Copper-Mediated Domino Cyclization/Trifluoromethylation/Deprotection with $TMSCF_3$: Synthesis of 4-Trifluoromethylpyrazoles

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General Experimental. Unless otherwise noted, the domino reactions were carried out open to air in a glass tube with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was done under a UV lamp (254 nm). Organic solutions were concentrated by rotary evaporation at 23-35 °C. Purification of products were generally done by flash column chromatography with Grace Materials Technologies 230-400 mesh silica gel.

Materials. $TMSCF_3$ (98%) was purchased from J&K Scientific. Copper (II) triflate (98%) and potassium fluoride (99%, extra pure) were purchased from Acros. DMF was dried over Solvent Purification System. Terminal alkynes including phenyl acetylene, 4-ethynyltoluene, 1-ethynyl-4-fluorobenzene, 1-ethynyl-2-methylbenzene, 1-ethynyl-4-(trifluoromethyl)benzene, 3-ethynylpyridine and 3-ethynylthiophene were purchased from commercial sources. Other terminal alkynes are known compounds and prepared according to literature procedures.[1] Other chemicals for the substrate preparation were purchased from Acros, J&K Scientific and Aldrich.

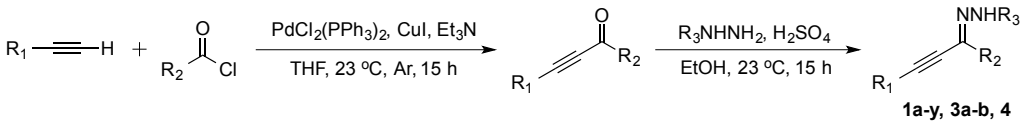
Instrumentation. Proton nuclear magnetic resonance spectra (^1H NMR) spectra, carbon nuclear magnetic resonance spectra (^{13}C NMR) and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 23 °C on a Bruker 400 spectrometer in $CDCl_3$ or Acetone-d_6 (400 MHz for ^1H and 100 MHz for ^{13}C and 376 MHz for ^{19}F). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.26 ppm and Acetone-d_6: 2.05 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak of $CDCl_3$ (77.16 ppm) and Acetone-d_6 (29.84 ppm) on the δ scale. Chemical shifts of ^{19}F NMR are reported as parts per million in δ scale using fluorobenzene (-113.15 ppm) or benzotrifluoride (-63.72 ppm) as internal standards. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br =

[1] TMS-Protected alkynes were prepared *via* Sonogashira coupling of the corresponding halide and trimethylsilylacetylene. Terminal alkynes were prepared by desilylation of the TMS-protected alkynes: U. Dutta, S. Maity, R. Kancherla, D. Maiti, *Org. Lett.* **2014**, *16*, 6302-6305.

broad), and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Thermo Scientific Q Exactive Focus Mass Spectrometer.

Experimental Procedures.

General procedure (A) for the synthesis of *α,β*-alkynic hydrazones:[2-3]



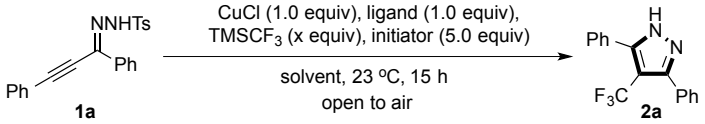
A mixture of acyl chloride (1.2 equiv), $PdCl_2(PPh_3)_2$ (0.02 equiv) and Et_3N (1.2 equiv) in anhydrous THF were stirred for 10 min at 23 °C under argon. CuI (0.04 equiv) was then added and the reaction mixture was stirred for another 10 min. Terminal alkyne (1.0 equiv) was then added in one portion, the resulting mixture was stirred at 23 °C for 15 h. After the reaction was complete, ethyl acetate was added, and the resulting solution was washed with 0.1N HCl in a separatory funnel. After the layers were separated, the organic phase was dried over Na_2SO_4 and evaporated on a rotary evaporator to give the crude product, which was purified by flash chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the corresponding *α, β*-alkynic ketones. Concentrated sulfuric acid (1.1 equiv) was added dropwise to a slurry of *α, β*-alkynic ketone (1.0 equiv) and hydrazine (1.1 equiv) in EtOH at 23 °C. The reaction mixture was stirred at 23 °C for 15 hours. After the reaction was complete, the mixture was concentrated and the crude product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the *α, β*-alkynic hyrazone.

General procedures (B) for the synthesis of 4-trifluoromethylpyrazoles 2 (Figure 1):

In a glove box, to a glass tube equipped with a stir bar was charged $Cu(OTf)_2$ (1.0 equiv), KF (5.0 equiv) and *α, β*-alkynic hydrazone (1.0 equiv). The tube was sealed with a septum and brought out. A solution of $TMSCF_3$ (5.0 equiv) in DMF (1.0 mL) was added into the glass tube in one portion at 23 °C. The reaction mixture was then stirred at 23 °C *under air* for 24 hours, diluted with water and extracted with diethyl ether for two times. The combined organic layers were evaporated to dryness and the crude residue was purified by column chromatography on silica gel using hexane:ethyl acetate as the eluent to afford the 4-trifluoromethylpyrazoles **2**.

[2] M. Zora and A. Kivrak, *J. Org. Chem.* **2011**, *76*, 9379-9390.
[3] J. T. DePinto, W. A. deProphetis, J. L. Menke, and R. J. McMahon, *J. Am. Chem. Soc.*, **2007**, *129*, 2308-2315.

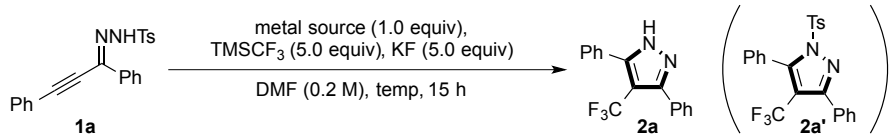
Table S1. Optimization studies for the formation of 2a (*c.f.* Scheme 2, Table 1).



initiator	x	ligand	solvent (concentration)	yield of 2a (%)[a]
CsF	5.0	-	DMF (0.2 M)	<5
TBAF	5.0	-	DMF (0.2 M)	<5
t-BuOK	5.0	-	DMF (0.2 M)	<5
Et_3N	5.0	-	DMF (0.2 M)	<5
NaOAc	5.0	-	DMF (0.2 M)	<5
K_2CO_3	5.0	-	DMF (0.2 M)	19
AgF	5.0	-	DMF (0.2 M)	61
KF	**5.0**	-	**DMF (0.2 M)**	**71**
KF	2.5	-	DMF (0.2 M)	20
KF	5.0	-	DMF (0.05 M)	47
KF	5.0	-	DMF (0.07 M)	60
KF	5.0	-	DMF (0.1 M)	68
KF	5.0	phen	DMF (0.2 M)	<5
KF	5.0	IPr	DMF (0.2 M)	<5
KF	5.0	*t*-Bu-bpy	DMF (0.2 M)	<5
KF	5.0	PPh_3	DMF (0.2 M)	31
KF	5.0	-	DCM (0.2 M)	<5
KF	5.0	-	$CHCl_3$ (0.2 M)	<5
KF	5.0	-	Toluene (0.2 M)	<5
KF	5.0	-	Dioxane (0.2 M)	<5
KF	5.0	-	THF (0.2 M)	<5
KF	5.0	-	MeCN (0.2 M)	14

[a] Yield of **2a** was determined by ^{19}F NMR analysis using benzotrifluoride as the internal standard.

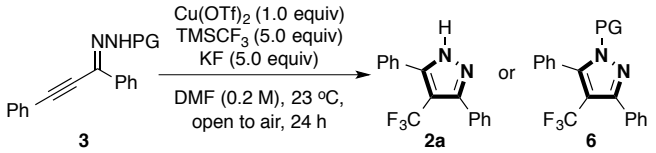
Table S2. Screening of metal sources and conditions for the formation of 2a (*c.f.* Table 1).

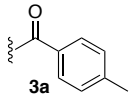
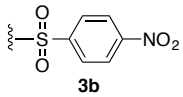
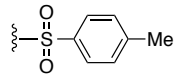


metal source	condition	temperature	yield of 2a (%)[a]
-	Open to air	23 °C	<5
$Cu(OH)_2$	Open to air	23 °C	<5
CuF_2	Open to air	23 °C	<5
$(CuOTf)_2$•benzene	Open to air	23 °C	<5
$Cu(OAc)_2$	Open to air	23 °C	25
CuBr	Open to air	23 °C	28
$CuBr_2$	Open to air	23 °C	44
CuCN	Open to air	23 °C	46
$Cu(CH_3CN)_4PF_6$	Open to air	23 °C	51
CuI	Open to air	23 °C	57
CuTc	Open to air	23 °C	66
CuCl	Open to air	23 °C	71
CuCl	Under argon	23 °C	<5 (19)[b]
$CuCl_2$	Open to air	23 °C	72
CuSCN	Open to air	23 °C	80
$Cu(OTf)_2$	**Open to air**	**23 °C**	**83**
$FeCl_2$	Open to air	23 °C	<5
$FeCl_3$	Open to air	23 °C	<5
FeF_3	Open to air	23 °C	<5
$Fe(OAc)_2$	Open to air	23 °C	<5
$ZnCl_2$	Open to air	23 °C	<5
$ZnBr_2$	Open to air	23 °C	<5
ZnI_2	Open to air	23 °C	<5
$Cu(OTf)_2$	Under argon	23 °C	<5 (46)[b]
$Cu(OTf)_2$	Under argon + Ag_2CO_3 (2.0 equiv)	23 °C	<5 (36)[b]
$Cu(OTf)_2$	Under oxygen	23 °C	73
$Cu(OTf)_2$	Bubbling air	23 °C	33
$Cu(OTf)_2$	Open to air	0 °C	39
$Cu(OTf)_2$	Open to air	50 °C	41

[a] Yield of **2a** was determined by ^{19}F NMR analysis using benzotrifluoride as the internal standard. [b] Yield of **2a'** is shown in the parentheses, determined by ^{19}F NMR analysis.

Table S3. Effects the *N*-protecting groups (*c.f.* Table 1).



PG	yield of 2a (%)[a]	yield of 6 (%)[a]
 3a	80[b]	<5
 3b	75[b]	<5
 3c	<5	37 (**6c**)
 1a	80	<5

[a] Isolated yield. [b] Observed 7% and 12% of **7** from **3a** and **3b**, respectively.

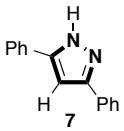
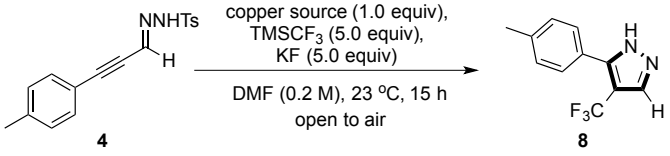


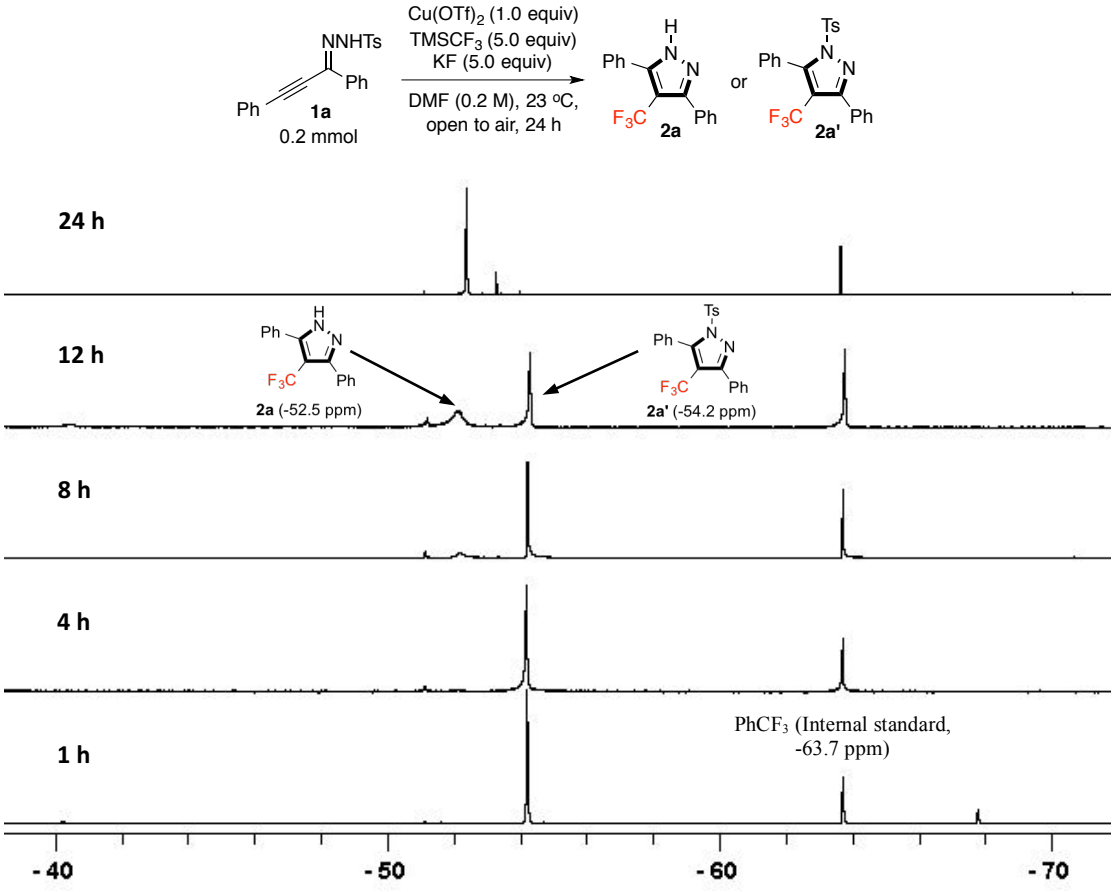
Table S4. Screening of copper sources for the domino reaction using substrate 4 (*c.f.* Scheme 3).



copper source	yield of 8[a]
$(CuOTf)_2$•benzene	<5
$Cu(CH_3CN)_4PF_6$	<5
CuBr	<5
CuI	<5
CuCN	<5
CuCl	18
$CuCl_2$	20
$Cu(OTf)_2$	28
CuTc	47
CuSCN	**63**

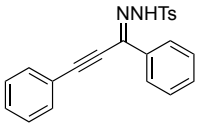
[a] Determined by ^{19}F NMR analysis using benzotrifluoride as the internal standard.

Scheme S1. ^{19}F NMR studies for the formation of 2a *vs.* 2a' over time. (Using $CDCl_3$ as the NMR solvent and benzotrifluoride as the internal standard)



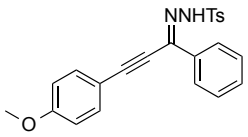
[a] Aliquots of the crude reaction solution were taken for the ^{19}F NMR analysis at various time intervals.

Characterization Data.

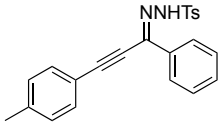


1a: *N'*-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to general procedure (A). Concentrated sulfuric acid (0.74 mL, 13.9 mmol) was added dropwise over 1 min to a slurry of 1,3-diphenylprop-2-yn-1-one (2.6 g, 12.6 mmol) and *p*-toluenesulfonyl hydrazide (2.6 g, 13.9 mmol) in EtOH (60 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1a** as a white solid (4.5 g, 95% yield), R_f = 0.28 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.58 (s, 1H), 7.93 - 7.88 (m, 4H), 7.61 (d, J = 7.6 Hz, 2H), 7.50 - 7.38 (m, 6H), 7.33 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H) ppm; The spectral data are in full accordance with the literature report.[4]

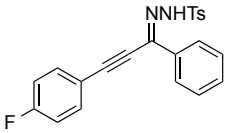
[4] N. Li, B. Li, S. Chen, *Synlett*. **2016**, *76*, 1597-1601.



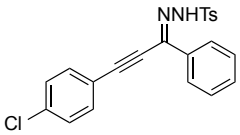
1b: ***N′*-(3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (60 μL, 1.1 mmol) was added dropwise over 1 min to a slurry of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (236 mg, 1.0 mmol) and *p*-toluenesulfonyl hydrazide (205 mg, 1.1 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1b** as a pale yellow solid (320 mg, 80% yield), R_f = 0.26 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.55 (s, 1H), 7.92 - 7.87 (m, 4H), 7.55 (d, J = 8.4 Hz, 2H), 7.39 - 7.37 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 161.4, 144.4, 136.3, 135.6, 134.2, 134.1, 130.2, 129.8, 128.5, 128.1, 126.7, 114.5, 112.2, 105.4, 76.7, 55.6, 21.7; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{20}N_2O_3SNa$ $[M+Na]^+$: 427.1087; found: 427.1082.



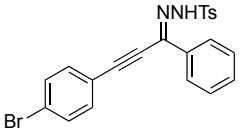
1c: 4-methyl-*N′*-(1-phenyl-3-(*p*-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (41 μL, 0.77 mmol) was added dropwise over 1 min to a slurry of 1-phenyl-3-(*p*-tolyl)prop-2-yn-1-one (154 mg, 0.7 mmol) and *p*-toluenesulfonyl hydrazide (143 mg, 0.77 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1c** as a white solid (232 mg, 85% yield), R_f = 0.34 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.57 (s, 1H), 7.92 - 7.86 (m, 4H), 7.50 (d, J = 8.1Hz, 2H), 7.40 - 7.37 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 2.42 (s 3H), 2.41 (s, 3H); The spectral data are in full accordance with the literature report.[4]



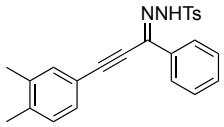
1d: ***N′*-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (58 μL, 1.08 mmol) was added dropwise over 1 min to a slurry of 3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one (220 mg, 0.98 mmol) and *p*-toluenesulfonyl hydrazide (200 mg, 1.08 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1d** as a white solid (320 mg, 83% yield), R_f = 0.18 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.57 (s, 1H), 7.93 - 7.86 (m, 4H), 7.62 - 7.59 (m, 2H), 7.40 - 7.38 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 8.4 Hz, 2H), 2.42 (s, 3H) ppm; The spectral data are in full accordance with the literature report.[4]



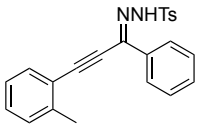
1e: ***N′*-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (50 μL, 0.91 mmol) was added dropwise over 1 min to a slurry of 3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (200 mg, 0.83 mmol) and *p*-toluenesulfonyl hydrazide (170 mg, 0.91 mmol) in EtOH (10 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1e** as a white solid (260 mg, 77% yield), R_f = 0.25 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.65 (s, 1H), 7.92 - 7.90 (m, 2H), 7.89 - 7.84 (m, 2H), 7.54 - 7.52 (m, 2H), 7.41 - 7.37 (m, 5H), 7.32 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H) ppm; The spectral data are in full accordance with the literature report.[4]



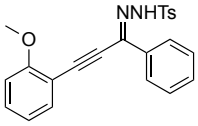
1f: ***N′*-(3-(4-bromophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (24 μL, 0.46 mmol) was added dropwise over 1 min to a slurry of 3-(4-bromophenyl)-1-phenylprop-2-yn-1-one (118 mg, 0.4 mmol) and *p*-toluenesulfonyl hydrazide (85 mg, 0.46 mmol) in EtOH (5 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 16:1 to afford **1f** as a white solid (150 mg, 80% yield), R_f = 0.32 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.55 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.87 - 7.85 (m, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.6, 2H), 7.40 - 7.38 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H) ppm; The spectral data are in full accordance with the literature report.[4]



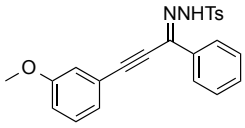
1g: ***N′*-(3-(3,4-dimethylphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (48 μL, 0.89 mmol) was added dropwise over 1 min to a slurry of 3-(3,4-dimethylphenyl)-1-phenylprop-2-yn-1-one (190 mg, 0.81 mmol) and *p*-toluenesulfonyl hydrazide (166 mg, 0.89 mmol) in EtOH (10 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1g** as a off-white solid (217 mg, 67% yield), R_f = 0.35 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.55 (s, 1H), 7.92 - 7.88 (m, 4H), 7.39 - 7.31 (m, 7H), 7.19 (d, J = 7.7 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.4, 140.0, 137.4, 136.2, 135.6, 134.2, 133.3, 130.2, 130.1, 129.9, 129.8, 128.5, 128.1, 126.7, 117.5, 105.5, 76.8, 21.7, 20.1, 19.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{24}H_{22}N_2O_2SNa$ $[M+Na]^+$: 425.1294; found: 425.1293.



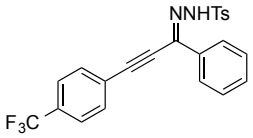
1h: 4-methyl-*N′*-(1-phenyl-3-(*o*-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (38 μL, 0.71 mmol) was added dropwise over 1 min to a slurry of 1-phenyl-3-(*o*-tolyl)prop-2-yn-1-one (143 mg, 0.65 mmol) and *p*-toluenesulfonyl hydrazide (133 mg, 0.71 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1h** as a white solid (184 mg, 73% yield), R_f = 0.36 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.58 (s, 1H), 7.92 - 7.89 (m, 4H), 7.58 (d, J = 7.6 Hz, 1H), 7.40 - 7.36 (m, 4H), 7.34 - 7.30 (m, 3H), 7.28 - 7.24 (m, 1H), 2.54 (s, 3H), 2.41 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.5, 140.9, 136.2, 135.6, 134.1, 132.9, 130.7, 130.3, 130.1, 129.9, 128.6, 128.1, 126.7, 126.2, 120.3, 104.0, 81.1, 21.8, 21.3 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{20}N_2O_2SNa$ $[M+Na]^+$: 411.1138; found: 411.1133.



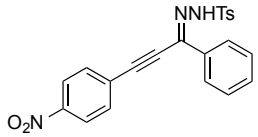
1i: *N′*-(3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (50 μL, 0.93 mmol) was added dropwise over 1 min to a slurry of 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one (200 mg, 0.85 mmol) and *p*-toluenesulfonyl hydrazide (173 mg, 0.93 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1i** as a white solid (242 mg, 71% yield), R_f = 0.22 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 9.47 (s, 1H), 7.93 - 7.88 (m, 4H), 7.53 - 7.44 (m, 2H), 7.41 - 7.37 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 7.05 - 7.00 (m, 2H), 4.16 (s, 3H), 2.40 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 160.8, 144.1, 136.1, 135.8, 133.8, 132.5, 132.3, 130.1, 129.8, 128.5, 127.9, 126.7, 120.9, 110.8, 109.8, 102.4, 83.3, 56.2, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{20}N_2O_3SNa$ $[M+Na]^+$: 427.1087; found: 427.1087.



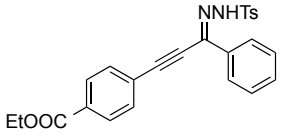
1j: *N′*-(3-(3-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (55 μL, 1.02 mmol) was added dropwise over 1 min to a slurry of 3-(3-methoxyphenyl)-1-phenylprop-2-yn-1-one (220 mg, 0.93 mmol) and *p*-toluenesulfonyl hydrazide (191 mg, 1.02 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1j** as a white solid (285 mg, 76% yield), R_f = 0.23 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.57 (s, 1H), 7.93 - 7.87 (m, 4H), 7.40 - 7.32 (m, 6H), 7.20 (d, J = 7.4 Hz, 1H), 7.11 - 7.10 (m, 1H), 7.03 (dd, J = 8.4 Hz, 2.6 Hz, 1H), 3.86 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 159.6, 144.4, 135.8, 135.5, 134.1, 130.2, 130.0, 129.8, 128.5, 128.0, 126.7, 124.9, 121.2, 117.2, 116.9, 104.6, 77.1, 55.6, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{20}N_2O_3SNa$ $[M+Na]^+$: 427.1087; found: 427.1087.



1k: 4-methyl-*N′*-(1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (47 μL, 0.88 mmol) was added dropwise over 1 min to a slurry of 1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (220 mg, 0.8 mmol) and *p*-toluenesulfonyl hydrazide (160 mg, 0.88 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1k** as a white solid (266 mg, 75% yield), R_f = 0.33 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.56 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.88 - 7.85 (m, 2H), 7.71 (dd, J = 8.5 Hz, 4.8 Hz, 4H), 7.41 - 7.39 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.6, 135.4, 135.2, 133.9, 132.7, 132.0 (q, J_{CF} = 32.4 Hz), 130.4, 129.9, 128.6, 128.1, 126.6, 125.7 (q, J_{CF} = 3.7 Hz), 124.2, 123.7 (q, J_{CF} = 270.8 Hz), 102.5, 79.2, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{18}F_3N_2O_2S$ $[M+H]^+$: 443.1036; found: 443.1031.

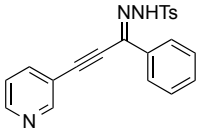


1l: 4-methyl-*N′*-(3-(4-nitrophenyl)-1-phenylprop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (40 μL, 0.74 mmol) was added dropwise over 1 min to a slurry of 3-(4-nitrophenyl)-1-phenylprop-2-yn-1-one (170 mg, 0.68 mmol) and *p*-toluenesulfonyl hydrazide (139 mg, 0.74 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using pure DCM to afford **1l** as a yellow solid (161 mg, 57% yield), R_f = 0.20 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.63 (s, 1H), 8.29 (d, J = 8.8 Hz, 2H), 7.92 (d, J =8.4 Hz, 2H), 7.87 - 7.84 (m, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.42 - 7.40 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.3, 144.7, 135.3, 134.8, 133.7, 133.3, 130.5, 129.9, 128.7, 128.1, 127.0, 126.6, 123.9, 101.5, 81.3, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{22}H_{17}N_3O_4SNa$ $[M+Na]^+$: 442.0832; found: 442.0830.

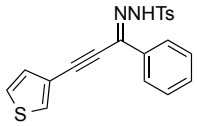


1m: Ethyl-4-(3-phenyl-3-(2-tosylhydrazono)prop-1-yn-1-yl)benzoate. Prepared according to the general procedure (A). Concentrated sulfuric acid (55 μL, 1.02 mmol) was added dropwise over 1 min to a slurry of ethyl 4-(3-oxo-3-phenylprop-1-yn-1-yl)benzoate (260 mg, 0.93 mmol) and *p*-toluenesulfonyl hydrazide (191 mg, 1.02 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1m** as a white solid (317 mg, 76% yield), R_f = 0.13 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.58 (s, 1H), 8.10 (d, J = 6.6 Hz, 2H), 7.93 - 7.86 (m, 4H), 7.67 (d, J = 6.5 Hz, 2H), 7.41 - 7.39 (m, 3H), 7.33 (d, J = 7.9

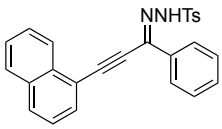
Hz, 2H), 4.42 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.7, 144.6, 135.5, 135.3, 133.9, 132.3, 132.0, 130.4, 129.9, 128.6, 128.1, 126.7, 124.6, 103.4, 79.5, 61.6, 21.8, 14.4 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{25}H_{22}N_2O_4SNa$ $[M+Na]^+$: 469.1193; found: 469.1193.



1n: 4-methyl-*N′*-(1-phenyl-3-(pyridin-4-yl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (63 µL, 1.06 mmol) was added dropwise over 1 min to a slurry of 1-phenyl-3-(pyridin-3-yl)prop-2-yn-1-one (200 mg, 0.96 mmol) and *p*-toluenesulfonyl hydrazide (198 mg, 1.06 mmol) in EtOH (5 mL) at 23 ^oC. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1n** as an off-white solid (250 mg, 69% yield), R_f = 0.03 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.84 (s, 1H), 8.69 (d, *J* = 4.3 Hz, 1H), 8.61 - 8.59 (m, 1H), 7.91 - 7.90 (m, 3H), 7.88 – 7.86 (m, 2H), 7.41 - 7.38 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 152.6, 150.6, 144.6, 139.3, 135.5, 135.1, 133.8, 130.4, 129.9, 128.7, 128.1, 126.7, 123.5, 117.8, 100.8, 80.4, 21.8 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{21}H_{18}N_3O_2S$ $[M+H]^+$: 376.1114; found: 376.1111.

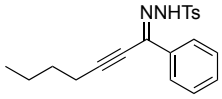


1o: 4-methyl-*N′*-(1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (42 µL, 0.78 mmol) was added dropwise over 1 min to a slurry of 1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-one (151 mg, 0.71 mmol) and *p*-toluenesulfonyl hydrazide (146 mg, 0.78 mmol) in EtOH (5 mL) at 23 ^oC. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1o** as a white solid (170 mg, 63% yield), R_f = 0.23 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.56 (s, 1H), 7.92 - 7.86 (m, 4H), 7.74 - 7.73 (m, 1H), 7.40 - 7.37 (m, 4H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.27 - 7.26 (m, 1H), 2.41 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.5, 135.9, 135.6, 134.1, 132.2, 130.3, 129.9, 129.9, 128.6, 128.1, 126.7, 126.6, 119.4, 99.9, 77.3, 21.8 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{20}H_{17}N_2O_2S_2$ $[M+H]^+$: 381.0726; found: 381.0721.

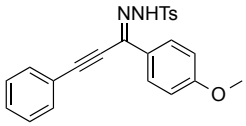


1p: 4-methyl-*N′*-(3-(naphthalen-1-yl)-1-phenylprop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (37 µL, 0.69 mmol) was added dropwise over 1 min to a slurry of 3-(naphthalen-1-yl)-1-phenylprop-2-yn-1-one (160 mg, 0.62 mmol) and *p*-toluenesulfonyl hydrazide (128 mg, 0.69 mmol) in EtOH (5 mL) at 23 ^oC. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1p** as a white solid

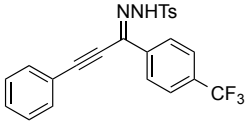
(207 mg, 78% yield), R_f = 0.19 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.00 - 7.92 (m, 6H), 7.87 (dd, J = 7.2 Hz, 1.1 Hz, 1H), 7.68 - 7.57 (m, 2H), 7.55 - 7.51 (m, 1H), 7.43 - 7.40 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.5, 136.1, 135.6, 134.2, 133.3, 133.0, 132.3, 131.3, 130.3, 129.9, 128.9, 128.7, 128.1, 128.0, 127.1, 126.8, 125.6, 125.4, 117.9, 103.1, 81.9, 21.8 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{26}H_{20}N_2O_2SNa$ $[M+Na]^+$: 447.1138; found: 447.1137.



1q: 4-methyl-*N′*-(1-phenylhept-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (21 μL, 0.39 mmol) was added dropwise over 1 min to a slurry of 1-phenylhept-2-yn-1-one (66 mg, 0.35 mmol) and *p*-toluenesulfonyl hydrazide (72 mg, 0.39 mmol) in EtOH (3 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1q** as a white solid (86 mg, 68% yield), R_f = 0.22 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.51 (s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.82 - 7.80 (m, 2H), 7.36 - 7.30 (m, 5H), 2.57 (t, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.70 - 1.63 (m, 2H), 1.54 - 1.45 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.3, 136.5, 135.7, 134.3, 130.1, 129.8, 128.4, 128.0, 126.7, 107.8, 70.1, 30.3, 22.2, 21.7, 19.5, 13.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{20}H_{22}N_2O_2SNa$ $[M+Na]^+$: 377.1294; found: 377.1294.

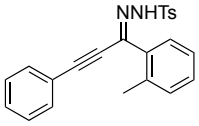


1r: *N′*-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (33 μL, 0.63 mmol) was added dropwise over 1 min to a slurry of 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (135 mg, 0.57 mmol) and *p*-toluenesulfonyl hydrazide (112 mg, 0.63 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **1r** as a white solid (162 mg, 70% yield), R_f = 0.23 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.46 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.85 - 7.81 (m, 2H), 7.62 - 7.59 (m, 2H), 7.50 - 7.41 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 6.92 - 6.88 (m, 2H), 3.84 (s, 3H), 2.41 (s, 3H) ppm; The spectral data are in full accordance with the literature report.[4]

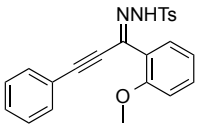


1s: 4-methyl-*N′*-(3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (58 μL, 1.08 mmol) was added dropwise over 1 min to a slurry of 3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (270 mg, 0.98 mmol) and *p*-toluenesulfonyl hydrazide (200 mg, 1.08 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1s** as a white solid (400 mg, 92% yield), R_f = 0.16 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):**

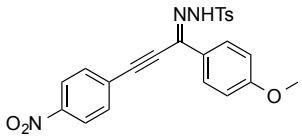
δ 8.68 (s, 1H), 7.99 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 8.4 Hz, 4H), 7.53 - 7.43 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.7, 137.4, 135.4, 134.1, 132.4, 131.7 (q, J_{CF} = 32.4 Hz), 130.8, 129.9, 128.9, 128.1, 126.9, 125.4 (q, J_{CF} = 3.5 Hz), 124.0 (d, J_{CF} = 270.7 Hz), 120.0, 105.5, 76.8, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{17}F_3N_2O_2SNa$ $[M+Na]^+$: 465.0855; found: 465.0855.



1t: 4-methyl-*N′*-(3-phenyl-1-(*o*-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (53 μL, 1.0 mmol) was added dropwise over 1 min to a slurry of 3-phenyl-1-(*o*-tolyl)prop-2-yn-1-one (200 mg, 0.91 mmol) and *p*-toluenesulfonyl hydrazide (186 mg, 1.0 mmol) in EtOH (5 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 16:1 to afford **1t** as a white solid (200 mg, 57% yield), R_f = 0.35 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.65 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.58 - 7.55 (m, 3H), 7.49 - 7.39 (m, 3H), 7.33 (d, J = 8.1 Hz, 2H), 7.29 - 7.25 (m, 3H), 7.23 - 7.19 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.5, 137.1, 136.7, 135.6, 133.5, 132.3, 131.6, 130.5, 129.9, 129.8, 129.4, 128.8, 128.2, 125.9, 120.4, 104.3, 78.7, 21.8, 21.8 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{20}N_2O_2SNa$ $[M+Na]^+$: 411.1138; found: 411.1136.

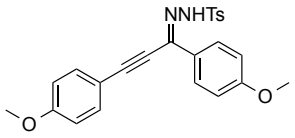


1u: *N′*-(1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (50 μL, 0.93 mmol) was added dropwise over 1 min to a slurry of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (200 mg, 0.85 mmol) and *p*-toluenesulfonyl hydrazide (173 mg, 0.85 mmol) in EtOH (5 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1u** as a white solid (234 mg, 68% yield), R_f = 0.19 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.72 (s, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.54 - 7.51 (m, 3H), 7.45 - 7.31 (m, 6H), 6.98 - 6.91 (m, 2H), 3.84 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 160.8, 144.1, 136.1, 135.8, 133.8, 132.4, 132.3, 130.1, 129.8, 128.5, 127.8, 126.7, 120.9, 110.8, 109.8, 102.4, 83.3, 56.2, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$: 405.1267; found: 405.1262.

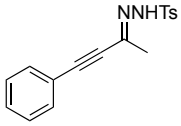


1v: *N′*-(1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (27 μL, 0.51 mmol) was added dropwise over 1 min to a slurry of 1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-one (130 mg, 0.46 mmol) and *p*-toluenesulfonyl hydrazide (95 mg, 0.51 mmol) in EtOH (5 mL) at 23 ^{o}C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 5:1 to afford **1v** as

a yellow solid (150 mg, 72% yield), R_f = 0.21 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.55 (s, 1H), 8.27 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 7.80 - 7.75 (m, 4H), 7.33 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 161.6, 148.4, 144.6, 135.5, 134.7, 133.2, 129.9, 128.2, 128.1, 127.0, 126.4, 124.0, 114.1, 101.1, 81.4, 55.6, 21.8 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{19}N_3O_5SNa$ $[M+Na]^+$: 472.0938; found: 472.0936.



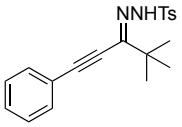
1w: ***N′*-(1,3-bis(4-methoxyphenyl)prop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide.** Prepared according to the general procedure (A). Concentrated sulfuric acid (44 µL, 0.83 mmol) was added dropwise over 1 min to a slurry of 1,3-bis(4-methoxyphenyl)prop-2-yn-1-one (200 mg, 0.75 mmol) and *p*-toluenesulfonyl hydrazide (154 mg, 0.83 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1w** as a light yellow solid (240 mg, 74% yield), R_f = 0.17 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.46 (s, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 2.40 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 161.4, 161.3, 144.3, 136.2, 135.7, 134.1, 129.8, 128.3, 128.1, 127.1, 114.5, 113.9, 112.3, 104.9, 76.7, 55.6, 55.5, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{24}H_{22}N_2O_4SNa$ $[M+Na]^+$: 457.1193; found: 457.1190.



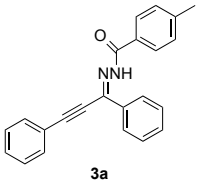
1x: 4-methyl-*N′*-(4-phenylbut-3-yn-2-ylidene)benzenesulfonohydrazide. To a 100 mL round-bottomed flask (RBF) equipped with magnetic stirring under argon at -78 °C were added the phenylacetylene (1.0 g, 10 mmol) and THF (50 mL). *n*-Butyllithium (4.2 mL, 10 mmol, 2.4 mol·L^{-1} solution in hexanes) was slowly added to the solution. The solution was warmed up to 0 °C, stirred at this temperature for 1 hour and then cooled to -78 °C prior to the addition of a solution of $ZnCl_2$ (1.36 g, 1.0 equiv, 10 mmol) in THF (10 mL). The solution was warmed and stirred at 23 °C for additional 15 min and then recooled at -78 °C. Acetyl chloride (0.8 mL, 12 mmol) was added in one portion. The reaction mixture was warmed to 23 °C and stirred for additional 1 hour, then diluted with hexane (15 mL) and washed with brine (3×15 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvents were evaporated and the residue purified by silica gel column chromatography (hexane:ethyl acetate = 50:1) gave the 4-phenylbut-3-yn-2-one as an orange oil (650 mg, 45% yield).[5] Concentrated sulfuric acid (120 µL, 2.2 mmol) was added dropwise over 1 min to a slurry of 4-phenylbut-3-yn-2-one (290 mg, 2 mmol) and *p*-toluenesulfonyl hydrazide (390 mg, 2.1 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **1x** as a white solid (356 mg, 57% yield), R_f = 0.2 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.27 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.52 - 7.49 (m, 2H), 7.46 - 7.37 (m, 3H), 7.32 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 2.15 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.3, 135.6,

[5] L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.,* **2009**, *11*, 3810-3813.

135.2, 132.2, 130.4, 129.7, 128.7, 128.0, 120.3, 102.5, 79.1, 22.9, 21.7 ppm; **HRMS** *m/z* (APCI) calcd. for $C_{17}H_{16}N_2O_2SNa$ $[M+Na]^+$: 335.0825; found: 335.0822.



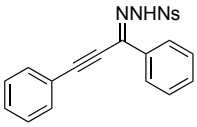
1y: *N′*-(4,4-dimethyl-1-phenylpent-1-yn-3-ylidene)-4-methylbenzenesulfonohydrazide. To a glass tube equipped with a magnetic stirrer bar was first charged with CuI (18.6 mg, 0.1 mmol), TMEDA (37 μL, 0.24 mmol), and pivaloyl chloride (0.73 mL, 5.9 mmol). The glass tube was then sealed with a septum and degassed with argon. Phenylacetylene (500 mg, 5 mmol) and Et_3N (2 mL, 14.7 mmol) were added successively. The mixture was then stirred at 23 °C for 1 h under argon. The reaction was monitored by TLC (hexane:ethyl acetate = 6:1). After the reaction was complete, sat. aqueous $NaHCO_3$ (15 mL) and EtOAc (50 mL) were added. The organic phase was separated and dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was purified by chromatography on silica gel using hexane:ethyl acetate = 100:1 to give 4,4-dimethyl-1-phenylpent-1-yn-3-one as a colorless oil (900 mg, 99% yield).[6] Concentrated sulfuric acid (32 μL, 0.59 mmol) was added dropwise over 1 min to a slurry of 4,4-dimethyl-1-phenylpent-1-yn-3-one (100 mg, 0.54 mmol) and *p*-toluenesulfonyl hydrazide (105 mg, 0.56 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 100:1 to afford **1y** as a white solid (161 mg, 85% yield), R_f = 0.32 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.52 - 7.49 (m, 2H), 7.46 - 7.37 (m, 3H), 7.31 (d, J = 7.4 Hz, 2H), 2.43 (s, 3H), 1.17 (s, 9H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.0, 144.1, 135.5, 132.2, 130.3, 129.5, 128.7, 128.0, 120.5, 104.1, 77.4, 38.1, 28.1, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{20}H_{22}N_2O_2SNa$ $[M+Na]^+$: 377.1294; found: 377.1294.



