# *Supporting Information*

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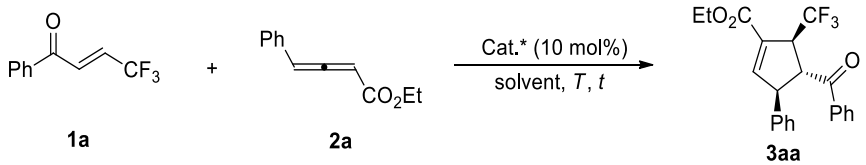
## 1. General Information

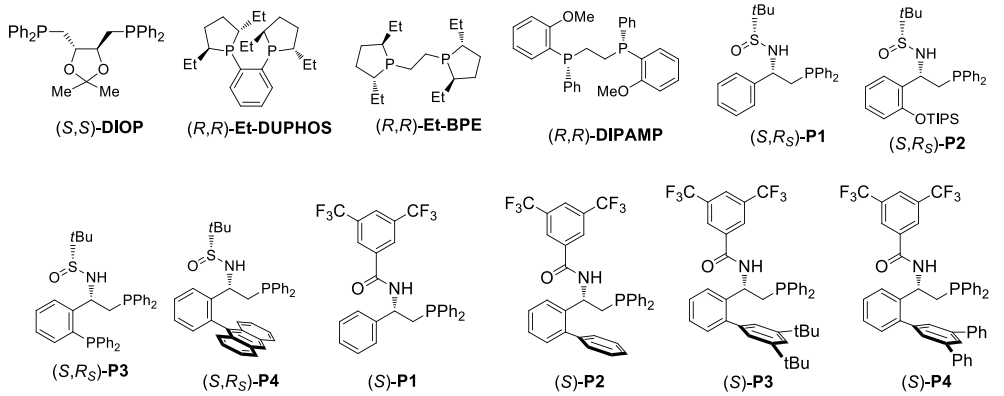
Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. $^{1}H$ NMR spectra, $^{13}C$ NMR spectra, $^{31}P$ NMR spectra and $^{19}F$ NMR spectra were recorded on a Bruker 400 (or 500) MHz spectrometer in chloroform-$d_3$. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta$ = 0 ppm) in $CDCl_3$ as an internal standard. $^{13}C$ NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ ($\delta$ = 77.00 ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Noteworthy, splitting signals between $^{13}C$ nucleus and $^{13}P$ nucleus in some chiral phosphine catalysts were difficult to distinguish and these $^{13}C$ NMR signals were reported as singlet entirely.

Trichloromethane ($CHCl_3$), dichloromethane, dichloroethane and ethyl acetate were freshly distilled from $CaH_2$; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

## 2. Optimization of Reaction Conditions for the Enantioselective [3+2] Cycloaddition of 1a and 2a[a]



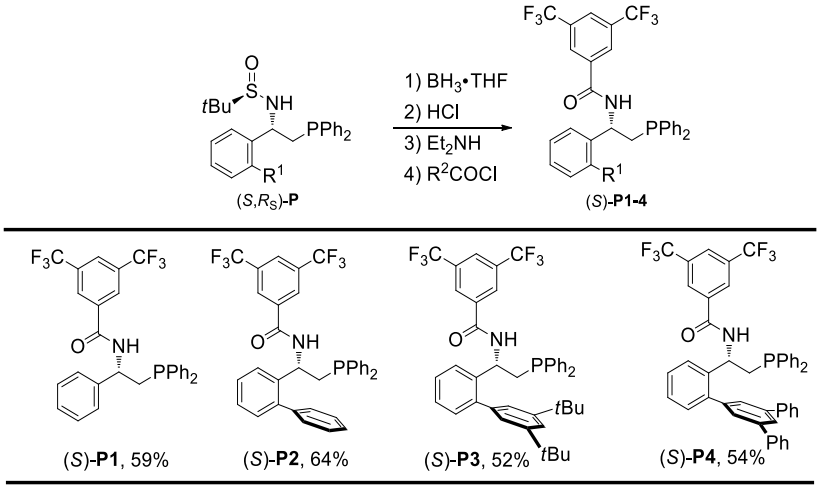




| Entry | Cat. | *T* (ºC) | *t* (h) | Solvent | Yield (%)[b] | *ee* (%)[c] |
|---|---|---|---|---|---|---|
| 1 | (*S*,*S*)-**DIOP** | 25 | 12 | toluene | <10 | -- |
| 2 | (*R*,*R*)-**Et-DUPHOS** | 25 | 12 | toluene | <10 | -- |
| 3 | (*R*,*R*)-**Et-BPE** | 25 | 8 | toluene | 64 | 39 |
| 4 | (*R*,*R*)-**DIPAMP** | 25 | 6 | toluene | 81 | 89 |
| 5 | (*S*,*R*$_S$)-**P1** | 25 | 12 | toluene | 51 | 5 |
| 6 | (*S*,*R*$_S$)-**P2** | 25 | 12 | toluene | 54 | 11 |
| 7 | (*S*,*R*$_S$)-**P3** | 25 | 12 | toluene | 62 | 30 |
| 8 | (*S*,*R*$_S$)-**P4** | 25 | 12 | toluene | 58 | 29 |
| 9 | (*S*)-**P1** | 25 | 3 | toluene | 79 | 3 |
| 10 | (*S*)-**P2** | 25 | 3 | toluene | 85 | 14 |
| 11 | (*S*)-**P3** | 25 | 3 | toluene | 84 | 40 |
| 12 | (*S*)-**P4** | 25 | 3 | toluene | 86 | 21 |
| 13 | (*R*,*R*)-**DIPAMP** | 25 | 6 | DCM | 51 | 72 |
| 14 | (*R*,*R*)-**DIPAMP** | 25 | 6 | $CHCl_3$ | 68 | 84 |
| 15 | (*R*,*R*)-**DIPAMP** | 25 | 6 | EA | 79 | 86 |
| 16 | (*R*,*R*)-**DIPAMP** | 25 | 6 | acetone | 62 | 26 |
| 17 | (*R*,*R*)-**DIPAMP** | 25 | 6 | $Et_2O$ | 74 | 87 |
| 18 | (*R*,*R*)-**DIPAMP** | 25 | 6 | MTBE | 73 | 88 |
| 19 | (*R*,*R*)-**DIPAMP** | 25 | 6 | THF | 60 | 86 |
| 20 | (*R*,*R*)-**DIPAMP** | 25 | 6 | $CH_3CN$ | 49 | 32 |
| 21 | (*R*,*R*)-**DIPAMP** | 0 | 6 | toluene | 84 | 90 |
| 22 | (*R*,*R*)-**DIPAMP** | -10 | 8 | toluene | 81 | 91 |
| 23 | (*R*,*R*)-**DIPAMP** | -20 | 12 | toluene | 78 | 92 |
| 24 | (*R*,*R*)-**DIPAMP** | -25 | 20 | toluene | 63 | 92 |

[a] Unless otherwise specified, all reactions were carried out with (*E*)-**1a** (0.1 mmol), recemic **2a** (0.15 mmol) in solvent (1 mL). [b] Yield of isolated products; both diastereoselectivity and regioselectivity were more than 20:1. [c] Determined by HPLC analysis using a chiral stationary phase.

# 3. Typical Synthetic Procedure and Data for Novel Chiral Phosphines Catalyst

## 3.1 Typical Procedure for the Synthesis of Phosphines (*S*)-P1~4



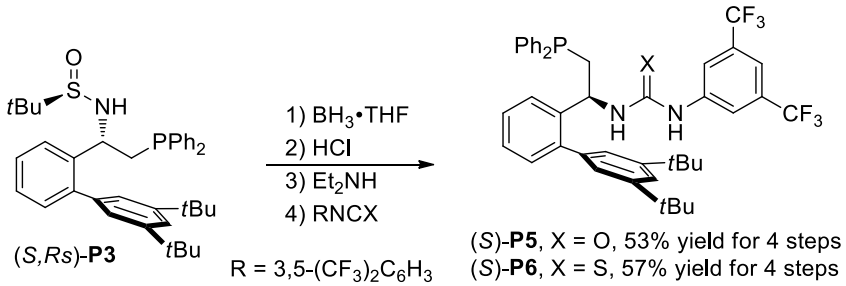

**Step 1**: $BH_3$•THF (3.0 mmol) was added slowly to the solution of ($S$,$R_S$)-**P** (2.0 mmol)[1] in dry THF (5 mL) at – 30 ºC and the reaction mixture was stirred for 2 h until completion of the material as indicated by TLC followed by adding 10 mL of water and 20 mL EtOAc. The aqueous phase was separated and extracted three times with 20 mL EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo.

**Step 2**: 4 M HCl (1 mL) was added slowly to the above residue which disolved in MeOH (10 mL) and the reaction mixture was stirred at room temperature for 3 h until completion of material as indicated by TLC analysis, followed by washing with aq $NaHCO_3$ and 10 mL aq brine water. The organic layers was separated and extracted three times with 20 mL EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo.

