

Supporting Information

Copper-Catalyzed Carbonylative Multi-Component Borylamidation of Alkenes for Synthesizing γ -Boryl Amides with CO as both Methylene and Carbonyl Sources

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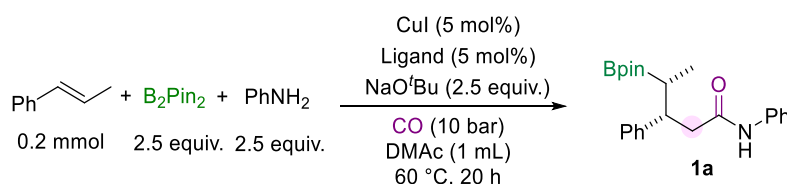
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1. General information

All experiments were carried out under a carbon monoxide or nitrogen atmosphere, unless otherwise stated. All chemical reagents were purchased from Sigma-Aldrich, TCI, abcr GmbH Germany, and BLD pharm of the highest purity grade and used without purification. In addition, B₂Pin₂ and NAOEt are stored in the glove box. Internal aryl olefins were prepared according to previous references. All solvents were dried by standard techniques. Silica gel column chromatography was carried out using silica gel (200–300 mesh). *n*-Pentane and ethyl acetate were used as eluent. Analytical thin layer chromatography (TLC) was performed on silica gel (silica gel 60 DC-Platten ALUGRAM® Xtra SIL G / UV₂₅₄). TLC plates were visualized with UV light, and/or submersion in KMnO₄ solution and/or phosphomolybdic acid. Bruker Avance III HD 300 NMR (¹H, 300 MHz; ¹³C{¹H}, 75 MHz; ¹¹B, 96 MHz), and Bruker ARX 400 NMR spectrometers (¹H, 400 MHz; ¹³C{¹H}, 101 MHz) recorded all NMR spectra. The chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ¹H NMR) and TMS (δ 0.00 for ¹H NMR) chloroform (δ 77.16 for ¹³C{¹H} NMR) in parts per million (ppm). The following abbreviations are used for the NMR spectra' multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quartet, m: multiplet, and br: broad signal for proton spectra. All ¹³C NMR spectra were broad-band ¹H decoupled. However, it is hard to observe the signals for the carbon attached to boron in the ¹³C{¹H} NMR spectra. Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using argon as carrier gas. High-resolution mass spectra were recorded on an Agilent 6210 system. All the reactions which used CO were performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

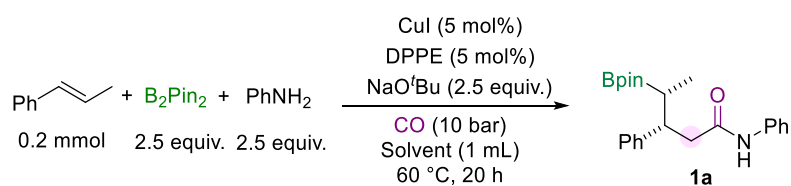
2. Optimization of reaction conditions.

Table S1. Screening of ligand



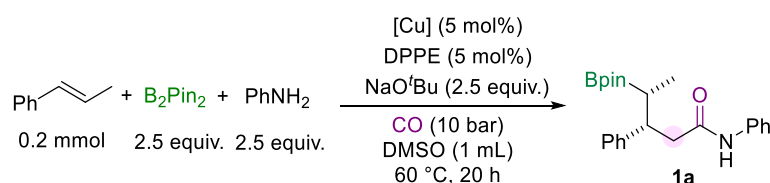
Entry	Base	1a (%)
1	DPPE	24
2	DPPB	8
3	DPPP	11
4	DPPPe	n.d.
5	DPPBz	13
6	Xantphos	n.d.
7	DPPM	n.d.

Reaction conditions: (*E*)-prop-1-en-1-ylbenzene (0.2 mmol), CuI (5 mol%), Ligand (5 mol%), NaO^tBu (2.5 equiv.), B₂Pin₂ (2.5 equiv.), PhNH₂ (2.5 equiv.), DMAc (1 mL), CO (10 bar), 60 °C, 20 h; Yields are determined by GC with hexadecane as an internal standard; n.d.: not detected.

Table S2. Screening of solvent

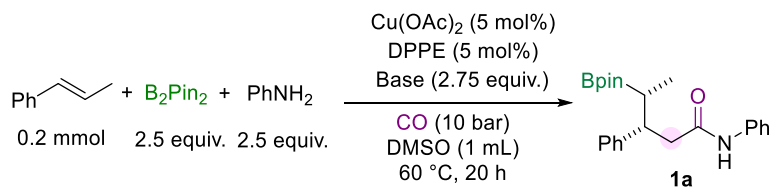
Entry	Solvent	1a (%)
1	DMF	21
2	DMSO	68
3	NMP	11
4	Toluene	n.d.
5	THF	33
6	CH_3CN	n.d.

Reaction conditions: *(E)*-prop-1-en-1-ylbenzene (0.2 mmol), CuI (5 mol%), $DPPE$ (5 mol%), NaO^tBu (2.5 equiv.), B_2Pin_2 (2.5 equiv.), $PhNH_2$ (2.5 equiv.), solvent (1 mL), CO (10 bar), $60\text{ }^\circ C$, 20 h; Yields are determined by GC with hexadecane as an internal standard; n.d.: not detected.

Table S3. Screening of copper catalyst

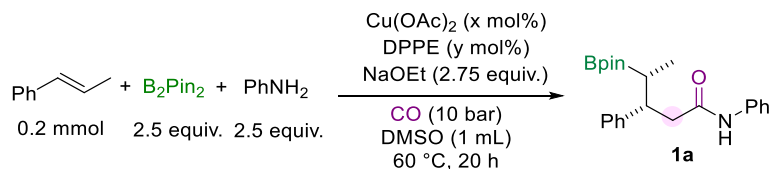
Entry	Solvent	1a (%)
1	$CuCl_2$	54
2	$Cu(OTf)_2$	13
3	$CuCN$	4
4	$CuSO_4$	n.d.
5	CuI	68
6	$CuBr_2$	10
7	$CuBr \cdot Me_2S$	Trace
8	$CuBr$	Trace
9	$Cu(OAc)_2$	69
10	$IPrCuCl$	Trace
11	$IPrCuCl$ (w/o $DPPE$)	Trace
12	$IMesCuCl$	6
13	$IMesCuCl$ (w/o $DPPE$)	Trace

Reaction conditions: *(E)*-prop-1-en-1-ylbenzene (0.2 mmol), $[Cu]$ (5 mol%), $DPPE$ (5 mol%), NaO^tBu (2.5 equiv.), B_2Pin_2 (2.5 equiv.), $PhNH_2$ (2.5 equiv.), $DMSO$ (1 mL), CO (10 bar), $60\text{ }^\circ C$, 20 h; Yields are determined by GC with hexadecane as an internal standard; n.d.: not detected.

Table S4. Screening of the base

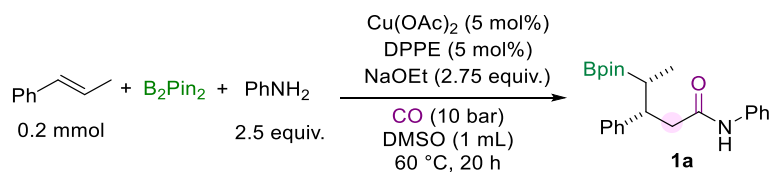
Entry	Base	1a (%)
1	NaO ^t Bu	69
2	LiO ^t Bu	41
3	KO ^t Bu	Trace
4	NaOEt	74
5	Cs ₂ CO ₃	11
6	LiOMe	Trace
7	KOMe	17

Reaction conditions: *(E)*-prop-1-en-1-ylbenzene (0.2 mmol), $Cu(OAc)_2$ (5 mol%), DPPE (5 mol%), base (2.5 equiv.), B_2Pin_2 (2.5 equiv.), $PhNH_2$ (2.5 equiv.), DMSO (1 mL), CO (10 bar), 60 °C, 20 h; Yields are determined by GC with hexadecane as an internal standard.

Table S5. Screening of the amount of catalytic system

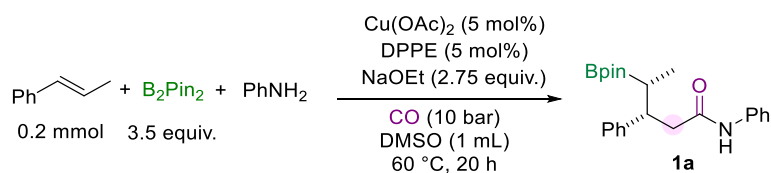
Entry	$Cu(OAc)_2$	DPPE	1a (%)
1	2.5 mol%	2.5 mol%	66
2	5 mol%	5 mol%	74
3	7.5 mol%	7.5 mol%	56
4	10 mol%	10 mol%	60
5	5 mol%	7.5 mol%	49
6	5 mol%	10 mol%	32

Reaction conditions: *(E)*-prop-1-en-1-ylbenzene (0.2 mmol), $Cu(OAc)_2$ (x mol%), DPPE (y mol%), NaOEt (2.5 equiv.), B_2Pin_2 (2.5 equiv.), $PhNH_2$ (2.5 equiv.), DMSO (1 mL), CO (10 bar), 60 °C, 20 h; Yields are determined by GC with hexadecane as an internal standard.

Table S6. Screening of the amount of B₂pin₂

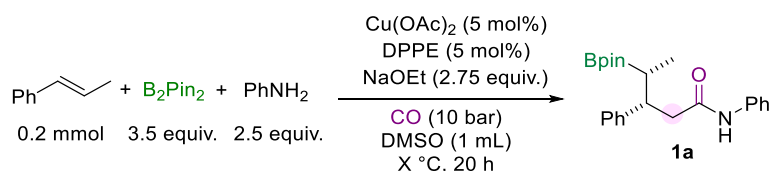
Entry	B ₂ pin ₂	1a (%)
1	3.0 eq.	71
2	3.5 eq.	79
3	3.75 eq.	73
4	4.0 eq.	68

Reaction conditions: (*E*)-prop-1-en-1-ylbenzene (0.2 mmol), Cu(OAc)₂ (5 mol%), DPPE (5 mol%), NaOEt (2.5 equiv.), B₂Pin₂ (x equiv.), PhNH₂ (2.5 equiv.), DMSO (1 mL), CO (10 bar), 60 °C, 20 h; Yields are determined by GC with hexadecane as an internal standard.

Table S7. Screening of the amount of PhNH₂

Entry	PhNH ₂	1a (%)
1	1.5 eq.	64
2	1.75 eq	70
3	2.0 eq.	75
4	2.5 eq.	79
5	2.75 eq.	74

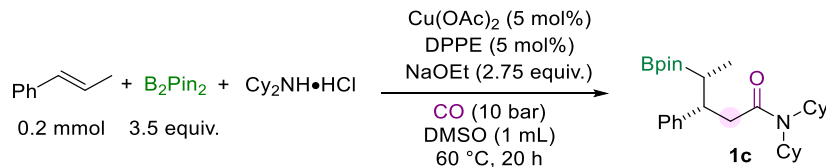
Reaction conditions: (*E*)-prop-1-en-1-ylbenzene (0.2 mmol), Cu(OAc)₂ (5 mol%), DPPE (5 mol%), NaOEt (2.5 equiv.), B₂Pin₂ (3.5 equiv.), PhNH₂ (x equiv.), DMSO (1 mL), CO (10 bar), 60 °C, 20 h; Yields are determined by GC with hexadecane as an internal standard.

Table S8. Screening of the temperature

Entry	Temperature	1a (%)
1	r.t.	38
2	80 °C	44
3	100 °C	25

Reaction conditions: (*E*)-prop-1-en-1-ylbenzene (0.2 mmol), Cu(OAc)₂ (5 mol%), DPPE (5 mol%), NaOEt (2.75 equiv.), B₂Pin₂ (3.5 equiv.), PhNH₂ (2.5 equiv.), DMSO (1 mL), CO (10 bar), x °C, 20 h; Yields are determined by GC with hexadecane as an internal standard.

Table S9. Optimization the reaction conditions for secondary amines.

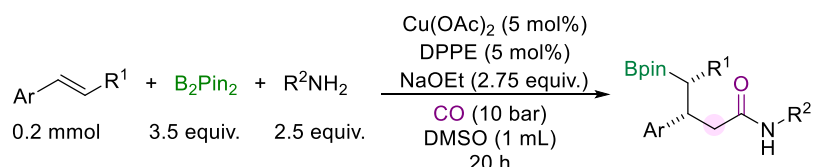


Entry	Deviation from the above conditions	1a (%)
1	Cy ₂ NH (2.5 equiv.)	19
2	Cy ₂ NH·HCl (2.5 equiv.)	46
3	Cy ₂ NH·HCl (2.0 equiv.)	59
4	Cy ₂ NH·HCl (1.5 equiv.)	65
5	Cy ₂ NH·HCl (1.0 equiv.)	47
6 ^b	Cy ₂ NH·HCl (1.5 equiv.)	71

Reaction conditions: (*E*)-prop-1-en-1-ylbenzene (0.2 mmol), Cu(OAc)₂ (5 mol%), DPPE (5 mol%), NaOEt (2.75 equiv.), B₂Pin₂ (3.5 equiv.), amines (x equiv.), DMSO (1 mL), CO (10 bar), 60 °C, 20 h; yields are determined by ¹H NMR spectra of the crude reaction mixture. [b] Cu(OAc)₂ (10 mol%), DPPE (10 mol%)

3. General procedure.

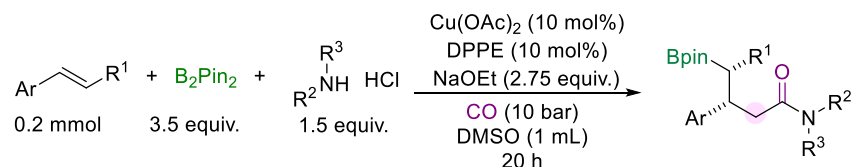
3.1 General procedure A for primary amines.



A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, internal aryl olefins (0.2 mmol), aryl amines or alkyl amines (2.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding products was afforded by directly purified by fast column chromatography. (For NMR yield: The

organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

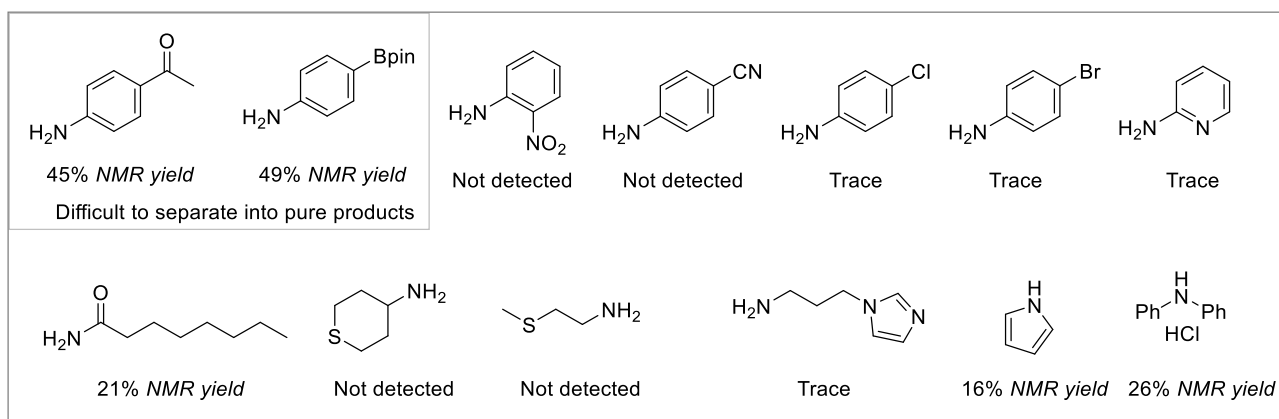
3.2 General procedure B for secondary amines-hydrochloride.



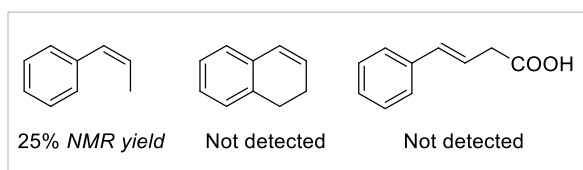
A dried vial (4 mL) was charged with Cu(OAc)₂ (10 mol%), DPPE (10 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, internal aryl olefins (0.2 mmol), secondary amines hydrochloride (1.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding products was afforded by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

3.3 Failed examples.

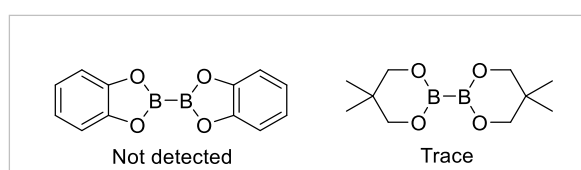
Failed examples of amines



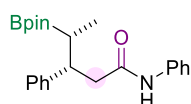
Failed examples of alkenes



Failed examples of boronate ester



4. Characterization Data.



***N*,3-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (1a)**

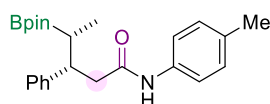
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (41 mg, 54%).

^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.16 (m, 7H), 7.10 – 6.91 (m, 2H), 3.16 (td, J = 10.2, 4.1 Hz, 1H), 2.80 (dd, J = 14.0, 4.1 Hz, 1H), 2.62 (dd, J = 14.0, 10.3 Hz, 1H), 1.53 – 1.40 (m, 1H), 1.29 (d, J = 1.6 Hz, 12H), 0.81 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 143.7, 137.8, 128.7, 128.6, 127.8, 126.6, 123.9, 119.7, 83.4, 45.7, 45.3, 24.9, 24.6, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 33.4.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{23}\text{H}_{30}^{11}\text{BNO}_3$ 402.2215, found: 402.2221.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*p*-tolyl)pentanamide (2a)

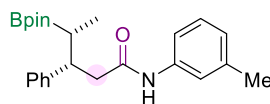
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and *p*-toluidine (2.5 equiv., 54 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (31 mg, 40%).

^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.21 (m, 5H), 7.17 – 7.00 (m, 4H), 6.93 (s, 1H), 3.17 (td, J = 10.2, 4.1 Hz, 1H), 2.81 (dd, J = 14.0, 4.1 Hz, 1H), 2.62 (dd, J = 14.0, 10.3 Hz, 1H), 2.28 (s, 3H), 1.52 – 1.43 (m, 1H), 1.31 (d, J = 1.2 Hz, 12H), 0.83 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.9, 143.7, 135.2, 133.5, 129.2, 128.6, 127.9, 126.6, 119.8, 83.4, 45.8, 45.3, 24.9, 24.7, 20.8, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 34.3

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{32}^{10}\text{BNO}_3$ 415.2404, found: 415.2404.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*m*-tolyl)pentanamide (3a)

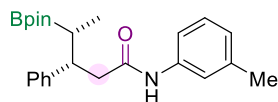
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and *m*-toluidine (2.5 equiv., 54 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (32 mg, 41%).

^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 (s, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.95 (d, J = 12.5 Hz, 2H), 6.84 (d, J = 7.4 Hz, 1H), 3.15 (td, J = 10.2, 4.1 Hz, 1H), 2.79 (dd, J = 14.0, 4.1 Hz, 1H), 2.60 (dd, J = 14.0, 10.3 Hz, 1H), 2.27 (s, 3H), 1.50 – 1.40 (m, 1H), 1.29 (d, J = 1.8 Hz, 12H), 0.81 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.9, 143.7, 138.7, 137.7, 128.6, 128.5, 127.9, 126.6, 124.7, 120.4, 116.7, 83.4, 45.7, 45.4, 24.9, 24.6, 21.4, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 32.9.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{32}^{10}\text{BNO}_3$ 415.2404, found: 415.2406.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(*o*-tolyl)pentanamide (4a)

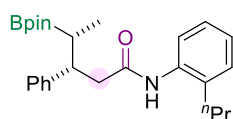
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and *o*-toluidine (2.5 equiv., 54 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (44 mg, 56%).

^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, J = 8.0 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.25 – 7.17 (m, 2H), 7.13 – 6.93 (m, 3H), 6.67 (s, 1H), 3.18 (td, J = 10.6, 3.9 Hz, 1H), 2.85 (dd, J = 14.1, 3.7 Hz, 1H), 2.73 – 2.62 (m, 1H), 1.82 (s, 3H), 1.42 (t, J = 8.5 Hz, 1H), 1.28 (d, J = 1.8 Hz, 12H), 0.80 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 143.5, 135.6, 130.2, 129.0, 128.7, 128.0, 126.7, 126.5, 124.9, 123.1, 83.4, 45.7, 45.0, 24.9, 24.6, 17.3, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.8.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{32}^{10}\text{BNO}_3$ 415.2404, found: 415.2408.



3-Phenyl-N-(2-propylphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (5a)

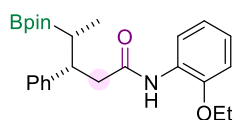
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-propylaniline (2.5 equiv., 68 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (35 mg, 41%).

^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, J = 7.8 Hz, 1H), 7.35 – 7.22 (m, 5H), 7.18 – 7.03 (m, 3H), 6.74 (s, 1H), 3.22 (td, J = 10.6, 3.7 Hz, 1H), 2.88 (dd, J = 14.0, 3.7 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.16 (dq, J = 15.8, 7.6 Hz, 2H), 1.43 (q, J = 7.4 Hz, 3H), 1.32 – 1.27 (m, 12H), 0.92 – 0.81 (m, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.1, 143.5, 135.0, 133.4, 129.2, 128.7, 127.9, 126.7, 126.4, 125.0, 123.8, 83.4, 45.6, 45.1, 32.8, 24.9, 24.6, 22.6, 13.9, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 34.2.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{26}\text{H}_{36}^{11}\text{BNO}_3$ 422.2866, found: 422.2866.



N-(2-Ethoxyphenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (6a)

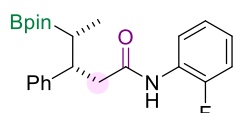
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-ethoxyaniline (2.5 equiv., 69 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (49 mg, 58%).

^1H NMR (300 MHz, CDCl_3) δ 8.24 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.54 (s, 1H), 7.25 (d, $J = 5.8$ Hz, 4H), 7.18 – 7.11 (m, 1H), 6.89 (dtd, $J = 24.2, 7.6, 1.6$ Hz, 2H), 6.77 (dd, $J = 8.0, 1.5$ Hz, 1H), 4.00 (q, $J = 7.0, 4.1$ Hz, 2H), 3.22 (td, $J = 10.1, 4.4$ Hz, 1H), 2.86 (dd, $J = 14.3, 4.4$ Hz, 1H), 2.66 (dd, $J = 14.4, 10.4$ Hz, 1H), 1.51 – 1.41 (m, 1H), 1.39 (t, $J = 7.0$ Hz, 3H), 1.26 (d, $J = 2.0$ Hz, 12H), 0.80 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.7, 146.9, 143.6, 137.0, 128.3, 127.9, 126.3, 123.2, 120.8, 119.8, 110.8, 83.3, 64.0, 45.2, 45.1, 25.0, 24.9, 24.6, 14.8, 13.8.

^{11}B NMR (96 MHz, CDCl_3) δ 30.1.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{25}\text{H}_{34}^{10}\text{BNO}_3$ 445.2509, found: 445.2511.



***N*-(2-Fluorophenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (7a)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-fluoroaniline (2.5 equiv., 55.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, $R_f = 0.2$) to give the product as a white solid (46 mg, 59%).

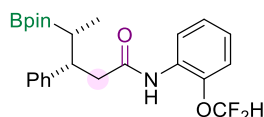
^1H NMR (400 MHz, CDCl_3) δ 8.20 (t, $J = 7.8$ Hz, 1H), 7.35 (s, 1H), 7.32 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 7.11 – 6.95 (m, 3H), 3.20 (td, $J = 10.1, 4.1$ Hz, 1H), 2.88 (dd, $J = 14.2, 4.1$ Hz, 1H), 2.70 (dd, $J = 14.2, 10.2$ Hz, 1H), 1.51 – 1.43 (m, 1H), 1.30 (d, $J = 2.3$ Hz, 12H), 0.83 (d, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 152.1 (d, $J = 243.0$ Hz), 143.4, 128.5, 127.7, 126.5, 126.4 (d, $J = 10.2$ Hz), 124.3 (d, $J = 3.6$ Hz), 123.8 (d, $J = 7.5$ Hz), 121.6, 114.5 (d, $J = 19.2$ Hz), 83.4, 45.6, 45.2, 24.8, 24.6, 14.0.

^{11}B NMR (128 MHz, CDCl_3) δ 35.3.

^{19}F NMR (282 MHz, CDCl_3) δ -131.2.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{23}\text{H}_{29}^{10}\text{BFNO}_3$ 397.2334, found: 397.2337.



***N*-(2-(Difluoromethoxy)phenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (8a)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-(difluoromethoxy)aniline (2.5 equiv., 32 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, $R_f = 0.2$) to give the product as a white solid (20 mg, 22%).

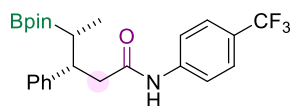
^1H NMR (300 MHz, CDCl_3) δ 8.15 (d, $J = 8.1$ Hz, 1H), 7.28 (s, 1H), 7.22 – 7.16 (m, 3H), 7.15 – 6.99 (m, 3H), 6.96 – 6.88 (m, 2H), 6.24 (t, $J = 73.6$ Hz, 1H), 3.11 (td, $J = 10.3, 4.2$ Hz, 1H), 2.80 (dd, $J = 14.2, 4.2$ Hz, 1H), 2.60 (dd, $J = 14.2, 10.5$ Hz, 1H), 1.39 – 1.30 (m, 1H), 1.20 (d, $J = 2.0$ Hz, 12H), 0.73 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.1, 143.3, 139.9, 129.9, 128.5, 127.8, 126.5, 126.0, 123.8, 121.6, 118.4, 116.2 (d, $J = 261.1$ Hz), 83.3, 45.4, 45.1, 25.0, 24.8, 24.6, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.2.

^{19}F NMR (282 MHz, CDCl_3) δ -79.75 (d, $J = 6.4$ Hz), -80.01 (d, $J = 6.1$ Hz).

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{30}^{11}\text{BF}_2\text{NO}_4$ 468.2132, found: 468.2128.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(trifluoromethyl)phenyl)pentanamide (9a)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 4-(trifluoromethyl)aniline (2.5 equiv., 80.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (47 mg, 53%).

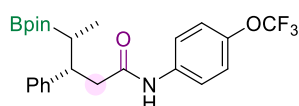
¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.12 (m, 5H), 7.06 (d, *J* = 8.2 Hz, 3H), 3.13 (td, *J* = 10.2, 4.0 Hz, 1H), 2.80 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.61 (dd, *J* = 14.0, 10.3 Hz, 1H), 1.52 – 1.39 (m, 1H), 1.29 (d, *J* = 1.6 Hz, 12H), 0.81 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.1, 143.6, 136.4, 128.7, 127.8, 126.7, 121.5, 120.8, 120.4 (q, *J* = 257.4 Hz), 83.5, 45.8, 45.3, 24.9, 24.6, 14.0.

¹¹B NMR (96 MHz, CDCl₃) δ 33.4.

¹⁹F NMR (282 MHz, CDCl₃) δ -58.2.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₄H₂₉¹⁰BF₃NO₃ 447.2302, found: 447.2293.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(trifluoromethoxy)phenyl)pentanamide (10a)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 4-(trifluoromethoxy)aniline (2.5 equiv., 88.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 7:1, R_f = 0.2) to give the product as a white solid (28 mg, 30%).

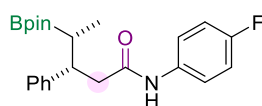
¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 5H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 3.13 (td, *J* = 10.3, 3.9 Hz, 1H), 2.80 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.61 (dd, *J* = 13.9, 10.3 Hz, 1H), 1.50 – 1.41 (m, 1H), 1.29 (d, *J* = 1.5 Hz, 12H), 0.81 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.1, 143.6, 136.5, 128.8, 127.9, 126.8, 121.6, 120.8, 120.4 (q, *J* = 256.8 Hz), 83.5, 45.8, 45.4, 24.9, 24.7, 14.1.

¹¹B NMR (96 MHz, CDCl₃) δ 34.6.

¹⁹F NMR (282 MHz, CDCl₃) δ -58.2.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₄H₂₉¹⁰BF₃NO₄ 463.2251, found: 463.2252.



N-(4-Fluorophenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (11a)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 4-fluoroaniline (2.5 equiv., 55.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (46 mg, 58%).

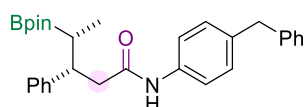
^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 7.19 – 7.10 (m, 2H), 7.02 – 6.83 (m, 3H), 3.14 (td, $J = 10.3, 4.1$ Hz, 1H), 2.79 (dd, $J = 13.9, 4.1$ Hz, 1H), 2.59 (dd, $J = 13.9, 10.4$ Hz, 1H), 1.50 – 1.40 (m, 1H), 1.28 (d, $J = 1.4$ Hz, 12H), 0.81 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 159.2 (d, $J = 243.6$ Hz), 143.6, 133.7 (d, $J = 2.3$ Hz), 128.7, 127.8, 126.7, 121.6 (d, $J = 7.8$ Hz), 115.4 (d, $J = 22.4$ Hz), 83.4, 45.8, 45.2, 24.9, 24.7, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 33.6.

^{19}F NMR (282 MHz, CDCl_3) δ -118.48 (tt, $J = 9.1, 5.1$ Hz).

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{23}\text{H}_{29}^{11}\text{BFNO}_3$ 398.2302, found: 398.2306.



***N*-(4-Benzylphenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (12a)**

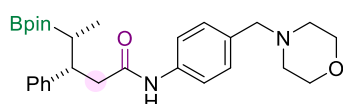
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 4-benzylaniline (2.5 equiv., 91.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, $R_f = 0.2$) to give the product as a white solid (50 mg, 49%).

^1H NMR (300 MHz, CDCl_3) δ 7.32 – 7.21 (m, 7H), 7.21 – 7.11 (m, 5H), 7.09 – 6.99 (m, 3H), 3.91 (s, 2H), 3.17 (td, $J = 10.1, 4.1$ Hz, 1H), 2.81 (dd, $J = 14.0, 4.1$ Hz, 1H), 2.62 (dd, $J = 14.0, 10.3$ Hz, 1H), 1.57 – 1.39 (m, 1H), 1.30 (d, $J = 1.4$ Hz, 12H), 0.83 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 143.7, 141.1, 136.8, 135.9, 129.2, 128.9, 128.7, 128.4, 127.9, 126.7, 126.0, 120.0, 83.5, 45.8, 45.3, 41.3, 24.9, 24.6, 14.0.

^{11}B NMR (128 MHz, CDCl_3) δ 33.3.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{30}\text{H}_{36}^{10}\text{BNO}_3$ 491.2717, found: 491.2720.



***N*-(4-(Morpholinomethyl)phenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (13a)**

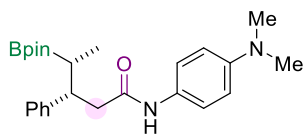
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 4-(morpholinomethyl)aniline (2.5 equiv., 96 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 1:1, $R_f = 0.2$) to give the product as a white solid (39 mg, 41%).

^1H NMR (300 MHz, CDCl_3) δ 7.37 – 7.27 (m, 2H), 7.26 – 7.04 (m, 7H), 7.00 (s, 1H), 3.79 – 3.66 (m, 4H), 3.45 (s, 2H), 3.14 (td, $J = 10.2, 4.1$ Hz, 1H), 2.79 (dd, $J = 14.0, 4.0$ Hz, 1H), 2.61 (d, $J = 3.7$ Hz, 1H), 2.51 – 2.33 (m, 4H), 1.45 (dd, $J = 10.1, 7.5$ Hz, 1H), 1.28 (d, $J = 1.7$ Hz, 12H), 0.80 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 143.7, 129.9, 128.7, 128.7, 127.9, 126.7, 119.6, 83.4, 66.6, 62.7, 53.3, 45.7, 45.3, 24.9, 24.7, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 35.1.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{28}\text{H}_{39}^{10}\text{BN}_2\text{O}_4$ 478.3112, found: 478.3108.



***N*-(4-(Dimethylamino)phenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (14a)**

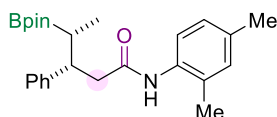
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and *N,N'*-dimethylbenzene-1,4-diamine (2.5 equiv., 68 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 1:1, R_f = 0.2) to give the product as a white solid (36 mg, 43%).

¹H NMR (300 MHz, CDCl₃) δ 7.32 – 7.16 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.00 – 6.40 (m, 3H), 3.15 (td, *J* = 10.2, 4.1 Hz, 1H), 2.85 (dd, *J* = 38.5, 12.4 Hz, 6H), 2.73 (s, 1H), 2.58 (dd, *J* = 13.8, 10.4 Hz, 1H), 1.45 (dd, *J* = 9.5, 6.9 Hz, 1H), 1.28 (d, *J* = 1.5 Hz, 12H), 0.81 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 169.8, 143.8, 128.6, 127.9, 126.6, 121.6, 83.4, 45.8, 45.1, 41.7, 24.9, 24.7, 14.0.

¹¹B NMR (96 MHz, CDCl₃) δ 34.0.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₅H₃₅¹⁰BN₂O₃ 422.2850, found: 422.2847.



***N*-(2,4-Dimethylphenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (15a)**

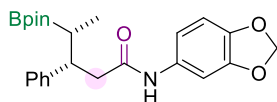
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 2,4-dimethylaniline (2.5 equiv., 60.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (36 mg, 44%).

¹H NMR (300 MHz, CDCl₃) δ 7.34 (s, 1H), 7.23 – 7.10 (m, 5H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.2 Hz, 1H), 6.56 (s, 1H), 3.11 (td, *J* = 10.6, 3.9 Hz, 1H), 2.77 (dd, *J* = 13.8, 3.9 Hz, 1H), 2.59 (dd, *J* = 13.9, 11.0 Hz, 1H), 2.17 (s, 3H), 1.70 (s, 3H), 1.25 (d, *J* = 7.8 Hz, 1H), 1.21 (d, *J* = 2.2 Hz, 12H), 0.73 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.0, 155.7, 143.6, 136.2, 135.4, 129.9, 128.7, 128.0, 126.7, 125.8, 125.6, 123.6, 83.4, 45.7, 45.1, 24.9, 24.6, 21.0, 16.8, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 34.1.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₅H₃₄¹⁰BNO₃ 407.2741, found: 407.2741.



***N*-(Benzo[*d*][1,3]dioxol-5-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (16a)**

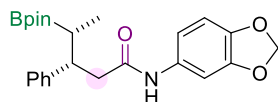
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and benzo[*d*][1,3]dioxol-5-amine (2.5 equiv., 68.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 6:1, R_f = 0.2) to give the product as a white solid (49 mg, 58%).

¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.22 (d, *J* = 6.9 Hz, 3H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.87 (s, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 6.44 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.88 (s, 2H), 3.13 (td, *J* = 10.3, 4.1 Hz, 1H), 2.77 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.56 (dd, *J* = 13.9, 10.4 Hz, 1H), 1.52 – 1.42 (m, 1H), 1.29 – 1.27 (m, 12H), 0.80 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.9, 147.5, 144.0, 143.7, 132.0, 128.6, 127.8, 126.7, 113.0, 107.8, 102.9, 101.1, 83.4, 45.8, 45.2, 24.9, 24.7, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 34.6.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{30}^{11}\text{BNO}_5$ 424.2294, found: 424.2294.



***N*-(2,2-Difluorobenzo[*d*][1,3]dioxol-5-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (17a)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2,2-difluorobenzo[*d*][1,3]dioxol-5-amine (2.5 equiv., 86.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 7:1, R_f = 0.2) to give the product as a white solid (36 mg, 40%).

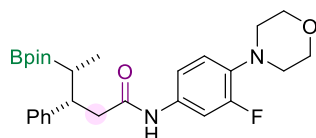
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 3H), 7.22 (td, J = 6.4, 1.7 Hz, 3H), 6.98 (s, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.59 (dd, J = 8.6, 2.1 Hz, 1H), 3.12 (td, J = 10.3, 4.0 Hz, 1H), 2.79 (dd, J = 13.9, 4.0 Hz, 1H), 2.59 (dd, J = 13.9, 10.4 Hz, 1H), 1.45 (dd, J = 10.2, 7.4 Hz, 1H), 1.29 (d, J = 2.3 Hz, 12H), 0.81 (d, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 143.7, 143.5, 139.9, 133.9, 131.7 (t, J = 231.5 Hz), 128.7, 127.8, 126.8, 114.4, 109.0, 103.1, 83.5, 45.9, 45.3, 24.9, 24.7, 14.0.

^{11}B NMR (128 MHz, CDCl_3) δ 35.4.

^{19}F NMR (282 MHz, CDCl_3) δ -50.0.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{24}\text{H}_{28}^{10}\text{BF}_2\text{NO}_5$ 481.1957, found: 481.1956.



***N*-(3-Fluoro-4-morpholinophenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (18a)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 3-fluoro-4-morpholinoaniline (2.5 equiv., 98 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.3) to give the product as a white solid (58 mg, 60%).

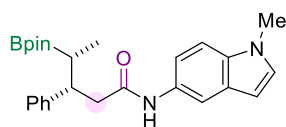
^1H NMR (300 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.11 (m, 4H), 7.02 (s, 1H), 6.88 – 6.62 (m, 2H), 3.89 – 3.80 (m, 4H), 3.13 (dt, J = 10.2, 5.1 Hz, 1H), 3.05 – 2.92 (m, 4H), 2.77 (dd, J = 14.0, 4.1 Hz, 1H), 2.58 (dd, J = 14.0, 10.3 Hz, 1H), 1.56 – 1.37 (m, 1H), 1.27 (d, J = 1.7 Hz, 12H), 0.80 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 155.3 (d, J = 245.7 Hz), 143.6, 135.7 (d, J = 16.6 Hz), 133.3 (d, J = 12.6 Hz), 128.6, 127.8, 126.7, 118.7 (d, J = 3.6 Hz), 115.5 (d, J = 3.3 Hz), 108.9 (d, J = 25.4 Hz), 83.4, 66.8, 51.1, 45.7, 45.2, 24.9, 24.6, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 33.9.

^{19}F NMR (282 MHz, CDCl_3) δ -121.2.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{27}\text{H}_{36}^{10}\text{BFN}_2\text{O}_4$ 504.2680, found: 504.2679.



***N*-(1-Methyl-1*H*-indol-5-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (19a)**

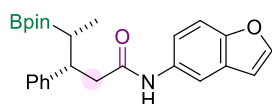
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 1-methyl-1*H*-indol-5-amine (2.5 equiv., 73 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 3:1, *R*_f = 0.2) to give the product as a white solid (42 mg, 49%).

¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.22 (m, 5H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.01 – 6.90 (m, 3H), 6.37 (dd, *J* = 3.1, 0.7 Hz, 1H), 3.71 (s, 3H), 3.21 (td, *J* = 10.2, 4.2 Hz, 1H), 2.83 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.62 (dd, *J* = 13.9, 10.4 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.30 (d, *J* = 1.3 Hz, 12H), 0.84 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 169.9, 143.9, 134.0, 130.1, 129.4, 128.5, 128.3, 127.9, 126.5, 115.8, 112.6, 109.0, 100.9, 83.3, 45.8, 45.2, 32.8, 24.9, 24.6, 14.0.

¹¹B NMR (96 MHz, CDCl₃) δ 32.9.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₆H₃₃¹¹BN₂O₃ 433.2662, found: 433.2670.



***N*-(Benzofuran-5-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (20a)**

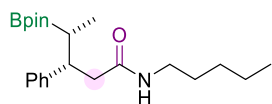
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and benzo[*d*][1,3]dioxol-5-amine (2.5 equiv., 68.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 6:1, *R*_f = 0.2) to give the product as a white solid (51 mg, 61%).

¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.20 (m, 3H), 7.10 (s, 1H), 6.89 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.66 (dd, *J* = 2.1, 0.8 Hz, 1H), 3.18 (td, *J* = 10.2, 4.2 Hz, 1H), 2.83 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.63 (dd, *J* = 13.9, 10.3 Hz, 1H), 1.50 – 1.42 (m, 1H), 1.30 – 1.27 (m, 12H), 0.82 (d, *J* = 7.5 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.1, 151.8, 145.6, 143.7, 132.9, 128.6, 127.9, 127.6, 126.6, 117.5, 113.0, 111.1, 106.7, 83.4, 45.8, 45.1, 24.9, 24.7, 14.0.

¹¹B NMR (96 MHz, CDCl₃) δ 33.0.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₅H₃₀¹¹BNO₃ 420.2345, found: 420.2343.



***N*-Pentyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (1b)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and pentan-1-amine (2.5 equiv., 39 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, *R*_f = 0.2) to give the product as a white solid (33 mg, 44%).

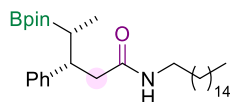
¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.26 (m, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.20 – 7.13 (m, 3H), 5.12 (s, 1H), 3.12 – 2.89 (m, 3H), 2.64 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.39 (dd, *J* = 13.9, 11.0 Hz, 1H), 1.41 – 1.33 (m, 1H), 1.26

(d, $J = 2.0$ Hz, 12H), 1.17 (ddd, $J = 9.4, 6.3, 2.6$ Hz, 4H), 1.01 (ddd, $J = 12.6, 7.5, 2.3$ Hz, 2H), 0.84 – 0.73 (m, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.6, 143.7, 128.4, 127.8, 126.4, 83.3, 45.6, 44.1, 39.2, 36.3, 29.0, 28.8, 24.8, 24.6, 22.2, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 34.2.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{22}\text{H}_{36}^{10}\text{BNO}_3$ 395.2717, found: 395.2721.



***N*-Hexadecyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2b)**

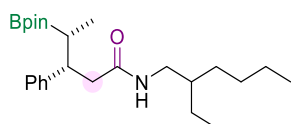
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and hexadecan-1-amine (2.5 equiv., 120 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, $R_f = 0.2$) to give the product as a white solid (60 mg, 57%).

^1H NMR (300 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.44 (s, 1H), 3.09 – 2.97 (m, 3H), 2.66 (dd, $J = 14.0, 4.6$ Hz, 1H), 2.44 (dd, $J = 14.0, 10.6$ Hz, 1H), 1.34 (d, $J = 7.5$ Hz, 1H), 1.29 – 1.18 (m, 40H), 0.90 – 0.85 (m, 3H), 0.77 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 172.0, 143.7, 128.4, 127.8, 126.4, 83.3, 45.5, 43.6, 39.5, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 26.7, 24.8, 24.7, 22.8, 22.7, 14.5, 14.1, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 32.8.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{33}\text{H}_{58}^{10}\text{BNO}_3$ 527.4619, found: 527.4622.



***N*-(2-Ethylhexyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (3b)**

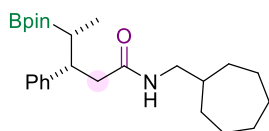
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-ethylhexan-1-amine (2.5 equiv., 129 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, $R_f = 0.2$) to give the product as a white solid (49 mg, 59%).

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 2H), 7.20 – 7.12 (m, 3H), 5.07 (s, 1H), 3.06 (td, $J = 10.5, 3.8$ Hz, 1H), 3.02 – 2.84 (m, 2H), 2.64 (dd, $J = 14.0, 4.0$ Hz, 1H), 2.44 (dd, $J = 14.0, 11.1$ Hz, 1H), 1.36 – 1.31 (m, 1H), 1.25 (d, $J = 3.3$ Hz, 12H), 1.19 (dd, $J = 8.1, 5.7$ Hz, 2H), 1.14 – 1.06 (m, 3H), 1.02 – 0.89 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H), 0.76 (d, $J = 7.4$ Hz, 3H), 0.71 (td, $J = 7.4, 2.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.7, 143.7, 128.5, 127.9, 126.5, 83.3, 45.5, 44.1, 41.9, 39.1, 30.7, 28.8, 24.9, 24.7, 23.9, 22.9, 14.1, 13.9, 10.8.

^{11}B NMR (128 MHz, CDCl_3) δ 33.3.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{25}\text{H}_{42}^{10}\text{BNO}_3$ 415.3367, found: 415.3372.



***N*-(Cycloheptylmethyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4b)**

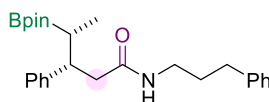
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and cycloheptylmethanamine (2.5 equiv., 63.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (48 mg, 58%).

¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 7.20 – 7.11 (m, 3H), 5.31 (s, 1H), 3.06 (td, *J* = 10.6, 4.1 Hz, 1H), 2.91 (dt, *J* = 12.8, 6.3 Hz, 1H), 2.79 (dt, *J* = 13.1, 5.9 Hz, 1H), 2.65 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.43 (dd, *J* = 13.9, 11.1 Hz, 2H), 1.60 – 1.41 (m, 5H), 1.35 (ddt, *J* = 19.0, 6.3, 2.8 Hz, 6H), 1.26 – 1.24 (m, 12H), 0.92 – 0.82 (m, 2H), 0.76 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.8, 143.6, 128.4, 127.9, 126.4, 83.3, 45.9, 45.5, 44.0, 39.3, 31.9, 31.8, 28.2, 28.1, 26.3, 26.2, 24.9, 24.7, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.1.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₅H₄₀¹⁰BNO₃ 413.3210, found: 413.3210.



3-Phenyl-*N*-(3-phenylpropyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (5b)

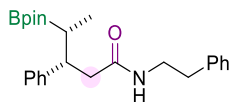
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 3-phenylpropan-1-amine (2.5 equiv., 67.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (55 mg, 65%).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.22 (m, 4H), 7.21 – 7.12 (m, 4H), 7.10 – 6.96 (m, 2H), 5.13 (t, *J* = 5.1 Hz, 1H), 3.21 – 2.89 (m, 3H), 2.64 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.54 – 2.19 (m, 3H), 1.51 (p, *J* = 7.2 Hz, 2H), 1.40 – 1.36 (m, 1H), 1.26 (d, *J* = 2.2 Hz, 12H), 0.77 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.6, 143.7, 141.4, 128.4, 128.3, 127.9, 126.4, 125.8, 83.2, 45.5, 44.1, 38.7, 32.8, 30.9, 24.8, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.0.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₆H₃₆¹¹BNO₃ 422.2866, found: 422.2870.



***N*-Phenethyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (6b)**

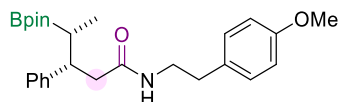
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 2-phenylethan-1-amine (2.5 equiv., 60.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (42 mg, 52%).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.19 (m, 5H), 7.16 (ddd, *J* = 7.8, 4.2, 1.7 Hz, 3H), 7.06 – 6.84 (m, 2H), 5.24 (s, 1H), 3.37 (dq, *J* = 13.5, 6.4 Hz, 1H), 3.28 – 2.96 (m, 2H), 2.63 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.58 – 2.30 (m, 3H), 1.38 – 1.32 (m, 1H), 1.25 (d, *J* = 2.2 Hz, 12H), 0.76 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.7, 143.7, 138.9, 128.6, 128.5, 128.4, 127.9, 126.4, 126.3, 83.2, 45.4, 44.0, 40.4, 35.5, 24.8, 24.6, 13.8.

^{11}B NMR (96 MHz, CDCl_3) δ 33.3.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{25}\text{H}_{34}^{11}\text{BNO}_3$ 430.2528, found: 430.2529.



***N*-(4-Methoxyphenethyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (7b)**

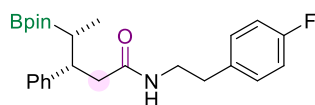
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-(4-methoxyphenyl)ethan-1-amine (2.5 equiv., 75.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 4:1, R_f = 0.2) to give the product as a white solid (48 mg, 55%).

^1H NMR (300 MHz, CDCl_3) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 6.92 – 6.85 (m, 2H), 6.83 – 6.74 (m, 2H), 5.29 (s, 1H), 3.80 (s, 3H), 3.35 (dq, J = 13.4, 6.4 Hz, 1H), 3.23 – 3.05 (m, 2H), 2.64 (dd, J = 13.9, 4.2 Hz, 1H), 2.54 – 2.35 (m, 3H), 1.40 – 1.32 (m, 1H), 1.27 (d, J = 2.3 Hz, 12H), 0.78 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.6, 158.1, 143.7, 130.9, 129.5, 128.3, 127.8, 126.3, 113.8, 83.2, 55.2, 45.3, 43.9, 40.5, 34.5, 24.8, 24.6, 13.8.

^{11}B NMR (96 MHz, CDCl_3) δ 32.7.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{26}\text{H}_{36}^{11}\text{BNO}_4$ 460.2634, found: 460.2635.



***N*-(4-Fluorophenethyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (8b)**

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-(4-fluorophenyl)ethan-1-amine (2.5 equiv., 69.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (36 mg, 42%).

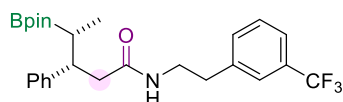
^1H NMR (300 MHz, CDCl_3) δ 7.30 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 6.97 – 6.85 (m, 4H), 5.34 (s, 1H), 3.35 (dq, J = 13.4, 6.4 Hz, 1H), 3.22 – 3.02 (m, 2H), 2.66 – 2.30 (m, 4H), 1.34 (d, J = 4.1 Hz, 1H), 1.25 (d, J = 2.2 Hz, 12H), 0.75 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.9, 161.5 (d, J = 244.4 Hz), 143.7, 134.5 (d, J = 3.4 Hz), 130.1 (d, J = 7.8 Hz), 128.4, 127.9, 126.5, 115.27 (d, J = 21.1 Hz), 83.3, 45.4, 43.8, 40.6, 34.7, 24.9, 24.7, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 32.8.

^{19}F NMR (282 MHz, CDCl_3) δ -116.89 (p, J = 7.0 Hz).

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{25}\text{H}_{33}^{11}\text{BFNO}_3$ 448.2434, found: 448.2434.



3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(3-(trifluoromethyl)phenethyl)pentanamide (9b)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 2-(3-(trifluoromethyl)phenyl)ethan-1-amine (2.5 equiv., 94.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (44 mg, 46%).

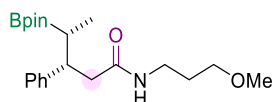
¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.20 – 7.10 (m, 4H), 5.36 (s, 1H), 3.36 (dt, *J* = 13.7, 6.9 Hz, 1H), 3.20 (td, *J* = 13.0, 7.2 Hz, 1H), 3.05 (td, *J* = 10.5, 4.2 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.49 (dt, *J* = 14.1, 7.4 Hz, 1H), 2.38 (dd, *J* = 14.0, 10.8 Hz, 1H), 1.35 – 1.32 (m, 1H), 1.25 (d, *J* = 1.9 Hz, 12H), 0.76 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.9, 143.6, 139.9, 132.1, 130.8 (q, *J* = 31.5 Hz), 128.9, 128.4, 127.8, 126.4, 125.3 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 3.7 Hz), 119.8 (q, *J* = 251.0 Hz), 83.3, 45.5, 43.8, 40.2, 35.3, 24.8, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 32.9.

¹⁹F NMR (282 MHz, CDCl₃) δ -62.5.

HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₆H₃₃¹¹BF₃NO₃ 498.2402, found: 498.2405.



N-(3-Methoxypropyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (10b)

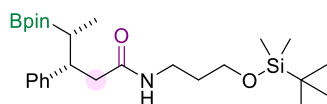
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 3-methoxypropan-1-amine (2.5 equiv., 44.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 1:1, R_f = 0.2) to give the product as a white solid (40 mg, 53%).

¹H NMR (300 MHz, CDCl₃) δ 7.23 – 7.16 (m, 2H), 7.15 – 7.02 (m, 3H), 5.48 (s, 1H), 3.17 (s, 3H), 3.15 – 2.94 (m, 5H), 2.57 (dd, *J* = 13.8, 4.3 Hz, 1H), 2.31 (dd, *J* = 13.6, 10.7 Hz, 1H), 1.43 – 1.25 (m, 3H), 1.19 (d, *J* = 2.7 Hz, 12H), 0.70 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.5, 143.7, 128.3, 127.8, 126.3, 83.2, 70.9, 58.5, 45.4, 43.9, 37.2, 28.9, 24.8, 24.6, 24.5, 13.8.

¹¹B NMR (96 MHz, CDCl₃) δ 33.5.

HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₁H₃₄¹¹BNO₄ 398.2477, found: 398.2478.



N-(3-((*tert*-Butyldimethylsilyloxy)propyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (11b)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and 3-((*tert*-butyldimethylsilyloxy)propyl)propan-1-amine (2.5 equiv., 94.5 mg), according to general procedure. The crude residue

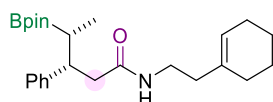
was purified by flash chromatography (*n*-pentane/EA = 4:1, R_f = 0.2) to give the product as a white solid (52 mg, 54%).

¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, *J* = 2.3 Hz, 2H), 7.20 – 7.14 (m, 3H), 5.59 (s, 1H), 3.53 – 3.38 (m, 2H), 3.18 – 3.01 (m, 3H), 2.64 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.34 (dd, *J* = 13.8, 10.8 Hz, 1H), 1.48 – 1.33 (m, 3H), 1.26 (d, *J* = 1.9 Hz, 12H), 0.88 (s, 9H), 0.78 (d, *J* = 7.4 Hz, 3H), 0.02 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 171.4, 143.8, 128.3, 127.9, 126.2, 83.2, 61.6, 45.4, 44.0, 37.3, 31.6, 25.9, 24.8, 24.6, 18.2, 13.9, -5.4.

¹¹B NMR (96 MHz, CDCl₃) δ 33.7.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₆H₄₆¹¹BNO₄Si 476.3367, found: 476.3370.



***N*-(2-(Cyclohex-1-en-1-yl)ethyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (12b)**

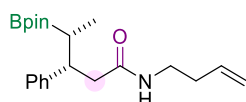
The title compound was prepared from *trans*-β-methylstyrene (0.2 mmol, 26 μL) and 2-(cyclohex-1-en-1-yl)ethan-1-amine (2.5 equiv., 62.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (52 mg, 63%).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.24 (m, 2H), 7.16 (ddd, *J* = 8.2, 4.8, 1.7 Hz, 3H), 5.39 – 4.86 (m, 2H), 3.07 (dq, *J* = 10.0, 5.3 Hz, 3H), 2.64 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.39 (dd, *J* = 13.9, 10.7 Hz, 1H), 1.93 (d, *J* = 1.8 Hz, 2H), 1.88 – 1.67 (m, 4H), 1.52 (tdd, *J* = 7.8, 6.2, 3.3 Hz, 4H), 1.40 – 1.33 (m, 1H), 1.25 (d, *J* = 2.2 Hz, 12H), 0.76 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.6, 143.7, 134.5, 128.3, 127.8, 126.4, 123.1, 83.2, 45.4, 43.9, 37.2, 36.9, 27.7, 25.1, 24.8, 24.7, 22.7, 22.3, 13.8.

¹¹B NMR (96 MHz, CDCl₃) δ 33.3.

HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₅H₃₈¹¹BNO₃ 434.2841, found: 434.2838.



***N*-(But-3-en-1-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (13b)**

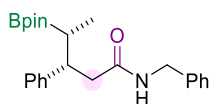
The title compound was prepared from *trans*-β-methylstyrene (0.2 mmol, 26 μL) and but-3-en-1-amine (2.5 equiv., 30.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (44 mg, 61%).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.24 (m, 2H), 7.17 (ddq, *J* = 6.8, 3.1, 1.8 Hz, 3H), 5.52 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.30 (s, 1H), 5.01 – 4.77 (m, 2H), 3.17 – 3.00 (m, 3H), 2.65 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.40 (dd, *J* = 13.9, 10.7 Hz, 1H), 2.05 – 1.85 (m, 2H), 1.39 – 1.32 (m, 1H), 1.26 (d, *J* = 1.9 Hz, 12H), 0.77 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.8, 143.7, 135.1, 128.4, 127.9, 126.4, 116.9, 83.3, 45.5, 43.8, 38.3, 33.4, 24.8, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.3.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₁H₃₂¹⁰BNO₃ 357.2585, found: 357.2593.



***N*-Benzyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (14b)**

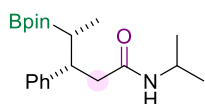
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and phenylmethanamine (2.5 equiv., 53.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (30 mg, 38%).

¹H NMR (300 MHz, CDCl₃) δ 7.22 – 7.14 (m, 3H), 7.11 (ddt, *J* = 4.4, 2.2, 1.1 Hz, 5H), 6.93 – 6.57 (m, 2H), 5.42 (d, *J* = 5.1 Hz, 1H), 4.24 (dd, *J* = 14.9, 6.2 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.06 (td, *J* = 10.8, 4.1 Hz, 1H), 2.65 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.37 (dd, *J* = 13.9, 11.1 Hz, 1H), 1.32 – 1.26 (m, 1H), 1.18 (d, *J* = 1.7 Hz, 12H), 0.71 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.5, 143.6, 138.1, 128.4, 128.4, 127.9, 127.4, 127.1, 126.4, 83.2, 45.5, 44.0, 43.2, 24.8, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.2.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₄H₃₂¹⁰BNO₃ 393.2585, found: 393.2588.



***N*-Isopropyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (15b)**

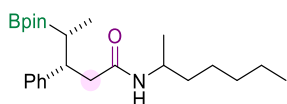
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and propan-2-amine (2.5 equiv., 29.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (38 mg, 55%).

¹H NMR (300 MHz, CDCl₃) δ 7.30 – 7.26 (m, 1H), 7.24 (s, 1H), 7.21 – 7.14 (m, 3H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.92 – 3.71 (m, 1H), 3.04 (td, *J* = 10.6, 4.4 Hz, 1H), 2.62 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.36 – 2.32 (m, 1H), 1.42 – 1.33 (m, 1H), 1.27 (d, *J* = 1.3 Hz, 12H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.80 – 0.73 (m, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 171.0, 143.7, 128.4, 127.9, 126.4, 83.3, 45.8, 44.2, 41.0, 24.8, 24.6, 22.4, 22.3, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.6.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₀H₃₂¹¹BNO₃ 346.2552, found: 346.2555.



***N*-(Heptan-2-yl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (16b)**

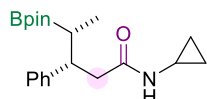
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and heptan-2-amine (2.5 equiv., 57.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (51 mg, 64%).

¹H NMR (300 MHz, CDCl₃) δ 7.23 – 7.17 (m, 2H), 7.14 – 7.08 (m, 3H), 4.94 (d, *J* = 8.8 Hz, 1H), 3.72 – 3.57 (m, 1H), 2.97 (td, *J* = 10.8, 4.2 Hz, 1H), 2.58 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.32 (dd, *J* = 13.8, 11.1 Hz, 1H), 1.37 – 1.27 (m, 1H), 1.20 (d, *J* = 1.6 Hz, 12H), 1.16 – 0.96 (m, 8H), 0.77 (t, *J* = 7.0 Hz, 3H), 0.71 (d, *J* = 7.4 Hz, 3H), 0.65 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.1, 143.6, 128.4, 127.9, 126.4, 83.3, 45.7, 44.9, 44.1, 36.6, 31.6, 25.4, 24.8, 24.7, 22.5, 20.5, 14.0, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.1.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{40}^{10}\text{BNO}_3$ 401.3210, found: 401.3219.



***N*-Cyclopropyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (17b)**

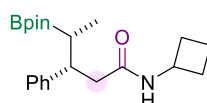
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and cyclopropanamine (2.5 equiv., 28.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (28 mg, 41%).

^1H NMR (300 MHz, CDCl_3) δ 7.28 – 7.26 (m, 1H), 7.23 (q, J = 1.4 Hz, 1H), 7.20 – 7.12 (m, 3H), 5.21 (s, 1H), 3.03 (td, J = 10.6, 4.2 Hz, 1H), 2.60 (dd, J = 13.7, 4.3 Hz, 1H), 2.43 (tq, J = 7.0, 3.8 Hz, 1H), 2.31 (dd, J = 13.7, 11.0 Hz, 1H), 1.47 – 1.34 (m, 1H), 1.25 (d, J = 1.6 Hz, 12H), 0.76 (d, J = 7.4 Hz, 3H), 0.62 – 0.49 (m, 2H), 0.19 – -0.09 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 173.1, 143.7, 128.3, 127.8, 126.4, 83.3, 45.7, 44.0, 24.8, 24.6, 22.1, 13.9, 6.5, 6.3.

^{11}B NMR (96 MHz, CDCl_3) δ 33.3.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{20}\text{H}_{30}^{10}\text{BNO}_3$ 365.2247, found: 365.2255.



***N*-Cyclobutyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (18b)**

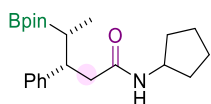
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and cyclobutanamine (2.5 equiv., 35.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (35 mg, 49%).

^1H NMR (300 MHz, CDCl_3) δ 7.28 (dt, J = 7.2, 1.2 Hz, 1H), 7.25 (d, J = 0.7 Hz, 1H), 7.21 – 7.09 (m, 3H), 5.23 (d, J = 6.9 Hz, 1H), 4.15 (h, J = 7.9 Hz, 1H), 3.03 (td, J = 10.5, 4.2 Hz, 1H), 2.59 (dd, J = 13.7, 4.3 Hz, 1H), 2.33 (dd, J = 13.7, 10.8 Hz, 1H), 2.09 (dddd, J = 17.3, 6.2, 4.6, 2.8 Hz, 2H), 1.53 (dt, J = 5.0, 3.2 Hz, 2H), 1.46 – 1.28 (m, 3H), 1.26 (d, J = 1.6 Hz, 12H), 0.77 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 143.8, 128.4, 127.9, 126.4, 83.3, 45.7, 44.3, 44.1, 31.0, 30.8, 24.8, 24.6, 14.9, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.2.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{21}\text{H}_{32}^{10}\text{BNO}_3$ 357.2585, found: 357.2585.



***N*-Cyclopentyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (19b)**

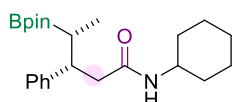
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and cyclopentanamine (2.5 equiv., 42.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (34 mg, 47%).

¹H NMR (300 MHz, CDCl₃) δ 7.28 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.21 – 7.12 (m, 3H), 5.05 (d, *J* = 7.0 Hz, 1H), 3.97 (h, *J* = 7.1 Hz, 1H), 3.03 (td, *J* = 10.7, 4.2 Hz, 1H), 2.61 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.35 (dd, *J* = 13.7, 11.0 Hz, 1H), 1.80 – 1.59 (m, 2H), 1.41 (dtdd, *J* = 11.9, 8.2, 4.1, 2.2 Hz, 5H), 1.26 (d, *J* = 1.6 Hz, 12H), 1.06 (dd, *J* = 13.3, 7.2 Hz, 1H), 0.92 – 0.85 (m, 1H), 0.77 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.2, 143.7, 128.4, 127.9, 126.4, 83.3, 50.7, 45.8, 44.2, 32.8, 32.7, 24.8, 24.6, 23.5, 23.4, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.5.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₂H₃₄¹⁰BNO₃ 371.2741, found: 371.2750.



***N*-Cyclohexyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (20b)**

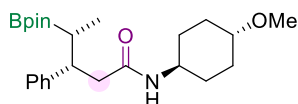
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and cyclohexanamine (2.5 equiv., 50.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, R_f = 0.2) to give the product as a white solid (42 mg, 55%).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 4.99 (d, *J* = 8.1 Hz, 1H), 3.64 – 3.45 (m, 1H), 3.03 (td, *J* = 10.7, 4.2 Hz, 1H), 2.60 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.34 (dd, *J* = 13.7, 11.0 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.48 (dt, *J* = 9.6, 7.3, 3.5 Hz, 4H), 1.26 (d, *J* = 1.8 Hz, 12H), 1.18 – 0.81 (m, 4H), 0.77 (d, *J* = 7.4 Hz, 3H), 0.72 – 0.60 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 170.6, 143.7, 128.3, 127.9, 126.3, 83.2, 47.5, 45.7, 44.3, 32.8, 32.7, 25.4, 24.8, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 34.4.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₃H₃₆¹¹BNO₃ 386.2865, found: 386.2870.



***N*-((1*r*,4*r*)-4-Methoxycyclohexyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (21b)**

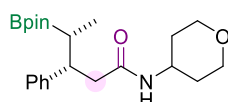
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and (1*r*,4*r*)-4-methoxycyclohexan-1-amine (2.5 equiv., 64.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 2:1, R_f = 0.2) to give the product as a white solid (31 mg, 37%).

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 2H), 7.17 (td, $J = 6.7, 1.4$ Hz, 3H), 4.94 (d, $J = 8.1$ Hz, 1H), 3.53 (dtt, $J = 15.1, 8.0, 4.0$ Hz, 1H), 3.27 (s, 3H), 3.08 – 2.95 (m, 2H), 2.61 (dd, $J = 13.7, 4.1$ Hz, 1H), 2.34 (dd, $J = 13.7, 11.1$ Hz, 1H), 1.91 – 1.73 (m, 3H), 1.59 – 1.51 (m, 1H), 1.35 (ddd, $J = 12.1, 7.4, 3.7$ Hz, 1H), 1.26 (d, $J = 2.9$ Hz, 12H), 1.21 – 1.07 (m, 2H), 0.94 – 0.86 (m, 1H), 0.77 (d, $J = 7.4$ Hz, 3H), 0.74 – 0.64 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.0, 143.6, 128.4, 127.9, 126.4, 83.3, 78.1, 55.7, 47.2, 45.8, 44.3, 30.3, 30.1, 29.9, 29.8, 24.8, 24.6, 13.9.

^{11}B NMR (128 MHz, CDCl_3) δ 35.7.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+ \text{C}_{24}\text{H}_{38}^{11}\text{BNO}_4$ 438.2790, found: 438.2794.



3-Phenyl-N-(tetrahydro-2H-pyran-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (22b)

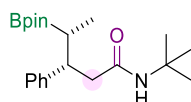
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and tetrahydro-2H-pyran-4-amine (2.5 equiv., 50.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 1:1, $R_f = 0.3$) to give the product as a white solid (40 mg, 52%).

^1H NMR (300 MHz, CDCl_3) δ 7.42 – 7.00 (m, 5H), 5.06 (d, $J = 8.0$ Hz, 1H), 3.74 (ddq, $J = 16.9, 11.2, 3.5$ Hz, 3H), 3.32 (tdd, $J = 11.8, 9.5, 2.4$ Hz, 2H), 3.03 (td, $J = 10.7, 4.1$ Hz, 1H), 2.63 (dd, $J = 13.6, 4.2$ Hz, 1H), 2.36 (dd, $J = 13.6, 11.1$ Hz, 1H), 1.64 (ddq, $J = 11.6, 4.6, 2.5$ Hz, 1H), 1.40 (dddd, $J = 21.0, 10.8, 5.2, 2.8$ Hz, 2H), 1.26 (d, $J = 1.8$ Hz, 12H), 1.20 – 1.10 (m, 1H), 1.04 – 0.93 (m, 1H), 0.77 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.0, 143.5, 128.4, 127.9, 126.5, 83.3, 66.5, 45.8, 45.0, 44.2, 32.7, 32.6, 24.8, 24.6, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.5.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{22}\text{H}_{34}^{10}\text{BNO}_4$ 387.2690, found: 387.2693.



N-(tert-Butyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (23b)

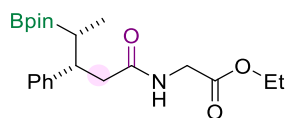
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and 2-methylpropan-2-amine (2.5 equiv., 36.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, $R_f = 0.3$) to give the product as a white solid (36 mg, 50%).

^1H NMR (300 MHz, CDCl_3) δ 7.24 – 7.18 (m, 2H), 7.15 – 7.07 (m, 3H), 4.77 (s, 1H), 2.94 (td, $J = 10.9, 4.1$ Hz, 1H), 2.49 (dd, $J = 13.4, 4.1$ Hz, 1H), 2.21 (dd, $J = 13.4, 11.3$ Hz, 1H), 1.33 – 1.24 (m, 1H), 1.20 (s, 12H), 0.97 (s, 9H), 0.70 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.1, 143.8, 128.3, 128.0, 126.3, 83.2, 50.6, 46.1, 45.3, 28.4, 24.8, 24.6, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.7.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+ \text{C}_{21}\text{H}_{34}^{11}\text{BNO}_3$ 360.2708, found: 360.2709.



Ethyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoyl glycinate (24b)

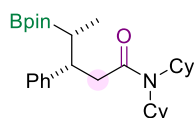
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and ethyl glycinate hydrogen chloride (1.5 equiv., 41.7 mg), according to general procedure B. The crude residue was purified by flash chromatography (*n*-pentane/EA = 4:1, R_f = 0.3) to give the product as a white solid (29 mg, 37%).

¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 5.75 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.97 – 3.67 (m, 2H), 3.12 (td, *J* = 10.2, 4.2 Hz, 1H), 2.71 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.52 (dd, *J* = 14.2, 10.5 Hz, 1H), 1.42 – 1.33 (m, 1H), 1.26 (d, *J* = 2.3 Hz, 12H), 1.24 (t, *J* = 2.1 Hz, 3H), 0.78 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.7, 169.9, 143.7, 128.3, 127.8, 126.4, 83.3, 61.3, 45.2, 43.4, 41.3, 24.9, 24.6, 14.1, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.9.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₁H₃₂¹¹BNO₅ 390.2450, found: 390.2451.



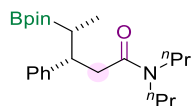
N,N-Dicyclohexyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (1c)

The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and dicyclohexylamine hydrochloride (1.5 equiv., 65 mg), according to general procedure B. The crude residue was purified by flash chromatography (*n*-pentane/EA = 7:1, R_f = 0.3) to give the product as a white solid (55 mg, 59%).

¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.15 (m, 5H), 3.39 (t, *J* = 10.5 Hz, 1H), 3.15 (td, *J* = 9.8, 5.4 Hz, 1H), 2.80 – 2.46 (m, 3H), 2.31 – 2.24 (m, 1H), 1.90 – 1.30 (m, 12H), 1.28 (s, 12H), 1.22 – 1.00 (m, 8H), 0.79 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 171.1, 144.0, 128.2, 128.0, 125.9, 82.9, 58.0, 56.0, 45.6, 41.3, 31.5, 30.9, 29.9, 29.8, 26.6, 26.6, 25.9, 25.2, 24.9, 24.7, 14.1.

¹¹B NMR (96 MHz, CDCl₃) δ 32.5.



3-Phenyl-*N,N*-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2c)

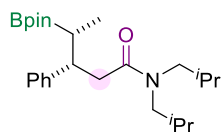
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μ L) and dipropylamine hydrochloride (1.5 equiv., 41 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 7:1, R_f = 0.3) to give the product as a white solid (45 mg, 58%).

¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.20 (m, 1H), 7.18 – 7.11 (m, 4H), 3.28 – 3.05 (m, 2H), 2.94 (qt, *J* = 14.9, 8.5 Hz, 3H), 2.74 – 2.48 (m, 2H), 1.44 – 1.21 (m, 5H), 1.20 (s, 12H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.69 (dd, *J* = 13.2, 7.4 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 171.7, 144.3, 128.1, 128.1, 126.1, 83.0, 49.7, 47.8, 45.1, 39.2, 24.9, 24.8, 22.1, 20.7, 14.1, 11.2.

^{11}B NMR (96 MHz, CDCl_3) δ 31.4.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{23}\text{H}_{38}^{11}\text{BNO}_3$ 388.3022, found: 388.3028.



***N,N*-Diisobutyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (3c)**

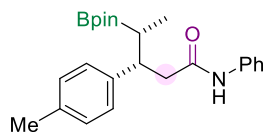
The title compound was prepared from *trans*- β -methylstyrene (0.2 mmol, 26 μL) and diisobutylamine hydrochloride (1.5 equiv., 49.5 mg), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 7:1, R_f = 0.3) to give the product as a white solid (51 mg, 61%).

^1H NMR (300 MHz, CDCl_3) δ 7.24 – 7.16 (m, 4H), 7.11 (ddd, J = 8.5, 5.3, 2.1 Hz, 1H), 3.39 – 3.14 (m, 2H), 3.04 (dd, J = 14.6, 7.3 Hz, 1H), 2.87 – 2.68 (m, 3H), 2.58 (dd, J = 14.6, 4.6 Hz, 1H), 1.76 (dhept, J = 27.5, 6.9 Hz, 2H), 1.36 (d, J = 3.7 Hz, 1H), 1.24 (s, 12H), 0.84 (dd, J = 6.7, 1.7 Hz, 6H), 0.77 (d, J = 7.4 Hz, 3H), 0.60 (dd, J = 6.7, 1.4 Hz, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ 172.0, 144.3, 128.0, 128.0, 125.9, 82.9, 55.8, 53.5, 45.2, 39.3, 28.0, 26.4, 24.9, 24.7, 20.0, 19.9, 14.1.

^{11}B NMR (96 MHz, CDCl_3) δ 32.6.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{25}\text{H}_{42}^{11}\text{BNO}_3$ 416.3335, found: 416.3335.



***N*-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)pentanamide (1d)**

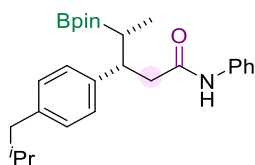
The title compound was prepared from (*E*)-1-methyl-4-(prop-1-en-1-yl)benzene (0.2 mmol, 26.4 mg) and aniline (2.5 equiv., 45 μL), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (37 mg, 47%).

^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.20 (m, 4H), 7.11 (s, 5H), 7.05 – 7.00 (m, 1H), 3.11 (td, J = 10.2, 4.1 Hz, 1H), 2.77 (dd, J = 14.1, 4.1 Hz, 1H), 2.61 (dd, J = 14.1, 10.2 Hz, 1H), 2.31 (s, 3H), 1.46 – 1.39 (m, 1H), 1.29 (d, J = 2.3 Hz, 12H), 0.80 (d, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.2, 140.5, 137.9, 136.1, 129.3, 128.7, 127.7, 123.9, 119.7, 83.4, 45.3, 45.3, 24.9, 24.6, 21.0, 14.0.

^{11}B NMR (128 MHz, CDCl_3) δ 33.4.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{32}^{11}\text{BNO}_3$ 394.2552, found: 394.2560.



3-(4-Isobutylphenyl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2d)

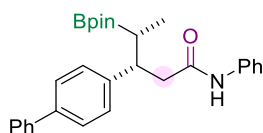
The title compound was prepared from (*E*)-1-isobutyl-4-(prop-1-en-1-yl)benzene (0.2 mmol, 34.8 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, *R_f* = 0.2) to give the product as a white solid (51 mg, 58%).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 4.3 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.01 (td, *J* = 8.4, 4.1 Hz, 2H), 3.12 (td, *J* = 10.2, 4.1 Hz, 1H), 2.78 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.62 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.83 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.43 (dt, *J* = 9.9, 7.5 Hz, 1H), 1.28 (d, *J* = 3.0 Hz, 12H), 0.87 (d, *J* = 1.6 Hz, 3H), 0.86 (d, *J* = 1.6 Hz, 3H), 0.81 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.2, 140.8, 140.0, 137.8, 129.4, 128.7, 127.6, 123.9, 119.7, 83.4, 45.3, 45.3, 45.0, 30.2, 24.9, 24.6, 22.3, 22.3, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 30.2.

HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₇H₃₈¹⁰BNO₃ 457.2873, found: 457.2878.



3-([1,1'-Biphenyl]-4-yl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (3d)

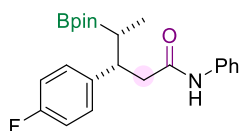
The title compound was prepared from (*E*)-4-(prop-1-en-1-yl)-1,1'-biphenyl (0.2 mmol, 38.8 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, *R_f* = 0.2) to give the product as a white solid (46 mg, 51%).

¹H NMR (300 MHz, CDCl₃) δ 7.56 (ddd, *J* = 10.8, 7.7, 1.6 Hz, 4H), 7.46 – 7.39 (m, 2H), 7.32 (tt, *J* = 8.2, 1.7 Hz, 3H), 7.27 – 7.16 (m, 4H), 7.13 – 6.96 (m, 2H), 3.22 (td, *J* = 10.1, 4.1 Hz, 1H), 2.84 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.65 (dd, *J* = 14.0, 10.2 Hz, 1H), 1.50 (dd, *J* = 9.9, 7.5 Hz, 1H), 1.30 (d, *J* = 1.4 Hz, 12H), 0.87 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.0, 142.8, 140.9, 139.4, 137.8, 128.8, 128.7, 128.3, 127.3, 127.1, 127.0, 123.9, 119.7, 83.4, 45.4, 45.3, 24.9, 24.7, 14.1.

¹¹B NMR (96 MHz, CDCl₃) δ 33.7.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₉H₃₄¹¹BNO₃ 456.2710, found: 456.2711.



3-(4-Fluorophenyl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (4d)

The title compound was prepared from (*E*)-1-fluoro-4-(prop-1-en-1-yl)benzene (0.2 mmol, 27.2 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, *R_f* = 0.2) to give the product as a white solid (34 mg, 43%).

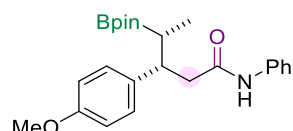
^1H NMR (300 MHz, CDCl_3) δ 7.31 – 7.15 (m, 6H), 7.15 – 7.01 (m, 2H), 7.00 – 6.90 (m, 2H), 3.17 (td, $J = 10.1$, 4.2 Hz, 1H), 2.79 (dd, $J = 14.0$, 4.2 Hz, 1H), 2.55 (dd, $J = 14.0$, 10.1 Hz, 1H), 1.42 (dd, $J = 10.3$, 7.2 Hz, 1H), 1.28 (d, $J = 1.1$ Hz, 12H), 0.80 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.8, 161.5 (d, $J = 244.4$ Hz), 139.3 (d, $J = 3.2$ Hz), 137.7, 129.21 (d, $J = 7.8$ Hz), 128.9, 124.1, 119.7, 115.3 (d, $J = 21.1$ Hz), 83.5, 45.2, 44.9, 24.9, 24.7, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.8.

^{19}F NMR (282 MHz, CDCl_3) δ -116.5.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{23}\text{H}_{29}^{11}\text{BFNO}_3$ 420.2121, found: 420.2124.



3-(4-Methoxyphenyl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (5d)

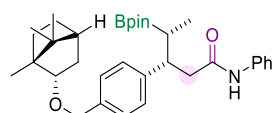
The title compound was prepared from (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene (0.2 mmol, 29.6 mg) and aniline (2.5 equiv., 45 μL), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, $R_f = 0.3$) to give the product as a white solid (28 mg, 34%).

^1H NMR (300 MHz, CDCl_3) δ 7.28 – 7.19 (m, 4H), 7.15 (d, $J = 8.6$ Hz, 2H), 7.02 (t, $J = 6.6$ Hz, 2H), 6.88 – 6.75 (m, 2H), 3.77 (s, 3H), 3.10 (td, $J = 10.2$, 4.0 Hz, 1H), 2.77 (dd, $J = 14.0$, 4.0 Hz, 1H), 2.58 (dd, $J = 14.0$, 10.3 Hz, 1H), 1.44 – 1.36 (m, 1H), 1.28 (d, $J = 1.5$ Hz, 12H), 0.80 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.1, 158.2, 137.9, 135.6, 128.8, 123.9, 119.7, 114.0, 83.4, 55.2, 45.5, 44.9, 24.9, 24.7, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.9.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{24}\text{H}_{32}^{10}\text{BNO}_4$ 431.2353, found: 431.2363.



N-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(((1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)phenyl)pentanamide (6d)

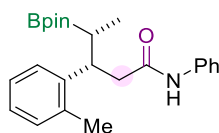
The title compound was prepared from (1*S*,2*R*,4*R*)-1,7,7-trimethyl-2-(((*E*)-prop-1-en-1-yl)benzyl)oxy)bicyclo[2.2.1]heptane (0.2 mmol, 56 mg) and aniline (2.5 equiv., 45 μL), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 5:1, $R_f = 0.2$) to give the product as a white solid (47 mg, 43%).

^1H NMR (300 MHz, CDCl_3) δ 7.29 – 7.18 (m, 8H), 7.07 – 6.95 (m, 2H), 4.55 – 4.38 (m, 2H), 3.67 (ddd, $J = 9.4$, 3.3, 1.8 Hz, 1H), 3.15 (td, $J = 10.1$, 4.0 Hz, 1H), 2.79 (dd, $J = 14.0$, 4.0 Hz, 1H), 2.61 (dd, $J = 14.0$, 10.2 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.67 (ddd, $J = 22.0$, 8.5, 4.5 Hz, 3H), 1.49 – 1.42 (m, 1H), 1.29 – 1.28 (m, 12H), 1.07 (dd, $J = 12.8$, 3.1 Hz, 2H), 0.88 – 0.80 (m, 12H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 142.6, 137.9, 137.9, 128.8, 127.7, 127.5, 123.9, 119.7, 84.4, 83.4, 71.4, 49.3, 47.8, 45.5, 45.0, 36.1, 31.5, 30.1, 29.7, 28.2, 26.7, 24.9, 24.7, 19.8, 18.9, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 32.8.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{34}\text{H}_{48}^{11}\text{BNO}_4$ 568.3574, found: 568.3581.



***N*-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl)pentanamide (7d)**

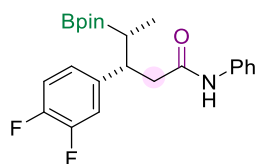
The title compound was prepared from (*E*)-1-methyl-2-(prop-1-en-1-yl)benzene (0.2 mmol, 26.4 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (51 mg, 65%).

^1H NMR (300 MHz, CDCl_3) δ 7.26 – 7.18 (m, 6H), 7.11 (dd, J = 5.5, 1.9 Hz, 2H), 7.01 (ddd, J = 8.6, 5.9, 2.7 Hz, 1H), 6.89 (s, 1H), 3.48 (td, J = 10.4, 3.9 Hz, 1H), 2.80 (dd, J = 13.7, 3.9 Hz, 1H), 2.59 (dd, J = 13.7, 10.3 Hz, 1H), 2.33 (s, 3H), 1.48 – 1.40 (m, 1H), 1.30 (s, 12H), 0.81 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.2, 142.6, 137.9, 137.2, 130.5, 128.8, 126.5, 126.1, 125.3, 123.8, 119.6, 83.4, 45.4, 40.1, 24.9, 24.6, 20.1, 14.0.

^{11}B NMR (96 MHz, CDCl_3) δ 33.9.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{32}^{11}\text{BNO}_3$ 394.2552, found: 394.2556.



3-(3,4-Difluorophenyl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (8d)

The title compound was prepared from (*E*)-1,2-difluoro-4-(prop-1-en-1-yl)benzene (0.2 mmol, 30 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (39 mg, 47%).

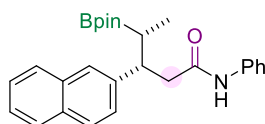
^1H NMR (300 MHz, CDCl_3) δ 7.36 – 7.23 (m, 5H), 7.05 (qd, J = 8.3, 3.6 Hz, 3H), 6.94 (d, J = 2.0 Hz, 1H), 3.19 (td, J = 9.8, 4.3 Hz, 1H), 2.80 (dd, J = 14.2, 4.3 Hz, 1H), 2.53 (dd, J = 14.2, 9.9 Hz, 1H), 1.42 – 1.34 (m, 1H), 1.28 (s, 12H), 0.81 (d, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.5, 148.9 (d, J = 259.2 Hz), 145.9, 140.9 (t, J = 4.3 Hz), 139.3 (d, J = 242.7 Hz), 128.9, 124.2, 123.9, (dd, J = 6.1, 3.3 Hz), 119.8, 117.0 (d, J = 16.5 Hz), 116.3 (d, J = 16.9 Hz), 83.6, 44.8, 44.6, 24.9, 24.7, 13.9.

^{11}B NMR (96 MHz, CDCl_3) δ 33.2.

^{19}F NMR (282 MHz, CDCl_3) δ -136.48 – -138.67 (m), -139.95 – -141.22 (m).

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{23}\text{H}_{28}^{10}\text{BF}_2\text{NO}_3$ 437.2059, found: 437.2069.



3-(Naphthalen-2-yl)-*N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (9d)

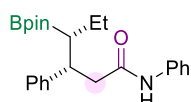
The title compound was prepared from (*E*)-2-(prop-1-en-1-yl)naphthalene (0.2 mmol, 33.6 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (45 mg, 53%).

^1H NMR (300 MHz, CDCl_3) δ 7.83 – 7.73 (m, 3H), 7.68 (s, 1H), 7.47 – 7.36 (m, 3H), 7.25 – 7.10 (m, 4H), 7.07 (s, 1H), 6.99 (dq, $J = 8.6, 4.2$ Hz, 1H), 3.35 (td, $J = 9.9, 4.2$ Hz, 1H), 2.88 (dd, $J = 14.2, 4.2$ Hz, 1H), 2.73 (dd, $J = 14.1, 9.9$ Hz, 1H), 1.60 – 1.51 (m, 1H), 1.30 (d, $J = 2.0$ Hz, 12H), 0.83 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 141.2, 137.8, 133.5, 132.4, 128.7, 128.4, 127.7, 127.6, 126.9, 126.0, 125.6, 125.4, 123.9, 119.7, 83.5, 45.8, 45.2, 24.9, 24.7, 14.1.

^{11}B NMR (96 MHz, CDCl_3) δ 33.6.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{27}\text{H}_{32}^{10}\text{BNO}_3$ 451.2404, found: 451.2409.



***N*,3-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (10d)**

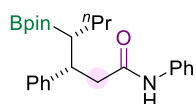
The title compound was prepared from (*E*)-but-1-en-1-ylbenzene (0.2 mmol, 26.4 mg) and aniline (2.5 equiv., 45 μL), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, $R_f = 0.2$) to give the product as a white solid (33 mg, 42%).

^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 7H), 7.01 (dt, $J = 12.5, 6.2$ Hz, 2H), 3.22 (td, $J = 10.3, 3.9$ Hz, 1H), 2.77 (dd, $J = 13.9, 3.9$ Hz, 1H), 2.58 (dd, $J = 13.9, 10.5$ Hz, 1H), 1.54 – 1.35 (m, 1H), 1.32 (s, 12H), 1.23 (d, $J = 6.3$ Hz, 2H), 0.83 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0, 144.1, 137.8, 128.8, 128.7, 127.8, 126.7, 124.0, 119.8, 83.5, 45.6, 44.5, 25.0, 24.9, 22.7, 13.4.

^{11}B NMR (96 MHz, CDCl_3) δ 33.3.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{32}^{10}\text{BNO}_3$ 393.2585, found: 393.2596.



***N*,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanamide (11d)**

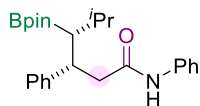
The title compound was prepared from (*E*)-pent-1-en-1-ylbenzene (0.2 mmol, 29.2 mg) and aniline (2.5 equiv., 45 μL), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, $R_f = 0.2$) to give the product as a white solid (43 mg, 53%).

^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 7H), 7.01 (dt, $J = 12.0, 5.9$ Hz, 2H), 3.20 (td, $J = 10.3, 3.9$ Hz, 1H), 2.76 (dd, $J = 13.9, 3.9$ Hz, 1H), 2.59 (dd, $J = 13.9, 10.5$ Hz, 1H), 1.49 – 1.39 (m, 1H), 1.31 (s, 12H), 1.23 (d, $J = 2.8$ Hz, 2H), 1.14 (ddd, $J = 17.6, 8.4, 3.6$ Hz, 2H), 0.77 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 169.9, 144.1, 137.8, 128.7, 128.7, 127.7, 126.6, 123.9, 119.7, 83.4, 45.5, 44.7, 32.0, 25.0, 24.8, 22.1, 14.3.

^{11}B NMR (96 MHz, CDCl_3) δ 33.0.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{25}\text{H}_{34}^{10}\text{BNO}_3$ 429.2560, found: 429.2566.



5-Methyl-*N*,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (**12d**)

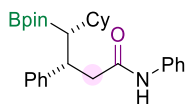
The title compound was prepared from (*E*)-(3-methylbut-1-en-1-yl)benzene (0.2 mmol, 29.2 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (42 mg, 51%).

¹H NMR (300 MHz, CDCl₃) δ 7.35 – 7.26 (m, 2H), 7.26 – 7.16 (m, 7H), 7.07 – 6.95 (m, 1H), 6.86 (s, 1H), 3.33 (td, *J* = 10.9, 3.5 Hz, 1H), 2.72 (dd, *J* = 13.7, 3.5 Hz, 1H), 2.51 (dd, *J* = 13.7, 10.7 Hz, 1H), 1.50 – 1.37 (m, 2H), 1.33 (d, *J* = 2.9 Hz, 12H), 0.88 (dd, *J* = 15.8, 6.8 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 169.9, 143.9, 137.8, 128.8, 128.7, 127.7, 126.6, 123.9, 119.7, 83.5, 46.2, 43.0, 27.2, 25.3, 25.0, 23.4, 19.1.

¹¹B NMR (96 MHz, CDCl₃) δ 33.7.

HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₅H₃₄¹¹BNO₃ 430.2528, found: 430.2533.



4-Cyclohexyl-*N*,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (**13d**)

The title compound was prepared from (*E*)-(2-cyclohexylvinyl)benzene (0.2 mmol, 37.2 mg) and aniline (2.5 equiv., 45 μ L), according to general procedure. The crude residue was purified by flash chromatography (*n*-pentane/EA = 10:1, R_f = 0.2) to give the product as a white solid (43 mg, 48%).

¹H NMR (300 MHz, CDCl₃) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.10 (m, 7H), 7.01 (dt, *J* = 8.6, 4.2 Hz, 1H), 6.94 (s, 1H), 3.39 (td, *J* = 10.8, 3.6 Hz, 1H), 2.71 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.53 (dd, *J* = 13.8, 10.7 Hz, 1H), 1.64 – 1.51 (m, 4H), 1.33 (d, *J* = 4.5 Hz, 12H), 1.17 – 0.80 (m, 8H).

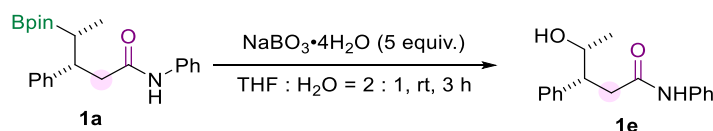
¹³C NMR (75 MHz, CDCl₃) δ 170.0, 144.0, 137.8, 128.7, 128.7, 127.6, 126.5, 123.9, 119.7, 83.5, 45.8, 42.0, 37.3, 33.8, 30.3, 26.7, 26.7, 26.4, 25.2, 25.0.

¹¹B NMR (96 MHz, CDCl₃) δ 31.0.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₂₈H₃₈¹¹BNO₃ 448.3023, found: 448.3025.

5. Derivatization of **1a**.

5.1 Oxidation of **1a**.



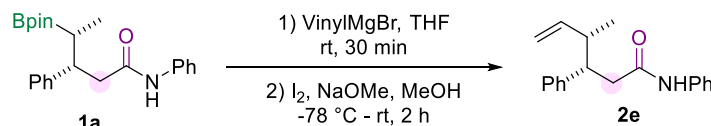
The title compound **1e** was synthesized according to the following literature¹: A 25 mL flask charged with **1a** (0.1 mmol) and THF/H₂O (1.0 mL/0.5 mL). Then the NaBO₃•4H₂O (5 equiv.) was added to a solution. The resulting mixture was stirred vigorously for 3 h at room temperature, then quenched with water and extracted with ethyl acetate (5 mL). The combined organic layers were washed with brine (15 mL), dried over Na₂SO₄ and concentrated. Purification by column chromatography on silica gel gave the corresponding product **1e** as a colorless oil (98% yield).

4-Hydroxy-*N*,3-diphenylpentanamide (**1e**)

^1H NMR (300 MHz, CDCl_3) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.24 (m, 5H), 7.23 – 7.19 (m, 2H), 7.09 (td, $J = 6.2$, 2.8 Hz, 1H), 4.01 (s, 1H), 3.12 (dt, $J = 8.4$, 6.3 Hz, 1H), 2.98 (dd, $J = 14.6$, 5.9 Hz, 1H), 2.75 (dd, $J = 14.6$, 6.6 Hz, 1H), 2.64 (d, $J = 5.7$ Hz, 1H), 1.10 (d, $J = 6.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 171.4, 142.3, 137.7, 128.8, 128.7, 127.9, 126.9, 124.3, 120.2, 71.7, 50.8, 41.4, 22.1.

5.2 Vinylation of **1a**.



The title compound **2e** was synthesized according to the modified following literature²: an oven-dried round bottom flask was charged with a stirring bar, **1a** (0.1 mmol) in THF (1 mL). Vinylmagnesium bromide (1 M, 0.4 mL, 4.0 equiv.) was added dropwise to the mixture at room temperature. The resulting mixture was stirred for 0.5 h and then cooled to -78°C . A solution of I_2 (4.0 equiv.) in methanol (1.0 mL) was added dropwise and the mixture was allowed to stir 0.5 h at the same temperature. A solution of NaOMe (8.0 equiv.) in methanol (1.5 mL) was added dropwise. Then the reaction mixture was warmed to room temperature and stirred for another 1.5 h. The reaction mixture was quenched by saturated $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) and diluted with EtOAc (10 mL) and water 10 mL. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the corresponding product **2e** as a colorless oil (93%).

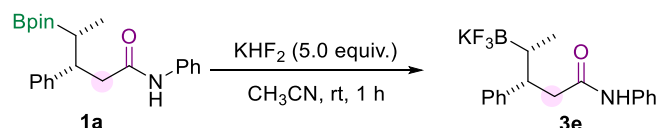
4-Methyl-*N*,3-diphenylhex-5-enamide (**2e**)

^1H NMR (300 MHz, CDCl_3) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.10 (m, 7H), 7.06 – 6.90 (m, 1H), 6.79 (s, 1H), 5.75 (ddd, $J = 17.1$, 10.1, 8.9 Hz, 1H), 5.19 – 4.98 (m, 2H), 2.99 (td, $J = 9.9$, 4.3 Hz, 1H), 2.89 (dd, $J = 14.3$, 4.3 Hz, 1H), 2.57 – 2.32 (m, 2H), 0.84 (d, $J = 6.7$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.2, 142.8, 142.7, 137.6, 128.8, 128.7, 128.1, 126.8, 124.1, 119.9, 115.1, 48.1, 44.3, 43.5, 19.1.

HRMS (ESI-TOF): calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{19}\text{H}_{21}\text{NO}$ 302.1515, found: 302.1518.

5.3 Preparation of trifluoroboration salt of **1a**.



The title compound **3e** was prepared according to the following literature⁴: an oven-dried 25 mL Schlenk tube was charged with **1a** (0.1 mmol) and MeCN (0.2 mL). The reaction mixture was stirred vigorously for 1 h at room temperature after KHF_2 (4.0 equiv.) was added. The resulting slurry was stirred concentrated, then placed under high vacuum for 1 h. The dried solids were triturated with hot acetone and filtered to remove inorganic salts. The combined organic layers were concentrated and Et_2O (5 mL) was added, then the mixture was sonicated for 15 minutes, and the organic layer was removed, and this step was repeated. The trifluoroboration salt **4e** was obtained as a white solid (82% yield).

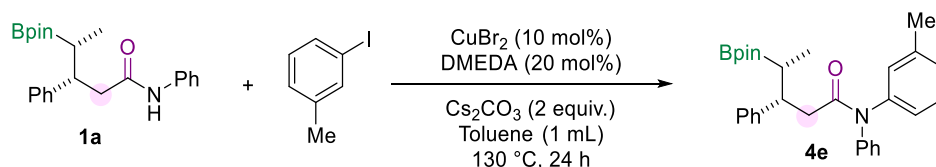
***N*,3-Diphenyl-4-(trifluoro-*λ*4-borane)pentanamide, potassium salt (**3e**)**

¹H NMR (300 MHz, DMSO) δ 9.38 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.22 – 7.05 (m, 6H), 6.98 (tt, *J* = 6.3, 2.9 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 3.09 (dd, *J* = 14.9, 3.9 Hz, 1H), 2.85 (td, *J* = 10.9, 3.7 Hz, 1H), 2.50 – 2.42 (m, 1H), 0.40 (s, 3H).

