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Supporting Information

Copper-catalyzed B–H bond insertion reaction of azide-ynamide with borane adducts via α -imino copper carbenes

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General Information

All reactions were carried out with a Titan HMS-14 digital magnetic stirrer with hot plate. Ethyl acetate (ACS grade), hexanes (ACS grade), anhydrous 1,2-dichloroethane (ACS grade) and toluene (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (200-300 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm⁻¹). Mass spectra were recorded with Agilent 1290-6545XT Ultra-High performance liquid chromatography-quadrupole time-of-flight mass spectrometer using electron spray ionization.

¹H NMR spectra and ¹³C NMR spectra, were recorded on a Bruker AV-400 spectrometer in chloroform-d, acetone-d₆ and methanol-d₄. For ¹H NMR spectra, chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as the standard. For ¹³C NMR spectra, chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as the standard, acetone at 30.0 ppm as a standard and methanol at 49.7 ppm as a standard.

More Reaction Condition Study

Table S1. Screening of Other Lewis Base-Borane Adducts ^a

MBS LB
$$\rightarrow$$
 BH₃ (2 equiv) LB \rightarrow BH₂ MBS DCE, 50 °C, 10 h

Entry	LB	Yield (%) ^b
1	ⁿ Bu₃P	n.r.
2	Ph ₃ P	n.r.
3	ⁿ Bu₃N	n.r.
4	Et ₃ N	trace
5	Et ₂ MeN	trace
6	EtMe ₂ N	trace
7	DMAP	n.r.
8	pyridine	n.r.
9	Me N N Me	n.r.

 $[^]a$ Reaction conditions: **1a** (0.05 mmol), Cu(CH₃CN)₄PF₆ (0.01 mmol), borane (0.1 mmol), DCE (1 mL), 50 °C, 10 h, in vials. b Measured by 1 H NMR using 1,3,5-trimethoxybenzene as internal reference.

Our attempts to extend the reaction to other Lewis base-borane adducts only led to the formation of complicated mixtures or no reaction.

Representative synthetic procedure for the preparation of ynamides $1^{1,2}$

N-((2-(azidomethyl)phenyl)ethynyl)-N-ethyl-4-methoxybenzenesulfonamide (1a)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1a** was afforded as a pale yellow oil (55%, 203.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.41 – 7.27 (m, 4H), 7.02 (d, J = 8.8 Hz, 2H), 4.45 (s, 2H), 3.87 (s, 3H), 3.51 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 136.3, 131.8, 129.7, 129.1, 128.5, 128.1, 127.9, 122.6, 114.4, 87.1, 68.5, 55.6, 53.1, 46.6, 13.3; IR (neat):2936, 2203, 2083, 1589, 1362, 1262, 1158, 1092, 996, 804, 756 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₈N₄NaO₃S]⁺ (M + Na⁺) 393.0992, found 393.0997.

N-((2-(azidomethyl)phenyl)ethynyl)-*N*-ethyl-4-methylbenzenesulfonamide (1b)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1b** was afforded as a pale yellow oil (48%, 170.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.0 Hz, 2H), 7.41 – 7.25 (m, 6H), 4.40 (s, 2H), 3.51 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 136.1, 134.5, 131.6, 129.7, 128.4, 127.9, 127.8, 127.3, 122.4, 86.8, 68.3, 52.9, 46.5, 21.3, 13.1; IR (neat): 2980, 2287, 2096, 1627, 1452, 1342, 1260, 1178, 1090, 997 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₈N₄NaO₂S]⁺ (M + Na⁺) 377.1043, found 377.1048.

N-((2-(azidomethyl)phenyl)ethynyl)-4-bromo-N-ethylbenzenesulfonamide (1c)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1c** was afforded as a pale yellow oil (34%, 142.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.42 – 7.27 (m, 4H), 4.45 (s, 2H), 3.53 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 136.3, 132.5, 131.9, 128.9, 128.8, 128.7, 128.2, 122.3, 86.2, 68. 7, 53.0, 46.8, 13.3; IR (neat): 2939, 2787, 2256, 2102, 1587, 1448, 1397, 1019, 862 cm⁻¹; HRESIMS Calcd for [C₁₇H₁₅N₄BrNaO₂S]⁺ (M + Na⁺) 440.9991, found: 440.9997.

N-((2-(azidomethyl)phenyl)ethynyl)-N-ethylbenzenesulfonamide (1d)

$$SO_2Ph$$
 N
Et
 N_3

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1d** was afforded as a pale yellow oil (52%, 176.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.6

Hz, 2H), 7.41 - 7.39 (m, 1H), 7.33 - 7.24 (m, 3H), 4.43 (s, 2H), 3.52 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 137.3, 136.2, 133.6, 131.7, 129.1, 128.5, 128.0, 127.9, 127.2, 122.3, 86.5, 68.3, 52.8, 46.6, 13.1; IR (neat): 3057, 2829, 2787, 2153, 2122, 1379, 1097, 1019, 950, 730 cm⁻¹; HRESIMS Calcd for $[C_{17}H_{16}N_4NaO_2S]^+$ (M + Na⁺) 363.0886, found: 363.0894.

N-((2-(azidomethyl)phenyl)ethynyl)-4-methoxy-N-methylbenzenesulfonamide (1e)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1e** was afforded as a pale yellow oil (74%, 263.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 9.2 Hz, 2H), 7.40 – 7.26 (m, 4H), 7.03 (d, J = 8.8 Hz, 2H), 4.45 (s, 2H), 3.87 (s, 3H), 3.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 136.4, 131.8, 129.9, 128.5, 128.1, 128.0, 127.6, 122.4, 114.4, 88.9, 66.6, 55.6, 53.0, 39.0; IR (neat): 2968, 2233, 2097, 1595, 1498, 1363, 1311, 1261, 1159, 805 cm⁻¹; HRESIMS Calcd for [C₁₇H₁₆N₄NaO₃S]⁺ (M + Na⁺) 379.0835, found: 379.0845.

N-((2-(azidomethyl)phenyl)-4-methoxy-N-propylbenzenesulfonamide (1f)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1f** was afforded as a pale yellow oil (36%, 138.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.8 Hz, 2H), 7.40 – 7.26 (m, 4H), 7.01 (d, J = 8.8 Hz, 2H), 4.44 (s, 2H), 3.86 (s, 3H), 3.39 (t, J = 7.2 Hz, 2H), 1.79 – 1.70 (m, 2H), 0.96 (t, J

= 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 163.7, 136.3, 131.7, 129.7, 129.0, 128.5, 128.1, 127.9, 122.6, 114.3, 87.4, 68.2, 55.6, 53.0(2), 52.9(8), 21.3, 10.8; IR (neat): 2968, 2306, 2057, 1598, 1498, 1324, 1260, 1096, 1027, 835 cm⁻¹; HRESIMS Calcd for $[C_{19}H_{20}N_4NaO_3S]^+$ (M + Na⁺) 407.1148, found: 407.1155.

N-((2-(azidomethyl)phenyl)ethynyl)-*N*-butyl-4-methoxybenzenesulfonamide (1g)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1g** was afforded as a pale yellow oil (30%, 119.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 9.2 Hz, 2H), 7.41 – 7.27 (m, 4H), 7.02 (d, J = 8.8 Hz, 2H), 4.45 (s, 2H), 3.87 (s, 3H), 3.43 (t, J = 7.2 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.42 – 1.37 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 136.2, 131.7, 129.7, 129.0, 128.5, 128.1, 127.9, 122.6, 114.3, 87.4, 68.3, 55.6, 53.0, 51.1, 29.9, 19.4, 13.5; IR (neat): 3040, 2306, 2057, 1597, 1462, 1231, 1027, 918, 802, 741 cm⁻¹; HRESIMS Calcd for [C₂₀H₂₂N₄NaO₃S]⁺ (M + Na⁺) 421.1305, found: 421.1314.

N-((2-(azidomethyl)phenyl)ethynyl)-N-cyclohexyl-4-methoxybenzenesulfonamide (1h)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1h** was afforded as a pale yellow oil (35%, 148.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.8 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.37 – 7.32 (m, 1H), 7.29 – 7.26 (m, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.45 (s, 2H), 3.88 – 3.81 (m, 4H), 1.79 – 1.72 (m, 4H), 1.61 – 1.51 (m, 3H), 1.36 – 1.26 (m, 2H), 1.12 – 1.03 (m, 1H); ¹³C NMR

(100 MHz, CDCl₃) δ 163.4, 135.9, 131.6, 130.4, 129.3, 128.5, 128.0, 127.6, 122.8, 114.2, 85.3, 69.9, 59.4, 55.5, 52.9, 31.1, 25.2, 24.7; IR (neat): 3025, 2229, 2102, 1593, 1447, 1361, 1025, 986, 810 cm⁻¹; HRESIMS Calcd for [C₂₂H₂₄N₄NaO₃S]⁺ (M + Na⁺) 447.1461, found: 447.1469.

N-((2-(azidomethyl)phenyl)ethynyl)-*N*-benzyl-4-methoxybenzenesulfonamide (1i)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1i** was afforded as a pale yellow oil (37%, 168.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.8 Hz, 2H), 7.33 (s, 5H), 7.26 – 7.19 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 4.60 (s, 2H), 4.13 (s, 2H), 3.86 (s, 3H); 13 C NMR (100 MHz, CDCl₃) δ 163.8, 136.2, 134.2, 131.5, 129.9, 129.0, 128.8, 128.6, 128.4, 128.1, 127.9, 122.2, 114.4, 87.5, 69.1, 55.7, 55.4, 52.6; IR (neat): 2980, 2230, 2094, 1635, 1454, 1339, 1188, 1339, 996, 752 cm⁻¹; HRESIMS Calcd for [C₂₃H₂₀N₄NaO₃S]⁺ (M + Na⁺) 455.1148, found: 455.1139.

N-((2-(azidomethyl)phenyl)ethynyl)-4-methoxy-N-phenylbenzenesulfonamide (1j)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product 1j was afforded as a pale yellow oil (52%, 217.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 9.2 Hz, 2H), 7.28 – 7.11 (m, 9H), 6.79 (d, J = 9.2 Hz, 2H), 4.33 (s, 2H), 3.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 138.6, 136.4, 131.8, 130.2, 129.1, 128.5, 128.2, 128.1(1), 128.0(5), 127.2, 126.1, 122.2, 114.0, 87.8,

68.0, 55.5, 52.9; IR (neat): 3066, 2237, 2091, 1576, 1456, 1263, 1113, 1090, 888, 692 cm⁻¹; HRESIMS Calcd for [C₂₂H₁₈N₄NaO₃S]⁺ (M + Na⁺) 441.0992, found: 441.0994.

N-((2-(azidomethyl)-4-fluorophenyl)ethynyl)-N-ethyl-4-methoxybenzenesulfonamide (1k)

$$N_3$$

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1k** was afforded as a pale yellow oil (39%, 151.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.8 Hz, 2H), 7.31 (dd, J = 8.4, 5.6 Hz, 1H), 7.08 (dd, J = 8.8, 2.8 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.98 (td, J = 8.4, 2.8 Hz, 1H), 4.43 (s, 2H), 3.87 (s, 3H), 3.51 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 161.9 (d, J = 246.0 Hz), 132.1 (d, J = 3.0 Hz), 130.4 (d, J = 9.0 Hz), 129.7, 129.0, 124.7 (d, J = 10.0 Hz), 118.0 (d, J = 23.0 Hz), 115.0, 114.6 (d, J = 21.0 Hz), 114.4, 88.1, 67.9 (d, J = 3.0 Hz), 55.6, 52.3, 46.5, 13.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.6; IR (neat): 3066, 2235, 2093, 1609, 1497, 1261, 1092, 916, 730, 556 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₇FN₄NaO₃S]⁺ (M + Na⁺) 411.0898, found: 411.0905.

N-((2-(azidomethyl)-4-chlorophenyl)ethynyl)-*N*-ethyl-4-methoxybenzenesulfonamide (1l)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **11** was afforded as a pale yellow oil (51%, 206.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.8 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.22 (dd, J = 8.4, 2.0 Hz, 1H), 7.02 (d, J = 8.8 Hz, 2H), 4.44 (s, 2H), 3.87 (s, 3H), 3.51 (q, J = 7.2 Hz,

2H), 1.28 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 163.7, 138.1, 133.5, 132.7, 129.6, 128.9, 128.2, 128.1, 120.8, 114.3, 88.0, 67.5, 55.5, 52.4, 46.4, 13.2; IR (neat): 3035, 2212, 2105, 1595, 1497, 1332, 1263, 1159, 995, 834 cm⁻¹; HRESIMS Calcd for $[C_{18}H_{17}CIN_4NaO_3S]^+$ (M + Na⁺) 427.0602, found: 427.0599.

N-((2-(azidomethyl)-4-bromophenyl)ethynyl)-*N*-ethyl-4-methoxybenzenesulfonamide (1m)

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1m** was afforded as a pale yellow oil (49%, 219.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 1.6 Hz, 1H), 7.40 (dd, J = 8.4, 1.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 4.41 (s, 2H), 3.88 (s, 3H), 3.51 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 135.1, 133.9, 130.8, 129.9, 129.7, 129.0, 124.6, 121.7, 114.4, 88.5, 67.6, 55.6, 52.5, 46.5, 13.3; IR (neat): 2937, 2231, 2097, 1597, 1497, 1363, 1259, 1158, 835, 764 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₇BrN₄NaO₃S]⁺ (M + Na⁺) 471.0097, found: 471.0089.

N-((2-(azidomethyl)-4-methylphenyl)ethynyl)-N-ethyl-4-methoxybenzenesulfonamide (1n)

$$N_3$$
 Me N_3 N_3

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1n** was afforded as a pale yellow oil (53%, 203.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 4.41 (s, 2H), 3.85 (s, 3H), 3.49 (q, J

= 7.2 Hz, 2H), 2.34 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 138.2, 136.3, 131.8, 129.6, 129.2, 129.0, 128.8, 119.4, 114.3, 86.1, 68.3, 55.5, 53.0, 46.5, 21.2, 13.2; IR (neat): 2978, 2232, 2093, 1594, 1362, 1260, 1089, 926, 834, 671 cm⁻¹; HRESIMS Calcd for [C₁₉H₂₀N₄NaO₃S] $^+$ (M + Na $^+$) 407.1148, found: 407.1152.

N-((2-(azidomethyl)-5-methylphenyl)ethynyl)-N-ethyl-4-methoxybenzenesulfonamide (10)

$$\begin{array}{c} \text{MBS} \\ \text{N} \\ \text{Et} \\ \\ \text{N}_3 \\ \\ \text{10} \\ \end{array}$$

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **10** was afforded as a pale yellow oil (49%, 188.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 4.41 (s, 2H), 3.86 (s, 3H), 3.50 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 163.7, 138.3, 136.3, 131.9, 129.7, 129.3, 129.1, 128.9, 119.5, 114.3, 86.2, 68.3, 55.6, 53.0, 46.5, 21.3, 13.2; IR (neat): 3066, 2273, 2023, 1608, 1491, 1361, 1089, 883, 651, 542 cm⁻¹; HRESIMS Calcd for [C₁₉H₂₀N₄NaO₃S] $^+$ (M + Na $^+$) 407.1148, found: 407.1152.

N-((2-(azidomethyl)-5-methoxyphenyl)ethynyl)-N-ethyl-4-methoxybenzenesulfonamide (1p)

MeO N₃

$$1p$$

Prepared according to typical procedure, after a flash column chromatography (PE:EA = 10:1) the product **1p** was afforded as a pale yellow oil (42%, 168.2 mg). ¹H NMR

(400 MHz, CDCl₃) δ 7.90 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 2.4 Hz, 1H), 6.83 (dd, J = 8.4, 2.8 Hz, 1H), 4.38 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.51 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 159.1, 130.2, 129.6, 129.0, 128.4, 123.9, 116.5, 114.3, 114.0, 86.7, 68.6, 55.5, 55.2, 52.5, 46.5, 13.2; IR (neat): 3100, 2242, 2087, 1593, 1193, 1089, 987, 834, 671 cm⁻¹; HRESIMS Calcd for [C₁₉H₂₀N₄NaO₄S] + (M + Na⁺) 423.1097, found: 423.1099.

General procedure for the synthesis of organoboron compound 2:

Cu(CH₃CN)₄PF₆ (0.06 mmol, 20 mol %) was added to a solution of the azide-ynamide 1 (0.3 mmol, 1 equiv) and borane adduct (0.6 mmol, 2 equiv) in DCM (0.05 M) at room temperature. The reaction mixture was stirred at 50 °C in sealed tubes under N₂ atmosphere, and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (PE:EA = 3:1) to afford the desired organoboron compound 2.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2a)

Compound **2a** was prepared in 78% yield (103.2 mg) according to the general procedure (Table 2, entry 1). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a brown solid (mp 81–83 °C). ¹H NMR (400 MHz,

CDCl₃) δ 7.49 (d, J = 8.8 Hz, 2H), 7.15 – 7.05 (m, 4H), 6.72 (d, J = 8.8 Hz, 2H), 4.56 (s, 2H), 4.13 (s, 1H), 3.75 (s, 3H), 3.71 – 3.61 (m, 2H), 3.30 – 3.24 (m, 1H), 3.08 – 3.02 (m, 1H), 2.97 – 2.91 (m, 1H), 2.82 – 2.76 (m, 1H), 2.69 (s, 3H), 2.02 – 1.92 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.0, 162.6, 143.8, 133.4, 130.0, 129.6, 126.1, 125.1, 124.8, 123.9, 113.6, 62.0, 61.6, 55.4, 53.0, 48.3, 43.6, 22.6, 22.3, 14.4; ¹¹B NMR (128 MHz, CDCl₃) δ -5.40; IR (neat): 3447, 2382, 1628, 1596, 1340, 1150, 1088, 1025, 833, 750 cm⁻¹; HRESIMS Calcd for [C₂₃H₃₂BN₃NaO₃S]⁺ (M + Na⁺) 464.2150, found 464.2144.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methylbenzenesulfonamide (2b)

Compound **2b** was prepared in 65% yield (82.9 mg) according to the general procedure (Table 2, entry 2). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 2H), 7.14 – 7.04 (m, 6H), 4.56 (s, 2H), 4.13 (s, 1H), 3.74 – 3.63 (m, 2H), 3.27 – 3.20 (m, 1H), 3.04 – 2.97 (m, 1H), 2.92 – 2.88 (m, 1H), 2.79 – 2.72 (m, 1H), 2.65 (s, 3H), 2.27 (s, 3H), 1.99 – 1.88 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.7, 143.7, 143.0, 135.2, 133.4, 129.0, 127.4, 126.0, 125.0, 124.8, 123.8, 61.9, 61.5, 52.9, 48.2, 43.5, 42.7, 22.5, 22.2, 21.3, 14.4; 11 B NMR (128 MHz, CDCl₃) δ -5.78; IR (neat): 3340, 2381, 1633, 1340, 1260, 1150, 1090, 1024, 750 cm $^{-1}$; HRESIMS Calcd for [C₂₃H₃₃BN₃O₂S] $^{+}$ (M + H $^{+}$) 426.2381, found 426.2390.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-4-bromo-N-ethylbenzenesulfonamide (2c)

Compound **2c** was prepared in 78% yield (114.4 mg) according to the general procedure (Table 2, entry 3). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a brown oil. 1 H NMR (400 MHz, CDCl₃) δ 7.42 (dd, J = 15.6, 8.8 Hz, 4H), 7.14 – 7.04 (m, 4H), 4.57 (s, 2H), 4.04 (s, 1H), 3.74 – 3.63 (m, 2H), 3.27 – 3.20 (m, 1H), 3.03 – 2.97 (m, 1H), 2.96 – 2.88 (m, 1H), 2.78 – 2.74 (m, 1H), 2.65 (s, 3H), 2.01 – 1.90 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.5, 143.4, 137.3, 133.3, 131.6, 129.2, 127.3, 126.2, 125.3, 124.9, 124.1, 62.1, 61.6, 53.0, 48.3, 43.8, 22.6, 22.3, 14.5; 11 B NMR (128 MHz, CDCl₃) δ -5.78; IR (neat): 3340, 2987, 2073, 1636, 1334, 1096, 991, 789, 595 cm $^{-1}$; HRESIMS Calcd for [C₂₂H₂₉BBrN₃NaO₂S] $^{+}$ (M + Na $^{+}$) 512.1149, found 512.1152.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-*N*-ethylbenzenesulfonamide (2d)

Compound **2d** was prepared in 51% yield (62.9 mg) according to the general procedure (Table 2, entry 4). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a brown oil. 1 H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.13 – 7.04 (m, 4H), 4.56 (s, 2H), 4.13 (s, 1H), 3.80 – 3.64 (m, 2H), 3.29 – 3.22 (m, 1H), 3.05 – 2.98 (m, 1H), 2.94 – 2.89 (m, 1H), 2.79 – 2.73 (m, 1H), 2.66 (s, 3H), 1.99 – 1.90 (m, 4H), 1.25 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.7, 143.6, 138.4, 133.4, 132.3, 128.4, 127.5, 126.1, 125.2, 124.9, 124.0, 62.1, 61.6, 53.0, 48.3, 43.7, 22.6, 22.3, 14.5; 11 B NMR (128 MHz,

CDCl₃) δ -5.57; IR (neat): 3340, 3447, 1632, 1597, 1341, 1300, 1150, 1025, 833, 751 cm⁻¹; HRESIMS Calcd for $[C_{22}H_{30}BN_3NaO_2S]^+$ (M + Na⁺) 434.2044, found 434.2039.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-4-methoxy-N-methylbenzenesulfonamide (2e)

Compound **2e** was prepared in 63% yield (80.7 mg) according to the general procedure (Table 2, entry 5). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a black solid (mp 101-102 °C). 1 H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 9.2 Hz, 2H), 7.19 – 7.04 (m, 4H), 6.76 (d, J = 9.2 Hz, 2H), 4.66 – 4.52 (m, 2H), 4.30 (s, 1H), 3.76 (s, 3H), 3.21 – 3.17 (m, 1H), 3.13 (s, 3H), 3.04 – 2.93 (m, 2H), 2.85 – 2.78 (m, 1H), 2.72 (s, 3H), 2.01 – 1.94 (m, 4H); 13 C NMR (100 MHz, CDCl₃) δ 171.2, 163.2, 141.9, 132.2, 129.8, 127.7, 126.6, 125.4, 125.1, 124.3, 113.9, 61.9, 61.8, 55.5, 52.1, 48.1, 42.0, 36.7, 22.4(2), 22.3(9); 11 B NMR (128 MHz, CDCl₃) δ -5.97; IR (neat): 3340, 3374, 1635, 1558, 1260, 1151, 822, 734, 555 cm $^{-1}$; HRESIMS Calcd for [C₂₂H₃₀BN₃NaO₃S]⁺ (M + Na⁺) 450.1993, found 450.1995.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-4-methoxy-N-propylbenzenesulfonamide (2f)

Compound **2f** was prepared in 62% yield (84.7 mg) according to the general procedure (Table 2, entry 6). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.4 Hz, 2H),

7.17 – 7.07 (m, 4H), 6.80 (d, J = 8.8 Hz, 2H), 4.60 (s, 2H), 4.11 (s, 1H), 3.78 (s, 3H), 3.72 – 3.65 (m, 1H), 3.61 – 3.56 (m, 1H), 3.23 – 3.16 (m, 1H), 2.93 – 2.86 (m, 2H), 2.74 – 2.69 (m, 1H), 2.62 (s, 3H), 1.99 – 1.87 (m, 4H), 1.74 – 1.66 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 163.3, 144.3, 142.0, 129.8, 129.3, 126.6, 125.4, 125.1, 124.6, 114.0, 62.3, 61.6, 55.6, 51.6, 50.3, 48.2, 42.7, 22.6, 22.4, 22.1, 11.4; ¹¹B NMR (128 MHz, CDCl₃) δ -5.54; IR (neat): 3340, 2383, 1704, 1635, 1558, 1455, 1380, 1264, 1151, 1086 cm⁻¹; HRESIMS Calcd for [C₂₄H₃₄BN₃NaO₃S]⁺ (M + Na⁺) 478.2306, found 478.2311.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-N-butyl-4-methoxybenzenesulfonamide (2g)

Compound **2g** was prepared in 66% yield (92.9 mg) according to the general procedure (Table 2, entry 7). The product was isolated through silica gel column chromatography (PE:EA = 5:1) as a yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 9.2 Hz, 2H), 7.12 – 7.04 (m, 4H), 6.71 (d, J = 8.8 Hz, 2H), 4.54 (s, 2H), 4.15 (s, 1H), 3.74 (s, 3H), 3.70 – 3.65 (m, 1H), 3.55 – 3.48 (m, 1H), 3.31 – 3.24 (m, 1H), 3.08 – 3.01 (m, 1H), 2.95 – 2.90 (m, 1H), 2.81 – 2.75 (m, 1H), 2.68 (s, 3H), 2.00 – 1.91 (m, 4H), 1.67 – 1.60 (m, 2H), 1.39 – 1.33 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 162.6, 144.0, 133.7, 130.0, 129.6, 126.0, 125.2, 124.8, 123.9, 113.6, 62.0, 61.6, 55.4, 53.0, 48.4(2), 48.3(8), 42.9, 30.8, 22.7, 22.4, 20.3, 13.8; 11 B NMR (128 MHz, CDCl₃) δ -5.62; IR (neat): 3340, 2105 1704, 1635, 1518, 1339, 1259, 1149, 871, 561 cm⁻¹; HRESIMS Calcd for [C₂₅H₃₆BN₃NaO₃S]⁺ (M + Na⁺) 492.2463, found 492.2467.

