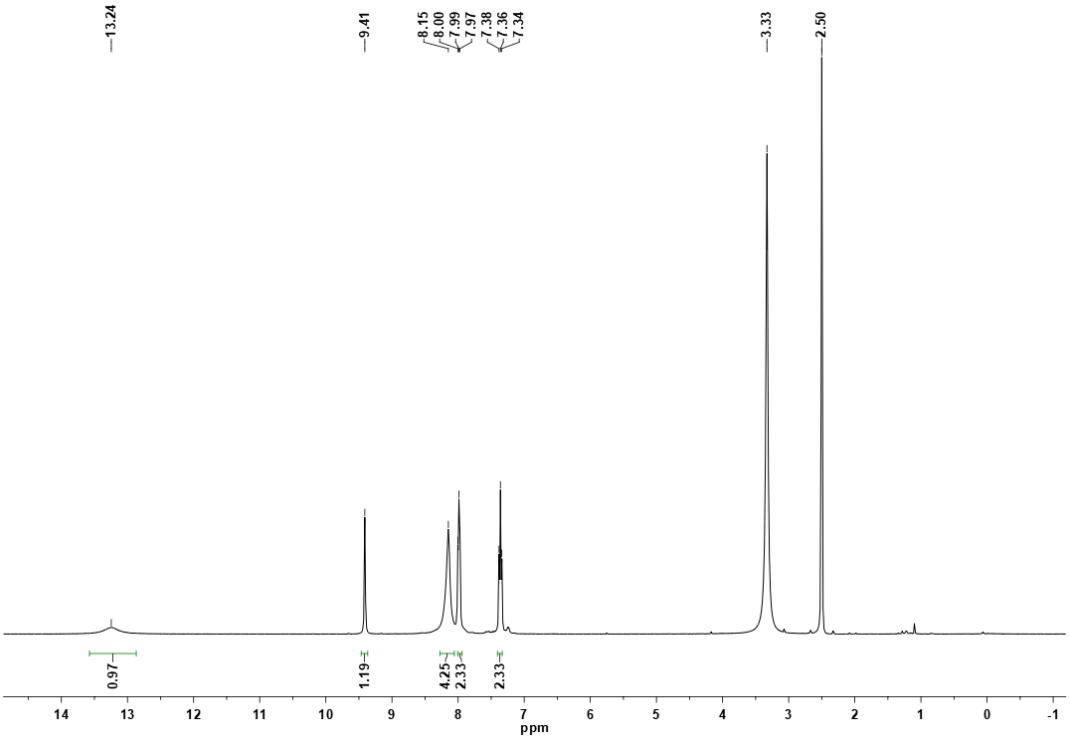


Figure S136. ^{1}H NMR spectrum of triazole **7d** measured in DMSO-d_6.

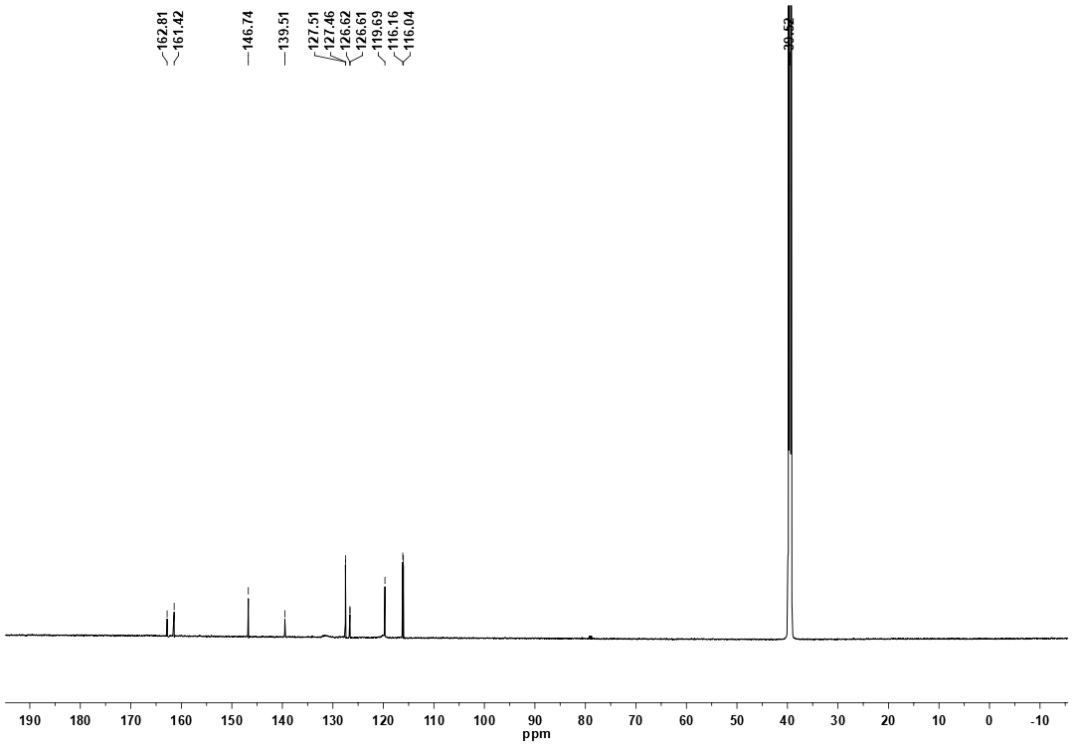


Figure S137. ^{13}C NMR spectrum of triazole **7d** measured in DMSO-d_6.