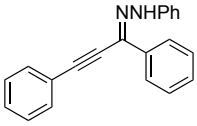
3a

3a: *N′*-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (85 μL, 1.6 mmol) was added dropwise over 1 min to a slurry of 1,3-diphenylprop-2-yn-1-one (300 mg, 1.45 mmol) and *p*-toluic hydrazide (240 mg, 1.6 mmol) in EtOH (10 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 20:1 to afford **3a** as a light yellow solid (285 mg, 58% yield), R_f = 0.23 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.17 (br s, 0.74H), 9.64 (br s, 0.22H), 8.12 (br s, 2H), 7.86 (br s, 2H), 7.65 (d, J = 6.8 Hz, 2H), 7.51 - 7.42 (m, 6H), 7.30 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.0, 143.0, 136.2, 134.2, 132.1, 130.5, 130.2, 129.6, 128.9, 128.5, 127.3, 127.0, 120.4, 105.4, 77.9, 21.6 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{18}N_2ONa$ $[M+Na]^+$: 361.1311; found: 361.1311.

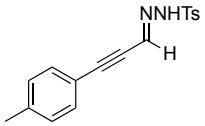
[6] W. Yin, H. He, Y. Zhang, D. Luo, H. He, *Synthesis* **2014**, *46*, 2617-2621.



3b: *N′*-(1,3-diphenylprop-2-yn-1-ylidene)-4-nitrobenzenesulfonohydrazide. Prepared according to the general procedure (A). Concentrated sulfuric acid (28 μL, 0.53 mmol) was added dropwise over 1 min to a slurry of 1,3-diphenylprop-2-yn-1-one (100 mg, 0.48 mmol) and 4-nitrobenzenesulfonohydrazide (120 mg, 0.53 mmol) in EtOH (5 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 to afford **3b** as a light yellow solid (160 mg, 81% yield), R_f = 0.16 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.68 (s, 1H), 8.39 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 7.90 - 7.87 (m, 2H), 7.64 - 7.61 (m, 2H), 7.53 - 7.39 (m, 6H) ppm; **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 150.6, 144.1, 137.4, 133.6, 132.4, 130.8, 130.8, 129.4, 128.9, 128.7, 126.8, 124.4, 120.0, 105.4, 77.1 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{21}H_{15}N_3O_4SNa$ $[M+Na]^+$: 428.0676; found: 428.0675.



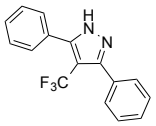
3c: 1-(1,3-diphenylprop-2-yn-1-ylidene)-2-phenylhydrazine. Prepared according to the general procedure (A). A mixture of phenylhydrazine (262 mg, 2.4 mmol) and 1,3-diphenylprop-2-yn-1-one (500 mg, 2.4 mmol) in a glass tube was heated at 80 °C under argon for 5 h. After the reaction was complete, the residue was purified by flash column chromatography on silica gel using hexane as the eluent to afford the desired product **3c** as yellow solid (120 mg, 18% yield). R_f = 0.61 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.73 (s, 1H), 7.99 (d, J = 7.4 Hz, 2H), 7.65 - 7.63 (m, 2H), 7.45 - 7.39 (m, 5H), 7.32 (t, J = 7.3 Hz, 3H), 7.25 - 7.23 (m, 2H), 6.93 (t, J = 7.2 Hz, 1H) ppm; The spectral data are in full accordance with the literature report.[7]



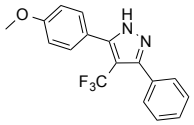
4: 4-methyl-*N′*-(3-(p-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide. 4-Ethynyltoluene (1.2 g, 10 mmol) was dissolved in THF (25 mL) and the solution was cooled to -78 °C under argon. *n*-Butyllithium (4.2 mL, 10 mmol, 2.4 mol·L^{-1} solution in hexanes) was added dropwise and then DMF (1.55 mL, 20 mmol) was added in one portion and the cold bath was removed. The reaction mixture was warmed to 23 °C and stirred at this temperature for 2 hours. The THF solution was poured into a vigourously stirred biphasic solution of 10% aqueous KH_2PO_4 (5.44 g, 40 mmol) and methyl *tert*-butyl ether (MTBE) cooled over ice. The organic extracts were separated, washed with water, dried over Na_2SO_4, filtered and concentrated to dryness. The crude residue was purified by chromatography on silica gel using hexane:ethyl acetate = 100:1 to give 3-(*p*-tolyl)propiolaldehyde as yellow oil (1.26 g, 88% yield).[8] Concentrated sulfuric acid (0.12 mL, 2.29 mmol) was added dropwise over 1 min to a slurry of 3-(*p*-tolyl)propiolaldehyde (300 mg, 2.08 mmol) and *p*-toluenesulfonyl hydrazide (426 mg, 2.29 mmol) in EtOH (8 mL) at 23 °C. The reaction mixture was stirred at the same temperature for 15 hours. The crude product was purified by flash column chromatography on silica gel using

[7] M. Zora, A. Kivrak, and C. Yazici, *J. Org. Chem.* **2011**, *76*, 6726–6742.
[8] M. Journet, D. Cai, L. M. DiMichele, R. D. Larsen, *Tetrahedron Lett.*, **1998**, *39*, 6427-6427.

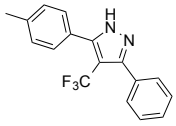
hexane:ethyl acetate = 15:1 to afford **4** as a white solid (200 mg, 31% yield), R_f = 0.30 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.83 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.5, 141.1, 135.4, 132.2, 129.8, 129.5, 128.0, 125.7, 117.1, 103.9, 77.3, 21.8, 21.7 ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{16}N_2O_2SNa$ $[M+Na]^+$: 335.0825; found: 335.0825.



2a: 3,5-diphenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1a** (75.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2a** was obtained as a white solid (46.0 mg, 80% yield), R_f = 0.15 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.69 (d, J = 6.8 Hz, 4H), 7.55 - 7.48 (m, 6H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 148.7, 131.5, 129.9, 129.6, 129.3, 124.8 (q, J_{CF} = 264.9 Hz), 107.0 (q, J_{CF} = 35.8 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{16}H_{12}F_3N_2$ $[M+H]^+$: 289.0947; found: 289.0947.

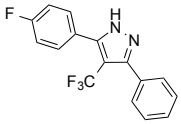


2b: 5-(4-methoxyphenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1b** (81.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2b** was obtained as a white solid (52.6 mg, 83% yield), R_f = 0.11 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.65 (d, J = 6.9 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.53 - 7.46 (m, 3H), 7.08 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 161.4, 149.2, 148.0, 132.1, 130.9, 129.8, 129.6, 129.2, 124.9 (q, J_{CF} = 264.9 Hz), 123.3, 114.8, 106.6 (q, J_{CF} = 34.2 Hz), 55.9 ppm; **^{19}F NMR (376 MHz, Acetone-d_6)**: δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$: 319.1053; found: 319.1052.

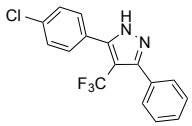


2c: 3-phenyl-5-(*p*-tolyl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1c** (77.7 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2c** was obtained as a pale yellow solid (48.0 mg, 79% yield), R_f = 0.22 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.66 (d, J = 6.6 Hz, 2H), 7.56 - 7.46 (m, 5H), 7.34 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 149.1, 148.5, 141.0, 131.9, 129.9, 129.8, 129.6, 129.5, 129.2, 128.4, 124.5 (q, J_{CF} = 264.9 Hz), 106.8 (q, J_{CF} = 34.0 Hz), 21.3 ppm; **^{19}F NMR (376 MHz, Acetone-d_6)**: δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2$ $[M+H]^+$: 303.1104; found:

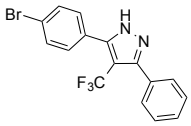
303.1106.



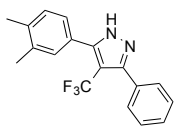
2d: 5-(4-fluorophenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1d** (78.5 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2d** was obtained as a off-white solid (45.0 mg, 74% yield), R_f = 0.17 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.74 - 7.66 (m, 4H), 7.55 - 7.48 (m, 3H), 7.32 - 7.27 (m, 2H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 164.1 (d, J_{CF} = 245.3 Hz), 148.2, 131.8, 131.8, 131.0, 130.1, 129.7, 129.4, 128.3, 124.7 (q, J_{CF} = 264.9 Hz), 116.2 (d, J_{CF} = 21.8 Hz), 107.1 (q, J_{CF} = 35.8 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.6 (s, 3F), -114.58 (m, 1F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{16}H_{11}F_4N_2$ $[M+H]^+$: 307.0853; found: 307.0852.



2e: 5-(4-chlorophenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1e** (81.8 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2e** was obtained as a pale yellow solid (41.0 mg, 64% yield), R_f = 0.21 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.70 - 7.65 (m, 4H), 7.57 - 7.49 (m, 5H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 148.3, 147.9, 135.4, 131.3, 130.9, 130.7, 130.2, 129.7, 129.4, 129.4, 124.6 (q, J_{CF} = 265.0 Hz), 107.1 (q, J_{CF} = 35.8 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6)**: δ -52.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{16}H_{11}ClF_3N_2$ $[M+H]^+$: 323.0557; found: 323.0560.

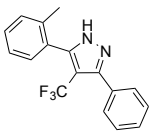


2f: 5-(4-bromophenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1f** (90.7 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2f** was obtained as a white solid (49.4 mg, 67% yield), R_f = 0.20 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.73 - 7.70 (m, 2H), 7.67 - 7.61 (m, 4H), 7.56 - 7.49 (m, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.4, 147.9, 132.4, 131.5, 131.4, 130.7, 130.2, 129.7, 129.4, 124.6 (q, J_{CF} = 265.0 Hz), 123.6, 107.1 (q, J_{CF} = 36.2 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{16}H_{11}BrF_3N_2$ $[M+H]^+$: 367.0052; found: 367.0053.

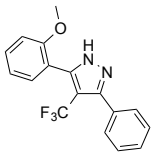


2g: 5-(3,4-dimethylphenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the

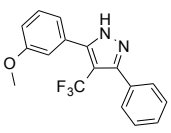
general procedure (B). Reaction was run using **1g** (80.5 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2g** was obtained as a yellow oil (51.4 mg, 81% yield), R_f = 0.29 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.66 (d, J = 6.6 Hz, 2H), 7.53 - 7.43 (m, 4H), 7.37 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 149.3, 148.2, 138.7, 137.5, 132.2, 130.6, 130.5, 129.7, 129.6, 129.2, 128.6, 127.1, 124.8 (q, J_{CF} = 264.8 Hz), 106.8 (q, J_{CF} = 35.7 Hz), 19.8, 19.6 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.4 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{18}H_{16}F_3N_2$ $[M+H]^+$: 317.1260; found: 317.1262.



2h: 3-phenyl-5-(*o*-tolyl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1h** (77.7 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2h** was obtained as a pale yellow solid (37.0 mg, 61% yield), R_f = 0.31 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.72 (d, J = 6.8 Hz, 2H), 7.54 - 7.46 (m, 3H), 7.42 - 7.36 (m, 3H), 7.32 - 7.29 (m 1H), 2.26 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.8, 146.6, 138.2, 132.1, 131.1, 130.9, 130.3, 129.7, 129.4, 129.4, 129.3, 126.4, 124.7 (q, J_{CF} = 264.9 Hz), 108.2 (q, J_{CF} = 35.1 Hz), 19.8 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -53.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2$ $[M+H]^+$: 303.1104; found: 303.1103.

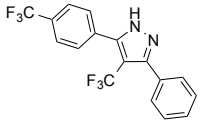


2i: 5-(2-methoxyphenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1i** (81.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2i** was obtained as a pale yellow oil (41.5 mg, 65% yield), R_f = 0.13 (hexane: ethyl acetate = 4: 1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.71 (d, J = 7.2 Hz, 2H), 7.52 - 7.42 (m, 5H), 7.16 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 158.4, 149.4, 143.6, 132.8, 131.9, 131.9, 129.5, 129.3, 129.2, 124.8 (q, J_{CF} = 264.8 Hz), 121.1, 119.7, 112.0, 108.4 (q, J_{CF} = 35.5 Hz), 55.8 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -54.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$: 319.1053; found: 319.1051.

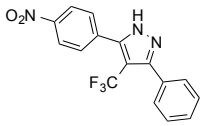


2j: 5-(3-methoxyphenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1j** (81.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified

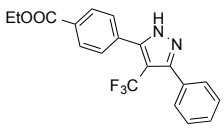
by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2j** was obtained as a pale yellow oil (47.4 mg, 75% yield), R_f = 0.17 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.68 - 7.66 (m, 2H), 7.55 - 7.41 (m, 4H), 7.25 - 7.23 (m, 2H), 7.08 - 7.05 (m, 1H), 3.89 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 160.6, 148.7, 148.4, 132.7, 131.6, 130.4, 129.9, 129.7, 129.3, 124.7 (q, J_{CF} = 264.9 Hz), 121.9, 115.5, 115.1, 107.0 (q, J_{CF} = 35.9 Hz), 55.6 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$: 319.1053; found: 319.1050.



2k: 3-phenyl-4-(trifluoromethyl)-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1k** (88.5 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2k** was obtained as an off-white solid (47.8 mg, 67% yield), R_f = 0.26 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.93 - 7.87 (q, J = 8.4 Hz, 4H), 7.68 - 7.66 (m, 2H), 7.58 - 7.53 (m, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.7, 147.6, 136.5, 131.1 (q, J_{CF} = 32.1 Hz), 130.4, 130.3, 130.2, 129.8, 129.5, 126.2 (q, J_{CF} = 3.8 Hz), 124.9 (q, J_{CF} = 269.8 Hz), 124.3 (q, J_{CF} = 265.0 Hz), 107.4 (q, J_{CF} = 35.7 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -50.5 (s, 3F), -61.7 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{11}F_6N_2$ $[M+H]^+$: 357.0821; found: 357.0821.

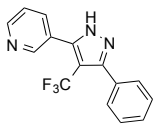


2l: 5-(4-nitrophenyl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1l** (62.9 mg, 0.15 mmol), $Cu(OTf)_2$ (54.2 mg, 0.15 mmol), KF (43.5 mg, 0.75 mmol), $TMSCF_3$ (107.0 mg, 0.75 mmol) and DMF (0.75 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 4:1). Compound **2l** was obtained as a pale yellow solid (33.8 mg, 68% yield), R_f = 0.20 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 8.39 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.68 - 7.66 (m, 2H), 7.56 - 7.55 (m, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 149.0, 148.5, 147.3, 139.1, 130.6, 130.6, 129.8, 129.7, 129.5, 124.5 (q, J_{CF} = 264.9 Hz), 124.4, 107.6 (q, J_{CF} = 33.5 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{16}H_{11}F_3N_3O_2$ $[M+H]^+$: 334.0798; found: 334.0792.

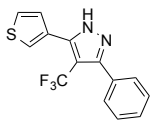


2m: Ethyl 4-(3-phenyl-4-(trifluoromethyl)-1*H*-pyrazol-5-yl)benzoate. Prepared according to the general procedure (B). Reaction was run using **1m** (89.3 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2m** was obtained as an off-white solid (48.0 mg, 67% yield), R_f = 0.20 (hexane: ethyl acetate = 4: 1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 8.16 - 8.14 (d, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.70 - 7.67 (m, 2H), 7.57 - 7.50 (m, 3H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR (100 MHz,**

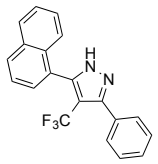
Acetone-d_6): δ 166.3, 148.8, 147.9, 136.6, 131.7, 130.5, 130.3, 130.2, 129.7, 129.4, 129.3, 124.6 (q, J_{CF} = 265.0 Hz), 107.4 (q, J_{CF} = 35.9 Hz), 61.7, 14.6 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{19}H_{16}F_3N_2O_2$ $[M+H]^+$: 361.1158; found: 361.1155.



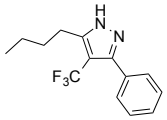
2n: 3-(3-phenyl-4-(trifluoromethyl)-1*H*-pyrazol-5-yl)pyridine. Prepared according to the general procedure (B). Reaction was run using **1n** (75.1 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 1:1). Compound **2n** was obtained as a white solid (15.0 mg, 26% yield), R_f = 0.45 (hexane:ethyl acetate = 1:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 8.87 - 8.86 (m, 1H), 8.68 (dd, J = 4.8 Hz, 1.7 Hz, 1H), 8.04 (dt, J = 7.9 Hz, 2.0 Hz, 1H), 7.68 - 7.66 (m, 2H), 7.58 - 7.51 (m, 4H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 150.8, 150.1, 147.6, 147.0, 136.8, 130.4, 130.3, 129.7, 129.5, 128.5, 124.6 (q, J_{CF} = 264.9 Hz), 124.2, 107.5 (q, J_{CF} = 35.9 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.7 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{15}H_{11}F_3N_3$ $[M+H]^+$: 290.0900; found: 290.0900.



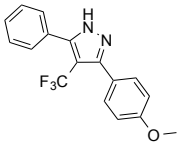
2o: 3-phenyl-5-(thiophen-3-yl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1o** (76.1 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2o** was obtained as a pale yellow solid (46.1 mg, 78% yield), R_f = 0.26 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.82 - 7.81 (m, 1H), 7.64 - 7.62 (m, 3H), 7.54 - 7.47 (m, 4H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.4, 144.0, 131.7, 131.4, 129.9, 129.7, 129.2, 128.5, 127.0, 125.8, 124.4 (q, J_{CF} = 264.9 Hz), 106.6 (q, J_{CF} = 34.5 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -53.2 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{14}H_{10}F_3N_2S$ $[M+H]^+$: 295.0511; found: 295.0512.



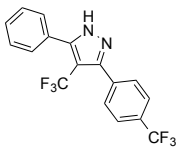
2p: 5-(naphthalen-1-yl)-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1p** (84.9 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2p** was obtained as a yellow oil (36.0 mg, 53% yield), R_f = 0.39 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 8.09 - 8.01 (m, 2H), 7.81 - 7.78 (m, 3H), 7.68 - 7.62 (m, 2H), 7.61 - 7.49 (m, 5H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.7, 146.3, 134.4, 133.3, 131.9, 130.5, 129.9, 129.5, 129.4, 129.2, 129.1, 128.9, 127.6, 127.1, 126.1, 125.9, 124.6 (q, J_{CF} = 264.9 Hz), 109.3 (q, J_{CF} = 35.4 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -54.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{20}H_{14}F_3N_2$ $[M+H]^+$: 339.1104; found: 339.1106.



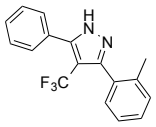
2q: 5-butyl-3-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1q** (70.9 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2q** was obtained as a pale yellow solid (21.5 mg, 40% yield), R_f = 0.24 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.61 - 7.59 (m, 2H), 7.48 - 7.41 (m, 3H), 2.84 (t, J = 7.9 Hz, 2H), 1.75 - 1.68 (m, 2H), 1.47 - 1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 149.0, 148.2, 132.6, 129.5, 129.4, 129.1, 125.1 (q, J_{CF} = 264.4 Hz), 106.7 (q, J_{CF} = 35.6 Hz), 32.2, 26.2, 23.0, 14.0 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -53.7 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{14}H_{16}F_3N_2$ $[M+H]^+$: 269.1260; found: 269.1261.



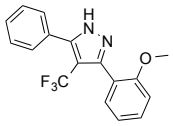
2r: 3-(4-methoxyphenyl)-5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1r** (81.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2r** was obtained as an off-white solid (52.0 mg, 82% yield), R_f = 0.10 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.67 - 7.65 (m, 2H), 7.62 - 7.59 (m, 2H), 7.53 - 7.46 (m, 3H), 7.10 - 7.06 (m, 2H), 3.87 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 161.4, 149.2, 148.0, 132.1, 130.9, 129.8, 129.6, 129.2, 124.9 (q, J_{CF} = 264.8 Hz), 123.3, 106.6 (q, J_{CF} = 35.6 Hz), 55.7 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$: 319.1053; found: 319.1054.



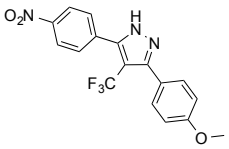
2s: 5-phenyl-4-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1s** (88.5 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2s** was obtained as a white solid (42.5 mg, 60% yield), R_f = 0.17 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.90 (q, J = 9.5 Hz, 4H), 7.69 - 7.67 (m, 2H), 7.58 - 7.51 (m, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.7, 147.6, 136.5, 131.1 (q, J_{CF} = 32.1 Hz), 130.4, 130.3, 130.2, 129.8, 129.5, 126.2 (q, J_{CF} = 3.8 Hz), 125.3 (q, J_{CF} = 269.8 Hz), 124.6 (q, J_{CF} = 265.0 Hz), 107.4 (q, J_{CF} = 36.1 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -50.5 (s, 3F), -61.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{11}F_6N_2$ $[M+H]^+$: 357.0821; found: 357.0821.



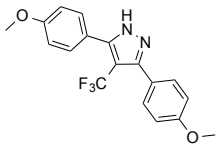
2t: 5-phenyl-3-(o-tolyl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1t** (77.7 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2t** was obtained as a pale yellow solid (46.0 mg, 76% yield), R_f = 0.25 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.74 - 7.72 (d, J = 7.1 Hz, 2H), 7.54 - 7.46 (m, 3H), 7.42 - 7.29 (m, 4H), 2.26 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 148.9, 147.0, 138.2, 132.2, 131.1, 130.9, 130.2, 129.4, 129.4, 129.3, 126.4, 124.7 (q, J_{CF} = 264.9 Hz), 108.2 (q, J_{CF} = 35.3 Hz), 19.8 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -53.7 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2$ $[M+H]^+$: 303.1104; found: 303.1108.



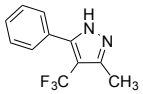
2u: 3-(2-methoxyphenyl)-5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1u** (81.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2u** was obtained as a pale yellow oil (45.8 mg, 72% yield), R_f = 0.13 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.73 - 7.70 (m, 2H), 7.53 - 7.42 (m, 5H), 7.16 (d, J = 8.2 Hz, 1H), 7.07 (td, J = 7.5 Hz, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 158.4, 149.4, 143.7, 132.8, 131.9, 131.9, 129.5, 129.3 (q, J_{CF} = 5.8 Hz), 129.2, 124.8 (q, J_{CF} = 264.7 Hz), 121.1, 119.6, 112.0, 108.3 (q, J_{CF} = 35.6 Hz), 55.8 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -54.5 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$: 319.1053; found: 319.1053.



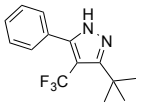
2v: 3-(4-methoxyphenyl)-5-(4-nitrophenyl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1v** (89.9 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 4:1). Compound **2v** was obtained as a pale yellow solid (42.0 mg, 58% yield), R_f = 0.08 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 8.38 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 161.9, 148.9, 146.9, 139.5, 131.1, 130.6, 129.4, 124.6 (q, J_{CF} = 265.0 Hz), 124.3, 121.5, 115.0, 107.1 (q, J_{CF} = 37.9 Hz), 55.8 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{17}H_{13}F_3N_3O_3$ $[M+H]^+$: 364.0904; found: 364.0899.



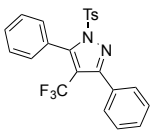
2w: 3,5-bis(4-methoxyphenyl)-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1w** (87.0 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 5:1). Compound **2w** was obtained as a white solid (55.4 mg, 80% yield), R_f = 0.27 (hexane:ethyl acetate = 2:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.59 (d, J = 8.5 Hz, 4H), 7.06 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 161.3, 148.5, 130.9, 125.0 (q, J_{CF} = 264.9 Hz), 123.9, 114.7, 106.3 (q, J_{CF} = 35.1 Hz), 55.7 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.6 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{18}H_{16}F_3N_2O_2$ $[M+H]^+$: 349.1158; found: 349.1154.



2x: 3-methyl-5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1x** (62.5 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2x** was obtained as a pale yellow solid (15.0 mg, 33% yield), R_f = 0.15 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.62 - 7.60 (m, 2H), 7.48 - 7.41 (m, 3H), 2.45 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 149.0, 144.0, 132.4, 129.5, 129.3, 129.2, 125.3 (q, J_{CF} = 264.1 Hz), 107.2 (q, J_{CF} = 35.6 Hz), 11.52 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -54.1 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{11}H_{10}F_3N_2$ $[M+H]^+$: 227.0791; found: 227.0792.

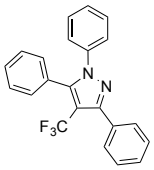


2y: 3-(tert-butyl)-5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **1y** (70.9 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 10:1). Compound **2y** was obtained as a white solid (27.0 mg, 50% yield), R_f = 0.29 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.51 - 7.51 (m, 5H), 1.46 (s, 9H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6):** δ 132.6, 129.9, 129.5, 129.0, 125.2 (q, J_{CF} = 264.6 Hz), 106.1 (q, J_{CF} = 36.1 Hz), 33.7, 30.2 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -49.8 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{14}H_{16}F_3N_2$ $[M+H]^+$: 269.1260; found: 269.1263.

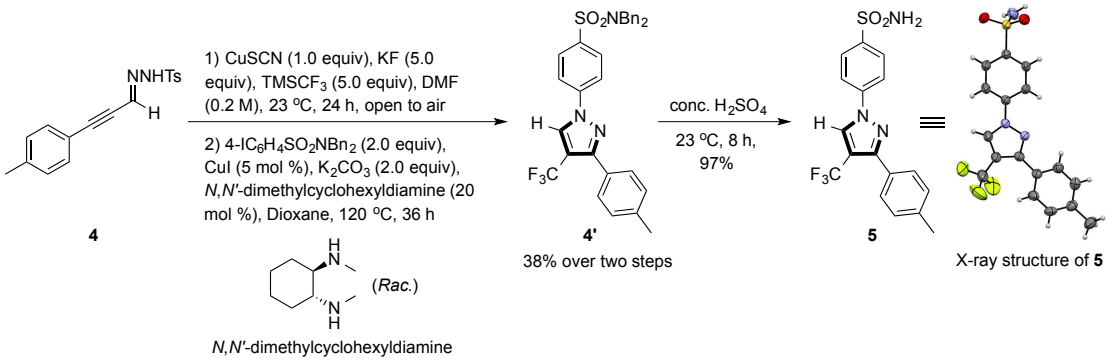


2a': 3,5-diphenyl-1-tosyl-4-(trifluoromethyl)-1*H*-pyrazole. A solution of compound **2a** (100 mg, 0.35 mmol), TsCl (73 mg, 0.38 mmol) and Et_3N (63 µL, 0.45 mmol) was stirred at 23 ^oC for 15 hours.

The crude product was purified by flash column chromatography (hexane:ethyl acetate = 40:1) to provide the compound **2a'** as a white solid (120.0 mg, 78% yield). R_f = 0.41 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.74 - 7.70 (m, 2H), 7.66 - 7.58 (m, 3H), 7.56 - 7.49 (m, 5H), 7.47 - 7.44 (m, 4H), 2.43 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 153.0 (q, J = 1.4 Hz), 148.3 (q, J = 3.2 Hz), 147.8, 135.0, 131.7, 131.1, 131.0, 130.5, 129.6 (q, J = 1.0 Hz), 129.3, 129.2, 129.0, 128.7, 128.1, 123.0 (q, J_{CF} = 266.9 Hz), 113.4 (q, J_{CF} = 35.5 Hz), 21.6 ppm; **^{19}F NMR (376 MHz, Acetone-d_6)**: δ -54.1 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{23}H_{17}F_3N_2O_2SNa$ $[M+Na]^+$: 465.0855; found: 465.0855.



6c (*c.f.* Table S3): 1,3,5-triphenyl-4-(trifluoromethyl)-1*H*-pyrazole. Prepared according to the general procedure (B). Reaction was run using **3c** (59.3 mg, 0.2 mmol), $Cu(OTf)_2$ (72.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol), $TMSCF_3$ (142.2 mg, 1.0 mmol) and DMF (1.0 mL). The product was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 80:1). Compound **6c** was obtained as an off-white solid (26.9 mg, 37% yield), R_f = 0.63 (hexane:ethyl acetate = 4:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 7.78 - 7.76 (d, J = 7.2 Hz, 2H), 7.54 - 7.43 (m, 8H), 7.39 - 7.35 (m, 5H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 151.0, 145.2, 140.0, 133.1, 131.2, 130.4, 129.7, 129.6, 129.5, 129.5, 129.3, 129.2, 129.1, 126.6, 124.2 (q, J_{CF} = 265.5 Hz), 110.2 (q, J_{CF} = 35.4 Hz) ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -52.8 (s, 3F) ppm; **HRMS** *m/z* (ESI) calcd. for $C_{22}H_{15}F_3N_2Na$ $[M+Na]^+$: 387.1080; found: 387.1078.



In a glove box, to a glass tube equipped with a stir bar was charged CuSCN (24.3 mg, 0.2 mmol), KF (58.1 mg, 1.0 mmol) and **4** (45.2 mg, 0.2 mmol). The tube was sealed with a septum and brought out. A solution of $TMSCF_3$ (142.2 mg, 1.0 mmol) in DMF (1.0 mL) was added in one portion at 23 °C. The reaction mixture was then stirred at 23 °C *under air* for 24 hours, diluted with water and extracted with diethyl ether for two times. The combined organic layers were evaporated to dryness and the crude residue was passed through a short pad of silica gel to afford the crude cyclized 4-CF_3 pyrazole precursor **8** (20 mg, *c.f.* Table S4) as an off-white solid. Without further purification, to a 10 mL round-bottom flask were added CuI (1.9 mg, 0.01 mmol), pyrazole precursor **8** (20 mg), *N,N*-dibenzyl-4-iodobenzenesulfonamide[9] (185 mg, 0.4 mmol), K_2CO_3 (55 mg, 0.4 mmol) and a

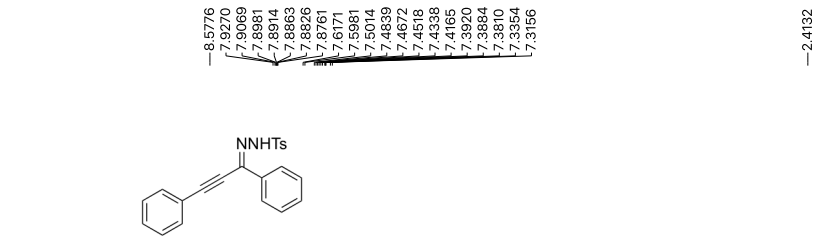
[9] The *N, N*-dibenzyl-4-iodobenzenesulfonamide was prepared according to literature procedure: S. M. Gaulier, R. McKay, N. A. Swain, *Tetrahedron Lett.* **2011**, *52*, 6000-6002.

magnetic stir bar. The round-bottom flask was sealed with a rubber septum, evacuated and back-filled with argon for three times. A solution of *N,N'*-dimethylcyclohexyldiamine[10] (5.7 mg, 0.04 mmol) in 0.5 mL dioxane was then added under argon. The flask was sealed and the reaction mixture was stirred at 120 °C for 36 h,[11] then cooled to 23 °C, and dioxane was removed by rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel (hexane:ethyl acetate = 20:1) to provide product **4'** (43.2 mg, 38% yield over two steps) as a white solid. R_f = 0.32 (hexane:ethyl acetate = 6:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.29 (s, 1H), 7.86 (q, J = 8.2 Hz, 4H), 7.66 (d, J = 7.9 Hz, 5H), 7.21 - 7.19 (m, 7H), 7.06 - 7.04 (m, 4H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 151.6, 141.9, 139.6, 139.5, 135.4, 129.5, 129.0, 128.7, 128.2, 128.0, 122.7 (q, J_{CF} = 265.5 Hz), 119.3, 113.9 (q, J_{CF} = 37.3 Hz), 50.7, 21.5 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -56.5 (s, 3F) ppm; **HRMS** *m/z* (APCI) calcd. for $C_{31}H_{26}F_3N_3O_2SNa$ $[M+Na]^+$: 584.1590; found: 584.1588.

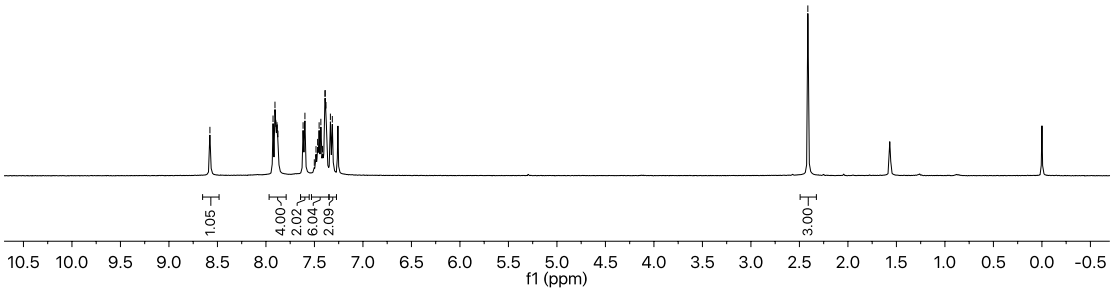
Compound **4'** (43.2 mg, 0.077 mmol) and concentrated H_2SO_4 (1 mL) were added to a 10 mL round-bottom flask with a magnetic stir bar. The reaction mixture was stirred at 23 °C for 8 h.[11] The mixture was then added carefully to water before extracting with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and then concentrated by rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel using hexane: ethyl acetate = 1:1 to afford product **5** (28.5 mg, 97% yield) as a white solid. R_f = 0.42 (hexane:ethyl acetate = 2:1). **^{1}H NMR (400 MHz, Acetone-d_6):** δ 9.06 (s, 1H), 8.19 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.76 (br s, 1H), 2.40 (s, 3H) ppm; **^{13}C NMR (100 MHz, Acetone-d_6)**: δ 151.5, 143.7, 142.3, 140.1, 131.2 (q, J_{CF} = 3.7 Hz), 130.1, 129.2, 128.8, 128.6, 124.0 (q, J_{CF} = 264.6 Hz), 120.1, 113.3 (q, J_{CF} = 37.0 Hz), 21.3 ppm; **^{19}F NMR (376 MHz, Acetone-d_6):** δ -56.2 (s, 3F) ppm; **HRMS** *m/z* (APCI) calcd. for $C_{17}H_{15}F_3N_3O_2S$ $[M+H]^+$: 382.0832; found: 382.0830. The structure of **5** was confirmed by X-ray crystallography (CCDC 1525831).

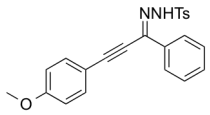
[10] The *N, N'*-dimethylcyclohexyldiamine was prepared according to literature procedure: N. Duguet, A. Donaldson, S.M. Leckie, J. Douglas, P. Shapland, T. B. Brown, G. Churchill, A. M. Z. Slawin, A. D. Smith, *Tetrahedron: Asymmetry* **2010**, *21*, 582-600.
[11] For literature procedures for the synthesis of Celecoxib, see: (a) F. Li, J. Nie, L. Sun, Y. Zheng, J. Ma, *Angew. Chem. Int. Ed.* **2013**, *52*, 6255-6258. (b) Y. Wang, J. Han, J. Chen, W. Cao, *Tetrahedron* **2015**, *71*, 8256-8262

Spectra

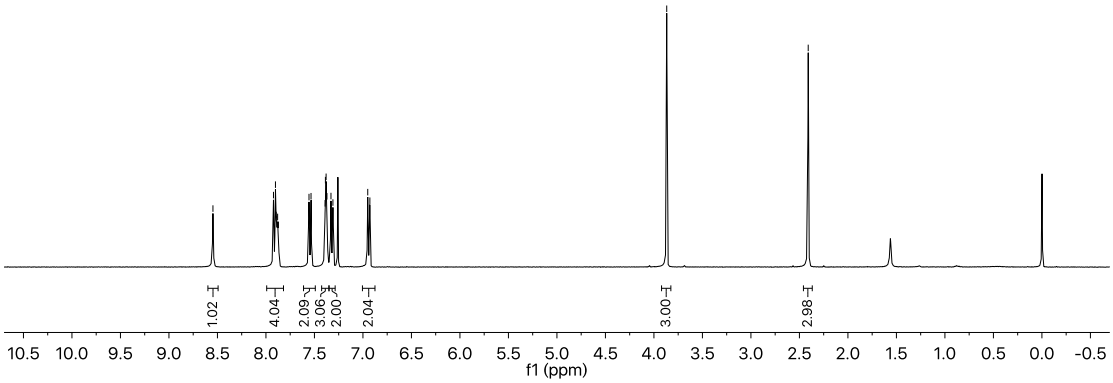


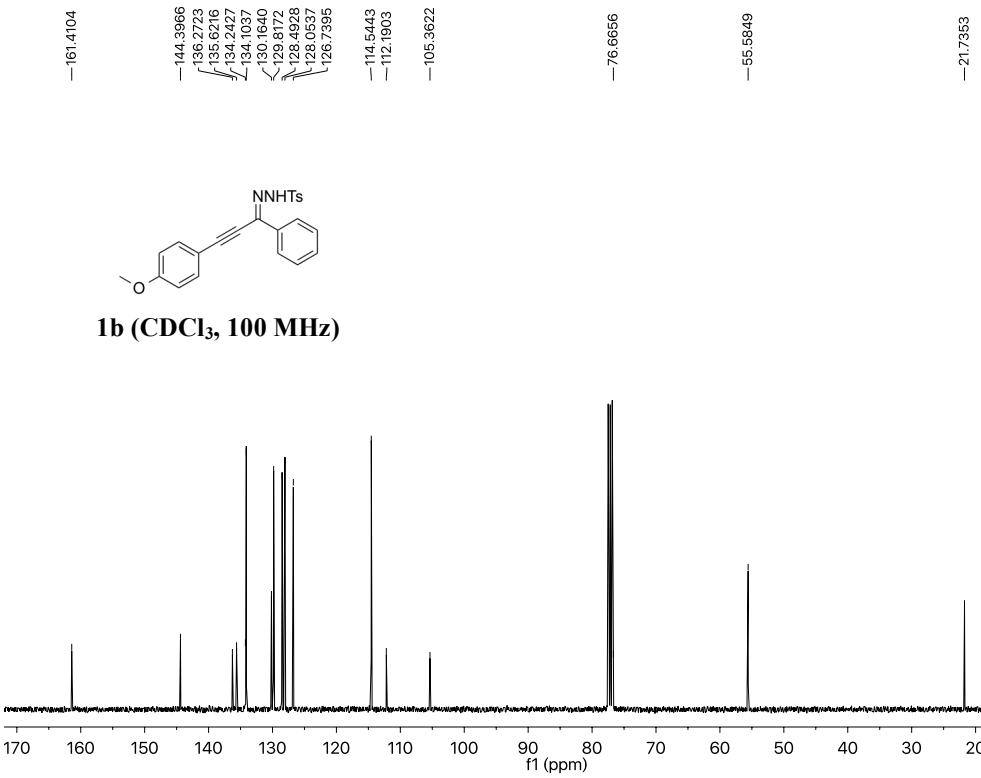
1a ($CDCl_3$, 400 MHz)



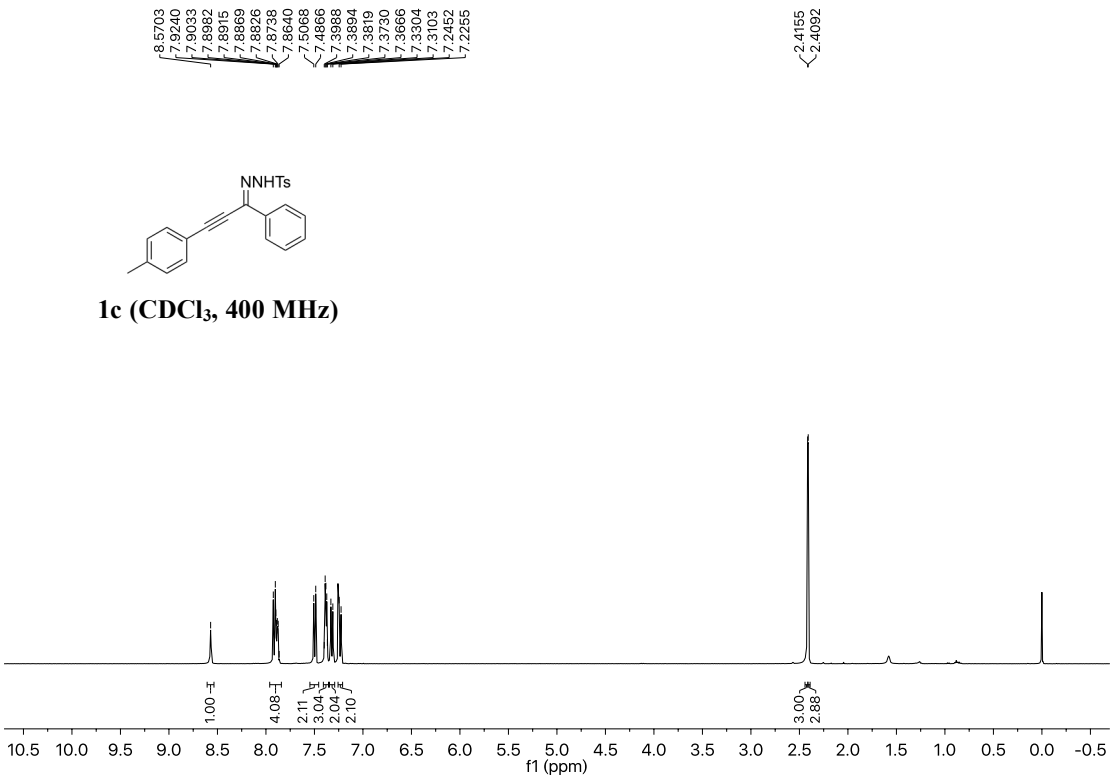


1b ($CDCl_3$, 400 MHz)





