# Enantioselective Synthesis of Polycyclic Pyrrole Derivatives by Iridium-Catalyzed Asymmetric Allylic Dearomatization and Ring-expansive Migration Reactions

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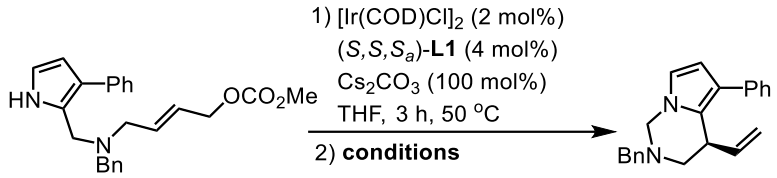
## General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian instrument (400 MHz and 101 Hz respectively) or an Agilent instrument (400, 600 MHz and 101, 151 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protic solvent signals. $^{19}F$ NMR spectra were recorded on a Varian instrument (376 MHz, respectively) and referenced relative to $CFCl_3$. Data for $^{1}H$ NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for $^{13}C$ NMR are reported in terms of chemical shift (δ, ppm).

## Optimization of Reaction Conditions

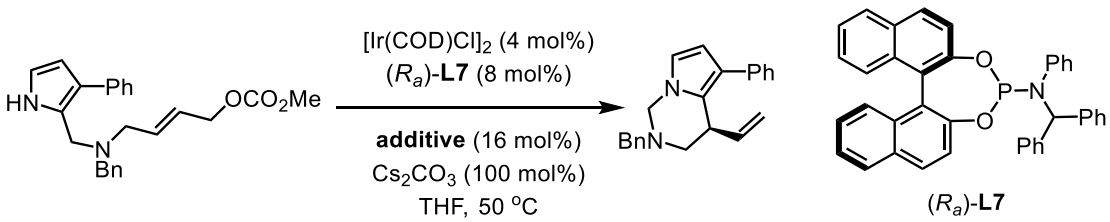
**Table S1.** Screening of post-process conditions.[a]




| entry | **conditions** | time (h) | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | THF/50 °C | 72 | 52 | 83 |
| 2 | THF/100 °C | 15 | 55 | 83 |
| 3 | dioxane/100 °C | 10 | 63 | 84 |
| 4 | toluene/100 °C | 10 | 53 | 83 |
| 5[d] | $HCO_2H$/THF/50 °C | 15 | < 5 | --- |
| 6[e] | HOAc/THF/50 °C | 72 | < 5 | --- |
| 7[f] | TsOH·$H_2O$/THF/50 °C | 72 | 36 | 85 |
| 8 | THF/50 °C | 11 | 57 | 84 |

[a] Reaction conditions: **1a** (0.2 mmol), $[Ir(cod)Cl]_2$ (2 mol%), **L1** (4 mol%) and $Cs_2CO_3$ (100 mol%) in THF (4 mL) at 50 °C. Catalyst was prepared by $^nPrNH_2$ activation. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase. [d] $HCO_2H$ (0.5 mL)/THF (1 mL). [e] HOAc (0.5 mL)/THF (1 mL). [f] TsOH·$H_2O$ (30 mol%).

**Table S2.** Screening of additives.[a]

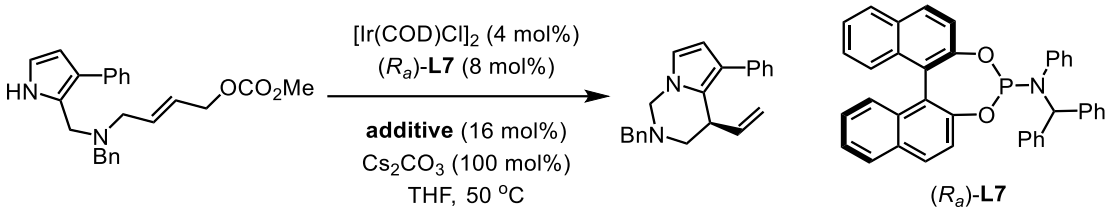



| entry | **additive** | time (h) | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | Ag(*S*)-TRIP-CPA | 10 | 67 | 96 |

| | | | | |
|---|---|---|---|---|
| 2 | $Ag_2CO_3$ | 10 | 62 | 96 |
| 3 | AgOAc | 10 | 65 | 95 |
| 4 | AgOTf | 10 | 65 | 96 |
| 5 | $AgBF_4$ | 10 | 36 | 95 |

[a] Reaction conditions: **1a** (0.2 mmol), $[Ir(cod)Cl]_2$ (4 mol%), **L7** (8 mol%), additive (16 mol%) and $Cs_2CO_3$ (100 mol%) in THF (4 mL) at 50 °C. Catalyst was prepared by $^nPrNH_2$ activation. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase.

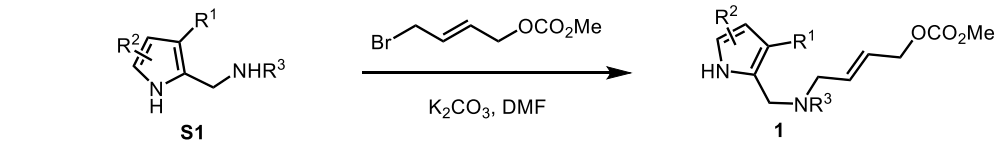
**Table S3.** Screening of concentration.[a]




| entry | **additive** | *c* (mol/L) | time (h) | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|---|
| 1 | Ag(*S*)-TRIP-CPA | 0.05 | 10 | 67 | 96 |
| 2 | Ag(*S*)-TRIP-CPA | 0.02 | 35 | 45 | 93 |
| 3 | Ag(*S*)-TRIP-CPA | 0.01 | 35 | 49 | 95 |
| 4 | AgOAc | 0.05 | 10 | 65 | 95 |
| 5 | AgOAc | 0.02 | 35 | 53 | 95 |
| 6 | AgOAc | 0.01 | 35 | 45 | 95 |
| 7 | AgOTf | 0.05 | 10 | 65 | 96 |
| 8 | AgOTf | 0.02 | 14 | 73 | 97 |
| 9 | AgOTf | 0.01 | 14 | 72 | 96 |

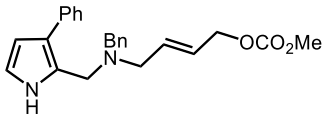
[a] Reaction conditions: **1a** (0.2 mmol), $[Ir(cod)Cl]_2$ (4 mol%), **L7** (8 mol%), additive (16 mol%) and $Cs_2CO_3$ (100 mol%) in THF at 50 °C. Catalyst was prepared by $^nPrNH_2$ activation. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase.

**General procedure for the synthesis of substituted pyrrole tethered allylic carbonates**

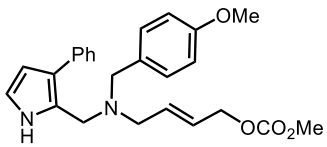



(1*H*-Pyrrol-2-yl)methanamine derivatives **S1** were synthesized according to literature procedures.[1-3]

(*E*)-4-Bromobut-2-en-1-yl methyl carbonate (0.50 g, 2.4 mmol, 1.2 equiv) was added to a solution of **S1** (2 mmol, 1 equiv) and $K_2CO_3$ (0.55 g, 4 mmol, 2 equiv) in DMF (25 mL). The reaction mixture was stirred at rt for 12 h, the starting material was consumed completely as monitored by TLC. Then the crude reaction mixture was quenched with water and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 4/1, 2/1) to afford the desired product (**1a-1s**).

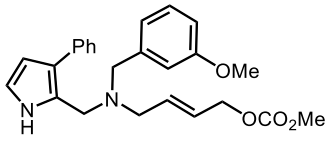



**1a**, viscous yellow oil, 1.82 g, 34% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.35-7.34 (m, 4H), 7.30-7.25 (m, 4H), 7.23-7.18 (m, 2H), 6.76 (t, $J$ = 2.8 Hz, 1H), 6.31 (t, $J$ = 2.8 Hz, 1H), 5.89-5.74 (m, 1H), 5.73-5.60 (m, 1H), 4.55 (d, $J$ = 6.0 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 2H), 3.54 (s, 2H), 3.04 (d, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.7, 138.9, 136.8, 133.1, 128.9, 128.44, 128.41, 128.1, 127.2, 126.6, 125.9, 125.5, 122.7, 116.7, 108.9, 68.0, 58.3, 55.2, 54.9, 49.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3423, 3026, 2803, 1743, 1601, 1500, 1442, 1377, 1257, 1116, 940, 791, 766, 724, 697, 562. HRMS-ESI calcd for $C_{24}H_{27}N_2O_3$ $[M+H]^+$: 391.2016, Found: 391.2015.

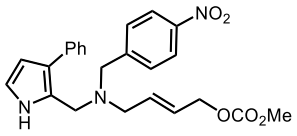



**1b**, viscous yellow oil, 718.1 mg, 41% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (s,

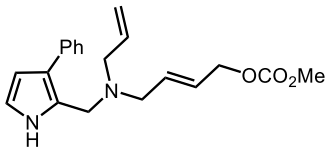
1H), 7.40-7.29 (m, 4H), 7.19-7.12 (m, 3H), 6.78 (d, $J$ = 8.4 Hz, 2H), 6.70 (t, $J$ = 2.4 Hz, 1H), 6.30 (t, $J$ = 2.4 Hz, 1H), 5.85-5.71 (m, 1H), 5.69-5.56 (m, 1H), 4.51 (d, $J$ = 6.0 Hz, 2H), 3.71 (s, 6H), 3.66 (s, 2H), 3.44 (s, 2H), 2.98 (d, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.6, 155.5, 136.7, 132.9, 130.5, 130.0, 128.3, 127.9, 126.3, 125.8, 125.2, 122.5, 116.6, 113.6, 108.7, 67.8, 57.4, 55.1, 54.8, 54.7, 49.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3417, 2953, 2832, 1743, 1606, 1507, 1442, 1245, 1175, 1099, 1032, 940, 764, 725, 700, 519. HRMS-ESI calcd for $C_{25}H_{29}N_2O_4$ $[M+H]^+$: 421.2122, Found: 421.2110.



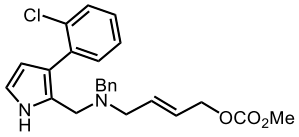

**1c**, viscous yellow oil, 564.3 mg, 34% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.38-7.28 (m, 4H), 7.22-7.14 (m, 2H), 6.84 (d, $J$ = 7.6 Hz, 2H), 6.75 (d, $J$ = 8.4 Hz, 1H), 6.70 (s, 1H), 6.30 (s, 1H), 5.84-5.72 (m, 1H), 5.71-5.58 (m, 1H), 4.51 (d, $J$ = 6.0 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 5H), 3.49 (s, 2H), 3.01 (d, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.7, 155.7, 140.5, 136.8, 132.9, 129.4, 128.4, 128.1, 126.6, 125.8, 125.4, 122.7, 121.2, 116.8, 114.6, 112.3, 108.9, 67.9, 58.2, 55.2, 54.9, 49.6. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3421, 3026, 2951, 2807, 1741, 1603, 1504, 1442, 1376, 1256, 1087, 1030, 939, 791, 766, 724, 698, 575. HRMS-ESI calcd for $C_{25}H_{29}N_2O_4$ $[M+H]^+$: 421.2122, Found: 421.2112.



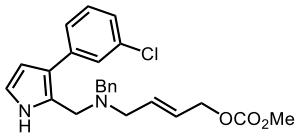

**1d**, viscous yellow oil, 384.7 mg, 26% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.10 (d, $J$ = 8.4 Hz, 2H), 7.41-7.33 (m, 6H), 7.25-7.21 (m, 1H), 6.77 (s, 1H), 6.30 (s, 1H), 5.87-5.76 (m, 1H), 5.75-5.63 (m, 1H), 4.56 (d, $J$ = 5.6 Hz, 2H), 3.76 (s, 3H), 3.73 (s, 2H), 3.59 (s, 2H), 3.05 (d, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 147.0, 146.9, 136.5, 132.2, 129.3, 128.4, 128.1, 127.1, 125.6, 125.0, 123.5, 123.3, 117.1, 109.0, 67.7, 57.4, 55.5, 54.9, 49.7. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3417, 2953, 2818, 1742, 1600, 1515, 1442, 1342, 1259, 1104, 941, 844, 791, 726, 698, 566. HRMS-ESI calcd for $C_{24}H_{26}N_3O_5$ $[M+H]^+$: 436.1867, Found: 436.1866.




**1e**, viscous yellow oil, 337.7 mg, 24% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.39-7.31 (m, 4H), 7.24-7.14 (m, 1H), 6.73 (t, *J* = 2.8 Hz, 1H), 6.31 (t, *J* = 2.8 Hz, 1H), 5.85-5.71 (m, 2H), 5.70-5.59 (m, 1H), 5.17-5.06 (m, 2H), 4.53 (d, *J* = 5.6 Hz, 2H), 3.75 (s, 3H), 3.70 (s, 2H), 3.04 (s, 2H), 3.02 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.7, 135.3, 132.8, 128.3, 128.0, 126.4, 125.8, 125.3, 122.5, 117.8, 116.6, 108.8, 67.9, 56.9, 55.0, 54.8, 49.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3418, 3021, 2954, 2810, 1662, 1743, 1602, 1502, 1442, 1257, 1092, 937, 791, 765, 723, 699, 566. HRMS-ESI calcd for $C_{20}H_{25}N_2O_3$ $[M+H]^+$: 341.1860, Found: 341.1860.

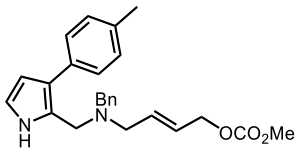



**1f**, viscous yellow oil, 369.9 mg, 18% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.45-7.39 (m, 1H), 7.27-7.19 (m, 8H), 6.77 (t, *J* = 2.8 Hz, 1H), 6.25 (t, *J* = 2.8 Hz, 1H), 5.83-5.71 (m, 1H), 5.70-5.58 (m, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 3.49 (d, *J* = 2.4 Hz, 4H), 2.99 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 138.9, 135.5, 133.8, 133.1, 132.3, 129.67, 128.8, 128.3, 127.6, 127.1, 126.9, 126.4, 120.0, 116.3, 110.3, 67.9, 58.1, 55.0, 54.9, 49.3. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3433, 3026, 2953, 2803, 1742, 1493, 1443, 1378, 1259, 1119, 1032, 941, 791, 732, 551, 460. HRMS-ESI calcd for $C_{24}H_{26}ClN_2O_3$ $[M+H]^+$: 425.1626, Found: 425.1622.

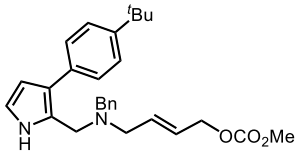



**1g**, viscous yellow oil, 489.2 mg, 44% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.38 (t, *J* = 1.6 Hz, 1H), 7.31-7.21 (m, 7H), 7.20-7.14 (m, 1H), 6.73 (t, *J* = 2.8 Hz, 1H), 6.28 (t, *J* = 2.8 Hz, 1H), 5.88-5.76 (m, 1H), 5.74-5.63 (m, 1H), 4.55 (dd, *J* = 6.0, 0.8 Hz, 2H), 3.75 (s, 3H), 3.68 (s, 2H), 3.53 (s, 2H), 3.03 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 138.7, 138.6, 134.1, 132.9, 129.6, 128.8, 128.4, 127.9,

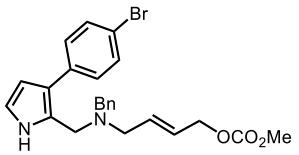
127.2, 126.6, 126.3, 126.1, 125.3, 121.3, 117.0, 108.8, 67.9, 58.3, 55.2, 54.9, 49.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3432, 3027, 2954, 2799, 1742, 1596, 1494, 1444, 1259, 1077, 941, 786, 724, 697. HRMS-ESI calcd for $C_{24}H_{26}ClN_2O_3$ $[M+H]^+$: 425.1626, Found: 425.1622.



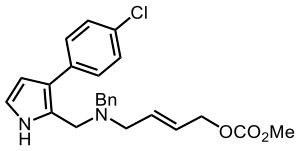

**1h**, viscous yellow oil, 482.5 mg, 47% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.30-7.24 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 2.8 Hz, 1H), 6.28 (t, *J* = 2.8 Hz, 1H), 5.88-5.76 (m, 1H), 5.74-5.61 (m, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.76 (s, 3H), 3.70 (s, 2H), 3.53 (s, 2H), 3.03 (d, *J* = 6.4 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.5, 138.8, 134.7, 133.7, 132.9, 129.0, 128.7, 128.2, 127.9, 127.0, 126.3, 125.4, 122.5, 116.6, 108.7, 67.8, 58.1, 54.9, 54.7, 49.4, 21.0. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3424, 3025, 2920, 2801, 1743, 1515, 1444, 1259, 1111, 941, 821, 791, 730, 699, 554. HRMS-ESI calcd for $C_{25}H_{29}N_2O_3$ $[M+H]^+$: 405.2173, Found: 405.2170.



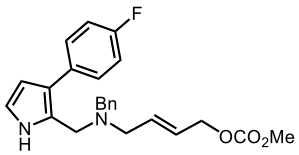

**1i**, viscous yellow oil, 323.6 mg, 40% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.22-7.18 (m, 1H), 6.70 (t, *J* = 2.8 Hz, 1H), 6.29 (t, *J* = 2.8 Hz, 1H), 5.86-5.74 (m, 1H), 5.71-5.58 (m, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 2H), 3.52 (s, 2H), 3.02 (d, *J* = 6.0 Hz, 2H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 148.0, 138.8, 133.8, 133.0, 128.8, 128.5, 128.3, 127.7, 127.1, 126.4, 125.5, 125.2, 122.5, 116.6, 108.8, 67.9, 58.2, 55.1, 54.8, 49.4, 34.4, 31.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3417, 2957, 2867, 2803, 1744, 1513, 1444, 1363, 1260, 1116, 942, 834, 791, 726, 568. HRMS-ESI calcd for $C_{28}H_{35}N_2O_3$ $[M+H]^+$: 447.2642, Found: 447.2639.



**1j**, viscous yellow oil, 184.5 mg, 30% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.49-7.40 (m, 2H), 7.29-7.17 (m, 7H), 6.73 (t, *J* = 2.8 Hz, 1H), 6.27 (t, *J* = 2.8 Hz, 1H), 5.92-5.62 (m, 2H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 3.66 (s, 2H), 3.52 (s, 2H), 3.02 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6, 138.6, 135.6, 132.8, 131.4, 129.6, 128.8, 128.4, 127.2, 126.6, 126.0, 121.5, 119.1, 116.9, 108.7, 67.8, 58.2, 55.2, 54.9, 49.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3429, 3026, 2955, 2802, 1743, 1495, 1443, 1258, 1070, 1008, 941, 897, 826, 790, 729, 700. HRMS-ESI calcd for $C_{24}H_{26}BrN_2O_3$ $[M+H]^+$: 469.1121, Found: 469.1121.

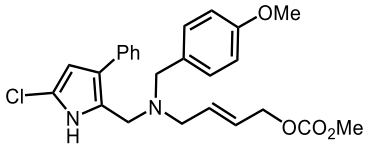



**1k**, viscous yellow oil, 505.8 mg, 22% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.33-7.16 (m, 9H), 6.70 (t, *J* = 2.8 Hz, 1H), 6.26 (t, *J* = 2.8 Hz, 1H), 5.85-5.73 (m, 1H), 5.72-5.58 (m, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 3.73 (s, 3H), 3.64 (s, 2H), 3.50 (s, 2H), 3.00 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.5, 138.6, 135.1, 132.7, 130.9, 129.1, 128.7, 128.4, 128.3, 127.1, 126.5, 125.9, 121.4, 116.9, 108.6, 67.7, 58.1, 55.0, 54.8, 49.4. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3432, 3027, 2954, 2802, 1743, 1498, 1444, 1258, 1091, 941, 829, 790, 732. HRMS-ESI calcd for $C_{24}H_{26}ClN_2O_3$ $[M+H]^+$: 425.1626, Found: 425.1624.

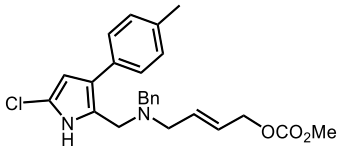



**1l**, viscous yellow oil, 192.3 mg, 33% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.37-7.23 (m, 7H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 6.26 (s, 1H), 5.88-5.76 (m, 1H), 5.74-5.63 (m, 1H), 4.56 (d, *J* = 6.0 Hz, 2H), 3.76 (s, 3H), 3.66 (s, 2H), 3.53 (s, 2H), 3.04 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 244.0 Hz), 155.6, 138.7, 132.9, 132.7 (d, *J* = 3.1 Hz), 129.5 (d, *J* = 7.7 Hz), 128.9, 128.4, 127.2, 126.6, 125.7, 121.8, 116.8, 115.2 (d, *J* = 21.1 Hz), 108.8, 67.9, 58.2, 55.1, 54.9, 49.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -118.0 (m). IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3429, 3027,

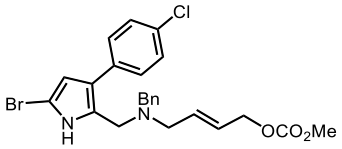
2956, 2803, 1743, 1511, 1444, 1260, 1157, 1096, 941, 836, 791, 731, 699, 593. HRMS-ESI calcd for $C_{24}H_{26}FN_2O_3$ $[M+H]^+$: 409.1922, Found: 409.1926.




**1m**, viscous yellow oil, 134.1 mg, 45% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.36-7.26 (m, 4H), 7.24-7.18 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.12 (d, *J* = 1.6 Hz, 1H), 5.87-5.74 (m, 1H), 5.71-5.60 (m, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.61 (s, 2H), 3.47 (s, 2H), 3.03 (d, *J* = 6.4 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.8, 155.7, 135.7, 132.8, 130.3, 130.2, 128.5, 128.0, 126.8, 125.9, 125.3, 123.7, 113.8, 113.2, 106.6, 67.9, 57.5, 55.3, 55.0, 54.9, 48.8. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3399, 3339, 2954, 2910, 2833, 1743, 1607, 1507, 1442, 1393, 1246, 1175, 1033, 941, 791, 760, 699, 516. HRMS-ESI calcd for $C_{25}H_{28}ClN_2O_4$ $[M+H]^+$: 455.1732, Found: 455.1725.

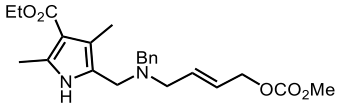



**1n**, viscous yellow oil, 116.5 mg, 36% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.32-7.13 (m, 9H), 6.09 (d, *J* = 2.8 Hz, 1H), 5.87-5.74 (m, 1H), 5.71-5.60 (m, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.76 (s, 3H), 3.62 (s, 2H), 3.52 (s, 2H), 3.03 (d, *J* = 6.0 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.7, 138.6, 135.6, 132.7, 129.2, 128.9, 128.5, 128.0, 127.3, 126.8, 124.9, 123.7, 113.1, 106.7, 67.9, 58.3, 55.2, 54.9, 49.1, 21.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3350, 3025, 2919, 2800, 1743, 1515, 1443, 1385, 1259, 1116, 941, 822, 789, 738, 698, 477. HRMS-ESI calcd for $C_{25}H_{28}ClN_2O_3$ $[M+H]^+$: 439.1783, Found: 439.1781.

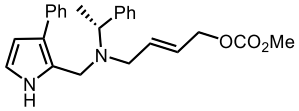



**1o**, viscous yellow oil, 199.3 mg, 49% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.34-7.16 (m, 9H), 6.19 (d, *J* = 2.8 Hz, 1H), 5.89-5.76 (m, 1H), 5.73-5.60 (m, 1H),

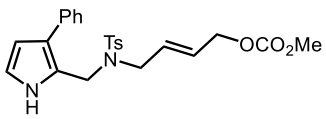
4.57 (d, *J* = 4.8 Hz, 2H), 3.78 (s, 3H), 3.61 (s, 2H), 3.53 (s, 2H), 3.05 (d, *J* = 5.2 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.7, 138.3, 134.0, 132.5, 131.7, 129.2, 128.9, 128.6, 128.5, 127.4, 127.4, 127.0, 123.5, 110.6, 97.4, 67.8, 58.3, 55.2, 55.0, 49.1. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3411, 3337, 3027, 2953, 2802, 1739, 1495, 1444, 1378, 1259, 1090, 939, 832, 789, 740, 698, 509. HRMS-ESI calcd for $C_{24}H_{25}BrClN_2O_3$ $[M+H]^+$: 503.0732, Found: 503.0726.




**1p**, pale yellow solid, m.p. = 66.6-68.7 °C, 410.0 mg, 28% yield.$^1$H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.28-7.19 (m, 5H), 5.91-5.62 (m, 2H), 4.57 (d, *J* = 5.6 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 3.51 (s, 2H), 3.41 (s, 2H), 3.02 (d, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 2.16 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.4, 155.6, 138.8, 134.9, 133.1, 128.8, 128.3, 127.0, 126.5, 123.5, 118.4, 110.7, 67.9, 59.0, 57.8, 54.8, 54.7, 48.0, 14.5, 14.0, 11.0. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3312, 3027, 2954, 2925, 2803, 1746, 1668, 1441, 1378, 1255, 1088, 942, 787, 735, 699. HRMS-ESI calcd for $C_{23}H_{31}N_2O_5$ $[M+H]^+$: 415.2227, Found: 415.2227.

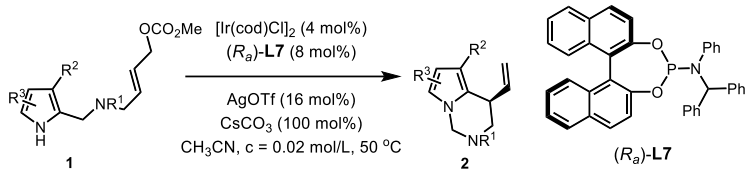



**1q**, viscous yellow oil, 204.1 mg, 36% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.38-7.26 (m, 8H), 7.24-7.16 (m, 2H), 6.76 (t, *J* = 2.8 Hz, 1H), 6.30 (t, *J* = 2.8 Hz, 1H), 5.83-5.70 (m, 1H), 5.66-5.49 (m, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 3.87 (q, *J* = 6.8 Hz, 1H), 3.80-3.68 (m, 4H), 3.63 (d, *J* = 14.4 Hz, 1H), 3.15 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.95 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.7, 142.8, 136.8, 133.7, 128.4, 128.3, 128.1, 127.8, 127.04, 126.5, 126.2, 125.3, 122.3, 116.5, 108.9, 67.9, 58.4, 54.8, 51.5, 45.7, 15.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3428, 3026, 2956, 2820, 1745, 1601, 1494, 1442, 1377, 1257, 1120, 1084, 939, 790, 763, 698, 546. HRMS-ESI calcd for $C_{25}H_{29}N_2O_3$ $[M+H]^+$: 405.2173, Found: 405.2167.

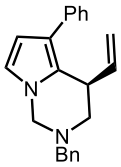


**1s**, viscous yellow oil, 346.2 mg, 22% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.72-7.64 (m, 2H), 7.32-7.18 (m, 7H), 6.79 (t, *J* = 2.8 Hz, 1H), 6.22 (t, *J* = 2.8 Hz, 1H), 5.27-5.15 (m, 1H), 5.01-4.89 (m, 1H), 4.34 (s, 2H), 4.15 (d, *J* = 5.6 Hz, 2H), 3.73 (s, 3H), 3.59 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.3, 143.6, 137.0, 136.3, 129.9, 128.43, 128.40, 127.8, 127.0, 125.8, 124.9, 122.1, 118.5, 108.6, 66.8, 54.7, 48.3, 41.3, 21.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3406, 2955, 2923, 2855, 1745, 1599, 1501, 1442, 1259, 1154, 1089, 940, 898, 730, 700, 653, 546. HRMS-ESI calcd for $C_{24}H_{30}N_3O_5S$ $[M+H]^+$: 472.1901, Found: 472.1898.

**General procedure for Ir-catalyzed asymmetric allylic dearomatization of pyrrole derivatives/migration reaction**

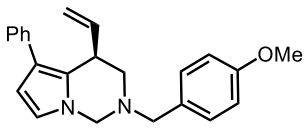



A flame-dried Schlenk tube was cooled to rt and filled with argon. To this flask were added $[Ir(cod)Cl]_2$ (5.4 mg, 0.008 mmol, 4 mol%), phosphoramidite ligand (BHPphos) **L7** (9.2 mg, 0.016 mmol, 8 mol%), THF (0.5 mL) and *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed *in vacuo* to give a pale-yellow solid. After that, substrate **1** (0.20 mmol), AgOTf (8.2 mg, 0.032 mmol, 16 mol%), $Cs_2CO_3$ (65.2 mg, 0.20 mmol, 100 mol%) and $CH_3CN$ (10 mL) were added. The reaction mixture was stirred at 50 °C for 2 h, and the starting material was consumed completely as monitored by TLC. The crude reaction mixture was quenched with water and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtrated and concentrated *in vacuo*. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1, 10/1) to afford the desired product (**2a-2r**). The analytical data of the products are summarized below.

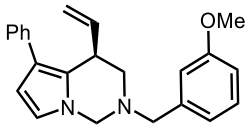



**2a**, viscous yellow oil, 48.4 mg, 77% yield, 98% ee [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 4.76 min, t (minor) = 5.13 min]. $[\alpha]_D^{29}$ = -25.0 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 8.4 Hz, 2H), 7.38-7.29 (m, 7H), 7.15 (t, $J$ = 7.2 Hz, 1H), 6.55 (d, $J$ = 2.4 Hz, 1H), 6.36 (d, $J$ = 2.4 Hz, 1H), 5.76 (ddd, $J$ = 17.2, 9.6, 7.6 Hz, 1H), 4.98-4.88 (m, 2H), 4.75 (d, $J$ = 10.0 Hz, 1H), 4.48 (d, $J$ = 10.0 Hz, 1H), 3.98 (dd, $J$ = 12.4, 6.0 Hz, 1H), 3.78 (s, 2H), 3.03 (dd, $J$ = 12.4, 5.6 Hz, 1H), 2.93 (dd, $J$ = 12.4, 6.0 Hz, 1H). $^{13}$C

NMR (101 MHz, $CDCl_3$) δ 138.9, 137.7, 136.8, 129.0, 128.6, 128.1, 128.0, 127.6, 125.2, 124.8, 121.8, 117.5, 116.0, 108.7, 66.6, 58.0, 55.6, 36.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2962, 2852, 2792, 1669, 1600, 1498, 1449, 1260, 1021, 912, 798, 738, 695. HRMS-ESI calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1856, Found: 315.1854.

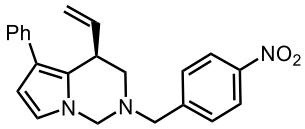



**2b**, viscous yellow oil, 51.0 mg, 74% yield, 98% ee [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 0.5 mL·$min^{-1}$, λ = 254 nm, t (major) = 16.41 min, t (minor) = 20.07 min]. $[\alpha]_D^{29}$ = -41.8 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.54 (d, *J* = 2.8 Hz, 1H), 6.35 (d, *J* = 2.8 Hz, 1H), 5.75 (ddd, *J* = 17.2, 9.6, 7.6 Hz, 1H), 4.93 (d, *J* = 16.4 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.45 (d, *J* = 10.0 Hz, 1H), 3.97 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 2H), 3.00 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.90 (dd, *J* = 12.4, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.1, 138.9, 136.7, 130.2, 129.6, 128.04, 127.97, 125.2, 124.8, 121.8, 117.5, 116.0, 113.9, 108.7, 66.5, 57.3, 55.43, 55.38, 36.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2957, 2833, 2782, 1605, 1508, 1454, 1409, 1353, 1301, 1243, 1174, 1095, 1031, 948, 911, 813, 753, 697, 515. HRMS-ESI calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1961, Found: 345.1966.

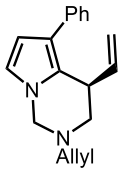



**2c**, viscous yellow oil, 56.5 mg, 82% yield, 99% ee [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 0.5 mL·$min^{-1}$, λ = 254 nm, t (major) = 16.06 min, t (minor) = 17.56 min]. $[\alpha]_D^{29}$ = -18.5 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 9.2 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 5.77 (ddd, *J* = 17.2, 10.0, 7.6 Hz, 1H), 4.94 (d, *J* = 12.8 Hz, 1H), 4.93 (d, *J* = 15.2 Hz, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.48 (d, *J* = 10.0 Hz, 1H),

3.97 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.81 (s, 3H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.72 (d, *J* = 13.6 Hz, 1H), 3.00 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.92 (dd, *J* = 12.4, 6.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.9, 139.4, 139.0, 136.7, 129.5, 128.1, 127.9, 125.2, 124.7, 121.8, 121.2, 117.5, 116.0, 114.1, 113.3, 108.7, 66.7, 57.9, 55.5, 55.3, 36.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2917, 2832, 2787, 1672, 1598, 1489, 1455, 1353, 1260, 1152, 1043, 989, 911, 758, 694. HRMS-ESI calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1961, Found: 345.1960.

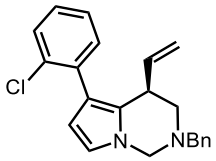



**2d**, pale yellow solid, m.p. = 71.2-74.9 °C, 45.3 mg, 63% yield, 99% ee [Daicel Chiralpak AD-H (0.46 cm × 25 cm), n-hexane/2-propanol = 95/5, *v* = 1.0 mL·$min^{-1}$, λ = 254 nm, t (major) = 14.45 min, t (minor) = 15.81 min]. $[\alpha]_D^{29}$ = -30.3 (*c* = 1.0, $CHCl_3$).$^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 5.77 (ddd, *J* = 17.6, 10.4, 7.6 Hz, 1H), 4.97 (d, *J* = 8.8 Hz, 1H), 4.94 (d, *J* = 16.4 Hz, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 3.97 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.90 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 14.4 Hz, 1H), 3.02 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.93 (dd, *J* = 12.4, 6.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.6, 138.7, 136.5, 129.4, 128.1, 127.9, 125.4, 124.4, 123.9, 122.1, 117.6, 116.4, 108.9, 66.8, 57.1, 55.6, 36.8. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 2921, 2853, 1640, 1601, 1516, 1446, 1341, 1229, 1160, 1093, 987, 906, 846, 742, 697. HRMS-ESI calcd for $C_{22}H_{22}N_3O_2$ $[M+H]^+$: 360.1707, Found: 360.1707.

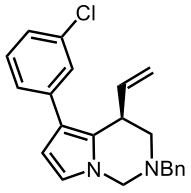



**2e**, viscous yellow oil, 37.5 mg, 71% yield, > 99% ee [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 0.5 mL·$min^{-1}$, λ = 254 nm, t (minor) = 10.72 min, t (major) = 11.76 min]. $[\alpha]_D^{29}$ = -43.8 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H),

6.58 (d, *J* = 2.8 Hz, 1H), 6.35 (d, *J* = 2.8 Hz, 1H), 5.97-5.83 (m, 1H), 5.74 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.26 (d, *J* = 20.4 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.95 (d, *J* = 17.6 Hz, 1H), 4.94 (d, *J* = 9.6 Hz, 1H), 4.76 (d, *J* = 10.0 Hz, 1H), 4.52 (d, *J* = 10.0 Hz, 1H), 3.95 (dd, *J* = 12.4, 6.0 Hz, 1H), 3.33-3.18 (m, 2H), 3.00 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.90 (dd, *J* = 12.8, 6.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.7, 134.6, 128.0, 128.0, 125.2, 124.6, 121.8, 118.7, 117.5, 116.1, 108.7, 66.6, 56.7, 55.4, 36.8. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3075, 2918, 2852, 2780, 1693, 1601, 1502, 1406, 1350, 1160, 1097, 992, 915, 791, 761, 696. HRMS-ESI calcd for $C_{18}H_{21}N_2$ $[M+H]^+$: 265.1699, Found: 265.1698.

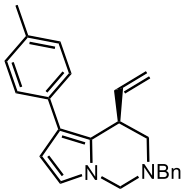



**2f**, viscous yellow oil, 46.7 mg, 67% yield, 97% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·$min^{-1}$, λ = 254 nm, t (minor) = 7.88 min, t (major) = 9.50 min]. $[\alpha]_D^{27}$ = -50.6 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 7H), 7.21-7.11 (m, 2H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.23 (d, *J* = 2.8 Hz, 1H), 5.46 (ddd, *J* = 17.2, 10.0, 8.4 Hz, 1H), 4.76 (d, *J* = 10.4 Hz, 1H), 4.75 (d. *J* = 17.2 Hz, 1H), 4.67-4.55 (m, 2H), 3.90 (dd, *J* = 14.8, 8.4 Hz, 1H), 3.82 (s, 2H), 3.07 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.81 (dd, *J* = 12.8, 8.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.3, 136.2, 134.0, 132.3, 129.0, 128.9, 128.5, 127.5, 127.4, 126.0, 125.7, 119.3, 116.4, 115.5, 109.9, 66.0, 57.1, 54.8, 36.6. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3062, 3003, 2919, 2784, 1699, 1670, 1494, 1454, 1304, 1209, 1054, 914, 746, 697, 462. HRMS-ESI calcd for $C_{22}H_{22}ClN_2$ $[M+H]^+$: 349.1466, Found: 349.1463.

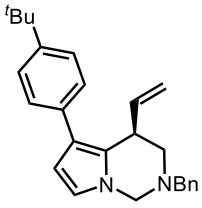



**2g**, viscous yellow oil, 56.5 mg, 81% yield, 99% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·$min^{-1}$, λ = 254 nm, t (minor) = 10.79 min, t (major) = 11.91 min]. $[\alpha]_D^{27}$ = -14.9 (*c* = 1.0, $CHCl_3$).$^1$H NMR (400 MHz, $CDCl_3$)

δ 7.41 (t, *J* = 2.0 Hz, 1H), 7.38-7.27 (m, 6H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 5.81-5.64 (m, 1H), 4.98 (d, *J* = 16.4 Hz, 1H), 4.97 (d, *J* = 10.0 Hz, 1H), 4.73 (d, *J* = 10.0 Hz, 1H), 4.47 (d, *J* = 10.0 Hz, 1H), 3.95 (dd, *J* = 13.2, 6.8 Hz, 1 H), 3.77 (s, 2H), 3.03 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.91 (dd, *J* = 12.8, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.43, 138.39, 137.5, 133.7, 129.1, 128.9, 128.5, 127.8, 127.56, 125.9, 125.1, 125.0, 120.4, 117.6, 116.4, 108.5, 66.5, 57.7, 55.4, 36.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3063, 2960, 2923, 2787, 1664, 1595, 1564, 1495 1453, 1351, 1259, 1076, 996, 916, 785, 749, 696, 614. HRMS-ESI calcd for $C_{22}H_{22}ClN_2$ $[M+H]^+$: 349.1466, Found: 349.1463.

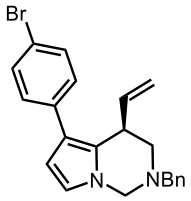



**2h**, viscous yellow oil, 40.7 mg, 62% yield, 98% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 6.96 min, t (minor) = 9.47 min]. $[\alpha]_D^{25}$ = -33.1 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 7H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 2.8 Hz, 1H), 6.33 (d, *J* = 2.8 Hz, 1H), 5.77 (ddd, *J* = 17.6, 10.0, 7.6 Hz, 1H), 4.98-4.88 (m, 2H), 4.73 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 10.0 Hz, 1H), 3.96 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.81-3.72 (m, 2H), 3.05-2.97 (m, 1H), 2.91 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.7, 134.6, 133.8, 129.0, 128.8, 128.6, 127.8, 127.6, 124.4, 121.7, 117.4, 116.0, 108.7, 66.6, 57.9, 55.6, 36.9, 21.2. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3062, 3026, 2918, 2787, 1673, 1551, 1511, 1494, 1415, 1260, 1187, 1097, 1017, 949, 913, 818, 739, 698. HRMS-ESI calcd for $C_{23}H_{25}N_2$ $[M+H]^+$: 329.2012, Found: 329.2011.

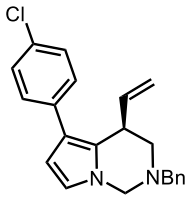



**2i**, viscous yellow oil, 51.1 mg, 69% yield, 99% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 6.36

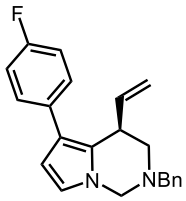
min, t (minor) = 8.30 min]. $[\alpha]_D^{25}$ = -11.5 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.24 (m, 9H), 6.52 (d, *J* = 2.8 Hz, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 5.82 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.02-4.88 (m, 2H), 4.73 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 3.93 (dd, *J* = 12.4, 5.6 Hz, 1H), 3.81-3.67 (m, 2H), 3.03-2.85 (m, 2H), 1.32 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.9, 139.4, 137.7, 133.7, 129.0, 128.6, 127.6, 127.4, 125.0, 124.6, 121.5, 117.4, 115.9, 108.7, 66.7, 58.1, 55.6, 37.0, 34.5, 31.5. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3080, 3028, 2957, 2865, 2787, 1674, 1637, 1550, 1508, 1455, 1411, 1357, 1267, 1092, 986, 950, 913, 833, 745, 697, 614, 569. HRMS-ESI calcd for $C_{26}H_{31}N_2$ $[M+H]^+$: 371.2482, Found: 371.2480.



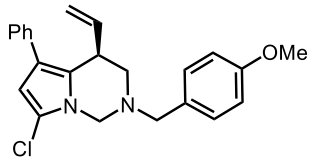

**2j**, viscous yellow oil, 59.0 mg, 75% yield, 97% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 7.79 min, t (minor) = 11.19 min]. $[\alpha]_D^{29}$ = -41.1 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.24 (m, 9H), 6.53 (d, *J* = 2.8 Hz, 1H), 6.31 (d, *J* = 2.8 Hz, 1H), 5.72 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 10.0 Hz, 1H), 3.92 (dd, dd, *J* = 12.8, 6.4 Hz, 1H), 3.83-3.67 (m, 2H), 3.02 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.90 (dd, *J* = 12.8, 6.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.6, 135.7, 131.1, 129.5, 128.9, 128.6, 127.7, 124.9, 120.6, 118.9, 117.7, 116.4, 108.5, 66.6, 57.8, 55.5, 36.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3061, 3028, 2918, 2786, 1655, 1590, 1544, 1597, 1452, 1412, 1353, 1184, 1097, 1069, 1006, 946, 915, 823, 738, 696, 612. HRMS-ESI calcd for $C_{22}H_{22}BrN_2$ $[M+H]^+$: 393.0961, Found: 393.0961.



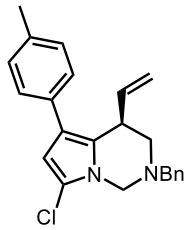
**2k**, viscous yellow oil, 54.4 mg, 78% yield, 98% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 6.90 min, t (minor) = 9.24 min]. $[\alpha]_D^{25}$ = -42.8 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.23 (m, 9H), 6.54 (d, $J$ = 2.8 Hz, 1H), 6.31 (d, $J$ = 2.8 Hz, 1H), 5.72 (ddd, $J$ = 17.6 Hz, 10.4, 7.2 Hz, 1H), 4.94 (d, $J$ = 9.6 Hz, 1H), 4.93 (d, $J$ = 17.2 Hz, 1H), 4.73 (d, $J$ = 10.0 Hz, 1H), 4.47 (d, $J$ = 10.0 Hz, 1H), 3.92 (dd, $J$ = 13.2, 6.8 Hz, 1H), 3.81-3.71 (m, 2H), 3.02 (ddd, $J$ = 12.4, 5.6, 0.8 Hz, 1H), 2.90 (dd, $J$ = 12.4, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.5, 135.1, 130.7, 129.1, 128.9, 128.5, 128.1, 127.6, 124.8, 120.6, 117.6, 116.3, 108.5, 66.5, 57.8, 55.4, 36.8. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3029, 2920, 2786, 1637, 1545, 1498, 1453, 1412, 1352, 1184, 1089, 1010, 947, 914, 827, 746, 697, 613, 543, 505. HRMS-ESI calcd for $C_{22}H_{22}ClN_2$ $[M+H]^+$: 349.1466, Found: 349.1464.




**2l**, viscous yellow oil, 57.8 mg, 87% yield, 98% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 6.36 min, t (minor) = 8.21 min]. $[\alpha]_D^{29}$ = -42.3 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 7H), 7.02-6.93 (m, 2H), 6.54 (d, $J$ = 2.8 Hz, 1H), 6.30 (d, $J$ = 2.8 Hz, 1H), 5.73 (ddd, $J$ = 18.0, 10.0, 6.4 Hz, 1H), 4.92 (d, $J$ = 10.0 Hz, 1H), 4.91 (d, $J$ = 16.8 Hz, 1H), 4.74 (d, $J$ = 10.0 Hz, 1H), 4.49 (d, $J$ = 10.0 Hz, 1H), 3.92 (dd, $J$ = 13.2, 6.4 Hz, 1H), 3.83-3.68 (m, 2H), 3.03 (dd, $J$ = 12.4, 5.6 Hz, 1H), 2.91 (dd, $J$ = 12.4, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, $J$ = 243.6 Hz), 138.7, 137.6, 132.8, 129.5 (d, $J$ = 7.6 Hz) 129.0, 128.6, 127.7, 124.6, 120.9, 117.5, 116.2, 114.8 (d, $J$ = 21.1 Hz), 108.7, 66.6, 57.9, 55.6, 36.9. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -118.3 (m). IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3061, 2921, 2852, 2788, 1665, 1551, 1507, 1452, 1353, 1219, 1156, 1094, 987, 915, 834, 739, 697, 592. HRMS-ESI calcd for $C_{22}H_{22}FN_2$ $[M+H]^+$: 333.1762, Found: 333.1762.

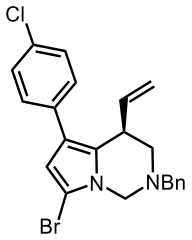



**2m**, viscous yellow oil, 61.4 mg, 81% yield, 99% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 5.95 min, t (minor) = 7.53 min]. $[\alpha]_D^{25}$ = -34.0 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.33-7.26 (m, 4H), 7.20-7.13 (m, 1H), 6.93-6.86 (m, 2H), 6.24 (s, 1H), 5.71 (ddd, $J$ = 17.2, 10.4, 7.2 Hz, 1H), 4.97-4.87 (m, 2H), 4.69 (d, $J$ = 10.4 Hz, 1H), 4.45 (d, $J$ = 10.4 Hz, 1H), 3.90 (dd, $J$ = 13.2, 6.4 Hz, 1H), 3.82 (s, 3H), 3.75 (d, $J$ = 13.2 Hz, 1H), 3.70 (d, $J$ = 13.2 Hz, 1H), 2.95 (dd, $J$ = 12.4, 5.6 Hz, 1H), 2.87 (dd, $J$ = 12.4, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.2, 138.7, 135.8, 130.2, 129.4, 128.2, 128.0, 125.7, 124.6, 121.9, 116.3, 114.0, 113.5, 106.6, 64.7, 57.3, 55.4, 54.6, 36.7. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 2958, 2911, 2833, 1607, 1509, 1458, 1244, 1175, 1030, 914, 802, 756, 696. HRMS-ESI calcd for $C_{23}H_{24}ClN_2O$ $[M+H]^+$: 379.1572, Found: 379.1562.

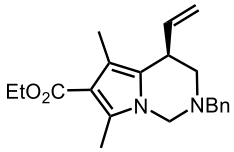



**2n**, viscous yellow oil, 64.6 mg, 89% yield, 98% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 5.89 min, t (minor) = 10.30 min]. $[\alpha]_D^{25}$ = -29.7 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 7H), 7.11 (d, $J$ = 8.0 Hz, 2H), 6.22 (s, 1H), 5.73 (ddd, $J$ = 17.2, 10.4, 7.2 Hz, 1H), 5.00-4.87 (m, 2H), 4.71 (d, $J$ = 10.4 Hz, 1H), 4.45 (d, $J$ = 10.4 Hz, 1H), 3.90 (dd, $J$ = 12.8, 6.0 Hz, 1H), 3.82 (d, $J$ = 13.2 Hz, 1H), 3.75 (d, $J$ = 13.2 Hz, 1H), 2.95 (dd, $J$ = 13.2, 5.6 Hz, 1H), 2.88 (dd, $J$ = 13.2, 6.0 Hz, 1H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.4, 135.2, 132.8, 129.0, 128.9, 128.6, 127.8, 127.7, 124.2, 121.9, 116.3, 113.4, 106.5, 64.8, 57.9, 54.7, 36.7, 21.2. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3026, 2918, 2857, 2805, 1553, 1509, 1454, 1407, 1330, 1181, 1152, 1072, 1022,

914, 821, 780, 738, 697, 530. HRMS-ESI calcd for $C_{23}H_{24}ClN_2$ $[M+H]^+$: 363.1623, Found: 363.1623.

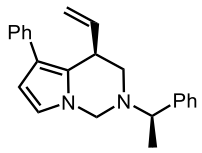



**2o**, viscous yellow oil, 58.2 mg, 68% yield, 99% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min$^{-1}$, λ = 254 nm, t (major) = 5.76 min, t (minor) = 12.02 min]. $[\alpha]_D^{25}$ = -31.4 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.23 (m, 9H), 6.32 (s, 1H), 5.67 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 4.99-4.86 (m, 2H), 4.70 (d, *J* = 10.4 Hz, 1H), 4.48 (d, *J* = 10.4 Hz, 1H), 3.91-3.71 (m, 3H), 2.97 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.88 (dd, *J* = 12.8, 6.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.3, 134.2, 131.4, 129.2, 129.0, 128.7, 128.3, 127.8, 126.5, 122.0, 116.7, 110.5, 99.0, 66.2, 57.8, 54.6, 36.8. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 1637, 1598, 1544, 1490, 1453, 1407, 1330, 1179, 1090, 1013, 915, 831, 785, 740, 697, 549, 500. HRMS-ESI calcd for $C_{22}H_{21}BrClN_2$ $[M+H]^+$: 427.0571, Found: 427.0570.

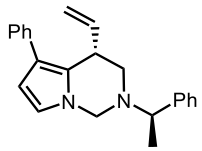



**2p**, viscous yellow oil, 46.0 mg, 68% yield, 97% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min$^{-1}$, λ = 254 nm, t (minor) = 10.09 min, t (major) = 10.54 min]. $[\alpha]_D^{30}$ = -68.3 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 5.82 (ddd, *J* = 17.2, 10.8, 8.0 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 5.06 (d, *J* = 16.4 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.33-4.19 (m, 3H), 3.72 (s, 2H), 3.61 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.96 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.88 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.36 (s, 3H), 2.15 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.6, 139.2, 137.5, 132.6, 128.9, 128.6, 127.7, 123.5, 117.2, 115.4, 111.0, 63.9, 59.1, 57.7, 54.9, 36.3, 14.7, 11.2, 11.0. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 2975, 2923, 1686, 1520,

1413, 1249, 1161, 1098, 913, 783, 740, 698. HRMS-ESI calcd for $C_{21}H_{27}N_2O_2$ $[M+H]^+$: 339.2067, Found: 339.2070.