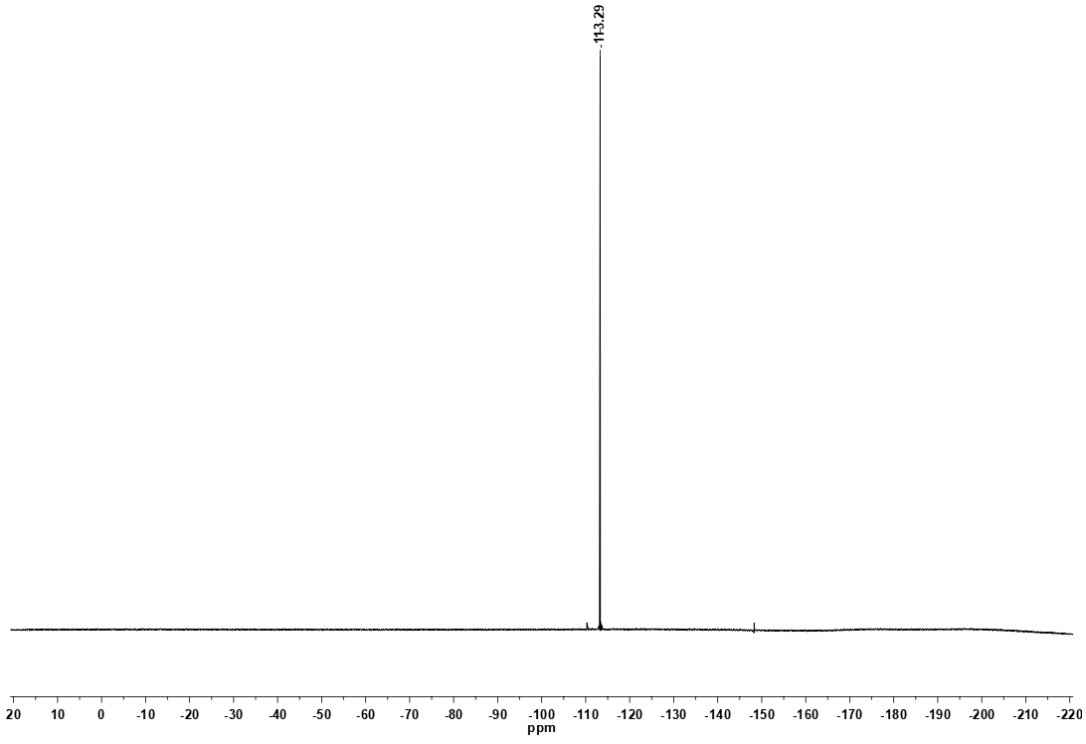


Figure S138. ^{19}F NMR spectrum of triazole **7d** measured in DMSO-d_6.

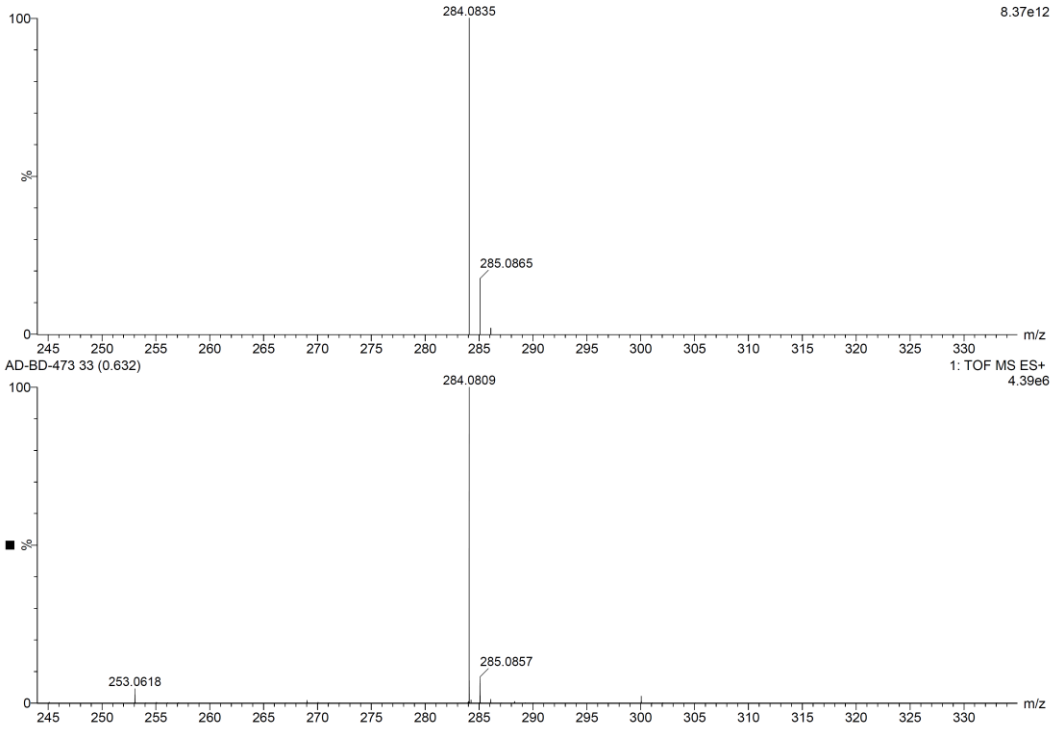
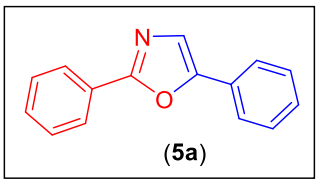