¹³C NMR (75 MHz, DMSO) δ 171.7, 148.0, 139.5, 128.3, 128.2, 127.2, 124.5, 122.4, 118.9, 45.8, 43.4, 15.9.

¹¹B NMR (96 MHz, DMSO) δ 6.6.

5.4 *N*-Arylation of **1a**.



The title compound **4e** was prepared according to the following literature³: an oven-dried 25 mL Schlenk tube was charged with **1a** (0.1 mmol), CuBr₂ (10 mol%), and Cs₂CO₃ (2.0 equiv.). The tube was evacuated under vacuum and recharged with argon for three times. Then 1-iodo-3-methylbenzene (2.0 equiv.), 1,2-dimethylethylenediamine (DMEDA, 20 mol%), and toluene (1 mL) was injected into the tube. The resulted mixture was allowed to stir at 130 °C for 24 h. Then the reaction mixture was cooled to room temperature. Then the solution was extracted by EtOAc (5 mLx2) and dried over Na₂SO₄. The combined organic layer was concentrated under reduced pressure and purified by column chromatography to give the corresponding **3e** in 61% yield.

***N*,3-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(*m*-tolyl)pentanamide (**4e**)**

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 7.09 (m, 6H), 7.11 – 6.95 (m, 4H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.55 (s, 2H), 3.20 (dt, *J* = 9.9, 7.6 Hz, 1H), 2.56 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H), 1.19 (d, *J* = 6.1 Hz, 1H), 1.14 (s, 12H), 0.67 (d, *J* = 7.4 Hz, 3H).

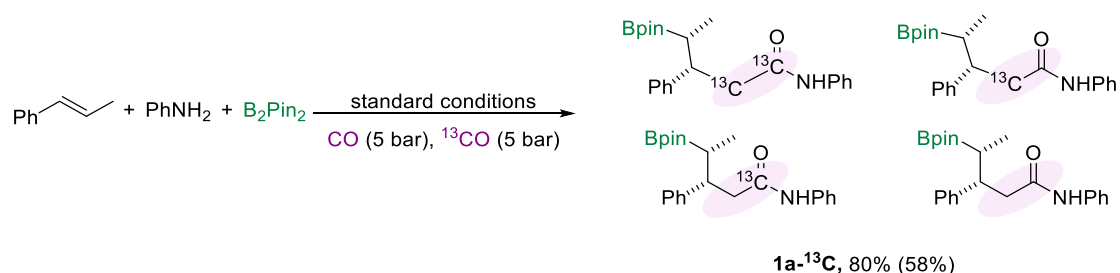
¹³C NMR (75 MHz, CDCl₃) δ 172.0, 144.0, 143.0, 142.8, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.4, 128.0, 126.1, 83.0, 45.8, 41.1, 24.8, 24.6, 21.2, 14.1.

¹¹B NMR (96 MHz, CDCl₃) δ 33.3.

HRMS (ESI-TOF): calcd for [M+H]⁺ C₃₀H₃₆¹¹BNO₃ 470.2867, found: 470.2872.

6. Mechanism studies.

6.1 ¹³C labeling experiment.



A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three

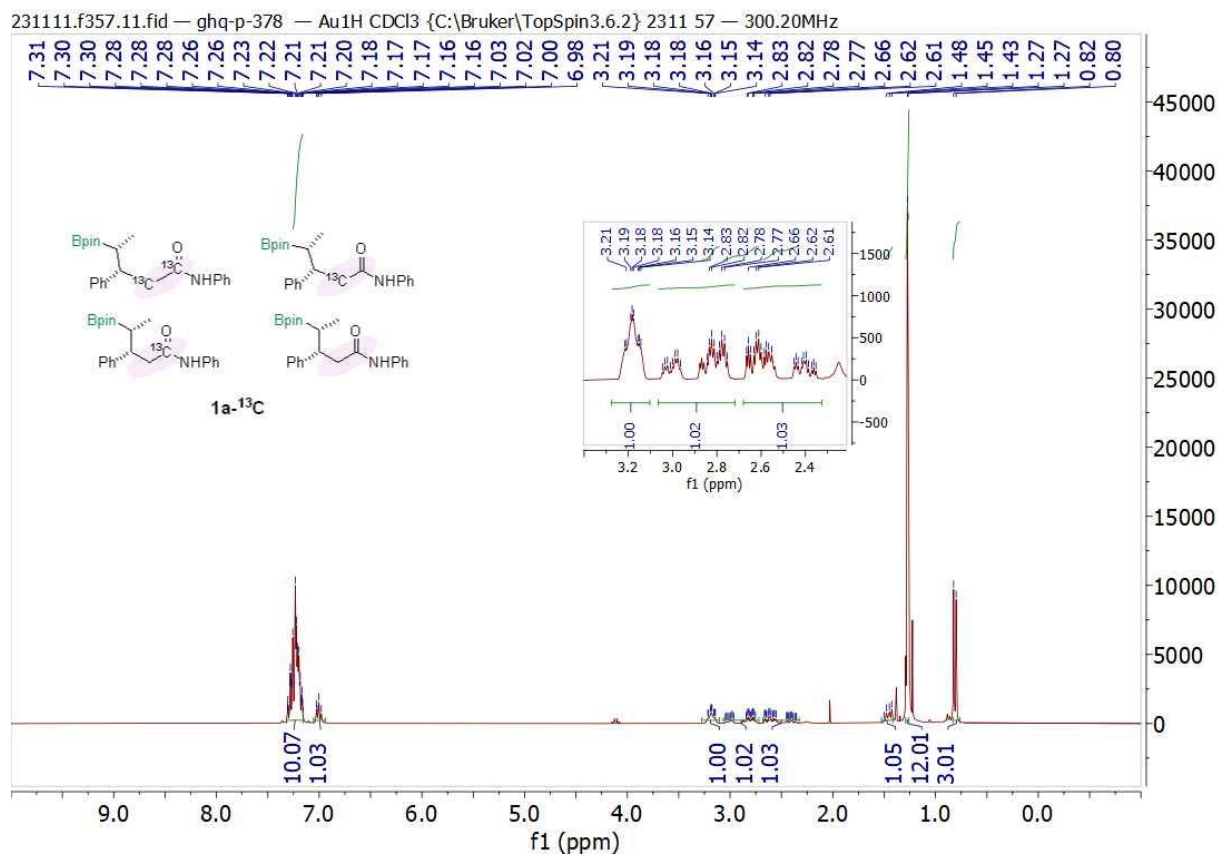
times with a needle. Then, *trans*- β -methylstyrene (0.2 mmol), aniline (2.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with ^{13}CO (5 bar) and CO (5 bar) after flushing two times with N_2 and two times with CO . The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that the corresponding products **1a- ^{13}C** was afforded as a white solid in 80% NMR yield and 58% isolated yield by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na_2SO_4 , an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

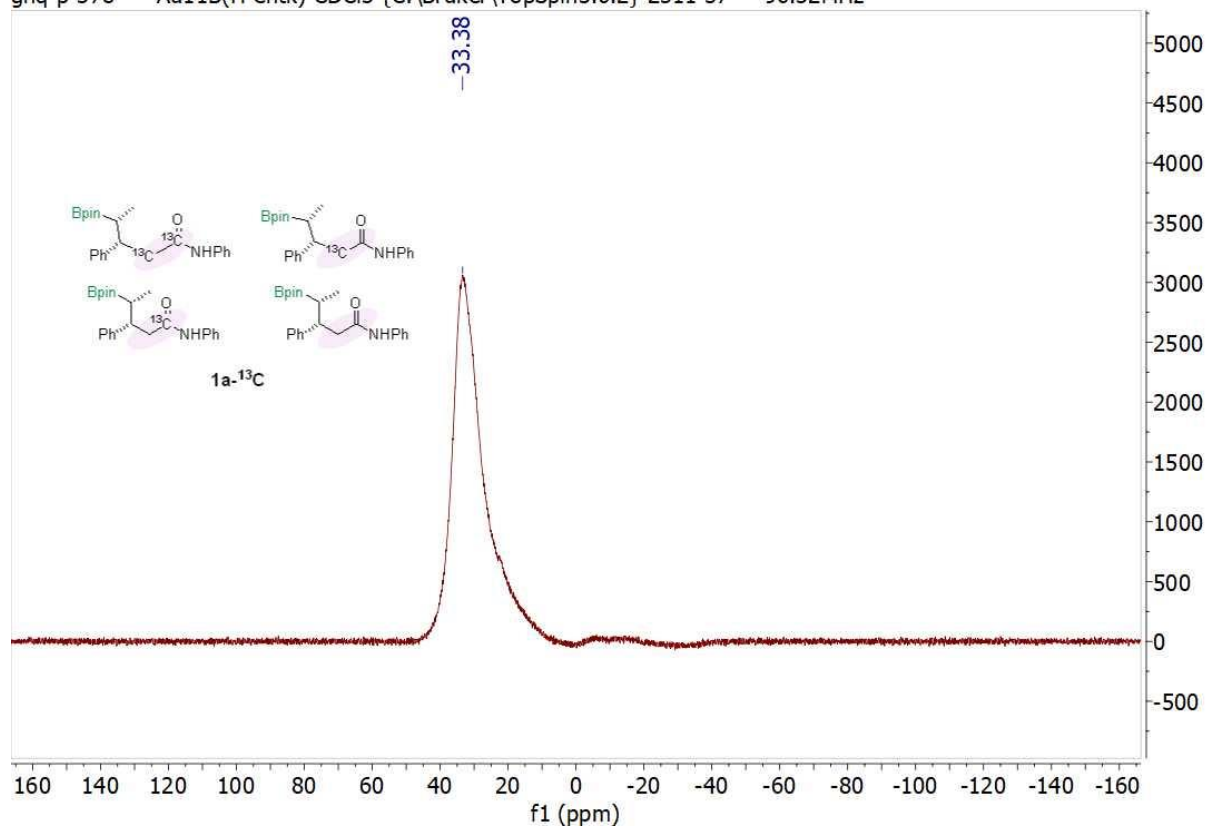
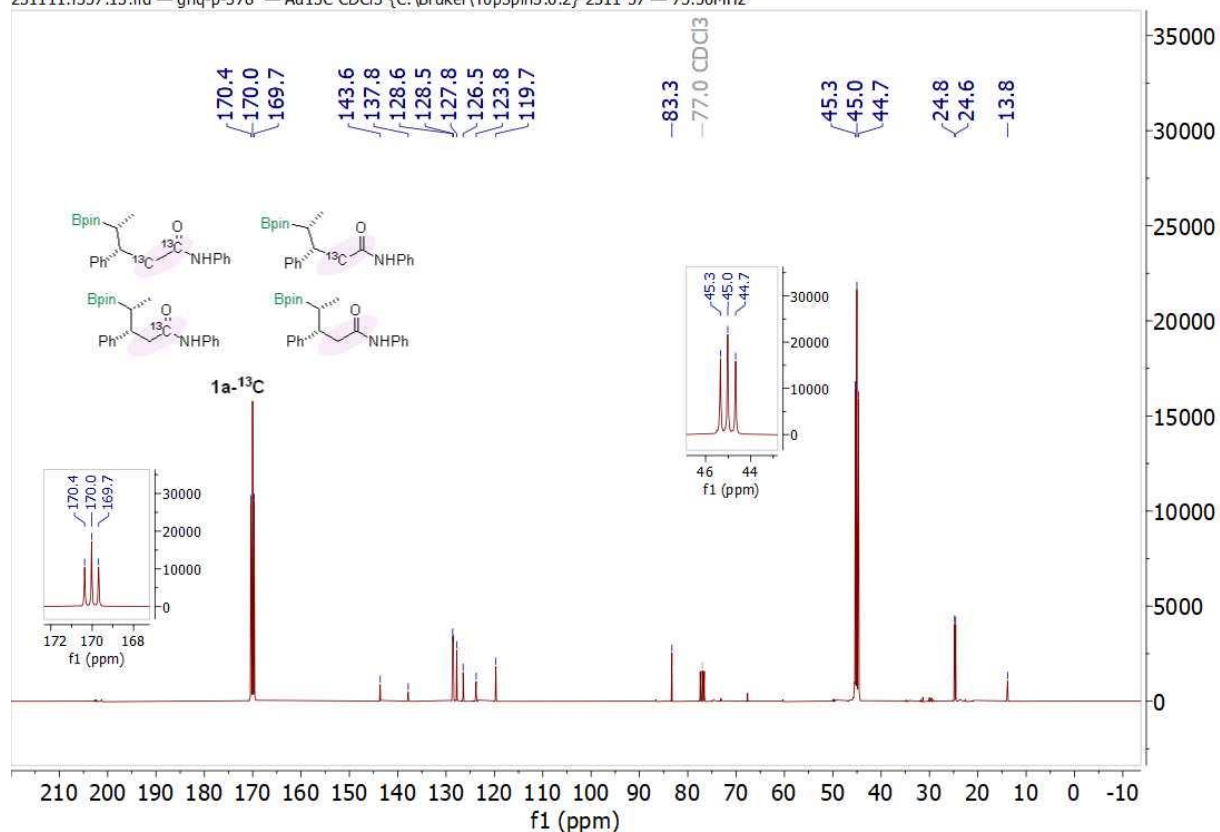
^1H NMR (300 MHz, CDCl_3) δ 7.32 – 7.16 (m, 10H), 7.05 – 6.94 (m, 1H), 3.18 (ddd, $J = 10.0, 6.0, 2.0$ Hz, 1H), 3.07 – 2.72 (m, 1H), 2.68 – 2.33 (m, 1H), 1.46 (dd, $J = 15.5, 7.3$ Hz, 1H), 1.27 (d, $J = 2.1$ Hz, 12H), 0.81 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.0 (d, $J = 51.3$ Hz), 170.0, 169.7, 143.6, 137.8, 128.6, 128.5, 127.8, 126.5, 123.8, 119.7, 83.3, 45.0 (d, $J = 50.6$ Hz), 45.0, 24.8, 24.6, 13.8.

^{11}B NMR (96 MHz, CDCl_3) δ 33.4.

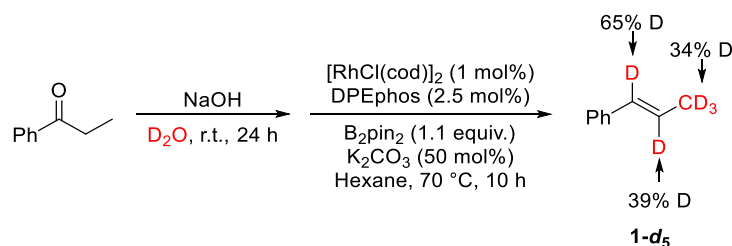
(Note: Through the NMR spectra, we can clearly see that the carbonyl and methylene carbon atoms are labelled by ^{13}C).





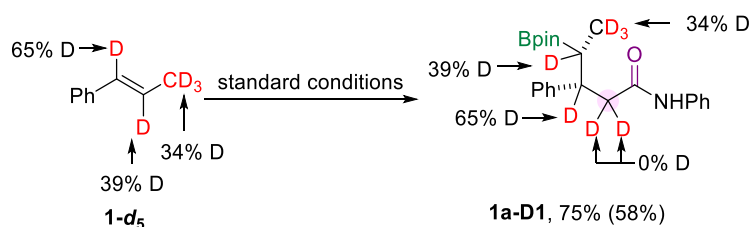
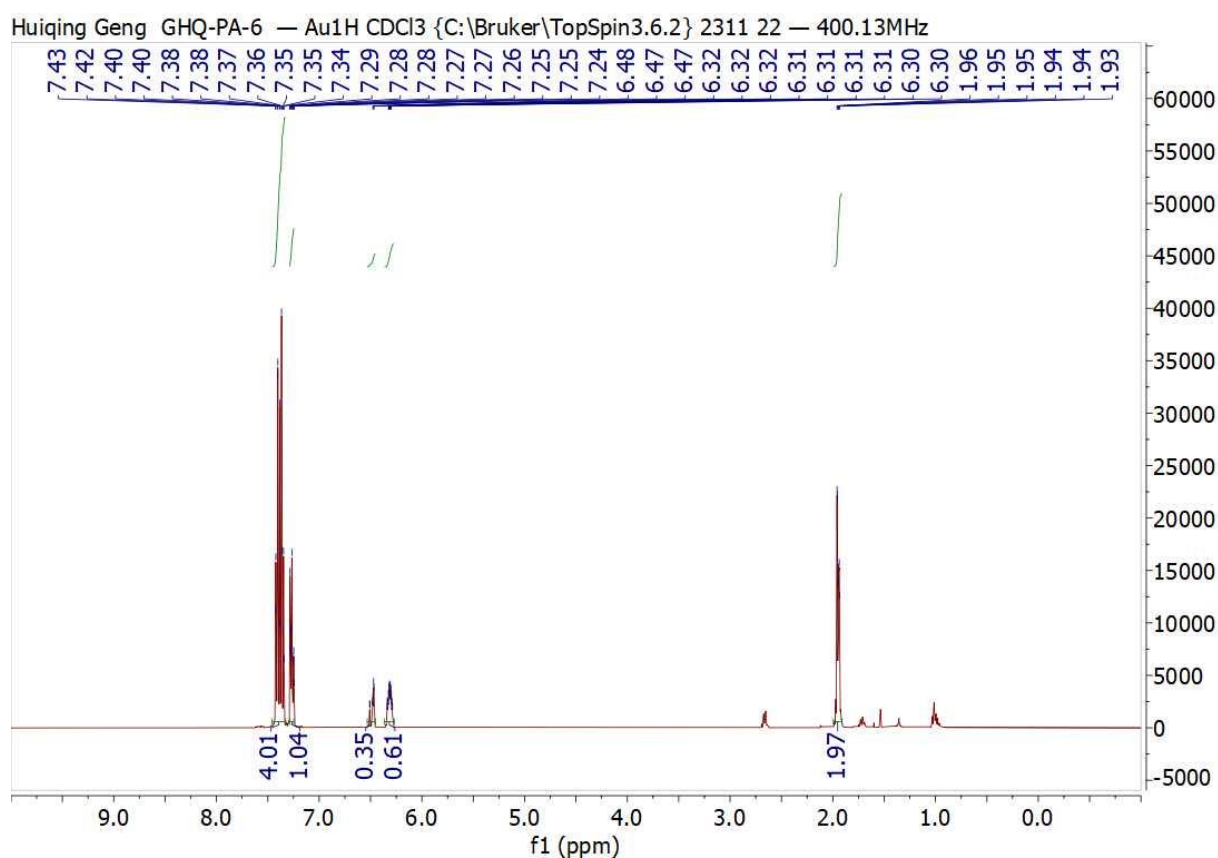
6.2 Deuterium labeling experiment.

6.2.1 Deuterated *trans*- β -methylstyrene.



(*E*)-(prop-1-en-1-yl-*d*₅)benzene (**1-d₅**) was synthesized according to the existed literature.⁵

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.33 (m, 4H), 7.29 – 7.24 (m, 1H), 6.47 (dd, *J* = 4.5, 1.8 Hz, 0.35H), 6.31 (dddd, *J* = 10.1, 5.6, 2.5, 1.1 Hz, 0.61H), 1.96 – 1.93 (m, 1.97H).



A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, (*E*)-(prop-1-en-1-yl-*d*₅)benzene (**1-d₅**) (0.2 mmol), aniline (2.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with

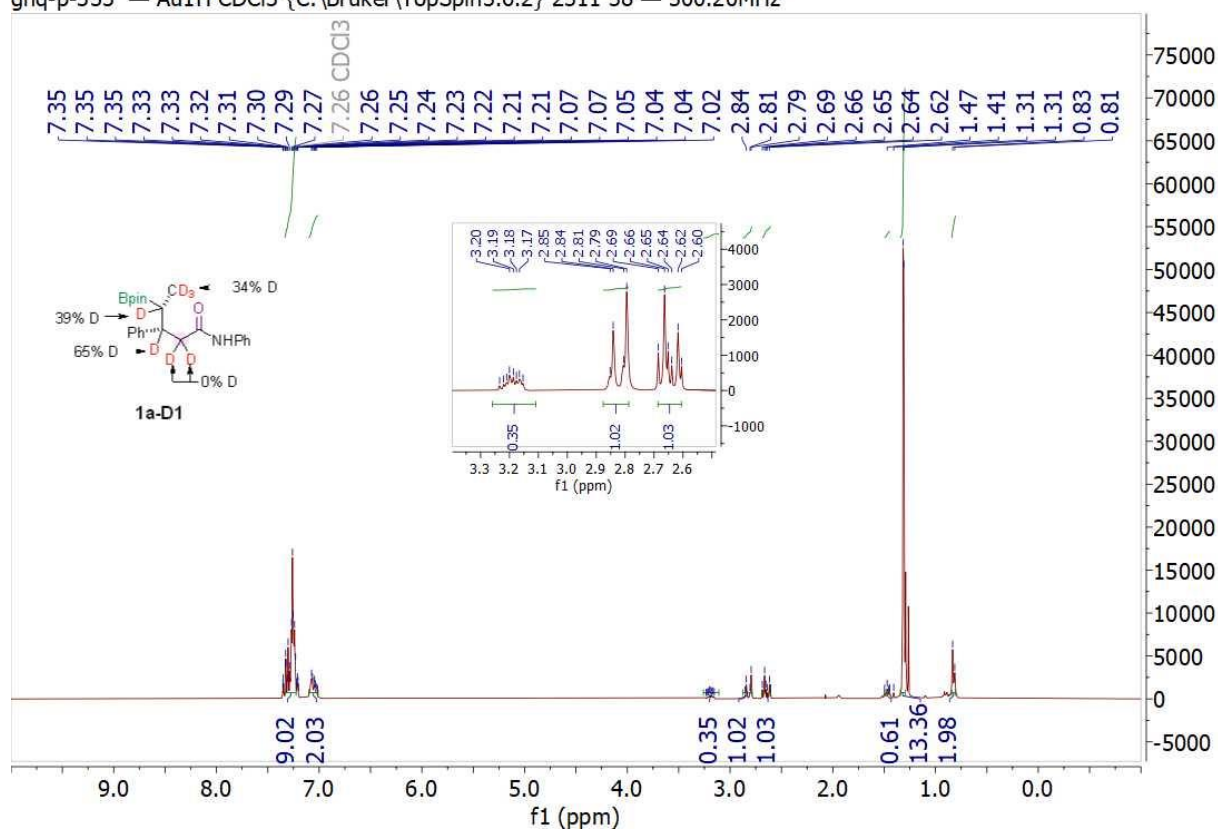
CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D1**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

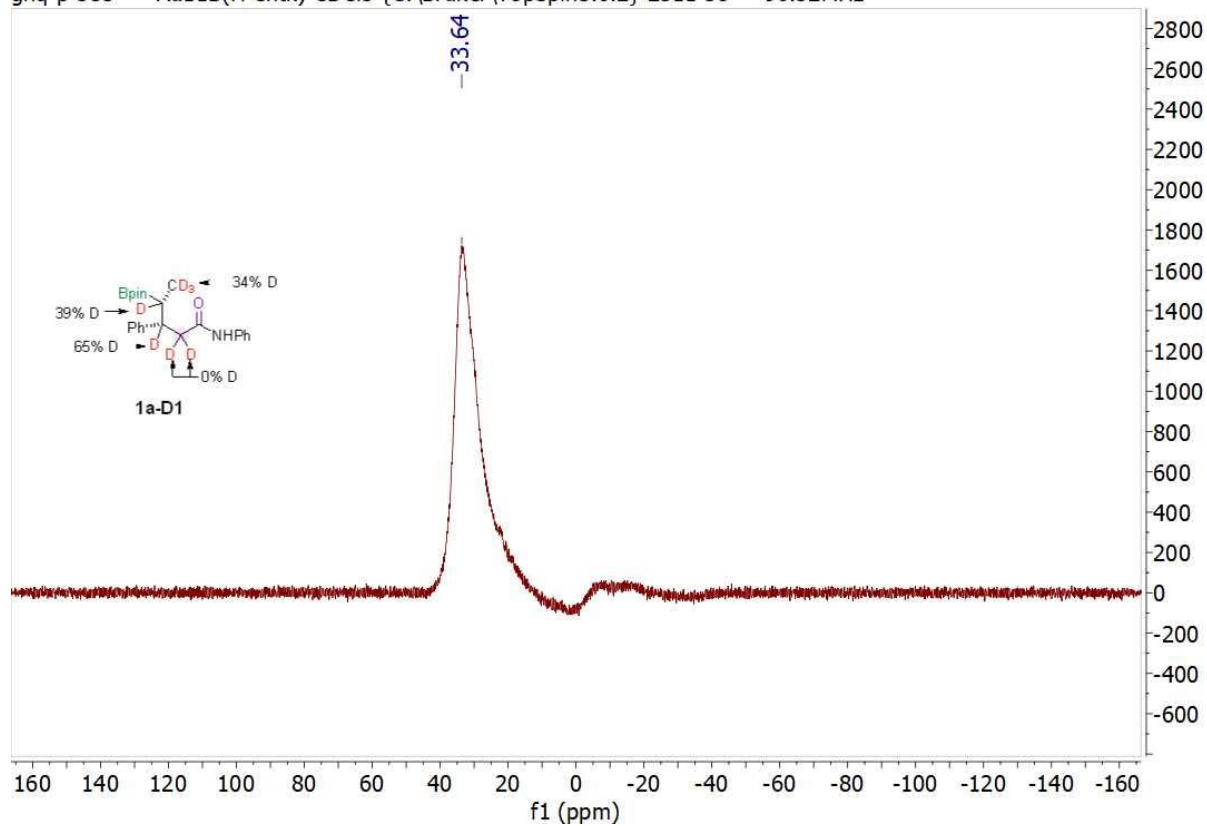
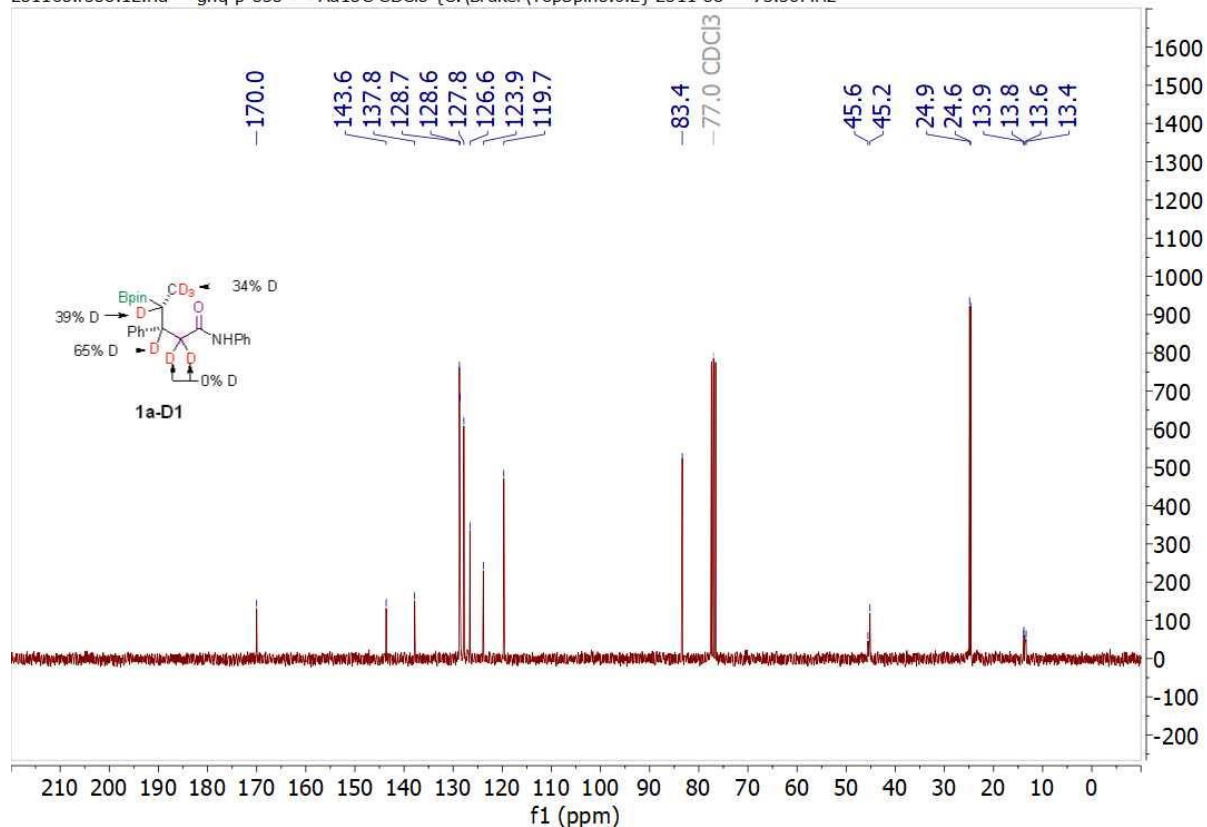
¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.22 (m, 9H), 7.04 (ddd, *J* = 8.5, 6.3, 2.4 Hz, 2H), 3.19 (ddt, *J* = 10.0, 6.8, 4.0 Hz, 1H), 2.82 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.70 – 2.53 (m, 1H), 1.50 – 1.44 (m, 0.61H), 1.31 (d, *J* = 1.8 Hz, 13H), 0.82 (d, *J* = 6.3 Hz, 1.97H).

¹³C NMR (75 MHz, CDCl₃) δ 170.0, 143.6, 137.8, 128.7, 128.6, 127.8, 126.6, 123.9, 119.7, 83.4, 45.6, 45.2, 24.9, 24.6, 13.9 – 13.4 (m).

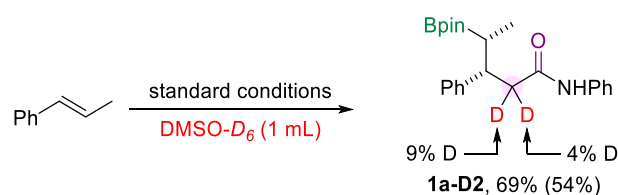
¹¹B NMR (96 MHz, CDCl₃) δ 33.6.

ghq-p-353 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 38 — 300.20MHz





6.2.2 DMSO-*d*₆.



A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*- β -methylstyrene (0.2 mmol), aniline (2.5 equiv.) and DMSO-*d*₆ (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D2**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

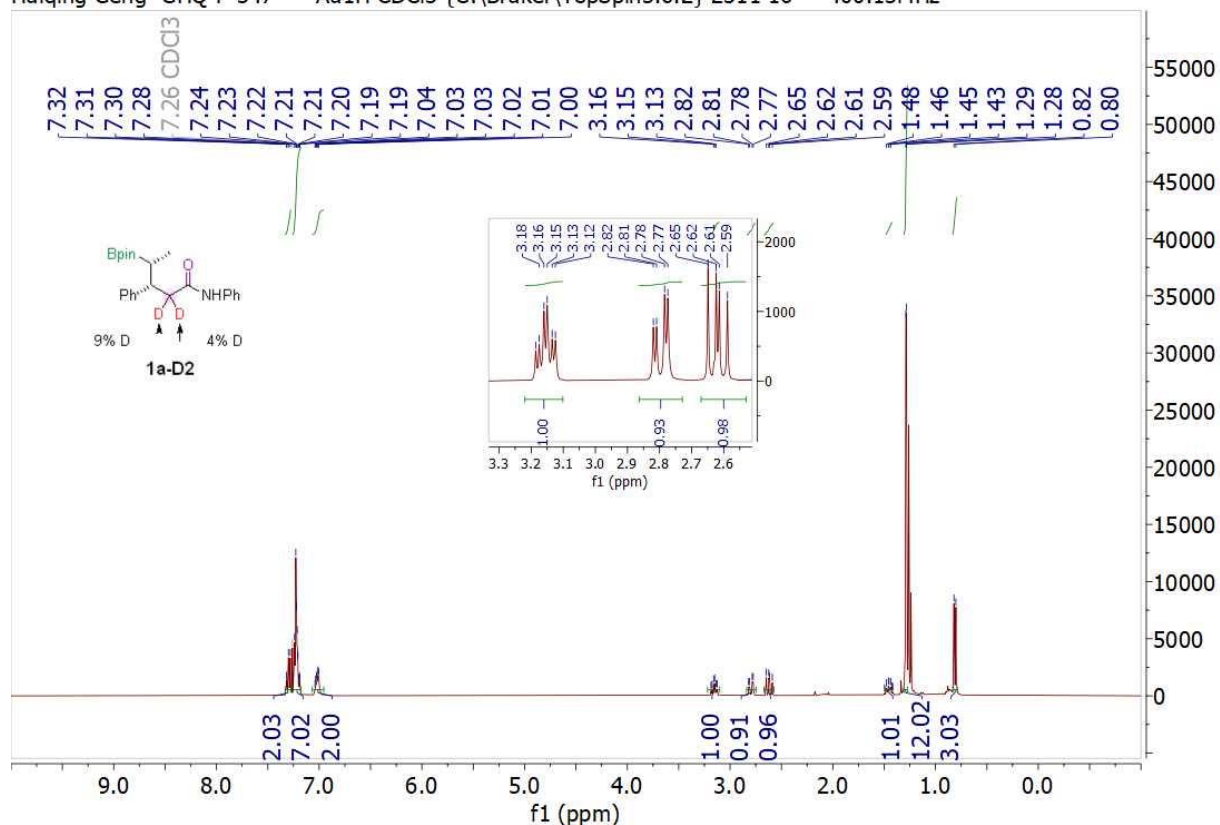
¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 7H), 7.07 – 6.96 (m, 2H), 3.15 (td, *J* = 10.2, 4.1 Hz, 1H), 2.80 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.62 (dd, *J* = 14.0, 10.3 Hz, 1H), 1.49 – 1.42 (m, 1H), 1.29 (d, *J* = 2.4 Hz, 12H), 0.81 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.0, 143.7, 137.8, 128.8, 128.6, 127.8, 126.6, 123.9, 119.7, 83.4, 45.7, 45.3, 24.9, 24.6, 14.0.

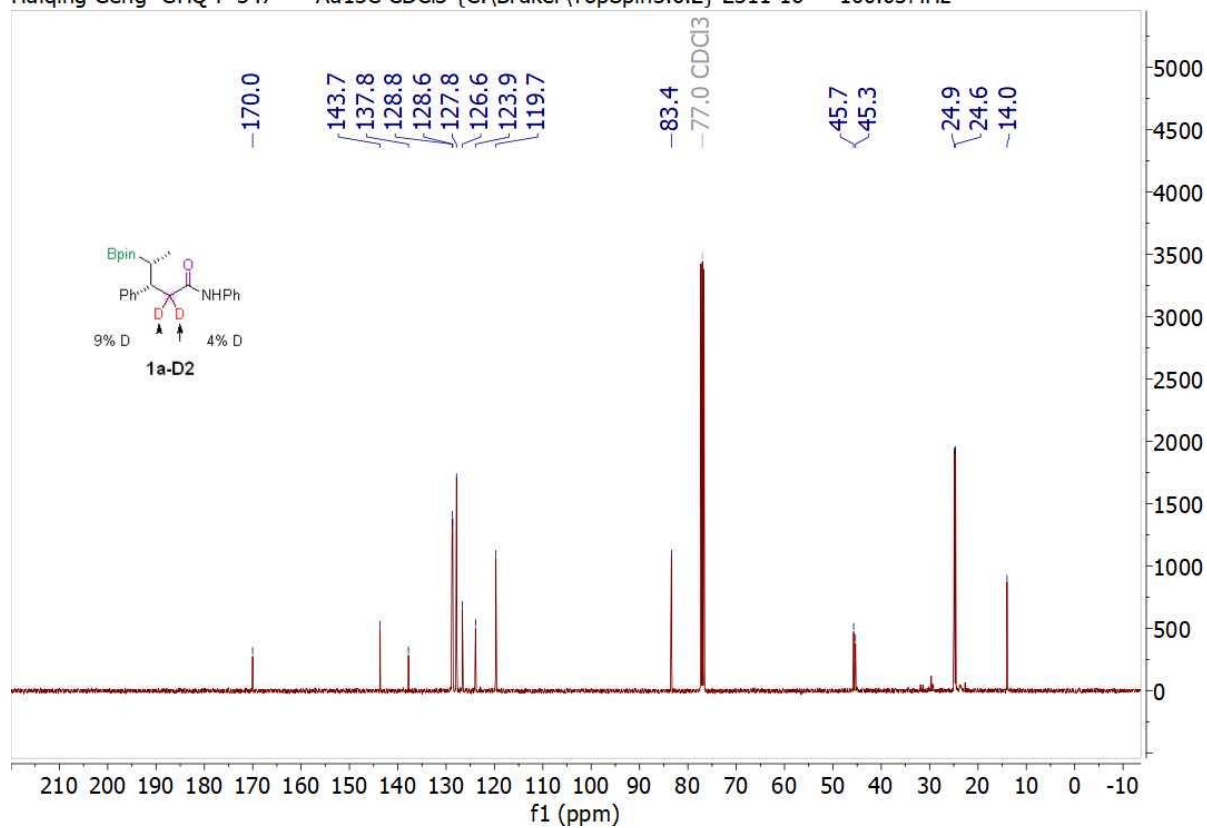
¹¹B NMR (96 MHz, CDCl₃) δ 33.3.

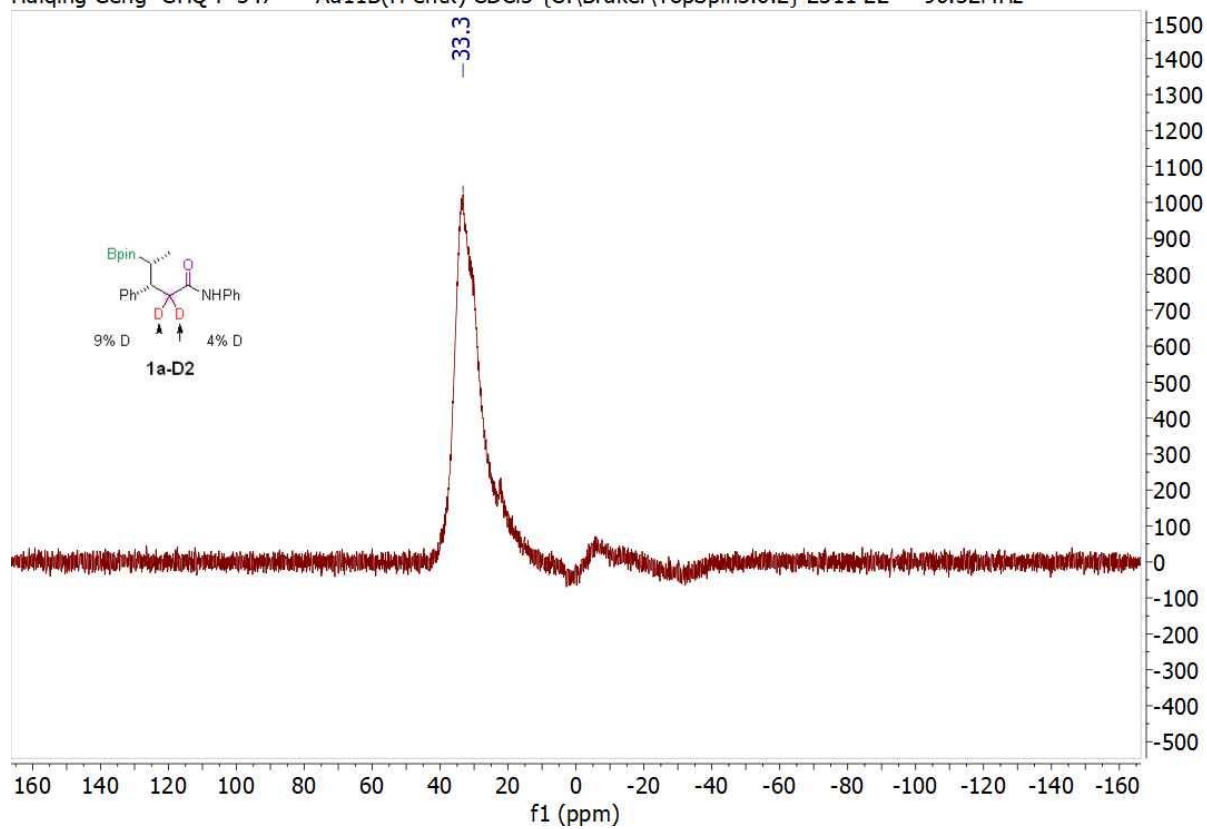
HRMS (ESI-TOF): calcd for [M+Na]⁺ C₂₇H₃₀¹⁰BNO₃ 401.2247, found: 401.2251.

Huiqing Geng GHQ-P-347 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 16 — 400.13MHz

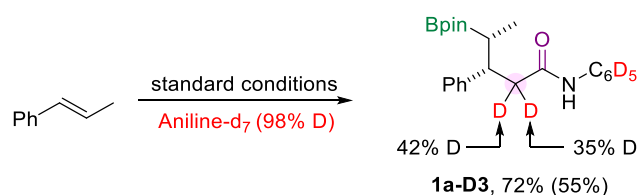


Huiqing Geng GHQ-P-347 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 16 — 100.63MHz





6.2.3 Aniline-*d*₇.

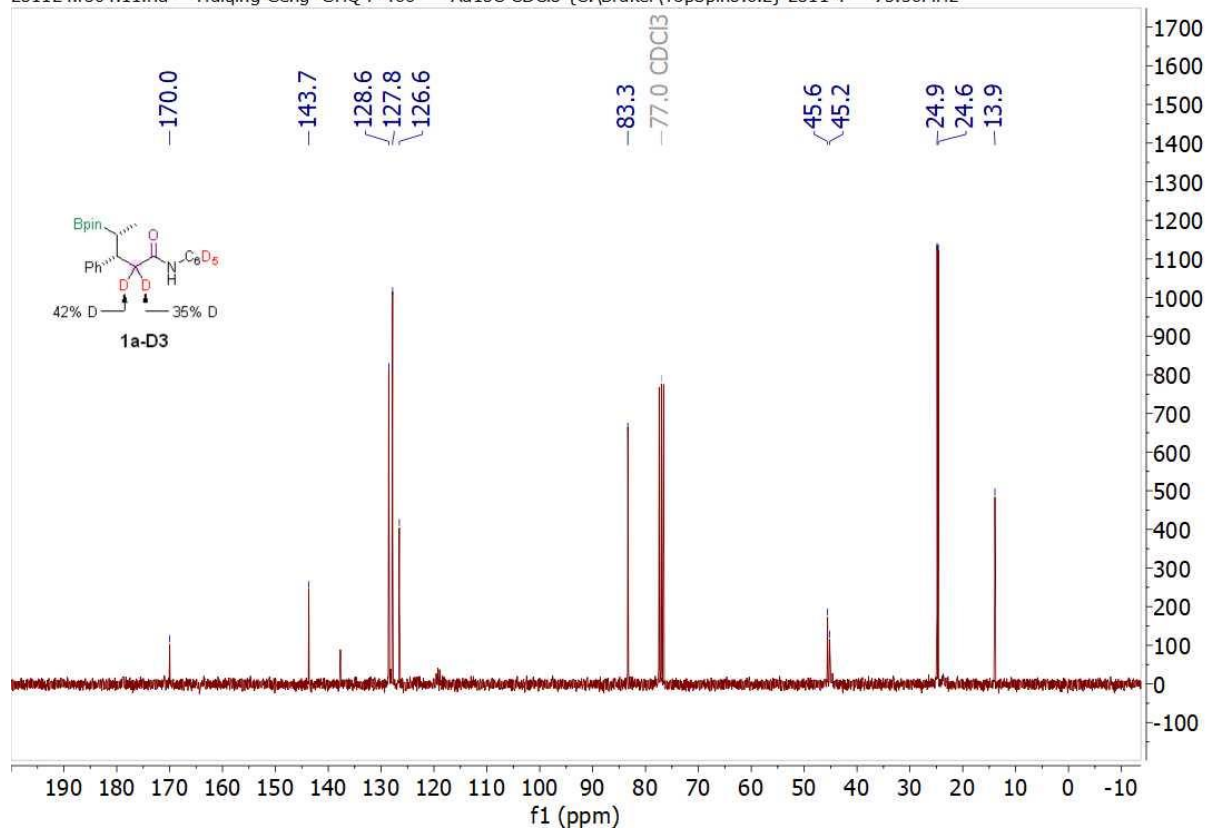
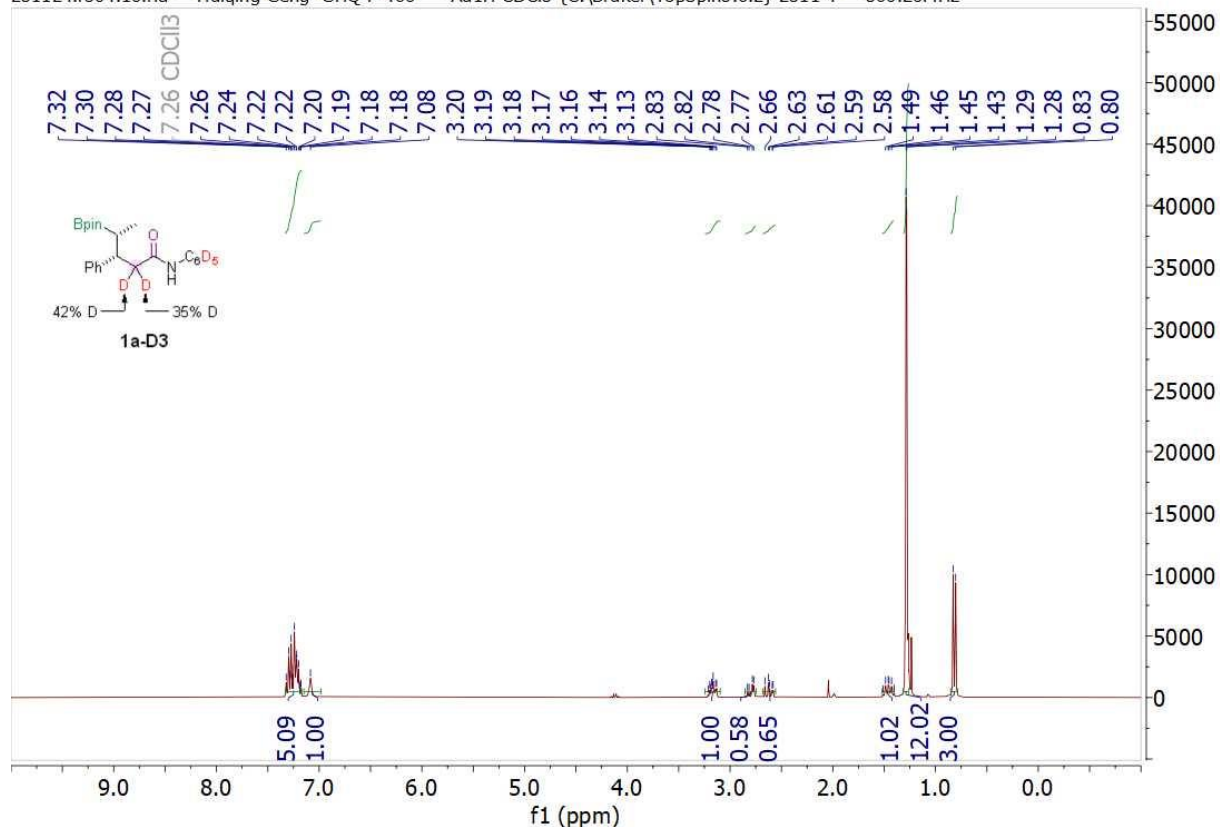


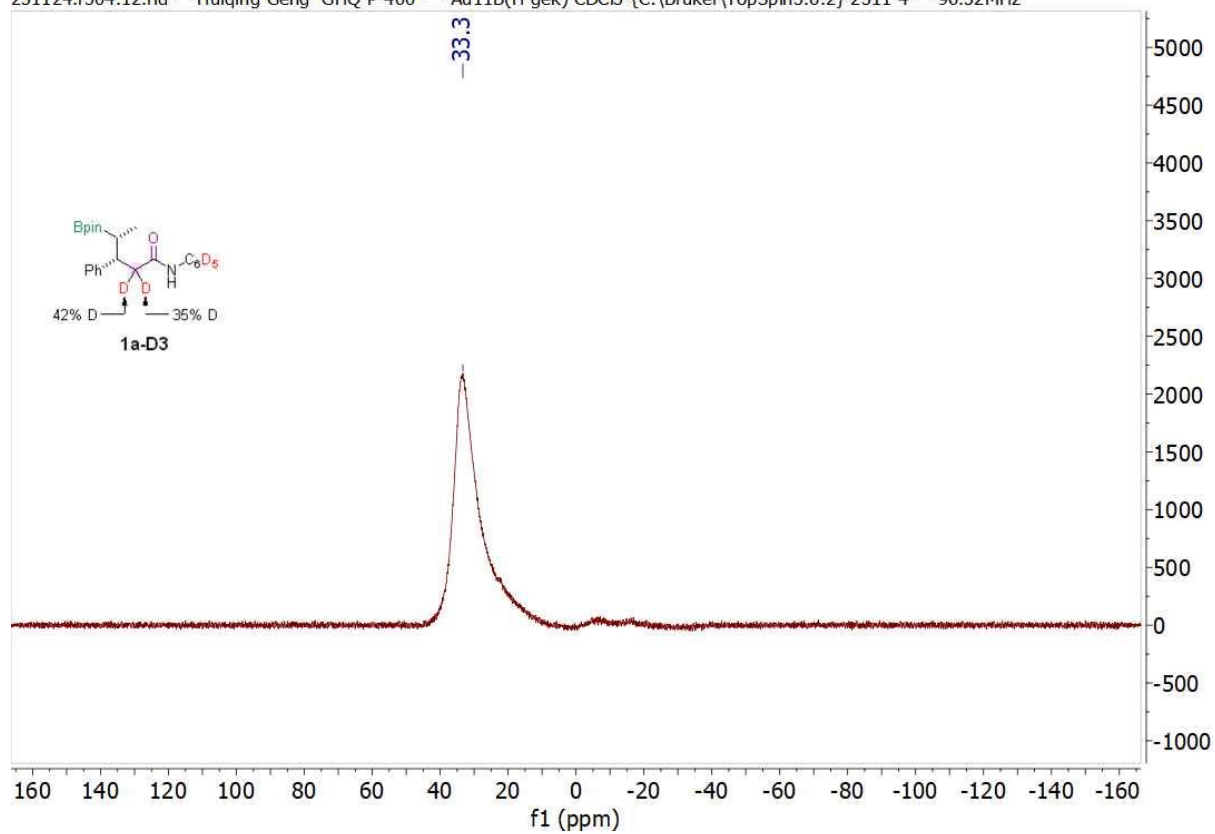
A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*-β-methylstyrene (0.2 mmol), aniline-*d*₇ (2.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D3**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.17 (m, 5H), 7.08 (s, 1H), 3.33 – 3.05 (m, 1H), 2.80 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.67 – 2.58 (m, 1H), 1.46 (dd, *J* = 10.0, 7.5 Hz, 1H), 1.28 (d, *J* = 1.8 Hz, 12H), 0.82 (d, *J* = 7.4 Hz, 3H).

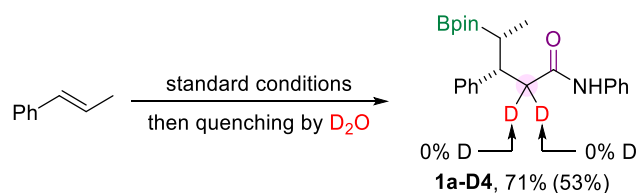
¹³C NMR (75 MHz, CDCl₃) δ 170.0, 143.7, 128.6, 127.8, 126.6, 83.3, 45.6, 45.2, 24.9, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.3.





6.2.4 Quenching with D₂O.

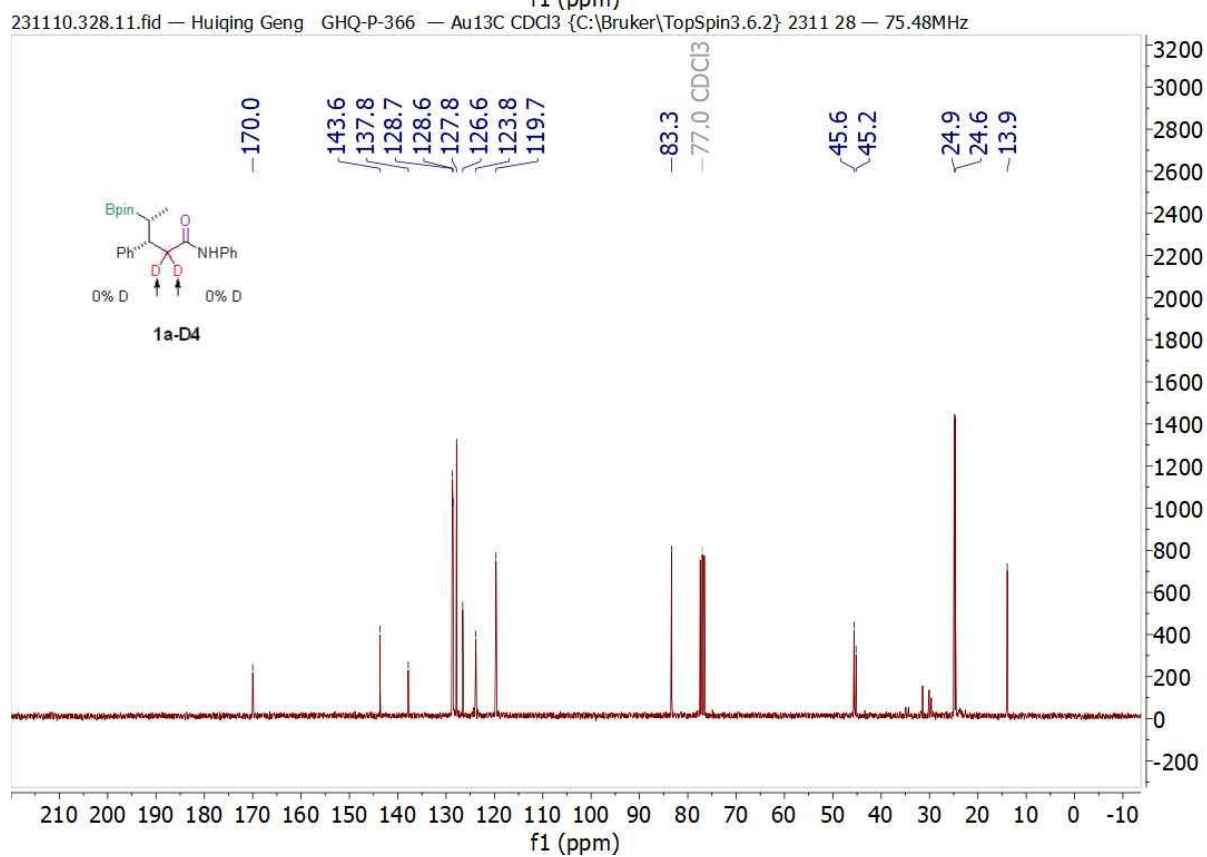
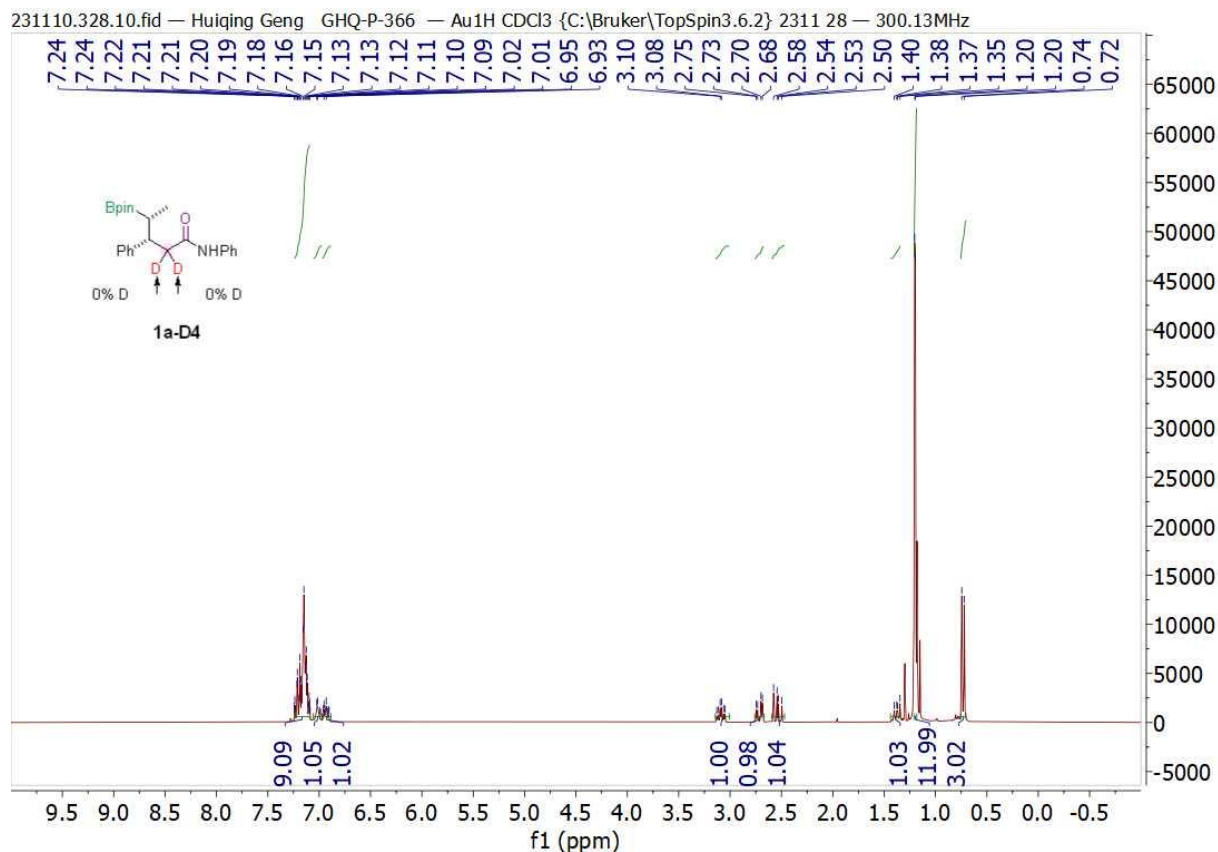


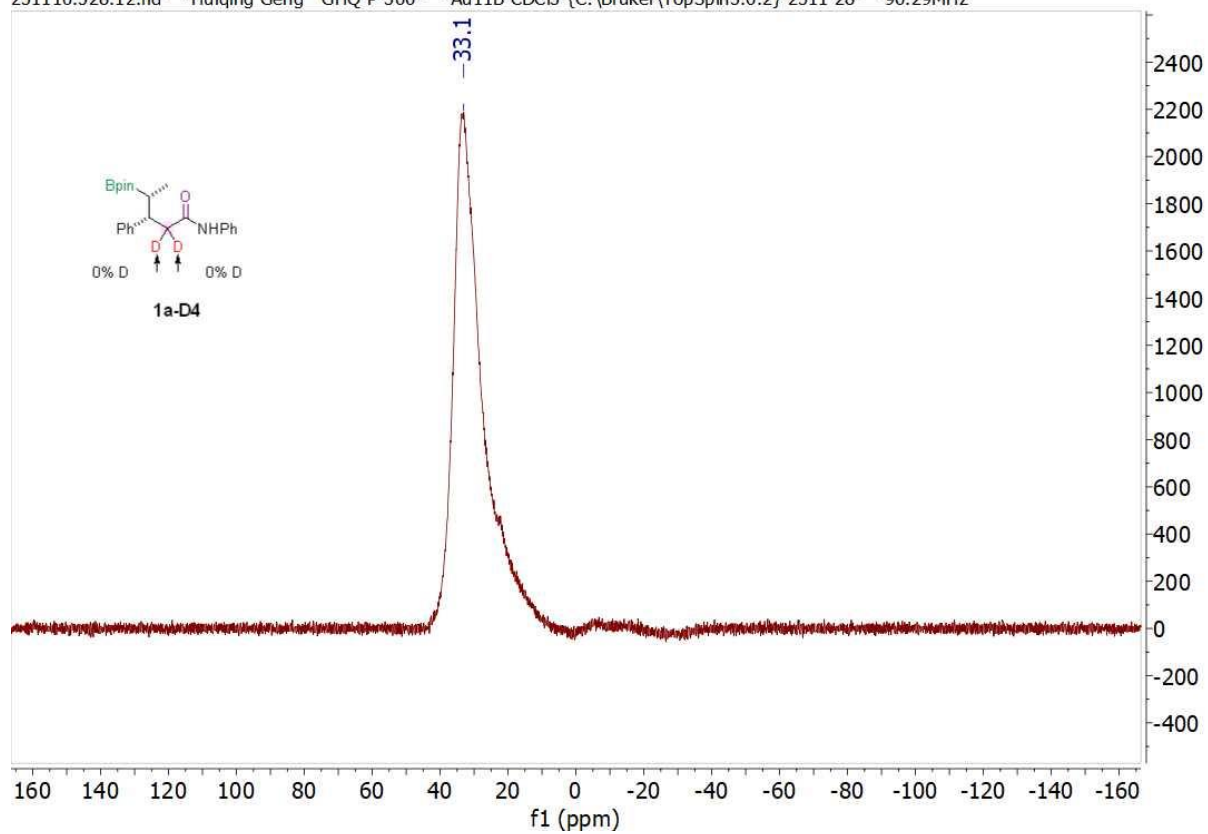
A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*- β -methylstyrene (0.2 mmol), aniline (2.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with D₂O (2 mL) and stirring for 5 minutes, then extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D4**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.)

¹H NMR (300 MHz, CDCl₃) δ 7.24 – 7.09 (m, 9H), 7.01 (dd, J = 8.4, 2.5 Hz, 1H), 6.97 – 6.88 (m, 1H), 3.09 (td, J = 10.1, 4.1 Hz, 1H), 2.72 (dd, J = 14.0, 4.2 Hz, 1H), 2.54 (dd, J = 14.0, 10.2 Hz, 1H), 1.37 (dd, J = 9.8, 7.3 Hz, 1H), 1.20 (d, J = 1.9 Hz, 12H), 0.73 (d, J = 7.4 Hz, 3H).

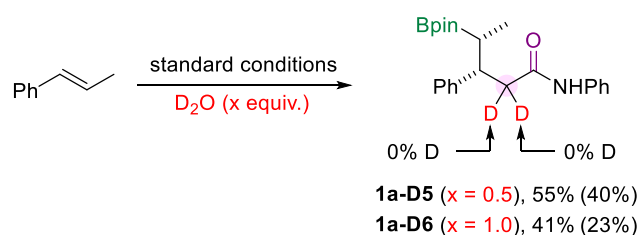
¹³C NMR (75 MHz, CDCl₃) δ 170.0, 143.6, 137.8, 128.7, 128.6, 127.8, 126.6, 123.8, 119.7, 83.3, 45.6, 45.2, 24.9, 24.6, 13.9.

¹¹B NMR (96 MHz, CDCl₃) δ 33.1.





6.2.5 Additional D₂O.



A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*- β -methylstyrene (0.2 mmol), aniline (2.5 equiv.), D₂O (0.5 equiv.) and DMSO (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D5**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.). The same procedure, but with 1.0 eq. of water, gives the product **1a-D6**.

1a-D5

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.14 (m, 7H), 7.06 – 6.90 (m, 2H), 3.16 (td, $J = 10.2$, 4.0 Hz, 1H), 2.80 (dd, $J = 14.0$, 4.1 Hz, 1H), 2.62 (dd, $J = 14.0$, 10.3 Hz, 1H), 1.49 – 1.42 (m, 1H), 1.29 (d, $J = 2.4$ Hz, 12H), 0.81 (d, $J = 7.4$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.0, 143.7, 137.8, 128.8, 128.6, 127.9, 126.6, 123.9, 119.7, 83.4, 45.7, 45.3, 24.9, 24.7, 14.0.

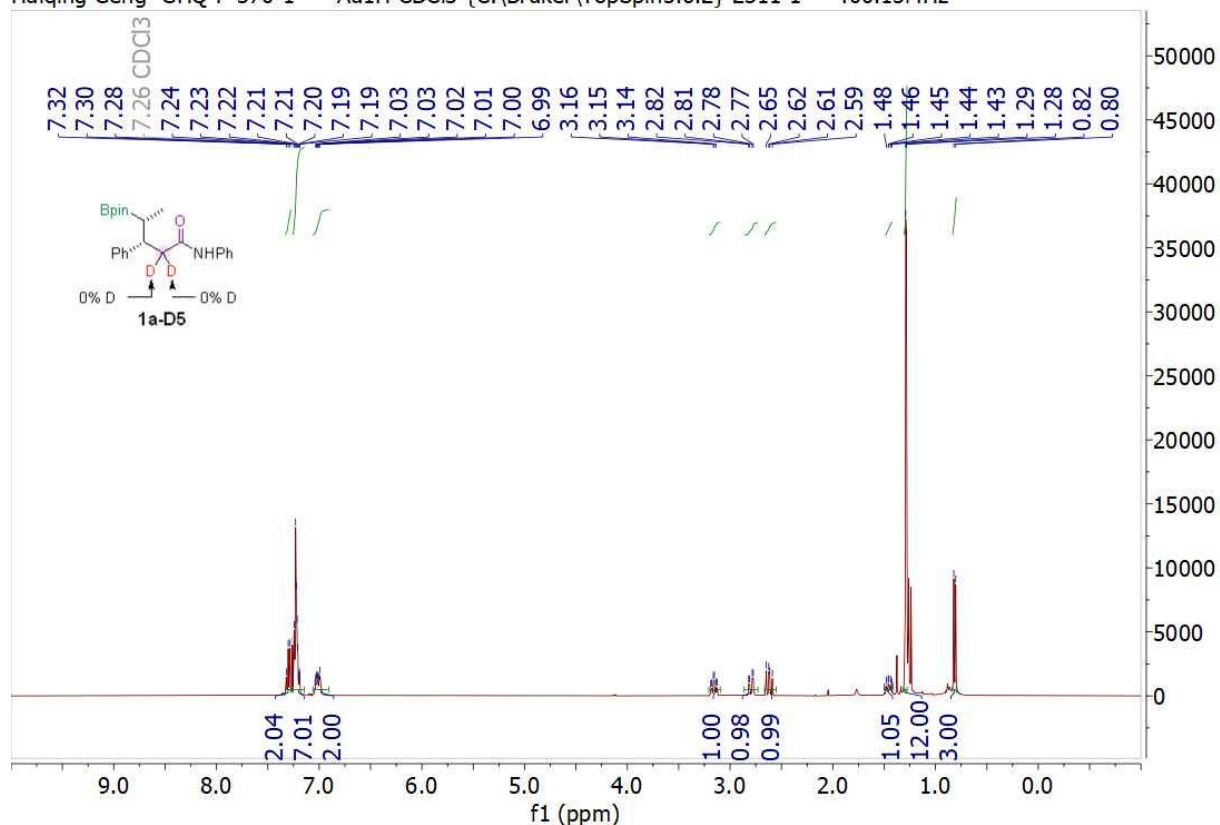
1a-D6

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.29 (m, 2H), 7.23 (t, $J = 5.2$ Hz, 7H), 7.02 (dt, $J = 8.6$, 4.2 Hz, 1H), 6.94 (s, 1H), 3.15 (td, $J = 10.2$, 4.0 Hz, 1H), 2.80 (dd, $J = 14.1$, 4.0 Hz, 1H), 2.62 (dd, $J = 14.0$, 10.3 Hz, 1H), 1.46 (dd, $J = 10.1$, 7.6 Hz, 1H), 1.29 (d, $J = 2.3$ Hz, 12H), 0.81 (d, $J = 7.4$ Hz, 3H).

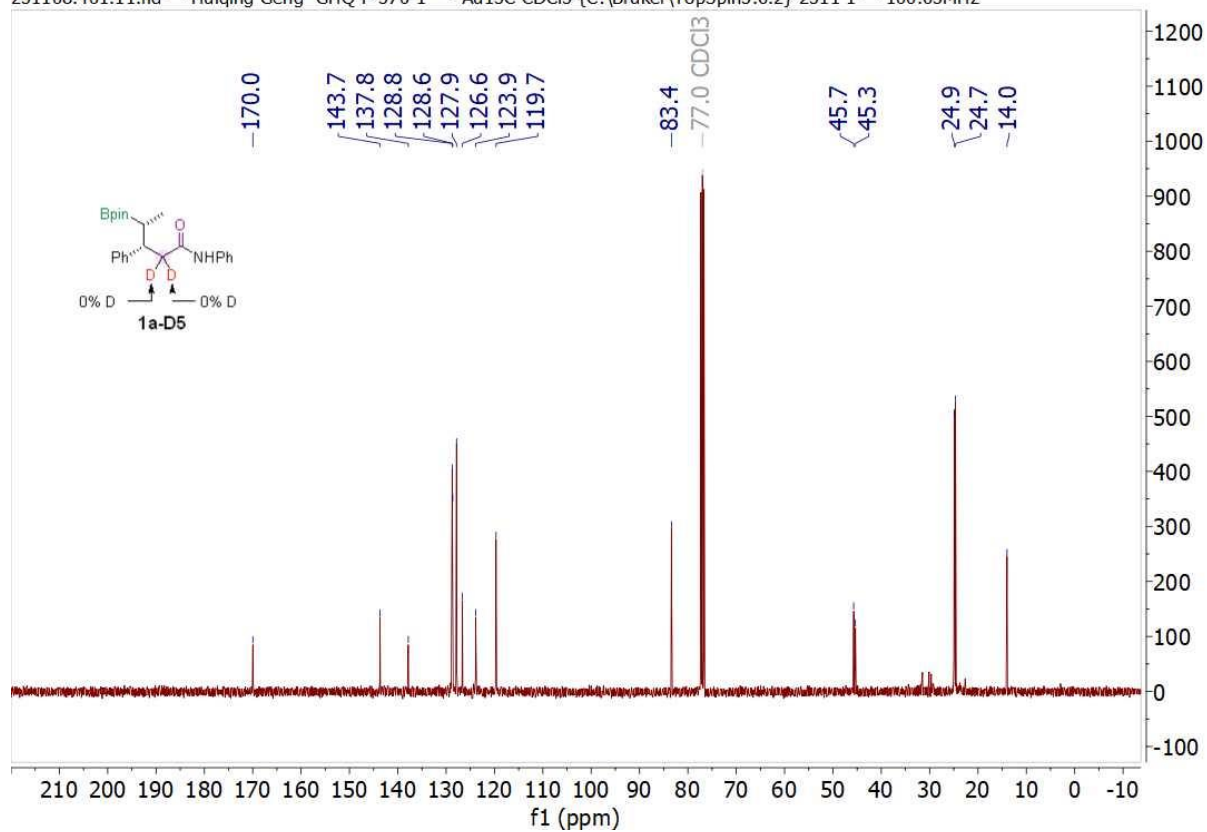
¹³C NMR (101 MHz, CDCl₃) δ 170.0, 143.7, 137.9, 128.8, 128.7, 127.9, 126.7, 124.0, 119.7, 83.5, 45.8, 45.4, 24.9, 24.7, 14.1.

¹¹B NMR (128 MHz, CDCl₃) δ 36.3.

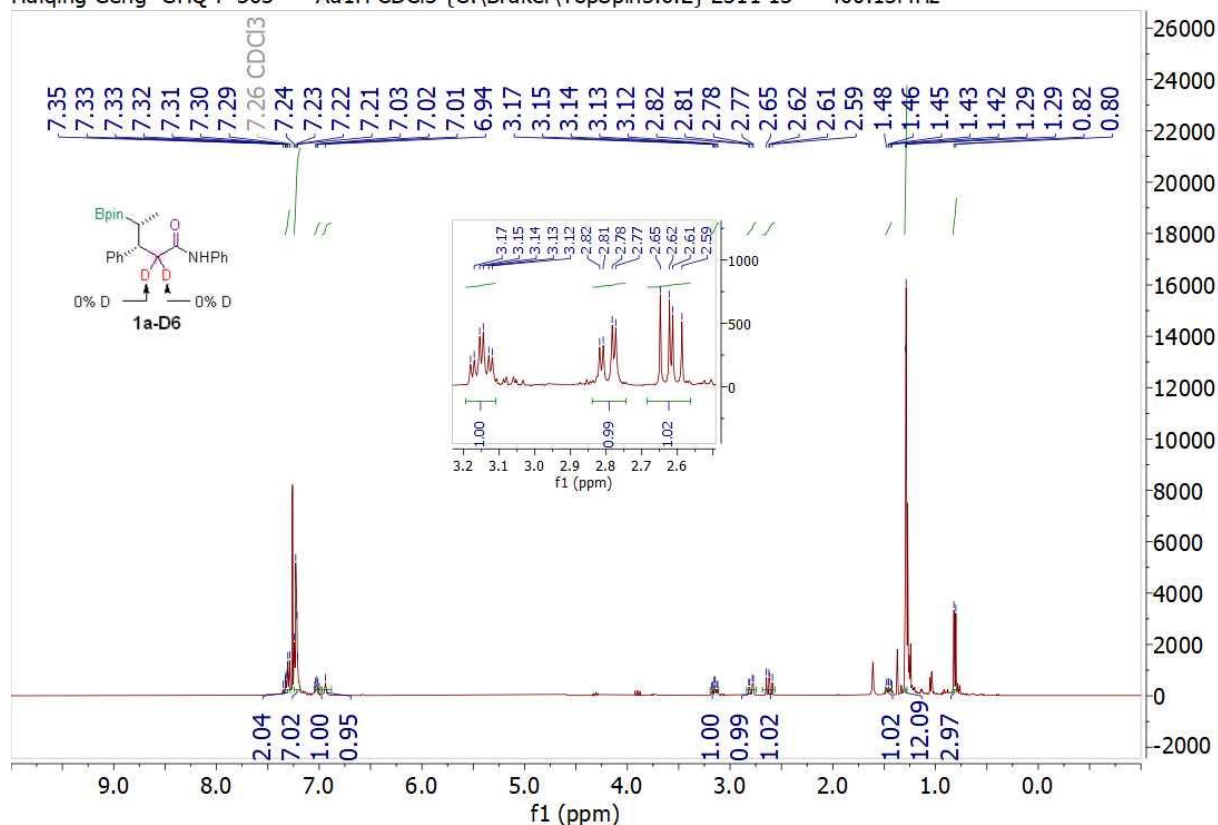
Huiqing Geng GHQ-P-370-1 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 1 — 400.13MHz



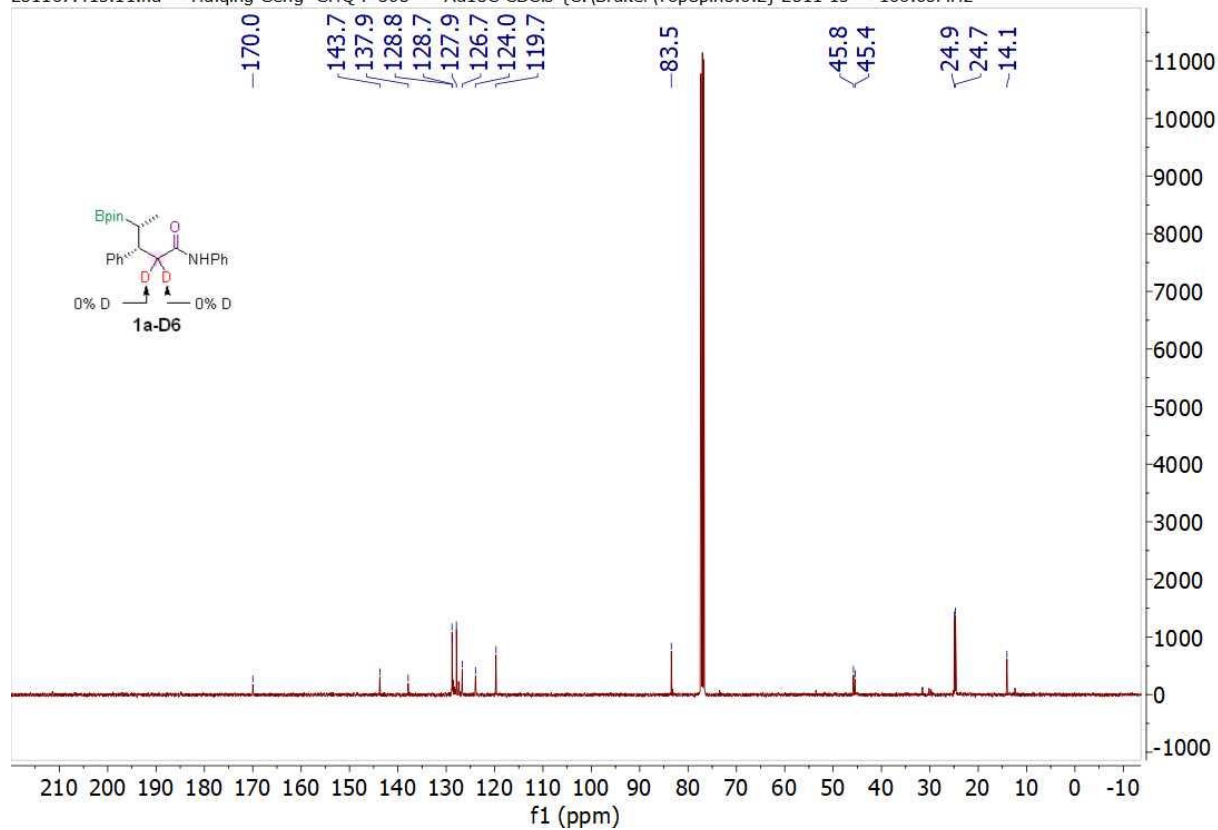
231108.401.11.fid — Huiqing Geng GHQ-P-370-1 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 1 — 100.63MHz

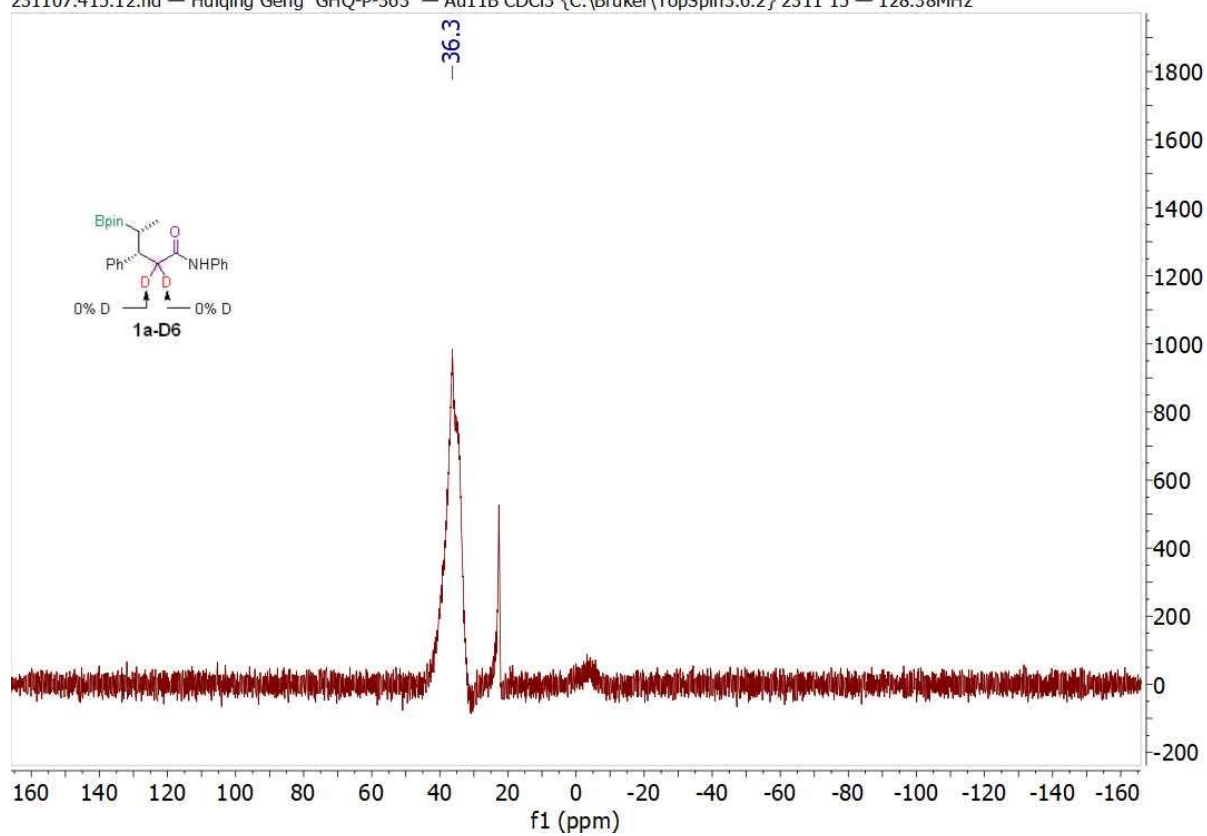


Huiqing Geng GHQ-P-363 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 15 — 400.13MHz

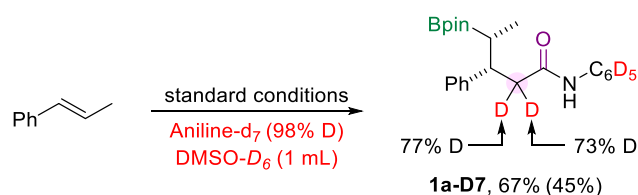


231107.415.11.fid — Huiqing Geng GHQ-P-363 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 15 — 100.63MHz





6.2.6 Mixed deuterated reagents of aniline- d_7 and DMSO- d_6 .

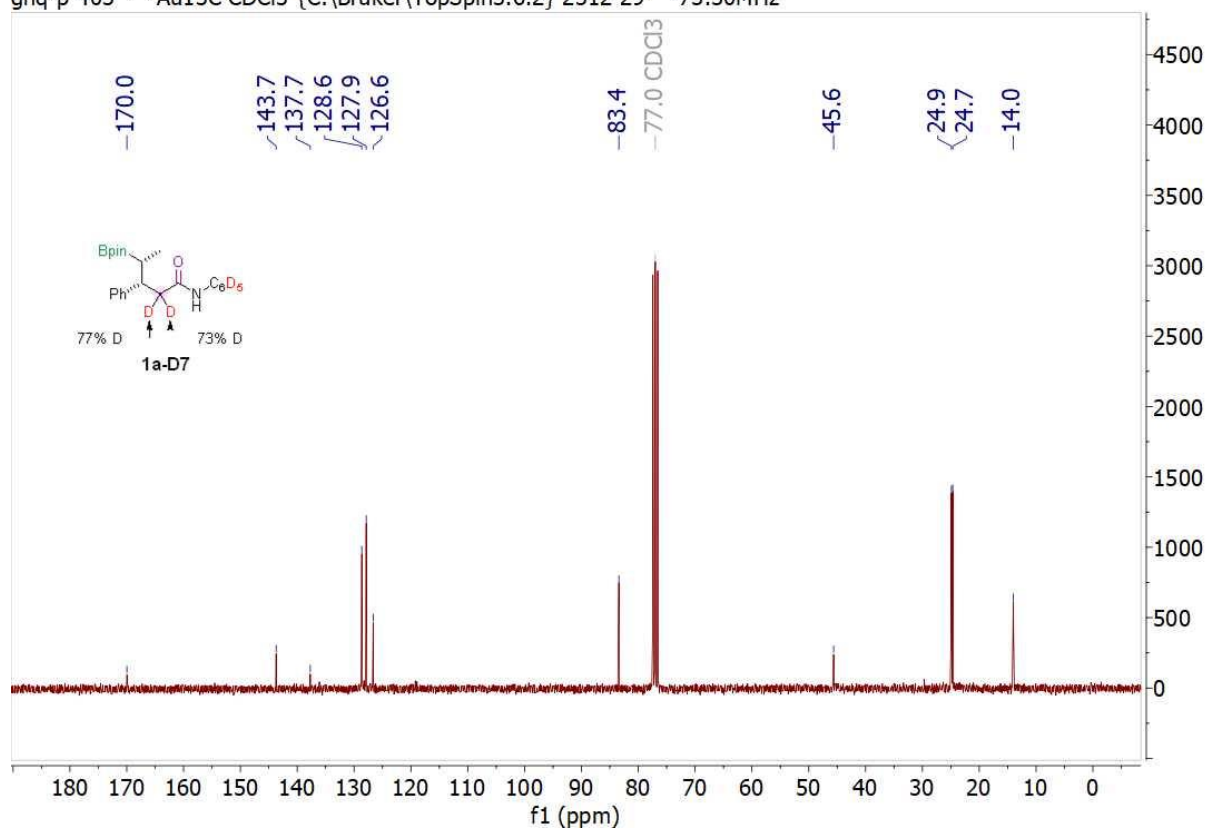
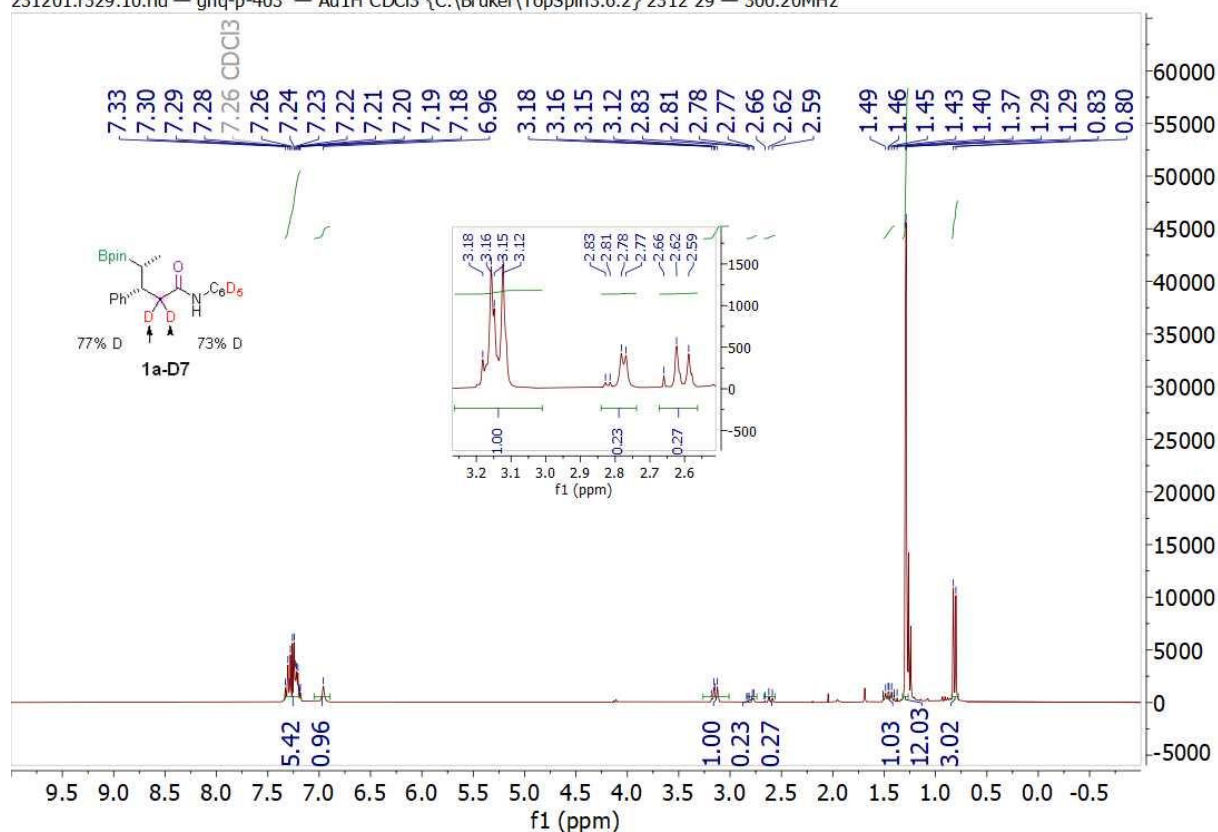


A dried vial (4 mL) was charged with $Cu(OAc)_2$ (5 mol%), DPPE (5 mol%), B_2pin_2 (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*- β -methylstyrene (0.2 mmol), aniline- d_7 (2.5 equiv.), and DMSO- d_6 (1.0 mL) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N_2 and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that the corresponding product (**1a-D7**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na_2SO_4 , an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.).

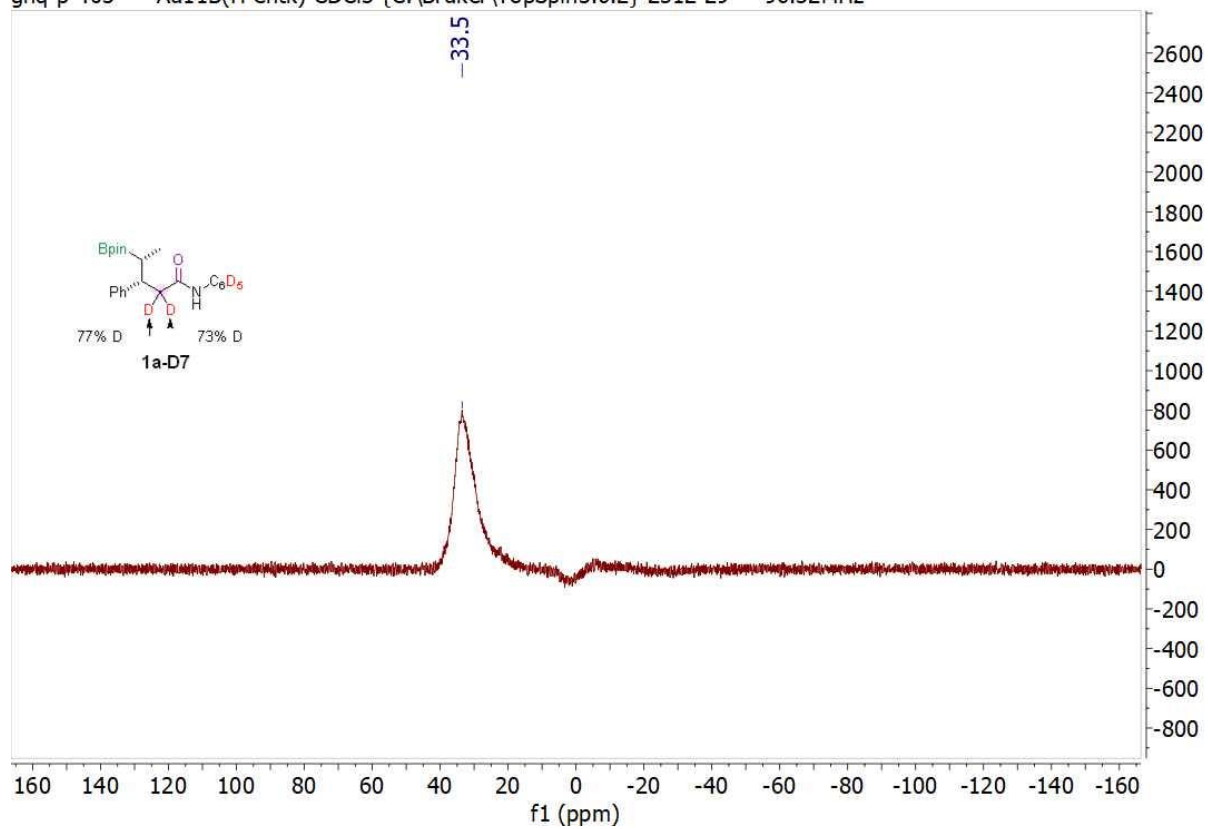
1H NMR (300 MHz, $CDCl_3$) δ 7.25 (ddt, $J = 15.1, 11.1, 7.1$ Hz, 5H), 6.96 (s, 1H), 3.15 (dd, $J = 10.0, 7.4$ Hz, 1H), 1.51 – 1.40 (m, 1H), 1.29 (d, $J = 1.5$ Hz, 12H), 0.81 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 143.7, 137.7, 128.6, 127.9, 126.6, 83.4, 45.6, 24.9, 24.7, 14.0.

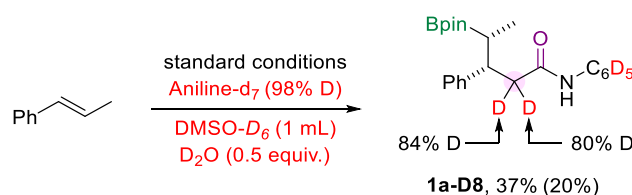
^{11}B NMR (96 MHz, $CDCl_3$) δ 33.5.



ghq-p-403 — Au11B(H-entk) CDCl3 {C:\Bruker\TopSpin3.6.2} 2312 29 — 96.32MHz



6.2.7 Mixed deuterated reagents of aniline-*d*₇, DMSO-*d*₆, and D₂O.



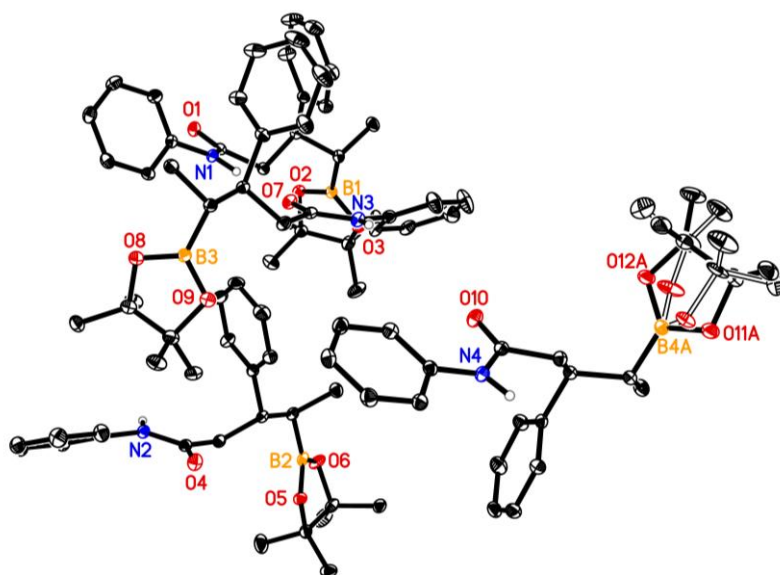
A dried vial (4 mL) was charged with Cu(OAc)₂ (5 mol%), DPPE (5 mol%), B₂pin₂ (3.5 equiv.), and a stirring bar. When the NaOEt (2.75 equiv.) is added, the vial was sealed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap immediately. The vial was evacuated under vacuum and recharged with argon for three times with a needle. Then, *trans*-β-methylstyrene (0.2 mmol), aniline-*d*₇ (2.5 equiv.), DMSO-*d*₆ (1.0 mL) and D₂O (0.5 equiv.) were added under argon by using a syringe. The vial (or several vials) was placed in an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. The autoclave was charged with CO (10 bar) after flushing two times with N₂ and two times with CO. The autoclave was then placed into an aluminum block on a magnetic stirrer. The reaction was performed for 20 h at 60 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction was quenched with water (2 mL) and extracted with EtOAc (2 mLx3). The organic layer was washed with water (10 mL) and dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. After that the corresponding product (**1a-D8**) was afforded as white solid by directly purified by fast column chromatography. (For NMR yield: The organic layer was washed with water and 0.1 mmol of 1,3,5-trimethoxybenzene was added. After drying with anhydrous Na₂SO₄, an appropriate amount of organic layer was concentrated under reduced pressure to test the NMR yield.).

¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 6.93 (s, 1H), 3.13 (d, *J* = 10.1 Hz, 1H), 1.46 (dd, *J* = 10.1, 7.5 Hz, 1H), 1.29 (d, *J* = 1.5 Hz, 12H), 0.81 (d, *J* = 7.4 Hz, 3H).

7. X-ray crystal analysis of 1a.

1a

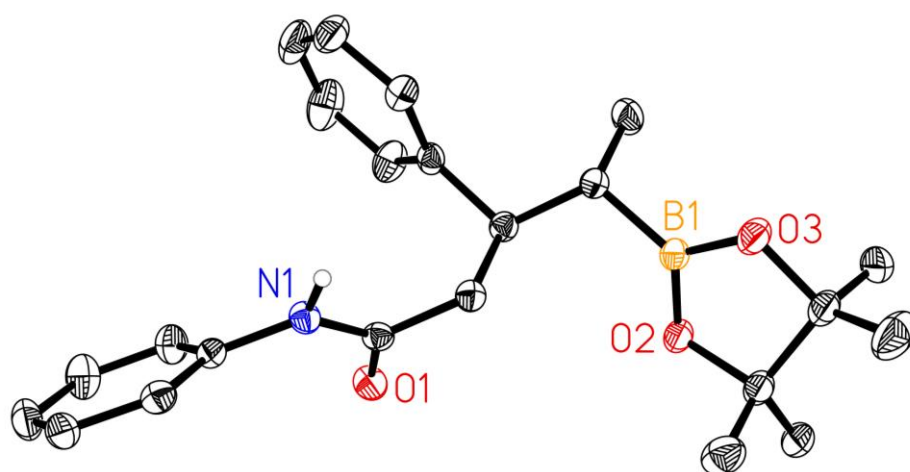
Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2019: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations. CCDC 2283170 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.