**Step 3**: $Et_2NH$ (5.0 mL) was added to the above residue and the mixture was stirred at 55 ºC for 6 h under the protection of $N_2$ until completion of material as indicated by TLC analysis. The solvent was then removed in vacuo and the residue was used directly for the next step.

**Step 4**: Under the protection of Ar, 3,5-bis(trifluoromethyl)benzoyl chloride (1.1 eq.) was added slowly to the above residue which was disolved in dry DCM (0.1 M) at 0 ºC. This reaction mixture was then stirred at 25 ºC for another 1 h, after completion of the reaction, the solvent was then removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired (*S*)-**P1~4**.

### 3.2 Typical Procedure for the Synthesis of Phosphines (*S*)-P5 and (*S*)-P6



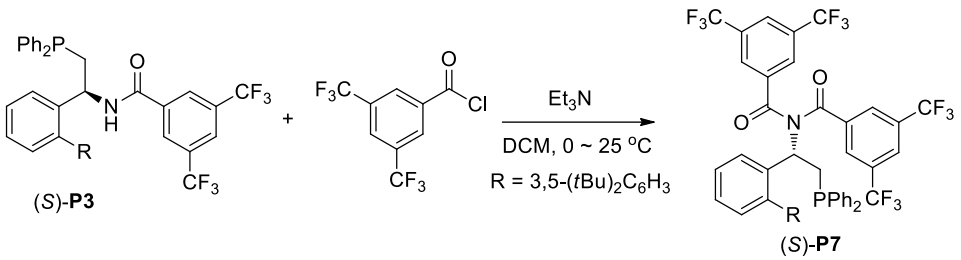

**Step 1**: $BH_3$•THF (3.0 mmol) was added slowly to the solution of ($S$,$R_S$)-**P3** (2.0 mmol)[1] in dry THF (5 mL) at –30 ºC and the reaction mixture was stirred for 2 h until completion of the material as indicated by TLC followed by adding 10 mL of water and 20 mL of EtOAc. The aqueous phase was separated and extracted three times with 20 mL EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo.

**Step 2**: 4 M HCl (1 mL) was added slowly to the above residue which disolved in MeOH (10 mL) and the reaction mixture was stirred at room temperature for 3 h until completion of material as indicated by TLC analysis, followed by washing with aq $NaHCO_3$ and 10 mL of aq brine water. The organic layers was separated and extracted three times with 20 mL of EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo.

**Step 3**: $Et_2NH$ (5.0 mL) was added to the above residue and the mixture was stirred at 55 ºC for 6 h under the protection of $N_2$ until completion of material as indicated by TLC analysis. The solvent was then removed in vacuo and the residue was used directly for the next step.

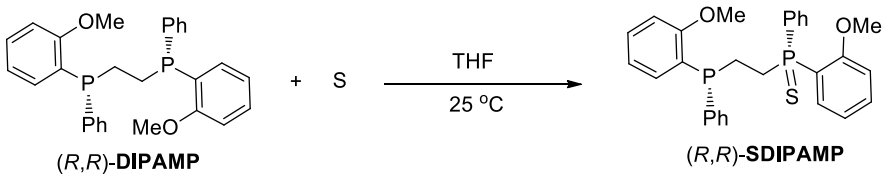
**Step 4**: Under the protection of Ar, 3,5-Bis(trifluoromethyl)phenylisocyanate or 3,5-Bis(trifluoromethyl)phenyl isothiocyanate (1.2 eq.) was added slowly to the above residue which was disolved in dry DCM (0.1 M) at 0 °C. This reaction mixture was then stirred at 25 °C for another 1 h, after completion of the reaction, the solvent was then removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired (*S*)-**P5** and (*S*)-**P6**.

### 3.3 Typical Procedure for the Synthesis of Phosphines (*S*)-P7




Under the protection of Ar, 3,5-bis(trifluoromethyl)benzoyl chloride (2 eq.) was added slowly to the solution of (*S*)-**P3** (0.2 mmol) in dry DCM (2 mL) at 0 °C and the reaction mixture was stirred for 1 h at this temperature. This reaction mixture was then stirred at 25 °C for another 4 h, until completion of the material as indicated by TLC followed by adding 5 mL of water and 10 mL of EtOAc. The aqueous phase was separated and extracted three times with 15 mL of EtOAc. The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. The residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired (*S*)-**P7** (36% yield).

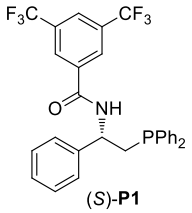
### 3.4 Typical Procedure for the Synthesis of Phosphines (*R*,*R*)-SDIPAMP




Under the protection of Ar, (*R*,*R*)-**DIPAMP** (0.2 mmol) was added to the solution of

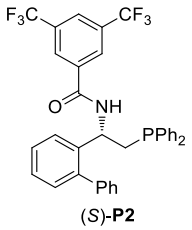
sulfur (0.2 mmol) in dry THF (2 mL) at 25 ºC and the reaction mixture was stirred for 0.5 h at this temperature. After completion of the material as indicated by TLC, the solvent was then removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired (*R*,*R*)-**SDIPAMP** (51% yield).

## General Data for (*S*)-P1~7 and (*R*,*R*)-SDIPAMP



(*S*)-**P1**

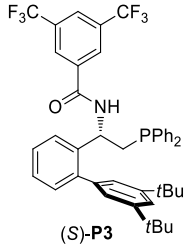
(*S*)-**P1**; white solid; $[\alpha]_D^{20}$ = + 15.0 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 2H), 7.97 (s, 1H), 7.55–7.51 (m, 2H), 7.45–7.42 (m, 2H), 7.35–7.34 (m, 9H), 7.30–7.26 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 5.42–5.36 (m, 1H), 2.90–2.85 (m, 1H), 2.73–2.69 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.62, 141.94 (d, *J* = 6.50 Hz), 137.78 (d, *J* = 12.13 Hz), 136.16, 132.98 (d, *J* = 19.38 Hz), 132.63 (d, *J* = 19.0 Hz), 131.94 (q, *J* = 33.63 Hz), 130.49 (q, *J* = 5.63 Hz), 129.25, 128.98, 128.88, 128.81, 128.75, 128.72, 128.67, 127.90, 127.28 (d, *J* = 2.88 Hz), 126.40, 125.85, 124.98–124.93 (m), 122.87 (q, *J* = 271.25 Hz), 53.00 (d, *J* = 17.13 Hz), 35.91 (d, *J* = 16.38 Hz); $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ = -22.82 ppm; HRMS (ESI) m/z calcd. for $C_{29}H_{22}F_6NNaOP$ $[M+Na]^+$ = 568.1258, found = 568.1235.



(*S*)-**P2**

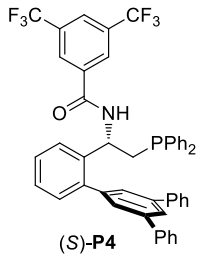
(*S*)-**P2**; white solid; $[\alpha]_D^{20}$ = -43.0 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 2H), 8.02 (s, 1H), 7.52–7.50 (m, 1H), 7.44–7.36 (m, 9H), 7.35–7.25 (m, 7H), 7.21–7.17 (m, 2H), 6.82 (d, *J* = 7.0 Hz, 1H), 5.62–5.57 (m, 1H), 2.69–2.63 (m, 1H), 2.57–2.53 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.27, 140.89, 140.62, 139.90 (d, *J* = 6.38 Hz), 137.39 (d, *J* = 11.75, Hz), 136.85 (d, *J* = 12.13 Hz), 136.10, 132.62 (d, *J*

= 19.38 Hz), 132.32 (d, *J* = 19.0 Hz), 131.88 (q, *J* = 33.5 Hz), 130.79, 129.24, 128.95, 128.75, 128.62 (d, *J* = 1.38 Hz), 128.56 (d, *J* = 1.50 Hz), 128.39, 127.95, 127.33 (d, *J* = 2.25 Hz), 127.23 (d, *J* = 2.63 Hz), 125.52, 124.88–124.83 (m), 122.83 (q, *J* = 271.25 Hz), 50.70 (d, *J* = 15.0 Hz), 36.21 (d, *J* = 17.13 Hz); $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ = -23.13 ppm; HRMS (ESI) m/z calcd. for $C_{35}H_{26}F_6NNaOP$ [M+Na] $^+$ = 644.1548, found = 644.1540.



(*S*)-**P3**

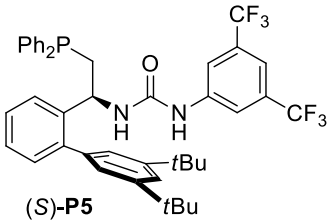
(*S*)-**P3**; white solid; $[\alpha]_D^{20}$ = -34.7 (*c* = 0.33, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 3H), 7.46–7.16 (m, 15H), 7.09–7.06 (m, 2H), 6.45–6.46 (m, 1H), 5.65–5.58 (m, 1H), 2.54–2.44 (m, 2H), 1.30 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.29, 150.87, 142.00, 140.05, 139.95, 137.85 (d, *J* = 11.9 Hz), 136.99 (d, *J* = 11.90 Hz), 136.53, 132.75, 132.56, 132.36, 132.17, 131.82, 131.49, 130.97, 128.99, 128.71, 128.67, 128.64, 128.60, 128.57, 127.72, 127.33, 127.22, 125.21, 124.87, 124.23, 123.65, 121.52, 121.05, 50.86 (d, *J* = 15.60 Hz), 36.42 (d, *J* = 16.70 Hz), 34.91, 31.44; $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ = -62.72 ppm; HRMS (ESI) m/z calcd. for $C_{44}H_{43}F_6NOP$ [M+H] $^+$ = 734.2981, found = 734.2998.



