Ligand-Controlled Regiodivergent and Enantioselective C–H Cyanation of Secondary Amines

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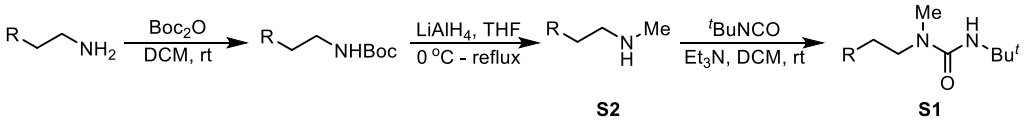
1. General Information

Unless otherwise stated, all experiments were carried out under air atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III 400/600 instrument in $CDCl_3$ using TMS as an internal standard, operating at 400/600 MHz and 101MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; $CHCl_3$ δH (7.26 ppm) and $CDCl_3$ δC (77.03 ppm). ^{19}F NMR were recorded on a Bruker AVANCE III. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. HPLC experiments were carried out using Agilent 1260 Infinity II. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra (HRMS (ESI-TOF)) were obtained on an Agilent 6545 Q-TOF LC-MS spectrometer equipped with an ESI source. Enantiomeric ratio was determined by an Agilent 1260 chromatography, using chiral HPLC columns Chiralpak® with hexane and *i*-PrOH as solvents.

2. Synthesis of Starting Materials and Ligands

2.1 Procedure for the synthesis of urea substrates S1

Method A:

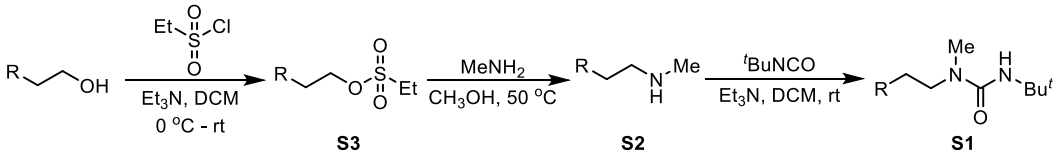


To a stirred solution of primary amine (5 mmol, 1.0 equiv) in DCM (15 mL) was added Boc_2O (6 mmol, 1.2 equiv) dropwise. The mixture was stirred at room temperature for 3 h, then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide Boc-protected amines.

To a stirred solution of Boc-protected amines (5 mmol) in THF (10 mL) was added $LiAlH_4$ (10 mmol, 2.0 equiv) in several portions (*caution: gas extrusion!*) at 0 °C under N_2 atmosphere. The reaction was reflux for 6 h. After completed, the mixture was cooled to room temperature and carefully quenched with EtOAc. Then solvent was removed under reduced pressure and DCM (50 mL) was added. The insoluble substance was filtered, washed with DCM (3 × 50 mL) and the collected solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 3 / 1 to MeOH) to provide **S2**.

To a stirred solution of **S2** (3.5 mmol) in DCM (15 mL) was dropwise added ^{t}BuNCO (4.2 mmol, 1.2 equiv) and Et_3N (4.2 mmol, 1.2 equiv). After stirring for 3 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide the target compound **S1**.

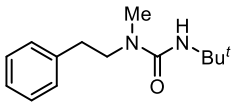
Method B:



To a stirred solution of primary alcohol (10 mmol, 1.0 equiv) in DCM (50 mL) was dropwise added $EtSO_2Cl$ (12 mmol, 1.2 equiv) and Et_3N (12 mmol, 1.2 equiv) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. After completed, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (PE / EA = 10 / 1) to provide **S3**.

To a stirred solution of **S3** (8 mmol) in MeOH (4 mL) was added $MeNH_2$ (3.31g, 30% wt in MeOH, 4 equiv) and the mixture was stirred at 50 °C overnight. After completed, the mixture was cooled to room temperature, concentrated, and purified by flash column chromatography (PE / EA = 3 / 1 to MeOH) to provide **S2**.

To a stirred solution of **S2** (5.4 mmol) in DCM (20 mL) was dropwise added ^{t}BuNCO (6.5 mmol, 1.2 equiv) and Et_3N (6.5 mmol, 1.2 equiv). After stirring for 3 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide the target compound **S1**.



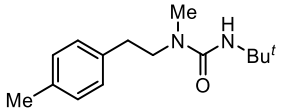
S1a

3-(*tert*-Butyl)-1-methyl-1-phenethylurea (S1a): Prepared *via* Method A from *N*-methyl-2-phenylethan-1-amine (**S3a**, 5 mmol) in 95% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31–7.27 (m, 2H), 7.24–7.18 (m, 3H), 3.86 (s, 1H), 3.42 (t, J = 7.0 Hz, 2H), 2.80 (t, J = 7.0 Hz, 2H), 2.80 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 139.5, 128.9 (2C), 128.7 (2C), 126.4, 51.2, 50.4, 34.6, 34.5, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{22}N_2ONa$: 257.1624, found: 257.1635.



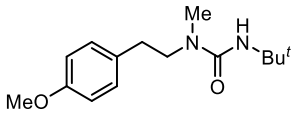
S1b

3-(*tert*-Butyl)-1-methyl-1-(4-methylphenethyl)urea (S1b): Prepared *via* Method A from 2-(p-tolyl)ethan-1-amine (5 mmol) in 55% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.12–7.06 (m, 4H), 3.83 (s, 1H), 3.39 (t, J = 7.0 Hz, 2H), 2.81 (s, 3H), 2.76 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.5, 136.4, 136.0, 129.4 (2C), 128.8 (2C), 51.4, 50.4, 34.5, 34.1, 29.3 (3C), 21.0.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{24}N_2ONa$: 271.1781, found: 271.1788.



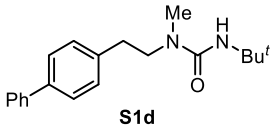
S1c

3-(*tert*-Butyl)-1-(4-methoxyphenethyl)-1-methylurea (S1c): Prepared *via* Method B from 2-(4-methoxyphenyl)ethan-1-ol (10 mmol) in 42% yield as a pale-yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.10 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.85 (s, 1H), 3.78 (s, 3H), 3.38 (t, J = 7.0 Hz, 2H), 2.80 (s, 3H), 2.74 (t, J = 7.0 Hz, 2H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 158.3, 157.4, 131.5, 129.9 (2C), 114.1 (2C), 55.3, 51.4, 50.4, 34.5, 33.6, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{24}N_2O_2Na$: 287.1730, found: 287.1743.



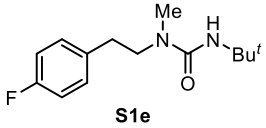
S1d

1-(2-([1,1'-Biphenyl]-4-yl)ethyl)-3-(*tert*-butyl)-1-methylurea (S1d): Prepared *via* Method B from 2-([1,1'-biphenyl]-4-yl)ethan-1-ol (10 mmol) in 44% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.55 (dd, *J* = 13.5, 7.9 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 1H), 3.47 (t, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H), 2.84 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 140.9, 139.5, 138.6, 129.4 (2C), 128.8 (2C), 127.5 (2C), 127.2, 127.0 (2C), 51.2, 50.5, 34.6, 34.3, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{26}N_2ONa$: 333.1937, found: 333.1950.



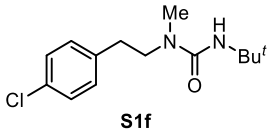
S1e

3-(*tert*-Butyl)-1-(4-fluorophenethyl)-1-methylurea (S1e): Prepared *via* Method A from 2-(4-fluorophenyl)ethan-1-amine (5 mmol) in 51% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.14 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 3.93 (s, 1H), 3.41 (t, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.77 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.6 (d, *J* = 244.3 Hz), 157.3, 135.2 (d, *J* = 3.1 Hz), 130.3 (d, *J* = 7.8 Hz, 2C), 115.4 (d, *J* = 21.0 Hz, 2C), 51.0, 50.5, 34.7, 33.8, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OFNa$: 275.1530, found: 275.1540.



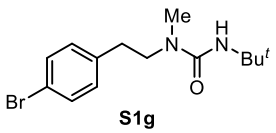
S1f

3-(*tert*-Butyl)-1-(4-chlorophenethyl)-1-methylurea (S1f): Prepare *via* Method A from 2-(4-chlorophenyl)ethan-1-amine (5 mmol) in 56% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 1H), 3.41 (t, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 138.0, 132.2, 130.3 (2C), 128.7 (2C), 50.8, 50.6, 34.7, 34.0, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OClNa$: 291.1235, found: 291.1246.



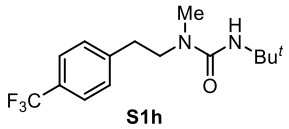
S1g

1-(4-Bromophenethyl)-3-(*tert*-butyl)-1-methylurea (S1g): Prepared *via* Method B from 2-(4-bromophenyl)ethan-1-ol (10 mmol) in 43% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.42–7.38 (m, 2H), 7.08–7.05 (m, 2H), 4.06 (s, 1H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 9.0 Hz, 2H), 2.76 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.0, 138.4, 131.7 (2C), 130.7 (2C), 120.2, 50.8, 50.7, 34.9, 34.0, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OBrNa$: 335.0729, found: 335.0734.



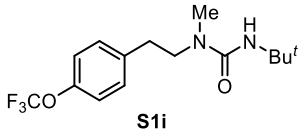
S1h

3-(*tert*-Butyl)-1-methyl-1-(4-(trifluoromethyl)phenethyl)urea (S1h): Prepared *via* Method A from 2-(4-(trifluoromethyl)phenyl)ethan-1-amine (5 mmol) in 57% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.53 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 3.96 (s, 1H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.78 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.1, 143.7, 129.3 (2C), 128.7 (q, *J* = 32.5 Hz), 125.5 (q, *J* = 3.8 Hz, 2C), 124.3 (q, *J* = 272.8 Hz), 50.6, 50.5, 34.8, 34.5, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{21}N_2OF_3Na$: 325.1498, found: 325.1508.



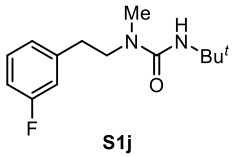
S1i

3-(*tert*-Butyl)-1-methyl-1-(4-(trifluoromethoxy)phenethyl)urea (S1i): Prepared *via* Method A from 2-(4-(trifluoromethoxy)phenyl)ethan-1-amine (5 mmol) in 49% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.94 (s, 1H), 3.44 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.78 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 147.8 (d, *J* = 1.9 Hz), 138.3, 130.2 (2C), 121.1 (2C), 120.5 (q, *J* = 257.8 Hz), 50.7, 50.6, 34.7, 33.9, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{21}N_2O_2F_3Na$: 341.1447, found: 341.1459.



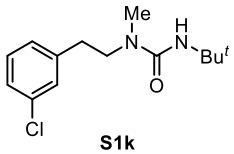
S1j

3-(*tert*-Butyl)-1-(3-fluorophenethyl)-1-methylurea (S1j): Prepared *via* Method A from 2-(3-fluorophenyl)ethan-1-amine (5 mmol) in 59% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.28–7.22 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93–6.88 (m, 2H), 4.02 (s, 1H), 3.44 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 163.0 (d, *J* = 246.0 Hz), 157.1, 142.1 (d, *J* = 7.2 Hz), 130.1 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 2.9 Hz), 115.8 (d, *J* = 20.8 Hz), 113.3 (d, *J* = 21.0 Hz), 50.8, 50.6, 34.8, 34.4 (d, *J* = 1.7 Hz), 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OFNa$: 275.1530, found: 275.1540.



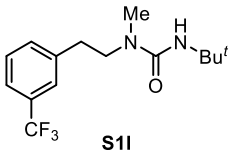
S1k

3-(*tert*-Butyl)-1-(3-chlorophenethyl)-1-methylurea (S1k): Prepared *via* Method A from 2-(3-chlorophenyl)ethan-1-amine (5 mmol) in 62% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.26–7.18 (m, 3H), 7.09–7.06 (m, 1H), 3.95 (s, 1H), 3.43 (t, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 141.6, 134.3, 129.9, 123.0, 127.2, 126.6, 50.7, 50.6, 34.7, 34.3, 29.4 (2C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OClNa$: 291.1235, found: 291.1247.



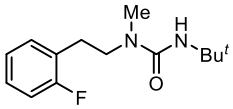
S1l

3-(*tert*-Butyl)-1-methyl-1-(3-(trifluoromethyl)phenethyl)urea (S1l): Prepared *via* Method A from 2-(3-(trifluoromethyl)phenyl)ethan-1-amine (5 mmol) in 52% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.48– 7.45 (m, 1H), 7.44–7.33 (m, 3H), 3.99 (s, 1H), 3.47 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.76 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.1, 140.4, 132.4 (d, *J* = 1.4 Hz), 130.8 (q, *J* = 32.0 Hz), 123.0, 125.6 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 273.3 Hz,), 123.2 (q, *J* = 3.8 Hz), 50.6, 50.6, 34.8, 34.4, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{21}N_2OF_3Na$: 325.1498, found: 325.1508.



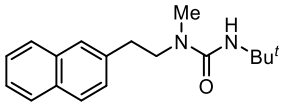
S1m

3-(*tert*-Butyl)-1-(2-fluorophenethyl)-1-methylurea (S1m): Prepared *via* Method A from 2-(2-fluorophenyl)ethan-1-amine (5 mmol) in 47% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.23–7.17 (m, 2H), 7.08–6.99 (m, 2H), 4.13 (s, 1H), 3.41 (t, *J* = 7.3 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.82 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.4 (d, *J* = 244.7 Hz), 157.2, 131.4 (d, *J* = 4.8 Hz), 128.3 (d, *J* = 8.1 Hz), 126.8 (d, *J* = 15.8 Hz), 124.3 (d, *J* = 3.7 Hz), 115.3 (d, *J* = 22.0 Hz), 50.6, 49.5, 34.6, 29.4 (3C), 28.1 (d, *J* = 1.8 Hz).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{21}N_2OFNa$: 275.1530, found: 275.1538.



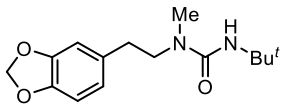
S1n

3-(*tert*-Butyl)-1-methyl-1-(2-(naphthalen-2-yl)ethyl)urea (S1n): Prepared *via* Method A from 2-(naphthalen-2-yl)ethan-1-amine (5 mmol) in 41% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (q, *J* = 7.2 Hz, 3H), 7.65 (s, 1H), 7.45 (tt, *J* = 7.0, 5.2 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.86 (s, 1H), 3.52 (t, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 137.1, 133.7, 132.2, 128.3, 127.6, 127.5, 127.4, 127.3, 126.1, 125.5, 51.1, 50.4, 34.8, 34.7, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{18}H_{24}N_2ONa$: 307.1781, found: 307.1792.



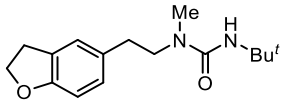
S1o

1-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-3-(*tert*-butyl)-1-methylurea (S1o): Prepared *via* Method A from 2-(benzo[*d*][1,3]dioxol-5-yl)ethan-1-amine (5 mmol) in 55% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.73 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.91 (s, 2H), 3.91 (s, 1H), 3.37 (t, *J* = 7.0 Hz, 2H), 2.79 (s, 3H), 2.71 (t, *J* = 7.0 Hz, 2H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 147.8, 146.1, 133.3, 121.7, 109.3, 108.5, 100.9, 51.3, 50.5, 34.6, 34.3, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{22}N_2O_3Na$: 301.1523, found: 301.1532.



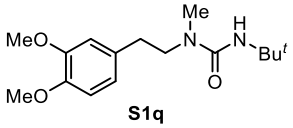
S1p

3-(*tert*-Butyl)-1-(2-(2,3-dihydrobenzofuran-5-yl)ethyl)-1-methylurea (S1p): Prepared *via* Method B from 2-(2,3-dihydrobenzofuran-5-yl)ethan-1-ol (10 mmol) in 63% yield as awhite solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.01 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.52 (t, *J* = 8.7 Hz, 2H), 3.83 (s, 1H), 3.35 (t, *J* = 7.0 Hz, 2H), 3.15 (t, *J* = 8.7 Hz, 2H), 2.81 (s, 3H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 158.8, 157.5, 131.4, 128.2, 127.4, 125.5, 109.3, 71.2, 51.6, 50.4, 34.4, 33.9, 29.7, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{24}N_2O_2Na$: 299.1730, found: 299.1737.



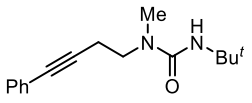
S1q

3-(*tert*-Butyl)-1-(3,4-dimethoxyphenethyl)-1-methylurea (S1q): Prepared *via* Method A from 2-(3,4-dimethoxyphenyl)ethan-1-amine (5 mmol) in 55% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.79 (d, *J* = 7.8 Hz, 1H), 6.73–6.69 (m, 2H), 3.97 (s, 1H), 3.84 (s, 3H), 3.84 (s, 3H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 2.74 (t, *J* = 7.1 Hz, 2H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 149.1, 147.7, 131.9, 120.8, 112.0, 111.5, 55.9, 55.9, 51.3, 50.5, 34.7, 34.1, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{26}N_2O_3Na$: 317.1836, found: 317.1846.



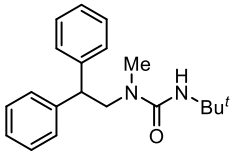
S1r

3-(*tert*-Butyl)-1-methyl-1-(4-phenylbut-3-yn-1-yl)urea (S1r): Prepared *via* Method B from 4-phenylbut-3-yn-1-ol (10 mmol, prepared according to the reference procedure[1]) in 46% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.38–7.36 (m, 2H), 7.27 (d, *J* = 3.3 Hz, 3H), 4.38 (s, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.94 (s, 3H), 2.62 (t, *J* = 6.7 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 131.6, 128.3 (2C), 127.9 (2C), 123.5, 87.9, 82.0, 50.7, 48.3, 35.0, 29.5 (3C), 19.4.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{22}N_2ONa$: 281.1624, found: 281.1636.



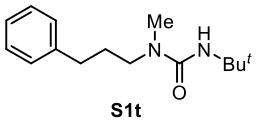
S1s

3-(*tert*-Butyl)-1-(2,2-diphenylethyl)-1-methylurea (S1s): Prepared *via* Method A from 2,2-diphenylethan-1-amine (5 mmol) in 46% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29–7.23 (m, 8H), 7.21–7.17 (m, 2H), 4.26 (t, J = 7.9 Hz, 1H), 3.84 (d, J = 7.9 Hz, 2H), 3.71 (s, 1H), 2.66 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.5, 142.5 (2C), 128.6 (4C), 128.3 (4C), 126.7 (2C), 54.6, 50.4, 49.7, 34.8, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{26}N_2ONa$: 333.1937, found: 333.1948.



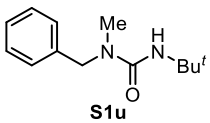
S1t

3-(*tert*-Butyl)-1-methyl-1-(3-phenylpropyl)urea (S1t): Prepared *via* Method A from 3-phenylpropan-1-amine (5 mmol) in 59% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.30–7.26 (m, 2H), 7.19–7.17 (m, 3H), 4.17 (s, 1H), 3.23 (t, J = 7.7 Hz, 2H), 2.81 (s, 3H), 2.61 (t, J = 7.7 Hz, 2H), 1.85 (p, J = 7.6 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 141.7, 128.5 (2C), 128.3 (2C), 126.0, 50.7, 48.3, 34.3, 33.0, 29.5 (3C), 29.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{24}N_2ONa$: 271.1781, found: 271.1793.



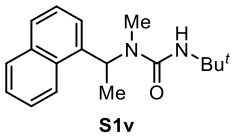
S1u

1-Benzyl-3-(*tert*-butyl)-1-methylurea (S1u): Prepared *via* Method A from *N*-methyl-1-phenylmethanamine (**S3t**, 5 mmol) in 96% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35–7.31 (m, 2H), 7.28–7.22 (m, 3H), 4.45 (s, 2H), 4.30 (s, 1H), 2.85 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.6, 138.2, 128.7 (2C), 127.3, 127.2 (2C), 52.2, 50.8, 34.6, 29.5 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{20}N_2ONa$: 243.1468, found: 243.1476.



S1v

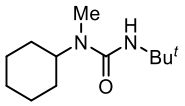
3-(*tert*-Butyl)-1-methyl-1-(1-(naphthalen-1-yl)ethyl)urea (S1v): Prepared *via* Method A from 1-(naphthalen-1-yl)ethan-1-amine (5 mmol) in 54% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.21 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.53–7.43 (m, 4H), 6.33 (q, J = 6.9 Hz, 1H), 4.19 (s, 1H), 2.37 (s, 3H), 1.61 (d, J = 6.9 Hz, 3H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 137.4, 133.8, 132.1, 128.5, 128.4, 126.5, 125.8, 124.8,

124.5, 124.4, 50.8, 48.5, 29.6 (3C), 28.3, 16.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{18}H_{24}N_2ONa$: 307.1781, found: 307.1794.



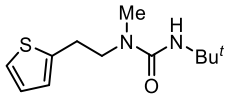
S1w

3-(*tert*-Butyl)-1-cyclohexyl-1-methylurea (S1w): Prepared *via* Method A from cyclohexylamine (5 mmol) in 39% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 4.17 (s, 1H), 3.99 (t, *J* = 10.8 Hz, 1H), 2.66 (s, 3H), 1.77–1.74 (m, 2H), 1.65–1.60 (m, 3H), 1.33 (s, 9H), 1.39–1.24 (m, 4H), 1.08–0.98 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 53.2, 50.7, 30.6 (2C), 29.6 (3C), 28.3, 25.9 (2C), 25.7.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{24}N_2ONa$: 235.1781, found: 235.1788.



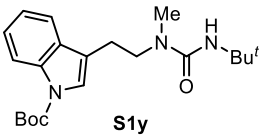
S1x

3-(*tert*-Butyl)-1-methyl-1-(2-(thiophen-2-yl)ethyl)urea (S1x): Prepared *via* Method A from 2-(thiophen-2-yl)ethan-1-amine (5 mmol) in 35% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.15 (d, *J* = 5.0 Hz, 1H), 6.93 (t, *J* = 4.4 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 3.99 (s, 1H), 3.46 (t, *J* = 7.0 Hz, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.81 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 141.6, 127.2, 125.4, 123.9, 51.2, 50.6, 34.6, 29.4 (3C), 28.6.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{20}N_2OSNa$: 263.1189, found: 263.1180.



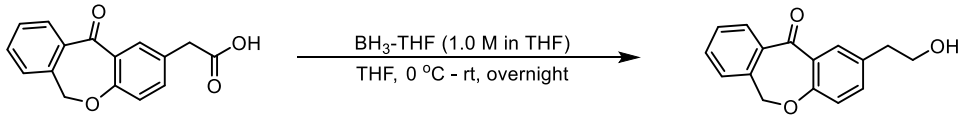
S1y

***tert*-Butyl 3-(2-(3-(*tert*-butyl)-1-methylureido)ethyl)-1H-indole-1-carboxylate (S1y)**: Prepared *via* Method A from tryptamine (5 mmol) in 58% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.14 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.39 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.91 (s, 1H), 3.51 (t, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.84 (s, 3H), 1.65 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.4, 149.7, 135.6, 130.3, 124.6, 123.4, 122.7, 118.7, 117.9, 115.4, 83.6, 50.4, 49.2, 34.6, 29.2 (3C), 28.2 (3C), 23.8.

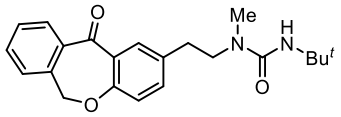
HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{21}H_{31}N_3O_3Na$: 396.2258, found: 396.2276.



Isoxepac **S4**

The Isoxepac (10 mmol, 1.0 equiv) was dissolved in dry THF (15 mL) in a 50 mL flame-dried Schlenk tube under N_2 atmosphere. Then the solution was cooled to 0 °C and BH_3-THF (10 mL, 1.0 M in THF, 1.0 equiv,) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After completed, the EtOAc (30 mL) was added carefully to quench the reaction, and the mixture was washed with water (3 × 30 mL). The collected aqueous phase was extracted with EtOAc

(30 mL) for twice. The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to provide the **S4**. The **S4** could be used to synthesize compound **S1z** under Method B.



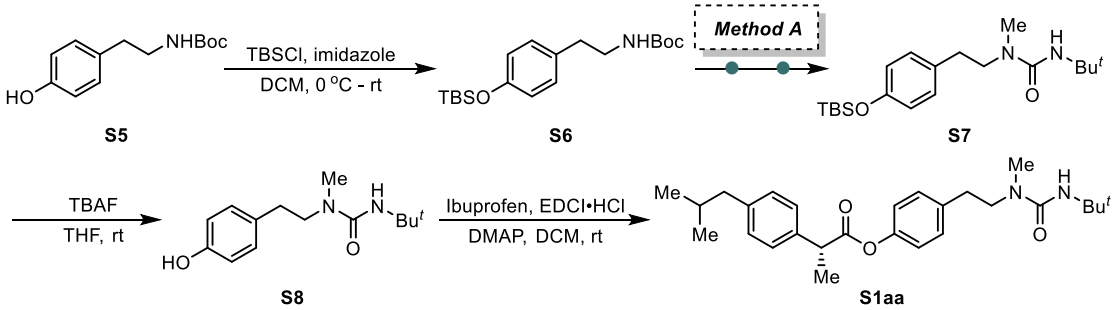
S1z

3-(*tert*-Butyl)-1-methyl-1-(2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)ethyl)urea (S1z): Prepared *via* Method B from Isoxepac (5 mmol, CAS: 55453-87-7) in 36% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 2H), 4.02 (s, 1H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.82 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 191.1, 160.0, 157.2, 140.5, 136.3, 135.7, 133.2, 132.8, 131.5, 129.5, 129.2, 127.8, 125.2, 121.0, 73.6, 50.7, 50.6, 34.7, 33.6, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{22}H_{26}N_2O_3Na$: 389.1836, found: 389.1848.



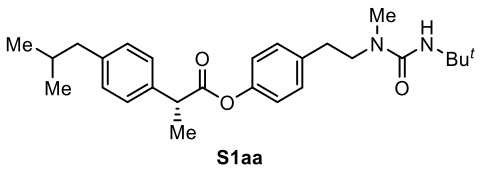
S5 **S6** **S7** **S8** **S1aa**

The **S5** was easily prepared from tyramine and Boc_2O in MeOH according to the reference procedure.[2]

To a stirred solution of 4-*N*-(*tert*-butoxycarbonyl)tyramine (20 mmol, 1.0 equiv) and imidazole (24 mmol, 1.2 equiv) in DCM (50 mL) was added TBSCl (24 mmol, 1.2 equiv) dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. After completed, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (PE / EA = 5 / 1) to provide **S6**.

The **S7** could be obtained from **S6** according to Method A. To a stirred solution of **S7** (10 mmol) in THF (30 mL) was added ^{t}Bu$_4$NF (15 mL, 1.0 mL in THF, 1.5 equiv) and the mixture was stirred at room temperature overnight. After completed, the mixture was concentrated and purified by flash column chromatography (PE / EA = 3 / 1) to provide **S8**.

To a stirred solution of **S8** (3 mmol) and Ibuprofen (3 mmol) in DCM (20 mL) was added EDCI·HCl (3.6 mmol, 1.2 equiv) and DMAP (3.6 mmol, 1.2 equiv). After stirred for 6 h, water (15 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine and evaporated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide **S1aa**.



S1aa

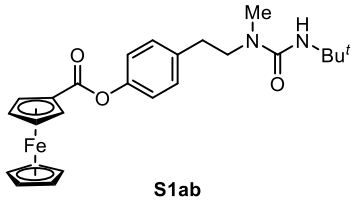
4-(2-(3-(*tert*-Butyl)-1-methylureido)ethyl)phenyl (*R*)-2-(4-isobutylphenyl)propanoate (S1aa):

Prepared from Ibuprofen (3 mmol) and **S8** in 62% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 1H), 3.92 (q, *J* = 7.2 Hz, 1H), 3.41 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.75 (s, 3H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.59 (d, *J* = 7.1 Hz, 3H), 1.27 (s, 9H), 0.91 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 173.3, 157.3, 149.4, 140.8, 137.3, 136.9, 129.7 (2C), 129.5 (2C), 127.2 (2C), 121.5 (2C), 51.0, 50.6, 45.3, 45.1, 34.8, 34.0, 30.2, 29.4 (3C), 22.4 (2C), 18.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{27}H_{38}N_2O_3Na$: 461.2775, found: 461.2792.



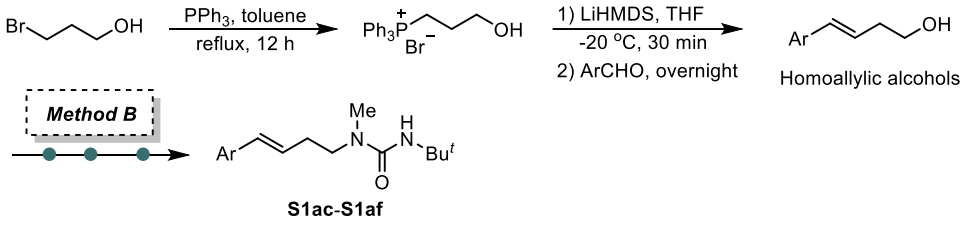
S1ab

4-(2-(3-(*tert*-Butyl)-1-methylureido)ethyl)phenyl ferrocenecarboxylate (S1ab): Prepared from ferrocenecarboxylic acid and **S8** in 45% yield as an orange-yellow solid by taking the similar synthesis procedure of **S1aa**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.95 (t, *J* = 2.0 Hz, 2H), 4.49 (t, *J* = 2.0 Hz, 2H), 4.29 (s, 5H), 4.00 (s, 1H), 3.46 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.3, 157.3, 149.5, 136.8, 129.8 (2C), 121.8 (2C), 71.9 (2C), 70.6 (2C), 70.1, 70.0 (5C), 51.1, 50.6, 34.8, 34.1, 29.5 (3C).

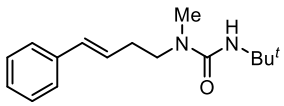
HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{25}H_{30}N_2O_3FeNa$: 485.1498, found: 485.1517.



S1ac-S1af

The corresponding homoallylic alcohols were prepared according to the reference procedure.[3] To a stirred solution of PPh_3 (10 mmol, 1.0 equiv) in dry toluene (9 mL) was added 3-bromopropan-1-ol (10 mmol, 1.0 equiv) under N_2 and refluxed for 12 h. After this time, the reaction was allowed to cool to room temperature, solids filtered, washed with cold diethyl ether and dried under vacuum to afford 3-(triphenylphsophonium)propan-1-ol-bromide as a white powder which was used without purification in the next step.

LiHMDS (2.8 mL, 1 M in THF, 3.5 equiv) was added dropwise to 3-(triphenylphsophonium)propan-1-ol-bromide (1 mmol, 1.25 equiv) in THF (5 mL) under N_2 at −20 °C. This was allowed to stir for 30 min before addition of the aldehyde (0.8 mmol, 1.0 equiv). This solution was then stirred overnight and allowed to warm to room temperature. The reaction was quenched by addition of aqueous NH_4Cl. 1 M HCl was added to take the solution to pH 1, extracted with CH_2Cl_2, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield corresponding homoallylic alcohol, which could be used to synthesize **S1ac-S1af** under Method B.



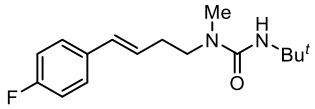
S1ac

3-(*tert*-Butyl)-1-methyl-1-(4-phenylbut-3-en-1-yl)urea (S1ac): Prepared *via* Method B from benzaldehyde in 39% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.32 (t, *J* = 7.2 Hz, 3H), 7.27–7.25 (m, 1H), 7.21–7.15 (m, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.4, 7.2 Hz, 1H), 4.21 (s, 1H), 3.37 (t, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 2.43 (q, *J* = 7.0 Hz, 2H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 137.4, 131.9, 128.5 (2C), 127.3, 127.2, 126.0 (2C), 50.6, 48.7, 34.6, 32.0, 29.5 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{24}N_2ONa$: 283.1781, found: 283.1787.



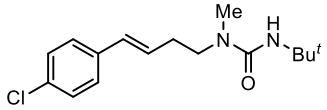
S1ad

3-(*tert*-Butyl)-1-(4-(4-fluorophenyl)but-3-en-1-yl)-1-methylurea (S1ad): Prepared *via* Method B from 2-fluorobenzaldehyde in 34% yield as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.30–7.27 (m, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.13–6.05 (m, 1H), 4.20 (s, 1H), 3.36 (t, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 2.41 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.1 (d, *J* = 246.0 Hz), 157.3, 133.6 (d, *J* = 3.2 Hz), 130.7, 127.5 (d, *J* = 7.9 Hz, 2C), 127.1 (d, *J* = 2.3 Hz), 115.4 (d, *J* = 21.6 Hz, 2C), 50.7, 48.6, 34.5, 31.9, 29.5 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_2OFNa$: 301.1687, found: 301.1696.



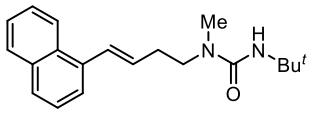
S1ae

3-(*tert*-Butyl)-1-(4-(4-chlorophenyl)but-3-en-1-yl)-1-methylurea (S1ae): Prepared *via* Method B from 4-chlorobenzaldehyde in 42% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.24 (s, 4H), 6.38 (dt, *J* = 15.8, 1.2 Hz, 1H), 6.16 (dt, *J* = 15.8, 7.2 Hz, 1H), 4.19 (s, 1H), 3.37 (t, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 2.53–2.30 (m, 2H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 135.9, 132.7, 130.7, 128.6 (2C), 128.2, 127.2 (2C), 50.7, 48.5, 34.5, 32.0, 29.5 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_2OClNa$: 317.1391, found: 317.1401.



S1af

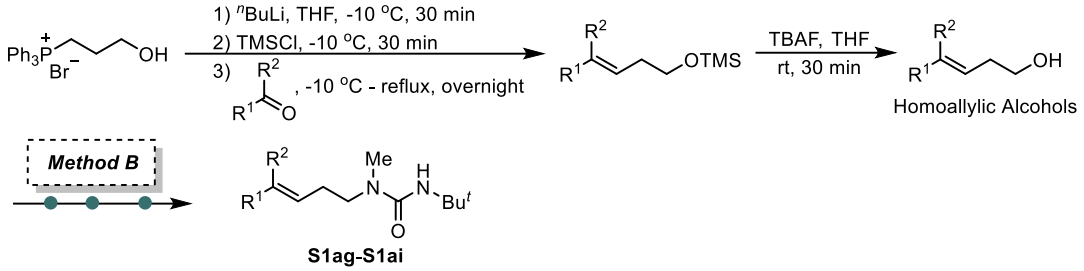
3-(*tert*-Butyl)-1-methyl-1-(4-(naphthalen-2-yl)but-3-en-1-yl)urea (S1af): Prepared *via* Method B from 2-naphthaldehyde in 34% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.12–8.09 (m, 1H), 7.83 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.52–7.45 (m, 2H), 7.44–7.40 (m, 1H), 7.18 (d, *J* = 15.6 Hz, 1H),

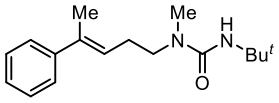
6.21 (dt, J = 15.4, 7.2 Hz, 1H), 4.23 (s, 1H), 3.47 (t, J = 7.1 Hz, 2H), 2.90 (s, 3H), 2.59–2.53 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 135.2, 133.6, 131.0, 130.7, 129.1, 128.5, 127.6, 125.9, 125.7, 125.7, 123.8, 123.7, 50.7, 48.6, 34.7, 32.4, 29.6 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{26}N_2ONa$: 333.1937, found: 333.1934.



The corresponding homoallylic alcohols were prepared according to the reference procedure.[4] To a suspension of (3-hydroxypropyl)triphenylphosphonium bromide (11 mmol, 1.1 equiv) in THF (20 mL) was added *n*-BuLi (8.8 mL, 2.5 M in hexanes, 2.2 equiv) over 10 min at -10 °C. The reaction mixture was stirred for 30 min and then TMSCl (11 mmol, 1.1 equiv) was added. After stirring for another 30 min, a solution of ketone (10 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. The cold bath was removed and the mixture was refluxed overnight. The mixture was quenched with saturated NH_4Cl (10 mL). The two layers were separated and the aqueous solution was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude material was dissolved in THF (10 mL), a solution of TBAF (10.0 mL, 1.0 M in THF, 1.0 equiv) was added and stirred for 30 min at room temperature, The solvent was removed by rotary evaporation and the crude product was purified by flash column chromatography (PE / EA = 5 / 1) to afford corresponding homoallylic alcohol, which could be used to synthesize **S1ag-S1ai** under Method B.



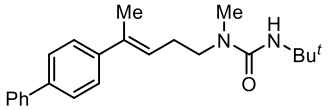
S1ag

3-(*tert*-Butyl)-1-methyl-1-(4-phenylpent-3-en-1-yl)urea (S1ag): Prepared *via* Method B from acetophenone in 27% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.37 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 5.77 (t, J = 7.5 Hz, 1H), 4.22 (s, 1H), 3.34 (t, J = 7.1 Hz, 2H), 2.87 (s, 3H), 2.44 (q, J = 7.3 Hz, 2H), 2.06 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 143.5, 136.9, 128.2 (2C), 126.8, 125.6 (2C), 124.7, 50.6, 48.7, 34.7, 29.5 (3C), 27.8, 15.8.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{26}N_2ONa$: 297.1937, found: 297.1942.



S1ah

1-(4-([1,1'-Biphenyl]-4-yl)pent-3-en-1-yl)-3-(*tert*-butyl)-1-methylurea (S1ah): Prepared *via* Method B from 4-phenylacetophenone in 27% yield as a white solid (major isomer : minor isomer = 2 : 1).

Major isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.60–7.53 (m, 4H), 7.46–7.31 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 5.48 (t, *J* = 7.4 Hz, 1H), 4.15 (s, 1H), 3.21 (t, *J* = 7.1 Hz, 1H), 2.72 (s, 3H), 2.25 (q, *J* = 7.1 Hz, 2H), 2.07 (s, 3H), 1.30 (s, 9H).

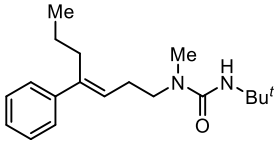
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 140.8, 140.7, 139.6, 138.4, 128.8 (2C), 128.3 (2C), 127.3, 127.0 (2C), 126.9 (2C), 124.2, 50.6, 48.9, 34.3, 29.5 (3C), 27.9, 25.8.

Minor isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.60–7.53 (m, 4H), 7.46–7.31 (m, 5H), 5.85 (t, *J* = 7.7 Hz, 1H), 4.24 (s, 1H), 3.36 (t, *J* = 7.1 Hz, 2H), 2.88 (s, 3H), 2.47 (q, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.1, 142.4, 140.8, 139.6, 136.4, 128.8 (2C), 127.2, 127.0 (2C), 126.9 (2C), 126.0 (2C), 124.7, 50.7, 48.7, 34.7, 29.6 (3C), 27.8, 15.8.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{23}H_{30}N_2ONa$: 373.2250, found: 373.2262.



S1ai

3-(*tert*-Butyl)-1-methyl-1-(4-phenylhept-3-en-1-yl)urea (S1ai): Prepared *via* Method B from butyrylbenzene in 22% yield as a white solid (major isomer : minor isomer = 2 : 1).

Major isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34–7.22 (m, 3H), 7.11 (d, *J* = 7.7 Hz, 2H), 5.42 (t, *J* = 7.4 Hz, 1H), 4.10 (s, 1H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.68 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.14 (q, *J* = 7.3 Hz, 2H), 1.39–1.25 (m, 2H), 1.30 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H).

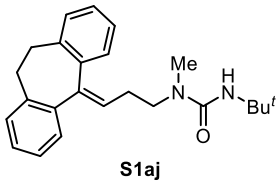
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 143.6, 141.0, 128.3 (2C), 128.1 (2C), 126.6, 123.3, 50.5, 48.9, 41.5, 34.2, 29.5 (3C), 27.6, 21.1, 13.6.

Minor isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34–7.22 (m, 5H), 5.63 (t, *J* = 7.5 Hz, 1H), 4.22 (s, 1H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.88 (s, 3H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.39–1.25 (m, 2H), 1.33 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 142.9, 142.1, 128.2 (2C), 126.7, 126.4 (2C), 125.3, 50.6, 49.1, 34.8, 31.7, 29.5 (3C), 27.6, 21.9, 14.0.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{19}H_{30}N_2ONa$: 325.2251, found: 325.2239.



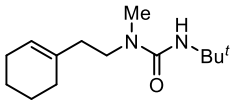
S1aj

3-(*tert*-Butyl)-1-(3-(10,11-dihydro-5H-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-1-methylurea (S1aj): Prepared *via* Method A from Nortriptyline (5 mmol, CAS: 72-69-5) in 92% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29–7.26 (m, 1H), 7.21–7.10 (m, 6H), 7.04–7.02 (m, 1H), 5.85 (t, *J* = 7.5 Hz, 1H), 4.17 (s, 1H), 3.39–3.28 (m, 4H), 2.98–2.91 (m, 1H), 2.78–2.72 (m, 1H), 2.74 (s, 3H), 2.35 (q, *J* = 7.3 Hz, 2H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.1, 144.6, 141.0, 139.9, 139.4, 136.9, 130.03, 128.6, 128.1, 128.1, 128.0, 127.6, 127.2, 126.1, 125.8, 50.7, 48.6, 34.4, 33.8, 32.0, 29.5 (3C), 28.3.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{24}H_{30}N_2ONa$: 385.2250, found: 385.2265.



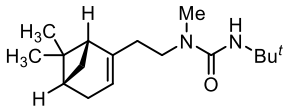
S1ak

3-(*tert*-Butyl)-1-(2-(cyclohex-1-en-1-yl)ethyl)-1-methylurea (S1ak): Prepared *via* Method A from 2-(1-cyclohexenyl)ethylamine in 63% yield as a pale-yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 5.42 (p, *J* = 2.2 Hz, 1H), 4.21 (s, 1H), 3.26 (t, *J* = 7.3 Hz, 2H), 2.81 (s, 3H), 2.10 (t, *J* = 7.3 Hz, 2H), 1.97–1.94 (m, 4H), 1.63–1.48 (m, 4H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.3, 135.3, 123.1, 50.6, 47.9, 36.4, 34.3, 29.6 (3C), 28.5, 25.3, 22.9, 22.3.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{26}N_2ONa$: 261.1937, found: 261.1947.



S1al

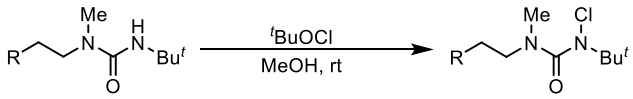
3-(*tert*-Butyl)-1-(2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)-1-methylurea (S1al): Prepared *via* Method B from (1*R*)-(-)-Nopol (CAS: 35836-73-8) in 48% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 5.25 (dt, *J* = 3.0, 1.5 Hz, 1H), 4.16 (s, 1H), 3.28–3.13 (m, 2H), 2.81 (s, 3H), 2.35 (dt, *J* = 8.5, 5.6 Hz, 1H), 2.26–2.12 (m, 4H), 2.05 (d, *J* = 5.6 Hz, 2H), 1.33 (s, 9H), 1.26 (s, 3H), 1.12 (d, *J* = 8.5 Hz, 1H), 0.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.2, 145.5, 117.9, 50.6, 47.2, 45.8, 40.7, 38.0, 35.3, 34.2, 31.7, 31.3, 29.6 (3C), 26.3, 21.2.

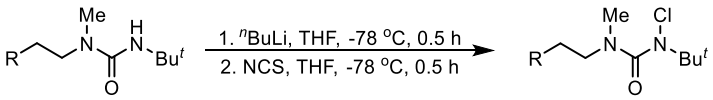
HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{30}N_2ONa$: 301.2250, found: 301.2244.

2.2 Procedure for the synthesis of *N*-chloro compounds 1



S1 **1**

Method C: To a stirred solution of urea **S1** (0.5 mmol, 1.0 equiv) in MeOH (5 mL) was added ^{t}BuOCl (0.55 mmol, 1.1 equiv). The reaction mixture was stirring at room temperature for 0.5 h. After that, the solvent was removed under reduced pressure at low temperature, and the residue was purified by flash column chromatography (PE / EA = 10 / 1) to provide the desired *N*-chloro compound **1**.



S1 **1**

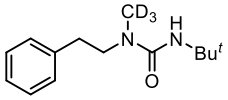
Method D: Synthesized according to the reference procedure.[8] To a 25 mL flame-dried Schlenk tube equipped with a stir bar was charged with urea **S1** (0.5 mmol, 1.0 equiv) and fitted with a rubber septum. The flask was evacuated and backfilled with N_2 (this process was repeated a total of three times). Then THF (3 mL) was added and the resulting solution was cooled to -78 °C. *n*-BuLi (0.33 mL, 1.6 M, 1.05 equiv) was added dropwise over a span of 5 min, and the resulting mixture was stirred for additional 30 min at -78 °C. At the same temperature, a solution of NCS (0.52 mmol, 1.05 equiv) in THF (2 mL) was then added dropwise. The mixture was stirred at -78 °C for another 30 min and allowed to warm to room

temperature. The reaction was quenched with a saturated NH_4Cl aqueous solution (15 mL) and was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure at low temperature. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to provide the desired *N*-chloro compound **1**.

The compounds **1a**, **1b**, **1d-1n**, **1s-1w**, **1z** were synthesized according to Method C; Compounds **1c**, **1o-1r**, **1x**, **1y**, **1aa-1al** were synthesized according to Method D.

*Notice: The N-chloro compounds **1** are unstable in storage, especially under thermal conditions or in the presence of bright light, therefore are recommended to immediately use.*

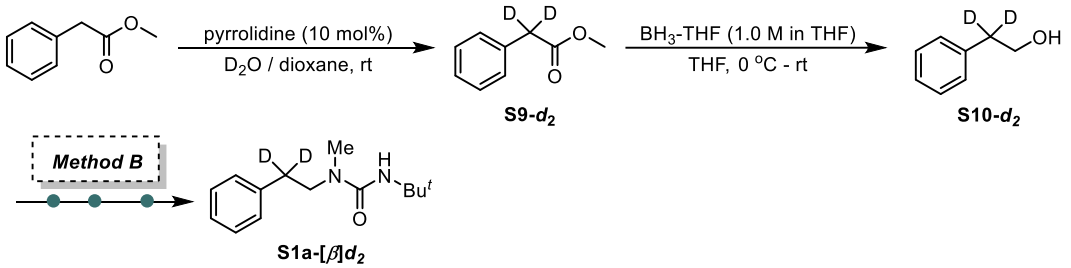
2.3 Procedure for the synthesis of deuterated substrates



S1a-[α']d_3

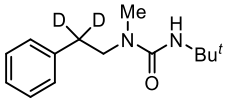
3-(*tert*-Butyl)-1-(methyl-d_3)-1-phenethylurea (S1a-[α']d_3): Deuterated ratio over 99%, prepared *via* Method A (with $LiAlD_4$ as the reducing agent) from phenethylamine in 54% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.32–7.28 (m, 2H), 7.24–7.18 (m, 3H), 3.85 (s, 1H), 3.42 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 2H), 1.22 (s, 9H).



The **S9-d_2** was synthesized according to the reference procedure.[5] To a stirred solution of methyl phenylacetate (10 mmol, 1.0 equiv) in D_2O (6 mL) and anhydrous dioxane (6 mL) was added pyrrolidine (1 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 36 h, followed by water (10 mL) and then extracted with DCM (2 × 15 mL). The organic layer was washed with water (15 mL) and brine (15 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated to afford **S9-d_2**, which was used without any purification in the next step.

The **S9-d_2** (10 mmol, 1.0 equiv) was dissolved in dry THF (15 mL) in a 100 mL flame-dried Schlenk tube under N_2 atmosphere. The solution was cooled to 0 °C and BH_3-THF (15 mL, 1.0 M in THF, 1.5 equiv,) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After completed, the EtOAc (30 mL) was added carefully to quench the reaction, and the mixture was washed with water (3 × 30 mL). Then the collected aqueous phase was extracted with EtOAc (30 mL) for twice. The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to provide the **S10-d_2**. The **S10-d_2** could be used to synthesize compound **S1a-[β]d_2** under Method B.

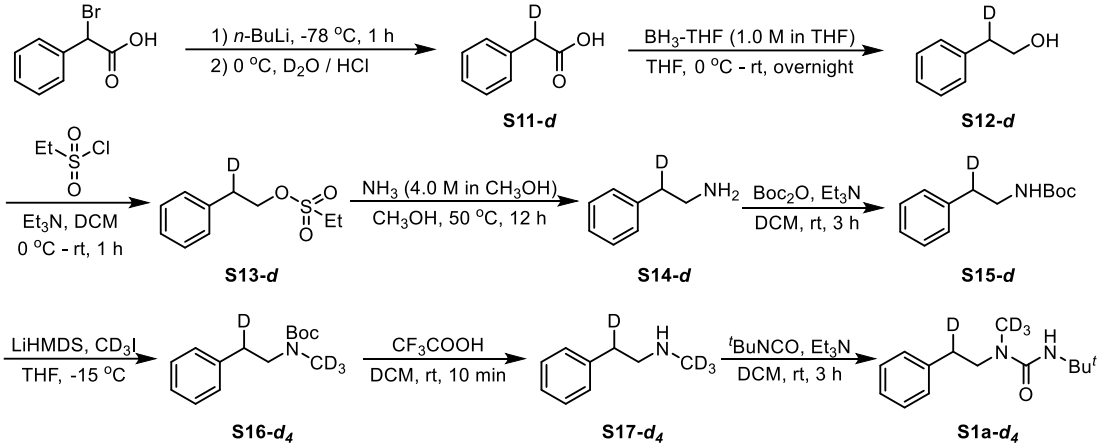


S1a-[β]d_2

3-(*tert*-Butyl)-1-methyl-1-(2-phenylethyl-2,2-d_2)urea (S1a-[β]d_2): Deuterated ratio over 99%,

prepared from methyl phenylacetate (10 mmol) in 35% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34–7.27 (m, 2H), 7.25–7.16 (m, 3H), 3.86 (s, 1H), 3.42 (s, 2H), 2.80 (s, 3H), 1.22 (s, 9H).



The **S11-*d*** was synthesized according to the reference procedure.[6] To a stirred solution of 2-bromo-2-phenylacetic acid (20 mmol, 1.0 equiv) in dry THF (50 mL) at -78 °C under N_2 atmosphere was added *n*-BuLi (41 mmol, 25.6 mL, 1.6 M in hexane) dropwise. The reaction mixture was left stirred for 1 h at -78 °C, and was then gradually brought to 0 °C, followed by quenching with D_2O (2 mL). The reaction mixture was acidified with 6N HCl and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to provide **S11-*d***, which was used without any purification in the next step.

The **S11-*d*** (18 mmol, 1.0 equiv) was dissolved in dry THF (20 mL) in a 100 mL flame-dried Schlenk tube under N_2 atmosphere. The solution was cooled to 0 °C and BH_3-THF (27 mL, 1.0 M in THF, 1.5 equiv,) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After completed, the EtOAc (30 mL) was added carefully to quench the reaction, and the mixture was washed with water (3 × 30 mL). Then the collected aqueous phase was extracted with EtOAc (30 mL) for twice. The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to provide the **S12-*d***.

To a stirred solution of **S12-*d*** (17 mmol, 1.0 equiv) in DCM (50 mL) was dropwise added $EtSO_2Cl$ (20.4 mmol, 1.2 equiv) and Et_3N (20.4 mmol, 1.2 equiv) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. After completed, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (PE / EA = 10 / 1) to provide **S13-*d***.

To a stirred solution of **S13-*d*** (15 mmol) in MeOH (4 mL) was added NH_3 (15 mL, 4.0 M in CH_3OH, 4 equiv) and the mixture was stirred at 50 °C for 12 h. After completed, the mixture was cooled to room temperature and concentrated under reduced pressure to provide the **S14-*d***, which was used without any purification in the next step.

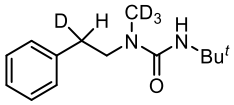
To a stirred solution of **S14-*d*** (10 mmol, 1.0 equiv) in DCM (15 mL) was dropwise added Boc_2O (12 mmol, 1.2 equiv) and Et_3N (12 mmol, 1.2 equiv). The mixture was stirred at room temperature for 3 h, then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to provide **S15-*d***.

To a cooled solution of **S15-*d*** (6.5 mmol,) in THF (20 mL) at -15 °C was added LiHMDS (7.8 mL, 1.0 M in THF, 1.2 equiv) under N_2 atmosphere. After stirring at -15 °C for 15 min, CD_3I (7.8 mmol, 1.2 equiv) was added dropwise to the above solution. The solution was then slowly warmed to room

temperature. After 1 h, the reaction was diluted with EtOAc (30 mL) and quenched with water (20 mL). After removing the organic phase, the aqueous phase was extracted again with EtOAc twice (2 × 30 mL). The combined organic extract was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to provide the **S16-*d*$_4$**.

To a stirred solution of **S16-*d*$_4$** in DCM (10 mL) was dropwise added CF_3COOH (10 mL) at room temperature. The reaction was then stirred for 10 minutes and the solvent was removed under reduced pressure. To the residue was added NaOH solution (1 N, 10 mL), and the aqueous phase was extracted with DCM (3 × 10 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide the **S17-*d*$_4$**, which was used without any purification in the next step.

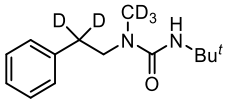
To a stirred solution of **S17-*d*$_4$** (5 mmol, 1.0 equiv) in DCM (20 mL) was dropwise added ^{t}BuNCO (6 mmol, 1.2 equiv) and Et_3N (6 mmol, 1.2 equiv). After stirring for 3 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide **S1a-*d*$_4$**.



S1a-*d*$_4$

3-(*tert*-Butyl)-1-(methyl-*d*$_3$)-1-(2-phenylethyl-2-*d*)urea (S1a-*d*$_4$): Deuterated ratio over 99%, prepared from methyl phenylacetate 2-bromo-2-phenylacetic acid (20 mmol) in 22% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.32–7.28 (m, 2H), 7.24–7.18 (m, 3H), 3.85 (s, 1H), 3.42 (d, J = 6.9 Hz, 2H), 2.79 (t, J = 7.0 Hz, 1H), 1.22 (s, 9H).



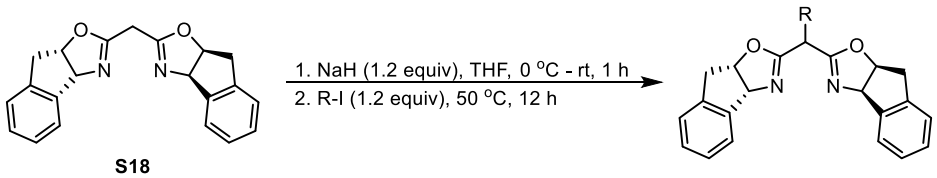
S1a-*d*$_5$

3-(*tert*-Butyl)-1-(methyl-*d*$_3$)-1-(2-phenylethyl-2,2-*d*$_2$)urea (S1a-*d*$_5$): Deuterated ratio over 99%, prepared from **S10-*d*$_2$** (12 mmol) in 23% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31–7.28 (m, 2H), 7.24–7.18 (m, 3H), 3.94 (s, 1H), 3.41 (s, 2H), 1.22 (s, 9H).

2.4 Procedure for the synthesis of new developed chiral ligands

A. Chiral bisoxazoline ligands:

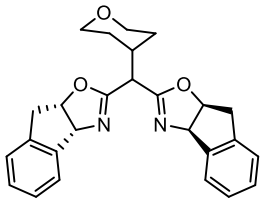


S18

The **S18**[7] (1 mmol, 1.0 equiv) was dissolved in dry THF (5 mL) in a flame-dried Schlenk tube. The solution was cooled to 0 °C and NaH (48 mg, 60% wt in oil, 1.2 equiv,) was added in portions. The resulting mixture was allowed to warm to room temperature and stirred for 1 h, then a solution of iodoalkane (1.2 mmol, 1.2 equiv) in THF (2 mL) was added dropwise. After stirring at 50 °C for 12 h, sat. NH_4Cl solution (5 mL) and water (15 mL) were added and the mixture was extracted with DCM (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced

pressure. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide the desired ligands **L21-L24**.

Selected analytical data of chiral bisoxazoline ligands:



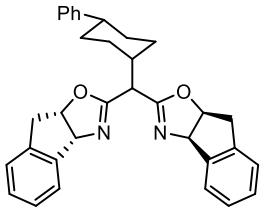
L21

(3a*R*,3a'*R*,8a*S*,8a'*S*)-2,2'-((Tetrahydro-2*H*-pyran-4-yl)methylene)bis(3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole) (L21): Prepared from **S18** (0.5 mmol) in 46% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.49–7.45 (m, 2H), 7.28–7.20 (m, 6H), 5.56– 5.52 (m, 2H), 5.31–5.25 (m, 2H), 3.82 (t, *J* = 12.5 Hz, 2H), 3.37–3.29 (m, 4H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.99 (t, *J* = 17.7 Hz, 2H), 2.27 (q, *J* = 11.3 Hz, 1H), 1.48 (d, *J* = 12.7 Hz, 1H), 1.37 (d, *J* = 12.4 Hz, 1H), 1.28– 1.15 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 163.7, 163.6, 141.8, 141.6, 139.5, 139.3, 128.4 (2C), 127.4, 127.4, 125.5, 125.5, 125.2, 125.1, 83.3, 83.1, 76.4, 76.3, 67.5 (2C), 45.3, 39.6, 39.5, 35.4, 30.6, 30.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{26}H_{26}N_2O_3Na$: 437.1836, found: 437.1825.



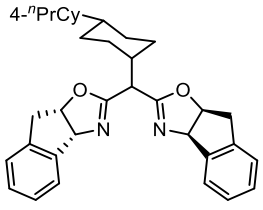
L22

(3a*R*,3a'*R*,8a*S*,8a'*S*)-2,2'-(((1*s*,4*R*)-4-Phenylcyclohexyl)methylene)bis(3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole) (L22): Prepared from **S18** (0.5 mmol) in 62% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.49–7.45 (m, 2H), 7.27– 7.12 (m, 11H), 5.53 (dd, *J* = 7.6, 4.6 Hz, 2H), 5.28 (t, *J* = 8.0 Hz, 2H), 3.31 (dt, *J* = 15.8, 7.7 Hz, 2H), 3.17 (d, *J* = 9.9 Hz, 1H), 2.97 (dd, *J* = 26.4, 17.9 Hz, 2H), 2.33 (t, *J* = 12.1 Hz, 1H), 2.09 (q, *J* = 11.7 Hz, 1H), 1.80–1.62 (m, 4H), 1.41 (q, *J* = 12.1 Hz, 2H), 1.11–0.93 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 164.3, 164.3, 147.2, 141.9, 141.7, 139.6, 139.5, 128.3 (2C), 128.3 (2C), 127.4, 127.4, 126.8 (2C), 125.9, 125.5, 125.5, 125.1, 125.1, 83.1, 83.1, 76.4, 76.3, 45.8, 44.0, 39.7, 39.6, 37.8, 33.7, 33.6, 30.9, 30.8.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{33}H_{32}N_2O_2Na$: 511.2356, found: 511.2368.



L23

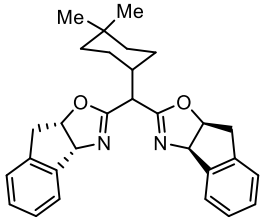
(3a*R*,3a'*R*,8a*S*,8a'*S*)-2,2'-(((1*R*,4*s*)-4'-Propyl-[1,1'-bi(cyclohexan)]-4-yl)methylene)bis(3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole) (L23): Prepared from **S18** (0.5 mmol) in 69% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47–7.43 (m, 2H), 7.26–7.17 (m, 6H), 5.50 (dd, *J* = 7.5, 5.3 Hz, 2H), 5.25 (t, *J* = 8.3 Hz, 2H), 3.29 (dt, *J* = 16.3, 7.8 Hz, 2H), 3.09 (d, *J* = 10.0 Hz, 1H), 2.95 (dd, *J* =

25.4, 18.0 Hz, 2H), 1.92 (q, *J* = 10.8 Hz, 1H), 1.75–1.49 (m, 9H), 1.33–1.23 (m, 2H), 1.12–1.09 (m, 3H), 0.90–0.75 (m, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 164.4, 164.4, 141.9, 141.8, 139.6, 139.5, 128.3 (2C), 127.3, 127.3, 125.5, 125.5, 125.1 (2C), 83.0, 83.0, 76.4, 76.3, 46.0, 43.2, 42.8, 39.8, 39.7, 39.6, 38.3, 37.6, 33.6 (2C), 30.9, 30.9, 30.0, 29.9, 29.5, 29.4, 20.0, 14.4.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{36}H_{44}N_2ONa$: 559.3295, found: 559.3279.



(1*R*,2*S*)-**L24**

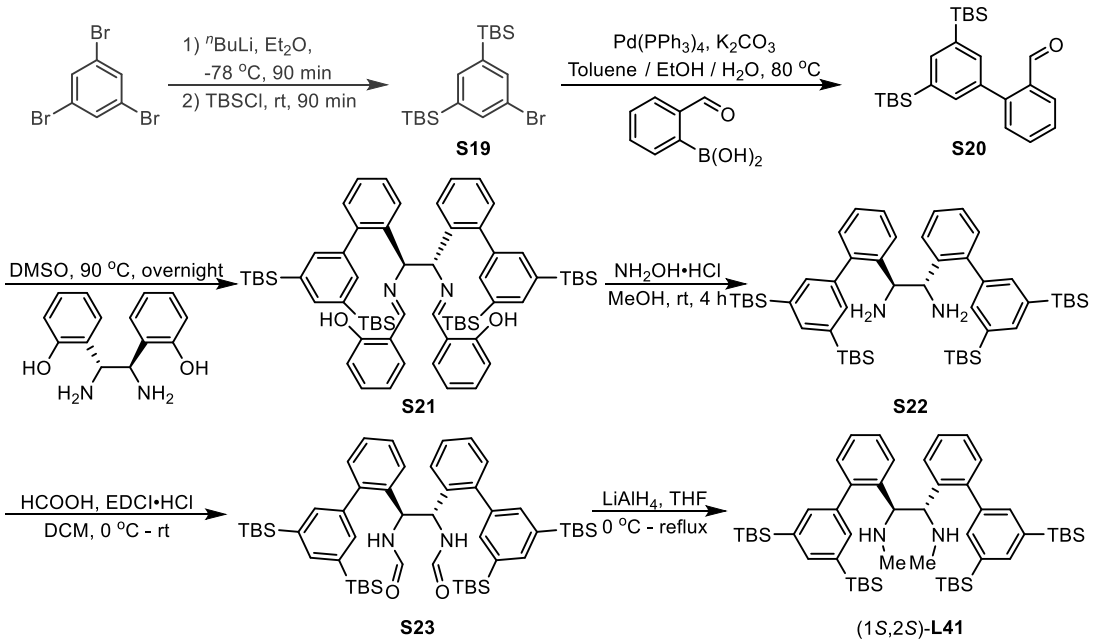
(3a*R*,3a'*R*,8a*S*,8a'*S*)-2,2'-((4,4-Dimethylcyclohexyl)methylene)bis(3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole ((1*R*,2*S*)-**L24)**: Prepared from **S18** (1 mmol) in 75% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47–7.43 (m, 2H), 7.26–7.17 (m, 6H), 5.51 (t, *J* = 7.6 Hz, 2H), 5.26 (qd, *J* = 6.9, 1.7 Hz, 2H), 3.31 (dt, *J* = 17.8, 7.5 Hz, 2H), 3.18 (d, *J* = 9.6 Hz, 1H), 2.99 (dd, *J* = 24.5, 17.9 Hz, 2H), 1.36–0.92 (m, 9H), 0.80 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 164.4, 164.4, 141.9, 141.8, 139.6, 139.5, 128.3 (2C), 127.4, 127.3, 125.5, 125.4, 125.1 (2C), 83.1, 83.0, 76.4, 76.2, 45.5, 39.7, 39.6, 38.6, 38.5, 38.0, 32.5, 29.7, 26.3, 26.2, 24.2.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{29}H_{32}N_2ONa$: 463.2356, found: 463.2371.

B. Chiral diamine ligands:



To a stirred solution of 1,3,5-tribromobenzene (20 mmol, 1.0 equiv) in Et_2O (125 mL) at -78 °C was added *n*-BuLi (25.6 mL, 1.6 M in hexane, 2.05 equiv) dropwise under N_2 atmosphere. The solution was stirred for 90 min before adding trihexylsilylchloride (44 mmol, 2.2 equiv) dropwise *via* a syringe. The solution was allowed to warm to room temperature. After stirring for another 90 min, the reaction mixture was washed with water, dried over $MgSO_4$ and filtered. The solution was concentrated and purified by

flash column chromatography (PE) to provide **S19** (mixed with a small amount of 1,3,5-tris(*tert*-butyldimethylsilyl)benzene and (3-bromophenyl)(*tert*-butyl)dimethylsilane).

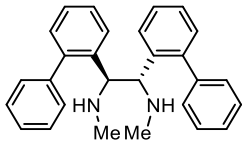
The **S19** (17 mmol, 1.0 equiv), (2-formylphenyl)boronic acid (20.4 mmol, 1.2 equiv), K_2CO_3 (61.2 mmol, 3.6 equiv) and $Pd(PPh_3)_4$ (0.51 mmol, 0.03 equiv) were dissolved in a degassed toluene/EtOH/H_2O mixture (10:6:3, 50 mL). The solution was heated to 80 °C under vigorous stirring for 1 day, then cooled to rt, treated with H_2O (20 mL) and separated. The aqueous phase was extracted with CH_2Cl_2 (3×20 mL), and the organic phases were combined, washed with H_2O (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to provide **S20**.

The **S20** (2.4 mmol, 2.4 equiv) and (*R*,*R*)-Mother diamine (1 mmol, 1.0 equiv) were dissolved in anhydrous DMSO (6 mL) and stirred at 90 °C under N_2 atmosphere overnight. After completed, the mixture was poured into water. The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue (crude **S21**, 1 mmol, 1.0 equiv) was dissolved in MeOH (15 mL) and $NH_2OH{\cdot}HCl$ (5 mmol, 5.0 equiv) was added. The mixture was stirred at rt for 4 h. NaOH (20 mL, 2 M) was added to the reaction mixture and the aqueous layer was extracted with CH_2Cl_2 (5 × 15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude diamine **S22** was purified by flash column chromatography (PE / EA = 3 / 1 to 1 / 1).

To a stirred solution of **S22** (0.74 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at 0 °C was added formic acid (4.44 mmol, 6.00 equiv) dropwise, and then EDCI·HCl (2.22 mmol, 3.00 equiv) was added portionwise over 2 min. Next, the mixture was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was added water (15 mL), separated, and the aqueous was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with an aqueous solution of HCl (25 mL, 1.0 M) and then water (20 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (PE / EA = 5 / 1 to 3 / 1) to provide **S23**.

To a stirred solution of **S23** (0.65 mmol, 1.0 equiv) in anhydrous THF (4 mL) under N_2 at 0 °C was added $LiAlH_4$ (powder; 3.9 mmol, 6.0 equiv) in ~10 portions over 5 min. The mixture was heated at reflux for 2 h. After completed, the reaction mixture was allowed to cool to 0 °C in an ice–water bath. The excess $LiAlH_4$ was quenched by the very careful addition of EtOAc (0.5 mL), then solvent was removed under reduced pressure and DCM (10 mL) was added. The insoluble substance was filtered, washed with DCM (3 × 10 mL) and the collected solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to provide the desired ligands **L35**-**L41**.

Selected analytical data of chiral diamine ligands:



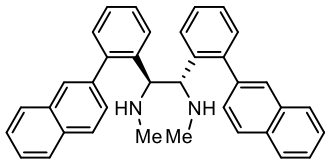
L35

(1*S*,2*S*)-1,2-Di([1,1'-biphenyl]-2-yl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine (L35): Prepared from bromobenzene and (*R*,*R*)-Mother diamine in 58% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31–7.23 (m, 7H), 7.17 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.99–6.93 (m, 7H), 3.81 (s, 2H), 2.28 (s, 6H), 2.13 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.2, 141.3, 138.5, 129.8, 129.6, 127.8, 127.6, 127.5, 126.5, 126.1, 65.3, 34.2.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{28}H_{29}N_2$: 393.2325, found: 393.2337.



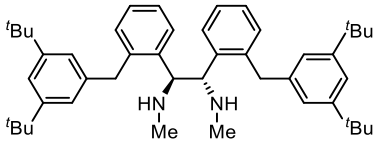
L36

(1*S*,2*S*)-*N*^{1},*N*^{2}-Dimethyl-1,2-bis(2-(naphthalen-2-yl)phenyl)ethane-1,2-diamine (L36): Prepared from 2-bromonaphthalene and (*R*,*R*)-Mother diamine in 52% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.88–7.86 (m, 2H), 7.74–7.68 (m, 4H), 7.53–7.48 (m, 5H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.04–6.88 (m, 9H), 3.84 (s, 2H), 2.28 (s, 6H), 2.11 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.1, 138.8, 138.6, 132.9, 132.1, 129.8, 128.5, 128.1, 127.8, 127.7, 127.63, 126.9, 126.2, 126.0, 125.7, 62.7, 34.3.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{36}H_{33}N_2$: 493.2638, found: 493.2651.



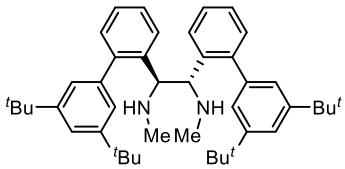
L37

(1*S*,2*S*)-1,2-Bis(2-(3,5-di-*tert*-butylbenzyl)phenyl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine (L37): Prepared from 1-(bromomethyl)-3,5-di-*tert*-butylbenzene and (*R*,*R*)-Mother diamine in 43% yield as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 4H), 3.97 (s, 2H), 3.42 (d, *J* = 15.9 Hz, 2H), 3.24 (d, *J* = 15.9 Hz, 2H), 2.99 (s, 2H), 1.96 (s, 6H), 1.26 (s, 36H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 150.6, 140.7, 139.7, 139.5, 129.9, 127.2, 127.1, 126.4, 123.5, 119.8, 65.3, 38.5, 34.7, 34.1, 31.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{46}H_{65}N_2$: 645.5142, found: 645.5130.



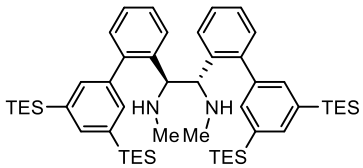
L38

(1*S*,2*S*)-1,2-Bis(3',5'-di-*tert*-butyl-[1,1'-biphenyl]-2-yl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine (L38): Prepared from 1-bromo-3,5-di-*tert*-butylbenzene and (*R*,*R*)-Mother diamine in 52% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.40 (s, 2H), 7.15–7.09 (m, 4H), 7.00–6.89 (m, 8H), 4.00 (s, 2H), 2.31 (s, 6H), 2.22 (s, 2H), 1.37 (s, 36H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.8, 143.9, 140.8, 138.2, 130.3, 127.7, 127.1, 126.1, 124.1, 120.8, 64.8, 34.9, 34.3, 31.7.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{44}H_{61}N_2$: 617.4829, found: 617.4842.



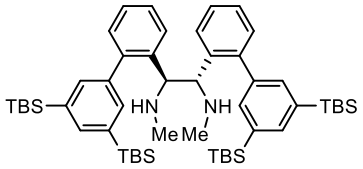
L40

(1*S*,2*S*)-1,2-Bis(3',5'-bis(triethylsilyl)-[1,1'-biphenyl]-2-yl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine (L40): Prepared from 1,3,5-tribromobenzene and (*R*,*R*)-Mother diamine in 59% yield as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 (s, 2H), 7.13–6.99. (m, 7H), 6.96–6.88 (m, 5H), 4.06 (s, 2H), 2.31 (s, 6H), 2.14 (s, 2H), 1.03 (t, *J* = 7.7 Hz, 36H), 0.87–0.82 (m, 24H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.6, 139.9, 138.7, 138.1, 136.0, 135.3, 130.3, 127.4, 127.2, 126.2, 64.0, 34.1, 7.6, 3.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{52}H_{84}N_2Si_4Na$: 849.5784, found: 849.5796.



(1*S*,2*S*)-**L41**

(1*S*,2*S*)-1,2-Bis(3',5'-bis(*tert*-butyldimethylsilyl)-[1,1'-biphenyl]-2-yl)-*N*^{1},*N*^{2}-dimethylethane-1,2-diamine ((1*S*,2*S*)-L41): Prepared from 1,3,5-tribromobenzene and (*R*,*R*)-Mother diamine in 62% yield as a white solid.

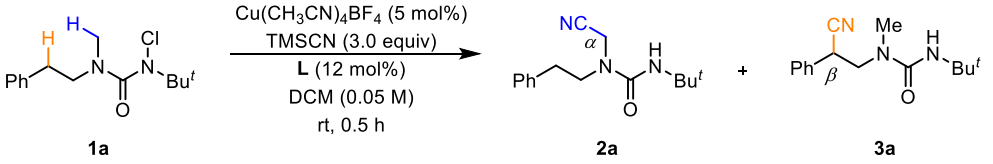
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.60 (s, 2H), 7.12 (t, *J* = 7.2 Hz, 4H), 7.03–6.93 (m, 8H), 5.41 (s, 2H), 4.40–4.36 (m, 2H), 2.35–2.44 (m, 6H), 0.89 (s, 36H), 0.32–0.30 (m, 24H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.5, 139.3, 138.7, 135.8, 135.3, 130.8, 127.7, 127.4, 127.3, 127.3, 63.0, 33.0, 26.6, 17.0, -6.0.

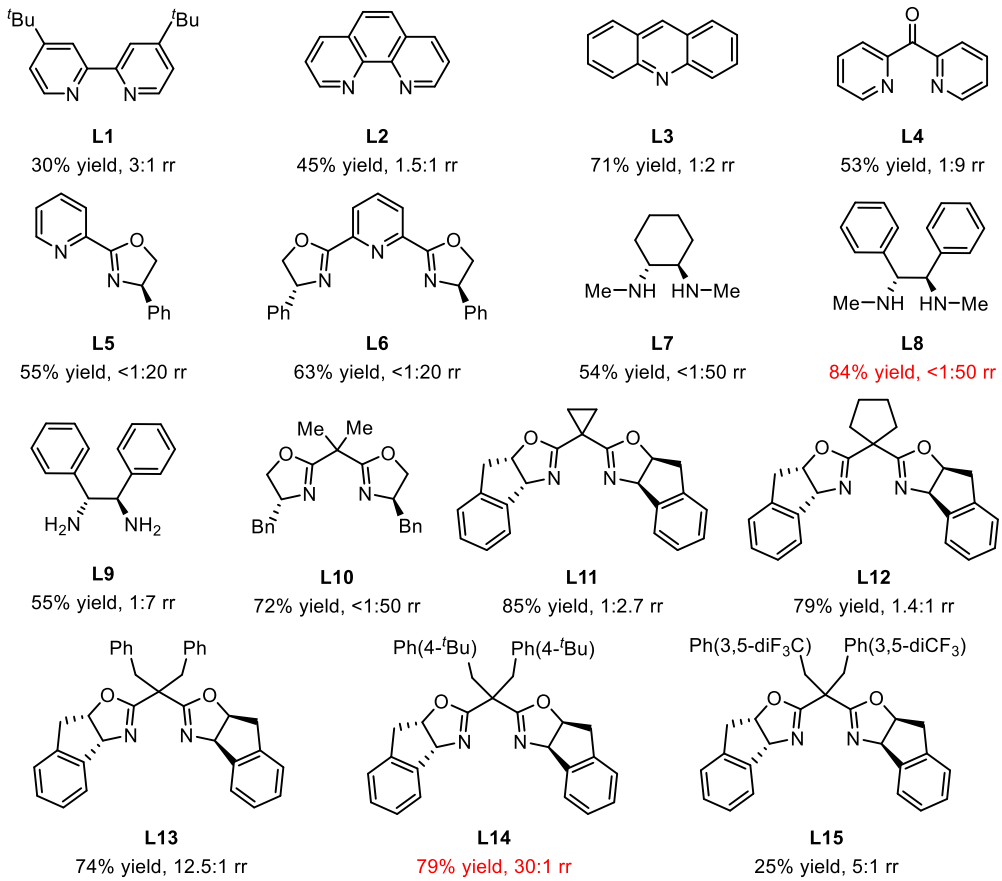
HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{52}H_{85}N_2Si_4$: 849.5784, found: 849.5792.

3. Optimization of the Reaction Conditions

Table S1. Preliminary screening of ligands for regioselective cyanation of α'/β-C(sp^3)–H



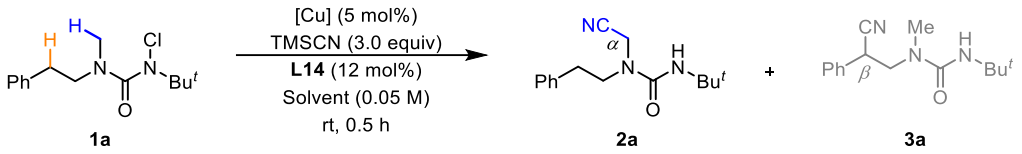
1a **2a** **3a**



L1 30% yield, 3:1 rr	**L2** 45% yield, 1.5:1 rr	**L3** 71% yield, 1:2 rr	**L4** 53% yield, 1:9 rr
L5 55% yield, <1:20 rr	**L6** 63% yield, <1:20 rr	**L7** 54% yield, <1:50 rr	**L8** 84% yield, <1:50 rr
L9 55% yield, 1:7 rr	**L10** 72% yield, <1:50 rr	**L11** 85% yield, 1:2.7 rr	**L12** 79% yield, 1.4:1 rr
L13 74% yield, 12.5:1 rr	**L14** 79% yield, 30:1 rr	**L15** 25% yield, 5:1 rr	

Reaction conditions: **1a** (0.1 mmol), $Cu(CH_3CN)_4BF_4$ (5 mol%), **L** (12 mol%), TMSCN (3.0 equiv), DCM (2 mL), N_2, rt, 0.5 h. The yields (**2a**+**3a**) and regioselectivity ratio (rr, **2a**/**3a**) were determined by GC-MS using dodecane as internal standard.

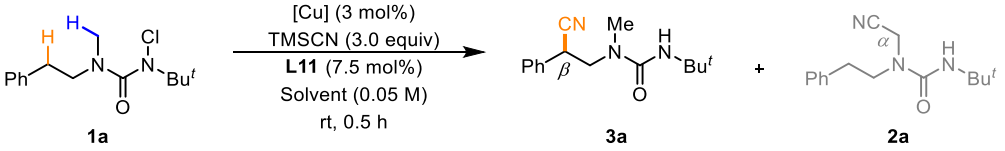
Table S2. Screening other conditions for selective cyanation of α'-C(sp^3)–H



Entry	Catalyst	Solvent	Yield of **2a** (%)	rr (**2a**/**3a**)
1	CuSCN	DCM	67%	20:1
2	CuSCN	DCE	65%	30:1
3	CuSCN	CH_3CN	10%	10:1
4	CuSCN (3 mol%)	DCM	35%	15:1
5[a]	CuSCN (3 mol%)	DCM	50%	10:1
6	CuSCN	DCM (1 mL)	65%	10:1
7	CuI	DCM	30%	1.5:1
8	$Cu(OTf)_2$	DCM	25%	5:1
9	**$Cu(CH_3CN)_4BF_4$**	**DCM**	**76% (69%)[b]**	**30:1**
10[c]	$Cu(CH_3CN)_4BF_4$	DCM	43%	12:1

Reaction conditions: **1a** (0.1 mmol), [Cu] (5 mol%), **L14** (12 mol%), TMSCN (3.0 equiv), solvent (2 mL), N_2, rt, 0.5 h. The yields and regioselectivity ratio (rr) were determined by GC-MS using dodecane as internal standard. [a]**L14** (7.5 mol%). [b]Isolated yield of **2a** was in parentheses. [c]Racemic **L14** was used.

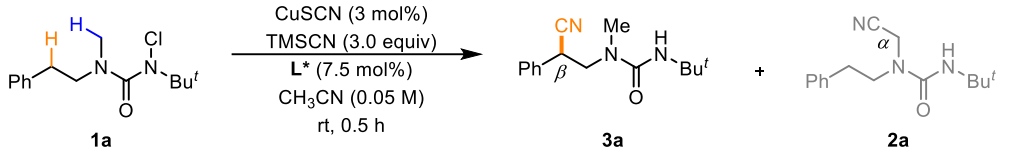
Table S3. Screening other conditions for enantioselective cyanation of β-C(sp^3)–H

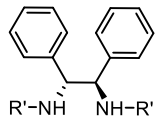


Entry	Catalyst	Solvent	Yield of **3a** (%)	Er of **3a**	rr (**2a**/**3a**)
1	$Cu(CH_3CN)_4BF_4$	DCM	62%	82.5:17.5	1:2.7
2	CuI	DCM	72%	86.5:13.5	1:2.9
3	$Cu(OTf)_2$	DCM	64%	90:10	1:2.9
4	CuOAc	DCM	25%	85.5:14.5	2.7:1
5	CuTc	DCM	51%	89:11	1:7.3
6	CuSCN	DCM	67%	90.5:9.5	1:2.7
7	**CuSCN**	**CH_3CN**	**75%**	**91.5:8.5**	**1:15**
8	CuSCN	THF	32%	82:18	1:9
9	CuSCN	$PhCF_3$	45%	91:9	1:2.5
10	CuSCN	dioxane	15%	85:15	1:13
11	CuSCN	DMA	/	/	/

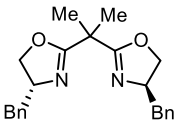
Reaction conditions: **1a** (0.1 mmol), [Cu] (3 mol%), **L11** (7.5 mol%), TMSCN (3.0 equiv), solvent (2 mL), N_2, rt, 0.5 h. The yields and regioselectivity ratio (rr, **2a**/**3a**) were determined by GC-MS using dodecane as internal standard. Enantiomeric ratio (er) values detected by HPLC on a chiral stationary phase.

Table S4. Screening chiral ligands for enantioselective cyanation of β-C(sp^3)–H

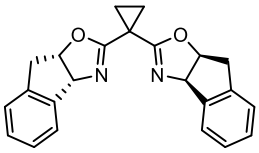




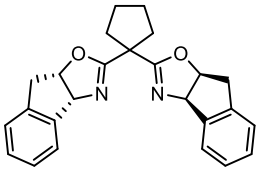
L8, R' = Me, 84% yield, 53:47 er
L9, R' = H, 50:50 er



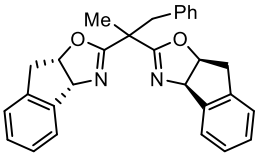
L10
72% yield, 75:25 er



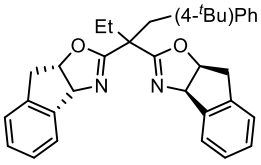
L11
75% yield, 91.5:8.5 er



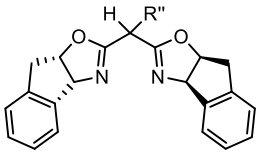
L12
33% yield, 89:11 er



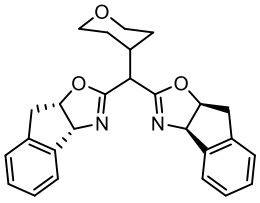
L16
58% yield, 90:10 er



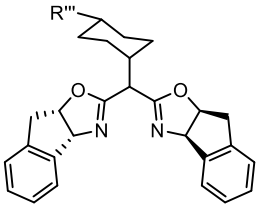
L17
56% yield, 92:8 er



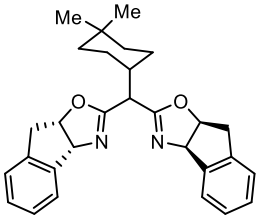
L18, R'' = ^{i}Pr, 56% yield, 95:5 er
L19, R'' = cyclopentyl, 59% yield, 95.5:4.5 er
L20, R'' = Cy, 68% yield, 95.5:4.5 er



L21
60% yield, 94:6 er



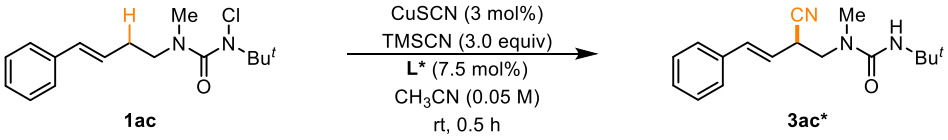
L22, R''' = Ph, 44% yield, 96.5:3.5 er, 1:1.5 rr
L23, R''' = 4-^{n}PrCy, 64% yield, 96:4 er, 1:22 rr



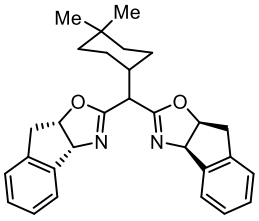
(1*R*,2*S*)-**L24**
73% yield (68%)[a], 97:3 er, 1:25 rr

Reaction conditions: **1a** (0.1 mmol), CuSCN (3 mol%), **L*** (7.5 mol%), TMSCN (3.0 equiv), CH_3CN (2 mL), N_2, rt, 0.5 h. The yields of **3a** and regioselectivity ratio (rr, **2a**/**3a**) were determined by GC-MS using dodecane as internal standard. Enantiomeric ratio (er) values detected by HPLC on a chiral stationary phase. [a]Isolated yield of **3a** was in parentheses.

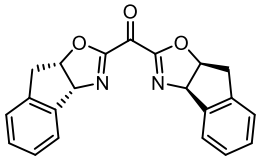
Table S5. Screening chiral ligands for enantioselective cyanation of allylic C(sp^3)–H



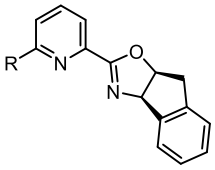
1ac → **3ac***



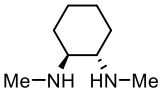
(1*R*, 2*S*)-**L24**
trace



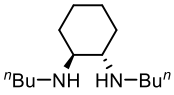
L25
42% yield, 50:50 er



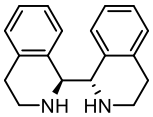
L26, R = H, 82% yield, 57:43 er
L27, R = Me, 45% yield, 55:45 er



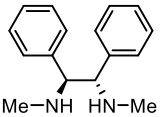
L7
35% yield, 65:35 er



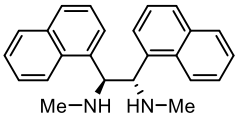
L28
46% yield, 60.5:39.5 er



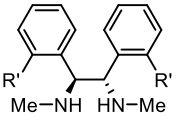
L29
32% yield, 60:40 er



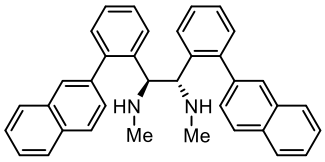
L8
75% yield, 65:35 er



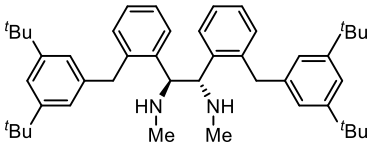
L30
51% yield, 68.5:31.5 er



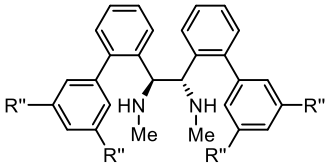
L31, R' = OMe, 51% yield, 64.5:35.5 er
L32, R' = Et, 75% yield, 72:28 er
L33, R' = ^{i}Pr, 62% yield, 75:25 er
L34, R' = Bn, 65% yield, 78:22 er
L35, R' = Ph, 63% yield, 80:20 er



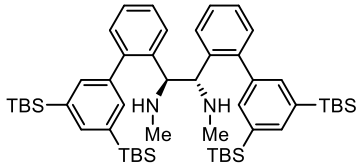
L36
48% yield, 79:21 er



L37
58% yield, 75:25 er



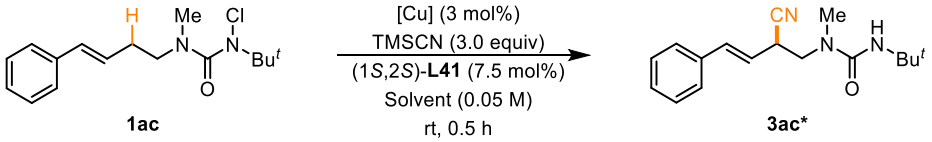
L38, R'' = ^{t}Bu, 55% yield, 89.5:10.5 er
L39, R'' = TMS, 52% yield, 91.5:8.5 er
L40, R'' = TES, 53% yield, 89:11 er



(1*S*,2*S*)-**L41**
rt, 58% yield (55%)[a], 93:7 er

Reaction conditions: **1ac** (0.1 mmol), CuSCN (3 mol%), **L*** (7.5 mol%), TMSCN (3.0 equiv), CH_3CN (2 mL), N_2, rt, 0.5 h. The yields of **3ac*** were determined by GC-MS analysis using dodecane as internal standard. Enantiomeric ratio (er) values detected by HPLC on a chiral stationary phase. [a]Isolated yield of **3ac*** was in parentheses.

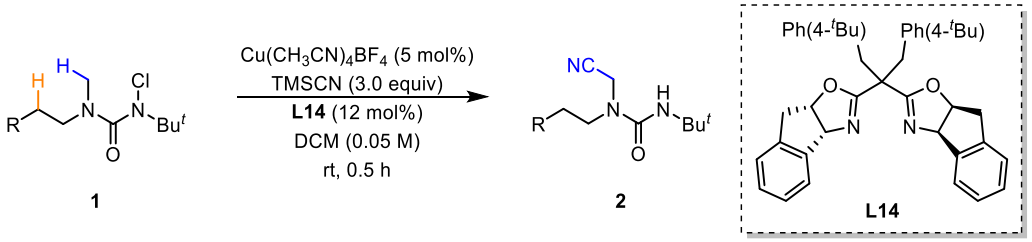
Table S6. Screening other conditions for enantioselective cyanation of allylic C(sp^3)–H



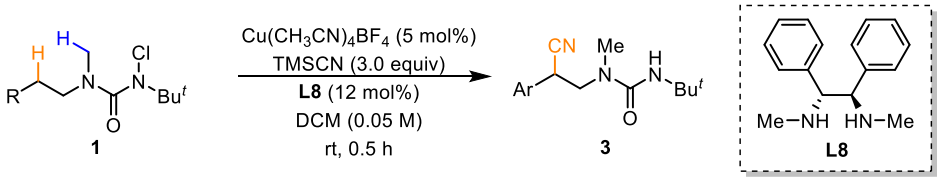
Entry	Catalyst	Solvent	Yield of **3ac*** (%)	er
1	**CuSCN**	**CH_3CN**	**58%**	**93:7**
2	CuI	CH_3CN	49%	90:10
3	$Cu(CH_3CN)_4BF_4$	CH_3CN	65%	88:12
4	CuTc	CH_3CN	41%	91:9
5	CuOAc	CH_3CN	50%	88.5:11.5
6	Cu_2O	CH_3CN	65%	91:9
7	$Cu(OTf)_2$	CH_3CN	30%	88.5:11.5
8	$Cu(NTf)_2$	CH_3CN	25%	88:12
9	CuSCN	Toluene	56%	75:25
10	CuSCN	PhCl	47%	75:25
11	CuSCN	Et_2O	57%	77.5:22.5
12	CuSCN	THF	72%	90:10
13	CuSCN	EtOAc	81%	88.5:11.5

Reaction conditions: **1ac** (0.1 mmol), [Cu] (3 mol%), (1*S*,2*S*)-**L41** (7.5 mol%), TMSCN (3.0 equiv), solvent (2 mL), N_2, rt, 0.5 h. The yields were determined by GC-MS using dodecane as internal standard.

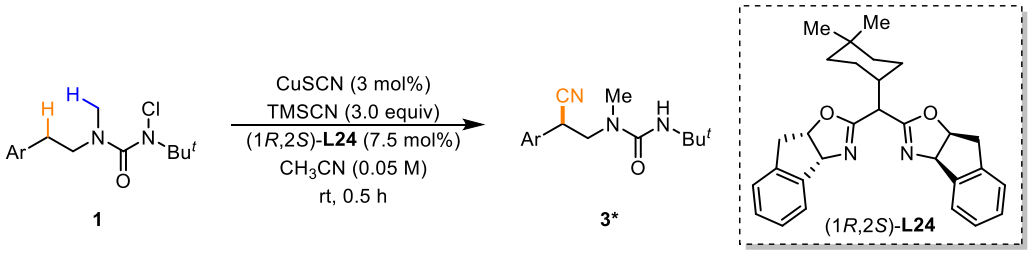
4. General Procedure for Selective Cyanation of α'/β-C(sp^3)–H



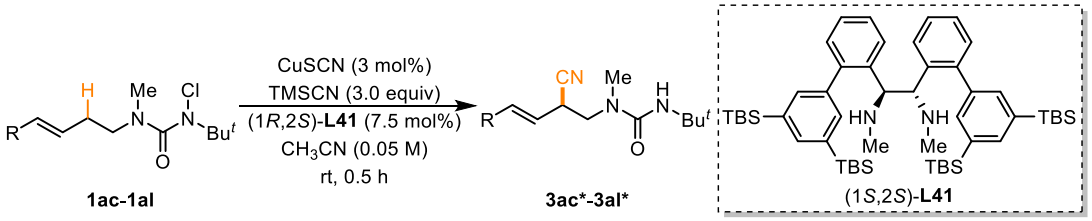
Regioselective 1,4'-HAT cyanation of α'-C(sp^3)–H (condition A): In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%) and *N*-chloro substrate **1** (0.2 mmol) were dissolved in degassed DCM (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 h. After completed (the color of solution generally changed from blue to colorless), the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography or preparative thin-layer chromatography (PE / EA = 10 / 1) to provide desired products **2**.



Regioselective 1,5-HAT cyanation of *β*-C(sp^3)–H (condition A): In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L8** (0.024 mmol, 12 mol%) and *N*-chloro substrate **1** (0.2 mmol) were dissolved in degassed DCM (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 h. After completed (the color of solution generally changed from blue to colorless), the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography or preparative thin-layer chromatography (PE / EA = 10 / 1) to provide desired products **3**.



Enantioselective 1,5-HAT cyanation of *β*-C(sp^3)–H (condition B): In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%) and *N*-chloro substrate **1** (0.2 mmol) were dissolved in degassed CH_3CN (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 h. After completed (the color of solution generally changed from blue to colorless), the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography or preparative thin-layer chromatography (PE / EA = 10 / 1) to provide desired products **3***.



Enantioselective 1,5-HAT cyanation of allylic *β*-C(sp^3)–H (condition B): In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*S*,2*S*)-**L41** (0.015 mmol, 7.5 mol%) and *N*-chloro substrate **1ac-1al** (0.2 mmol) were dissolved in degassed CH_3CN (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at rt for 0.5 h. After completed (the color of solution generally changed from pink to pale-yellow), the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography or preparative thin-layer chromatography (PE / EA = 10 / 1) to provide desired products **3ac*-3al***.

5. Crude ^{1}H NMR Analysis for Regiodivergent Cyanation

The reactions were done following the *α'*/*β*-C(sp^3)–H cyanation procedures as stated above. After the reaction completed, the mixture was concentrated, and the residue (not purified) was dissolved in $CDCl_3$ and subjected to the ^{1}H NMR test. Analysis of ^{1}H NMR spectra indicated that the *α'*/*β*-regioselectivity of C(sp^3)–H cyanation conducted by ligands **L14** and **L8** were excellent, which is accordance with the GC-MS detected.

