

The Asymmetric Cu(II)-Indolinylmethanol Complex Catalyzed Diels-Alder Reaction of 2-Vinyldoles with β,γ - Unsaturated α -Ketoesters: An Efficient Route to Functionalized Tetrahydrocarbazoles

Banlai Ouyang,^a Tingting Yu,^a Renshi Luo,^a and Gui Lu^{a,b,*}

^a *Institute of Medicinal Chemistry, School of Pharmaceutical Sciences, Sun Yat-sen University,
Guangzhou 510006, P. R. China*

^b *Institute of Human Virology, Sun Yat-sen University, Guangzhou 510080, P. R. China.*

Fax: (+86)-20-39943048

E-mail: lugui@mail.sysu.edu.cn

Supporting Information

- 1. General information**
- 2. Preparation of ligands**
- 3. Synthesis of β,γ -unsaturated α -ketoesters 1a-f, 1h, 1j-k, 1m-n and 1p**
- 4. Synthesis of β,γ -unsaturated α -ketoesters 1g, 1i, 1l and 1o**
- 5. Preparation of 2-vinyldoles 2**
- 6. General procedure for the asymmetric Diels-Alder reaction**
- 7. References**
- 8. HPLC spectra**
- 9. ^1H and ^{13}C NMR spectra**

1. General information

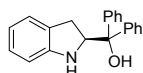
All reactions were carried out under an atmosphere of nitrogen in flame dried glassware with magnetic stirring. The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200-300 mesh).

^1H NMR spectra were recorded on a Bruker Advance III spectrometer (400 MHz). Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). ^{13}C NMR spectra were recorded on Bruker spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference (CDCl_3 , $\delta = 77.0$ ppm). HPLC analyses were conducted on an Agilent 1200 instrument using Daicel columns (0.46 cm diameter $\times$ 25 cm length). Optical rotations were recorded on a Perkin Elmer polarimeter (Model 341). MS spectra were recorded on an ESI-ion trap Mass spectrometer (Shimadzu LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Preparation of ligands

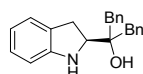
The ligands were prepared following the literature methods.

(S)-Indolin-2-ylidiphenylmethanol (L1)¹



$[\alpha]_D^{20} = -105.0$ ($c = 1.0$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ : 7.62 (d, $J = 7.4$ Hz, 2H), 7.53 (d, $J = 7.4$ Hz, 2H), 7.40-7.15 (m, 6H), 6.99 (t, $J = 7.7$ Hz, 2H), 6.71 (t, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 7.7$ Hz, 1H), 5.12 (t, $J = 9.6$ Hz, 1H), 3.81 (s, 1H), 3.56 (s, 1H), 3.07 (dd, $J = 16.1, 10.5$ Hz, 1H), 2.76 (dd, $J = 16.1, 8.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 150.09, 146.95, 144.08, 129.22, 128.67, 128.21, 127.24, 127.04, 126.77, 125.82, 125.50, 124.75, 119.67, 109.79, 77.18, 66.86, 31.18.

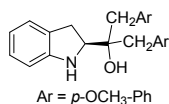
(S)-2-(Indolin-2-yl)-1,3-diphenylpropan-2-ol (L2)



$[\alpha]_D^{20} = -18.4$ ($c = 1.0$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ : 7.33-7.19 (m, 9H), 7.07 (d, $J = 7.3$ Hz, 1H), 6.98 (dd, $J = 14.0, 6.4$ Hz, 2H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 7.7$ Hz, 1H), 3.94 (t,

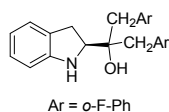
$J = 9.5$ Hz, 1H), 3.57 (s, 1H), 3.21-3.00 (m, 3H), 2.79 (s, 2H), 2.71 (d, $J = 13.8$ Hz, 1H), 2.42 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 150.58, 137.52, 137.16, 130.82, 130.27, 128.48, 128.41, 128.26, 127.30, 126.67, 126.52, 124.52, 119.00, 109.52, 75.31, 65.83, 44.09, 42.21, 31.52.

(S)-2-(Indolin-2-yl)-1,3-bis(4-methoxyphenyl)propan-2-ol (L3)



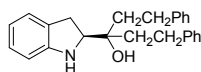
$[\alpha]_D^{20} = -10.5$ ($c = 0.9$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.21 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.84 (dd, $J = 10.9, 8.6$ Hz, 4H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.51 (d, $J = 7.7$ Hz, 1H), 3.91 (t, $J = 9.5$ Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.07 (ddd, $J = 27.5, 18.4, 11.9$ Hz, 3H), 2.72 (s, 2H), 2.63 (d, $J = 14.0$ Hz, 1H), 2.34 (s, 1H), 1.61 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 158.45, 158.33, 150.64, 131.72, 131.17, 129.39, 129.07, 128.48, 127.27, 124.52, 118.93, 113.91, 113.70, 109.47, 75.25, 65.73, 55.27, 55.24, 43.01, 41.08, 31.47.

(S)-1,3-bis(2-Fluorophenyl)-2-(indolin-2-yl)propan-2-ol (L4)



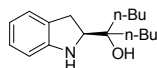
$[\alpha]_D^{20} = +5.6$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.39 (td, $J = 7.6, 1.5$ Hz, 1H), 7.24-7.14 (m, 3H), 7.13-6.92 (m, 6H), 6.70 (t, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 1H), 3.91 (t, $J = 9.3$ Hz, 1H), 3.13 (d, $J = 9.3$ Hz, 2H), 3.02 (dd, $J = 17.5, 14.4$ Hz, 2H), 2.83 (dd, $J = 14.0, 9.9$ Hz, 2H), 2.37 (s, 1H), 1.67 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 161.70 ($^1J_{\text{CF}} = 243.5$ Hz), 161.60 ($^1J_{\text{CF}} = 243.5$ Hz), 150.67, 133.12 (d, $^2J_{\text{CF}} = 20.8$ Hz), 133.08 (d, $^2J_{\text{CF}} = 20.8$ Hz), 128.67, 128.50, 128.42, 128.33, 127.36, 124.61, 124.12, 124.04, 123.98, 119.03, 115.34 (d, $^2J_{\text{CF}} = 23.4$ Hz), 115.27 (d, $^2J_{\text{CF}} = 23.4$ Hz), 109.63, 76.15, 64.95, 35.33, 33.92, 31.43.

(S)-3-(Indolin-2-yl)-1,5-diphenylpentan-3-ol (L5)



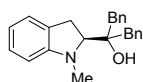
$[\alpha]_D^{20} = -44.8$ ($c = 0.65$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.39-7.29 (m, 4H), 7.29-7.19 (m, 6H), 7.11 (d, $J = 7.3$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.77 (td, $J = 7.4, 0.9$ Hz, 1H), 6.67 (d, $J = 7.7$ Hz, 1H), 4.08 (dd, $J = 10.6, 9.2$ Hz, 1H), 3.84 (s, 1H), 3.19 (dd, $J = 15.5, 10.7$ Hz, 1H), 2.99 (dd, $J = 15.6, 9.1$ Hz, 1H), 2.93-2.61 (m, 4H), 2.46 (s, 1H), 2.11-1.74 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ : 150.33, 142.25, 142.09, 129.25, 128.59, 128.54, 128.31, 128.29, 127.28, 126.05, 126.03, 124.76, 119.70, 110.09, 73.64, 66.17, 39.73, 36.18, 30.27, 30.14, 30.00.

(S)-5-(Indolin-2-yl)nonan-5-ol (L6)



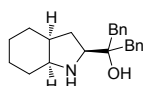
$[\alpha]_D^{20} = -52.9$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.08 (d, $J = 7.3$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.73 (td, $J = 7.4, 0.7$ Hz, 1H), 6.66 (d, $J = 7.7$ Hz, 1H), 3.95 (dd, $J = 10.8, 9.0$ Hz, 1H), 3.10 (dd, $J = 15.6, 10.9$ Hz, 1H), 2.90 (dd, $J = 15.6, 9.0$ Hz, 1H), 2.24 (s, 1H), 1.62-1.14 (m, 12H), 0.94 (td, $J = 7.1, 4.6$ Hz, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ : 150.53, 129.51, 127.13, 124.70, 119.42, 109.88, 73.62, 66.43, 37.46, 34.04, 30.12, 25.82, 25.55, 23.43, 14.11, 14.03.

(S)-2-(1-Methylindolin-2-yl)-1,3-diphenylpropan-2-ol (L7)



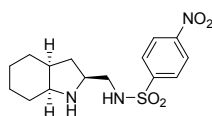
$[\alpha]_D^{20} = -2.6$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.33-7.14 (m, 9H), 7.06 (dd, $J = 16.2, 7.7$ Hz, 2H), 6.95 (dd, $J = 18.3, 6.6$ Hz, 1H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 3.41 (dd, $J = 10.2, 8.3$ Hz, 1H), 3.29 (dd, $J = 16.1, 10.3$ Hz, 1H), 3.16 (d, $J = 13.7$ Hz, 1H), 2.96 (dd, $J = 16.1, 8.1$ Hz, 1H), 2.90 (s, 3H), 2.82 (d, $J = 14.2$ Hz, 1H), 2.73 (dd, $J = 14.0, 7.5$ Hz, 2H), 1.66 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 154.32, 136.99, 136.72, 131.09, 130.43, 128.25, 128.23, 127.88, 127.60, 126.56, 126.48, 123.92, 117.59, 107.83, 77.76, 71.67, 43.63, 40.53, 38.64, 32.19.

2-((2S)-octahydro-1H-indol-2-yl)-1,3-diphenylpropan-2-ol (L8)



$[\alpha]_D^{20} = -1.3$ ($c = 0.62$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.09 (m, 10H), 3.82-3.54 (m, 1H), 3.24 (t, $J = 8.3$ Hz, 1H), 3.05-2.91 (m, 2H), 2.64 (t, $J = 10.7$ Hz, 3H), 2.03-1.88 (m, 2H), 1.78-1.10 (m, 10H). ^{13}C NMR (101 MHz, CDCl_3) δ : 138.69, 138.30, 130.75, 130.28, 128.55, 128.11, 128.02, 126.11, 73.99, 63.61, 55.95, 45.33, 43.10, 37.61, 31.06, 31.00, 27.91, 22.92, 22.82.

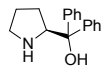
4-Nitro-N-(((2S)-octahydro-1H-indol-2-yl)methyl)benzenesulfonamide (L9)²



$[\alpha]_D^{20} = +7.0$ ($c = 1.3$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ : 8.36 (d, $J = 8.8$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 3.60-3.32 (m, 3H), 3.18-3.07 (m, 2H), 2.92 (dd, $J = 12.4, 7.4$ Hz, 1H), 2.04 (dt, $J = 13.0, 6.5$ Hz, 1H), 1.99-1.87 (m, 1H), 1.66-1.36 (m, 6H), 1.35-1.16 (m, 3H). ^{13}C NMR (101 MHz,

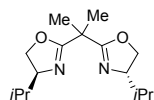
CDCl₃) δ : 149.91, 146.42, 128.22, 124.30, 57.41, 56.57, 48.43, 38.17, 33.57, 29.65, 27.98, 23.10, 22.24.

(S)-diPhenyl(pyrrolidin-2-yl)methanol (L10)³



$[\alpha]_D^{20} = -68.6$ ($c = 1.0$, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.66-7.35 (m, 4H), 7.32-6.92 (m, 6H), 4.56 (s, 1H), 4.25 (t, $J = 7.6$ Hz, 1H), 3.09-2.68 (m, 2H), 1.80-1.41 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ : 148.17, 145.41, 128.22, 127.96, 126.45, 126.34, 125.86, 125.53, 77.11, 64.49, 46.76, 26.28, 25.51.

(4S,4'S)-2,2'-(Propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (L11)⁴

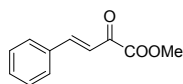


$[\alpha]_D^{20} = -82.3$ ($c = 0.8$, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ : 4.24-4.16 (m, 2H), 4.03-3.94 (m, 4H), 1.84-1.75 (m, 2H), 1.52 (s, 6H), 0.92 (d, $J = 6.8$ Hz, 6H), 0.86 (d, $J = 6.8$ Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ : 168.81, 71.52, 69.94, 38.59, 32.20, 24.45, 18.52, 17.36.

3. Synthesis of β,γ -unsaturated α -ketoesters **1a-f**, **1h**, **1j-k**, **1m-1n** and **1p**.

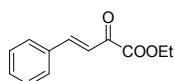
The β,γ -unsaturated α -ketoesters **1a-1f**, **1h**, **1j-k**, **1m-n** and **1p** were prepared following the literature methods.⁵

(E)-Methyl 2-oxo-4-phenylbut-3-enoate (1a)



¹H NMR (400 MHz, CDCl₃) δ : 7.89 (d, $J = 16.1$ Hz, 1H), 7.64 (dd, $J = 7.4, 1.1$ Hz, 2H), 7.49-7.33 (m, 4H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 182.43, 162.56, 148.66, 133.99, 131.70, 129.10, 129.07, 120.48, 53.03.

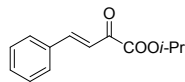
(E)-Ethyl 2-oxo-4-phenylbut-3-enoate (1b)



¹H NMR (400 MHz, CDCl₃) δ : 7.85 (d, $J = 16.1$ Hz, 1H), 7.68-7.57 (m, 2H), 7.45-7.31 (m, 4H),

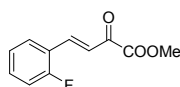
4.38 (q, $J = 7.1$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.92, 162.22, 148.47, 134.01, 131.63, 129.08, 129.03, 120.58, 62.50, 14.05.

(E)-isoPropyl 2-oxo-4-phenylbut-3-enoate (1c)



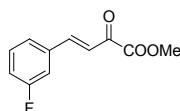
^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 16.1$ Hz, 1H), 7.62 (d, $J = 5.9$ Hz, 2H), 7.49-7.37 (m, 3H), 7.33 (d, $J = 16.1$ Hz, 1H), 5.23 (dt, $J = 16.3, 6.2$ Hz, 1H), 1.39 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ : 183.32, 161.92, 148.21, 134.11, 131.53, 129.06, 128.97, 120.79, 70.65, 21.64.

(E)-Methyl 4-(2-fluorophenyl)-2-oxobut-3-enoate (1d)



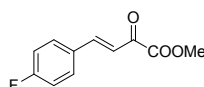
^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, $J = 16.3$ Hz, 1H), 7.65 (td, $J = 7.7, 1.6$ Hz, 1H), 7.49-7.39 (m, 2H), 7.24-7.17 (m, 1H), 7.14 (m, $J = 10.5, 8.3, 1.0$ Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.48, 162.40, 161.97 (d, $J = 256.2$ Hz), 140.91 (d, $J = 3.1$ Hz), 133.15 (d, $J = 8.9$ Hz), 129.55 (d, $J = 2.4$ Hz), 124.65 (d, $J = 3.7$ Hz), 122.64 (d, $J = 6.6$ Hz), 122.21 (d, $J = 11.3$ Hz), 116.42 (d, $J = 21.8$ Hz), 53.04.

(E)-Methyl 4-(3-fluorophenyl)-2-oxobut-3-enoate (1e)



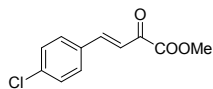
^1H NMR (400 MHz, CDCl_3) δ : 7.83 (d, $J = 16.1$ Hz, 1H), 7.43-7.30 (m, 4H), 7.19-7.12 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.14, 163.01 (d, $J = 247.7$ Hz), 162.27, 146.92 (d, $J = 2.7$ Hz), 136.18 (d, $J = 7.6$ Hz), 130.67 (d, $J = 8.2$ Hz), 125.09 (d, $J = 2.8$ Hz), 121.61, 118.50 (d, $J = 21.5$ Hz), 115.04 (d, $J = 22.0$ Hz), 53.09.

(E)-Methyl 4-(4-fluorophenyl)-2-oxobut-3-enoate (1f)



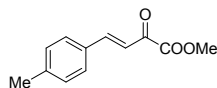
^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 16.1$ Hz, 1H), 7.64 (dd, $J = 8.6, 5.5$ Hz, 2H), 7.31 (d, $J = 16.1$ Hz, 1H), 7.12 (t, $J = 8.6$ Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.15, 164.74 (d, $J = 253.9$ Hz), 162.47, 147.18, 131.11 (d, $J = 8.8$ Hz), 130.31 (d, $J = 3.4$ Hz), 120.17, 116.38 (d, $J = 22.1$ Hz), 53.04.

(E)-Methyl 4-(4-chlorophenyl)-2-oxobut-3-enoate (1h)



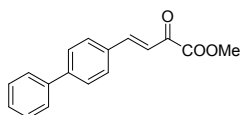
^1H NMR (400 MHz, CDCl_3) δ : 7.83 (d, $J = 16.1$ Hz, 1H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 16.1$ Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.13, 162.39, 146.96, 137.75, 132.49, 130.15, 129.44, 120.87, 53.06.

(E)-Methyl 2-oxo-4-(p-tolyl)but-3-enoate (1j)



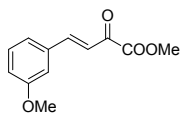
^1H NMR (400 MHz, CDCl_3) δ : 7.86 (d, $J = 16.1$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 16.1$ Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 2H), 3.93 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.45, 162.70, 148.76, 142.56, 131.33, 129.86, 129.14, 119.51, 52.95, 21.63.

(E)-Methyl 4-([1,1'-biphenyl]-4-yl)-2-oxobut-3-enoate (1k)



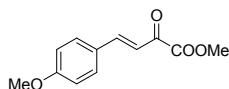
^1H NMR (400 MHz, CDCl_3) δ : 7.92 (d, $J = 16.1$ Hz, 1H), 7.73-7.59 (m, 6H), 7.42 (m, $J = 13.5$, 10.5, 5.7 Hz, 4H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.32, 162.62, 148.17, 144.48, 139.84, 132.94, 129.63, 128.97, 128.16, 127.71, 127.09, 120.26, 53.02.

(E)-Methyl 4-(3-methoxyphenyl)-2-oxobut-3-enoate (1m)



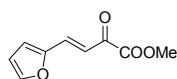
^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 16.1$ Hz, 1H), 7.33 (dd, $J = 12.0$, 4.0 Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.14 (s, 1H), 7.07-6.94 (m, 1H), 3.94 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.41, 162.56, 160.04, 148.54, 135.34, 130.06, 121.85, 120.77, 117.77, 113.57, 55.36, 52.96.

(E)-Methyl 4-(4-methoxyphenyl)-2-oxobut-3-enoate (1n)



^1H NMR (400 MHz, CDCl_3) δ : 7.86 (d, $J = 16.0$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.26 (d, $J = 16.0$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 2H), 3.94 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.26, 162.88, 162.69, 148.52, 131.09, 126.83, 118.16, 114.63, 55.47, 52.91.

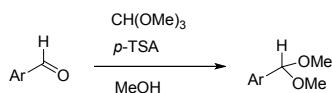
(E)-Methyl 4-(furan-2-yl)-2-oxobut-3-enoate (1p)



^1H NMR (400 MHz, CDCl_3) δ : 7.63 (d, J = 15.8 Hz, 1H), 7.60-7.56 (m, 1H), 7.26-7.19 (m, 1H), 6.83 (d, J = 3.5 Hz, 1H), 6.55 (dd, J = 3.4, 1.7 Hz, 1H), 3.92 (d, J = 0.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 181.96, 162.41, 151.06, 146.37, 133.67, 118.60, 118.04, 113.17, 52.94.

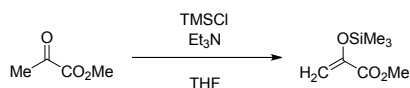
4. Synthesis of β,γ -unsaturated α -ketoesters 1g, 1i, 1l and 1o.

a) Preparation of aryl acetal derivatives^{5a}



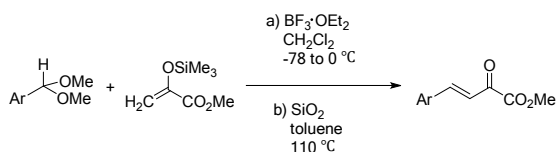
A solution of aldehyde (50 mmol), *p*-toluenesulfonic acid monohydrate (2.5 mmol) and trimethyl orthoformate (0.5 mol) in dry methanol (100 mL) was heated to reflux for 24 h. Part of the solvent was evaporated *in vacuo*, then Et_2O (125 mL) was added to the residue (*ca.* 25 mL), and the mixture was washed with saturated NaHCO_3 solution (125 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography.

b) Preparation of methyl 2-((trimethylsilyl)oxy)acrylate⁶



TEA (18.8 mL, 13.66 g, 135 mmol) was added dropwise to a mixture of methyl pyruvate (10.21 g, 100 mmol) and TMSCl (14.2 mL, 12.17 g, 112 mmol) in THF (100 mL) under N_2 . After 3.5 h, pentane (150 mL) was added, and the reaction mixture was filtered. The filtrate was washed with water (50 mL) and brine (50 mL) in turn, dried over Na_2SO_4 and evaporated to give methyl 2-((trimethylsilyl)oxy)acrylate as a clear liquid (14.8 g, 85% yield), which was used without further purification.

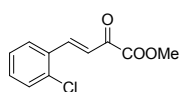
c) Preparation of methyl 2-oxo-4-arylbut-3-enoate^{5a,7}



To a mixture of acetal (20 mmol) and methyl 2-((trimethylsilyl)oxy)acrylate (24 mmol) in dry dichloromethane (100 mL) was added boron trifluoridediethyl ether (22 mmol) dropwise under N_2

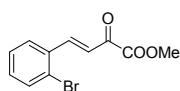
at -78 °C. The reaction mixture was warmed to 0 °C and stirred at the same temperature for 2 h. Saturated NaHCO₃ was added, the mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to afford crude γ -alkoxy- α -oxo ester, which was dissolved in toluene (100 mL). Then silica gel (30 g) was added and the mixture was heated at 110 °C with vigorous stirring for 12 h. After being cooled to room temperature, the mixture was filtered and the residue was washed with DCM for several times. The filtrate was combined, concentrated to give the crude β,γ -unsaturated α -ketoester. The purification was carried out by flash column chromatography with petroleum ether/ethyl acetate to afford yellow oil or solid.

(E)-Methyl 4-(2-chlorophenyl)-2-oxobut-3-enoate (1g)



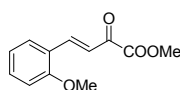
¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, J = 16.2 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.50-7.28 (m, 4H), 3.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 182.25, 162.37, 144.05, 136.19, 132.26, 130.44, 127.97, 127.21, 122.73, 99.99, 53.05.

(E)-Methyl 4-(2-bromophenyl)-2-oxobut-3-enoate (1i)



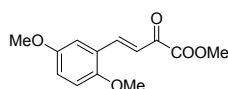
¹H NMR (400 MHz, CDCl₃) δ : 8.28 (d, J = 16.1 Hz, 1H), 7.75 (dd, J = 7.8, 1.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.34-7.31 (m, 1H), 7.31-7.28 (m, 1H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 182.19, 162.36, 146.70, 133.74, 132.38, 129.39, 128.10, 127.84, 126.65, 122.96, 53.08.

(E)-Methyl 4-(2-methoxyphenyl)-2-oxobut-3-enoate (1l)



¹H NMR (400 MHz, CDCl₃) δ : 8.21 (d, J = 16.2 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.49-7.35 (m, 2H), 7.05-6.90 (m, 2H), 3.93 (s, 3H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 183.05, 162.95, 159.29, 144.15, 133.11, 129.53, 123.02, 120.92, 120.84, 111.35, 55.57, 52.87.

(E)-Methyl 4-(2,5-dimethoxyphenyl)-2-oxobut-3-enoate (1o)



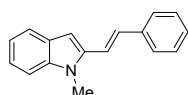
¹H NMR (400 MHz, CDCl₃) δ : 8.21 (d, J = 16.2 Hz, 1H), 7.40 (d, J = 16.2 Hz, 1H), 7.15 (d, J =

3.0 Hz, 1H), 7.01 (dd, $J = 9.0, 3.0$ Hz, 1H), 6.89 (d, $J = 9.0$ Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 182.89, 162.90, 153.89, 153.53, 143.84, 123.42, 120.96, 119.30, 113.22, 112.62, 56.09, 55.84, 52.89.

5. Preparation of 2-vinylindoles 2

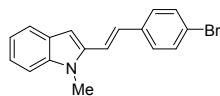
The 2-vinylindoles were prepared following the literature methods.⁸

(*E*)-1-Methyl-2-styryl-1*H*-indole (2a)



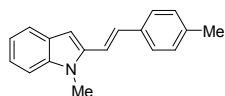
^1H NMR (400 MHz, CDCl_3) δ : 7.59 (d, $J = 7.9$ Hz, 1H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.33-7.27 (m, 2H), 7.21 (d, $J = 7.0$ Hz, 1H), 7.18 (s, 2H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.81 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 138.42, 138.18, 137.18, 130.93, 128.78, 128.00, 127.85, 126.45, 121.78, 120.43, 119.91, 117.09, 109.14, 99.08, 29.92.

(*E*)-2-(4-Bromostyryl)-1-methyl-1*H*-indole (2b)



^1H NMR (400 MHz, CDCl_3) δ : 7.59 (d, $J = 7.9$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 1H), 7.20 (dd, $J = 15.0, 7.1$ Hz, 1H), 7.15-7.05 (m, 3H), 6.80 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 138.25, 137.98, 136.13, 131.87, 129.44, 127.93, 127.86, 121.99, 121.51, 120.51, 120.00, 117.75, 109.17, 99.44, 29.92.

(*E*)-1-Methyl-2-(4-methylstyryl)-1*H*-indole (2c)



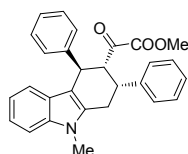
^1H NMR (400 MHz, CDCl_3) δ : 7.57 (d, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.26-7.04 (m, 7H), 6.76 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 138.67, 138.14, 137.85, 134.44, 130.97, 129.52, 128.08, 126.40, 121.65, 120.37, 119.87, 116.10, 109.12, 98.78, 29.90, 21.32.

6. General procedure for the asymmetric Diels–Alder reaction

To a 10 mL tube was added chiral ligand **L2** (3.3 mg, 0.01 mmol), enone **1** (0.12 mmol), $\text{Cu}(\text{OTf})_2$ (3.6 mg, 0.01 mmol) and 1.5 mL DCM (containing 0.1 mmol H_2O) under N_2 . The solution was

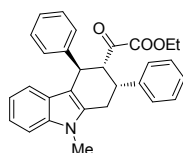
stirred at 30 °C for 30 min, then 2-vinylindole **2** (0.8 mmol) was added. After completion of the reaction (about 10 min), the mixture was quenched with saturated NaHCO₃ solution (1 mL) and extracted with DCM (3 × 3 mL). The DCM layer was combined, dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure to give the crude product, which was purified by column chromatography on silica gel to provide pure **3**.

Methyl 2-((2*R*,2*R*,4*R*)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3a**)**



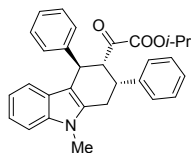
Yield: 90%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 21.34 min, t_{minor} = 26.97 min, 95% ee. $[\alpha]_D^{25}$ = -42.6 (c = 0.76, CH₂Cl₂). mp 150-153 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.34-7.18 (m, 9H), 7.18-7.12 (m, 1H), 7.10 (dd, J = 7.8, 1.4 Hz, 2H), 6.95-6.86 (m, 2H), 4.63 (d, J = 4.1 Hz, 1H), 4.17 (dd, J = 4.1, 3.0 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.67-3.56 (m, 2H), 3.25 (q, J = 9.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.35, 161.47, 143.56, 141.37, 137.68, 136.17, 128.67, 128.52, 128.43, 128.02, 127.04, 126.68, 126.58, 121.02, 118.96, 118.83, 108.67, 107.78, 56.22, 52.92, 39.11, 38.07, 29.33, 25.60. HRMS (ESI) m/z calcd. for C₂₈H₂₆NO₃ [M+H]⁺: 424.1907, found: 424.1905.

Ethyl 2-((2*R*,3*R*,4*R*)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3b**)**



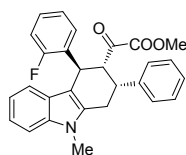
Yield: 89%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 25.88 min, t_{minor} = 37.77 min, 53% ee. $[\alpha]_D^{25}$ = -32.5 (c = 0.67, CH₂Cl₂). mp 172-176 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.36-7.06 (m, 12H), 6.92 (dt, J = 14.5, 7.3 Hz, 2H), 4.64 (d, J = 3.6 Hz, 1H), 4.31-4.07 (m, 3H), 3.73 (s, 3H), 3.68-3.57 (m, 2H), 3.32-3.07 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.77, 161.17, 143.65, 141.51, 137.70, 136.29, 128.82, 128.64, 128.49, 128.41, 128.02, 126.98, 126.64, 121.00, 118.95, 118.78, 108.65, 107.71, 62.43, 56.11, 39.20, 37.98, 29.30, 25.53, 13.90. HRMS (ESI) m/z calcd. for C₂₉H₂₈NO₃ [M+H]⁺: 438.2064, found: 438.2066.

***iso*Propyl 2-((2*R*,3*R*,4*R*)-9-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (**3c**)**



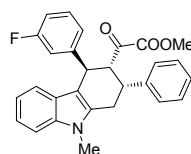
Yield: 95%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 12.86 min, t_{minor} = 18.88 min, 34% ee. $[\alpha]_D^{25}$ = -21.5 (c = 0.86, CH₂Cl₂). mp 115-118 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.39-7.20 (m, 9H), 7.20-7.14 (m, 3H), 7.03-6.92 (m, 2H), 5.15-5.04 (m, 1H), 4.69 (d, J = 3.6 Hz, 1H), 4.21 (t, J = 3.0 Hz, 1H), 3.77 (s, 3H), 3.71 (t, J = 8.0 Hz, 1H), 3.68-3.64 (m, 1H), 3.26 (dd, J = 14.8, 4.5 Hz, 1H), 1.31 (dd, J = 10.6, 6.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ : 194.13, 160.85, 143.73, 141.62, 137.70, 136.39, 128.65, 128.52, 128.43, 128.05, 126.98, 126.66, 121.01, 118.97, 118.76, 108.69, 107.70, 70.77, 56.01, 39.26, 37.97, 29.33, 25.53, 21.56. HRMS (ESI) m/z calcd. for C₃₀H₃₀NO₃ [M+H]⁺: 452.2220, found: 452.2224.

Methyl 2-((2R,3R,4S)-4-(2-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3d)



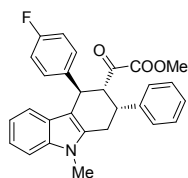
Yield: 96%, pale yellow solid. HPLC: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 22.68 min, t_{minor} = 26.33 min, 93% ee. $[\alpha]_D^{25}$ = -23.9 (c = 0.82, CH₂Cl₂). mp 198-201 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.30 (d, J = 8.2 Hz, 1H), 7.28-7.05 (m, 8H), 7.02-6.86 (m, 4H), 4.88 (d, J = 3.6 Hz, 1H), 4.23 (dd, J = 20.4, 16.7 Hz, 1H), 3.74 (d, J = 13.2 Hz, 3H), 3.68 (s, 3H), 3.67-3.61 (m, 1H), 3.52 (dd, J = 16.0, 9.1 Hz, 1H), 3.23 (dt, J = 22.1, 11.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 194.27, 161.84, 160.72 ($^1J_{CF}$ = 247.2 Hz), 140.97, 137.69, 136.28, 130.97, 130.13 (d, $^2J_{CF}$ = 13.7 Hz), 128.58, 128.53, 127.87, 127.17, 126.26, 123.99, 121.12, 119.06, 118.44, 115.6 (d, $^2J_{CF}$ = 21.9 Hz), 108.76, 106.82, 53.83, 52.77, 38.45, 33.03, 29.34, 25.33. HRMS (ESI) m/z calcd. for C₂₈H₂₅FNO₃ [M+H]⁺: 442.1813, found: 442.1814.