$N\hbox{-}(4\hbox{-}(1\hbox{-methylpyrrolidine-boranyl})\hbox{-}1,4\hbox{-}dihydroisoquinolin-3-yl})\hbox{-}N\hbox{-}cyclohexyl-4-methoxybenzenesulfonamide (2h)}$

Compound **2h** was prepared in 54% yield (80.3 mg) according to the general procedure (Table 2, entry 8). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.8 Hz, 2H), 7.09 – 7.01 (m, 3H), 6.95 (d, J = 7.2 Hz, 1H), 6.78 (d, J = 9.2 Hz, 2H), 4.68 – 4.57 (m, 2H), 3.81 – 3.73 (m, 5H), 3.25 – 3.19 (m, 1H), 3.02 – 2.95 (m, 1H), 2.90 – 2.84 (m, 1H), 2.73 – 2.68 (m, 1H), 2.61 (s, 3H), 2.15 – 2.09 (m, 2H), 1.97 – 1.88 (m, 4H), 1.68 – 1.55 (m, 6H), 1.19 – 1.06 (m, 2H); 13 C NMR (100 MHz, CDCl₃) δ 169.4, 162.2, 143.3, 133.5, 133.1, 130.2, 125.9, 125.4, 124.9, 124.0, 113.4, 62.4, 62.2, 61.7, 55.4, 53.1, 48.3, 42.3, 34.2, 31.0, 26.9, 26.7, 25.5, 22.7, 22.3; 11 B NMR (128 MHz, CDCl₃) δ -4.23; IR (neat): 3340, 2388, 1682, 1622, 1397, 1260, 1076, 749 cm $^{-1}$; HRESIMS Calcd for [C₂₇H₃₈BN₃NaO₃S] $^{+}$ (M + Na $^{+}$) 518.2619, found 518.2614.

N-benzyl-*N*-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-4-methoxybenzenesulfonamide (2i)

Compound **2i** was prepared in 66% yield (99.9 mg) according to the general procedure (Table 2, entry 9). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.51 – 7.46 (m, 4H), 7.28 – 7.20 (m, 3H), 7.08 – 6.96 (m, 4H), 6.69 (d, J = 9.2 Hz, 2H), 5.11 (d, J = 14.4 Hz, 1H), 4.75 (d, J = 14.4 Hz, 1H), 4.59 – 4.50 (m, 2H), 4.06 (s, 1H), 3.72 (s, 3H), 2.90 – 2.83 (m, 2H), 2.67 – 2.58 (m, 2H), 2.42 (s, 3H), 1.80 – 1.75 (m, 4H); 13 C NMR (100 MHz, CDCl₃) δ 168.6, 162.6, 143.7, 137.9, 133.5, 130.3, 129.7, 129.4, 127.9, 127.0, 126.0,

125.0, 124.8, 123.7, 113.5, 61.5(1), 61.4(9), 55.4, 52.7, 51.1, 47.9, 22.4, 22.3; 11 B NMR (128 MHz, CDCl₃) δ -3.88; IR (neat): 3340, 2970, 2381, 1704, 1632, 1558, 1340, 1153, 1091, 1024, 750 cm⁻¹; HRESIMS Calcd for [C₂₈H₃₄BN₃NaO₃S]⁺ (M + Na⁺) 526.2306, found 526.2302.

N-(4-(1-methylpyrrolidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-4-methoxy-N-phenylbenzenesulfonamide (2j)

Compound **2j** was prepared in 61% yield (89.5 mg) according to the general procedure (Table 2, entry 10). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a colorless oil. 1 H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.8 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.15 – 7.12 (m, 3H), 7.07 (dd, J = 5.6, 3.2 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.74 (dd, J = 5.2, 3.2 Hz, 1H), 4.82 (s, 2H), 3.83 (s, 3H), 3.03 – 2.98 (m, 2H), 2.87 – 2.82 (m, 1H), 2.78 – 2.71 (m, 1H), 2.63 – 2.57 (m, 1H), 2.38 (s, 3H), 1.91 – 1.83 (m, 4H); 13 C NMR (100 MHz, CDCl₃) δ 169.8, 163.9, 139.5, 136.8, 131.6, 131.0, 129.9, 129.5, 129.2, 128.8, 126.9, 125.4(1), 125.3(7), 124.9, 113.7, 62.3, 61.8, 55.7, 50.4, 47.7, 41.6, 22.4, 22.0; 11 B NMR (128 MHz, CDCl₃) δ -6.13; IR (neat): 3340, 2380, 1646, 1595, 1349, 1260, 1161, 1089, 750, 698 cm $^{-1}$; HRESIMS Calcd for [C₂₇H₃₂BN₃NaO₃S]⁺ (M + Na⁺) 512.2150, found 512.2158.

N-(4-(1-methylpyrrolidine-boranyl)-7-fluoro-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2k)

Compound **2k** was prepared in 36% yield (49.6 mg) according to the general procedure (Table 2, entry 11). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale red oil. 1 H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.8 Hz, 2H), 7.00 (t, J = 6.4 Hz, 1H), 6.76 – 6.72 (m, 4H), 4.56 – 4.46 (m, 2H), 4.09 (s, 1H), 3.75 (s, 3H), 3.72 – 3.62 (m, 2H), 3.28 – 3.22 (m, 1H), 3.08 – 3.05 (m, 1H), 2.96 – 2.93 (m, 1H), 2.84 – 2.81 (m, 1H), 2.70 (s, 3H), 2.01 – 1.94 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.5, 162.7, 161.7 (d, J = 241.0 Hz), 146.5 (d, J = 8.0 Hz), 129.8, 129.6, 129.1 (d, J = 2.0 Hz), 126.2 (d, J = 8.0 Hz), 113.6, 111.4 (d, J = 21.0 Hz), 110.4 (d, J = 21.0 Hz), 62.0, 61.6, 55.4, 52.3, 48.4, 43.6, 22.6, 22.3, 14.4; 11 B NMR (128 MHz, CDCl₃) δ -6.67; 19 F NMR (376 MHz, CDCl₃) δ -110.8; IR (neat): 3340, 2373, 1633, 1577, 1496 1341, 1152, 1089, 962, 804, 733 cm $^{-1}$; HRESIMS Calcd for $[C_{23}H_{31}BFN_3NaO_3S]^+$ (M + Na $^+$) 482.2055, found 482.2058.

N-(4-(1-methylpyrrolidine-boranyl)-7-chloro-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (21)

21

Compound **2l** was prepared in 72% yield (102.9 mg) according to the general procedure (Table 2, entry 12). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 8.8 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 9.2 Hz, 2H), 4.52 (s, 2H), 4.12 (s, 1H), 3.76 (s, 3H), 3.71 – 3.61 (m, 2H), 3.28 – 3.21 (m, 1H), 3.06 – 3.00 (m, 1H), 2.96 – 2.90 (m, 1H), 2.82 – 2.76 (m, 1H), 2.68 (s, 3H), 2.02 – 1.90 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 169.1, 162.7, 142.6, 135.3, 129.7, 129.6, 129.3, 126.1, 125.9, 125.2, 113.7, 62.1, 61.6, 55.4, 52.6, 48.4, 43.6, 42.5, 22.6, 22.3, 14.4; 11 B NMR (128 MHz, CDCl₃) δ -4.58; IR (neat): 3340, 2382, 1635,

1590 1339, 1259, 1150, 803, 749 cm $^{-1}$; HRESIMS Calcd for $[C_{23}H_{31}BClN_3NaO_3S]^+$ (M + Na $^+$) 498.1760, found 498.1766.

N-(4-(1-methylpyrrolidine-boranyl)-7-bromo-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2m)

2m

Compound **2m** was prepared in 65% yield (101.3 mg) according to the general procedure (Table 2, entry 13). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a dark oil. 1 H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.8 Hz, 2H), 7.25 – 7.21 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 4.52 (s, 2H), 4.10 (s, 1H), 3.76 (s, 3H), 3.72 – 3.61 (m, 2H), 3.25 – 3.20 (m, 1H), 3.03 – 2.98 (m, 1H), 2.94 – 2.89 (m, 1H), 2.82 – 2.77 (m, 1H), 2.67 (s, 3H), 2.03 – 1.91 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.8, 162.6, 143.1, 135.8, 129.7, 129.5, 128.9, 128.0, 126.3, 117.2, 113.6, 62.0, 61.6, 55.4, 52.4, 48.3, 43.5, 42.4, 22.5, 22.2, 14.3; 11 B NMR (128 MHz, CDCl₃) δ -6.41; IR (neat): 3340, 2377, 1622, 1558, 1507, 1417, 1260, 1077, 803, 750 cm⁻¹; HRESIMS Calcd for [C₂₃H₃₁BBrN₃NaO₃S]⁺ (M + Na⁺) 542.1255, found 542.1259.

N-(4-(1-methylpyrrolidine-boranyl)-7-methyl-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2n)

Compound **2n** was prepared in 69% yield (94.2 mg) according to the general procedure (Table 2, entry 14). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 9.2 Hz, 2H), 7.57 – 6.95 (m, 5H), 4.74 – 4.63 (m, 2H), 3.94 – 3.82 (m, 6H), 3.06 – 3.01 (m, 1H), 2.93 – 2.86 (m, 1H), 2.71 – 2.59 (m, 2H), 2.53 (s, 3H), 2.29 (s, 3H), 1.92 – 1.83 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 168.7, 162.6, 158.2, 145.5, 130.0, 129.7, 126.0, 125.9, 113.6, 111.0, 108.7, 62.0, 61.7, 55.4, 55.3, 52.4, 48.5, 43.6, 43.2, 22.7, 22.4, 14.4; 11 B NMR (128 MHz, CDCl₃) δ -5.35; IR (neat): 3340, 2377, 1704, 1635, 1558, 1339, 1260, 1150, 749, 567 cm $^{-1}$; HRESIMS Calcd for [C₂₄H₃₄BN₃NaO₃S] $^{+}$ (M + Na $^{+}$) 478.2306, found 478.2311.

N-(4-(1-methylpyrrolidine-boranyl)-6-methyl-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamidee (20)

Compound **20** was prepared in 64% yield (87.4 mg) according to the general procedure (Table 2, entry 15). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.8 Hz, 2H), 7.03 – 6.89 (m, 5H), 4.69 – 4.58 (m, 2H), 3.98 (s, 1H), 3.82 – 3.77 (m, 5H), 3.12 – 3.07 (m, 1H), 2.91 – 2.87 (m, 1H), 2.78 – 2.73 (m, 1H), 2.66 – 2.62 (m, 1H), 2.57 (s, 3H), 2.30 (s, 3H), 1.97 – 1.86 (m, 4H), 1.29 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 171.7, 163.8, 134.6, 130.7, 130.0, 128.6, 127.9, 126.2, 125.3, 114.3, 62.5, 61.6, 55.7, 50.3, 47.9, 44.0, 22.5, 21.9, 20.9, 15.0; 11 B NMR (128 MHz, CDCl₃) δ -5.15; IR (neat): 3340, 2381, 1703, 1625, 1554, 1342, 1260, 1150, 750, 551 cm $^{-1}$; HRESIMS Calcd for [C₂₄H₃₄BN₃NaO₃S] $^{+}$ (M + Na $^{+}$) 478.2306, found 478.2302.

N-(4-(1-methylpyrrolidine-boranyl)-6-methoxy-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2p)

Compound **2p** was prepared in 80% yield (113.1 mg) according to the general procedure (Table 2, entry 16). The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a yellow oil. 1 H NMR (400 MHz, CD₃OD) δ 7.52 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.57 – 6.54 (m, 2H), 4.37 (dd, J = 28.4, 16.0 Hz, 2H), 3.89 (s, 1H), 3.73 – 3.61 (m, 8H), 3.25 (s, 1H), 3.04 – 2.93 (m, 1H), 2.85 – 2.75 (m, 1H), 2.75 – 2.65 (m, 1H), 2.65 – 2.56 (m, 1H), 2.46 (s, 3H), 1.88 – 1.73 (m, 4H), 1.15 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CD₃OD) δ 173.5, 165.7, 160.8, 145.5, 131.7, 127.8, 126.5, 115.9, 112.9, 111.6, 64.0, 63.4, 56.9, 56.0, 52.8, 45.6, 24.2, 23.7, 16.0; 11 B NMR (128 MHz, CD₃OD) δ -5.39; IR (neat): 2919, 2379, 1573, 1506, 1372, 1272, 1174, 1067, 744, 585 cm⁻¹; HRESIMS Calcd for [C₂₄H₃₄BN₃NaO₄S]⁺ (M + Na⁺) 494.2255, found 494.2247.

N-(4-(1-methylpiperidine-boranyl)-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2q)

Compound **2q** was prepared in 75% yield (102.4 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.8 Hz, 2H), 7.15 – 7.05 (m, 4H), 6.70 (d, J = 8.8 Hz, 2H), 4.55 (s, 2H), 4.12 (s, 1H), 3.74 – 3.60 (m, 5H), 3.07 – 2.97 (m, 2H), 2.89 – 2.78 (m, 2H), 2.65 (s, 3H), 1.80 – 1.77 (m, 1H), 1.71 – 1.63

(m, 4H), 1.47 - 1.44 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, Acetone-d₆) δ 170.0, 164.0, 145.2, 134.8, 132.1, 130.7, 127.0, 126.3, 126.0, 124.8, 114.7, 59.4, 59.3, 56.2, 53.4, 46.7, 44.2, 42.5, 23.4, 21.0, 20.9, 15.3; 11 B NMR (128 MHz, CDCl₃) δ -4.30; IR (neat): 3447, 1704, 1635, 1581, 1497, 1339, 1260, 750, 671 cm⁻¹; HRESIMS Calcd for [C₂₄H₃₅BN₃NaO₃S]⁺ (M + H⁺) 456.2487, found 456.2493.

N-(4-(trimethylamine-boranyl)-1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (2r)

Compound **2r** was prepared in 80% yield (99.6 mg) according to the general procedure. The product was isolated through silica gel column chromatography (PE:EA = 3:1) as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.8 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.08 – 7.06 (m, 3H), 6.73 (d, J = 8.8 Hz, 2H), 4.56 (s, 2H), 4.11 (s, 1H), 3.75 (s, 3H), 3.72 – 3.64 (m, 2H), 2.65 (s, 9H), 1.24 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 169.2, 162.7, 143.5, 133.3, 129.6(9), 129.6(5), 126.3, 125.2, 124.9, 124.1, 113.7, 55.4, 52.9, 52.6, 43.6, 42.5, 14.4; 11 B NMR (128 MHz, CDCl₃) δ -6.27; IR (neat): 3340, 2381, 1704, 1635, 1558, 1339, 1260, 1087, 749 cm $^{-1}$; HRESIMS Calcd for $[C_{21}H_{30}BN_3NaO_3S]^+$ (M + Na $^+$) 438.1993, found 438.1998.

Gram-scale synthesis of 2a

Cu(CH₃CN)₄PF₆ (0.24 g, 0.64 mmol) was added to a solution of the azide-ynamide **1a** (1.18 g, 3.2 mmol) and borane (0.63 g, 6.4 mmol) in DCM (10 mL) in a 50 mL sealed tube under N_2 atmosphere. The reaction mixture was stirred at 50 °C for 10 h. Upon

completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (PE:EA = 3:1) to afford the desired organoboron compound **2a** (0.96 g, 68% yield).

N-(1,4-dihydroisoquinolin-3-yl)-N-ethyl-4-methoxybenzenesulfonamide (3)

MBS

$$K_2CO_3 (10 \text{ equiv})$$
 $K_2CO_3 (10 \text{ equiv})$
 $K_2CO_3 (10 \text{ equiv})$

Compound **3** was prepared in 82% yield (56.5 mg) according to the following procedure. The powered potassium carbonate (276 mg, 2.0 mmol) was introduced to a Schelenk tube under argon atmosphere, followed by a solution of **2a** (88.3 mg, 0.2 mmol) in THF (2 mL) and H₂O (0.5 mL) was injected into the Schelenk tube. The reaction mixture were stirred at 90 °C for 5 hours. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (PE:EA = 5:1) to give **3** as a yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.8 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.17 – 7.12 (m, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.73 (t, J = 3.2 Hz, 2H), 3.85 – 3.82 (m, 5H), 3.71 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 163.0, 156.0, 133.1, 131.3, 131.0, 129.4, 127.2, 127.0, 126.8, 125.1, 114.2, 55.6, 52.6, 43.0, 34.7, 14.2; IR (neat): 2982, 1908, 1693, 1521, 1407, 1294, 1086, 842, 711, 540 cm⁻¹; HRESIMS Calcd for [C₁₈H₂₀N₂NaO₃S]⁺ (M + Na⁺) 367.1087, found 367.1085.

N-ethyl-N-(isoquinolin-3-yl)-4-methoxybenzenesulfonamide

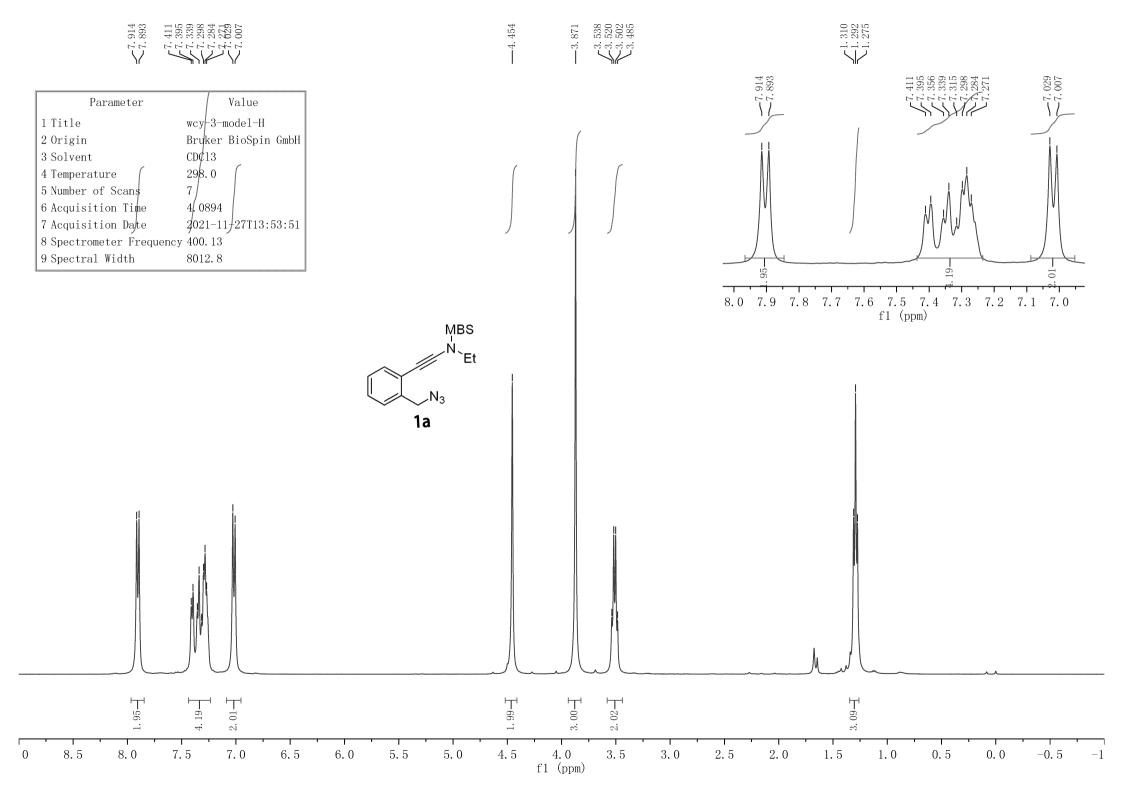
MBS
$$O_2$$
 (1 atm) O_2 (1 atm) O_3 Et O_3 (1 atm) O_4 O_5 O_5 O_7 O_8 O_8

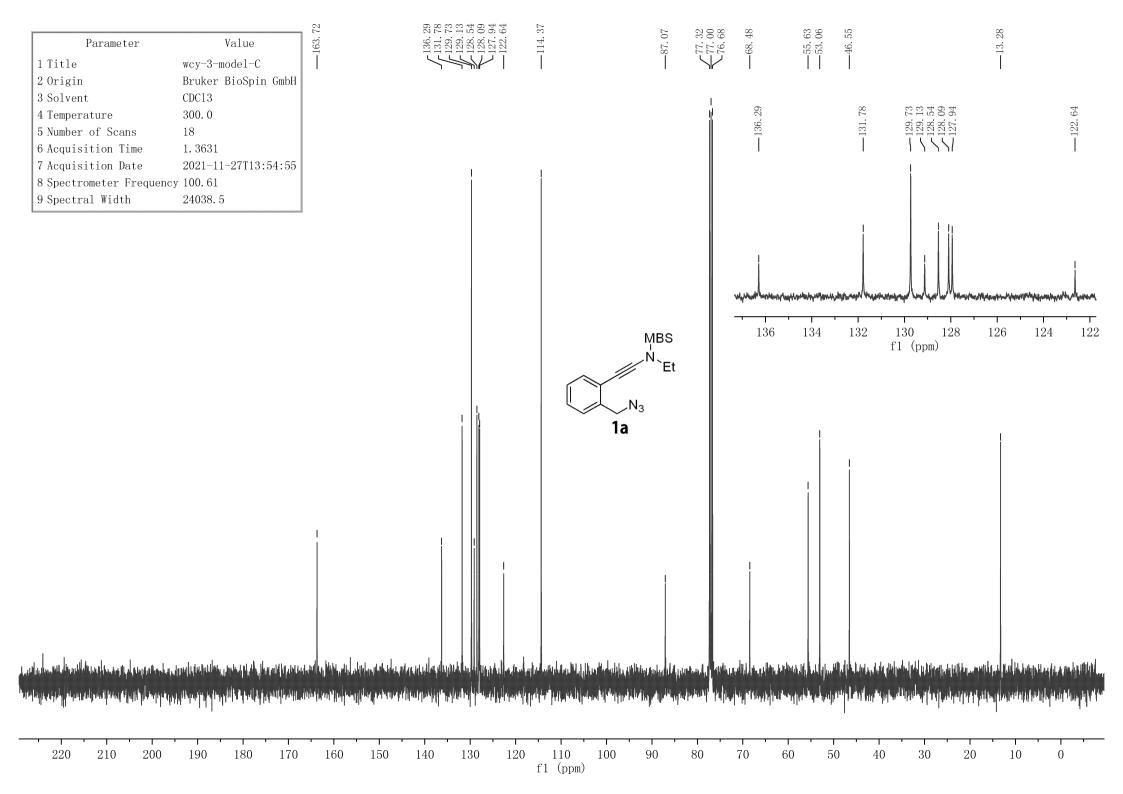
Compound 4 was prepared in 99% yield (67.8 mg) according to the following procedures. 2a (88.3 mg, 0.2 mmol) in toluene (5 mL) was introduced to an oven-dried eggplant-shaped bottle. Then the mixture was heated to 80 °C for 2 hours with an

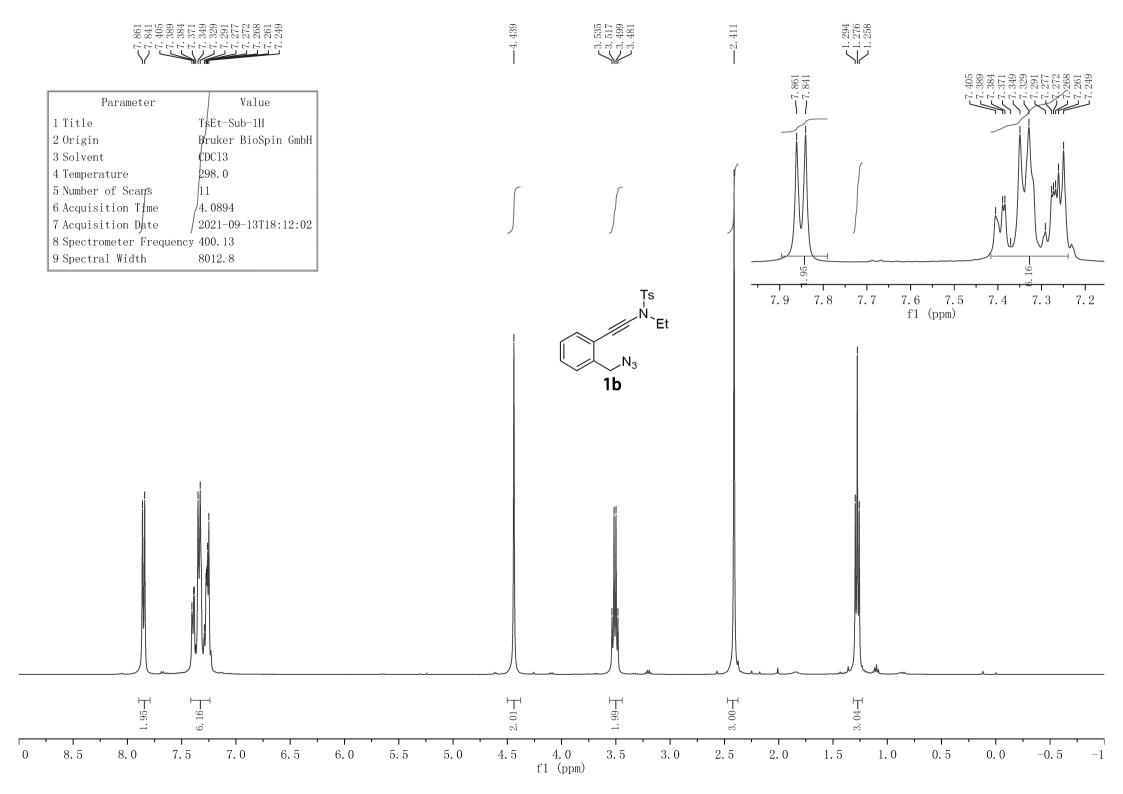
oxygen ball. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (PE:EA = 3:1) to afford the desired **4** as a pale yellow oil. 1 H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 7.97 – 7.86 (m, 3H), 7.71 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.93 – 3.78 (m, 5H), 1.11 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 162.8, 151.4, 146.6, 137.2, 130.7, 130.5, 129.7, 127.4(4), 127.3(9), 127.3, 127.0, 120.4, 113.9, 55.5, 43.3, 14.1; IR (neat): 3081, 1711, 1605, 1559, 1422, 1332, 1112, 957, 714, 517 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₈N₂NaO₃S]⁺ (M + Na⁺) 365.0930, found 365.0921.