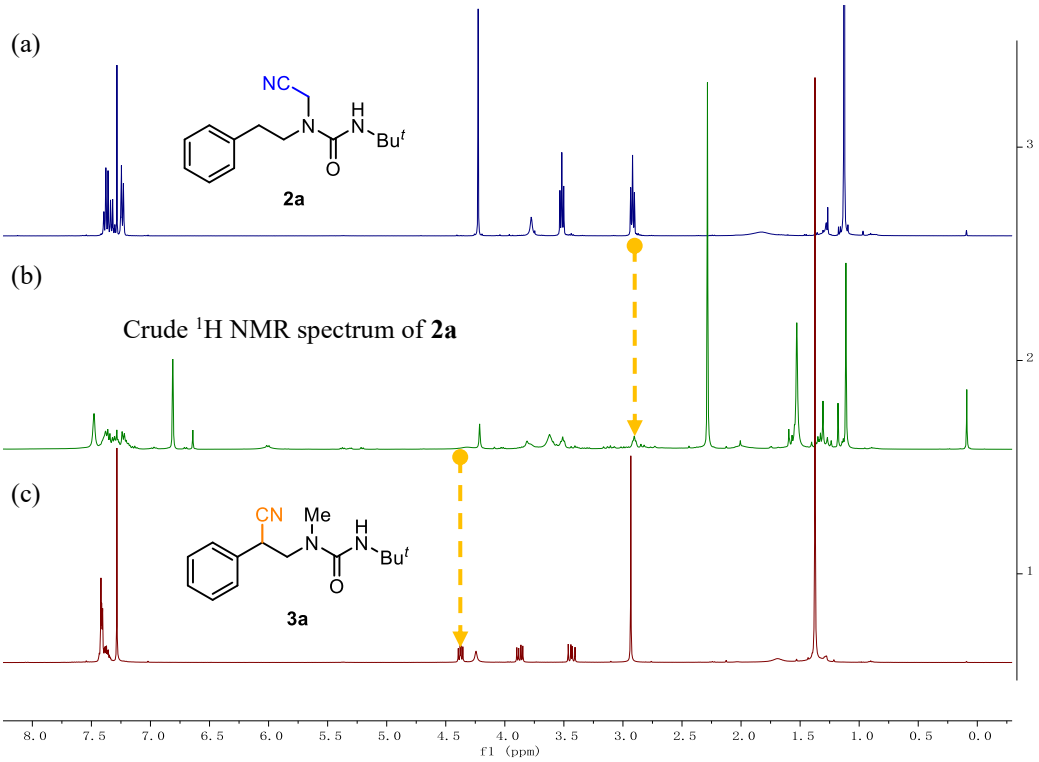


Figure S1. (a) ^{1}H NMR of **2a**; (b) Crude ^{1}H NMR of **2a**; (c) ^{1}H NMR of **3a**

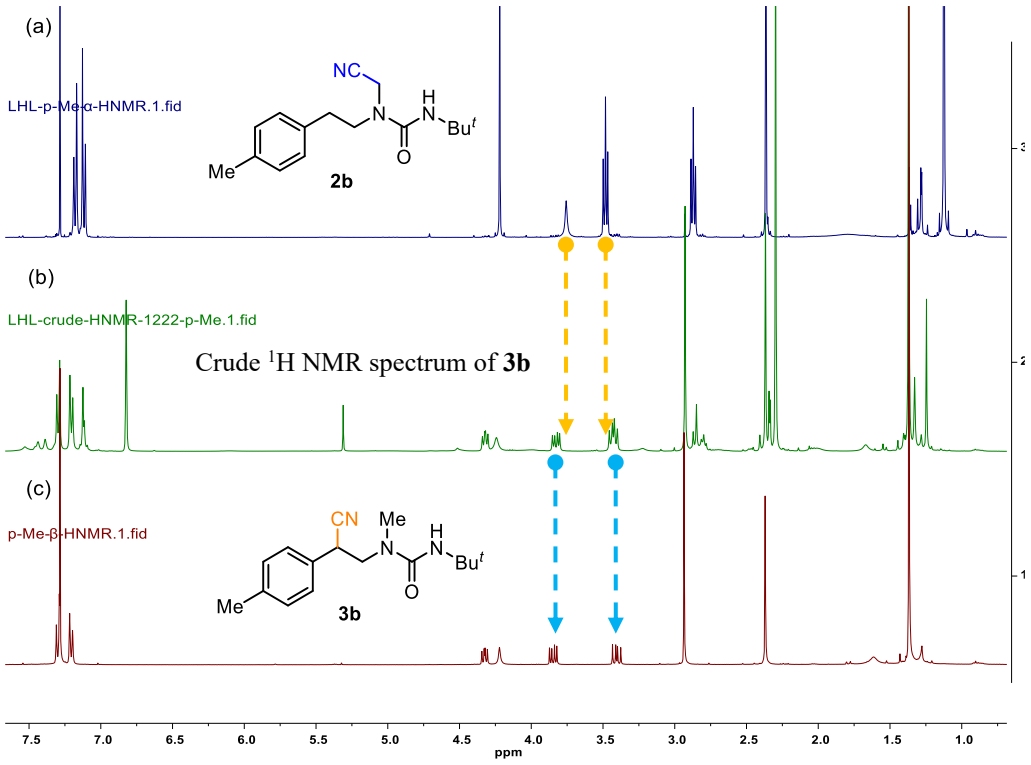


Figure S2. (a) ^{1}H NMR of **2b**; (b) Crude ^{1}H NMR of **3b**; (c) ^{1}H NMR of **3b**

6. Mechanistic Studies

6.1. Nonlinear relationship between enantiopurity of L24 and product 3a*

The reactions were done following the same *β*-C(sp^3)–H cyanation procedures as stated above (condition

B) by using the chiral bisoxazoline ligand **L24** in different ees which were obtained by mixing (1*R*,2*S*)-**L24** and (1*S*,2*R*)-**L24** in specific ratios. After the completion of reaction, the product **3a*** was purified and detected by HPLC analysis to provide the ee values. The ee values of (1*R*,2*S*)-**L24** and **3a*** were shown in the table below.

Ee value of **L24**	20%	40%	60%	80%	100%
Ee value of **3a***	22%	37%	57%	74.5%	94%

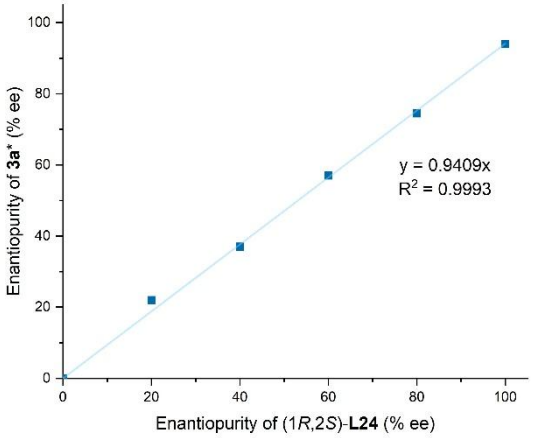
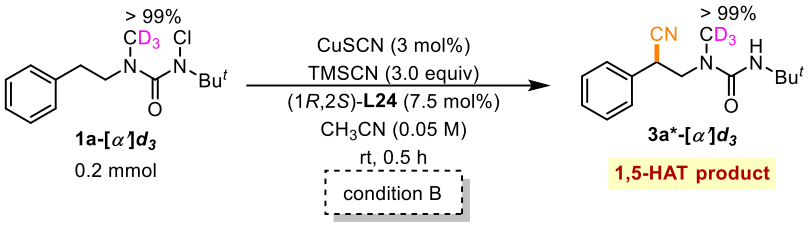


Figure S3. Non-linear effect study

6.2. Deuteration experiments



The reaction was conducted according to the general procedure. In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%) and **1a-[*α'*]*d*$_3$** (0.2 mmol) were dissolved in degassed CH_3CN (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 h. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide **3a*-[*α'*]*d*$_3$**.

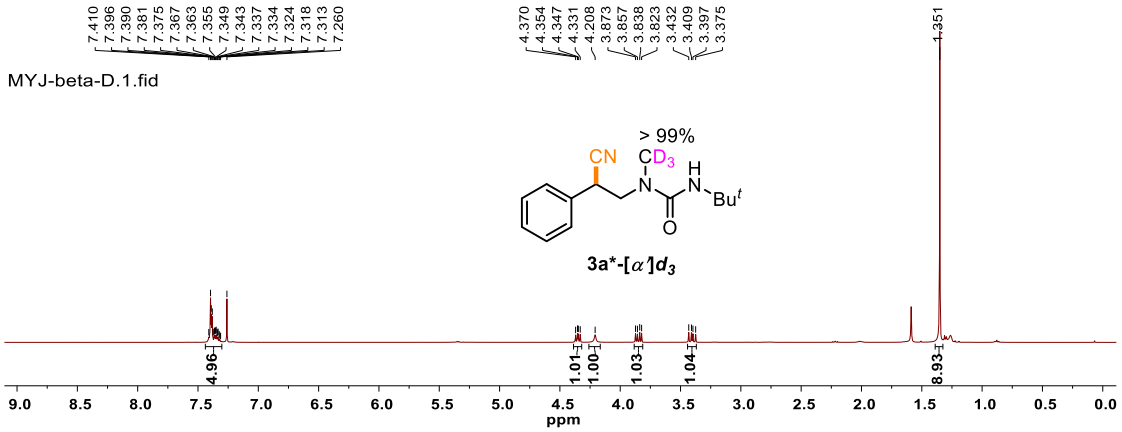
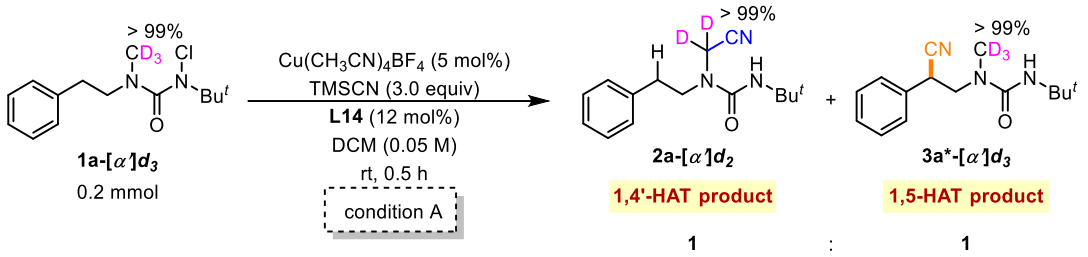


Figure S4. ^{1}H NMR spectrum of **3a*-[*α'*]*d*$_3$**



The reaction was conducted according to the general procedure. In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%) and **1a-[*α'*]*d*$_3$** (0.2 mmol) were dissolved in degassed DCM (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 h. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide the mixture of **2a-[*α'*]*d*$_2$** and **3a*-[*α'*]*d*$_3$**, which were difficult to separate and purified by column chromatography, and the ratio were determined by GC-MS.

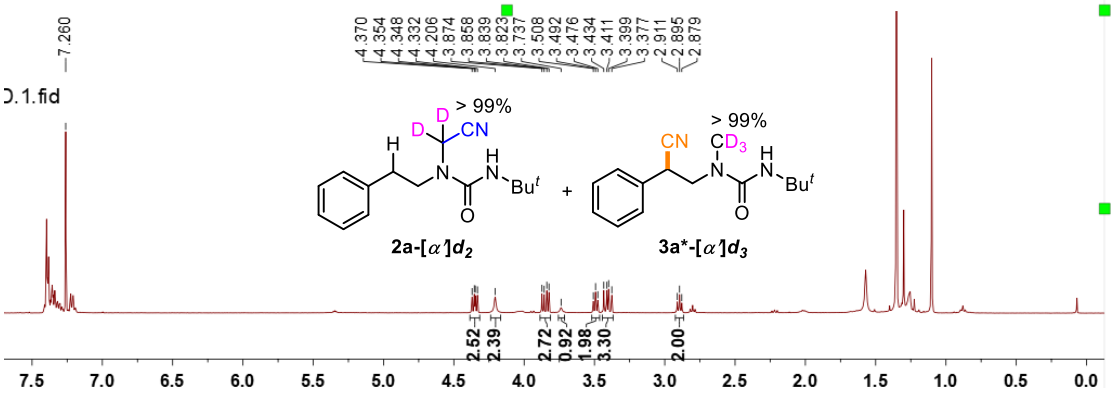


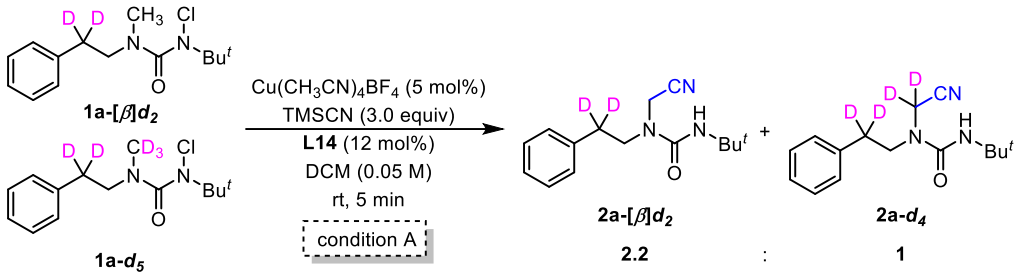
Figure S5. ^{1}H NMR spectrum of **2a-[*α'*]*d*$_2$** and **3a*-[*α'*]*d*$_3$**

The intact of deuterated atoms on products **2a-[*α'*]*d*$_2$** and **3a*-[*α'*]*d*$_3$** showed in Figure S4 and S5 indicated that the compound **1a** possibly underwent the direct 1,4'-HAT with **L14** to provide *α'*-cyanation product **2a**, and 1,5-HAT with (1*R*,2*S*)-**L24** to provide *β*-cyanation product **3a***, rather than reversible HAT process[9] or radical transfer process (*e.g.* *β*-position transfer to *α'*-position).

6.3. KIE experiments

(1) KIE of α'-C(sp³)–H cyanation

a) KIE determined from 1a-[β]d_2 and 1a-d_5 under condition A



Intramolecular cyanation of 1a-d_4 under condition A: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%), **1a-[β]d_2** (0.1 mmol) and **1a-d_5** (0.1 mmol) were dissolved in degassed DCM (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide the mixture of **2a-[β]d_2** and **2a-d_4**. Based on the integrations between **2a-[β]d_2** and **2a-d_4**, the KIE is calculated to be 2.2 (Figure S9).

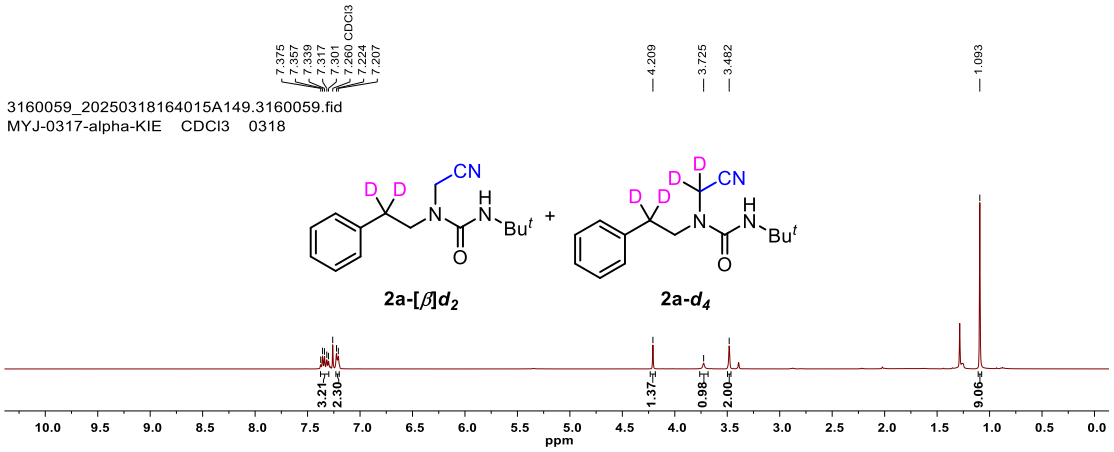
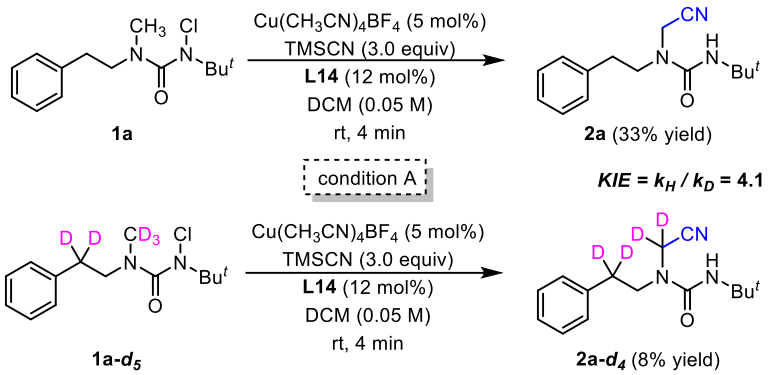


Figure S9. ^{1}H NMR spectrum of **2a** and **2a-d_4**

b) KIE determined from parallel reactions under condition A



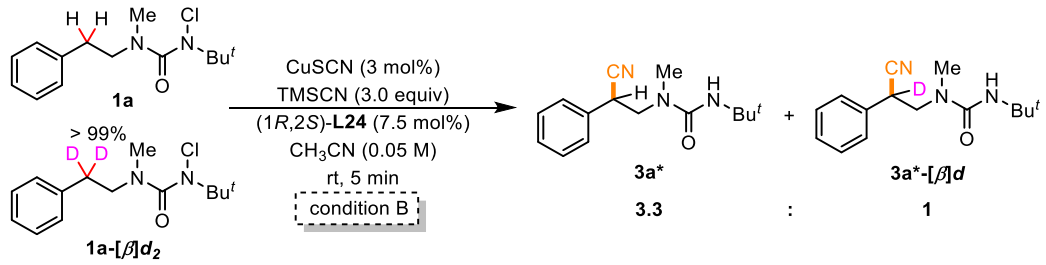
Parallel reactions of 1a and 1a-d_4 under condition A: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%), **1a** (0.1 mmol) were

dissolved in degassed DCM (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 4 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide **2a** (8.6 mg, 33% yield).

In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%), **1a-*d*$_5$** (0.1 mmol) were dissolved in degassed DCM (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide **2a-*d*$_4$** (2.1 mg, 8% yield).

(2) KIE of *β*-C(sp^3)–H cyanation

a) KIE determined from 1a and 1a-*d*$_5$ under condition B



One-pot cyanation of 1a and 1a-[*β*]*d*$_2$ under condition B: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%), **1a** (0.1 mmol) and **1a-[*β*]*d*$_2$** (0.1 mmol) were dissolved in degassed CH_3CN (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide the mixture of **3a*** and **3a*-[*β*]*d***. Based on the integrations between **3a*** and **3a*-[*β*]*d***, the KIE is calculated to be 3.3 (Figure S6).

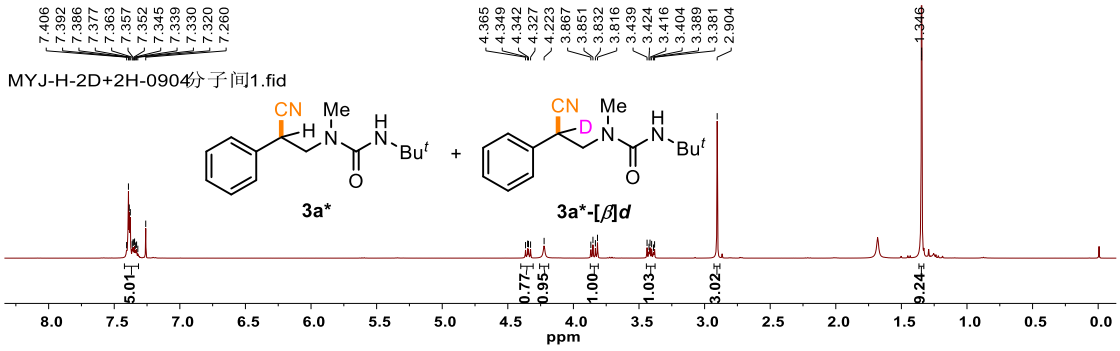
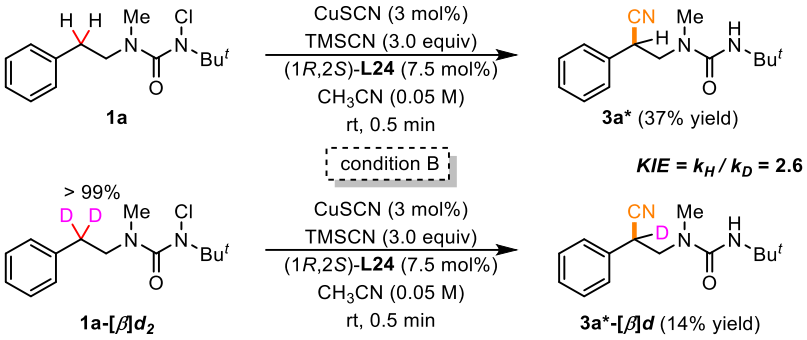


Figure S6. ^{1}H NMR spectrum of **3a*** and **3a*-[*β*]*d***

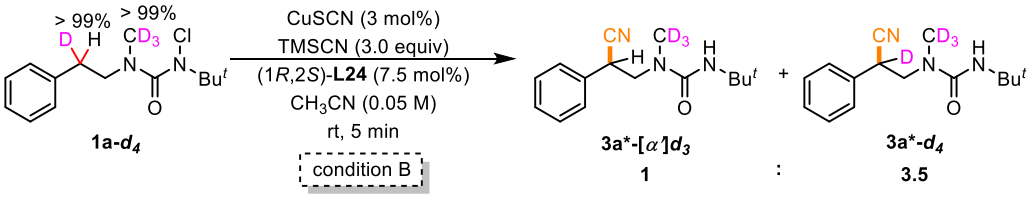
b) KIE determined from parallel reactions under condition B



Parallel reactions of 1a and 1a-[*β*]d_2 under condition B: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%), **1a** (0.1 mmol) was dissolved in degassed CH_3CN (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide **3a*** (9.6 mg, 37% yield).

In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%), **1a-[*β*]d_2** (0.1 mmol) was dissolved in degassed CH_3CN (4 mL) under N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 0.5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide **3a*-[*β*]*d*** (3.7 mg, 14% yield).

c) KIE determined from 1a-d_4 under condition B



Intramolecular cyanation of 1a-d_4 under condition B: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, CuSCN (0.006 mmol, 3 mol%), chiral bisoxazoline ligand (1*R*,2*S*)-**L24** (0.015 mmol, 7.5 mol%), **1a-d_4** (0.2 mmol) were dissolved in degassed CH_3CN (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide the mixture of **3a*-[*α'*]d_3** and **3a*-d_4**. Based on the integrations between **3a*-[*α'*]d_3** and **3a*-d_4**, the KIE is calculated to be 3.5 (Figure S7).

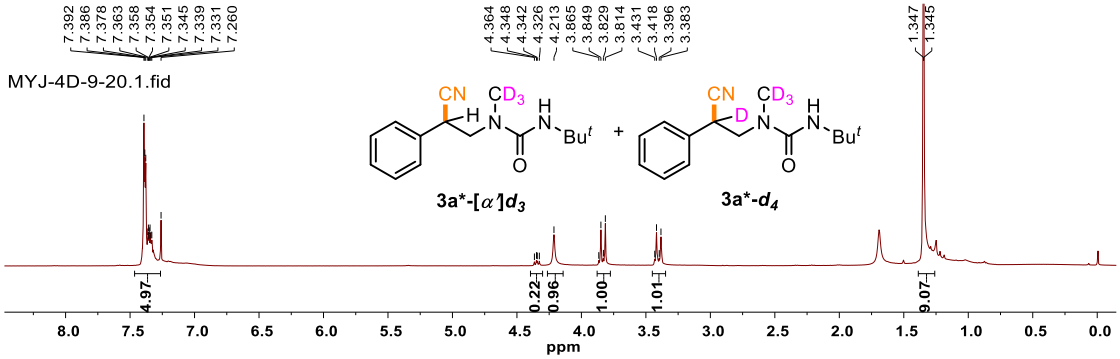
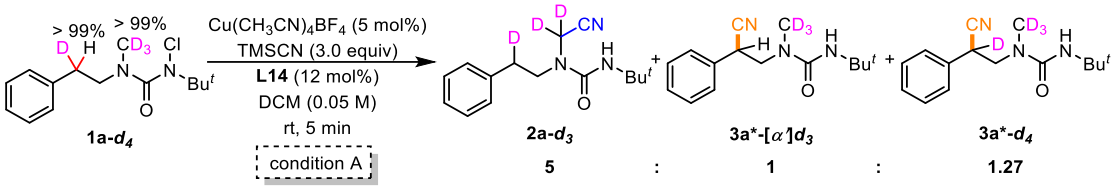


Figure S7. ^{1}H NMR spectrum of **3a*-[*α'*]*d*$_3$** and **3a*-*d*$_4$**

(3) KIE of *β*-C(sp^3)–H cyanation under condition A



Intramolecular cyanation of 1a-*d*$_4$ under condition A: In a dried sealed 10 mL Schlenk tube equipped with a stir bar, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L14** (0.024 mmol, 12 mol%) and **1a-*d*$_4$** (0.2 mmol) were dissolved in degassed DCM (4 mL) under a N_2 atmosphere, then TMSCN (80 μL, 0.6 mmol, 3.0 equiv) was added. The tube was sealed with Teflon septum and stirred at room temperature for 5 min. After completed, the mixture was concentrated under reduced pressure, and the residue was purified by preparative thin-layer chromatography (PE / EA = 10 / 1) to provide the mixture of **3a*-[*α'*]*d*$_3$** and **3a*-*d*$_4$**. Based on the integrations between **3a*-[*α'*]*d*$_3$** and **3a*-*d*$_4$**, the KIE is calculated to be 1.27 (Figure S8).

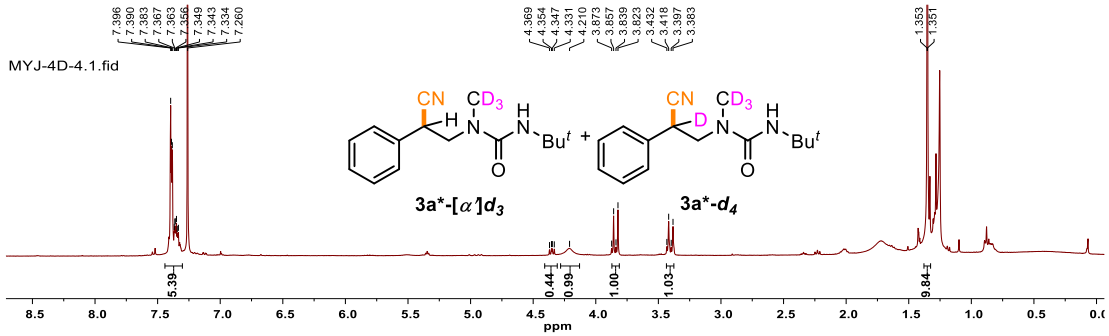


Figure S8. ^{1}H NMR spectrum of **3a*-[*α'*]*d*$_3$** and **3a*-*d*$_4$** under condition A

6.4. Proposed mechanism

Based on the above observations and previous literatures,[10,11] a plausible mechanism involving a selective HAT process as well as the proposed energy profile diagrams are depicted in Fig. S10. Firstly, the [LCu^{I}CN] species **I/I′**, formed *via* a transmetalation of each LCu^{I} catalysts with TMSCN under condition A or B, could undergo a single electron transfer with *N*-Cl urea **1** to generate a *N*-centered radical **II** and [LCu^{II}(Cl)CN] intermediates **III/III′**. For *α'*-cyanation process under condition A, the radical **II** would undergo the selective 1,4'-HAT to form a *α'*-aminomethyl radical **IV′** in the presence of [**L14**-Cu^{II}(X)CN] intermediate **III′**, which probably retards the radical trapping at the sterically more demanding *β*-position by sterically encumbered ligand **L14** and therefore facilitates the *α'*-C–H

cyanation at the less congest *N*-methyl group. We speculate that the entire activation free energy for *β* C-centered radical cyanation is probably higher than 1,4'-HAT process under condition A, thus *α'*-C–H cyanation should be kinetically more feasible (Fig. S10B, condition A). As a result, increasing the BDE of *α'*-C–H bonds (also the activation free energy of 1,4'-HAT is increased) by replacing *N*-CH_3 (~93 kcal/mol) with *N*-CD_3 (~96 kcal/mol) leads to the poor *α'*/*β* regioselectivity (1:1, see Fig. 5D). Finally, the combination of *α'*-radical **IV′** and Cu^{II}-cyanide adduct **III′** affords the *α'*-cyanation products **2** and [**L14**-Cu^{I}X] species **VI′**, which then regenerates the [**L14**-Cu^{I}CN] species **I′** with TMSCN.[12,13] However, another pathway involved an iminium ion intermediate also cannot be totally excluded.[14,15] For *β*-cyanation process under condition B, the radical **II** would undergo the entropically and enthalpically favored 1,5-HAT (see Fig. S10B, condition B) to form a benzylic *β* C-centered radical **IV**, which recombines with [**L'**-Cu^{II}(X)CN] intermediate **III** to form a Cu^{III} complex **V**. Lastly, reductive elimination of **V** provides the *β*-cyanation products **3** or **3*** along with the regenerated Cu^{I} catalyst.

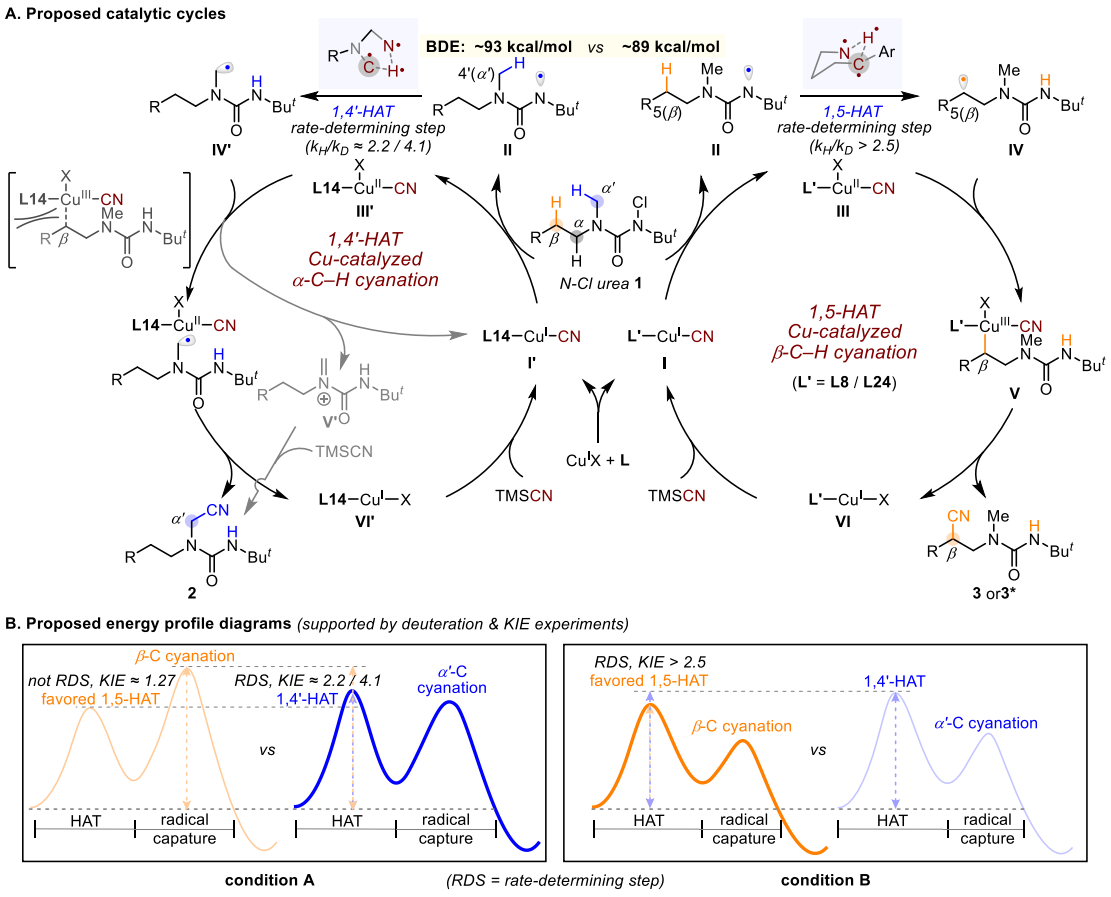


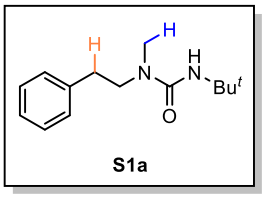
Figure S10. Proposed mechanism for selective *α'*/*β*-cyanation

6.5. DFT calculations for BDE analysis

All calculations were carried out with the Gaussian 16 software.[16] The M06-2X functional was adopted for all calculations. For geometry optimization and frequency calculations, the def2-SVP basis set was used. The single point energy calculations were performed with a larger basis set def2-TZVP basis set. The DFT-D3 dispersion correction was applied to correct the weak interaction to improve the calculation accuracy. The SMD implicit solvation model was used to account for the solvation effect. Finally, the single point energy of each compound was added to the free energy correction terms calculated before to obtain the Gibbs free energy. Bond dissociation energies for the C–H bonds were determined by

calculating the difference in energies between the optimized starting substrates and their radical energies plus hydrogen atom energies.

BDE = [E(radical) + E(H)] – E(molecule)



S1a

S1a = -458763.5 kcal/mol

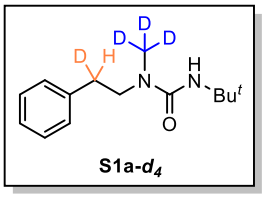
α'-rad-**S1a** = -458359.6 kcal/mol

β-rad-**S1a** = -458364.1 kcal/mol

H_{atom} = -310.6 kcal/mol

α'-C–H BDE: 93 kcal/mol

β-C–H BDE: 89 kcal/mol



S1a-*d*$_4$

S1a-*d*$_4$ = -458771.3 kcal/mol

α'-D-rad-**S1a** = -458365.0 kcal/mol

β-D-rad-**S1a** = -458370.0 kcal/mol

β-rad-**S1a** = -458371.8 kcal/mol

D_{atom} = -310.6 kcal/mol

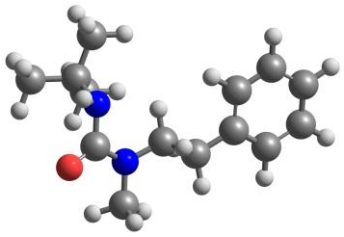
H_{atom} = -310.6 kcal/mol

α'-C–D BDE: 96 kcal/mol

β-C–D BDE: 91 kcal/mol

β-C–H BDE: 89 kcal/mol

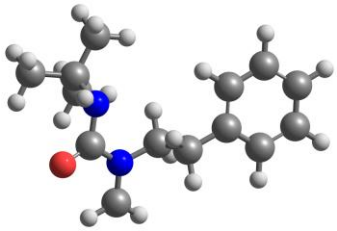
N-phenethyl-*N*-methyl urea (**S1a**)



C	-2.68361	0.1146	-0.16833
C	-1.30067	0.09996	-0.2212
C	-0.54669	0.43011	0.89678
C	-1.20463	0.76836	2.07324
C	-2.58633	0.78411	2.12835
C	-3.32976	0.4568	1.00674
H	-3.25804	-0.14133	-1.04671
H	-0.80124	-0.1656	-1.14247
H	-0.62564	1.02369	2.94937
H	-3.0855	1.05274	3.048
H	-4.40884	0.46926	1.04862
C	0.95256	0.37007	0.86198
H	1.30926	0.49617	-0.16093
H	1.37558	1.16291	1.48194
C	1.41906	-0.98526	1.42657
H	1.12382	-1.78706	0.74081
H	0.93369	-1.13547	2.38981
N	2.84517	-1.04086	1.63497
C	3.68265	-1.0095	0.4584
H	4.71299	-1.16914	0.7702
H	3.37657	-1.80174	-0.22711
H	3.62219	-0.04699	-0.05489

C	3.42579	-0.86455	2.84778
O	4.60912	-0.62307	2.98359
N	2.52721	-0.95472	3.94308
H	2.86284	-0.31452	4.65931
C	2.36446	-2.27351	4.59005
C	2.28695	-3.39767	3.55707
H	1.43337	-3.27351	2.89773
H	3.19336	-3.43075	2.95725
H	2.18322	-4.34908	4.07338
C	1.06084	-2.21289	5.39191
H	0.89093	-3.15558	5.90498
H	1.10702	-1.41785	6.1322
H	0.21962	-2.01671	4.73162
C	3.55006	-2.54189	5.52699
H	3.57631	-1.80725	6.33026
H	3.47609	-3.53234	5.96924
H	4.48278	-2.47487	4.97044

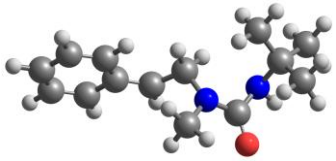
α'-radical-*N*-phenethyl-*N*-methyl urea (*α'*-rad-**S1a**)



C	-2.68361	0.1146	-0.16833
C	-1.30067	0.09996	-0.2212
C	-0.54669	0.43011	0.89678
C	-1.20463	0.76836	2.07324
C	-2.58633	0.78411	2.12835
C	-3.32976	0.4568	1.00674
H	-3.25804	-0.14133	-1.04671
H	-0.80124	-0.1656	-1.14247
H	-0.62564	1.02369	2.94937
H	-3.0855	1.05274	3.048
H	-4.40884	0.46926	1.04862
C	0.95256	0.37007	0.86198
H	1.30926	0.49617	-0.16093
H	1.37558	1.16291	1.48194
C	1.41906	-0.98526	1.42657
H	1.12382	-1.78706	0.74081
H	0.93369	-1.13547	2.38981
N	2.84517	-1.04086	1.63497
C	3.68265	-1.0095	0.4584

H	4.71299	-1.16914	0.7702
H	3.37657	-1.80174	-0.22711
C	3.42579	-0.86455	2.84778
O	4.60912	-0.62307	2.98359
N	2.52721	-0.95472	3.94308
H	2.86284	-0.31452	4.65931
C	2.36446	-2.27351	4.59005
C	2.28695	-3.39767	3.55707
H	1.43337	-3.27351	2.89773
H	3.19336	-3.43075	2.95725
H	2.18322	-4.34908	4.07338
C	1.06084	-2.21289	5.39191
H	0.89093	-3.15558	5.90498
H	1.10702	-1.41785	6.1322
H	0.21962	-2.01671	4.73162
C	3.55006	-2.54189	5.52699
H	3.57631	-1.80725	6.33026
H	3.47609	-3.53234	5.96924
H	4.48278	-2.47487	4.97044

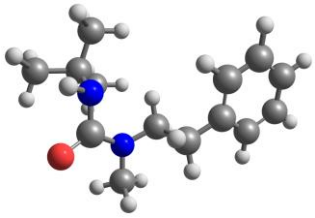
β-radical-*N*-phenethyl-*N*-methyl urea (*β*-rad-**S1a**)



C	-2.68361	0.1146	-0.16833
C	-1.30067	0.09996	-0.2212
C	-0.54669	0.43011	0.89678
C	-1.20463	0.76836	2.07324
C	-2.58633	0.78411	2.12835
C	-3.32976	0.4568	1.00674
H	-3.25804	-0.14133	-1.04671
H	-0.80124	-0.1656	-1.14247
H	-0.62564	1.02369	2.94937
H	-3.0855	1.05274	3.048
H	-4.40884	0.46926	1.04862
C	0.95256	0.37007	0.86198
H	1.37558	1.16291	1.48194
C	1.41906	-0.98526	1.42657
H	1.12382	-1.78706	0.74081
H	0.93369	-1.13547	2.38981
N	2.84517	-1.04086	1.63497
C	3.68265	-1.0095	0.4584
H	4.71299	-1.16914	0.7702

H	3.37657	-1.80174	-0.22711
H	3.62219	-0.04699	-0.05489
C	3.42579	-0.86455	2.84778
O	4.60912	-0.62307	2.98359
N	2.52721	-0.95472	3.94308
H	2.86284	-0.31452	4.65931
C	2.36446	-2.27351	4.59005
C	2.28695	-3.39767	3.55707
H	1.43337	-3.27351	2.89773
H	3.19336	-3.43075	2.95725
H	2.18322	-4.34908	4.07338
C	1.06084	-2.21289	5.39191
H	0.89093	-3.15558	5.90498
H	1.10702	-1.41785	6.1322
H	0.21962	-2.01671	4.73162
C	3.55006	-2.54189	5.52699
H	3.57631	-1.80725	6.33026
H	3.47609	-3.53234	5.96924
H	4.48278	-2.47487	4.97044

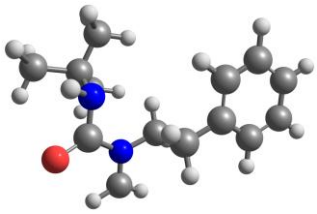
S1a-*d*$_4$



H(Iso=2)	-0.70771	3.49152	-0.38121
H(Iso=2)	-0.43742	3.12467	1.35149
H(Iso=2)	-2.09845	3.22487	0.68802
H(Iso=2)	1.51581	2.24728	-0.48712
C	4.77808	0.13419	0.61186
C	3.6395	0.90278	0.36711
C	2.5535	0.37061	-0.33543
C	2.62994	-0.95494	-0.78282
C	3.76497	-1.72598	-0.54071
C	4.84396	-1.18237	0.15822
H	5.61823	0.56739	1.15717
H	3.59412	1.93556	0.72125
H	1.78618	-1.38153	-1.33236
H	3.81008	-2.75483	-0.9017
H	5.7346	-1.78381	0.34634
C	1.29651	1.17133	-0.55931
H	0.90157	0.98064	-1.56983

C	0.2089	0.78435	0.45339
H	0.55669	1.00101	1.47685
H	0.03365	-0.2931	0.38165
N	-1.04606	1.47933	0.22611
C	-1.07007	2.90707	0.48077
C	-2.04091	0.9794	-0.56846
O	-2.88207	1.69738	-1.0799
N	-2.01065	-0.42267	-0.76653
H	-2.45399	-0.58213	-1.6702
C	-2.72437	-1.27817	0.22628
C	-2.44144	-0.8351	1.66228
H	-1.36923	-0.86119	1.89801
H	-2.81769	0.17962	1.85432
H	-2.95511	-1.52271	2.34879
C	-2.22361	-2.70655	0.01599
H	-2.75547	-3.40679	0.67654
H	-2.38925	-3.024	-1.02461
H	-1.14611	-2.76904	0.22655
C	-4.23518	-1.20086	-0.02936
H	-4.47536	-1.57108	-1.03829
H	-4.78819	-1.81243	0.69858
H	-4.58216	-0.16005	0.04302

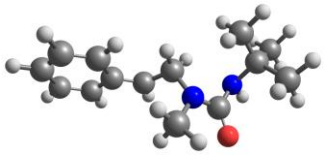
α-D-rad-**S1a**-d_4



H(Iso=2)	-0.70771	3.49152	-0.38121
H(Iso=2)	-0.43742	3.12467	1.35149
H(Iso=2)	1.51581	2.24728	-0.48712
C	4.77808	0.13419	0.61186
C	3.6395	0.90278	0.36711
C	2.5535	0.37061	-0.33543
C	2.62994	-0.95494	-0.78282
C	3.76497	-1.72598	-0.54071
C	4.84396	-1.18237	0.15822
H	5.61823	0.56739	1.15717
H	3.59412	1.93556	0.72125
H	1.78618	-1.38153	-1.33236
H	3.81008	-2.75483	-0.9017
H	5.7346	-1.78381	0.34634

C	1.29651	1.17133	-0.55931
H	0.90157	0.98064	-1.56983
C	0.2089	0.78435	0.45339
H	0.55669	1.00101	1.47685
H	0.03365	-0.2931	0.38165
N	-1.04606	1.47933	0.22611
C	-1.07007	2.90707	0.48077
C	-2.04091	0.9794	-0.56846
O	-2.88207	1.69738	-1.0799
N	-2.01065	-0.42267	-0.76653
H	-2.45399	-0.58213	-1.6702
C	-2.72437	-1.27817	0.22628
C	-2.44144	-0.8351	1.66228
H	-1.36923	-0.86119	1.89801
H	-2.81769	0.17962	1.85432
H	-2.95511	-1.52271	2.34879
C	-2.22361	-2.70655	0.01599
H	-2.75547	-3.40679	0.67654
H	-2.38925	-3.024	-1.02461
H	-1.14611	-2.76904	0.22655
C	-4.23518	-1.20086	-0.02936
H	-4.47536	-1.57108	-1.03829
H	-4.78819	-1.81243	0.69858
H	-4.58216	-0.16005	0.04302

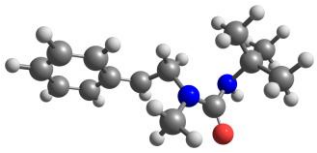
β-D-rad-**S1a**-d_4



H(Iso=2)	-0.70771	3.49152	-0.38121
H(Iso=2)	-0.43742	3.12467	1.35149
H(Iso=2)	-2.09845	3.22487	0.68802
C	4.77808	0.13419	0.61186
C	3.6395	0.90278	0.36711
C	2.5535	0.37061	-0.33543
C	2.62994	-0.95494	-0.78282
C	3.76497	-1.72598	-0.54071
C	4.84396	-1.18237	0.15822
H	5.61823	0.56739	1.15717
H	3.59412	1.93556	0.72125
H	1.78618	-1.38153	-1.33236
H	3.81008	-2.75483	-0.9017
H	5.7346	-1.78381	0.34634

C	1.29651	1.17133	-0.55931
H	0.90157	0.98064	-1.56983
C	0.2089	0.78435	0.45339
H	0.55669	1.00101	1.47685
H	0.03365	-0.2931	0.38165
N	-1.04606	1.47933	0.22611
C	-1.07007	2.90707	0.48077
C	-2.04091	0.9794	-0.56846
O	-2.88207	1.69738	-1.0799
N	-2.01065	-0.42267	-0.76653
H	-2.45399	-0.58213	-1.6702
C	-2.72437	-1.27817	0.22628
C	-2.44144	-0.8351	1.66228
H	-1.36923	-0.86119	1.89801
H	-2.81769	0.17962	1.85432
H	-2.95511	-1.52271	2.34879
C	-2.22361	-2.70655	0.01599
H	-2.75547	-3.40679	0.67654
H	-2.38925	-3.024	-1.02461
H	-1.14611	-2.76904	0.22655
C	-4.23518	-1.20086	-0.02936
H	-4.47536	-1.57108	-1.03829
H	-4.78819	-1.81243	0.69858
H	-4.58216	-0.16005	0.04302

β-rad-**S1a**-*d*$_4$

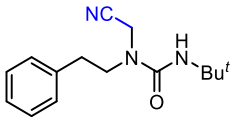


H(Iso=2)	0.6255	2.32845	0.78822
H(Iso=2)	0.70298	0.98744	1.96656
H(Iso=2)	-0.68806	2.1192	1.97111
C	4.35592	-1.05977	1.04483
C	3.02419	-0.8754	0.70051
C	2.66315	-0.1022	-0.43621
C	3.72072	0.46899	-1.19646
C	5.04701	0.27853	-0.84408
C	5.37748	-0.48809	0.27969
H	4.60505	-1.65733	1.92335
H	2.24989	-1.33243	1.31742
H	3.46908	1.06829	-2.07401
H	5.83667	0.72992	-1.44697
H	6.42164	-0.63756	0.55672

C	1.31838	0.12316	-0.83571
H(Iso=2)	1.15403	0.7643	-1.7064
C	0.08764	-0.39086	-0.15732
H	0.33151	-1.13954	0.61106
H	-0.55987	-0.87612	-0.89702
N	-0.69313	0.69119	0.44664
C	0.0273	1.58328	1.33744
C	-1.83871	1.18328	-0.12463
O	-2.18181	2.34361	0.01183
N	-2.60126	0.26101	-0.87373
H	-3.2222	0.833	-1.44408
C	-3.45559	-0.7038	-0.12241
C	-2.63272	-1.83208	0.49896
H	-2.07672	-2.38732	-0.26928
H	-1.92582	-1.44547	1.24535
H	-3.31074	-2.53362	1.00591
C	-4.41843	-1.29404	-1.15264
H	-5.07748	-2.03569	-0.68031
H	-5.0515	-0.50753	-1.59189
H	-3.85788	-1.78308	-1.9619
C	-4.24204	0.02099	0.97683
H	-4.81194	0.86245	0.55619
H	-4.94319	-0.66782	1.47017
H	-3.56147	0.42435	1.74196

7. Characterization of Cyanation Compounds

7.1 α'-Cyanation products



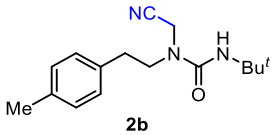
2a

3-(*tert*-Butyl)-1-(cyanomethyl)-1-phenethylurea (2a): Prepared *via* condition A from **1a** (0.2 mmol) in 69% yield (35.8 mg) and 30:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.38–7.28 (m, 3H), 7.23–7.20 (m, 2H), 4.20 (s, 2H), 3.75 (s, 1H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.0, 138.5, 129.3 (2C), 129.0 (2C), 127.2, 116.8, 50.9, 50.8, 35.0, 34.7, 28.9 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{21}N_3ONa$: 282.1577, found: 282.1578.



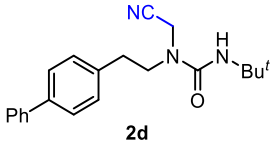
2b

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(4-methylphenethyl)urea (2b): Prepared *via* condition A from **1b** (0.2 mmol) in 70% yield (38.2 mg) and 20:1 rr as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.15 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.20 (s, 2H), 3.73 (s, 1H), 3.46 (t, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 6.3 Hz, 2H), 2.34 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.2, 137.0, 135.5, 130.1 (2C), 128.9 (2C), 117.0, 51.0, 50.9, 35.0, 34.3, 28.9 (3C), 21.1.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_3ONa$: 296.1733, found: 296.1735.



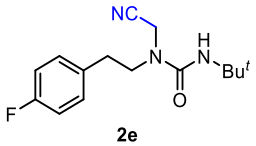
2d

1-(2-([1,1'-Biphenyl]-4-yl)ethyl)-3-(*tert*-butyl)-1-(cyanomethyl)urea (2d): Prepared *via* condition A from **1d** (0.2 mmol) in 72% yield (48.3 mg) and 20:1 rr as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.57 (t, *J* = 7.6 Hz, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.25 (s, 2H), 3.80 (s, 1H), 3.53 (t, *J* = 6.3 Hz, 2H), 2.94 (t, *J* = 6.3 Hz, 2H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.1, 140.5, 140.3, 137.6, 129.5 (2C), 128.9 (2C), 128.0 (2C), 127.5, 127.0 (2C), 116.9, 50.9, 50.8, 35.0, 34.3, 28.9 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{21}H_{25}N_3ONa$: 358.1890, found: 358.1892.



2e

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(4-fluorophenethyl)urea (2e): Prepared *via* condition A from **1e** (0.2 mmol) in 61% yield (33.8 mg) and 16:1 rr as a colorless oil.

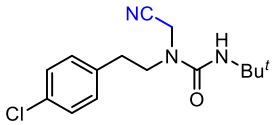
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.18 (t, *J* = 6.2 Hz, 2H), 7.04 (t, *J* = 8.3 Hz, 2H), 4.18 (s, 2H),

3.81 (s, 1H), 3.46 (t, J = 6.2 Hz, 2H), 2.87 (t, J = 6.1 Hz, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.0 (d, J = 246.0 Hz), 155.8, 134.1 (d, J = 3.3 Hz), 130.5 (d, J = 7.9 Hz, 2C), 116.8, 116.1 (d, J = 21.3 Hz, 2C), 51.0, 50.8, 35.1, 33.8, 28.9 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -115.36.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1483.



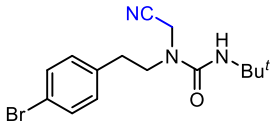
2f

3-(*tert*-Butyl)-1-(4-chlorophenethyl)-1-(cyanomethyl)urea (2f): Prepared *via* condition A from **1f** (0.2 mmol) in 62% yield (36.4 mg) and 8:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 4.17 (s, 2H), 3.80 (s, 1H), 3.45 (t, J = 6.0 Hz, 2H), 2.86 (t, J = 6.0 Hz, 2H), 1.13 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.8, 136.9, 133.2, 130.3 (2C), 129.4 (2C), 116.8, 51.1, 50.6, 35.1, 34.0, 28.9 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}ClN_3ONa$: 316.1187; found: 316.1186.



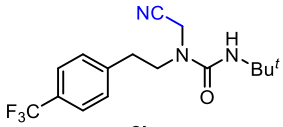
2g

1-(4-Bromophenethyl)-3-(*tert*-butyl)-1-(cyanomethyl)urea (2g): Prepared *via* condition A from **1g** (0.2 mmol) in 66% yield (44.6 mg) and 20:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.44–7.41 (m, 2H), 7.08–7.05 (m, 2H), 3.57 (s, 2H), 3.56 (t, J = 7.3 Hz, 2H), 2.82 (t, J = 7.3 Hz, 2H), 1.57 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.5, 157.4, 137.1, 131.8 (2C), 130.3 (2C), 120.7, 58.0, 49.9, 43.7, 33.6, 28.6 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}BrN_3ONa$: 360.0682, found: 360.0685.



2h

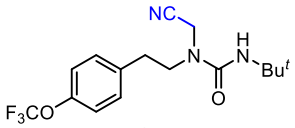
3-(*tert*-Butyl)-1-(cyanomethyl)-1-(4-(trifluoromethyl)phenethyl)urea (2h): Prepared *via* condition A from **1h** (0.2 mmol) in 69% yield (45.2 mg) and 20:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 7.7 Hz, 2H), 4.21 (s, 2H), 3.76 (s, 1H), 3.51 (t, J = 6.2 Hz, 2H), 2.98 (t, J = 6.1 Hz, 2H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.6, 142.6, 129.7 (q, J = 32.6 Hz), 129.4 (2C), 126.1 (q, J = 3.7 Hz, 2C), 124.0 (q, J = 272.0 Hz), 116.7, 51.1, 50.4, 35.1, 34.5, 28.8 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -62.61.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3ONa$: 350.1451, found: 350.1455.



2i

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(4-(trifluoromethoxy)phenethyl)urea (2i): Prepared *via* condition A

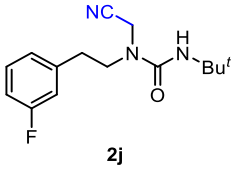
from **1i** (0.2 mmol) in 68% yield (46.7 mg) and 11:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29–7.21 (m, 4H), 4.23 (s, 2H), 3.83 (s, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.93 (t, J = 6.1 Hz, 2H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.8, 148.4, 137.2, 130.4 (2C), 121.8 (2C), 120.4 (q, J = 258.5 Hz), 116.8, 51.1, 50.6, 35.1, 33.9, 28.8 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -57.88.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3O_2Na$: 366.1400, found: 366.1398.



2j

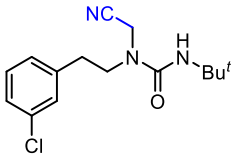
3-(*tert*-Butyl)-1-(cyanomethyl)-1-(3-fluorophenethyl)urea (2j): Prepared *via* condition A from **1j** (0.2 mmol) in 68% yield (37.7 mg) and 20:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.32 (q, J = 7.3 Hz, 1H), 7.00 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 9.4 Hz, 1H), 4.20 (s, 2H), 3.83 (s, 1H), 3.49 (t, J = 6.3 Hz, 2H), 2.90 (t, J = 6.3 Hz, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 163.2 (d, J = 247.6 Hz), 155.8, 141.0 (d, J = 7.1 Hz), 130.9 (d, J = 8.3 Hz), 124.7 (d, J = 2.9 Hz), 116.7, 115.9 (d, J = 21.0 Hz), 114.2 (d, J = 20.9 Hz), 51.0, 50.5, 35.1, 34.4, 28.9 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -111.97.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1482.



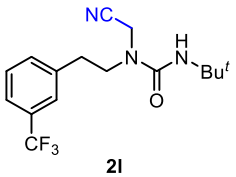
2k

3-(*tert*-Butyl)-1-(3-chlorophenethyl)-1-(cyanomethyl)urea (2k): Prepared *via* condition A from **1k** (0.2 mmol) in 70% yield (41.1 mg) and 20:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29–7.28 (m, 2H), 7.22–7.21 (m, 1H), 7.12–7.09 (m, 1H), 4.21 (s, 2H), 3.81 (s, 1H), 3.49 (t, J = 6.5 Hz, 2H), 2.88 (t, J = 6.5 Hz, 2H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.8, 140.5, 135.1, 130.6, 129.0, 127.4, 127.3, 116.7, 51.0, 50.5, 35.1, 34.3, 28.9 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}ClN_3ONa$: 316.1187, found: 316.1185.



2l

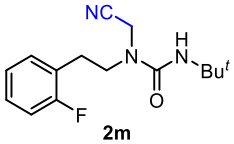
3-(*tert*-Butyl)-1-(cyanomethyl)-1-(3-(trifluoromethyl)phenethyl)urea (2l): Prepared *via* condition A from **1l** (0.2 mmol) in 65% yield (45.2 mg) and 49:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.56 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.4 Hz, 1H), 4.21 (s, 2H), 3.81 (s, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.98 (t, J = 6.4 Hz, 2H), 1.13 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.6, 139.4, 132.5, 131.6 (q, J = 32.4 Hz), 129.7, 125.5 (q, J = 3.7 Hz), 124.1 (q, J = 3.7 Hz), 123.9 (q, J = 273.5 Hz), 116.7, 51.1, 50.4, 35.2, 34.4, 28.9 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -62.83.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3ONa$: 350.1451, found: 350.1457.



2m

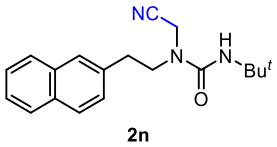
3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2-fluorophenethyl)urea (2m): Prepared *via* condition A from **1m** (0.2 mmol) in 71% yield (39.4 mg) and 7:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31–7.26 (m, 1H), 7.25–7.20 (m, 1H), 7.12 (td, *J* = 7.5, 1.2 Hz, 1H), 7.07 (ddd, *J* = 9.4, 8.2, 1.0 Hz, 1H), 4.29 (s, 1H), 4.27 (s, 2H), 3.46 (t, *J* = 7.3 Hz, 2H), 2.97 (t, *J* = 7.1 Hz, 2H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.3 (d, *J* = 244.1 Hz), 155.5, 131.4 (d, *J* = 4.7 Hz), 129.2 (d, *J* = 8.3 Hz), 124.9 (d, *J* = 3.7 Hz), 124.8 (d, *J* = 16.0 Hz), 116.8, 115.7 (d, *J* = 21.8 Hz), 51.1, 48.6, 34.9, 29.0 (3C), 28.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -118.97.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1480.



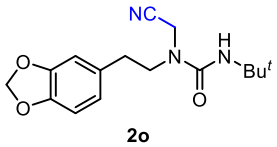
2n

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2-(naphthalen-2-yl)ethyl)urea (2n): Prepared *via* condition A from **1n** (0.2 mmol) in 65% yield (40.2 mg) and 18:1 rr as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.85–7.78 (m, 3H), 7.67 (s, 1H), 7.52–7.45 (m, 2H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.22 (s, 2H), 3.68 (s, 1H), 3.56 (t, *J* = 6.3 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H), 0.91 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.0, 135.9, 133.7, 132.4, 129.1, 127.7, 127.6, 127.6, 126.9, 126.6, 126.1, 116.9, 50.8, 50.7, 35.1, 34.9, 28.7 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{19}H_{23}N_3ONa$: 332.1733, found: 332.1734.



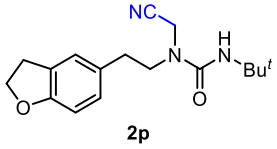
2o

1-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-3-(*tert*-butyl)-1-(cyanomethyl)urea (2o): Prepared *via* condition A from **1o** (0.2 mmol) in 58% yield (35.2 mg) and 17:1 rr as a brown yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.78 (d, *J* = 7.8 Hz, 1H), 6.68–6.64 (m, 2H), 5.94 (s, 2H), 4.19 (s, 2H), 3.86 (s, 1H), 3.43 (t, *J* = 6.0 Hz, 2H), 2.80 (t, *J* = 6.0 Hz, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.0, 148.3, 146.8, 132.1, 121.9, 116.9, 109.2, 109.0, 101.2, 50.9, 50.9, 35.0, 34.4, 29.0 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{21}N_3O_3Na$: 326.1475, found: 326.1471.



2p

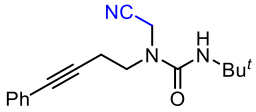
3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2-(2,3-dihydrobenzofuran-5-yl)ethyl)urea (2p): Prepared *via*

condition A from **1p** (0.2 mmol) in 55% yield (33.2 mg) and 10:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.03 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 2H), 4.21 (s, 2H), 3.76 (s, 1H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.18 (t, *J* = 8.7 Hz, 2H), 2.81 (t, *J* = 6.2 Hz, 2H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.4, 156.2, 130.3, 128.3, 128.1, 125.7, 116.9, 110.0, 71.4, 51.3, 50.8, 35.0, 34.1, 29.7, 28.9 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{23}N_3O_2Na$: 324.1682, found: 324.1680.



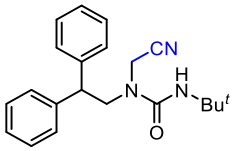
2r

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(4-phenylbut-3-yn-1-yl)urea (2r): Prepared *via* condition A from **1v** (0.2 mmol) in 57% yield (32.3 mg) and 10:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.41–7.38 (m, 2H), 7.32–7.29 (m, 3H), 4.88 (s, 1H), 4.31 (s, 2H), 3.53 (t, *J* = 6.3 Hz, 2H), 2.74 (t, *J* = 6.3 Hz, 2H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.2, 131.7, 128.5 (2C), 128.4 (2C), 122.6, 116.6, 86.4, 83.4, 51.2, 47.6, 35.1, 29.1 (3C), 19.6.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{21}N_3ONa$: 306.1577, found: 306.1578.



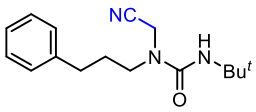
2s

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2,2-diphenylethyl)urea (2s): Prepared *via* condition A from **1r** (0.2 mmol) in 69% yield (46.3 mg) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.40–7.36 (m, 4H), 7.33–7.27 (m, 6H), 4.26 (t, *J* = 7.4 Hz, 1H), 4.14 (s, 2H), 3.90 (d, *J* = 7.4 Hz, 2H), 3.71 (s, 1H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.1, 141.7 (2C), 129.2 (4C), 128.0 (4C), 127.4 (2C), 116.8, 54.8, 50.9, 49.5, 35.3, 28.8 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{21}H_{25}N_3ONa$: 358.1890, found: 358.1892.



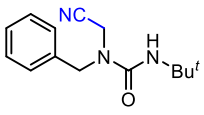
2t

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(3-phenylpropyl)urea (2t): Prepared *via* condition A from **1s** (0.2 mmol) in 72% yield (39.4 mg) and 9:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.33–7.28 (m, 2H), 7.24–7.15 (m, 3H), 4.21 (s, 2H), 4.14 (s, 1H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 1.97 (p, *J* = 7.2 Hz, 2H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.6, 140.3, 128.8 (2C), 128.3 (2C), 126.5, 116.8, 51.2, 47.1, 34.8, 32.4, 29.2, 28.8 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_3ONa$: 296.1733, found: 296.1737.



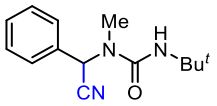
2u

1-Benzyl-3-(*tert*-butyl)-1-(cyanomethyl)urea (2u): Prepared *via* condition A from **1t** (0.2 mmol) in 43% yield (21.1 mg) and 1:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.40–7.30 (m, 4H), 7.26–7.24 (m, 1H), 4.46 (s, 2H), 4.41 (s, 1H), 4.31 (s, 2H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.1, 135.6, 129.3, 128.4, 126.8, 116.4, 51.7, 51.4, 35.6, 29.1 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{19}N_3ONa$: 268.1420, found: 268.1424.



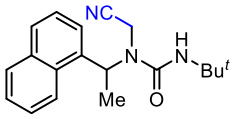
2u'

3-(*tert*-Butyl)-1-(cyano(phenyl)methyl)-1-methylurea (2u'): Prepared *via* condition A from **1t** (0.2 mmol) in 40% yield (19.6 mg) and 1:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.44–7.34 (m, 5H), 6.88 (s, 1H), 4.49 (s, 1H), 2.69 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.1, 133.1, 129.1 (2C), 129.0 (2C), 127.0, 117.0, 51.5, 49.8, 30.4, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{19}N_3ONa$: 268.1420, found: 268.1423.



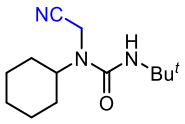
2v

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(1-(naphthalen-1-yl)ethyl)urea (2v): Prepared *via* condition A from **1u** (0.2 mmol) in 58% yield (35.9 mg) and 15:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.97–7.95 (m, 1H), 7.90–7.85 (m, 2H), 7.59–7.48 (m, 4H), 5.87 (q, *J* = 6.9 Hz, 1H), 4.45 (s, 1H), 4.05 (d, *J* = 18.1 Hz, 1H), 3.65 (d, *J* = 18.1 Hz, 1H), 1.79 (d, *J* = 7.0 Hz, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.4, 135.1, 134.0, 131.3, 129.5, 129.1, 127.1, 126.3, 125.2, 124.5, 122.9, 116.9, 51.6, 51.2, 30.6, 29.3 (3C), 17.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{19}H_{23}N_3ONa$: 332.1733, found: 332.1734.



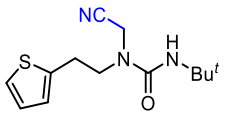
2w

3-(*tert*-Butyl)-1-(cyanomethyl)-1-cyclohexylurea (2w): Prepared *via* condition A from **1w** (0.2 mmol) in 72% yield (34.2 mg) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 4.38 (s, 1H), 4.11 (s, 2H), 3.44–3.35 (m, 1H), 1.84 (d, *J* = 10.6 Hz, 4H), 1.68–1.65 (m, 1H), 1.49–1.39 (m, 2H), 1.33 (s, 9H), 1.30–1.18 (m, 2H), 1.16–1.05 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.6, 117.9, 56.3, 51.3, 31.1 (2C), 29.7, 29.3 (3C), 25.8 (2C), 25.2.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{23}N_3ONa$: 260.1733, found: 260.1734.



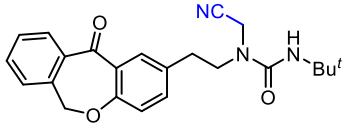
2x

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2-(thiophen-2-yl)ethyl)urea (2x): Prepared *via* condition A from **1x** (0.2 mmol) in 57% yield (30.3 mg) and 15:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25 (d, *J* = 4.7 Hz, 1H), 7.00–6.83 (m, 2H), 4.24 (s, 2H), 3.95 (s, 1H), 3.53 (t, *J* = 5.6 Hz, 2H), 3.14 (t, *J* = 5.5 Hz, 2H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.0, 140.1, 127.8, 126.5, 125.0, 116.8, 51.0, 50.8, 34.9, 28.9 (3C), 28.7.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{19}N_3OSNa$: 288.1141, found: 288.1141.



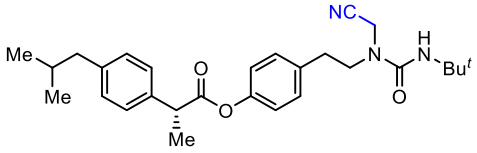
2z

3-(*tert*-Butyl)-1-(cyanomethyl)-1-(2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)ethyl)urea (2z): Prepared *via* condition A from **1z** (0.2 mmol) in 58% yield (45.4 mg) and 17:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.07 (d, *J* = 2.2 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (ddd, *J* = 16.6, 7.9, 1.8 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 5.18 (s, 2H), 4.22 (s, 2H), 3.98 (s, 1H), 3.50 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.6 Hz, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 190.8, 160.5, 155.7, 140.3, 136.2, 135.5, 133.0, 132.0, 131.5, 129.5, 129.4, 127.9, 125.6, 121.7, 116.7, 73.7, 51.0, 50.4, 35.1, 33.6, 29.0 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{23}H_{25}N_3O_3Na$: 414.1788, found: 414.1788.



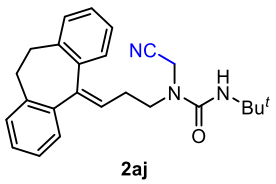
2aa

4-(2-(3-(*tert*-Butyl)-1-(cyanomethyl)ureido)ethyl)phenyl (*R*)-2-(4-isobutylphenyl)propanoate (2aa): Prepared *via* condition A from **1aa** (0.2 mmol) in 61% yield (56.6 mg) and 12:1 rr as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.28 (d, *J* = 7.9 Hz, 2H), 7.18–7.13 (m, 4H), 6.98 (d, *J* = 7.8 Hz, 2H), 4.17 (s, 2H), 3.96–3.90 (m, 1H), 3.86 (s, 1H), 3.46 (t, *J* = 6.3 Hz, 2H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.91–1.81 (m, 1H), 1.60 (d, *J* = 7.1 Hz, 3H), 1.16 (s, 9H), 0.91 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 173.1, 155.8, 150.1, 140.9, 137.1, 135.7, 129.8 (2C), 129.5 (2C), 127.2 (2C), 122.2 (2C), 116.8, 51.1, 50.6, 45.2, 45.0, 35.2, 34.0, 30.2 (3C), 29.0, 22.4 (2C), 18.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{28}H_{37}N_3O_3Na$: 486.2727, found: 486.2729.



2aj

3-(*tert*-Butyl)-1-(3-(10,11-dihydro-5H-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-1-methylurea (2aj): Prepared *via* condition A from **1aj** (0.2 mmol) in 62% yield (48.1 mg) and 20:1 rr as a colorless

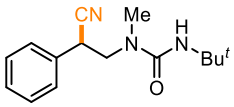
oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.27–714 (m, 6H), 7.09–7.04 (m, 2H), 5.83 (t, *J* = 7.5 Hz, 1H), 4.22 (s, 1H), 4.20–4.01 (m, 2H), 3.37–3.23 (m, 4H), 3.00–2.94 (m, 1H), 2.79 (d, *J* = 11.4 Hz, 1H), 2.50–2.41 (m, 2H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 155.6, 146.6, 140.3, 139.4, 139.3, 137.0, 130.3, 128.3 (2C), 128.0, 127.8, 127.6, 126.2, 126.1, 125.9, 116.6, 51.2, 47.8, 34.6, 33.8, 31.9, 29.1 (3C), 28.0.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{25}H_{29}N_3ONa$: 410.2203; found: 410.2204.

7.2 *β*-Cyanation products



3a*

3-(*tert*-Butyl)-1-(2-cyano-2-phenylethyl)-1-methylurea (3a*): Prepared *via* condition B from **1a** (0.2 mmol) in 68% yield (35.3 mg) and 97:3 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.41–7.32 (m, 5H), 4.37 (dd, *J* = 9.0, 6.3 Hz, 1H), 4.24 (s, 1H), 3.87 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.43 (dd, *J* = 13.9, 9.0 Hz, 1H), 2.93 (s, 3H), 1.37 (s, 9H).

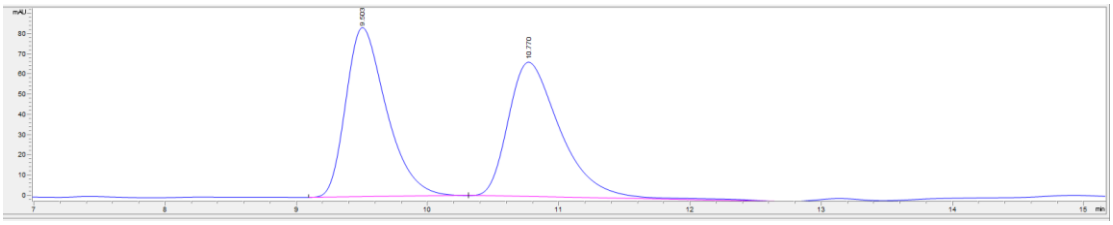
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 133.4, 129.2 (2C), 128.4, 127.7 (2C), 120.4, 55.4, 51.0, 37.2, 36.9, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{21}N_3ONa$: 282.1577, found: 282.1578.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 9.7 min, t_R (major) = 10.9 min.

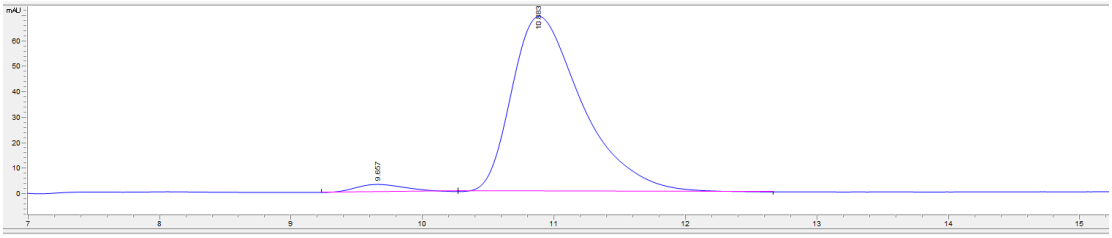
$[\alpha]_D^{21}$ = -11.5 (c = 0.8, CH_2Cl_2).

Racemic sample:



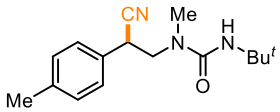
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.503	1799.6	83.7	0.327	0.653	49.278	BB
2	10.77	1852.3	66.5	0.4229	0.586	50.722	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.657	80.9	3	0.4133	0.748	3.037	BB
2	10.883	2583	69.1	0.5681	0.587	96.963	BB

Enriched sample:



3b*

3-(*tert*-Butyl)-1-(2-cyano-2-(p-tolyl)ethyl)-1-methylurea (3b*): Prepared *via* condition B from **1b** (0.2 mmol) in 74% yield (40.5 mg) and 96:4 er as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.27–7.25 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.31 (dd, *J* = 9.0, 6.4 Hz, 1H), 4.22 (s, 1H), 3.82 (dd, *J* = 13.9, 6.4 Hz, 1H), 3.41 (dd, *J* = 13.9, 9.0 Hz, 1H), 2.92 (s, 3H), 2.36 (s, 3H), 1.36 (s, 9H).

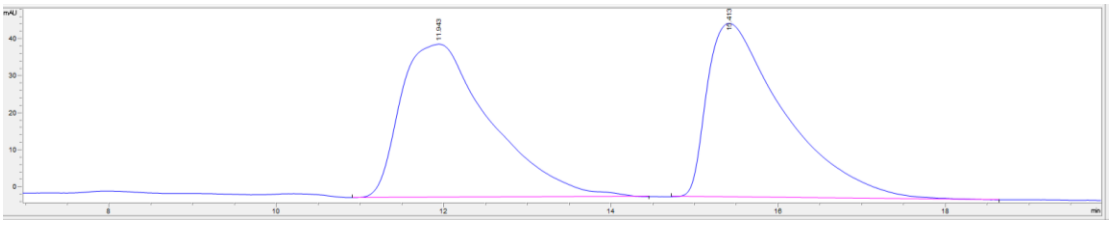
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 138.2, 130.3 (2C), 129.8 (2C), 127.5, 120.6, 55.4, 51.0, 36.8, 36.8, 29.4 (3C), 21.1.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_3ONa$: 296.1733, found: 296.1735.

Chiral HPLC: Chiralcel IB column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (major) = 12.0 min, t_R (minor) = 15.7 min.

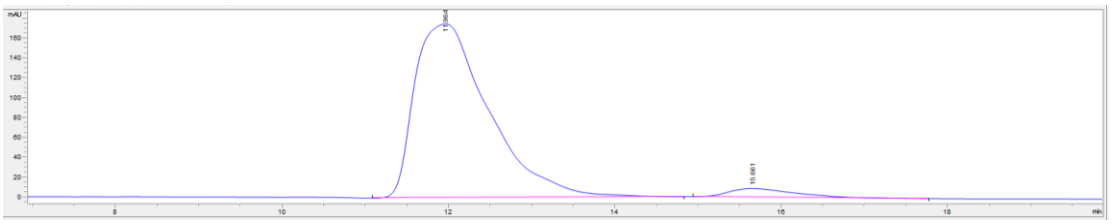
$[\alpha]_D^{21}$ = -9.3 (c = 0.8, CH_2Cl_2).

Racemic sample:

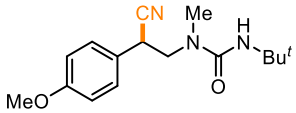


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.943	3087.6	41.3	0.9746	0.678	50.619	BB
2	15.413	3012.1	46.9	0.9118	0.364	49.381	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.964	10862.9	175.7	0.9272	0.634	95.823	BB
2	15.661	473.5	8.6	0.6709	0.553	4.177	BB



3c*

3-(*tert*-Butyl)-1-(2-cyano-2-(4-methoxyphenyl)ethyl)-1-methylurea (3c*): Prepared *via* condition B from **1c** (0.2 mmol) in 71% yield (41.1 mg) and 95:5 er as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.30–7.27 (m, 2H), 6.90–6.86 (m, 2H), 4.29 (dd, *J* = 8.9, 6.4 Hz, 1H), 4.17 (s, 1H), 3.80 (s, 3H), 3.77 (dd, 1H), 3.41 (dd, *J* = 13.9, 8.9 Hz, 1H), 2.90 (s, 3H), 1.35 (s, 9H).

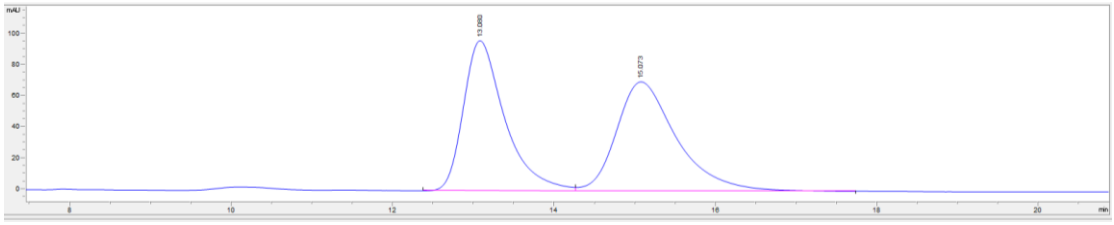
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.6, 156.9, 128.8 (2C), 125.3, 120.6, 114.5 (2C), 55.4, 55.3, 50.9, 36.8, 36.3, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{23}N_3O_2Na$: 312.1682, found: 312.1680.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 13.1 min, t_R (major) = 15.1 min.

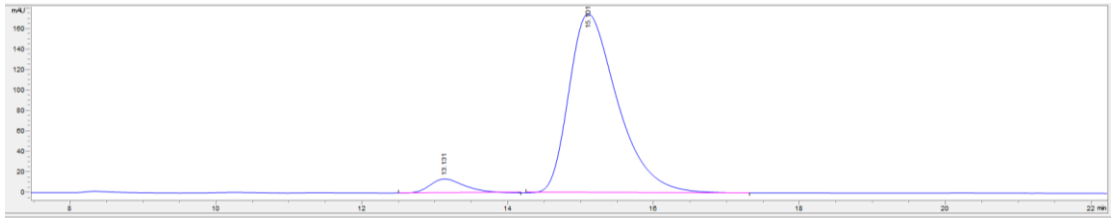
$[\alpha]_D^{21}$ = -7.4 (c = 0.5, CH_2Cl_2).

Racemic sample:

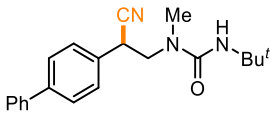


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.08	3451.2	96.8	0.528	0.626	48.668	BV
2	15.073	3640.1	70.4	0.7756	0.647	51.332	VB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.131	451	13.6	0.503	0.671	5.283	BB
2	15.101	8086.2	174.7	0.7001	0.618	94.717	BB



3d*

1-(2-([1,1'-Biphenyl]-4-yl)-2-cyanoethyl)-3-(*tert*-butyl)-1-methylurea (3d*): Prepared *via* condition B from **1d** (0.2 mmol) in 65% yield (43.6 mg) and 97:3 er as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61–7.56 (m, 4H), 7.44 (dd, *J* = 14.3, 7.9 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 4.39 (dd, *J* = 8.9, 6.3 Hz, 1H), 4.26 (s, 1H), 3.88 (dd, *J* = 13.9, 6.3 Hz, 1H), 3.45 (dd, *J* = 13.9, 9.0 Hz, 1H), 2.93 (s, 3H), 1.35 (s, 9H).

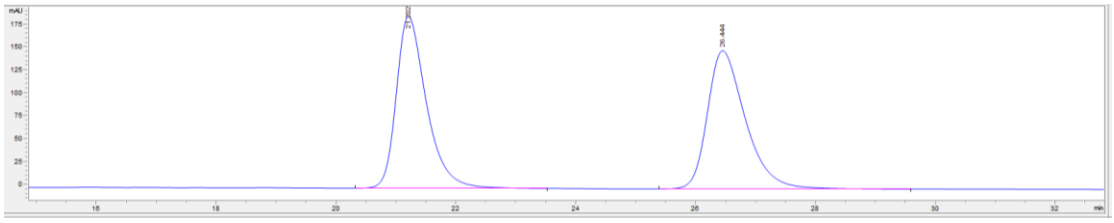
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 141.4, 140.2, 132.3, 128.9 (2C), 128.1 (2C), 127.8 (2C), 127.7, 127.1 (2C), 120.4, 55.3, 51.0, 36.9, 36.8, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{21}H_{25}N_3ONa$: 358.1890, found: 358.1885.

Chiral HPLC: Chiralcel IF column, hexane:*i*PrOH (95:5), 1.0 mL/min, 254 nm, t_R (minor) = 21.5 min, t_R (major) = 26.6 min.

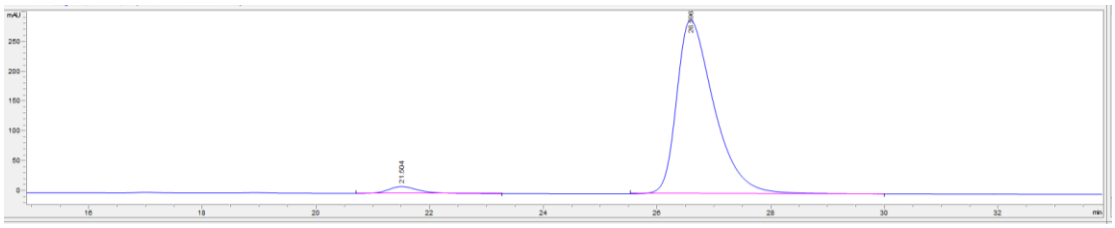
$[\alpha]_D^{21}$ = -26.8 (c = 0.8, CH_2Cl_2).

Racemic sample:

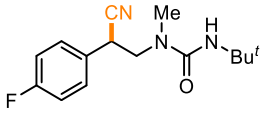


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.202	6570	188.3	0.5251	0.639	49.687	BB
2	26.444	6652.7	151.1	0.6637	0.632	50.313	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.504	420.8	11.5	0.5405	0.727	3.071	BB
2	26.596	13279.5	290.4	0.6935	0.554	96.929	BB



3e*

3-(*tert*-Butyl)-1-(2-cyano-2-(4-fluorophenyl)ethyl)-1-methylurea (3e*): Prepared *via* condition B from **1e** (0.2 mmol) in 60% yield (33.3 mg) and 95:5 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.38–7.35 (m, 2H), 7.09–7.05 (m, 2H), 4.34 (ddd, *J* = 8.7, 6.2, 2.0 Hz, 1H), 4.25 (s, 1H), 3.82 (ddd, *J* = 13.8, 6.2, 2.1 Hz, 1H), 3.38 (ddd, *J* = 13.8, 9.1, 2.0 Hz, 1H), 2.91 (d, *J* = 2.0 Hz, 3H), 1.35 (d, *J* = 2.0 Hz, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.6 (d, *J* = 247.6 Hz), 156.8, 129.4 (d, *J* = 8.3 Hz, 2C), 129.2 (d, *J* = 3.3 Hz), 120.3, 116.1 (d, *J* = 21.9 Hz, 2C), 55.4, 51.0, 36.9, 36.4, 29.4 (3C).

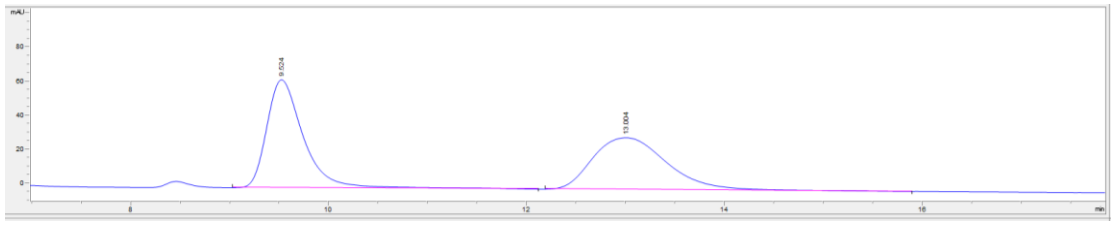
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -113.37.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1485.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 9.5 min, t_R (major) = 12.9 min.

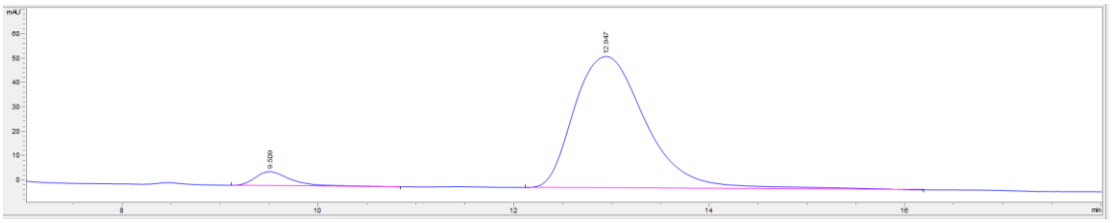
$[\alpha]_D^{21}$ = -13.4 (c = 1.0, CH_2Cl_2).

Racemic sample:

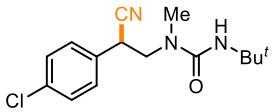


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.524	1656.7	63.7	0.3894	0.609	50.681	BB
2	13.004	1612.2	30.7	0.8276	0.743	49.319	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.509	143.1	5.7	0.3662	0.662	4.932	BB
2	12.947	2758	53.8	0.8023	0.726	95.068	BB



3f*

3-(*tert*-Butyl)-1-(2-(4-chlorophenyl)-2-cyanoethyl)-1-methylurea (3f*): Prepared *via* condition B from **1f** (0.2 mmol) in 67% yield (39.4 mg) and 96:4 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.36–7.31 (m, 4H), 4.37 (dd, *J* = 9.1, 6.1 Hz, 1H), 4.23 (s, 1H), 3.84 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.39 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.93 (s, 3H), 1.37 (s, 9H).

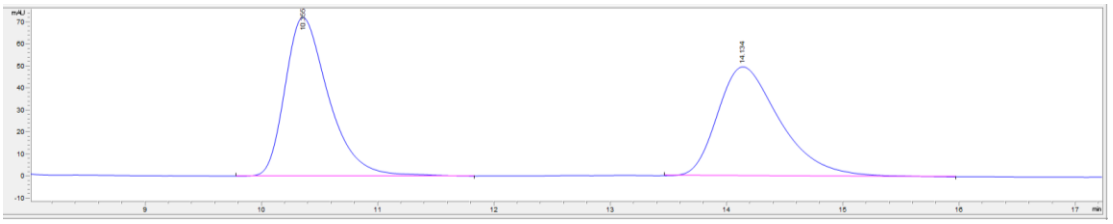
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 134.4, 131.9, 129.3 (2C), 129.0 (2C), 120.1, 55.3, 51.0, 37.0, 36.6, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}ClN_3ONa$: 316.1187, found: 316.1189.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 10.6 min, t_R (major) = 14.3 min.

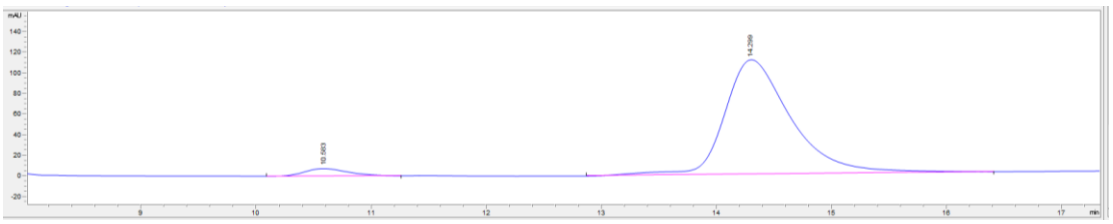
$[\alpha]_D^{21}$ = -8.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

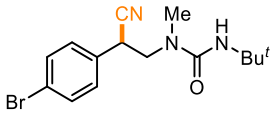


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.355	1861.6	71.8	0.3926	0.65	50.298	BB
2	14.134	1839.6	49.3	0.567	0.638	49.702	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.583	187.1	7.2	0.3958	0.735	4.023	BB
2	14.299	4463.3	110.9	0.5995	0.655	95.977	BB



3g*

1-(2-(4-Bromophenyl)-2-cyanoethyl)-3-(*tert*-butyl)-1-methylurea (3g*): Prepared *via* condition B from **1g** (0.2 mmol) in 55% yield (37.2 mg) and 90:10 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.51–7.49 (m, 2H), 7.29–7.27 (m, 2H), 4.34 (dd, *J* = 9.1, 6.1 Hz, 1H), 4.26 (s, 1H), 3.83 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.37 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.92 (s, 3H), 1.35 (s, 9H).

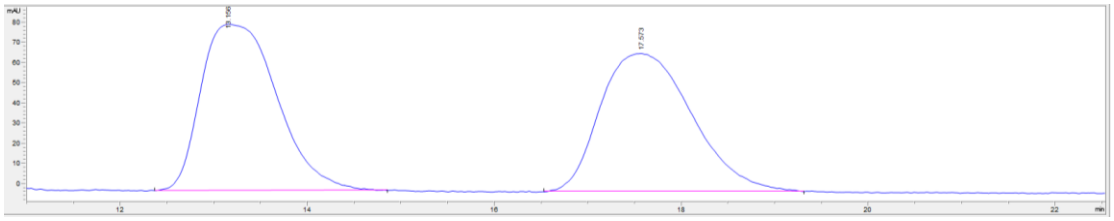
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 132.4, 132.3 (2C), 129.3 (2C), 122.5, 120.0, 55.3, 51.1, 37.0, 36.7, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}BrN_3ONa$: 360.0682, found: 360.0682.

Chiral HPLC: Chiralcel OD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 13.2 min, t_R (major) = 17.5 min.

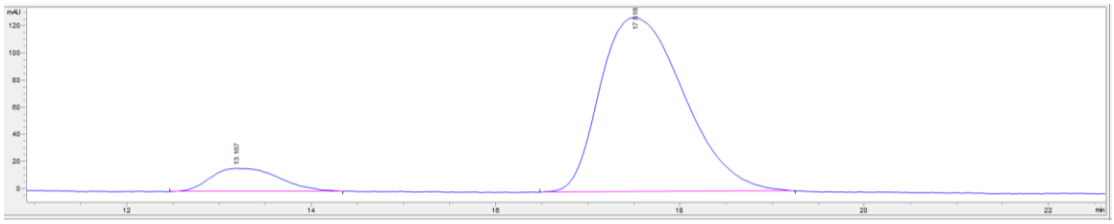
$[\alpha]_D^{21}$ = -32.5 (c = 1.0, CH_2Cl_2).

Racemic sample:

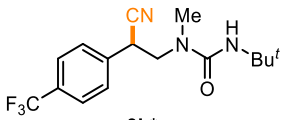


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.156	4672.4	82.7	0.6773	0.566	49.995	BV R
2	17.573	4673.4	68.6	0.8113	0.786	50.005	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.187	889.3	17.1	0.6271	0.587	9.842	BB
2	17.518	8146.6	128.8	0.7662	0.708	90.158	BB



3h*

3-(*tert*-Butyl)-1-(2-cyano-2-(4-(trifluoromethyl)phenyl)ethyl)-1-methylurea (3h*): Prepared *via* condition B from **1h** (0.2 mmol) in 56% yield (36.7 mg) and 93:7 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 4.45 (dd, *J* = 9.1, 6.0 Hz, 1H), 4.28 (s, 1H), 3.88 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.39 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.93 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 137.3, 130.7 (q, *J* = 32.9 Hz), 128.1 (2C), 126.1 (q, *J* = 3.8 Hz, 2C), 123.8 (q, *J* = 272.7 Hz), 119.7, 55.2, 51.1, 37.0, 37.0, 29.3 (3C).

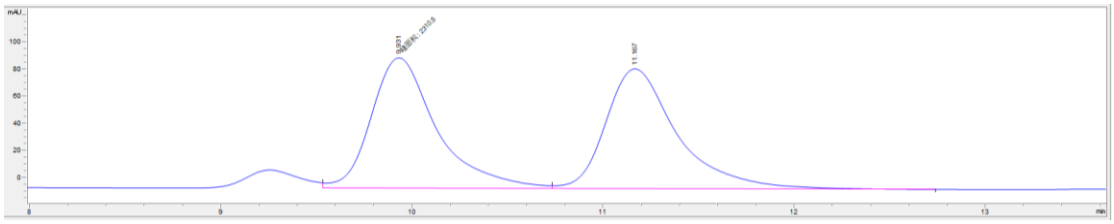
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -62.71.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3ONa$: 350.1451, found: 350.1452.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 10.0 min, t_R (major) = 11.2 min.

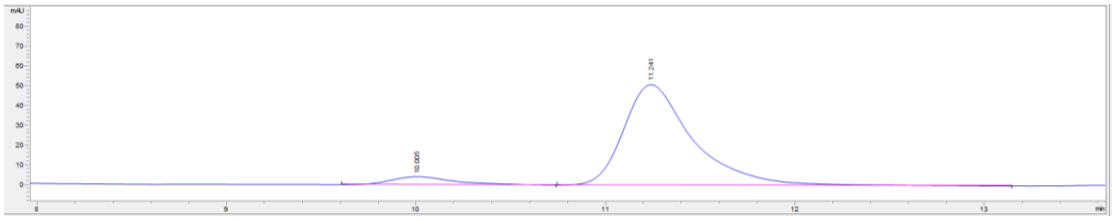
$[\alpha]_D^{21}$ = -9.1 (c = 1.0, CH_2Cl_2).

Racemic sample:

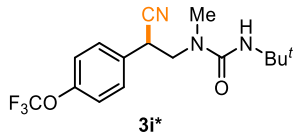


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.931	2310.5	96.6	0.3988	0.707	49.971	FM
2	11.167	2313.2	88.8	0.3901	0.639	50.029	VB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.005	94.9	4.1	0.3409	0.655	6.787	BB
2	11.241	1304	51.1	0.3756	0.602	93.213	BB



3i*

3-(*tert*-Butyl)-1-(2-cyano-2-(4-(trifluoromethoxy)phenyl)ethyl)-1-methylurea (3i*): Prepared *via* condition B from **1i** (0.2 mmol) in 57% yield (39.1 mg) and 93:7 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.44 (d, *J* = 8.3 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 4.39 (t, *J* = 7.5 Hz, 1H), 4.27 (s, 1H), 3.87 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.37 (dd, *J* = 13.9, 9.4 Hz, 1H), 2.94 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 149.2, 132.1, 129.2 (2C), 121.6 (2C), 120.4 (q, *J* = 258.2 Hz), 120.1, 55.3, 51.1, 36.9, 36.6, 29.4 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -57.91.

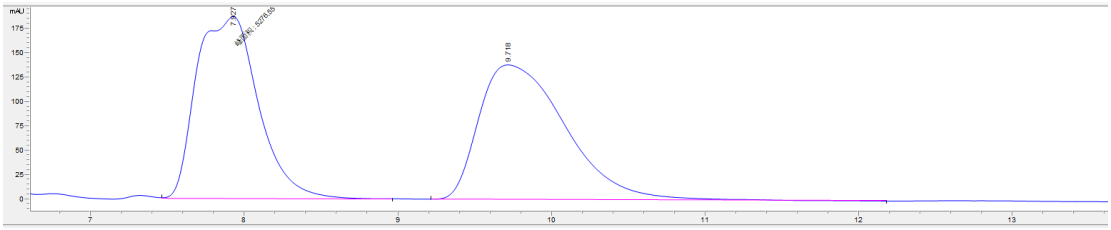
HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3O_2Na$: 366.1400, found: 366.1397.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 7.7 min,

t_R (major) = 9.8 min.

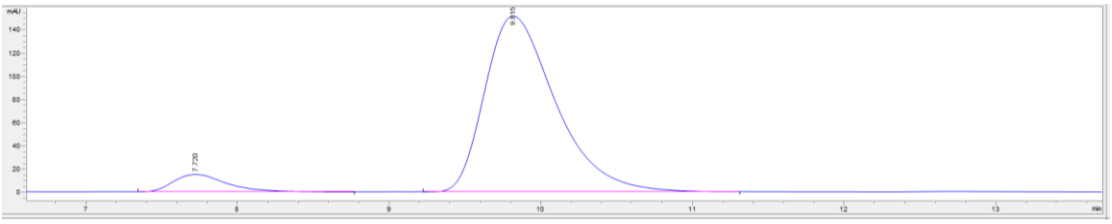
$[\alpha]_D^{21}$ = -9.0 (c = 0.8, CH_2Cl_2).