Methyl 2-((2R,3R,4R)-4-(3-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3e)



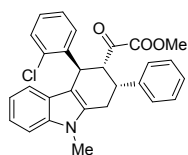
Yield: 94%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 96/4, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 23.38 min, t_{minor} = 27.66 min, 50% ee. $[\alpha]_D^{25}$ = -36.3 (c = 0.81, CH₂Cl₂). mp 140-145 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.31 (d, J = 7.8 Hz, 1H), 7.24-7.07 (m, 8H), 6.99 (d, J = 10.1 Hz, 1H), 6.96-6.88 (m, 3H), 4.62 (d, J = 4.1 Hz, 1H), 4.18-4.10 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.65-3.56 (m, 2H), 3.26 (q, J = 10.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.04, 163.01 (d, J = 245.6 Hz), 161.36, 146.44 (d, J = 6.6 Hz), 141.10, 137.72, 136.23, 129.89 (d, J = 8.3 Hz), 128.60, 128.01, 127.18, 126.40, 124.41, 121.18, 119.14, 118.70, 115.65 (d, J = 21.7 Hz), 113.73 (d, J = 21.2 Hz), 108.81, 107.29, 56.10, 53.01, 38.89, 38.20, 29.36, 25.62. HRMS (ESI) m/z calcd. for C₂₈H₂₅FNO₃ [M+H]⁺: 442.1813, found: 442.1818.

Methyl 2-((2*R*,3*R*,4*R*)-4-(4-fluorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3f)



Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 94/6, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 18.88 min, t_{minor} = 22.82 min, 52% ee. $[\alpha]_D^{25}$ = -38.1 (c = 0.70, CH₂Cl₂). mp 179-183 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.34 (d, J = 8.2 Hz, 1H), 7.31-7.15 (m, 6H), 7.11 (dd, J = 7.7, 1.6 Hz, 2H), 7.02-6.87 (m, 4H), 4.62 (d, J = 4.6 Hz, 1H), 4.14 (dd, J = 4.6, 3.1 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.69-3.56 (m, 2H), 3.29 (dd, J = 15.1, 4.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.15, 161.71 ($^1J_{CF}$ = 246.5 Hz), 161.40, 141.13, 139.18, 137.69, 136.06, 130.24, 128.56, 127.99, 127.14, 126.38, 121.12, 119.05, 118.77, 108.75, 107.83, 56.38, 52.98, 38.31, 38.21, 29.33, 25.74. HRMS (ESI) m/z calcd. for C₂₈H₂₅FNO₃ [M+H]⁺: 442.1813, found: 442.1818.

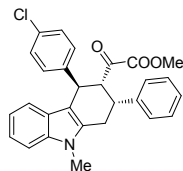
Methyl 2-((2*R*,3*R*,4*S*)-4-(2-chlorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3g)



Yield: 91%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 220 nm), t_{major} = 13.05 min, t_{minor} = 33.68 min, 67% ee. $[\alpha]_D^{25}$ = -12.8 (c = 0.74, CH₂Cl₂). mp 180-184 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.46 (d, J = 7.6 Hz, 1H), 7.35-7.11 (m, 8H), 7.07 (t, J = 7.3 Hz, 1H), 7.02-6.89 (m, 3H), 5.00 (s, 1H), 4.15 (s, 1H), 3.75 (s, 3H), 3.55 (s, 4H), 3.42 (dd, J = 16.0, 10.6 Hz, 1H), 3.19 (d, J = 12.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ :

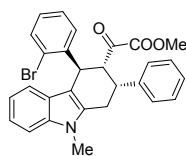
195.42, 162.22, 140.78, 140.57, 137.76, 136.48, 133.70, 130.67, 129.93, 128.57, 128.20, 127.77, 127.23, 126.77, 126.23, 121.18, 119.09, 118.57, 108.76, 107.19, 53.29, 52.58, 38.45, 36.64, 29.34, 24.53. HRMS (ESI) m/z calcd. for $C_{28}H_{25}ClNO_3$ $[M+H]^+$: 458.1517, found: 458.1518.

Methyl 2-((2*R*,3*R*,4*R*)-4-(4-chlorophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3h)



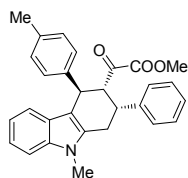
Yield: 84%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 28.32 min, t_{minor} = 31.49 min, 56% ee. $[\alpha]_D^{25}$ = -41.7 (c = 0.70, CH_2Cl_2). mp 170-176 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.31 (d, J = 8.2 Hz, 1H), 7.26-7.21 (m, 6H), 7.17 (ddd, J = 9.5, 8.5, 3.8 Hz, 2H), 7.08 (dd, J = 7.7, 1.6 Hz, 2H), 6.91 (ddd, J = 16.3, 11.7, 4.2 Hz, 2H), 4.58 (d, J = 4.6 Hz, 1H), 4.11 (dd, J = 4.6, 3.1 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.60 (dd, J = 20.7, 7.2 Hz, 2H), 3.27 (dd, J = 14.3, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ : 193.05, 161.36, 142.11, 141.04, 137.70, 136.13, 132.46, 130.13, 128.59, 128.00, 127.19, 126.34, 121.18, 119.12, 118.76, 108.79, 107.51, 56.24, 53.02, 38.48, 38.26, 29.36, 25.73. HRMS (ESI) m/z calcd. for $C_{28}H_{25}ClNO_3$ $[M+H]^+$: 458.1517, found: 458.1518.

Methyl 2-((2*R*,3*R*,4*S*)-4-(2-bromophenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3i)



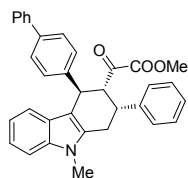
Yield: 80%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 220 nm), t_{major} = 15.00 min, t_{minor} = 32.64 min, 71% ee. $[\alpha]_D^{25}$ = -8.2 (c = 0.80, CH_2Cl_2). mp 143-147 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.71-7.62 (m, 1H), 7.35-7.19 (m, 4H), 7.14 (ddd, J = 16.7, 7.2, 2.6 Hz, 5H), 6.95 (dt, J = 14.5, 7.3 Hz, 3H), 4.97 (s, 1H), 4.13 (s, 1H), 3.74 (s, 3H), 3.63-3.54 (m, 1H), 3.49 (s, 3H), 3.36 (dd, J = 15.8, 11.4 Hz, 1H), 3.17 (dd, J = 16.0, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ : 195.64, 162.18, 142.31, 140.66, 137.77, 136.43, 133.23, 130.72, 128.58, 128.53, 127.77, 127.42, 127.28, 126.22, 124.53, 121.21, 119.11, 118.69, 108.77, 107.48, 53.64, 52.57, 39.27, 38.47, 29.36, 24.25. HRMS (ESI) m/z calcd. for $C_{28}H_{25}BrNO_3$ $[M+H]^+$: 502.1012, found: 502.1013.

Methyl 2-((2*R*,3*R*,4*R*)-9-methyl-2-phenyl-4-(*p*-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3j)



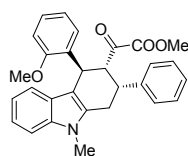
Yield: 77%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 21.14 min, t_{minor} = 30.94 min, 59% ee. $[\alpha]_D^{25}$ = -48.3 (c = 0.77, CH₂Cl₂). mp 140-147 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.30 (d, J = 8.2 Hz, 1H), 7.25-7.05 (m, 10H), 6.92 (dt, J = 14.1, 7.2 Hz, 2H), 4.60 (d, J = 3.8 Hz, 1H), 4.18-4.10 (m, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.66-3.57 (m, 2H), 3.28-3.15 (m, 1H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.48, 161.51, 141.50, 140.54, 137.68, 136.15, 129.15, 128.84, 128.51, 128.05, 127.01, 126.65, 120.99, 118.95, 118.88, 108.66, 107.92, 56.31, 52.91, 38.76, 38.03, 29.33, 25.56, 21.10. HRMS (ESI) m/z calcd. for C₂₉H₂₈NO₃ [M+H]⁺: 438.2064, found: 438.2063.

Methyl 2-((2R,3R,4R)-4-([1,1'-biphenyl]-4-yl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3k)



Yield: 68%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 93/7, flow rate 0.5 mL/min, λ = 210 nm), t_{major} = 41.16 min, t_{minor} = 23.45 min, 57% ee. $[\alpha]_D^{25}$ = -65.0 (c = 0.65, CH₂Cl₂). mp 167-174 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.64-7.58 (m, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.48-7.31 (m, 7H), 7.29-7.20 (m, 2H), 7.16 (dd, J = 9.1, 7.4 Hz, 3H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 (t, J = 7.3 Hz, 1H), 4.70 (d, J = 4.1 Hz, 1H), 4.28-4.20 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.67 (dd, J = 21.0, 7.3 Hz, 2H), 3.30 (dd, J = 14.0, 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.32, 161.45, 142.67, 141.35, 140.88, 139.42, 137.69, 136.18, 129.07, 128.72, 128.53, 128.02, 127.11, 127.06, 126.99, 126.58, 121.06, 119.00, 118.87, 108.70, 107.72, 56.18, 52.94, 38.82, 38.13, 29.34, 25.61. HRMS (ESI) m/z calcd. for C₃₄H₃₀NO₃ [M+H]⁺: 500.2220, found: 500.2220.

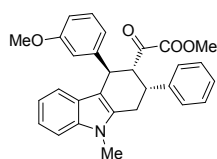
Methyl 2-((2R,3R,4S)-4-(2-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3l)



Yield: 80%, yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min,

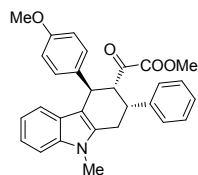
$\lambda = 220$ nm), $t_{\text{major}} = 18.46$ min, $t_{\text{minor}} = 21.14$ min, 87% ee. $[\alpha]_D^{25} = +6.7$ ($c = 0.72$, CH_2Cl_2). mp 167-171 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.31 (d, $J = 8.2$ Hz, 1H), 7.28-7.23 (m, 1H), 7.23-7.11 (m, 6H), 7.04 (d, $J = 7.7$ Hz, 1H), 6.98-6.90 (m, 2H), 6.82 (dd, $J = 7.5, 1.7$ Hz, 1H), 6.74 (td, $J = 7.4, 0.9$ Hz, 1H), 4.92 (s, 1H), 4.12 (dd, $J = 3.3, 1.8$ Hz, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 3.63 (s, 3H), 3.57-3.43 (m, 2H), 3.11 (dd, $J = 15.2, 4.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 196.05, 162.80, 156.68, 141.75, 137.74, 137.00, 131.37, 129.93, 128.46, 127.92, 127.82, 126.89, 126.66, 120.91, 120.25, 118.82, 118.69, 110.30, 108.63, 106.93, 55.31, 52.86, 52.44, 38.30, 33.72, 29.30, 24.80. HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 454.2013, found: 454.2010.

Methyl 2-((2*R*,3*R*,4*R*)-4-(3-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3m)



Yield: 84%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min, $\lambda = 220$ nm), $t_{\text{major}} = 36.73$ min, $t_{\text{minor}} = 27.95$ min, 58% ee. $[\alpha]_D^{25} = -38.3$ ($c = 0.78$, CH_2Cl_2). mp 80-82 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.30 (d, $J = 8.2$ Hz, 1H), 7.20 (ddd, $J = 13.2, 7.9, 4.3$ Hz, 4H), 7.12 (dd, $J = 8.0, 6.6$ Hz, 3H), 7.00-6.86 (m, 4H), 6.77 (dd, $J = 7.9, 2.1$ Hz, 1H), 4.61 (d, $J = 3.9$ Hz, 1H), 4.17 (dd, $J = 4.8, 2.2$ Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.66-3.58 (m, 2H), 3.23 (q, $J = 10.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 193.35, 161.46, 159.68, 145.37, 141.41, 137.70, 136.14, 129.35, 128.50, 128.03, 127.01, 126.63, 121.11, 121.00, 118.97, 118.80, 114.90, 111.68, 108.64, 107.64, 56.09, 55.17, 52.88, 39.20, 38.09, 29.30, 25.52. HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 454.2013, found: 454.2014.

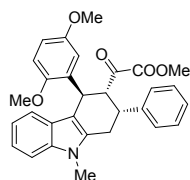
Methyl 2-((2*R*,3*R*,4*R*)-4-(4-methoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3n)



Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 0.4 mL/min, $\lambda = 220$ nm), $t_{\text{major}} = 32.85$ min, $t_{\text{minor}} = 26.14$ min, 78% ee. $[\alpha]_D^{25} = -56.7$ ($c = 0.78$, CH_2Cl_2). mp 188-191 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.31 (d, $J = 8.2$ Hz, 1H), 7.24-7.08 (m, 8H), 6.97-6.88 (m, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 4.58 (d, $J = 4.1$ Hz, 1H), 4.17-4.08 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.64-3.56 (m, 2H), 3.24 (q, $J = 9.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ : 193.47, 161.49, 158.33, 141.46, 137.68, 136.05, 135.62, 129.65, 128.51, 128.04,

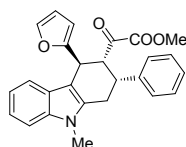
127.02, 126.61, 121.00, 118.95, 118.91, 113.81, 108.66, 108.14, 56.46, 55.21, 52.90, 38.32, 38.10, 29.32, 25.64. HRMS (ESI) m/z calcd. for $C_{29}H_{28}NO_4$ $[M+H]^+$: 454.2013, found: 454.2015.

Methyl 2-((2*R*,3*R*,4*S*)-4-(2,5-dimethoxyphenyl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3o)



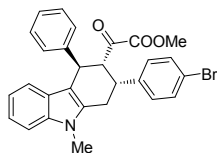
Yield: 84%, yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 20.40 min, t_{minor} = 15.60 min, 91% ee. $[a]_D^{25}$ = +1.2 (c = 0.82, CH_2Cl_2). mp 197-203 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.32-7.23 (m, 2H), 7.23-7.10 (m, 5H), 7.06 (d, J = 7.8 Hz, 1H), 6.96-6.89 (m, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 3.1 Hz, 1H), 6.44 (d, J = 3.1 Hz, 1H), 4.89 (s, 1H), 4.17-4.05 (m, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.59 (s, 3H), 3.53 (d, J = 11.1 Hz, 2H), 3.10 (q, J = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ : 195.88, 162.75, 153.27, 151.09, 141.69, 137.77, 136.87, 133.02, 128.45, 127.81, 126.87, 126.62, 120.86, 118.81, 118.61, 117.63, 110.90, 110.77, 108.59, 106.70, 55.80, 55.55, 52.78, 52.43, 38.17, 33.81, 29.27, 24.80. HRMS (ESI) m/z calcd. for $C_{30}H_{30}NO_5$ $[M+H]^+$: 484.2118, found: 484.2115.

Methyl 2-((2*R*,3*R*,4*S*)-4-(furan-2-yl)-9-methyl-2-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3p)



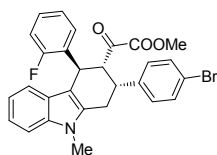
Yield: 86%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 15.03 min, t_{minor} = 13.58 min, 42% ee. $[a]_D^{25}$ = -0.4 (c = 0.71, CH_2Cl_2). mp 140-146 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.39 (dd, J = 1.8, 0.8 Hz, 1H), 7.34-7.10 (m, 8H), 7.06-6.96 (m, 1H), 6.27 (dd, J = 3.1, 1.9 Hz, 1H), 6.07-5.96 (m, 1H), 4.69 (d, J = 4.0 Hz, 1H), 4.45-4.35 (m, 1H), 3.78-3.72 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.57-3.47 (m, 1H), 3.20 (dd, J = 16.3, 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ : 193.62, 161.46, 155.63, 141.84, 141.08, 137.47, 135.62, 128.58, 127.97, 127.18, 126.46, 121.11, 119.18, 118.46, 110.24, 108.79, 108.14, 106.27, 52.89, 52.35, 38.83, 33.48, 29.29, 25.29. HRMS (ESI) m/z calcd. for $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1704.

Methyl 2-((2*R*,3*R*,4*R*)-2-(4-bromophenyl)-9-methyl-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3q)



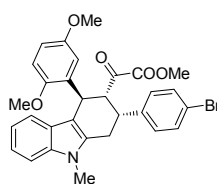
Yield: 82%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 18.48 min, t_{minor} = 34.28 min, 59% ee. $[\alpha]_D^{25}$ = -56.7 (c = 0.82, CH₂Cl₂). mp 171-177 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.41-7.36 (m, 2H), 7.36-7.22 (m, 6H), 7.18 (ddd, J = 8.2, 4.6, 3.6 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 4.2 Hz, 2H), 4.65 (d, J = 4.2 Hz, 1H), 4.16 (dd, J = 4.2, 3.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.67-3.57 (m, 2H), 3.26 (dd, J = 19.3, 9.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.11, 161.36, 143.32, 140.42, 137.70, 135.72, 131.59, 129.83, 128.62, 128.49, 126.79, 126.47, 121.16, 120.94, 119.06, 118.85, 108.72, 107.71, 56.15, 53.02, 39.03, 37.60, 29.36, 25.54. HRMS (ESI) m/z calcd. for C₂₈H₂₅BrNO₃ [M+H]⁺: 502.1012, found: 502.1015.

Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2-fluorophenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3r)



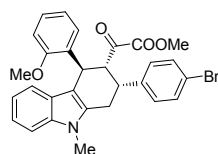
Yield: 79%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 20.00 min, t_{minor} = 24.34 min, 56% ee. $[\alpha]_D^{25}$ = -28.8 (c = 0.82, CH₂Cl₂). mp 203-208 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.2 Hz, 1H), 7.26-7.19 (m, 1H), 7.15 (ddd, J = 8.2, 5.7, 2.5 Hz, 1H), 7.13-7.06 (m, 1H), 7.02-6.89 (m, 6H), 4.86 (d, J = 4.0 Hz, 1H), 4.16 (t, J = 3.7 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.61 (ddd, J = 9.0, 5.7, 3.4 Hz, 1H), 3.56-3.44 (m, 1H), 3.24 (dd, J = 16.2, 5.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 193.90, 161.75, 160.69 (¹ J_{CF} = 247.4 Hz), 140.04, 137.69, 135.80, 131.64, 130.97, 130.93, 129.83 (d, ² J_{CF} = 13.3 Hz), 129.67, 128.72, 128.64, 126.14, 124.04, 124.01, 121.24, 121.04, 119.15, 118.43, 115.63 (d, ² J_{CF} = 20.47 Hz), 108.79, 106.79, 53.67, 52.88, 37.97, 32.96, 29.35, 25.40. HRMS (ESI) m/z calcd. for C₂₈H₂₄BrFNO₃ [M+H]⁺: 520.0918, found: 520.0920.

Methyl 2-((2R,3R,4S)-2-(4-bromophenyl)-4-(2,5-dimethoxyphenyl)-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)-2-oxoacetate (3s)



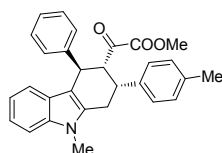
Yield: 82%, yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 18.82 min, t_{minor} = 15.42 min, 68% ee. $[\alpha]_D^{25}$ = +11.0 (*c* = 0.92, CH₂Cl₂). mp 185-187 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.41-7.33 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.18-7.10 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 3H), 6.97-6.90 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.41 (d, *J* = 3.1 Hz, 1H), 4.88 (s, 1H), 4.06 (dd, *J* = 3.1, 2.2 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.59 (s, 3H), 3.56-3.38 (m, 2H), 3.08 (dd, *J* = 15.3, 4.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 195.53, 162.77, 153.27, 151.04, 140.82, 137.76, 136.49, 132.73, 131.51, 129.66, 126.51, 121.00, 120.72, 118.90, 118.58, 117.64, 110.95, 110.81, 108.64, 106.59, 55.80, 55.53, 52.66, 52.56, 37.64, 33.75, 29.29, 24.83. HRMS (ESI) *m/z* calcd. for C₃₀H₂₉BrNO₅ [M+H]⁺: 562.1224, found: 562.1225.

Methyl 2-((2*R*,3*R*,4*S*)-2-(4-bromophenyl)-4-(2-methoxyphenyl)-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3t)



Yield: 69%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 220 nm), t_{major} = 16.46 min, t_{minor} = 30.33 min, 90% ee. $[\alpha]_D^{25}$ = -5.2 (*c* = 0.73, CH₂Cl₂). mp 171-178 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.39 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.24 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.21-7.14 (m, 1H), 7.07 (dd, *J* = 7.6, 5.5 Hz, 3H), 7.00-6.91 (m, 2H), 6.82 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.76 (td, *J* = 7.4, 0.8 Hz, 1H), 4.94 (s, 1H), 4.08 (dt, *J* = 22.1, 11.1 Hz, 1H), 3.93 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.62-3.51 (m, 1H), 3.49-3.38 (m, 1H), 3.12 (dd, *J* = 15.8, 5.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ : 195.67, 162.79, 156.62, 140.88, 137.72, 136.61, 131.51, 131.07, 129.90, 129.66, 128.03, 126.54, 121.03, 120.72, 120.28, 118.90, 118.65, 110.32, 108.65, 106.79, 55.30, 52.70, 52.57, 37.75, 33.65, 29.32, 24.83. HRMS (ESI) *m/z* calcd. for C₂₉H₂₇BrNO₄ [M+H]⁺: 532.1118, found: 532.1118.

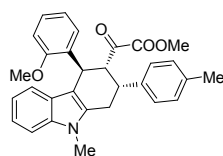
Methyl 2-((2*R*,3*R*,4*R*)-9-methyl-4-phenyl-2-(*p*-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3u)



Yield: 73%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 220 nm), t_{major} = 18.82 min, t_{minor} = 28.65 min, 56% ee. $[\alpha]_D^{25}$ = -59.1 (*c* = 0.64, CH₂Cl₂). mp 176-180 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.33-7.18 (m, 6H), 7.14 (dt, *J* = 8.2, 4.1

Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 2H), 6.98 (d, $J = 8.2$ Hz, 2H), 6.90 (d, $J = 3.9$ Hz, 2H), 4.61 (d, $J = 4.4$ Hz, 1H), 4.15 (dd, $J = 4.4, 3.1$ Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.66-3.51 (m, 2H), 3.24 (dd, $J = 15.2, 4.9$ Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 193.39, 161.46, 143.59, 138.31, 137.66, 136.63, 136.18, 129.19, 128.72, 128.40, 127.88, 126.63, 126.59, 120.96, 118.93, 118.86, 108.64, 107.92, 56.29, 52.89, 39.03, 37.81, 29.31, 25.87, 20.98. HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{28}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 438.2064, found: 438.2063.

Methyl 2-((2*R*,3*R*,4*S*)-4-(2-methoxyphenyl)-9-methyl-2-(*p*-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)-2-oxoacetate (3v)



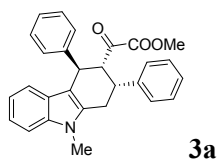
Yield: 91%, pale yellow solid. HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, $\lambda = 220$ nm), $t_{\text{major}} = 15.60$ min, $t_{\text{minor}} = 25.67$ min, 50% ee. $[\alpha]_D^{25} = -2.2$ ($c = 0.85$, CH_2Cl_2). mp 174-178 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.30 (d, $J = 8.2$ Hz, 1H), 7.22-7.18 (m, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.09-7.00 (m, 5H), 6.97-6.88 (m, 2H), 6.82 (dd, $J = 7.5, 1.6$ Hz, 1H), 6.74 (t, $J = 7.3$ Hz, 1H), 4.91 (s, 1H), 4.10 (dt, $J = 15.0, 7.5$ Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.58-3.36 (m, 2H), 3.09 (dd, $J = 15.3, 4.6$ Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 196.11, 162.78, 156.68, 138.70, 137.70, 137.09, 136.42, 131.40, 129.94, 129.11, 127.86, 127.68, 126.67, 120.85, 120.23, 118.78, 118.68, 110.26, 108.59, 106.92, 55.28, 52.88, 52.42, 37.94, 33.69, 29.28, 24.98, 20.97. HRMS (ESI) m/z calcd. for $\text{C}_{30}\text{H}_{30}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 468.2169, found: 468.2167.

7. References

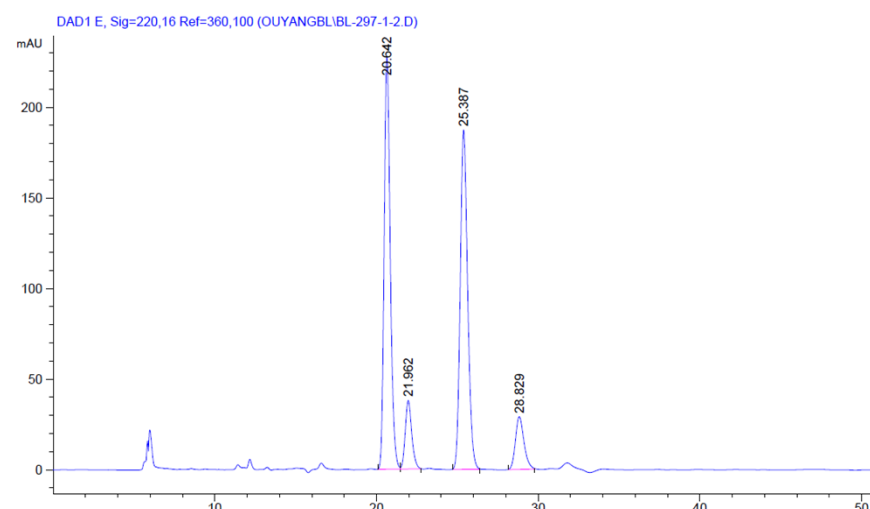
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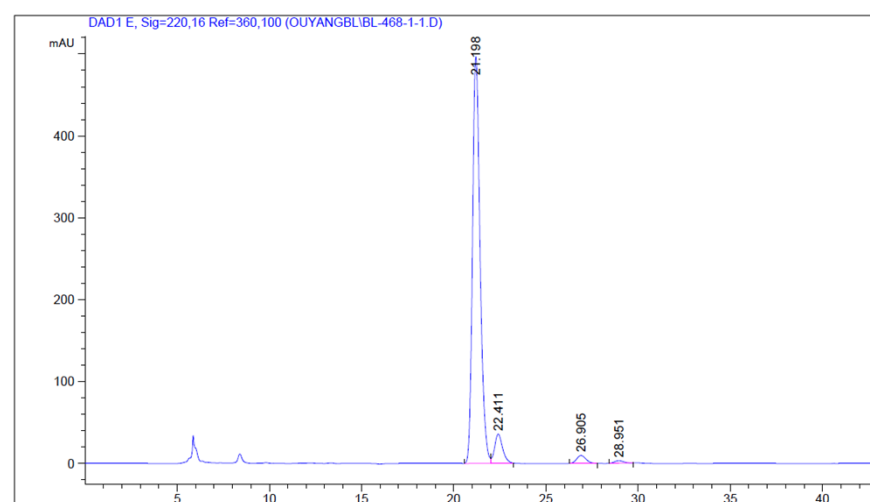
8. HPLC spectra

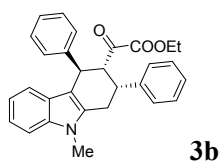


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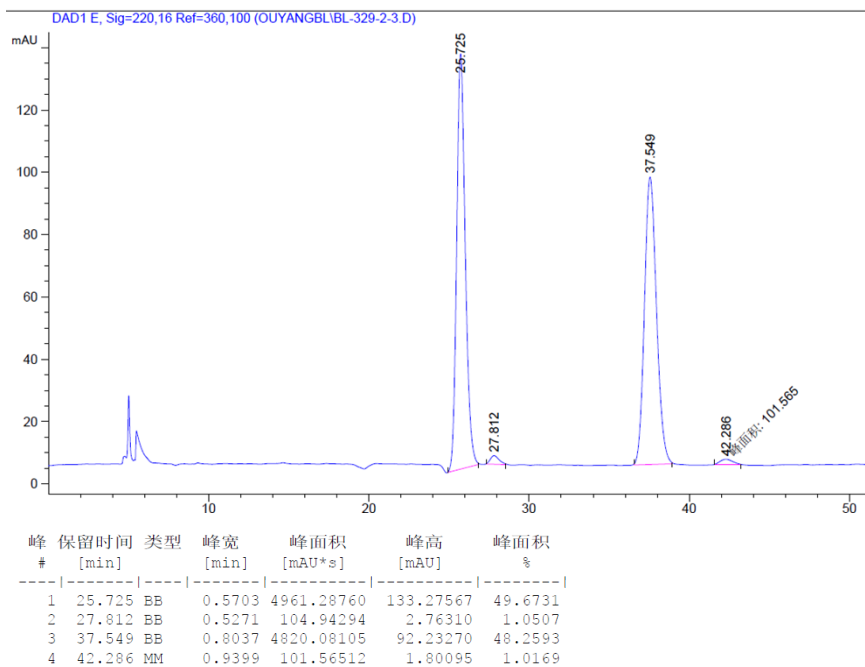


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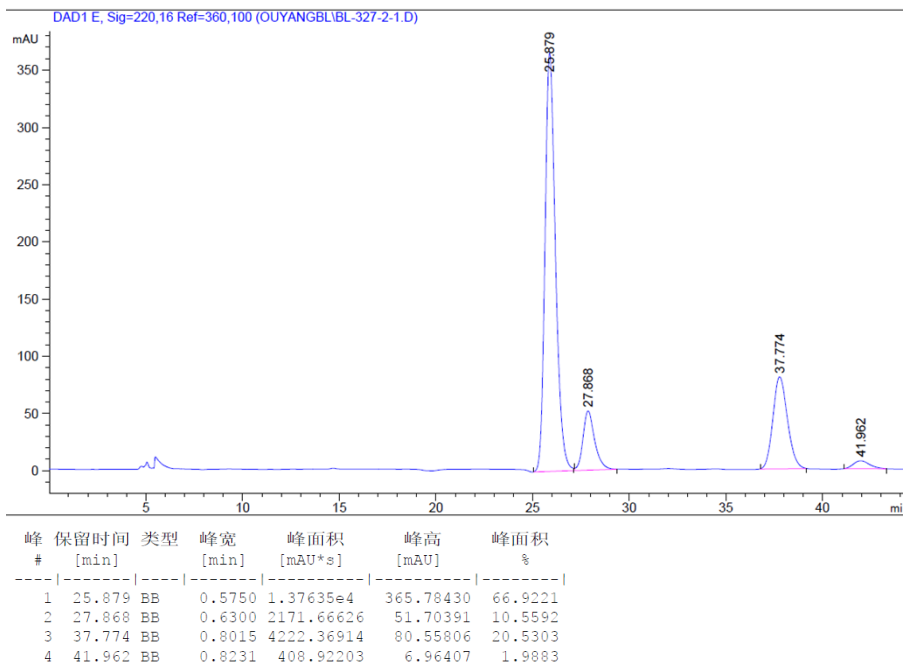