Figure S139. HRMS spectrum of triazole **7d** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of oxazole (5a)

The grinded reaction mixture was purified by silica gel (100-200 mesh) column chromatography



(10% EtOAc/hexane mixture) which afforded an orange solid (9 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.14–8.10 (m, 2H), 7.75–7.72 (m, 2H), 7.51–7.43 (m, 6H), and 7.35 (t, *J* = 6.8 Hz, 1H) ppm. ^{13}C NMR and HRMS spectral data are similar to the aforementioned data prepared by the other method.

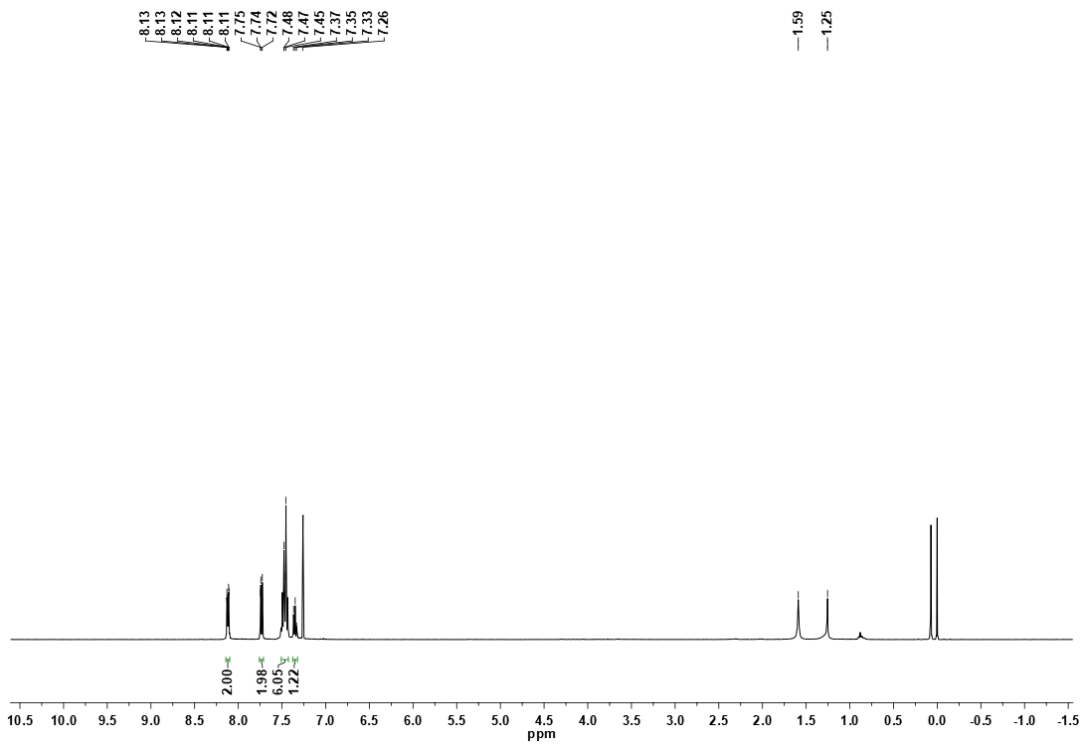


Figure S140. ^{1}H NMR spectrum of oxazole **5a** measured in $CDCl_3$.

Synthetic procedure of 5a and 6a by shaking method

The alkyne (1.2 equiv.), azide (1 equiv), and the pre-cat.**3a** (2 mol%/triazole, or 10 mol%/oxazole) were taken in a closed glass vial, and shaked for 4h using the Spinix vertex mixer. **5a** (Figure S142) and **6a** were obtained in 27% and 94% yields respectively. **6a** (Figure S143) was isolated by flash column chromatrography using ethyl acetate as an eluent.

