Supporting Information for

Asymmetric amination of unstrained C(sp^3)-C(sp^3) bonds

Yang Liu[1], Ye-Wei Chen[1,2], Yuan-Xiang Yang[1], John F. Hartwig[2]*, and Zhi-Tao He[1,3,4]*

[1]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Shanghai, 200032, China.

[2]Department of Chemistry, University of California, Berkeley; California 94720, United States.

[3]School of Chemistry and Materials Science, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China.

[4]Ningbo Zhongke Creation Center of New Materials, Ningbo, 315899, China.

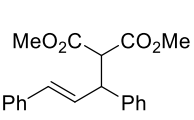
*Correspondence to: jhartwig@berkeley.edu (J.F.H.); hezt@sioc.ac.cn (Z.T.H.)

Table of Contents

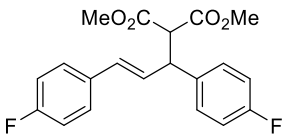
1. General information

All air-sensitive manipulations were conducted with Schlenk techniques under argon. Unless otherwise indicated, all commercially available starting materials and dry solvents were purchased and used directly without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz Bruker or 500 MHz Agilent instruments at Shanghai Institute of Organic Chemistry. For high-resolution mass spectra: ESI mass spectra were recorded on Thermo Scientific Q Exactive HF Orbitrap-FTMS; MALDI was measured on Voyager-DE STR; EI mass spectra were recorded on Waters Premier GC-TOF MS; FI mass spectra were recorded on JEOL-AccuTOF-GCv4G-GCT MS. Optical rotation was measured using a 1 mL cell with 1.0 dm path length on a JASCO P-1030 polarimeter. HPLC analysis was conducted on a Shimadzu HPLC system equipped with Daicel or Chiralpak chiral-stationary-phase columns (ϕ 4.6 mm × 250 mm). Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard or $CHCl_3$ in $CDCl_3$ (7.26 ppm) for ^{1}H NMR, $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR, and $CFCl_3$ (0 ppm) for ^{19}F NMR. Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Column chromatography was performed with 300-400 mesh silica gel using standard techniques for flash column chromatography.

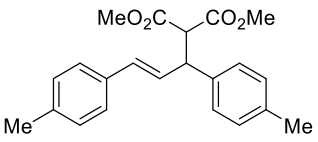
2. Synthesis of substrates and racemic products



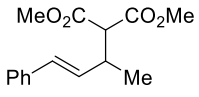
1a



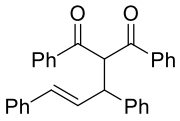
1b



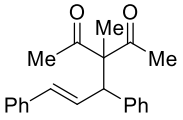
1c



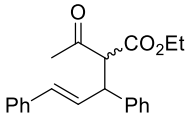
1d



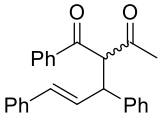
1e



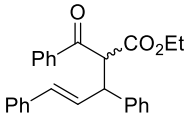
1f



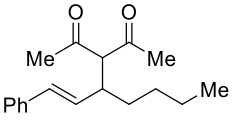
1g



1h

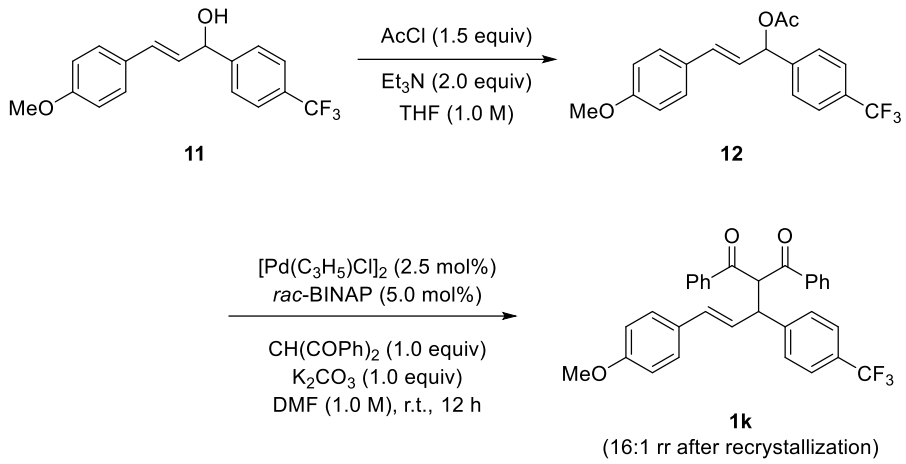


1i



1j

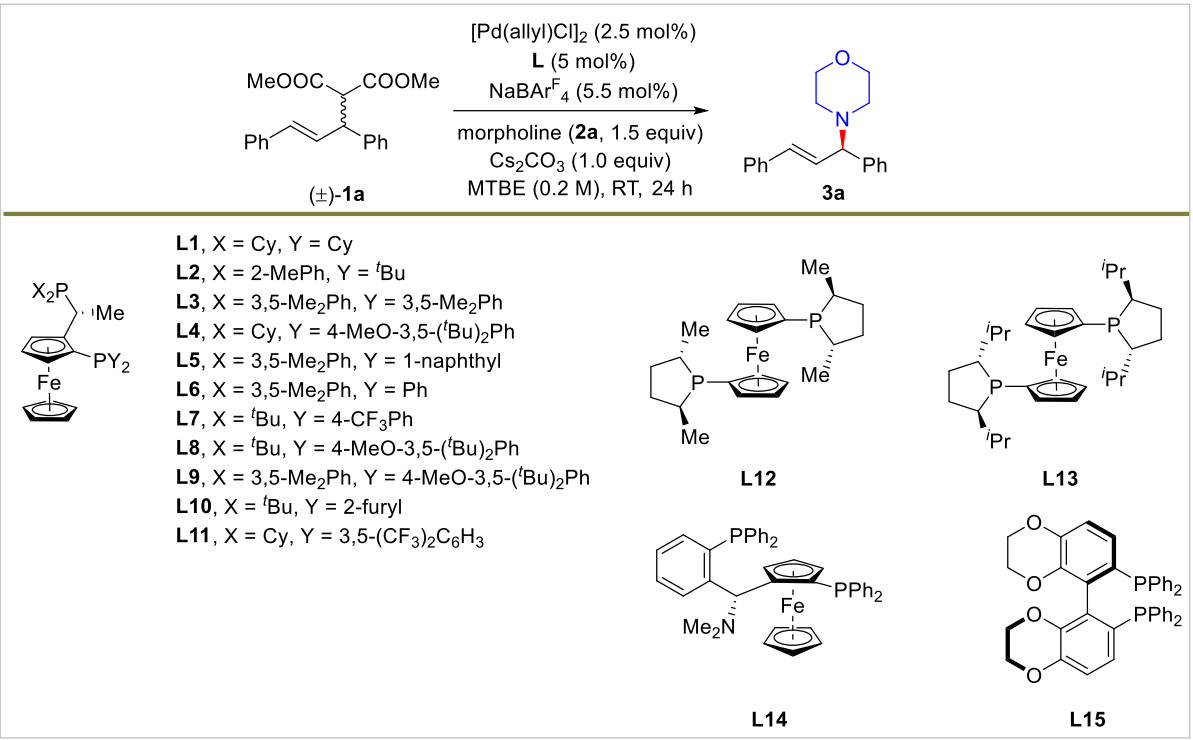
All these substrates are reported and prepared according to the literatures[1-7].



(*E*)-2-(3-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)allyl)-1,3-diphenylpropane-1,3-dione (**1k**). In a nitrogen-filled glovebox, to a 50 mL flask with alcohol **11** (3.1 g, 10 mmol) and Et_3N (2.0 g, 20 mmol) were added AcCl (1.2 g, 15 mmol) and dry THF (10 mL). Then the reaction was stirred at room temperature for 12 h. After this time, the reaction was washed by brine and extracted with ethyl acetate, dried over Na_2SO_4, concentrated and purified by flash column chromatography to provide **12** as a light-yellow oil in 80% yield (2.8 g). Then in a nitrogen-filled glovebox, to a 25 mL flask with $[Pd(allyl)Cl]_2$ (73 mg, 0.20 mmol) and *rac*-BINAP (0.25 g, 0.40 mmol) were added $CH(COPh)_2$ (1.8 g, 8.0 mmol), K_2CO_3 (1.1 g, 8.0 mmol), the prepared **12** (8.0 mmol) and dry DMF (8.0 mL). Then the mixture was stirred at room temperature for 12 h. After this time, the reaction was washed with brine and extracted by ethyl acetate, dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford **1k** with 2:1 regioselectivity. The corresponding regioselectivity was elevated to 16:1 after repeated recrystallization with toluene and hexane. In this case, **1k** was obtained in 19% yield (0.79 g) as a white solid. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.06 – 7.94 (m, 2H), 7.89 – 7.76 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.40 (m, 5H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.87 – 6.71 (m, 2H), 6.40 (dd, *J* = 15.8, 7.9 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.91 (d, *J* = 10.4 Hz, 1H), 4.77 (dd, *J* = 10.4, 7.8 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 194.5, 193.7, 158.5, 140.4, 137.2, 136.8, 133.7, 133.4, 133.1, 132.4, 130.3, 129.4, 129.0, 128.8, 128.7, 128.8 (q, *J* = 32.3 Hz), 128.6, 126.4, 125.3 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 272.3 Hz), 114.2, 62.6, 55.2, 49.2. ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.54. HRMS (EI): $[M]^{\oplus}$ calcd for $C_{32}H_{25}F_3O_3Na^{\oplus}$ 537.1648, found 537.1653.

3. Development of reaction conditions

3.1 The evaluations of chiral ligands

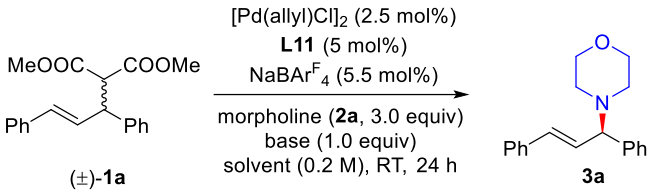


Entry	L	Yield (%)[a]	er (%)[b]
1	**L1**	37	50:50
2	**L2**	4	55:45
3	**L3**	10	30:70
4	**L4**	32	75:25
5	**L5**	34	19:81
6	**L6**	30	72:28
7	**L7**	41	69:31
8	**L8**	76	40:60
9	**L9**	12	75:25
10	**L10**	72	58:42
11	**L11**	10	94:6
12	**L12**	64	24:76

13	**L13**	10	26:74
14	**L14**	9	55:45
15	**L15**	77	58:42

[a]Determined by crude ^{1}H NMR. [b]Determined by HPLC analysis.

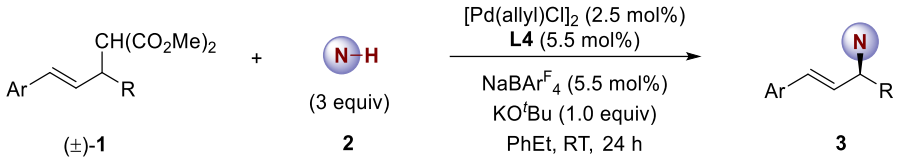
3.2 The evaluations of other conditions



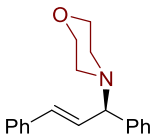
Entry	Base	Solvent	Yield (%)[a]	er (%)[b]
1	Cs_2CO_3	MTBE	22	95:5
2	Cs_2CO_3	mesitylene	61	90:10
3	Cs_2CO_3	cyclohexane	69	82:18
4	Cs_2CO_3	PhOMe	59	80:20
5	Cs_2CO_3	DME	n.d.	
6	Cs_2CO_3	DCE	38	62:38
7	Cs_2CO_3	MeOH	18	53:47
8[c]	Cs_2CO_3	PhEt	56	91:9
9[c]	Na_2CO_3	PhEt	26	50:50
10[c]	K_2CO_3	PhEt	28	50:50
11[c]	Et_3N	PhEt	28	50:50
12[c]	NaO^{t}Bu	PhEt	76	50:50
13[c]	LiO^{t}Bu	PhEt	76	50:50
14[c]	KHMDS	PhEt	95	57:43
15[c,d]	KO^{t}Bu	PhEt	86	95:5

[a]Determined by crude ^{1}H NMR. [b]Determined by HPLC analysis. [c]The reaction concentration was 0.5 M. [d]Isolated yield. n.d., not detected.

4. General procedure for the asymmetric C-C σ bond aminations

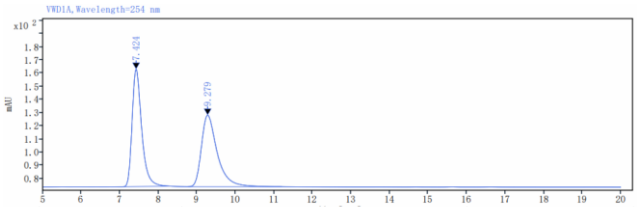


General procedure: in a nitrogen-filled glovebox, to a 4 mL vial with $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L11** (4.8 mg, 0.0055 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol) were added alkene **1** (0.10 mmol), KO^{t}Bu (11 mg, 0.10 mmol) and dry PhEt (0.20 mL) sequentially. Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2** (0.30 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3**.

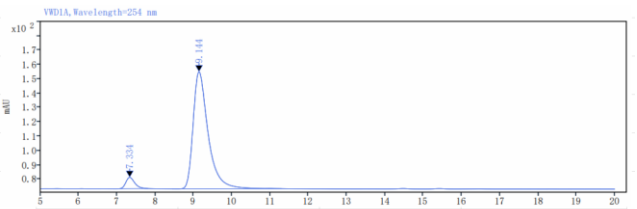


(*R*,*E*)-4-(1,3-Diphenylallyl)morpholine (3a)

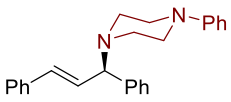
Known compound[8]. Yellow oil, 86% yield, $[\alpha]_D^{25}$ -3.3 (*c* 0.46, $CHCl_3$) for 95:5 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.51 – 7.37 (m, 2H), 7.37 – 7.16 (m, 8H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.28 (dd, *J* = 15.8, 8.9 Hz, 1H), 3.79 (d, *J* = 8.9 Hz, 1H), 3.70 (t, *J* = 4.8 Hz, 4H), 2.54 (d, *J* = 11.8 Hz, 2H), 2.39 (dt, *J* = 11.8, 4.8 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 141.6, 136.8, 131.6, 131.5, 128.8, 128.6, 128.1, 127.6, 127.4, 126.5, 74.9, 67.2, 52.3. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{19}H_{22}ON^{\oplus}$ 280.1696, found 280.1696. HPLC analysis: chiral OJ-H column; detected at 254 nm, 40 °C; 10% ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 7.3 min (minor), 9.1 min (major).



Peak	Retention time/min	Area%
1	7.424	49.80
2	9.279	50.20

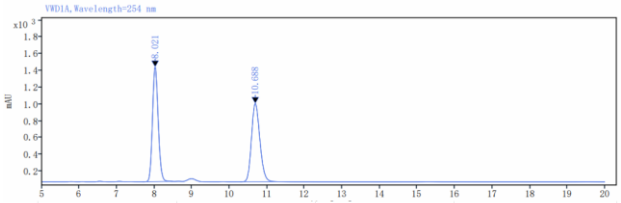


Peak	Retention time/min	Area%
1	7.334	5.37
2	9.144	94.63

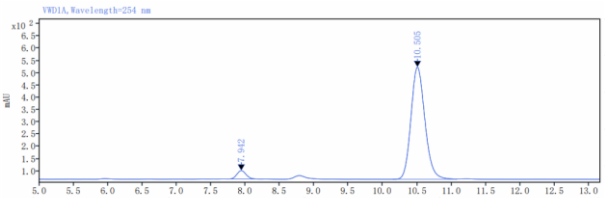


(*R*,*E*)-1-(1,3-Diphenylallyl)-4-phenylpiperazine (**3b**)

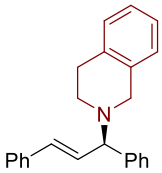
[Pd(allyl)Cl]$_2$ (4 mol%), **L11** (8.8 mol%), NaBAr$^F{}_4$ (8.8 mol%) and **2b** (5 equiv) were used. Yellow oil, 52% yield, $[\alpha]_D^{25}$ -19.5 (*c* 0.65, $CHCl_3$) for 95:5 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.18 (m, 10H), 6.95 – 6.88 (m, 2H), 6.84 (td, *J* = 7.2, 1.0 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.34 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H), 3.19 (t, *J* = 5.1 Hz, 4H), 2.72 (dt, *J* = 10.7, 5.0 Hz, 2H), 2.57 (dt, *J* = 11.0, 5.0 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 151.4, 141.9, 136.9, 131.7, 131.5, 129.2, 128.8, 128.6, 128.1, 127.6, 127.4, 126.5, 119.6, 116.0, 74.4, 51.6, 49.3. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{25}H_{27}N_2^{\oplus}$ 355.2169, found 355.2170. HPLC analysis: chiral OD-H column; detected at 254 nm, 40 °C; 10% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 7.9 min (minor), 10.5 min (major).



Peak	Retention time/min	Area%
1	8.021	50.01
2	10.688	49.99

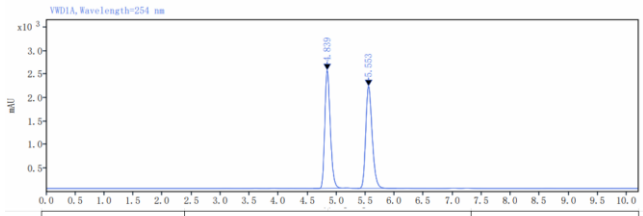


Peak	Retention time/min	Area%
1	7.942	4.69
2	10.505	95.31

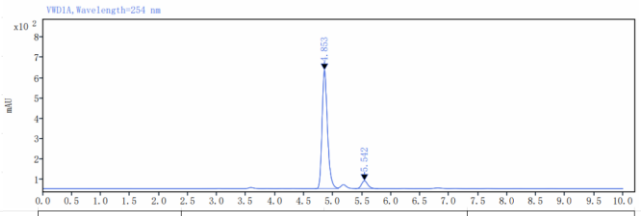


(*R*,*E*)-2-(1,3-Diphenylallyl)-1,2,3,4-tetrahydroisoquinoline (**3c**)

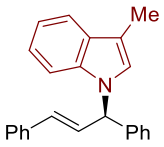
Known compound[9].White solid, 65% yield, $[\alpha]_D^{25}$ -19.5 (*c* 0.80, $CHCl_3$) for 93:7 er; ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.57 – 7.47 (m, 2H), 7.47 – 7.21 (m, 8H), 7.09 – 7.19 (m, 3H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.44 (dd, *J* = 15.8, 8.8 Hz, 1H), 4.06 (d, *J* = 8.8 Hz, 1H), 3.84 (d, *J* = 15.1 Hz, 1H), 3.64 (d, *J* = 15.1 Hz, 1H), 2.91 (q, *J* = 6.5 Hz, 2H), 2.82 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 142.2, 136.9, 135.1, 134.7, 131.8, 131.3, 128.8, 128.7, 128.6, 128.0, 127.6, 127.4, 126.9, 126.5, 126.2, 125.7, 73.9, 54.8, 48.6, 29.2. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{24}N^{\oplus}$ 326.1903, found 326.1904. HPLC analysis: chiral AD-H column; detected at 254 nm, 25 °C; 5% ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 4.9 min (major), 5.5 min (minor).



Peak	Retention time/min	Area%
1	4.839	49.59
2	5.553	50.41

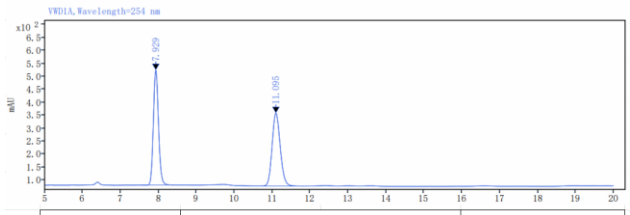


Peak	Retention time/min	Area%
1	4.853	92.99
2	5.542	7.01

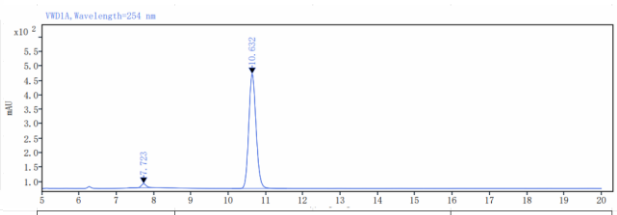


(*R*,*E*)-1-(1,3-Diphenylallyl)-3-methyl-1*H*-indole (3d)

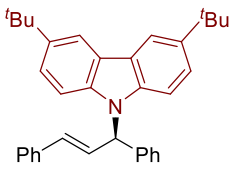
Known compound.[10] Yellow oil, 60% yield, $[\alpha]_D^{25}$ -57.1 (*c* 0.48, $CHCl_3$) for 98:2 er; ^1H NMR (500 MHz, chloroform-*d*) δ 7.66 – 7.56 (m, 1H), 7.40 – 7.22 (m, 11H), 7.20 – 7.08 (m, 2H), 6.96 (s, 1H), 6.70 (dd, *J* = 15.9, 6.5 Hz, 1H), 6.41 (dd, *J* = 15.9, 1.5 Hz, 1H), 6.24 (d, *J* = 6.5 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 139.9, 136.5, 136.3, 133.5, 129.2, 128.8, 128.7, 128.1, 128.0, 127.9, 127.6, 126.8, 123.9, 121.6, 119.1, 119.0, 110.9, 110.0, 61.4, 9.8. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{22}N^{\oplus}$ 324.1747, found 324.1750. HPLC analysis: chiral OD-H column; detected at 254 nm, 40 °C; 10% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 7.7 min (minor), 10.6 min (major).



Peak	Retention time/min	Area%
1	7.929	49.85
2	11.095	50.15



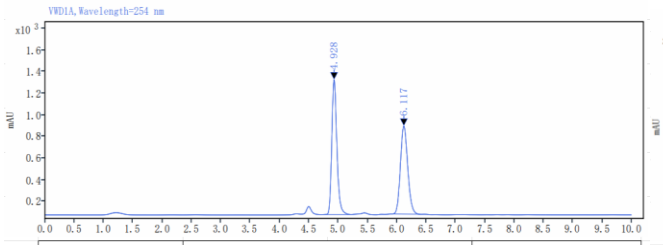
Peak	Retention time/min	Area%
1	7.723	2.48
2	10.632	97.52



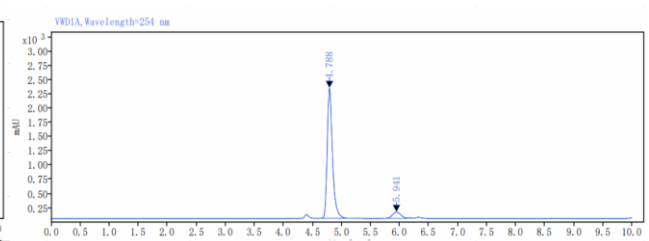
(*R*,*E*)-3,6-Di-*tert*-butyl-9-(1,3-diphenylallyl)-9*H*-carbazole (3e)

Reaction time was 12 h. Colorless oil, 51% yield, $[\alpha]_D^{25}$ -2.7 (*c* 0.51, $CHCl_3$) for 93:7 er; ^1H NMR (500 MHz, chloroform-*d*) δ 8.11 (s, 2H), 7.44 – 7.16 (m, 14H), 6.91 (dd, *J* = 15.9, 7.1, 1H), 6.59 (d,

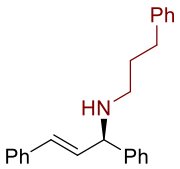
J = 15.9 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 1.44 (s, 18H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 141.9, 139.4, 138.6, 136.4, 134.0, 128.7, 128.6, 128.0, 127.7, 127.4, 126.8, 126.3, 123.5, 123.3, 116.3, 109.8, 60.0, 34.7, 32.1 (two aromatic carbon signals were not observed). HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{35}H_{37}NNa^{\oplus}$ 494.2818, found 494.2822. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 °C; 10% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 4.8 min (major), 5.9 min (minor).



Peak	Retention time/min	Area%
1	4.928	51.61
2	6.117	48.39

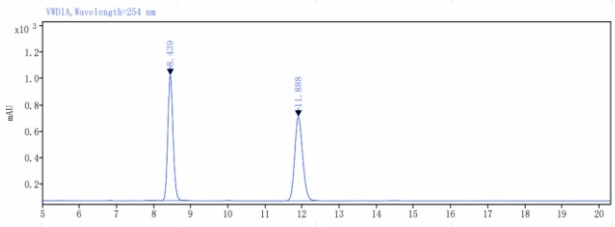


Peak	Retention time/min	Area%
1	4.788	92.74
2	5.941	7.26

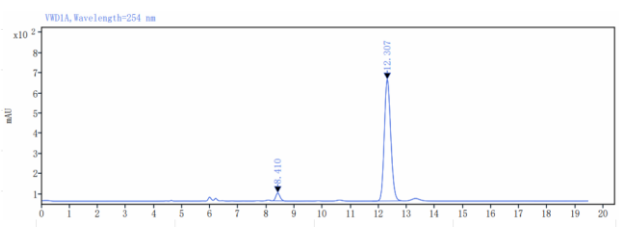


(*R*,*E*)-1,3-Diphenyl-*N*-(3-phenylpropyl)prop-2-en-1-amine (3f)

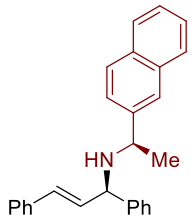
p-Xylene was used as the solvent. Yellow oil, 84% yield, $[\alpha]_D^{25}$ -2.0 (*c* 0.90, $CHCl_3$) for 96:4 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.54 – 7.08 (m, 15H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.33 (d, *J* = 7.4 Hz, 1H), 2.85 – 2.45 (m, 4H), 1.84 (m, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.1, 142.2, 137.0, 132.8, 130.2, 128.7, 128.6, 128.45, 128.39, 127.5, 127.4, 127.3, 126.5, 125.8, 65.7, 47.3, 33.7, 31.9. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{26}N^{\oplus}$ 328.2060, found 328.2061. HPLC analysis: chiral OD-H column; detected at 254 nm, 40 °C; 10% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 8.4 min (minor), 12.3 min (major).



Peak	Retention time/min	Area%
1	8.439	49.69
2	11.888	50.31

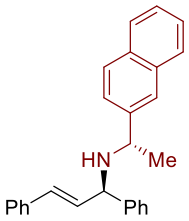


Peak	Retention time/min	Area%
1	8.410	4.02
2	12.307	95.98



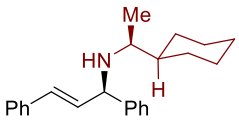
(*R*,*E*)-*N*-((*R*)-1-(Naphthalen-2-yl)ethyl)-1,3-diphenylprop-2-en-1-amine (**3g**)

p-Xylene was used as the solvent. Yellow oil, 77% yield, $[\alpha]_D^{25}$ -7.4 (*c* 0.98, $CHCl_3$) for >20:1 dr; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 – 7.75 (m, 3H), 7.63 (d, *J* = 1.7 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.39 – 7.32 (m, 2H), 7.32 – 7.20 (m, 7H), 7.20 – 7.13 (m, 1H), 6.44 (dd, *J* = 15.9, 1.2 Hz, 1H), 6.29 (dd, *J* = 15.9, 6.6 Hz, 1H), 4.20 (dd, *J* = 6.6, 1.2 Hz, 1H), 3.82 (q, *J* = 6.6 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.0, 137.1, 133.6, 133.2, 132.9, 129.7, 128.7, 128.5, 128.4, 127.8, 127.7, 127.6, 127.4, 127.3, 126.4, 126.0, 125.6, 125.5, 125.0, 62.3, 55.0, 24.6 (one aromatic carbon signal was not observed because of overlapping). HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{27}H_{26}N^{\oplus}$ 364.2060, found 364.2061.



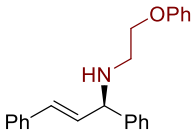
(*R*,*E*)-*N*-((*S*)-1-(Naphthalen-2-yl)ethyl)-1,3-diphenylprop-2-en-1-amine (**3h**)

p-Xylene was used as the solvent. Yellow oil, 81% yield, $[\alpha]_D^{25}$ -131.8 (*c* 0.48, $CHCl_3$) for 9:1 dr; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 – 7.79 (m, 3H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.41 – 7.35 (m, 4H), 7.34 – 7.28 (m, 4H), 7.27 – 7.19 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.27 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.19 (d, *J* = 8.0 Hz, 1H), 4.14 (q, *J* = 6.6 Hz, 1H), 1.47 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.4, 143.0, 137.0, 133.5, 132.9, 132.0, 131.1, 128.58, 128.57, 128.4, 127.8, 127.7, 127.5, 127.20, 127.18, 126.4, 126.0, 125.5, 124.8, 62.1, 55.2, 24.5 (one aromatic carbon signal was not observed because of overlapping). HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{27}H_{26}N^{\oplus}$ 364.2060, found 364.2060.



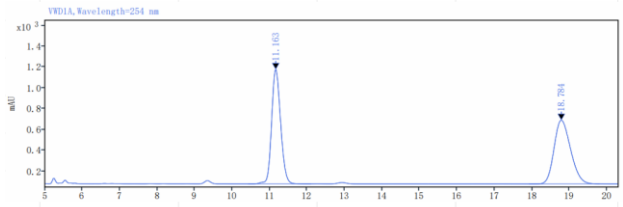
(*R*,*E*)-*N*-((*S*)-1-Cyclohexylethyl)-1,3-diphenylprop-2-en-1-amine (**3i**)

p-Xylene was used as the solvent. Yellow oil, 51% yield, $[\alpha]_D^{25}$ +20.5 (*c* 0.76, $CHCl_3$) for 13:1 dr; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 6H), 7.29 – 7.23 (m, 3H), 7.22 – 7.16 (m, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.1 Hz, 1H), 4.49 (d, *J* = 7.1 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.76 – 1.69 (m, 3H), 1.67 – 1.60 (m, 2H), 1.36 – 1.05 (m, 5H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.99 – 0.90 (m, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.4, 137.2, 133.8, 129.6, 128.5, 127.6, 127.4, 127.1, 126.5, 62.7, 54.3, 43.5, 29.8, 28.4, 26.9, 26.8, 26.6, 17.0 (one aromatic carbon signal was not observed because of overlapping). HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{30}N^{\oplus}$ 320.2373, found 320.2374.

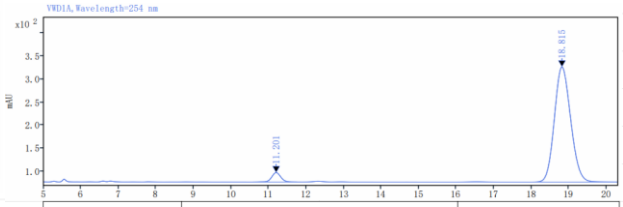


(*R*,*E*)-*N*-(2-Phenoxyethyl)-1,3-diphenylprop-2-en-1-amine (**3j**)

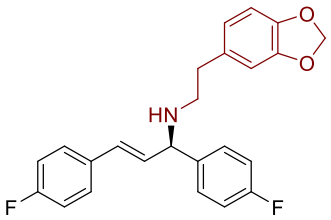
$[Pd(allyl)Cl]_2$ (4 mol%), **L11** (8.8 mol%), $NaBAr^F{}_4$ (8.8 mol%) and **2j** (5 equiv) with *p*-xylene as the solvent were used. Yellow oil, 65% yield, $[\alpha]_D^{25}$ +1.2 (*c* 0.58, $CHCl_3$) for 96:4 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 4H), 7.31 – 7.23 (m, 5H), 7.23 – 7.17 (m, 1H), 6.97 – 6.92 (m, 1H), 6.92 – 6.88 (m, 2H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.44 (d, *J* = 7.5 Hz, 1H), 4.10 (t, *J* = 5.2 Hz, 2H), 3.05 (dt, *J* = 12.7, 5.2 Hz, 1H), 2.95 (dt, *J* = 12.7, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 158.9, 142.8, 137.0, 132.6, 130.4, 129.5, 128.7, 128.6, 127.6, 127.42, 127.41, 126.5, 120.9, 114.6, 67.4, 65.6, 46.7. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{24}ON^{\oplus}$ 330.1852, found 330.1853. HPLC analysis: chiral OD-H column; detected at 254 nm, 40 °C; 20% ^{i}PrOH in *n*-hexane; flow = 0.8 mL/min; Retention time: 11.2 min (minor), 18.8 min (major).



Peak	Retention time/min	Area%
1	11.163	49.47
2	18.784	50.53

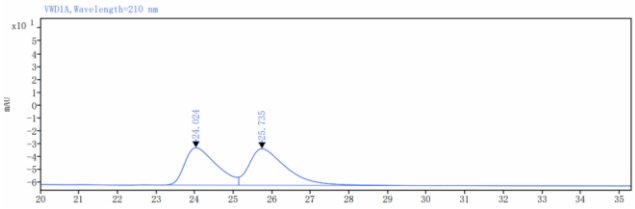


Peak	Retention time/min	Area%
1	11.201	4.29
2	18.815	95.71

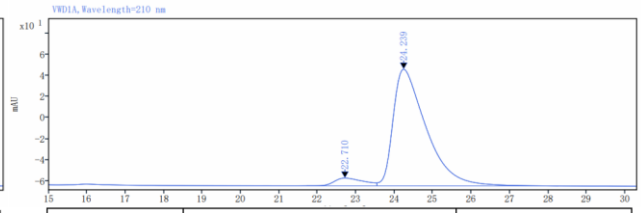


(*R*,*E*)-*N*-(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)-1,3-bis(4-fluorophenyl)prop-2-en-1-amine (**3k**)

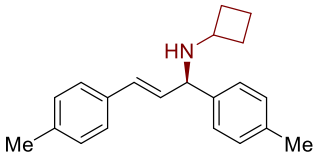
$[Pd(allyl)Cl]_2$ (4 mol%), **L11** (8.8 mol%) and $NaBAr^F{}_4$ (8.8 mol%) with *p*-xylene as the solvent were used. Yellow oil, 55% yield, $[\alpha]_D^{25}$ -5.6 (*c* 0.49, $CHCl_3$) for 95:5 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 (tdd, *J* = 7.0, 5.3, 2.2 Hz, 4H), 7.05 – 6.93 (m, 4H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69 – 6.61 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 7.4 Hz, 1H), 5.92 (s, 2H), 4.32 (d, *J* = 7.4 Hz, 1H), 2.91 – 2.69 (m, 4H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 163.2 (d, *J* = 33.0 Hz), 161.2 (d, *J* = 31.5 Hz), 147.8, 146.0, 138.5, 133.7, 133.0 (d, *J* = 3.4 Hz), 132.2, 129.2, 128.8 (d, *J* = 7.9 Hz), 128.0 (d, *J* = 8.1 Hz), 121.6, 115.6 (d, *J* = 1.7 Hz), 115.4, 109.1, 108.3, 100.9, 64.9, 49.0, 36.1. ^{19}F NMR (376 MHz, chloroform-*d*) δ -114.30 (s), -115.25 (s). HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{22}O_2NF_2{}^{\oplus}$ 394.1613, found 394.1617. HPLC analysis: chiral OJ-H column; detected at 254 nm, 40 °C; 20% ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 22.7 min (minor), 24.2 min (major).



Peak	Retention time/min	Area%
1	24.024	46.88
2	25.735	53.12



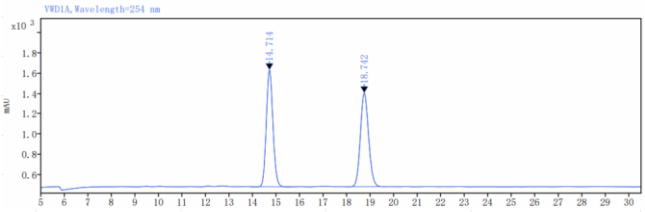
Peak	Retention time/min	Area%
1	22.710	5.41
2	24.239	94.59



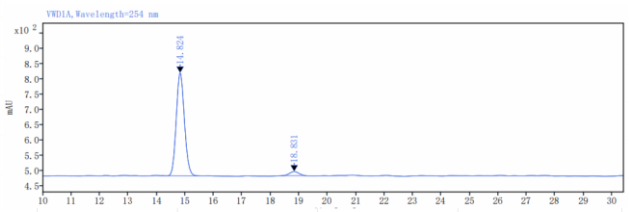
(*R*,*E*)-*N*-(1,3-Di-*p*-tolylallyl)cyclobutanamine (**3l**)

Yellow oil, 61% yield, $[\alpha]_D^{25}$ -1.5 (*c* 0.61, $CHCl_3$) for 96:4 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.29 – 7.21 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.8, 7.7 Hz, 1H), 4.30 (d, *J* = 7.6 Hz, 1H), 3.35 – 3.15 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.27 – 2.12 (m, 2H), 1.75 – 1.65 (m, 3H), 1.60 – 1.52 (m, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 140.2, 137.2, 136.9, 134.3, 131.9, 129.8, 129.3, 129.2, 127.3, 126.4, 62.8, 51.8,

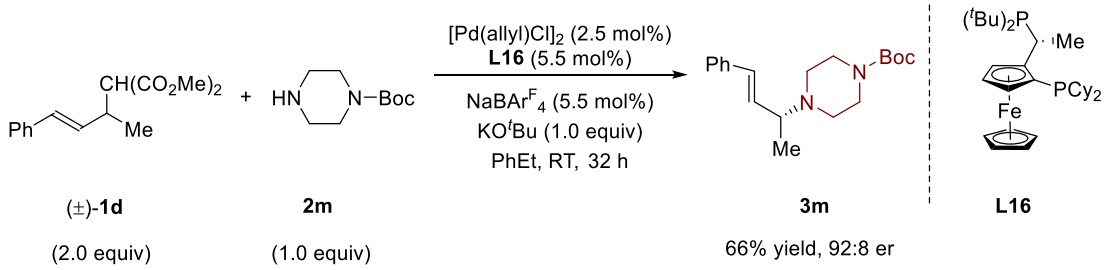
31.74, 31.71, 21.24, 21.17,14.8. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{21}H_{26}N^{\oplus}$ 292.2060, found 292.2059. HPLC analysis: chiral AD-H column; detected at 254 nm, 30 °C; 1% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 14.8 min (major), 18.8 min (minor).



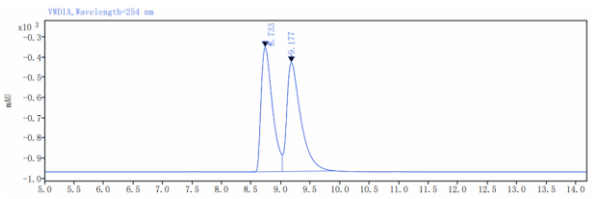
Peak	Retention time/min	Area%
1	14.714	50.14
2	18.742	49.86



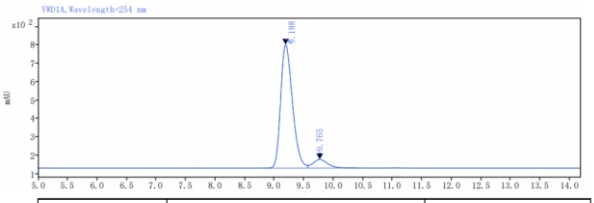
Peak	Retention time/min	Area%
1	14.824	95.72
2	18.831	4.28



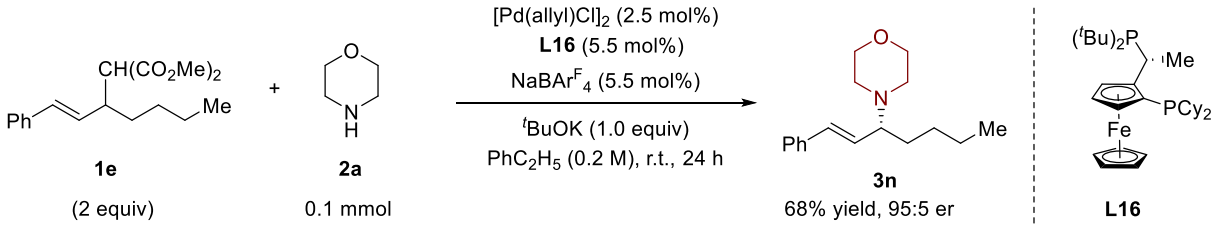
***tert*-Butyl (*S*,*E*)-4-(4-phenylbut-3-en-2-yl)piperazine-1-carboxylate** (**3m**). In a nitrogen-filled glovebox, to a 4 mL vial with $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L16** (3.0 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBArF_4$, 4.9 mg, 0.0055 mmol), alkene **1d** (52 mg, 0.20 mmol), amine **2m** (0.10 mmol) and KO^{t}Bu (11 mg, 0.10 mmol) was added dry PhEt (0.20 mL). The resulting mixture was stirred at room temperature for 32 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3m** as a light-yellow oil (21 mg) in 66% yield. $[\alpha]_D^{25}$ +49.9 (c 1.01, $CHCl_3$) for 92:8 er. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 8.0 Hz, 1H), 3.44 (t, *J* = 5.2 Hz, 4H), 3.12 – 3.06 (m, 1H), 2.61 – 2.43 (m, 7.5 Hz, 4H), 1.45 (s, 9H), 1.26 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 154.8, 137.0, 131.9, 131.2, 128.6, 127.5, 126.3, 79.6, 62.6, 49.8, 28.5, 17.7 (one alkyl carbon signal was not observed because of overlapping). HRMS (EI): $[M]^{\oplus}$ calcd for $C_{19}H_{28}N_2O_2^{\oplus}$ 316.2145, found 316.2141. HPLC analysis: Chiracel IE column; detected at 254 nm, 25 ºC; 2% ^{i}PrOH in *n*-hexane; flow = 1.5 mL/min; Retention time: 9.2 min (major), 9.8 min (minor).