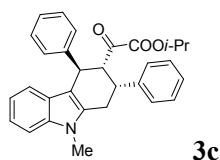


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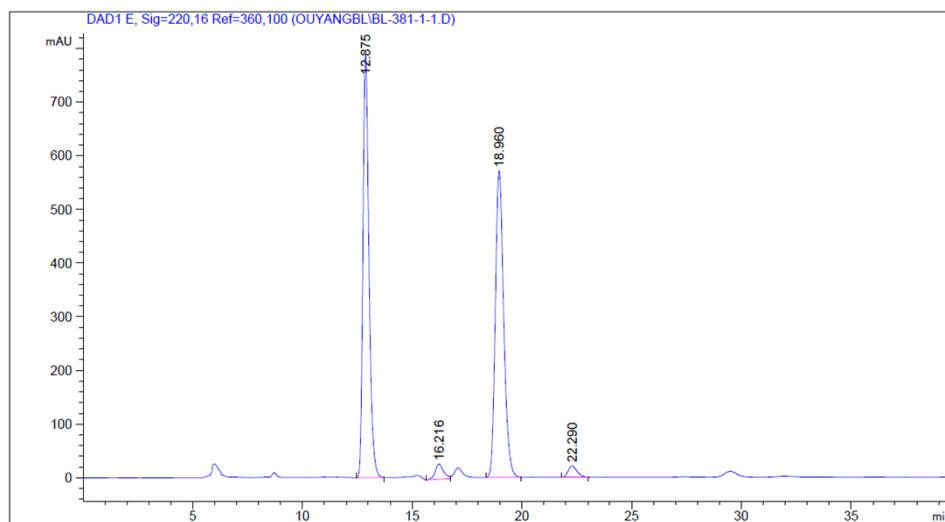
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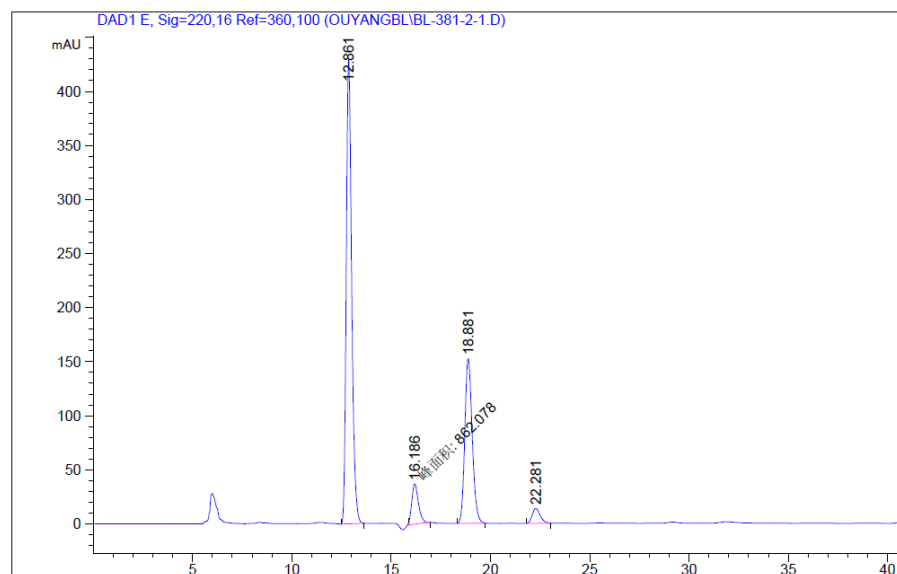
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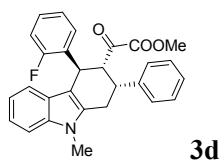


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1	12.875	BB	0.2893	1.49283e4	787.09833	47.6909
2	16.216	VV	0.3952	749.62262	28.28336	2.3948
3	18.960	BB	0.4050	1.50363e4	571.47455	48.0358
4	22.290	BB	0.4241	588.02087	21.16405	1.8785

Optically enriched product

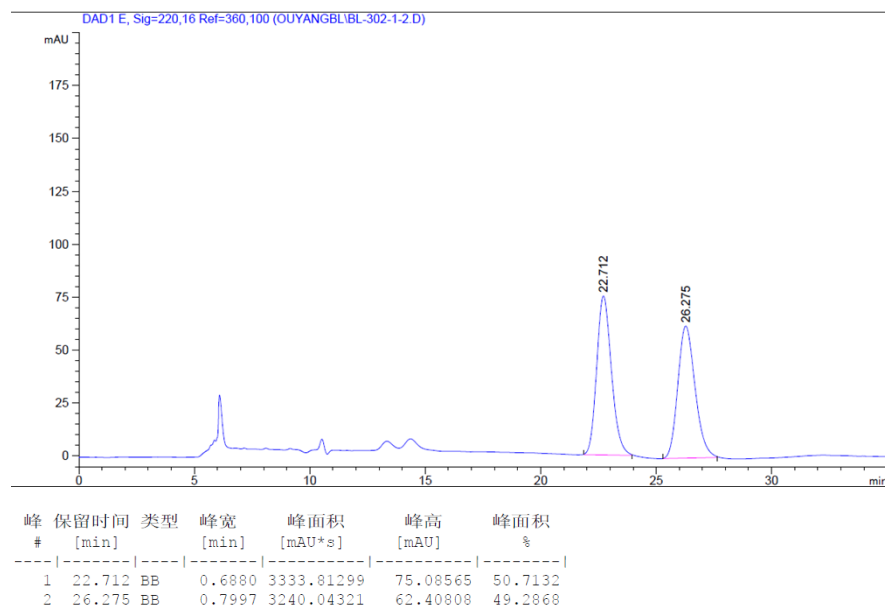


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1	12.861	BB	0.2875	8071.68213	429.10522	60.8407
2	16.186	MM	0.3864	862.07849	37.17944	6.4980
3	18.881	BB	0.3984	3949.57935	152.39470	29.7702
4	22.281	BB	0.4237	383.56976	13.74125	2.8912

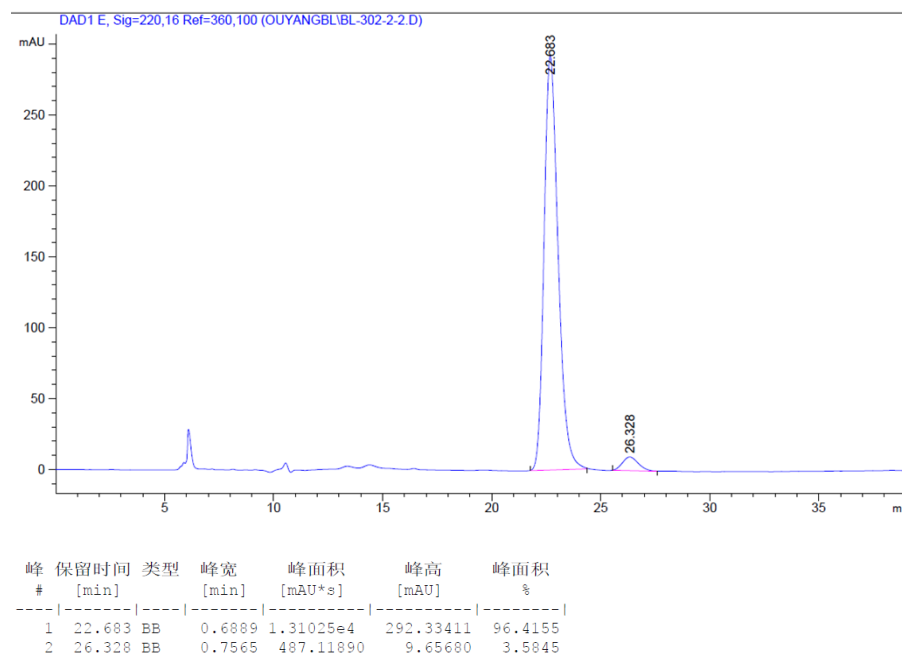


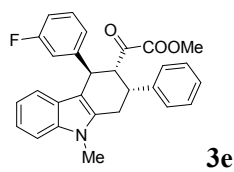
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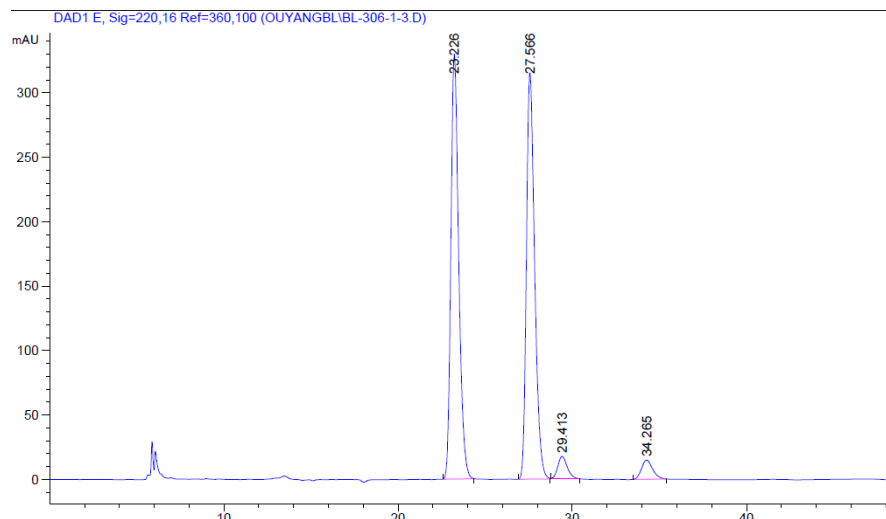


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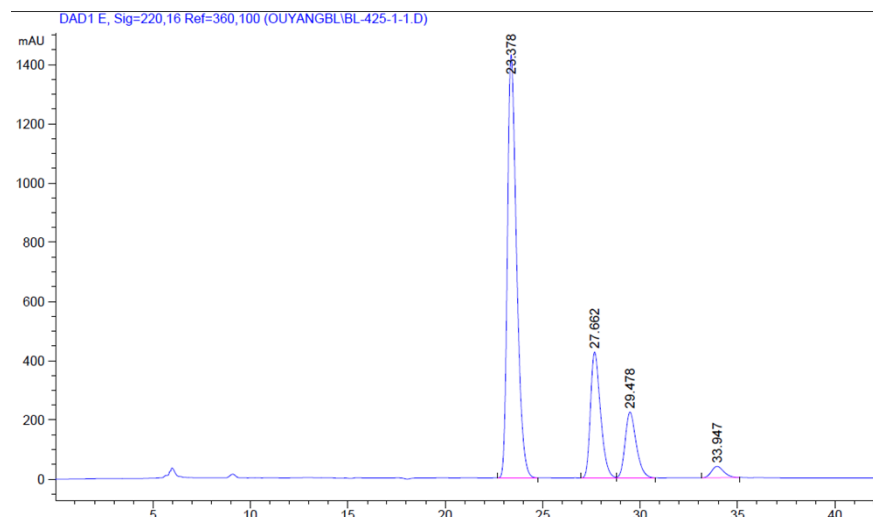


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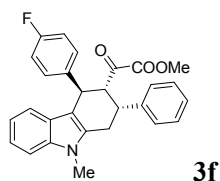


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1	23.226	BB	0.4756	1.02823e4	329.89203	46.8676
2	27.566	BB	0.4996	1.03171e4	315.41476	47.0259
3	29.413	BB	0.5852	676.00842	17.63449	3.0813
4	34.265	BB	0.6646	663.71570	14.87499	3.0253

Optically enriched product

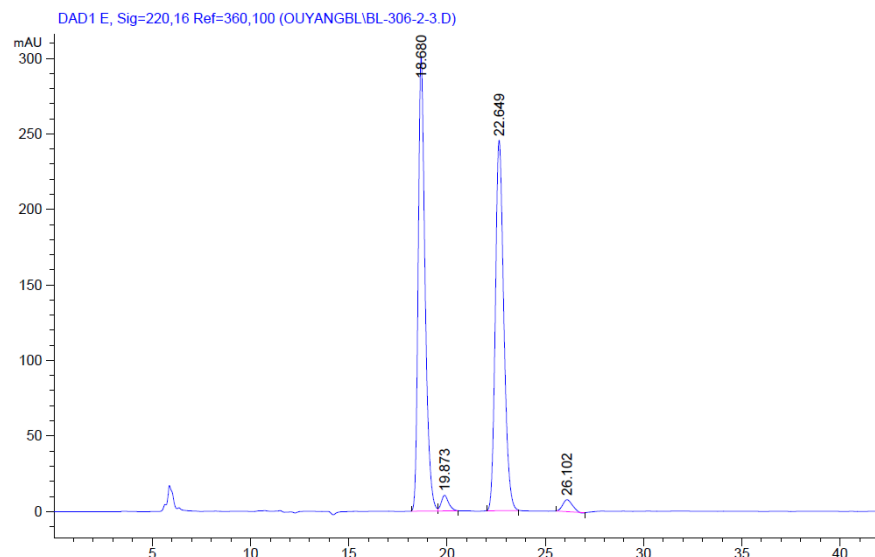


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1	23.378	BB	0.5009	4.69144e4	1429.38599	64.6014
2	27.662	BV	0.5466	1.51933e4	425.45050	20.9213
3	29.478	VB	0.6053	8845.65430	222.75992	12.1805
4	33.947	BB	0.6596	1667.93079	38.33458	2.2967



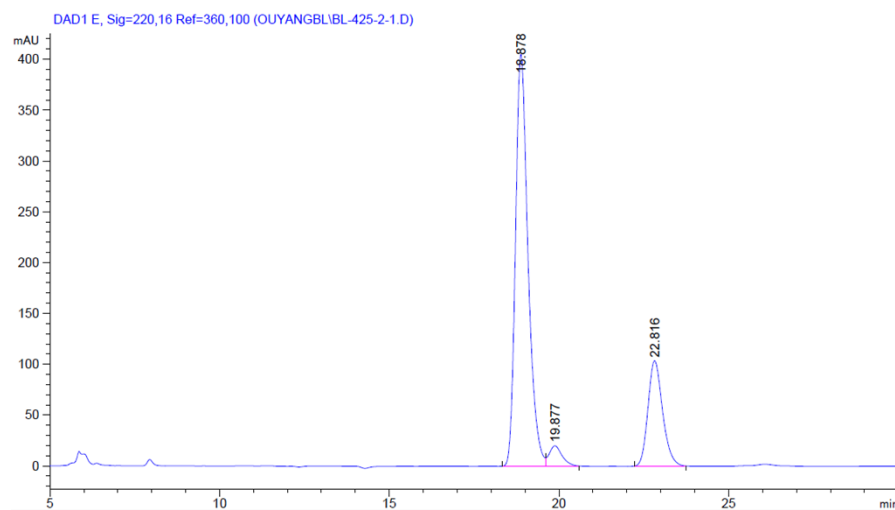
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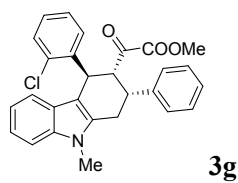


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1	18.680	BB	0.3667	7333.72900	300.48849	48.2027
2	19.873	BB	0.3942	271.48804	10.34366	1.7844
3	22.649	BB	0.4592	7343.45703	245.34579	48.2666
4	26.102	BB	0.5083	265.67932	7.90097	1.7462

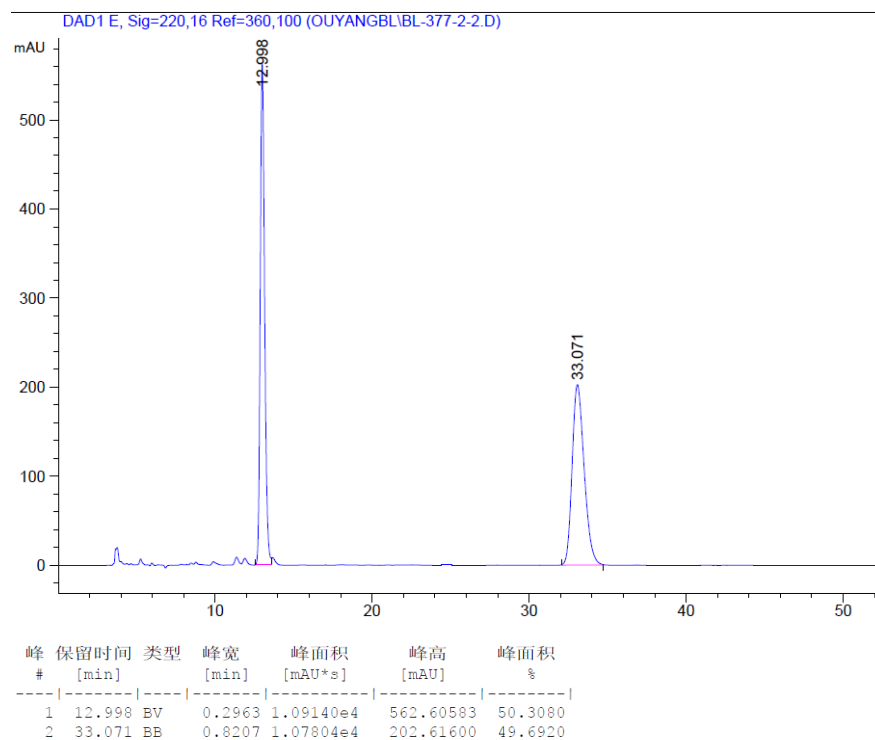
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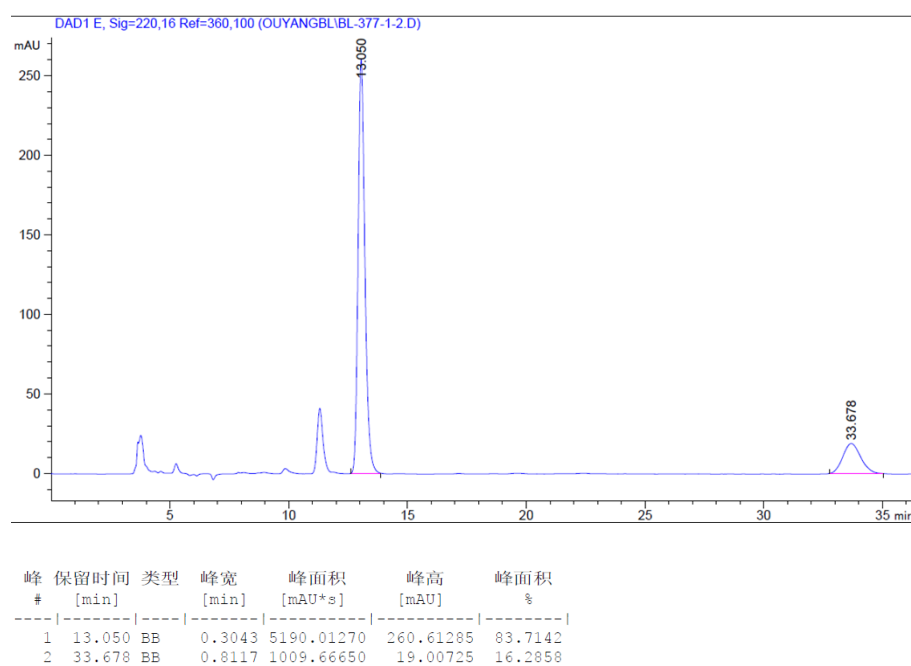
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1	18.878	BV	0.3899	1.04289e4	405.67743	73.9999
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3	22.816	BB	0.4605	3120.08252	103.86281	22.1390

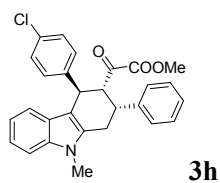


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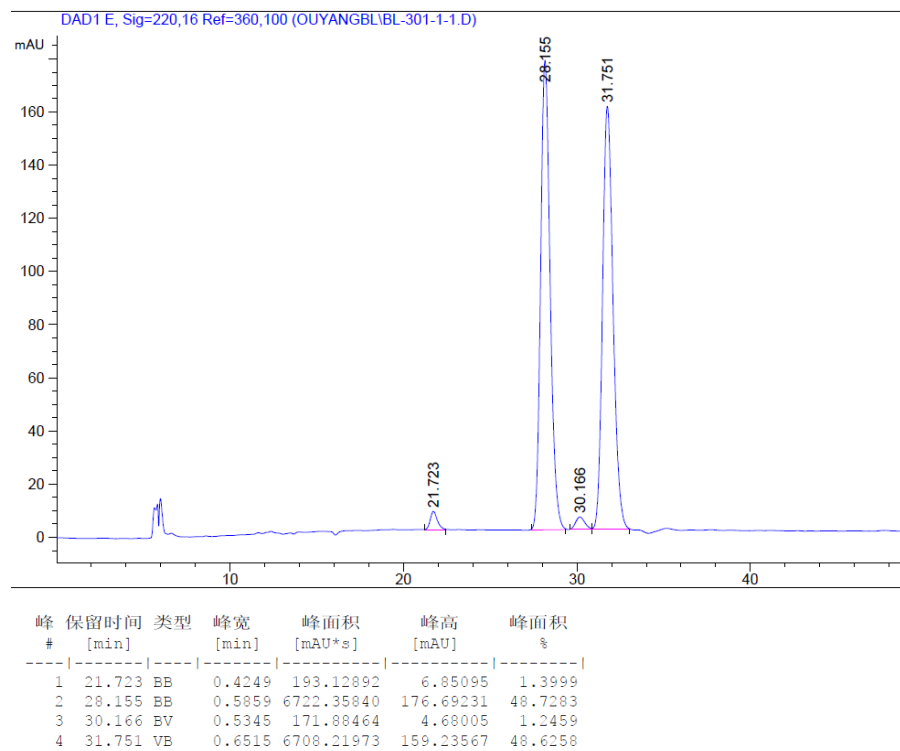


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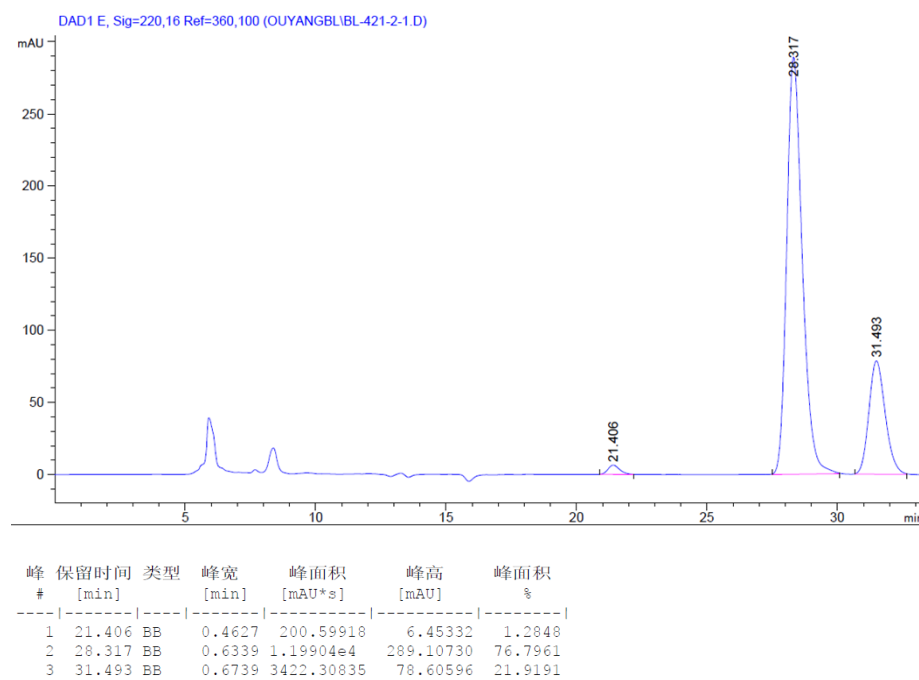


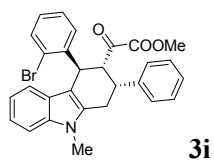


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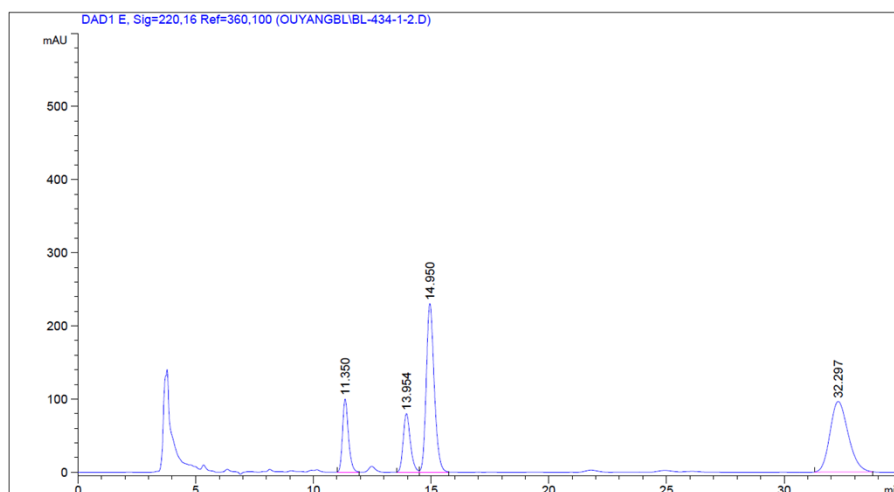


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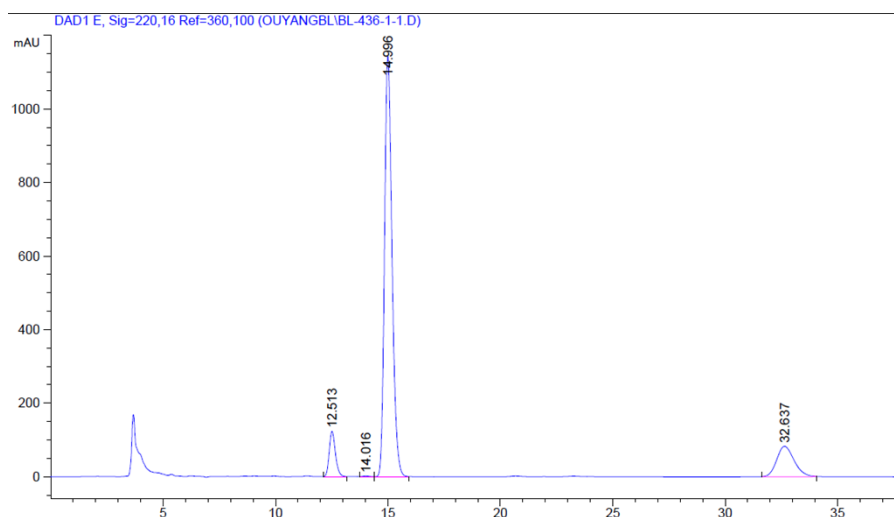


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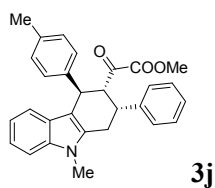


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1	11.350	BB	0.2642	1728.07336	99.72685	12.3082
2	13.954	BV	0.3226	1692.22241	80.04690	12.0529
3	14.950	VB	0.3598	5409.98877	230.52582	38.5326
4	32.297	BB	0.8373	5209.72900	96.58315	37.1063

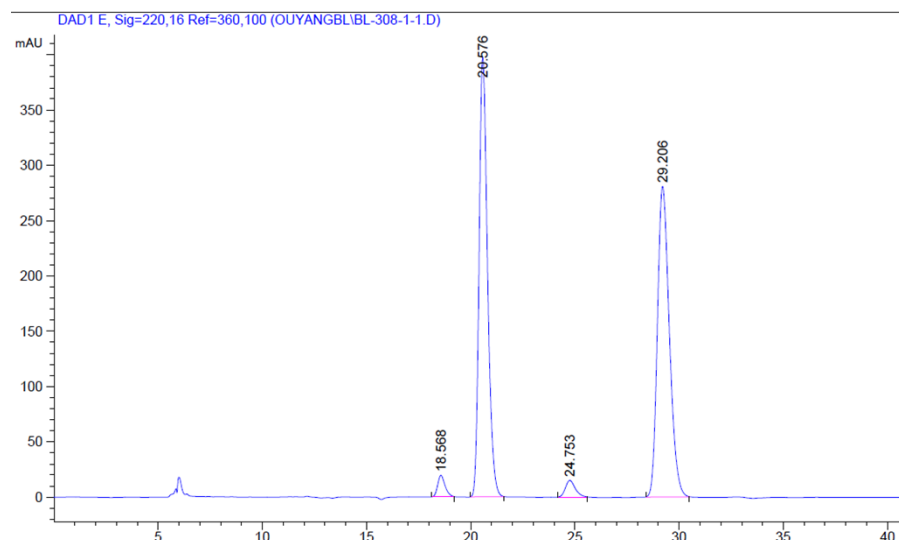
Optically enriched product



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1	12.513	BB	0.2935	2363.94946	123.40984	7.0894
2	14.016	BV	0.2767	26.48514	1.48079	0.0794
3	14.996	VB	0.3563	2.64892e4	1143.30603	79.4399
4	32.637	BB	0.8310	4465.32568	82.82526	13.3913

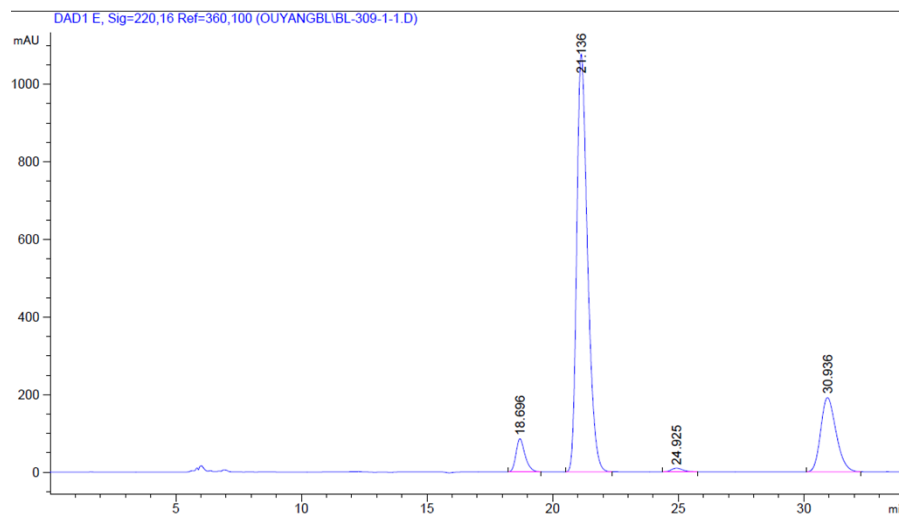


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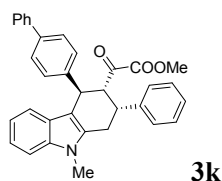


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1	18.568	BB	0.3744	483.74014	19.56830	2.0816
2	20.576	BB	0.4248	1.11293e4	397.34753	47.8908
3	24.753	BB	0.4952	494.84872	15.06671	2.1294
4	29.206	BB	0.6102	1.11310e4	280.95950	47.8982

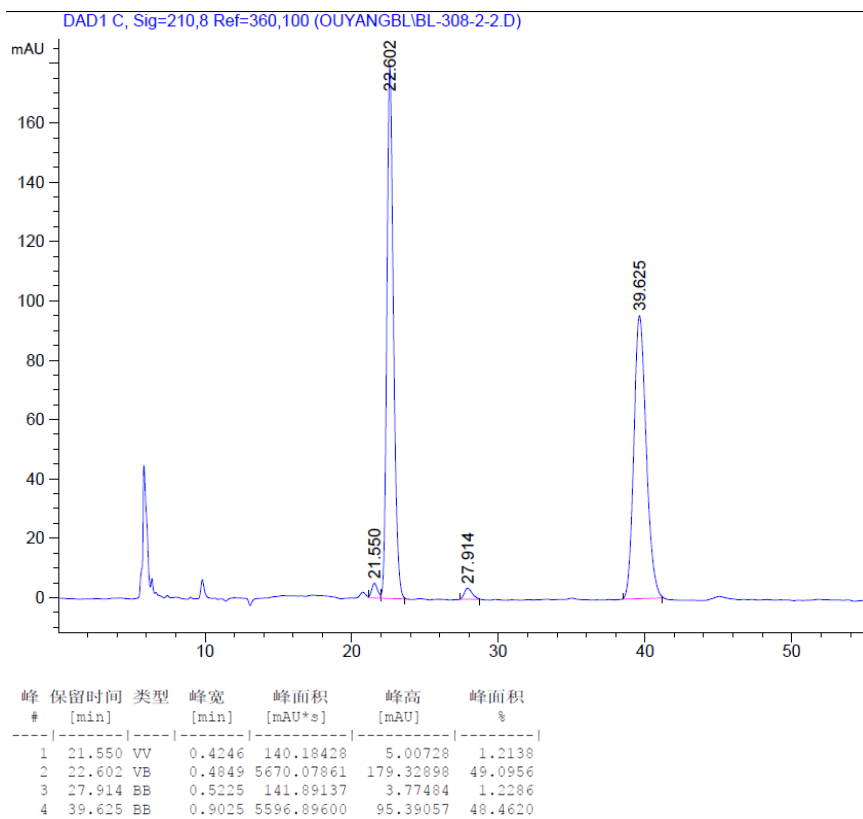
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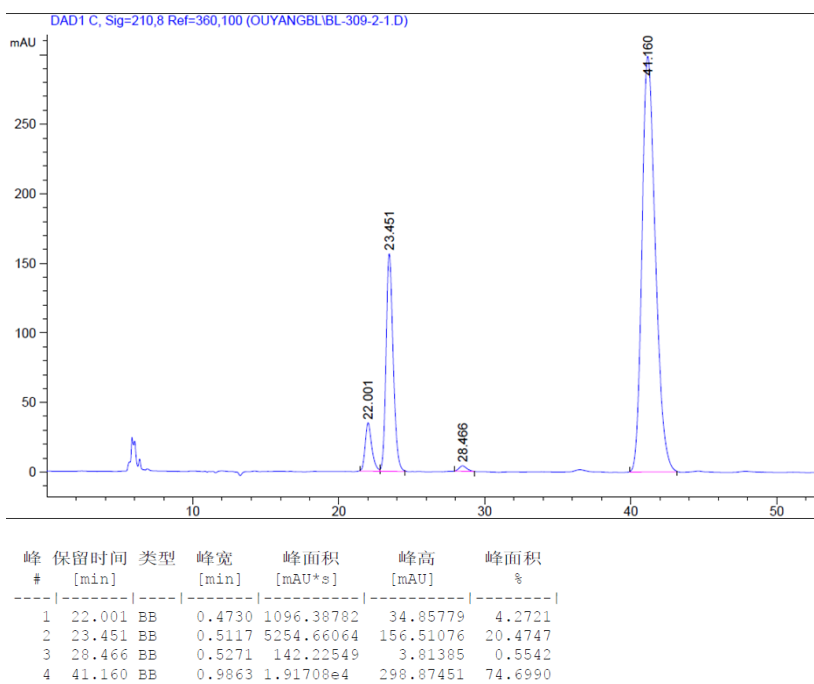
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1	18.696	BB	0.3808	2163.39648	85.61875	5.0472
2	21.136	BB	0.4564	3.21746e4	1077.56104	75.0631
3	24.925	BB	0.4945	328.68707	9.92151	0.7668
4	30.936	BB	0.6584	8196.71484	191.87932	19.1229