1b ($CDCl_3$, 100 MHz)



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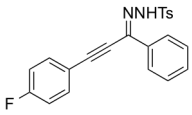

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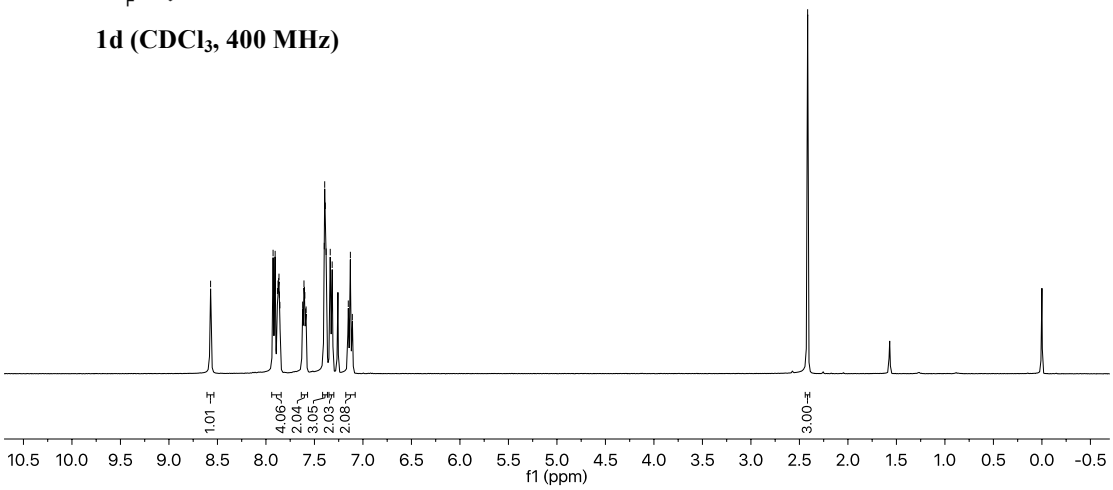

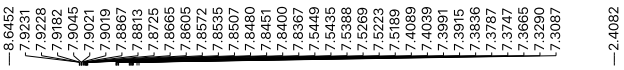

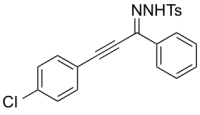

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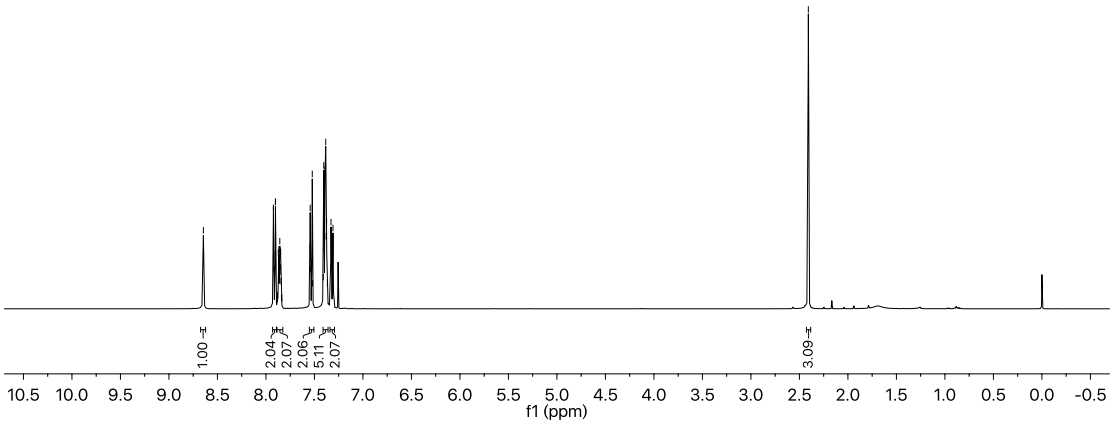

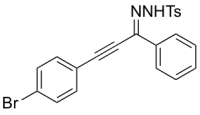

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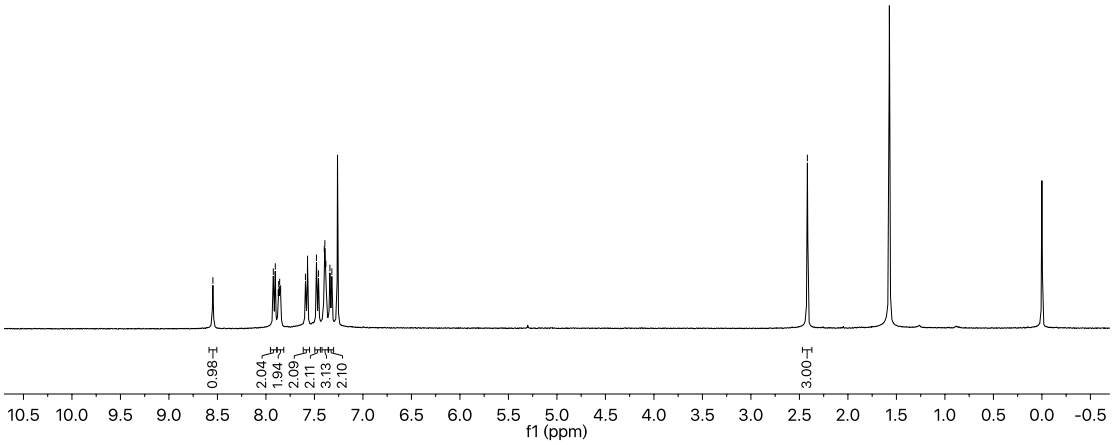

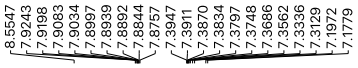

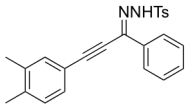

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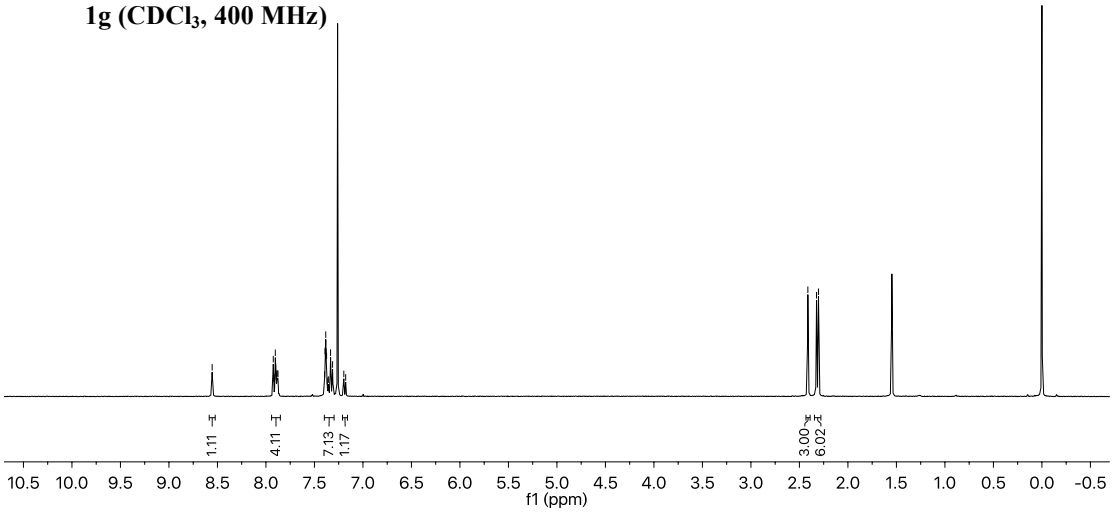
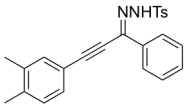
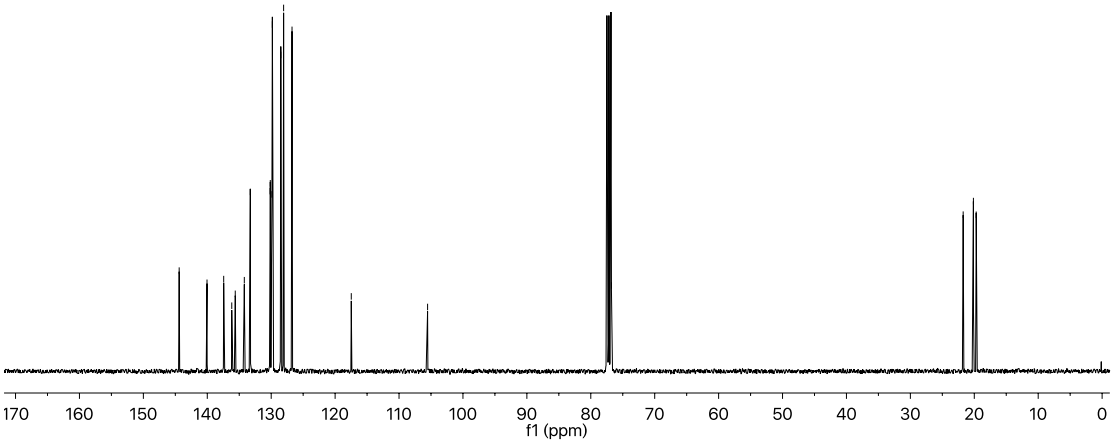
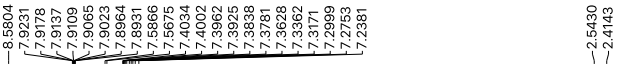
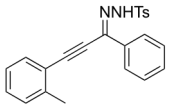




1g ($CDCl_3$, 100 MHz)







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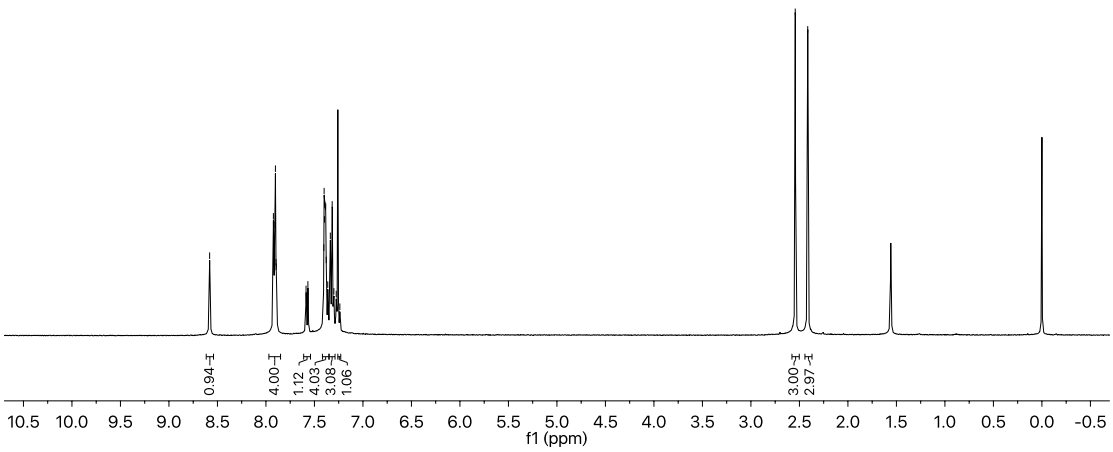

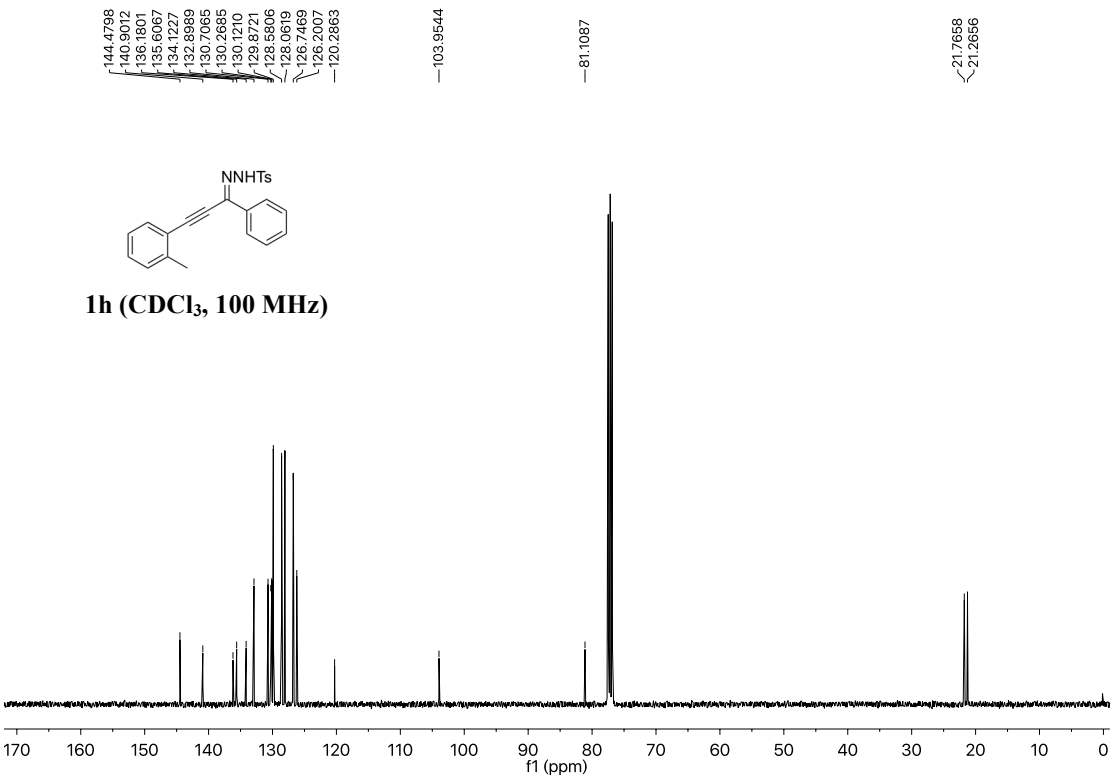

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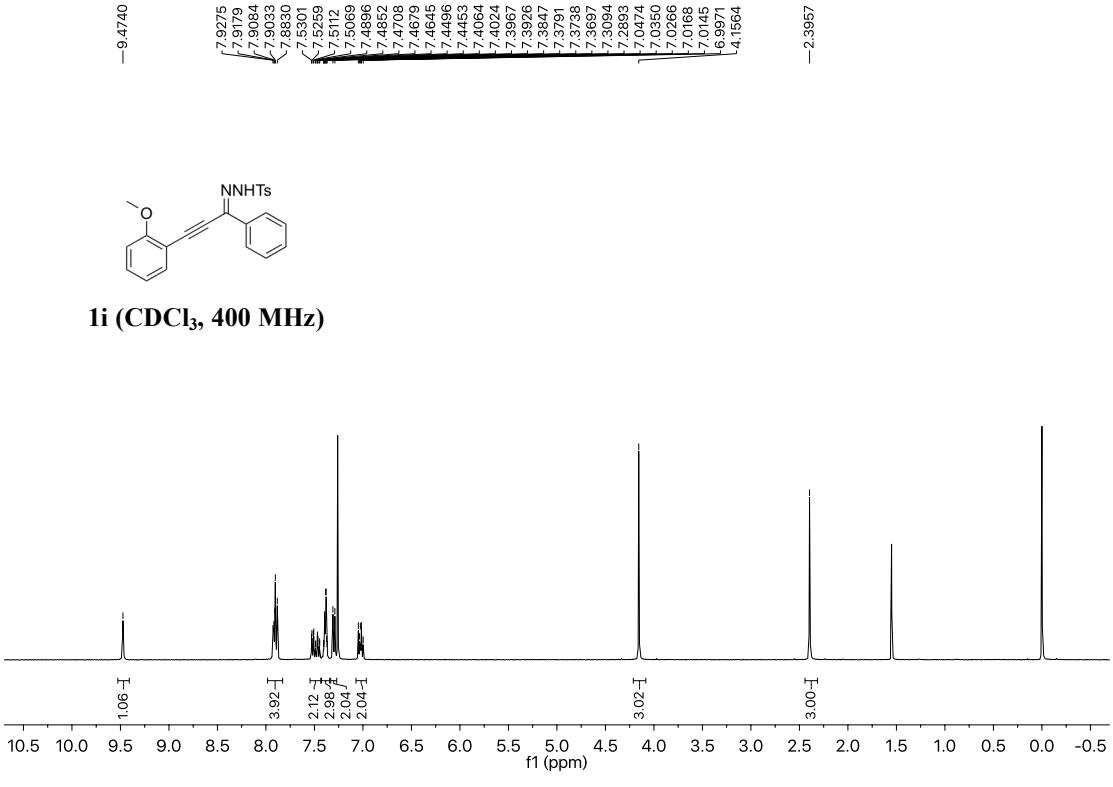

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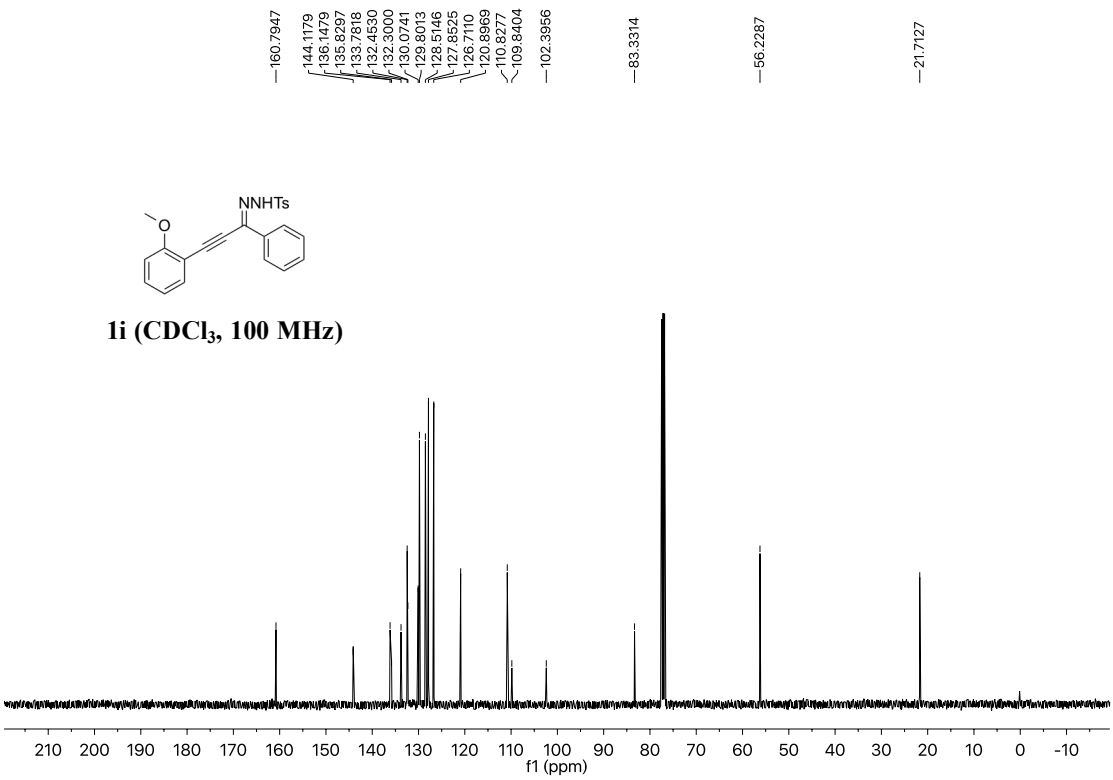

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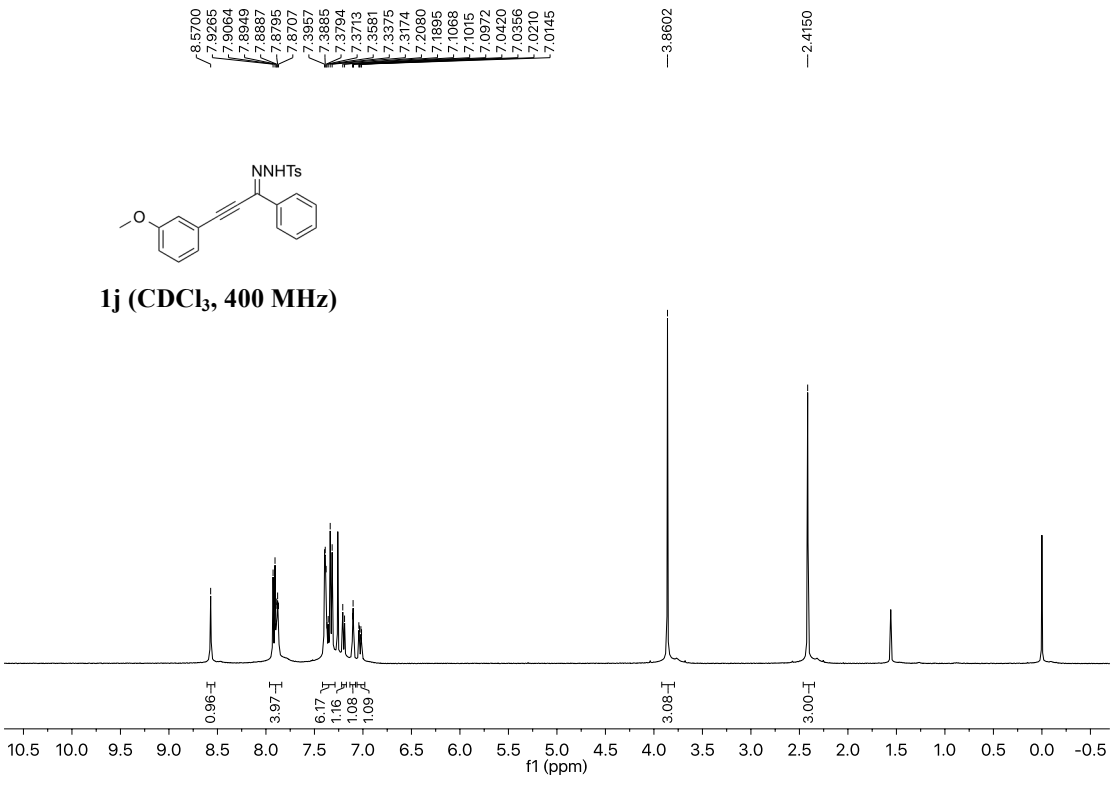

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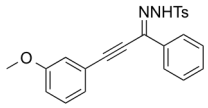

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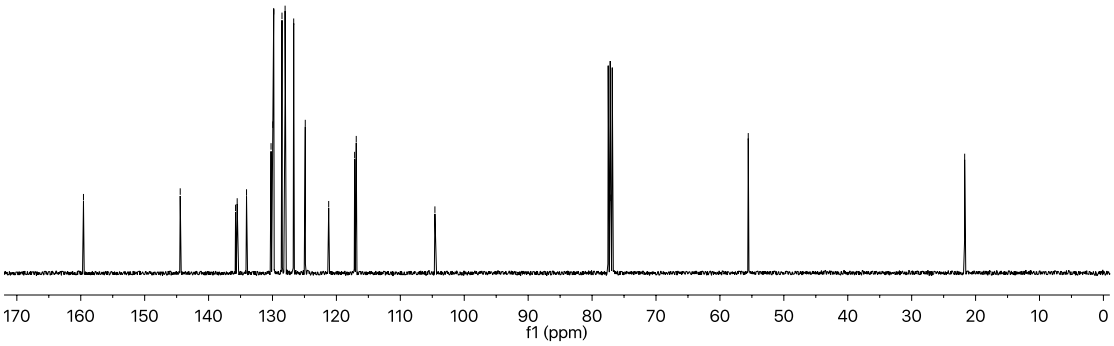

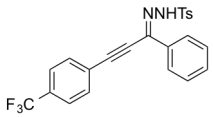

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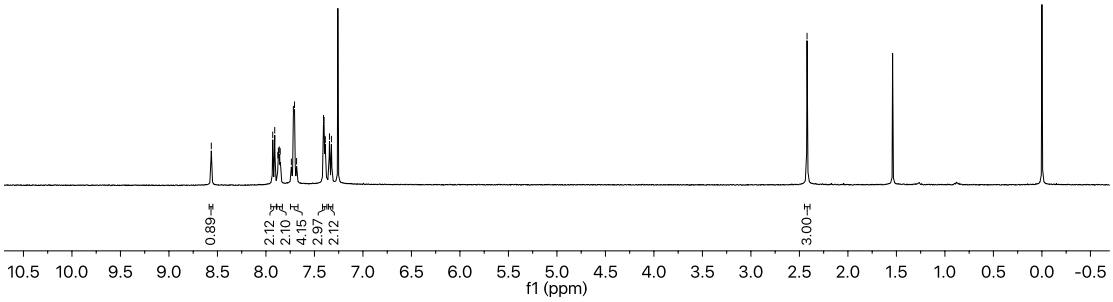

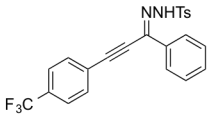

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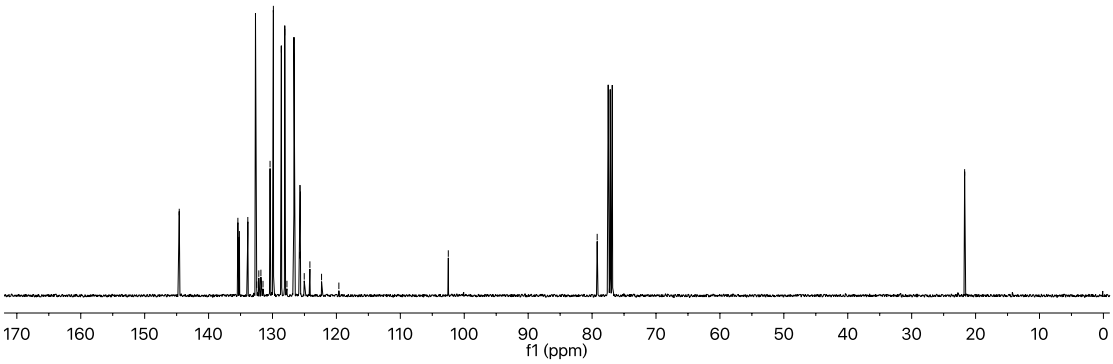

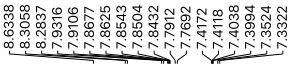

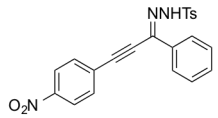

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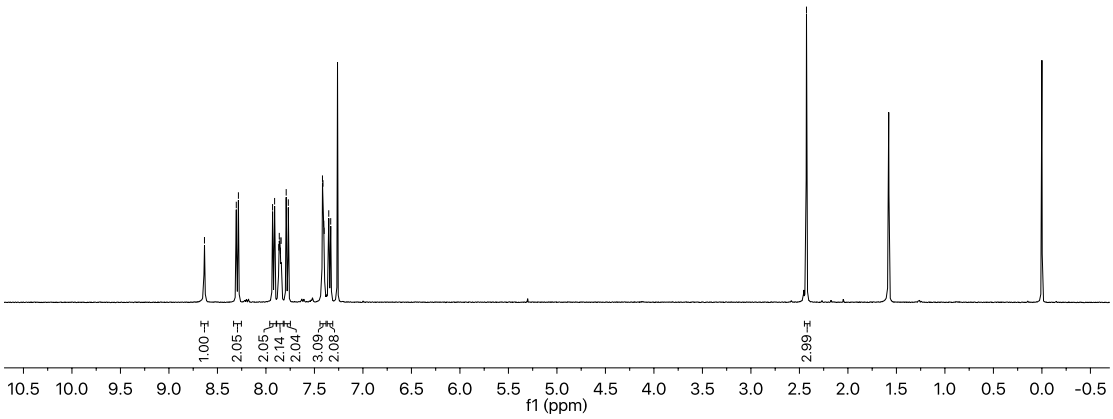

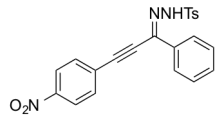

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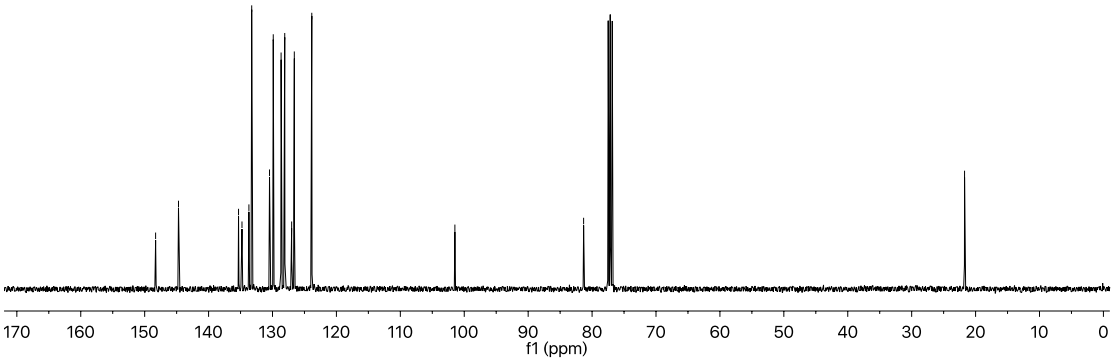

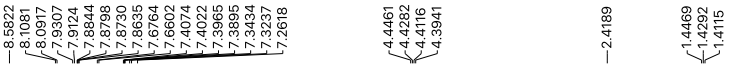

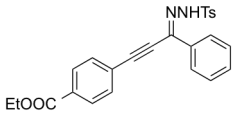

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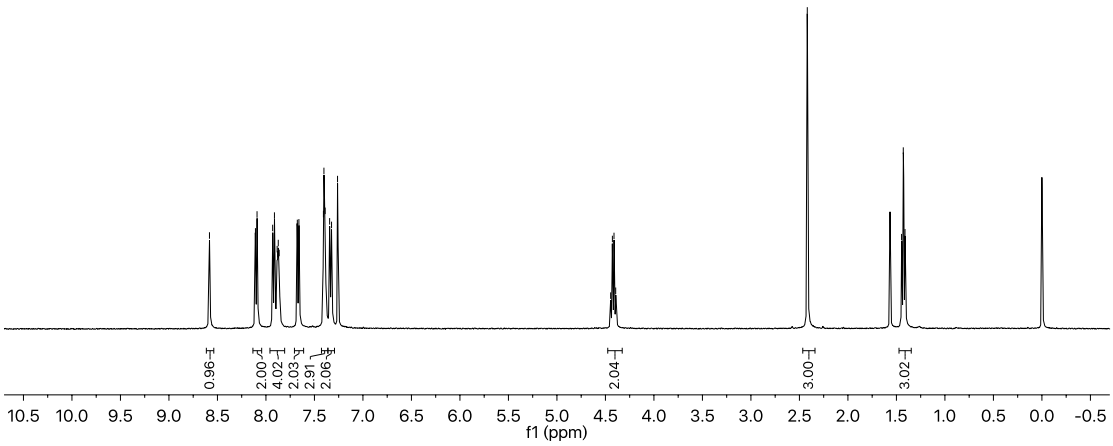

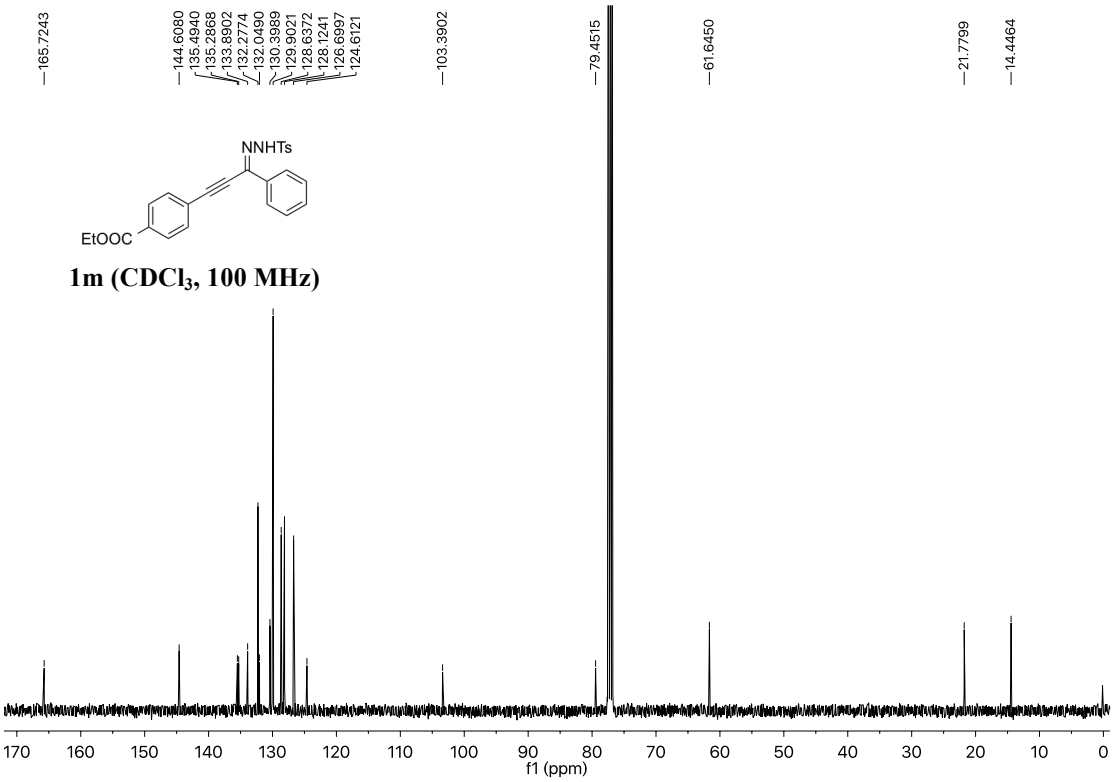

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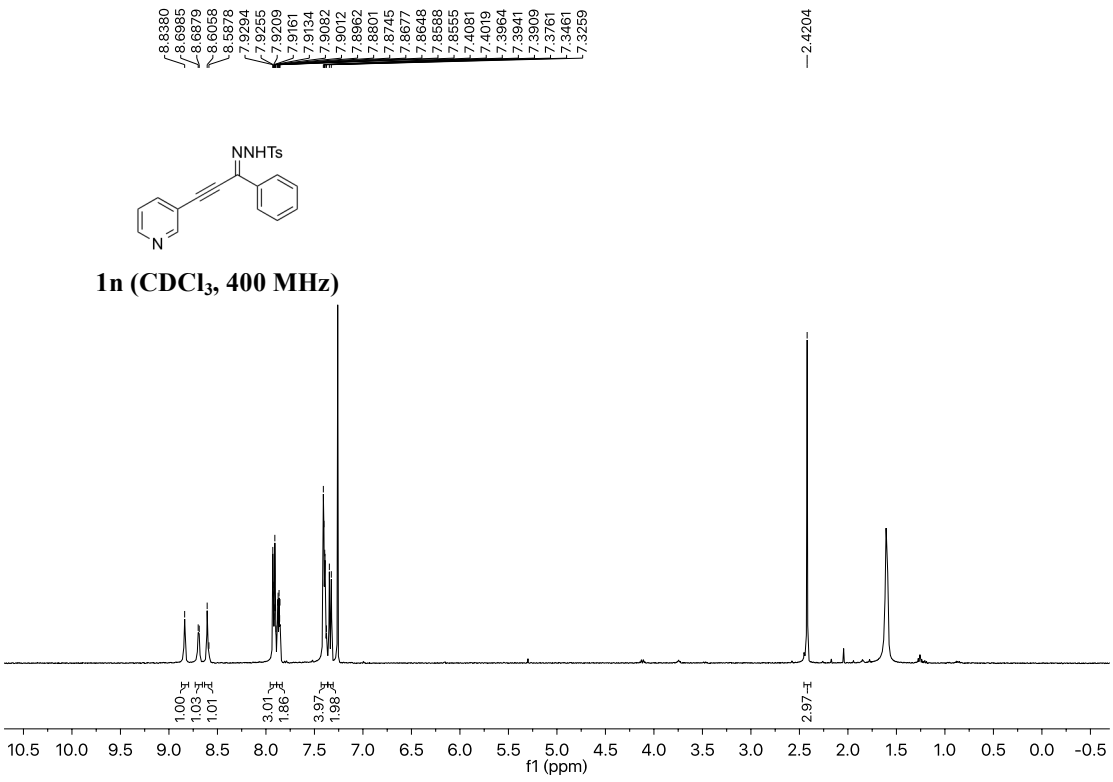
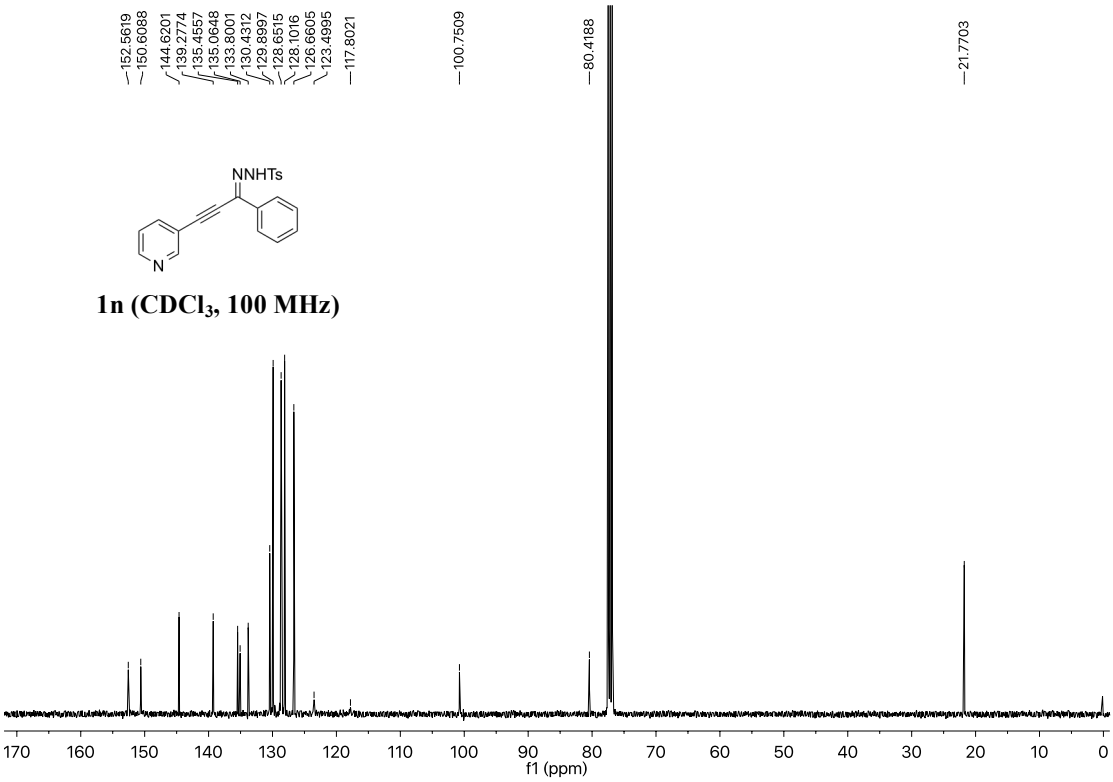


1n ($CDCl_3$, 400 MHz)