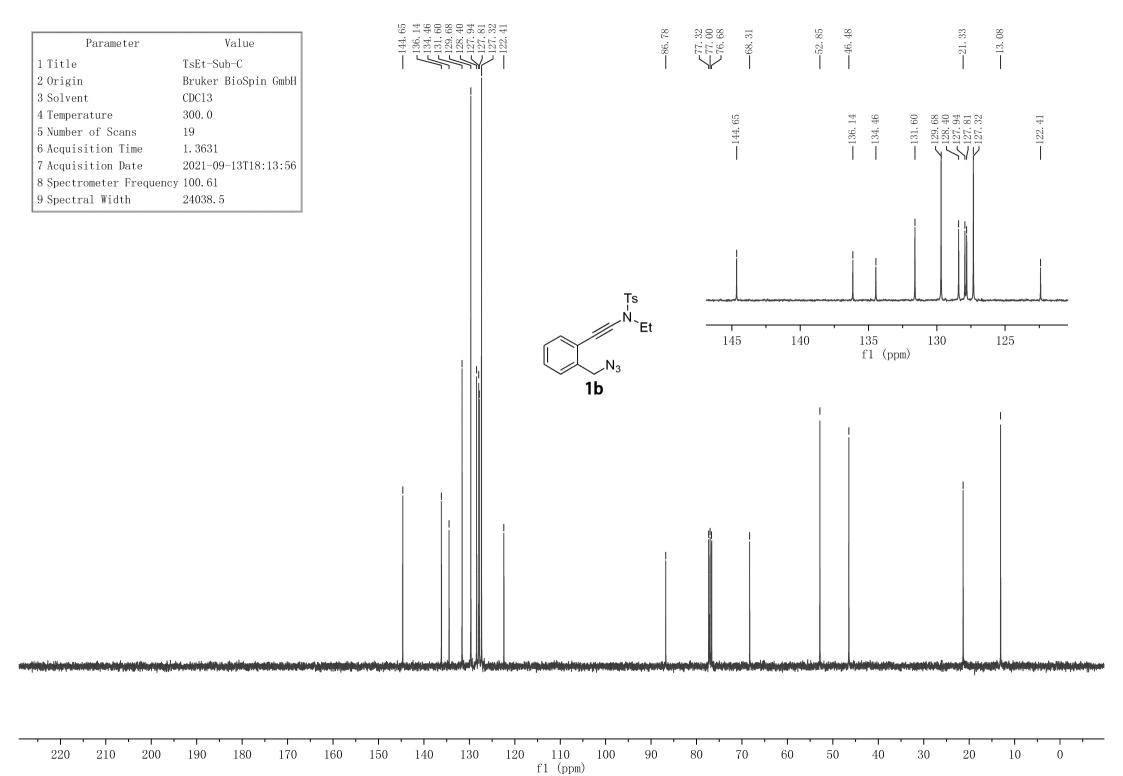
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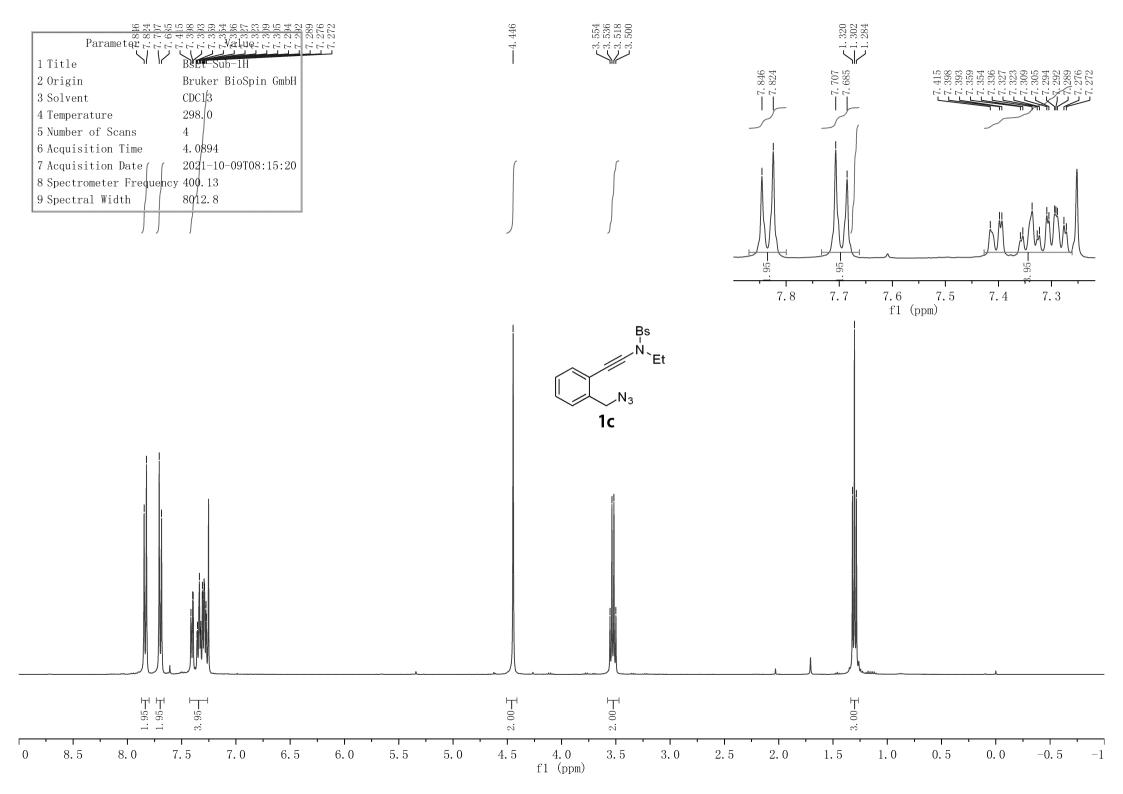
- W.-B. Shen, B. Zhou, Z.-X. Zhang, H. Yuan, W. Fang and L.-W. Ye, *Org. Chem. Front.*, 2018, 5, 2468–2472.
- 2. Y. Pan, G.-W. Chen, C.-H. Shen, W. He, L.-W. Ye, *Org. Chem. Front.*, 2016, **3**, 491–495.

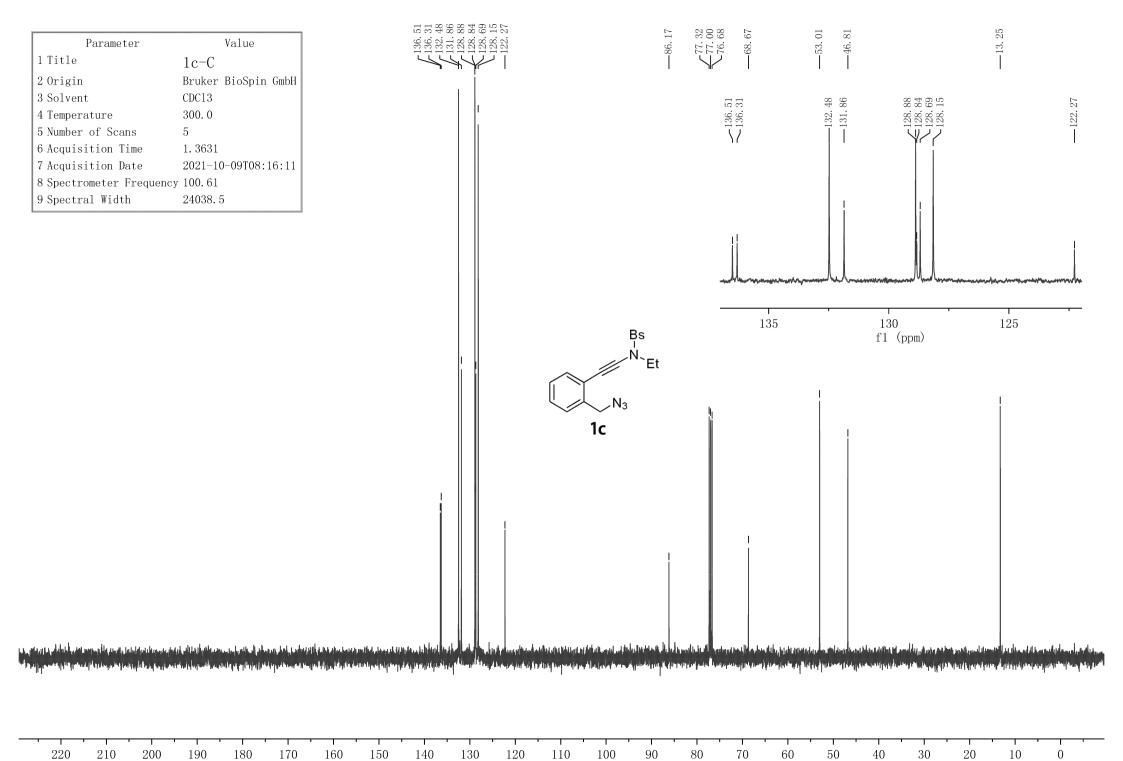




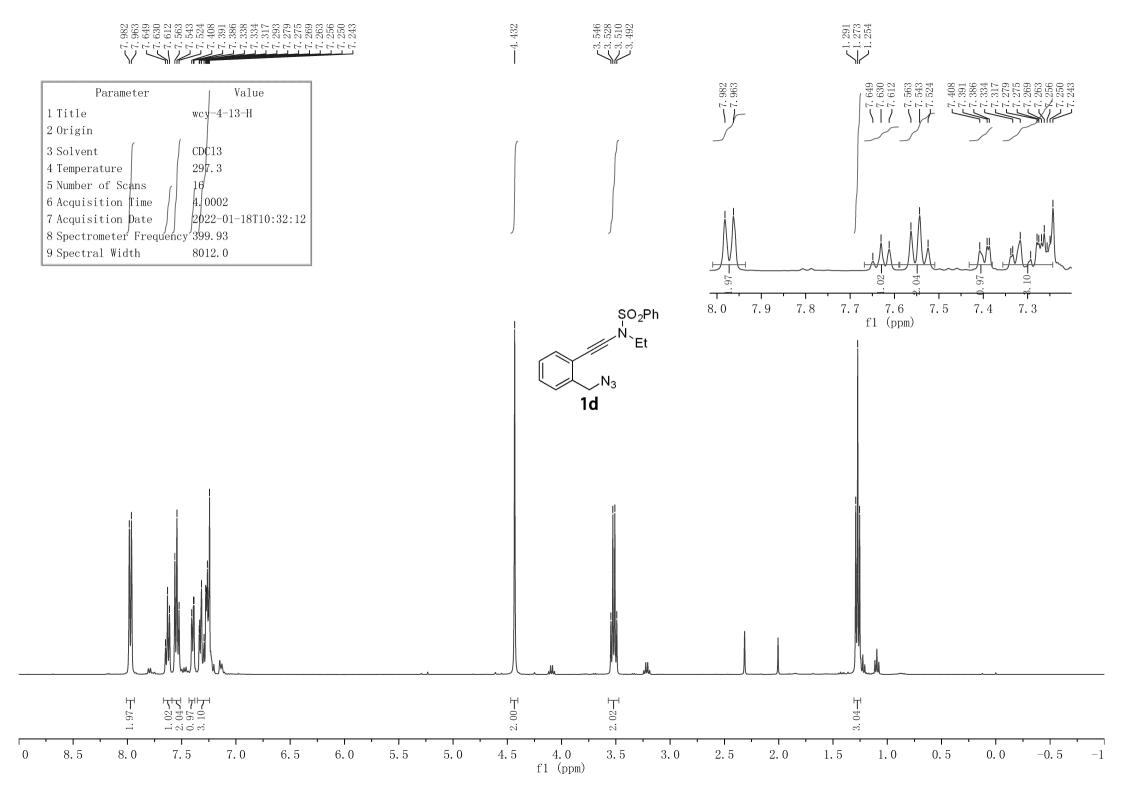


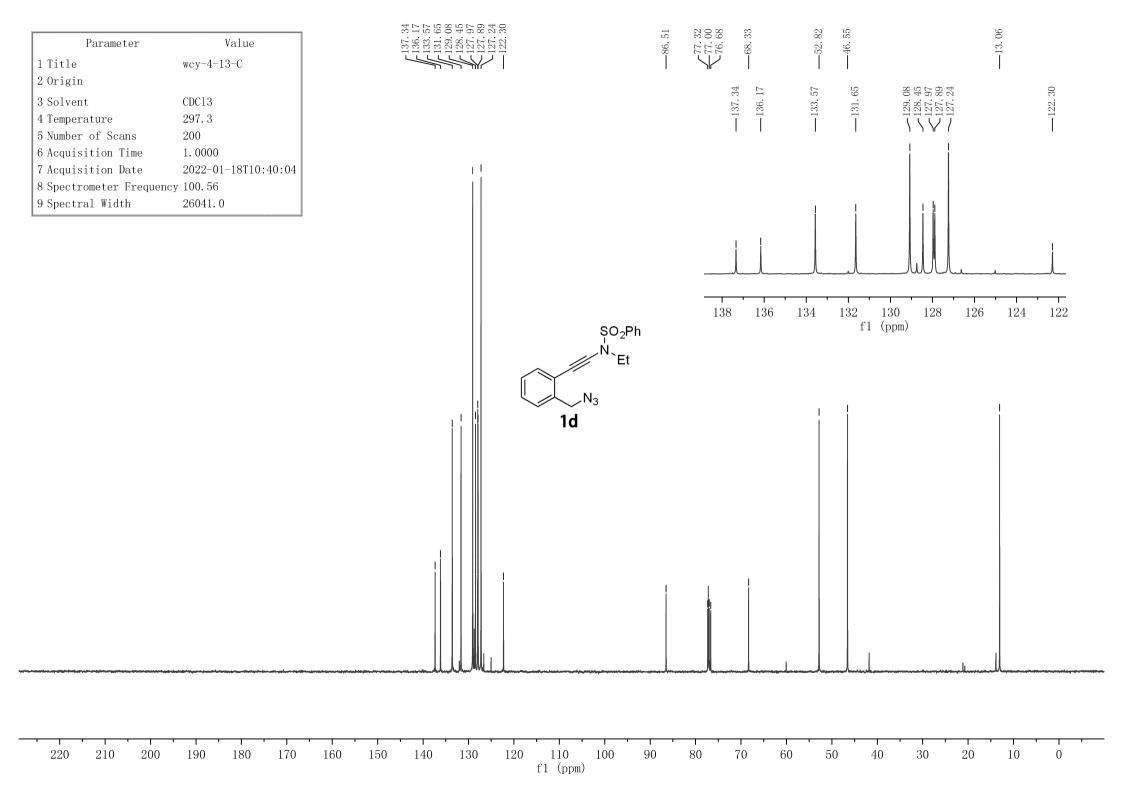


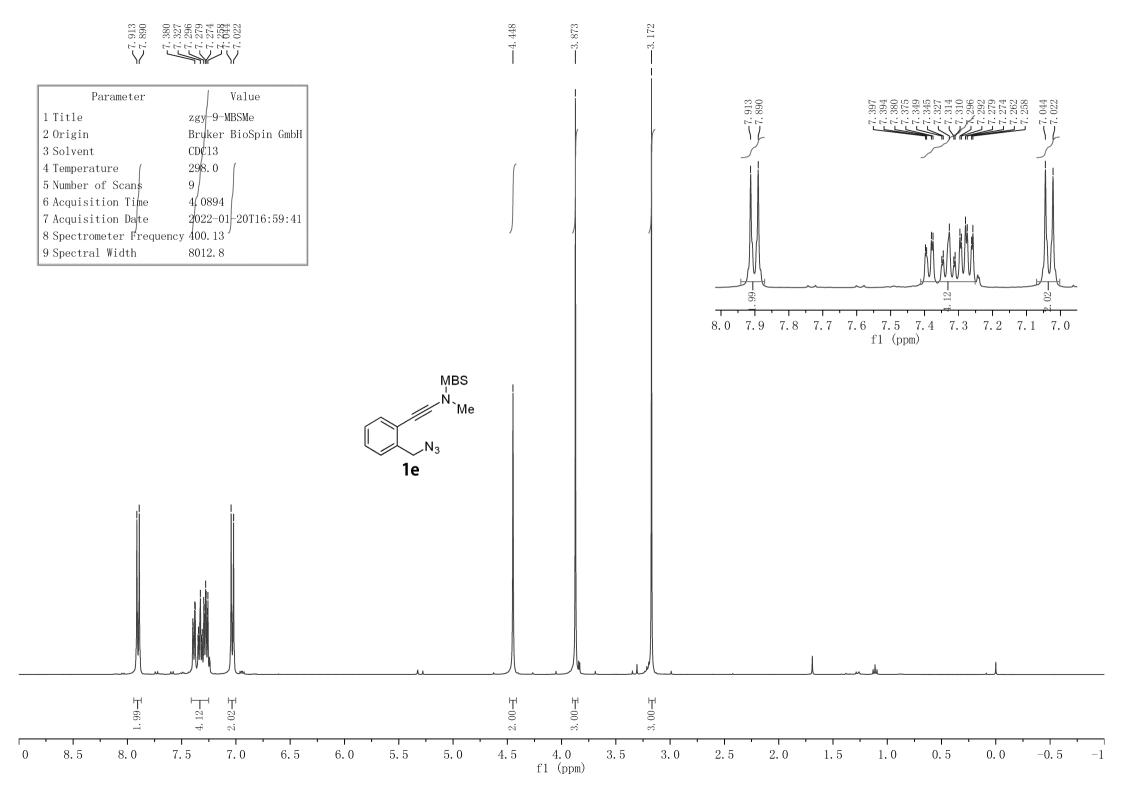


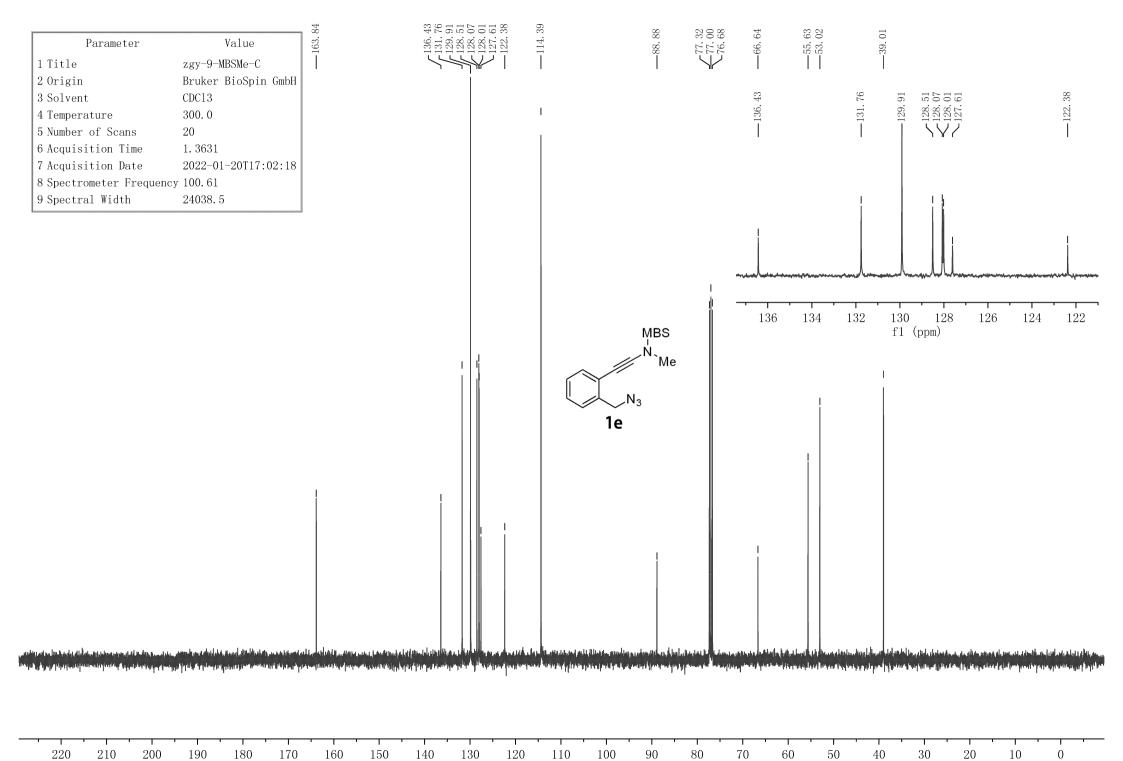


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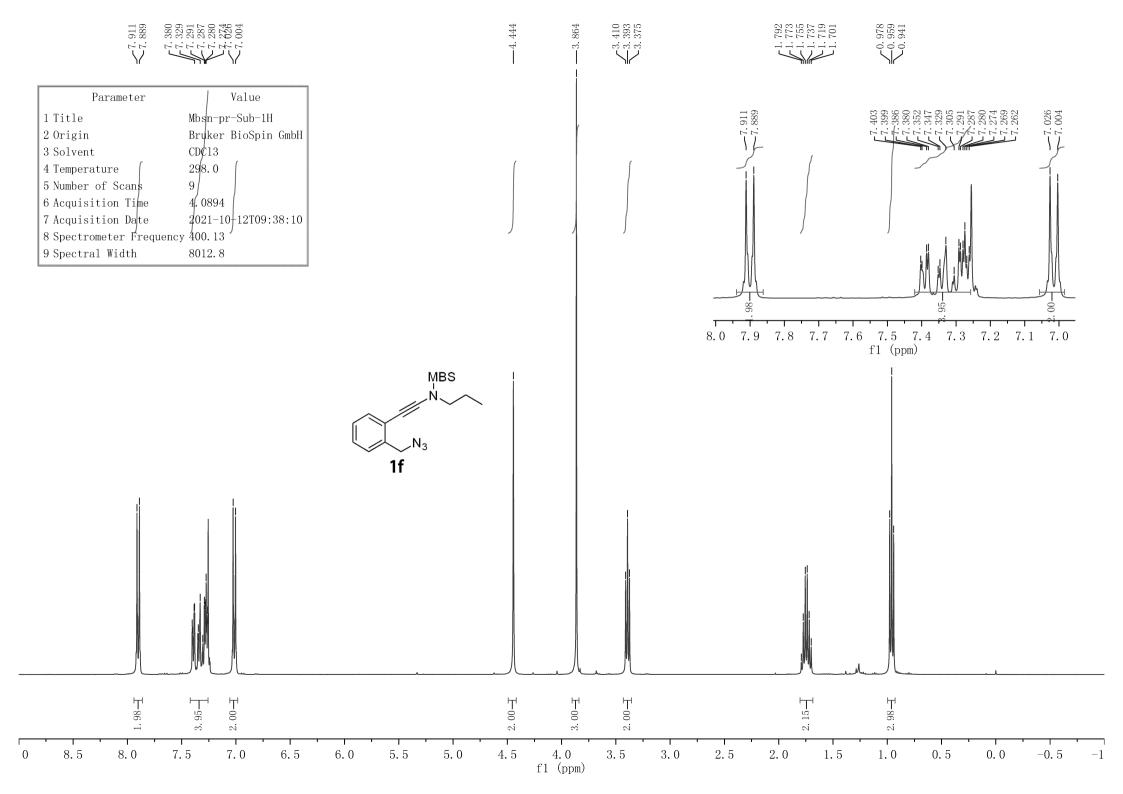