Racemic sample:

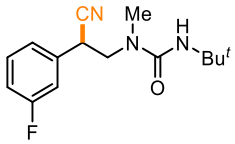


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.927	5276.5	187.1	0.47	0.394	49.295	MM T
2	9.718	5427.4	138	0.6248	0.485	50.705	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.72	365	14.9	0.3861	0.647	6.949	BB
2	9.815	4888	150.9	0.4979	0.628	93.051	BB



3j*

3-(*tert*-Butyl)-1-(2-cyano-2-(3-fluorophenyl)ethyl)-1-methylurea (3j*): Prepared *via* condition B from **1j** (0.2 mmol) in 61% yield (33.8 mg) and 95:5 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35 (td, *J* = 8.0, 5.8 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.12 (dt, *J* = 9.4, 2.1 Hz, 1H), 7.06–7.01 (m, 1H), 4.38 (dd, *J* = 9.1, 6.2 Hz, 1H), 4.26 (s, 1H), 3.85 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.40 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.92 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 163.0 (d, *J* = 247.9 Hz), 156.8, 135.7 (d, *J* = 7.5 Hz), 130.8 (d, *J* = 8.3 Hz), 123.4 (d, *J* = 3.1 Hz), 120.0, 115.5 (d, *J* = 21.0 Hz), 114.9 (d, *J* = 22.7 Hz), 55.3, 51.1, 37.0, 36.9 (d, *J* = 2.0 Hz), 29.4 (3C).

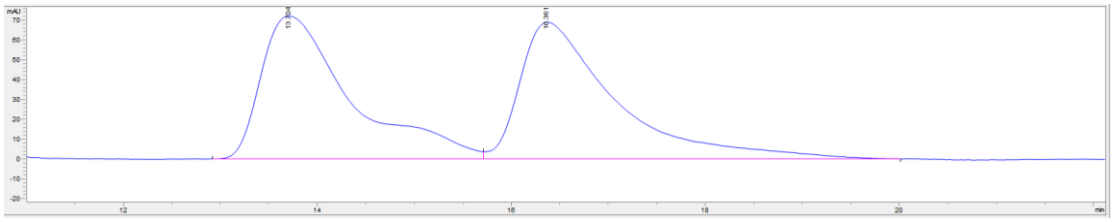
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -111.53.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1486.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (97:3), 1.0 mL/min, 220 nm, t_R (minor) = 13.6 min, t_R (major) = 16.4 min.

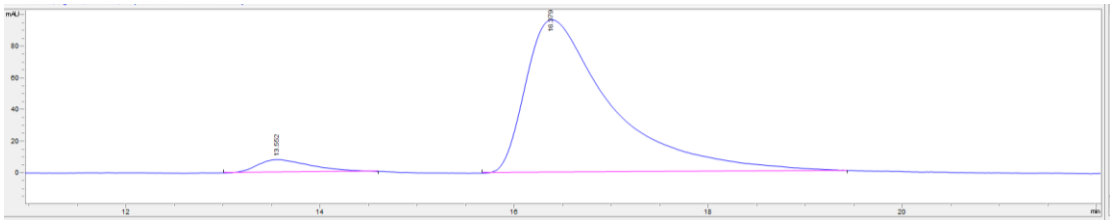
$[\alpha]_D^{21}$ = -25.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

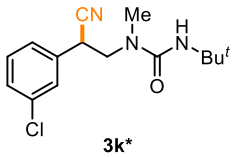


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.704	4592.2	71.8	0.8945	0.418	49.633	BV
2	16.361	4660.2	68.7	0.9072	0.371	50.367	VB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.552	313.6	8.1	0.4694	0.545	5.023	BB
2	16.379	5929.9	96.8	0.8484	0.404	94.977	BB



3k*

3-(*tert*-Butyl)-1-(2-(3-chlorophenyl)-2-cyanoethyl)-1-methylurea (3k*): Prepared *via* condition B from **1k** (0.2 mmol) in 62% yield (36.5 mg) and 96:4 er as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.42 (q, *J* = 1.5 Hz, 1H), 7.33 (m, 3H), 4.38 (d, *J* = 2.9 Hz, 1H), 4.29 (s, 1H), 3.86 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.41 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.93 (s, 3H), 1.37 (s, 9H).

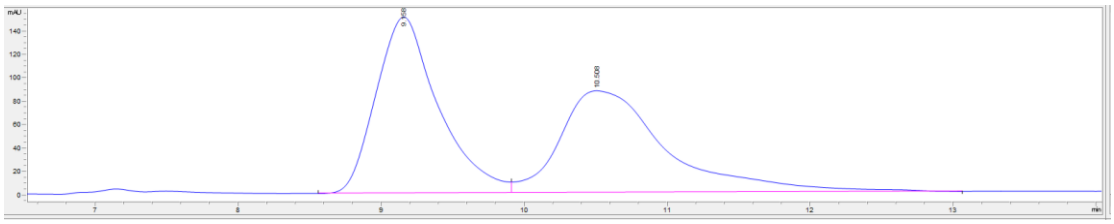
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 135.3, 135.0, 130.4, 128.6, 127.8, 125.9, 119.9, 55.3, 51.1, 37.0, 36.8, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}ClN_3ONa$: 316.1188, found: 316.1185.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 8.8 min, t_R (major) = 10.3 min.

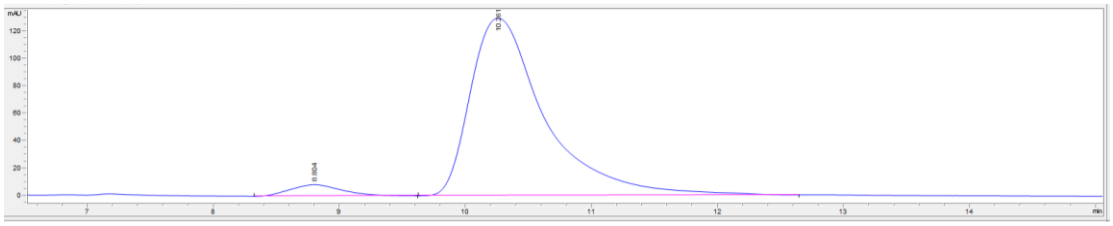
$[\alpha]_D^{21}$ = -6.2 (c = 0.7, CH_2Cl_2).

Racemic sample:

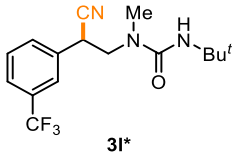


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.158	4561.3	150.1	0.4546	0.739	50.370	BV
2	10.508	4494.3	86.6	0.7735	0.497	49.630	VB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.804	235.8	8.2	0.4124	0.841	4.263	BB
2	10.261	5295.6	129.1	0.6164	0.537	95.737	BB



3l*

3-(*tert*-Butyl)-1-(2-cyano-2-(3-(trifluoromethyl)phenyl)ethyl)-1-methylurea (3l*): Prepared *via* condition B from **1l** (0.2 mmol) in 52% yield (34.0 mg) and 95:5 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63–7.59 (m, 3H), 7.54–7.50 (m, 1H), 4.48 (dd, *J* = 9.1, 6.3 Hz, 1H), 4.28 (s, 1H), 3.84 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.43 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.90 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 134.4, 132.6 (q, *J* = 32.7 Hz), 131.1, 129.8, 125.3 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 267.5 Hz), 124.5 (q, *J* = 3.8 Hz), 119.7, 55.3, 51.1, 37.0, 36.9, 29.3 (3C).

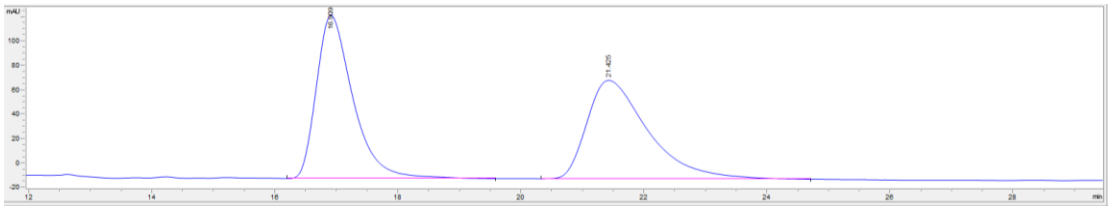
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -62.64.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3N_3ONa$: 350.1451, found: 350.1453.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (98:2), 1.0 mL/min, 220 nm, t_R (minor) = 17.7 min, t_R (major) = 23.1 min.

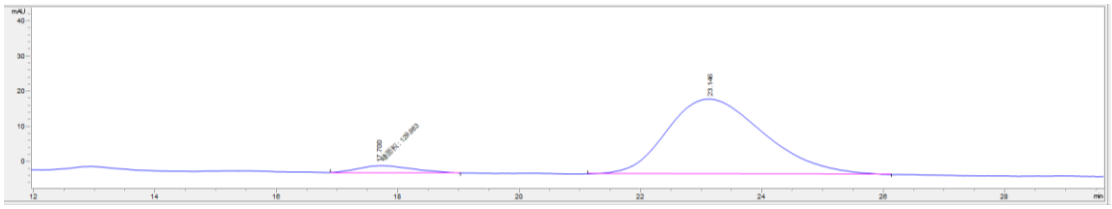
$[\alpha]_D^{21}$ = -11.7 (c = 1.0, CH_2Cl_2).

Racemic sample:

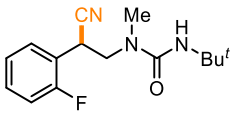


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.909	5506.5	133.2	0.6222	0.616	49.922	BB
2	21.425	5523.6	80.4	1.0117	0.523	50.078	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.7	130	2.1	1.0564	0.665	5.193	MM T
2	23.146	2373.2	21.2	1.3195	0.773	94.807	BB



3m*

3-(*tert*-Butyl)-1-(2-cyano-2-(2-fluorophenyl)ethyl)-1-methylurea (3m*): Prepared *via* condition B from **1m** (0.2 mmol) in 65% yield (36.0 mg) and 99:1 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.44 (td, *J* = 7.6, 1.7 Hz, 1H), 7.36–7.30 (m, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08 (ddd, *J* = 9.5, 8.4, 0.9 Hz, 1H), 4.52 (dd, *J* = 8.4, 6.6 Hz, 1H), 4.24 (s, 1H), 3.75 (dd, *J* = 13.9, 6.7 Hz, 1H), 3.65 (dd, *J* = 13.9, 8.4 Hz, 1H), 2.89 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 160.3 (d, *J* = 248.4 Hz), 156.7, 130.5 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 3.4 Hz), 124.9 (d, *J* = 3.6 Hz), 120.7 (d, *J* = 14.2 Hz), 119.3, 116.0 (d, *J* = 21.2 Hz), 52.9 (d, *J* = 1.6 Hz), 51.0, 36.5, 31.5 (d, *J* = 1.9 Hz), 29.3 (3C).

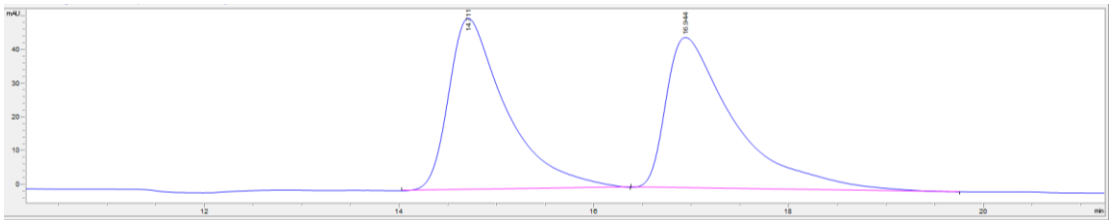
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -117.36.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{20}FN_3ONa$: 300.1483, found: 300.1480.

Chiral HPLC: Chiralcel IB column, hexane:*i*PrOH (97:3), 1.0 mL/min, 220 nm, t_R (major) = 14.6 min, t_R (minor) = 17.3 min.

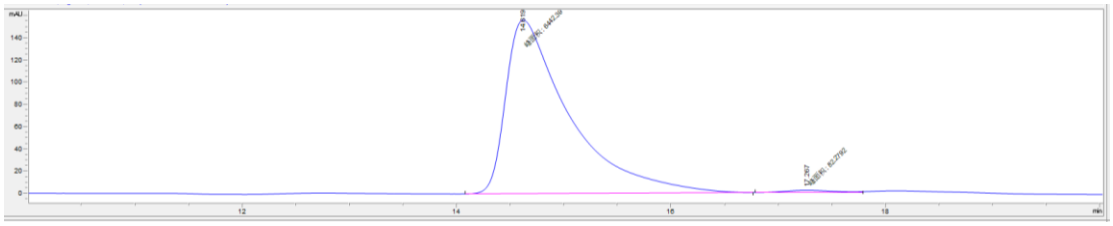
$[\alpha]_D^{21}$ = -9.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

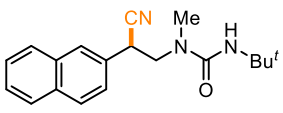


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.711	2087.8	50.8	0.5955	0.48	48.923	BB
2	16.944	2179.7	44.6	0.6861	0.364	51.077	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.619	6442.4	156.9	0.6844	0.367	98.739	MM
2	17.267	82.3	2.3	0.5984	0.7	1.261	MM



3n*

3-(*tert*-Butyl)-1-(2-cyano-2-(naphthalen-2-yl)ethyl)-1-methylurea (3n*): Prepared *via* condition B from **1n** (0.2 mmol) in 65% yield (40.2 mg) and 95:5 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.86–7.80 (m, 4H), 7.51–7.46 (m, 3H), 4.52 (dd, *J* = 9.0, 6.3 Hz,

1H), 4.23 (s, 1H), 3.91 (dd, J = 13.9, 6.3 Hz, 1H), 3.48 (dd, J = 13.9, 9.0 Hz, 1H), 2.89 (s, 3H), 1.33 (s, 9H).

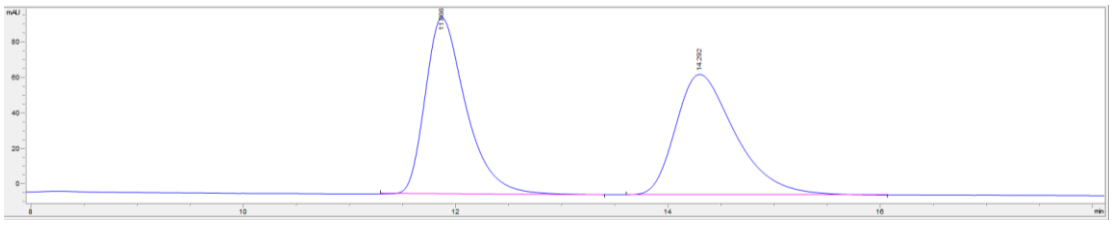
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 133.3, 132.9, 130.7, 129.1, 127.9, 127.8, 126.8, 126.8, 126.6, 125.1, 120.5, 55.4, 51.0, 37.3, 36.9, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{19}H_{23}N_3ONa$: 332.1734, found: 332.1733.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 11.8 min, t_R (major) = 14.2 min.

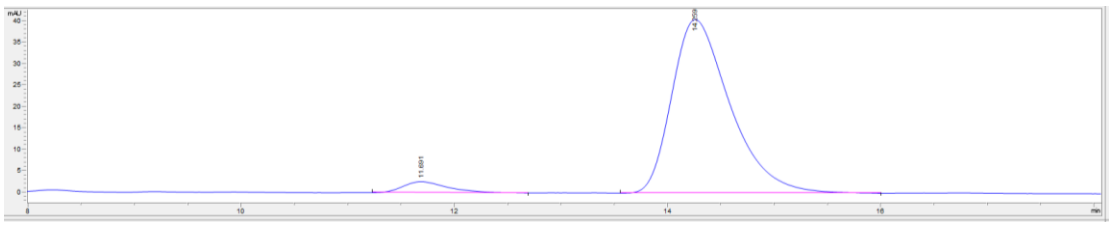
$[\alpha]_D^{21}$ = -15.6 (c = 1.0, CH_2Cl_2).

Racemic sample:

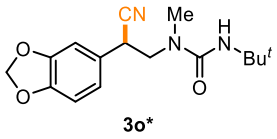


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.866	2638.3	99.3	0.4019	0.647	49.990	BB
2	14.292	2639.3	67.8	0.5884	0.635	50.010	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.691	76.6	2.6	0.4215	0.65	4.712	BB
2	14.259	1548.7	40.7	0.5737	0.63	95.288	BB



3o*

1-(2-(Benzo[*d*][1,3]dioxol-5-yl)-2-cyanoethyl)-3-(*tert*-butyl)-1-methylurea (3o*): Prepared *via* condition B from **1o** (0.2 mmol) in 67% yield (40.7 mg) and 98:2 er as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.84–6.80 (m, 2H), 6.76 (d, J = 7.9 Hz, 1H), 5.94 (s, 2H), 4.22 (dd, J = 8.9, 6.3 Hz, 2H), 3.73 (dd, J = 13.8, 6.4 Hz, 1H), 3.37 (dd, J = 13.8, 8.9 Hz, 1H), 2.87 (s, 3H), 1.31 (d, J = 1.7 Hz, 9H).

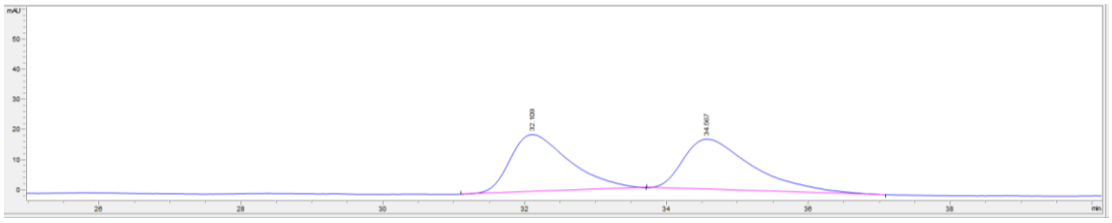
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 148.3, 147.7, 127.0, 121.1, 120.5, 108.7, 108.0, 101.4, 55.4, 50.9, 36.9, 36.7, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{16}H_{21}N_3O_3Na$: 326.1475, found: 326.1473.

Chiral HPLC: Chiralcel IF column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 32.4 min, t_R (major) = 33.9 min.

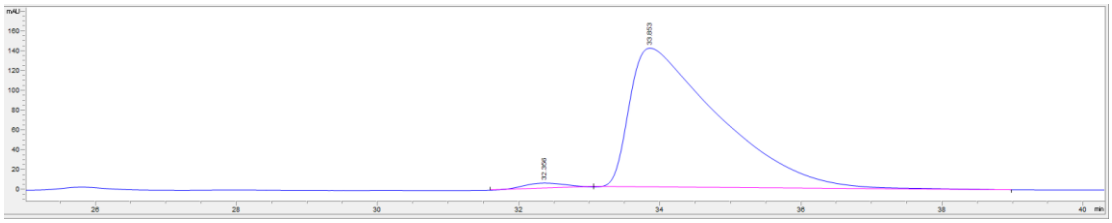
$[\alpha]_D^{21}$ = -27.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

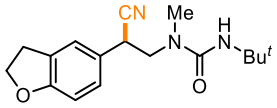


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	32.109	1102.1	19	0.8213	0.578	49.166	BB
2	34.567	1139.5	16.8	0.9217	0.488	50.834	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	32.356	229.2	5.4	0.5667	0.938	1.820	BB
2	33.853	12364.7	140.2	1.2106	0.274	98.180	BB



3p*

3-(*tert*-Butyl)-1-(2-cyano-2-(2,3-dihydrobenzofuran-5-yl)ethyl)-1-methylurea (3p*): Prepared *via* condition B from **1p** (0.2 mmol) in 64% yield (38.6 mg) and 93:7 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.23 (s, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 4.58 (td, J = 8.8, 2.5 Hz, 2H), 4.24 (dd, J = 14.6, 7.9 Hz, 2H), 3.81 (dd, J = 13.9, 6.2 Hz, 1H), 3.34 (dd, J = 13.6, 9.4 Hz, 1H), 3.20 (t, J = 8.9 Hz, 2H), 2.93 (s, 3H), 1.34 (s, 9H).

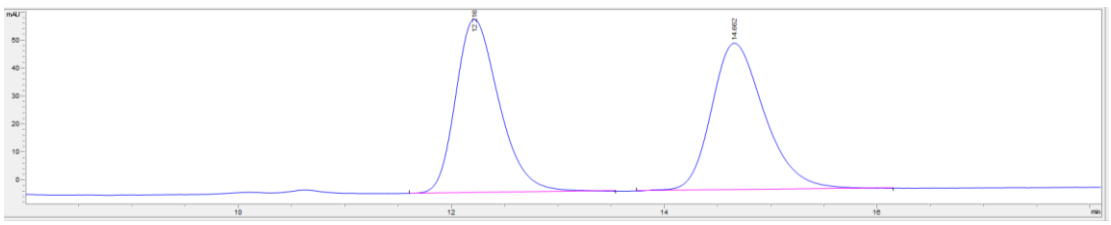
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 160.2, 156.9, 128.2, 127.5, 125.2, 124.3, 120.9, 109.7, 71.5, 55.6, 51.0, 36.8, 36.6, 29.5, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{23}N_3O_2Na$: 324.1682, found: 324.1673.

Chiral HPLC: Chiralcel OD-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 220 nm, t_R (minor) = 12.3 min, t_R (major) = 14.5 min.

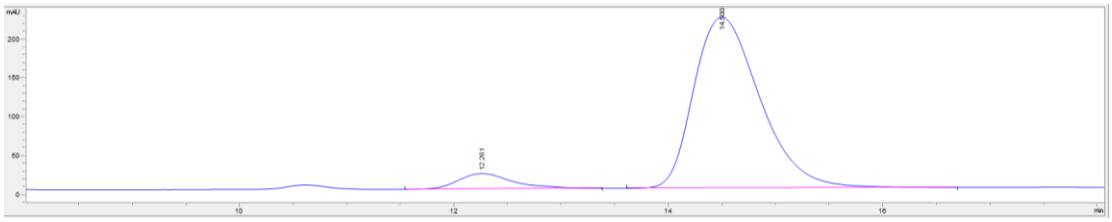
$[\alpha]_D^{21}$ = -17.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

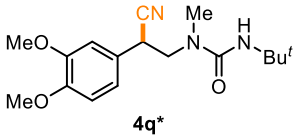


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.216	1751.1	61.8	0.4327	0.702	49.092	BB
2	14.662	1815.9	52.2	0.5395	0.72	50.908	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.261	697.6	19.8	0.5226	0.719	6.905	BB
2	14.5	9405.1	219.9	0.6651	0.691	93.095	BB



4q*

3-(*tert*-Butyl)-1-(2-cyano-2-(3,4-dimethoxyphenyl)ethyl)-1-methylurea (4q*): Prepared *via* condition B from **2q** (0.2 mmol) in 71% yield (45.4 mg) and 94:6 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.94 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.85 (dd, *J* = 5.2, 3.1 Hz, 2H), 4.30 (dd, *J* = 9.1, 6.4 Hz, 1H), 4.22 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.82 (dd, *J* = 13.8, 6.5 Hz, 1H), 3.38 (dd, *J* = 13.9, 9.1 Hz, 1H), 2.92 (s, 3H), 1.35 (s, 9H).

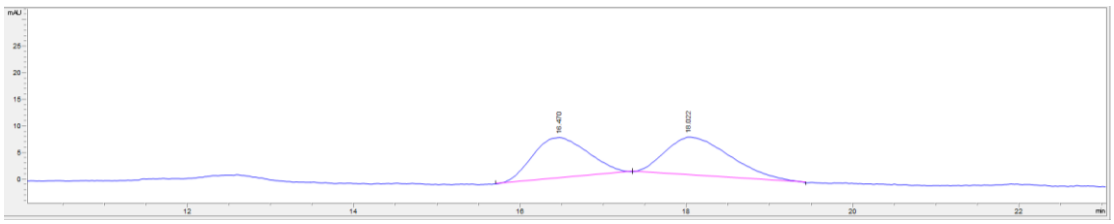
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 149.4, 149.0, 125.7, 120.6, 119.9, 111.5, 110.6, 56.1, 56.0, 55.4, 56.0, 36.9, 36.7, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{25}N_3O_3Na$: 342.1788, found: 342.1793.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 17.4 min, t_R (major) = 19.0 min.

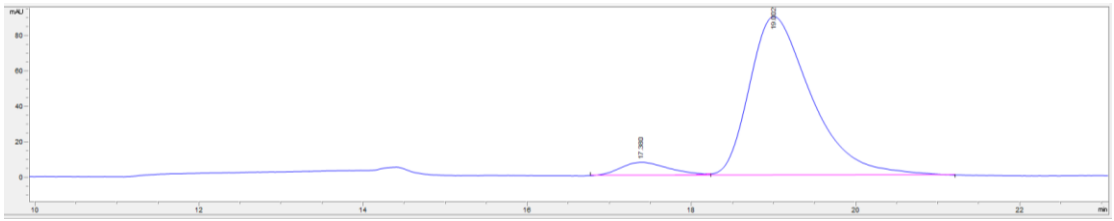
$[\alpha]_D^{21}$ = -27.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

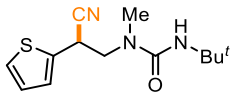


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.47	357	7.7	0.5477	0.944	47.262	BB
2	18.022	398.4	7.2	0.662	0.528	52.738	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.38	311.5	7.5	0.5043	0.688	6.198	BV E
2	19.002	4714.3	89.9	0.7701	0.847	93.802	VB R



3x*

3-(*tert*-Butyl)-1-(2-cyano-2-(thiophen-2-yl)ethyl)-1-methylurea (3x*): Prepared *via* condition B from **1x** (0.2 mmol) in 52% yield (27.6 mg) and 91:9 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.28 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.09 (dt, *J* = 3.6, 1.0 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.64 (dd, *J* = 8.5, 6.8 Hz, 1H), 4.27 (s, 1H), 3.88 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.50 (dd, *J* = 13.8, 8.8 Hz, 1H), 2.93 (s, 3H), 1.35 (s, 9H).

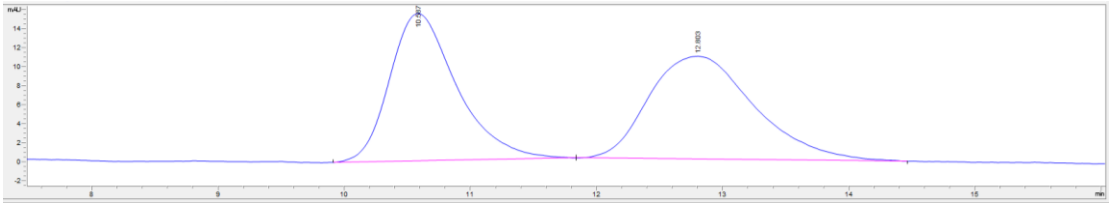
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 135.0, 127.3, 126.7, 126.0, 119.6, 55.4, 51.0, 37.0, 32.3, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{19}N_3OSNa$: 288.1141, found: 288.1144.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 10.5 min, t_R (major) = 12.6 min.

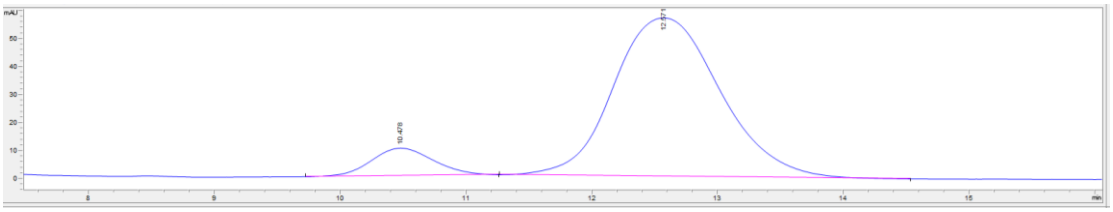
$[\alpha]_D^{21}$ = -6.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

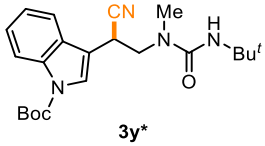


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.587	570.1	15.4	0.5579	0.695	47.736	BB
2	12.803	624.2	10.8	0.6909	0.837	52.264	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.478	341.4	9.9	0.5083	0.884	9.256	BB
2	12.571	3346.6	56.8	0.9137	0.867	90.744	BB



3y*

***tert*-Butyl 3-(2-(3-(*tert*-butyl)-1-methylureido)-1-cyanoethyl)-1H-indole-1-carboxylate (3y*)**: Prepared *via* condition B from **1y** (0.2 mmol) in 55% yield (43.8 mg) and 96:4 er as a Colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.17 (d, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.67 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 4.60 (t, *J* = 7.9 Hz, 1H), 4.25 (s, 1H), 4.06 (dd, *J* = 14.3,

5.8 Hz, 1H), 3.45 (dd, J = 14.1, 9.8 Hz, 1H), 2.96 (s, 3H), 1.67 (s, 9H), 1.36 (s, 9H).

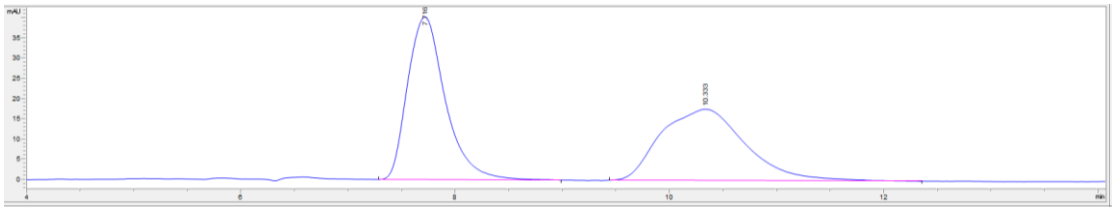
^{13}C NMR (101 MHz, Chlo-roform-*d*) δ = 156.9, 149.3, 135.0, 128.0, 125.2, 124.1, 123.2, 120.0, 119.1, 115.5, 113.0, 84.3, 53.6, 51.0, 37.1, 29.4 (3C), 28.8, 28.2 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{22}H_{30}N_4O_3Na$: 421.2210, found: 421.2212.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (major) = 7.7 min, t_R (minor) = 10.4 min.

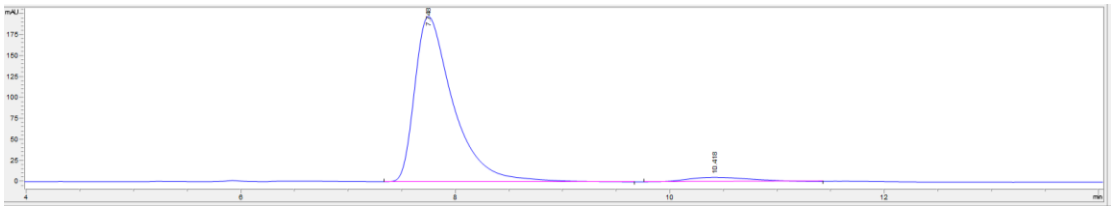
$[\alpha]_D^{21}$ = -25.2 (c = 0.8, CH_2Cl_2).

Racemic sample:

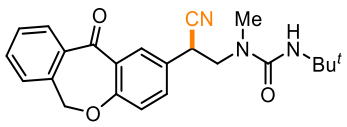


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.716	992.8	40.5	0.3821	0.78	50.514	BB
2	10.333	972.6	17.7	0.7343	1.031	49.486	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.748	4900.1	196.8	0.3705	0.507	95.881	BB
2	10.418	210.5	5.1	0.4932	0.713	4.119	BB



3z*

3-(*tert*-Butyl)-1-(2-cyano-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)ethyl)-1-methylurea (3z*): Prepared *via* condition B from **1z** (0.2 mmol) in 62% yield (48.5 mg), and 94:6 er ((1*R*,2*S*)-**L24**) or 5:95 er ((1*S*,2*R*)-**L24**) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.23 (d, J = 2.5 Hz, 1H), 7.88 (dd, J = 7.7, 1.4 Hz, 1H), 7.57 (td, J = 7.5, 1.4 Hz, 1H), 7.59–7.46 (m, 2H), 7.37 (dd, J = 7.4, 1.3 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H), 5.19 (s, 2H), 4.36 (dd, J = 9.0, 6.3 Hz, 1H), 4.27 (s, 1H), 3.85 (dd, J = 13.8, 6.4 Hz, 1H), 3.45 (dd, J = 13.8, 9.0 Hz, 1H), 2.95 (s, 3H), 1.35 (s, 9H).

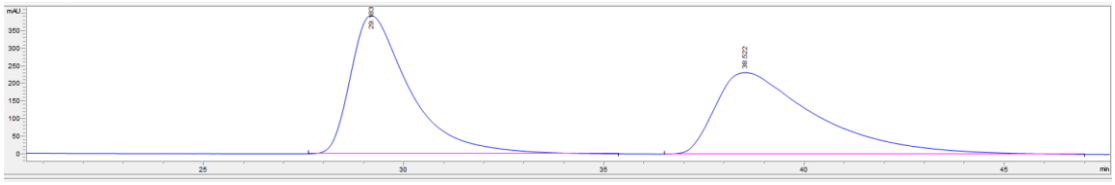
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 190.4, 161.1, 156.8, 140.3, 135.3, 134.5, 133.0, 131.0, 129.5, 129.4, 127.9, 127.2, 125.5, 121.9, 120.1, 73.6, 54.8, 51.0, 36.8, 36.3, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{23}H_{25}N_3O_3Na$: 414.1788, found: 414.1788.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 220 nm, t_R (minor) = 29.0 min, t_R (major) = 39.0 min.

$[\alpha]_D^{21}$ = -29.7 (c = 1.0, CH_2Cl_2).

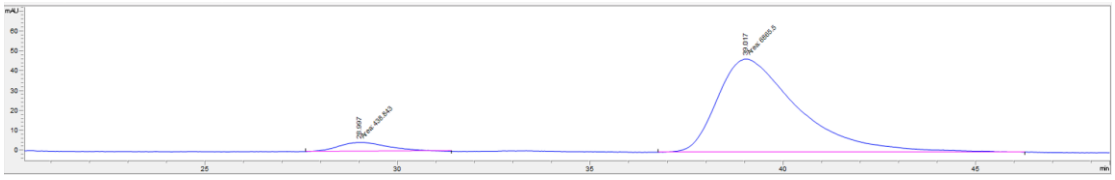
Racemic sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	29.183	40627.1	396.5	1.4235	0.499	49.931	BB
2	38.522	40739.2	233.6	2.0684	0.411	50.069	BB

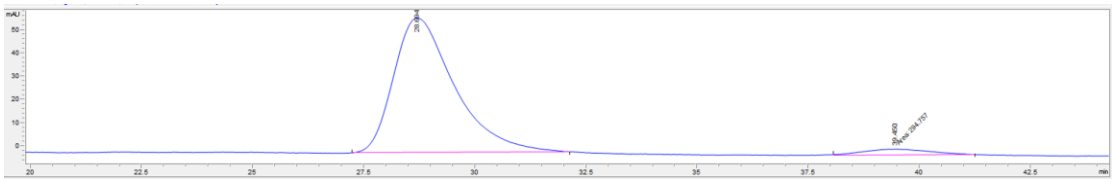
Enriched sample:

With (1*R*,2*S*)-**L24:**

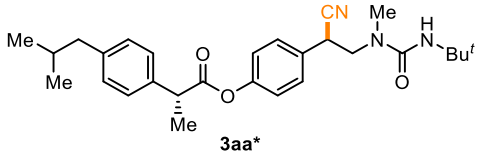


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	28.997	438.8	4.6	1.5764	1.33E-3	6.008	MM T
2	39.017	6865.5	47.1	2.4272	7.18E-5	93.992	MM T

With (1*S*,2*R*)-**L24:**



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	28.694	5507.6	58	1.1687	0.59	94.920	BB
2	39.45	294.8	2.7	1.8121	0.933	5.080	MM



3aa*

4-(2-(3-(*tert*-Butyl)-1-methylureido)-1-cyanoethyl)phenyl (*R*)-2-(4-isobutylphenyl)propanoate (3aa*): Prepared *via* condition B from **1aa** (0.2 mmol) in 67% yield (62.1 mg) and 95:5 er as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.36 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.36 (dd, *J* = 9.1, 6.3 Hz, 1H), 4.24 (s, 1H), 3.93 (q, *J* = 7.1 Hz, 1H), 3.80 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.38 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.88 (s, 3H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dp, *J* = 13.6, 6.7 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 9H), 0.91 (d, *J* = 6.7 Hz, 6H).

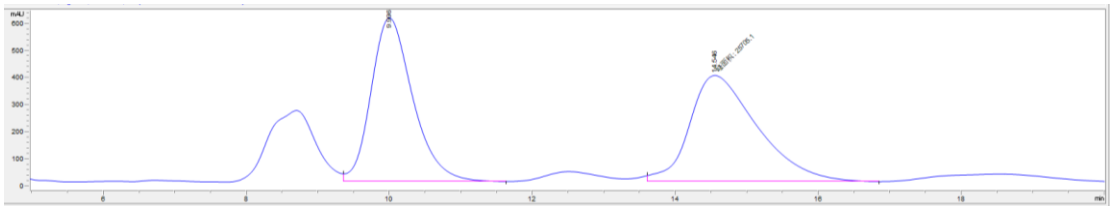
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 173.1, 156.8, 150.8, 141.0, 137.0, 130.8, 129.6 (2C), 128.7 (2C), 127.2 (2C), 122.2 (2C), 120.2, 55.5, 51.0, 45.2, 45.1, 37.0, 36.6, 30.2, 29.4 (3C), 22.4 (2C), 18.5.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{28}H_{37}N_3O_3Na$: 486.2727, found: 486.2725.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 220 nm, t_R (minor) = 10.8 min, t_R (major) = 15.9 min.

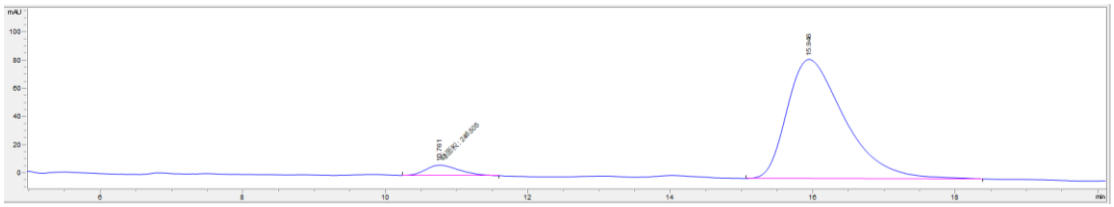
$[\alpha]_D^{21}$ = -20.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

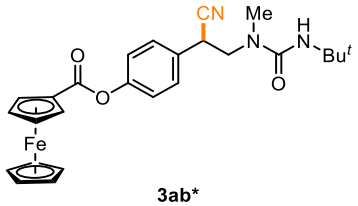


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.996	24444.1	602.2	0.6156	0.751	48.743	VB
2	14.546	25705.1	389.6	1.0995	0.586	51.257	FM

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.761	246.5	7.5	0.5514	0.695	4.941	MM T
2	15.946	4742.8	84.7	0.8314	0.592	95.059	BB



3ab*

4-(2-(3-(*tert*-Butyl)-1-methylureido)-1-cyanoethyl)phenyl ferrocenecarboxylate (3ab*): Prepared *via* condition B from **1ab** (0.2 mmol) in 51% yield (49.7 mg) and 95:5 er as a yellow brown oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.45 (d, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 4.95 (d, *J* = 2.0 Hz, 2H), 4.51 (d, *J* = 2.1 Hz, 2H), 4.43–4.39 (m, 1H), 4.30 (s, 5H), 4.27 (s, 1H), 3.85 (dd, *J* = 12.1, 6.4 Hz, 1H), 3.42 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.92 (s, 3H), 1.36 (s, 9H).

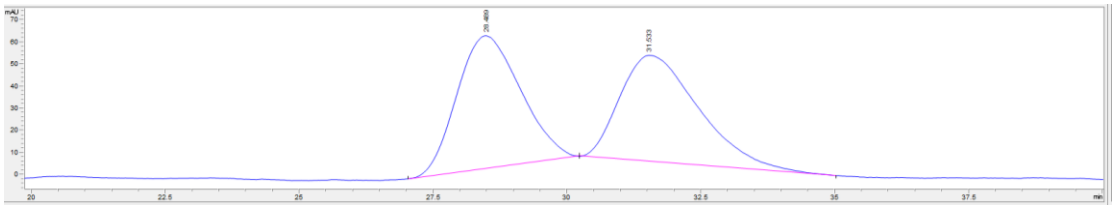
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.2, 156.8, 150.9, 130.6, 128.8 (2C), 122.5 (2C), 120.3, 72.1 (2C), 70.7 (2C), 70.0 (5C), 69.7, 55.5, 51.0, 37.0, 36.7, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{26}H_{29}FeN_3O_3Na$: 510.1451, found: 510.1454.

Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (minor) = 28.6 min, t_R (major) = 31.5 min.

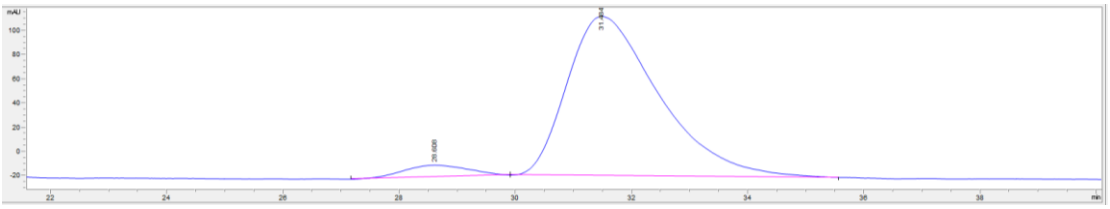
$[\alpha]_D^{21}$ = -32.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

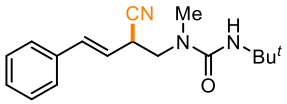


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	28.489	4992.2	60.3	0.9795	0.838	50.128	BB
2	31.533	4966.6	48.2	1.2358	0.557	49.872	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	28.608	764.8	9.7	0.9263	0.962	5.028	BB
2	31.484	14444.2	131.4	1.3189	0.583	94.972	BB



3ac*

3-(*tert*-Butyl)-1-(2-cyano-4-phenylbut-3-en-1-yl)-1-methylurea (3ac*): Prepared *via* condition B from **1ac** (0.2 mmol) in 55% yield (31.4 mg) and 93:7 er as a yellow oil.

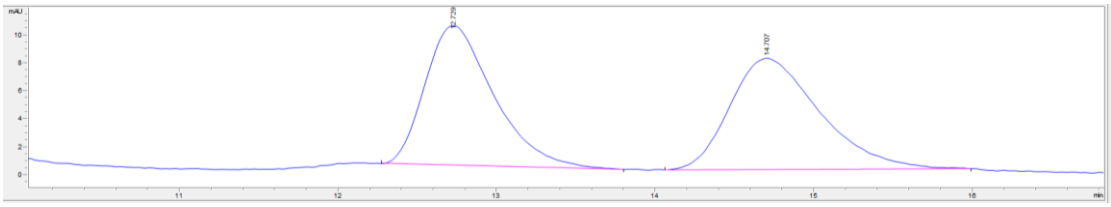
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.38–7.30 (m, 5H), 6.79–6.75 (m, 1H), 6.04 (dd, J = 15.9, 6.4 Hz, 1H), 4.32 (s, 1H), 3.95–3.89 (m, 1H), 3.84 (dd, J = 13.7, 5.6 Hz, 1H), 3.34 (dd, J = 13.6, 8.5 Hz, 1H), 3.03 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 135.6, 134.5, 128.7 (2C), 128.4, 126.6 (2C), 120.3, 119.9, 52.5 51.1, 36.8, 34.7, 29.3 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{23}N_3ONa$: 308.1733, found: 308.1741.

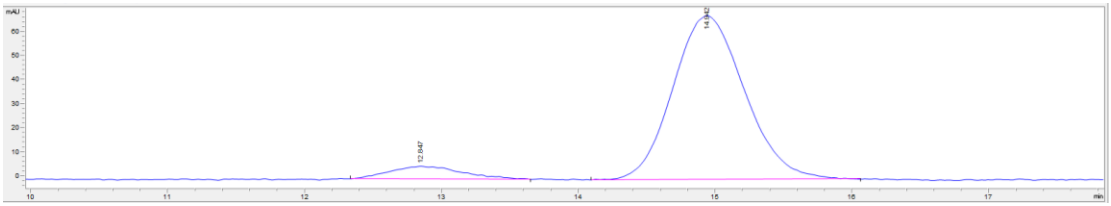
Chiral HPLC: Chiralcel OD-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 254 nm, t_R (minor) = 12.8 min, t_R (major) = 14.9 min. $[\alpha]_D^{21}$ = -15.0 (c = 1.0, CH_2Cl_2).

Racemic sample:

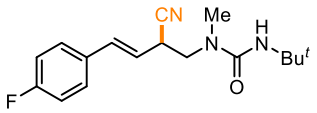


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.729	298.9	9.9	0.4274	0.675	48.944	BB
2	14.707	311.8	7.9	0.5278	0.664	51.056	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.847	194.4	5.3	0.438	0.713	7.287	BV R
2	14.942	2473.4	67.8	0.4638	0.895	92.713	BV R



3ad*

3-(*tert*-Butyl)-1-(2-cyano-4-(4-fluorophenyl)but-3-en-1-yl)-1-methylurea (3ad*): Prepared *via* condition B from **1ad** (0.2 mmol) in 49% yield (29.7 mg) and 93:7 er as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35–7.31 (m, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 16.0 Hz, 1H), 5.96 (dd, *J* = 15.8, 6.2 Hz, 1H), 4.31 (s, 1H), 3.93–3.83 (m, 2H), 3.34 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.03 (s, 3H), 1.34 (s, 9H).

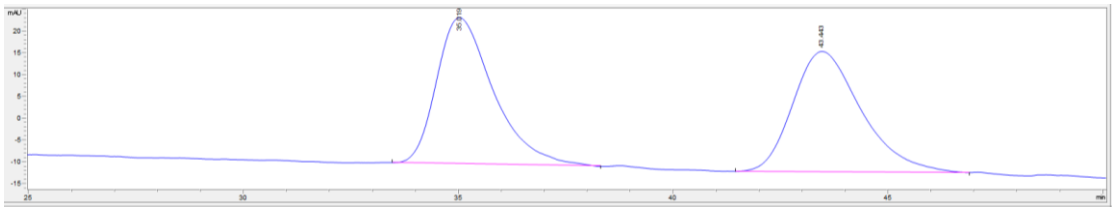
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.7 (d, *J* = 248.1 Hz), 156.9, 133.2, 131.8 (d, *J* = 3.5 Hz), 128.2 (d, *J* = 8.1 Hz, 2C), 120.1 (d, *J* = 2.3 Hz), 119.9, 115.7 (d, *J* = 21.7 Hz, 2C), 52.4, 51.0, 36.7, 34.7, 29.4 (3C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -113.15.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{22}FN_3ONa$: 326.1639, found: 326.1637.

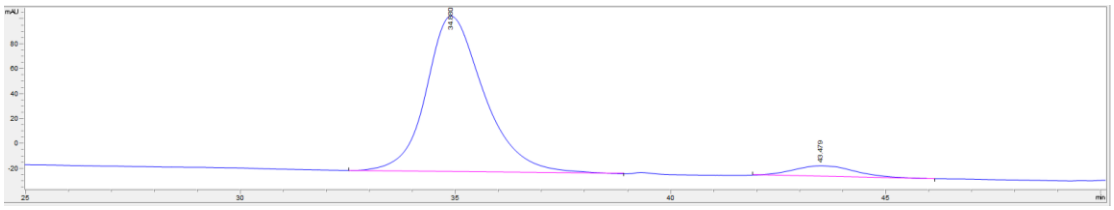
Chiral HPLC: Chiralcel IC column, hexane:*i*PrOH (95:5), 1.0 mL/min, 254 nm, t_R (major) = 34.9 min, t_R (minor) = 43.5 min. $[\alpha]_D^{21}$ = -6.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

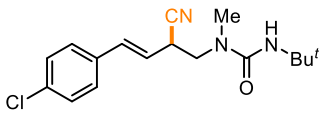


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	35.019	3093.1	33.6	1.2688	0.634	50.276	BB
2	43.443	3059.1	27.6	1.329	0.684	49.724	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	34.88	11686.6	124.7	1.3738	0.723	93.185	BB
2	43.479	854.7	8.5	1.1783	0.779	6.815	BB



3ae*

3-(*tert*-Butyl)-1-(4-(4-chlorophenyl)-2-cyanobut-3-en-1-yl)-1-methylurea (3ae*): Prepared *via* condition B from **1ae** (0.2 mmol) in 41% yield (26.2 mg) and 91:9 er as a yellow oil.

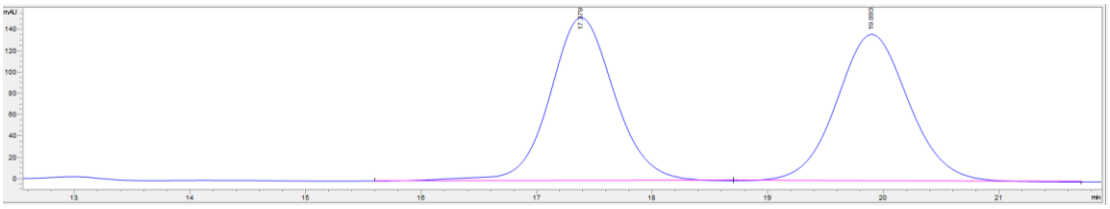
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29 (s, 4H), 6.72 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.03 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.31 (s, 1H), 3.94–3.82 (m, 2H), 3.35 (dd, *J* = 13.6, 8.3 Hz, 1H), 3.03 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 134.1, 133.2, 128.9 (2C), 127.8 (2C), 121.1, 119.7, 52.3, 51.1, 36.7, 34.7, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{17}H_{22}ClN_3ONa$: 342.1344, found: 342.1352.

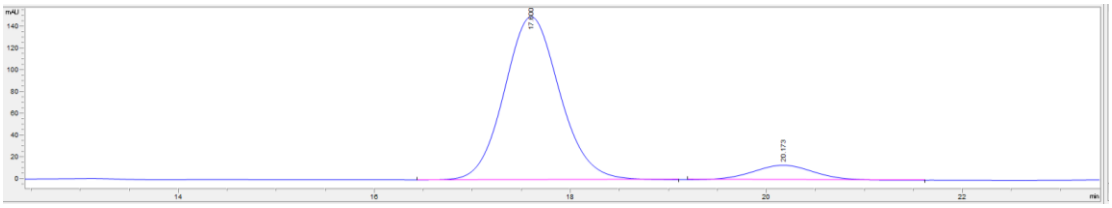
Chiral HPLC: Chiralcel IC column, hexane:*i*PrOH (90:10), 1.0 mL/min, 254 nm, t_R (major) = 17.6 min, t_R (minor) = 20.2 min. $[\alpha]_D^{21}$ = -1.9 (c = 1.0, CH_2Cl_2).

Racemic sample:

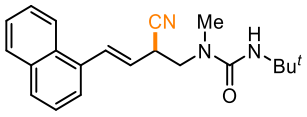


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.379	6010.4	153.9	0.5996	0.927	49.897	BB
2	19.893	6035.2	138.4	0.6687	0.922	50.103	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.6	5890.8	149.8	0.6066	0.903	91.003	BB
2	20.173	582.4	13.4	0.6064	0.972	8.997	BB



3af*

3-(*tert*-Butyl)-1-(2-cyano-4-(naphthalen-2-yl)but-3-en-1-yl)-1-methylureaa (3af*): Prepared *via* condition B from **1af** (0.2 mmol) in 39% yield (26.2 mg) and 90:10 er as a yellow oil.

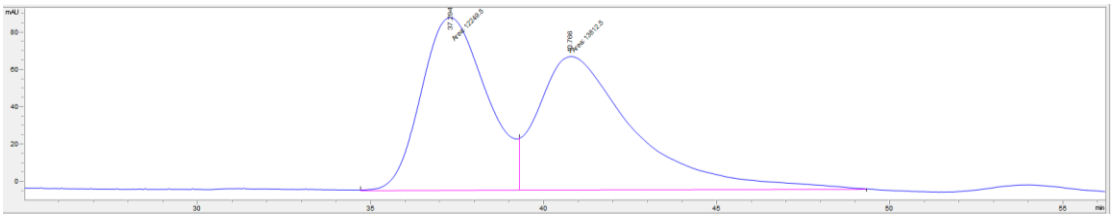
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.08 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 18.6, 7.9 Hz, 2H), 7.56–7.49 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.09 (dd, *J* = 15.6, 6.5 Hz, 1H), 4.34 (s, 1H), 4.05 (q, *J* = 6.7 Hz, 1H), 3.91 (dd, *J* = 13.8, 5.8 Hz, 1H), 3.46 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.06 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 133.5, 133.4, 132.0, 131.0, 128.7, 128.6, 126.4, 126.0, 125.6, 124.3, 123.6, 123.6, 119.9, 52.5, 51.1, 36.9, 35.0, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{21}H_{25}N_3ONa$: 358.1890, found: 358.1888.

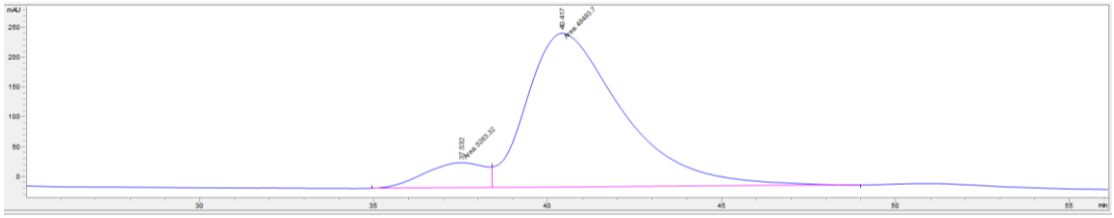
Chiral HPLC: Chiralcel OJ-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 230 nm, t_R (minor) = 37.5 min, t_R (minor) = 40.4 min. $[\alpha]_D^{21}$ = -1.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

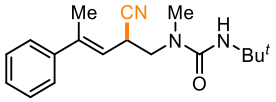


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	37.294	12249.5	92.8	2.3204	0	47.001	MF T
2	40.766	13812.5	71.7	3.2092	0.487	52.999	FM T

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	37.532	5263.3	42.6	2.0606	1.431	9.612	MF T
2	40.417	49493.7	259.2	3.1822	0.566	90.388	FM T



3ag*

3-(*tert*-Butyl)-1-(2-cyano-4-phenylpent-3-en-1-yl)-1-methylurea (3ag*): Prepared *via* condition B from **1ag** (0.2 mmol) in 53% yield (31.7 mg) and 94:6 er as a yellow oil.

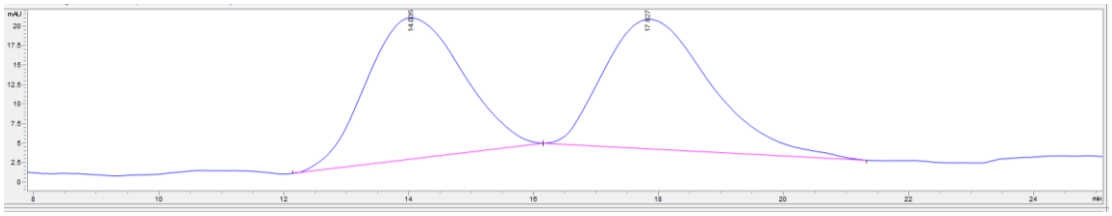
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.37–7.29 (m, 5H), 5.60 (d, J = 9.2 Hz, 1H), 4.30 (s, 1H), 4.12 (q, J = 8.7 Hz, 1H), 3.73 (dd, J = 13.8, 6.8 Hz, 1H), 3.40 (dd, J = 13.8, 8.6 Hz, 1H), 3.00 (s, 3H), 2.14 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 142.0, 141.9, 128.4 (2C), 127.9, 125.9 (2C), 120.5, 118.5, 52.3, 51.0, 37.0, 30.7, 29.4 (3C), 16.6.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{18}H_{25}N_3ONa$: 322.1890, found: 322.1879.

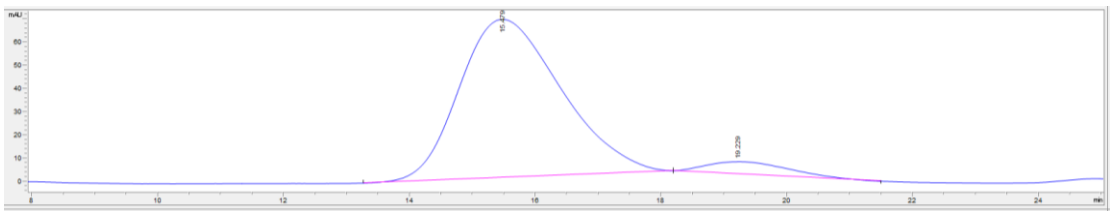
Chiral HPLC: Chiralcel IC column, hexane:*i*PrOH (95:5), 1.0 mL/min, 254 nm, t_R (major) = 15.5 min, t_R (minor) = 19.2 min. $[\alpha]_D^{21}$ = -2.3 (c = 1.0, CH_2Cl_2).

Racemic sample:

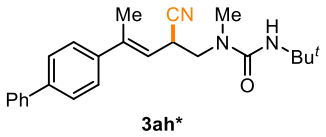


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.035	1931	18	1.3024	0.867	49.649	BB
2	17.827	1958.4	16.5	1.4045	0.67	50.351	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.479	7656.5	68.3	1.6387	0.721	93.985	BB
2	19.229	490.1	5.3	1.086	0.564	6.015	BB



3ah*

1-(4-([1,1'-Biphenyl]-4-yl)-2-cyanopent-3-en-1-yl)-3-(*tert*-butyl)-1-methylurea (3ah*): Prepared *via* condition B from **1ah** (0.2 mmol) in 43% yield (32.3 mg) and 92:8 er as a yellow oil.

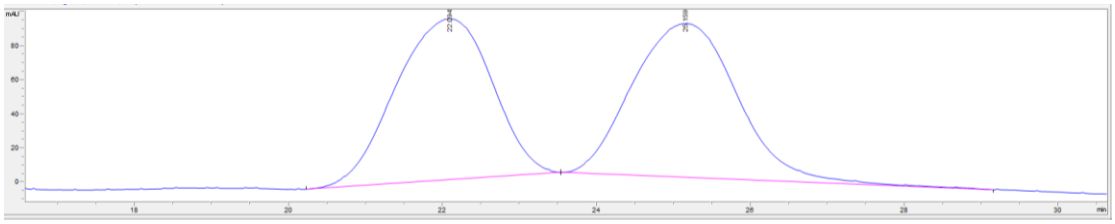
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.37–7.29 (m, 5H), 5.60 (d, *J* = 9.2 Hz, 1H), 4.30 (s, 1H), 4.12 (q, *J* = 8.7 Hz, 1H), 3.73 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.40 (dd, *J* = 13.8, 8.6 Hz, 1H), 3.00 (s, 3H), 2.14 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 142.0, 141.9, 128.4 (2C), 127.9, 125.9 (2C), 120.5, 118.5, 52.3, 51.0, 37.0, 30.7, 29.4 (3C), 16.6.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{24}H_{29}N_3ONa$: 398.2203, found: 398.2199.

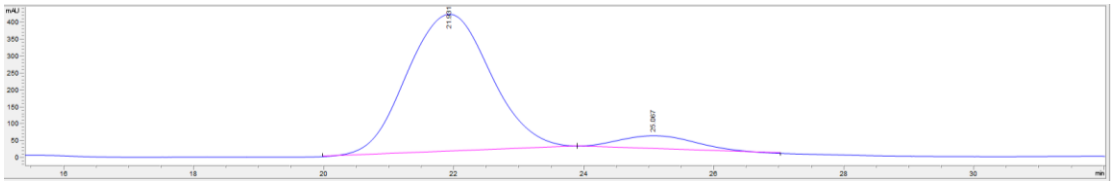
Chiral HPLC: Chiralcel IC column, hexane:*i*PrOH (85:15), 1.0 mL/min, 254 nm, t_R (major) = 22.1 min, t_R (minor) = 25.2min. $[\alpha]_D^{21}$ = -7.9 (c = 1.0, CH_2Cl_2).

Racemic sample:

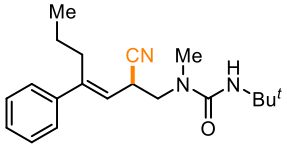


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	22.094	8182.6	94.2	1.027	1.272	49.014	BB
2	25.159	8511.8	90	1.1715	0.964	50.986	BV R

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.931	36317.9	406.4	1.3945	0.998	91.897	BB
2	25.067	3202.4	38.7	1.0342	0.751	8.103	BB



3ai*

3-(*tert*-Butyl)-1-(2-cyano-4-phenylhept-3-en-1-yl)-1-methylurea (3ai*): Prepared *via* condition B from **1ai** (0.2 mmol) in 41% yield (26.9 mg) and 87:13 er as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.34–7.27 (m, 5H), 5.46 (d, *J* = 9.6 Hz, 1H), 4.29 (s, 1H), 4.11–

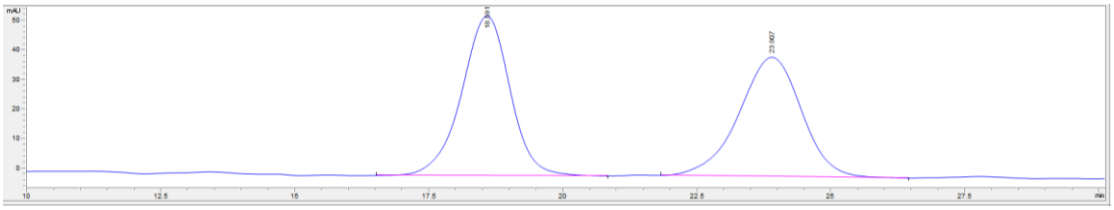
4.06 (m, 1H), 3.66 (dd, J = 13.8, 7.0 Hz, 1H), 3.46 (dd, J = 13.8, 8.1 Hz, 1H), 2.99 (s, 3H), 2.57–2.47 (m, 2H), 1.36 (s, 9H), 1.41–1.33 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 147.2, 141.4, 128.4 (2C), 127.7, 126.6 (2C), 120.4, 119.2, 52.5, 51.0, 37.0, 32.2, 30.5, 29.4 (3C), 21.5, 13.8.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{29}N_3ONa$: 350.2203, found: 350.2210.

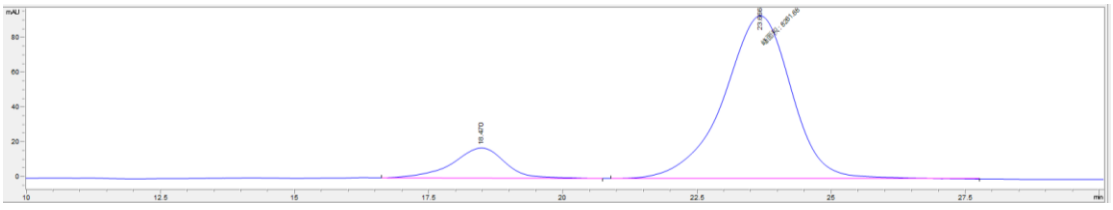
Chiral HPLC: Chiralcel IC column, hexane:*i*PrOH (90:10), 1.0 mL/min, 254 nm, t_R (minor) = 18.4 min, t_R (major) = 23.7 min. $[\alpha]_D^{21}$ = -8.1 (c = 1.0, CH_2Cl_2).

Racemic sample:

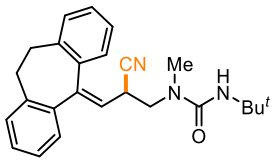


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	18.591	3419	54.2	0.9617	1.082	50.930	BB
2	23.907	3294.1	40.5	1.1855	1.086	49.070	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	18.472	1371.4	20	0.9821	1.193	12.654	BB
2	23.662	9465.9	108.7	1.3318	1.163	87.346	BB



3aj*

3-(*tert*-Butyl)-1-(2-cyano-3-(10,11-dihydro-5H-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-1-methylurea (3aj*): Prepared *via* condition B from **1aj** (0.2 mmol) in 57% yield (44.1 mg) and 89:11 er as a colorless oil (major isomer : minor isomer = 1.25 : 1).

Major isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34–7.04 (m, 8H), 5.78 (d, J = 10.0 Hz, 1H), 4.18 (s, 1H), 3.82–3.69 (m, 2H), 3.62–3.26 (m, 3H), 3.00–2.93 (m, 1H), 2.81–2.75 (m, 1H), 2.68 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.6, 149.4, 139.4, 139.1, 138.2, 137.1, 130.2, 128.5 (2C), 128.4, 128.1, 127.7, 126.5, 126.4, 121.6, 119.8, 51.4, 50.9, 35.4, 33.6, 31.9, 31.1, 29.3 (3C).

Minor isomer:

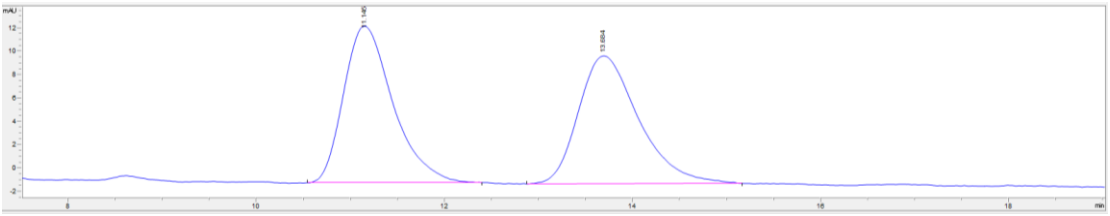
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34–7.04 (m, 8H), 5.74 (d, J = 9.4 Hz, 1H), 4.37 (s, 1H), 3.82–3.69 (m, 2H), 3.62–3.26 (m, 3H), 3.04 (s, 3H), 3.00–2.93 (m, 1H), 2.81–2.75 (m, 1H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 148.9, 139.3, 139.1, 138.5, 137.2, 130.4, 128.6, 128.5 (2C), 128.4, 128.0, 126.9, 126.2, 121.7, 119.5, 51.3, 50.9, 36.4, 33.6, 31.7, 31.2, 29.4 (3C).

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{25}H_{29}N_3ONa$: 410.2203, found: 410.2202.

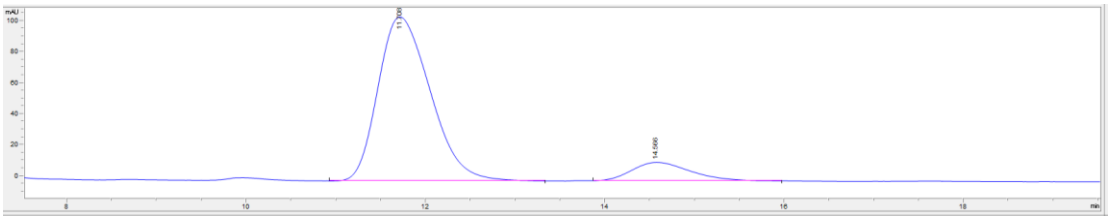
Chiral HPLC: Chiralcel AD-H column, hexane:*i*PrOH (95:5), 1.0 mL/min, 254 nm, t_R (major) = 11.7 min, t_R (minor) = 14.6 min. $[\alpha]_D^{21}$ = -1.8 (c = 1.0, CH_2Cl_2).

Racemic sample:

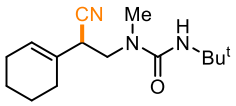


#	时间	峰面积	峰高	峰宽	对称因子	Area%	Type
1	11.145	487.6	13.4	0.5593	0.696	50.086	BB
2	13.684	485.9	10.9	0.6325	0.687	49.914	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型	Area%	Type
1	11.708	4267.2	105.7	0.6329	0.684	88.933	BB	88.933	BB
2	14.566	531	11.8	0.5919	0.691	11.067	BB	11.067	BB



3ak*

3-(*tert*-Butyl)-1-(2-cyano-2-(cyclohex-1-en-1-yl)ethyl)-1-methylurea (3ak*): Prepared *via* condition B from **1ak** (0.2 mmol) in 34% yield (17.9 mg) and 78:22 er as a colorless oil.

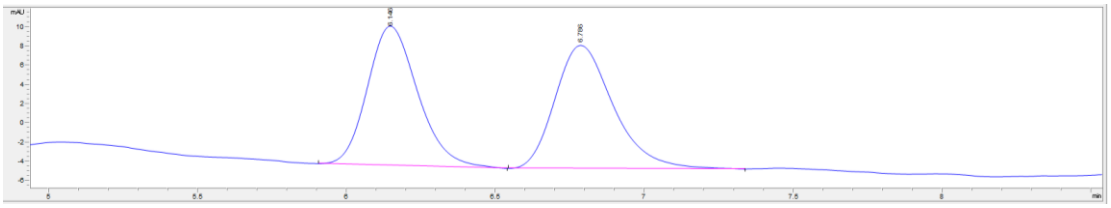
^{1}H NMR (600 MHz, Chloroform-*d*) δ = 5.80–5.78 (m, 1H), 4.27 (s, 1H), 3.80 (dd, *J* = 13.9, 5.9 Hz, 1H), 3.55–3.50 (m, 1H), 3.22 (dd, *J* = 13.8, 8.8 Hz, 1H), 2.97 (s, 3H), 2.05–1.99 (m, 4H), 1.67–1.63 (m, 2H), 1.58–1.53 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 129.9, 127.3, 120.4, 51.3, 50.9, 38.9, 36.5, 29.4 (3C), 26.4, 25.2, 22.5, 21.8.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{15}H_{25}N_3ONa$: 286.1890, found: 286.1887.

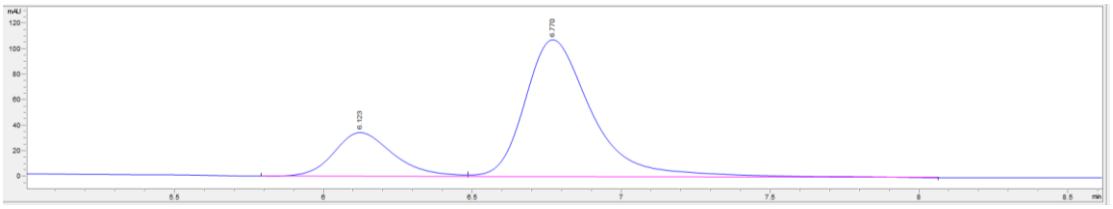
Chiral HPLC: Chiralcel OD-H column, hexane:*i*PrOH (90:10), 1.0 mL/min, 220 nm, t_R (minor) = 6.1 min, t_R (major) = 6.8 min. $[\alpha]_D^{21}$ = -4.3 (c = 1.0, CH_2Cl_2).

Racemic sample:

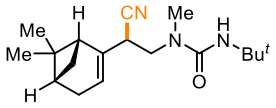


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.146	170.3	14.5	0.1814	0.79	49.365	BB
2	6.786	174.6	12.8	0.2113	0.738	50.635	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.123	476	34.2	0.2123	0.756	21.982	BV
2	6.77	1689.4	107.2	0.2379	0.65	78.018	VB



3al*

3-(*tert*-Butyl)-1-(2-cyano-2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)-1-methylurea (3al*): Prepared *via* condition B from **1al** (0.2 mmol) in 37% yield (22.5 mg) and 80:20 er as a colorless oil (major isomer : minor isomer = 4 : 1).

Major isomer:

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 5.70 (s, 1H), 4.29 (s, 1H), 3.91 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.63–3.59 (m, 1H), 3.02 (s, 3H), 2.94 (dd, *J* = 13.8, 10.5 Hz, 1H), 2.46–2.40 (m, 1H), 2.34–2.20 (m, 3H), 2.12–2.07 (td, *J* = 5.7, 2.8 Hz, 1H), 1.35 (s, 9H), 1.29 (s, 3H), 1.15 (d, *J* = 8.8 Hz, 1H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.9, 139.7, 121.9, 120.3, 51.4, 51.0, 44.5, 40.4, 38.2, 38.1, 36.8, 31.8, 31.3, 29.4 (3C), 26.0, 21.2.

Minor isomer:

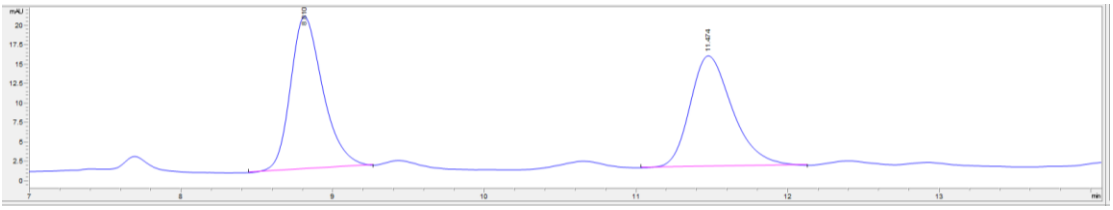
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 5.70 (s, 1H), 4.29 (s, 1H), 3.87 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.69–3.65 (m, 1H), 3.00 (s, 3H), 2.95 (dd, *J* = 13.8, 10.0 Hz, 1H), 2.46–2.40 (m, 1H), 2.34–2.20 (m, 3H), 2.12–2.07 (td, *J* = 5.7, 2.8 Hz, 1H), 1.35 (s, 9H), 1.29 (s, 3H), 1.14 (d, *J* = 8.8 Hz, 1H), 0.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.8, 139.5, 122.2, 120.0, 51.2, 51.0, 44.1, 40.4, 38.2, 37.9, 36.7, 31.7, 31.3, 29.4 (3C), 25.9, 21.1.

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{18}H_{29}N_3ONa$: 326.2203, found: 326.2208.

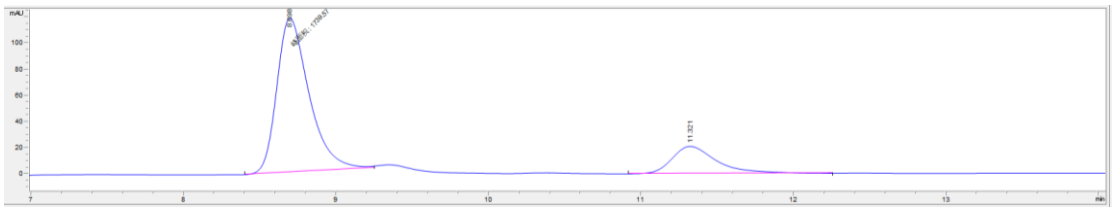
Chiral HPLC: Chiralcel IF column, hexane:*i*PrOH (95:5), 1.0 mL/min, 220 nm, t_R (major) = 8.7 min, t_R (minor) = 11.3 min. $[\alpha]_D^{21}$ = -7.1 (c = 1.0, CH_2Cl_2).

Racemic sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.81	293	19.7	0.2254	0.728	51.238	BB
2	11.474	278.9	14.3	0.2976	0.719	48.762	BB

Enriched sample:



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.698	1739.6	118.3	0.2452	0.663	80.240	MM
2	11.321	428.4	20.9	0.3072	0.628	19.760	BB

8. X-Ray Data for 2d and 3k

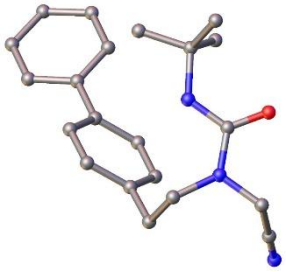


Figure S11. X-Ray crystal data of **2d**

Table S7. Crystal data and structure refinement for **2d**

Identification code	cu_0414_6_0m
Expirical formula	$C_{21}H_{25}N_3O$
Formula weight	335.44
Temperature/K	150.00
Crystal system	monoclinic
Space group	C2/c
a/Å	31.7800(8)
b/Å	6.1176(1)
c/Å	19.0293(5)
α/°	90
β/°	90.186(2)
γ/°	90
Volume/Å^3	3699.61(15)
Z	8
ρ_{calc}g/cm^3	1.204
μ/mm^{-1}	0.590
F(000)	1440.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.562 to 144.242
Index ranges	$-38 \le h \le 37$, $-7 \le k \le 7$, $-23 \le l \le 23$
Reflections collected	16077
Independent reflections	3583 [R_{int} = 0.0408, R_{sigma} = 0.0313]
Data/restraints/parameters	3583/0/229
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1027
Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1082
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

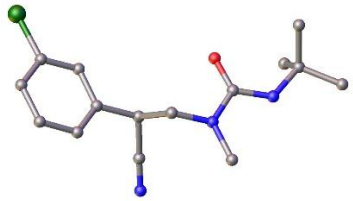


Figure S12. X-Ray crystal data of **3k**

Table S8. Crystal data and structure refinement for **3k**

Identification code	cu_0508_8_0ma
Empirical formula	$C_{15}H_{20}ClN_3O$
Formula weight	293.79
Temperature/K	150.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.0770(3)
b/Å	10.3211(2)
c/Å	18.8000(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3119.53(11)
Z	8
ρ_{calc}g/cm^3	1.251
μ/mm^{-1}	2.160
F(000)	1248.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.408 to 149.186
Index ranges	$-20 \leq h \leq 16$, $-12 \leq k \leq 11$, $-23 \leq l \leq 19$
Reflections collected	19520
Independent reflections	3191 [R_{int} = 0.0380, R_{sigma} = 0.0261]
Data/restraints/parameters	3191/0/185
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0674, wR_2 = 0.1710
Final R indexes [all data]	R_1 = 0.0736, wR_2 = 0.1824
Largest diff. peak/hole / e Å^{-3}	0.55/-0.18

9. References

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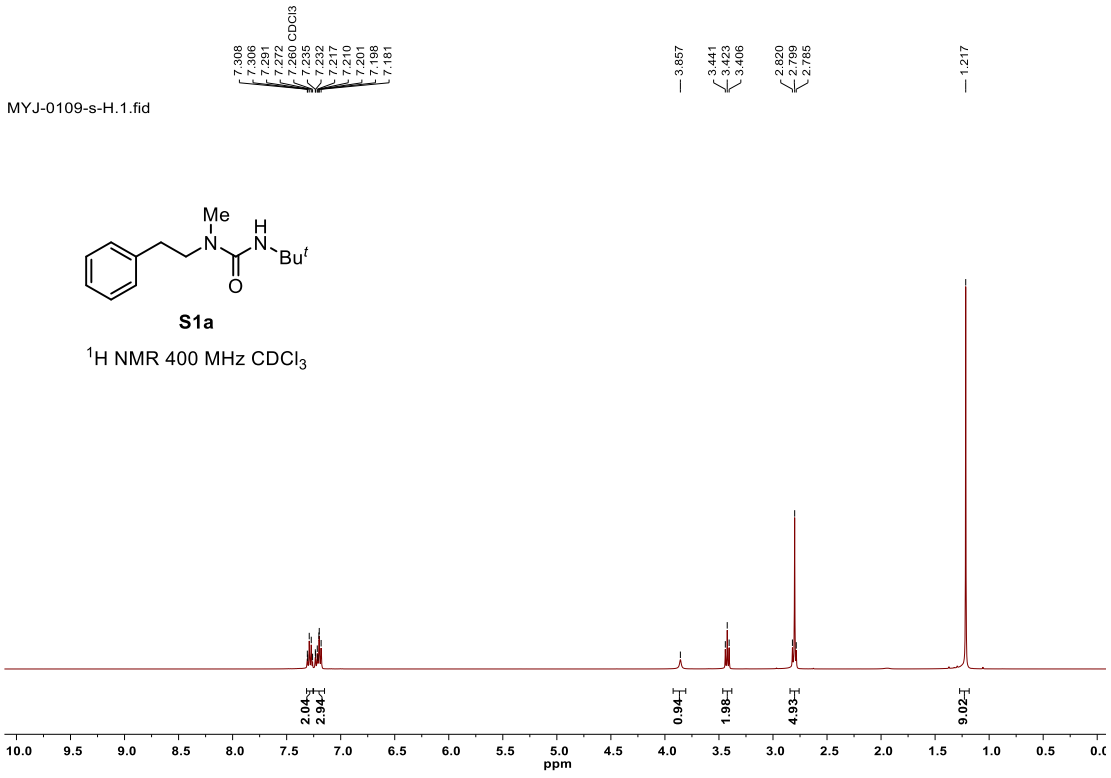
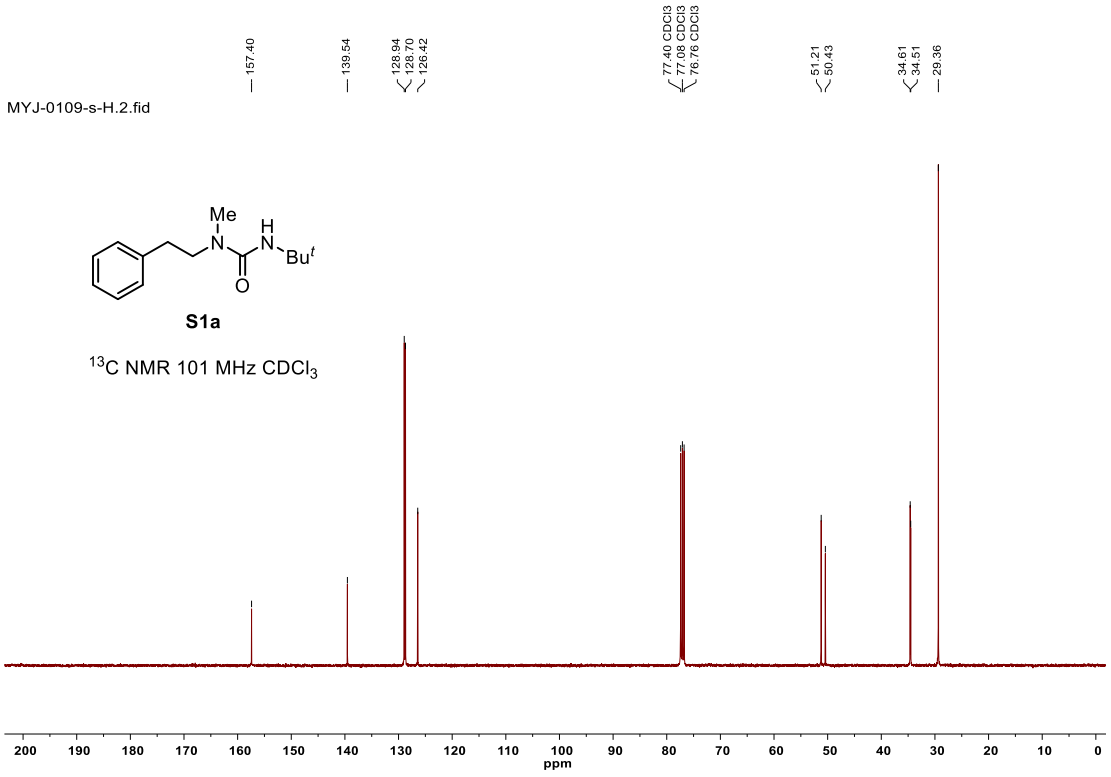
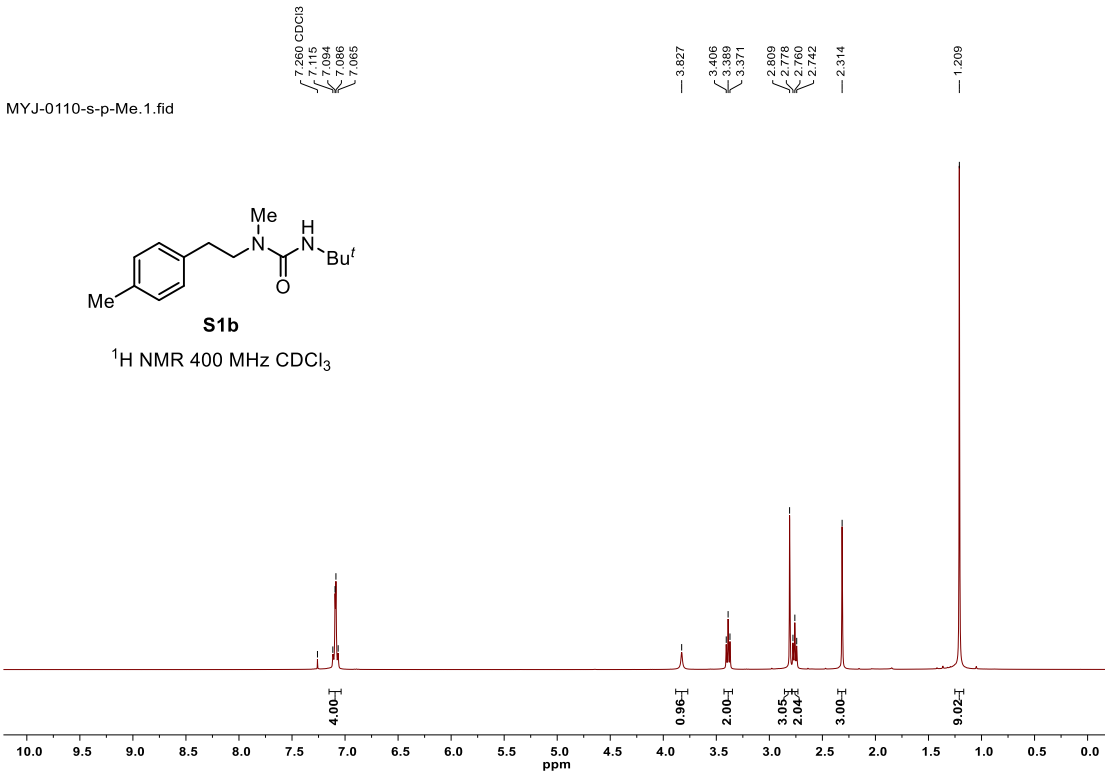
10. NMR Spectra

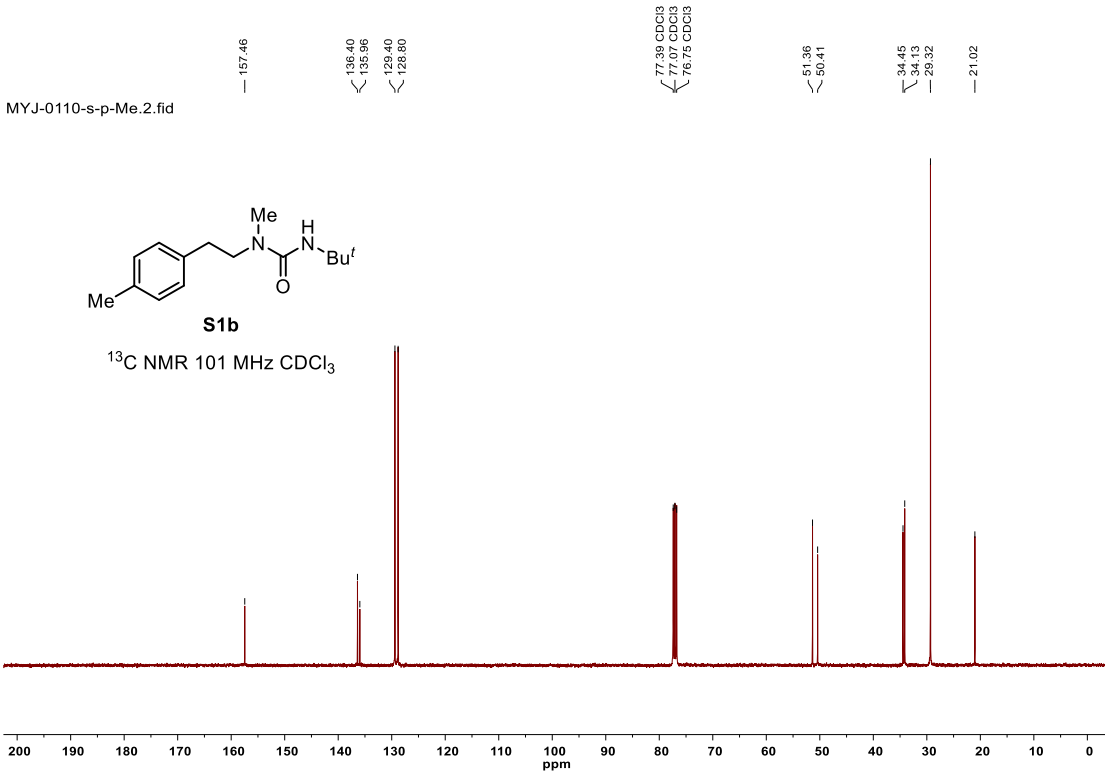






S1b

^{1}H NMR 400 MHz $CDCl_3$



S1b

^{13}C NMR 101 MHz $CDCl_3$

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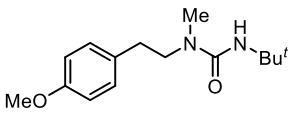

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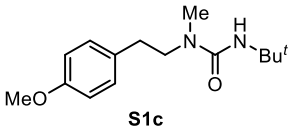

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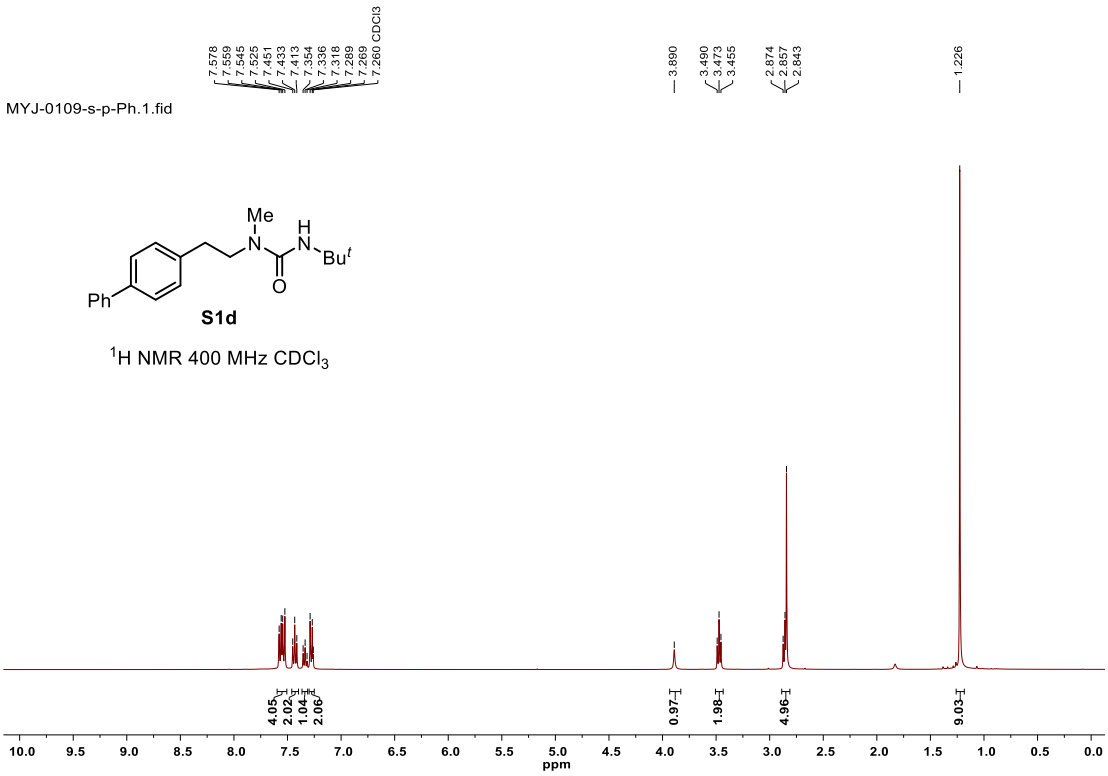
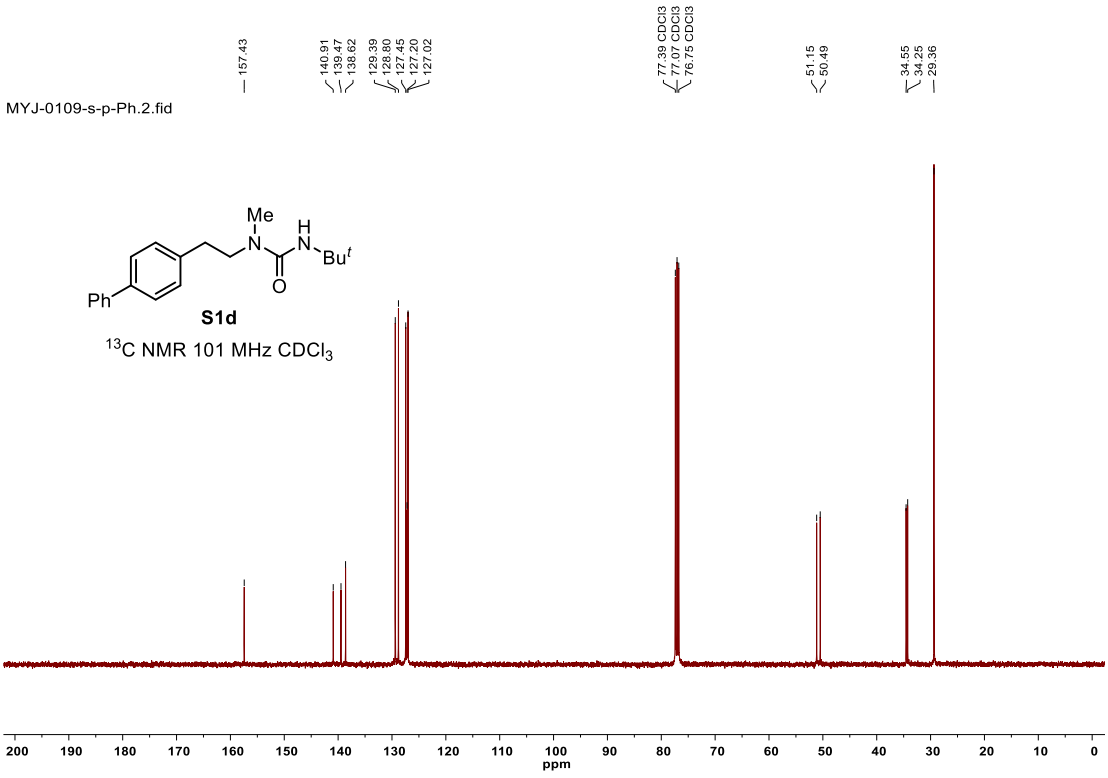
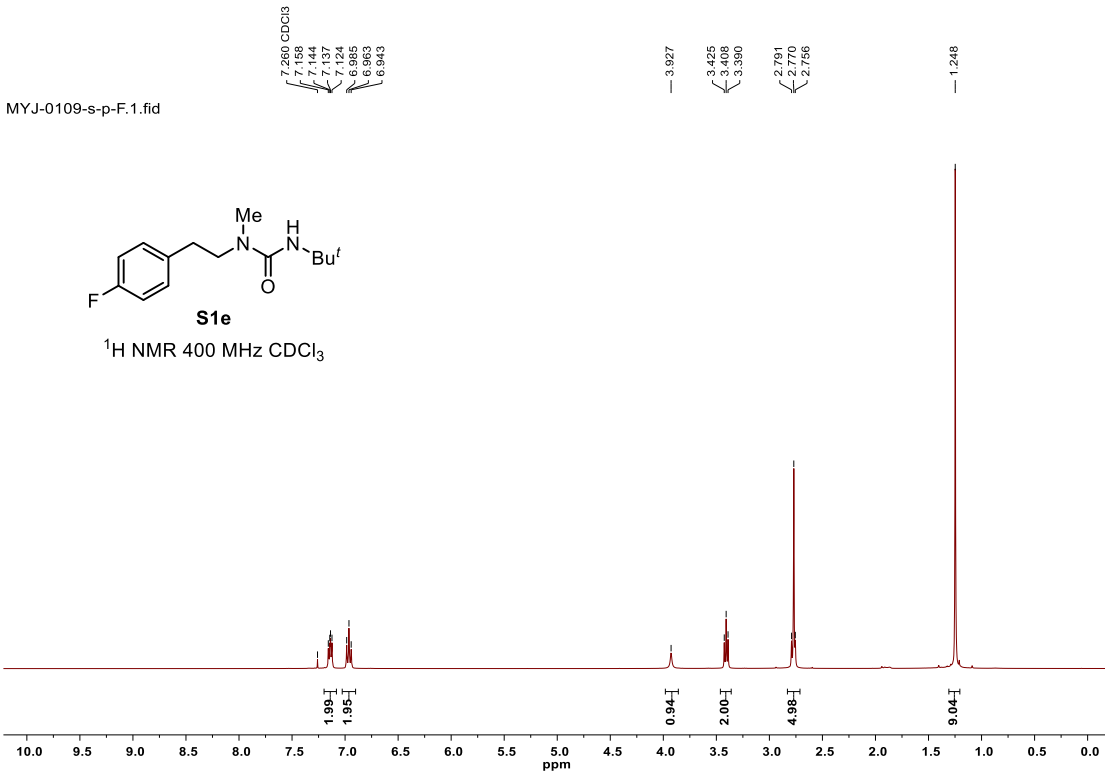
^{13}C NMR 101 MHz $CDCl_3$