(*S*)-**P4**

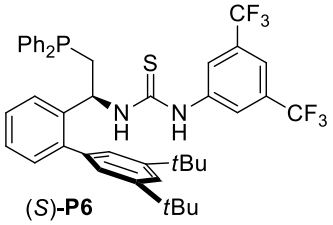
(*S*)-**P4**; white solid; $[\alpha]_D^{20}$ = -41.6 (*c* = 0.33, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 2H), 7.88 (s, 1H), 7.82–7.81 (m, 1H), 7.61–7.59 (m, 6H), 7.48–7.46 (m, 1H), 7.41–7.27 (m, 11H), 7.17–7.03 (m, 8H), 6.72 (d, *J* = 6.8 Hz, 1H), 5.64–5.57 (m, 1H), 2.68–2.62 (m, 1H), 2.57–2.52 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.32, 141.74, 141.67, 140.81, 140.52, 139.99 (d, *J* = 6.40 Hz), 137.23 (d, *J* = 12.0 Hz), 136.89 (d, *J* = 12.30 Hz), 136.25, 132.58 (d, *J* = 19.40 Hz), 132.26 (d, *J* = 19.20 Hz),

131.88 (q, $J$ = 33.7 Hz), 130.80, 128.99, 128.75, 128.61, 128.54, 128.48, 128.16, 127.50, 127.43, 127.19, 126.89, 125.52, 124.90, 124.82, 124.78, 122.81 (q, $J$ = 271.4 Hz), 50.87 (d, $J$ = 15.60 Hz), 36.60 (d, $J$ = 17.10 Hz); $^{31}$P NMR (121.5 MHz, $CDCl_3$) δ = -22.96 ppm; HRMS (ESI) m/z calcd. for $C_{47}H_{34}F_6NNaOP$ $[M+Na]^+$ = 796.2174, found = 796.2171.



(*S*)-**P5**

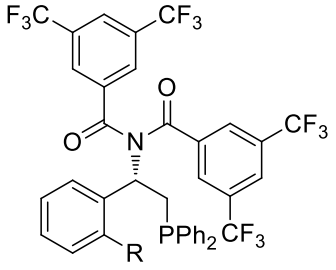
(*S*)-**P5**; white solid; $[\alpha]_D^{20}$ = -16.6 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CD_3COCD_3$): δ 8.80 (s, 1H), 8.17 (s, 2H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.57–7.52 (m, 3H), 7.34–7.31 (m, 1H), 7.28–7.13 (m, 10H), 7.01–6.98 (m, 2H), 6.88 (d, $J$ = 7.0 Hz, 1H), 5.51–5.46 (m, 1H), 3.74 (s, 1H), 2.48–2.43 (m, 1H), 2.37–2.31 (m, 1H), 1.36 (s, 18H); $^{13}$C NMR (125 MHz, $CD_3COCD_3$): δ 154.66, 151.28, 143.51, 142.99 (d, $J$ = 4.63 Hz), 142.80, 141.04, 140.17 (d, $J$ = 13.88 Hz), 138.28 (d, $J$ = 13.75 Hz), 133.16 (d, $J$ = 12.25 Hz), 133.01 (d, $J$ = 12.63 Hz), 132.31 (q, $J$ = 32.63 Hz), 131.12, 129.45, 129.39, 129.20, 129.15, 129.11, 129.10, 128.43, 127.63, 126.24, 124.95, 124.49 (q, $J$ = 270.13 Hz), 121.56, 118.41 (d, $J$ = 3.5 Hz), 114.69 (m), 49.73 (d, $J$ = 16.25 Hz), 38.18 (d, $J$ = 16.38 Hz), 35.52, 31.81; $^{31}$P NMR (202.5 MHz, $CD_3COCD_3$) δ = -24.58 ppm; $^{19}$F NMR (376 MHz, $CD_3COCD_3$) δ = -63.56 ppm; HRMS (ESI) m/z calcd. for $C_{43}H_{44}F_6N_2OP$ $[M+H]^+$ = 749.3090, found = 749.3082.



(*S*)-**P6**

(*S*)-**P6**; white solid; $[\alpha]_D^{20}$ = -8.8 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CD_3COCD_3$): δ 9.55 (s, 1H), 8.42 (s, 2H), 7.76 (s, 1H), 7.63–7.59 (m, 3H), 7.34–7.18 (m, 10H), 7.00–6.97 (m, 2H), 6.06 (br, 1H), 3.75 (d, $J$ = 4.0 Hz, 1H), 2.64–2.60 (m, 1H), 2.45–2.40 (m, 1H), 1.39 (s, 18H); $^{13}$C NMR (125 MHz, $CD_3COCD_3$): δ 181.11,

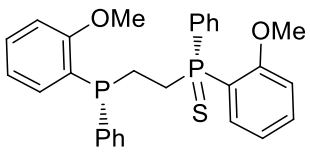
151.29, 142.67 (d, $J$ = 16.00 Hz), 141.92 (d, $J$ = 5.38 Hz), 141.03, 139.96 (d, $J$ = 13.38 Hz), 138.04 (d, $J$ = 13.13 Hz), 133.29 (d, $J$ = 19.25 Hz), 132.92 (d, $J$ = 19.25 Hz), 132.51 (q, $J$ = 32.88 Hz), 131.29, 129.41 (d, $J$ = 6.5 Hz), 129.11 (d, $J$ = 8.00 Hz), 129.01 (d, $J$ = 7.00 Hz), 128.30, 127.61, 125.42, 124.58, 124.29 (q, $J$ = 270.75 Hz), 121.68, 117.36-117.30 (m), 54.43 (d, $J$ = 15.25 Hz), 37.19 (d, $J$ = 17.00 Hz), 35.50, 31.88; $^{31}$P NMR (202.5 MHz, $CD_3COCD_3$) δ = -23.86 ppm; $^{19}$F NMR (376 MHz, $CD_3COCD_3$) δ = -67.71 ppm; HRMS (ESI) m/z calcd. for $C_{43}H_{44}F_6N_2SP$ $[M+H]^+$ = 765.2862, found = 765.2865.




R = 3,5-(*t*Bu)$_2$C$_6$H$_3$

(*S*)-**P7**

(*S*)-**P6**; white solid; $[\alpha]_D^{20}$ = -70.8 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CD_3COCD_3$): δ 8.18–8.17 (m, 1H), 7.77–7.34 (m, 6H), 7.61–7.60 (m, 1H), 7.54–7.51 (m, 1H), 7.40–7.19 (m, 10H), 7.10–7.06 (m, 2H), 6.99–6.96 (m, 2H), 6.34–6.30 (m, 1H), 3.15–3.08 (m, 1H), 2.83–2.78 (m, 1H), 1.39–1.29 (m, 18H); $^{13}$C NMR (125 MHz, $CD_3COCD_3$): δ 170.67, 150.87, 142.38, 139.80, 139.65, 139.381 (d, $J$ = 7.25 Hz), 138.14 (d, $J$ = 10.38 Hz), 138.81 (d, $J$ = 10.88 Hz), 132.85 (d, $J$ = 20.05 Hz), 132.191 (q, $J$ = 34.25 Hz), 131.64 (d, $J$ = 17.75 Hz), 131.06, 129.35, 129.21 (d, $J$ = 7.38 Hz), 128.61, 128.35, 128.34, 128.30, 128.21, 127.73, 126.68, 124.84, 123.70, 122.23 (q, $J$ = 271.63 Hz), 58.33 (d, $J$ = 13.50 Hz), 34.99, 32.49 (d, $J$ = 17.13 Hz), 31.44; $^{31}$P NMR (202.5 MHz, $CD_3COCD_3$) δ = -21.96 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -63.57 ppm; HRMS (ESI) m/z calcd. for $C_{52}H_{45}F_{12}NO_2P$ $[M+H]^+$ = 974.2991, found = 974.2993.