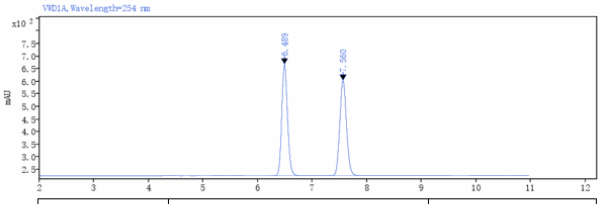
Peak	Retention time/min	Area%
1	8.733	47.99
2	9.177	52.01



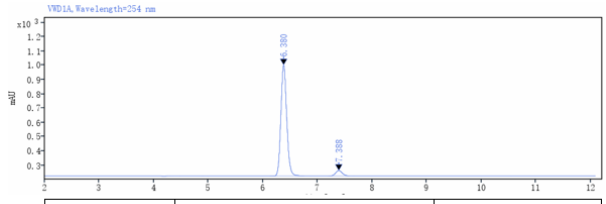
Peak	Retention time/min	Area%
1	9.188	92.00
2	9.765	8.00



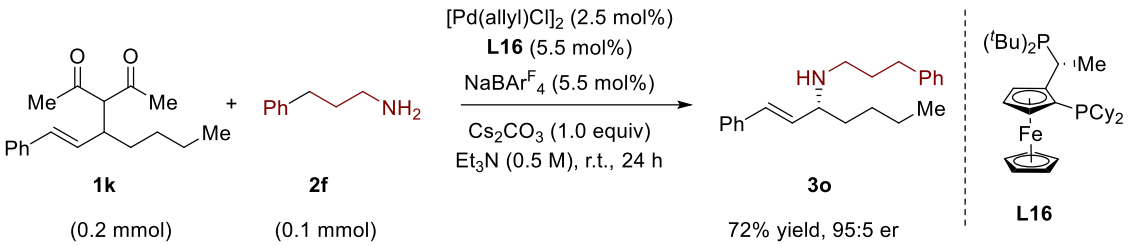
(*S*,*E*)-1-(1-phenylhept-1-en-3-yl)piperazine (**3n**). Known compound.[11] In a nitrogen-filled glovebox, to a 4 mL vial were added [Pd(allyl)Cl]$_2$ (0.9 mg, 0.0025 mmol), **L16** (3.0 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr$^F_4$, 4.9 mg, 0.0055 mmol), racemic alkene **1e** (0.20 mmol), KO^{t}Bu (11 mg, 0.10 mmol) and dry PhEt (0.50 mL). Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2a** (0.10 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3n** as a colorless oil in 68% yield. $[\alpha]_D^{25}$ +15.1 (c 0.88, $CHCl_3$) for 95:5 er.^{1}H NMR (500 MHz, chloroform-*d*) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.10 (dd, *J* = 15.9, 9.1 Hz, 1H), 3.77 – 3.65 (m, 4H), 2.89 – 2.79 (m, 1H), 2.71 – 2.47 (m, 4H), 1.78 – 1.67 (m, 1H), 1.55 – 1.45 (m, 1H), 1.39 – 1.20 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 137.0, 132.9, 129.9, 128.6, 127.5, 126.4, 68.5, 67.4, 50.7, 31.7, 28.6, 22.9, 14.2. HPLC analysis: Chiracel OD-H column; detected at 254 nm, 40 ºC; 20% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 6.4 min (major), 7.4 min (minor).



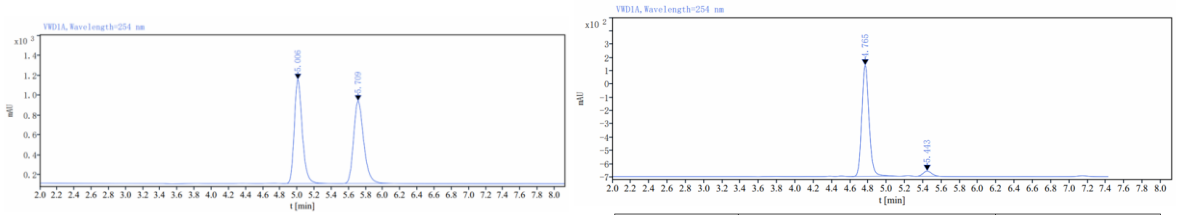
Peak	Retention time/min	Area%
1	6.489	49.95
2	7.560	50.05



Peak	Retention time/min	Area%
1	6.380	94.85
2	7.388	5.15

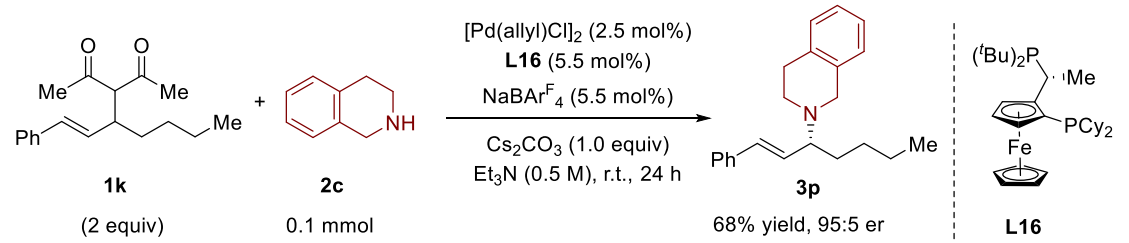


(*S*,*E*)-1-Phenyl-*N*-(3-phenylpropyl)hept-1-en-3-amine (**3o**). In a nitrogen-filled glovebox, to a 4 mL vial were added $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L16** (3.0 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol), racemic alkene **1k** (0.20 mmol), Cs_2CO_3 (33 mg, 0.10 mmol) and dry Et_3N (0.20 mL). Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2f** (0.10 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3o** as a light yellow oil in 72% yield; $[\alpha]_D^{25}$ +42.9 (*c* 0.74, $CHCl_3$) for 95:5 er; ^1H NMR (400 MHz, chloroform-*d*) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 - 7.20 (m, 3H), 7.20 - 7.14 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.4 Hz, 1H), 3.23 – 3.04 (m, 1H), 2.79 – 2.52 (m, 4H), 1.87 – 1.79 (m, 2H), 1.65 – 1.43 (m, 2H), 1.37 – 1.20 (m, 5H), 0.98 – 0.81 (m, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 142.2, 137.2, 133.4, 131.1, 128.6, 128.44, 128.39, 127.4, 126.4, 125.8, 61.6, 47.1, 35.9, 33.8, 31.9, 28.4, 22.8, 14.1. HRMS (EI): $[M]^{\oplus}$ calcd for $C_{22}H_{30}N^{\oplus}$ 308.2373, found 308.2371. HPLC analysis: Chiracel OD-H column; detected at 254 nm, 40 ºC; 20% ^{i}PrOH in *n*-hexane; flow = 0.8 mL/min; Retention time: 4.8 min (major), 5.4 min (minor).

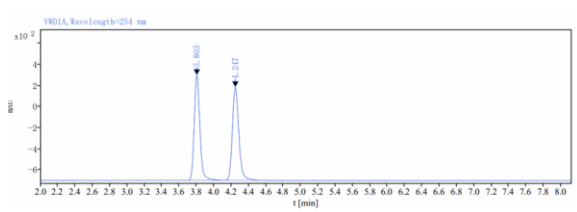


Peak	Retention time/min	Area%
1	5.006	49.90
2	5.709	50.10

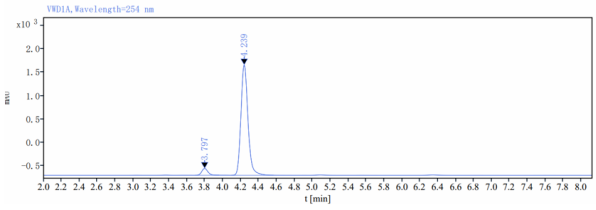
Peak	Retention time/min	Area%
1	4.765	94.94
2	5.443	5.06



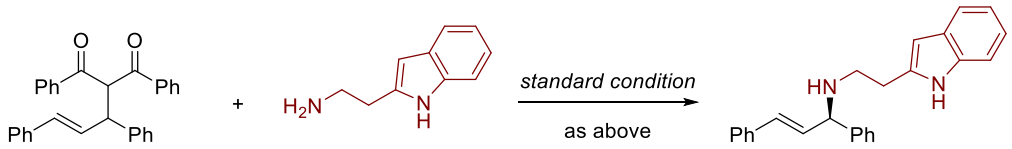
(*S*,*E*)-2-(1-Phenylhept-1-en-3-yl)-1,2,3,4-tetrahydroisoquinoline (**3p**). In a nitrogen-filled glovebox, to a 4 mL vial were added $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L16** (3.0 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol), racemic alkene **1k** (0.20 mmol), Cs_2CO_3 (32.5 mg, 0.10 mmol) and dry Et_3N (0.20 mL). Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2c** (0.10 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3p** as a light yellow oil in 68% yield; $[\alpha]_D^{25}$ +19.5 (*c* 0.76, $CHCl_3$) for 95:5 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.14 – 7.07 (m, 3H), 7.05 – 7.00 (m, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.86 (d, *J* = 14.9 Hz, 1H), 3.79 (d, *J* = 14.9 Hz, 1H), 3.20 – 3.10 (m, 1H), 3.05 – 2.97 (m, 1H), 2.91 (t, *J* = 5.7 Hz, 2H), 2.86 – 2.76 (m, 1H), 1.94 – 1.80 (m, 1H), 1.74 – 1.64 (m, 1H), 1.43 – 1.23 (m, 4H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 137.0, 134.9, 134.5, 133.1, 129.4, 128.73, 128.67, 127.6, 126.8, 126.4, 126.1, 125.7, 67.5, 52.8, 47.1, 32.1, 29.3, 28.8, 22.9, 14.2. HRMS (EI): $[M]^{\oplus}$ calcd for $C_{22}H_{28}N^{\oplus}$ 306.2216, found 306.2211. HPLC analysis: Chiracel AD-H column; detected at 254 nm, 25 ºC; 5% ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 3.8 min (minor), 4.2 min (major).



Peak	Retention time/min	Area%
1	3.803	49.93
2	4.247	50.07



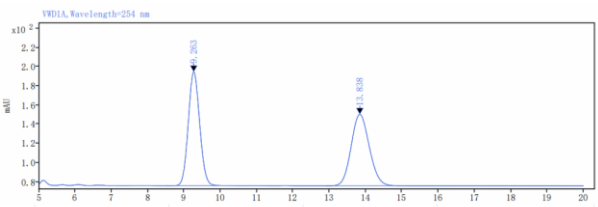
Peak	Retention time/min	Area%
1	3.797	5.03
2	4.239	94.97



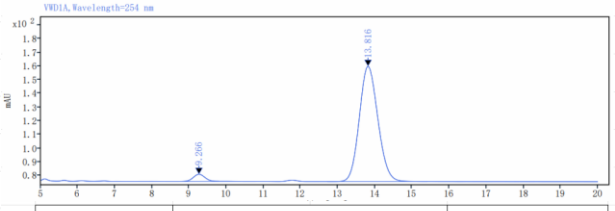
(±)-**1f** **2** (3 equiv) **3q**

(*R*,*E*)-*N*-(2-(1*H*-Indol-2-yl)ethyl)-1,3-diphenylprop-2-en-1-amine (**3q**). The procedure for this transformation was identical to that described above for the amination of allylic C-C bonds, except that *rac*-**1f** was used as the electrophile, Cs_2CO_3 (1 equiv) was used as the base and the reaction was stirred at 0 °C. Light yellow solid, 67% yield, $[\alpha]_D^{25}$ -11.4 (*c* 0.95, $CHCl_3$) for 96:4 er; ^{1}H NMR (400

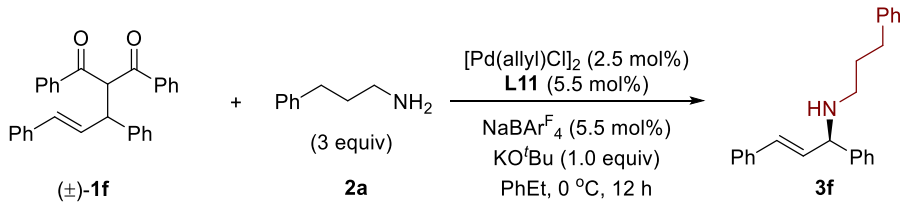
MHz, chloroform-*d*) δ 7.98 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.27 (m, 8H), 7.25 – 7.16 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J* = 15.9, 7.4 Hz, 1H), 4.38 (d, *J* = 7.4 Hz, 1H), 3.01 (m, 3H), 2.97 – 2.85 (m, 1H), 2.28 (br s, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.0, 137.0, 136.4, 132.8, 130.2, 128.6, 128.5, 127.51, 127.46, 127.4, 127.3, 126.5, 122.1, 122.0, 119.3, 119.0, 114.0, 111.2, 65.6, 47.6, 25.8. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{25}H_{25}N_2^{\oplus}$ 353.2012, found 353.2015. HPLC analysis: chiral OD-H column; detected at 254 nm, 40 °C; 20% ^{i}PrOH in *n*-hexane; flow = 1.5 mL/min; Retention time: 9.3 min (minor), 13.8 min (major).



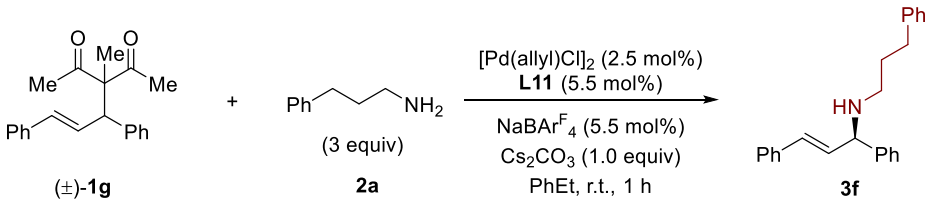
Peak	Retention time/min	Area%
1	9.263	50.07
2	13.838	49.93



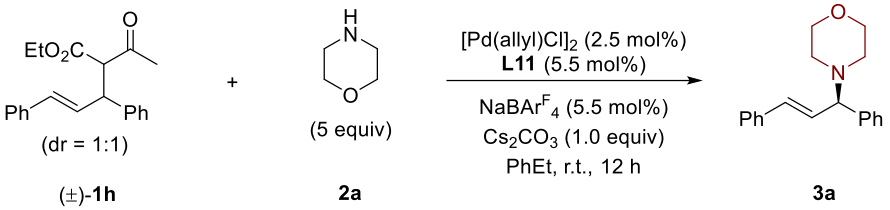
Peak	Retention time/min	Area%
1	9.266	3.67
2	13.816	96.33



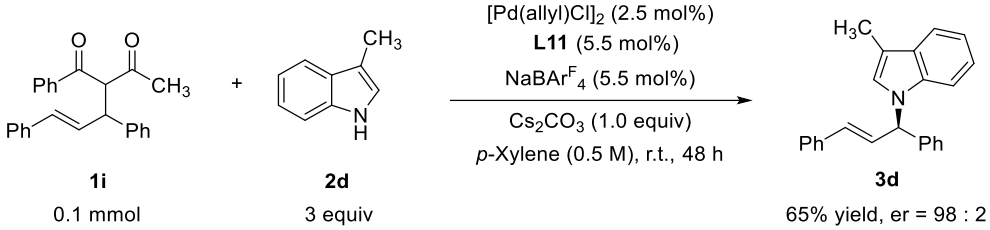
The procedure for this transformation was identical to that described above for the amination of allylic C-C bonds, except that *rac*-**3f** was used as the electrophile and the reaction was stirred at 0 °C for 12 h. The product **3f** was isolated in 52% yield and with 94:6 er.



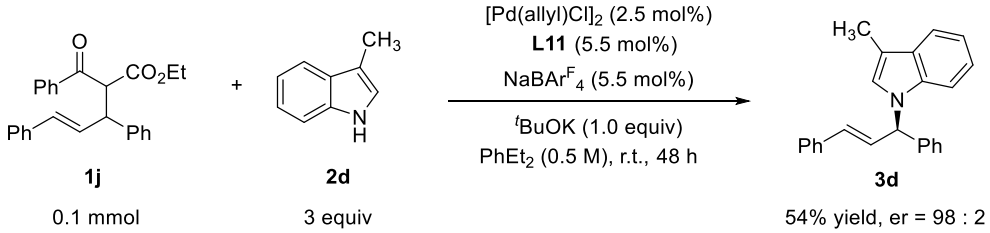
The procedure for this transformation was identical to that described above for the amination of allylic C-C bonds, except that *rac*-**1g** was used as the electrophile and Cs_2CO_3 was used as the base. The reaction time was 1 h and the product **3f** was isolated in 67% yield and with 93:7 er.



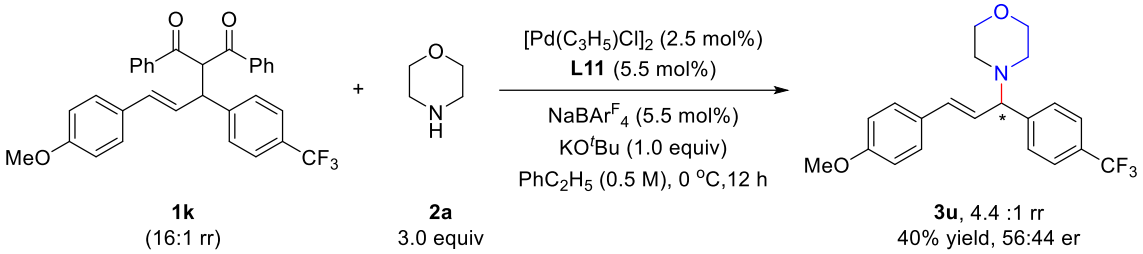
The procedure for this transformation was identical to that described above for the amination of allylic C–C bonds, except that *rac*-**1h** as the electrophile, **2a** (5 equiv) as the nucleophile and Cs_2CO_3 as the base were used. The reaction time was 12 h and the product **3a** was isolated in 58% yield and with 94:6 er.



In a nitrogen-filled glovebox, to a 4 mL vial were added alkene **1i** (0.10 mmol), $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L11** (4.8 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol), Cs_2CO_3 (32.5 mg, 0.10 mmol), amine nucleophile **2d** (0.30 mmol) and dry *p*-Xylene (0.20 mL). Then the resulting mixture was stirred at room temperature for 48 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product. In this case, the product **3d** was isolated in 65% yield and with 98:2 er.

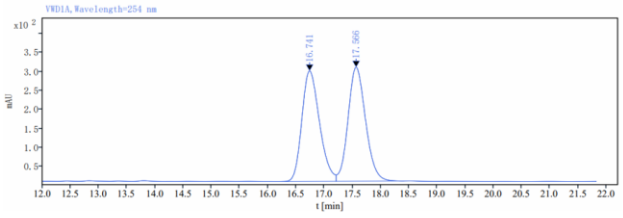


In a nitrogen-filled glovebox, to a 4 mL vial were added alkene **1j** (0.10 mmol), $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L11** (4.8 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol), KO^{t}Bu (11.2 mg, 0.10 mmol), amine nucleophile **2d** (0.30 mmol) and dry PhEt (0.20 mL). Then the resulting mixture was stirred at room temperature for 48 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product. In this case, the product **3d** was isolated in 54% yield and with 98:2 er.

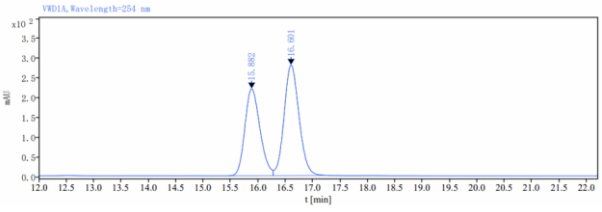


1k (16:1 rr) + **2a** 3.0 equiv → **3u**, 4.4 :1 rr, 40% yield, 56:44 er

(*E*)-4-(3-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)allyl)morpholine (**3u**). The procedure for this transformation was identical to that described above for the amination of allylic C-C bonds, except that *rac*-**1k** was used as the electrophile and the reaction was stirred at 0 °C for 12 h. The regioselectivity of the products was 4.4:1 and the two regioisomers could be isolated from each other. The pure product **3u** was isolated in 40% yield and with 56:44 er as a yellow oil. $[\alpha]_D^{25}$ +1.8 (*c* 0.76, $CHCl_3$) for 56:44 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.28 (m, 2H), 6.93 – 6.85 (m, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.39 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.80 (s, 3H), 3.77 (d, *J* = 8.8 Hz, 1H), 3.71 (t, *J* = 4.7 Hz, 4H), 2.58 – 2.46 (m, 2H), 2.44 – 2.34 (m, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 159.1, 140.3, 134.5, 133.4, 129.9, 129.3 (q, *J* = 32.6 Hz), 129.1, 126.6, 125.5 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.4 Hz), 114.2, 74.0, 67.2, 55.3, 52.2. ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.6. HRMS (ESI): [M-morpholine]$^{\oplus}$ calcd for $C_{17}H_{14}F_3O^{\oplus}$ 291.0991, found 291.0993. HPLC analysis: chiral (OD-H) + (OD-H) column (the two columns were connected to each other); detected at 254 nm, 25 °C; 2.0 % ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 15.9 min (minor), 16.6 min (major).

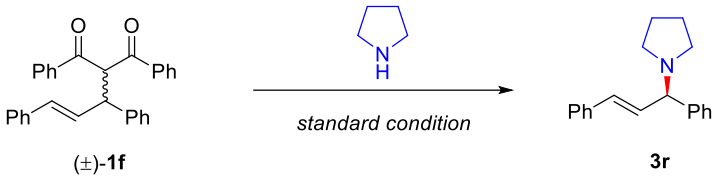


Peak	Retention time/min	Area
1	16.741	49.33
2	17.566	50.67



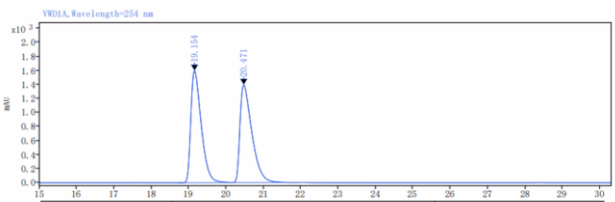
Peak	Retention time/min	Area
1	15.882	44.16
2	16.601	55.84

5. Applications of C-C bond aminations

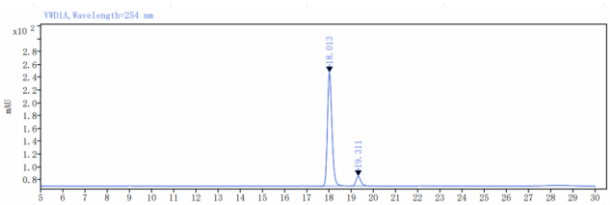


(±)-**1f** **3r**

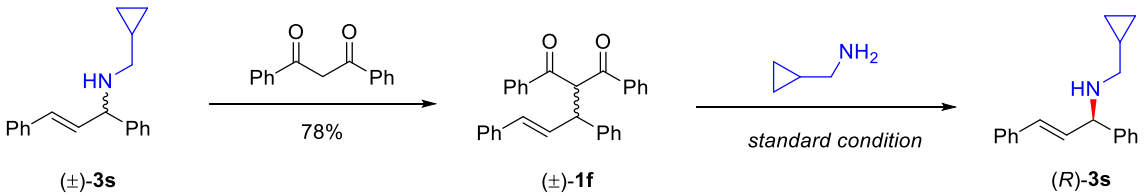
(*R*,*E*)-1-(1,3-Diphenylallyl)pyrrolidine (**3r**). Known compound[12]. The procedure for this transformation was identical to that described above for the amination of allylic C–C bonds, except that THF (0.10 mL) as the solvent and Cs_2CO_3 (1 equiv) as the base were used. The reaction was stirred at 0 °C for 12 h. Yellow oil, 70% yield, $[\alpha]_D^{25}$ -0.80 (*c* 0.62, $CHCl_3$) for 92:8 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.15 (m, 8H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.43 (dd, *J* = 15.8, 8.5 Hz, 1H), 3.77 (d, *J* = 8.5 Hz, 1H), 2.75 – 2.50 (m, 2H), 2.45 (m, 2H), 1.91 – 1.66 (m, 4H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.0, 137.1, 133.0, 130.1, 128.63, 128.55, 127.8, 127.5, 127.2, 126.5, 74.5, 53.2, 23.4. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{19}H_{22}N^{\oplus}$ 264.1747, found 264.1749. HPLC analysis: chiral (OD-H) + (OD-H) column (the two columns were connected to each other); detected at 254 nm, 25 °C; 0.5% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 18.0 min (major), 19.3 min (minor).



Peak	Retention time/min	Area%
1	19.154	50.02
2	20.471	49.98



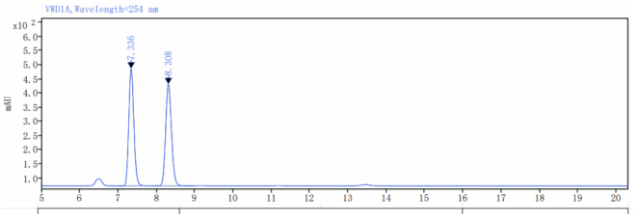
Peak	Retention time/min	Area%
1	18.013	91.72
2	19.311	8.28



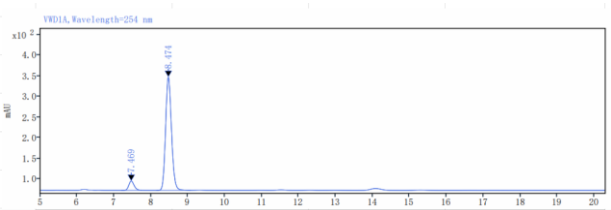
(±)-**3s** (±)-**1f** (*R*)-**3s**

(±)-**1f**. In a nitrogen-filled glovebox, to a 4 mL vial with amine (±)-**3s** (0.10 mmol), $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), dppf (3.3 mg, 0.0060 mmol) and Et_3N (30 mg, 0.30 mmol) were added 1,3-diphenylpropane-1,3-dione (0.30 mmol) and dry CH_3OH (0.40 mL). The resulting mixture was stirred at room temperature for 20 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure (±)-**1f** (33 mg) in 78% yield.

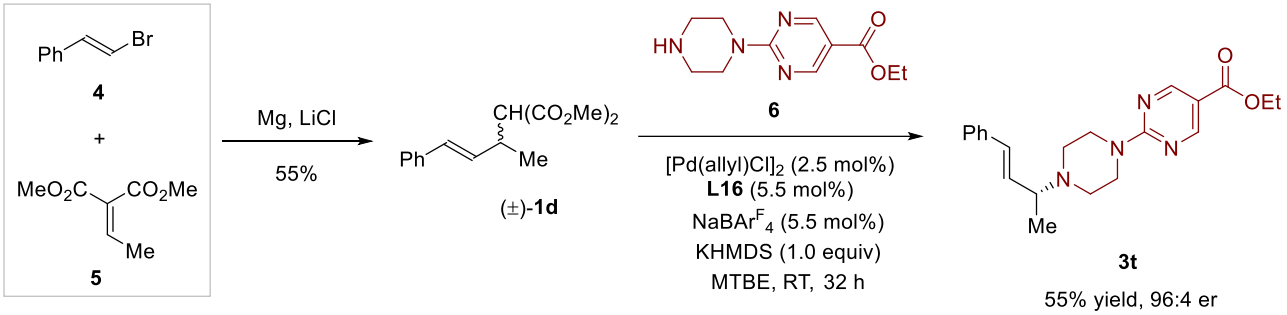
(*R*,*E*)-*N*-(Cyclopropylmethyl)-1,3-diphenylprop-2-en-1-amine (**3s**). The procedure for this transformation was identical to that described above for the amination of allylic C–C bonds, except that Cs_2CO_3 (1 equiv) was used as the base and the reaction was stirred at 0 °C for 12 h. Yellow oil, 65% yield, $[\alpha]_D^{25}$ +8.5 (*c* 0.73, $CHCl_3$) for 93:7 er; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.49 – 7.09 (m, 10H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.40 (d, *J* = 7.5 Hz, 1H), 2.54 (dd, *J* = 12.1, 6.8 Hz, 1H), 2.37 (dd, *J* = 12.1, 6.8 Hz, 1H), 1.00 (m, 1H), 0.54 – 0.40 (m, 2H), 0.09 (m, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 143.0, 137.0, 132.8, 130.2, 128.7, 128.6, 127.5, 127.4, 127.3, 126.5, 65.6, 52.9, 11.4, 3.5. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{19}H_{22}N^{\oplus}$ 264.1747, found 264.1747. HPLC analysis: chiral OD-H column; detected at 254 nm, 25 °C; 2% ^{i}PrOH in *n*-hexane; flow = 0.7 mL/min; Retention time: 7.5 min (minor), 8.5 min (major).



Peak	Retention time/min	Area%
1	7.336	49.99
2	8.308	50.01

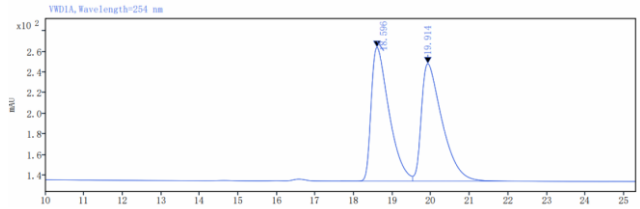


Peak	Retention time/min	Area%
1	7.469	6.82
2	8.474	93.18

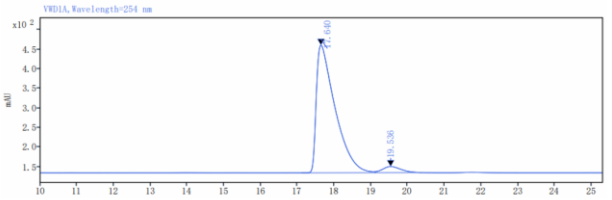


Dimethyl (*E*)-2-(4-phenylbut-3-en-2-yl)malonate ((±)-**1d**): To a dry 25 mL Schlenk tube with Mg (72 mg, 0.30 mmol) and LiCl (42 mg, 0.1 mmol) were added **4** (37 mg, 0.20 mmol) in THF (0.40 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 30 min and the solution gradually turned dark green. Then unsaturated ester **5** (16 mg, 0.10 mmol) in THF (0.20 mL) was added to the solution dropwise. The reaction continued to stir at 0 °C for 5 h. After this time, the reaction was quenched with EtOAc (5 mL) dropwise at 0 °C, diluted with water (5 mL), extracted by EtOAc (5 mL × 3), condensed and purified by preparative HPLC (IE column, *i*-PrOH:*n*-hexane = 20:80, 25 °C, 1.0 mL/min) to give racemic **1d** (14 mg) as a colorless oil in 55% yield.

Ethyl (*E*)-2-(4-(4-phenylbut-3-en-2-yl)piperazin-1-yl)pyrimidine-5-carboxylate (**3t**). In a nitrogen-filled glovebox, to a 4 mL vial with $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L16** (3.0 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBArF_4$, 4.9 mg, 0.0055 mmol), alkene **1d** (52 mg, 0.20 mmol), amine nucleophile **6** (0.10 mmol) and KHMDS (20 mg, 0.10 mmol) was added dry MTBE (0.20 mL). The resulting mixture was stirred at room temperature for 32 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3t** as a white solid (21 mg) in 55% yield. $[\alpha]_D^{25}$ +74.8 (c 0.93, $CHCl_3$) for 96:4 er. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.82 (s, 2H), 7.39 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 8.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.95 (t, *J* = 5.2 Hz, 4H), 3.15 (p, *J* = 6.8 Hz, 1H), 2.64 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 165.0, 162.1, 159.8, 136.9, 131.7, 131.4, 128.7, 127.6, 126.4, 112.5, 62.6, 60.6, 49.8, 44.2, 17.8, 14.4. HRMS (EI): $[M]^{\oplus}$ calcd for $C_{21}H_{26}N_4O_2^{\oplus}$ 366.2050, found 366.2055. HPLC analysis: Chiracel IE column; detected at 254 nm, 40 ºC; 20% ^{i}PrOH in *n*-hexane; flow = 1.0 mL/min; Retention time: 17.6 min (major), 19.5 min (minor).



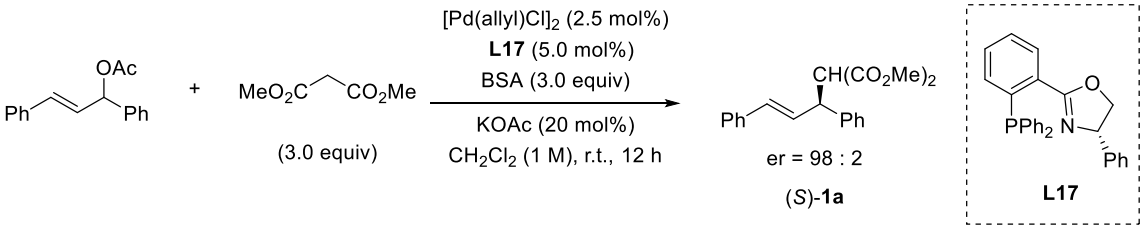
Peak	Retention time/min	Area%
1	18.60	50.02
2	19.91	49.98



Peak	Retention time/min	Area%
1	17.64	95.52
2	19.54	4.48

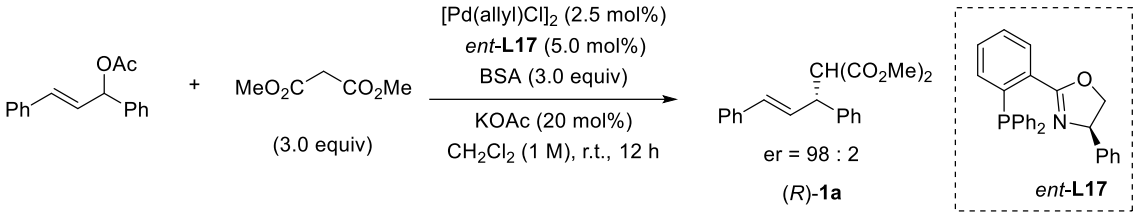
6. Mechanistic studies

6.1 Comparison of initial rates

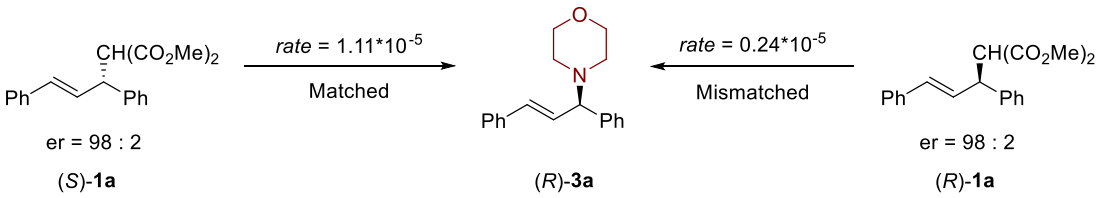


Preparation of (*S*)-**1a**: to a 25 mL flask under nitrogen with $[Pd(allyl)Cl]_2$ (18 mg, 0.050 mmol), **L17** (41 mg, 0.10 mmol), allyl electrophile (2.0 mmol), BSA (1.2 g, 6.0 mmol) and KOAc (39 mg, 0.40 mmol) were added dimethyl malonate (6.0 mmol) and dry CH_2Cl_2 (2 mL). The resulting

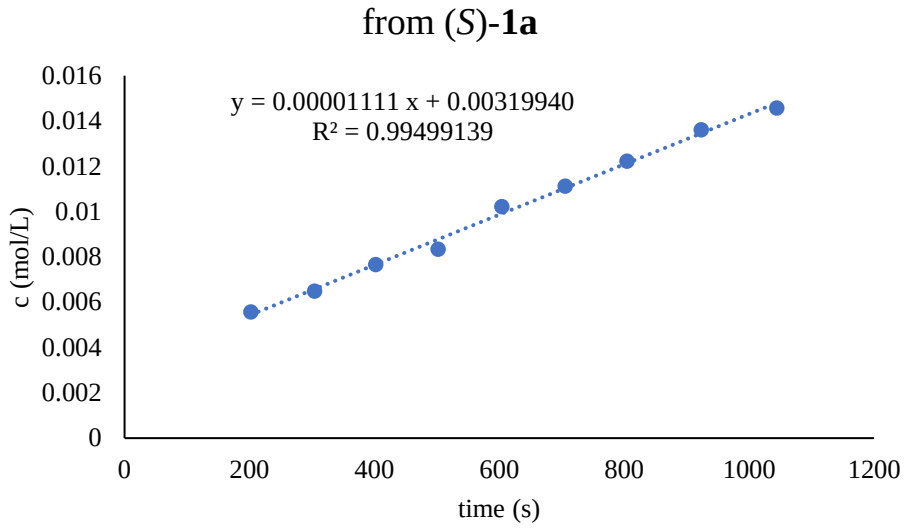
mixture was stirred at room temperature for 12 h. After this time, the reaction was quenched with saturated NH_4Cl aqueous solution (10 mL) and water (40 mL), extracted with EtOAc (40 mL × 3). The combined organic phase was dried over anhydrous sodium sulfate, filtered, concentrated and purified by flash column chromatography to provide pure compound (*S*)-**1a** in 98% yield (0.64 g) and 98:2 er.

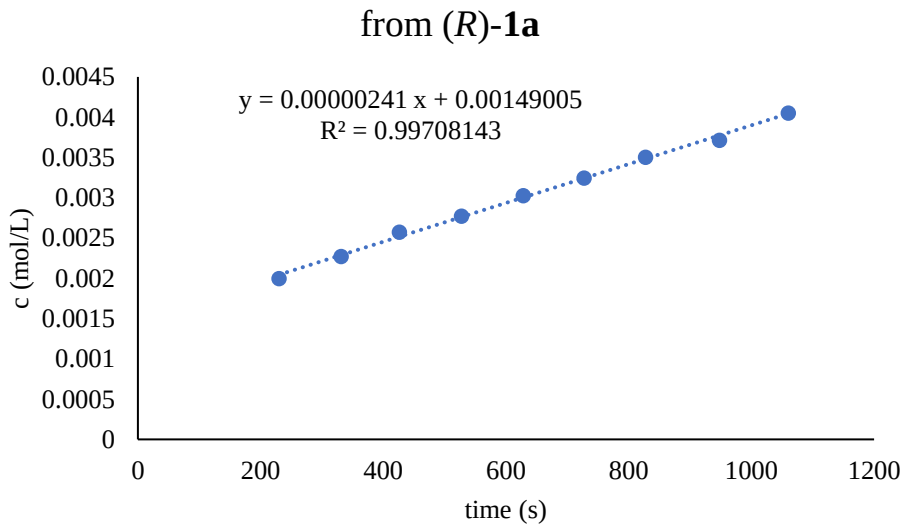


Preparation of (*R*)-**1a**: the procedure was the same to that described for the synthesis of (*S*)-**1a**, except that *ent*-**L17** was used.

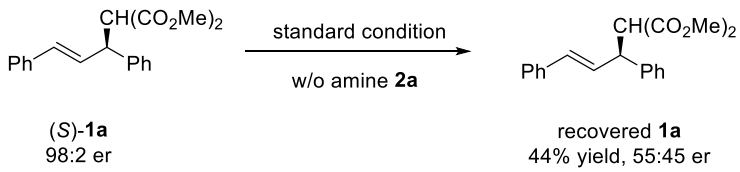


In a nitrogen-filled glovebox, to a 4 mL vial were added $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), ligand **L11** (4.8 mg, 0.0055 mmol), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 4.9 mg, 0.0055 mmol), (*S*)-**1a** or (*R*)-**1a** (0.1 mmol), KO^{t}Bu (11 mg, 0.10 mmol) and dry PhC_2H_5 (0.2 mL). The mixture was stirred at room temperature for 1 min. Then, dodecane (25 μL, 18 mg, 0.11 mmol) and morpholine **2a** (0.30 mmol) were added to the solution. The resulting mixture was stirred at room temperature and analyzed by GC. The GC samples were prepared by taking an aliquot of the reaction mixture with syringe and filtered over a short pad of silica with DCM as eluent at the indicated time points.





6.2 Racemization test

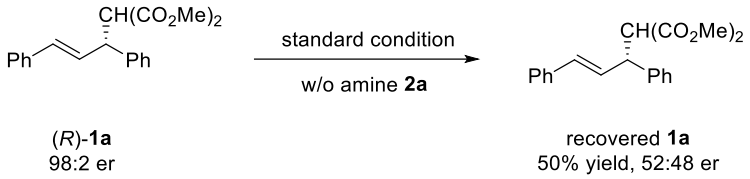


(*S*)-**1a**
98:2 er

recovered **1a**
44% yield, 55:45 er

In a nitrogen-filled glovebox, to a 4 mL vial with $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), ligand **L11** (4.4 mg, 0.0050 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F{}_4$, 4.9 mg, 0.0055 mmol) were added (*S*)-**1a** (0.1 mmol), KO^{t}Bu (11 mg, 0.10 mmol) and dry PhC_2H_5 (0.20 mL). The mixture was stirred at room temperature for 24 h. After this time, the reaction was

condensed and analyzed by crude ^{1}H NMR. The yield of recovered **1a** was determined to be 44%. The enantioselectivity of recovered **1a** was further determined by HPLC analysis as 55:45 er.



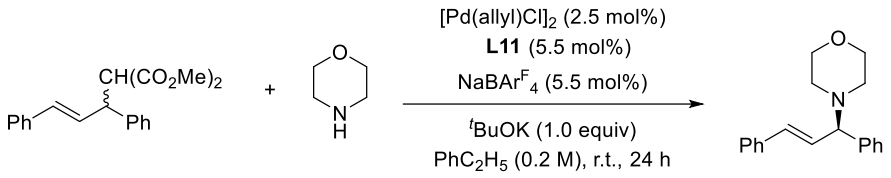
(*R*)-**1a**
98:2 er

recovered **1a**
50% yield, 52:48 er

In a nitrogen-filled glovebox, to a 4 mL vial with [Pd(allyl)Cl]$_2$ (0.9 mg, 0.0025 mmol), ligand **L11** (4.4 mg, 0.0050 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr$^F{}_4$, 4.9 mg, 0.0055 mmol) were added (*R*)-**1a** (0.1 mmol), KO^{t}Bu (11 mg, 0.10 mmol) and dry PhC_2H_5 (0.20 mL). The mixture was stirred at room temperature for 24 h. After this time, the reaction was condensed and analyzed by crude ^{1}H NMR. The yield of recovered **1a** was determined to be 50%. The enantioselectivity of recovered **1a** was further determined by HPLC analysis as 52:48 er.