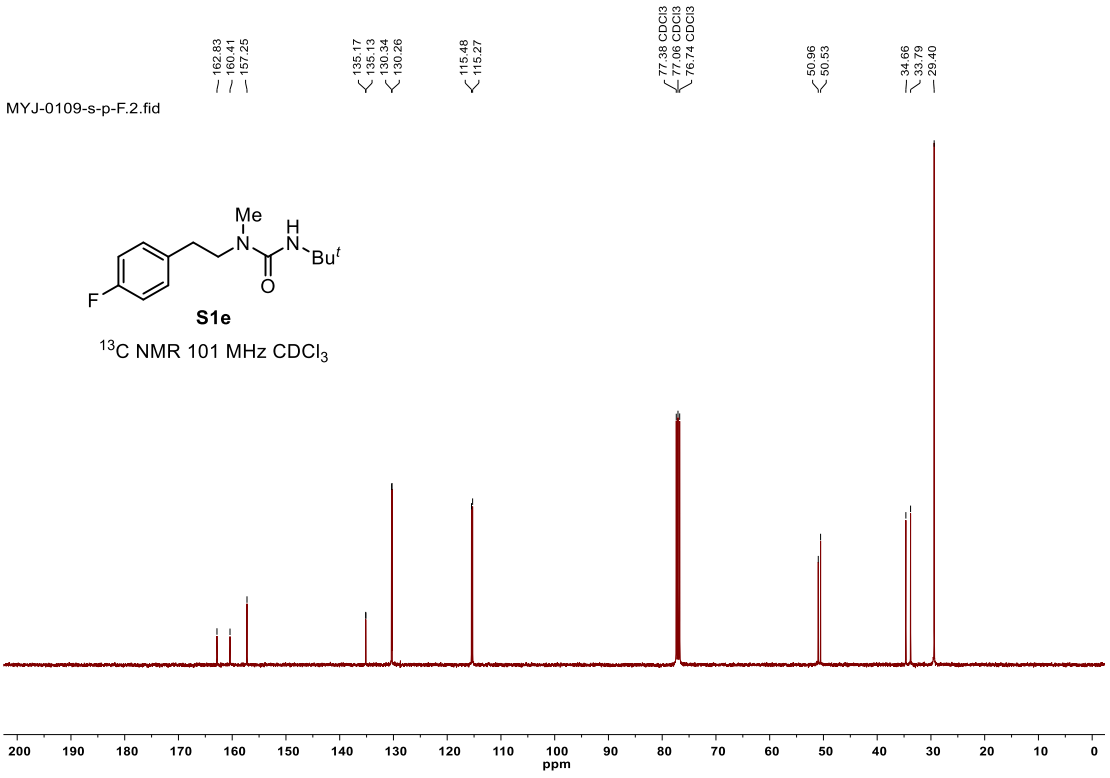

7.578
7.559
7.545
7.525
7.451
7.433
7.413
7.354
7.336
7.318
7.289
7.269
7.260 CDCl3
3.890
3.490
3.473
3.455
2.874
2.857
2.843
1.226
MYJ-0109-s-p-Ph.1.fid
Me
N
H
N
Bu^t
O
Ph
S1d
^{1}H NMR 400 MHz CDCl$_3$
4.05
2.02
1.04
2.06
0.97
1.98
4.96
9.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


157.43
140.91
139.47
138.62
129.39
128.80
127.45
127.20
127.02
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
51.15
50.49
34.55
34.25
29.36
MYJ-0109-s-p-Ph.2.fid
Me
N
H
N
Bu^t
O
Ph
S1d
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



S1e

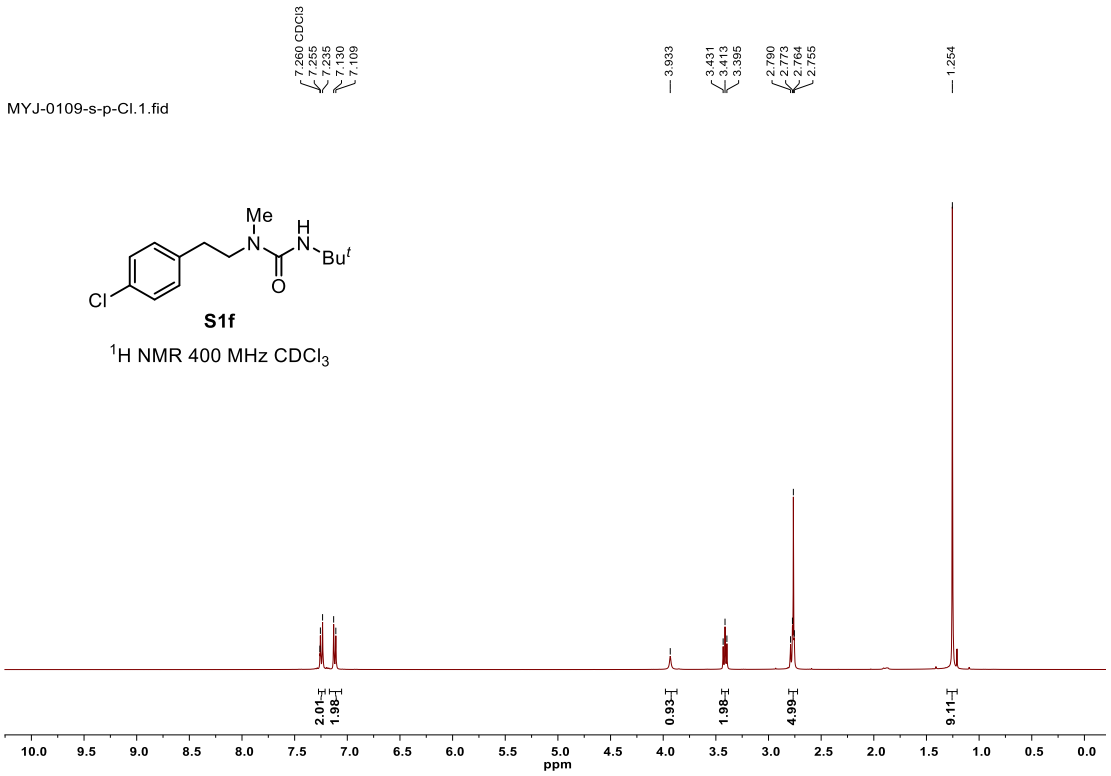
^{1}H NMR 400 MHz $CDCl_3$



S1e

^{13}C NMR 101 MHz $CDCl_3$

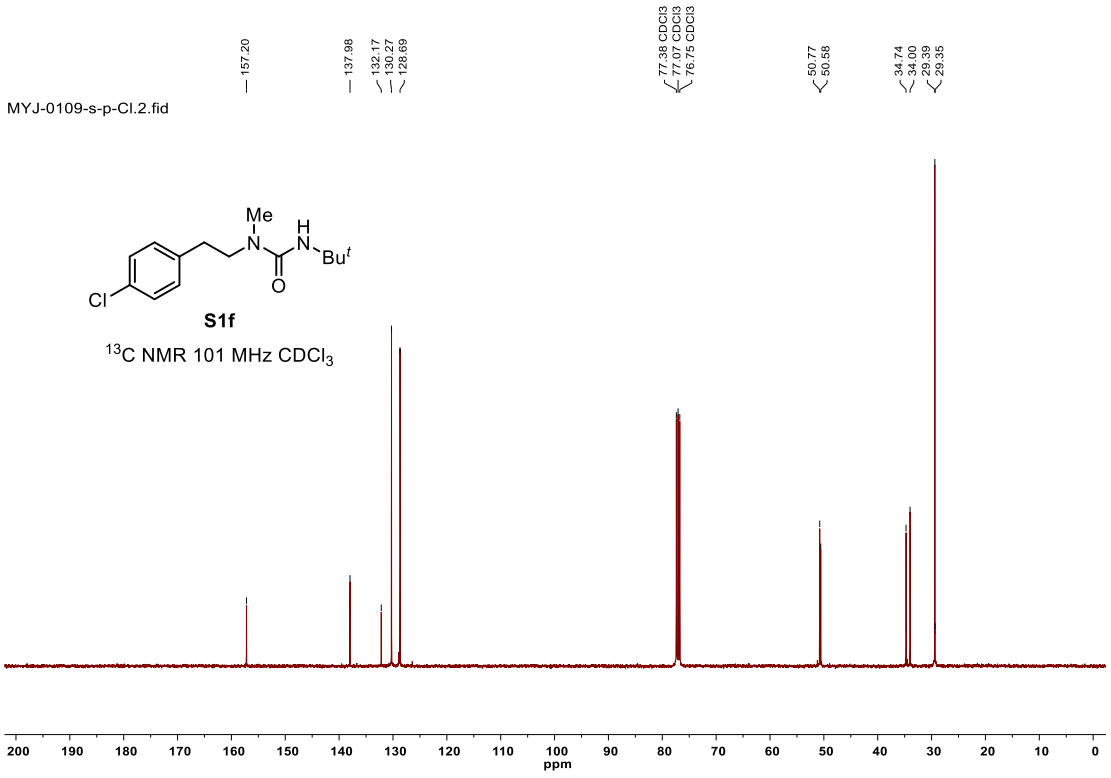
MYJ-0109-s-p-Cl.1.fid



S1f

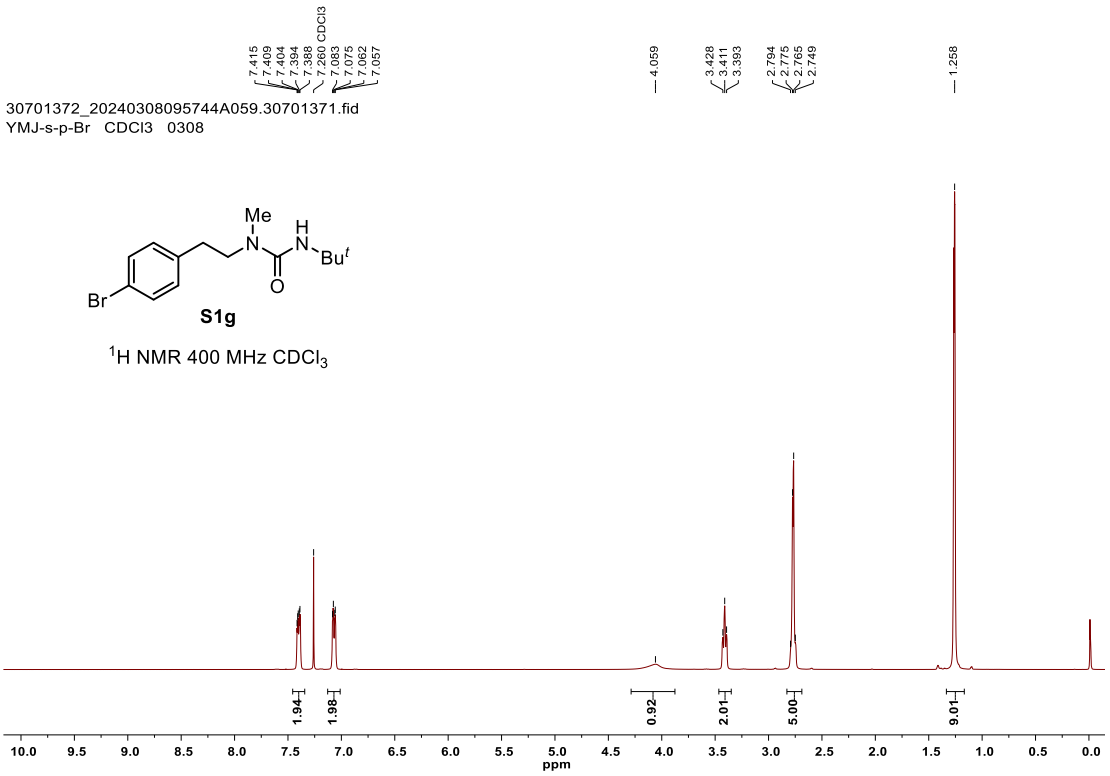
^{1}H NMR 400 MHz $CDCl_3$

MYJ-0109-s-p-Cl.2.fid



S1f

^{13}C NMR 101 MHz $CDCl_3$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7.388
7.260 CDCl3
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7.057
4.059
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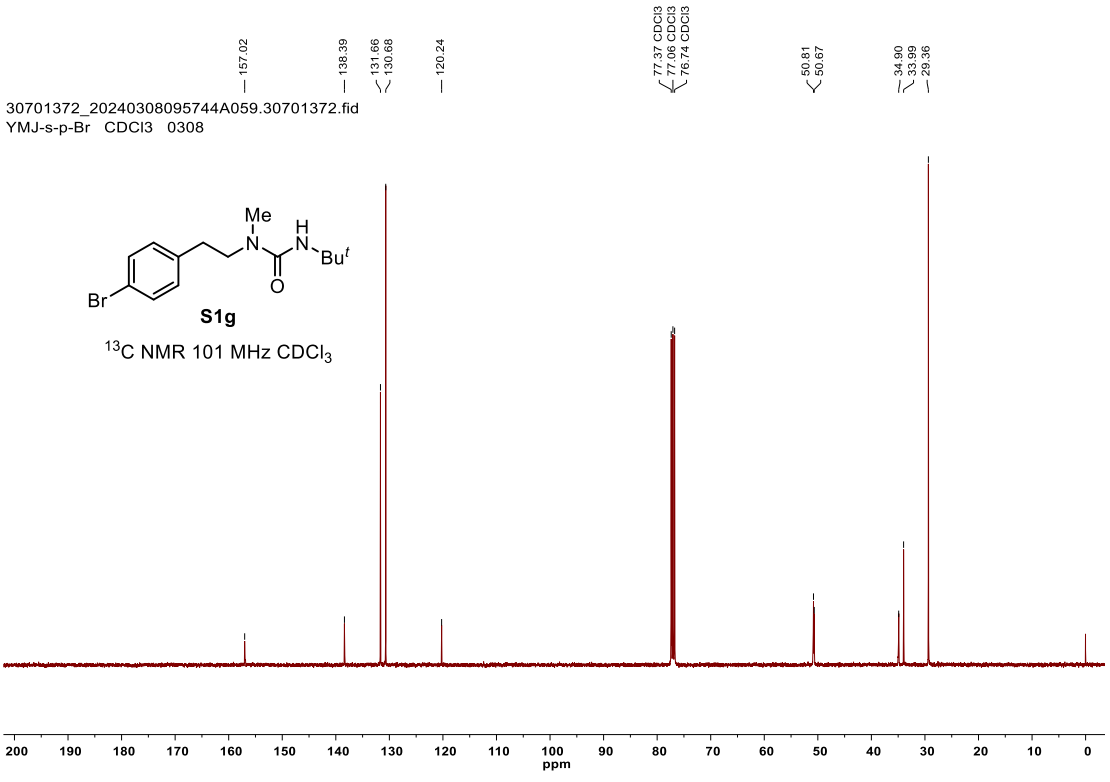
3.411
3.393
2.794
2.775
2.765
2.749
1.258
30701372_20240308095744A059.30701371.fid
YMJ-s-p-Br CDCl3 0308
Me
N
H
N
Bu^t
O
Br
S1g
^{1}H NMR 400 MHz CDCl$_3$
1.94
1.98
0.92
2.01
5.00
9.01
ppm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131.66
130.68
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76.74 CDCl3
50.81
50.67
34.90
33.99
29.36
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YMJ-s-p-Br CDCl3 0308
Me
N
H
N
Bu^t
O
Br
S1g
^{13}C NMR 101 MHz CDCl$_3$
ppm

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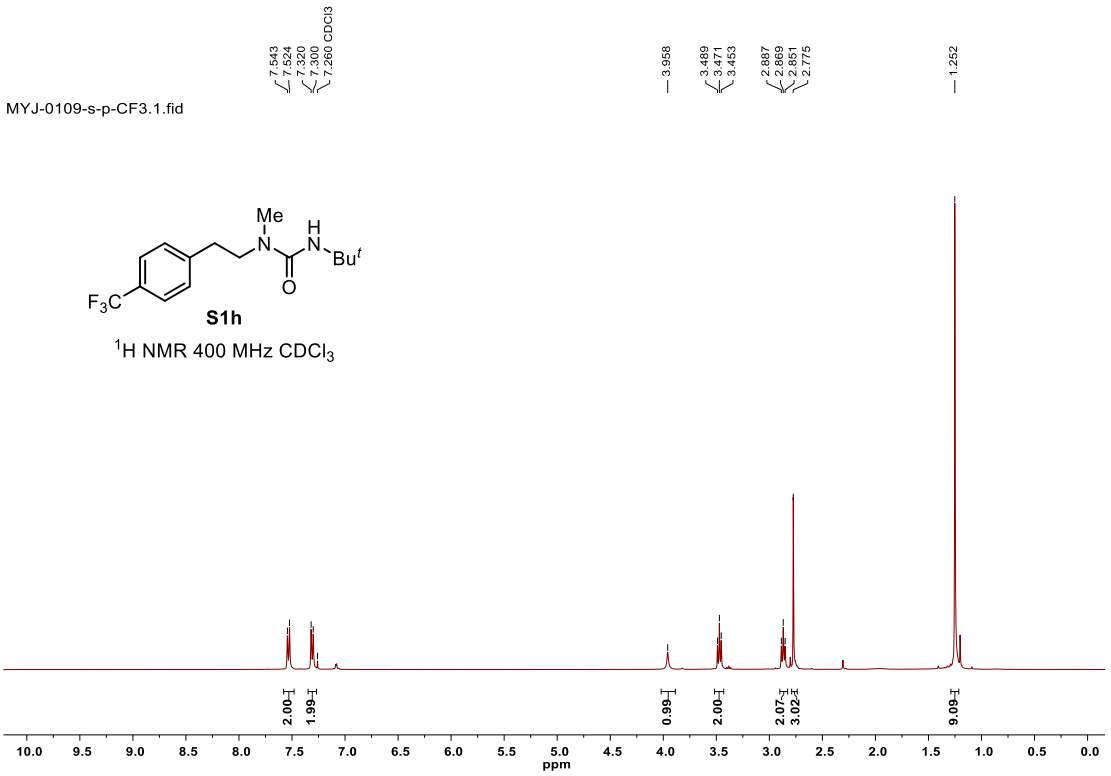

S1h

^{1}H NMR 400 MHz $CDCl_3$

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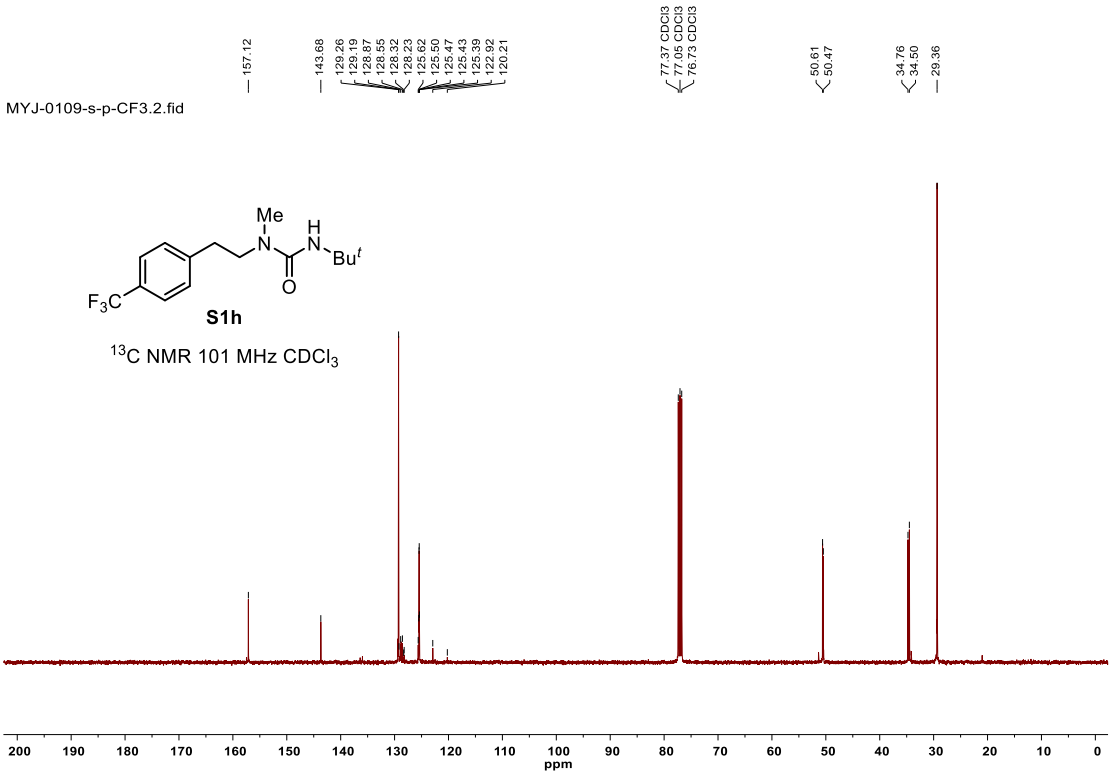

S1h

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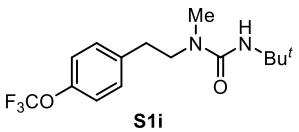
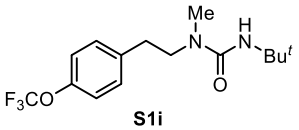


S1i

^{1}H NMR 400 MHz $CDCl_3$

MYJ-0109-s-p-OCF3.2.fid



S1i

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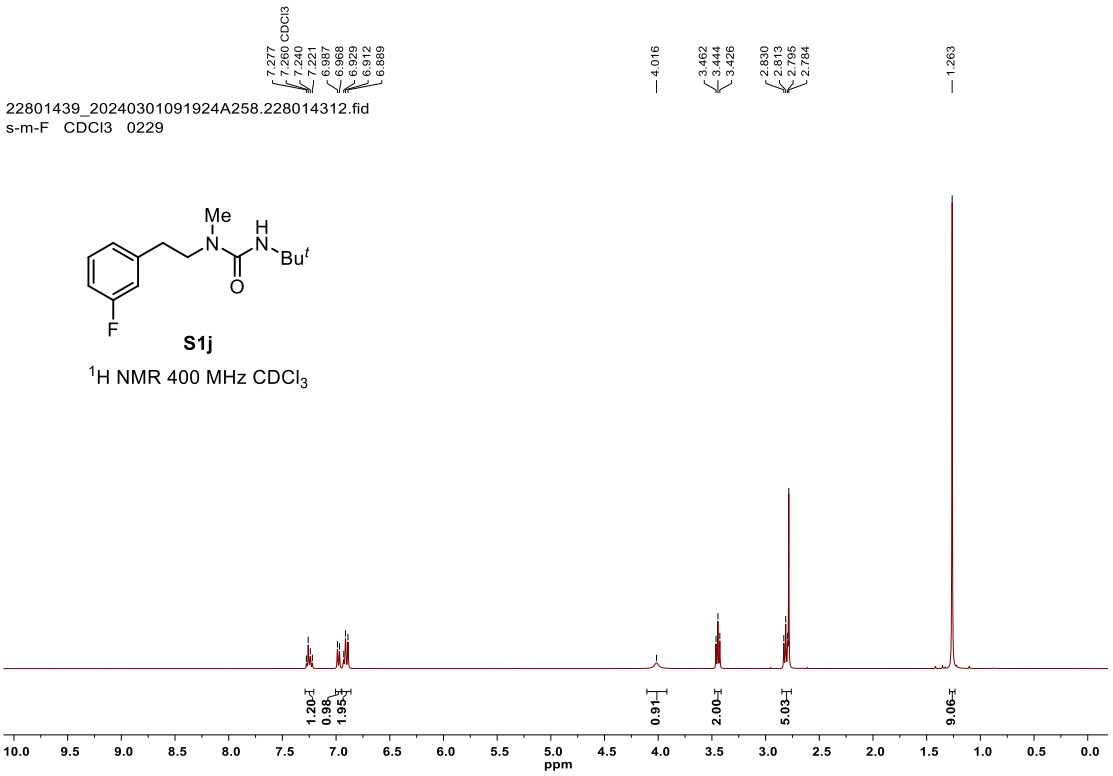

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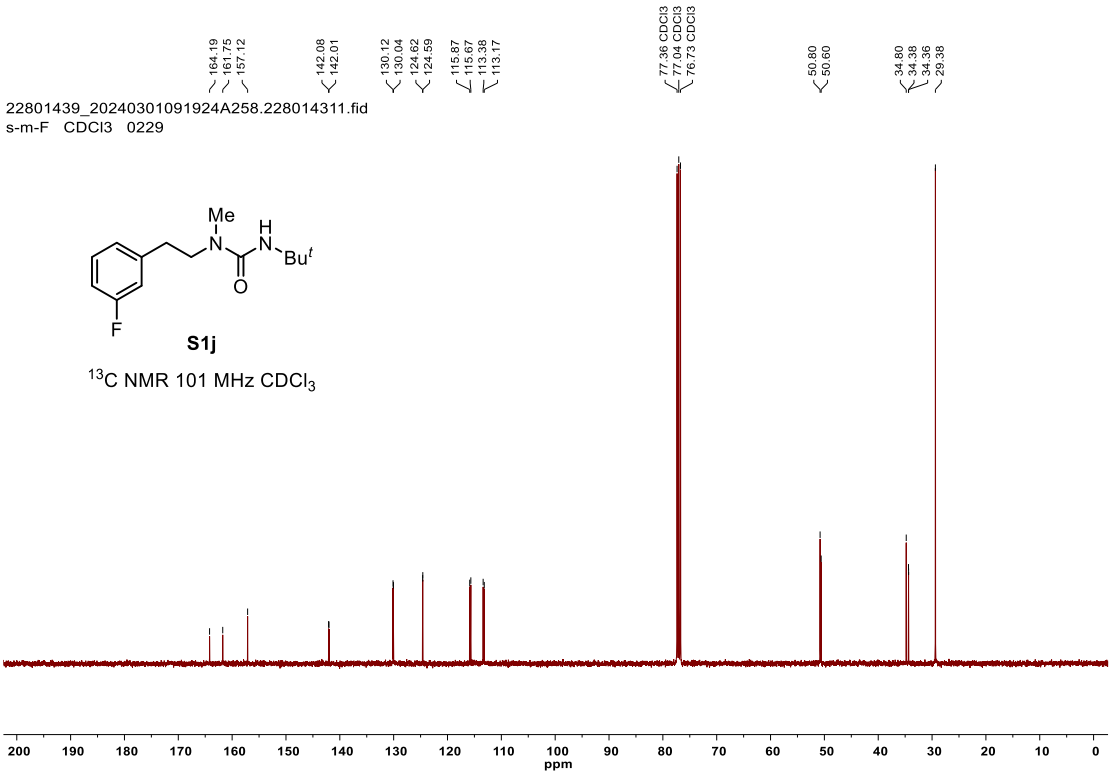

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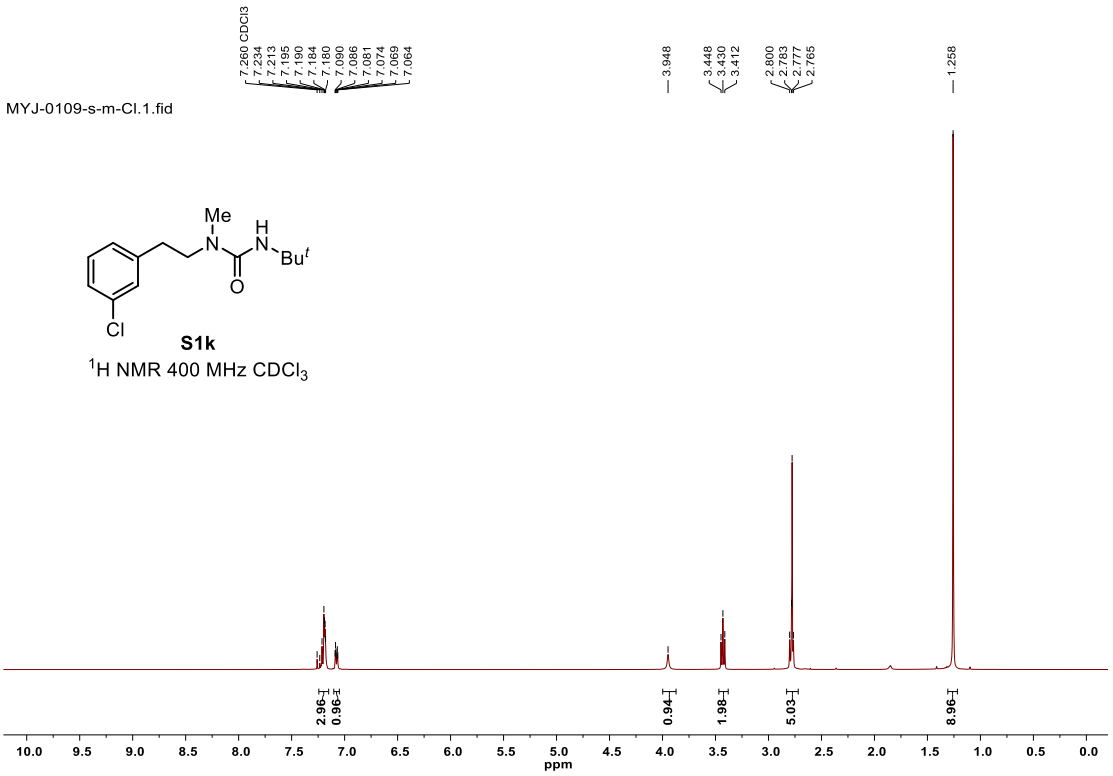

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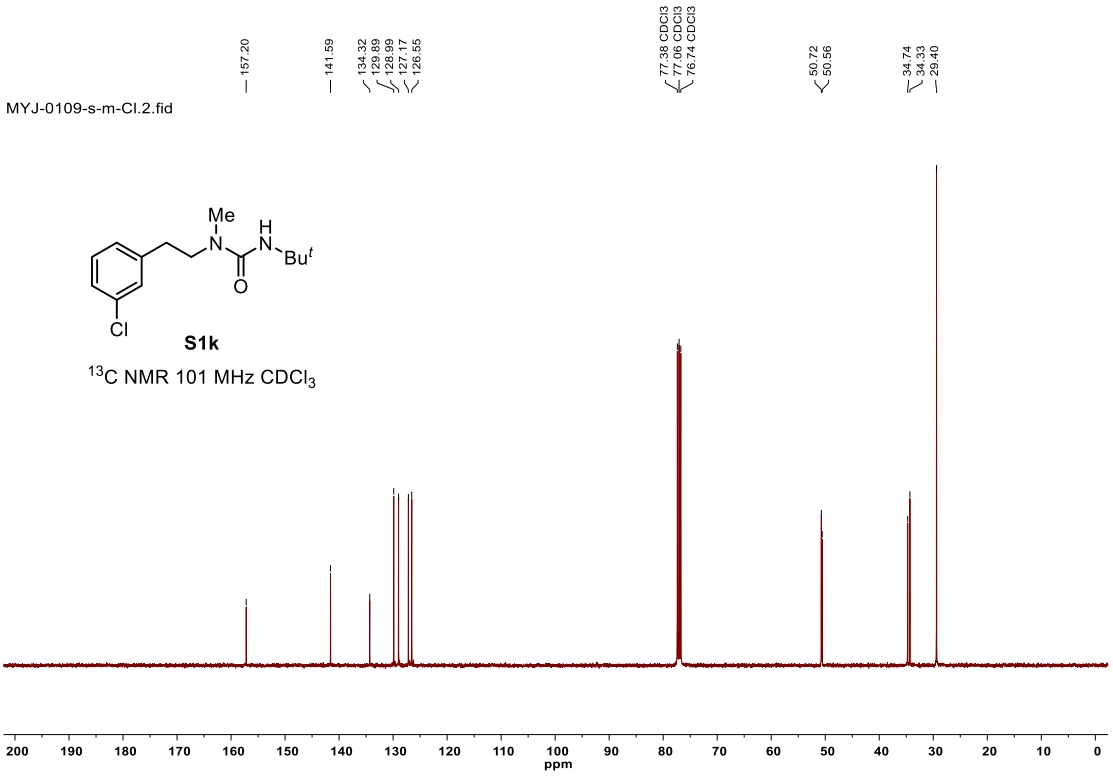

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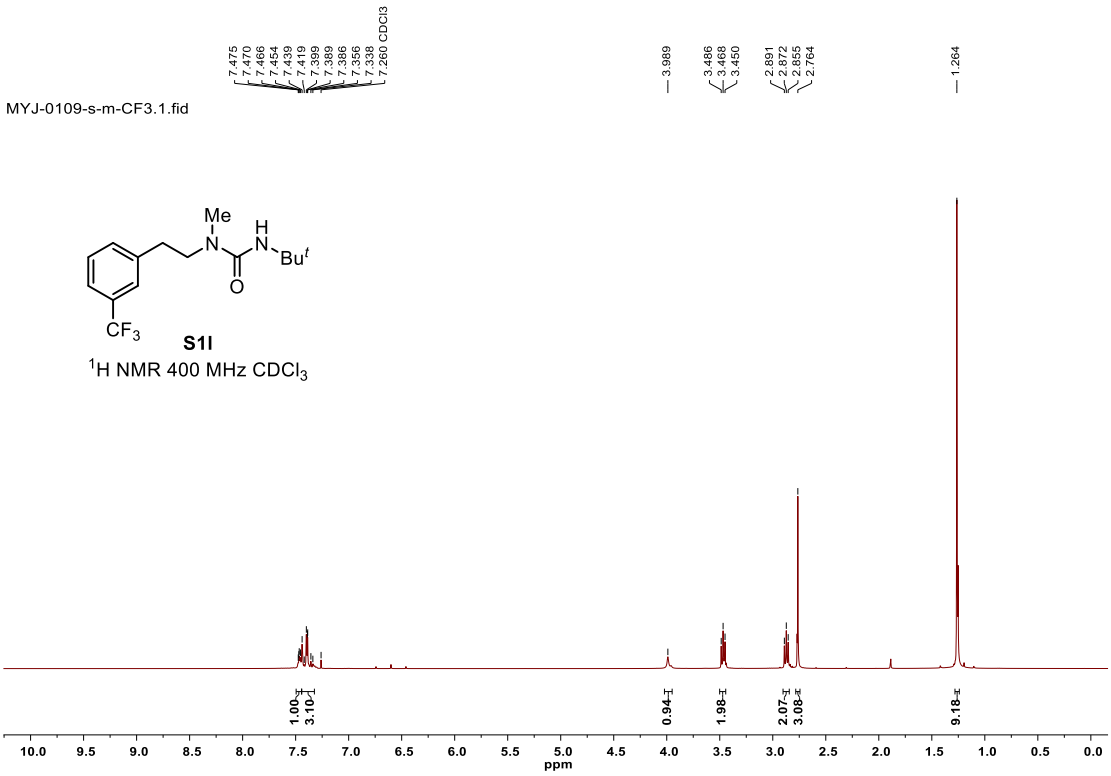

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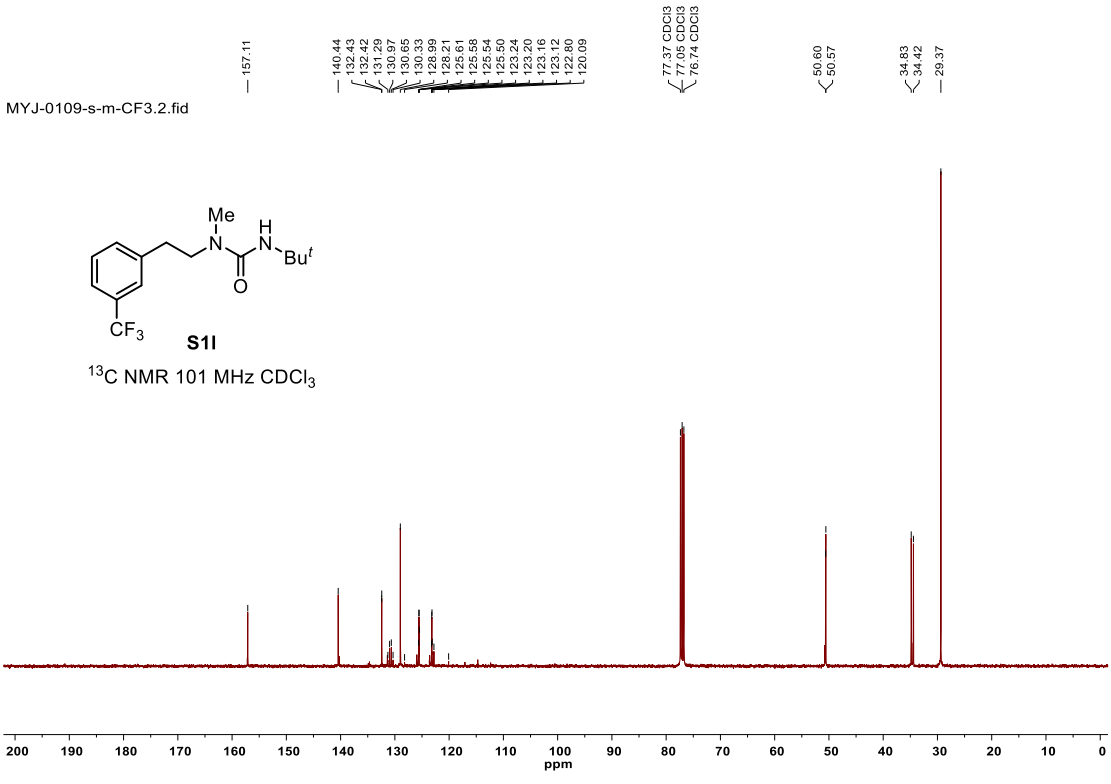

S1l

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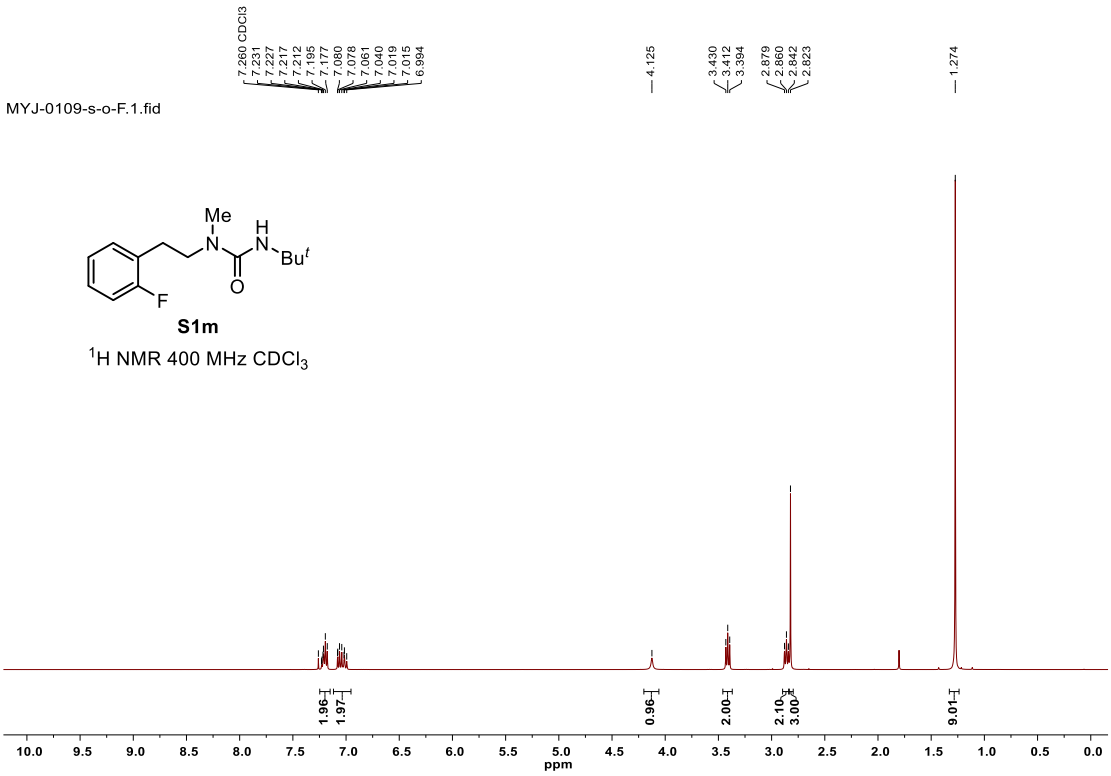

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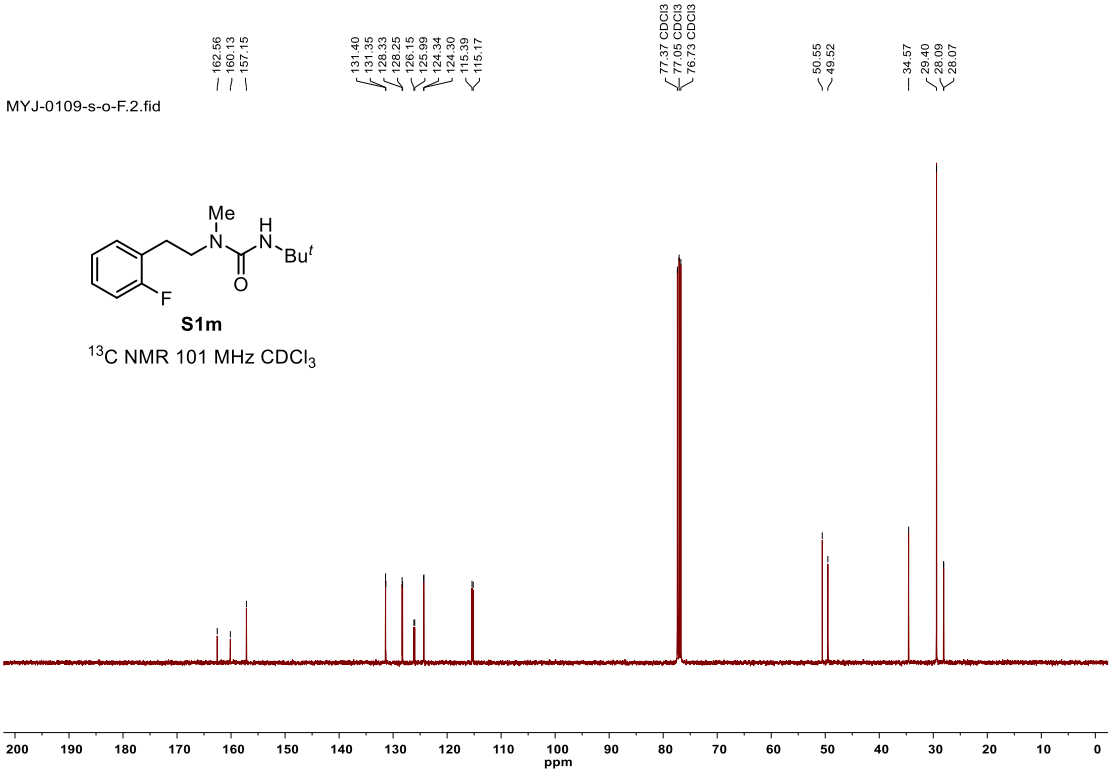

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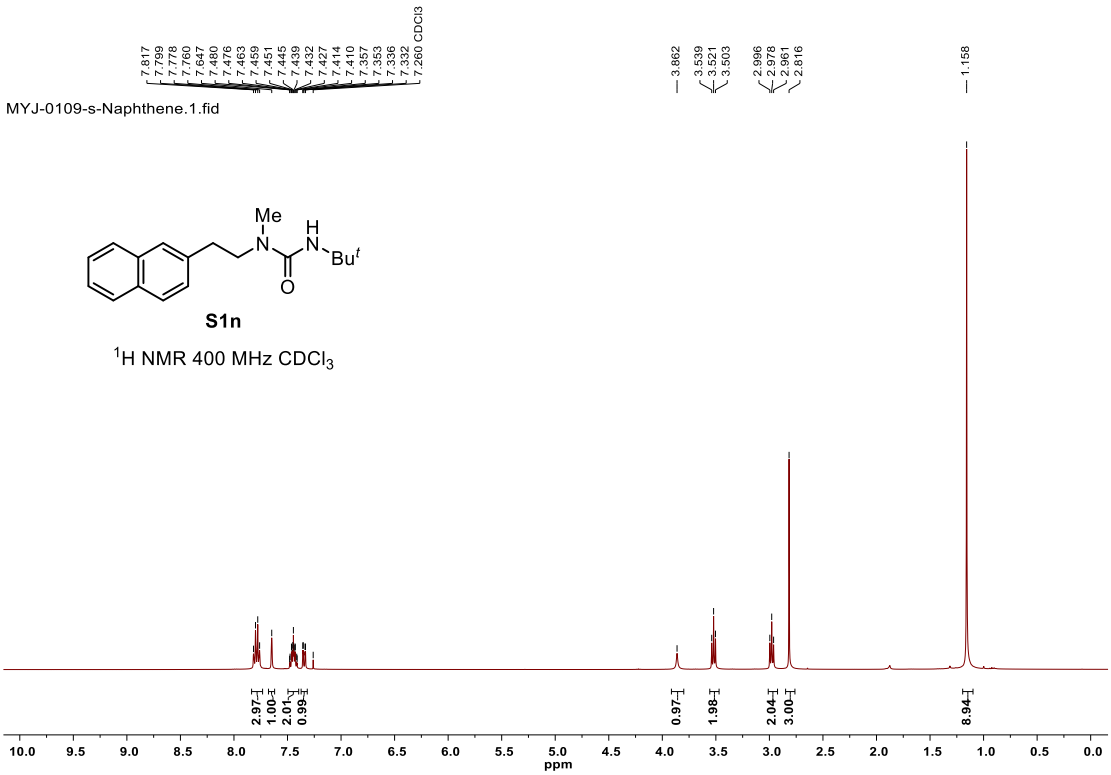
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7.451
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7.439
7.432
7.427
7.414
7.410
7.357
7.353
7.336
7.332
7.260 CDCl3
3.862
3.539
3.521
3.503
2.996
2.978
2.961
2.816
1.158
MYJ-0109-s-Naphthene.1.fid
Me
H
N
N
Bu^t
O
S1n
^{1}H NMR 400 MHz CDCl$_3$
2.97
1.00
2.01
0.99
0.97
1.98
2.04
3.00
8.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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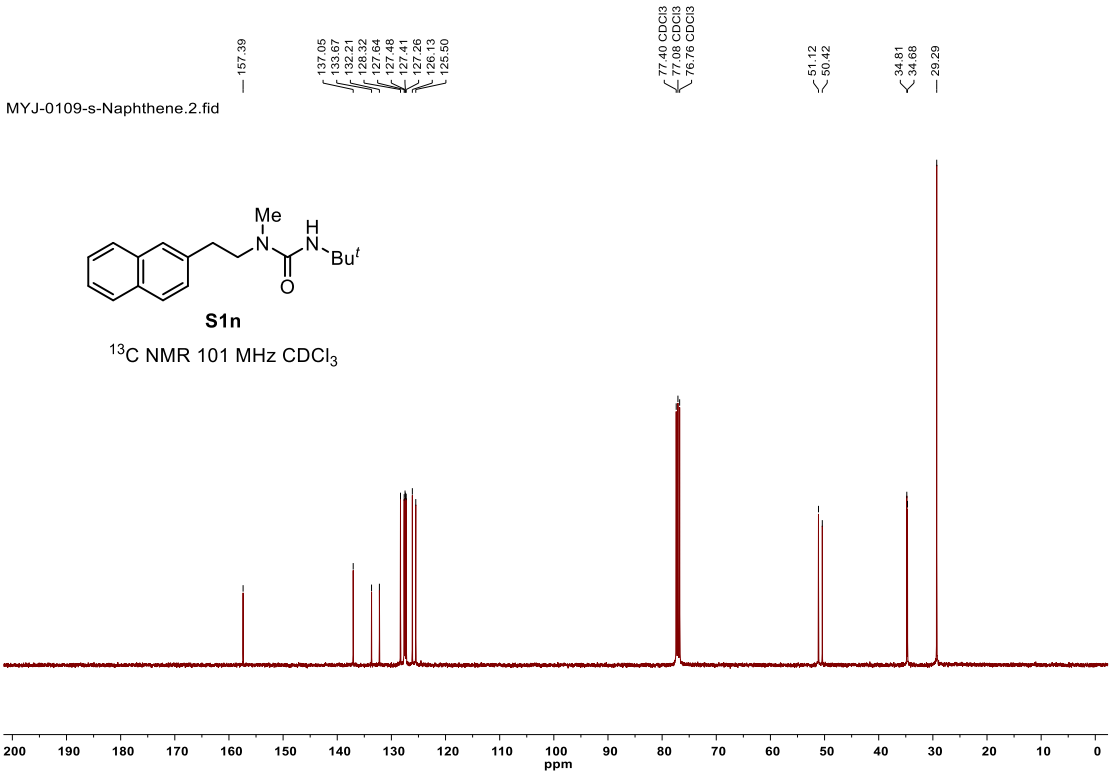
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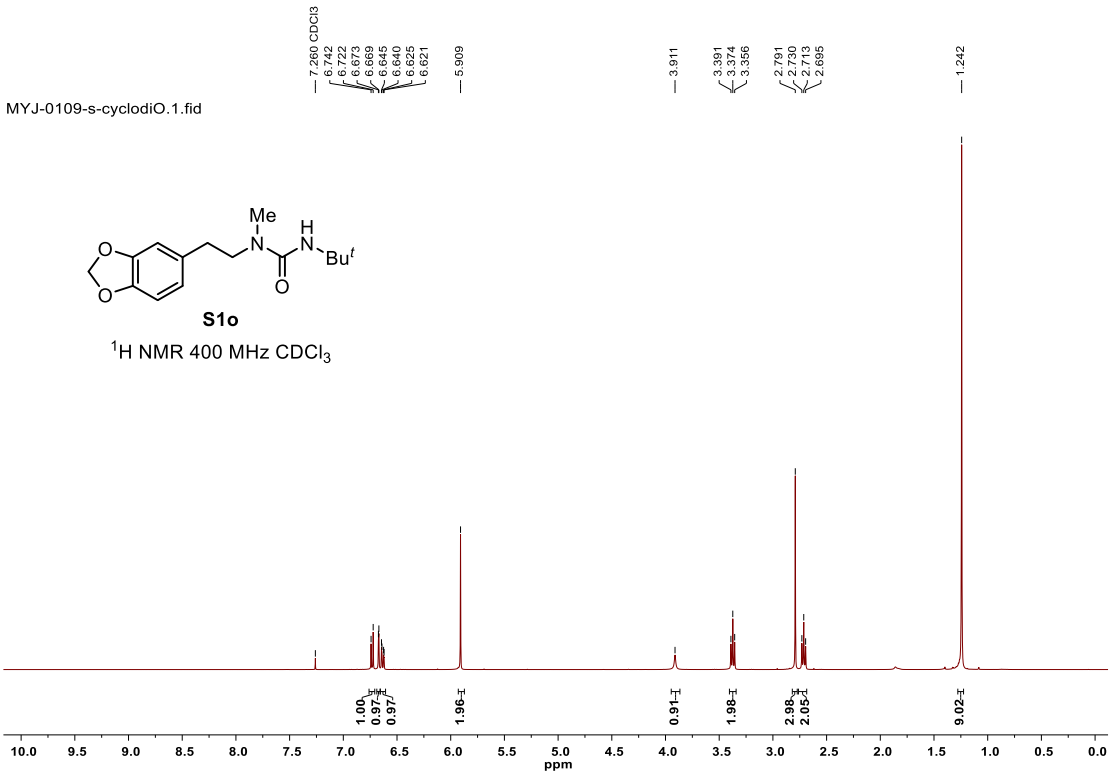
137.05
133.67
132.21
128.32
127.64
127.48
127.41
127.26
126.13
125.50
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
51.12
50.42
34.81
34.68
29.29
MYJ-0109-s-Naphthene.2.fid
Me
H
N
N
Bu^t
O
S1n
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



S1o

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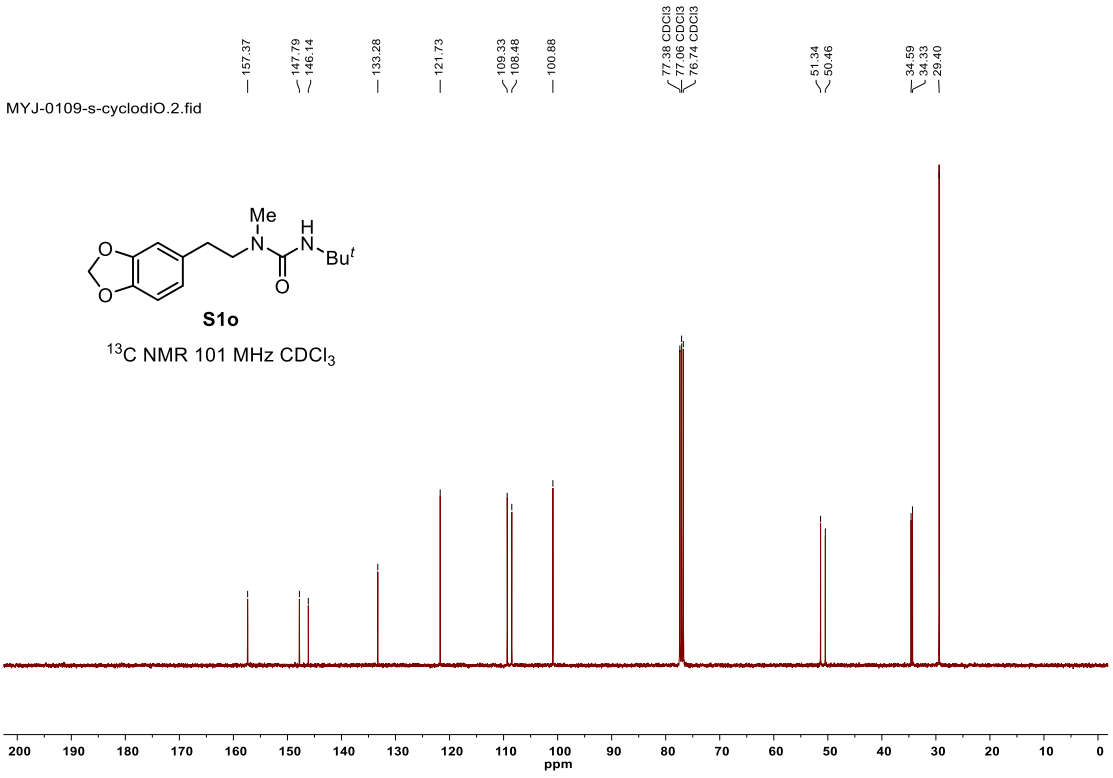

S1o

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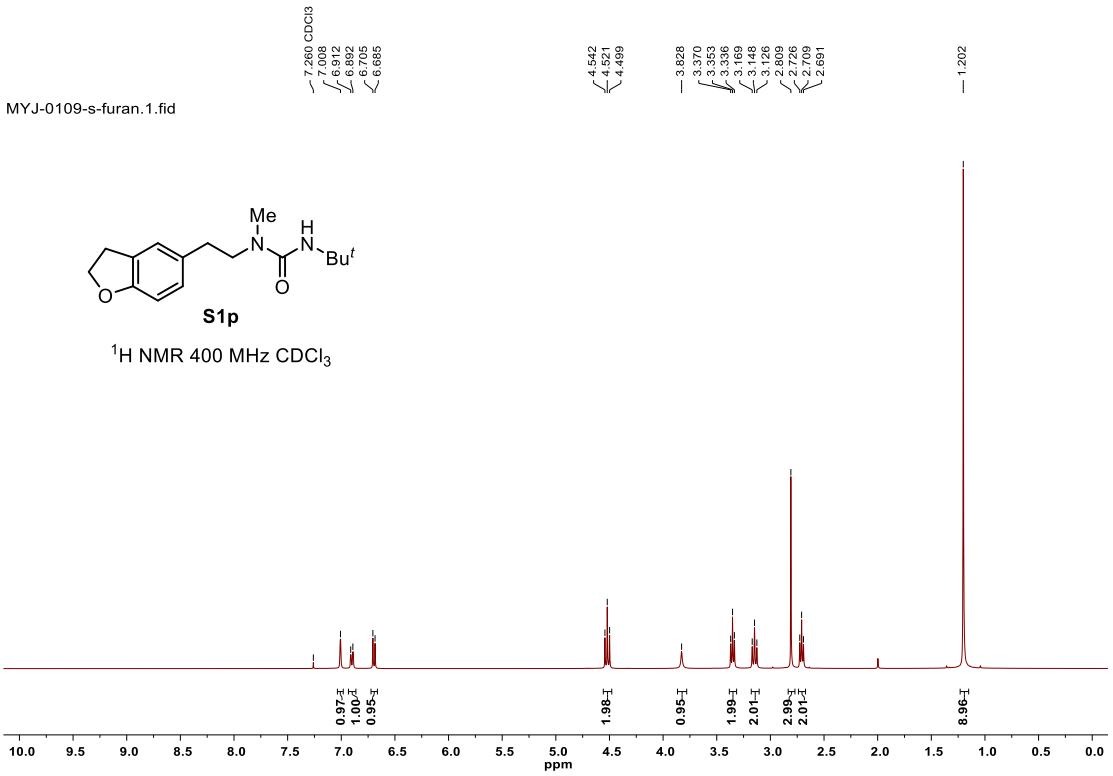

S1p

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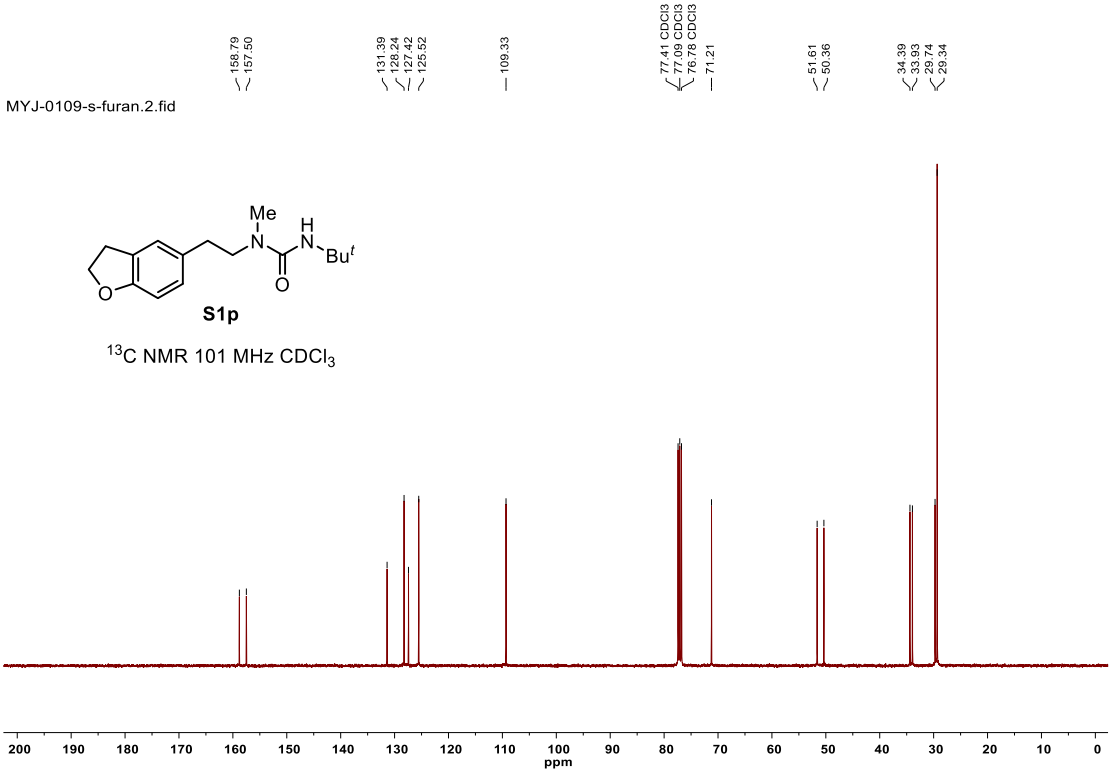
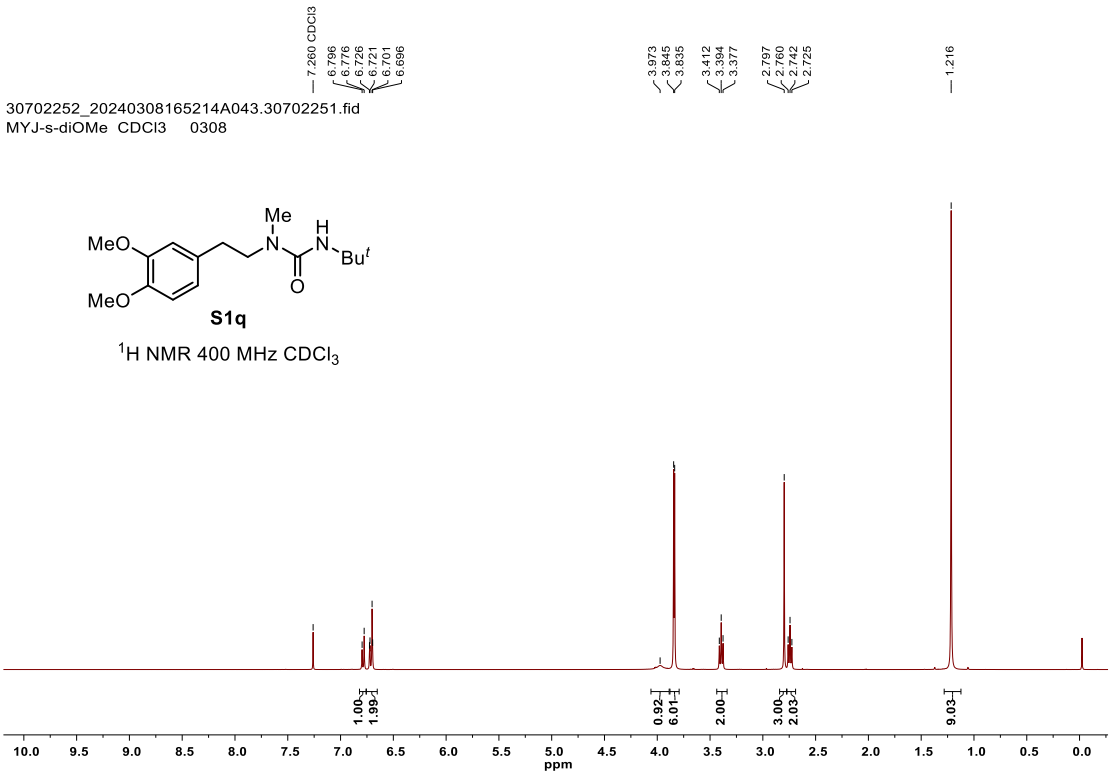


S1p

^{13}C NMR 101 MHz $CDCl_3$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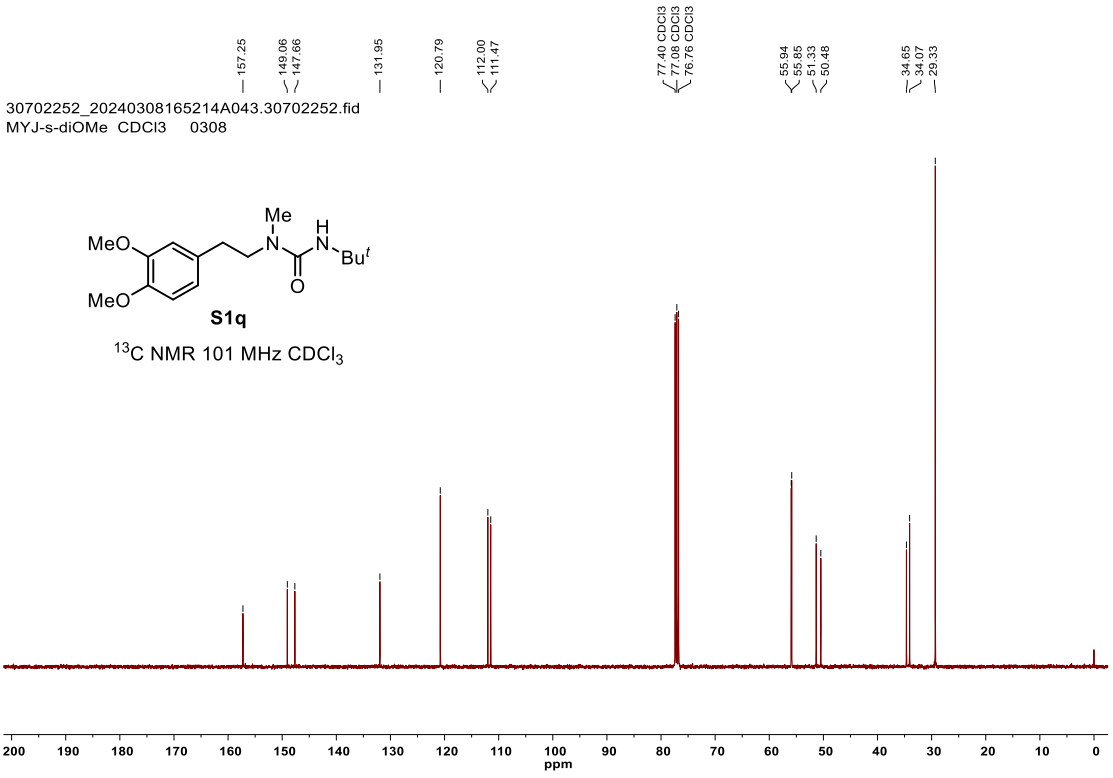
3.845
3.835
3.412
3.394
3.377
2.797
2.760
2.742
2.725
1.216
30702252_20240308165214A043.30702251.fid
MYJ-s-diOMe CDCl3 0308
Me
N
H
N
Bu^t
MeO
MeO
O
S1q
^{1}H NMR 400 MHz CDCl$_3$
1.00
1.99
0.92
6.01
2.00
3.00
2.03
9.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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147.66
131.95
120.79
112.00
111.47
77.40 CDCl3
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55.94
55.85
51.33
50.48
34.65
34.07
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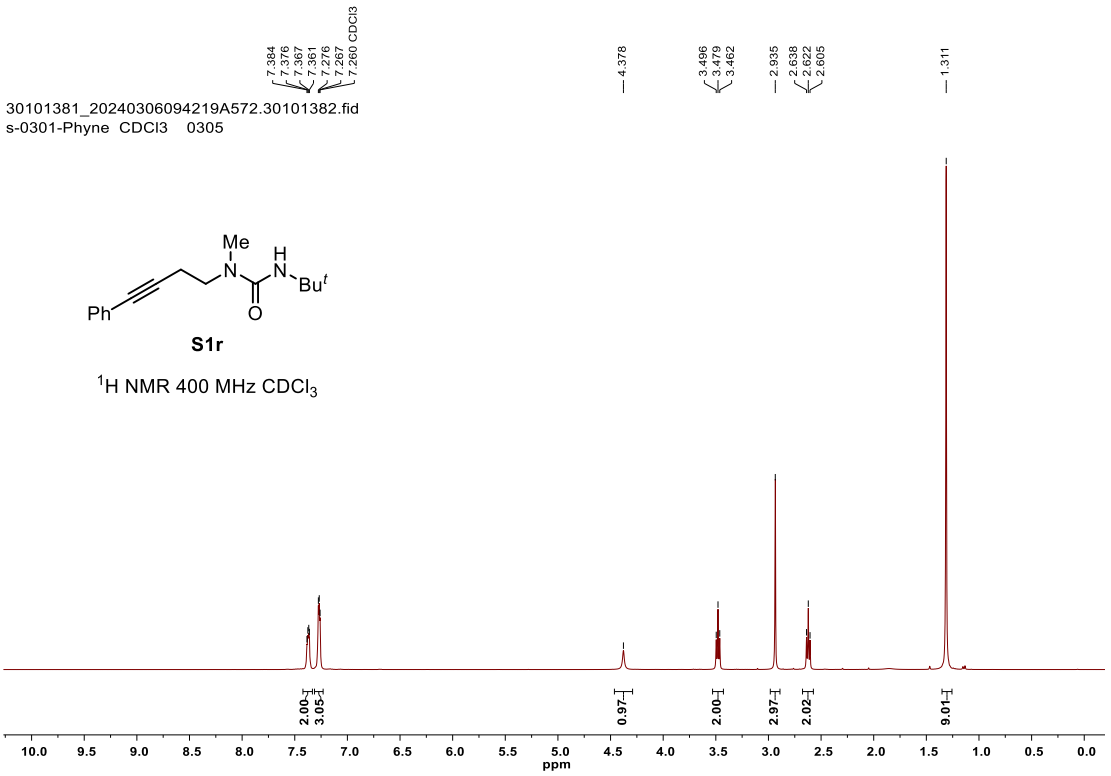
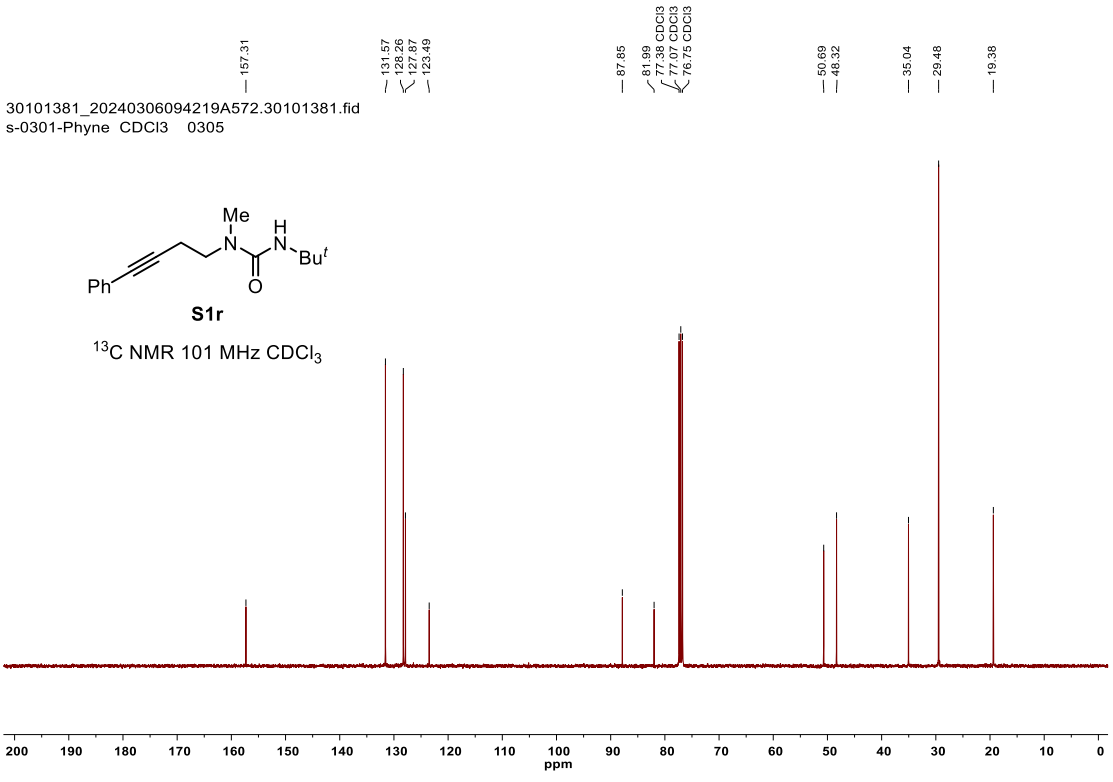
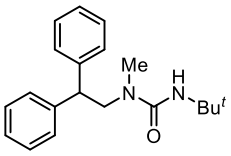
MYJ-s-diOMe CDCl3 0308
Me
N
H
N
Bu^t
MeO
MeO
O
S1q
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.384
7.376
7.367
7.361
7.276
7.267
7.260 CDCl3
4.378
3.496
3.479
3.462
2.935
2.638
2.622
2.605
1.311
30101381_20240306094219A572.30101382.fid
s-0301-Phyne CDCl3 0305
Me
N
H
N
Bu^t
Ph
O
S1r
^{1}H NMR 400 MHz CDCl$_3$
2.00
3.05
0.97
2.00
2.97
2.02
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


157.31
131.57
128.26
127.87
123.49
87.85
81.99
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
50.69
48.32
35.04
29.48
19.38
30101381_20240306094219A572.30101381.fid
s-0301-Phyne CDCl3 0305
Me
N
H
N
Bu^t
Ph
O
S1r
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

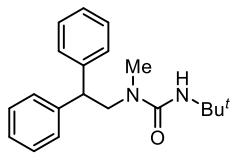
22801439_20240301091924A258.22801438.fid
s-1,1-diPh CDCl3 0229



S1s

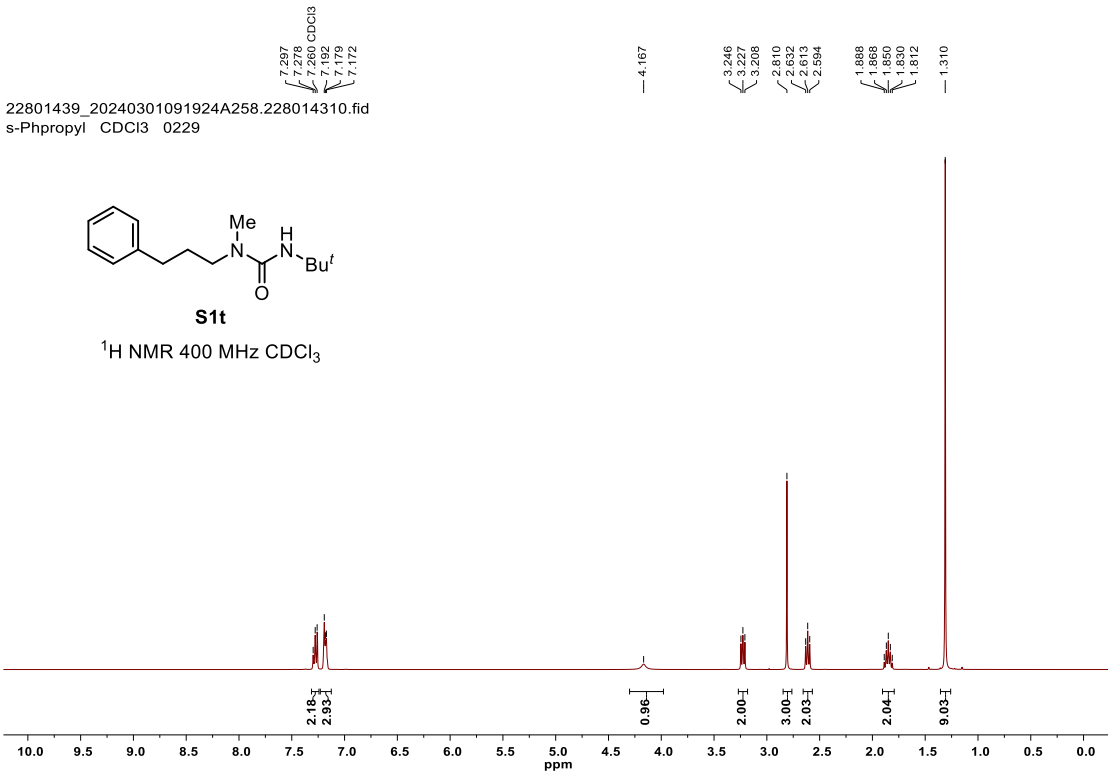
^{1}H NMR 400 MHz $CDCl_3$

22801439_20240301091924A258.22801437.fid
s-1,1-diPh CDCl3 0229



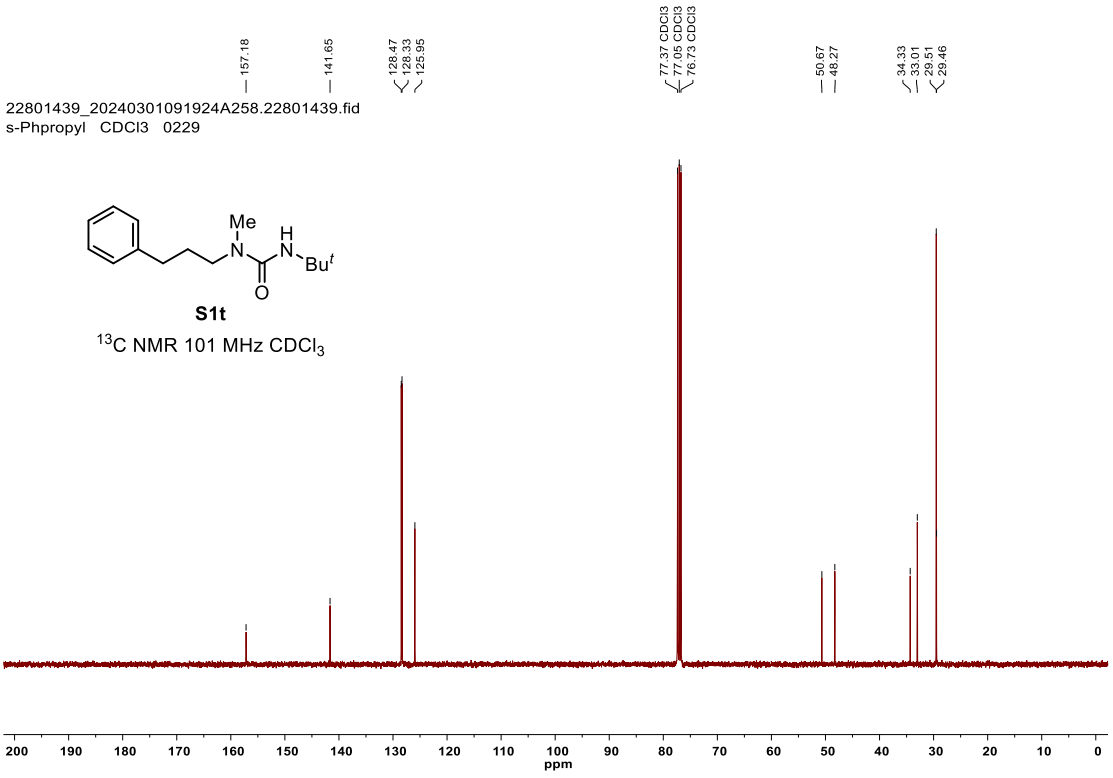
S1s

^{13}C NMR 101 MHz $CDCl_3$



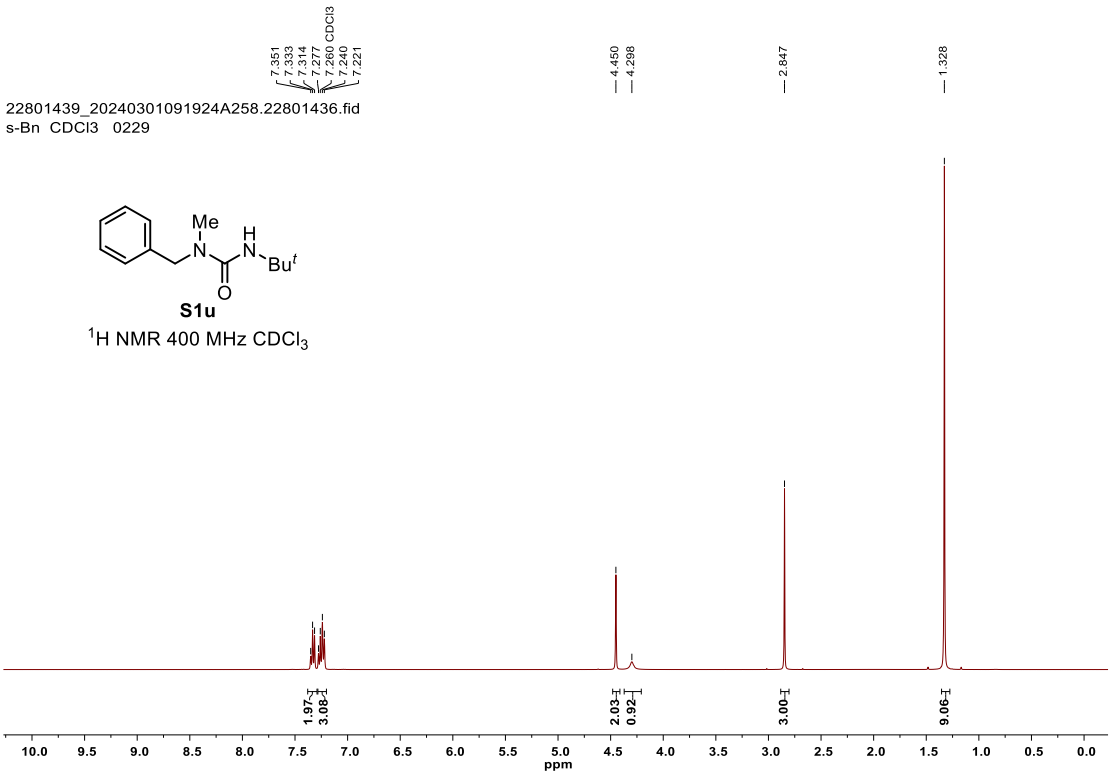
S1t

^{1}H NMR 400 MHz $CDCl_3$



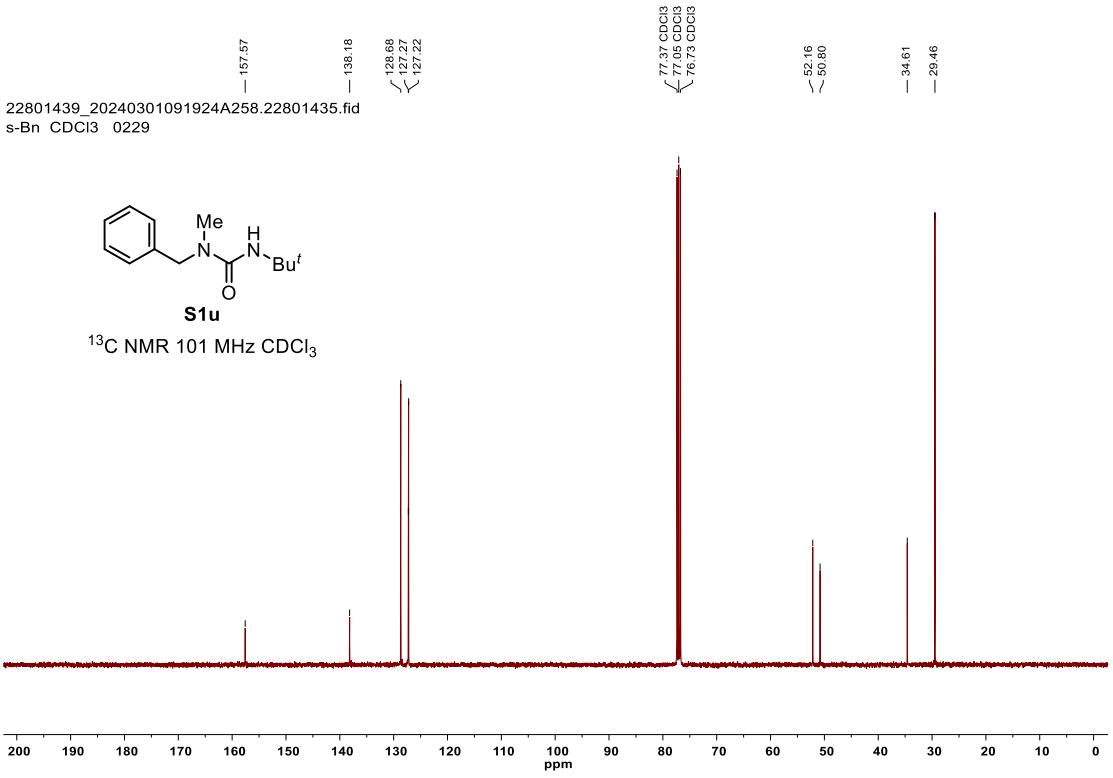
S1t

^{13}C NMR 101 MHz $CDCl_3$



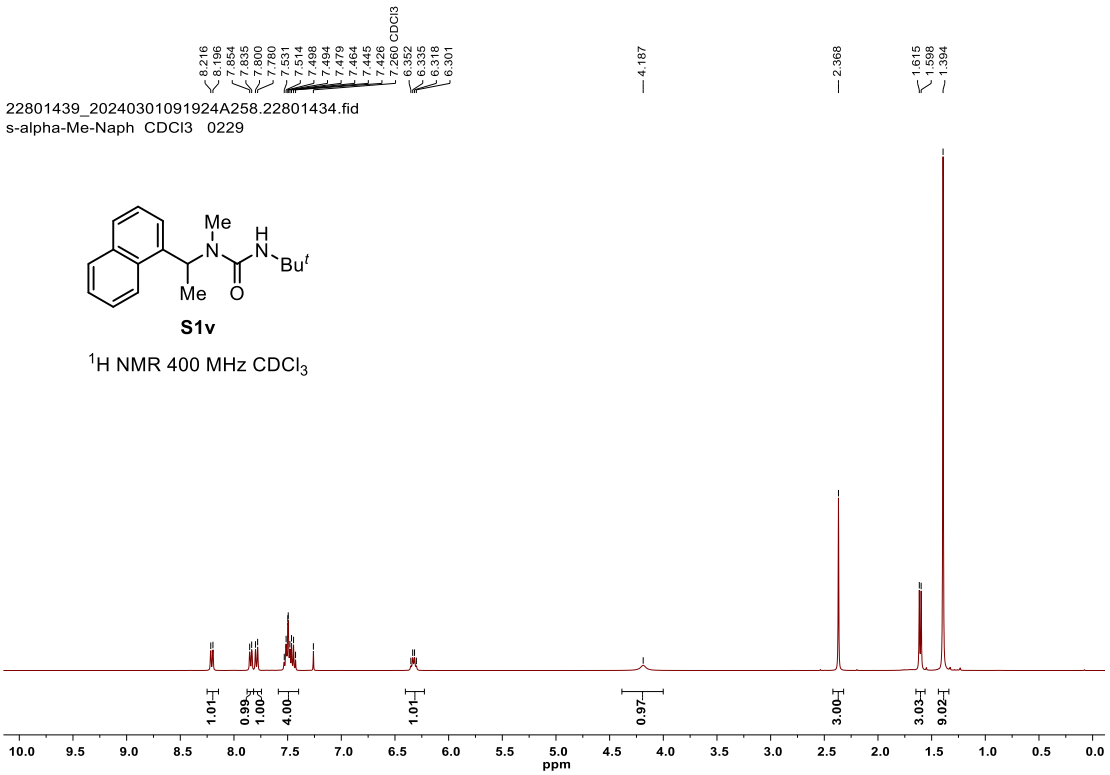
S1u

^{1}H NMR 400 MHz $CDCl_3$



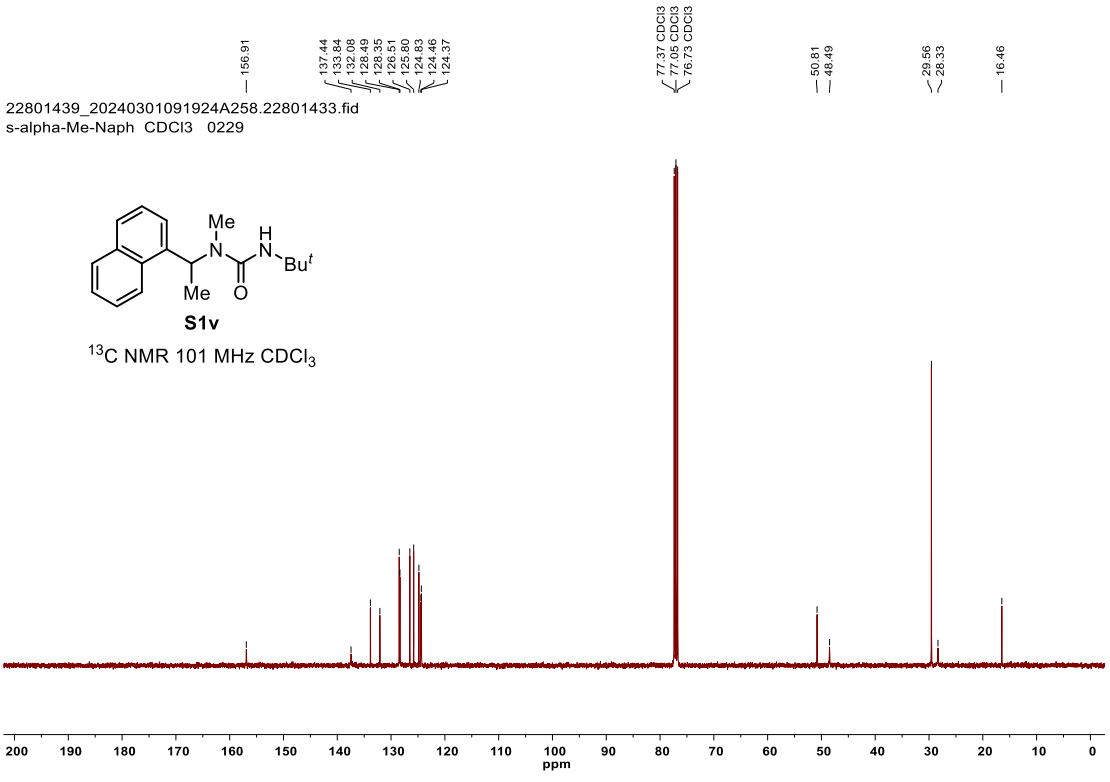
S1u

^{13}C NMR 101 MHz $CDCl_3$



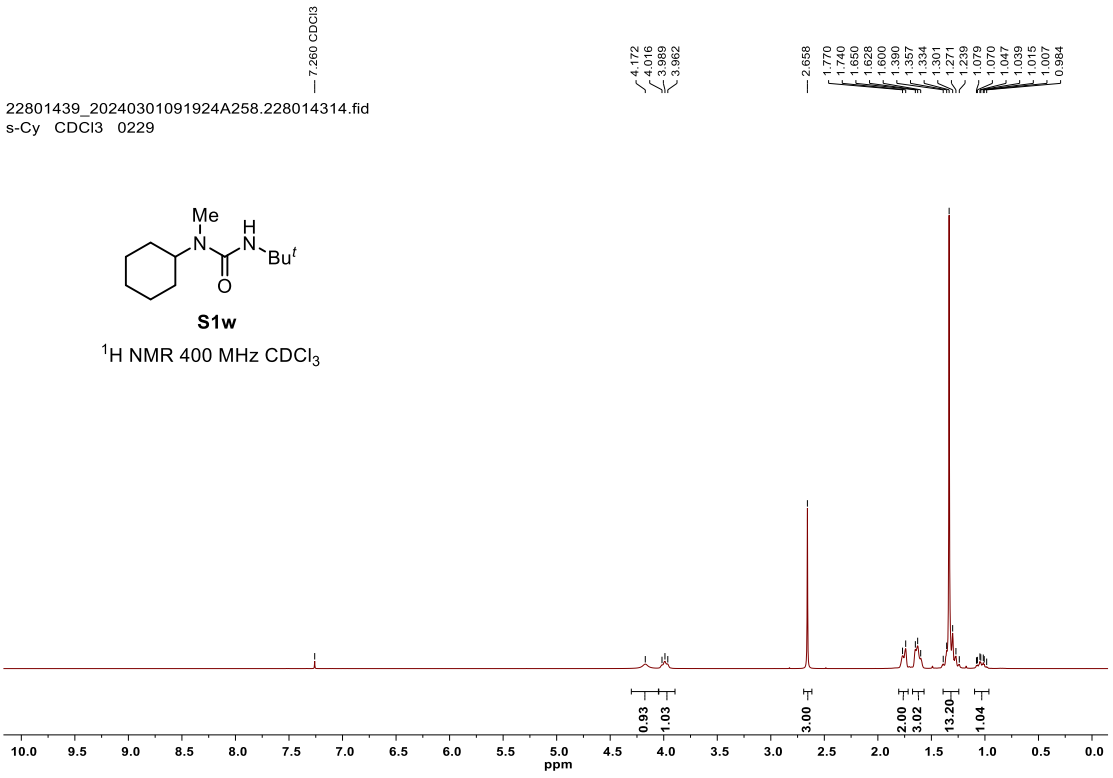
S1v

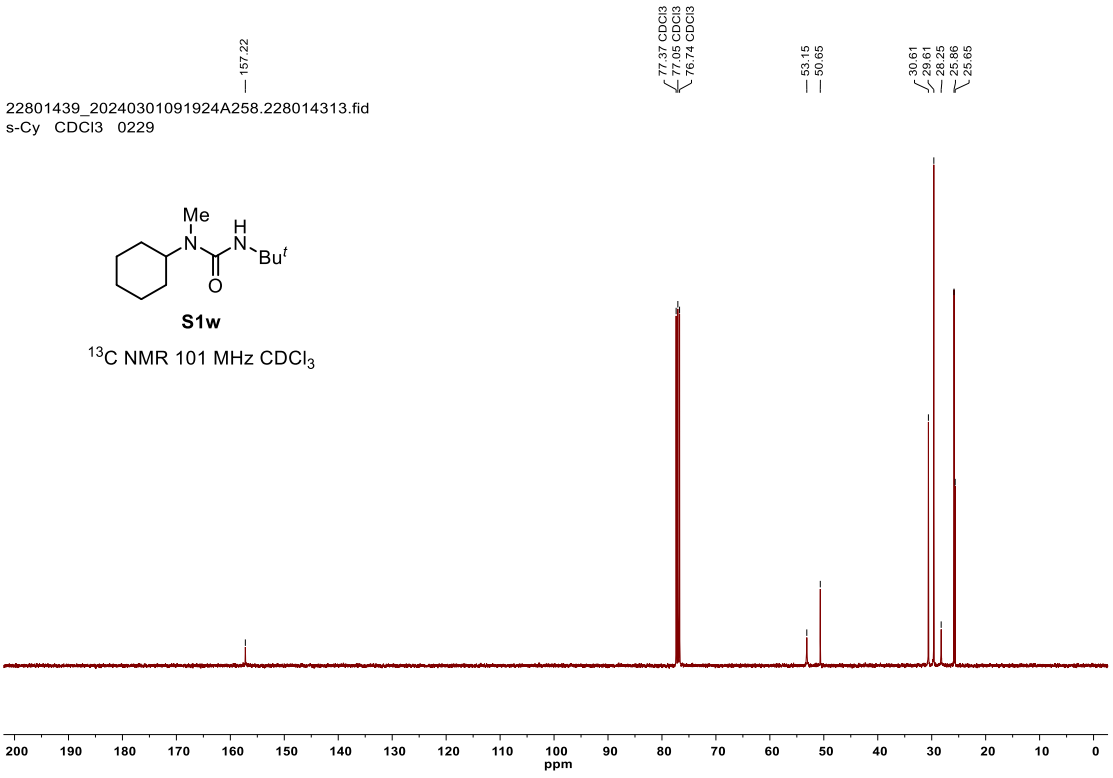
^{1}H NMR 400 MHz $CDCl_3$



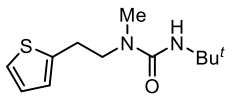
S1v

^{13}C NMR 101 MHz $CDCl_3$


7.260 CDCl3
4.172
4.016
3.989
3.962
2.658
1.770
1.740
1.650
1.628
1.600
1.390
1.357
1.334
1.301
1.271
1.239
1.079
1.070
1.047
1.039
1.015
1.007
0.984
22801439_20240301091924A258.228014314.fid
s-Cy CDCl3 0229
Me
N
H
N
Bu^t
O
S1w
^{1}H NMR 400 MHz CDCl$_3$
0.93
1.03
3.00
2.00
3.02
13.20
1.04
ppm


157.22
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
53.15
50.65
30.61
29.61
28.25
25.86
25.65
22801439_20240301091924A258.228014313.fid
s-Cy CDCl3 0229
Me
N
H
N
Bu^t
O
S1w
^{13}C NMR 101 MHz CDCl$_3$
ppm