Molecular structure of **1a**. Displacement ellipsoids correspond to 30% probability. The pinacol boronic esters (tetramethyl-1,3,2-dioxaborolanes or “Bpin esters” for short) unit of one molecule is disordered over two sites with occupancies of 0.675(3):0.325(3). The lower occupied unit is shown with unfilled bonds. C-bound hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Details

chemical formula	C ₂₃ H ₃₀ BNO ₃
formula weight	379.29
crystal system	triclinic
unit cell dimensions	
<i>a</i> [Å]	13.6717(12)
<i>b</i> [Å]	16.5727(14)
<i>c</i> [Å]	19.6345(17)
<i>a</i> [deg]	85.336(2)
<i>b</i> [deg]	85.800(2)
<i>g</i> [deg]	78.852(2)
<i>V</i> [Å ³]	4342.8(7)
<i>T</i> [K]	110(2)
space group	$P\bar{1}$
<i>Z</i>	8
<i>m</i> [mm ⁻¹]	0.075
density [g/cm ³]	1.160
no. of reflections measured	140929
no. of independent reflections	20961 ($R_{\text{int}} = 0.0378$)
no. of observed reflections ($I > 2\sigma(I)$)	16120
no. of parameters	1105
R_1 ($I > 2s(I)$)	0.0561
wR_2 (all data)	0.1572
Goodness of fit on F^2	1.025
largest diff. peak and hole [e/Å ³]	1.425 and -0.373



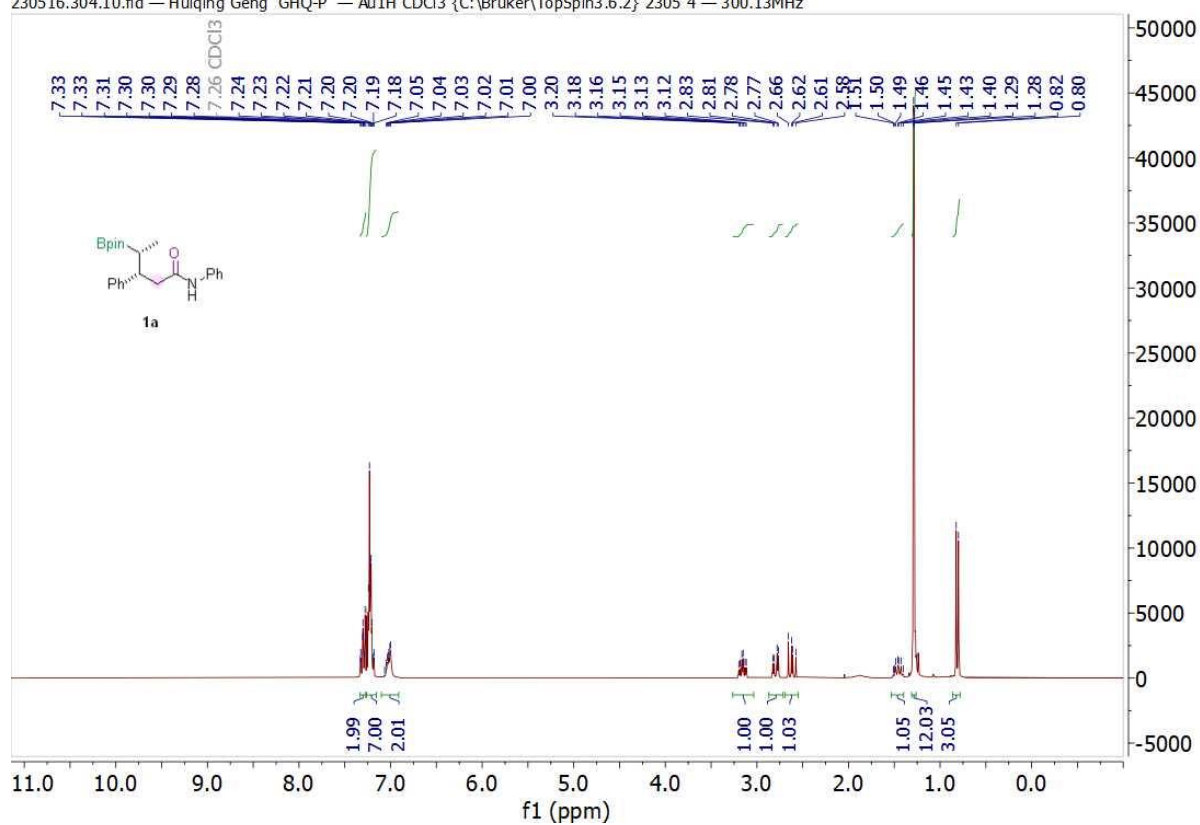
Molecular structure of one molecule of the asymmetric unit of **1a**. Displacement ellipsoids correspond to 50% probability. C-bound hydrogen atoms are omitted for clarity.

8. References.

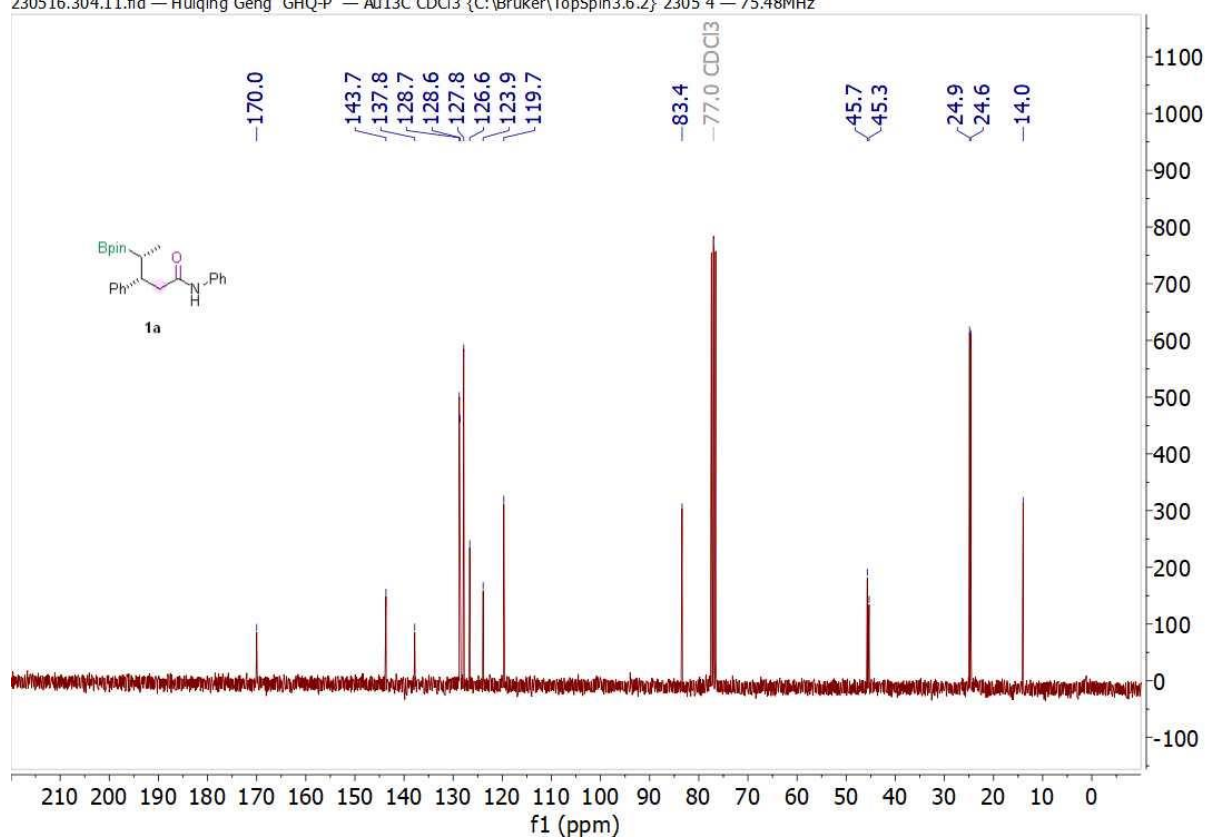
- (1) C. N. Farthing, S. P. Marsden, *Tetrahedron Lett.* **2000**, *41*, 4235-4238.
- (2) R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott, V. K. Aggarwal, *Angew. Chem., Int. Ed.* **2011**, *50*, 3760-3763.
- (3) M. Wang, H. Yu, X. You, J. Wu, Z. Shang, *Chin. J. Chem.* **2012**, *30*, 2356-2362.
- (4) D. L. Sandrock, L. Jean-Gérard, C.-Y. Chen, S. D. Dreher, G. A. Molander, *J. Am. Chem. Soc.* **2010**, *132*, 17108-17110.

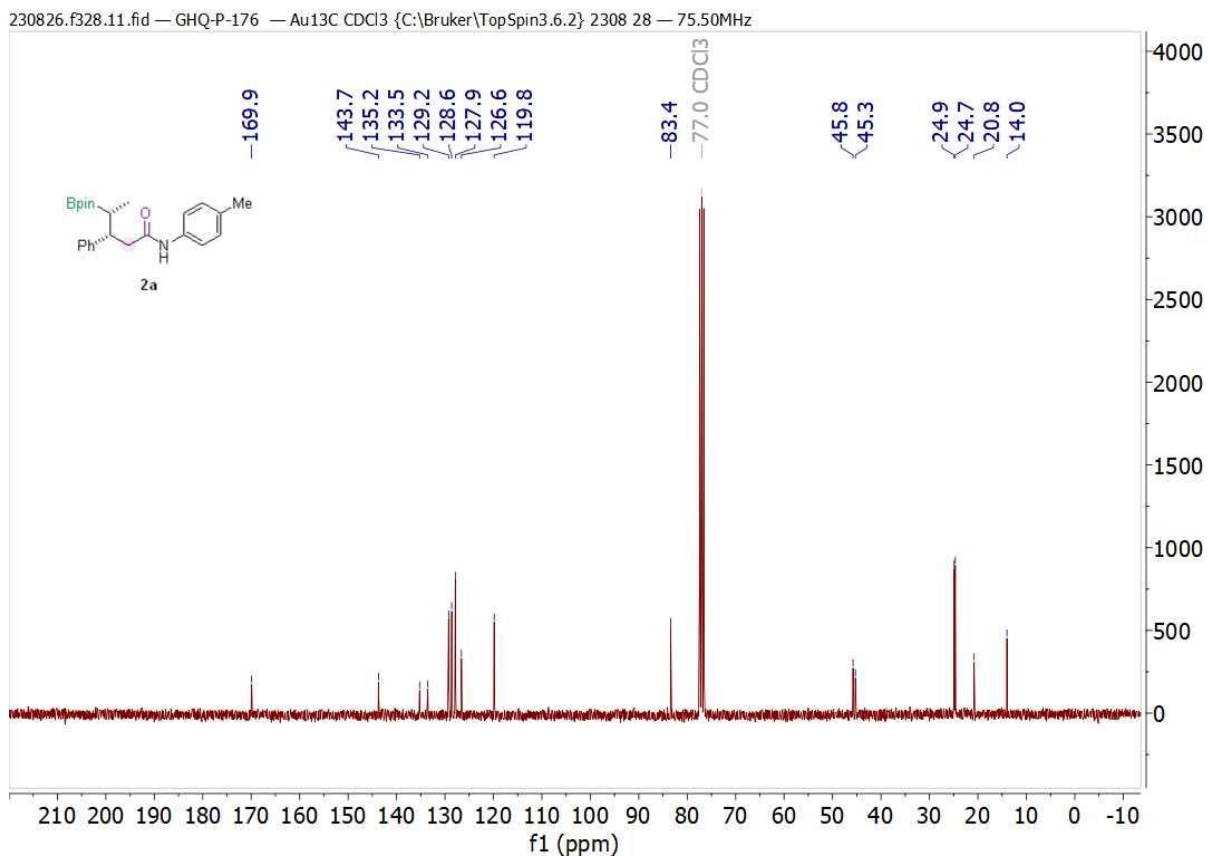
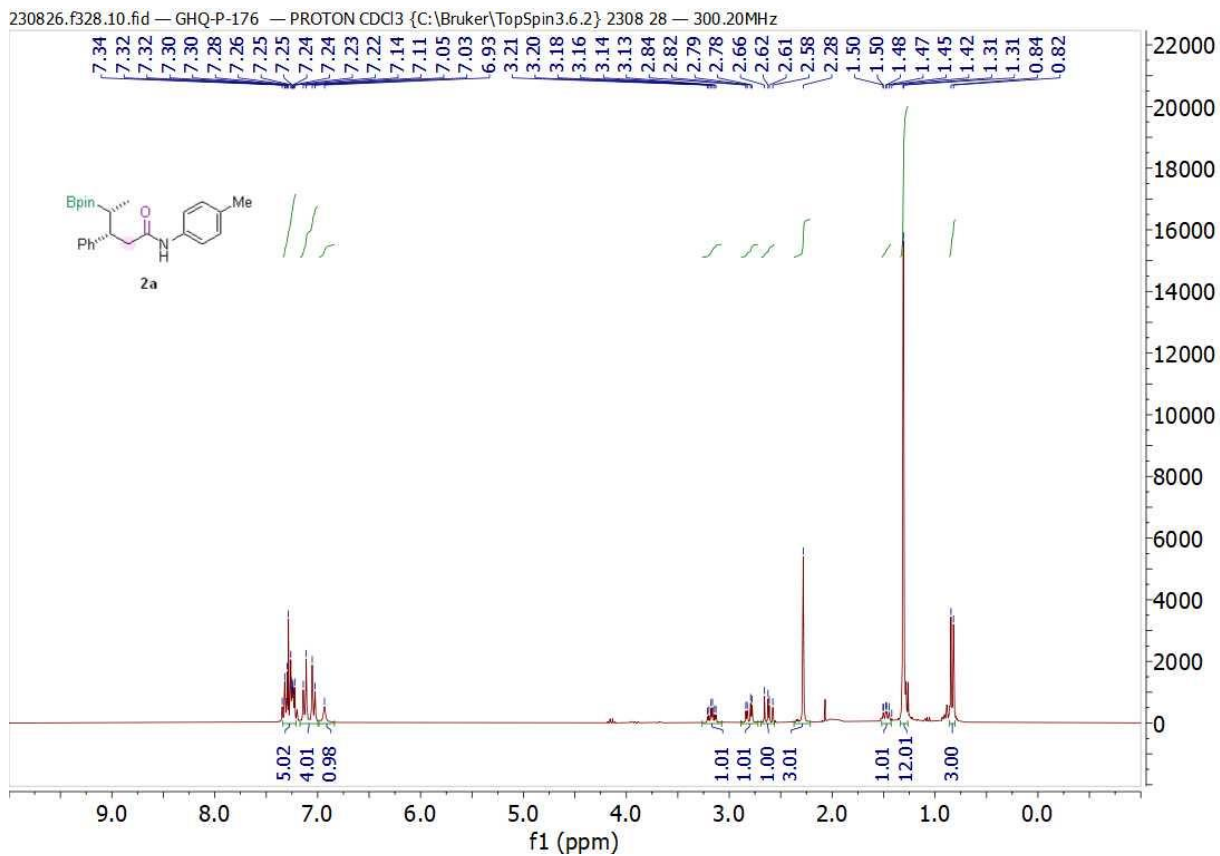
9. NMR spectra

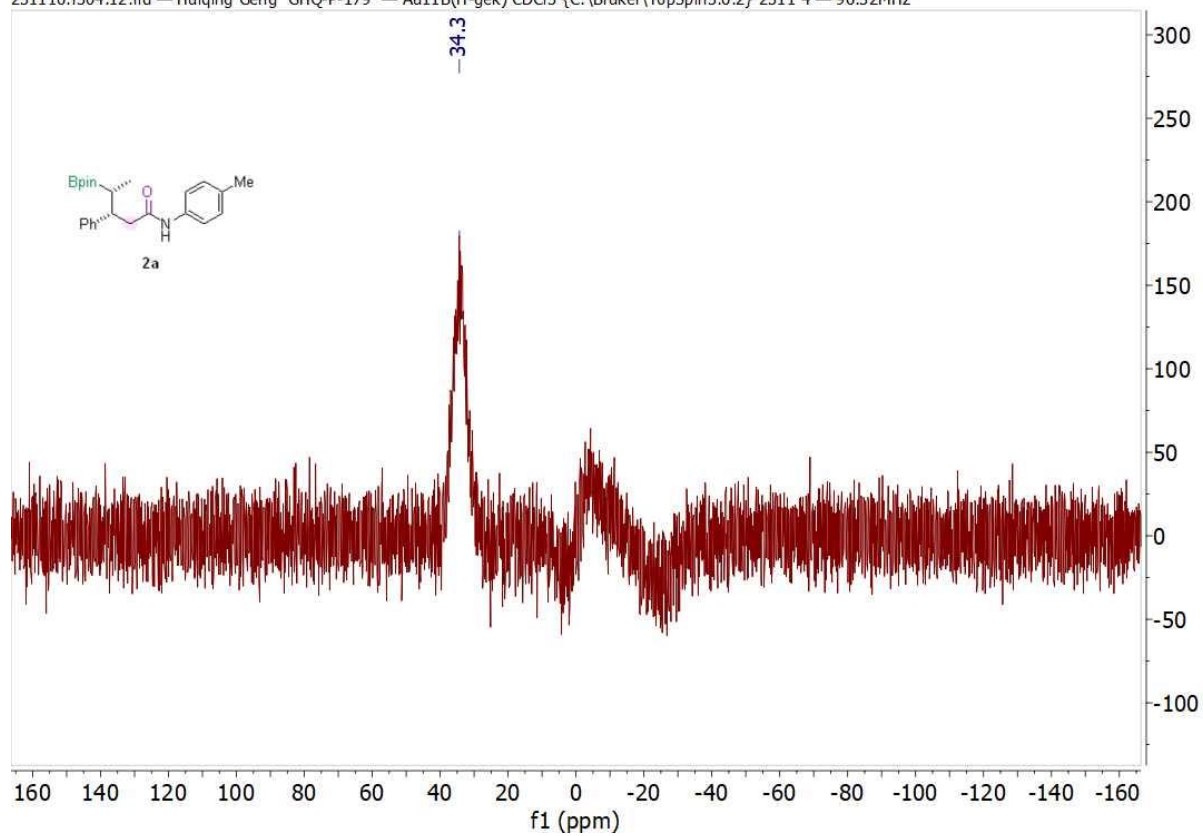
230516.304.10.fid — Huiqing Geng GHQ-P — Au1H CDCl₃ {C:\Bruker\TopSpin3.6.2} 2305 4 — 300.13MHz

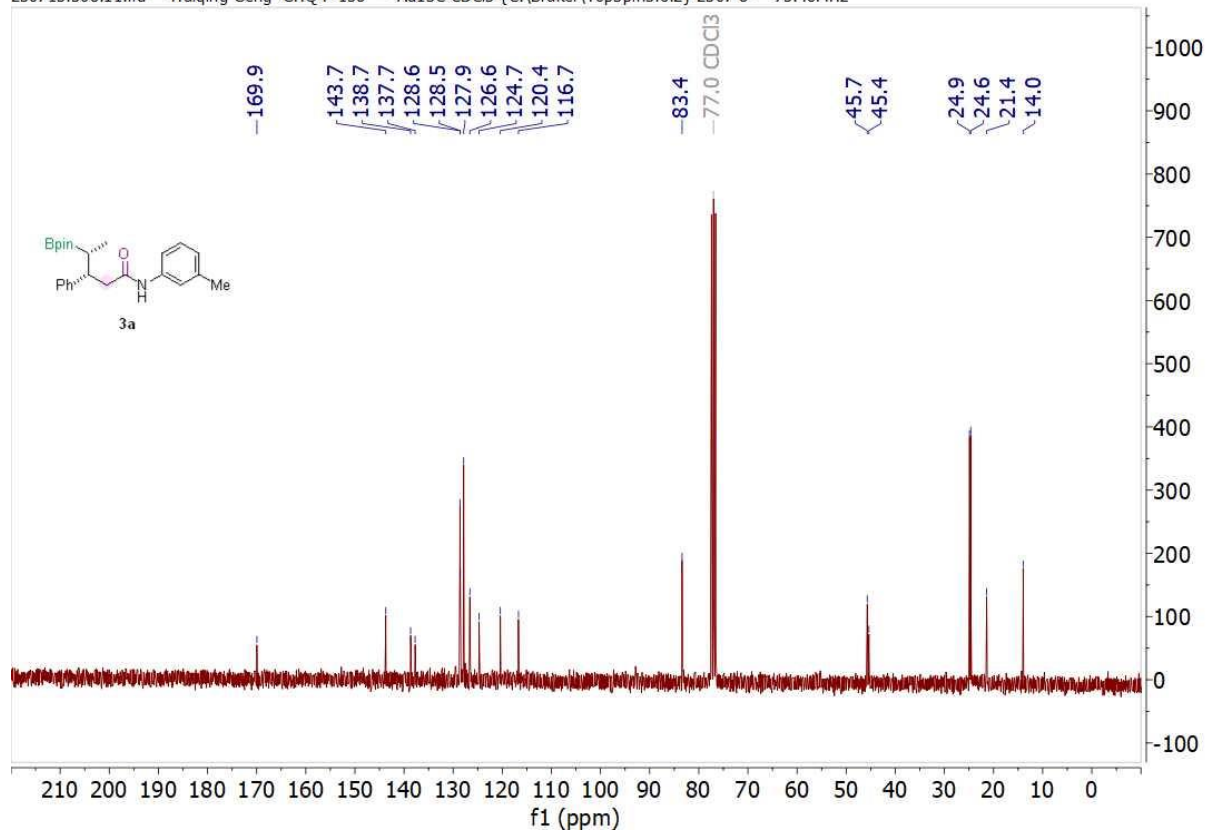
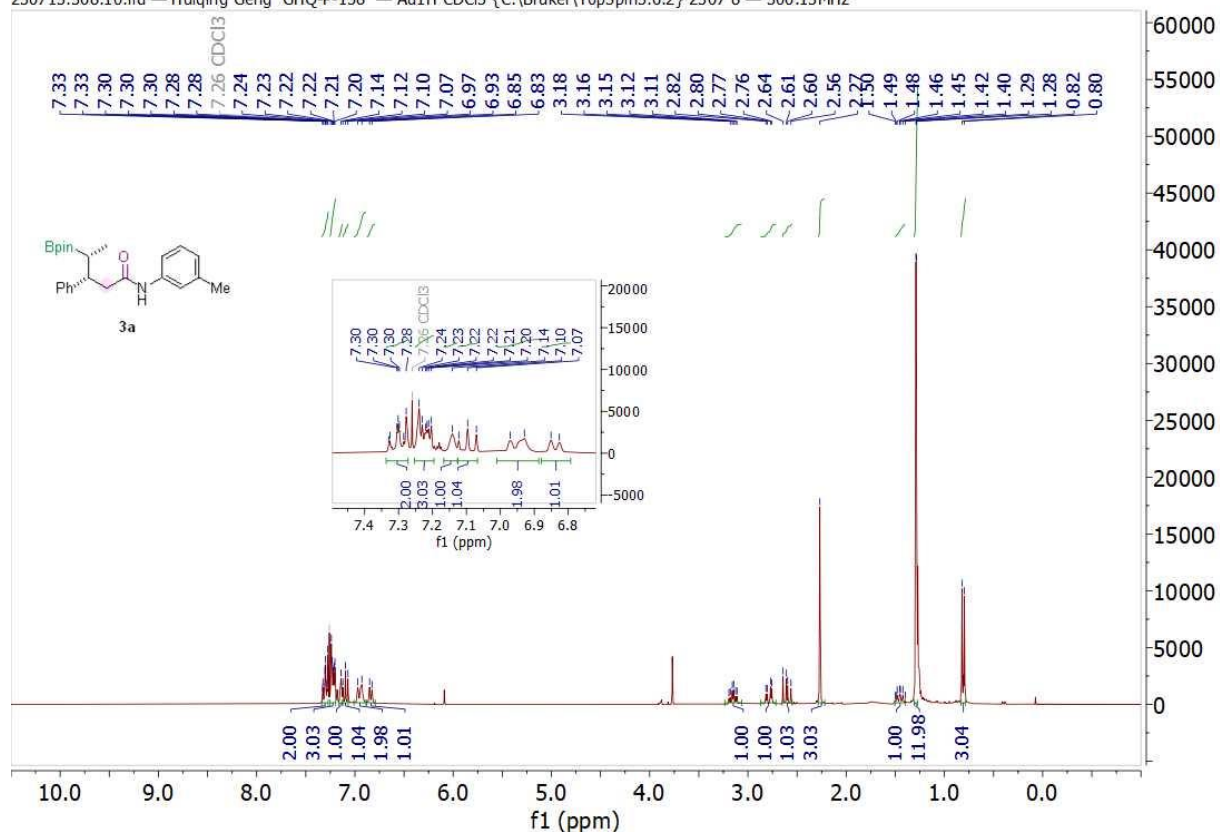


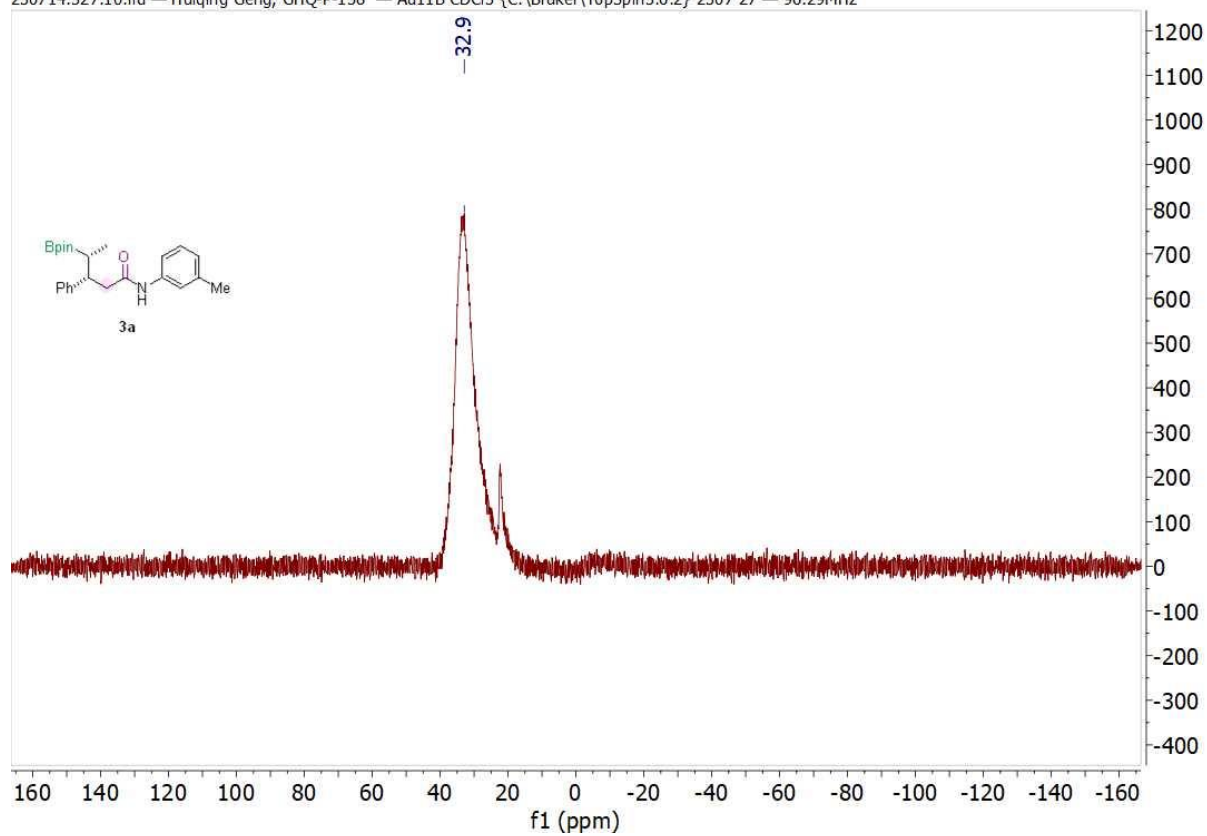
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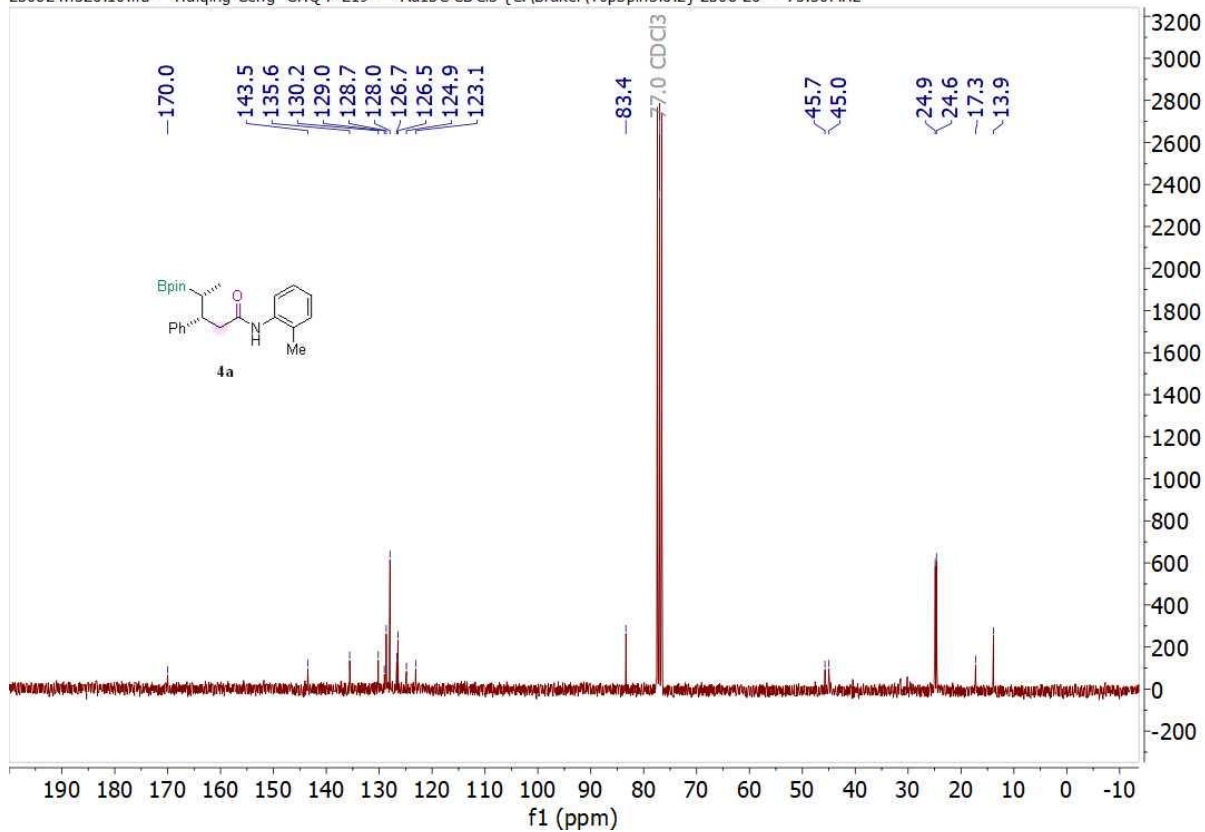
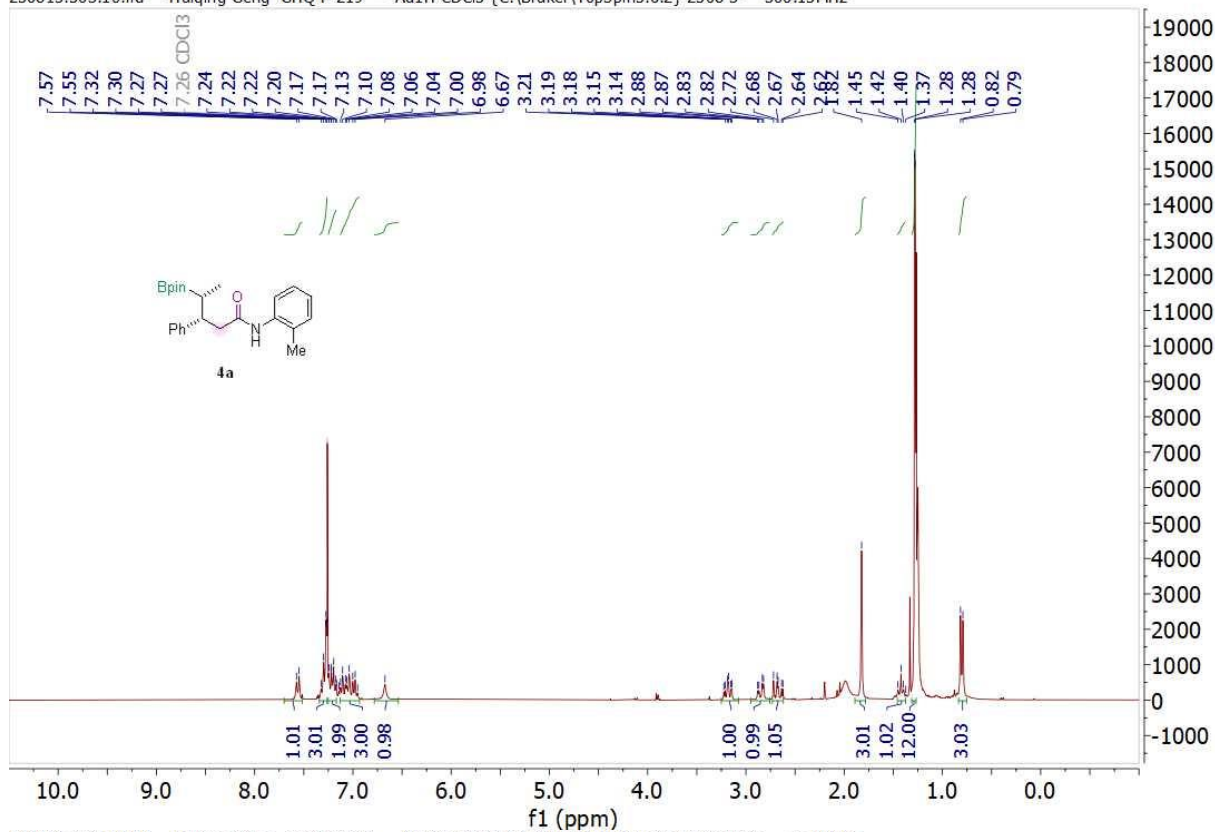


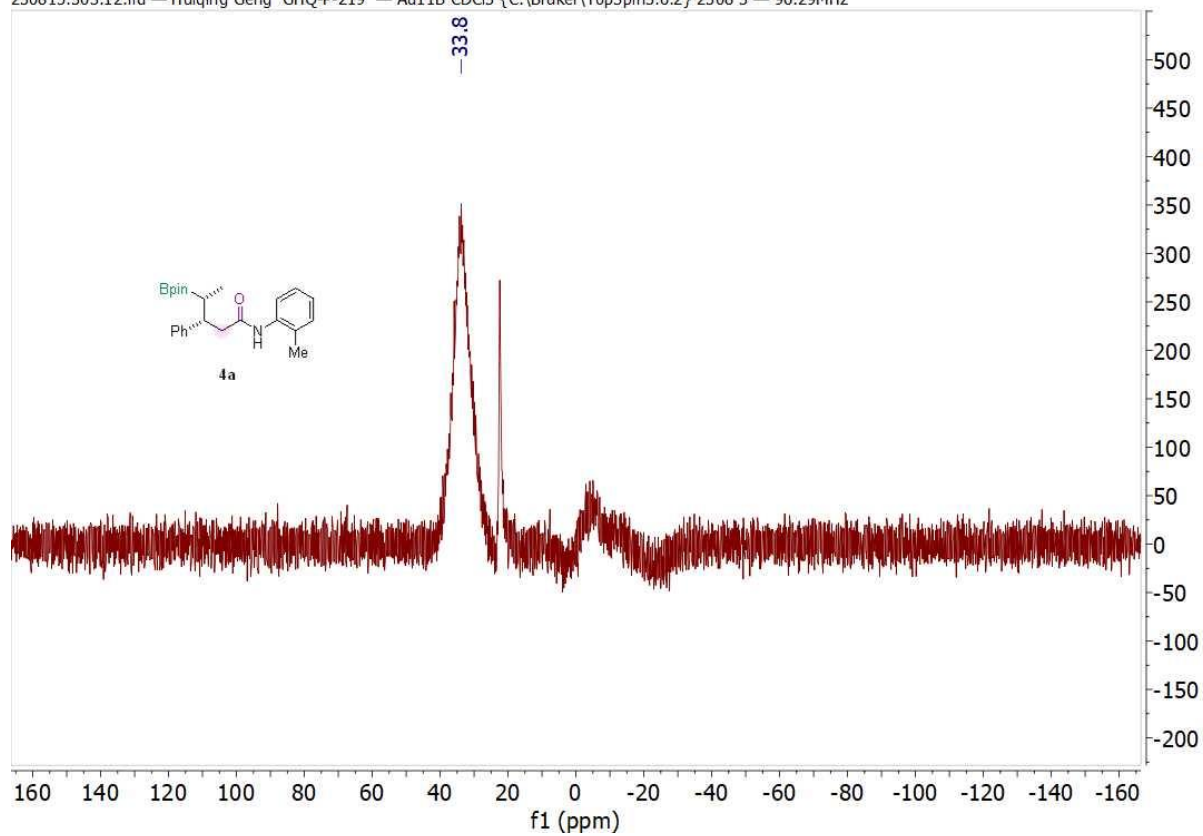


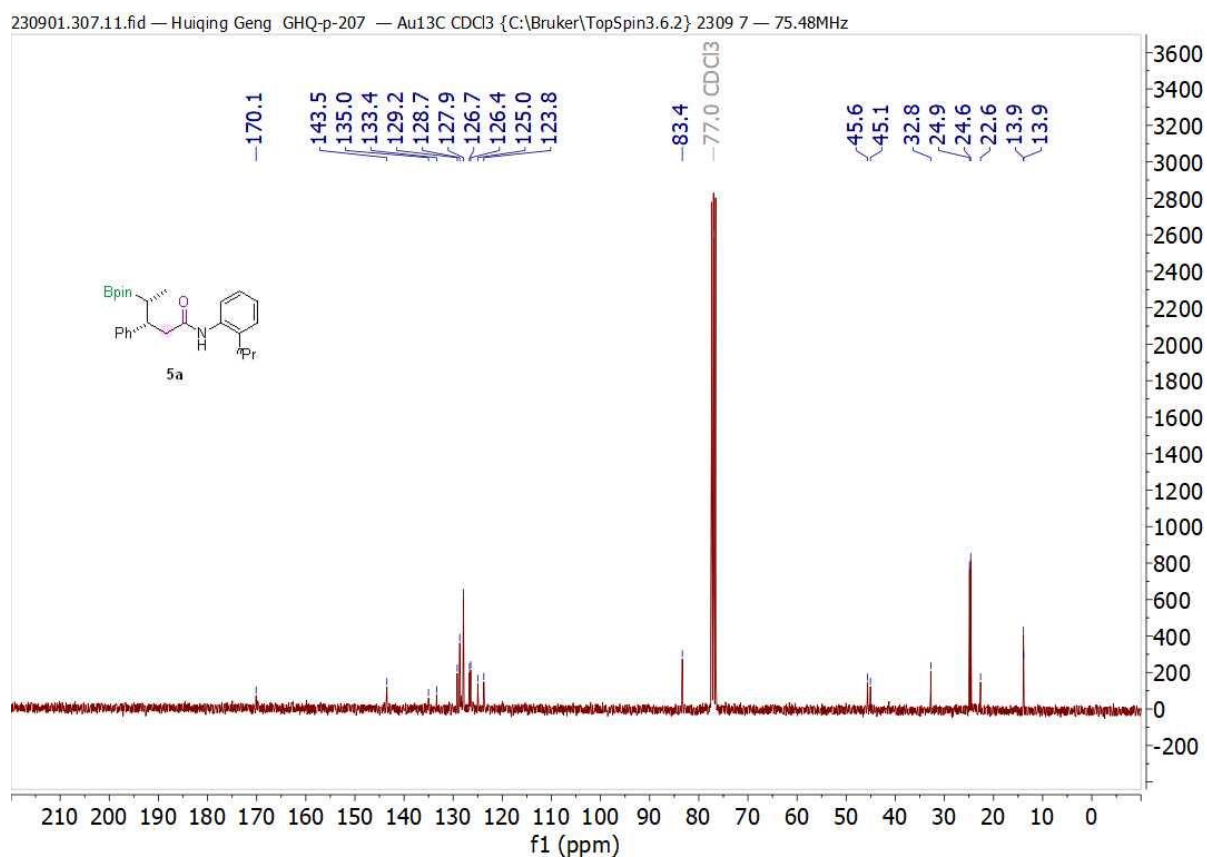
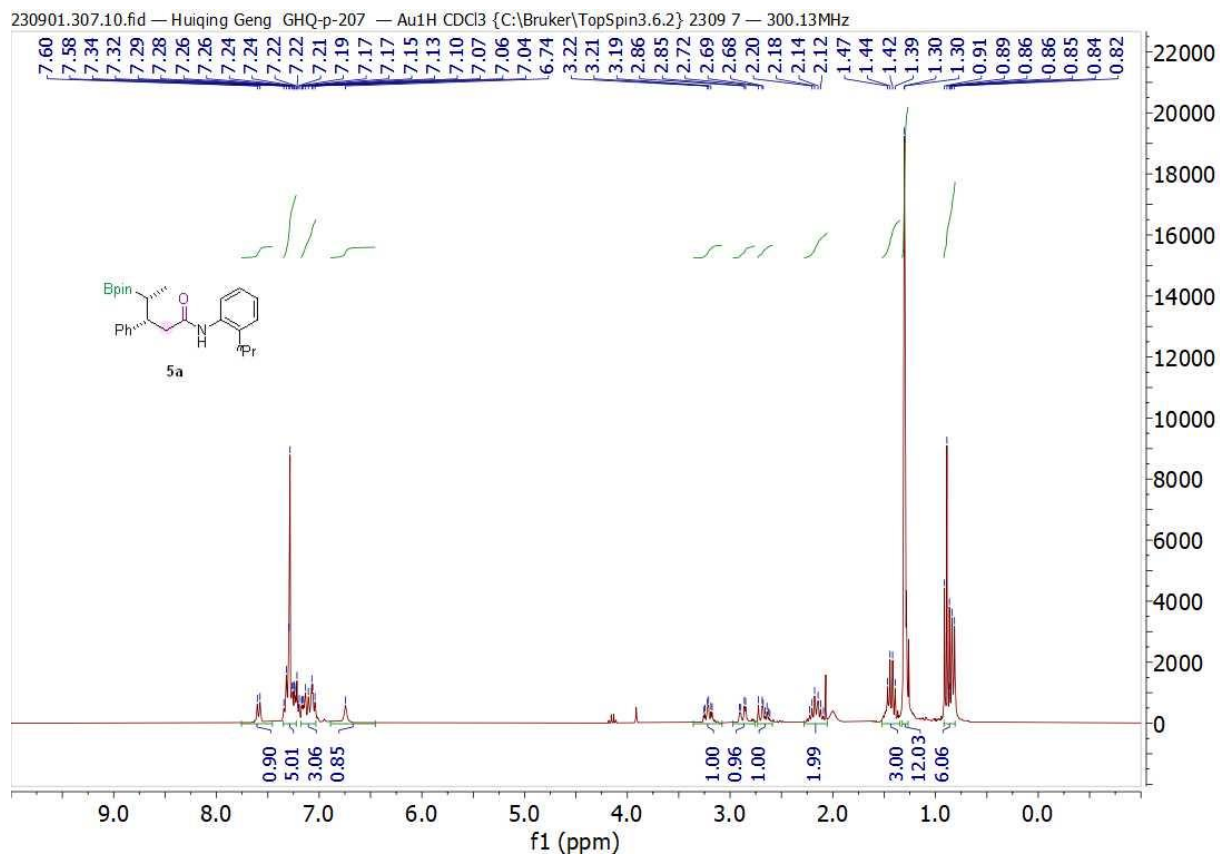


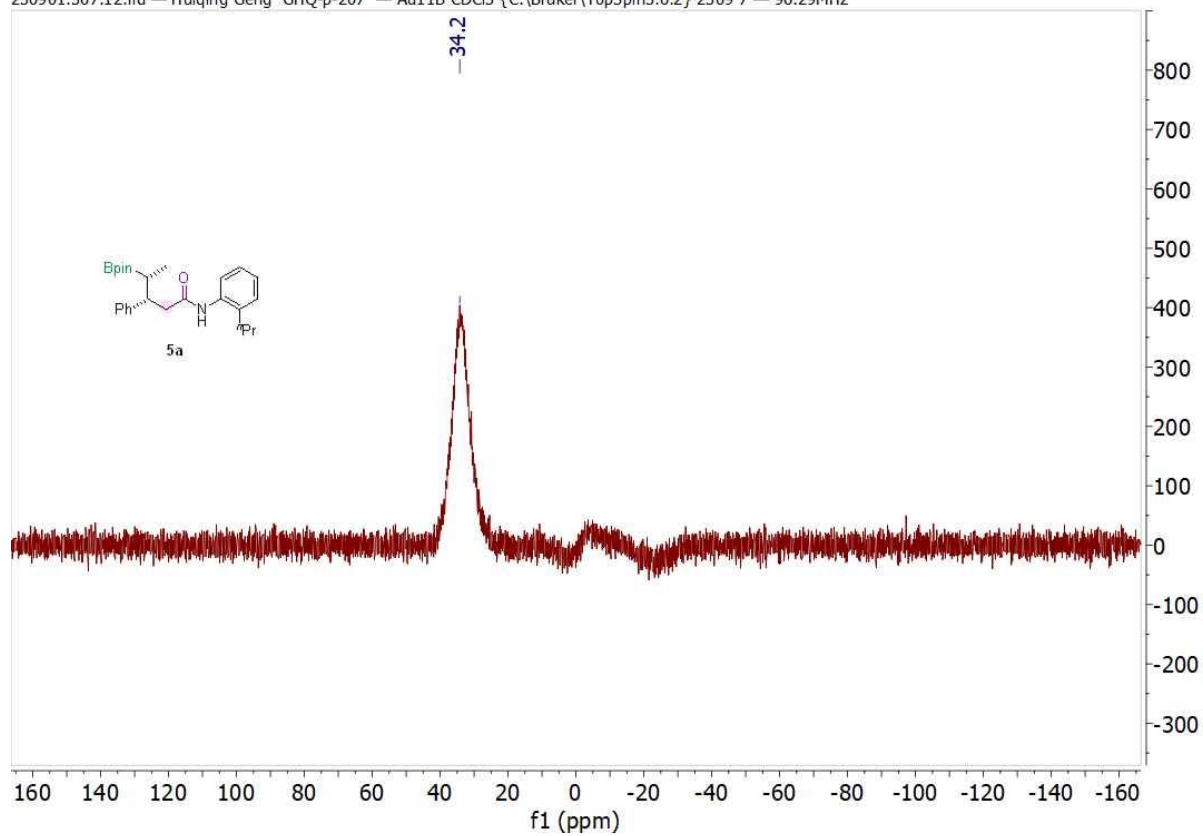


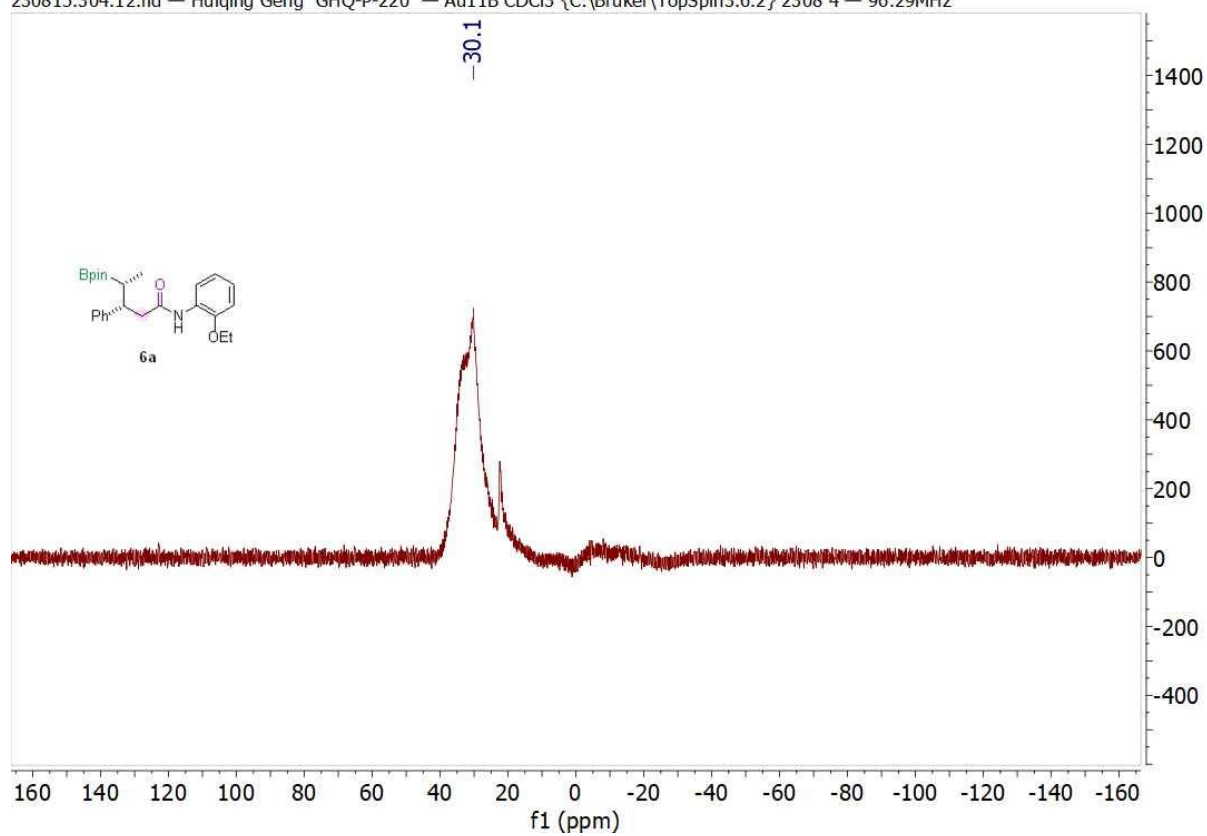


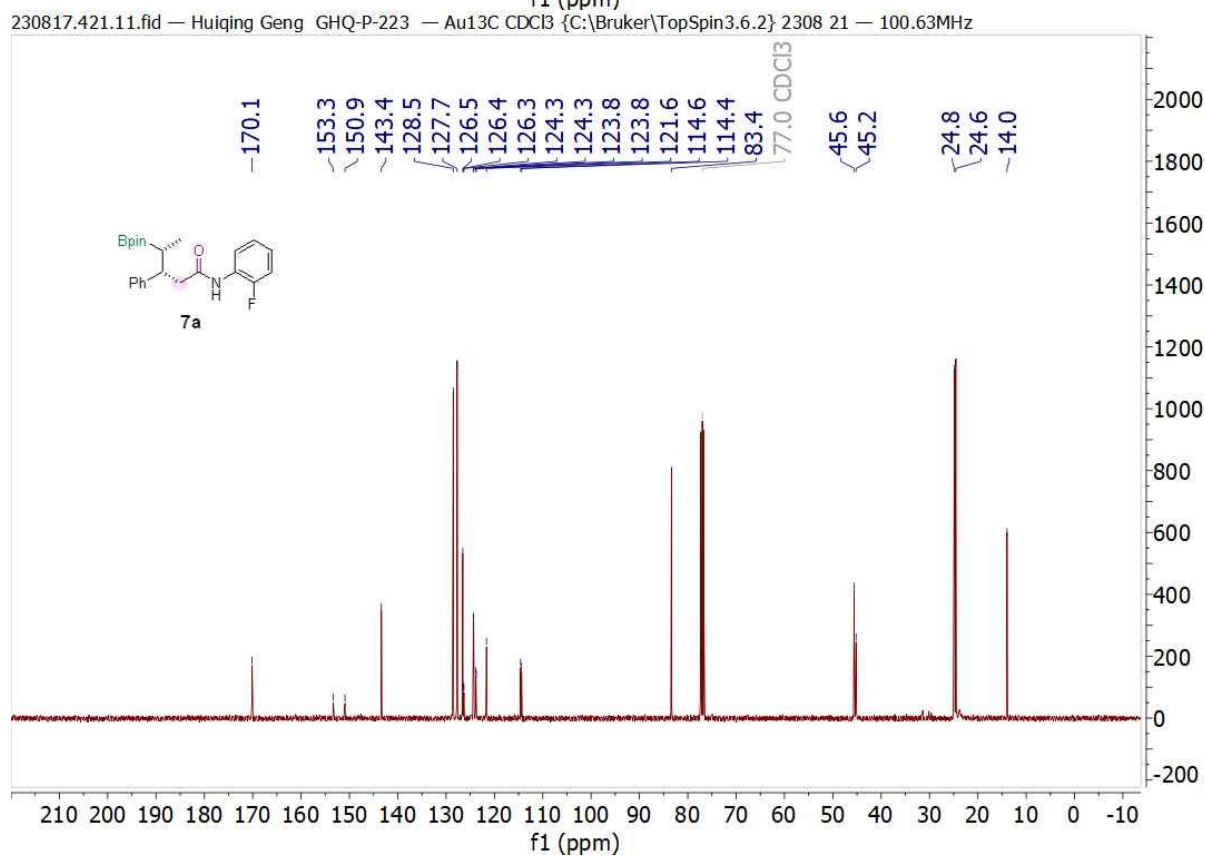
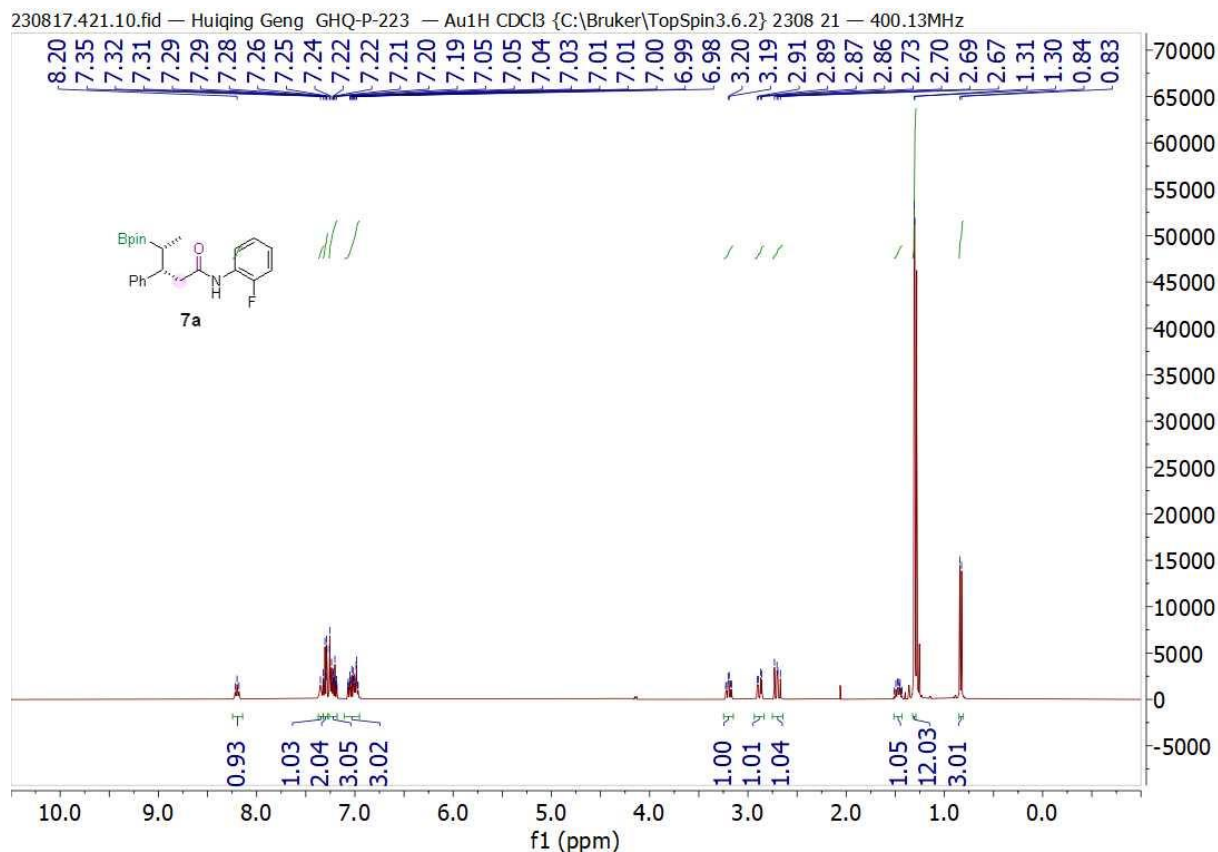




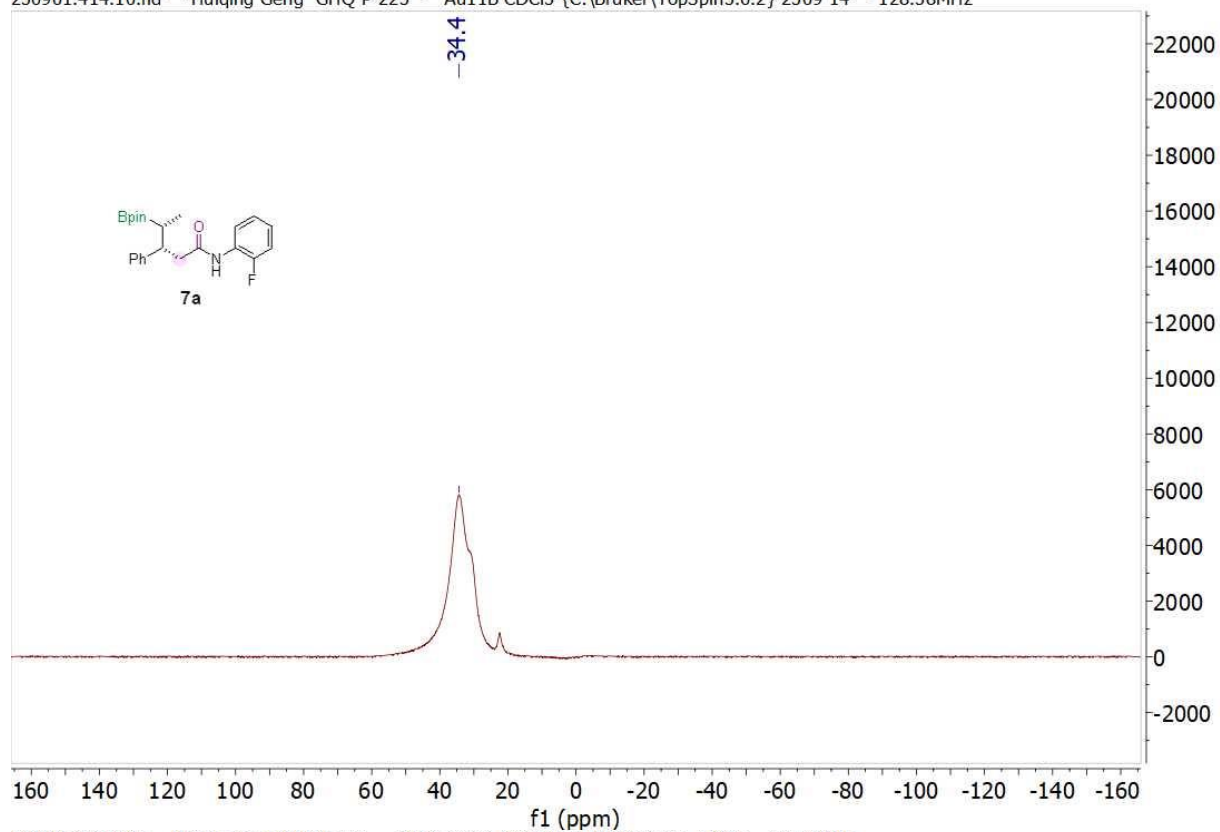




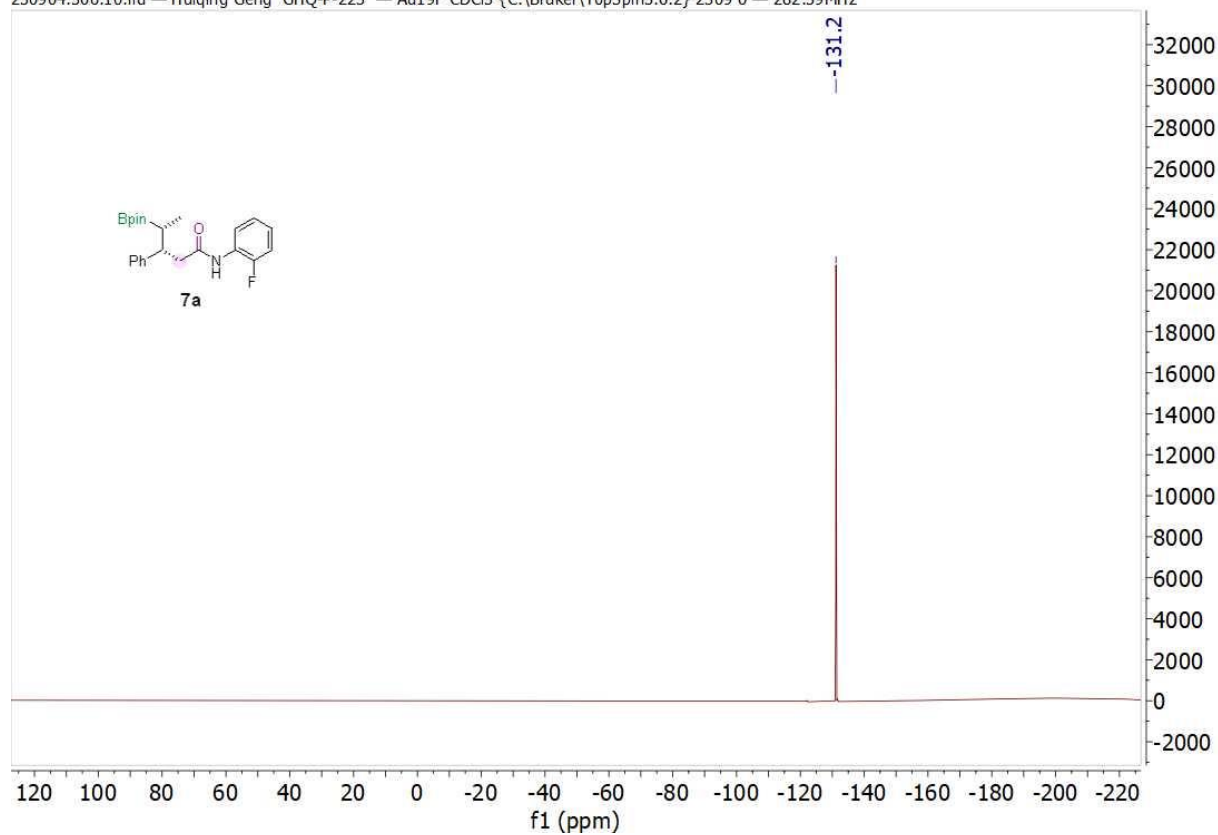


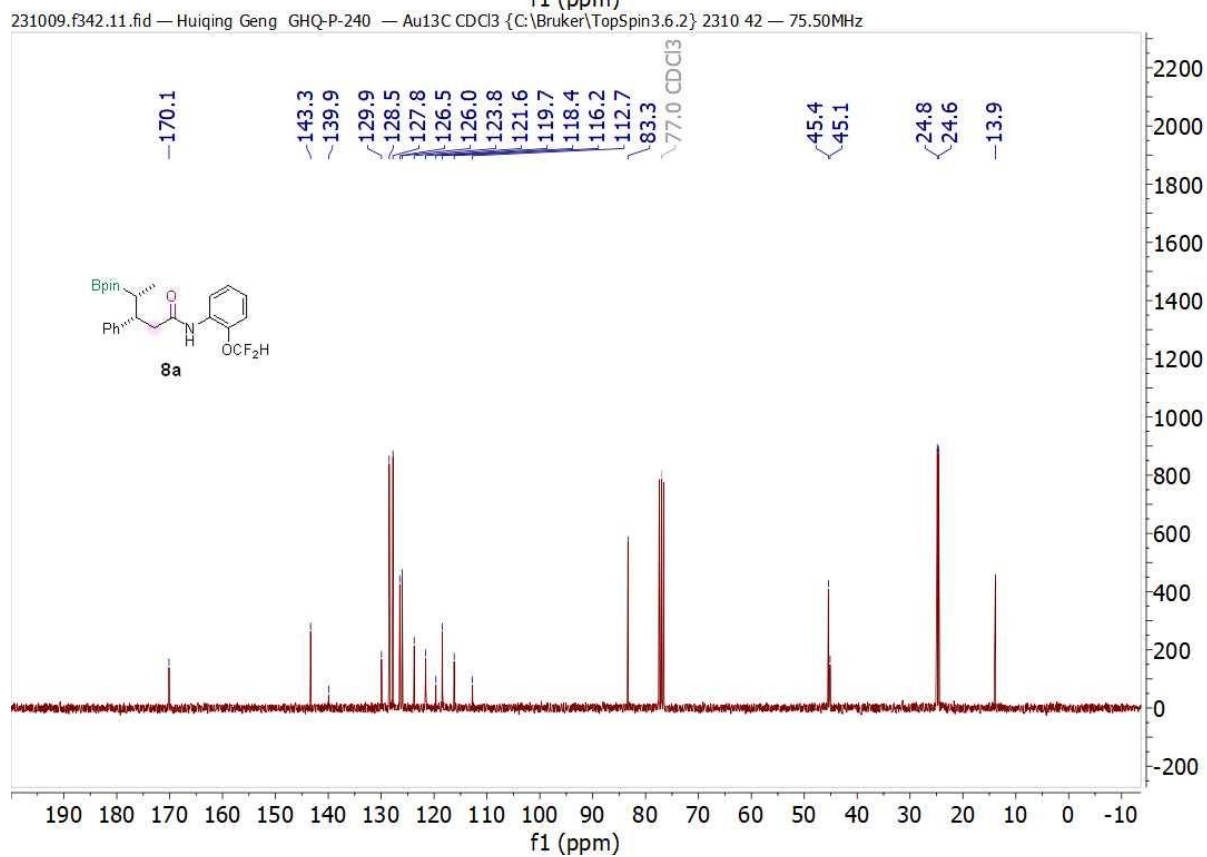
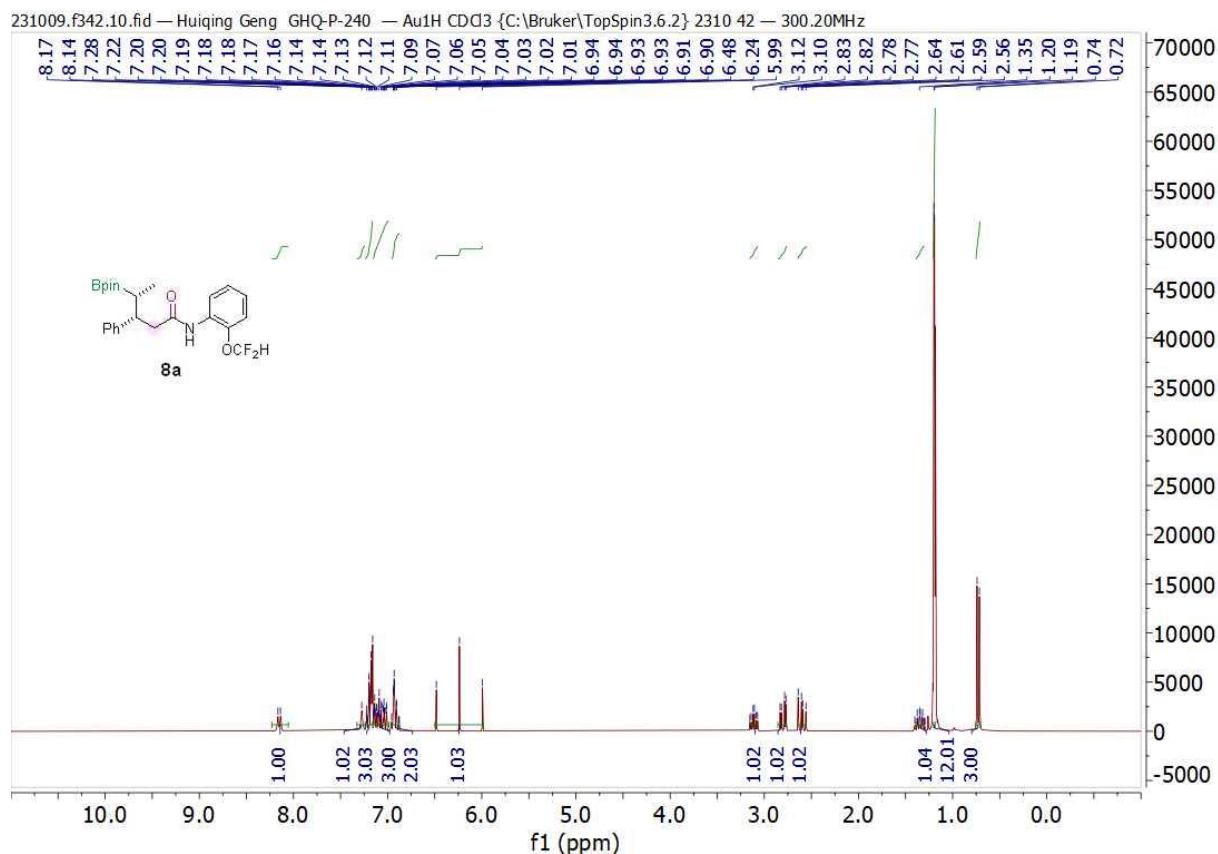


230901.414.10.fid — Huiqing Geng GHQ-P-223 — Au11B CDCl3 {C:\Bruker\TopSpin3.6.2} 2309 14 — 128.38MHz

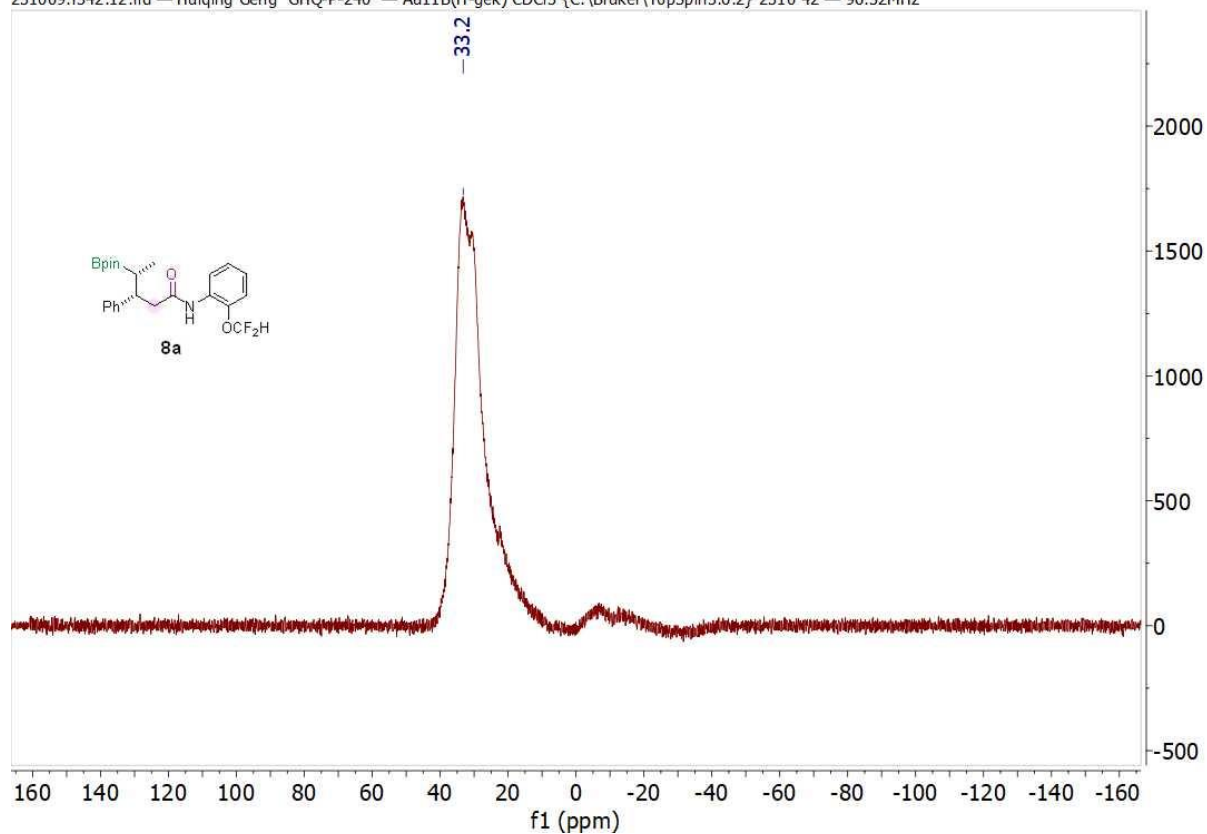


230904.306.10.fid — Huiqing Geng GHQ-P-223 — Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2309 6 — 282.39MHz

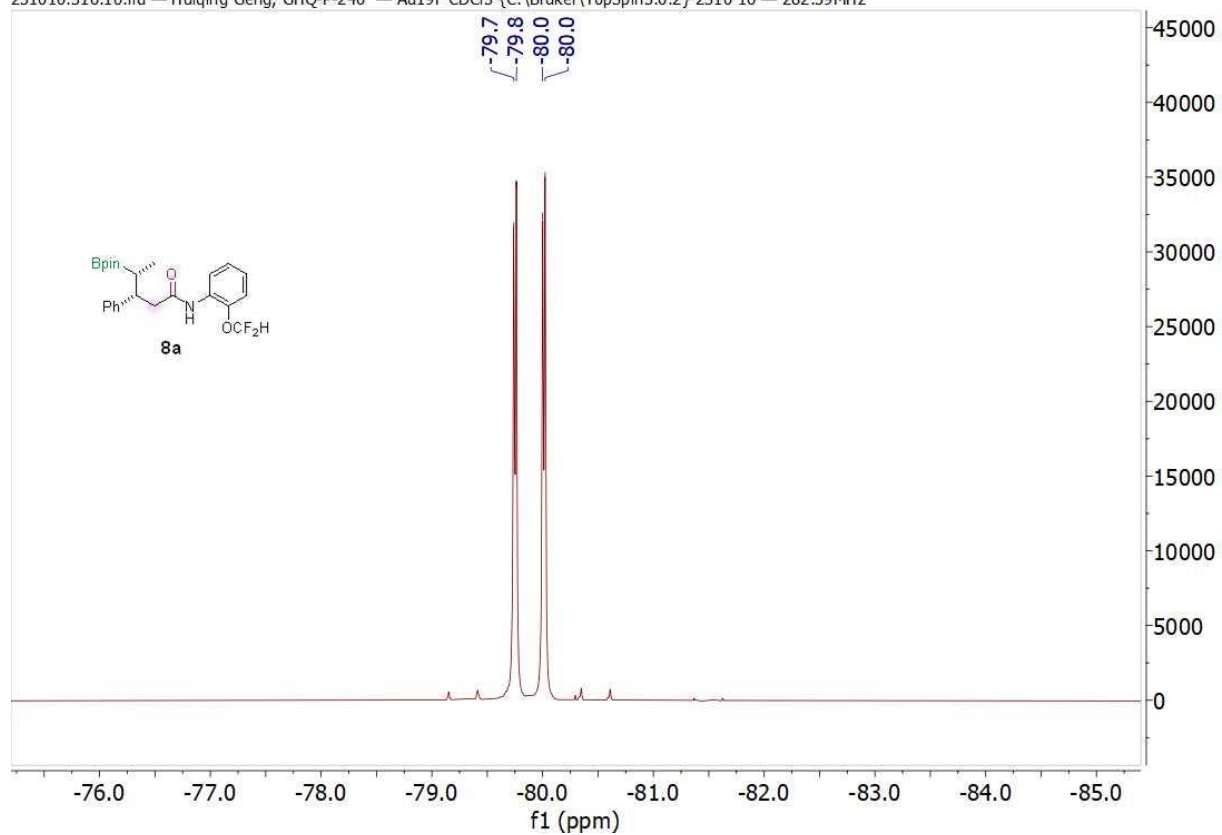


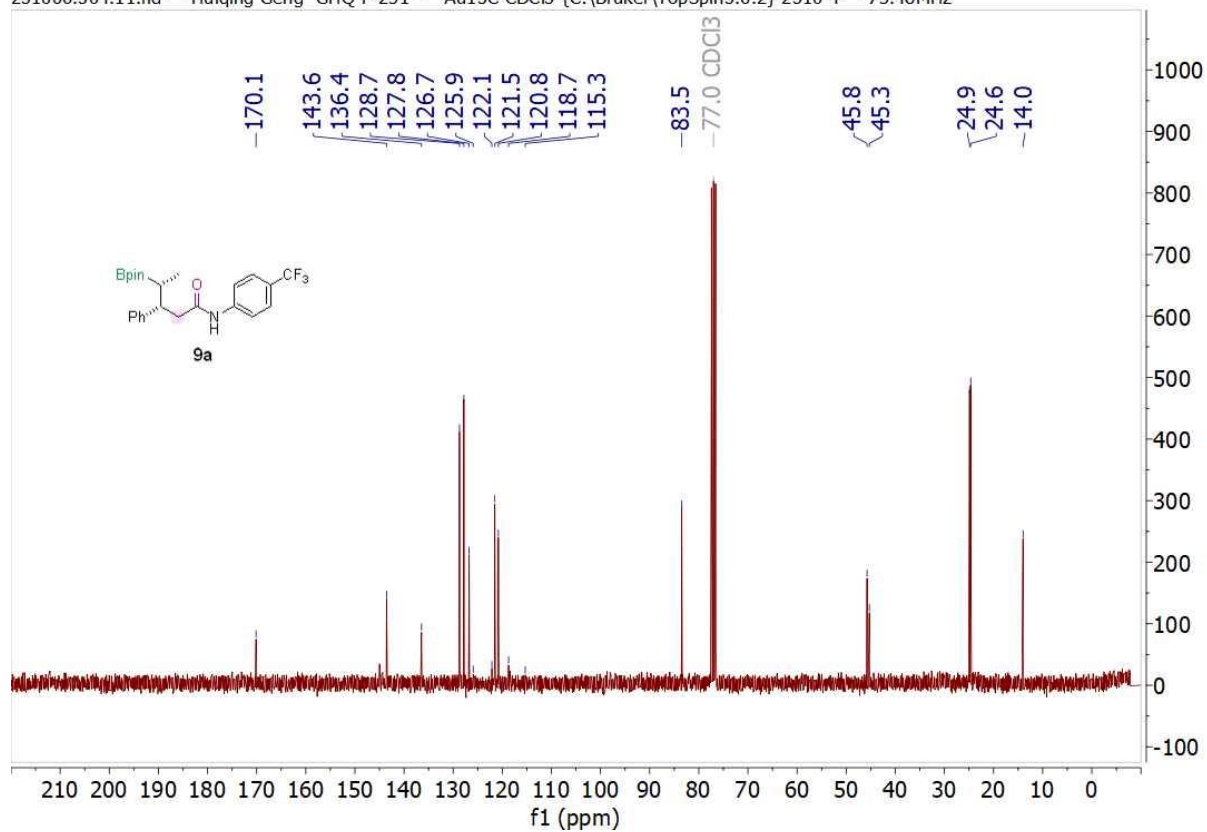
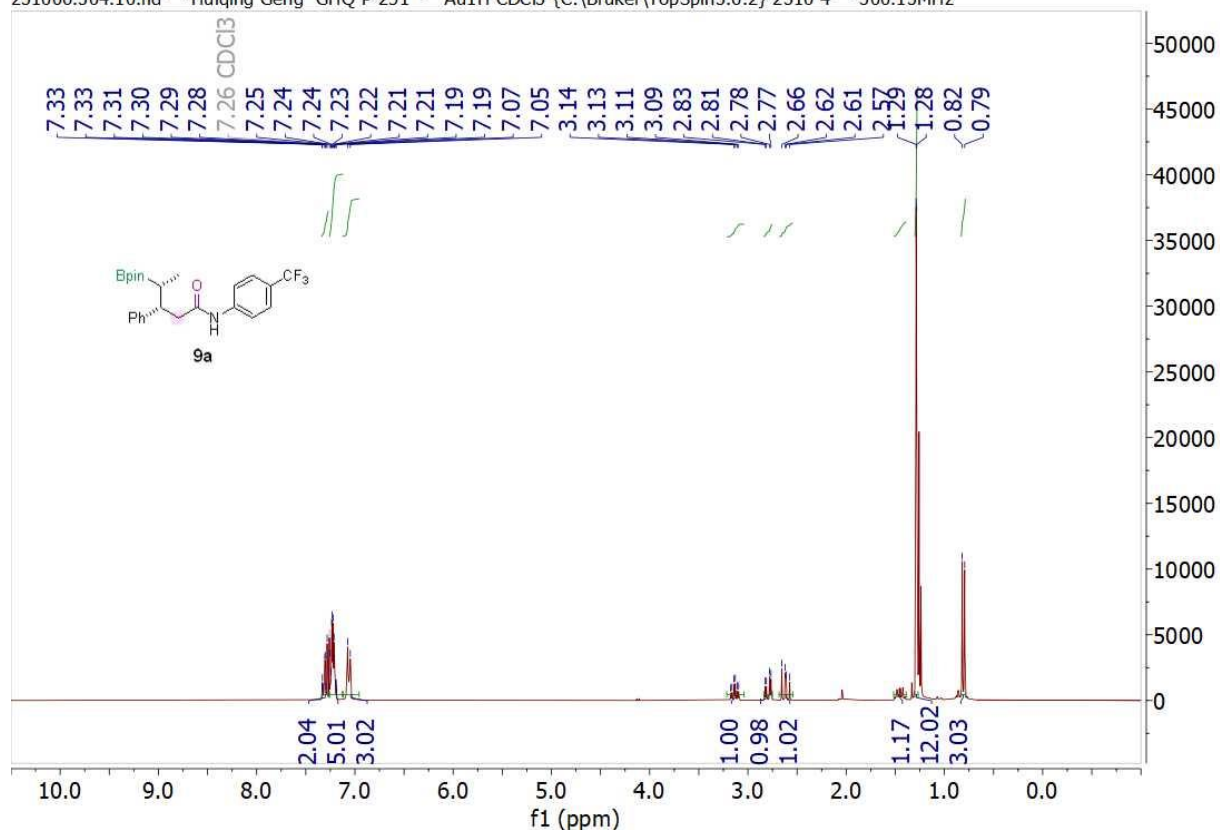


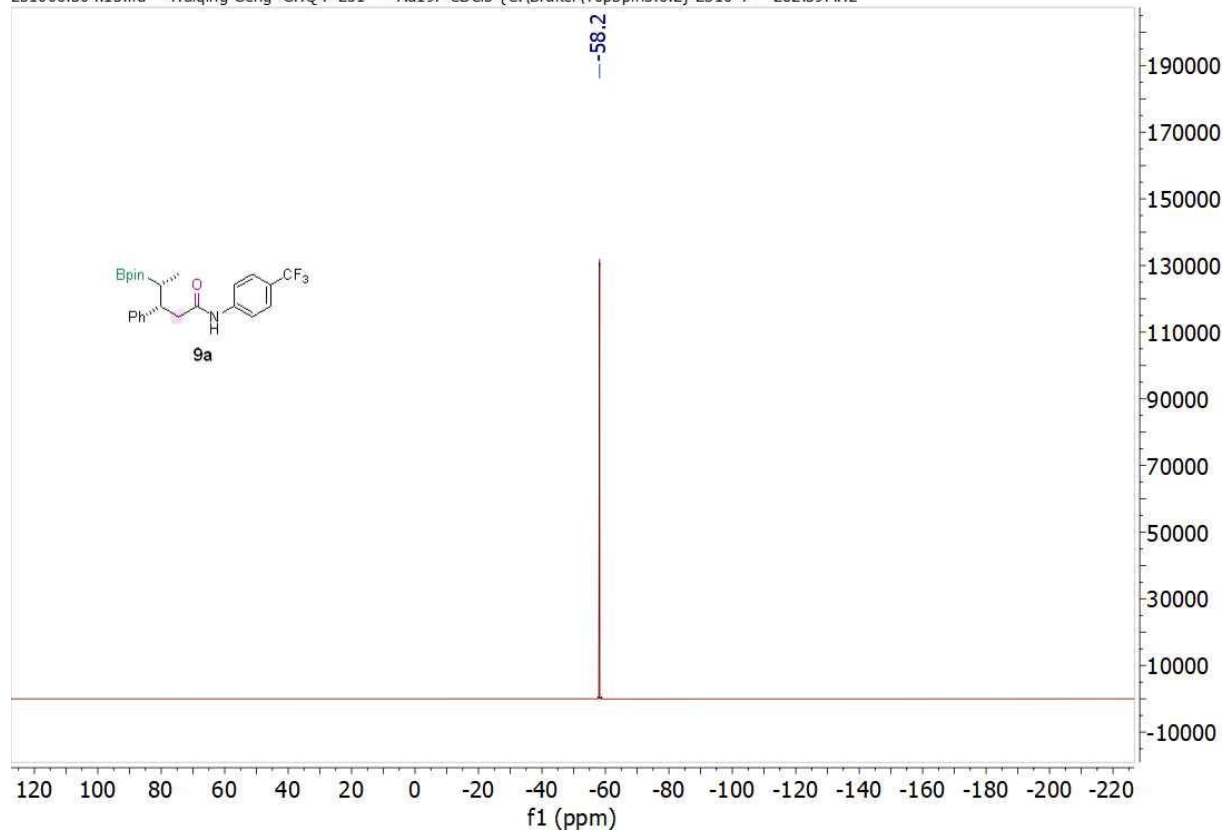
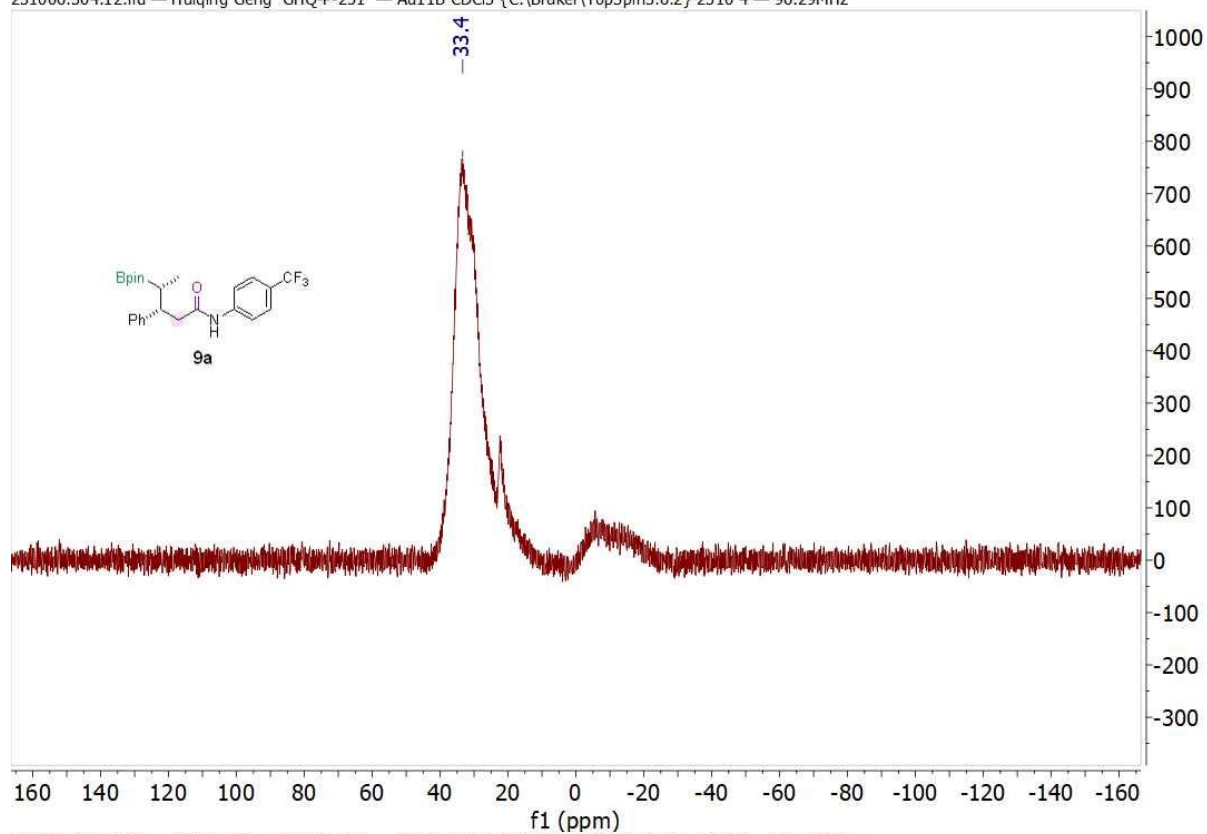
231009.f342.12.fid — Huiqing Geng GHQ-P-240 — Au11B(H-gek) CDCl3 {C:\Bruker\TopSpin3.6.2} 2310 42 — 96.32MHz

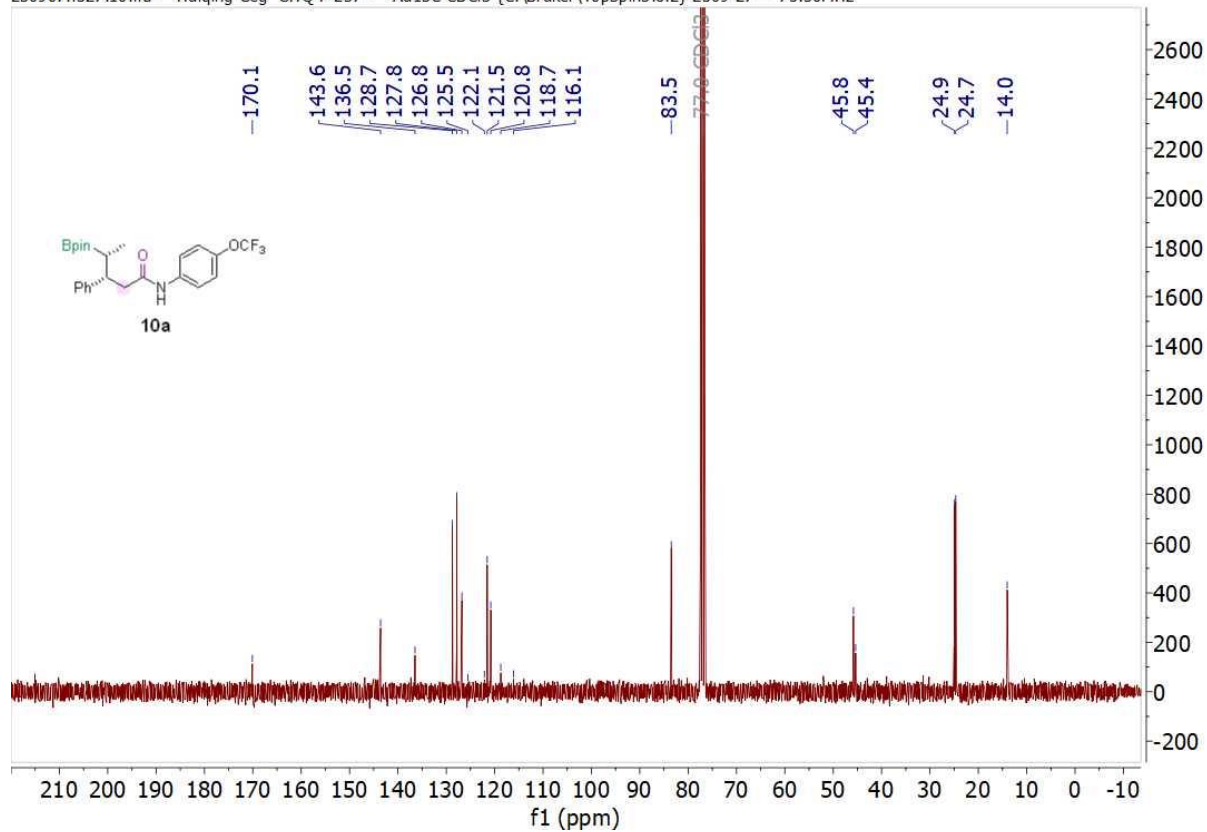
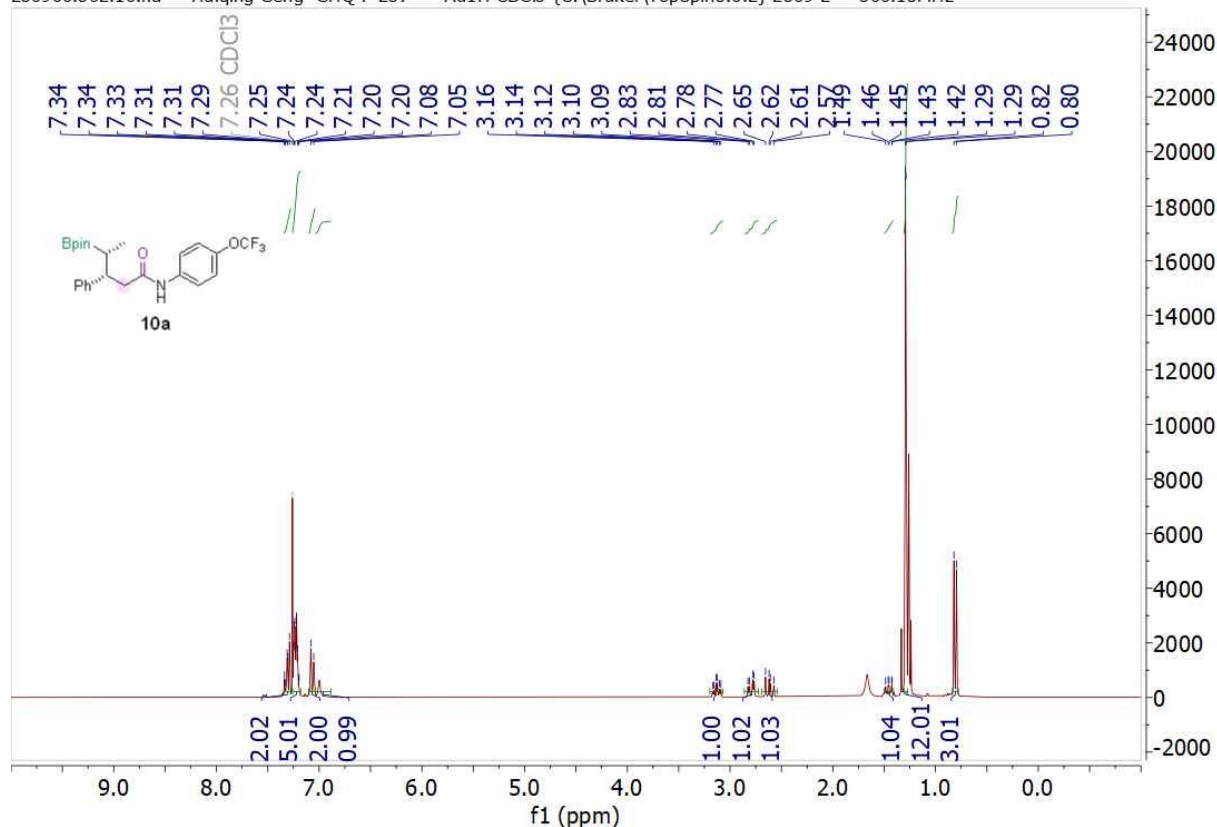