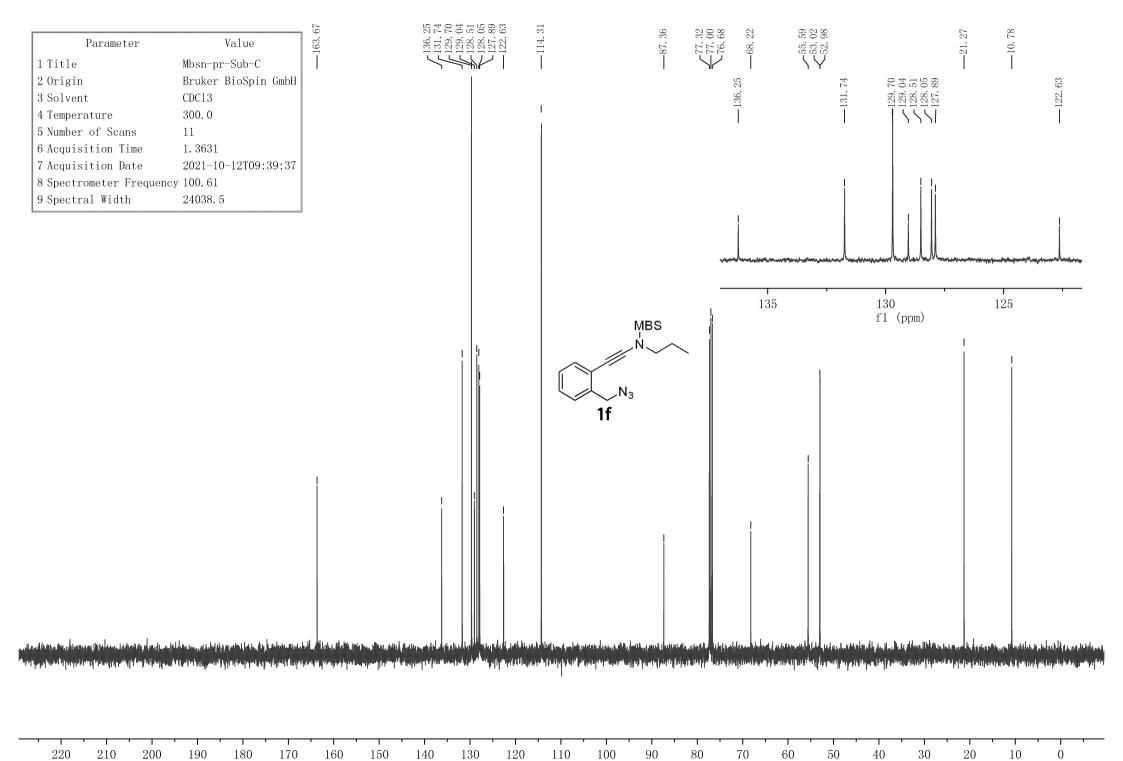




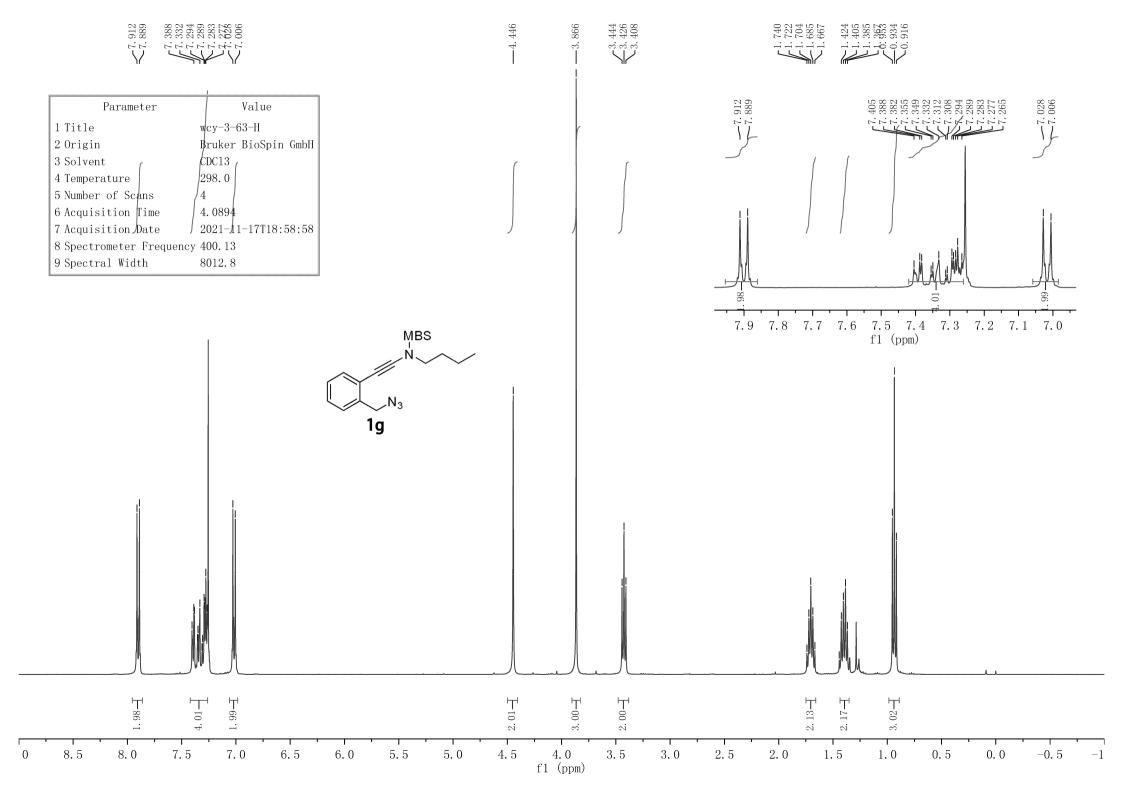


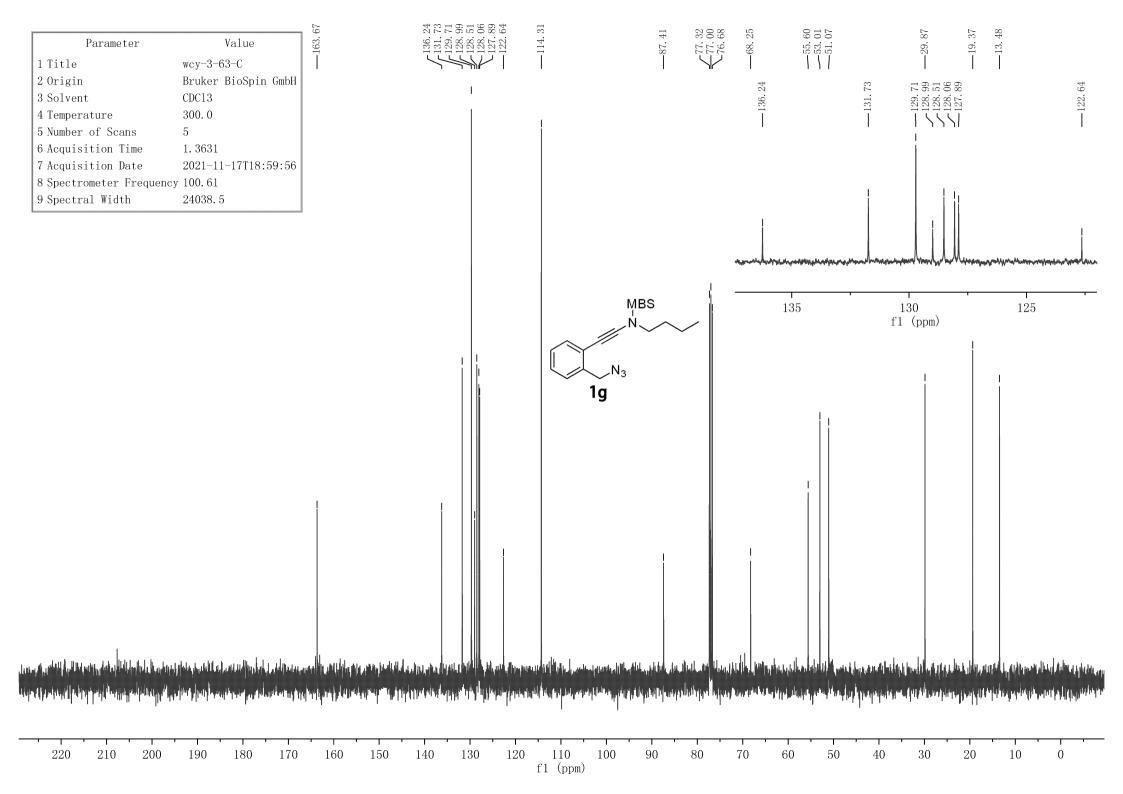
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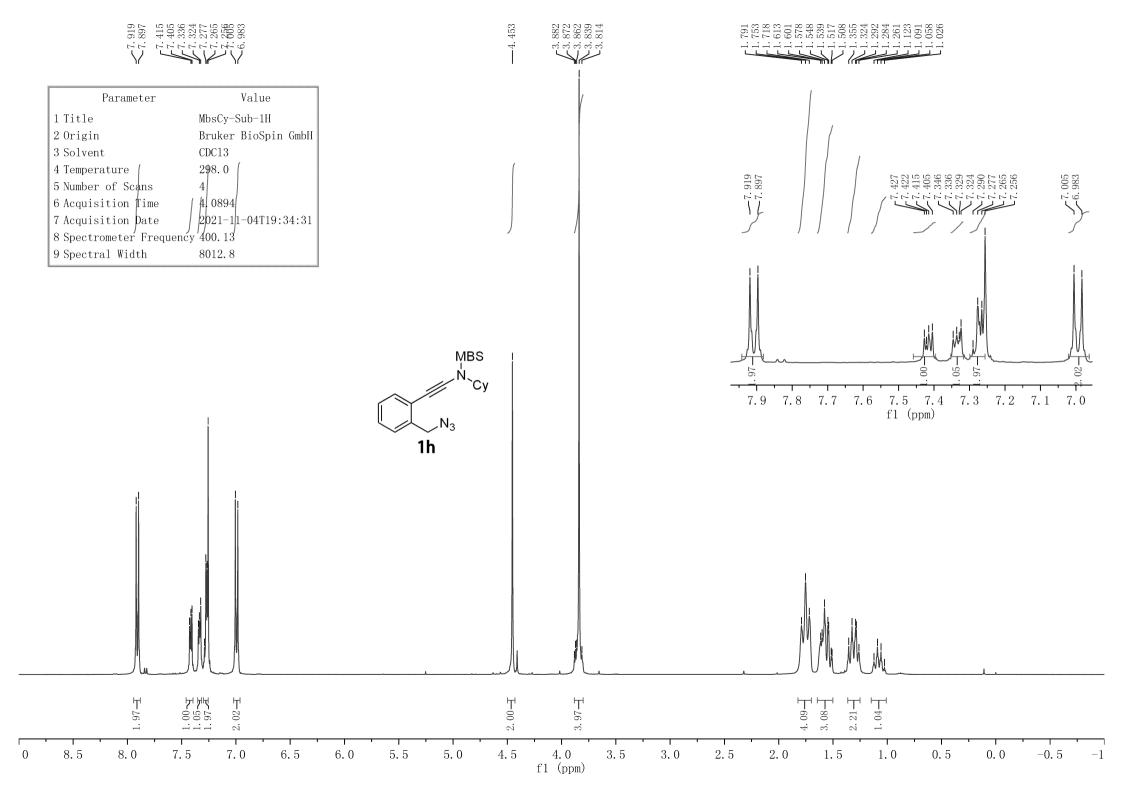


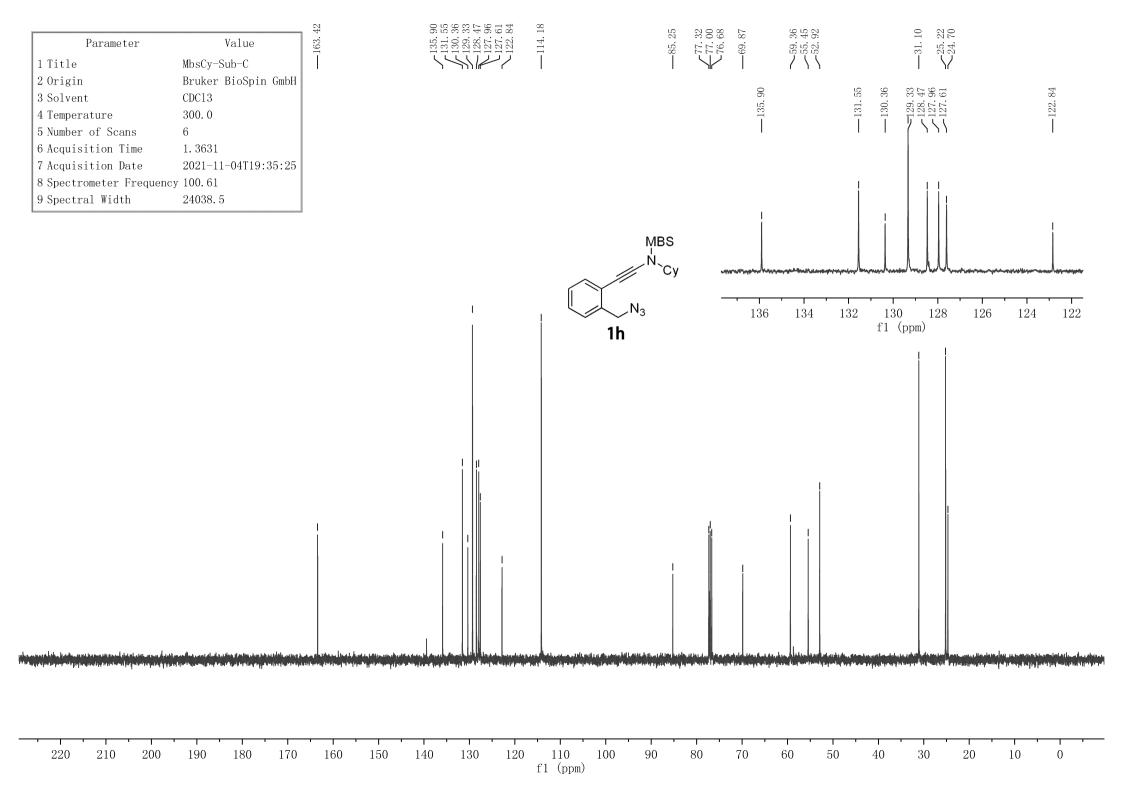


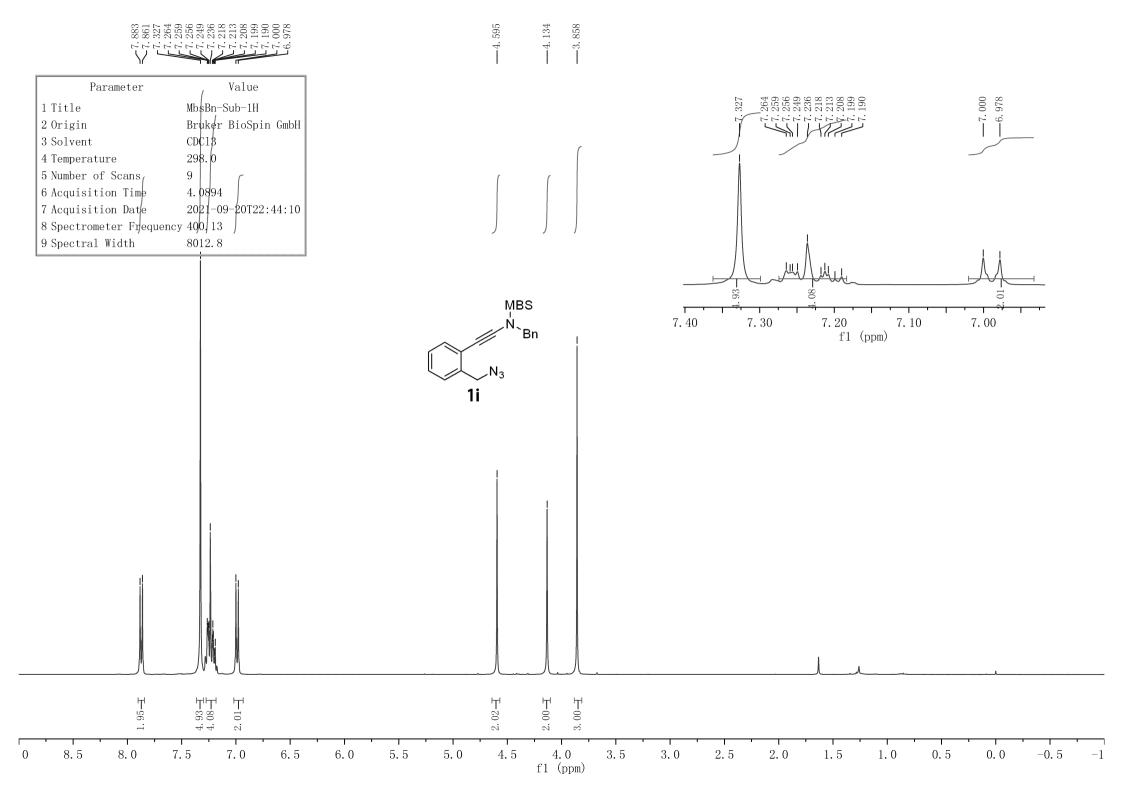
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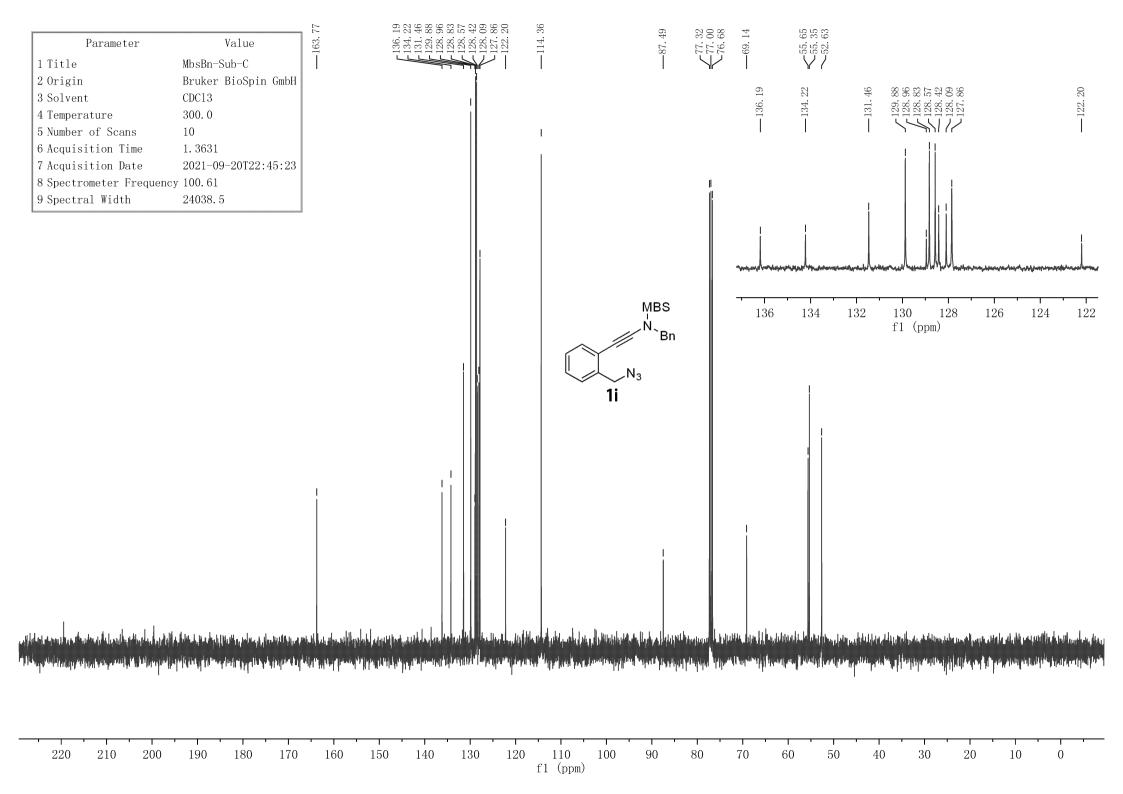


