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Supporting Information For

Asymmetric Petasis Reactions for the Synthesis of Chiral α- and β-Butadienyl Amines

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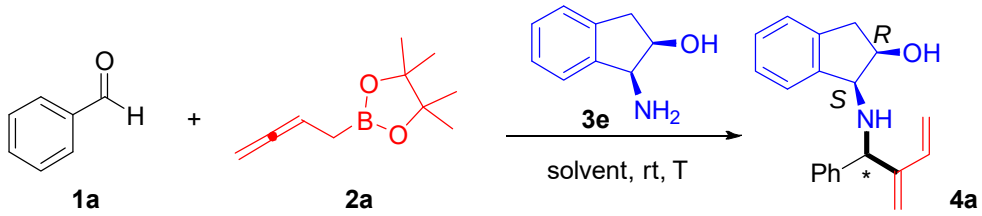
General information. All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. Anhydrous toluene, and THF were distilled from sodium benzophenone ketyl. All reactions were monitored by TLC, and TLC analysis was performed by illumination with a UV lamp (254 nm). Flash chromatography was packed with silica gel as the stationary phase. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts (δ) were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.2 ppm). ^{19}F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. Coupling constants (J) were measured in hertz (Hz). Infrared spectra were recorded on a NICOLET FT/IR-200 spectrometer. High-resolution MS (ESI-orbitrap) were obtained on a Thermo Fisher Q Exactive mass spectrometer.

Table S1: Control experiments



1a **2a** **4a**

entry	solvent/additive	t/h	yield/%[b]	*dr*[c]
1	CH_3CN + 5 equiv MeOH	72	85	3.6:1
2	1,4-dioxane + 5 equiv MeOH	72	60	3.1:1
3	DMF+ 5 equiv MeOH	72	65	5:1
7	DMSO + 1 equiv MeOH	48	95	8.4:1
8	DMSO + 3 equiv MeOH	48	93	10:1
9	DMSO + 5 equiv MeOH	20	95	11.3:1
10	DMSO + 10 equiv MeOH	72	96	7.3:1

[a] Reaction conditions: **1** (0.2 mmol), **3** (0.24 mmol), solvent (0.4 mL) were stirred at rt for 2 h, then **2a** (0.30 mmol) was added. [b] Isolated yield. [c] Diastereomeric ratio (*dr*) was determined by ^{1}H NMR.

General Procedure for the Asymmetric Petasis Butadienylation Reaction.
To a 2 mL test tube with a stir bar was added aldehyde **1** (0.20 mmol), **3e** (0.24 mmol), DMSO (0.4 mL) and MeOH (5 equiv) at rt. After 2 h, pinacol homoallenylboronate **2a** (0.30 mmol) was added, and the reaction mixture was stirred at rt for the time indicated in the main article. Finally the reaction mixture was directly subjected to the preparative thin-layer chromatography to obtain compound **4**.

To a 2 mL test tube with a stir bar was added aldehyde **1** (0.20 mmol), **3e** (0.24 mmol), DMSO (0.2 mL) and MeOH (5 equiv) at rt. After 2 h, pinacol isoprenylboronate **2b** (0.30 mmol) was added, and the reaction mixture was stirred at rt for the time indicated in the main article. Finally the reaction mixture was directly subjected to the preparative thin-layer chromatography to obtain compound **5**.

Characterization Data of the Reaction Adducts.

*(1S,2R)-1-((2-methylene-1-phenylbut-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4a**).* Brown oil, 55.4 mg, 95% yield, dr = 11.3:1. $[\alpha]_D^{25}$ = -21.3 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.29–7.25 (m, 2H), 7.23–7.17 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.34 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.46 (s, 1H), 5.37 (s, 1H), 5.35 (d, *J* = 19.5 Hz, 1H), 5.05 (d, *J* = 11.1 Hz, 1H), 4.80 (s, 1H), 4.47–4.41 (m, 1H), 4.12 (d, *J* = 4.8 Hz, 1H), 3.02 (dd, *J* = 5.0, 16.5 Hz, 1H), 2.96–2.90 (m, 1H), 2.43 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.2, 142.7, 142.0, 140.9, 136.8, 128.7, 128.1, 127.6, 127.4, 126.8, 125.6, 123.7, 115.7, 115.0, 71.4, 63.8, 62.8, 39.6. IR (KBr): 3402, 3065, 2920, 1645, 1454, 1265, 1051, 908, 744, 702 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NO$, 292.1696; found, 292.1692.

*(1S,2R)-1-((2-methylene-1-(p-tolyl)but-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4b**).* Brown oil, 59.9 mg, 98% yield, dr = 5.3:1. $[\alpha]_D^{25}$ = -10.0 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.6 Hz, 2H), 7.24–7.10 (m, 6H), 6.33 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.46 (s, 1H), 5.36(s, 1H), 5.35 (d, *J* = 18.0 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.76 (s, 1H), 4.45–4.40 (m, 1H), 4.11 (d, *J* = 4.7 Hz, 1H), 3.05–2.90 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.3, 142.8, 140.9, 139.0, 137.3, 136.9, 129.4, 128.0, 127.3, 126.8, 125.6, 123.7, 115.2, 115.0, 71.4, 63.9, 62.5, 39.6, 21.1. IR (KBr): 3397, 3020, 2919, 1635, 1456, 1265, 1050, 907, 816, 706 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO$, 306.1852; found, 306.1848.

*(1S,2R)-1-((1-(4-methoxyphenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4c**).* Brown oil, 59.8 mg, 93% yield, dr = 6.5:1. $[\alpha]_D^{25}$ = -5.6 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40–7.30 (m, 2H), 7.24–7.12 (m, 4H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.33 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.46 (s, 1H), 5.35 (s, 1H), 5.34 (d, *J* = 18.5 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.75 (s, 1H), 4.45–4.40 (m, 1H), 4.11 (d, *J* = 4.7 Hz, 1H), 3.78 (s, 3H), 3.06–2.88 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 147.4, 142.8, 140.9, 136.9, 134.1, 128.8, 128.5, 128.0, 126.8, 125.6, 123.7, 115.4, 114.9, 114.1, 71.4, 63.8, 62.2, 55.3, 39.6. IR (KBr): 3403, 3004, 2911, 1608, 1460, 1267, 1035, 907, 830, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO_2$, 322.1802; found, 292.1798.

*(1S,2R)-1-((1-(4-fluorophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4d**).* Brown oil, 58.2 mg, 94% yield, dr >20:1. $[\alpha]_D^{25}$ = -30.3 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.15–7.05 (m, 4H), 6.97–6.93 (m, 2H), 6.24 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.37 (s, 1H), 5.29 (s, 1H), 5.26 (d, *J* = 17.5 Hz, 1H), 4.98 (d, *J* = 11.1 Hz, 1H), 4.72 (s, 1H), 4.38–4.35 (m, 1H), 4.00 (d, *J* = 5.2 Hz, 1H), 3.00–2.83 (m, 2H). ^{13}C NMR (126 MHz, CDCl3): δ 162.2 (d, *J* = 246.5 Hz), 147.2, 142.7, 140.8, 137.8 (d, *J* = 3.2 Hz), 136.7, 129.0 (d, *J* = 8.1 Hz),

128.1, 126.8, 125.6, 123.8, 115.8, 115.5 (d, J = 21.4 Hz), 115.1, 71.5, 63.8, 62.0, 39.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -114.9 (s, 1F). IR (KBr): 3356, 3072, 2922, 1601, 1506, 1222, 1050, 908, 833, 745 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}FNO$, 310.1602; found, 310.1598.

*(1S,2R)-1-((1-(4-chlorophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1 H-inden-2-ol (**4e**)*. Brown oil, 58.7 mg, 90% yield, dr >20:1. $[\alpha]_D^{25}$ = -48.3 (*c* 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.32 (m, 4H), 7.23–7.16 (m, 4H), 6.33 (dd, J = 17.7, 11.1 Hz, 1H), 5.46 (s, 1H), 5.39 (s, 1H), 5.35 (d, J = 17.5 Hz, 1H), 5.08 (d, J = 11.1 Hz, 1H), 4.79 (s, 1H), 4.48–4.43 (m, 1H), 4.09 (d, J = 5.1 Hz, 1H), 3.04 (dd, J = 5.5, 16.5 Hz, 1H), 2.95 (dd, J = 2.5, 16.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.0, 142.6, 140.8, 140.6, 136.5, 133.3, 128.9, 128.8, 128.1, 126.9, 125.6, 123.7, 116.0, 115.2, 71.5, 63.8, 62.0, 39.6. IR (KBr): 3386, 3012, 2921, 1646, 1511, 1256, 1020, 905, 840, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}ClNO$, 326.1306; found, 326.1302.

*(1S,2R)-1-((1-(4-bromophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1 H-inden-2-ol (**4f**)*. Brown oil, 68.1 mg, 92% yield, dr >20:1. $[\alpha]_D^{25}$ = -9.1 (*c* 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25–7.19 (m, 4H), 6.35 (dd, J = 17.6, 11.2 Hz, 1H), 5.48 (s, 1H), 5.41 (s, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.10 (d, J = 11.1 Hz, 1H), 4.80 (s, 1H), 4.50–4.46 (m, 1H), 4.11 (d, J = 4.4 Hz, 1H), 3.06 (dd, J = 4.5, 16.5 Hz, 1H), 3.00–2.94 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.9, 142.5, 141.1, 140.7, 136.5, 131.8, 129.2, 128.2, 126.8, 125.6, 123.7, 121.4, 116.1, 115.3, 71.5, 63.8, 62.0, 39.6. IR (KBr): 3043, 3023, 2921, 1634, 1481, 1265, 1009, 908, 865, 756 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}BrNO$, 370.0801; found, 370.0796.

*Methyl4-(1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-2-methylene but-3-en-1-yl)benzoate (**4g**)*. Brown oil, 65.6 mg, 94% yield, dr >20:1. $[\alpha]_D^{25}$ = +6.3 (*c* 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.27–7.18 (m, 4H), 6.36 (dd, J = 17.6, 11.1 Hz, 1H), 5.48 (s, 1H), 5.41 (s, 1H), 5.39 (d, J = 7.5 Hz, 1H), 5.10 (d, J = 11.0 Hz, 1H), 4.89 (s, 1H), 4.51–5.48 (m, 1H), 4.11 (d, J = 4.7 Hz, 1H), 3.93 (s, 3H), 3.05 (dd, J = 5.0, 16.5 Hz, 1H), 3.00–2.92 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.8, 147.3, 147.0, 142.5, 140.7, 136.5, 130.0, 129.5, 128.1, 127.5, 126.8, 125.6, 123.8, 116.3, 115.29 , 71.5, 63.8, 62.4, 52.1, 39.6. IR (KBr): 3418, 3052, 2947, 1719, 1608, 1436, 1111, 909, 865, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NO_3$, 350.1751; found, 350.1746.

*(1S,2R)-1-((2-methylene-1-(4-nitrophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1H-i nden-2-ol (**4h**)*. Brown oil, 62.6 mg, 93% yield, dr >20:1. $[\alpha]_D^{25}$ = +9.5 (*c* 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.25 (s, 4H), 6.36 (dd, J = 17.6, 11.2 Hz, 1H), 5.49 (s, 1H), 5.44 (s, 1H), 5.42 (d, J = 17.5 Hz, 1H), 5.13 (d, J = 11.1 Hz, 1H), 4.96 (s, 1H), 4.55–4.51 (m, 1H), 4.08 (d, J = 4.4 Hz, 1H), 3.10–2.92 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.3, 146.7, 142.3, 140.5, 136.2, 128.4, 128.2, 126.9, 125.6, 124.0, 123.9, 116.9, 115.6, 71.8, 63.9, 61.9, 39.7, 24.8. IR (KBr): 3400, 3072, 2923, 1599, 1519, 1461, 1159, 911, 852, 760 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2O_3$, 337.1547; found, 337.1544.

*(1S,2R)-1-((1-(3-methoxyphenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4i**).* Brown oil, 61.1 mg, 95% yield, dr >20:1. $[\alpha]_D^{25}$ = -16.1 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35–7.14 (m, 5H), 7.07–6.98 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.38 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.48 (s, 1H), 5.41 (d, *J* = 17.5 Hz, 1H), 5.40 (s, 1H), 5.09 (d, *J* = 11.1 Hz, 1H), 4.79 (s, 1H), 4.50–4.45 (m, 1H), 4.16 (d, *J* = 4.5 Hz, 1H), 3.83 (s, 3H), 3.09–2.94 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.9, 147.2, 143.7., 142.7, 140.9, 136.8, 129.7, 128.1, 126.8, 125.6, 123.7, 119.8, 115.7, 115.0, 113.4, 112.6, 71.4, 63.9, 62.7, 55.2, 39.6, 24.9. IR (KBr): 3600, 3054, 2922, 1633, 1600, 1458, 1158, 906, 818, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO_2$, 322.1802; found, 322.1798.

*(1S,2R)-1-((1-(3-bromophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1 H-inden-2-ol (**4j**).* Brown oil, 72.6 mg, 98% yield, dr >20:1. $[\alpha]_D^{25}$ = -7.9 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.41(d, *J* = 7.5 Hz, H), 7.25–7.21 (m, 5H), 6.37 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.48 (s, 1H), 5.42 (s, 1H), 5.40 (d, *J* = 18.5 Hz, 1H), 5.12 (d, *J* = 11.0 Hz, 1H), 4.81 (s, 1H), 4.52–4.47 (m, 1H), 4.12 (d, *J* = 4.6 Hz, 1H), 3.07 (dd, *J* = 4.5, 16.5 Hz, 1H), 3.01–2.92 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.8, 144.5, 142.5, 140.8, 136.5, 130.7, 130.5, 130.2, 128.2, 126.9, 126.1, 125.6, 123.8, 122.9, 116.2, 115.3, 71.6, 63.8, 62.1, 39.6. IR (KBr): 3585, 3071, 2921, 1637, 1591, 1466, 1161, 908, 820, 745 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}BrNO_2$, 370.0810; found, 370.0797.

*(1S,2R)-1-((2-methylene-1-(3-(trifluoromethyl)phenyl)but-3-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**4k**).* Brown oil, 64.7 mg, 90% yield, dr >20:1. $[\alpha]_D^{25}$ = +5.6 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.25–7.21 (m, 4H), 6.37 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.48 (s, 1H), 5.43 (s, 1H), 5.41 (d, *J* = 17.5 Hz, 1H), 5.13 (d, *J* = 11.1 Hz, 1H), 4.92 (s, 1H), 4.54–4.49 (m, 1H), 4.11 (d, *J* = 5.1 Hz, 1H), 3.07 (dd, *J* = 4.5, 16.5 Hz, 1H), 3.00–2.93 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.9, 143.1, 142.5, 140.7, 136.4, 131.0 (q, *J* = 32.4 Hz), 130.9, 129.1, 128.2, 126.9, 124.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.8 Hz), 123.8, 116.4, 115.4, 71.6, 63.8, 62.2, 39.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.6 (s, 3F). IR (KBr): 3628, 3026, 2926, 1641, 1453, 1164, 1125, 909, 802, 747 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}F_3NO$, 360.1570; found, 360.1567.

3-*(1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-2-methylenebut-3-en-1-yl)benzonitrile (**4l**).* Brown oil, 55.7 mg, 88% yield, dr >20:1. $[\alpha]_D^{25}$ = -7.6 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.74–7.72 (m, 1H), 7.60–7.59 (m, 1H), 7.49 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.26–7.24 (m, 4H), 6.35 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.49 (s, 1H), 5.43 (s, 1H), 5.39 (d, *J* = 18.0 Hz, 1H), 5.12 (d, *J* = 11.1 Hz, 1H), 4.88 (s, 1H), 4.53–4.50 (m, 1H), 4.07 (d, *J* = 5.0 Hz, 1H), 3.10–3.05 (m, 1H), 2,97 (dd, *J* = 3.0, 16.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.6, 143.7, 142.4, 140.5, 136.2, 132.0, 131.2, 131.2, 129.4, 128.2, 126.9, 125.6, 123.9, 118.8, 116.7, 115.5, 112.7, 71.8, 63.8, 61.8, 39.6. IR (KBr): 3520, 3010, 2924, 1637, 1461, 1267, 1149, 909, 810, 695 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}N_2O$, 317.1648; found, 317.1647.

*Methyl3-(1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-2-methylene but-3-en-1-yl)benzoate (**4m**).* Brown oil, 64.3 mg, 92% yield, dr >20:1. $[\alpha]_D^{25}$ = -16.1 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.24–7.20 (m, 4H), 6.36 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.50 (s, 1H), 5.42 (s, 1H), 5.40 (d, *J* = 18.0 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H), 4.90 (s, 1H), 4.50–4.49 (m, 1H), 4.12 (d, *J* = 4.9 Hz, 1H), 3.94 (s, 3H), 3.05 (dd, *J* = 5.0, 16.5 Hz, 1H), 3.00–2.94 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 147.0, 142.5, 140.8, 136.5, 132.0, 130.6, 128.9, 128.8, 128.6, 128.1, 126.8, 125.6, 123.8, 116.2, 115.3, 71.5, 63.8, 62.3, 52.2, 39.6. IR (KBr): 3072, 3015, 2948, 1720, 1639, 1438, 1286, 1196, 909, 817, 749 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NO_3$, 350.1751; found, 350.1748

*(1S,2R)-1-((1-(2-fluorophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1H -inden-2-ol (**4n**).* Brown oil, 52.3 mg, 86% yield, dr >20:1. $[\alpha]_D^{25}$ = -16.0 (*c* 0.3, $CHCl_3$).^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (td, *J* = 7.6, 1.7 Hz, 1H), 7.33–7.27 (m, 2H), 7.25–7.17 (m, 4H), 7.15–7.09 (m, 2H), 6.39 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.51 (s, 1H), 5.44 (s, 1H), 5.38 (d, *J* = 17.7 Hz, 1H), 5.19 (s, 1H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.50 (dt, *J* = 2.5, 8.0 Hz, 1H), 4.14 (d, *J* = 5.1 Hz, 1H), 3.05 (dd, *J* = 5.0, 16.5 Hz, 1H), 3.00–2.97 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.8 (d, *J* = 245.7 Hz), 146.3, 142.4, 141.0, 136.8, 129.2 (d, *J* = 8.3 Hz), 129.0 (d, *J* = 13.9 Hz), 128.6 (d, *J* = 4.0 Hz), 128.1, 126.8, 125.6, 124.6 (d, *J* = 3.4 Hz), 123.6, 116.0, 115.6 (d, *J* = 22.6 Hz),, 114.7, 71.3, 64.2, 55.1, 39.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -118.9 (s, 1F). IR (KBr): 3063, 3011, 2927, 1637, 1600, 1466, 1152, 909, 812, 734 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}FNO$, 310.1602; found, 310.1599.

*(1S,2R)-1-((1-(3,5-dibromophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dihydr o-1H-inden-2-ol (**4o**).* Brown oil, 87.1 mg, 97% yield, dr >20:1. $[\alpha]_D^{25}$ = +7.7 (*c* 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.30–7.26 (m, 4H), 6.35 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.46 (s, 1H), 5.43 (s, 1H), 5.43 (d, *J* = 18.0 Hz, 1H), 5.15 (d, *J* = 11.1 Hz, 1H), 4.89 (s, 1H), 4.56–4.51 (m, 1H), 4.06 (d, *J* = 4.0 Hz, 1H), 3.12–2.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.9, 146.5, 143.7, 142.2, 140.3, 136.0, 135.1, 132.2, 128.3, 127.0, 125.6, 124.6, 124.1, 117.1, 115.8, 113.1, 71.9, 63.9, 61.2, 39.7. IR (KBr): 3427, 3010, 2923, 1637, 1555, 1420, 1265, 1048, 908, 810, 743 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}Br_2NO$, 449.9886; found, 449.9881.

(1S,2R)-1-((1-(4-bromo-3-nitrophenyl)-2-methylenebut-3-en-1-yl)amino)-2,3-dih ydro-1H-inden-2-ol (***4p***). Brown oil, 79.7 mg, 96% yield, dr >20:1. $[\alpha]_D^{25}$ = +5.7 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60–7.56 (m, 3H), 7.26 (s, 4H), 6.35 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.46 (s, 1H), 5.43 (s, 1H), 5.41 (d, *J* = 16.0 Hz, 1H), 5.15 (d, *J* = 11.1 Hz, 1H), 4.78 (s, 1H), 4.53–4.48 (m, 1H), 4.08 (d, *J* = 4.3 Hz, 1H), 3.15–2.88 (m, 2H), 2.40 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.5, 146.3, 142.3, 140.6, 136.2, 133.2, 129.4, 128.2, 127.0, 125.6, 124.0, 123.2, 116.7, 115.6, 71.7, 63.8, 61.6, 39.6. IR (KBr): 3428, 3089, 2919, 1635, 1534, 1264, 1157, 1035, 910, 825, 744 cm^{-1}. HRMS (ESI) m/z: [M+H]+ calcd for $C_{20}H_{20}BrN_2O_3$, 415.0652; found, 415.0647.

*(1S,2R)-1-((2-methylene-1-(naphthalen-2-yl)but-3-en-1-yl)amino)-2,3-dihydro-1 H-inden-2-ol (**4q**).* Brown oil, 62.8 mg, 92% yield, dr >20:1. $[\alpha]_D^{25}$ = -17.5 (*c* 0.3,

$CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.80–7.69 (m, 4H), 7.43 (d, J = 8.5 Hz, 1H), 7.40–7.34 (m, 2H), 7.10–7.06 (m, 4H), 6.27 (dd, J = 17.6, 11.1 Hz, 1H), 5.42 (s, 1H), 5.33 (d, J = 18.0 Hz, 1H), 5.32 (s, 1H), 4.95 (d, J = 11.1 Hz, 1H), 4.86 (s, 1H), 4.39–4.37 (m, 1H), 4.08 (d, J = 5.1 Hz, 1H), 2.92 (dd, J = 5.5, 16.5 Hz, 1H), 2.86 (dd, J = 2.0, 16.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.2, 142.7, 140.9, 139.3, 136.8, 133.4, 133.0, 128.7, 128.1, 127.9, 127.7, 126.8, 126.4, 126.3, 126.0, 125.6, 125.2, 123.8, 115.9, 115.2, 71.4, 63.9, 62.9, 39.6. IR (KBr): 3395, 3006, 2930, 1595, 1459, 1263, 1155, 1046, 908, 820, 701 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{24}NO$, 342.1852; found, 342.1852.

(1S,2R)-1-((3-methylenehept-1-en-4-yl)amino)-2,3-dihydro-1H-inden-2-ol (***4r***). Brown oil, 47.3 mg, 92% yield, dr >20:1. $[\alpha]_D^{25}$ = +20.8 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.29–7.17 (m, 4H), 6.41 (dd, J = 17.5, 10.9 Hz, 1H), 5.52 (d, J = 18.5 Hz, 1H), 5.29 (s, 1H), 5.21 (s, 1H), 5.16 (d, J = 11.1 Hz, 1H), 4.27 (dt, J = 3.0, 5.5 Hz, 1H), 4.04 (d, J = 5.3 Hz, 1H), 3.77 (dd, J = 2.0, 1.5 Hz, 1H), 3.02 (dd, J = 5.5, 16.5 Hz, 1H), 2.95–2.90 (m, 1H), 1.71–1.57 (m, 2H), 1.42–1.35 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.7, 143.3, 141.1, 136.6, 128.0, 126.8, 125.7, 123.6, 115.5, 114.4, 71.7, 64.0, 60.2, 39.3, 37.5, 19.6, 14.1. IR (KBr): 3500, 2957, 2960, 1636, 1458, 1083, 960, 821, 742, 451 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{24}NO$ 258.1852; found, 258.1849.

(1S,2R)-1-((2-methyl-4-methylenehex-5-en-3-yl)amino)-2,3-dihydro-1H-inden-2-ol (***4s***). Brown oil, 47.9 mg, 90% yield, dr >20:1. $[\alpha]_D^{25}$ = +50.3 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.29–7.28 (m, 1H), 7.23–7.22 (m, 3H), 6.41 (dd, J = 17.6, 11.1 Hz, 1H), 5.52 (d, J = 17.6 Hz, 1H), 5.34 (s, 1H), 5.19 (s, 1H), 5.14 (d, J = 11.1 Hz, 1H), 4.29–4.24 (m, 1H), 4.02 (d, J = 5.3 Hz, 1H), 3.45 (d, J = 7.6 Hz, 1H), 3.01 (dd, J = 5.5, 16.5 Hz, 1H), 2.95–2.88 (m, 1H), 1.95–1.84 (m, 1H), 1.04 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.2, 143.5, 141.0, 136.8, 128.0, 126.8, 125.7, 123.5, 116.4, 114.6, 71.8, 68.0, 64.9, 39.2, 31.7, 20.1, 19.4. IR (KBr): 3600, 2957, 2850, 1636, 1463, 1264, 1084, 990, 905, 748 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{24}NO$, 258.1852; found, 258.1850.

(1S,2R)-1-((1-cyclohexyl-2-methylenebut-3-en-1-yl)amino)-2,3-dihydro-1H-indene-2-ol (***4t***). Brown oil, 54.7 mg, 92% yield, dr >20:1. $[\alpha]_D^{25}$ = +60.6 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.31–7.23 (m, 4H), 6.42 (dd, J = 17.7, 11.1 Hz, 1H), 5.55 (dd, J = 17.7, 1.0 Hz, 1H), 5.35 (s, 1H), 5.18 (s, 1H), 5.16 (d, J = 11.0 Hz, 1H), 4.29–4.27 (m, 1H), 4.03 (d, J = 5.3 Hz, 1H), 3.51 (d, J = 7.8 Hz, 1H), 3.03 (dd, J = 5.5, 16.5 Hz, 1H), 2.97–2.93 (m, 2H), 2.00–1.97 (m, 1H), 1.83–1.69 (m, 5H), 1.62–1.55 (m, 1H), 1.29-1.18 (m, 4H), 1.13-0.98 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.0, 143.5, 141.0, 136.7, 128.0, 126.7, 125.7, 123.5, 116.4, 114.6, 71.8, 67.3, 64.9, 41.3, 39.2, 30.4, 30.1, 26.5, 26.3, 26.2. IR (KBr): 3424, 3010, 2851, 1634, 1450, 1265, 1080, 989, 904, 742 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{28}NO$, 298.2162; found, 298.2165.

(1S,2R)-1-(((S)-3-methylene-1-p-henylpent-4-en-1-yl)amino)-2,3-dihydro-1H-indene-2-ol (***5a***). Yellow oil, 59.2 mg, 97% yield, dr = 19:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.46 (m, 4H), 7.29–7.34 (m, 1H), 7.16–7.22 (m, 3H), 7.10–7.07 (m, 1H), 6.24 (dd, J = 10.5, 17.5 Hz, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 5.12

(s, 1H), 5.02 (s, 1H), 4.40–4.43 (m, 1H), 3.98–4.03 (m, 2H), 2.96 (d, J = 3.5 Hz, 2H), 2.67–2.71 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.0, 143.1, 142.4, 141.0, 128.7, 127.9, 127.5, 126.9, 126.7, 125.4, 123.8, 118.9, 114.1, 70.9, 63.7, 60.1, 41.1, 39.7. IR (KBr): 3415, 2919, 1453, 1160, 1051, 992, 903, 746, 701 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO$, 306.1852; found, 306.1851.

*(1S,2R)-1-(((S)-3-methylene-1-(p-tolyl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5b**)*. Yellow oil, 61.3 mg, 96% yield, dr = 8.5:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.24–7.17(m, 5H), 7.11–7.08 (m, 1H), 6.43 (dd, J = 11.0, 18.0 Hz, 1H), 5.37 (d, J = 18.0 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.43–4.39 (m, 1H), 4.02–3.96 (m, 2H), 2.96 (d, J = 3.5 Hz, 1H), 2.72–2.64 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.2, 142.4, 141.0, 140.9, 138.4, 137.1, 129.4, 127.9, 126.8, 126.6, 125.4, 123.7, 118.8, 114.1, 70.8, 63.6, 59.7, 41.1, 39.6, 21.1. IR (KBr): 3332, 3085, 3021, 2921, 1593, 1459, 1051, 901, 742 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}NO$, 320.2009; found, 320.2006.

*(1S,2R)-1-(((S)-1-(4-isopropylphenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5c**)*. Yellow oil, 61.3 mg, 96% yield, dr = 10:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.34 (m, 2H), 7.28–7.25 (m, 2H), 7.22–7.16 (m, 3H), 7.07 (d, J = 7.5 Hz, 1H), 6.44 (dd, J = 11.0, 17.5 Hz, 1H), 5.37 (d, J = 18.0 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 4.43–4.39 (m, 1H), 4.01 (d, J = 5.0 Hz, 1H), 3.98 (dd, J = 5.5, 9.0 Hz, 1H), 2.98–2.91 (m, 3H), 2.71 (dd, J = 5.5, 14.0 Hz, 1H), 2.65 (dd, J = 8.5, 14.0 Hz, 1H), 1.30 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.1, 143.2, 142.4, 141.3, 141.0, 138.4, 127.9, 126.7, 126.6, 125.4, 123.7, 118.8, 114.0, 70.8, 63.6, 59.7, 41.1, 39.6, 33.8, 24.0. IR (KBr): 2958, 1593, 1464, 1160, 1054, 992, 902, 830, 742 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}NO$, 348.2322; found, 348.2320.

*(1S,2R)-1-(((S)-1-(4-(tert-butyl)phenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5d**)*. Yellow oil, 67.2 mg, 93% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2H), 7.38–7.35 (m, 2H), 7.22–7.16 (m, 4H), 7.08–7.05 (m, 1H), 6.40 (dd, J = 10.5, 17.5 Hz, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 5.15 (s, 1H), 5.06 (s, 1H), 4.43–4.39 (m, 1H), 4.01 (d, J = 5.0 Hz, 1H), 3.98 (dd, J = 5.5, 9.0 Hz, 1H), 2.96 (d, J = 3.0 Hz, 1H), 2.72 (dd, J = 5.5, 14.0 Hz, 1H), 2.65 (dd, J = 9.0, 14.0 Hz, 1H), 2.58 (brs, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.3, 143.2, 142.5, 141.1, 140.9, 138.5, 127.9, 126.6, 126.4, 125.5, 125.4, 123.7, 118.8, 114.0, 70.8, 63.6, 59.6, 41.0, 39.6, 34.5, 31.4. IR (KBr): 3333, 3085, 2961, 1593, 1462, 1364, 1051, 901, 743 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{32}NO$, 362.2478; found, 362.2475.

*(1S,2R)-1-(((S)-1-(4-chlorophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5e**)*. Yellow oil, 64.4 mg, 95% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 4H), 7.24–7.19 (m, 3H), 7.17-7.14 (m, 1H), 6.42 (dd, J = 11.0, 17.5 Hz, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.20 (d, J = 11.0 Hz, 1H), 5.13 (s, 1H), 5.02 (s, 1H), 4.46–4.42 (m, 1H), 4.04 (dd, J = 6.5, 1.0 Hz, 1H), 3.96 (d, J = 4.5 Hz, 1H), 3.02–2.92 (m, 2H), 2.71–2.62 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.7, 142.5, 142.3, 140.8, 138.3, 133.0, 128.8, 128.3, 130.0, 126.7, 125.5, 123.8, 119.1, 114.2, 71.0, 63.7, 59.3, 41.2, 39.7. IR (KBr): 3331, 3083, 3023, 2916, 1489, 1089,

1050, 1013, 902, 826, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}ClNO$, 340.1463; found, 340.1460.

*4-((S)-1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-3-methylenepent-4-en-1-yl)benzonitrile (**5f**).* Yellow oil, 62.7 mg, 99% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.68–7.64 (m, 2H), 7.58–7.55(m, 2H), 7.22–7.15 (m, 4H), 6.38 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.33 (d, *J* = 18.0 Hz, 1H), 5.17 (d, *J* =10.5 Hz, 1H), 5.09 (s, 1H), 4.97 (s, 1H), 4.44–4.41 (m, 1H), 2.95 (dd, *J* = 5.0, 17.0 Hz, 1H), 2.90 (dd, *J* = 2.5, 16.5 Hz, 1H), 2.67–2.57 (s, 2H), 2.23 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.7, 142.2, 142.0, 140.5, 138.1, 132.5, 128.1, 127.8, 126.8, 125.4, 123.9, 119.4, 118.8, 114.4, 111.3, 71.2, 63.8, 59.5, 41.2, 39.7. IR (KBr): 2915, 2227, 1464, 1160, 1084, 1051, 992, 903, 841, 741 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O$, 331.1805; found, 331.1804.

*Methyl4-((S)-1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-3-methylenepent-4-en-1-yl)benzoate (**5g**).* Yellow oil, 69.0 mg, 95% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.19–7.15 (m, 3H), 7.12–7.09 (m, 1H), 6.38 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.33 (d, *J* = 17.5 Hz, 1H), 5.16 (d, *J* = 11.0 Hz, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.42–4.39 (m, 1H), 4.07 (dd, *J* = 3.0, 2.5 Hz, 1H), 3.93–3.89 (m, 4H), 2.95–2.91 (m, 2H), 2.70–2.61 (m, 2H), 2.52 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9, 149.4, 142.6, 142.1, 170.8, 138.2, 130.0, 129.4, 128.0, 127.0, 126.7, 125.4, 123.8, 119.2, 114.2, 71.0, 63.7, 59.7, 52.1, 41.0, 39.6. IR (KBr): 3331, 2949, 1722, 1609, 1460, 1436, 1280, 1190, 1112, 1051, 1018, 992, 905, 745, 709 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO_3$, 364.1907; found, 364.1905.

*(1S,2R)-1-(((S)-3-methylene-1-(m-tolyl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5h**).* Yellow oil, 54.3 mg, 85% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.24–7.29 (m, 2H), 7.23–7.19 (m, 2H), 7.18–7.13 (m, 3H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 6.5 Hz, 1H), 6.40 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.34 (d, *J* = 17.5 Hz, 1H), 5.14 (d, *J* = 11.0 Hz, 1H), 5.10 (s, 1H), 5.01 (s, 1H), 4.38 (m, 1H), 3.96 (d, *J* = 5.0 Hz, 1H), 3.92 (dd, *J* = 5.5, 8.5 Hz, 1H), 2.92 (d, *J* = 3.5 Hz, 2H), 2.67 (dd, *J* = 5.5, 14.0 Hz, 1H), 2.62 (dd, *J* = 8.5, 13.5 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.9, 143.1, 142.4, 141.0, 138.4, 138.3, 128.6, 128.2, 127.9, 127.6, 126.6, 125.4, 123.8, 123.7, 118.8, 114.1, 70.8, 63.6, 60.0, 41.1, 39.6, 21.5. IR (KBr): 3695, 2911, 1593, 1359, 1393, 1251, 1160, 1052, 993, 901, 787, 743, 704, 669 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}NO$, 320.2009; found, 320.2006.

*(1S,2R)-1-(((S)-1-(3-fluorophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5i**).* Yellow oil, 56.2 mg, 87% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 1H), 7.25–7.14 (m, 6H), 6.42 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.36 (d, *J* = 18.0 Hz, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.46–4.42 (m, 1H), 4.04 (t, *J* = 7.0 Hz, 1H), 3.98 (d, *J* = 5.0 Hz, 1H), 3.01–2.97 (m, 2H), 2.71–2.62 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.2 (d, *J* = 246.8 Hz), 146.9 (d, *J* = 6.3 Hz), 142.7, 142.2, 140.8, 138.3, 130.2 (d, *J* = 8.2 Hz), 128.0, 126.7, 125.4, 123.8, 122.6 (d, *J* = 2.6 Hz), 119.1, 114.3 (d, *J* = 21.3 Hz), 114.2 (d, *J* = 4.0 Hz), 123.7 (d, *J* = 21.3 Hz),71.0, 63.7, 59.5, 41.1, 39.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ -112.7 (s, 1F). IR (KBr): 3404, 3085, 2924, 1612, 1592, 1481, 1450, 1251, 1051,

902, 743 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}FNO$, 324.1758; found, 324.1755.

*(1S,2R)-1-(((S)-1-(3-chlorophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5j**)*. Yellow oil, 57.0 mg, 84% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.36–7.32 (m, 2H), 7.29–7.28(m, 1H), 7.23–7.20 (m, 3H), 7.17–7.15 (m, 1H), 7.45–7.39 (dd, J = 11.0, 17.5 Hz, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.20 (d, J = 11.0 Hz, 1H), 5.13 (s, 1H), 5.02 (s, 1H), 4.45–4.42 (s, 1H), 4.04 (dd, J = 6.5, 7.5 Hz, 1H), 3.96 (d, J = 4.5 Hz, 1H), 3.01–2.93 (m, 2H), 2.68 (dd, J= 8.0, 6.0 Hz), 2.64 (dd, J = 4.5, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.7, 142.5, 142.3, 140.8, 138.3, 133.0, 128.8, 128.3, 128.0, 126.7, 125.5, 123.8, 119.1, 114.2, 71.0, 63.70, 59.3, 41.2, 39.7. IR (KBr): 3329, 2903, 1594, 1463, 1428, 1346, 1161, 1076, 1051, 994, 901, 823, 786, 744, 694 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}ClNO$, 340.1463; found, 340.1461.

*(1S,2R)-1-(((S)-1-(3-bromophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5k**)*. Yellow oil, 69.7 mg, 91% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.30–7.25 (m, 1H), 7.24–7.20 (m, 3H), 7.18–7.15 (m, 1H), 6.42 (dd, J = 10.5, 17.5 Hz, 1H), 5.36 (d, J = 18.0 Hz, 1H), 5.19 (d, J = 11.0 Hz, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 4.46–4.42 (m, 1H), 4.01 (dd, J = 6.5, 8.0 Hz, 1H), 3.96 (d, J = 4.5 Hz, 1H), 3.02–2.92 (m, 2H), 2.67 (dd, J = 6.0, 14.0 Hz, 1H), 2.66–2.61 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.6, 142.6, 142.2, 140.8, 138.2, 130.6, 130.3, 130.1, 128.0, 126.8, 125.5, 125.4, 123.8, 122.8, 119.2, 114.3, 71.0, 63.7, 59.4, 41.2, 39.7. IR (KBr): 3331, 2922, 1593, 1570, 1464, 1426, 1050, 994, 903, 784, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}BrNO$, 384.0958; found, 384.0955.

*((S)-1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-3-methylenepent-4-en-1-yl)benzonitrile (**5l**)*. Yellow oil, 62.7 mg, 95% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.51 (dd, J = 8.0, 7.5 Hz, 1H), 7.24–7.21 (m, 4H), 6.41 (dd, J = 10.5, 17.5 Hz, 1H), 5.36 (d, J = 18.0 Hz, 1H), 5.20 (d, J = 11.0 Hz, 1H), 5.12 (s, 1H), 5.00 (s, 1H), 4.48–4.45 (m, 1H), 4.11 (dd, J = 6.0, 7.5 Hz, 1H), 3.89 (d, J = 4.5 Hz, 1H), 2.98 (dd, J = 4.5, 16.5 Hz, 1H), 2.93 (dd, J = 1.5, 16.5 Hz, 1H), 2.67 (dd, J = 8.0, 14 Hz, 1H), 2.62 (dd, J = 6.5, 14.5 Hz, 1H), 2.32 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.7, 142.2, 142.0, 140.5, 138.1, 131.5, 131.2, 130.8, 129.4, 128.1, 126.8, 125.4, 123.9, 119.4, 118.8, 114.4, 112.6, 71.2, 63.80, 59.1, 41.3, 39.7. IR (KBr): 2915, 2227, 1724, 1593, 1464, 1160, 1084, 992, 903, 841, 741cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O$, 331.1805; found, 331.1803.

*Methyl4-((S)-1-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-3-methylenepent-4-en-1-yl)benzoate (**5m**)*. Yellow oil, 71.2 mg, 98% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11(s, 1H), 7.96 (d, J = 2.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.45 (dd, J = 7.5, 7.5 Hz, 1H), 7.18–7.12 (m, 4H), 6.39 (dd, J = 10.5, 17.5 Hz, 1H), 5.34 (d, J = 17.5 Hz, 1H), 5.16 (d, J = 11.0 Hz, 1H), 5.01 (s, 1H), 5.00 (s, 1H), 4.42–4.39 (m, 1H), 4.08 (t, J = 7.0 Hz, 1H), 3.94 (s, 3H), 3.92 (d, J = 4.5 Hz, 1H), 2.92 (d, J = 3.0 Hz, 2H), 2.70–2.63 (m, 2H), 2.49 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0, 144.5, 142.7, 142.2, 140.8, 138.3, 131.6, 130.6, 128.8, 128.7, 128.1,

127.9, 125.4, 123.8, 119.1, 114.3, 71.0, 63.7, 59.6, 52.2, 41.1, 39.6. IR (KBr): 3331, 2949, 1722, 1609, 1460, 1436, 1280, 1190, 1112, 1051, 993, 905, 769, 744 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO_3$, 364.1907; found, 364.1905.