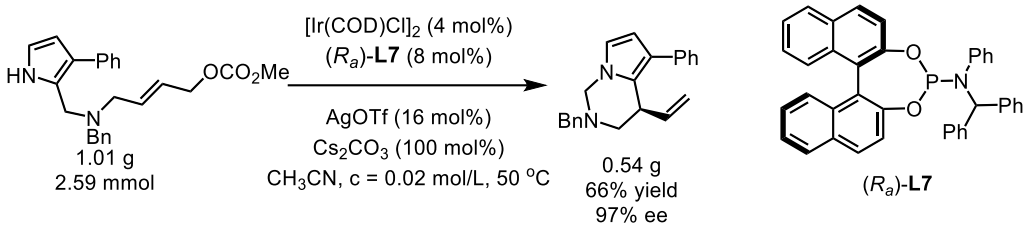



**2q**, viscous yellow oil, 57.8 mg, 88% yield, >20/1 dr. $[\alpha]_D^{31}$ = -65.9 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.33-7.25 (m, 7H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 6.31 (d, *J* = 2.8 Hz, 1H), 5.71 (ddd, *J* = 17.2, 10.0, 7.6 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 4.66 (d, *J* = 10.4 Hz, 1H), 4.42 (d, *J* = 10.4 Hz, 1H), 3.98 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.77 (q, *J* = 6.4 Hz, 1H), 3.21 (dd, *J* = 12.8, 5.6 Hz, 1H), 2.95 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.0, 138.6, 136.8, 128.7, 128.1, 128.0, 127.54, 127.46, 125.1, 124.9, 121.7, 117.4, 116.1, 108.5, 65.5, 59.3, 52.6, 36.5, 21.1. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3059, 2971, 2924, 2788, 1685, 1601, 1498, 1451, 1353, 1261, 1089, 1027, 912, 795, 758, 696. HRMS-ESI calcd for $C_{23}H_{25}N_2$ $[M+H]^+$: 329.2012, Found: 329.2010.



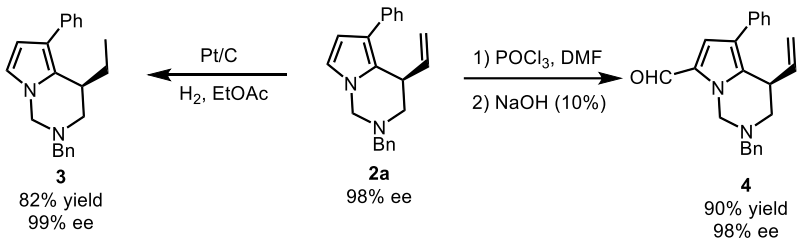

**2r**, viscous yellow oil, 52.6 mg, 80% yield, >20/1 dr. $[\alpha]_D^{31}$ = -0.74 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.39-7.26 (m, 7H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 5.72 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 4.93-4.80 (m, 3H), 4.63 (d, *J* = 10.0 Hz, 1H), 3.87 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.75 (q, *J* = 6.4 Hz, 1H), 2.86 (d, *J* = 6.0 Hz, 2H), 1.43 (d, *J* = 6.4 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.7, 139.0, 136.8, 128.7, 128.1, 127.9, 127.51, 127.47, 125.15, 125.10, 121.6, 117.5, 115.9, 108.6, 65.0, 60.3, 53.4, 37.0, 20.9. IR (thin film): $\nu_{max}$ ($cm^{-1}$) = 3058, 2972, 2920, 2789, 1688, 1601, 1497, 1451, 1409, 1328, 1086, 946, 910, 761, 696, 552. HRMS-ESI calcd for $C_{23}H_{25}N_2$ $[M+H]^+$: 329.2012, Found: 329.2009.

**Millimole-scale synthesis of 2a**




A flame-dried Schlenk tube was cooled to rt and filled with argon. To this flask were added $[Ir(cod)Cl]_2$ (69.5 mg, 0.10 mmol, 4 mol%), phosphoramidite ligand **L7** (118.7 mg, 0.21 mmol, 8 mol%), THF (2.5 mL) and *n*-propylamine (2.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed *in vacuo* to give a pale-yellow solid. After that, substrate **1a** (1.01 g, 2.59 mmol, 1 equiv), AgOTf (0.11 g, 0.41 mmol, 16 mol%), $Cs_2CO_3$ (0.84 g, 2.59 mmol, 100 mol%) and $CH_3CN$ (125 mL) were added. The reaction mixture was stirred at 50 °C for 2 h, and the starting material was consumed completely as monitored by TLC. The crude reaction mixture was quenched with water and extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtrated and concentrated *in vacuo*. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1, 10/1) to afford the desired product **2a** (0.54 g, 66% yield, 97% ee).

**Transformations of 2a**




Pt/C (39.0 mg, platinum on activated carbon, 5% Pt basis, 0.1 equiv) was added to a solution of **2a** (31.1 mg, 1 equiv, 98% ee) in EtOAc (2 mL). The reaction mixture was stirred under $H_2$ atmosphere (1 atm) at rt for 6 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated with celite and washed with EtOAc. The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1, 10/1) to afford the desired product **3**.

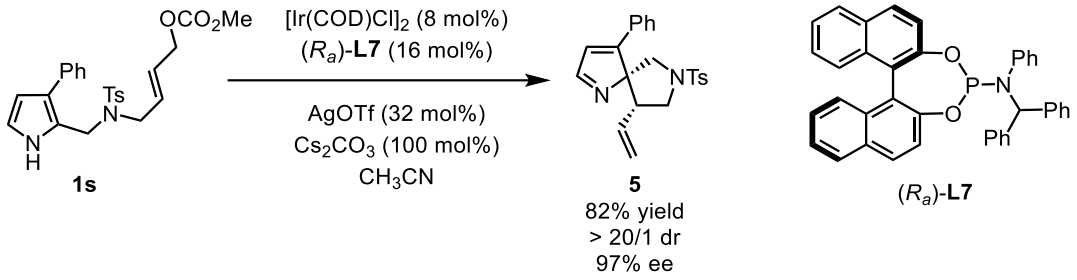
**3**, viscous yellow oil, 25.8 mg, 82% yield, 99% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 98/2, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (minor) = 8.80 min, t (major) = 9.71 min]. $[\alpha]_D^{31}$ = -41.6 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, $J$ = 7.6 Hz, 2H), 7.40-7.28 (m, 7H), 7.17 (t, $J$ = 7.6 Hz, 1H), 6.49 (d, $J$ = 2.8 Hz, 1H), 6.31 (d, $J$ = 2.8 Hz, 1H), 4.69 (d, $J$ = 9.6 Hz, 1H), 4.41 (d, $J$ = 9.6 Hz, 1H), 3.76 (d, $J$ = 13.2 Hz, 1H), 3.70 (d, $J$ = 13.2 Hz, 1H), 3.35-3.26 (m, 1H), 2.94 (dd, $J$ = 12.4, 5.2 Hz, 1H), 2.85 (dd, $J$ = 12.4, 6.0 Hz, 1H), 1.62-1.54 (m, 2H), 0.72 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.7, 137.6, 128.9, 128.4, 128.2, 127.48, 127.45, 127.3, 125.0, 120.1, 116.6, 108.5, 67.0, 58.3, 53.3, 33.8, 26.0, 11.4. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3028, 2960, 2926, 2871, 2782, 1675, 1601, 1500, 1452, 1260, 1151, 1097, 1062, 765, 733, 696. HRMS-ESI calcd for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, Found: 317.2011.

A solution of DMF (50 μL, 0.6 mmol, 7 equiv) and $POCl_3$ (28 μL, 0.3 mmol, 3.5 equiv) in DCM (2 mL) was stirred at 0 °C for 30 min before being treated with a solution of

compound **2a** (27.7 mg, 0.88 mmol, 1 equiv, 98% ee) in DCM (1 mL). The resulted mixture was stirred at rt for 5 h. Then, the crude reaction mixture was quenched with water and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtrated and concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (PE/EtOAc = 10/1, 5/1) to afford the desired product **4**.

**4**, pale yellow solid, 80.6-82.5 °C, 27.2 mg, 90% yield, 98% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (minor) = 8.18 min, t (major) = 14.22 min]. $[\alpha]_D^{32}$ = -56.5 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.43-7.19 (m, 10H), 7.04 (s, 1H), 5.68 (ddd, $J$ = 17.2, 10.0, 7.6 Hz, 1H), 5.27 (d, $J$ = 11.6 Hz, 1H), 5.07 (d, $J$ = 11.6 Hz, 1H), 4.91 (d, $J$ = 10.0 Hz, 1H), 4.84 (d, $J$ = 17.2 Hz, 1H), 3.97 (dd, $J$ = 12.4, 6.0 Hz, 1H), 3.85 (d, $J$ = 13.2 Hz, 1H), 3.74 (d, $J$ = 13.2 Hz, 1H), 2.95 (dd, $J$ = 12.4, 5.6 Hz, 1H), 2.84 (dd, $J$ = 12.4, 6.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.8, 137.1, 137.0, 135.6, 134.8, 129.9, 128.8, 128.5, 128.21, 128.19, 127.6, 126.4, 124.6, 123.6, 117.0, 67.4, 57.9, 53.1, 37.0. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3077, 2957, 2928, 2812, 1647, 1603, 1454, 1416, 1377, 1311, 1242, 1167, 1145, 1055, 1026, 923, 860, 744, 694, 601, 500. HRMS-ESI calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805, Found: 343.1804.

**Capture of the spiro-2*H*-pyrrole 5**




A flame-dried Schlenk tube was cooled to rt and filled with argon. To this flask were added [Ir(cod)Cl]$_2$ (5.4 mg, 0.008 mmol, 8 mol%), phosphoramidite ligand **L7** (9.2 mg, 0.016 mmol, 16 mol%), THF (0.5 mL) and *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed *in vacuo* to give a pale-yellow solid. After that, substrate **1s** (0.1 mmol, 41.6 mg, 1 equiv), AgOTf (8.2 mg, 0.032 mmol, 32 mol%), $Cs_2CO_3$ (32.6 mg, 0.1 mmol, 100 mol%) and $CH_3CN$ (2 mL) were added. The reaction mixture was stirred at 50 °C for 2 h, and the starting material was consumed completely as monitored by TLC. The crude reaction mixture was quenched with water and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtrated and concentrated *in vacuo*. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1, 10/1) to afford the desired product **5**.

**5**, pale yellow solid, 131.8-134.4 °C, 28.4 mg, 82% yield, >20/1 dr, 97% ee. [Daicel Chiralpak AD-H (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, $v$ = 1.0 mL·min$^{-1}$, λ = 254 nm, t (minor) = 22.37 min, t (major) = 26.58 min]. $[\alpha]_D^{29}$ = +4.05 ($c$ = 0.05, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 (d, $J$ = 8.4 Hz, 2H), 7.49-7.44 (m, 2H), 7.43-7.38 (m, 3H), 7.35 (d, $J$ = 8.0 Hz, 2H), 6.73 (s, 1H), 5.18 (ddd, $J$ = 17.6, 10.0, 7.6 Hz, 1H), 4.86 (dd, $J$ = 10.0, 0.4 Hz, 1H), 4.73 (dt, $J$ = 17.6, 1.2 Hz, 1H), 3.97 (m, 2H), 3.55 (dd, $J$ = 11.2, 9.2 Hz, 1H), 3.37-3.28 (m, 2H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.22, 163.16, 143.8, 133.6, 131.6, 130.7, 129.9, 129.4, 129.1, 127.8, 126.8, 124.7, 118.8, 88.8, 53.6, 52.9, 51.0, 21.8. IR (thin film): $\nu_{max}$ (cm$^{-1}$) = 3053, 2949,

2888, 1745, 1710, 1596, 1443, 1344, 1158, 1089, 1030, 991, 811, 764, 696, 661, 572, 543. HRMS-ESI calcd for $C_{22}H_{23}N_2O_2S$ $[M+H]^+$: 379.1475, Found: 379.1477.

**X-Ray crystal structure of spiro-2*H*-pyrrole 5**

The crystal was obtained by slow evaporation of **5** in hexane/dichloromethane (CCDC 2048880).

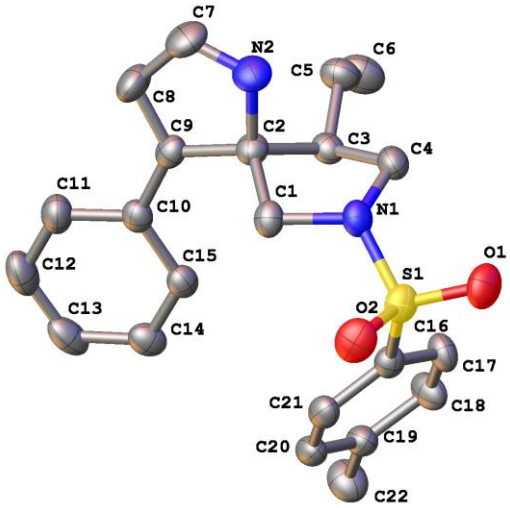



**Table S4.** Crystal data and structure refinement for mo_d8v17087_0m.

| | | |
|---|---|---|
| Identification code | mo_d8v17087_0m | |
| Empirical formula | C22 H22 N2 O2 S | |
| Formula weight | 378.47 | |
| Temperature | 300.88 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P1 | |
| Unit cell dimensions | a = 9.4904(7) Å | a= 71.155(2)°. |
| | b = 9.8661(7) Å | b= 70.007(2)°. |
| | c = 12.9696(9) Å | g = 61.631(2)°. |
| Volume | 985.04(12) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.276 Mg/m3 | |
| Absorption coefficient | 0.183 $mm^{-1}$ | |
| F(000) | 400 | |
| Crystal size | 0.33 × 0.3 × 0.25 $mm^3$ | |

| | |
|---|---|
| Theta range for data collection | 2.504 to 25.999°. |
| Index ranges | -11<=h<=11, -12<=k<=12, -15<=l<=15 |
| Reflections collected | 24092 |
| Independent reflections | 7641 [R(int) = 0.0546] |
| Completeness to theta = 25.242° | 99.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7461 and 0.6793 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7641 / 3 / 490 |
| Goodness-of-fit on $F^2$ | 1.048 |
| Final R indices [I>2sigma(I)] | $R^1$ = 0.0764, $wR^2$ = 0.1843 |
| R indices (all data) | $R^1$ = 0.0860, $wR^2$ = 0.2003 |
| Absolute structure parameter | 0.05(3) |
| Extinction coefficient | 0.21(4) |
| Largest diff. peak and hole | 1.418 and -0.272 e.$Å^{-3}$ |

## References

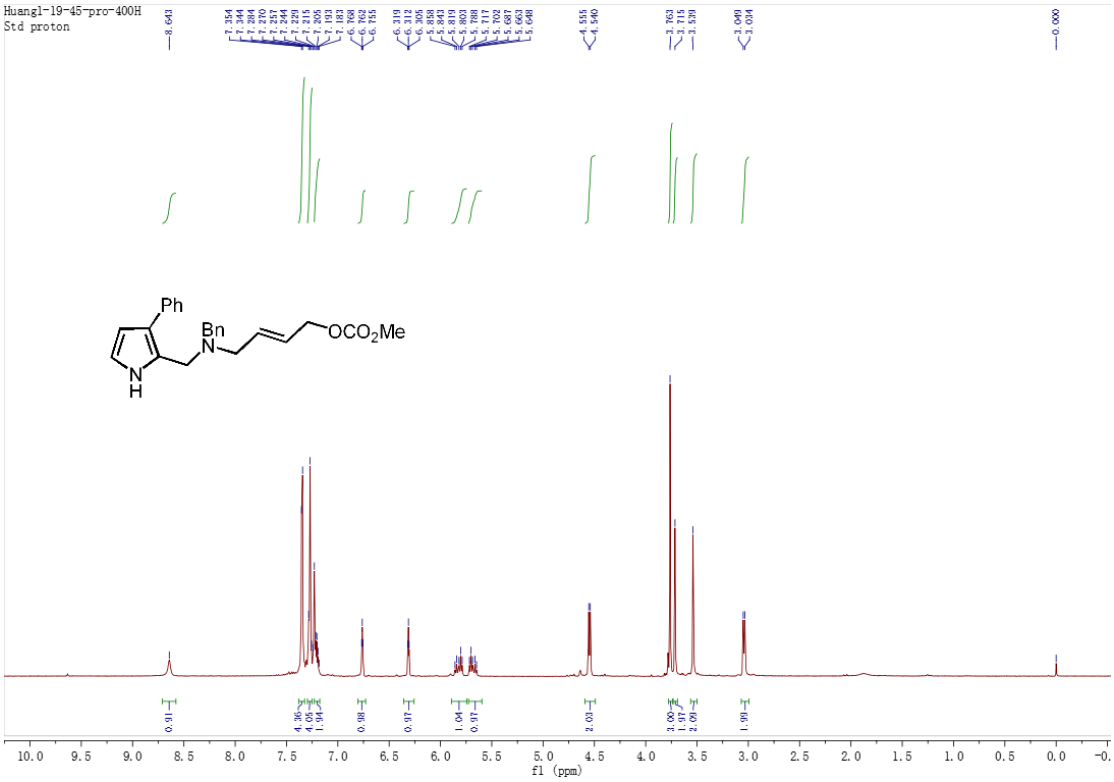

(1) Kim, H.-J.; Lindsey, J. S., De Novo Synthesis of Stable Tetrahydroporphyrinic Macrocycles: Bacteriochlorins and a Tetradehydrocorrin. *J. Org. Chem.* **2005**, *70*, 5475-5486.

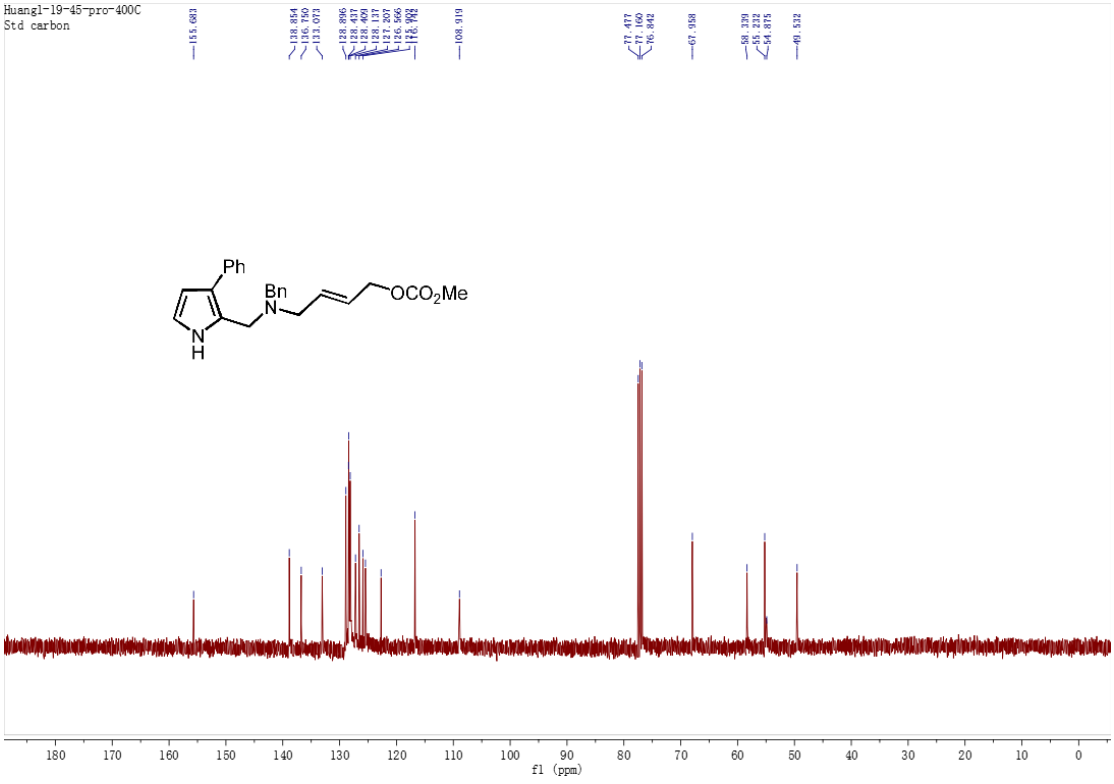
(2) Smith, N. D.; Huang, D.; Cosford, N. D. P. One-Step Synthesis of 3-Aryl- and 3,4-Diaryl-(1H)-Pyrroles Using Tosylmethyl Isocyanide (TOSMIC). *Org. Lett.* **2002**, *4*, 3537-3539.

(3) Trotter, B. W.; Bell, Ian M.; Zartman, C. B.; Lindsley, C.; Zhao, Z. Preparation of 2-carboxypyrroles as tyrosine kinase inhibitors. PCT Int. Appl., 2003035615, 01 May 2003.

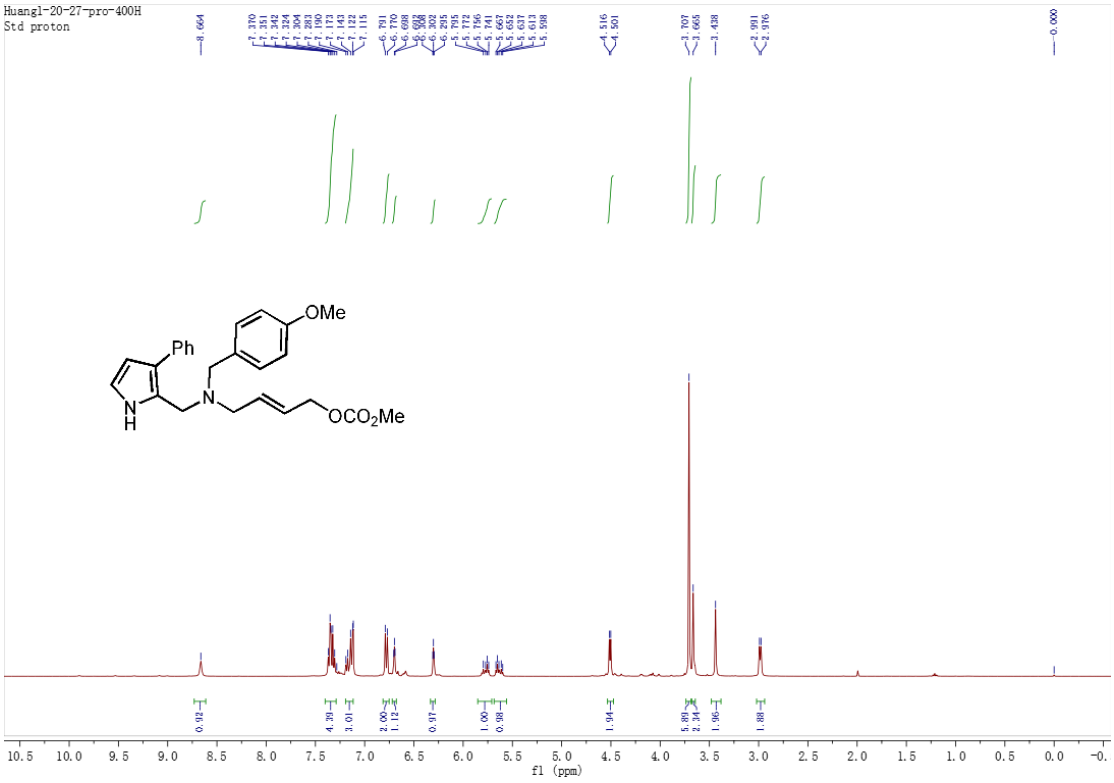
## Copies of NMR spectra and HPLC chromatograms