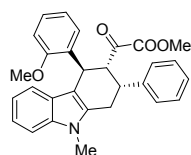


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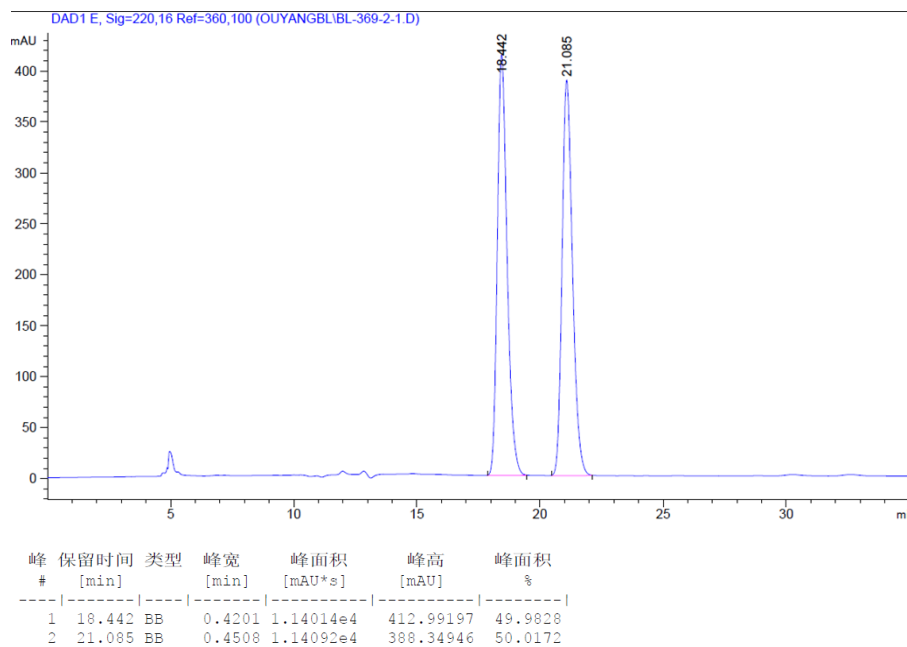
Optically enriched product



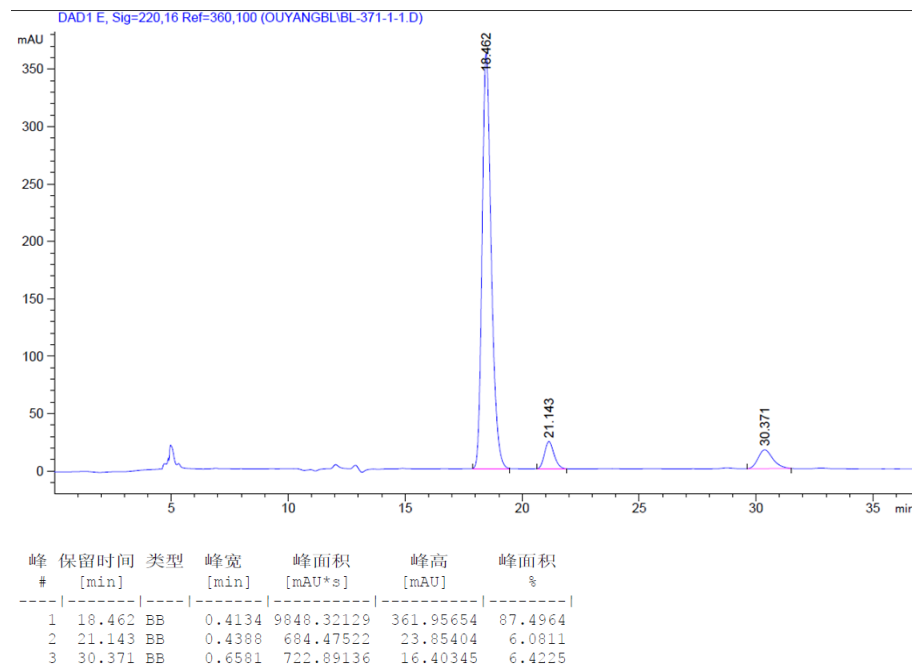


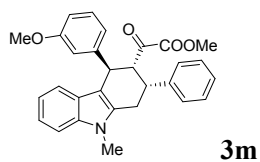
31

Racemic product

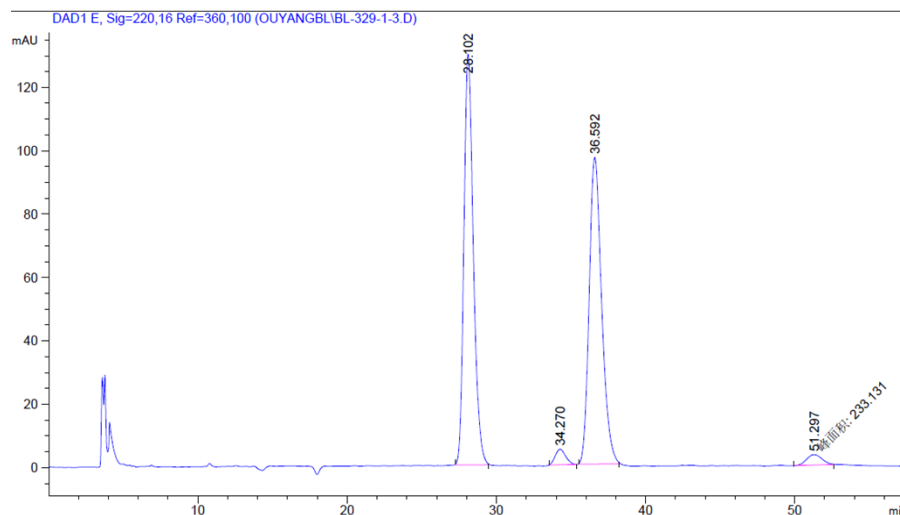


Optically enriched product



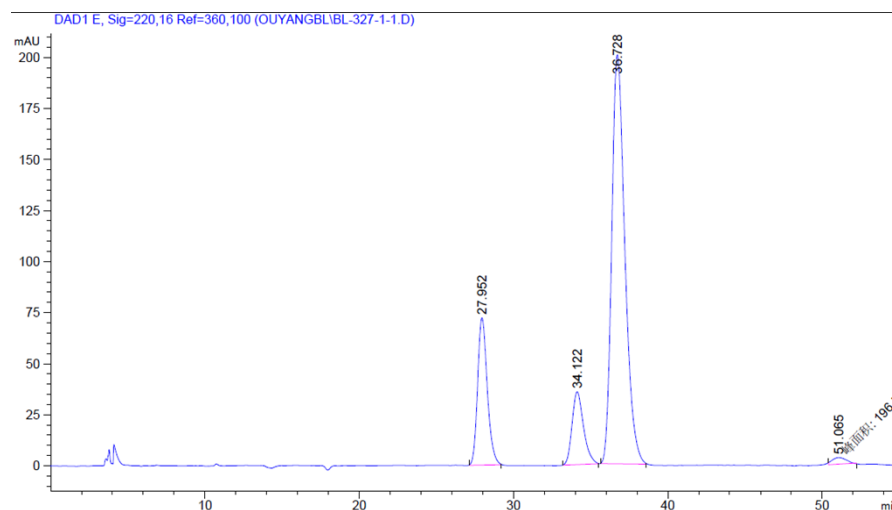


Racemic product

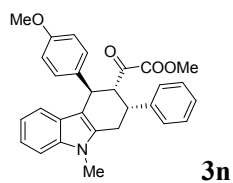


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.102	BB	0.6717	5685.87891	129.64398	48.3079
2	34.270	BB	0.6513	238.91438	4.93029	2.0298
3	36.592	BB	0.8846	5612.16748	96.77056	47.6816
4	51.297	MM	1.1834	233.13129	3.28322	1.9807

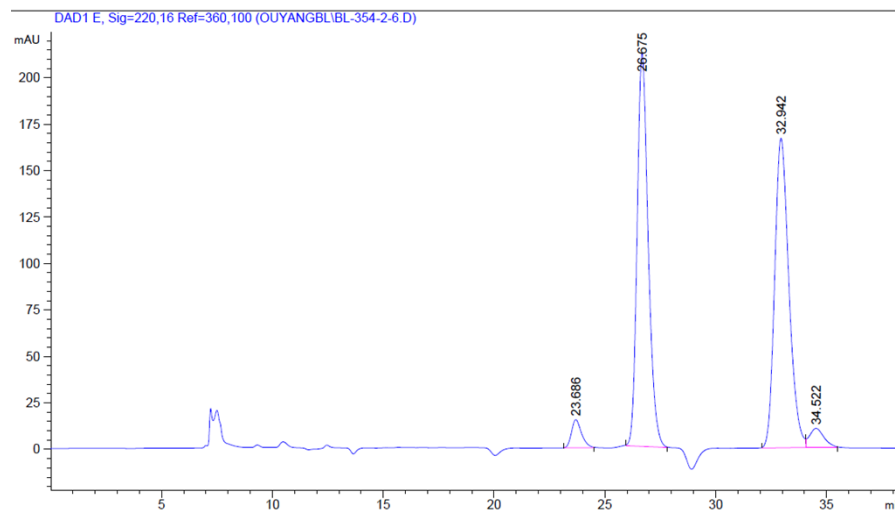
Optically enriched product



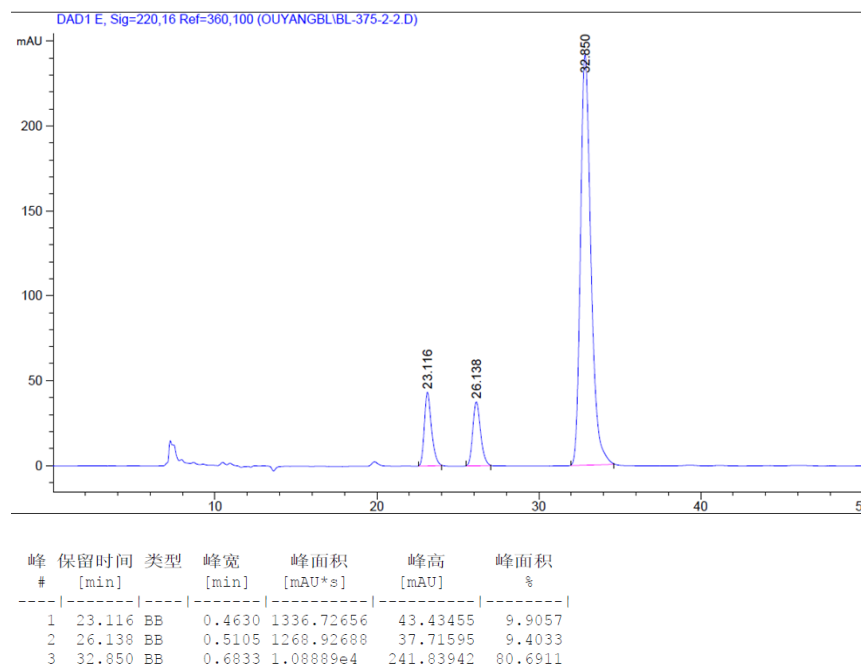
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.952	BB	0.6677	3141.00684	72.18289	18.4158
2	34.122	BB	0.7782	1836.83142	35.70697	10.7694
3	36.728	BB	0.9077	1.18816e4	200.39607	69.6624
4	51.065	MM	1.0104	196.55469	3.24209	1.1524

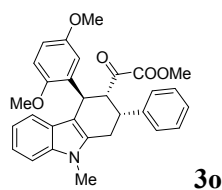


Racemic product



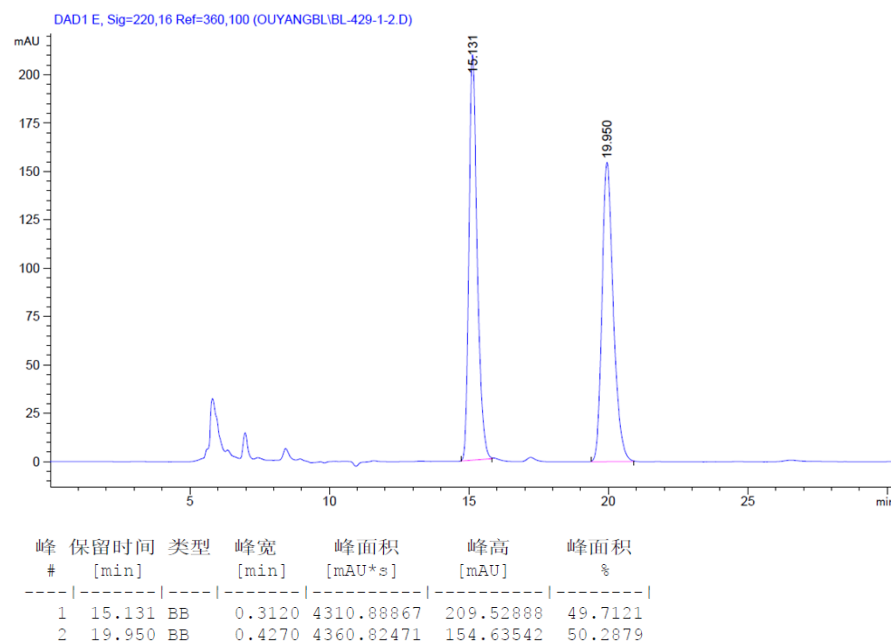
Optically enriched product



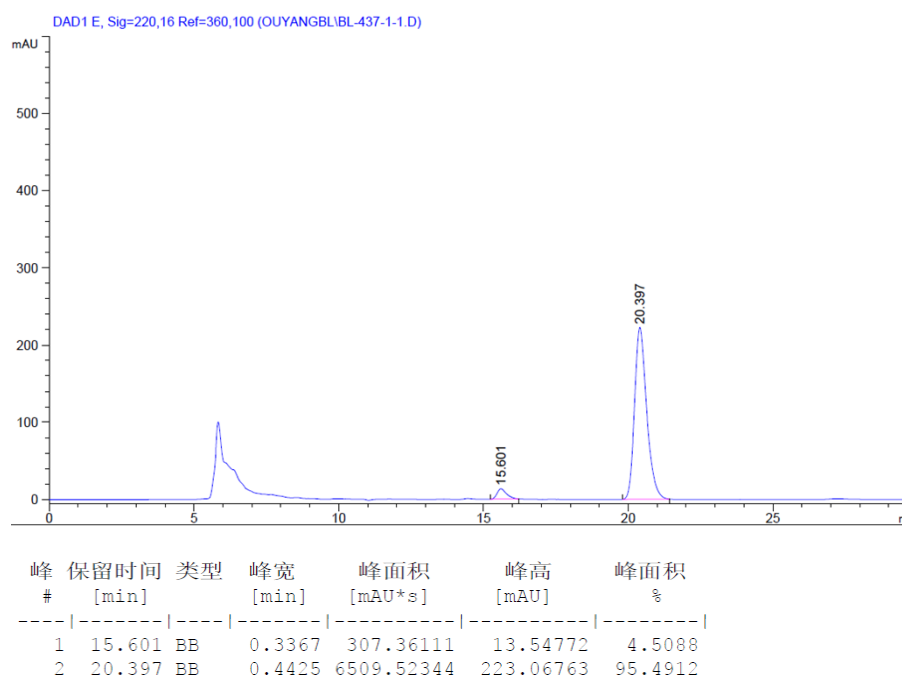


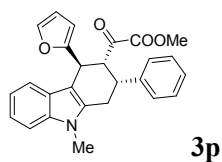
30

Racemic product

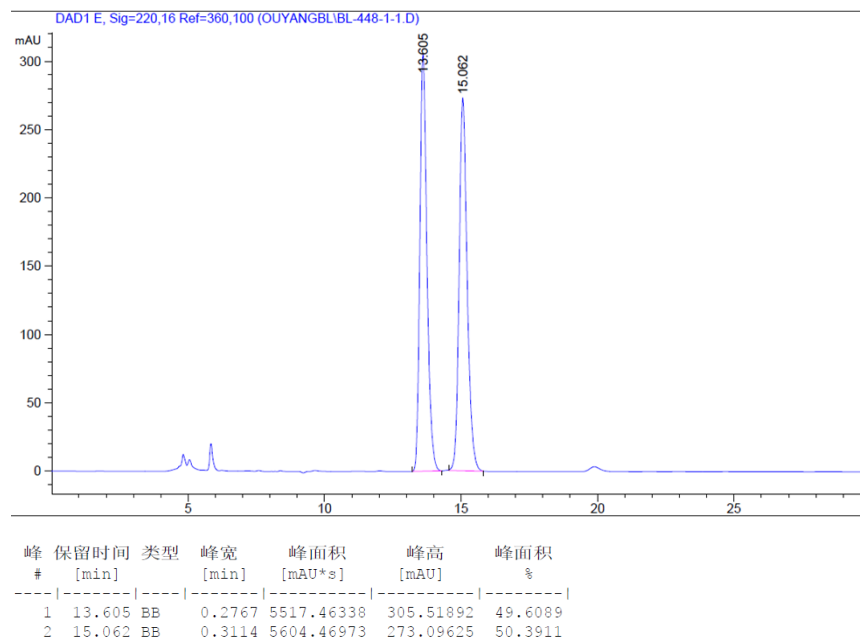


Optically enriched product

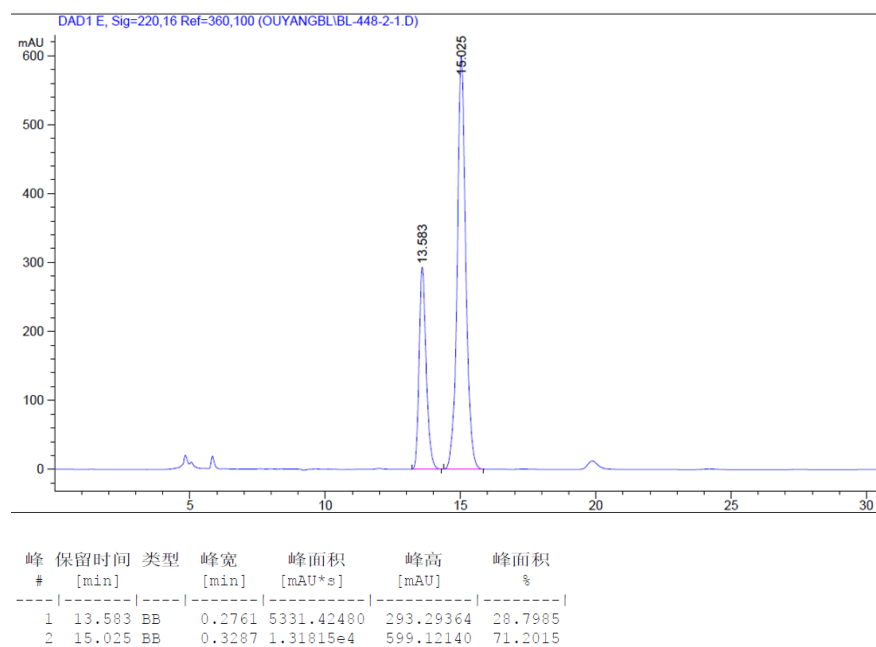


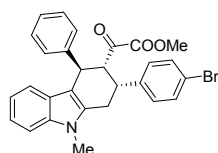


Racemic product



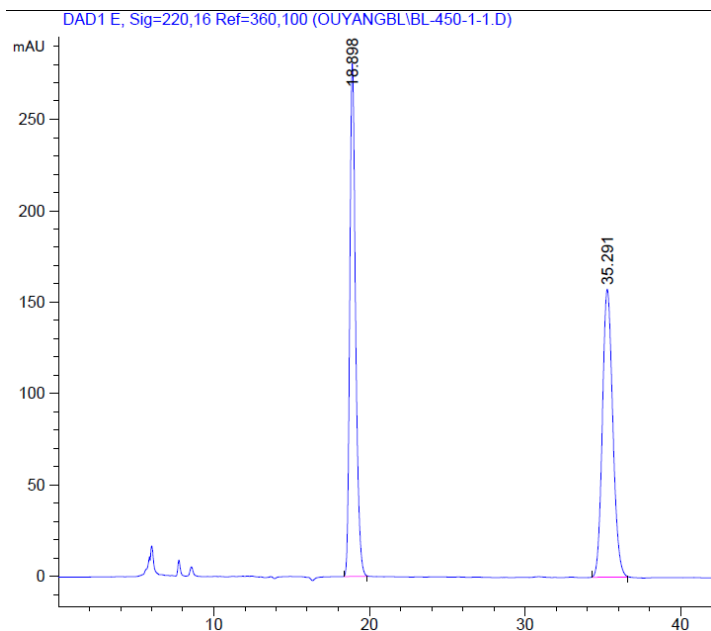
Optically enriched product



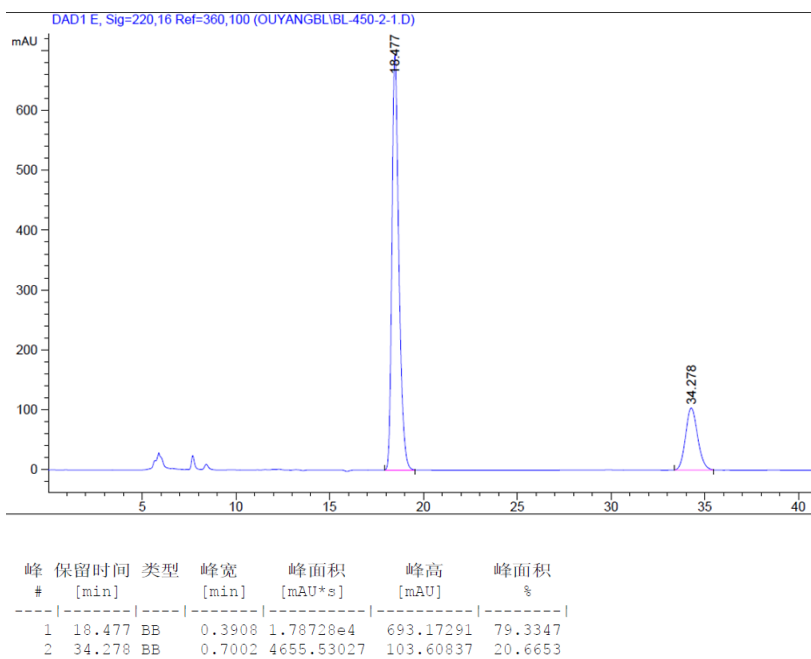


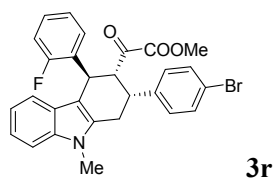
3q

Racemic product

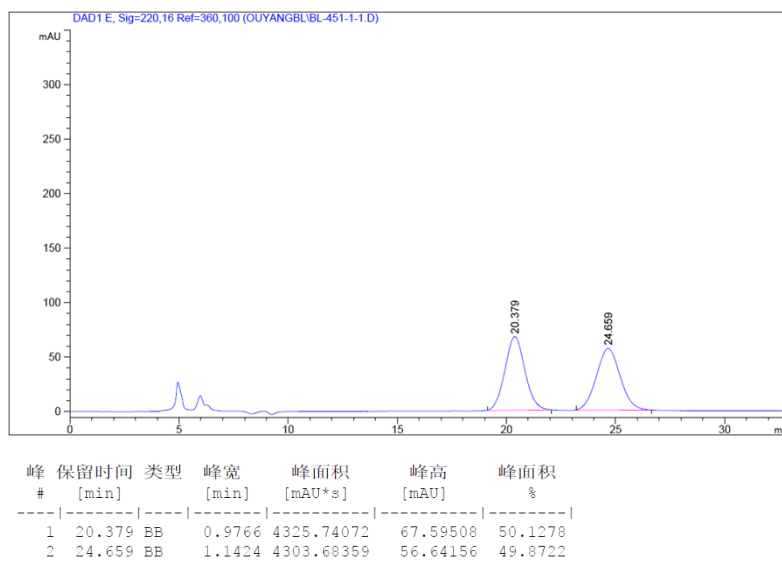


Optically enriched product

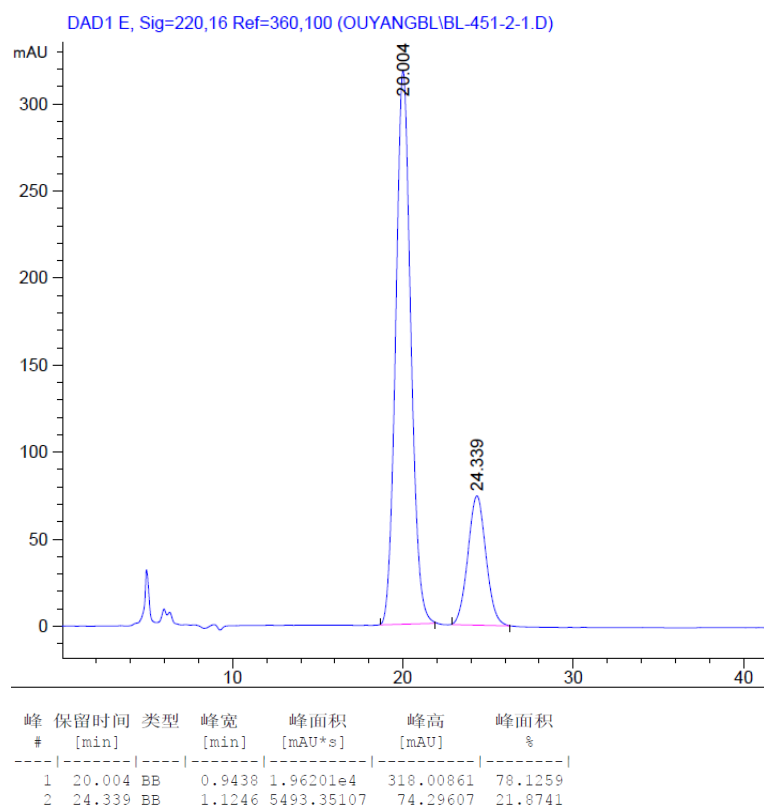


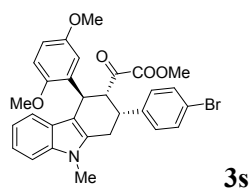


Racemic product

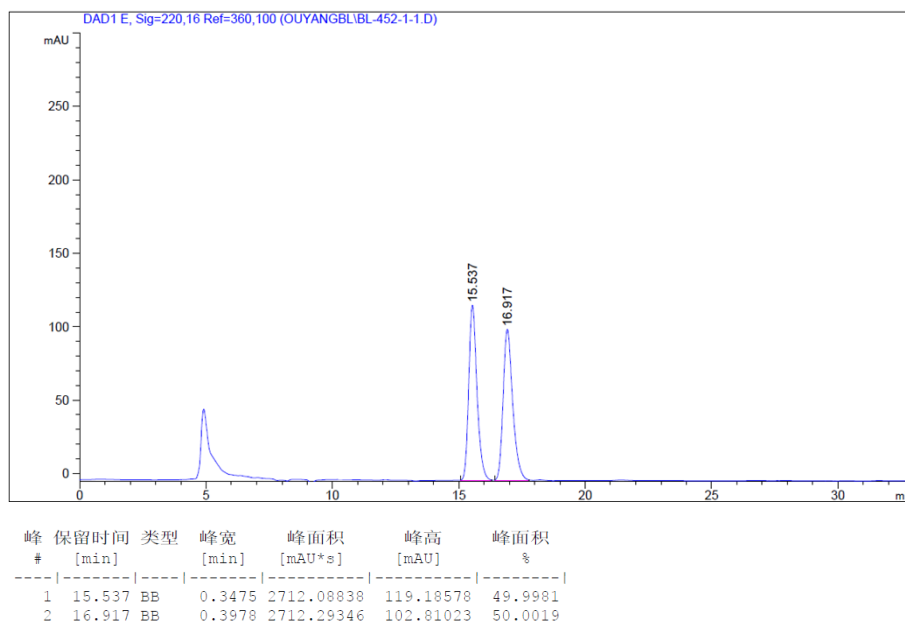


Optically enriched product

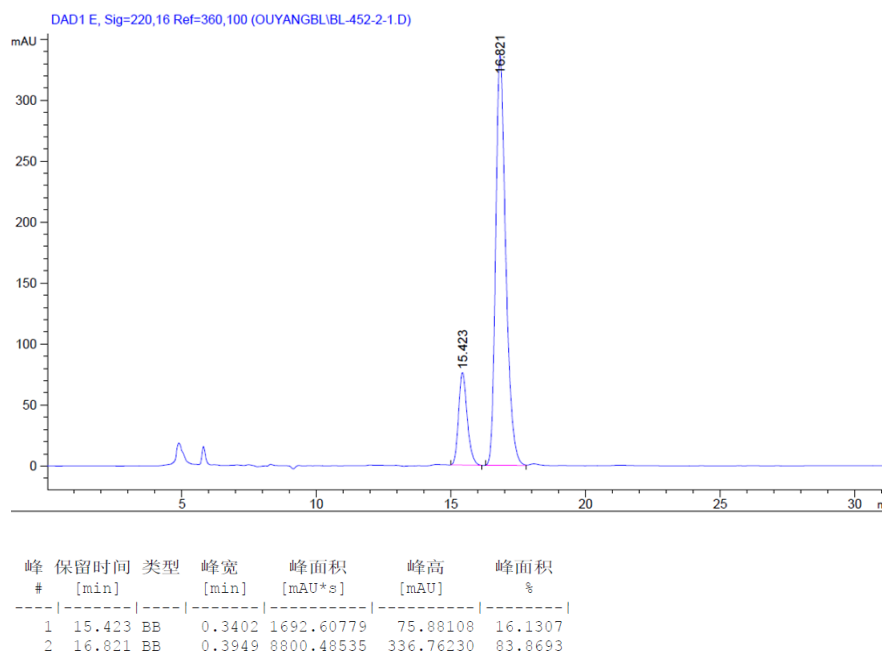


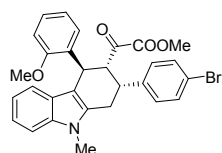


Racemic product



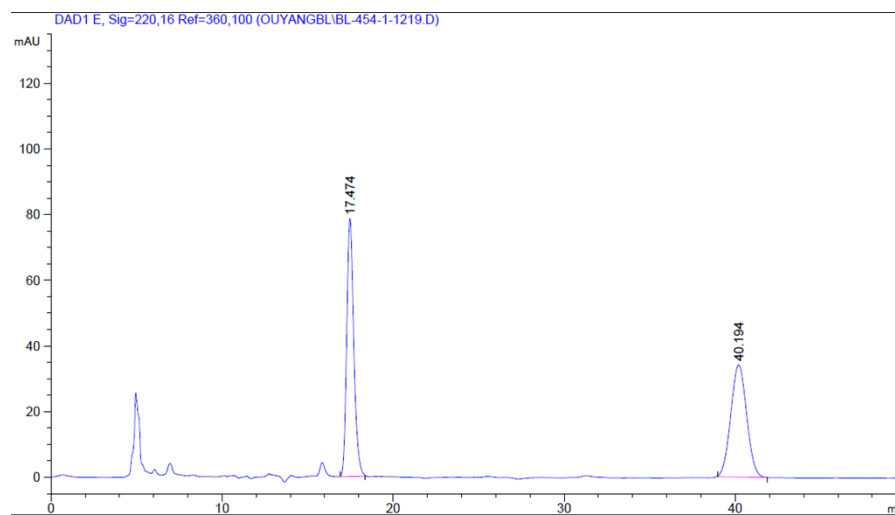
Optically enriched product





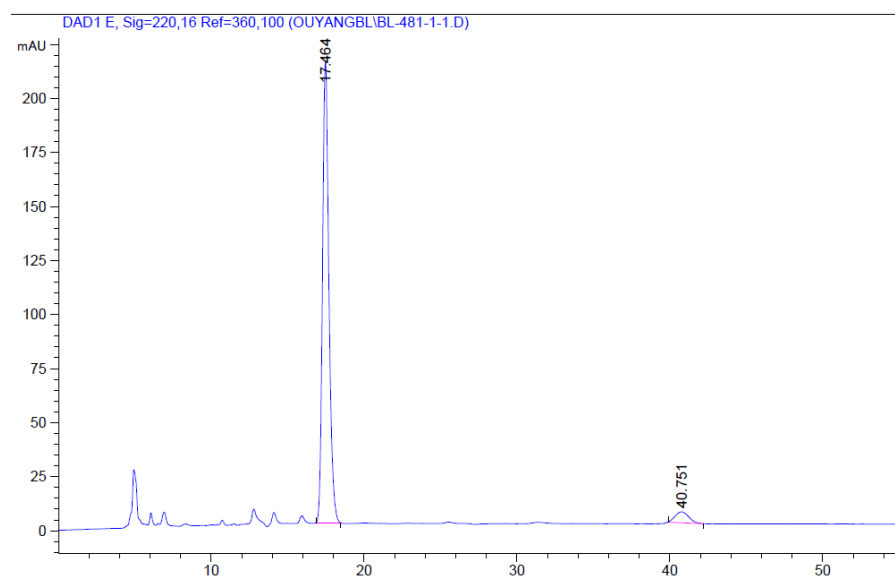
3t

Racemic product

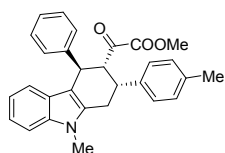


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.474	BB	0.4324	2238.46509	78.56823	50.4024
2	40.194	BB	0.9784	2202.72314	34.15456	49.5976