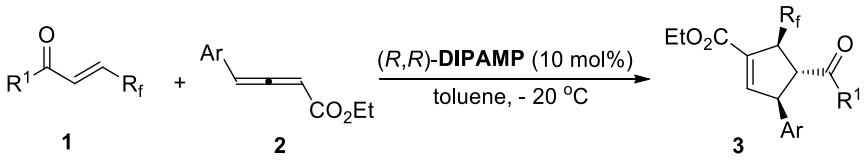



(*R*,*R*)-**SDIPAMP**

(*R*,*R*)-**SDIPAMP**; white solid; $[\alpha]_D^{20}$ = +39.9 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CD_3COCD_3$): δ 8.30–8.25 (m, 1H), 7.70–7.65 (m, 2H), 7.53–7.29 (m, 10H), 7.15–7.12 (m, 1H), 7.07–7.04 (m, 1H), 6.91–6.82 (m, 3H), 3.69 (s, 3H), 3.59 (s, 3H), 2.95–2.85 (m, 1H), 2.66–2.56 (m, 1H), 2.38–2.23 (m, 2H); $^{13}C$ NMR (125 MHz, $CD_3COCD_3$): δ 161.02 (d, *J* = 12.75 Hz), 159.75 (d, *J* = 2.50 Hz), 136.717 (d, *J* = 12.88 Hz), 136.31 (d, *J* = 9.75 Hz), 134.28, 133.94 (q, *J* = 2.13 Hz), 133.62, 133.23, 133.08, 132.09 (d, *J* = 4.38 Hz), 130.76 (d, *J* = 2.75 Hz), 130.59, 130.51, 130.10, 128.34, 128.32 (d, *J* = 6.88 Hz), 128.05 (d, *J* = 12.25 Hz), 125.69 (d, *J* = 15.75 Hz), 121.05 (d, *J* = 12.25 Hz), 120.80, 119.08, 118.47, 110.72 (d, *J* = 7.25 Hz), 110.24, 55.21 (d, *J* = 34.75 Hz), 27.61 (dd, *J* = 55, 19.63 Hz), 18.31 (dd, *J* = 14.25, 3.38, Hz); $^{31}P$ NMR (202.5 MHz, $CD_3COCD_3$) δ = 45.17, -21.96 ppm; HRMS (ESI) m/z calcd. for $C_{28}H_{29}O_2P_2S$ $[M+H]^+$ = 491.1358, found = 491.1370.

## 4. Typical Procedure for the Enantioselective [3+2] Cycloaddition of Allenes with β–Perfluoroalkyl α,β–Enones

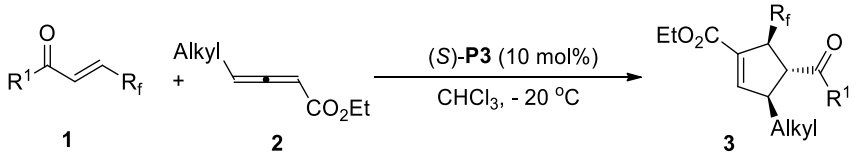
**Enantioselective [3+2] cycloadditions of γ-aryl substituted allenoates with enone**




1 2 3

Under Ar, a stirred solution of **1**[2] (0.2 mmol) and recemic **2** (0.3 mmol) in toluene (2 mL) was cooled to -20 °C. Subsequently, (*R*,*R*)-**DIPAMP** (0.02 mmol) was added in one portion. The reaction mixture was stirred at -20 °C until completion of the material as indicated by TLC. Then the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired cycloaddition product **3**.

**Enantioselective [3+2] cycloadditions of γ-alkyl substituted allenoates with enone**




1 2 3

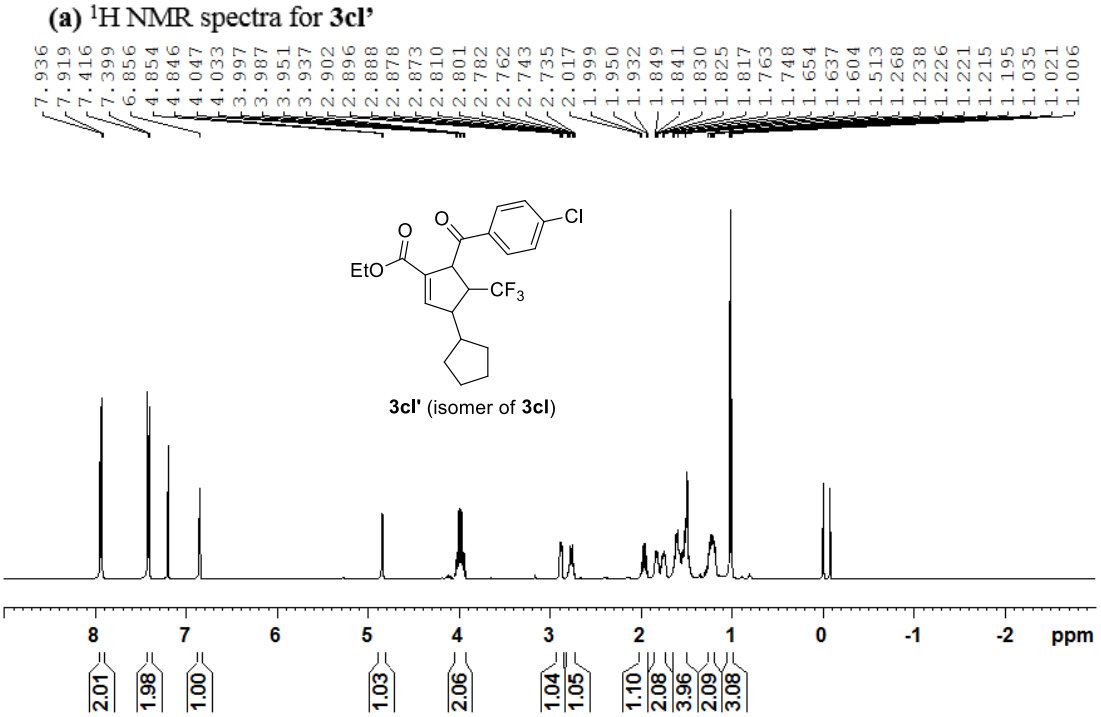
Under Ar, a stirred solution of **1** (0.2 mmol) and recemic **2** (0.44 mmol) in $CHCl_3$ (2

mL) was cooled to -20 ºC. Subsequently, (*S*)-**P3** (0.02 mmol) was added in one portion. The reaction mixture was stirred at -20 ºC until completion of the material as indicated by TLC. Then the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired cycloaddition product **3**.

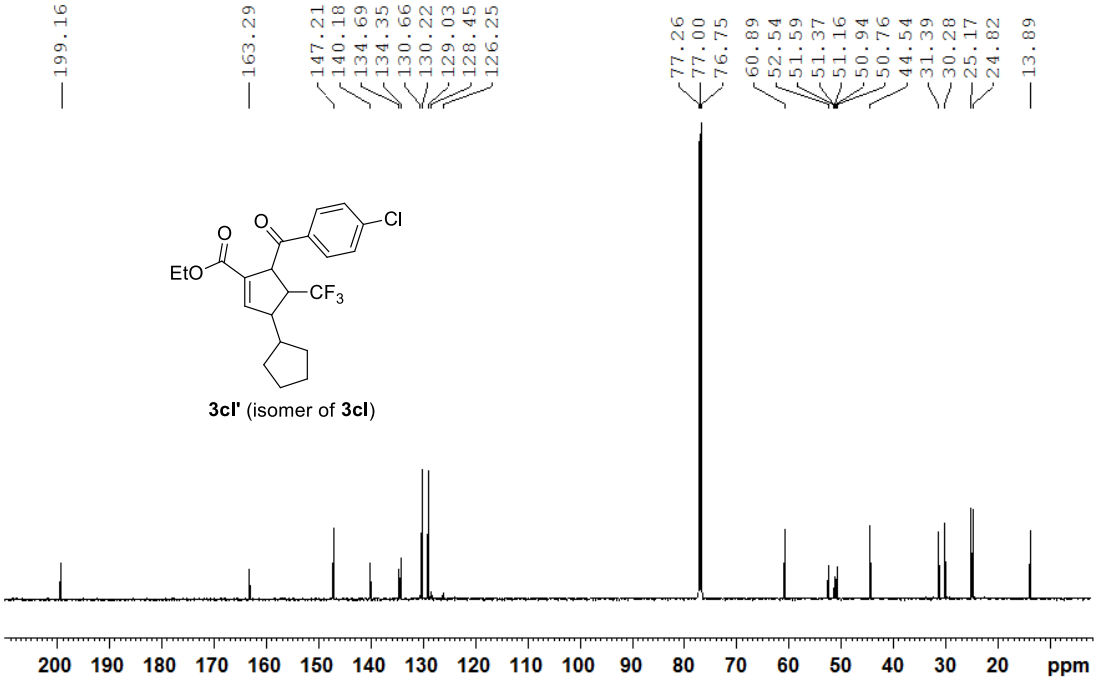
## 5. The Structural Assignment for the Regioisomer

In order to confirm the structure of the minor product which was observed in the (*S*)-**P3** catalyzed enantioselective [3+2] cycloadditions of *γ*-alkyl substituted allenoates with *β*-perfluoro substituted enone, we have isolated the isomer of **3cl** and confirmed its structurue by NMR analysis. According to these NMR spectra, the minor product **3cl'** was assigned to the regioisomer of **3cl**.