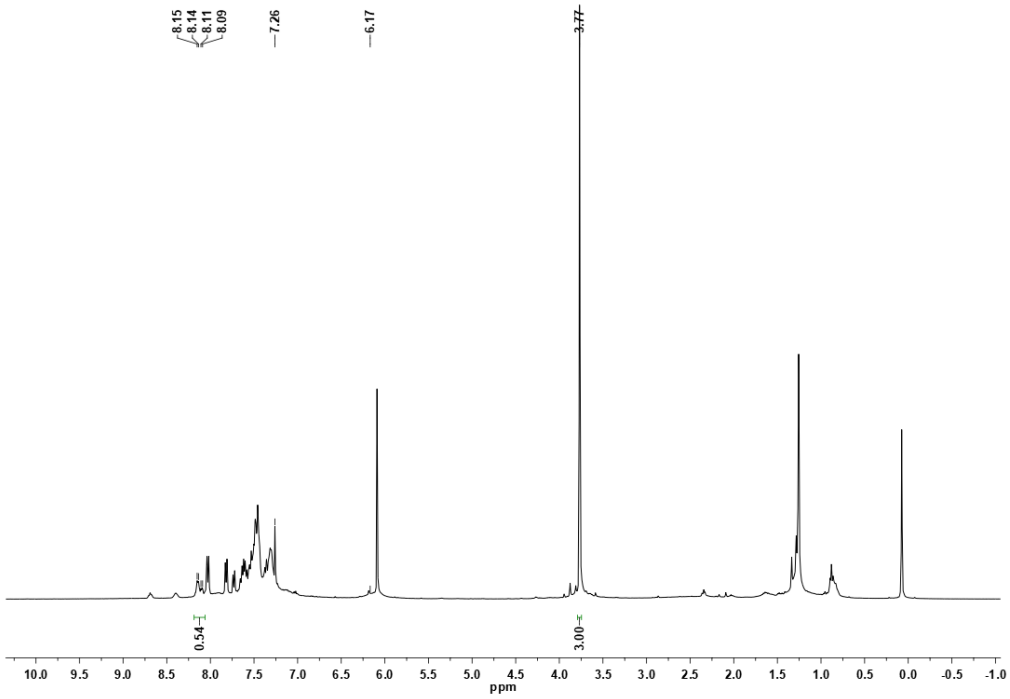


Figure S141. ^{1}H NMR spectrum of oxazole **5a** synthesized by shaking technique measured in $CDCl_3$ (yield (27%) was determined by ^{1}H NMR spectral data by using an internal standard; 1,3,5-trimethoxy benzene).

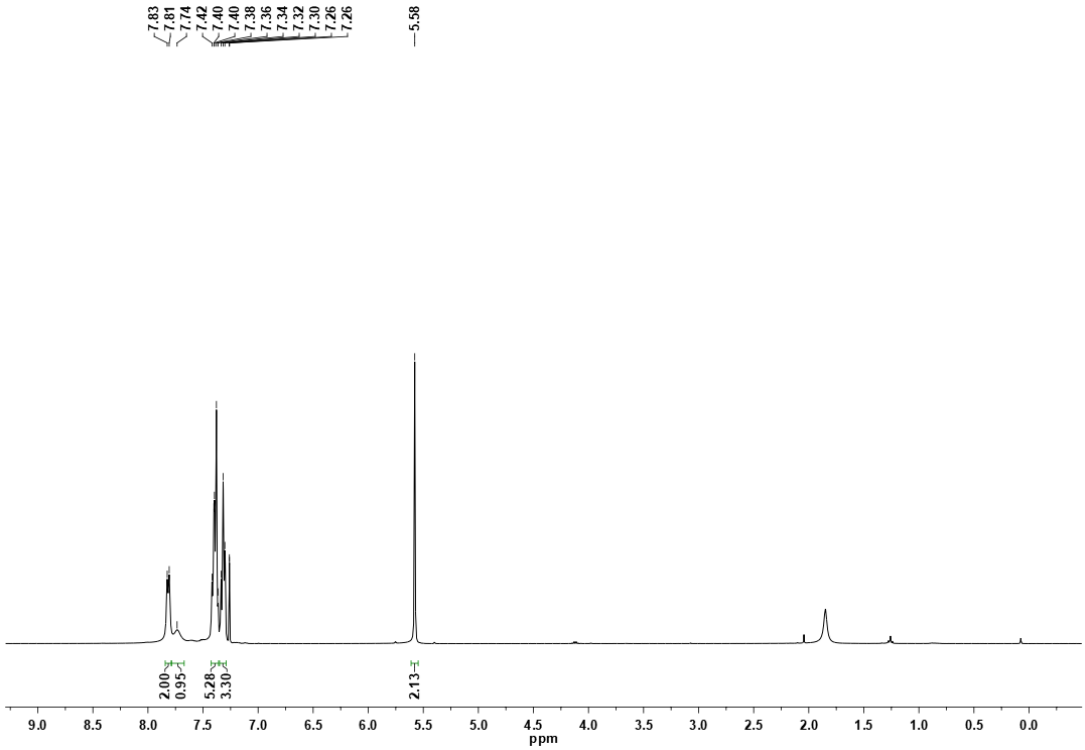


Figure S142. ^{1}H NMR spectrum of triazole **6a** synthesized by shaking method measured in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.82 (d, *J* = 7.2 Hz, 2H), 7.74 (s, 1H), 7.39 (dt, *J* = 12.7, 6.2 Hz, 5H), 7.32 (t, *J* = 6.8 Hz, 3H), and 5.58 (s, 2H) ppm (Yield; 94% isolated yield).