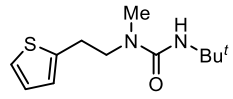
MYJ-0110-s-thiophene.1.fid



S1x

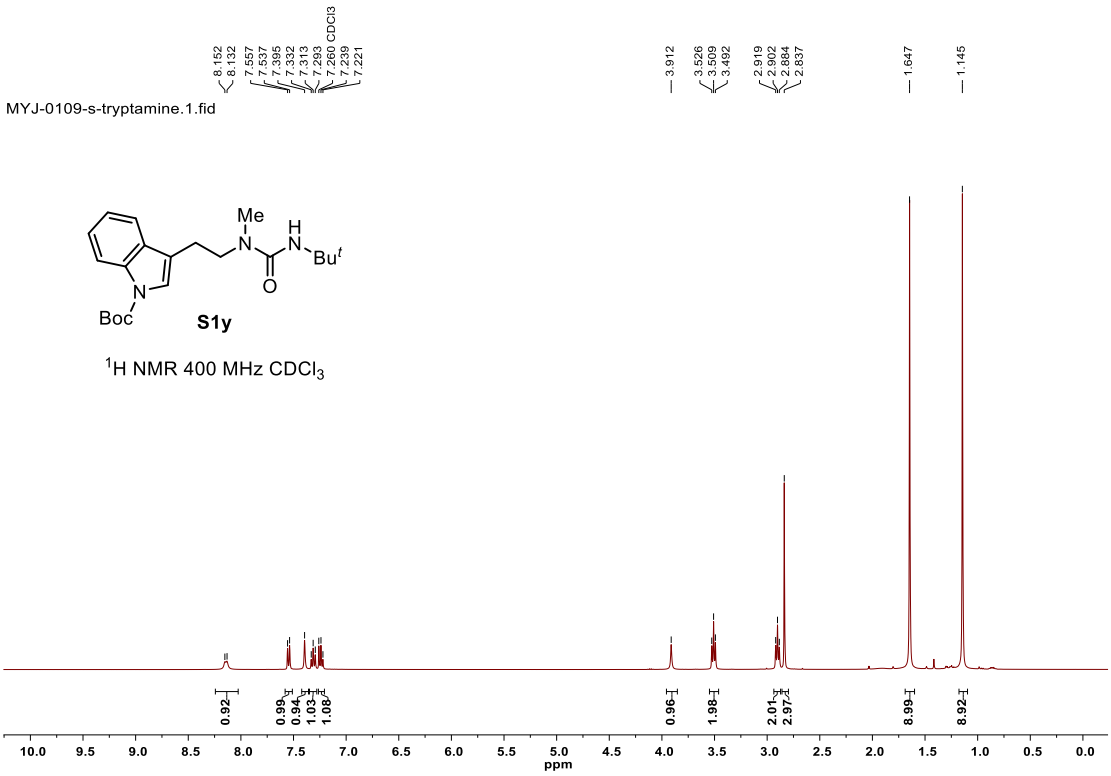
^{1}H NMR 400 MHz $CDCl_3$

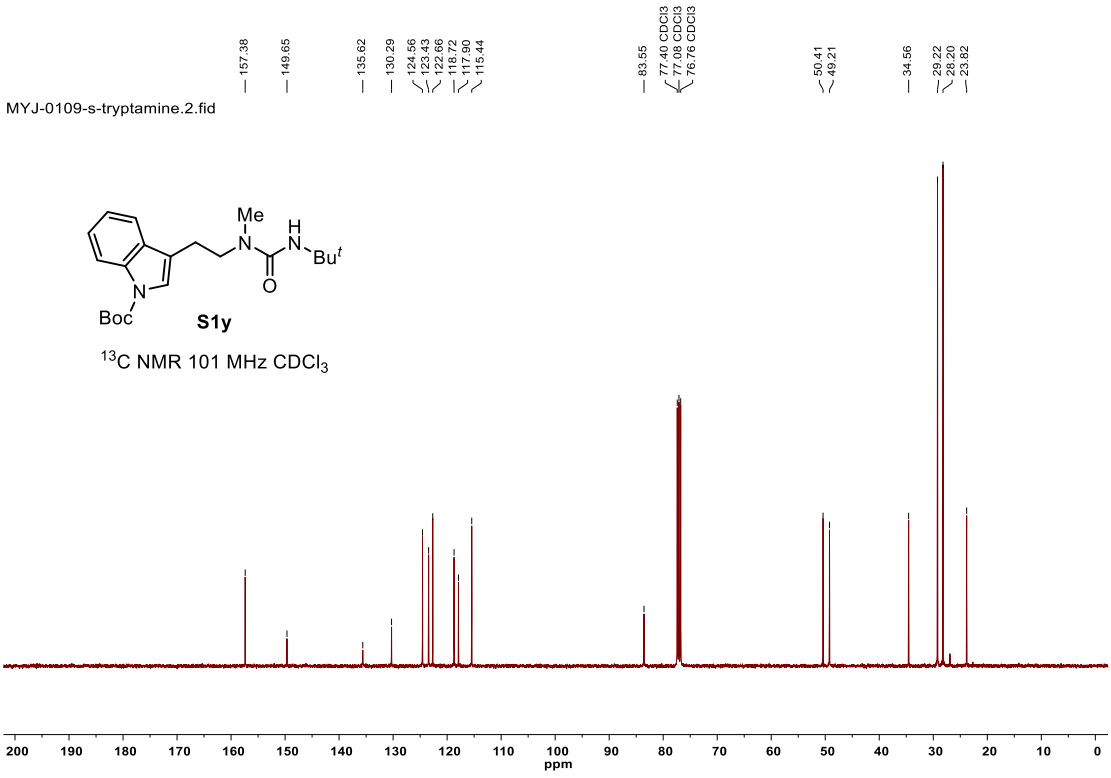
MYJ-0110-s-thiophene.2.fid

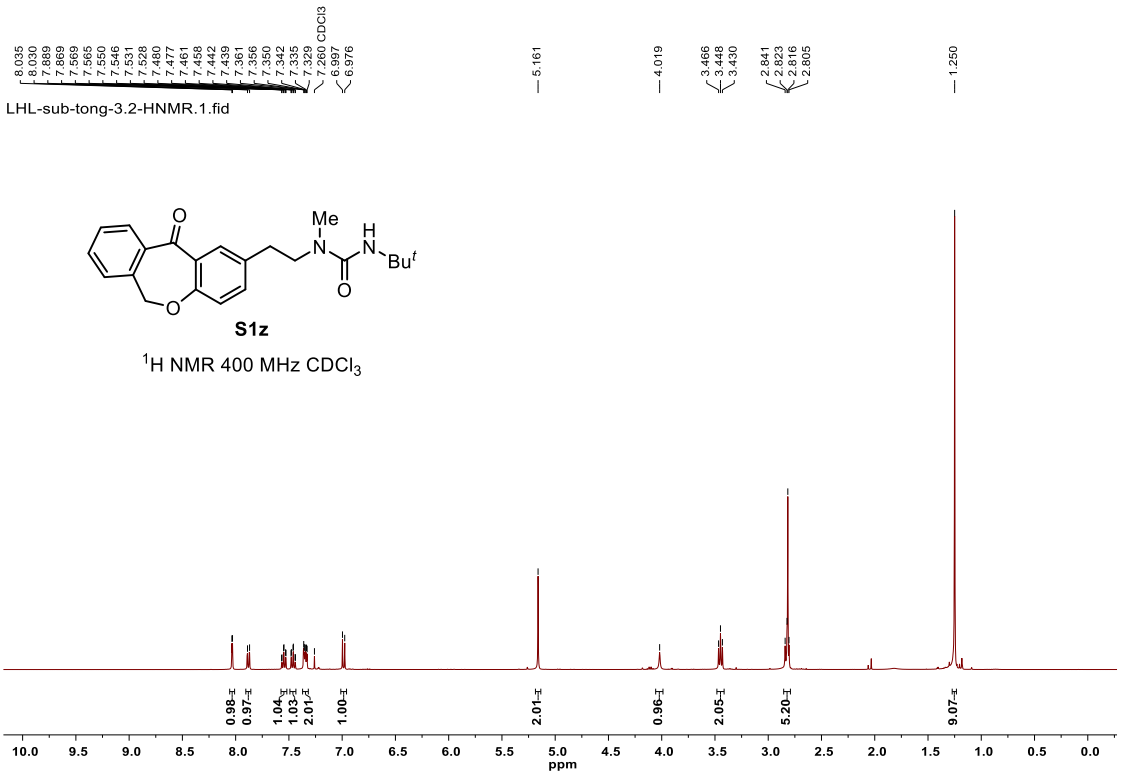


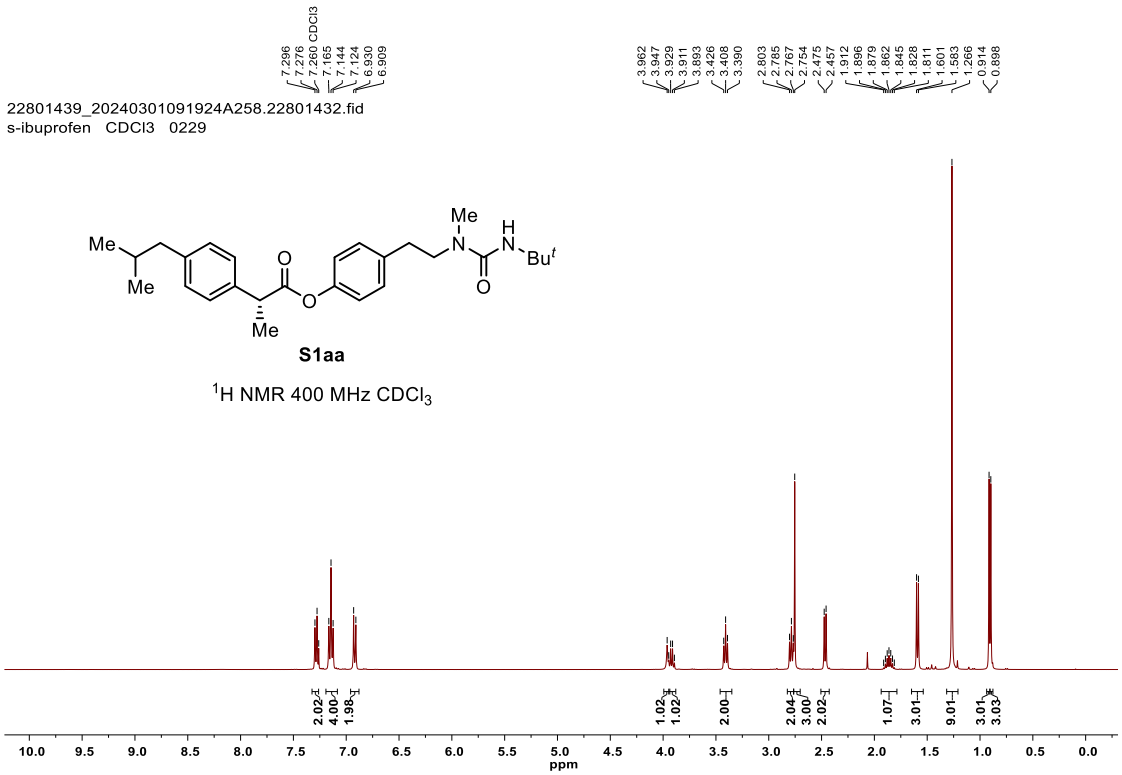
S1x

^{13}C NMR 101 MHz $CDCl_3$


8.152
8.132
7.557
7.537
7.395
7.332
7.313
7.293
7.260 CDCl3
7.239
7.221
3.912
3.526
3.509
3.492
2.919
2.902
2.884
2.837
1.647
1.145
MYJ-0109-s-tryptamine.1.fid
Me
N
H
N
Bu^t
O
N
Boc
S1y
^{1}H NMR 400 MHz CDCl$_3$
0.92
0.99
0.94
1.03
1.08
0.96
1.98
2.01
2.97
8.99
8.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

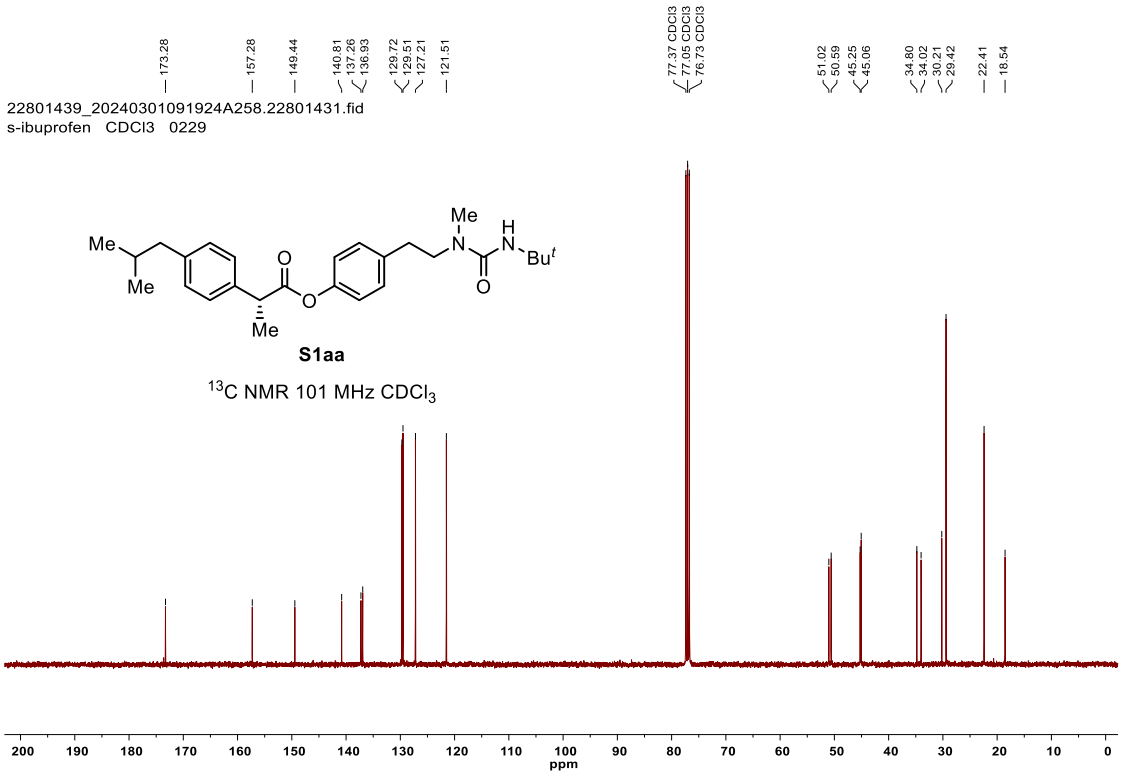

157.38
149.65
135.62
130.29
124.56
123.43
122.66
118.72
117.90
115.44
83.55
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
50.41
49.21
34.56
29.22
28.20
23.82
MYJ-0109-s-tryptamine.2.fid
Me
N
H
N
Bu^t
O
N
Boc
S1y
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.035
8.030
7.889
7.869
7.569
7.565
7.550
7.546
7.531
7.528
7.480
7.477
7.461
7.458
7.442
7.439
7.361
7.356
7.350
7.342
7.332
7.329
7.260 CDCl3
6.997
6.976
5.161
4.019
3.466
3.448
3.430
2.841
2.823
2.816
2.805
1.250
LHL-sub-tong-3.2-HNMR.1.fid
O
Me
N
H
N
Bu^t
O
O
S1z
^{1}H NMR 400 MHz CDCl$_3$
0.98
0.97
1.04
1.03
2.01
1.00
2.01
0.96
2.05
5.20
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
191.07
160.03
157.21
140.48
136.32
135.65
133.18
132.77
131.50
128.45
128.23
127.81
125.20
121.02
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
73.63
50.68
50.56
34.69
33.58
29.43
LHL-sub-tong-3.2-CNMR.1.fid
O
Me
N
H
N
Bu^t
O
O
S1z
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



S1aa

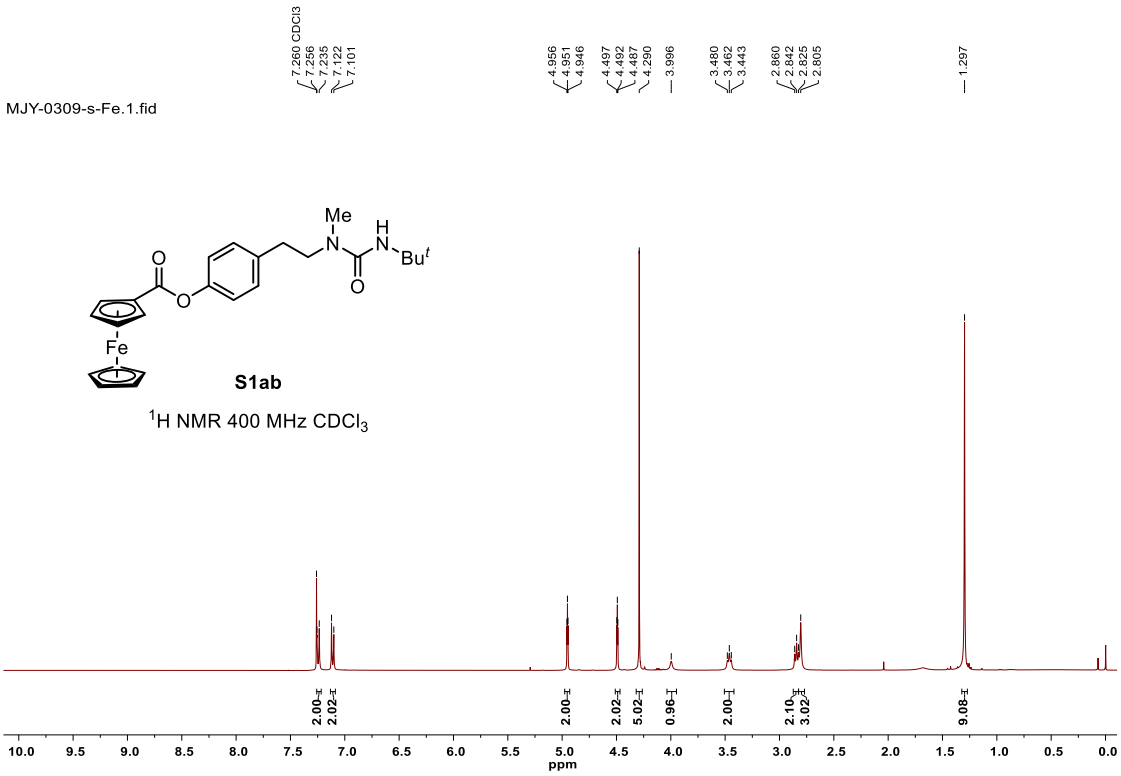
^{1}H NMR 400 MHz $CDCl_3$



S1aa

^{13}C NMR 101 MHz $CDCl_3$

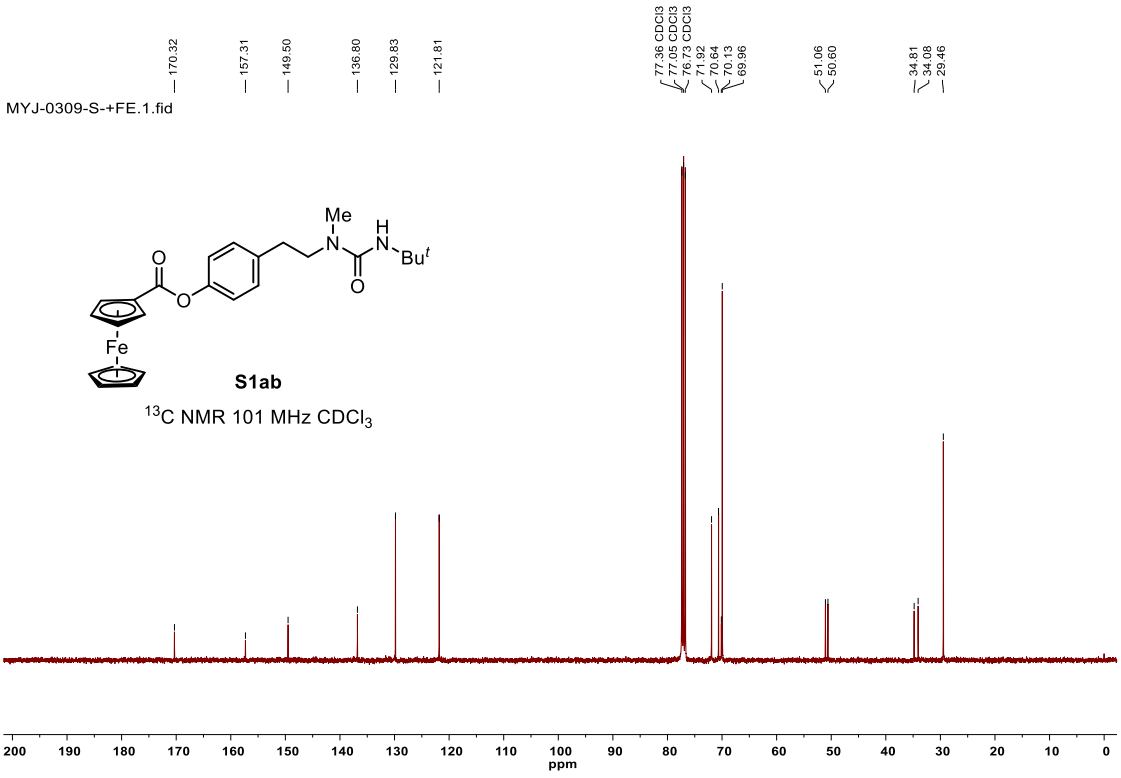
MJY-0309-s-Fe.1.fid



S1ab

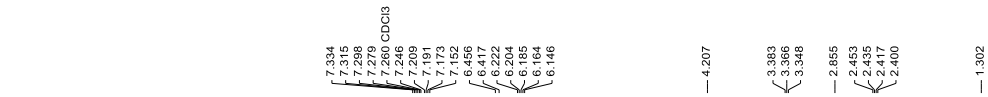
^{1}H NMR 400 MHz $CDCl_3$

MYJ-0309-S-+FE.1.fid

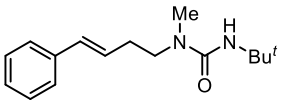


S1ab

^{13}C NMR 101 MHz $CDCl_3$

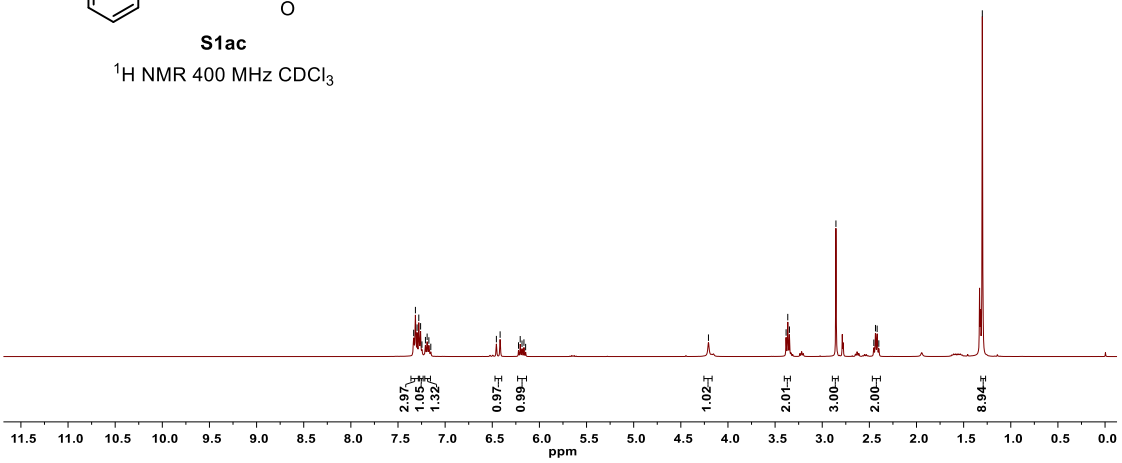


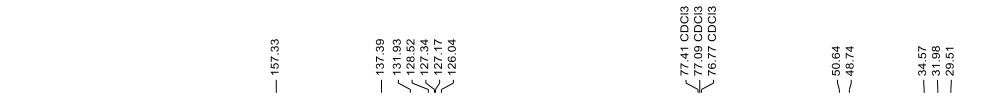
32801511_20240329093338A192.32801515.fid
MYJ-s-olefin-H CDCl3 0328



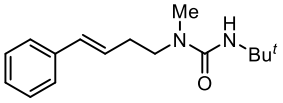
S1ac

^{1}H NMR 400 MHz $CDCl_3$



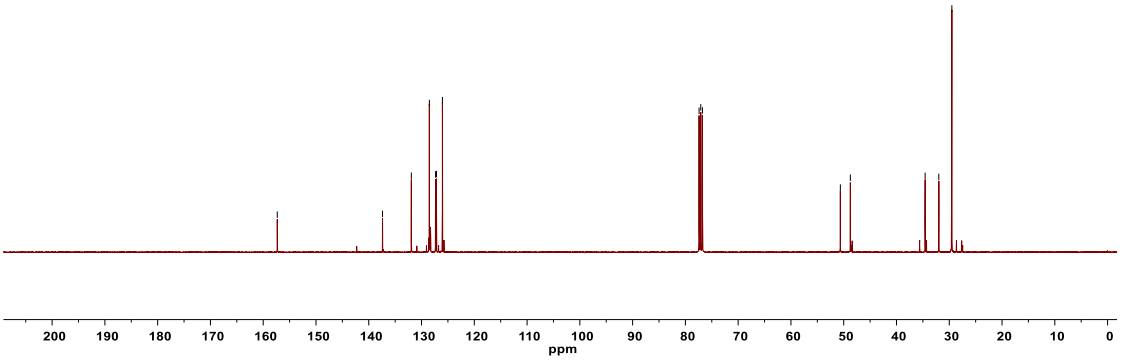


32801511_20240329093338A192.32801516.fid
MYJ-s-olefin-H CDCl3 0328

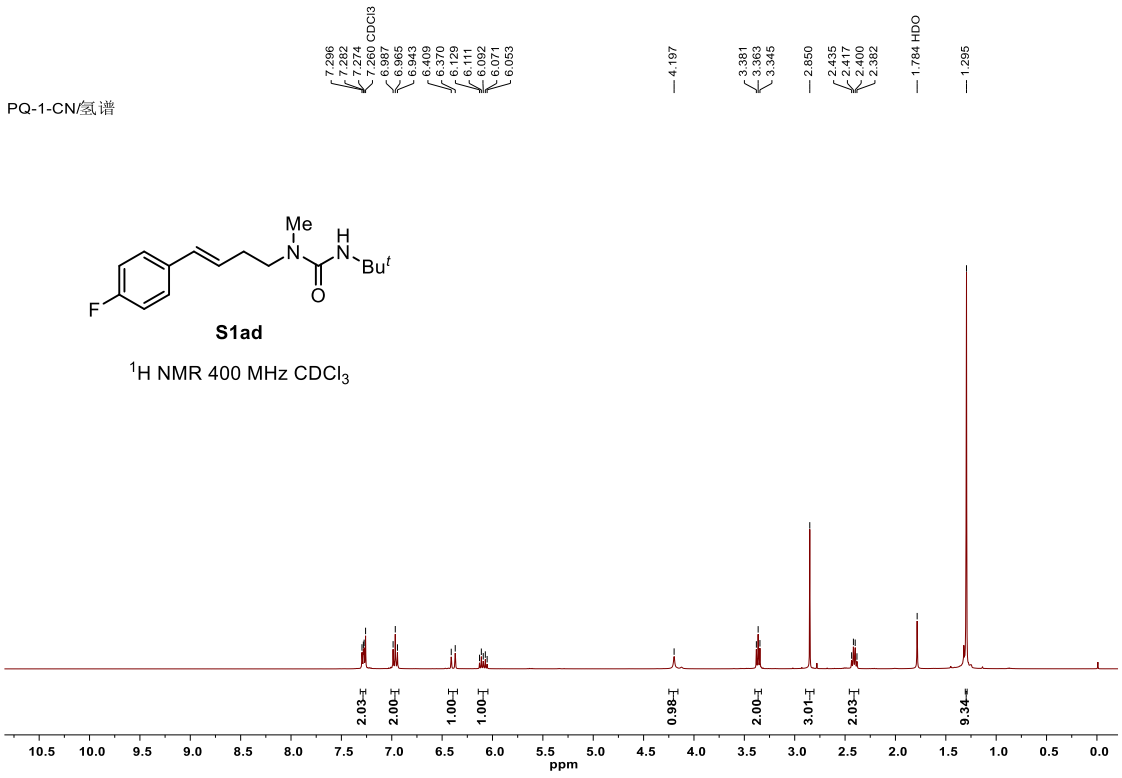


S1ac

^{13}C NMR 101 MHz $CDCl_3$



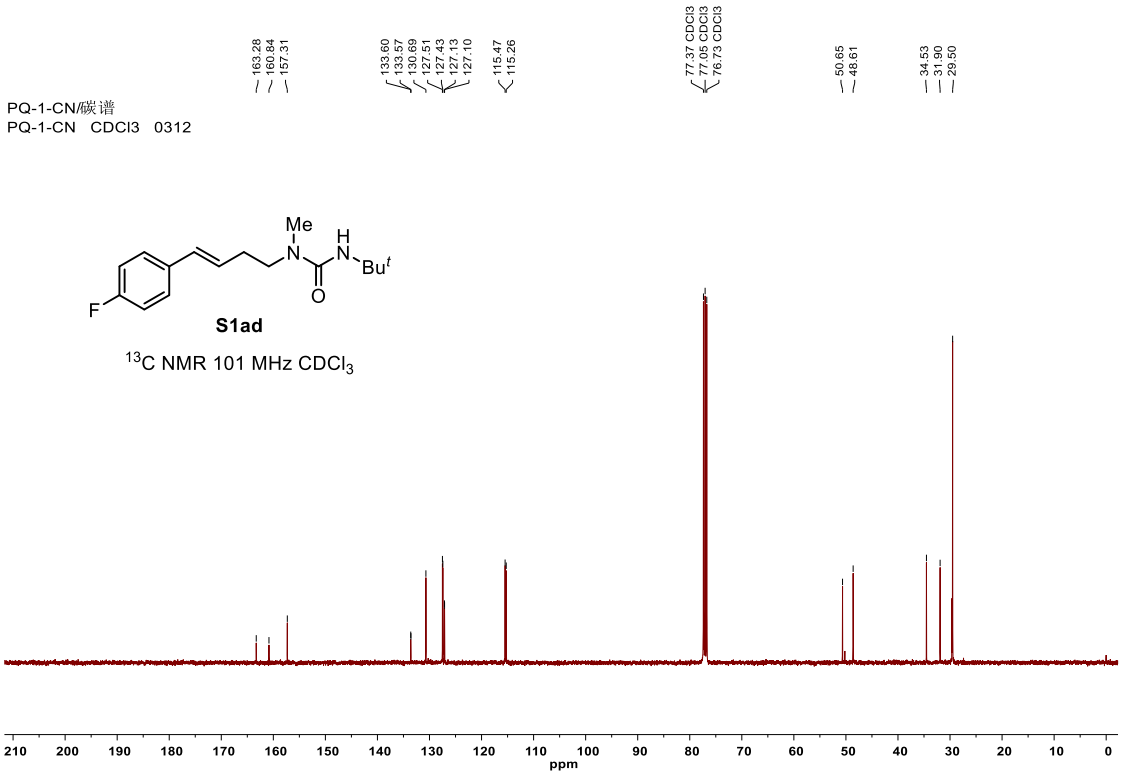
PQ-1-CN/氢谱



S1ad

^{1}H NMR 400 MHz $CDCl_3$

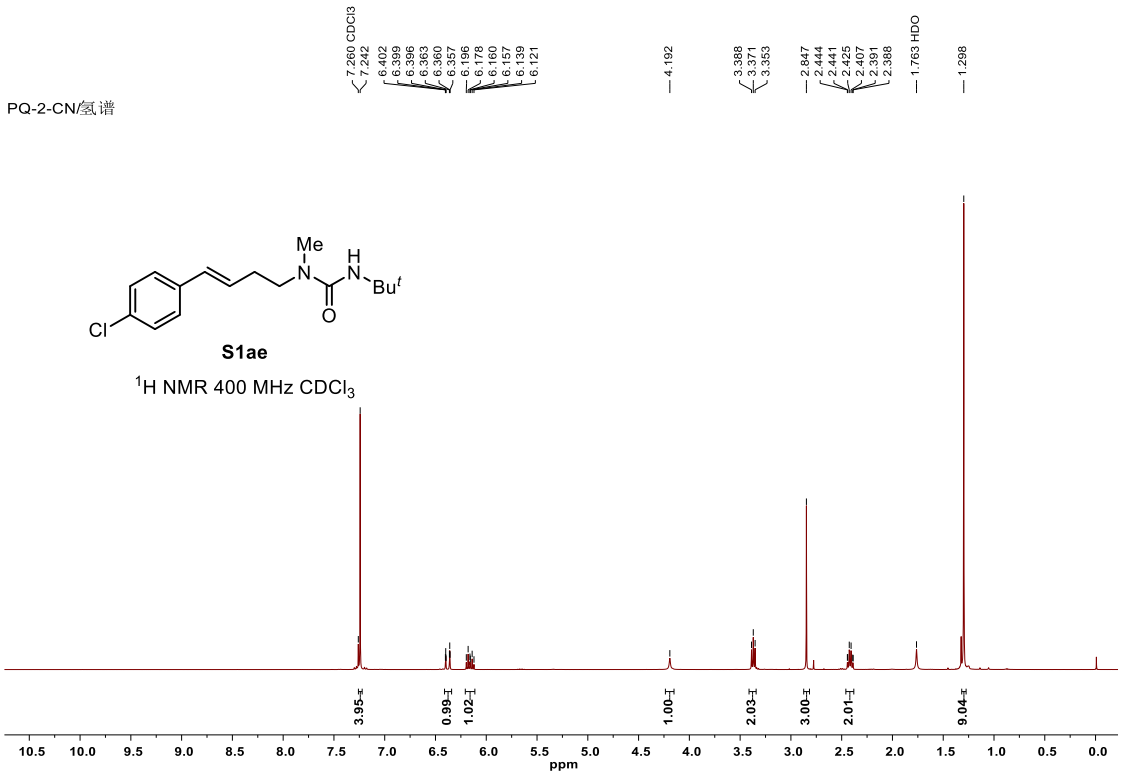
PQ-1-CN/碳谱
PQ-1-CN CDCl3 0312



S1ad

^{13}C NMR 101 MHz $CDCl_3$

PQ-2-CN/氢谱

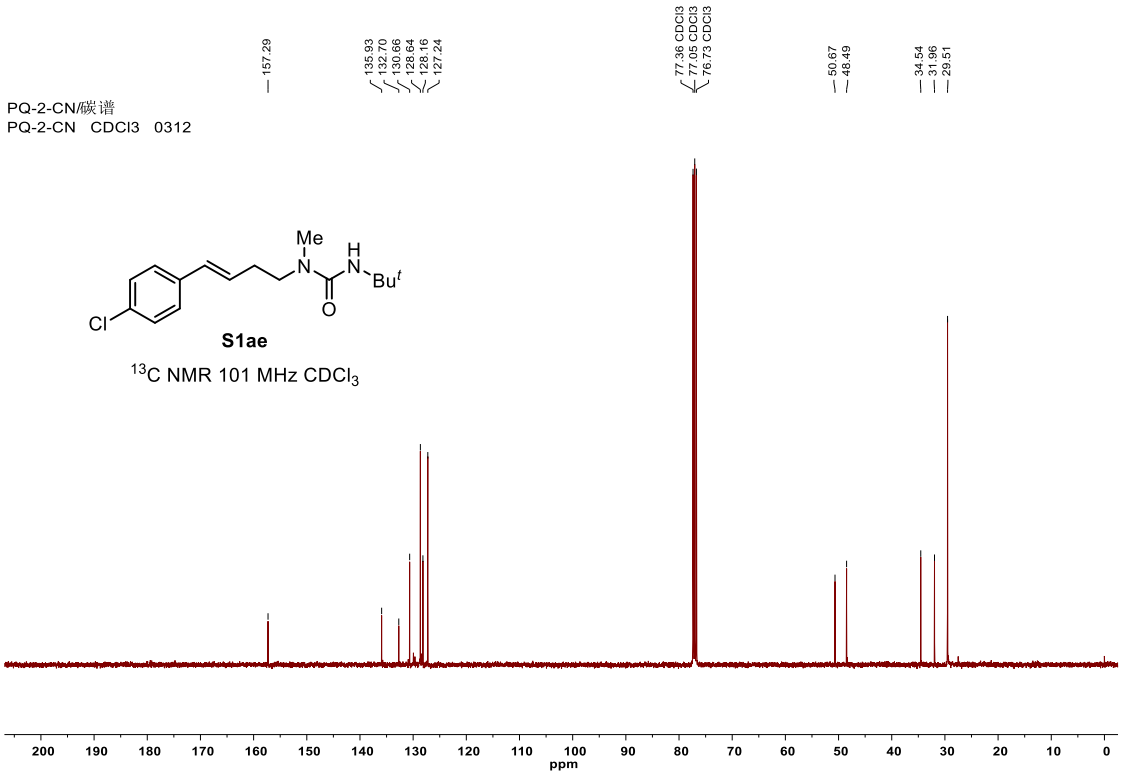


S1ae

^{1}H NMR 400 MHz $CDCl_3$

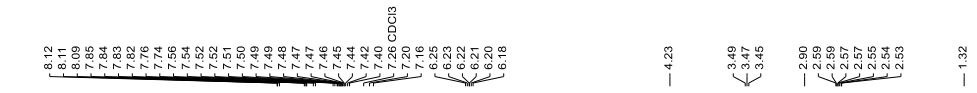
PQ-2-CN/碳谱

PQ-2-CN CDCl3 0312

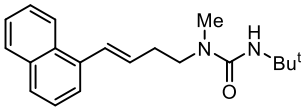


S1ae

^{13}C NMR 101 MHz $CDCl_3$



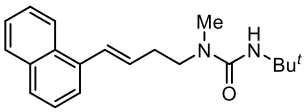
PQ-3-CN/氢谱



S1af

^{1}H NMR 400 MHz $CDCl_3$

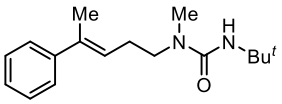
PQ-3-CN.3290175.fid
PQ-3-CN CDCl3 0403



S1af

^{13}C NMR 101 MHz $CDCl_3$

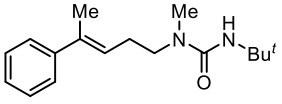
PQ-5-CN/氢谱
PQ-5-CN CDCl3 0321



S1ag

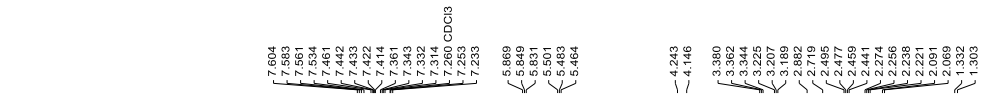
^{1}H NMR 400 MHz $CDCl_3$

PQ-5-CN/碳谱
PQ-5-CN CDCl3 0321

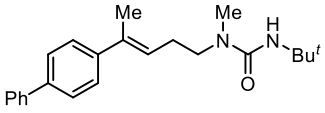


S1ag

^{13}C NMR 101 MHz $CDCl_3$



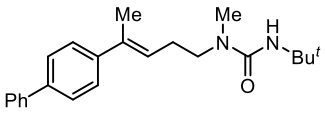
32801511_20240329093338A192.32801513.fid
PQ-10-CN CDCl3 0328



S1ah

^{1}H NMR 400 MHz $CDCl_3$

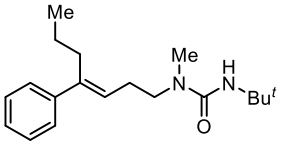
32801511_20240329093338A192.32801514.fid
PQ-10-CN CDCl3 0328



S1ah

^{13}C NMR 101 MHz $CDCl_3$

PQ-9-CN/氢谱
PQ-9-CN CDCl3 0321



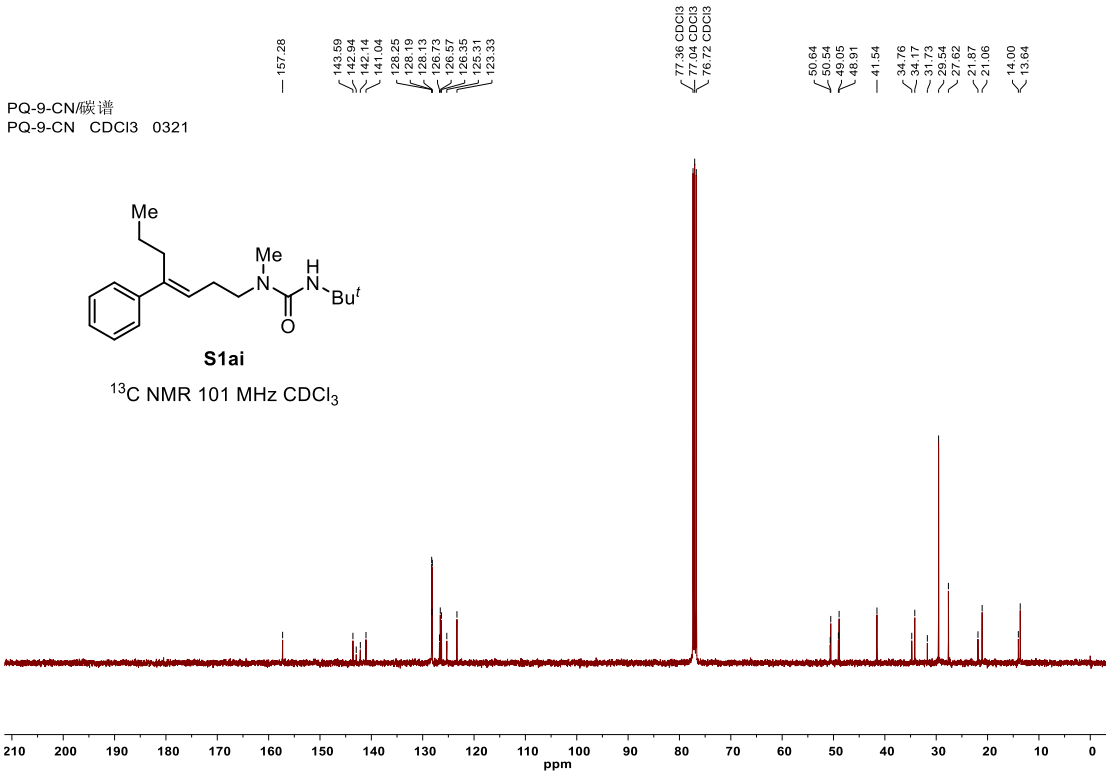
S1ai

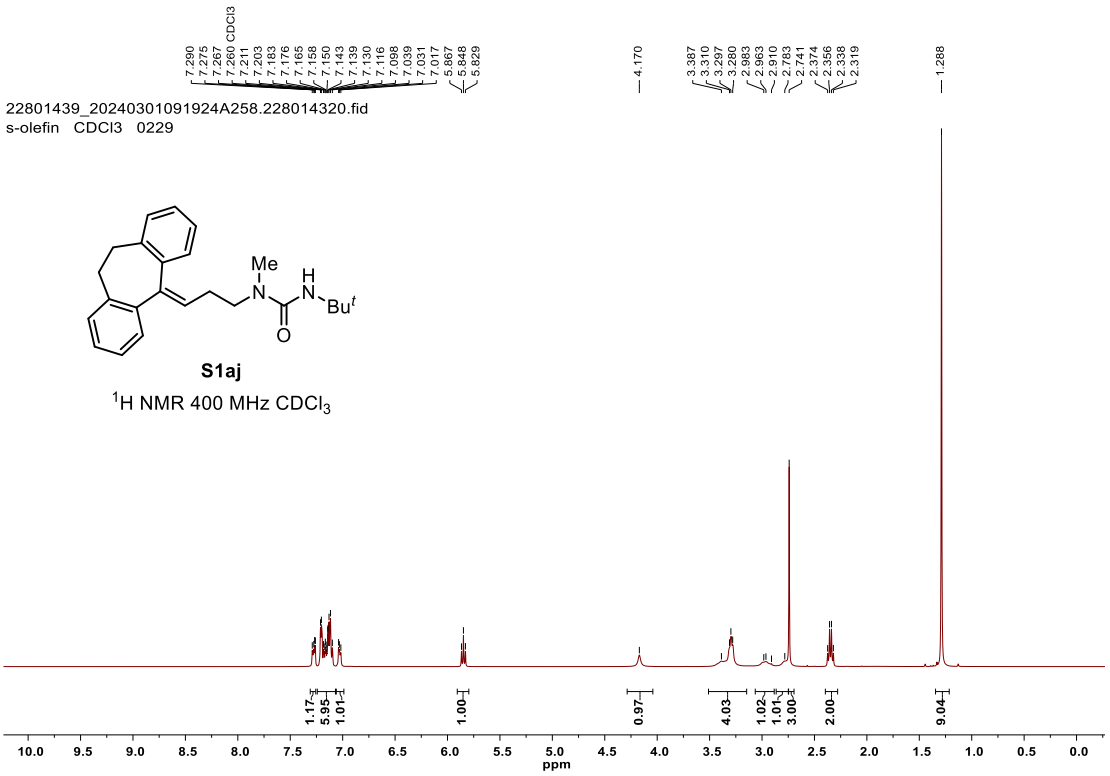
^{1}H NMR 400 MHz $CDCl_3$

PQ-9-CN/碳谱
PQ-9-CN CDCl3 0321

S1ai

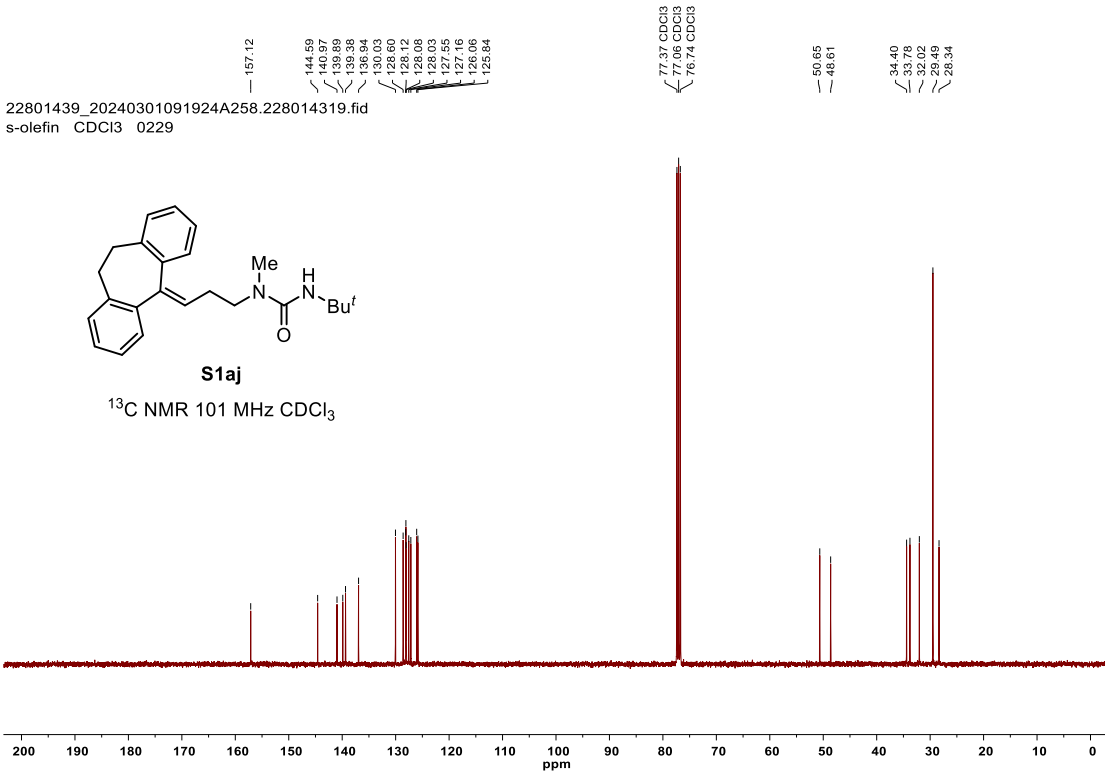
^{13}C NMR 101 MHz $CDCl_3$





S1aj

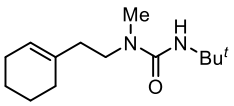
^{1}H NMR 400 MHz $CDCl_3$



S1aj

^{13}C NMR 101 MHz $CDCl_3$

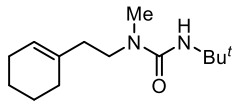
MYJ-cyclohexene.40201462.fid
MYJ-s-cyclohexen CDCl3 0403



S1ak

^{1}H NMR 400 MHz $CDCl_3$

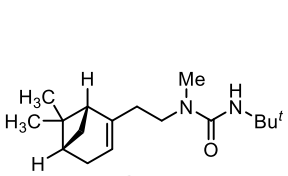
MYJ-cyclohexene.40201461.fid
MYJ-s-cyclohexen CDCl3 0403



S1ak

^{13}C NMR 101 MHz $CDCl_3$

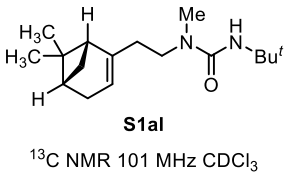
PQ-4-CN.1.fid



S1al

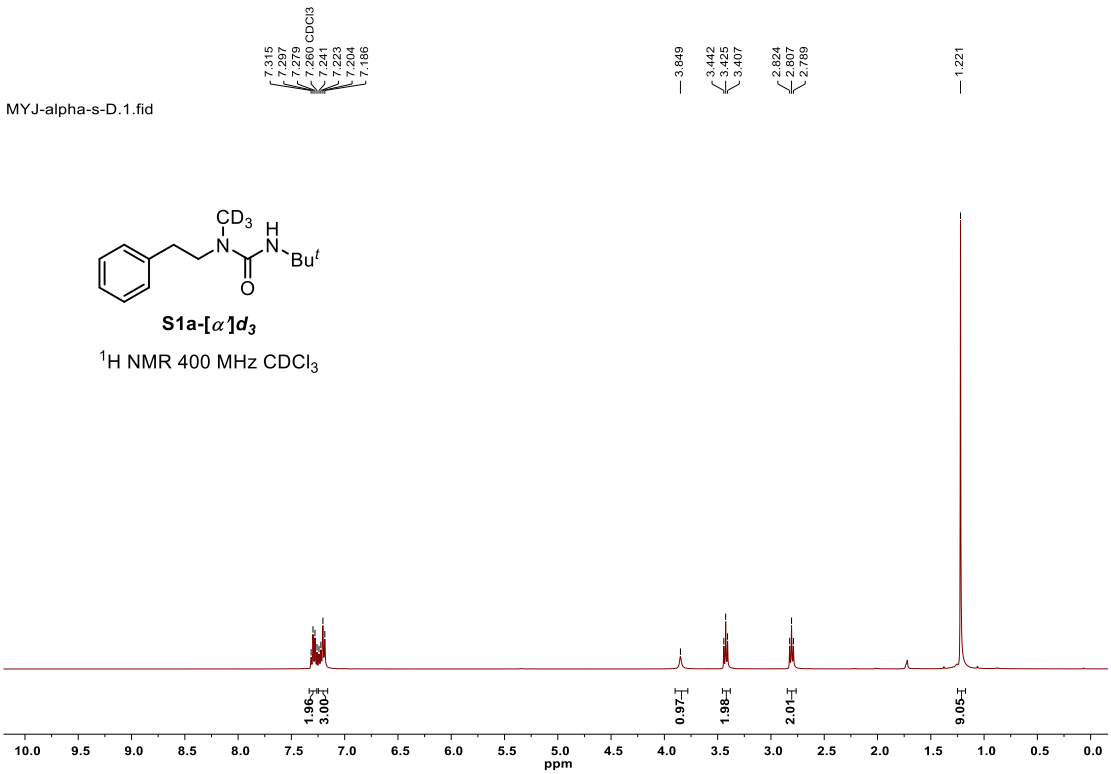
^{1}H NMR 400 MHz $CDCl_3$

PQ-4-CN.2.fid



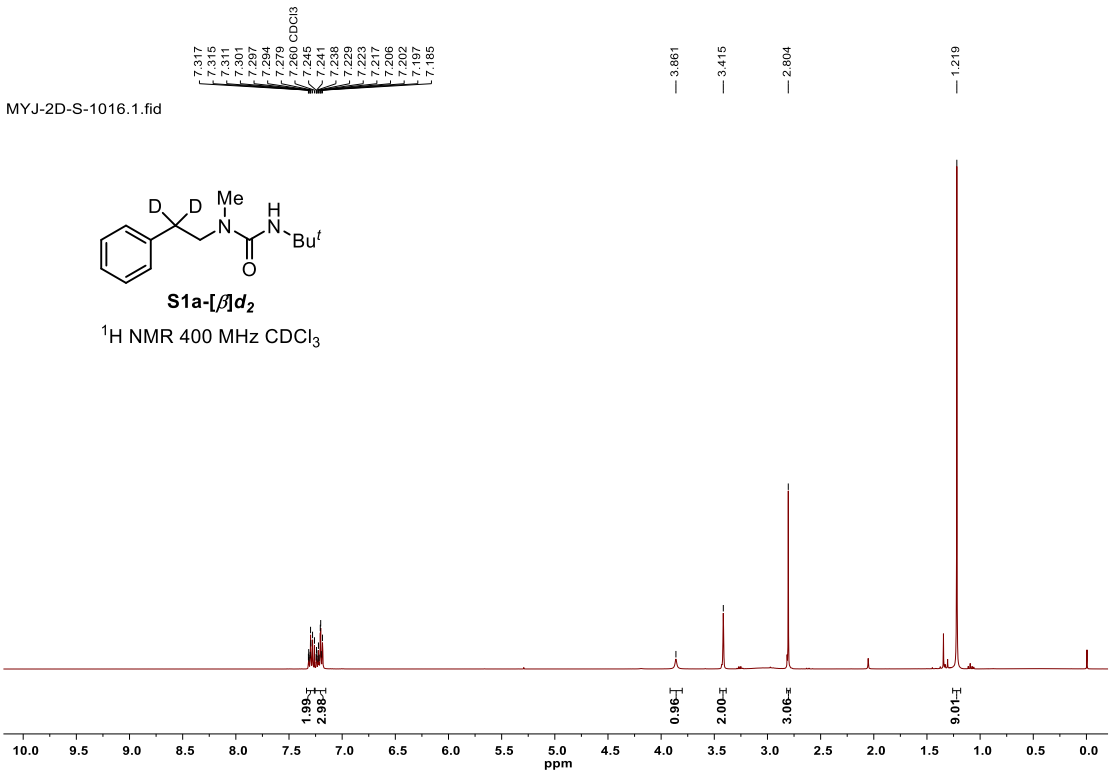
S1al

^{13}C NMR 101 MHz $CDCl_3$



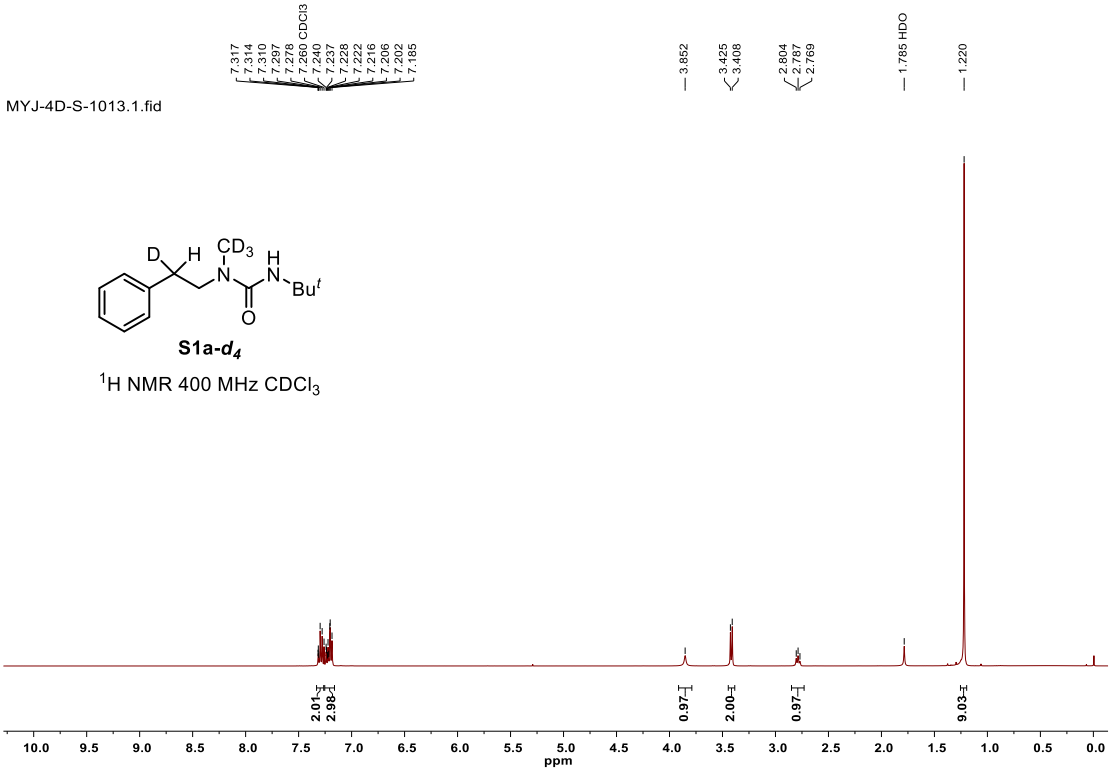
S1a-[α]d_3

^{1}H NMR 400 MHz $CDCl_3$



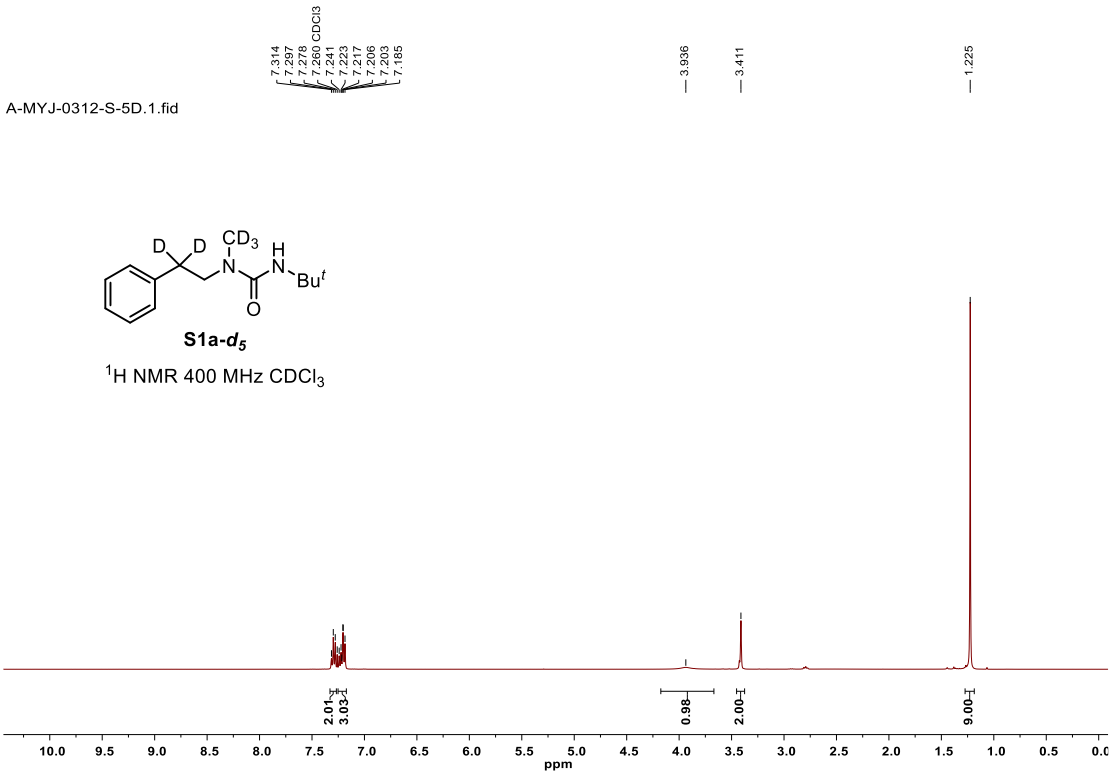
S1a-[β]d_2

^{1}H NMR 400 MHz $CDCl_3$



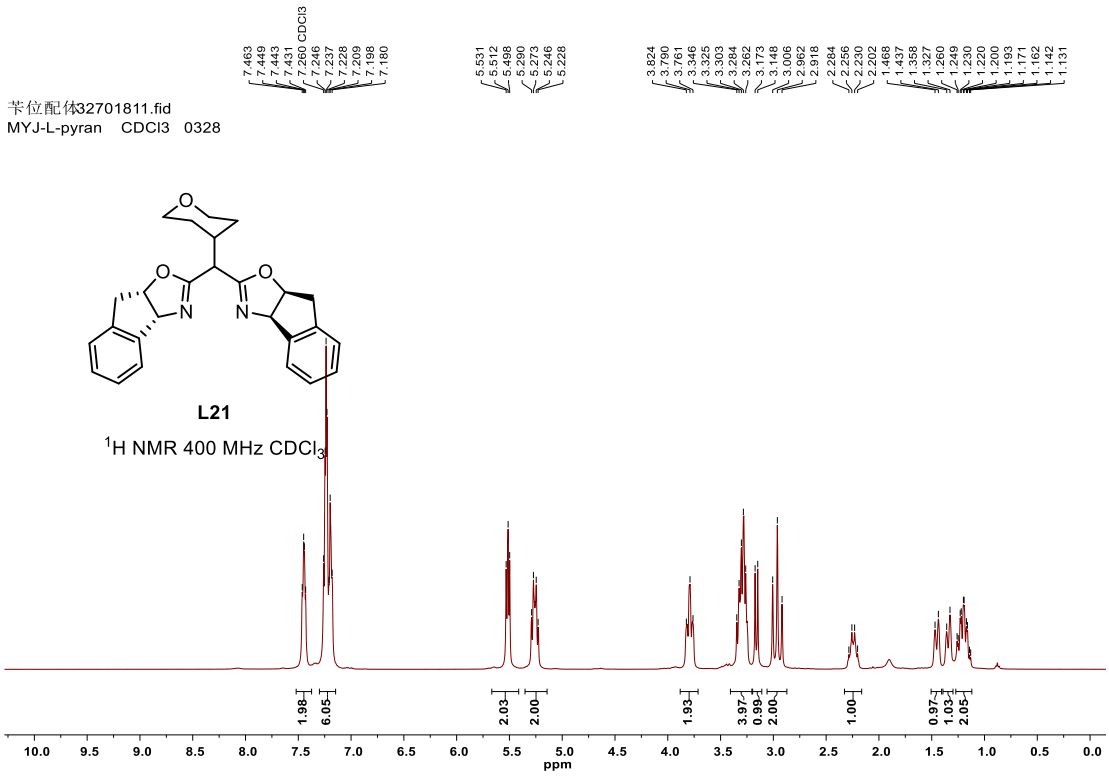
S1a-*d*$_4$

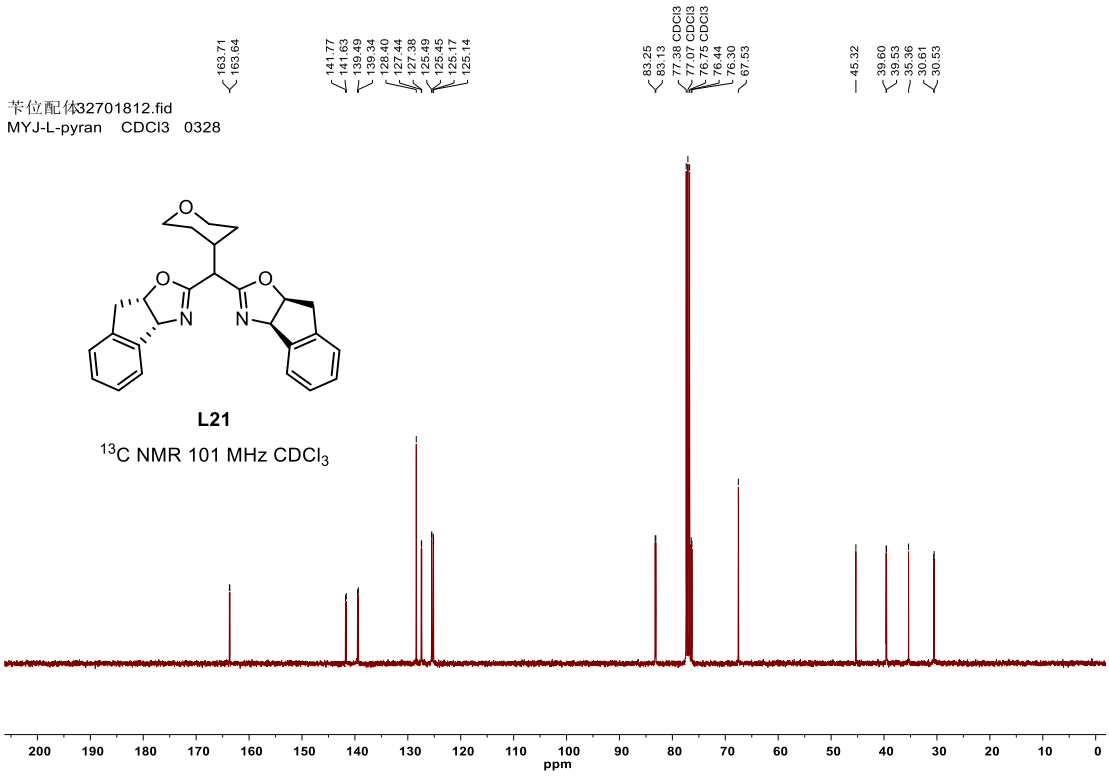
^{1}H NMR 400 MHz $CDCl_3$

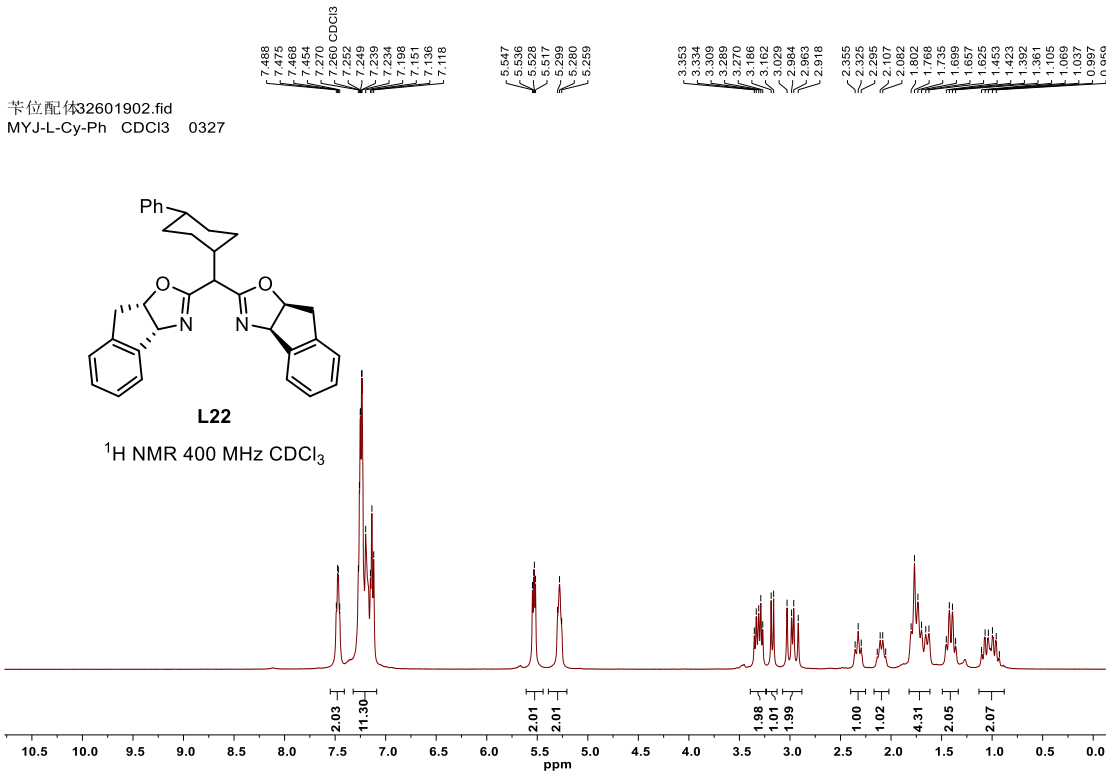


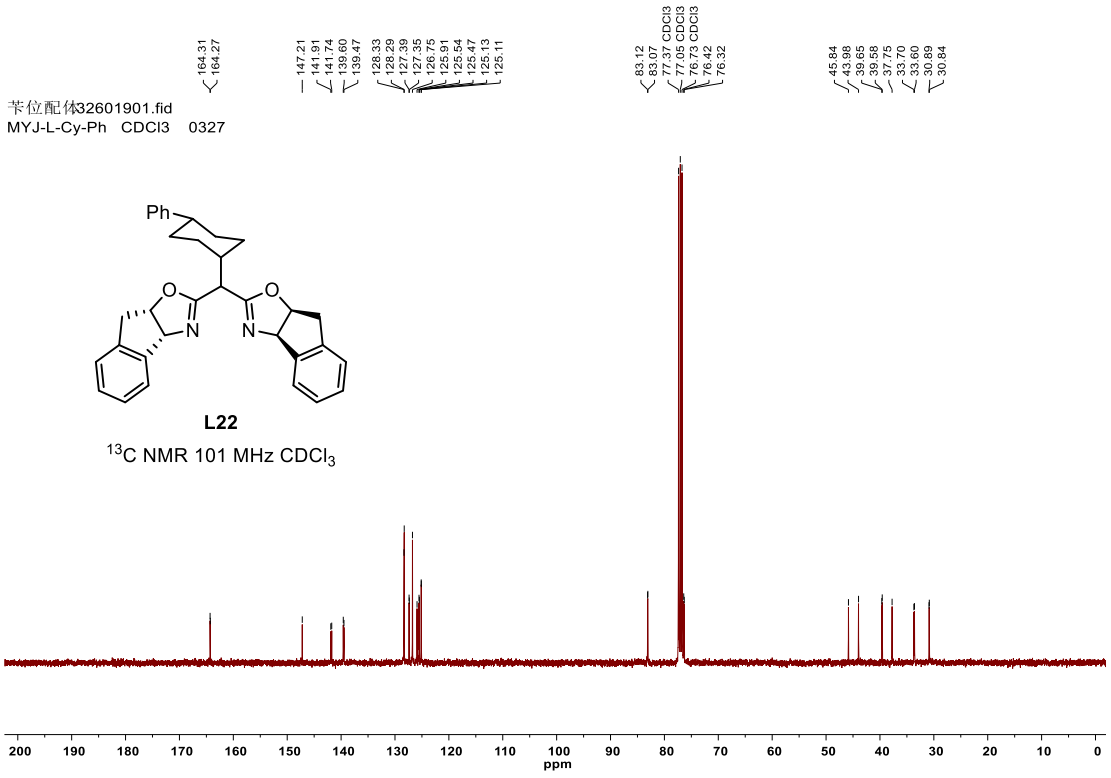
S1a-*d*$_5$

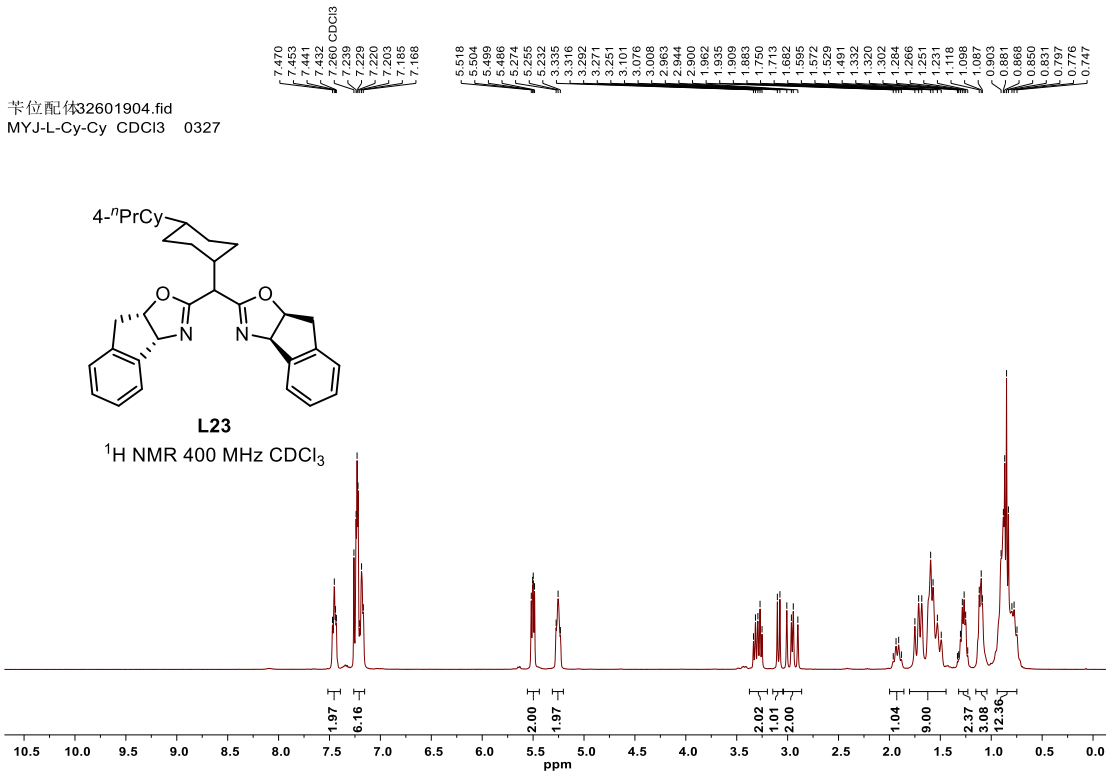
^{1}H NMR 400 MHz $CDCl_3$

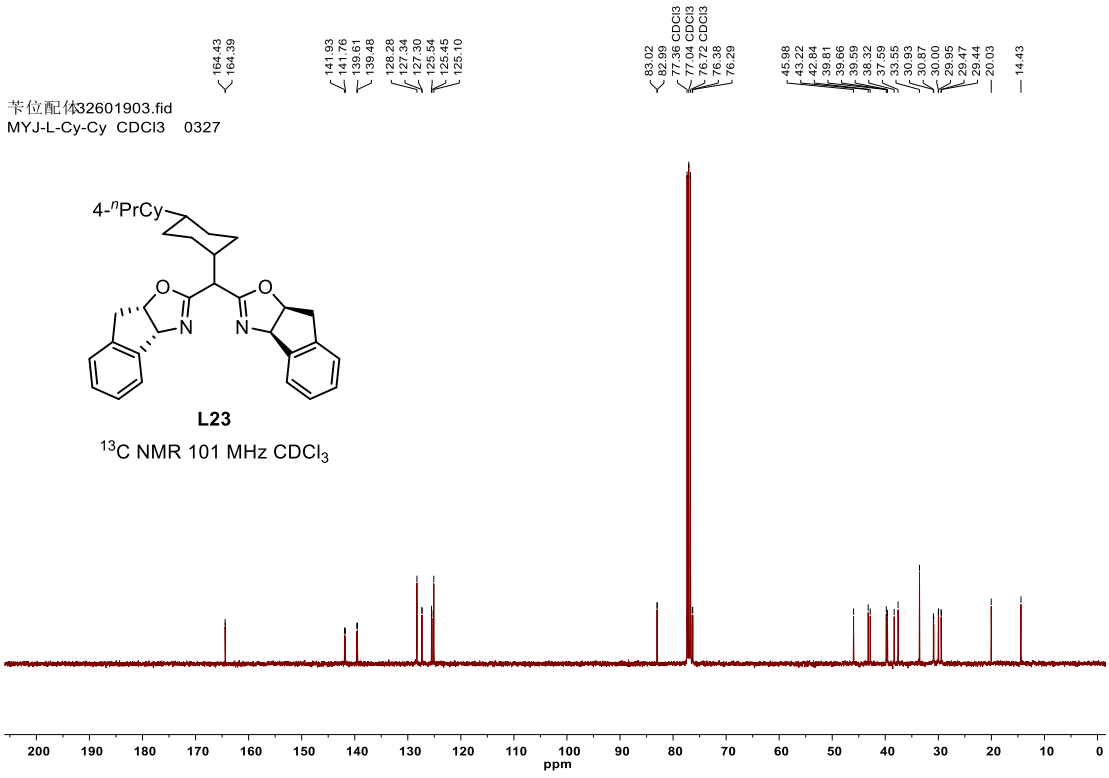

7.463
7.449
7.443
7.431
7.260 CDCl3
7.246
7.237
7.228
7.209
7.198
7.180
5.531
5.512
5.498
5.290
5.273
5.246
5.228
3.824
3.790
3.761
3.346
3.325
3.303
3.284
3.262
3.173
3.148
3.006
2.992
2.918
2.284
2.256
2.230
2.202
1.468
1.437
1.358
1.327
1.280
1.248
1.230
1.220
1.200
1.193
1.171
1.162
1.142
1.131
苄位配体32701811.fid
MYJ-L-pyran CDCl3 0328
L21
1H NMR 400 MHz CDCl3
1.98
6.05
2.03
2.00
1.93
3.97
0.99
2.00
1.00
0.97
1.03
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

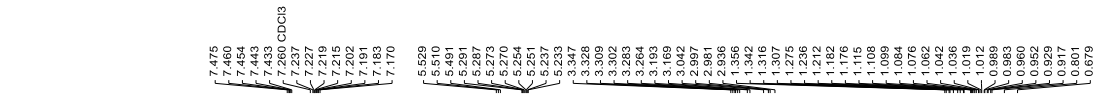

163.71
163.64
141.77
141.63
139.49
139.34
128.40
127.44
127.38
125.49
125.45
125.17
125.14
83.25
83.13
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
76.44
76.30
67.53
45.32
39.60
39.53
35.36
30.61
30.53
苄位配体32701812.fid
MYJ-L-pyran CDCl3 0328
L21
13C NMR 101 MHz CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.488
7.475
7.468
7.454
7.270
7.260 CDCl3
7.252
7.249
7.239
7.234
7.198
7.151
7.136
7.118
5.547
5.536
5.528
5.517
5.299
5.280
5.259
3.353
3.334
3.309
3.289
3.270
3.186
3.162
3.029
2.984
2.963
2.918
2.355
2.325
2.295
2.107
2.082
1.802
1.768
1.735
1.699
1.657
1.625
1.453
1.423
1.382
1.361
1.105
1.069
1.037
0.997
苄位配体32601902.fid
MYJ-L-Cy-Ph CDCl3 0327
Ph
O
N
O
N
L22
1H NMR 400 MHz CDCl3
2.03
11.30
2.01
2.01
1.98
1.01
1.99
1.00
1.02
4.31
2.05
2.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

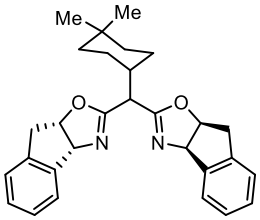

164.31
164.27
147.21
141.91
141.74
139.60
139.47
128.33
128.29
127.39
127.35
126.75
125.91
125.54
125.47
125.13
125.11
83.12
83.07
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
76.42
76.32
45.84
43.98
39.65
39.58
37.75
33.70
33.60
30.89
30.84
苄位配体32601901.fid
MYJ-L-Cy-Ph CDCl3 0327
Ph
O
N
O
N
L22
13C NMR 101 MHz CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.470
7.453
7.441
7.432
7.260 CDCl3
7.239
7.229
7.220
7.203
7.185
7.168
5.518
5.504
5.499
5.486
5.274
5.255
5.232
3.335
3.316
3.292
3.271
3.251
3.101
3.076
3.008
2.963
2.944
2.900
1.962
1.935
1.909
1.883
1.750
1.713
1.682
1.595
1.572
1.528
1.491
1.332
1.320
1.302
1.284
1.266
1.251
1.231
1.118
1.098
1.087
0.903
0.881
0.868
0.850
0.831
0.797
0.776
0.747
苄位配体32601904.fid
MYJ-L-Cy-Cy CDCl3 0327
4-nPrCy
L23
1H NMR 400 MHz CDCl3
1.97
6.16
2.00
1.97
2.02
1.01
2.00
1.04
9.00
2.37
3.08
12.36
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


164.43
164.39
141.93
141.76
139.61
139.48
128.28
127.34
127.30
125.54
125.45
125.10
83.02
82.99
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
76.38
76.29
45.98
43.22
42.84
39.81
39.66
39.59
38.32
37.59
33.55
30.93
30.87
30.00
29.95
29.47
29.44
20.03
14.43
苄位配体32601903.fid
MYJ-L-Cy-Cy CDCl3 0327
4-nPrCy
L23
13C NMR 101 MHz CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

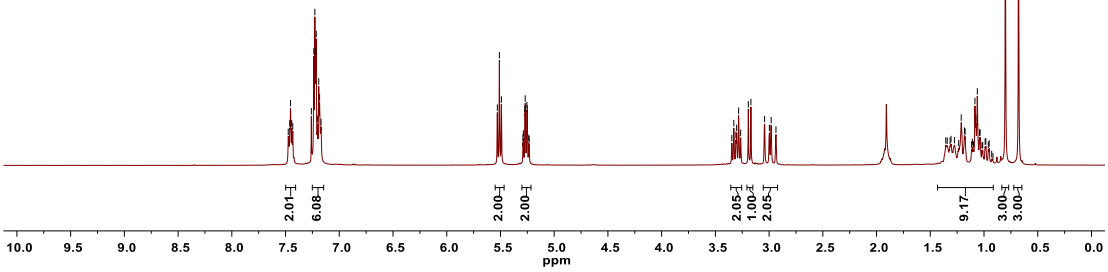


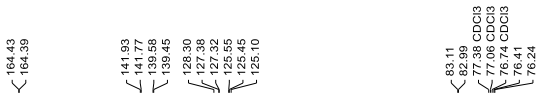
MYJ-0110-L.1.fid



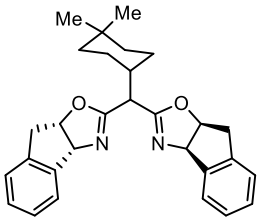
(1*R*,2*S*)-**L24**

^{1}H NMR 400 MHz $CDCl_3$



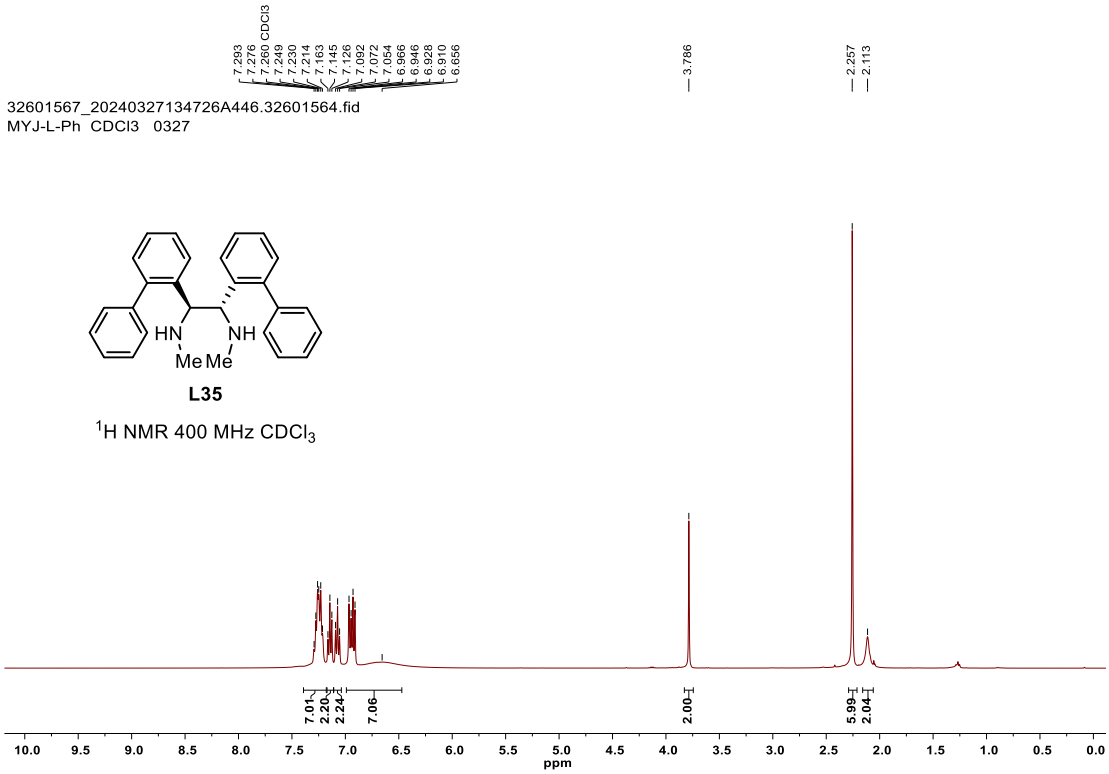


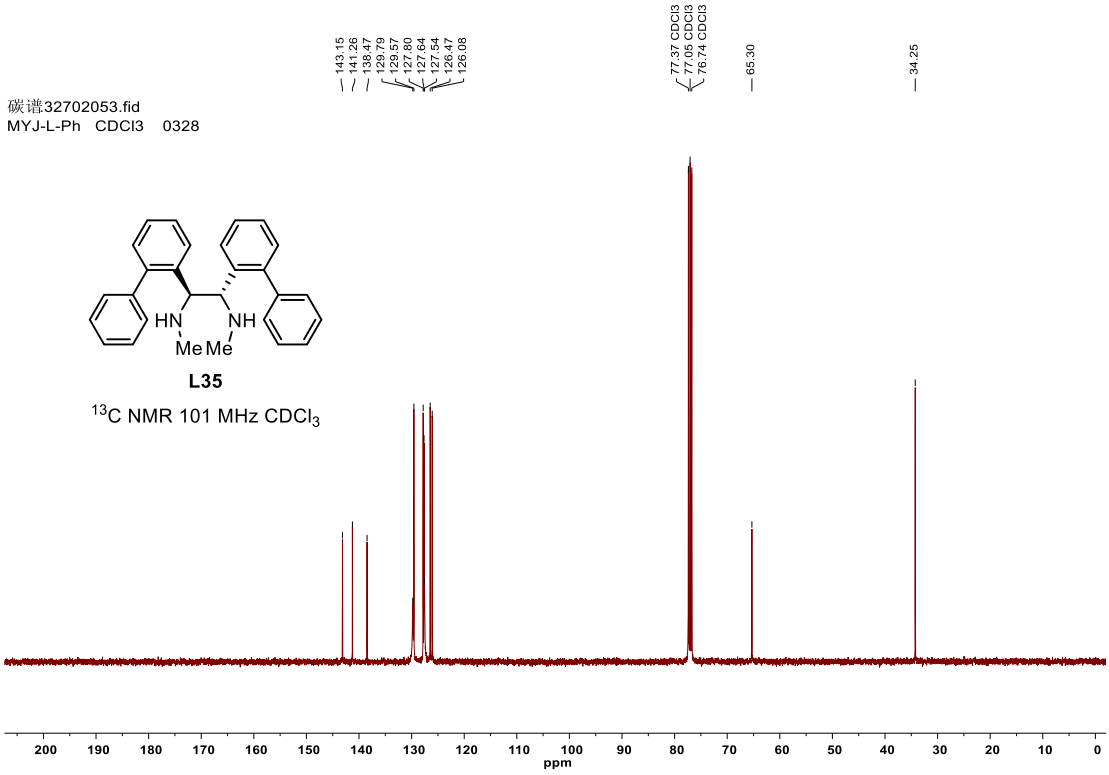
MYJ-0110-L.2.fid



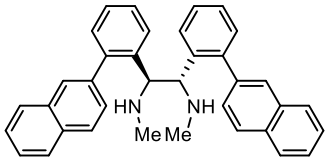
(1*R*,2*S*)-**L24**

^{13}C NMR 101 MHz $CDCl_3$


7.293
7.276
7.260 CDCl3
7.249
7.230
7.214
7.163
7.145
7.126
7.092
7.072
7.054
6.966
6.946
6.928
6.910
6.656
3.786
2.257
2.113
32601567_20240327134726A446.32601564.fid
MYJ-L-Ph CDCl3 0327
HN
NH
Me Me
L35
1H NMR 400 MHz CDCl3
7.01
2.20
2.24
7.06
2.00
5.99
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

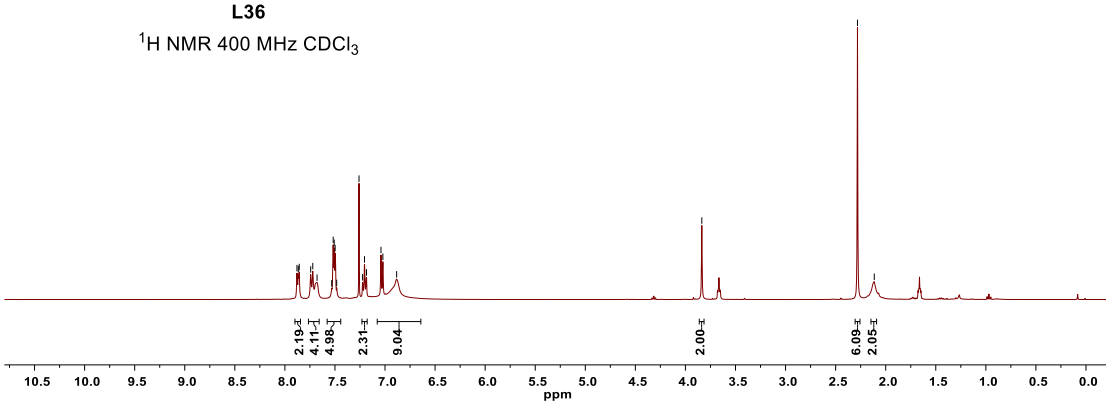

143.15
141.26
138.47
129.79
129.57
127.80
127.64
127.54
126.47
126.08
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
65.30
34.25
碳谱32702053.fid
MYJ-L-Ph CDCl3 0328
HN
NH
Me Me
L35
13C NMR 101 MHz CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

32601567_20240327134726A446.32601567.fid
MYJ-L-naphtha CDCl3 0327

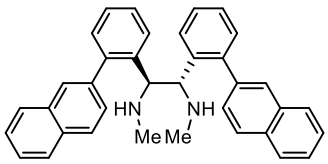


L36

^{1}H NMR 400 MHz $CDCl_3$

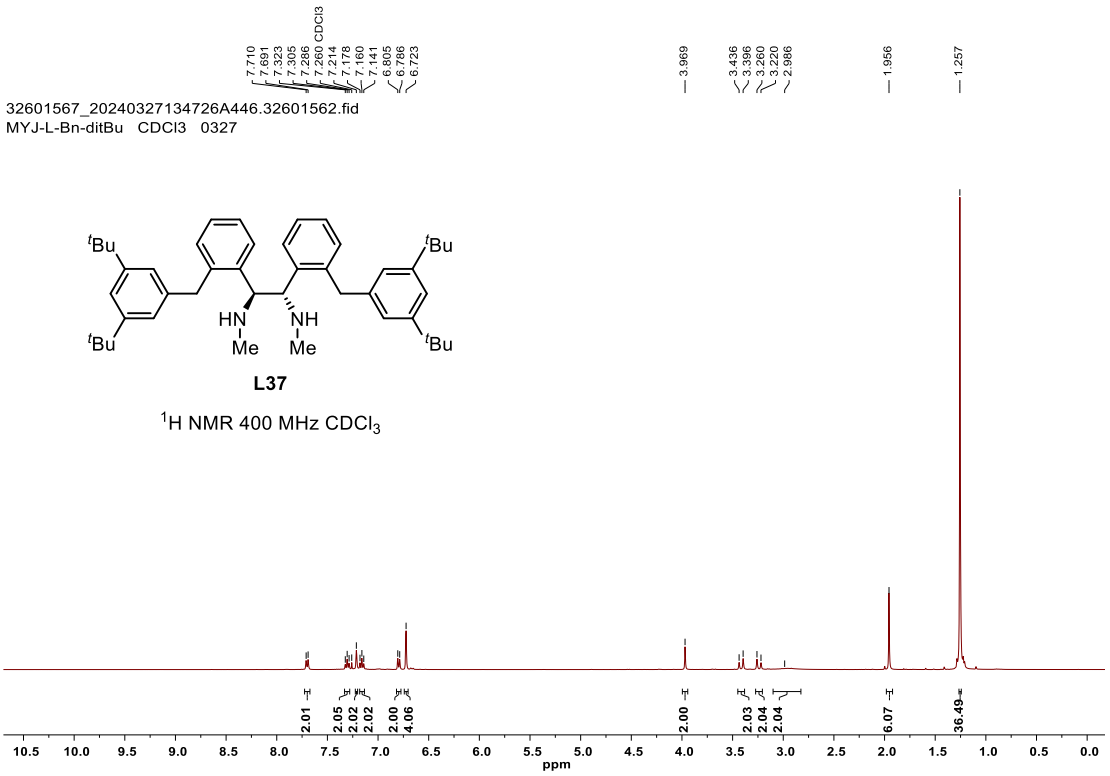


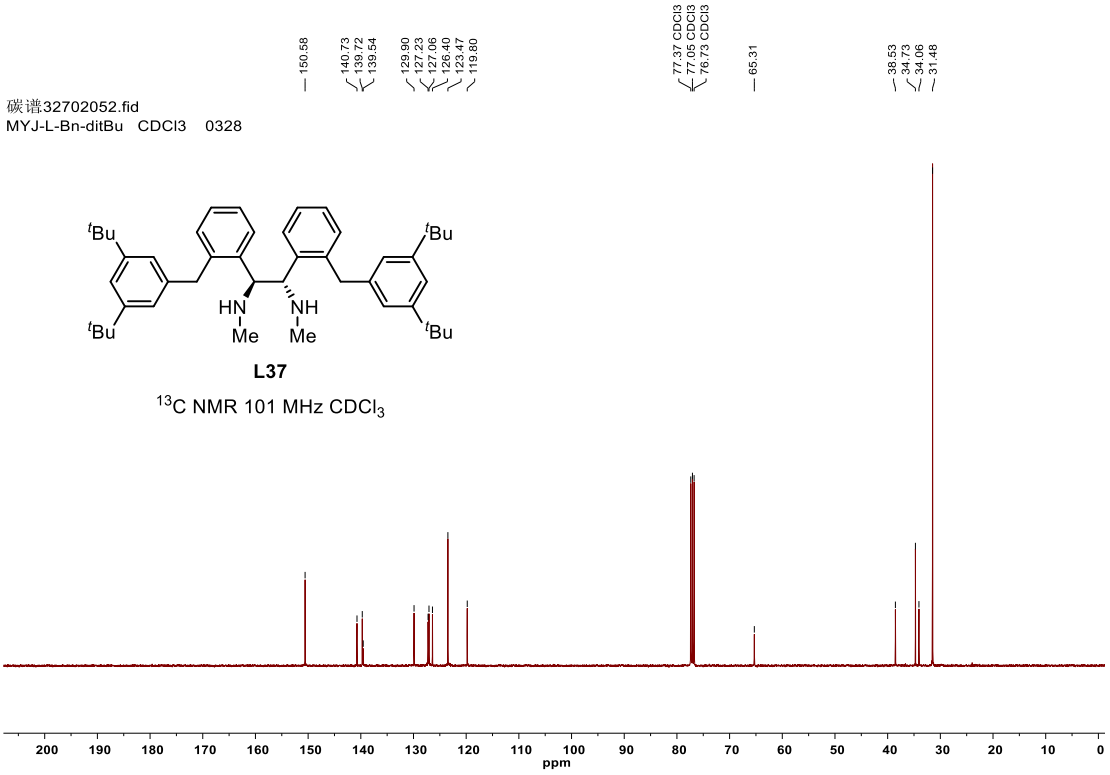
碳谱32702056.fid
MYJ-L-Naphtha CDCl3 0328

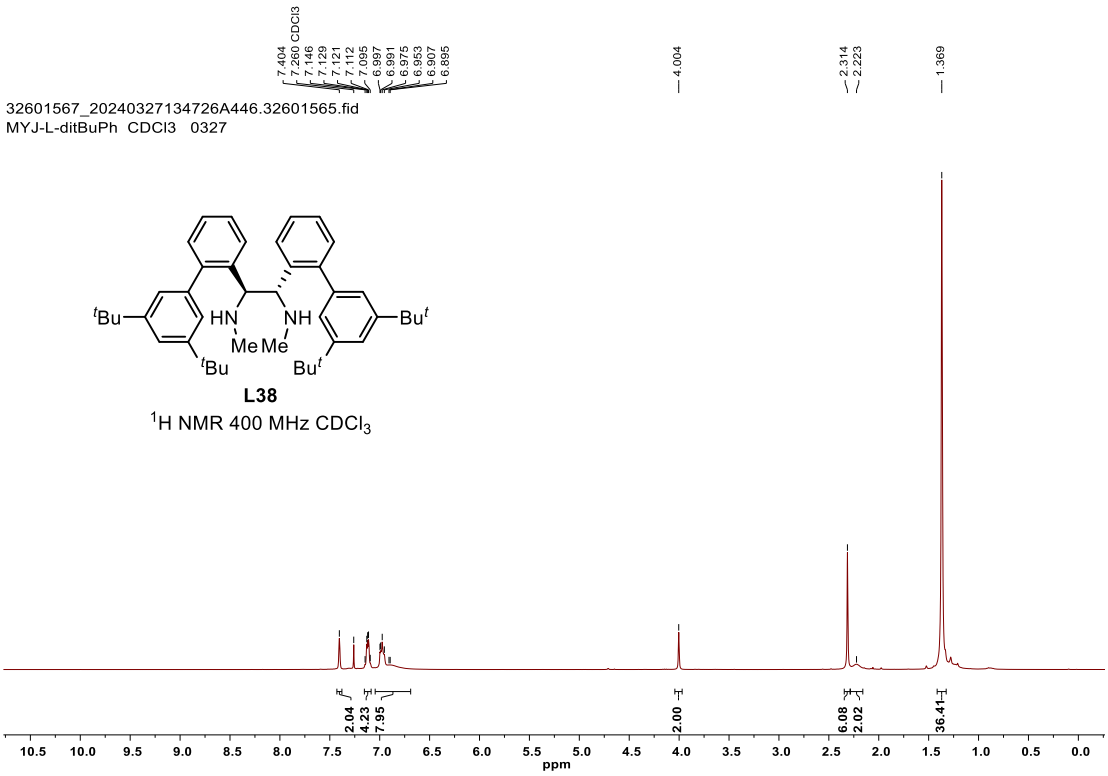


L36

^{13}C NMR 101 MHz $CDCl_3$

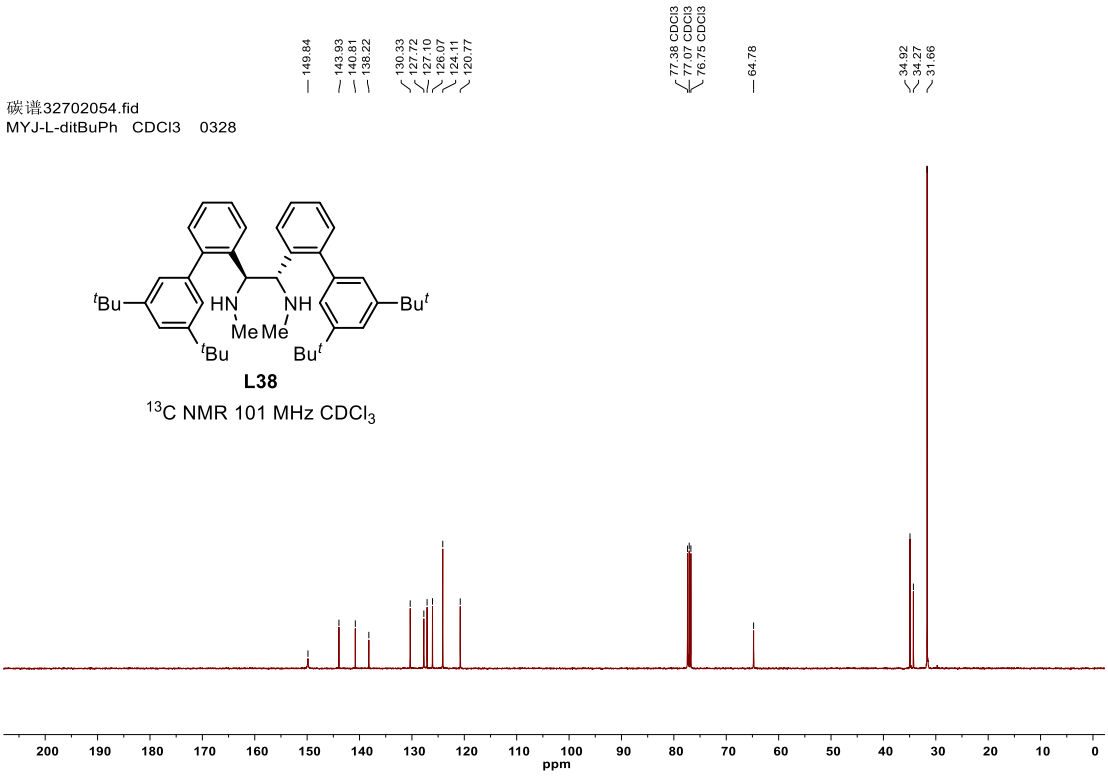

7.710
7.691
7.323
7.305
7.286
7.260 CDCl3
7.214
7.178
7.160
7.141
6.805
6.786
6.723
3.969
3.436
3.396
3.260
3.220
2.986
1.956
1.257
32601567_20240327134726A446.32601562.fid
MYJ-L-Bn-ditBu CDCl3 0327
tBu
tBu
tBu
tBu
HN
NH
Me
Me
L37
1H NMR 400 MHz CDCl3
2.01
2.05
2.02
2.02
2.00
4.06
2.00
2.03
2.04
2.04
6.07
36.49
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