*(1S,2R)-1-(((S)-1-(2-methoxyphenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5n**)*. Yellow oil, 56.9 mg, 85% yield, dr = 6:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 7.0 Hz, 1H), 7.30–7.27 (m, 1H), 7.22–7.14 (m, 3H), 7.01–6.95 (m, 3H), 6.42 (dd, J = 10.5, 17.5 Hz, 1H), 5.43 (d, J = 17.5 Hz, 1H), 5.16 (d, J = 11.0 Hz, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 4.37 (dt, J = 2.0, 5.0 Hz, 1H), 4.15–4.09 (m, 1H), 3.97–3.92 (m, 4H), 3.74 (brs, 1H), 2.99 (dd, J = 1.0, 16.5 Hz, 1H), 2.93 (dd, J = 5.0, 16.5 Hz, 1H), 2.50 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.5, 143.8, 142.5, 141.3, 138.5, 131.1, 128.8, 128.4, 127.7, 126.5, 125.4, 123.5, 120.7, 118.6, 114.0, 110.9, 70.4, 63.9, 55.2, 39.6, 38.8. IR (KBr): 3333, 3004, 2920, 2836, 1596, 1490, 1463, 1237, 1086, 1050, 1026, 902, 750 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}NO_2$, 336.1958; found: 336.1955.

*(1S,2R)-1-(((S)-1-(2-fluorophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5o**)*. Yellow oil, 58.1 mg, 90% yield, dr >20:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (dt, J = 1.5, 7.5 Hz, 1H), 7.33–7.27 (m, 1H), 7.24–7.17 (m, 4H), 7.15–7.08 (m, 2H), 6.42 (dd, J = 10.5, 17.5 Hz, 1H), 5.41 (d, J = 17.5 Hz, 1H), 5.19 (d, J = 11.0 Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 4.44–4.41 (m, 1H), 4.24 (dd, J = 6.0, 8.5 Hz, 1H), 3.97 (d, J = 5.0 Hz, 1H), 2.99 (dd, J = 2.0, 16.5 Hz, 1H), 2.95 (dd, J = 4.5, 16.5 Hz, 1H), 2.80 (dd, J = 6.0, 14.0 Hz, 1H), 2.73 (dd, J = 8.5, 14.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.3 (d, J = 245.1 Hz), 143.0, 142.1, 141.1, 138.2, 130.5 (d, J = 12.8 Hz), 128.9 (d, J = 8.6 Hz), 128.8 (d, J = 5.2 Hz), 127.9, 126.7, 125.5, 124.4 (d, J = 3.3 Hz), 123.5, 119.0, 115.9 (d, J = 22.0 Hz), 114.2, 70.6, 63.9, 55.4, 39.6, 39.5. ^{19}F NMR (471 MHz, $CDCl_3$): δ -118.9 (s, 1F). IR (KBr): 3331, 3083, 2910, 1592, 1486, 1454, 1220, 1052, 903, 757 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}FNO$, 324.1758; found, 324.1756.

*(1S,2R)-1-(((S)-3-methylene-1-(2-(trifluoromethyl)phenyl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5p**)*. Yellow oil, 64.2 mg, 86% yield, dr = 8:1. ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 8.0, 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 8.0 Hz, 1H), 7.26–7.19 (m, 4H), 6.48 (dd, J = 11.0, 18.0 Hz, 1H), 5.52 (d, J = 18.0 Hz, 1H), 5.29–5.24 (m, 2H), 5.22 (s, 1H), 4.84 (d, J = 12.0 Hz, 1H), 3.93 (d, J = 5.0 Hz, 1H), 3.77–3.74 (m, 1H), 2.91–2.83 (m, 2H), 2.79 (dd, J = 2.5, 14.0 Hz, 1H), 2.47 (dd, J = 10.5, 14.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 114.1, 142.9, 142.5, 140.7, 138.2, 132.4, 128.5 (q, J = 29.6 Hz), 127.9, 127.8, 127.2, 126.6, 125.6 (q, J = 4.6 Hz), 125.3, 124.5 (q, J = 274.6 Hz), 123.8, 119.2, 114.6, 70.1, 63.8, 54.0, 41.3, 39.5. ^{19}F NMR (471 MHz, $CDCl_3$): δ - 57.3 (s, 3F). IR (KBr): 3416, 2925, 1455, 1313, 1159, 1119, 1056, 1035, 770, 746 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}F_3NO$, 374.1726; found, 374.1724.

*(1S,2R)-1-(((S)-3-methylene-1-(2-nitrophenyl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5q**)*. Yellow oil, 58.8 mg, 84% yield, dr = 10:1. ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.68 (dd, J = 7.5, 8.0 Hz, 1H), 7.44 (dd, J = 7.5, 8.0 Hz, 1H), 7.27–7.23 (m, 1H), 7.23–7.19 (m, 3H), 6.42 (dd, J = 10.5, 17.5 Hz, 1H), 5.50 (d, J = 17.5 Hz, 1H), 5.21 (d, J = 11.0 Hz, 1H), 5.17 (s,

1H), 5.11 (s, 1H), 4.65 (dd, *J* = 5.0, 9.5 Hz, 1H), 4.51–4.48 (m, 1H), 3.86 (d, *J* = 4.5 Hz, 1H), 2.99–2.90 (m, 2H), 2.88 (dd, *J* = 5.0, 13.5 Hz, 1H), 2.64–2.58 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 150.4, 142.5, 142.2, 140.6, 138.9, 137.9, 133.0, 128.9, 128.1, 127.9, 126.7, 125.4, 124.0, 123.9, 119.5, 115.0, 71.2, 64.2, 54.1, 40.6, 39.5. IR (KBr): 2924, 1590, 1627, 1565, 1356, 1050, 993, 907, 855, 784, 746, 670 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_3$, 351.1703; found, 351.1701.

*(1S,2R)-1-(((S)-1-(3,4-dimethylphenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5r**).* Yellow oil, 64.1 mg, 96% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.21–7.17 (m, 6H), 7.11–7.09 (m, 1H), 6.43 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.38 (d, *J* = 18.0 Hz, 1H), 5.18 (d, *J* = 11 Hz, 1H), 5.13 (s, 1H), 5.05 (s, 1H), 4.42–3.39 (m, 1H), 4.01 (d, *J* = 5.0 Hz, 1H), 3.94 (dd, *J* = 5.5, 8.5 Hz, 1H), 2.99–2.92 (m, 2H), 2.70 (dd, *J* = 5.0, 14.5 Hz, 1H), 2.64 (dd, *J* = 9.0, 14.0 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 143.3, 142.5, 141.4, 141.1, 138.5, 136.8, 135.7, 129.9, 128.2, 127.8, 126.6, 125.4, 124.1, 123.7, 118.7, 114.0, 70.8, 63.6, 59.7, 41.1, 39.6, 19.9, 19.5. IR (KBr): 3332, 3083, 3005, 2920, 1593, 1456, 1159, 1085, 1051, 992, 901, 823, 742 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}NO$, 334.2165; found, 334.2163.

*(1S,2R)-1-(((S)-1-(3,5-dibromophenyl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5s**).* Yellow oil, 83.8 mg, 91% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.57 (dd, *J* = 2.0, 1.5 Hz, 1H), 7.53 (d, *J* = 1.0 Hz, 2H), 7.24–7.18 (m, 4H), 6.39 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.32 (d, *J* = 18.0 Hz, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 5.12 (s, 1H), 5.02 (s, 1H), 4.44–4.41 (m, 1H), 3.97 (dd, *J* = 5.5, 14.0 Hz, 1H), 3.90 (d, *J* = 4.5 Hz, 1H), 2.97 (dd, *J* = 5.0, 16.5 Hz, 1H), 2.90 (dd, *J* = 1.0, 16.5 Hz, 1H), 2.63–1.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 148.5, 142.3, 142.1, 140.5, 138.1, 133.1, 128.9, 128.1, 126.9, 125.4, 124.0, 123.2, 119.4, 114.4, 71.2, 63.7, 58.9, 41.3, 39.7. IR (KBr): 3326, 3072, 2920, 1583, 1555, 1423, 1160, 1048, 991, 904, 855, 685 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}Br_2NO$, 462.0063; found, 462.0058.

*(1S,2R)-1-(((S)-3-methylene-1-(naphthalen-2-yl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5t**).* Yellow solid, 58.3 mg, 82% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.93 (d, *J* = 8.5 Hz, 1H), 7.89–7.86 (m, 2H), 7.84 (s, 1H), 7.64 (dd, *J* = 1.5, 8.5 Hz, 1H), 7.55–7.548 (m, 2H), 7.21–7.15 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.45 (dd, *J* = 11.0 Hz, 17.5 Hz, 1H), 5.43 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.13 (s, 1H), 5.05 (s, 1H), 4.48–4.45 (m, 1H), 4.20 (t, *J* = 7.0 Hz, 1H), 4.04 (d, *J* = 4.5 Hz, 1H), 3.00–2.92 (m, 2H), 2.79 (d, *J* = 7.0 Hz, 2H), 2.60 (brs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 142.9, 142.3, 141.1, 140.9, 138.4, 133.3, 133.0, 128.7, 127.9, 127.7, 126.6, 126.3, 126.2, 125.8, 125.4, 124.3, 123.7, 119.0, 114.2, 70.9, 63.6, 60.1, 41.0, 39.6. IR (KBr): 2902, 1806, 1725, 1590, 1250, 1052, 901, 861, 802, 741, 669, 650, 478 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{26}NO$, 356.2009; found, 356.2006.

*(1S,2R)-1-(((S)-1-(furan-2-yl)-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5u**).* Yellow solid, 53.5 mg, 99% yield, dr = 8.5:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.46 (d, *J* = 1.0 Hz, 1H), 7.23–7.16 (m, 3H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.41 (dd, *J* = 11.0, 18.0 Hz, 1H), 6.37 (dd, *J* = 2.0, 3.0 Hz, 1H), 6.28 (d, *J* = 3.0 Hz, 1H),

5.31 (d, J = 18.0 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 5.15 (s, 1H), 5.04 (s, 1H), 5.36–5.32 (m, 1H), 4.10 (d, J = 5.0 Hz, 1H), 4.02 (dd, J = 6.5 Hz, 8.0 Hz, 1H), 3.03–2.95 (m, 2H), 2.82 (dd, J = 7.0, 14.5 Hz, 1H), 2.75 (dd, J = 8.0, 14.Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.7, 142.7, 142.2, 141.8, 141.2, 138.2, 128.0, 126.7, 125.5, 123.6, 118.8, 113.9, 110.1, 107.0, 70.6, 63.6, 54.3, 39.6, 37.8. IR (KBr): 3291, 2966, 2931, 1591, 1500, 1461, 1346, 1170, 1140, 1054, 944, 915, 811, 739 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}NO_2$, 296.1645; found, 296.1643.

*(1S,2R)-1-(((S)-3-methylene-1-(thiophen-2-yl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5v**).* Yellow solid, 53.5 mg, 86% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.28 (m, 1H), 7.24–7.18 (m, 3H), 7.14–7.12 (m, 1H), 7.05–7.03 (m, 1H), 7.00 (dd, J = 3.5, 5.0 Hz, 1H), 6.43 (dd, J = 10.5, 17.5 Hz, 1H), 5.36 (d, J = 18.0 Hz, 1H), 5.19 (d, J = 11.0 Hz, 1H), 5.16 (s, 1H), 5.08 (s, 1H), 4.45–4.40 (m, 1H), 4.32 (dd, J = 6.0, 8.0 Hz, 1H), 4.17 (d, J = 5.0 Hz, 1H), 3.04–2.94 (m, 2H), 2.81 (dd, J = 6.0, 14.0 Hz, 1H), 2.76 (dd, J = 8.0, 13.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.8, 142.7, 142.2, 140.9, 138.2, 127.9, 126.7, 126.6, 125.4, 124.6, 124.1, 123.8, 119.1, 114.1, 70.9, 63.7, 55.8, 42.0, 39.7. IR (KBr): 3286, 3070, 2908, 1589, 1462, 1431, 1338, 1054, 912, 827, 739, 704 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}NOS$, 312.1417; found, 312.1414.

*(1S,2R)-1-(((S)-3-methylene-1-(pyridin-2-yl)pent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5w**).* Yellow oil, 48.9 mg, 80% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (d, J = 4.5 Hz, 1H), 7.67 (dt, J = 1.5, 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.24–7.16 (m, 5H), 6.41 (dd, J = 10.5, 17.5 Hz, 1H), 5.37 (d, J = 17.5 Hz, 1H), 5.16 (d, J = 10.5 Hz, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 4.40 (t, J = 4.5 Hz, 1H), 4.02 (dd, J = 7.5, 7.0 Hz, 1H), 3.87 (d, J = 5.0 Hz, 1H), 3.04–2.99 (m, 1H), 2.94 (dd, J = 4.5, 16.0 Hz, 1H), 2.72 (d, J = 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 126.5, 149.9, 143.0, 142.1, 141.2, 138.3, 136.2, 127.9, 126.6, 125.4, 123.8, 122.8, 122.4, 118.9, 114.1, 70.5, 64.4, 61.3, 40.0, 39.6. IR (KBr): 3330, 3083, 2923, 1590, 1471, 1434, 1263, 1159, 1088, 1052, 994, 903, 747 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O$, 307.1805; found, 307.1803.

*(1S,2R)-1-(((R)-2-methyl-6-methyleneoct-7-en-4-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5x**).* Yellow oil, 46.7 mg, 82% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.23 (m, 4H), 6.45 (dd, J = 10.5, 17.5 Hz, 1H), 5.31 (d, J = 18.0 Hz, 1H), 5.20 (s, 1H), 5.15 (d, J = 11.0 Hz, 1H), 5.10 (s, 1H), 4.33–4.30 (m, 1H), 4.19 (d, J = 5.5 Hz, 1H), 3.08–2.99 (m, 3H), 2,63 (brs, 1H), 2.46 (dd, J = 6.0, 14.0 Hz, 1H), 2.35 (dd, J = 8.0, 14.0 Hz, 1H), 1.85–1.76 (m, 1H), 1.57–1.50 (m, 1H), 1.47–1.40 (m, 1H), 1.00 (d, J = 2.0 Hz, 3H), 0.98 (d, J = 2.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.8, 142.8, 141.4, 138.9, 128.0, 126.7, 125.7, 123.5, 118.6, 113.8, 71.3, 64.3, 54.0, 45.6, 39.5, 38.5, 25.2, 23.0, 22.9. IR (KBr): 3088, 2958, 2923, 1739, 1596, 1462, 1369, 1336, 1158, 1084, 1057, 993, 908, 869, 740 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{28}NO$, 286.2165; found, 286.2162.

*(1S,2R)-1-(((S)-1-cyclohexyl-3-methylenepent-4-en-1-yl)amino)-2,3-dihydro-1H-inden-2-ol (**5y**).* Yellow oil, 52.9 mg, 85% yield, dr >20:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 4H), 6.44 (dd, J = 11.0, 18.0 Hz, 1H), 5.28 (d, J = 17.5 Hz, 1H), 5.19 (s, 1H), 5.14 (d, J = 11.0 Hz, 1H), 5.09 (s, 1H), 5.30–5.27 (dt, J = 4.5, 2.5 Hz,

1H), 4.18 (d, *J* = 5.0 Hz, 1H), 3.02 (dd, *J* = 4.5, 16.5 Hz, 1H), 2.98 (dd, *J* = 2.0, 16.5 Hz, 1H), 2.84 (dt, *J* = 3.5, 9.5 Hz, 1H), 2.55 (dd, *J* = 3.5, 13.5 Hz, 1H), 2.12 (dd, *J* = 10.0, 14.0 Hz, 1H), 1.95–1.75 (m, 6H), 1.40–1.20 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 144.5, 142.9, 141.5, 138.6, 127.9, 126.7, 125.6, 123.5, 118.7, 113.9, 71.1, 64.6, 60.4, 41.5, 39.4, 34.4, 29.7, 27.7, 26.8, 26.7, 26.7. IR (KBr): 2924, 2851, 1593, 1449, 1263, 1084, 992, 897, 742, 889 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{30}NO$, 312.2322; found, 312.2320.

*Dimethyl4-(2-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-2-phenylethyl)cyclohex-4-ene-1,2-dicarboxylate (**6**).* To an oven-dried 2 mL test tube with a stir bar was added dimethyl fumarate (0.70 mmol, 100.0 mg) in a nitrogen atmosphere. To the tube was added anhydrous toluene (0.20 mL) followed by a solution of compound **5a** (0.35 mmol, 107.0 mg) in toluene (0.20 mL). The reaction mixture was stirred at 100 ºC for 6 h. Finally the reaction mixture was directly subjected to the preparative thin-layer chromatography (PE/EA = 10:1). Yellow oil, 138.3 mg, 88% yield, dr = 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.45–7.36 (m, 4H), 7.32–7.27 (m, 1H), 7.22–7.18 (m, 3H), 7.18-7.12 (m, 1H), 5.50–5.47 (m, 1H), 4.48–4.44 (m, 1H), 3.98 (t, *J* = 5.0 Hz, 1H), 3.96–3.91 (m, 1H), 3.73 (s, 3H of one diastereomer), 3.72 (s, 3H of one diastereomer), 3.68 (s, 3H of another diastereomer), 3.67 (s, 3H of another diastereomer), 2.98–2.95 (m, 2H), 2.94–2.74 (m, 3H), 2.51–2.31 (m, 5H), 2.23–2.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 175.3, 175.2, 144.0, 142.6, 140.8, 133.0, 128.7, 127.9, 127.5, 126.9, 126.7, 125.5, 123.9, 122.5, 70.8, 63.7, 59.6, 52.0, 51.8, 46.9, 41.6, 41.1, 40.0, 30.9, 27.9 (one diastereomer); 175.1, 175.0, 143.7, 142.5, 140.7, 132.9, 128.6, 127.8, 127.4, 126.8, 126.6, 125.4, 123.8, 122.4, 70.8, 63.6, 59.2, 51.9, 51.8, 46.4, 41.5, 40.9, 39.9, 30.9, 27.8 (another diastereomer). IR (KBr): 3451, 3024, 2949, 2847, 1737, 1437, 1375, 1314, 1197, 1174, 1049, 1022, 915, 746, 703 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{32}NO_5$, 450.2275; found, 450.2273.

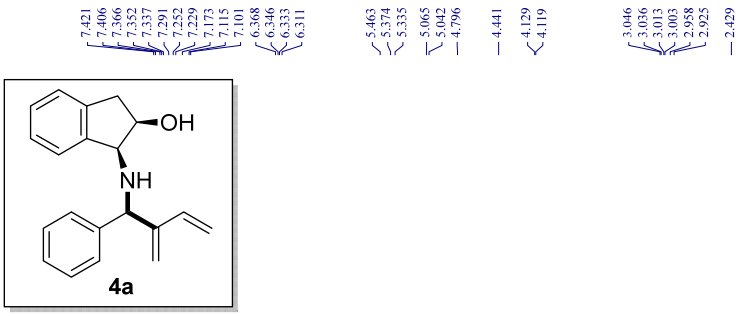
*Diethyl4-((S)-2-(((1S,2R)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)amino)-2-phenylethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**7**).* To an oven-dried 5 mL test tube with a stir bar was added diethyl acetylenedicarboxylate (0.26 mmol, 44.5 mg)、compound **5a** (0.20 mmol, 61.0 mg) and anisole (2.0 mL). The reaction mixture was stirred at 180 ºC for 1 h. And then the anisole was distilled off at reduced pressure. Finally the reaction mixture was subjected to the preparative thin-layer chromatography (PE/EA = 5:1). Yellow oil, 74.1 mg, 78% yield, dr = 99:1. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.45–7.37 (m, 4H), 7.32–7.29 (m, 1H), 7.22–7.16 (m, 3H), 7.13–7.10 (m, 1H), 5.50 (s, 1H), 4.47–4.43 (m, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.01–3.96 (m, 2H), 3.06–2.88 (m, 6H), 2.58–2.52 (m, 2H), 2.43 (dd, *J* = 6.0, 14.0 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 168.0, 167.9, 143.6, 142.5, 140.7, 132.3, 132.3, 130.5, 128.7, 127.9, 127.5, 126.9, 126.7, 125.4, 123.8, 120.1, 70.8, 63.6, 61.2, 61.1, 59.4, 45.9, 40.0, 30.8, 28.5, 14.0, 14.0. IR (KBr): 3510, 2927, 1720, 1653, 1456, 1392, 1367, 1260, 1174, 1067, 1044, 749, 702 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{34}NO_5$, 476.2432; found, 476.2431.

*Diethyl4-((S)-2-(((1S,2R)-2-methoxy-2,3-dihydro-1H-inden-1-yl)amino)-2-phenylethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (**8**).* To an oven-dried 5 mL test tube with a stir bar was added silver oxide (0.52 mmol, 121.1 mg)、CH_3I (0.70 mmol, 99.4

mg)、and compound **7** (0.14 mmol, 68.0 mg) in DCM (2.0 mL). The reaction mixture was stirred at room temperature for 48 h. The solution was filtered which was then washed with DCM. After evaporation of the solvent, the reaction mixture was subjected to the preparative thin-layer chromatography (PE/EA = 10:1). Yellow oil, 74.1 mg, 85% yield (Recovery yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.0 Hz, 1H), 7.34 (dd, J = 7.5, 7.0 Hz, 2H), 7.24–7.13 (m, 4H), 5.58 (s, 1H), 4.24 (q, J = 7.0 Hz, 2H), 4.19 (q, J = 7.0 Hz, 2H), 4.08 (t, J = 4.5 Hz, 1H), 3.99 (dd, J = 3.5, 10.5 Hz, 1H), 3.92 (d, J = 4.5 Hz, 1H), 3.35 (s, 3H), 3.25–3.15 (m, 1H), 3.07–2.97 (m, 3H), 2.94–2.85 (m, 1H), 2.69–2.63 (m, 1H), 2.42–2.36 (m, 1H), 2.34–2.28 (m, 1H), 1.97 (brs, 1H), 1.30 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.1, 167.9, 144.7, 144.2, 139.5, 132.5, 132.2, 130.5, 128.5, 127.3, 127.3, 127.1, 126.6, 124.8, 124.4, 120.0, 63.3, 61.1, 61.0, 57.3, 56.5, 47.7, 34.7, 30.0, 28.6, 14.1, 14.0. IR (KBr): 2899, 1717, 1652, 1540, 1457, 1366, 1260, 1157, 1093, 1066, 859, 750, 721, 702, 620 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{36}NO_5$, 490.2588; found, 490.2590.

*Diethyl4-((S)-2-(((1S,2R)-2-methoxy-2,3-dihydro-1H-inden-1-yl)amino)-2-pheny lethyl)phthalate(**9**).* To an oven-dried 5 mL test tube with a stir bar was added compound **8** (0.11 mmol, 53.8 mg) and activated manganese dioxide (220.0 mg) in dioxane (2.0 mL) at ambient temperature for 48 h. After filtration and evaporation of the solvent, the residue was subjected to the preparative thin-layer chromatography to provide compound **8** (PE/EA = 10:1). Yellow oil, 43.9 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 10.0 Hz, 1H), 7.56–7.51 (m, 3H), 7.43 (d, J = 9.0 Hz, 1H), 7.37–7.28 (m, 3H), 7.28–7.22 (m, 1H), 7.20–7.14 (m, 1H), 7.13–7.08 (m, 2H), 4.34 (q, J = 11.0 Hz, 2H), 4.32 (q, J = 11.0 Hz, 2H), 4.08 (dd, J = 6.0, 11.0 Hz, 1H), 3.96 (t, J = 5.5 Hz, 1H), 3.88 (d, J = 5.5 Hz, 1H), 3.14 (s, 3H), 3.05 (dd, J = 6.0, 16.5 Hz, 1H), 2.98–2.90 (m, 2H), 2.63 (dd, J = 5.5, 20.5 Hz, 1H), 1.35 (t, J = 9.0 Hz, 3H), 1.33 (t, J = 9.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.0, 167.4, 143.9, 143.6, 142.8, 139.5, 132.8, 131.7, 129.9, 129.4, 129.1, 128.5, 127.5, 127.4, 127.3, 126.5, 124.8, 124.4, 80.4, 63.4, 62.3, 61.6, 61.5, 56.7, 45.9, 34.9, 14.1, 14.1. IR (KBr): 2923, 2852, 1731, 1652, 1558, 1472, 1366, 1286, 1197, 1130, 1095, 1070, 1023, 751, 703 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{34}NO_5$, 488.2443; found, 488.2441.

^{1}H, ^{13}C and ^{19}F NMR spectra copies



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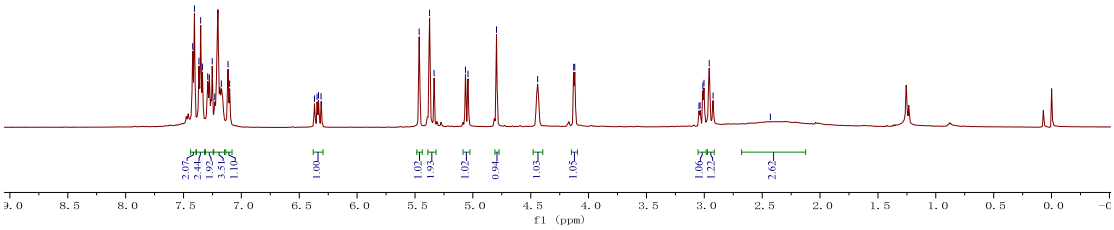

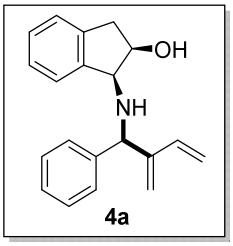

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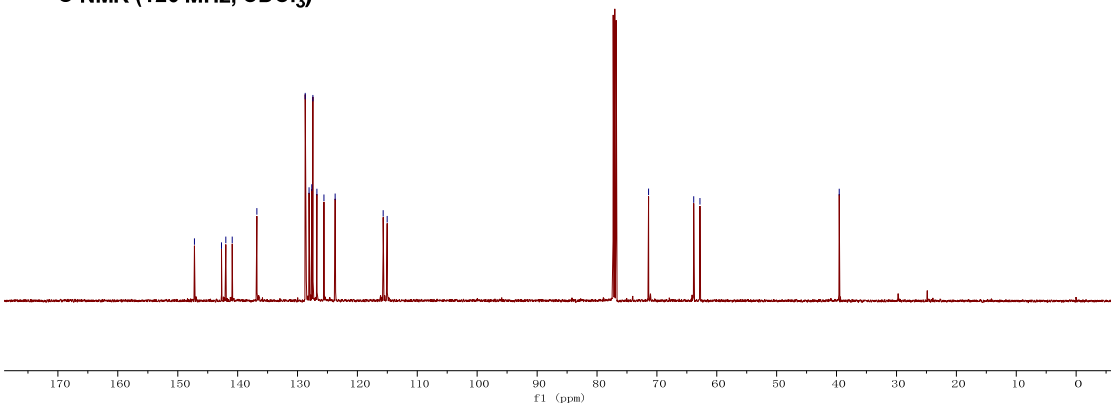

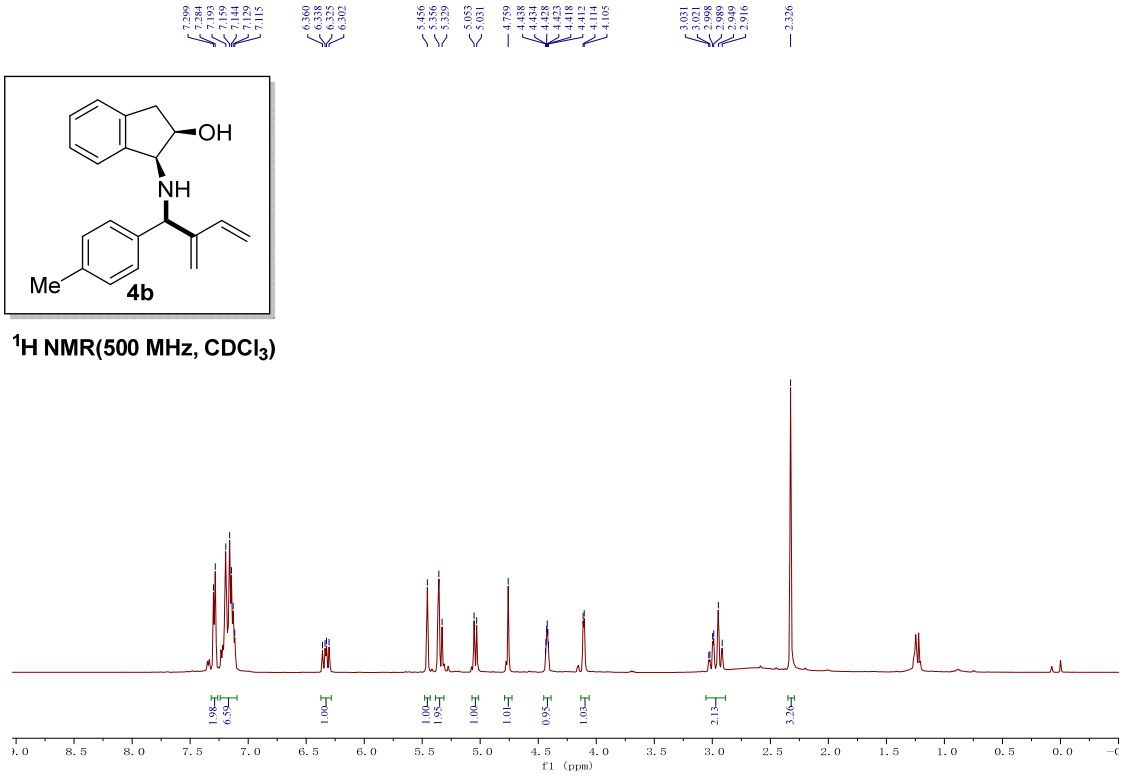

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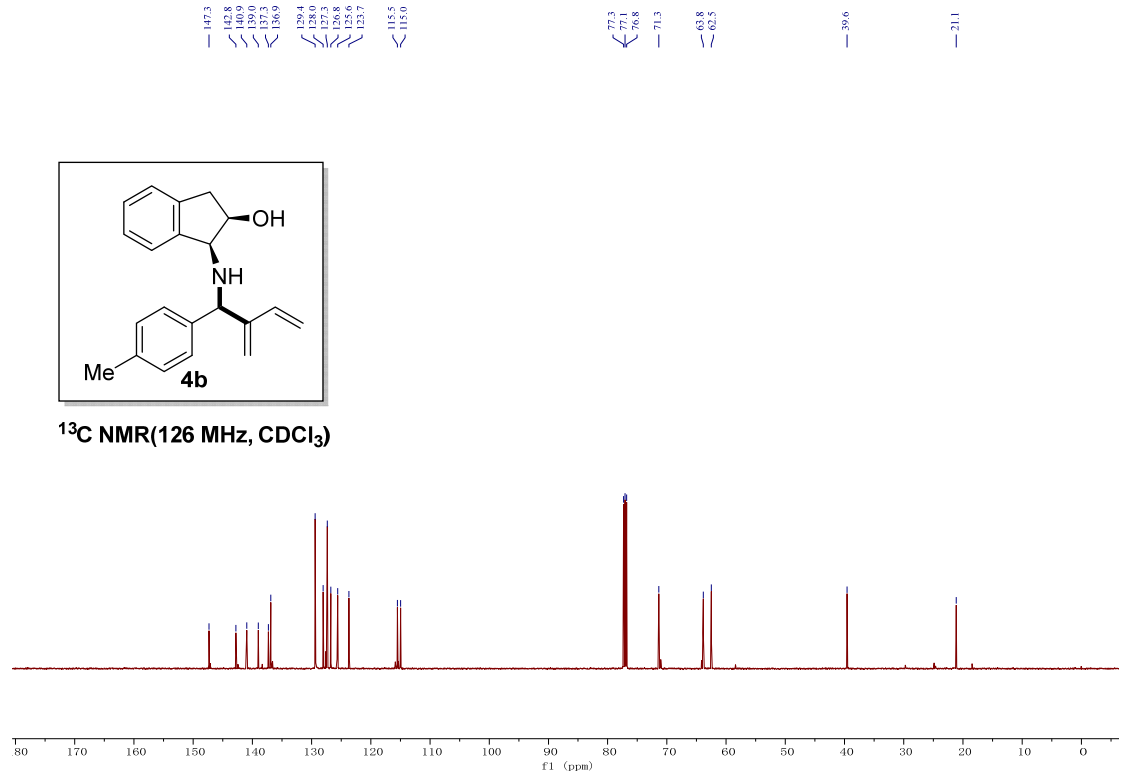

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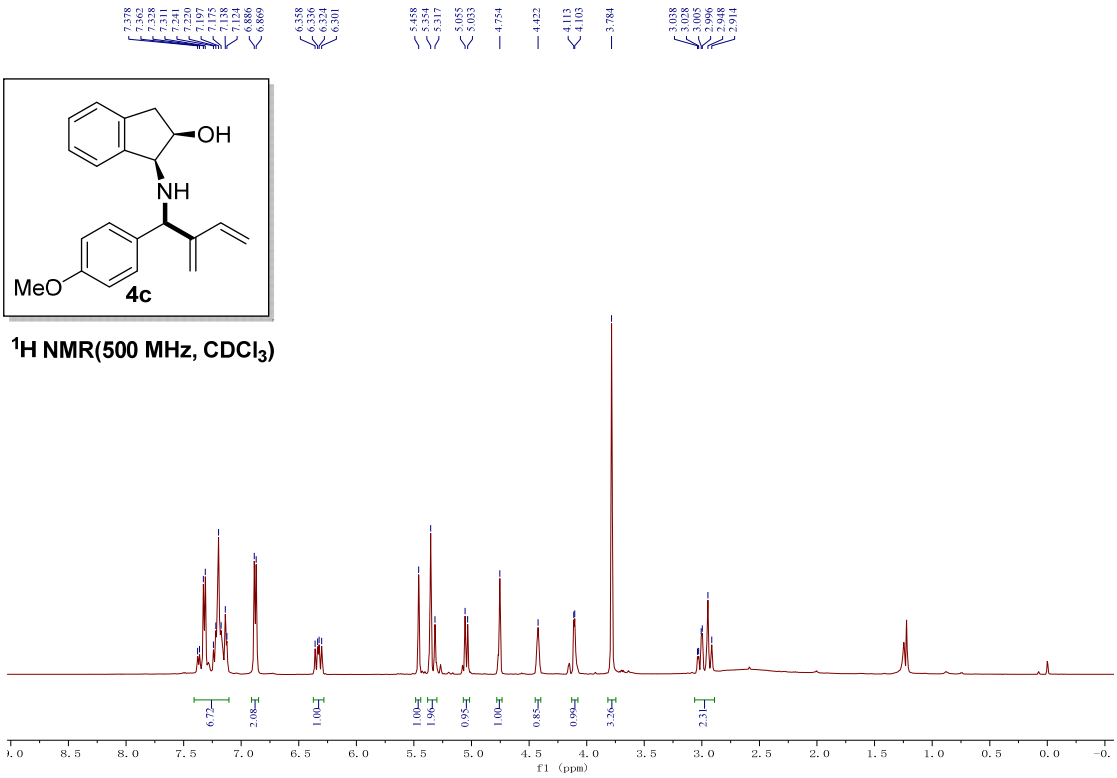

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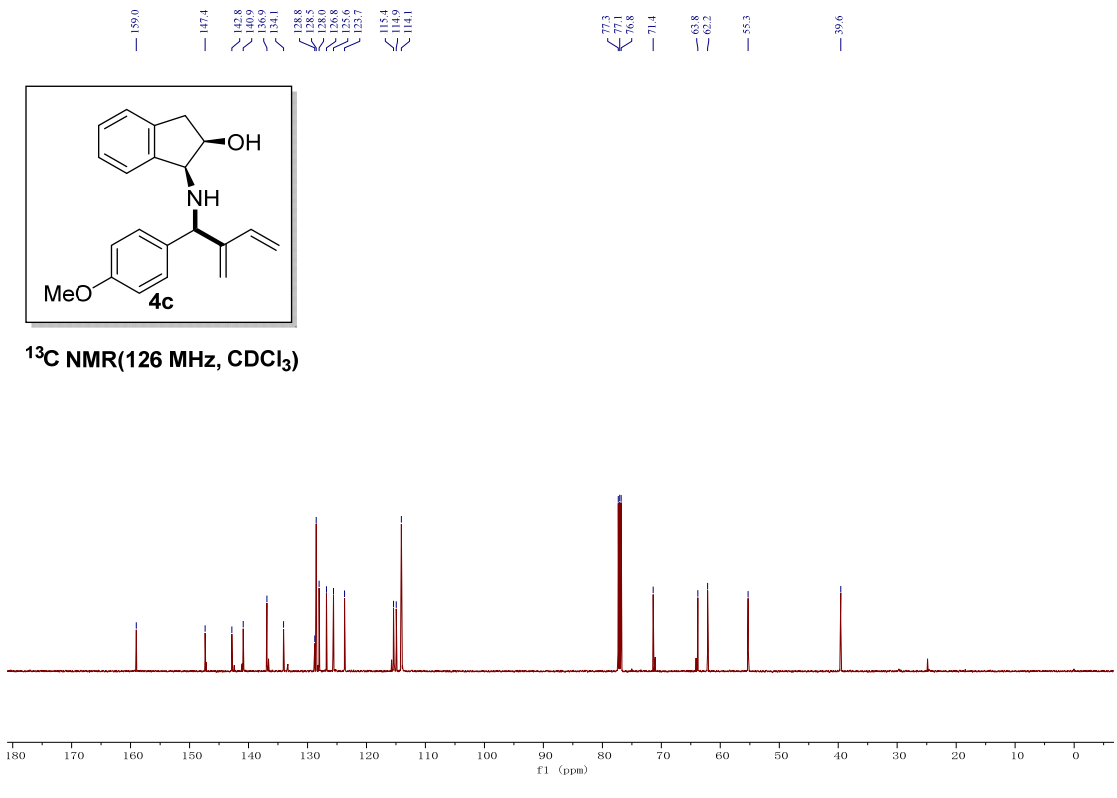

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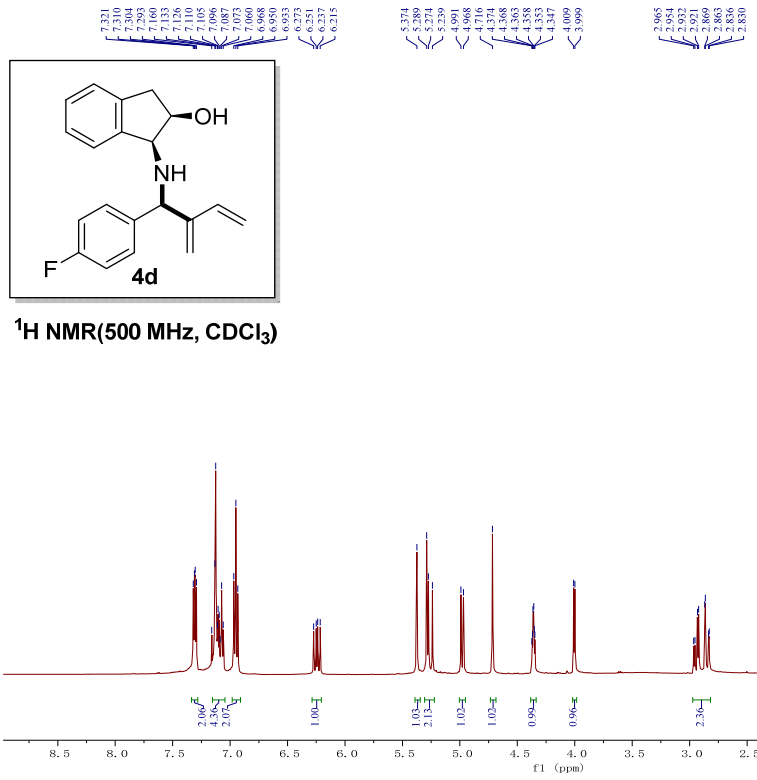