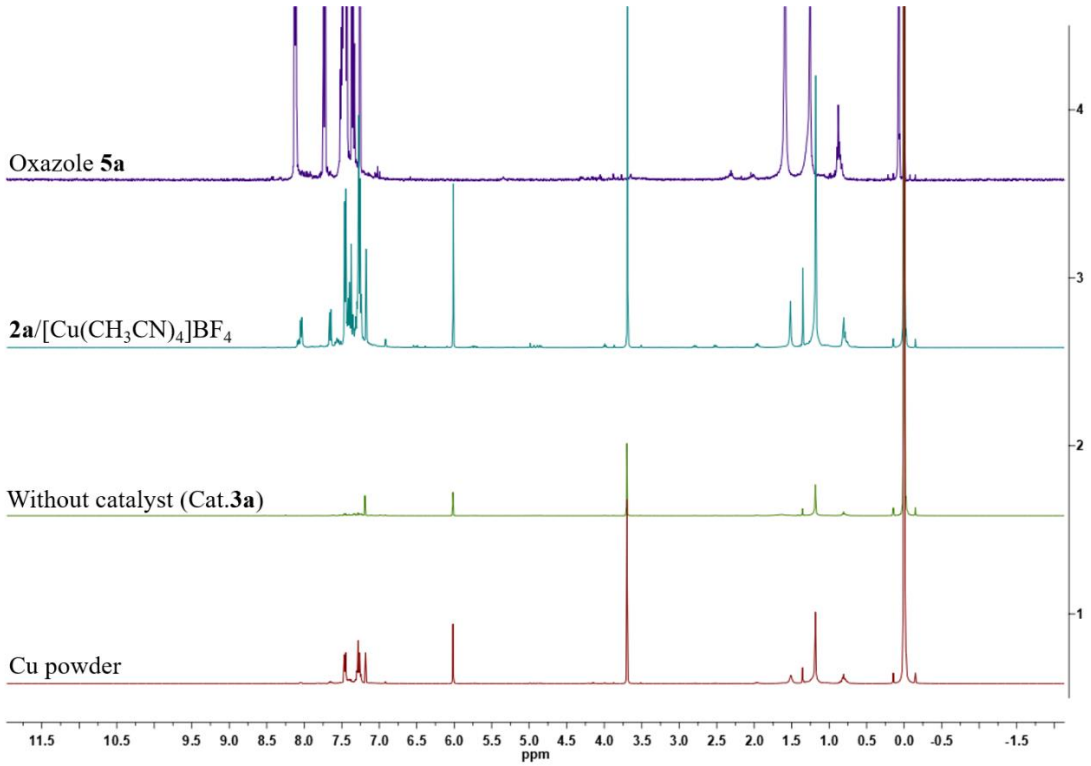
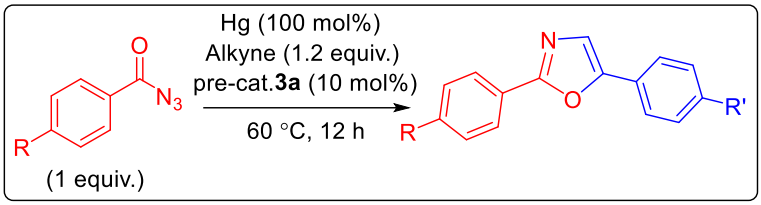


Figure S143. Stacked ^{1}H NMR spectra of a few controlled expeirments for the preparation of oxazole **5a** (measured in $CDCl_3$).

Figure S144. Mass spectrum of a controlled reaction, showing the product formation and the presence of active catalytic species; [(**2a**)Cu]$^{+}$ during the reaction.

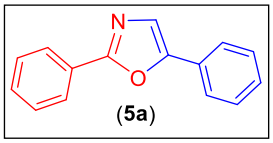
Homogeneity test with mercury metal

Under N_2 atmosphere, a 15 mL flame-dried Schlenk tube was charged with azide (1 equiv.), alkyne (1.2 equiv.), and pre-cat.**3a** (10 mol%) sequentially followed by mercury (100 mol%) was added into the tube. Then, the reaction mixture was allowed to stir for 12 h at 60 °C. After cooling to room temperature, the crude reaction mixture was purified by silica gel column chromatography (10% EtOAc/hexane mixture) to afford the corresponding substituted oxazoles.



Preparation of oxazole (5a)

5a was prepared according to the general procedure mentioned above. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (10 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.04 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.35 (m, 6H), 7.27 (t, *J* = 7.4 Hz, 1H) ppm. HRMS (ESI) m/z calcd for $C_{15}H_{11}NO$ $[M+H]^+$: 222.0919; found: 222.0919.