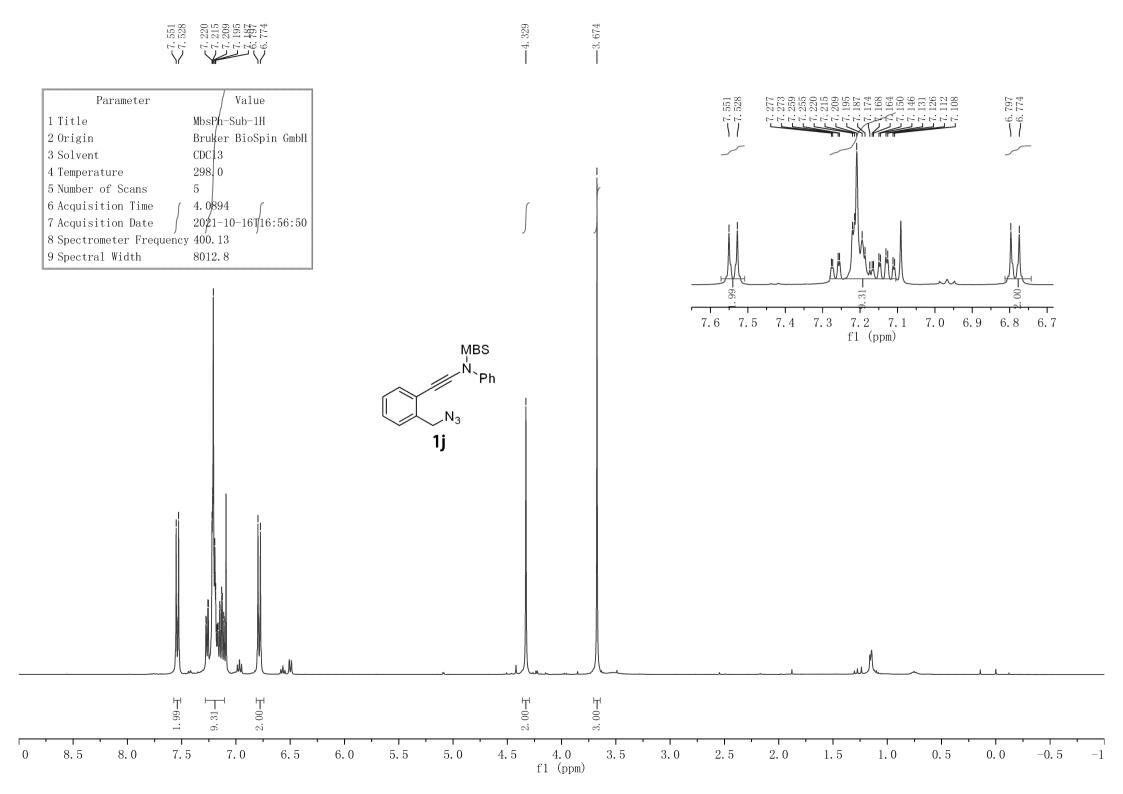


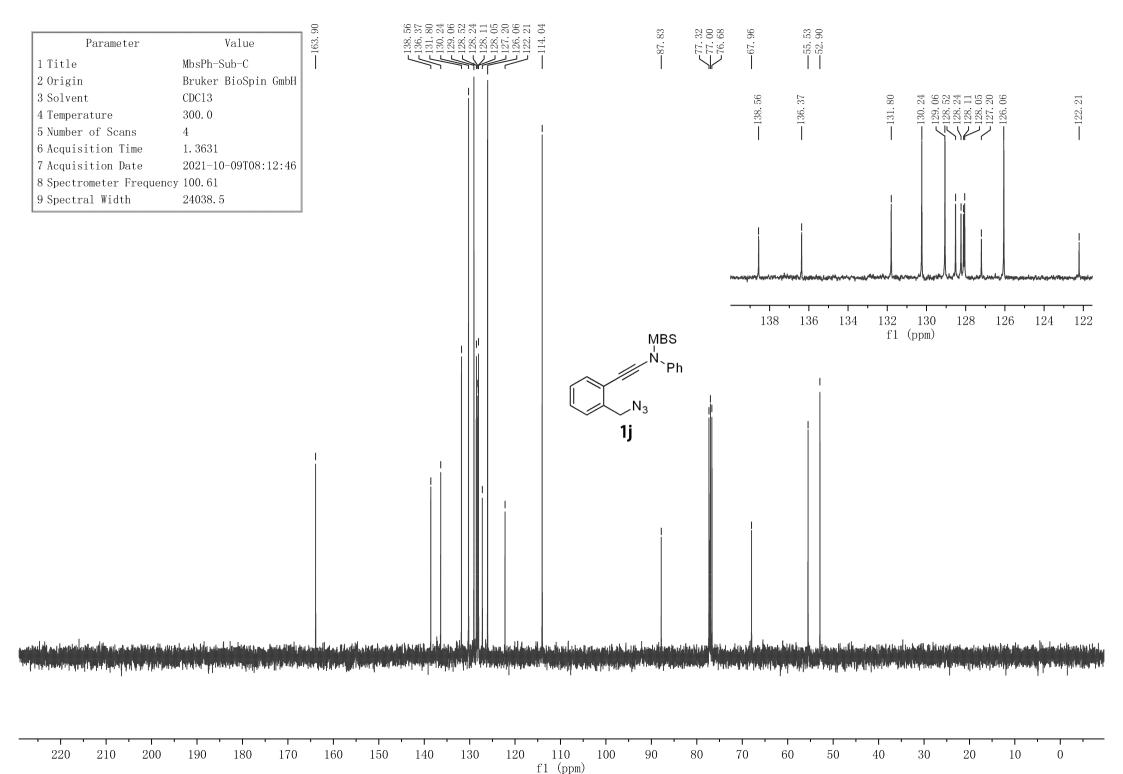


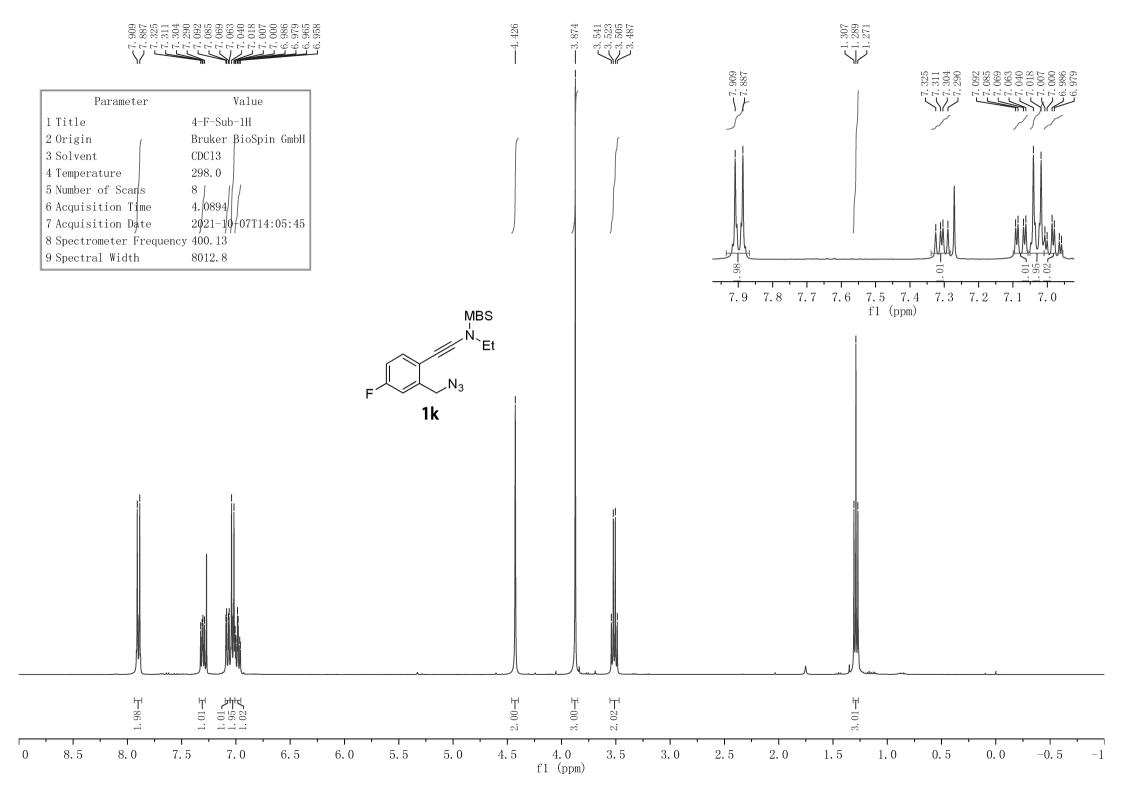


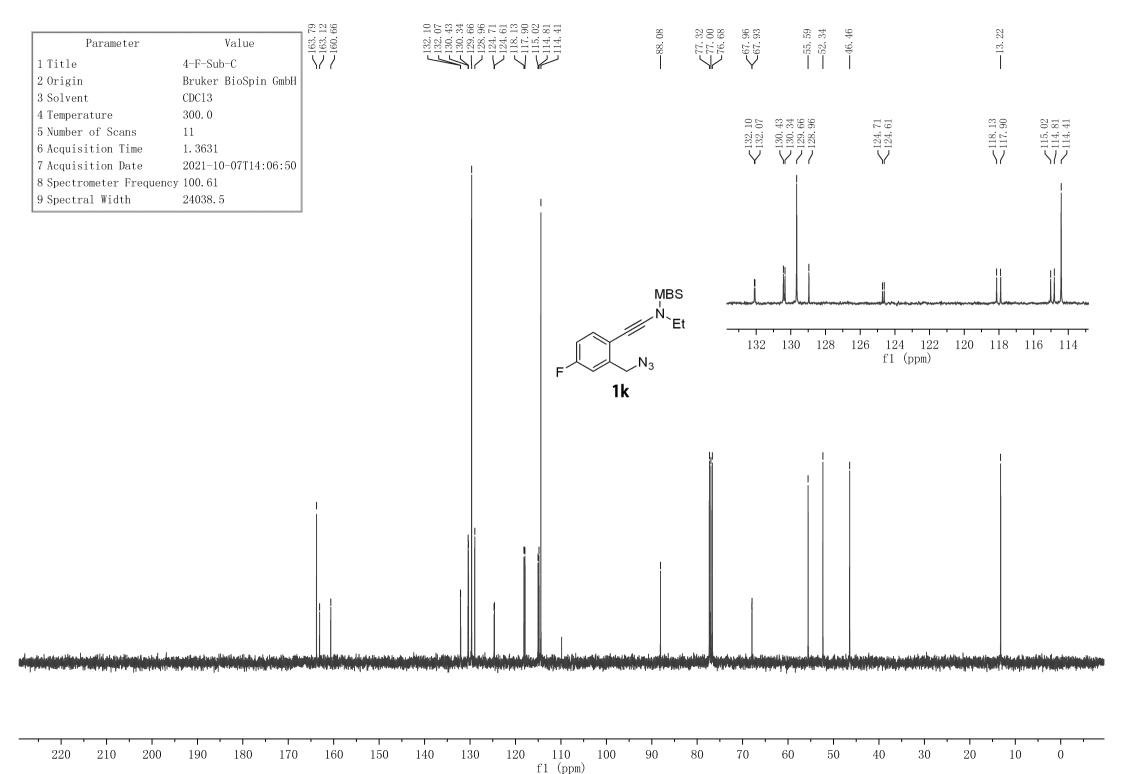




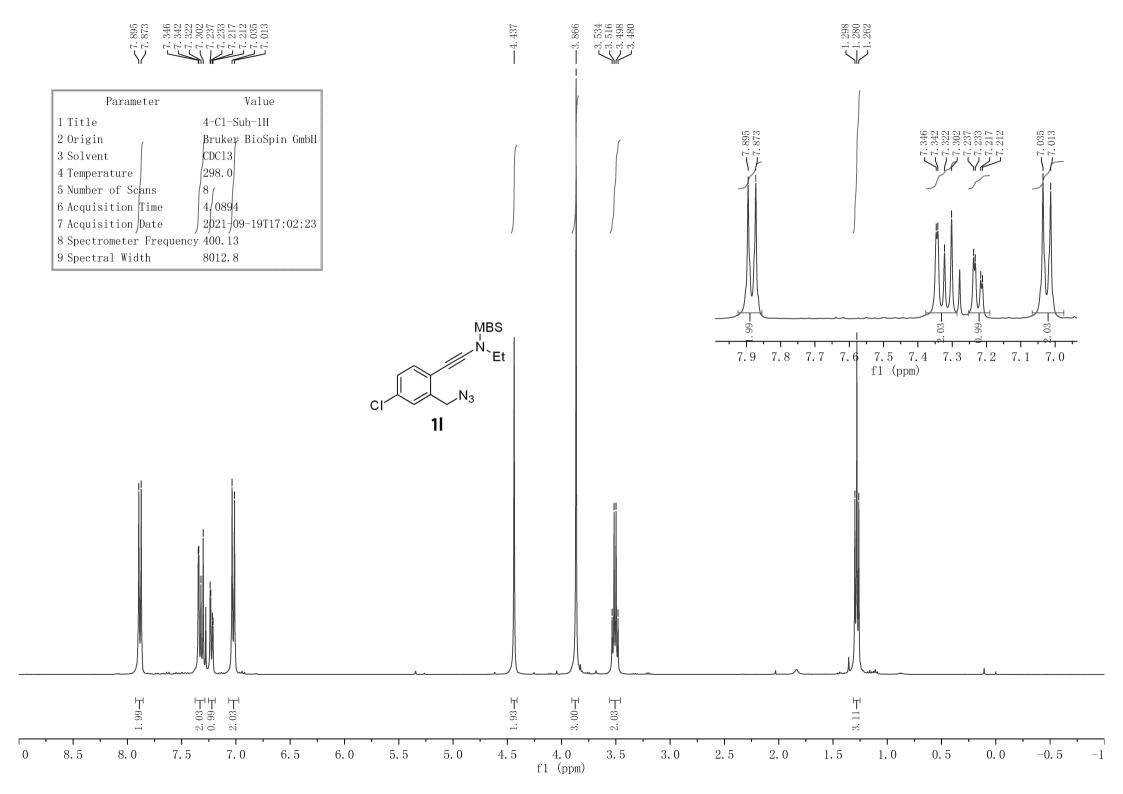


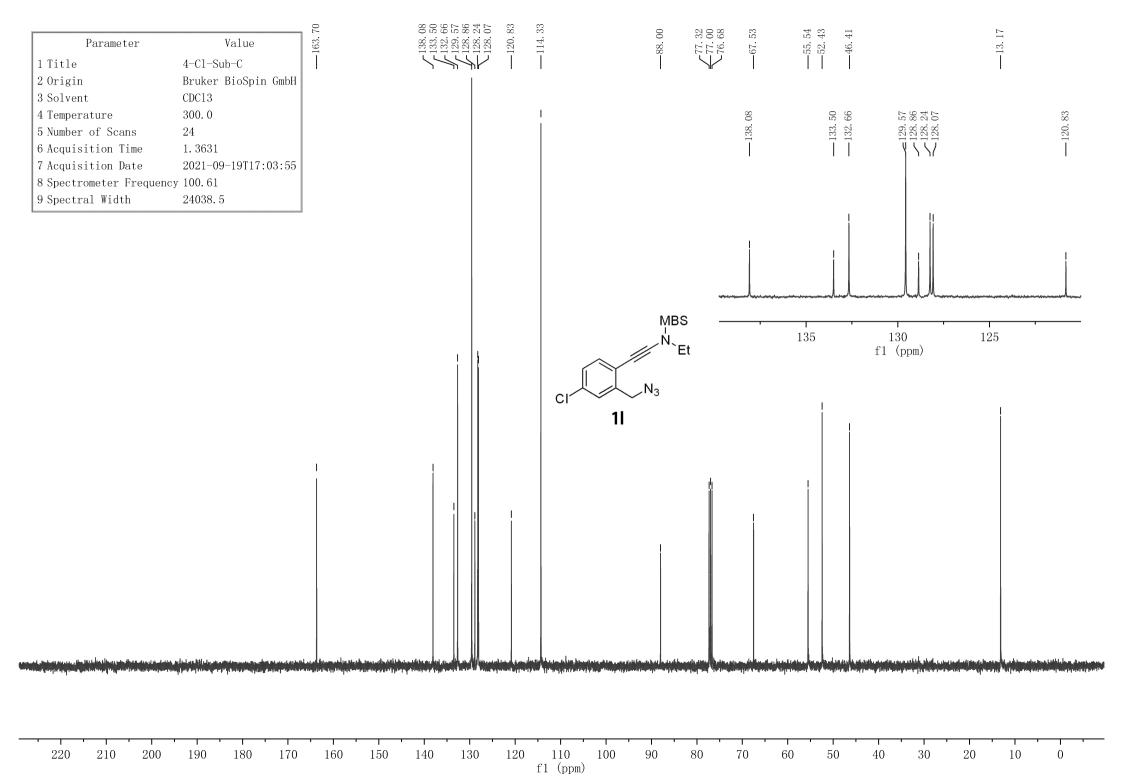


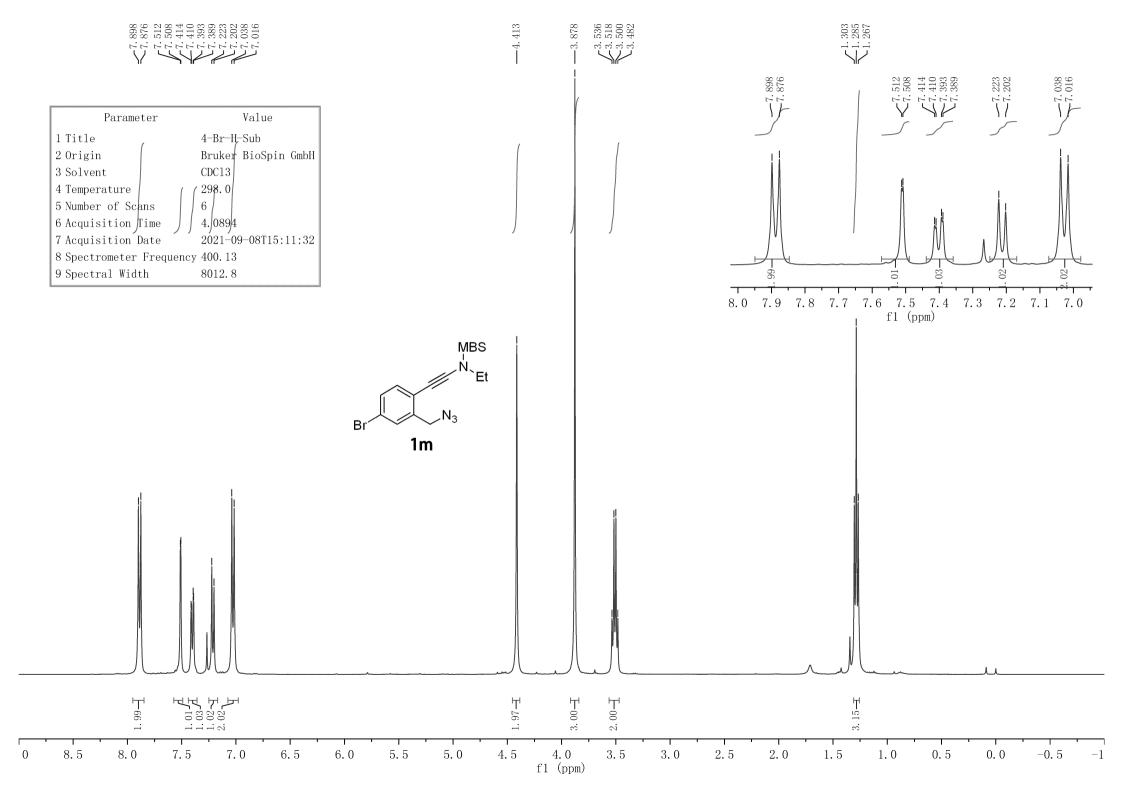


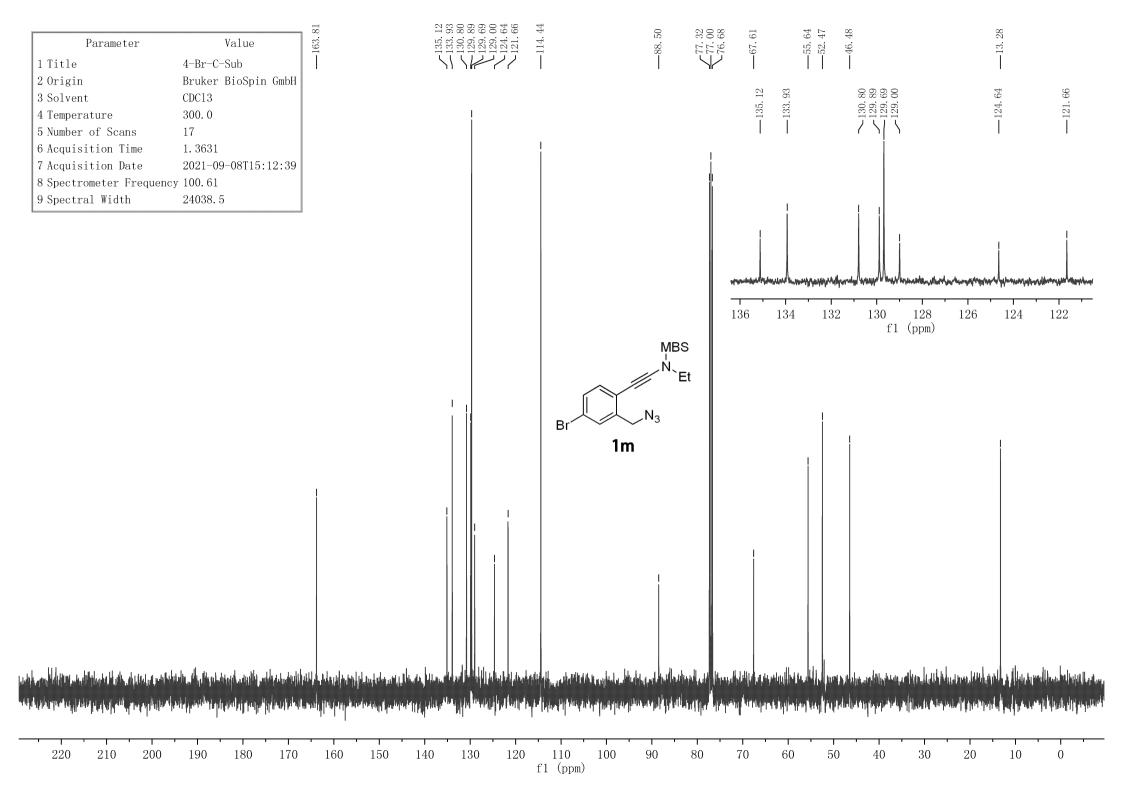


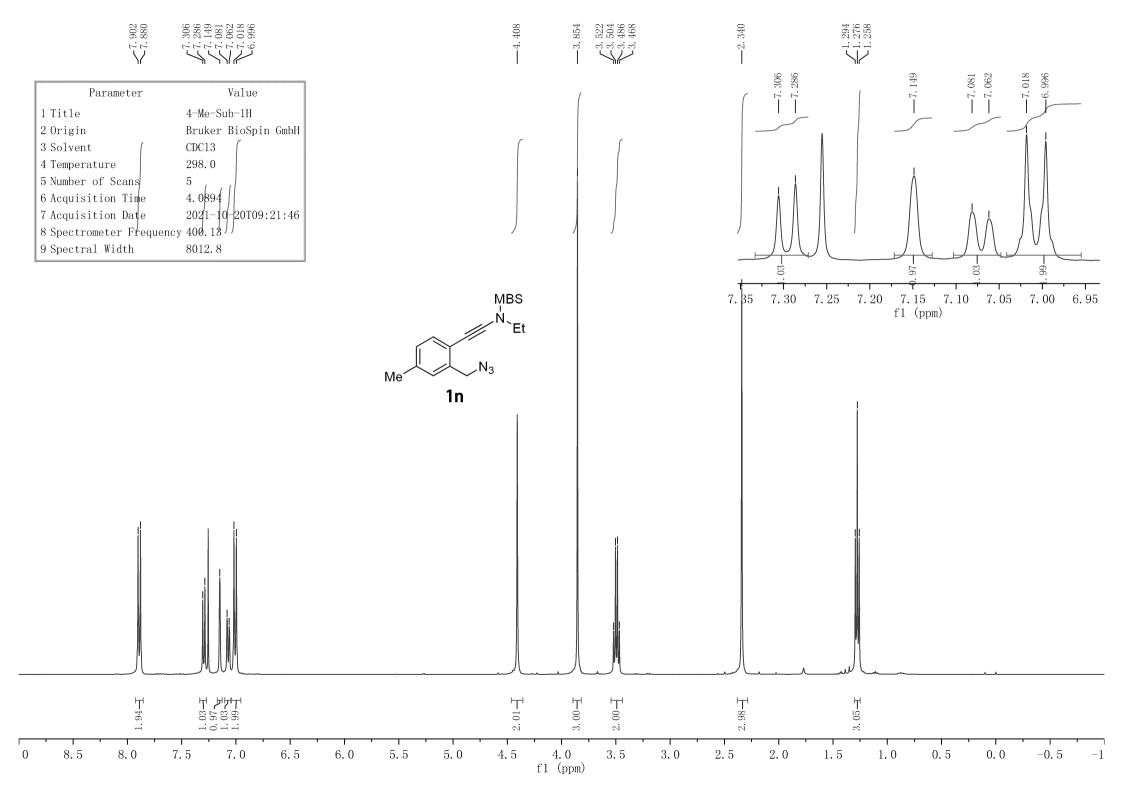
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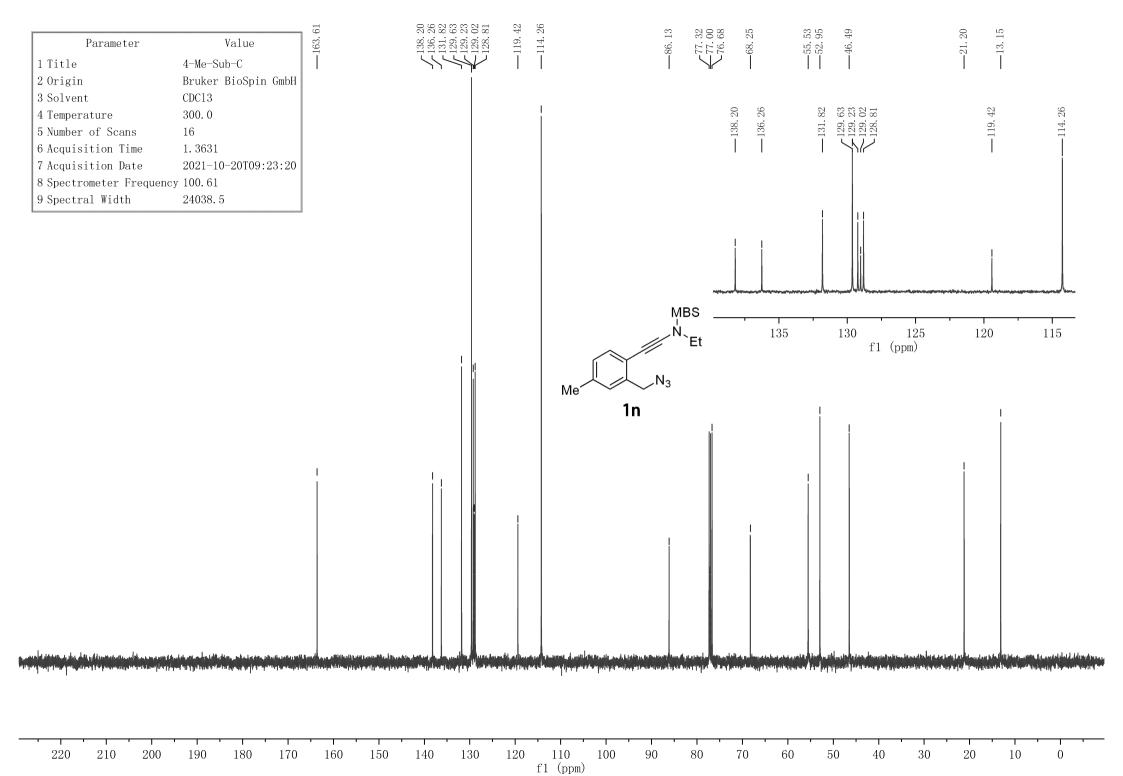