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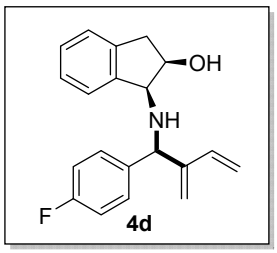
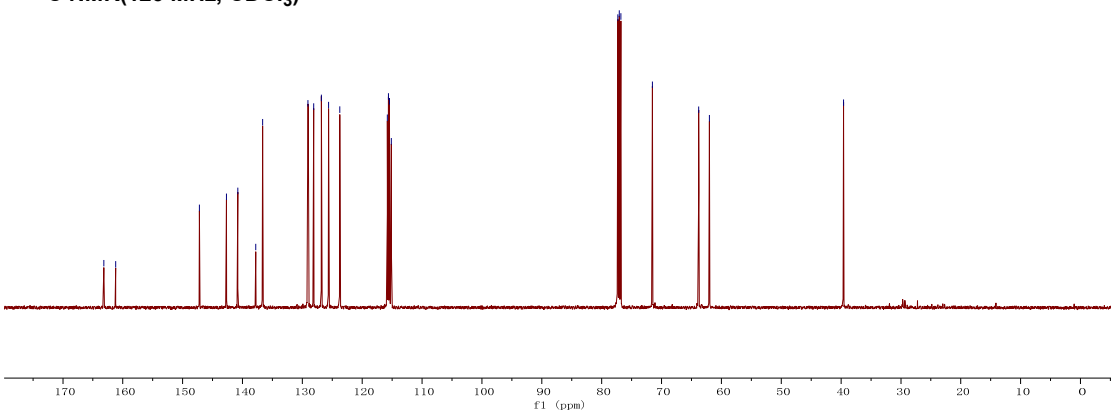
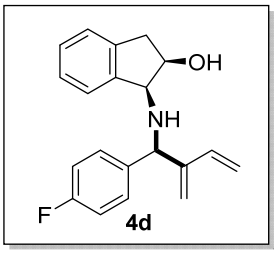
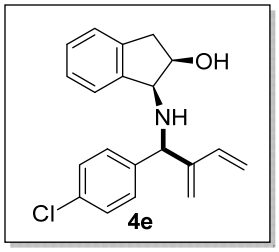


^{13}C NMR(126 MHz, $CDCl_3$)

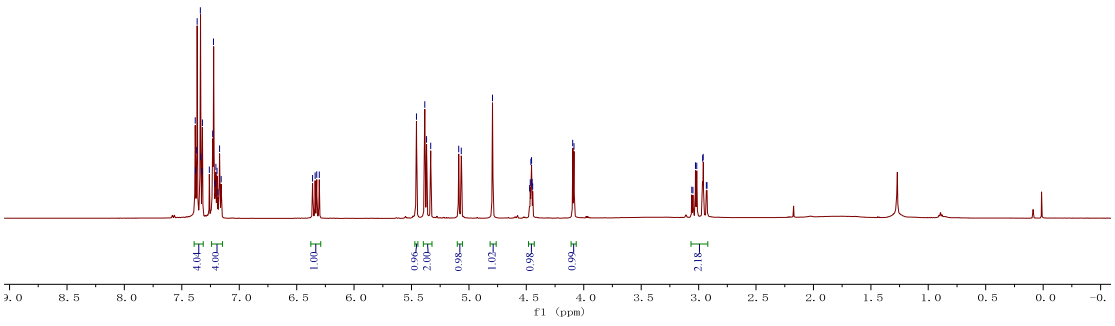


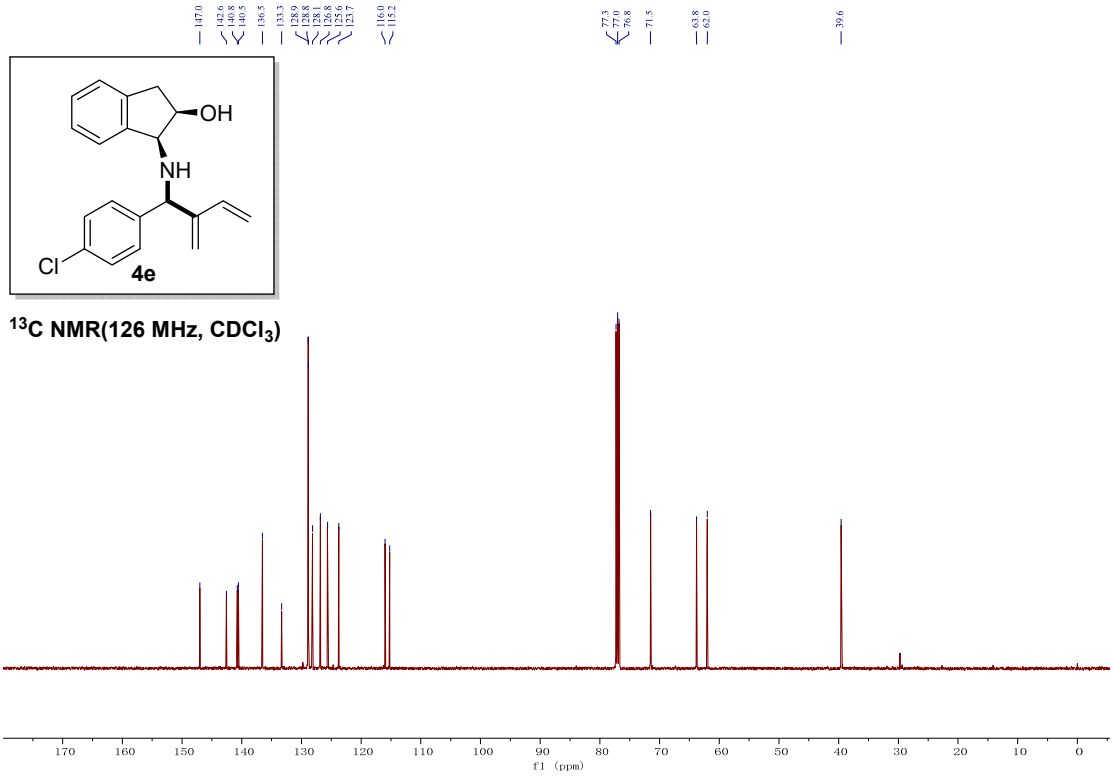


^{19}F NMR(471 MHz, $CDCl_3$)

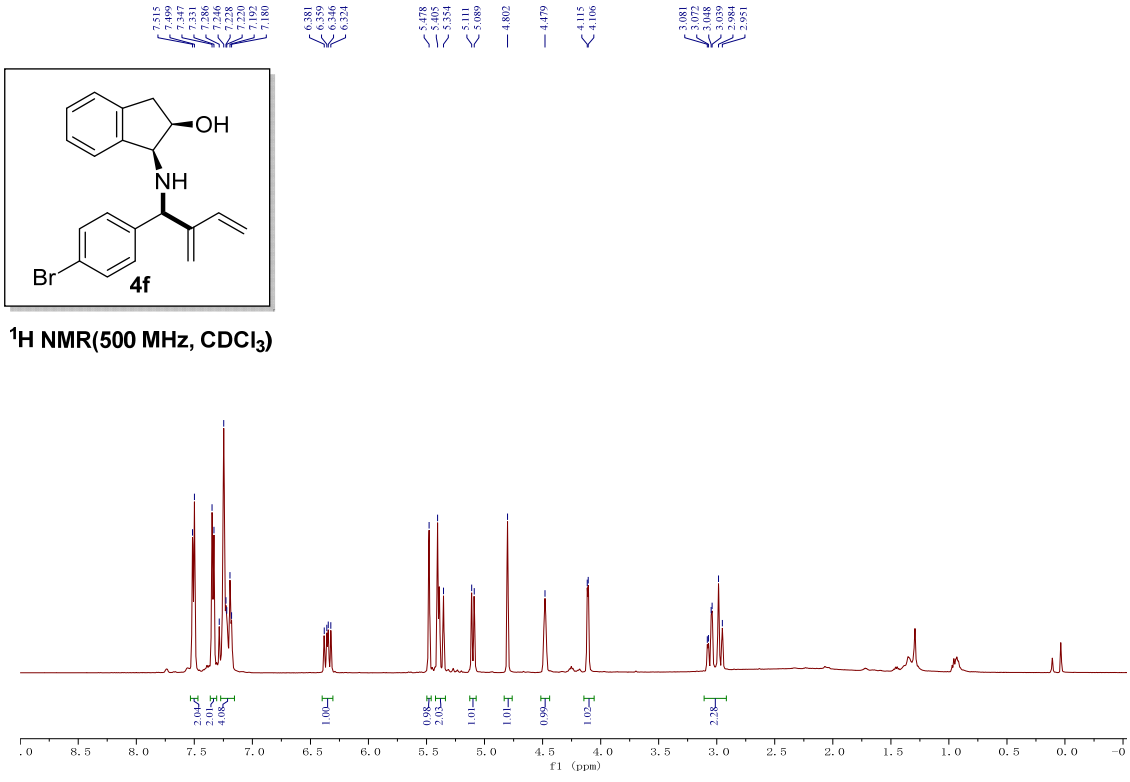


^{1}H NMR(500 MHz, $CDCl_3$)

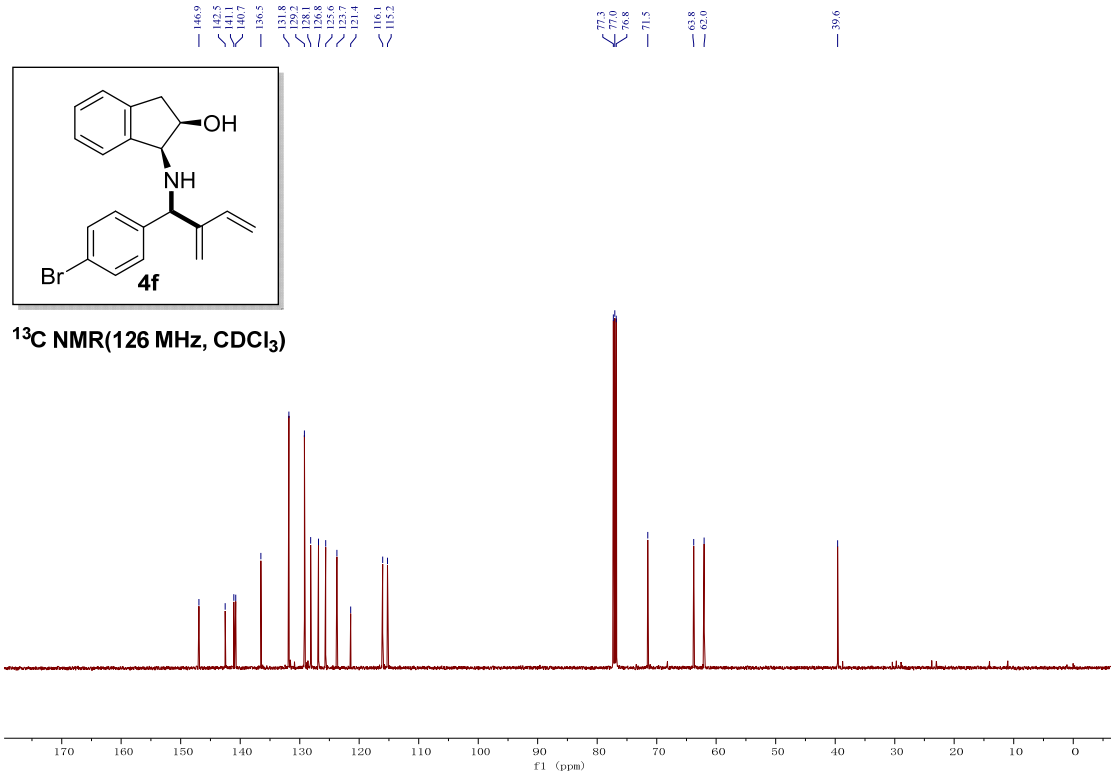




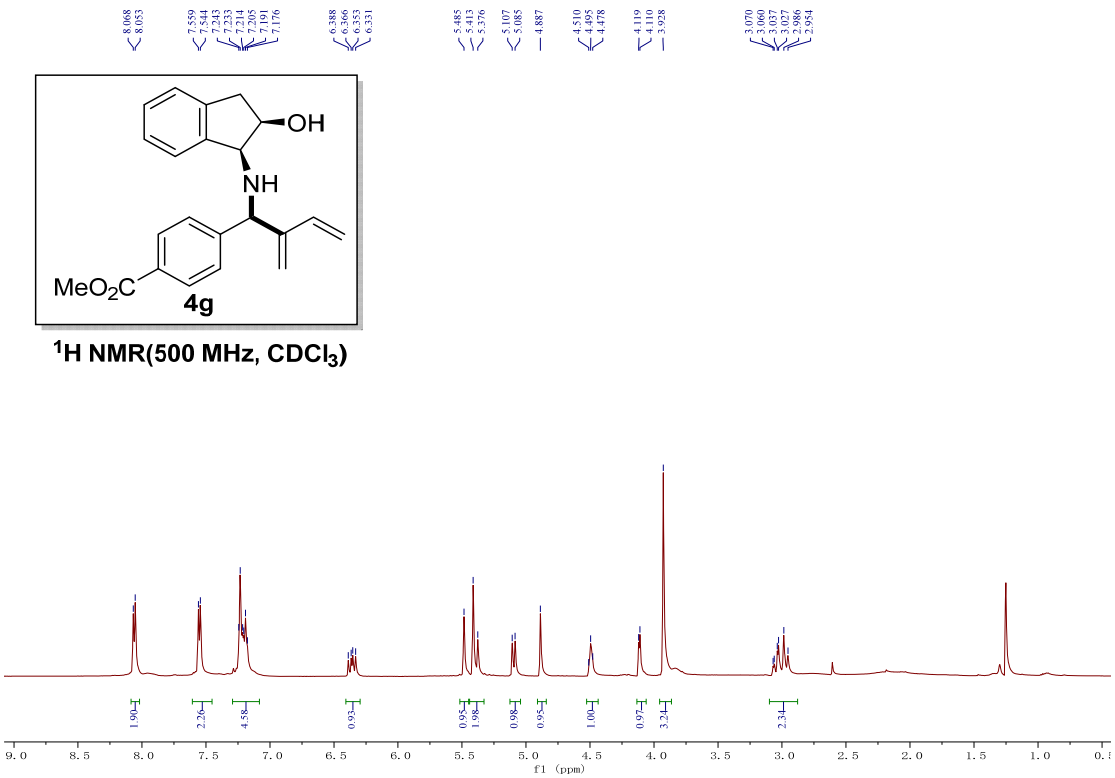
^{13}C NMR(126 MHz, $CDCl_3$)



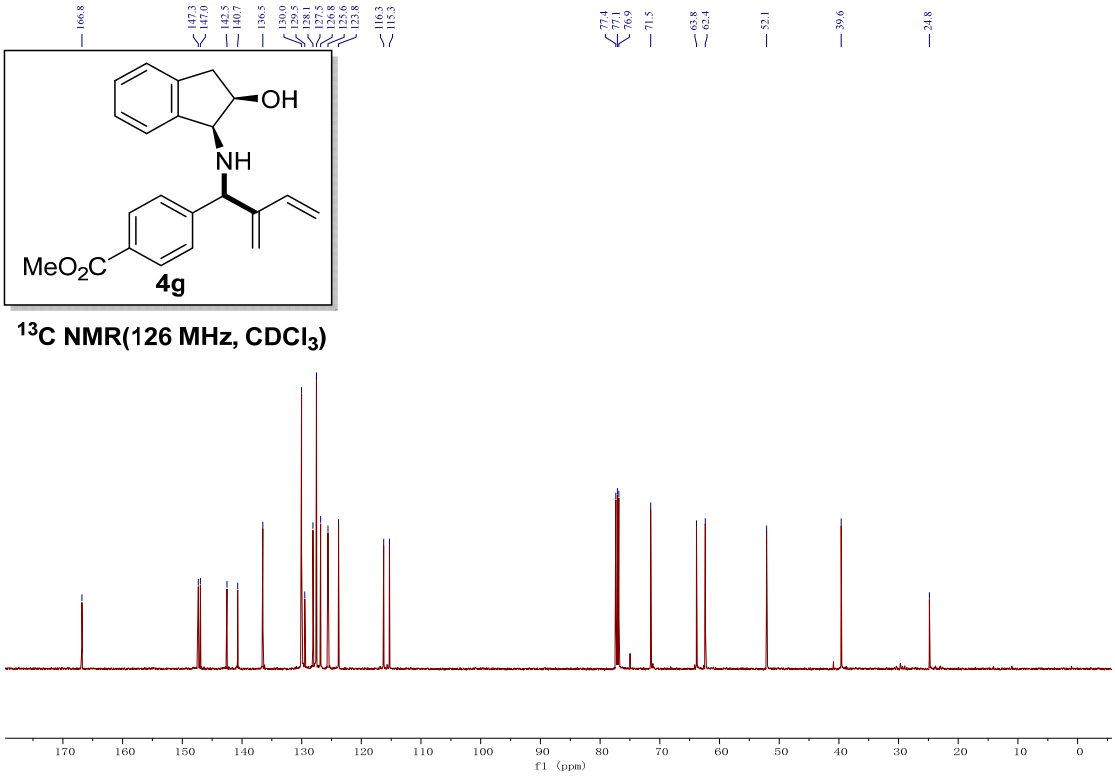
^{1}H NMR(500 MHz, $CDCl_3$)



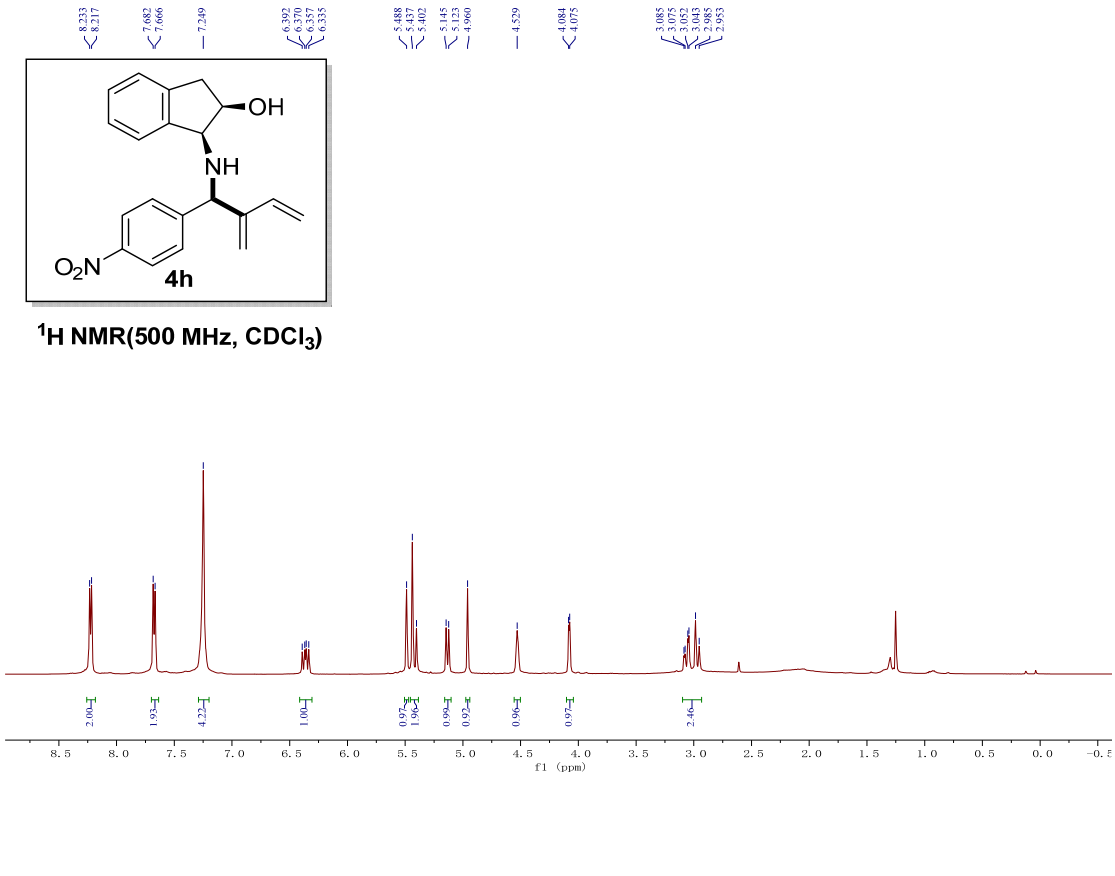
^{13}C NMR(126 MHz, $CDCl_3$)



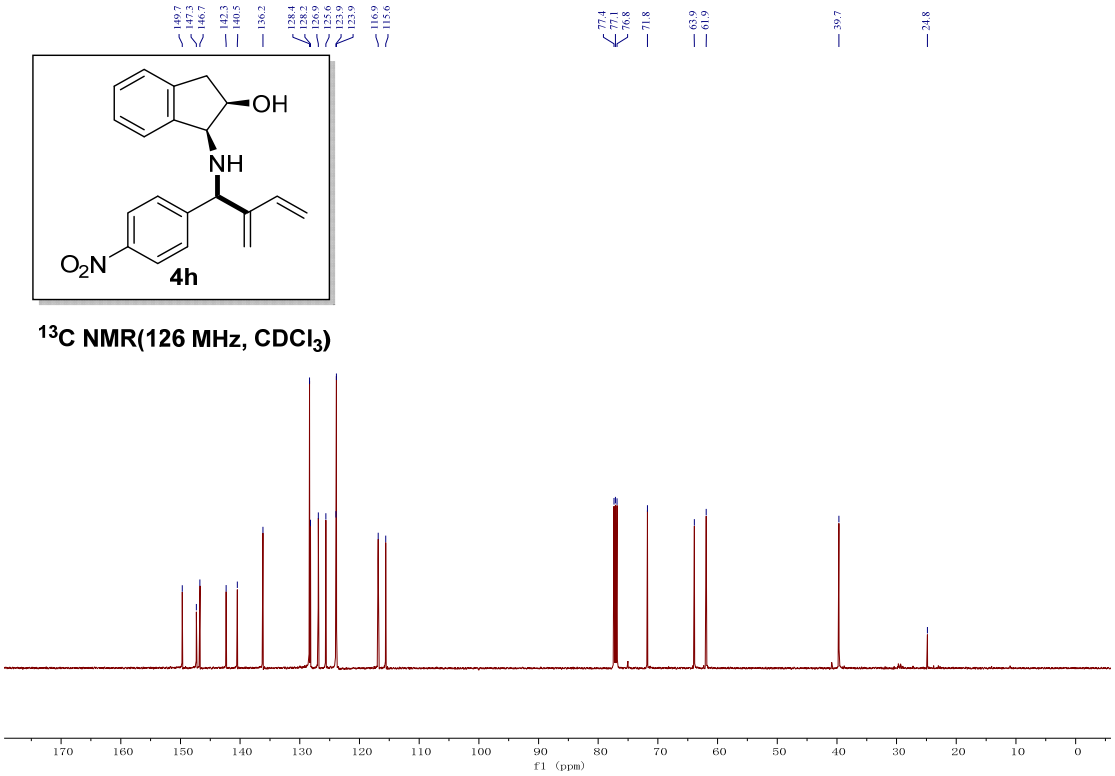
^{1}H NMR(500 MHz, $CDCl_3$)



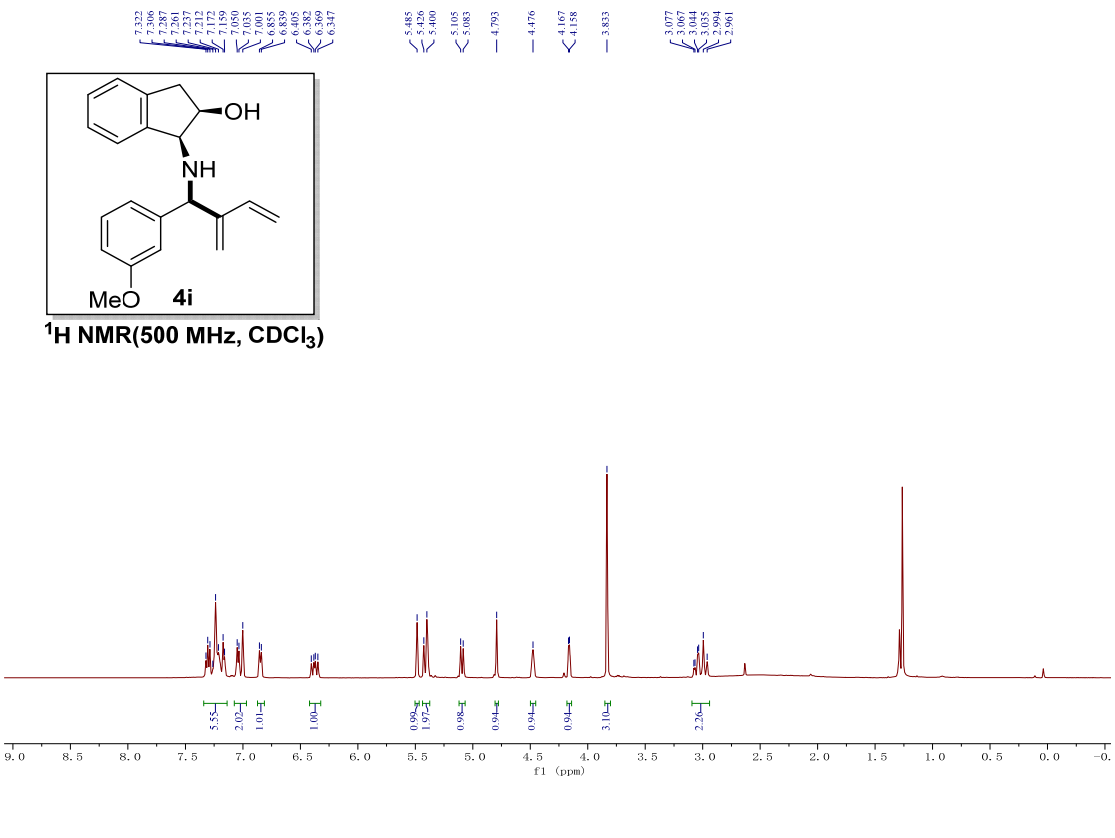
^{13}C NMR(126 MHz, $CDCl_3$)



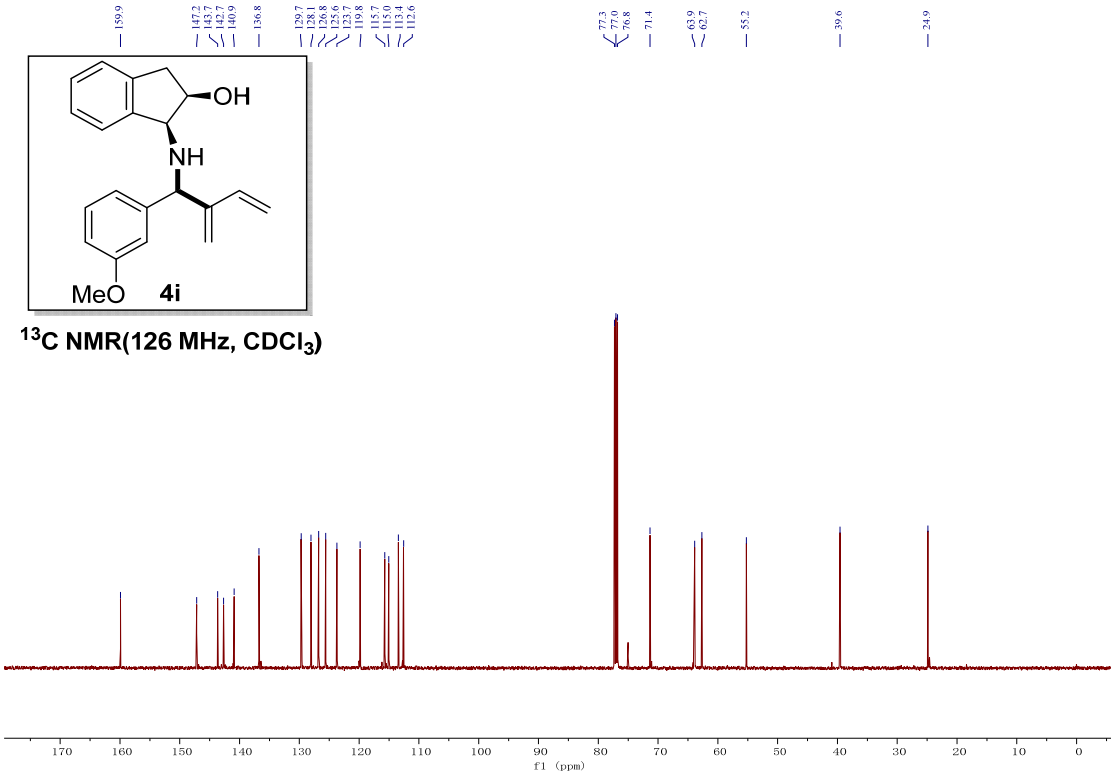
^{1}H NMR(500 MHz, $CDCl_3$)



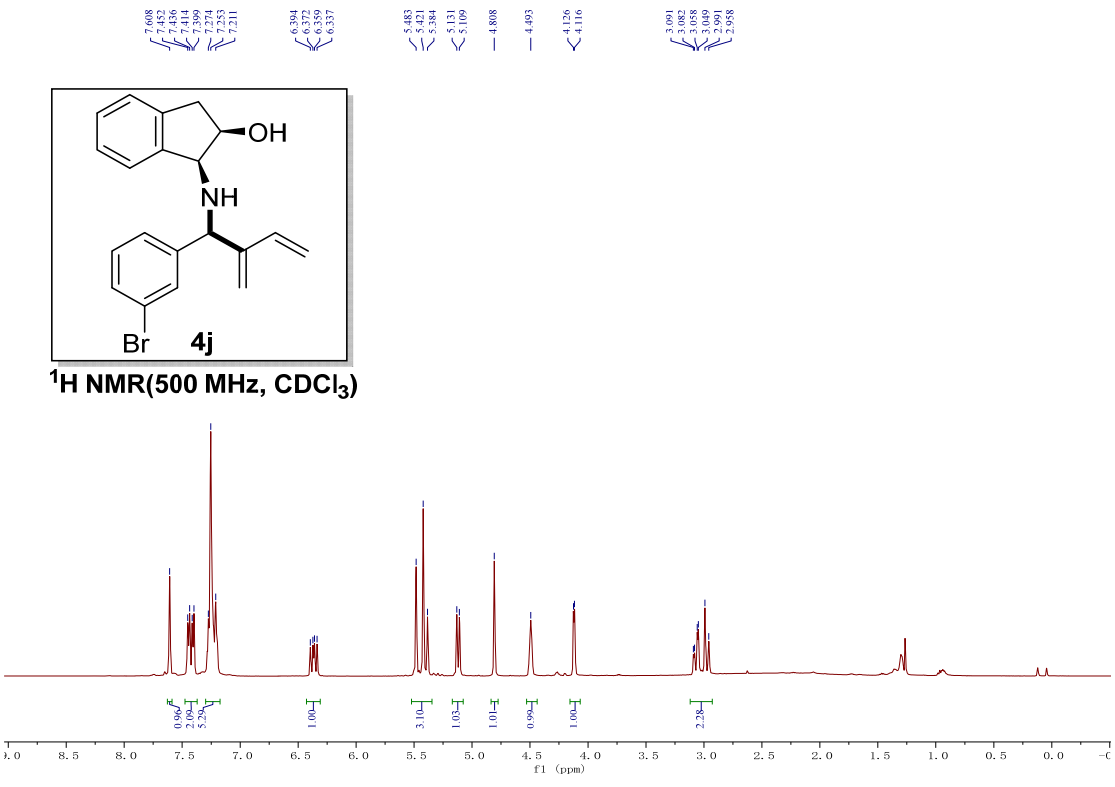
^{13}C NMR(126 MHz, $CDCl_3$)



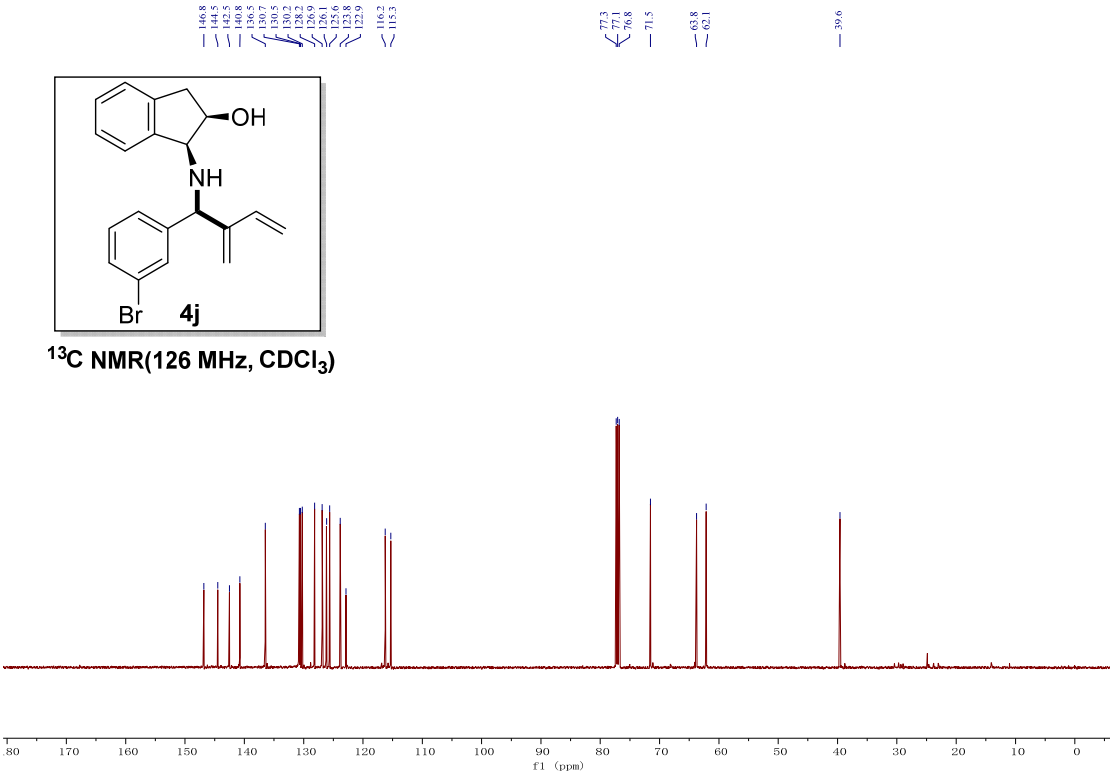
^{1}H NMR(500 MHz, $CDCl_3$)



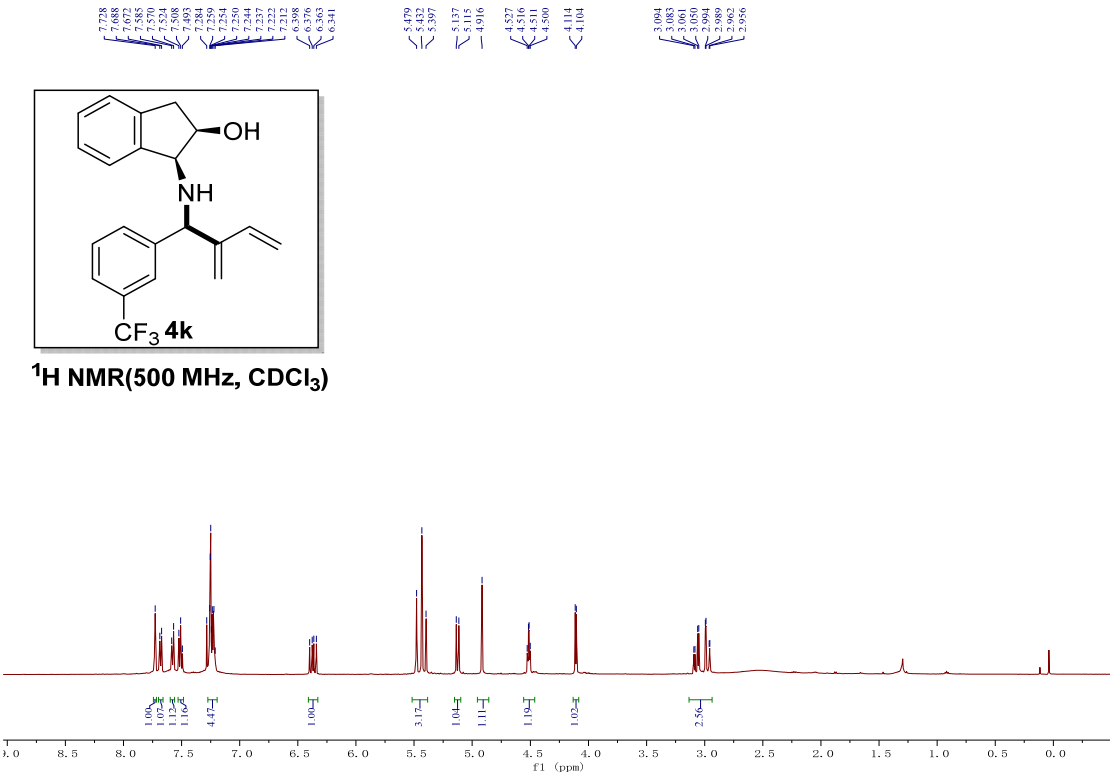
^{13}C NMR(126 MHz, $CDCl_3$)



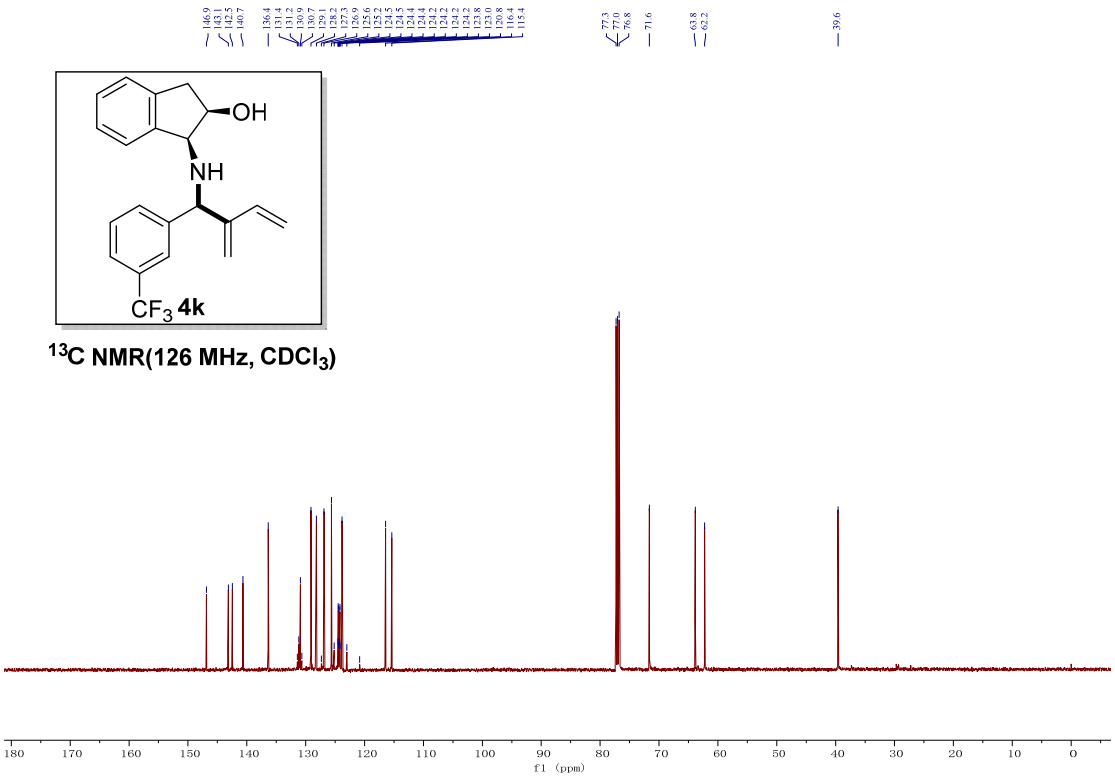
^{1}H NMR(500 MHz, $CDCl_3$)