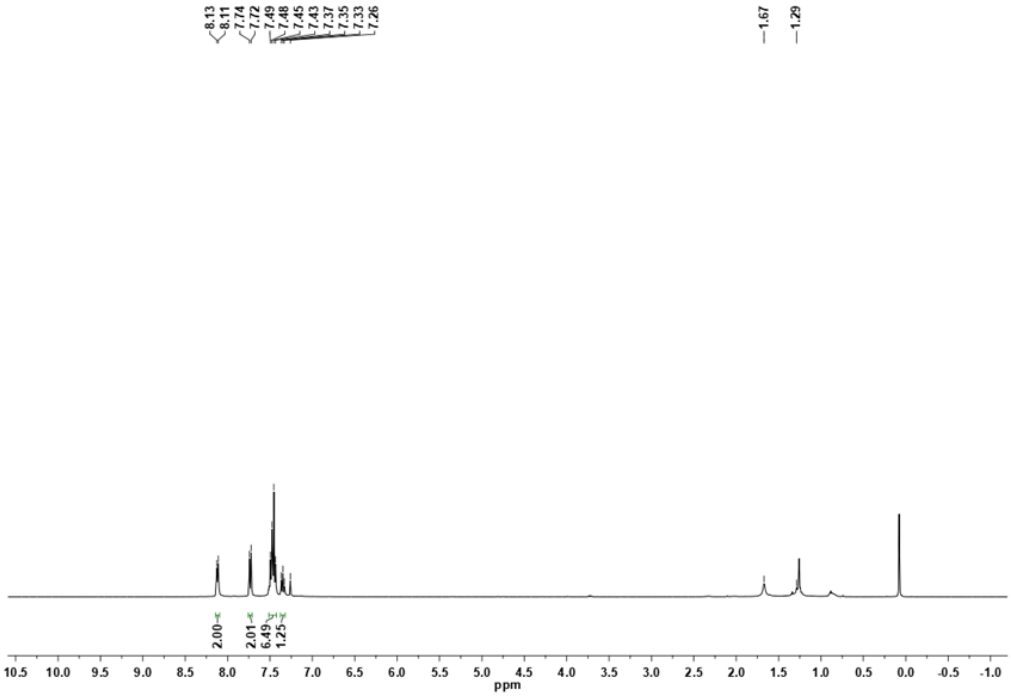


Figure S145. ^{1}H NMR spectrum of oxazole **5a** measured in $CDCl_3$.

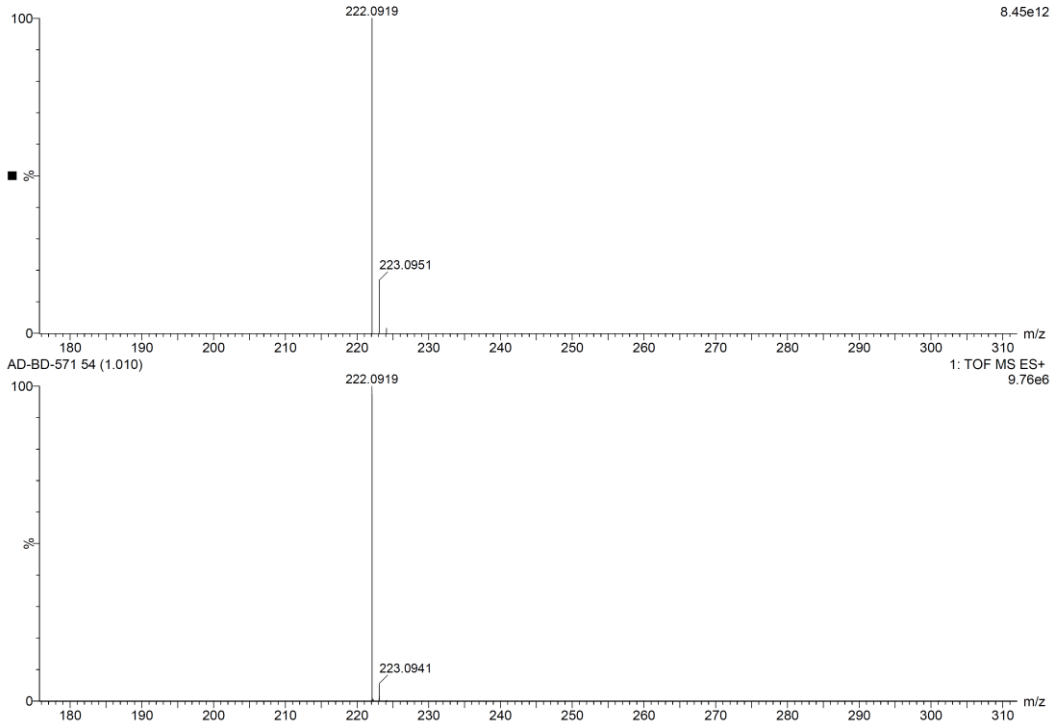
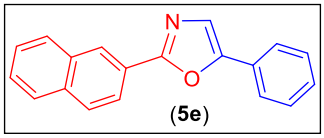


Figure S146. HRMS spectrum of oxazole **5a** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of oxazole (5e)

5e was prepared according to the general procedure mentioned above. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (15 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.61 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.96 (dd, *J* = 11.4, 5.8 Hz, 2H), 7.91 – 7.85 (m, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 3.3 Hz, 2H), 7.49 (dd, *J* = 13.4, 5.8 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 1H) ppm. HRMS (ESI) *m/z* calcd for $C_{15}H_{10}N_2O_3$ $[M+H]^+$: 272.1075; found: 272.1078.