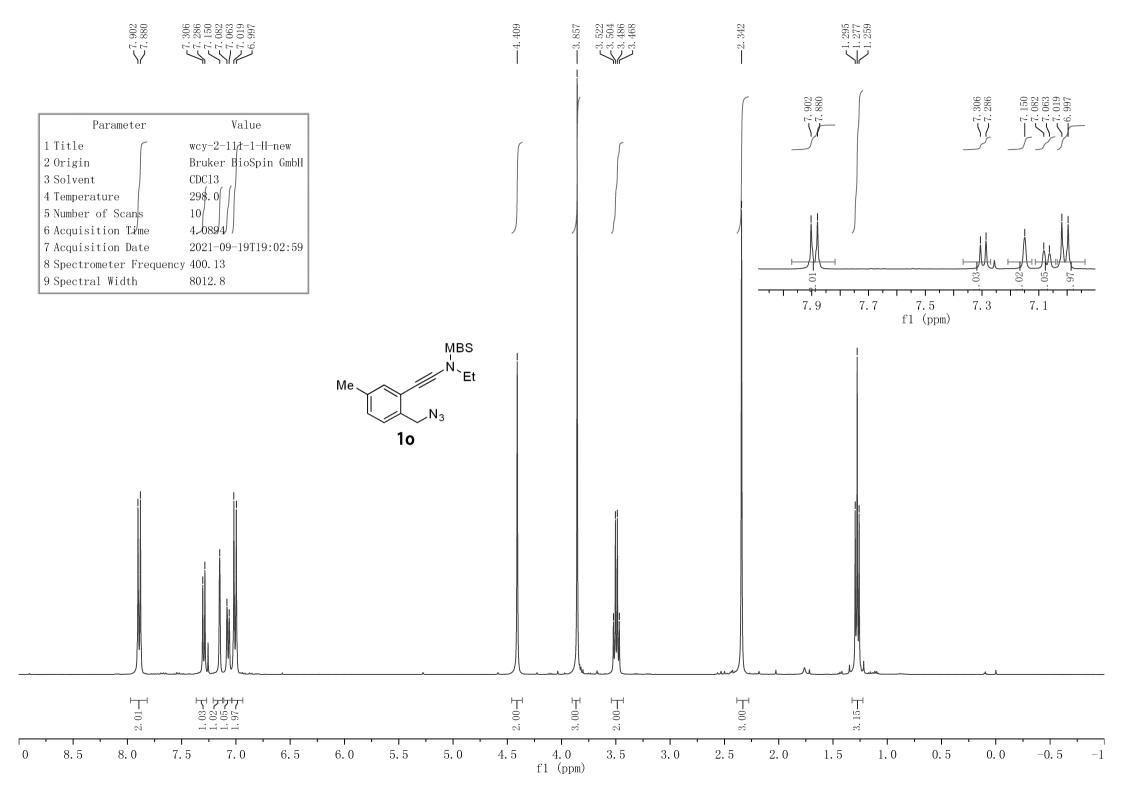


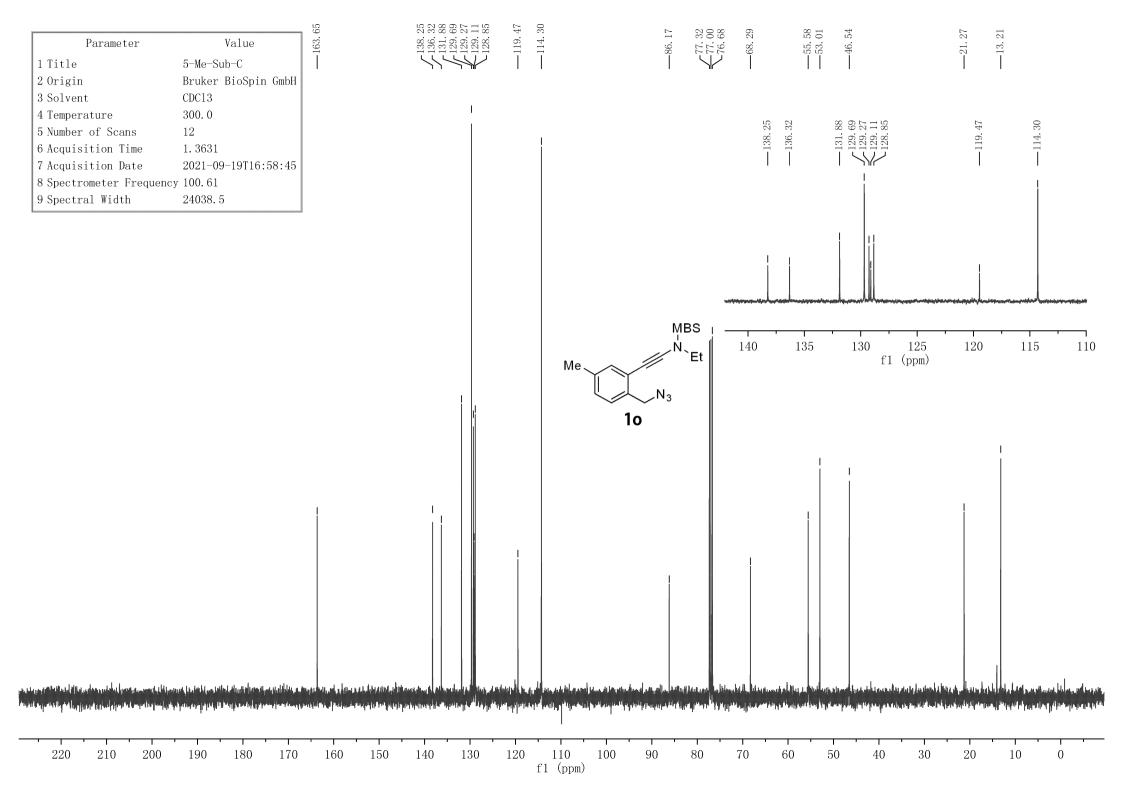


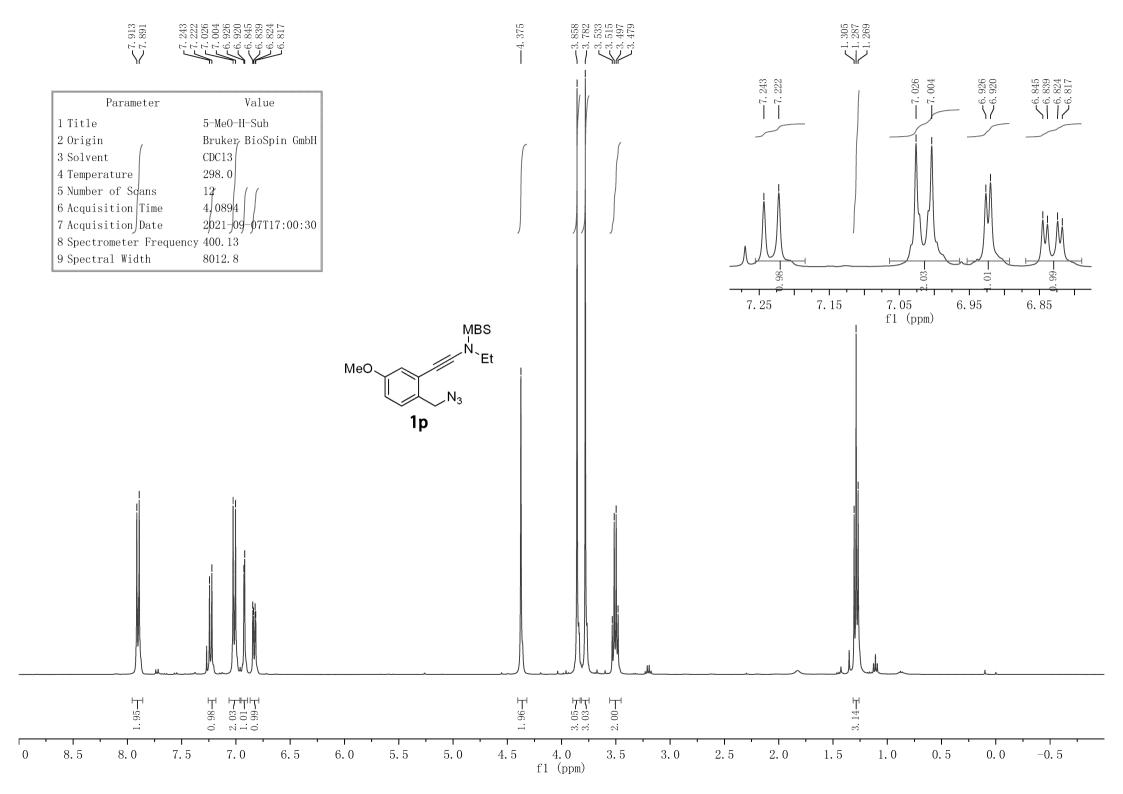


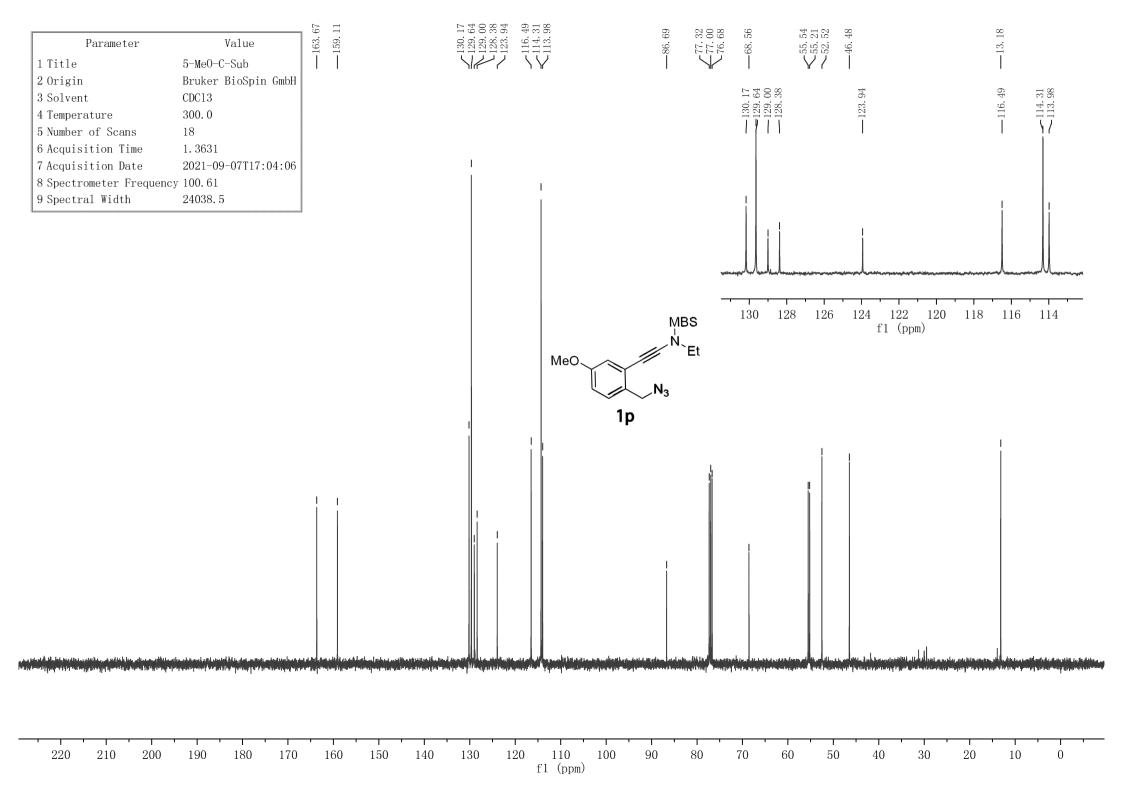


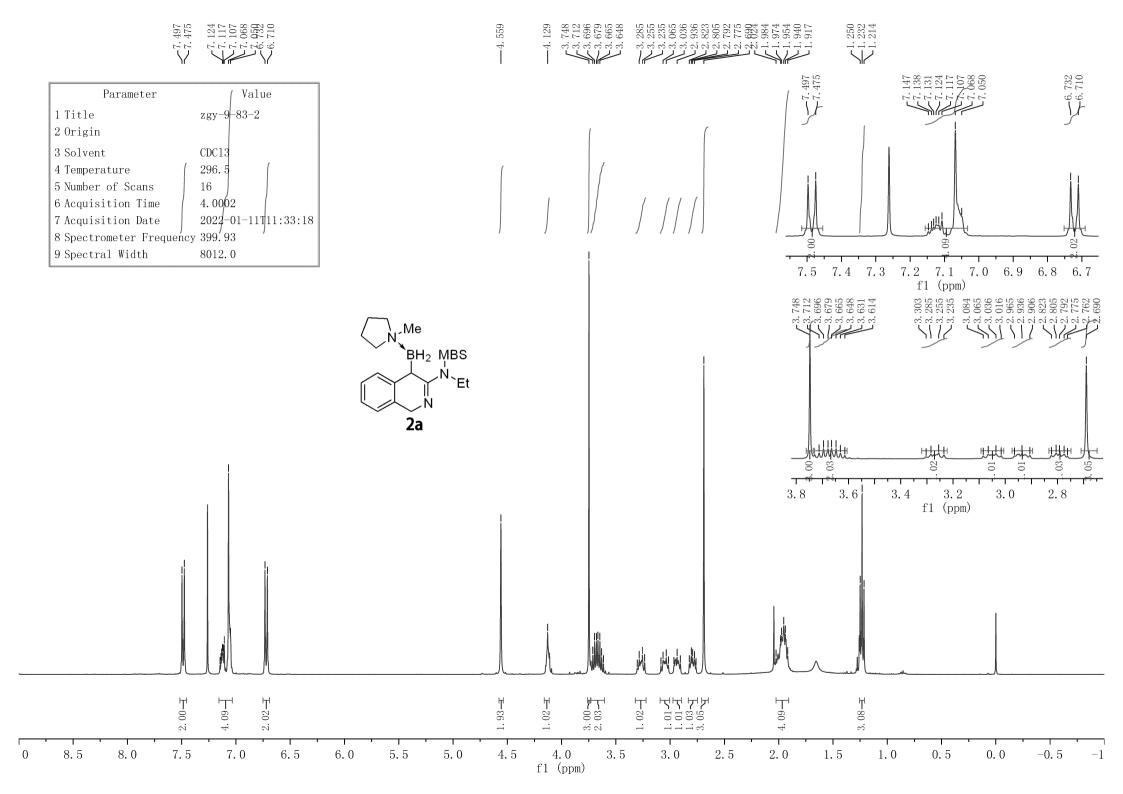


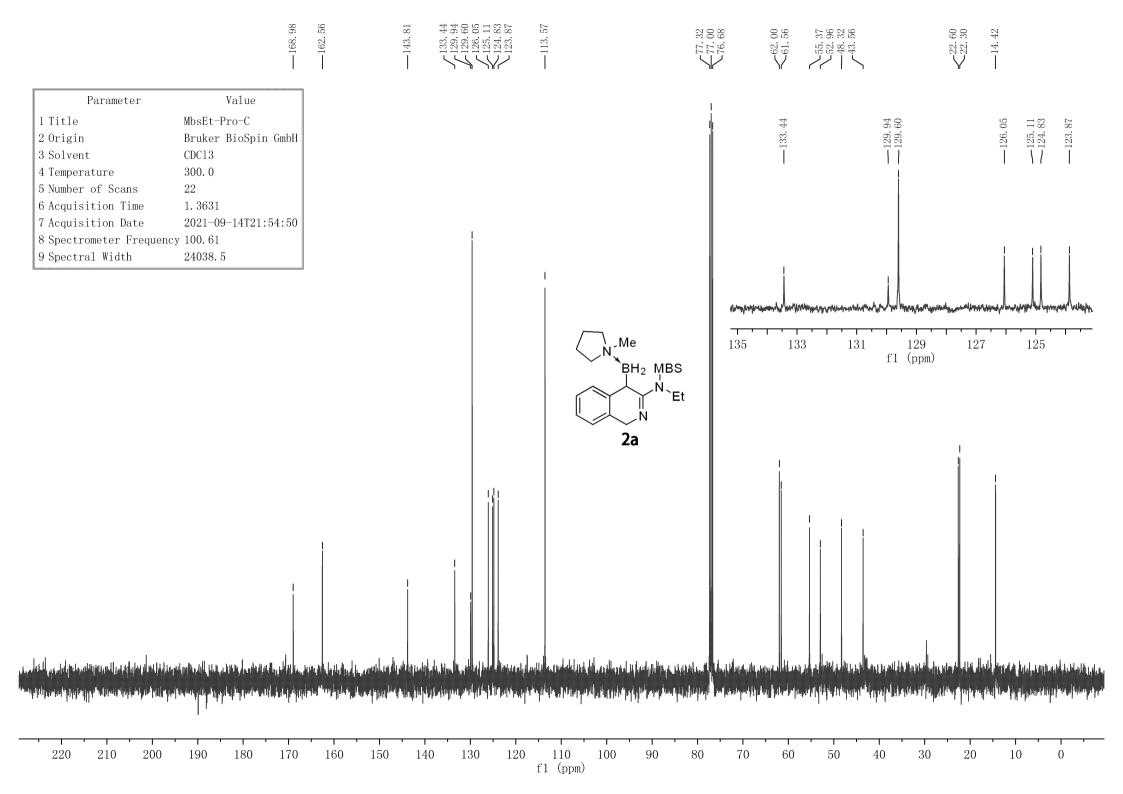


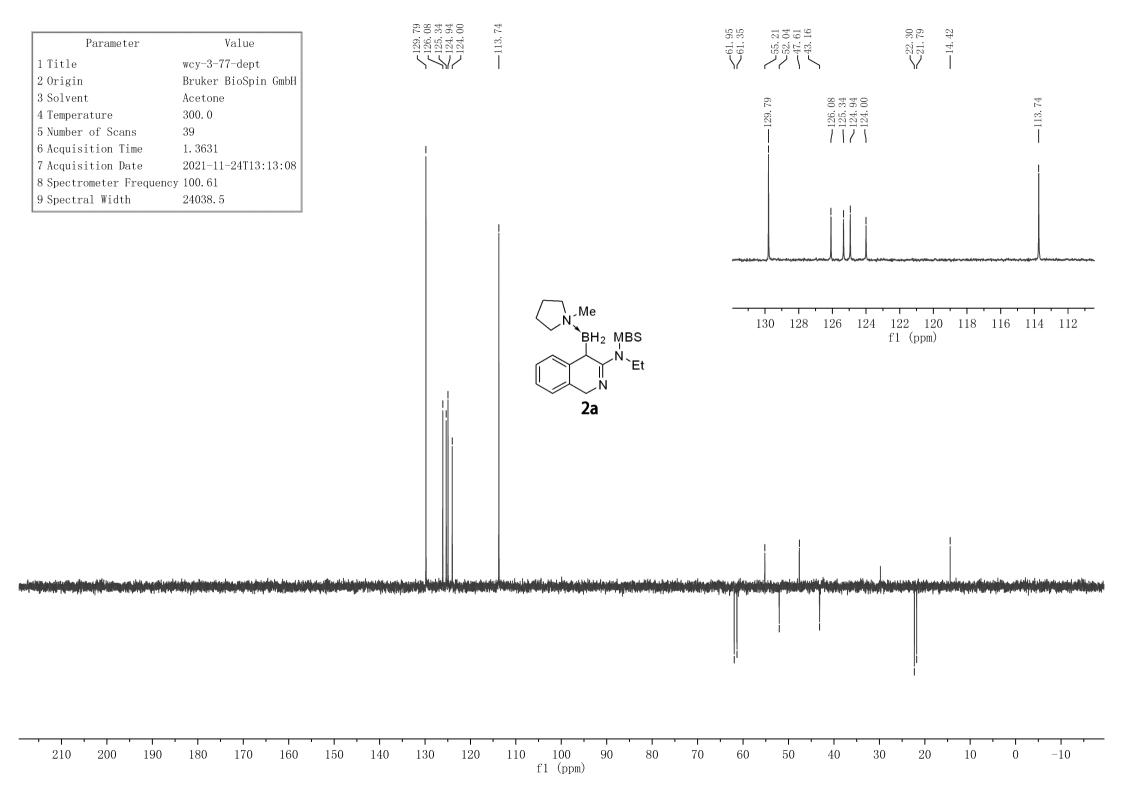


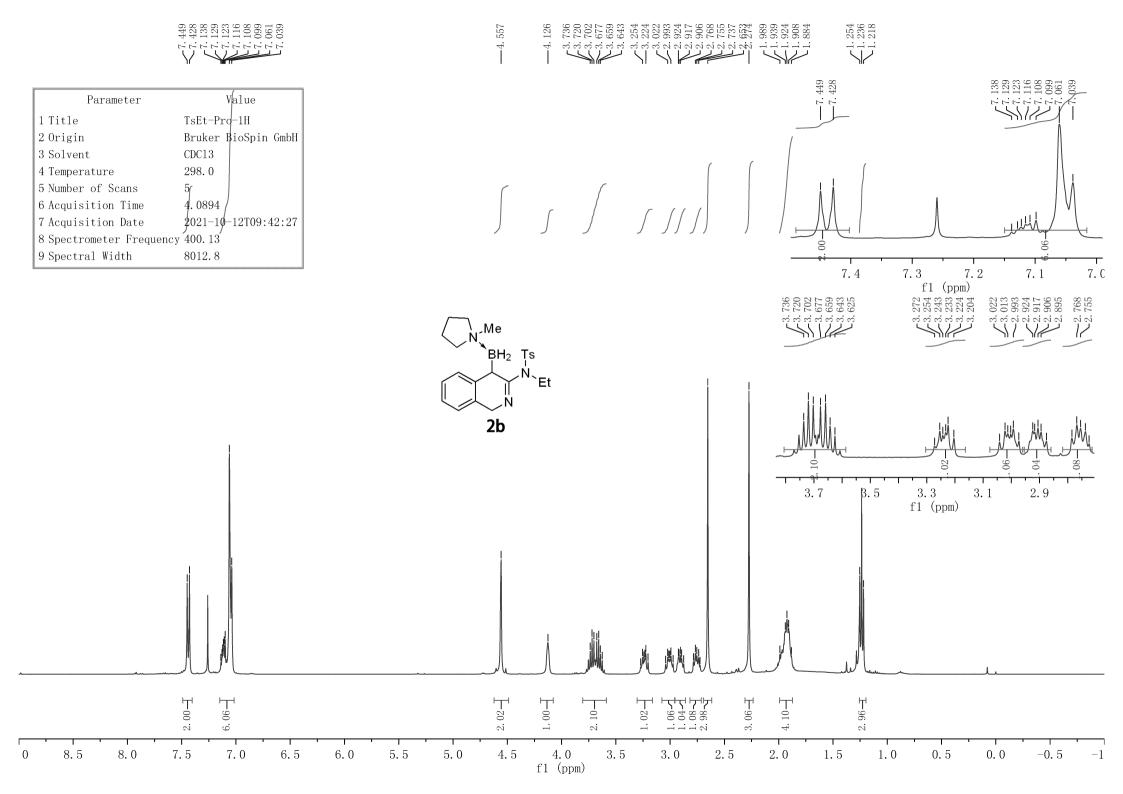


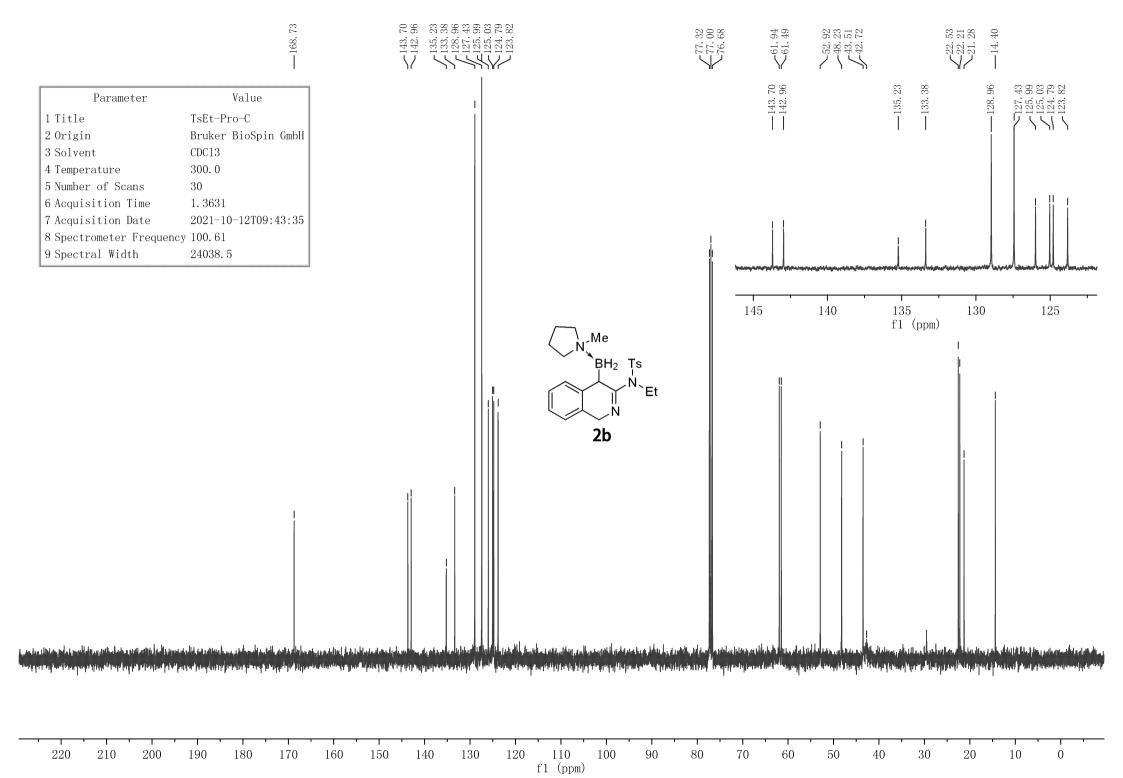