**(a)** $^{1}$H NMR spectra for **3cl'**

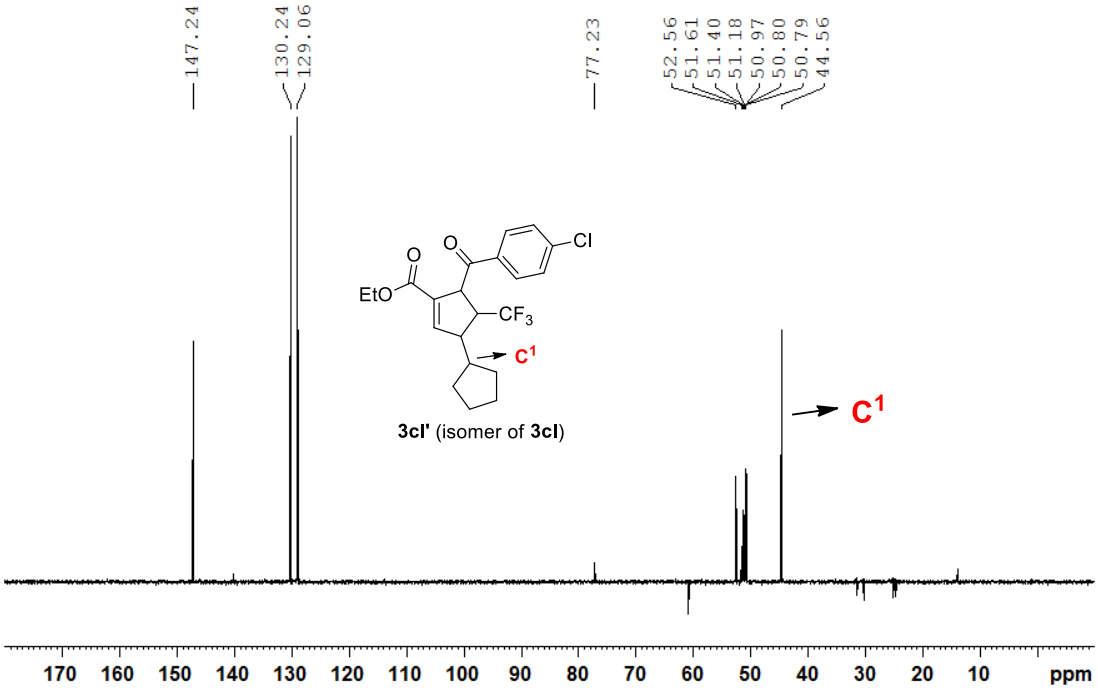


**(b)** $^{13}$C NMR spectra for **3cl'**



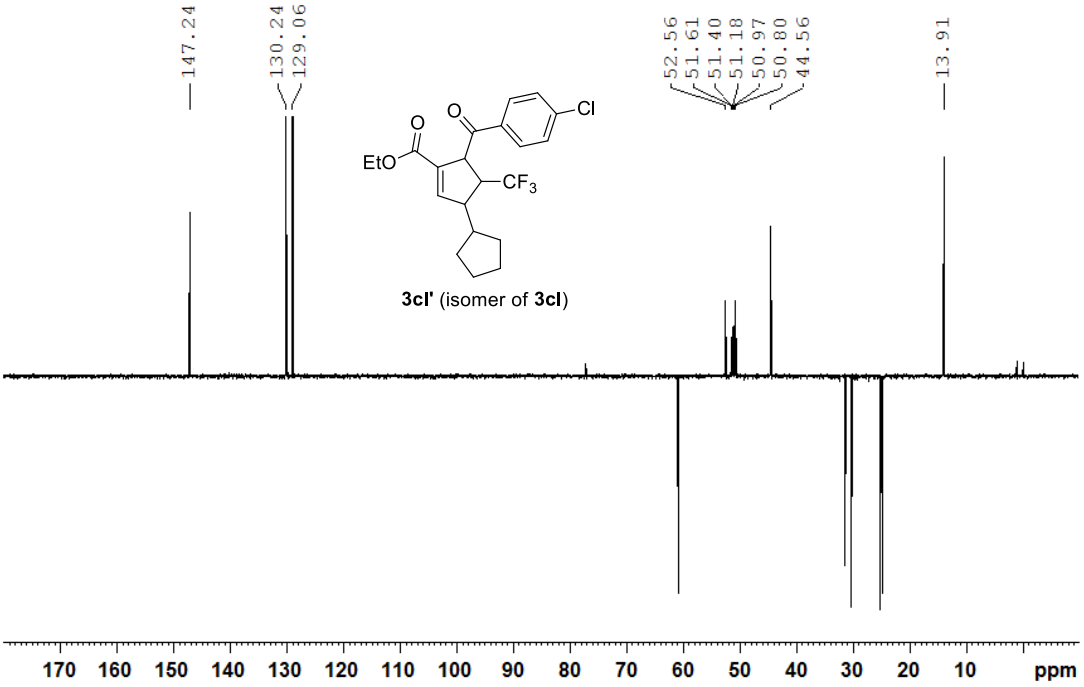

**3cl'** (isomer of **3cl**)

**(c)** DEPT 90 spectra for **3cl'**

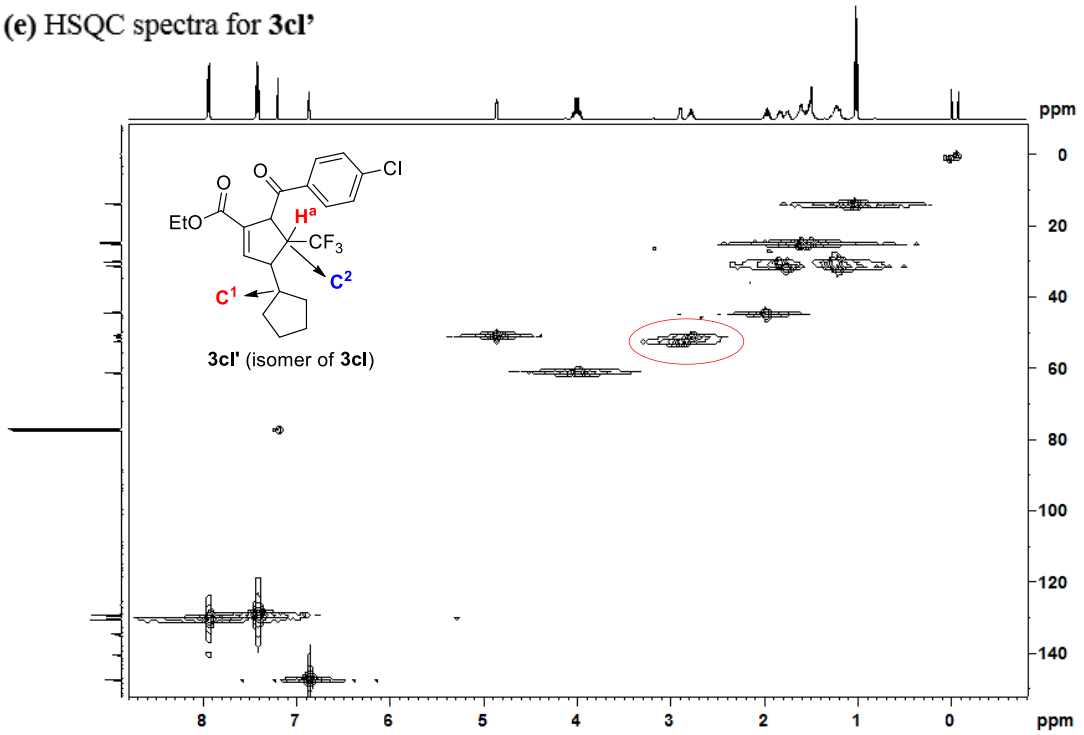



**3cl'** (isomer of **3cl**)

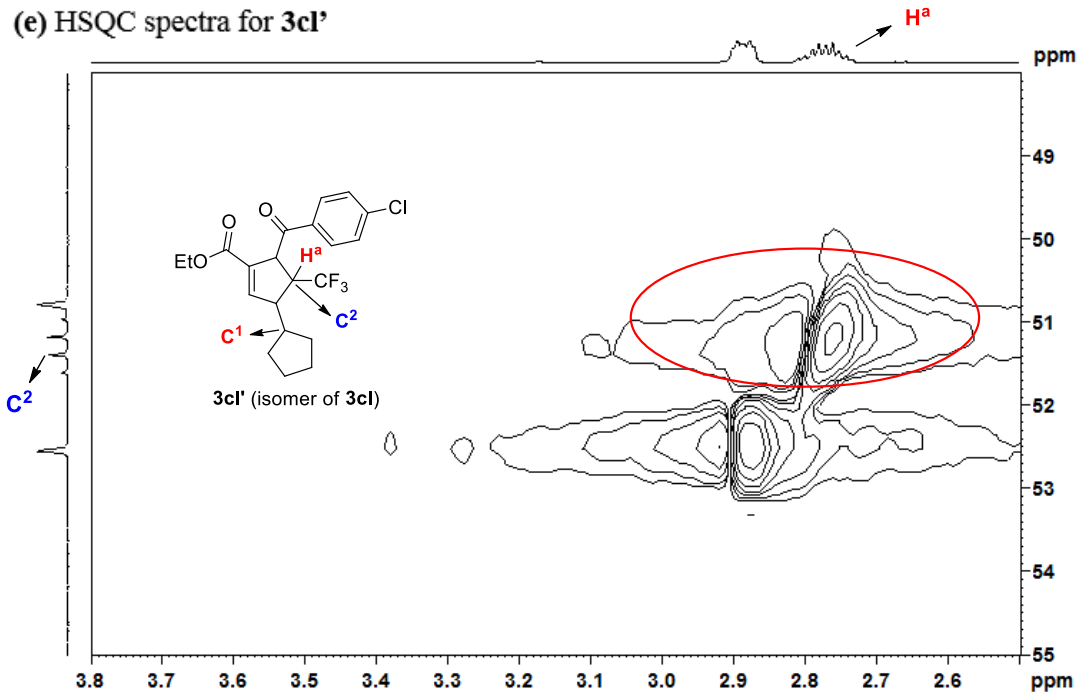
**(d)** DEPT 135 spectra for **3cl'**



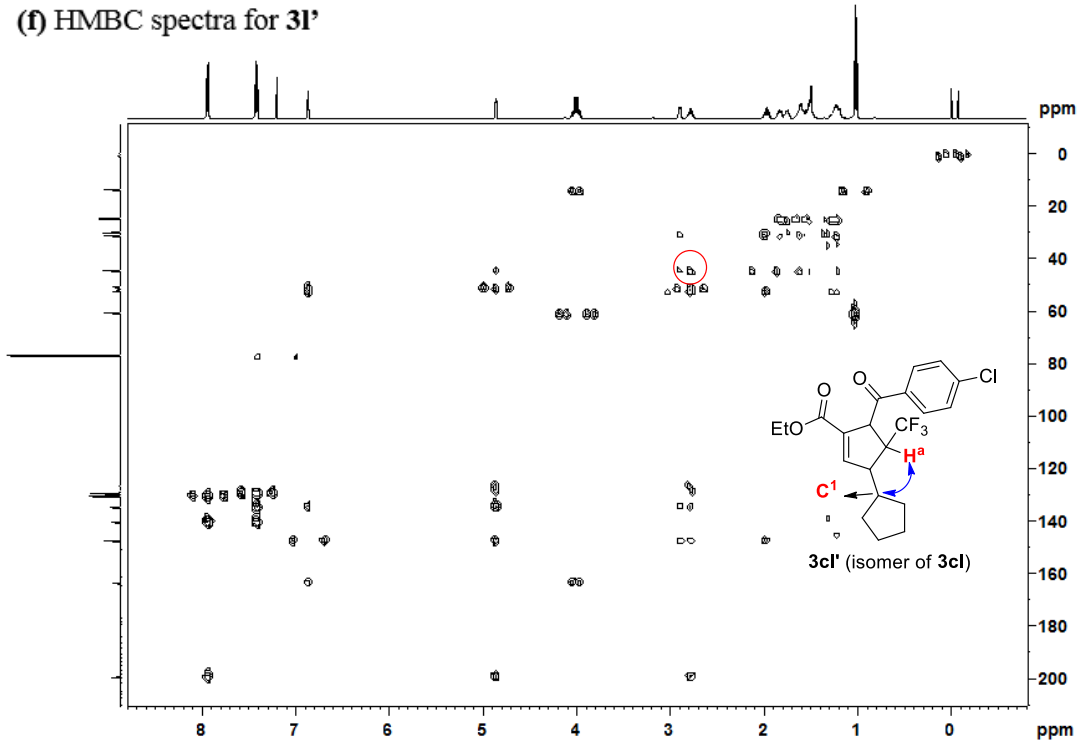

**(e)** HSQC spectra for **3cl'**

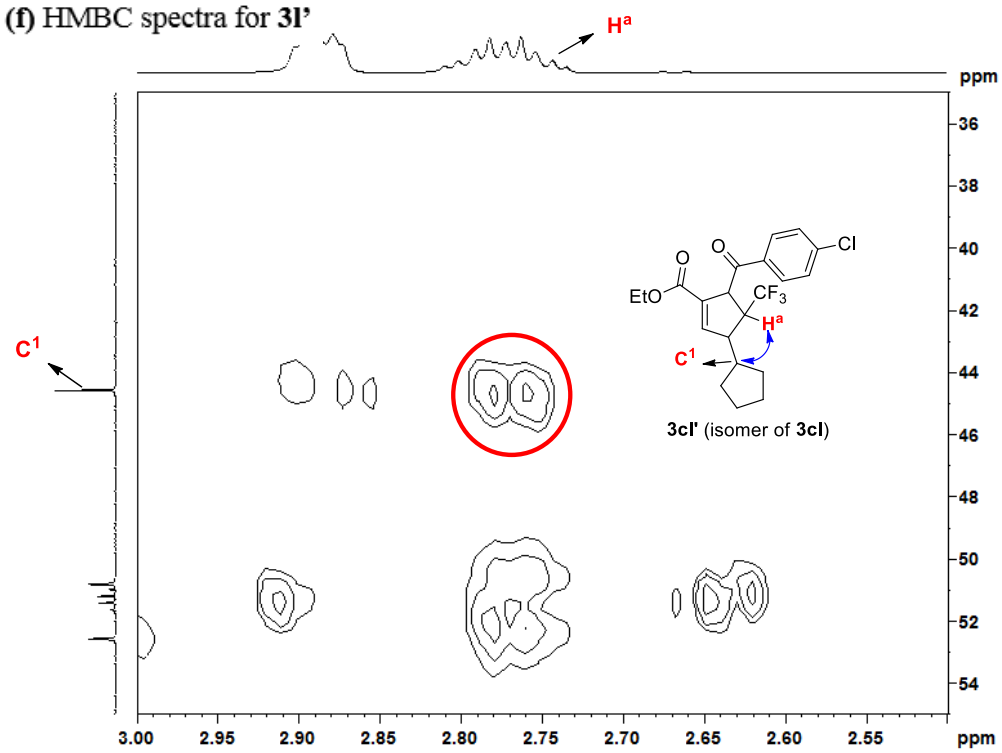


(e) HSQC spectra for **3cl'**



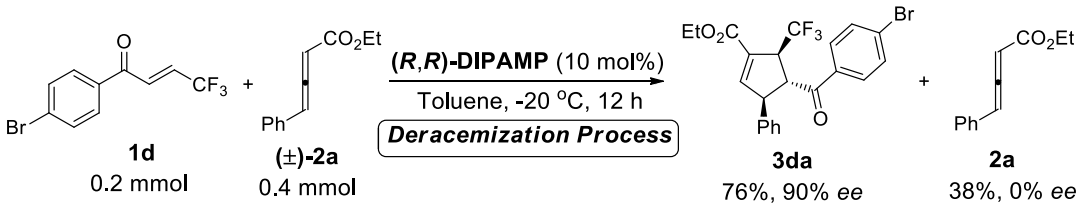

(f) HMBC spectra for **3l'**





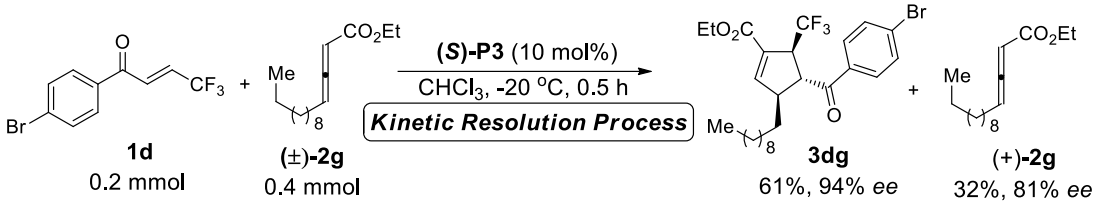

## 6. Procedure for the "Deracemization" and Kinetic Resolution of Recemic Allenoates

### Procedure for the "Deracemization" of Racemic 2a



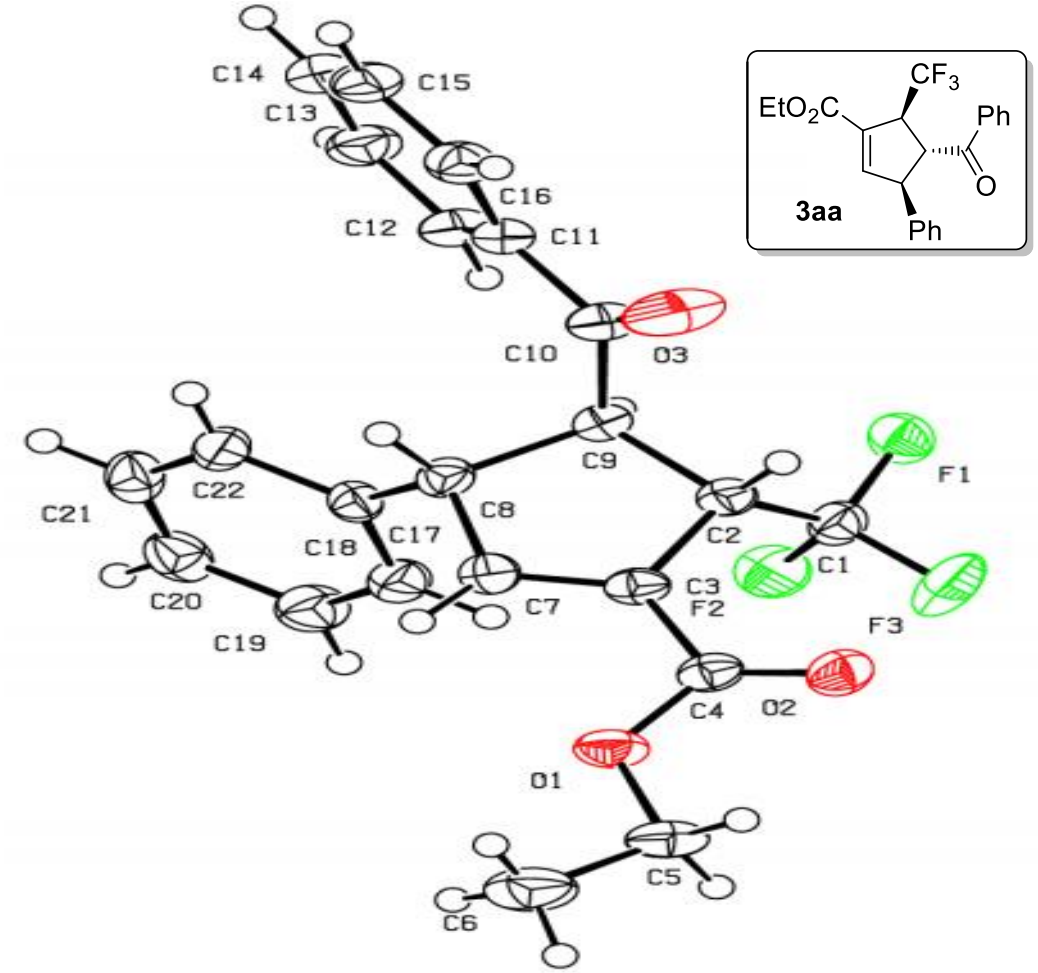

Under Ar, a stirred solution of **1d** (0.2 mmol) and racemic **2a** (0.4 mmol) in toluene (2 mL) was cooled to -20 °C. Subsequently, (*R*,*R*)-**DIPAMP** (0.02 mmol) was added in one portion. The reaction mixture was stirred at -20 °C for 12 h. Then the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the **3da** (76%, 90% *ee*) and **2a** (38%, 0% *ee*).

**Procedure for the Kinetic Resolution of Racemic 2g**

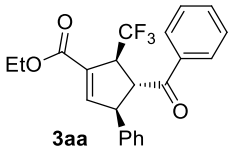