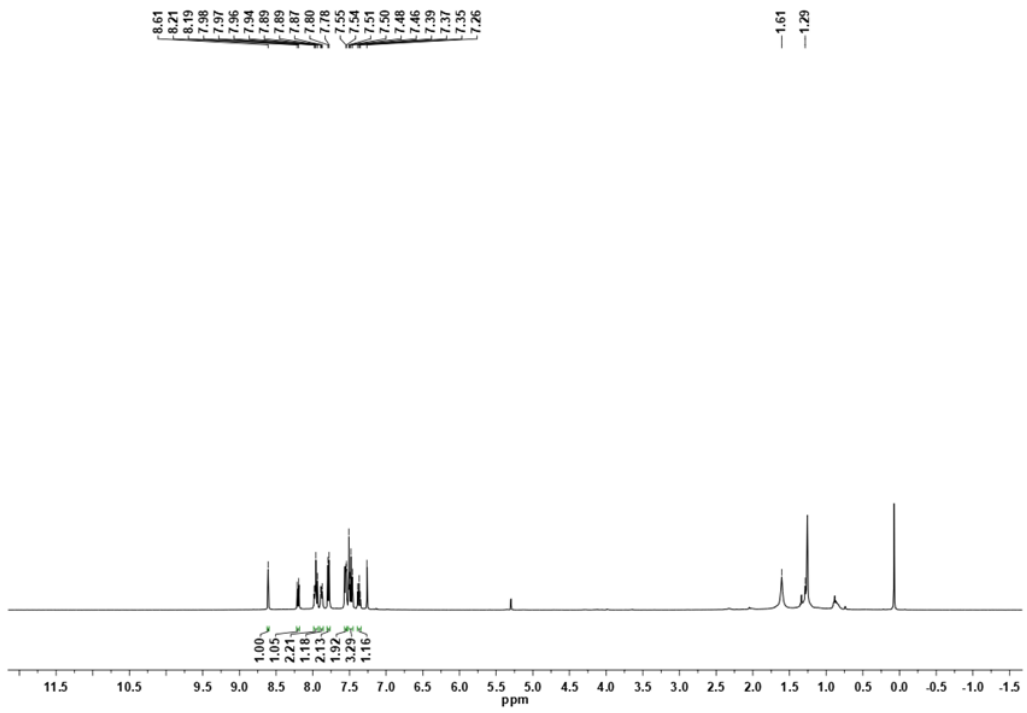


Figure S147. ^{1}H NMR spectrum of oxazole **5e** measured in $CDCl_3$.

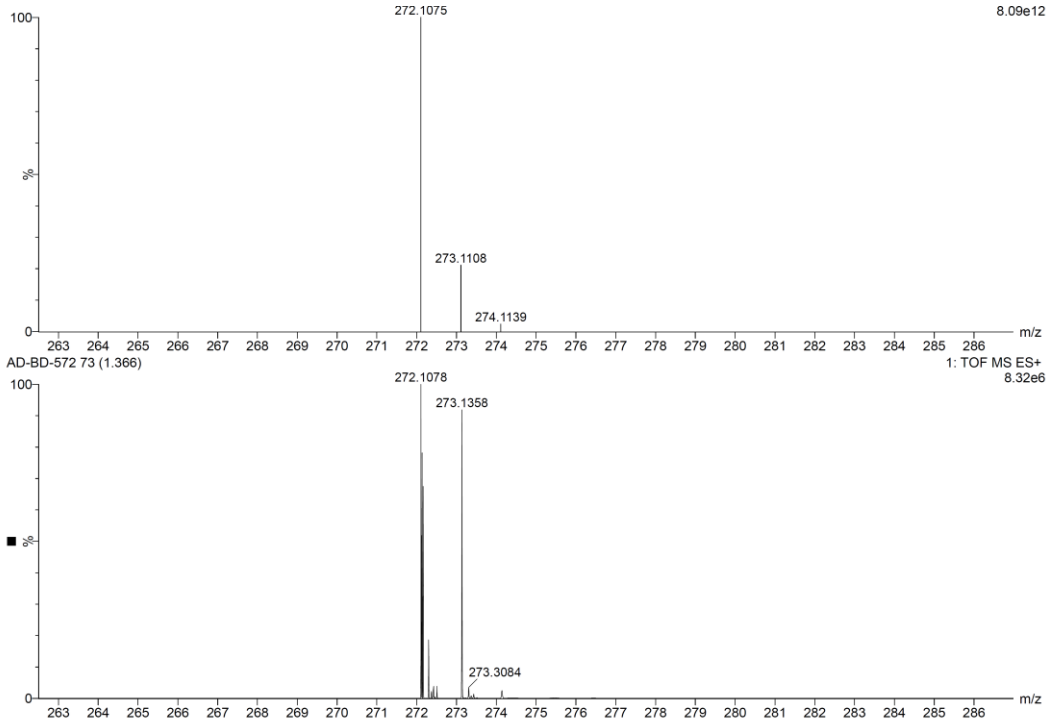
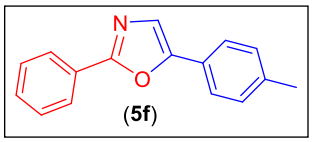


Figure S148. HRMS spectrum of oxazole **5e** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

Preparation of oxazole (5f)

5f was prepared according to the general procedure mentioned above. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography (10% EtOAc/hexane mixture) which afforded orange solid (10 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.97 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 2H), 7.34 (d, *J* = 7.6 Hz, 3H), 7.12 (d, *J* = 7.9 Hz, 3H), 2.26 (s, 3H) ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1075; found: 236.1083.