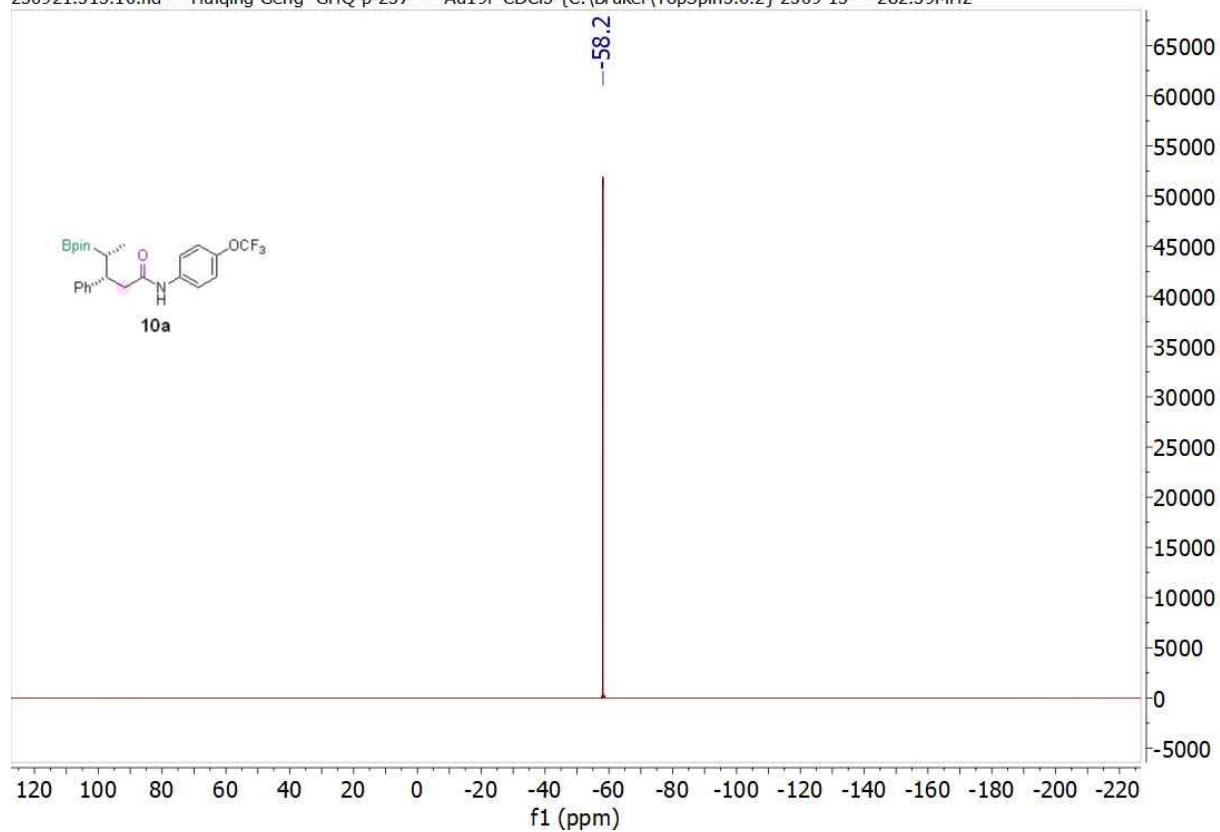
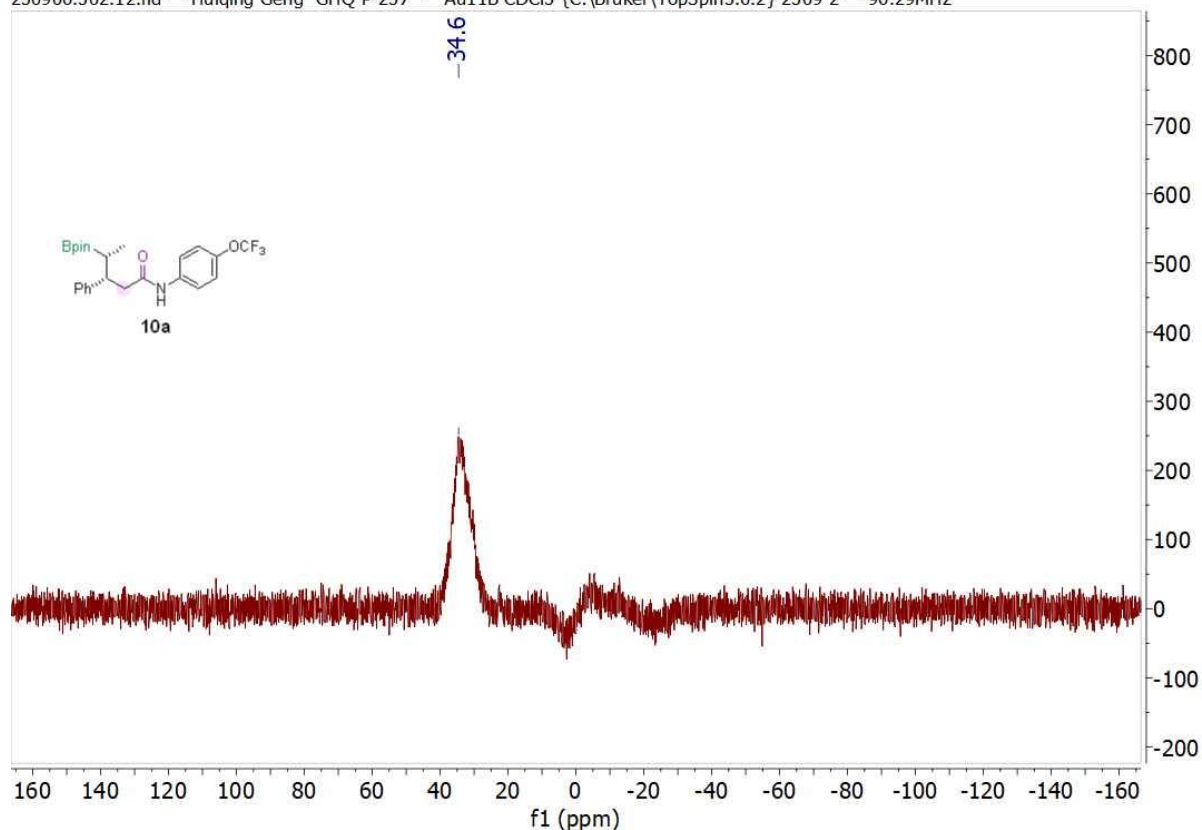
231010.316.10.fid — Huiqing Geng, GHQ-P-240 — Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2310 16 — 282.39MHz

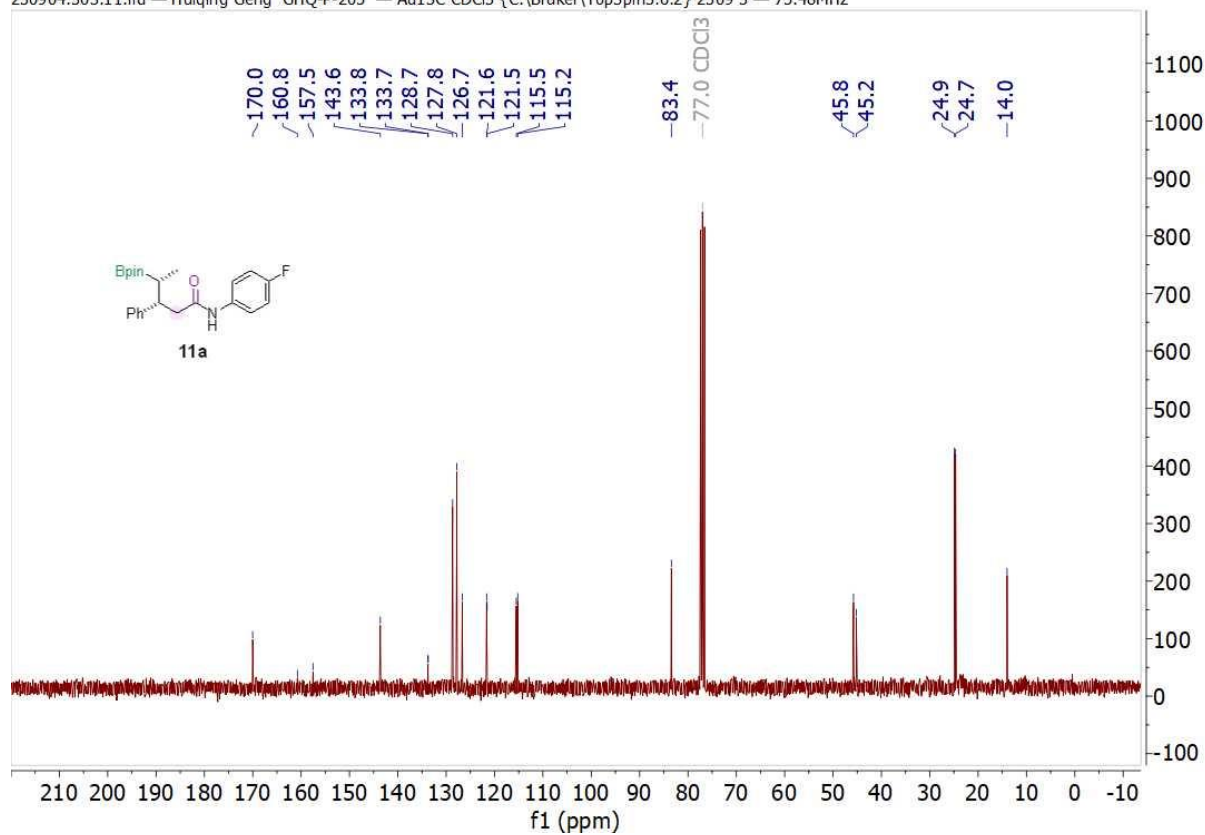
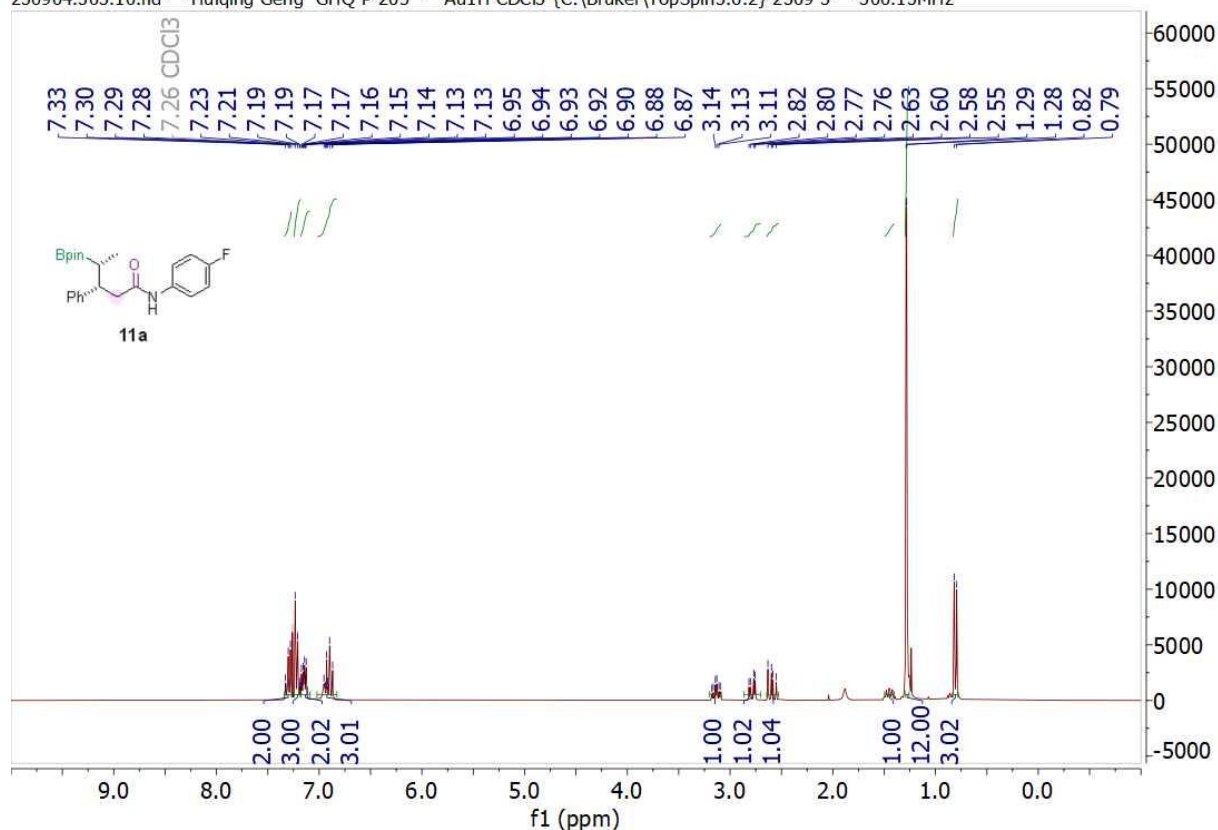


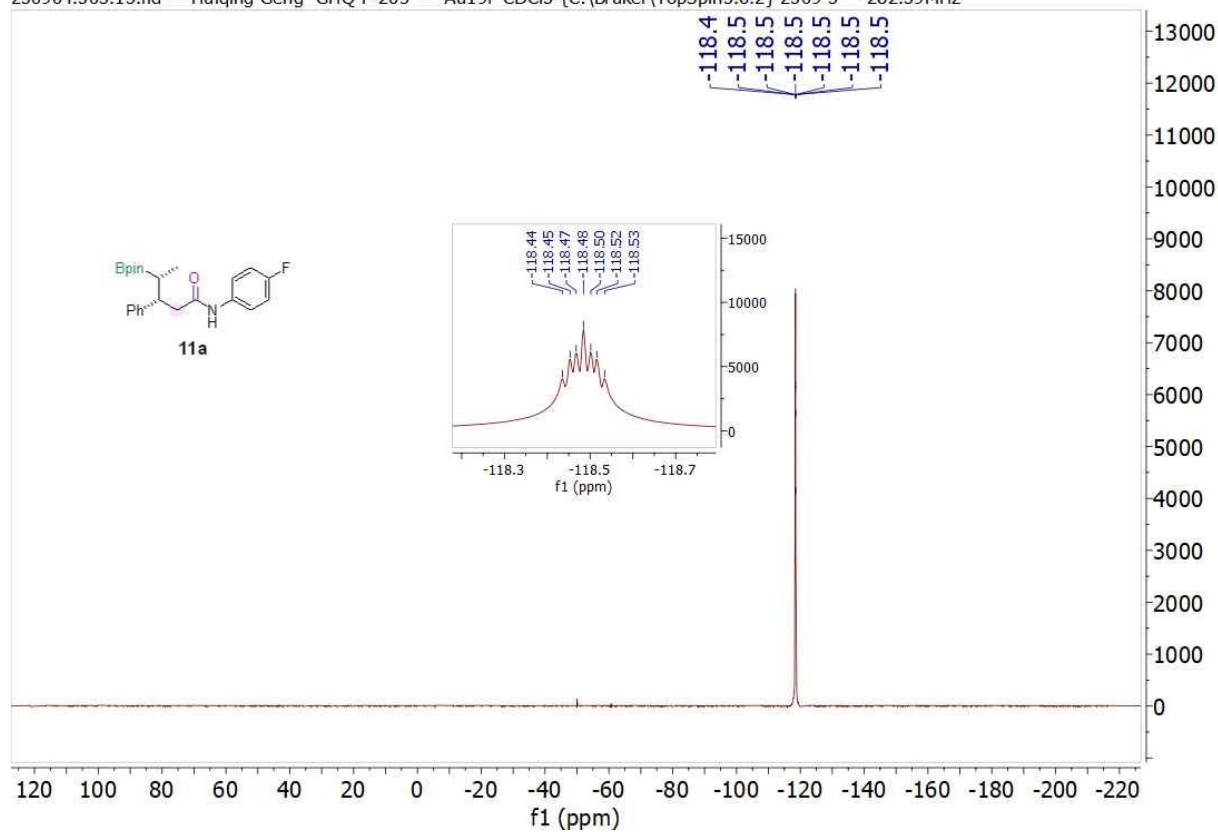
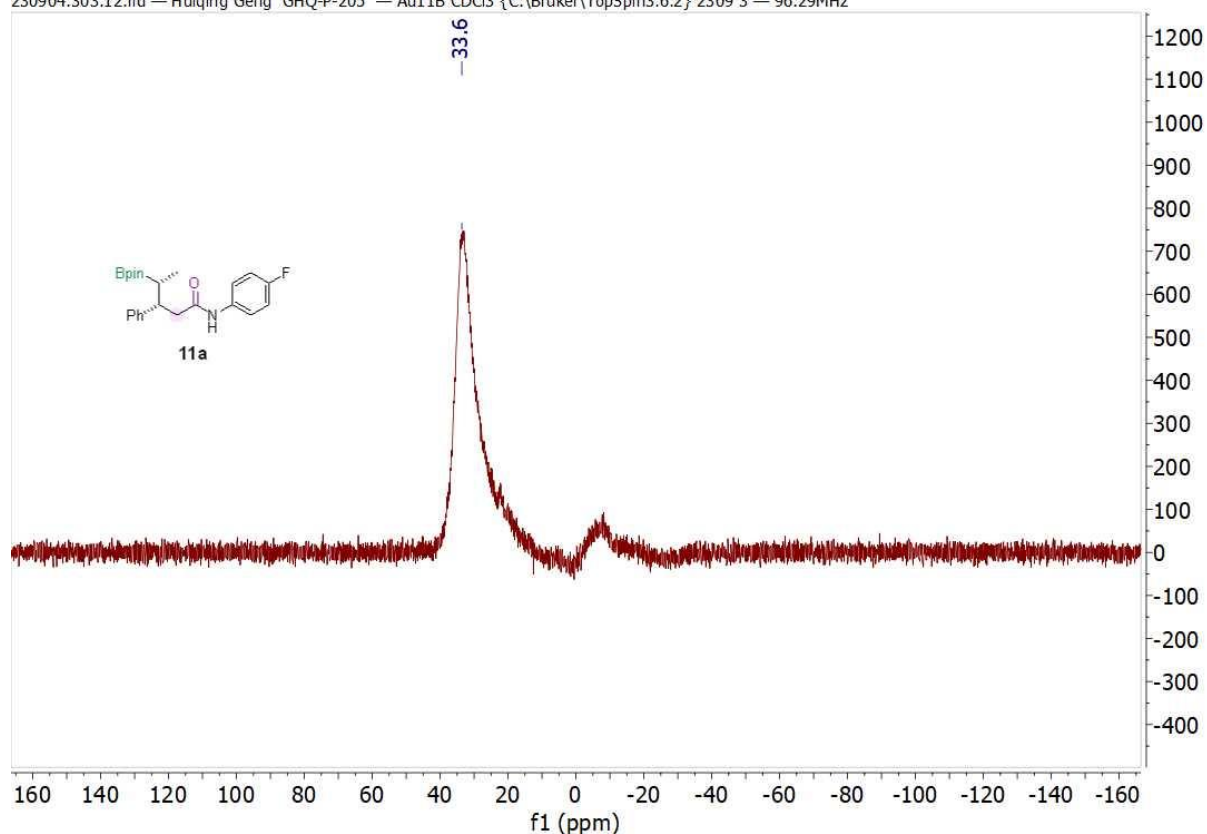


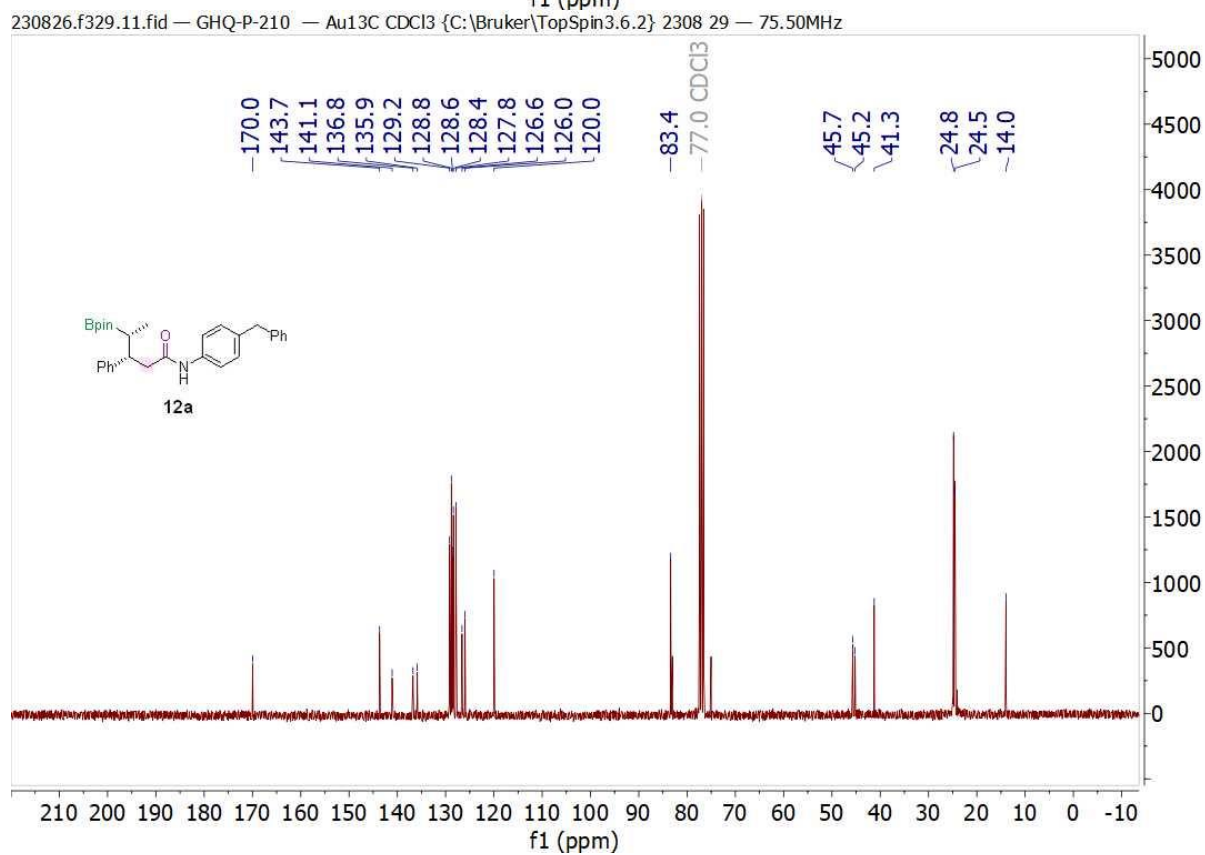
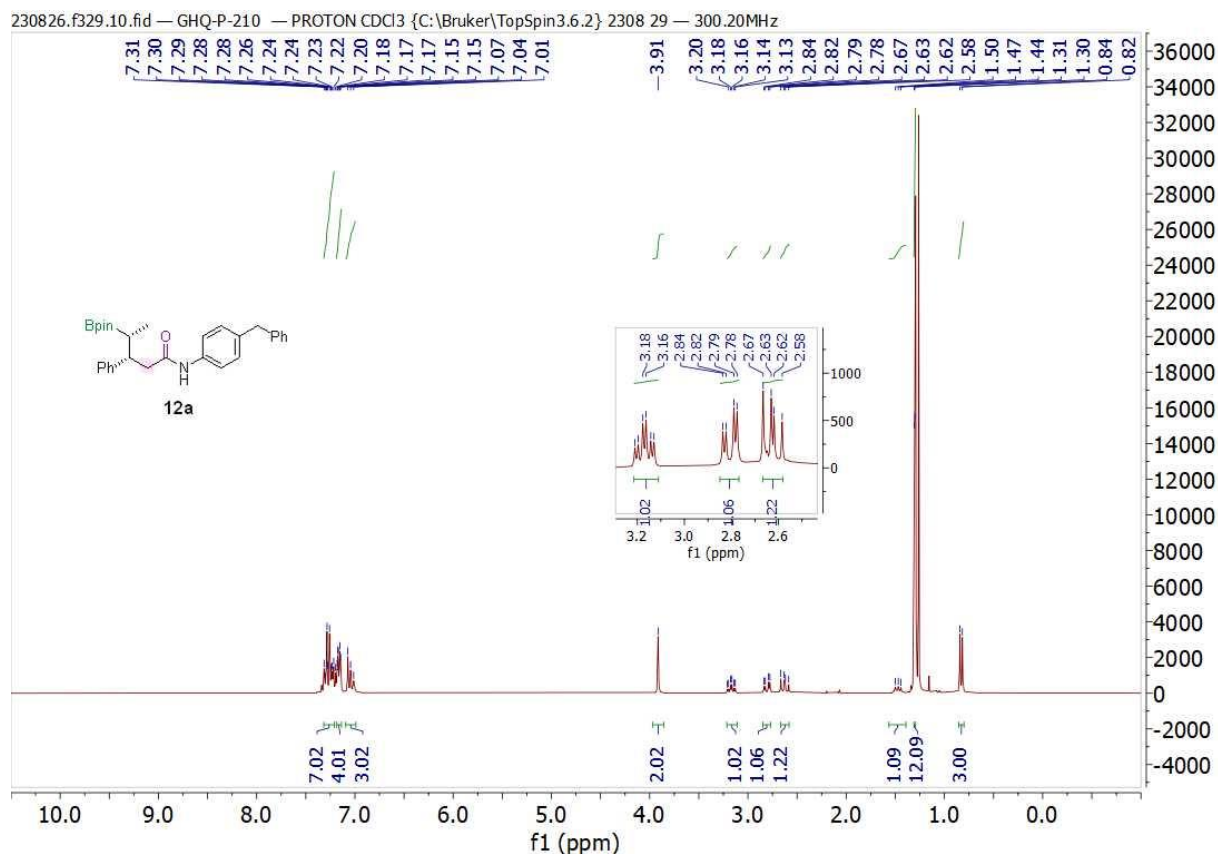


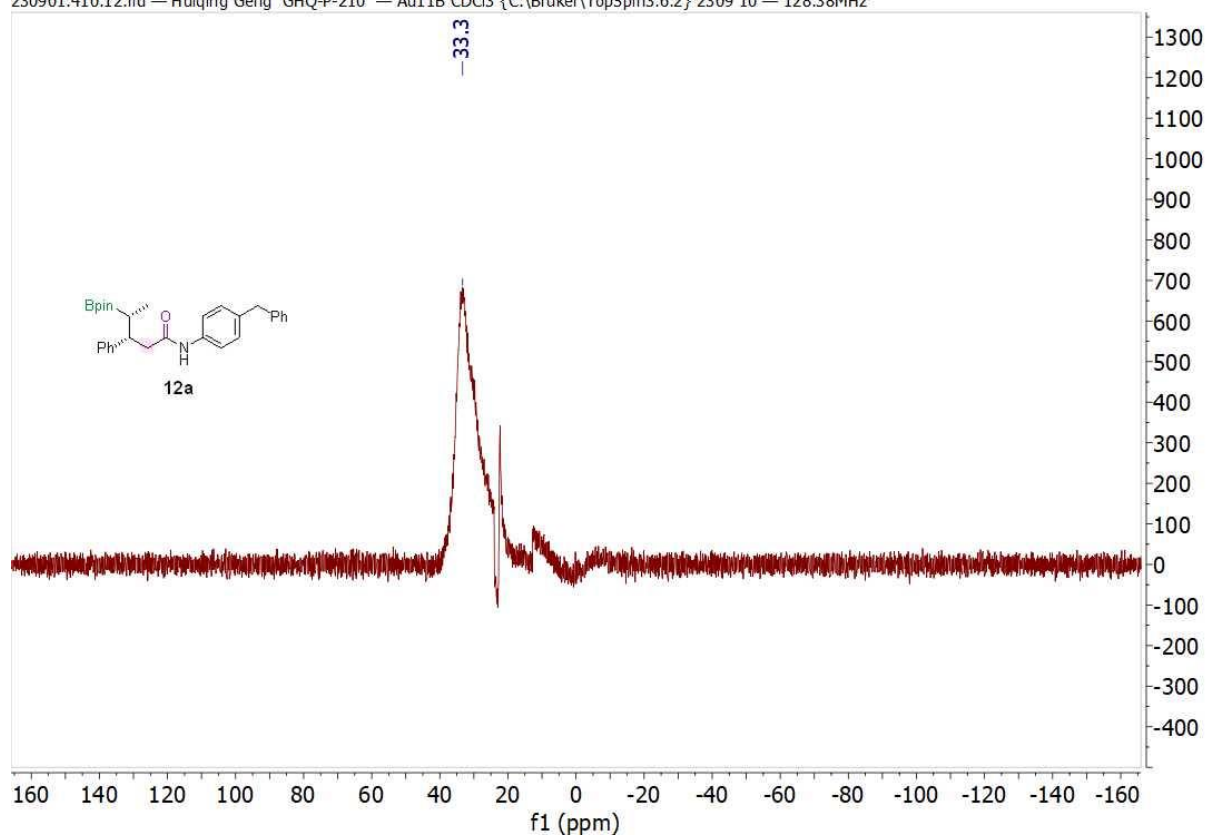


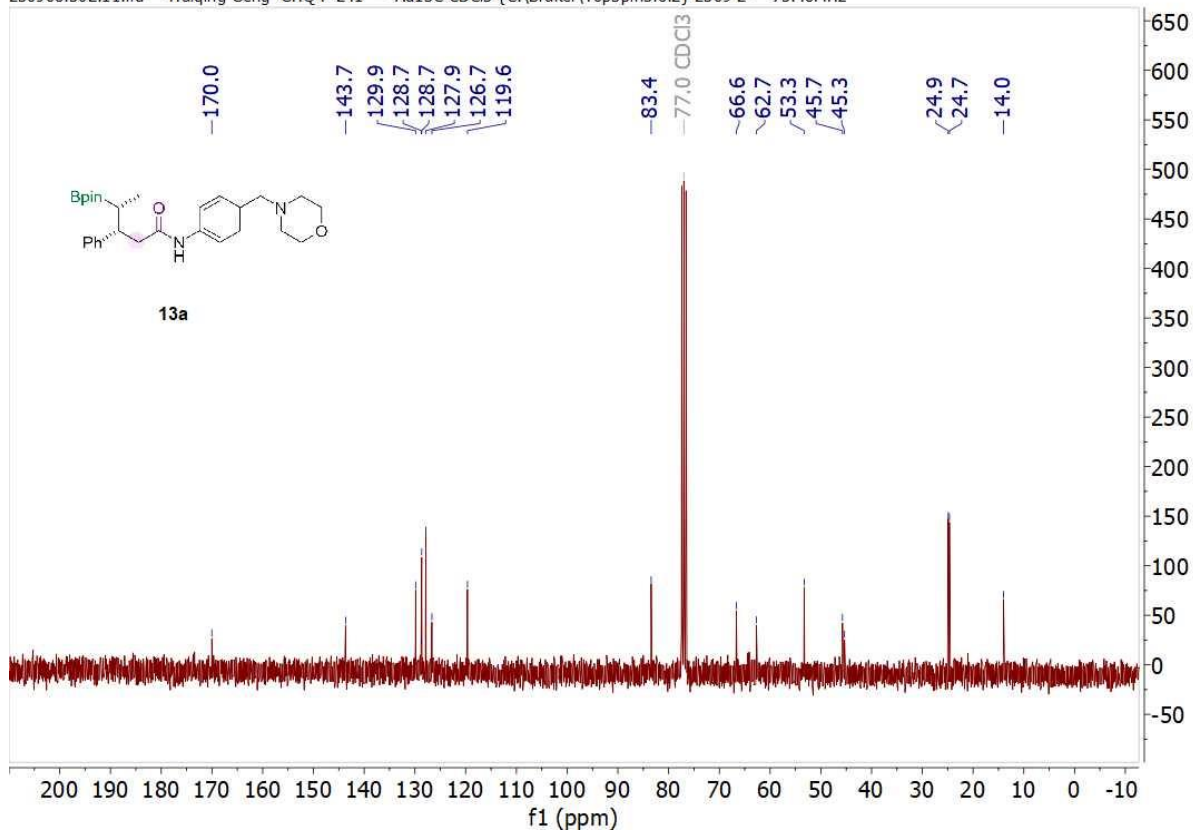
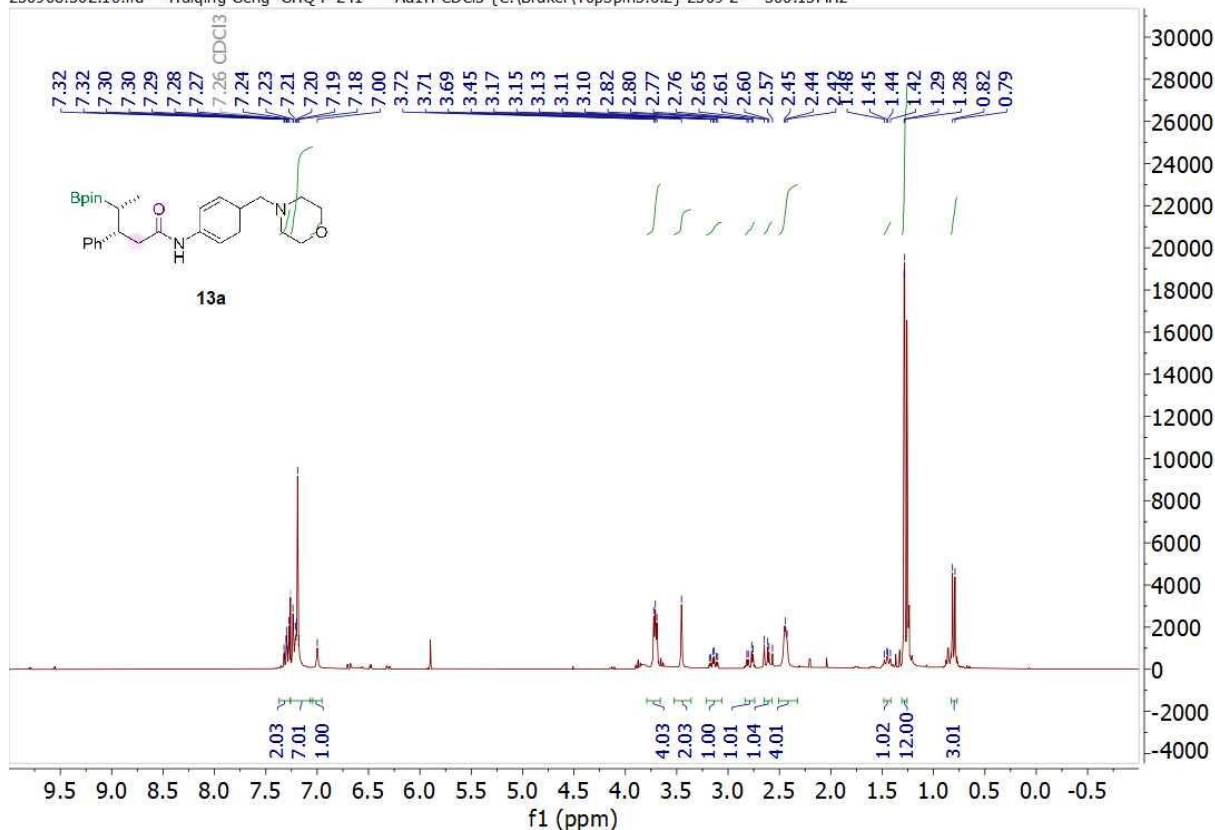


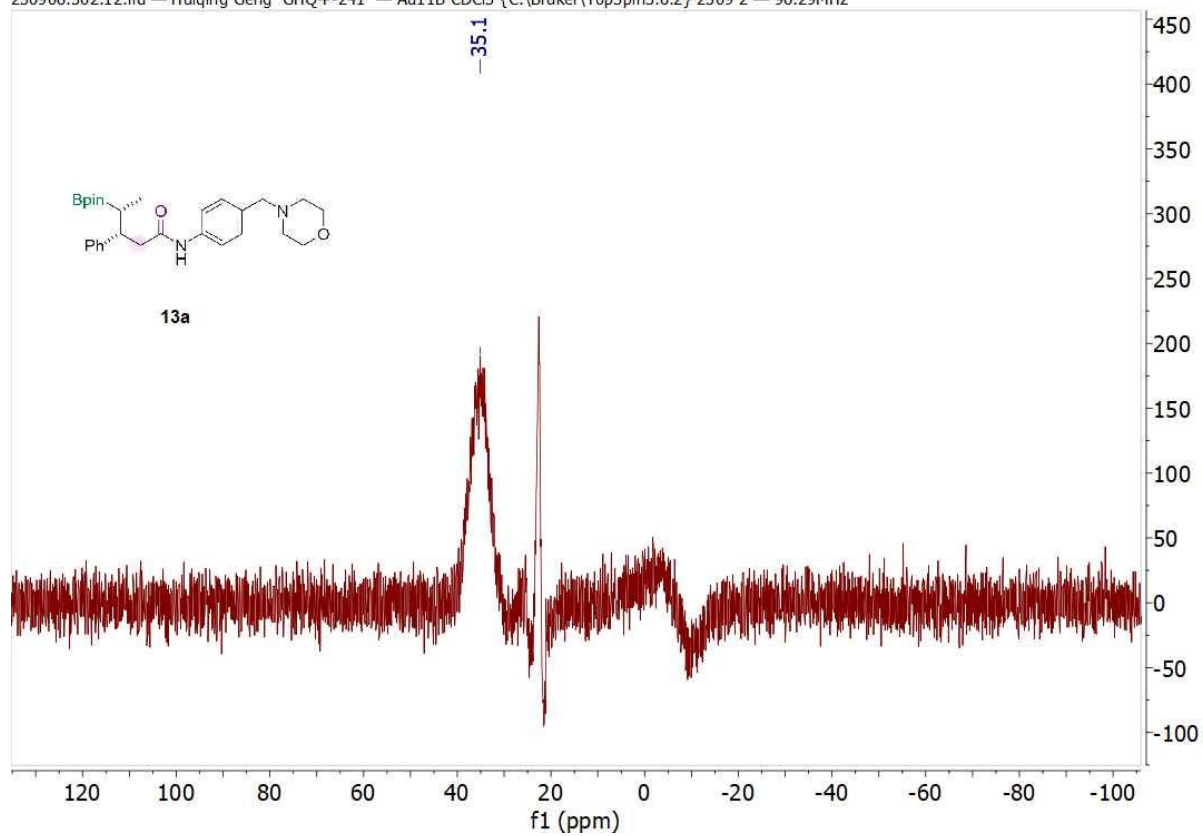


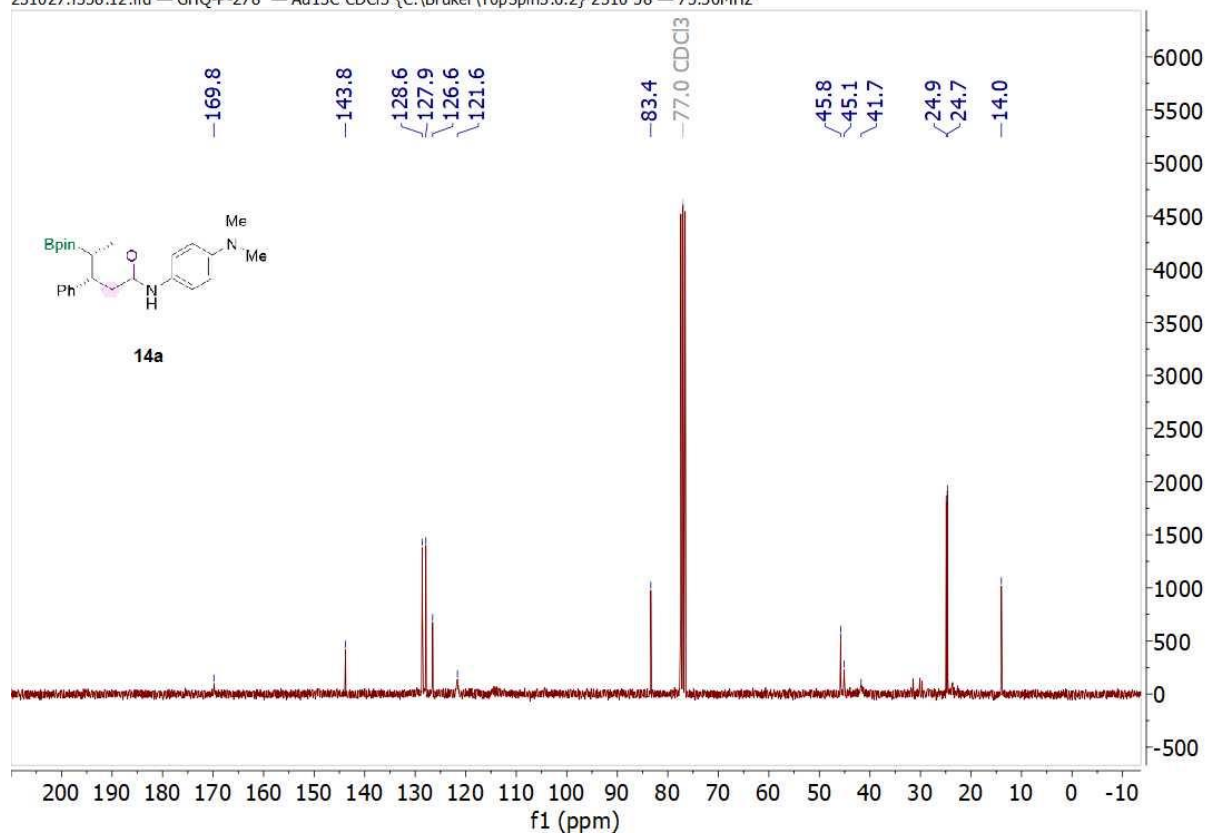
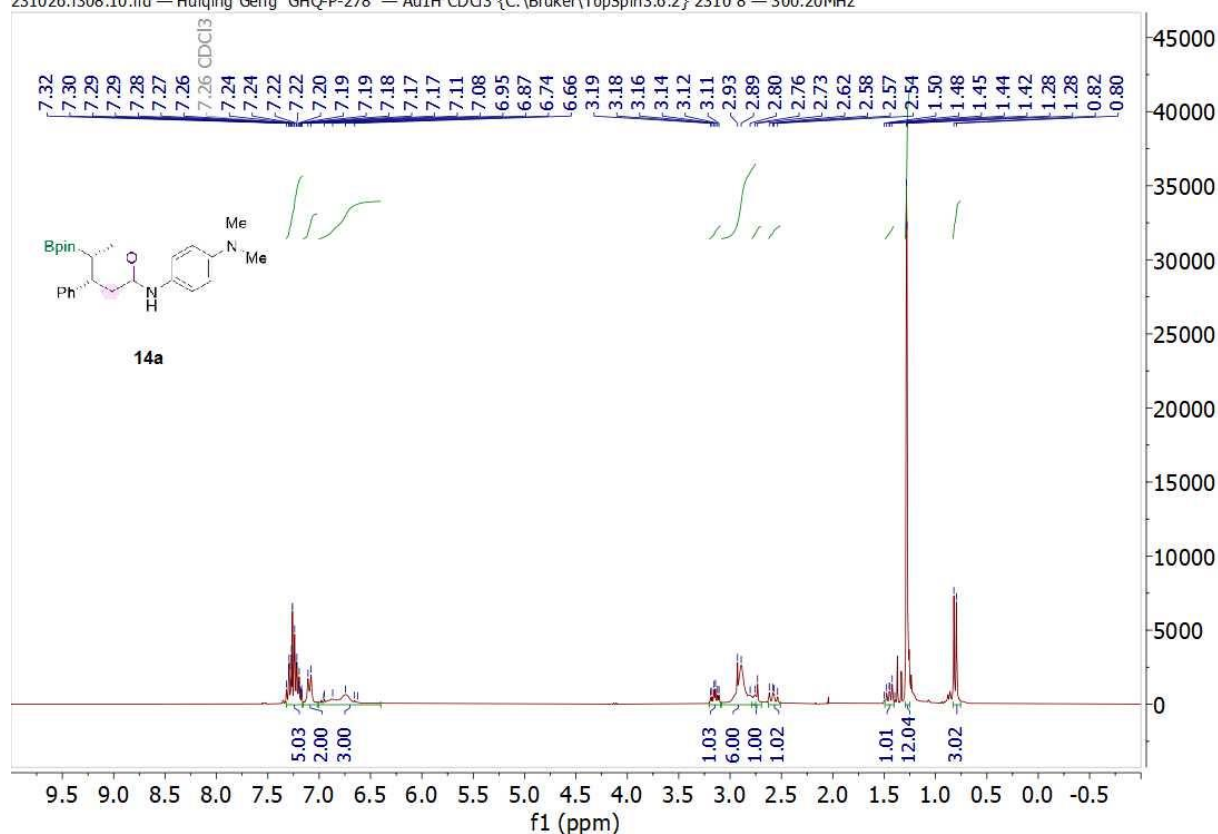


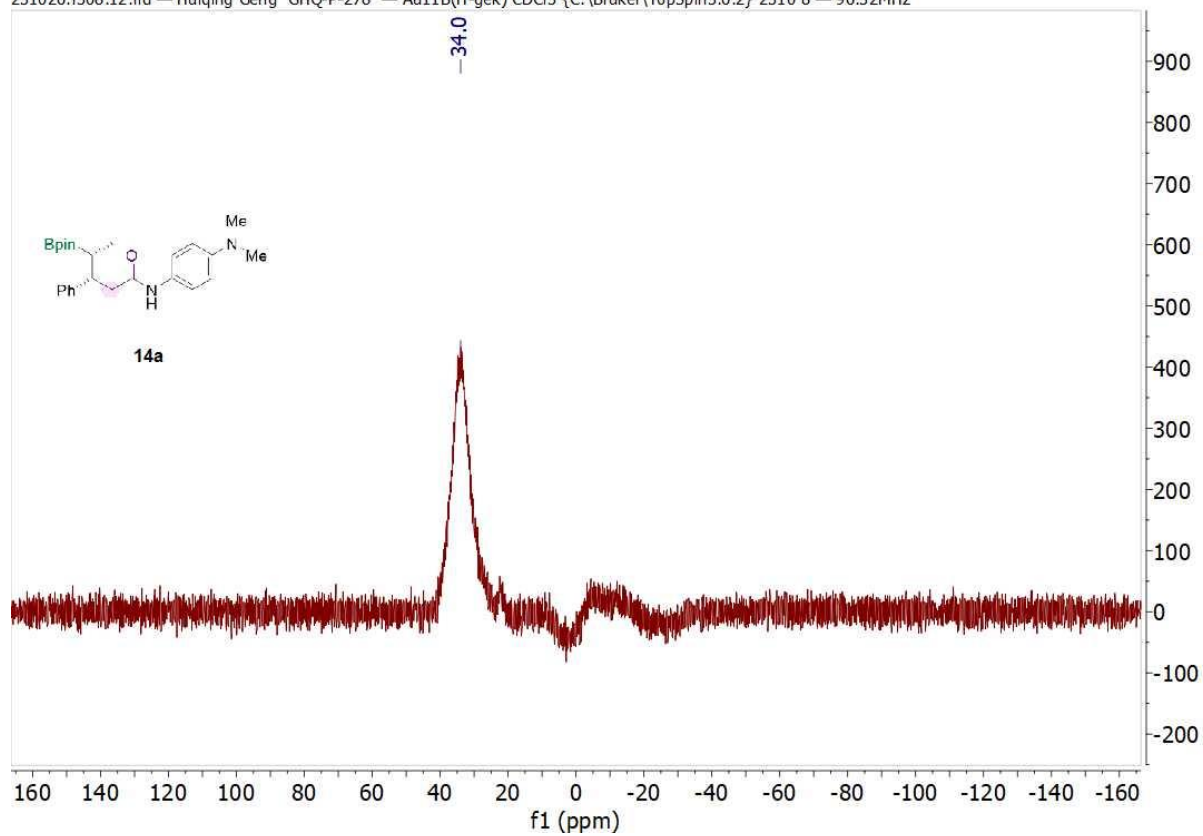


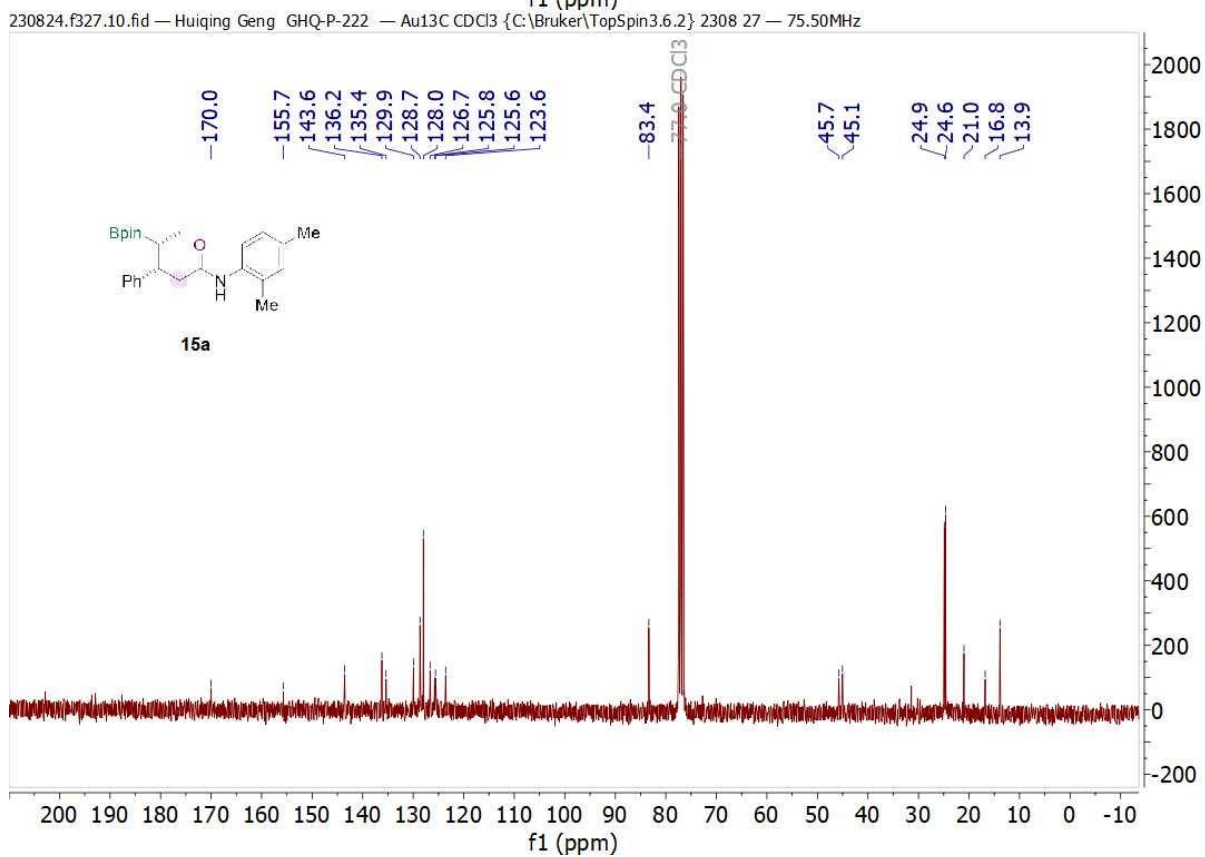
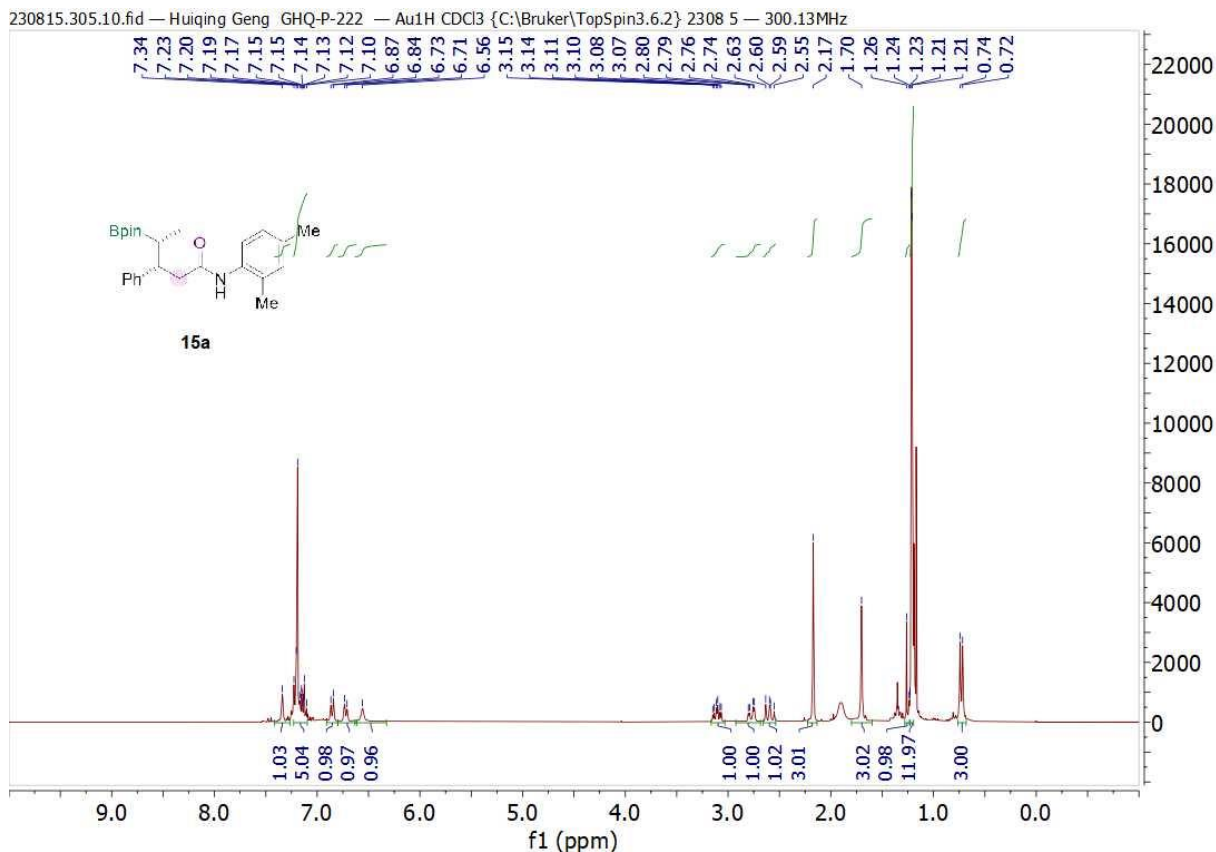


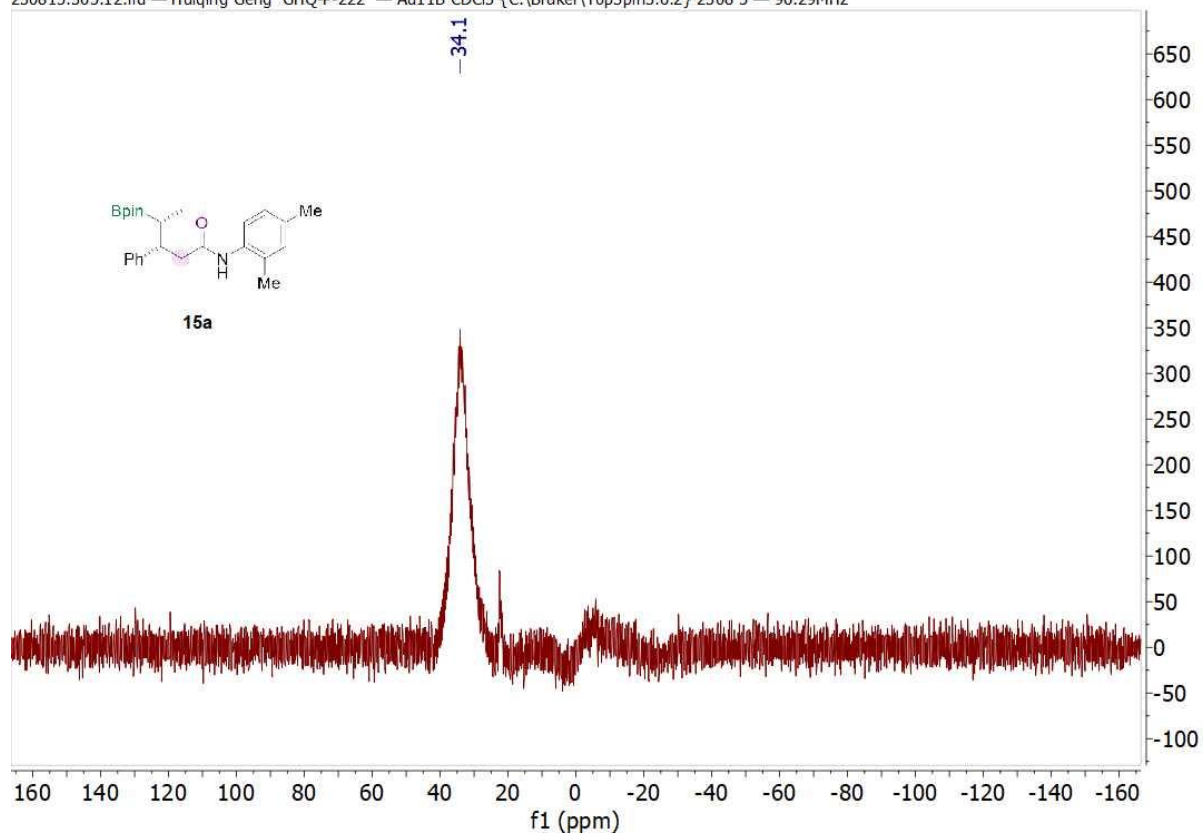


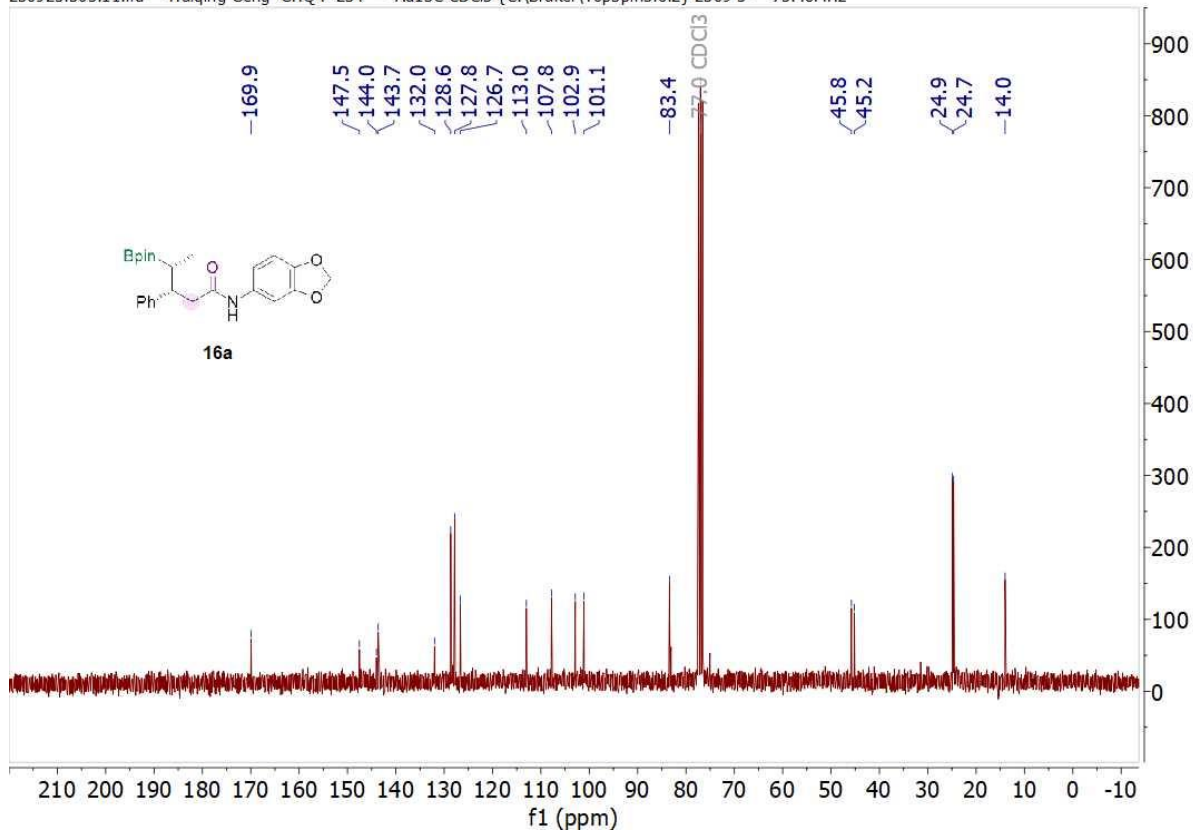
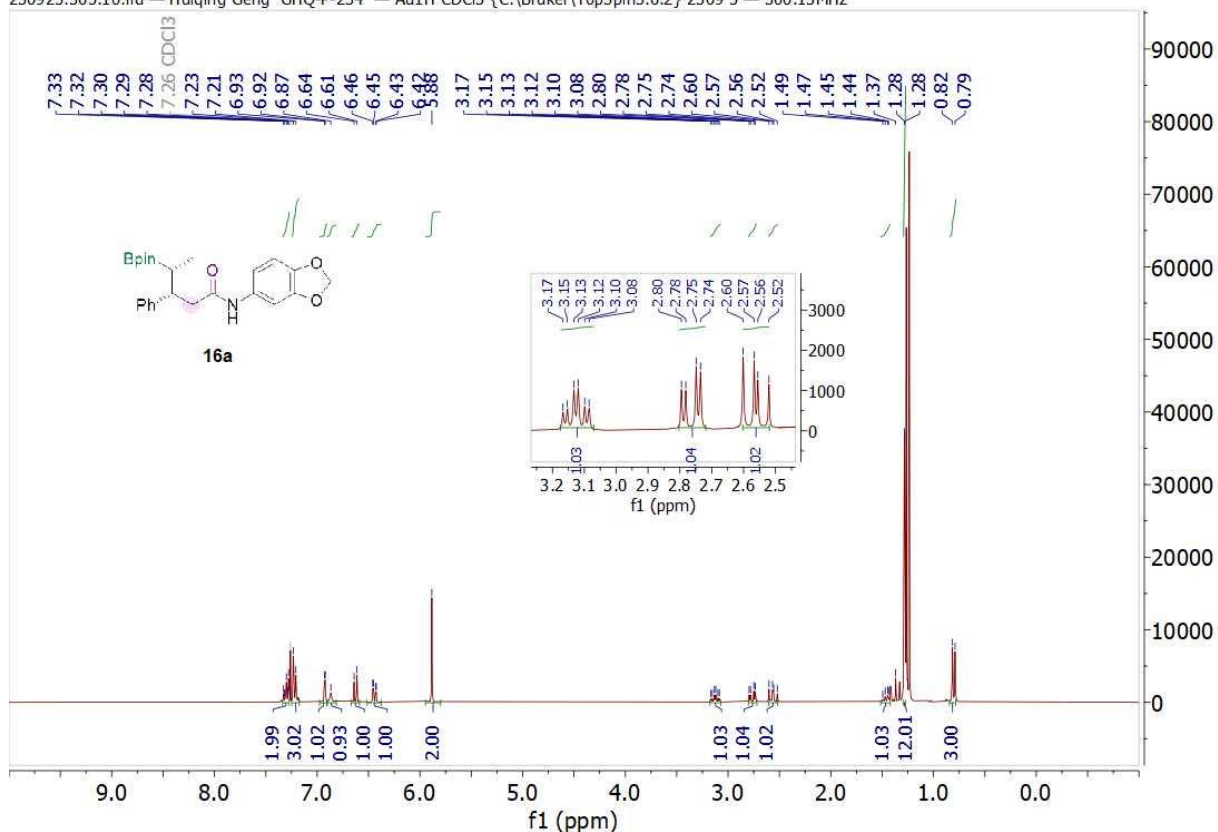


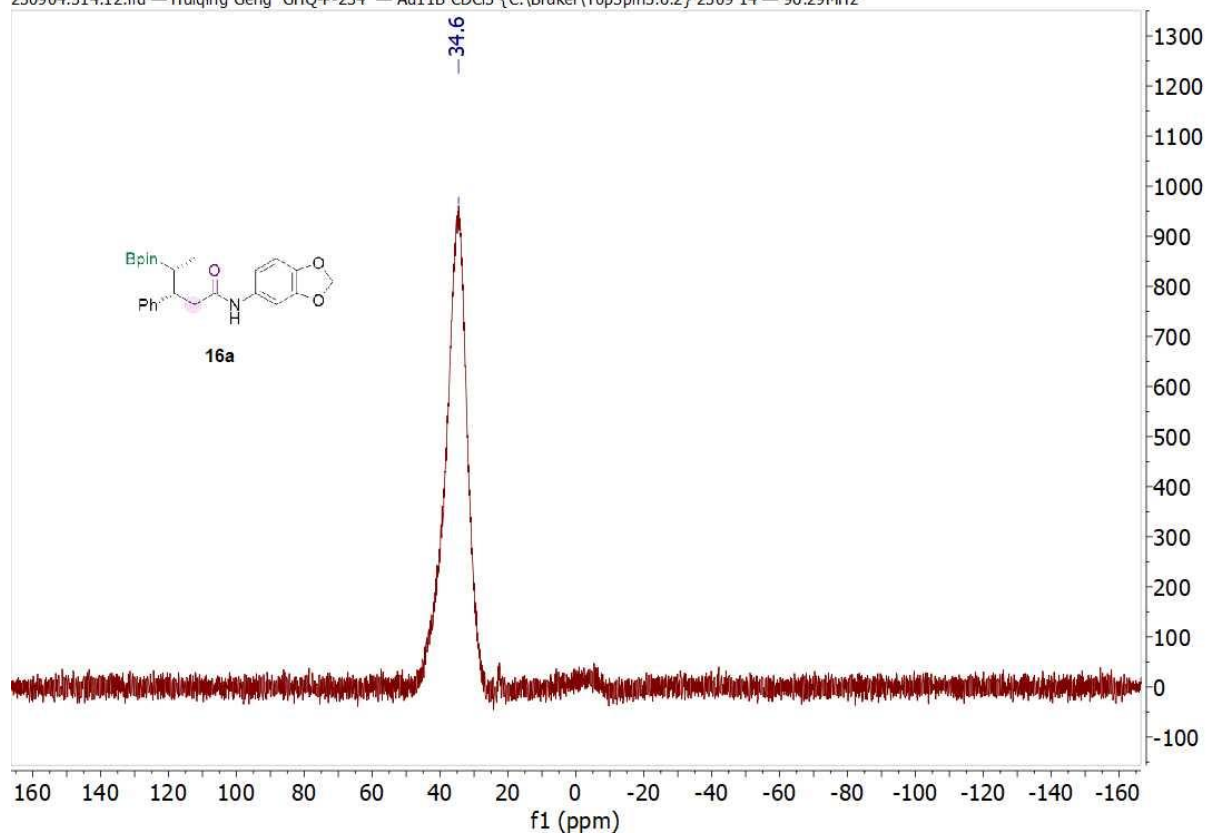


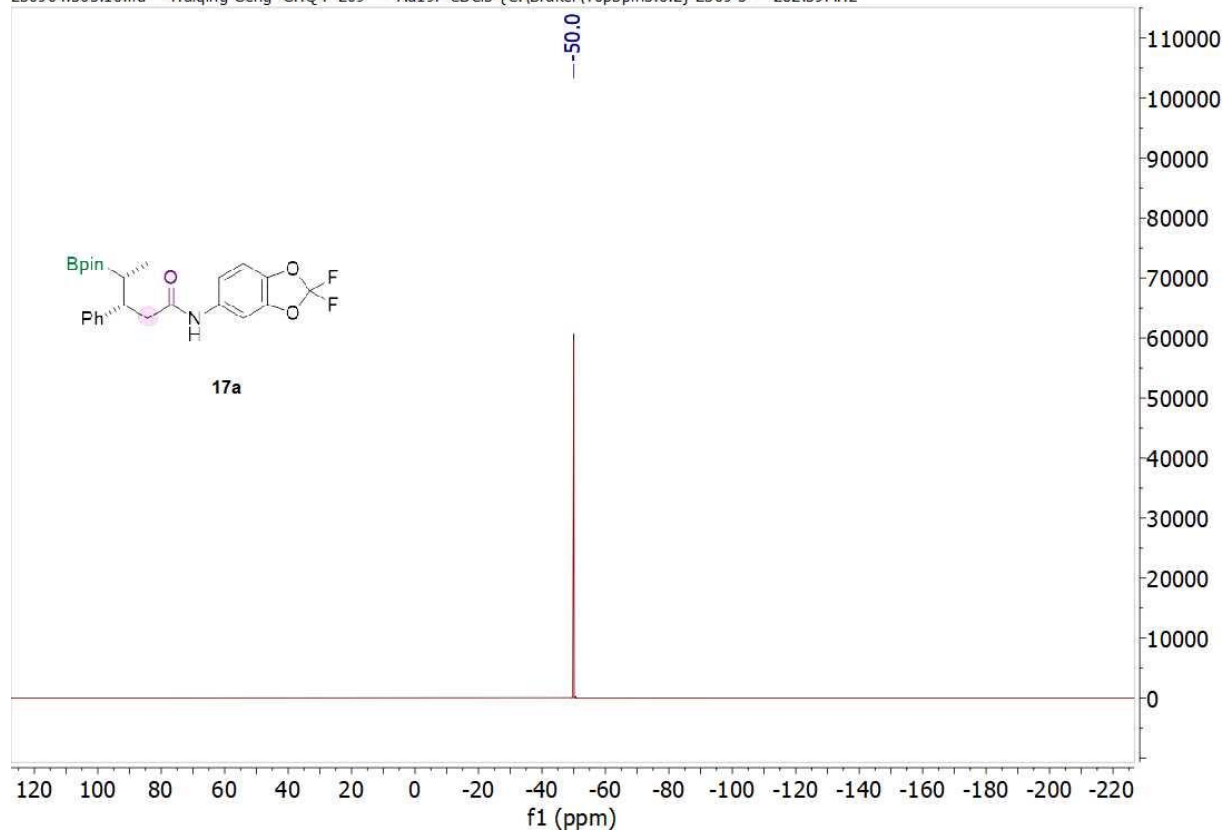
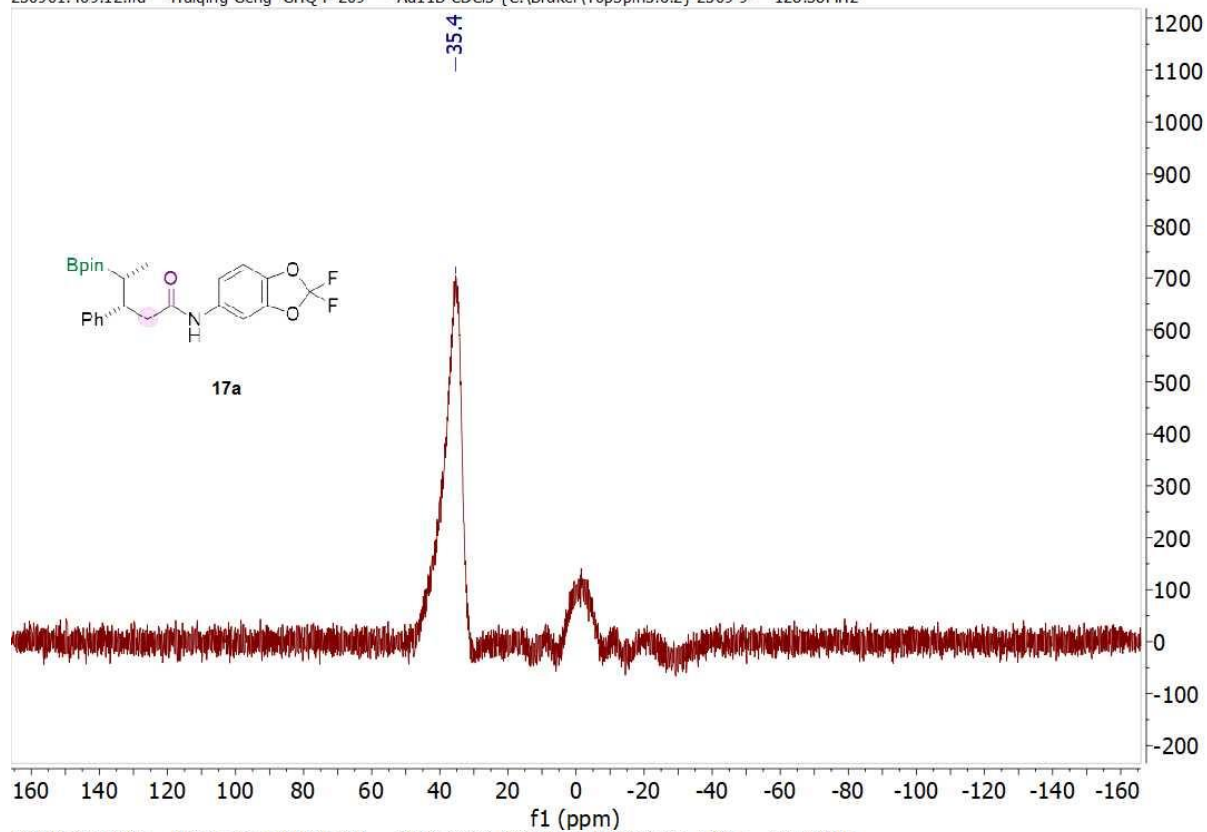


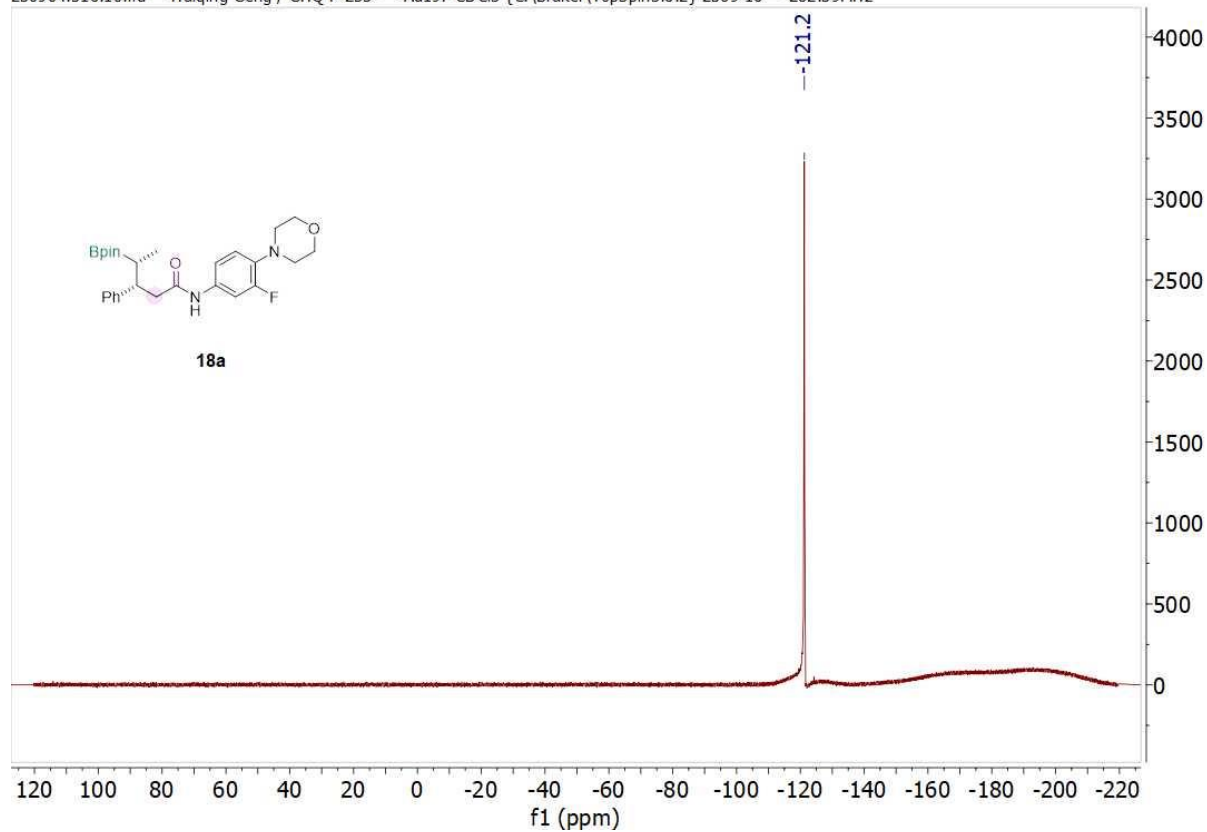
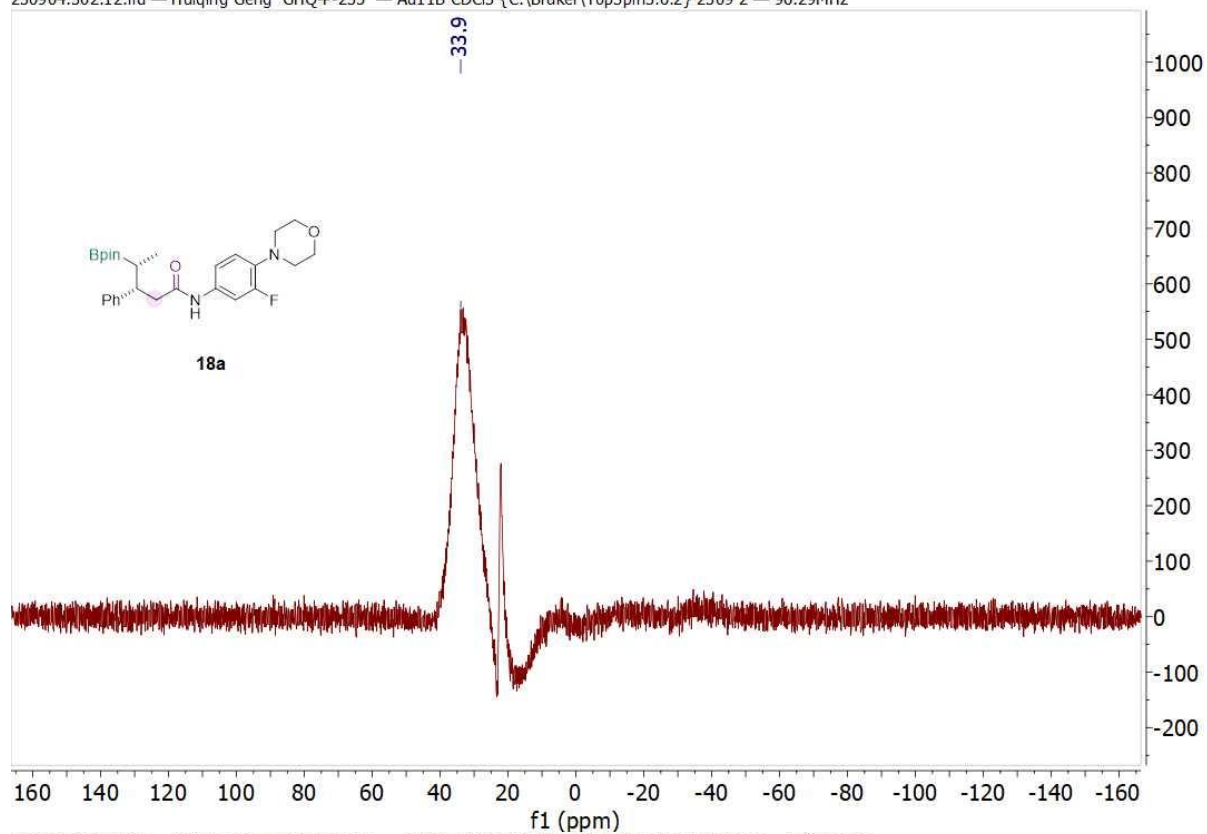


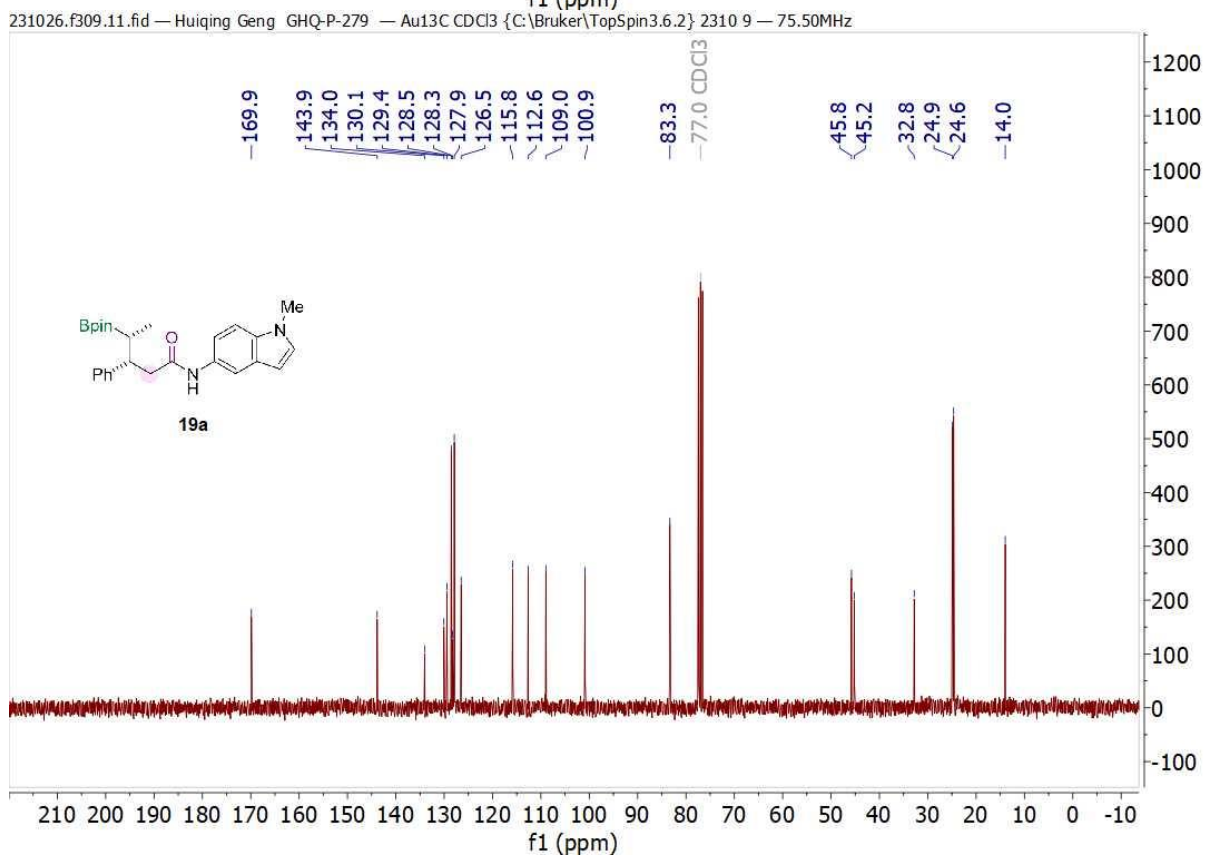
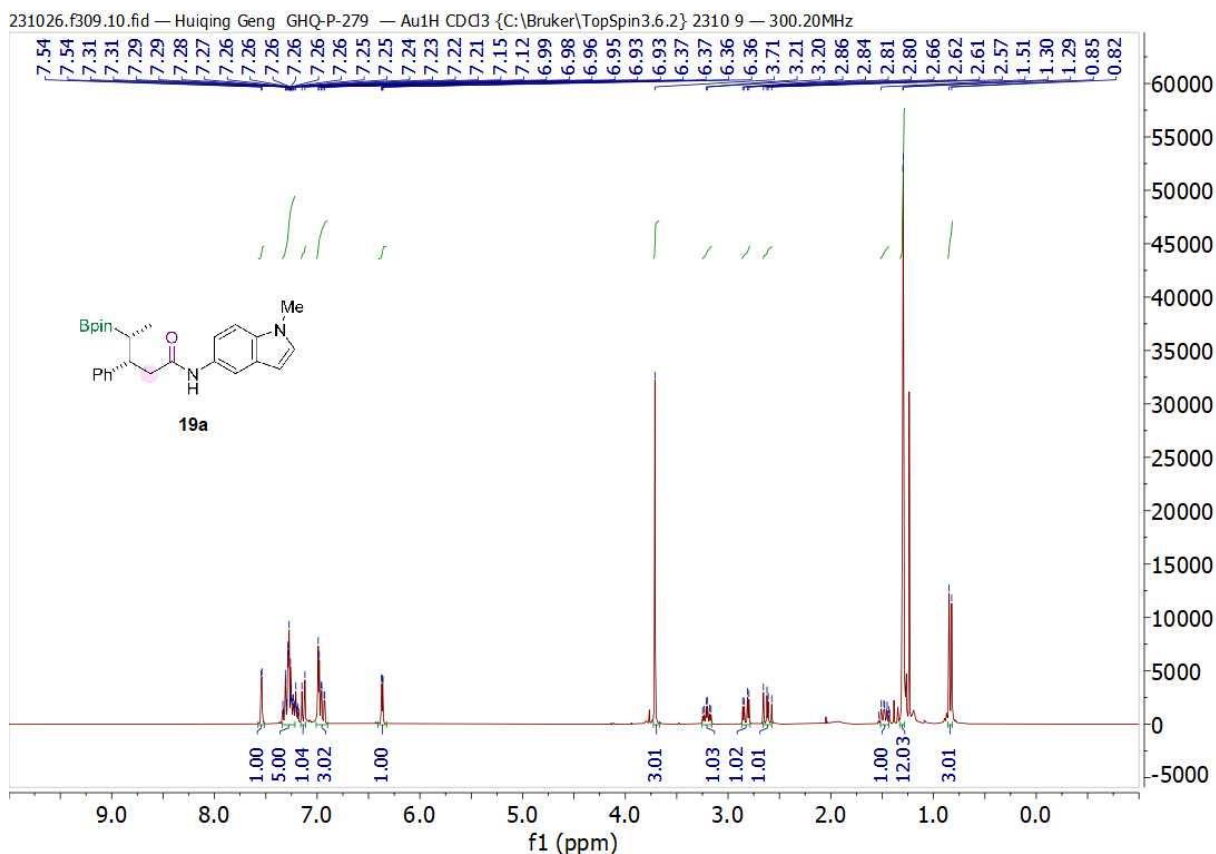


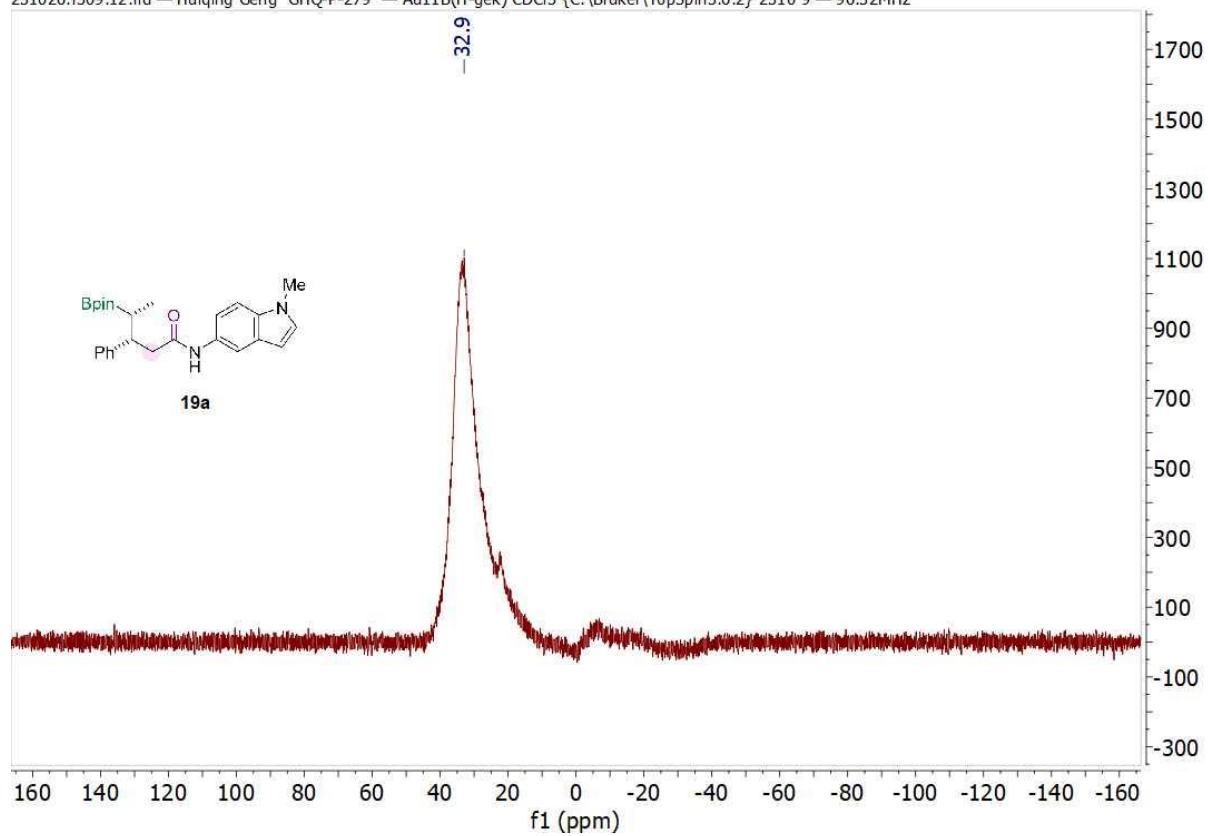


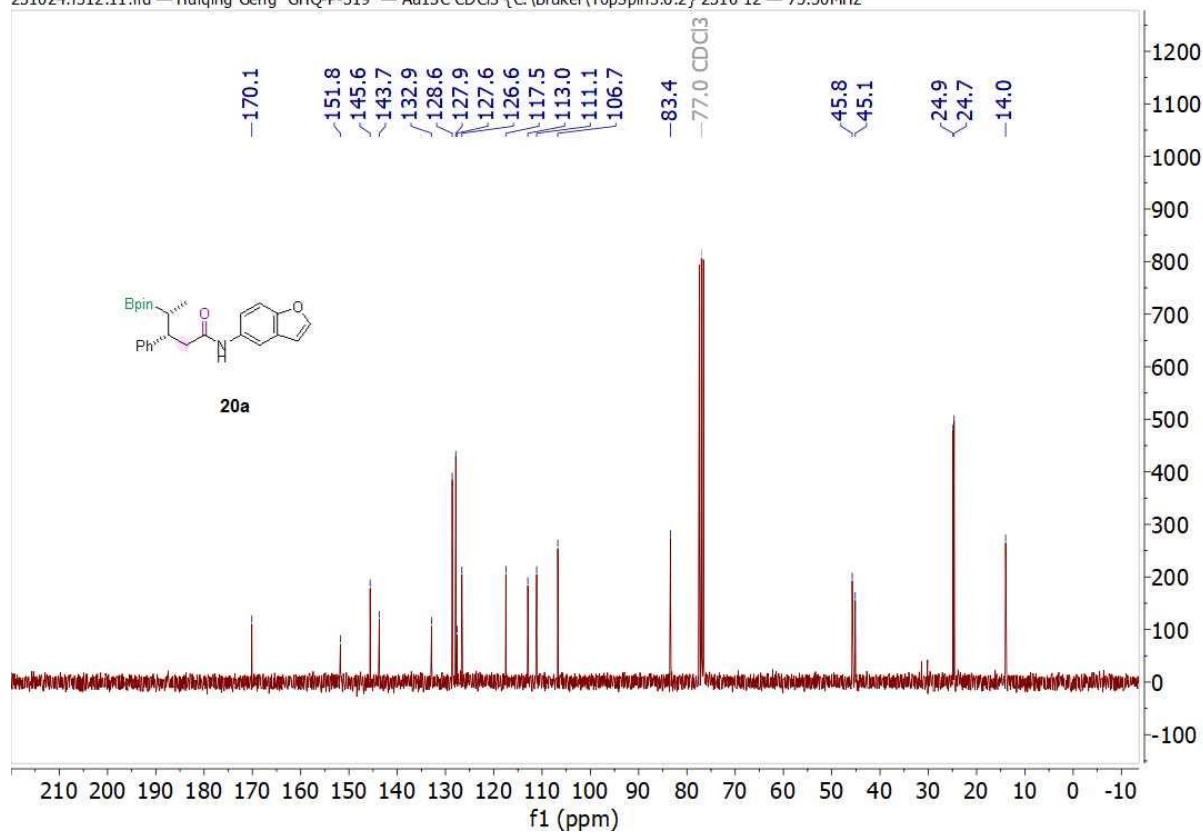
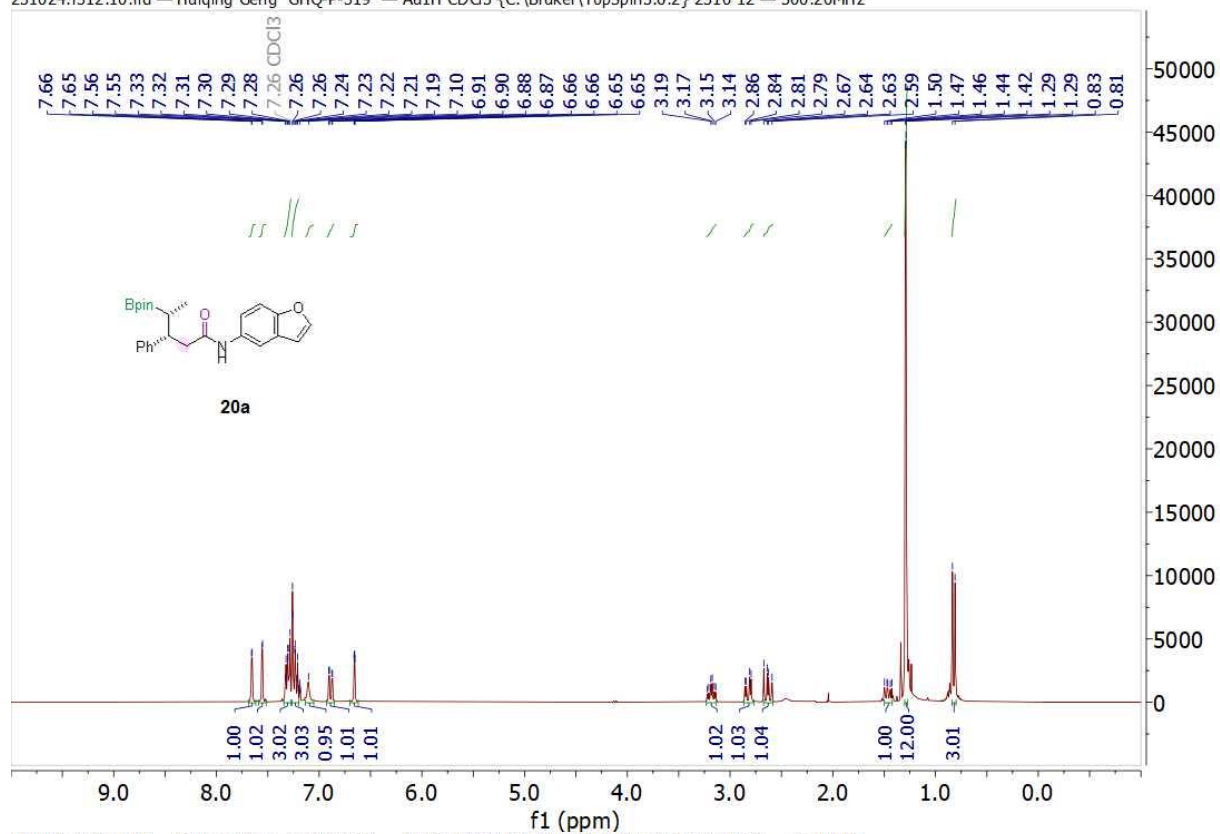