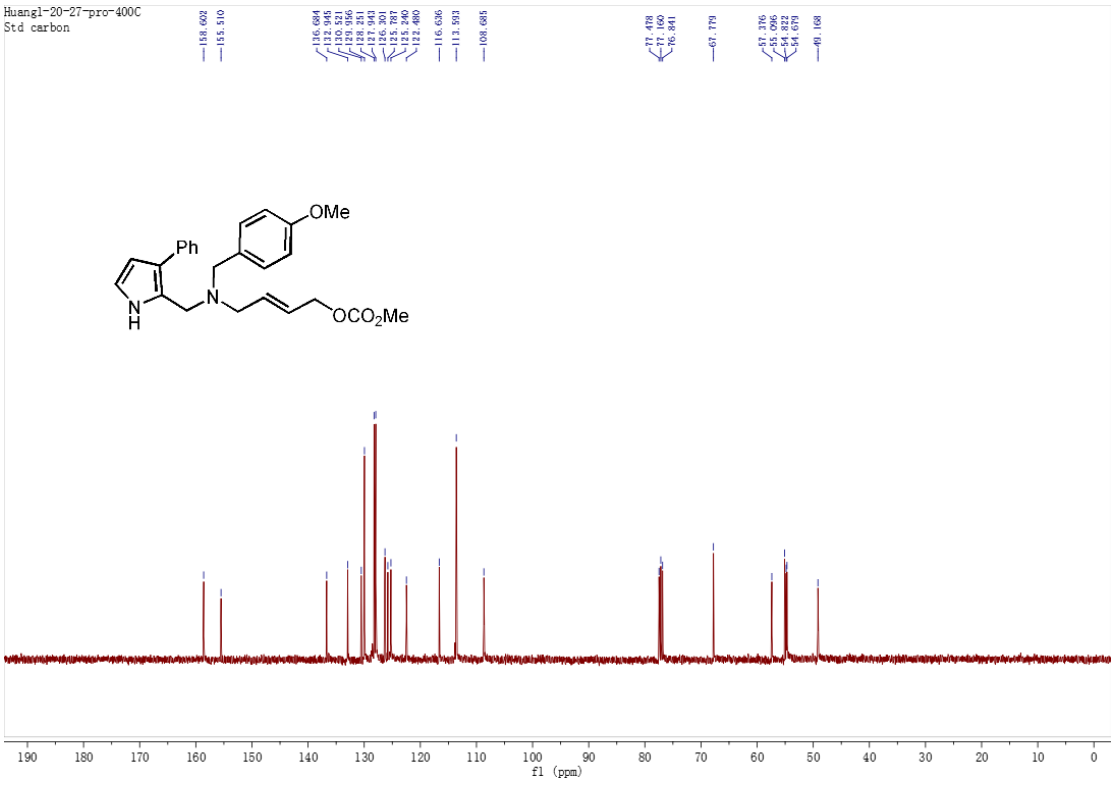
NMR Spectra of **1a**



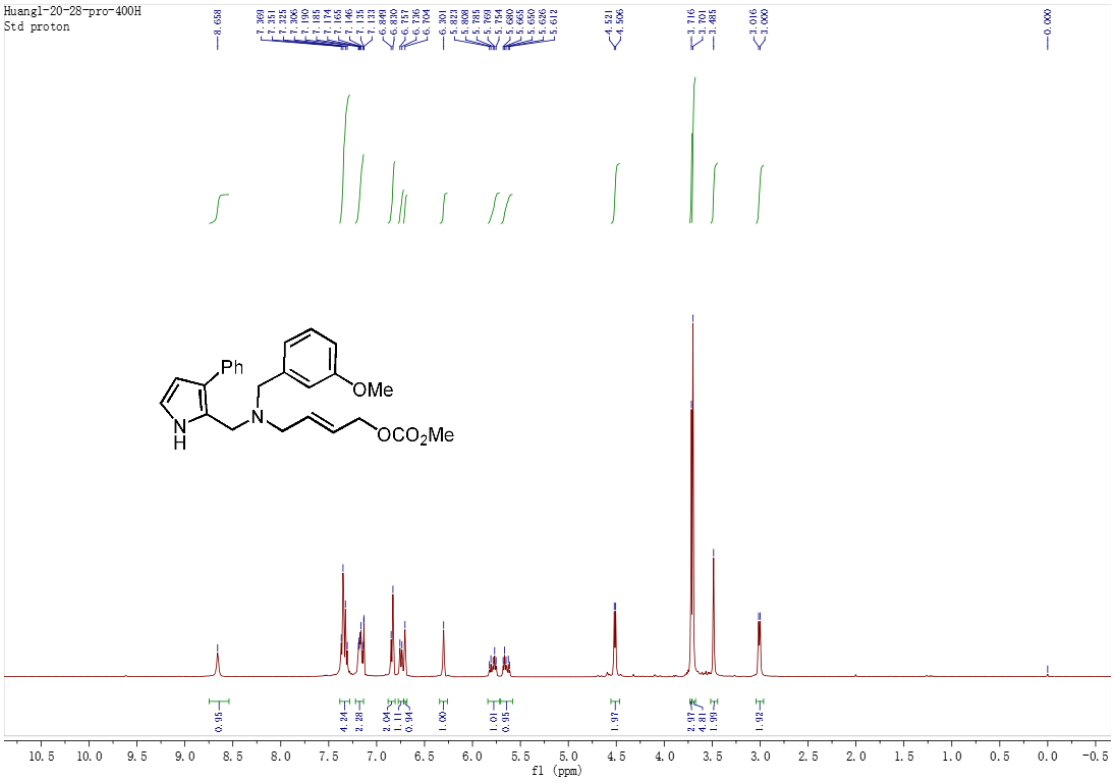



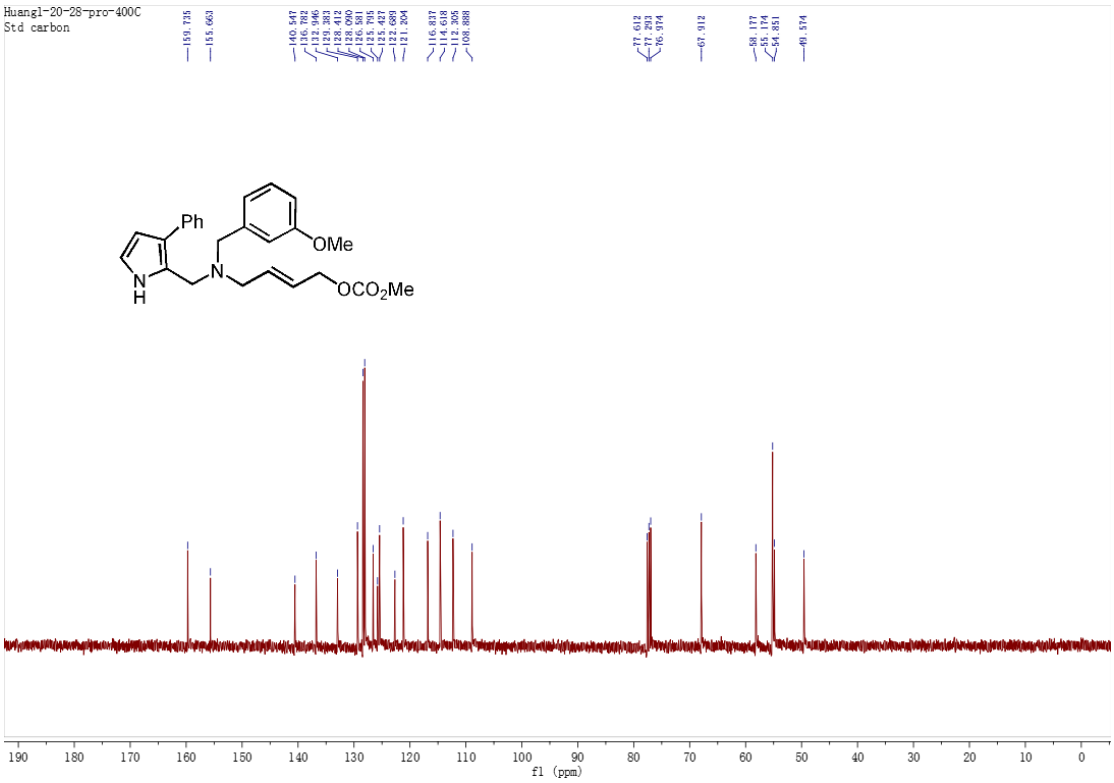
NMR Spectra of **1b**



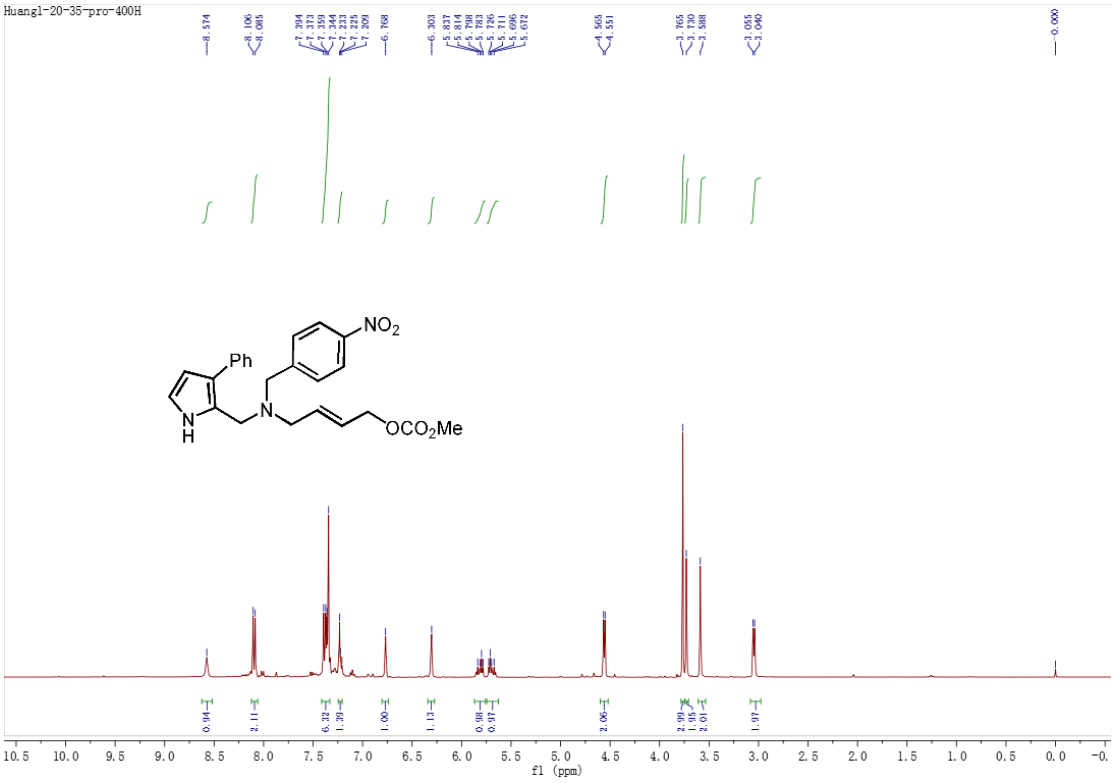



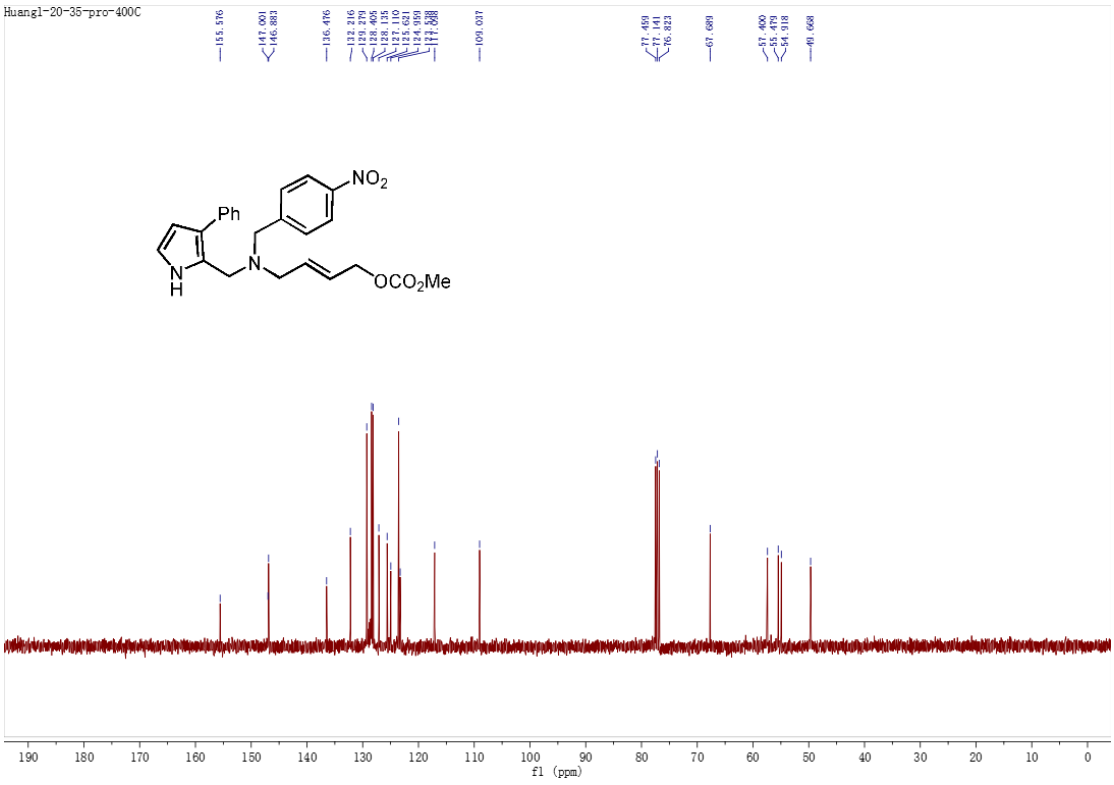
NMR Spectra of **1c**



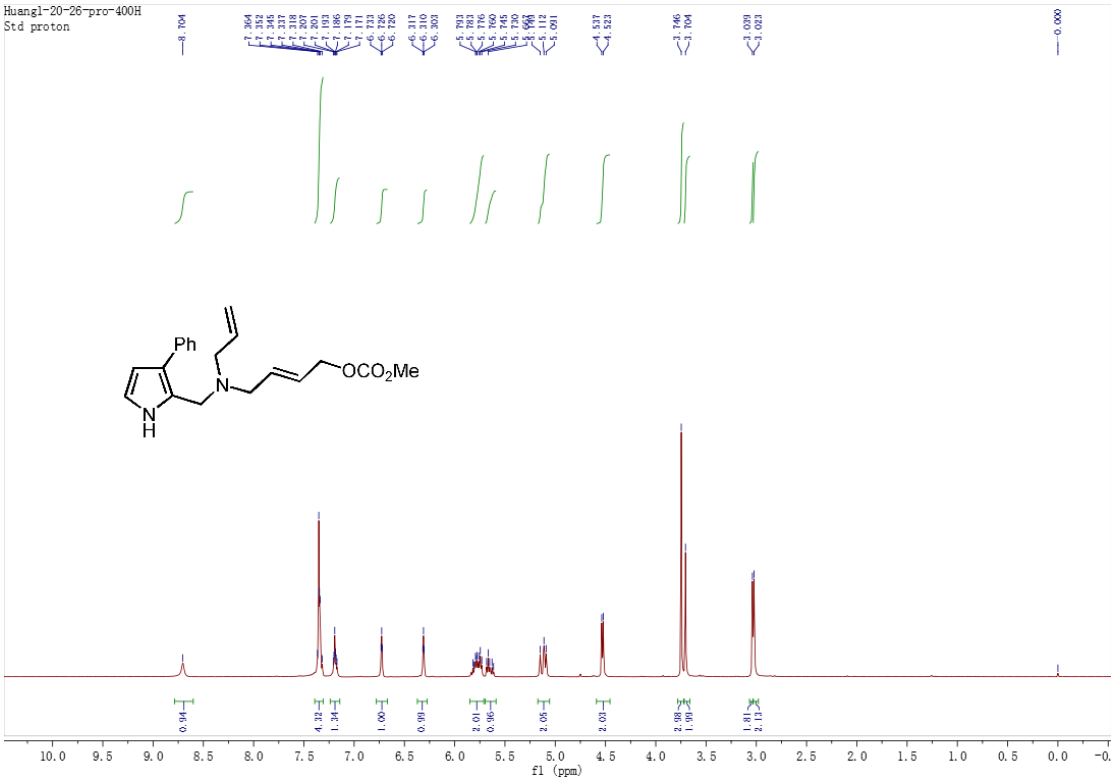



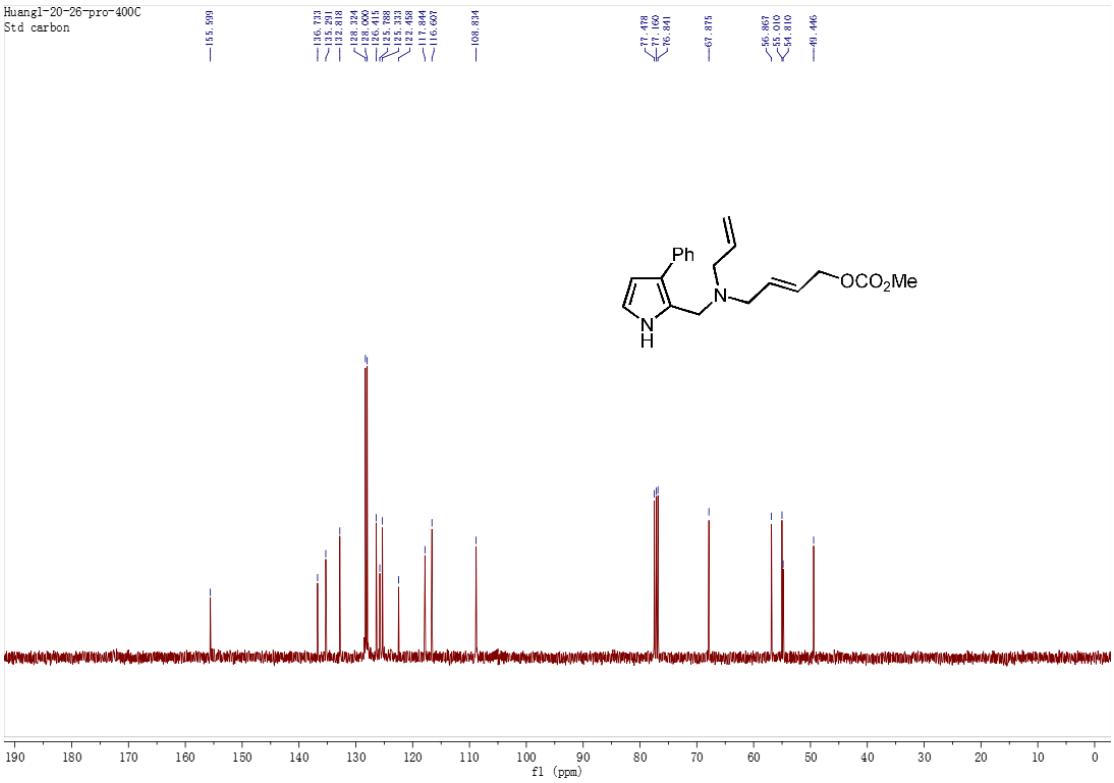
NMR Spectra of **1d**



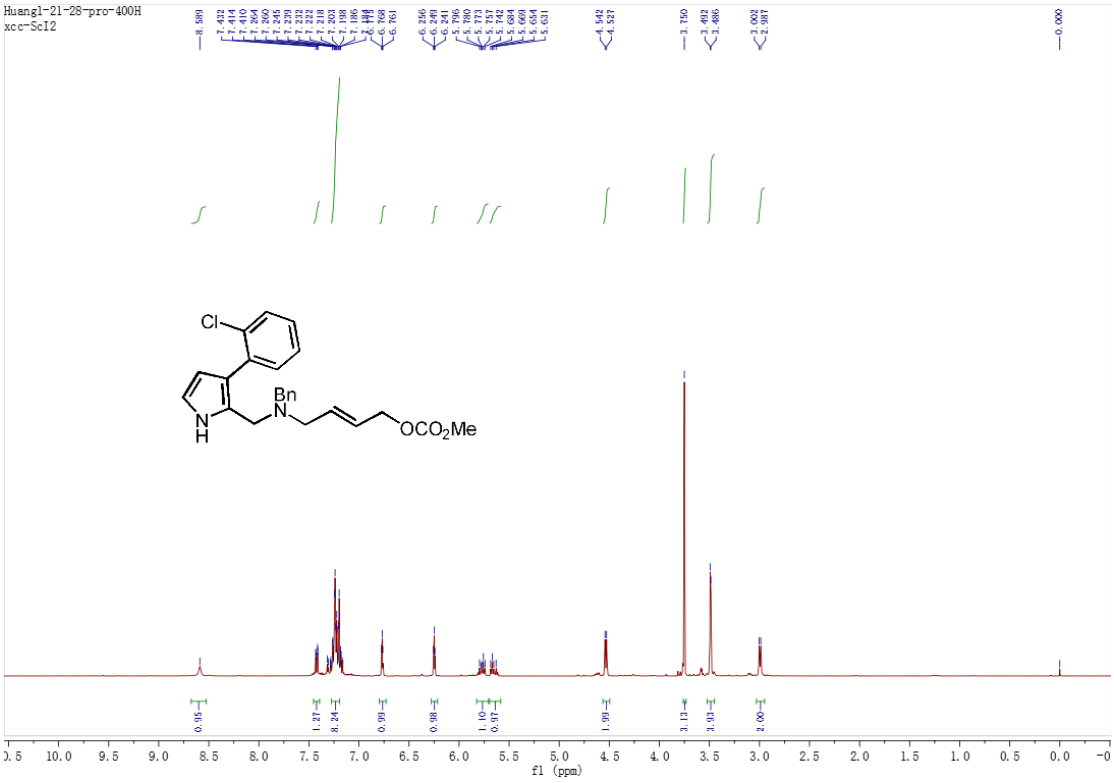



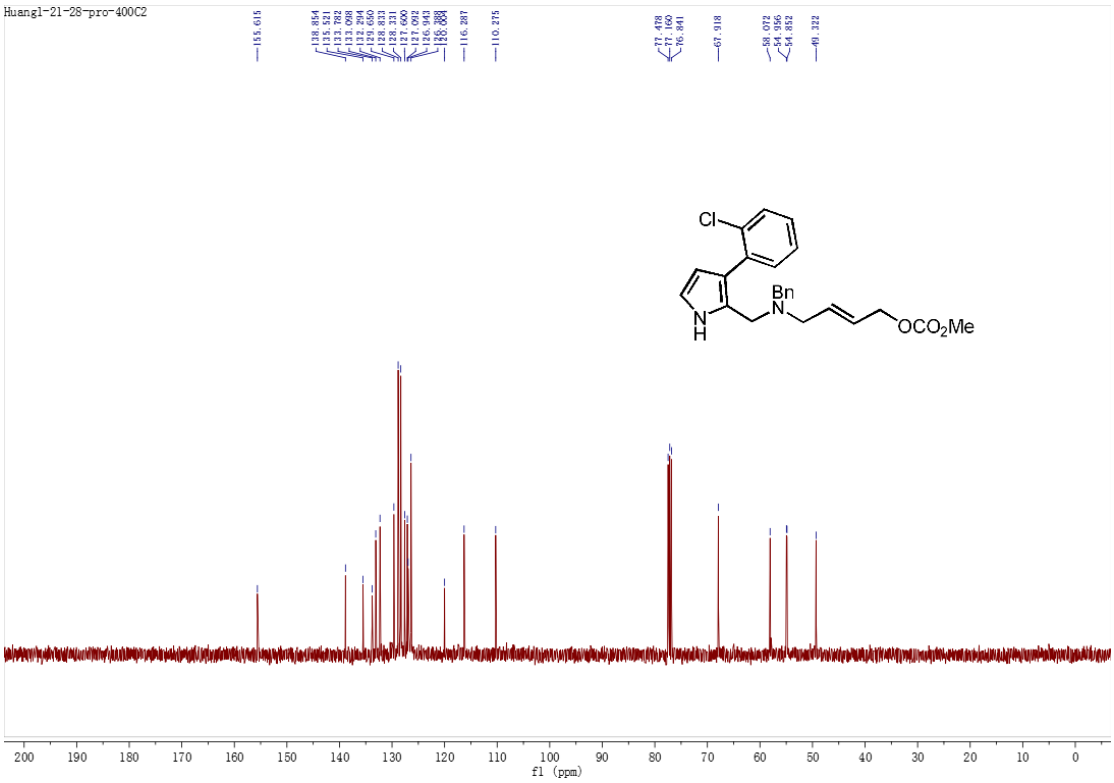
NMR Spectra of **1e**



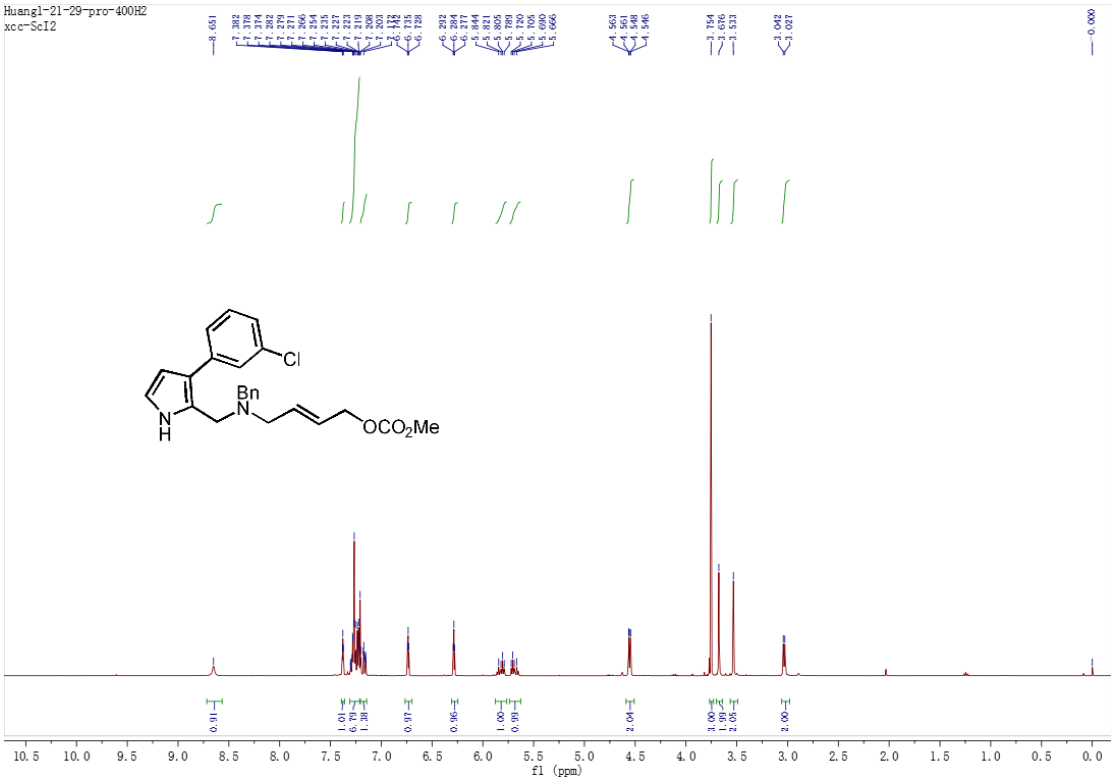



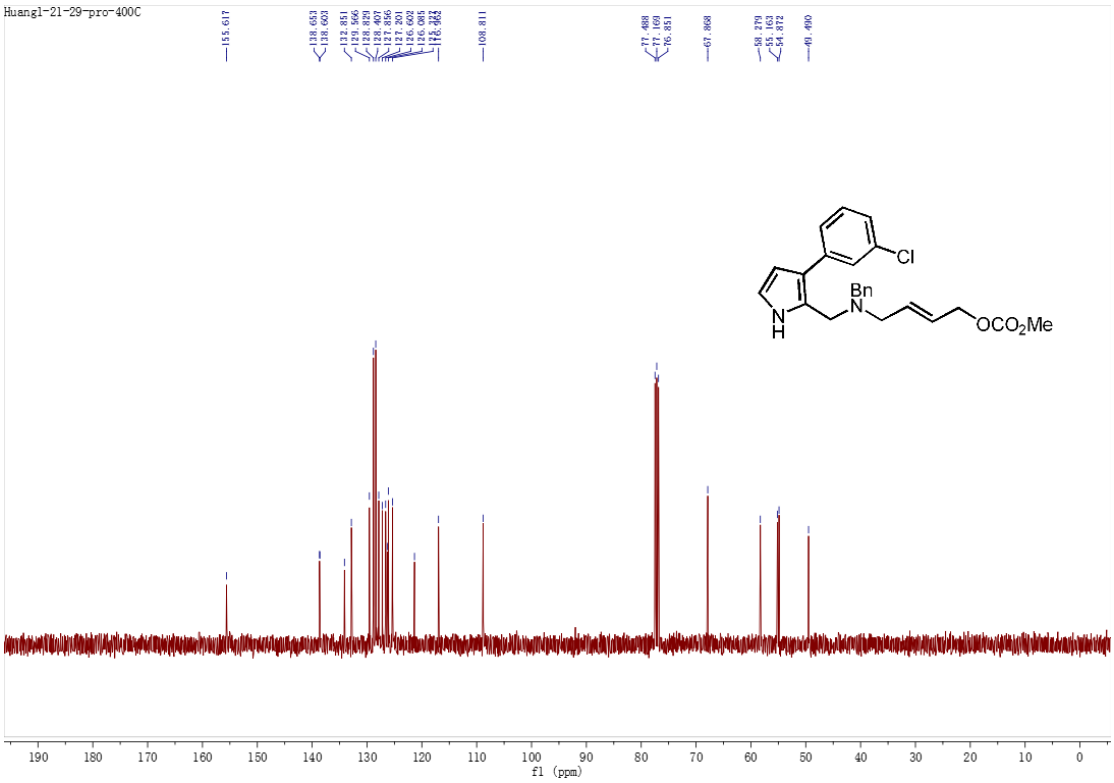
NMR Spectra of **1f**



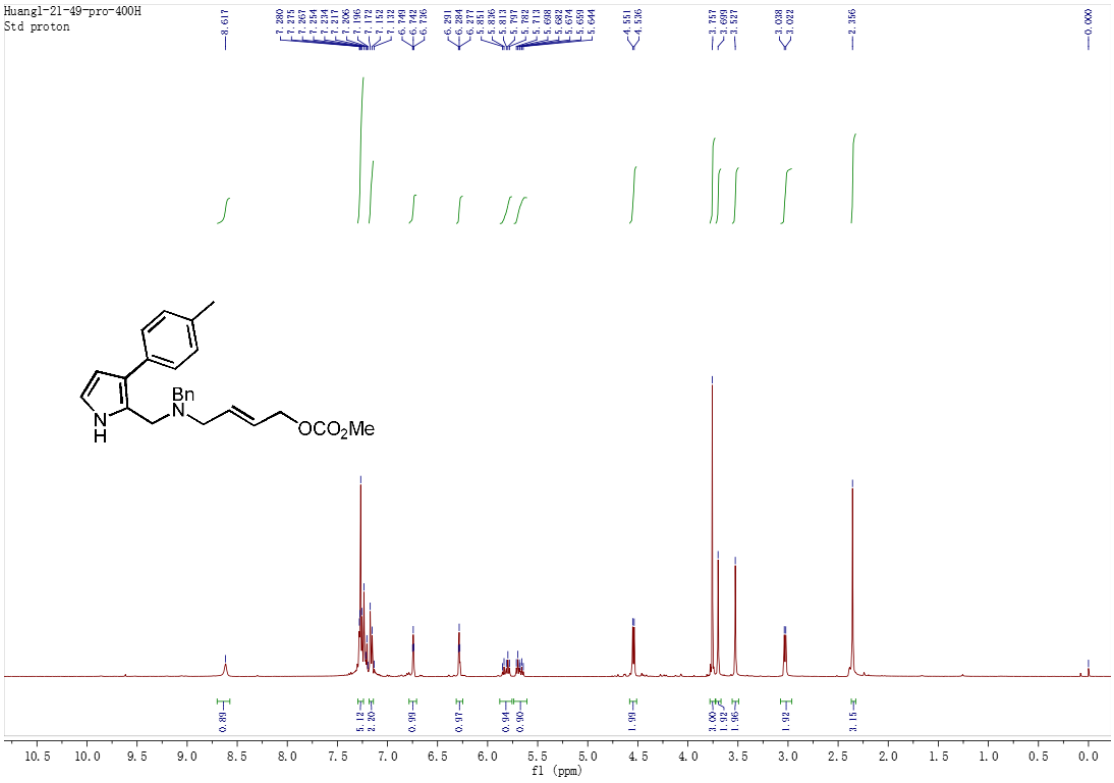



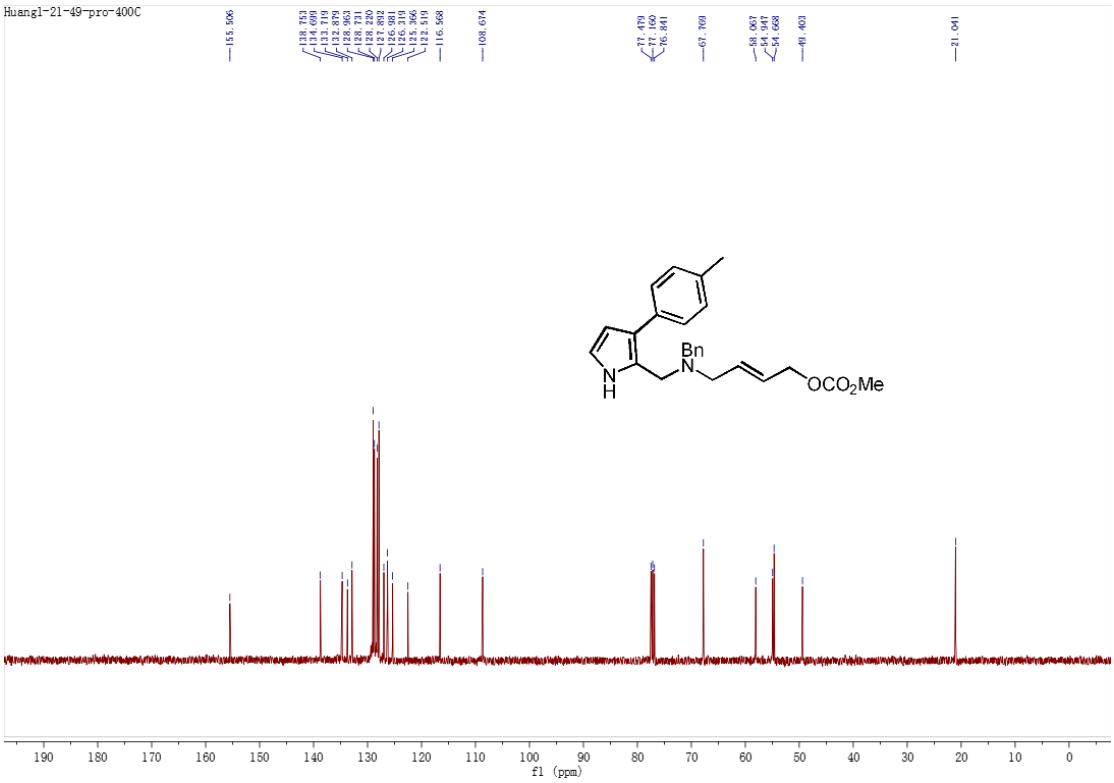
NMR Spectra of **1g**



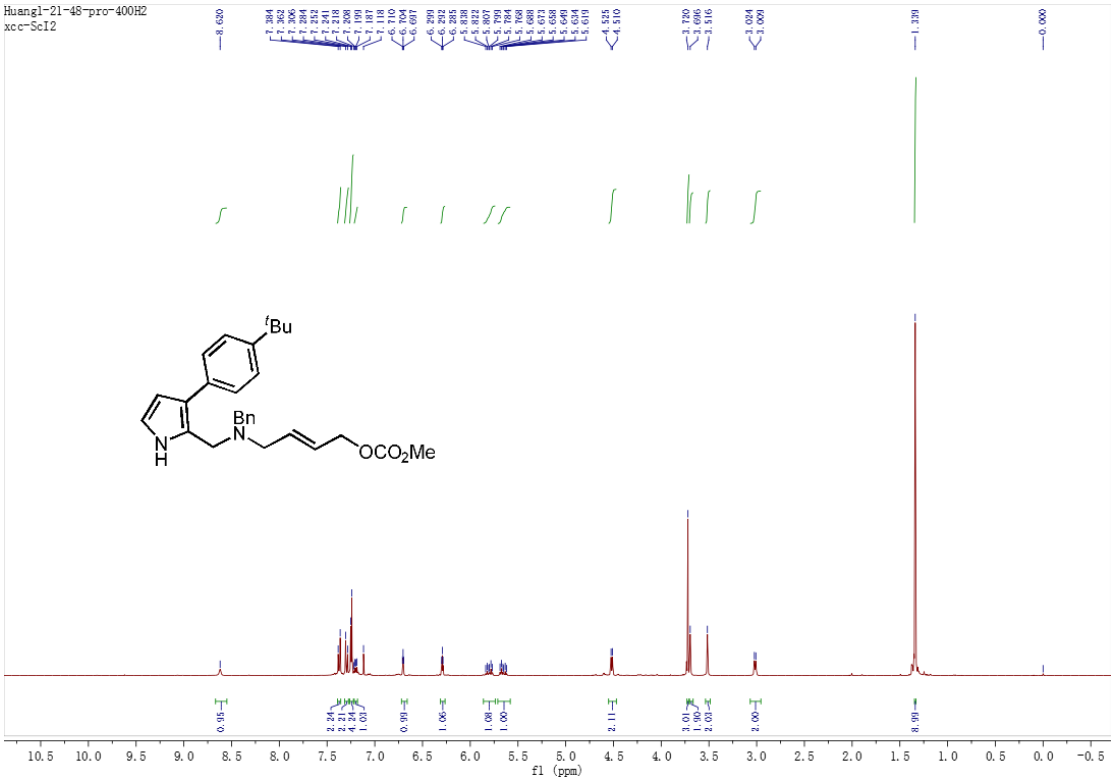



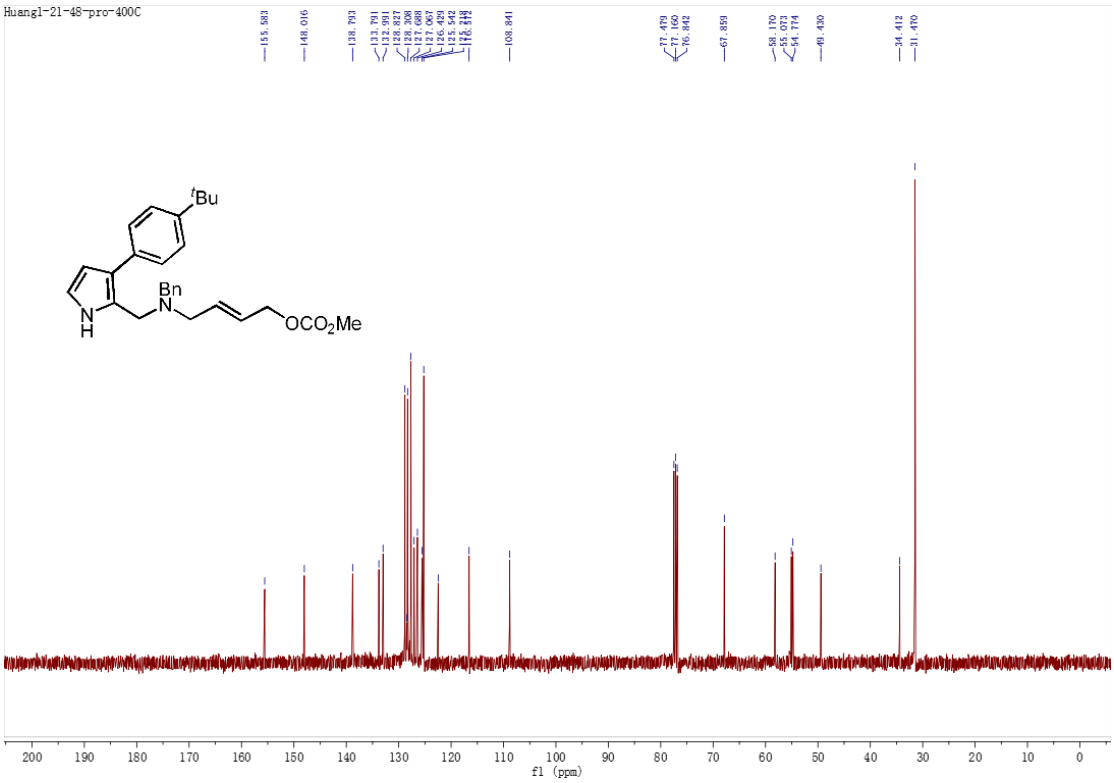
NMR Spectra of **1h**



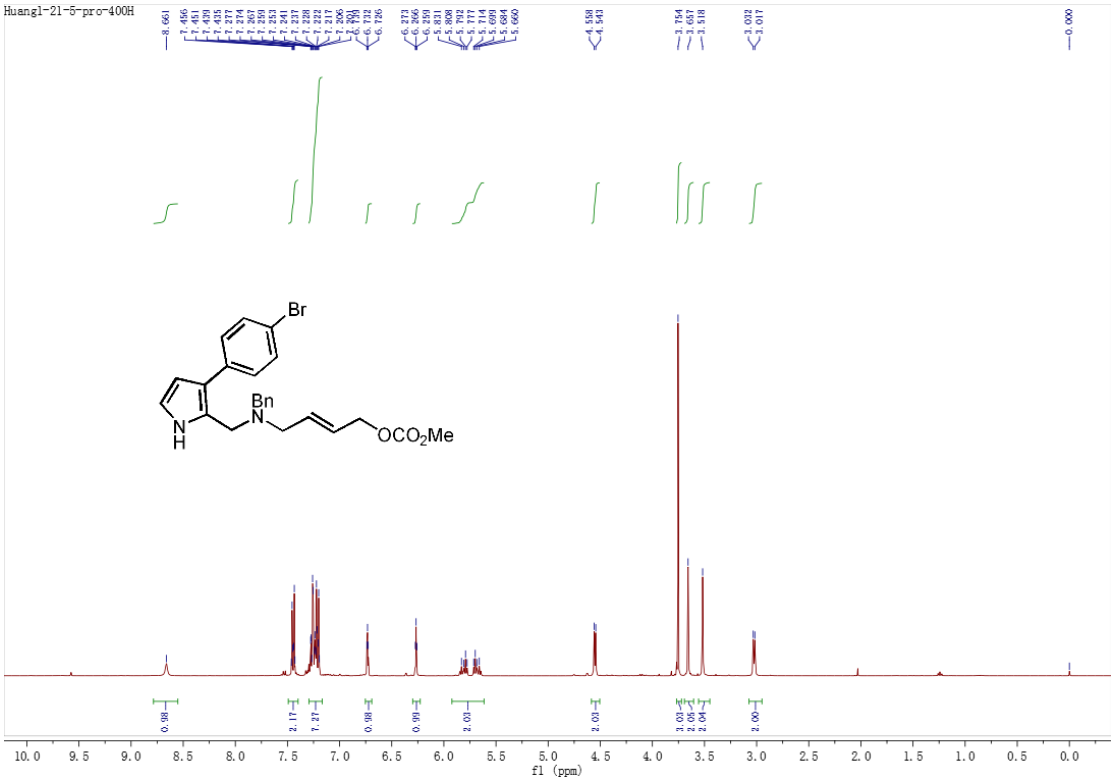



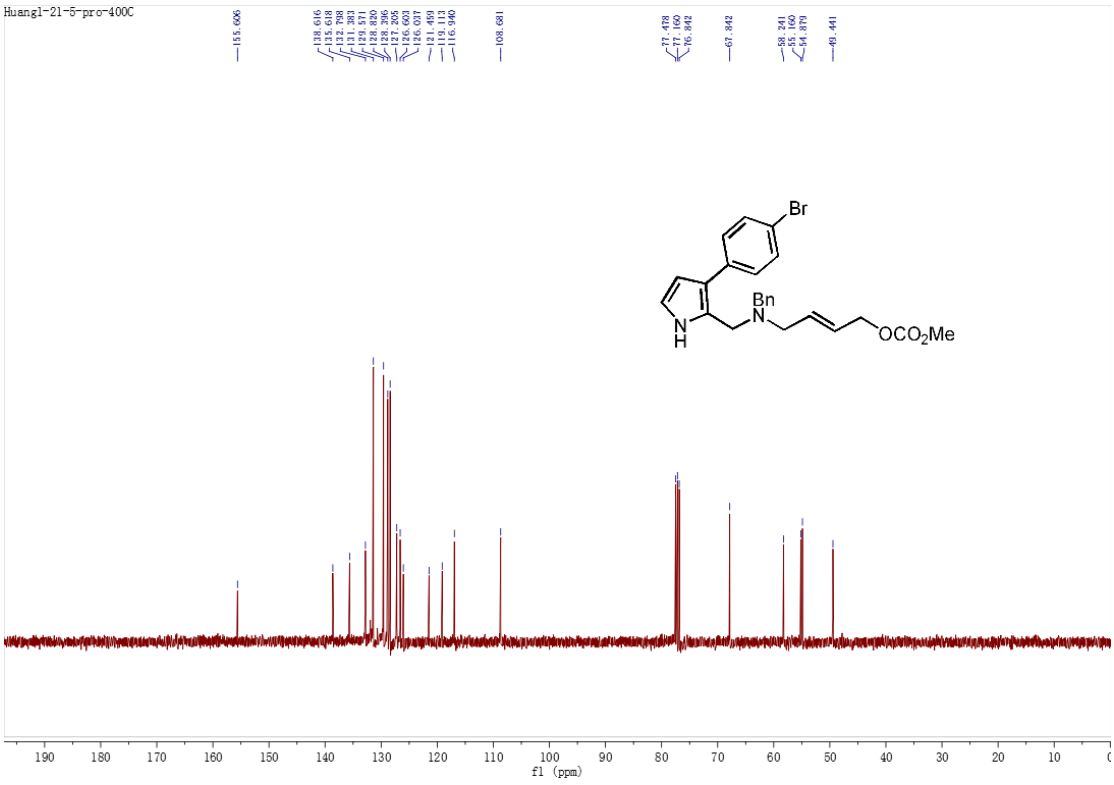
NMR Spectra of **1i**



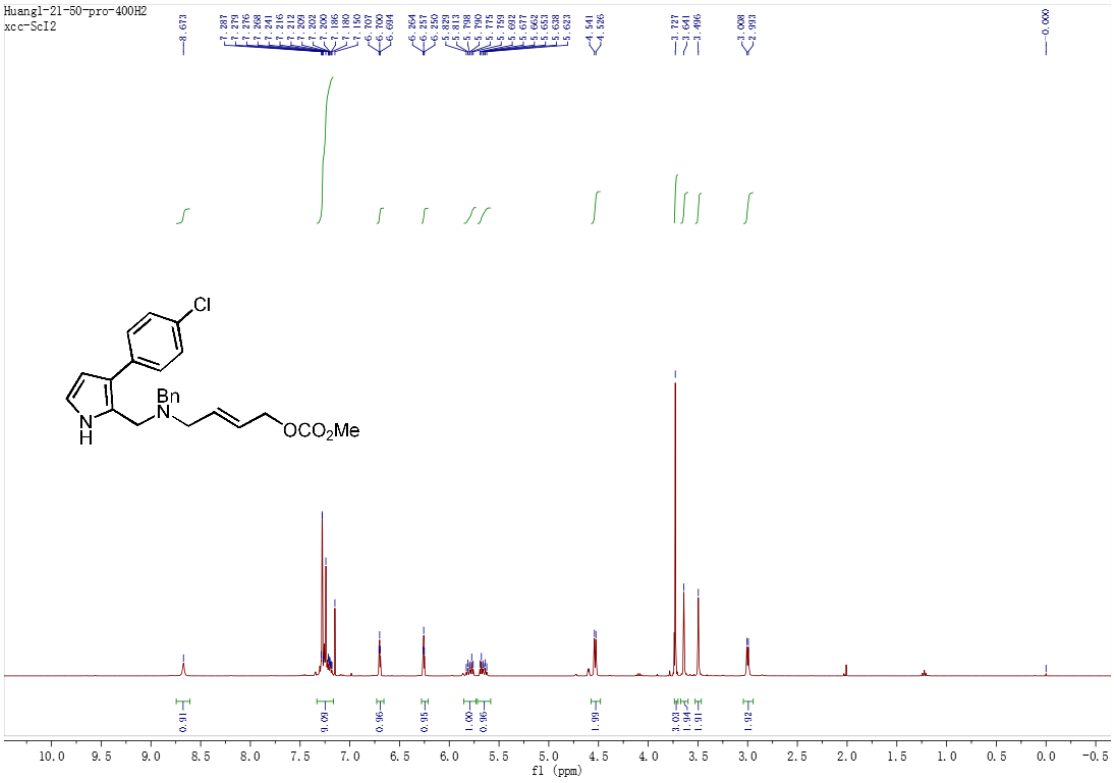



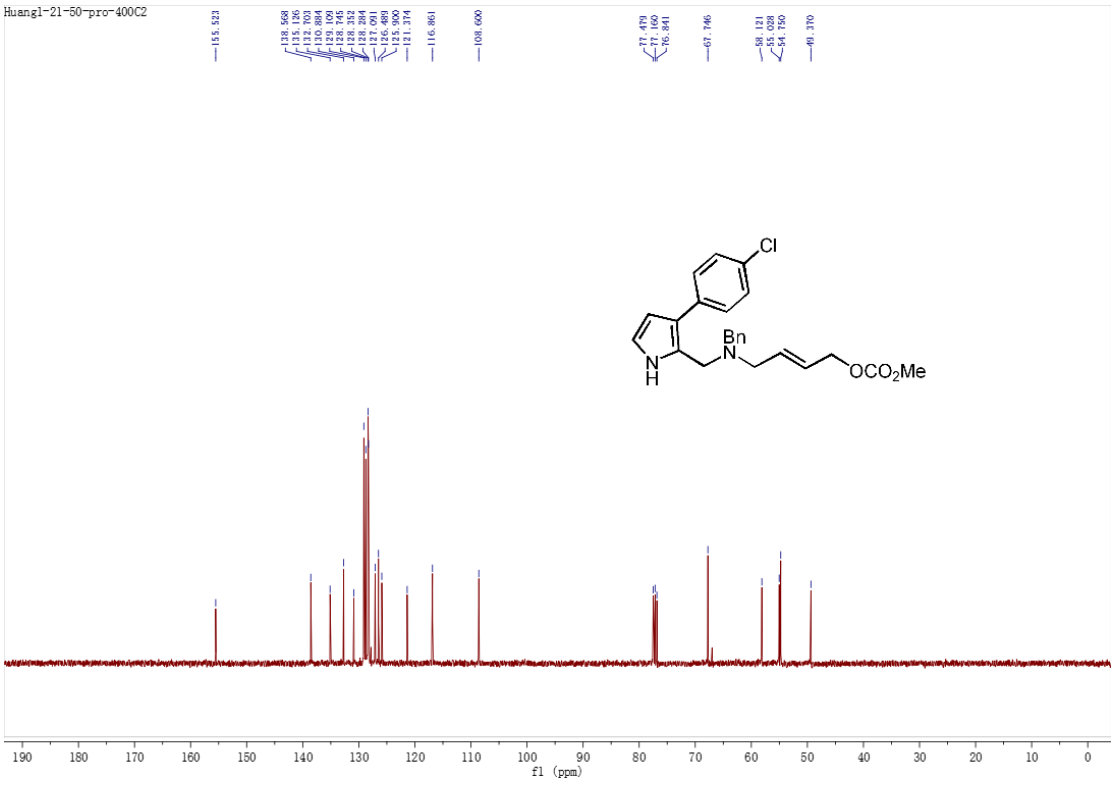
NMR Spectra of **1j**



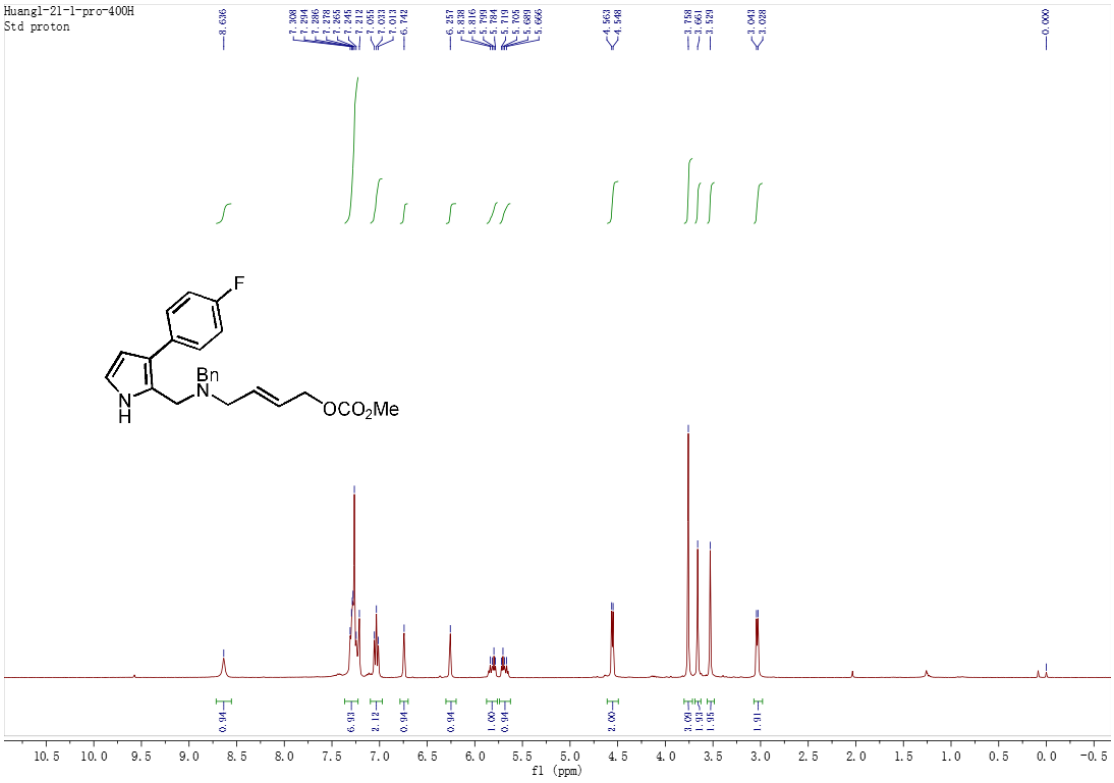



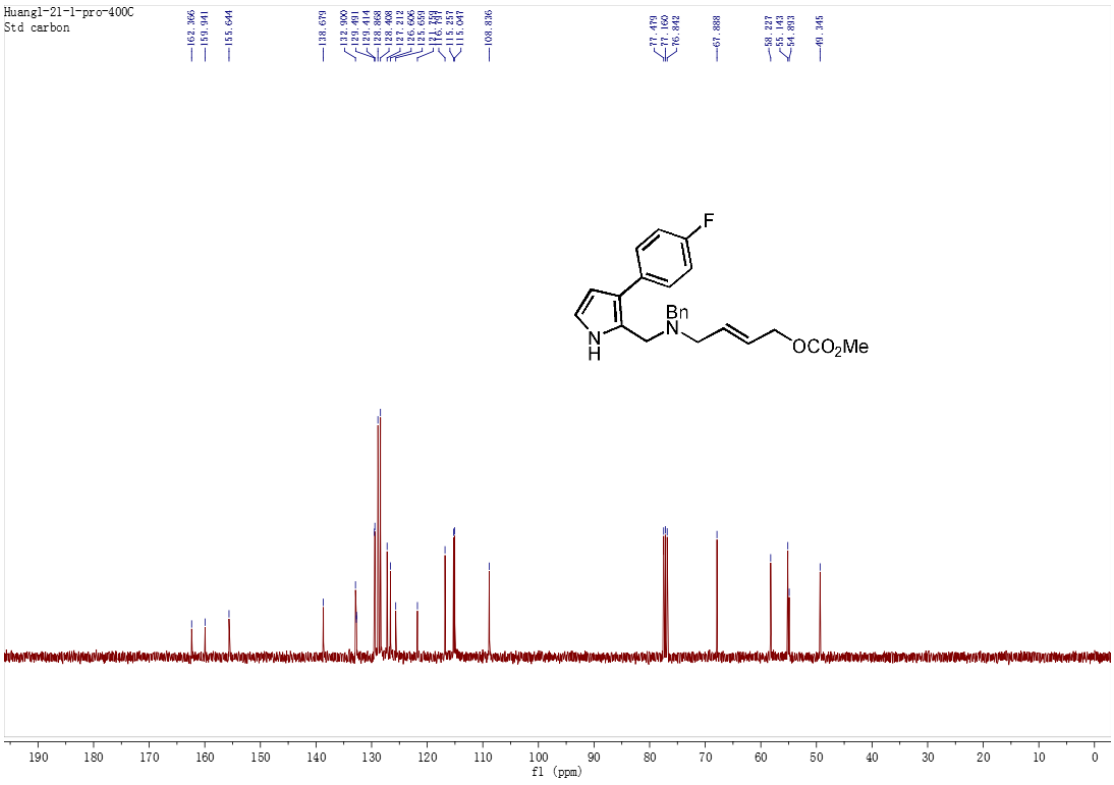
NMR Spectra of **1k**

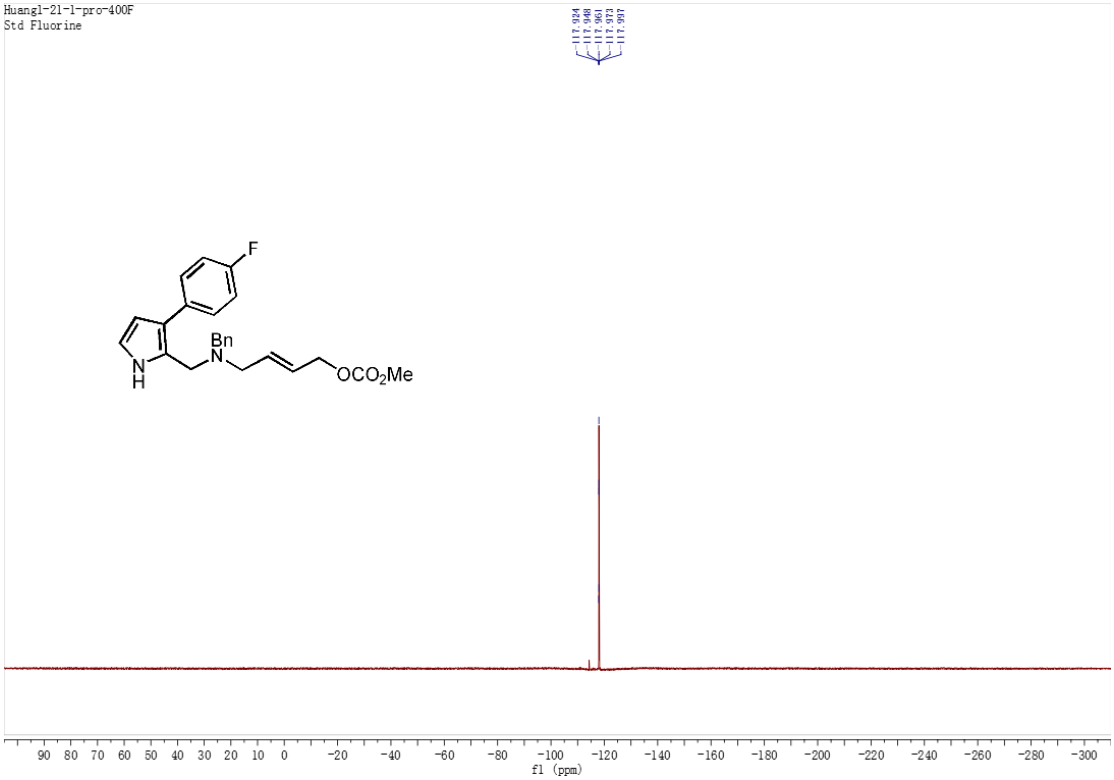


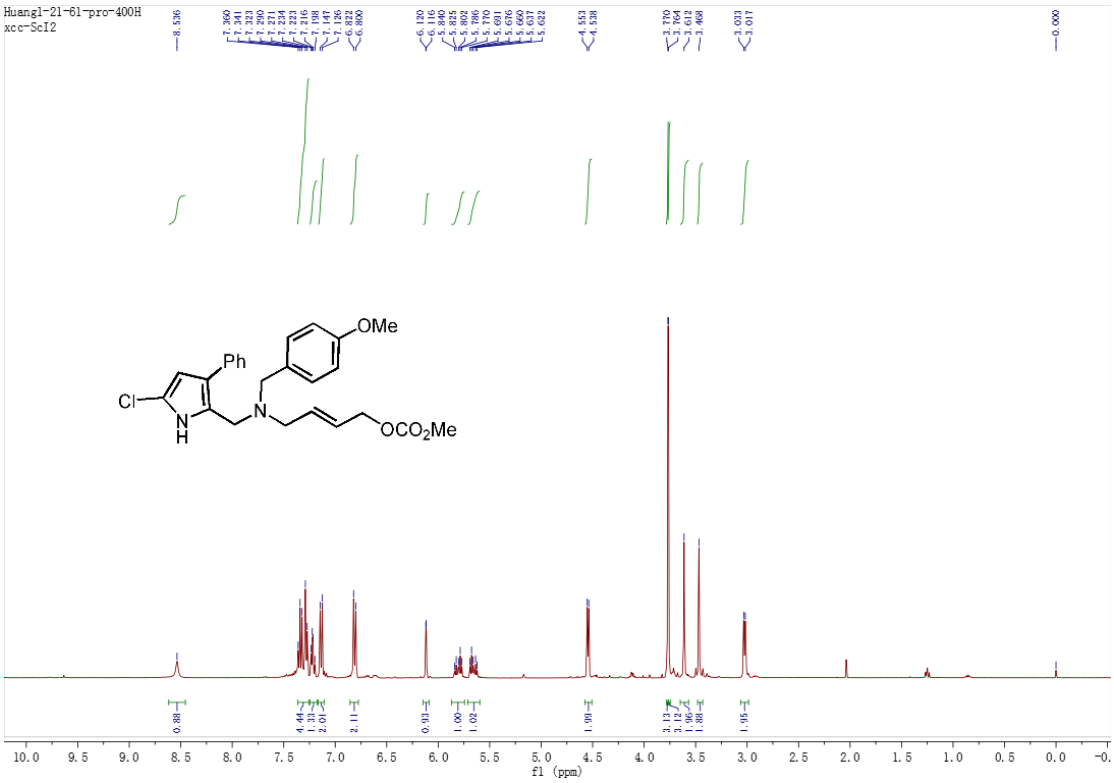
NMR Spectra of **1l**

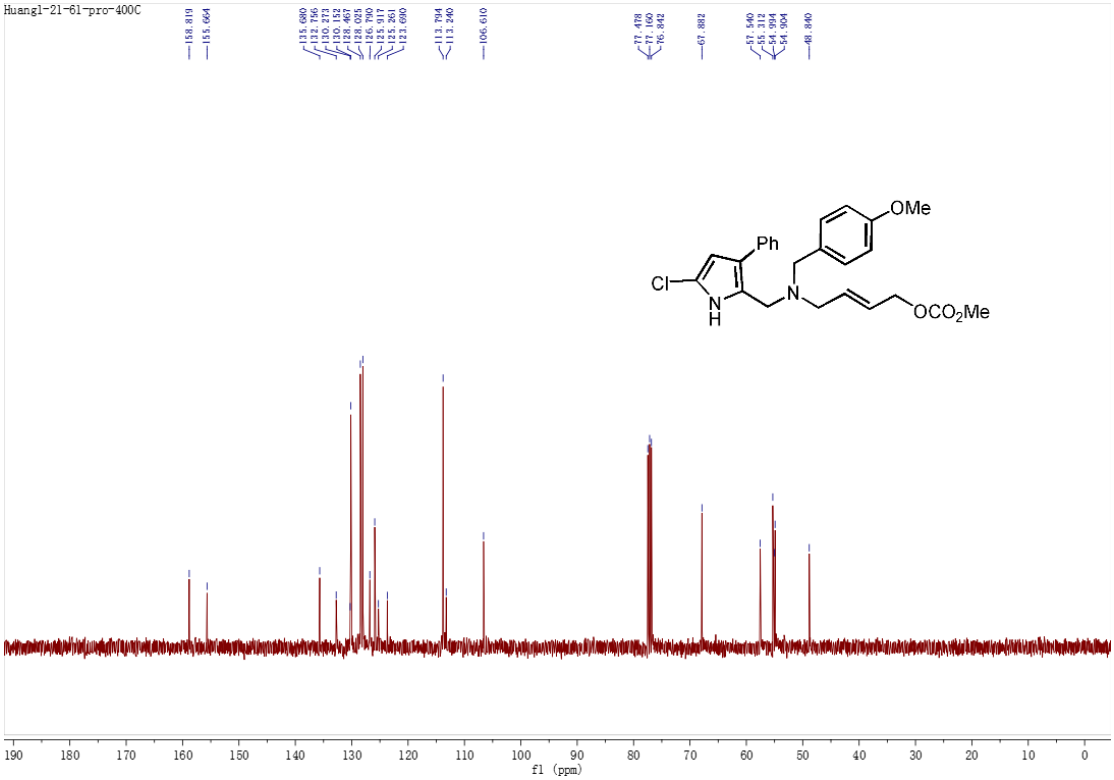


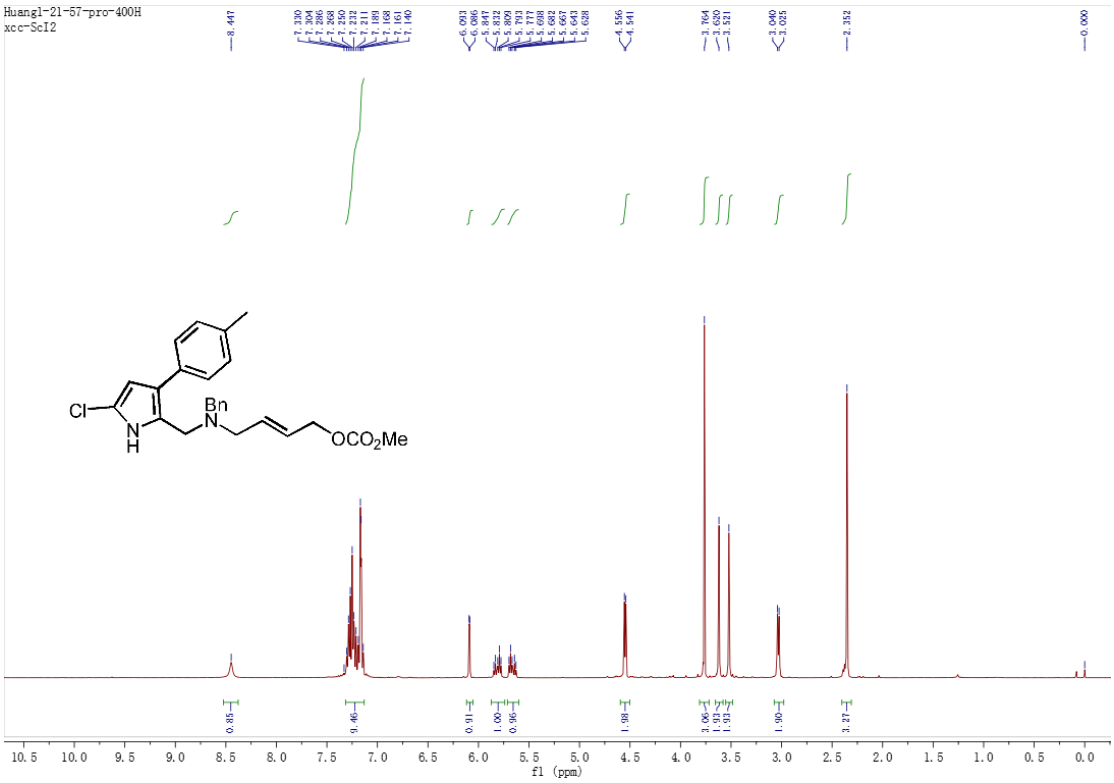


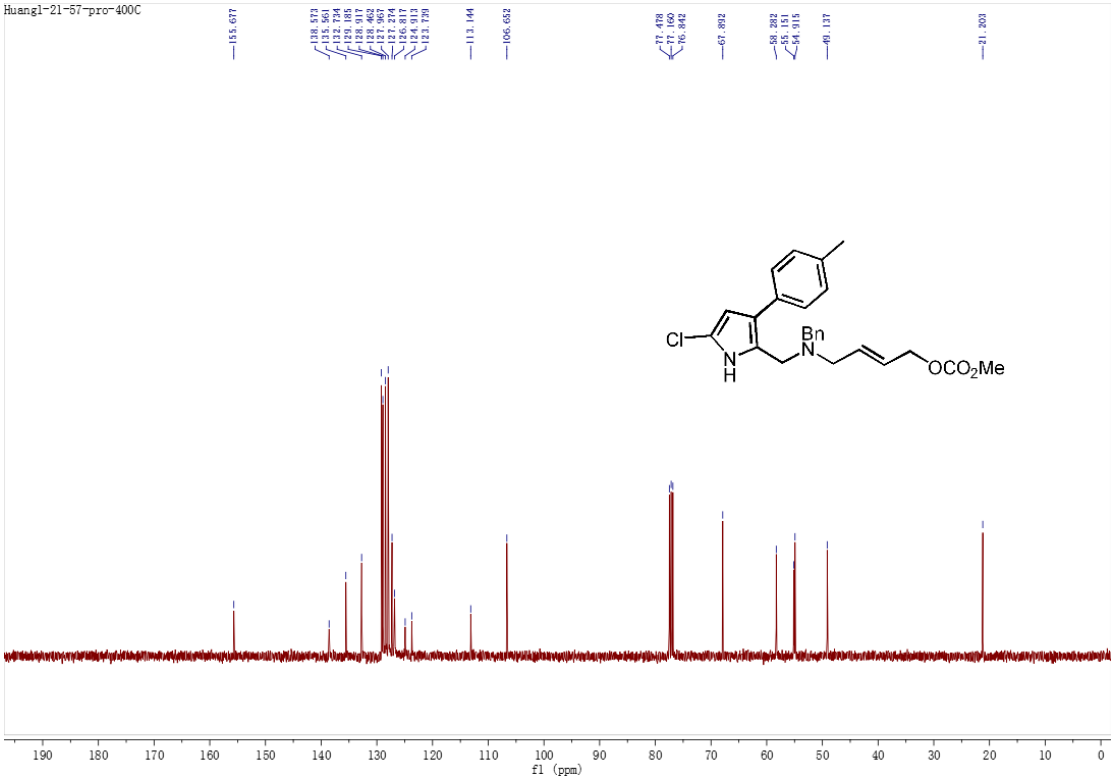

NMR Spectra of **1m**



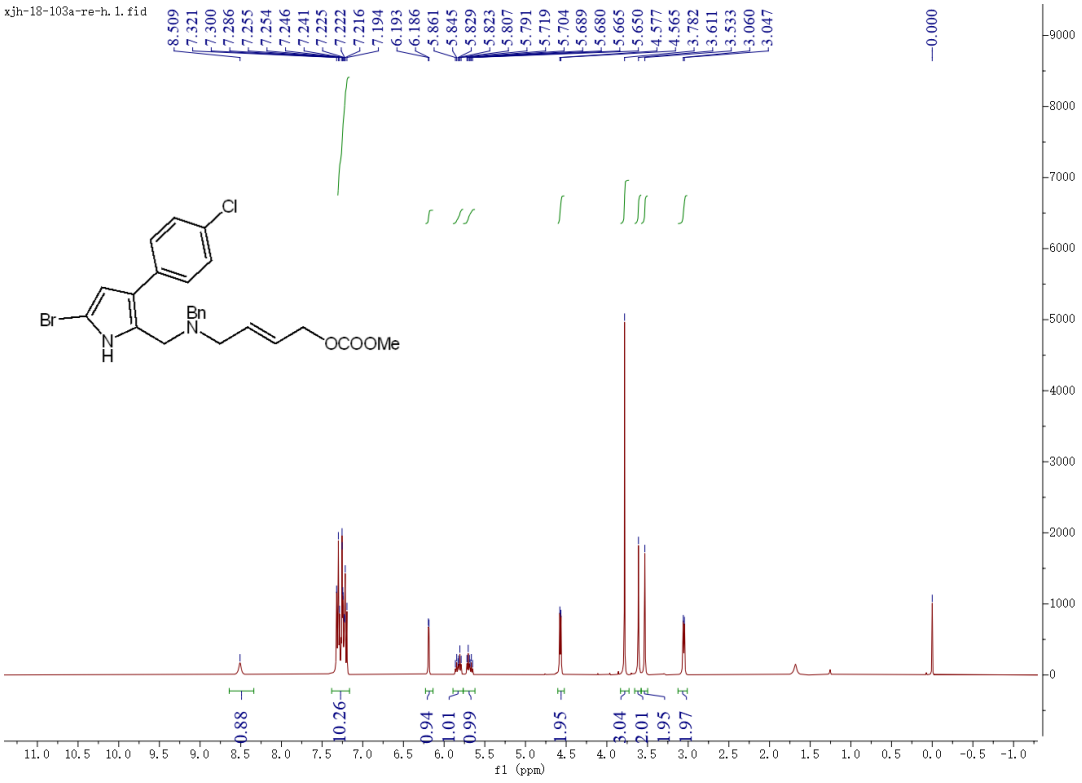


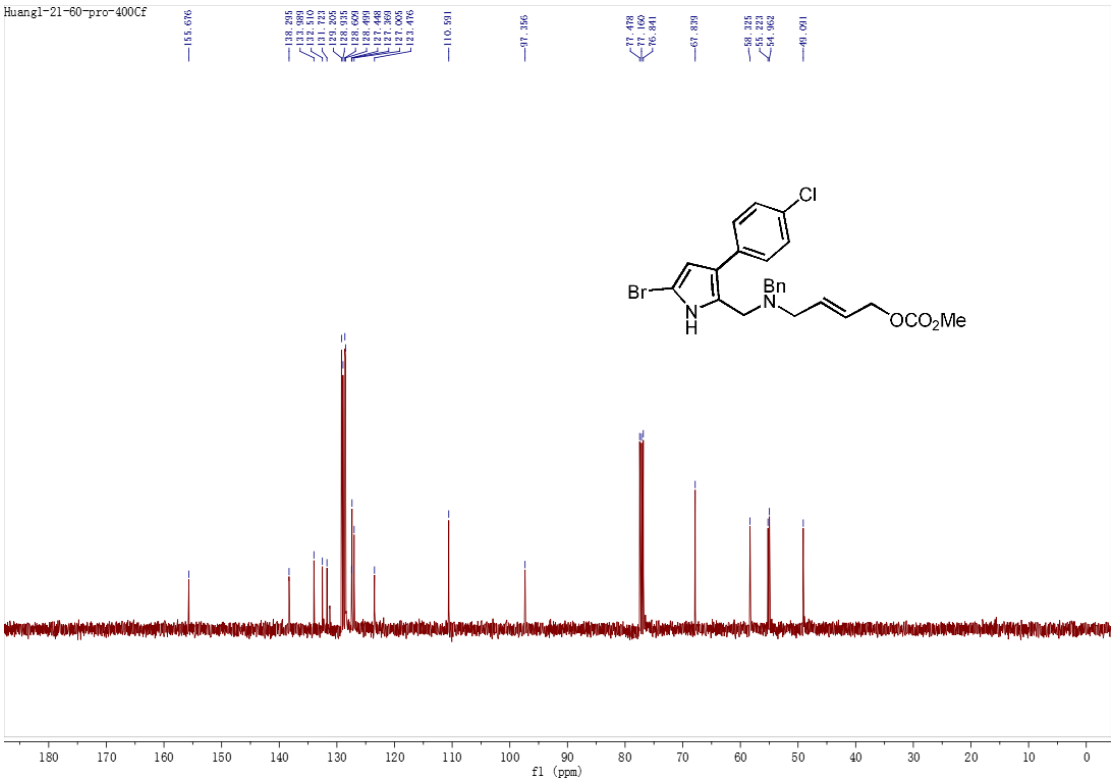

NMR Spectra of **1n**



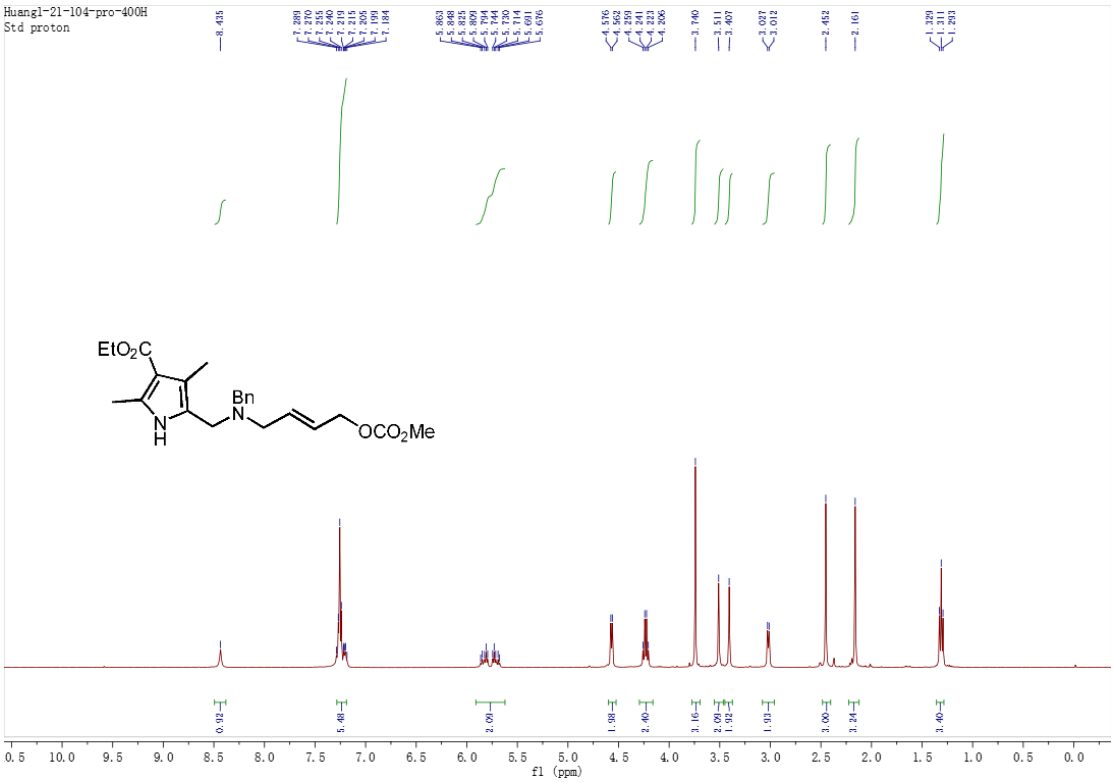


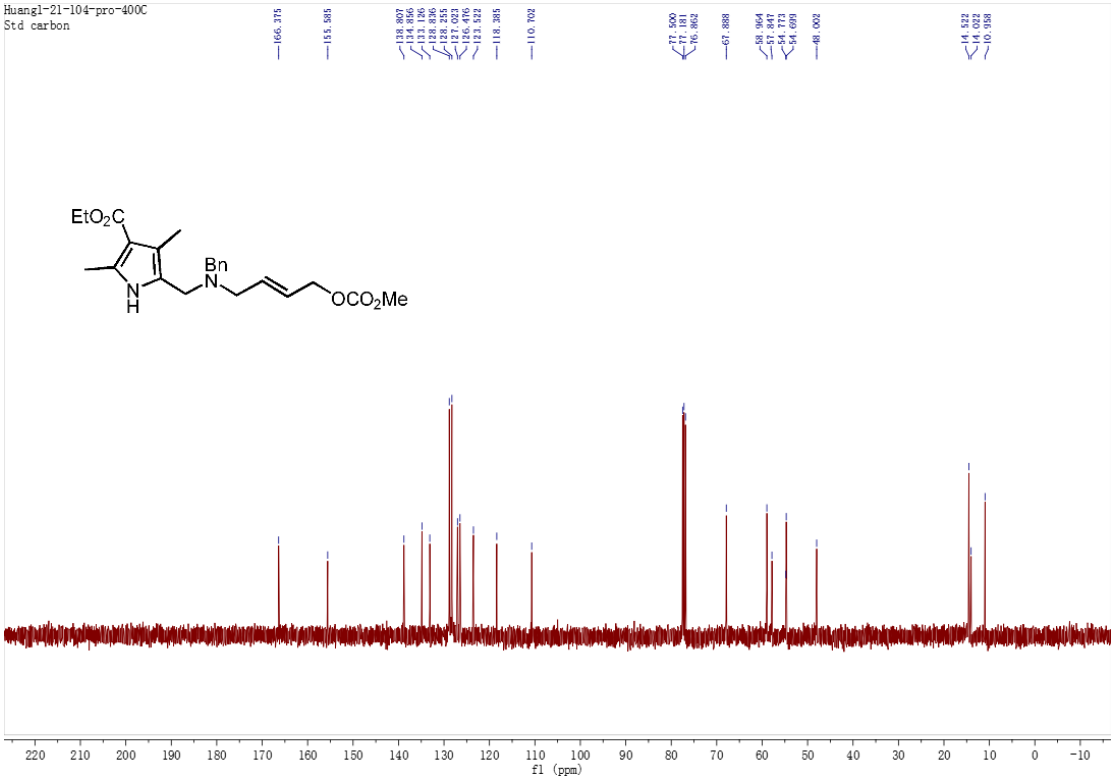

NMR Spectra of **1o**



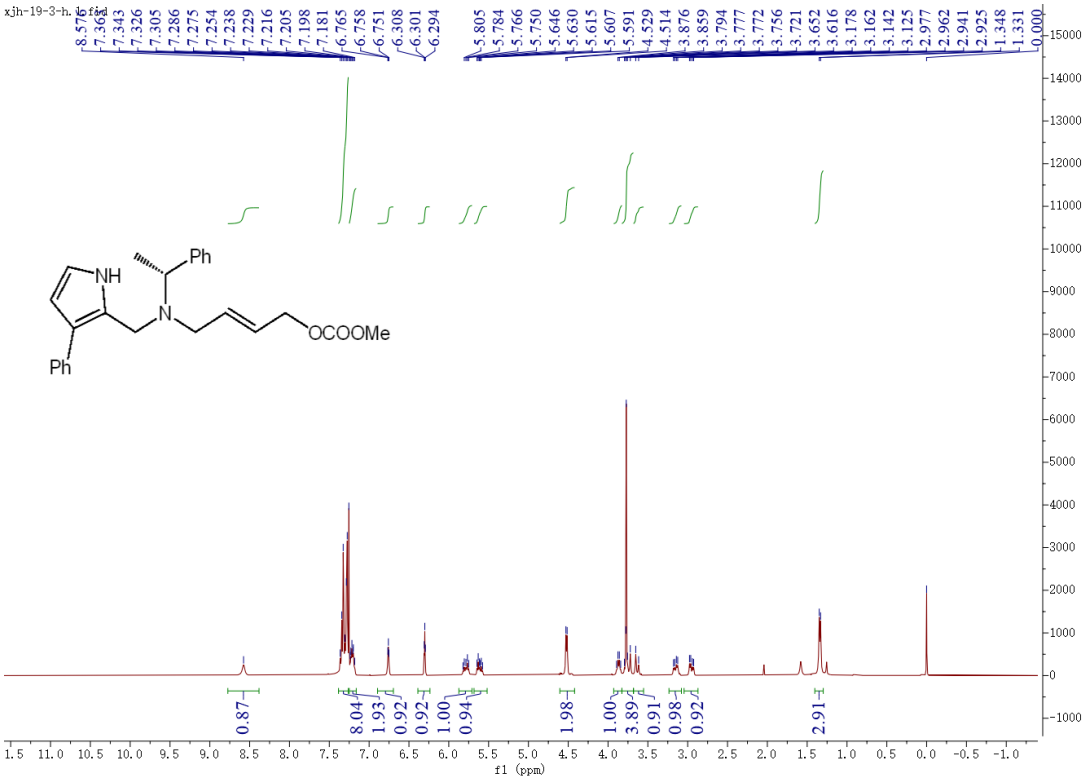


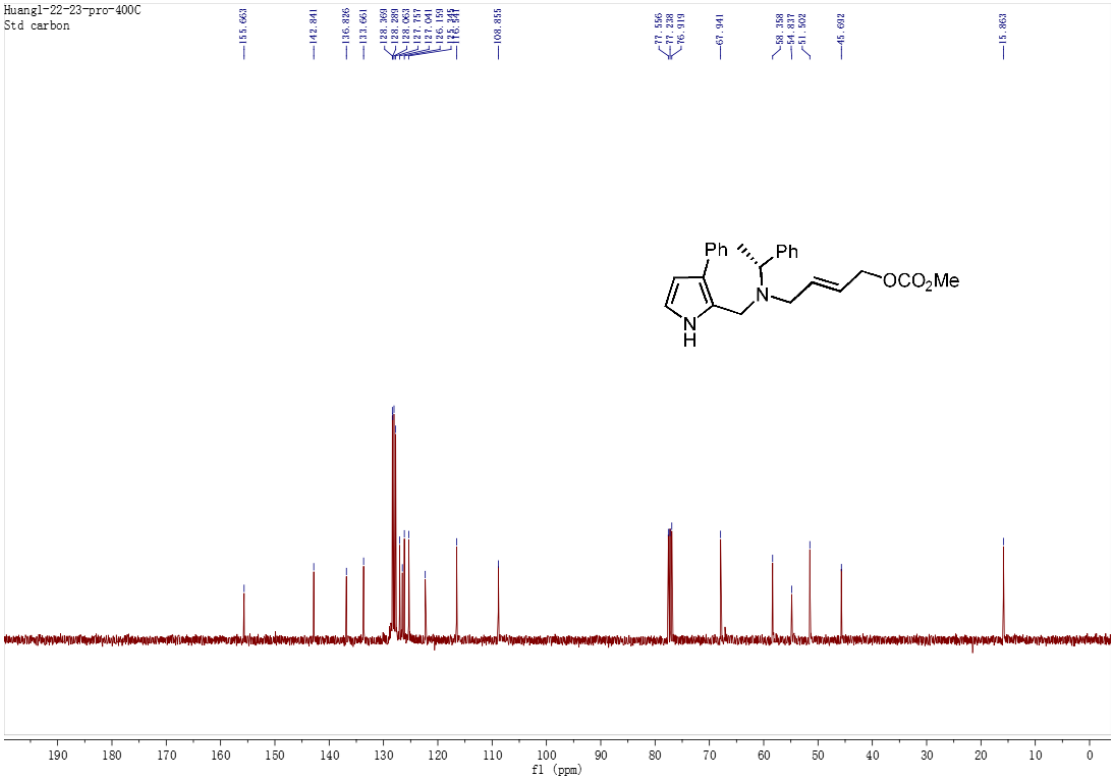

NMR Spectra of **1p**



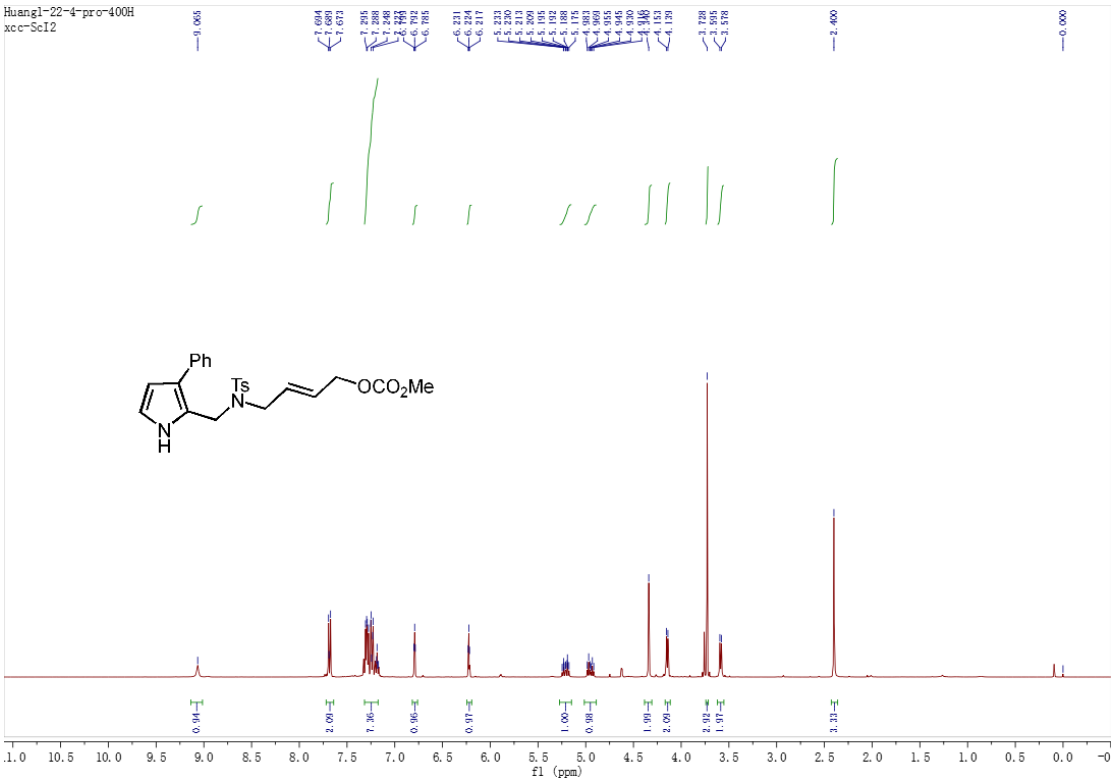


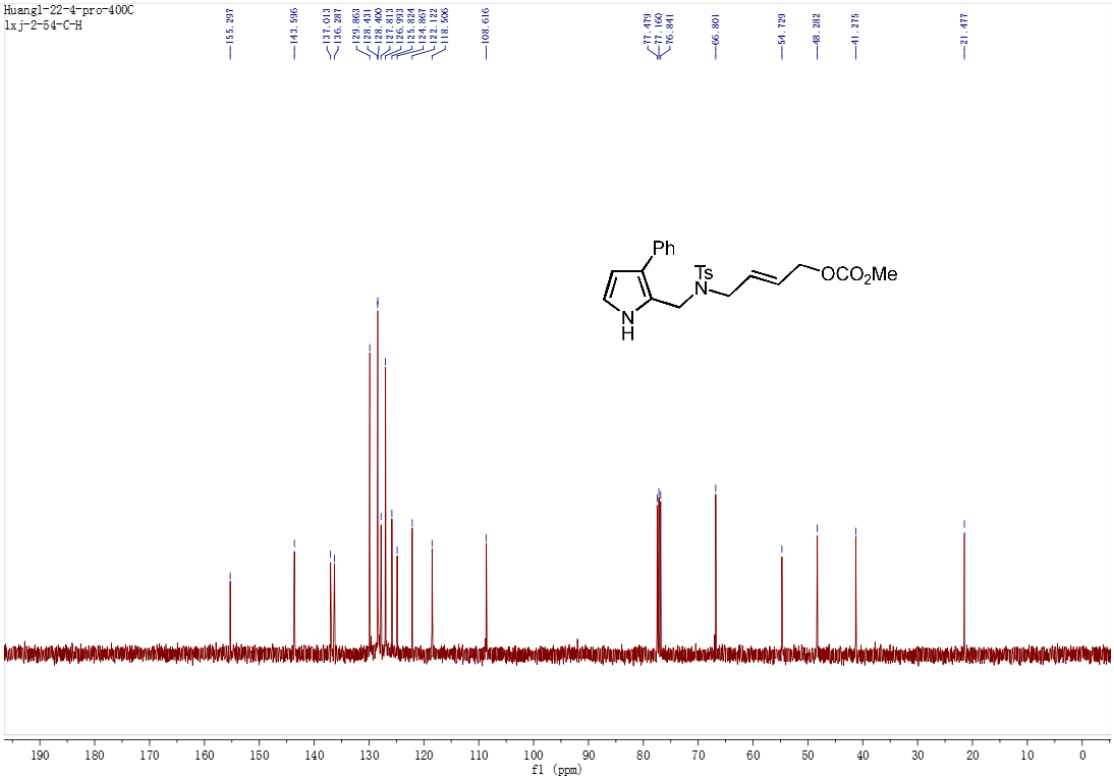

NMR Spectra of **1q**



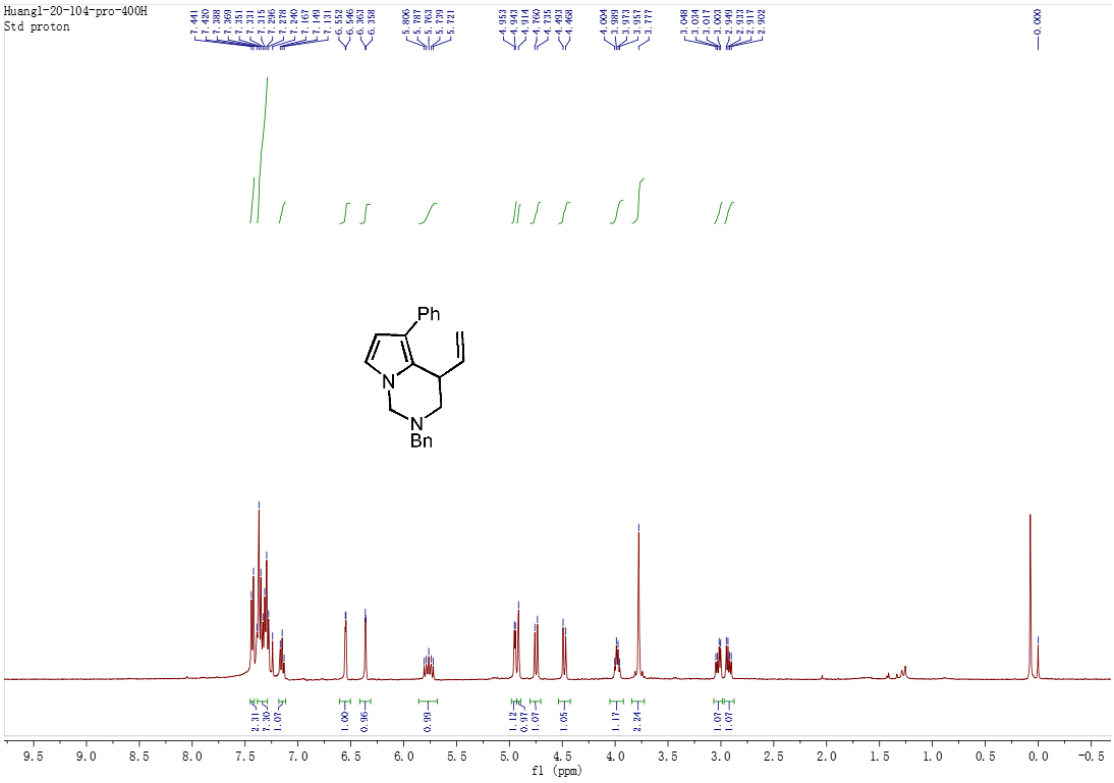


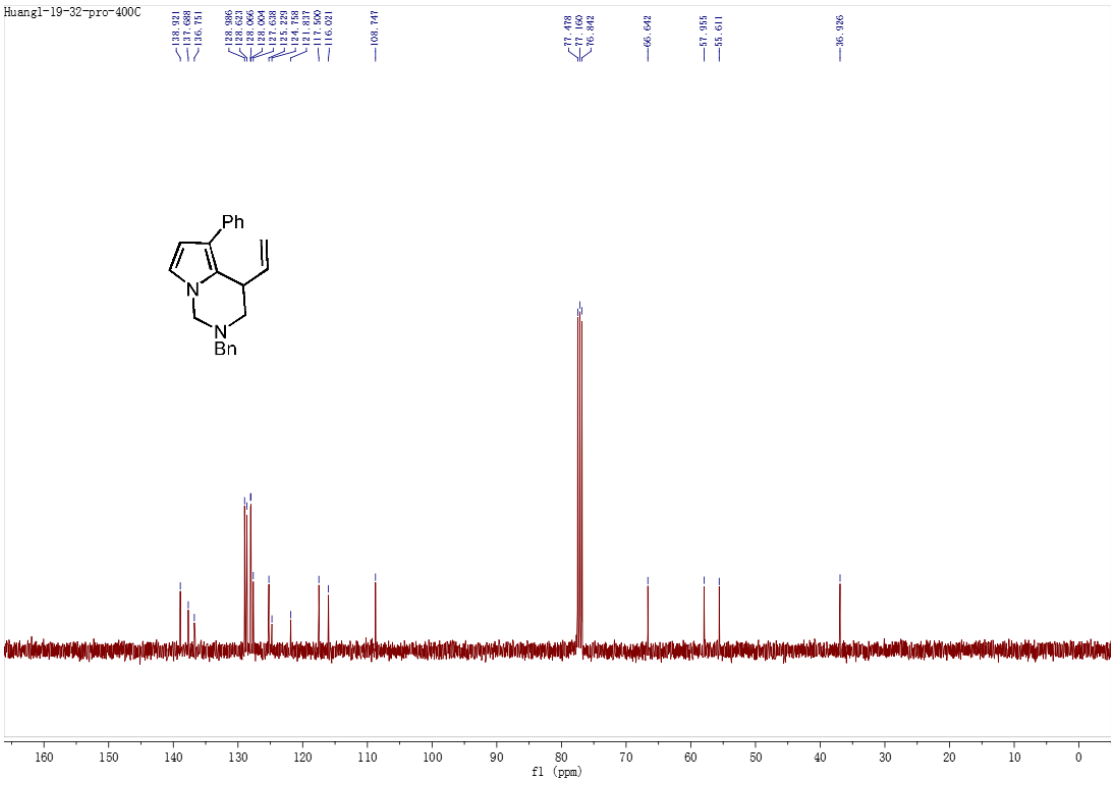

NMR Spectra of **1s**

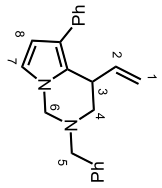



Huang1-22-4-pro-400C
1xj-2-54-C-H
155.297
143.596
137.013
136.287
129.863
128.411
128.406
127.813
126.993
125.824
124.969
122.122
118.506
108.616
77.479
77.160
76.841
66.801
54.729
48.282
41.376
21.477
Ph
Ts
N
OCO2Me
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

NMR Spectra and HPLC Chromatograms of **2a**






HL-19-59-pro-2D

Sample Name:
HL-19-59-pro-2D
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
HL-19-59-pro-2D_20161201_01
PidFile: gCOSY_01

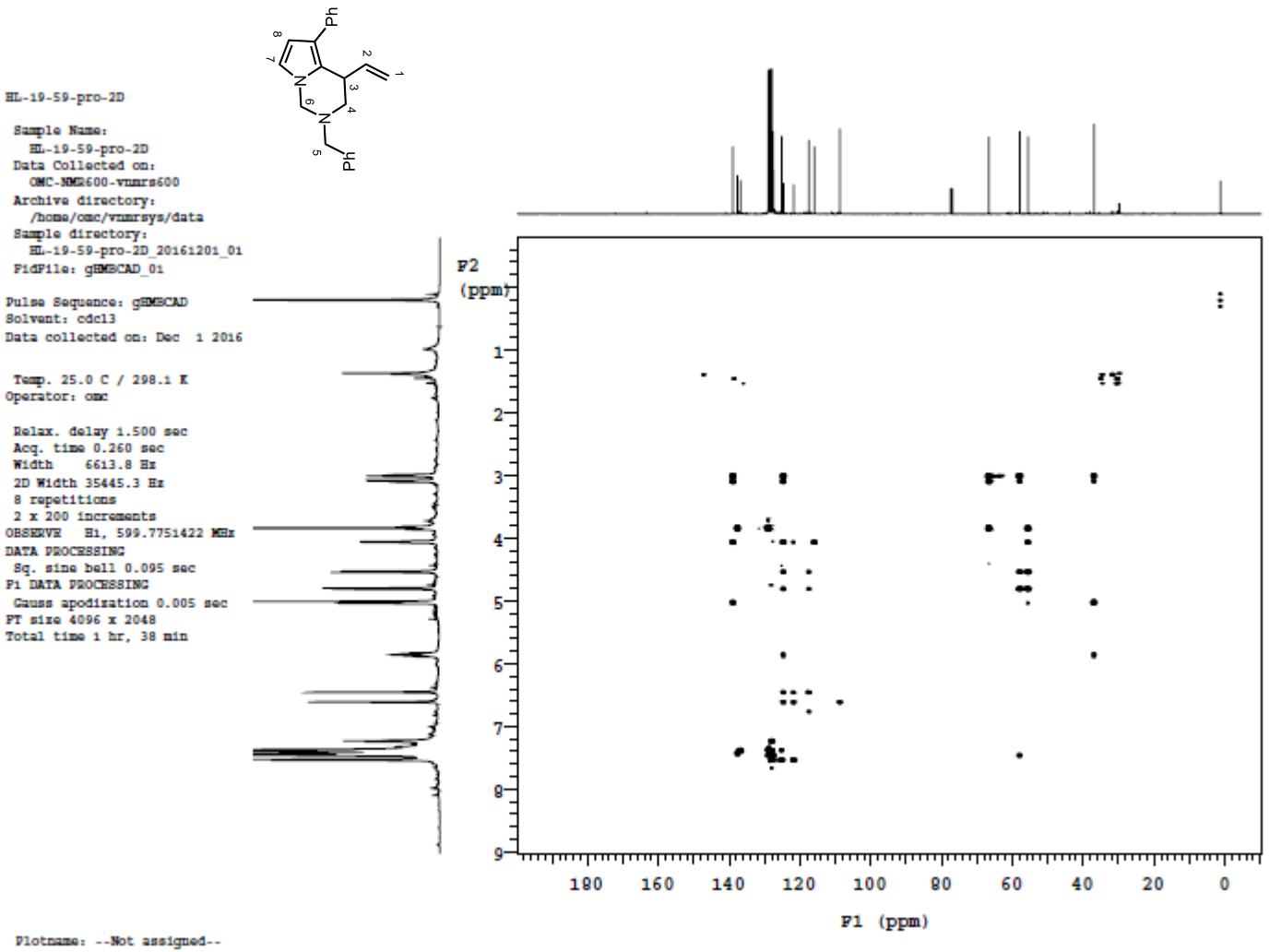
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Dec 1 2016

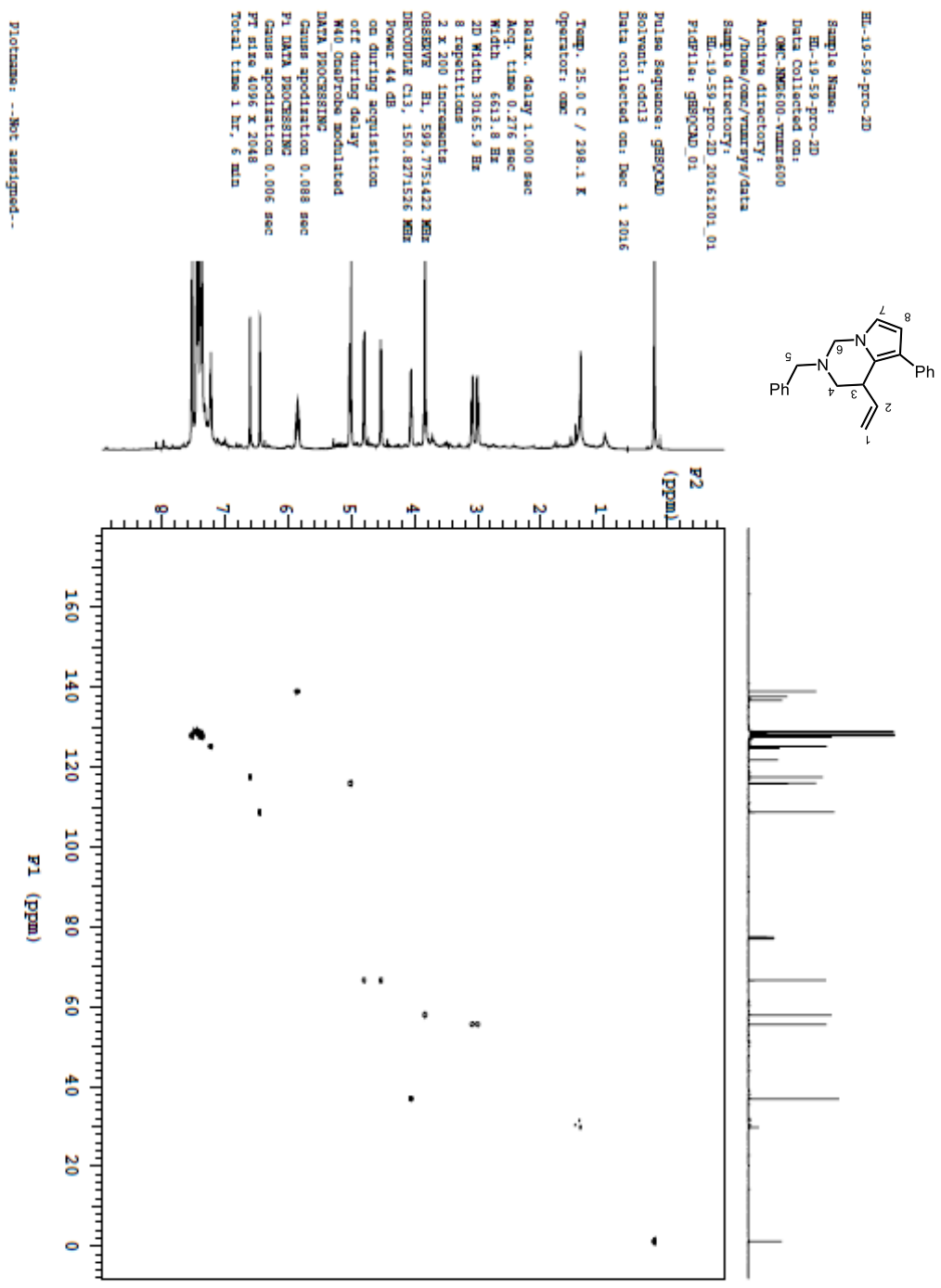
Temp. 25.0 C / 298.1 K
Operator: omc

Relax. delay 1.000 sec
Acq. time 0.453 sec
Width 6578.9 Hz
2D Width 6578.9 Hz
2 repetitions
128 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Sq. sine bell 0.106 sec
F1 DATA PROCESSING
Sq. sine bell 0.019 sec
FT size 4096 x 4096
Total time 5 min 50 sec




Plotname: --Not assigned--


HL-19-59-pro-2D
Sample Name:
HL-19-59-pro-2D
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
HL-19-59-pro-2D_20161201_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Dec 1 2016
Temp. 25.0 C / 298.1 K
Operator: omc
Relax. delay 1.500 sec
Acq. time 0.260 sec
Width 6613.8 Hz
2D Width 35445.3 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Sq. sine bell 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 1 hr, 38 min
Ph
Ph
F2 (ppm)