Optically enriched product

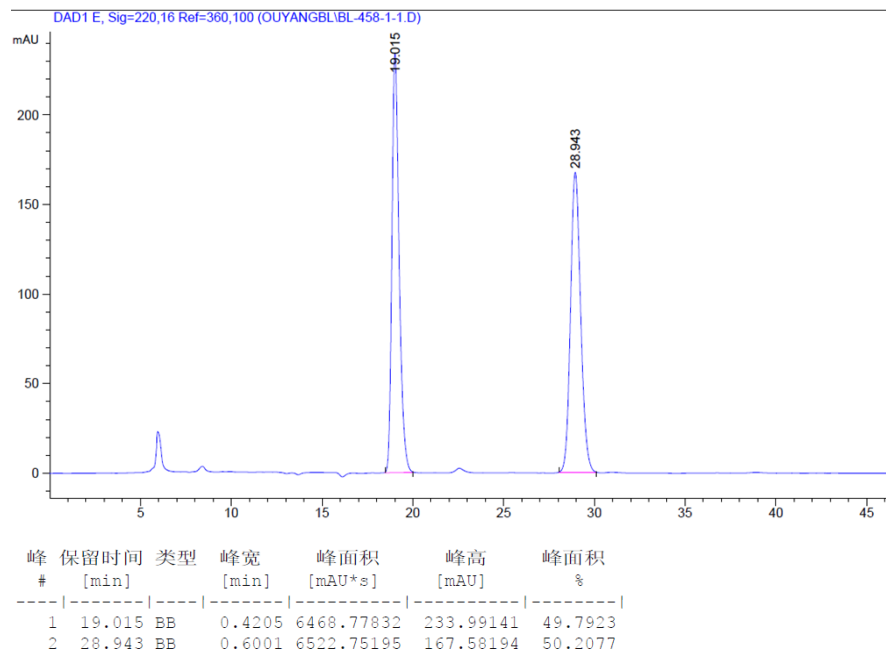


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.464	BB	0.4437	6214.64893	213.46040	95.1995
2	40.751	BB	0.7414	313.37692	5.02625	4.8005

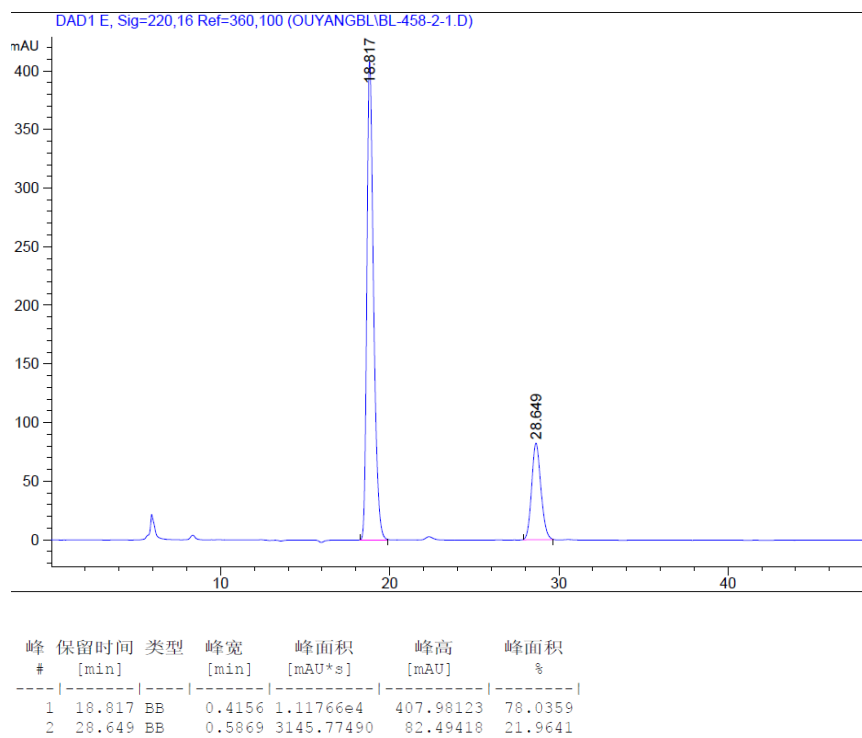


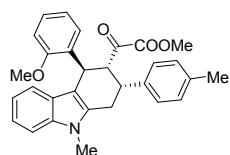
3u

Racemic product



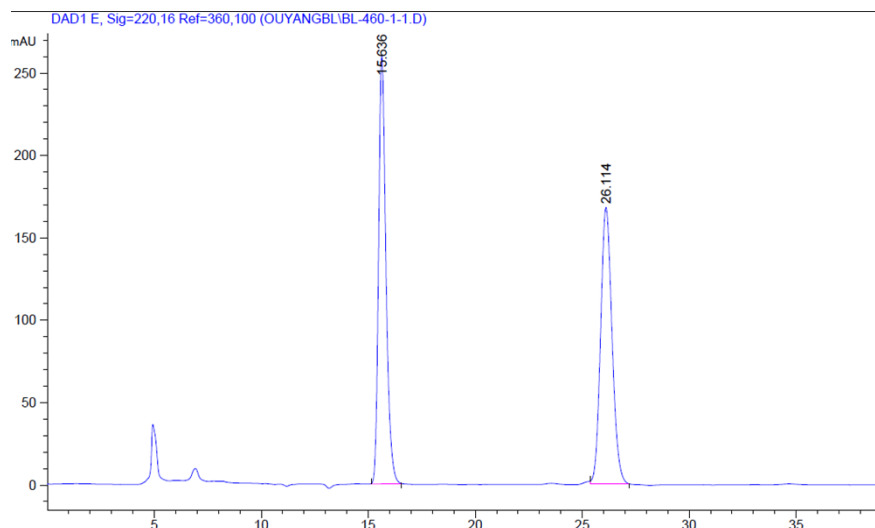
Optically enriched product





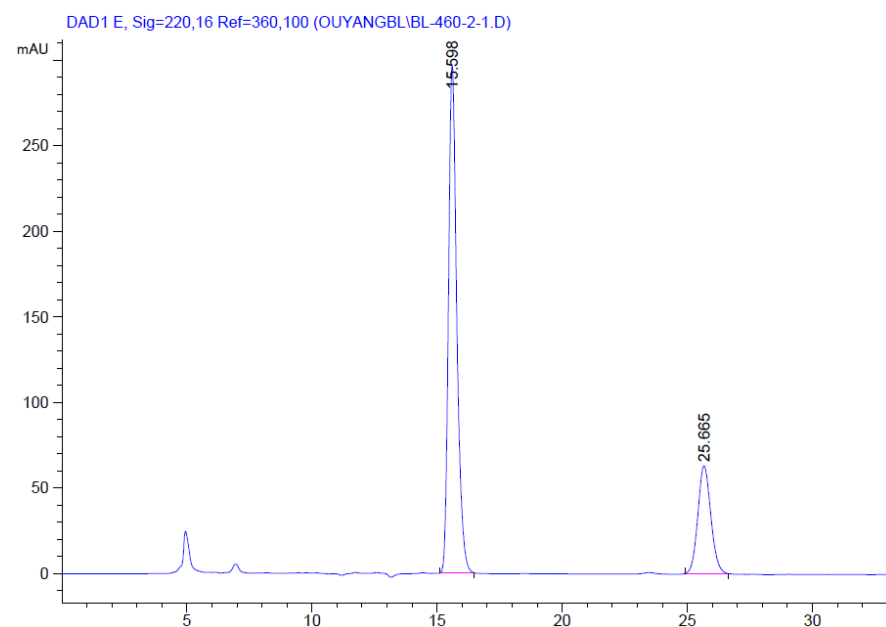
3v

Racemic product



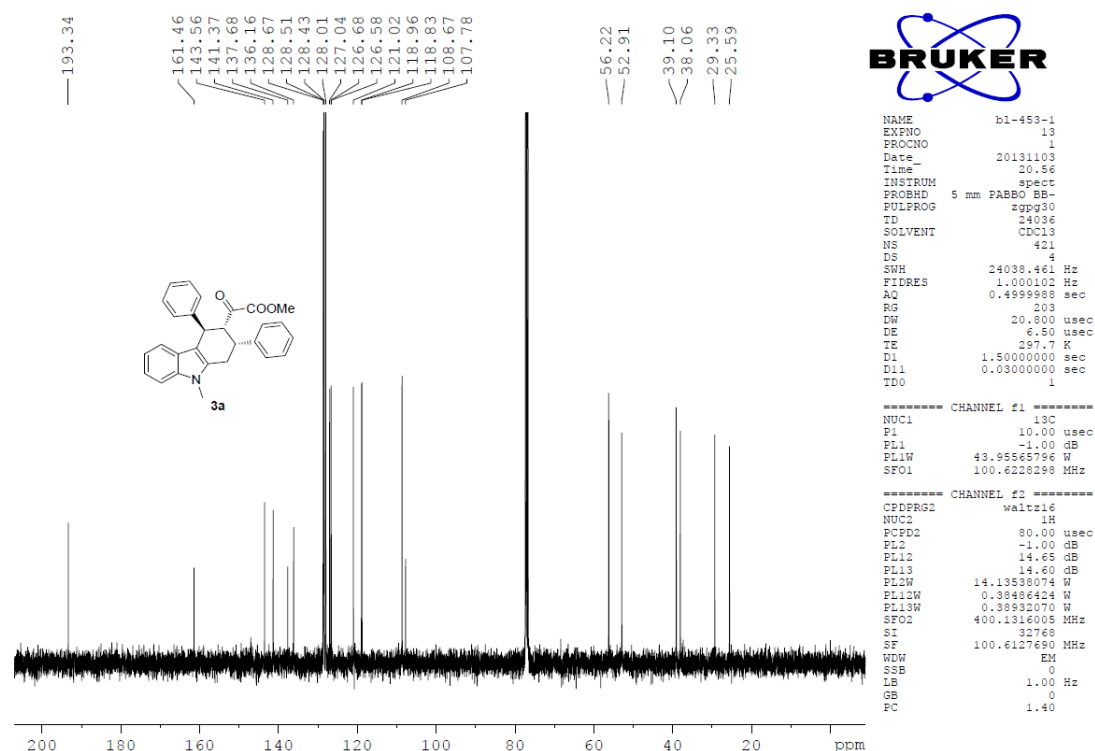
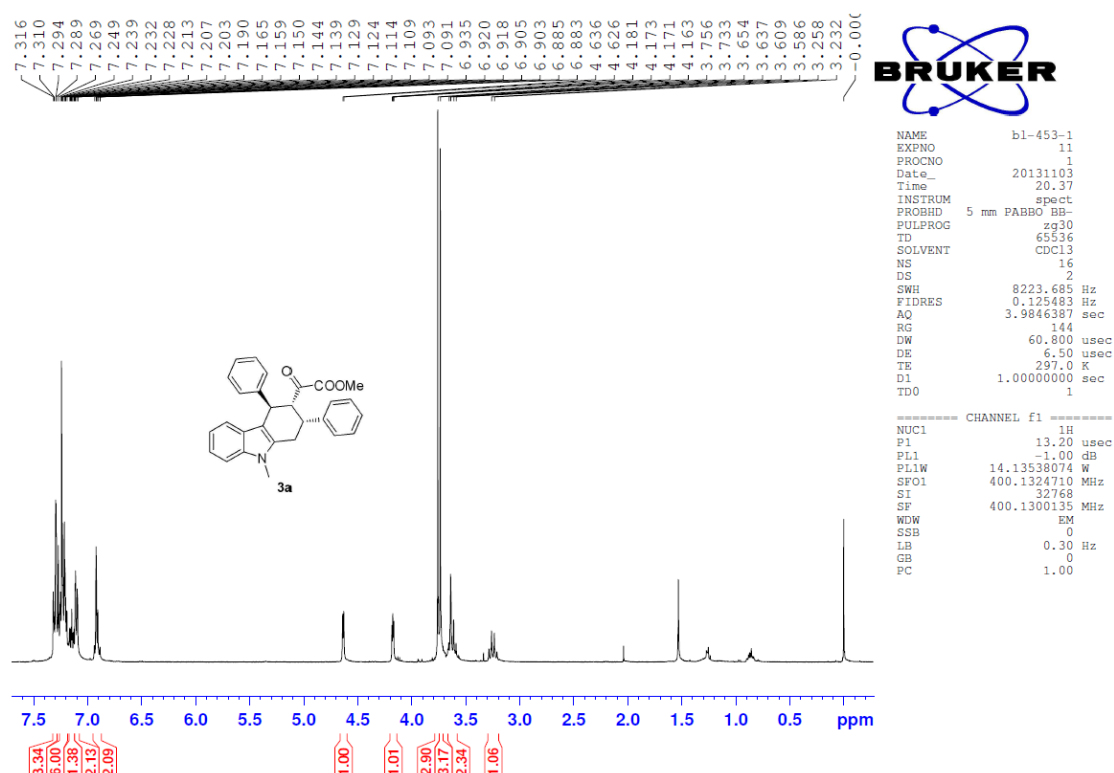
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.636	BB	0.3610	6216.07959	259.90289	49.9751
2	26.114	BB	0.5704	6222.27734	167.89534	50.0249

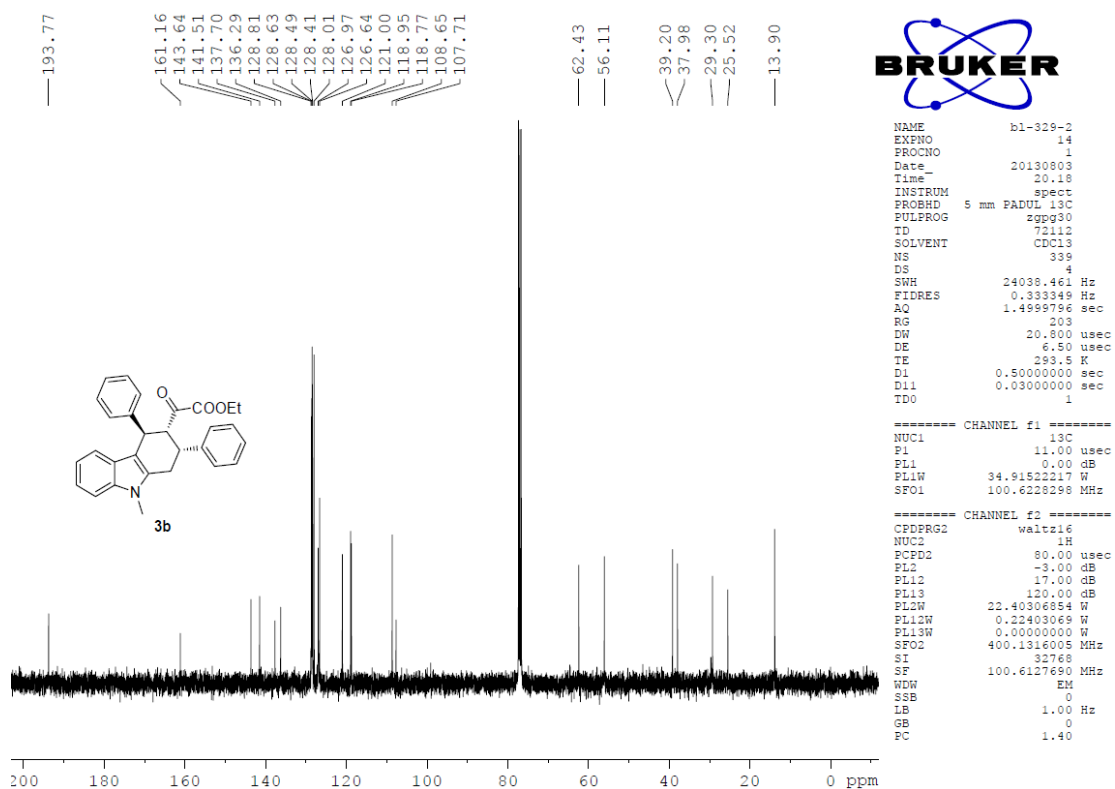
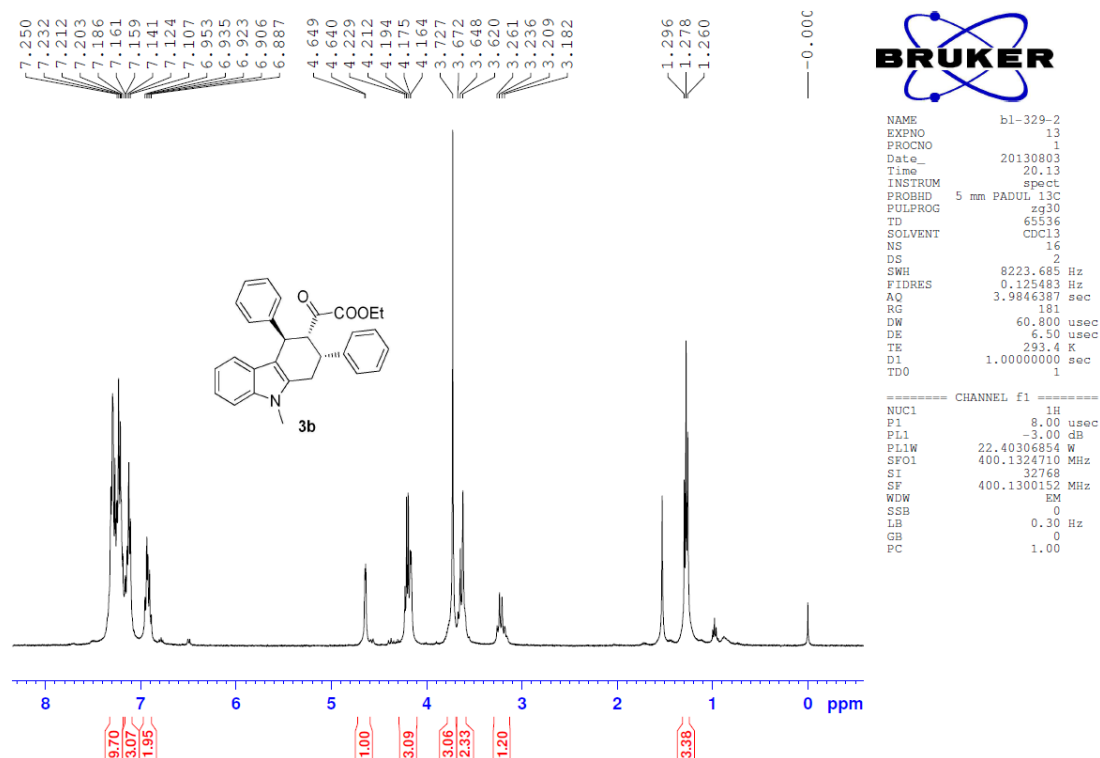
Optically enriched product

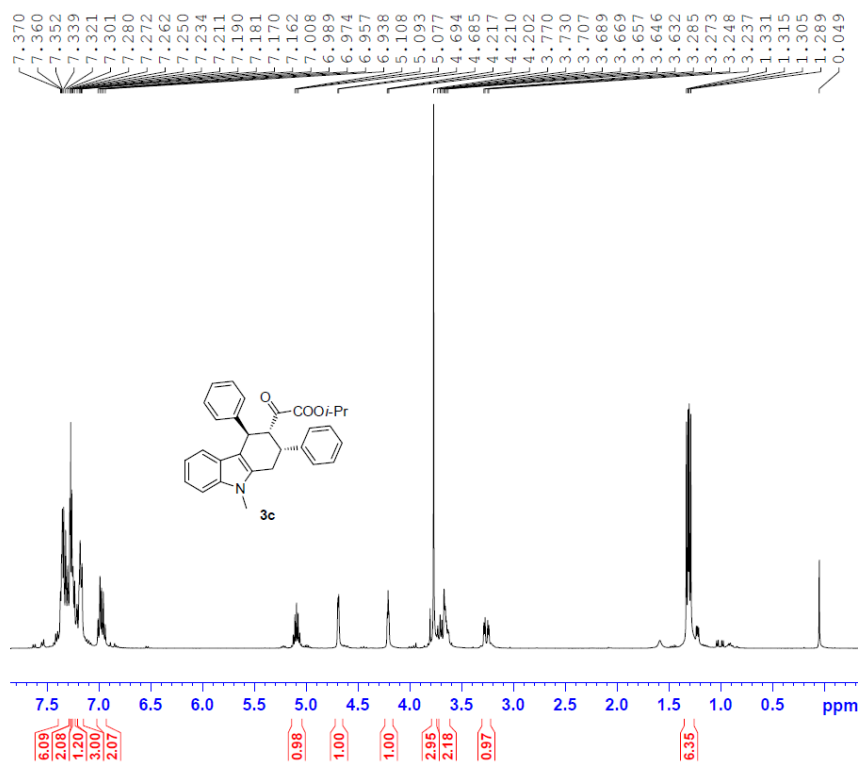


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.598	BB	0.3496	6853.91895	296.65063	75.0056
2	25.665	BB	0.5540	2283.95972	63.14785	24.9944

9. ^1H and ^{13}C NMR spectra





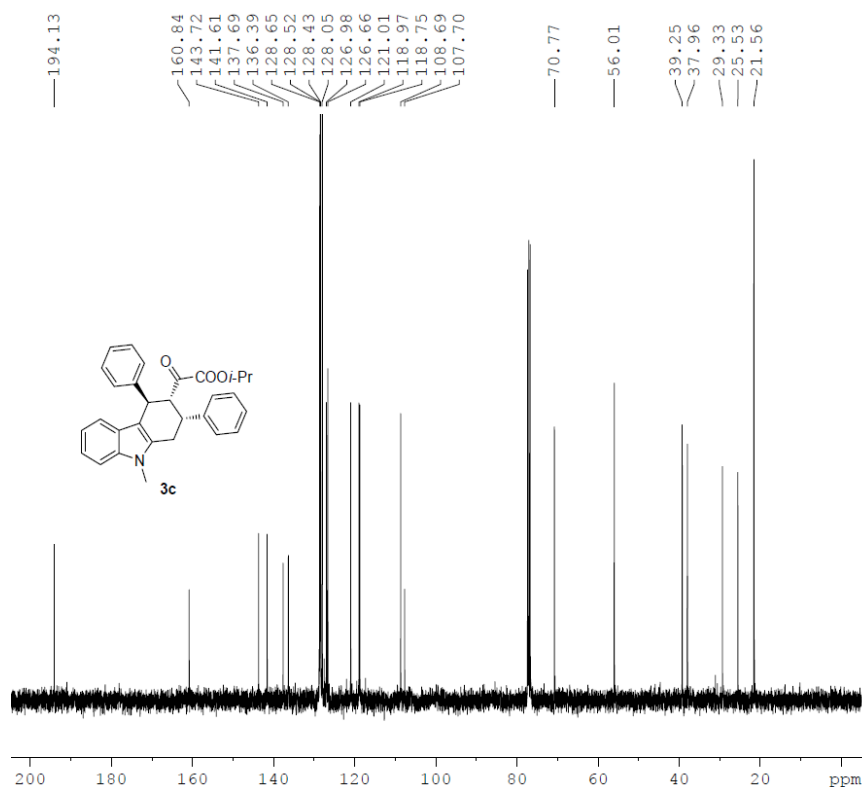


```

NAME      b1-381-1
EXPNO     10
PROCNO    1
Date_     20131108
Time      17.00
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         101
DW         60.800 usec
DE         6.50 usec
TE         296.9 K
D1         1.00000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.20 usec
PL1       -1.00 dB
PL1W      14.13538074 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```



```

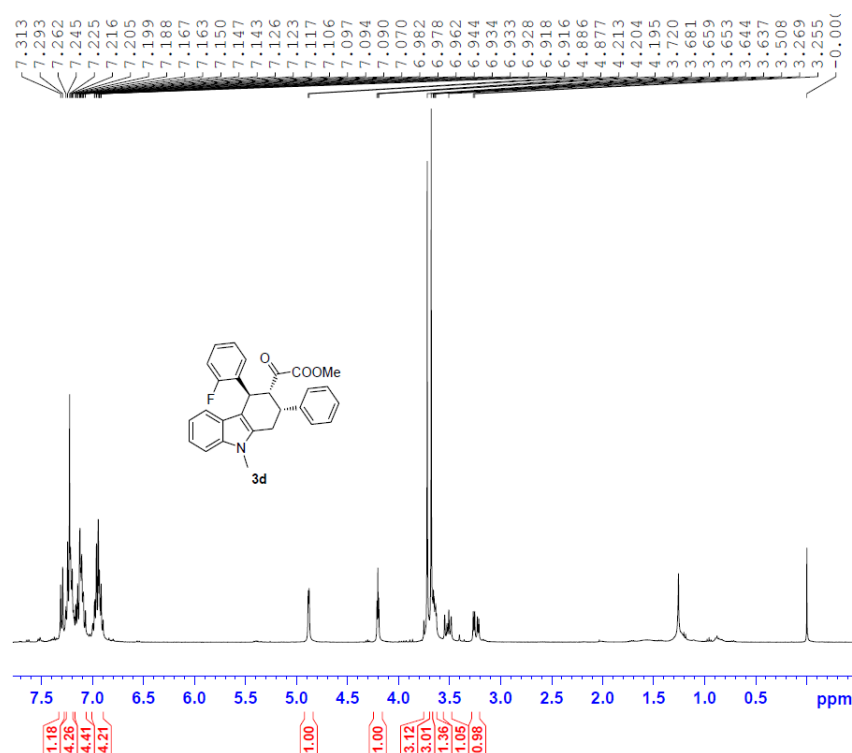
NAME      b1-381-1
EXPNO     12
PROCNO    1
Date_     20131108
Time      17.28
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         34036
SOLVENT   CDCl3
NS         190
DS         4
SWH       24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         298.4 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
PL1W      43.95565796 W
SFO1      100.6228298 MHz
  
```

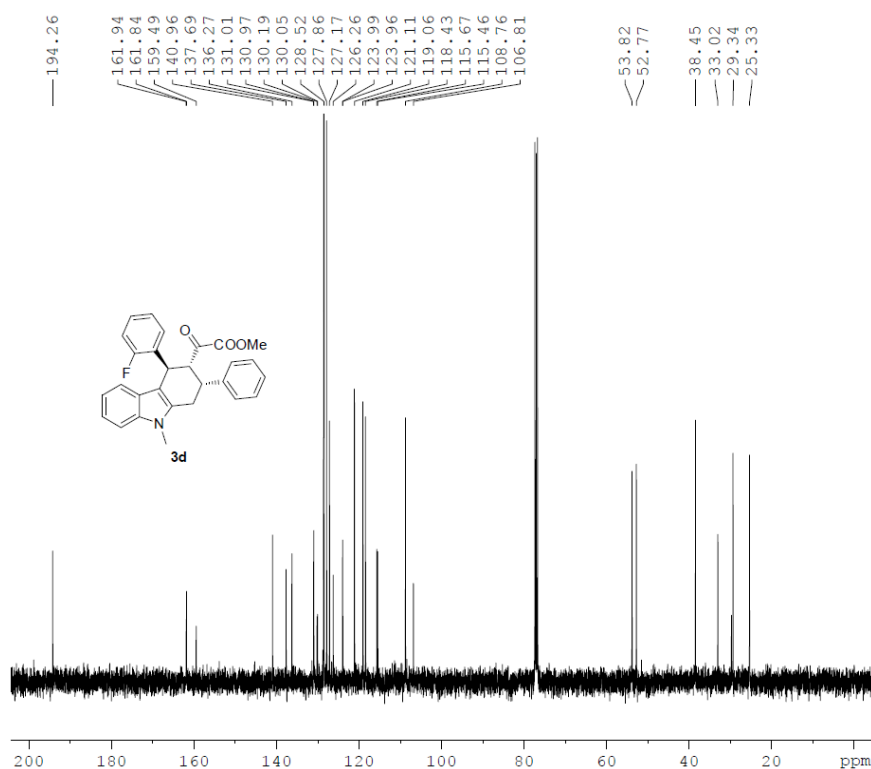
```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       -1.00 dB
PL12      14.65 dB
PL13      14.60 dB
PL2W      14.13538074 W
PL12W     0.38486424 W
PL13W     0.38932070 W
SFO2      400.1316005 MHz
SI        32768
SF        100.6127690 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```



NAME b1-302-1-1H
 EXPNO 10
 PROCNO 1
 Date 20131108
 Time 16.53
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 101
 DW 60.800 usec
 DE 6.50 usec
 TE 297.0 K
 D1 1.0000000 sec
 TD0 1