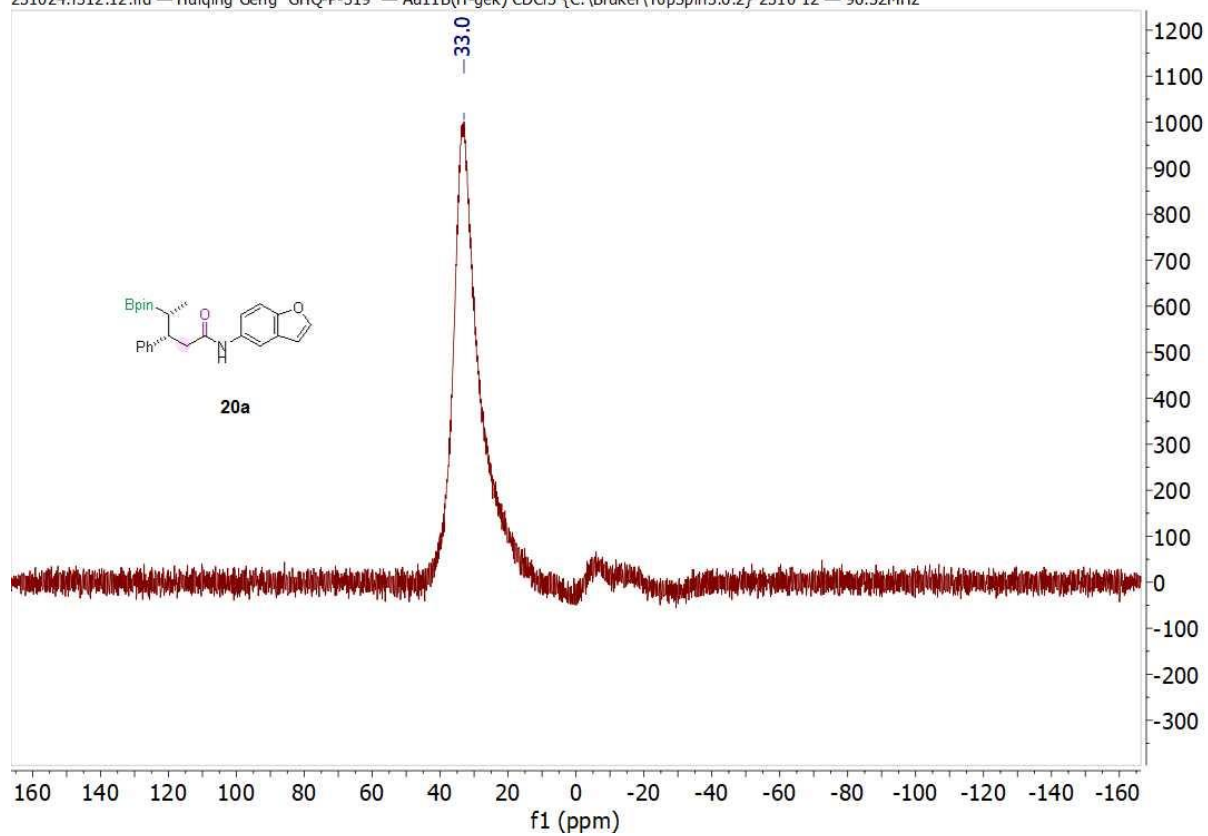


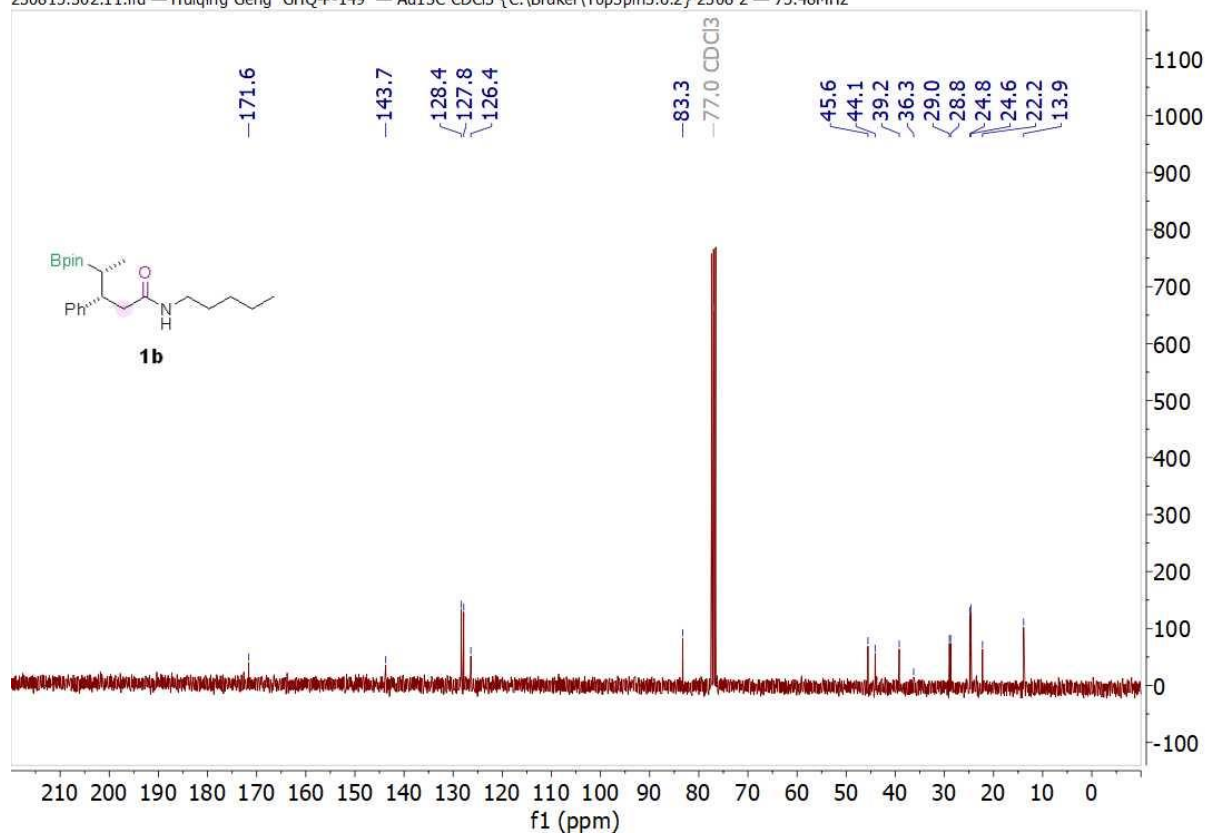
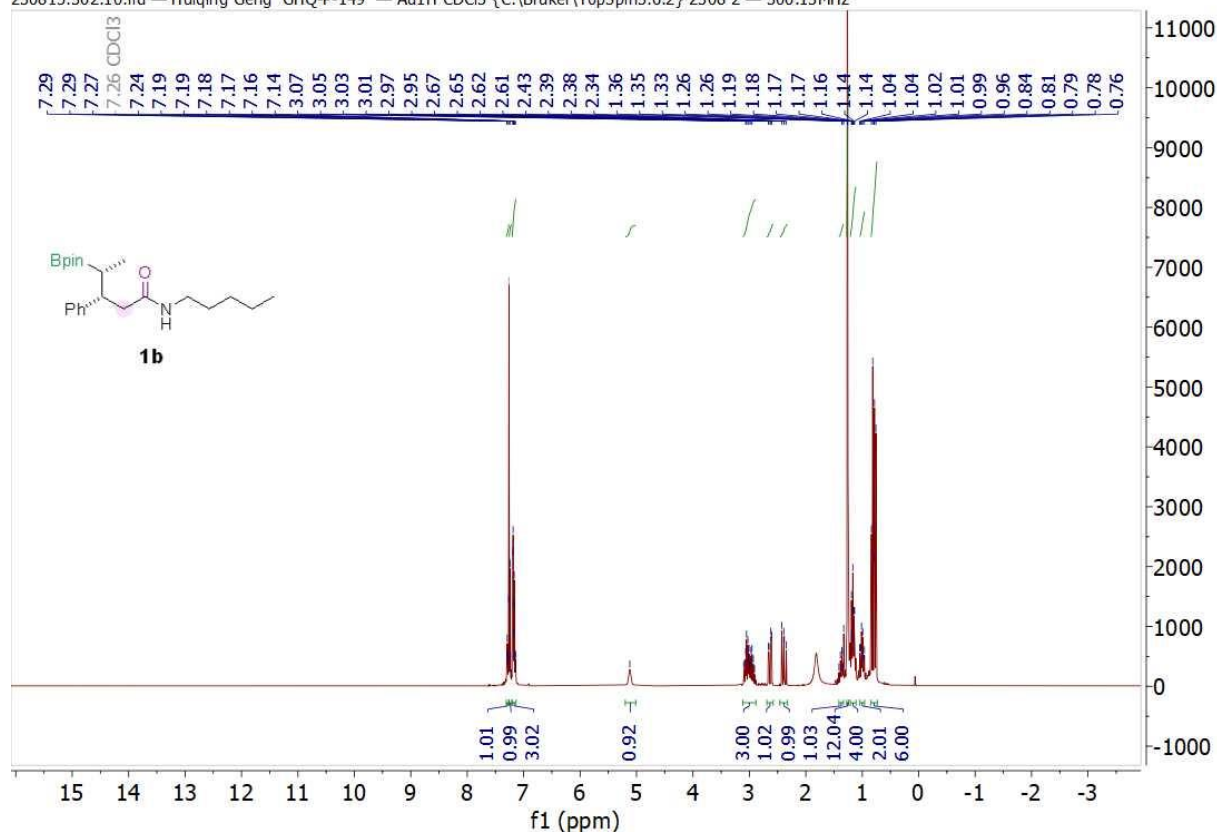


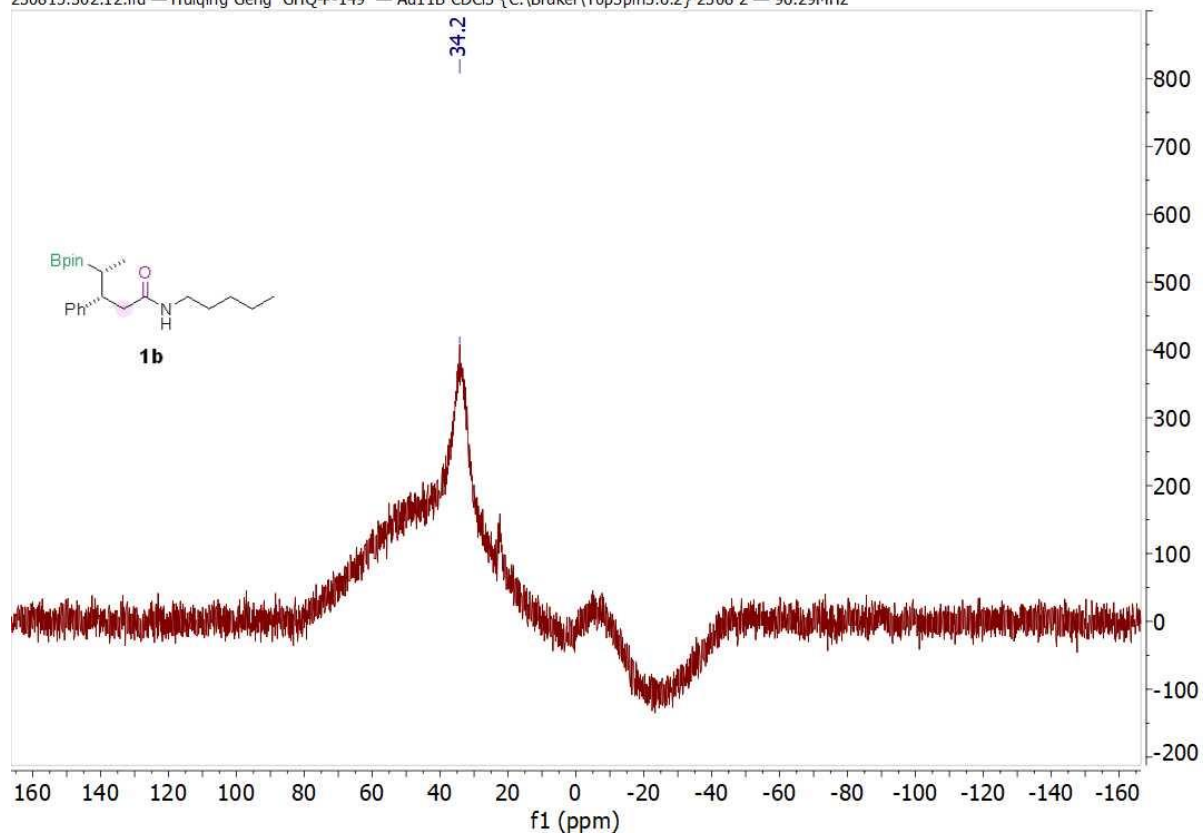


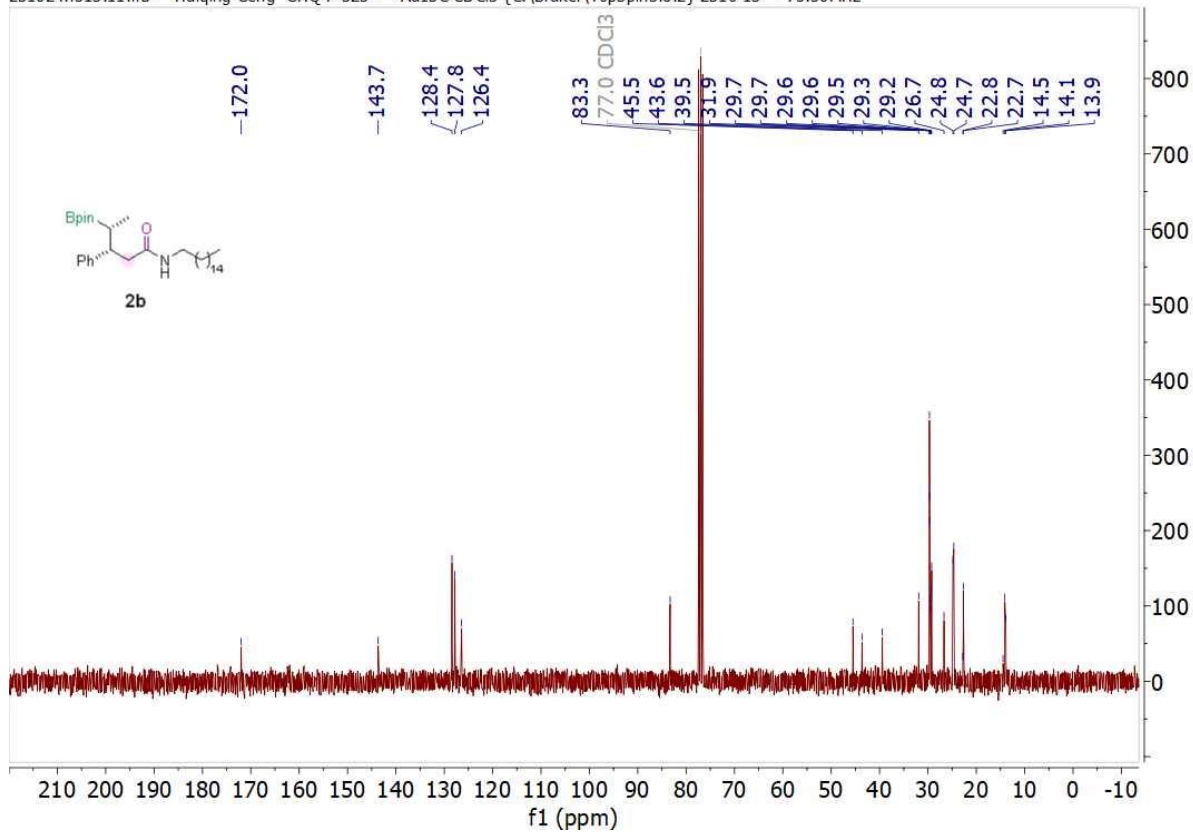
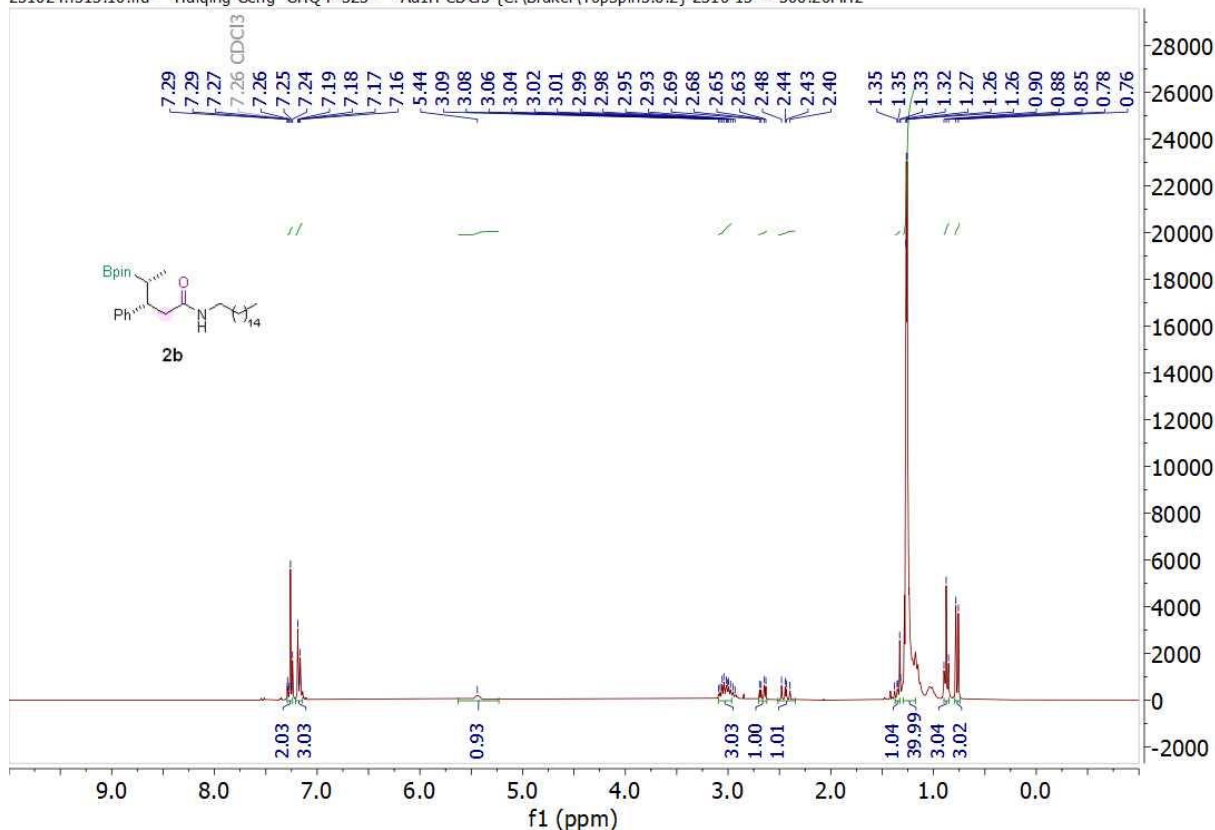


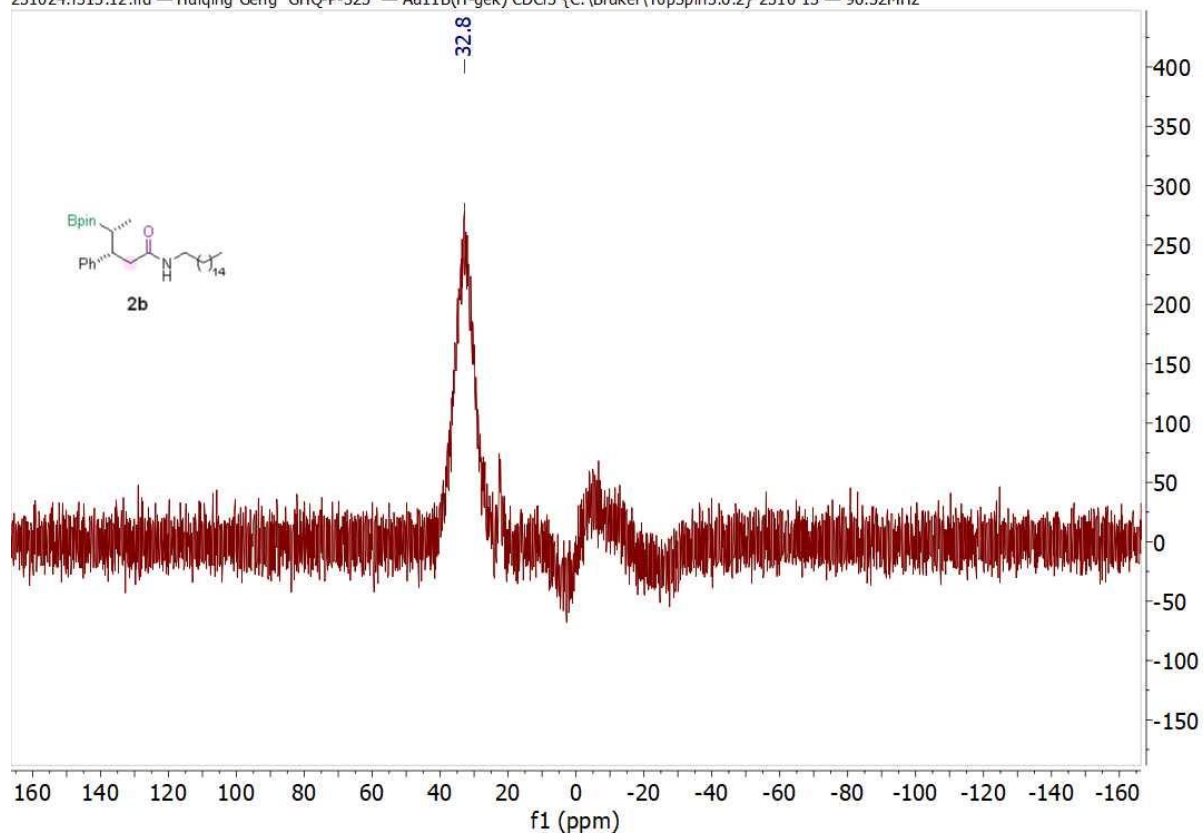


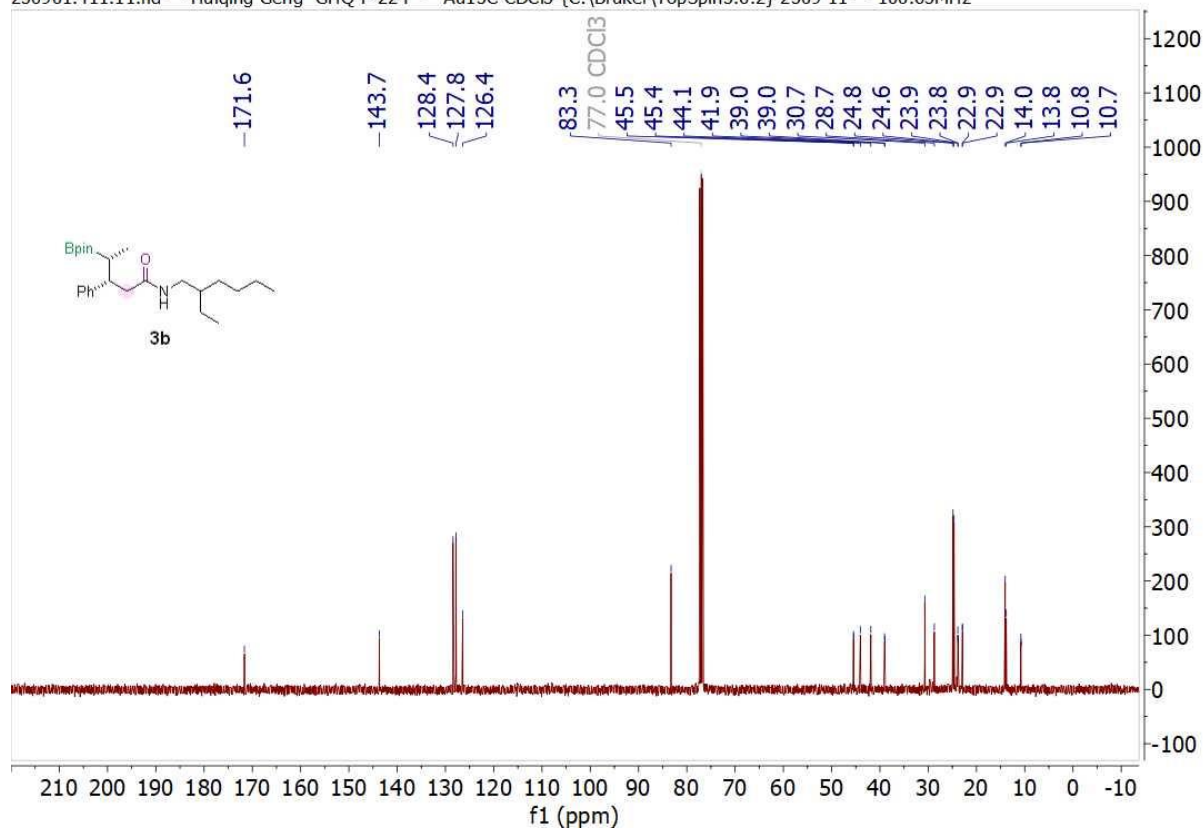
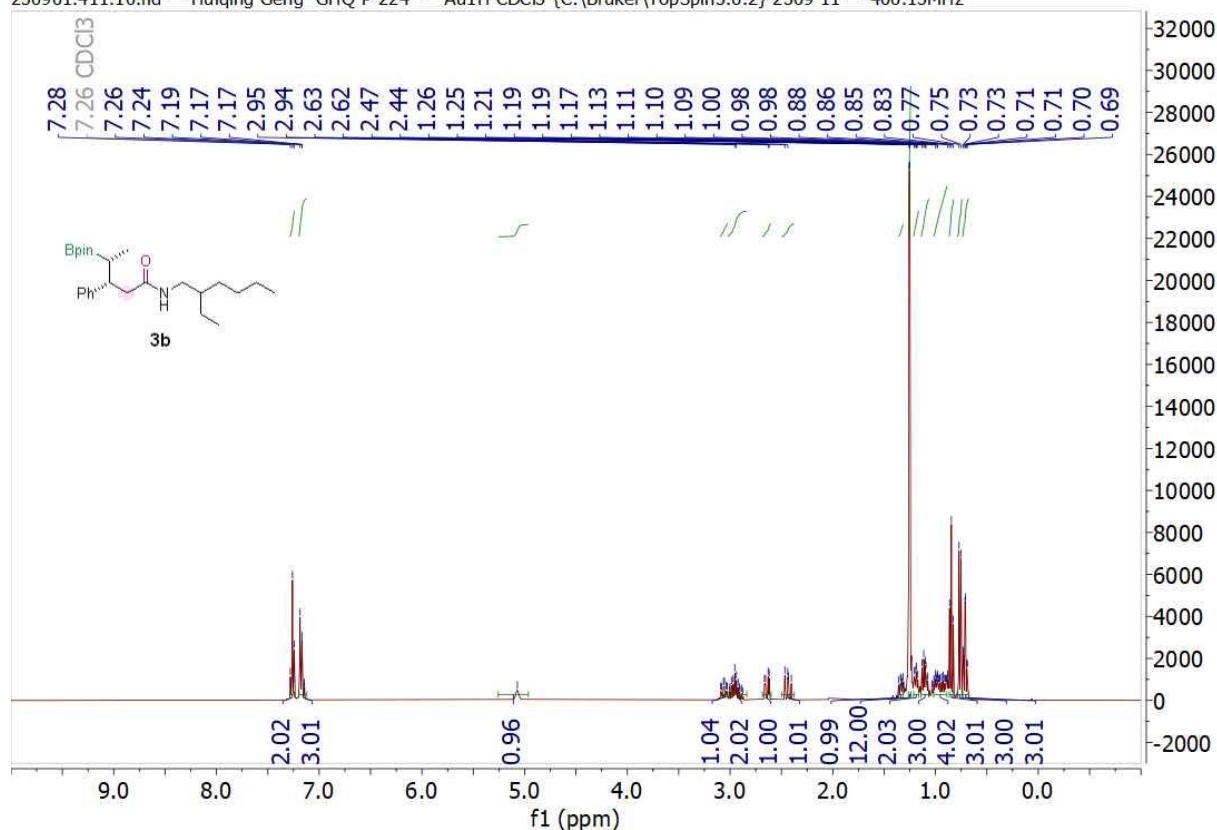


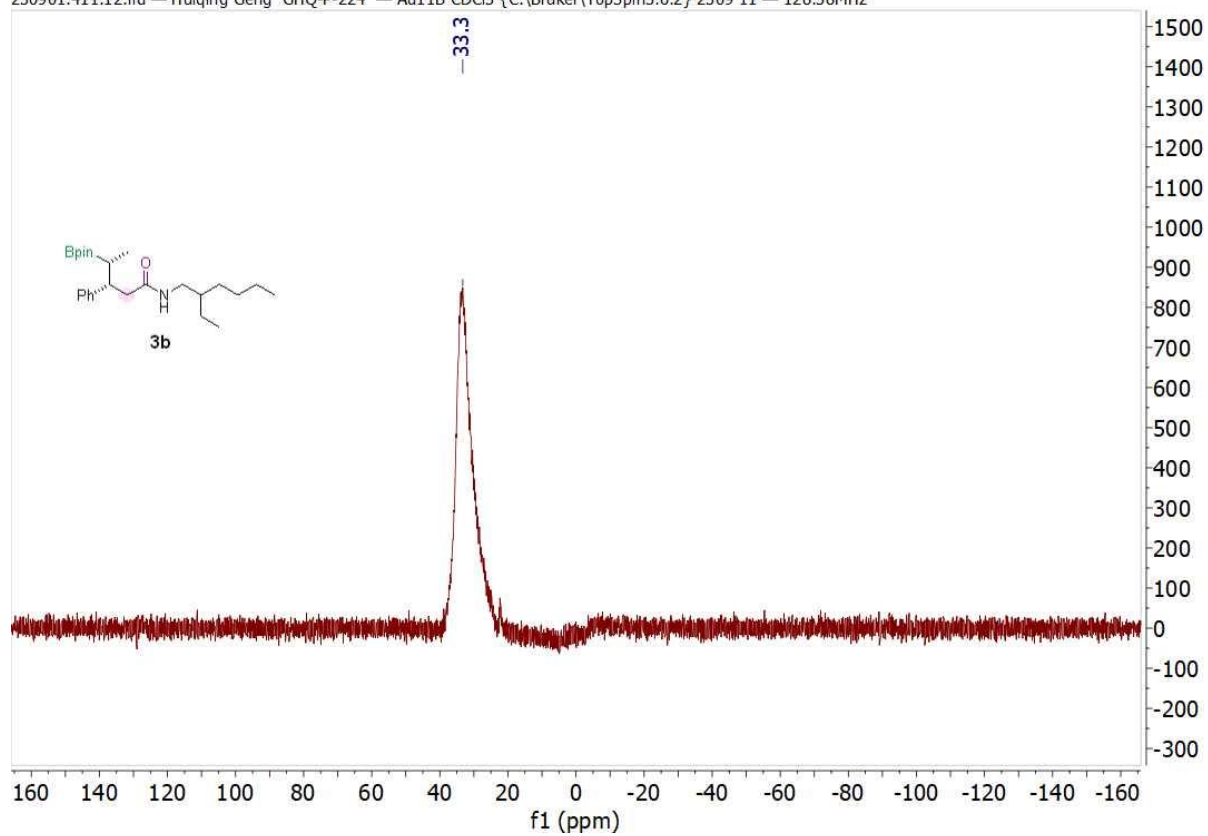


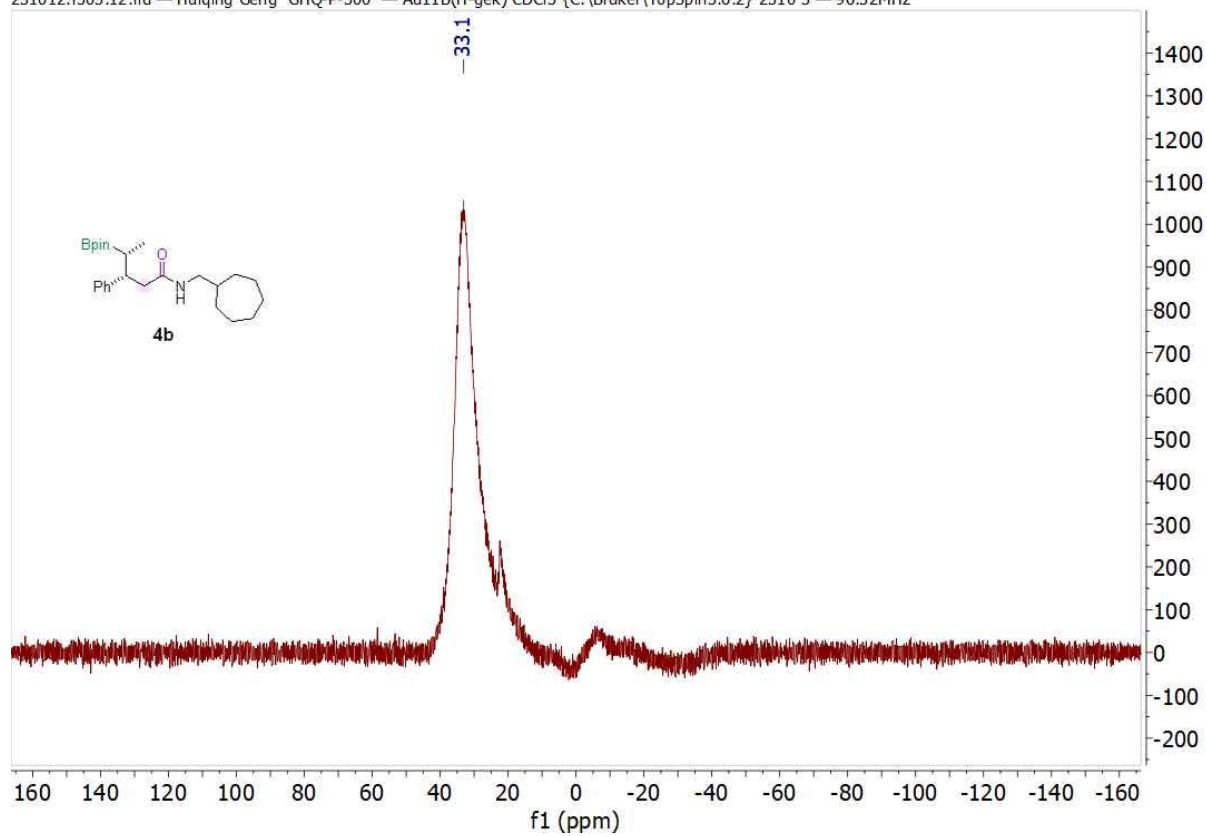


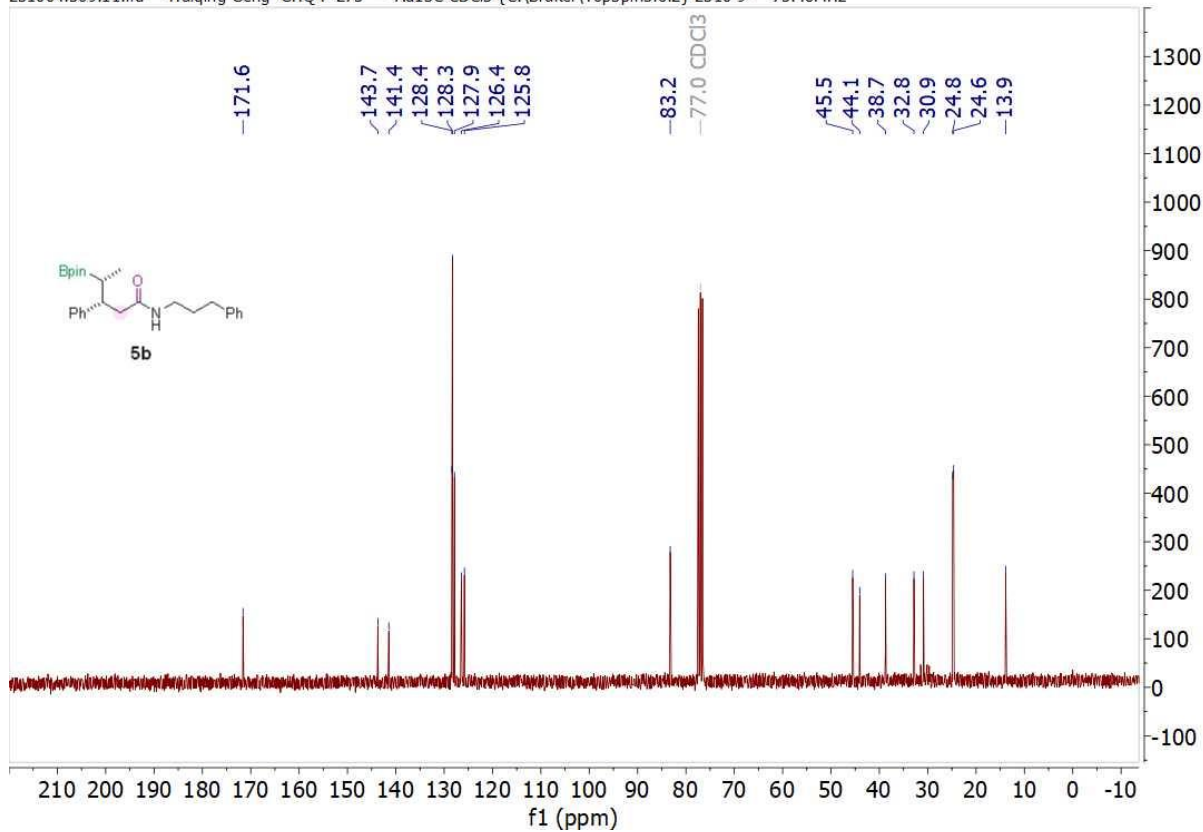
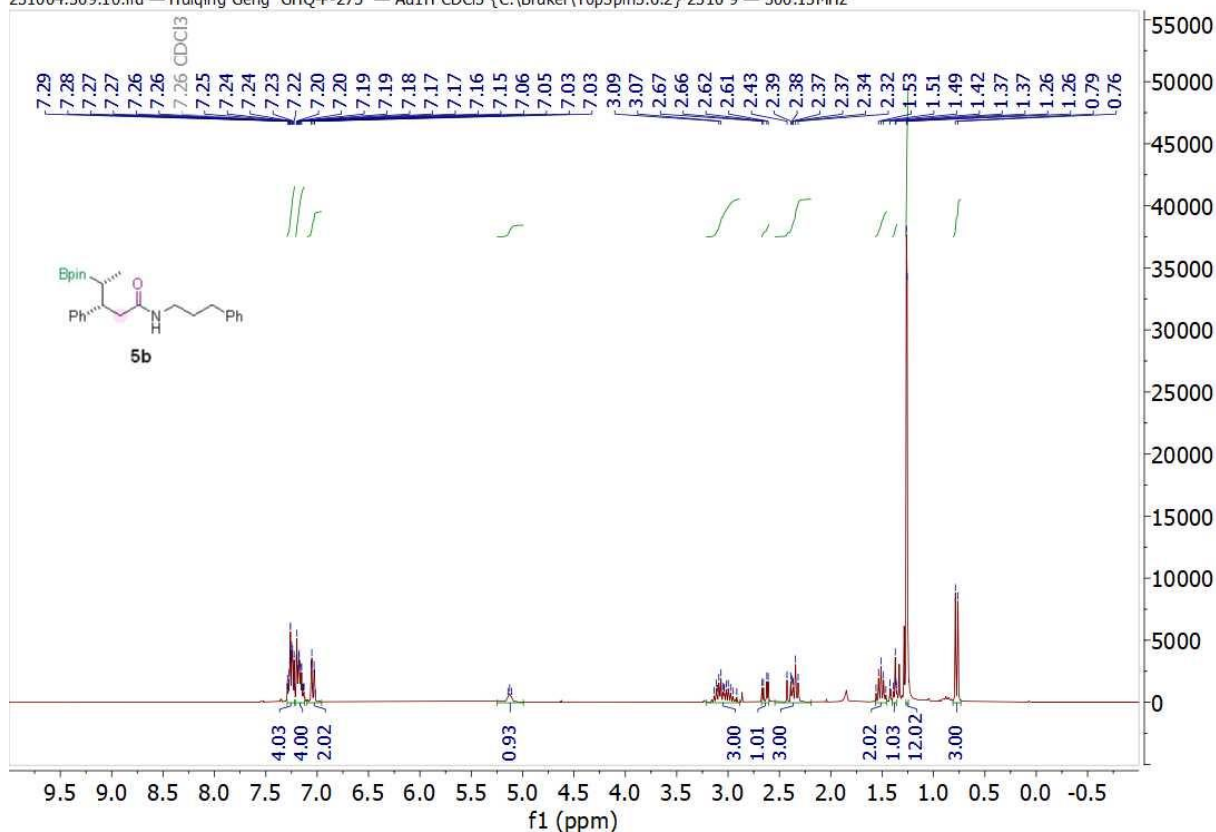


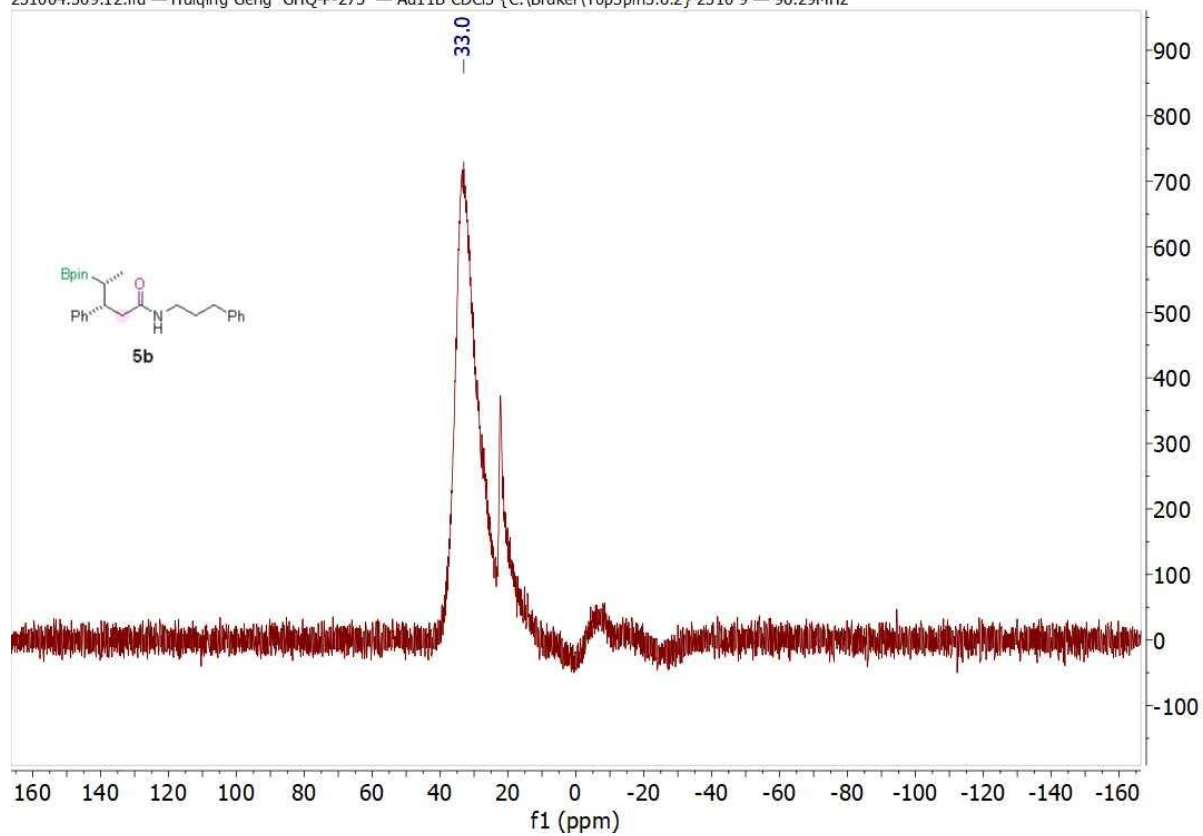


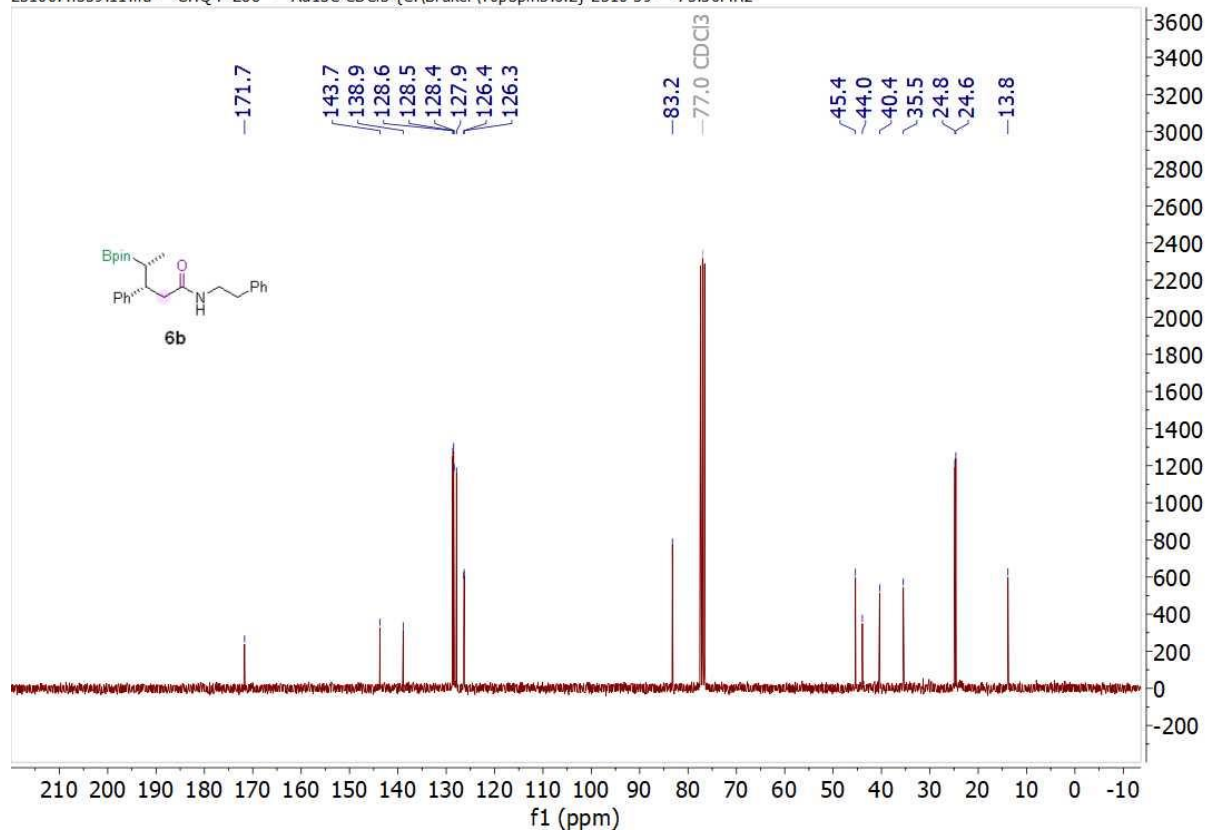
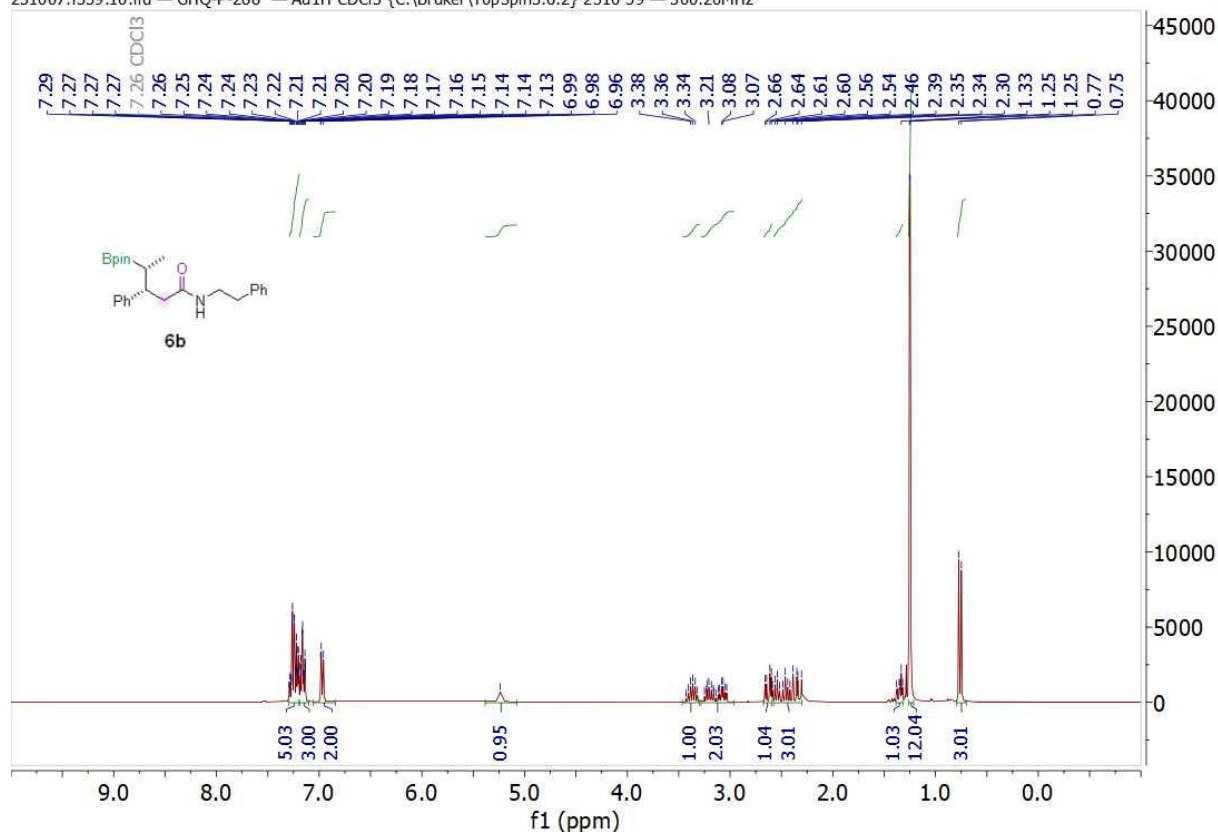


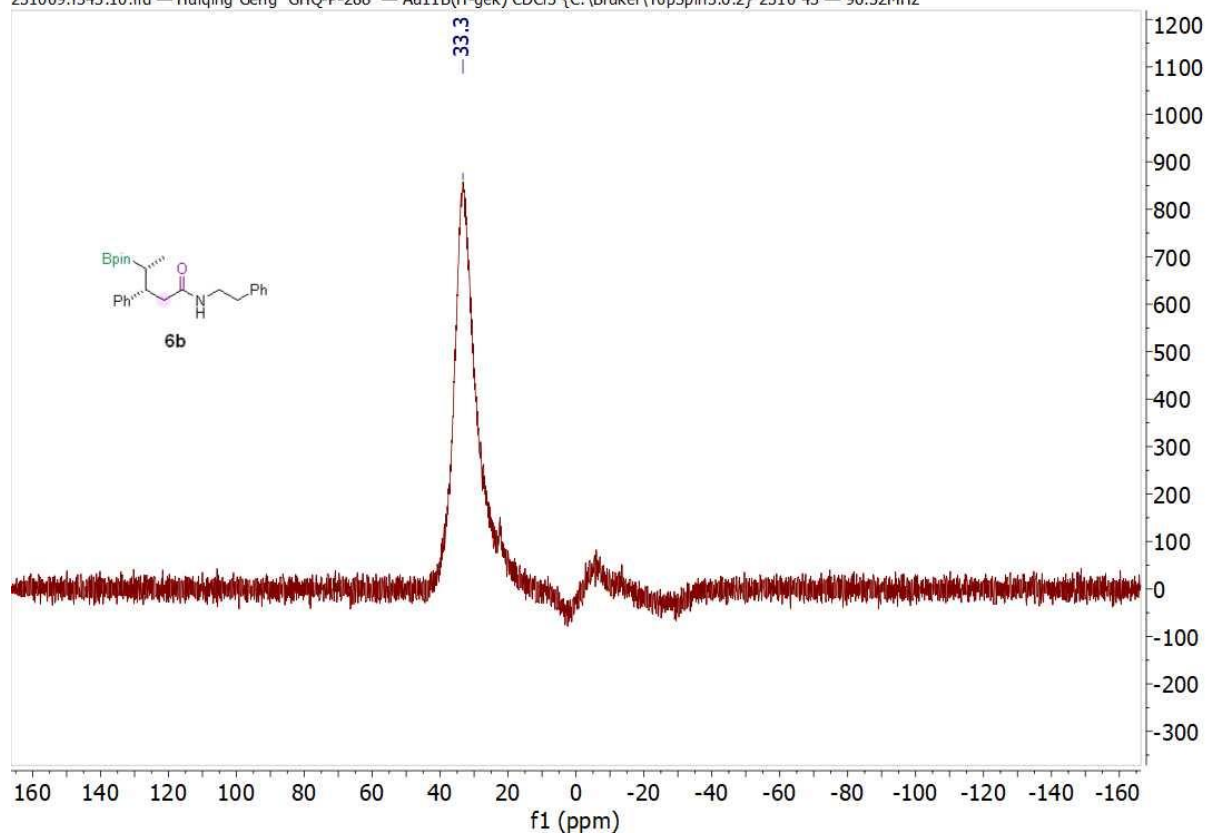


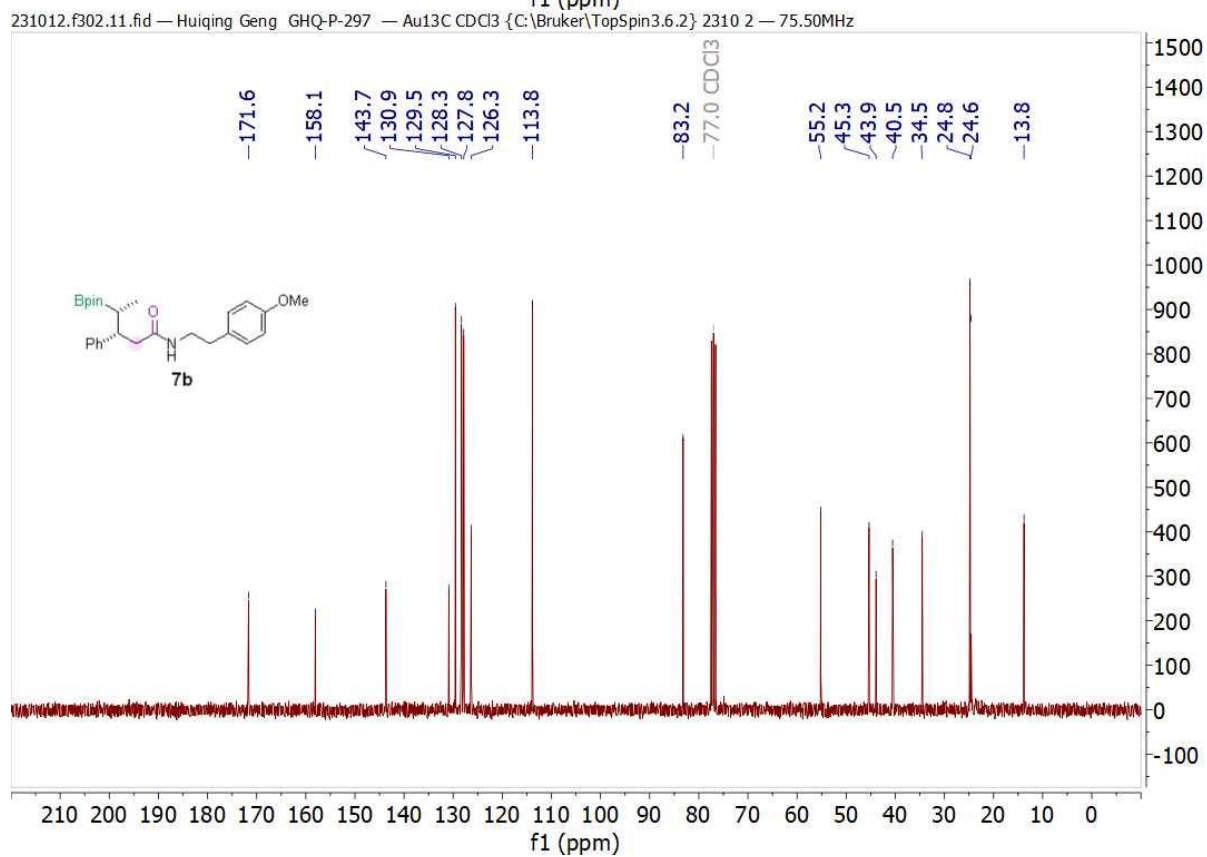
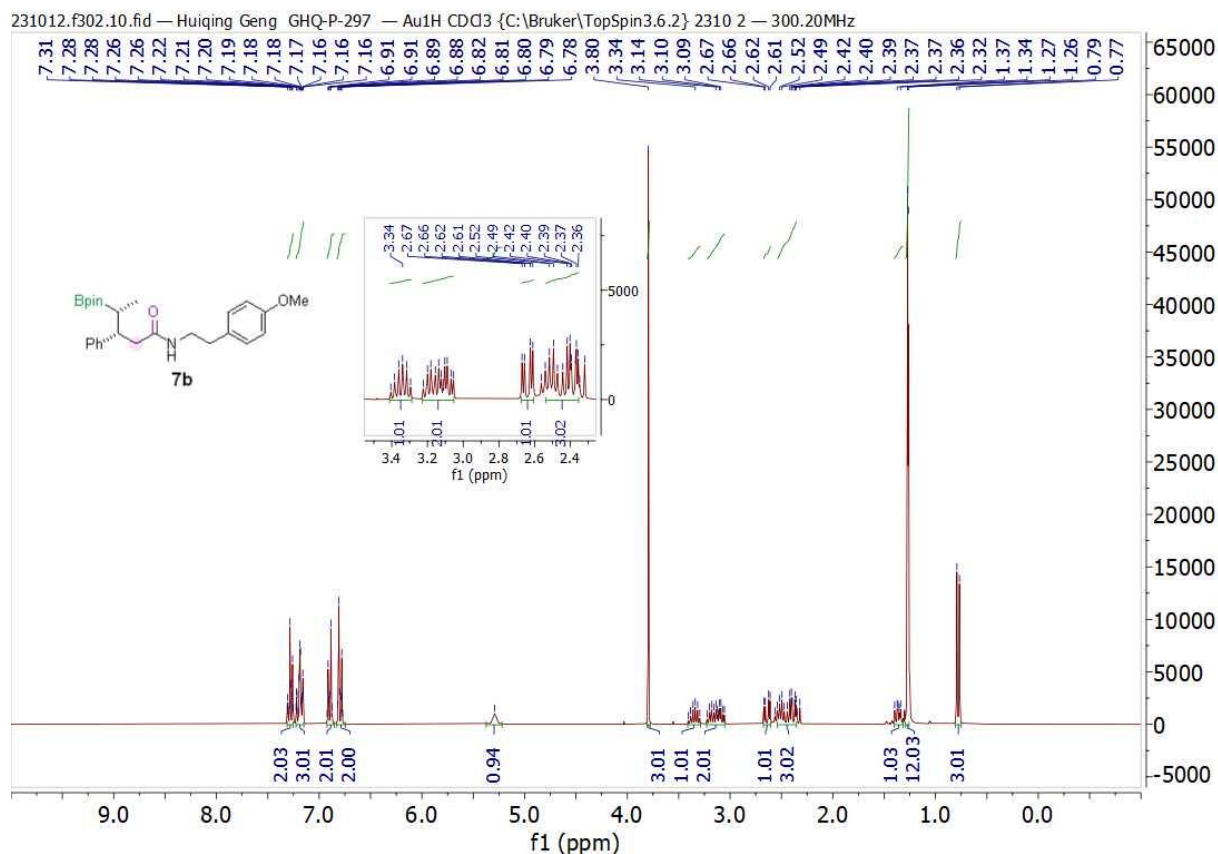


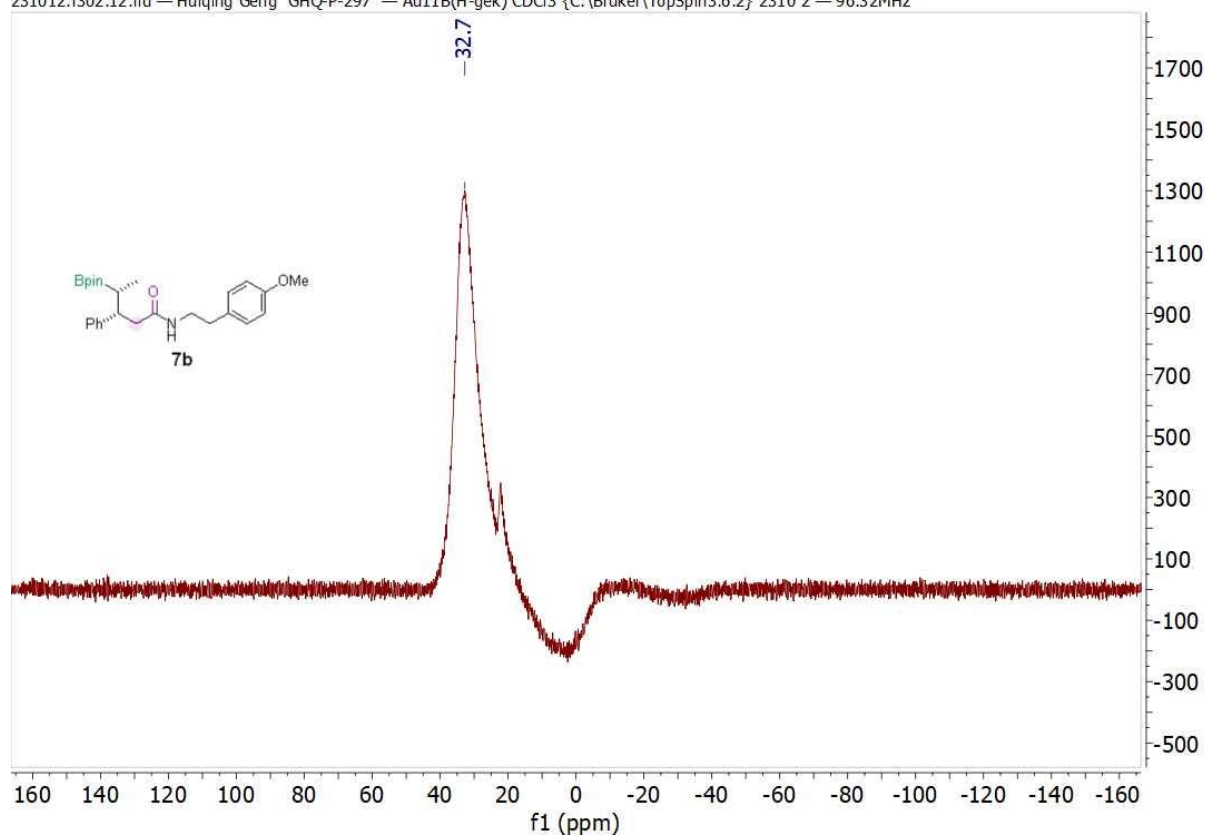


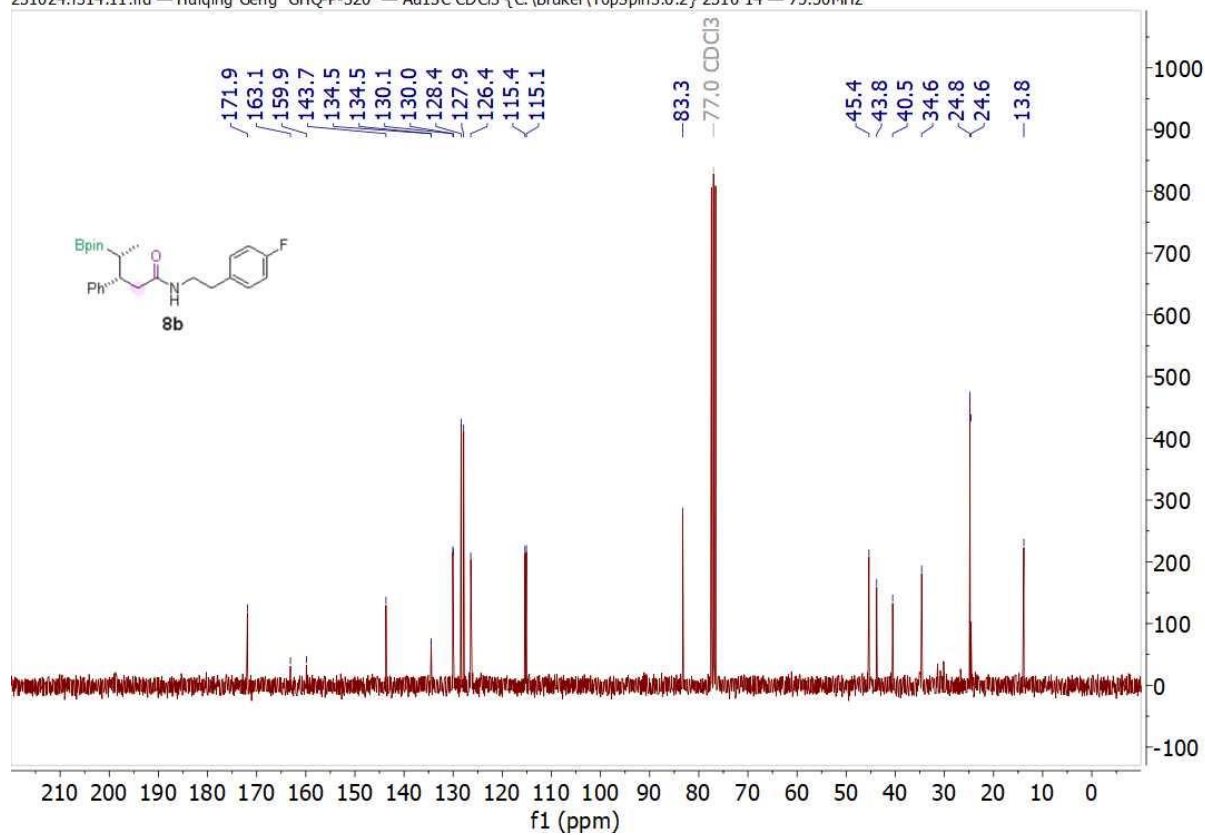
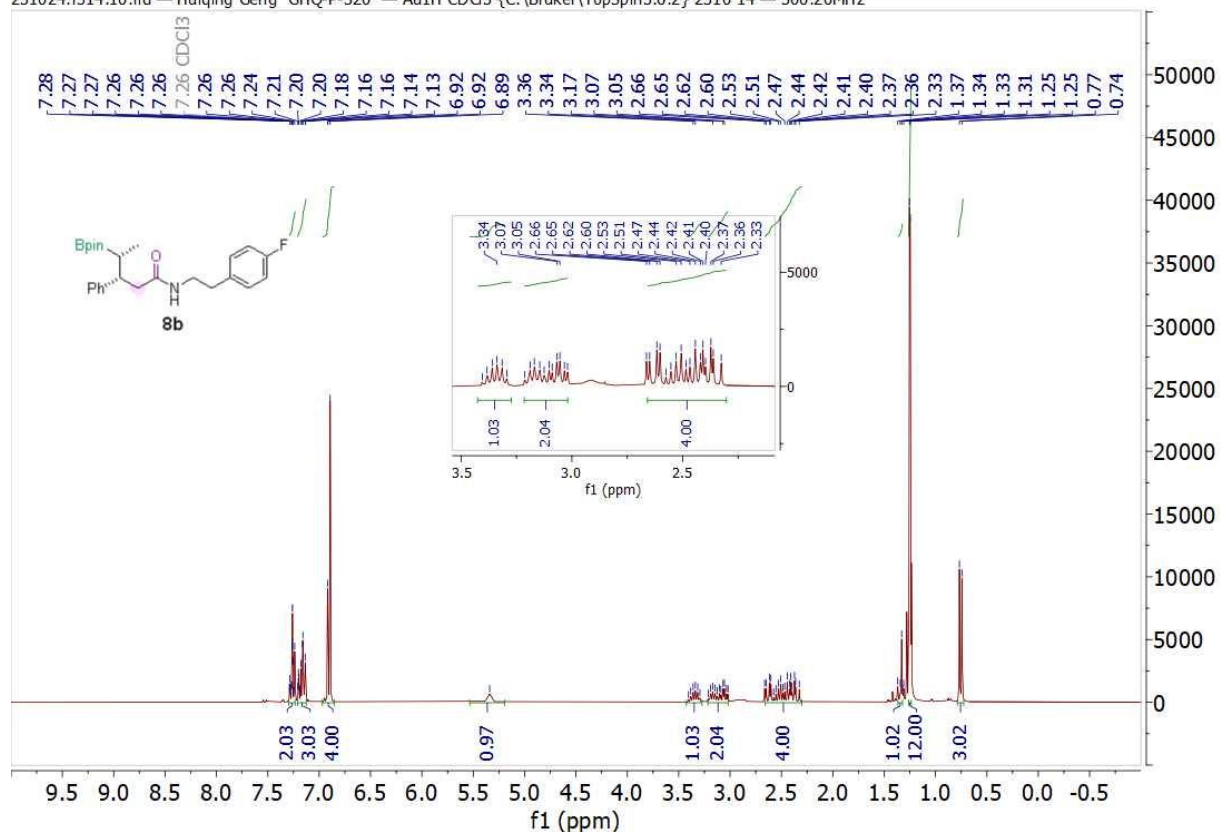


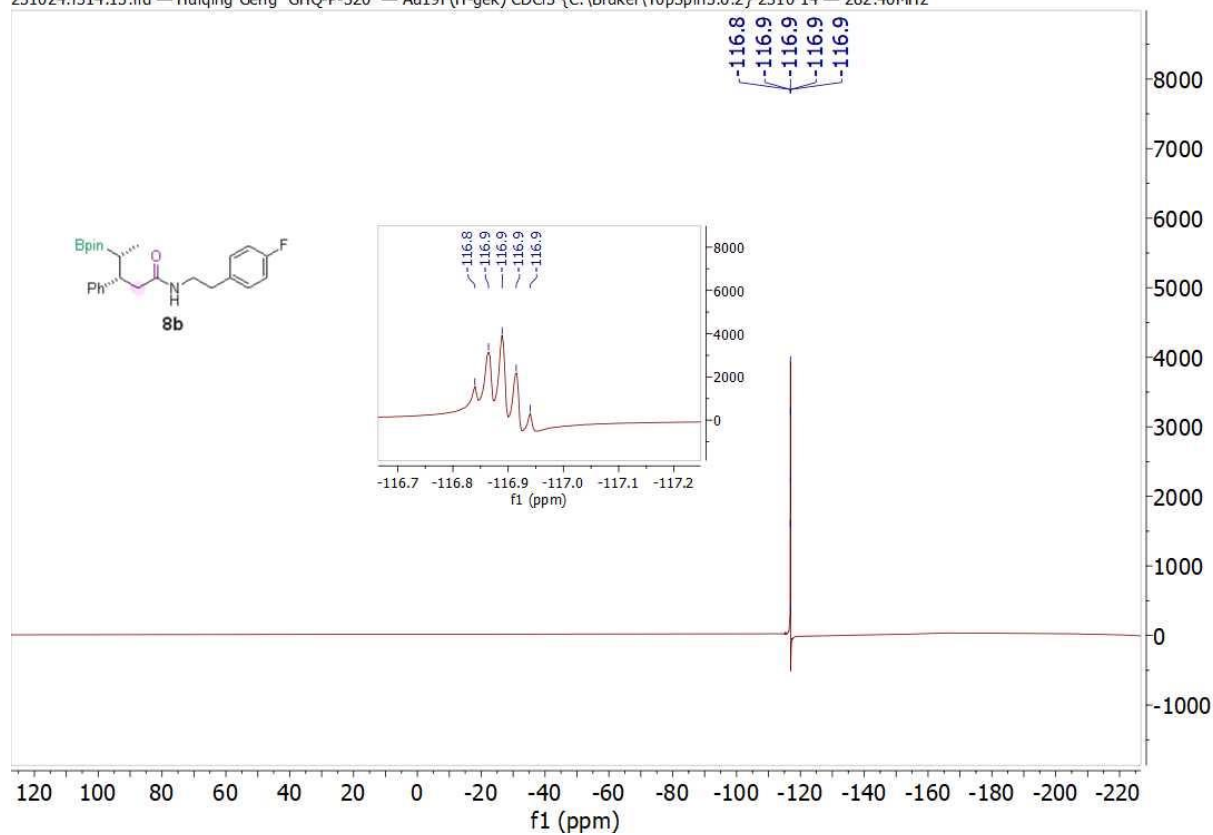
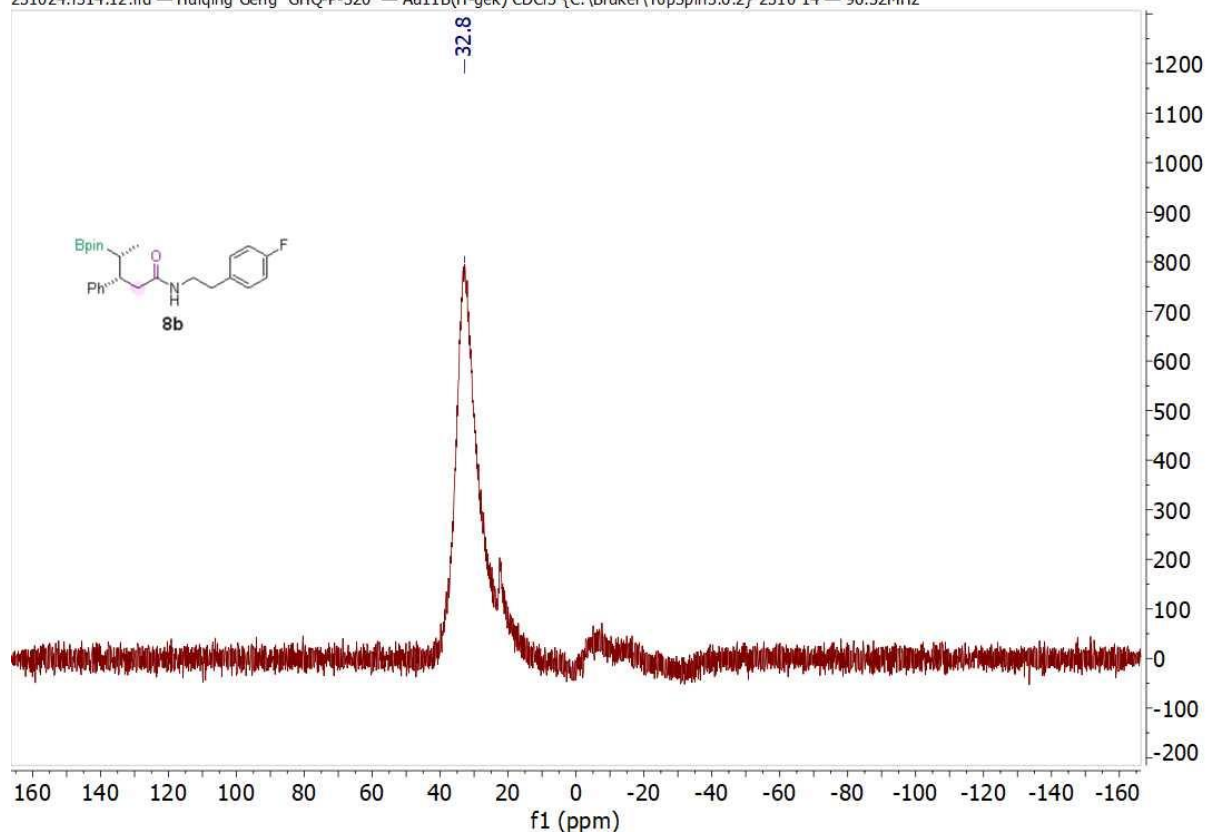


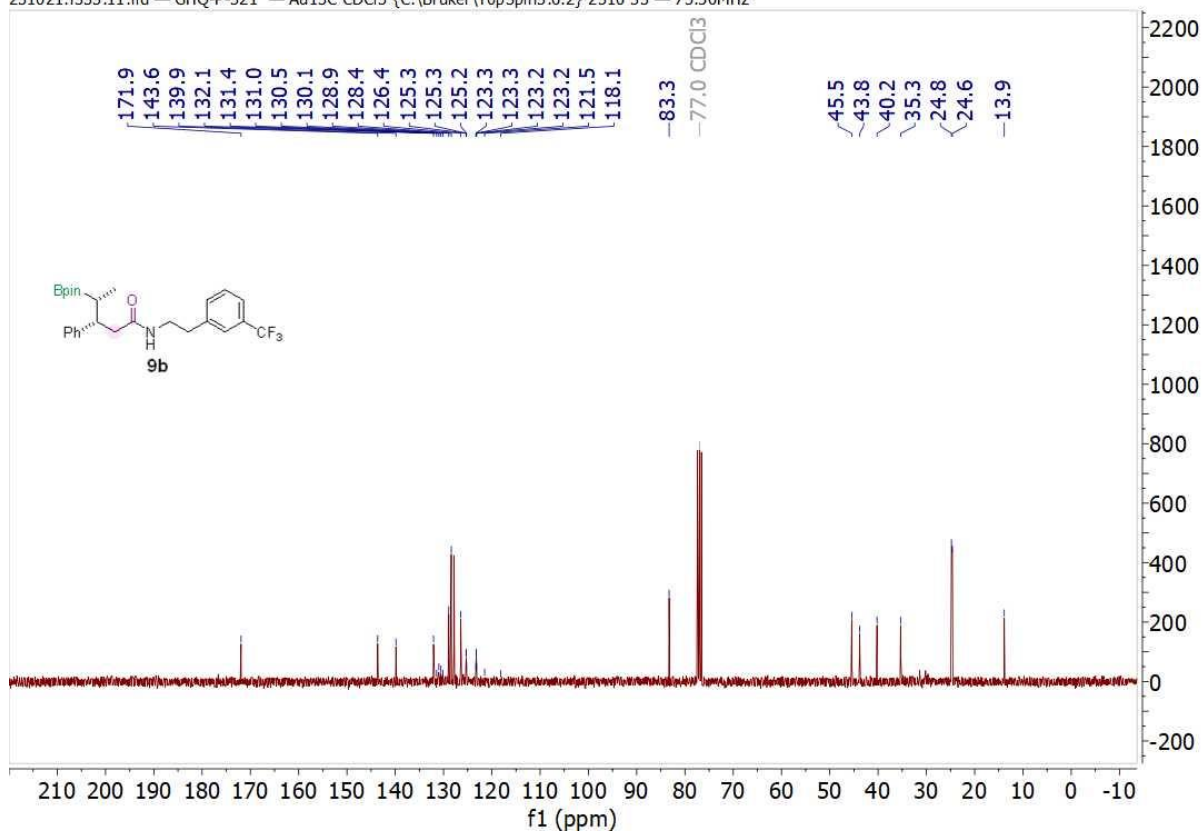
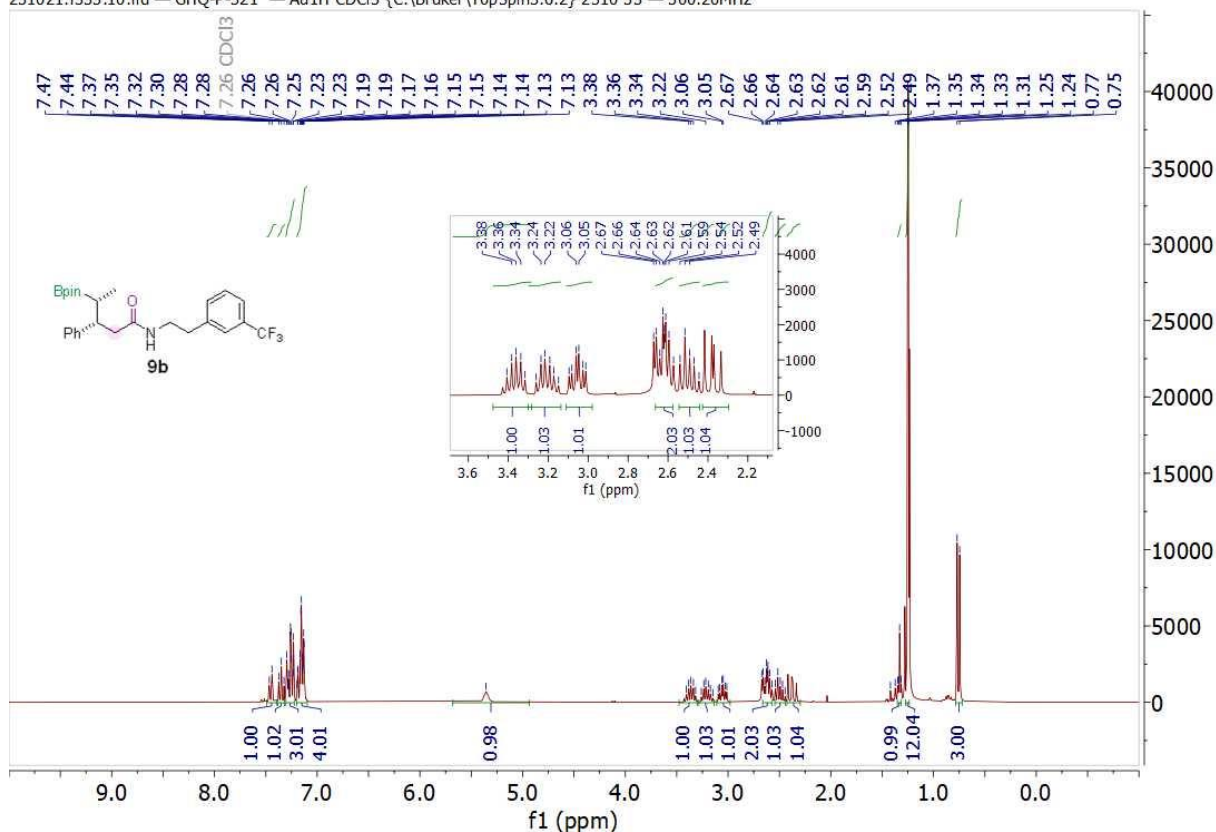


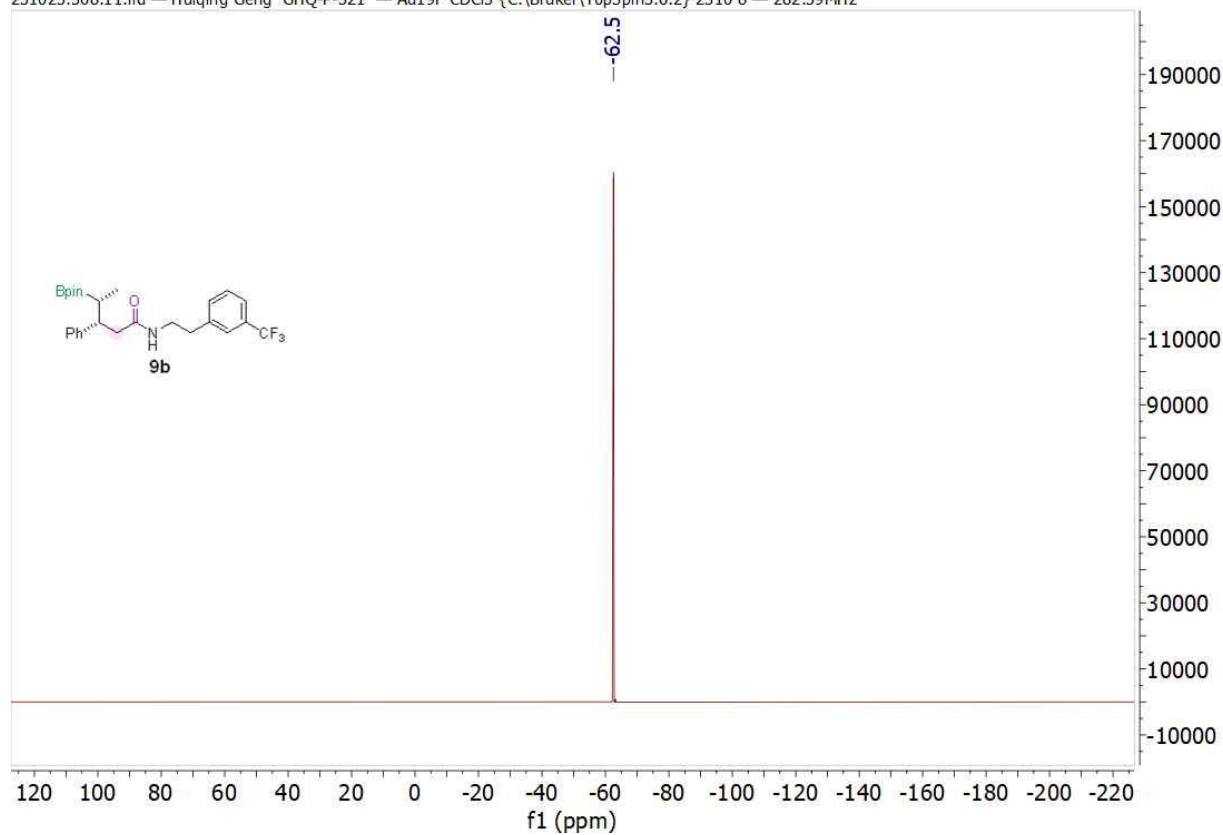
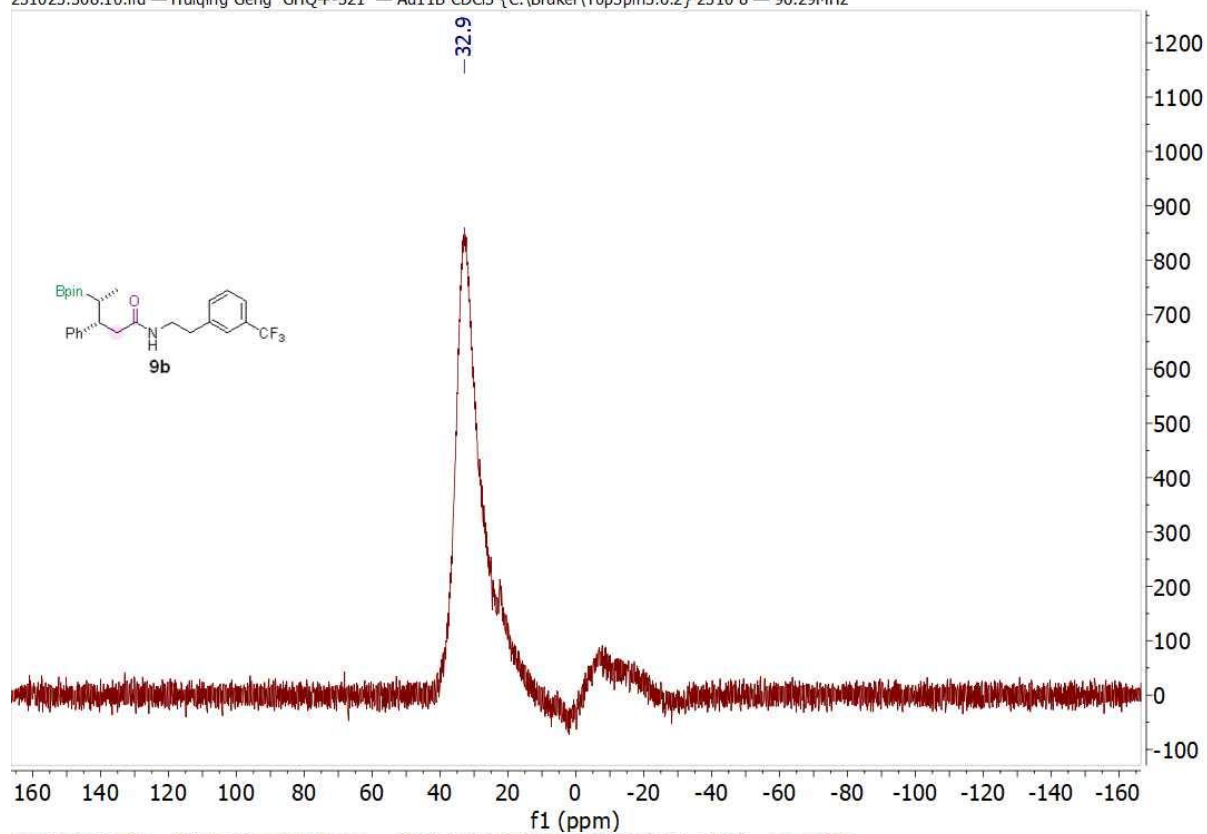


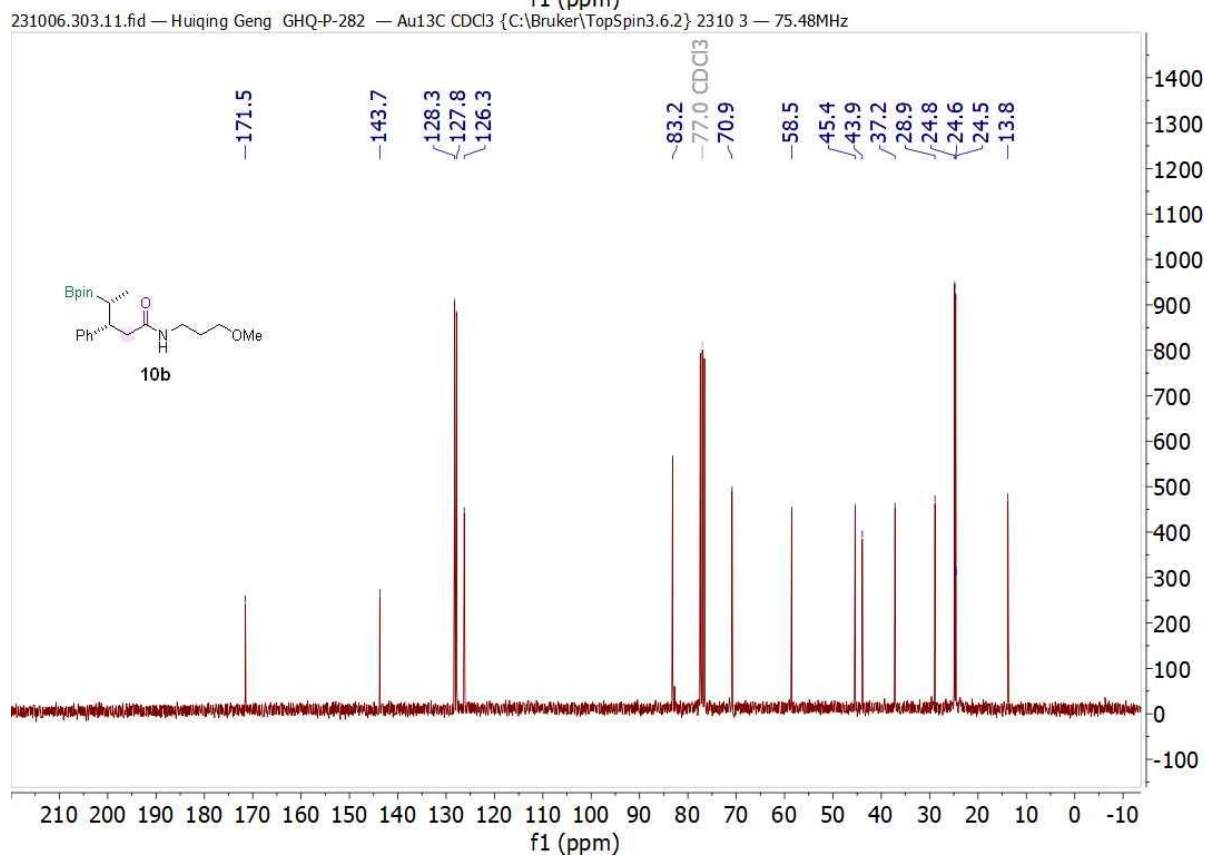
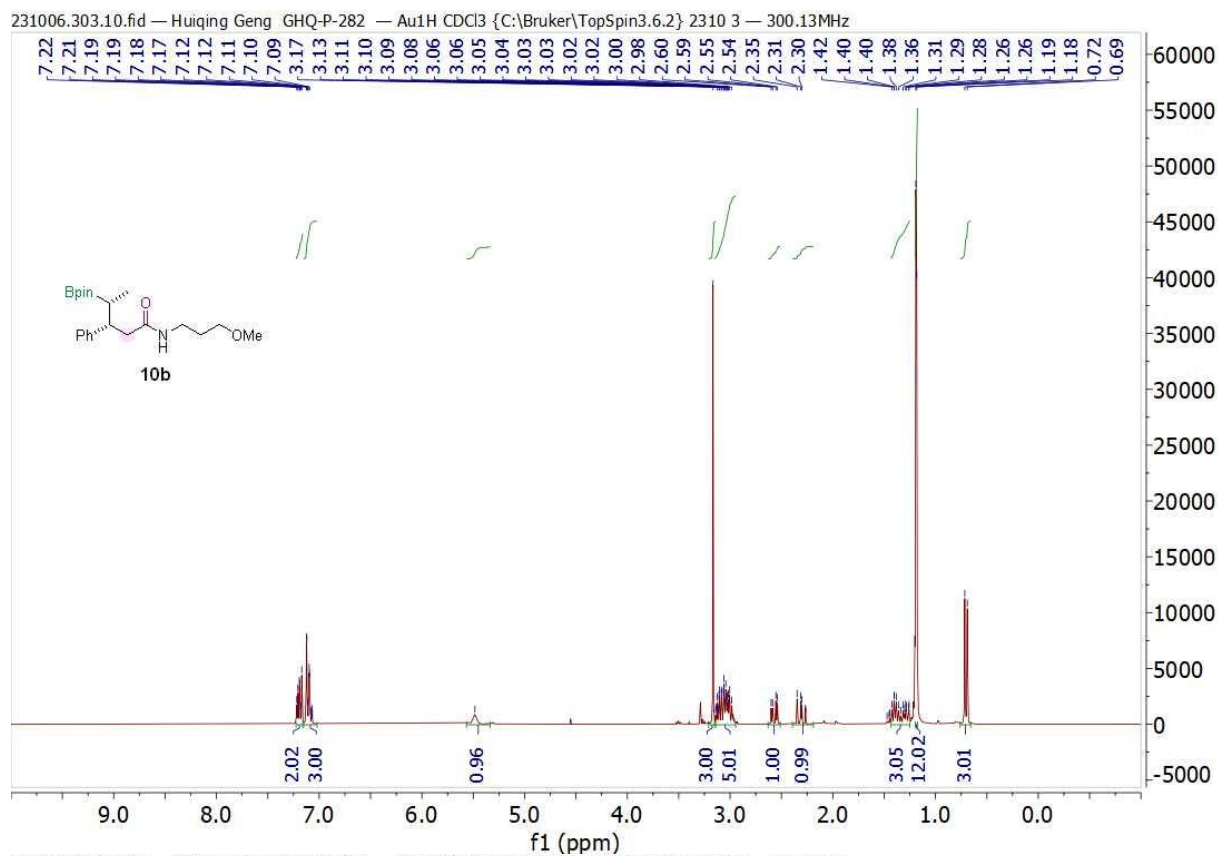