Note: for both cases above, the other side products mainly come from the homocoupling, decarboxylation and ester exchange with *tert*-butoxide, which lead to the consumption of starting substrate **1a**.

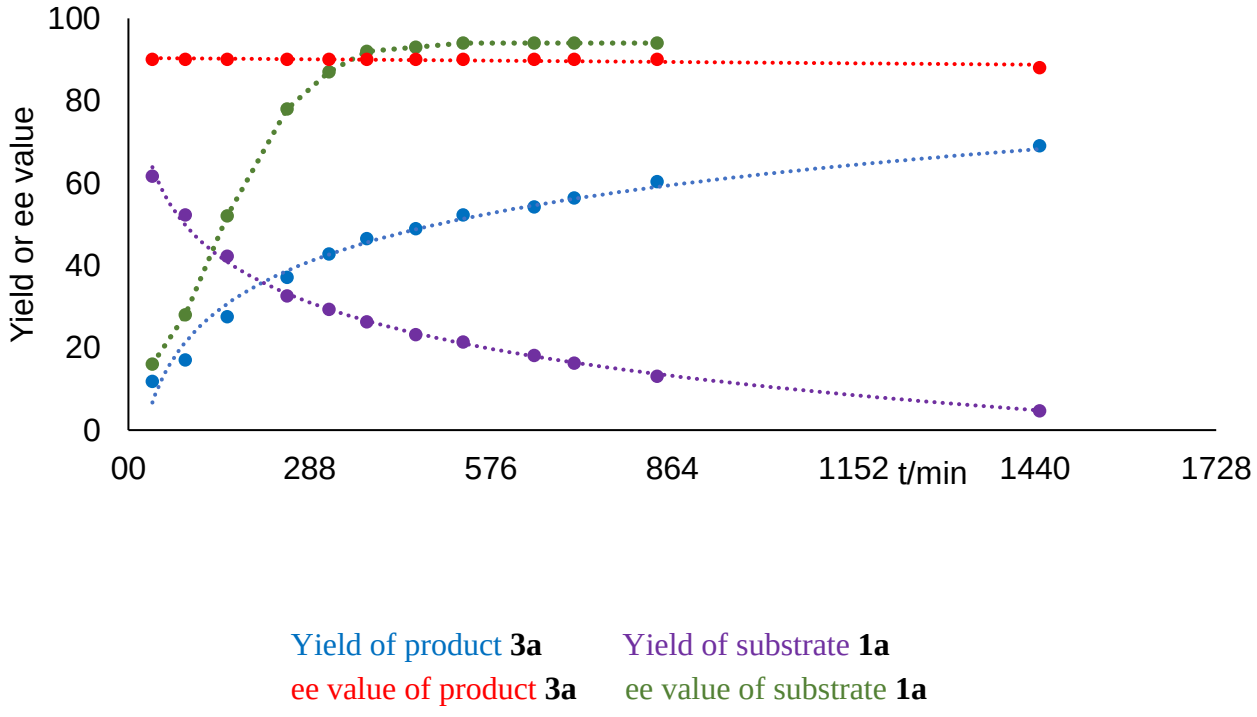
6.3 Reaction profile of asymmetric C–C bond amination



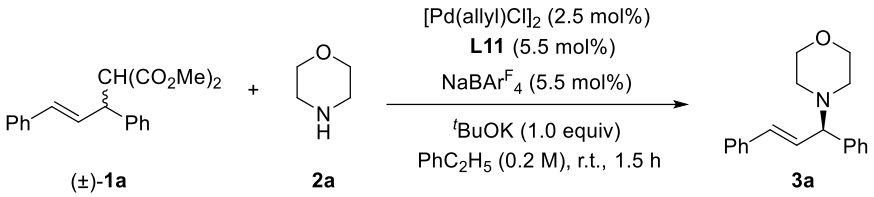
(±)-**1a** **2a** **3a**

In a nitrogen-filled glovebox, to a 4 mL vial were added [Pd(allyl)Cl]$_2$ (2.7 mg, 0.0075 mmol), ligand **L11** (14 mg, 0.0165 mmol), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr$^F{}_4$, 15 mg, 0.0165 mmol), *rac*-**1a** (0.30 mmol), KO^{t}Bu (34 mg, 0.30 mmol) and dry PhC_2H_5 (0.60 mL). The mixture was stirred at room temperature for 1 min. Then, dodecane (25 μL, 18 mg, 0.11 mmol) and nucleophile **2a** (0.90 mmol) were added to the solution. The resulting mixture was stirred at room temperature and analyzed by GC. The GC samples were prepared by removing an aliquot of the reaction mixture by syringe and filtered over a short pad of silica with DCM as eluent at the indicated time points. The enantioselectivity of recovered **1a** and corresponding product **3a** isolated from the reaction mixture for GC sample was determined by HPLC analysis.

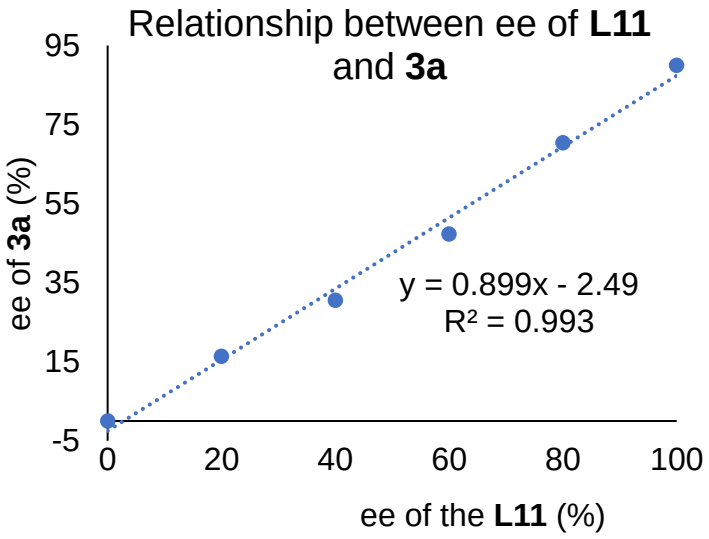
Entry	*t*/min	Yield of **3a**	ee of **3a**	ee of **1a**	Yield of **1a**
1	38	12%	90	16	62%
2	90	17%	90	28	52%
3	157	27%	90	52	42%
4	252	37%	90	78	33%
5	318	43%	90	87	29%
6	378	46%	90	92	26%
7	456	49%	90	93	23%
8	531	52%	90	94	21%
9	644	54%	90	94	18%
10	708	56%	90	94	16%
11	839	60%	90	94	13%
12	1447	69%	88	--	5%



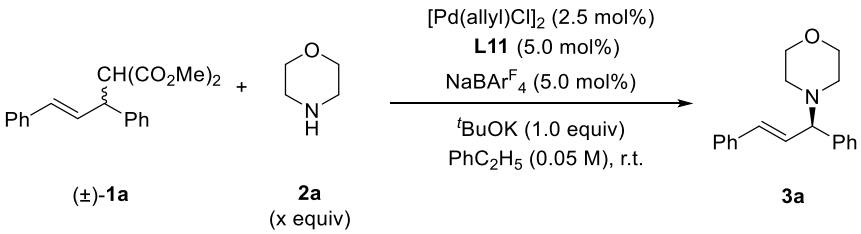
6.4 Nonlinear relationship experiments



Entry	ee of **L11**	ee of **3a**
1	100	90
2	80	70
3	60	47
4	40	30
5	20	16
6	0	0



6.5 Kinetic order of nucleophile 2a



To a 25 mL Schlenk tube in a N_2 box was added $[Pd(allyl)Cl]_2$, **L11**, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$), **1a** and ^{t}BuOK. Then dry PhEt was added and the mixture was then stirred at 25 °C for 3 min. Next, dodecane was added sequentially. After the mixture was stirred for 1 min, nucleophile **2a** was added to the reaction. The reaction was stirred at 25 °C and analyzed by GC along time. The detailed amount of each substrate was shown in the table below.

Entry	Pd	**L11**	^{t}BuOK	$NaBAr^F_4$	PhEt	**1a**	**2a**			Dodecane
	mg	mg	mg	mg	mL	mg	mg	mmol	c / mol*L^{-1}	mg
1	0.9	4.3	28.0	4.4	5	81.0	22.0	0.25	0.05	18.8
2	0.9	4.3	28.0	4.4	5	81.0	44.0	0.50	0.1	18.8
3	0.9	4.3	28.0	4.4	5	81.0	66.0	0.75	0.15	18.8
4	0.9	4.3	28.0	4.4	5	81.0	88.0	1.00	0.20	18.8

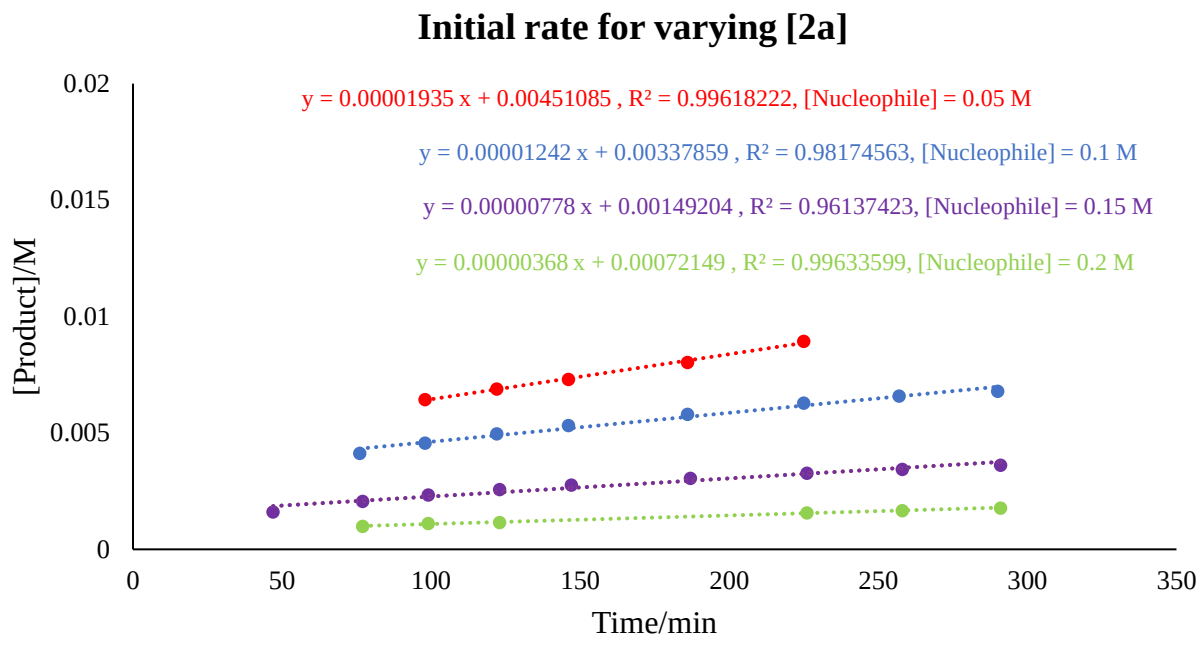


Fig. 1 Plot of concentration of **3a** over time with reactions performed with varying concentration of **2a**

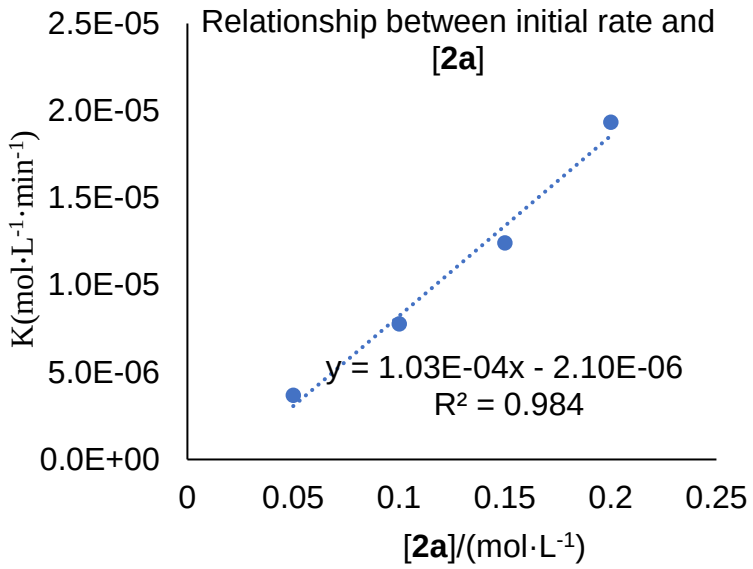


Fig. 2. Plot of the initial rates of formation of **3a** vs. [**2a**] for the C-C bond amination.

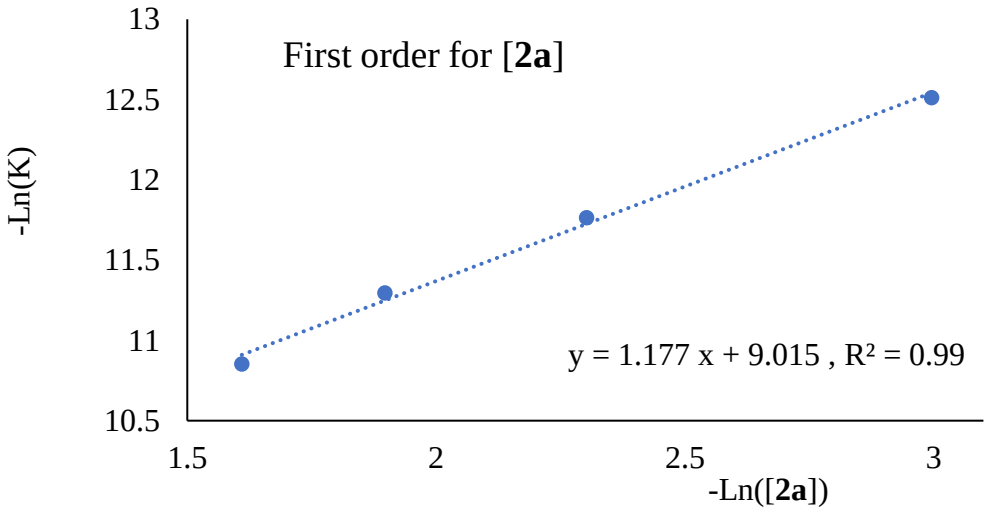
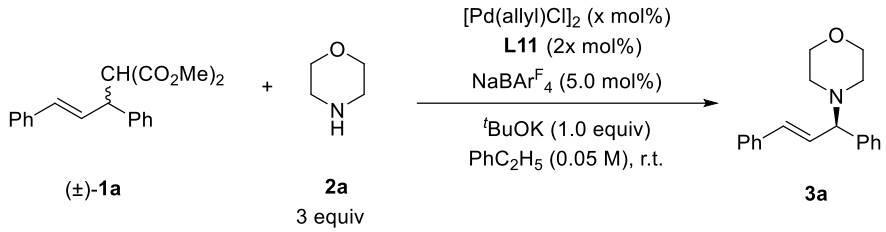


Fig. 3 Plot of ln(Initial Rates) *vs.* ln(**2a**) for the substitution reaction.

6.6 Kinetic order of catalyst



To a 25 mL Schlenk tube in a N_2 box was added $[Pd(allyl)Cl]_2$, **L11**, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$), **1a** and ^{t}BuOK. Then dry PhEt was added and the mixture was then stirred at 25 °C for 3 min. Next, dodecane was added sequentially. After the mixture was stirred for 1 min, nucleophile **2a** was added to the reaction. The reaction was stirred at 25 °C and analyzed by GC along time. The detailed amount of each substrate was shown in the table below.

Entry	Pd		**L11**		$NaBAr^F_4$		^{t}BuOK	PhEt	**1a**	**2a**	Dodecane
	mmol	mg	mmol	mg	mmol	mg	mg	mL	mg	mg	mg
1	0.0025	0.9	0.005	4.3	0.005	4.4	28.0	5	81.0	22.0	18.8
2	0.00375	1.4	0.0075	6.5	0.0075	6.5	28.0	5	81.0	22.0	18.8
3	0.0050	1.8	0.010	8.7	0.010	8.7	28.0	5	81.0	22.0	18.8
4	0.00625	2.3	0.0125	10.8	0.0125	10.8	28.0	5	81.0	22.0	18.8

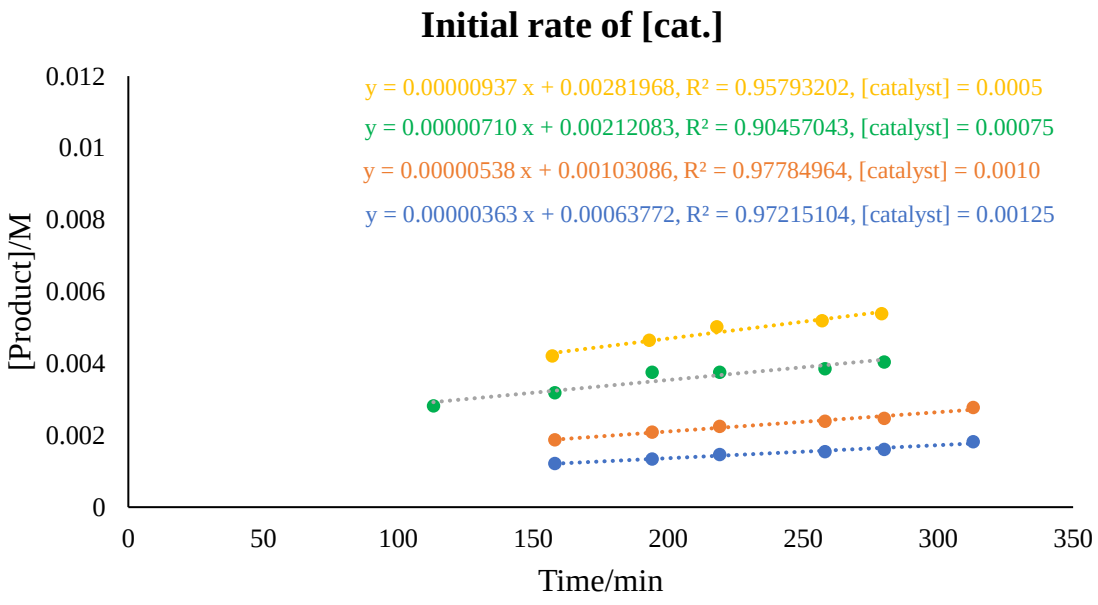


Fig. 4 Plot of concentration of **3a** over time with reactions performed with varying concentration of catalyst.

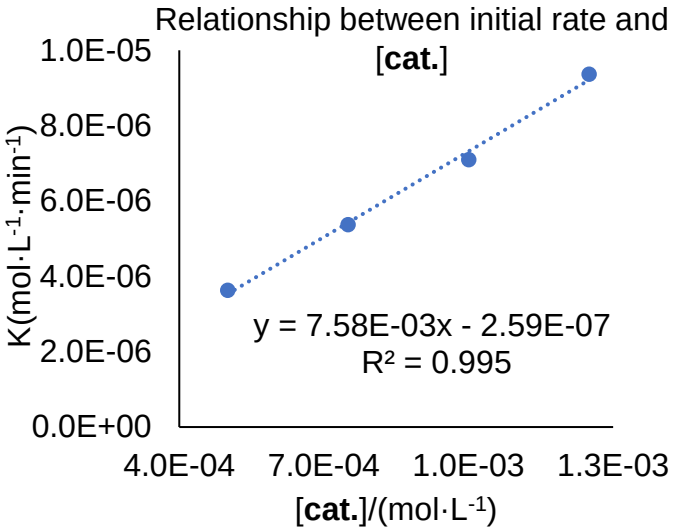


Fig. 5. Plot of the initial rates of formation of **3a** vs. [**cat.**] for the C-C bond amination.

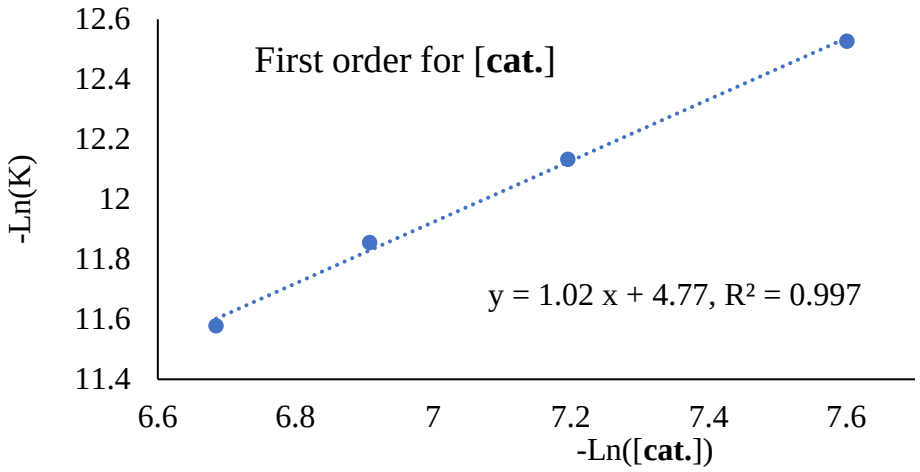
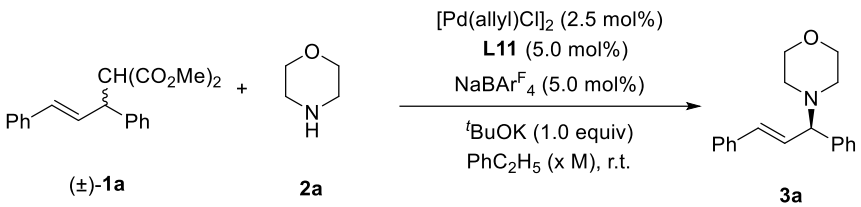


Fig. 6 Plot of ln(Initial Rates) *vs.* ln(catalyst) for the substitution reaction.

6.7 Kinetic studies on 1a



To a 25 mL Schlenk tube in a N_2 box was added $[Pd(allyl)Cl]_2$, **L11**, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$), **1a** and ^{t}BuOK. Then dry PhEt was added and the mixture was then stirred at 25 °C for 3 min. Next, dodecane was added sequentially. After the mixture was stirred for 1 min, nucleophile **2a** was added to the reaction. The reaction was stirred at 25 °C and analyzed by GC along time. The detailed amount of each substrate was shown in the table below.

Entry	Pd	**L4**	^{t}BuOK	$NaBAr^F_4$	PhEt	**1a**			**2a**	Dodecane
	mg	mg	mg	mg	mL	mg	mmol	c / mol*L^{-1}	mg	mg
1	2.3	10.8	28.0	11.1	5	81.0	0.25	0.05	22.0	18.8
2	2.3	10.8	28.0	11.1	5	121.6	0.375	0.075	22.0	18.8
3	2.3	10.8	28.0	11.1	5	162.1	0.500	0.10	22.0	18.8
4	2.3	10.8	28.0	11.1	5	202.6	0.625	0.125	22.0	18.8

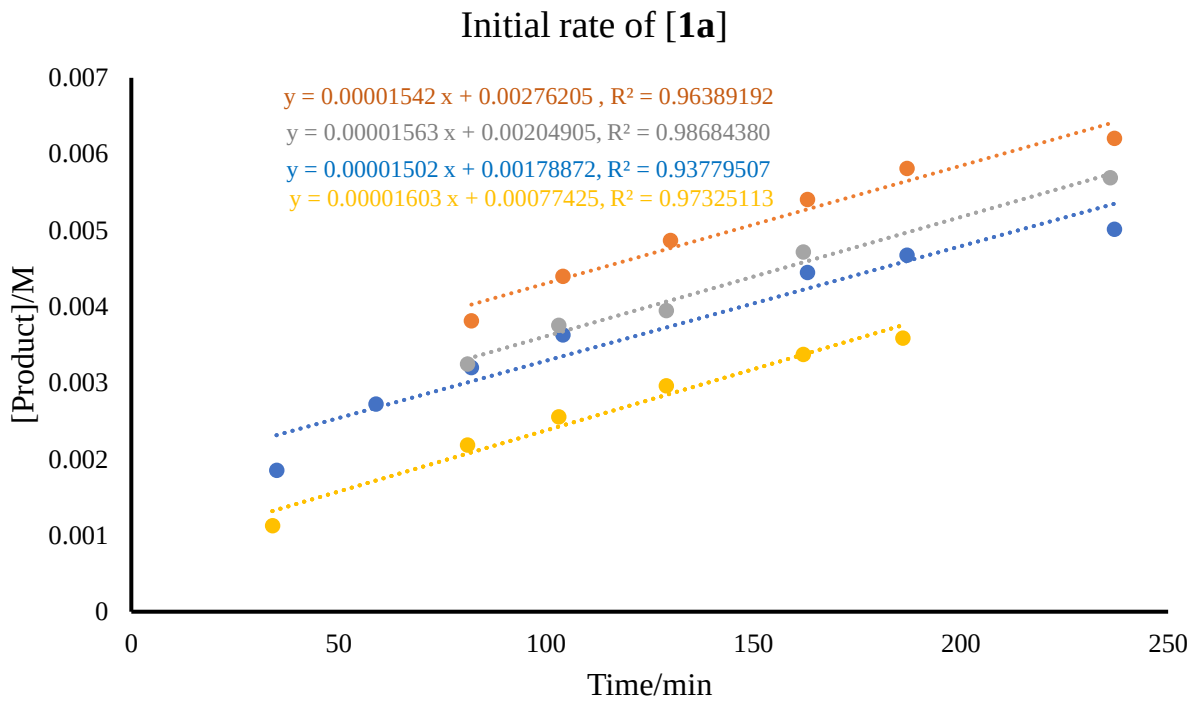


Fig. 7 Plot of concentration of **3a** over time with reactions performed with varying concentration of **1a**.

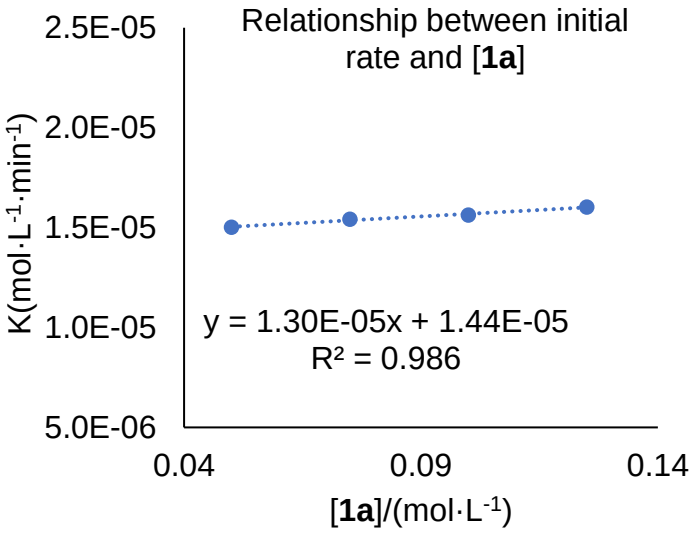


Fig. 8. Plot of the initial rates of formation of **3a** vs. [**1a**] for the C-C bond amination.

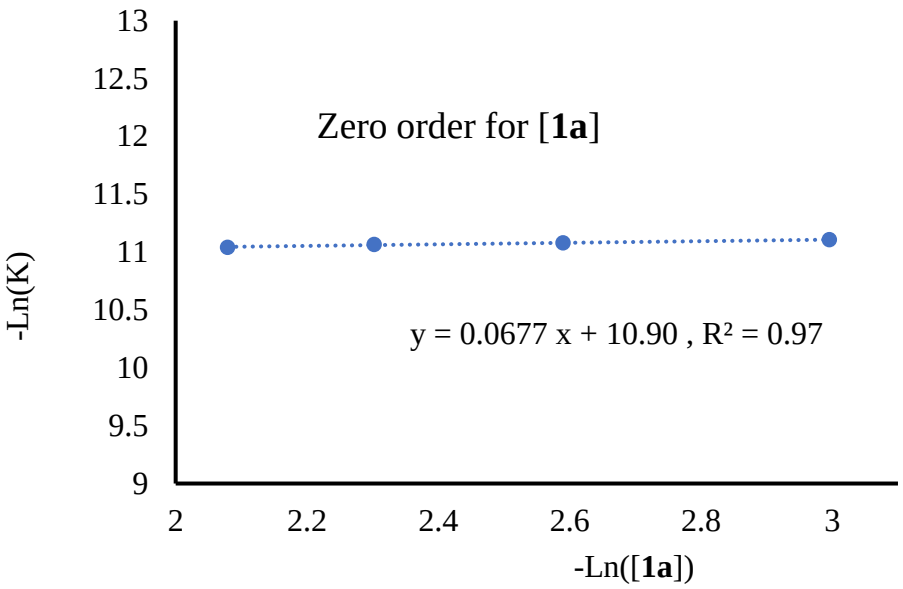
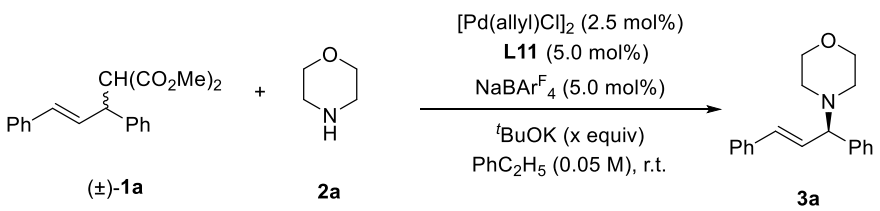


Fig. 9 Plot of ln(Initial Rates) *vs.* ln(**1a**) for the substitution reaction.

6.8 Kinetic order of ^{t}BuOK



To a 25 mL Schlenk tube in a N_2 box was added $[Pd(allyl)Cl]_2$, **L11**, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$), **1a** and ^{t}BuOK. Then dry PhEt was added and the mixture was then stirred at 25 °C for 3 min. Next, dodecane was added sequentially. After the mixture was stirred for 1 min, nucleophile **2a** was added to the reaction. The reaction was stirred at 25 °C and analyzed by GC along time. The detailed amount of each substrate was shown in the table below.

Entry	Pd	**L11**	^{t}BuOK			$NaBAr^F_4$	PhEt	**1a**	**2a**	Dodecane
	mg	mg	mg	mmol	c / mol*L^{-1}	mg	mL	mg	mg	mg
1	2.3	10.8	7.0	0.0625	0.0125	11.1	5	81.0	22.0	18.8
2	2.3	10.8	14.0	0.125	0.025	11.1	5	81.0	22.0	18.8
3	2.3	10.8	28.0	0.1875	0.0375	11.1	5	81.0	22.0	18.8
4	2.3	10.8	28.0	0.25	0.05	11.1	5	81.0	22.0	18.8

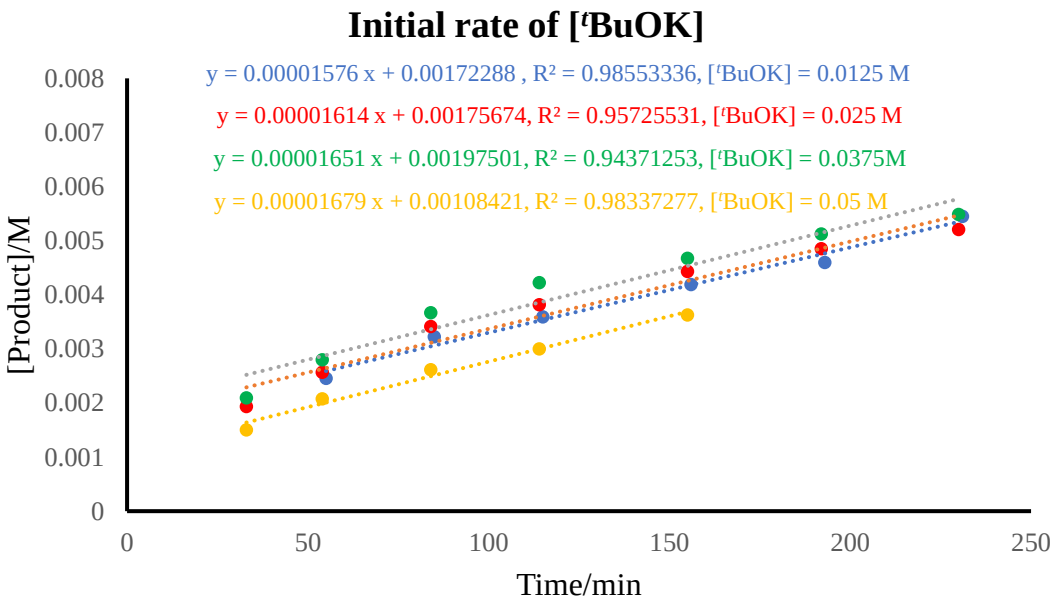


Fig. 10. Plot of concentration of **3a** over time with reactions performed with varying concentration of **^{t}BuOK**

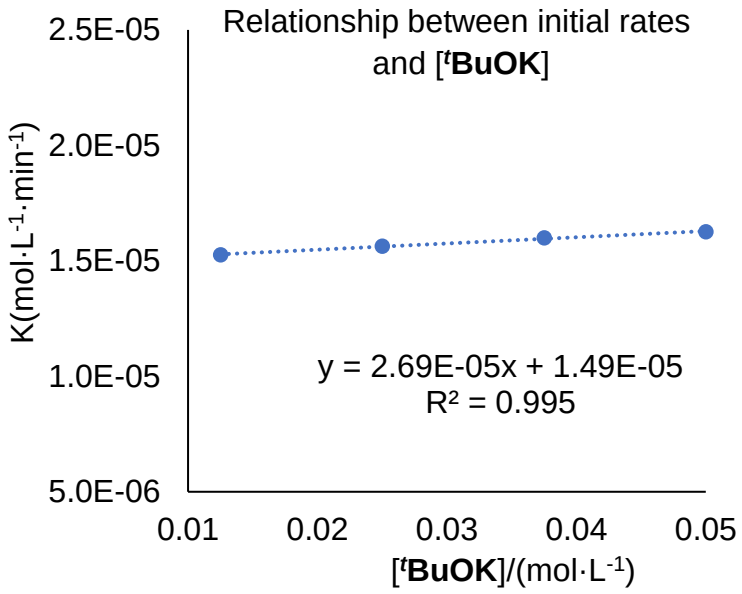


Fig. 11. Plot of the initial rates of formation of **3a** vs. [^{t}**BuOK**] for the C-C bond amination.

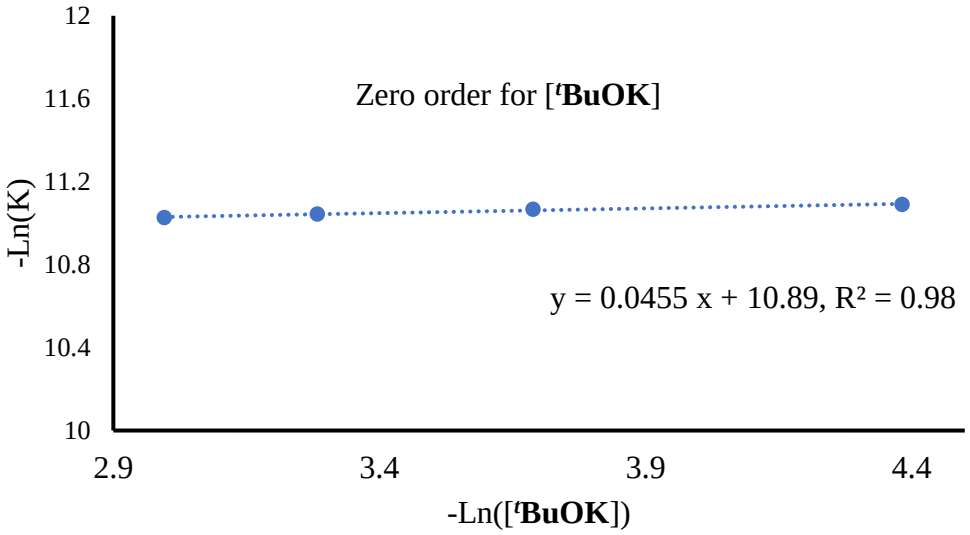
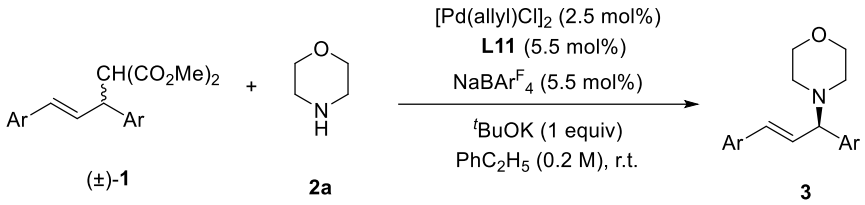


Fig. 12. Plot of ln(Initial Rates) *vs.* ln(*t*BuOK) for the substitution reaction.

6.9 Hammett curve



Ar = Ph, *p*-CH_3Ph, *m*-CH_3OPh, *p*-FPh, *p*-CF_3Ph

To a 25 mL Schlenk tube under N_2 was added $[Pd(allyl)Cl]_2$ (0.9 mg, 0.0025 mmol), **L11** (4.8 mg, 0.0055 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$) (4.9 mg, 0.0055 mmol), different electrophile (0.1 mmol) and ^{t}BuOK (11.2 mg, 0.1 mmol). Then dry PhEt (0.5 mL) was added to the reaction and the resulting mixture was stirred at 25 ^{o}C for 3 min. Next, dodecane (18 mg, 0.11 mmol) was added to the solution. After the mixture was stirred for 1 min, morpholine **2a** (26 mg, 0.30 mmol) was added to the reaction. The mixture continued to stir at room temperature and the reaction was analyzed by GC along time.

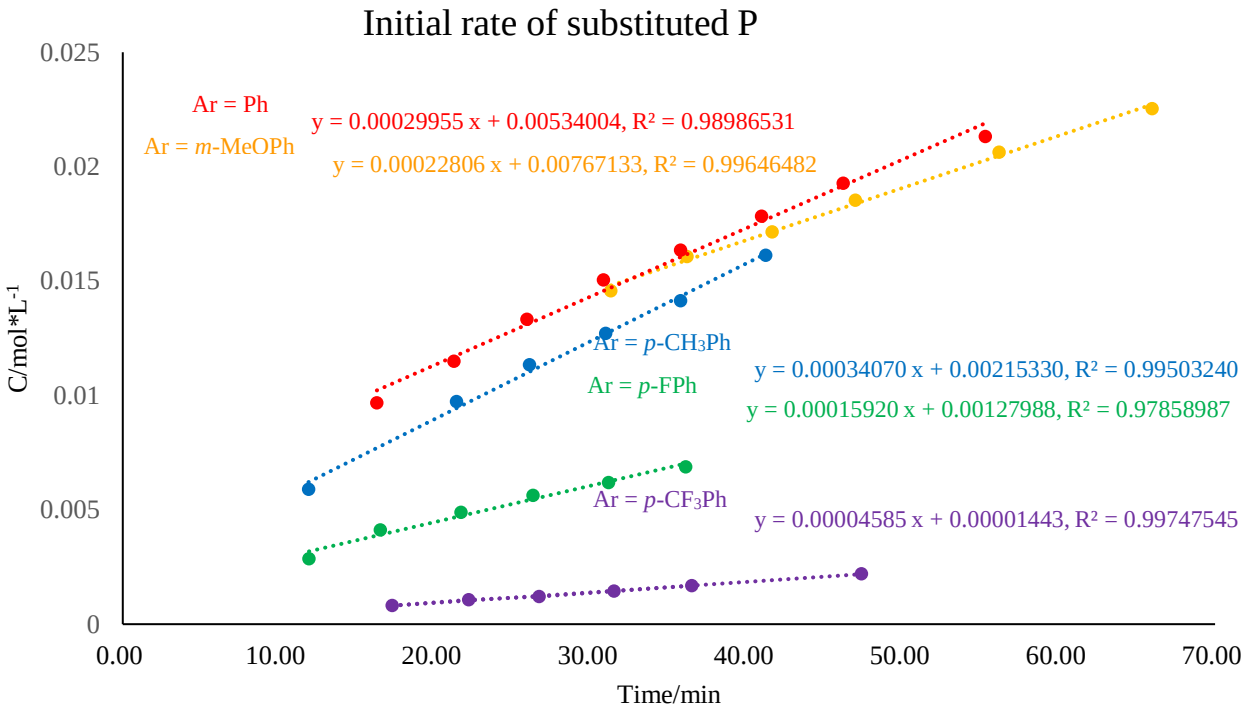


Fig. 13 Plot of **[product]** *vs.* time for the substitution reaction.