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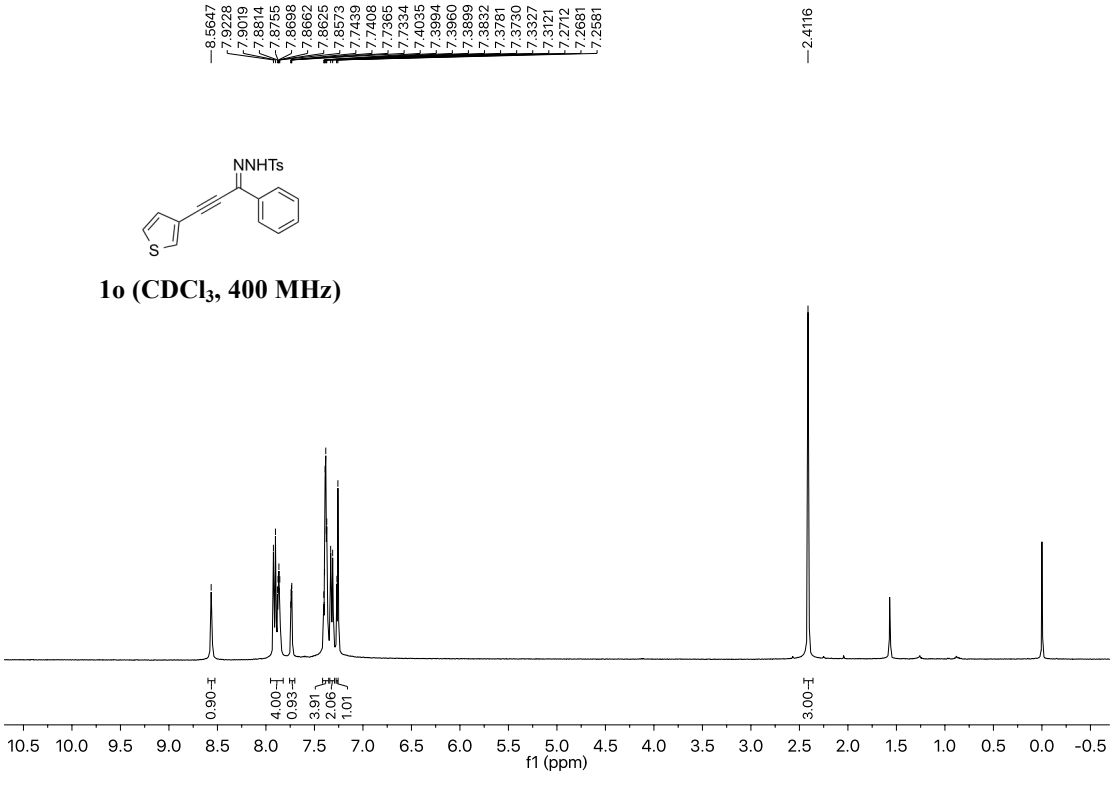
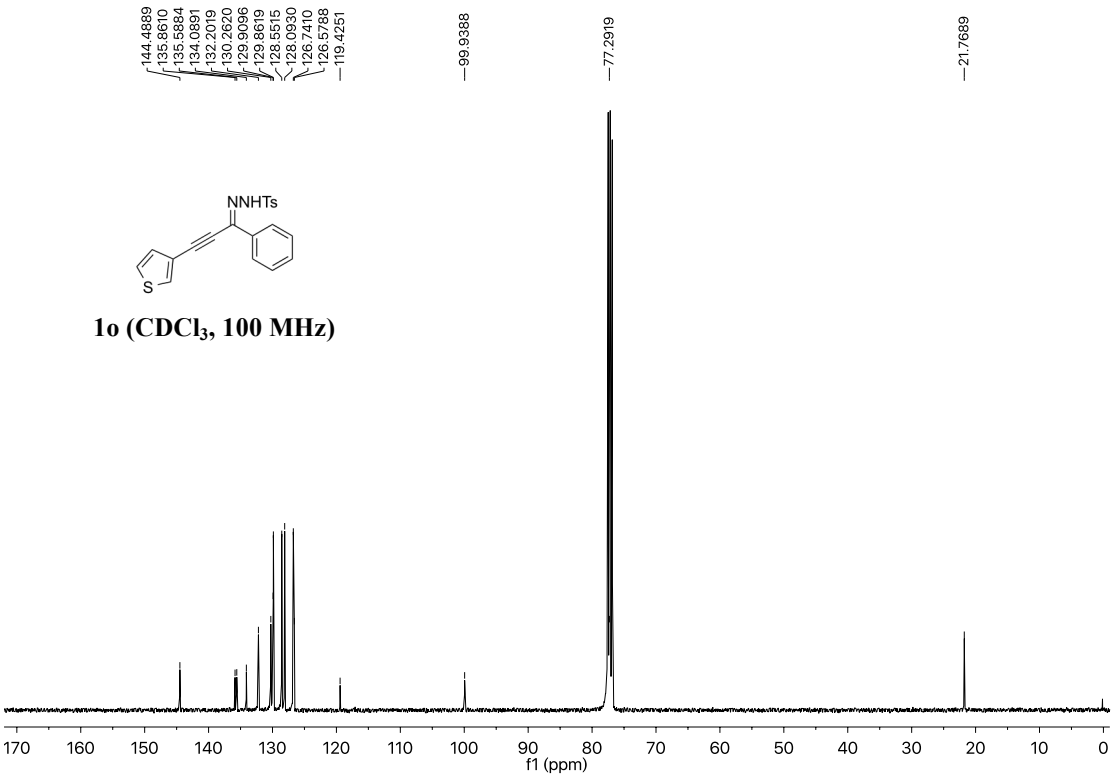
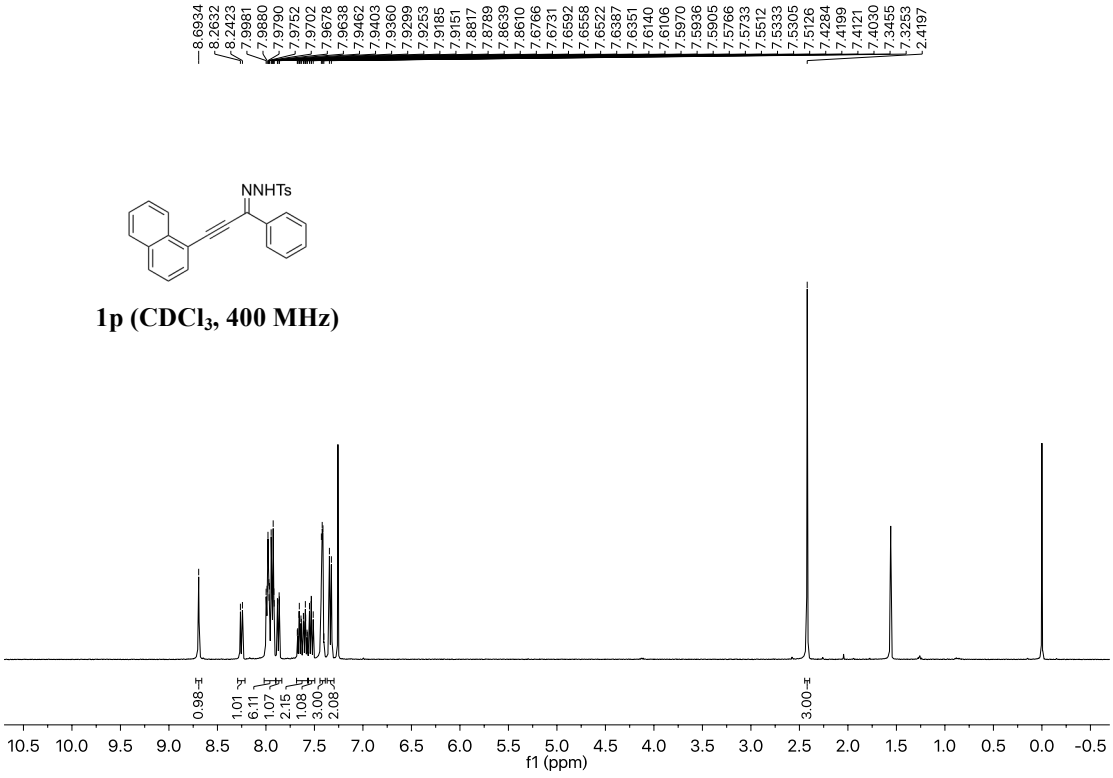


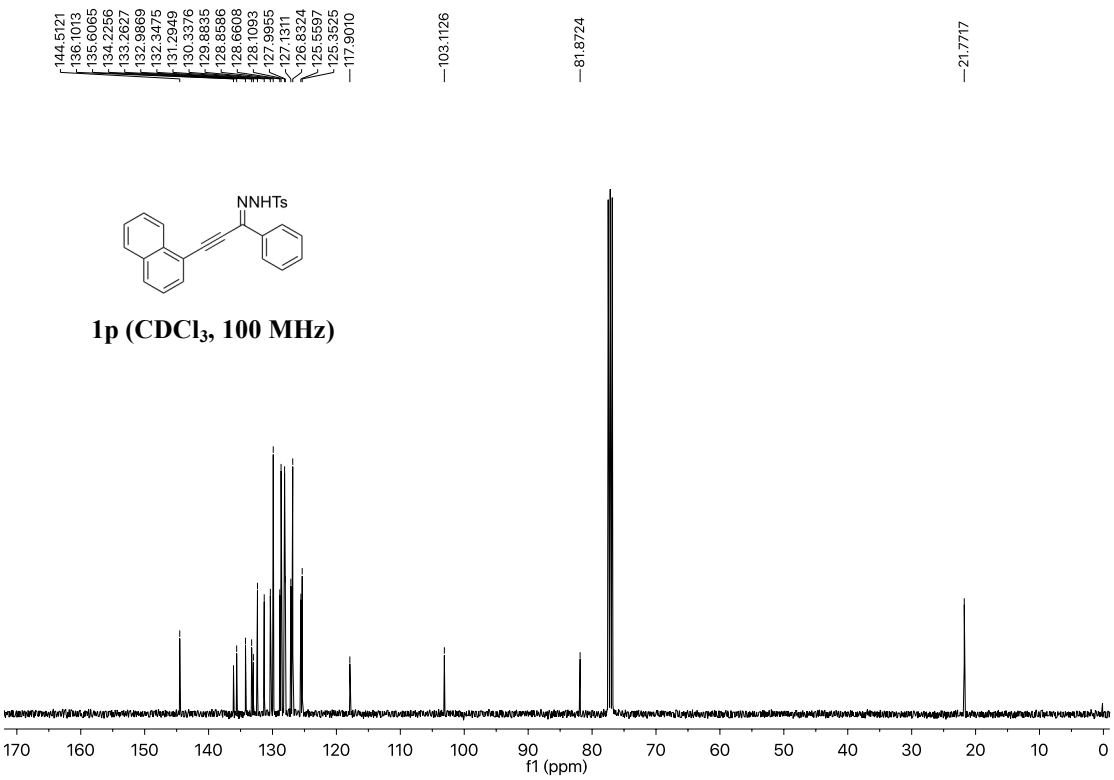
1o ($CDCl_3$, 400 MHz)



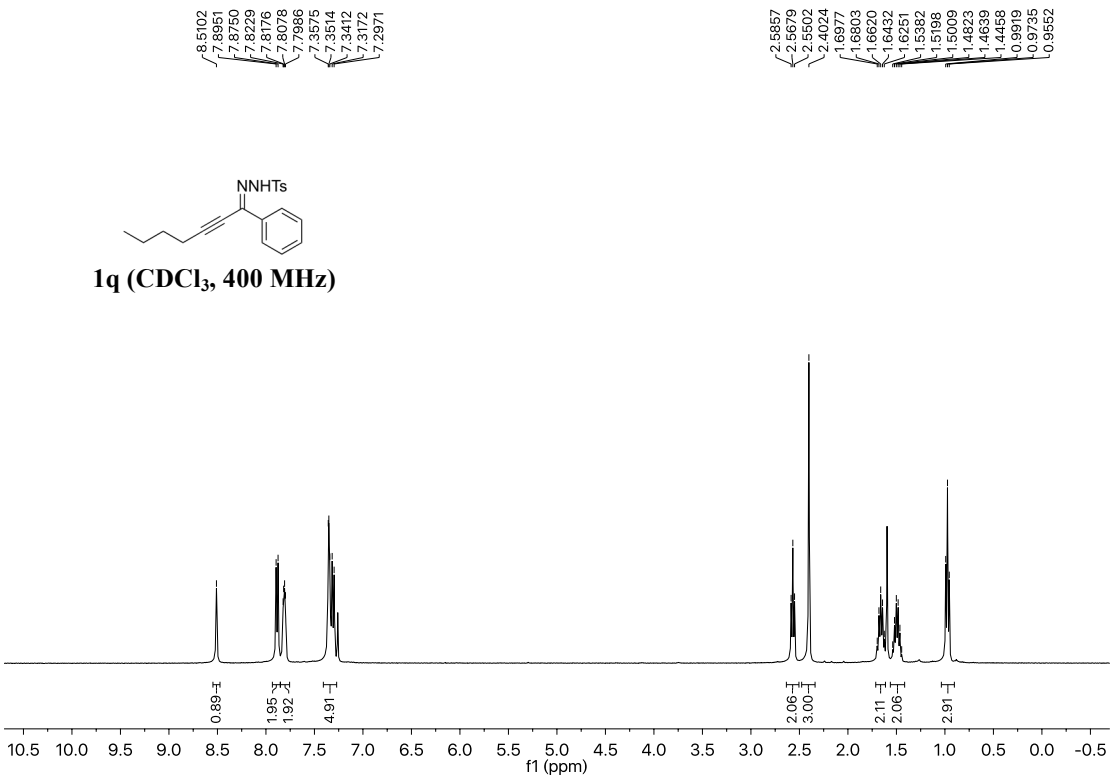
1o ($CDCl_3$, 100 MHz)



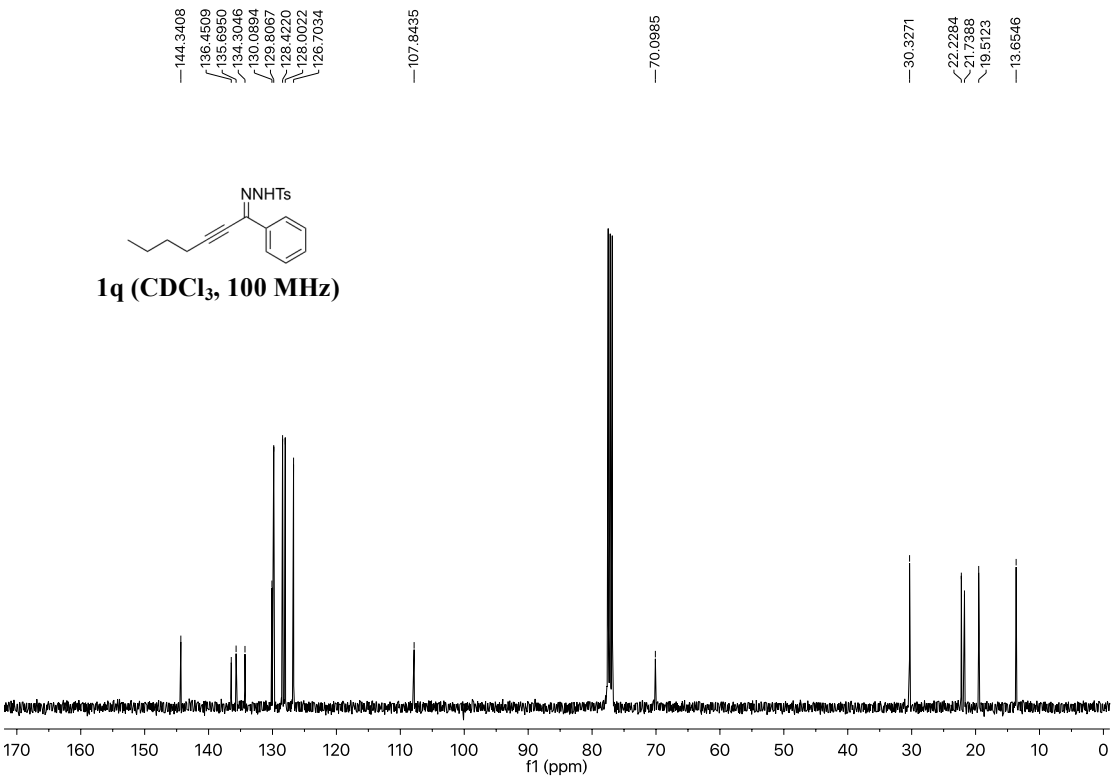
1p ($CDCl_3$, 400 MHz)



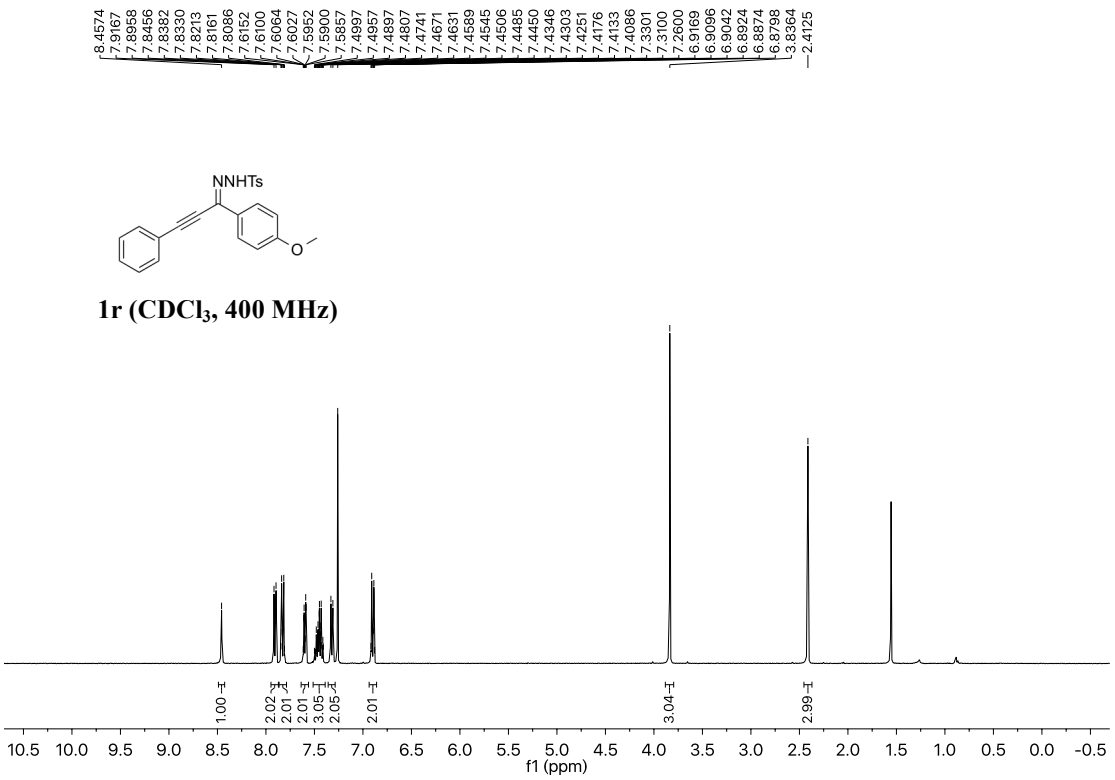
1p ($CDCl_3$, 100 MHz)



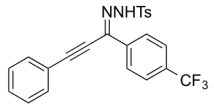
1q ($CDCl_3$, 400 MHz)



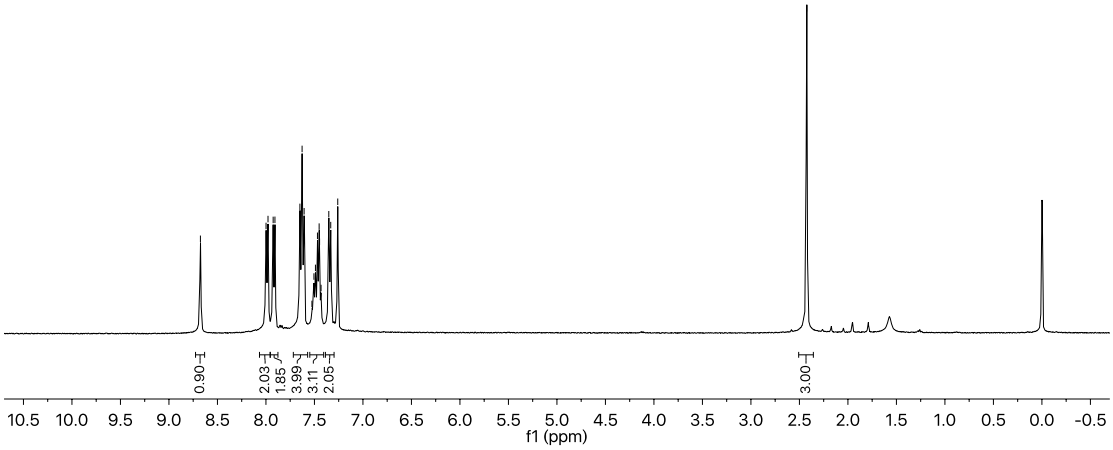
1q ($CDCl_3$, 100 MHz)

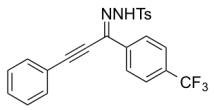


1r ($CDCl_3$, 400 MHz)

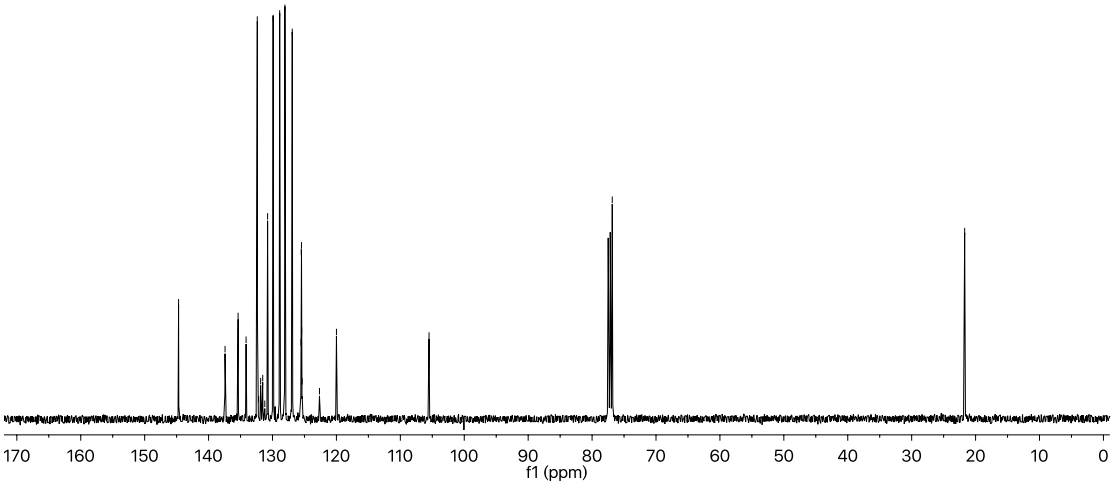


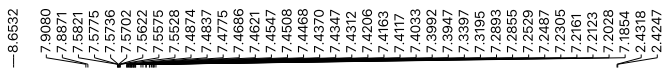
1s ($CDCl_3$, 400 MHz)

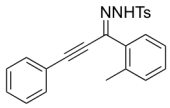




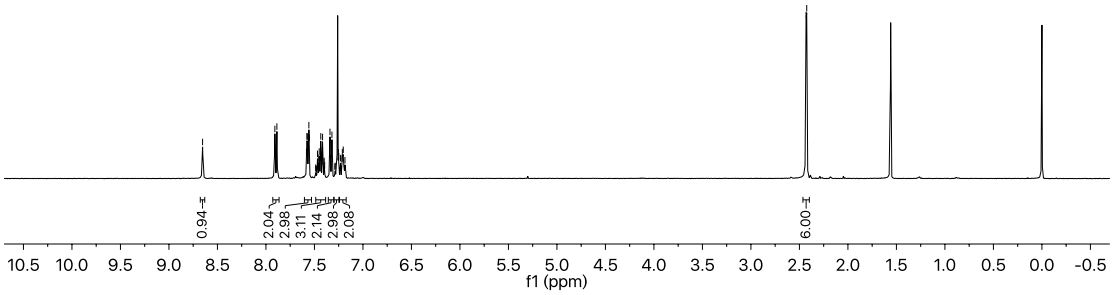
1s ($CDCl_3$, 100 MHz)

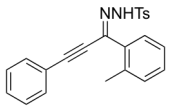




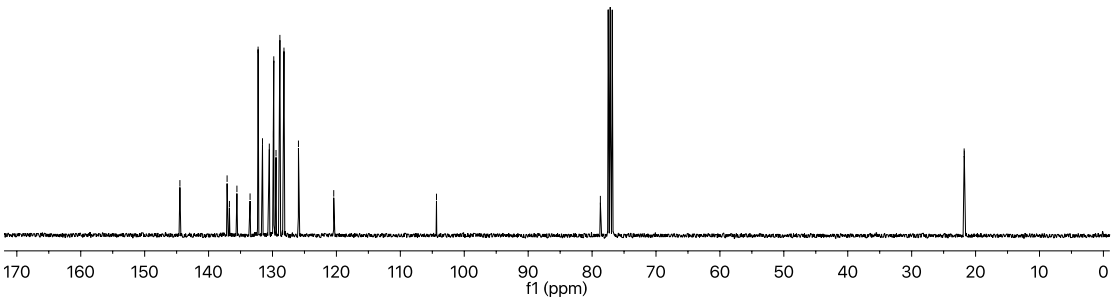


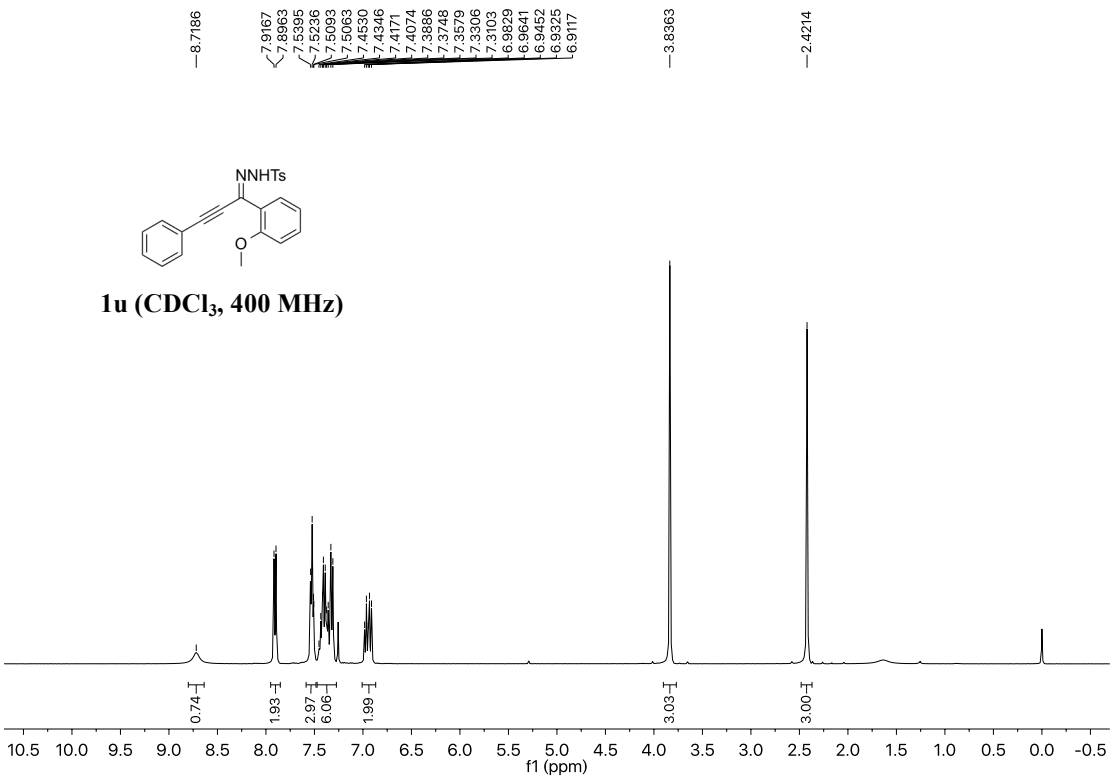
1t ($CDCl_3$, 400 MHz)



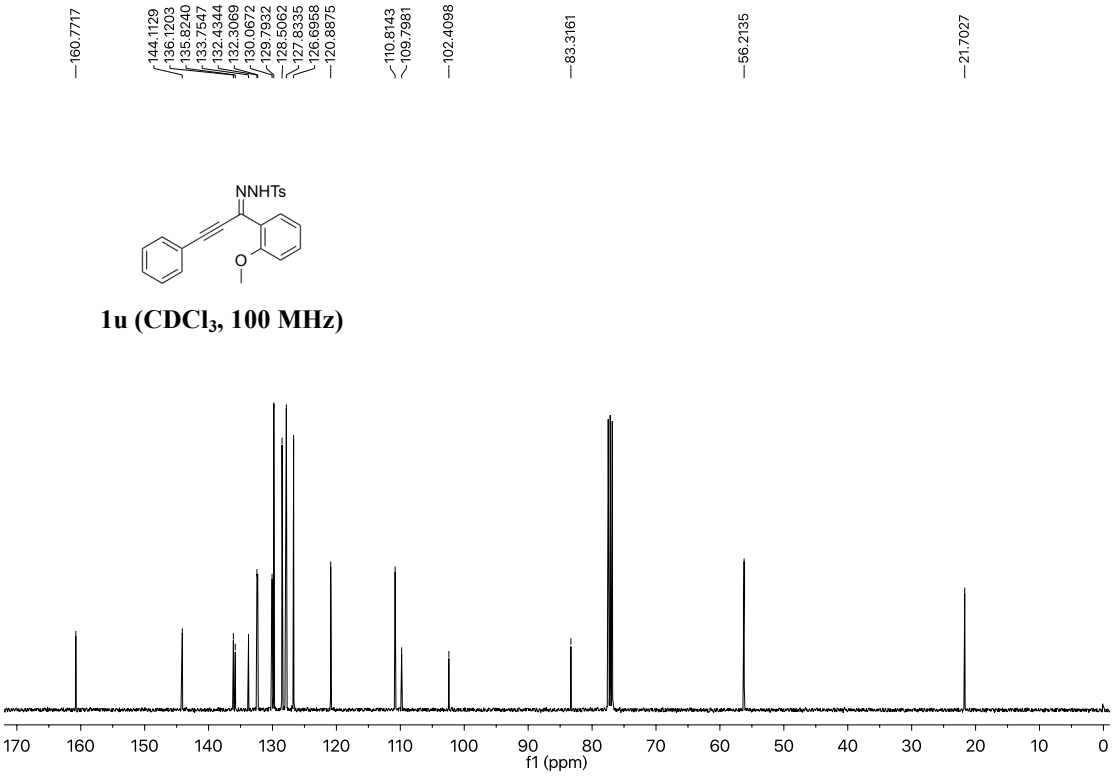


1t ($CDCl_3$, 100 MHz)

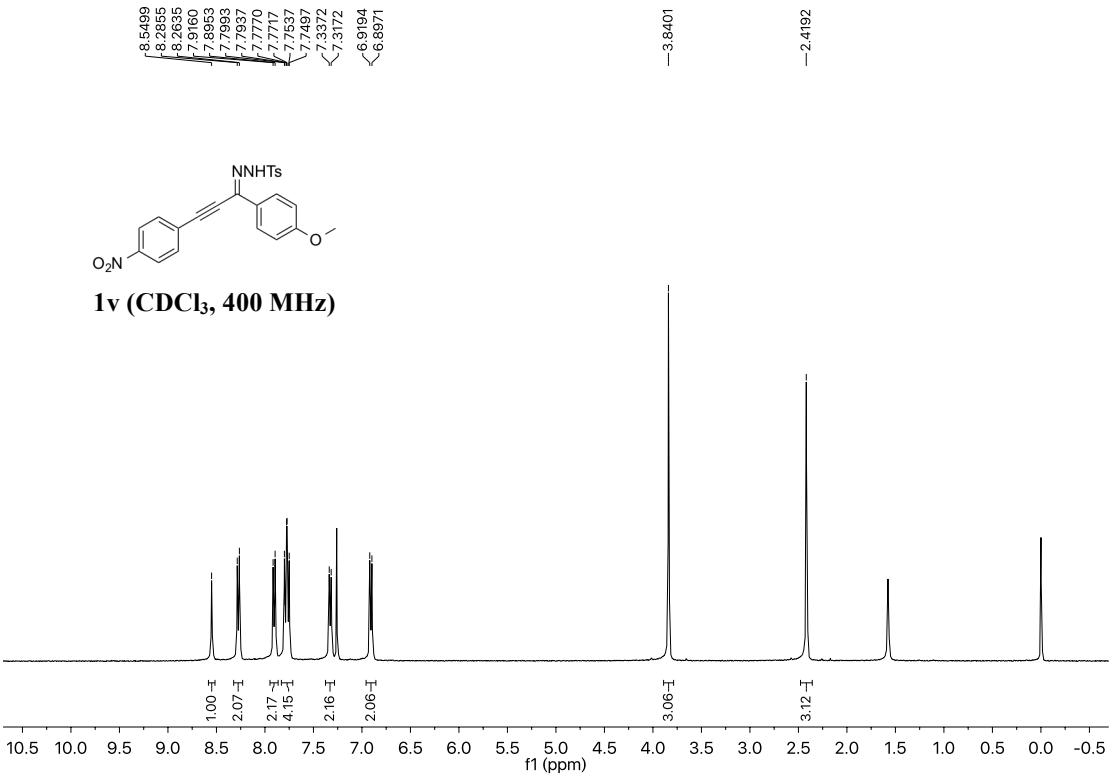




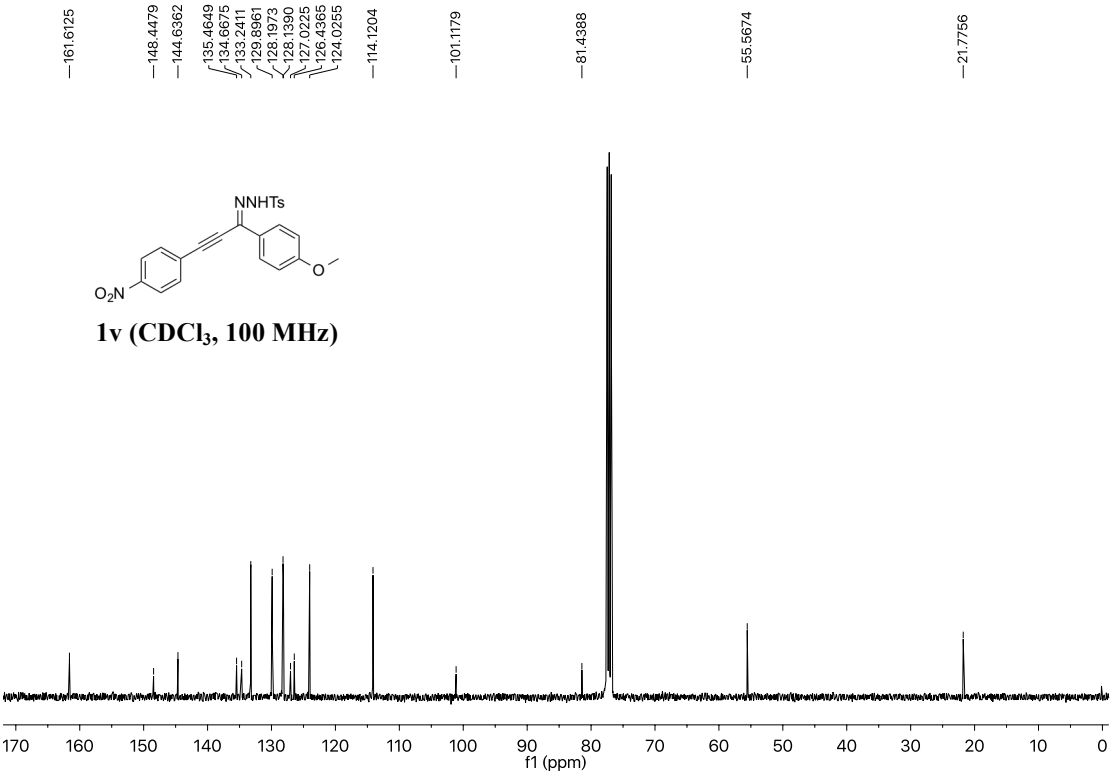
1u ($CDCl_3$, 400 MHz)



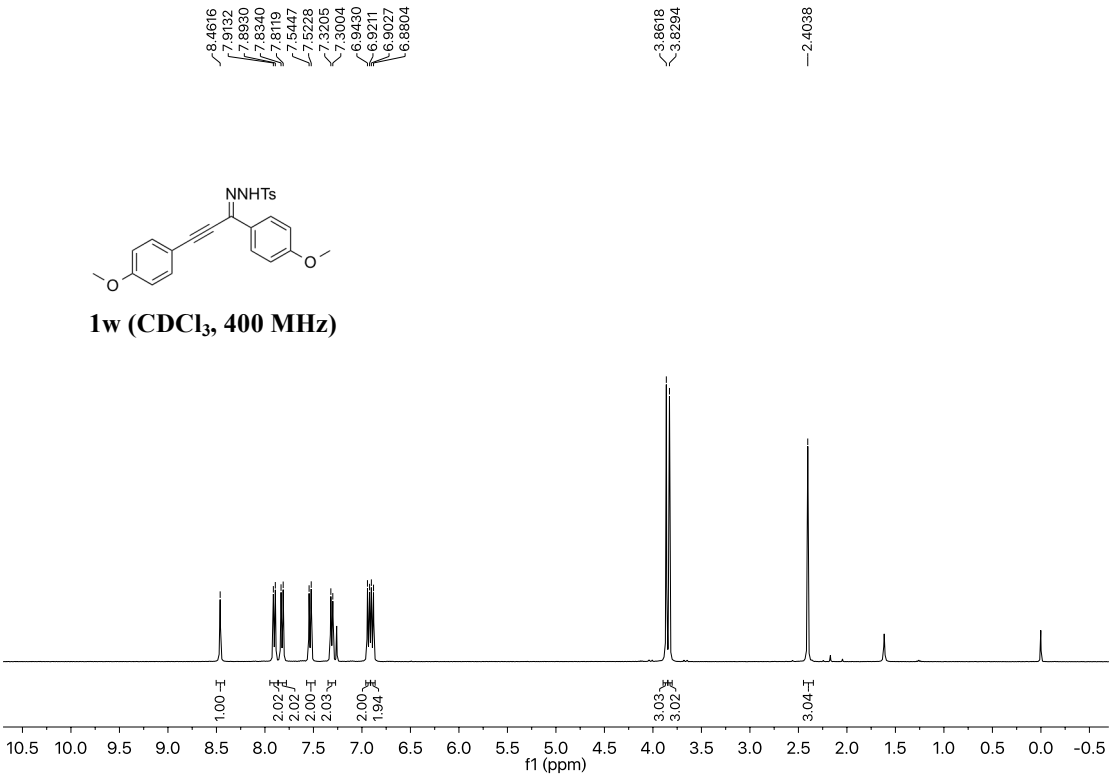
1u ($CDCl_3$, 100 MHz)



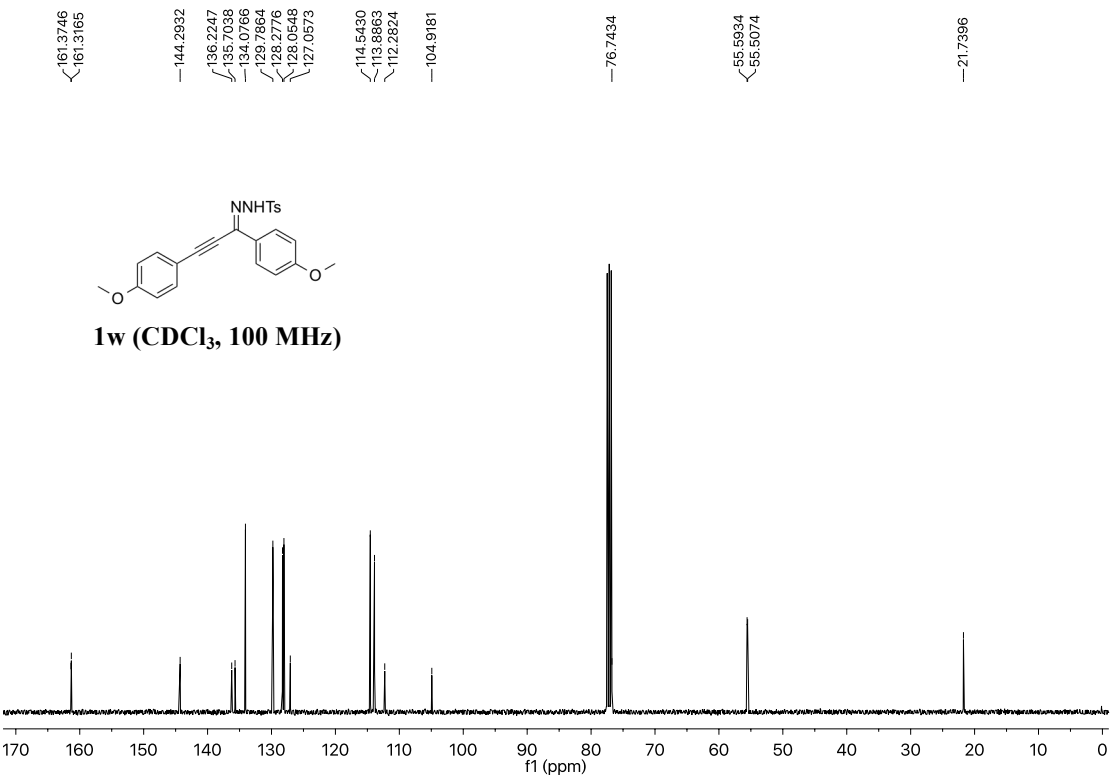
1v ($CDCl_3$, 400 MHz)