F1 (ppm)
Plotname: --Not assigned--


EM-19-59-pro-2D
Sample Name:
EM-19-59-pro-2D
Data Collected on:
CMC-NMR600-vnmrs600
Archive directory:
/home/cmc/vnmrsys/data
Sample directory:
EM-19-59-pro-2D_20161201_01
FidFile: gHBQCAD_01
Pulse Sequence: gHBQCAD
Solvent: cdcl3
Data collected on: Dec 1 2016
Temp. 25.0 C / 298.1 K
Operator: cmc
Relax. delay 1.000 sec
Acq. time 0.276 sec
Width 6613.8 Hz
2D Width 30165.9 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 599.7751422 MHz
DECOUPLE C13, 150.8271526 MHz
Power 44 dB
on during acquisition
off during delay
WALTZ16 modulated
DATA PROCESSING
Gauss apodization 0.088 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 4096 x 2048
Total time 1 hr, 6 min
Plotname: --Not assigned--
F2 (ppm)
F1 (ppm)
Ph
Ph

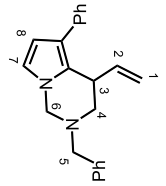
HL-19-59-pro-2D

Sample Name:
HL-19-59-pro-2D
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
HL-19-59-pro-2D_20161201_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Dec 1 2016

Temp. 25.0 C / 298.1 K
Operator: omc

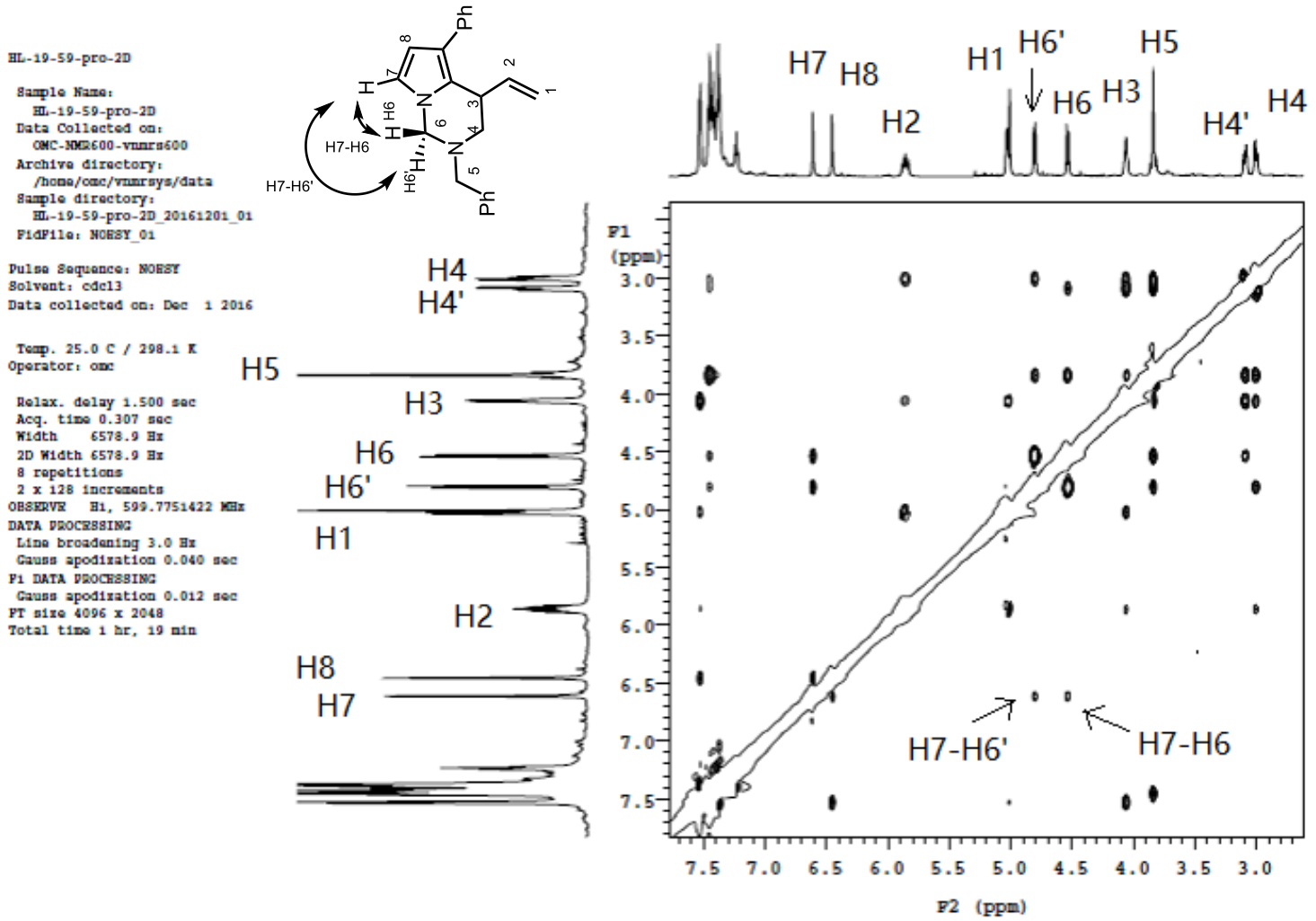
Relax. delay 1.500 sec
Acq. time 0.307 sec
Width 6578.9 Hz
2D Width 6578.9 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.040 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 2048
Total time 1 hr, 19 min

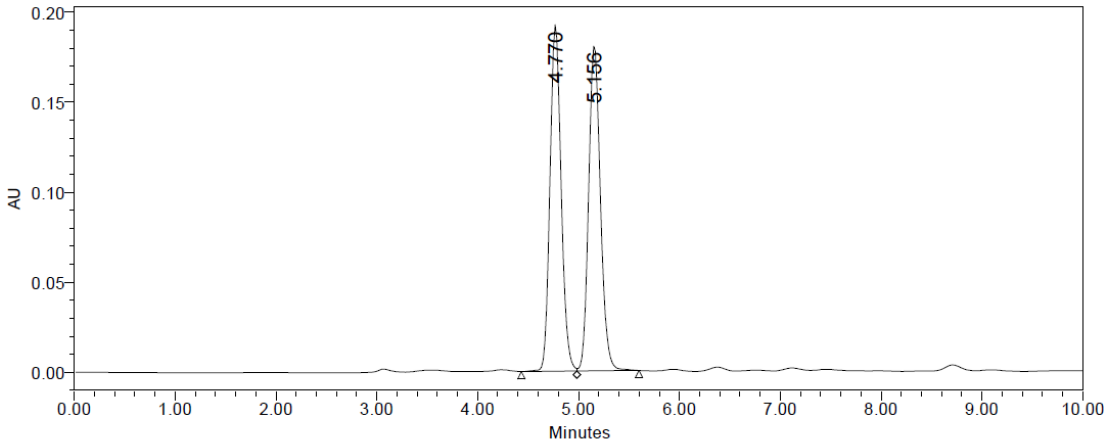






Plotname: --Not assigned--

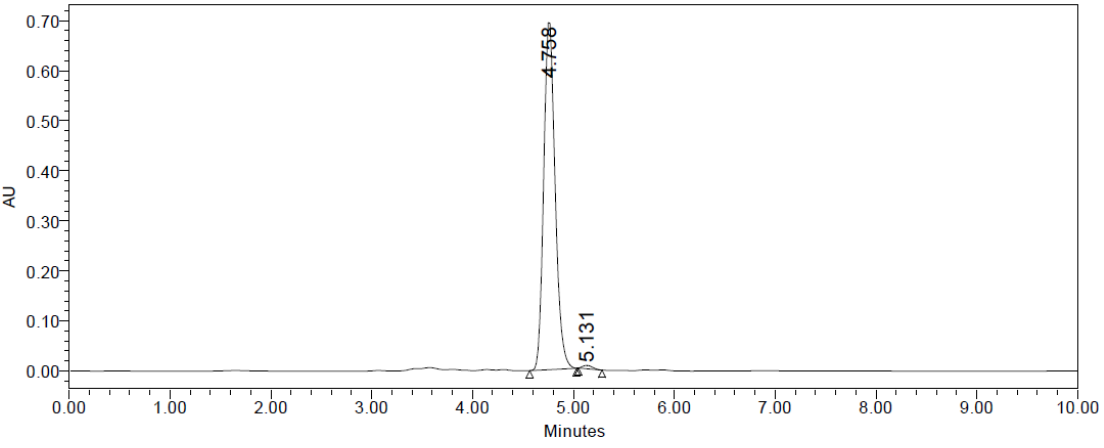

HL-19-59-pro-2D
Sample Name:
HL-19-59-pro-2D
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
HL-19-59-pro-2D_20161201_01
FidFile: NOESY_01
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Dec 1 2016
Temp. 25.0 C / 298.1 K
Operator: omc
Relax. delay 1.500 sec
Acq. time 0.307 sec
Width 6578.9 Hz
2D Width 6578.9 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.040 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 2048
Total time 1 hr, 19 min
Plotname: --Not assigned--
H7-H6
H7-H6'
H4
H4'
H5
H3
H6
H6'
H1
H2
H8
H7
F1 (ppm)
F2 (ppm)
H7-H6'
H7-H6




Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 11/21/2016 10:31:40 AM CST; Result Id: 4212; Processing Method: dfghdf

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 5.156 | 1474057 | 50.01 | 180932 |
| 2 | 1 | 4.770 | 1473697 | 49.99 | 192178 |
| Mean | | 4.963 | | | |
| Std. Dev. | | 0.273 | | | |
| % RSD | | 5.50 | | | |

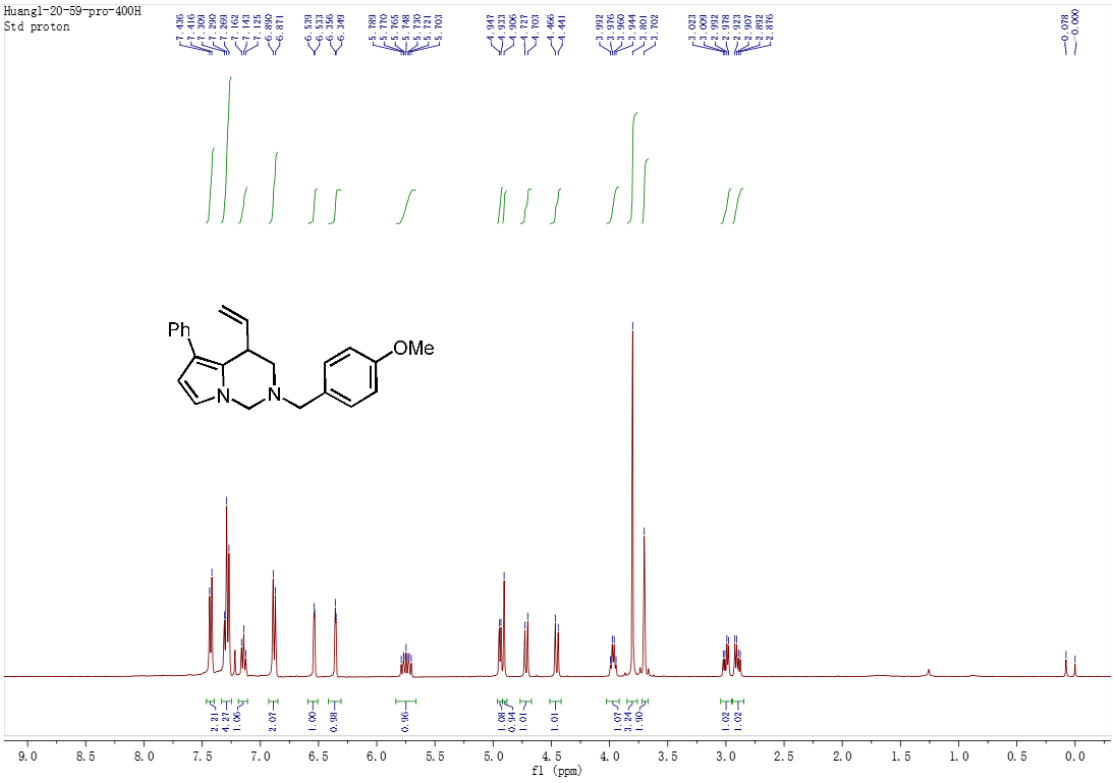


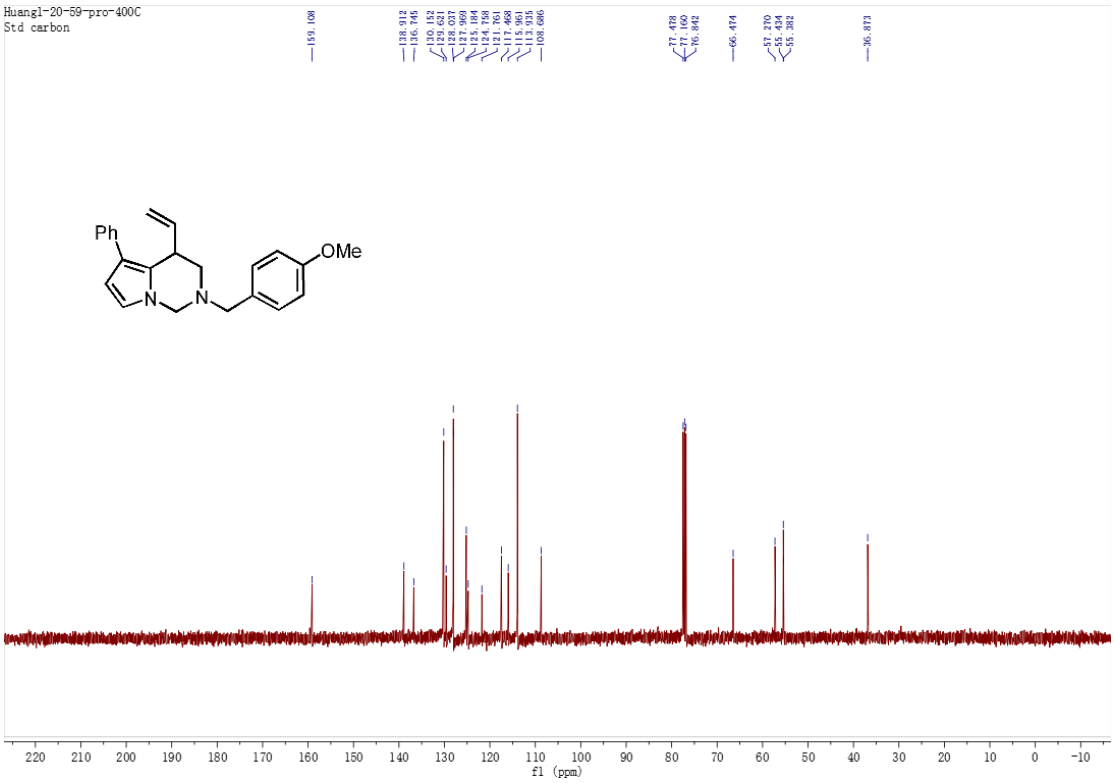

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 12/12/2016 5:02:17 PM CST; Result Id: 4214; Processing Method: gfhjudr

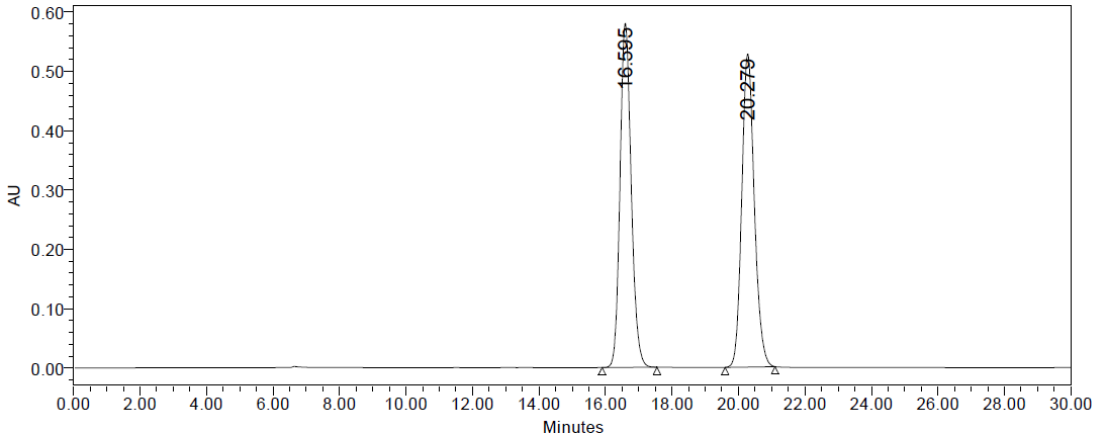
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 5.131 | 46123 | 0.84 | 6805 |
| 2 | 1 | 4.758 | 5446354 | 99.16 | 699635 |
| Mean | | 4.945 | | | |
| Std. Dev. | | 0.264 | | | |
| % RSD | | 5.33 | | | |

NMR Spectra and HPLC Chromatograms of **2b**



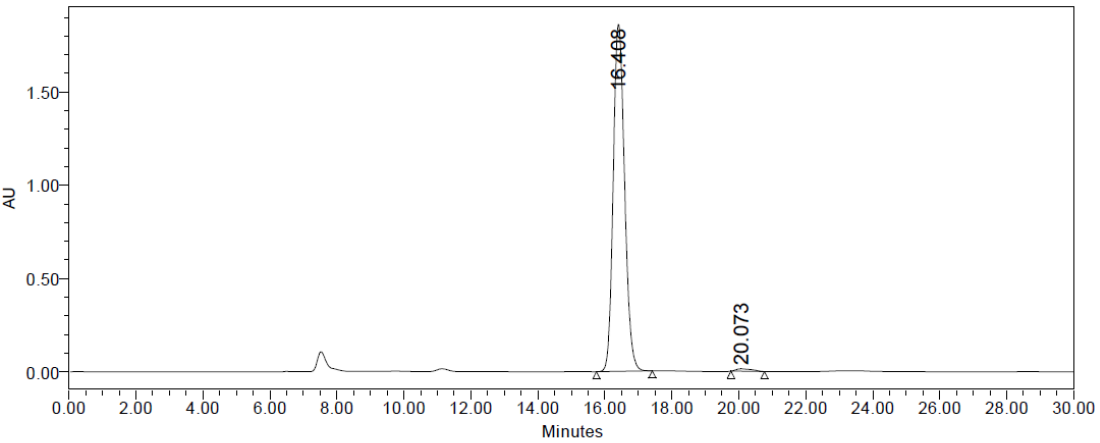






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/5/2017 4:11:35 PM CST; Result Id: 3938; Processing Method: 4524

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 16.595 | 13555076 | 49.42 | 580551 |
| 2 | 1 | 20.279 | 13870827 | 50.58 | 528057 |
| Mean | | 18.437 | | | |
| Std. Dev. | | 2.605 | | | |
| % RSD | | 14.13 | | | |

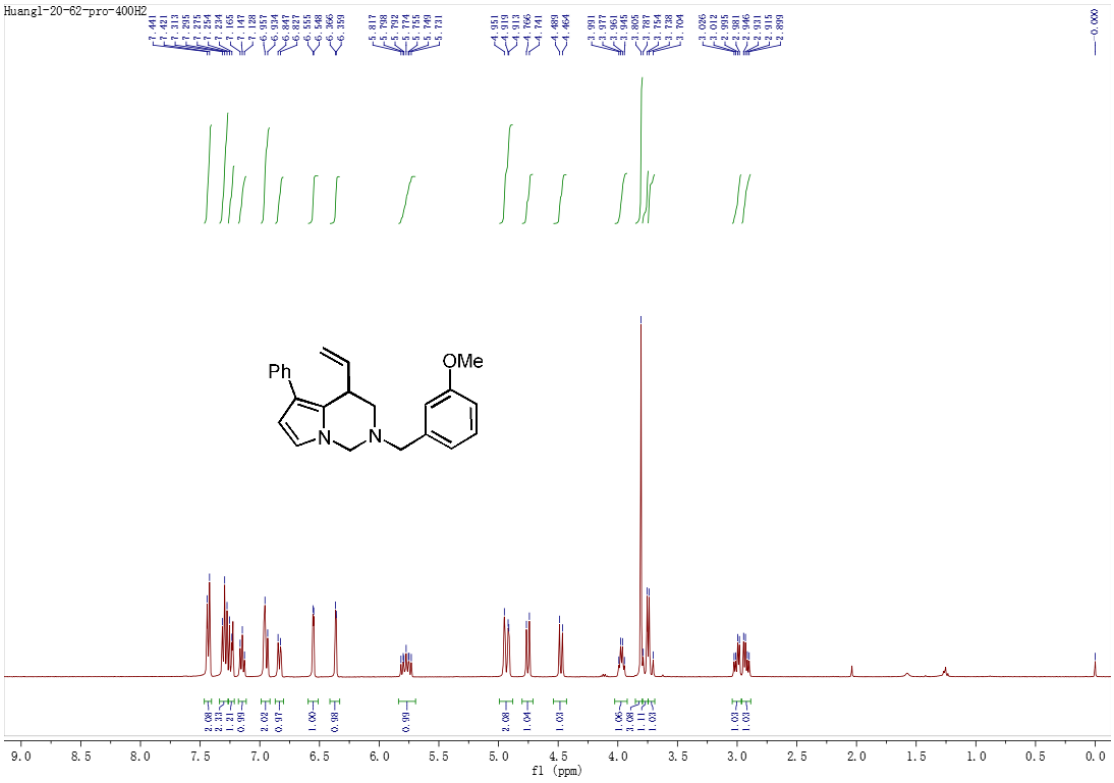


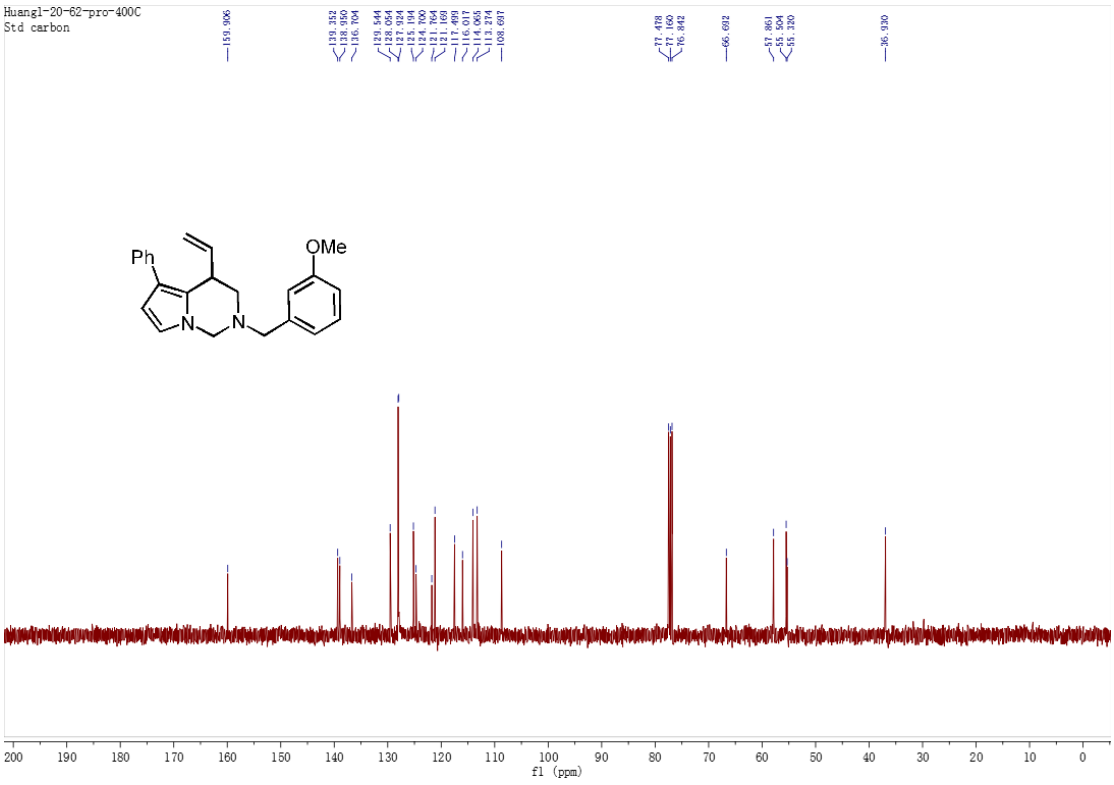

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/5/2017 6:21:54 PM CST; Result Id: 4038; Processing Method: thursd