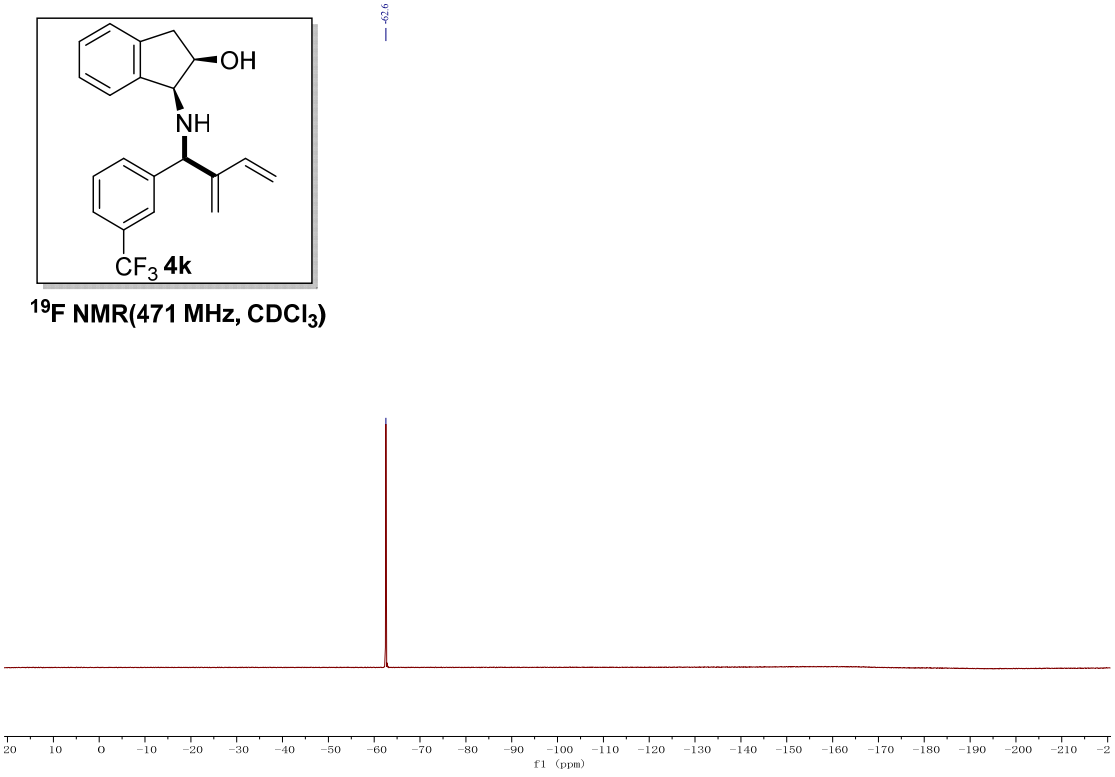
^{13}C NMR(126 MHz, $CDCl_3$)



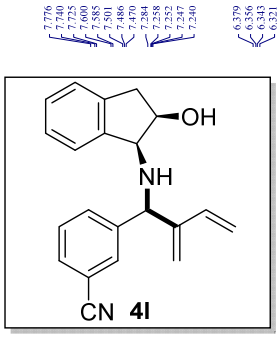
^{1}H NMR(500 MHz, $CDCl_3$)



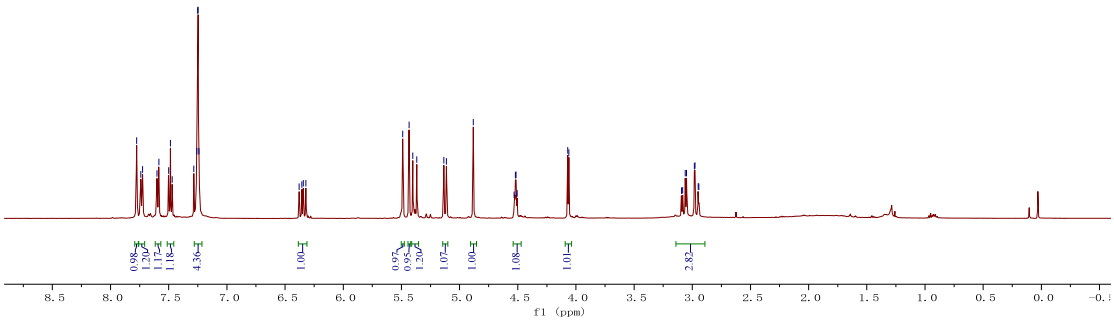
^{13}C NMR(126 MHz, $CDCl_3$)

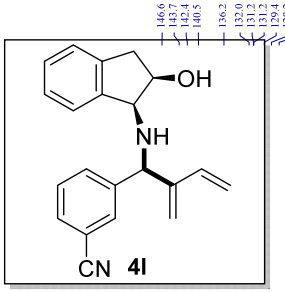


^{19}F NMR(471 MHz, $CDCl_3$)

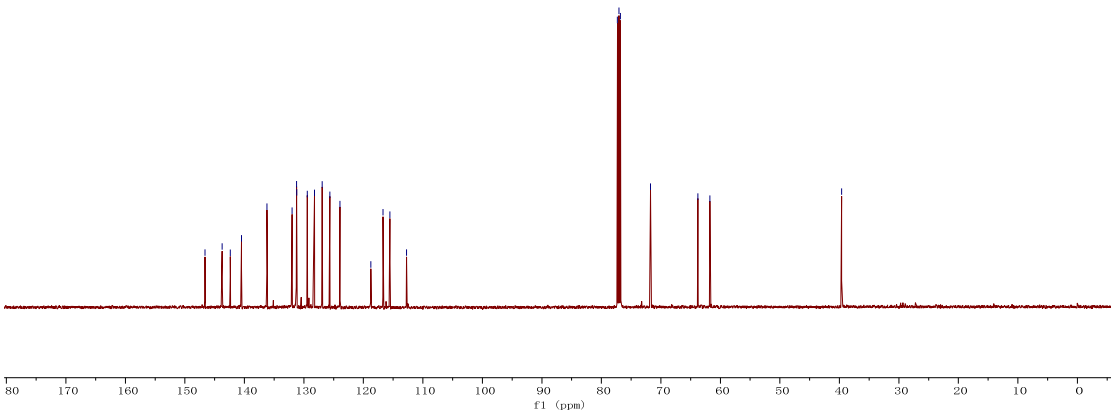


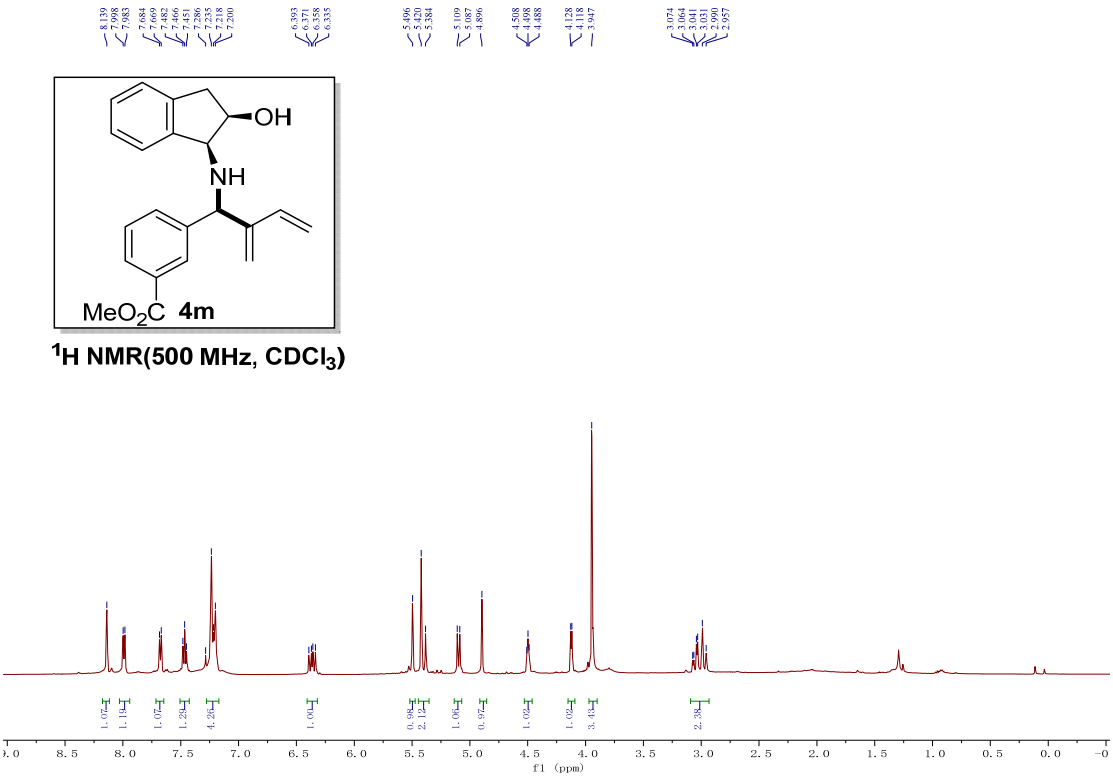
^{1}H NMR(500 MHz, $CDCl_3$)





^{13}C NMR(126 MHz, $CDCl_3$)





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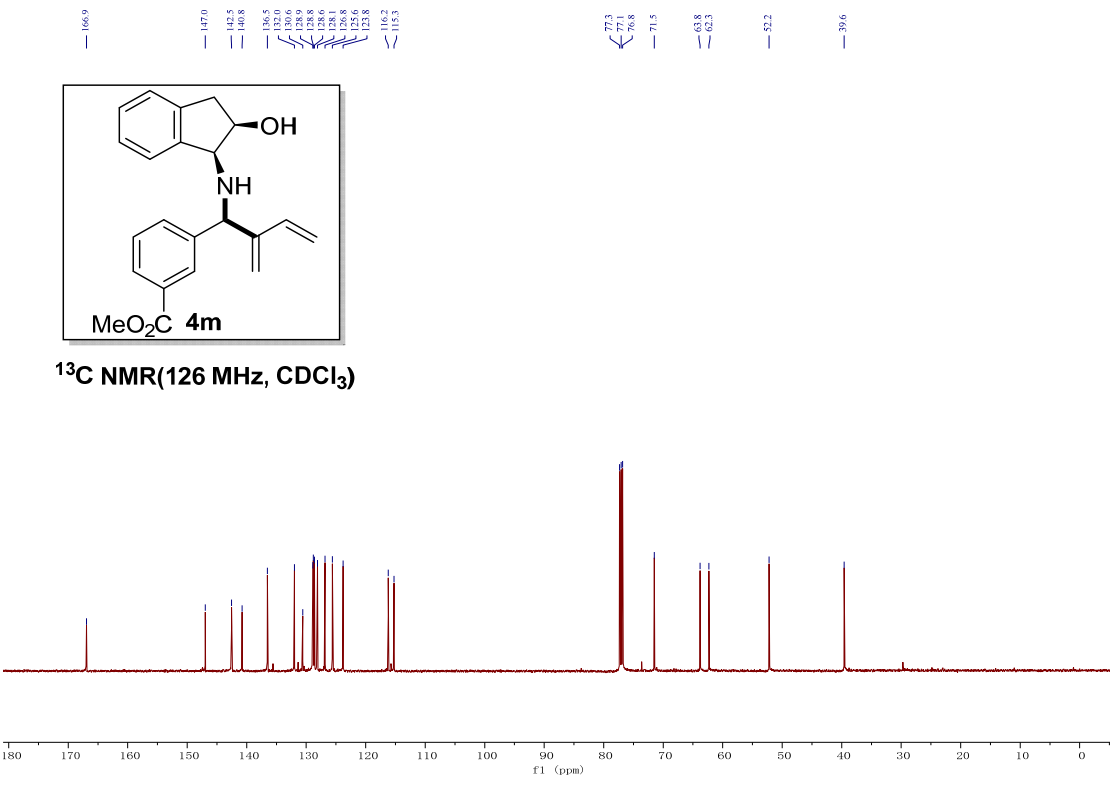
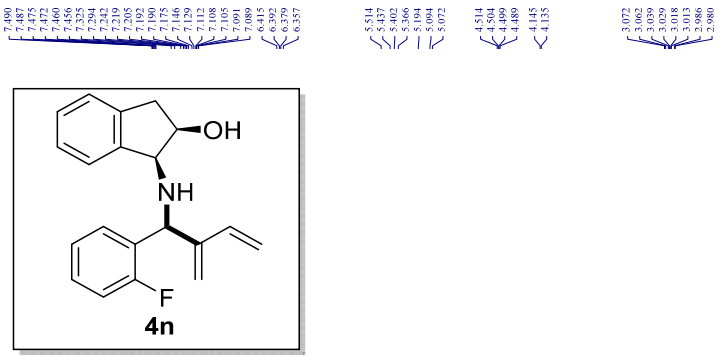


^{13}C NMR(126 MHz, $CDCl_3$)



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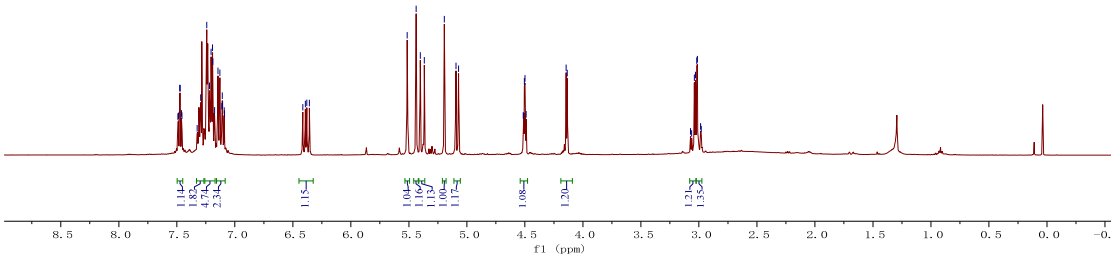
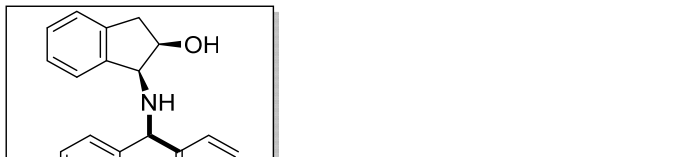
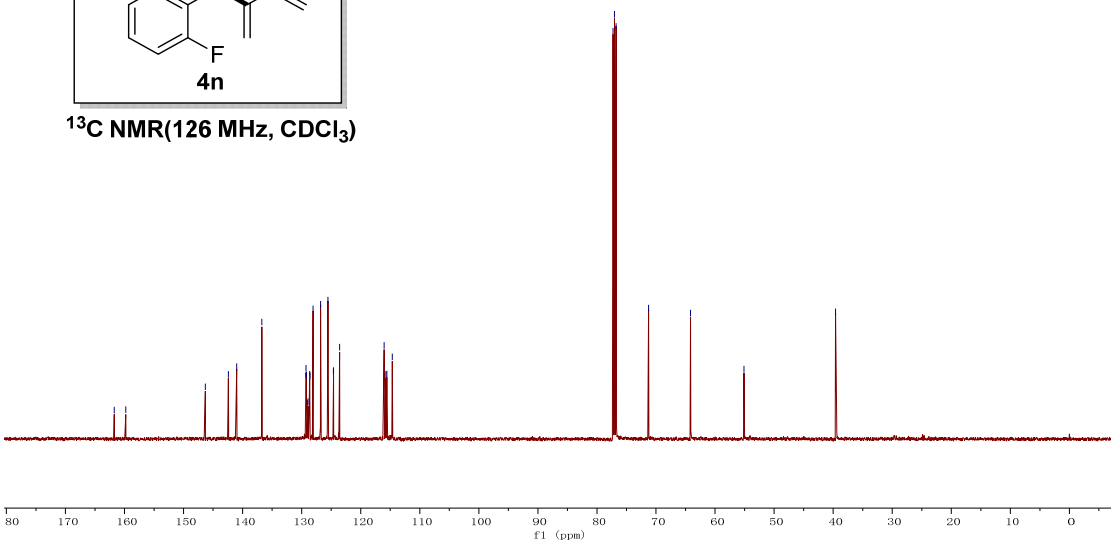
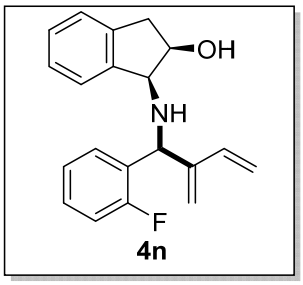


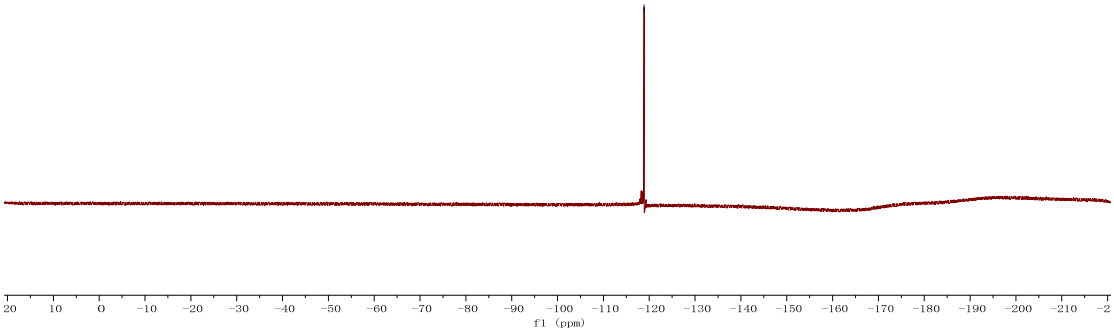


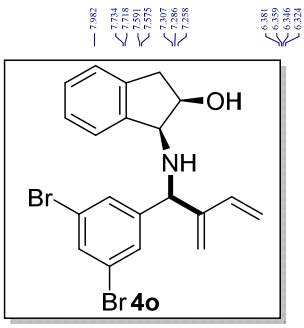
^{13}C NMR(126 MHz, $CDCl_3$)





^{19}F NMR(471 MHz, $CDCl_3$)





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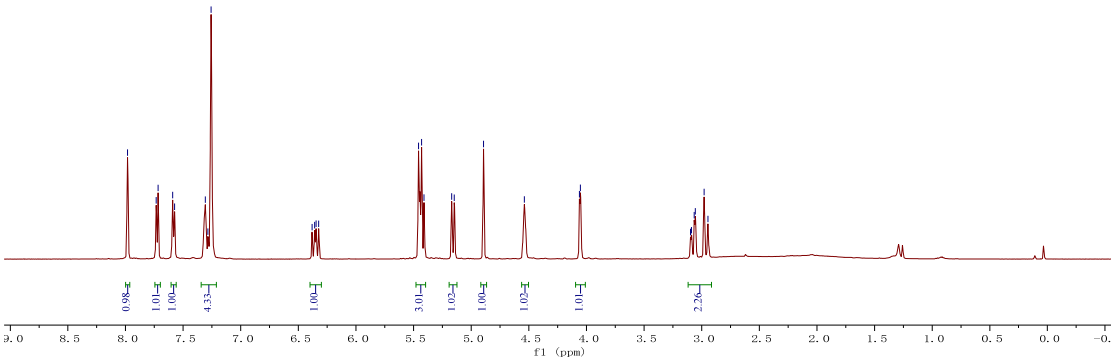

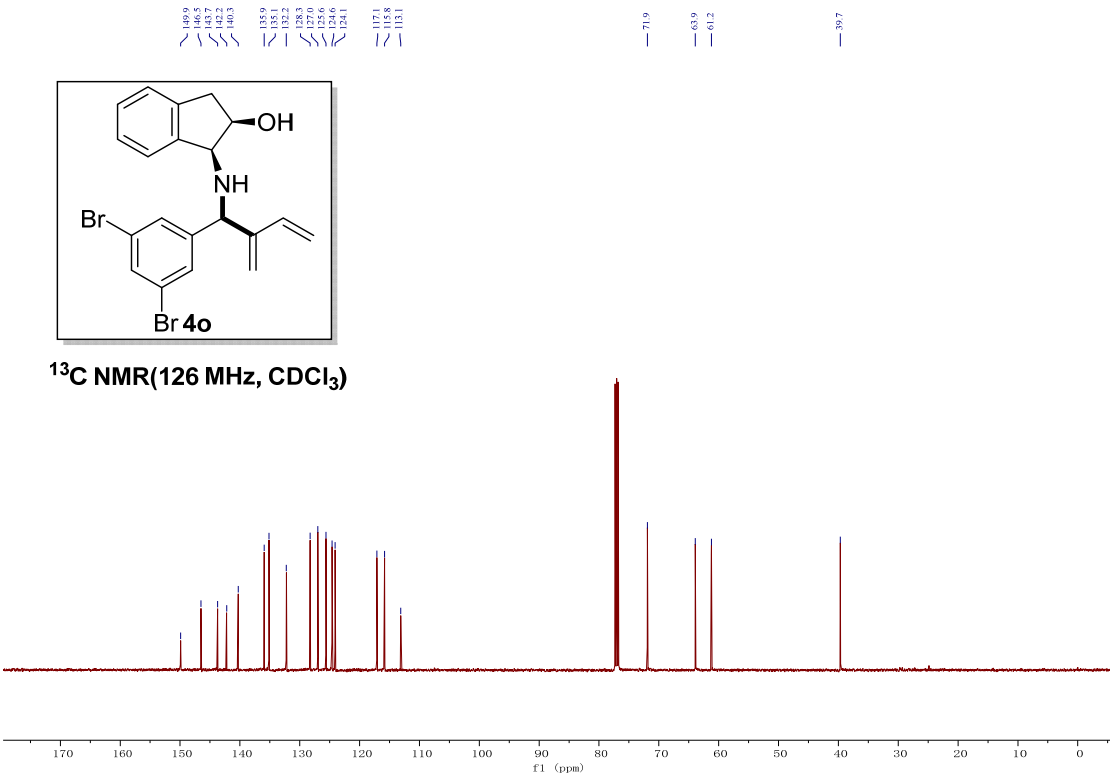

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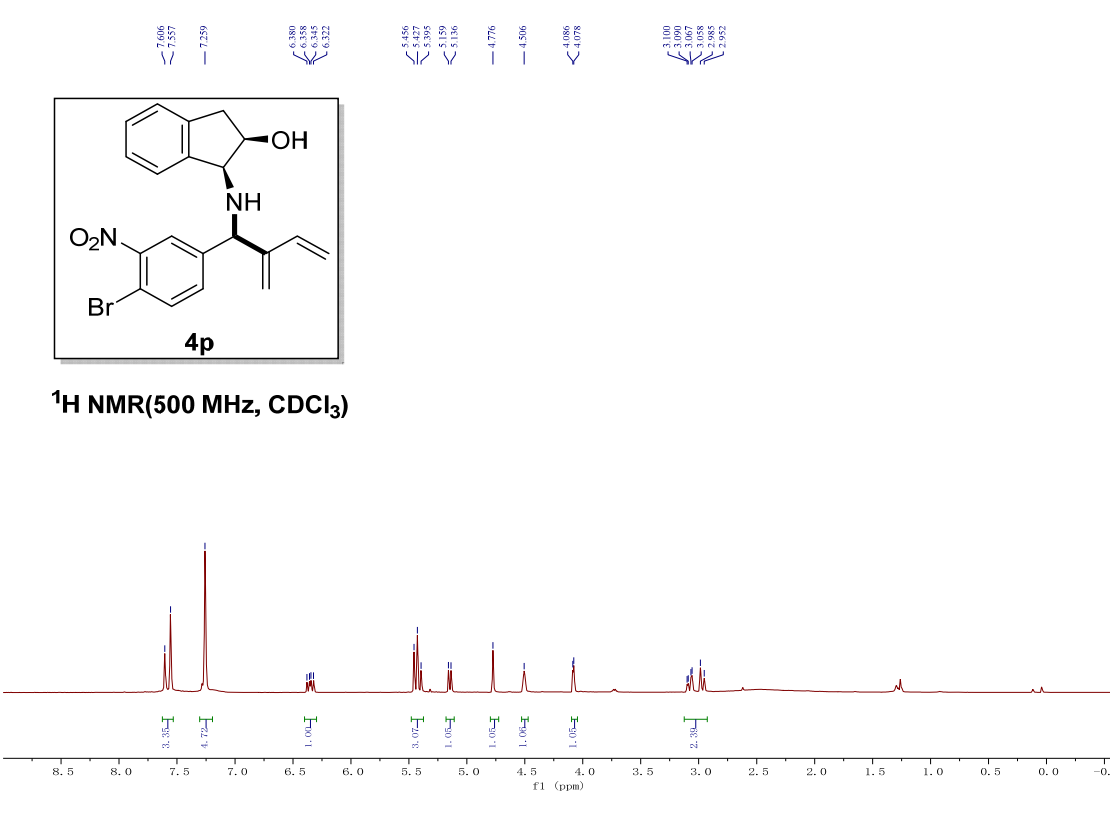
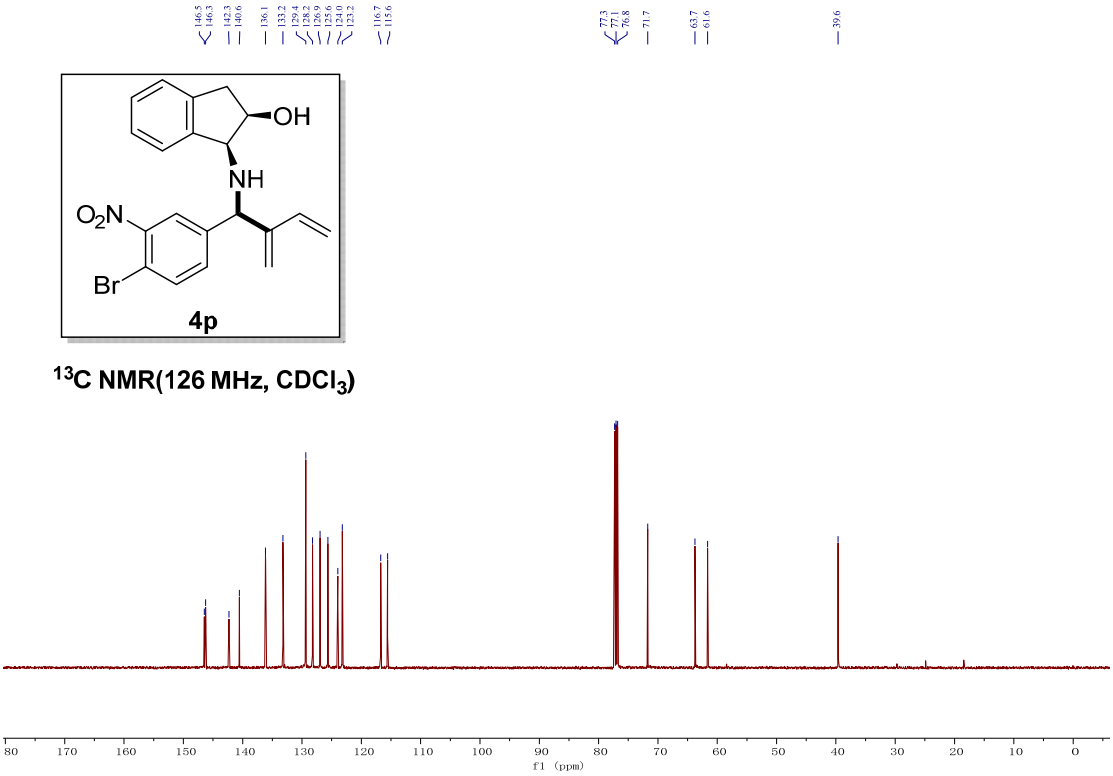


^{1}H NMR(500 MHz, $CDCl_3$)



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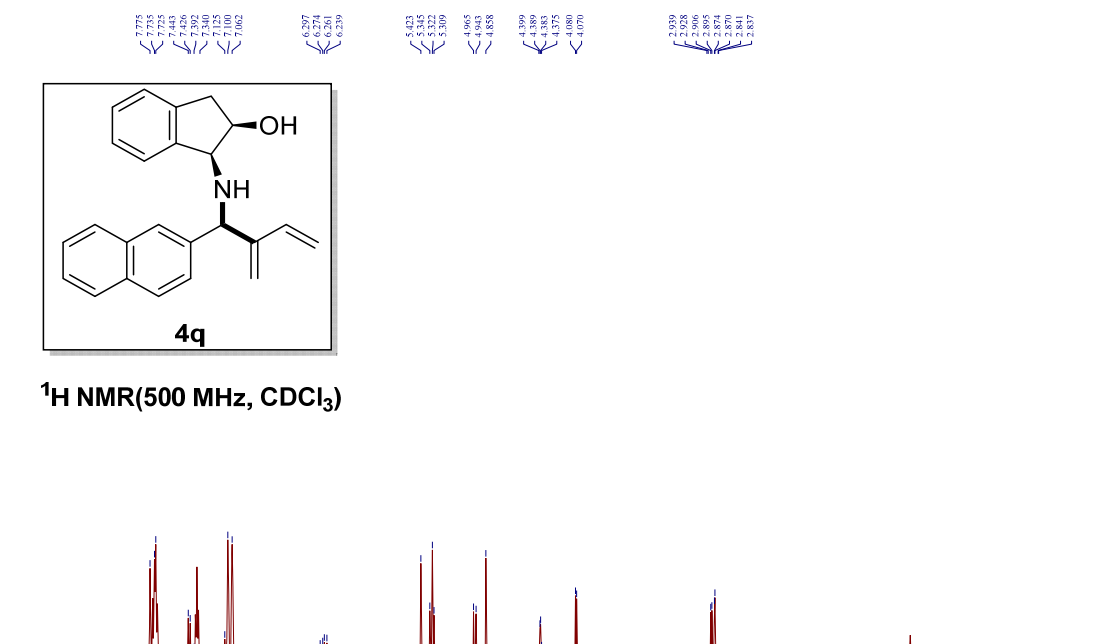

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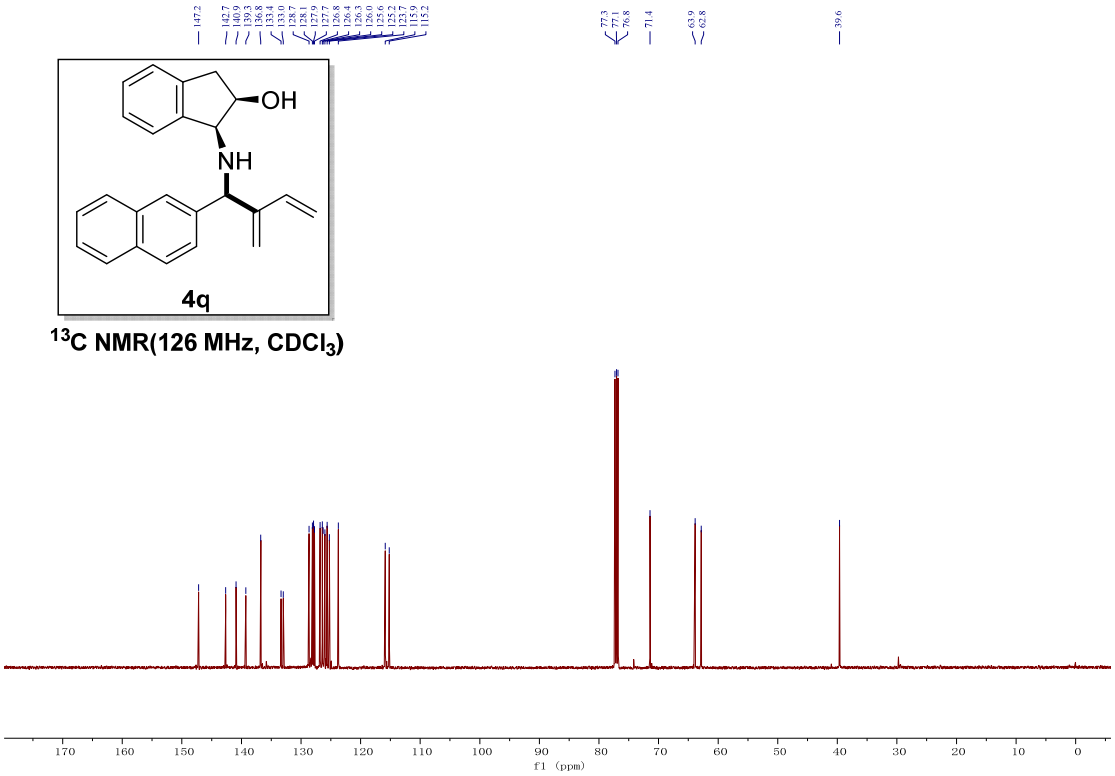

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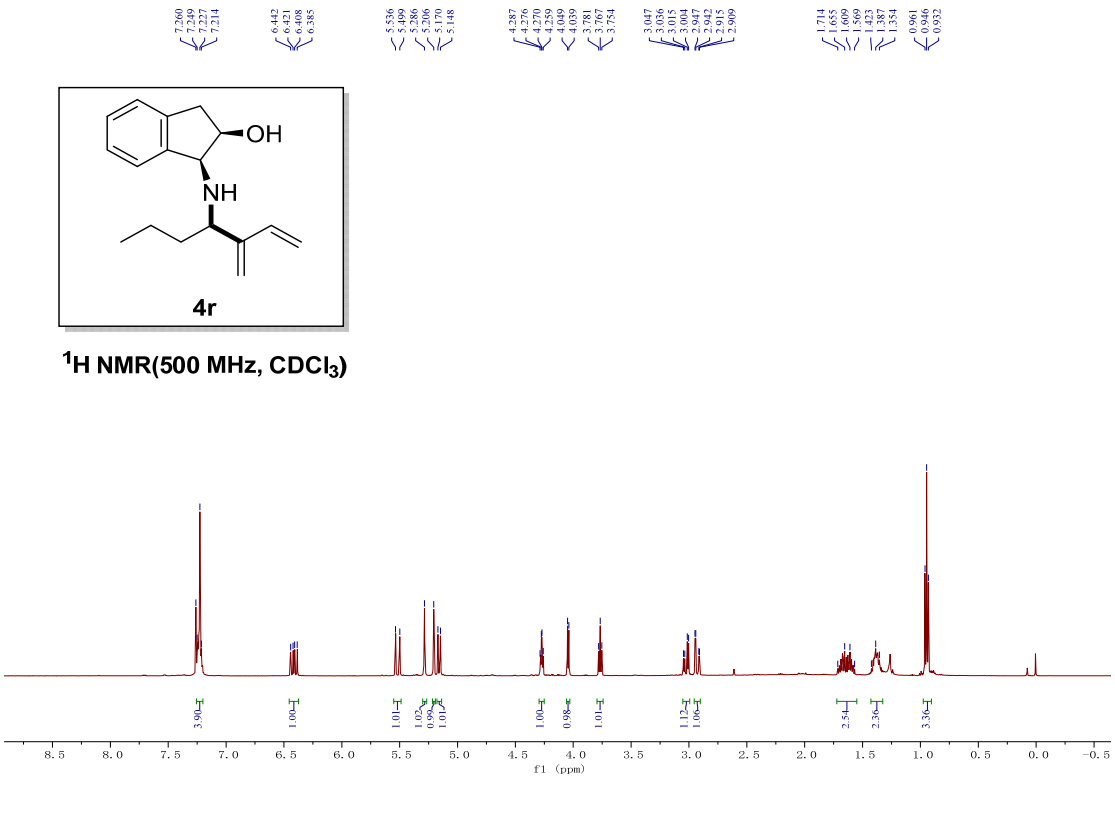
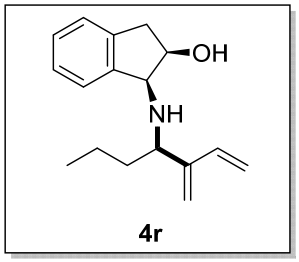
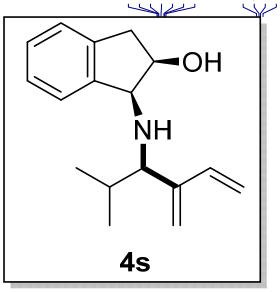


^{1}H NMR(500 MHz, $CDCl_3$)



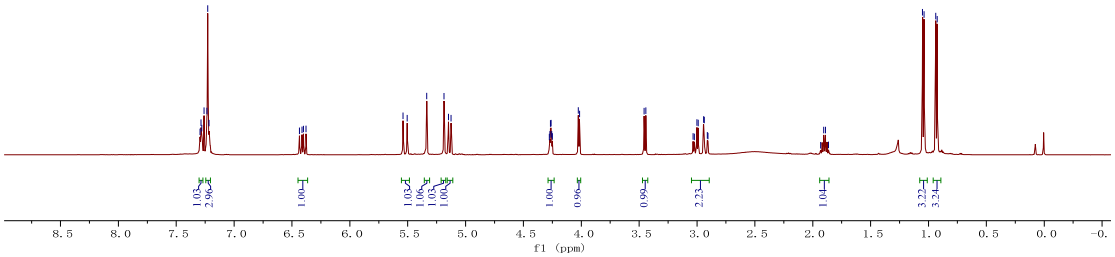
4r

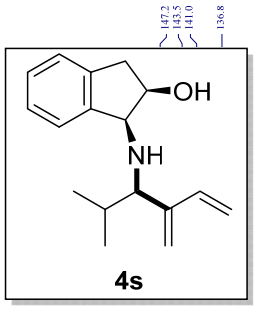
^{13}C NMR(126 MHz, $CDCl_3$)



4s

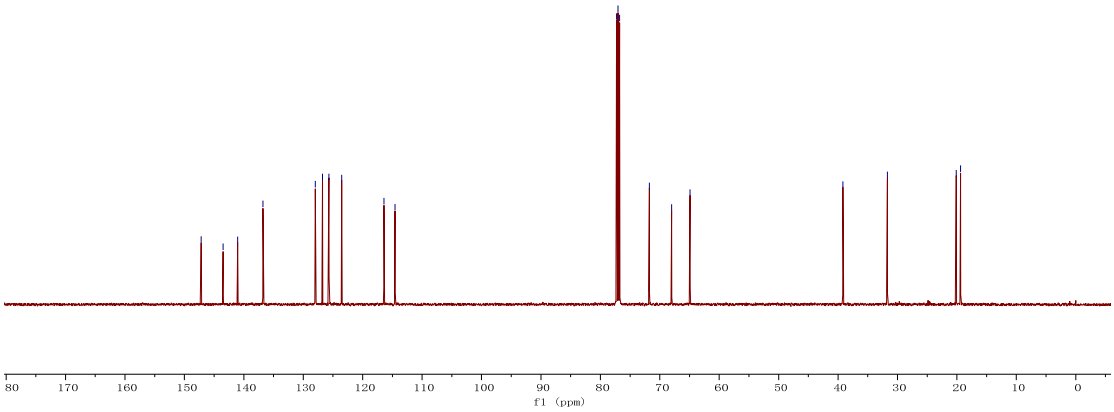
^{1}H NMR(500 MHz, $CDCl_3$)

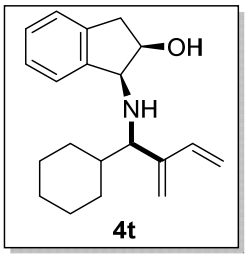




4s

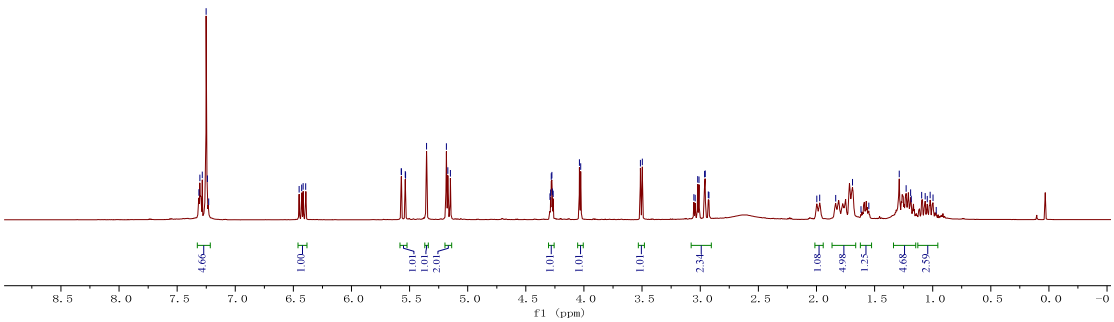
^{13}C NMR(126 MHz, $CDCl_3$)

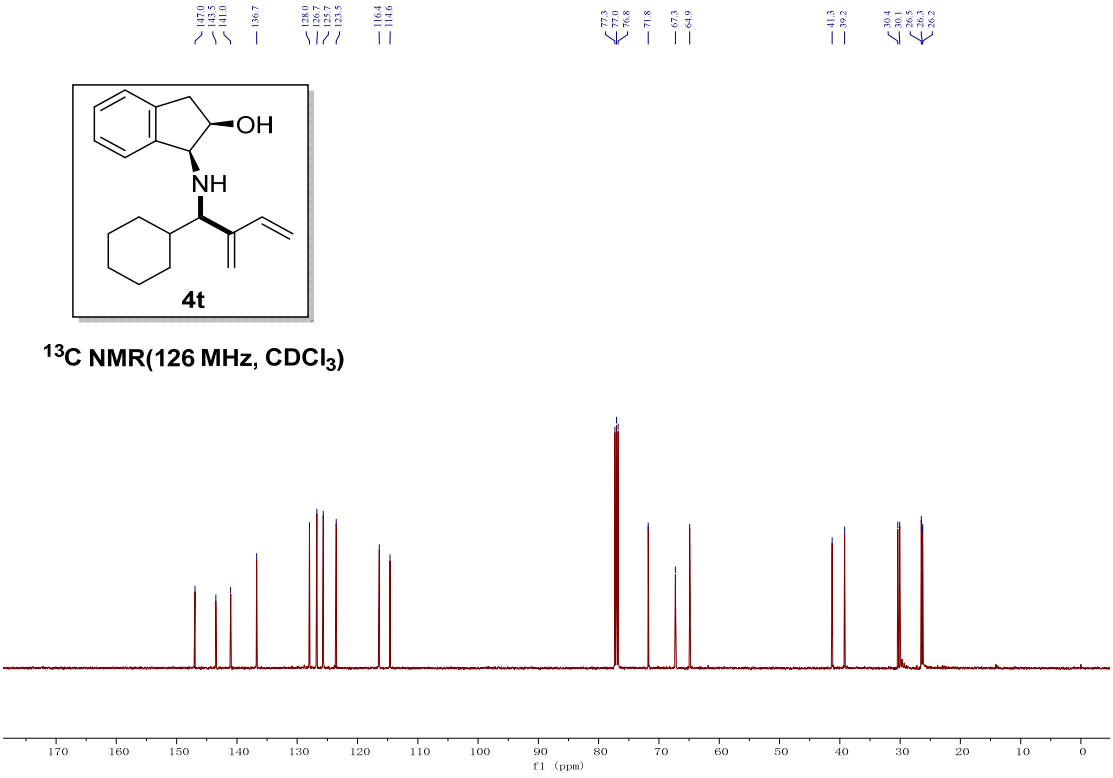




4t

^{1}H NMR(500 MHz, $CDCl_3$)