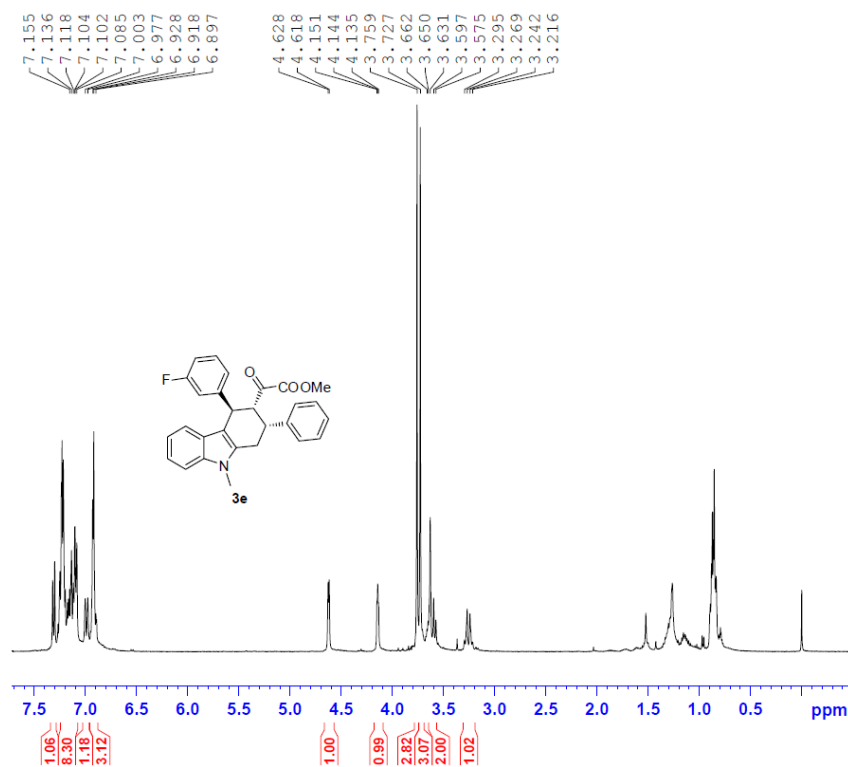
===== CHANNEL f1 =====
 NUC1 1H
 P1 13.20 usec
 PL1 -1.00 dB
 FL1W 14.13538074 W
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1300188 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME b1-302-1-C13
 EXPNO 10
 PROCNO 1
 Date 20131108
 Time 17.07
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 24036
 SOLVENT CDCl3
 NS 328
 DS 4
 SWH 24038.461 Hz
 FIDRES 1.000102 Hz
 AQ 0.4999988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 297.5 K
 D1 1.5000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -1.00 dB
 FL1W 43.95565796 W
 SFO1 100.6228298 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 14.65 dB
 PL13 14.60 dB
 PL2W 14.13538074 W
 FL12W 0.38486424 W
 FL13W 0.38932070 W
 SFO2 400.1316005 MHz
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

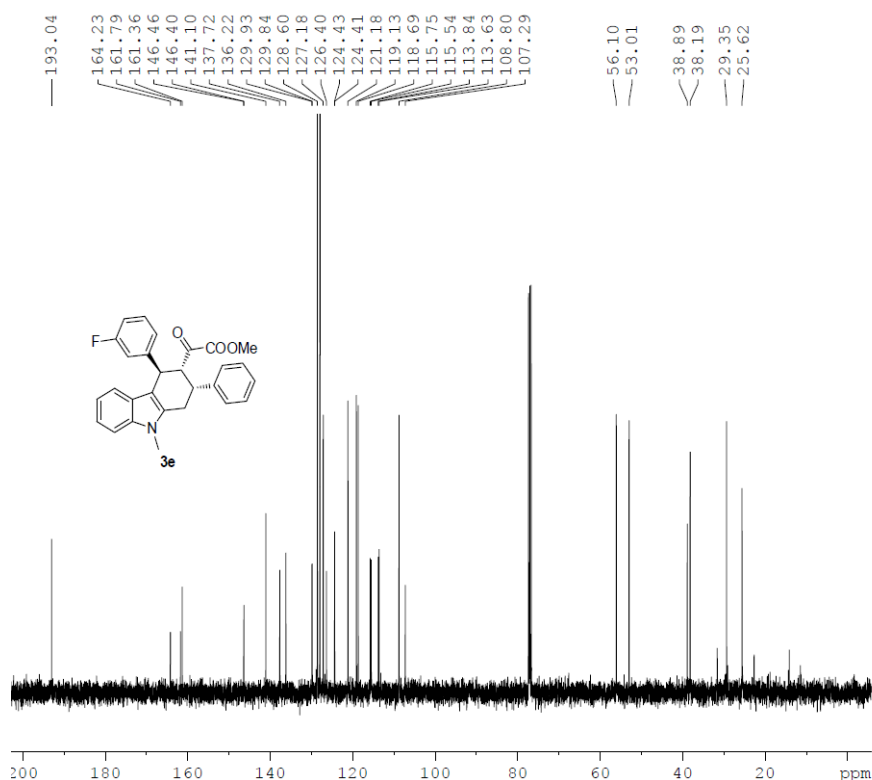


```

NAME      b1-470-1
EXPNO     10
PROCNO    1
Date_     20131205
Time      19.48
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         80.6
DW         60.800 usec
DE         6.50 usec
TE         297.3 K
D1         1.00000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.20 usec
PL1       -1.00 dB
PL1W      14.13538074 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300175 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



```

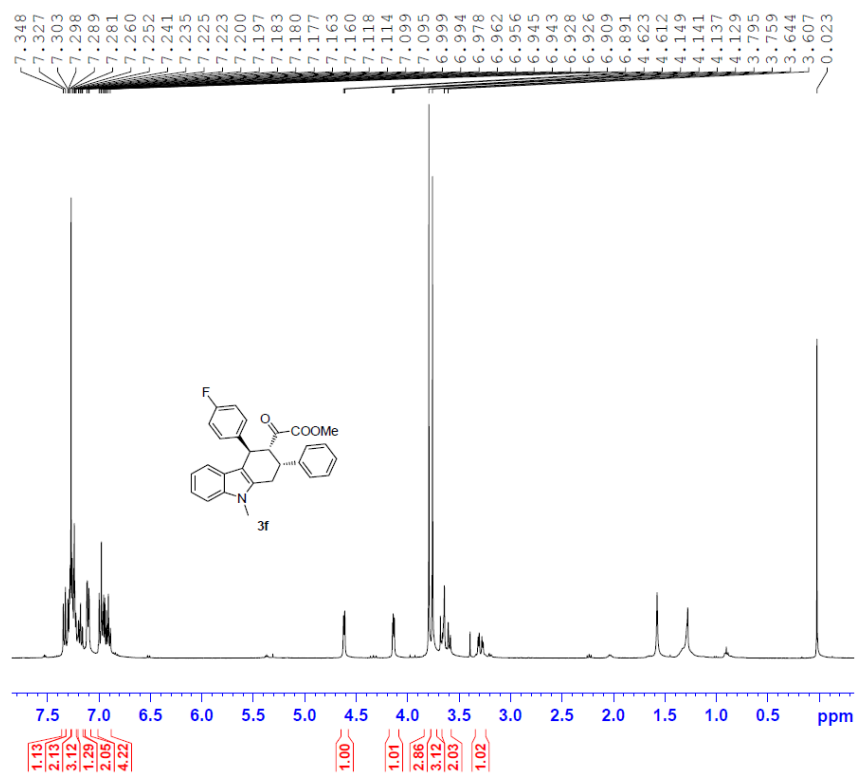
NAME      b1-470-1
EXPNO     11
PROCNO    1
Date_     20131205
Time      19.58
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD        24036
SOLVENT   CDCl3
NS         102
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         297.1 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
PL1W      43.95565796 W
SFO1      100.6228298 MHz
  
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       -1.00 dB
PL12      14.65 dB
PL13      14.60 dB
PL2W      14.13538074 W
PL12W     0.38486424 W
PL13W     0.38932070 W
SFO2      400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```



```

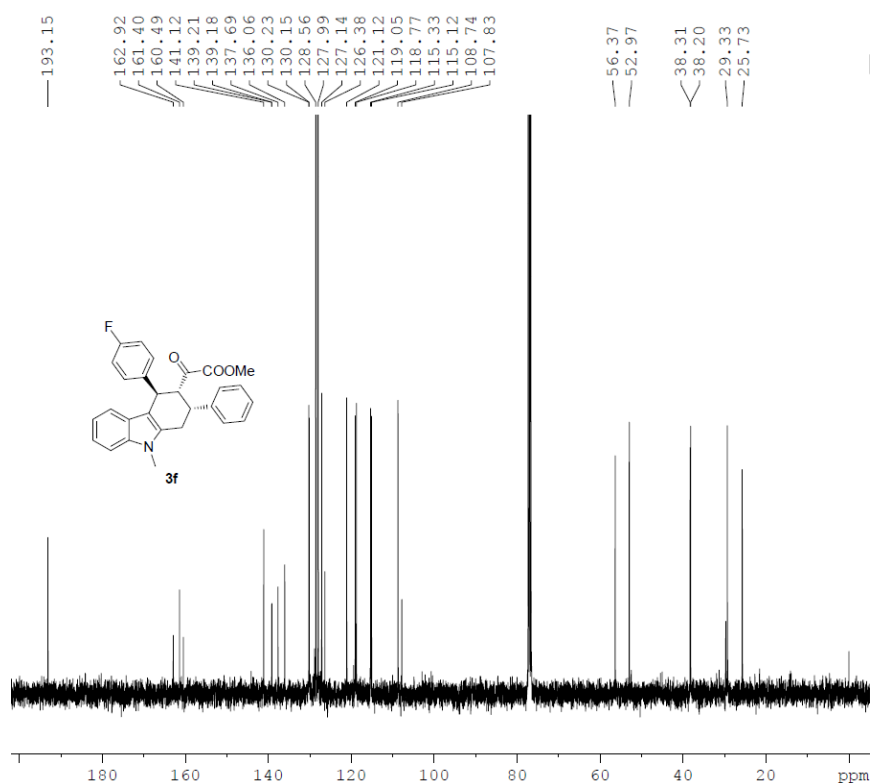
NAME      bl-425-2
EXPNO     1
PROCNO    1
Date_     20131104
Time      23.19
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8223.605 Hz
FIDRES     0.125493 Hz
AQ         3.9846387 sec
RG         203
DW         60.800 usec
DE         6.50 usec
TE         296.8 K
D1         1.00000000 sec
TD0        1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.20 usec
PL1       -1.00 dB
PL1W      14.13538074 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

NAME      bl-425-2
EXPNO     12
PROCNO    1
Date_     20131104
Time      23.50
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         24036
SOLVENT   CDCl3
NS         432
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         298.1 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1

```

```

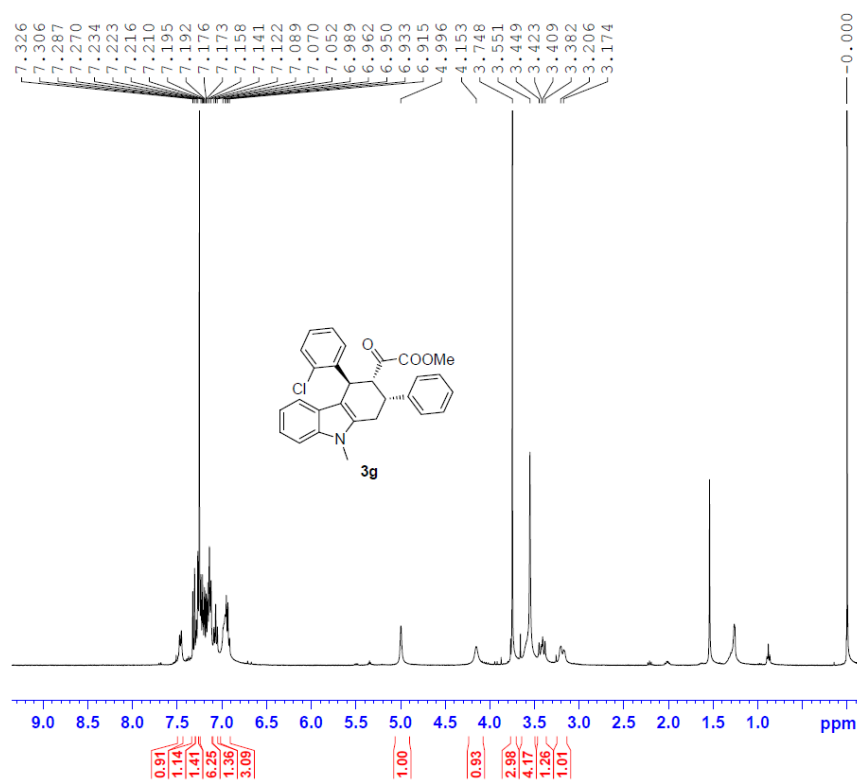
===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
PL1W      43.95565796 W
SFO1      100.6228298 MHz

```

```

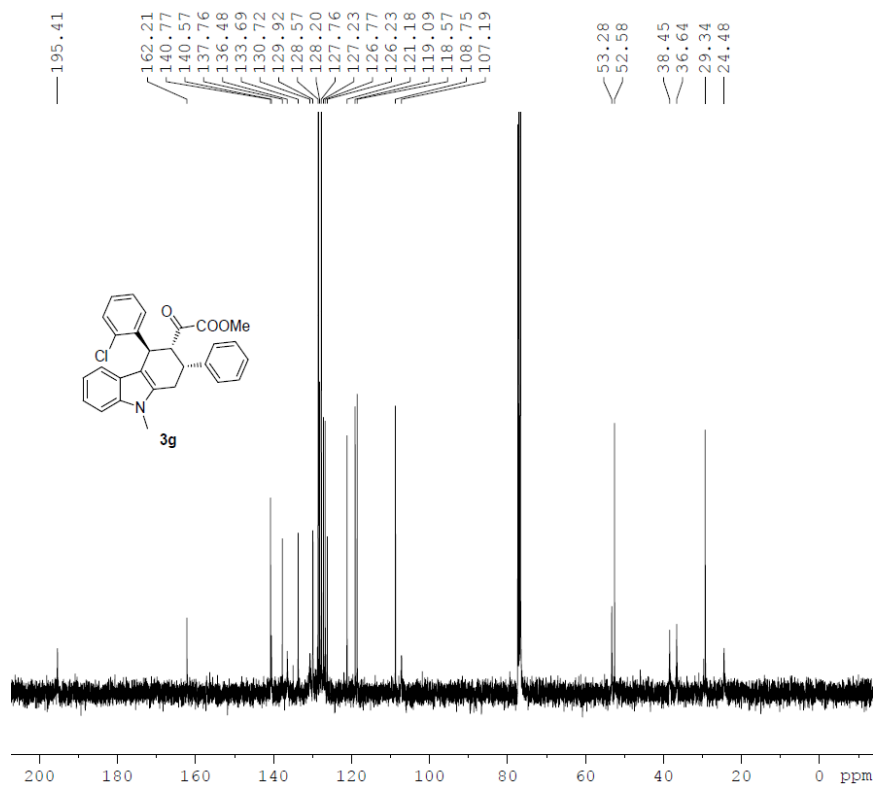
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       -1.00 dB
PL12      14.65 dB
PL13      14.60 dB
PL2W      14.13538074 W
PL12W     0.38486424 W
PL13W     0.38932070 W
SFO2      400.1316005 MHz
SI        32768
SF        100.6127693 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```



NAME b1-377-2
EXPNO 20
PROCNO 1
Date_ 20131104
Time_ 22.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125493 Hz
AQ 3.9846397 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
D10 1

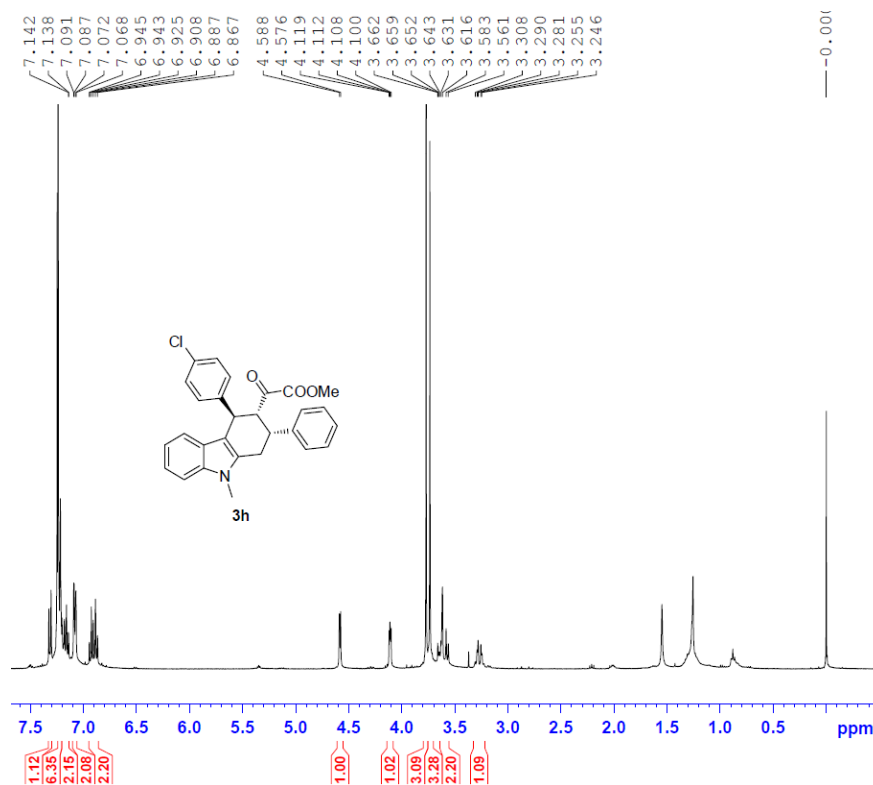
===== CHANNEL f1 =====
NUC1 1H
P1 13.20 usec
PL1 -1.00 dB
PL1W 14.13538074 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME b1-377-2
EXPNO 11
PROCNO 1
Date_ 20130910
Time_ 22.54
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 24036
SOLVENT CDCl3
NS 607
DS 4
SWH 24038.461 Hz
FIDRES 1.000102 Hz
AQ 0.4999988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.7 K
D1 1.50000000 sec
D11 0.03000000 sec
D10 1

===== CHANNEL f1 =====
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
PL1W 34.91522217 W
SFO1 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.00 dB
PL13 120.00 dB
PL2W 22.40306854 W
PL12W 0.22403068 W
PL13W 0.00000000 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

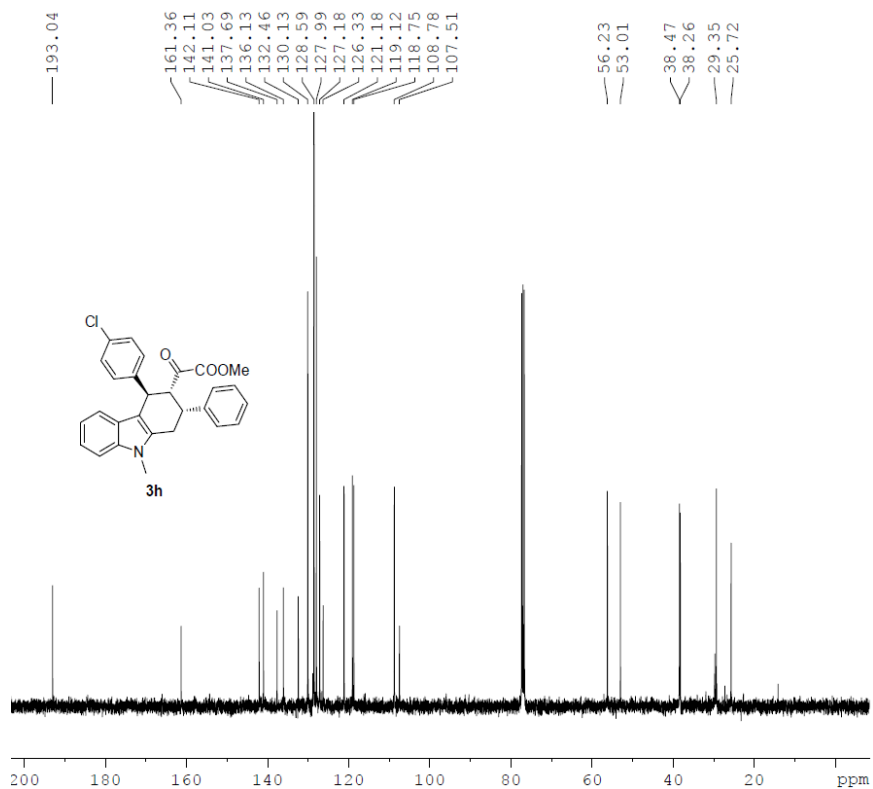


```

NAME          b1-421-2
EXPNO         10
PROCNO        1
Date_         20131104
Time_         23.13
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG            181
DW            60.800 usec
DE            6.50 usec
TE            297.1 K
D1            1.00000000 sec
TD0           1
  
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            13.20 usec
PL1           -1.00 dB
PL1W          14.13538074 W
SFO1          400.1324710 MHz
SI            32768
SF            400.1300097 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



```

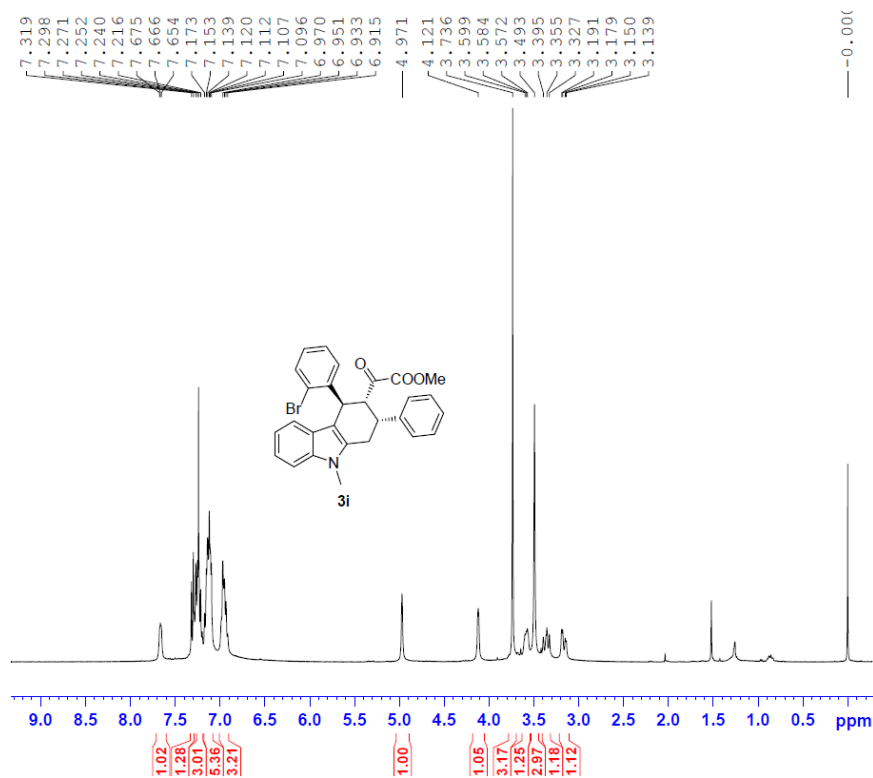
NAME          b1-421-2
EXPNO         12
PROCNO        1
Date_         20131104
Time_         23.26
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            24036
SOLVENT       CDCl3
NS            451
DS            4
SWH           24038.461 Hz
FIDRES        1.000102 Hz
AQ            0.4999988 sec
RG            203
DW            20.800 usec
DE            6.50 usec
TE            297.7 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0           1
  
```

```

===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
PL1           -1.00 dB
PL1W          43.95565796 W
SFO1          100.6228298 MHz
  
```

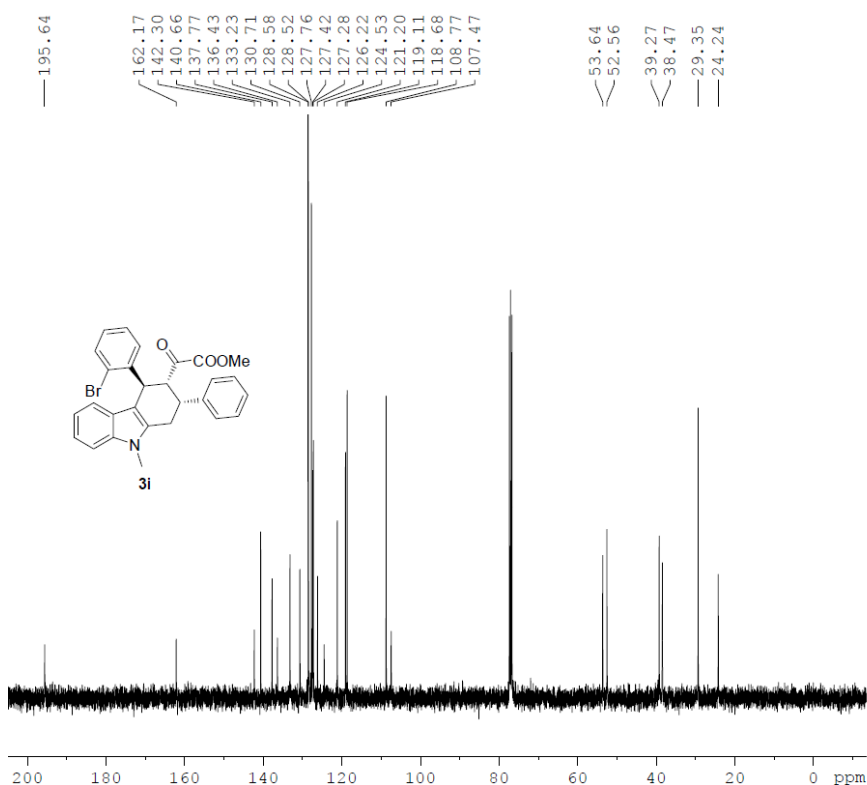
```

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           -1.00 dB
PL12          14.65 dB
PL13          14.60 dB
PL12W         14.13538074 W
PL12W         0.38486424 W
PL13W         0.38932070 W
SFO2          400.1316005 MHz
SI            32768
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```



NAME b1-474-1
 EXPNO 10
 PROCNO 1
 Date_ 20131207
 Time_ 19.34
 INSTRUM spect
 PROBHD 5 mm FAPBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125493 Hz
 AQ 3.9846387 sec
 RG 144
 DW 60.800 usec
 DE 6.50 usec
 TE 299.4 K
 D1 1.00000000 sec
 TD0 1

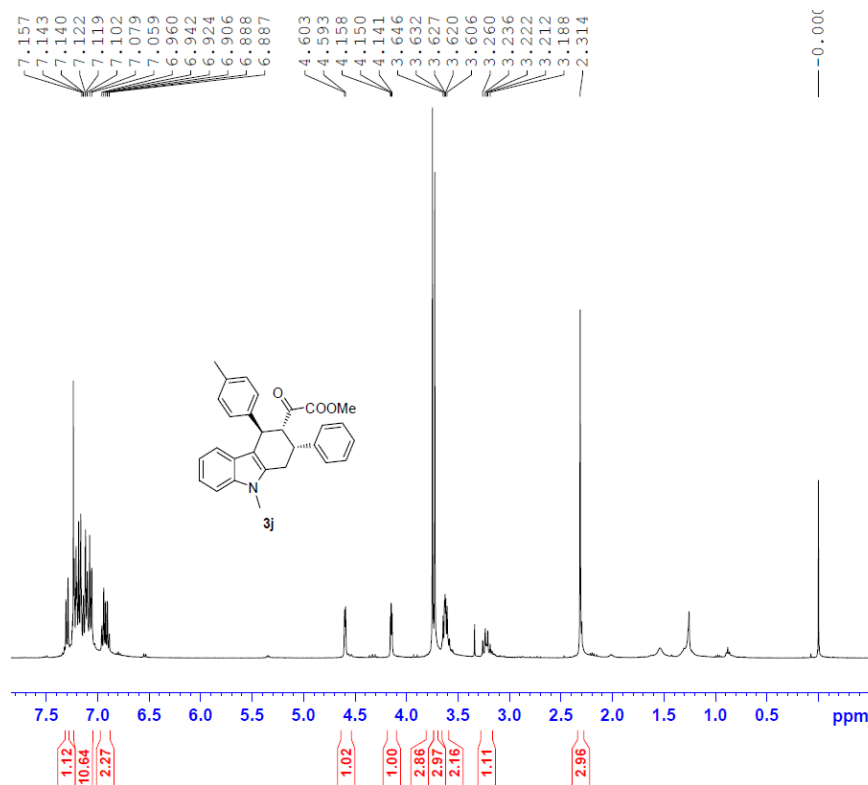
===== CHANNEL f1 =====
 NUC1 ¹H
 P1 13.20 usec
 PL1 -1.00 dB
 PL1W 14.13538074 W
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1300125 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME b1-474-1
 EXPNO 11
 PROCNO 1
 Date_ 20131207
 Time_ 19.41
 INSTRUM spect
 PROBHD 5 mm FAPBO BB-
 PULPROG zgpg30
 TD 24036
 SOLVENT CDCl3
 NS 162
 DS 4
 SWH 24038.461 Hz
 FIDRES 1.000102 Hz
 AQ 0.4999988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 299.5 K
 D1 1.50000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 10.00 usec
 PL1 -1.00 dB
 PL1W 43.95565796 W
 SFO1 100.6228298 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 14.65 dB
 PL13 14.60 dB
 PL2W 14.13538074 W
 PL12W 0.38486424 W
 PL13W 0.38932070 W
 SFO2 400.1316005 MHz
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



```

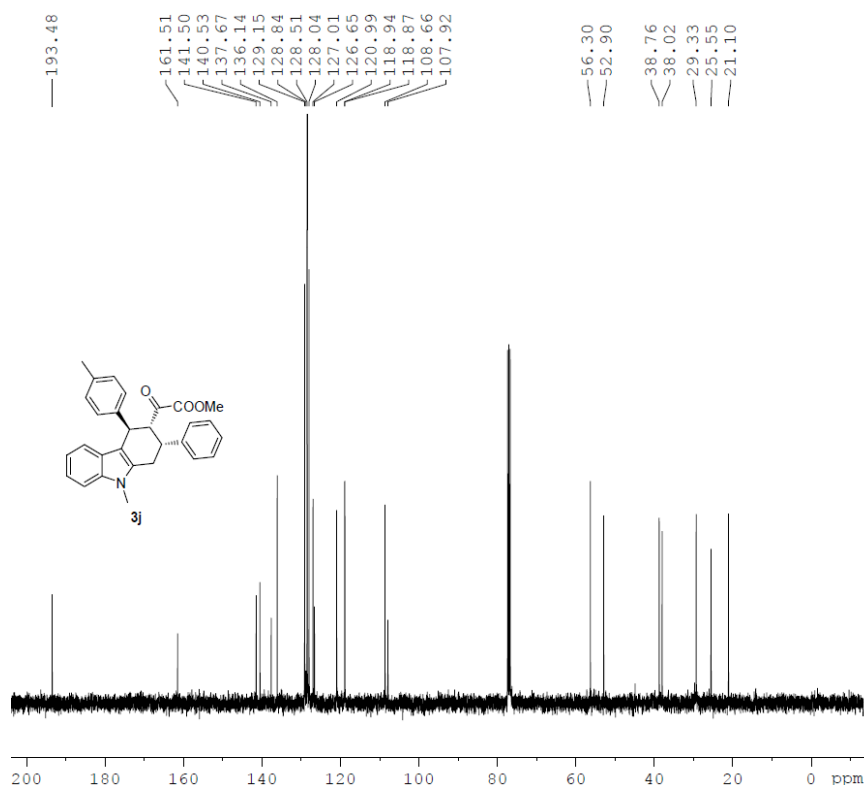
NAME          bl-445-1
EXPNO         10
PROCNO        1
Date_         20131102
Time          20.28
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG            128
DW            60.800 usec
DE            6.50 usec
TE            297.5 K
D1            1.00000000 sec
TD0           1

```

```

===== CHANNEL f1 =====
NUC1          1H
P1            13.20 usec
PL1           -1.00 dB
PL1W          14.13538074 W
SFO1          400.1324710 MHz
SI            32768
SF            400.1300140 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

```



```

NAME          bl-445-1
EXPNO         12
PROCNO        1
Date_         20131102
Time          20.40
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            24036
SOLVENT       CDCl3
NS            206
DS            4
SWH           24038.461 Hz
FIDRES        1.000102 Hz
AQ            0.4999988 sec
RG            203
DW            20.800 usec
DE            6.50 usec
TE            297.5 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0           1

```