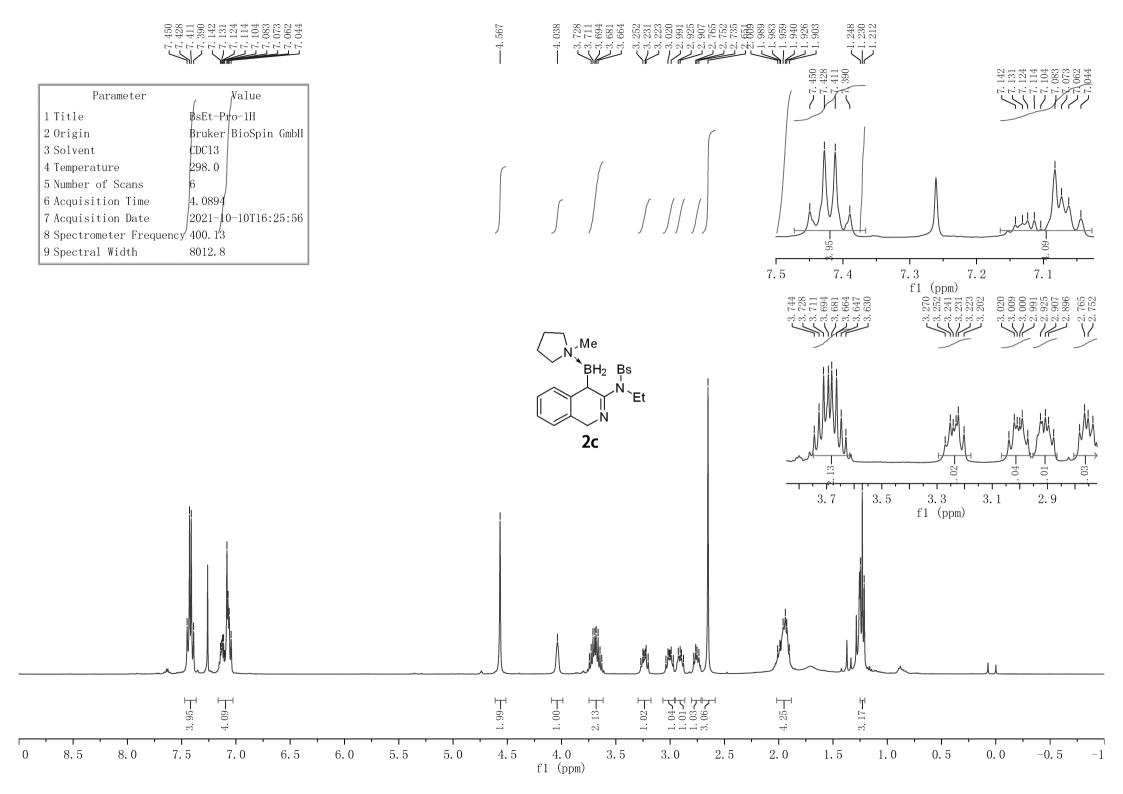


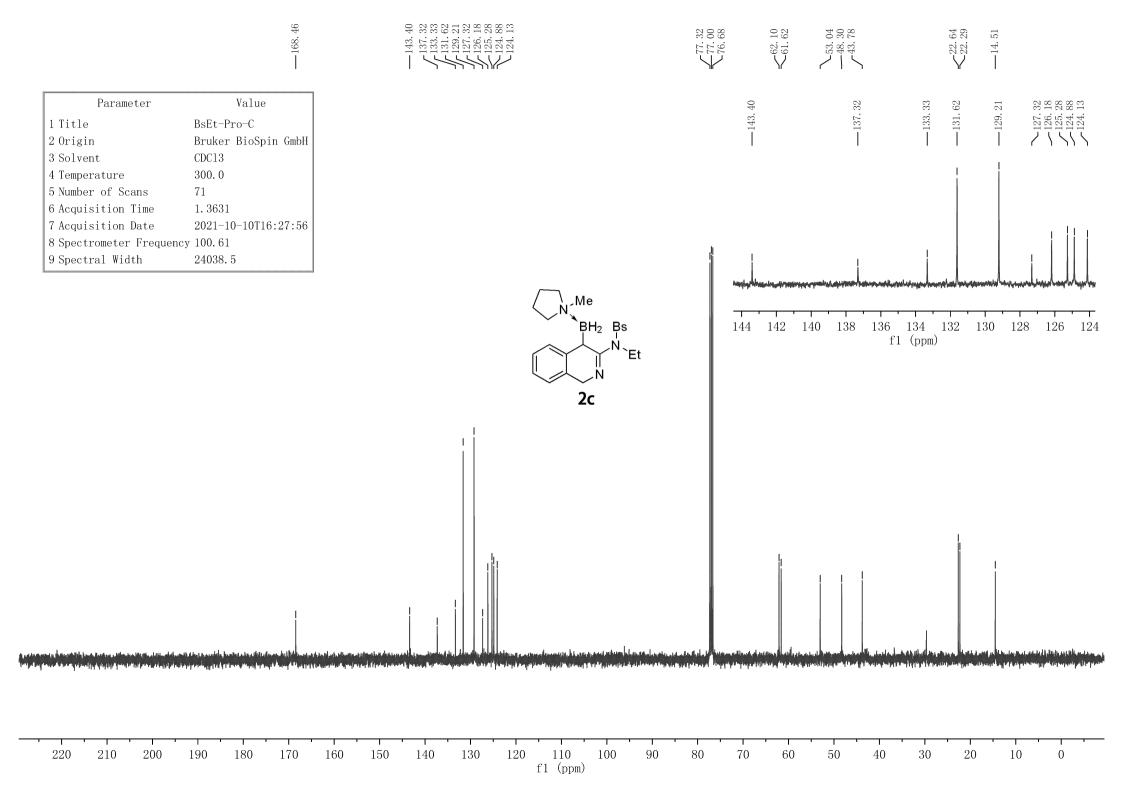


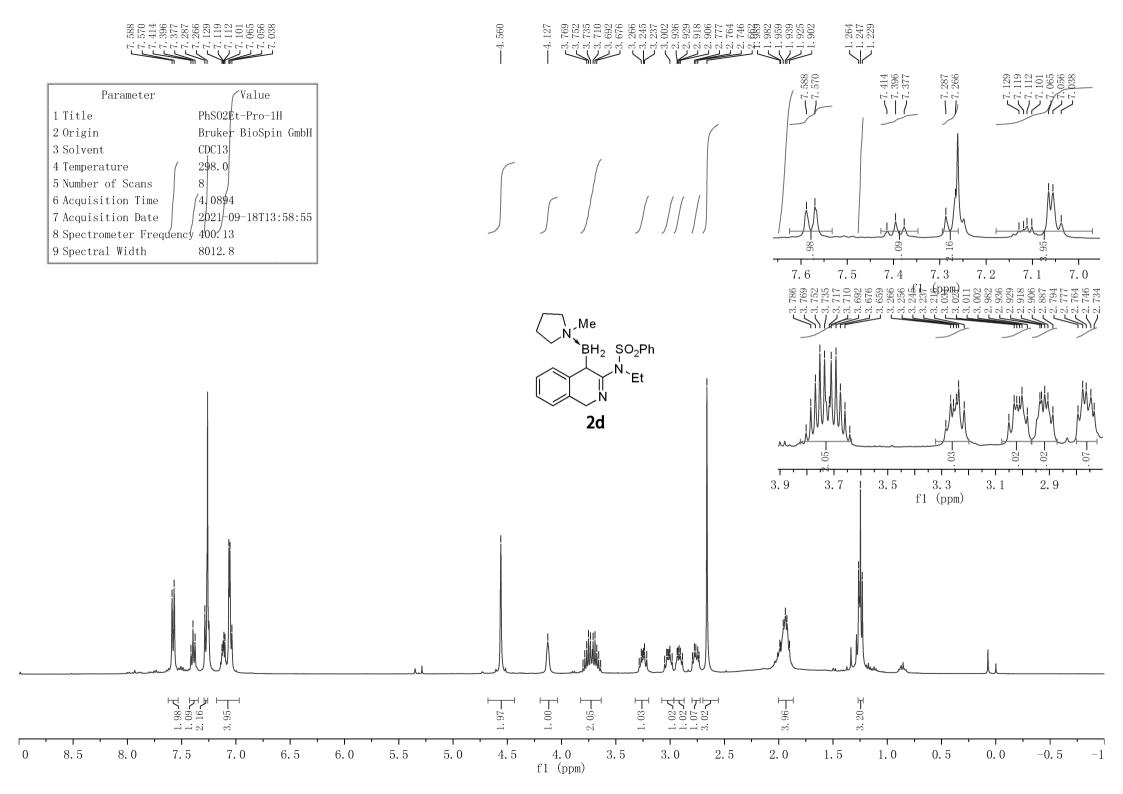


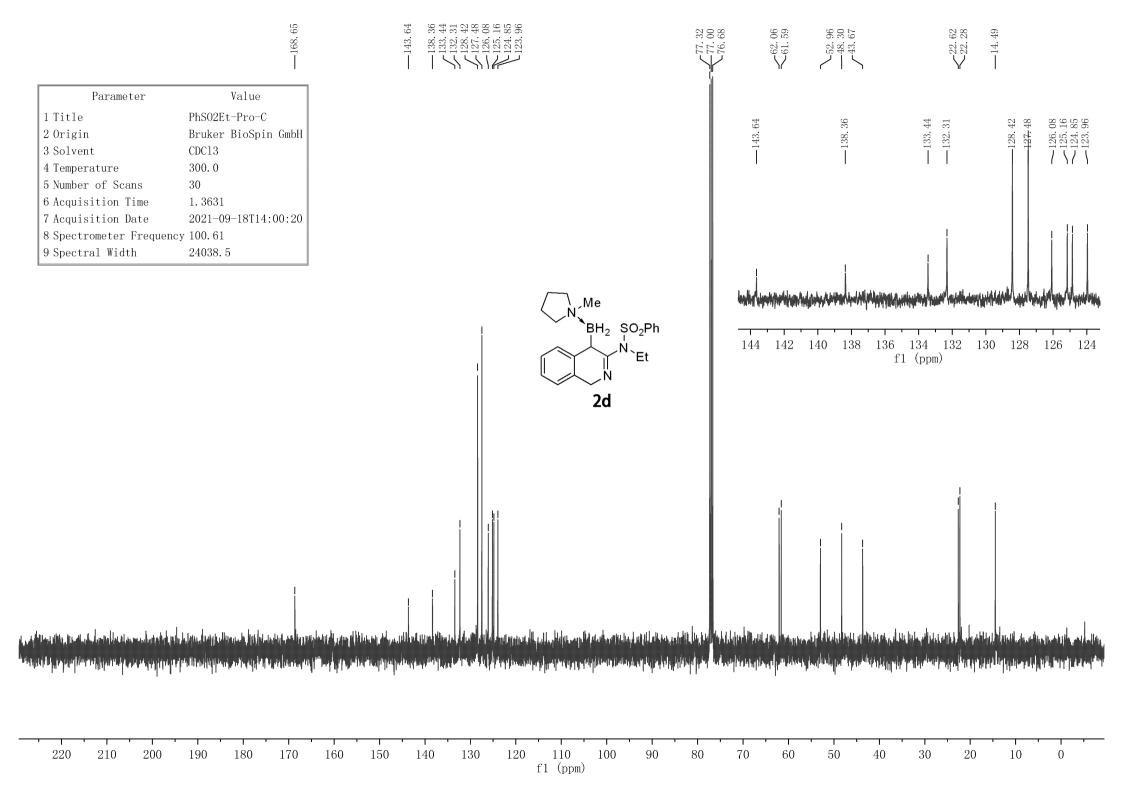


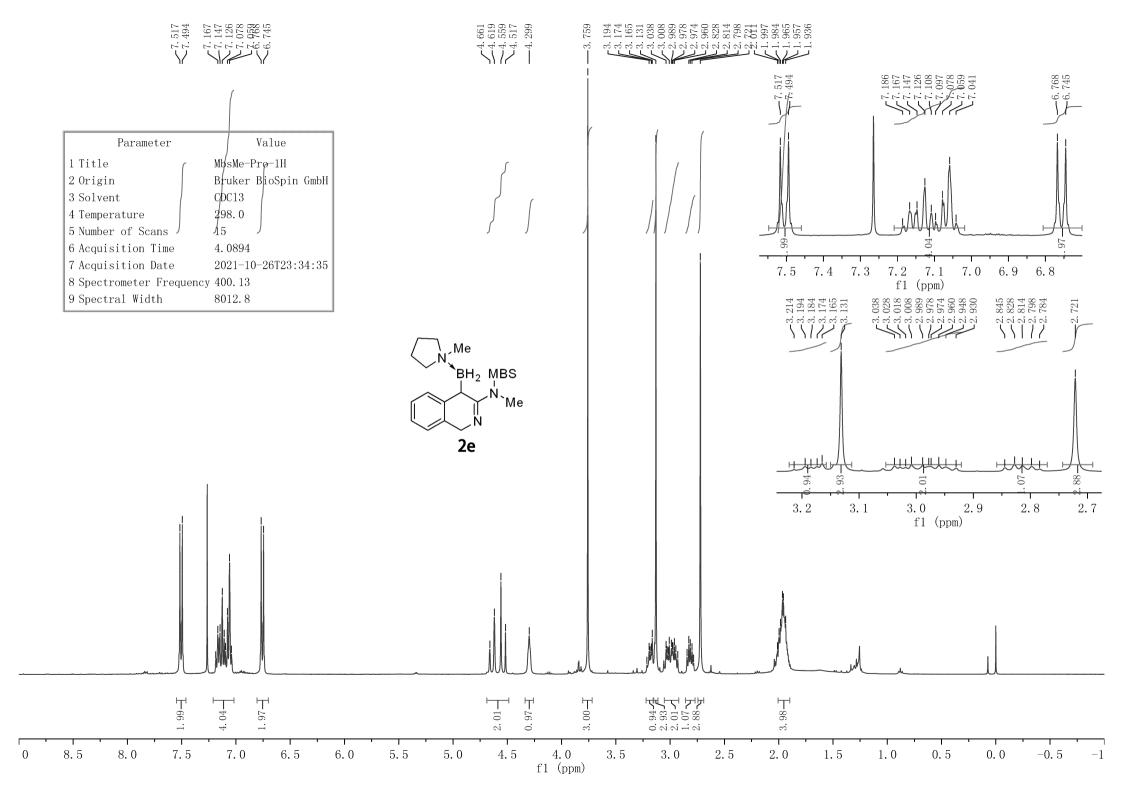


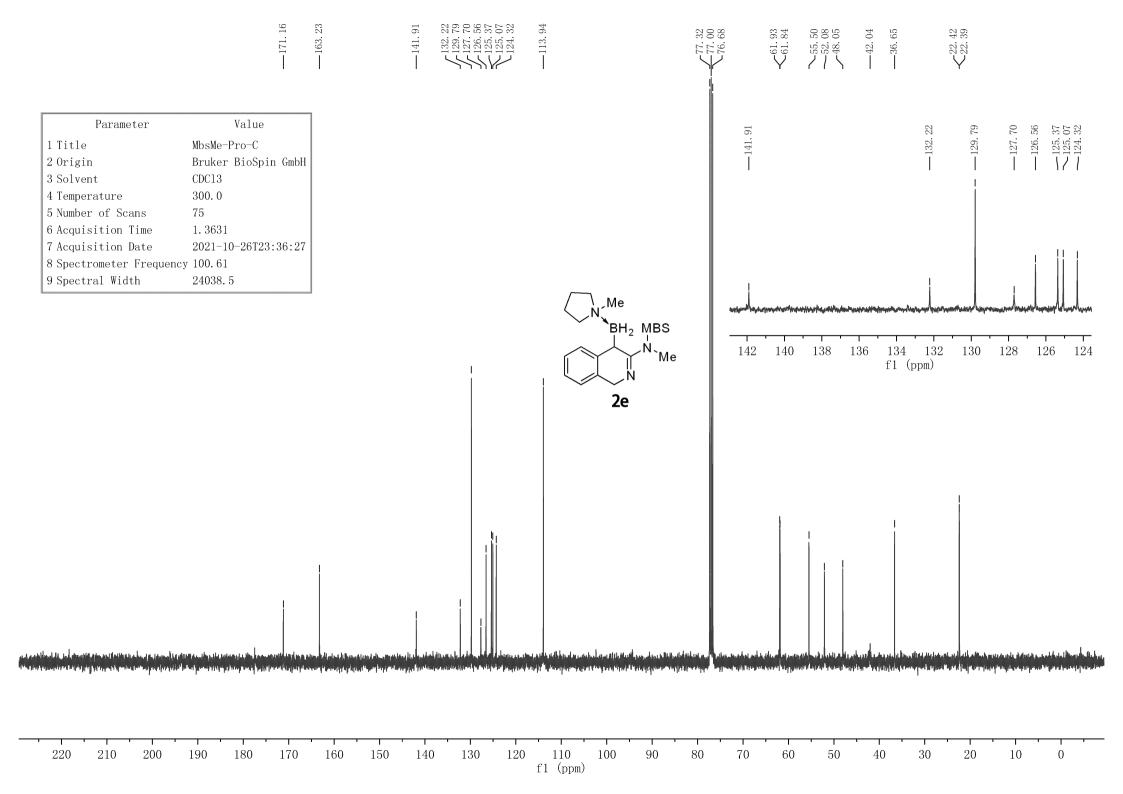


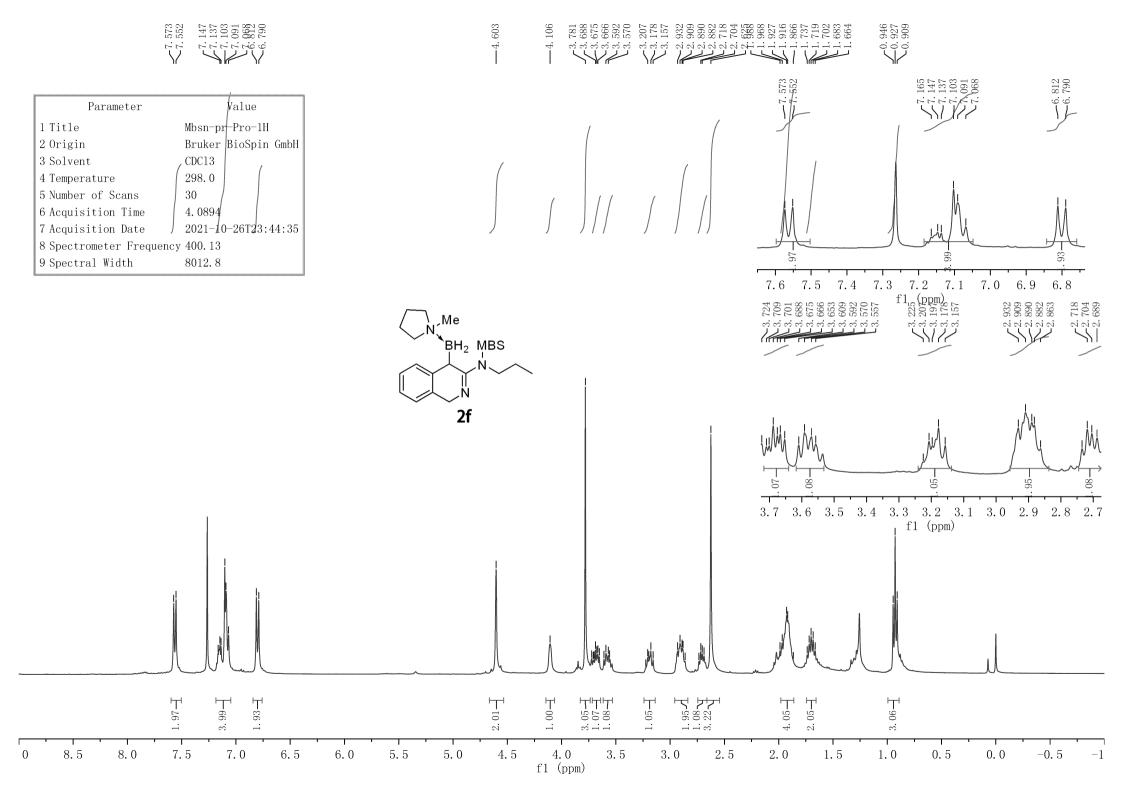


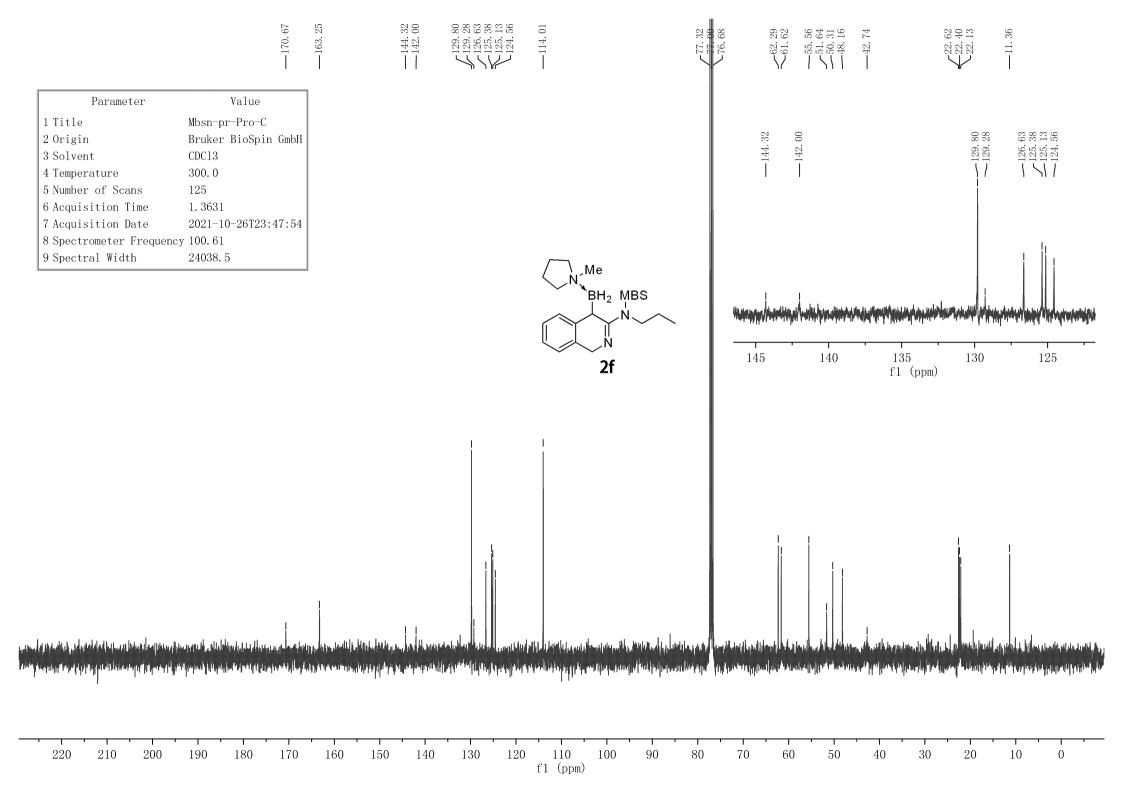


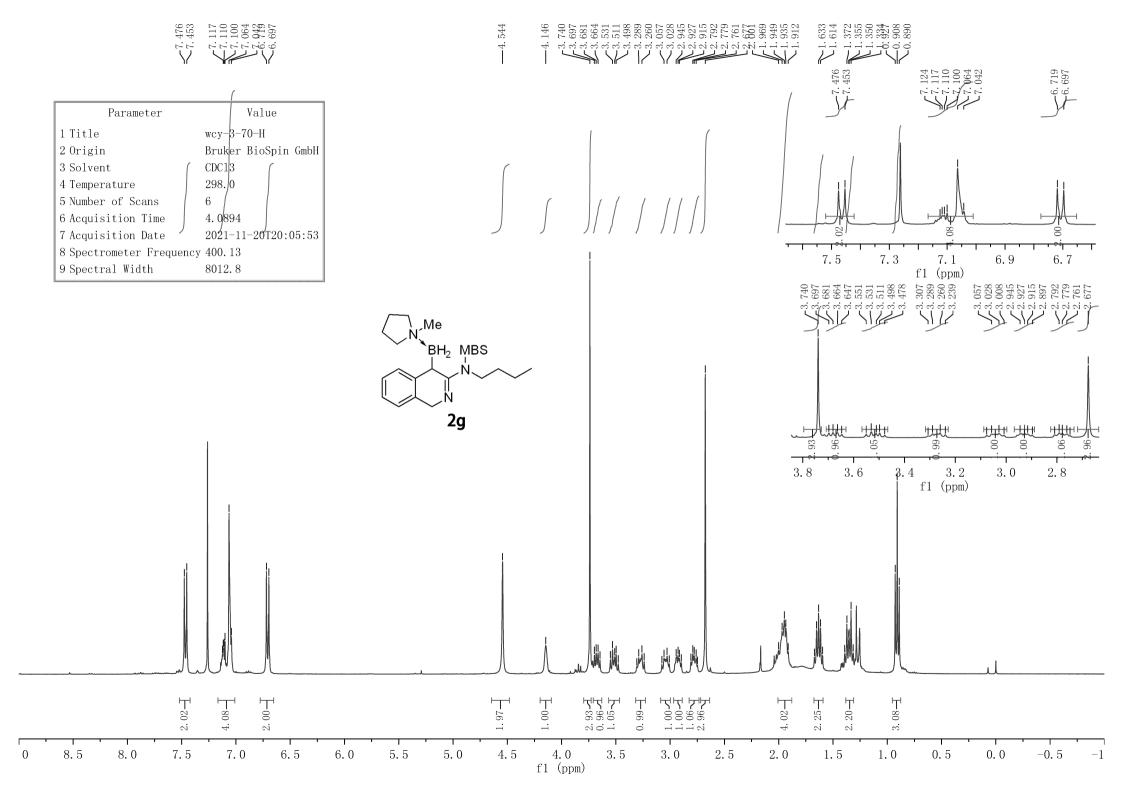


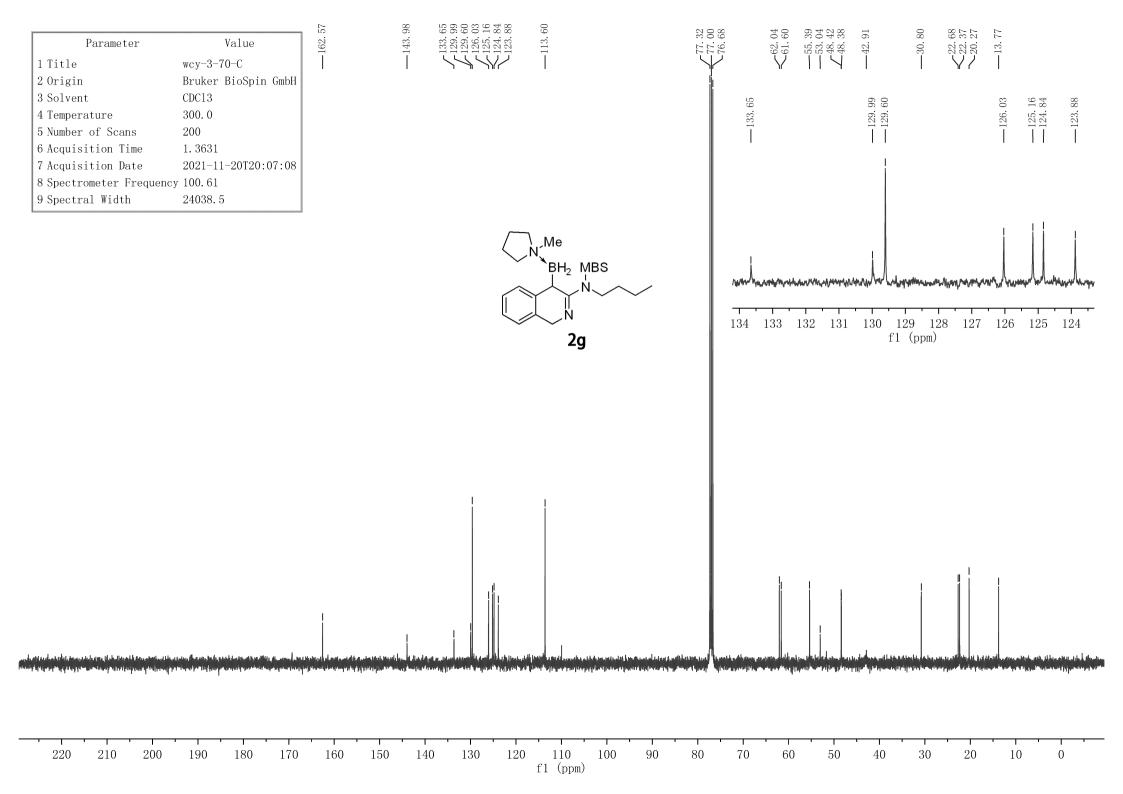