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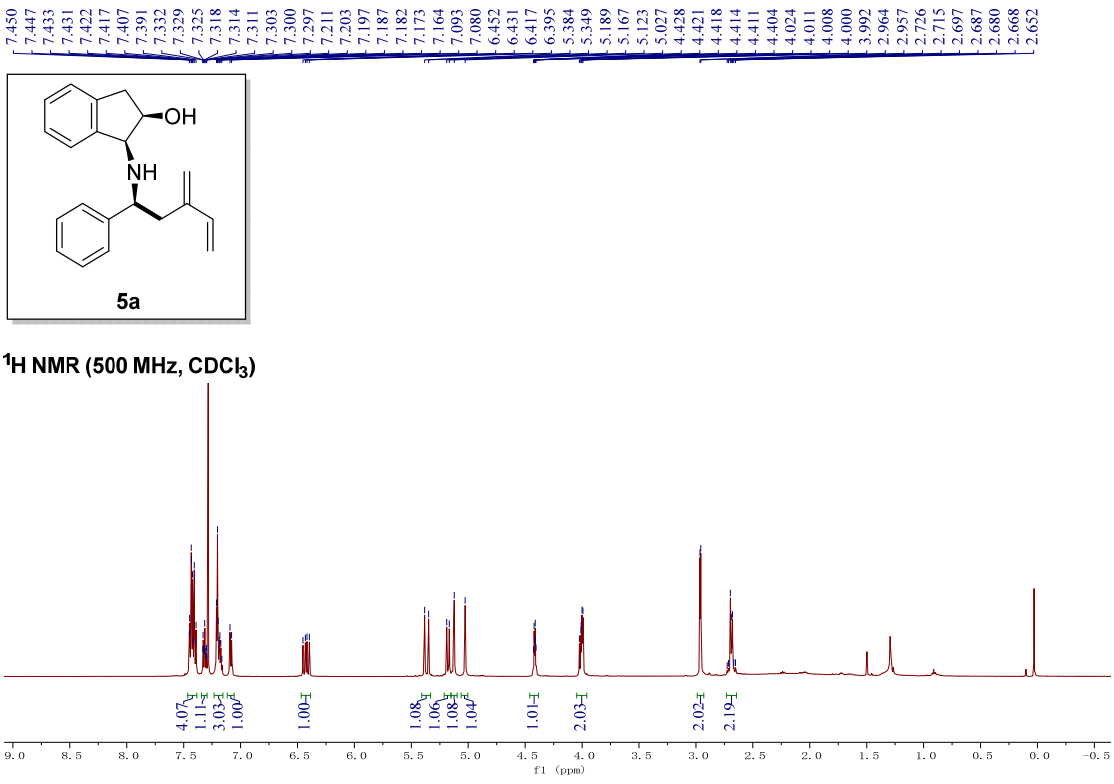
143.5
141.0
136.7
128.0
126.7
125.7
123.5
116.4
114.6
77.3
77.0
76.8
71.8
67.3
64.9
41.3
39.2
30.4
30.1
28.5
26.3
26.2
OH
NH
4t
13C NMR(126 MHz, CDCl3)
f1 (ppm)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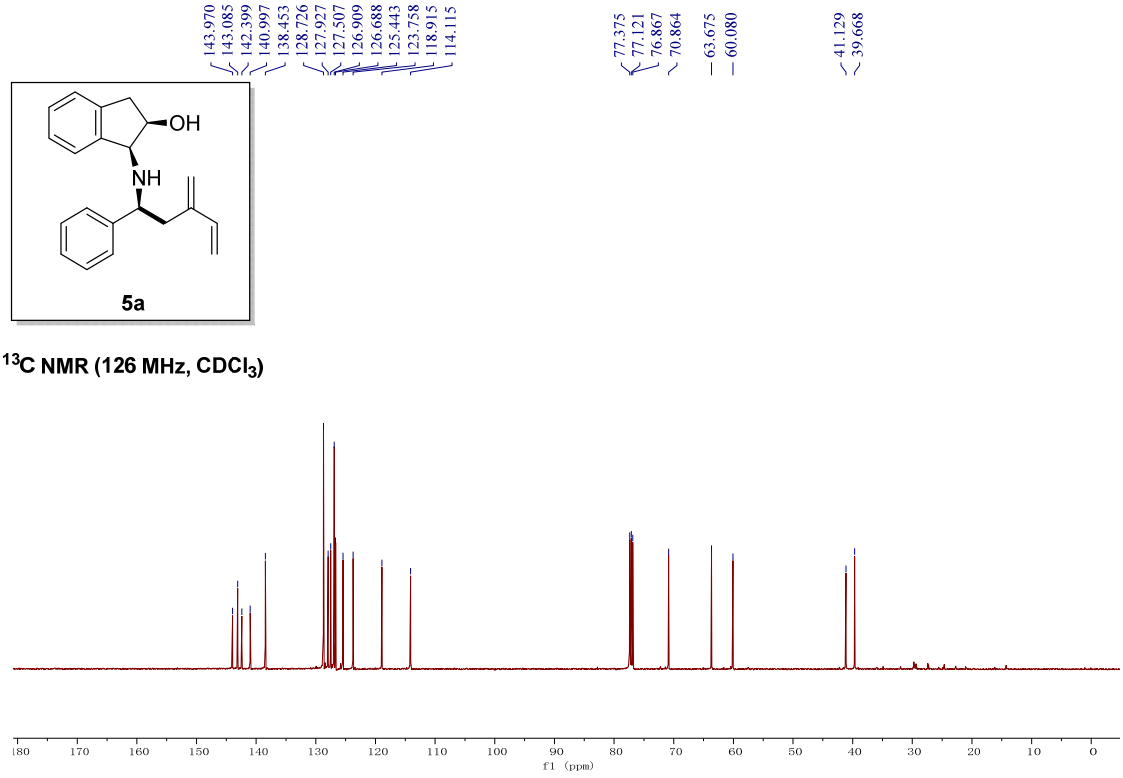
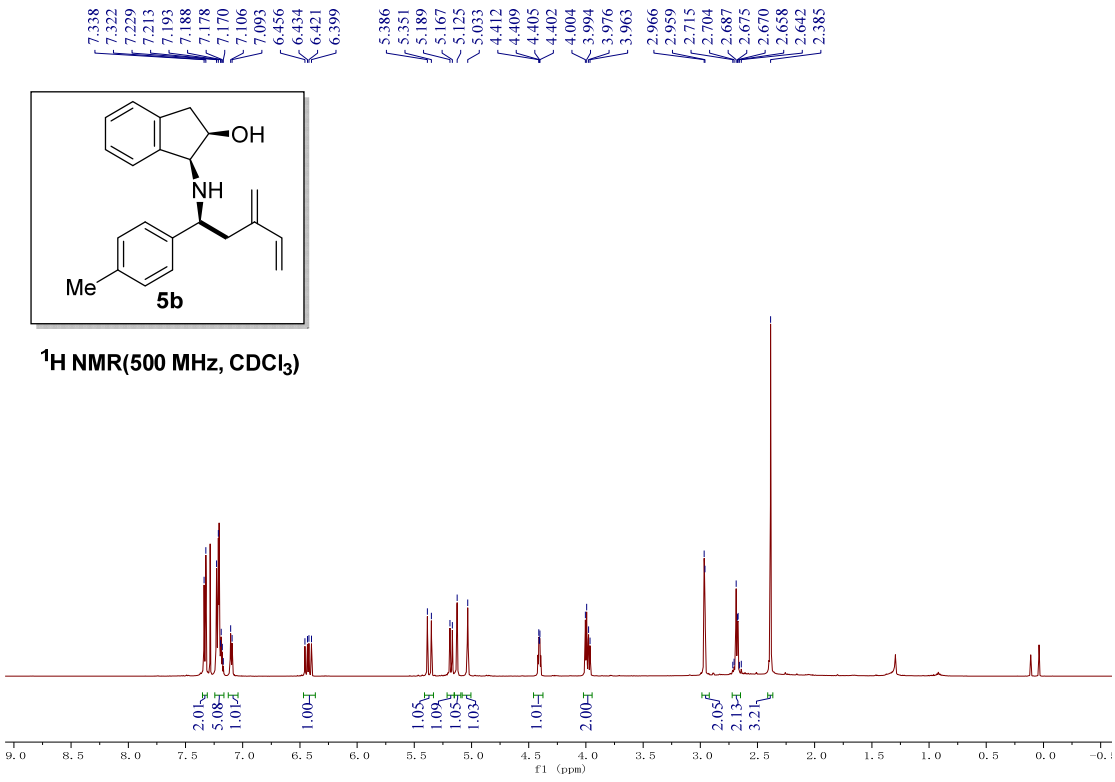
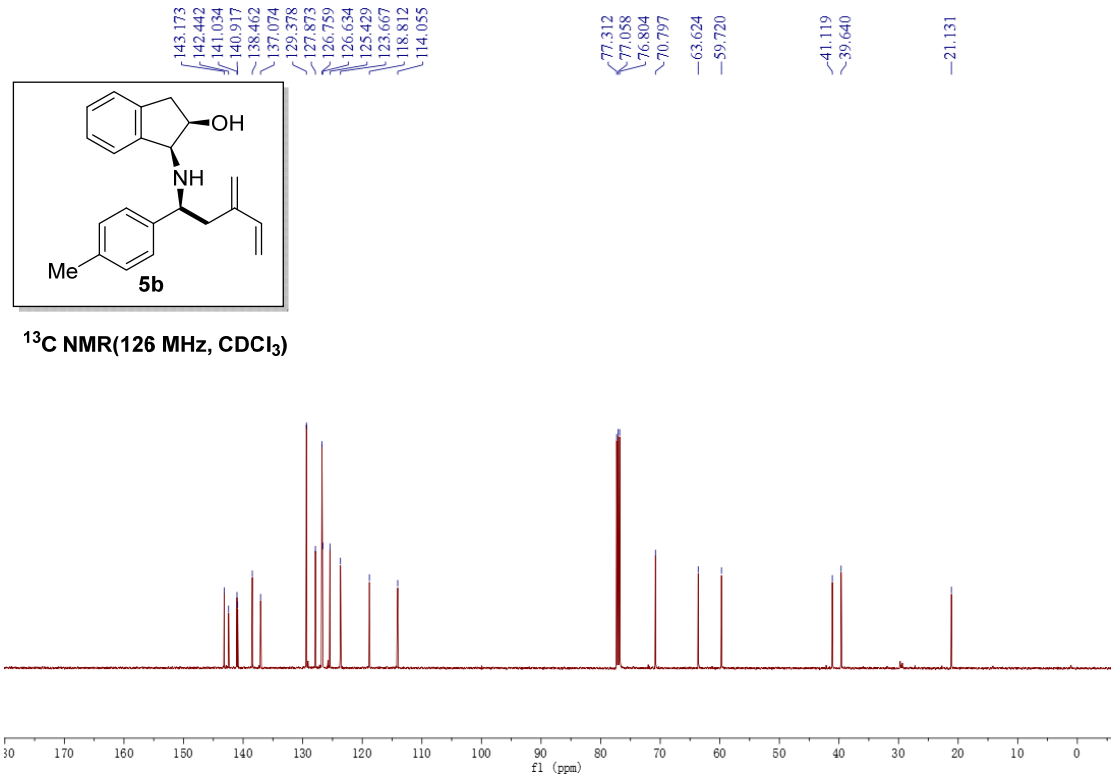
7.447
7.433
7.431
7.422
7.417
7.407
7.391
7.332
7.329
7.325
7.318
7.314
7.311
7.303
7.300
7.297
7.211
7.203
7.197
7.187
7.182
7.173
7.164
7.093
7.080
6.452
6.431
6.417
6.395
5.384
5.349
5.189
5.167
5.123
5.027
4.428
4.421
4.418
4.414
4.411
4.404
4.024
4.011
4.008
4.000
3.992
2.964
2.957
2.726
2.715
2.697
2.687
2.680
2.668
2.652
OH
NH
5a
1H NMR (500 MHz, CDCl3)
4.07
1.11
3.03
1.00
1.00
1.08
1.06
1.08
1.04
1.01
2.03
2.02
2.19
f1 (ppm)



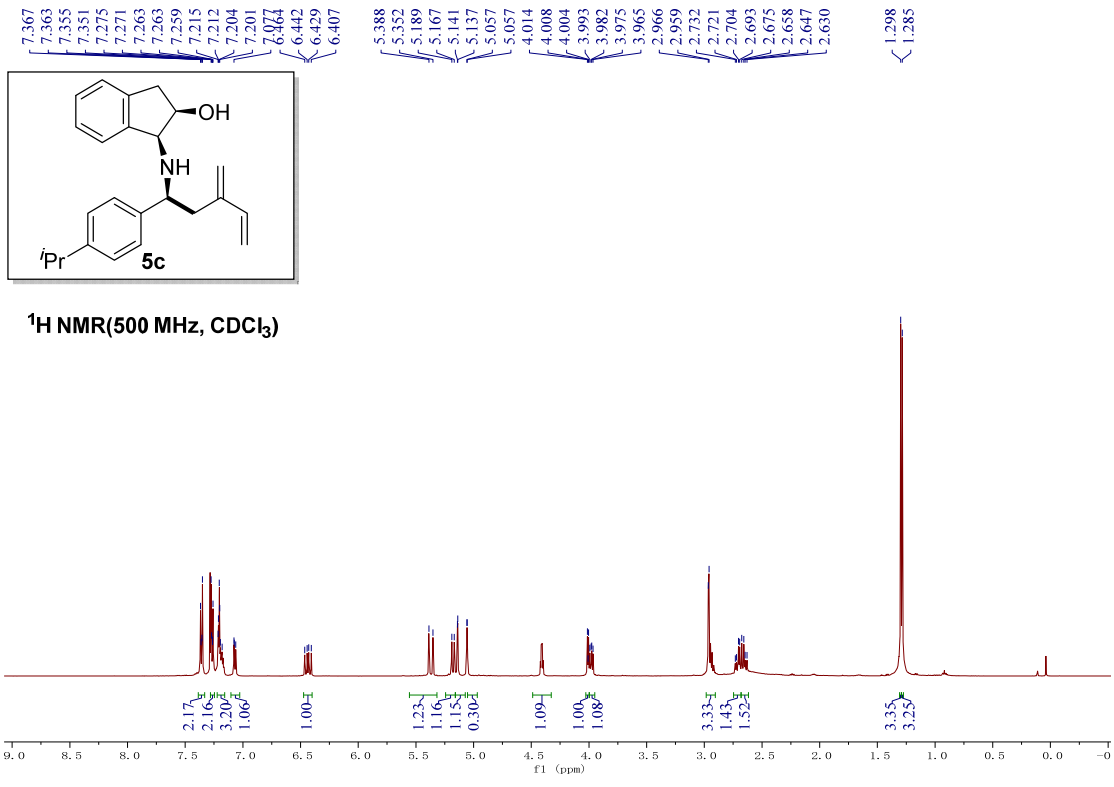
^{13}C NMR (126 MHz, $CDCl_3$)



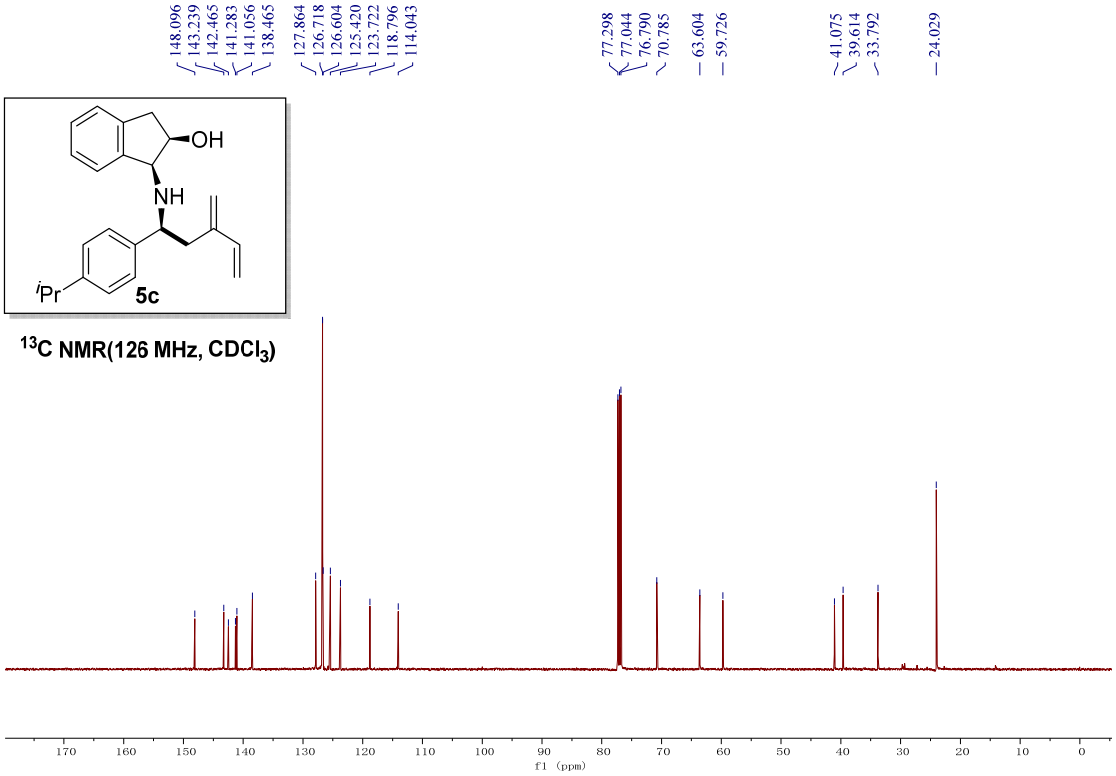
^{1}H NMR(500 MHz, $CDCl_3$)



^{13}C NMR(126 MHz, $CDCl_3$)



^{1}H NMR(500 MHz, $CDCl_3$)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138.465
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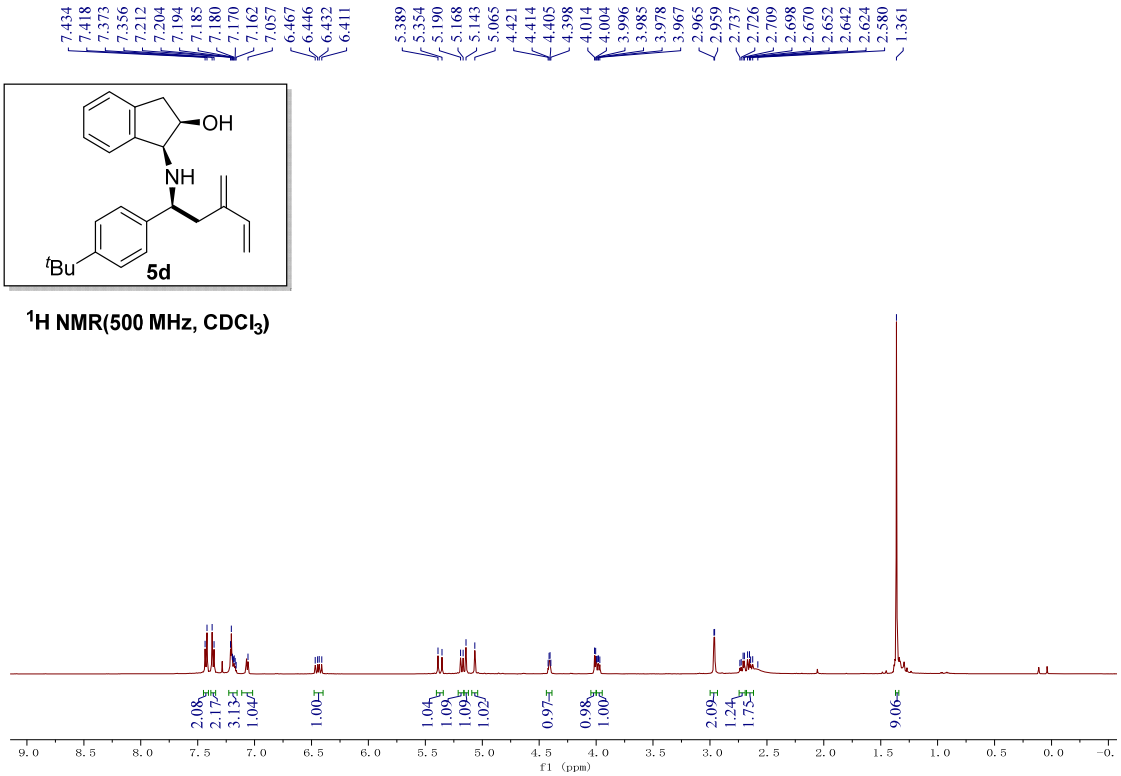
114.043
77.298
77.044
76.790
70.785
63.604
59.726
41.075
39.614
33.792
24.029
OH
NH
iPr
5c
13C NMR(126 MHz, CDCl3)
f1 (ppm)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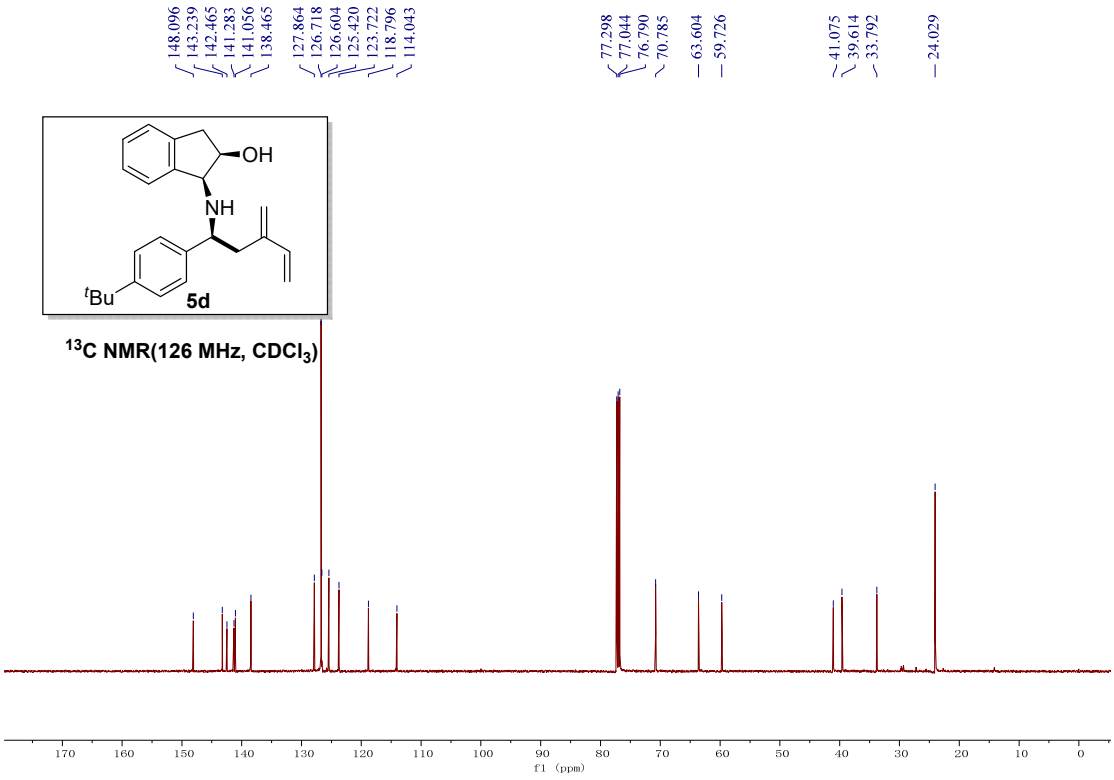
7.418
7.373
7.356
7.212
7.204
7.194
7.185
7.180
7.170
7.162
7.057
6.467
6.446
6.432
6.411
5.389
5.354
5.190
5.168
5.143
5.065
4.421
4.414
4.405
4.398
4.014
4.004
3.996
3.985
3.978
3.967
2.965
2.959
2.737
2.726
2.709
2.698
2.670
2.652
2.642
2.624
2.580
1.361
OH
NH
tBu
5d
1H NMR(500 MHz, CDCl3)
2.08
2.17
3.13
1.04
1.00
1.04
1.09
1.09
1.02
0.97
0.98
1.00
2.09
1.24
1.75
9.06
f1 (ppm)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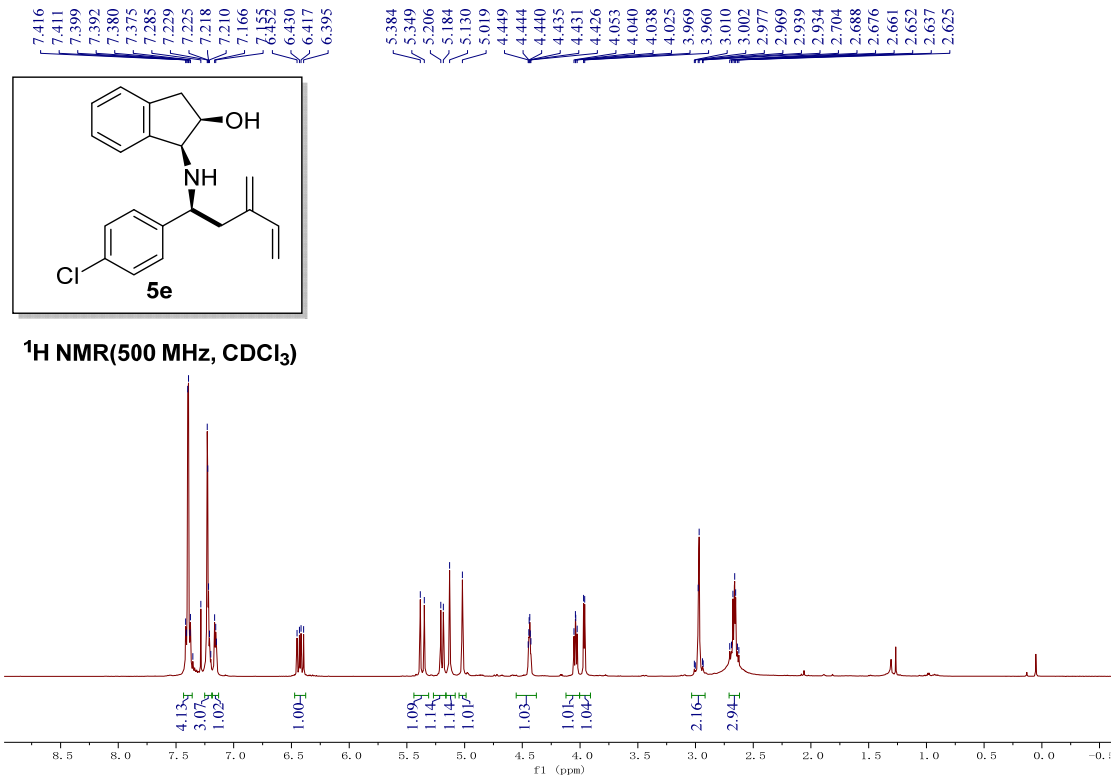
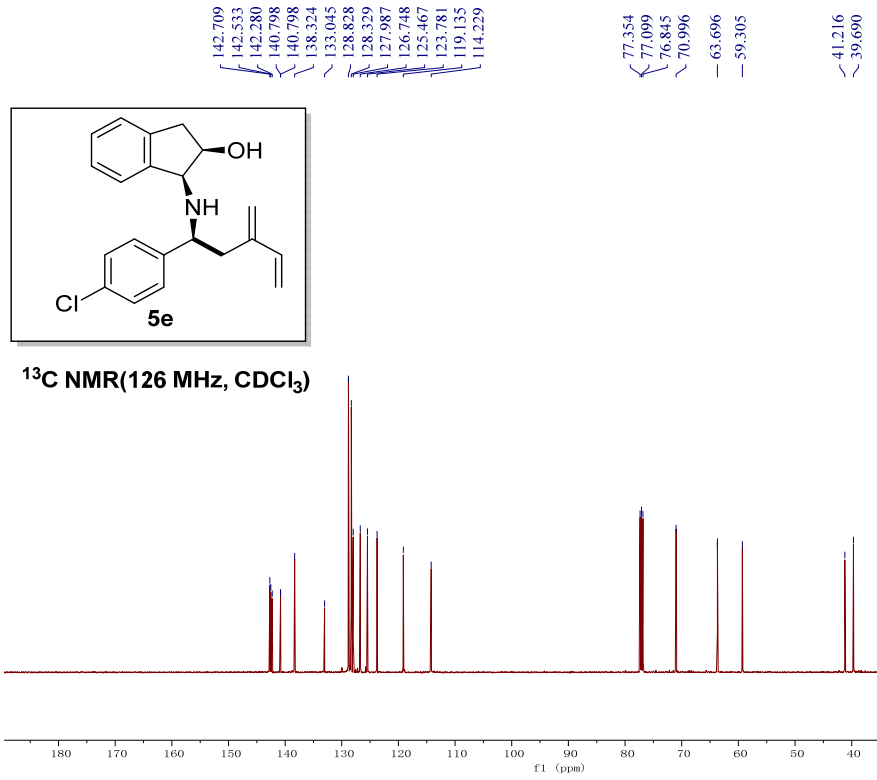
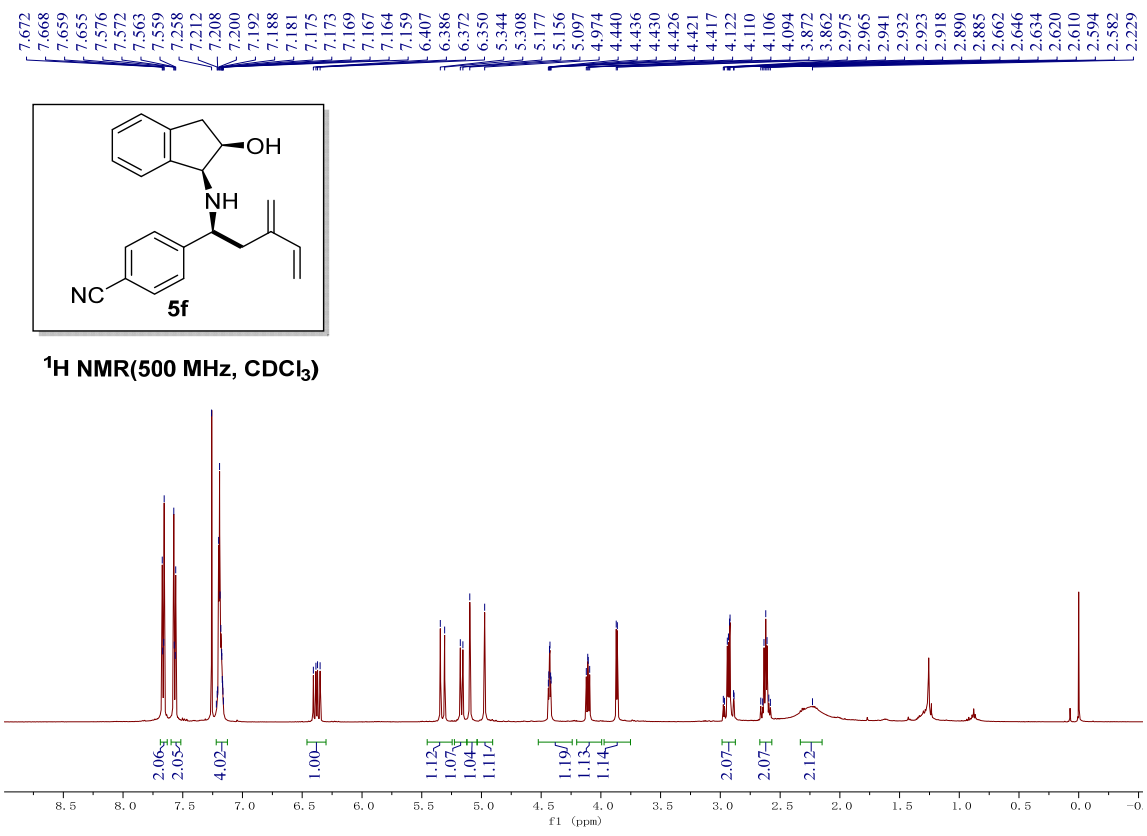
143.239
142.465
141.283
141.056
138.465
127.864
126.718
126.604
125.420
123.722
118.796
114.043
77.298
77.044
76.790
70.785
63.604
59.726
41.075
39.614
33.792
24.029
OH
NH
tBu
5d
13C NMR(126 MHz, CDCl3)
f1 (ppm)


7.416
7.411
7.399
7.392
7.380
7.375
7.285
7.229
7.225
7.218
7.210
7.166
7.155
6.452
6.430
6.417
6.395
5.384
5.349
5.206
5.184
5.130
5.019
4.449
4.444
4.440
4.435
4.431
4.426
4.053
4.040
4.038
4.025
3.969
3.960
3.010
3.002
2.977
2.969
2.939
2.934
2.704
2.688
2.676
2.661
2.652
2.637
2.625
OH
NH
Cl
5e
1H NMR(500 MHz, CDCl3)
4.13
3.07
1.02
1.00
1.09
1.14
1.14
1.01
1.03
1.01
1.04
2.16
2.94
f1 (ppm)


142.709
142.533
142.280
140.798
140.798
138.324
133.045
128.828
128.329
127.987
126.748
125.467
123.781
119.135
114.229
77.354
77.099
76.845
70.996
63.696
59.305
41.216
39.690
OH
NH
Cl
5e
13C NMR(126 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.672
7.668
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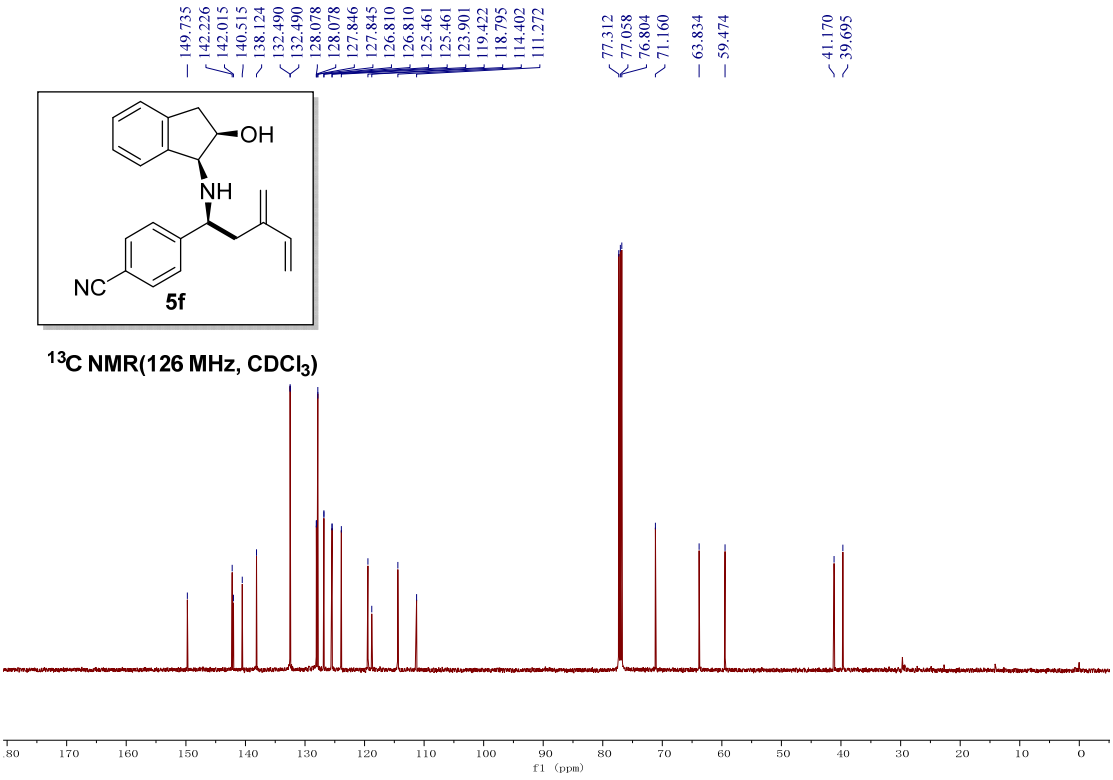
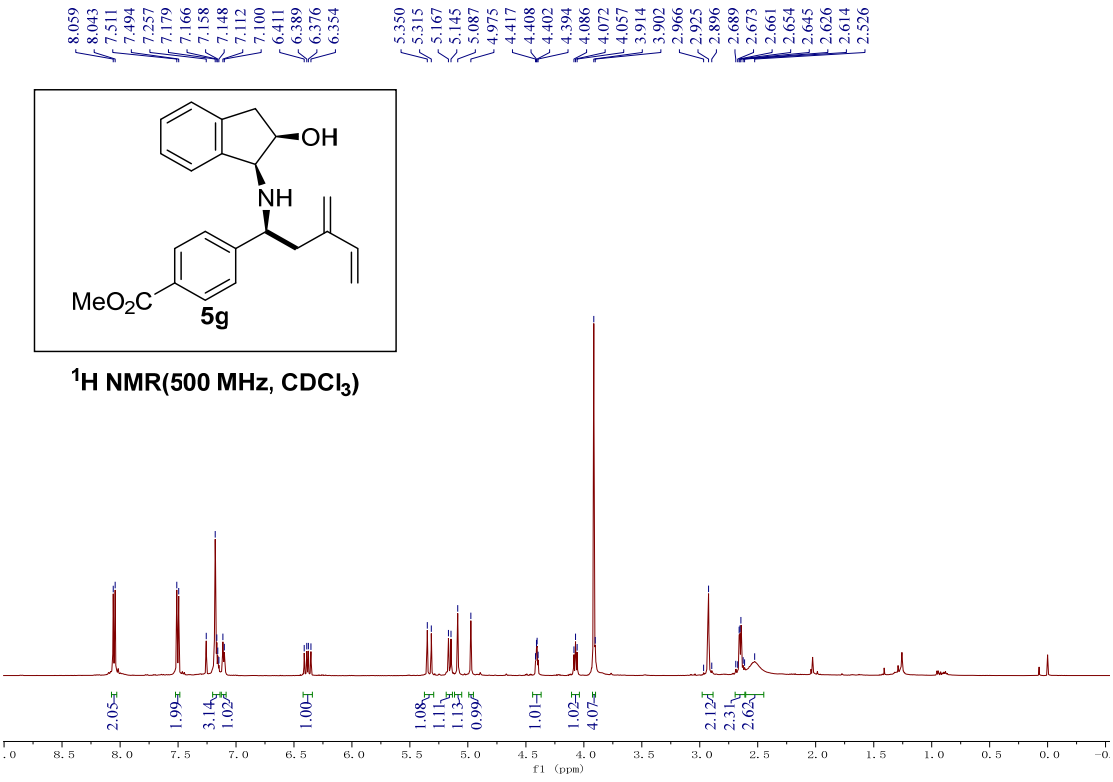
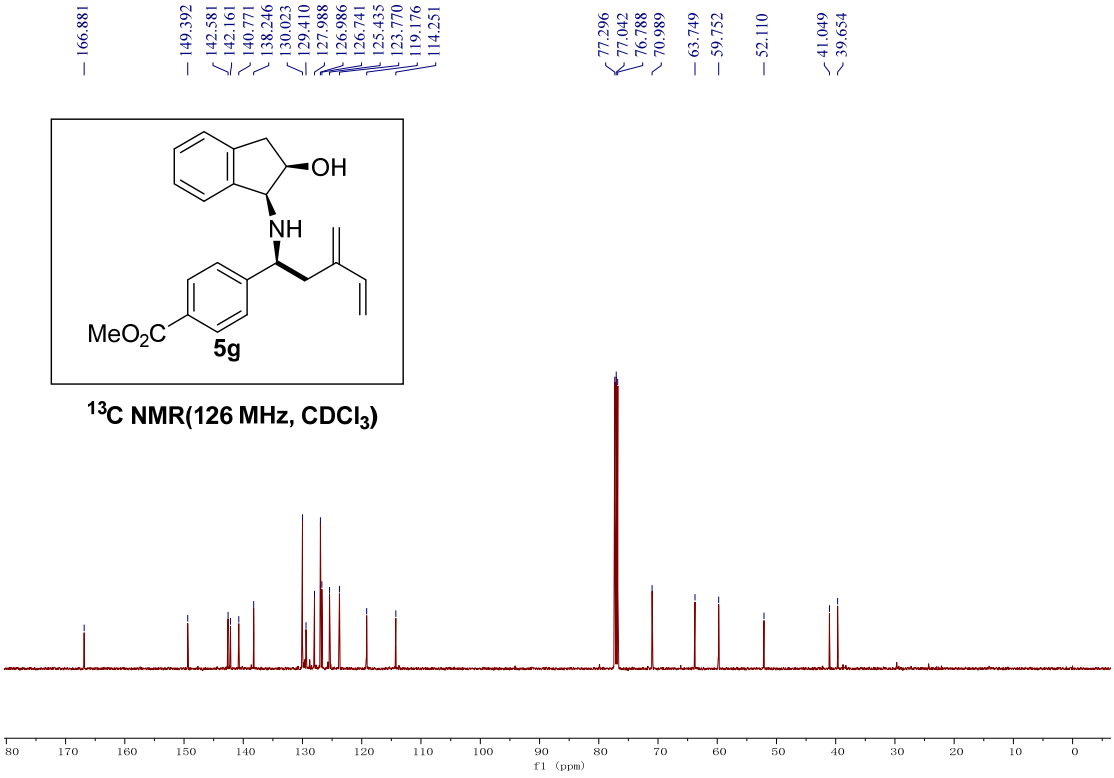
7.655
7.576
7.572
7.563
7.559
7.258
7.212
7.208
7.200
7.192
7.188
7.181
7.175
7.173
7.169
7.167
7.164
7.159
6.407
6.386
6.372
6.350
5.344
5.308
5.177
5.156
5.097
4.974
4.440
4.436
4.430
4.426
4.421
4.417
4.122
4.110
4.106
4.094
3.872
3.862
2.975
2.965
2.941
2.932
2.923
2.918
2.890
2.885
2.662
2.646
2.634
2.620
2.610
2.594
2.582
2.229
OH
NH
NC
5f
1H NMR(500 MHz, CDCl3)
2.06
2.05
4.02
1.00
1.12
1.07
1.04
1.11
1.19
1.13
1.14
2.07
2.07
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
f1 (ppm)