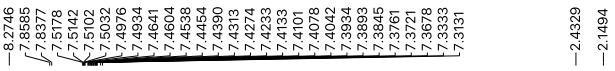
1v ($CDCl_3$, 100 MHz)

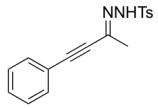


1w ($CDCl_3$, 400 MHz)

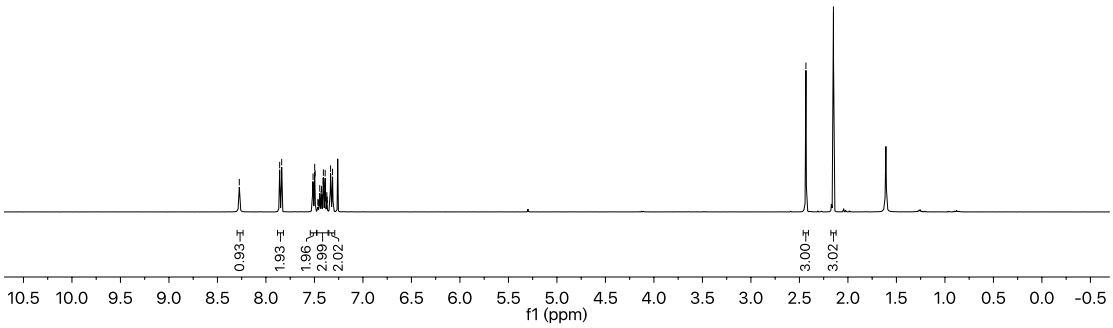


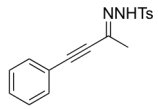
1w ($CDCl_3$, 100 MHz)



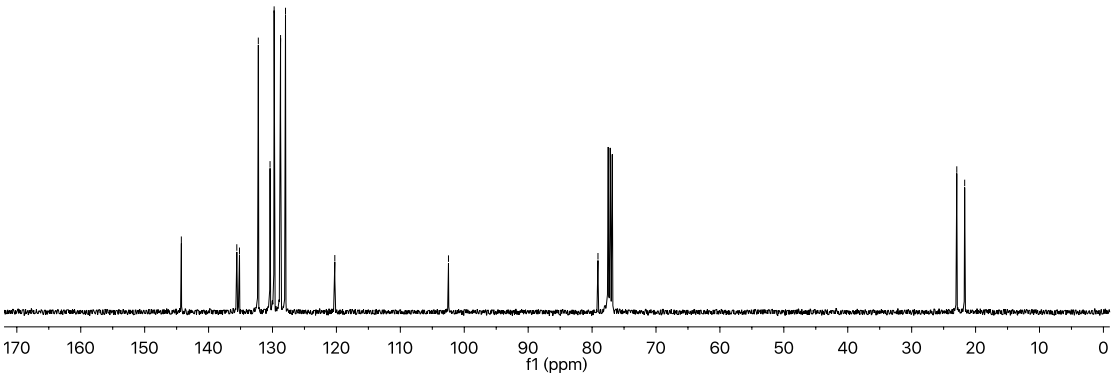


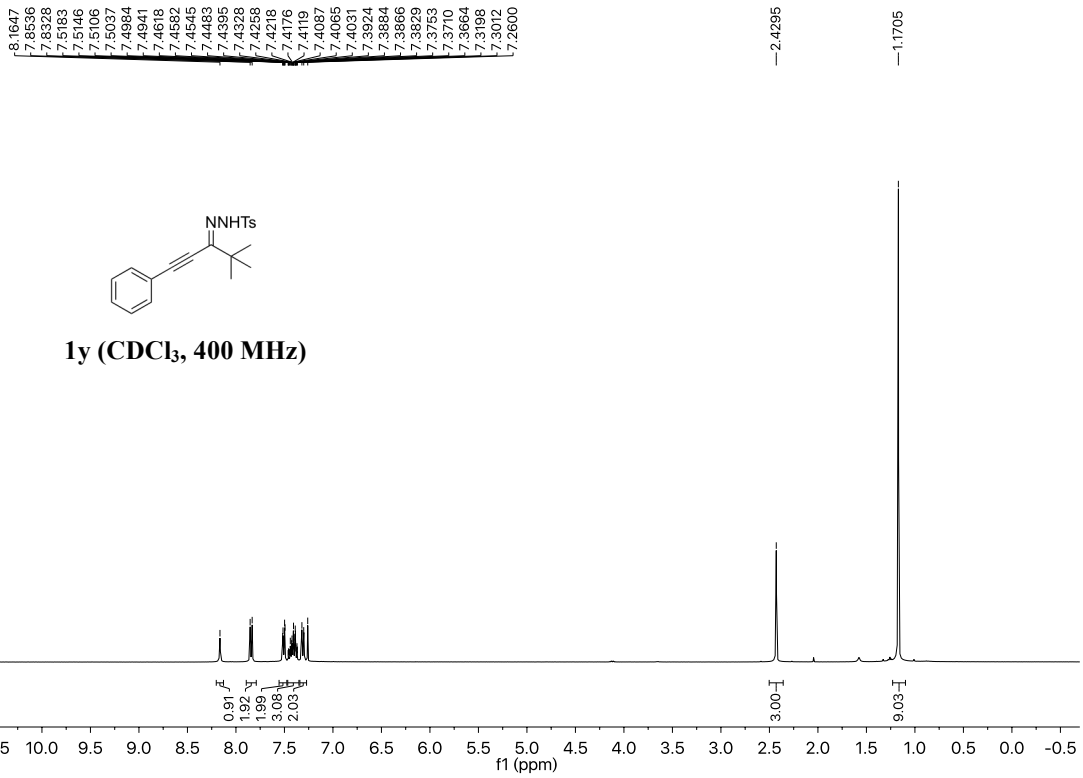
1x ($CDCl_3$, 400 MHz)



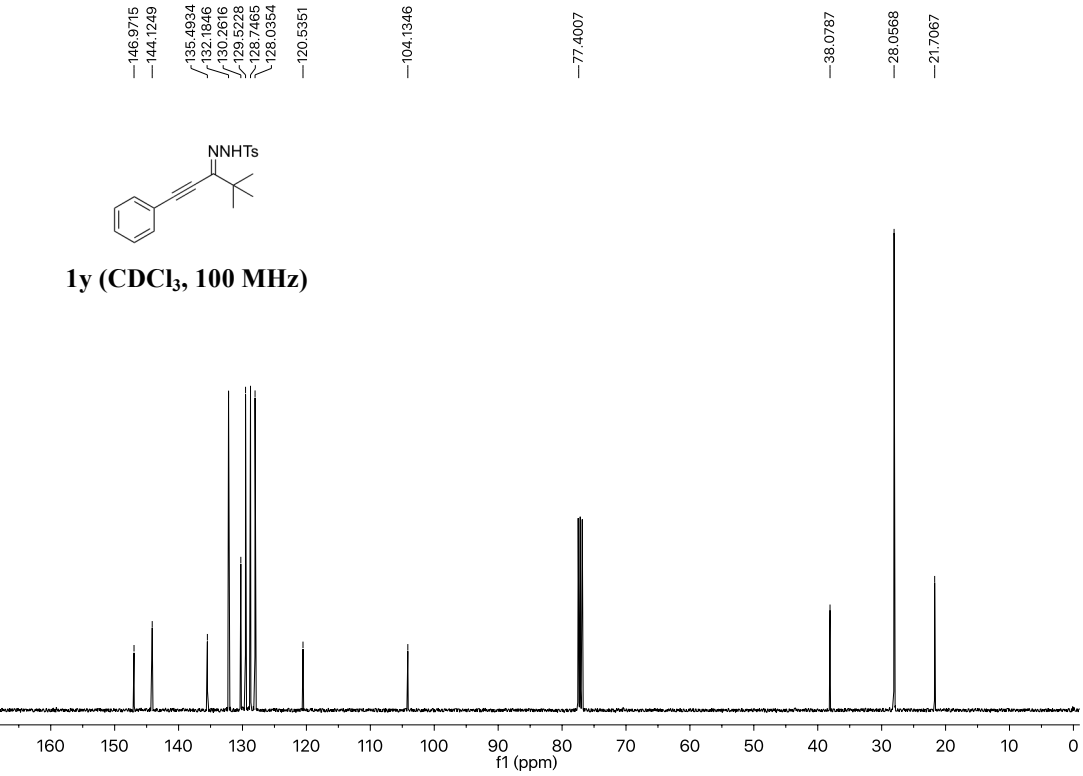


1x ($CDCl_3$, 100 MHz)

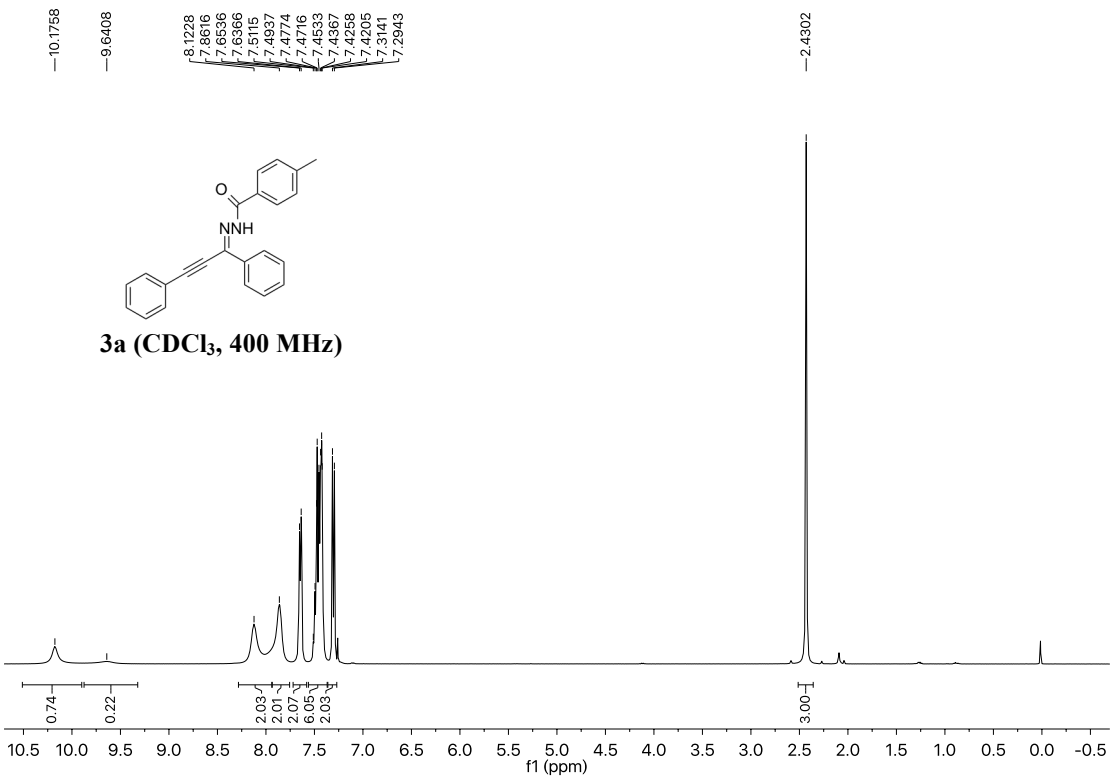




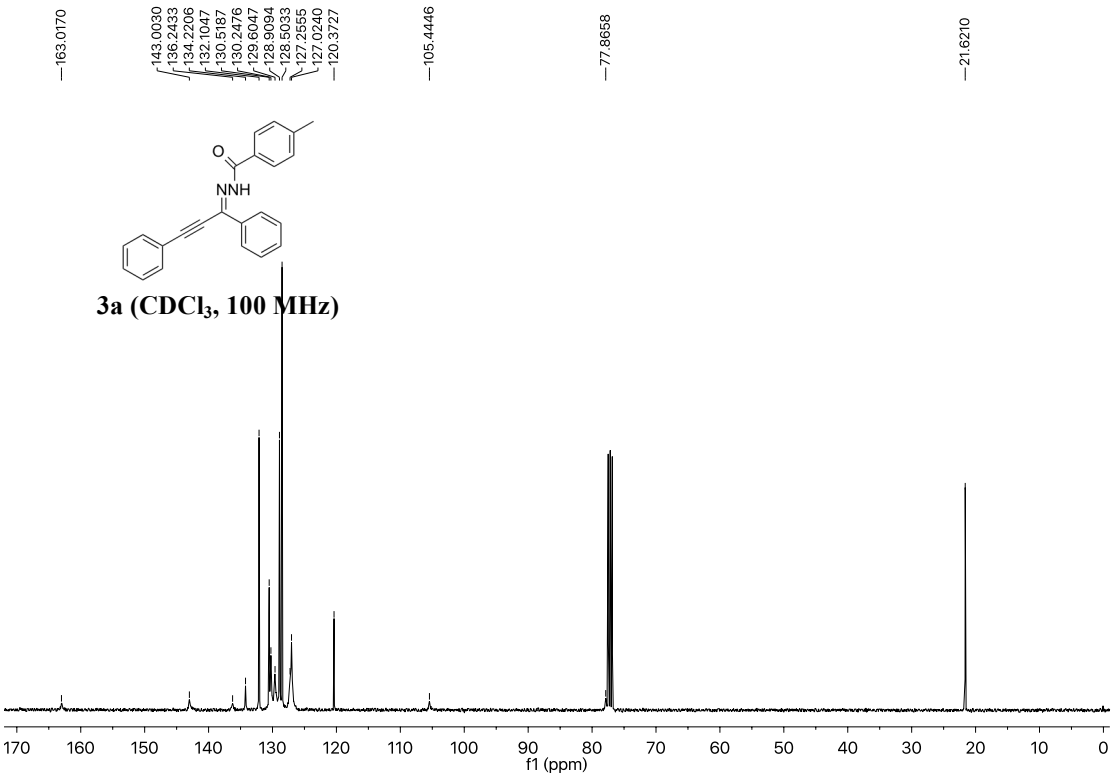
1y ($CDCl_3$, 400 MHz)



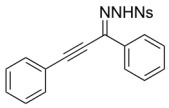
1y ($CDCl_3$, 100 MHz)



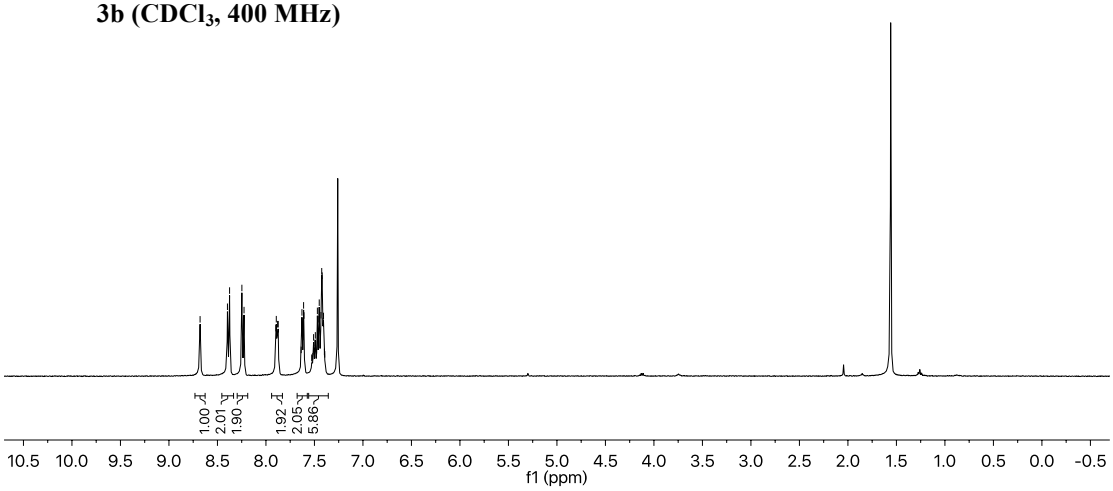
3a ($CDCl_3$, 400 MHz)

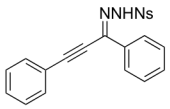


3a ($CDCl_3$, 100 MHz)

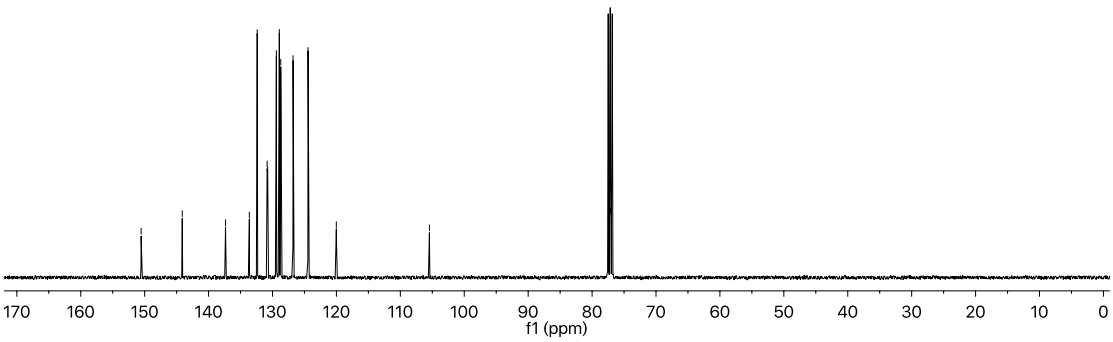


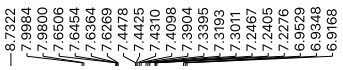
3b ($CDCl_3$, 400 MHz)

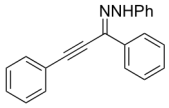




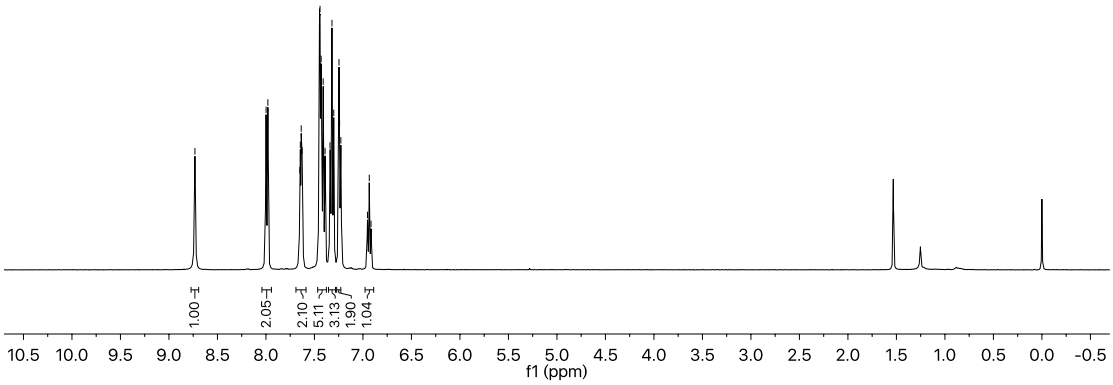
3b ($CDCl_3$, 100 MHz)

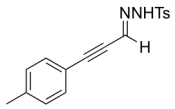




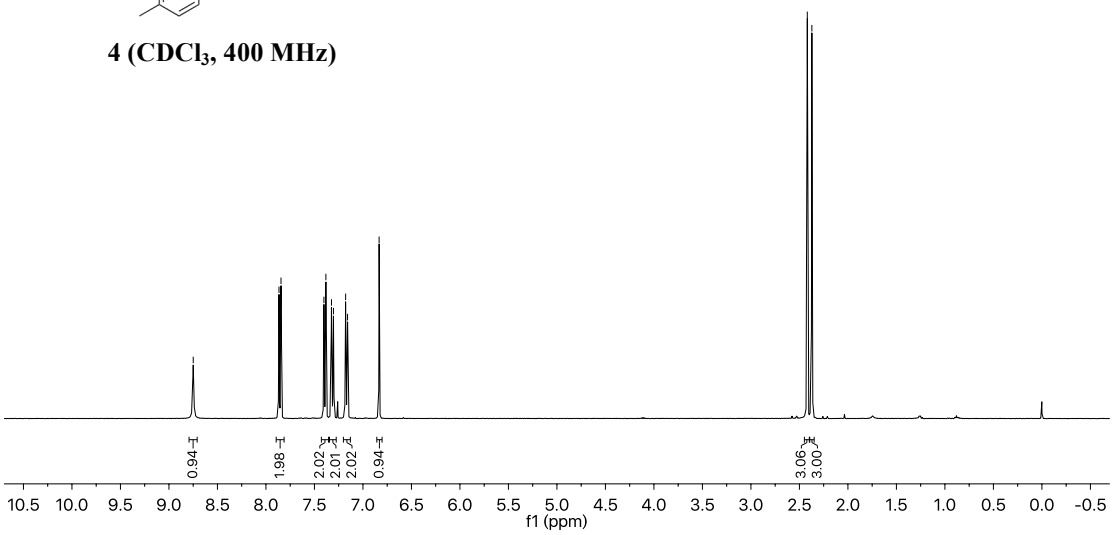


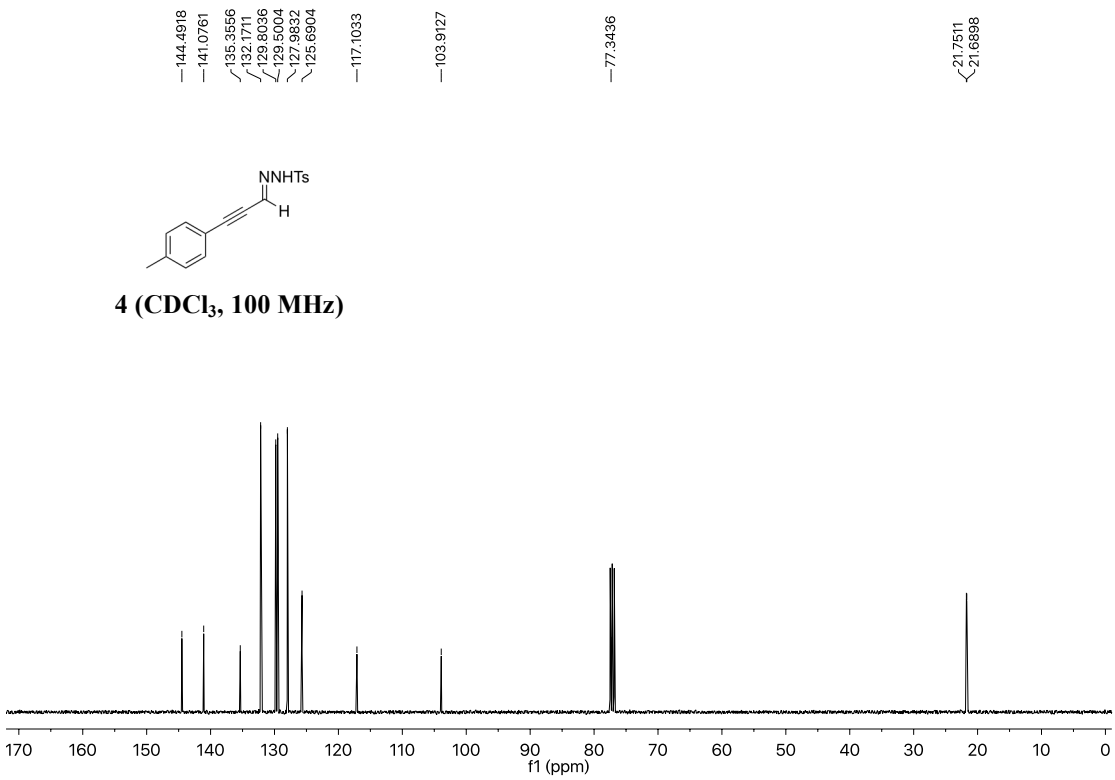
3c ($CDCl_3$, 400 MHz)



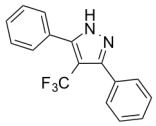


4 ($CDCl_3$, 400 MHz)

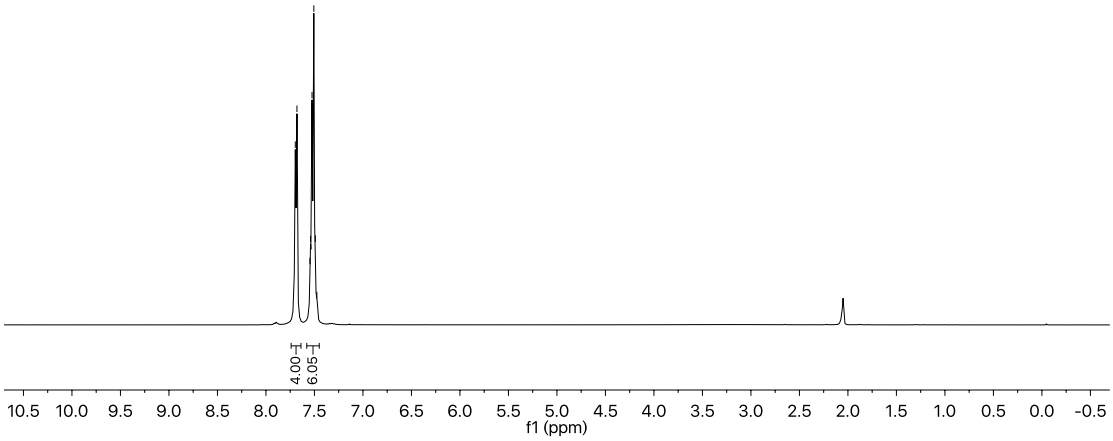


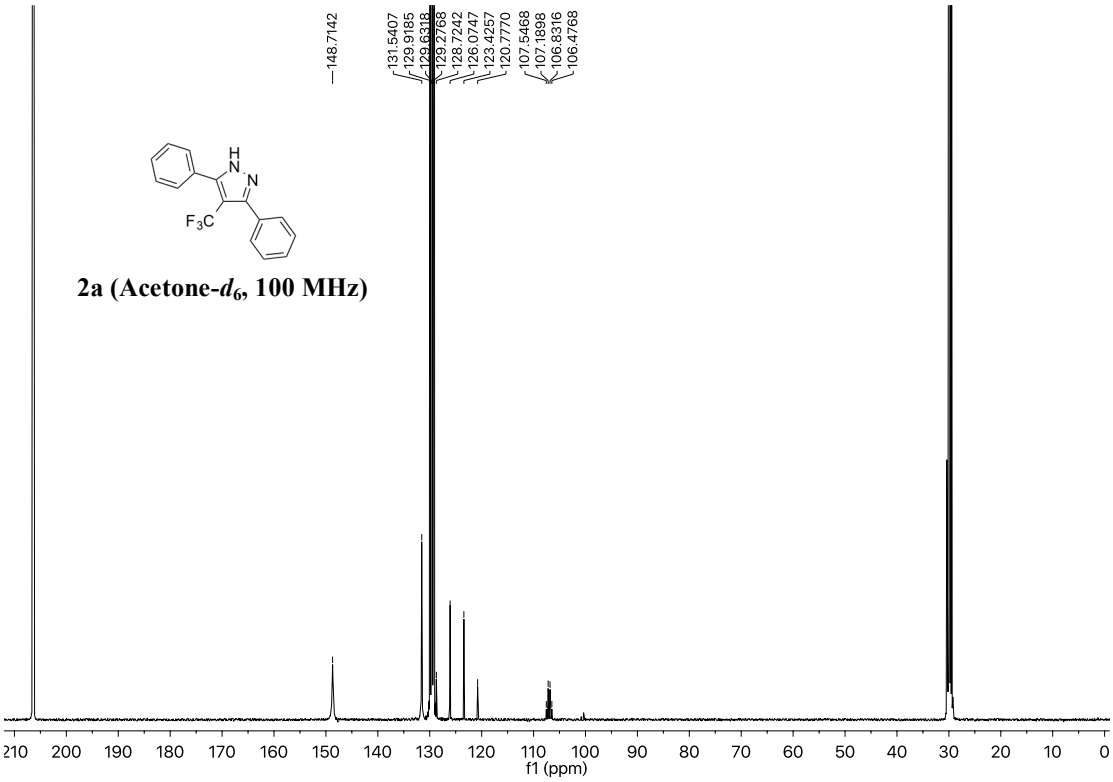


4 ($CDCl_3$, 100 MHz)

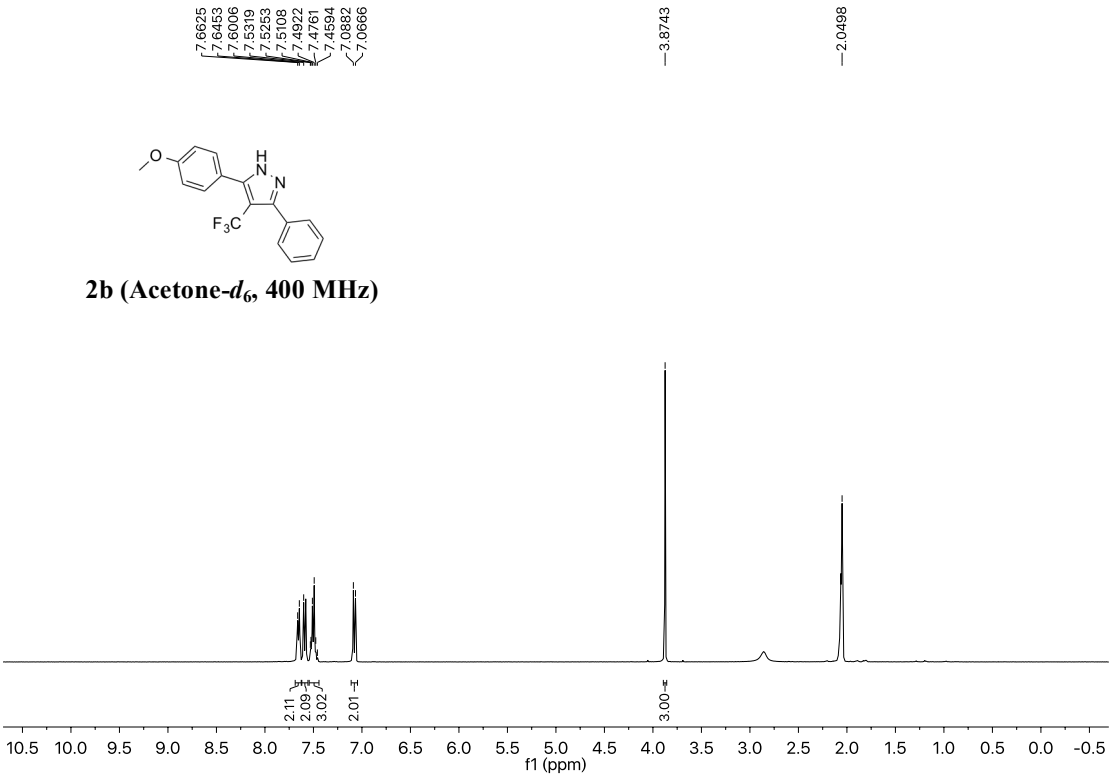


2a (Acetone-d_6, 400 MHz)

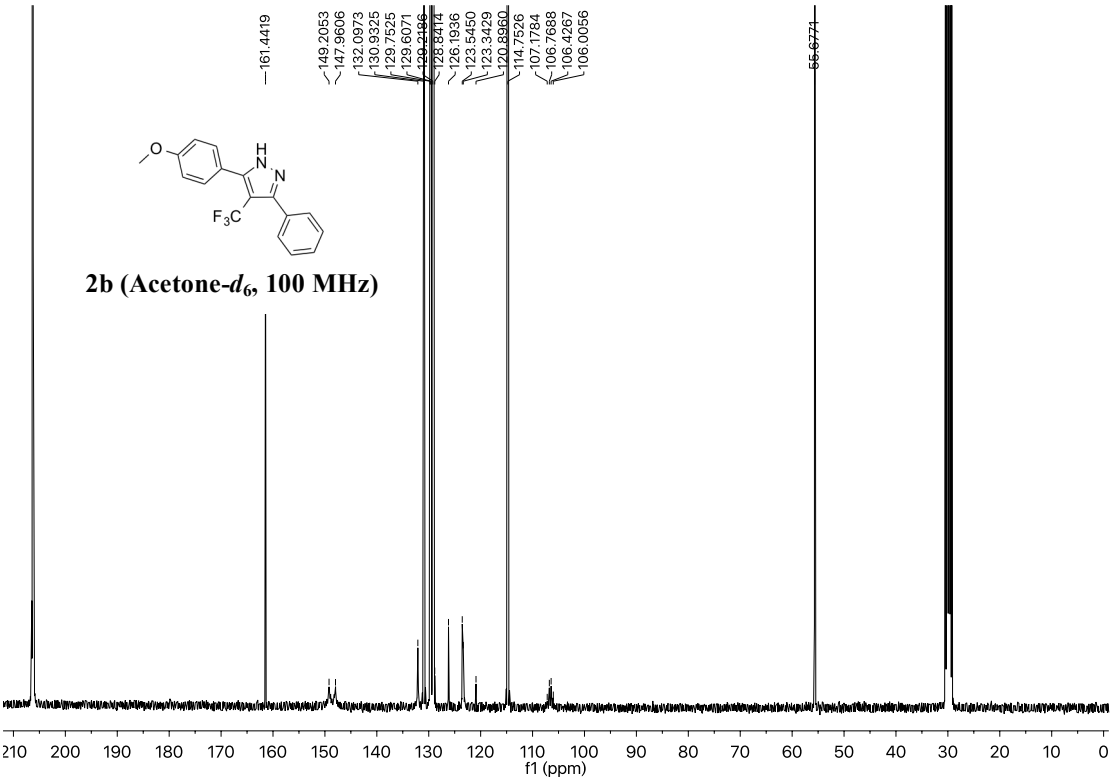




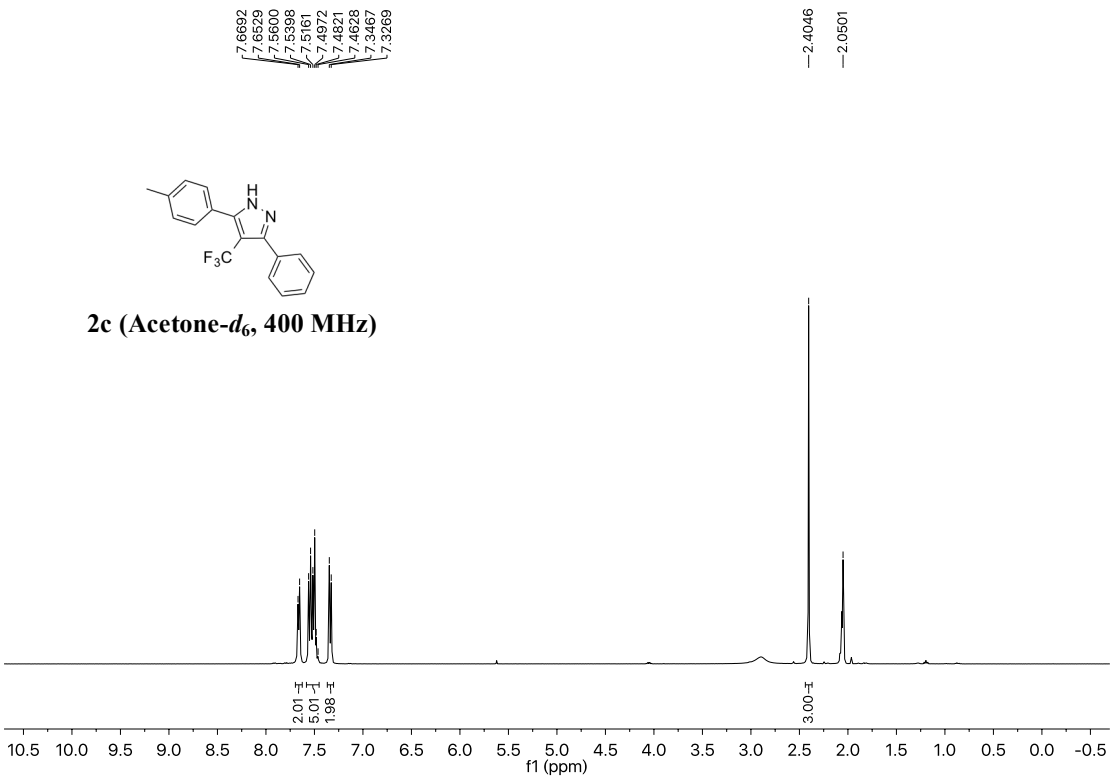
2a (Acetone-d_6, 100 MHz)



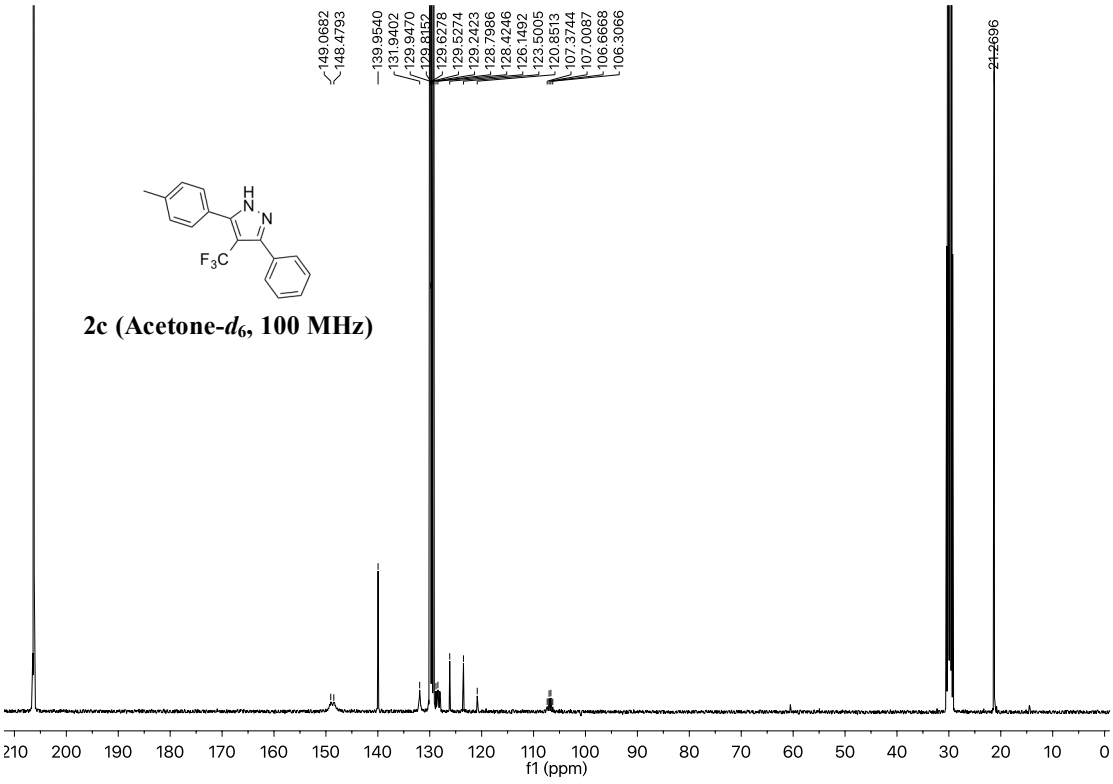
2b (Acetone-d_6, 400 MHz)



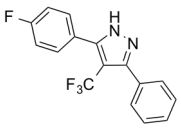
2b (Acetone-d_6, 100 MHz)



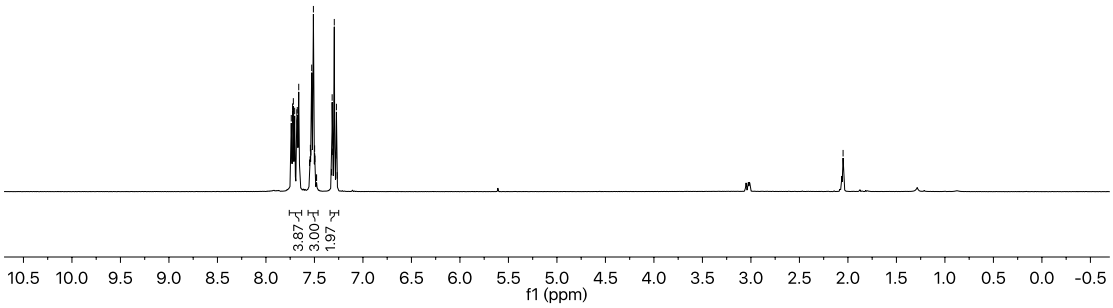
2c (Acetone-d_6, 400 MHz)