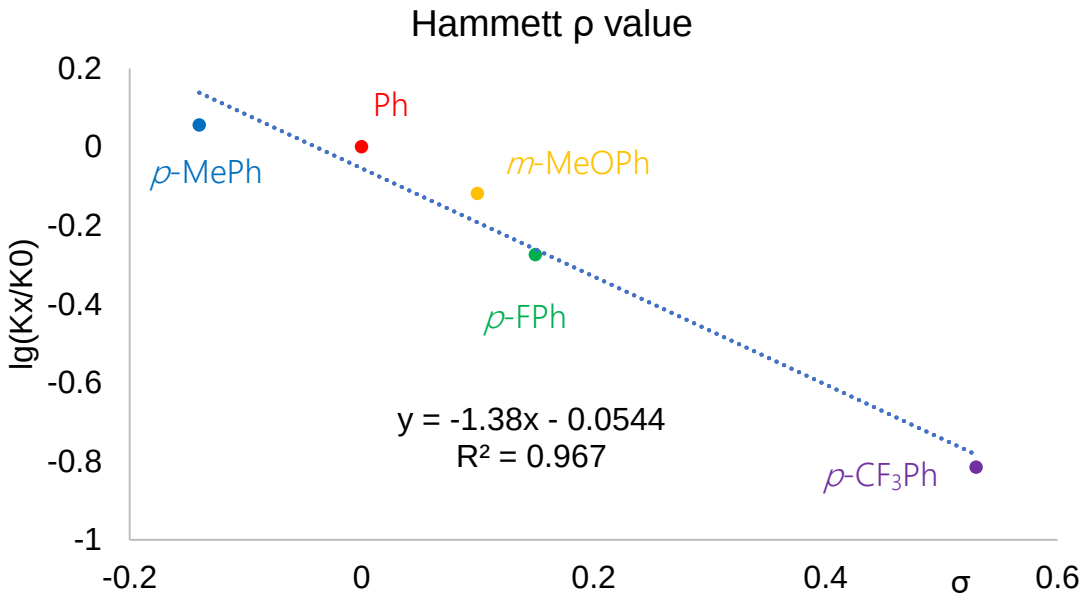
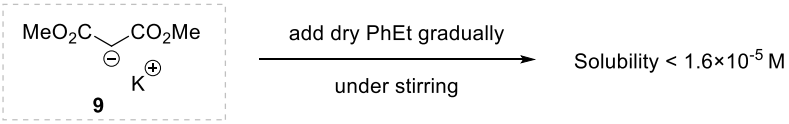


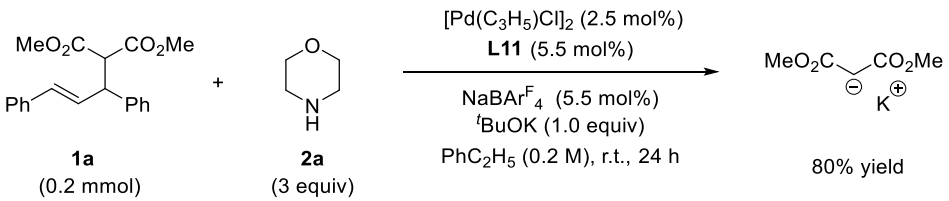
Fig. 14 Plot of lg(Kx/K0) *vs.* σ for the substitution reaction.

6.10 Solubility test



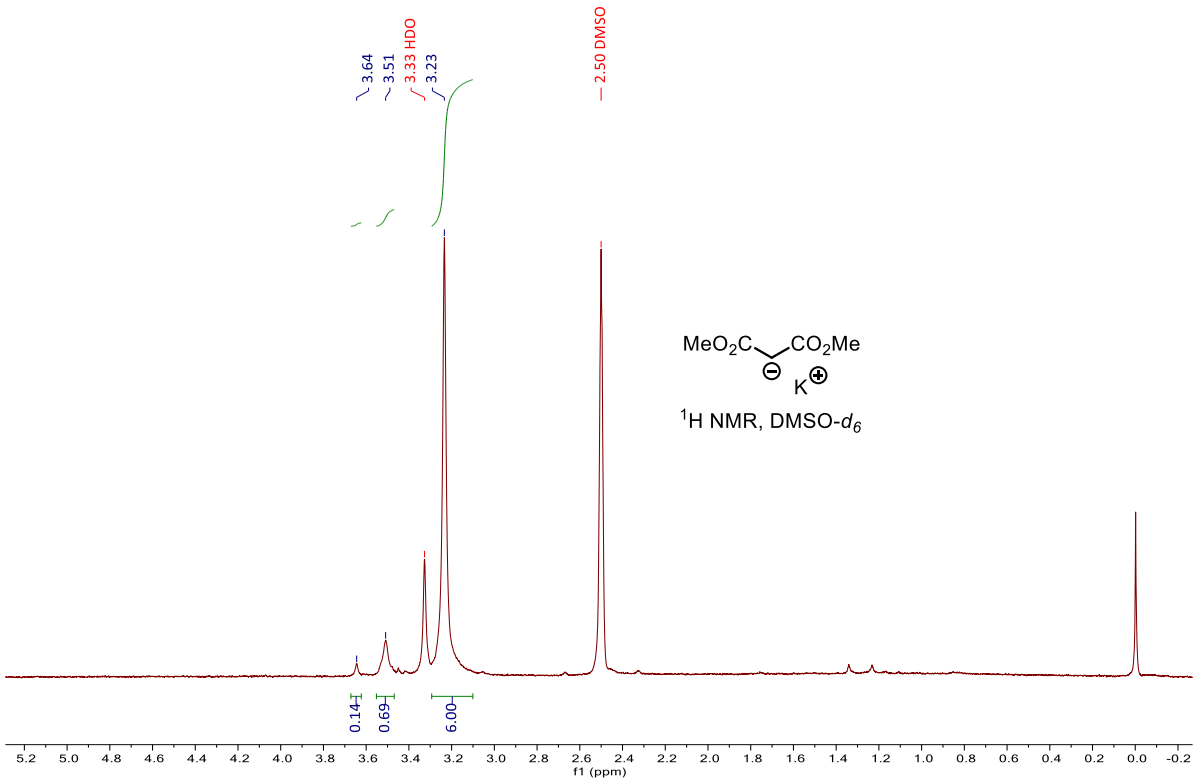
To a 50 mL dry flask under nitrogen was added $KHCH(CO_2Me)_2$ **9** (1.1 mg, 0.0065 mmol). Next, dry PhEt (5 mL) was added to the flask and the resulting mixture was stirred at 25 °C for 10 min. If the solid could not fully dissolve in the solvent, then repeat this process. Finally, we found that after PhEt (40 mL) was added into the flask, the solid still did not fully dissolve in the solvent. Thus, the solubility of $KHCH(CO_2Me)_2$ in PhEt is roughly determined to be less than 1.6×10^{-5} M.

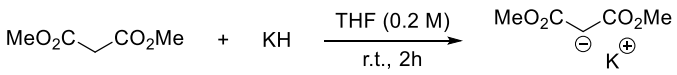
6.11 Detection of malonate potassium salt



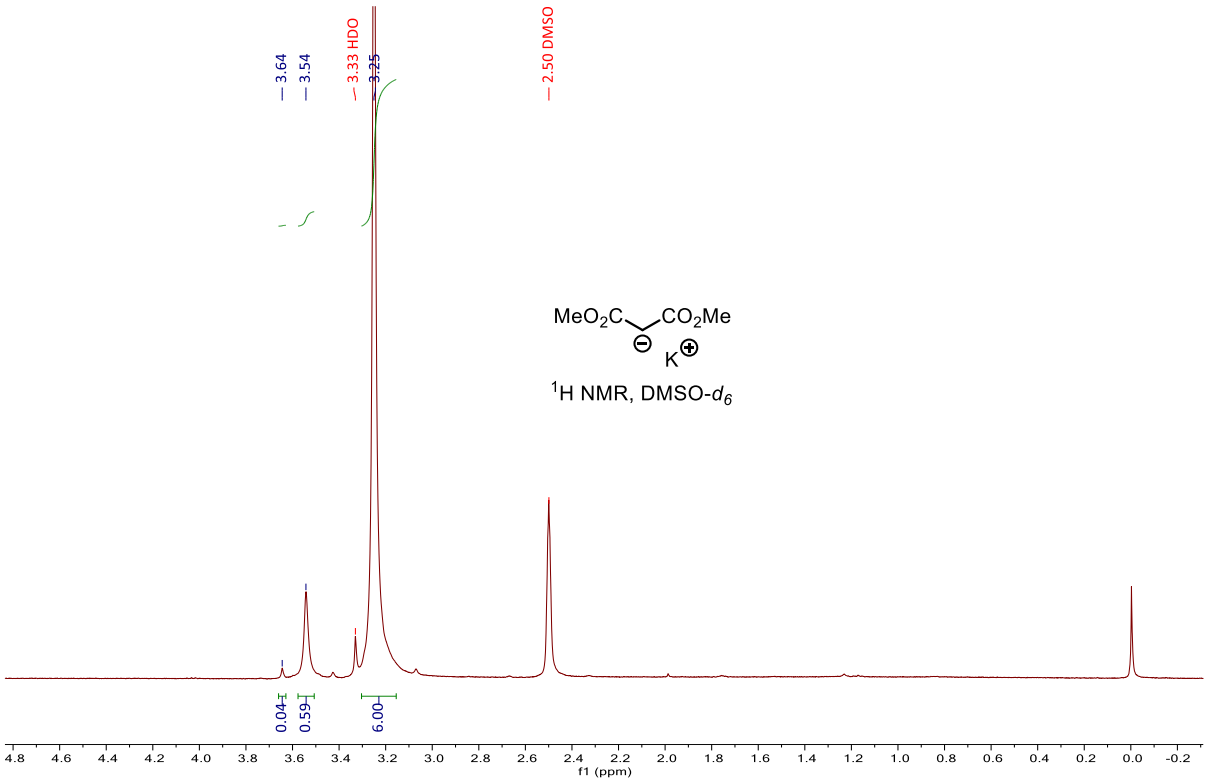
In a nitrogen-filled glovebox, to a 4 mL vial were added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol), **L11** (9.6 mg, 0.011 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 9.8 mg, 0.011 mmol), racemic alkene **1a** (0.20 mmol), ^{t}BuOK (22.4 mg, 0.20 mmol) and dry Et_3N (0.40 mL).

Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2a** (0.60 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was transferred to a centrifuge tube under nitrogen and washed by dry *n*-hexane (5 mL). The centrifuge tube was centrifugal separated in centrifuge. Then the supernate was removed from the tube and the precipitate was washed by THF (5 mL × 3). Finally, the solid was dried by vacuum to give the malonate potassium salt as a white solid in 80% yield (27.2 mg).

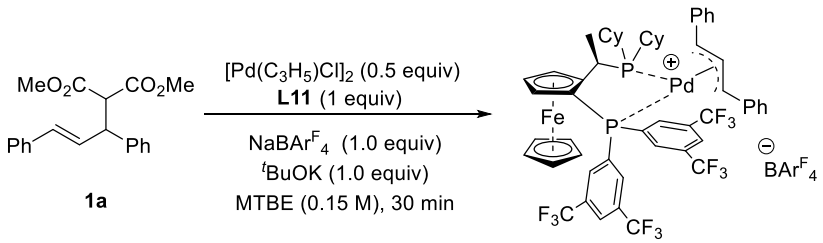




In a nitrogen-filled glovebox, to a 25 mL dry flask were added $CH_2(CO_2Me)_2$ (33 mg, 2.5 mmol) and dry THF (12.5 mL). Then KH (80 mg, 2.0 mmol) was added slowly to the reaction. Then the mixture was stirred at room temperature for 2 h. After this time, the reaction was transferred to a centrifuge tube under nitrogen and washed by dry THF (5 mL). The centrifuge tube was centrifugal separated in centrifuge. Then the supernate was removed from the tube and the precipitate was washed by THF (5 mL × 3). Finally, the solid was dried by vacuum to give the malonate potassium salt as a white solid in 88% yield (298 mg). The corresponding ^{1}H NMR was shown as below, which was same to that prepared from **1a** described above.

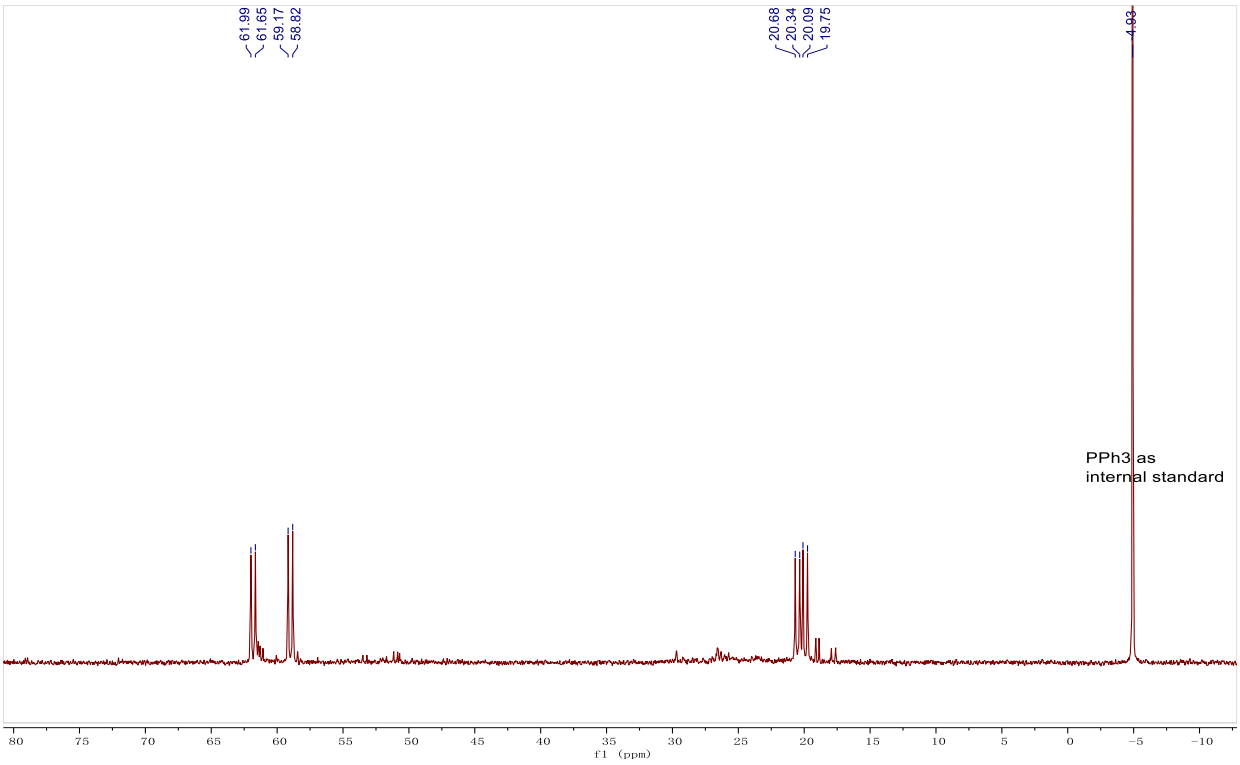


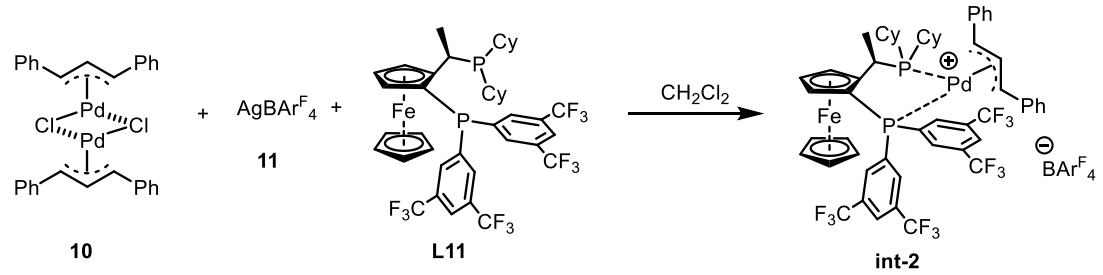
6.12 Detection of C-C cleavage species



int-2

In a nitrogen-filled glovebox, to a 4 mL vial were added alkene **1a** (0.03 mmol), $[Pd(allyl)Cl]_2$ (5.5 mg, 0.015 mmol), **L11** (26 mg, 0.030mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 27 mg, 0.030 mmol), ^{t}BuOK (3.4 mg, 0.030 mmol) and dry MTBE (0.20 mL). Then the resulting mixture was stirred at room temperature for 30 min. After this time, the solvent was removed by vacuum to provide the complex **int-2** which was detected by ^{31}P NMR (PPh_3 as the internal standard and $CDCl_3$ as the solvent as shown below). The structure of this complex was also confirmed by other method to prepare it as shown below.

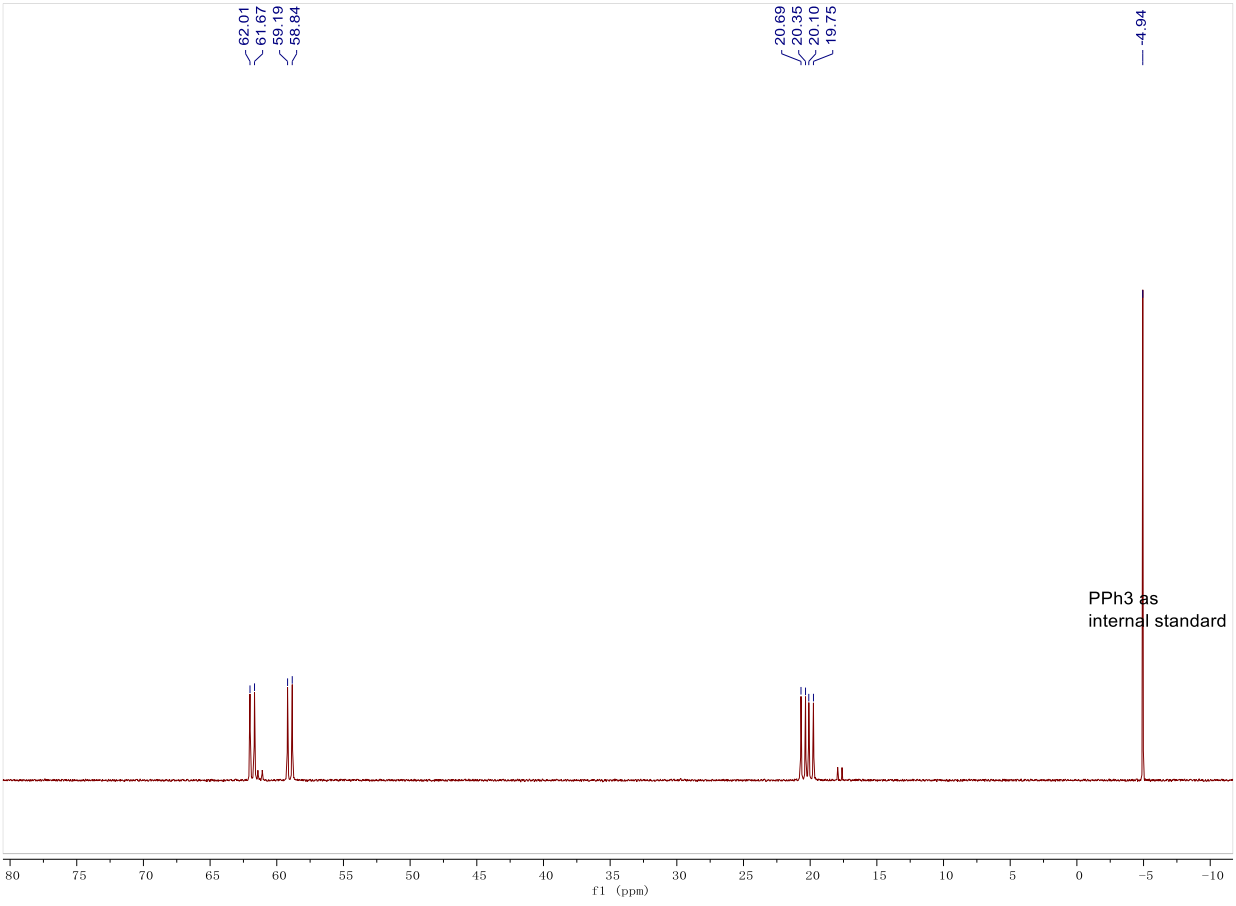




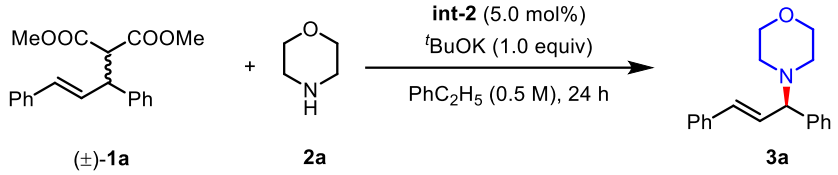
The direct preparation of **int-2** was based on a reported work[13]. In a nitrogen-filled glovebox, to a 25 mL flask were added palladium catalyst **10** (33 mg, 0.050 mmol), **L11** (87 mg, 0.10 mmol), silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($AgBAr^F_4$, 0.11 g, 0.11 mmol) and dry CH_2Cl_2 (2.0 mL). Then the resulting mixture was stirred at room temperature for 30 min. After this time, the flask was removed from the glovebox, filtered through a pad of celite (rinsing with CH_2Cl_2), and concentrated in vacuo to afford **int-2** as an orange solid in 96% yield as a mixture of *exo* and *endo* complexes (*ca.* 1:1 mixture)[14]. The corresponding spectra were complicated due to the mixture of isomers and peak overlapping. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.33 (s, 1H), 8.31 (s, 2H), 8.14 (s, 1H), 8.06 (s, 2H), 8.04 (s, 1H), 7.88 (s, 1H), 7.73 – 7 .68 (m , 18H), 7.53 – 7.48 (m, 12H), 7.44 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.08 (t, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 10.8 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 7.5 Hz, 2H), 6.56 – 6.49 (m, 3H), 6.15 – 6.07 (m, 1H), 5.21 – 5.14 (m, 1H), 5.05 (t, *J* = 12.1 Hz, 1H), 4.91 (t, *J* = 11.8 Hz, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.53 (t, *J* = 2.7 Hz, 1H), 4.45 (t, *J* = 2.7 Hz, 1H), 3.98 (s, 1H), 3.80 (s, 5H), 3.75 – 3.65 (m, 6H), 2.96

– 2.86 (m, 1H), 2.84 – 2.74 (m, 1H), 2.53 – 2.39 (m, 1H), 2.00 – 1.92 (m, 2H), 1.87 – 1.58 (m, 22H), 1.52 – 0.86 (m, 25H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 162.3, 161.9, 161.5, 161.1, 136.2, 135.4, 135.3, 135.1, 134.8, 134.24, 134.21, 134.20, 134.17, 133.5, 133.4, 133.3, 133.24, 133.22, 133.13, 133.06, 133.0, 132.9, 132.7, 132.66, 132.60, 132.5, 132.4, 132.3, 132.22, 132.19, 131.0, 130.5, 130.3, 130.1, 130.0, 129.9, 129.8, 129.4, 129.3, 129.0, 128.9, 128.79, 128.77, 128.74, 128.49, 128.46, 127.9, 127.0, 126.6, 125.7, 125.1, 124.8, 124.6, 123.5, 123.46, 123.40, 123.3, 121.4, 121.3, 121.2, 119.1, 117.4, 111.4, 110.2, 96.8, 94.1, 92.3, 92.1, 89.0, 88.8, 84.0, 83.8, 75.1, 74.6, 73.3, 72.9, 71.3, 71.2, 70.9, 70.8, 70.4, 70.3, 58.5, 36.8, 36.7, 35.5, 35.3, 34.0, 33.9, 32.5, 32.14, 32.08, 32.0, 31.9, 31.8, 31.6, 31.3, 31.25, 31.19, 31.15, 30.7, 30.6, 30.0, 29.4, 29.1, 27.9, 27.4, 27.3, 27.2, 26.93, 26.85, 26.8, 26.6, 26.5, 26.0, 25.9, 25.8, 25.6, 25.4, 25.3, 17.0, 16.9, 16.7, 16.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52, -63.06, -63.19, -63.27, -63.36. ^{31}P NMR (202 MHz, $CDCl_3$) δ 61.84 (d, *J* = 68.6 Hz), 59.01 (d, *J* = 70.9 Hz), 20.52 (d, *J* = 68.7 Hz), 19.93 (d, *J* = 70.3 Hz). HRMS (ESI): $[M - BAr^F{}_4]^{\oplus}$ calcd for $C_{55}H_{53}F_{12}FeP_2Pd^{\oplus}$ 1165.1810, found 1165.1826.

The corresponding ^{31}P NMR (PPh_3 as the internal standard and $CDCl_3$ as the solvent) was shown as below:



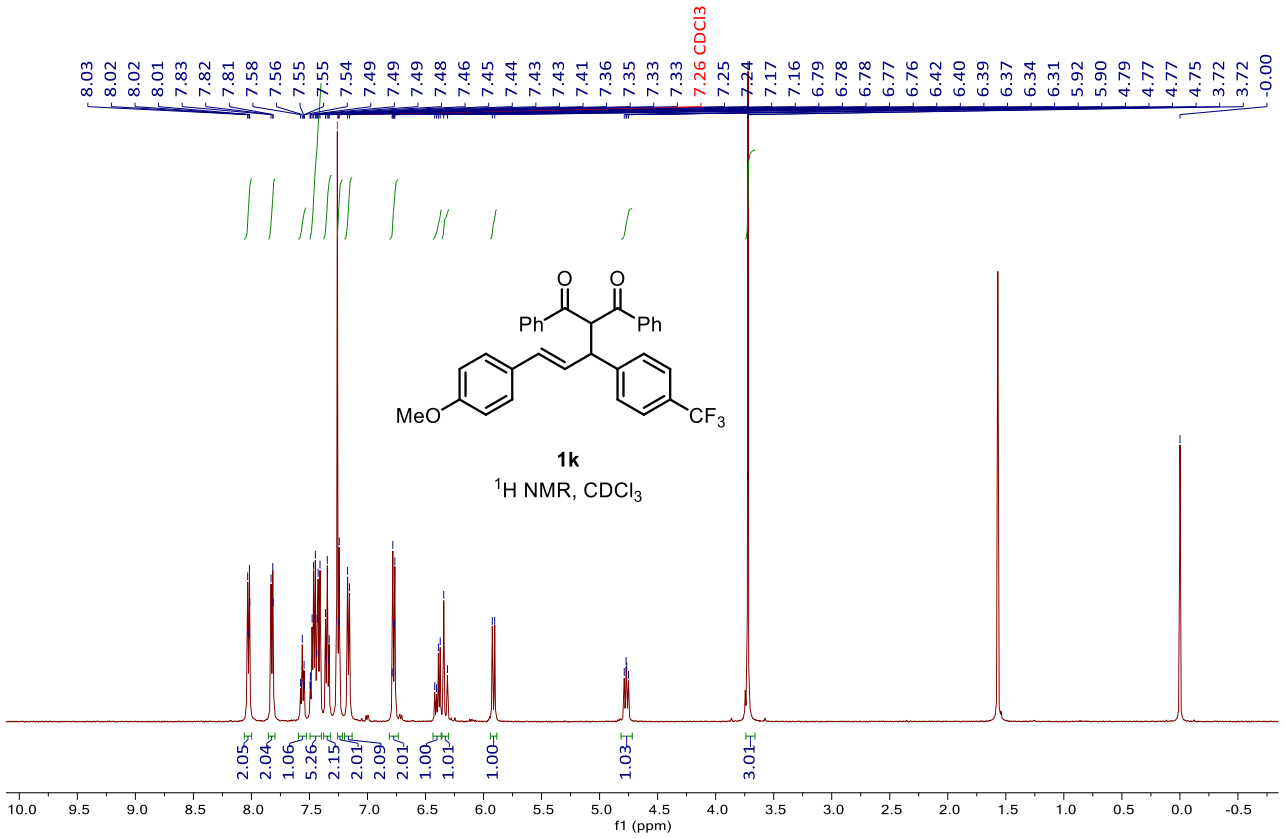
The effect of the prepared complex **int-2** was evaluated as shown below:

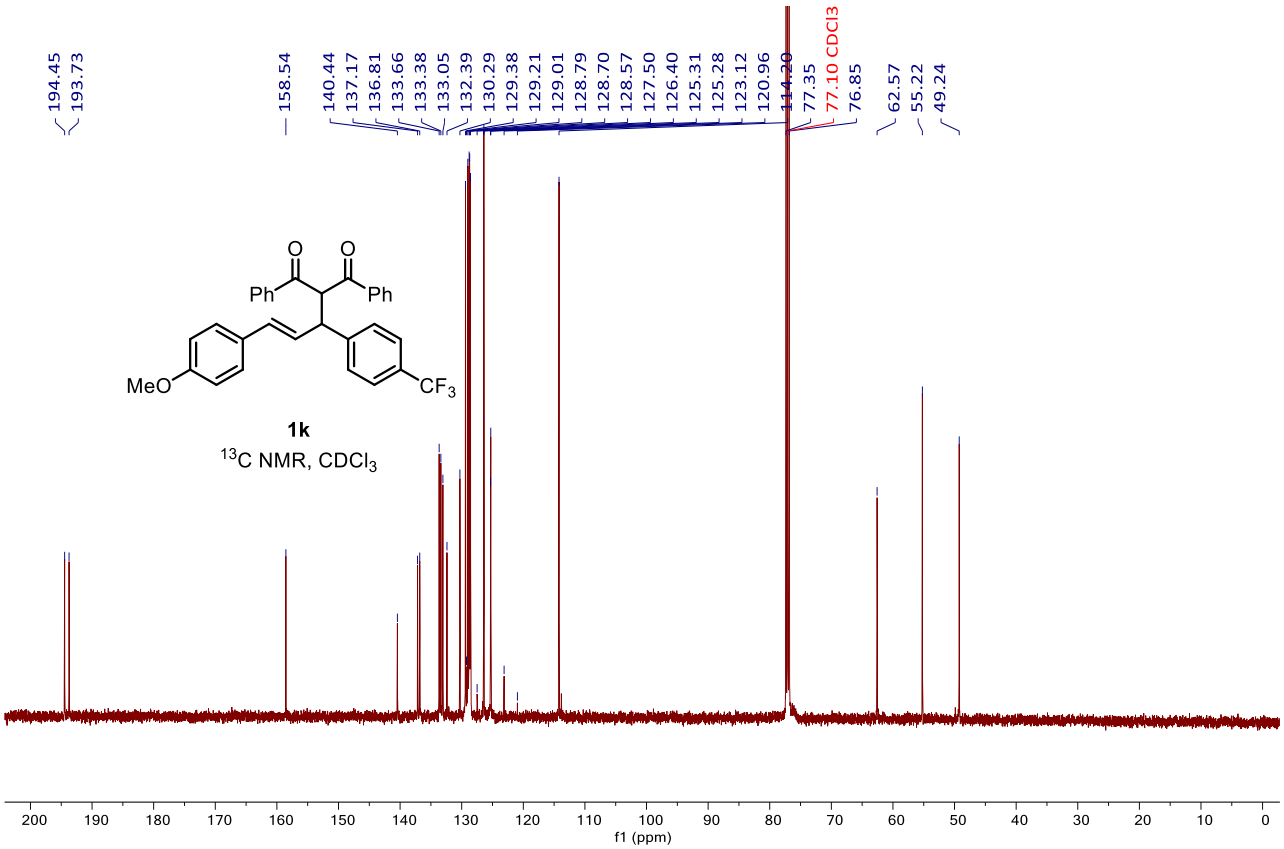


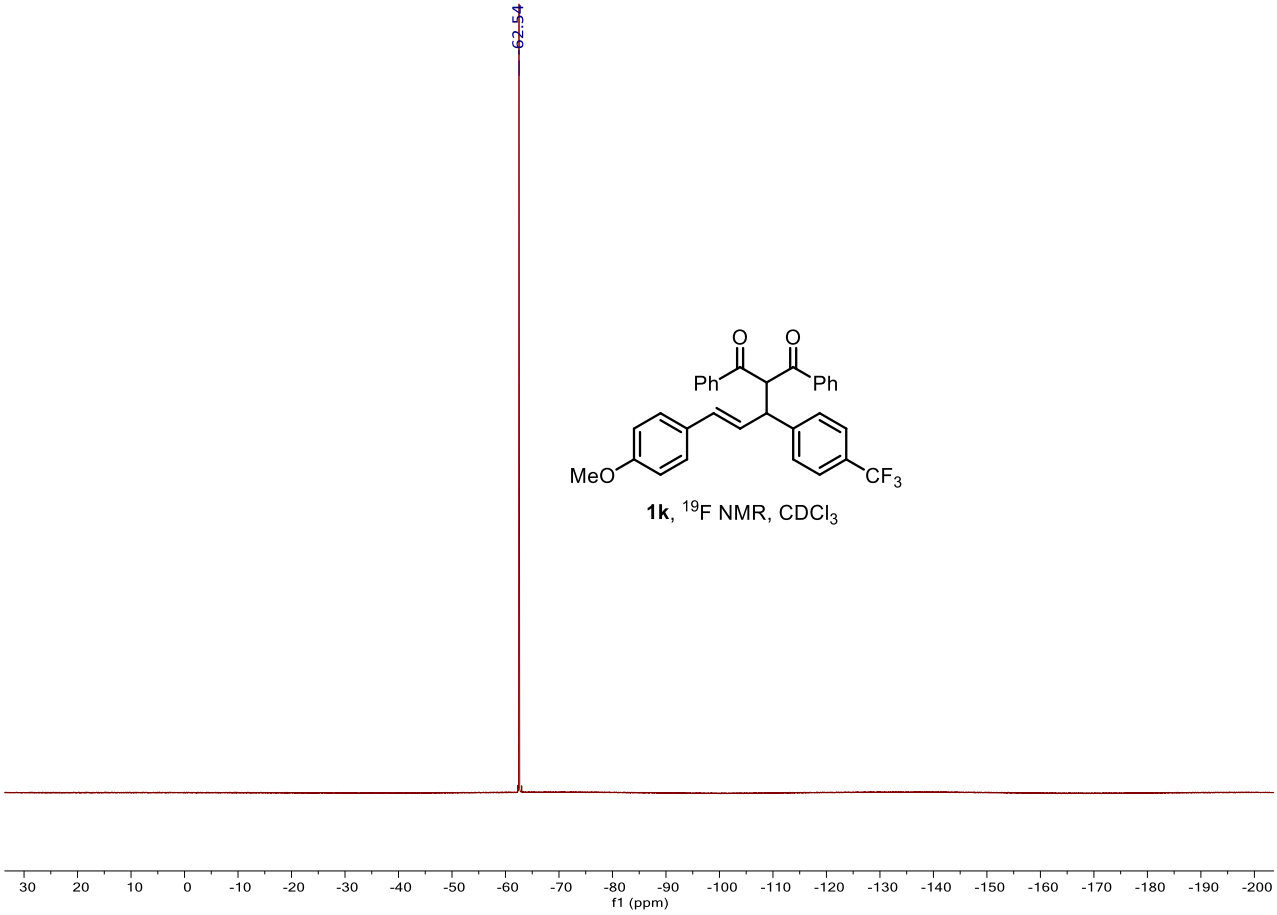
(±)-**1a** **2a** **3a**

In a nitrogen-filled glovebox, to a 4 mL vial with alkene **1a** (0.10 mmol), KO^{t}Bu (11 mg, 0.10 mmol), **int-2** and dry PhEt (0.20 mL) sequentially. Then the reaction was stirred at room temperature for 1 min. Next, amine nucleophile **2a** (0.30 mmol) was added to the reaction and the resulting mixture was stirred at room temperature for 24 h. After this time, the reaction was concentrated and purified by flash column chromatography to afford the pure product **3a** as a yellow oil (22 mg) in 78% yield and with 94:6 er. The results are comparable to that using separate Pd catalyst and chiral ligand **L11** under standard conditions.

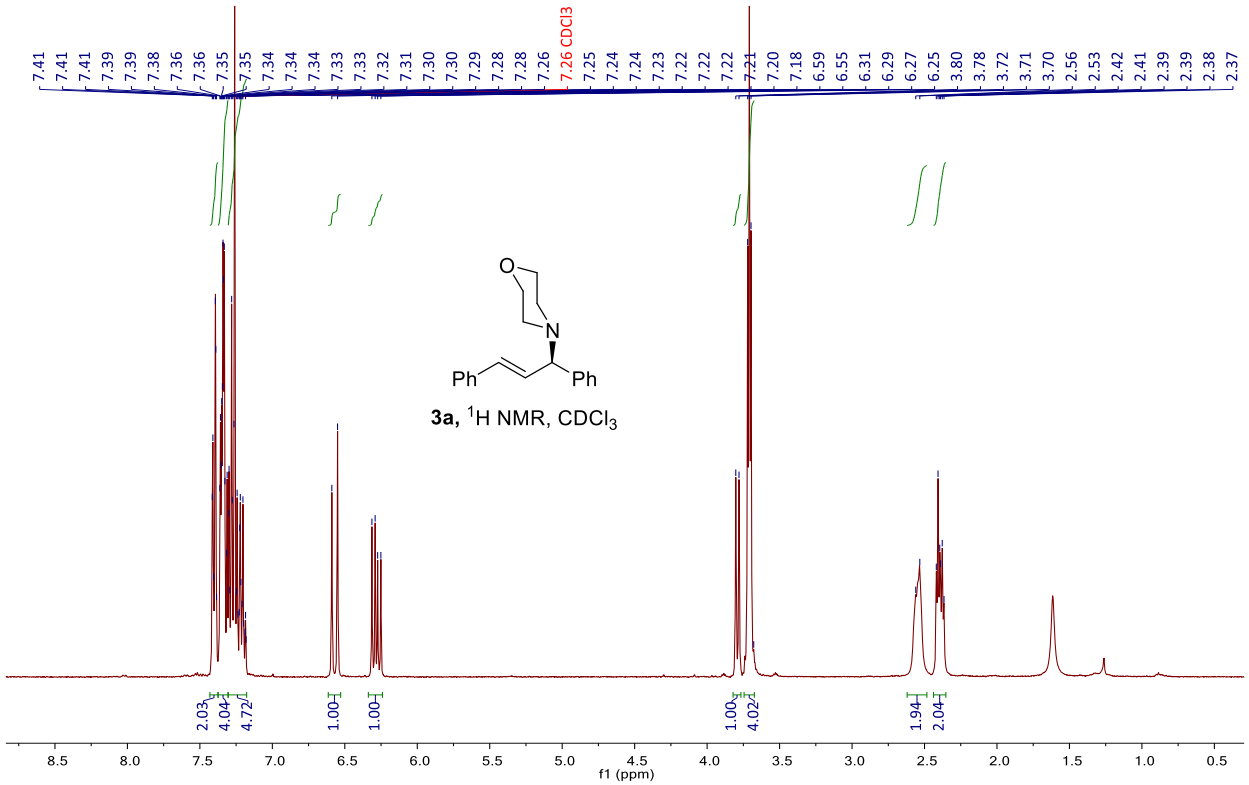
7. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra


8.03 8.02 8.02 8.01 7.83 7.82 7.81 7.58 7.56 7.55 7.55 7.54 7.49 7.49 7.49 7.48 7.46 7.45 7.44 7.43 7.43 7.41 7.36 7.35 7.33 7.33 7.26 CDCl3 7.25 7.24 7.17 7.16 6.79 6.78 6.78 6.77 6.76 6.42 6.40 6.39 6.37 6.34 6.31 5.92 5.90 4.79 4.77 4.77 4.75 3.72 3.72 -0.00
O
O
Ph
Ph
MeO
CF3
1k
1H NMR, CDCl3
2.05 2.04 1.06 5.26 2.15 2.01 2.09 2.01 1.00 1.01 1.00 1.03 3.01
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 -0.5
f1 (ppm)

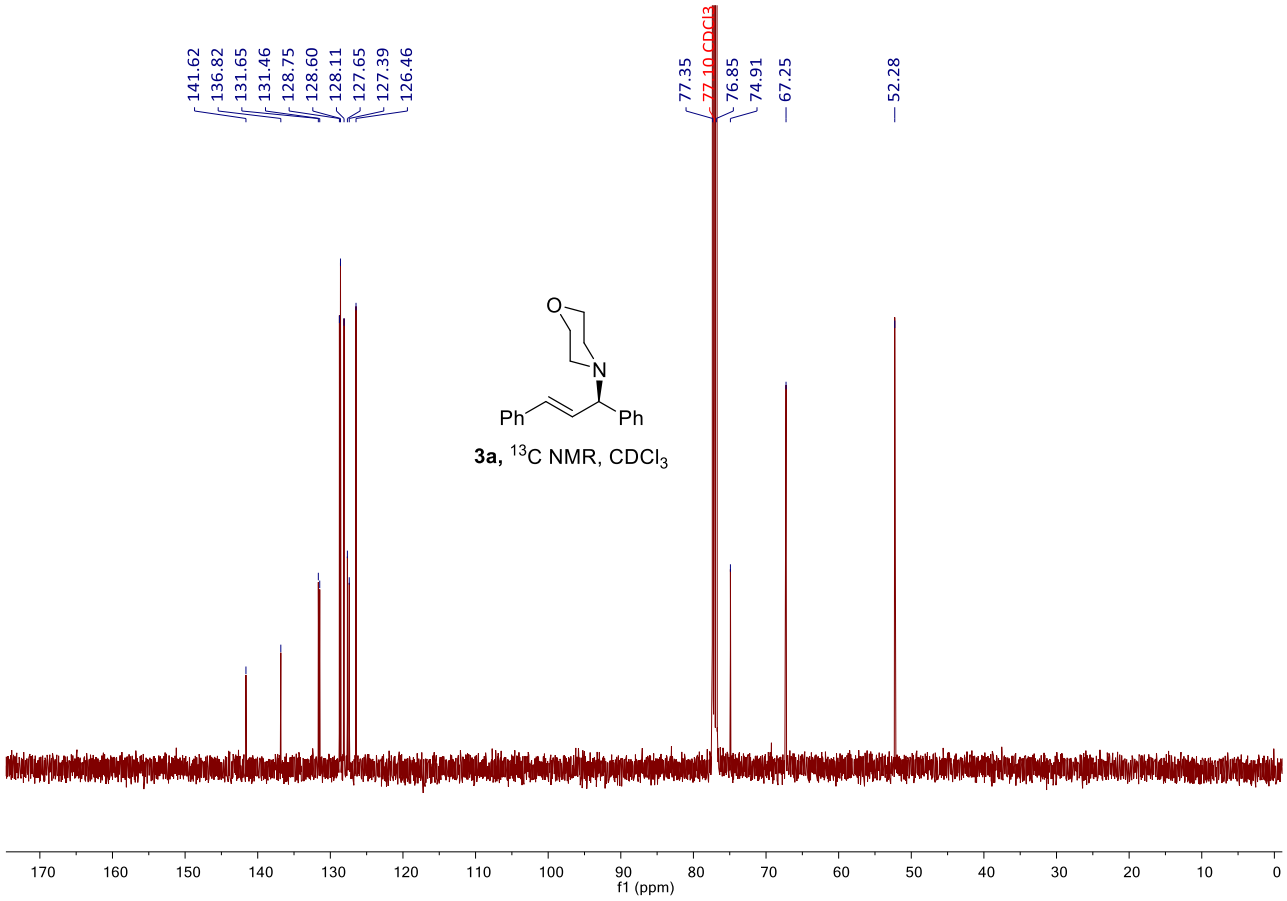

194.45 193.73 158.54 140.44 137.17 136.81 133.66 133.38 133.05 132.39 130.29 129.38 129.21 129.01 128.79 128.70 128.57 127.50 126.40 125.31 125.28 123.12 120.96 114.20 77.35 77.10 CDCl3 76.85 62.57 55.22 49.24
O
O
Ph
Ph
MeO
CF3
1k
13C NMR, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