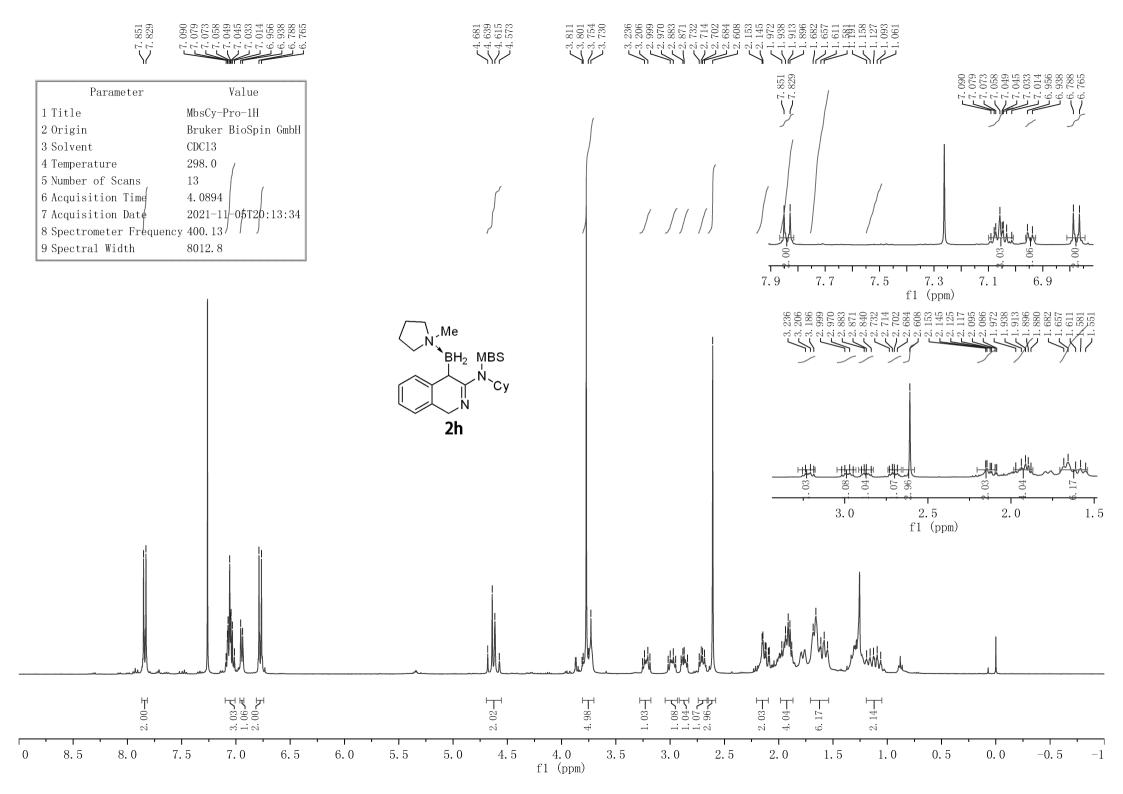


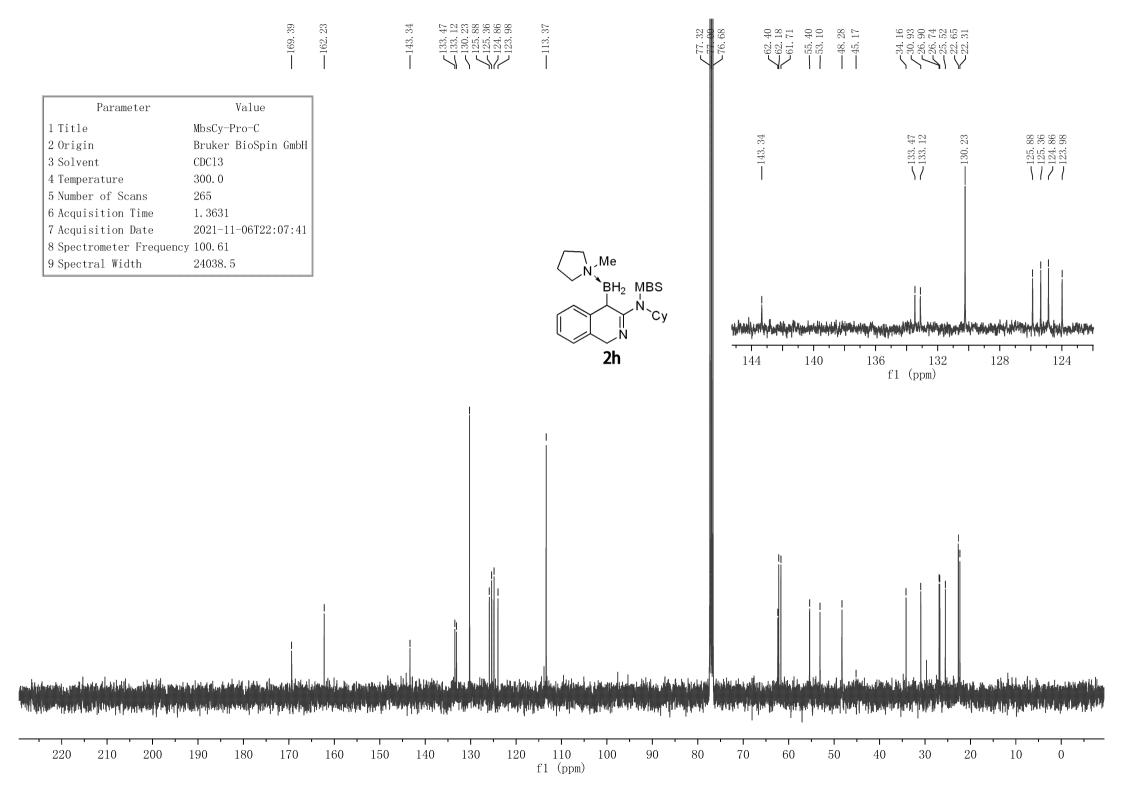


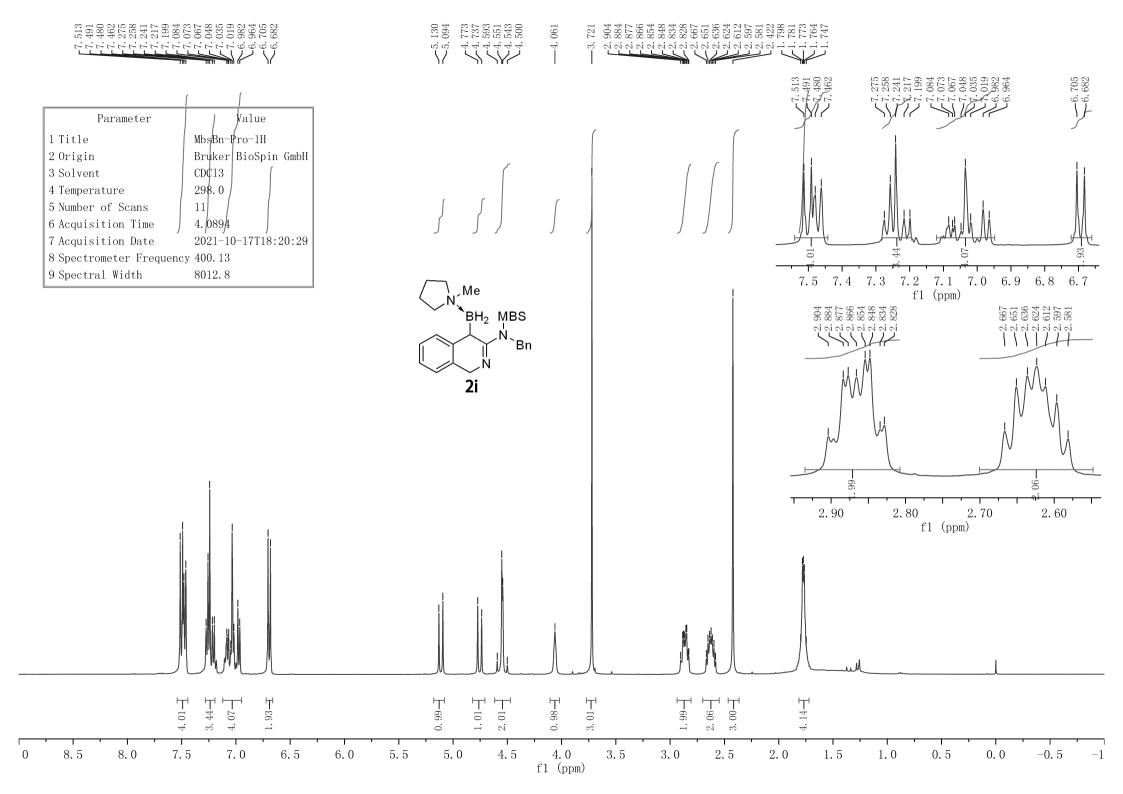


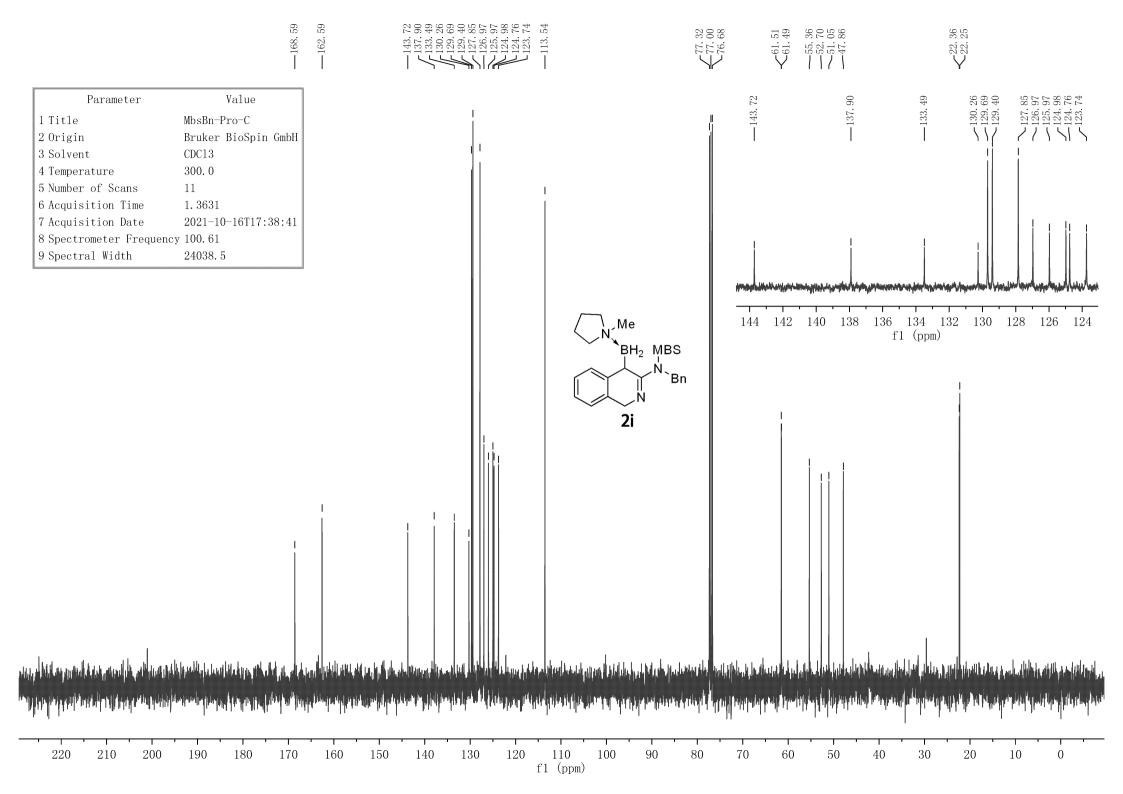


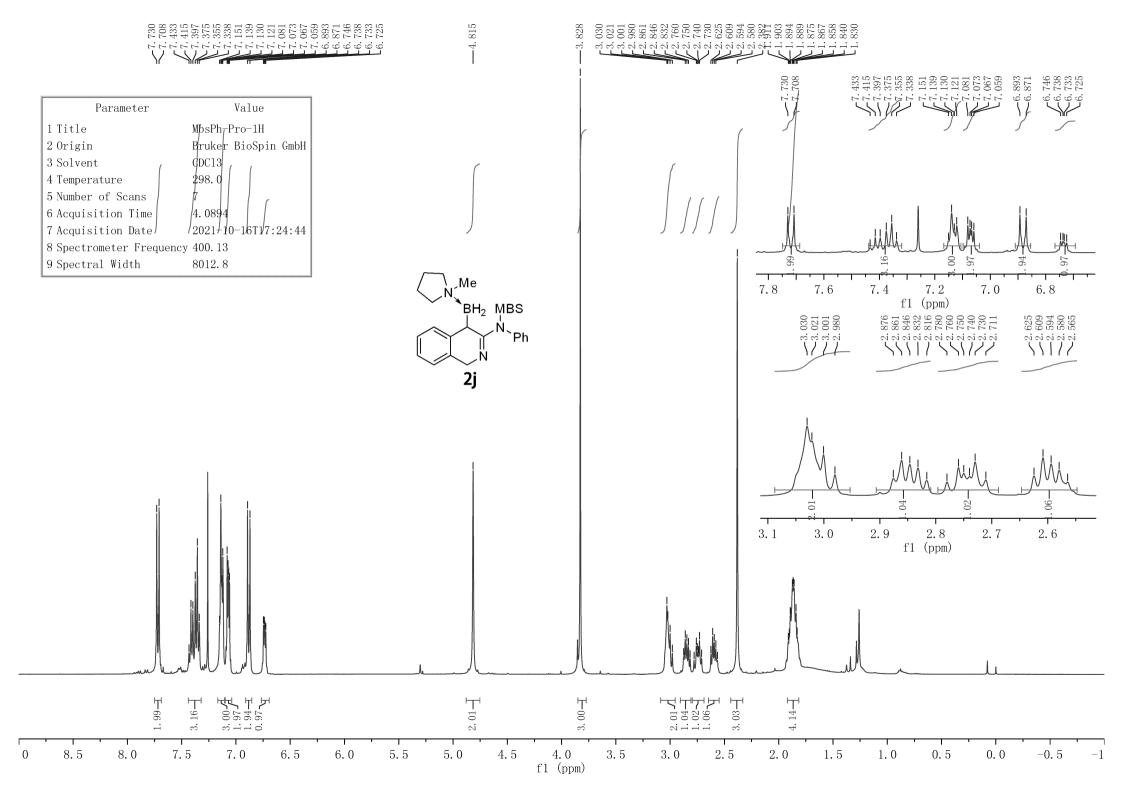


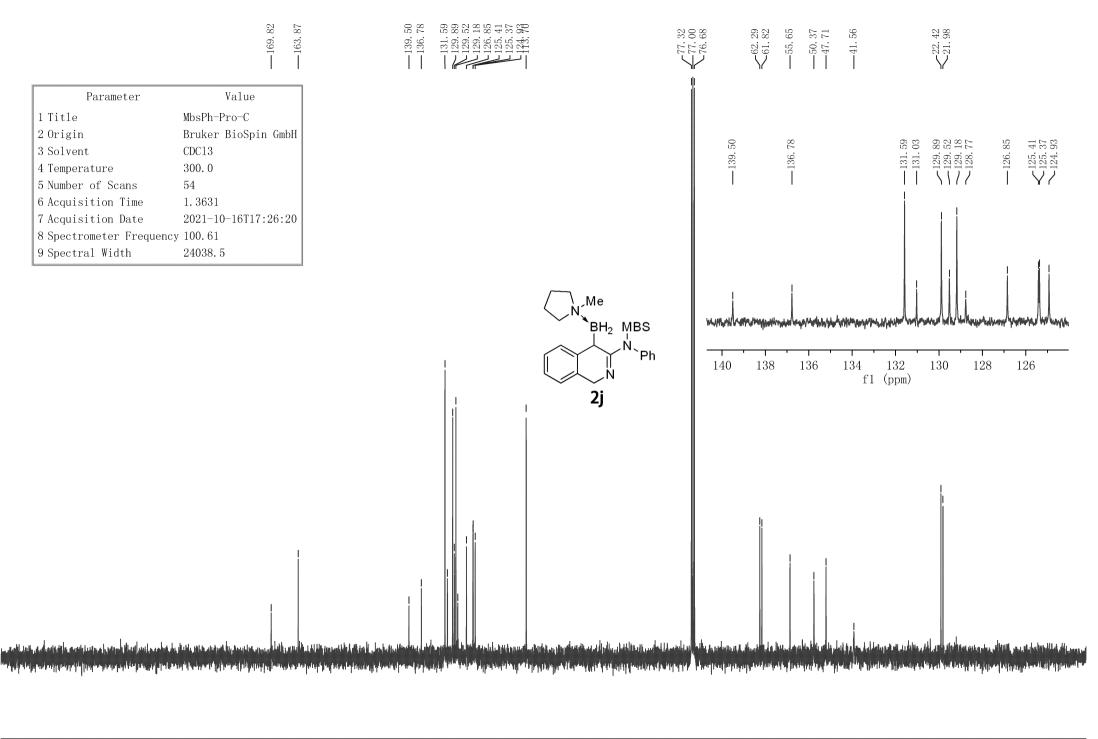


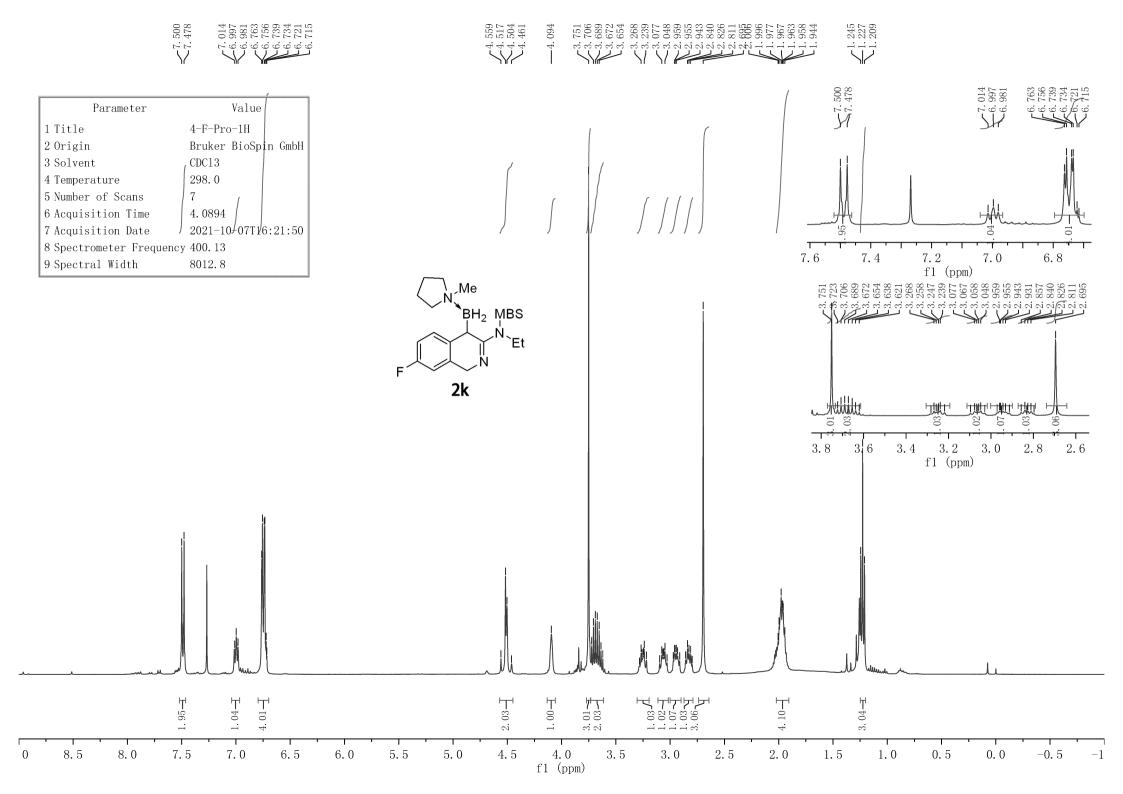


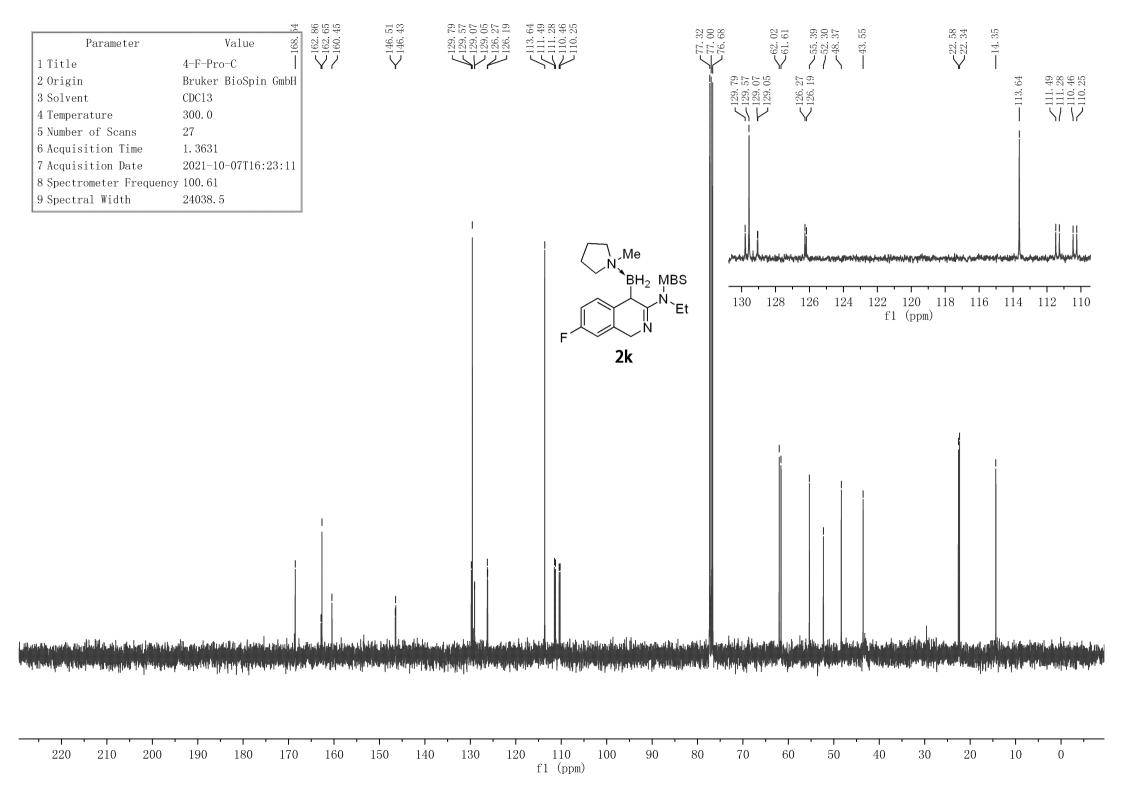












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