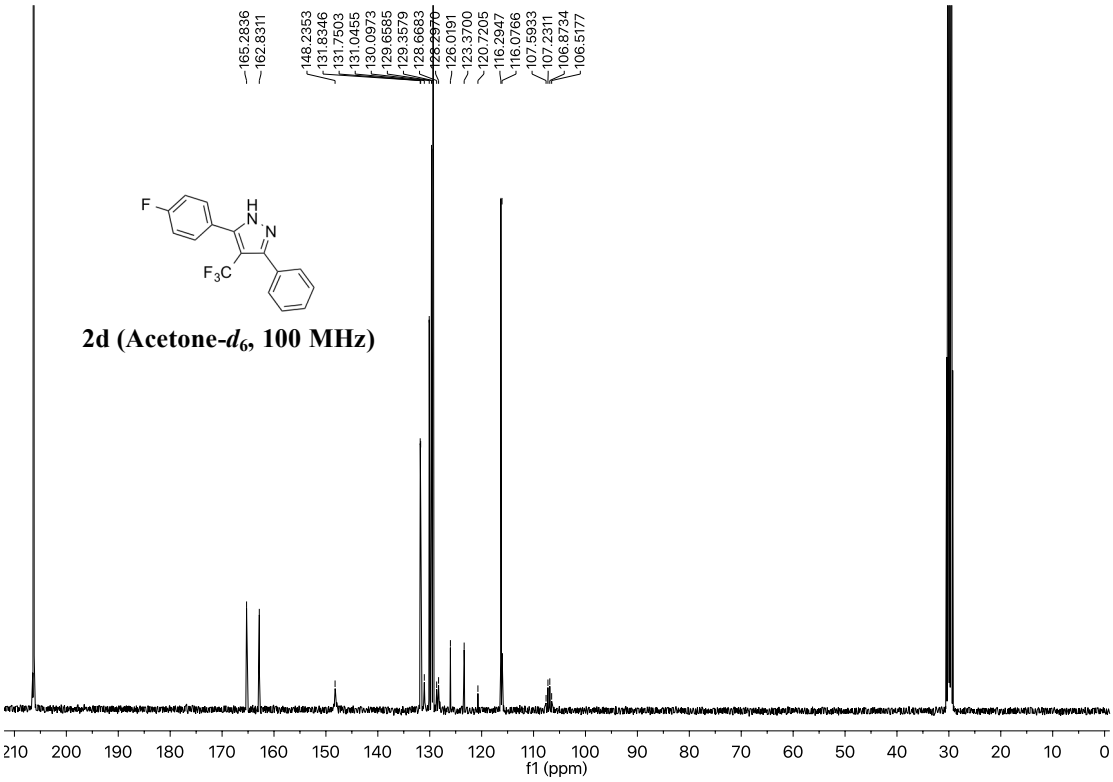


2c (Acetone-d_6, 100 MHz)

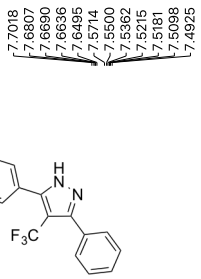


2d (Acetone-d_6, 400 MHz)

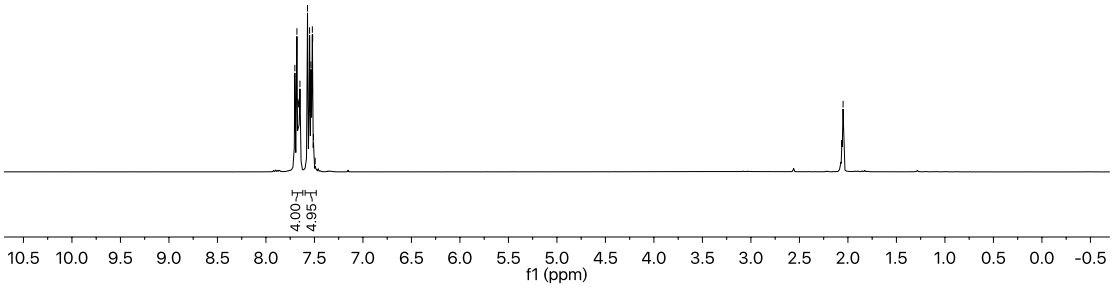


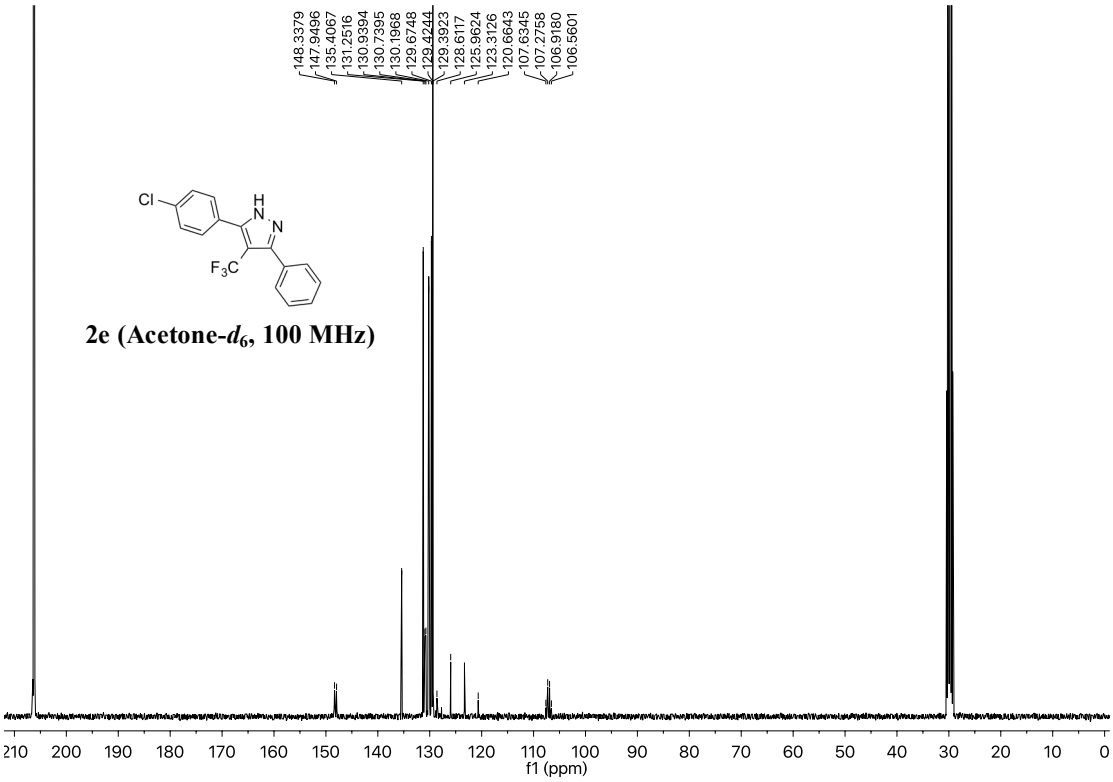


2d (Acetone-d_6, 100 MHz)

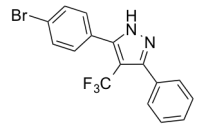


2e (Acetone-d_6, 400 MHz)

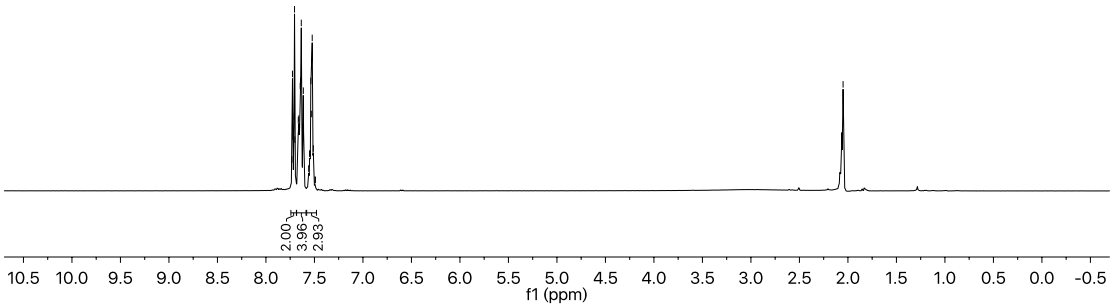


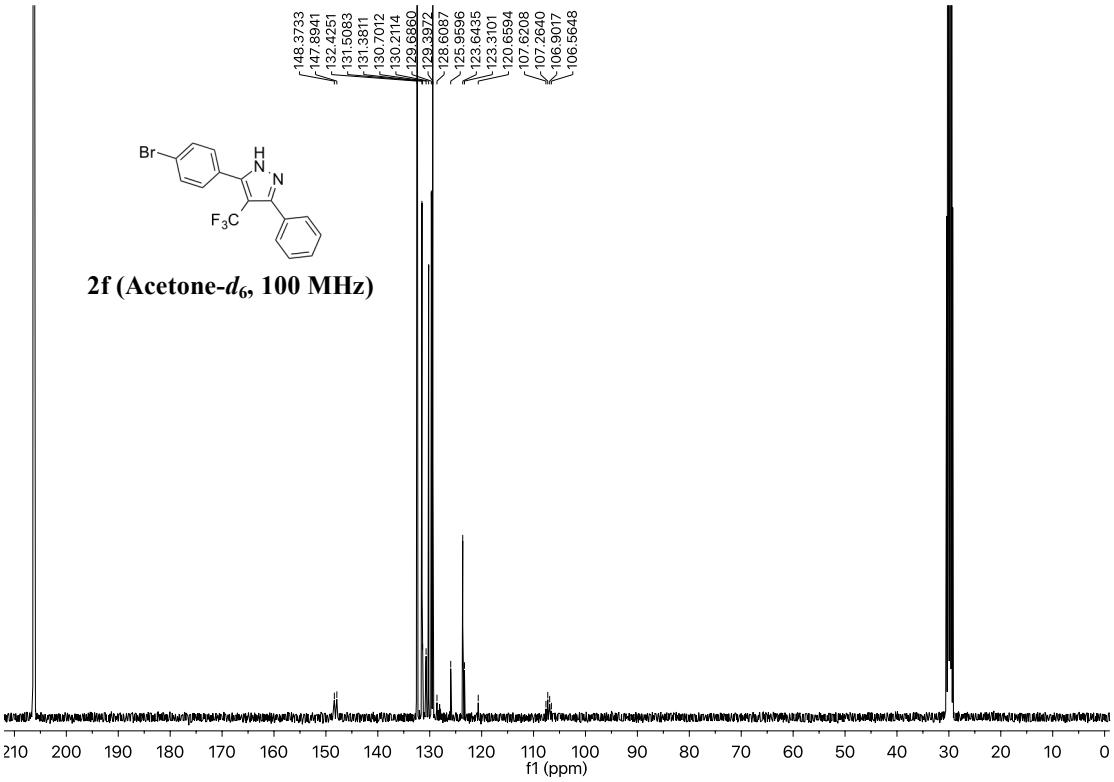


2e (Acetone-d_6, 100 MHz)

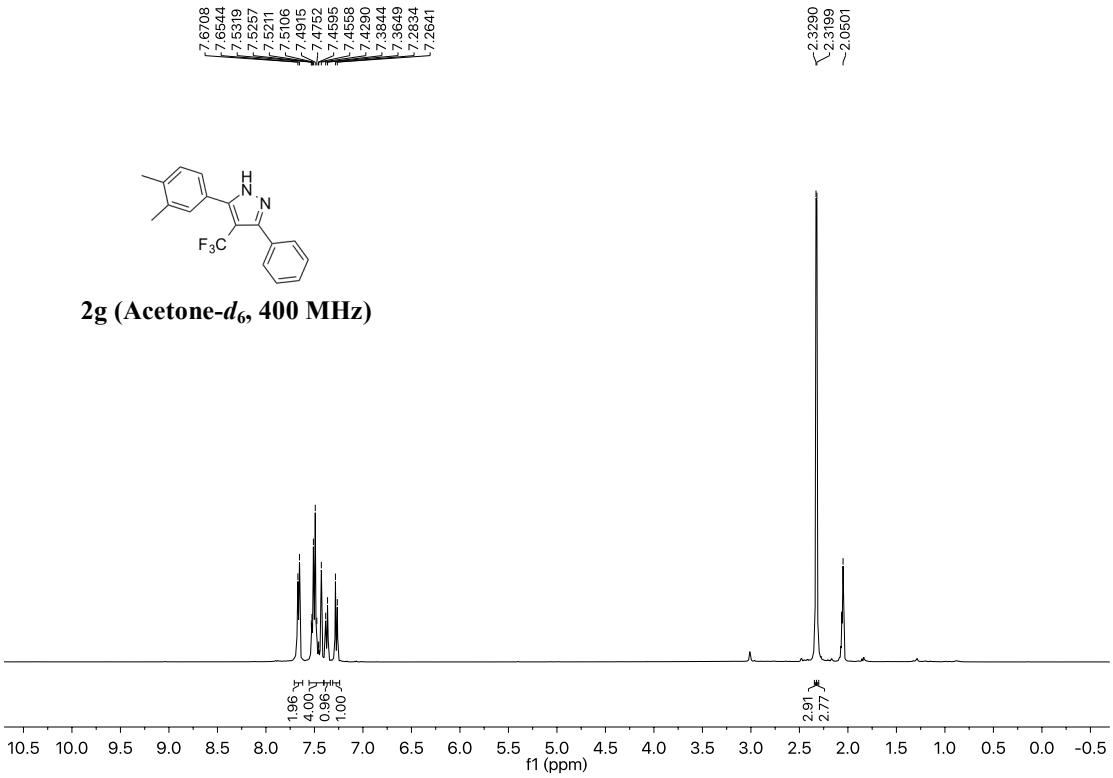


2f (Acetone-d_6, 400 MHz)

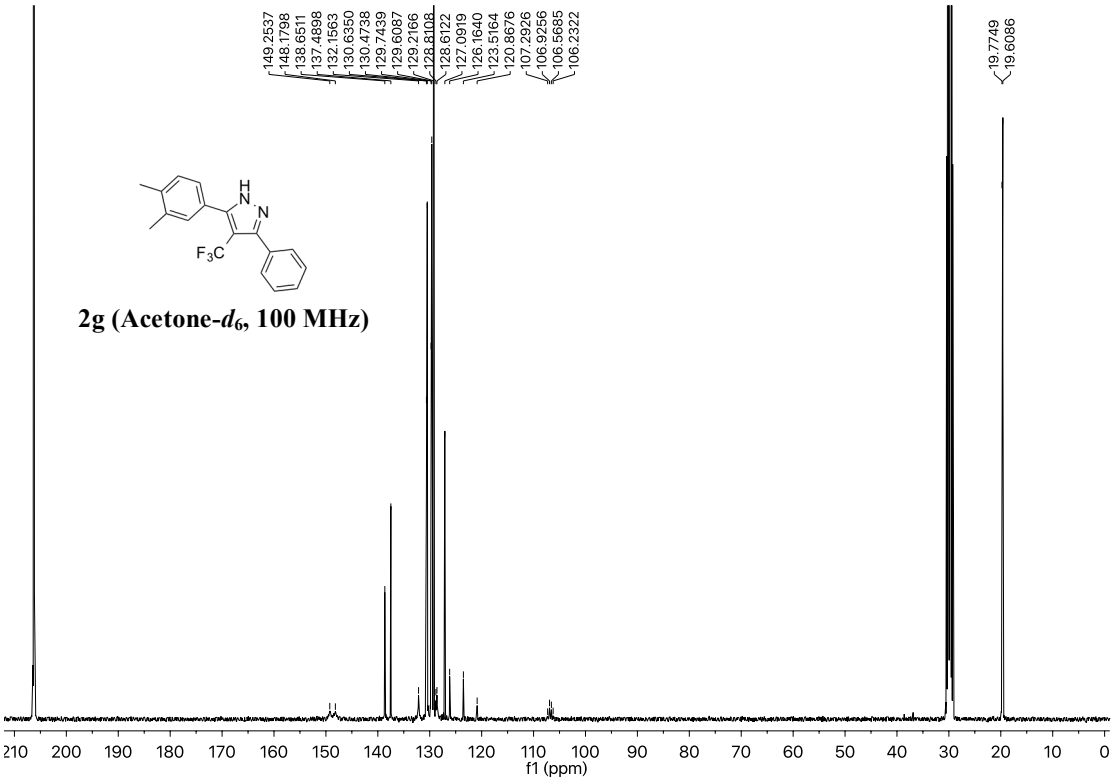




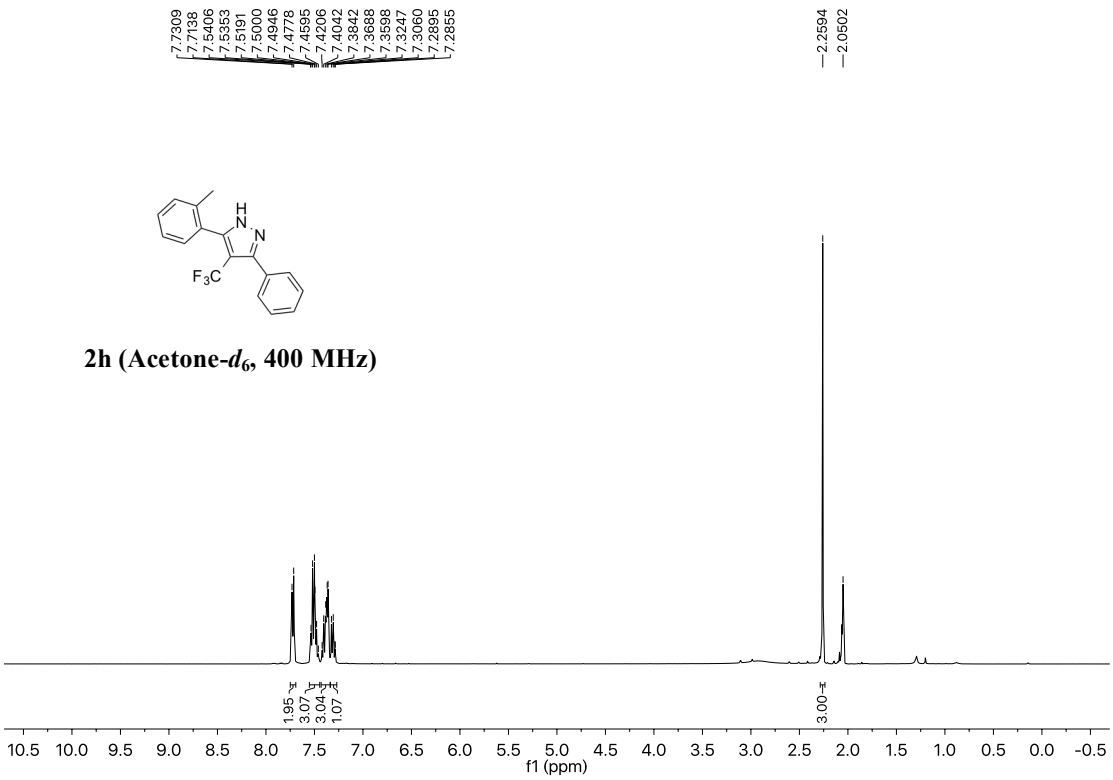
2f (Acetone-d_6, 100 MHz)



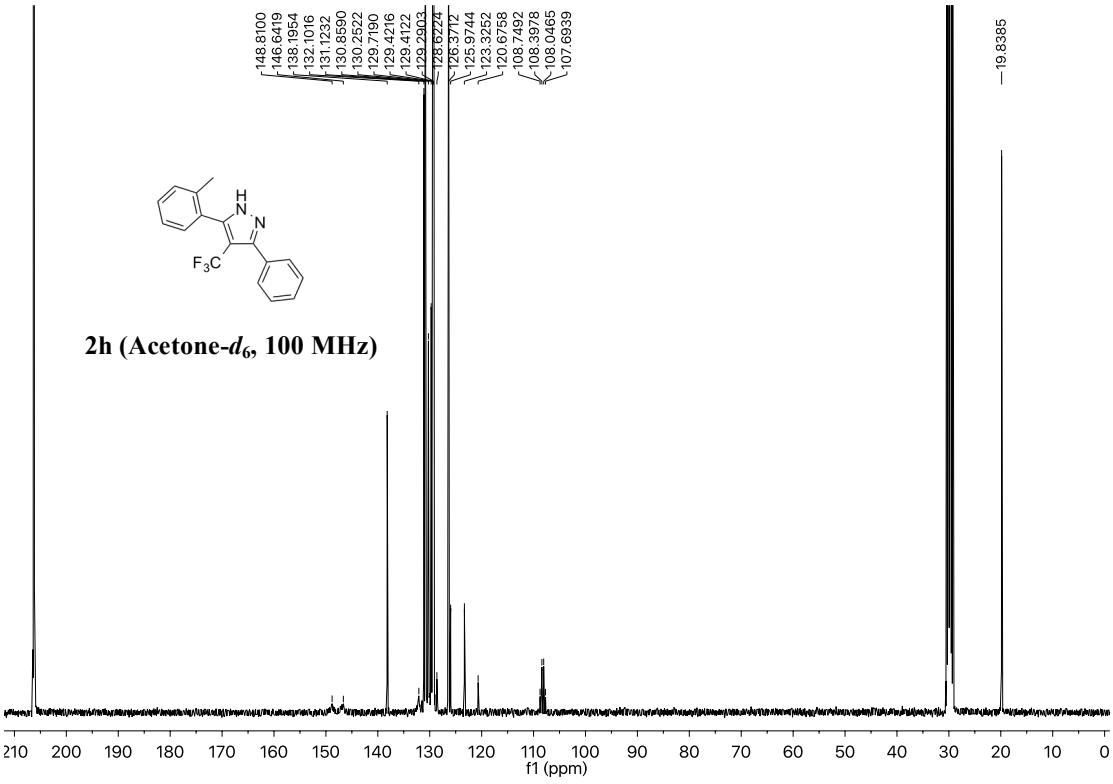
2g (Acetone-d_6, 400 MHz)



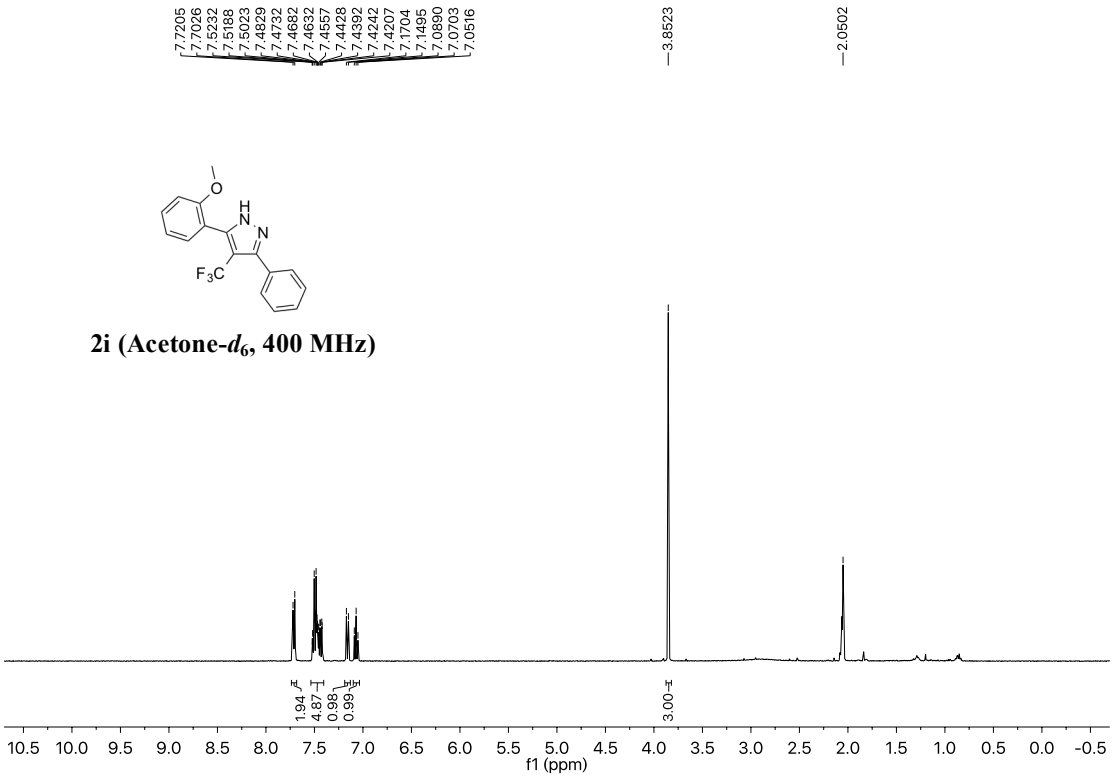
2g (Acetone-d_6, 100 MHz)



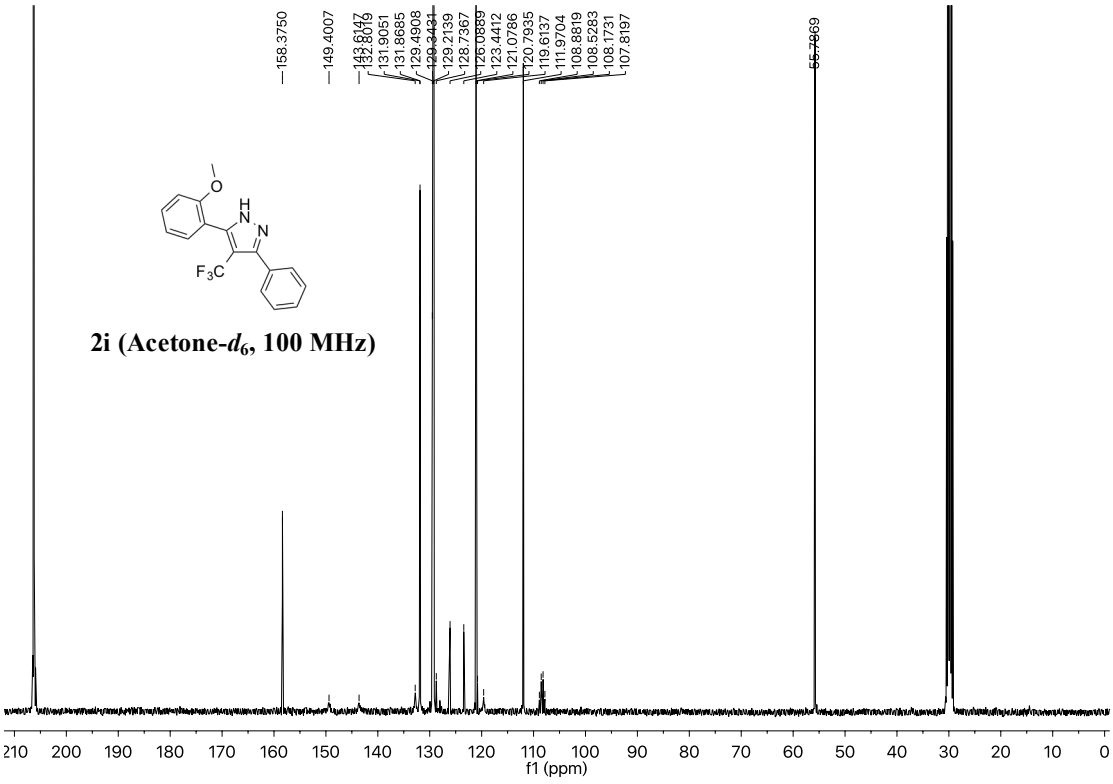
2h (Acetone-d_6, 400 MHz)



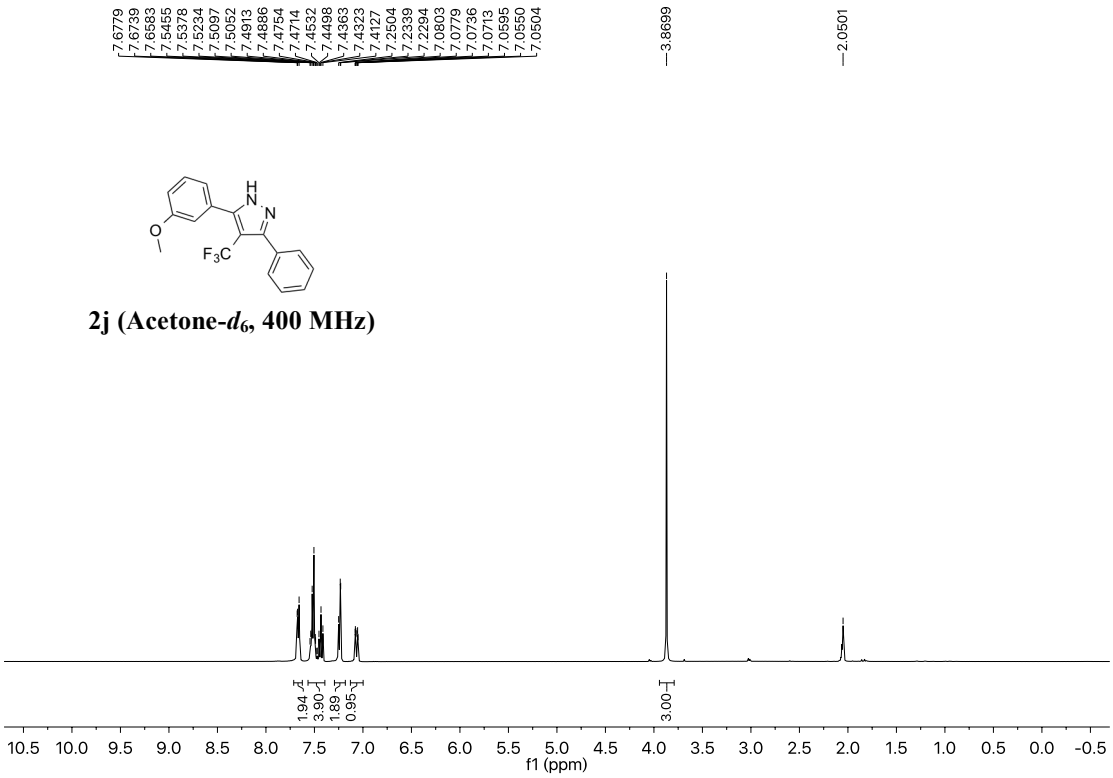
2h (Acetone-d_6, 100 MHz)



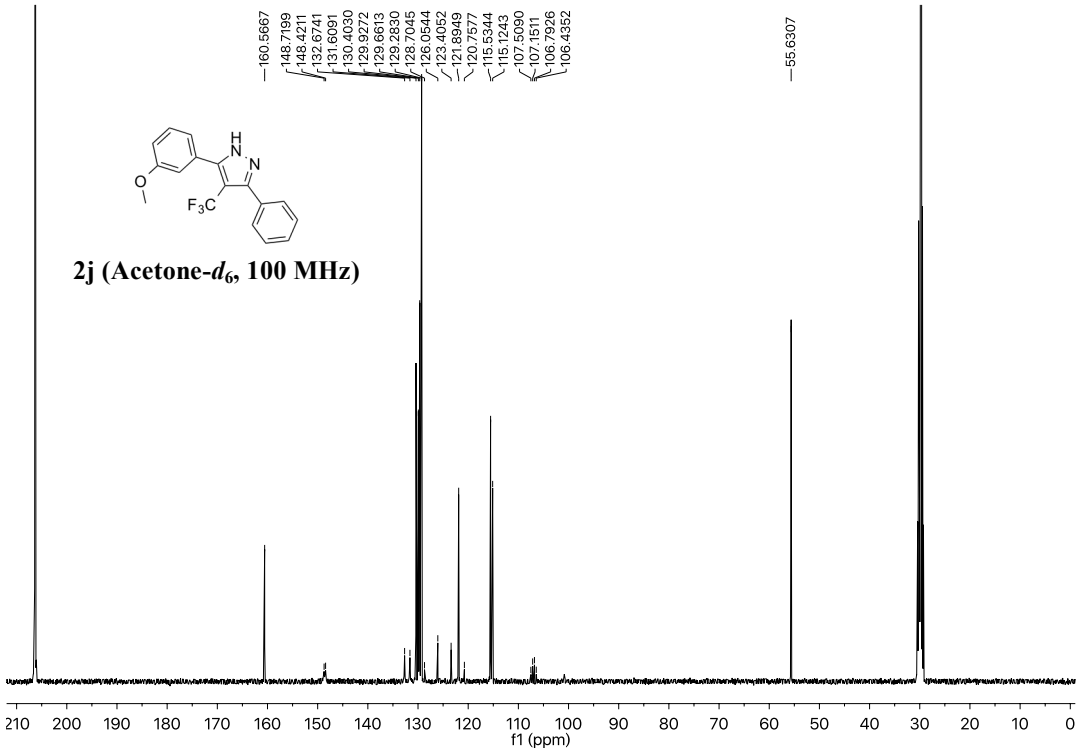
2i (Acetone-d_6, 400 MHz)



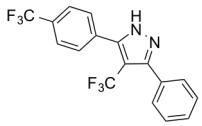
2i (Acetone-d_6, 100 MHz)



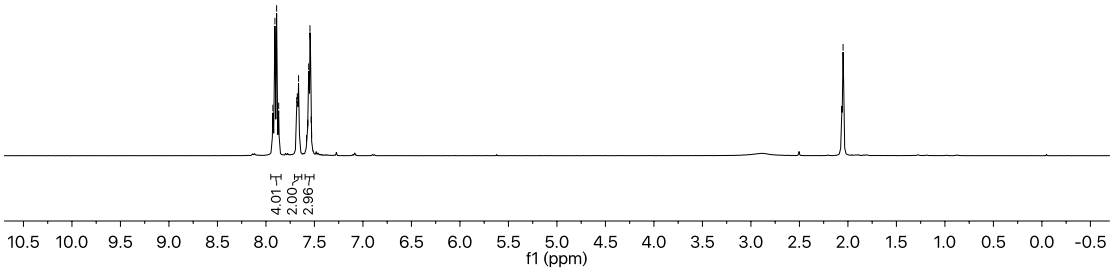
2j (Acetone-d_6, 400 MHz)

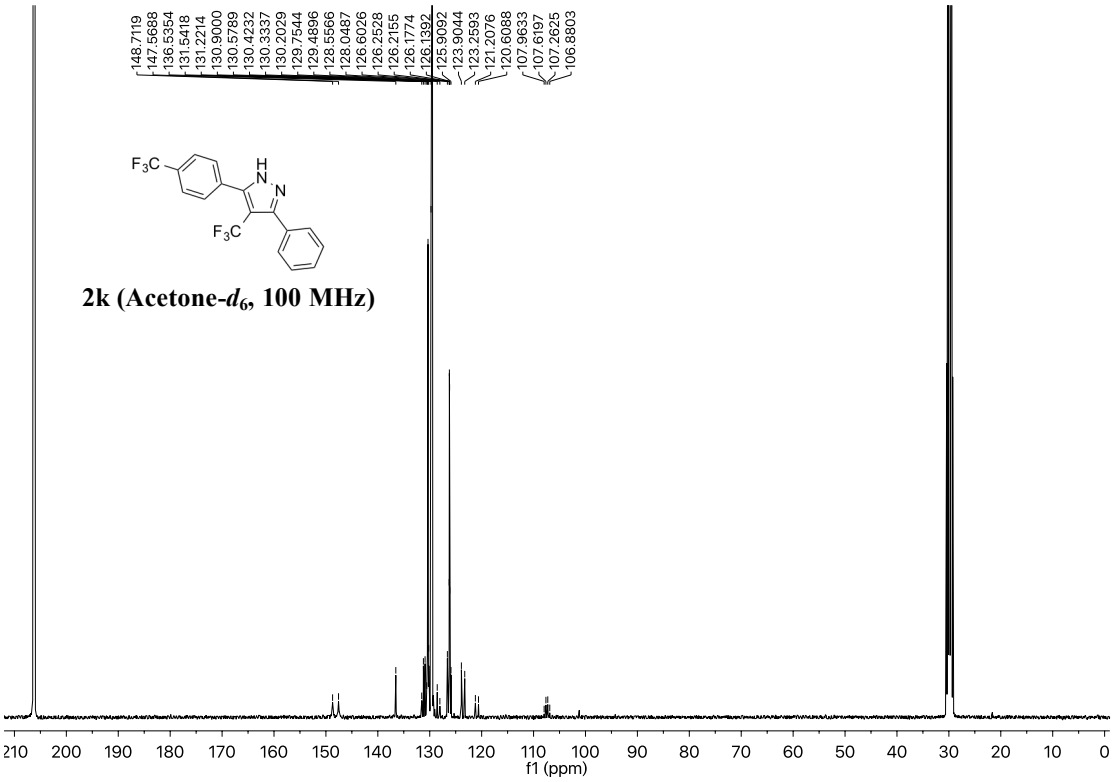


2j (Acetone-d_6, 100 MHz)

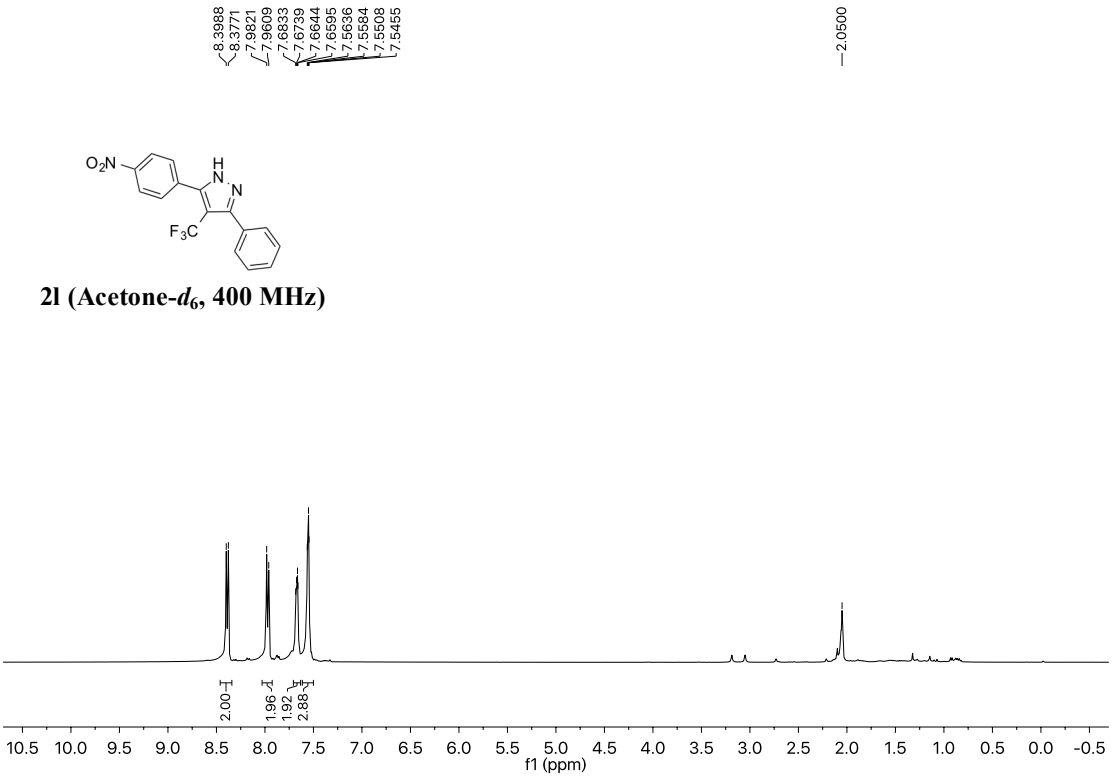


2k (Acetone-d_6, 400 MHz)

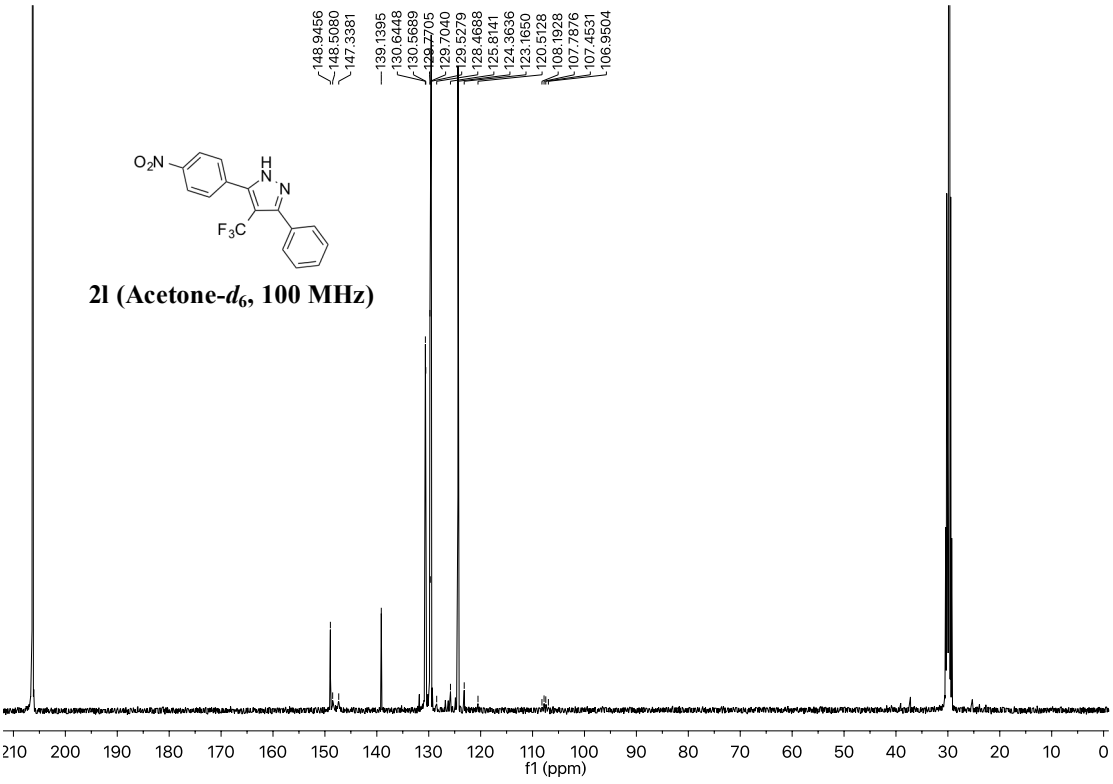




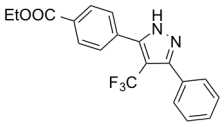
2k (Acetone-d_6, 100 MHz)