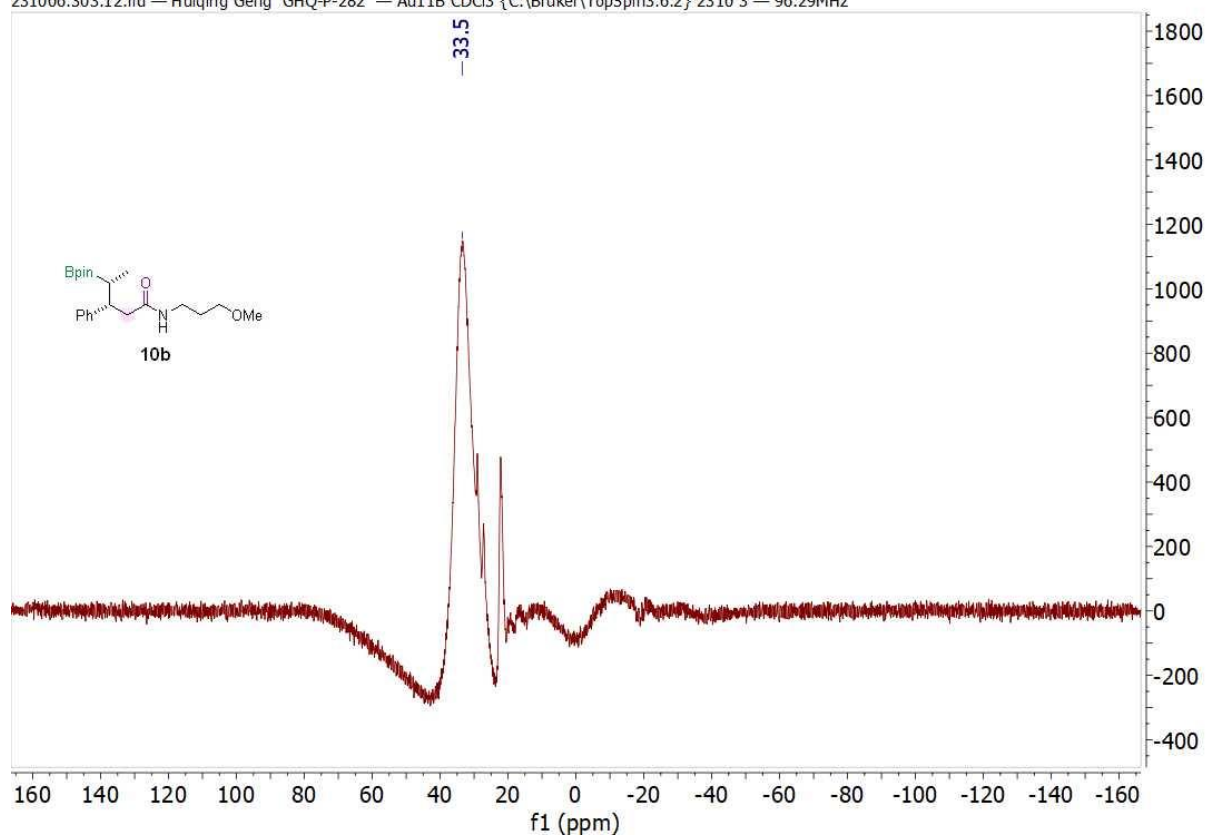


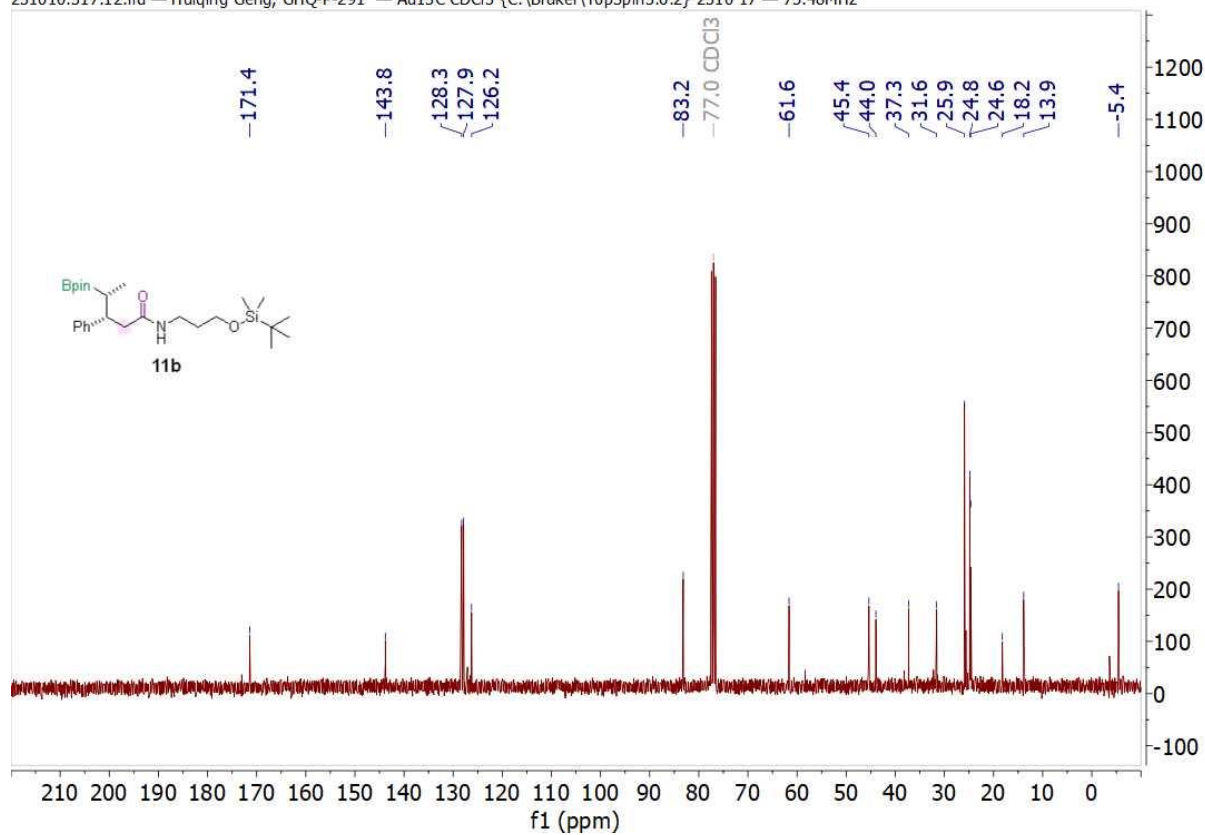
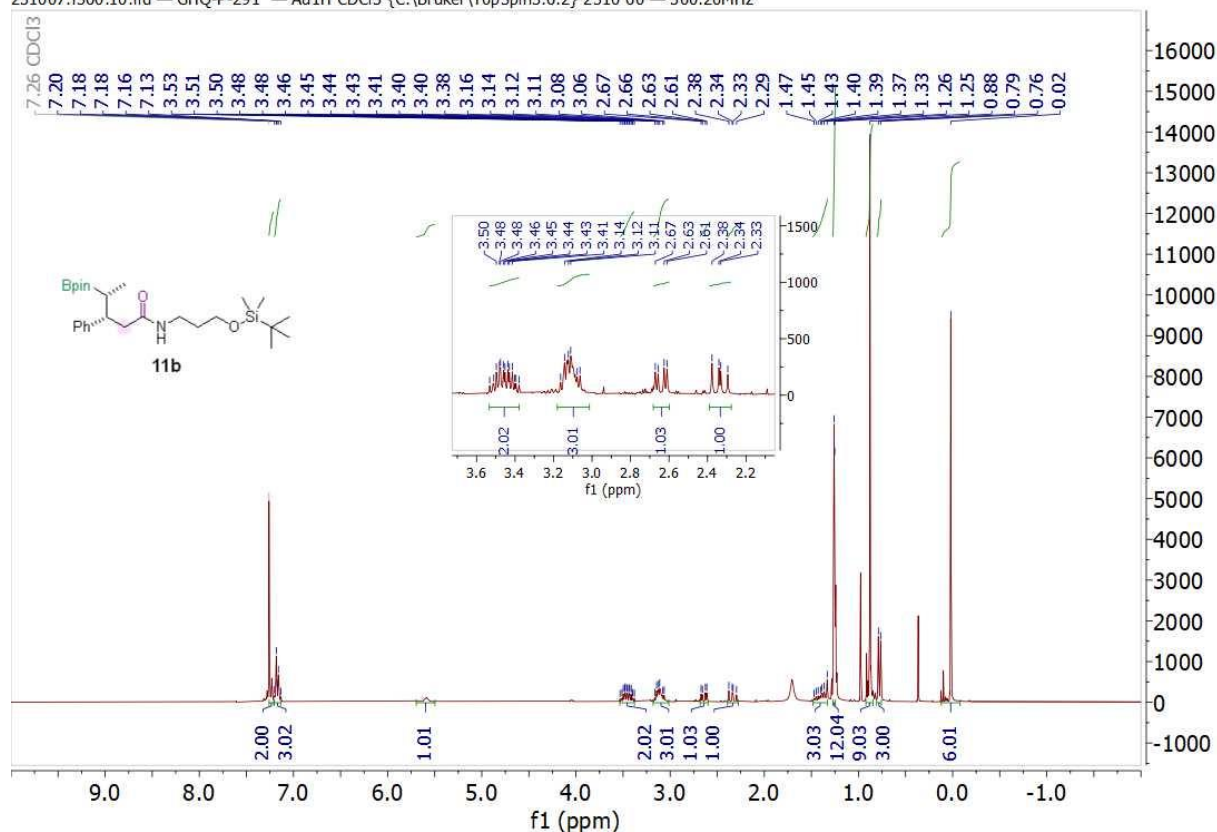


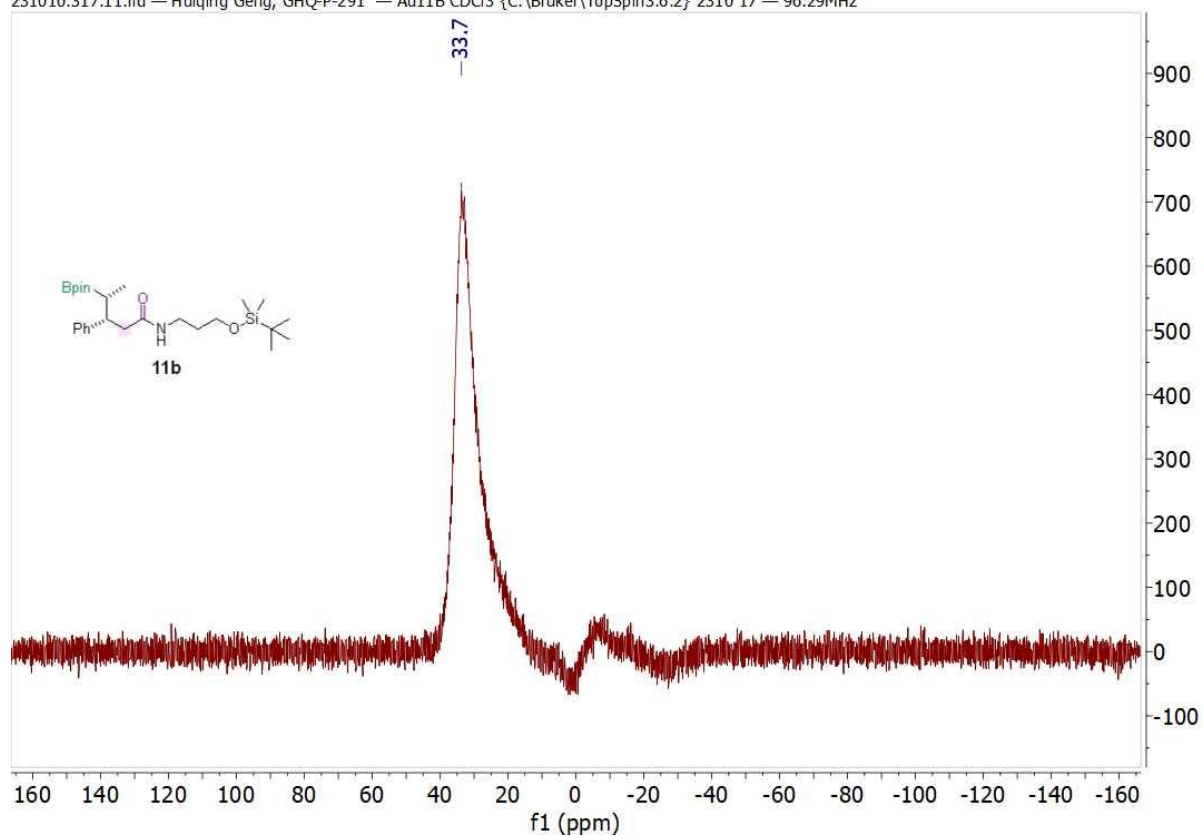


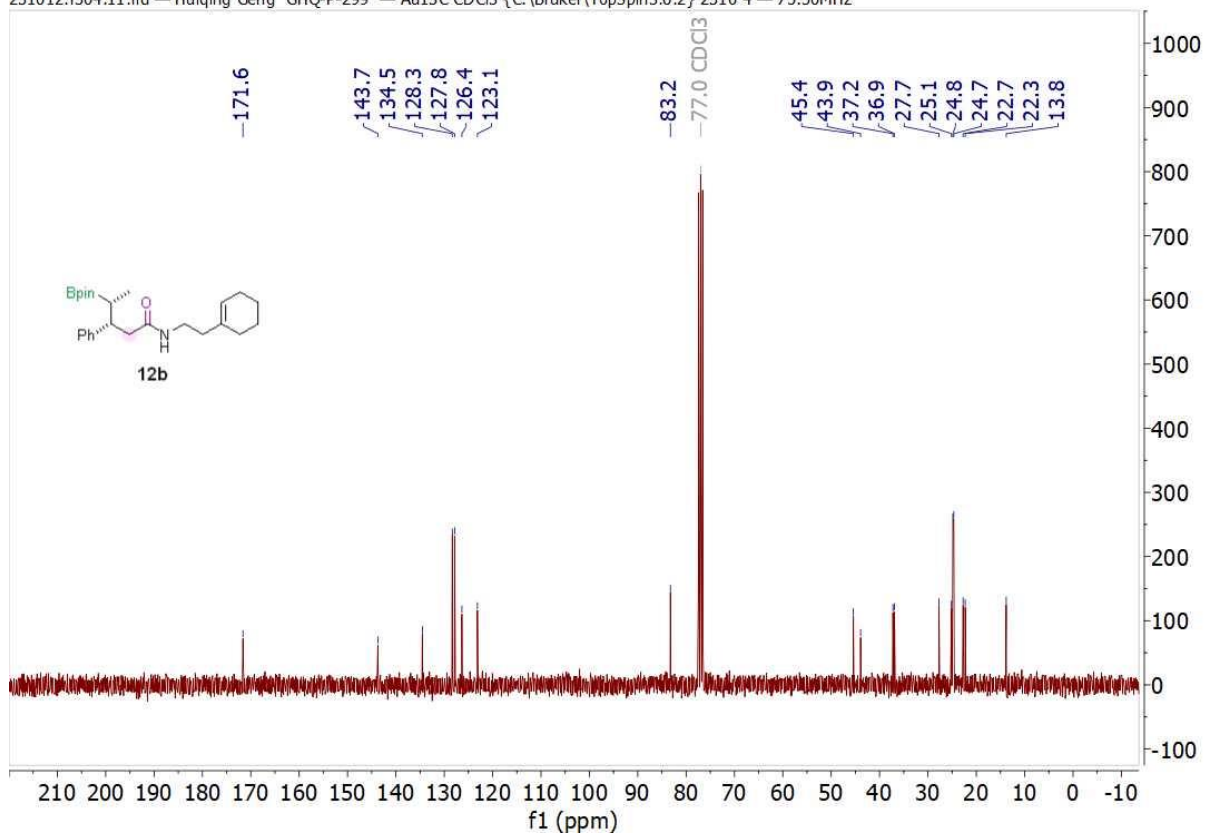
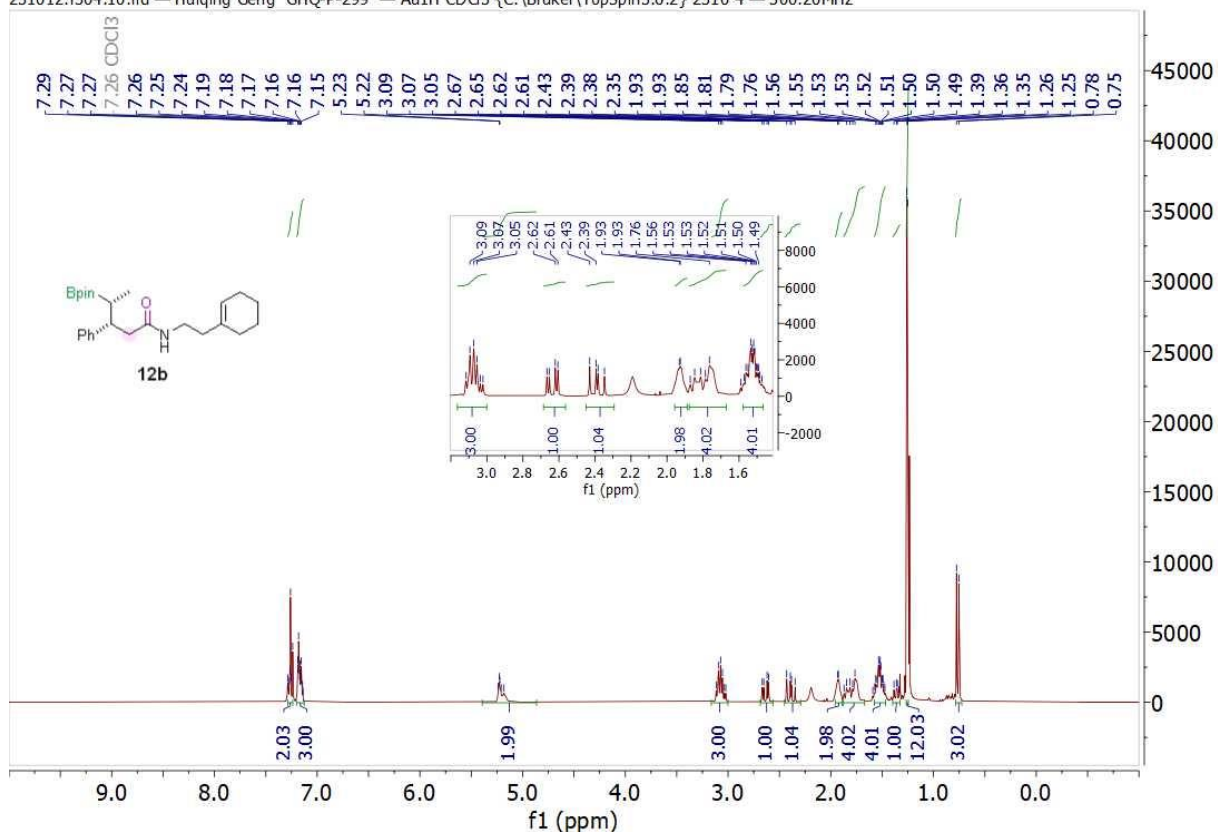


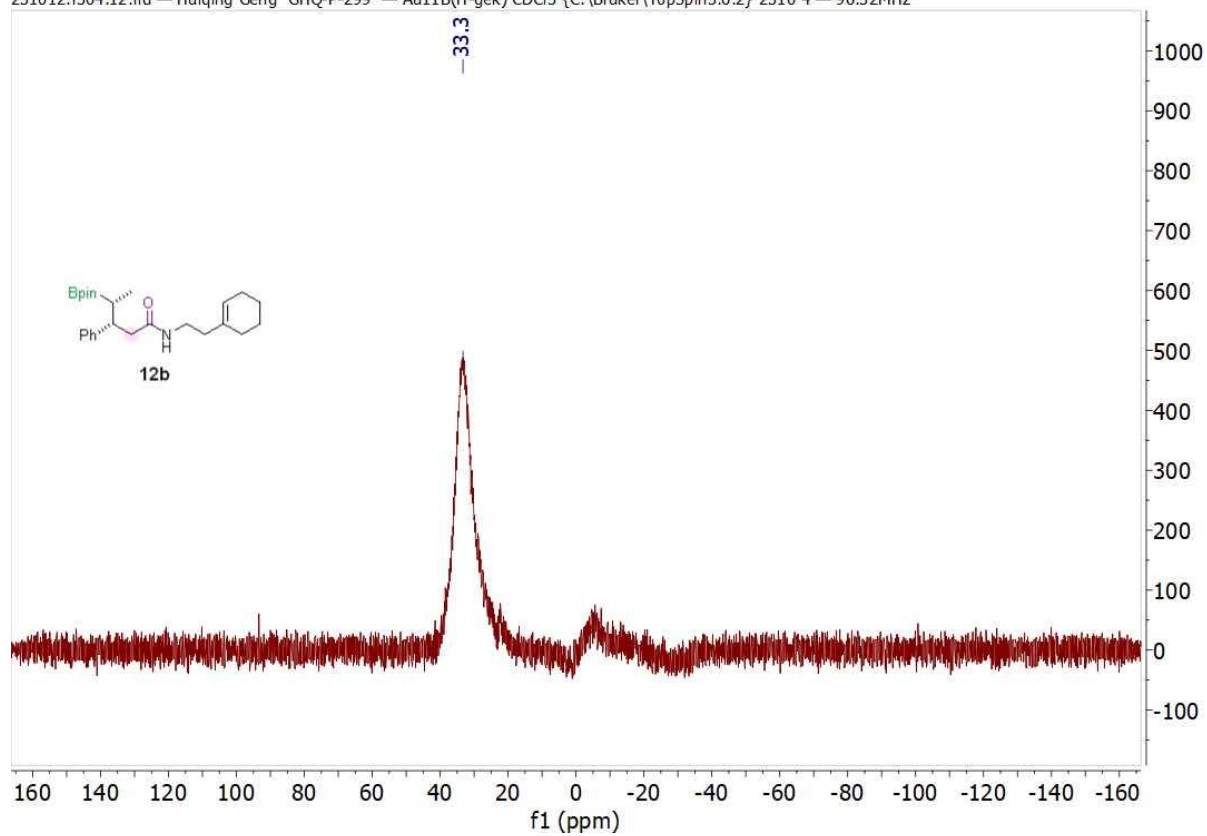


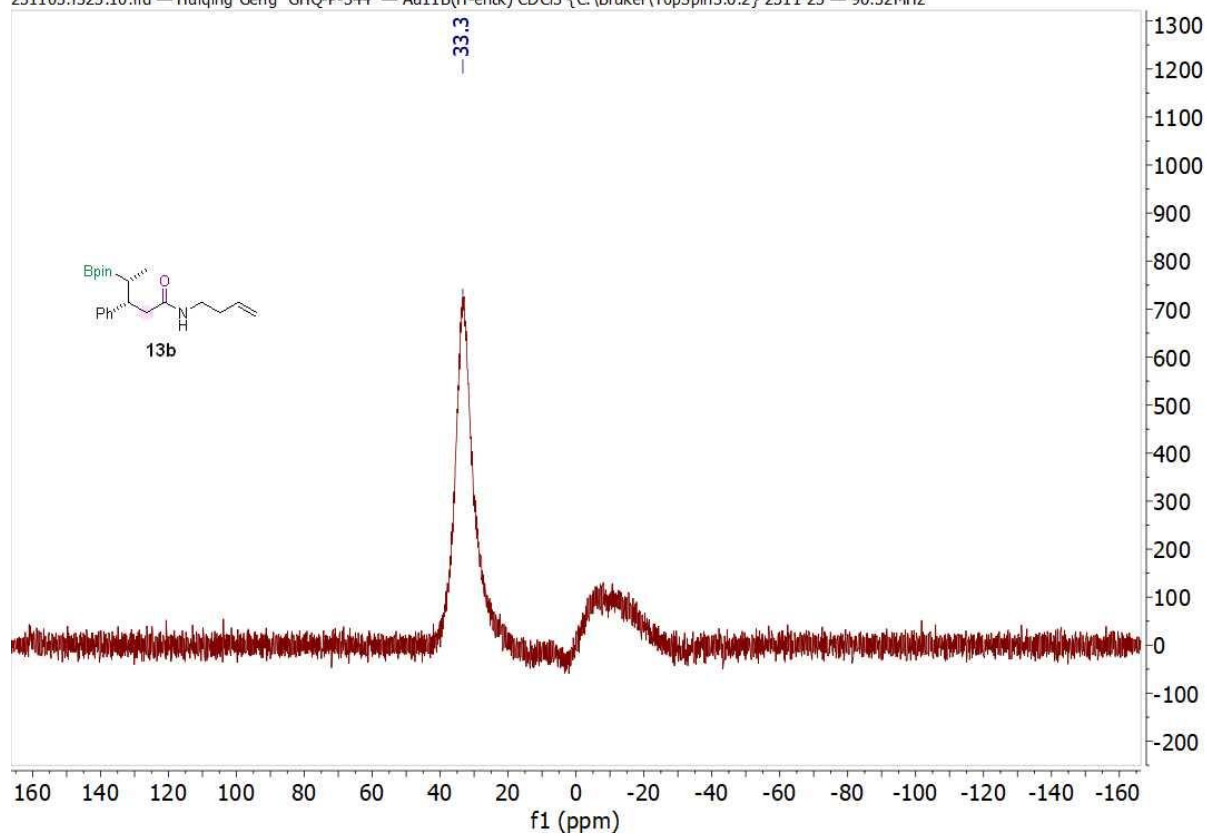


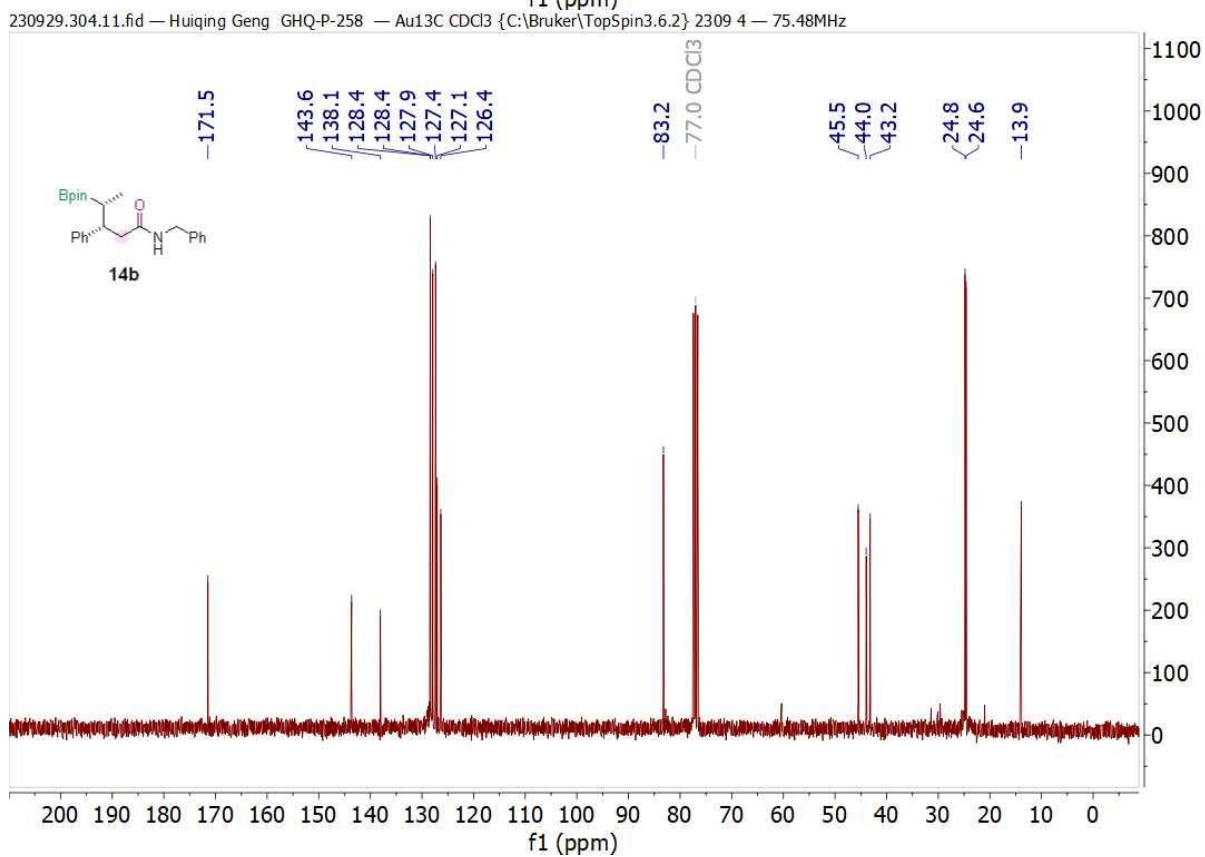
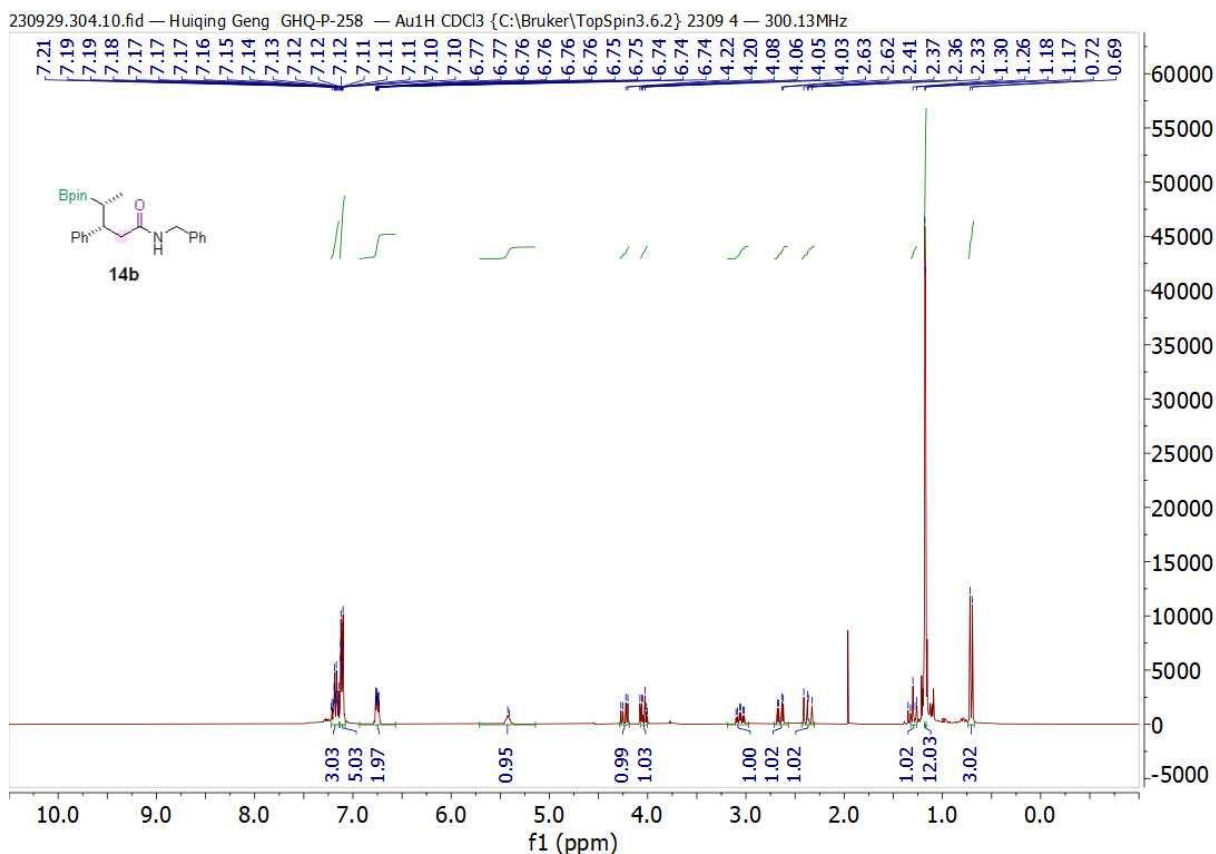


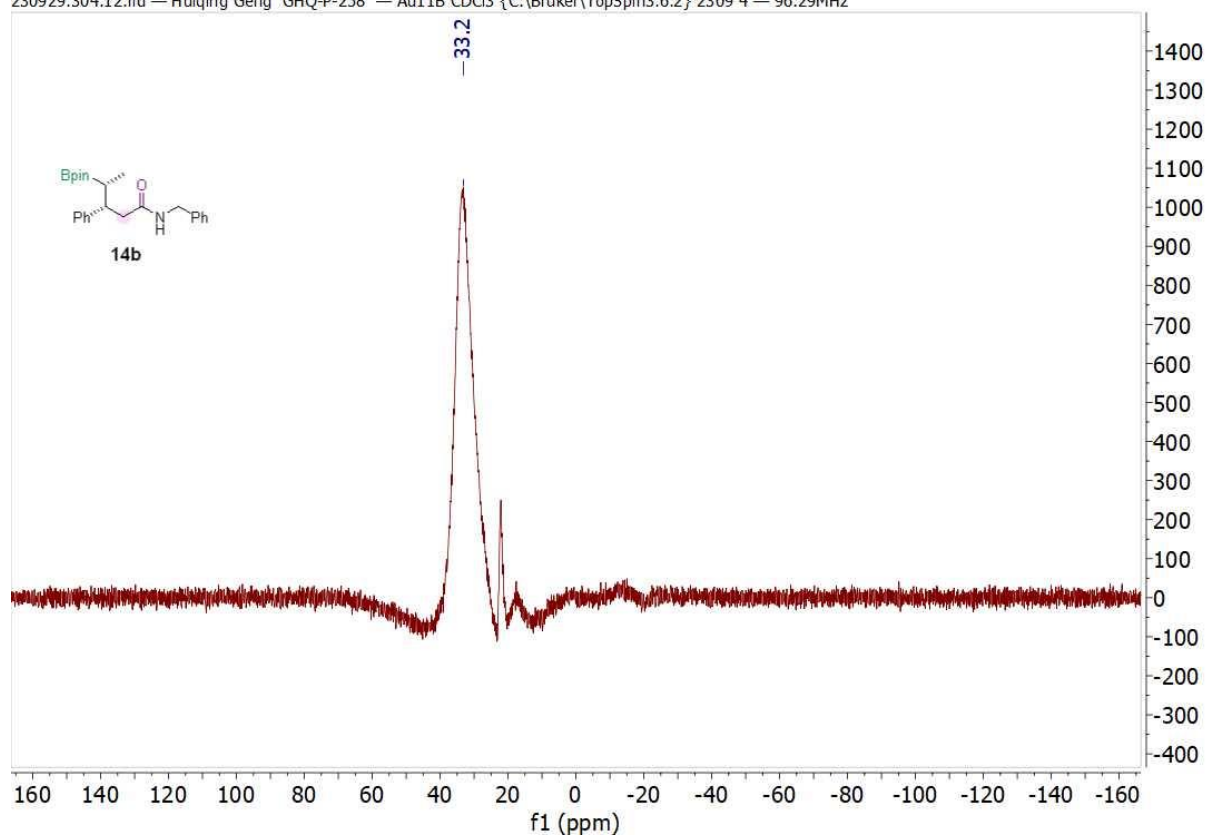


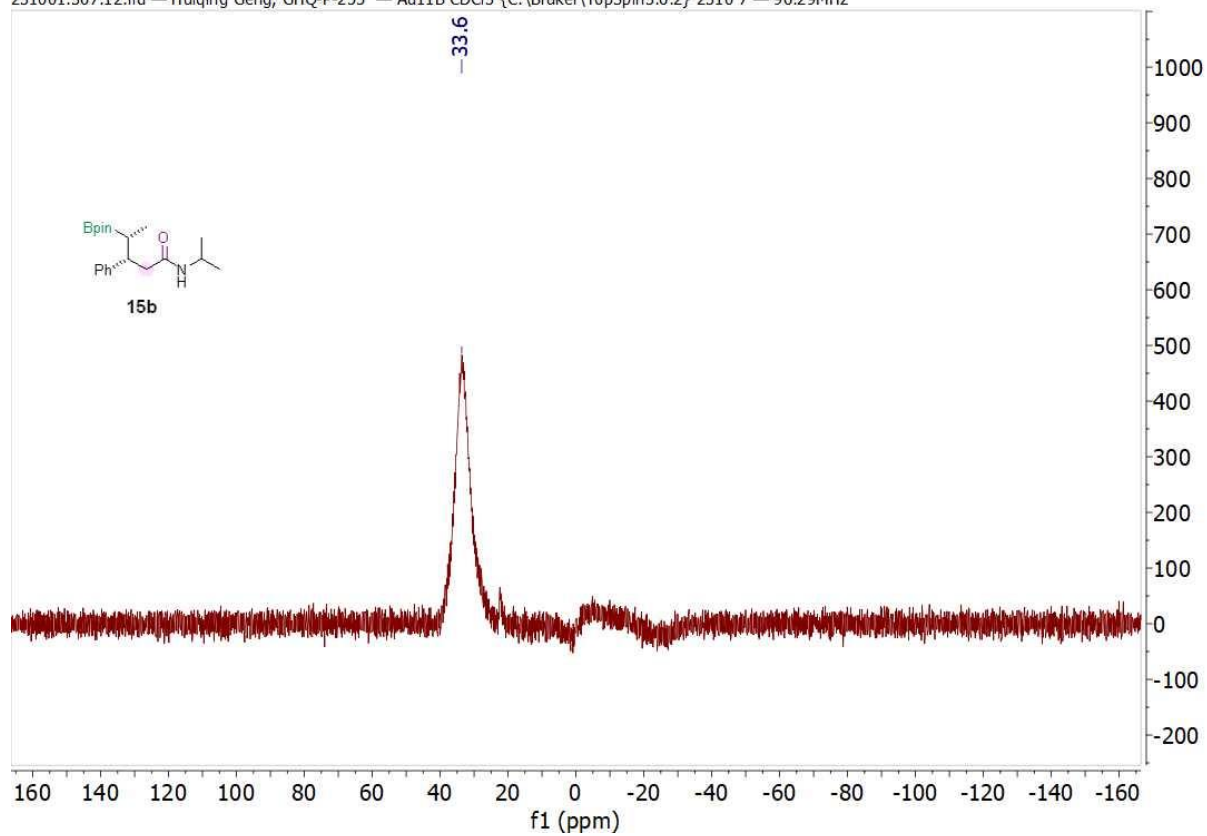




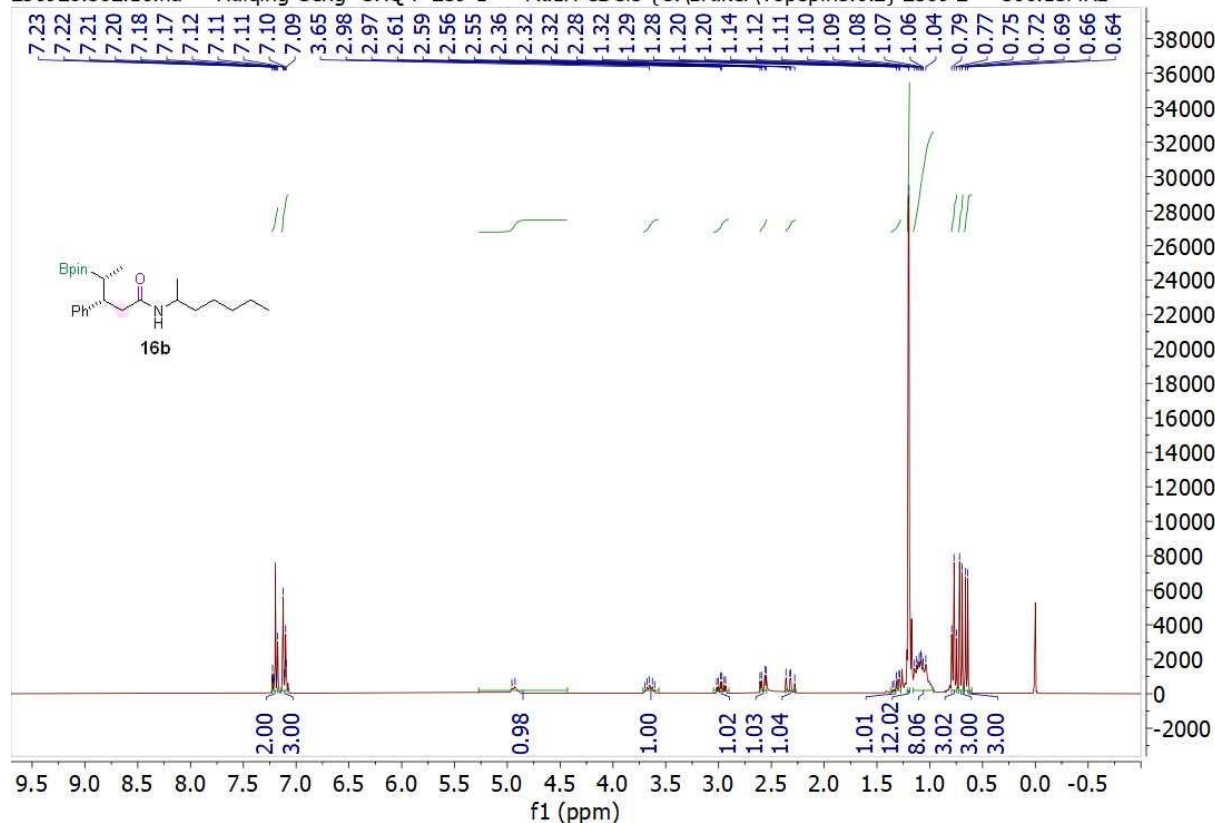




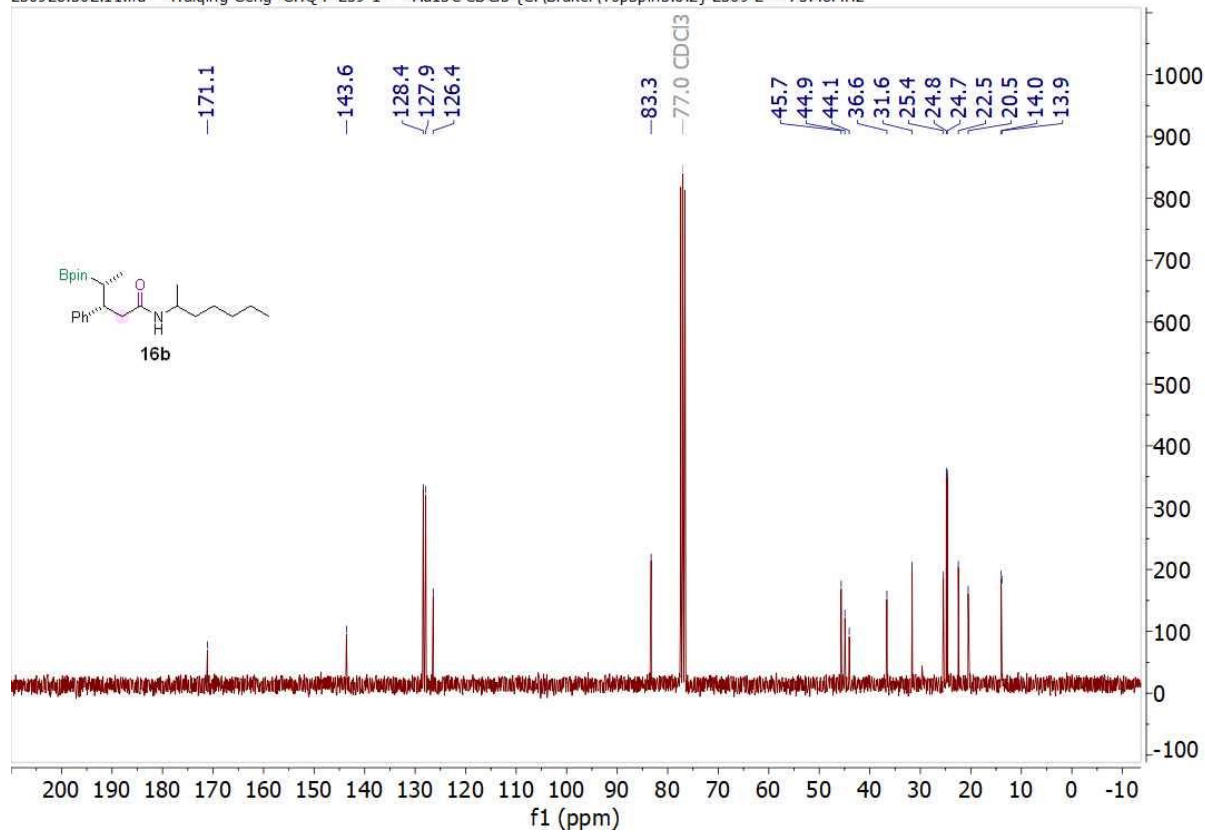


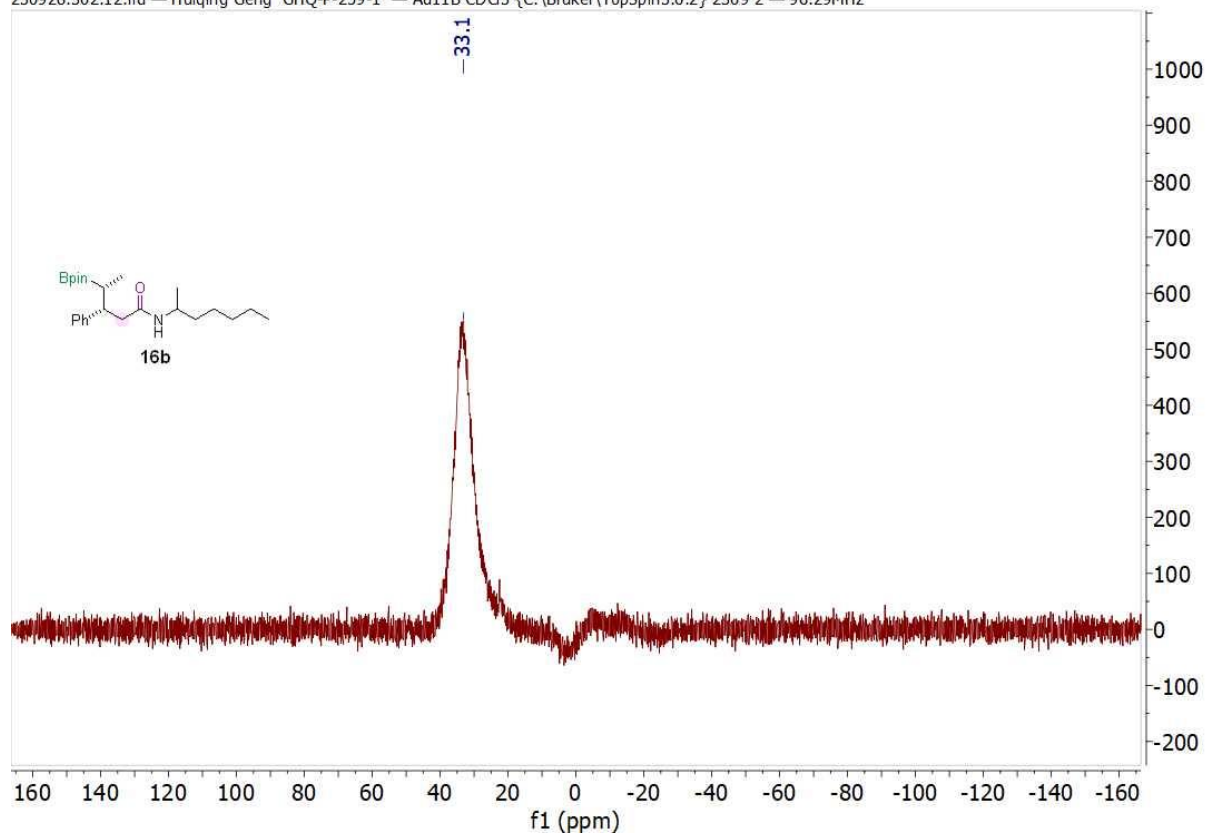


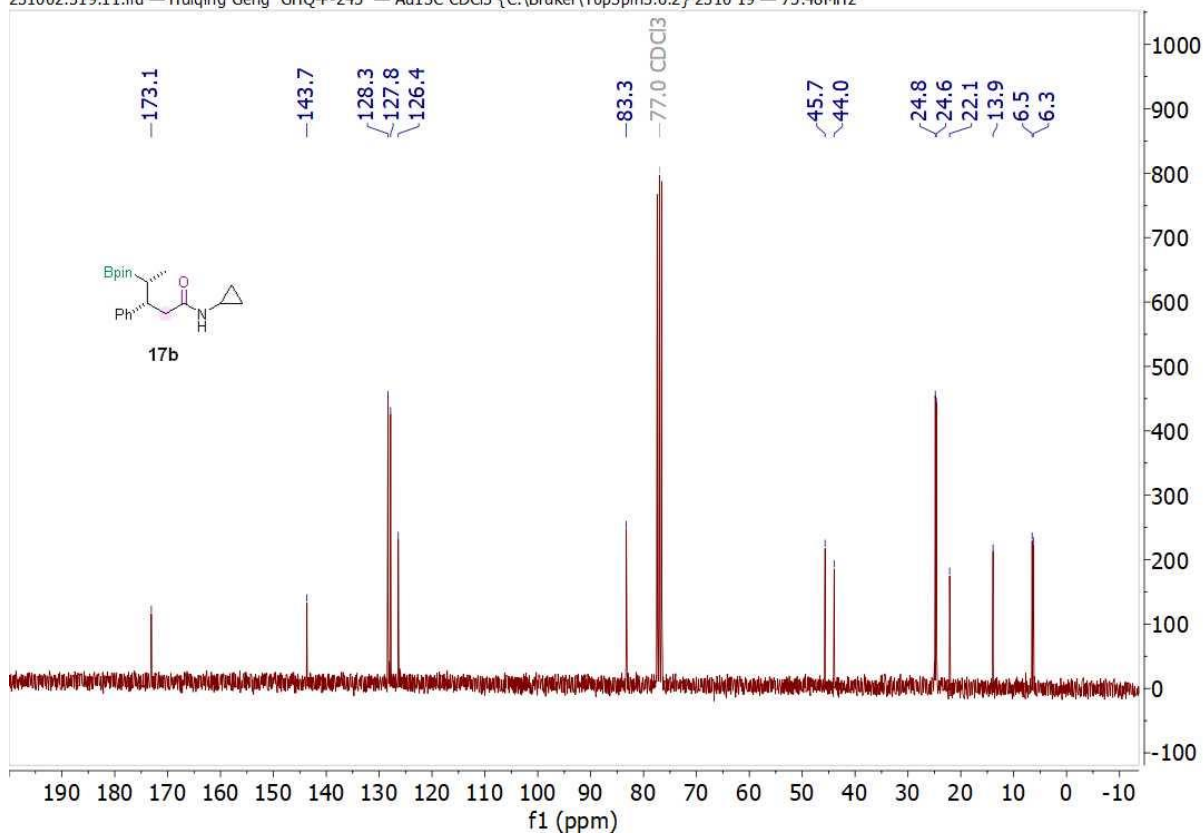
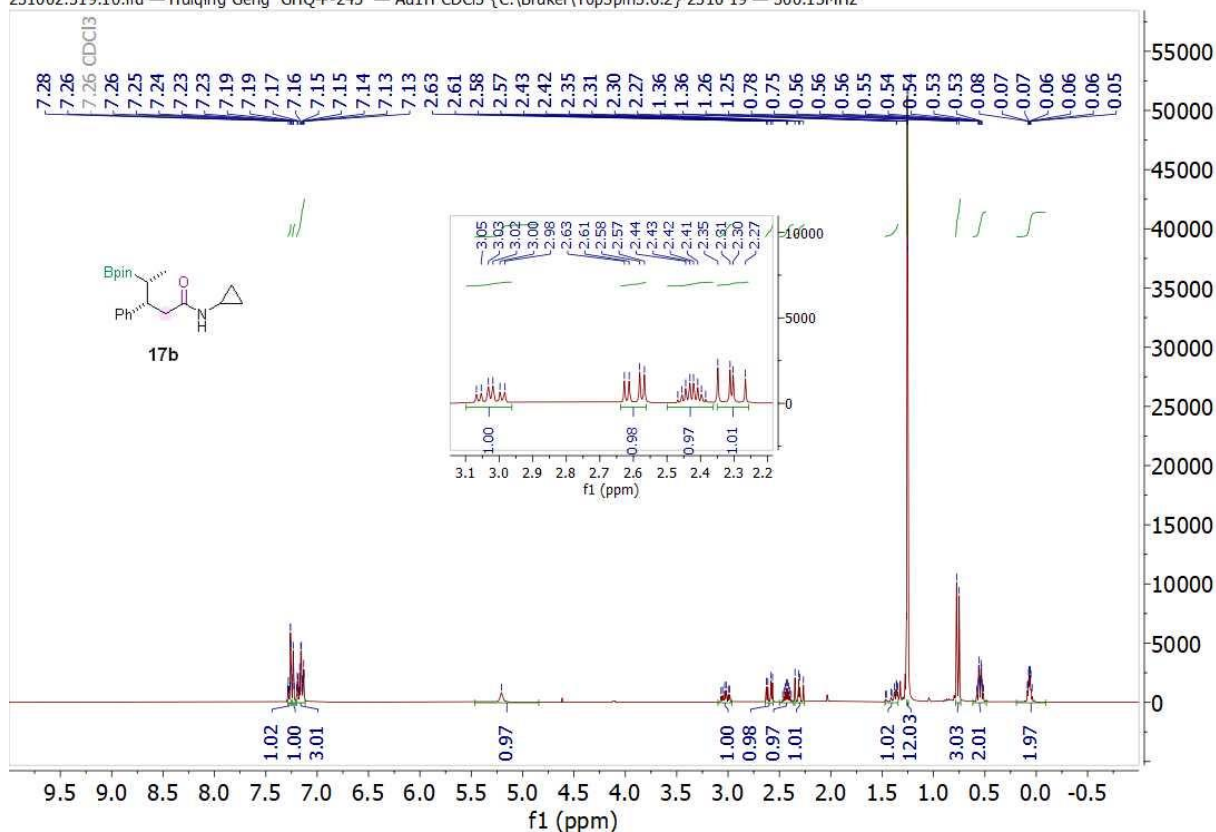
230928.302.10.fid — Huiqing Geng GHQ-P-259-1 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2309 2 — 300.13MHz

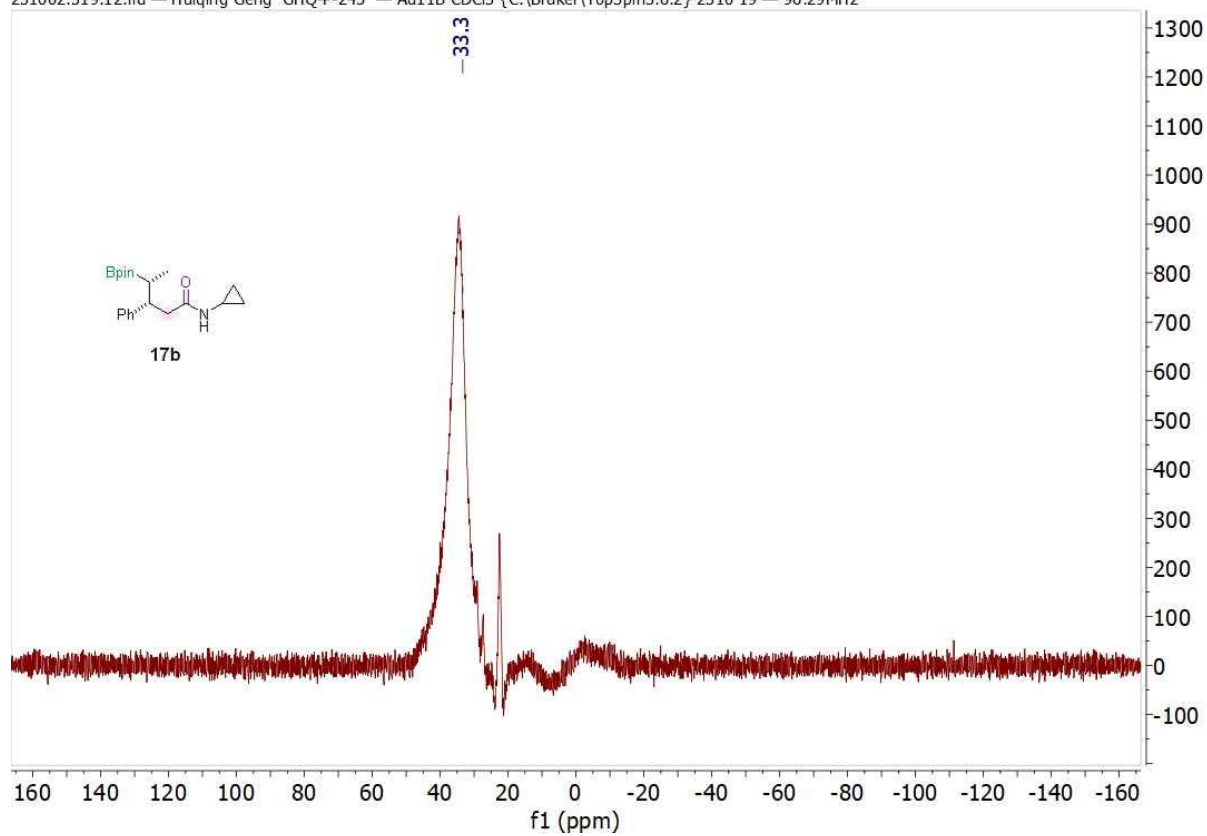


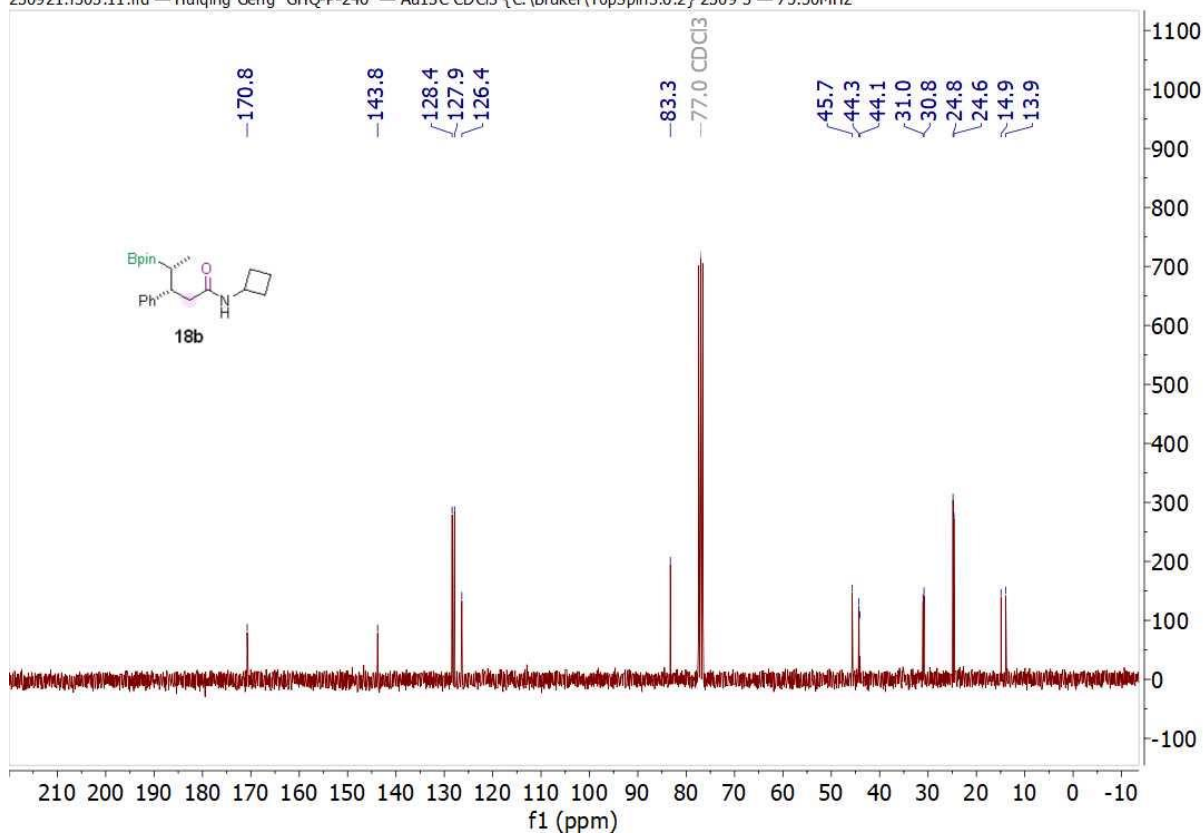
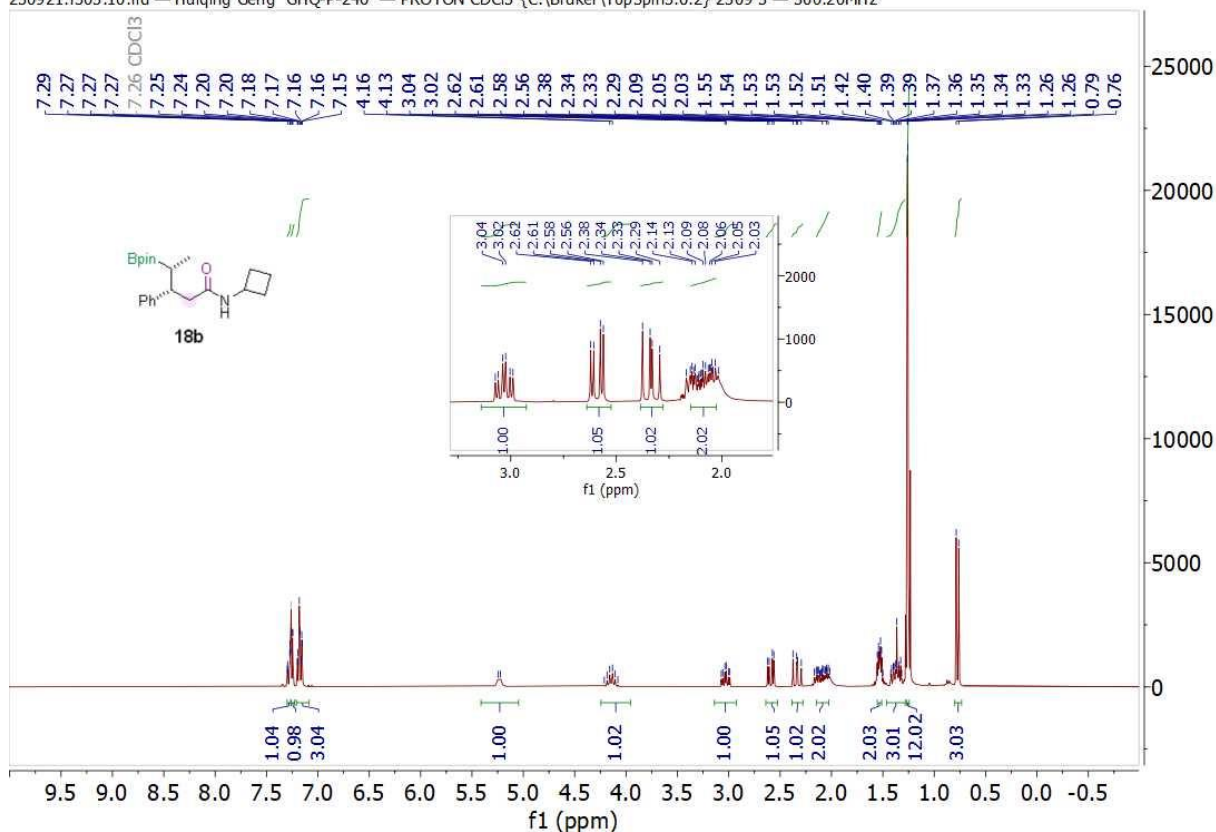
230928.302.11.fid — Huiqing Geng GHQ-P-259-1 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2309 2 — 75.48MHz

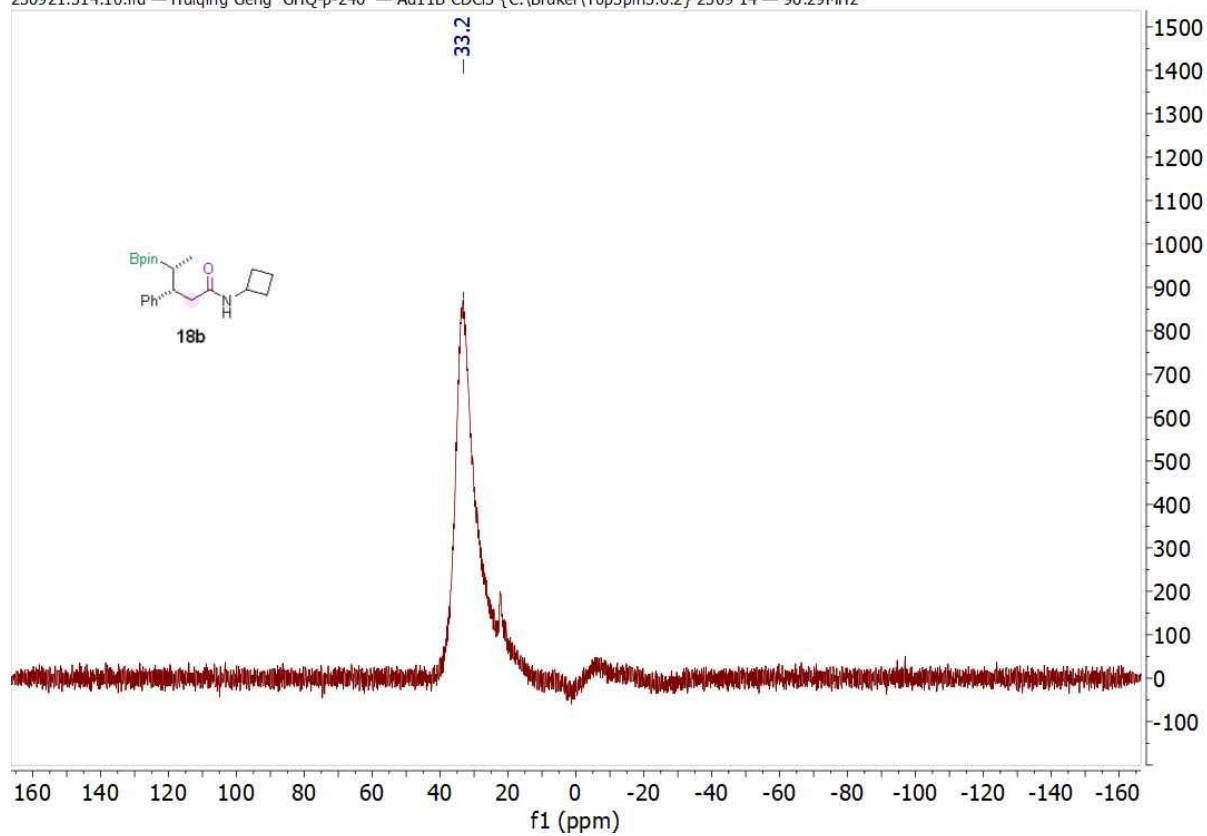


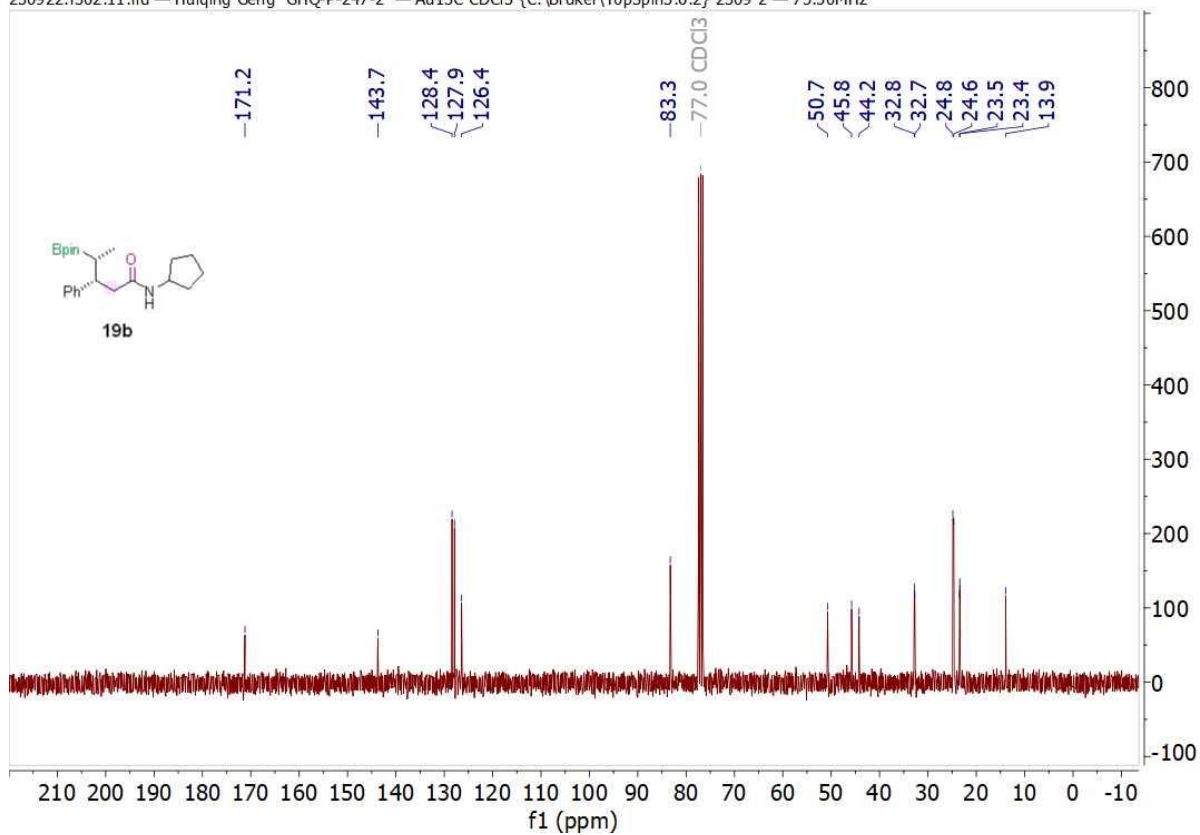
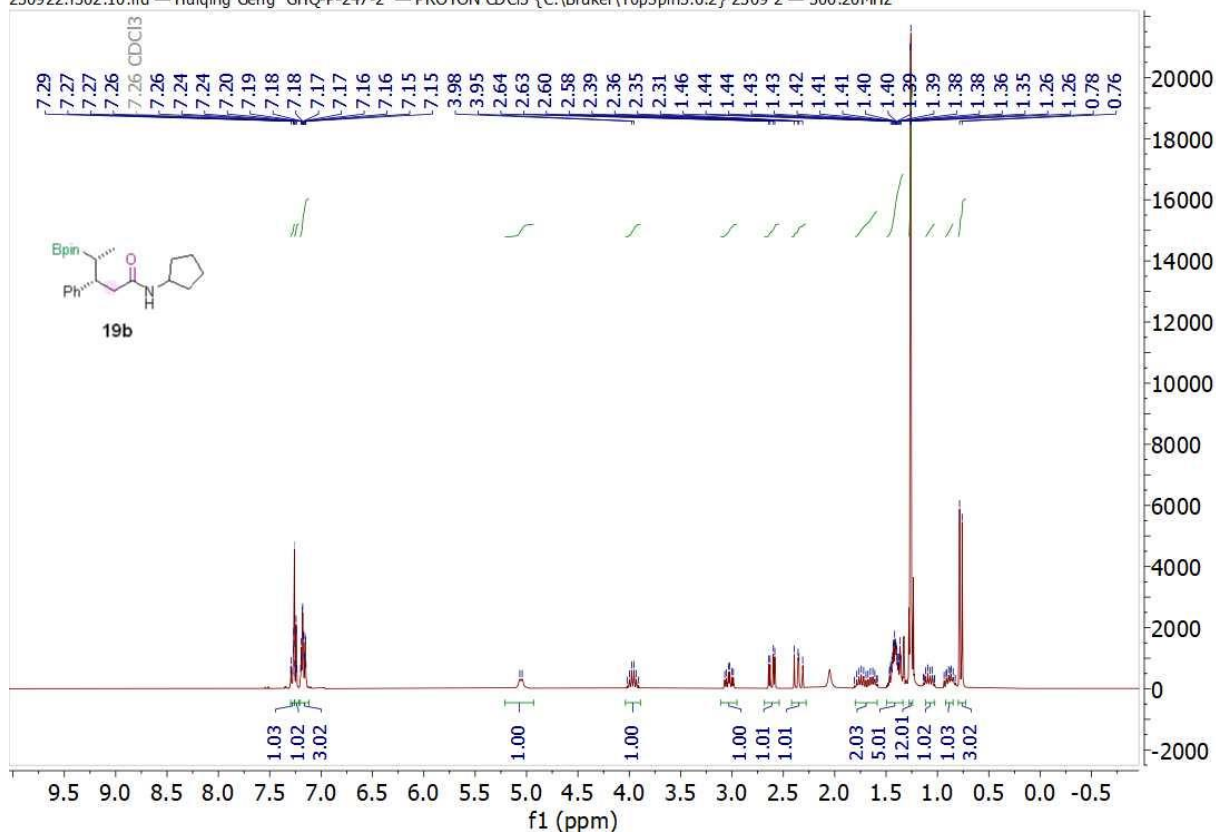


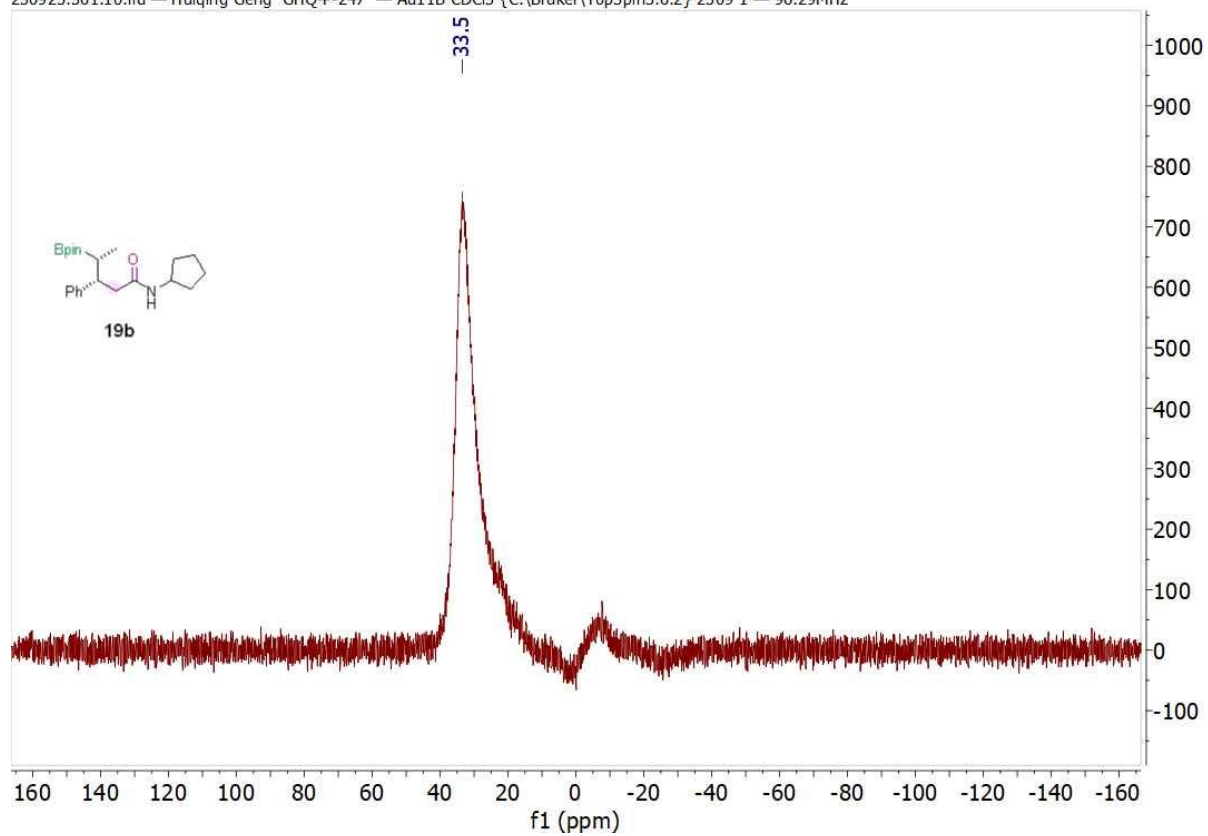


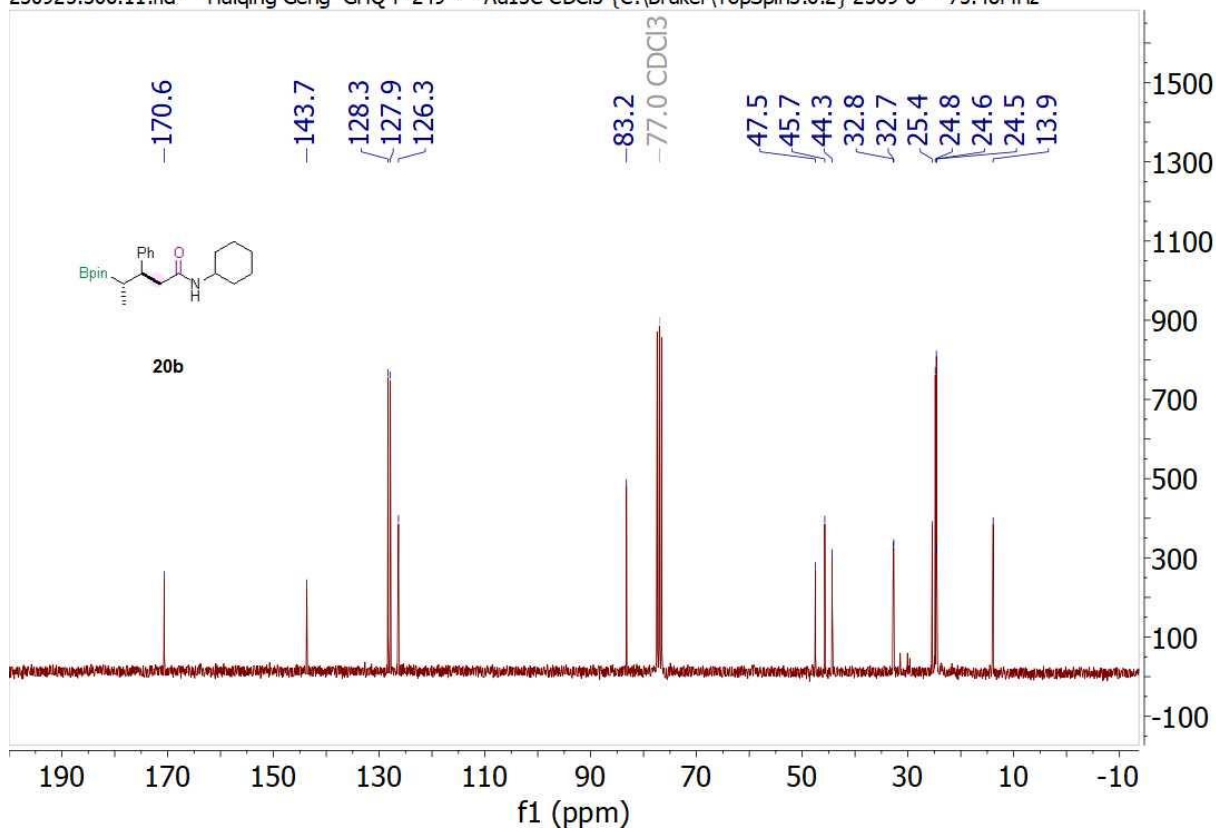
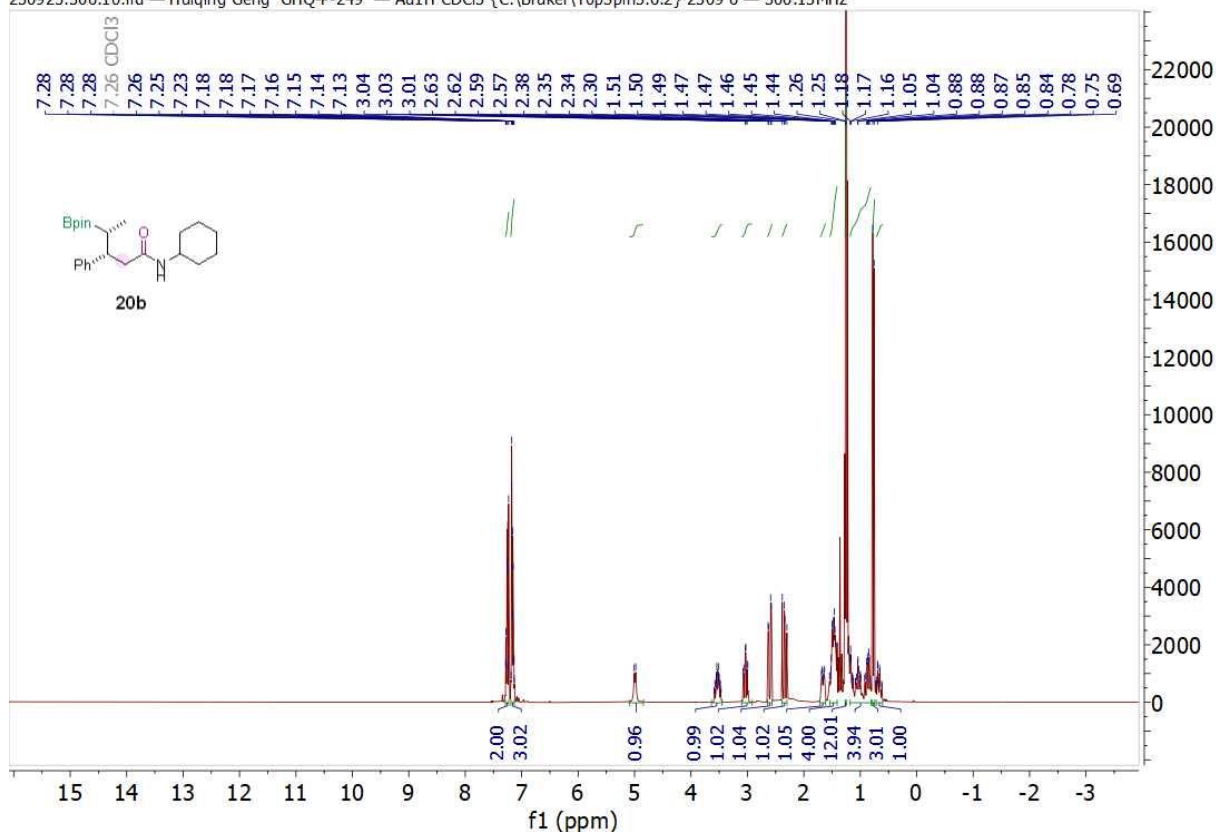


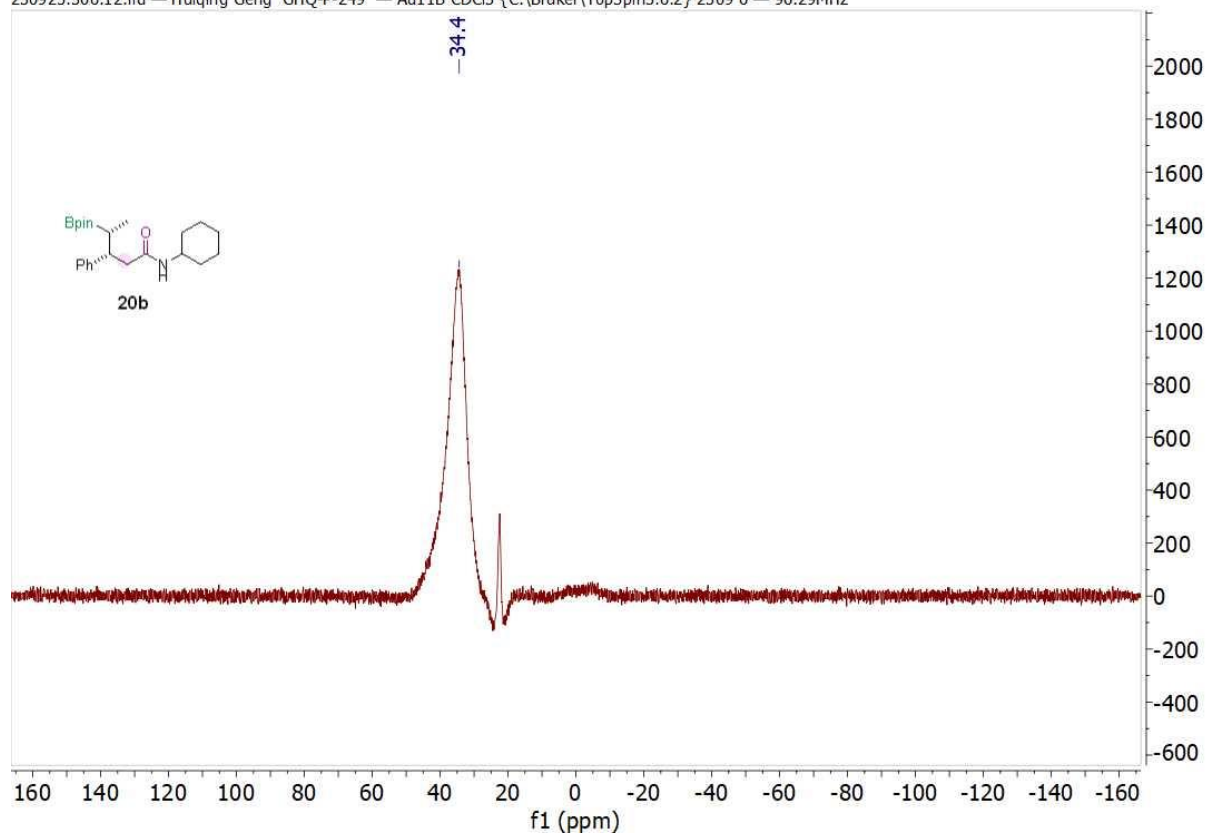


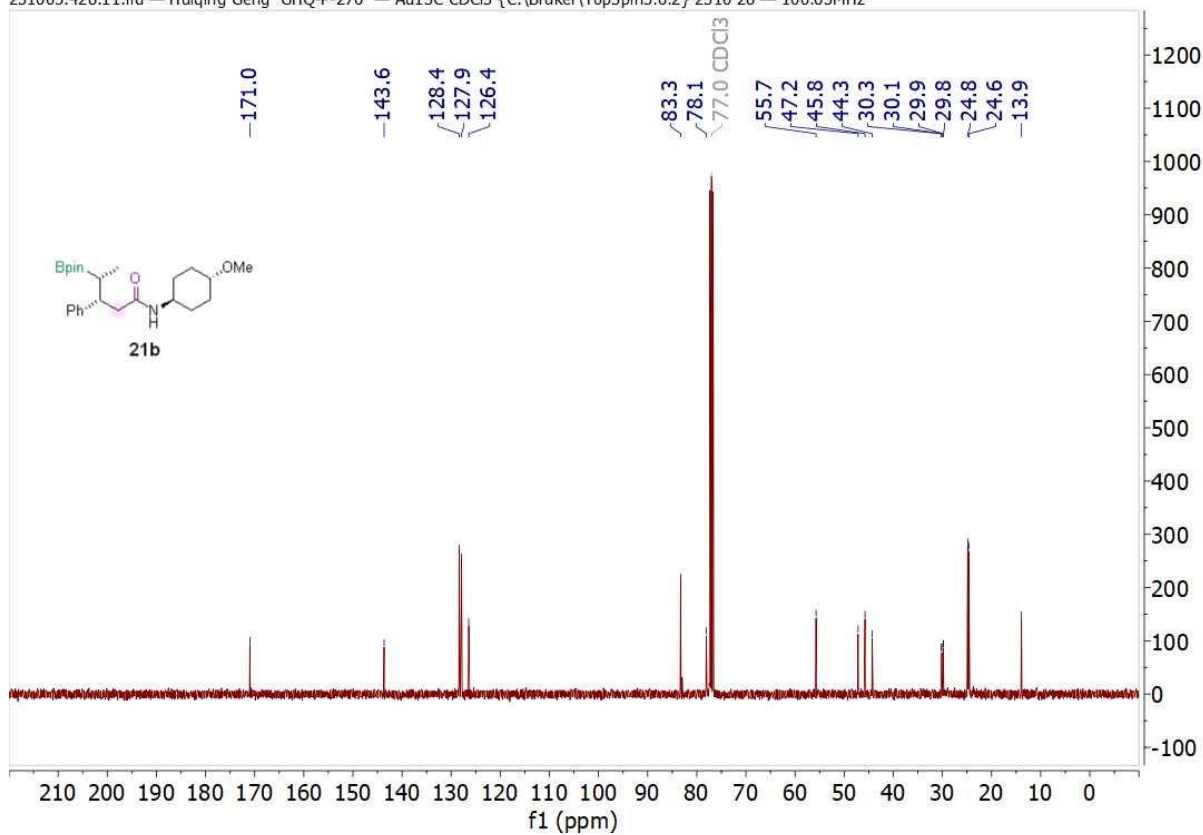
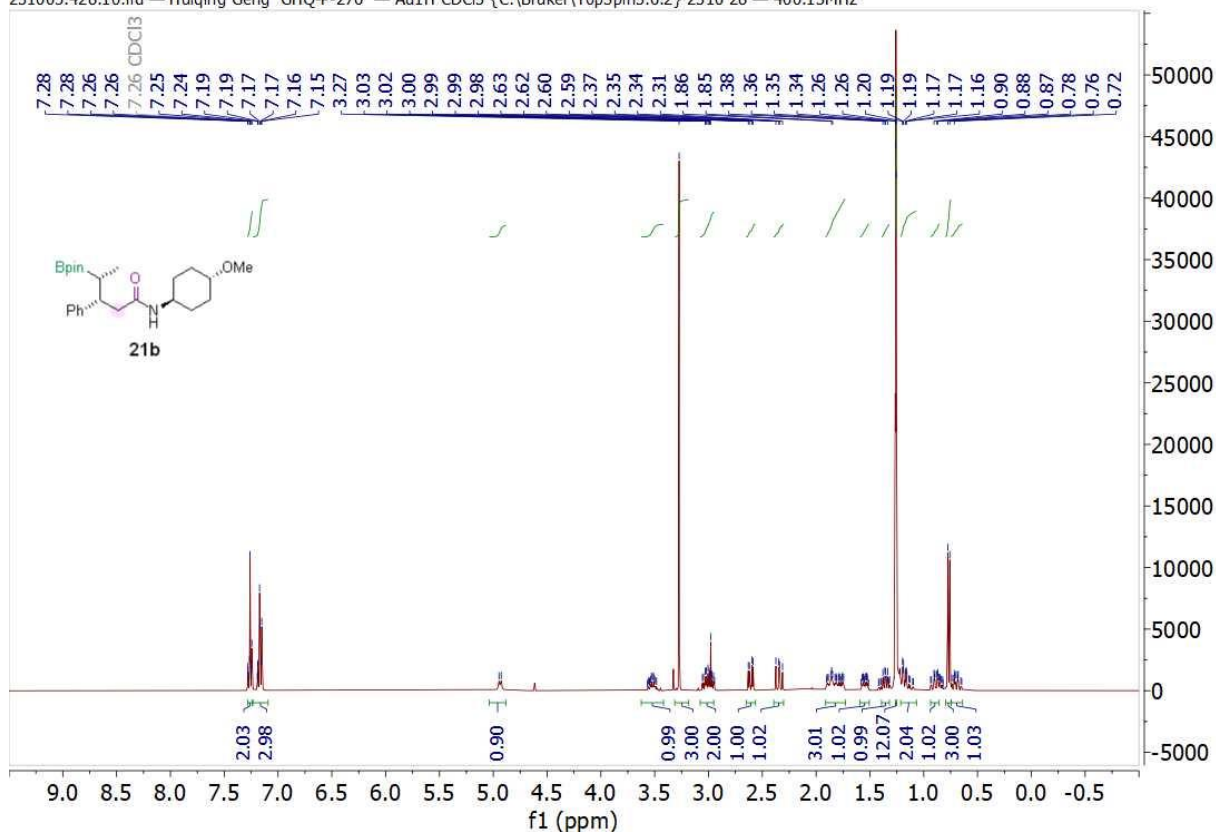


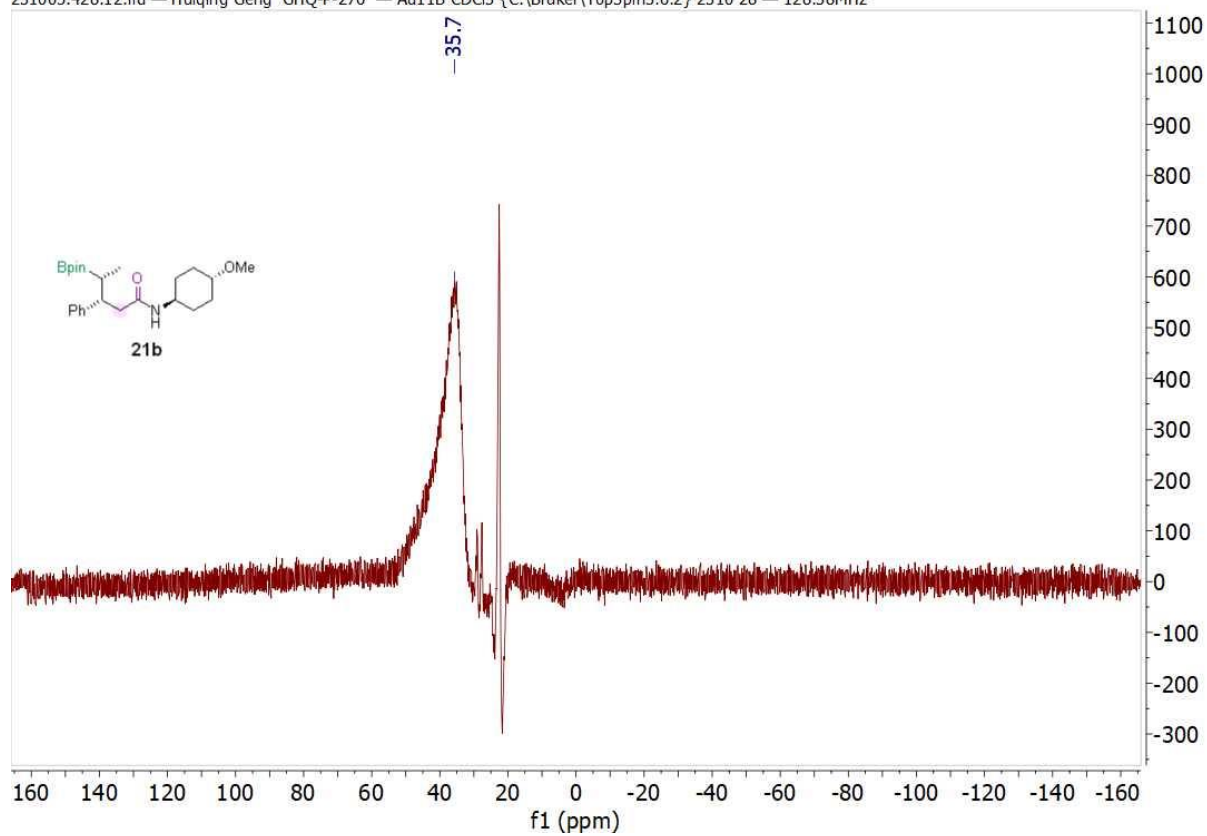


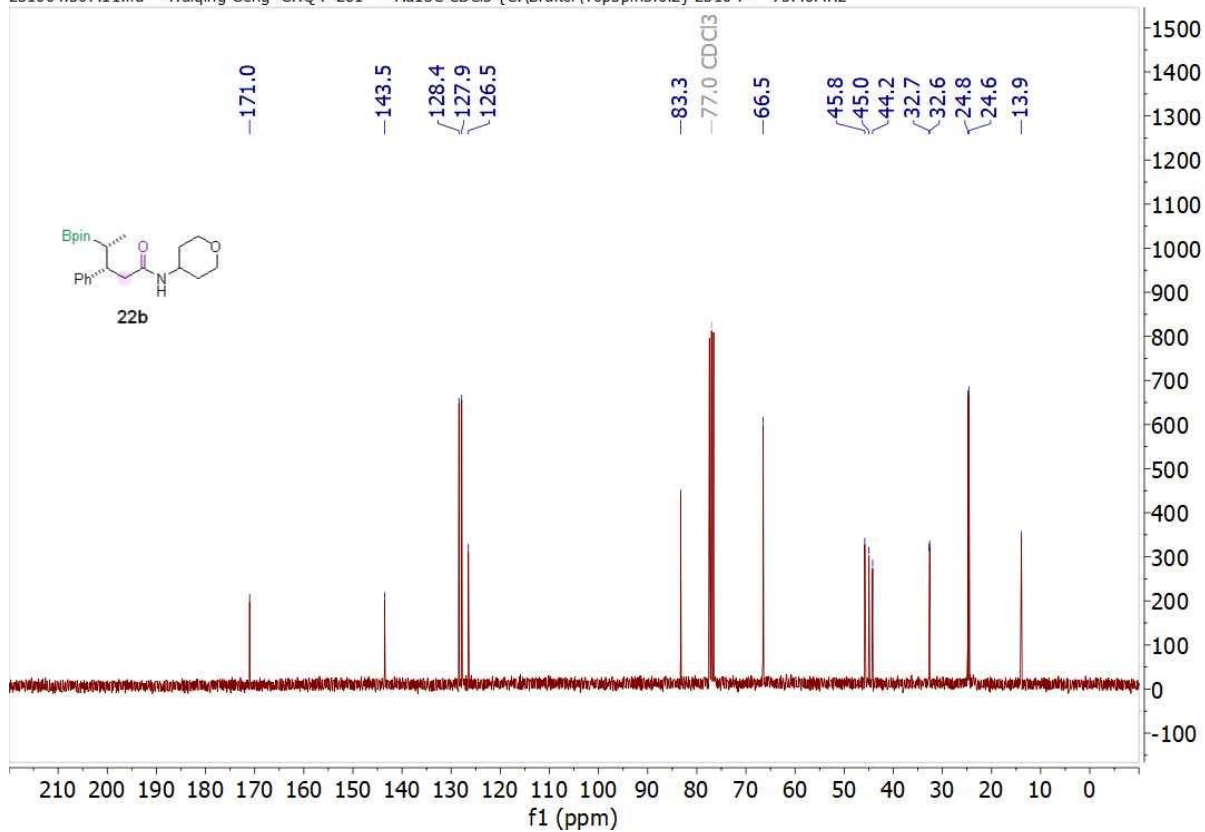
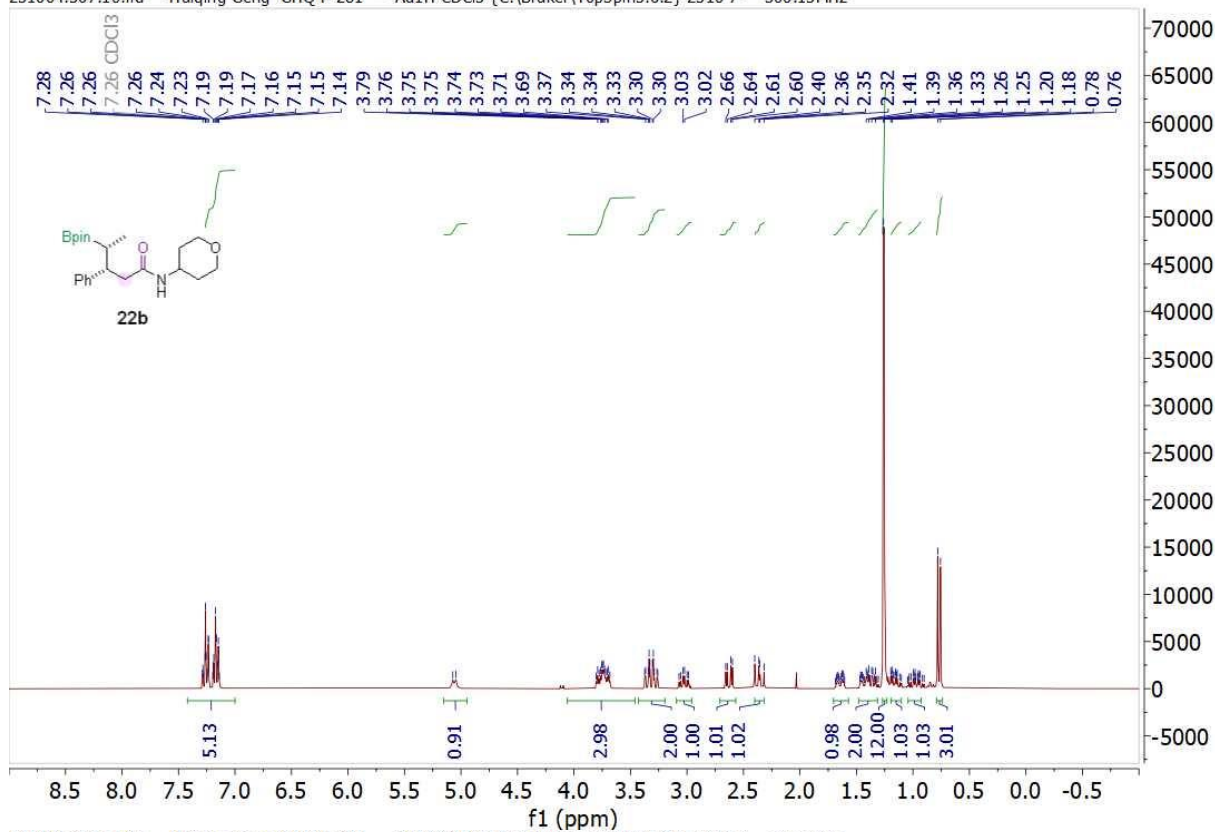