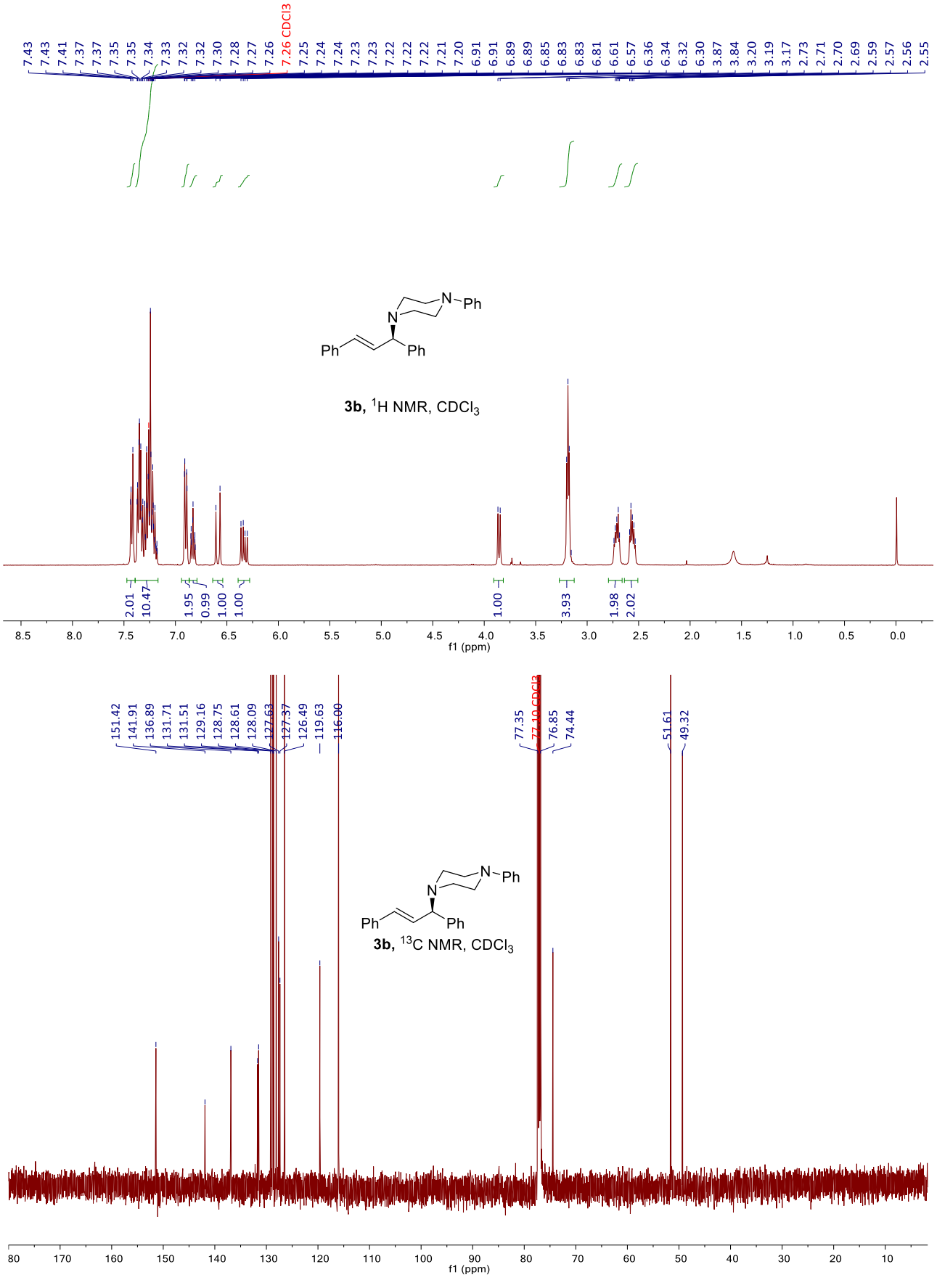
1k, ^{19}F NMR, $CDCl_3$

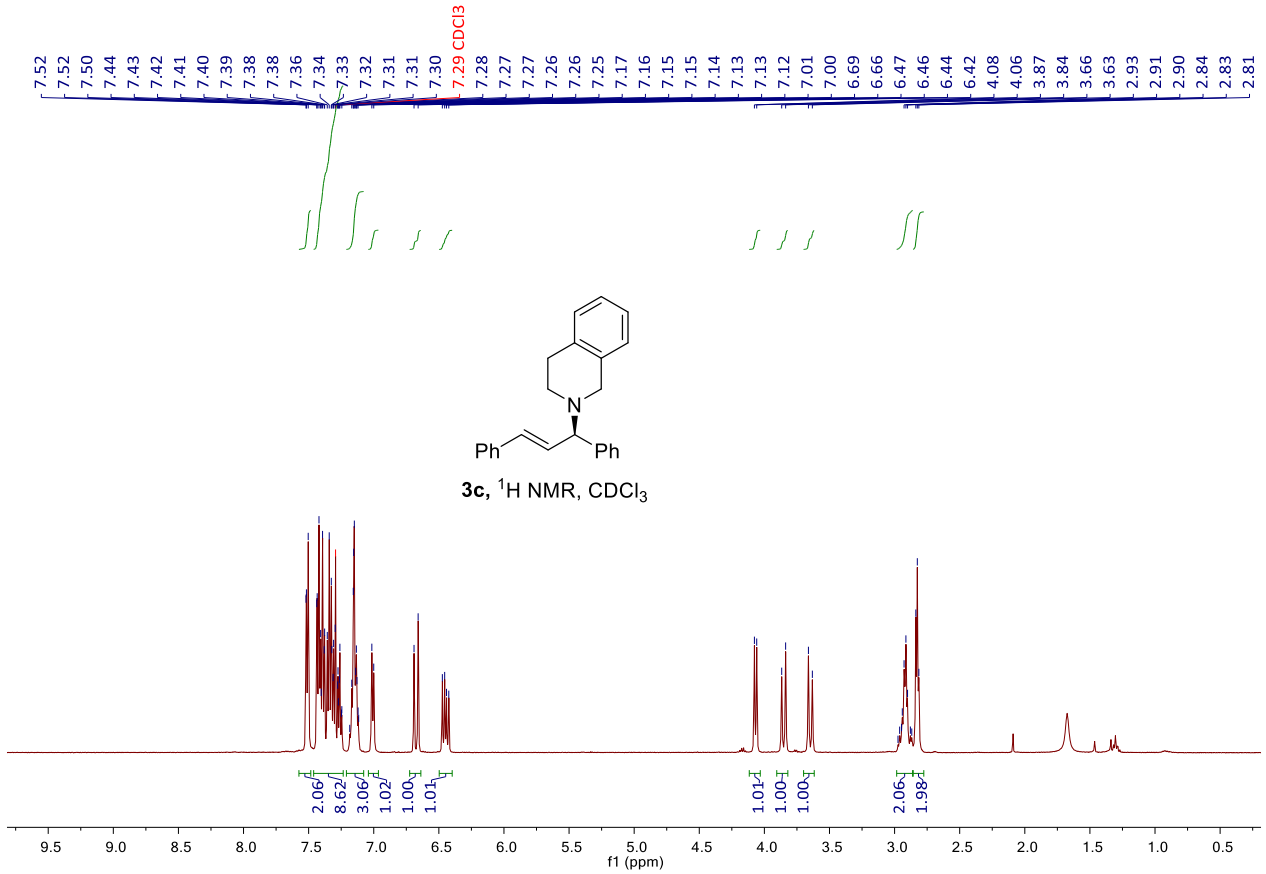


3a, ^{1}H NMR, $CDCl_3$

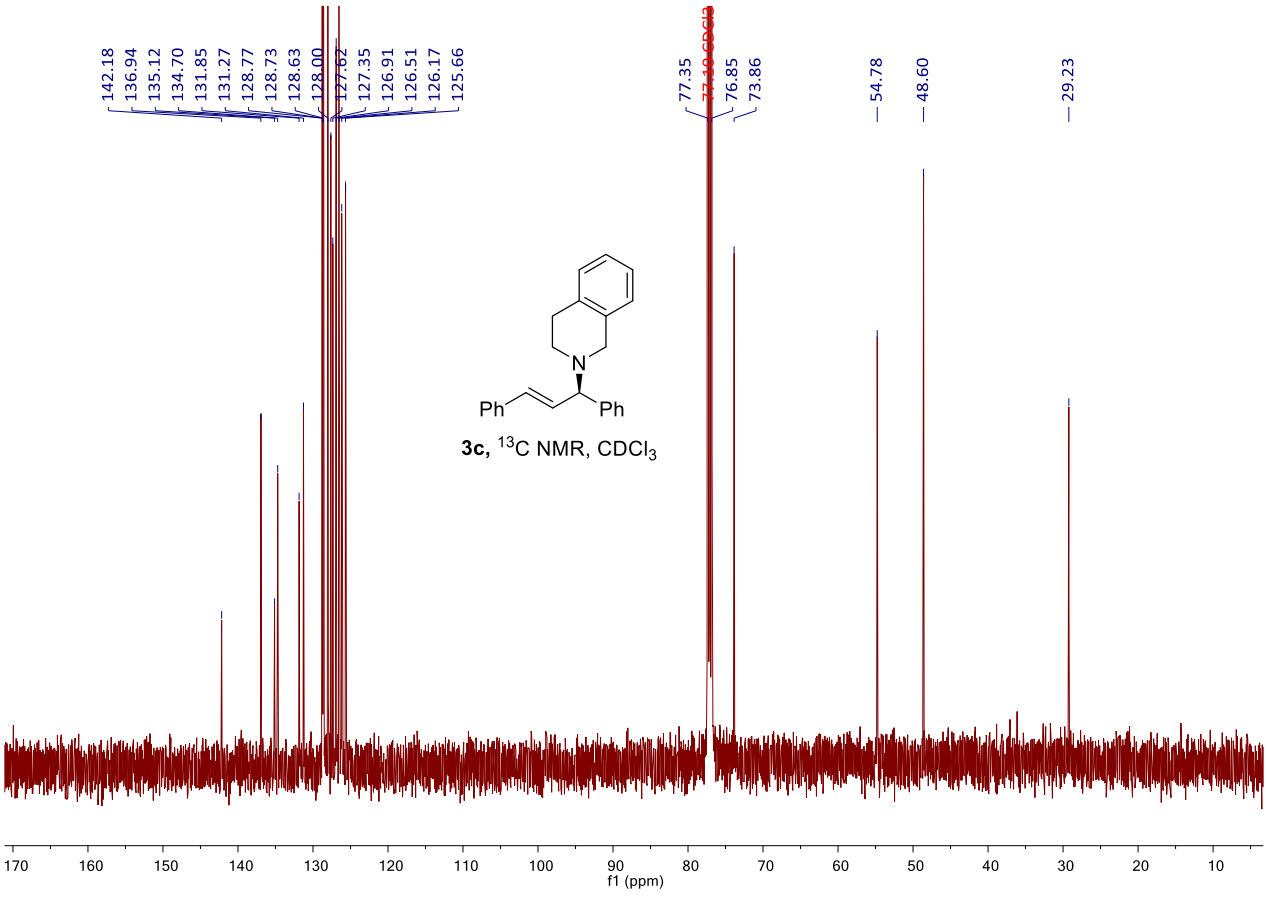


3a, ^{13}C NMR, $CDCl_3$

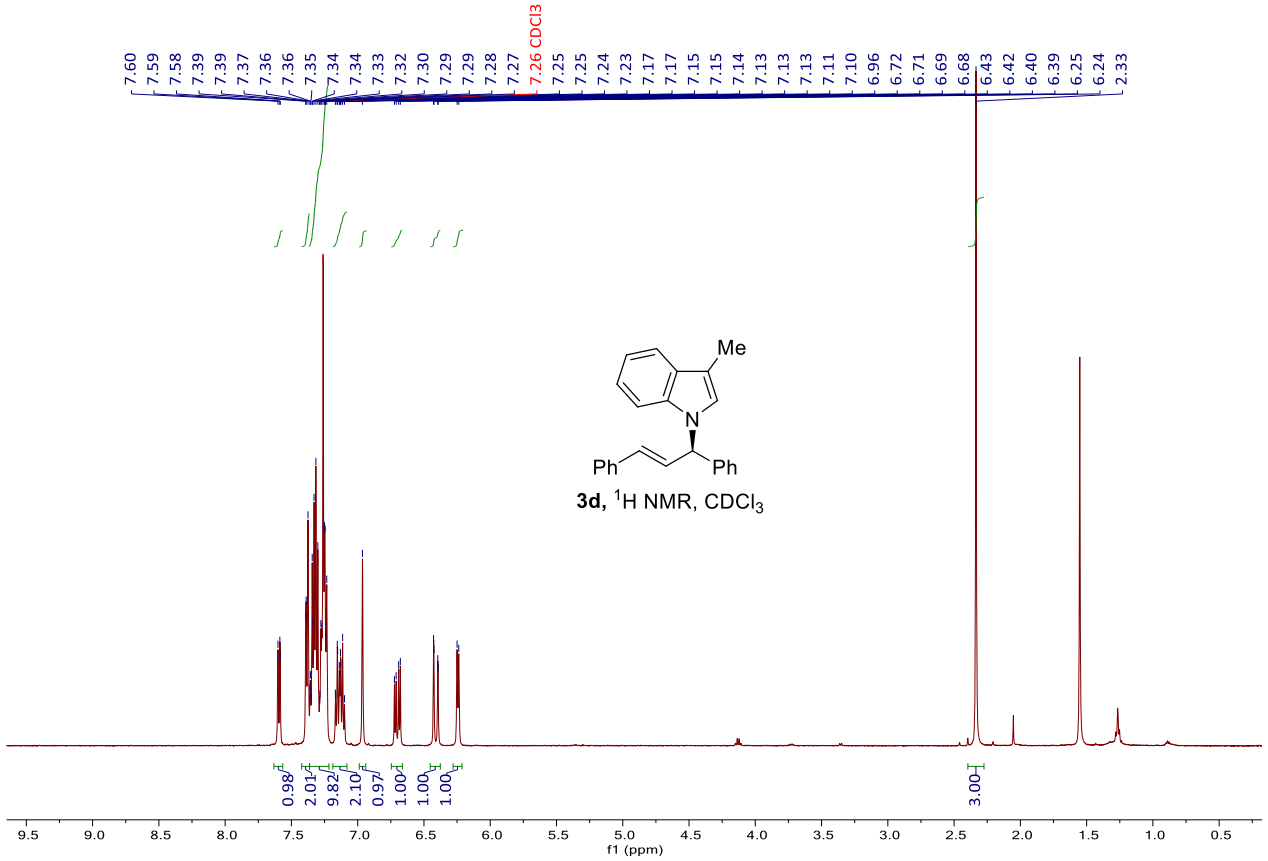

7.43 7.43 7.41 7.37 7.37 7.35 7.35 7.34 7.33 7.32 7.32 7.30 7.28 7.27 7.26 7.26 CDCl3 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.20 6.91 6.91 6.89 6.89 6.85 6.83 6.83 6.81 6.61 6.57 6.36 6.34 6.32 6.30 3.87 3.84 3.20 3.19 3.17 2.73 2.71 2.70 2.69 2.59 2.57 2.56 2.55
N
Ph
N
Ph
Ph
3b, 1H NMR, CDCl3
2.01 10.47 1.95 0.99 1.00 1.00 1.00 3.93 1.98 2.02
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
f1 (ppm)
151.42 141.91 136.89 131.71 131.51 129.16 128.75 128.61 128.09 127.63 127.37 126.49 119.63 116.00
77.35 77.10 CDCl3 76.85 74.44
51.61 49.32
N
Ph
N
Ph
Ph
3b, 13C NMR, CDCl3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



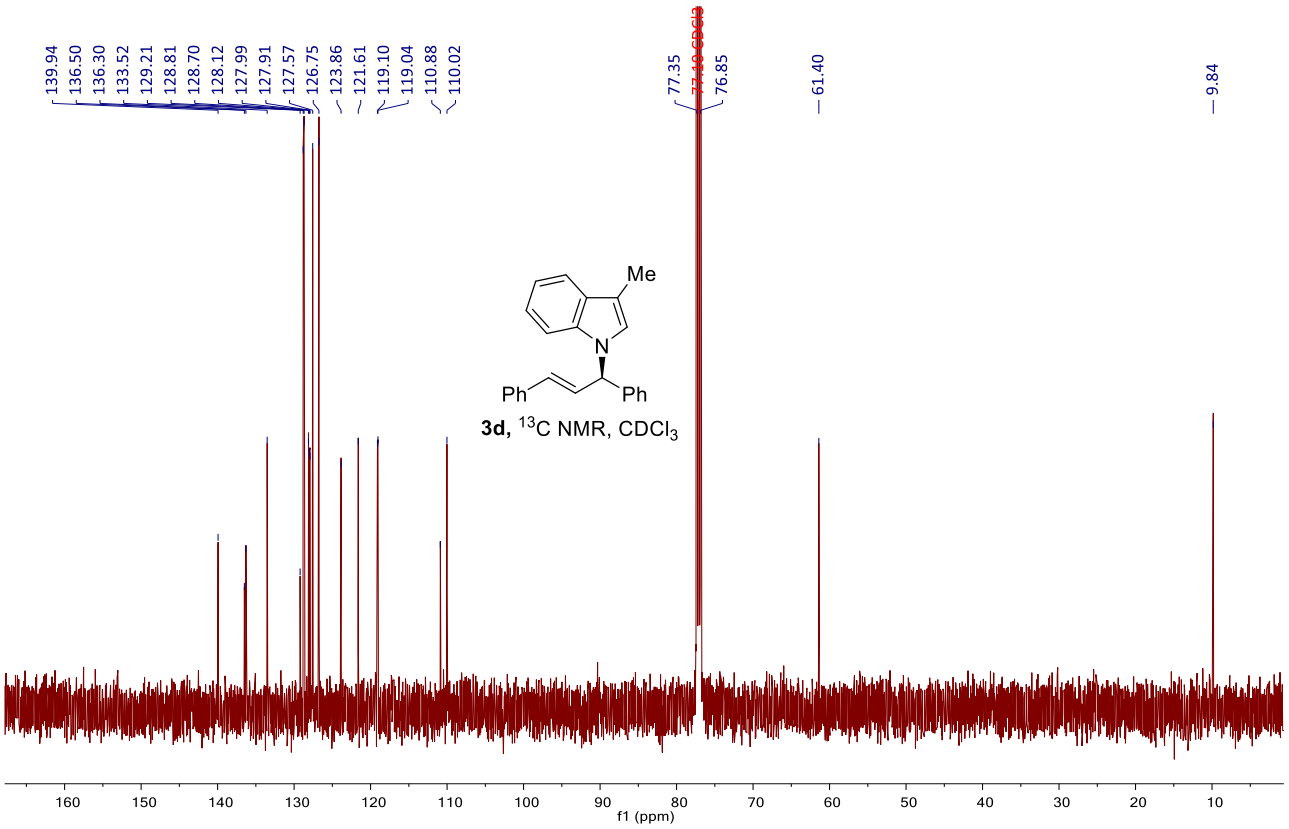
3c, ^{1}H NMR, $CDCl_3$



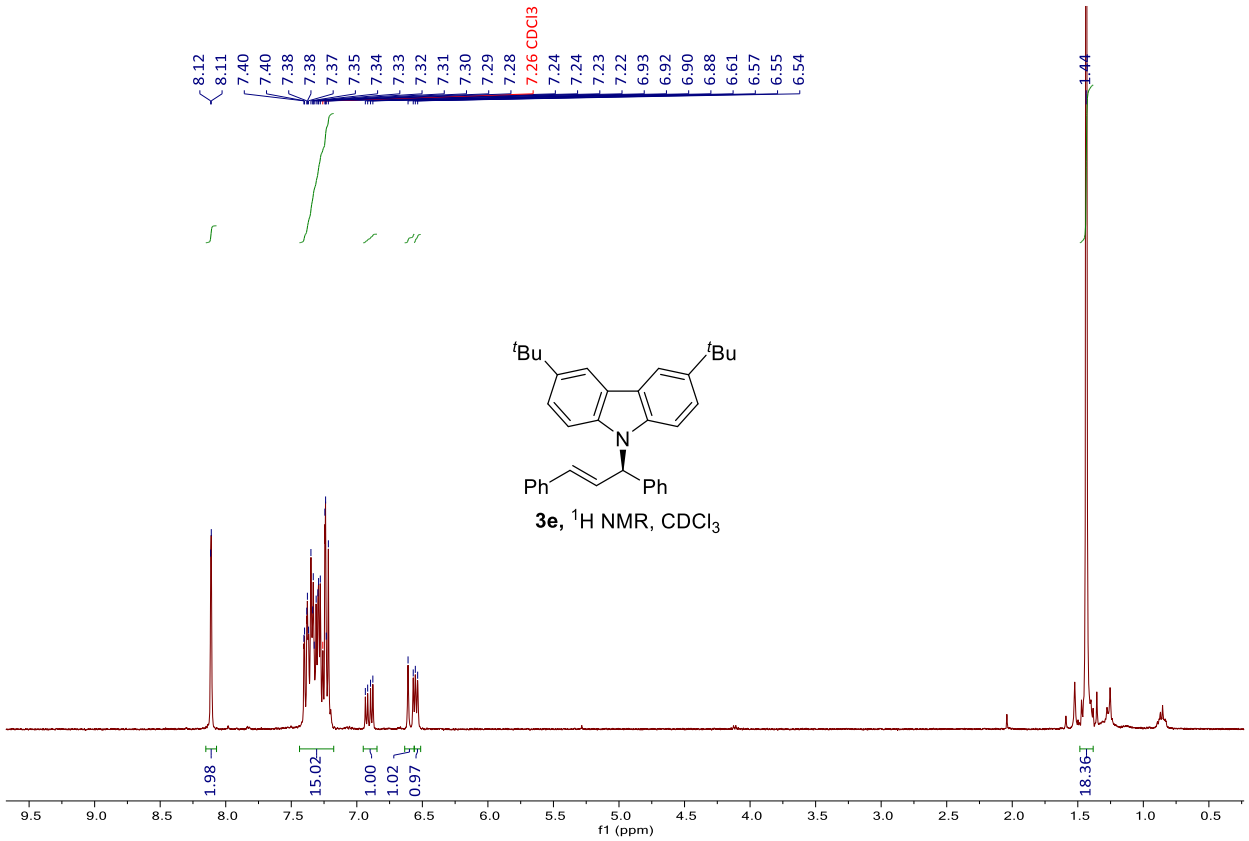
3c, ^{13}C NMR, $CDCl_3$



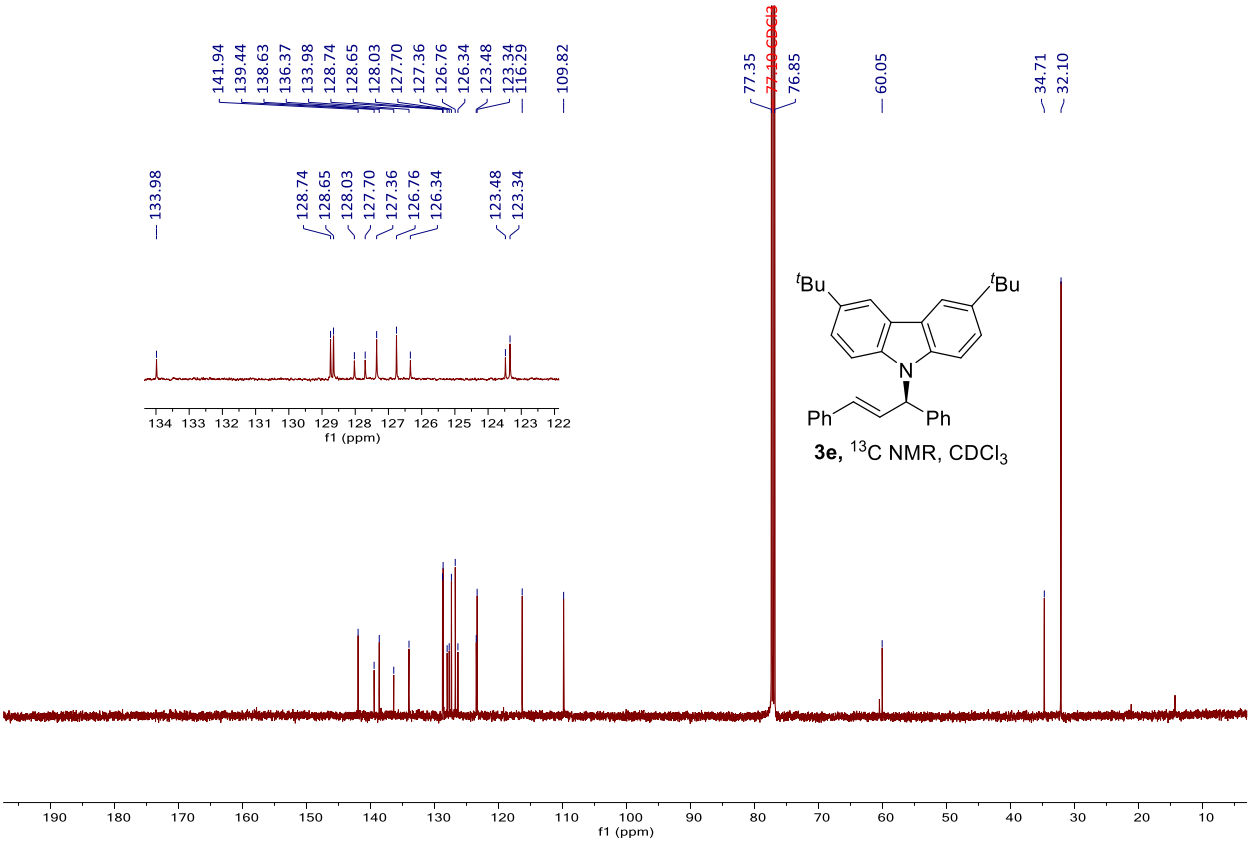
3d, ^{1}H NMR, $CDCl_3$



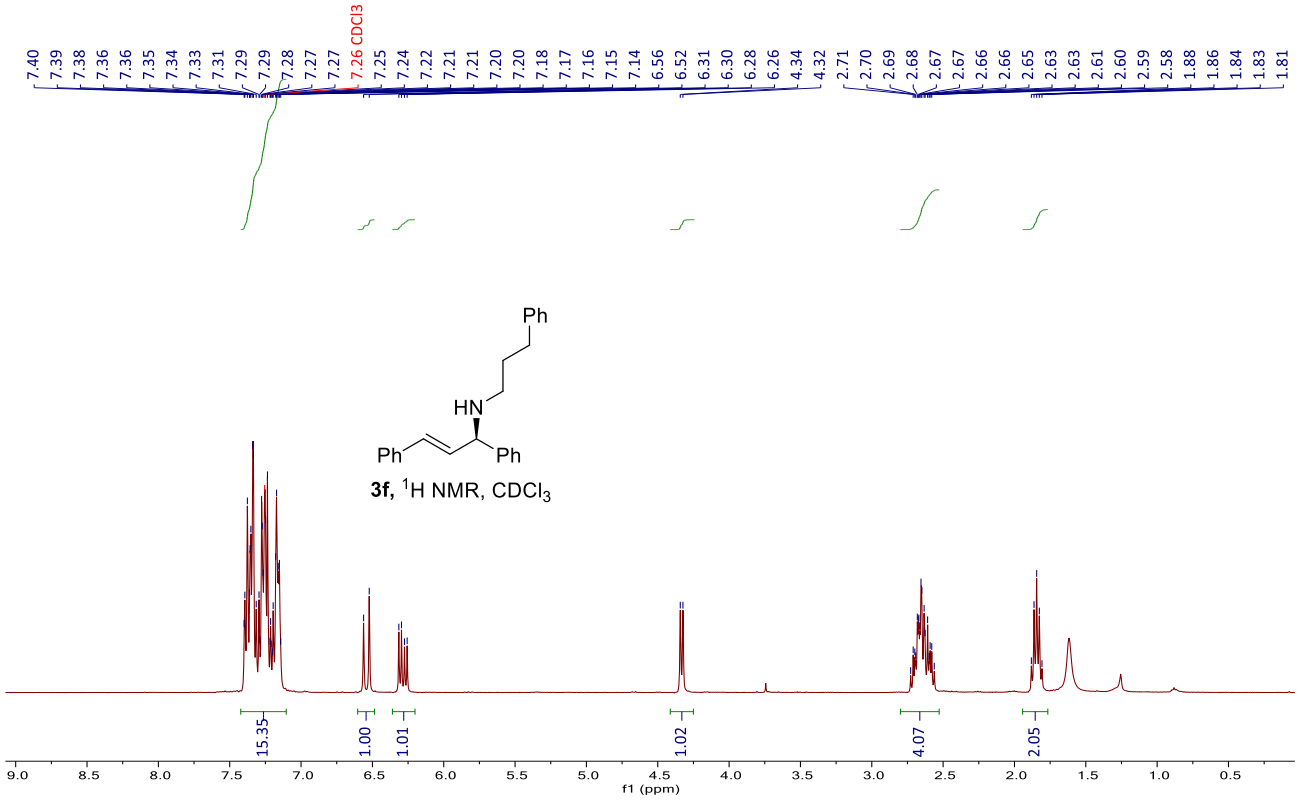
3d, ^{13}C NMR, $CDCl_3$

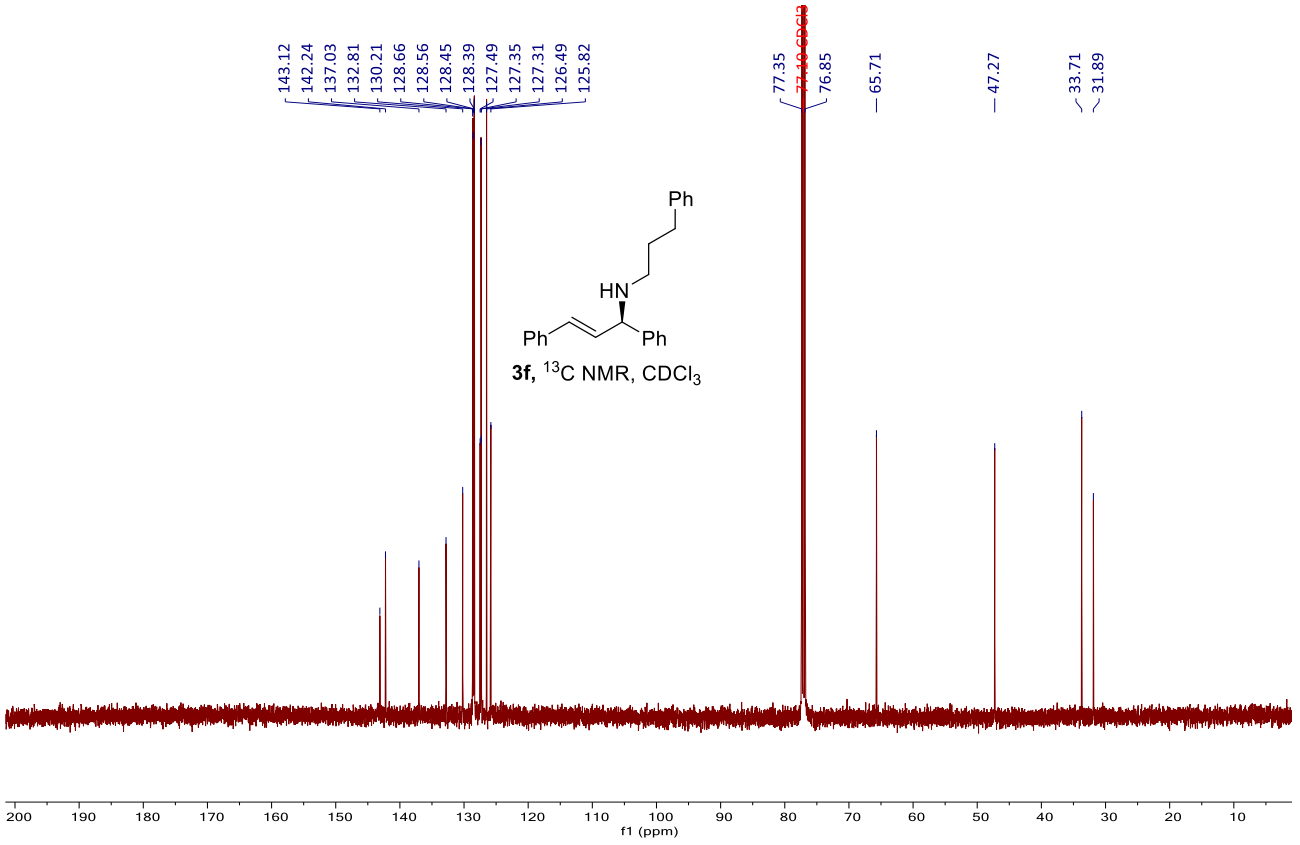


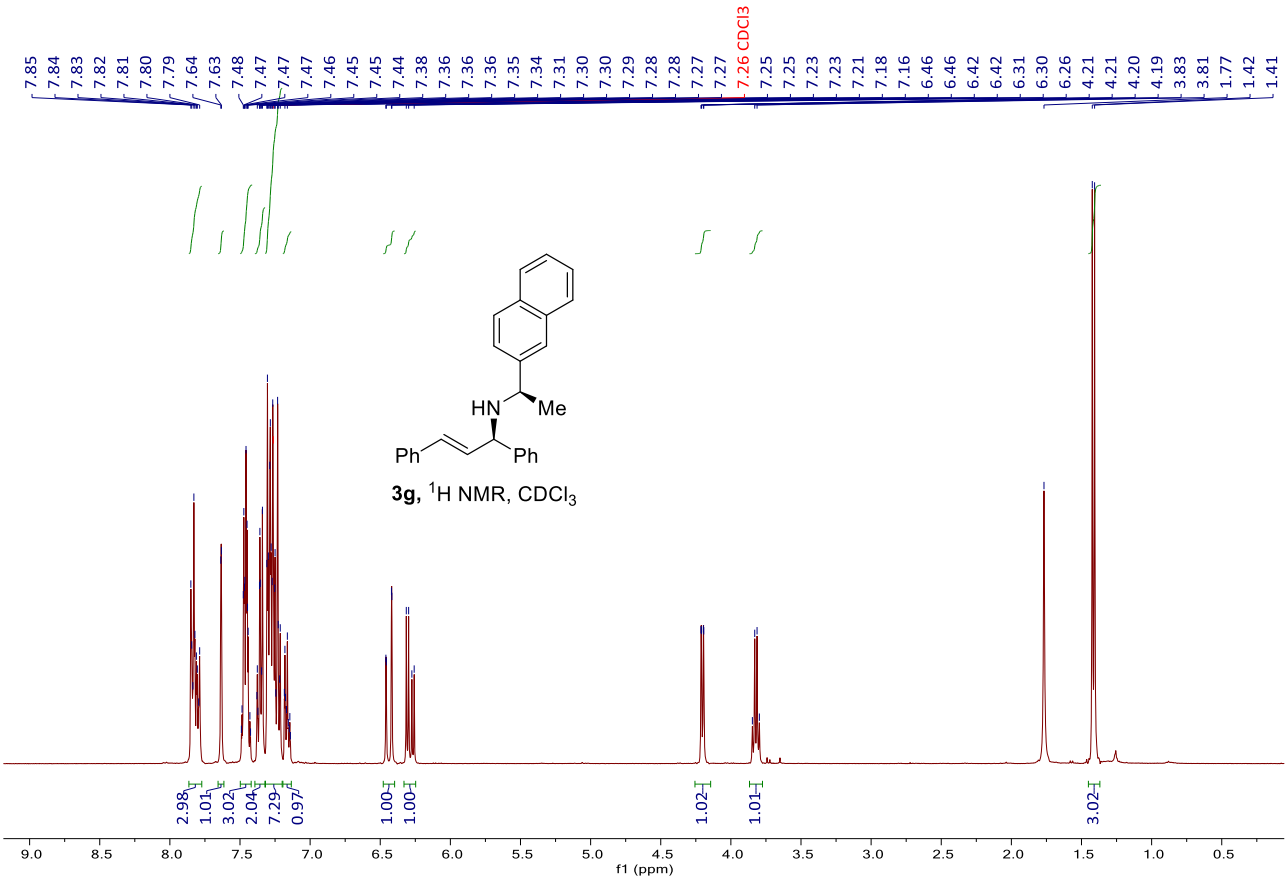
3e, ^{1}H NMR, $CDCl_3$



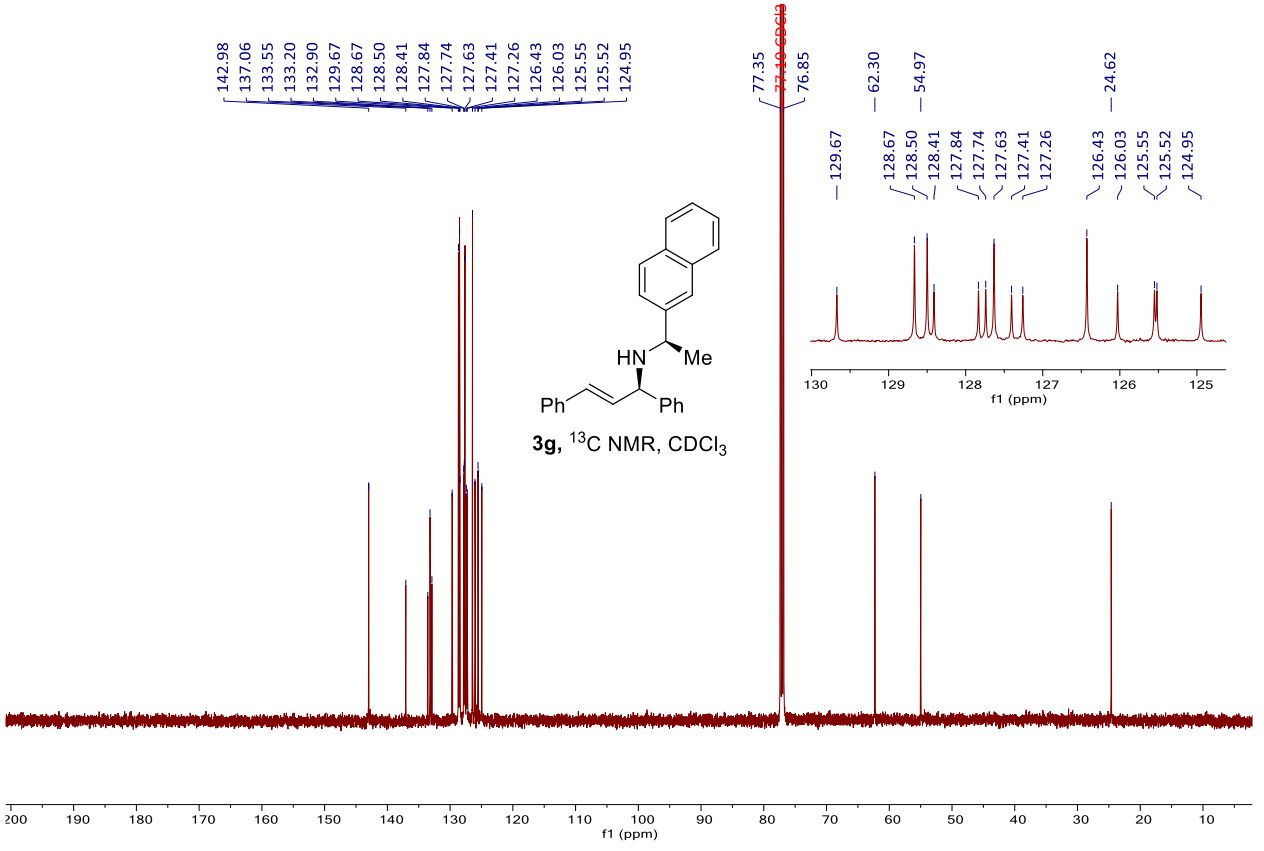
3e, ^{13}C NMR, $CDCl_3$


7.40 7.39 7.38 7.36 7.36 7.35 7.34 7.33 7.31 7.29 7.29 7.28 7.27 7.27 7.26 CDCl3 7.25 7.24 7.22 7.21 7.21 7.20 7.20 7.18 7.17 7.16 7.15 7.14 6.56 6.52 6.31 6.30 6.28 6.26 4.34 4.32 2.71 2.70 2.69 2.68 2.67 2.67 2.66 2.66 2.65 2.63 2.63 2.61 2.60 2.59 2.58 1.88 1.86 1.84 1.83 1.81
Ph
HN
Ph
Ph
3f, 1H NMR, CDCl3
15.35
1.00
1.01
1.02
4.07
2.05
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
f1 (ppm)