Under Ar, a stirred solution of **1d** (0.2 mmol) and racemic **2g** (0.4 mmol) in $CHCl_3$ (2 mL) was cooled to -20 °C. Subsequently, (*S*)-**P3** (0.02 mmol) was added in one portion. The reaction mixture was stirred at -20 °C for 0.5 h. Then the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the **3dg** (61%, 94% *ee*) and **2g** (32%, 81% *ee*).

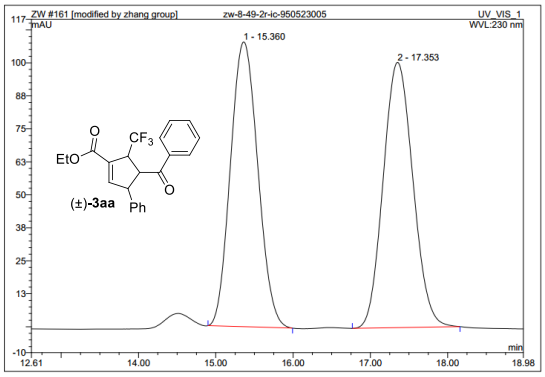
## 7. X-ray Crystal Structure for 3aa



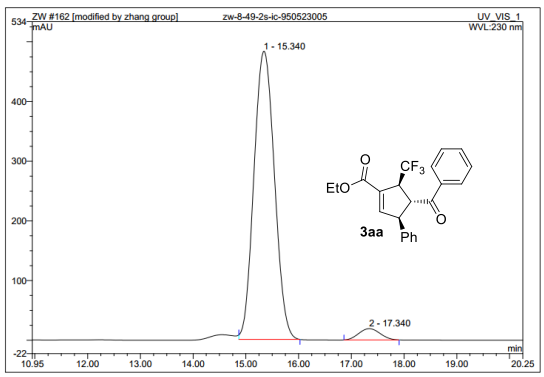
## 8. General Data and HPLC Spectra for Cycloaddition Product 3



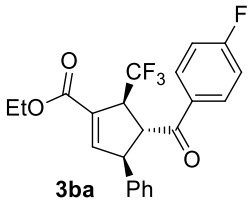

**3aa**; white solid; $[\alpha]_D^{20}$ = + 67.2 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.57–7.54 (m, 1H), 7.38–7.30 (m, 5H), 7.09–7.07 (m, 2H), 6.82 (s, 1H), 4.61–4.53 (m, 1H), 4.37–4.21 (m, 3H), 4.00–3.99 (m, 1H), 1.33 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.22, 163.27, 147.41, 140.19, 135.26, 133.82, 131.95, 129.13, 128.97, 128.62, 128.03, 127.86, 127.68, 126.29 (q, *J* = 277.90 Hz), 61.06, 55.47, 54.10, 51.35 (q, *J* = 28.90 Hz), 14.08; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.48 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 15.34 min, second peak: $t_R$ = 17.34 min; HRMS (ESI) m/z calcd. for $C_{22}H_{19}F_3NaO_3$ $[M+Na]^+$ = 411.1179, found = 411.1182.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 15.36 | n.a. | 107.931 | 44.250 | 49.68 | n.a. | BMB* |
| 2 | 17.35 | n.a. | 100.530 | 44.823 | 50.32 | n.a. | BMB* |