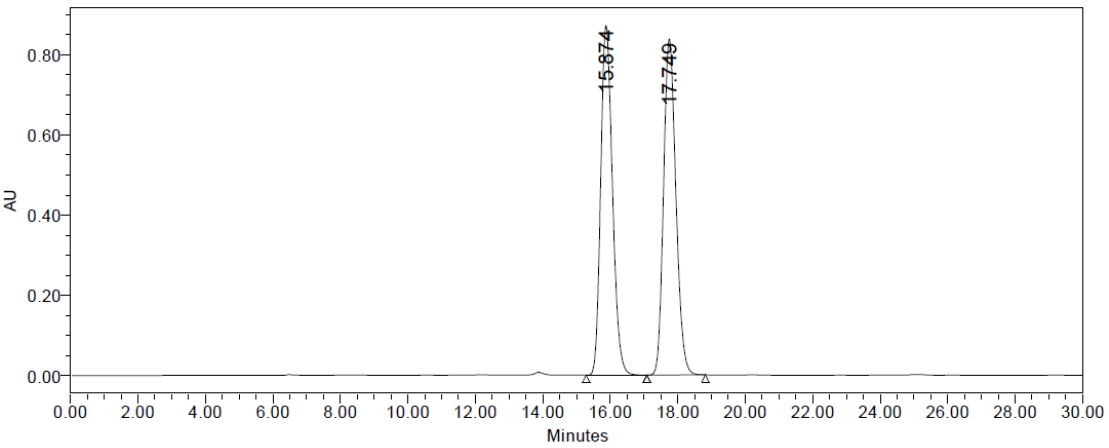
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 20.073 | 448058 | 1.01 | 13497 |
| 2 | 1 | 16.408 | 43863914 | 98.99 | 1862546 |
| Mean | | 18.241 | | | |
| Std. Dev. | | 2.591 | | | |
| % RSD | | 14.21 | | | |

NMR Spectra and HPLC Chromatograms of **2c**



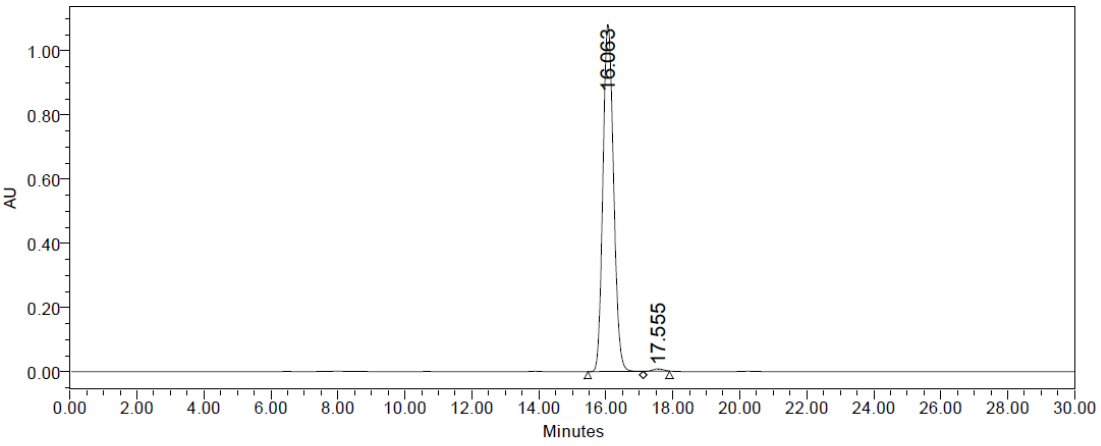






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/8/2017 2:16:49 PM CST; Result Id: 4032; Processing Method: fgh

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 17.749 | 21288947 | 50.29 | 837799 |
| 2 | 1 | 15.874 | 21045794 | 49.71 | 872275 |
| Mean | | 16.811 | | | |
| Std. Dev. | | 1.326 | | | |
| % RSD | | 7.89 | | | |

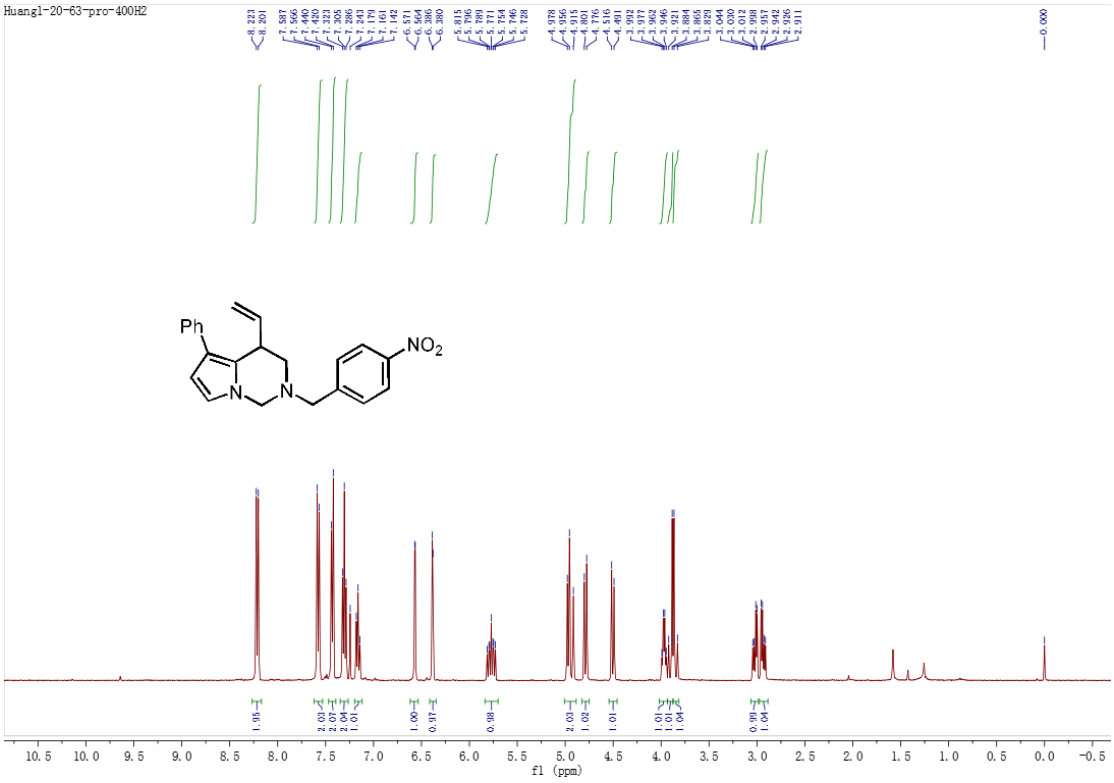


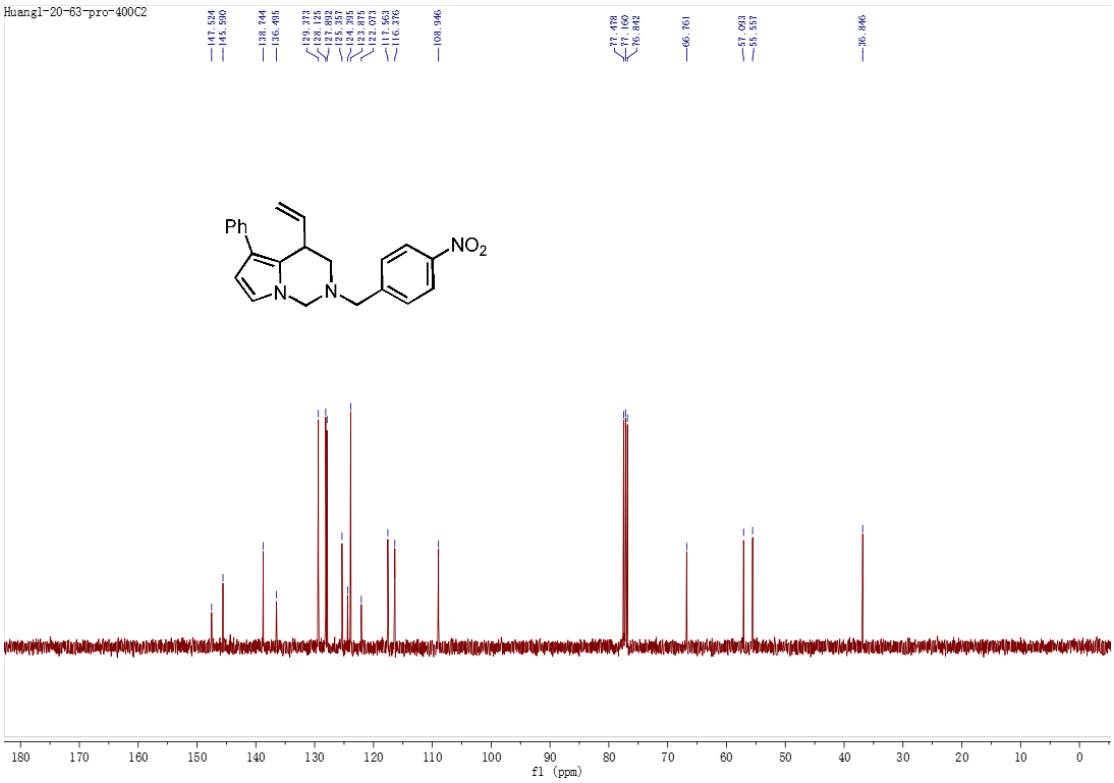

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/8/2017 4:19:06 PM CST; Result Id: 4030; Processing Method: dfhsdf

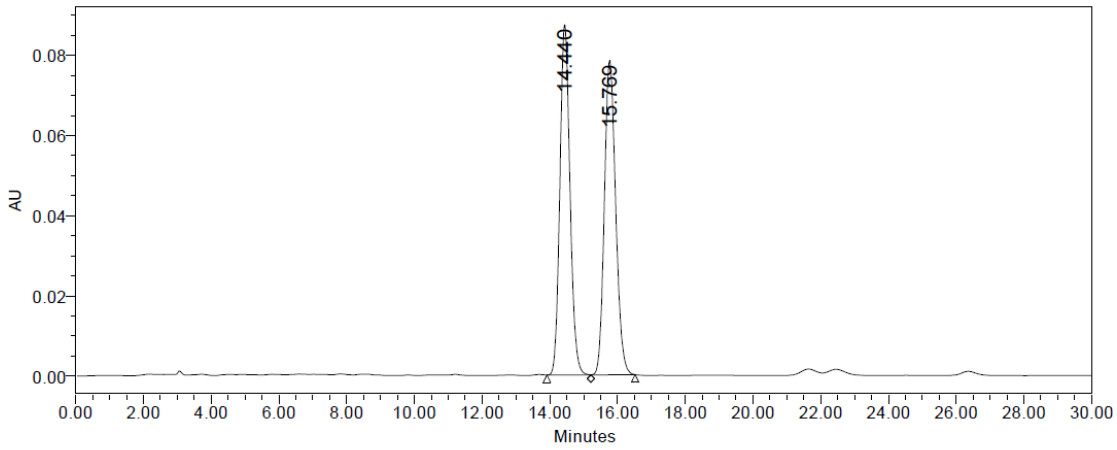
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 17.555 | 148203 | 0.62 | 7007 |
| 2 | 1 | 16.063 | 23849735 | 99.38 | 1081535 |
| Mean | | 16.809 | | | |
| Std. Dev. | | 1.055 | | | |
| % RSD | | 6.28 | | | |

NMR Spectra and HPLC Chromatograms of **2d**



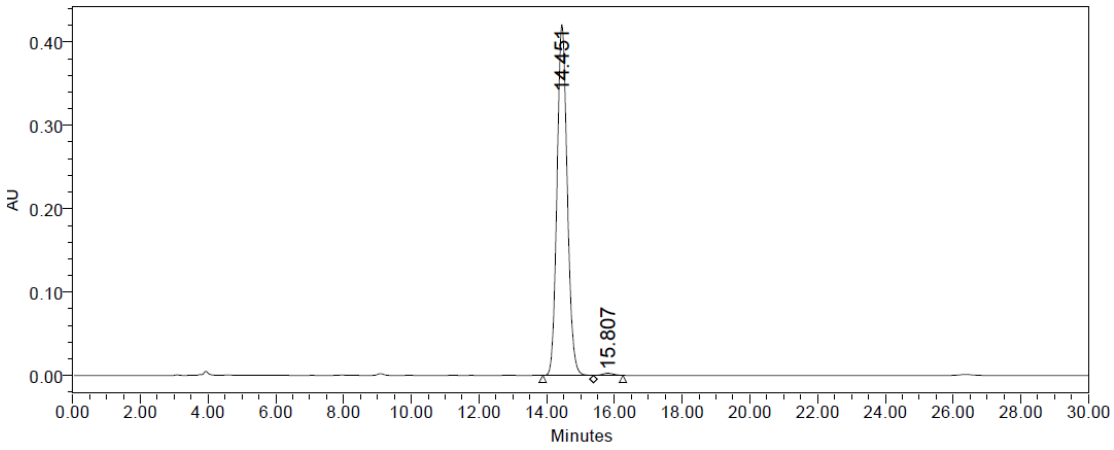






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/8/2017 4:59:52 PM CST; Result Id: 4034; Processing Method: deye

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 15.769 | 1816295 | 50.04 | 78406 |
| 2 | 1 | 14.440 | 1813376 | 49.96 | 87493 |
| Mean | | 15.104 | | | |
| Std. Dev. | | 0.939 | | | |
| % RSD | | 6.22 | | | |

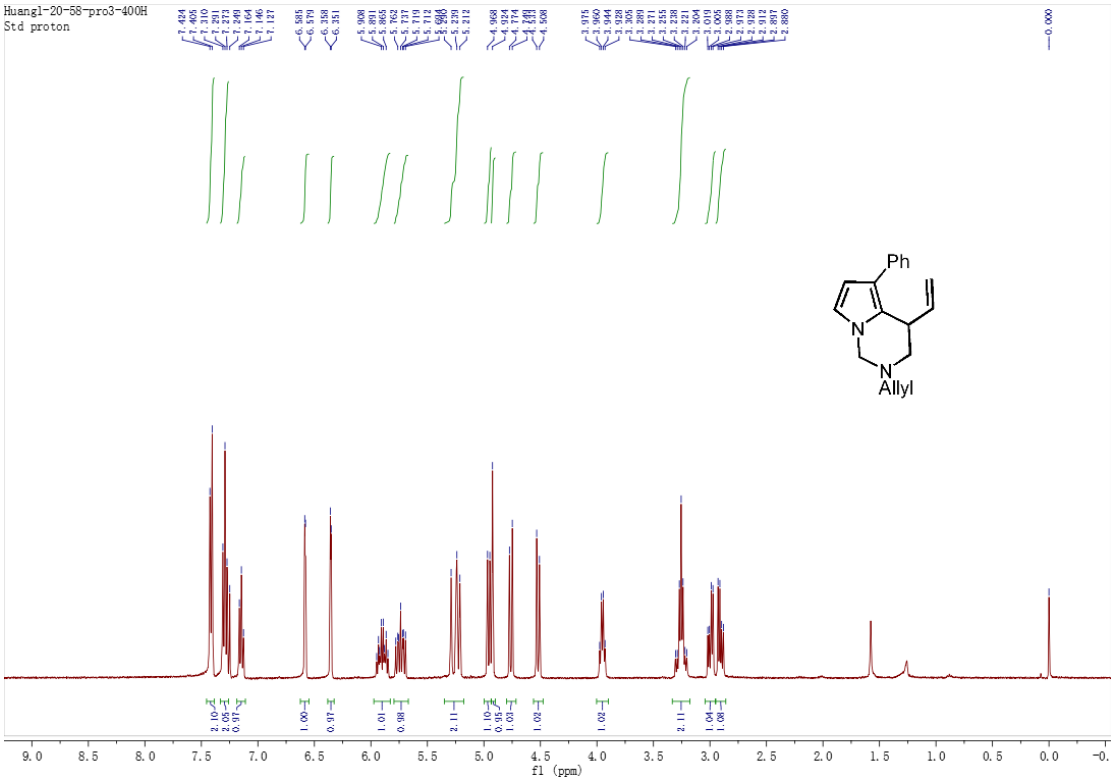


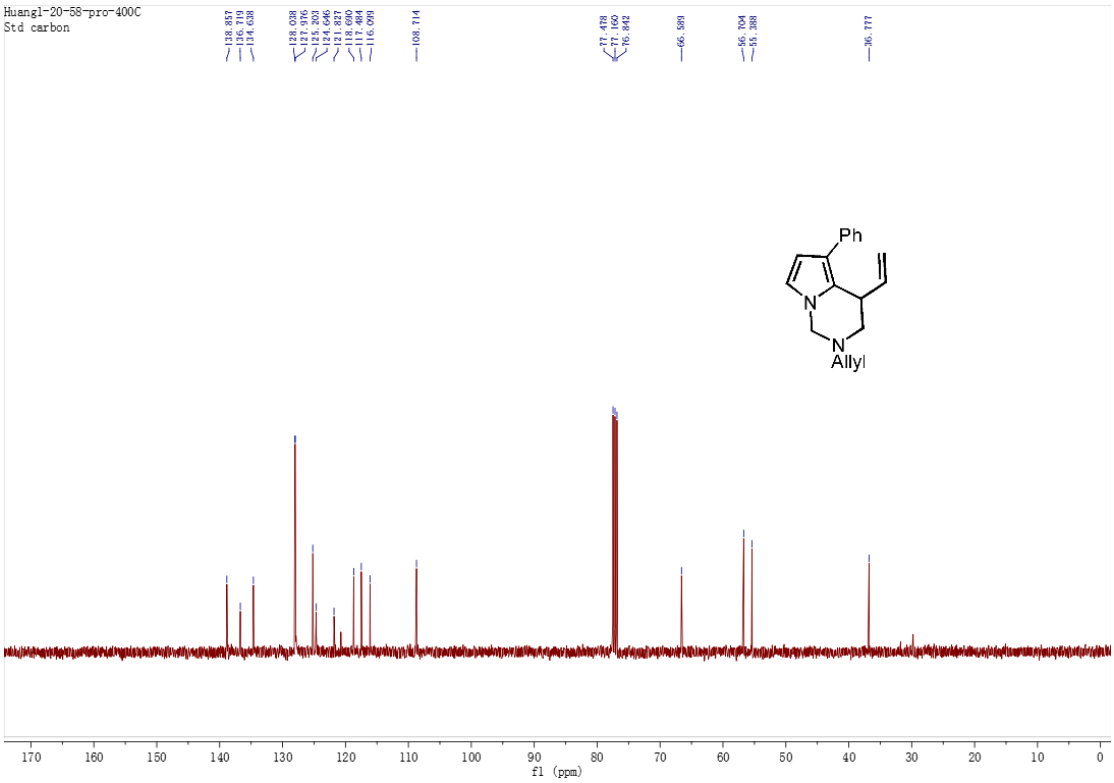

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/8/2017 5:30:13 PM CST; Result Id: 4036; Processing Method: dfhdghfr

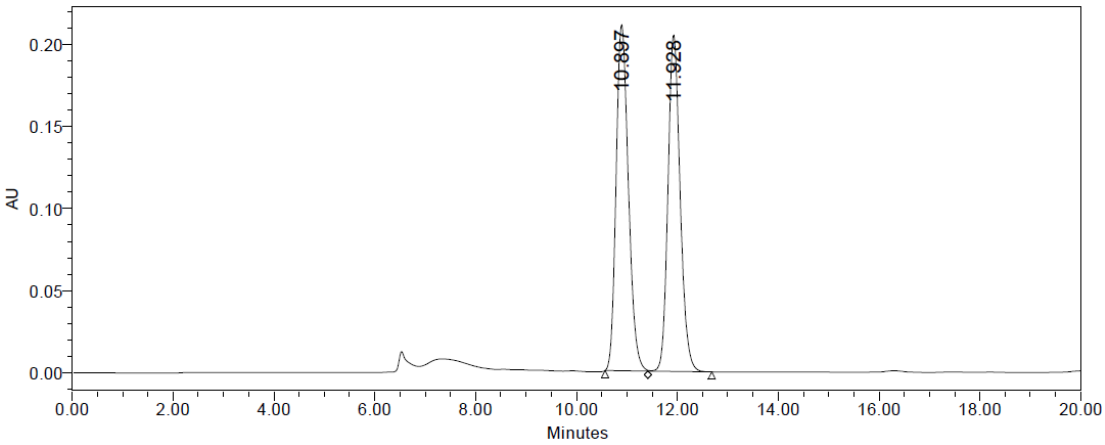
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 15.807 | 59169 | 0.66 | 2671 |
| 2 | 1 | 14.451 | 8849800 | 99.34 | 420618 |
| Mean | | 15.129 | | | |
| Std. Dev. | | 0.959 | | | |
| % RSD | | 6.34 | | | |

NMR Spectra and HPLC Chromatograms of **2e**



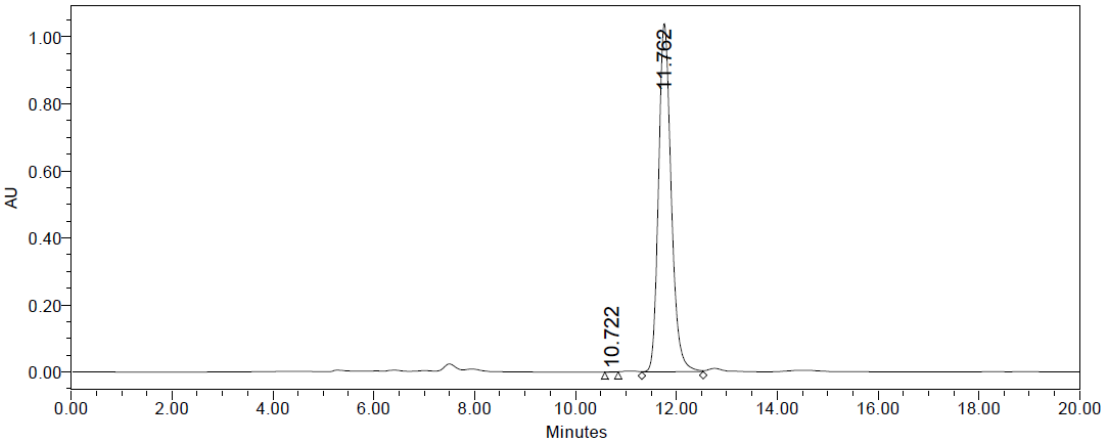






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/5/2017 2:57:04 PM CST; Result Id: 3934; Processing Method: 5646

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.928 | 3448585 | 49.15 | 205120 |
| 2 | 1 | 10.897 | 3567284 | 50.85 | 210906 |
| Mean | | 11.412 | | | |
| Std. Dev. | | 0.729 | | | |
| % RSD | | 6.39 | | | |

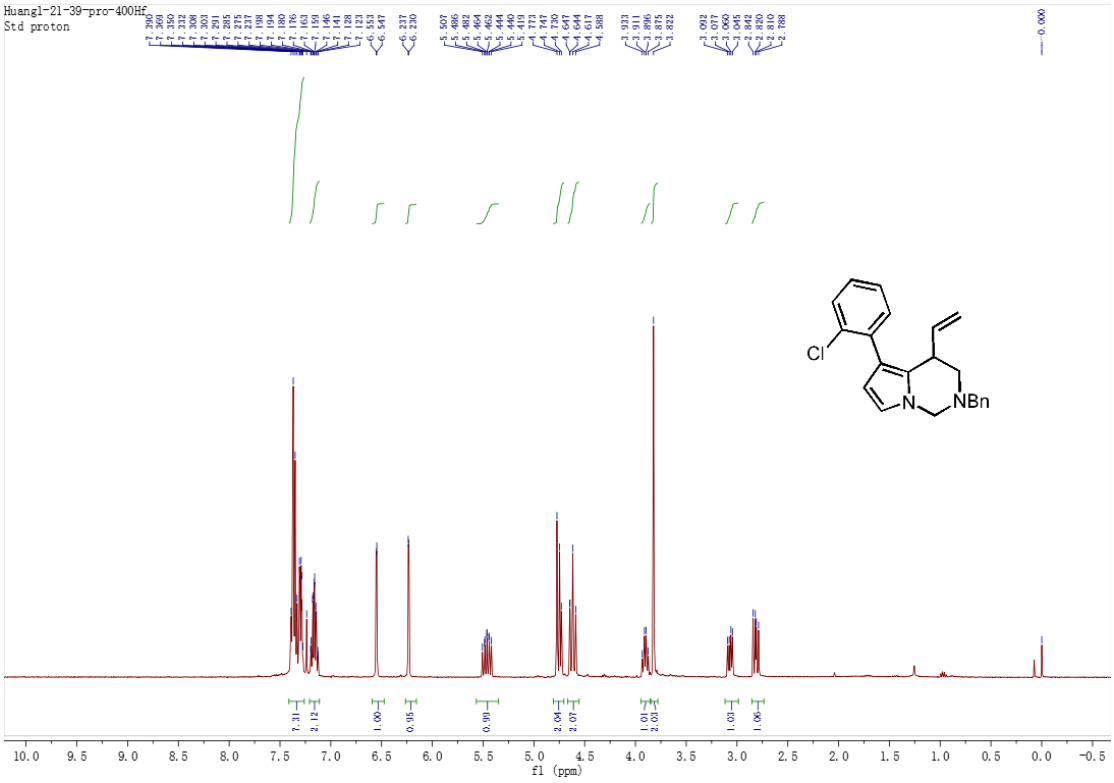


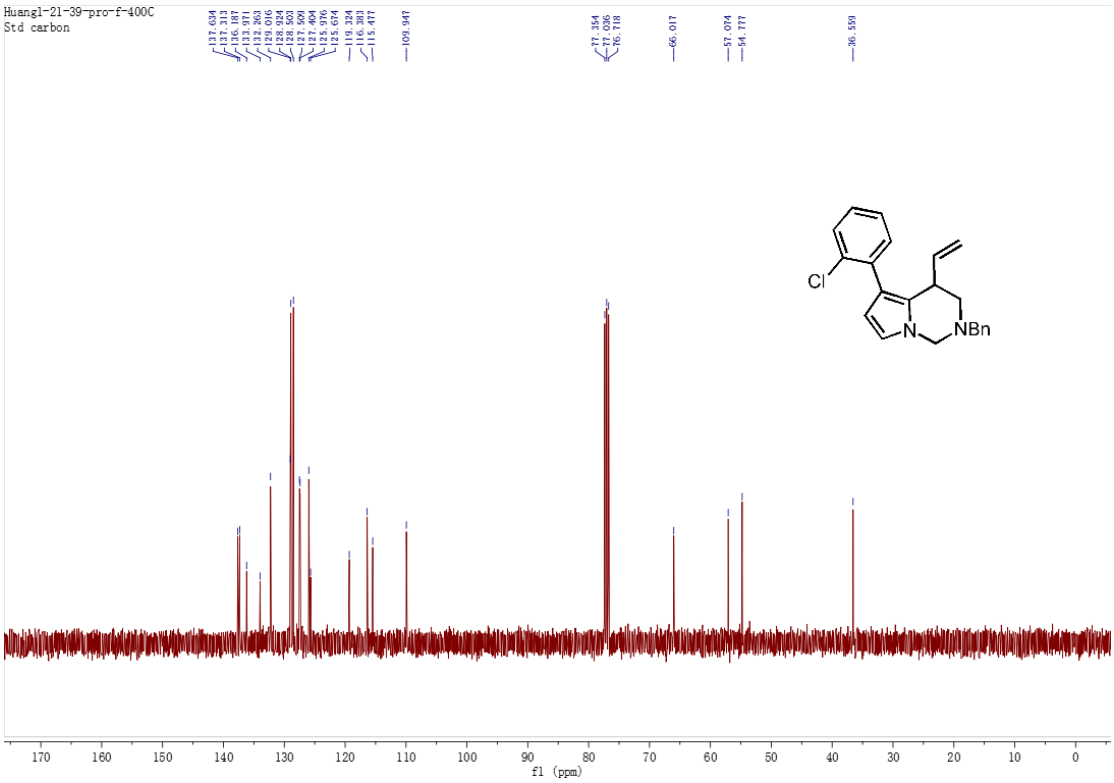

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 1/5/2017 6:01:29 PM CST; Result Id: 3961; Processing Method: ety

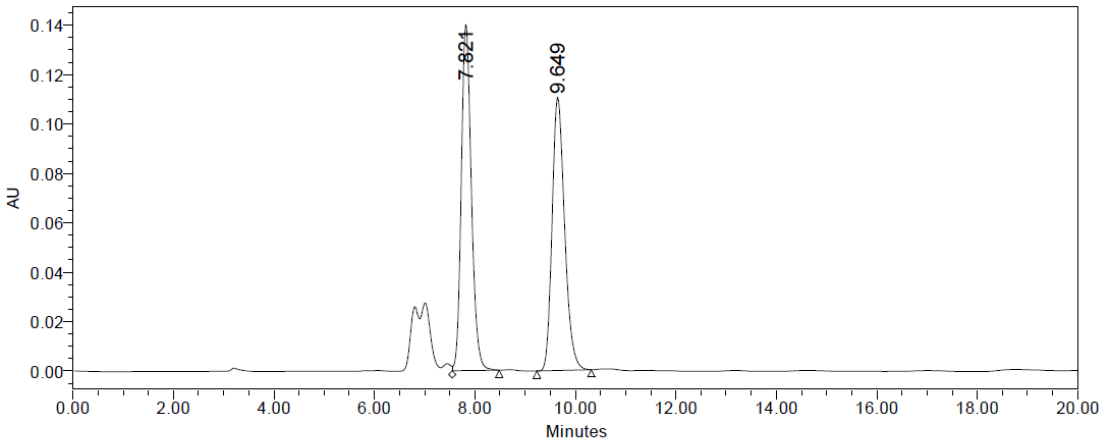
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.762 | 18151183 | 99.97 | 1039334 |
| 2 | 1 | 10.722 | 6075 | 0.03 | -598 |
| Mean | | 11.242 | | | |
| Std. Dev. | | 0.735 | | | |
| % RSD | | 6.54 | | | |

NMR Spectra and HPLC Chromatograms of **2f**



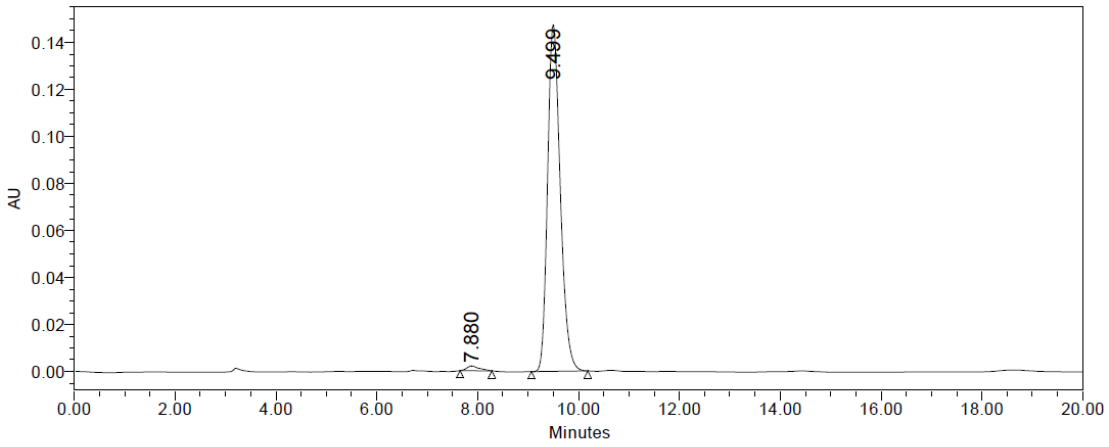






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 10:25:16 AM CST; Result Id: 4342; Processing Method: ghfghf

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.649 | 1922237 | 49.77 | 110643 |
| 2 | 1 | 7.821 | 1940269 | 50.23 | 140213 |
| Mean | | 8.735 | | | |
| Std. Dev. | | 1.292 | | | |
| % RSD | | 14.79 | | | |

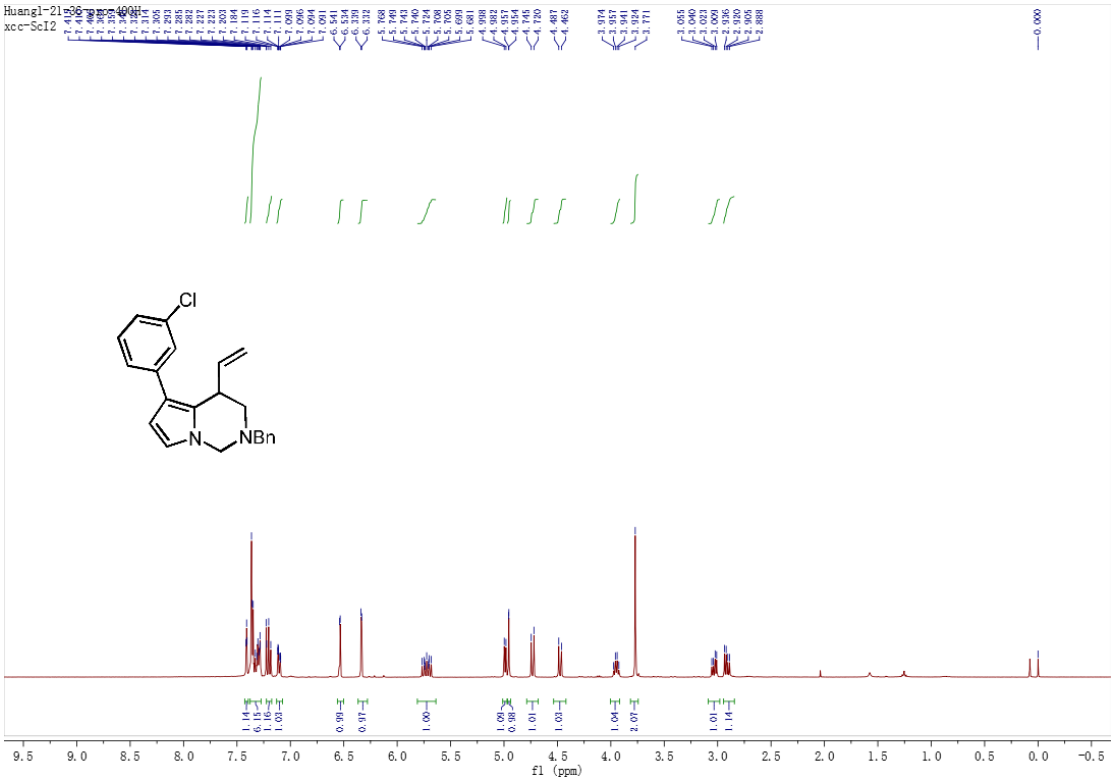


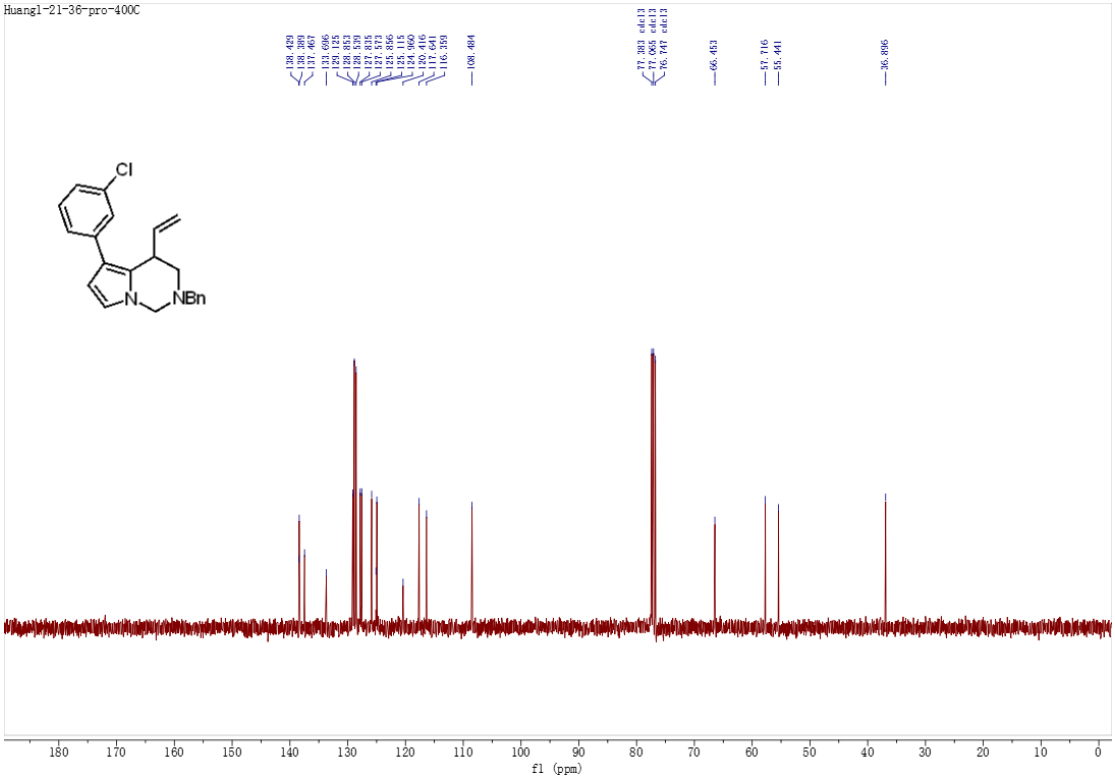

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 10:45:39 AM CST; Result Id: 4344; Processing Method: ghhdfg

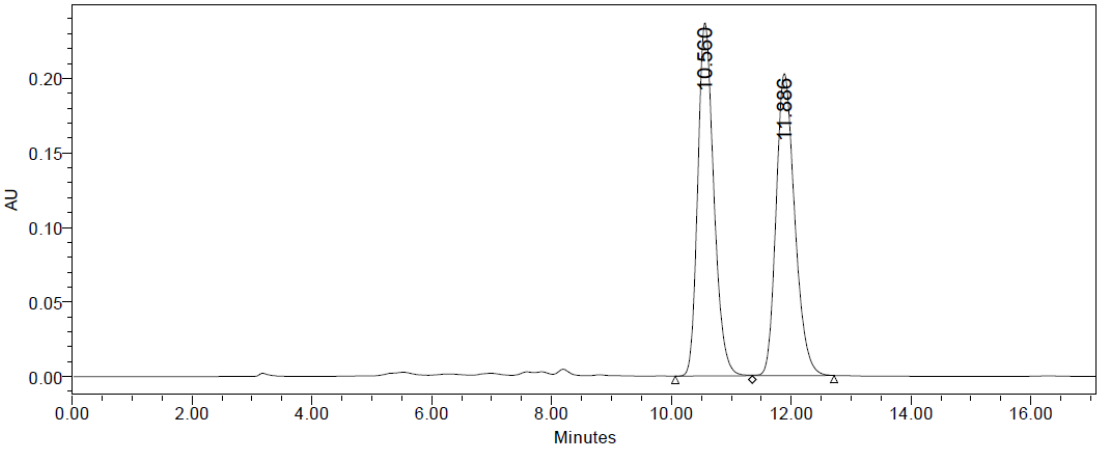
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.499 | 2570240 | 98.67 | 147492 |
| 2 | 1 | 7.880 | 34629 | 1.33 | 2047 |
| Mean | | 8.689 | | | |
| Std. Dev. | | 1.145 | | | |
| % RSD | | 13.18 | | | |

NMR Spectra and HPLC Chromatograms of **2g**



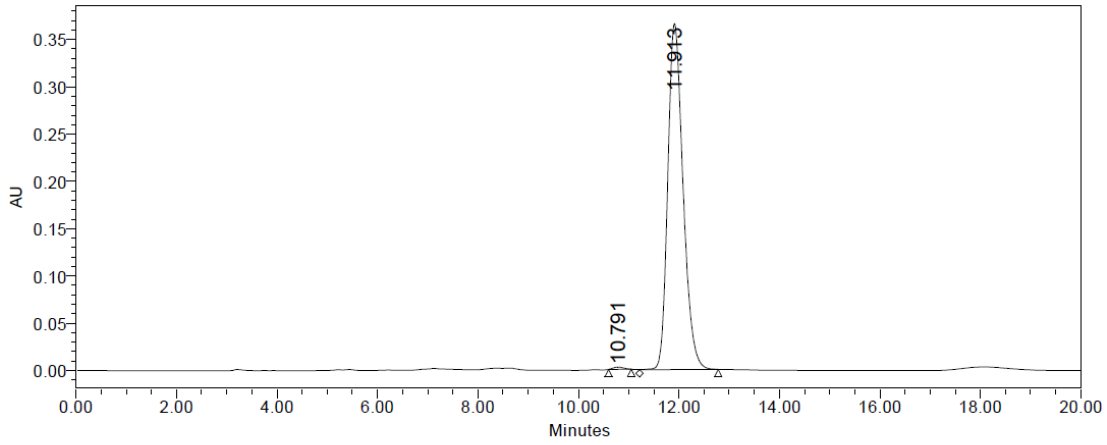






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/10/2017 2:09:56 PM CST; Result Id: 4266; Processing Method: fgjfgh

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.886 | 4387585 | 49.88 | 202647 |
| 2 | 1 | 10.560 | 4409085 | 50.12 | 237117 |
| Mean | | 11.223 | | | |
| Std. Dev. | | 0.938 | | | |
| % RSD | | 8.36 | | | |

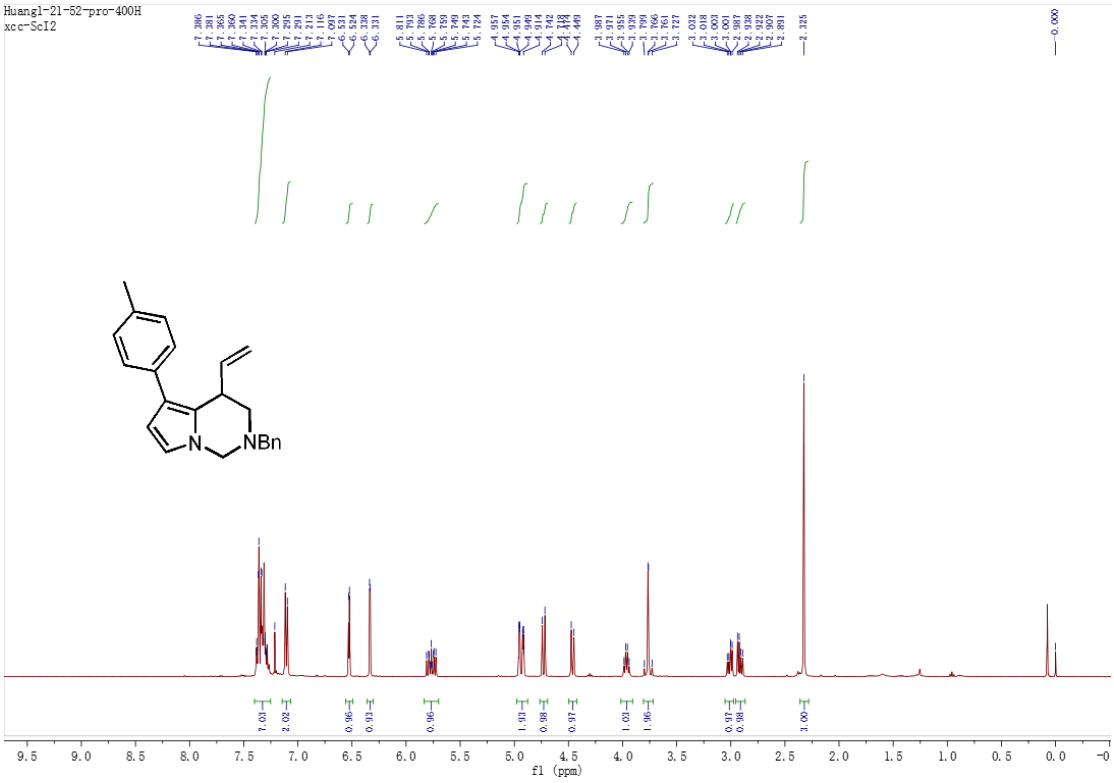


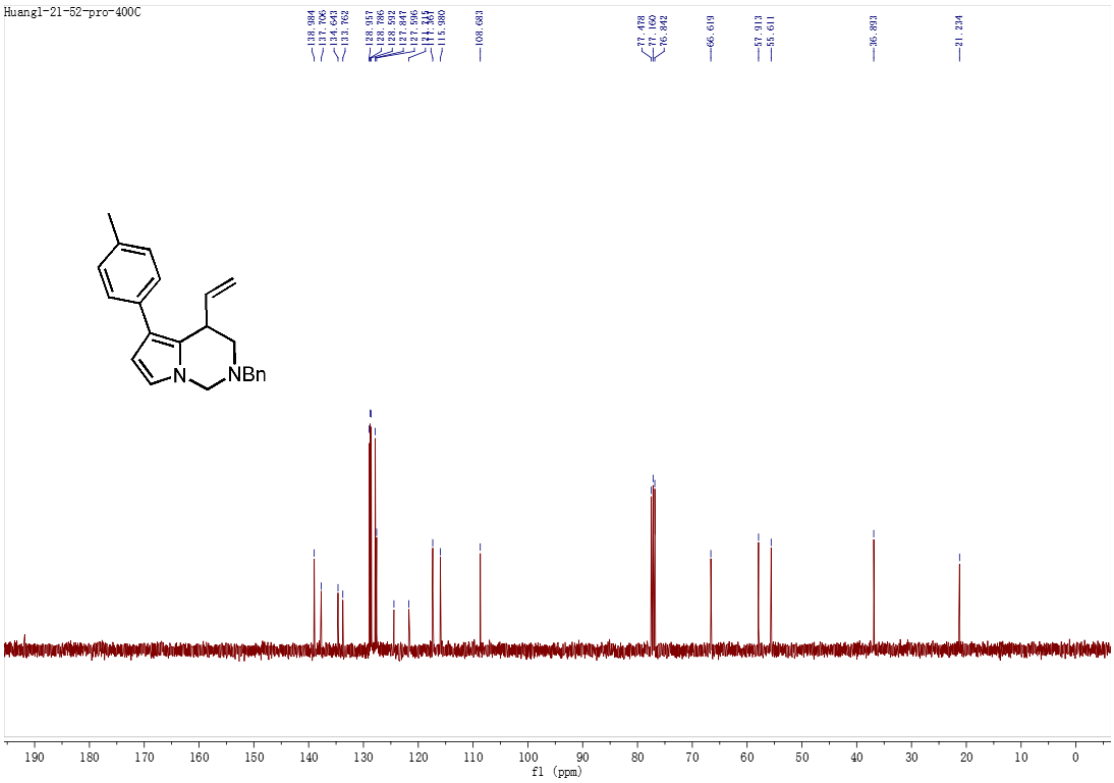

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/9/2017 12:06:28 AM CST; Result Id: 4268; Processing Method: fgdfgd

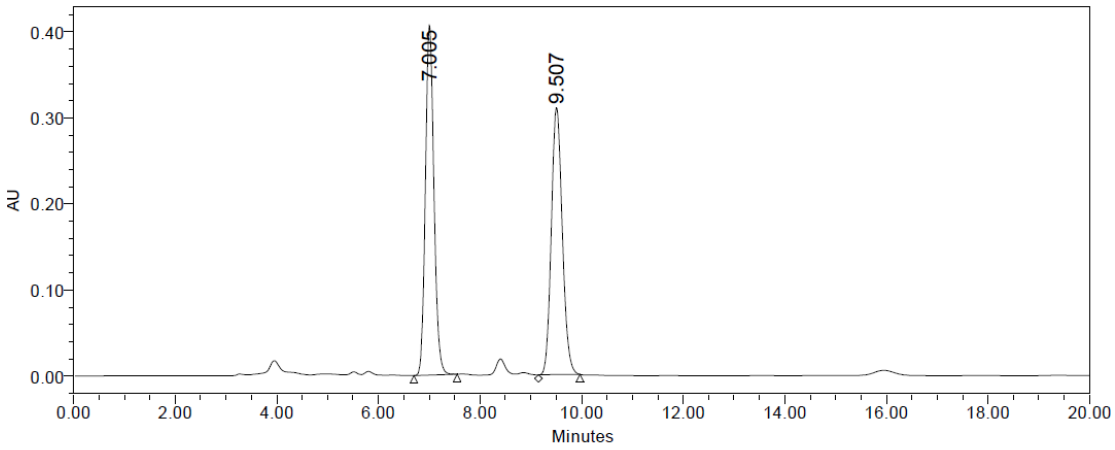
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.913 | 7746078 | 99.56 | 366006 |
| 2 | 1 | 10.791 | 33988 | 0.44 | 2351 |
| Mean | | 11.352 | | | |
| Std. Dev. | | 0.793 | | | |
| % RSD | | 6.99 | | | |

NMR Spectra and HPLC Chromatograms of **2h**



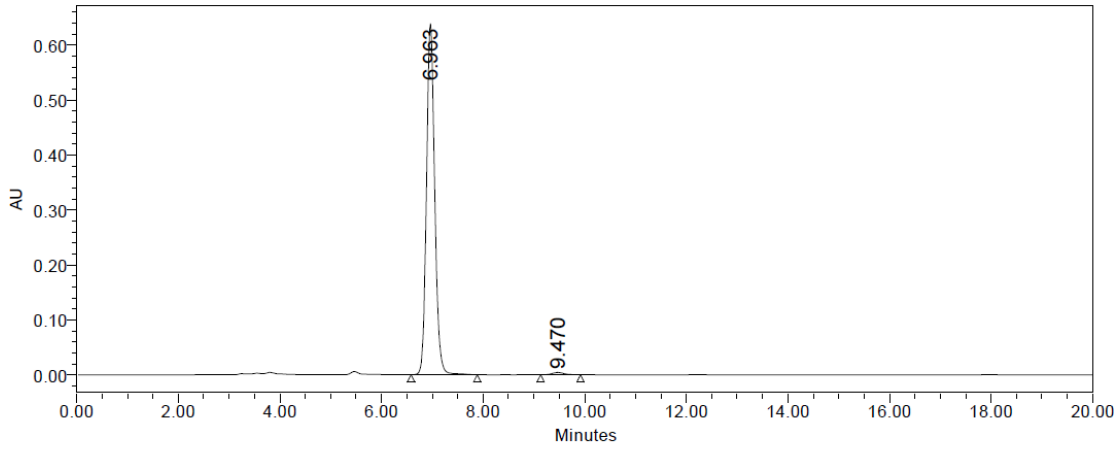






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 1:16:08 PM CST; Result Id: 4334; Processing Method: ghjgfjhgfv