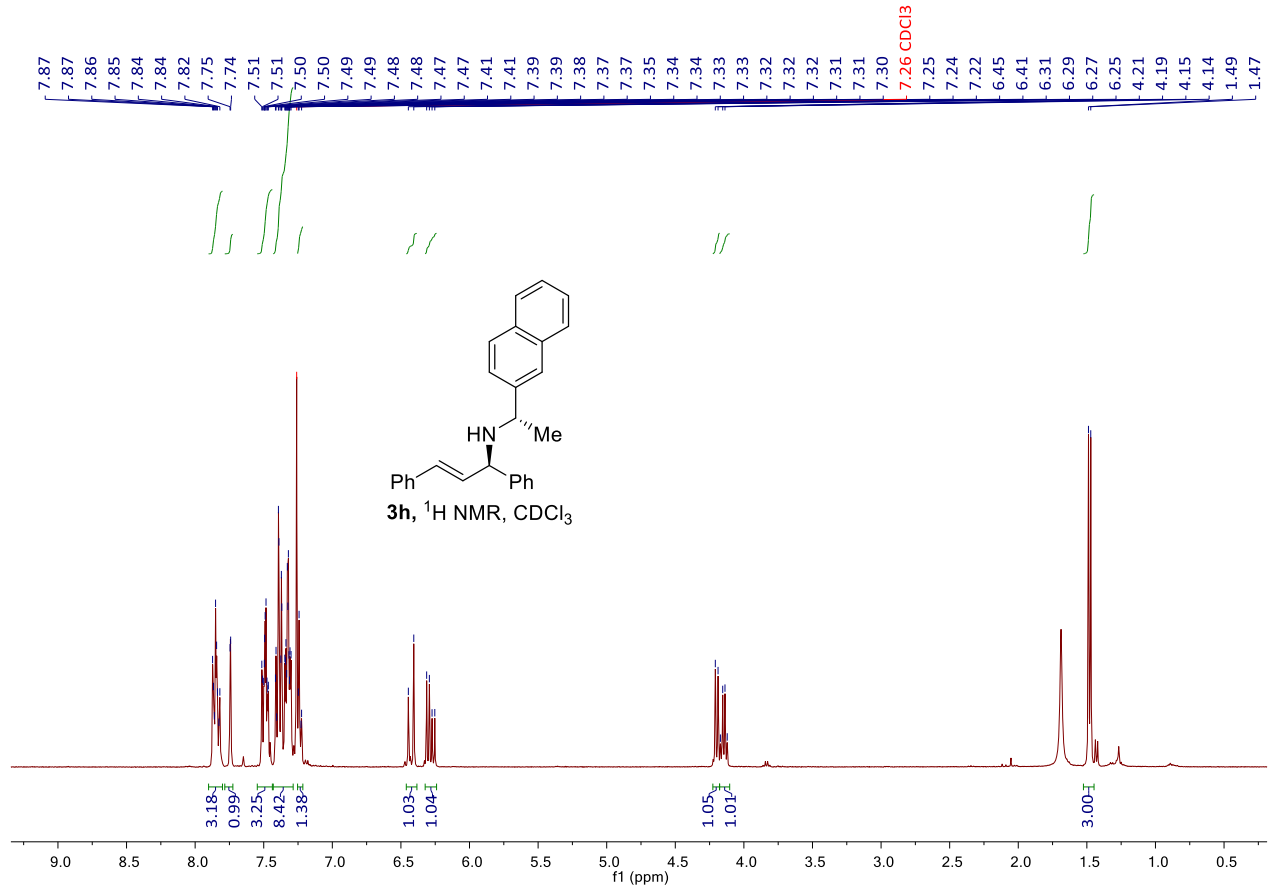

143.12 142.24 137.03 132.81 130.21 128.66 128.56 128.45 128.39 127.49 127.35 127.31 126.49 125.82
77.35 77.10 CDCl3 76.85
65.71
47.27
33.71
31.89
Ph
HN
Ph
Ph
3f, 13C NMR, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

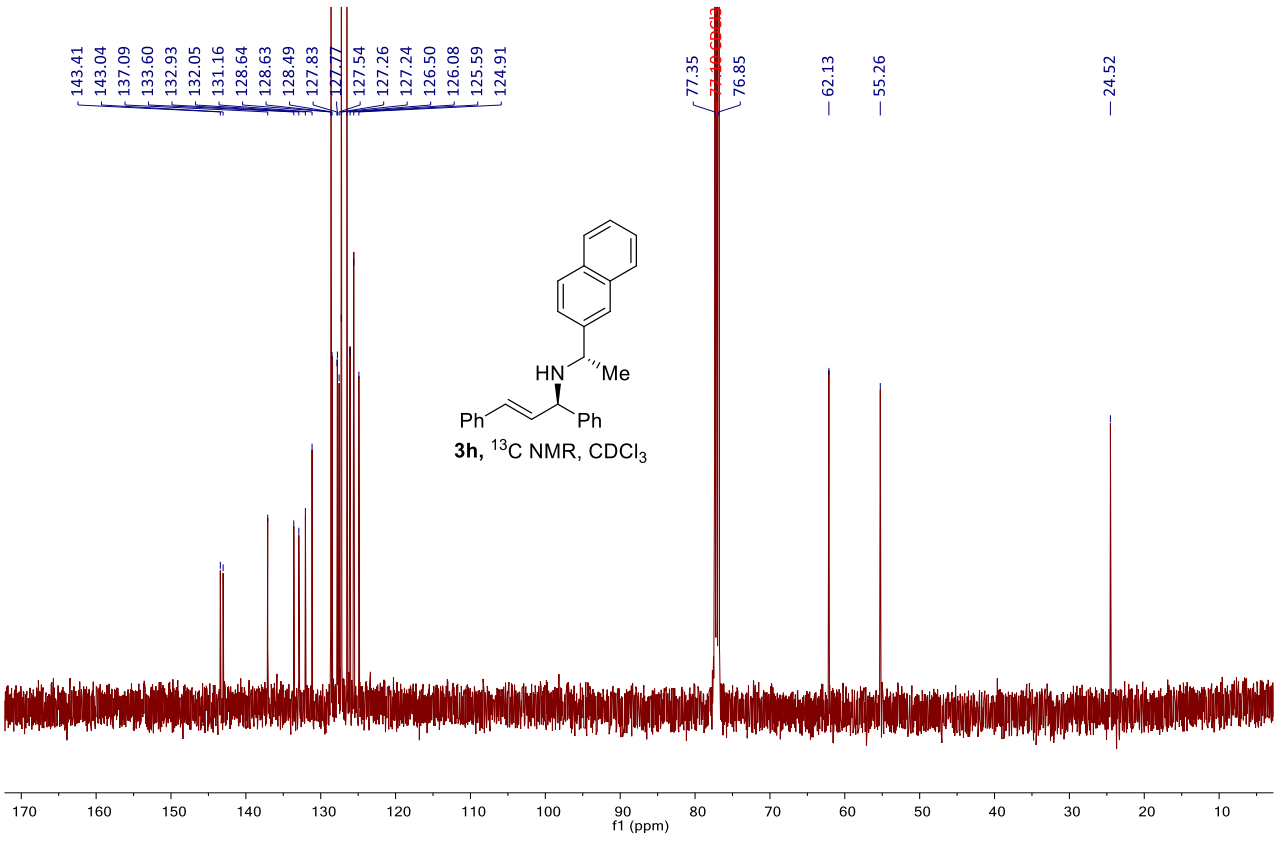


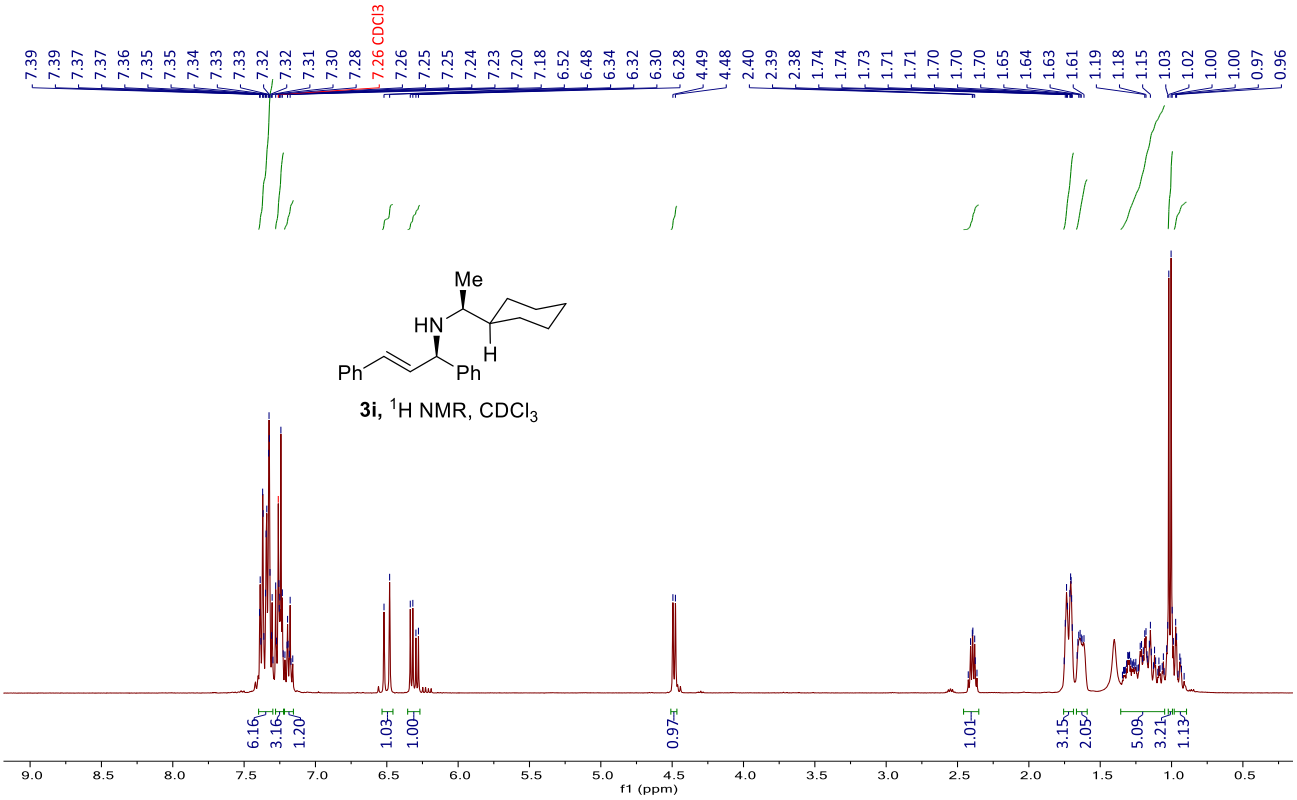
3g, ^{1}H NMR, $CDCl_3$

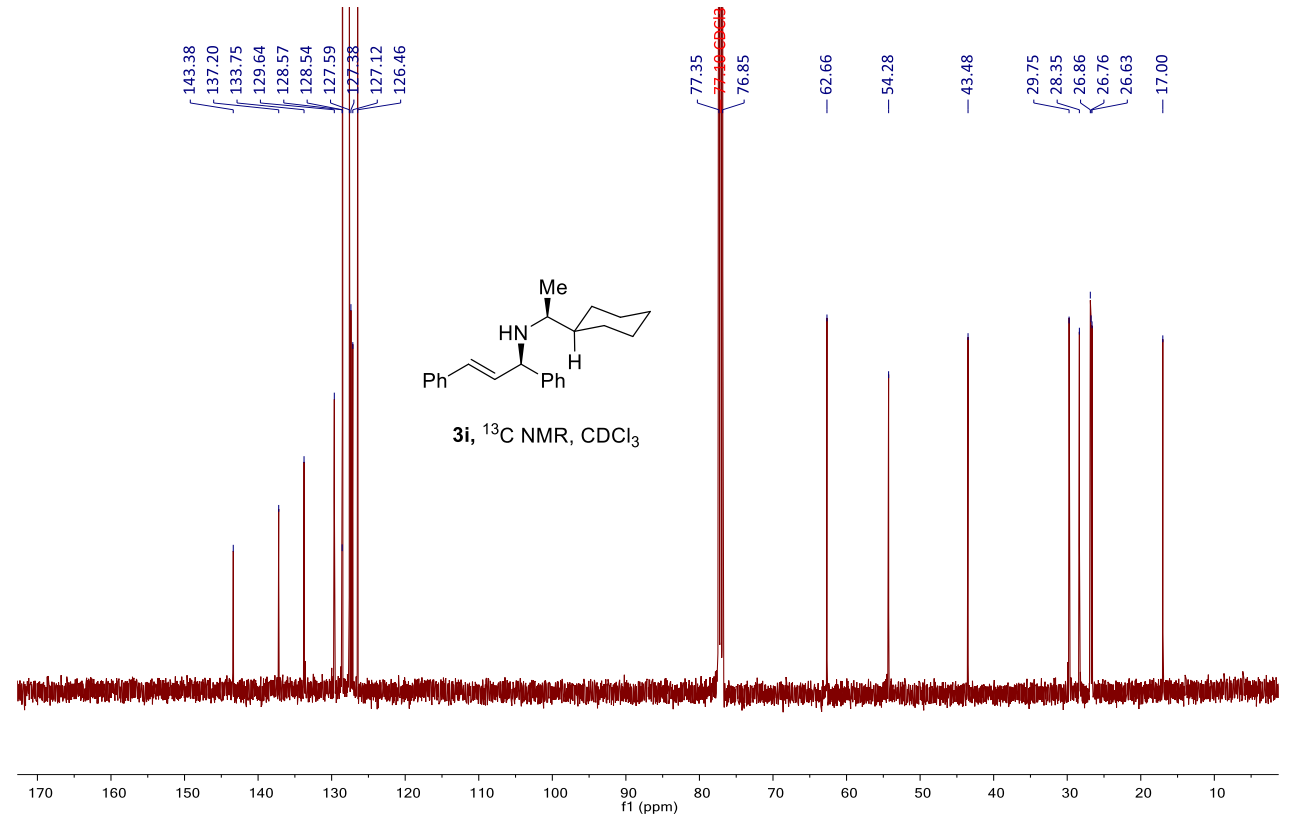


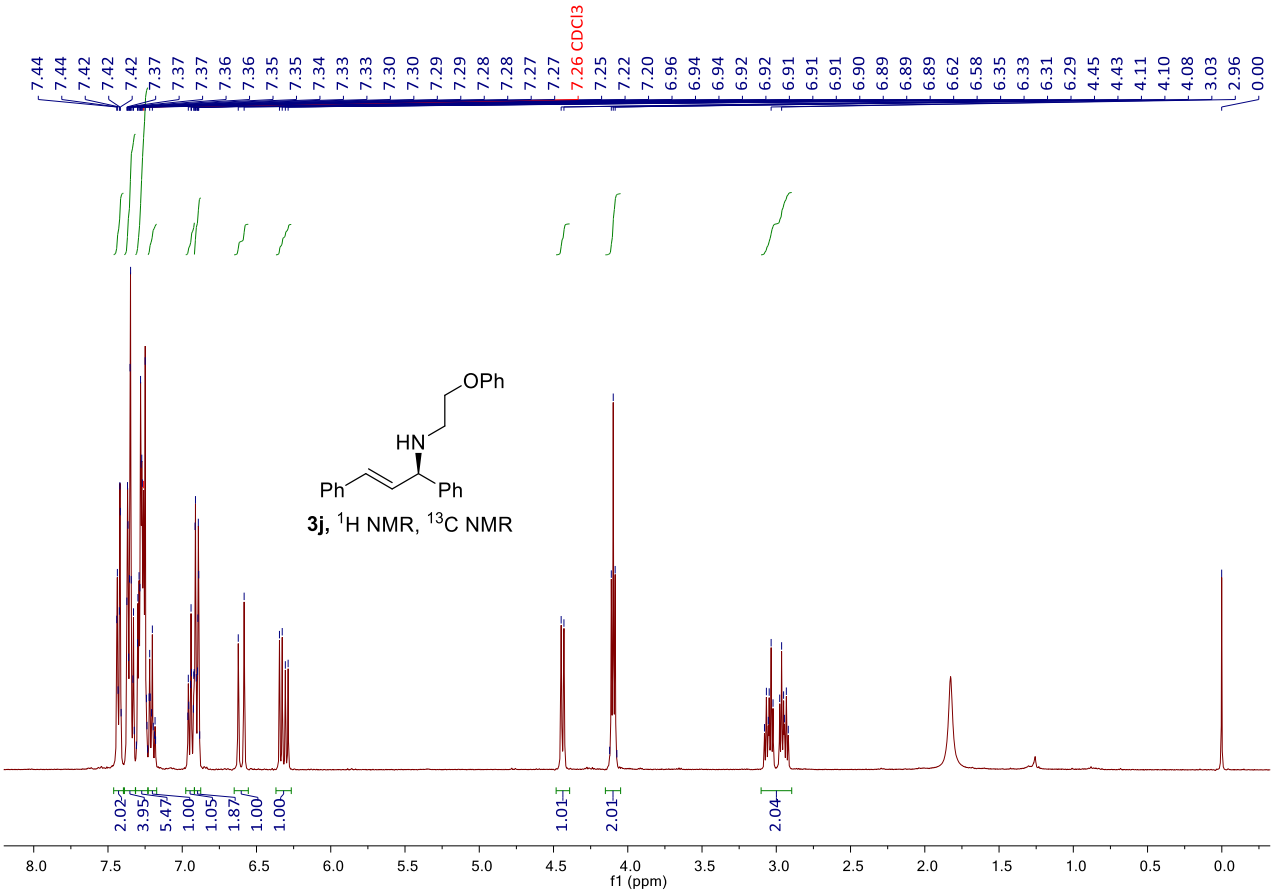
3g, ^{13}C NMR, $CDCl_3$

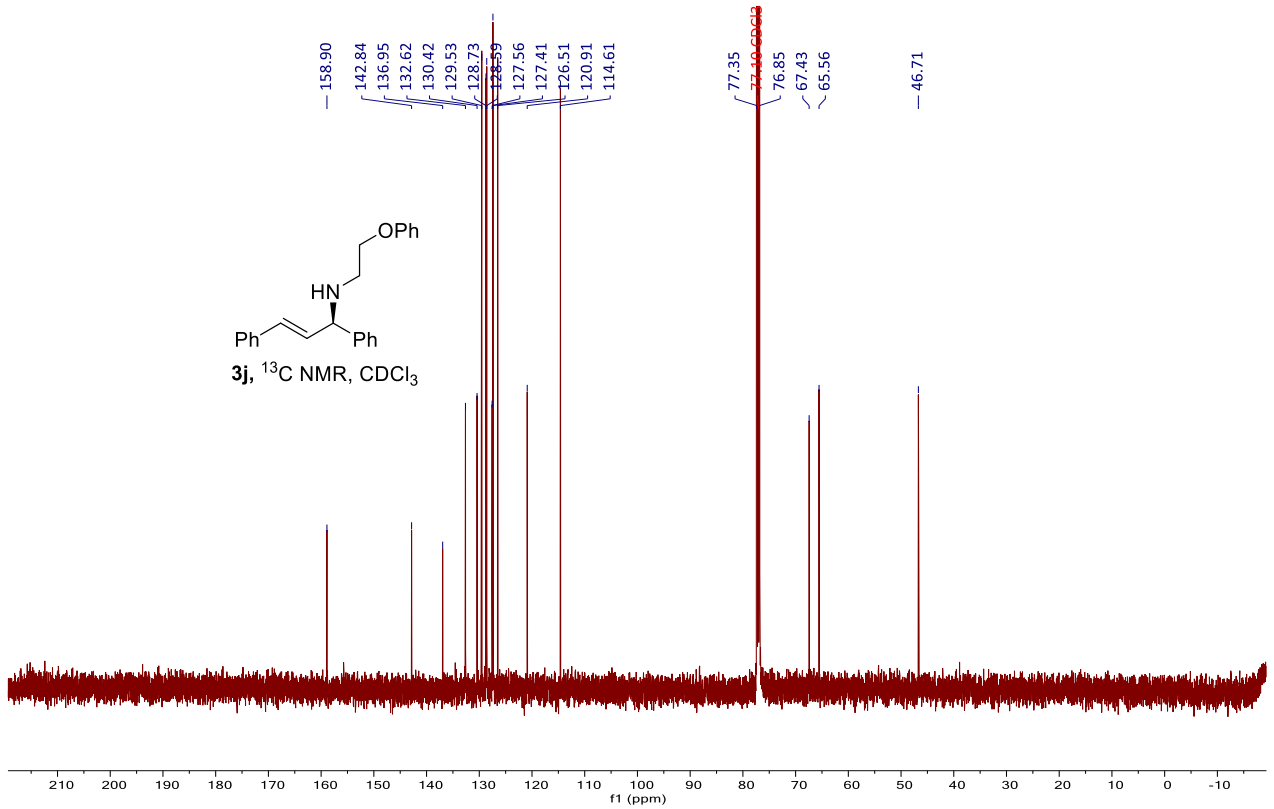

7.87 7.87 7.86 7.85 7.84 7.84 7.82 7.75 7.74 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.41 7.41 7.39 7.39 7.38 7.37 7.37 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.26 CDCl3 7.25 7.24 7.22 6.45 6.41 6.31 6.29 6.27 6.25 4.21 4.19 4.15 4.14 1.49 1.47
HN
Me
Ph
Ph
3h, 1H NMR, CDCl3
3.18 0.99 3.25 8.42 1.38 1.03 1.04 1.05 1.01 3.00
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
f1 (ppm)

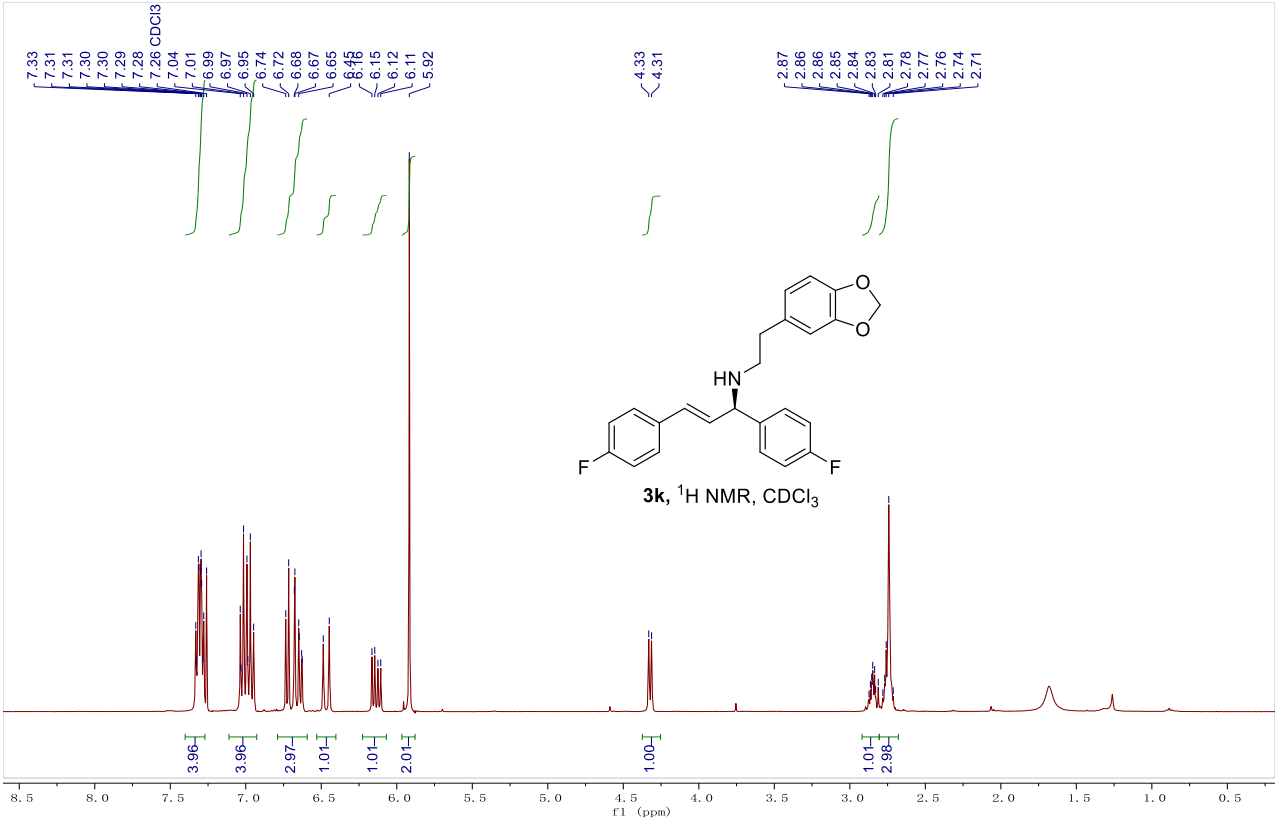

143.41 143.04 137.09 133.60 132.93 132.05 131.16 128.64 128.63 128.49 127.83 127.77 127.54 127.26 127.24 126.50 126.08 125.59 124.91
77.35 77.40 CDCl3 76.85
62.13
55.26
24.52
HN
Me
Ph
Ph
3h, 13C NMR, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.39 7.39 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.28 7.26 CDCl3 7.26 7.25 7.25 7.24 7.23 7.20 7.18 6.52 6.48 6.34 6.32 6.30 6.28 4.49 4.48 2.40 2.39 2.38 1.74 1.74 1.73 1.71 1.71 1.70 1.70 1.70 1.65 1.64 1.63 1.61 1.19 1.18 1.15 1.03 1.02 1.00 1.00 0.97 0.96
Me
HN
H
Ph
Ph
3i, 1H NMR, CDCl3
6.16 3.16 1.20 1.03 1.00 0.97 1.01 3.15 2.05 5.09 3.21 1.13
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
f1 (ppm)

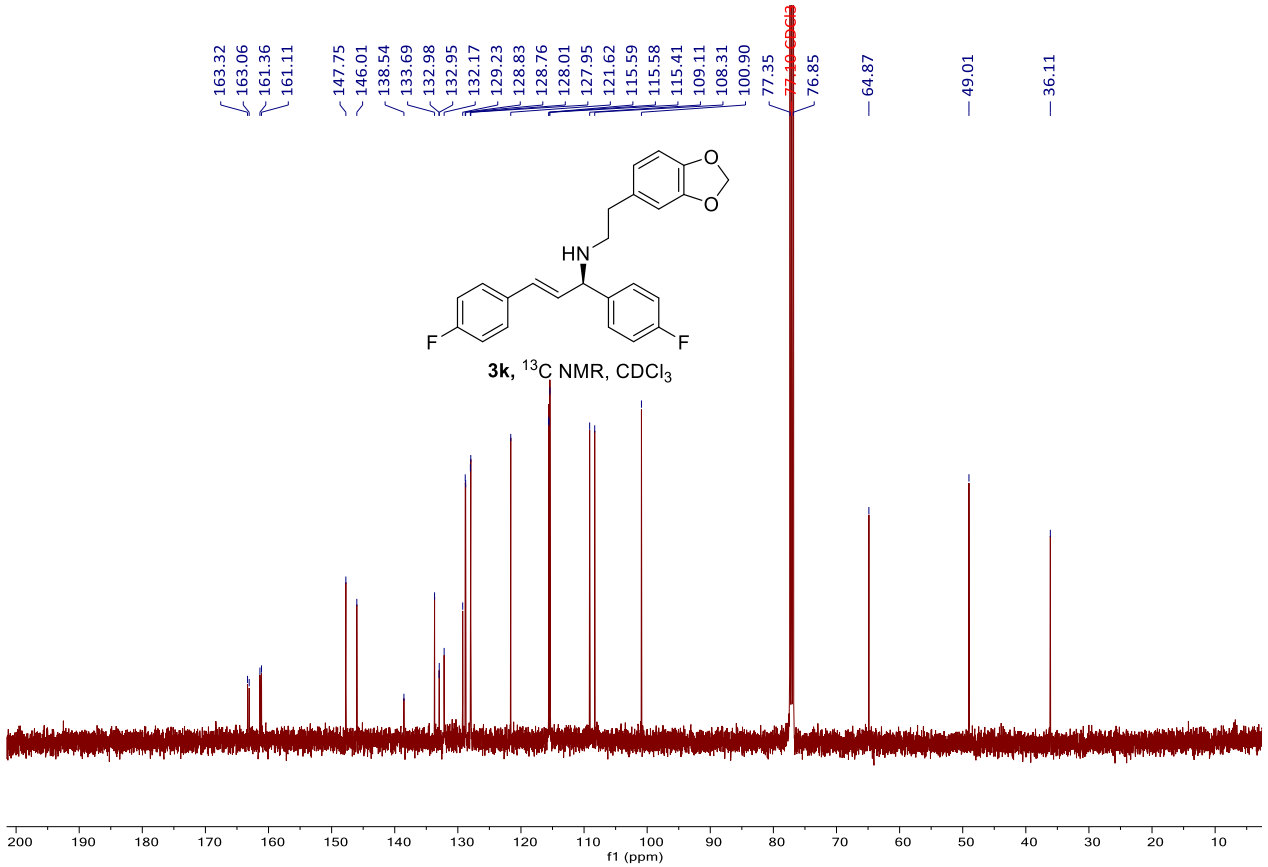

143.38 137.20 133.75 129.64 128.57 128.54 127.59 127.38 127.12 126.46
77.35 77.10 CDCl3 76.85 62.66 54.28 43.48 29.75 28.35 26.86 26.76 26.63 17.00
Me
HN
H
Ph
Ph
3i, 13C NMR, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.44 7.44 7.42 7.42 7.42 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.25 7.22 7.20 6.96 6.94 6.94 6.92 6.92 6.91 6.91 6.91 6.90 6.89 6.89 6.89 6.62 6.58 6.35 6.33 6.31 6.29 4.45 4.43 4.11 4.10 4.08 3.03 2.96 0.00
OPh
HN
Ph
Ph
3j, 1H NMR, 13C NMR
2.02 3.95 5.47 1.00 1.05 1.87 1.00 1.00 1.01 2.01 2.04
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
f1 (ppm)

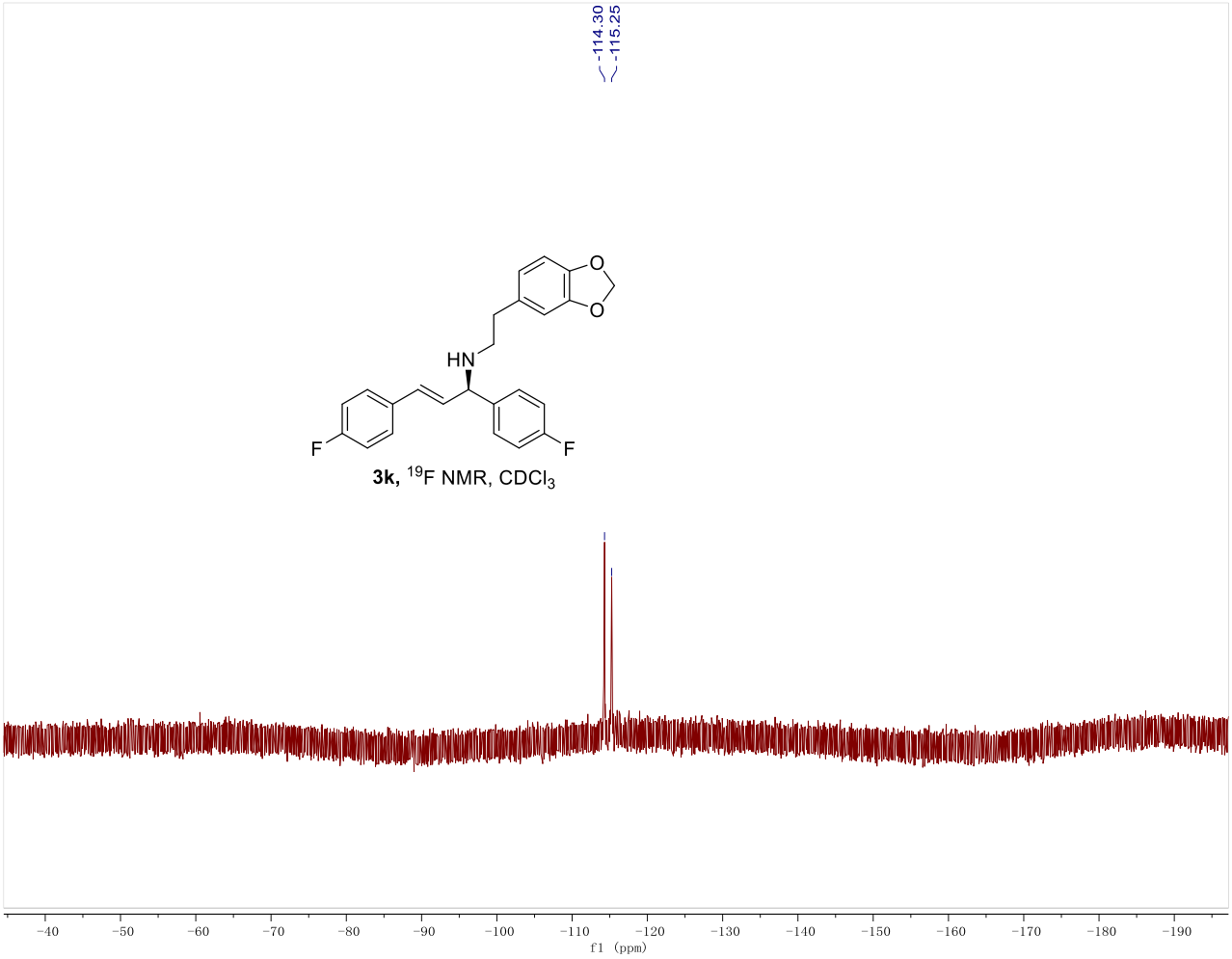

158.90 142.84 136.95 132.62 130.42 129.53 128.73 128.59 127.56 127.41 126.51 120.91 114.61
77.35 77.10 CDCl3 76.85 67.43 65.56 46.71
OPh
HN
Ph
Ph
3j, 13C NMR, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

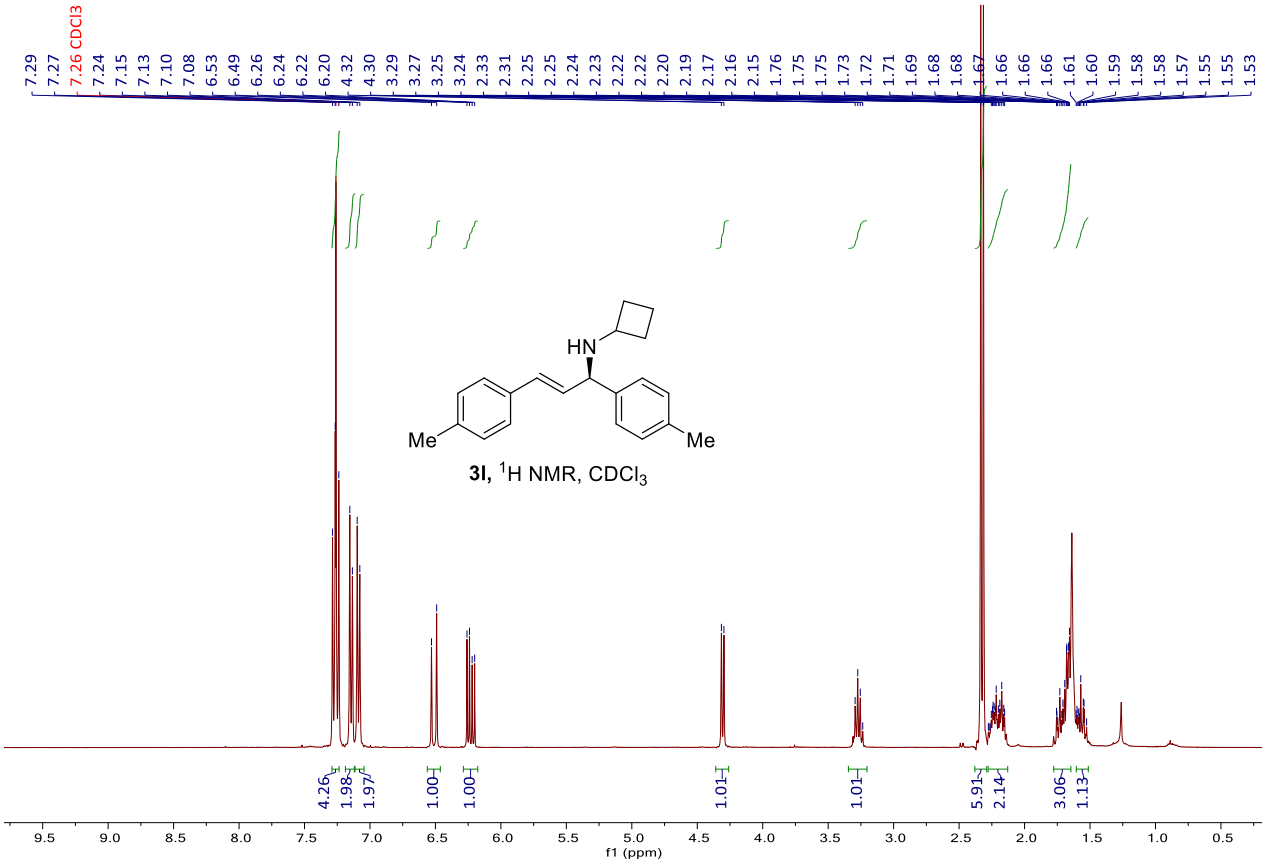


3k, ^{1}H NMR, $CDCl_3$

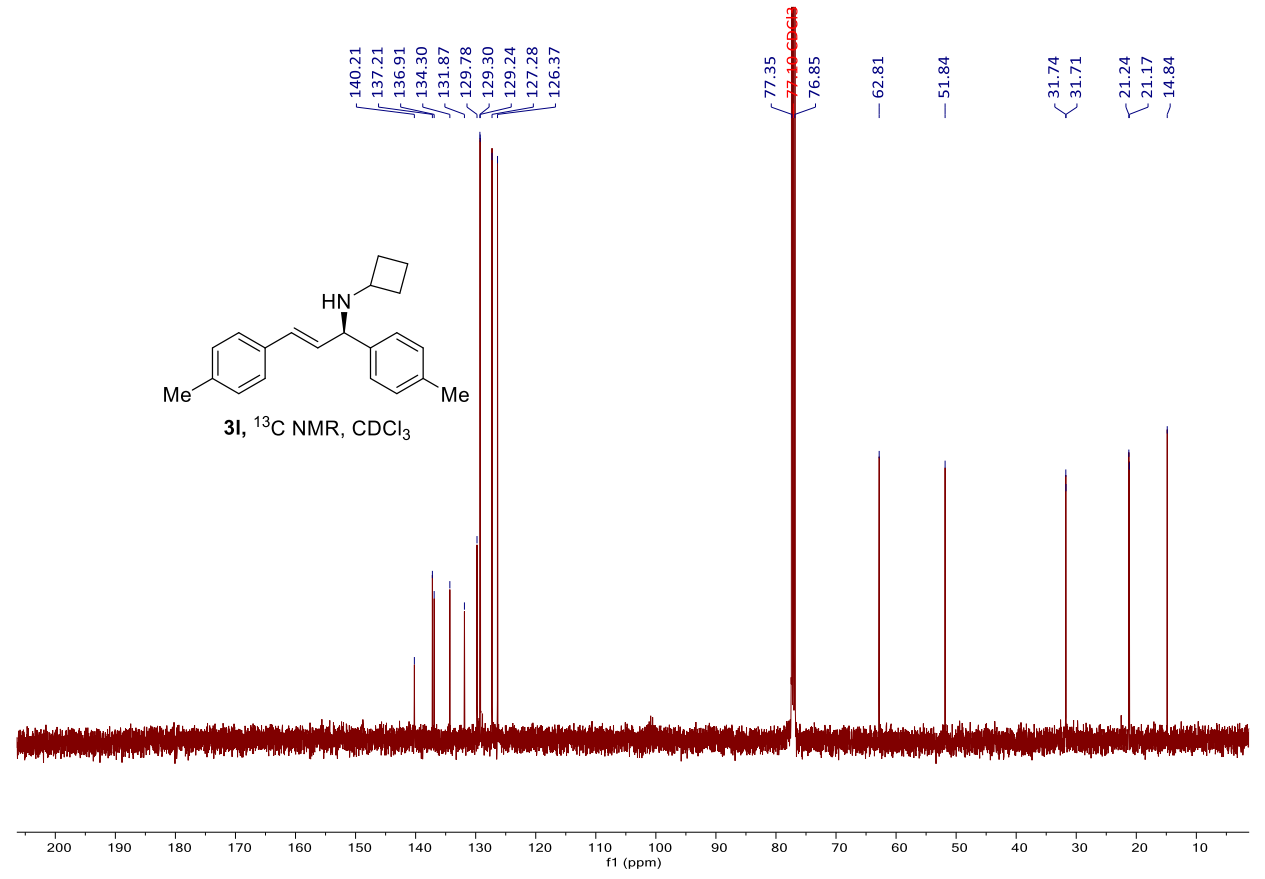


3k, ^{13}C NMR, $CDCl_3$

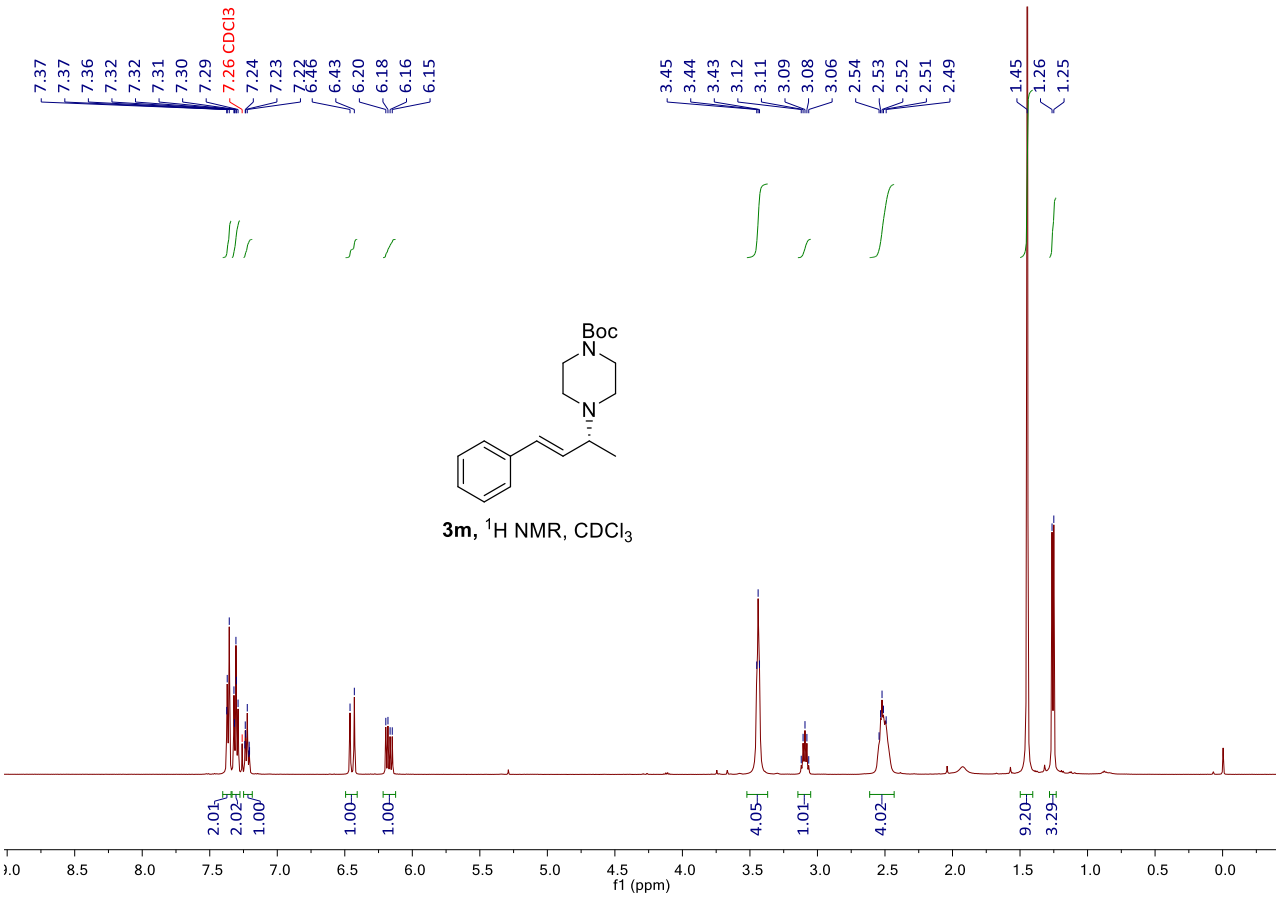

-114.30
-115.25
O
O
HN
F
F
3k, 19F NMR, CDCl3
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)