| Total: | | | 208.461 | 89.072 | 100.00 | 0.000 | |

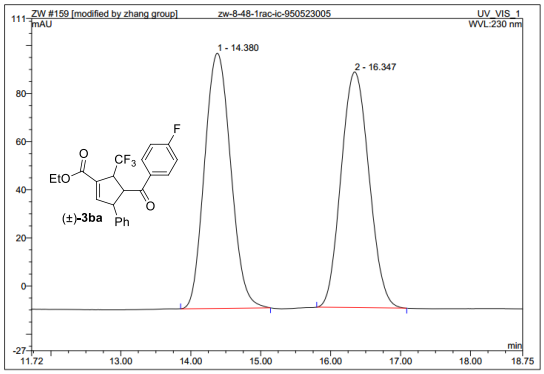


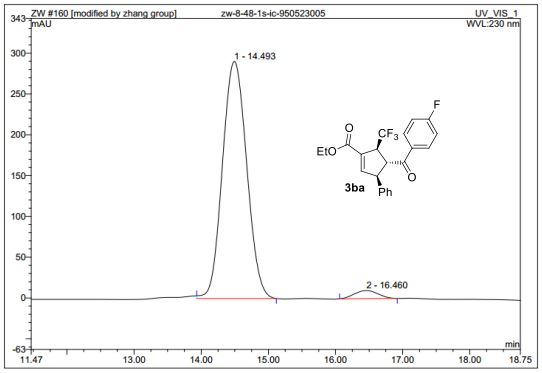

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 15.34 | n.a. | 482.951 | 217.640 | 96.11 | n.a. | MB* |
| 2 | 17.34 | n.a. | 18.914 | 8.816 | 3.89 | n.a. | BMB* |
| Total: | | | 501.865 | 226.456 | 100.00 | 0.000 | |




**3ba**; colorless oil; $[\alpha]_D^{20}$ = + 122.4 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.72–7.68 (m, 2H), 7.36–7.32 (m, 3H), 7.10–7.00 (m, 4H), 6.81 (s, 1H), 4.61–4.53 (m,

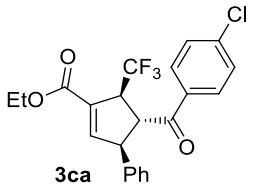
1H), 4.37–4.18 (m, 3H), 3.98–3.96 (m, 1H), 1.33 (t, $J$ = 7.20 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 196.61, 166.22 (d, $J$ = 255.00 Hz), 163.22, 147.26, 140.10, 131.85 (d, $J$ = 9.50 Hz), 131.67 (d, $J$ = 2.80 Hz), 129.08, 127.99, 126.25 (d, $J$ = 278.00 Hz), 115.81 (d, $J$ = 21.9 Hz), 61.10, 55.55, 54.22, 51.46 (q, $J$ = 29.00 Hz), 14.07; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.52, -103.61 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 14.49 min, second peak: $t_R$ = 16.46 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}F_4NaO_3$ $[M+Na]^+$ = 429.1084, found = 429.1093.