```

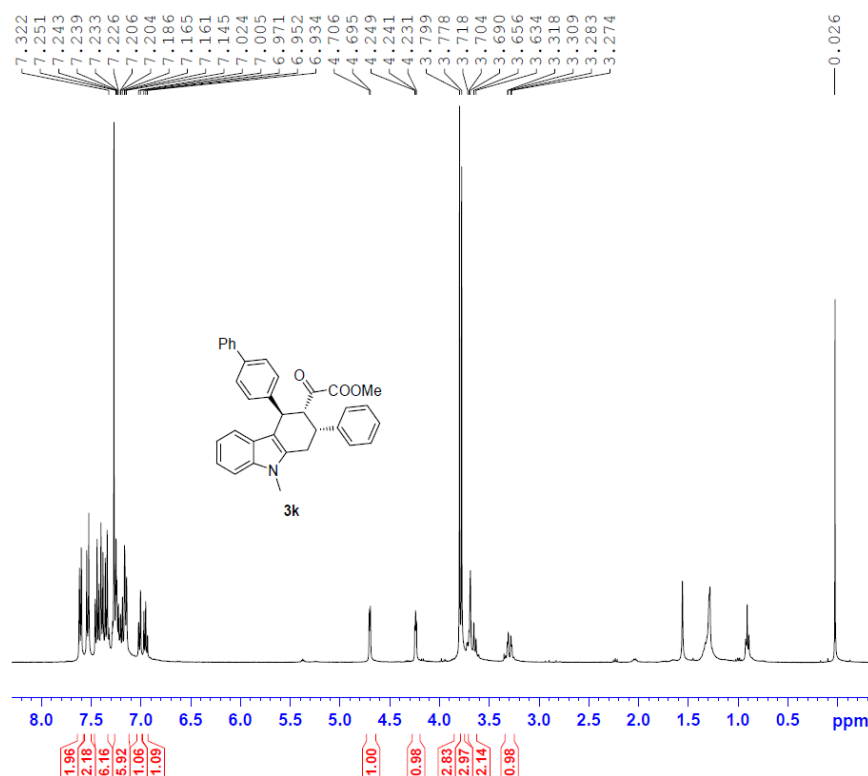
===== CHANNEL f1 =====
NUC1          13C
P1            10.00 usec
PL1           -1.00 dB
PL1W          43.95565796 W
SFO1          100.6228298 MHz

```

```

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           -1.00 dB
PL12          14.65 dB
PL13          14.60 dB
PL2W          14.13538074 W
PL12W         0.38486424 W
PL13W         0.38932070 W
SFO2          400.1316005 MHz
SI            32768
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```

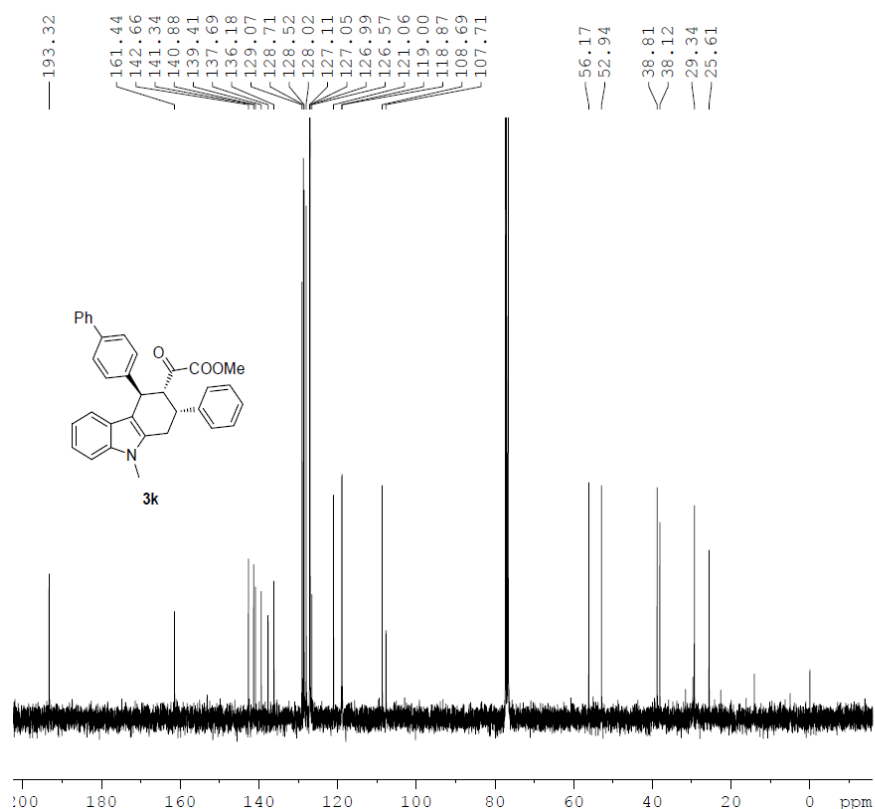


```

NAME      b1-445-2
EXPNO     10
PROCNO    1
Date_     20131102
Time      18.03
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         181
DW         60.800 usec
DE         6.50 usec
TE         297.3 K
D1         1.00000000 sec
D11        1
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.20 usec
PL1       -1.00 dB
PL1W      14.13538074 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



```

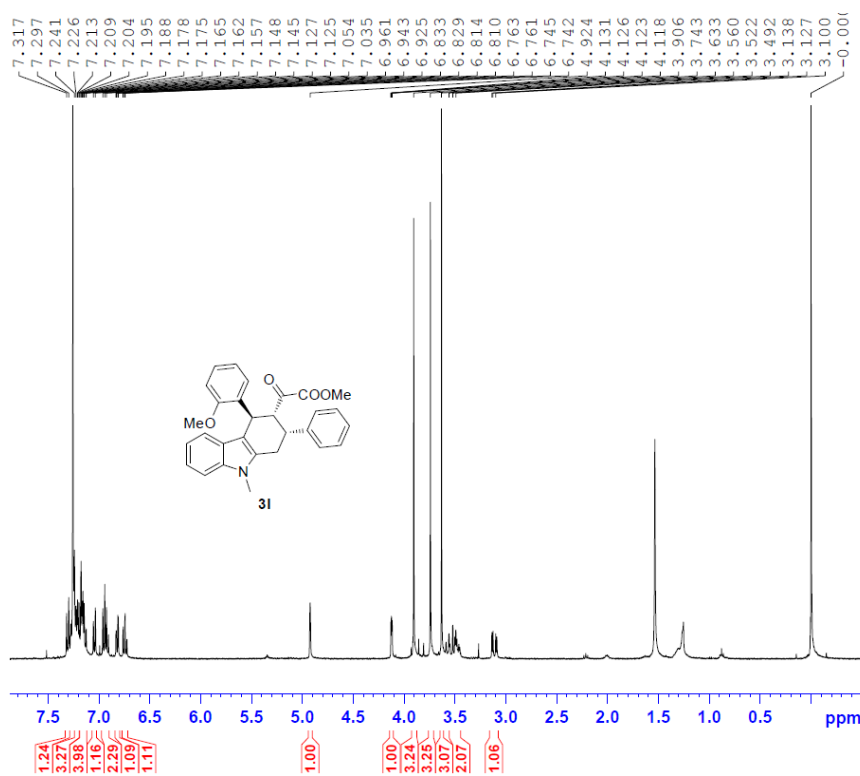
NAME      b1-445-2-C13
EXPNO     10
PROCNO    1
Date_     20131102
Time      20.24
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         24036
SOLVENT   CDCl3
NS         396
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         298.7 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
PL1W      43.95565796 W
SFO1      100.6228298 MHz
  
```

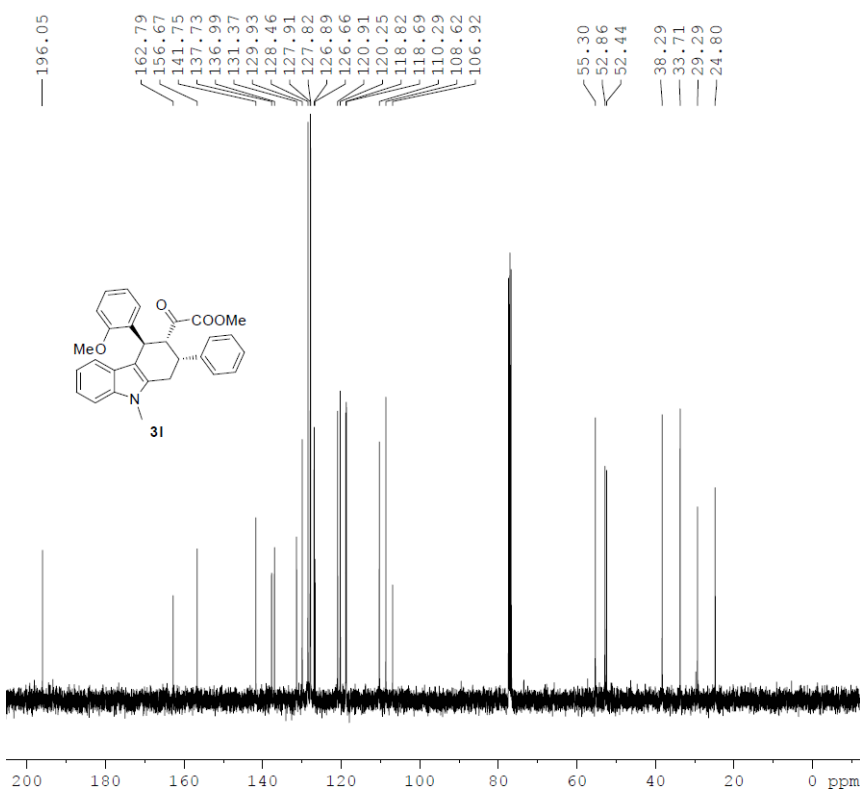
```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       -1.00 dB
PL12      14.65 dB
PL13      14.60 dB
PL2W      14.13538074 W
PL12W     0.38486424 W
PL13W     0.38932070 W
SFO2      400.1316005 MHz
SI        32768
SF        100.6127701 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```



NAME bl-369-2
EXPNO 10
PROCNO 1
Date 20131029
Time 18.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

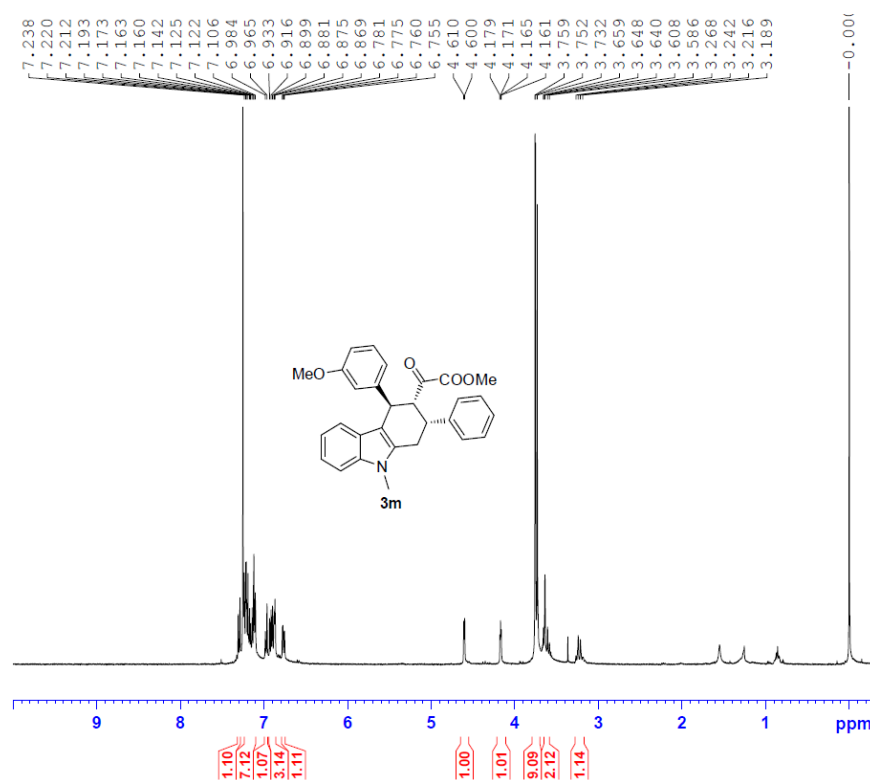
===== CHANNEL f1 =====
NUC1 1H
P1 13.20 usec
PL1 -1.00 dB
PL1W 14.13538074 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME bl-369-2
EXPNO 14
PROCNO 1
Date 20130905
Time 23.03
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 72112
SOLVENT CDCl3
NS 245
DS 4
SWH 24038.461 Hz
FIDRES 0.333349 Hz
AQ 1.4999796 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 292.5 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

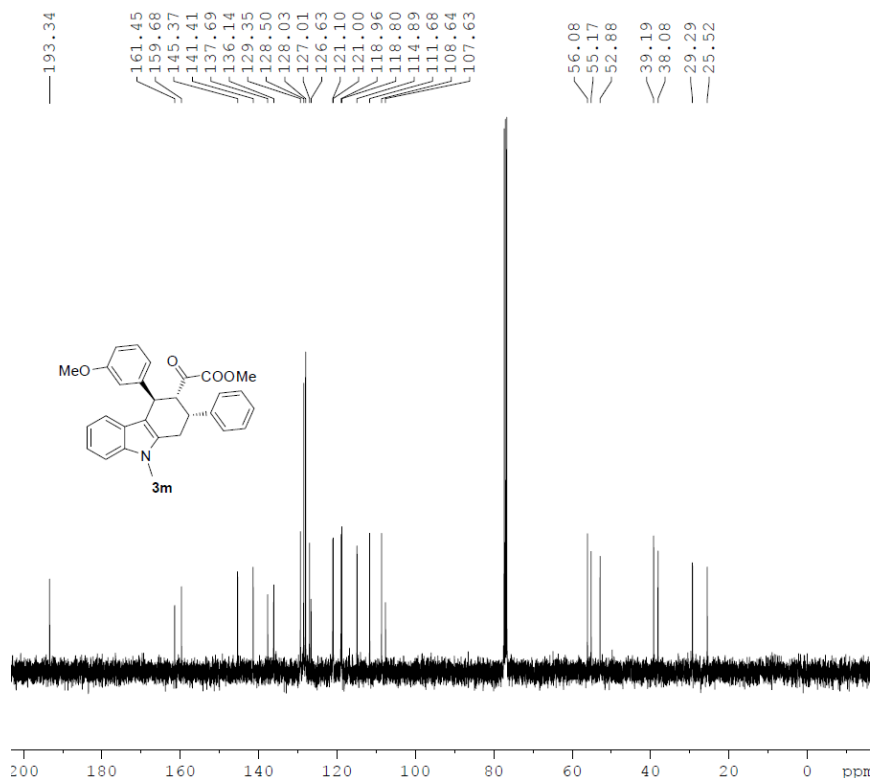
===== CHANNEL f1 =====
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
PL1W 34.91522217 W
SFO1 100.6228299 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -9.00 dB
PL12 17.00 dB
PL13 120.00 dB
PL2W 22.40306854 W
PL12W 0.22403069 W
PL13W 0.00000000 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



NAME b1-329-1-1122
EXPNO 10
PROCNO 1
Date_ 20131122
Time_ 12.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846379 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.1 K
DL 1.00000000 sec
TD0 1

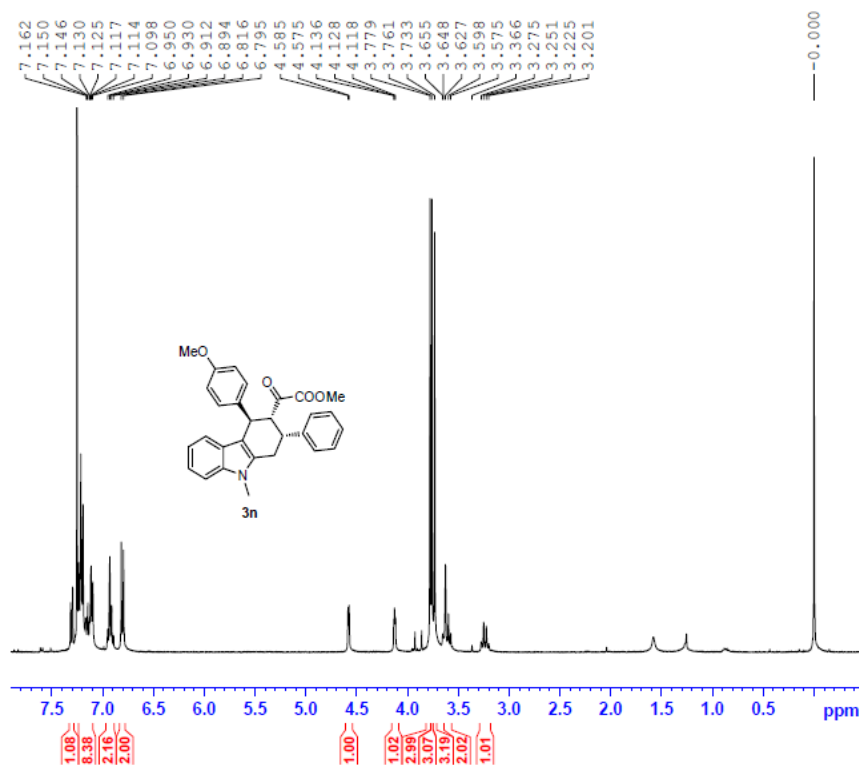
===== CHANNEL f1 =====
NUC1 1H
P1 13.20 usec
PL1 1.00 dB
PL1W 14.13538074 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME b1-329-1
EXPNO 13
PROCNO 1
Date_ 20130803
Time_ 20.00
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 72112
SOLVENT CDCl3
NS 216
DS 4
SWH 24038.461 Hz
FIDRES 0.333349 Hz
AQ 1.4999796 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 293.5 K
D1 0.50000000 sec
D11 0.03000000 sec
TD0 1

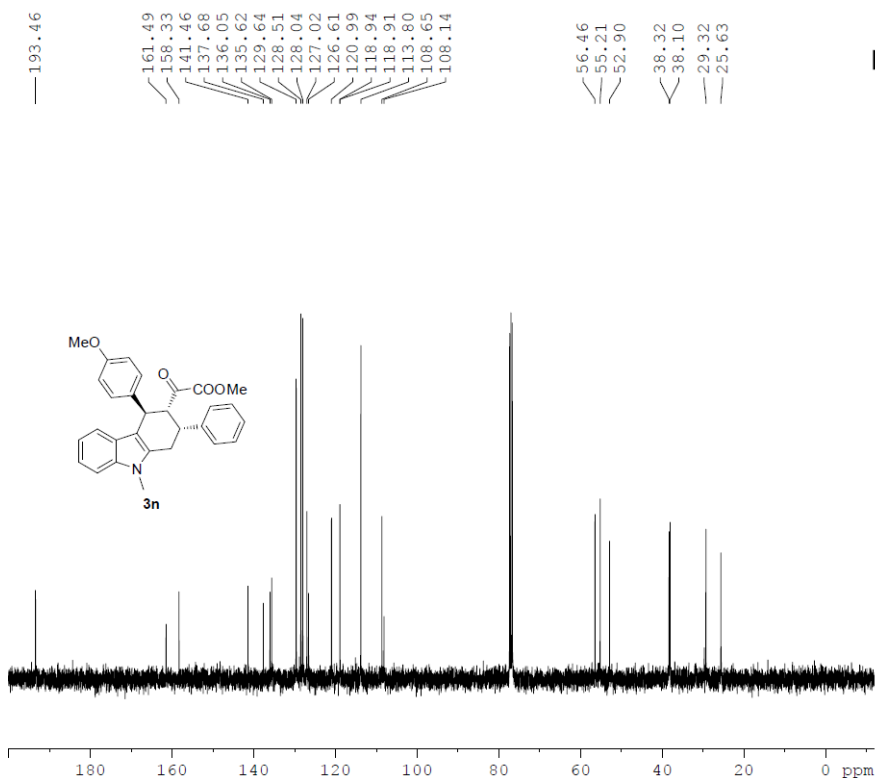
===== CHANNEL f1 =====
NUC1 13C
P1 11.00 usec
PL1 0.00 dB
PL1W 34.91522217 W
SFO1 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.00 dB
PL13 120.00 dB
PL12W 22.40306854 W
PL13W 0.22403069 W
PL13W 0.00000000 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



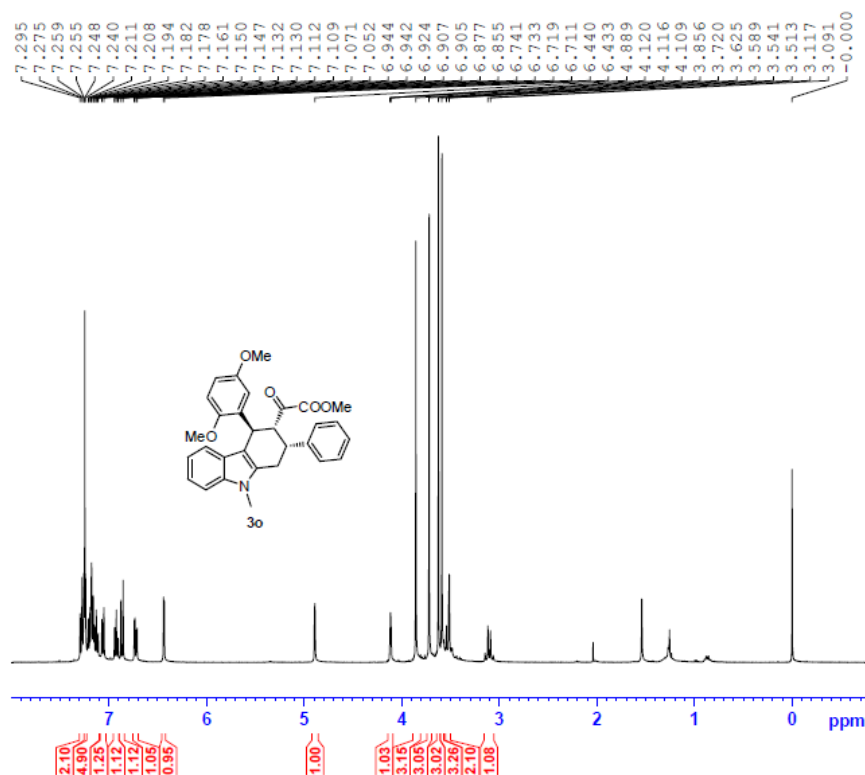
NAME b1-354-2-131108
EXPNO 10
PROCNO 1
Date_ 20131108
Time 17.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125489 Hz
AQ 3.9846287 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.20 usec
PL1 -1.00 dB
PL1W 14.13538074 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



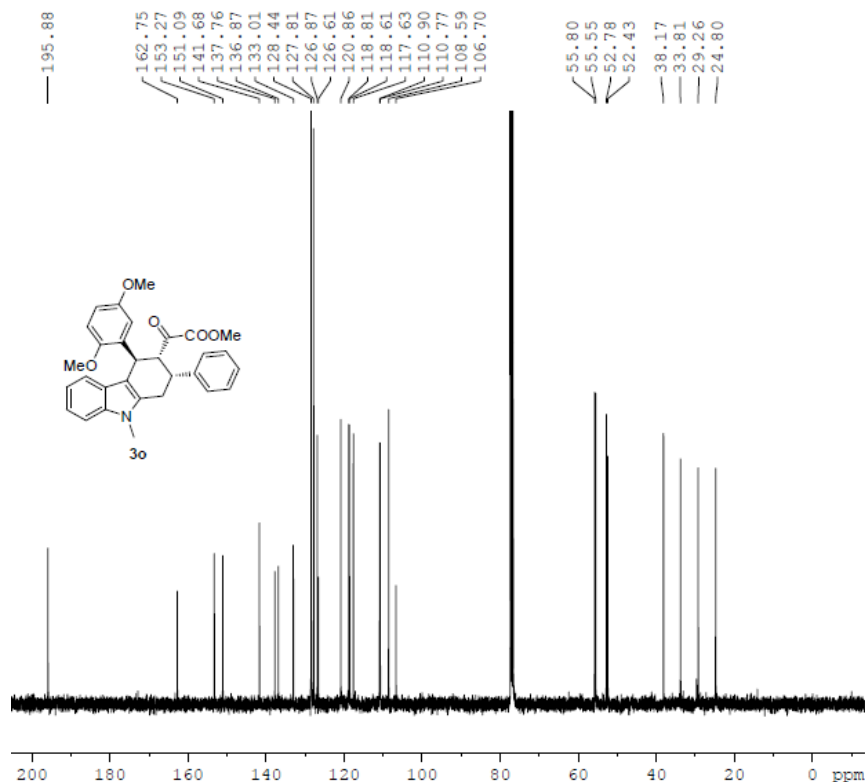
NAME b1-471-1-C13
EXPNO 10
PROCNO 1
Date_ 20131207
Time 19.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 24036
SOLVENT CDCl3
NS 125
DS 4
SWH 24038.461 Hz
FIDRES 1.000102 Hz
AQ 0.4999988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 -1.00 dB
PL1W 43.95565796 W
SFO1 100.6228298 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.65 dB
PL13 14.60 dB
PL2W 14.13538074 W
PL12W 0.38486424 W
PL13W 0.38932070 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



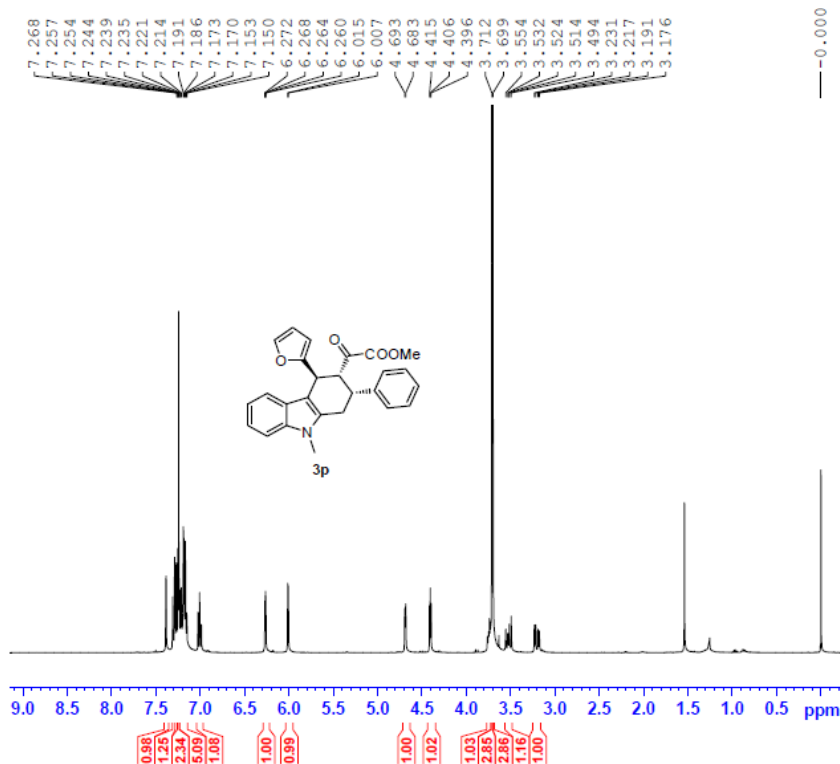
NAME b1-429-1
 EXPNO 10
 PROCNO 1
 Date_ 20131024
 Time_ 20.24
 INSTRUM spect
 PROBHD 5 mm FAPBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125488 Hz
 AQ 2.9846387 sec
 RG 161
 DW 60.300 usec
 DE 6.50 usec
 TE 298.1 K
 DL 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 13.20 usec
 PL1 -1.00 dB
 PL1W 14.18538074 W
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 FC 1.00



NAME b1-429-1
 EXPNO 11
 PROCNO 1
 Date_ 20131024
 Time_ 21.20
 INSTRUM spect
 PROBHD 5 mm FAPBO BB-
 PULPROG zgpg30
 TD 24036
 SOLVENT CDCl3
 NS 324
 DS 4
 SWH 24038.461 Hz
 FIDRES 1.000102 Hz
 AQ 0.4999988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 299.2 K
 DL 1.50000000 sec
 D11 0.02000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -1.00 dB
 PL1W 42.95565796 W
 SFO1 100.6228298 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL2W 14.65 dB
 PL3 14.60 dB
 PL12W 14.18538074 W
 PL12W 0.38486424 W
 PL13W 0.38932070 W
 SFO2 400.1316005 MHz
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 1.40

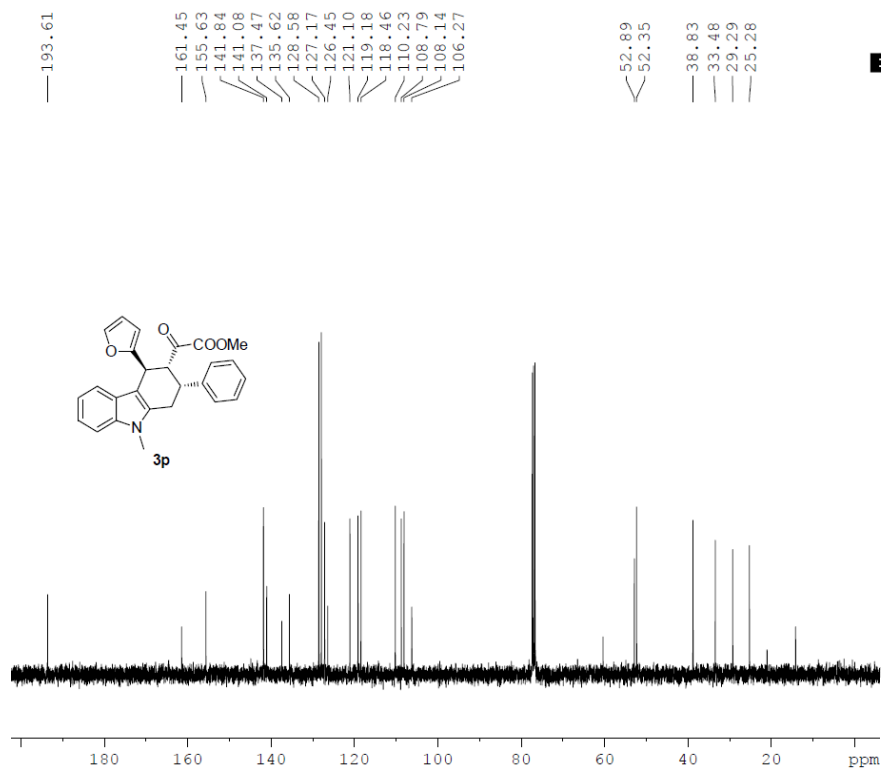


```

NAME      bl-448-1
EXPNO     1
PROCNO    1
Date_     20131102
Time      20.35
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zg30
TD         65536
SOLVENT    CDCl3
NS         16
DS         2
SWH         8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         161
SW         60.800 usec
DE         6.50 usec
TE         297.3 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         19.20 usec
PL1        -1.00 dB
PL1W       14.13538074 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300112 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