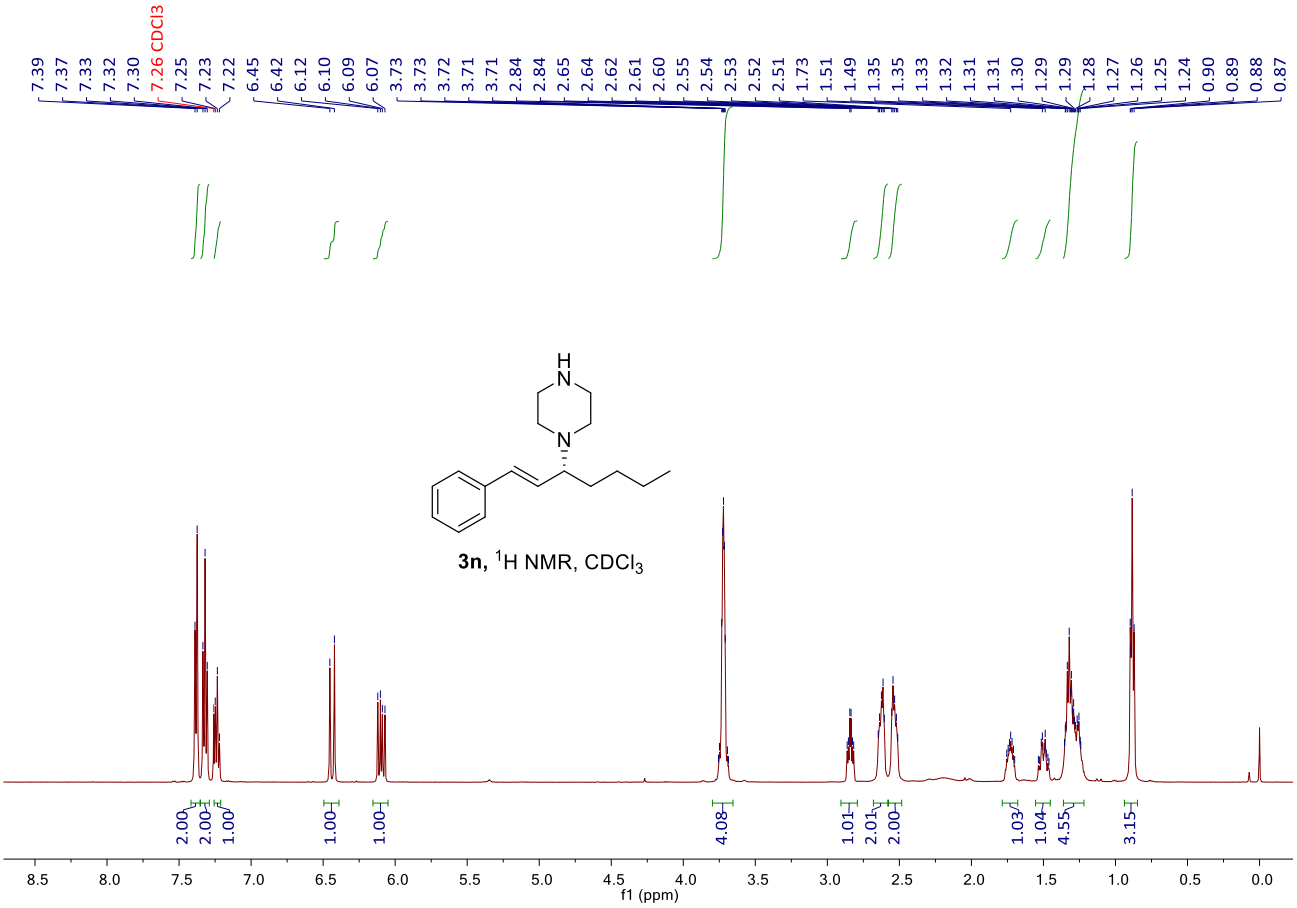
3l, ^{1}H NMR, $CDCl_3$



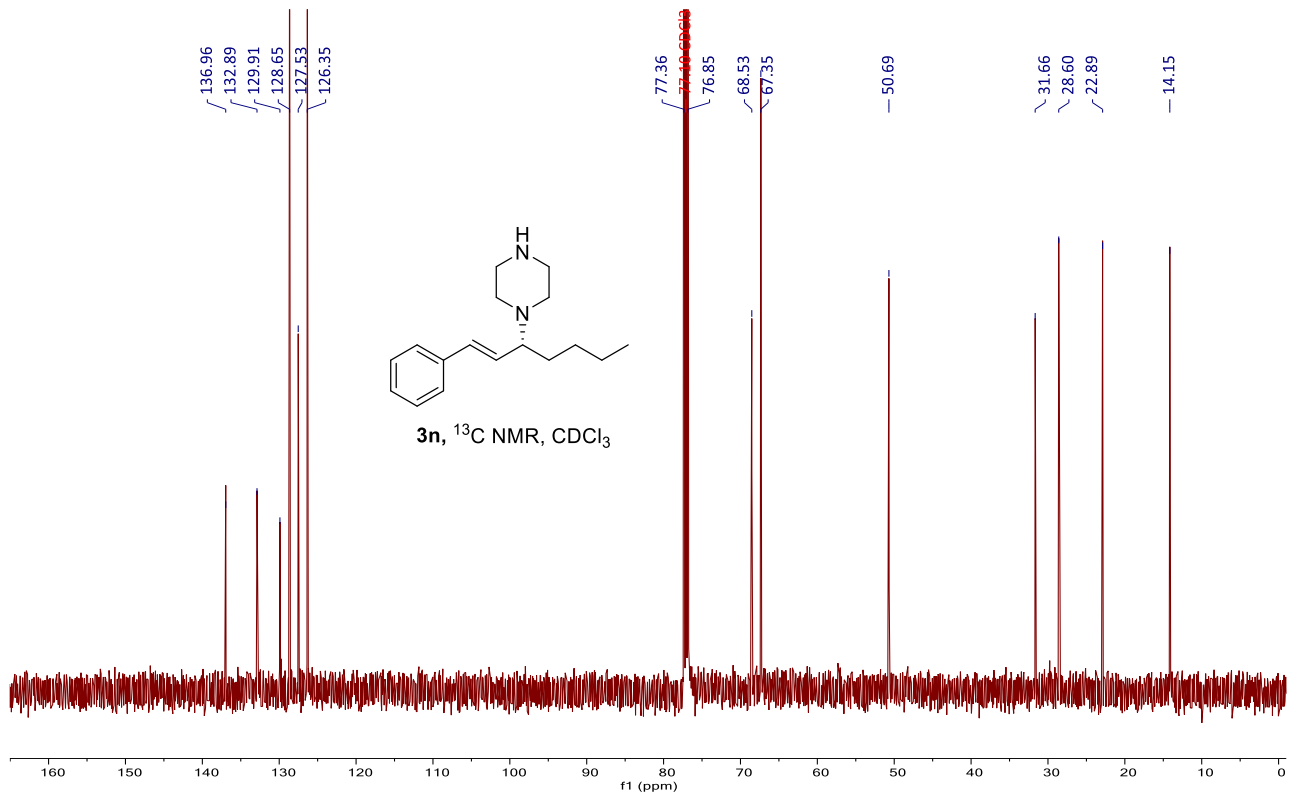
3l, ^{13}C NMR, $CDCl_3$



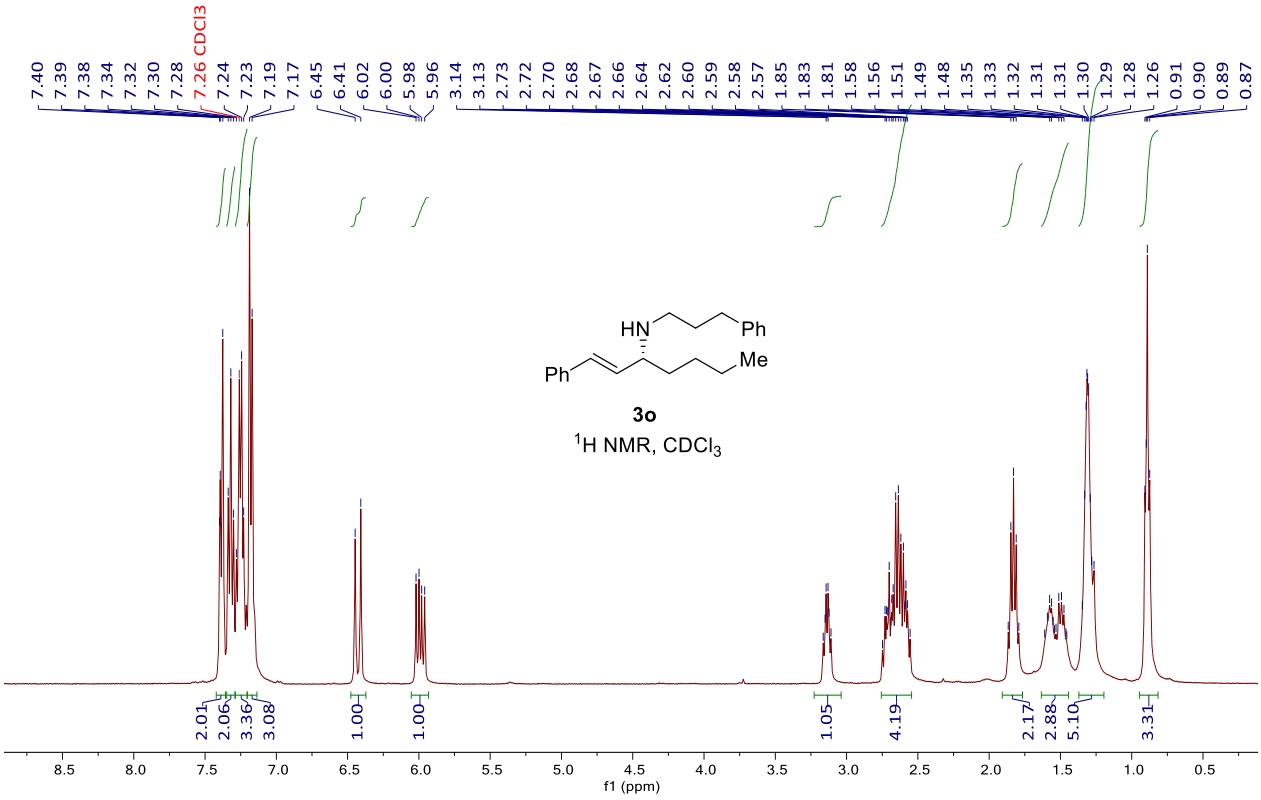
3m, ^{1}H NMR, $CDCl_3$

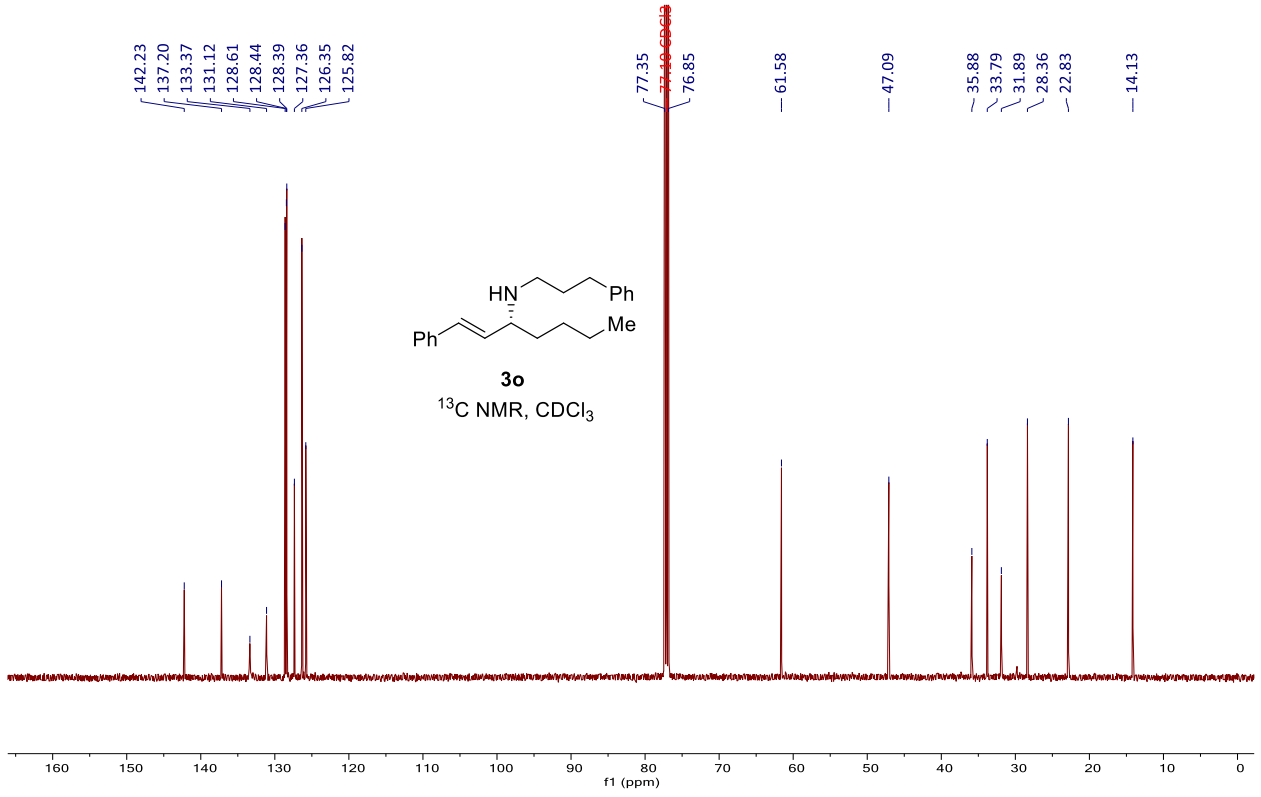


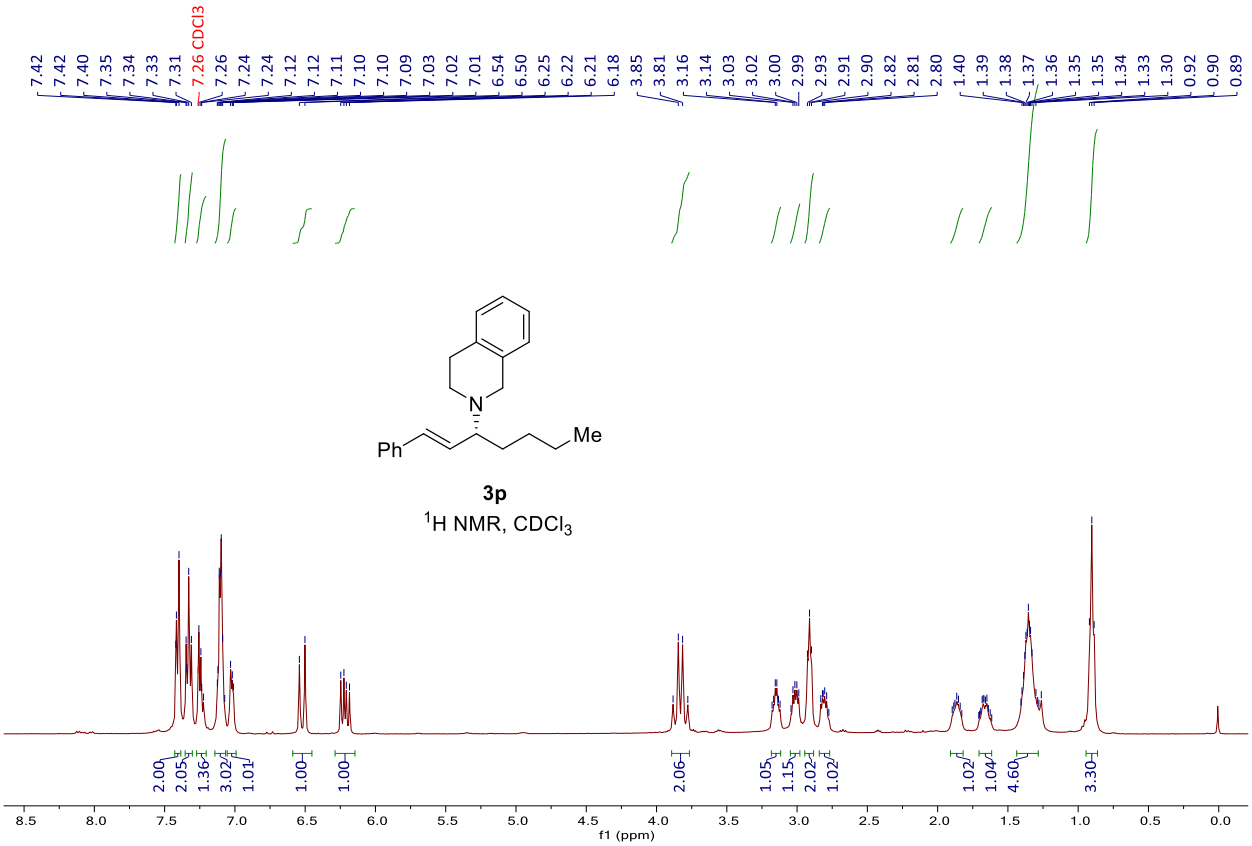
3n, ^{1}H NMR, $CDCl_3$

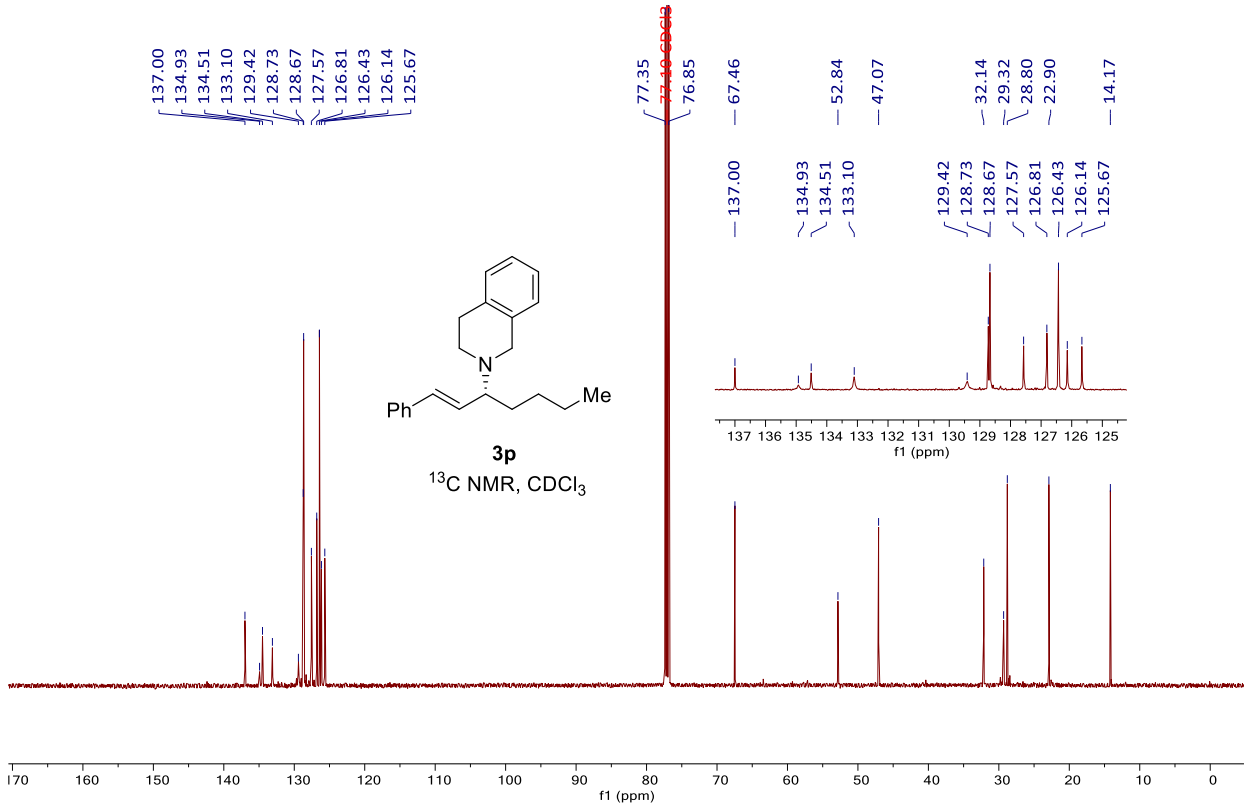


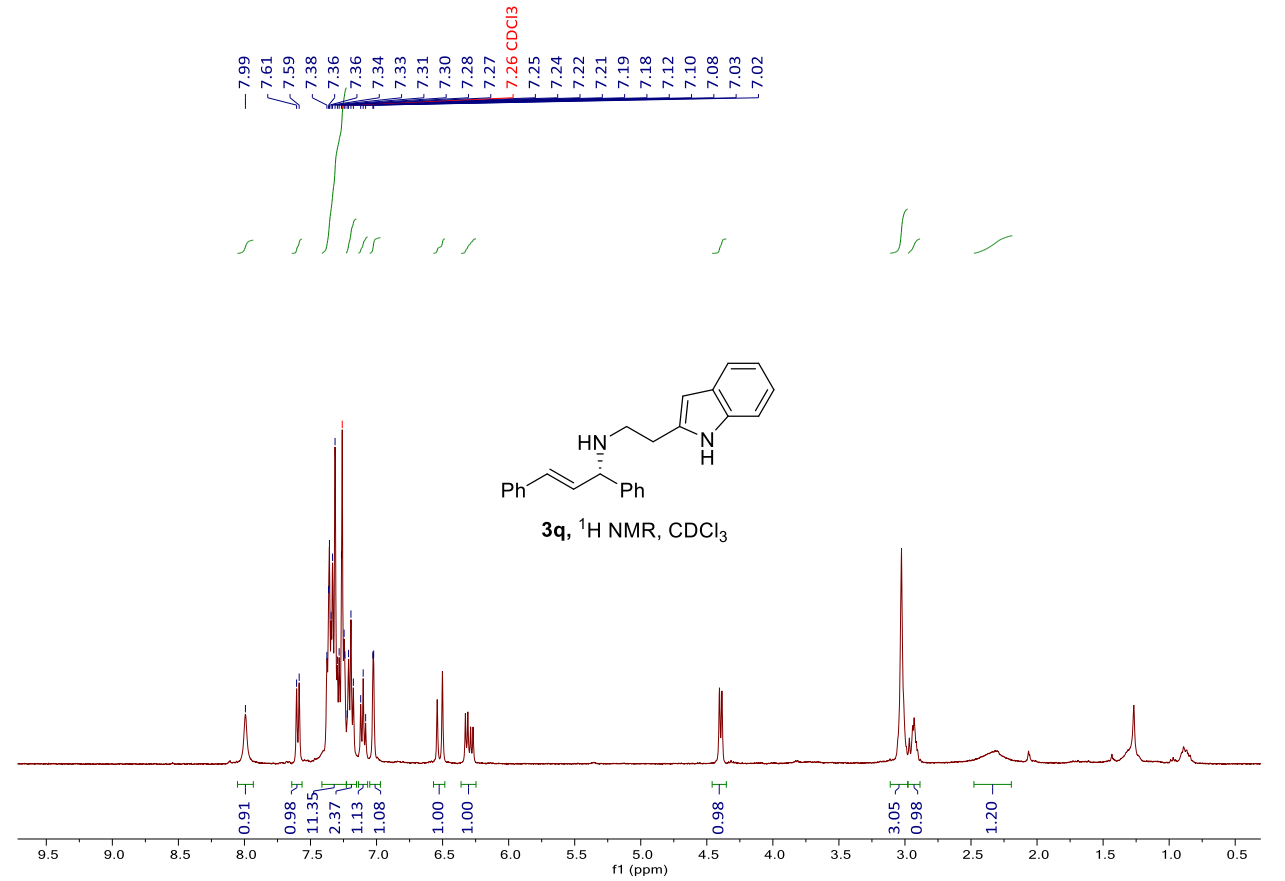
3n, ^{13}C NMR, $CDCl_3$


7.40 7.39 7.38 7.34 7.32 7.30 7.28 7.26 CDCl3 7.24 7.23 7.19 7.17 6.45 6.41 6.02 6.00 5.98 5.96 3.14 3.13 2.73 2.72 2.70 2.68 2.67 2.66 2.64 2.62 2.60 2.59 2.58 2.57 1.85 1.83 1.81 1.58 1.56 1.51 1.49 1.48 1.35 1.33 1.32 1.31 1.31 1.30 1.29 1.28 1.26 0.91 0.90 0.89 0.87
HN
Ph
Ph
Me
3o
1H NMR, CDCl3
2.01 2.06 3.36 3.08 1.00 1.00 1.05 4.19 2.17 2.88 5.10 3.31
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
f1 (ppm)

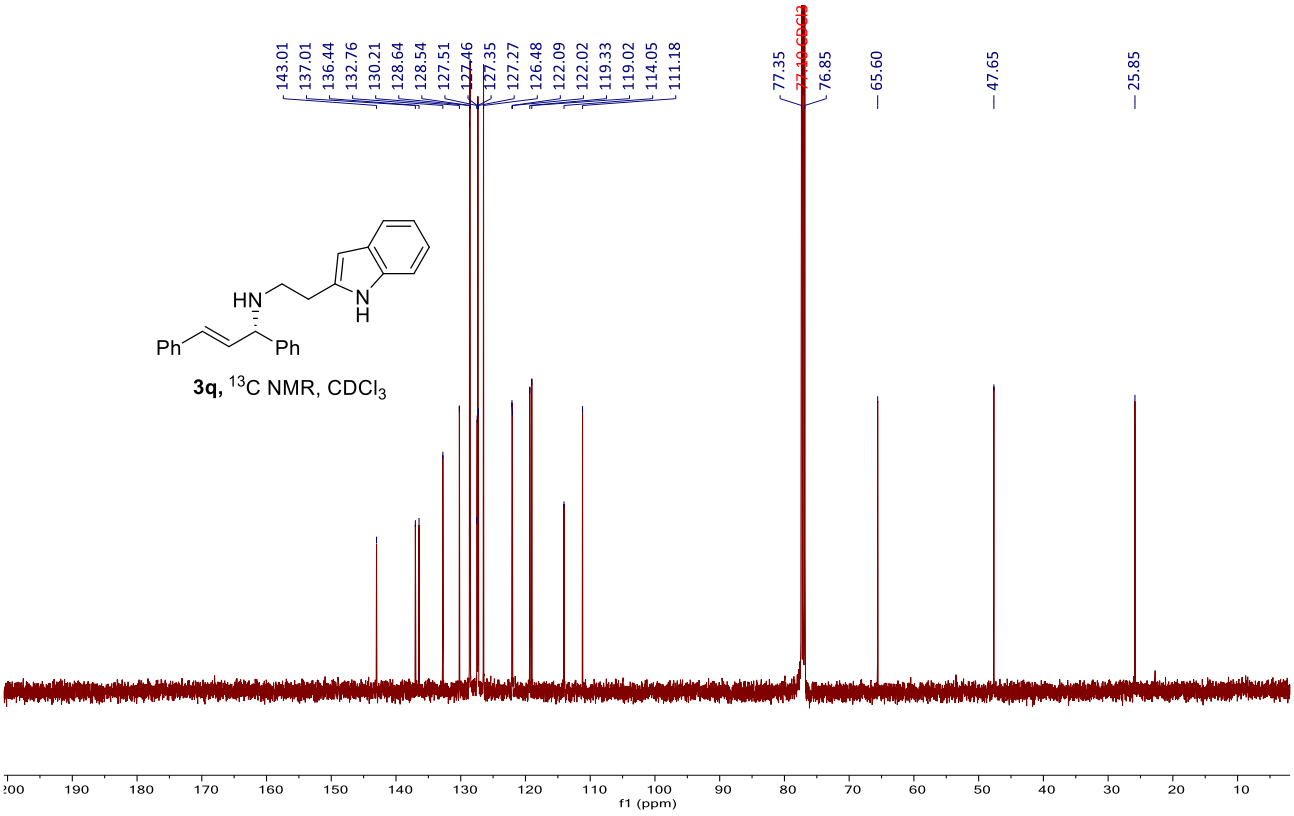

142.23 137.20 133.37 131.12 128.61 128.44 128.39 127.36 126.35 125.82
77.35 77.10 CDCl3 76.85 61.58 47.09 35.88 33.79 31.89 28.36 22.83 14.13
HN
Ph
Ph
Me
3o
13C NMR, CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42 7.42 7.40 7.35 7.34 7.33 7.31 7.26 CDCl3 7.26 7.24 7.24 7.12 7.12 7.11 7.10 7.10 7.09 7.03 7.02 7.01 6.54 6.50 6.25 6.22 6.21 6.18
3.85 3.81 3.16 3.14 3.03 3.02 3.00 2.99 2.93 2.91 2.90 2.82 2.81 2.80
1.40 1.39 1.38 1.37 1.36 1.35 1.35 1.34 1.33 1.30 0.92 0.90 0.89
N
Ph
Me
3p
1H NMR, CDCl3
2.00 2.05 1.36 3.02 1.01 1.00 1.00 2.06 1.05 1.15 2.02 1.02 1.02 1.04 4.60 3.30
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
f1 (ppm)

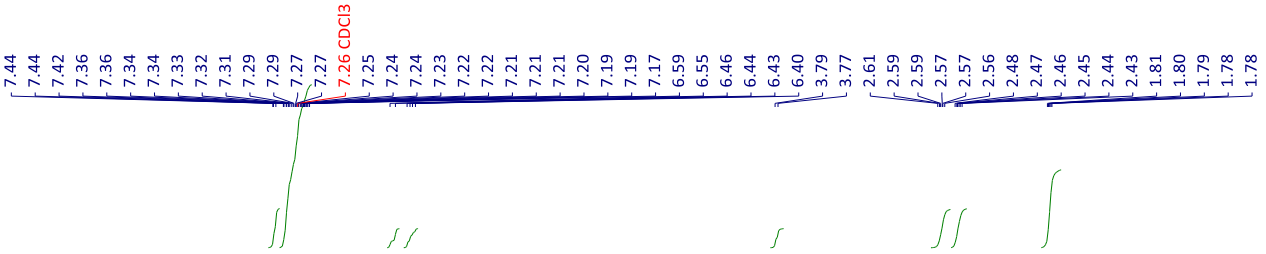

137.00 134.93 134.51 133.10 129.42 128.73 128.67 127.57 126.81 126.43 126.14 125.67
77.35 77.19 CDCl3 76.85
67.46
52.84
47.07
32.14 29.32 28.80 22.90
14.17
N
Ph
Me
3p
13C NMR, CDCl3
137 136 135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