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.507 | 4632572 | 49.29 | 310758 |
| 2 | 1 | 7.005 | 4765254 | 50.71 | 407532 |
| Mean | | 8.256 | | | |
| Std. Dev. | | 1.769 | | | |
| % RSD | | 21.43 | | | |

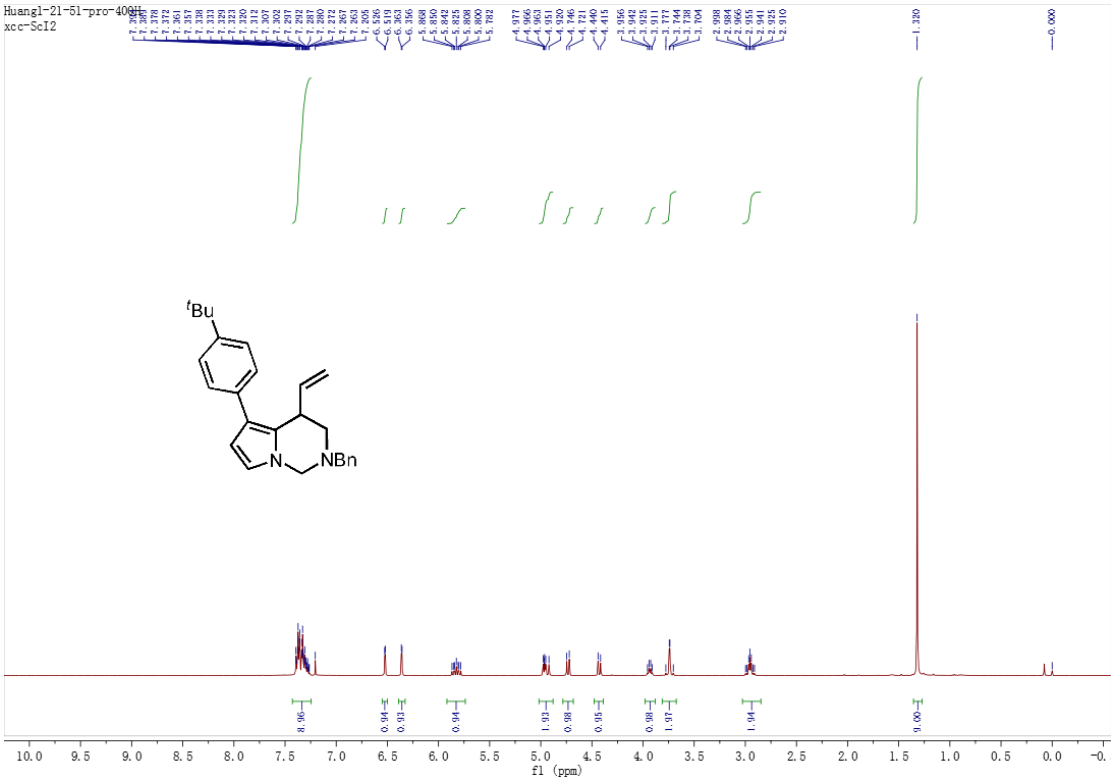


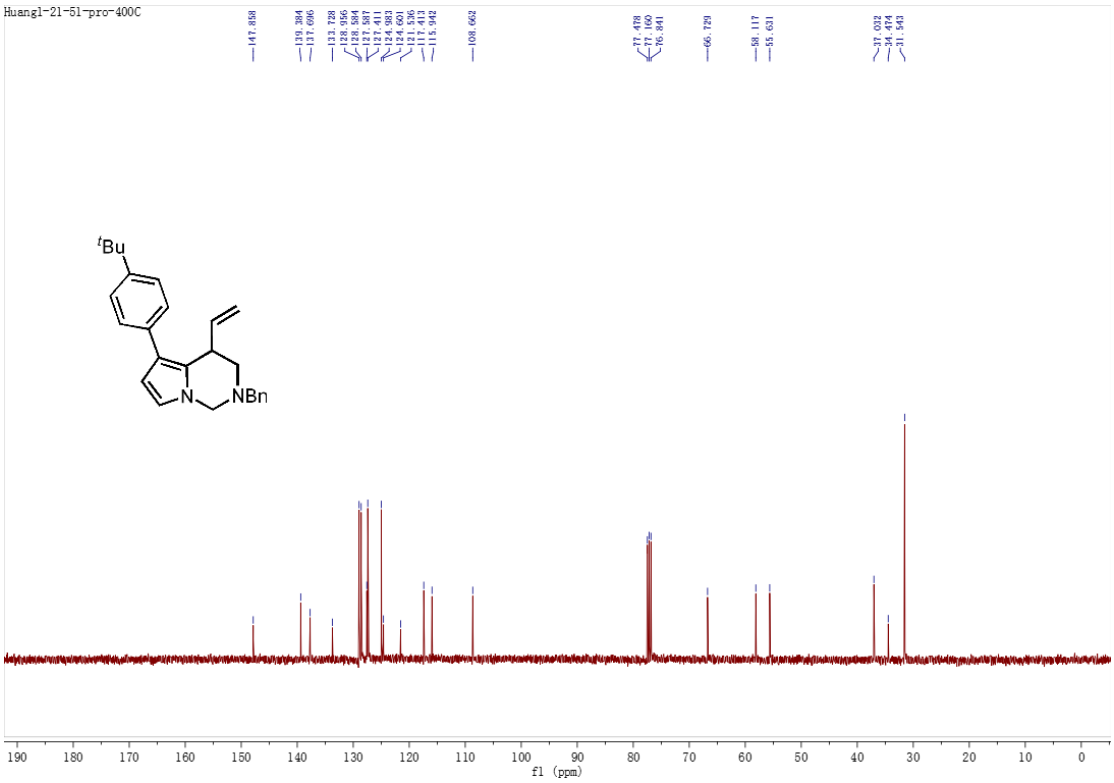

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 2:17:17 PM CST; Result Id: 4336; Processing Method: ghfcghgf

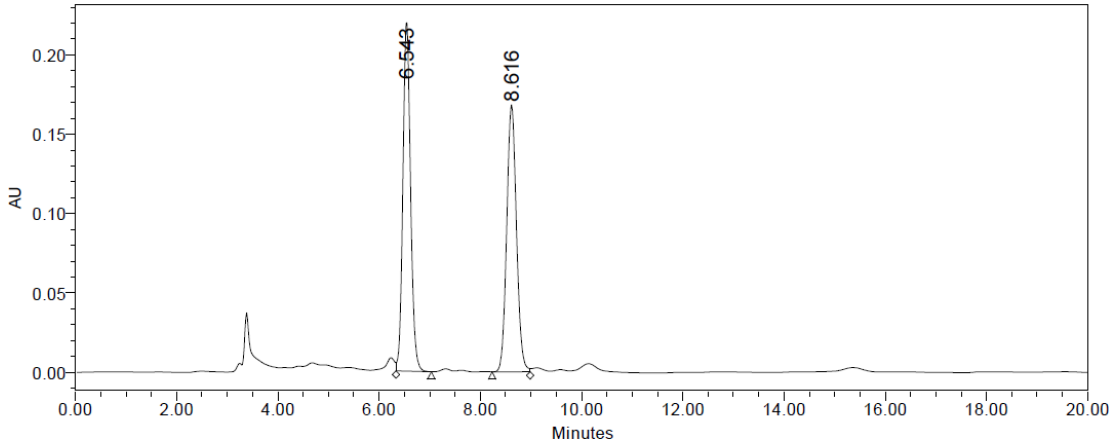
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.470 | 65936 | 0.91 | 4207 |
| 2 | 1 | 6.963 | 7218165 | 99.09 | 639400 |
| Mean | | 8.217 | | | |
| Std. Dev. | | 1.773 | | | |
| % RSD | | 21.58 | | | |

NMR Spectra and HPLC Chromatograms of **2i**



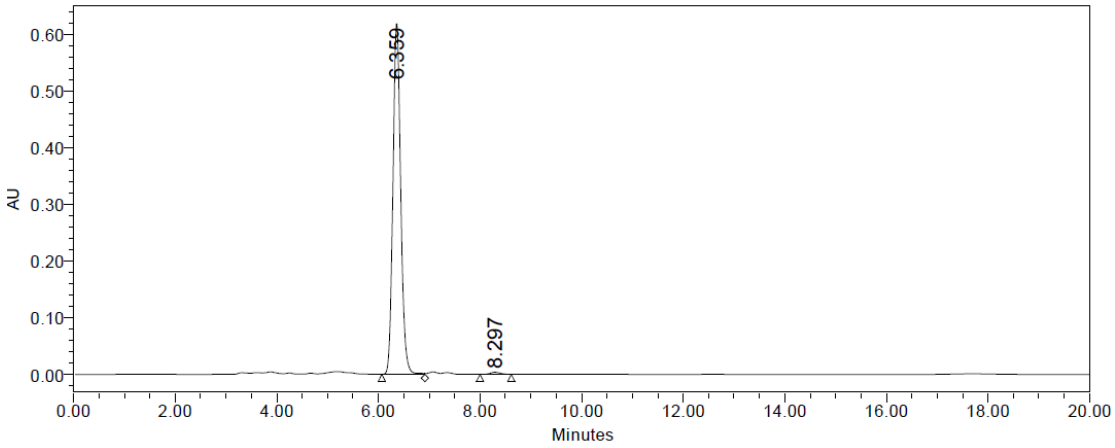






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 12:55:45 PM CST; Result Id: 4330; Processing Method: fghudfgh

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 6.543 | 2327532 | 50.76 | 220526 |
| 2 | 1 | 8.616 | 2257817 | 49.24 | 168262 |
| Mean | | 7.579 | | | |
| Std. Dev. | | 1.466 | | | |
| % RSD | | 19.34 | | | |

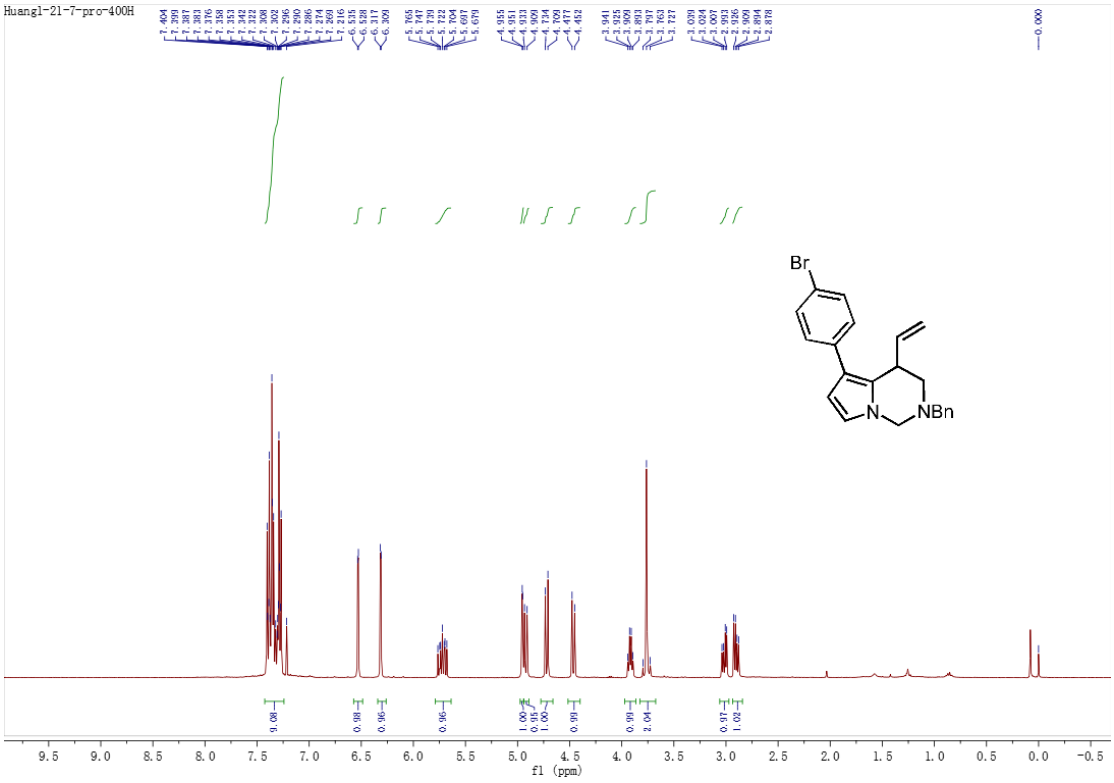


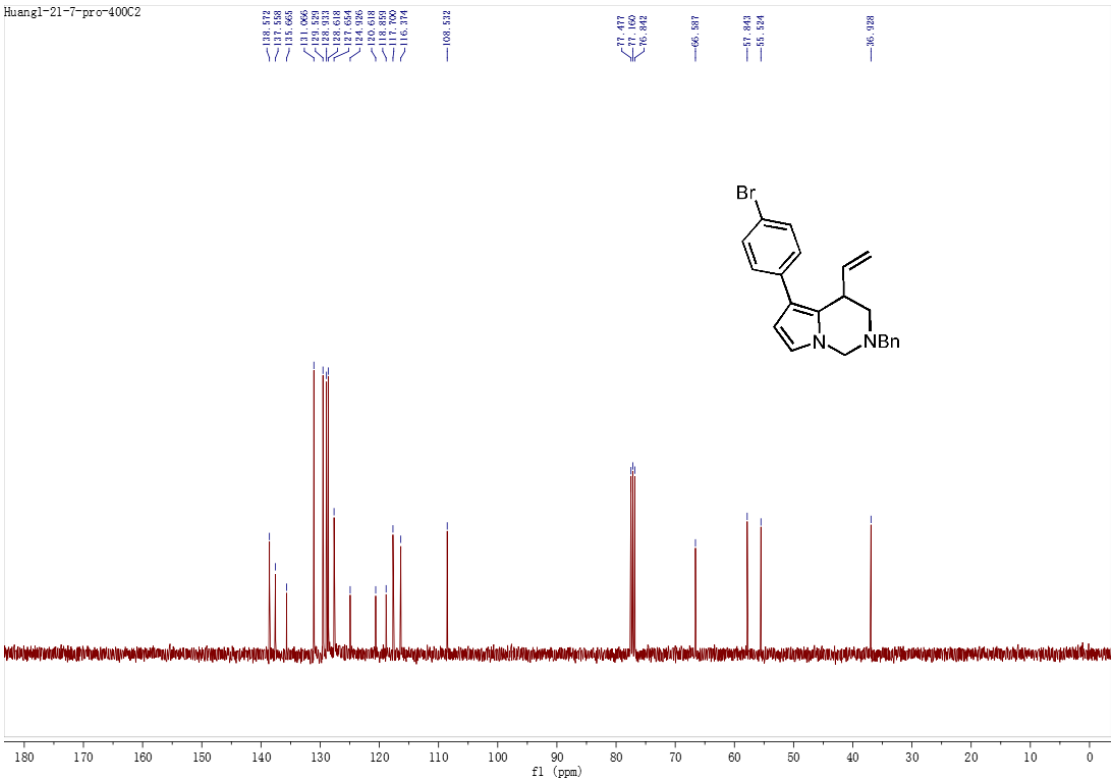

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 1:56:54 PM CST; Result Id: 4332; Processing Method: gfhnjfchgfg

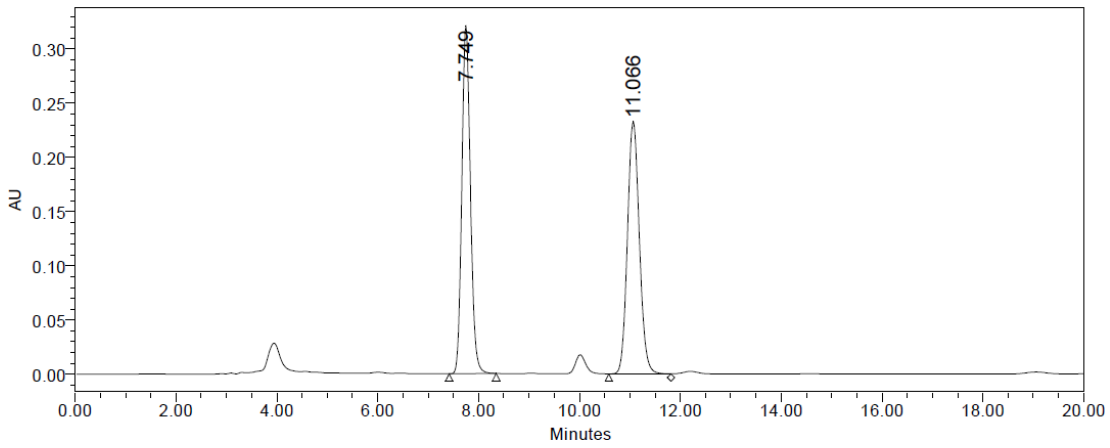
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 8.297 | 50030 | 0.75 | 3856 |
| 2 | 1 | 6.359 | 6600730 | 99.25 | 621085 |
| Mean | | 7.328 | | | |
| Std. Dev. | | 1.370 | | | |
| % RSD | | 18.70 | | | |

NMR Spectra and HPLC Chromatograms of **2j**



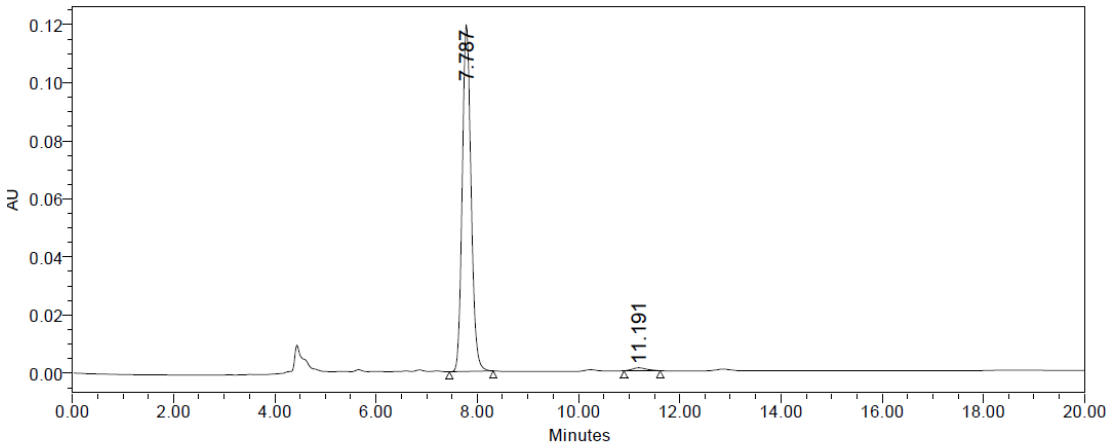






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/5/2017 3:21:27 PM CST; Result Id: 4270; Processing Method: ftyhrth

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.066 | 3801832 | 50.13 | 232679 |
| 2 | 1 | 7.749 | 3781398 | 49.87 | 320766 |
| Mean | | 9.408 | | | |
| Std. Dev. | | 2.345 | | | |
| % RSD | | 24.93 | | | |

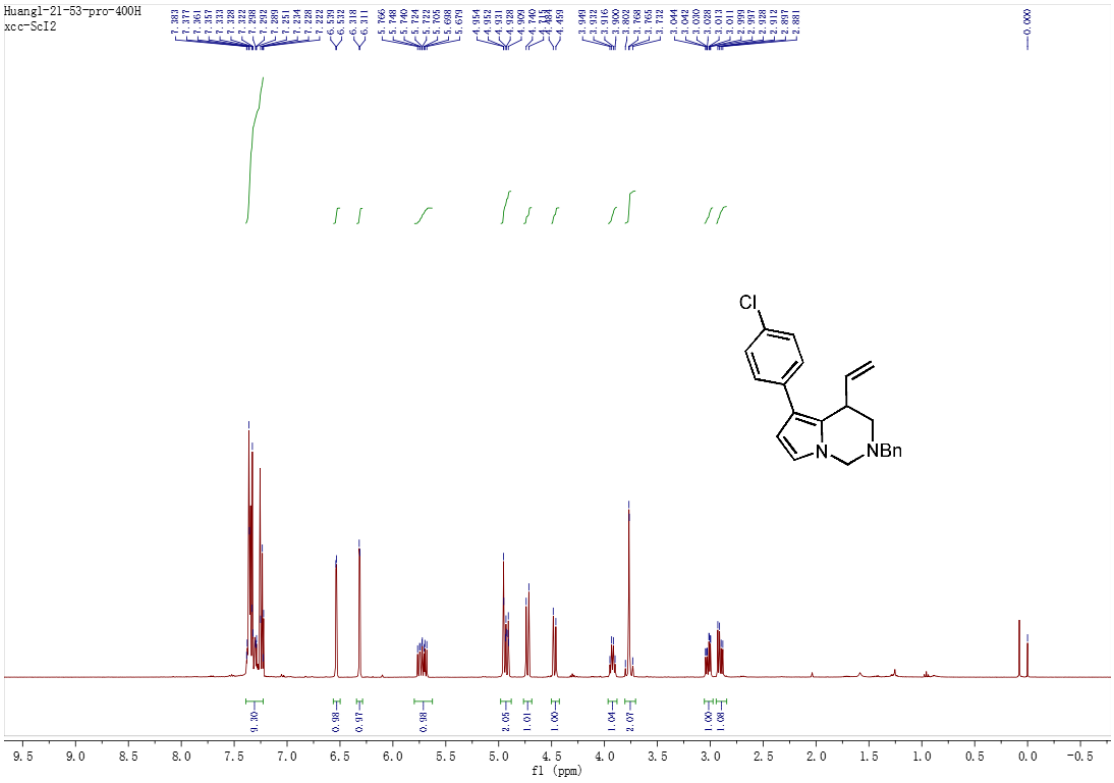


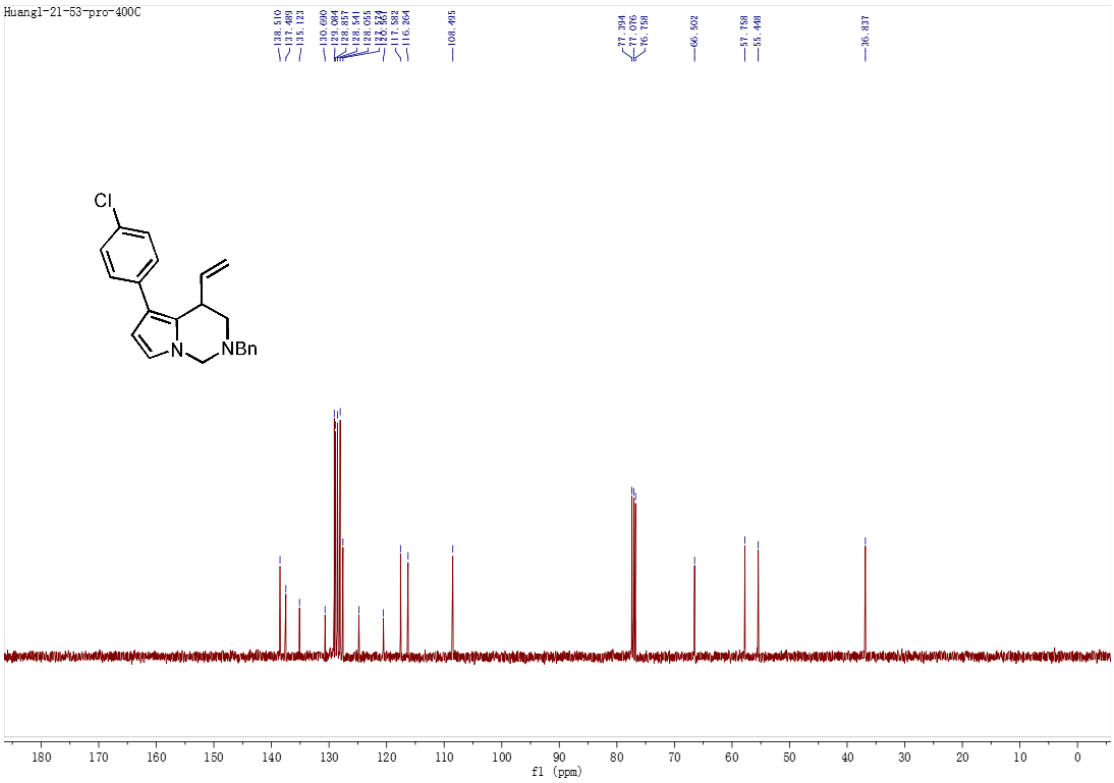

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/5/2017 4:30:51 PM CST; Result Id: 4272; Processing Method: fghdfg

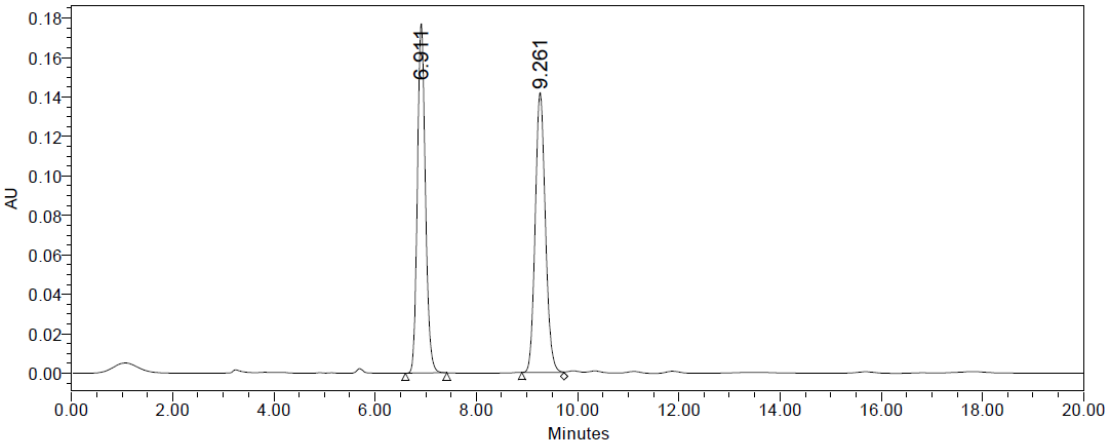
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 11.191 | 19177 | 1.32 | 992 |
| 2 | 1 | 7.787 | 1432942 | 98.68 | 119413 |
| Mean | | 9.489 | | | |
| Std. Dev. | | 2.407 | | | |
| % RSD | | 25.37 | | | |

NMR Spectra and HPLC Chromatograms of **2k**



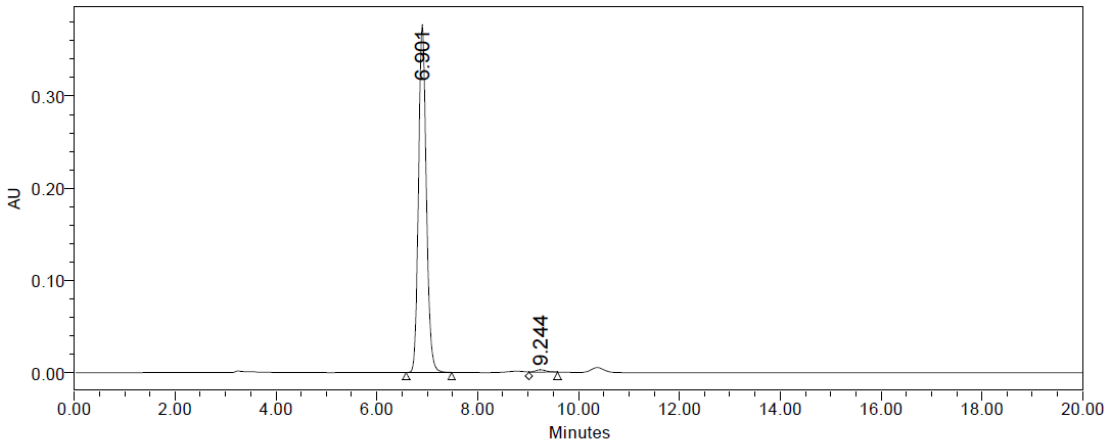






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 1:36:30 PM CST; Result Id: 4338; Processing Method: hjfgvhjgf

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.261 | 1993322 | 50.64 | 142079 |
| 2 | 1 | 6.911 | 1943261 | 49.36 | 177440 |
| Mean | | 8.086 | | | |
| Std. Dev. | | 1.662 | | | |
| % RSD | | 20.55 | | | |

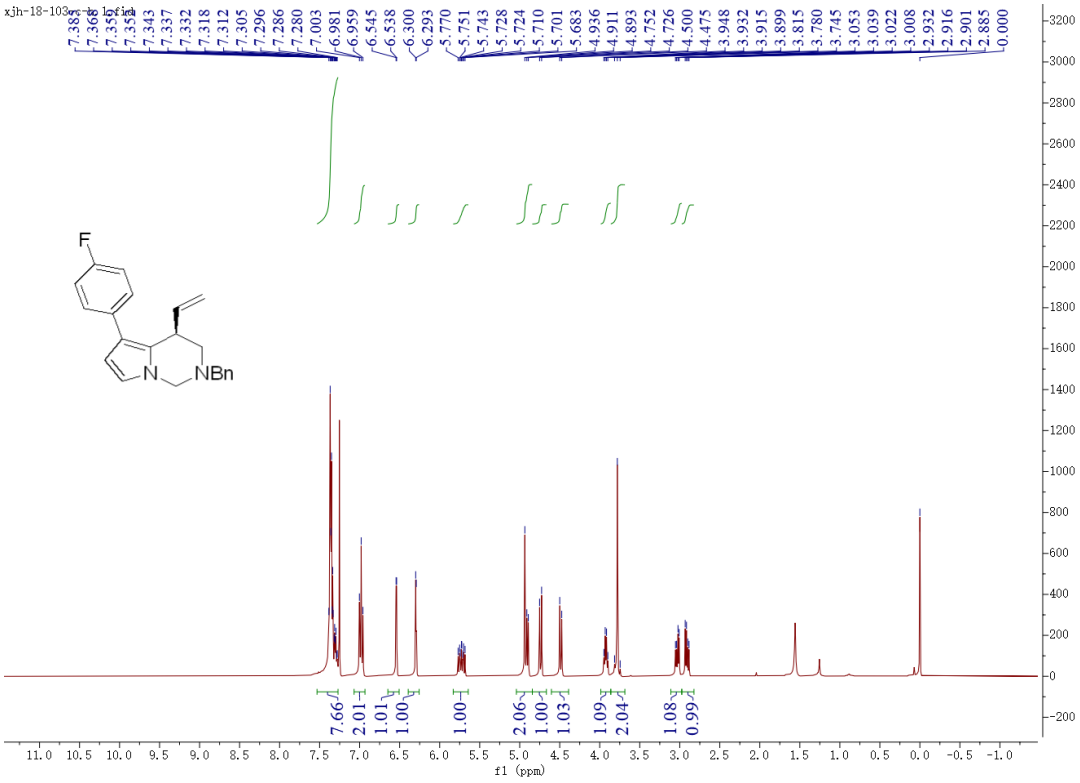


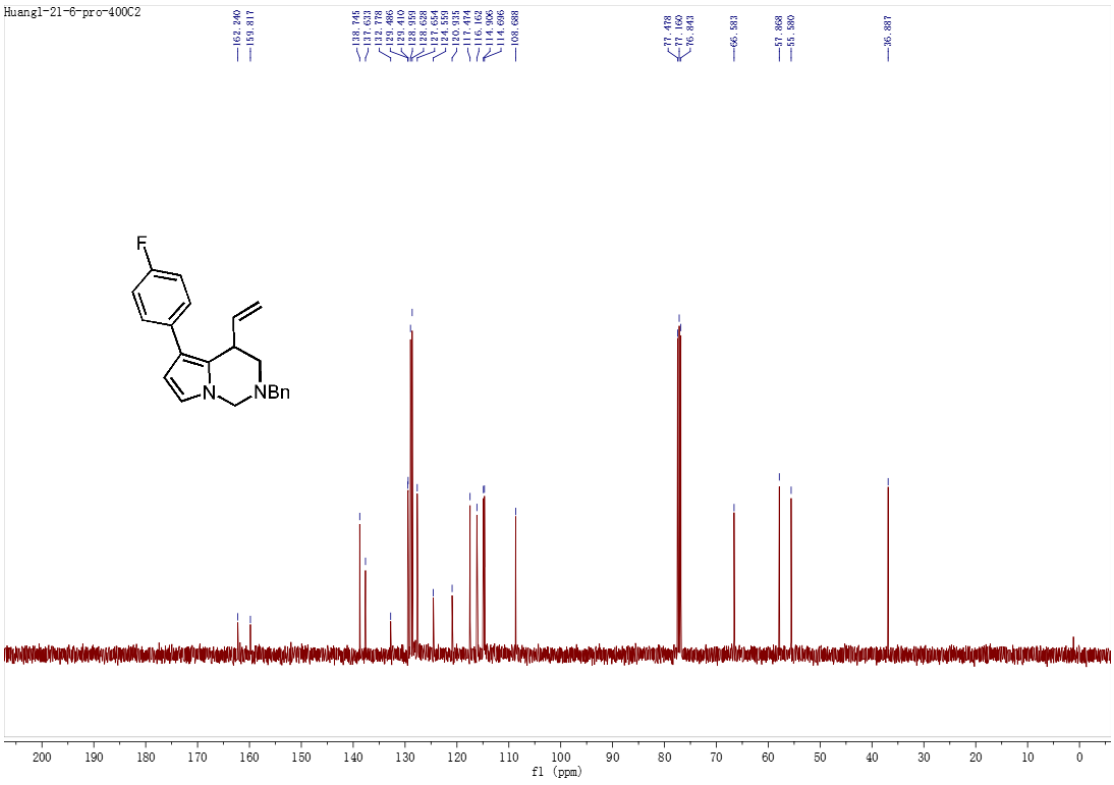

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/19/2017 2:37:40 PM CST; Result Id: 4340; Processing Method: vbhnmjvhbjn

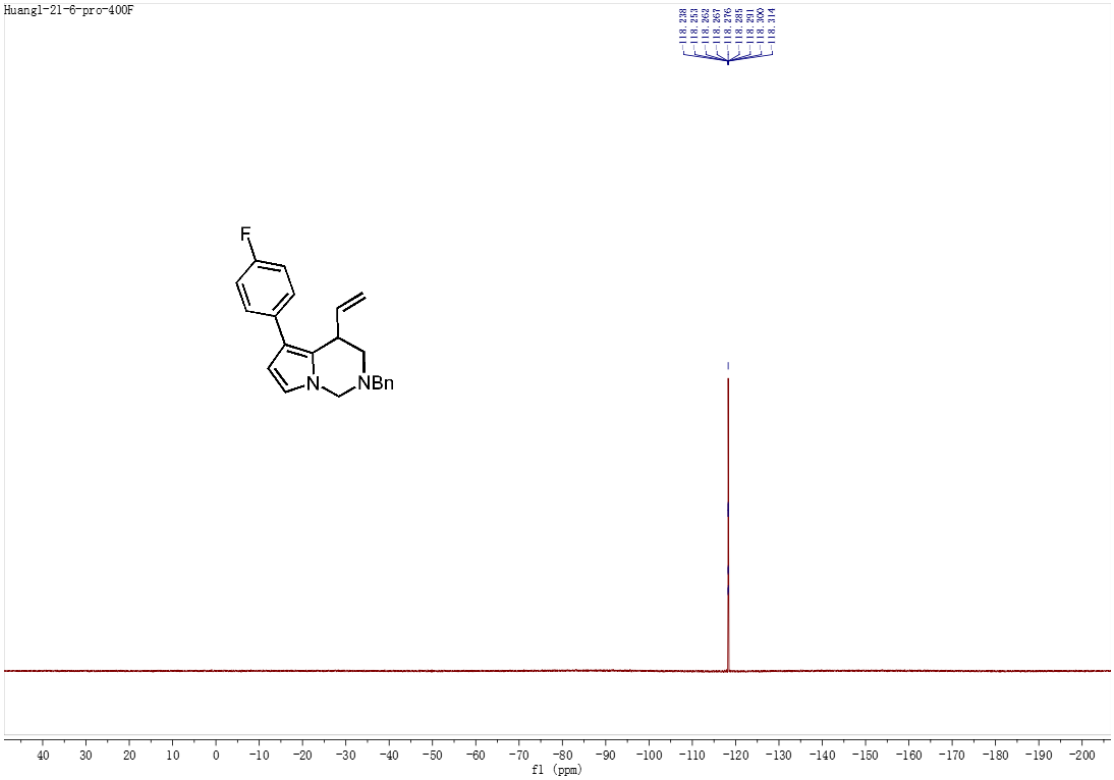
**Peak Name:**

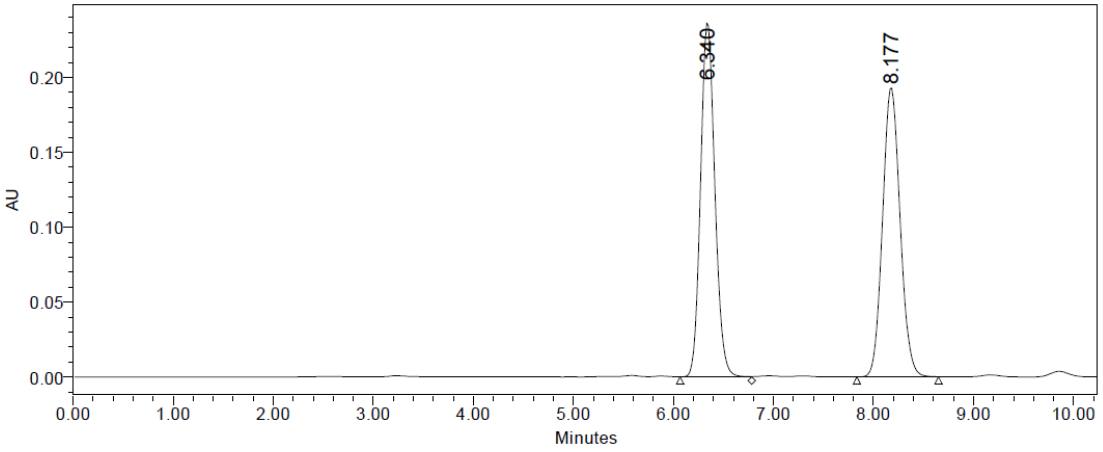
| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 9.244 | 38020 | 0.93 | 2633 |
| 2 | 1 | 6.901 | 4052780 | 99.07 | 376820 |
| Mean | | 8.073 | | | |
| Std. Dev. | | 1.657 | | | |
| % RSD | | 20.53 | | | |

NMR Spectra and HPLC Chromatograms of **2l**



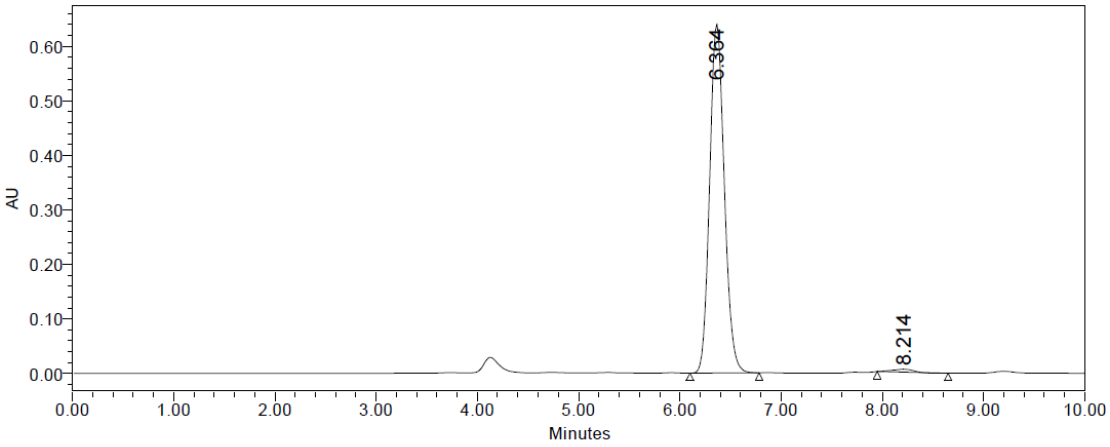



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 2/26/2017 11:08:55 AM CST; Result Id: 4190; Processing Method: dfhysdf

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 8.177 | 2347387 | 50.00 | 193354 |
| 2 | 1 | 6.340 | 2347637 | 50.00 | 236962 |
| Mean | | 7.258 | | | |
| Std. Dev. | | 1.299 | | | |
| % RSD | | 17.90 | | | |

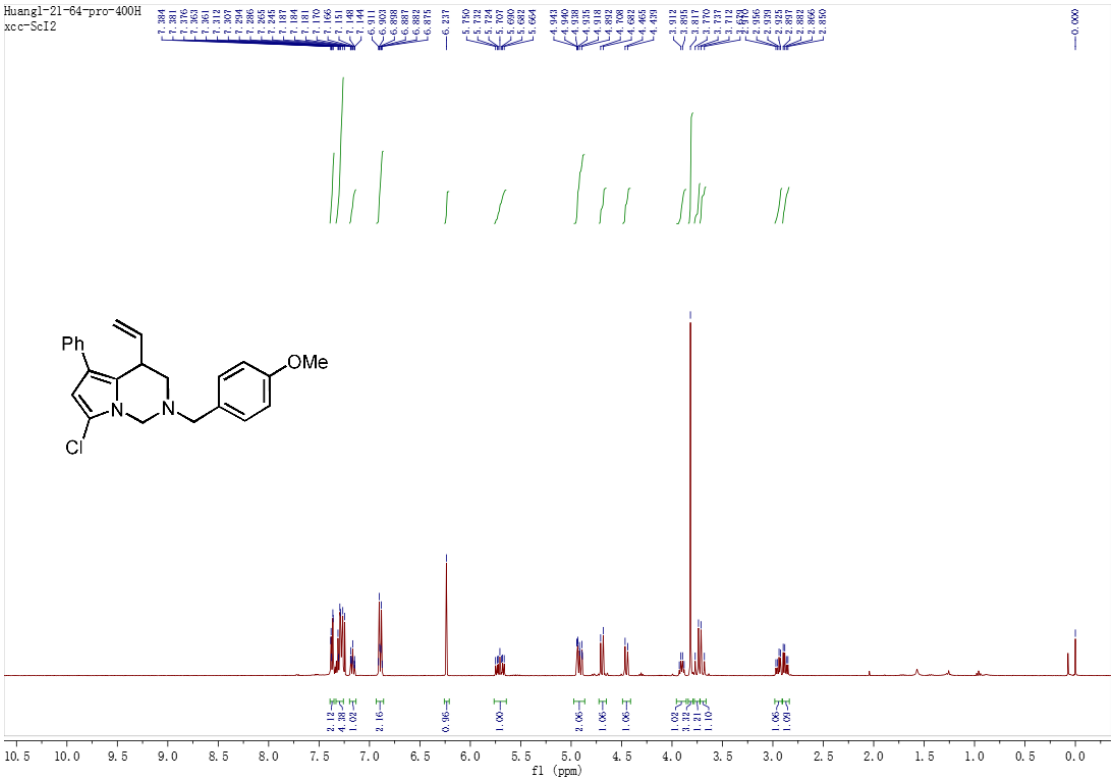


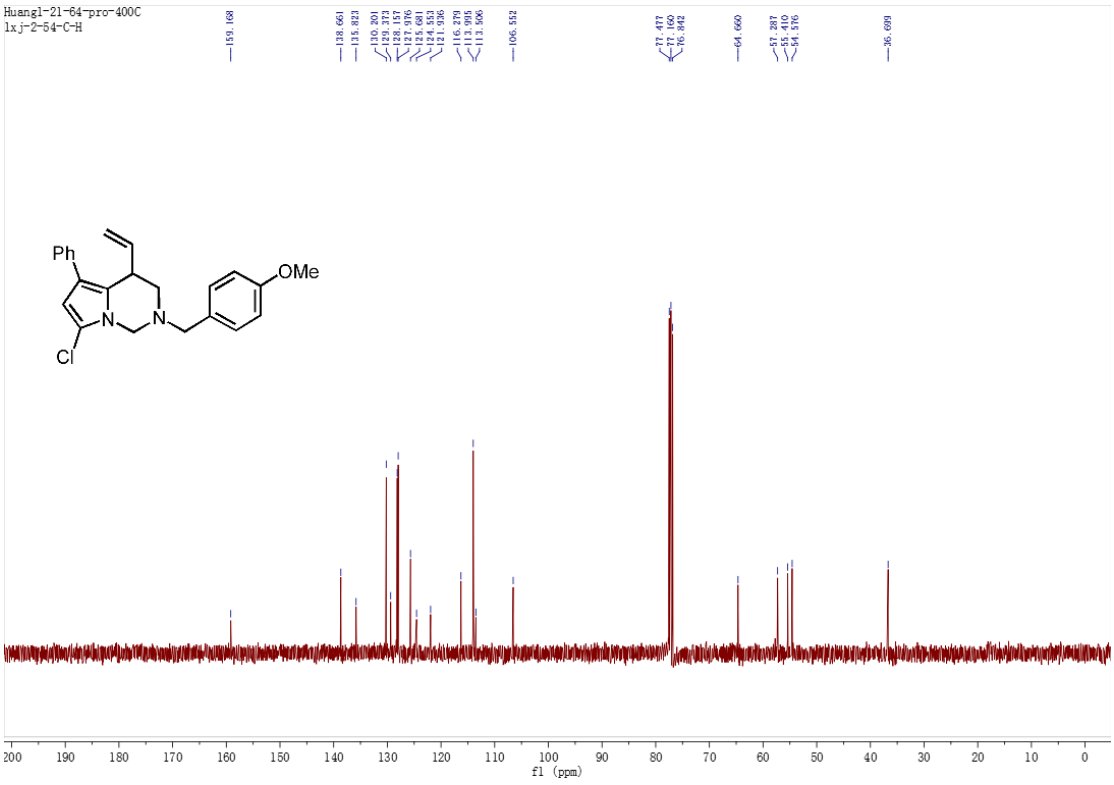

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 2/26/2017 11:31:16 AM CST; Result Id: 4192; Processing Method: cghdsf

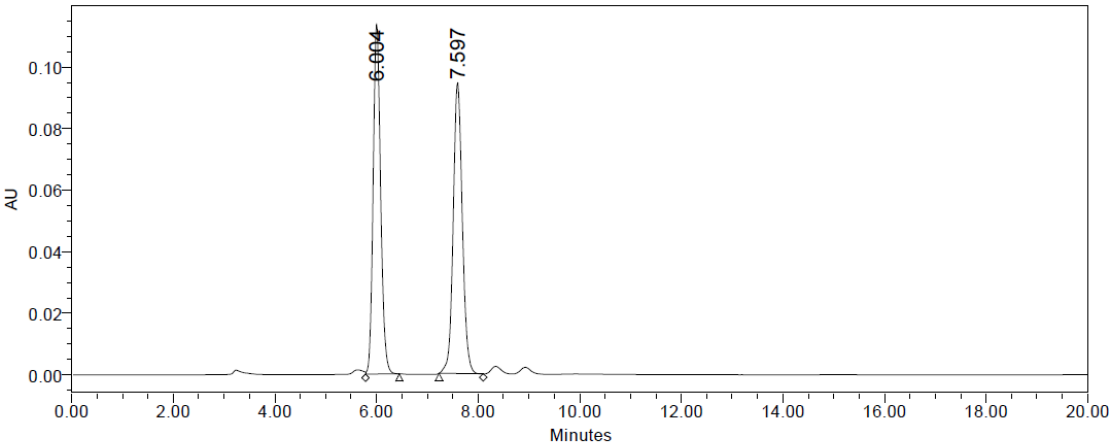
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 8.214 | 81004 | 1.24 | 5361 |
| 2 | 1 | 6.364 | 6439688 | 98.76 | 640897 |
| Mean | | 7.289 | | | |
| Std. Dev. | | 1.308 | | | |
| % RSD | | 17.94 | | | |

NMR Spectra and HPLC Chromatograms of **2m**



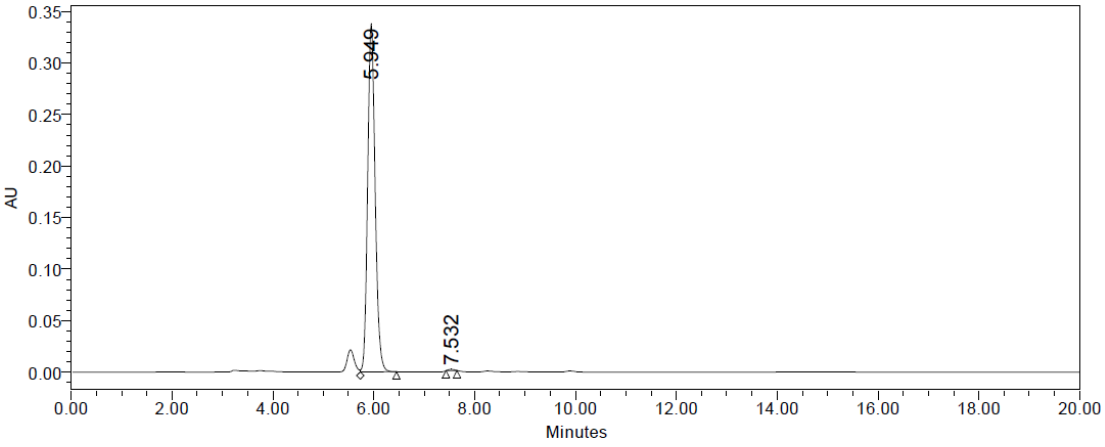






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/23/2017 8:26:33 PM CST; Result Id: 4388; Processing Method: fhgdfgds

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 7.597 | 1185512 | 50.37 | 94621 |
| 2 | 1 | 6.004 | 1168179 | 49.63 | 113935 |
| Mean | | 6.800 | | | |
| Std. Dev. | | 1.126 | | | |
| % RSD | | 16.56 | | | |