```



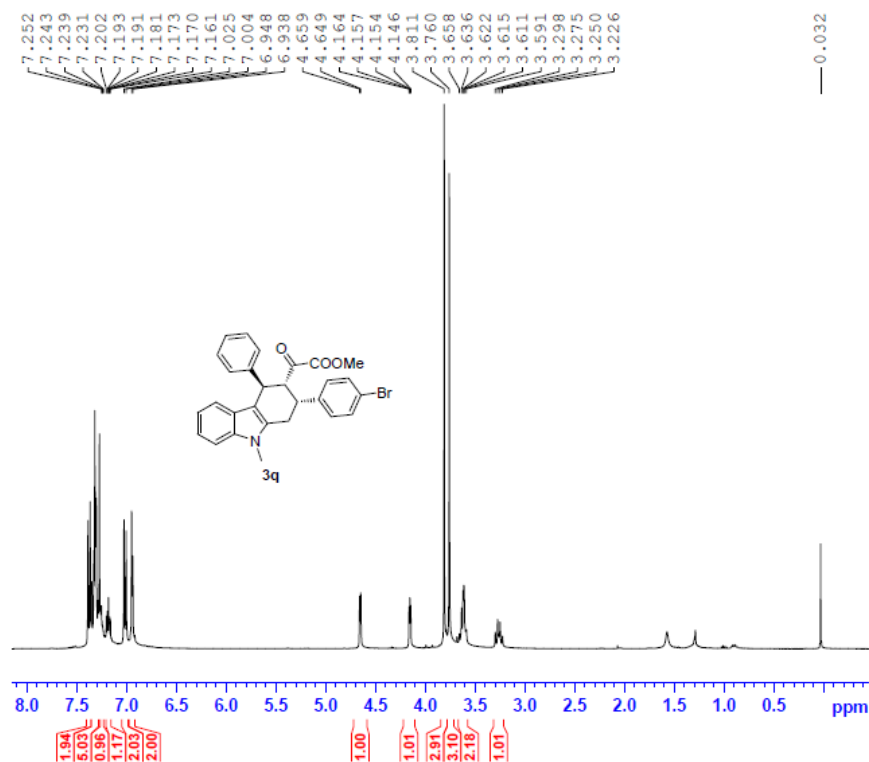
```

NAME      bl-448-1-C13
EXPNO     30
PROCNO    1
Date_     20131103
Time      15.33
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD         24036
SOLVENT    CDCl3
NS         117
DS         4
SWH         24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         297.2 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        -1.00 dB
PL1W       43.95565796 W
SFO1       100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -1.00 dB
PL2W       14.65 dB
PL13       14.60 dB
PL12W      14.13538074 W
PL12W      0.38486424 W
PL13W      0.38932070 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40

```

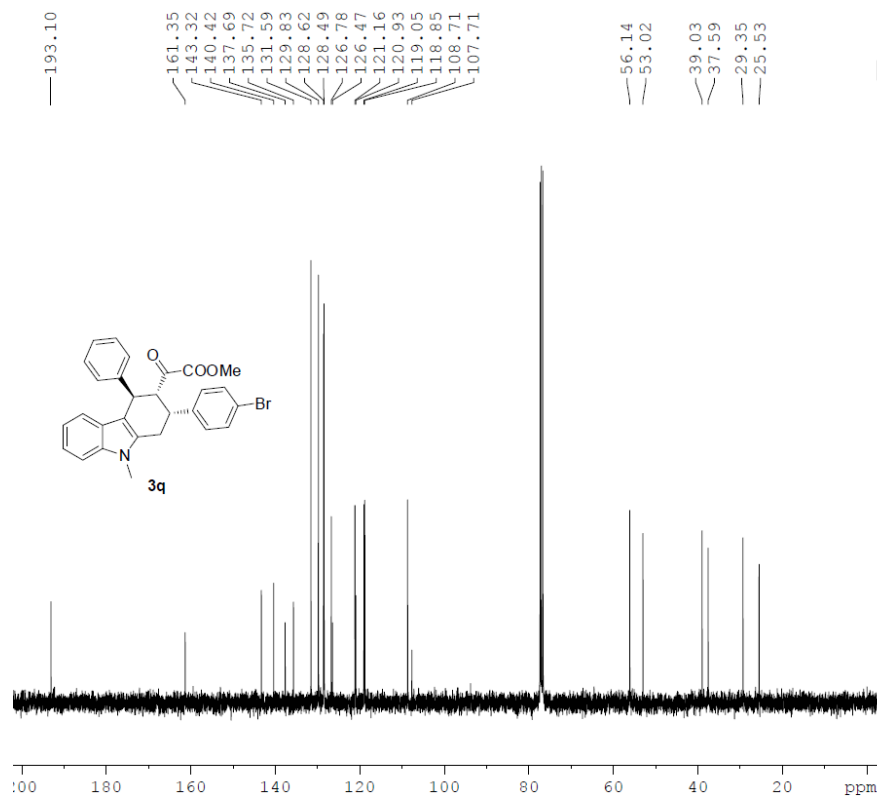


BRUKER

```

NAME      bl-450-2
EXPNO     10
PROCNO    1
Date_     20131102
Time      17.57
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         16
DS         2
SWH        8223.685 Hz
FIDRES     0.125489 Hz
AQ         3.9846387 sec
RG         128
DE         60.800 usec
TE         6.50 usec
TE         297.3 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         13.20 usec
PL1        -1.00 dB
PL1W       14.13538074 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



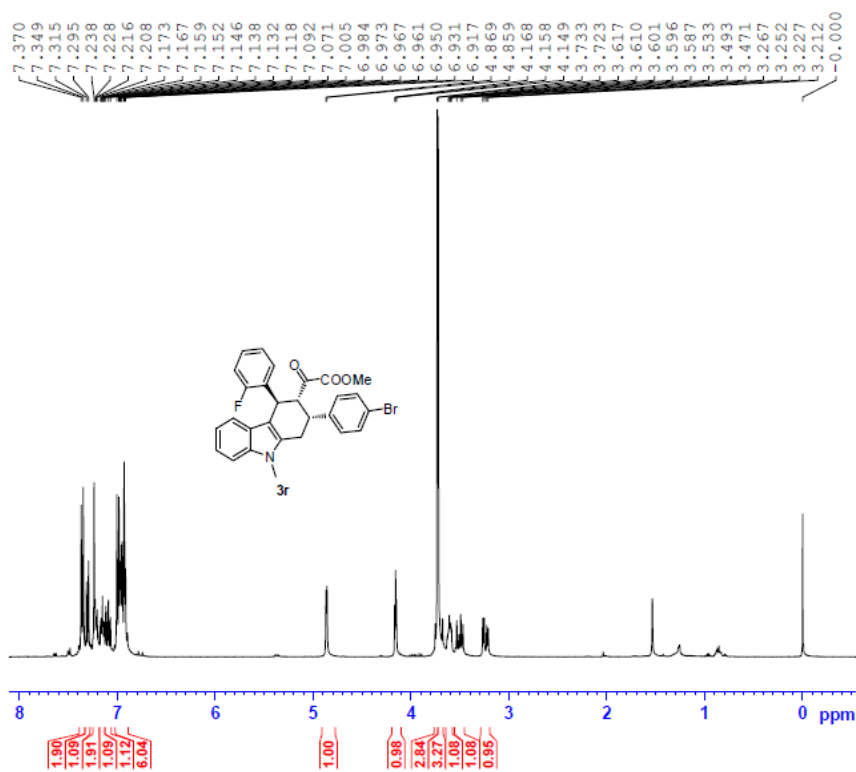
BRUKER

```

NAME      bl-450-2
EXPNO     12
PROCNO    1
Date_     20131102
Time      18.13
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD         24036
SOLVENT    CDCl3
NS         234
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DE         20.800 usec
TE         6.50 usec
TE         298.3 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        -1.00 dB
PL1W       43.95565796 W
SFO1       100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -1.00 dB
PL12       14.65 dB
PL13       14.60 dB
PL2W       14.13538074 W
PL12W      0.38486424 W
PL13W      0.38932070 W
SFO2       400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

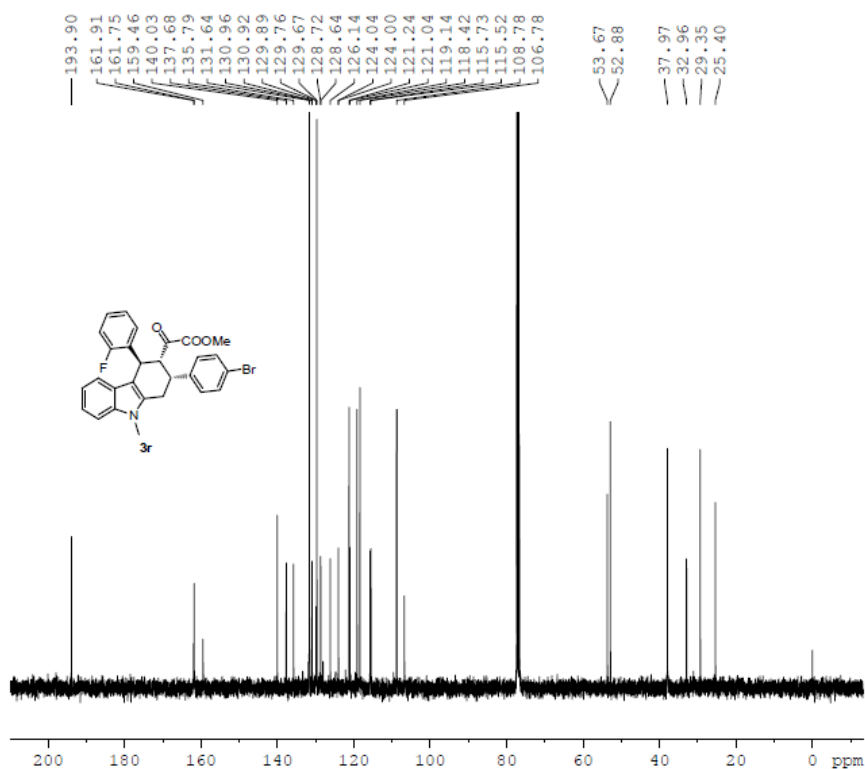


```

NAME      bl-451-1
EXPNO     12
PROCNO    1
Date_     20191102
Time      16.07
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8223.685 Hz
FIDRES     0.125482 Hz
AQ         3.984637 sec
RG         128
DW         60.800 usec
DE         6.50 usec
TE         297.1 K
D1         1.00000000 sec
TD0        1
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        12.20 usec
PL1       -1.00 dB
PL1W      14.13538074 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300137 MHz
WDW        EM
SSB        0
LB         0.40 Hz
GB         0
PC         1.00
  
```



```

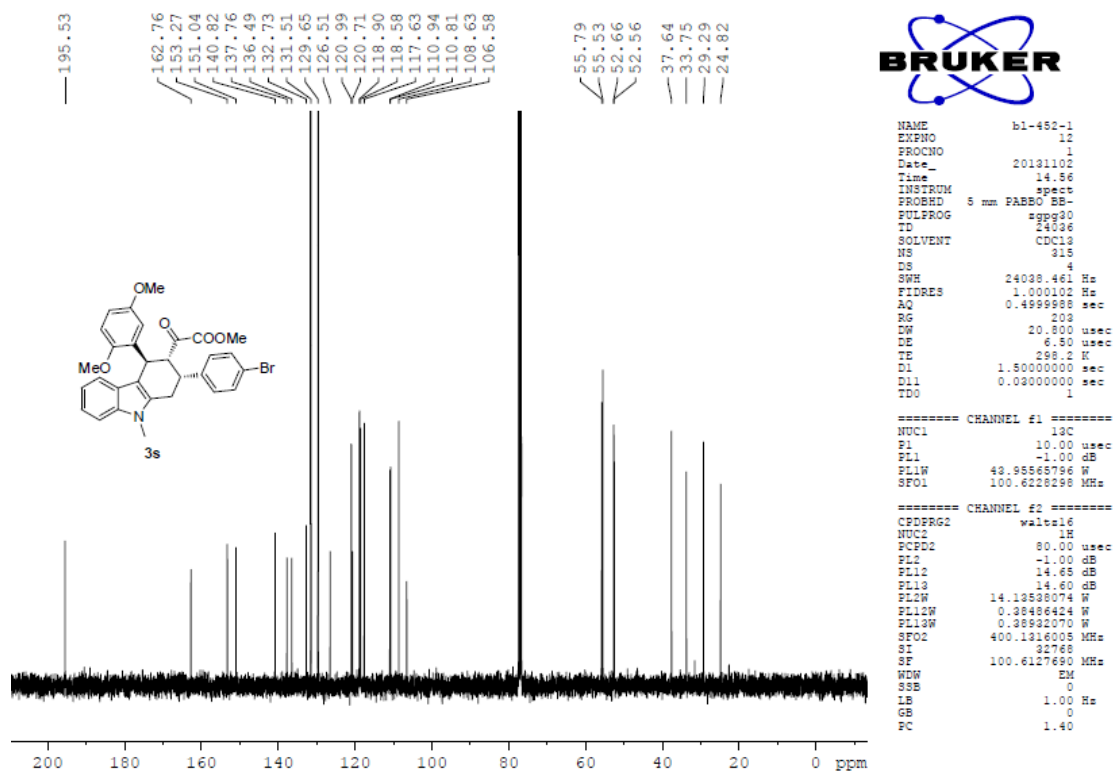
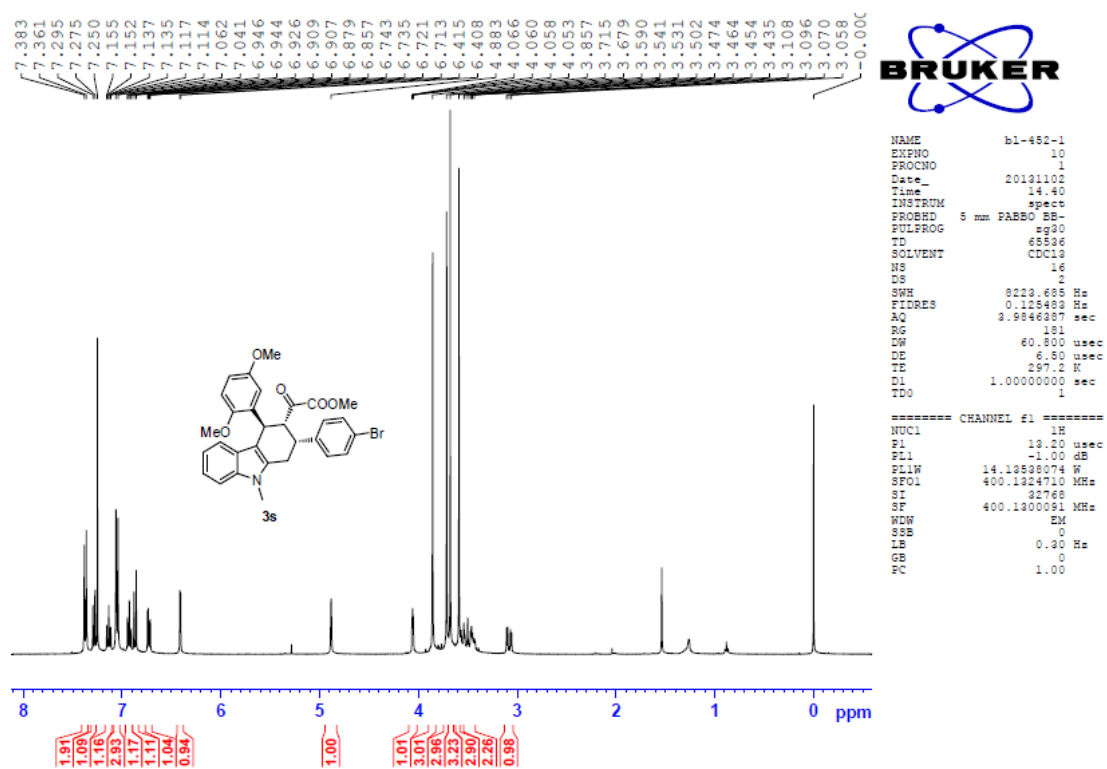
NAME      bl-451-1-C13
EXPNO     10
PROCNO    1
Date_     20191102
Time      17.51
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         24096
SOLVENT   CDCl3
NS         613
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         298.8 K
D1         1.50000000 sec
D11        0.03000000 sec
TD0        1
  
```

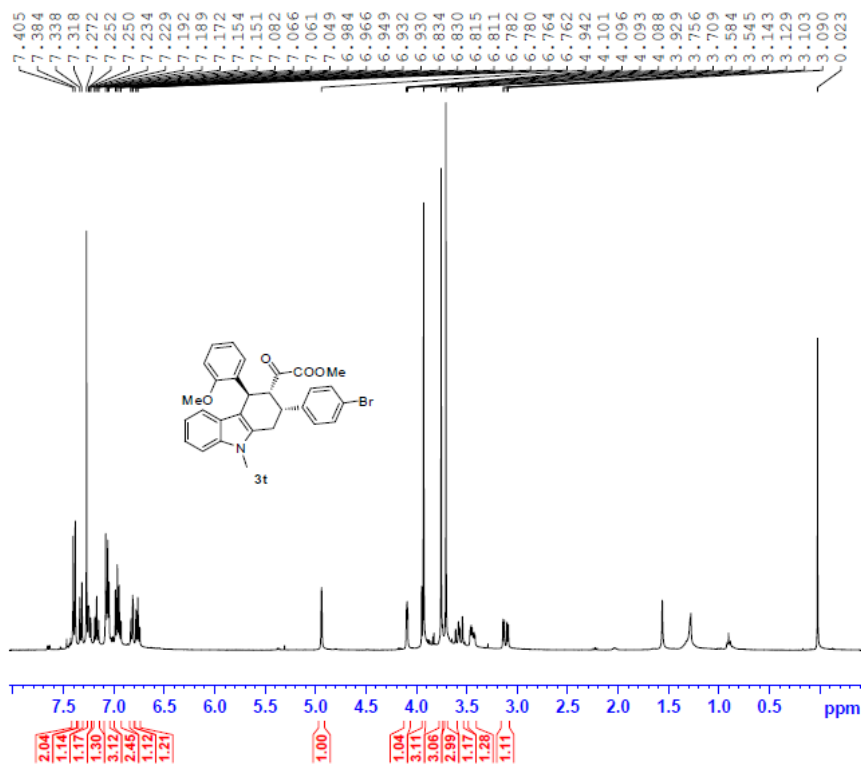
```

===== CHANNEL f1 =====
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
PL1W      43.95565796 W
SFO1      100.6228298 MHz
  
```

```

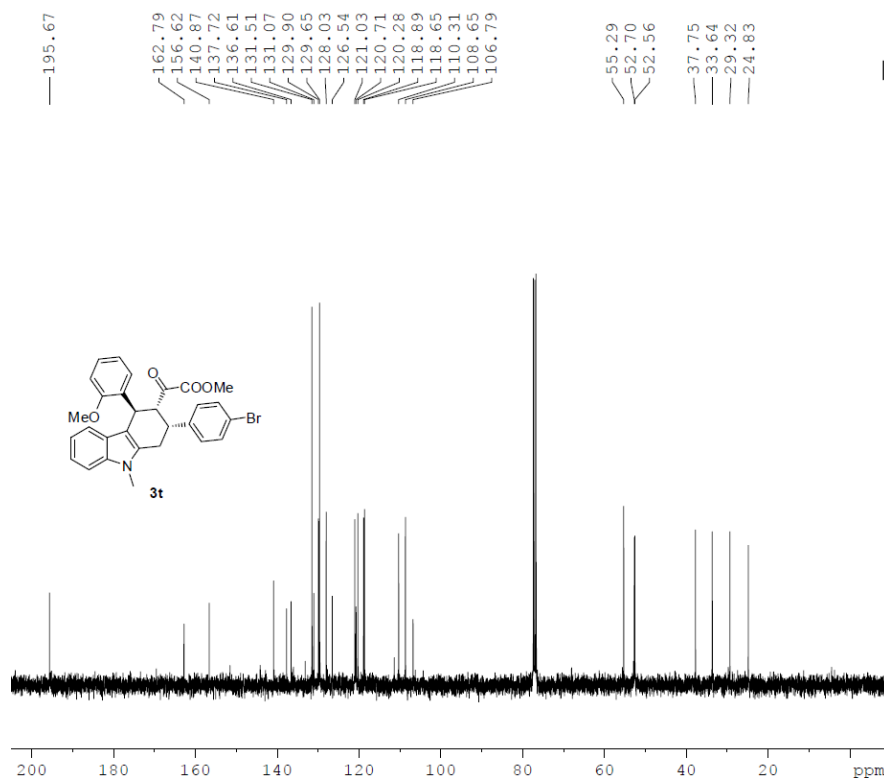
===== CHANNEL f2 =====
CQDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       -1.00 dB
PL12      24.65 dB
PL13      14.60 dB
PL12W     14.13538074 W
PL12W     0.38486424 W
PL13W     0.38932073 W
SFO2      400.1316005 MHz
SI         32768
SF         100.6127698 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```





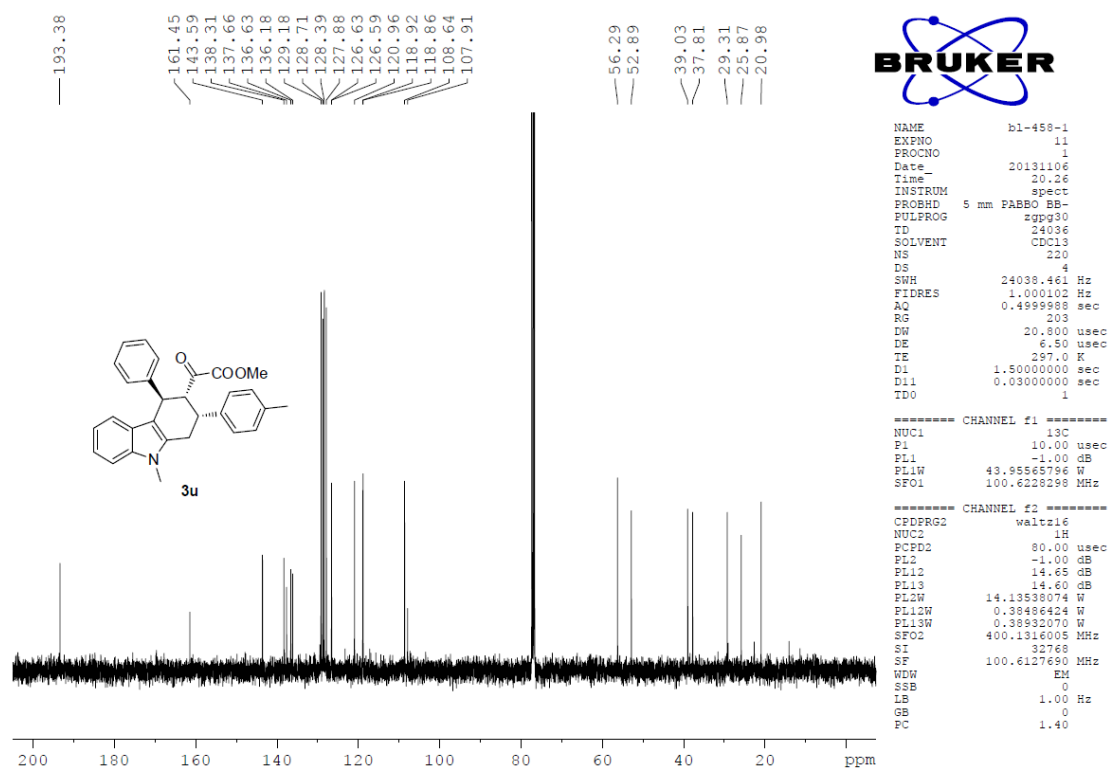
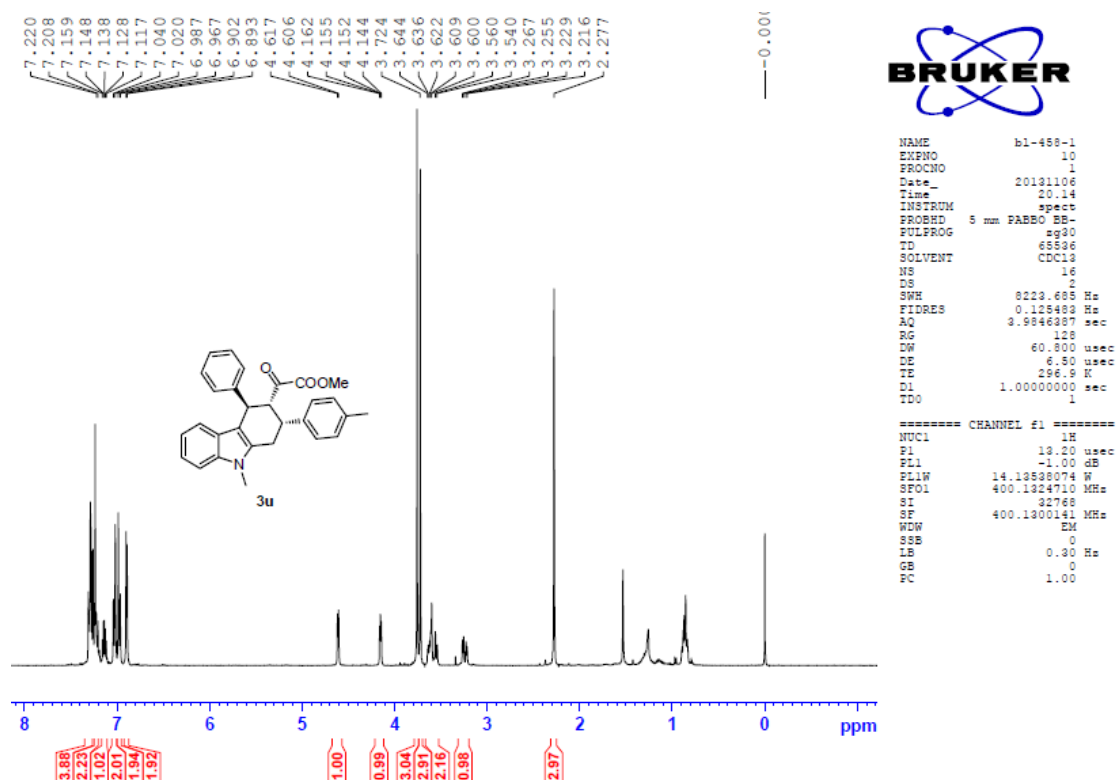
NAME bl-454-1
 EXPNO 10
 PROCNO 1
 Date_ 20131102
 Time 14.47
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8229.685 Hz
 FIDRES 0.125489 Hz
 AQ 2.9846387 sec
 RG 181
 DW 60.300 usec
 DE 6.50 usec
 TE 297.0 K
 DL 1.00000000 sec
 TDO 1

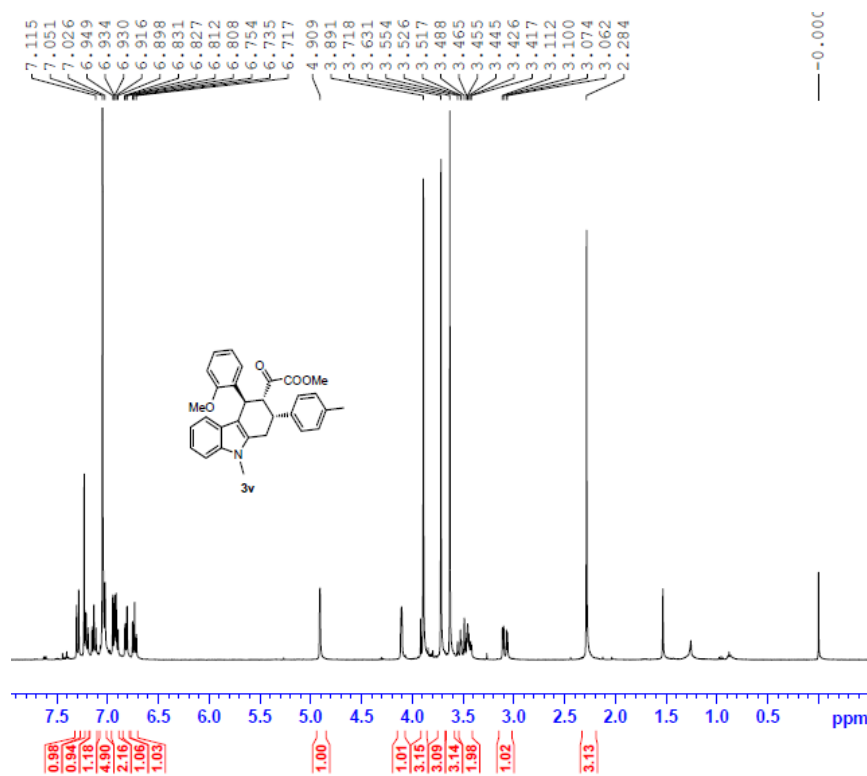
===== CHANNEL f1 =====
 NUC1 1H
 P1 13.20 usec
 PL1 -1.00 dB
 PL1W 14.13538074 W
 SF01 400.1324710 MHz
 SI 32768
 SF 400.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME bl-454-1
 EXPNO 12
 PROCNO 1
 Date_ 20131102
 Time 15.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 24036
 SOLVENT CDCl3
 NS 186
 DS 4
 SWH 24038.461 Hz
 FIDRES 1.000102 Hz
 AQ 0.4999988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 297.6 K
 DL 1.50000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -1.00 dB
 PL1W 43.95565796 W
 SF01 100.6228298 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 14.65 dB
 PL13 14.60 dB
 PL2W 14.13538074 W
 PL12W 0.38486424 W
 PL13W 0.38932070 W
 SF02 400.1316005 MHz
 SI 32768
 SF 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



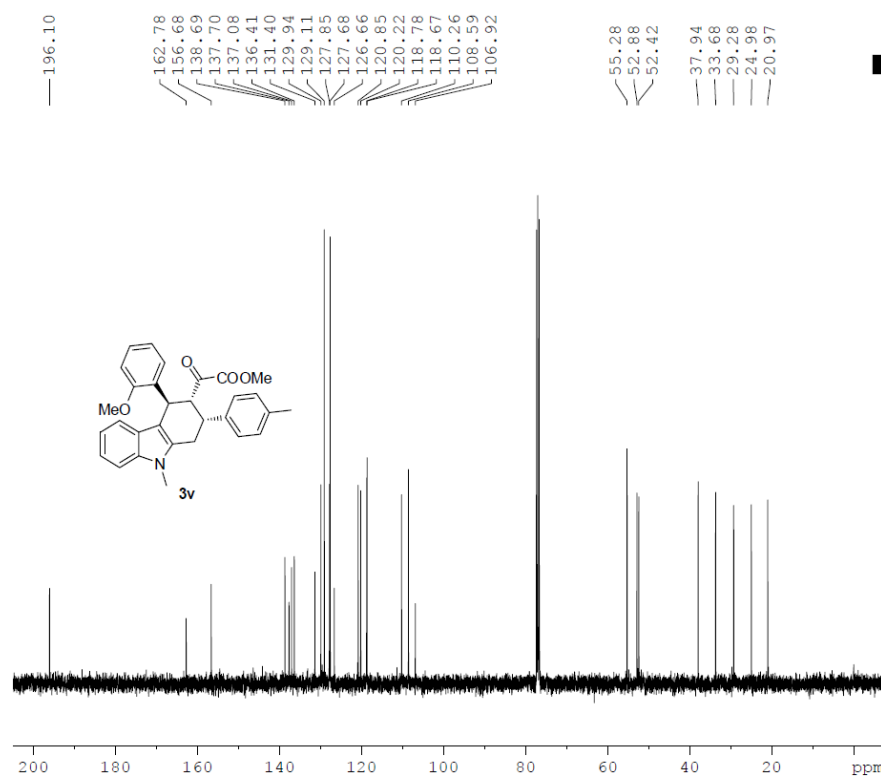


```

NAME      b1-460-1
EXPNO     10
PROCNO    1
Date_     20131106
Time      20.38
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        8123.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         114
DW         60.800 usec
DE         6.50 usec
TE         297.1 K
DL         1.00000000 sec
TDO        1
  
```

```

===== CHANNEL f1 =====
NUC1      1H
P1         13.20 usec
PL1        -1.00 dB
PL1W       14.13538074 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300164 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         1.00
PC         1.00
  
```



```

NAME      b1-460-1
EXPNO     11
PROCNO    1
Date_     20131106
Time      20.43
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         24036
SOLVENT   CDCl3
NS         345
DS         4
SWH        24038.461 Hz
FIDRES     1.000102 Hz
AQ         0.4999988 sec
RG         203
DW         20.800 usec
DE         6.50 usec
TE         299.1 K
DL         1.50000000 sec
D11        0.03000000 sec
TDO        1
  
```

```

===== CHANNEL f1 =====
NUC1      13C
P1         10.00 usec
PL1        -1.00 dB
PL1W       43.95565796 W
SFO1      100.6228298 MHz
  
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -1.00 dB
PL12       14.65 dB
PL13       14.60 dB
PL2W       14.13538074 W
PL12W      0.38496424 W
PL13W      0.38932070 W
SFO2      400.1316005 MHz
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```