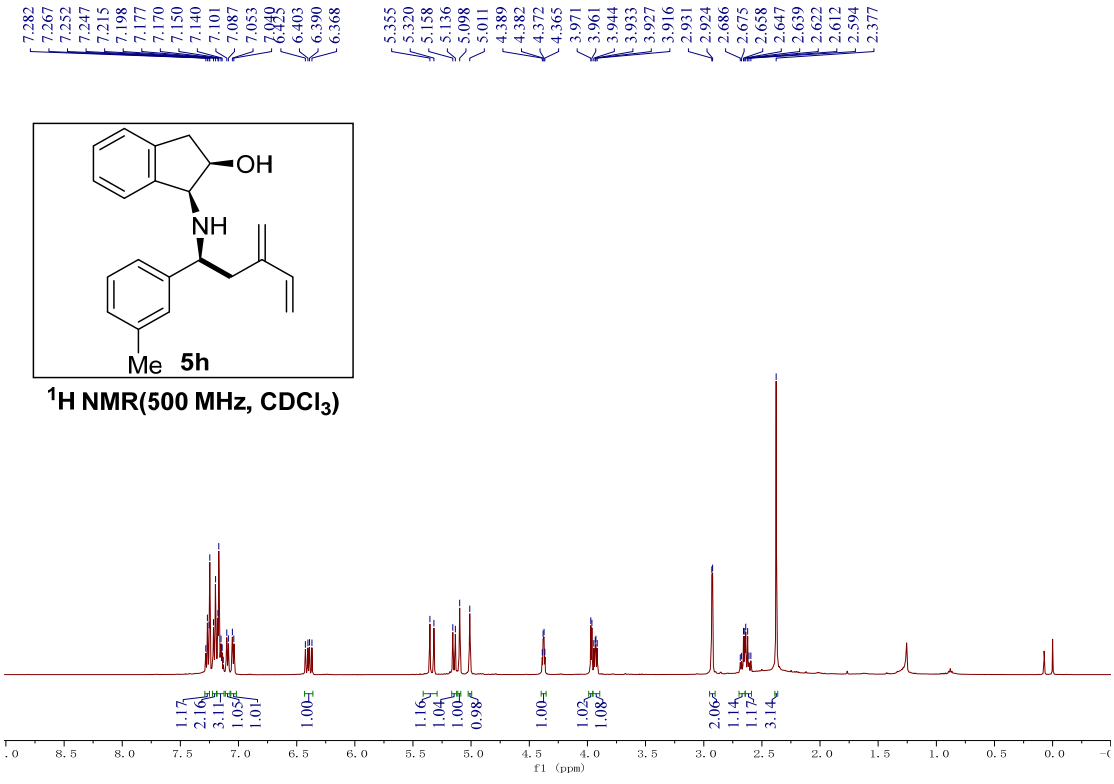


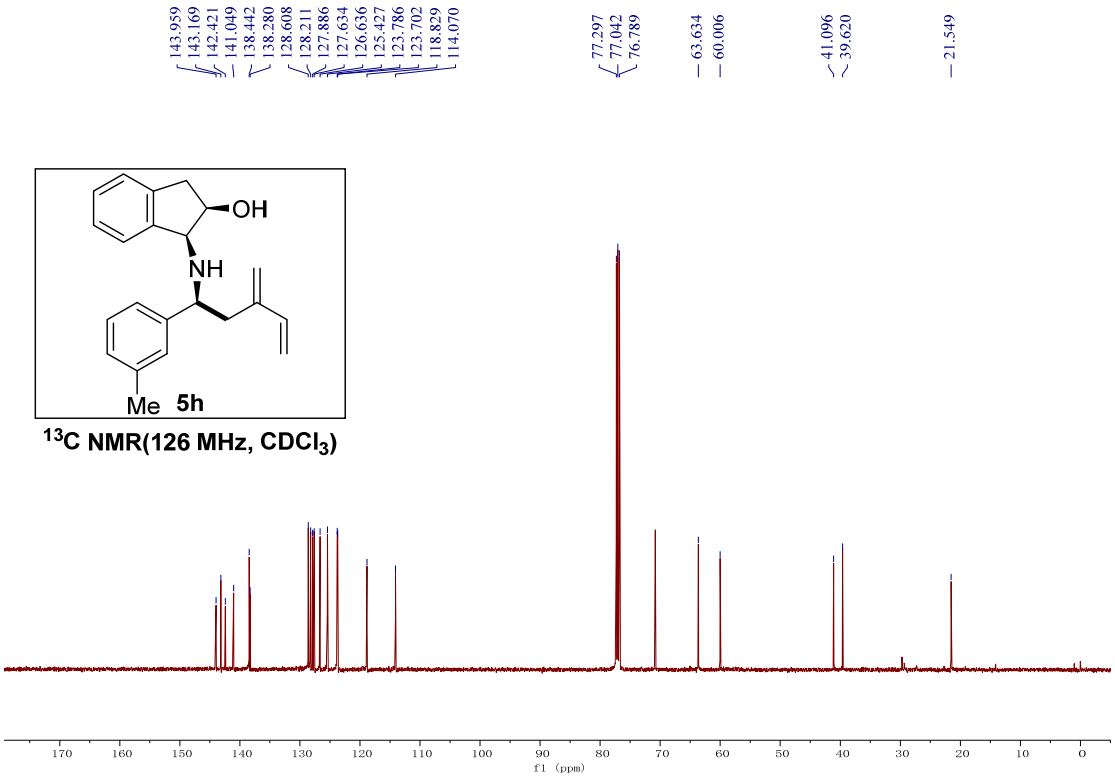
^{13}C NMR(126 MHz, $CDCl_3$)

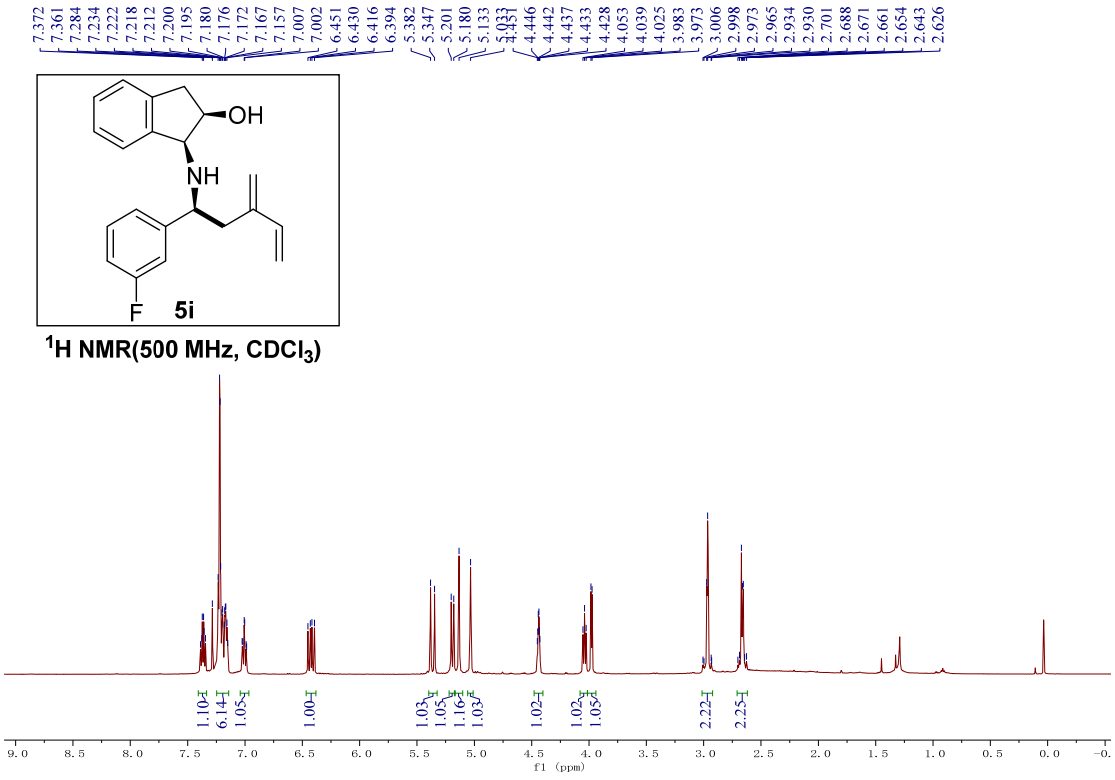


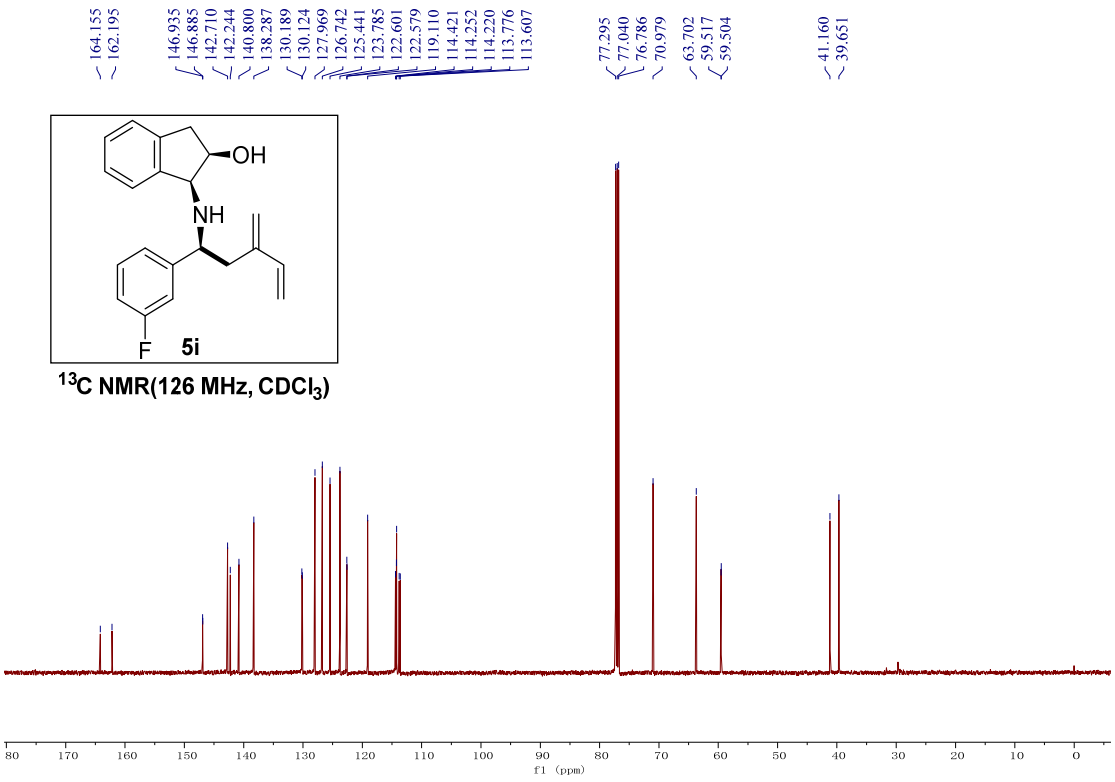
^{1}H NMR(500 MHz, $CDCl_3$)


166.881
149.392
142.581
142.161
140.771
138.246
130.023
129.410
127.988
126.986
126.741
125.435
123.770
119.176
114.251
77.296
77.042
76.788
70.989
63.749
59.752
52.110
41.049
39.654
OH
NH
MeO2C
5g
13C NMR(126 MHz, CDCl3)
f1 (ppm)

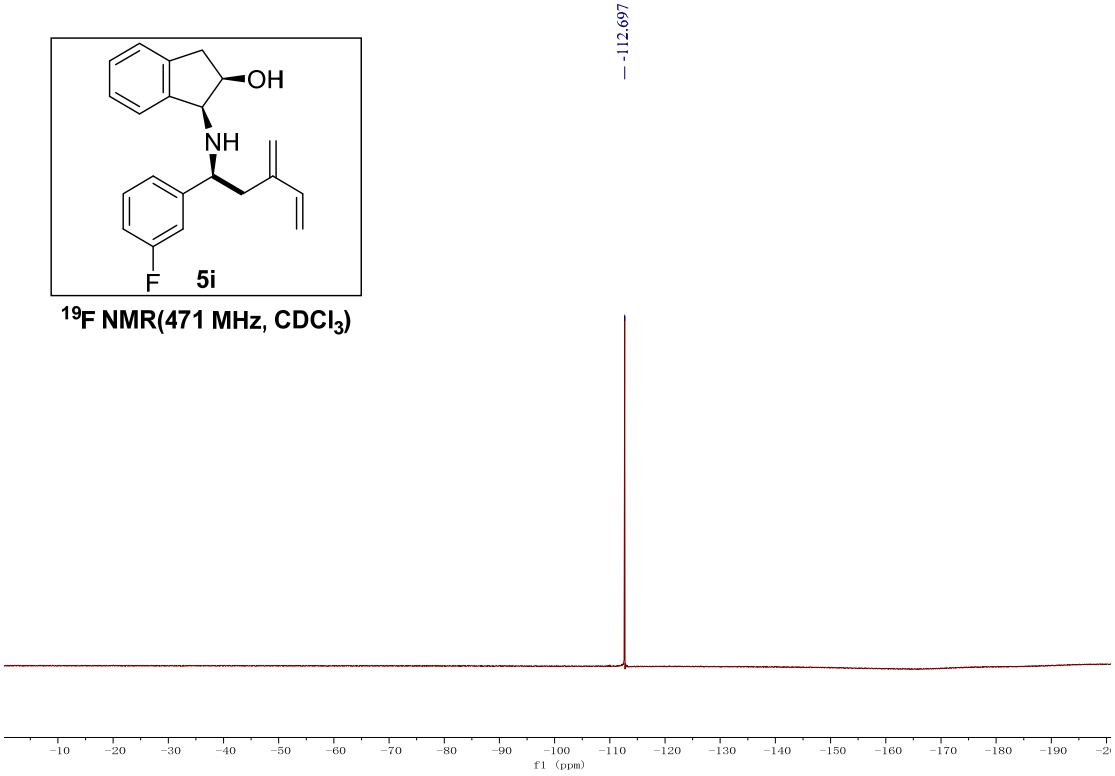

7.282
7.267
7.252
7.247
7.215
7.198
7.177
7.170
7.150
7.140
7.101
7.087
7.053
6.403
6.390
6.368
5.355
5.320
5.158
5.136
5.098
5.011
4.389
4.382
4.372
4.365
3.971
3.961
3.944
3.933
3.927
3.916
2.931
2.924
2.686
2.675
2.658
2.647
2.639
2.622
2.612
2.594
2.377
OH
NH
Me
5h
1H NMR(500 MHz, CDCl3)
1.17
2.16
3.11
1.05
1.01
1.00
1.16
1.04
1.00
0.98
1.00
1.02
1.08
2.06
1.14
1.17
3.14
f1 (ppm)


143.959
143.169
142.421
141.049
138.442
138.280
128.608
128.211
127.886
127.634
126.636
125.427
123.786
123.702
118.829
114.070
77.297
77.042
76.789
63.634
60.006
41.096
39.620
21.549
OH
NH
Me
5h
13C NMR(126 MHz, CDCl3)
f1 (ppm)

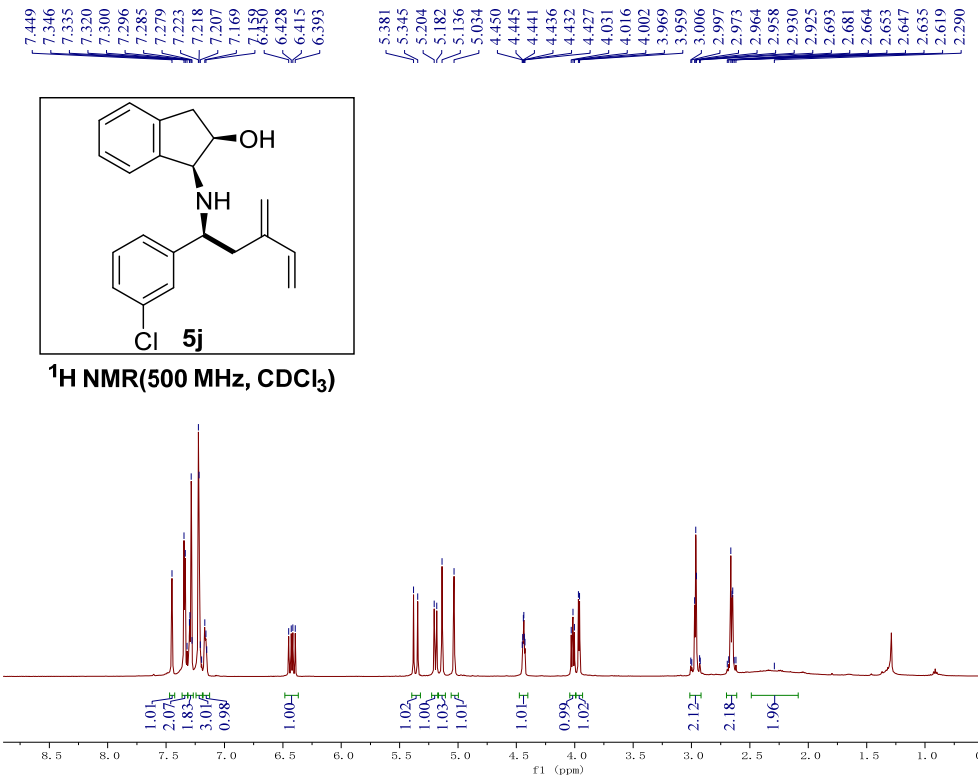

7.372
7.361
7.284
7.234
7.222
7.218
7.212
7.200
7.195
7.180
7.176
7.172
7.167
7.157
7.007
7.002
6.451
6.430
6.416
6.394
5.382
5.347
5.201
5.180
5.133
4.446
4.442
4.437
4.433
4.428
4.053
4.039
4.025
3.983
3.973
3.006
2.998
2.973
2.965
2.934
2.930
2.701
2.688
2.671
2.661
2.654
2.643
2.626
OH
NH
F
5i
1H NMR(500 MHz, CDCl3)
1.10
6.14
1.05
1.00
1.03
1.05
1.16
1.03
1.02
1.02
1.05
2.22
2.25
f1 (ppm)



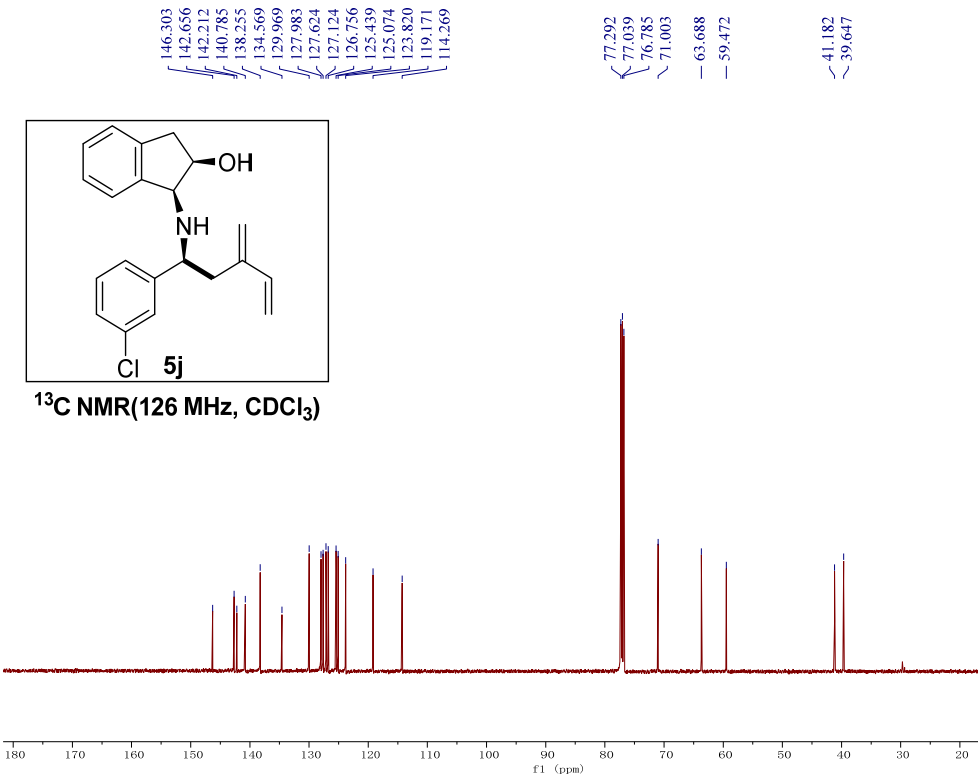
^{13}C NMR(126 MHz, $CDCl_3$)



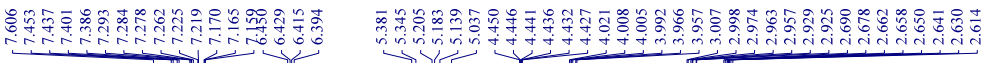
^{19}F NMR(471 MHz, $CDCl_3$)

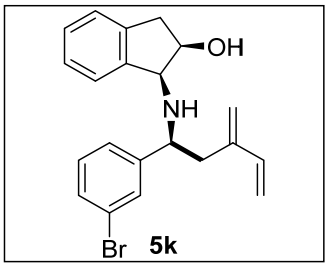


^{1}H NMR(500 MHz, $CDCl_3$)

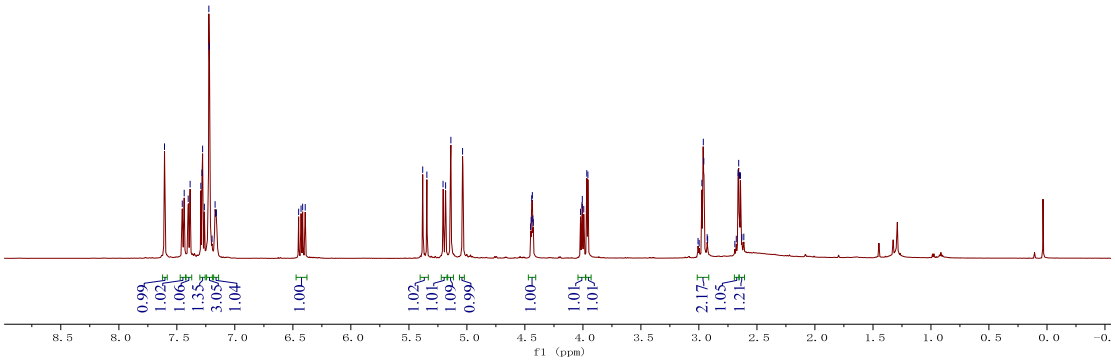


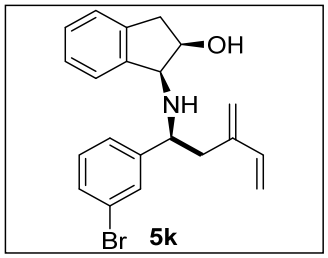
^{13}C NMR(126 MHz, $CDCl_3$)



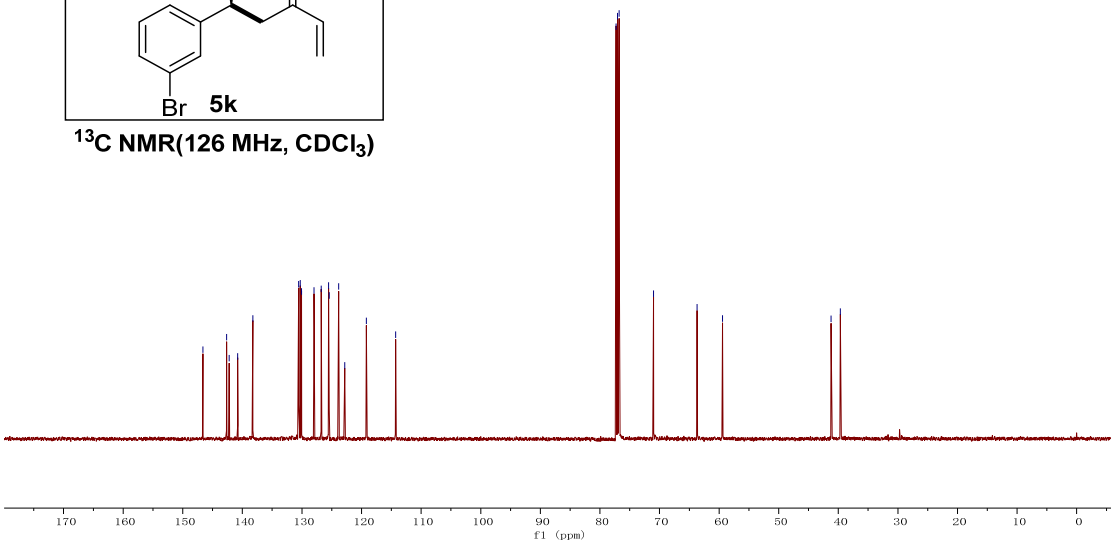


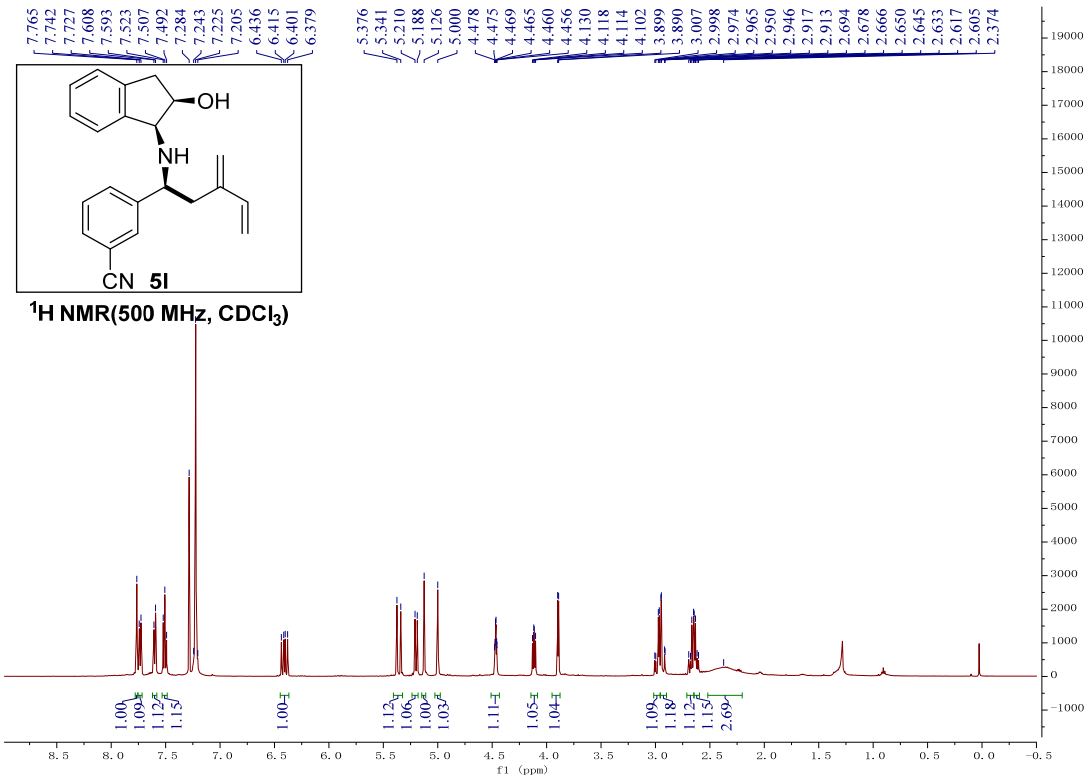
^{1}H NMR(500 MHz, $CDCl_3$)

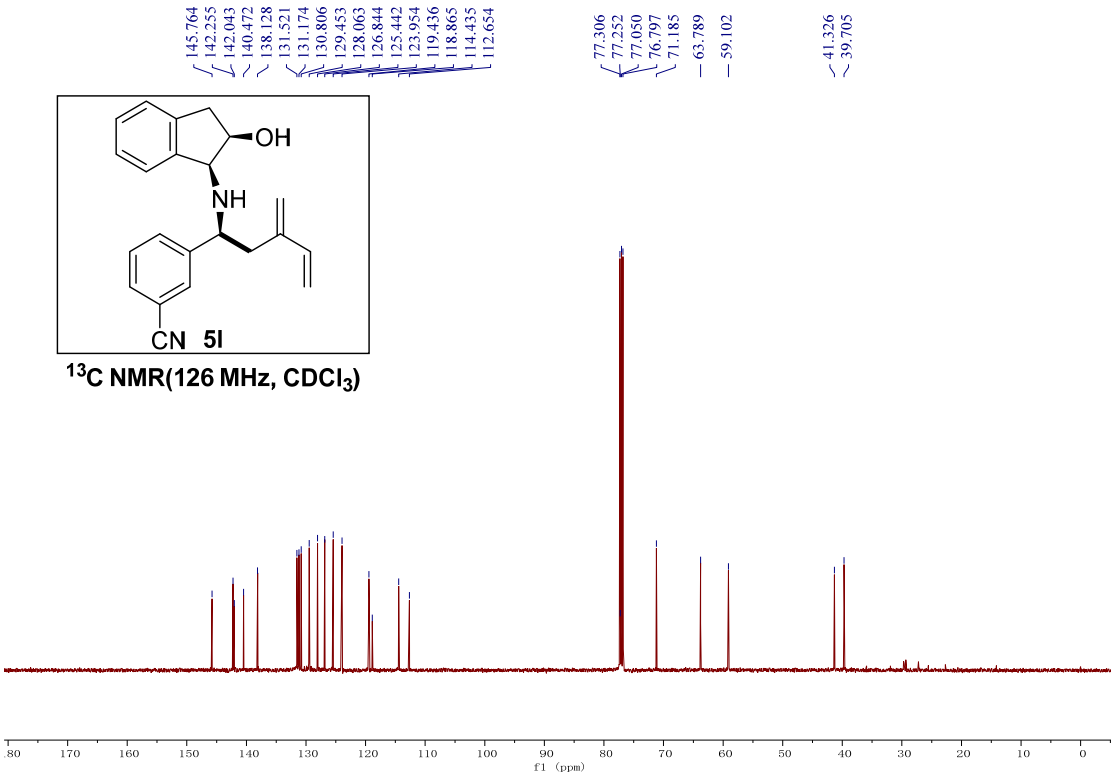


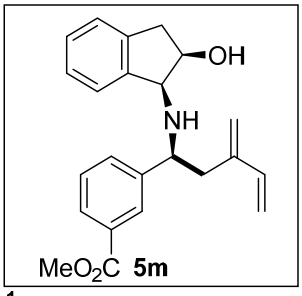


^{13}C NMR(126 MHz, $CDCl_3$)

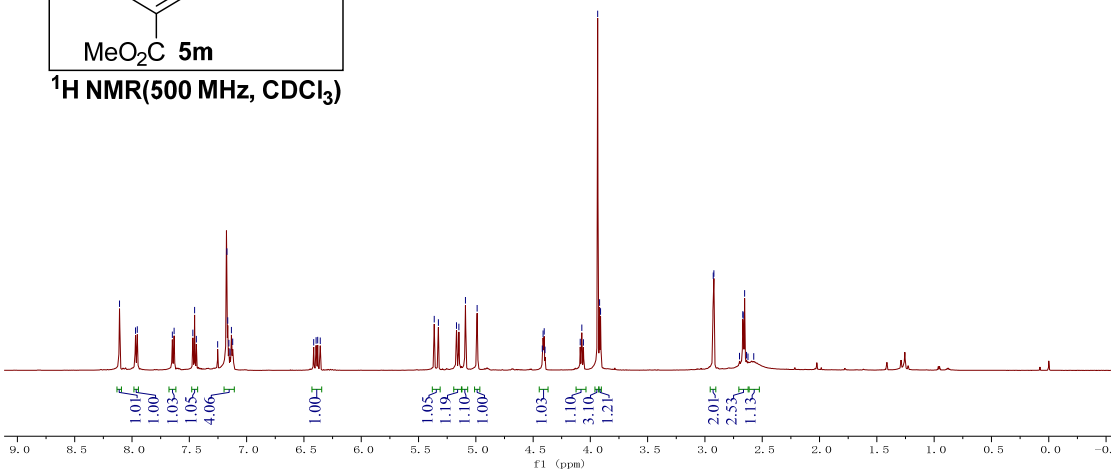


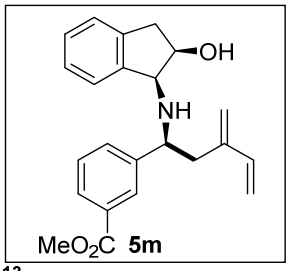

OH
NH
CN 5l
1H NMR(500 MHz, CDCl3)
f1 (ppm)


OH
NH
CN 5l
13C NMR(126 MHz, CDCl3)
f1 (ppm)

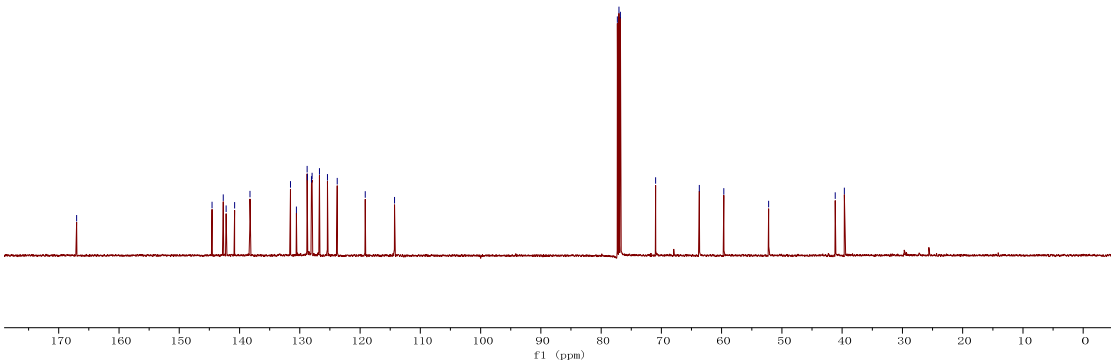


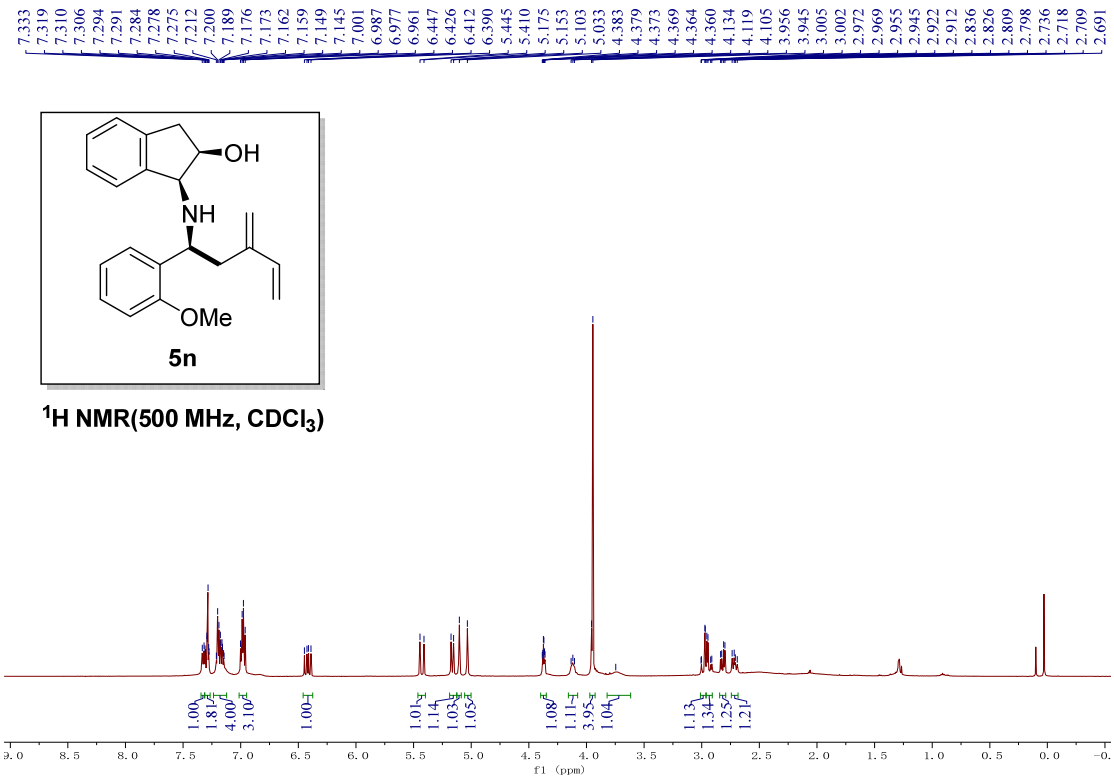
^{1}H NMR(500 MHz, $CDCl_3$)





^{13}C NMR(126 MHz, $CDCl_3$)