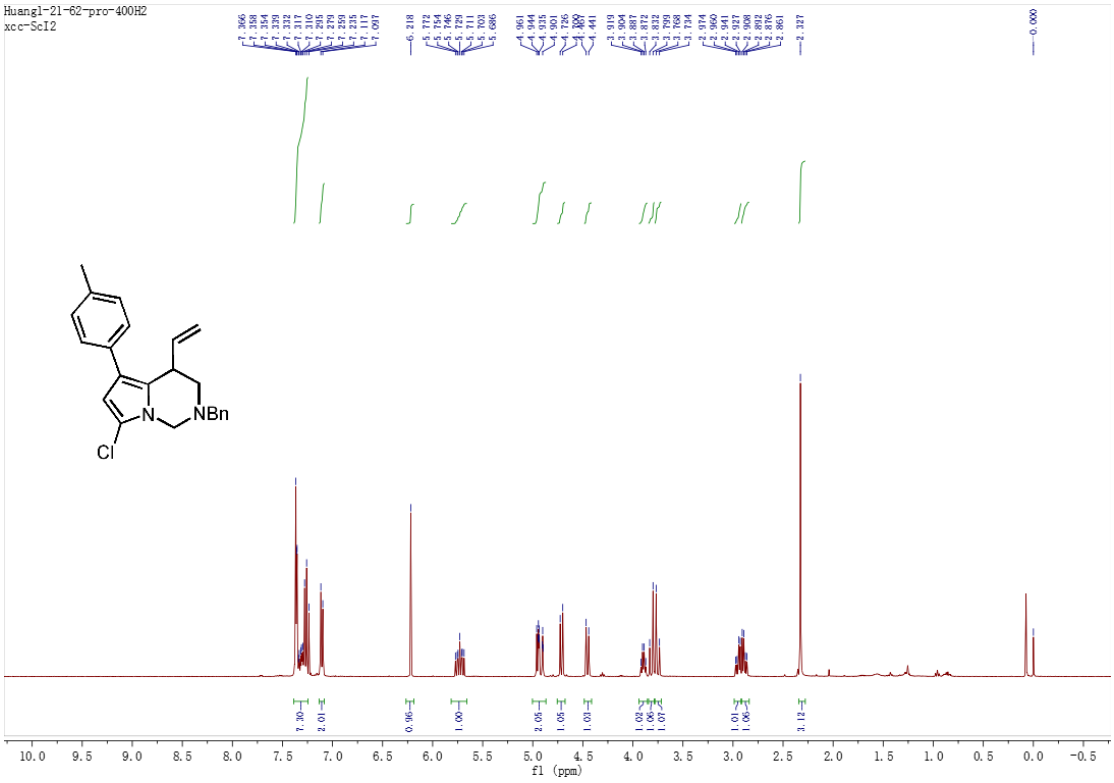


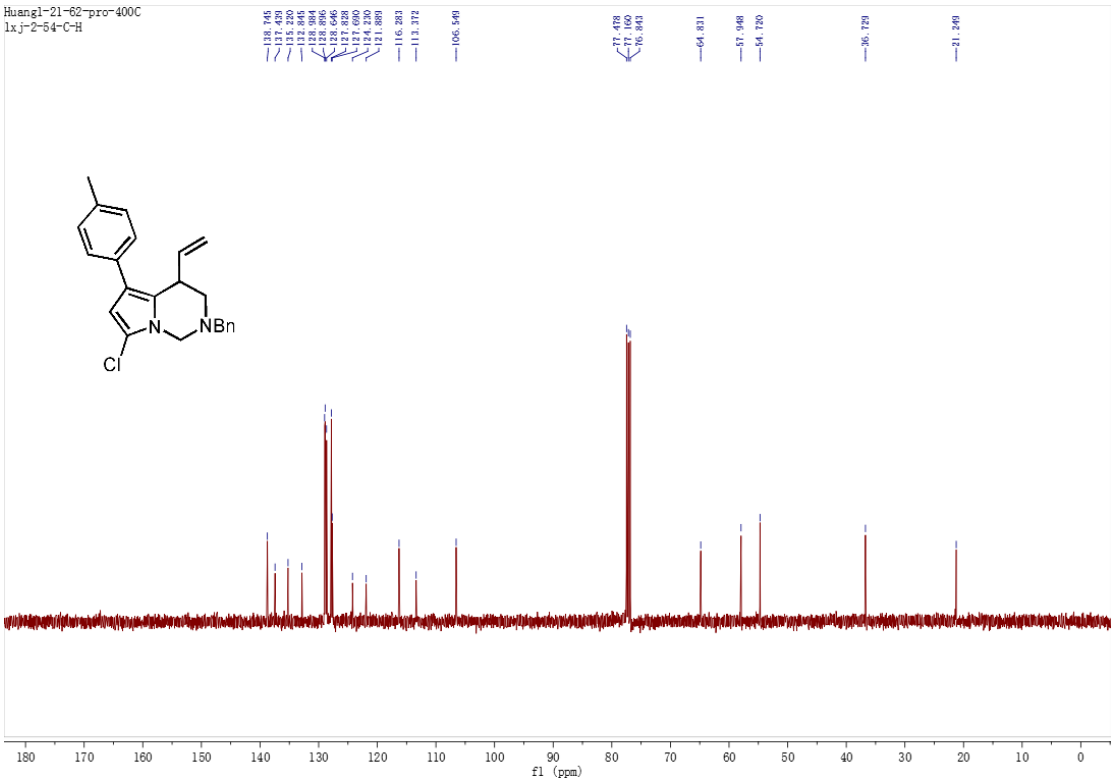

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/23/2017 6:48:57 PM CST; Result Id: 4390; Processing Method: ftghdfgh

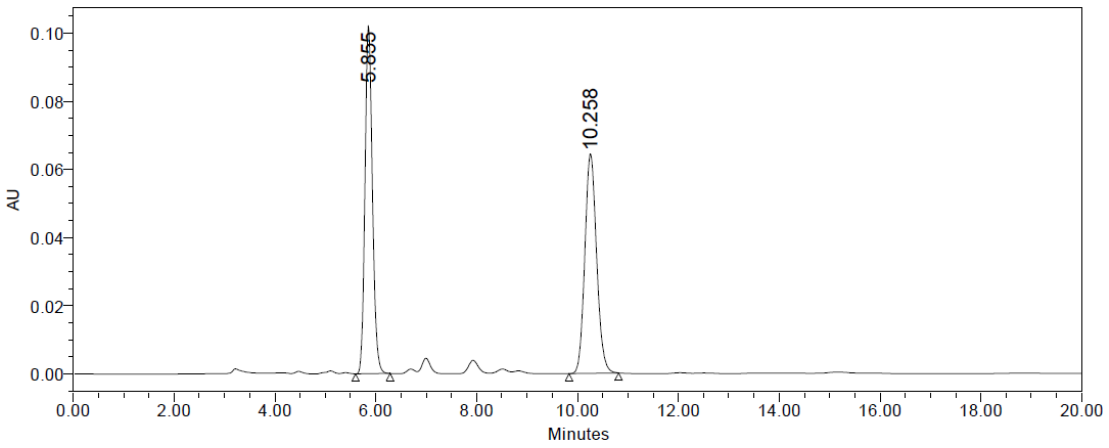
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 7.532 | 10407 | 0.30 | 1330 |
| 2 | 1 | 5.949 | 3487596 | 99.70 | 337583 |
| Mean | | 6.741 | | | |
| Std. Dev. | | 1.119 | | | |
| % RSD | | 16.61 | | | |

NMR Spectra and HPLC Chromatograms of **2n**



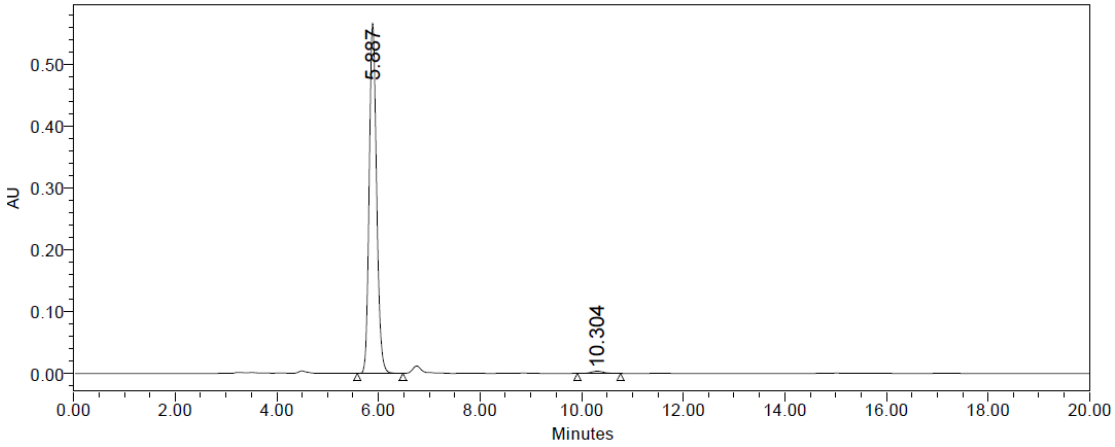






Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/23/2017 5:27:25 PM CST; Result Id: 4379; Processing Method: fgdsfgsdf

**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 10.258 | 1048350 | 50.01 | 64449 |
| 2 | 1 | 5.855 | 1047866 | 49.99 | 102309 |
| Mean | | 8.056 | | | |
| Std. Dev. | | 3.113 | | | |
| % RSD | | 38.65 | | | |

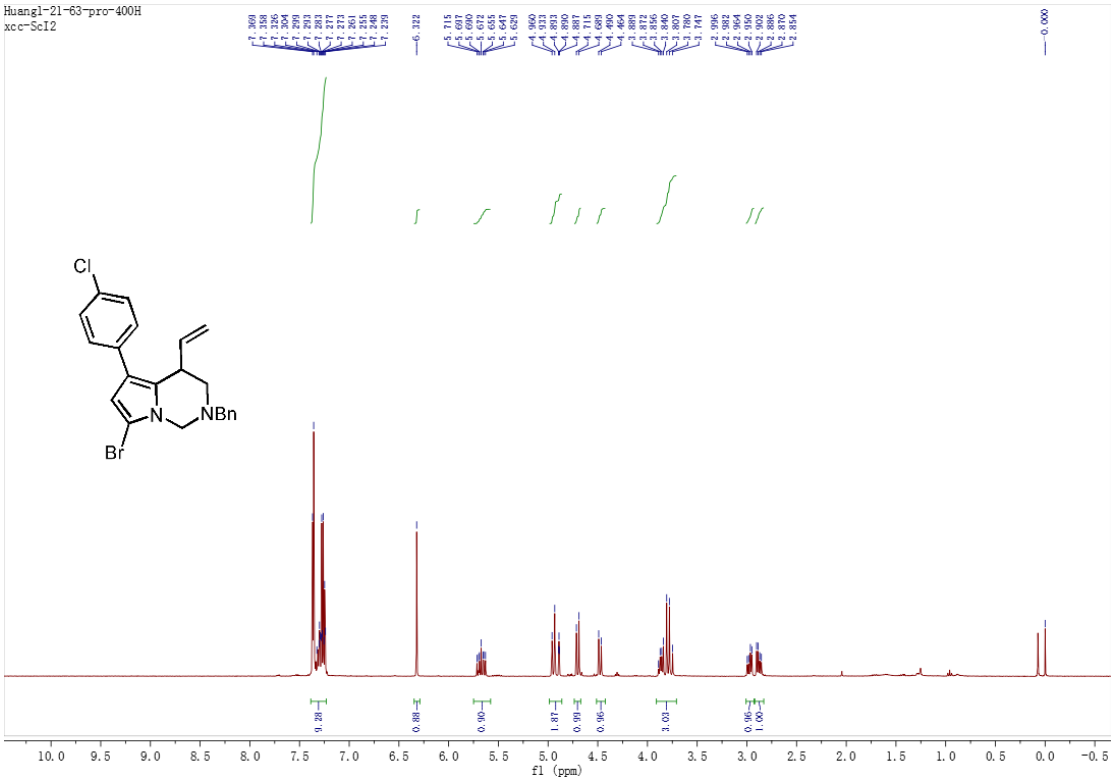


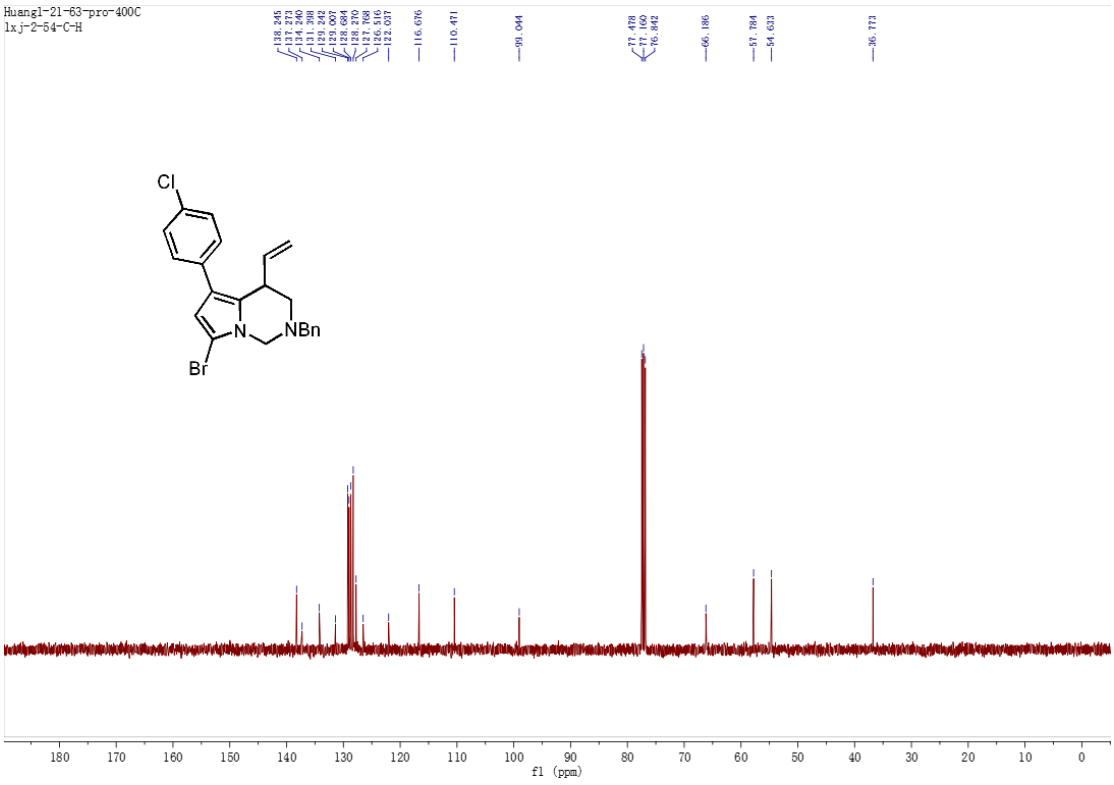

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 3/23/2017 6:08:11 PM CST; Result Id: 4381; Processing Method: ftgdfgdf

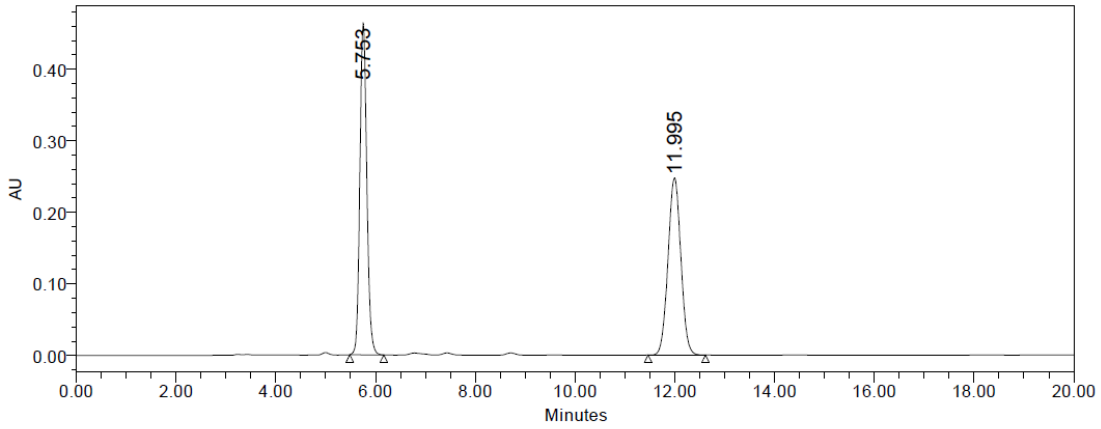
**Peak Name:**

| | Injection | RT | Area | % Area | Height |
|---|---|---|---|---|---|
| 1 | 1 | 10.304 | 61745 | 1.06 | 3730 |
| 2 | 1 | 5.887 | 5748214 | 98.94 | 567160 |
| Mean | | 8.095 | | | |
| Std. Dev. | | 3.124 | | | |
| % RSD | | 38.58 | | | |

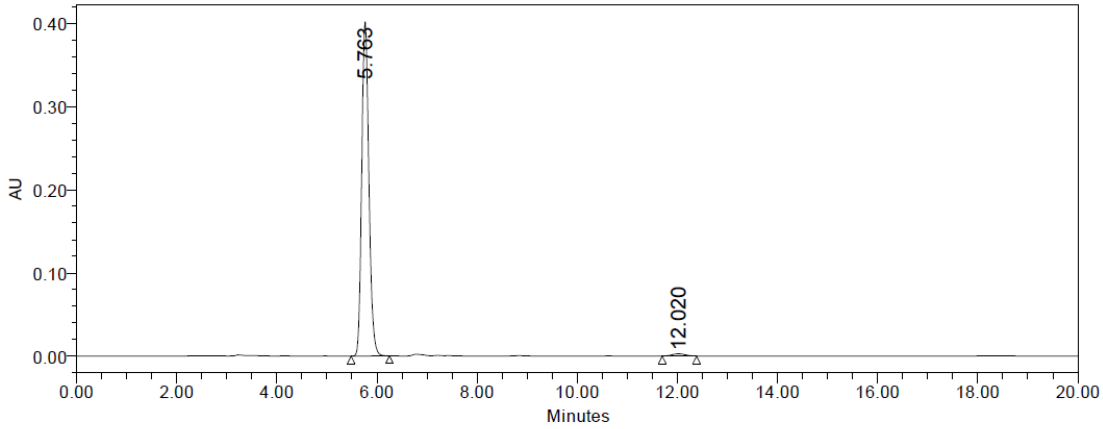
NMR Spectra and HPLC Chromatograms of **2o**



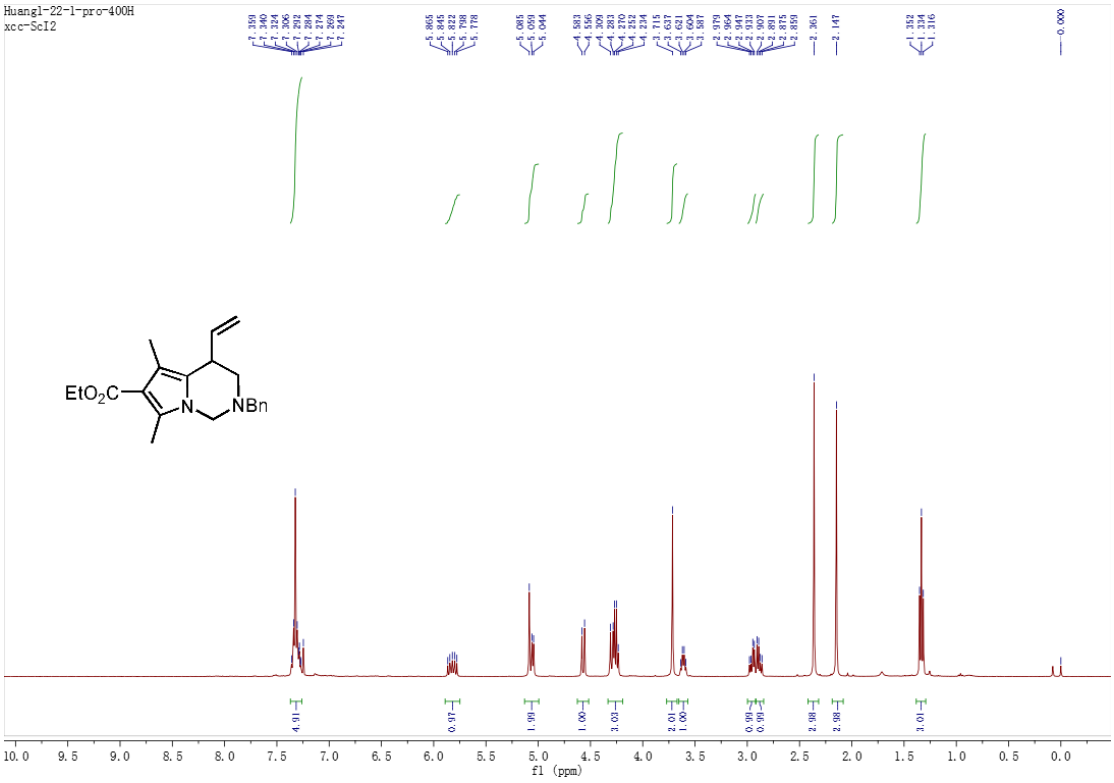


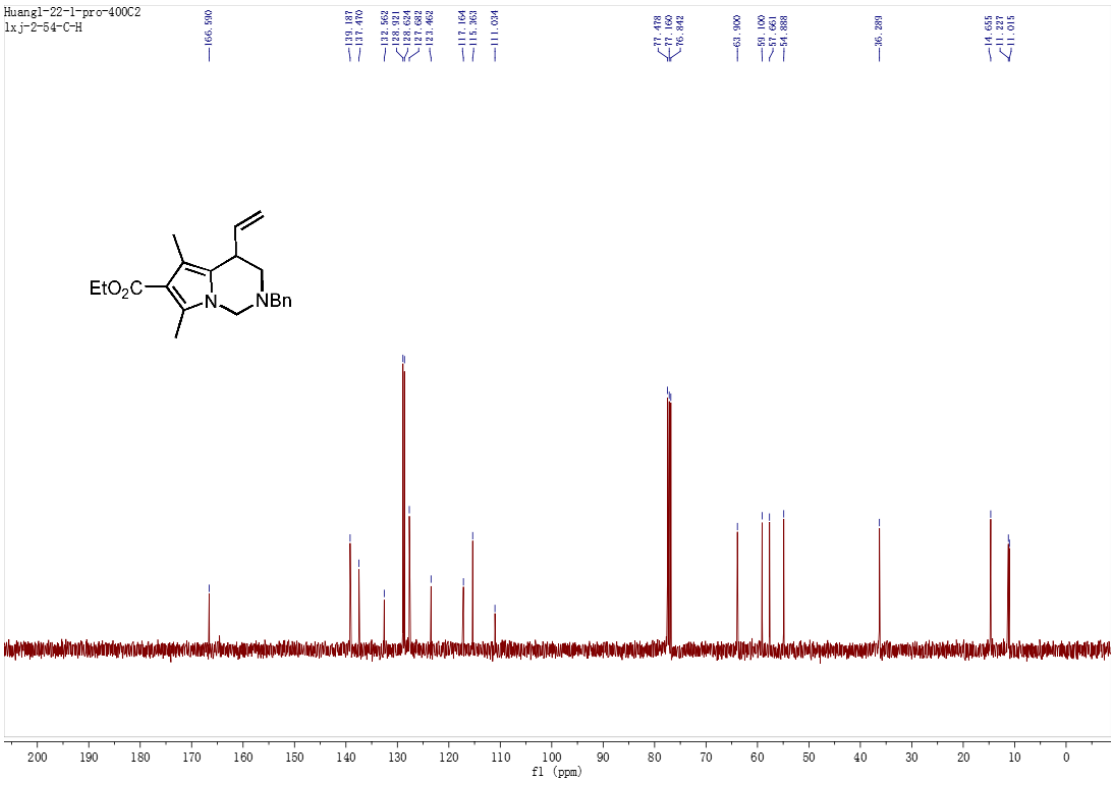

| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 5.753 | 4456503 | 50.27 | 463968 |
| 2 | 11.995 | 4409268 | 49.73 | 247855 |

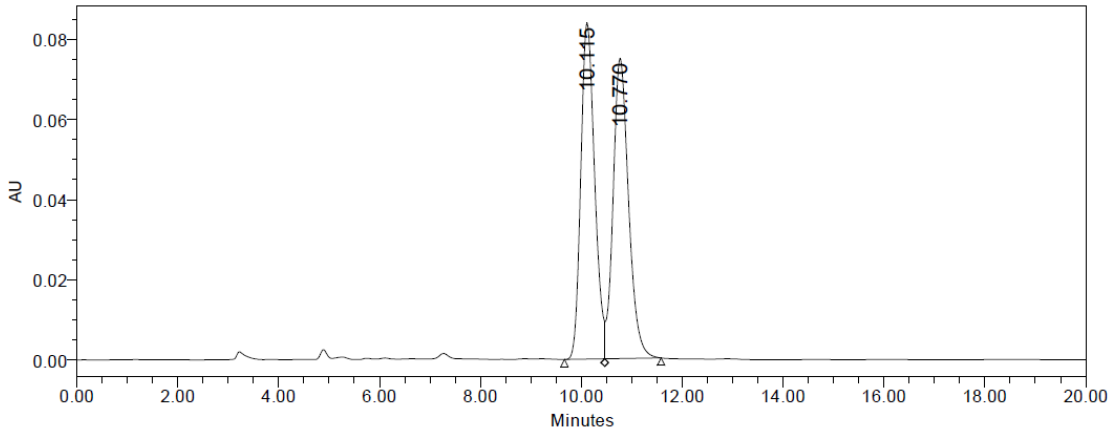



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 5.763 | 3978736 | 98.76 | 402009 |
| 2 | 12.020 | 49863 | 1.24 | 2809 |

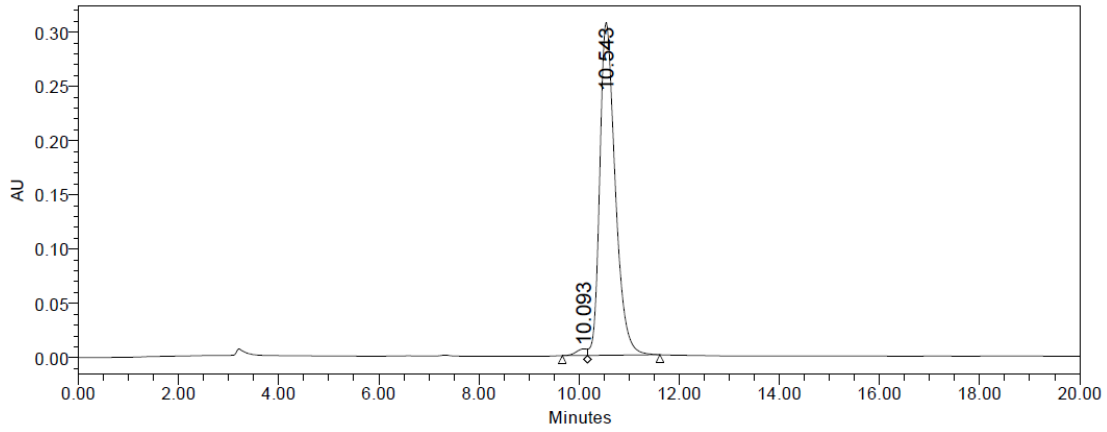
NMR Spectra and HPLC Chromatograms of **2p**



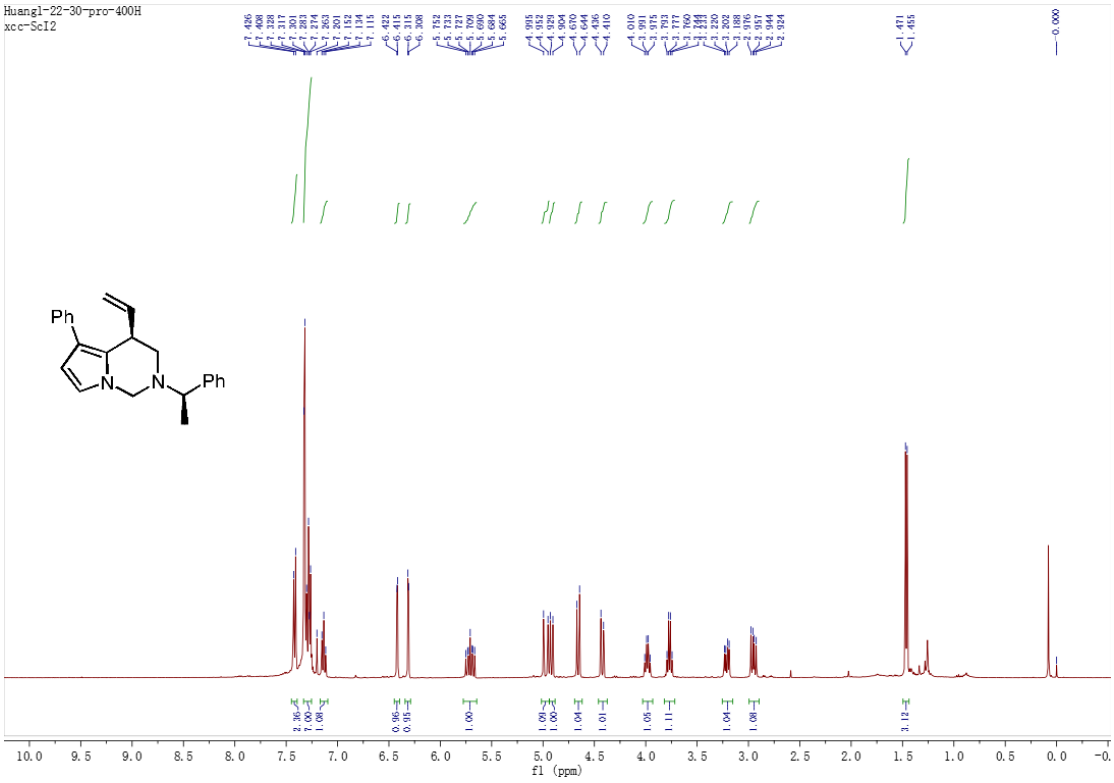


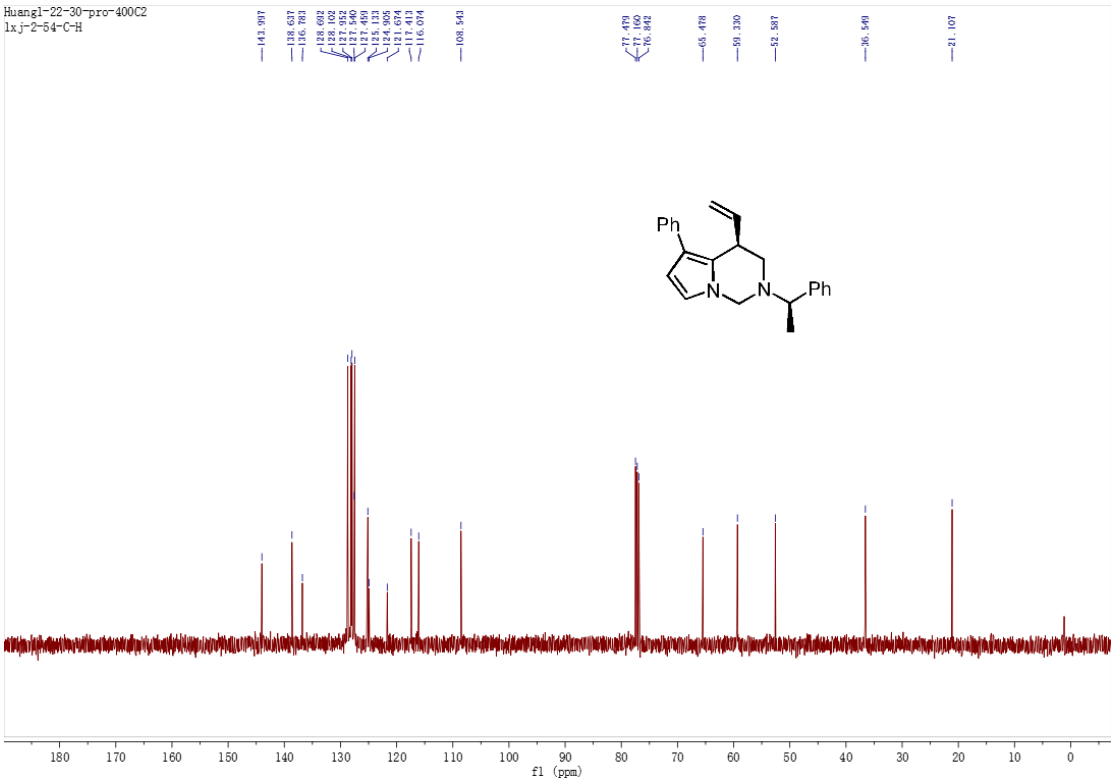

| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 10.115 | 1596547 | 49.95 | 83885 |
| 2 | 10.770 | 1599848 | 50.05 | 74936 |



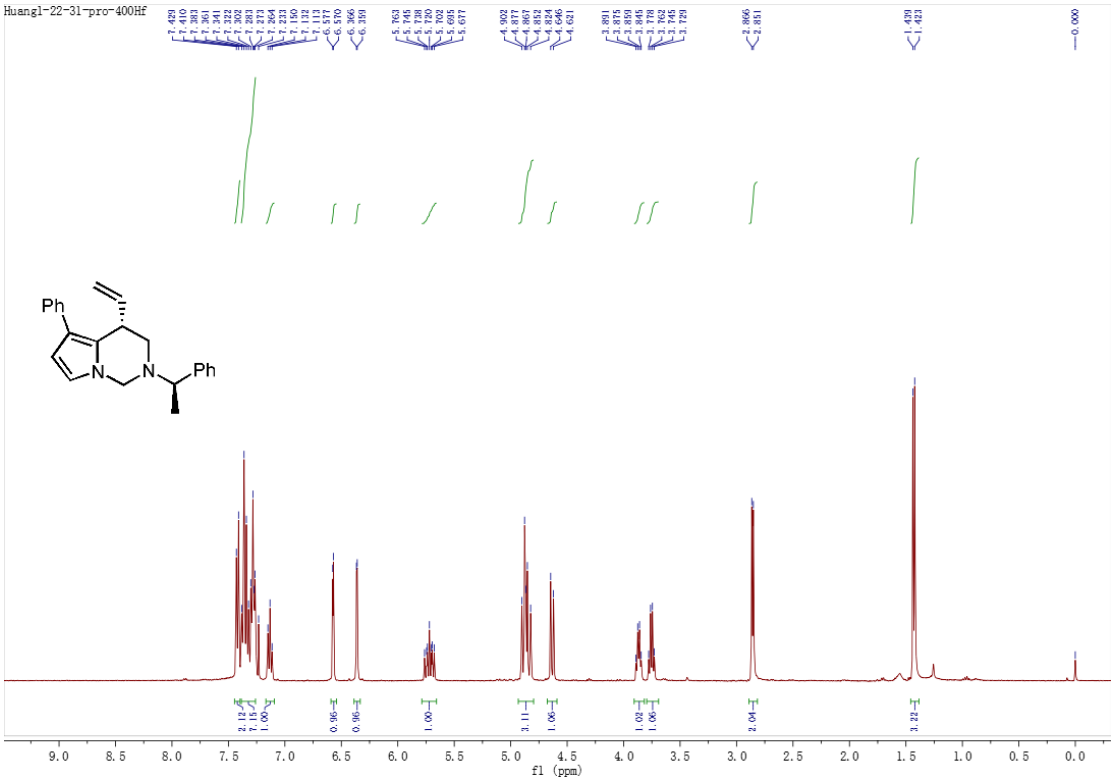

| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 10.093 | 88603 | 1.33 | 6088 |
| 2 | 10.543 | 6564770 | 98.67 | 306901 |

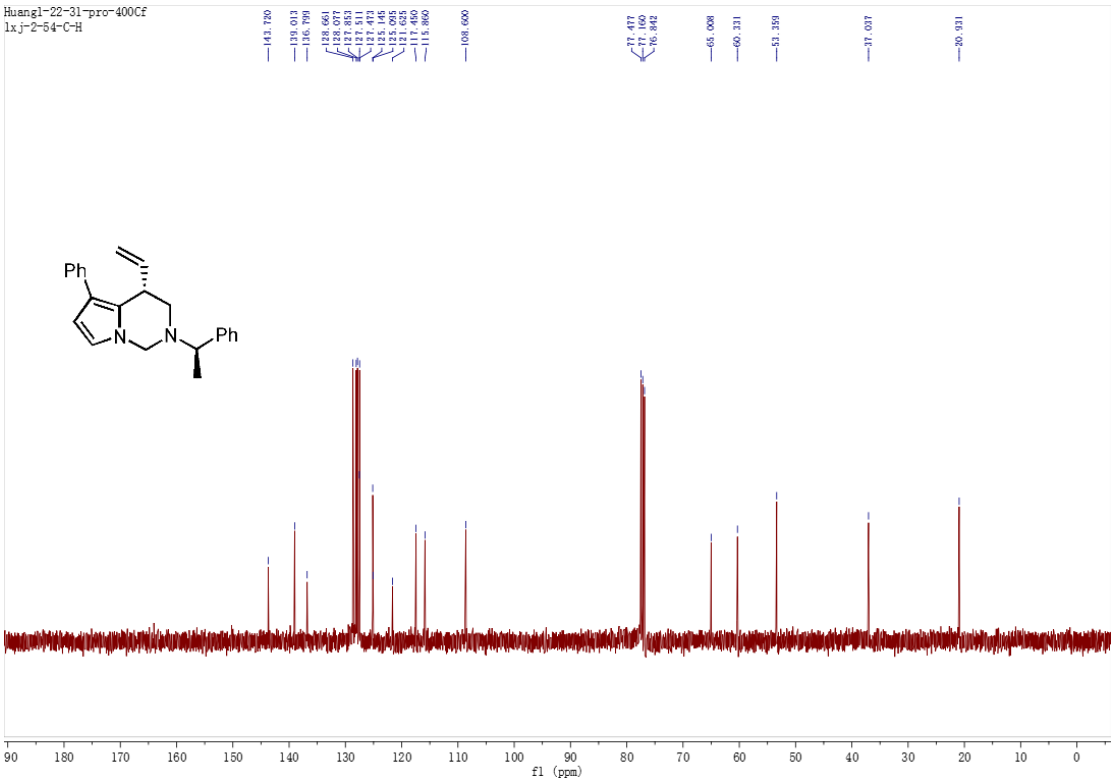
NMR Spectra of **2q**



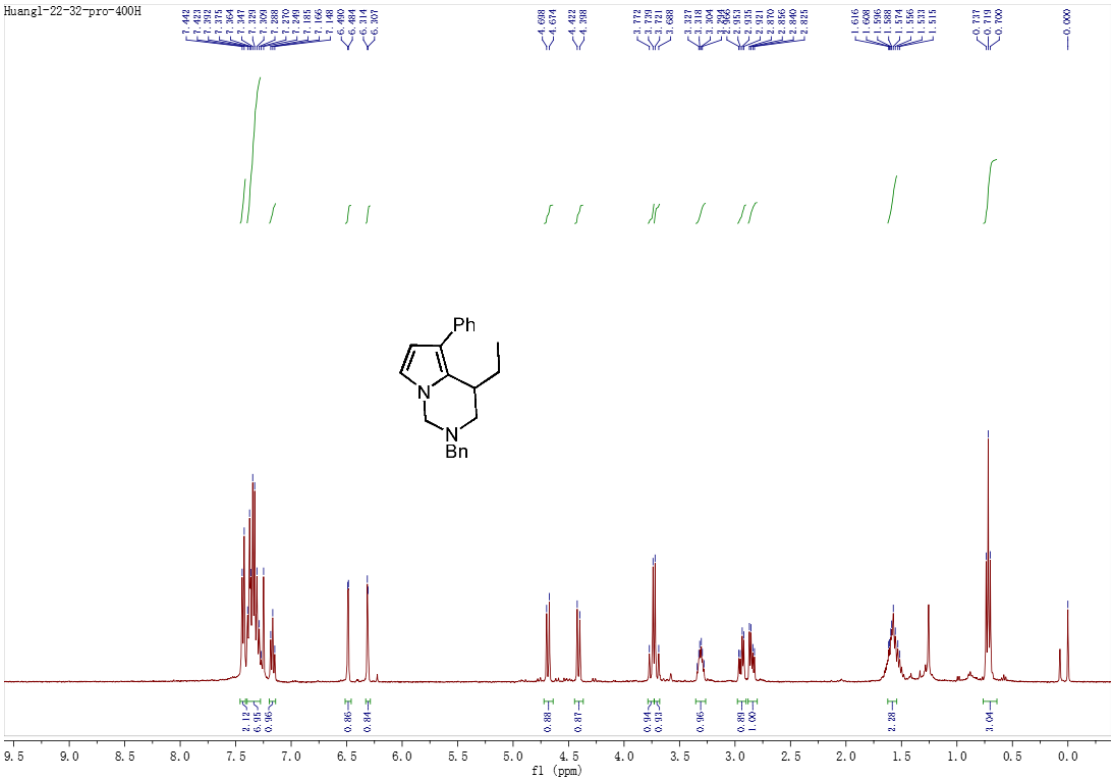



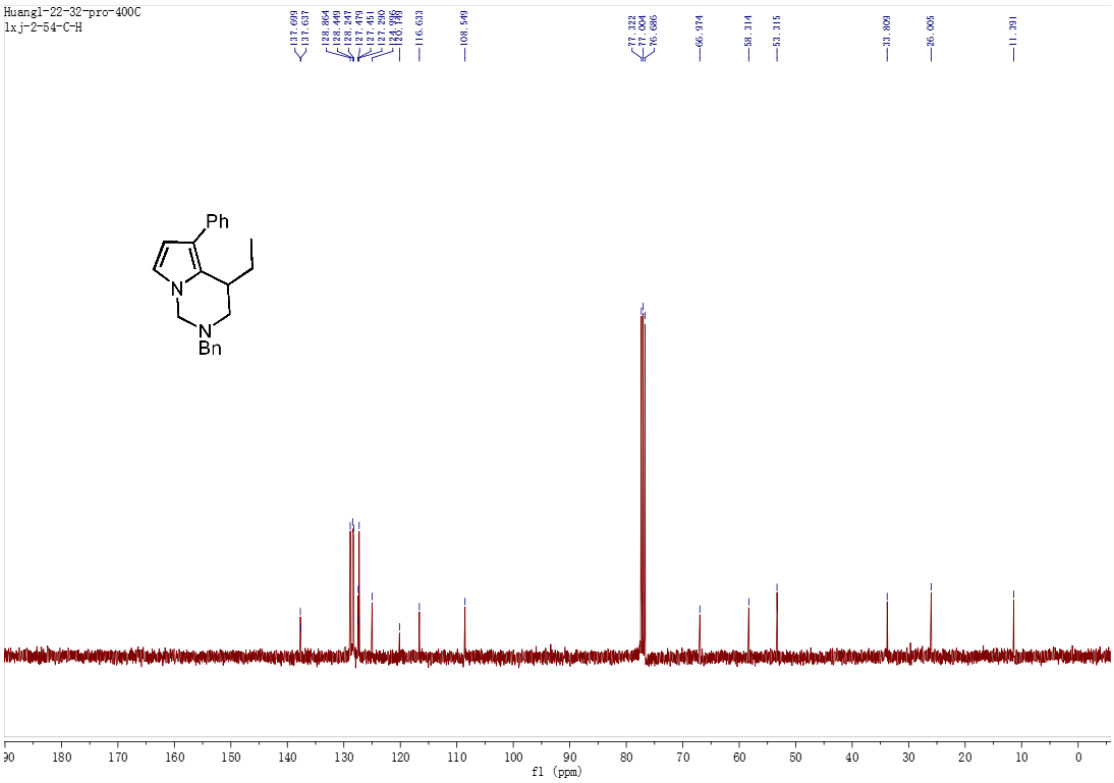
NMR Spectra of **2r**

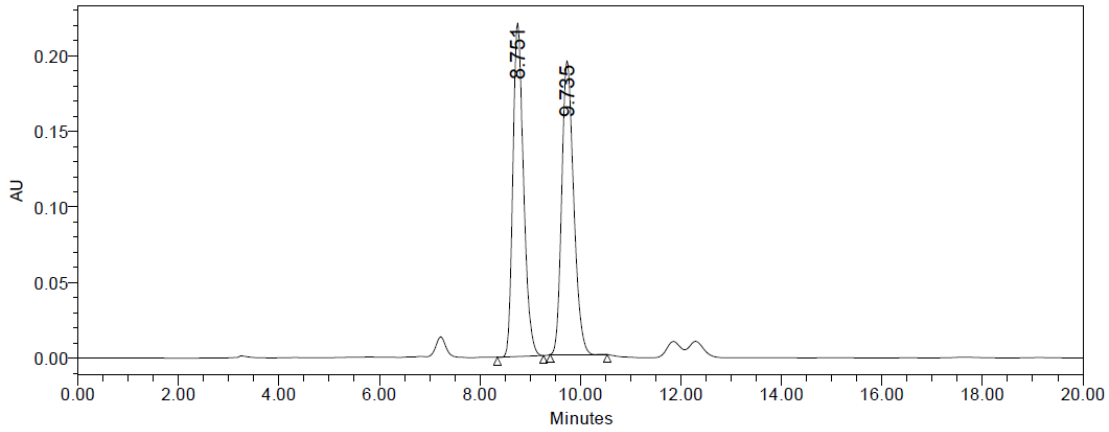


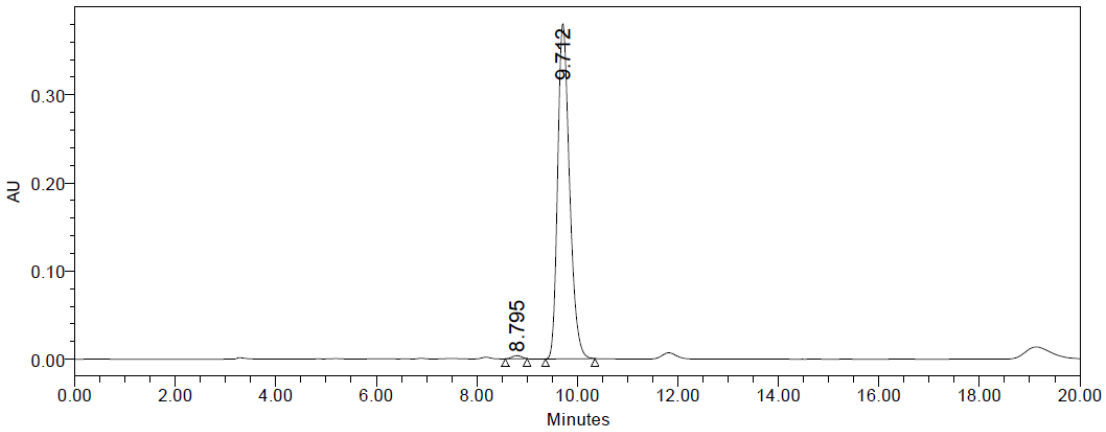
NMR Spectra and HPLC Chromatograms of **3**



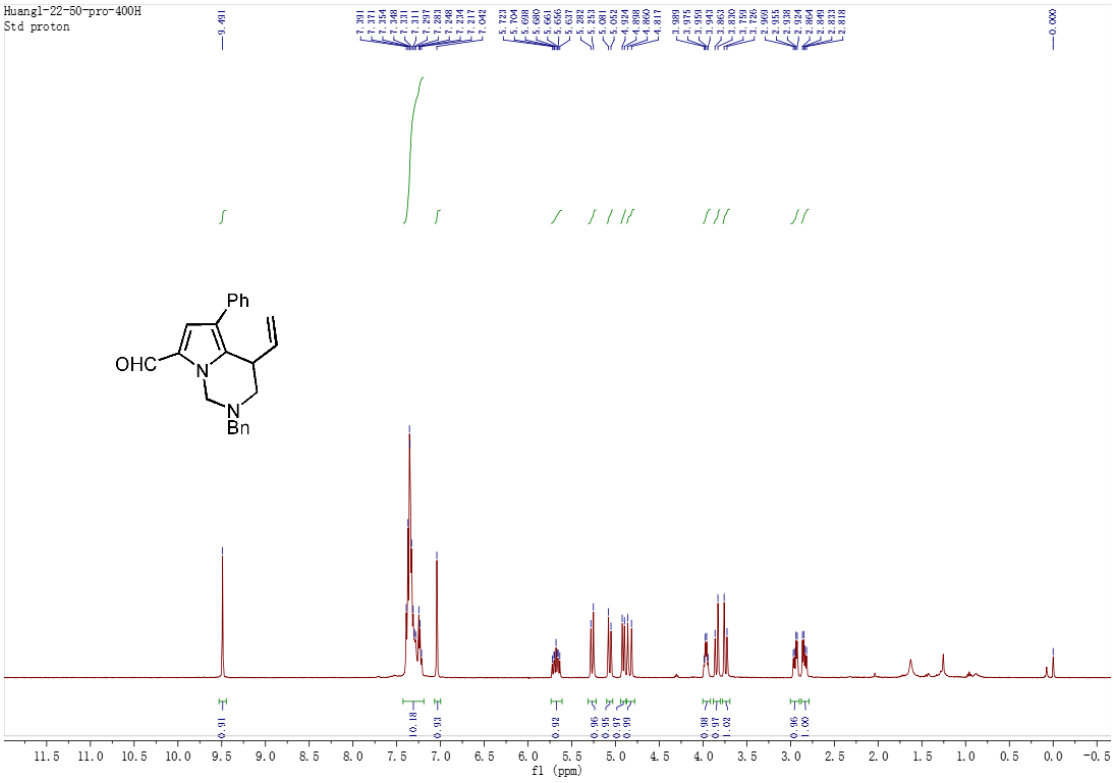


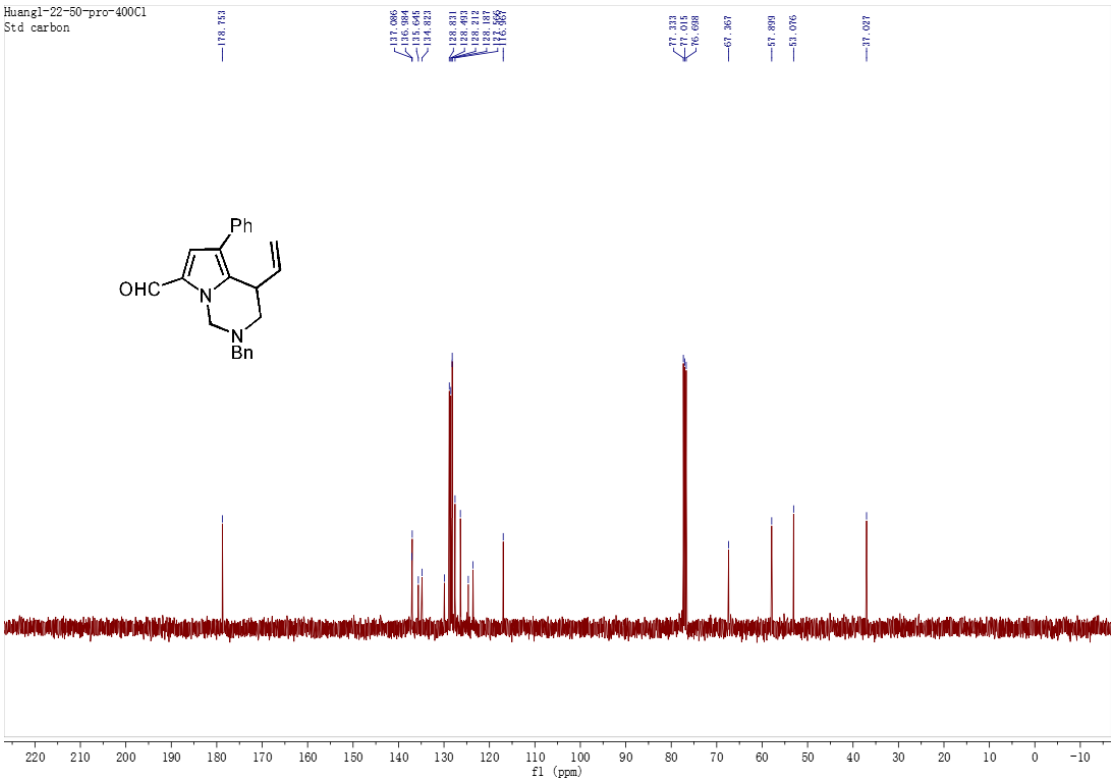

| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8.751 | 3224561 | 50.09 | 220751 |
| 2 | 9.735 | 3212782 | 49.91 | 194357 |