150.58
140.73
139.72
139.54
129.90
127.23
127.06
126.40
123.47
119.80
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
65.31
38.53
34.73
34.06
31.48
碳谱32702052.fid
MYJ-L-Bn-ditBu CDCl3 0328
tBu
tBu
tBu
tBu
HN
NH
Me
Me
L37
13C NMR 101 MHz CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



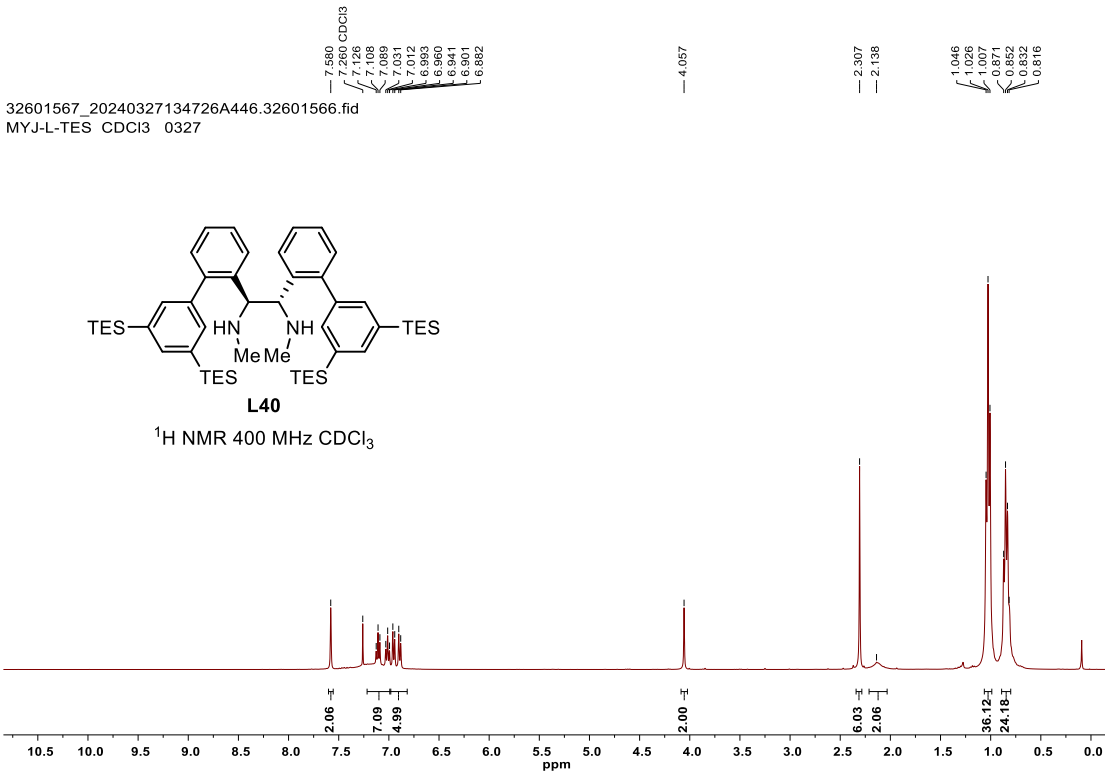
L38

^{1}H NMR 400 MHz $CDCl_3$



L38

^{13}C NMR 101 MHz $CDCl_3$


7.580
7.260 CDCl3
7.126
7.108
7.089
7.031
7.012
6.993
6.960
6.941
6.901
6.882
4.057
2.307
2.138
1.046
1.026
1.007
0.871
0.852
0.832
0.616
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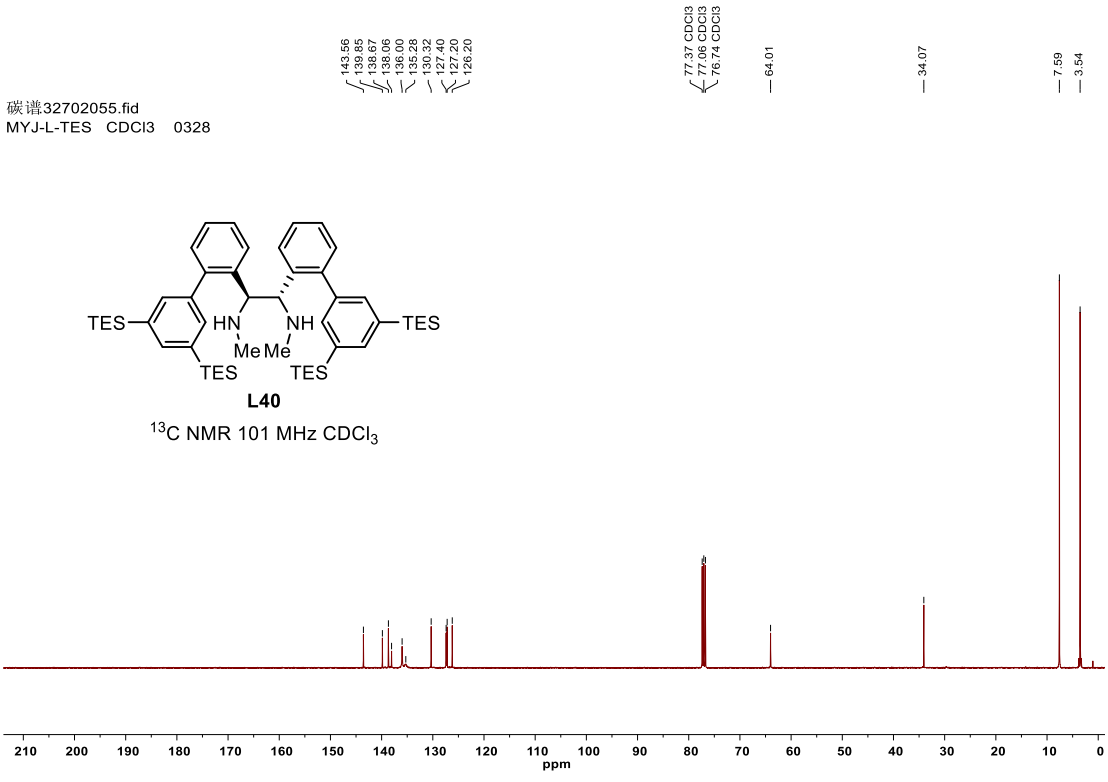
MYJ-L-TES CDCl3 0327
TES
HN
NH
TES
Me Me
TES
TES
L40
1H NMR 400 MHz CDCl3
2.06
7.09
4.99
2.00
6.03
2.06
36.12
24.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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139.85
138.67
138.06
136.00
135.28
130.32
127.40
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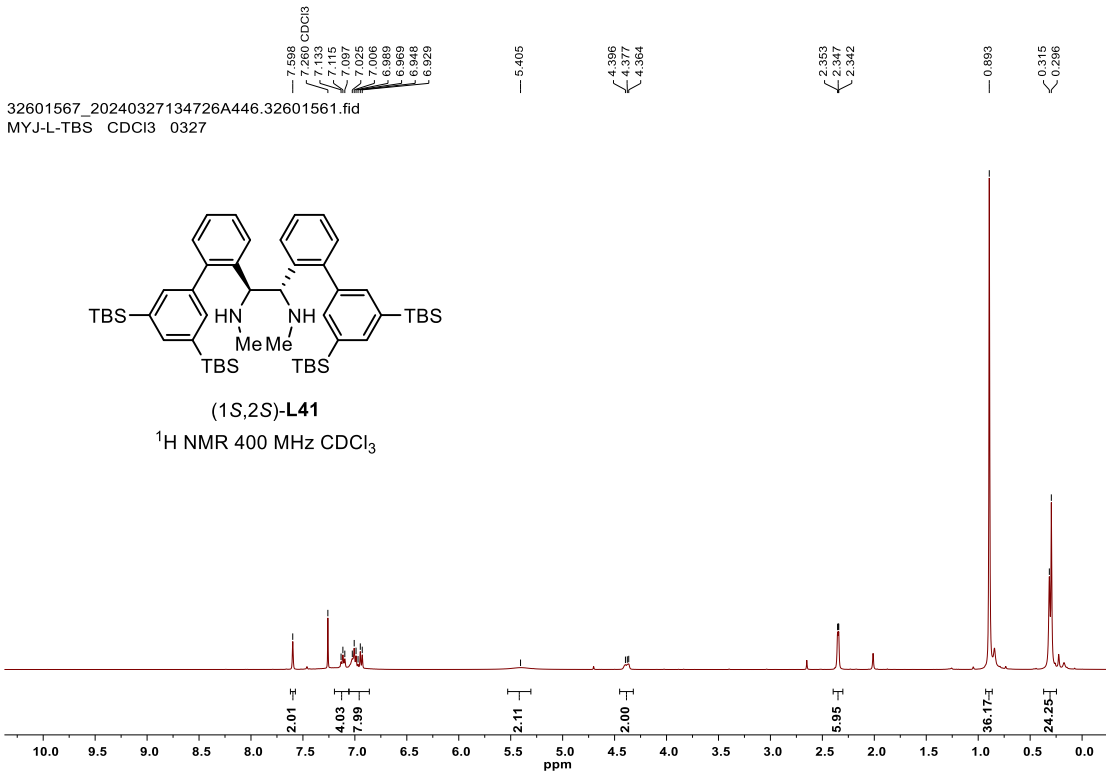
126.20
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
64.01
34.07
7.59
3.54
碳谱32702055.fid
MYJ-L-TES CDCl3 0328
TES
HN
NH
TES
Me Me
TES
TES
L40
13C NMR 101 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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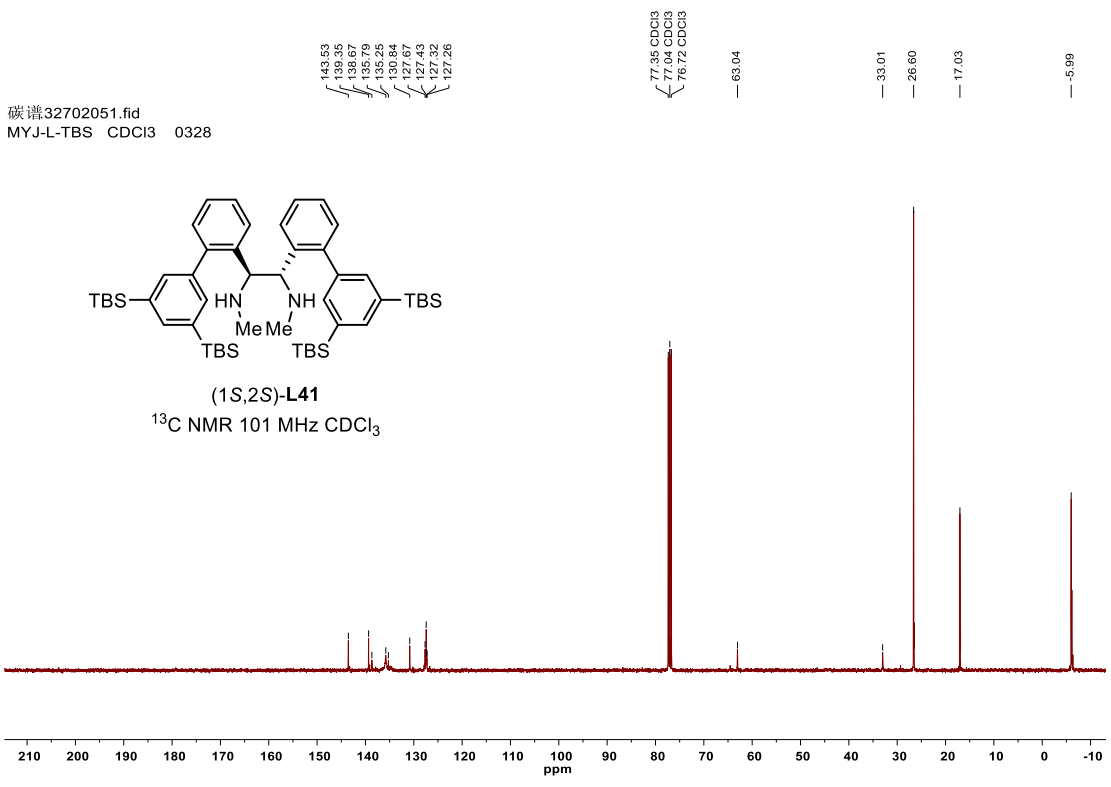
7.260 CDCl3
7.133
7.115
7.097
7.025
7.006
6.989
6.969
6.948
6.929
5.405
4.396
4.377
4.364
2.353
2.347
2.342
0.893
0.315
0.296
32601567_20240327134726A446.32601561.fid
MYJ-L-TBS CDCl3 0327
TBS
HN
NH
TBS
Me Me
TBS
TBS
(1S,2S)-L41
1H NMR 400 MHz CDCl3
2.01
4.03
7.99
2.11
2.00
5.95
36.17
24.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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139.35
138.77
138.79
135.25
130.84
127.67
127.43
127.32
127.26
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
63.04
33.01
26.60
17.03
-5.99
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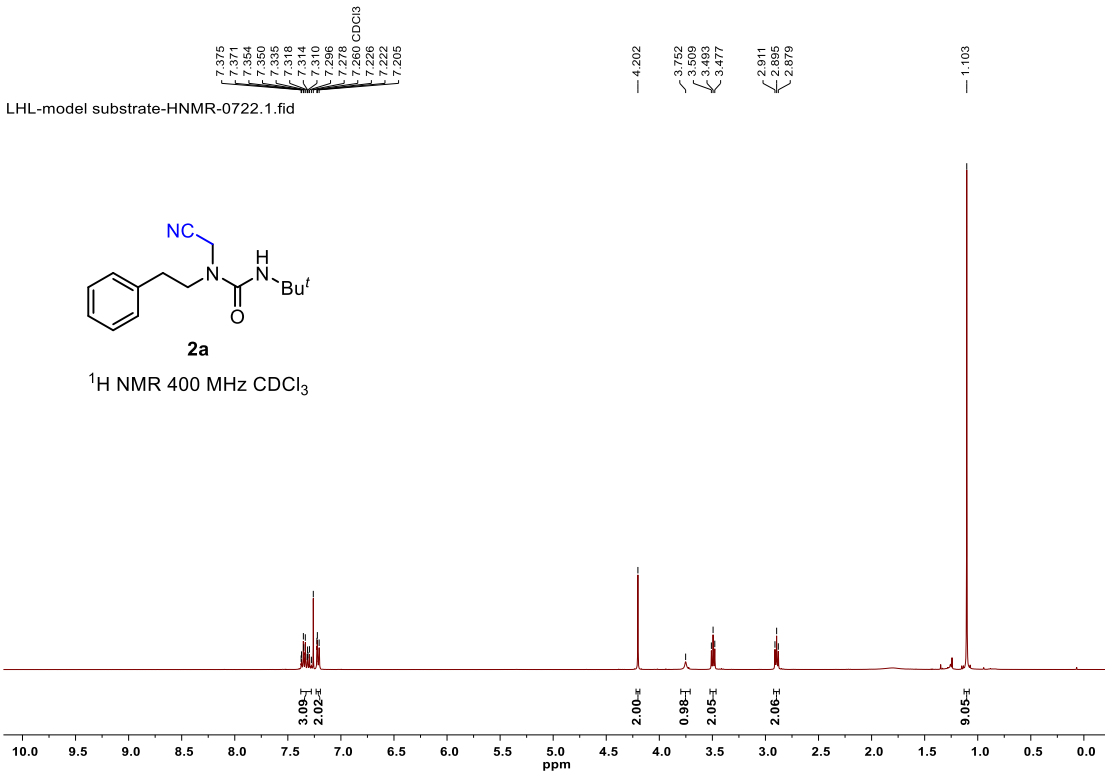
MYJ-L-TBS CDCl3 0328
TBS
HN
NH
TBS
Me Me
TBS
TBS
(1S,2S)-L41
13C NMR 101 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm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7.354
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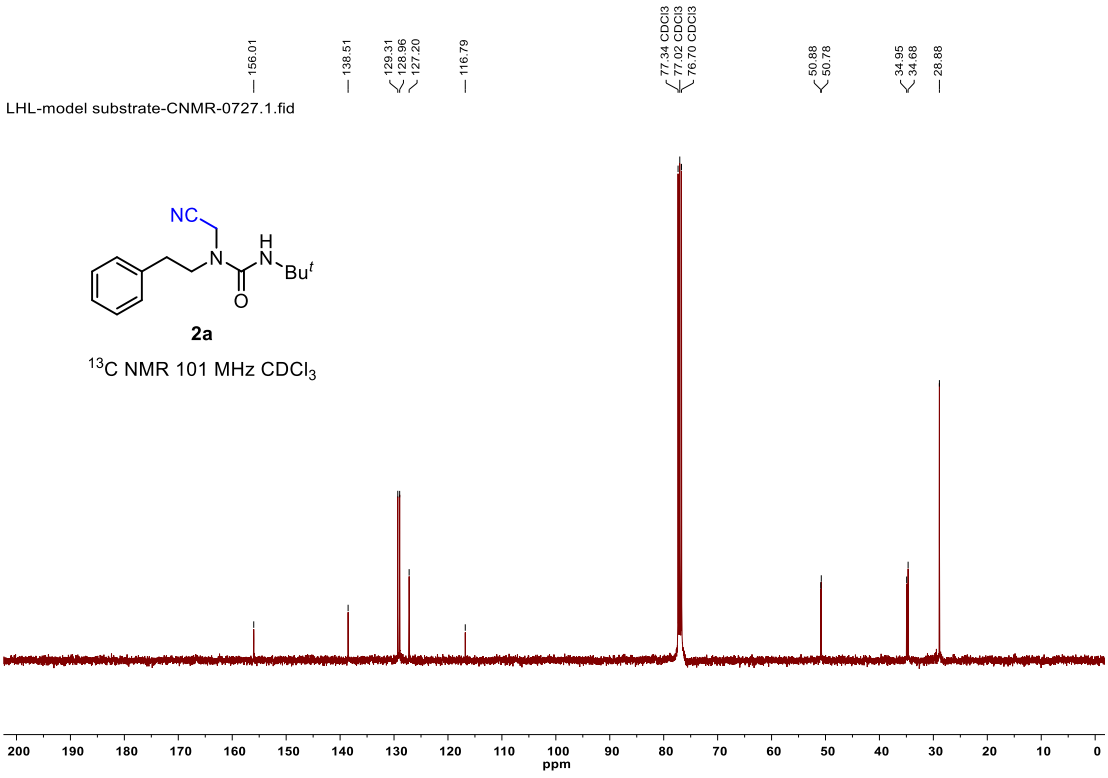
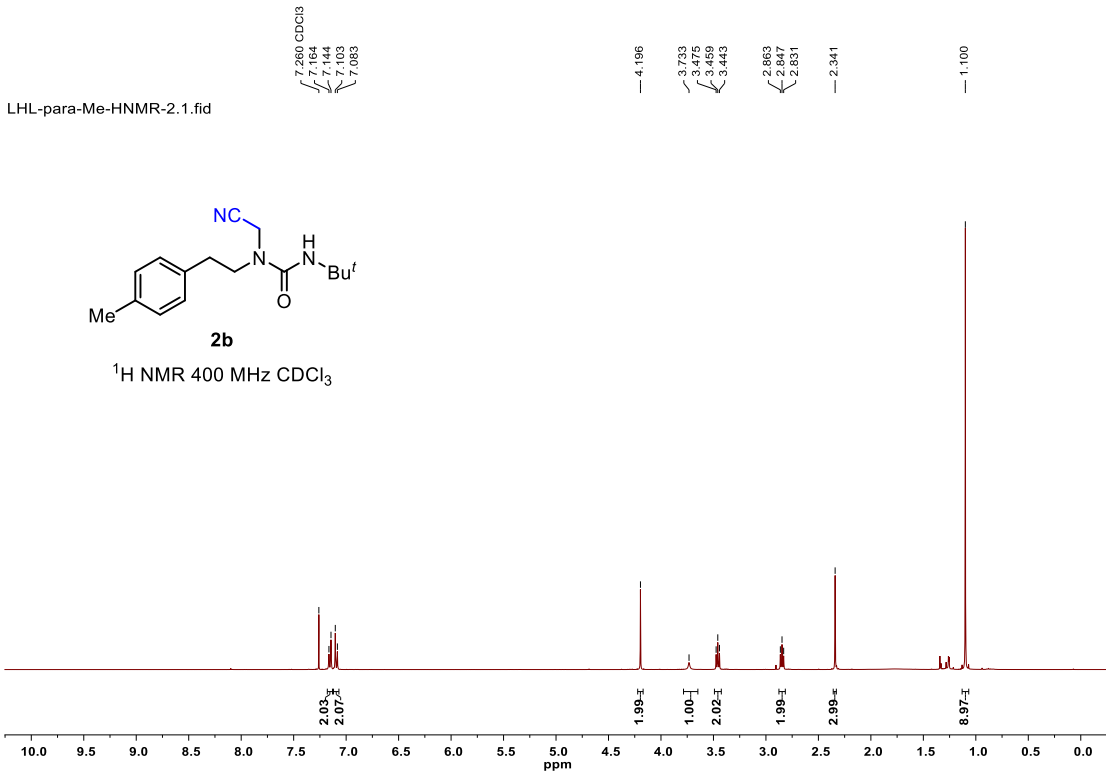
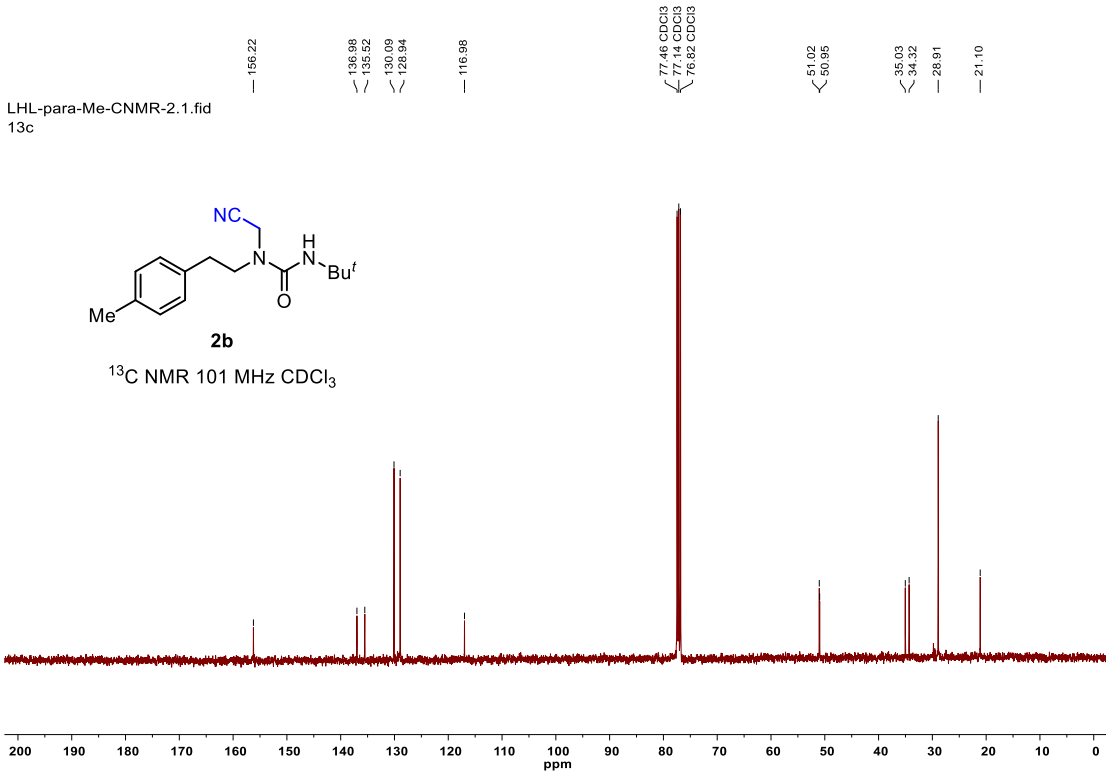
7.335
7.318
7.314
7.310
7.296
7.278
7.260 CDCl3
7.226
7.222
7.205
4.202
3.752
3.509
3.493
3.477
2.911
2.895
2.879
1.103
LHL-model substrate-HNMR-0722.1.fid
NC
N
H
N
Bu^t
O
2a
^{1}H NMR 400 MHz CDCl$_3$
3.09
2.02
2.00
0.98
2.05
2.06
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

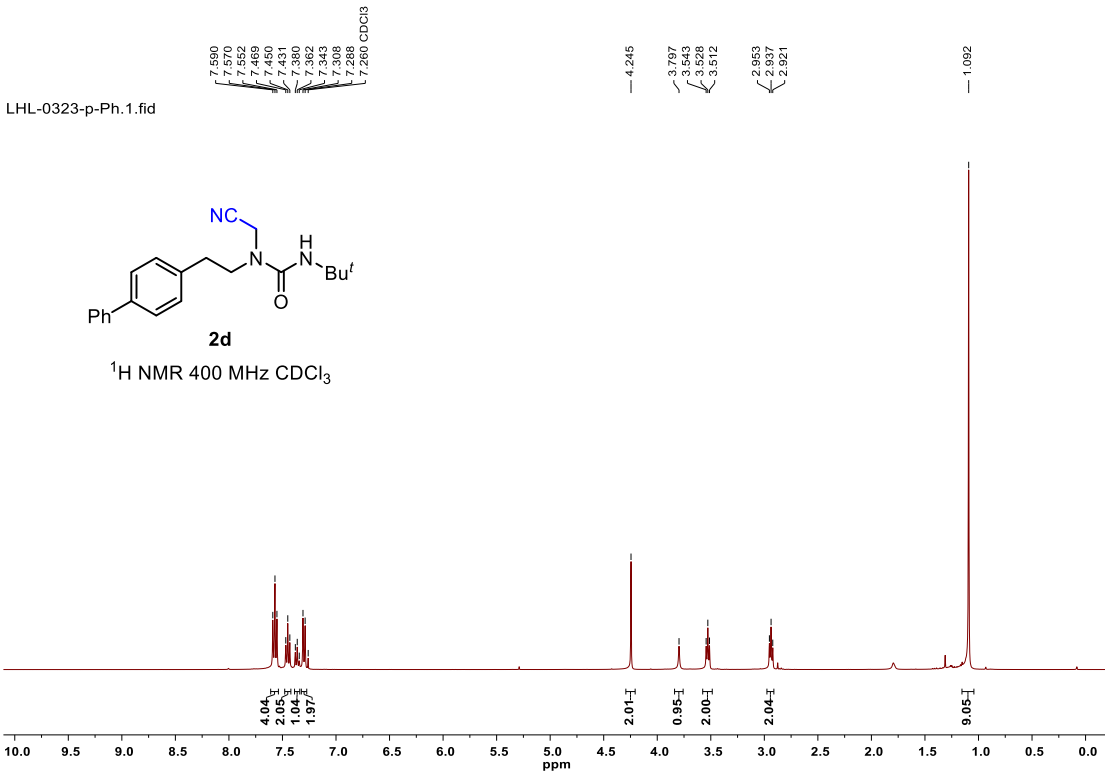

156.01
138.51
129.31
128.96
127.20
116.79
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
50.88
50.78
34.95
34.68
28.88
LHL-model substrate-CNMR-0727.1.fid
NC
N
H
N
Bu^t
O
2a
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

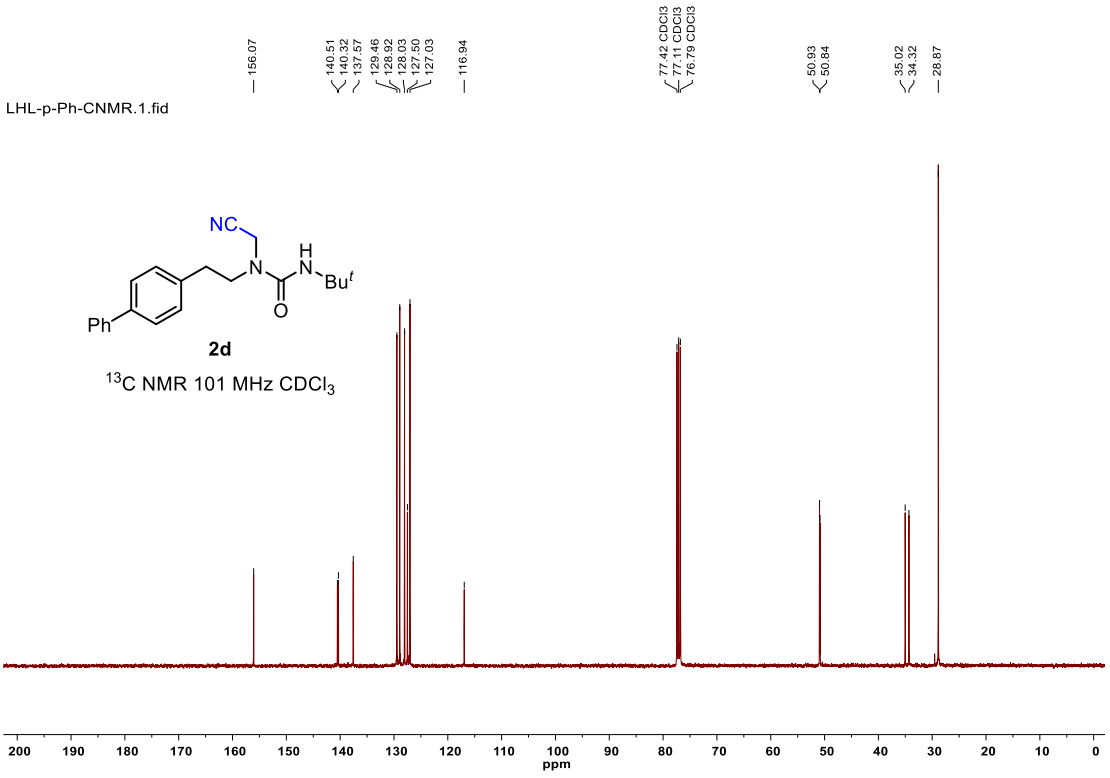
LHL-para-Me-HNMR-2.1.fid



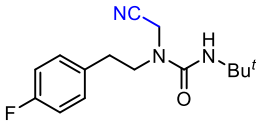
LHL-para-Me-CNMR-2.1.fid
13c




7.590
7.570
7.552
7.469
7.450
7.431
7.380
7.362
7.343
7.308
7.288
7.260 CDCl3
4.245
3.797
3.543
3.528
3.512
2.953
2.937
2.921
1.092
LHL-0323-p-Ph.1.fid
NC
H
N
N
Bu^t
O
Ph
2d
^{1}H NMR 400 MHz CDCl$_3$
4.04
2.05
1.04
1.97
2.01
0.95
2.00
2.04
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


156.07
140.51
140.32
137.57
129.46
128.92
128.03
127.50
127.03
116.94
77.42 CDCl3
77.11 CDCl3
76.79 CDCl3
50.93
50.84
35.02
34.32
28.87
LHL-p-Ph-CNMR.1.fid
NC
H
N
N
Bu^t
O
Ph
2d
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

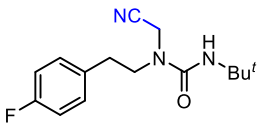
LHL-para-F-HNMR-7.1.fid



2e

^{1}H NMR 400 MHz $CDCl_3$

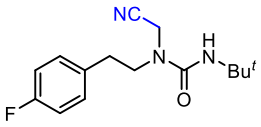
LHL-para-F-CNMR-7.1.fid



2e

^{13}C NMR 101 MHz $CDCl_3$

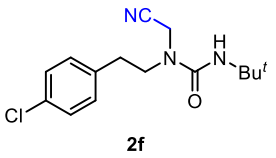
h60nihcyQE6Jdv+53pA6uQ.90800221.fid
MYJ-0909-alpha-p-F CDCl3 0910



2e

^{19}F NMR 376 MHz $CDCl_3$

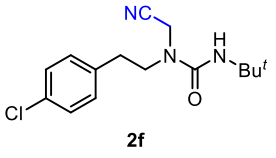
LHL-para-Cl-NMR-15.1.fid



2f

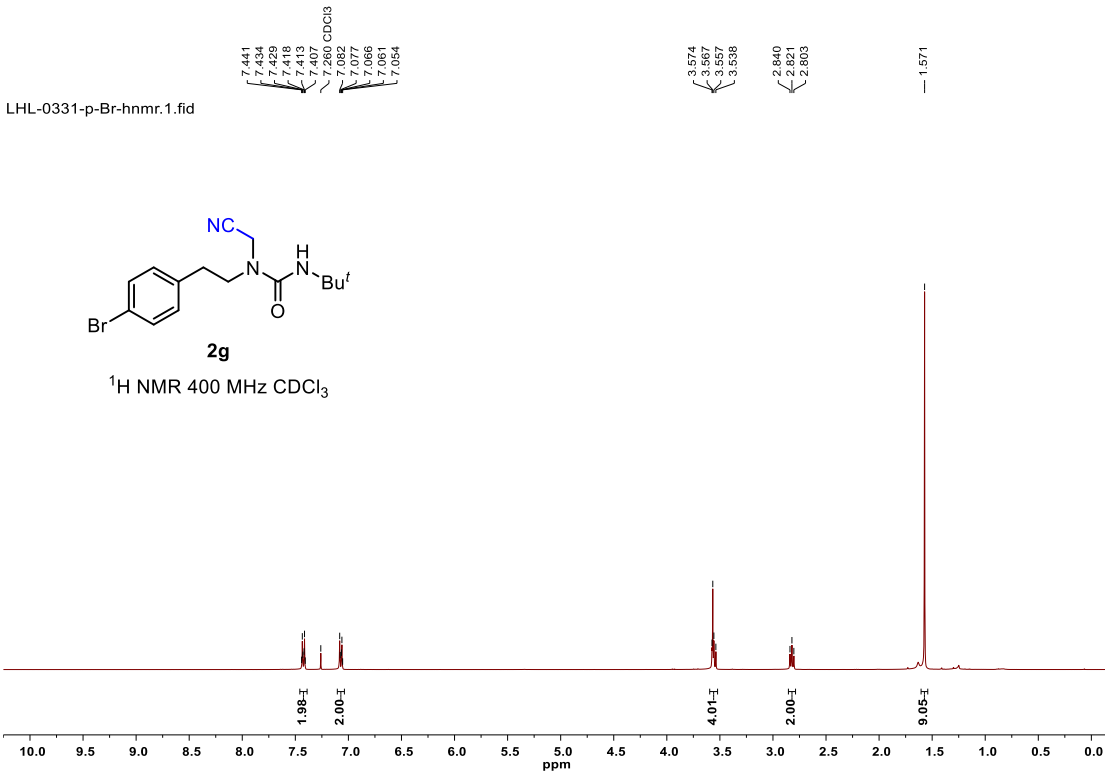
^{1}H NMR 400 MHz $CDCl_3$

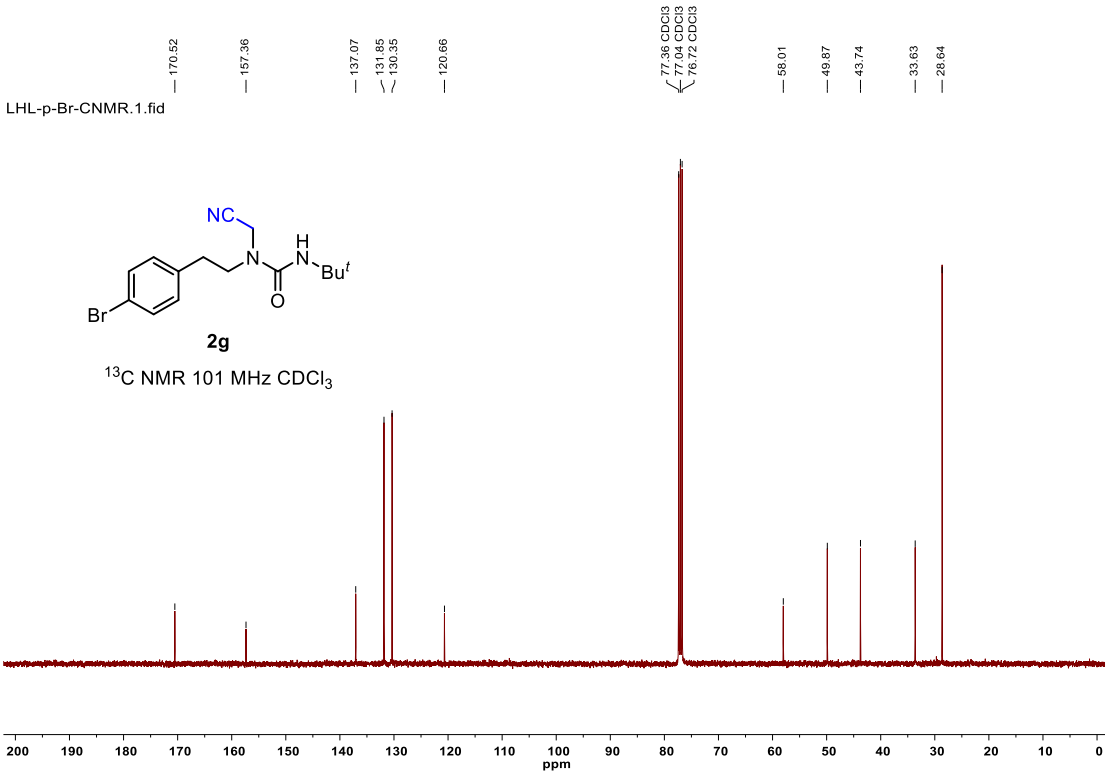
LHL-para-Cl-NMR-15.2.fid



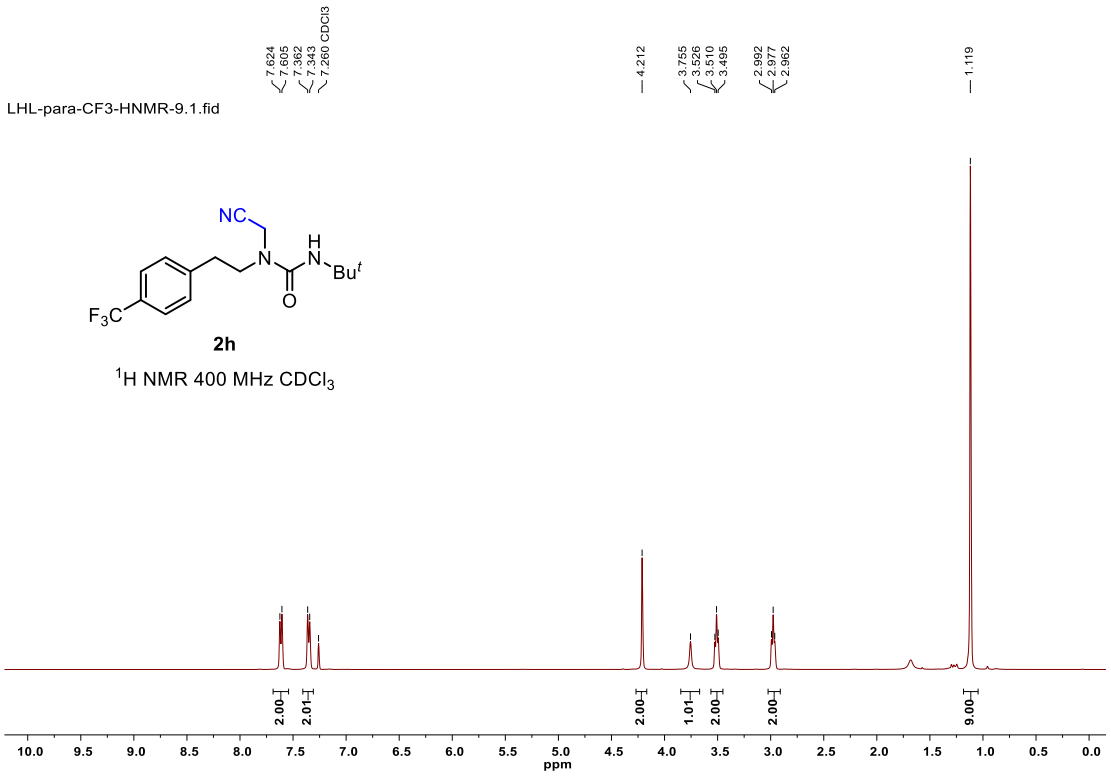
2f

^{13}C NMR 101 MHz $CDCl_3$


7.441
7.434
7.429
7.418
7.413
7.407
7.260 CDCl3
7.082
7.077
7.066
7.061
7.054
3.574
3.567
3.557
3.538
2.840
2.821
2.803
1.571
LHL-0331-p-Br-hnmr.1.fid
NC
H
N
N
Bu^t
O
Br
2g
^{1}H NMR 400 MHz CDCl$_3$
1.98
2.00
4.01
2.00
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


170.52
157.36
137.07
131.85
130.35
120.66
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
58.01
49.87
43.74
33.63
28.64
LHL-p-Br-CNMR.1.fid
NC
H
N
N
Bu^t
O
Br
2g
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

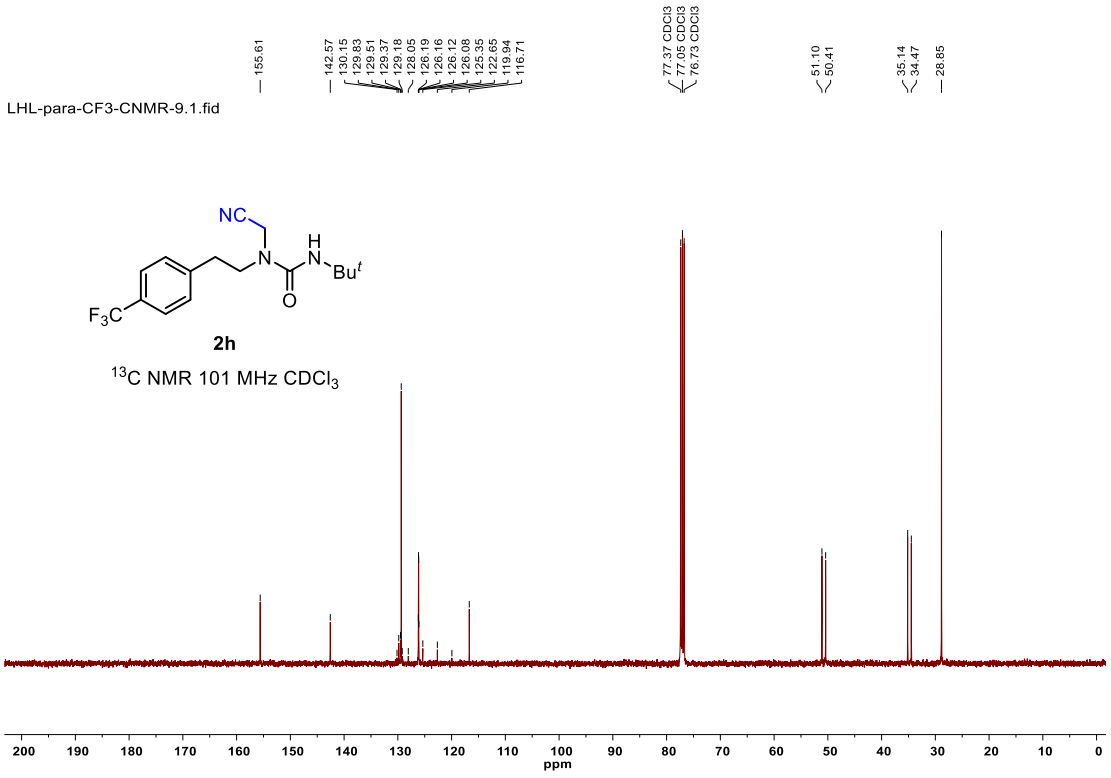
LHL-para-CF3-HNMR-9.1.fid



2h

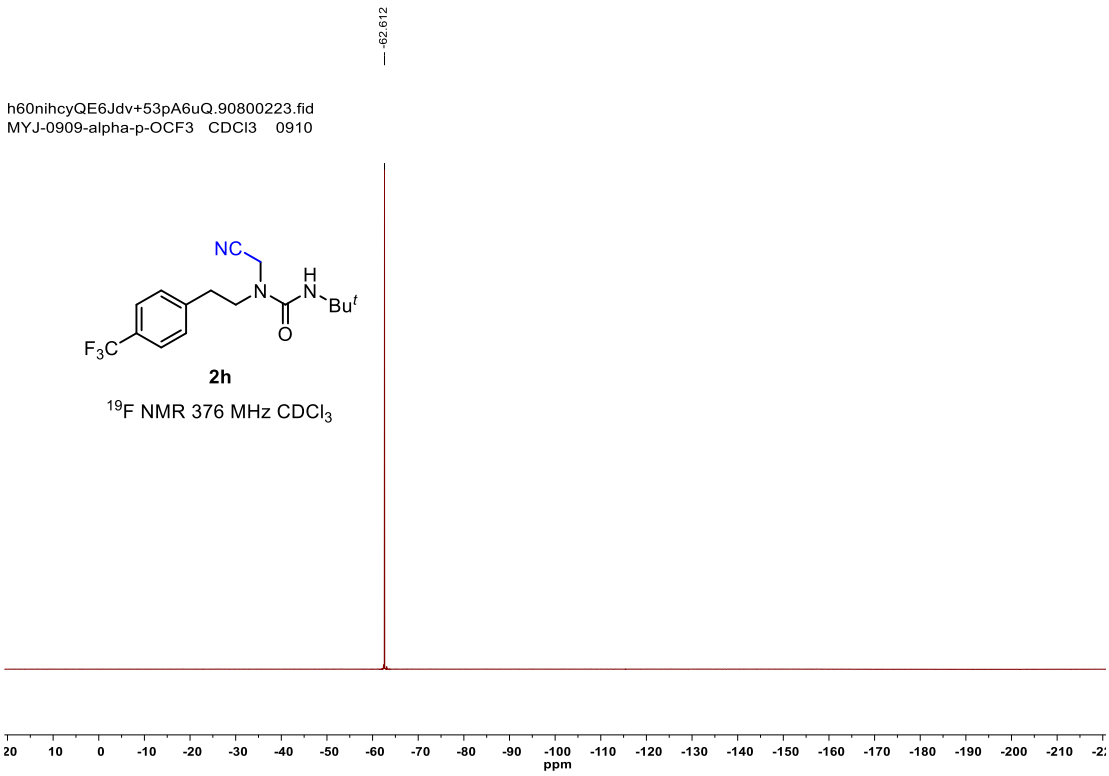
^{1}H NMR 400 MHz $CDCl_3$

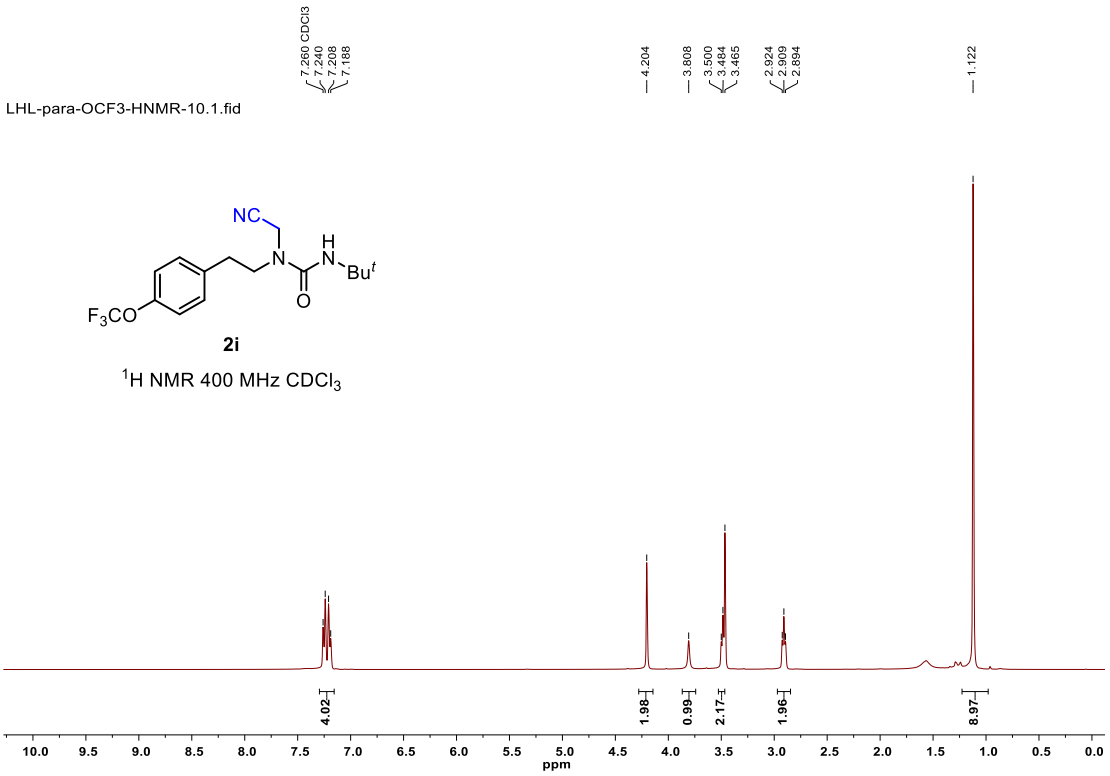
LHL-para-CF3-CNMR-9.1.fid



2h

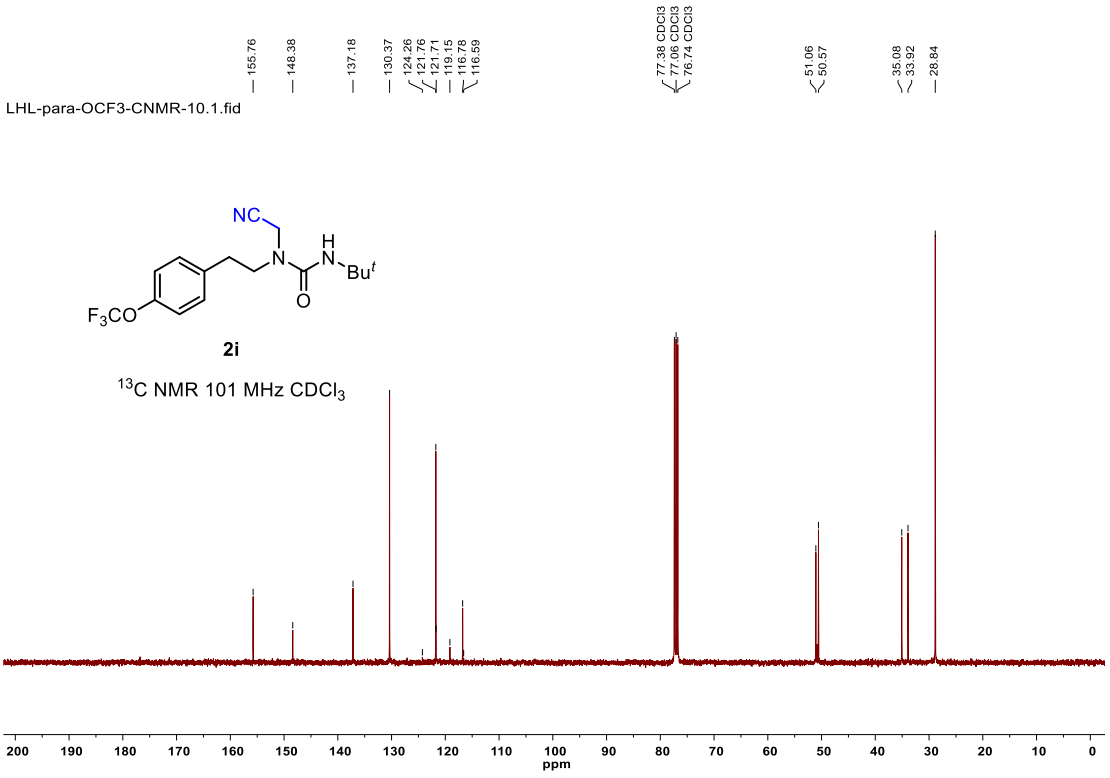
^{13}C NMR 101 MHz $CDCl_3$


-62.612
h60nihcyQE6Jdv+53pA6uQ.90800223.fid
MYJ-0909-alpha-p-OCF3 CDCl3 0910
NC
H
N
N
Bu^t
O
F_3C
2h
^{19}F NMR 376 MHz $CDCl_3$
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm



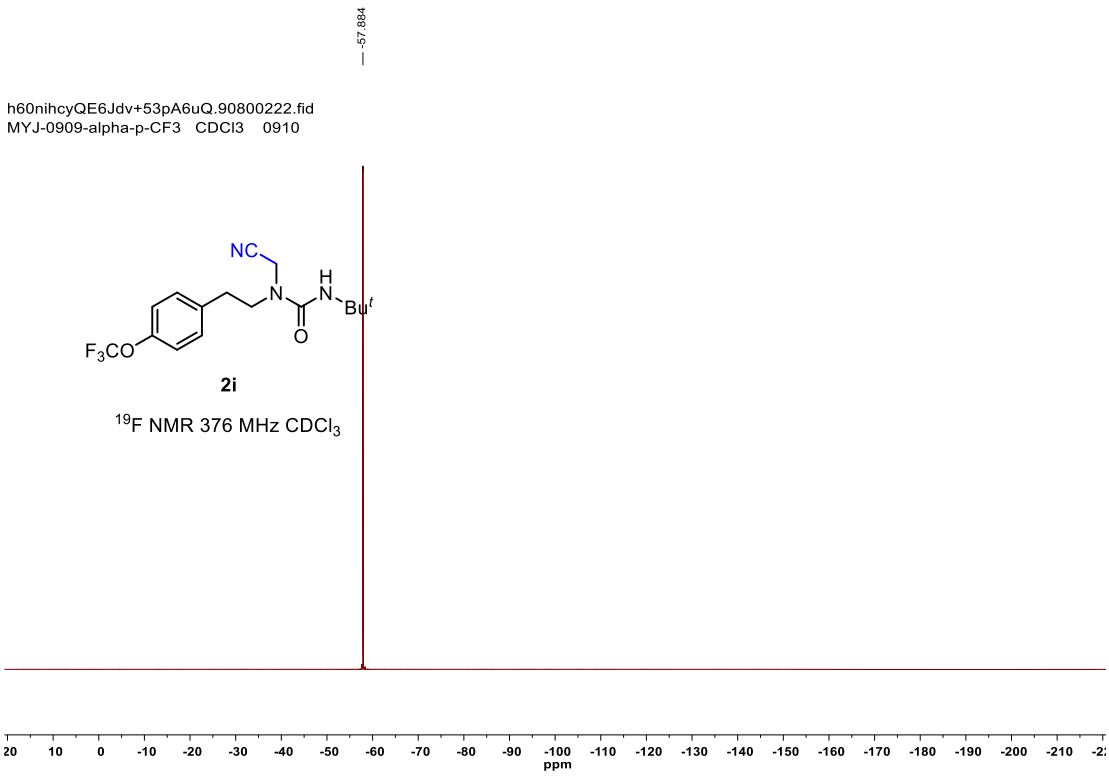
2i

^{1}H NMR 400 MHz $CDCl_3$



2i

^{13}C NMR 101 MHz $CDCl_3$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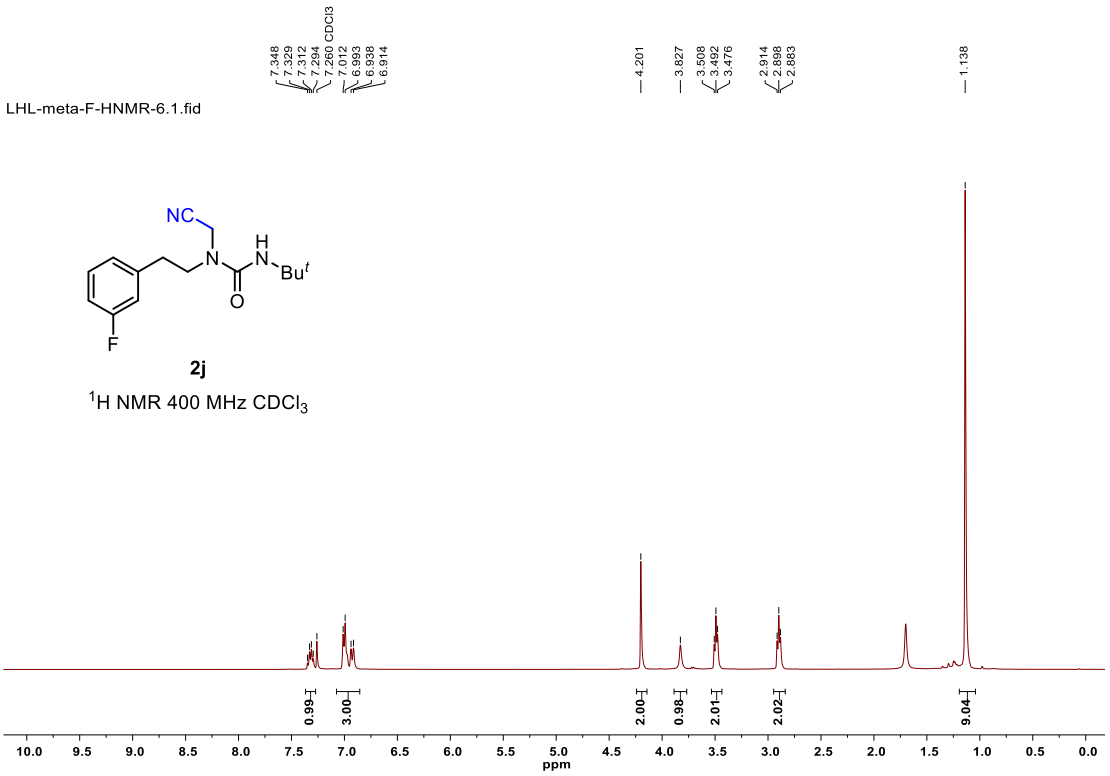
MYJ-0909-alpha-p-CF3 CDCl3 0910
NC
H
N
N
Bu t
O
F3CO
2i
19F NMR 376 MHz CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

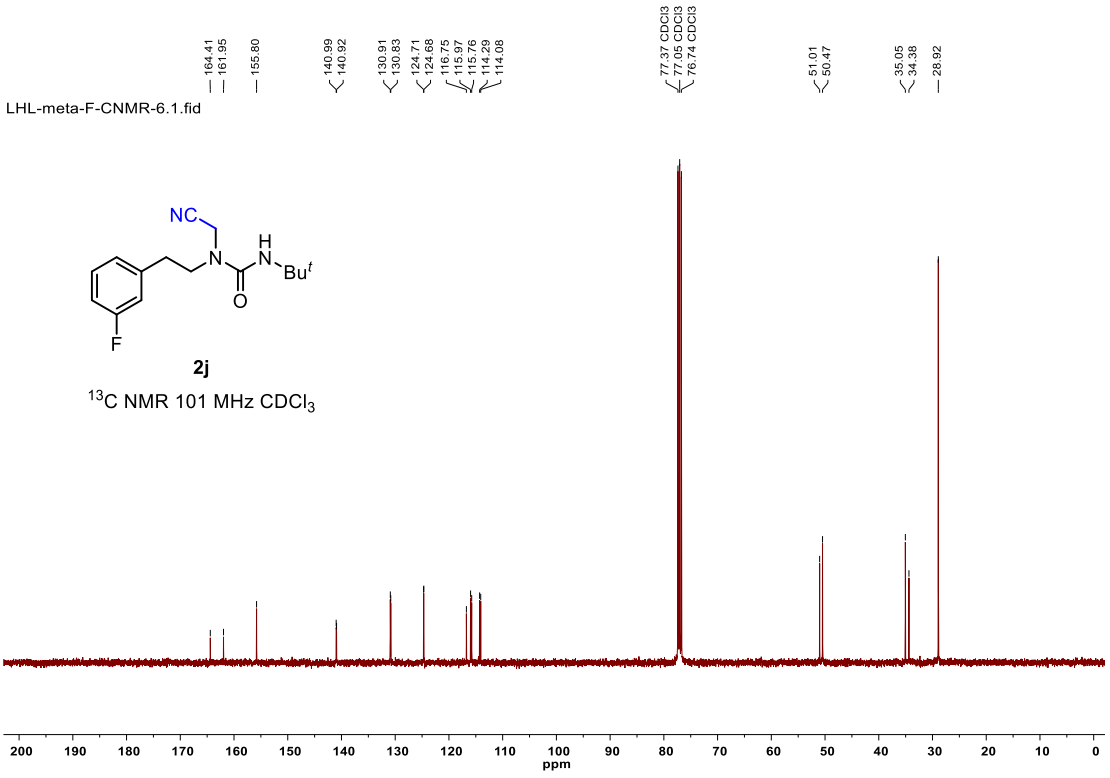
LHL-meta-F-HNMR-6.1.fid



2j

^{1}H NMR 400 MHz $CDCl_3$

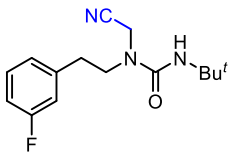
LHL-meta-F-CNMR-6.1.fid



2j

^{13}C NMR 101 MHz $CDCl_3$

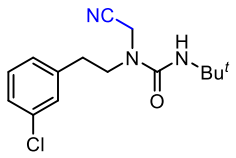
h60nihcyQE6Jdv+53pA6uQ.90800226.fid
MYJ-0909-alpha-o-F CDCl3 0910



2j

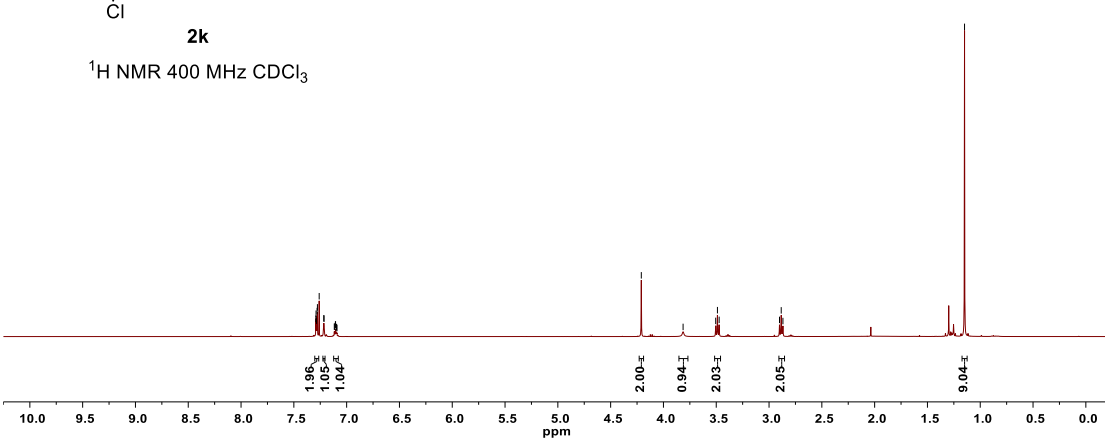
^{19}F NMR 376 MHz $CDCl_3$

LHL-meta-Cl-HNMR-3.1.fid

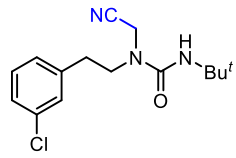


2k

^{1}H NMR 400 MHz $CDCl_3$

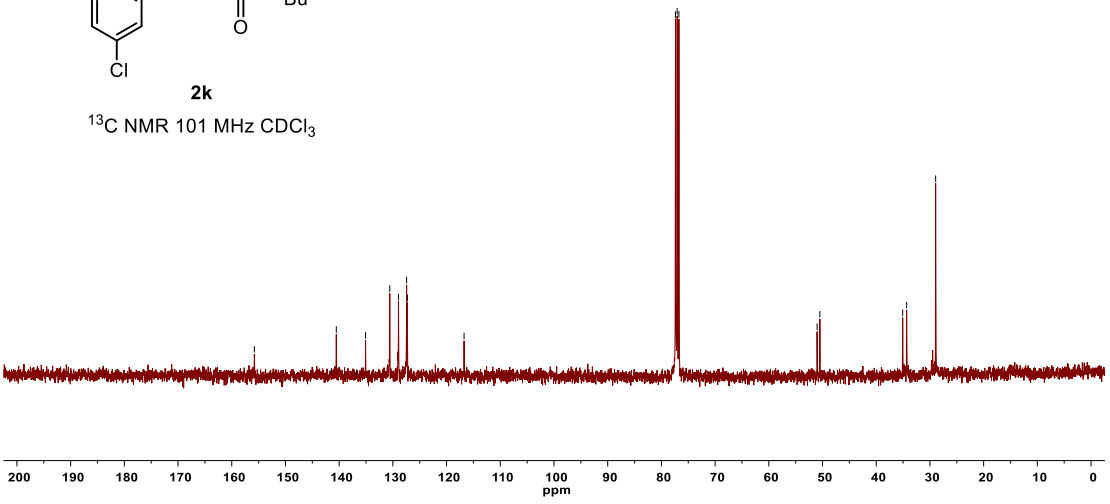


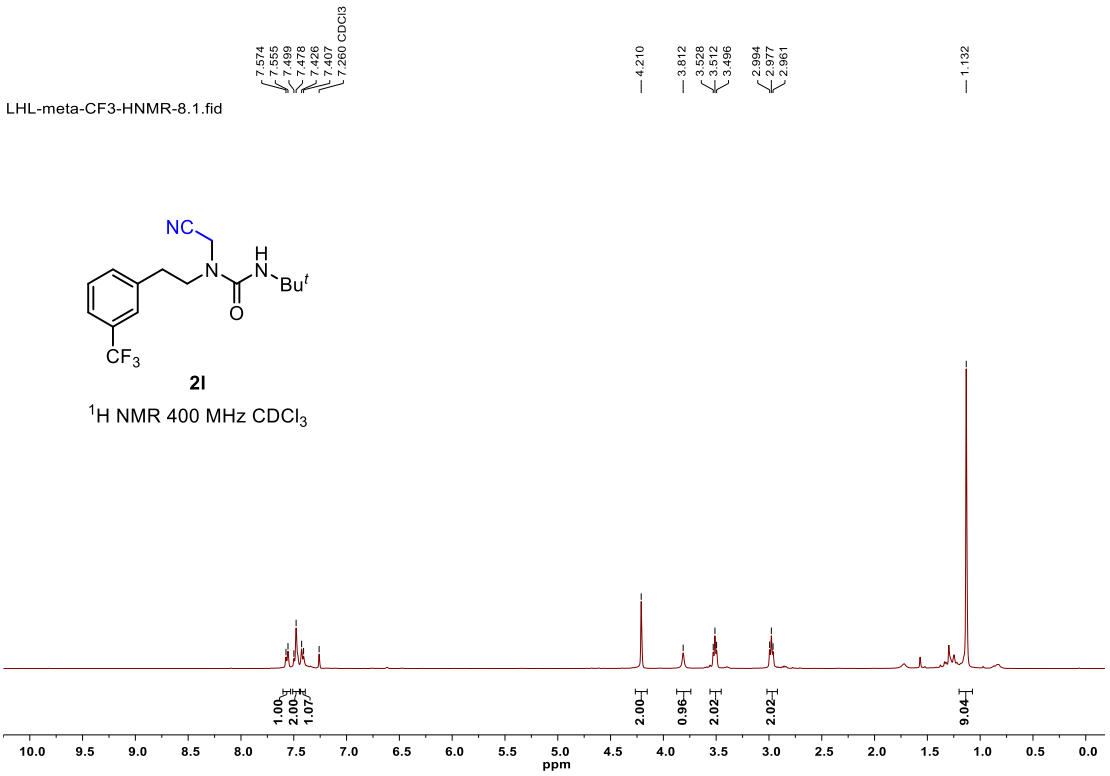
LHL-meta-Cl-CNMR-3.1.fid
13C



2k

^{13}C NMR 101 MHz $CDCl_3$




7.574
7.555
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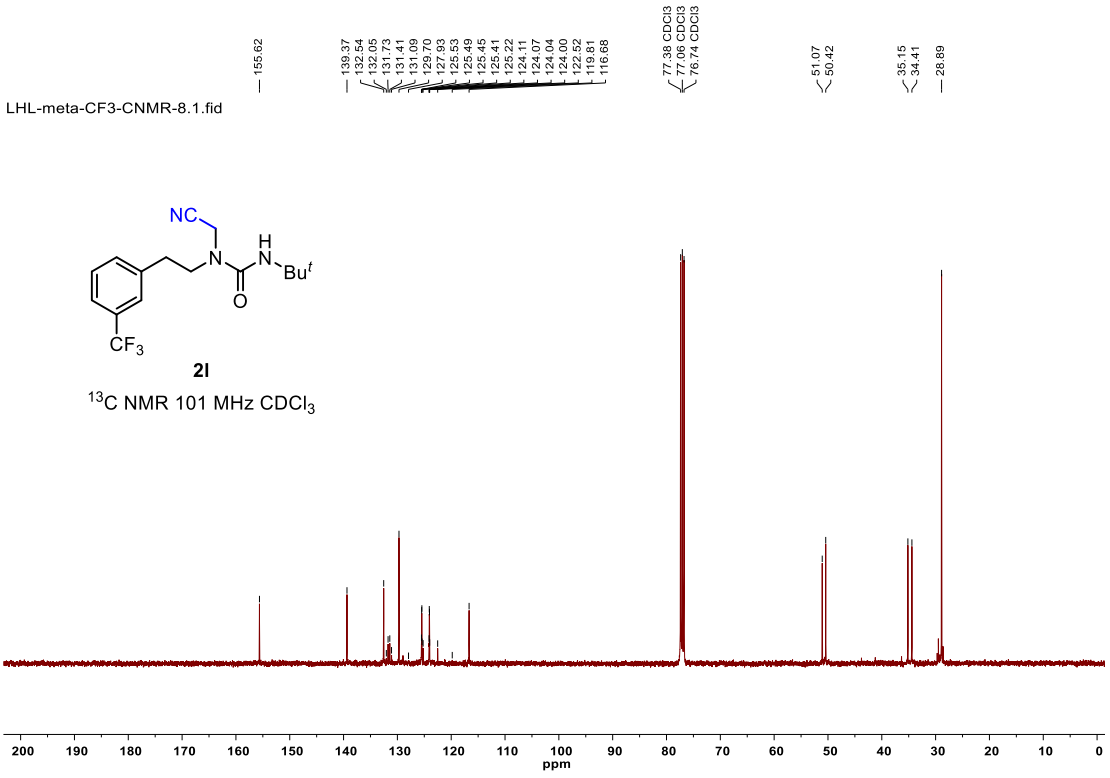
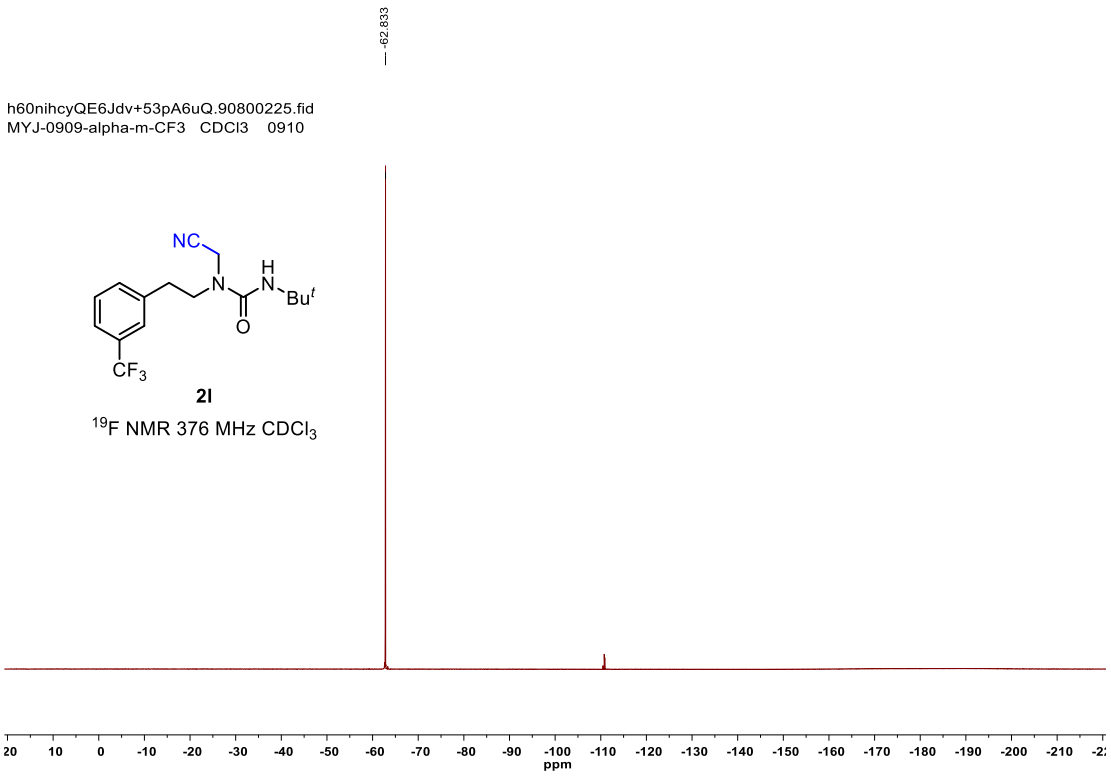
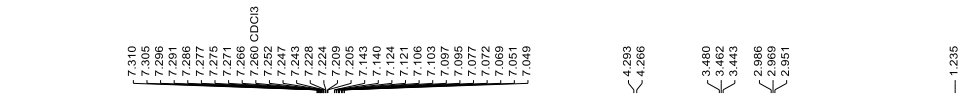
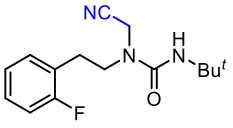
7.478
7.426
7.407
7.260 CDCl3
4.210
3.812
3.528
3.512
3.496
2.994
2.977
2.961
1.132
LHL-meta-CF3-HNMR-8.1.fid
NC
H
N
N
Bu^t
O
CF$_3$
2l
^{1}H NMR 400 MHz CDCl$_3$
1.00
2.00
1.07
2.00
0.96
2.02
2.02
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


155.62
139.37
132.54
132.05
131.73
131.41
131.09
129.70
127.93
125.53
125.49
125.45
125.41
125.22
124.11
124.07
124.04
124.00
122.52
119.81
116.68
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
51.07
50.42
35.15
34.41
28.89
LHL-meta-CF3-CNMR-8.1.fid
NC
H
N
N
Bu^t
O
CF$_3$
2l
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-62.833
h60nihcyQE6Jdv+53pA6uQ.90800225.fid
MYJ-0909-alpha-m-CF3 CDCl3 0910
NC
N
H
N
Bu^t
O
CF$_3$
2l
^{19}F NMR 376 MHz CDCl$_3$
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

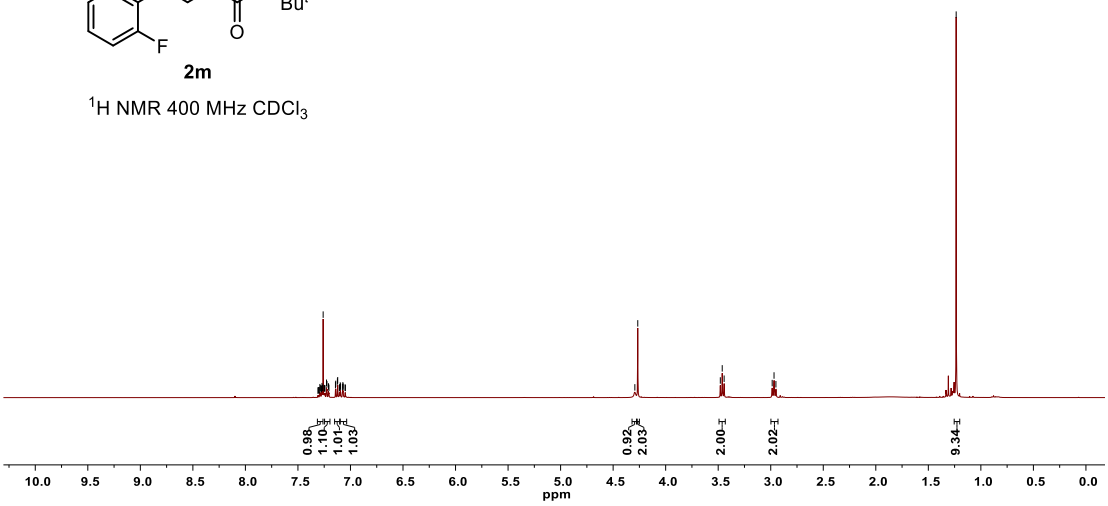


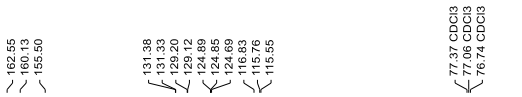
LHL-ortho-F-HNMR-1.1.fid



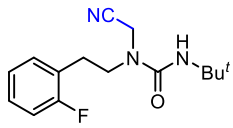
2m

^{1}H NMR 400 MHz $CDCl_3$



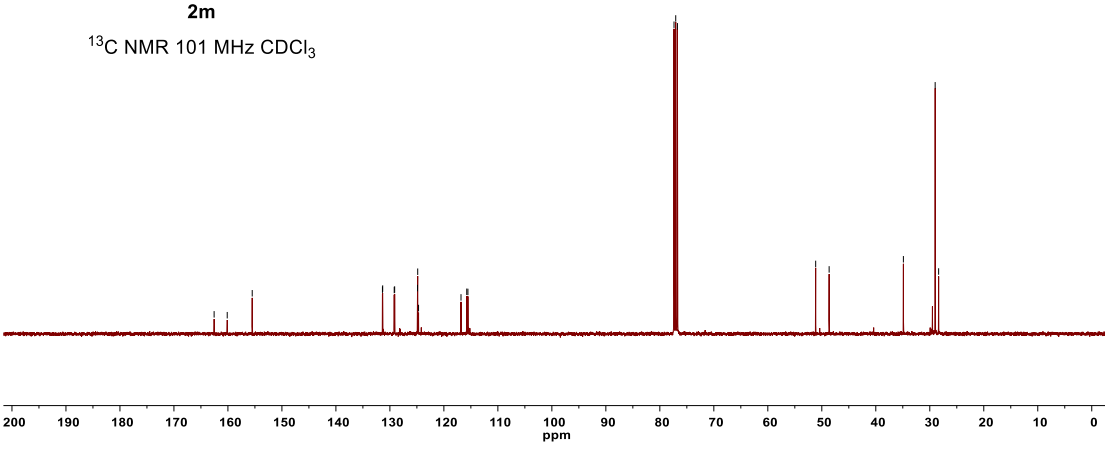


LHL-ortho-F-CNMR-1.1.fid

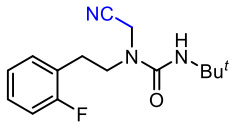


2m

^{13}C NMR 101 MHz $CDCl_3$

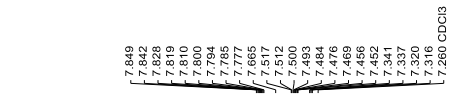


h60nihcyQE6Jdv+53pA6uQ.90800224.fid
MYJ-0909-alpha-m-F CDCl3 0910

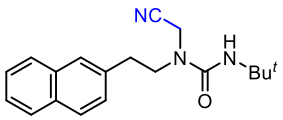


2m

^{19}F NMR 376 MHz $CDCl_3$



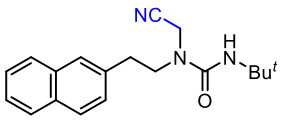
LHL-naiyian-HNMR-2.24.1.fid



2n

^{1}H NMR 400 MHz $CDCl_3$

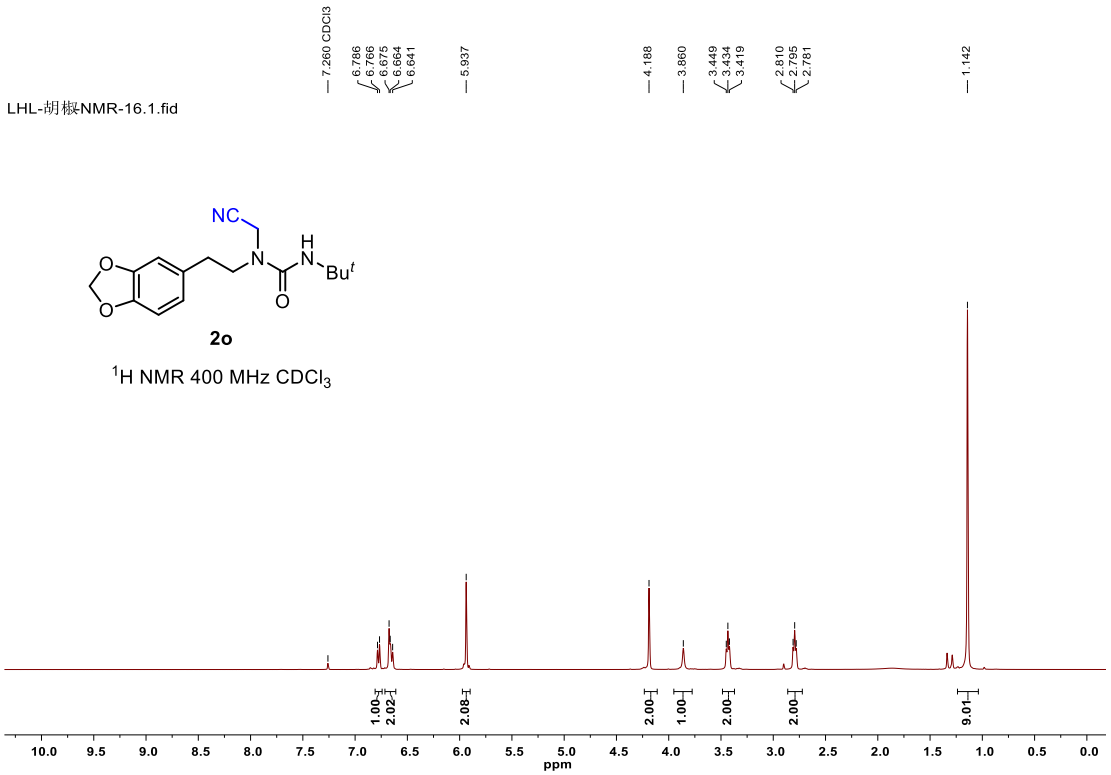
LHL-naiyian-CNMR-3.2.1.fid



2n

^{13}C NMR 101 MHz $CDCl_3$

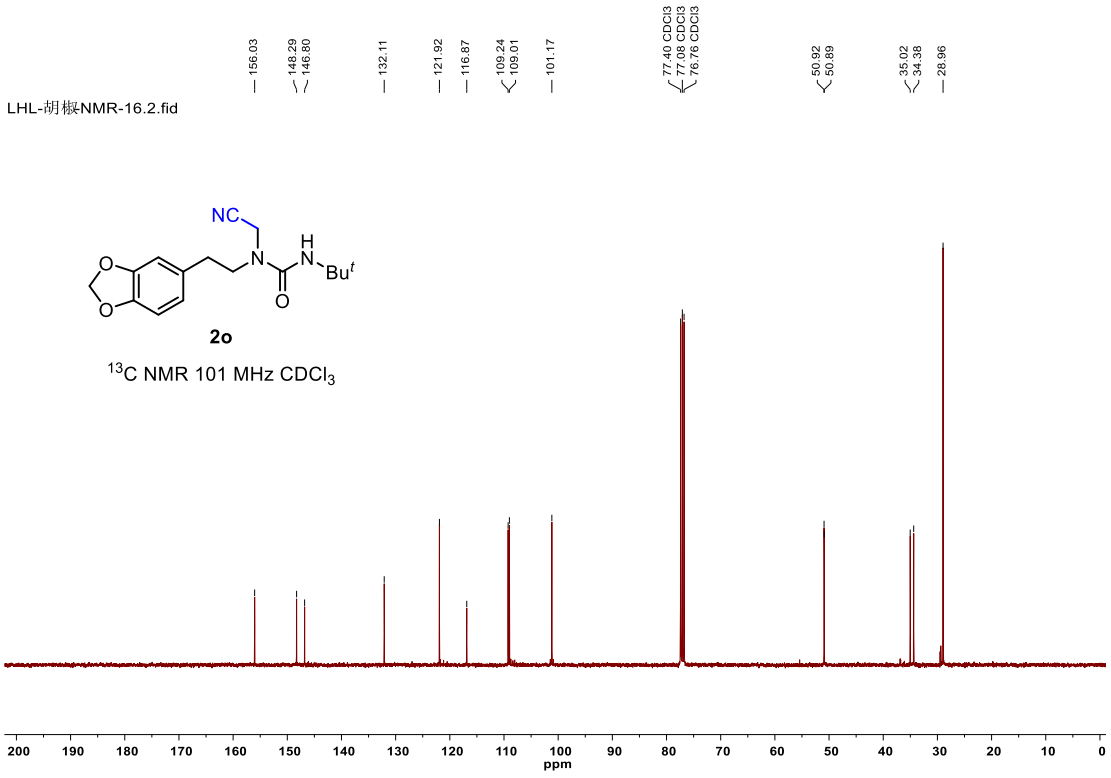
LHL-胡椒NMR-16.1.fid



2o

^{1}H NMR 400 MHz $CDCl_3$

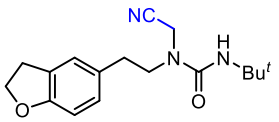
LHL-胡椒NMR-16.2.fid



2o

^{13}C NMR 101 MHz $CDCl_3$

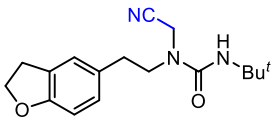
LHL-ph-funan-HNMR-20.1.fid



2p

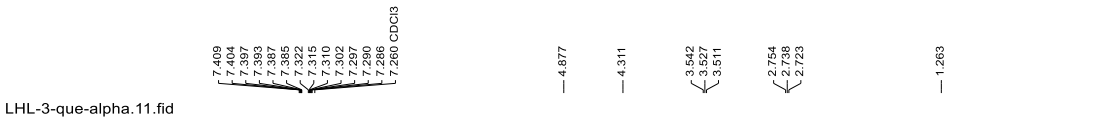
^{1}H NMR 400 MHz $CDCl_3$

LHL-Ph-funnan-3.2-CNMR.1.fid

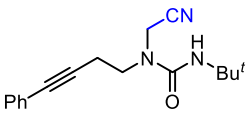


2p

^{13}C NMR 101 MHz $CDCl_3$

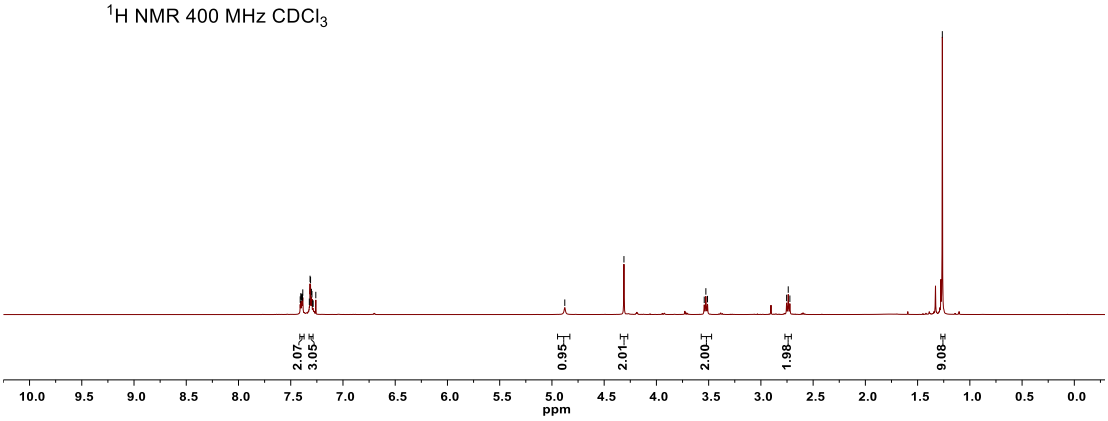


LHL-3-que-alpha.11.fid

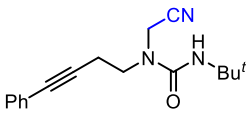


2r

^{1}H NMR 400 MHz $CDCl_3$

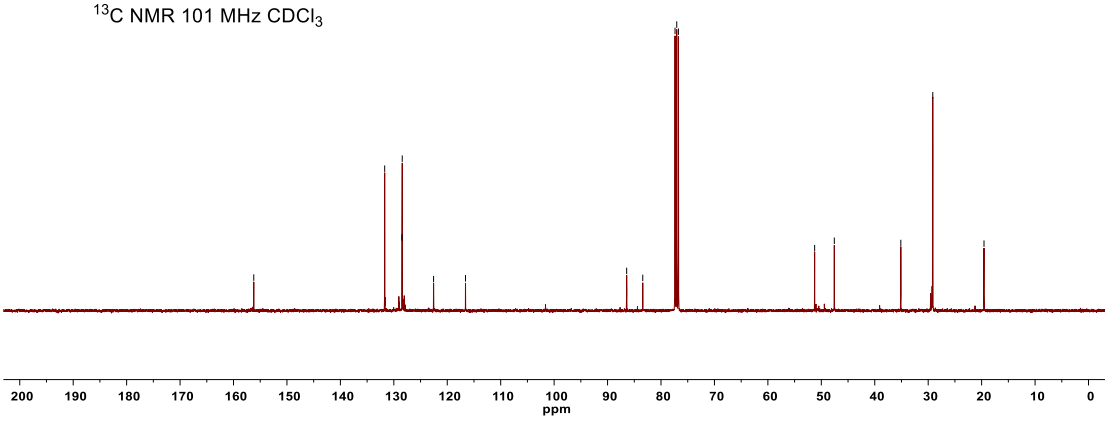


LHL-que-alpha-CNMR.1.fid

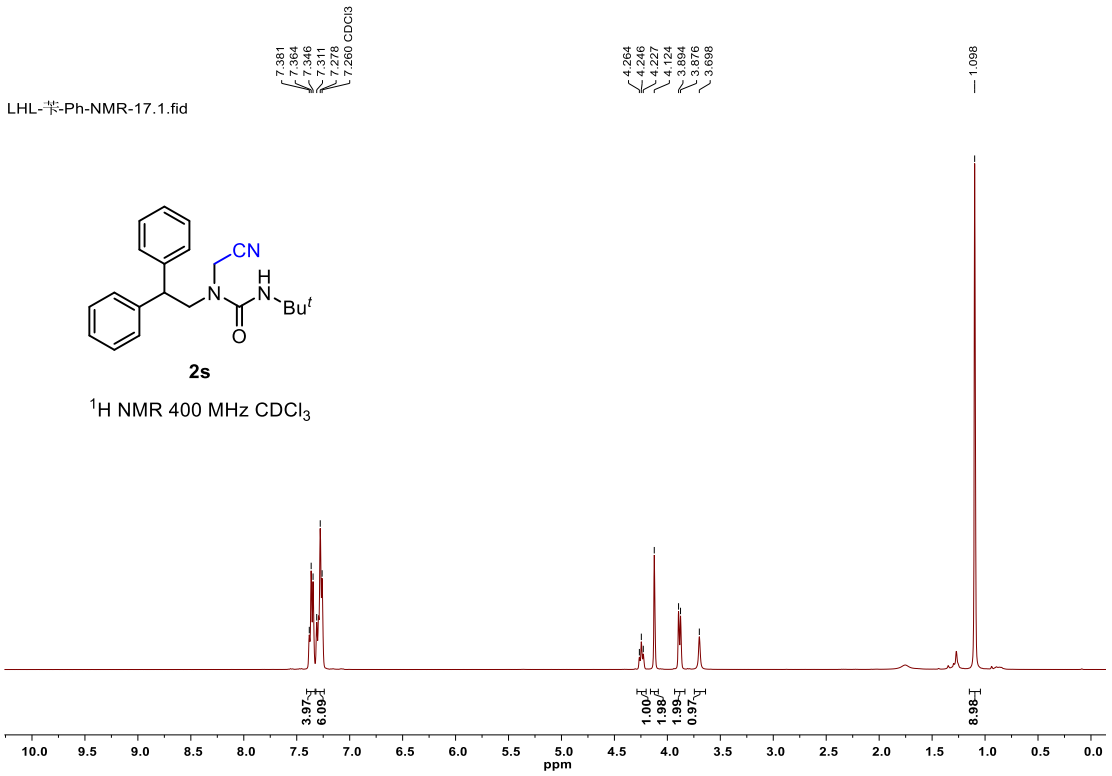


2r

^{13}C NMR 101 MHz $CDCl_3$



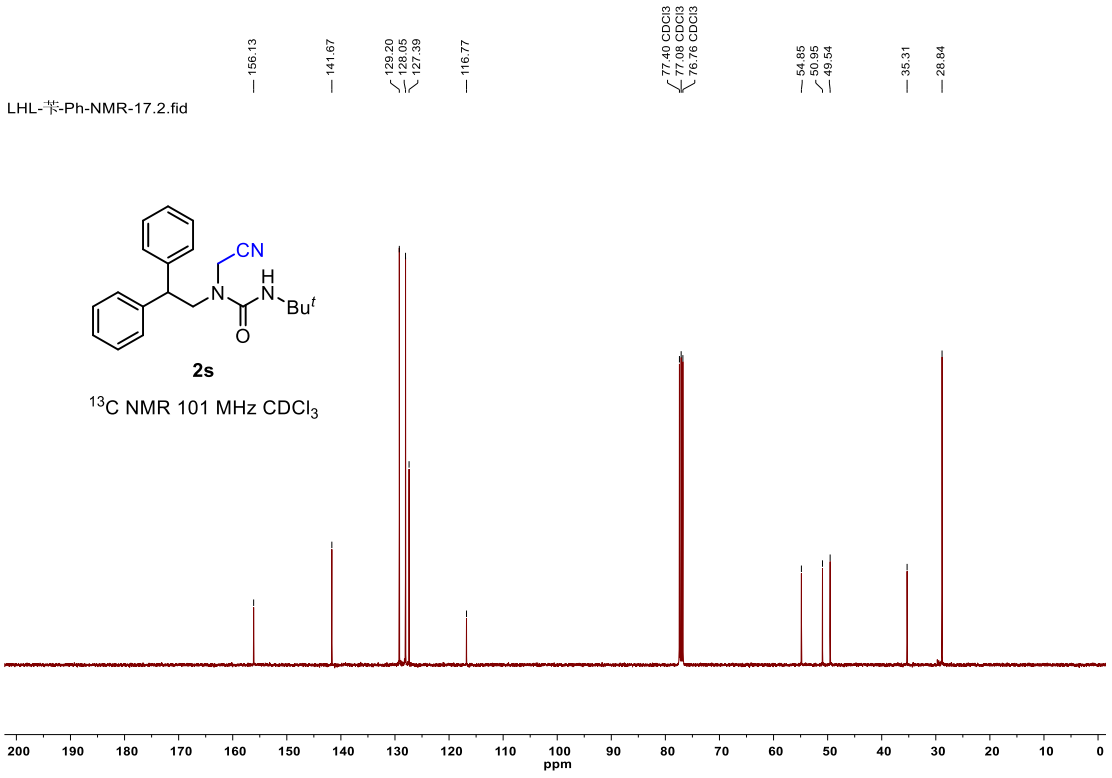
LHL-苄-Ph-NMR-17.1.fid



2s

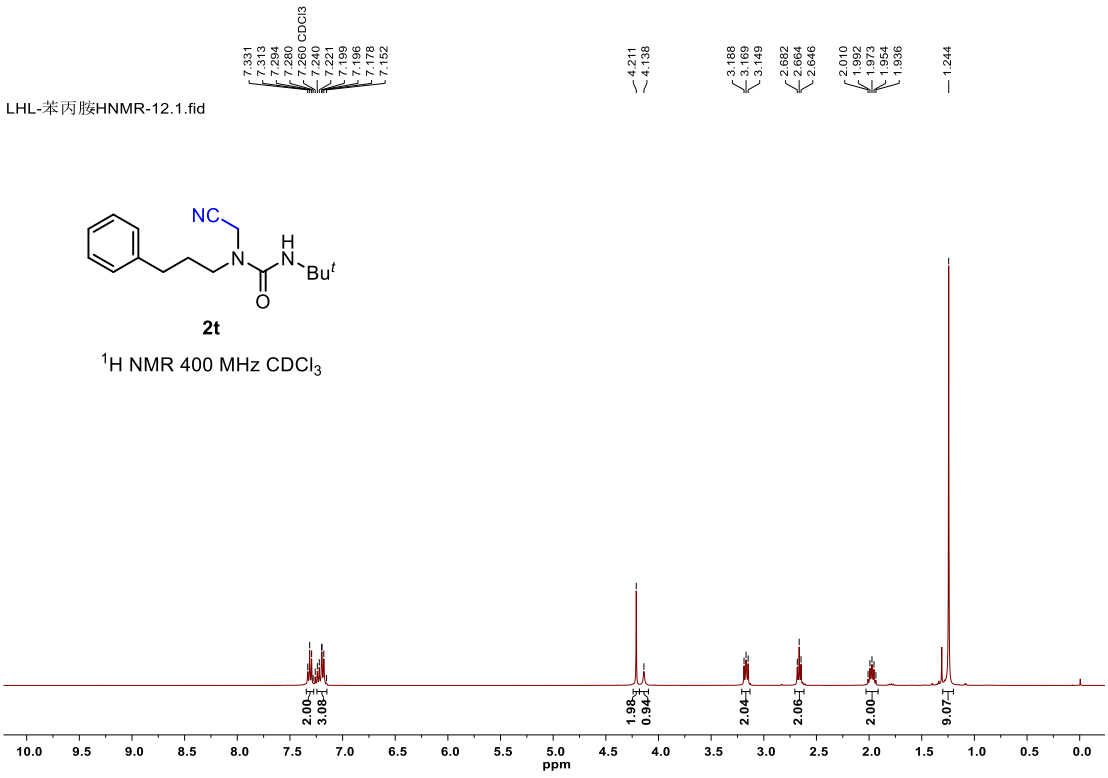
^{1}H NMR 400 MHz $CDCl_3$

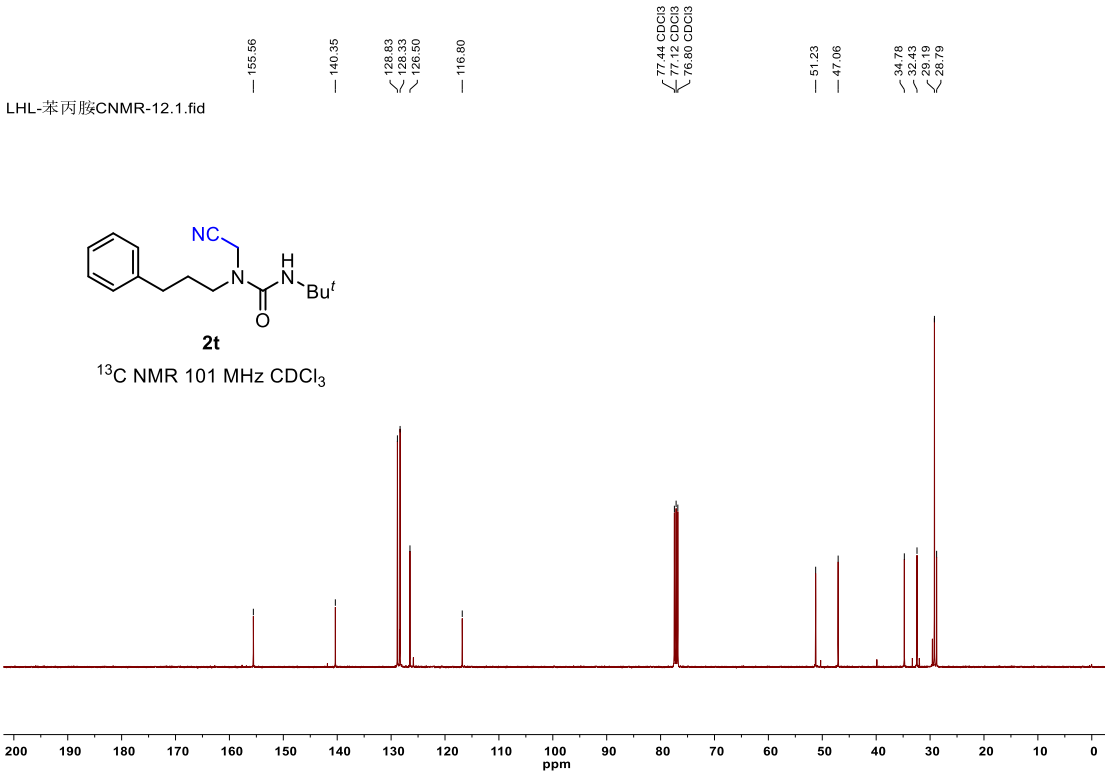
LHL-苄-Ph-NMR-17.2.fid



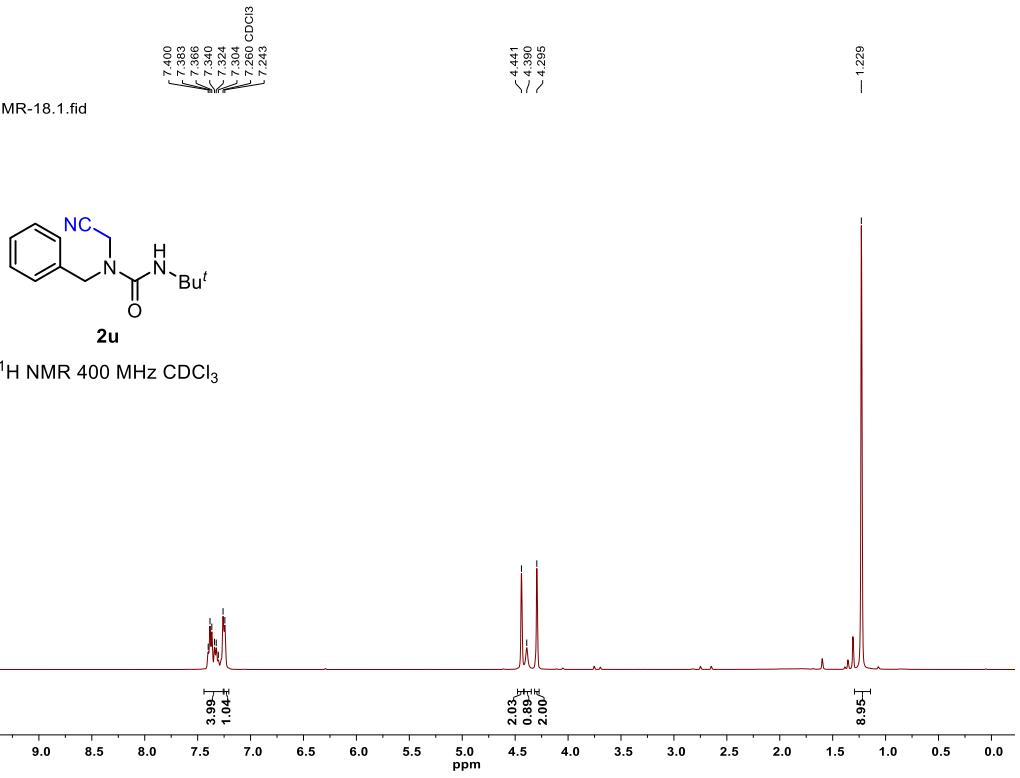
2s

^{13}C NMR 101 MHz $CDCl_3$


7.331
7.313
7.294
7.280
7.260 CDCl3
7.240
7.221
7.199
7.196
7.178
7.152
4.211
4.138
3.188
3.169
3.149
2.682
2.664
2.646
2.010
1.992
1.973
1.954
1.936
1.244
LHL-苯丙胺HNMR-12.1.fid
NC
H
N
N
Bu^t
O
2t
^{1}H NMR 400 MHz CDCl$_3$
2.00
3.08
1.98
0.94
2.04
2.06
2.00
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