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7.319
7.310
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7.212
7.200
7.189
7.176
7.173
7.162
7.159
7.149
7.145
7.001
6.987
6.977
6.961
6.447
6.426
6.412
6.390
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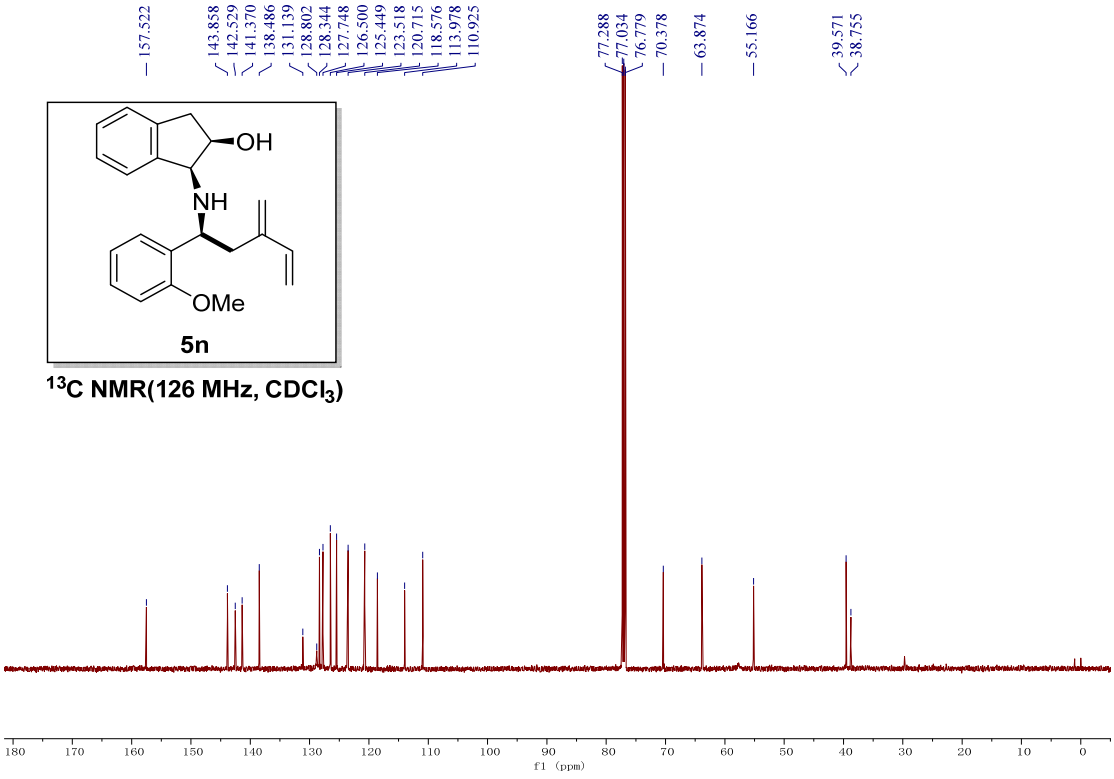
5.410
5.175
5.153
5.103
5.033
4.383
4.379
4.373
4.369
4.364
4.360
4.134
4.119
4.105
3.956
3.945
3.005
3.002
2.972
2.969
2.955
2.945
2.922
2.912
2.836
2.826
2.809
2.798
2.736
2.718
2.709
2.691
OH
NH
OMe
5n
1H NMR(500 MHz, CDCl3)
1.00
1.81
4.00
3.10
1.00
1.01
1.14
1.03
1.05
1.08
1.11
3.95
1.04
1.13
1.34
1.25
1.21
f1 (ppm)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141.370
138.486
131.139
128.802
128.344
127.748
126.500
125.449
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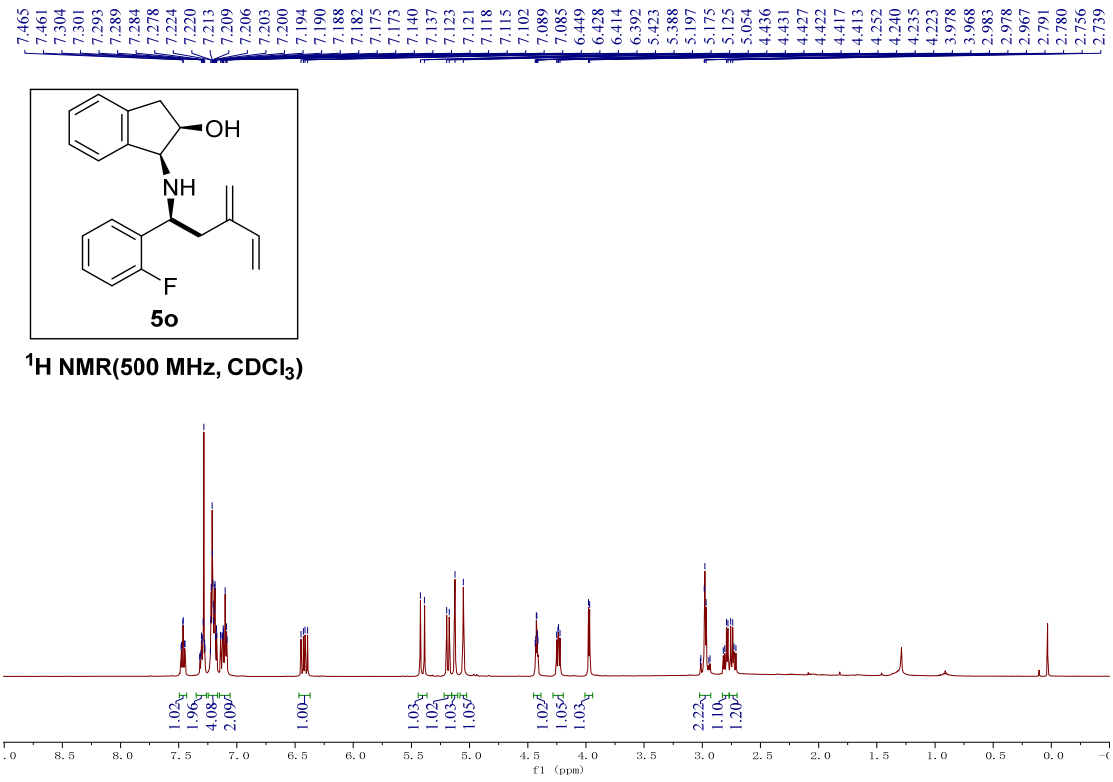
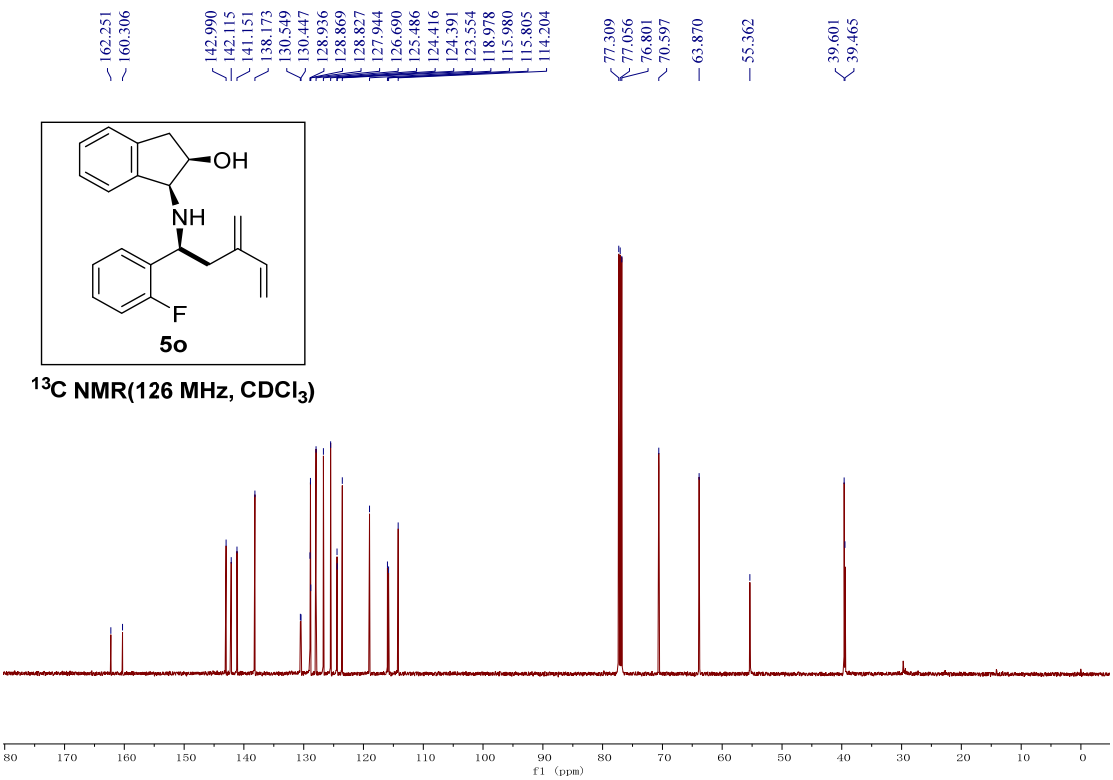
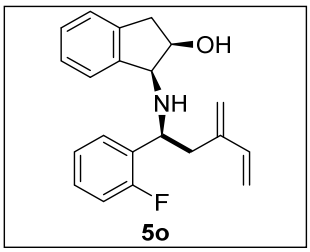
120.715
118.576
113.978
110.925
77.288
77.034
76.779
70.378
63.874
55.166
39.571
38.755
OH
NH
OMe
5n
13C NMR(126 MHz, CDCl3)
f1 (ppm)



^{1}H NMR(500 MHz, $CDCl_3$)

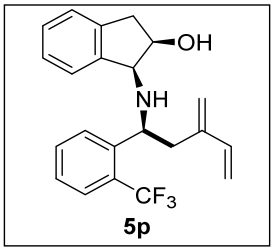


^{13}C NMR(126 MHz, $CDCl_3$)



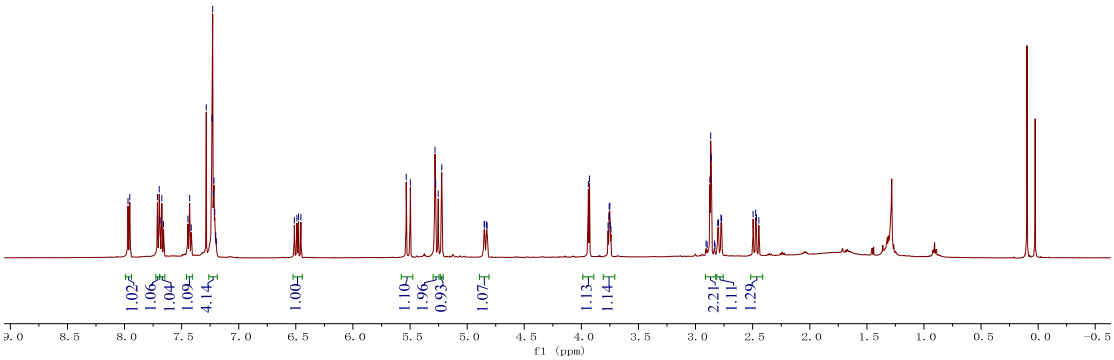
5o

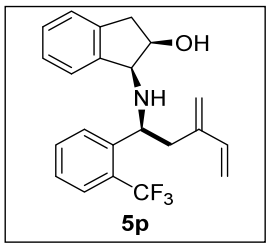
^{19}F NMR(471 MHz, $CDCl_3$)



5p

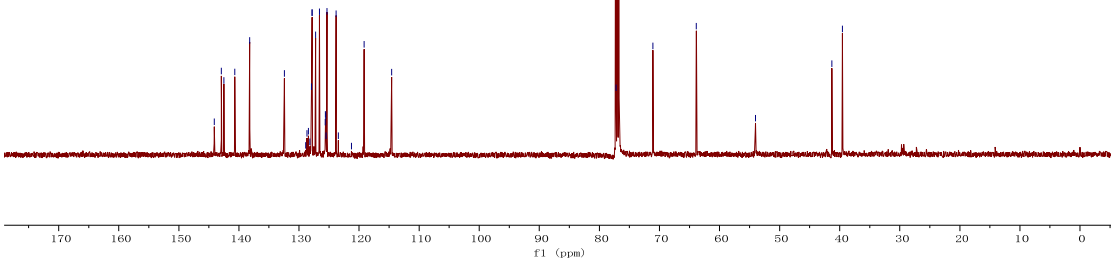
^{1}H NMR(500 MHz, $CDCl_3$)

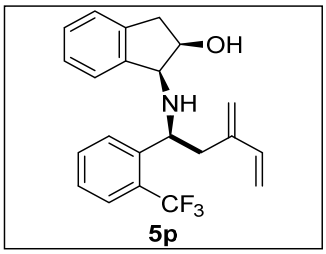




5p

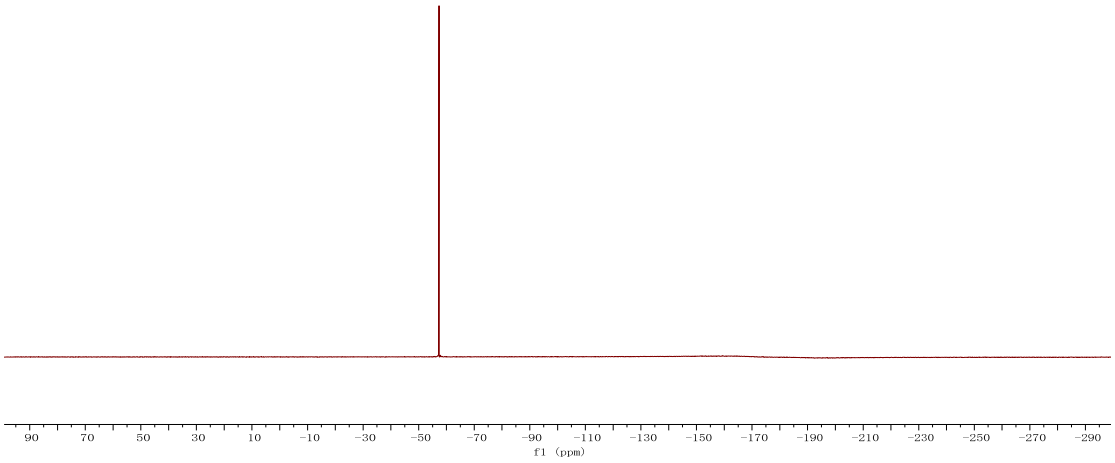
^{13}C NMR(126 MHz, $CDCl_3$)

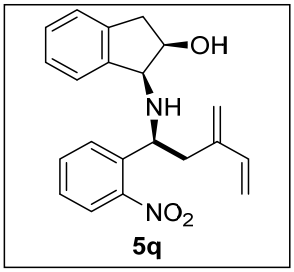




5p

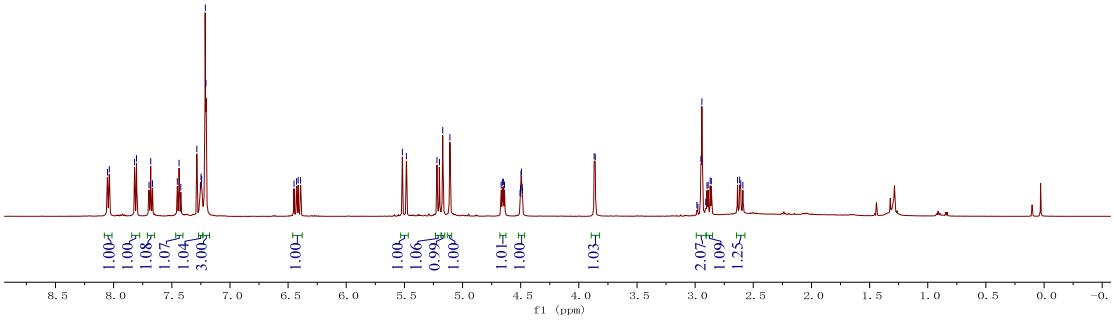
^{19}F NMR(471 MHz, $CDCl_3$)

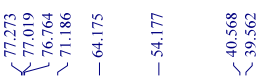


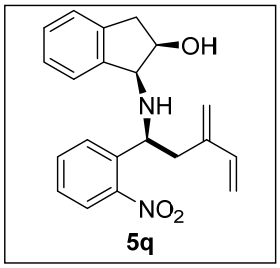


5q

^{1}H NMR(500 MHz, $CDCl_3$)

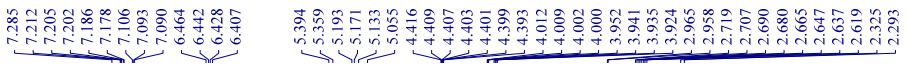


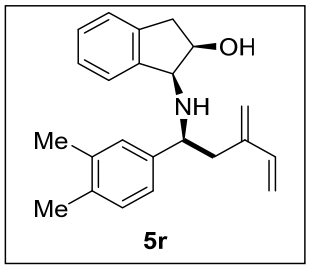




5q

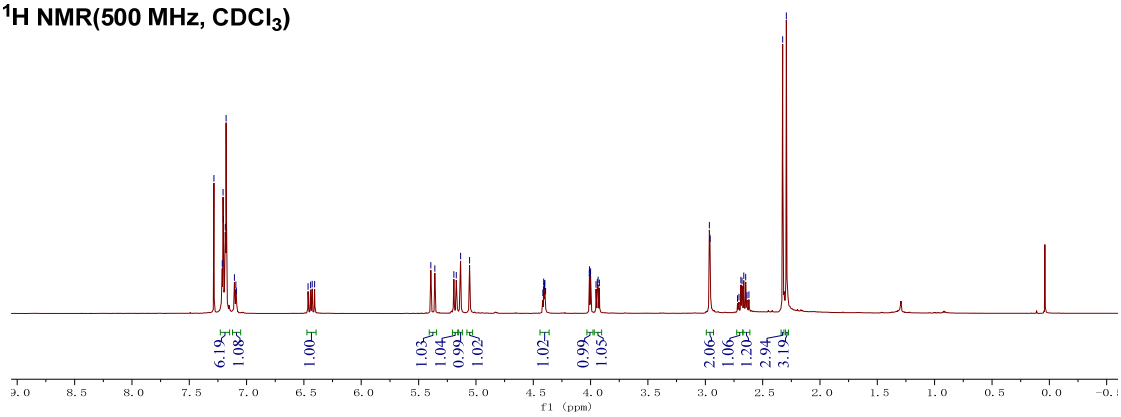
^{13}C NMR(126 MHz, $CDCl_3$)

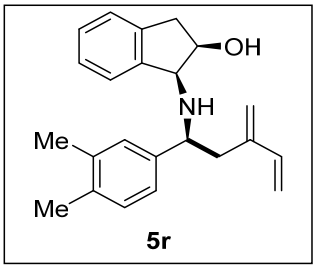




5r

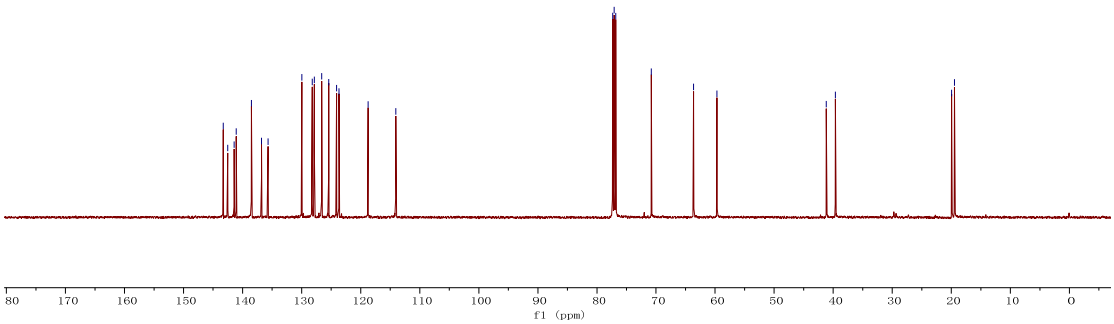
^{1}H NMR(500 MHz, $CDCl_3$)

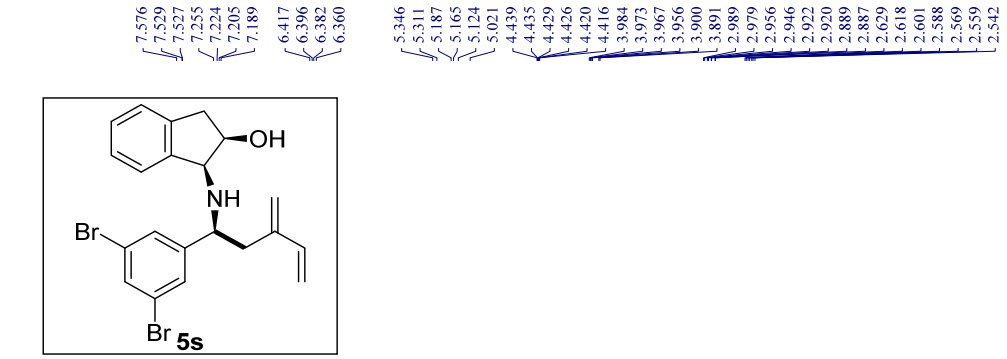




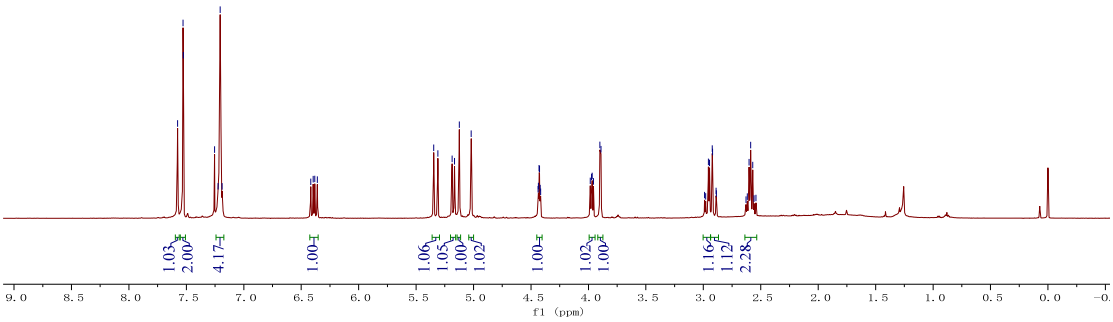
5r

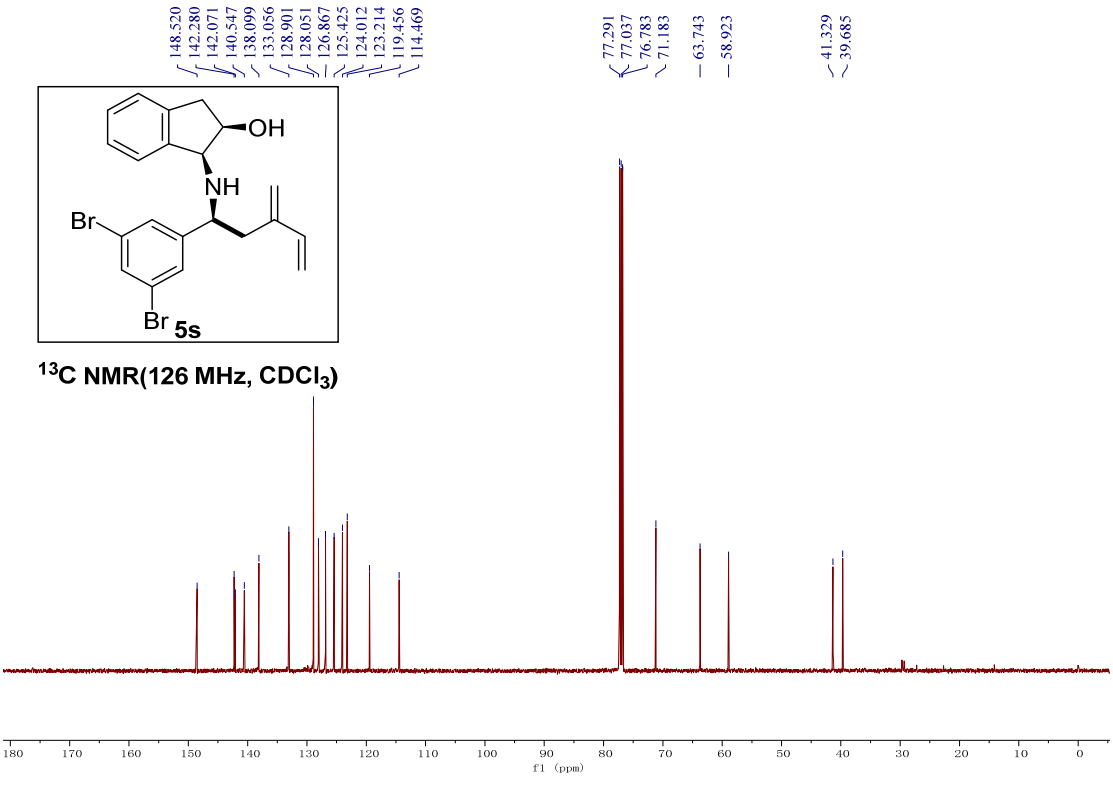
^{13}C NMR(126 MHz, $CDCl_3$)



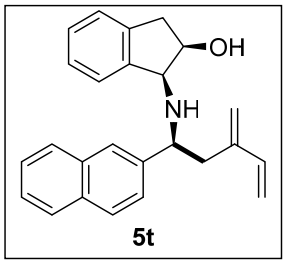


^{1}H NMR(500 MHz, $CDCl_3$)

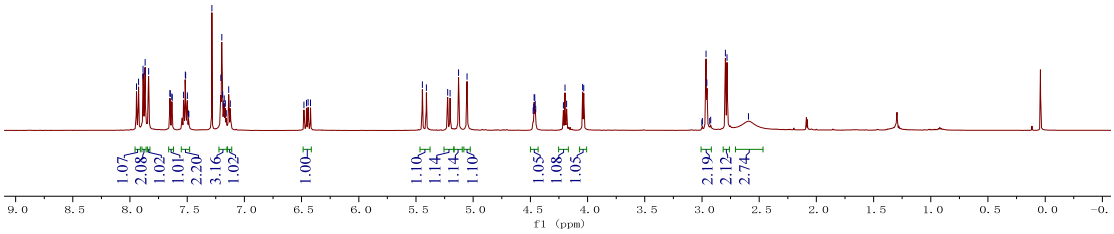


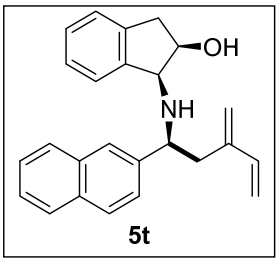


^{13}C NMR(126 MHz, $CDCl_3$)

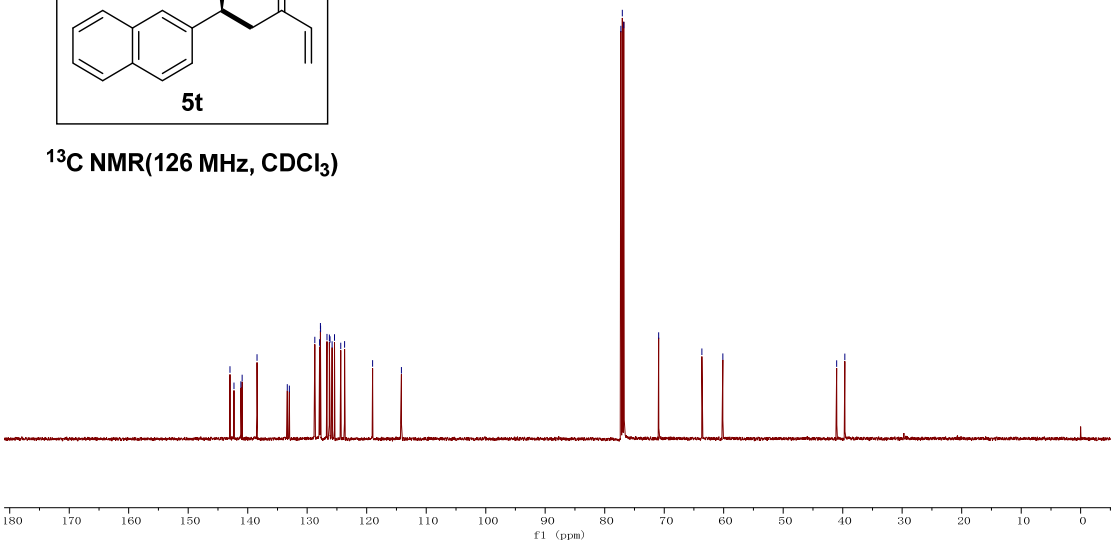


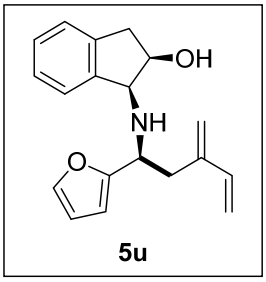
^{1}H NMR(500 MHz, $CDCl_3$)





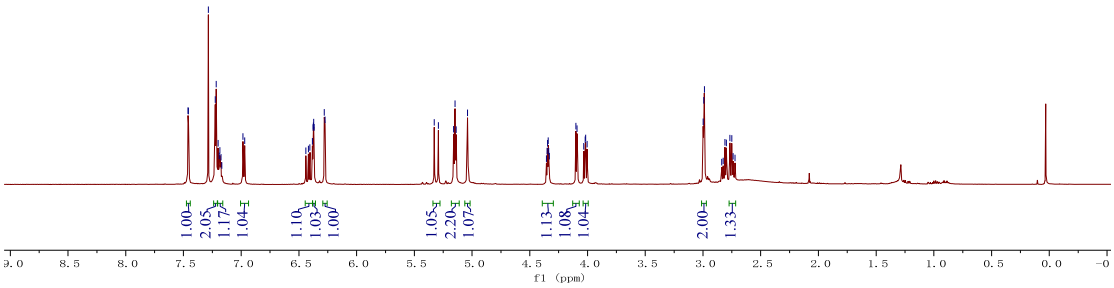
^{13}C NMR(126 MHz, $CDCl_3$)

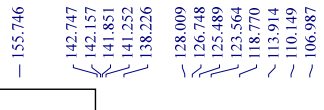


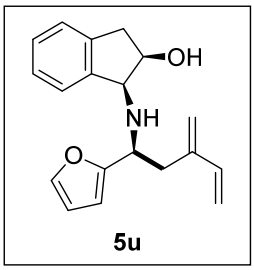


5u

^{1}H NMR(500 MHz, $CDCl_3$)

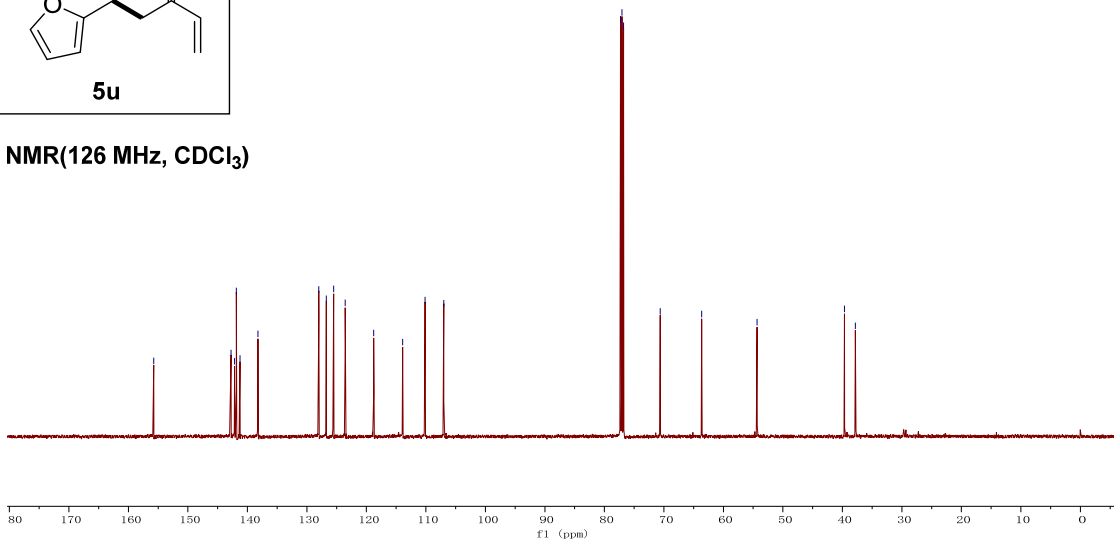


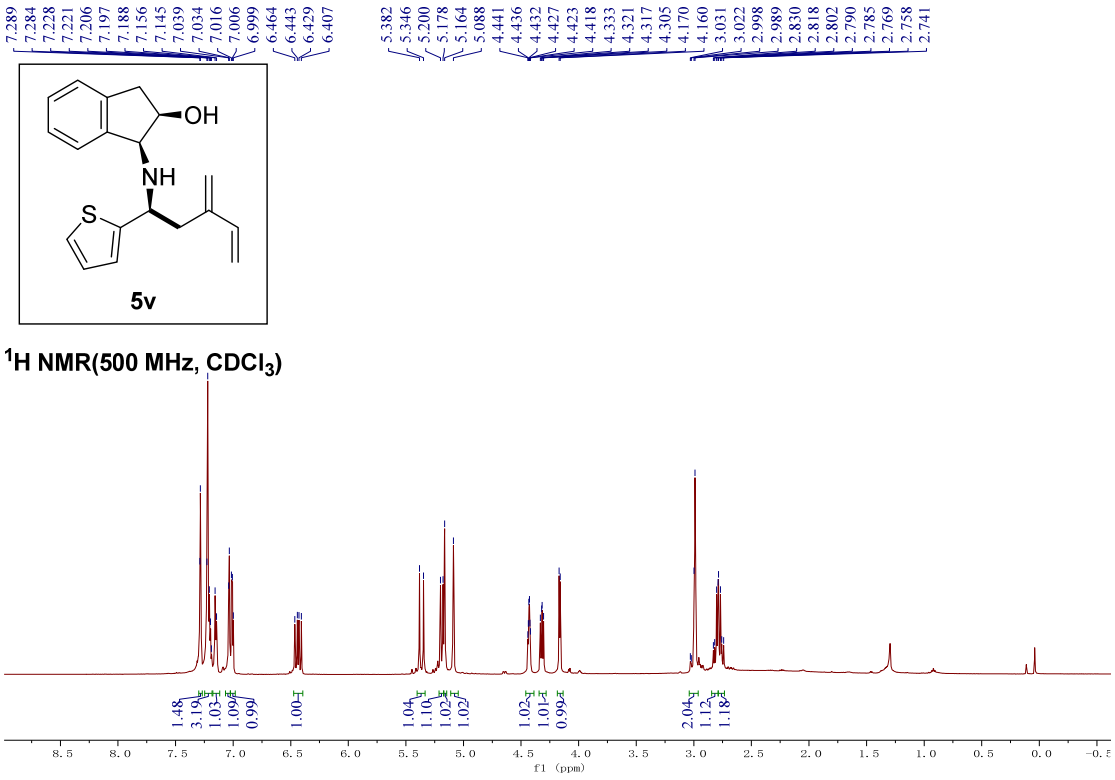




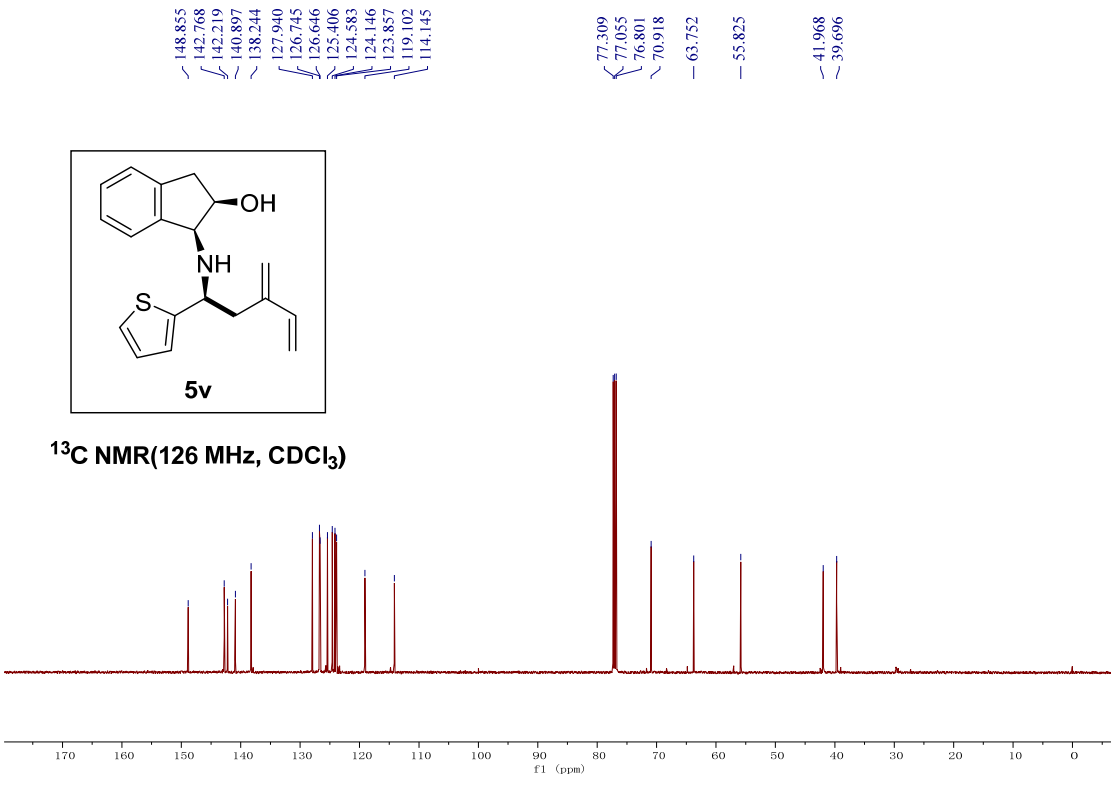
5u

^{13}C NMR(126 MHz, $CDCl_3$)

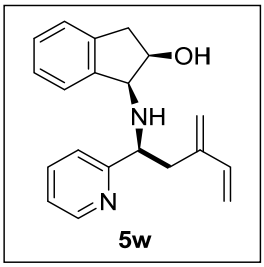




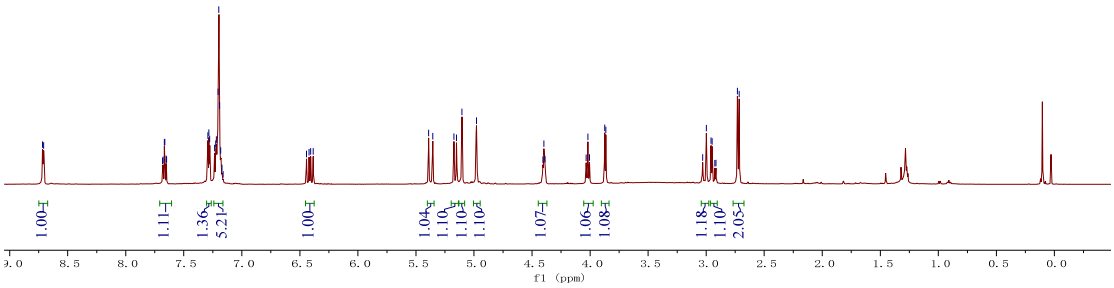
^{1}H NMR(500 MHz, $CDCl_3$)

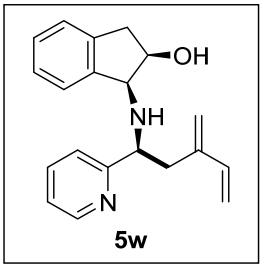


^{13}C NMR(126 MHz, $CDCl_3$)

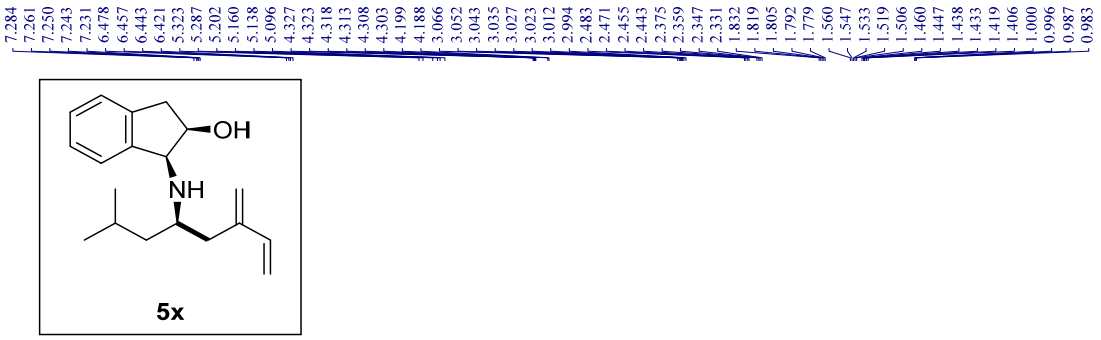


^{1}H NMR(500 MHz, $CDCl_3$)

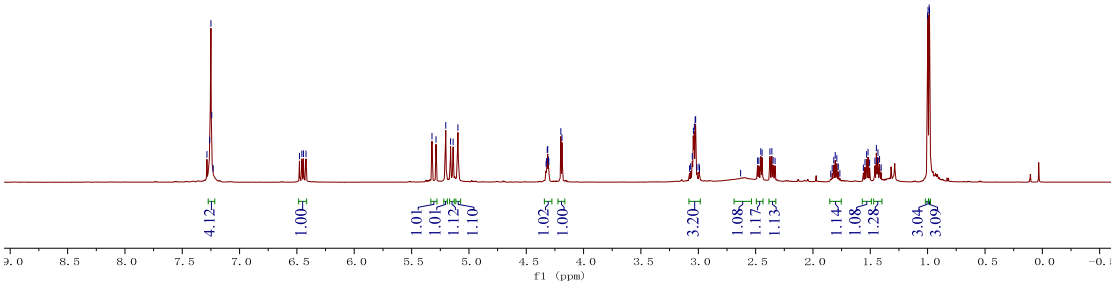


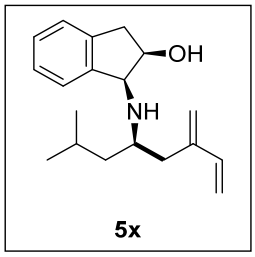


^{13}C NMR(126 MHz, $CDCl_3$)