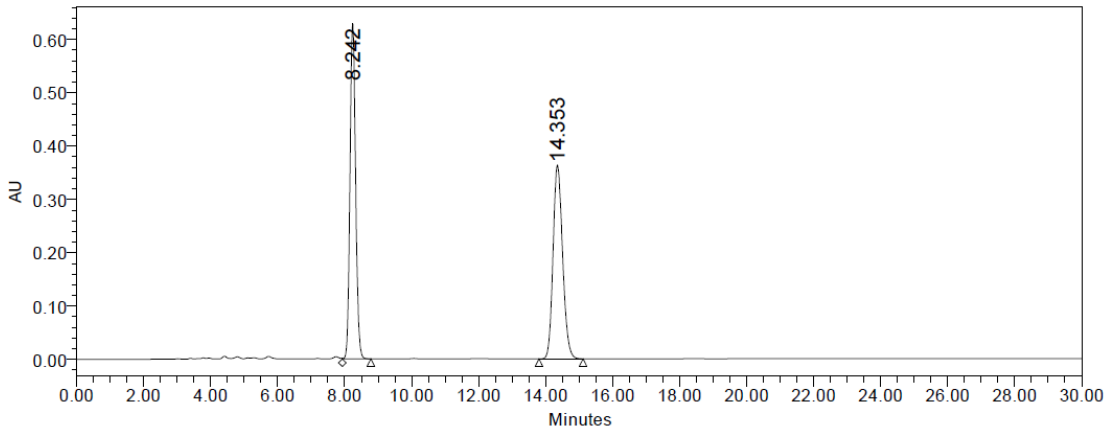



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8.795 | 46620 | 0.74 | 3722 |
| 2 | 9.712 | 6241238 | 99.26 | 380458 |

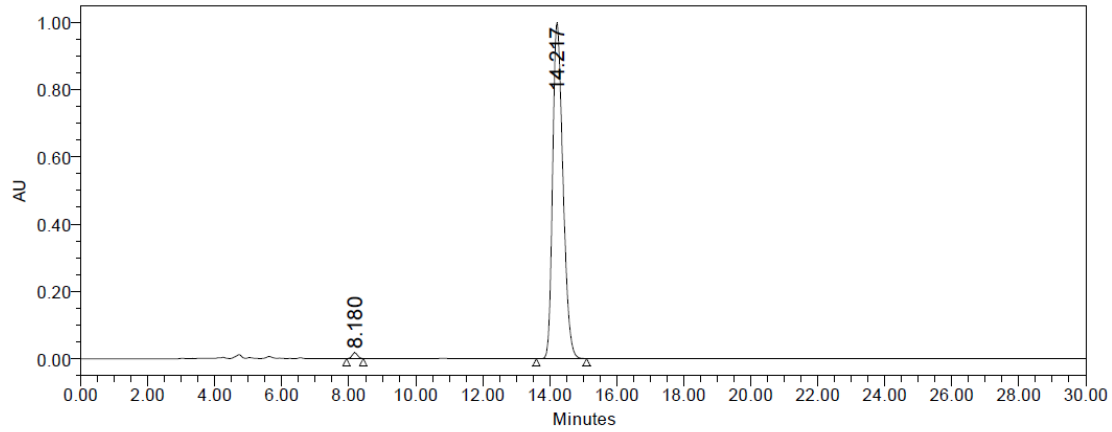
NMR Spectra and HPLC Chromatograms of **4**



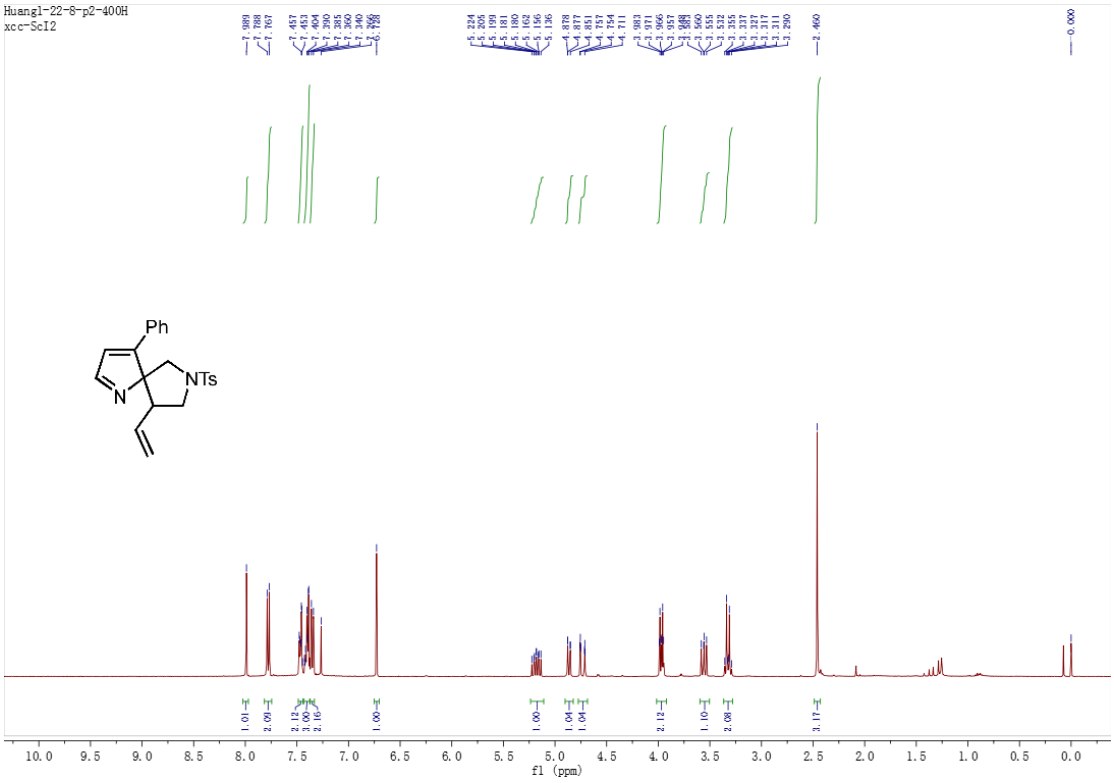


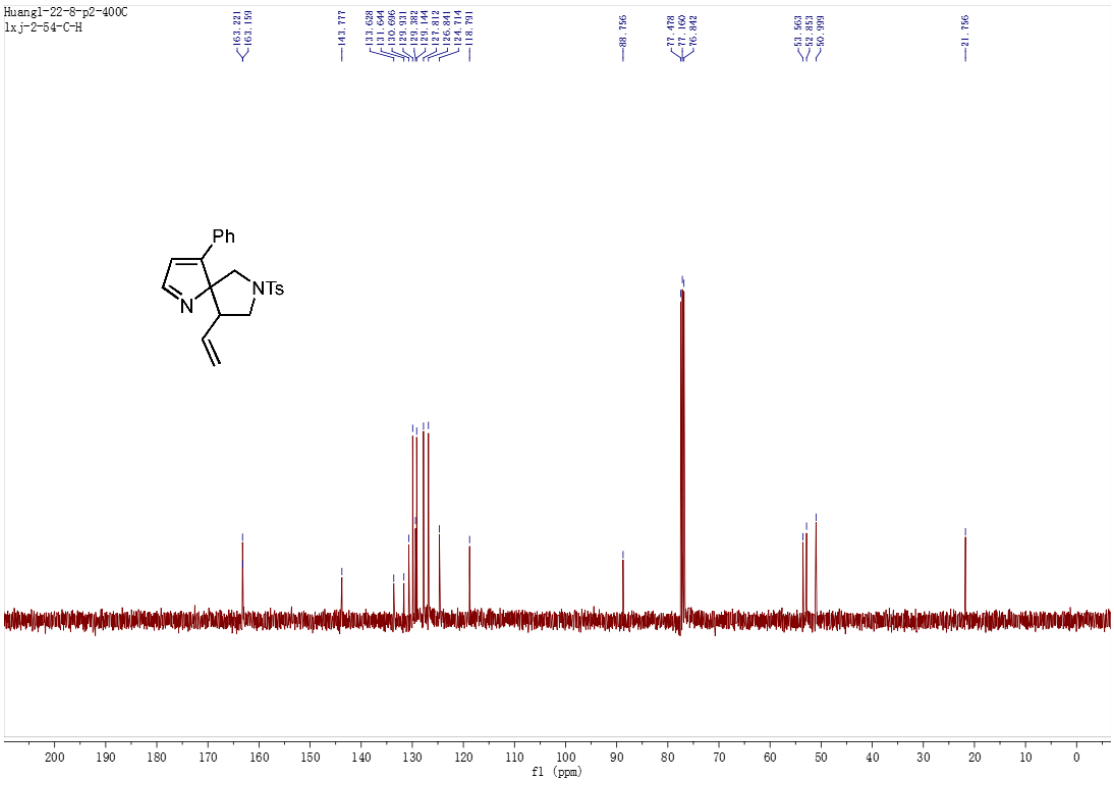

| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8.242 | 7329847 | 50.48 | 631097 |
| 2 | 14.353 | 7190502 | 49.52 | 363513 |

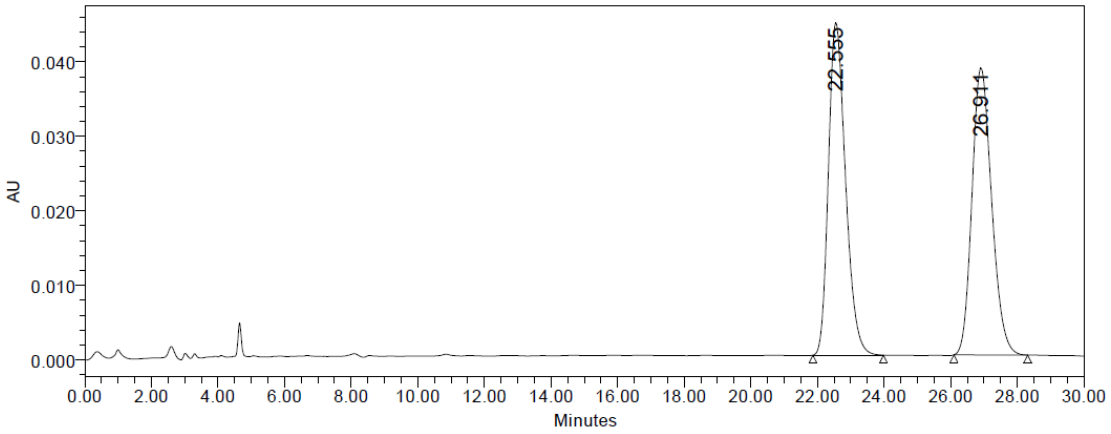



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8.180 | 198252 | 0.92 | 17253 |
| 2 | 14.217 | 21304034 | 99.08 | 997372 |

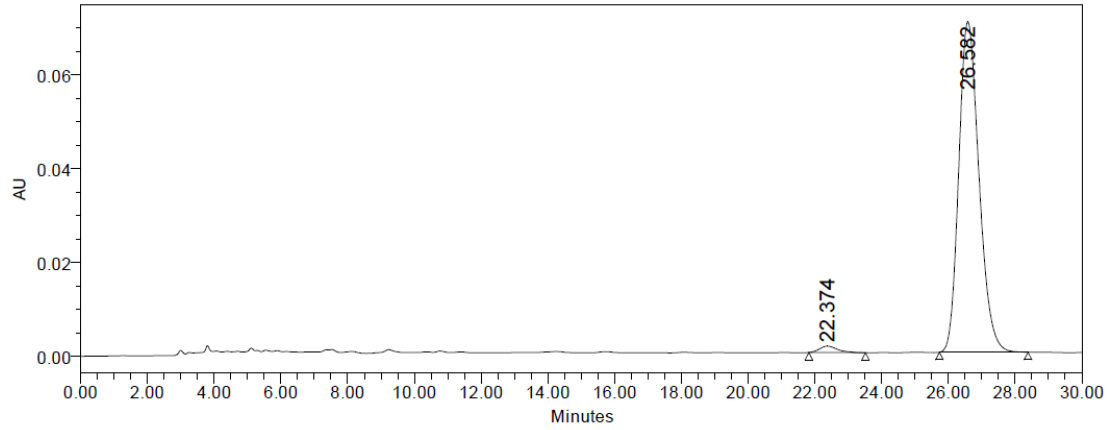
NMR Spectra and HPLC Chromatograms of **5**






| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 22.555 | 1592085 | 50.13 | 44601 |
| 2 | 26.911 | 1583523 | 49.87 | 38491 |




| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 22.374 | 51522 | 1.71 | 1370 |
| 2 | 26.582 | 2958245 | 98.29 | 70472 |

**DFT Calculations**

*Computational Methods*

All the calculations in this study were performed with Gaussian16 package.[1] The density functional theory (DFT) method was employed using the PBE1PBE functional.[2] The def2-TZVP basis sets[3] for all atoms were used. Optimizations were conducted without any constraint using implicit solvation model (SMD)[4] in acetonitrile ($\varepsilon = 35.688$). The Gibbs free energies in THF ($\Delta G$) were discussed throughout the paper. The 3D images of the calculated structures were prepared using CYLView.[5]

*Computational results*

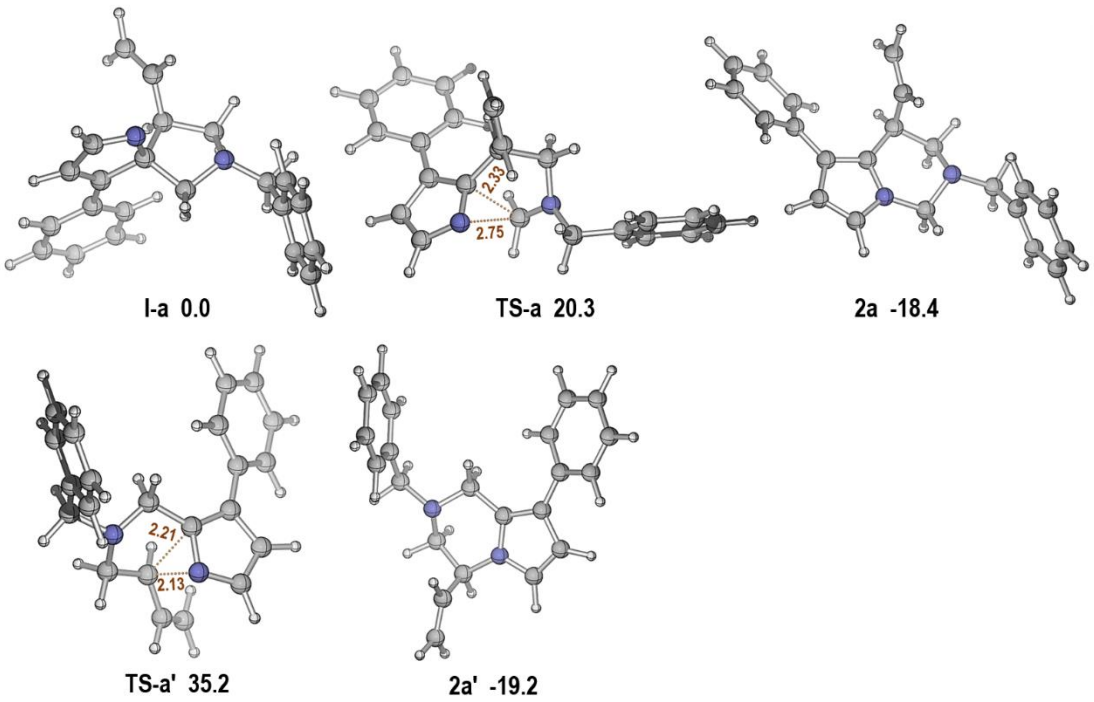


**Figure S1.** Optimized structures for the key transition states and intermediates in the possible ring-expansive migration pathways of spiro-2*H*-pyrrole intermediate **I-a**. Calculated at the PBE1PBE/def2-TZVP level of theory. Relative Gibbs free energies (in MeCN) are in kcal/mol. Values in brown are bond distances in Å.

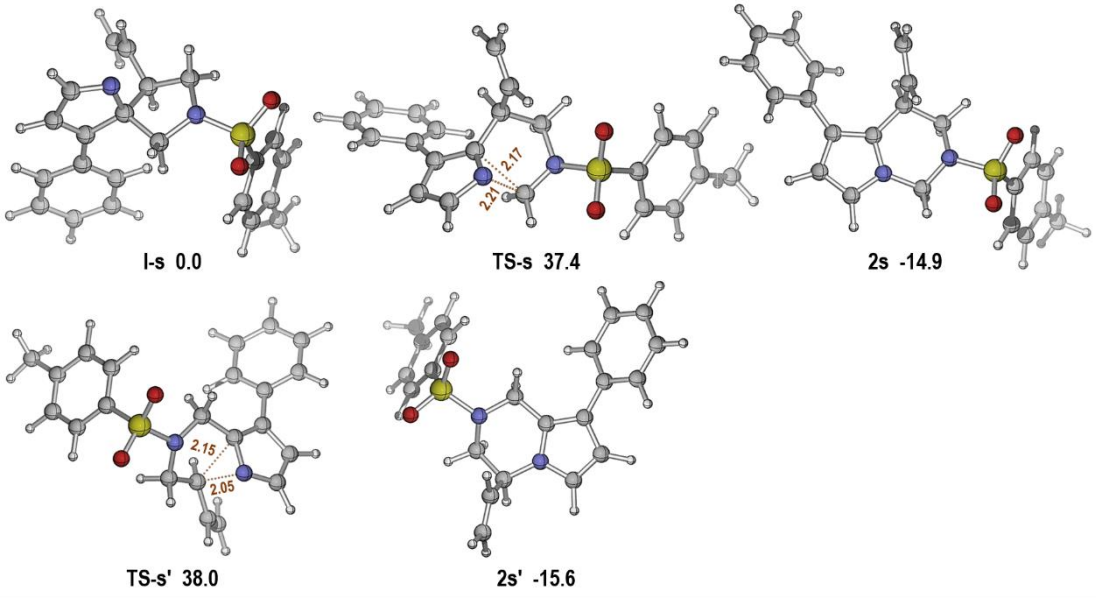



**Figure S2.** Optimized structures for the key transition states and intermediates in the possible ring-expansive migration pathways of spiro-2*H*-pyrrole intermediate **I-s**. Calculated at the PBE1PBE/def2-TZVP level of theory. Relative Gibbs free energies (in MeCN) are in kcal/mol. Values in brown are bond distances in Å.

*References*

1. Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.;

Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Iz-maylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

2. (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
3. (a) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297. (b) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
4. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
5. CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

*Cartesian coordinates of the calculated structures*

**I-a**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -960.250579695 a.u.

Zero-point correction = 0.387514 Hartree/Particle
Sum of electronic and thermal Free Energies = -959.914226 a.u.
---
N,0,-1.0400854301,-0.134028421,1.0972710808
N,0,0.1165307114,1.7207184616,-0.8994165893
C,0,-0.2134530959,-0.5128302345,-0.0301024497
H,0,-0.801666665,-0.6331651194,-0.9418621353
H,0,0.3285997555,-1.4536820166,0.1567782725
C,0,0.7747616908,0.6572881746,-0.1486310243
C,0,0.9807862721,1.0957157156,1.3527174155
H,0,1.9672527927,0.7637741672,1.6765789536
C,0,-0.1048527328,0.3122123779,2.1130859877
H,0,0.3612367849,-0.5421456608,2.6338895249
H,0,-0.6131721486,0.9208323949,2.8657422912
C,0,0.905714079,2.5714772672,1.5672492551
H,0,-0.0687494982,3.0316310989,1.4232084445
C,0,1.9379642191,3.3196528682,1.9387862011
H,0,2.923877076,2.8885324902,2.0928173584
H,0,1.8343768294,4.3877689656,2.1013138348
C,0,0.8783631518,2.0067737669,-1.8909229957
H,0,0.6043566954,2.7710611735,-2.6138389898
C,0,2.0893167423,1.2189569851,-1.9466695414
H,0,2.8540529167,1.3153673148,-2.7047464478
C,0,2.0579639338,0.3646343452,-0.8985041993
C,0,3.0723579698,-0.6381281328,-0.5670400168
C,0,4.1708152923,-0.8257421251,-1.4204653235
H,0,4.2594817756,-0.230432998,-2.3212368756
C,0,5.1479899293,-1.7625589267,-1.1406817036
H,0,5.983640881,-1.8836178647,-1.8214190324
C,0,5.0611957422,-2.5471482599,0.0042962072
H,0,5.8274224091,-3.2823047885,0.2241781886
C,0,3.98420439,-2.3789181355,0.8599424414
H,0,3.9017157548,-2.9825391436,1.757215512
C,0,3.0025701308,-1.4381756816,0.5798102842
H,0,2.1801425477,-1.337603814,1.2746617268
C,0,-1.9386073095,-1.1709862113,1.5589747185
H,0,-1.3916703576,-2.1027749262,1.7866318392
H,0,-2.3782964228,-0.8248463901,2.5010100506
C,0,-3.0454791015,-1.473278104,0.5836149185
C,0,-3.8749043292,-0.4556326769,0.1138575394
C,0,-3.2779954779,-2.7750484533,0.1522525925
C,0,-4.910946775,-0.7350483256,-0.7643513042
H,0,-3.7000779457,0.5648346495,0.4390106896
C,0,-4.3177164052,-3.0602796284,-0.7253409071
H,0,-2.6353678787,-3.5753686819,0.5067012655
C,0,-5.1372926056,-2.0405328365,-1.1864381919
H,0,-5.5480902359,0.0680916017,-1.1195780489
H,0,-4.4832408718,-4.0816464181,-1.0515417612
H,0,-5.9482761864,-2.2591728434,-1.8727370562
---

**TS-a**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -960.216307269 a.u.
Zero-point correction = 0.385683 Hartree/Particle
Sum of electronic and thermal Free Energies = -959.881941 a.u.
Imaginary frequency = -247.8991 $cm^{-1}$
---

N,0,-1.0091852935,-0.6822346509,-0.5989438489
N,0,0.6400192115,1.8800946156,-0.6380122739
C,0,-0.0672918243,-0.6301988014,-1.4995521613
H,0,-0.2628645485,-0.1453683122,-2.4476363724
H,0,0.7611141904,-1.318093042,-1.4172001534
C,0,1.1969072241,0.7368012331,-0.1026123472
C,0,0.5709103078,0.095538961,1.108689814
H,0,1.3474870668,-0.4484442878,1.6512796389
C,0,-0.5226674905,-0.9846460083,0.7218832979
H,0,-0.0520104012,-1.9680178345,0.7101753209
H,0,-1.3475021825,-1.0021184982,1.4323048211
C,0,-0.0073151843,1.1121475474,2.048261928
H,0,-0.7884374584,1.7524372718,1.6466437742
C,0,0.3731422349,1.2570947054,3.3119762657
H,0,1.1563381943,0.639091927,3.7438458572
H,0,-0.0804168768,2.0025338197,3.9575188739
C,0,1.5704225386,2.4164968228,-1.4276478749
H,0,1.3613505164,3.3082385788,-2.0094303001
C,0,2.761602391,1.6782965219,-1.4171732764
H,0,3.6560593036,1.882915715,-1.9908128947
C,0,2.5471879966,0.5964754845,-0.5568143347
C,0,3.5370865192,-0.4240454072,-0.2148088618
C,0,4.9059557634,-0.1187189457,-0.2711434908
H,0,5.2117803622,0.8845642691,-0.5468469017
C,0,5.8711474747,-1.0633927362,0.0349567826
H,0,6.92041769,-0.7911257622,-0.0147768522
C,0,5.5031148076,-2.3494882485,0.4137016288
H,0,6.2580218573,-3.0886656527,0.6580656183
C,0,4.1551601293,-2.6730671873,0.4740719669
H,0,3.848874788,-3.674049535,0.759946873
C,0,3.1880791022,-1.7272313803,0.1626806701
H,0,2.1463752032,-2.0202696985,0.1965003105
C,0,-2.2399753523,0.0885379733,-0.7380697494
H,0,-2.201696163,0.9423640282,-0.057702558
H,0,-2.2688825699,0.4718084346,-1.7595137575
C,0,-3.4621995784,-0.7433147178,-0.4530697724
C,0,-3.714683087,-1.9057749963,-1.1787723436
C,0,-4.3686197092,-0.3454617841,0.5230096886
C,0,-4.8545294536,-2.6549012423,-0.9313184892
H,0,-3.0130720638,-2.2255149634,-1.9430725758
C,0,-5.5143413355,-1.0922243504,0.7694842077
H,0,-4.1753418761,0.5574297203,1.0937325825
C,0,-5.7586742397,-2.248773826,0.0437123949
H,0,-5.0413508034,-3.5573981533,-1.5032963146
H,0,-6.2138731825,-0.7701850069,1.5332539197
H,0,-6.6507711988,-2.8348696003,0.2359712696
---

**2a**

Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -960.280791860 a.u.
Zero-point correction = 0.388498 Hartree/Particle
Sum of electronic and thermal Free Energies = -959.943562 a.u.
---
N,0,-1.6920240912,-1.1535531961,0.0598399222
N,0,-0.1453870218,-0.0753269435,-1.3578441785
C,0,-1.4844191834,-0.611049636,-1.2594731766
H,0,-2.1946298074,0.1934765752,-1.4535011736

H,0,-1.6181915543,-1.3902514694,-2.0315985741
C,0,0.9299887445,-0.5572690014,-0.6690709506
C,0,0.7067650794,-1.5256883853,0.4573221632
H,0,1.4394468446,-2.3340743504,0.4077501673
C,0,-0.680308652,-2.1622577874,0.3265744474
H,0,-0.6593317563,-2.9213885512,-0.4754418491
H,0,-0.9301413362,-2.6721579152,1.2589451163
C,0,0.864521167,-0.8285992348,1.7806132241
H,0,0.2009179981,0.0168624059,1.9512644243
C,0,1.7389575888,-1.1805057922,2.7149738683
H,0,2.4177589187,-2.01714353,2.5728756387
H,0,1.8062151827,-0.6446827906,3.6564833628
C,0,0.2495627762,0.8842609476,-2.2403005913
H,0,-0.4637650439,1.3602652763,-2.8959725384
C,0,1.6037567739,1.043334064,-2.1106202913
H,0,2.2188861446,1.7268111573,-2.6774382127
C,0,2.0544832354,0.13116329,-1.11389223
C,0,3.4430889033,0.01076938,-0.6579361227
C,0,4.2618255104,1.1453719856,-0.607170346
H,0,3.8474754272,2.1103266094,-0.8790262564
C,0,5.5851870234,1.0599704167,-0.202388618
H,0,6.1941828365,1.9573754598,-0.1694328954
C,0,6.1282314425,-0.1638917636,0.1668800257
H,0,7.1624034832,-0.231914036,0.4861954735
C,0,5.3316373588,-1.3002248086,0.1175912967
H,0,5.7449759468,-2.2653599501,0.3914135327
C,0,4.0093238408,-1.2151606455,-0.2931196385
H,0,3.4165721719,-2.1201713035,-0.3535997099
C,0,-3.0401305266,-1.6865413017,0.1946268724
H,0,-3.2632940866,-2.4221389375,-0.5960673595
H,0,-3.0747851003,-2.2234923812,1.1471821674
C,0,-4.1019063853,-0.6187123652,0.1911035077
C,0,-4.069498541,0.4144541518,1.126812698
C,0,-5.1472986855,-0.656880668,-0.7255517675
C,0,-5.0594362832,1.3851607167,1.1435551302
H,0,-3.2590226429,0.455299992,1.8473779816
C,0,-6.1436690047,0.3122993547,-0.7101133028
H,0,-5.180677053,-1.4552798204,-1.460740861
C,0,-6.1017095392,1.3365012172,0.2243897168
H,0,-5.0216263615,2.1816093567,1.8792751744
H,0,-6.9514690183,0.2672118873,-1.4327772267
H,0,-6.8766307243,2.0952853207,0.2381729591
---

**TS-a'**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -960.191143995 a.u.
Zero-point correction = 0.384133 Hartree/Particle
Sum of electronic and thermal Free Energies = -959.858122 a.u.
Imaginary frequency = -405.6992 $cm^{-1}$
---
N,0,-1.1575852047,0.399401759,1.1521843568
N,0,-0.4109738812,1.546560519,-1.2119227986
C,0,-0.0221221025,-0.2151738816,0.5123007407
H,0,-0.3301008584,-1.2051378951,0.1556457662
H,0,0.8219079971,-0.3873014276,1.2046427254
C,0,0.4524752611,0.6145322426,-0.6317452647
C,0,0.1702359424,2.3812475656,0.6593540854

H,0,1.1585114221,2.0443905923,0.9575047024
C,0,-0.9532987081,1.8101029999,1.4444912324
H,0,-0.6752165674,1.9580279432,2.5029685675
H,0,-1.8770864559,2.3690900592,1.2672460155
C,0,0.1459535308,3.7457492215,0.2086182798
H,0,-0.8245950875,4.197174639,0.0216159944
C,0,1.2730443716,4.4308959791,-0.0092553496
H,0,2.2453787704,3.9827644341,0.1703339662
H,0,1.2526956738,5.4576322415,-0.3582955176
C,0,0.2459609872,2.0607894728,-2.2629115465
H,0,-0.2017639137,2.8282427806,-2.8805545827
C,0,1.502392609,1.4809936418,-2.3973287862
H,0,2.2144465395,1.6696259274,-3.1910381628
C,0,1.6527185883,0.5414610588,-1.3566060975
C,0,2.8366565353,-0.2833565483,-1.1097383097
C,0,4.1047856213,0.1809342913,-1.4853870674
H,0,4.1974009617,1.1629139258,-1.9370492186
C,0,5.2423218056,-0.5823855686,-1.277210041
H,0,6.2101374833,-0.193777632,-1.576700501
C,0,5.1492514209,-1.8338001002,-0.6802364499
H,0,6.0392636056,-2.4304605488,-0.5132431045
C,0,3.9015401907,-2.3113095785,-0.3034982936
H,0,3.8103536416,-3.2911683897,0.1535249641
C,0,2.761142132,-1.5502554479,-0.5183874121
H,0,1.7972190682,-1.9621644253,-0.2455772099
C,0,-1.6705037598,-0.3445270096,2.2843668653
H,0,-0.8925293578,-0.5167456057,3.0475514635
H,0,-2.440297946,0.2765716709,2.7550637643
C,0,-2.2854769203,-1.6650510992,1.8999478933
C,0,-3.2651928395,-1.7313353754,0.9101260498
C,0,-1.9113788478,-2.8375957318,2.5478091345
C,0,-3.855419509,-2.9413508586,0.5784992222
H,0,-3.5609892392,-0.8239722946,0.3935715016
C,0,-2.5037393373,-4.0521007593,2.2214553876
H,0,-1.1452155782,-2.7994494423,3.3163963017
C,0,-3.4773007935,-4.1074410998,1.2349480416
H,0,-4.6168662042,-2.9761159197,-0.1936082666
H,0,-2.1986867428,-4.9566616582,2.7368680056
H,0,-3.9394893049,-5.0538216676,0.9756559525
---

**2a'**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -960.282315022 a.u.
Zero-point correction = 0.388317 Hartree/Particle
Sum of electronic and thermal Free Energies = -959.944894 a.u.
---
N,0,-1.0834748458,-1.1949918221,-0.9219172568
N,0,1.5400499934,-1.9119908134,-0.5900958553
C,0,-0.1022934437,-0.1396836506,-1.1086801084
H,0,-0.4019543154,0.7433171425,-0.5386683363
H,0,-0.0724063403,0.1659267284,-2.1731453856
C,0,1.2506885367,-0.5828827457,-0.6693574852
C,0,0.5790038953,-2.984646593,-0.8168204445
H,0,1.0551580794,-3.7370964527,-1.4515884072
C,0,-0.6173800602,-2.4075406249,-1.5646340228
H,0,-0.3341156331,-2.2236990912,-2.6162730496
H,0,-1.4170324688,-3.1501008635,-1.561801077

C,0,0.1884222385,-3.6237559133,0.483435506
H,0,-0.2699717213,-2.9652414193,1.2177709773
C,0,0.3666479136,-4.910337002,0.7489515878
H,0,0.8287243479,-5.5791309475,0.0274828458
H,0,0.055211095,-5.3420244569,1.6945263087
C,0,2.8232834947,-2.0845212942,-0.1548592753
H,0,3.2341562716,-3.0741575713,-0.0258416471
C,0,3.3733036932,-0.8473994175,0.0415693087
H,0,4.3859793422,-0.6496012498,0.3609997648
C,0,2.382610747,0.1254556215,-0.2855820993
C,0,2.5534943713,1.5761717218,-0.2056814643
C,0,3.4752954087,2.1262647035,0.6950203655
H,0,4.0451410725,1.4667705431,1.3407123873
C,0,3.6610172178,3.4962567058,0.7875441304
H,0,4.379928252,3.8919115497,1.4974563872
C,0,2.9271380192,4.3613829308,-0.0150682228
H,0,3.0691682446,5.4338830141,0.0595899994
C,0,2.0125857732,3.833965004,-0.9162884965
H,0,1.4394755784,4.494867213,-1.5582496723
C,0,1.8313389404,2.4616922401,-1.014702041
H,0,1.1354891909,2.075256699,-1.7497512691
C,0,-2.3910460834,-0.793501579,-1.4176922986
H,0,-2.3382307448,-0.476697618,-2.4732760319
H,0,-3.0361329086,-1.6768772164,-1.3796988547
C,0,-3.0169195934,0.3082595474,-0.6045914359
C,0,-3.2509531938,0.1358890546,0.7591817526
C,0,-3.393729112,1.5076766892,-1.1994491649
C,0,-3.8466891905,1.1395087972,1.5077745015
H,0,-2.9616928781,-0.795220322,1.2359132546
C,0,-3.9943505077,2.5153999015,-0.4536358833
H,0,-3.2129569409,1.6545518304,-2.2599876276
C,0,-4.2214774182,2.3340904303,0.9026503231
H,0,-4.0240216924,0.989276281,2.567522457
H,0,-4.2809879055,3.4446126703,-0.934526559
H,0,-4.6885267196,3.118739645,1.4880636148
---

**I-s**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -1508.69062075 a.u.
Zero-point correction = 0.397905 Hartree/Particle
Sum of electronic and thermal Free Energies = -1508.349104 a.u.
---
N,0,-0.405885013,-1.5767933674,-0.4612303436
N,0,-2.9455672066,-0.1524093471,-0.626690095
C,0,-0.6047982936,-0.3253591528,-1.1960475132
H,0,-0.9921262965,-0.5158188085,-2.1962836637
H,0,0.3211312192,0.2493454226,-1.2788719561
C,0,-1.6344836451,0.4177885214,-0.3373894539
C,0,-1.2211316192,0.0031632622,1.1044963923
H,0,-0.3164920604,0.5582444947,1.3598462814
C,0,-0.8633321357,-1.4726427602,0.9300927914
H,0,-0.0885946254,-1.7742632204,1.6371069617
H,0,-1.735985776,-2.112336853,1.0803387907
C,0,-2.2516457987,0.2474947222,2.153182413
H,0,-3.1830337079,-0.3044179428,2.0504787353
C,0,-2.0845418191,1.0735860888,3.1782855562
H,0,-1.1644505403,1.6365265169,3.3105627837

H,0,-2.8622386025,1.2150924645,3.921743122
C,0,-3.7005378809,0.82107176,-0.9839182051
H,0,-4.7396926902,0.6610294327,-1.2591839119
C,0,-3.0391529939,2.1069177288,-0.9840798721
H,0,-3.5113094415,3.0409917257,-1.2538938816
C,0,-1.759403099,1.9047000271,-0.5959402003
C,0,-0.7278517891,2.9330955786,-0.4438171673
C,0,-1.0568226075,4.2814130734,-0.6547018447
H,0,-2.0707633727,4.5529069879,-0.9226272452
C,0,-0.111889136,5.2815379785,-0.5234848106
H,0,-0.3988424704,6.3136339782,-0.6928648387
C,0,1.1977908746,4.9693224298,-0.175363374
H,0,1.9391859942,5.7538272544,-0.0718071798
C,0,1.5433948515,3.6447399393,0.0390822346
H,0,2.560130621,3.3834546457,0.3116575878
C,0,0.5949049839,2.639976736,-0.0921291226
H,0,0.908817416,1.6203545269,0.0820375945
S,0,0.8205778256,-2.5614216534,-0.8566458762
O,0,0.6240792251,-3.780829085,-0.1235223662
O,0,0.8805870024,-2.5807023033,-2.2920990782
C,0,2.3071762697,-1.8166985665,-0.2709650467
C,0,2.9896356524,-0.9102872316,-1.0783525592
C,0,2.771448578,-2.1061783359,1.0063952491
C,0,4.1305604518,-0.2939628627,-0.5960734283
H,0,2.6387826471,-0.704105439,-2.0821752777
C,0,3.9168346385,-1.4799981287,1.4735607403
H,0,2.2523750407,-2.8285469257,1.6245079654
C,0,4.6115424889,-0.5642518835,0.6863664492
H,0,4.6652427285,0.4058148707,-1.2304593346
H,0,4.2829125202,-1.7136593412,2.4678681919
C,0,5.8446252272,0.1137692147,1.1933718798
H,0,6.6800162745,-0.0245412971,0.5016358595
H,0,5.6829443338,1.1919561429,1.2875799816
H,0,6.1376067565,-0.2727330191,2.1704200853

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**TS-s**

Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -1508.62706049 a.u.
Zero-point correction = 0.394218 Hartree/Particle
Sum of electronic and thermal Free Energies = -1508.289462 a.u.
Imaginary frequency = -420.4130 $cm^{-1}$

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N,0,-0.7720395415,-0.0049972875,-0.3108104368
N,0,1.5669729453,1.4852211357,-1.0111993061
C,0,0.0438496973,-0.0728674271,-1.3776358432
H,0,-0.2304467456,0.5191101956,-2.2368583954
H,0,0.537339683,-1.0191080378,-1.5606759146
C,0,1.8522738258,0.3440761399,-0.2449340603
C,0,1.2061400529,0.1260852338,1.0951337679
H,0,1.8109610721,-0.5967984125,1.6474036976
C,0,-0.2012267956,-0.5235363069,0.9167411703
H,0,-0.0874908857,-1.6036687186,0.8117697171
H,0,-0.8604982807,-0.3233591096,1.7591426648
C,0,1.1460138937,1.3915337806,1.8999756872
H,0,0.5644120995,2.2065899743,1.4795037308
C,0,1.7572029479,1.5504258501,3.0671760985
H,0,2.3513519687,0.755897024,3.5113053293

H,0,1.6876685667,2.4827980293,3.6183085161
C,0,2.5029124855,1.5328025751,-1.9631627245
H,0,2.4786632234,2.2994032011,-2.7282517507
C,0,3.4247087321,0.490608906,-1.8307335818
H,0,4.279158272,0.3021371889,-2.4682741311
C,0,3.0249987432,-0.2804528337,-0.7343116611
C,0,3.7057062328,-1.4748730215,-0.2312759321
C,0,5.1034993296,-1.5598617179,-0.2730774261
H,0,5.6735602976,-0.7196928604,-0.655333631
C,0,5.7684086654,-2.6883364913,0.1795151575
H,0,6.852066528,-2.7242511985,0.1380971478
C,0,5.0556711334,-3.7653166355,0.6929985774
H,0,5.5757918524,-4.6469580085,1.0511426475
C,0,3.6699500113,-3.700233383,0.7386098935
H,0,3.0988184868,-4.5377817014,1.1254711257
C,0,3.0037272644,-2.5729345424,0.2784303806
H,0,1.9197711684,-2.5596049514,0.2900609614
S,0,-2.0698014874,1.0751272334,-0.2750346825
O,0,-1.9684032087,1.8516367106,0.9231214625
O,0,-2.0826529324,1.7108775457,-1.5577758057
C,0,-3.4463840941,0.0031478375,-0.1363156392
C,0,-4.0957766095,-0.127472052,1.0822814719
C,0,-3.877280652,-0.6972008137,-1.2602154407
C,0,-5.1929548586,-0.9705727779,1.1718541274
H,0,-3.7547641049,0.428459477,1.9467382746
C,0,-4.970376659,-1.532816894,-1.1498313356
H,0,-3.3655000511,-0.5849979979,-2.2091111812
C,0,-5.6457913402,-1.683958254,0.0653698269
H,0,-5.70834797,-1.0726101209,2.1207791332
H,0,-5.3129622271,-2.0788228342,-2.0225878502
C,0,-6.8288500158,-2.5918490041,0.1625383062
H,0,-7.615694364,-2.277797817,-0.5293642188
H,0,-6.5551067938,-3.6154016585,-0.1091703145
H,0,-7.2412815616,-2.6015581687,1.1720223895
---

**2s**

Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -1508.71416753 a.u.
Zero-point correction = 0.398189 Hartree/Particle
Sum of electronic and thermal Free Energies = -1508.372862 a.u.
---
N,0,-1.5898352915,-1.4827177868,-0.3282304263
N,0,-0.0588529511,-0.1868771662,-1.5328645385
C,0,-1.353799807,-0.8250077231,-1.596781286
H,0,-2.1143715919,-0.0671384247,-1.7716525044
H,0,-1.3616681223,-1.5536398251,-2.4189132083
C,0,0.9946778248,-0.6330939124,-0.7832891482
C,0,0.765500005,-1.667218413,0.2829405395
H,0,1.5729380782,-2.4019835325,0.2732750022
C,0,-0.530018987,-2.4331496601,-0.0014504541
H,0,-0.3780700274,-3.1245044866,-0.84022502
H,0,-0.8191985157,-3.0039905986,0.8784495548
C,0,0.7282394264,-1.0175394722,1.6388289798
H,0,-0.0385540967,-0.2577931704,1.778381746
C,0,1.556655832,-1.3129074277,2.6321689598
H,0,2.3346427902,-2.0631663736,2.5204838882
H,0,1.4849637099,-0.8142302172,3.5934143578

C,0,0.3320971991,0.8463086854,-2.3316628167
H,0,-0.3606121964,1.3061055735,-3.0199782221
C,0,1.6559069963,1.0900665233,-2.0821443341
H,0,2.2616971148,1.8465492937,-2.5590232015
C,0,2.0930749147,0.1572233159,-1.0989791517
C,0,3.4453153026,0.1094148716,-0.5323670632
C,0,4.1554007986,1.2965185638,-0.3200341967
H,0,3.6826994502,2.2454557291,-0.5500152579
C,0,5.4441086186,1.2803590166,0.1915909243
H,0,5.9695098717,2.2163668329,0.34977192
C,0,6.0580951831,0.0753056462,0.5075493066
H,0,7.0651012198,0.0613929942,0.909843463
C,0,5.3690738377,-1.1119580029,0.2979763152
H,0,5.840405569,-2.0616276744,0.5287621383
C,0,4.0817945963,-1.0955191545,-0.2187924315
H,0,3.5737874977,-2.034768719,-0.4034361081
S,0,-3.1404633,-1.8481787517,0.0680458643
O,0,-3.1055616781,-2.3327644202,1.4175569663
O,0,-3.9220073829,-0.6909372238,-0.2633751767
C,0,-3.6490090039,-3.171333345,-0.9749254574
C,0,-4.221134906,-2.8929416561,-2.2118697323
C,0,-3.4374692373,-4.4853132474,-0.5739831315
C,0,-4.5820704876,-3.9392954837,-3.042850433
H,0,-4.3929718415,-1.8676940535,-2.5165857611
C,0,-3.805285577,-5.5198602652,-1.4183373042
H,0,-2.9999263672,-4.6973688147,0.3939046266
C,0,-4.3827833133,-5.2666065473,-2.6617969781
H,0,-5.0308396885,-3.722276266,-4.0066485553
H,0,-3.6431164126,-6.5455991348,-1.104181993
C,0,-4.80651105,-6.3888710235,-3.5544353052
H,0,-5.8681650073,-6.6137574569,-3.4064299585
H,0,-4.6740858176,-6.1297213919,-4.6067775841
H,0,-4.2447020992,-7.2998482233,-3.3414188231

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**TS-s'**

Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -1508.62687423 a.u.
Zero-point correction = 0.394578 Hartree/Particle
Sum of electronic and thermal Free Energies = -1508.288569 a.u.
Imaginary frequency = -481.4856 $cm^{-1}$

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N,0,0.4823092758,-1.1655870128,-0.5978557206
N,0,-2.181272829,-1.4871744401,-0.1526054034
C,0,-0.3241753699,0.0219535957,-0.844374202
H,0,-0.3926003137,0.1645019792,-1.9256301008
H,0,0.1306343093,0.9229992792,-0.419527004
C,0,-1.6866223099,-0.1827828524,-0.2745687578
C,0,-0.8664081754,-1.2417558253,1.4028008912
H,0,-0.7229779827,-0.2180310215,1.7394955385
C,0,0.3053614663,-1.8275369459,0.6942922644
H,0,1.1791453855,-1.6722012292,1.3427367341
H,0,0.1711807365,-2.8987335605,0.545418628
C,0,-1.5953178511,-2.0448723206,2.3575952541
H,0,-1.6548021864,-3.1134188983,2.1701936987
C,0,-2.1992094689,-1.4976040512,3.4142393106
H,0,-2.1501478146,-0.4287856963,3.5984001547
H,0,-2.7502295462,-2.1028348482,4.1258208714

C,0,-3.4816775667,-1.3617615983,0.1613902101
H,0,-4.0931913105,-2.2310868836,0.3615948216
C,0,-3.8537764682,-0.0241140479,0.1983512528
H,0,-4.8480432812,0.3615491504,0.3860333553
C,0,-2.7079122112,0.7514915631,-0.0663990563
C,0,-2.6567774332,2.2163029938,-0.1254076391
C,0,-3.7159695931,2.9324271127,-0.6944401724
H,0,-4.5556985615,2.3907419399,-1.1168985368
C,0,-3.7023149456,4.318205353,-0.7386816018
H,0,-4.5348534125,4.8482092244,-1.1893222892
C,0,-2.6268378677,5.0259961316,-0.2175204671
H,0,-2.6134804729,6.1097086027,-0.255283949
C,0,-1.5709419863,4.3305645146,0.3566613769
H,0,-0.7304383144,4.8708811853,0.779437379
C,0,-1.5873133003,2.9442840617,0.4062331969
H,0,-0.767854196,2.4228440971,0.8882848527
S,0,1.9326360901,-1.3013145989,-1.3294647288
O,0,2.3815744057,-2.6427918563,-1.0844698566
O,0,1.7634012588,-0.8296143794,-2.6747883312
C,0,3.0359428359,-0.2026414727,-0.5063658362
C,0,3.1029043227,1.1311844056,-0.9012689455
C,0,3.8046717591,-0.6611767835,0.5559577436
C,0,3.9403527147,1.9986056862,-0.2239011407
H,0,2.5160676183,1.4819943056,-1.7415662491
C,0,4.6391022218,0.2224915054,1.2236502622
H,0,3.7643919016,-1.7035115764,0.8477227953
C,0,4.7196641393,1.5616326811,0.8493922275
H,0,3.9968731529,3.0362063155,-0.5370793505
H,0,5.2443824683,-0.1378191443,2.0488340788
C,0,5.622579963,2.5132958659,1.5675833012
H,0,5.053483736,3.3472946174,1.9883197172
H,0,6.1573358241,2.0181278634,2.3791303788
H,0,6.3589651832,2.9431490129,0.8823860436
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**2s'**
Opt @ PBE1PBE/def2-TZVP in acetonitrile (SMD model)
SCF Done: E(RPBE1PBE) = -1508.71766697 a.u.
Zero-point correction = 0.398317 Hartree/Particle
Sum of electronic and thermal Free Energies = -1508.373908 a.u.
---
N,0,-0.8713466672,-1.3165652415,-1.1574796437
N,0,1.7052254305,-1.9497409962,-0.5893900171
C,0,0.0631777393,-0.195606708,-1.2109979362
H,0,-0.3327917393,0.6328170707,-0.6239868596
H,0,0.1768317262,0.1483620217,-2.2507233942
C,0,1.3807214119,-0.626515548,-0.6591945326
C,0,0.804529597,-3.0526776483,-0.9049973784
H,0,1.3615122409,-3.7889557062,-1.4901531958
C,0,-0.3242437306,-2.5161809222,-1.7773564994
H,0,0.0596490739,-2.2864100088,-2.7796311236
H,0,-1.098699605,-3.2754610084,-1.8602798072
C,0,0.3002535667,-3.7012479342,0.3502670886
H,0,-0.2562529488,-3.0581996504,1.0286051176
C,0,0.4964618019,-4.979786267,0.639006578
H,0,1.0553228011,-5.6320694149,-0.0267217489
H,0,0.1037041571,-5.4202633798,1.5494591183
C,0,2.9492126207,-2.0913565364,-0.0437166235

H,0,3.379340858,-3.0707704576,0.0991112568
C,0,3.4360428503,-0.8436277552,0.2326676472
H,0,4.4083958404,-0.6217509057,0.6470689644
C,0,2.4472519682,0.1066306846,-0.1581507903
C,0,2.5625853331,1.5597466377,-0.0245130556
C,0,3.3605926266,2.1069057576,0.9885871523
H,0,3.8725811436,1.443899975,1.677645178
C,0,3.494985642,3.4780458385,1.1358040283
H,0,4.117623892,3.8722403482,1.9321583112
C,0,2.8316545708,4.345678211,0.2766130017
H,0,2.9338118607,5.4189579177,0.3933273706
C,0,2.0400172974,3.8209059397,-0.7354413543
H,0,1.5247564774,4.4845867539,-1.4219214725
C,0,1.9106723505,2.4476642867,-0.8879125834
H,0,1.3147170683,2.0659708572,-1.7083117839
S,0,-2.4642936536,-0.9830318284,-1.3694404677
O,0,-3.1673683061,-2.2161684792,-1.1562534394
O,0,-2.7494546026,0.1579083956,-0.5465469818
C,0,-2.6828663617,-0.5113754665,-3.0513331177
C,0,-2.5699293175,0.8251295556,-3.4128374332
C,0,-2.9299561188,-1.4854015413,-4.0147842086
C,0,-2.7059252631,1.1827010834,-4.7453785345
H,0,-2.3927566976,1.5817341835,-2.6581530483
C,0,-3.0626141957,-1.1106430634,-5.3394364486
H,0,-3.0334854367,-2.5245919702,-3.7269973736
C,0,-2.9507725069,0.2259796798,-5.7277995097
H,0,-2.624964808,2.2273934311,-5.0265046719
H,0,-3.2635491709,-1.8694774647,-6.0888138375
C,0,-3.0941181991,0.6123491679,-7.1653287503
H,0,-2.3089438436,0.1499576507,-7.7709462035
H,0,-4.0512897885,0.2695152003,-7.5680583322
H,0,-3.0329723249,1.6936615348,-7.2946013944
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