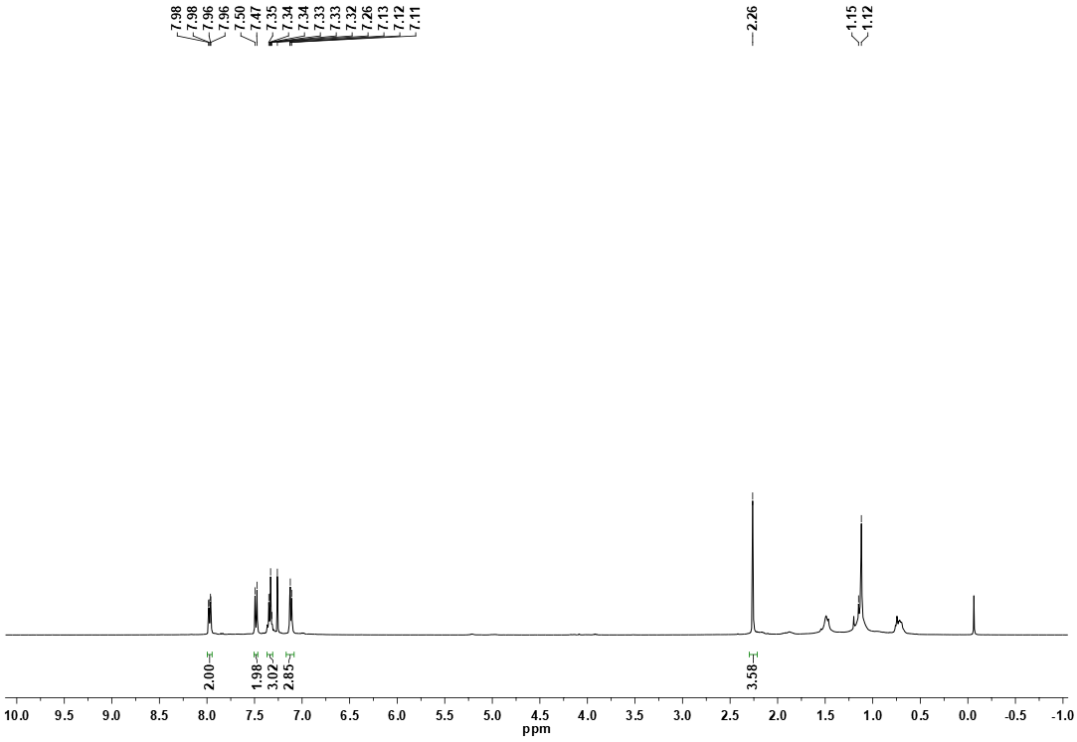


Figure S149. ^{1}H NMR spectrum of oxazole **5f** measured in $CDCl_3$.

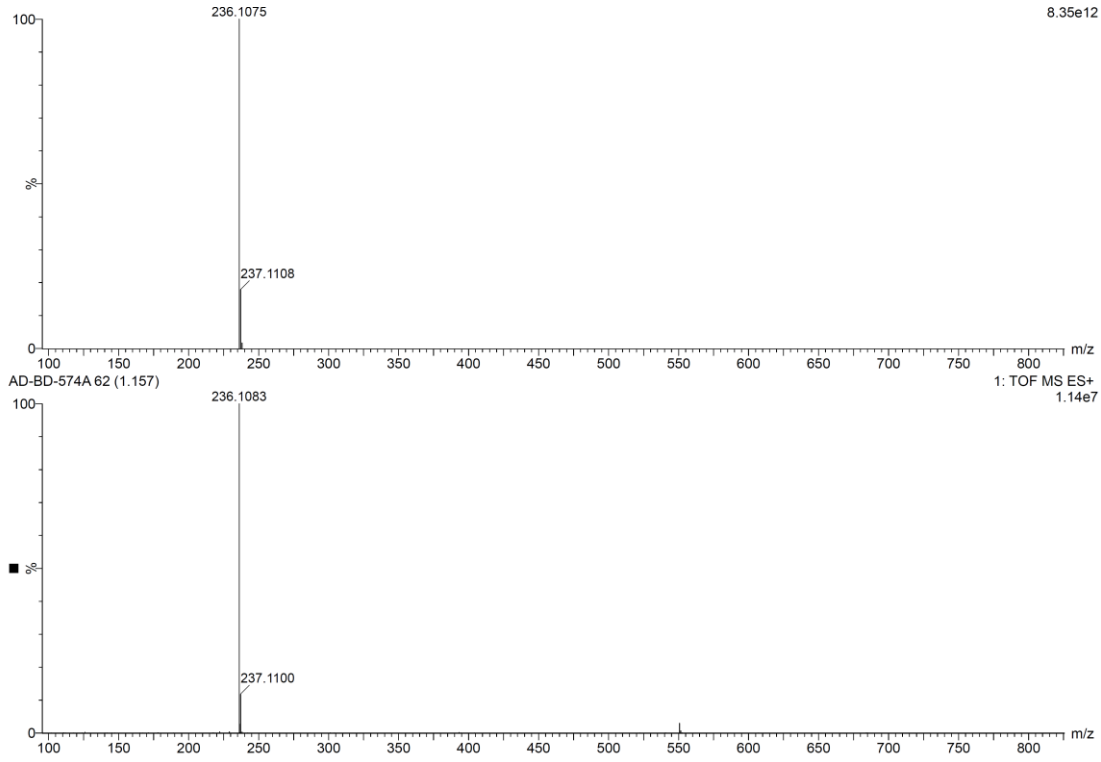


Figure S150. HRMS spectrum of oxazole **5f** measured in methanol, (*top*; theoretical isotopic pattern, *bottom*; calculated isotopic pattern).

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