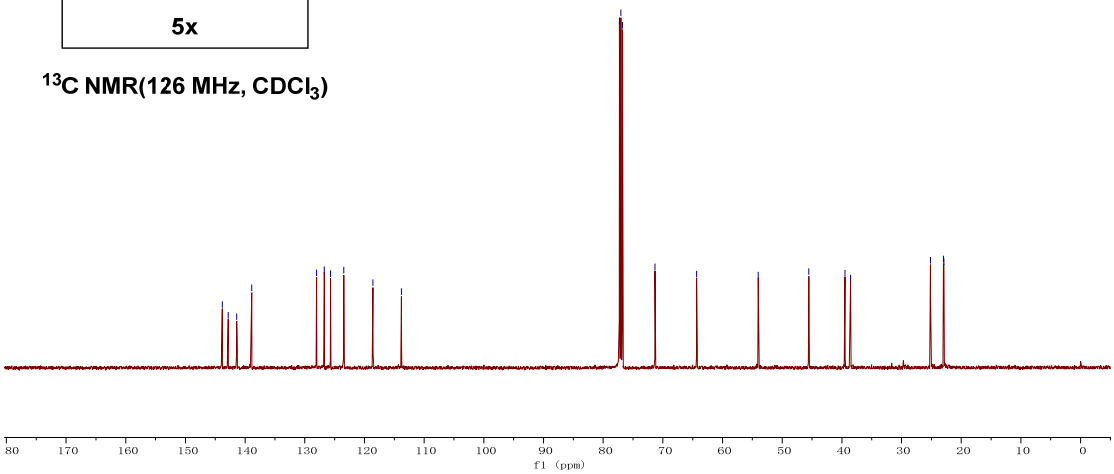


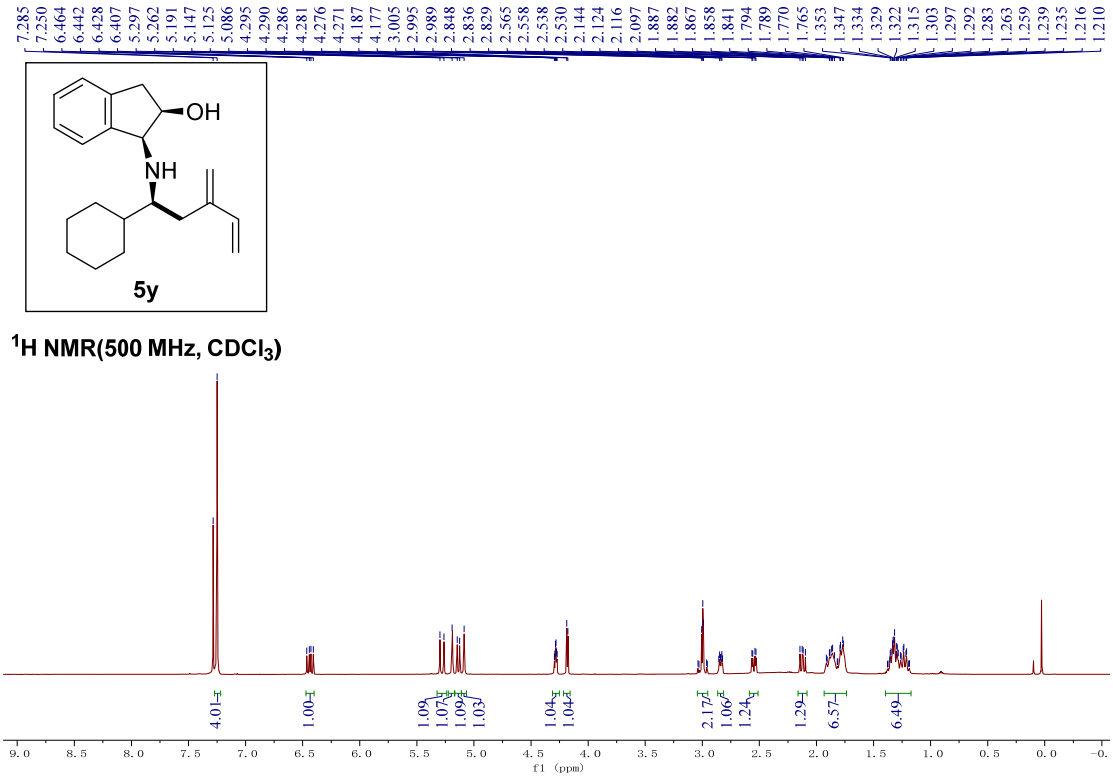
^{1}H NMR(500 MHz, $CDCl_3$)



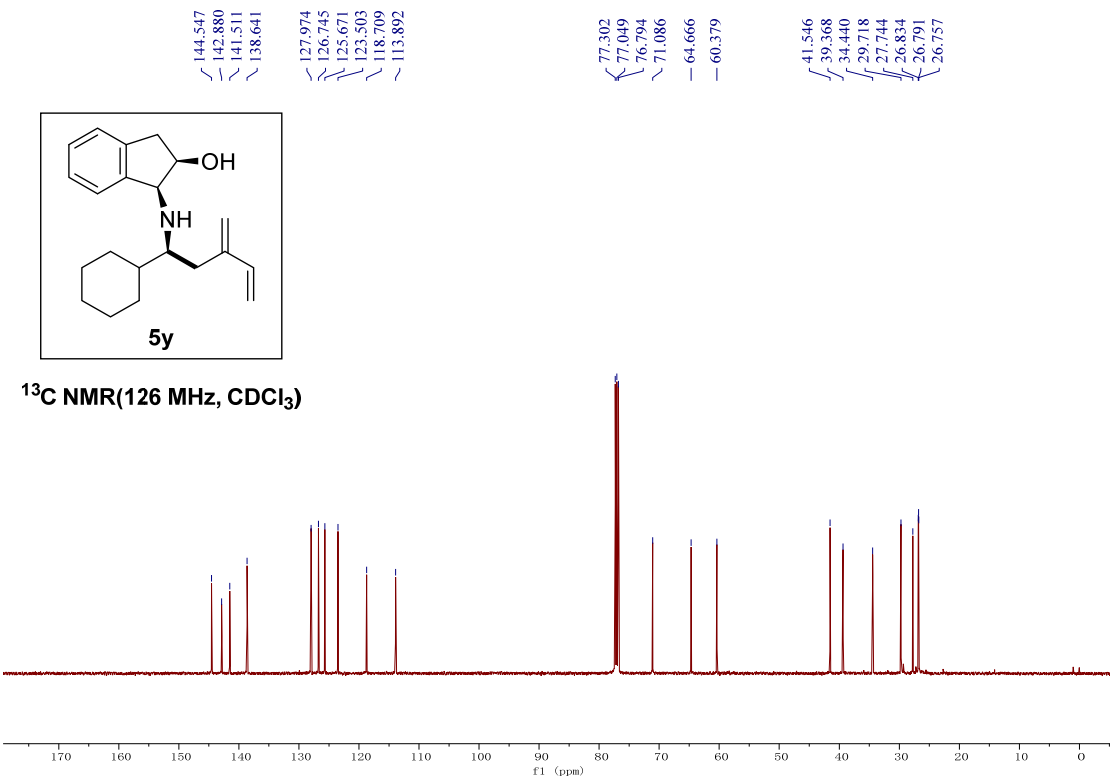


^{13}C NMR(126 MHz, $CDCl_3$)

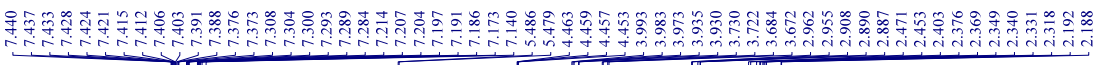


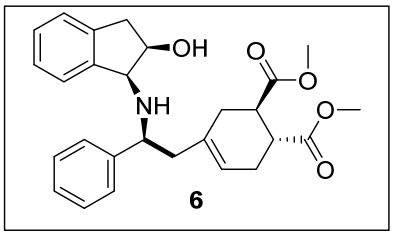


^{1}H NMR(500 MHz, $CDCl_3$)

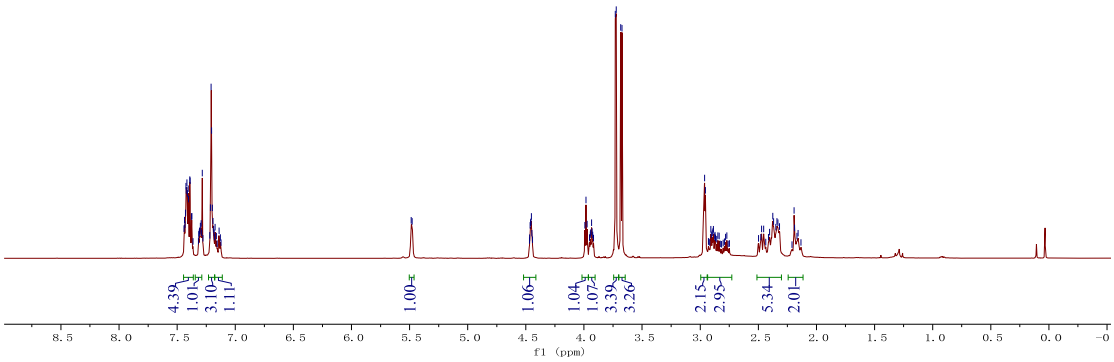


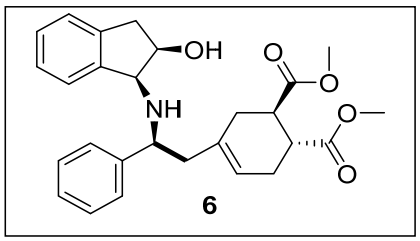
^{13}C NMR(126 MHz, $CDCl_3$)



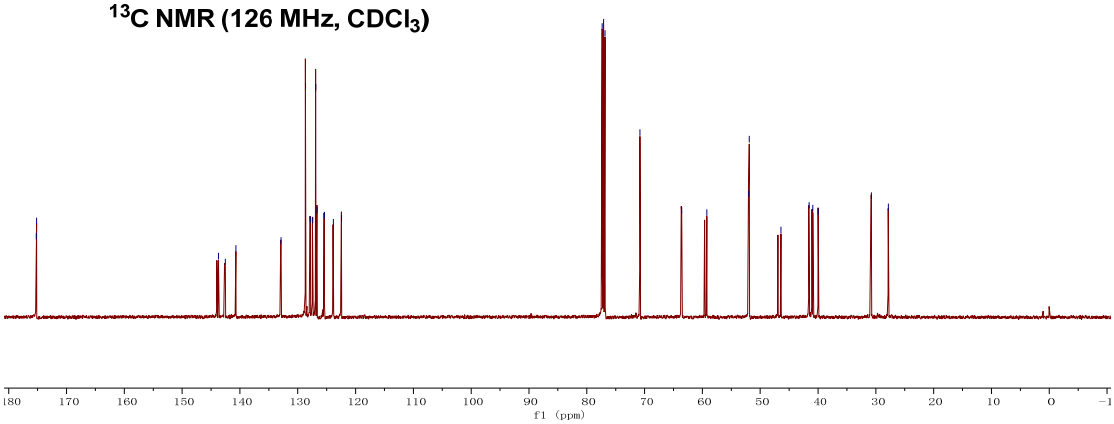


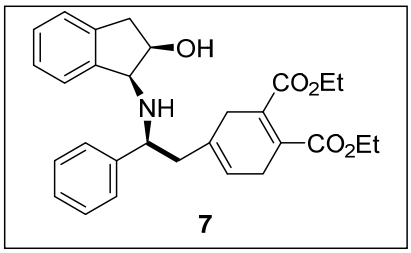
^{1}H NMR (500 MHz, $CDCl_3$)





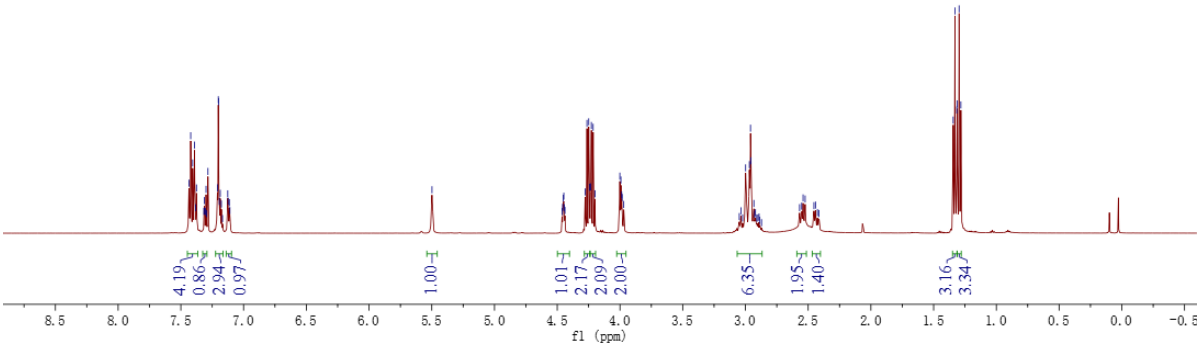
^{13}C NMR (126 MHz, $CDCl_3$)

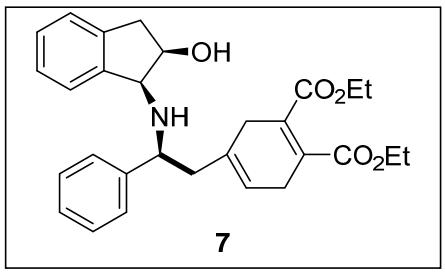




7

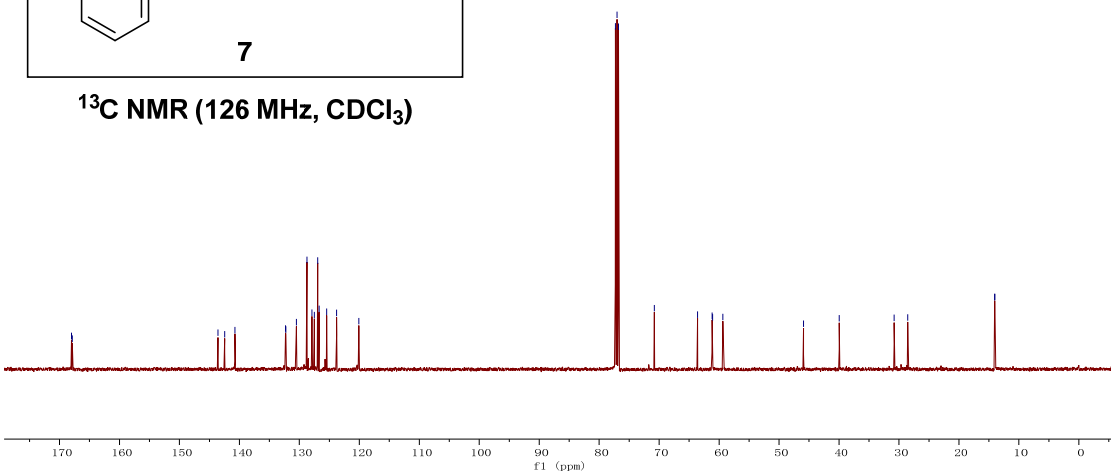
^{1}H NMR (500 MHz, $CDCl_3$)

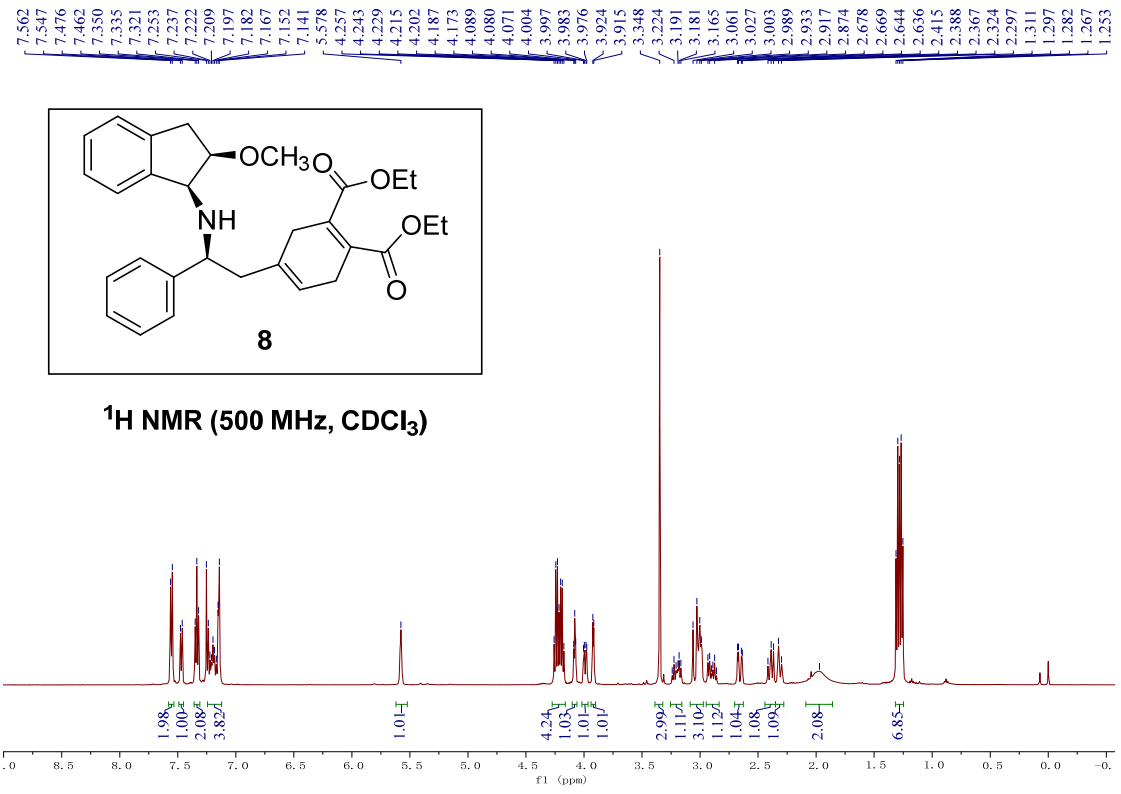


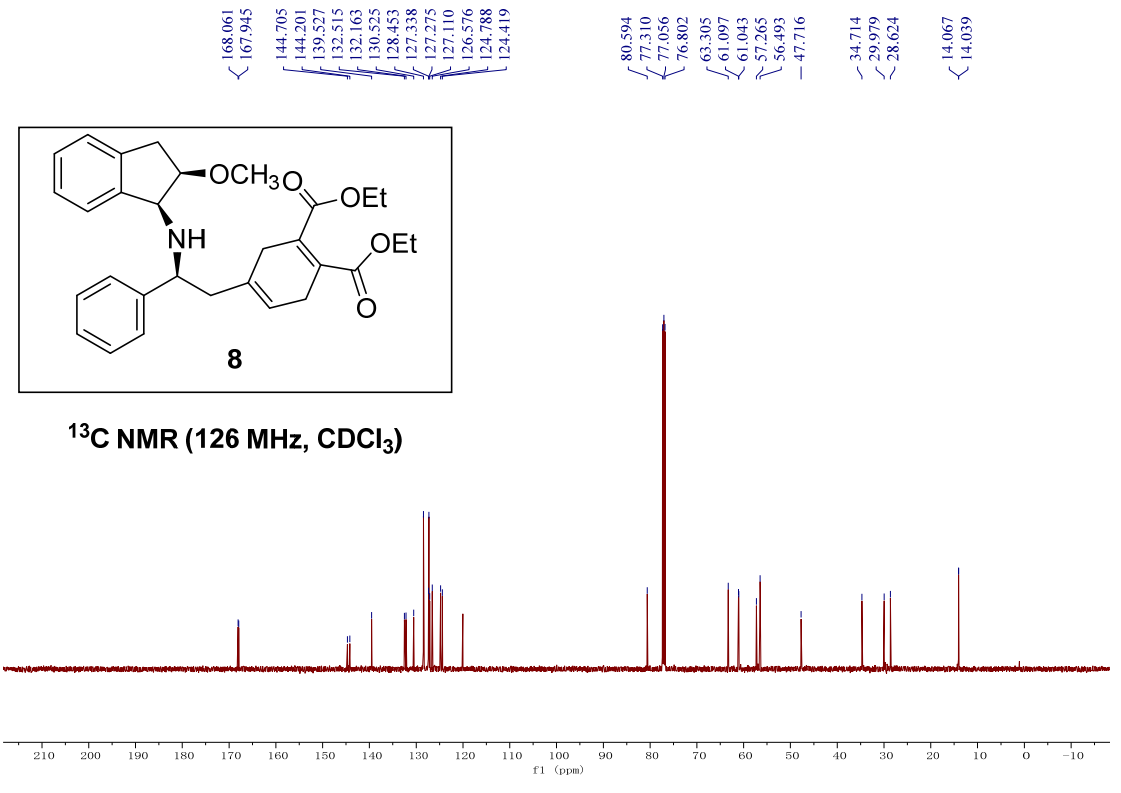


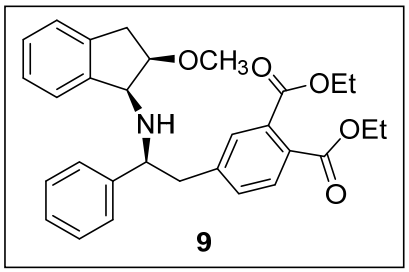
7

^{13}C NMR (126 MHz, $CDCl_3$)



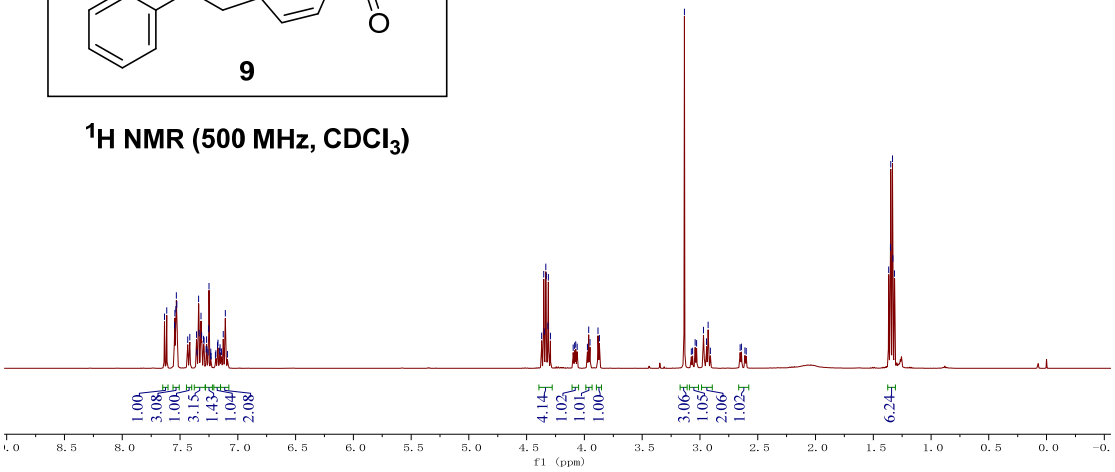

OCH3
O
OEt
NH
OEt
O
8
1H NMR (500 MHz, CDCl3)
f1 (ppm)

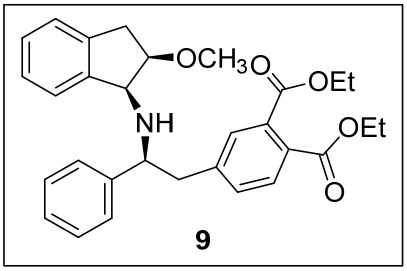

OCH3
O
OEt
NH
OEt
O
8
13C NMR (126 MHz, CDCl3)
f1 (ppm)



9

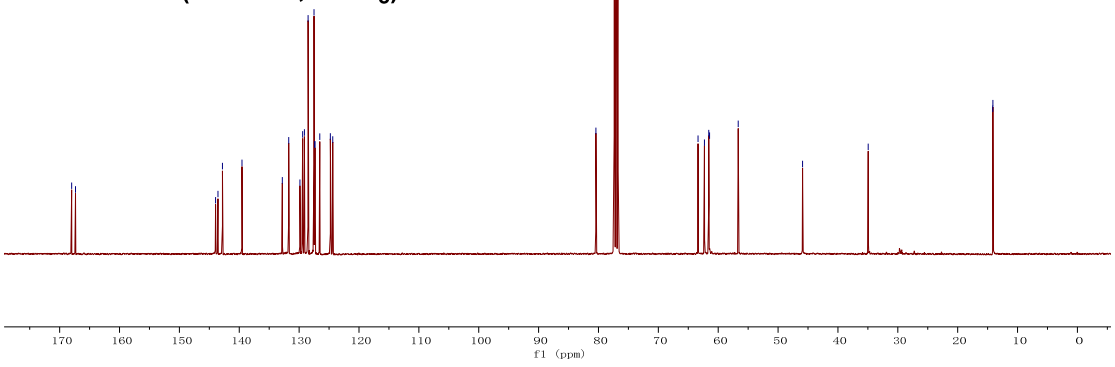
^{1}H NMR (500 MHz, $CDCl_3$)





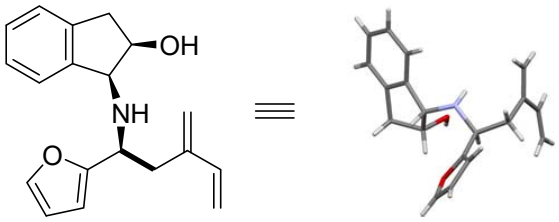
9

^{13}C NMR (126 MHz, $CDCl_3$)



X-ray crystal structure data of 5u

X-ray data of **5u** (CCDC 2023204).



5u ≡ **5u**

Table (1). Crystal data and structure refinement for **5u**.

Identification code	mo_191216e_0m	
Empirical formula	C19 H21 N O2	
Formula weight	295.37	
Temperature	273.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 27.510(2) Å	a= 90°.
	b = 5.7053(5) Å	b= 95.370(2)°.
	c = 10.3731(9) Å	g = 90°.
Volume	1620.9(2) $Å^3$	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	632	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.487 to 29.675°.	
Index ranges	-33<=h<=38, -7<=k<=7, -13<=l<=13	
Reflections collected	12012	
Independent reflections	4164 [R(int) = 0.0157]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6603	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4164 / 1 / 203
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.1025
R indices (all data)	R1 = 0.0402, wR2 = 0.1050
Absolute structure parameter	-0.6(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.262 and -0.141 e.Å^{-3}

Table (2). Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5u**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5966(1)	9560(3)	-86(1)	29(1)
C(2)	5896(1)	6911(3)	186(2)	32(1)
C(3)	5605(1)	6062(3)	-1064(2)	37(1)
C(4)	5816(1)	7521(3)	-2085(2)	34(1)
C(5)	6023(1)	9548(3)	-1526(2)	32(1)
C(6)	6243(1)	11184(3)	-2265(2)	40(1)
C(7)	6252(1)	10781(4)	-3586(2)	49(1)
C(8)	6049(1)	8760(5)	-4141(2)	52(1)
C(9)	5831(1)	7095(4)	-3398(2)	45(1)
C(10)	6377(1)	10509(3)	2089(2)	33(1)
C(11)	5940(1)	11588(3)	2607(2)	36(1)
C(12)	5868(1)	13729(4)	3084(2)	44(1)
C(13)	5384(1)	13789(5)	3459(2)	56(1)
C(14)	5193(1)	11706(6)	3176(2)	64(1)
C(15)	6844(1)	11716(4)	2710(2)	44(1)
C(16)	7308(1)	10691(5)	2292(2)	61(1)
C(17)	7476(1)	8462(7)	2859(4)	88(1)
C(18)	7306(2)	7353(6)	3785(4)	98(1)
C(19)	7559(1)	11845(10)	1422(3)	95(1)

N(1)	6364(1)	10788(2)	665(1)	31(1)
O(1)	6369(1)	5897(2)	347(1)	40(1)
O(2)	5531(1)	10285(3)	2649(2)	56(1)

Table (3). Bond lengths [Å] and angles [°] for **5u**.

C(1)-C(2)	1.553(2)
C(1)-C(5)	1.516(2)
C(1)-N(1)	1.463(2)
C(2)-C(3)	1.537(2)
C(2)-O(1)	1.420(2)
C(3)-C(4)	1.506(2)
C(4)-C(5)	1.392(2)
C(4)-C(9)	1.388(2)
C(5)-C(6)	1.383(2)
C(6)-C(7)	1.392(3)
C(7)-C(8)	1.383(3)
C(8)-C(9)	1.394(3)
C(10)-C(11)	1.494(2)
C(10)-C(15)	1.544(2)
C(10)-N(1)	1.483(2)
C(11)-C(12)	1.340(3)
C(11)-O(2)	1.352(2)
C(12)-C(13)	1.421(3)
C(13)-C(14)	1.322(4)
C(14)-O(2)	1.385(3)
C(15)-C(16)	1.505(3)
C(16)-C(17)	1.458(5)
C(16)-C(19)	1.358(5)
C(17)-C(18)	1.276(6)
C(5)-C(1)-C(2)	101.57(12)
N(1)-C(1)-C(2)	117.93(13)
N(1)-C(1)-C(5)	112.61(13)
C(3)-C(2)-C(1)	102.52(13)
O(1)-C(2)-C(1)	106.92(13)
O(1)-C(2)-C(3)	111.76(14)

C(4)-C(3)-C(2)	102.38(13)
C(5)-C(4)-C(3)	109.63(14)
C(9)-C(4)-C(3)	129.99(17)
C(9)-C(4)-C(5)	120.38(17)
C(4)-C(5)-C(1)	109.74(13)
C(6)-C(5)-C(1)	129.37(15)
C(6)-C(5)-C(4)	120.89(15)
C(5)-C(6)-C(7)	118.85(17)
C(8)-C(7)-C(6)	120.34(19)
C(7)-C(8)-C(9)	121.00(18)
C(4)-C(9)-C(8)	118.53(19)
C(11)-C(10)-C(15)	109.39(14)
N(1)-C(10)-C(11)	111.67(13)
N(1)-C(10)-C(15)	107.96(13)
C(12)-C(11)-C(10)	131.28(17)
C(12)-C(11)-O(2)	109.74(16)
O(2)-C(11)-C(10)	118.98(16)
C(11)-C(12)-C(13)	107.3(2)
C(14)-C(13)-C(12)	106.4(2)
C(13)-C(14)-O(2)	110.18(19)
C(16)-C(15)-C(10)	113.72(16)
C(17)-C(16)-C(15)	118.0(3)
C(19)-C(16)-C(15)	120.1(3)
C(19)-C(16)-C(17)	122.0(3)
C(18)-C(17)-C(16)	127.7(3)
C(1)-N(1)-C(10)	115.18(12)
C(11)-O(2)-C(14)	106.40(18)

Symmetry transformations used to generate equivalent atoms:

Table (4). Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5u**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

C(1)	34(1)	28(1)	27(1)	0(1)	4(1)	1(1)
C(2)	37(1)	30(1)	31(1)	2(1)	4(1)	-3(1)
C(3)	39(1)	35(1)	38(1)	-2(1)	1(1)	-7(1)
C(4)	35(1)	36(1)	32(1)	-1(1)	0(1)	0(1)
C(5)	35(1)	32(1)	28(1)	1(1)	4(1)	2(1)
C(6)	46(1)	38(1)	36(1)	3(1)	6(1)	-3(1)
C(7)	59(1)	55(1)	36(1)	8(1)	13(1)	-2(1)
C(8)	63(1)	64(1)	30(1)	-3(1)	7(1)	2(1)
C(9)	52(1)	48(1)	34(1)	-8(1)	-1(1)	-2(1)
C(10)	39(1)	31(1)	28(1)	0(1)	0(1)	2(1)
C(11)	40(1)	42(1)	27(1)	3(1)	3(1)	3(1)
C(12)	46(1)	40(1)	48(1)	-2(1)	10(1)	3(1)
C(13)	52(1)	72(2)	46(1)	-9(1)	8(1)	17(1)
C(14)	41(1)	95(2)	56(1)	-4(1)	10(1)	-4(1)
C(15)	41(1)	47(1)	41(1)	-11(1)	-4(1)	1(1)
C(16)	41(1)	76(2)	63(1)	-21(1)	-4(1)	3(1)
C(17)	63(2)	82(2)	112(3)	-26(2)	-27(2)	26(2)
C(18)	99(2)	64(2)	119(3)	8(2)	-51(2)	5(2)
C(19)	56(1)	138(3)	94(2)	-24(2)	25(1)	-15(2)
N(1)	36(1)	30(1)	29(1)	-2(1)	5(1)	-2(1)
O(1)	42(1)	29(1)	48(1)	4(1)	-1(1)	1(1)
O(2)	51(1)	57(1)	62(1)	-8(1)	8(1)	-9(1)

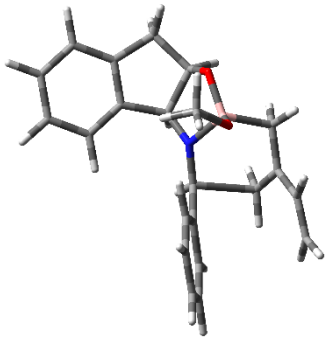
Table (5). Hydrogen coordinates (x 10^4) and isotropic isplacement parameters (Å^{2}x 10^3) for **5u**.

	x	y	z	U(eq)
H(1)	5660	10368	46	35
H(2)	5717	6657	946	39
H(3A)	5656	4403	-1204	45
H(3B)	5259	6357	-1044	45
H(6)	6383	12531	-1886	48
H(7)	6394	11876	-4097	59
H(8)	6058	8508	-5024	63

H(9)	5699	5729	-3773	54
H(10)	6389	8836	2305	39
H(12)	6093	14949	3157	53
H(13)	5233	15045	3829	68
H(14)	4876	11260	3312	76
H(15A)	6830	13367	2487	52
H(15B)	6850	11596	3644	52
H(17)	7738	7766	2502	105
H(18A)	7044	7965	4180	117
H(18B)	7444	5934	4066	117
H(19A)	7848	11216	1170	114
H(19B)	7443	13265	1077	114
H(1A)	6645(8)	10230(40)	450(20)	38
H(1B)	6345	4470	413	60

Table (6). Torsion angles [°] for **5u**.

Computational data



TS-Si (0.0 kcal/mol):

#P M06L/6-31G(d,p) opt=(calcfc,noeigentest,ts) freq=noraman SCRF=(SMD,Solvent=DiMethylSulfoxide)

Sum of electronic and thermal Free Energies = -1082.428760

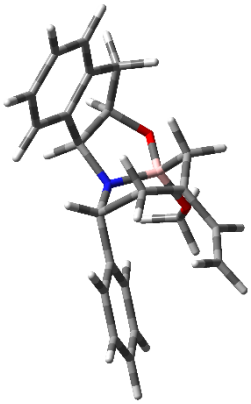
0 1

C	-0.66137565	0.52910050	0.00000000
C	0.53028835	-0.06511550	0.42733800
C	1.59057935	0.73035750	0.85379700
C	1.44108635	2.11768450	0.85630600
C	0.24328035	2.70568950	0.44429100
C	-0.81997265	1.91073550	0.01629400
C	-1.66416765	-0.52472250	-0.40549400
C	-1.06138965	-1.82341850	0.17815700
C	0.43770735	-1.56147650	0.33354700
O	-1.67469465	-1.97263550	1.43796400
N	-2.94758565	-0.34381350	0.27552400
C	-3.94810865	0.22056550	-0.42243800

C	-4.04675165	-2.68590450	0.60241600
C	-5.22160065	-2.05820350	0.05674400
C	-5.10415965	-1.40002350	-1.16197000
B	-3.03818865	-1.49747850	1.36751800
O	-3.61788465	-1.20525250	2.63305500
C	-4.98615165	1.06031650	0.20956700
C	-6.02678865	1.57521750	-0.57848800
C	-7.01057665	2.38068750	-0.01977000
C	-6.96908265	2.69532650	1.33940300
C	-5.92352265	2.21560650	2.12345600
C	-4.93563165	1.40931250	1.56339200
H	2.52096035	0.27911250	1.19184100
H	2.26143735	2.74706150	1.19162400
H	0.13824735	3.78718750	0.46345600
H	-1.76175165	2.36316850	-0.29072500
H	-1.79875465	-0.56176850	-1.49641700
H	-1.26698265	-2.69779950	-0.46102600
H	0.98724235	-1.93222050	-0.54150300
H	0.84245735	-2.08344550	1.20646900
H	-3.69360465	0.53356350	-1.43896900
H	-4.24543665	-3.37982950	1.42314100
H	-3.41266765	-3.14716950	-0.15870200
H	-5.95429765	-0.89081450	-1.60689100
H	-4.34508265	-1.73757050	-1.86426100
H	-6.06250465	1.33319950	-1.63865600
H	-7.81115465	2.76683150	-0.64504600
H	-7.73946465	3.32325550	1.77861400
H	-5.86894165	2.47601950	3.17729100
H	-4.10633165	1.05859450	2.16506500
C	-6.37304065	-1.86279650	0.93177200
H	-6.22655765	-2.17815650	1.96498400
C	-7.55547065	-1.34066950	0.57489800
H	-7.77423965	-1.03556250	-0.44615900
H	-8.35585865	-1.21803450	1.29882600
C	-2.78333865	-0.50254750	3.51777200
H	-1.99458365	-1.13932550	3.94262600
H	-2.27944265	0.35509850	3.03811100
H	-3.38965065	-0.11483550	4.34526900

TS-Re (4.4 kcal/mol):

#P M06L/6-31G(d,p) opt=(calcfc,noeigentest,ts) freq=noraman SCRF=(SMD,Solvent=DiMethylSulfoxide)



Sum of electronic and thermal Free Energies = -1082.421681

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C	-1.40211638	0.01763668	0.00000000
C	-2.36435438	0.58991668	0.84078700
C	-3.35138238	-0.20619632	1.41892700
C	-3.37757338	-1.57204532	1.14071700
C	-2.44464038	-2.13516632	0.26814200
C	-1.45867538	-1.34049832	-0.31459500
C	-0.41644838	1.05155468	-0.47744500
C	-0.97798638	2.41006268	0.04589800
C	-2.18486438	2.07244868	0.95374100
O	0.05471862	3.08796768	0.71411100
N	0.95626262	0.99076368	0.07994900
C	1.58359562	-0.19499332	0.14525600
C	0.73427562	1.39310668	2.63752300
C	1.59523662	0.25052968	2.77311100
C	1.22178162	-0.92238432	2.12663700
B	1.09482962	2.17986868	1.11434200
O	2.36058062	2.80099568	1.30888700
C	3.05437362	-0.31601232	0.04817600
C	3.66739862	-1.56209032	0.25449200
C	5.04657262	-1.70100732	0.16489500
C	5.84365462	-0.59833032	-0.14530900
C	5.24258962	0.63147868	-0.39875700
C	3.85973362	0.76954568	-0.31171900
H	-4.10006438	0.23438468	2.07375000
H	-4.14322738	-2.19958332	1.58948400
H	-2.49360038	-3.19494432	0.03330900
H	-0.75577238	-1.77959932	-1.01861900
H	-0.32091338	1.03210768	-1.57044100
H	-1.31019038	3.03322268	-0.79371300
H	-3.08994938	2.60547268	0.64040900
H	-1.98192438	2.39789768	1.98080300
H	1.04912562	-1.04857032	-0.27525500
H	-0.32399338	1.12793368	2.60687400
H	0.92215762	2.19976768	3.35033600
H	1.84779462	-1.80887332	2.17075000
H	0.16319062	-1.10808932	1.95706700

H	3.05368362	-2.42605232	0.49988600
H	5.50231462	-2.67233732	0.33680000
H	6.92305562	-0.70481032	-0.20797500
H	5.84949262	1.48975968	-0.67544100
H	3.39038162	1.71479768	-0.54976800
C	2.94406162	0.44520468	3.29655600
H	3.21932962	1.48137868	3.49089500
C	3.83286362	-0.52593532	3.55091000
H	3.60179562	-1.57926432	3.40507500
H	4.82371862	-0.29625932	3.93217300
C	2.68940062	3.83263768	0.41528800
H	2.17383862	4.77296468	0.65672400
H	3.76987562	4.01628068	0.46907100
H	2.44008762	3.59137868	-0.63108000