155.56
140.35
128.83
128.33
126.50
116.80
77.44 CDCl3
77.12 CDCl3
76.80 CDCl3
51.23
47.06
34.78
32.43
29.19
28.79
LHL-苯丙胺CNMR-12.1.fid
NC
H
N
N
Bu^t
O
2t
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

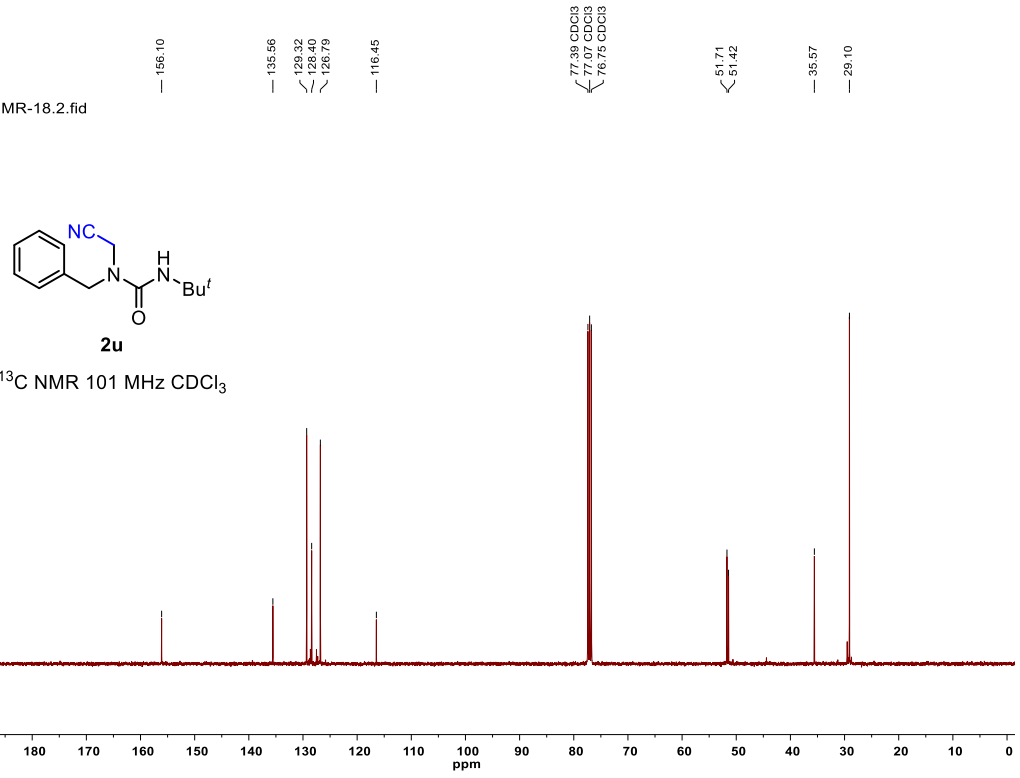
LHL-苄胺NMR-18.1.fid



2u

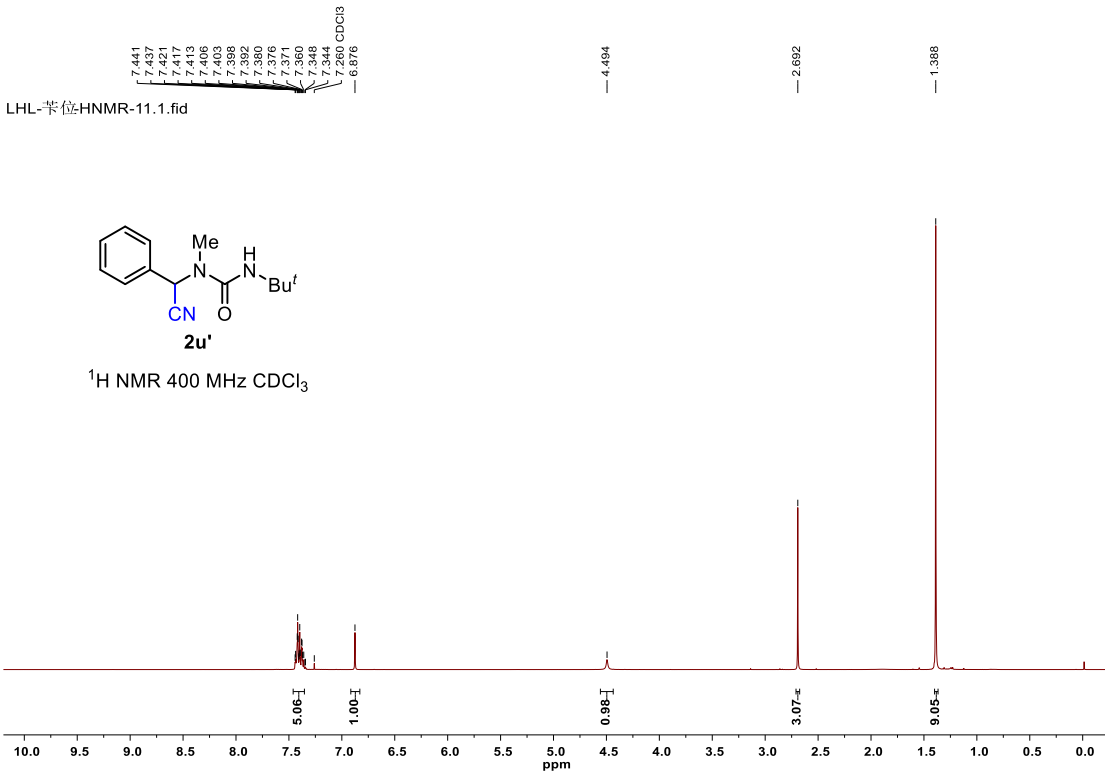
^{1}H NMR 400 MHz $CDCl_3$

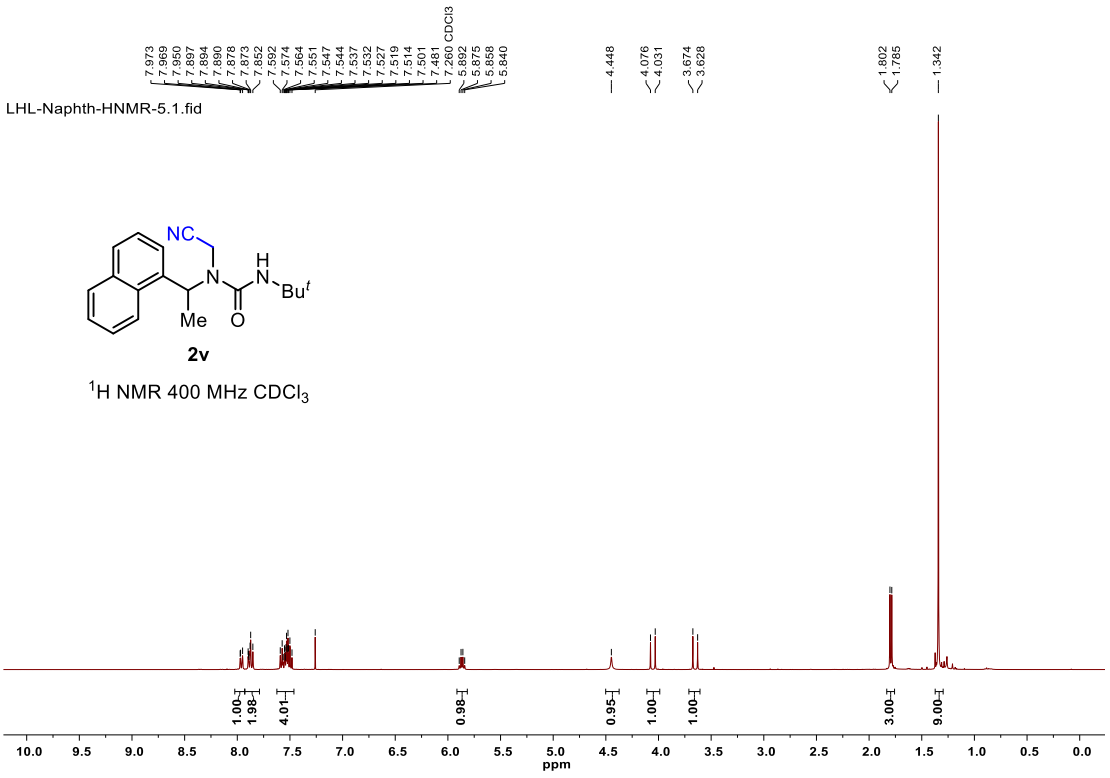
LHL-苄胺NMR-18.2.fid

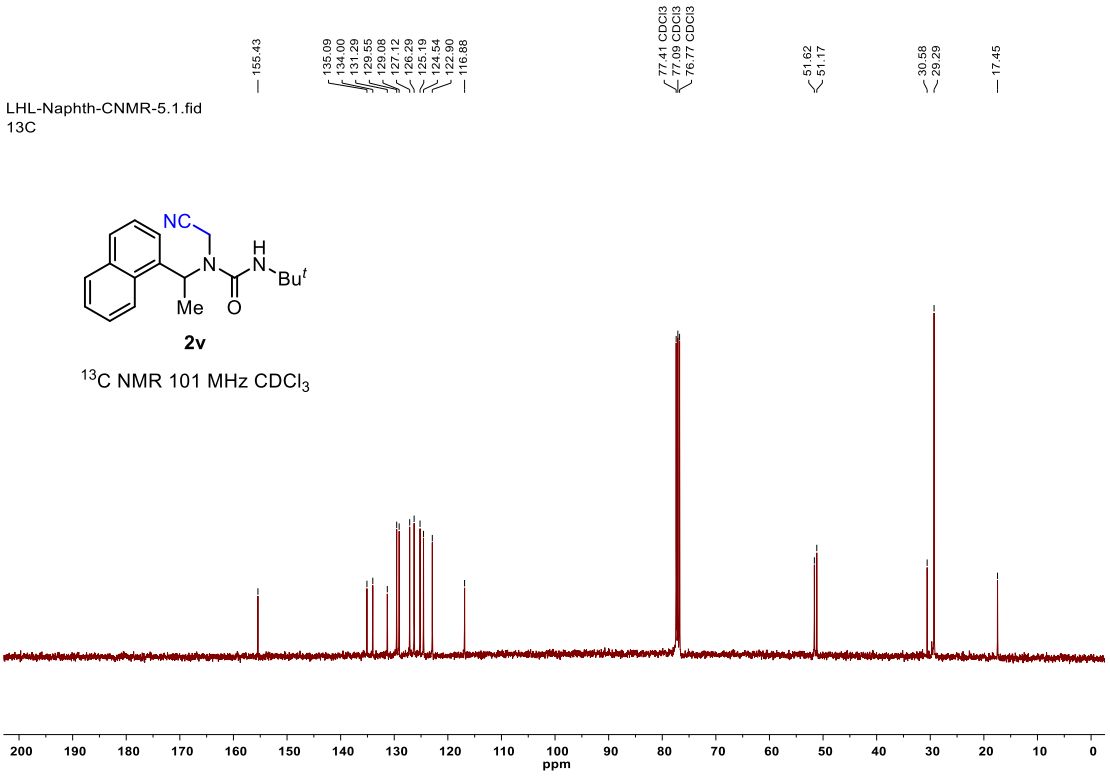


2u

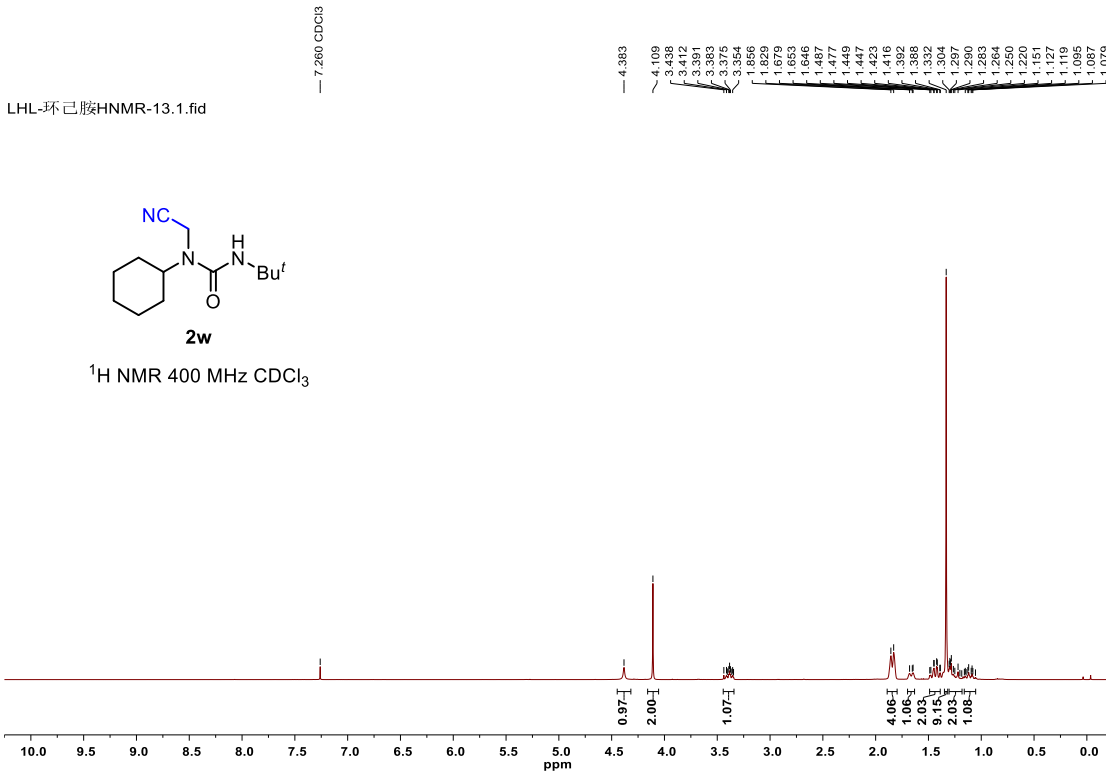
^{13}C NMR 101 MHz $CDCl_3$


7.441
7.437
7.421
7.417
7.413
7.406
7.403
7.398
7.392
7.380
7.376
7.371
7.360
7.348
7.344
7.260 CDCl3
6.876
4.494
2.692
1.388
LHL-苄位HNMR-11.1.fid
Me
N
H
N
Bu^t
CN
O
2u'
^{1}H NMR 400 MHz CDCl$_3$
5.06
1.00
0.98
3.07
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
156.14
133.11
129.07
128.98
127.02
117.04
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
51.46
49.84
30.43
29.30
LHL-苄位CNMR-11.1.fid
Me
N
H
N
Bu^t
CN
O
2u'
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.973
7.969
7.950
7.897
7.894
7.890
7.878
7.873
7.852
7.592
7.574
7.564
7.551
7.547
7.544
7.537
7.532
7.527
7.519
7.514
7.501
7.481
7.260 CDCl3
5.892
5.875
5.858
5.840
4.448
4.076
4.031
3.674
3.628
1.802
1.785
1.342
LHL-Naphth-HNMR-5.1.fid
NC
N
H
N
Bu^t
Me
O
2v
^{1}H NMR 400 MHz CDCl$_3$
1.00
1.98
4.01
0.98
0.95
1.00
1.00
3.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


155.43
135.09
134.00
131.29
129.55
129.08
127.12
126.29
125.19
124.54
122.90
116.88
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
51.62
51.17
30.58
29.29
17.45
LHL-Naphth-CNMR-5.1.fid
13C
NC
N
H
N
Bu^t
Me
O
2v
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

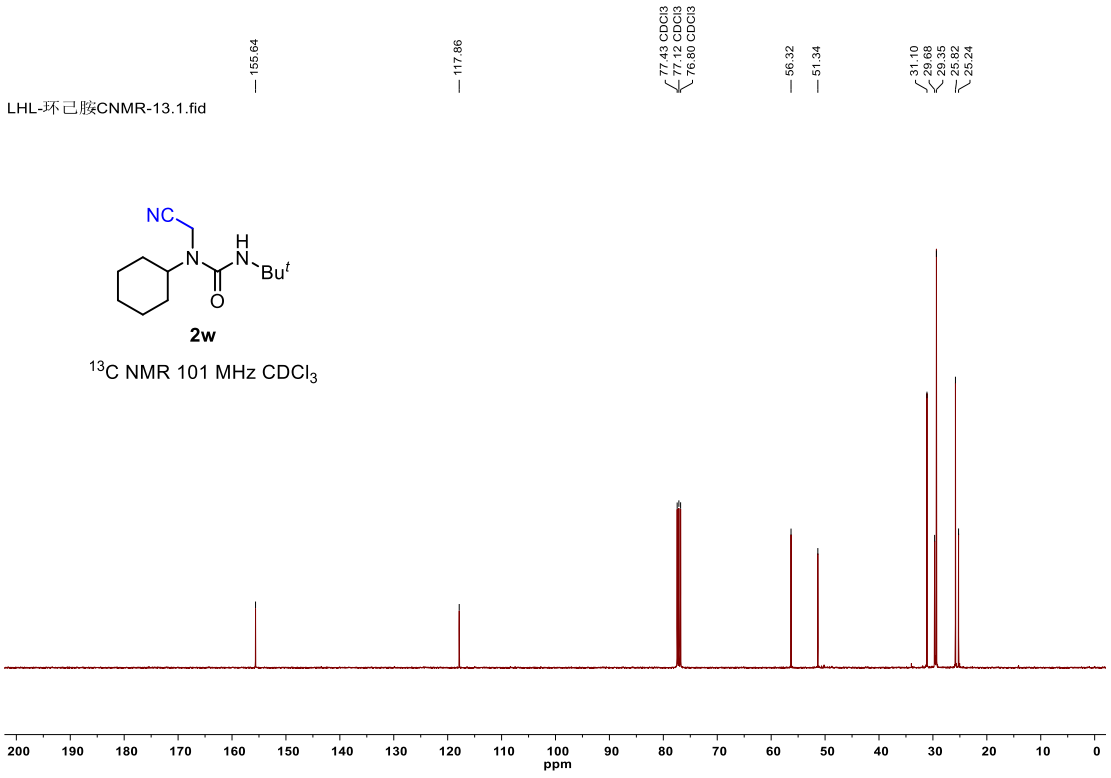
LHL-环己胺HNMR-13.1.fid



2w

^{1}H NMR 400 MHz $CDCl_3$

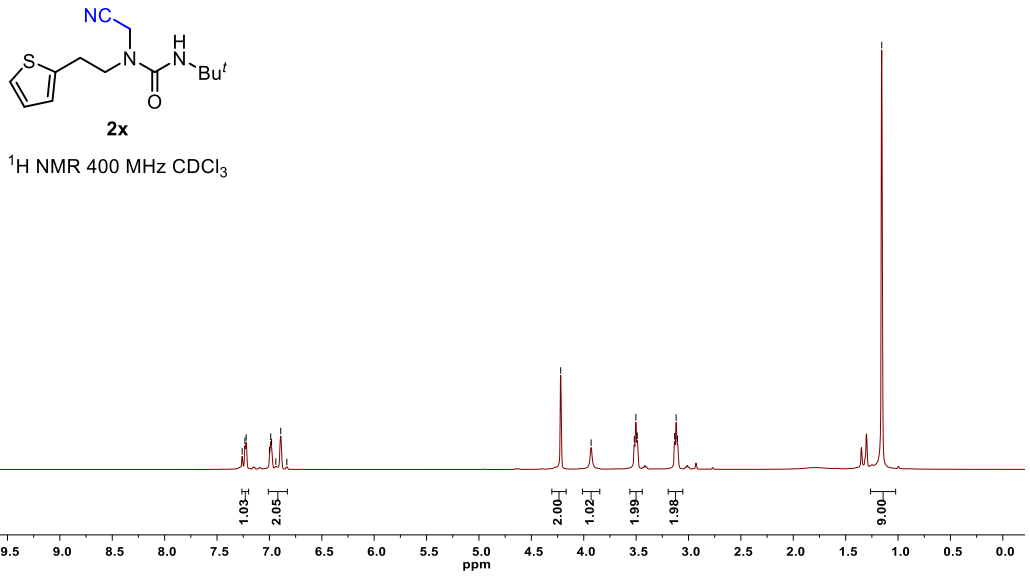
LHL-环己胺CNMR-13.1.fid



2w

^{13}C NMR 101 MHz $CDCl_3$

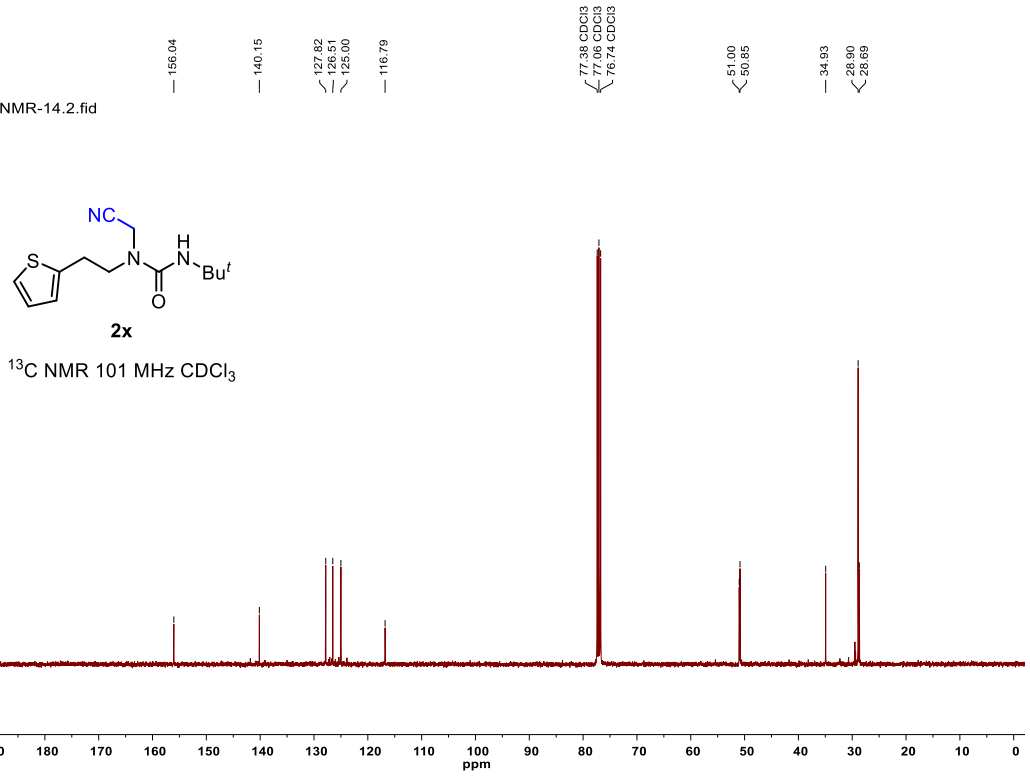
LHL-噻吩NMR-14.1.fid



2x

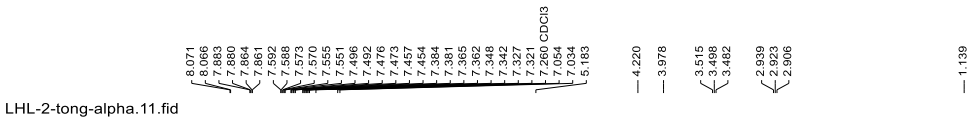
^{1}H NMR 400 MHz $CDCl_3$

LHL-噻吩NMR-14.2.fid

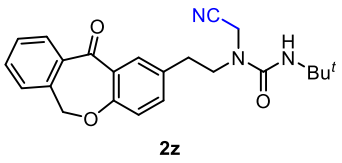


2x

^{13}C NMR 101 MHz $CDCl_3$

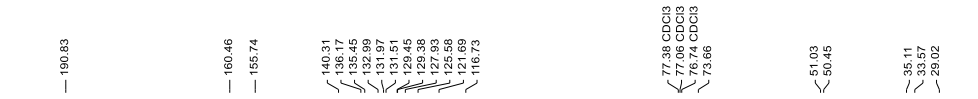


LHL-2-tong-alpha.11.fid

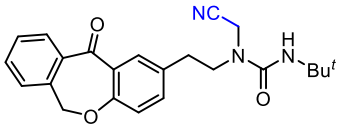


2z

^{1}H NMR 400 MHz $CDCl_3$



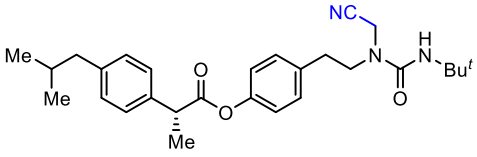
LHL-tong-alpha-CNMR.1.fid



2z

^{13}C NMR 101 MHz $CDCl_3$

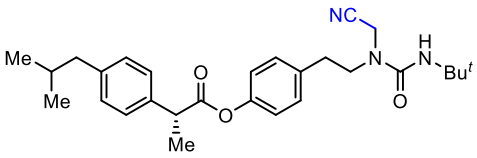
LHL-4-buluofen-alpha.11.fid



2aa

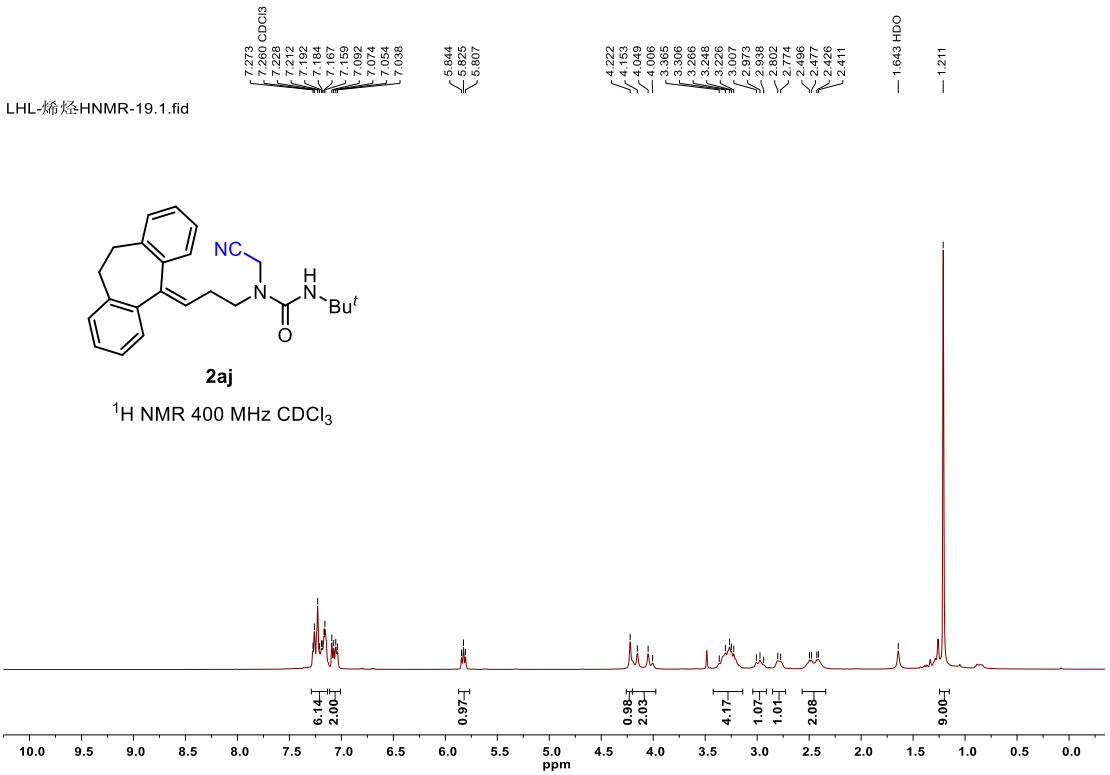
^{1}H NMR 400 MHz $CDCl_3$

LHL-Ibuprofen-alpha-CNMR.1.fid



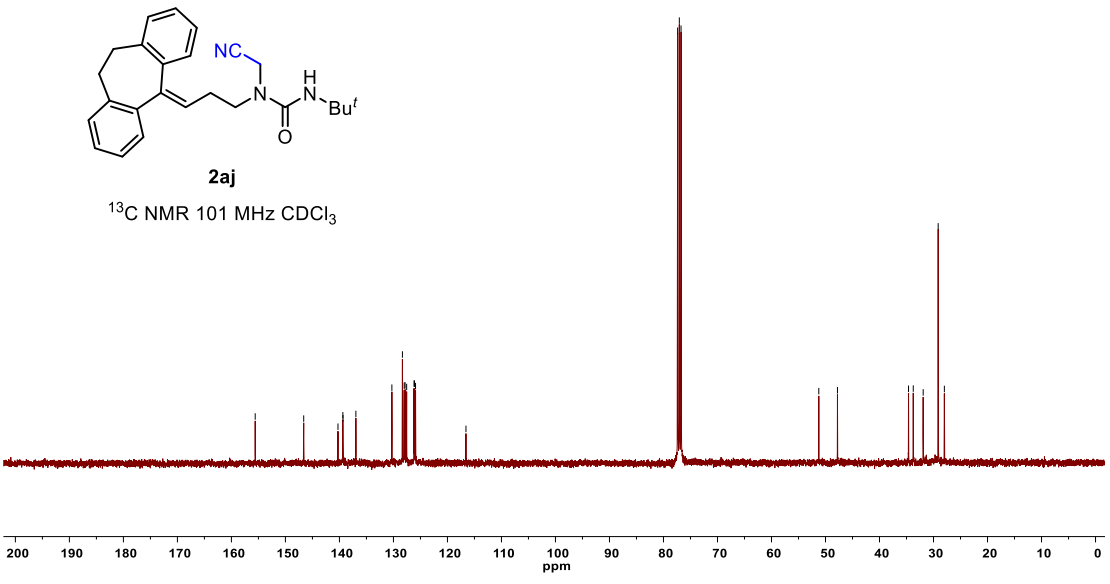
2aa

^{13}C NMR 101 MHz $CDCl_3$



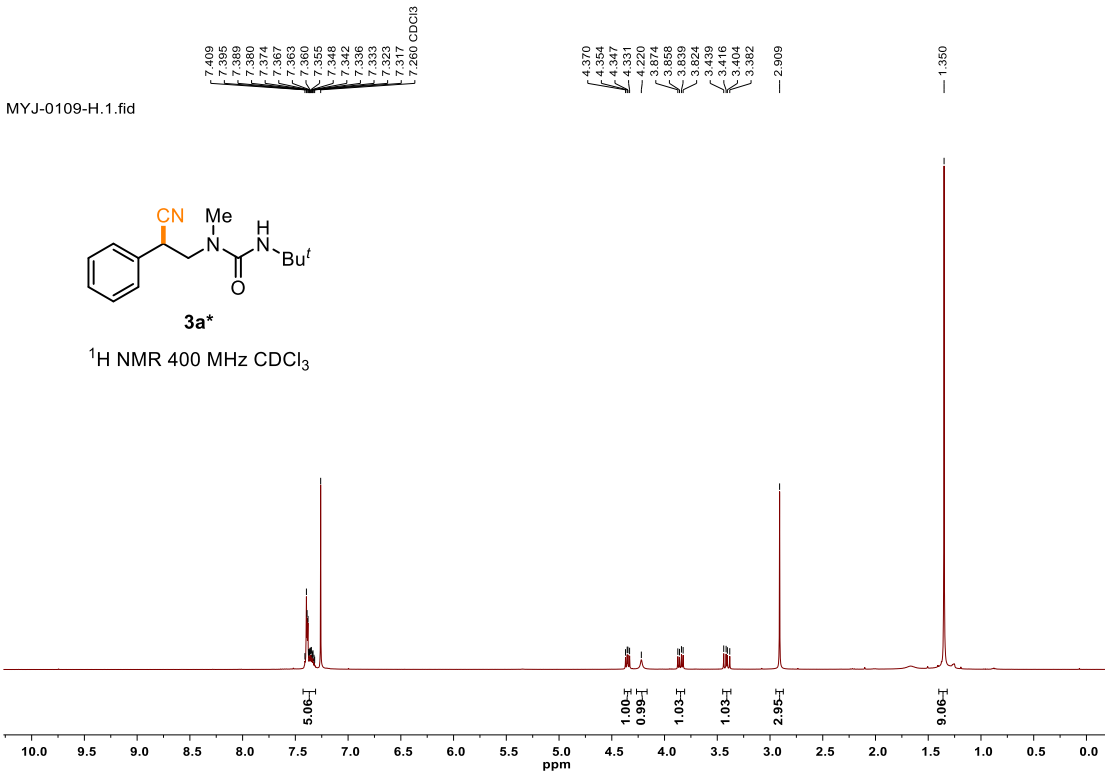
2aj

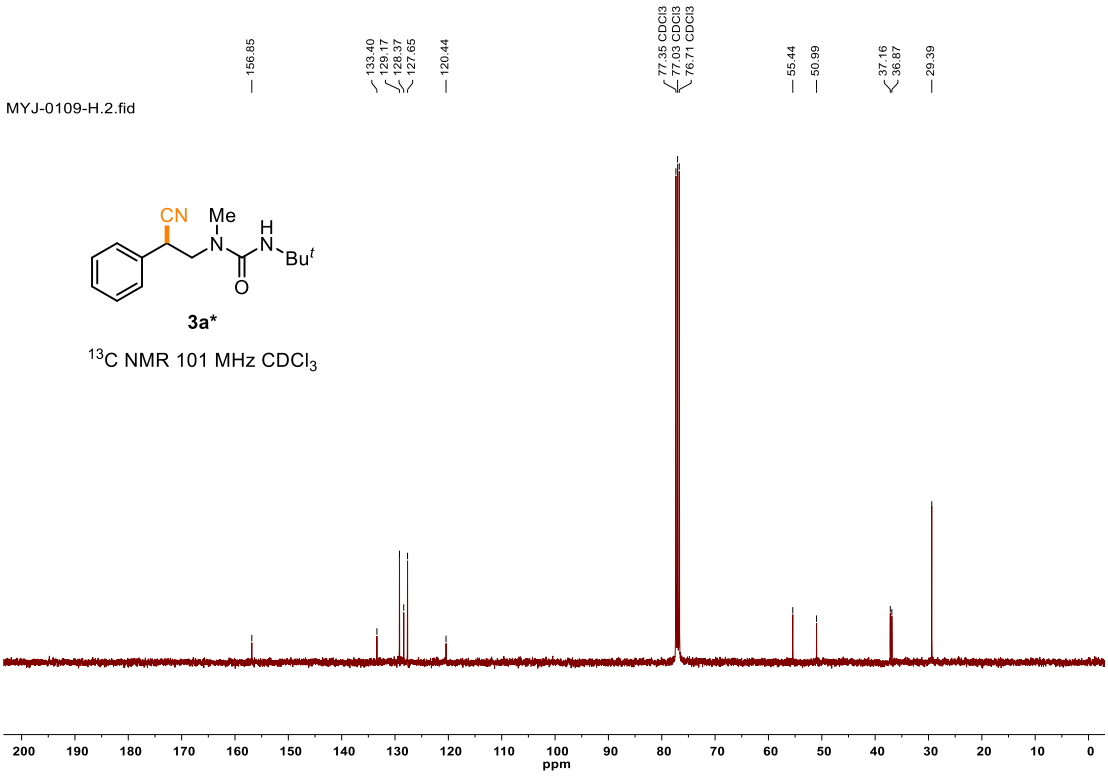
^{1}H NMR 400 MHz $CDCl_3$



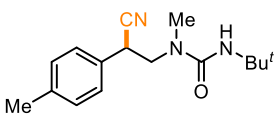
2aj

^{13}C NMR 101 MHz $CDCl_3$


MYJ-0109-H.1.fid
7.409
7.395
7.389
7.380
7.374
7.367
7.363
7.360
7.355
7.348
7.342
7.336
7.333
7.323
7.317
7.260 CDCl3
4.370
4.354
4.347
4.331
4.220
3.874
3.858
3.839
3.824
3.439
3.416
3.404
3.382
2.909
1.350
CN
Me
N
H
N
Bu^t
O
3a*
^{1}H NMR 400 MHz CDCl$_3$
5.06
1.00
0.99
1.03
1.03
2.95
9.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


MYJ-0109-H.2.fid
156.85
133.40
129.17
128.37
127.65
120.44
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
55.44
50.99
37.16
36.87
29.39
CN
Me
N
H
N
Bu^t
O
3a*
^{13}C NMR 101 MHz CDCl$_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

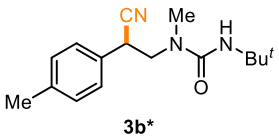
MYJ-0109-p-Me.1.fid



3b*

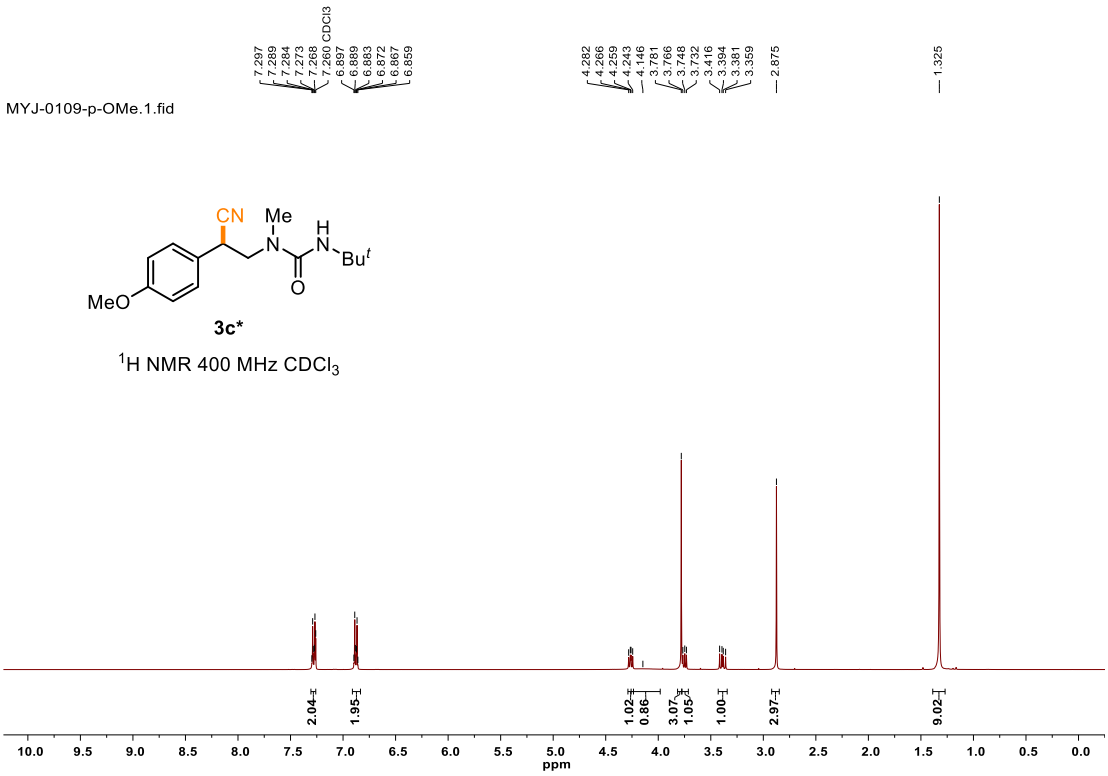
^{1}H NMR 400 MHz $CDCl_3$

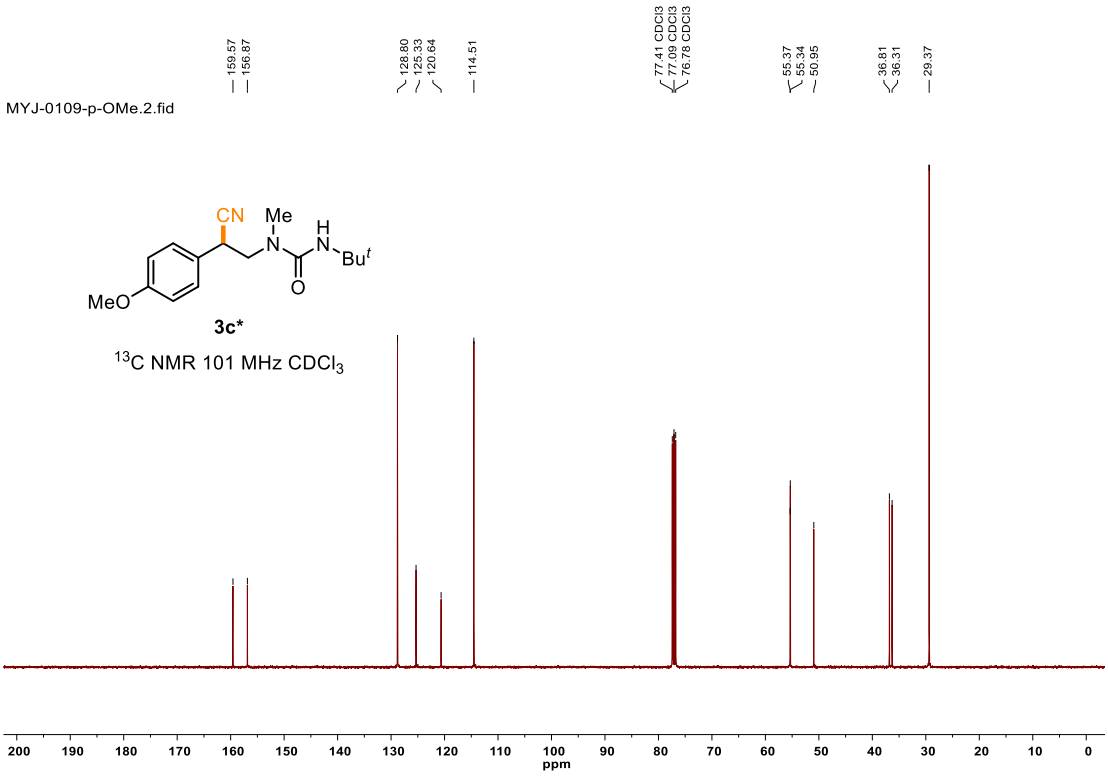
MYJ-0109-p-Me.2.fid

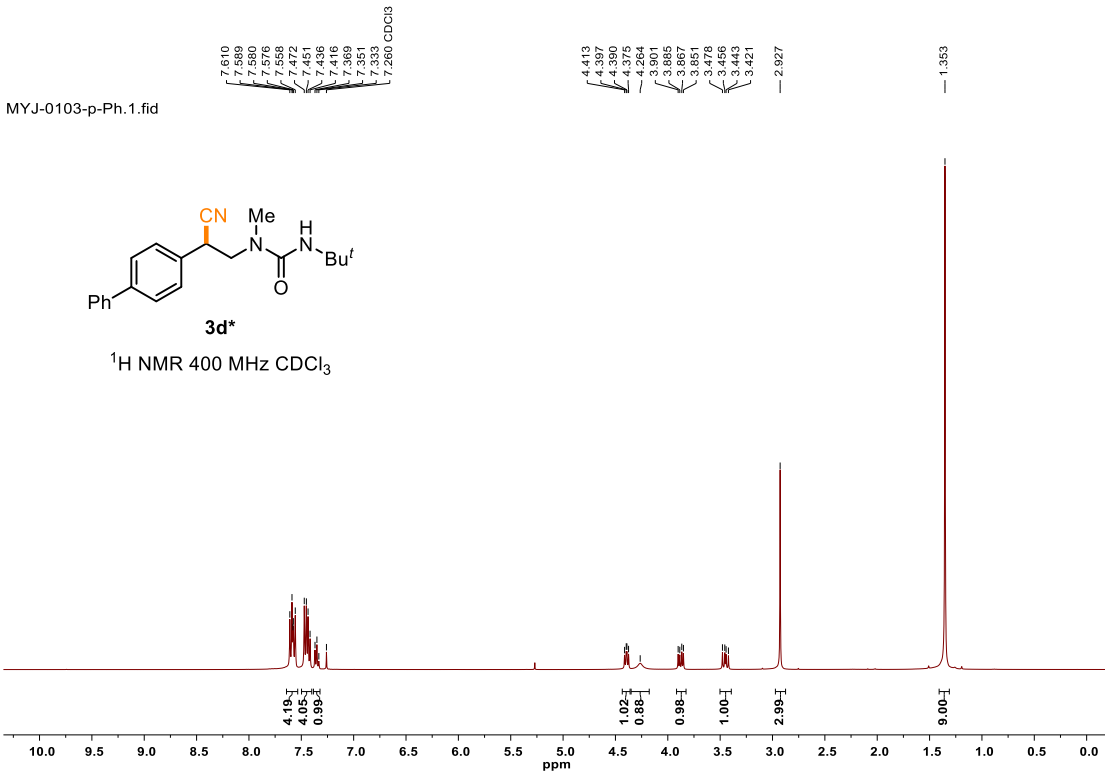


3b*

^{13}C NMR 101 MHz $CDCl_3$


7.297
7.289
7.284
7.273
7.268
7.260 CDCl3
6.897
6.889
6.883
6.872
6.867
6.859
4.282
4.266
4.259
4.243
4.146
3.781
3.766
3.748
3.732
3.416
3.394
3.381
3.359
2.875
1.325
MYJ-0109-p-OMe.1.fid
CN
Me
N
H
N
Bu^t
MeO
O
3c*
^{1}H NMR 400 MHz CDCl$_3$
2.04
1.95
1.02
0.86
3.07
1.05
1.00
2.97
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


159.57
156.87
128.80
125.33
120.64
114.51
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
55.37
55.34
50.95
36.81
36.31
29.37
MYJ-0109-p-OMe.2.fid
CN
Me
N
H
N
Bu^t
MeO
O
3c*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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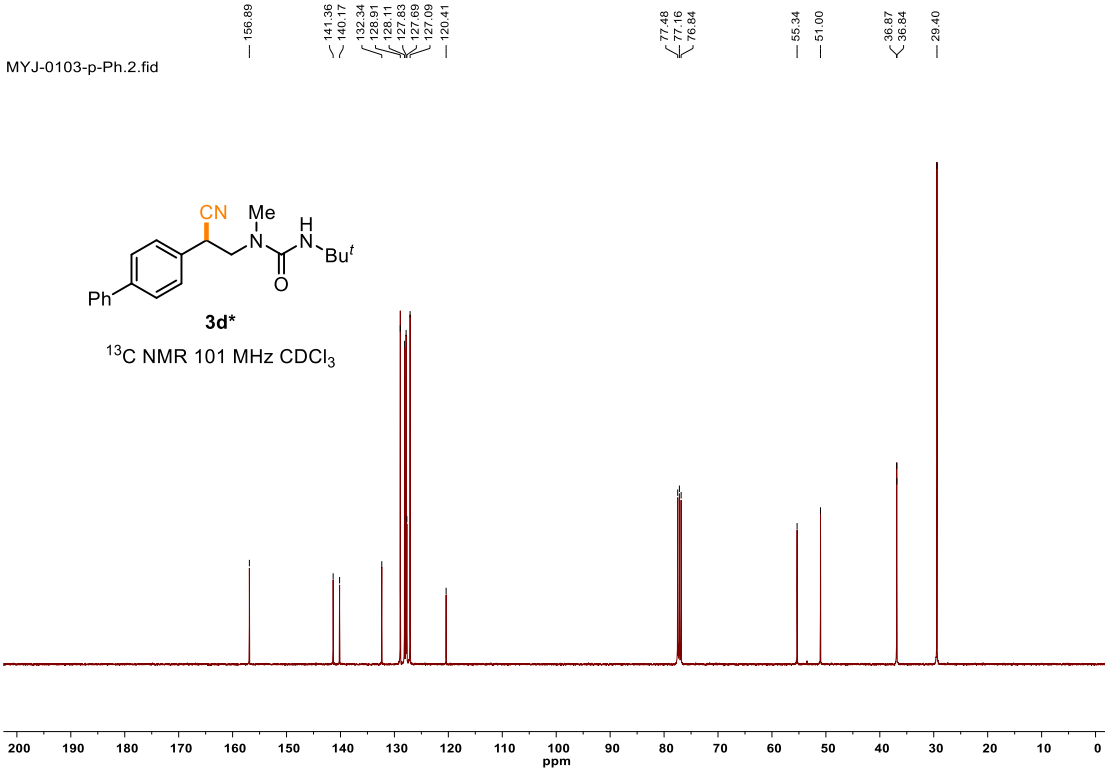
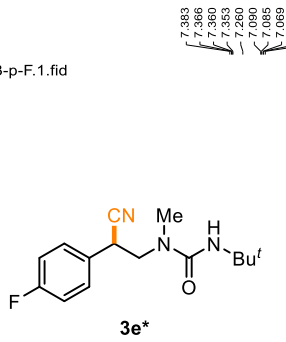
7.610
7.589
7.580
7.576
7.558
7.472
7.451
7.436
7.416
7.369
7.351
7.333
7.260 CDCl3
4.413
4.397
4.390
4.375
4.264
3.901
3.885
3.867
3.851
3.478
3.456
3.443
3.421
2.927
1.353
CN
Me
H
N
N
Bu^t
Ph
O
3d*
^{1}H NMR 400 MHz CDCl$_3$
4.19
4.05
0.99
1.02
0.88
0.98
1.00
2.99
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


MYJ-0103-p-Ph.2.fid
156.89
141.36
140.17
132.34
128.91
128.11
127.83
127.69
127.09
120.41
77.48
77.16
76.84
55.34
51.00
36.87
36.84
29.40
CN
Me
H
N
N
Bu^t
Ph
O
3d*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

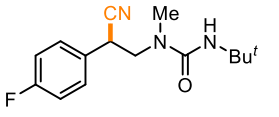
MYJ-0103-p-F.1.fid



3e*

^{1}H NMR 400 MHz $CDCl_3$

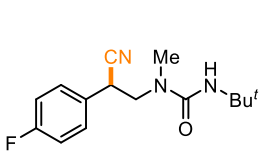
MYJ-0103-p-F.2.fid



3e*

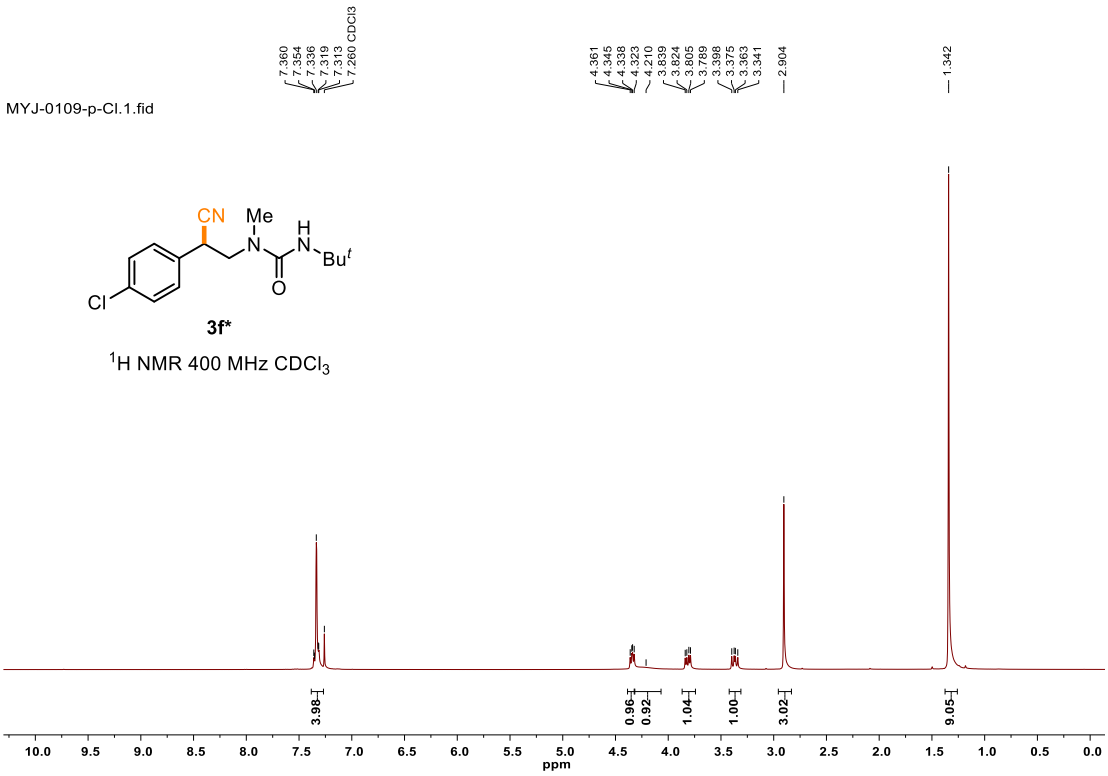
^{13}C NMR 101 MHz $CDCl_3$

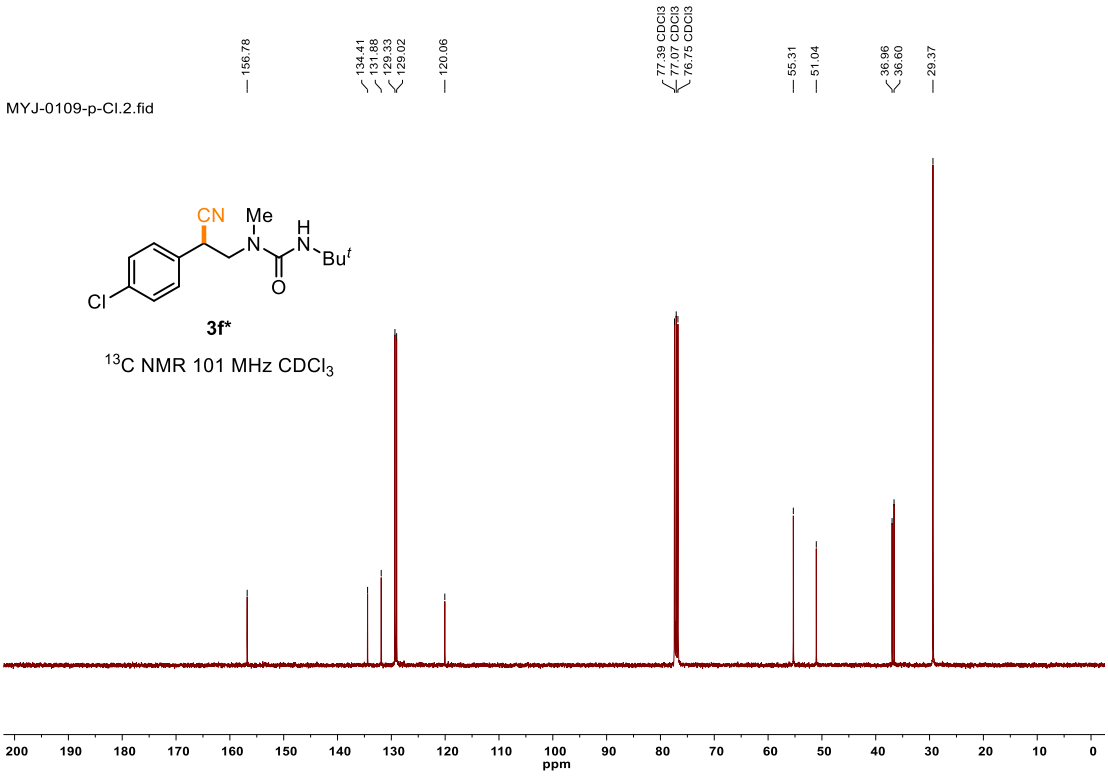
MYJ-0103-p-F.4.fid

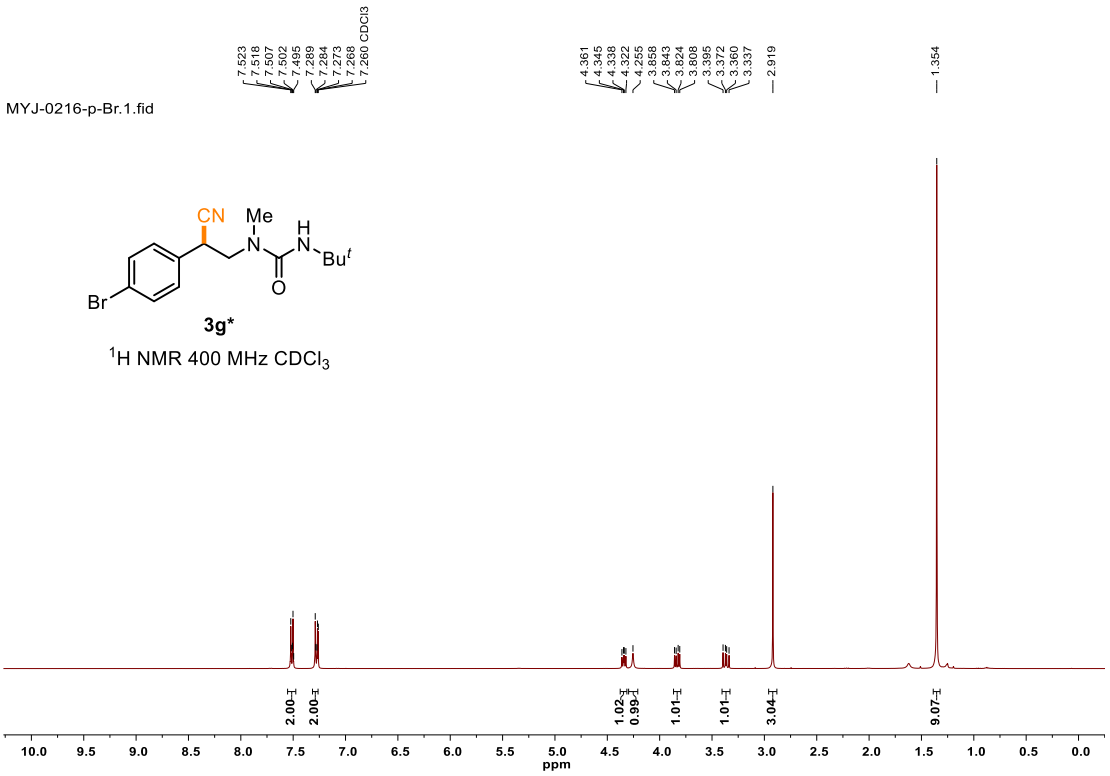


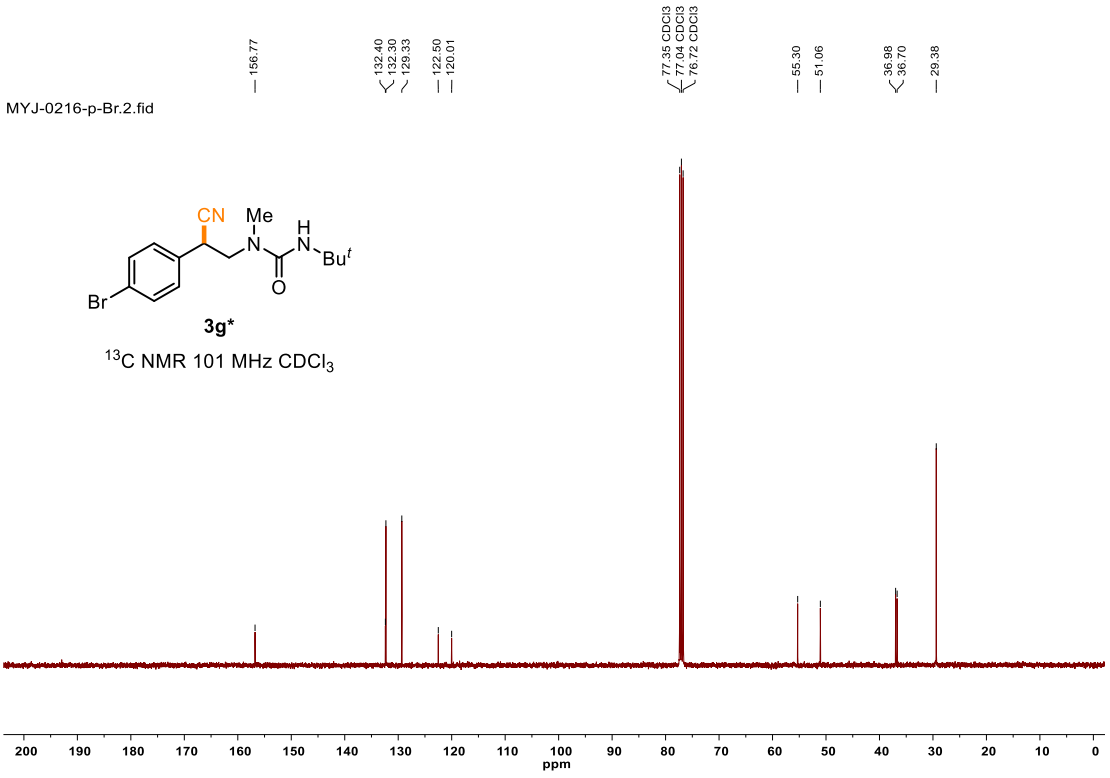
3e*

^{19}F NMR 376 MHz $CDCl_3$

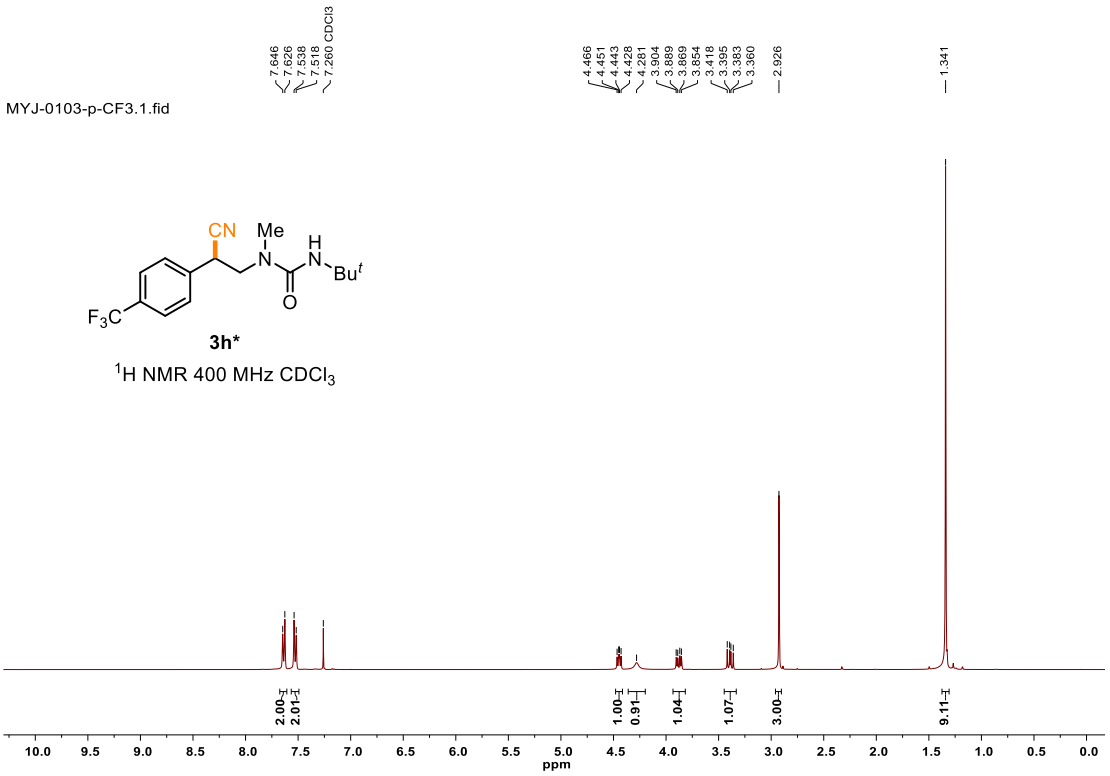

7.360
7.354
7.336
7.319
7.313
7.260 CDCl3
4.361
4.345
4.338
4.323
4.210
3.839
3.824
3.805
3.789
3.398
3.375
3.363
3.341
2.904
1.342
MYJ-0109-p-Cl.1.fid
CN
Me
N
H
N
Bu^t
Cl
O
3f*
^{1}H NMR 400 MHz $CDCl_3$
3.98
0.96
0.92
1.04
1.00
3.02
9.05
ppm


156.78
134.41
131.88
129.33
129.02
120.06
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
55.31
51.04
36.96
36.60
29.37
MYJ-0109-p-Cl.2.fid
CN
Me
N
H
N
Bu^t
Cl
O
3f*
^{13}C NMR 101 MHz $CDCl_3$
ppm


7.523
7.518
7.507
7.502
7.495
7.289
7.284
7.273
7.268
7.260 CDCl3
4.361
4.345
4.338
4.322
4.255
3.858
3.843
3.824
3.808
3.395
3.372
3.360
3.337
2.919
1.354
MYJ-0216-p-Br.1.fid
CN
Me
N
H
N
Bu^t
Br
O
3g*
^{1}H NMR 400 MHz CDCl$_3$
2.00
2.00
1.02
0.99
1.01
1.01
3.04
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


156.77
132.40
132.30
129.33
122.50
120.01
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
55.30
51.06
36.98
36.70
29.38
MYJ-0216-p-Br.2.fid
CN
Me
N
H
N
Bu^t
Br
O
3g*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

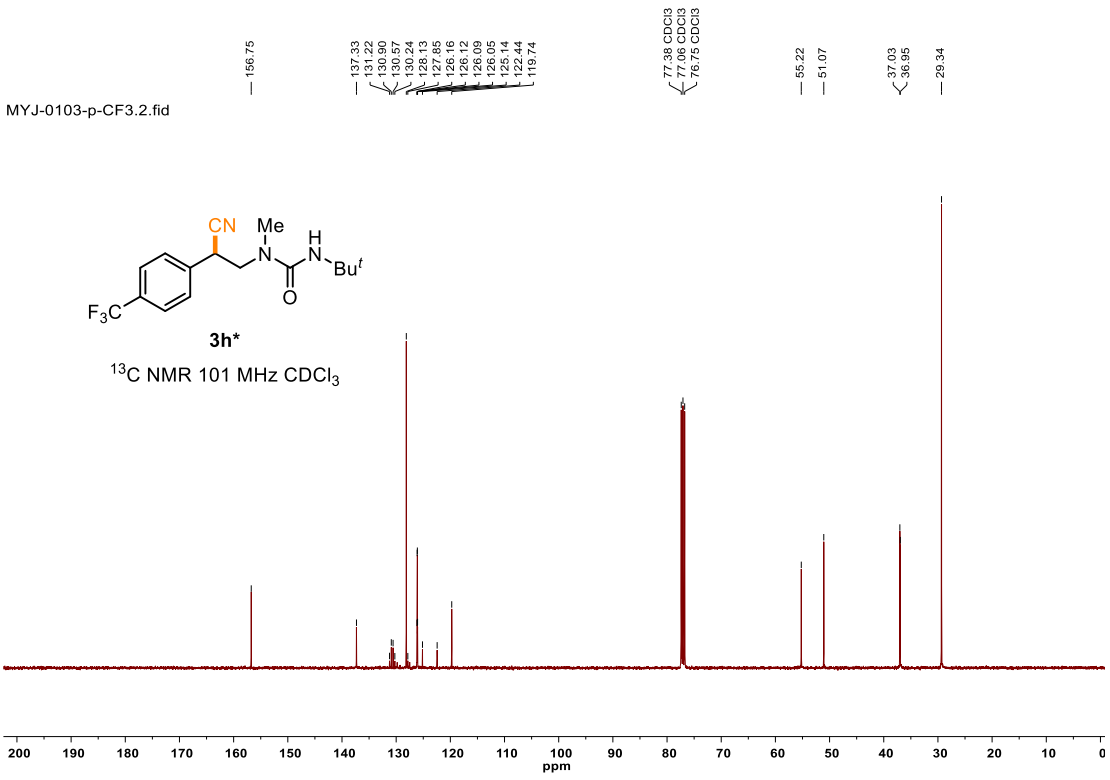
MYJ-0103-p-CF3.1.fid



3h*

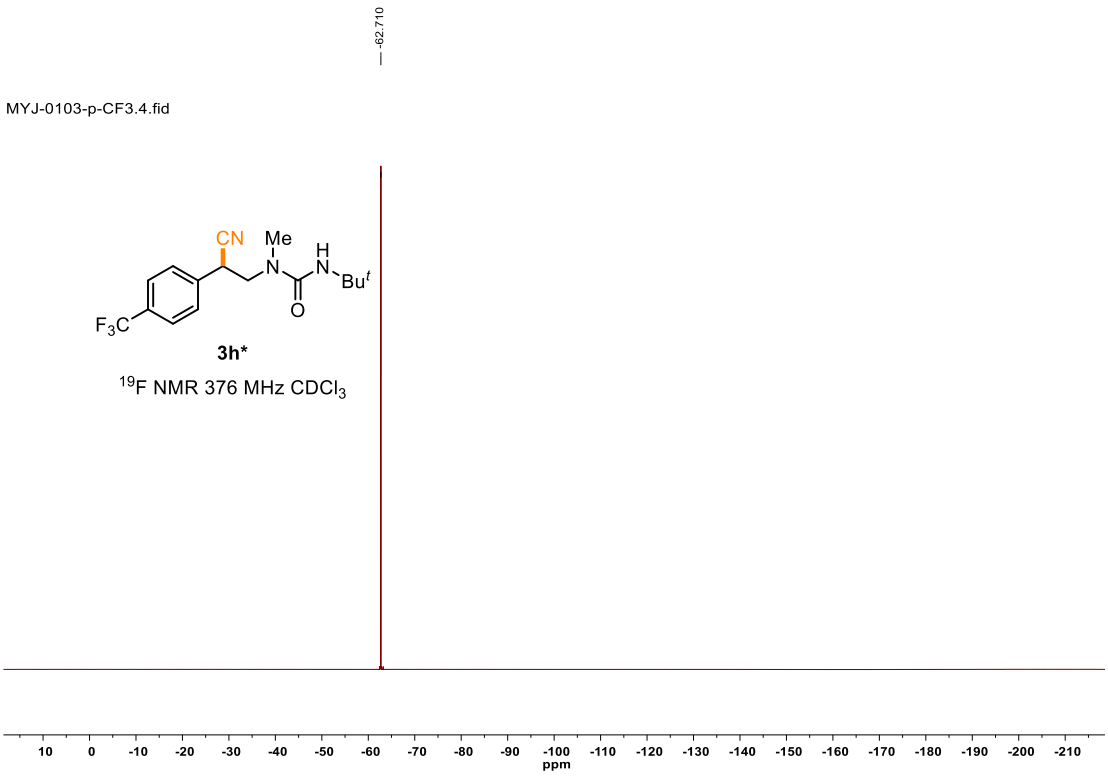
^{1}H NMR 400 MHz $CDCl_3$

MYJ-0103-p-CF3.2.fid



3h*

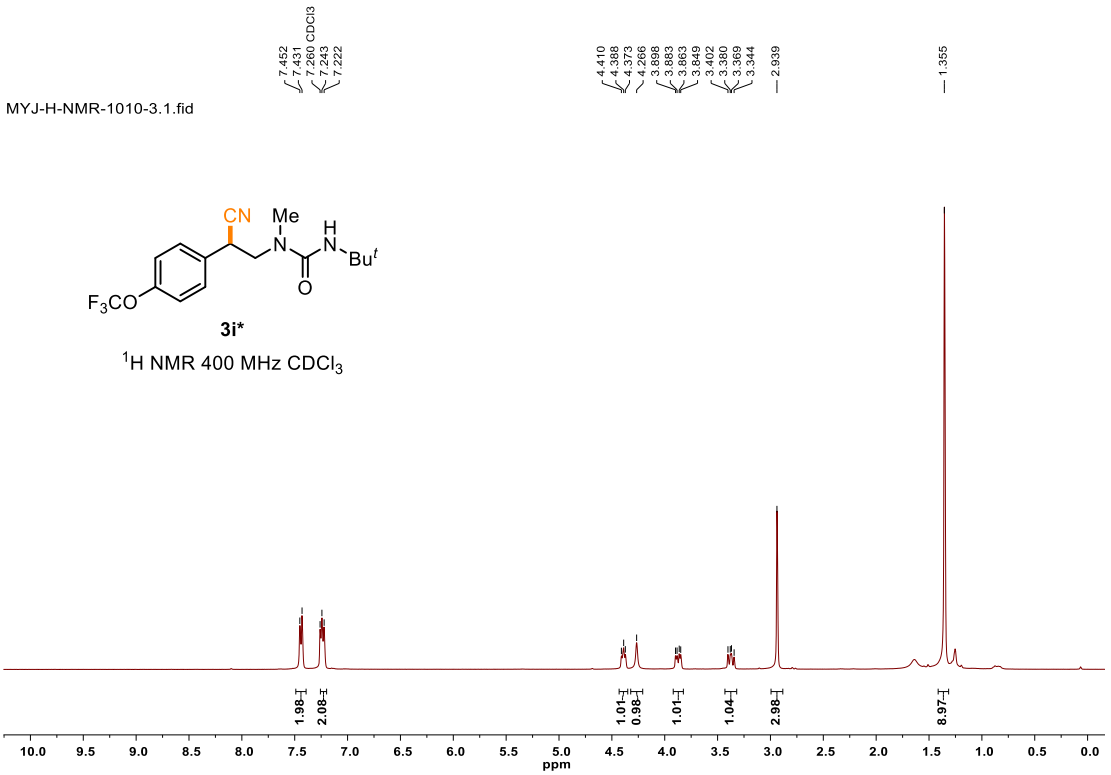
^{13}C NMR 101 MHz $CDCl_3$



3h*

^{19}F NMR 376 MHz $CDCl_3$

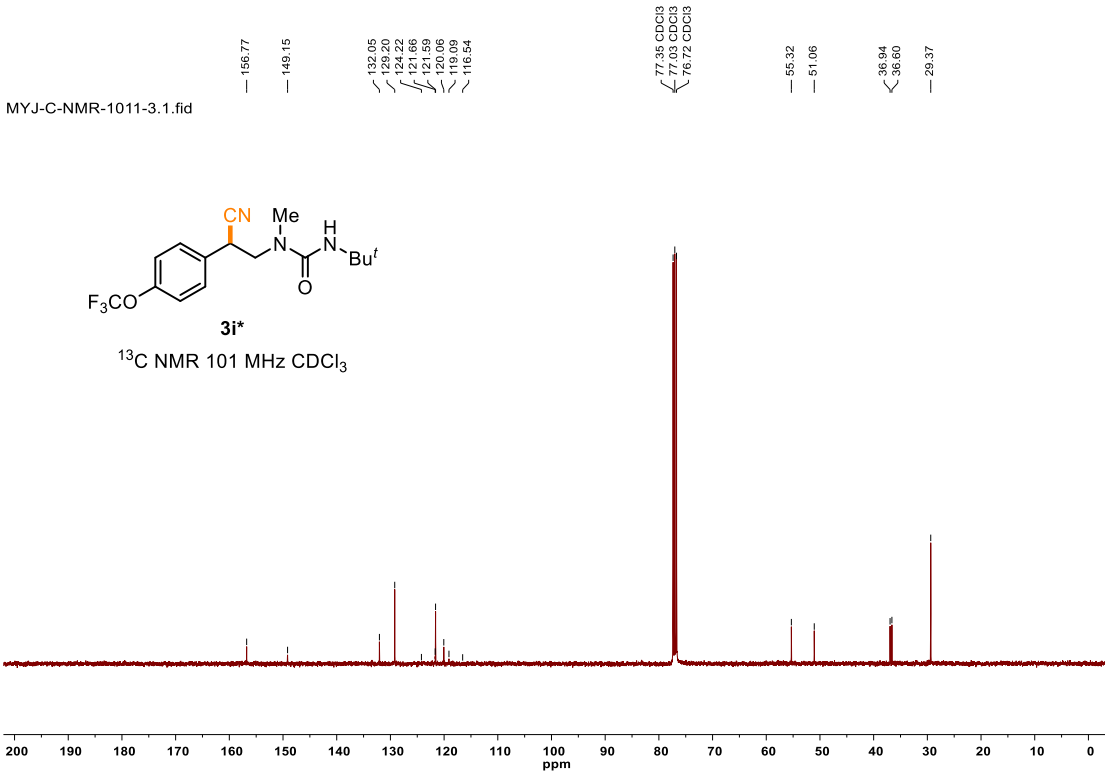
MYJ-H-NMR-1010-3.1.fid



3i*

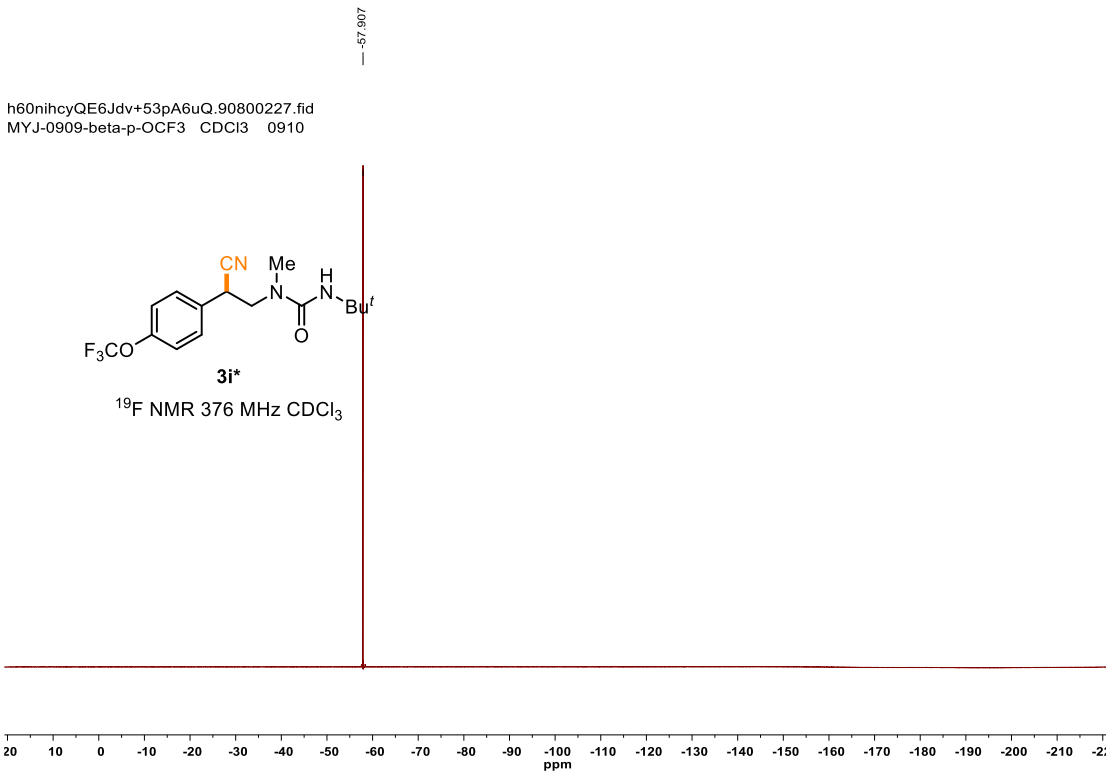
^{1}H NMR 400 MHz $CDCl_3$

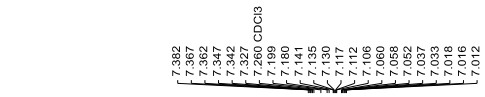
MYJ-C-NMR-1011-3.1.fid



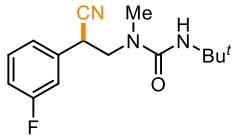
3i*

^{13}C NMR 101 MHz $CDCl_3$


-57.907
h60nihcyQE6Jdv+53pA6uQ.90800227.fid
MYJ-0909-beta-p-OCF3 CDCl3 0910
CN
Me
H
N
N
Bu^t
F_3CO
O
3i*
^{19}F NMR 376 MHz $CDCl_3$
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm