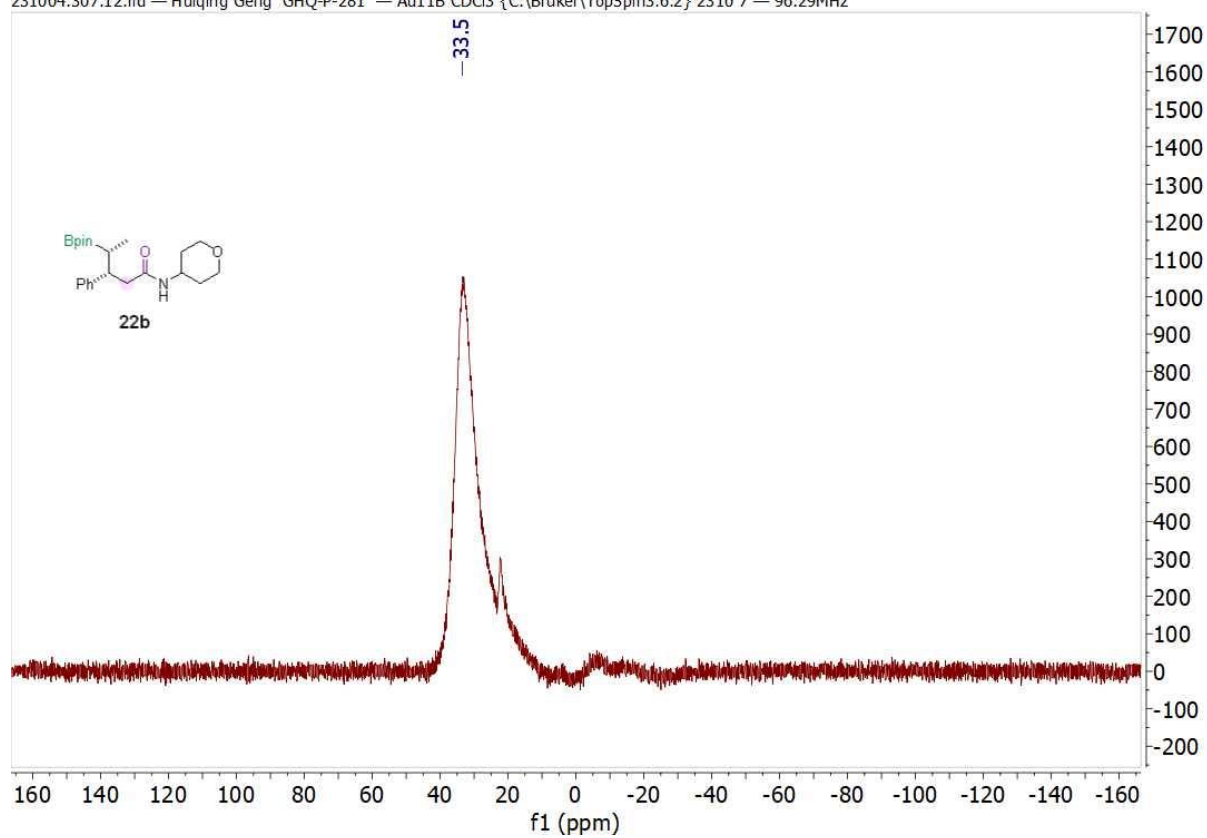


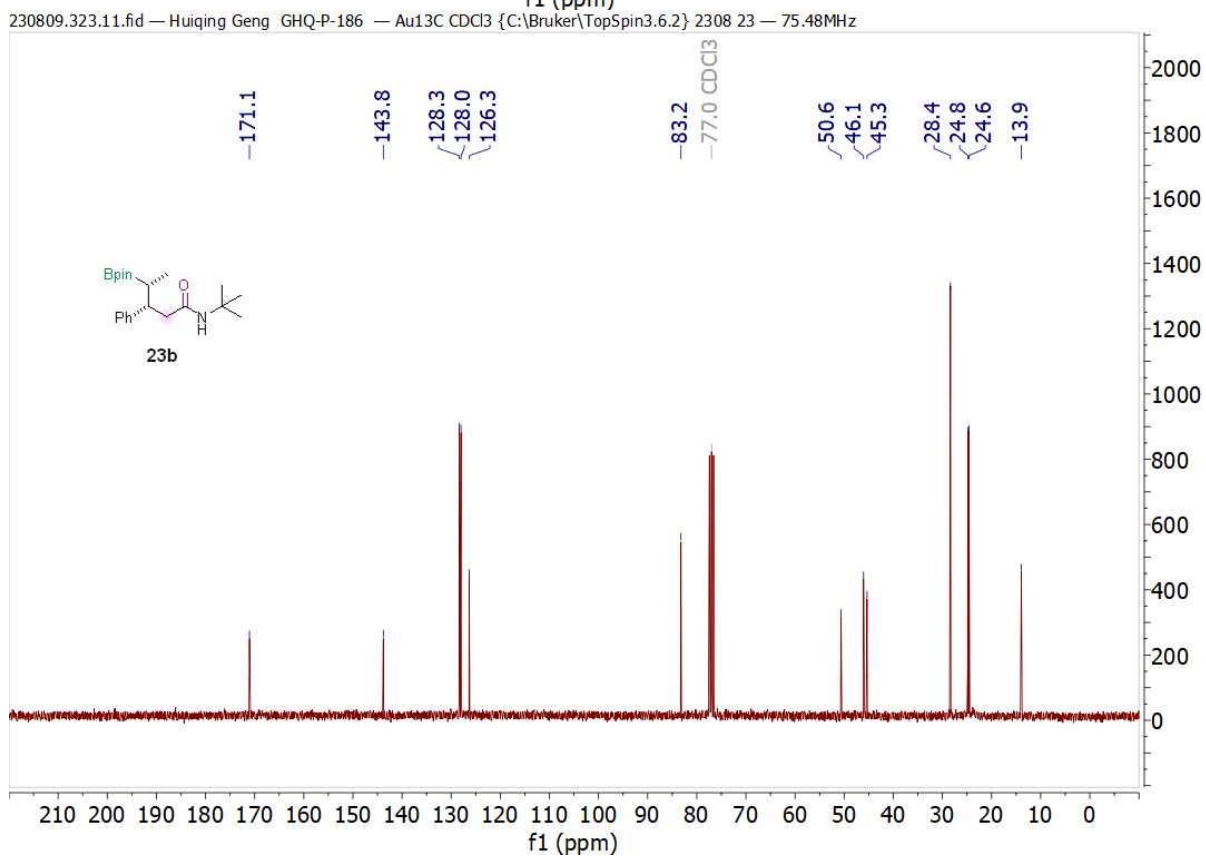
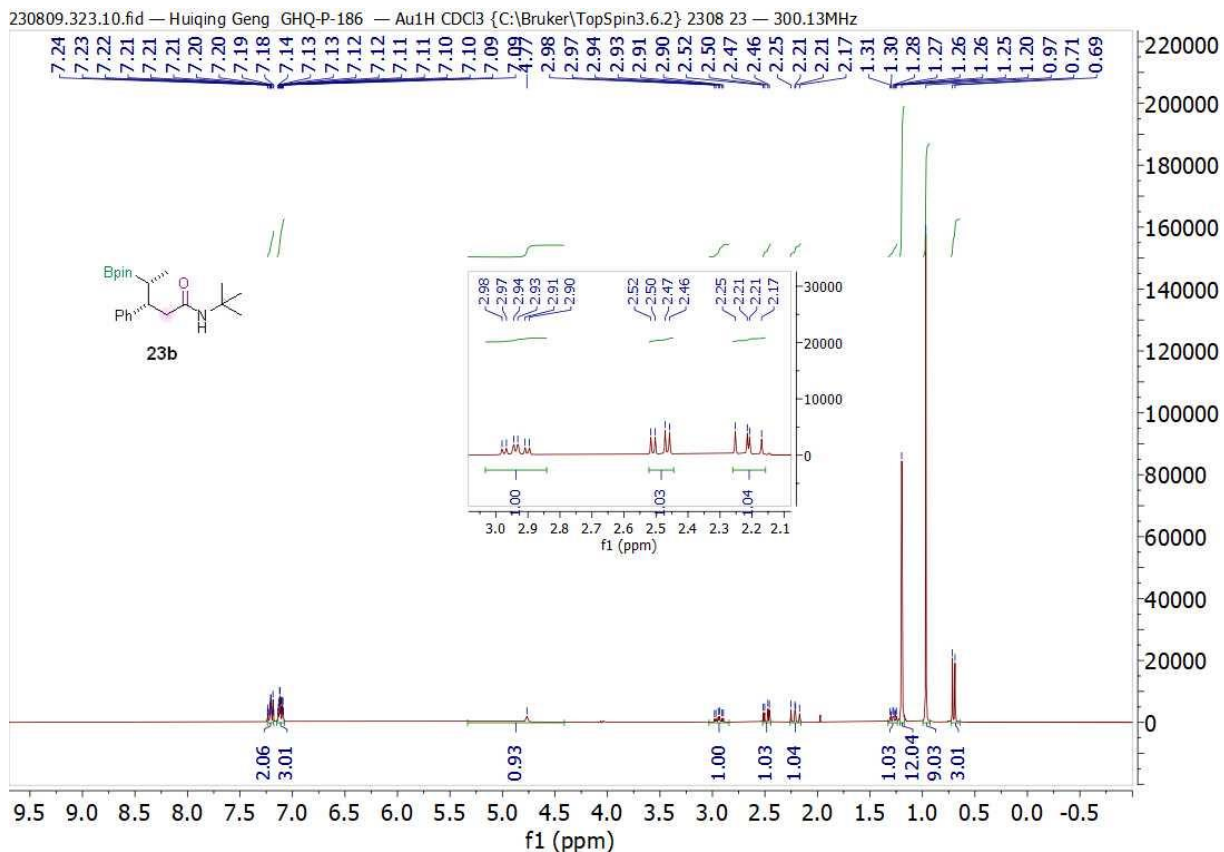


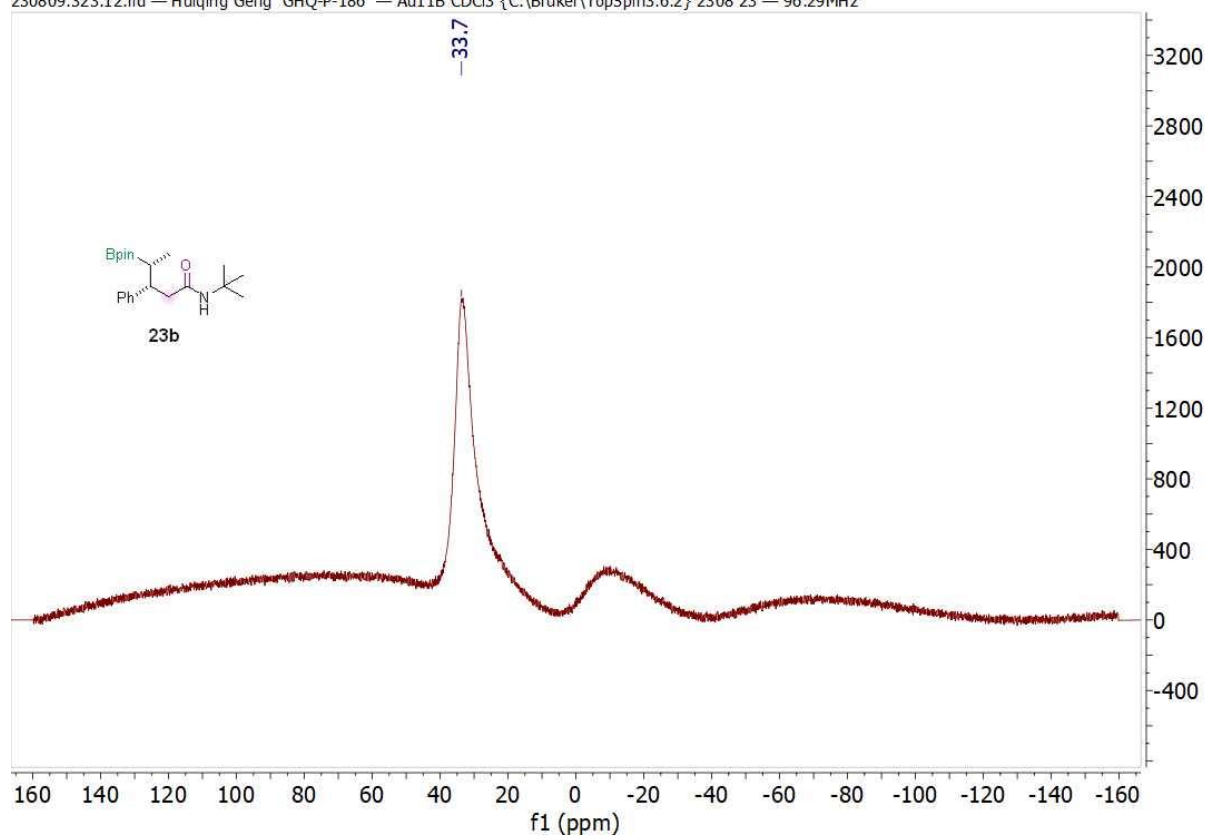


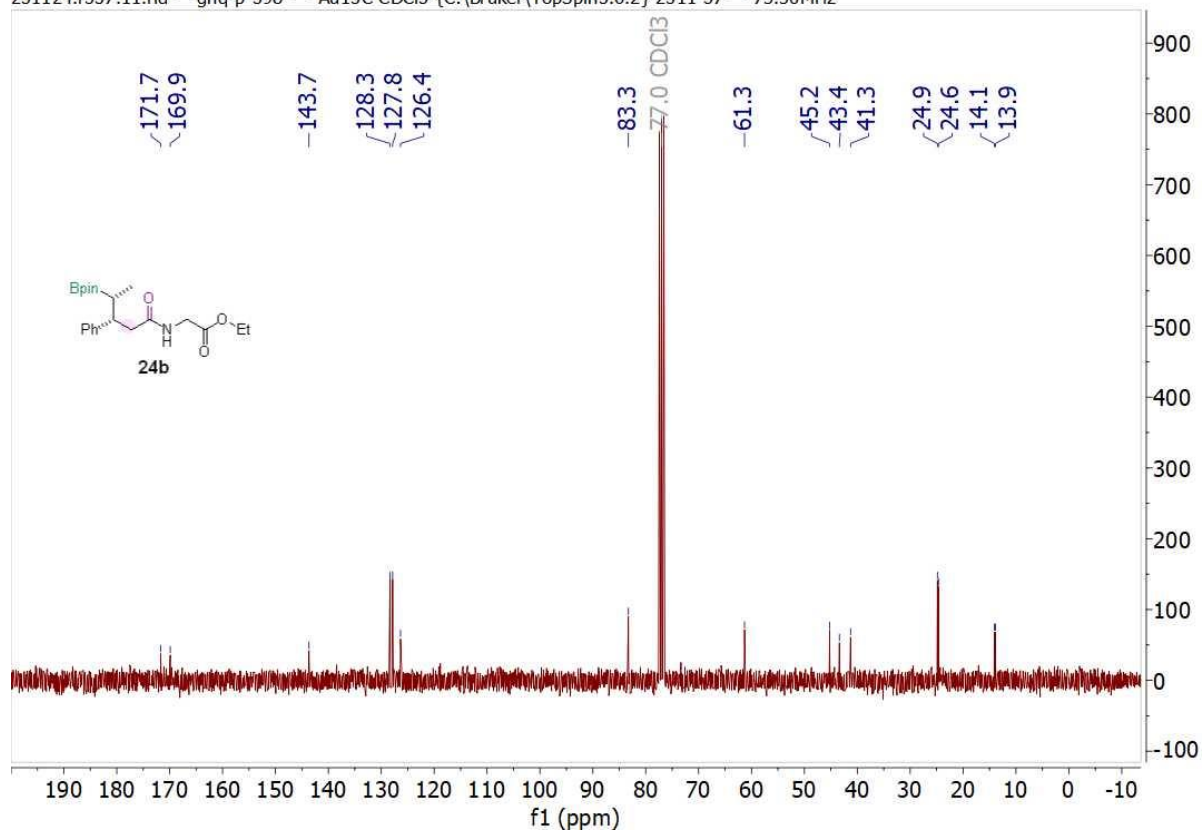
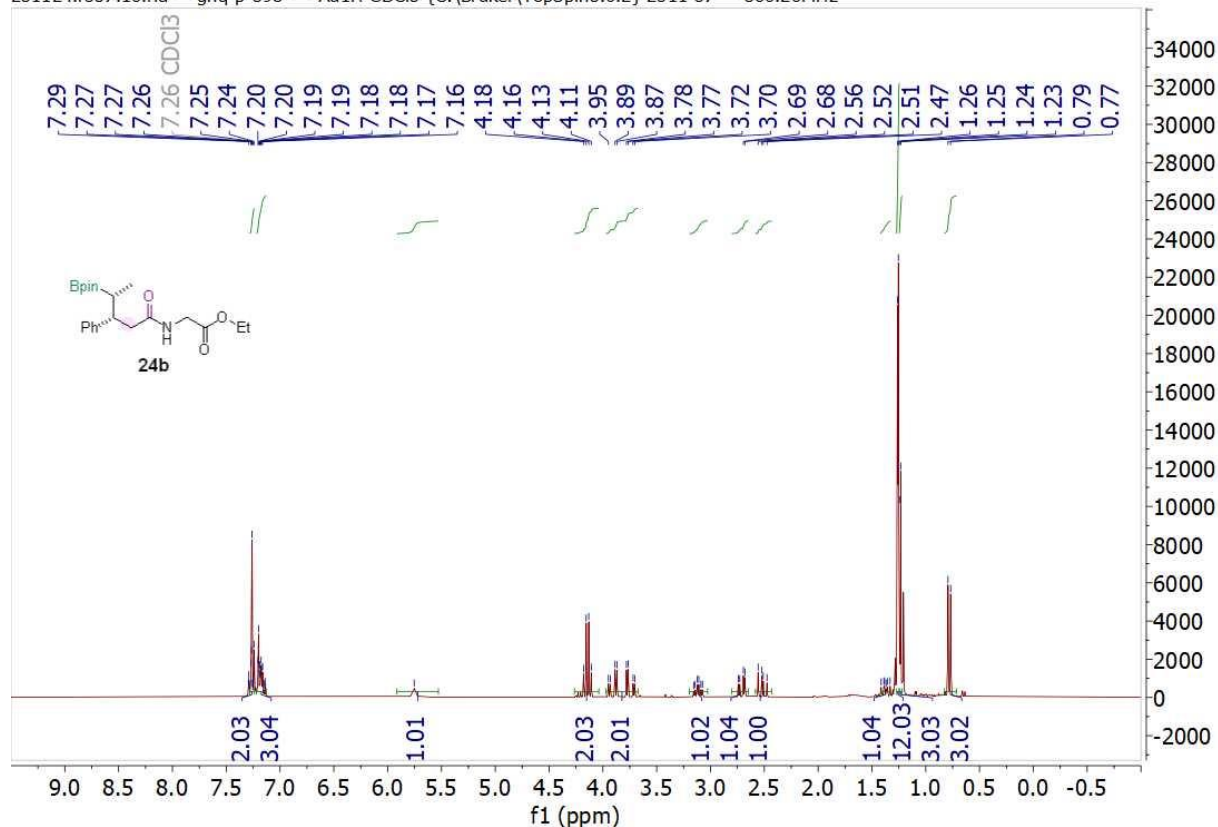


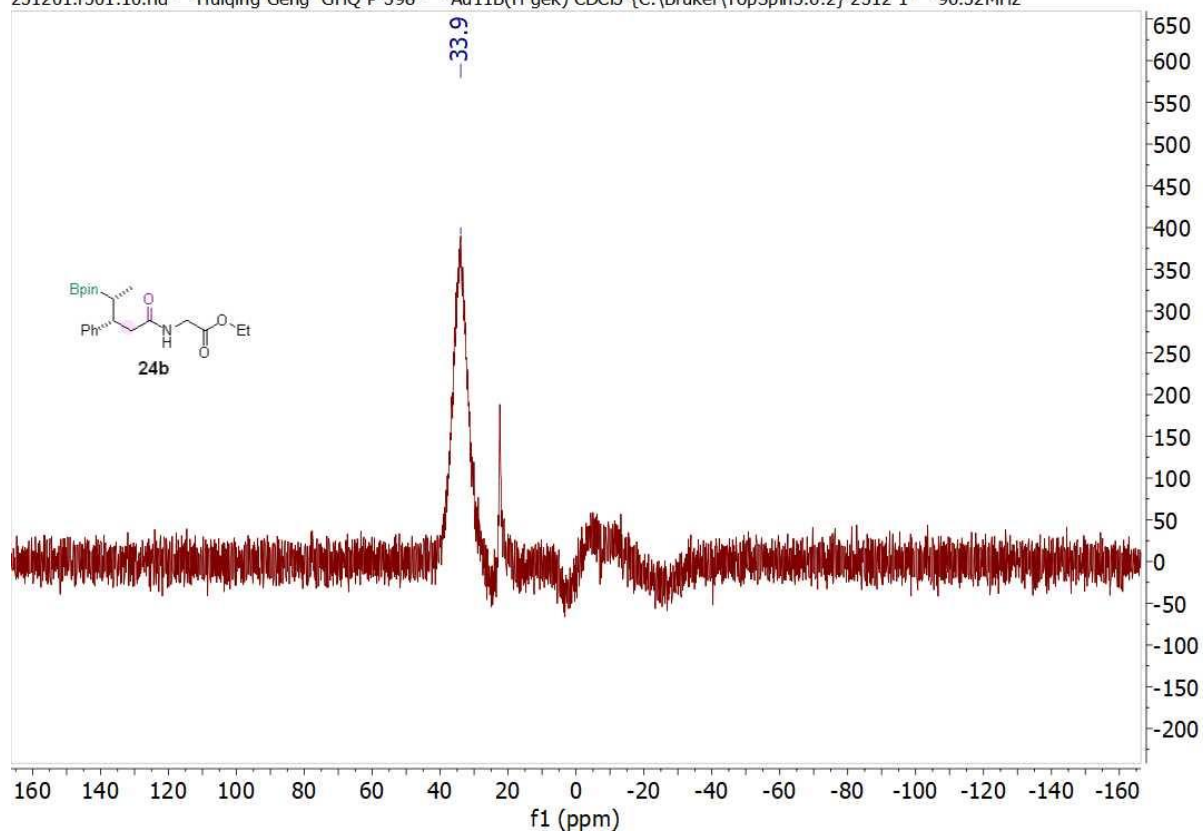


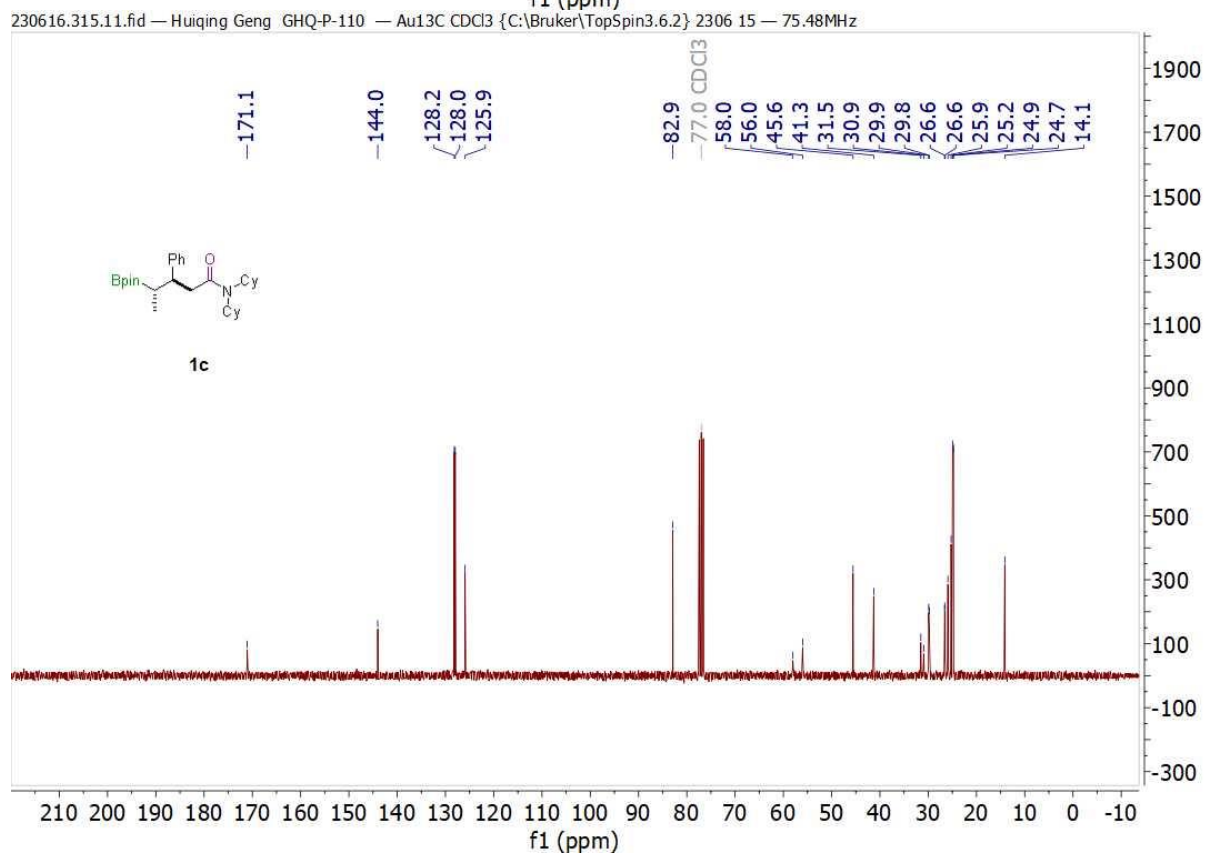
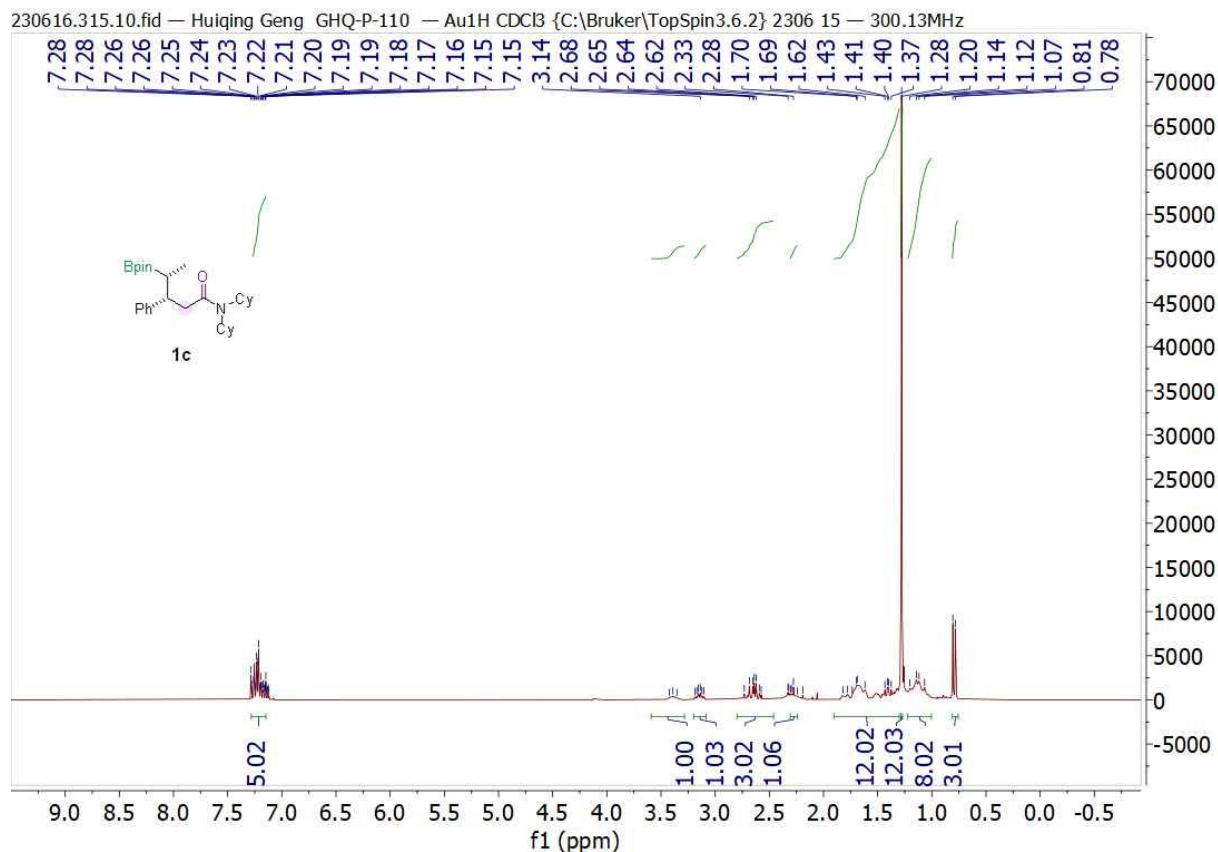


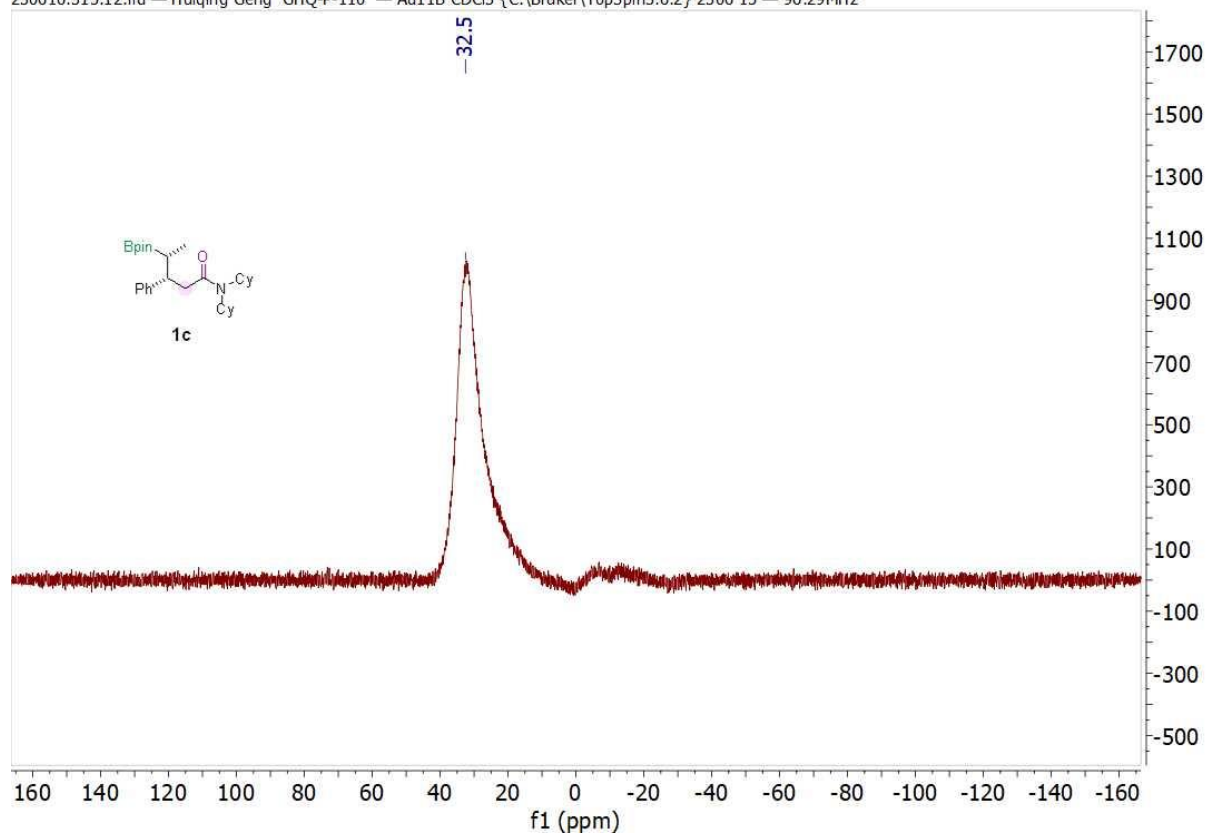




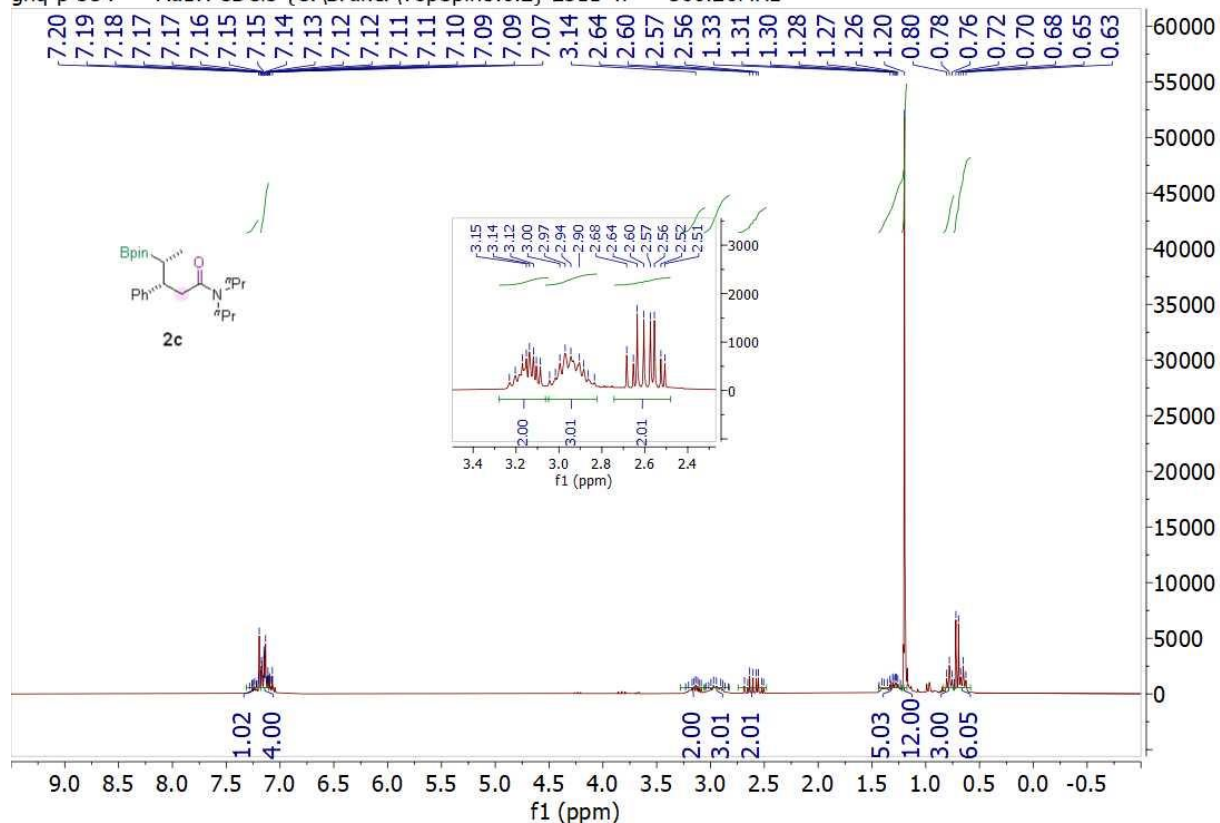




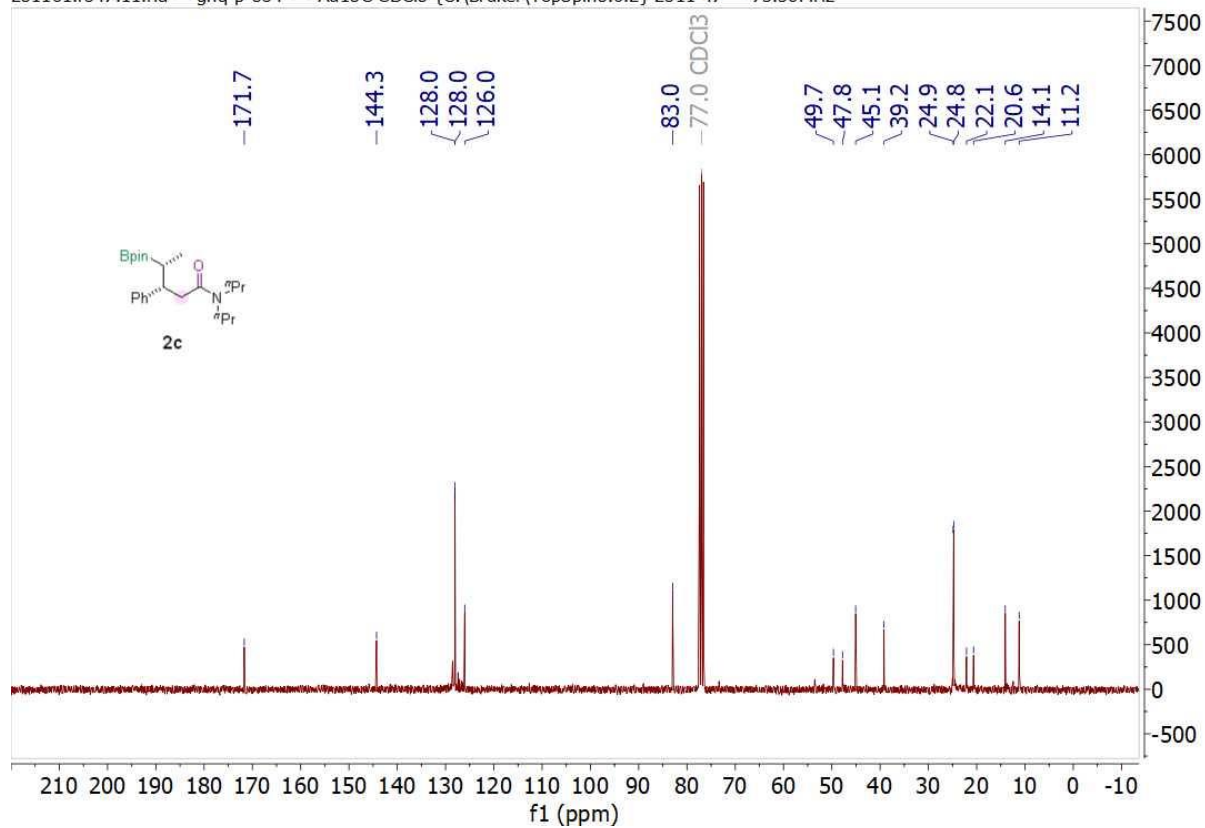




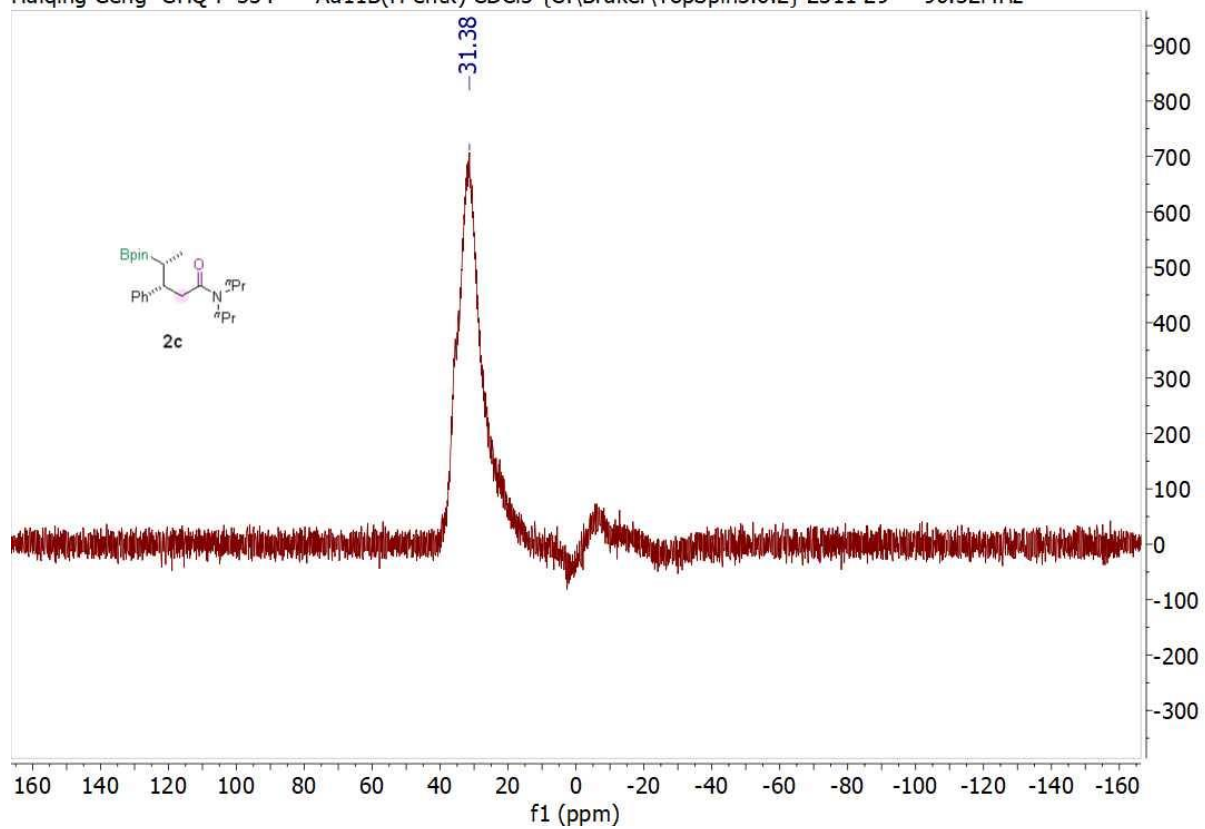
ghq-p-334 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 47 — 300.20MHz

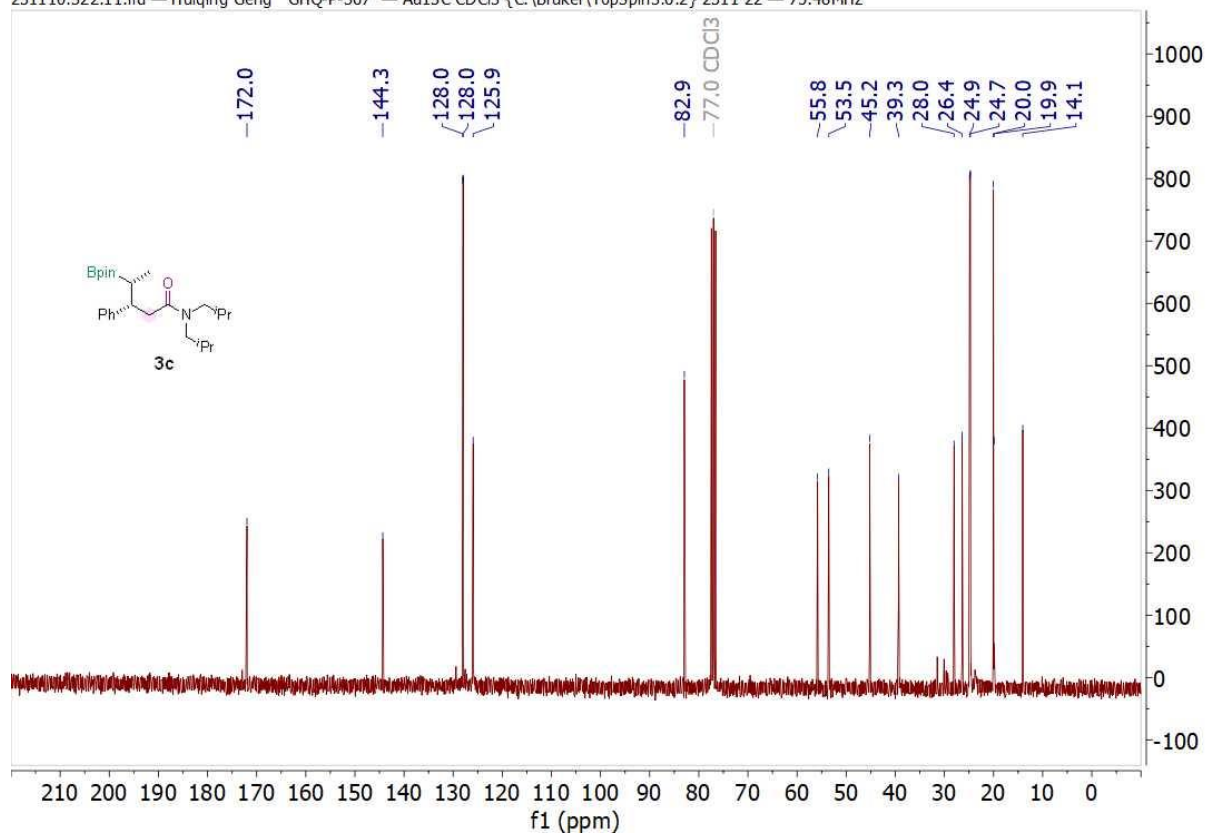
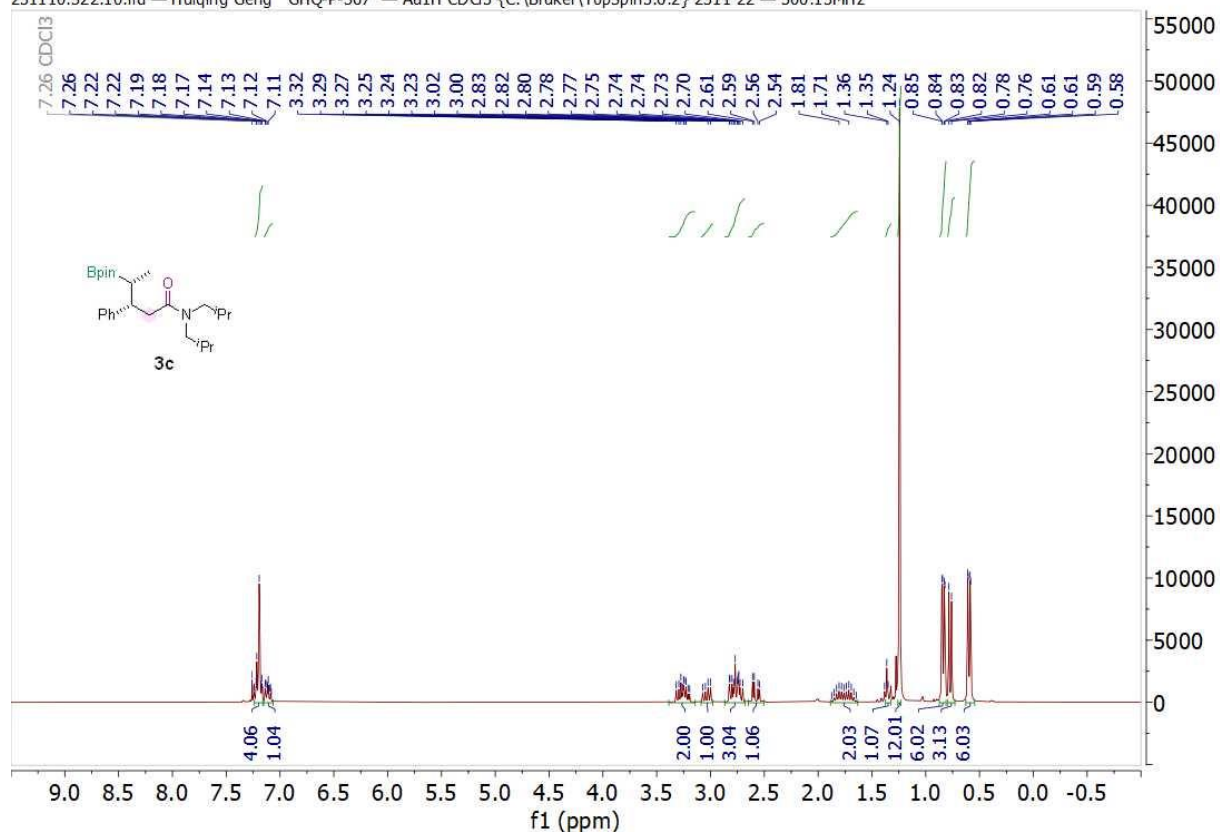


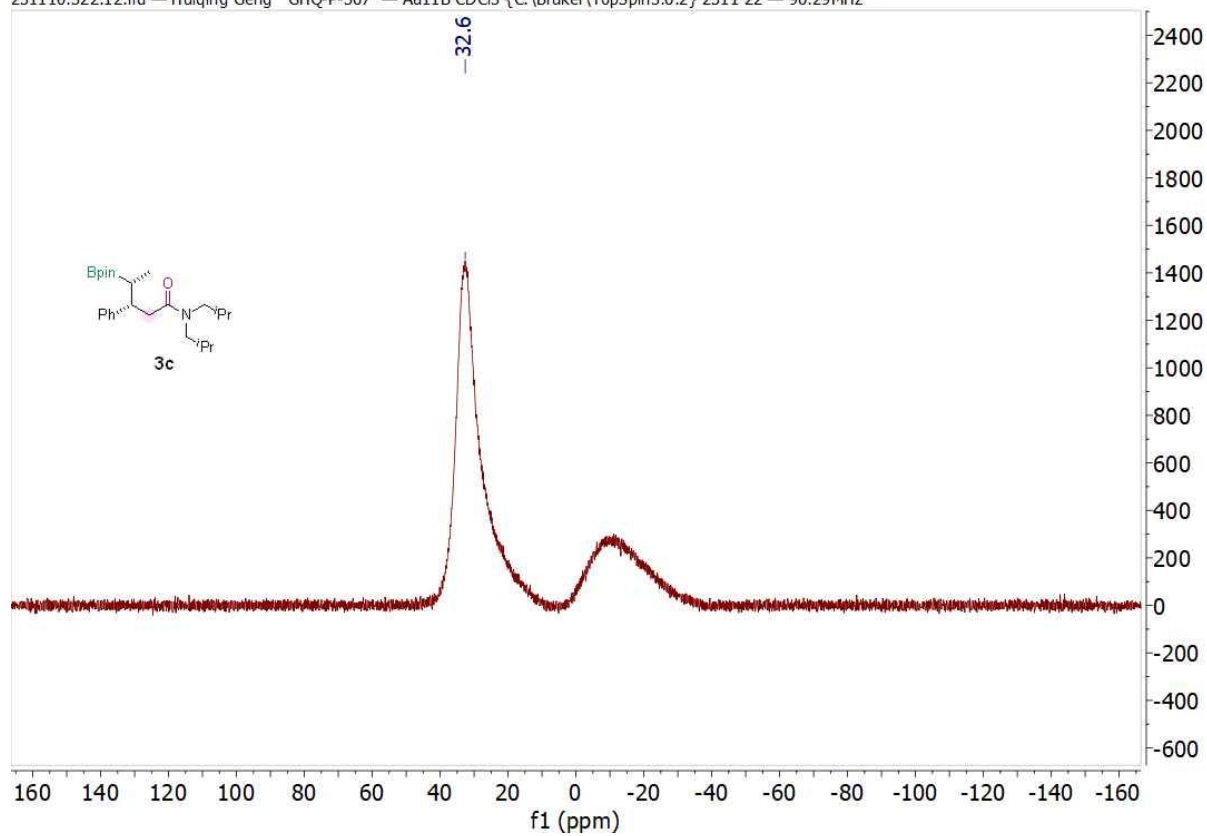
231101.f347.11.fid — ghq-p-334 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 47 — 75.50MHz

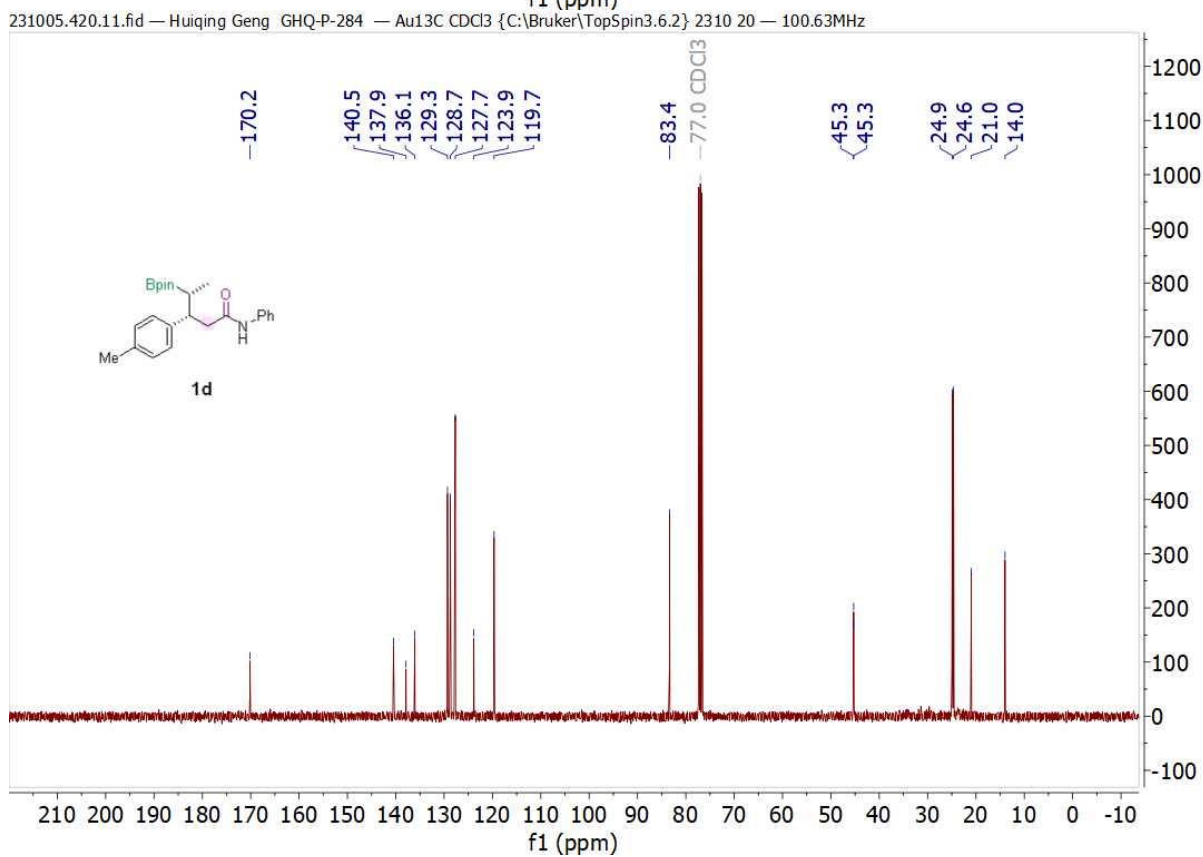
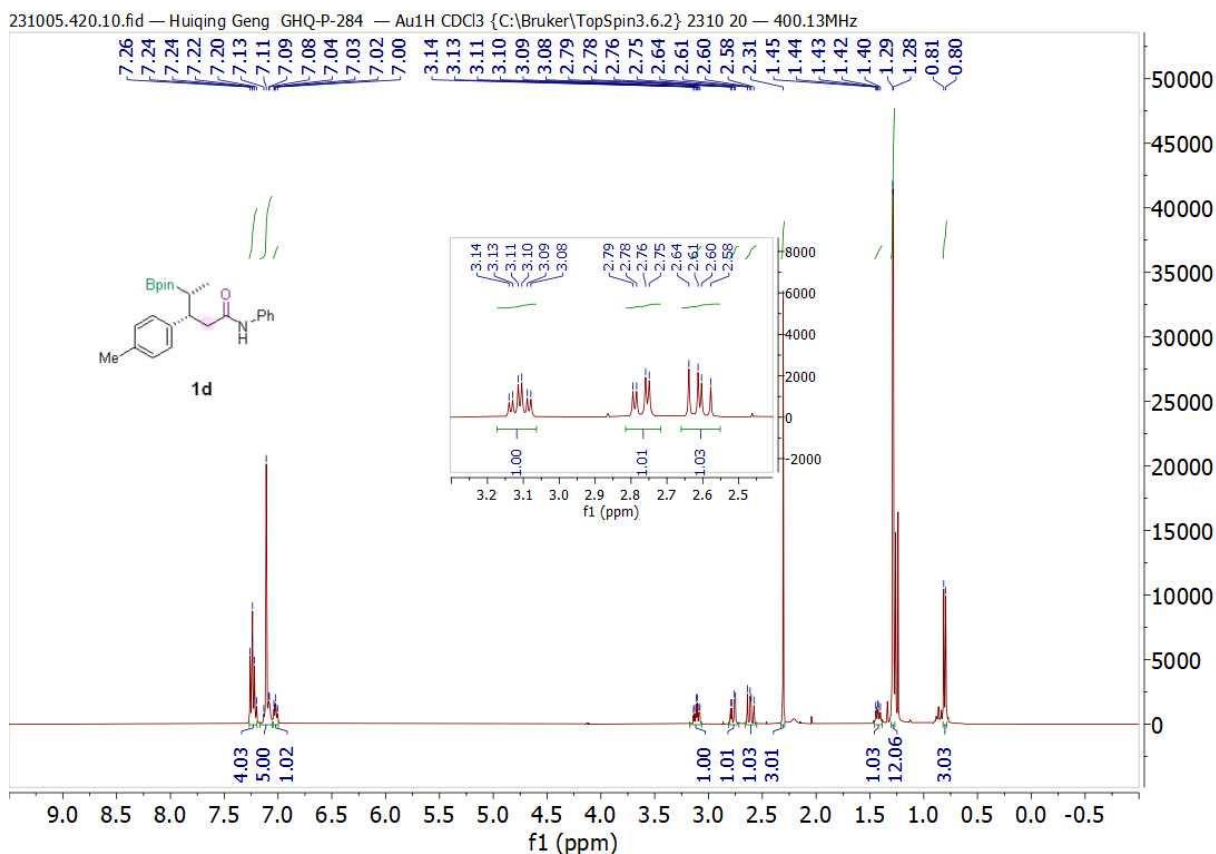


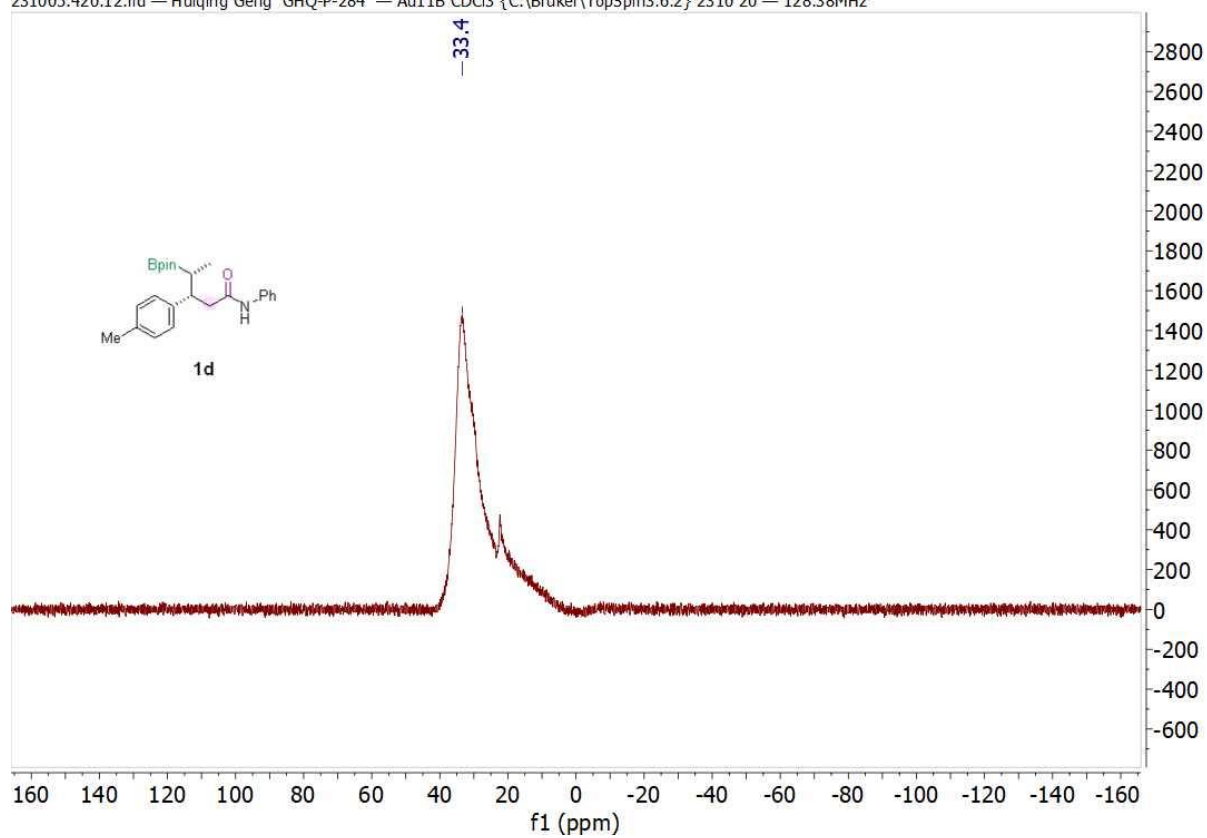
Huiqing Geng GHQ-P-334 — Au11B(H-entk) CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 29 — 96.32MHz

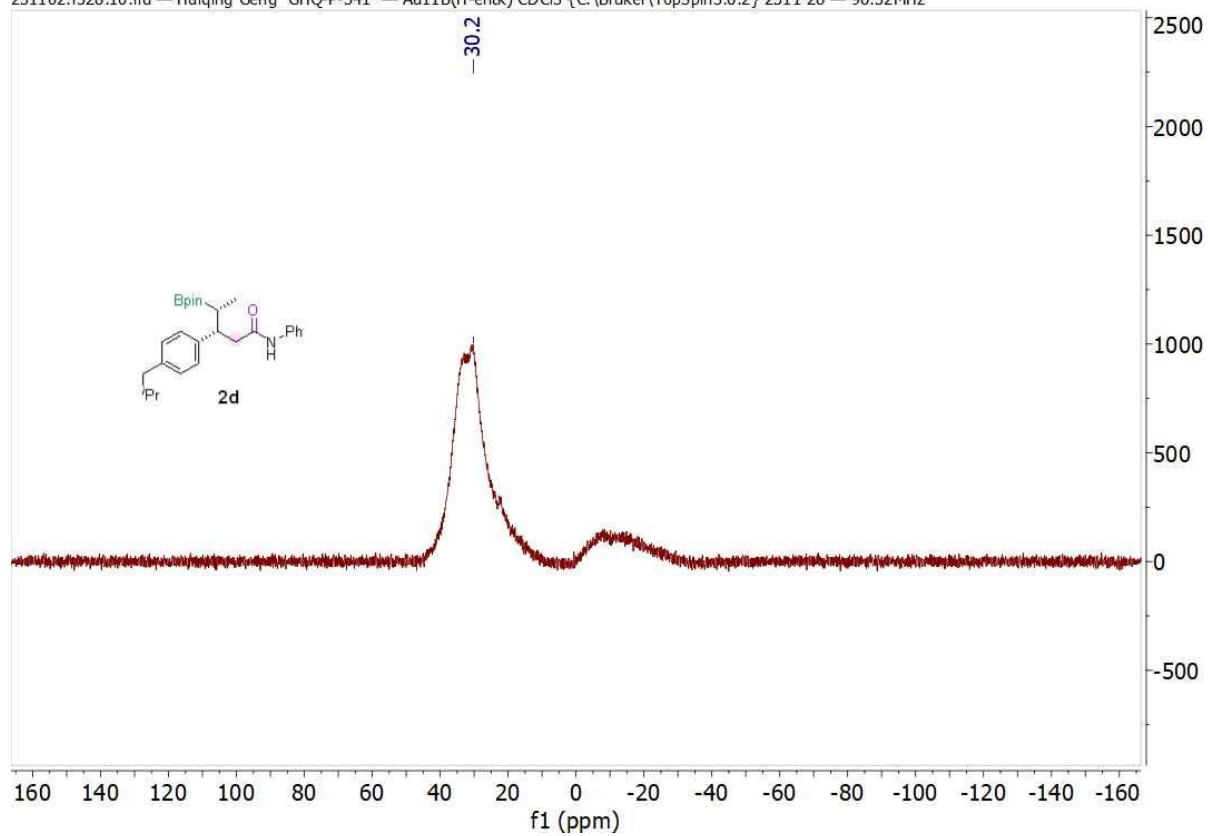


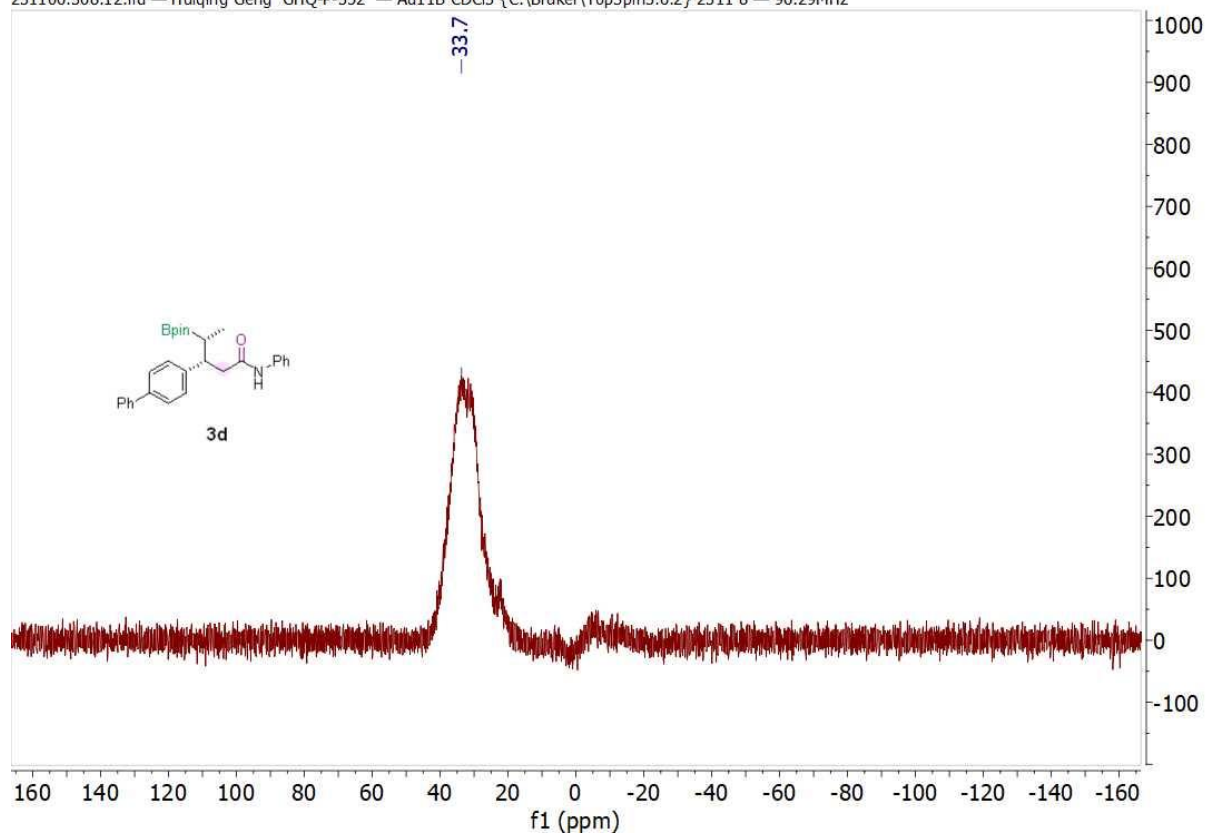


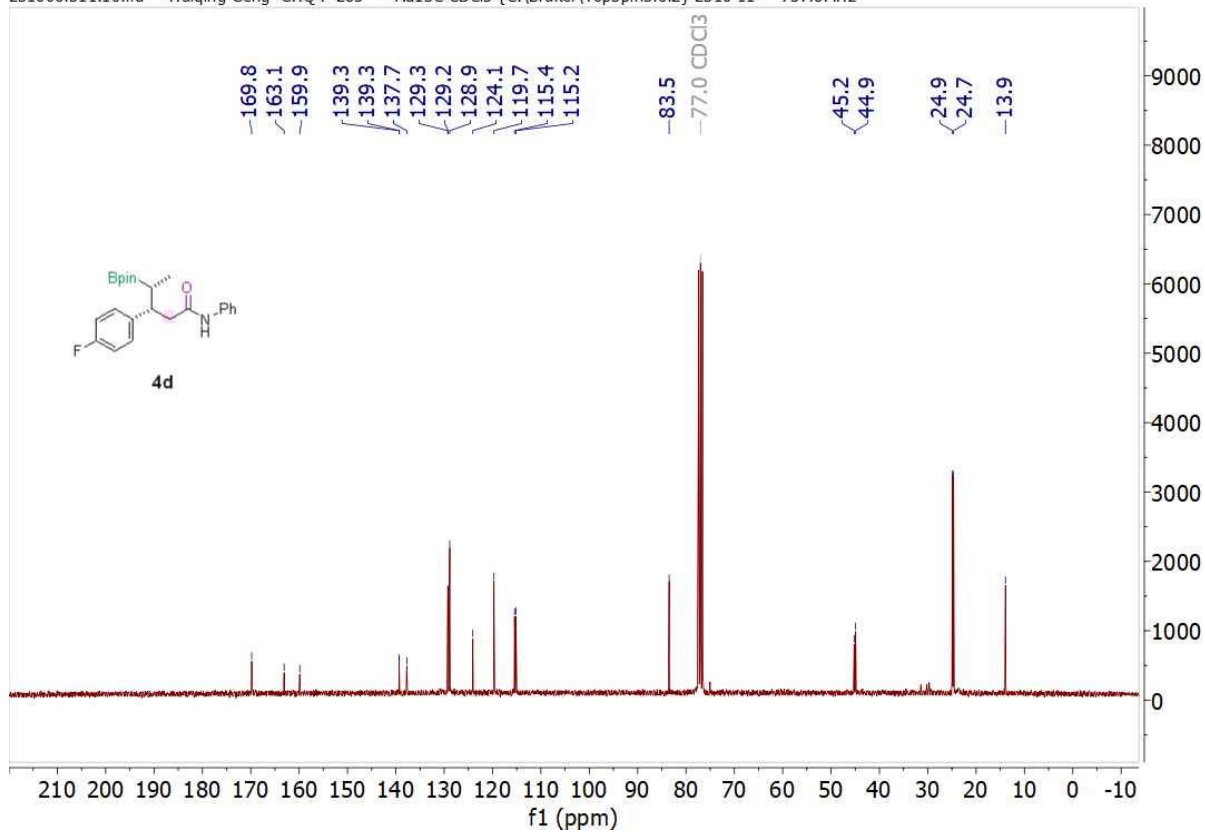
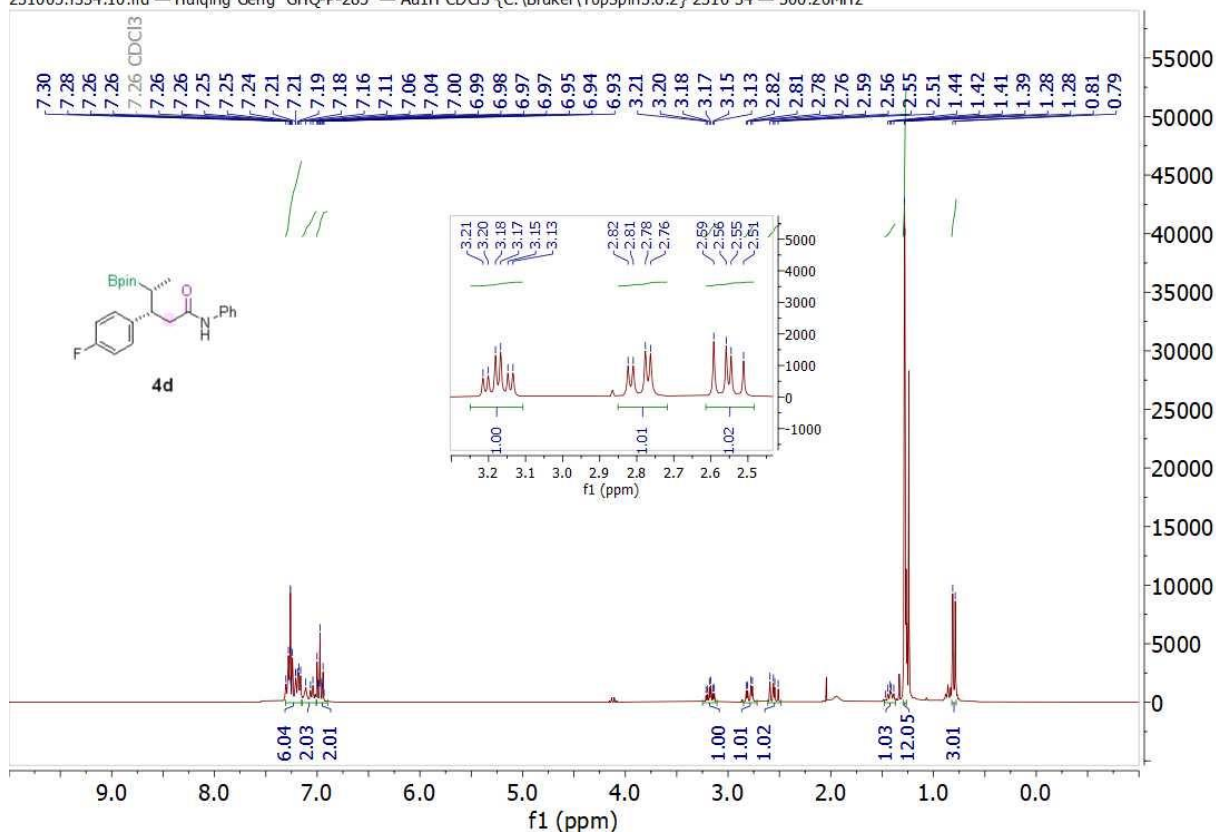




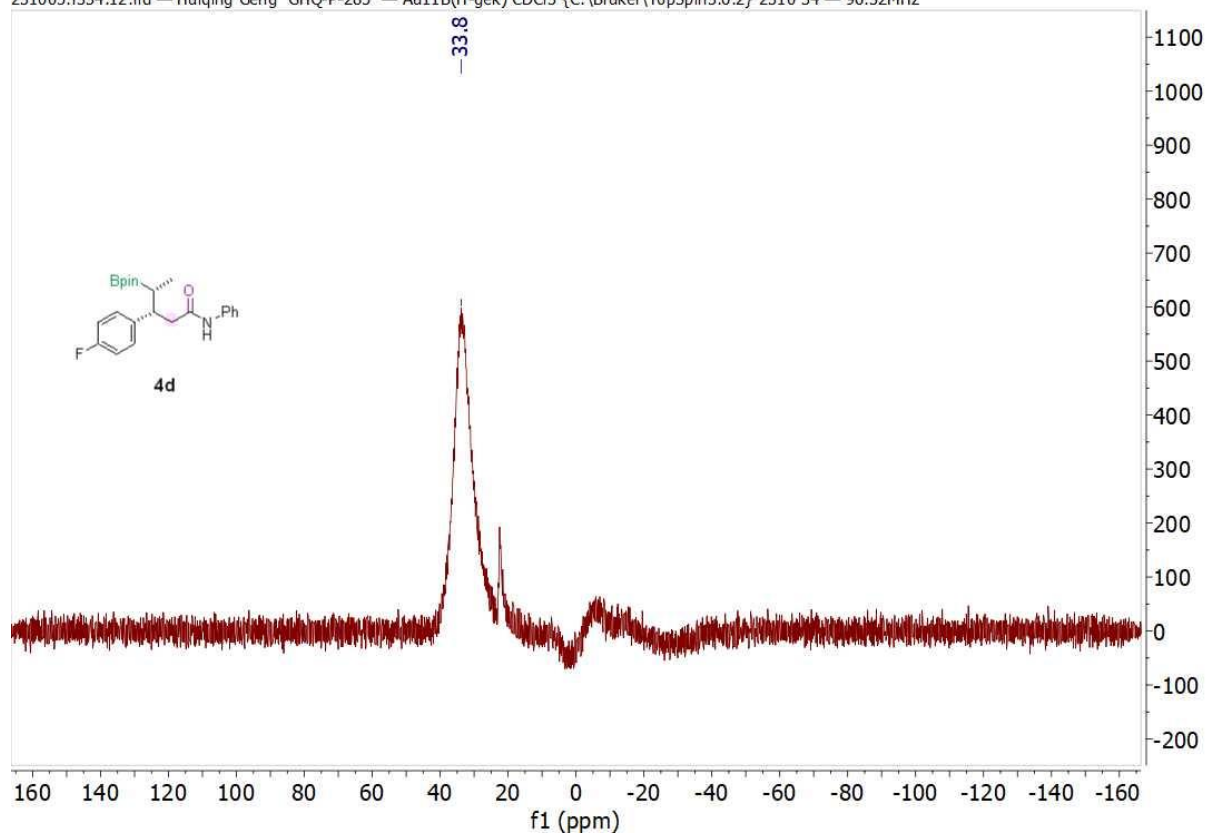




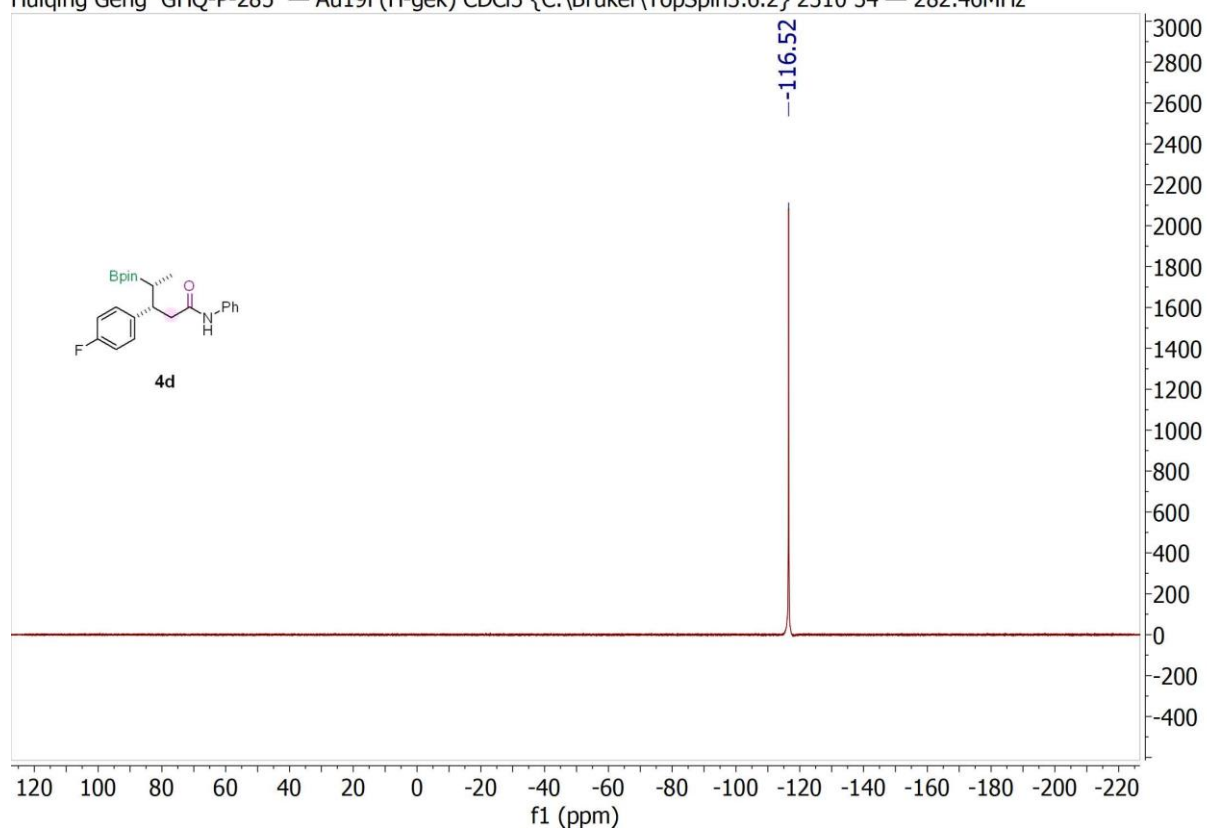


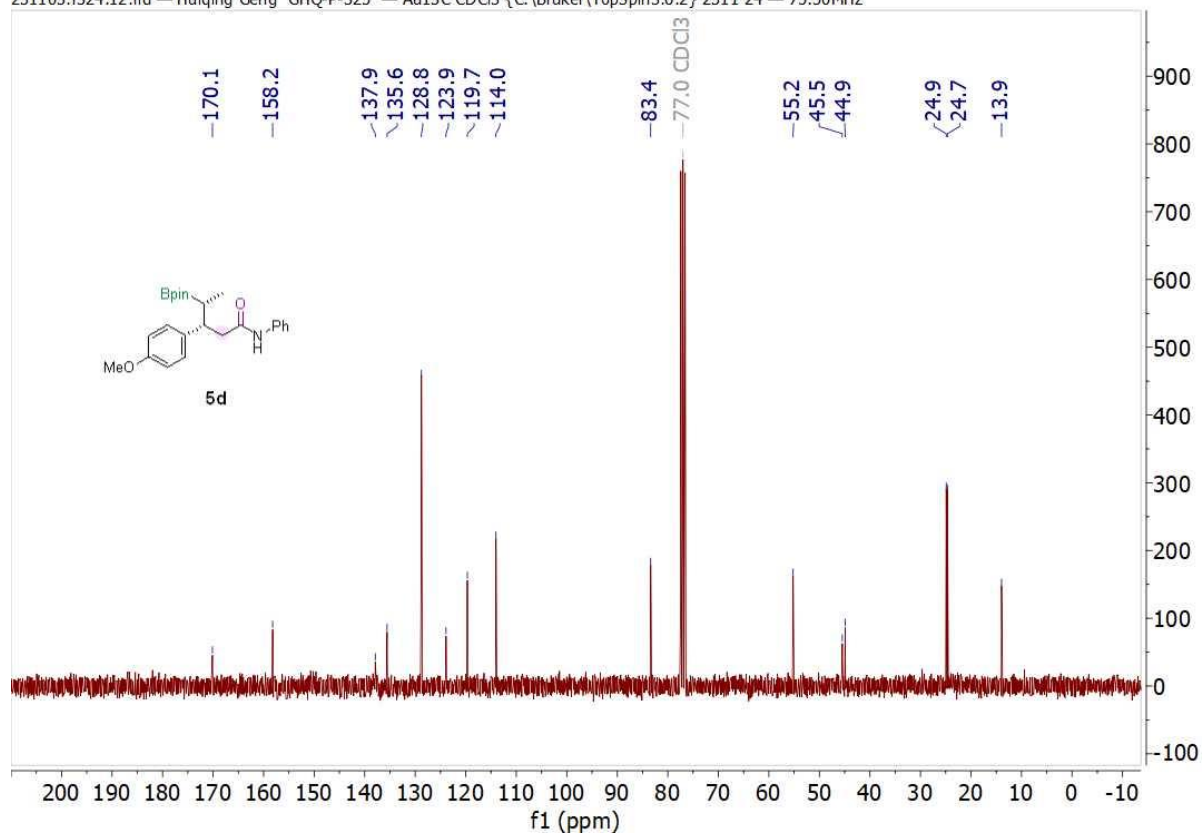
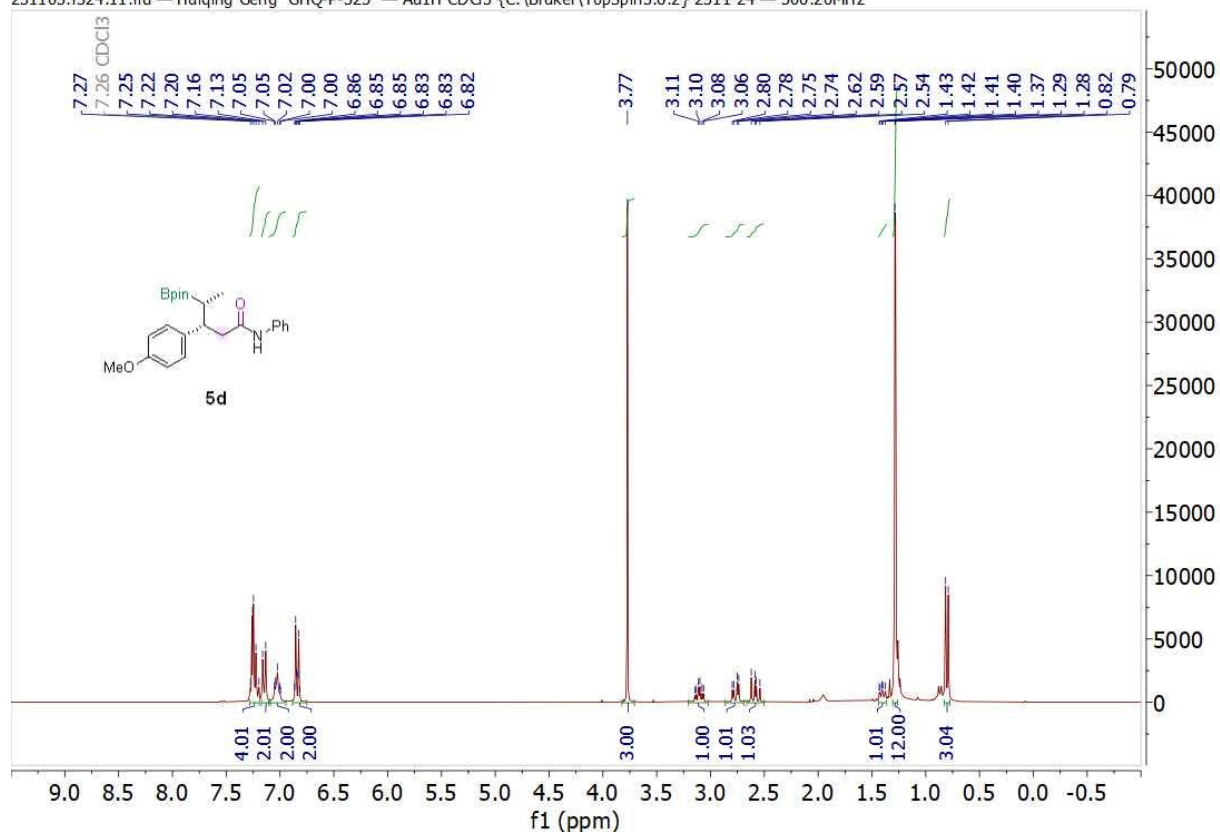


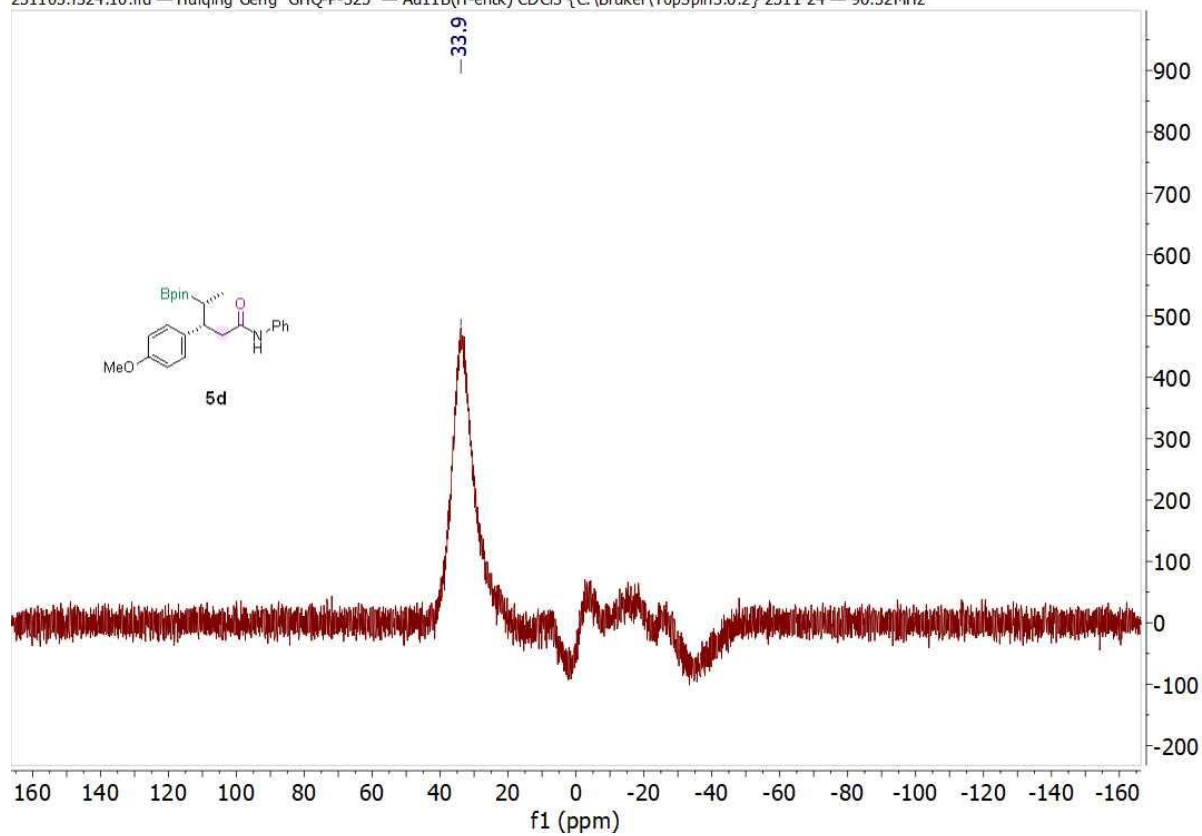
231005.f334.12.fid — Huiqing Geng GHQ-P-285 — Au11B(H-gek) CDCl3 {C:\Bruker\TopSpin3.6.2} 2310 34 — 96.32MHz