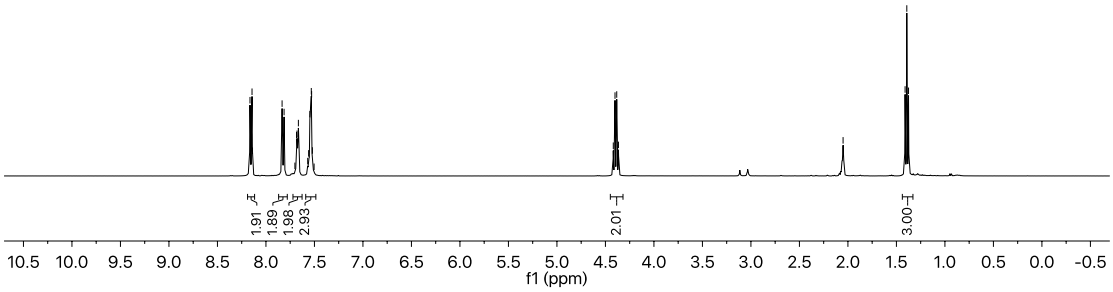
2l (Acetone-d_6, 400 MHz)

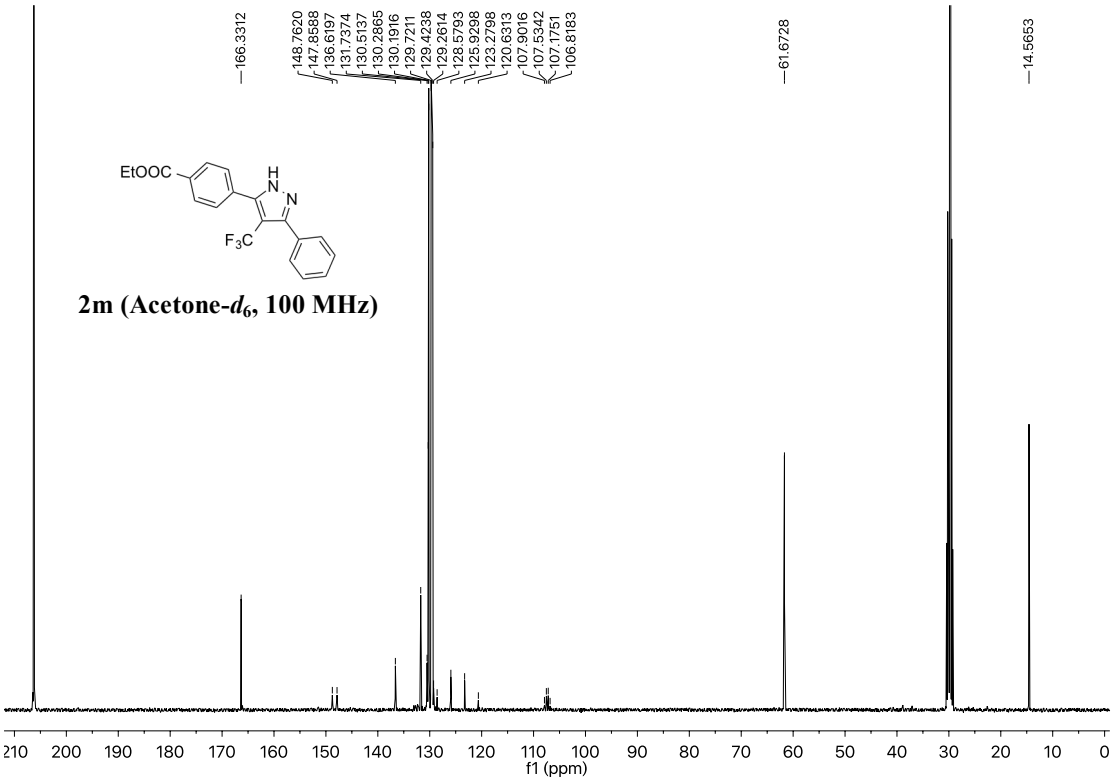


2l (Acetone-d_6, 100 MHz)

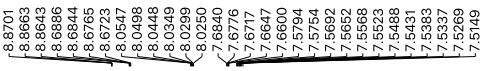


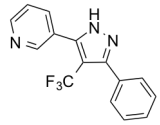
2m (Acetone-d_6, 400 MHz)



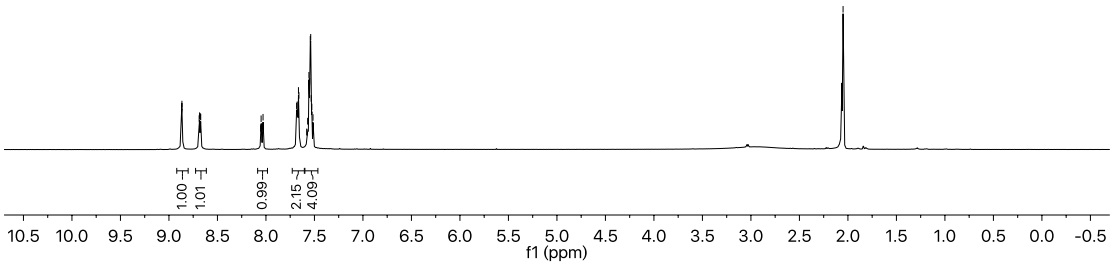


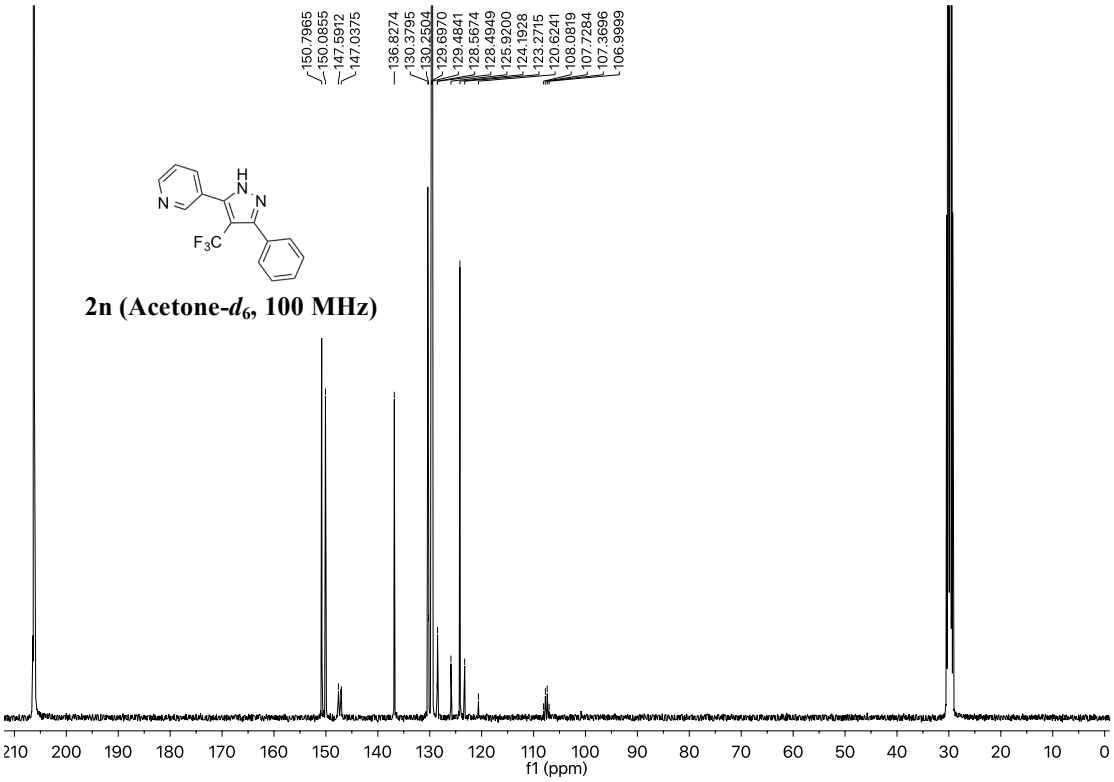
2m (Acetone-d_6, 100 MHz)



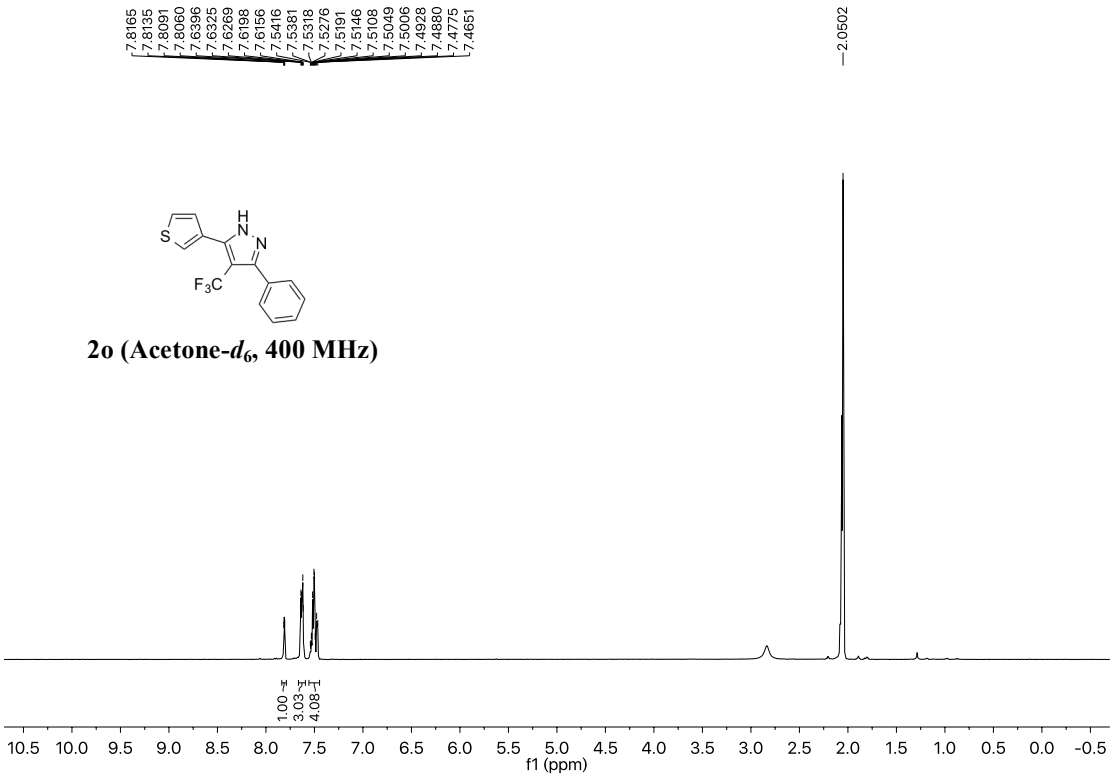


2n (Acetone-d_6, 400 MHz)

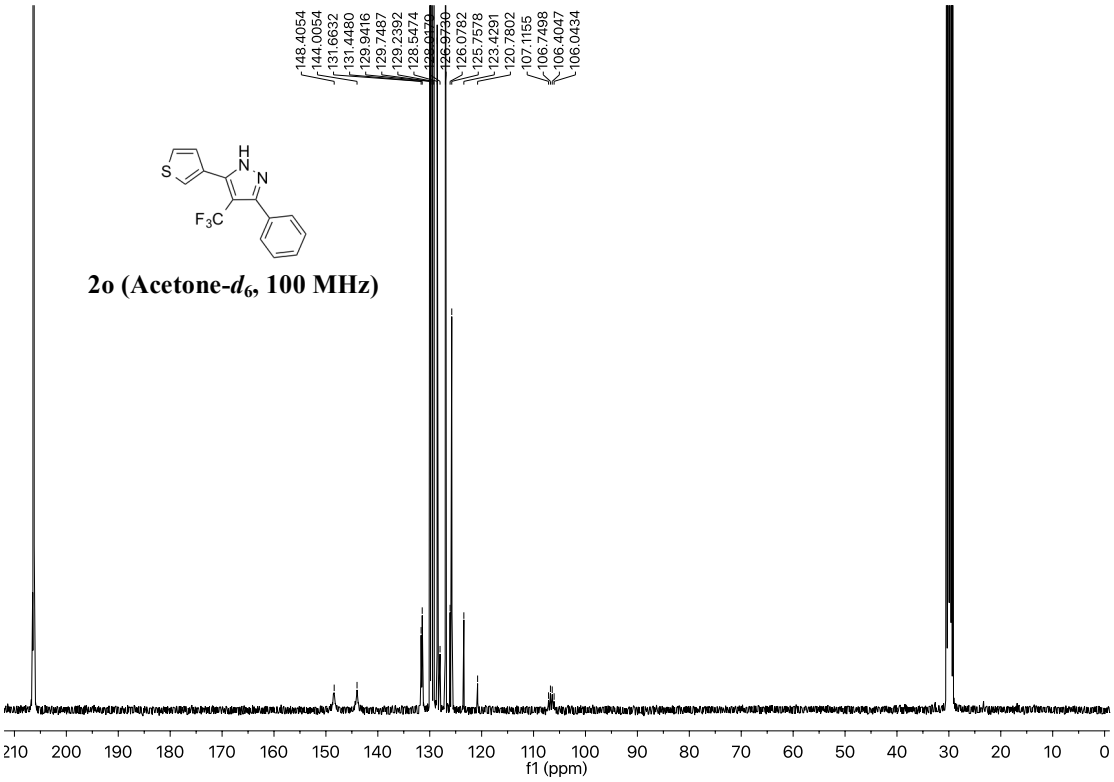




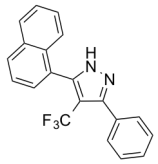
2n (Acetone-d_6, 100 MHz)



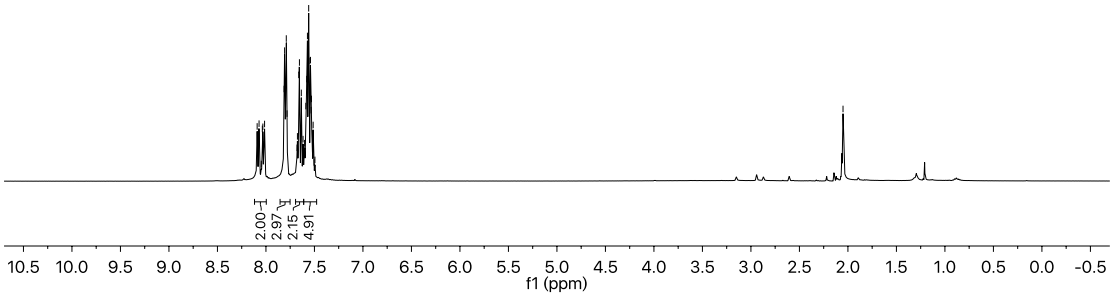
2o (Acetone-d_6, 400 MHz)

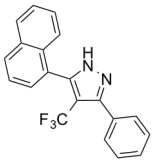


2o (Acetone-d_6, 100 MHz)

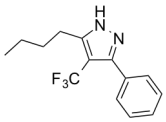


2p (Acetone-d_6, 400 MHz)

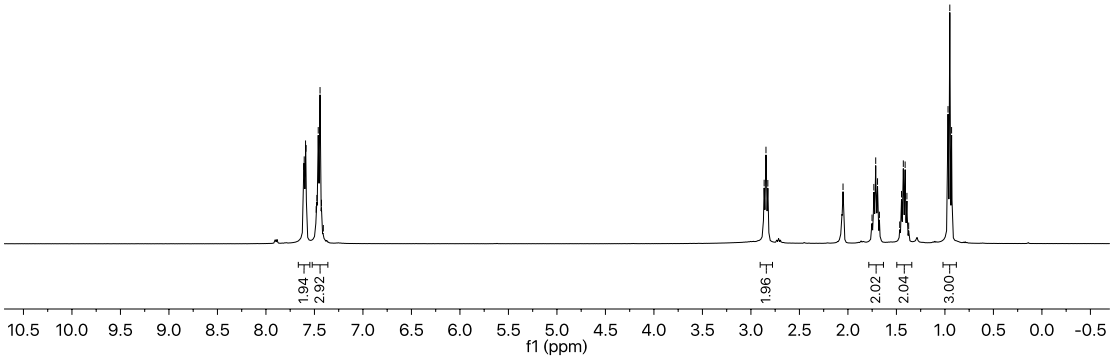


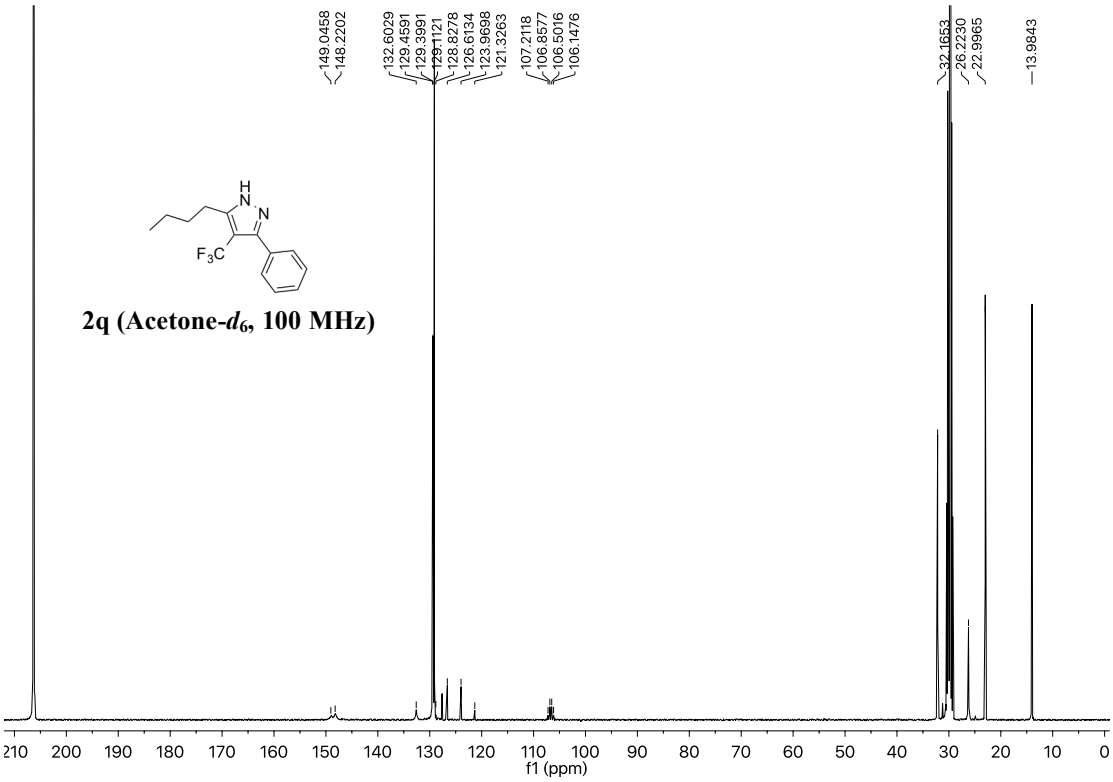


2p (Acetone-d_6, 100 MHz)

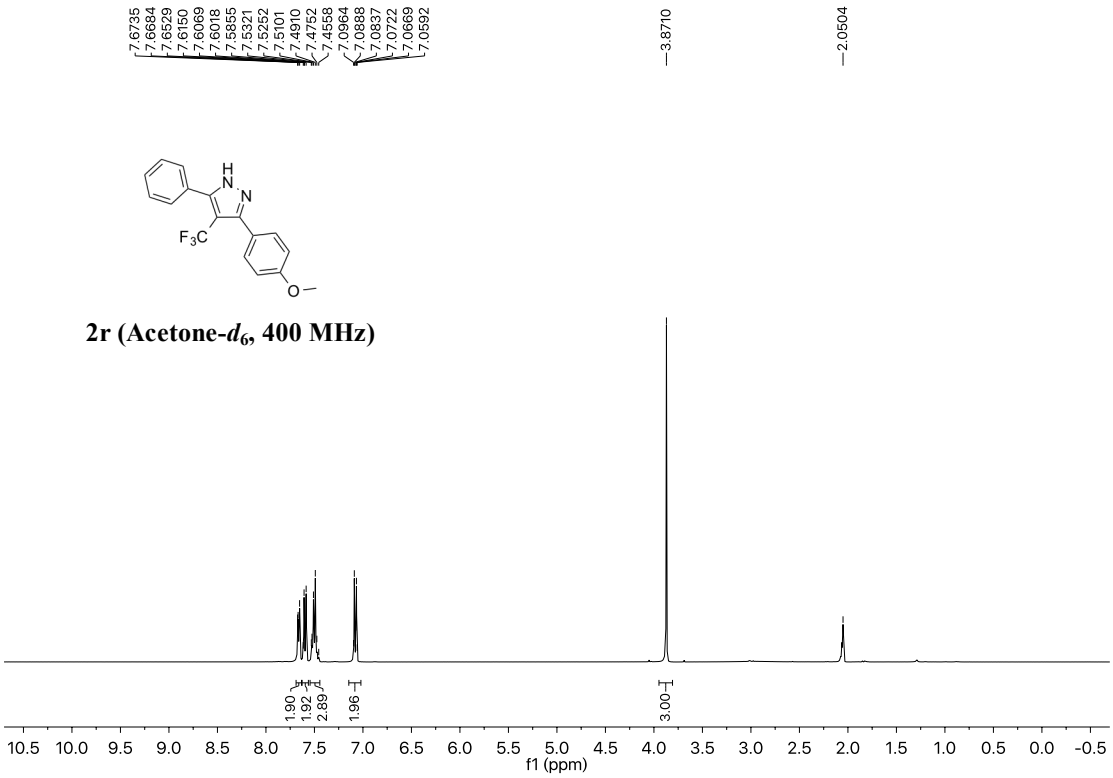


2q (Acetone-d_6, 400 MHz)

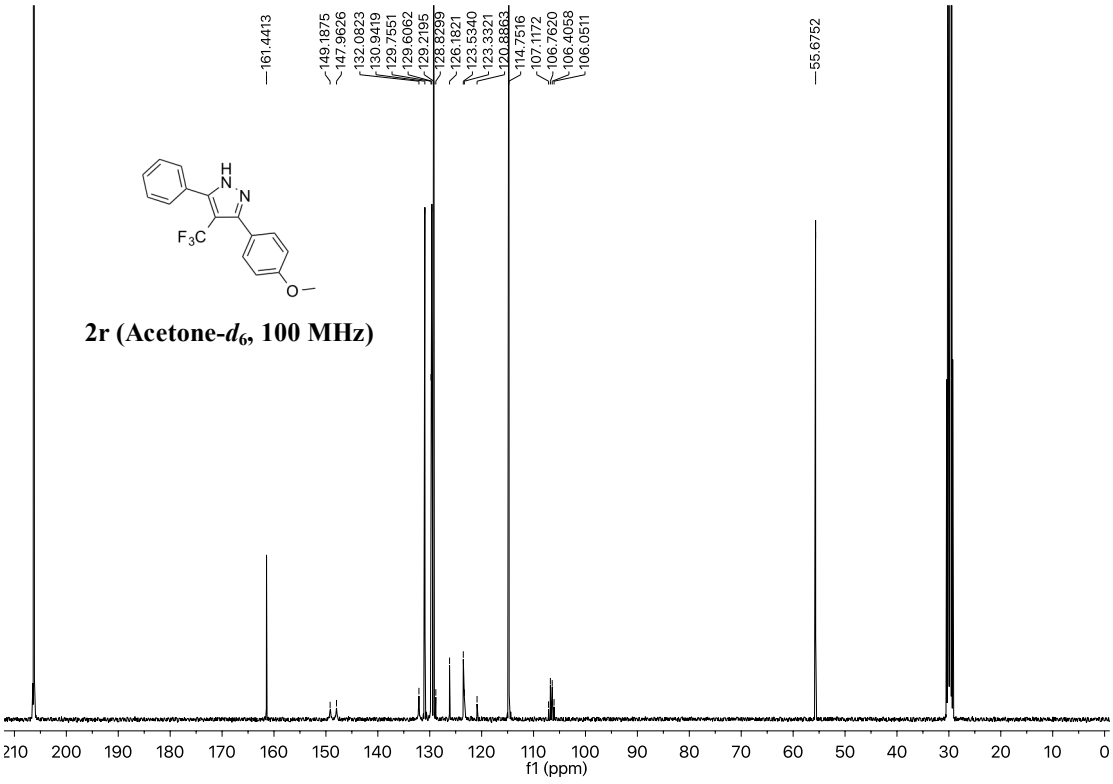




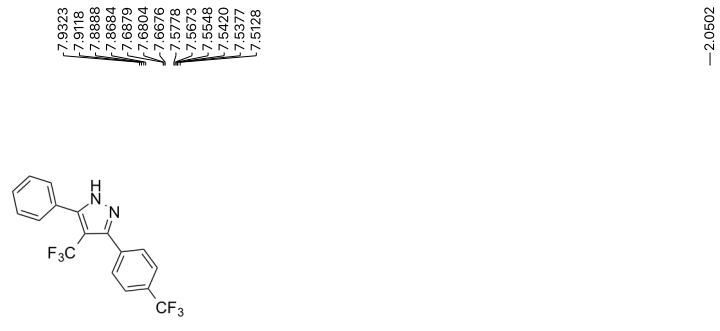
2q (Acetone-d_6, 100 MHz)



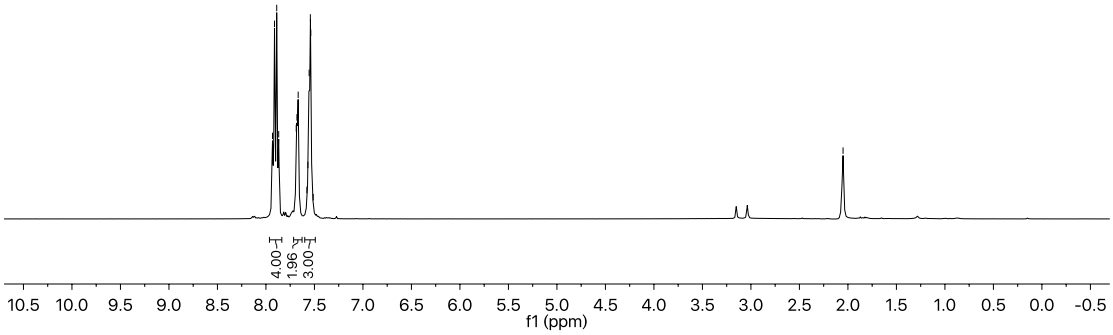
2r (Acetone-d_6, 400 MHz)

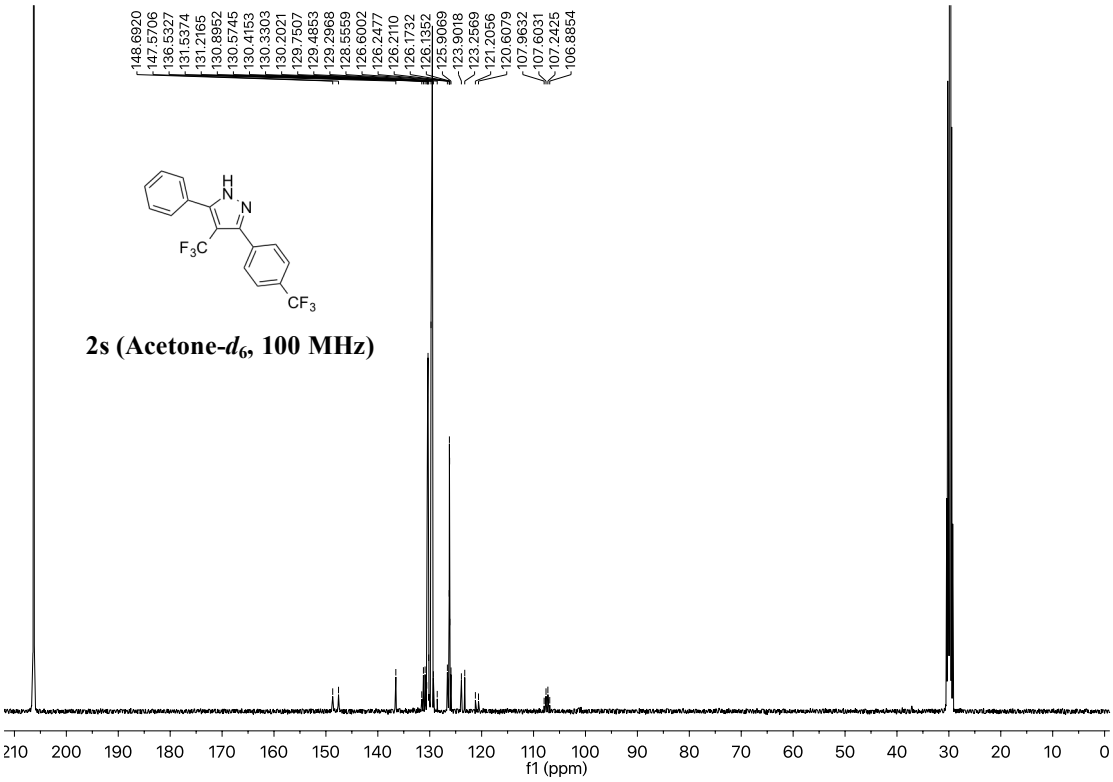


2r (Acetone-d_6, 100 MHz)

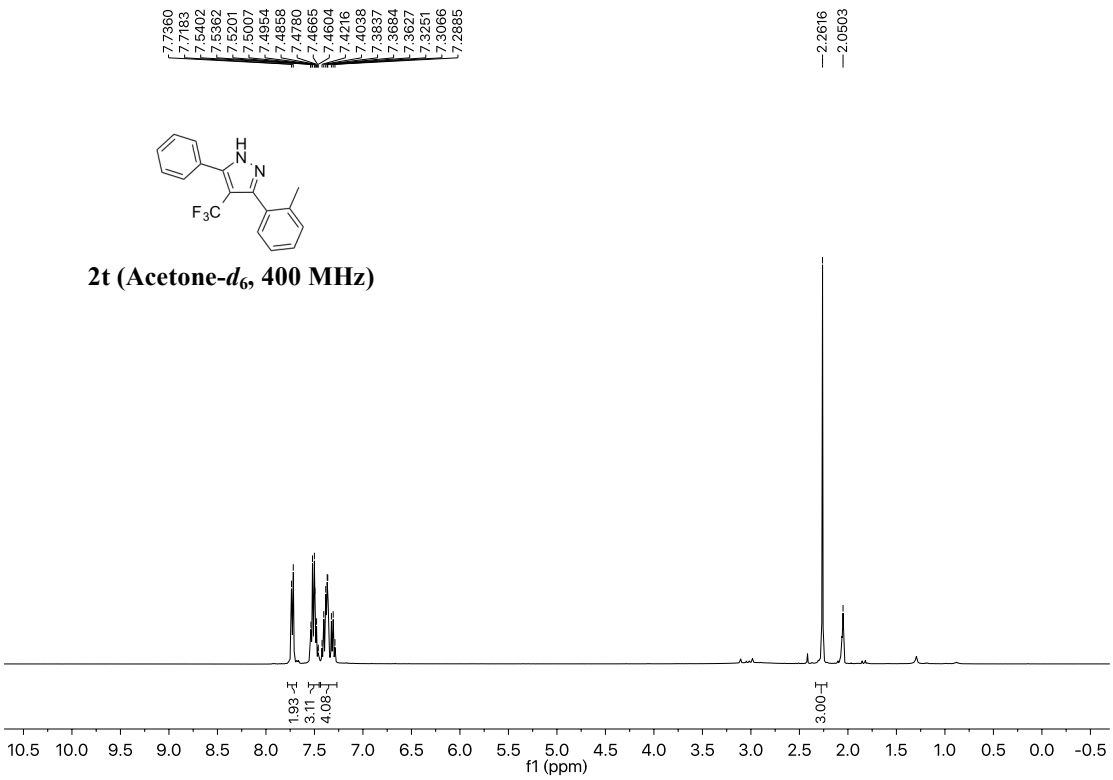


2s (Acetone-d_6, 400 MHz)

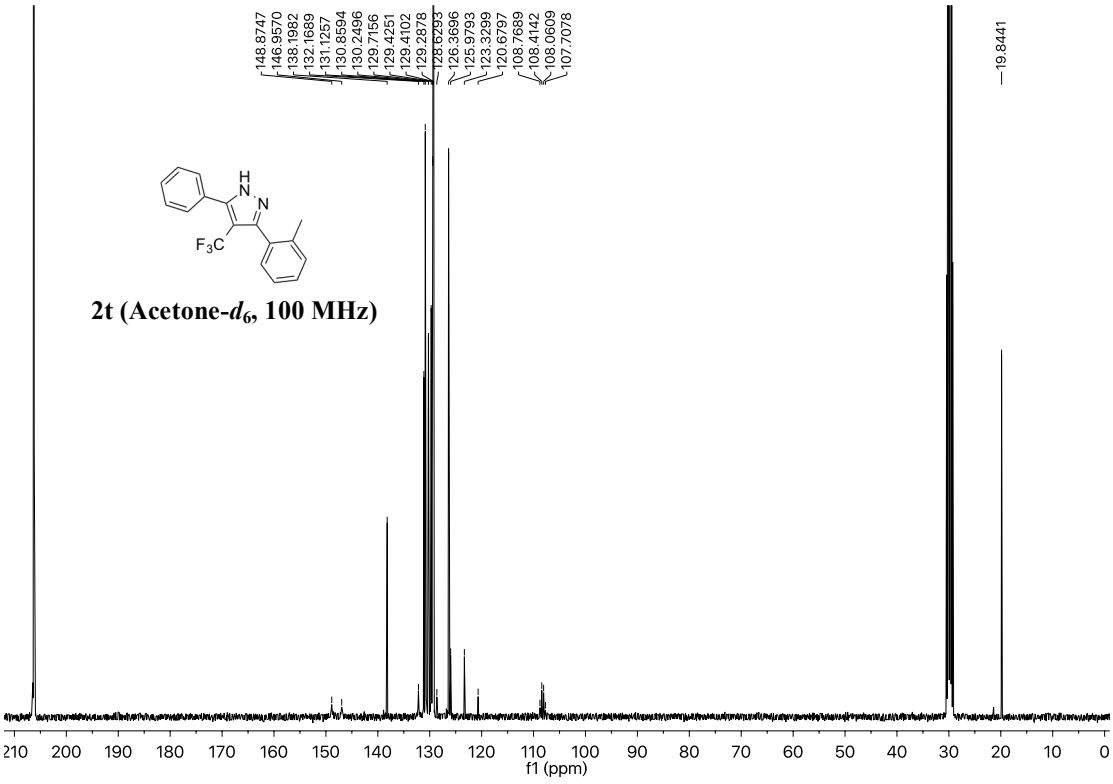




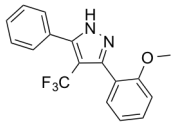
2s (Acetone-d_6, 100 MHz)



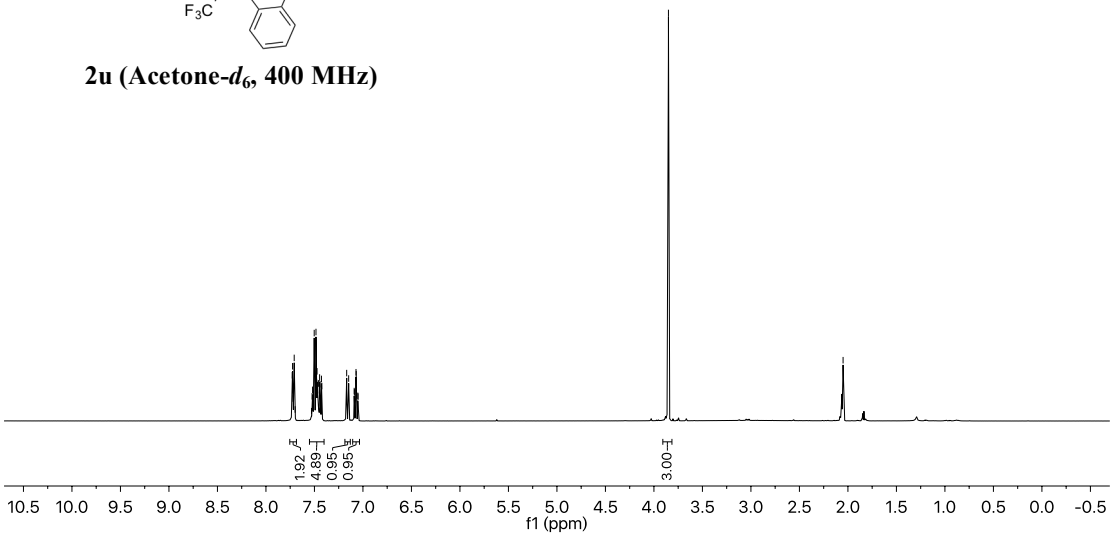
2t (Acetone-d_6, 400 MHz)

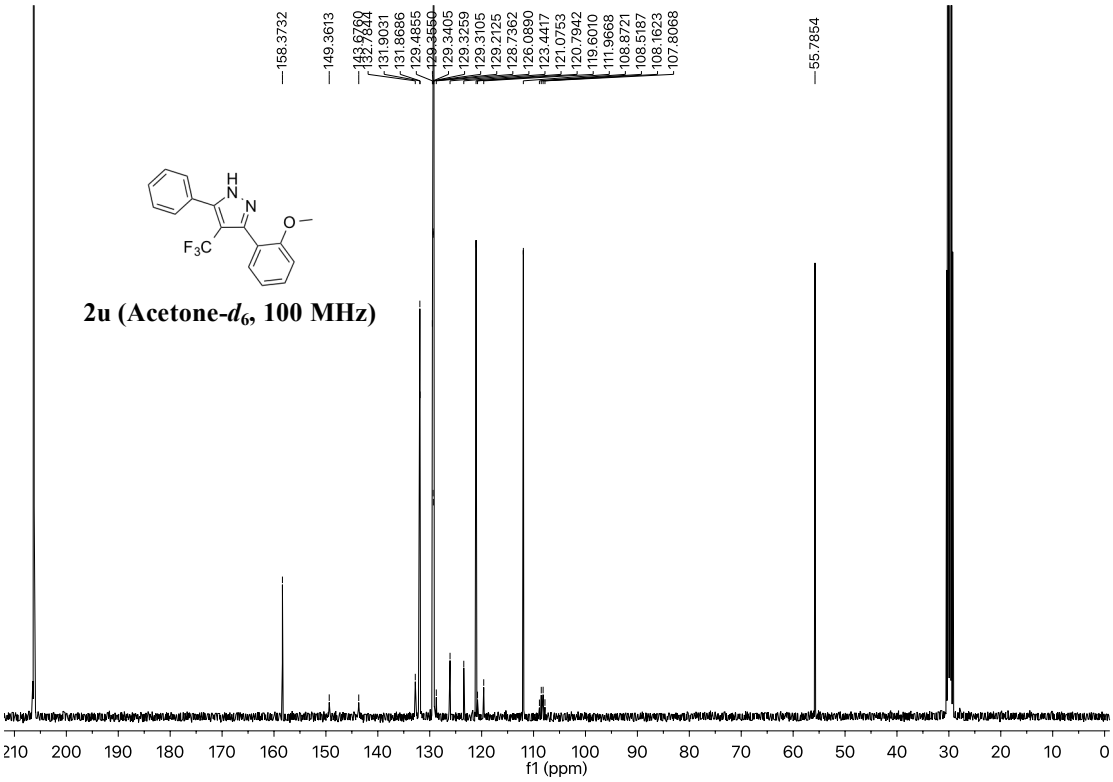


2t (Acetone-d_6, 100 MHz)