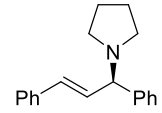


3q, ^{1}H NMR, $CDCl_3$

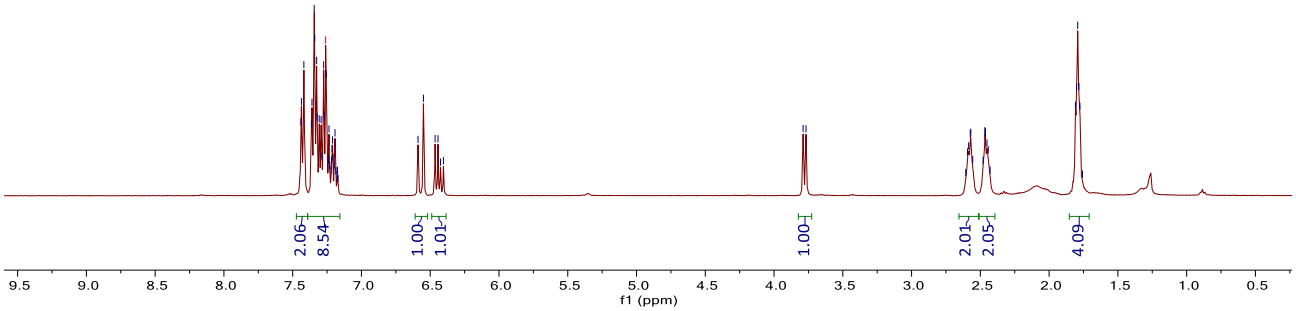


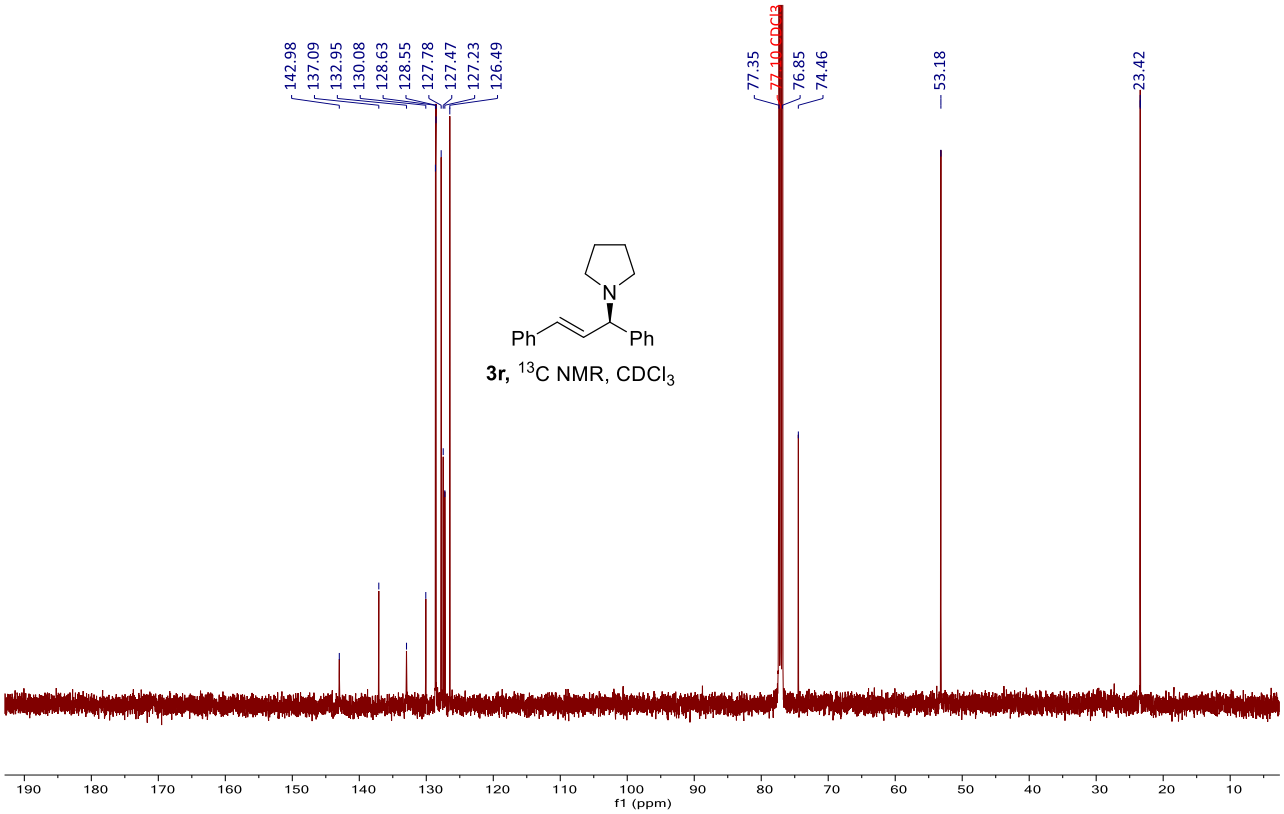
3q, ^{13}C NMR, $CDCl_3$



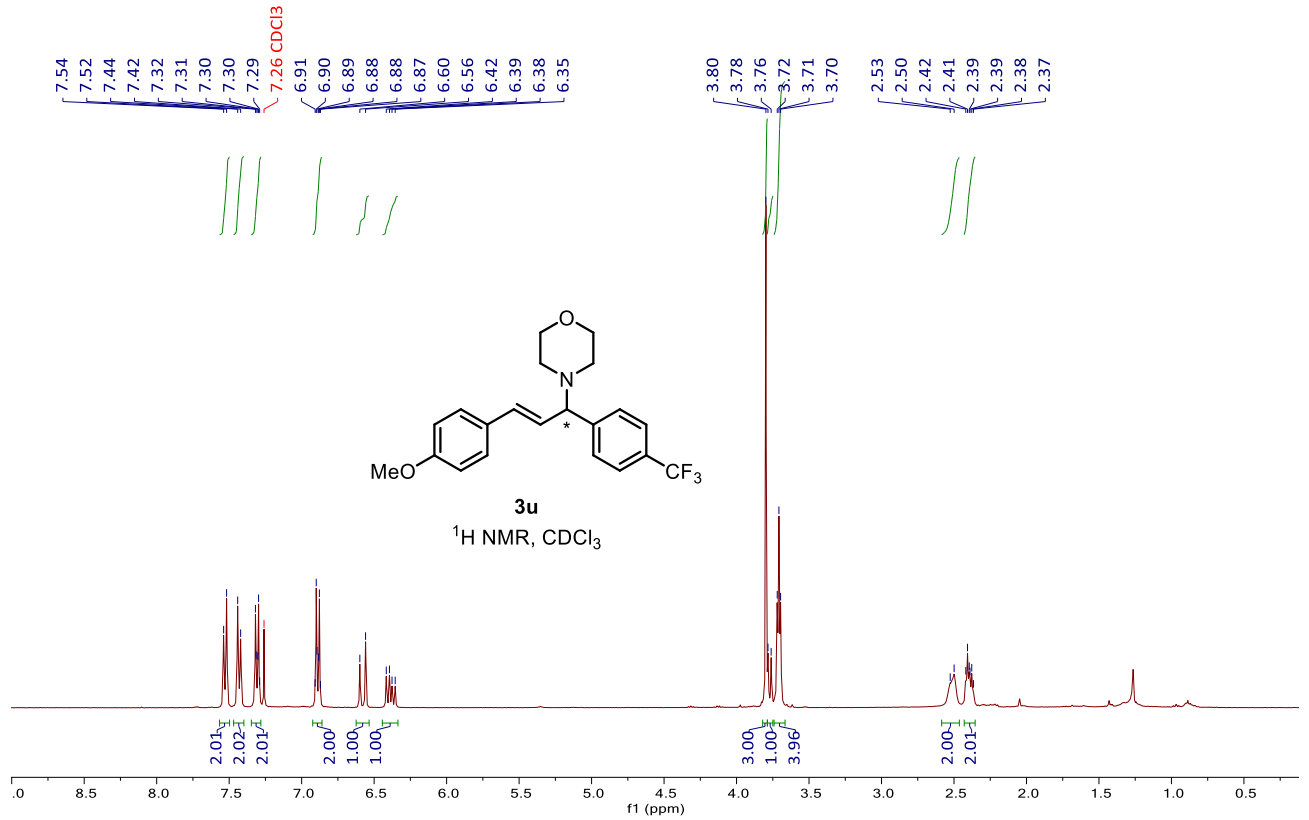


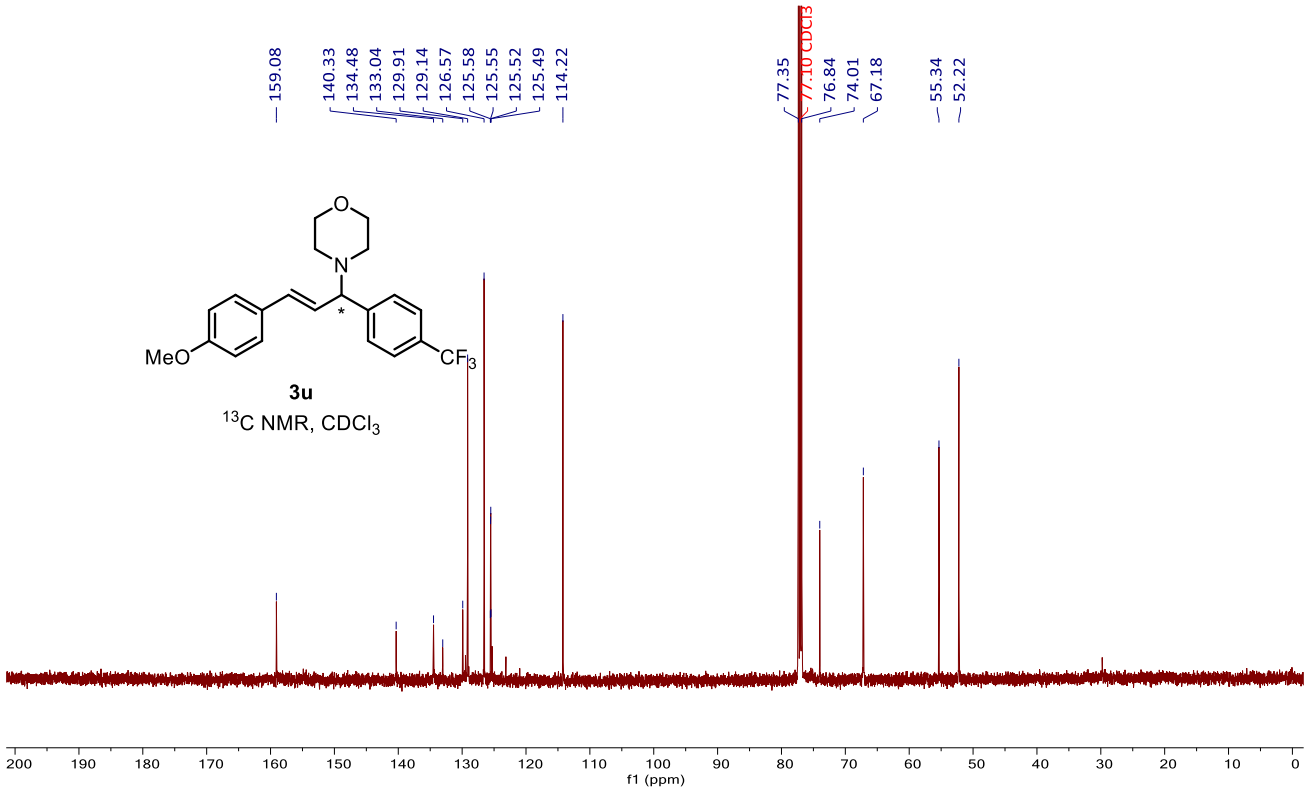
3r, ^{1}H NMR, $CDCl_3$

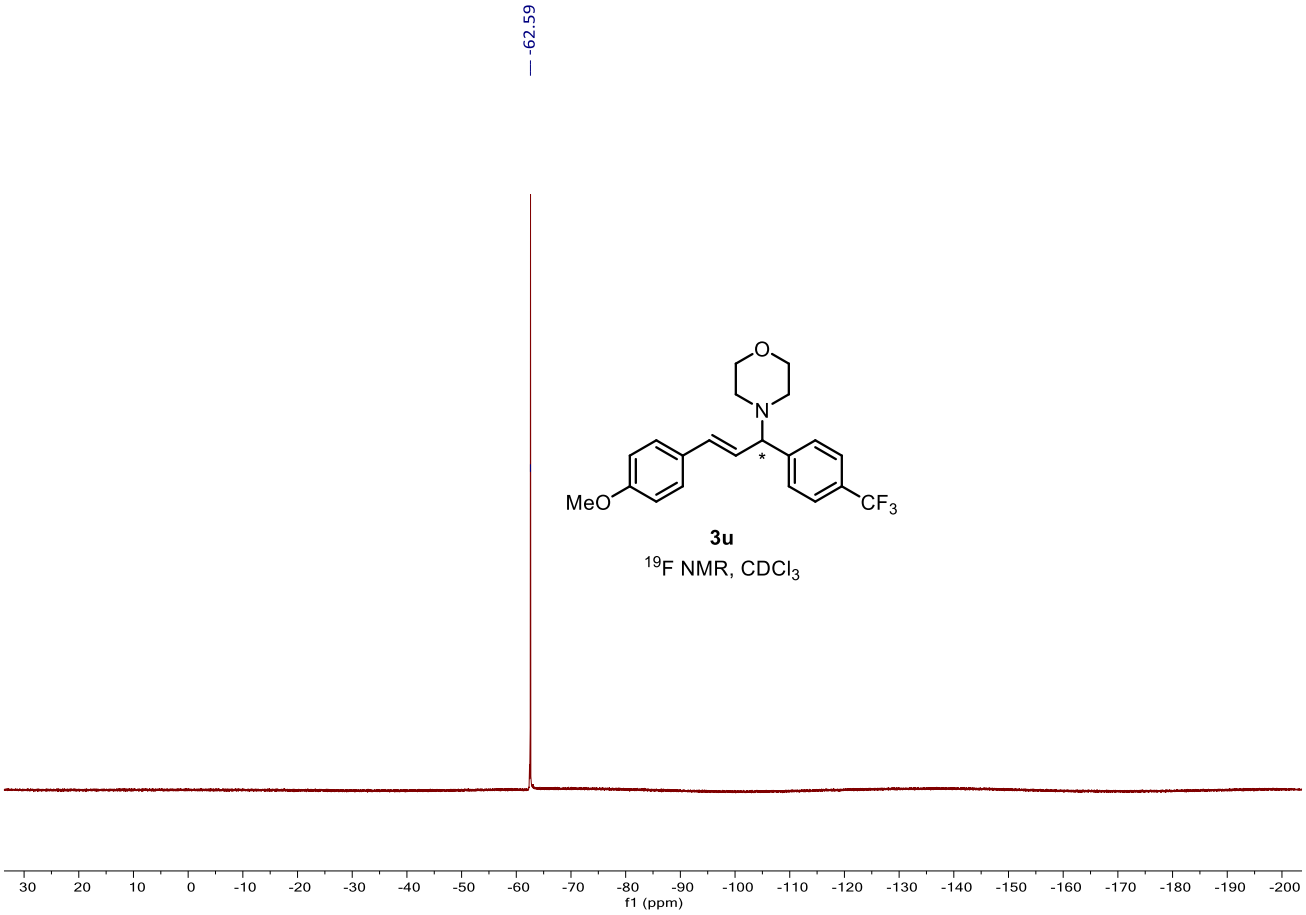


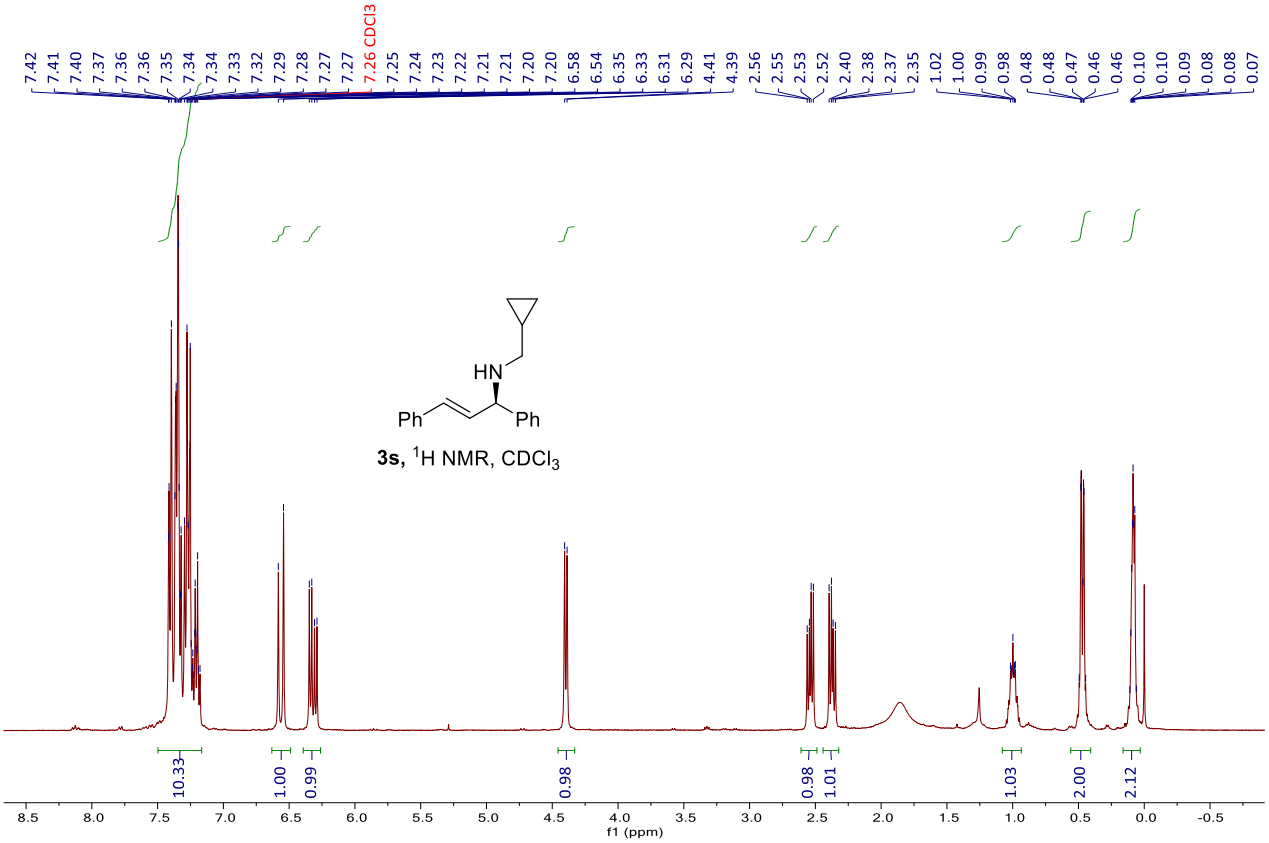


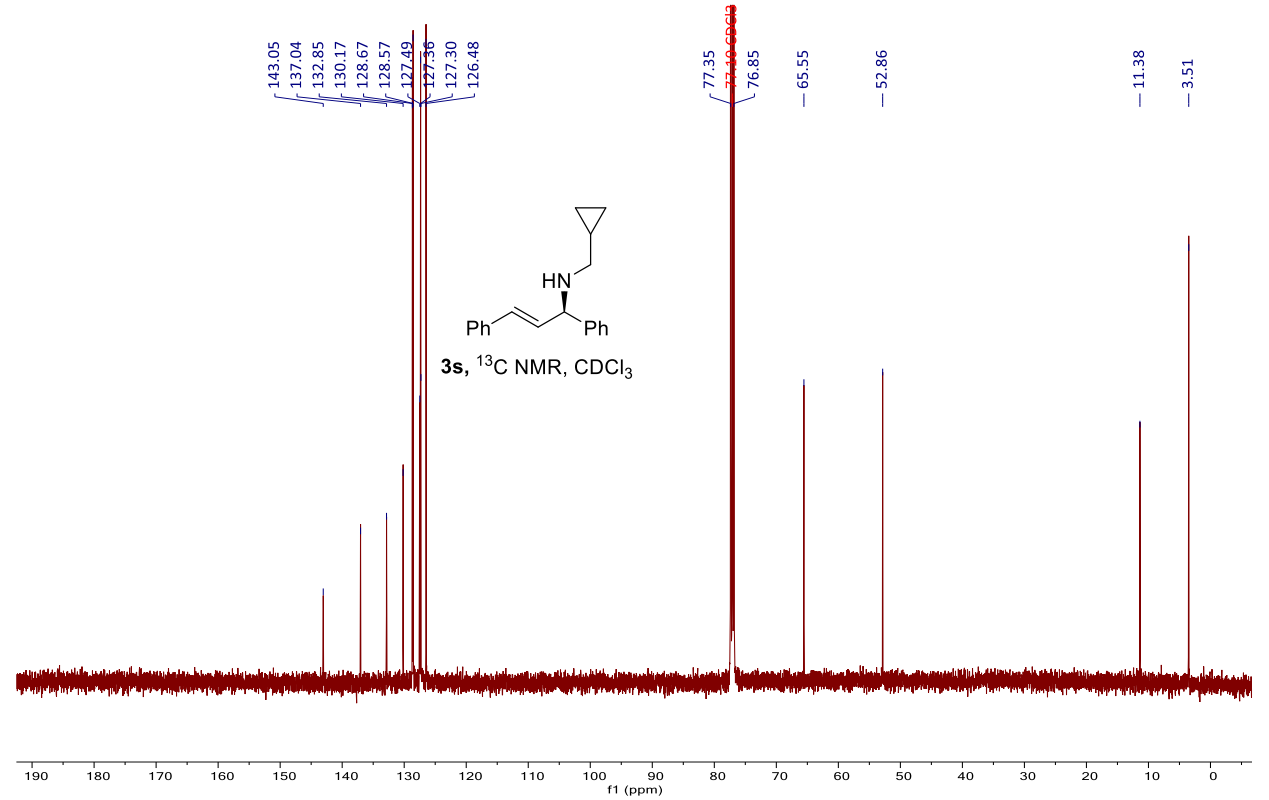
3r, ^{13}C NMR, $CDCl_3$

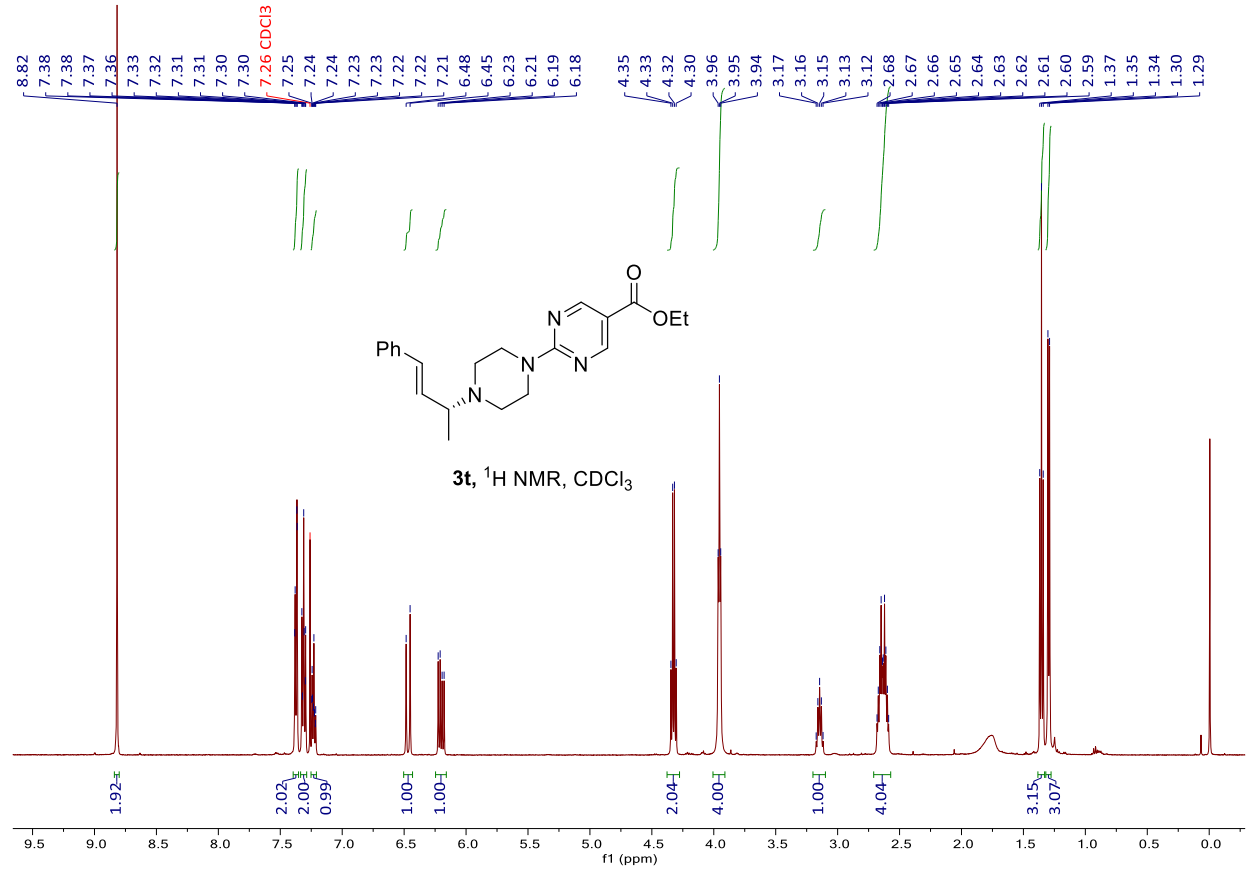

7.54
7.52
7.44
7.42
7.32
7.31
7.30
7.30
7.29
7.26 CDCl3
6.91
6.90
6.89
6.88
6.88
6.87
6.60
6.56
6.42
6.39
6.38
6.35
3.80
3.78
3.76
3.72
3.71
3.70
2.53
2.50
2.42
2.41
2.39
2.39
2.38
2.37
MeO
CF3
3u
1H NMR, CDCl3
2.01
2.02
2.01
2.00
1.00
1.00
3.00
1.00
3.96
2.00
2.01
f1 (ppm)

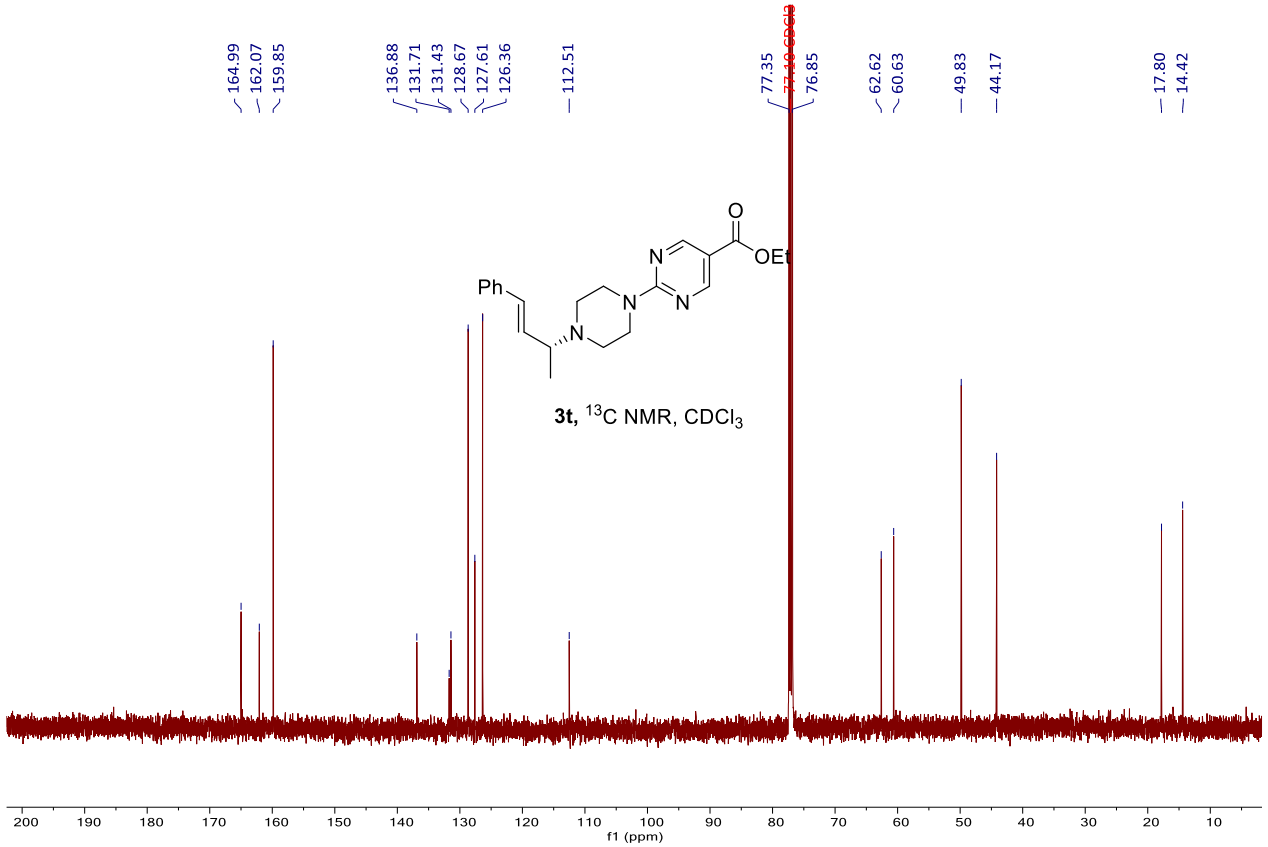

159.08
140.33
134.48
133.04
129.91
129.14
126.57
125.58
125.55
125.52
125.49
114.22
77.35
77.10 CDCl3
76.84
74.01
67.18
55.34
52.22
MeO
CF3
3u
13C NMR, CDCl3
f1 (ppm)

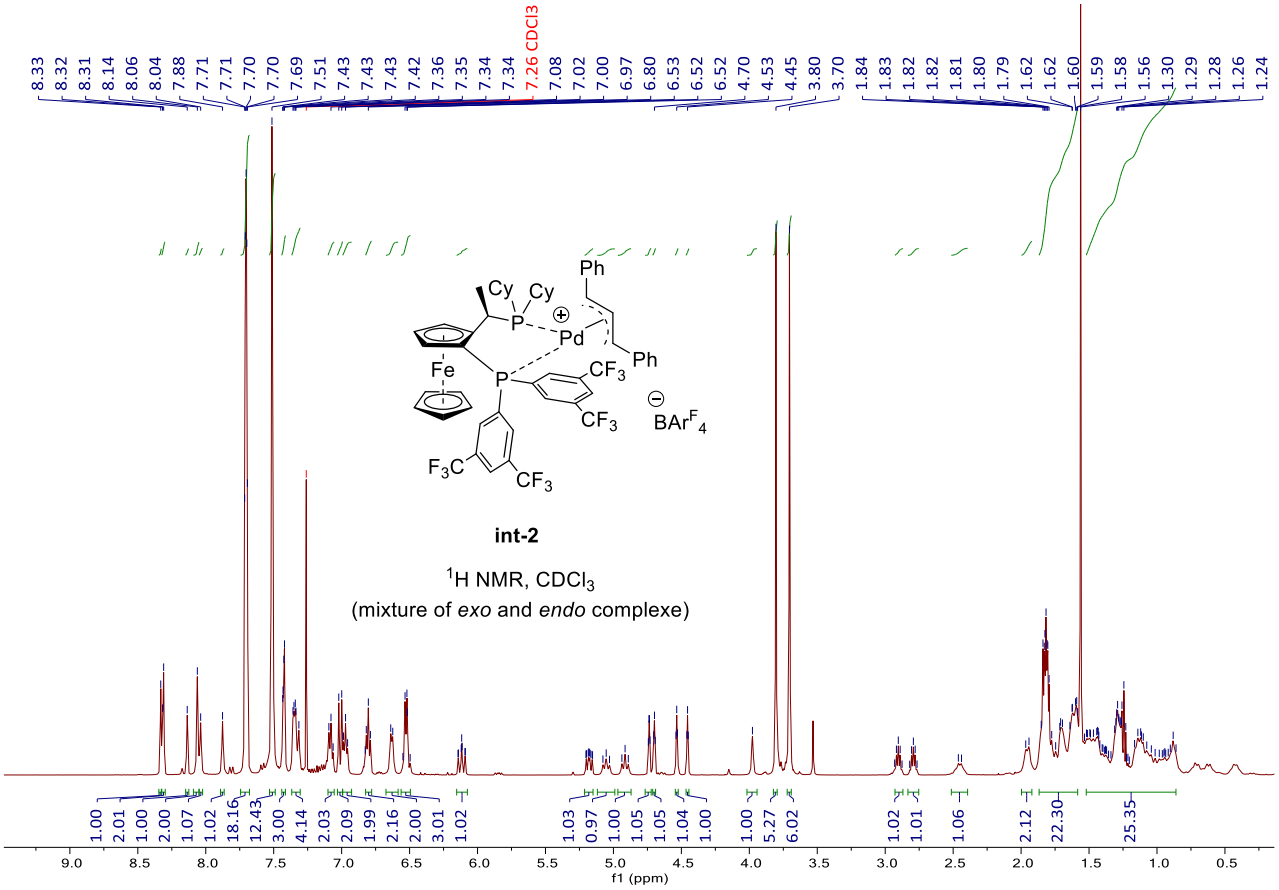

-62.59
O
N
*
MeO
CF3
3u
19F NMR, CDCl3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

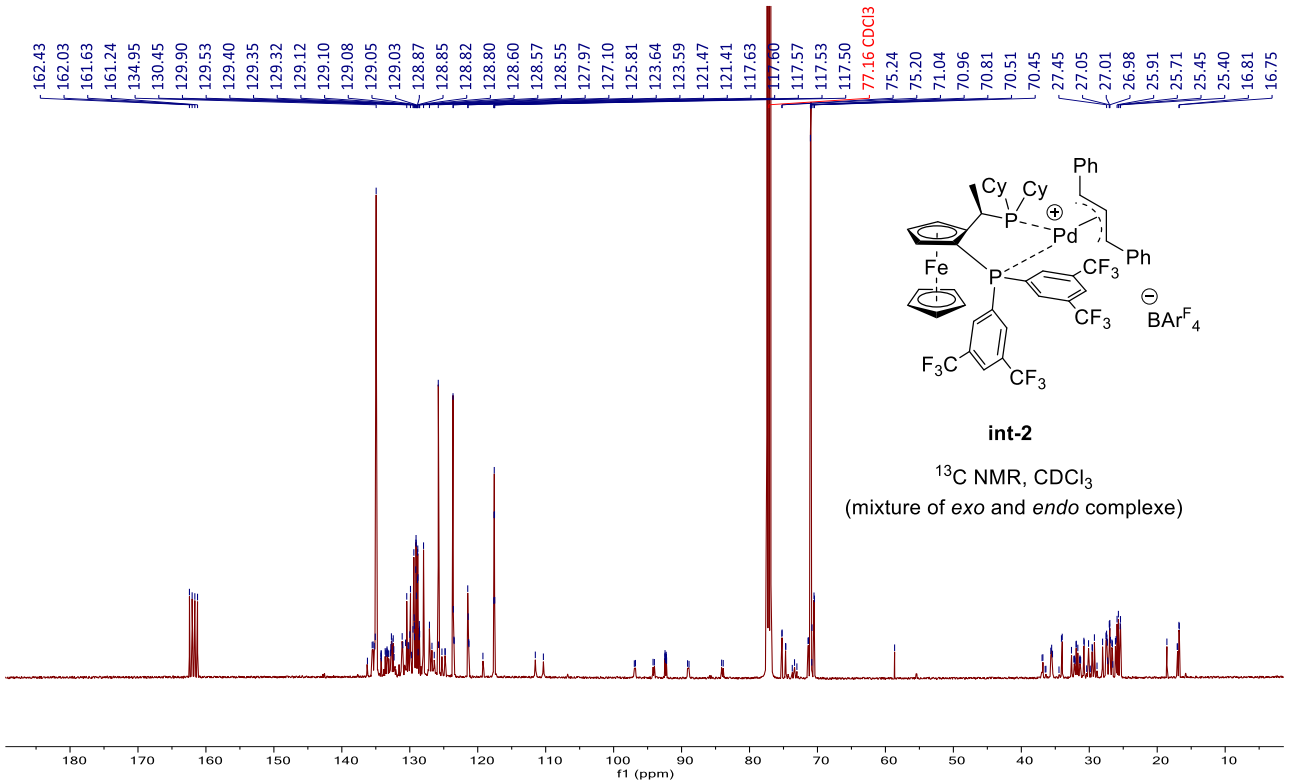

7.42 7.41 7.40 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.29 7.28 7.27 7.27 7.26 CDCl3 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 6.58 6.54 6.35 6.33 6.31 6.29 4.41 4.39 2.56 2.55 2.53 2.52 2.40 2.38 2.37 2.35 1.02 1.00 0.99 0.98 0.48 0.48 0.47 0.46 0.46 0.10 0.10 0.09 0.08 0.08 0.07
HN
Ph
Ph
3s, 1H NMR, CDCl3
10.33 1.00 0.99 0.98 0.98 1.01 1.03 2.00 2.12
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 -0.5
f1 (ppm)

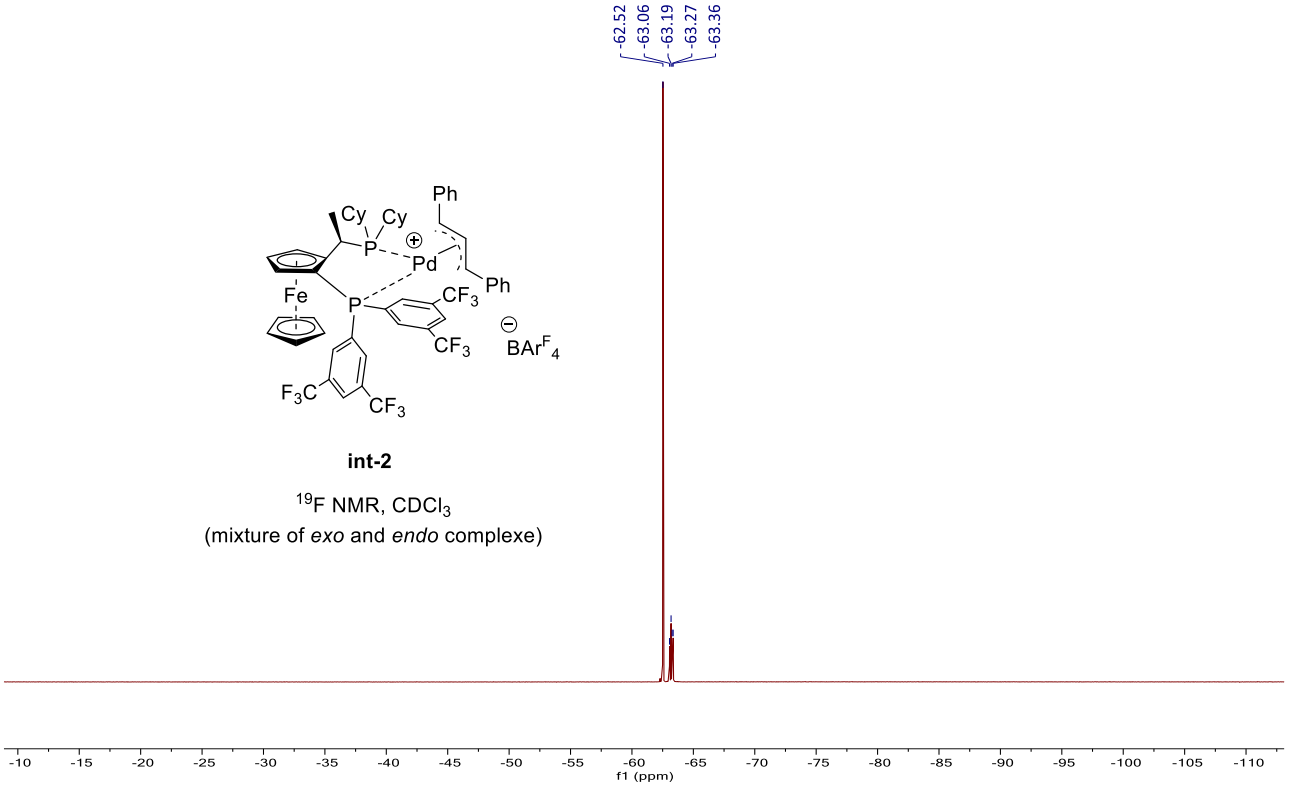

143.05 137.04 132.85 130.17 128.67 128.57 127.49 127.36 127.30 126.48
77.35 77.10 76.85
65.55
52.86
11.38
3.51
HN
Ph
Ph
3s, 13C NMR, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.82 7.38 7.38 7.37 7.36 7.33 7.32 7.31 7.31 7.30 7.30 7.26 CDCl3 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 6.48 6.45 6.23 6.21 6.19 6.18
4.35 4.33 4.32 4.30 3.96 3.95 3.94 3.17 3.16 3.15 3.13 3.12 2.68 2.67 2.66 2.65 2.64 2.63 2.62 2.61 2.60 2.59 1.37 1.35 1.34 1.30 1.29
O
OEt
N
N
N
N
Ph
3t, 1H NMR, CDCl3
1.92 2.02 2.00 0.99 1.00 1.00 2.04 4.00 1.00 4.04 3.15 3.07
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
f1 (ppm)


164.99 162.07 159.85 136.88 131.71 131.43 128.67 127.61 126.36 112.51 77.35 77.10 CDCl3 76.85 62.62 60.63 49.83 44.17 17.80 14.42
O
OEt
N
N
N
N
Ph
3t, 13C NMR, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


int-2
^{1}H NMR, $CDCl_3$
(mixture of *exo* and *endo* complexe)

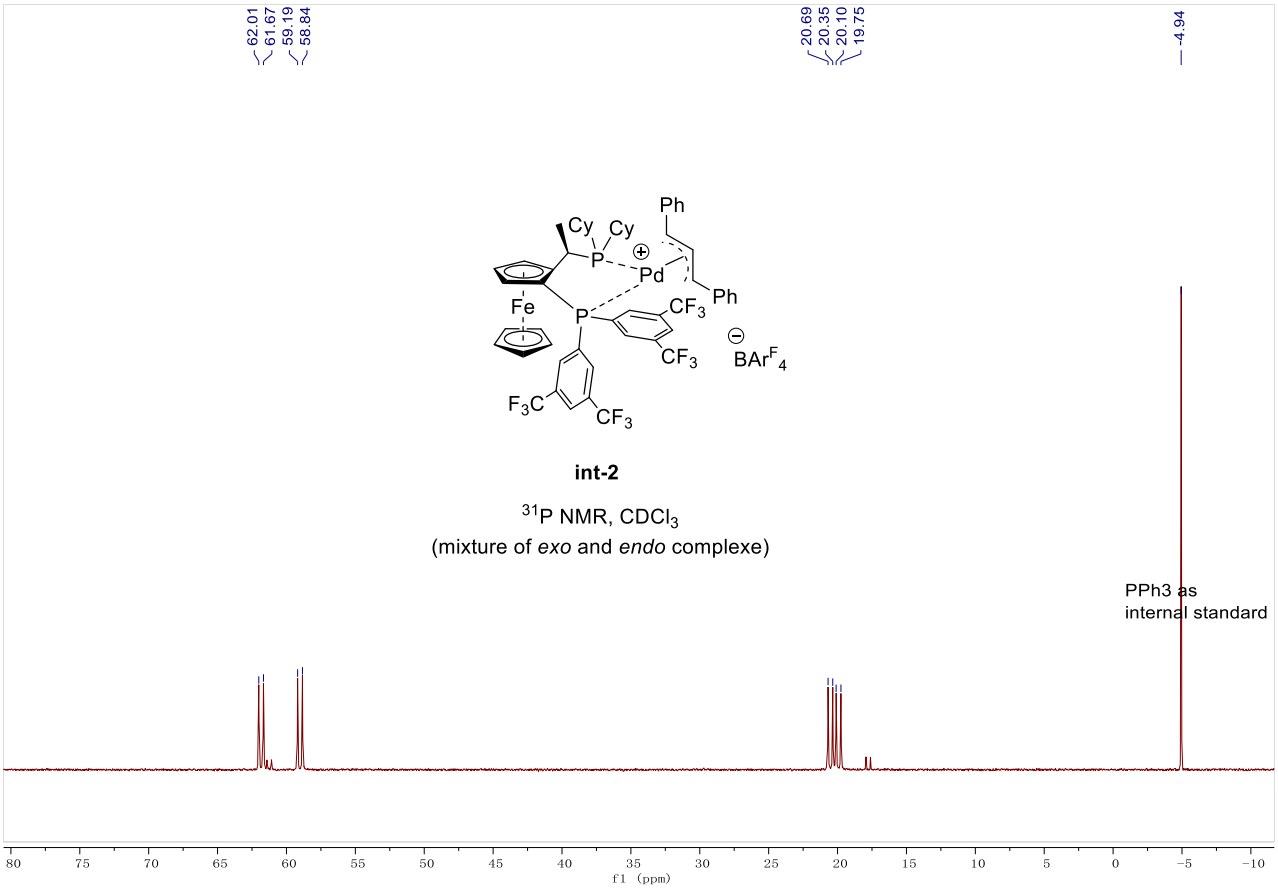

int-2
^{13}C NMR, $CDCl_3$
(mixture of *exo* and *endo* complexe)



int-2

^{19}F NMR, $CDCl_3$

(mixture of *exo* and *endo* complexe)



int-2

^{31}P NMR, $CDCl_3$

(mixture of *exo* and *endo* complexe)

8. References

1. Hussain, M. M. & Walsh, P. J. Allylic substitution versus Suzuki cross-coupling: capitalizing on chemoselectivity with bifunctional substrates. *Angew. Chem. Int. Ed.* **49**, 1834−1837 (2010).
2. Liu, J., Wang, L., Zheng, X., Wang, A. L., Zhu, M., Yu, J. & Shen, Q. $Yb(OTf)_3$-promoted effective benzylation and allylation with *N*-tosyl amino group as a stable leaving group. *Tetrahedron Lett*. **53**, 1843–1846 (2012).
3. Xiao, X., Huang, S., Tang, S., Jia, G., Ou, G. & Li, Y. Ligand-free, quinoline *N*-assisted copper-catalyzed nitrene transfer reaction to synthesize 8-quinolylsulfimides. *J. Org. Chem.* **84**, 7618−7629 (2019).
4. Sato, Y., Yoshino, T. & Mori, M. Pd-catalyzed allylic substitution using nucleophilic N-heterocyclic carbene as a ligand. *Org. Lett.* **5**, 31−33 (2003).
5. Cheng, H.-G., Feng, B., Chen, L.-Y., Guo, W., Yu, X.-Y., Lu, L.-Q., Chen, J.-R. & Xiao, W.-J. Rational design of sulfoxide–phosphine ligands for Pd-catalyzed enantioselective allylic alkylation reactions. *Chem. Commun.* **50**, 2873−2875 (2014).
6. Manabe, K. & Kobayashi, S. Palladium-catalyzed, carboxylic acid-assisted allylic substitution of carbon nucleophiles with allyl alcohols as allylating agents in water. *Org. Lett.* **5**, 3241−3244 (2003).
7. Danjo, H., Tanaka, D., Hayashi, T. & Uozumi, Y. Allylic substitution in water catalyzed by amphiphilic resin-supported palladium-phosphine complexes. *Tetrahedron* **55**, 14341−14352 (1999).
8. Faller, J. W. & Wilt, J. C. Palladium/BINAP(S)-catalyzed asymmetric allylic amination. *Org. Lett.* **7**, 633−636 (2005).
9. Feng, B., Cheng, H.-G., Chen, J.-R., Deng, Q.-H., Lu, L.-Q. & Xiao, W.-J. Palladium/sulfoxide–phosphine-catalyzed highly enantioselective allylic etherification and amination. *Chem. Commun.* **50**, 9550−9553 (2014).
10. Zhao, Q.; Zhuo, C.-X.; You, S.-L. Enantioselective synthesis of *N*-allylindoles *via* palladium-catalyzed allylic amination/oxidation of indolines. *RSC Adv*. **4**, 10875−10878 (2014).

11. Park, S. & Malcolmson, S. J. Development and mechanistic investigations of enantioselective Pd-Catalyzed intermolecular hydroaminations of internal dienes. *ACS Catal.* **8**, 8468−8476 (2018).
12. Wu, H., Xie, F., Wang, Y., Zhao, X., Liu, D. & Zhang, W. Pd-catalyzed asymmetric allylic amination using easily accessible metallocenyl P,N-ligands. *Org. Biomol. Chem.* **13**, 4248−4254 (2015).
13. Adamson, N. J., Wilbur, K. C. E. & Malcolmson, S. J. Enantioselective intermolecular Pd-catalyzed hydroalkylation of acyclic 1,3-dienes with activated pronucleophiles. *J. Am. Chem. Soc.* **140**, 2761−2764 (2018).
14. Behenna, D. C., Mohr, J. T., Sherden, N. H., Marinescu, S. C., Harned, A. M., Tani, K., Seto, M., Ma, S., Novák, Z., Krout, M. R., McFadden, R. M., Roizen, J. L., Enquist, J. A., White, D. E., Levine, S. R., Petrova, K. V., Iwashita, A., Virgil, S. C. & Stoltz, B. M. Enantioselective decarboxylative alkylation reactions: catalyst development, substrate scope, and mechanistic studies. *Chem. – Eur. J.* **17**, 14199–14223 (2011).