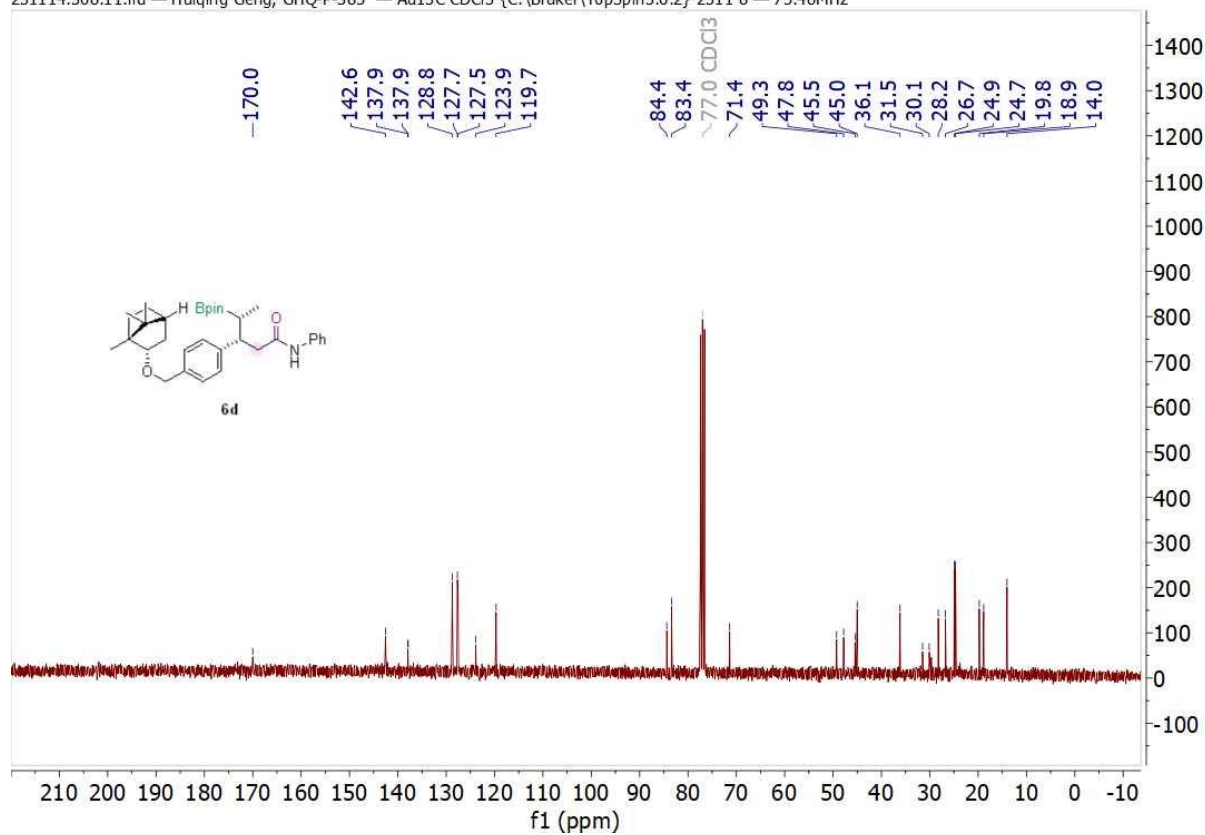
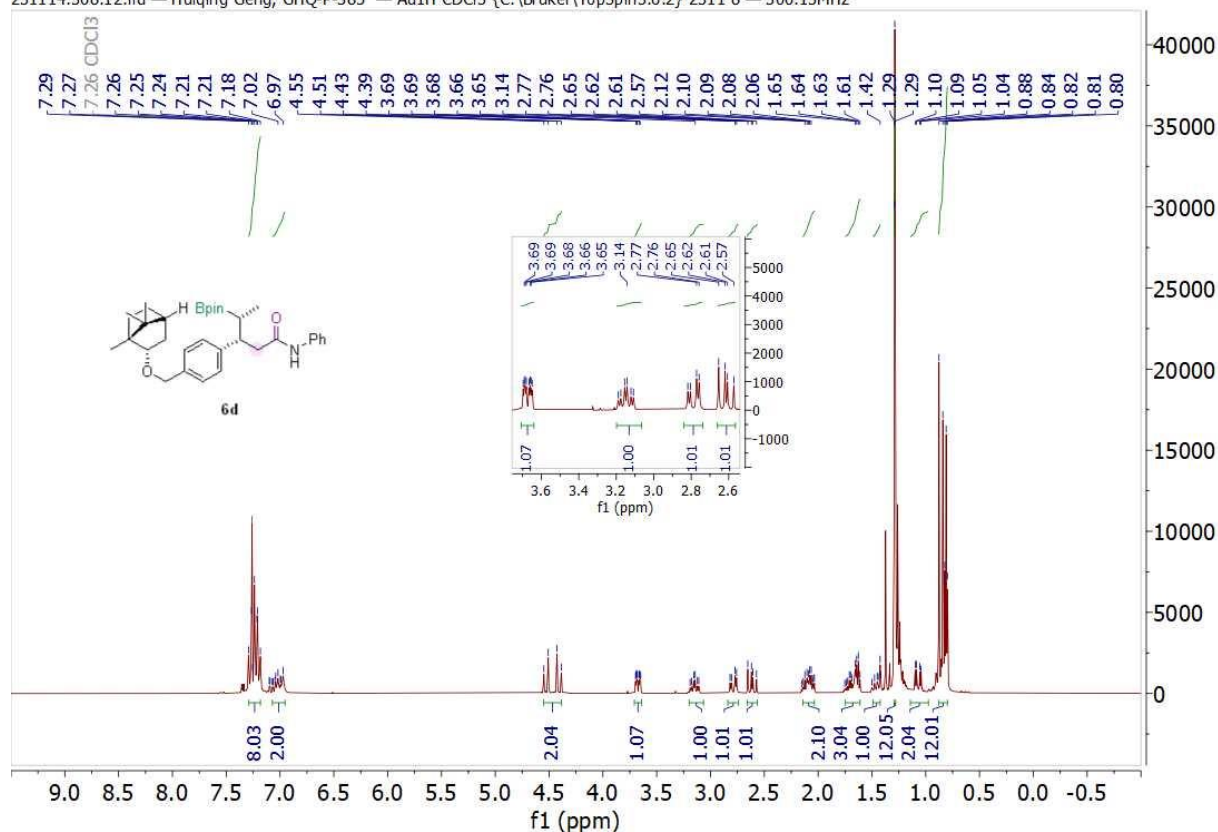


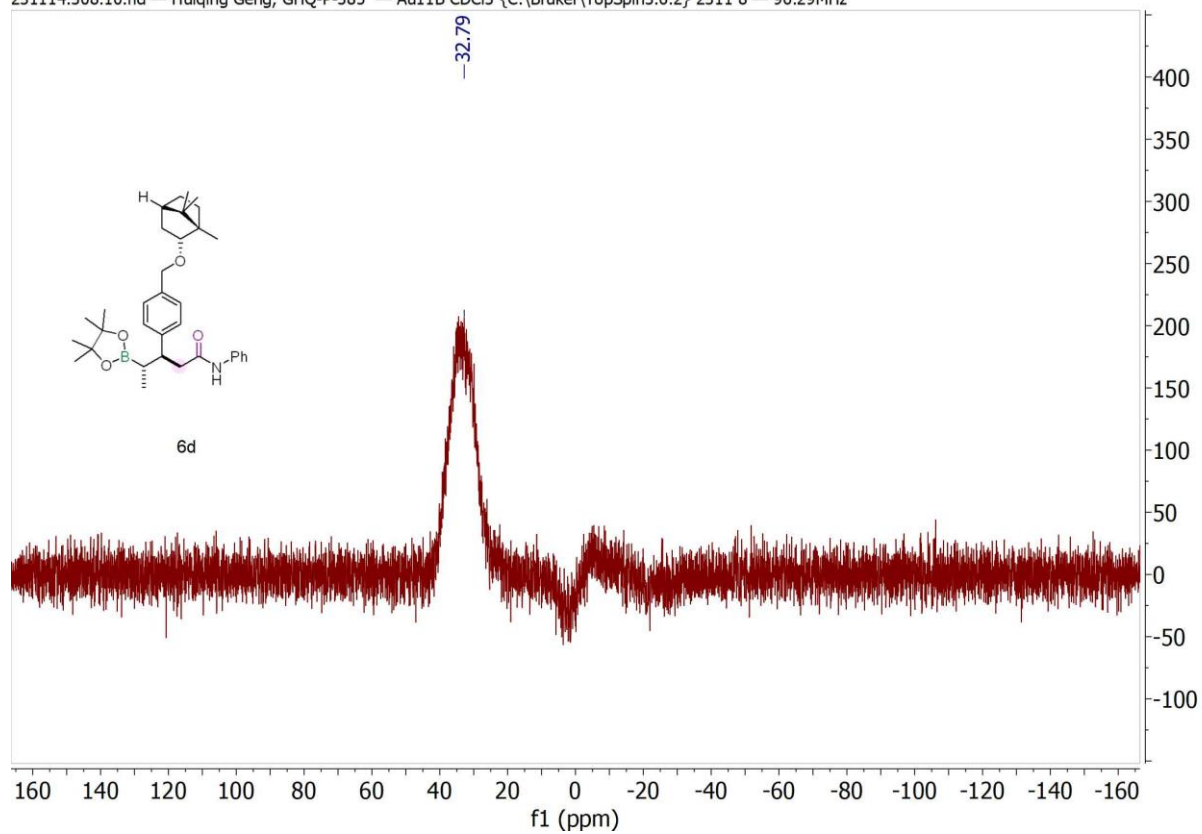
Huiqing Geng GHQ-P-285 — Au19F(H-gek) CDCl3 {C:\Bruker\TopSpin3.6.2} 2310 34 — 282.46MHz

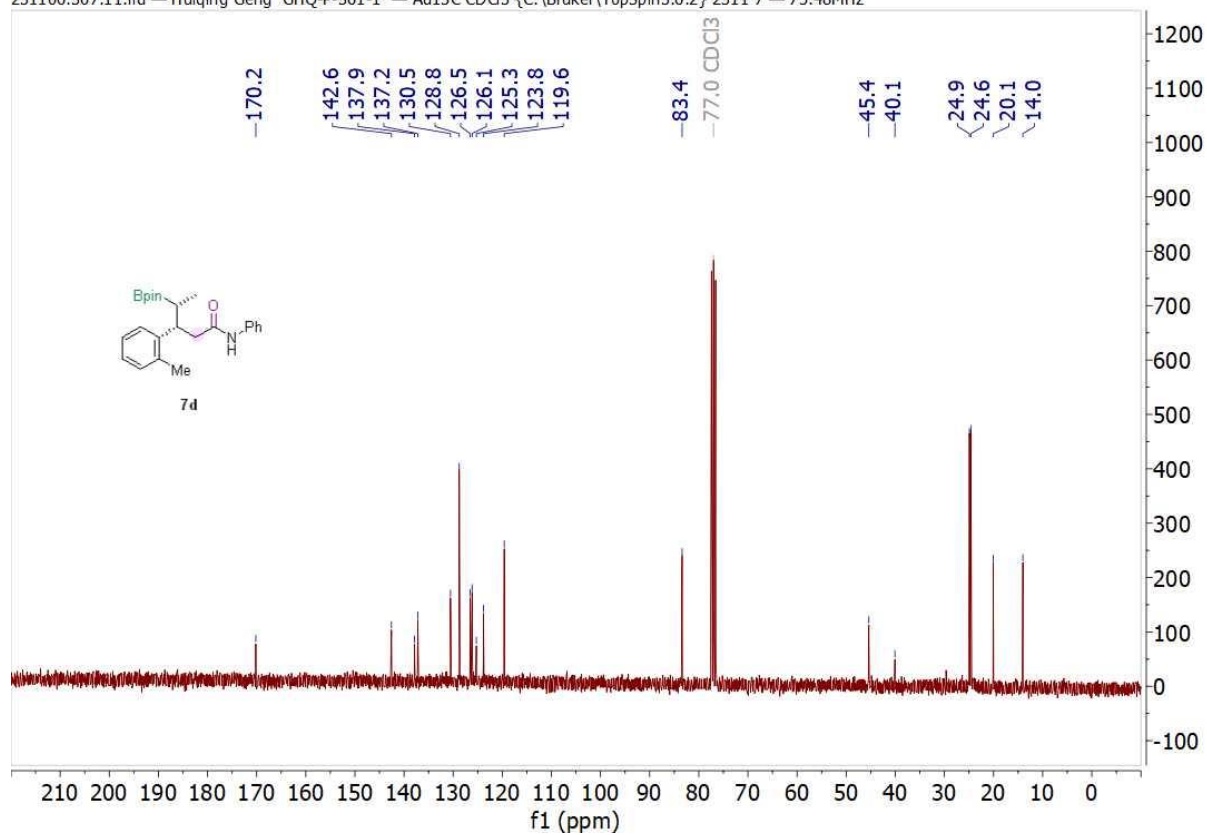
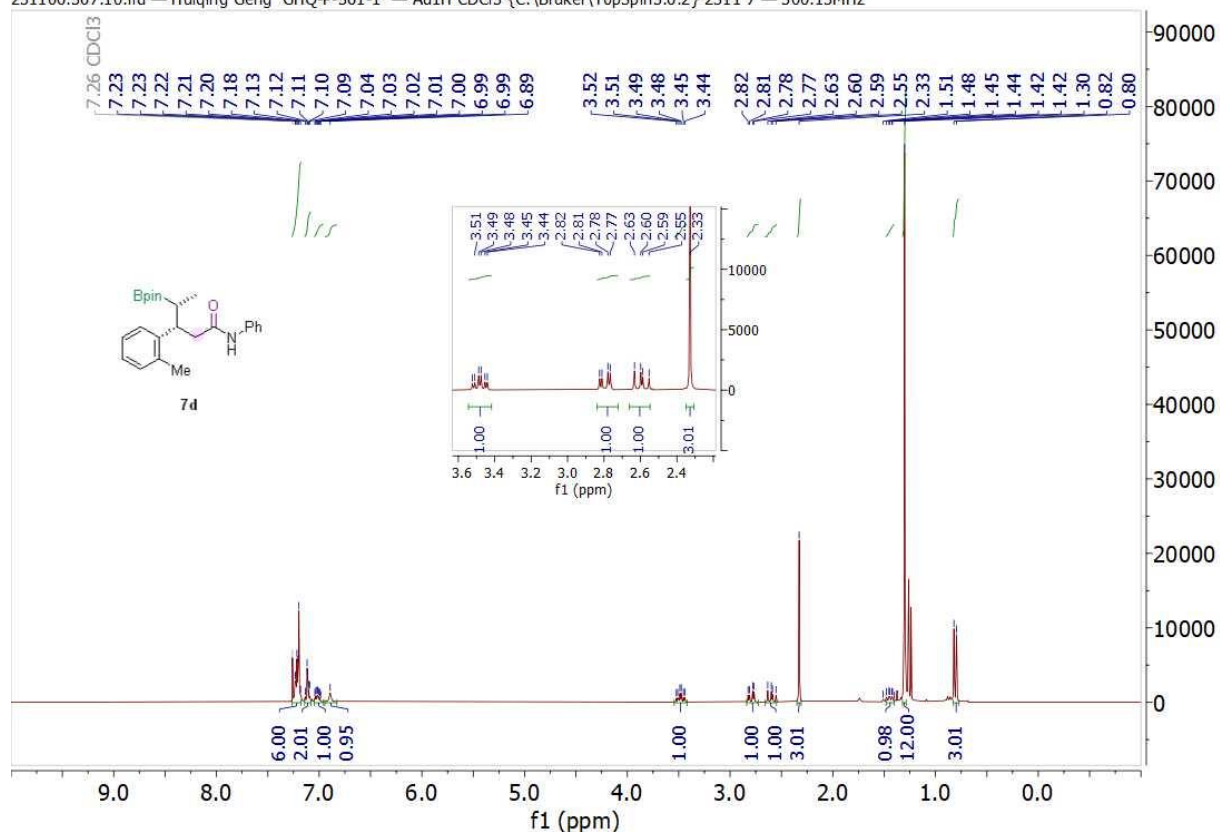


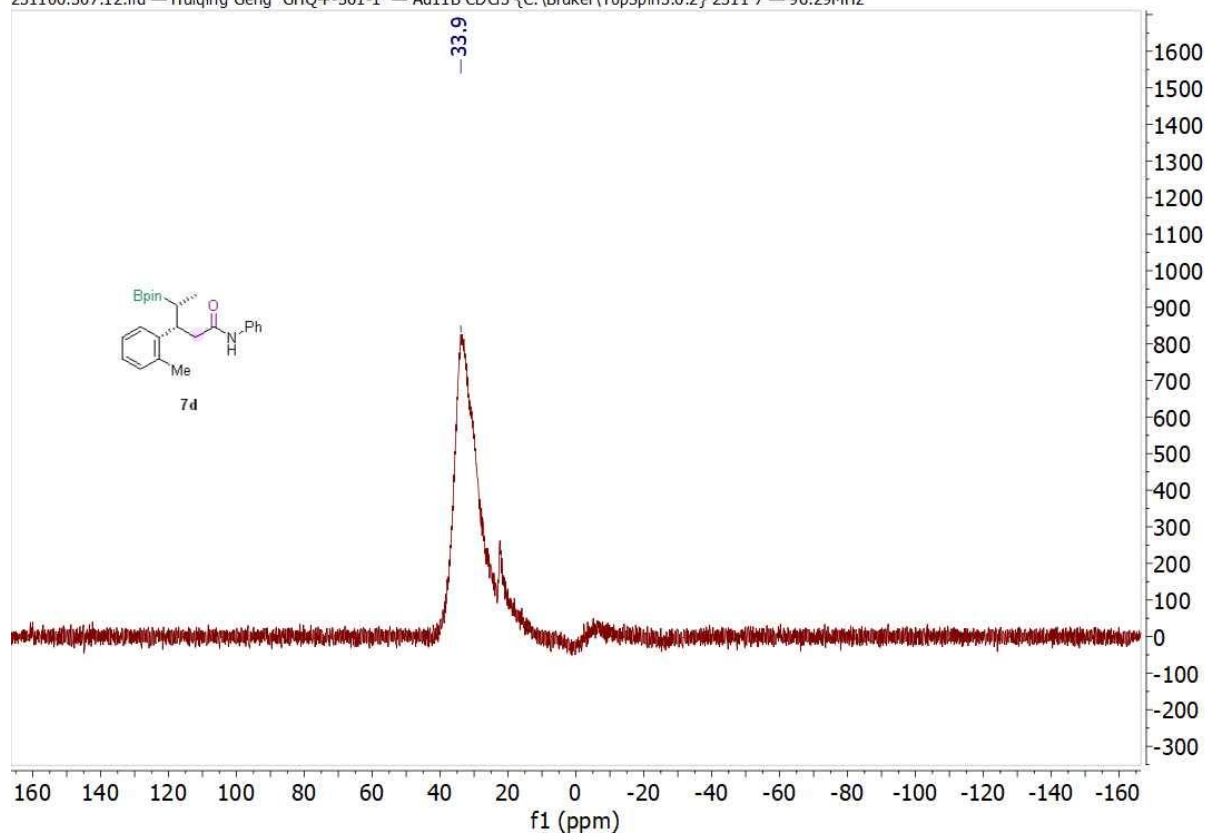


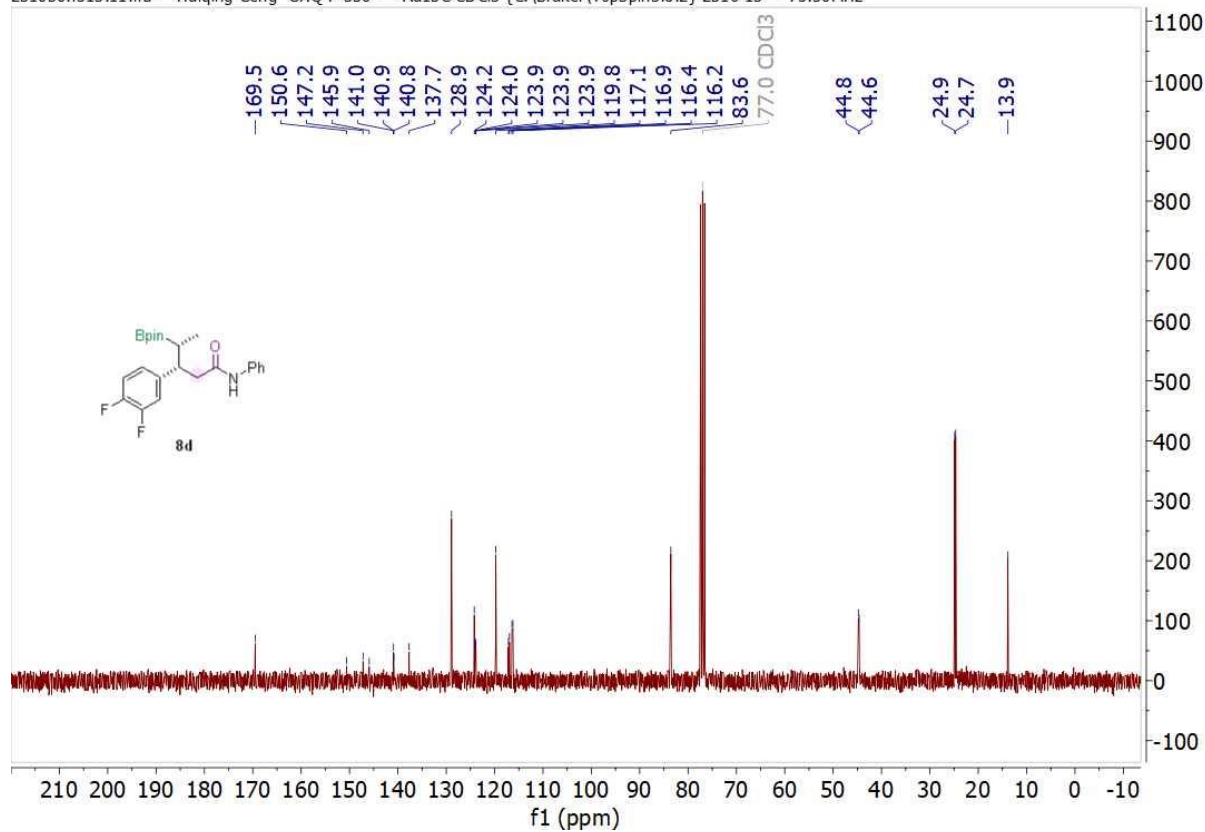
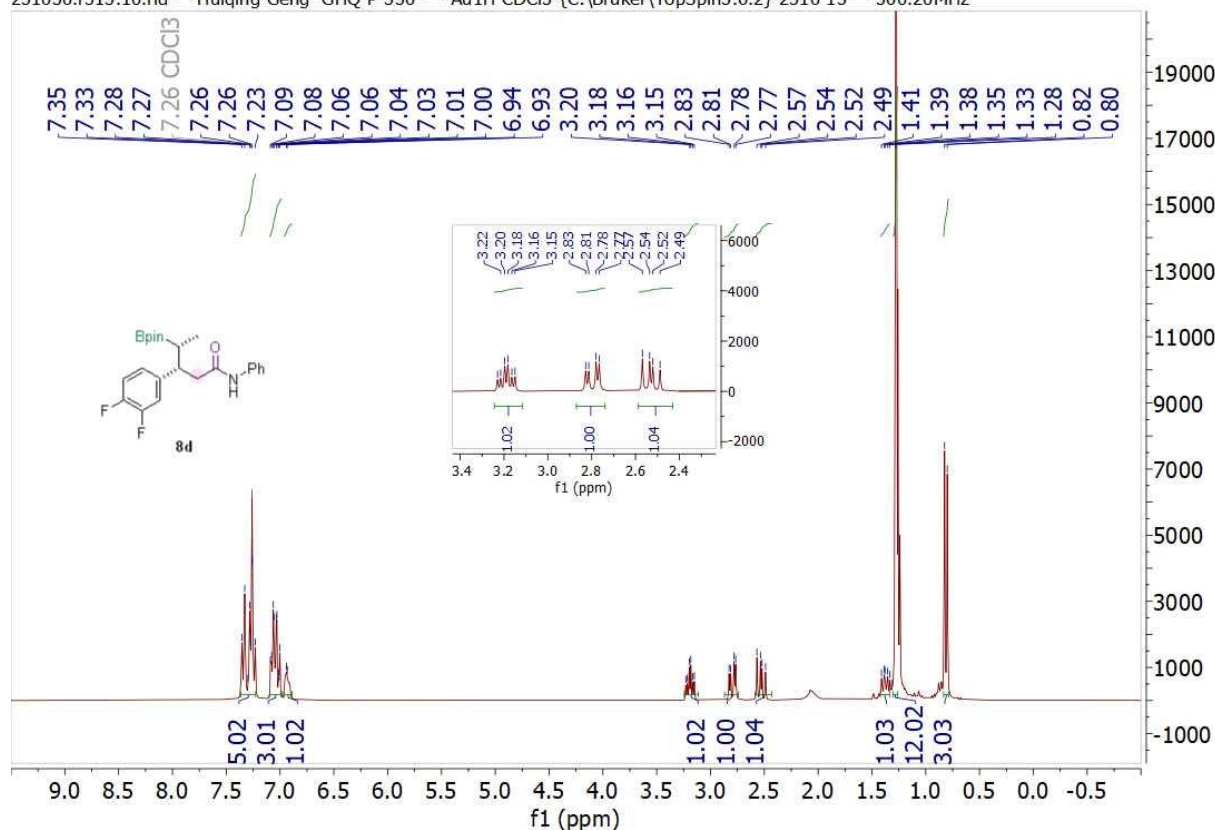


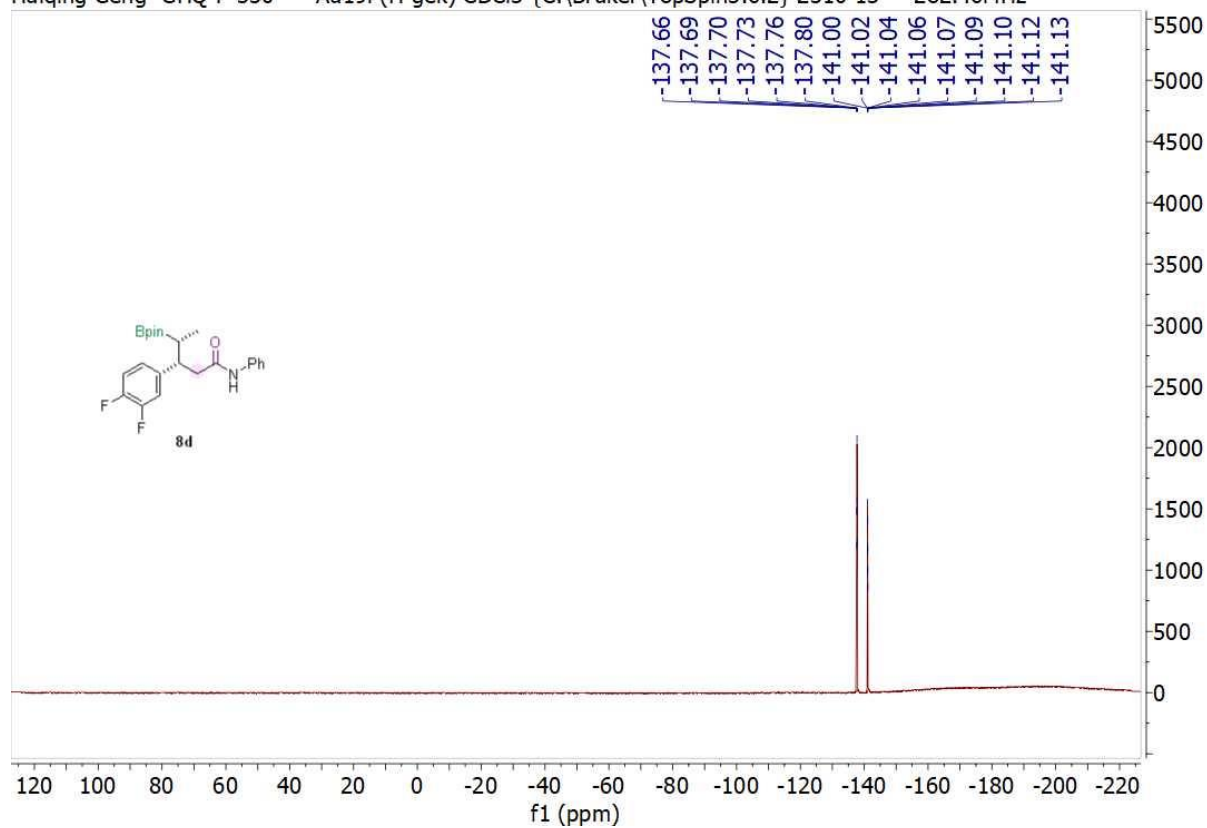
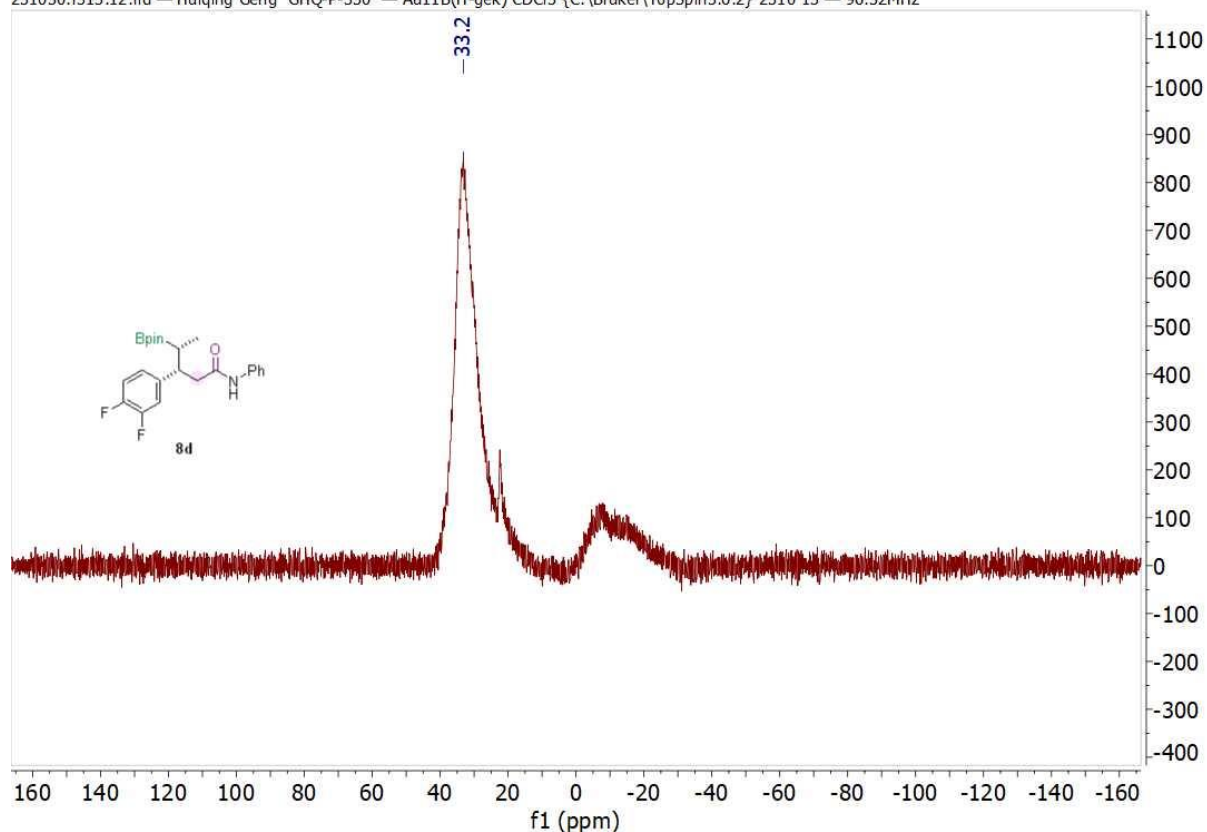


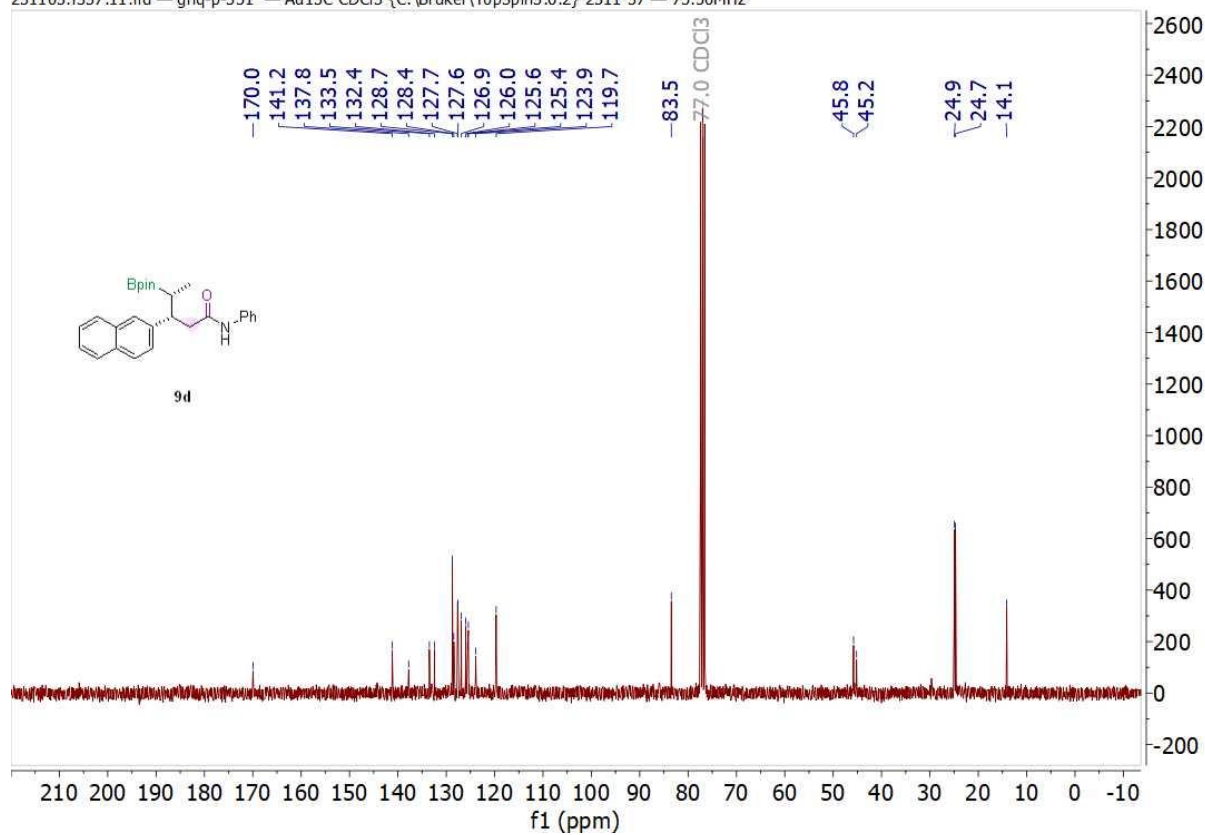
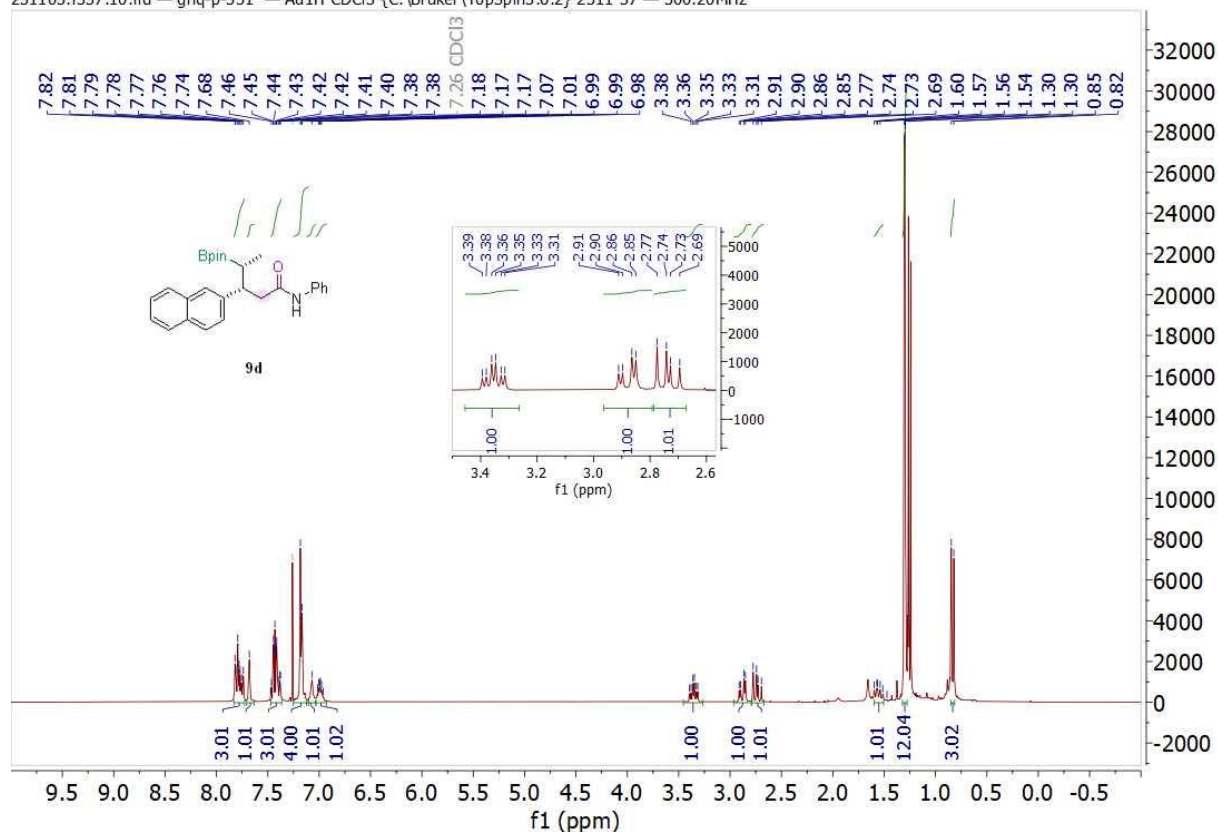


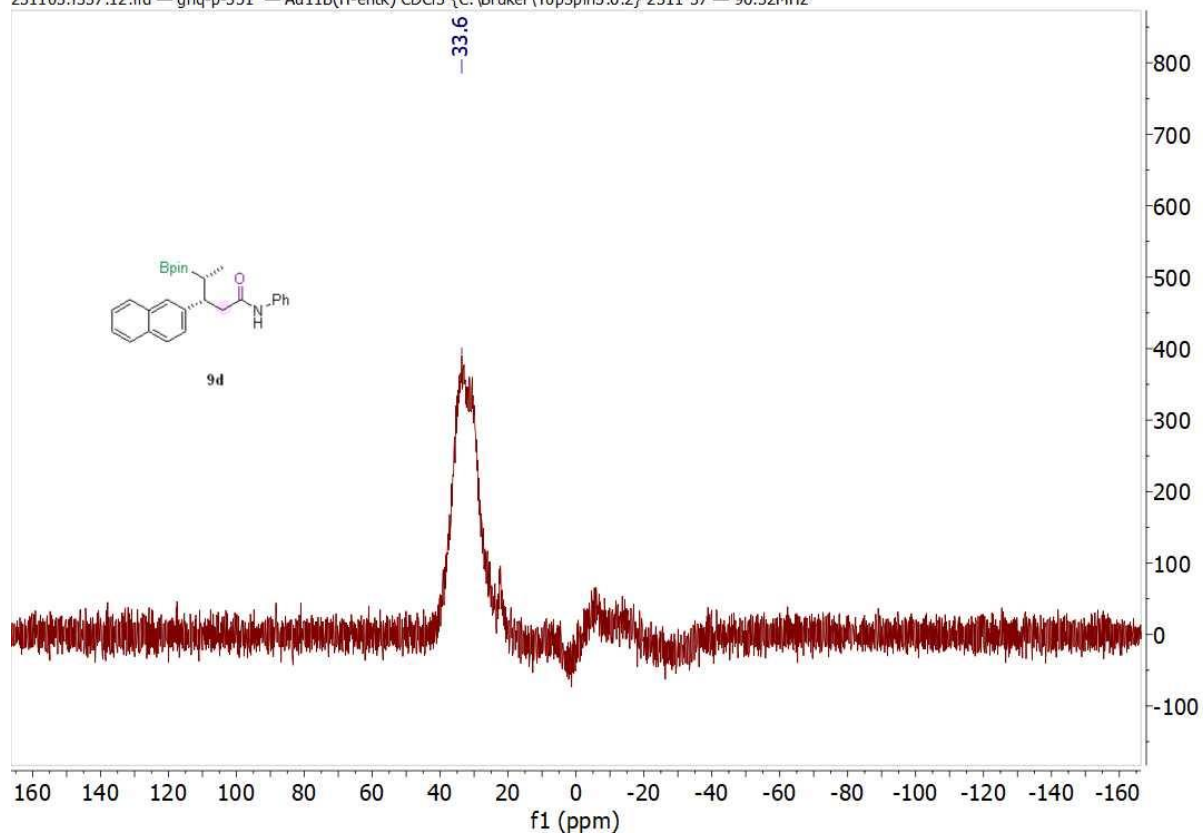


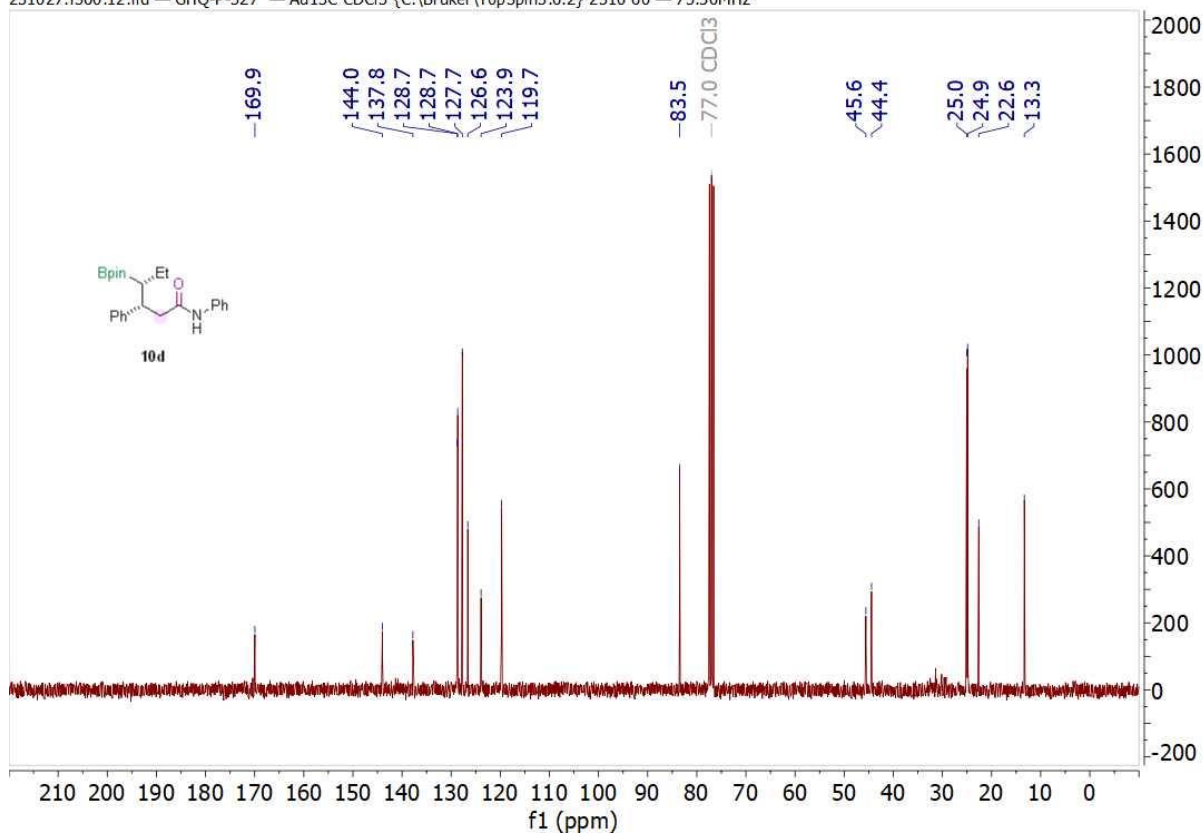
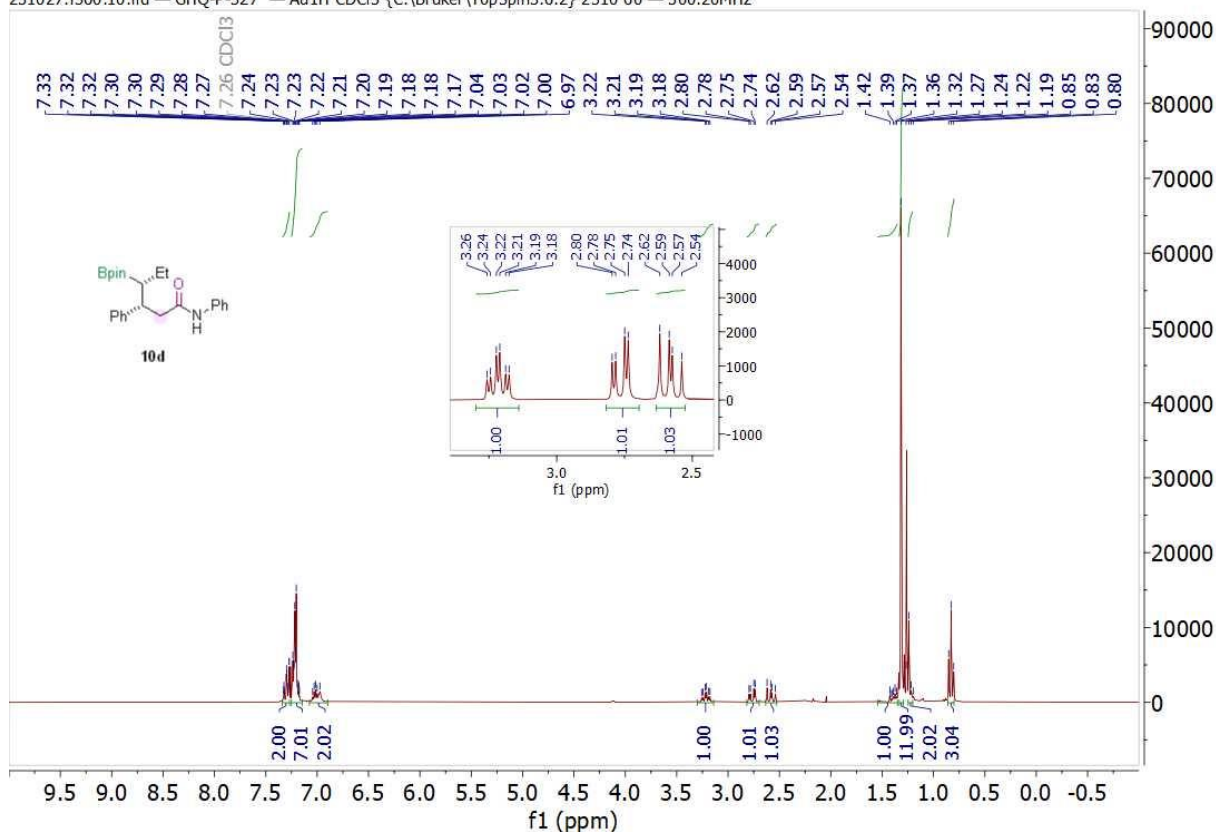


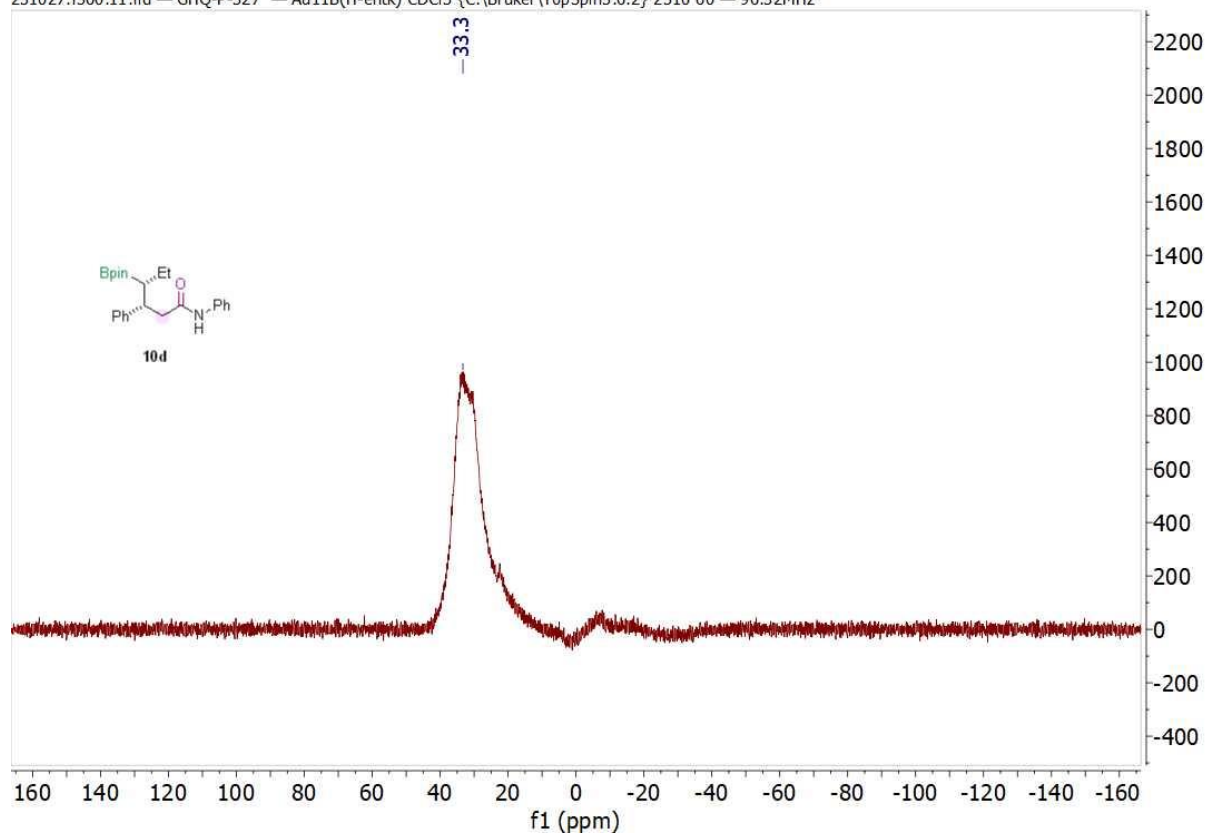


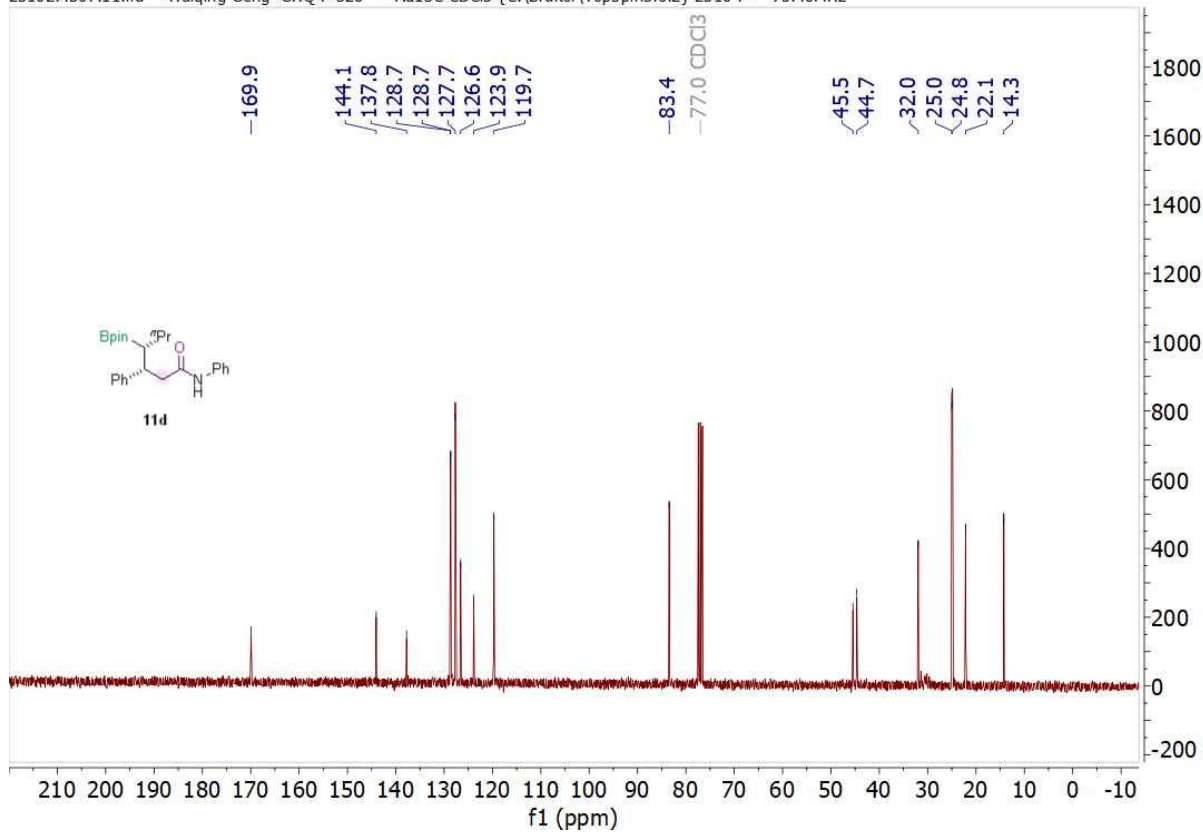
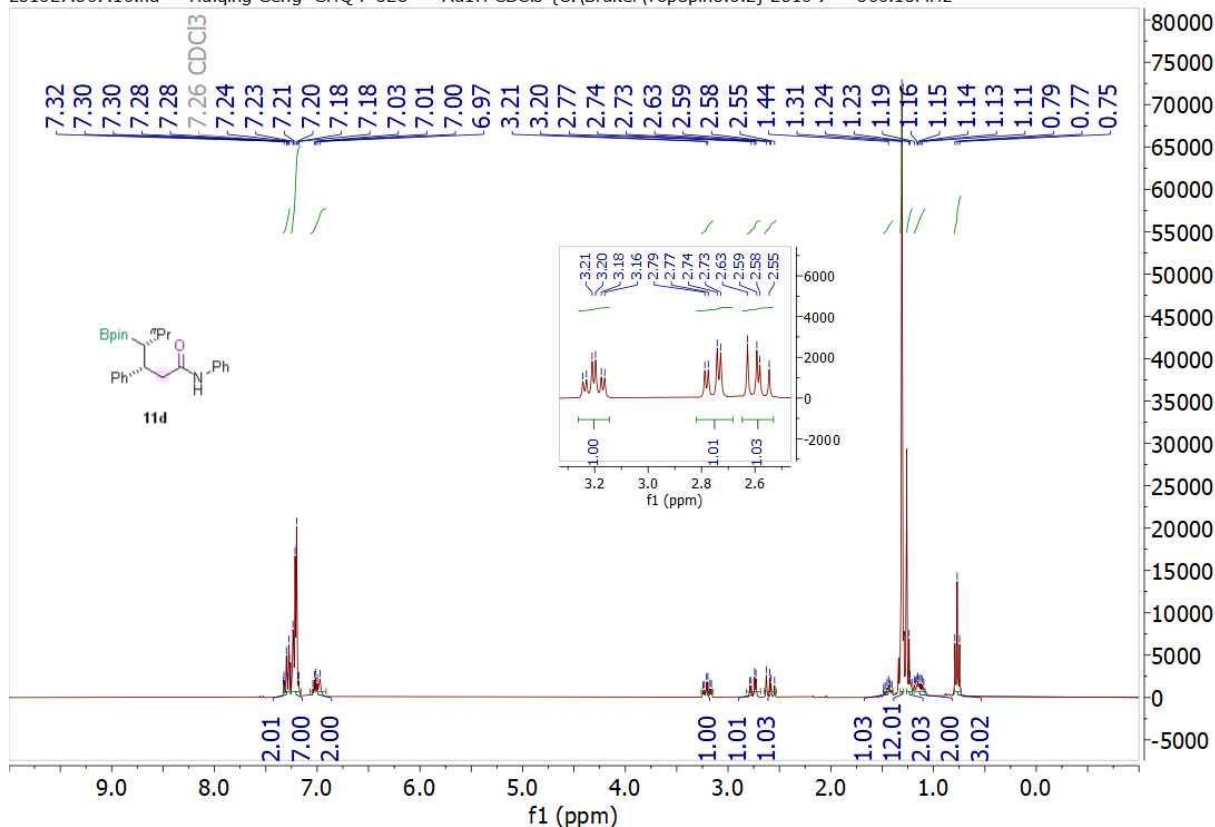


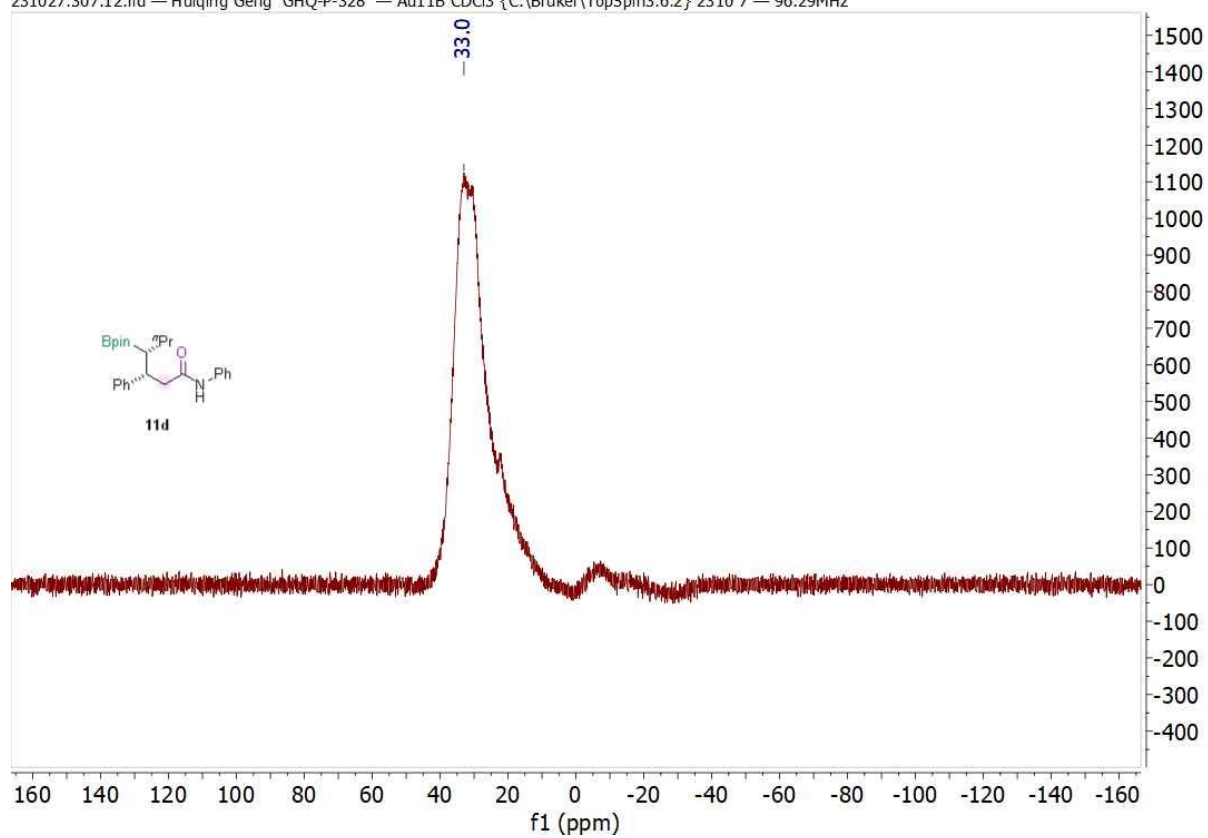


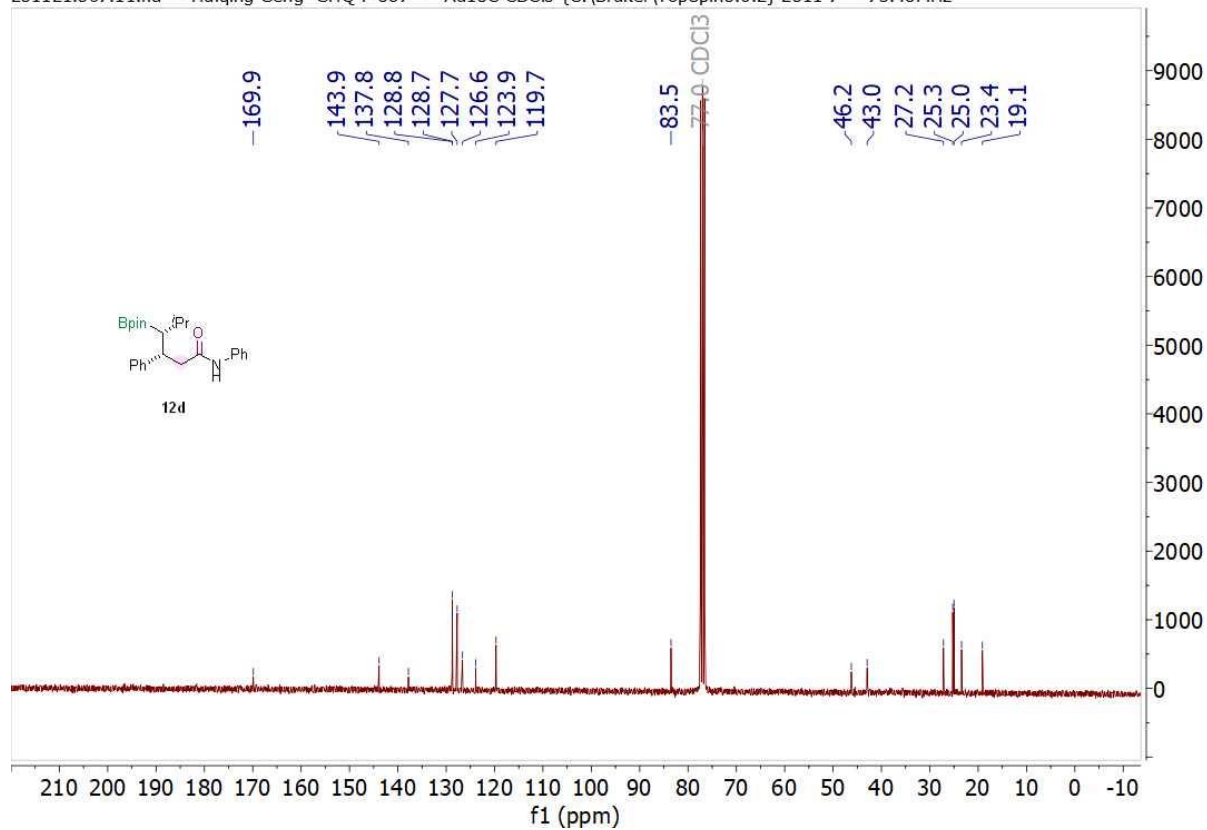
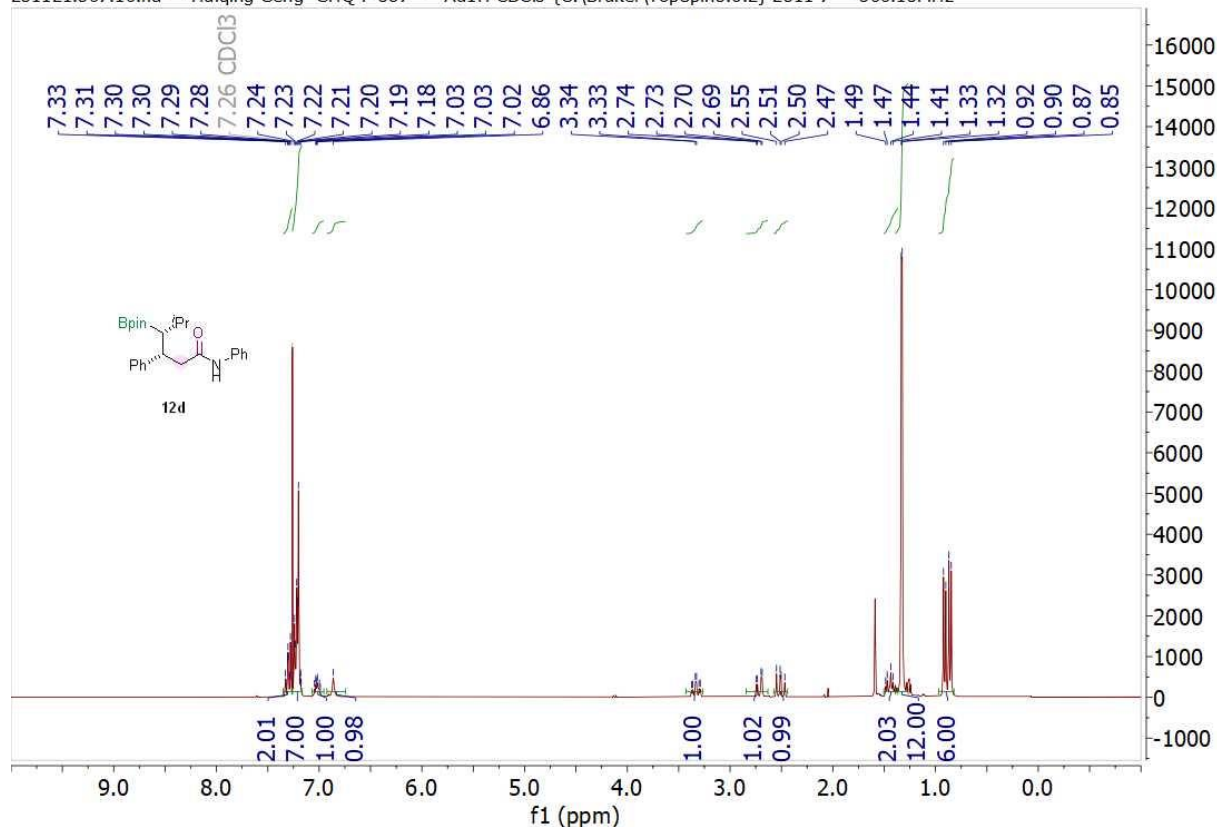


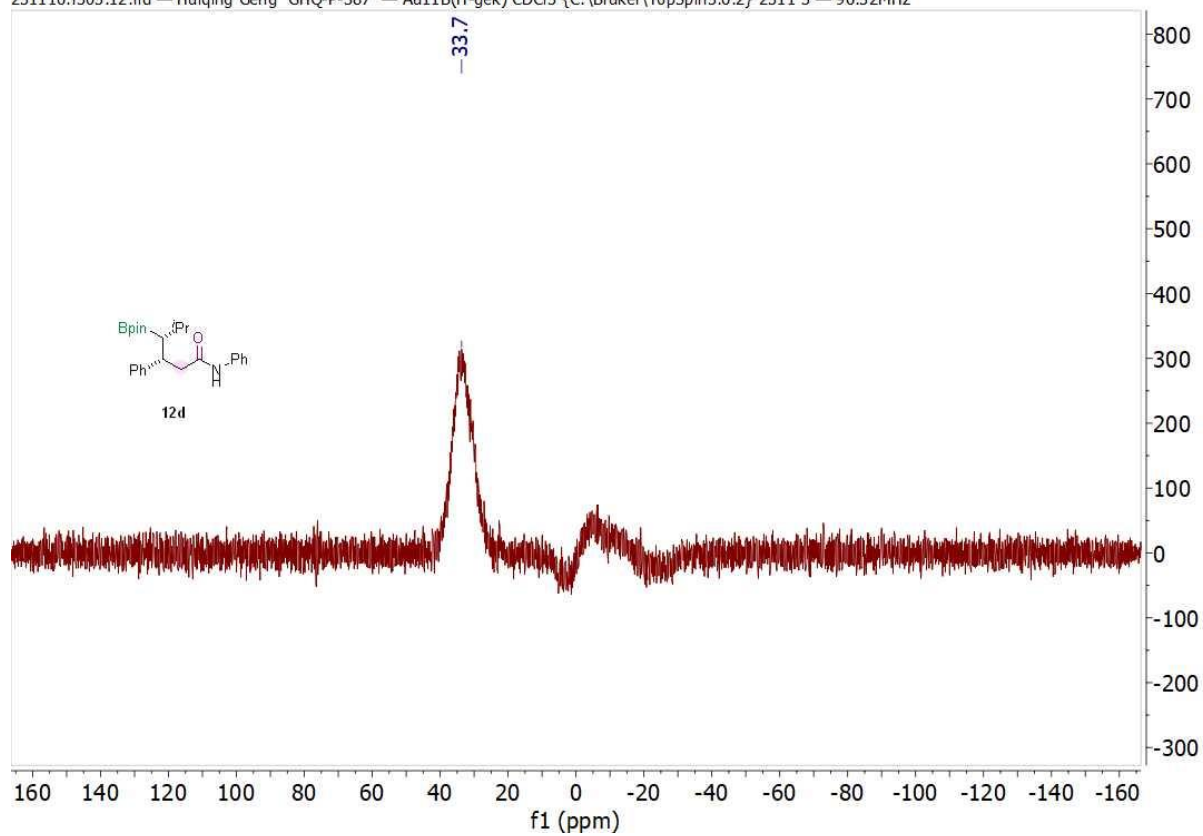




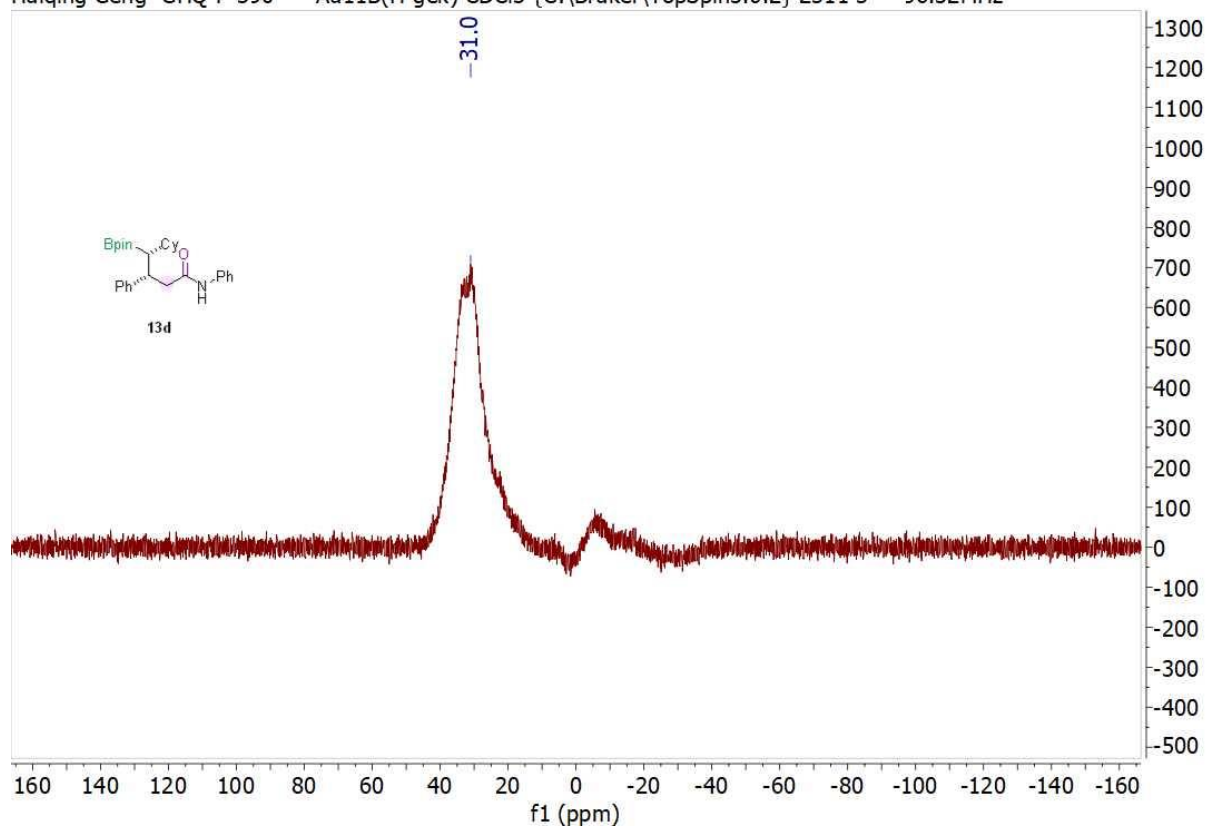




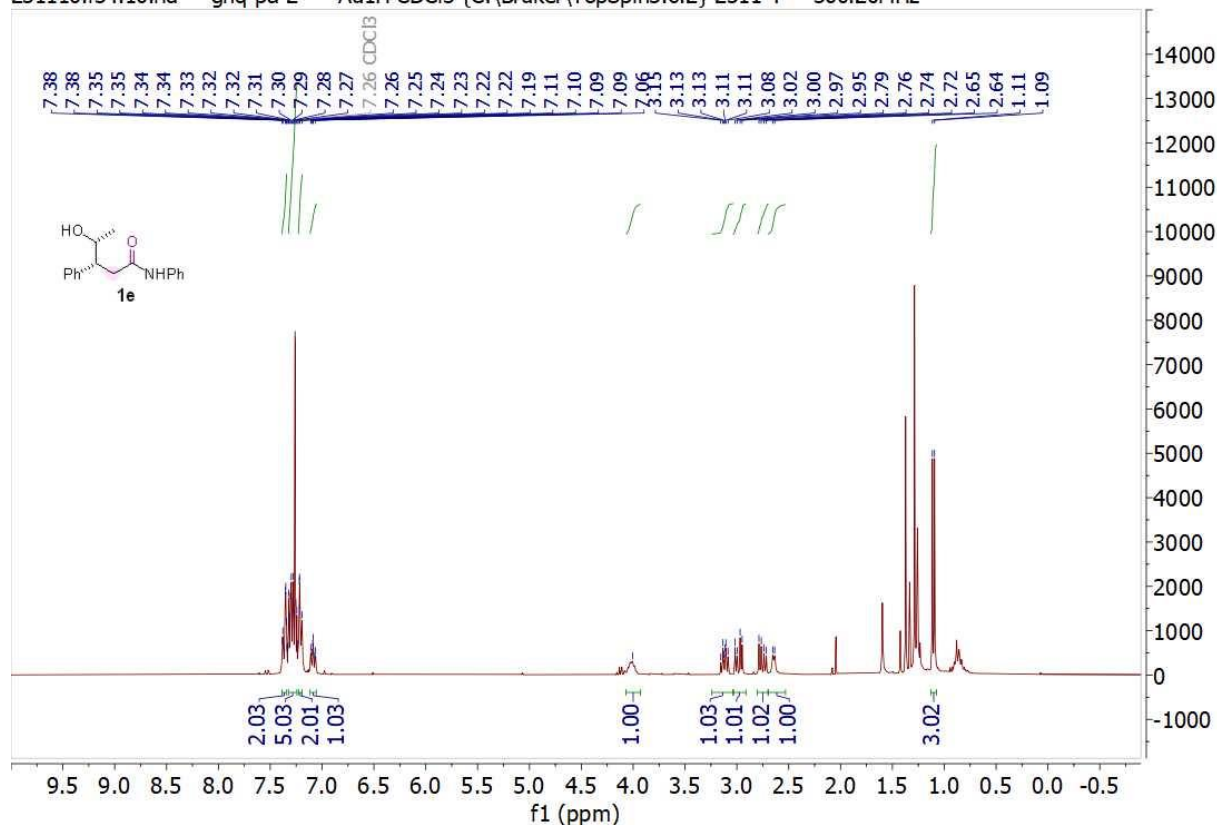




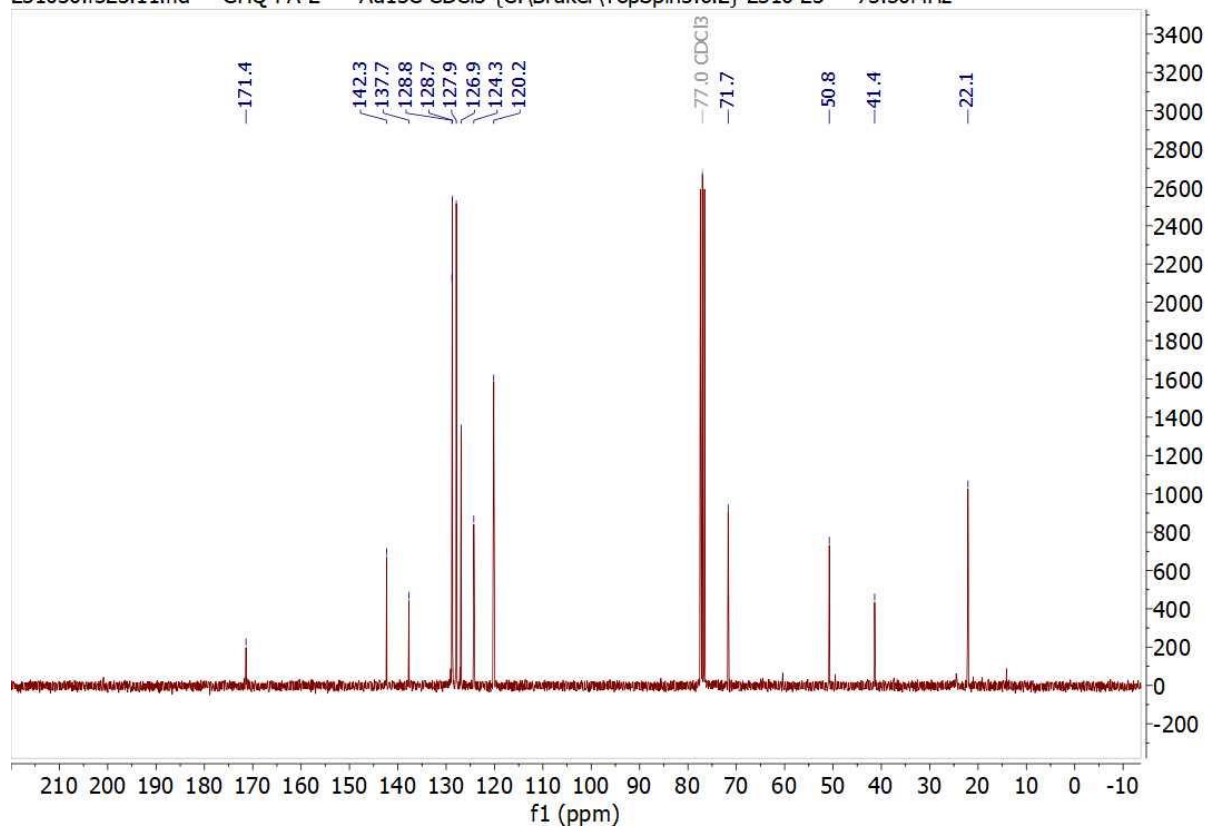
Huiqing Geng GHQ-P-390 — Au11B(H-gek) CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 3 — 96.32MHz



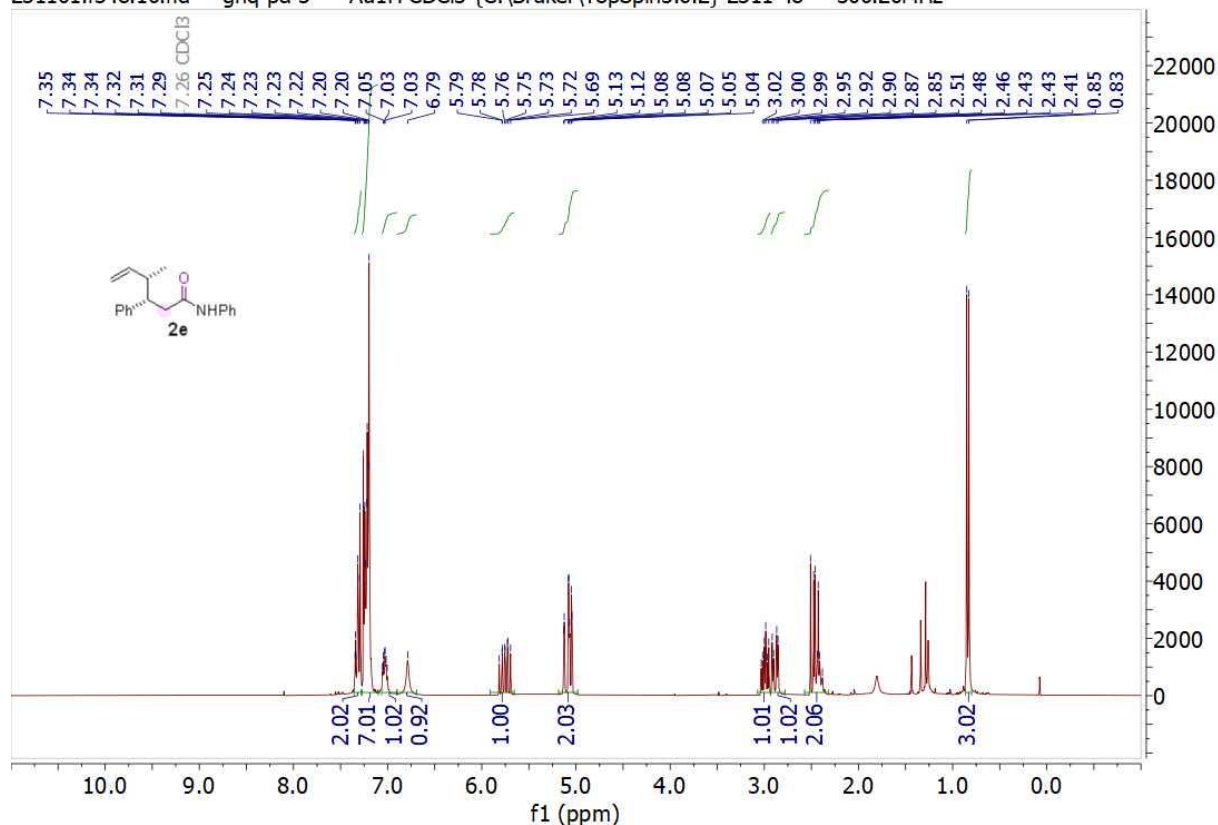
231110.f34.10.fid — ghq-pa-2 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 4 — 300.20MHz



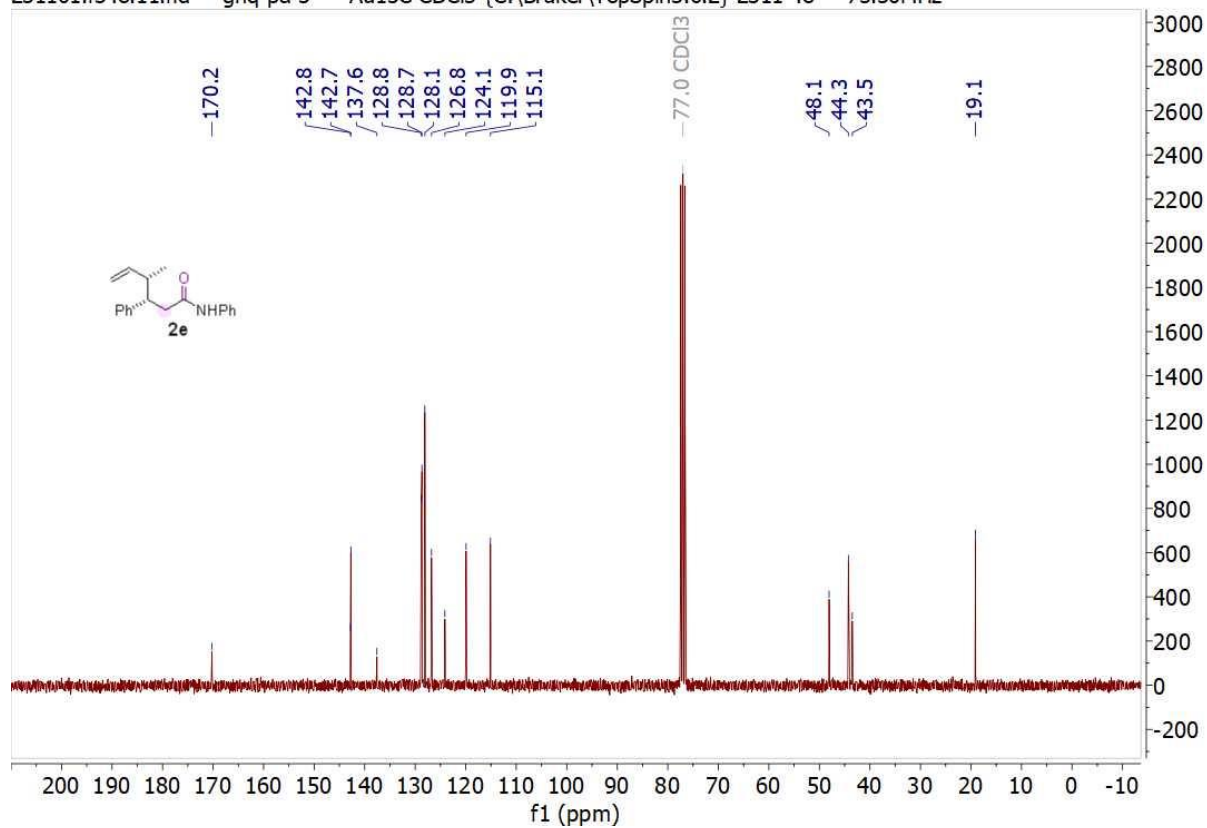
231030.f323.11.fid — GHQ-PA-2 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2310 23 — 75.50MHz



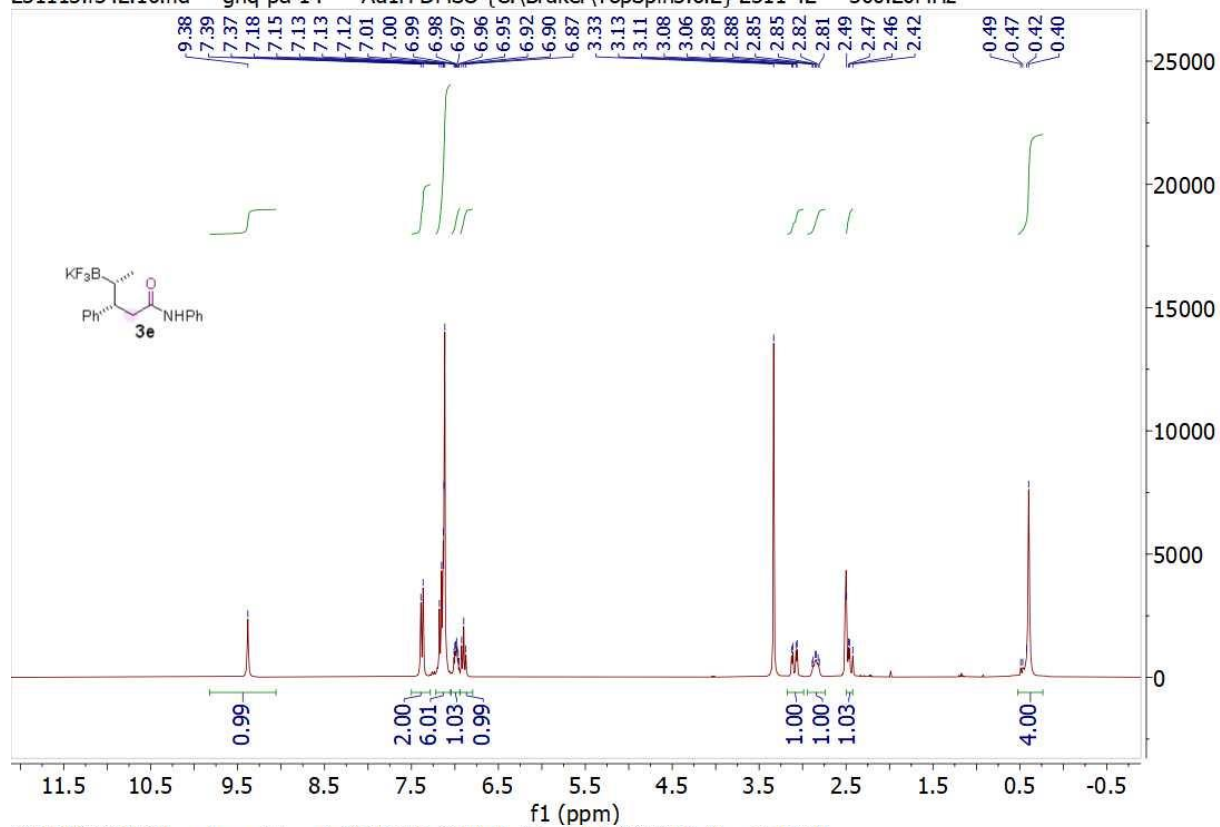
231101.f348.10.fid — ghq-pa-3 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 48 — 300.20MHz



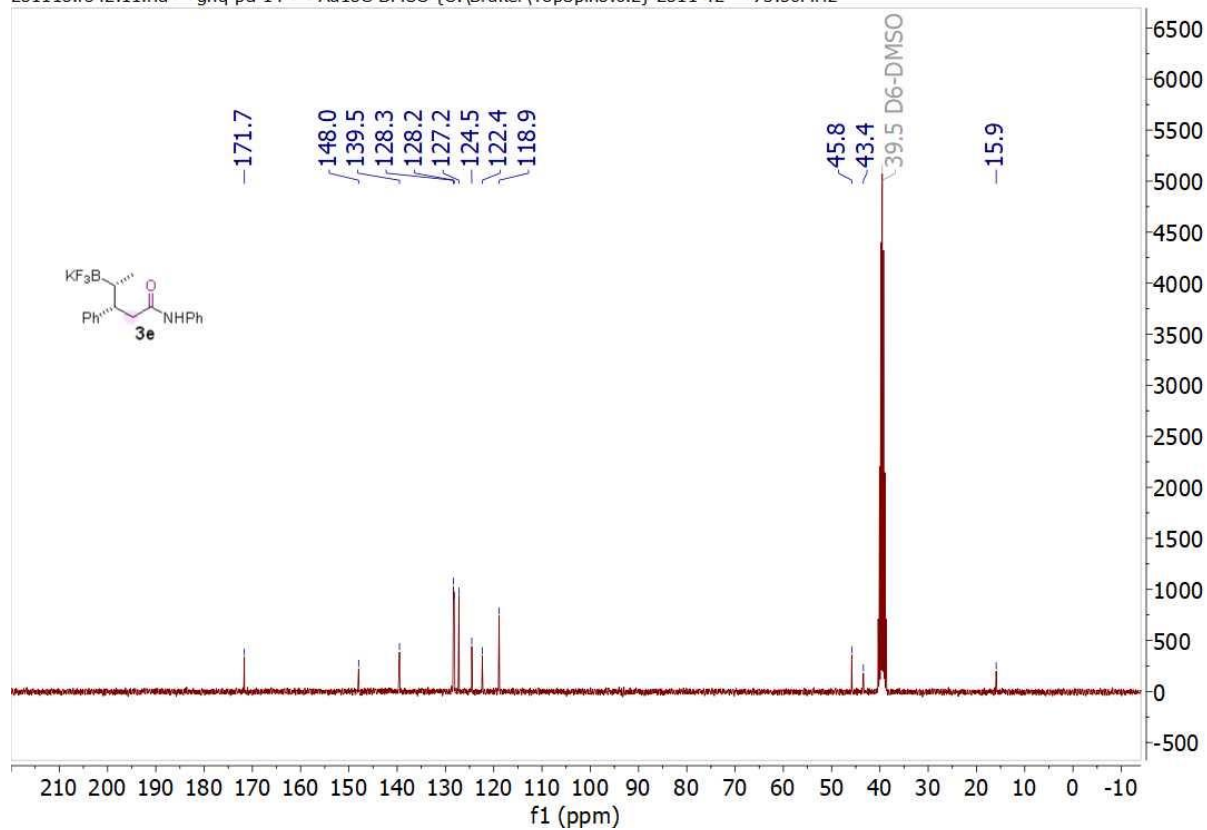
231101.f348.11.fid — ghq-pa-3 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 48 — 75.50MHz

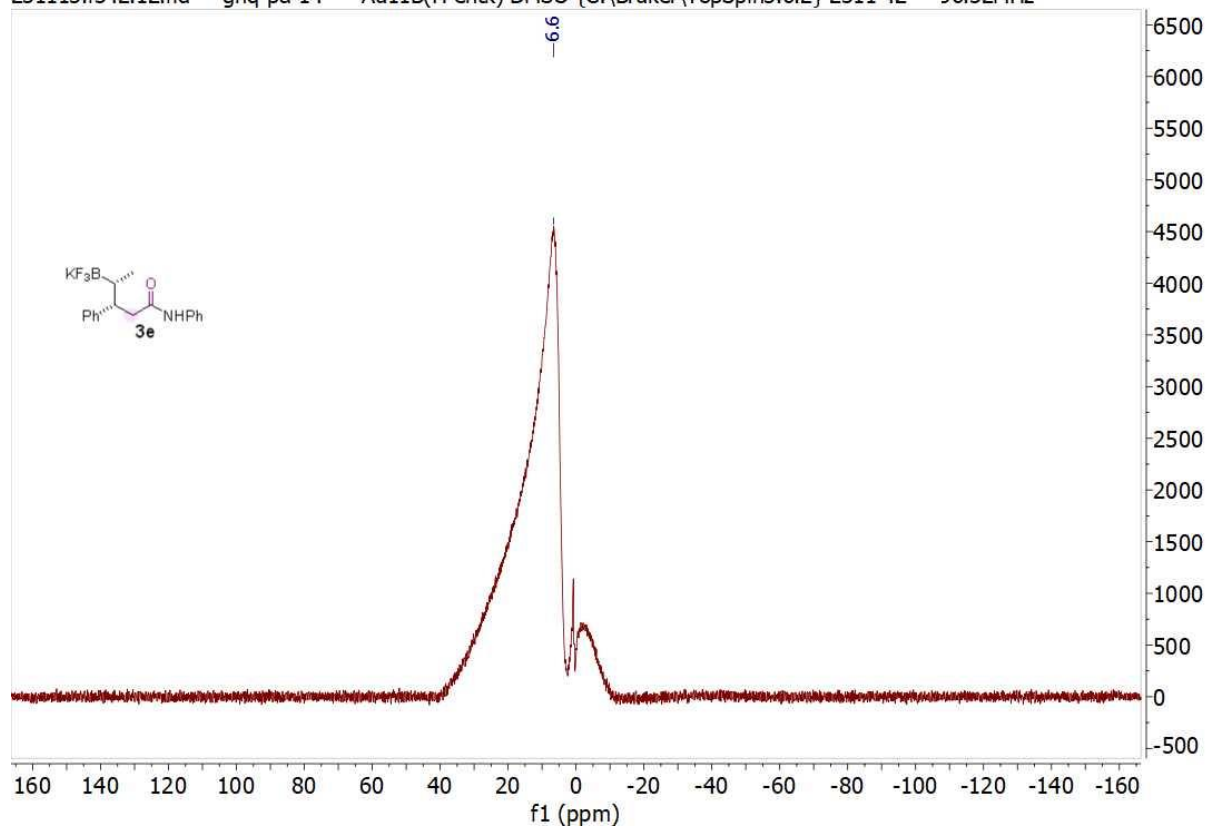


231113.f342.10.fid — ghq-pa-14 — Au1H DMSO {C:\Bruker\TopSpin3.6.2} 2311 42 — 300.20MHz

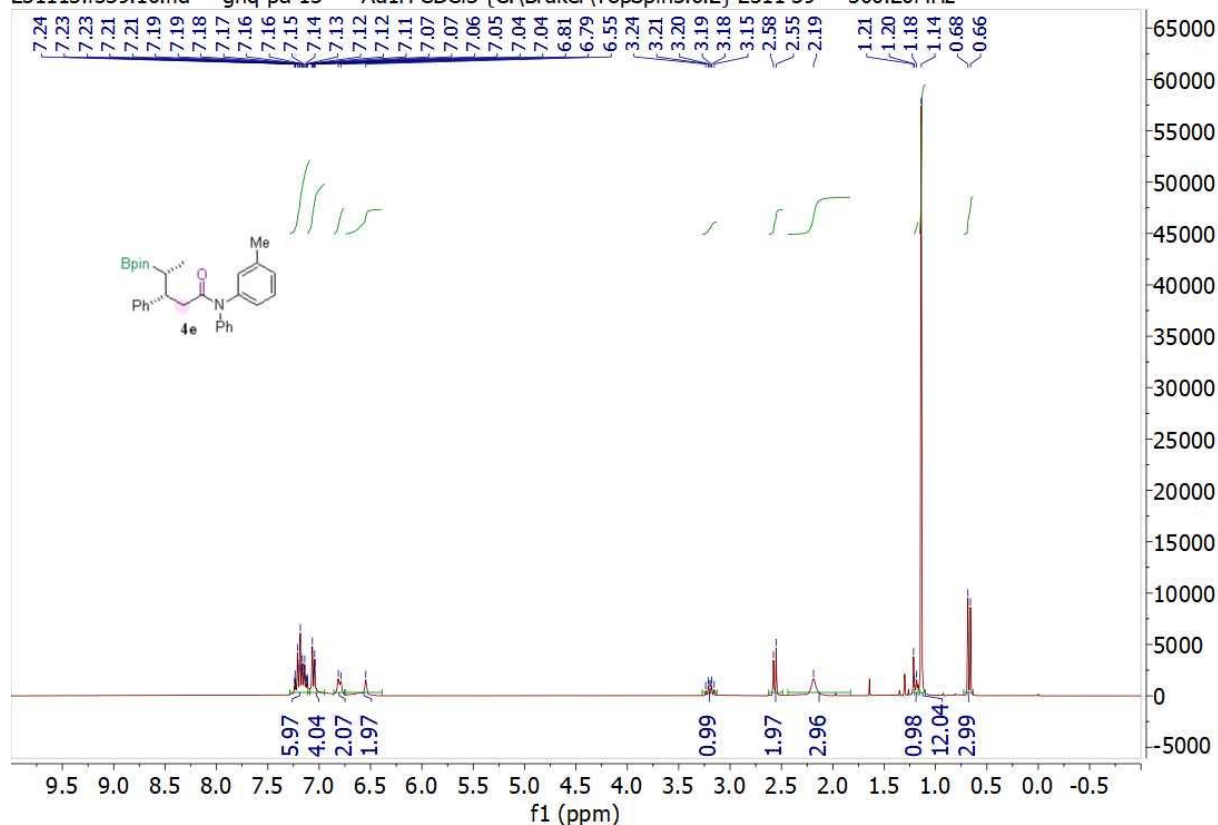


231113.f342.11.fid — ghq-pa-14 — Au13C DMSO {C:\Bruker\TopSpin3.6.2} 2311 42 — 75.50MHz





231113.f339.10.fid — ghq-pa-13 — Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 39 — 300.20MHz



231110.327.11.fid — Huiqing Geng GHQ-PA-13 — Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2311 27 — 75.48MHz