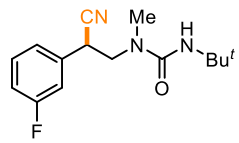
MYJ-0216-m-F.1.fid



3j*

^{1}H NMR 400 MHz $CDCl_3$

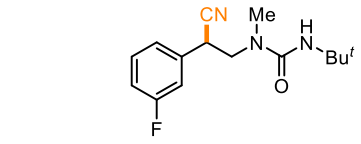
MYJ-0216-m-F.2.fid



3j*

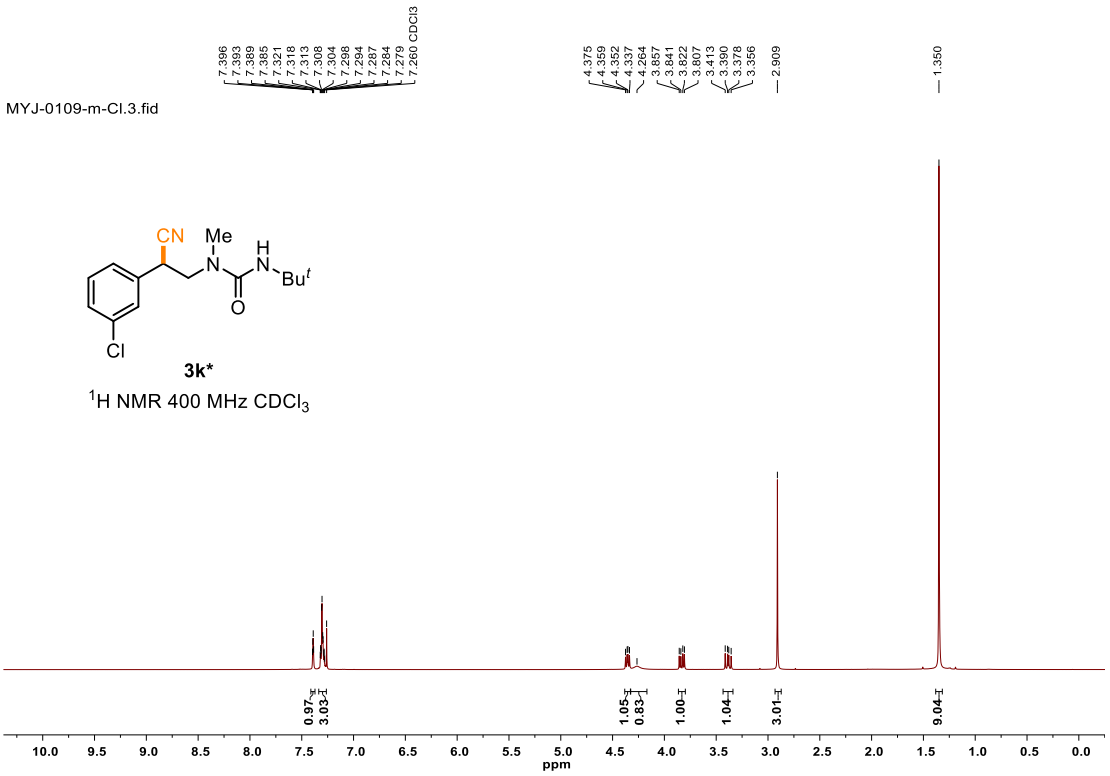
^{13}C NMR 101 MHz $CDCl_3$

MYJ-0216-m-F.3.fid



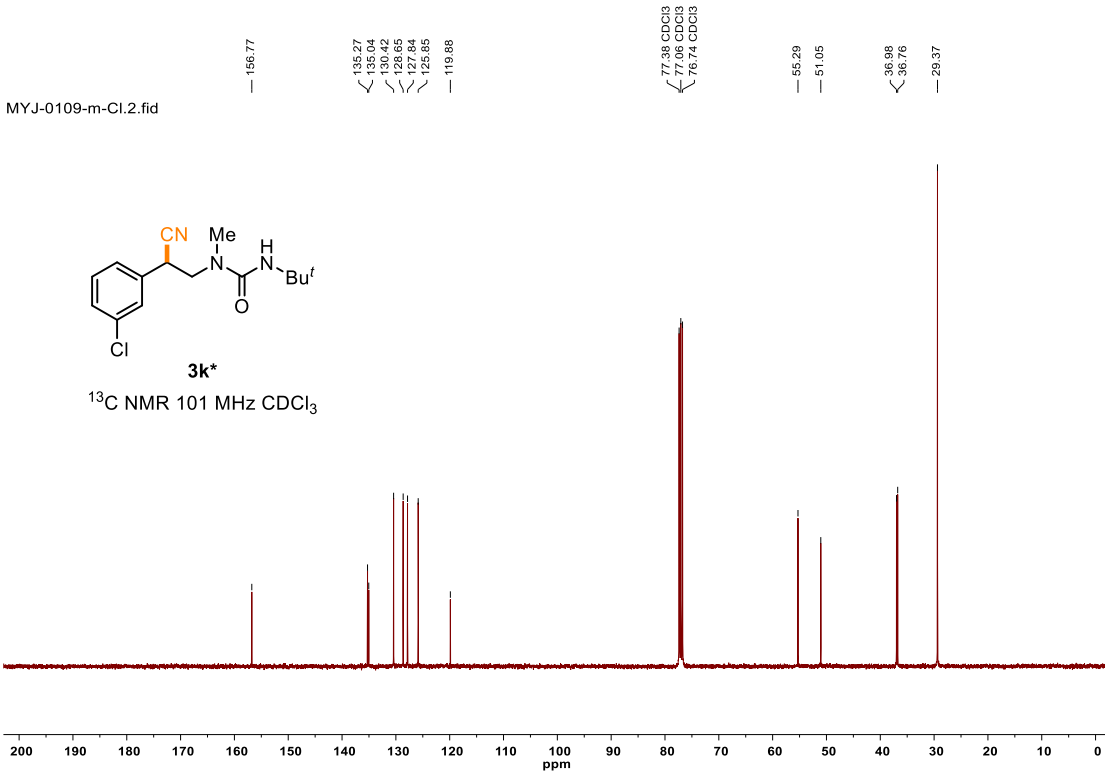
3j*

^{19}F NMR 376 MHz $CDCl_3$



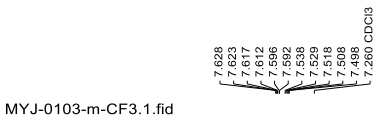
3k*

^{1}H NMR 400 MHz $CDCl_3$

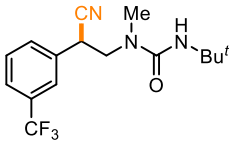


3k*

^{13}C NMR 101 MHz $CDCl_3$



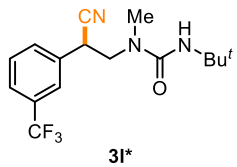
MYJ-0103-m-CF3.1.fid



3l*

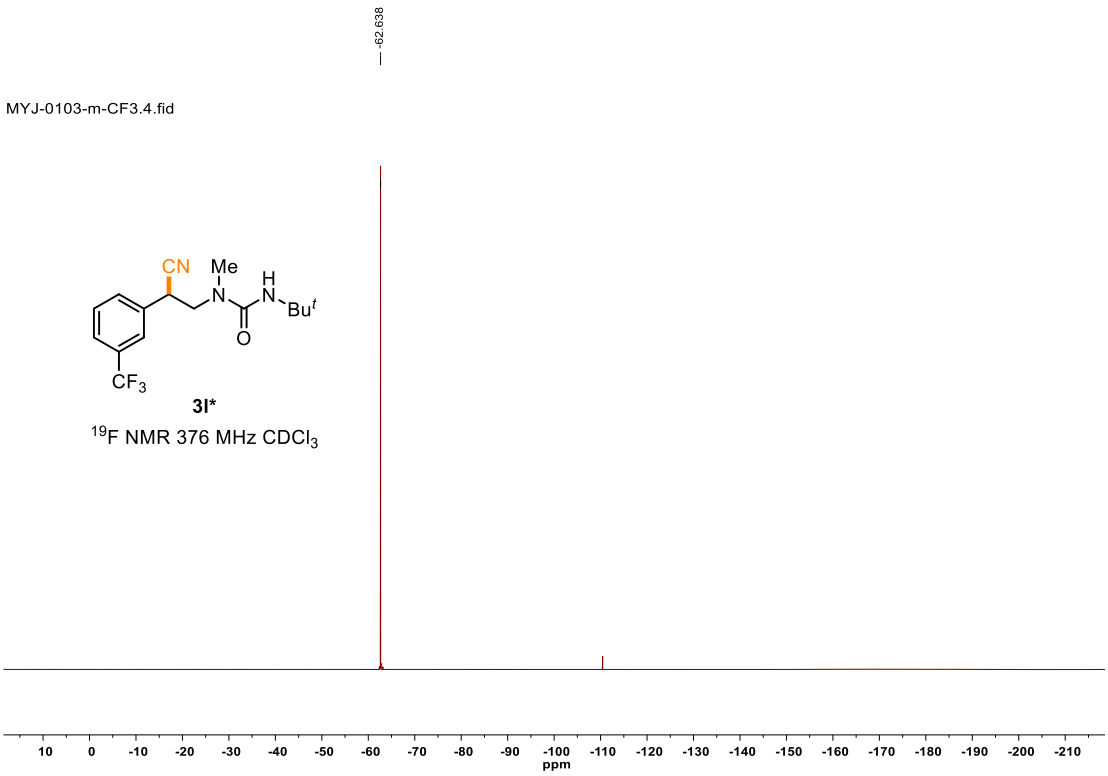
^{1}H NMR 400 MHz $CDCl_3$

MYJ-0103-m-CF3.2.fid



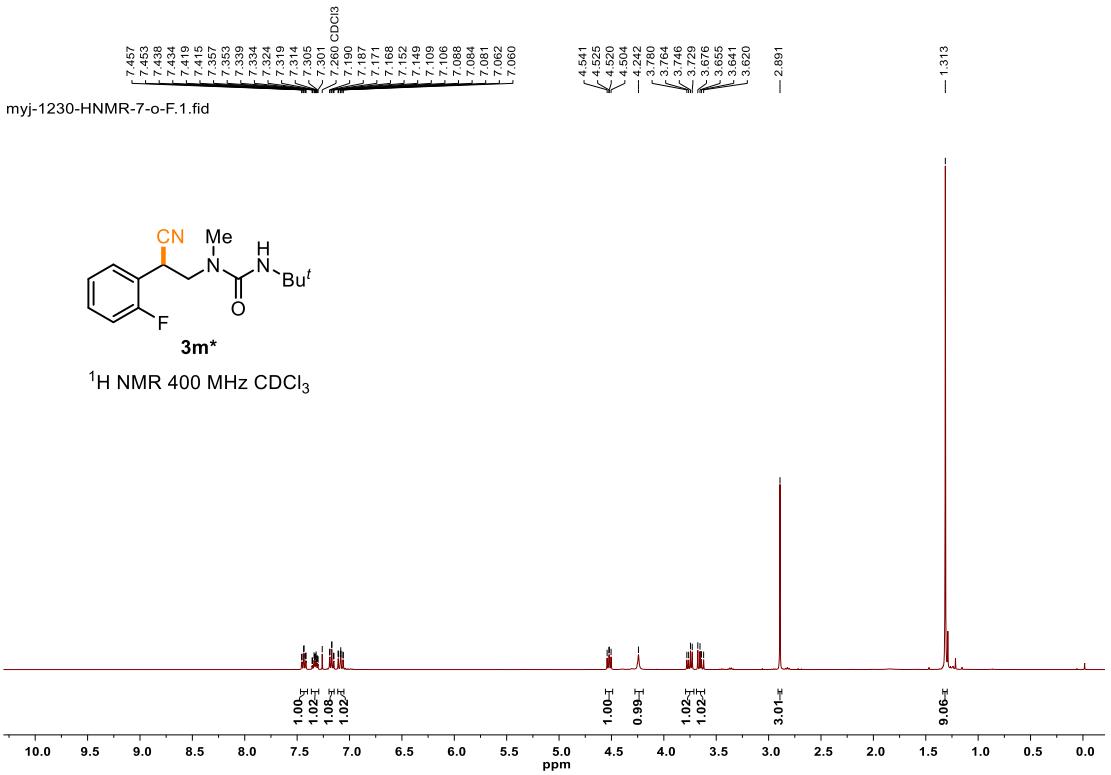
3l*

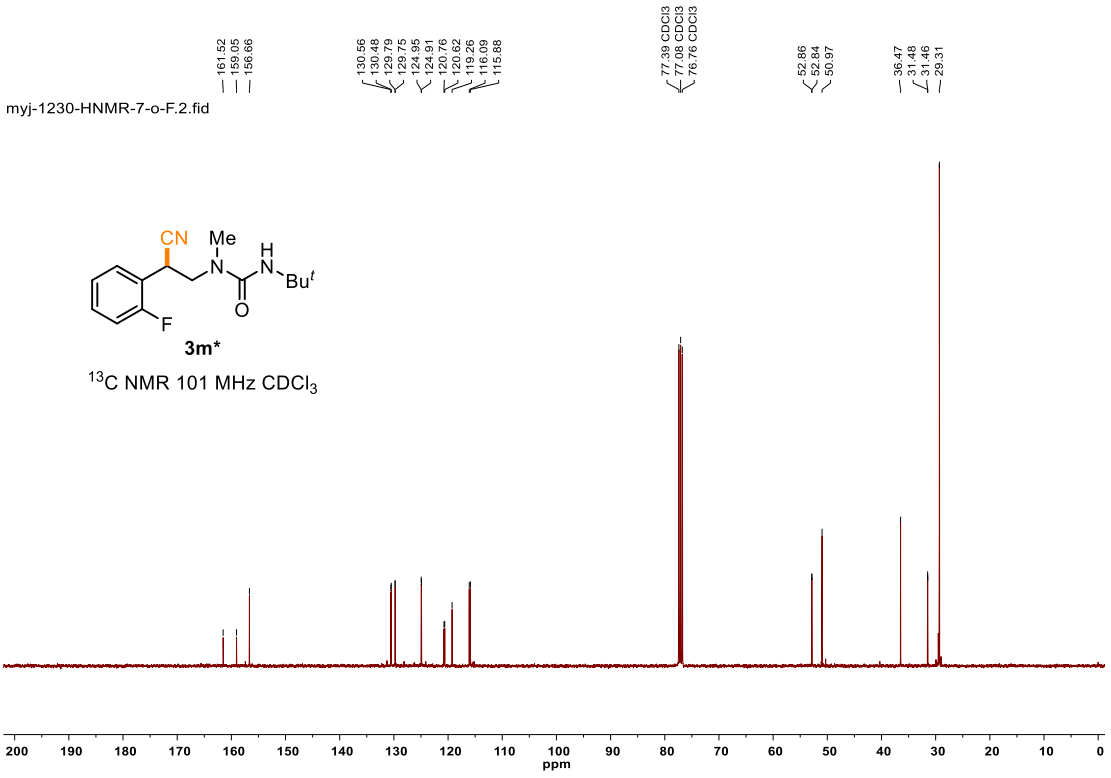
^{13}C NMR 101 MHz $CDCl_3$



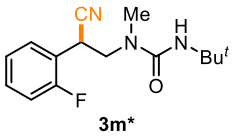
3l*

^{19}F NMR 376 MHz $CDCl_3$


7.457
7.453
7.438
7.434
7.419
7.415
7.357
7.353
7.339
7.334
7.324
7.319
7.314
7.305
7.301
7.260 CDCl3
7.190
7.187
7.171
7.168
7.152
7.149
7.109
7.106
7.088
7.084
7.081
7.062
7.060
4.541
4.525
4.520
4.504
4.242
3.780
3.764
3.746
3.729
3.676
3.655
3.641
3.620
2.891
1.313
myj-1230-HNMR-7-o-F.1.fid
CN
Me
N
H
N
Bu^t
O
F
3m*
^{1}H NMR 400 MHz CDCl$_3$
1.00
1.02
1.08
1.02
1.00
0.99
1.02
1.02
3.01
9.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


161.52
159.05
156.66
130.56
130.48
129.79
129.75
124.95
124.91
120.76
120.62
119.26
116.09
115.88
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
52.86
52.84
50.97
36.47
31.48
31.46
29.31
myj-1230-HNMR-7-o-F.2.fid
CN
Me
N
H
N
Bu^t
O
F
3m*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

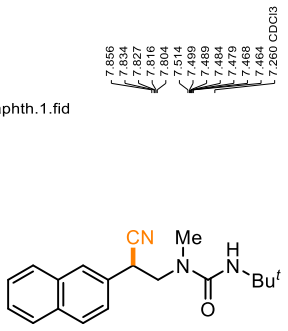
h60nihcyQE6Jdv+53pA6uQ.90800228.fid
MYJ-0909-beta-o-F CDCl3 0910



3m*

^{19}F NMR 376 MHz $CDCl_3$

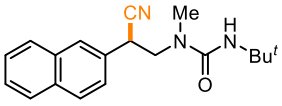
MYJ-0103-Naphth.1.fid



3n*

^{1}H NMR 400 MHz $CDCl_3$

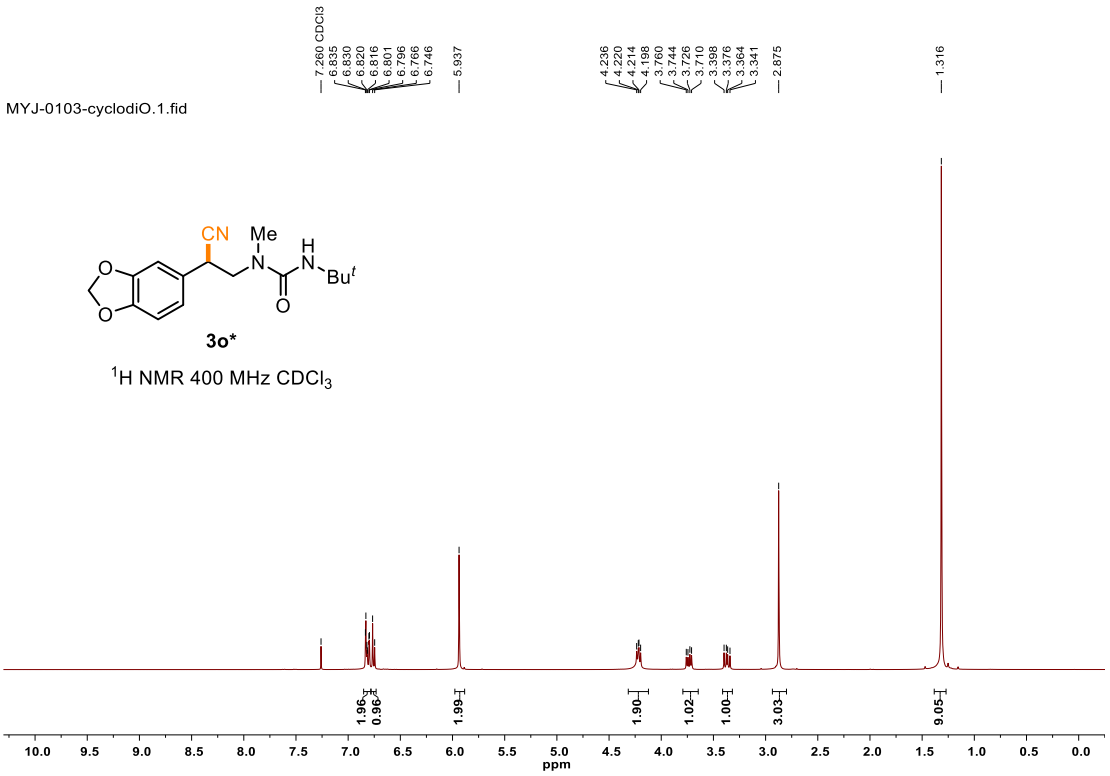
MYJ-0103-Naphth.2.fid



3n*

^{13}C NMR 101 MHz $CDCl_3$

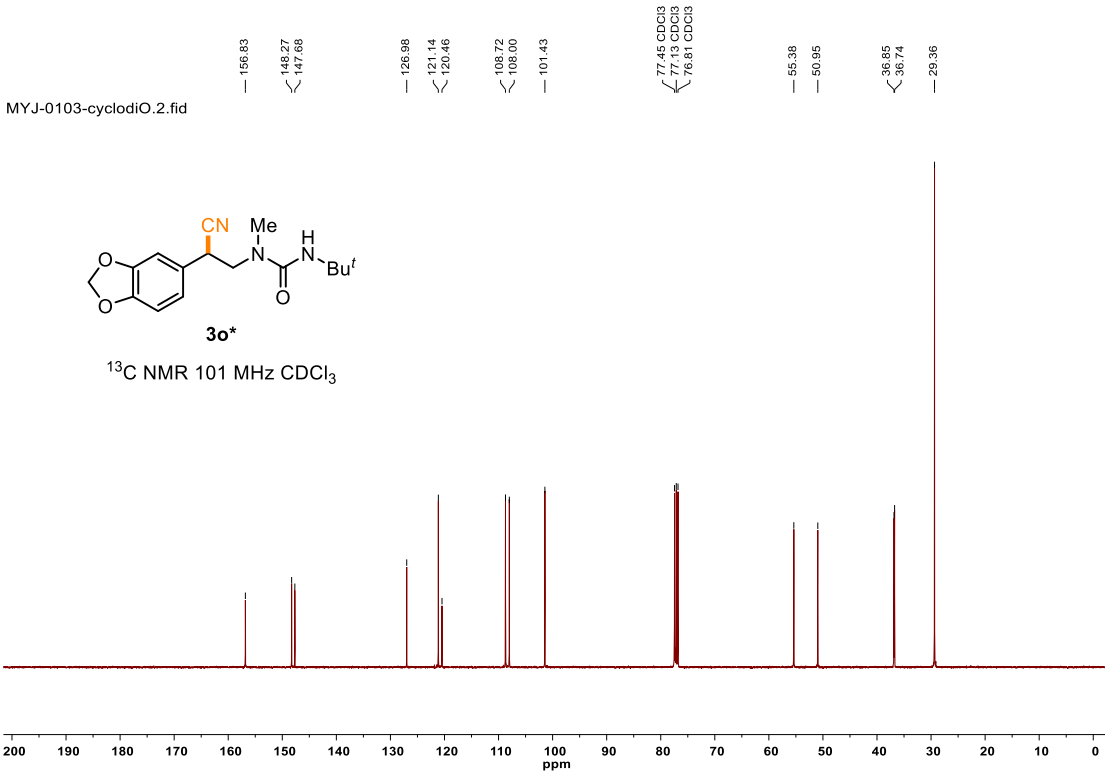
MYJ-0103-cyclodiO.1.fid



3o*

^{1}H NMR 400 MHz $CDCl_3$

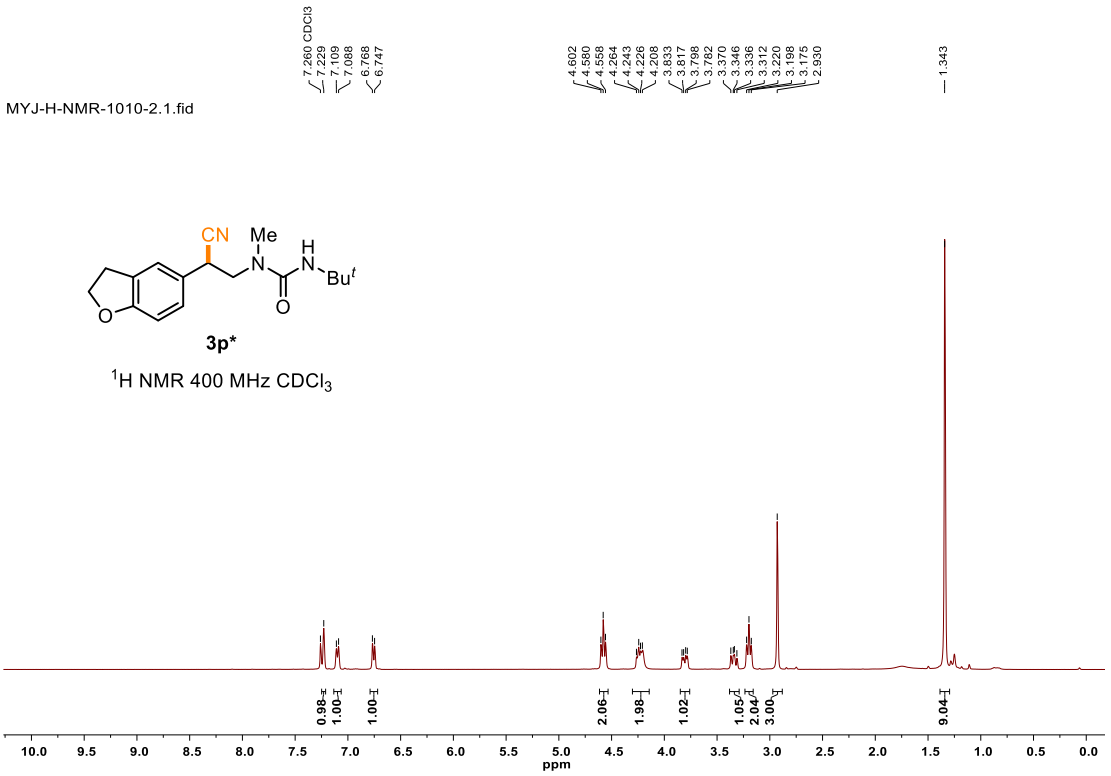
MYJ-0103-cyclodiO.2.fid



3o*

^{13}C NMR 101 MHz $CDCl_3$

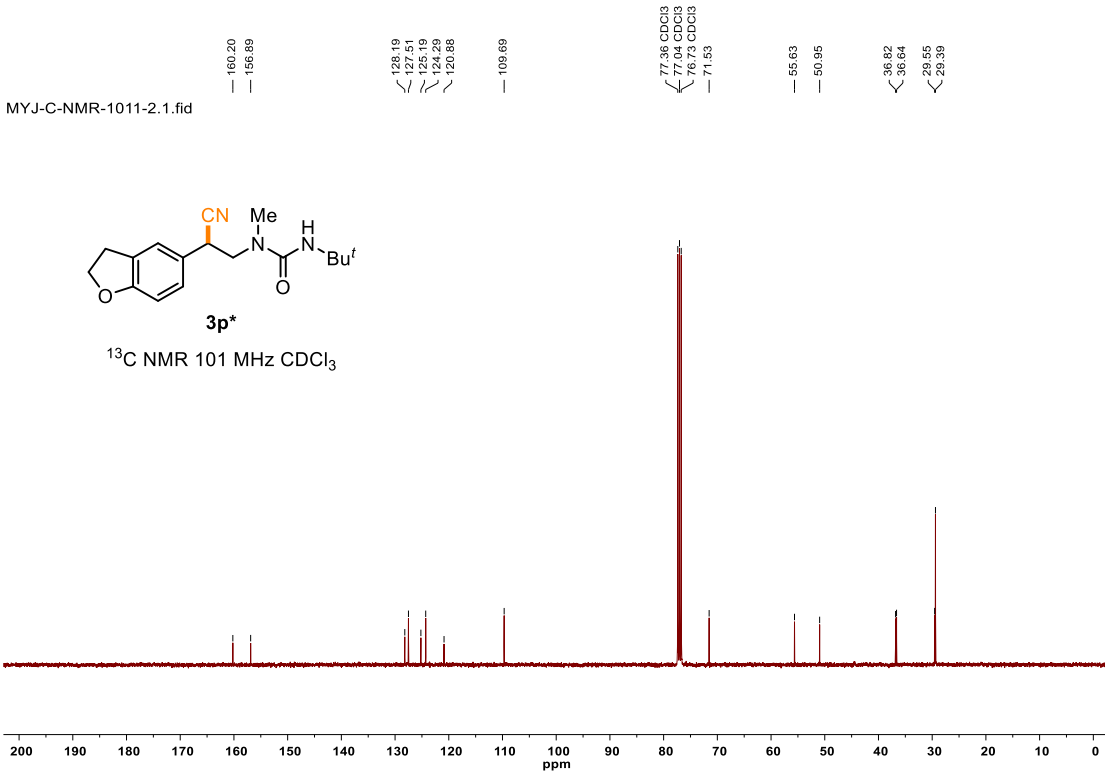
MYJ-H-NMR-1010-2.1.fid



3p*

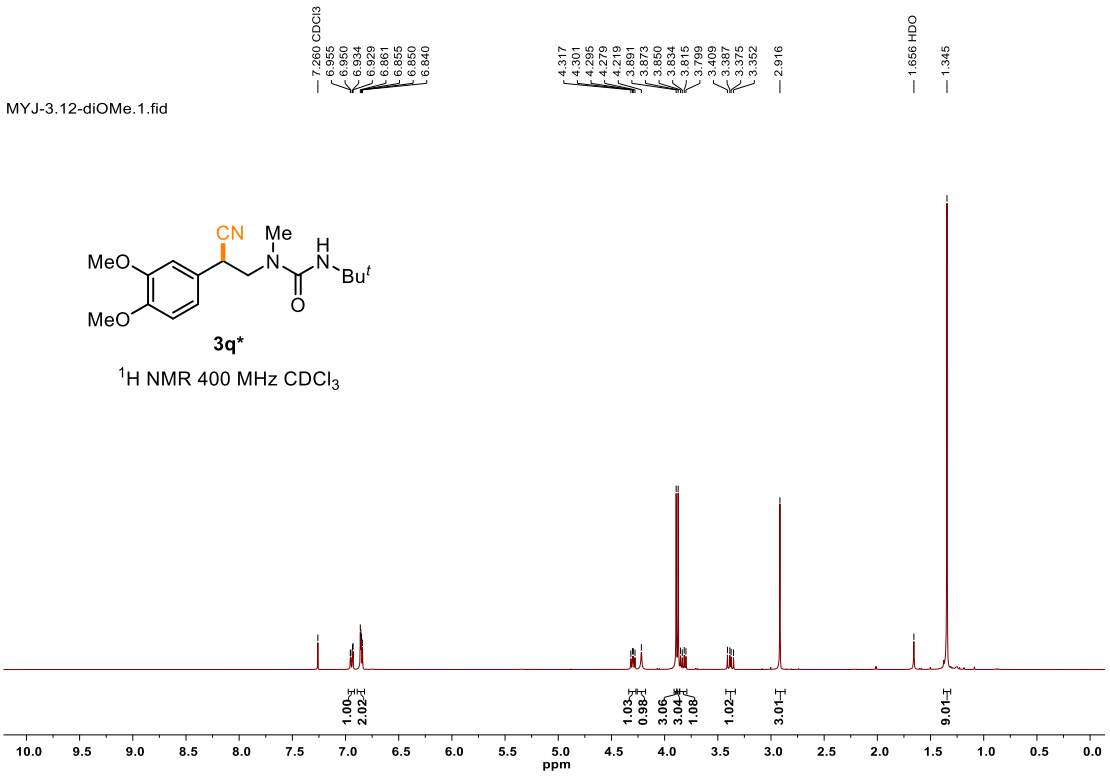
^{1}H NMR 400 MHz $CDCl_3$

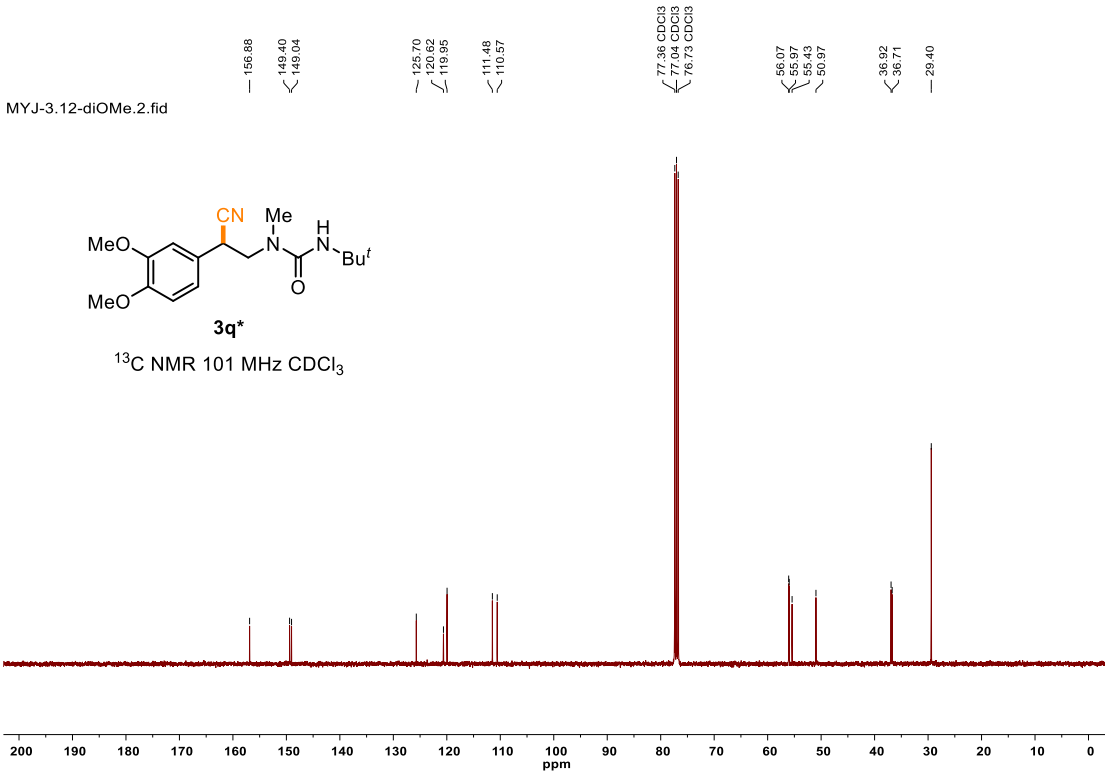
MYJ-C-NMR-1011-2.1.fid

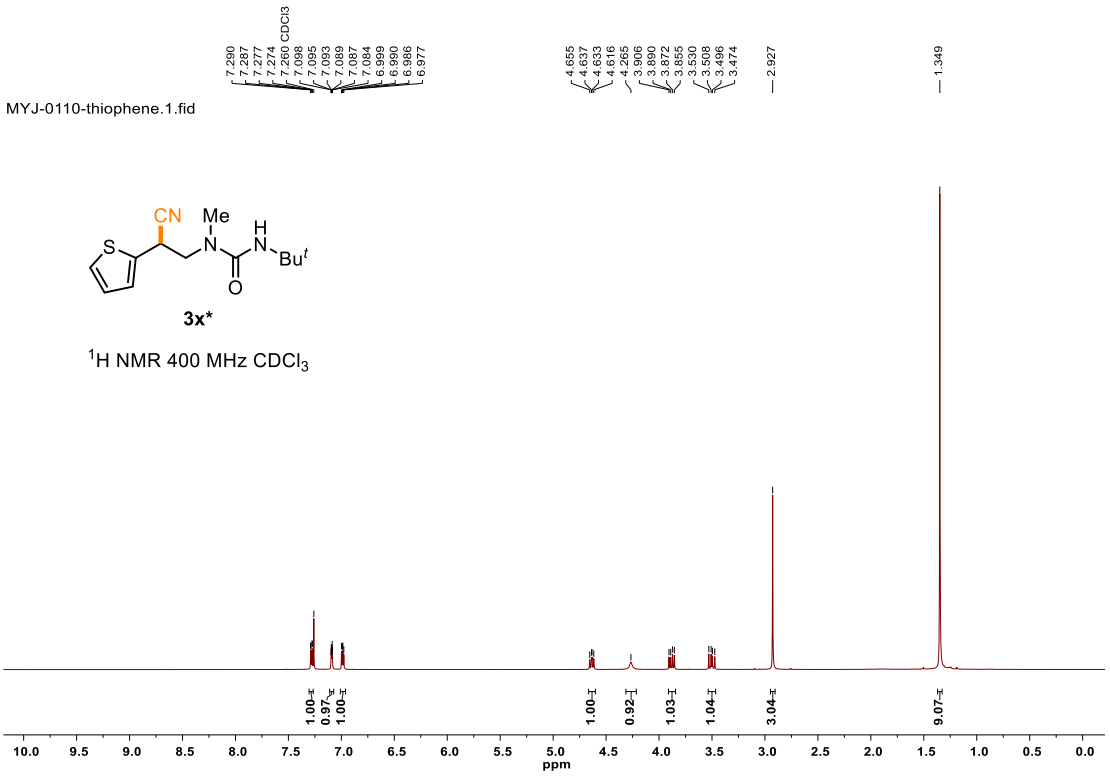


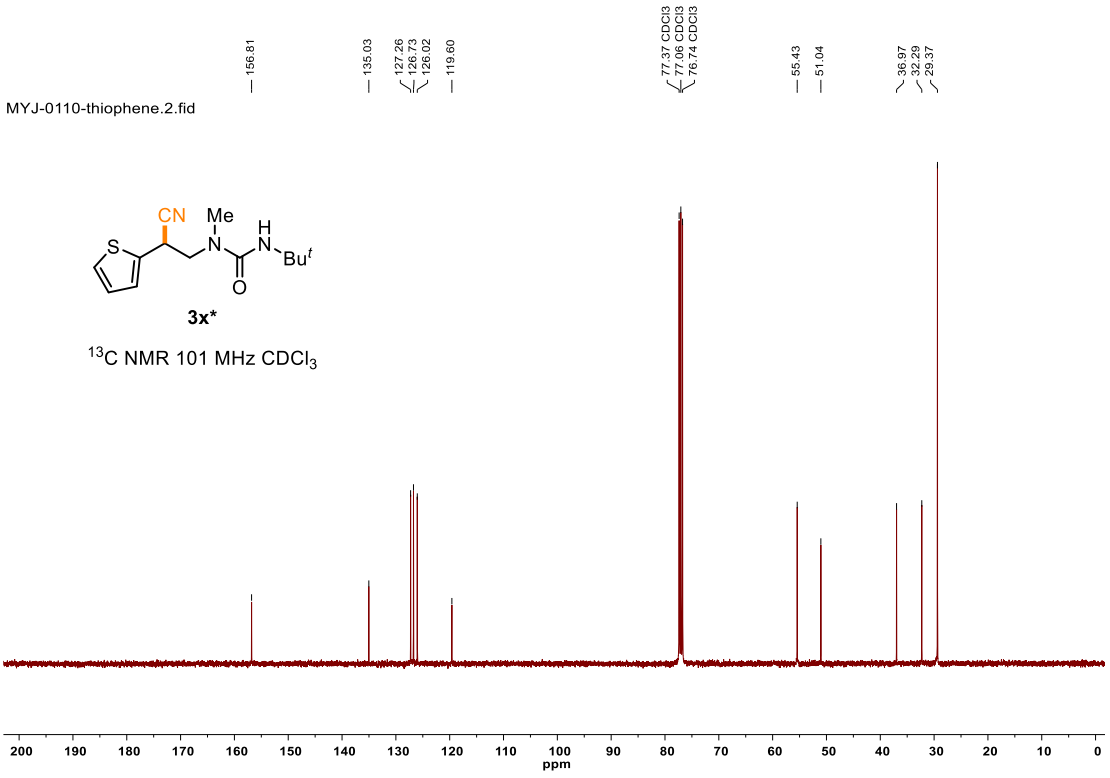
3p*

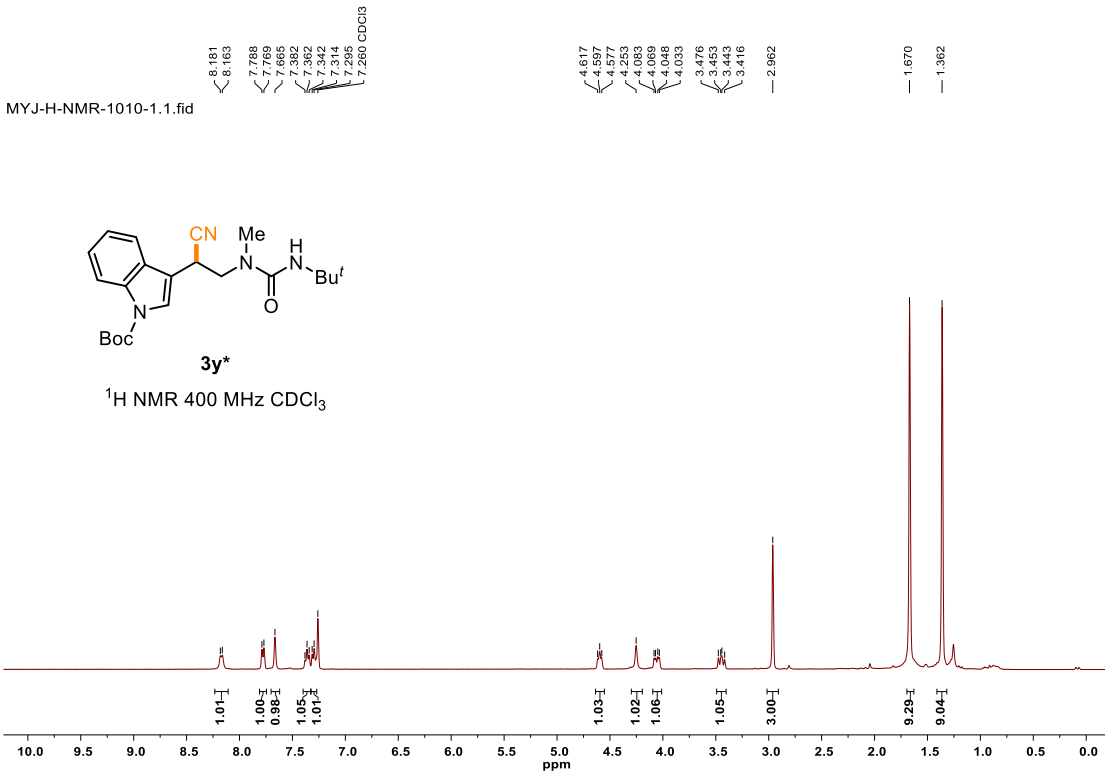
^{13}C NMR 101 MHz $CDCl_3$

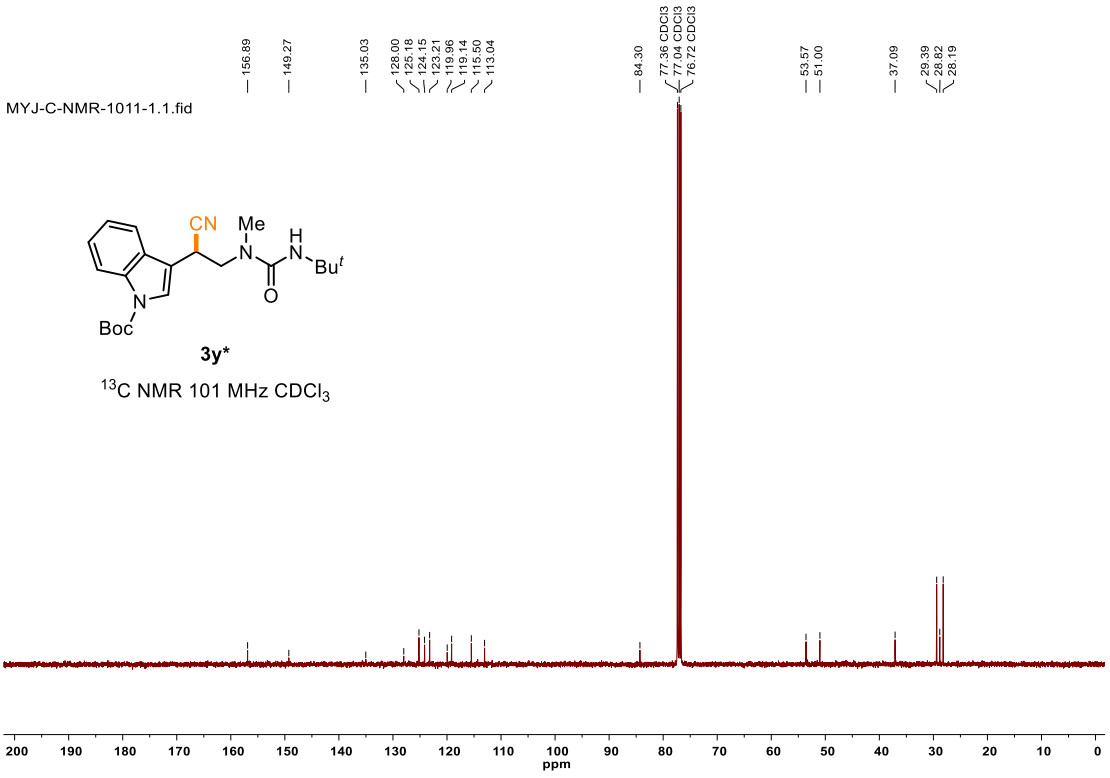

7.260 CDCl3
6.955
6.950
6.934
6.929
6.861
6.855
6.850
6.840
4.317
4.301
4.295
4.279
4.219
3.891
3.873
3.850
3.834
3.815
3.799
3.409
3.387
3.375
3.352
2.916
1.656 HDO
1.345
MYJ-3.12-diOMe.1.fid
CN
Me
H
N
MeO
MeO
N
O
Bu^t
3q*
^{1}H NMR 400 MHz CDCl$_3$
1.00
2.02
1.03
0.98
3.06
3.04
1.08
1.02
3.01
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

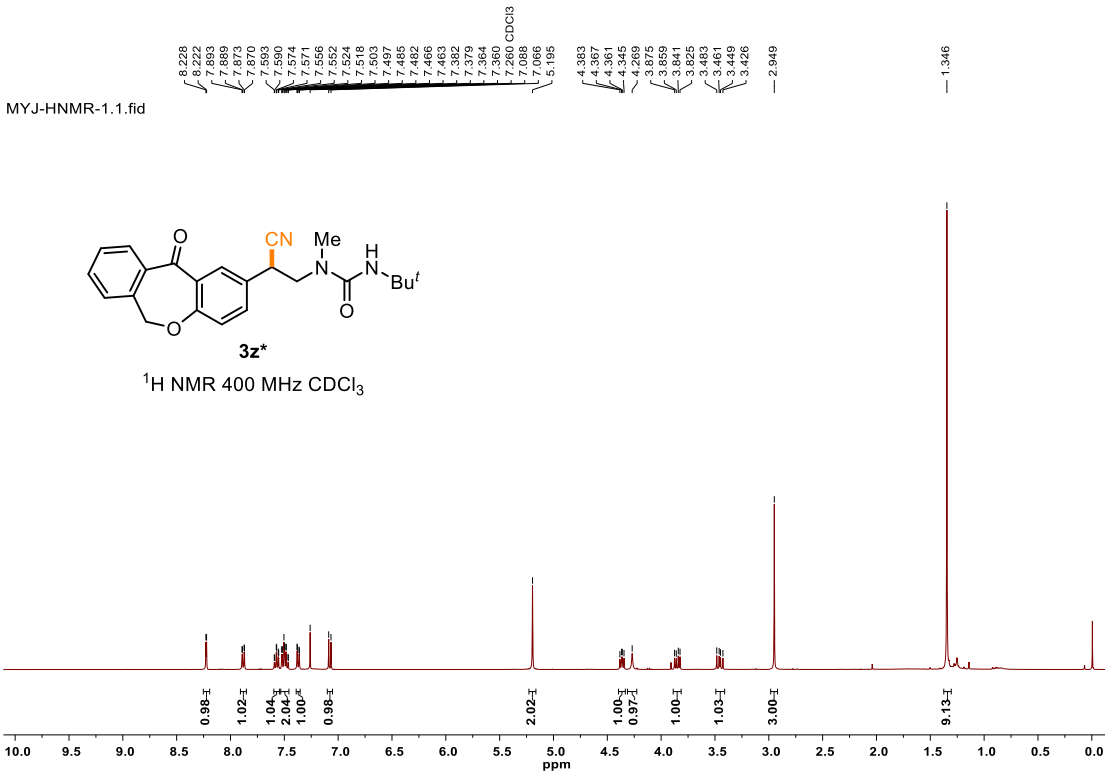

156.88
149.40
149.04
125.70
120.62
119.95
111.48
110.57
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
56.07
55.97
55.43
50.97
36.92
36.71
29.40
MYJ-3.12-diOMe.2.fid
CN
Me
H
N
MeO
MeO
N
O
Bu^t
3q*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.290
7.287
7.277
7.274
7.260 CDCl3
7.098
7.095
7.093
7.089
7.087
7.084
6.999
6.990
6.986
6.977
4.655
4.637
4.633
4.616
4.265
3.906
3.890
3.872
3.855
3.530
3.508
3.496
3.474
2.927
1.349
MYJ-0110-thiophene.1.fid
CN
Me
N
H
N
Bu^t
S
O
3x*
^{1}H NMR 400 MHz CDCl$_3$
1.00
0.97
1.00
1.00
0.92
1.03
1.04
3.04
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

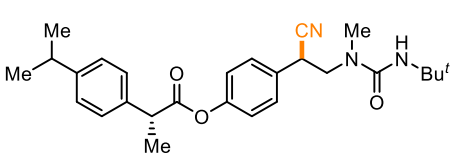

156.81
135.03
127.26
126.73
126.02
119.60
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
55.43
51.04
36.97
32.29
29.37
MYJ-0110-thiophene.2.fid
CN
Me
N
H
N
Bu^t
S
O
3x*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.181
8.163
7.788
7.769
7.665
7.382
7.362
7.342
7.314
7.295
7.260 CDCl3
4.617
4.597
4.577
4.253
4.083
4.069
4.048
4.033
3.476
3.453
3.443
3.416
2.962
1.670
1.362
MYJ-H-NMR-1010-1.1.fid
CN
Me
N
H
N
Bu^t
O
N
Boc
3y*
^{1}H NMR 400 MHz CDCl$_3$
1.01
1.00
0.98
1.05
1.01
1.03
1.02
1.06
1.05
3.00
9.29
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


156.89
149.27
135.03
128.00
125.18
124.15
123.21
119.96
119.14
115.50
113.04
84.30
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
53.57
51.00
37.09
29.39
28.82
28.19
MYJ-C-NMR-1011-1.1.fid
CN
Me
N
H
N
Bu^t
O
N
Boc
3y*
^{13}C NMR 101 MHz CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.228
8.222
7.893
7.889
7.873
7.870
7.593
7.590
7.574
7.571
7.556
7.552
7.524
7.518
7.503
7.497
7.485
7.482
7.466
7.463
7.382
7.379
7.364
7.360
7.260 CDCl3
7.088
7.066
5.195
4.383
4.367
4.361
4.345
4.269
3.875
3.859
3.841
3.825
3.483
3.461
3.449
3.426
2.949
1.346
MYJ-HNMR-1.1.fid
O
CN
Me
N
H
N
Bu^t
O
O
3z*
^{1}H NMR 400 MHz $CDCl_3$
0.98
1.02
1.04
2.04
1.00
0.98
2.02
1.00
0.97
1.00
1.03
3.00
9.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
190.41
161.13
156.79
140.32
135.27
134.48
132.98
131.02
129.51
129.44
127.92
127.20
125.53
121.90
120.12
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
73.65
54.79
51.02
36.84
36.25
29.37
LHL-CNMR-1219-1-Ph-C=O-7-O-Ph.1.fid
O
CN
Me
N
H
N
Bu^t
O
O
3z*
^{13}C NMR 101 MHz $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

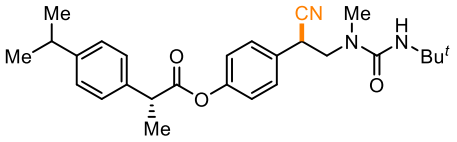
MYJ-0110-ibuprofen.2.fid



3aa*

^{1}H NMR 400 MHz $CDCl_3$

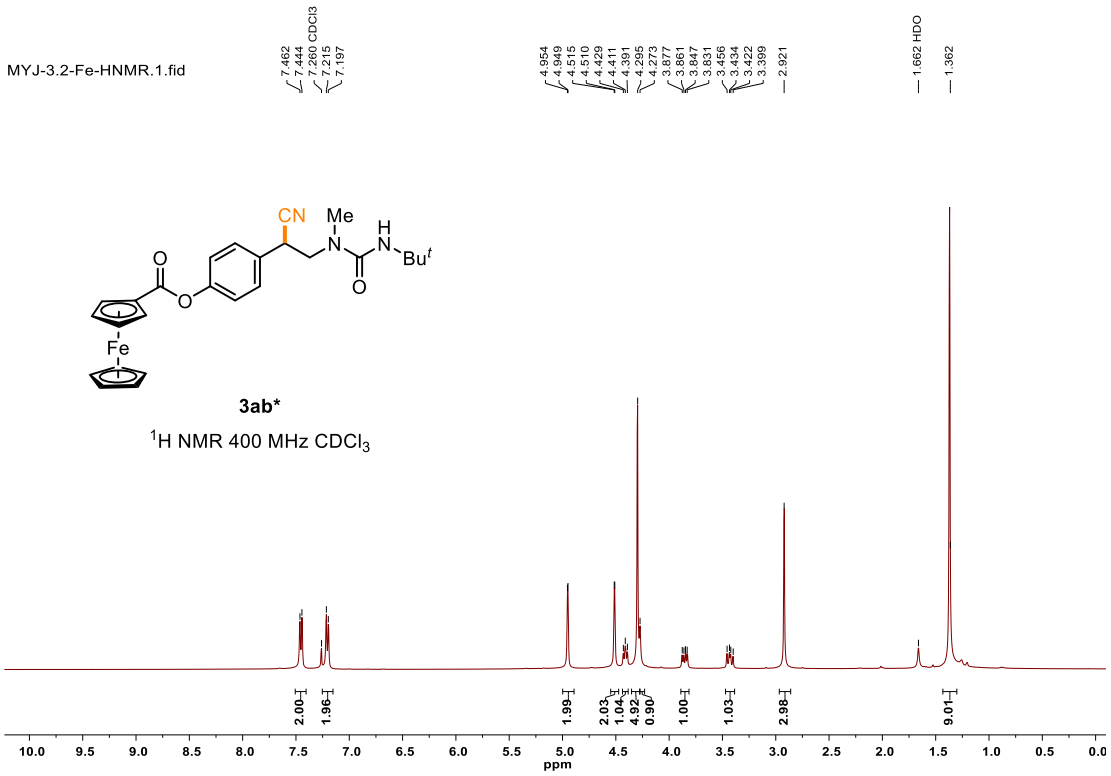
MYJ-0110-ibuprofen.3.fid



3aa*

^{13}C NMR 101 MHz $CDCl_3$

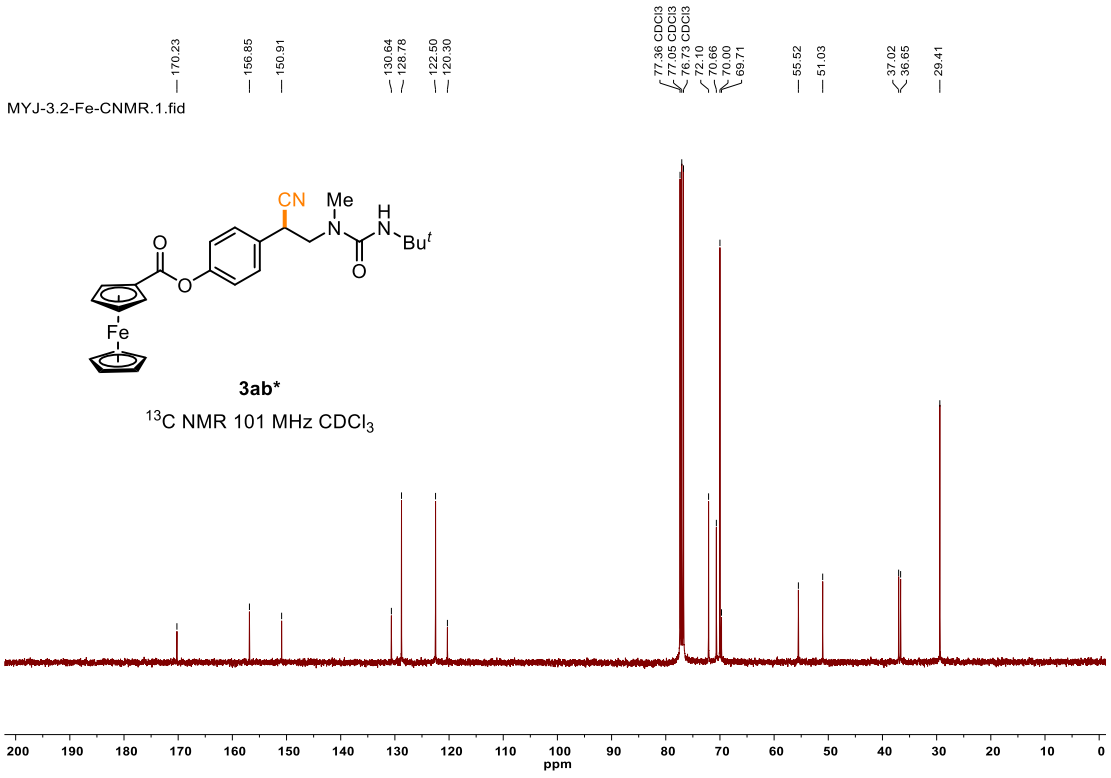
MYJ-3.2-Fe-HNMR.1.fid



3ab*

^{1}H NMR 400 MHz $CDCl_3$

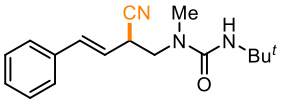
MYJ-3.2-Fe-CNMR.1.fid



3ab*

^{13}C NMR 101 MHz $CDCl_3$

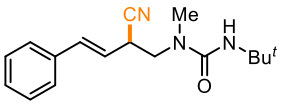
MYJ-Ph-olefin-CN.1.fid



3ac*

^{1}H NMR 400 MHz $CDCl_3$

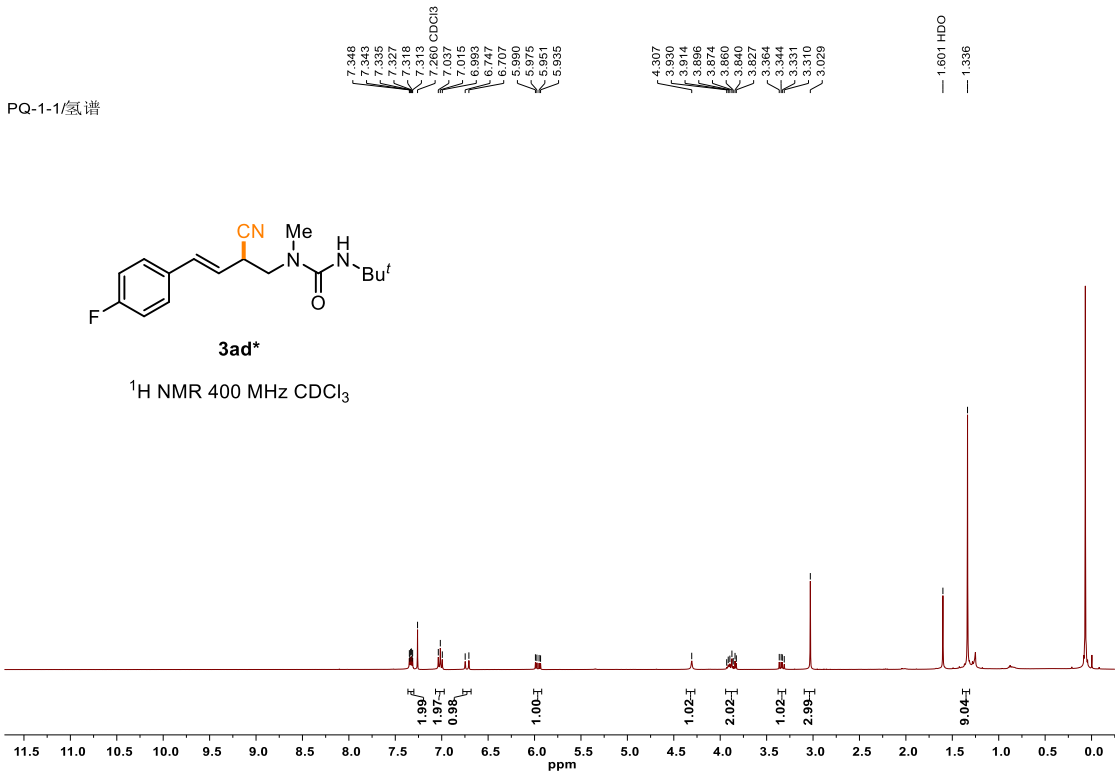
MYJ-Ph-olefin-CN.2.fid



3ac*

^{13}C NMR 101 MHz $CDCl_3$

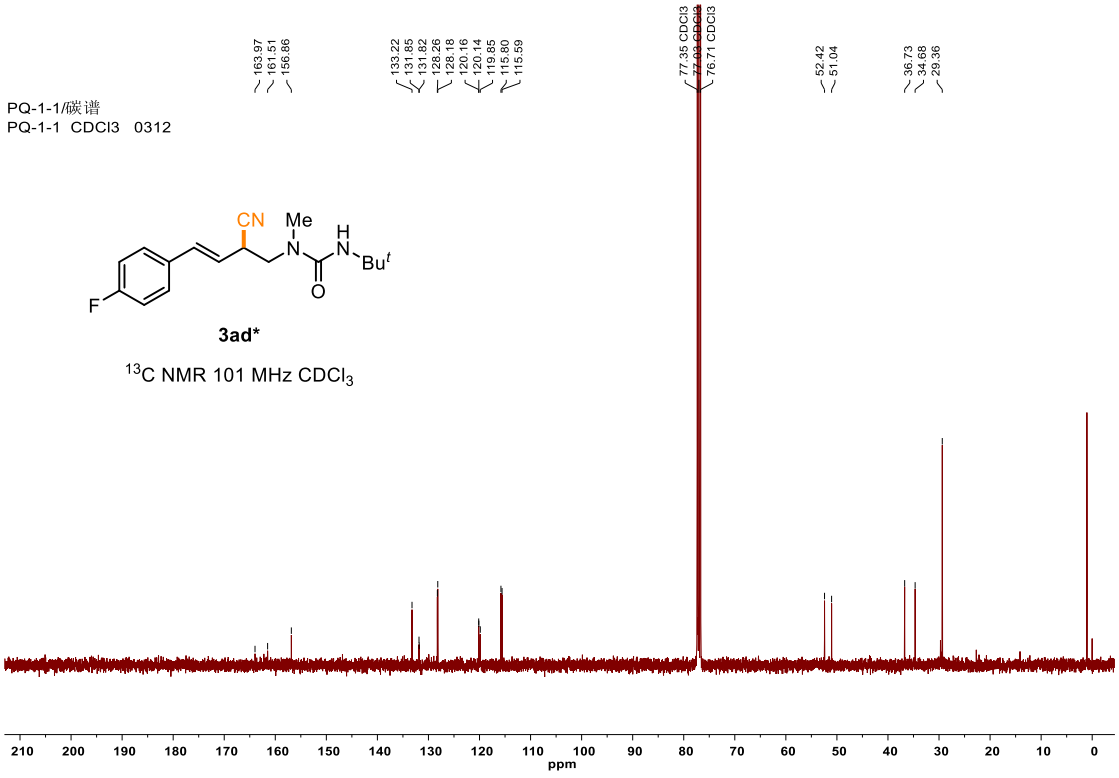
PQ-1-1/氢谱



3ad*

^{1}H NMR 400 MHz $CDCl_3$

PQ-1-1/碳谱
PQ-1-1 CDCl3 0312

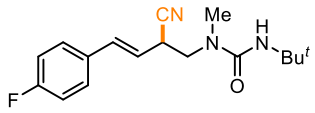


3ad*

^{13}C NMR 101 MHz $CDCl_3$

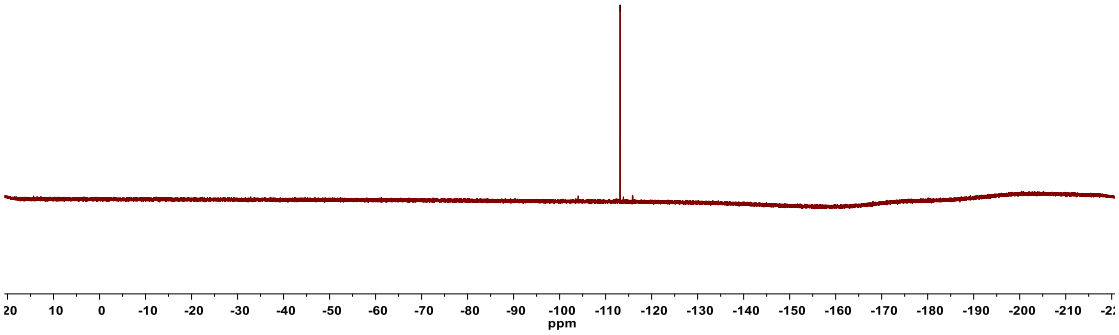
— -113.151

h60nihcyQE6Jdv+53pA6uQ.90800229.fid
MYJ-0909-olefin-F CDCl3 0910

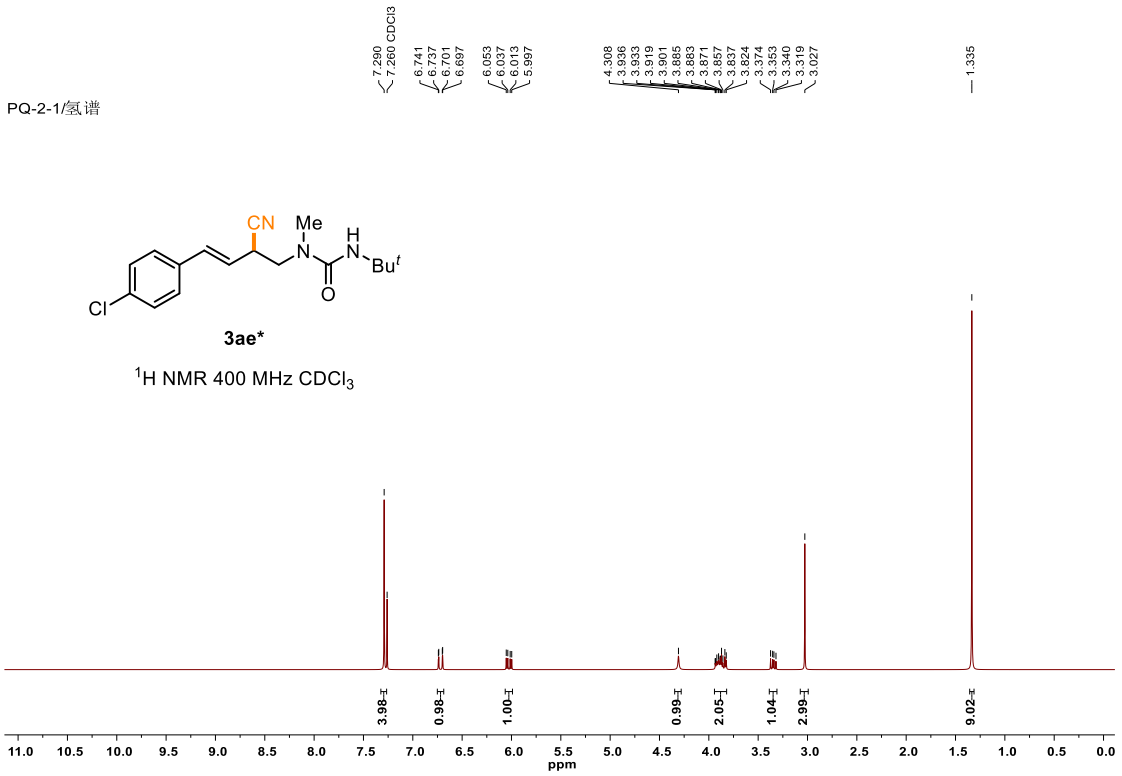


3ad*

^{19}F NMR 376 MHz $CDCl_3$



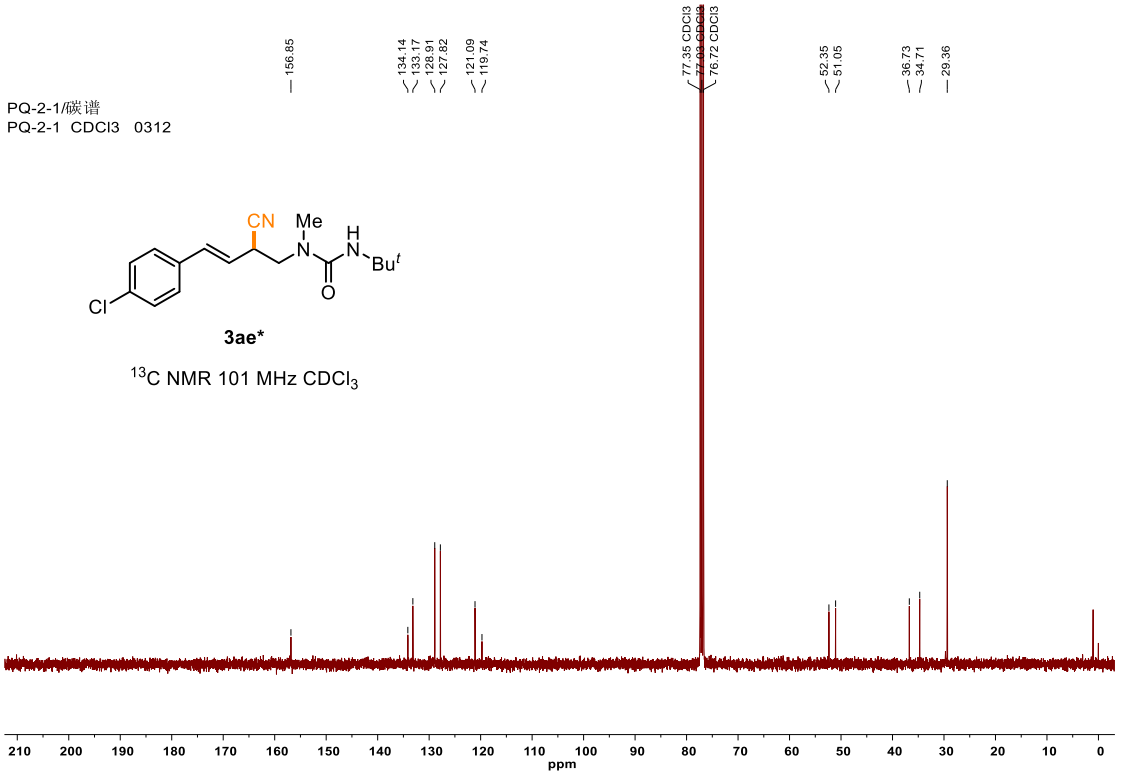
PQ-2-1/氢谱



3ae*

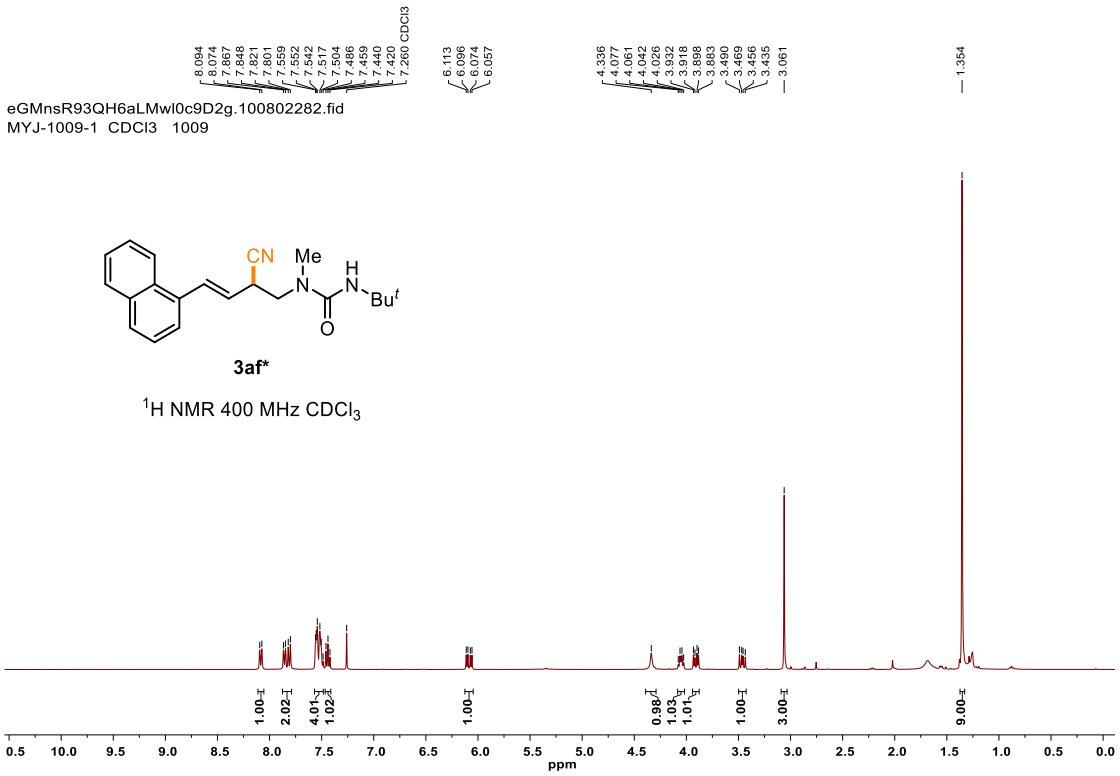
^{1}H NMR 400 MHz $CDCl_3$

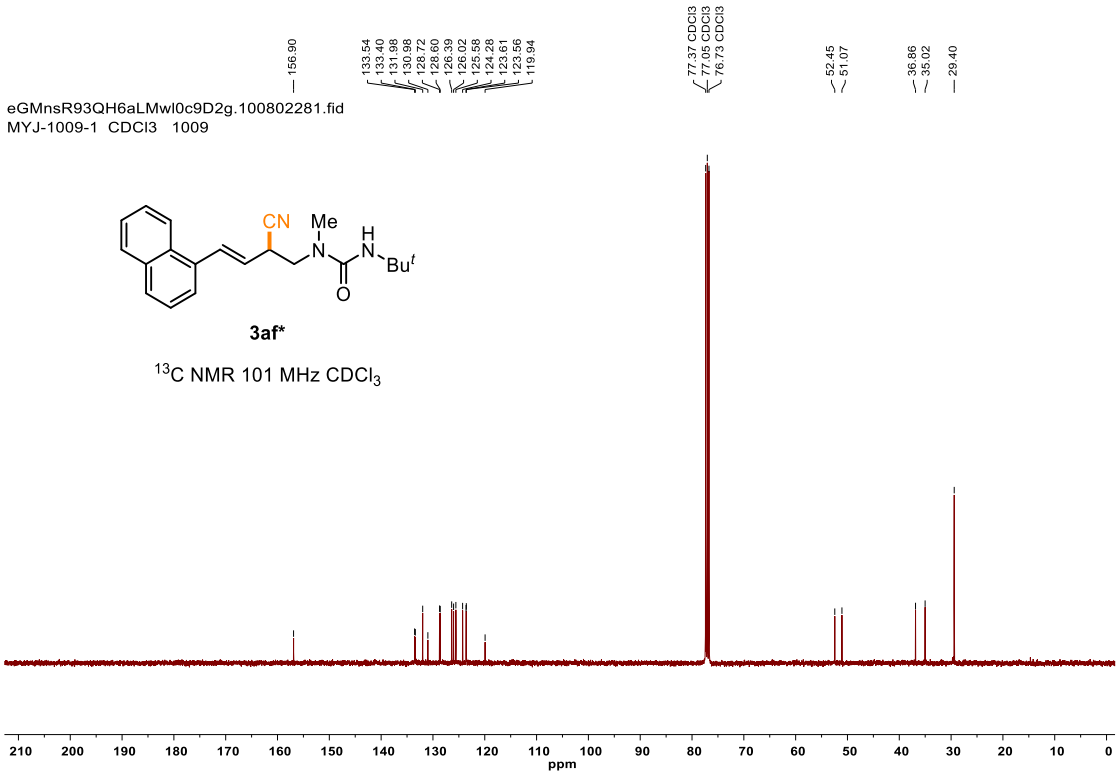
PQ-2-1/碳谱
PQ-2-1 CDCl3 0312

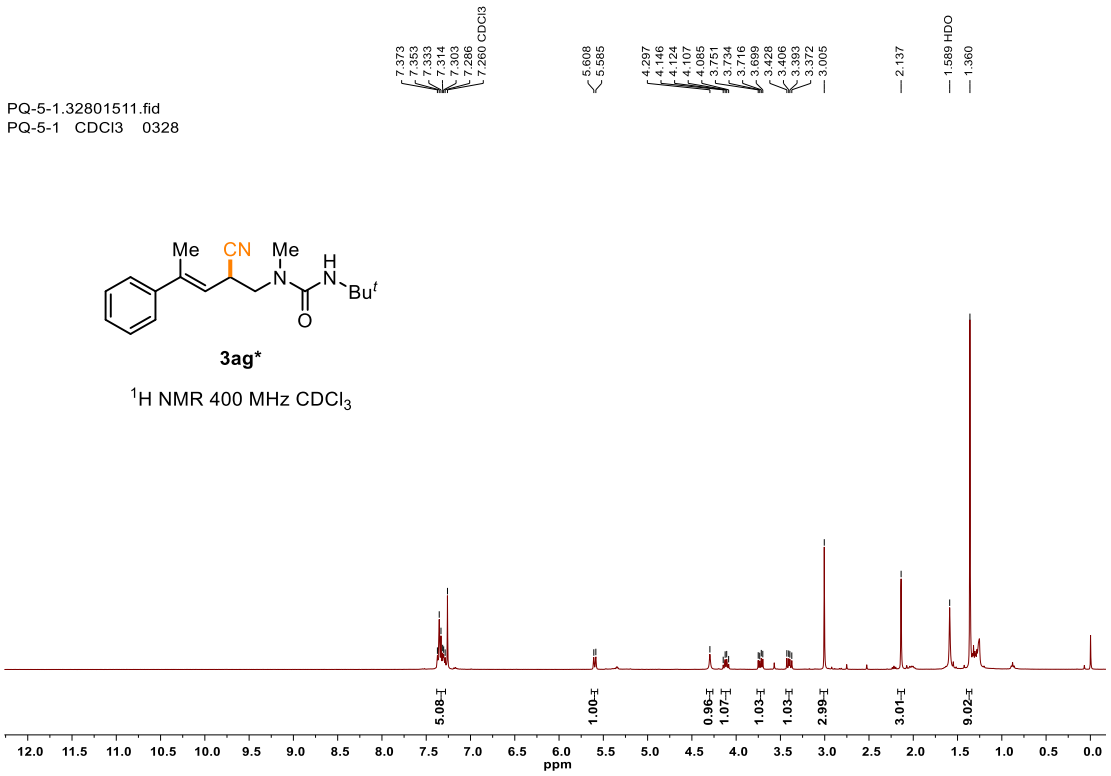


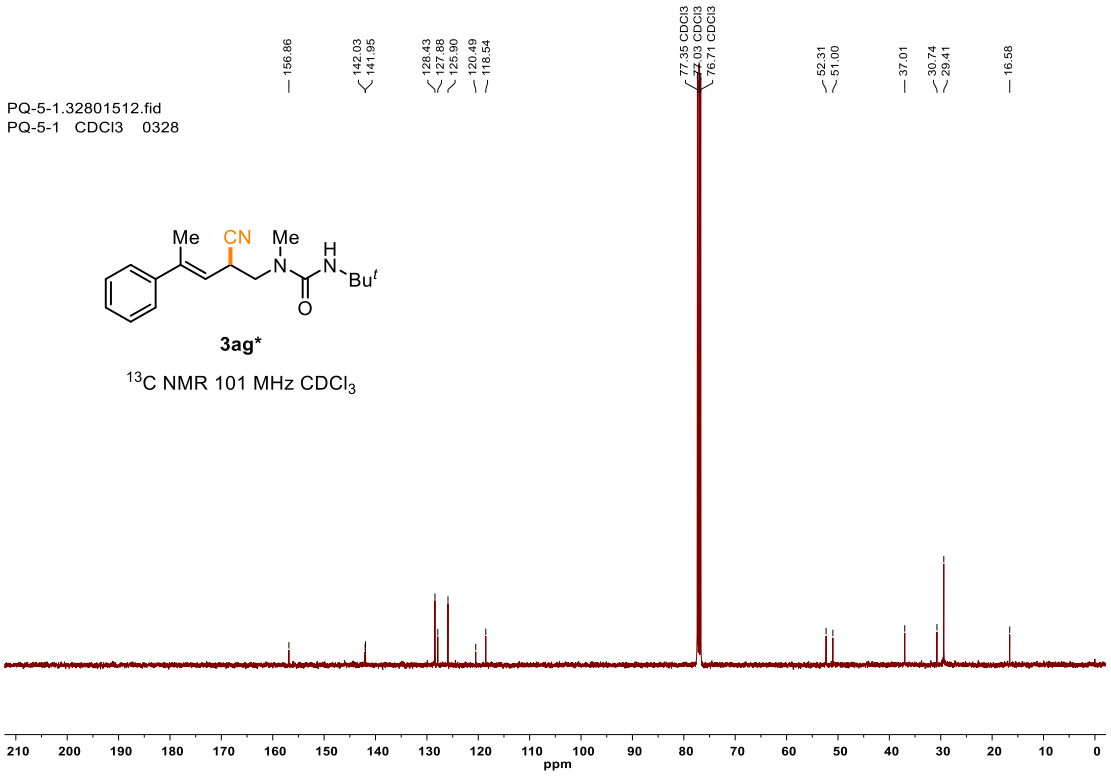
3ae*

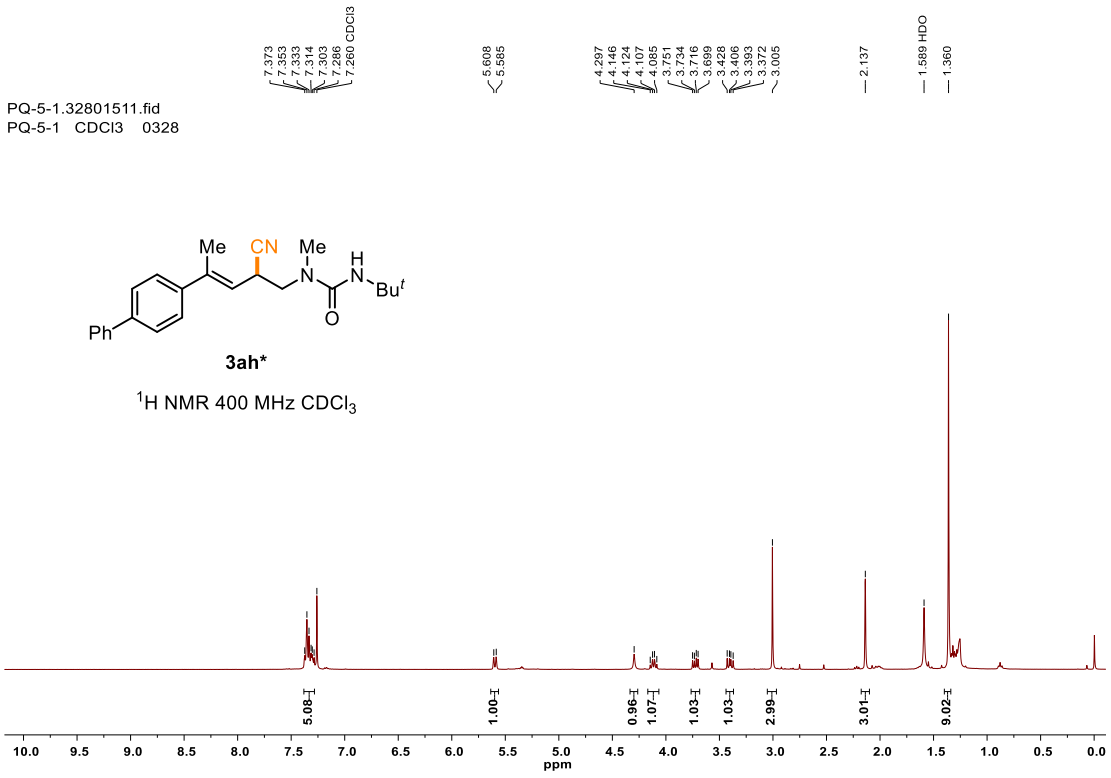
^{13}C NMR 101 MHz $CDCl_3$

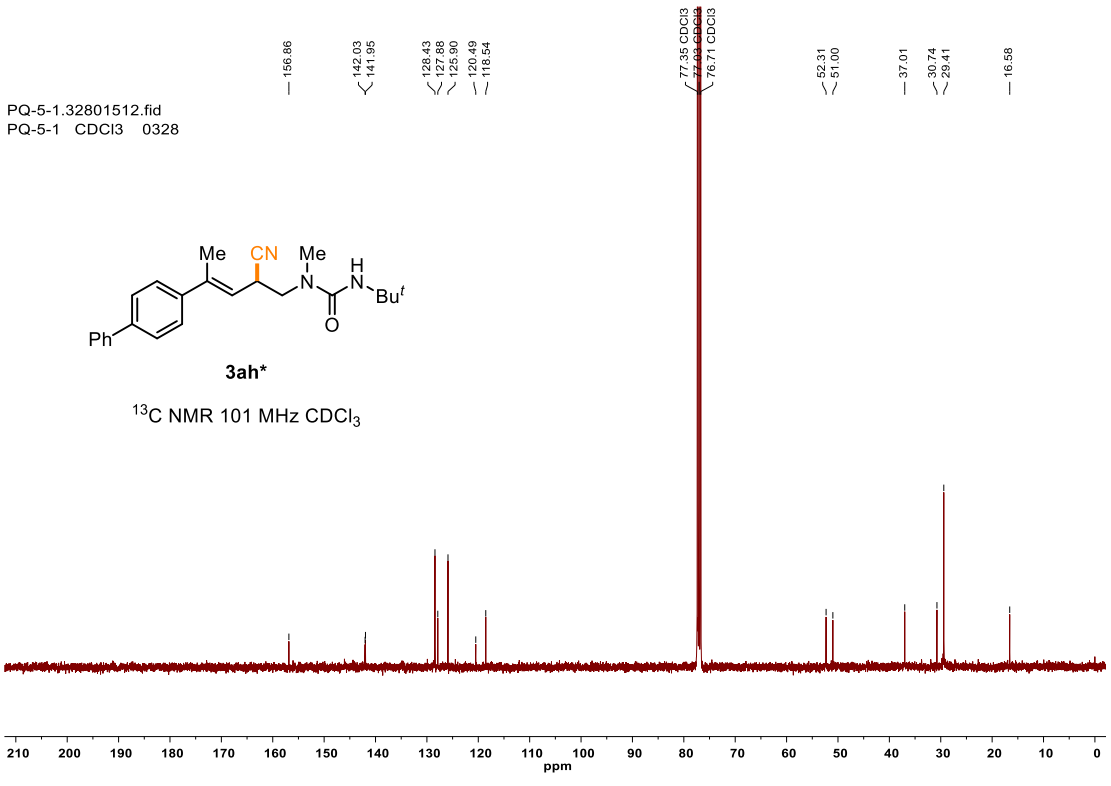

8.094
8.074
7.867
7.848
7.821
7.801
7.559
7.552
7.542
7.517
7.504
7.486
7.459
7.440
7.420
7.260 CDCl3
6.113
6.096
6.074
6.057
4.336
4.077
4.061
4.042
4.026
3.932
3.918
3.898
3.883
3.490
3.469
3.456
3.435
3.061
1.354
eGMnsR93QH6aLMwl0c9D2g.100802282.fid
MYJ-1009-1 CDCl3 1009
CN
Me
N
H
N
Bu^t
O
3af*
^{1}H NMR 400 MHz $CDCl_3$
1.00
2.02
4.01
1.02
1.00
0.98
1.03
1.01
1.00
3.00
9.00
ppm

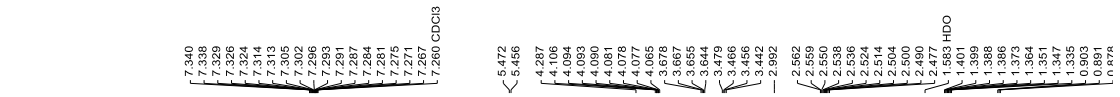

156.90
133.54
133.40
131.98
130.98
128.72
128.60
126.39
126.02
125.58
124.28
123.61
123.56
119.94
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
52.45
51.07
36.86
35.02
29.40
eGMnsR93QH6aLMwl0c9D2g.100802281.fid
MYJ-1009-1 CDCl3 1009
CN
Me
N
H
N
Bu^t
O
3af*
^{13}C NMR 101 MHz $CDCl_3$
ppm


7.373
7.353
7.333
7.314
7.303
7.286
7.260 CDCl3
5.608
5.585
4.297
4.146
4.124
4.107
4.085
3.751
3.734
3.716
3.699
3.428
3.406
3.393
3.372
3.005
2.137
1.589 HDO
1.360
PQ-5-1.32801511.fid
PQ-5-1 CDCl3 0328
Me
CN
Me
N
H
N
Bu^t
O
3ag*
^{1}H NMR 400 MHz $CDCl_3$
5.08
1.00
0.96
1.07
1.03
1.03
2.99
3.01
9.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


156.86
142.03
141.95
128.43
127.88
125.90
120.49
118.54
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
52.31
51.00
37.01
30.74
29.41
16.58
PQ-5-1.32801512.fid
PQ-5-1 CDCl3 0328
Me
CN
Me
N
H
N
Bu^t
O
3ag*
^{13}C NMR 101 MHz $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.373
7.353
7.333
7.314
7.303
7.286
7.260 CDCl3
5.608
5.585
4.297
4.146
4.124
4.107
4.085
3.751
3.734
3.716
3.699
3.428
3.406
3.393
3.372
3.005
2.137
1.589 HDO
1.360
PQ-5-1.32801511.fid
PQ-5-1 CDCl3 0328
Me
CN
Me
N
H
N
Bu^t
Ph
O
3ah*
^{1}H NMR 400 MHz $CDCl_3$
5.08
1.00
0.96
1.07
1.03
1.03
2.99
3.01
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


156.86
142.03
141.95
128.43
127.88
125.90
120.49
118.54
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
52.31
51.00
37.01
30.74
29.41
16.58
PQ-5-1.32801512.fid
PQ-5-1 CDCl3 0328
Me
CN
Me
N
H
N
Bu^t
Ph
O
3ah*
^{13}C NMR 101 MHz $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



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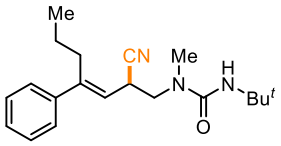
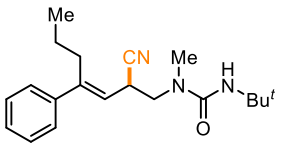


3ai*

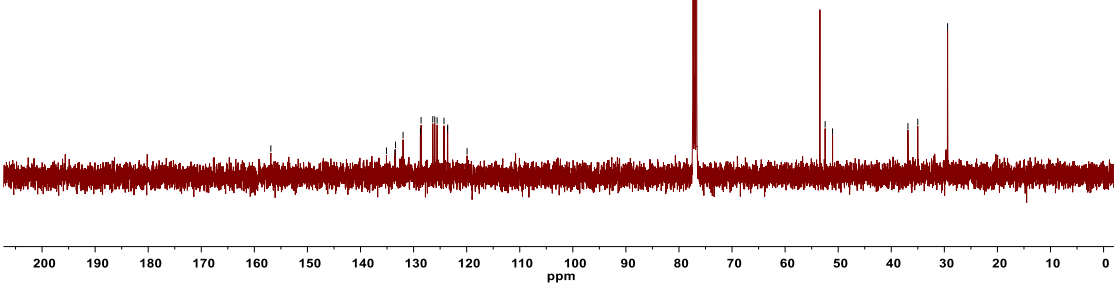
^{1}H NMR 600 MHz $CDCl_3$

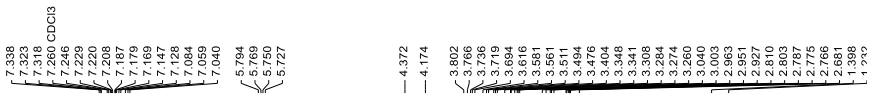
40802241_20240411170508A193.40802241.fid
PQ-3-1 CDCl3 0411



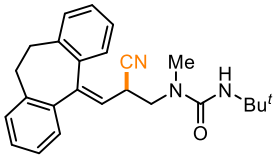
3ai*

^{13}C NMR 101 MHz $CDCl_3$



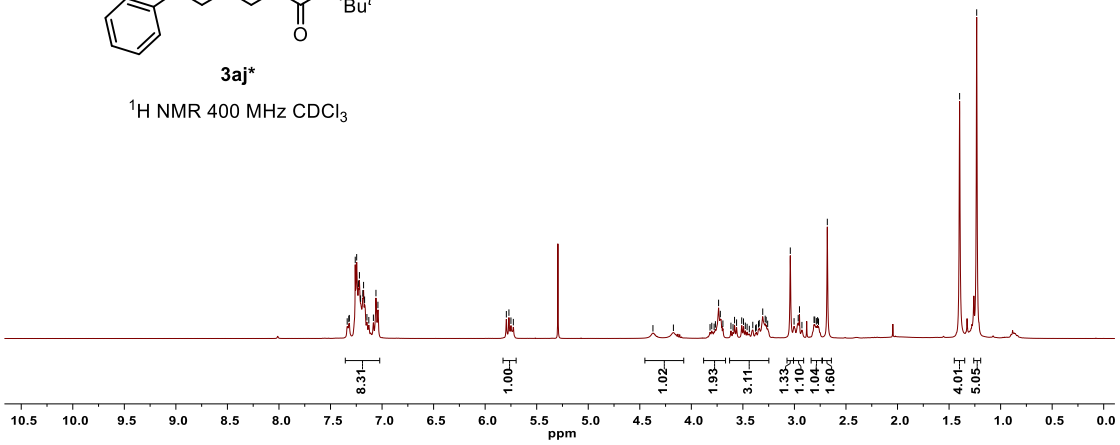


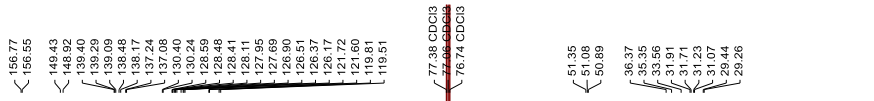
40702402_20240409102404A025.40702402.fid
PA-ai-1 CDCl3 0408



3aj*

^{1}H NMR 400 MHz $CDCl_3$





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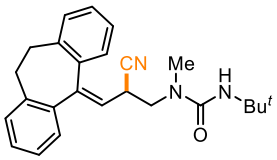
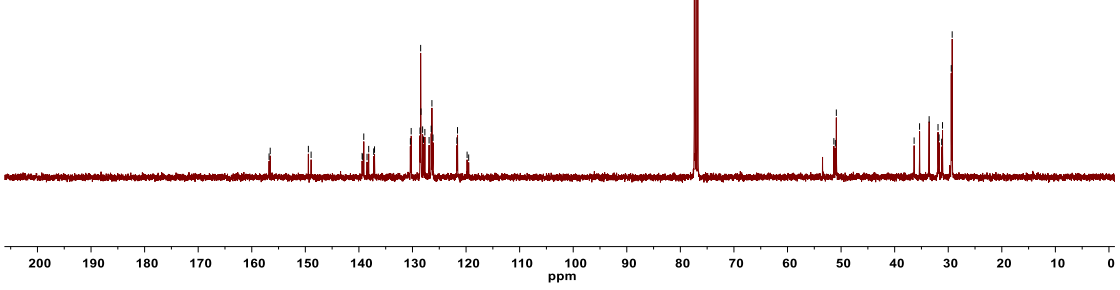
PA-ai-1 CDCl3 0408

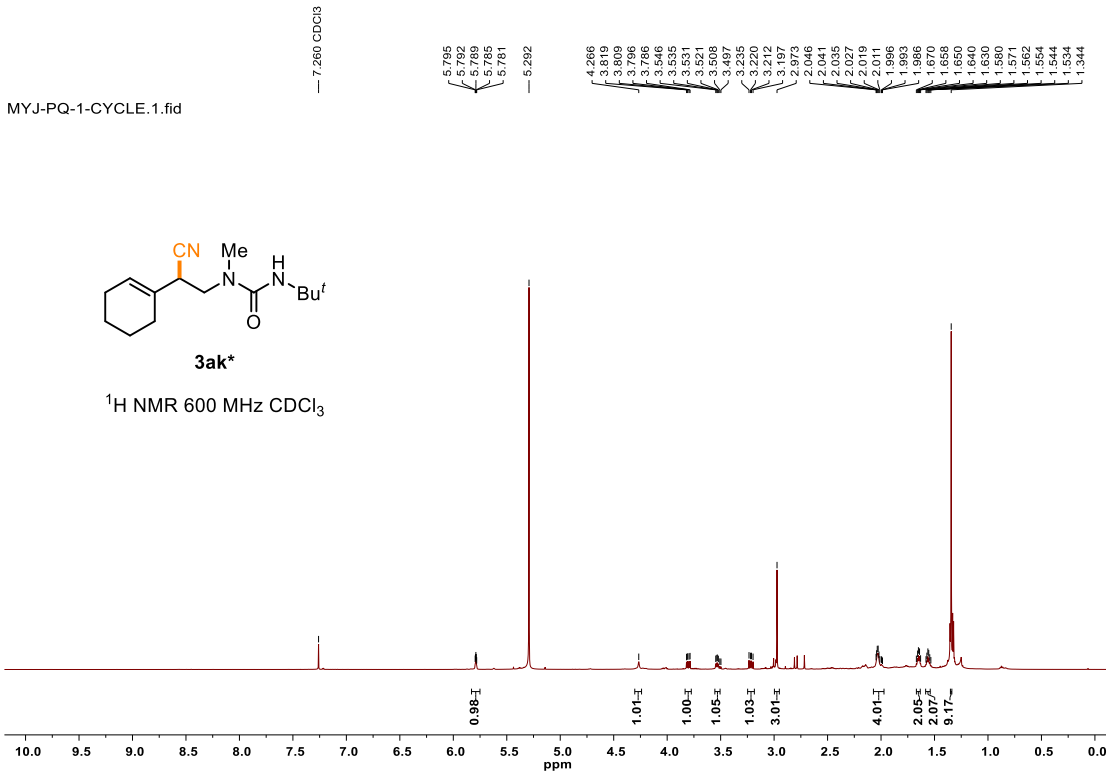


3aj*

^{13}C NMR 101 MHz $CDCl_3$



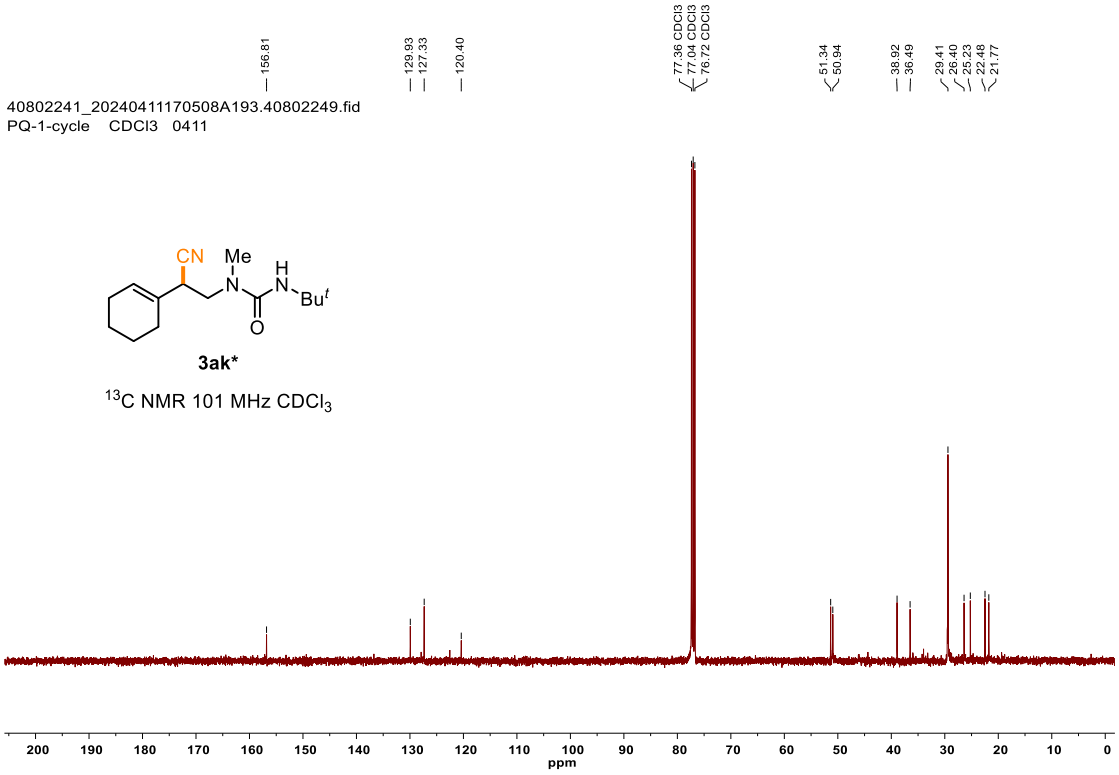
MYJ-PQ-1-CYCLE.1.fid



3ak*

^{1}H NMR 600 MHz $CDCl_3$

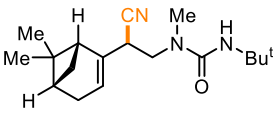
40802241_20240411170508A193.40802249.fid
PQ-1-cycle CDCl3 0411



3ak*

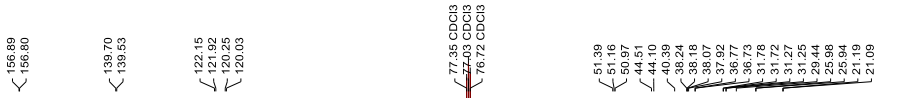
^{13}C NMR 101 MHz $CDCl_3$

4290065_20240430094743A105.4290065.fid
MYJ-Nopol-0429 CDCl3 0429



3al*

^{1}H NMR 400 MHz $CDCl_3$



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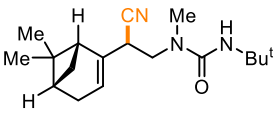
MYJ-nopol-0430 CDCl3 0430



3al*

^{13}C NMR 101 MHz $CDCl_3$