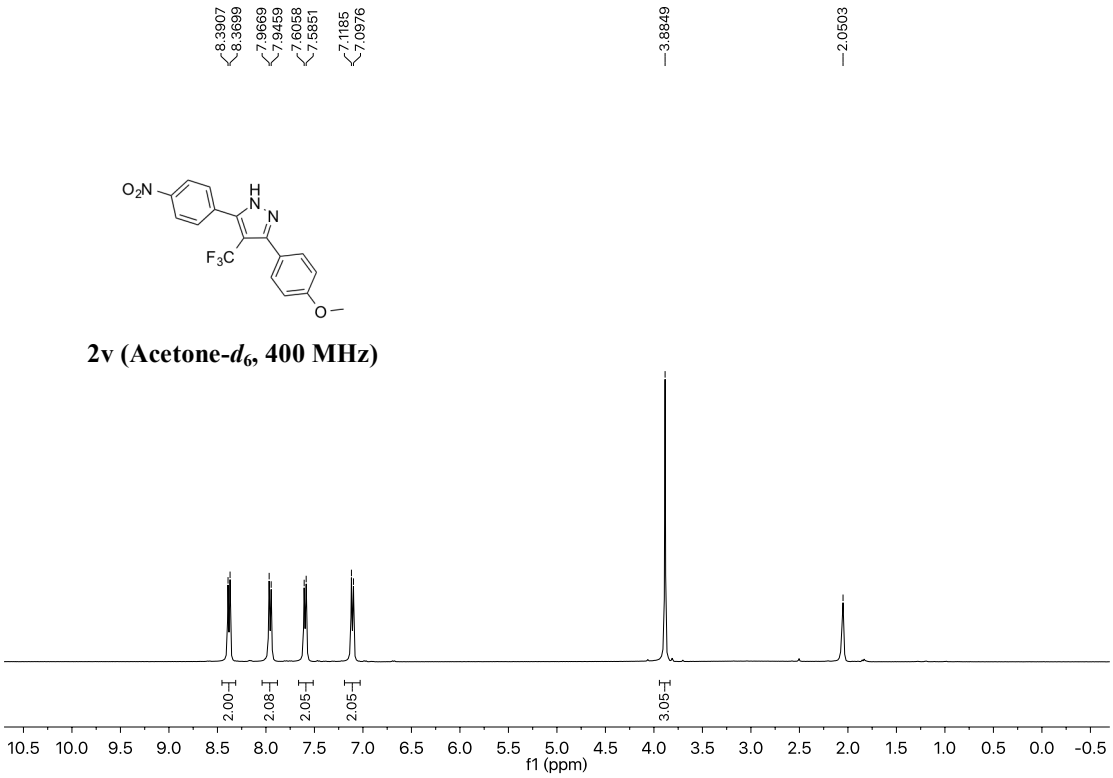


2u (Acetone-d_6, 400 MHz)

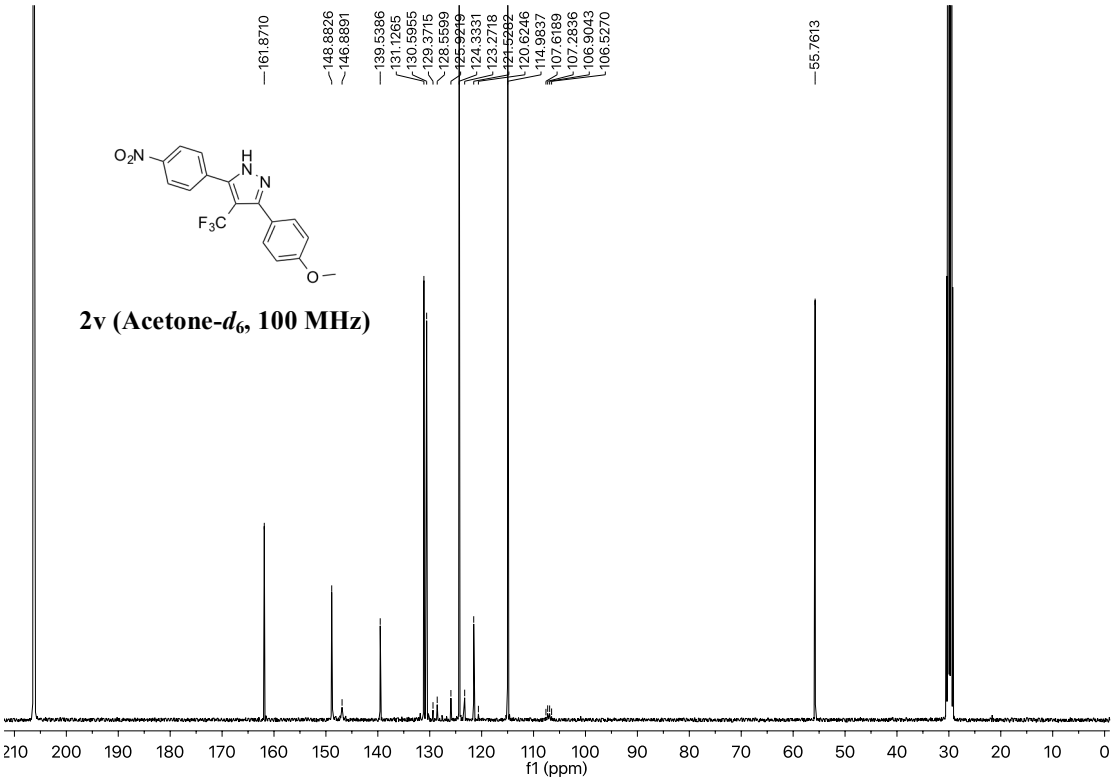




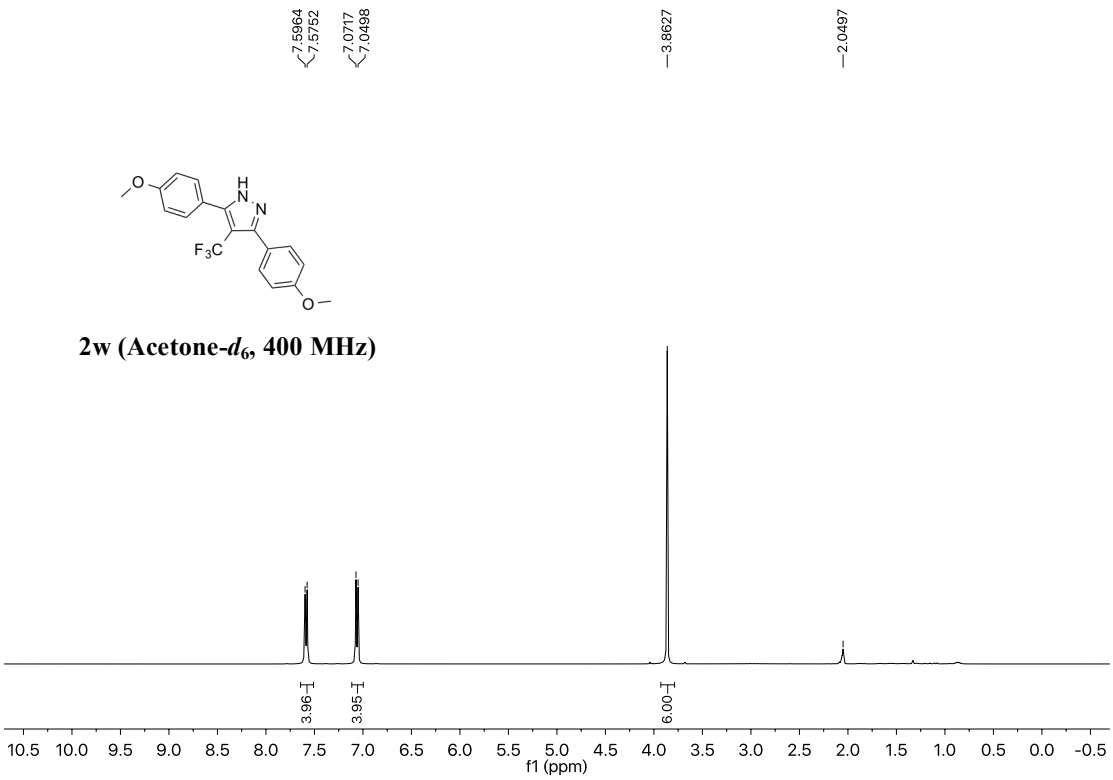
2u (Acetone-d_6, 100 MHz)



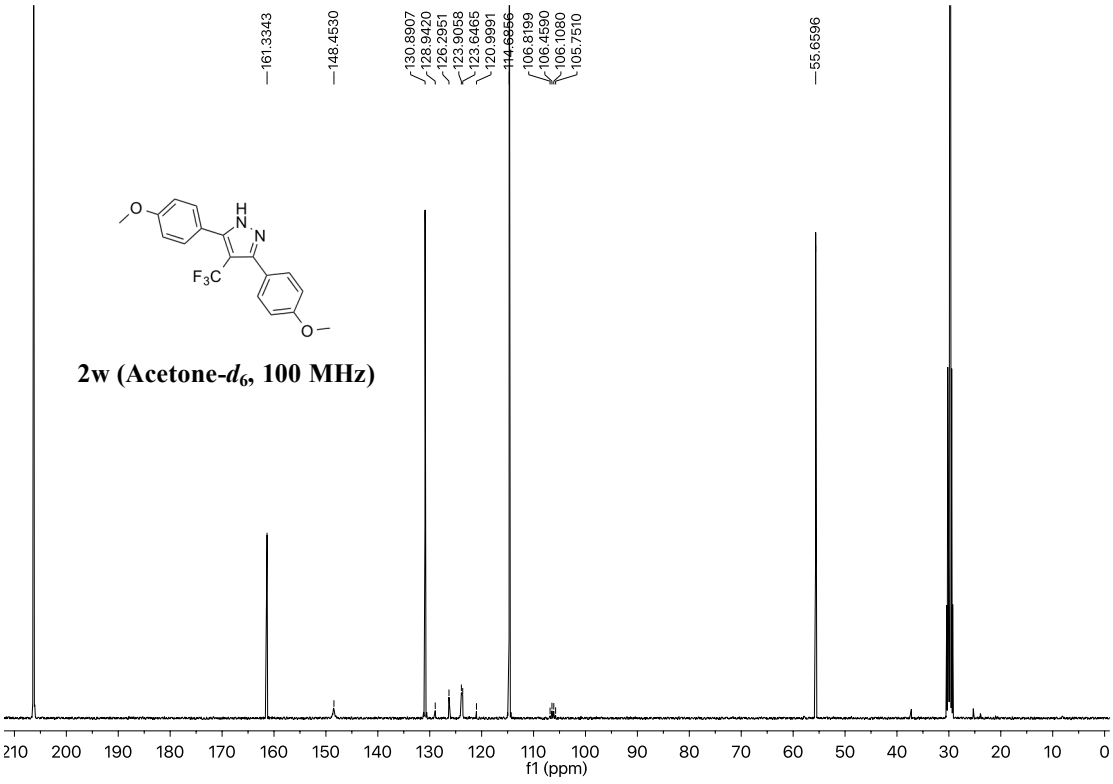
2v (Acetone-d_6, 400 MHz)



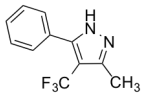
2v (Acetone-d_6, 100 MHz)



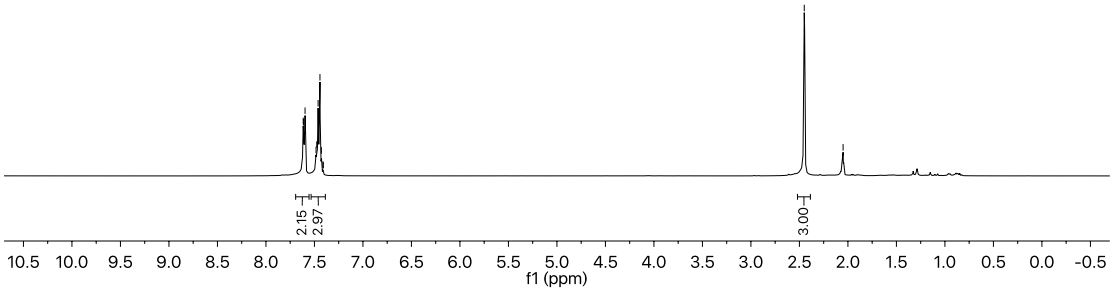
2w (Acetone-d_6, 400 MHz)

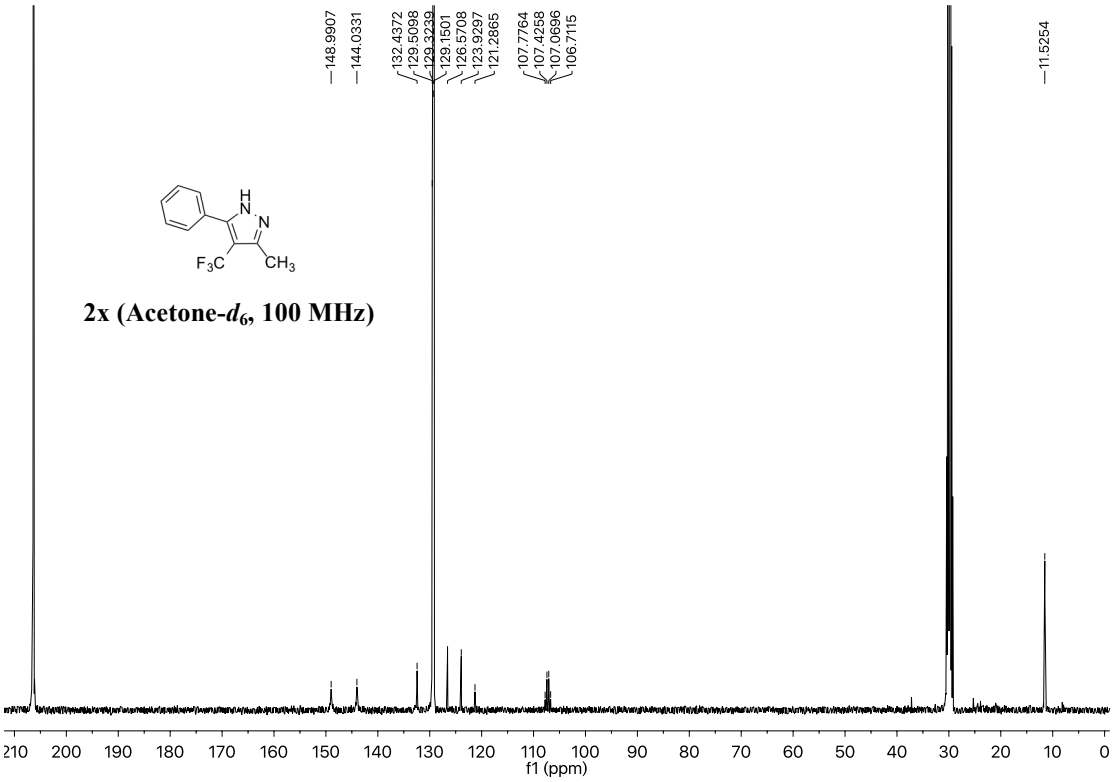


2w (Acetone-d_6, 100 MHz)

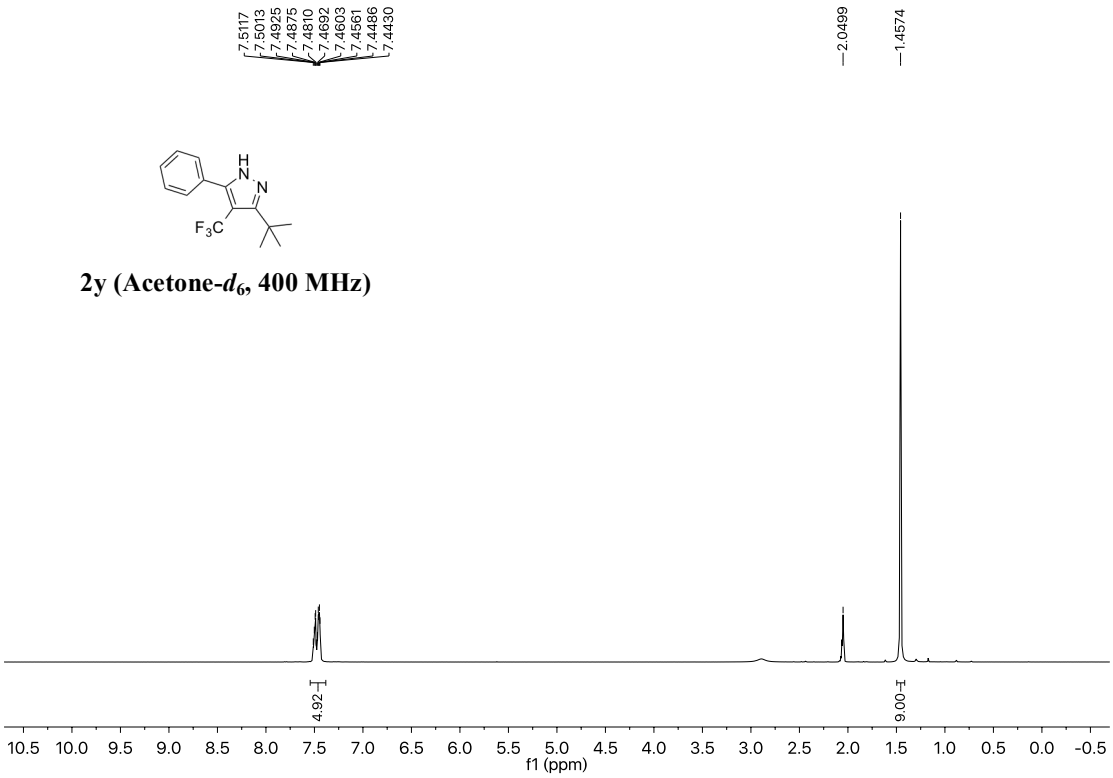


2x (Acetone-d_6, 400 MHz)

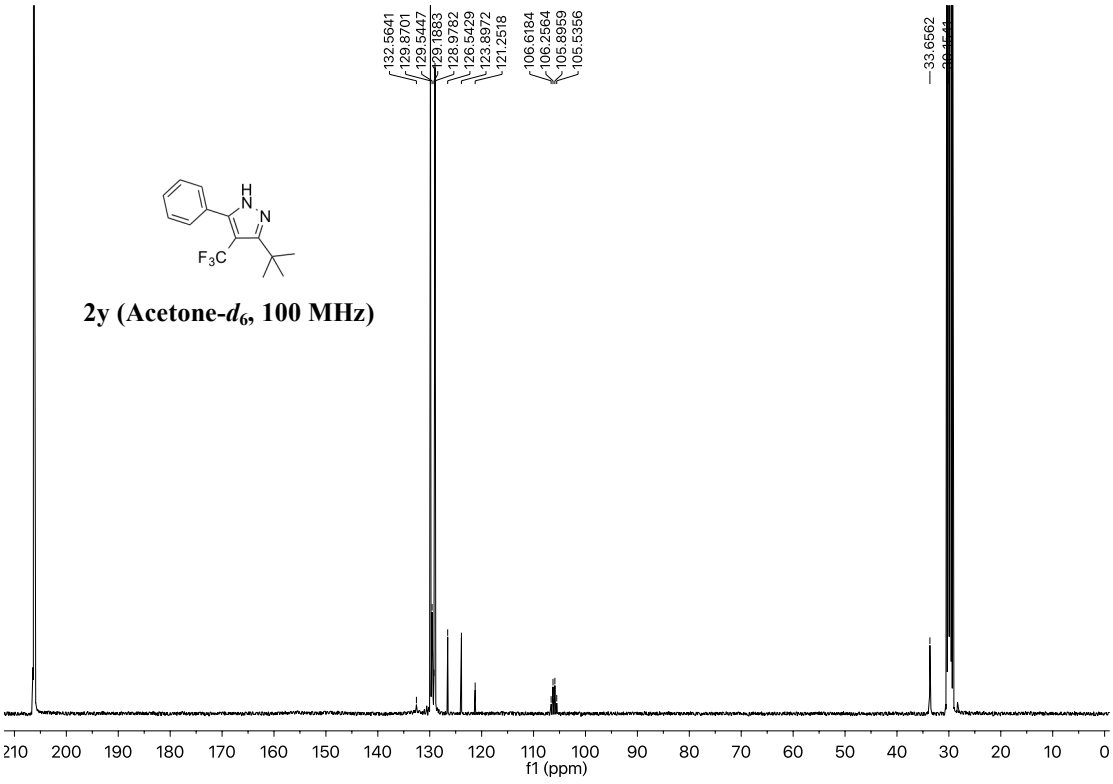




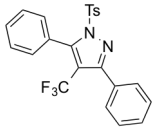
2x (Acetone-d_6, 100 MHz)



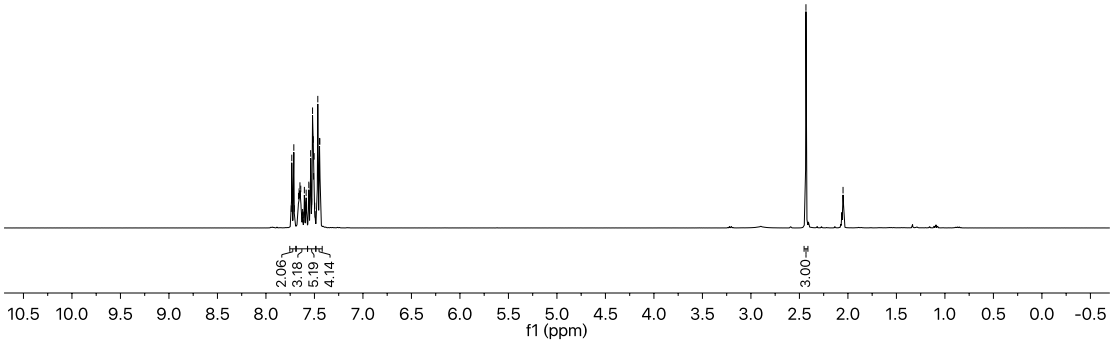
2y (Acetone-d_6, 400 MHz)

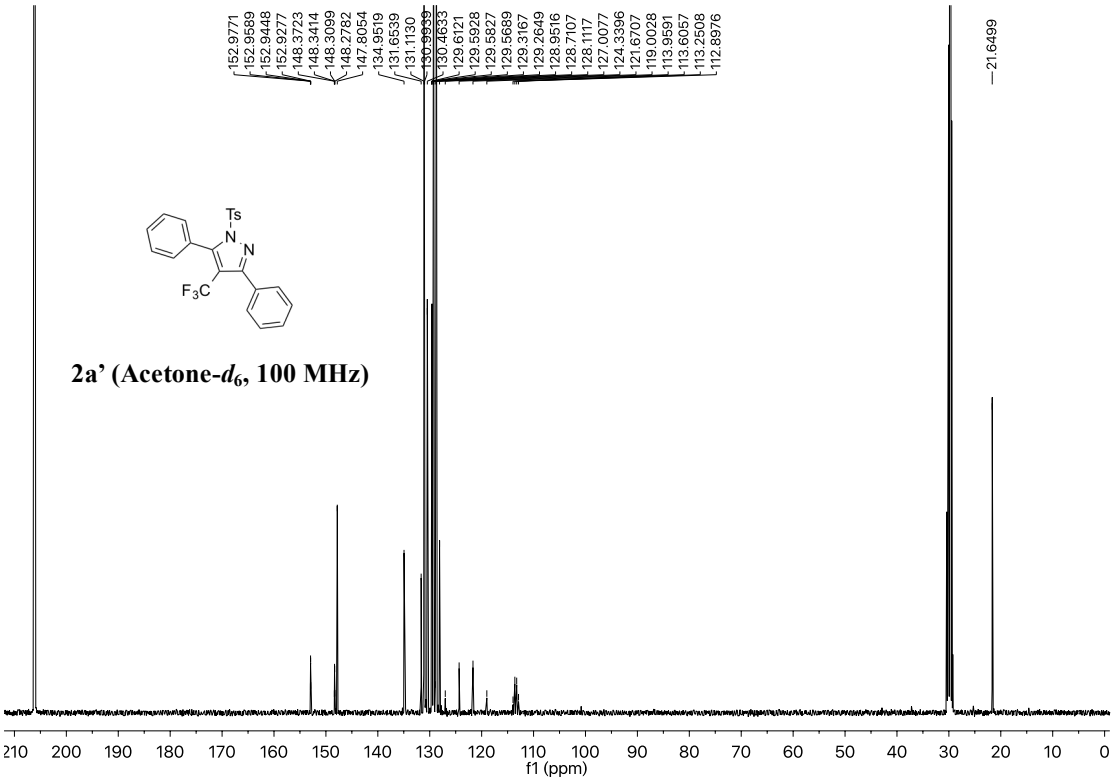


2y (Acetone-d_6, 100 MHz)

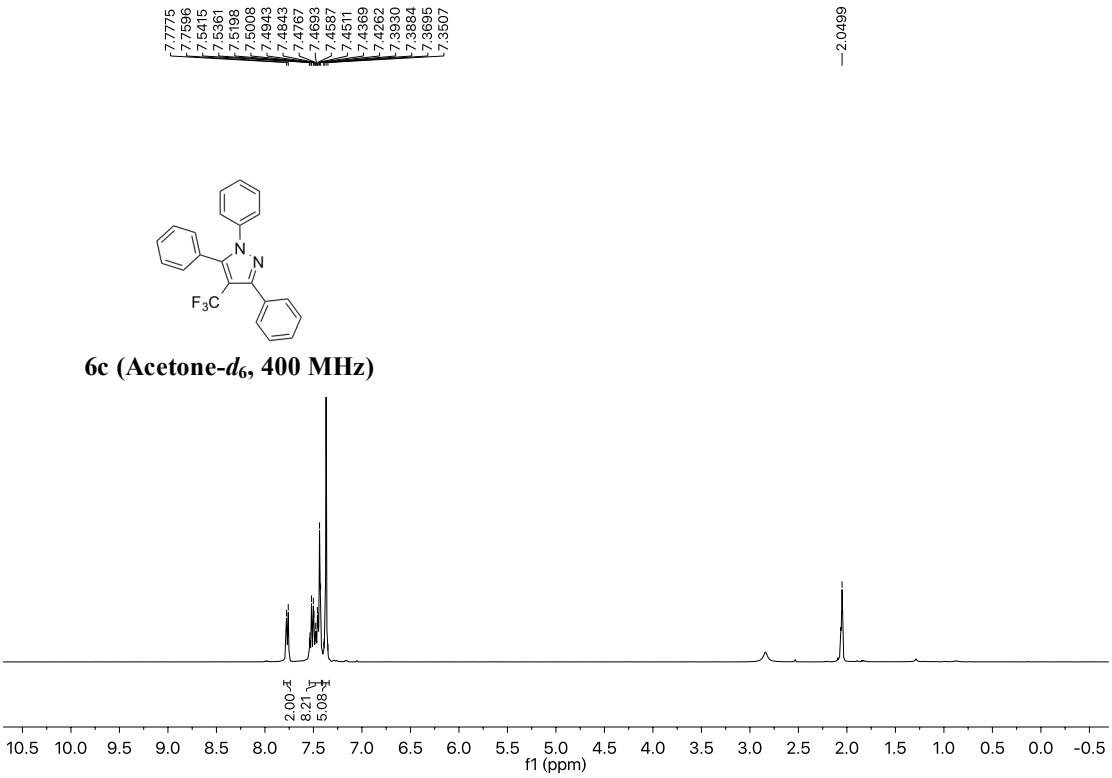


2a' (Acetone-d_6, 400 MHz)

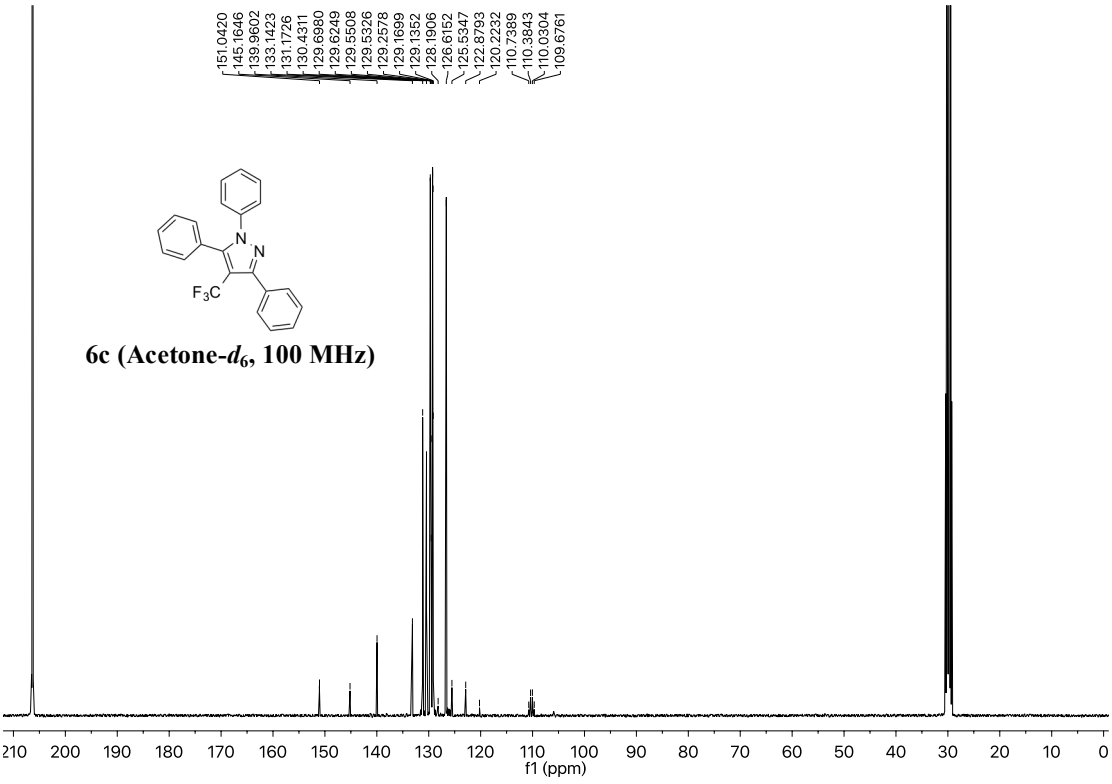




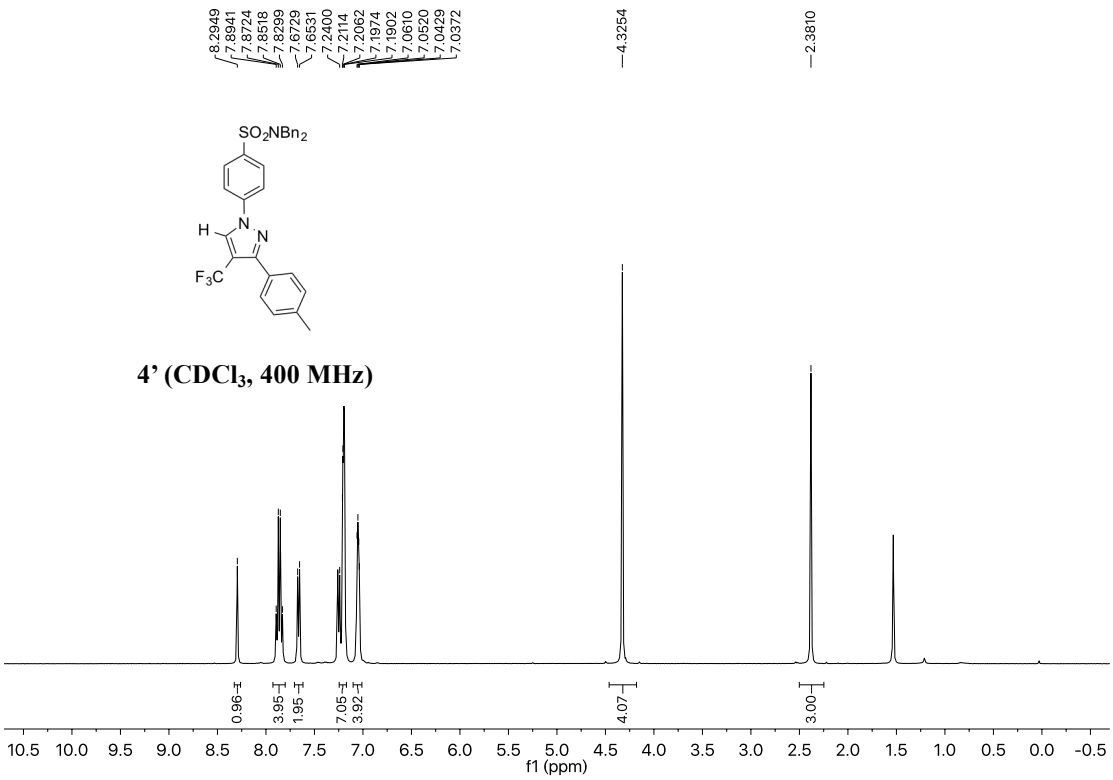
2a' (Acetone-d_6, 100 MHz)



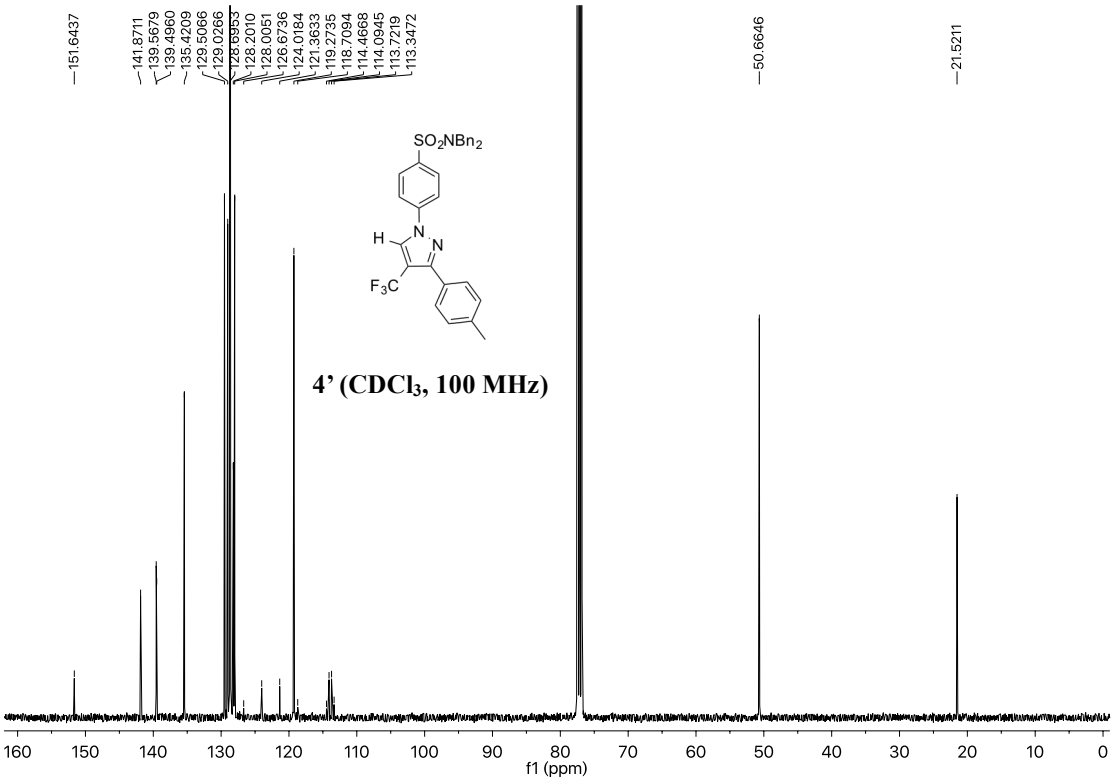
6c (Acetone-d_6, 400 MHz)



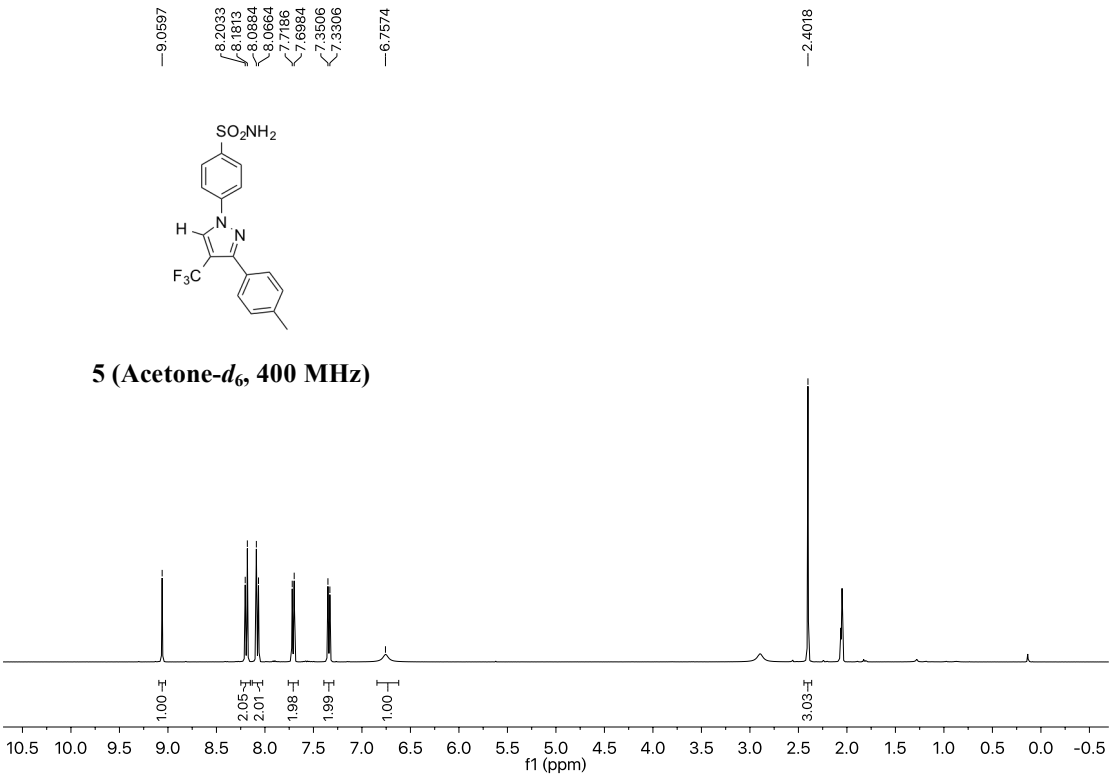
6c (Acetone-d_6, 100 MHz)



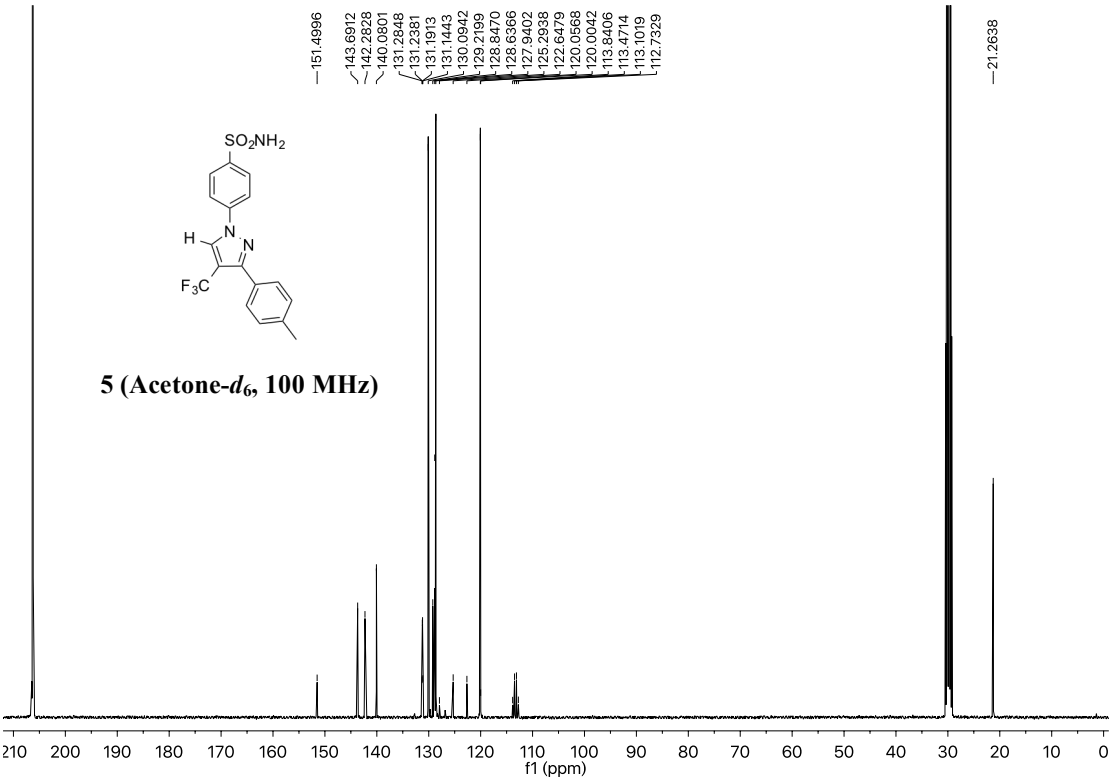
4' ($CDCl_3$, 400 MHz)



4' ($CDCl_3$, 100 MHz)



5 (Acetone-d_6, 400 MHz)



5 (Acetone-d_6, 100 MHz)