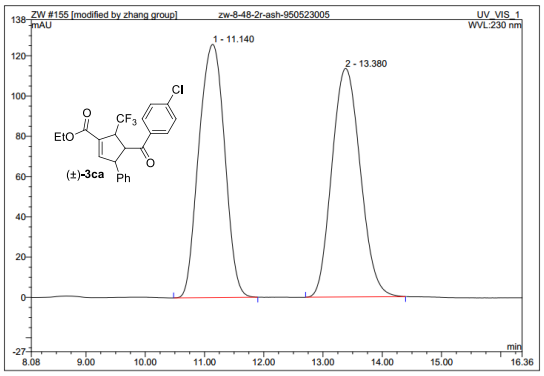



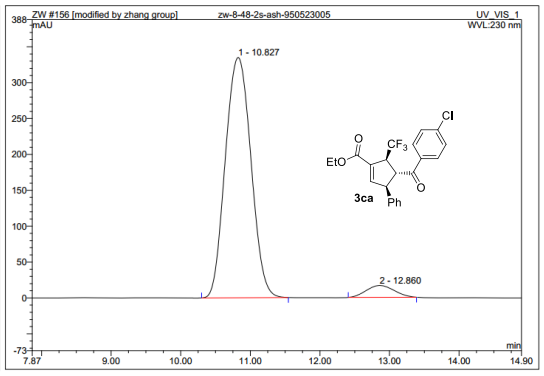

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 14.38 | n.a. | 106.085 | 45.973 | 50.38 | n.a. | BMB* |
| 2 | 16.35 | n.a. | 97.983 | 45.282 | 49.62 | n.a. | BMB* |
| Total: | | | 204.068 | 91.256 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 14.49 | n.a. | 290.623 | 121.731 | 96.79 | n.a. | MB* |
| 2 | 16.46 | n.a. | 9.933 | 4.034 | 3.21 | n.a. | BMB* |
| Total: | | | 300.556 | 125.765 | 100.00 | 0.000 | |



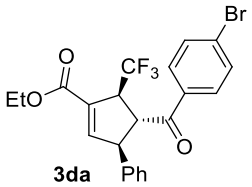

**3ca**; colorless oil; $[\alpha]_D^{20}$ = + 80.6 ($c$ = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.64–7.62 (m, 2H), 7.38–7.33 (m, 5H), 7.12–7.10 (m, 2H), 6.83 (s, 1H), 4.62–4.56 (m, 1H), 4.38–4.24 (m, 2H), 4.21–4.19 (m, 1H), 4.00–3.98 (m, 1H), 1.35 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 196.93, 163.16, 147.24, 140.49, 139.98, 133.48, 131.85 (d, $J$ = 1.75 Hz), 130.49, 129.08, 128.94, 128.01, 127.96, 126.19 (q, $J$ = 278.13 Hz), 61.09, 55.45, 54.21, 51.36 (q, $J$ = 29.00 Hz), 14.06; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.49 ppm; Enantiomeric excess: 90%, determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.82 min, second peak: $t_R$ = 12.86 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}ClF_3NaO_3$ $[M+Na]^+$ = 445.0789, found = 445.0794.



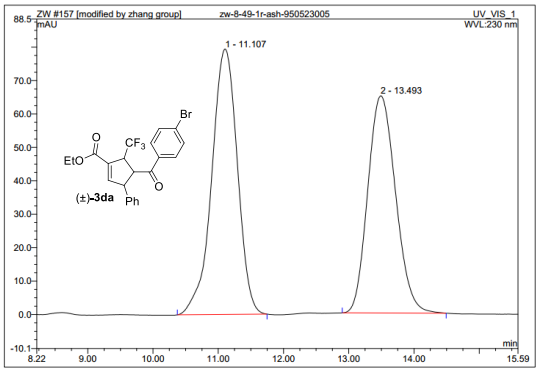



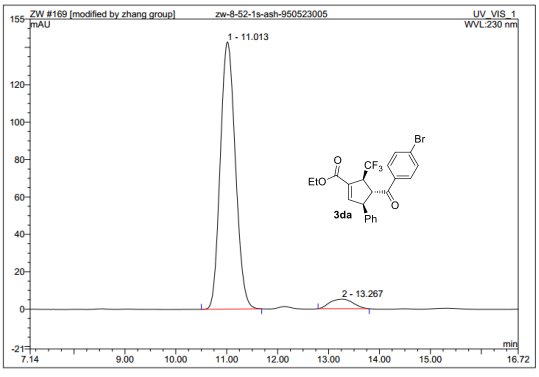

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.14 | n.a. | 125.749 | 63.568 | 50.17 | n.a. | BMB* |
| 2 | 13.38 | n.a. | 113.582 | 63.145 | 49.83 | n.a. | BMB* |
| Total: | | | 239.331 | 126.713 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.83 | n.a. | 334.926 | 142.934 | 94.92 | n.a. | BMB* |
| 2 | 12.86 | n.a. | 16.537 | 7.655 | 5.08 | n.a. | BMB* |
| Total: | | | 351.463 | 150.589 | 100.00 | 0.000 | |



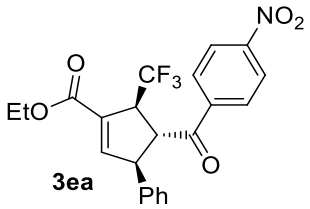

**3da**; colorless oil; $[\alpha]_D^{20}$ = + 92.8 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.54–7.48 (m, 4H), 7.36–7.32 (m, 3H), 7.10–7.08 (m, 2H), 6.80 (s, 1H), 4.60–4.52 (m, 1H), 4.37–4.21 (m, 2H), 4.18–4.16 (m, 1H), 3.98–3.95 (m, 1H), 1.33 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 197.19, 163.17, 147.22, 140.00, 133.95, 131.96, 131.90, 130.56, 129.31, 129.11, 128.04, 127.97, 126.20 (q, *J* = 278.20 Hz), 61.11, 55.46, 54.23, 51.43 (q, *J* = 28.90 Hz), 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.49 ppm; Enantiomeric excess: 90%, determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 11.01 min, second peak: $t_R$ = 13.26 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}BrF_3NaO_3$ $[M+Na]^+$ = 489.0284, found = 489.0287.



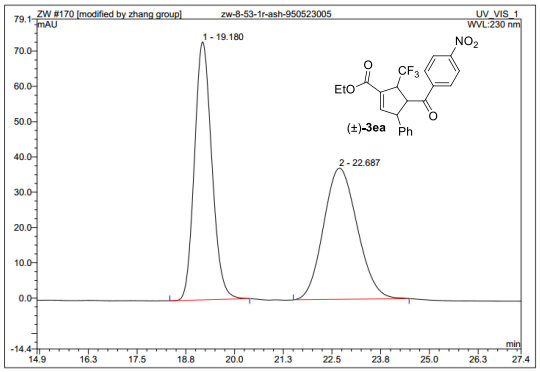




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.11 | n.a. | 79.420 | 36.236 | 53.01 | n.a. | BMB* |
| 2 | 13.49 | n.a. | 64.998 | 32.117 | 46.99 | n.a. | BMB* |
| Total: | | | 144.418 | 68.353 | 100.00 | 0.000 | |

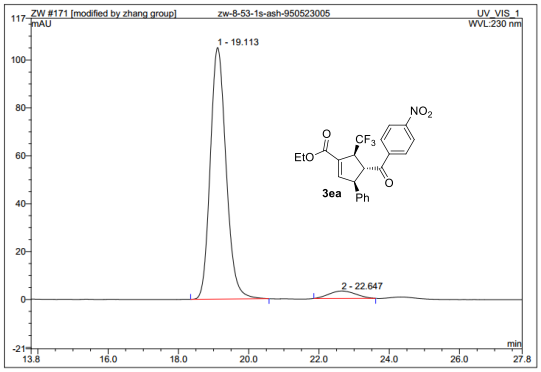
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.01 | n.a. | 142.859 | 49.184 | 94.79 | n.a. | BMB* |
| 2 | 13.27 | n.a. | 5.084 | 2.704 | 5.21 | n.a. | BMB* |
| Total: | | | 147.943 | 51.888 | 100.00 | 0.000 | |



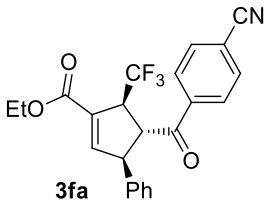

**3ea**; colorless oil; $[\alpha]_D^{20}$ = + 68.3 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.21–8.19 (m, 2H), 7.83–7.81 (m, 2H), 7.37–7.36 (m, 3H), 7.11–7.09 (m, 2H), 6.82 (s, 1H), 4.64–4.57 (m, 1H), 4.39–4.25 (m, 3H), 4.01–3.99 (m, 1H), 1.36 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 196.77, 163.02, 150.67, 146.94, 139.71, 139.65, 131.81, 130.09, 129.28, 128.32, 127.87, 126.06 (q, *J* = 280.25 Hz), 123.75, 61.22, 55.29, 55.04, 51.38 (q, *J* = 29.13 Hz), 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.49 ppm; Enantiomeric excess: 90%, determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 19.11 min, second peak: $t_R$ = 22.64 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}F_3NNaO_5$ $[M+Na]^+$ = 456.1029, found = 456.1042.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 19.18 | n.a. | 73.108 | 37.699 | 50.21 | n.a. | BMB* |
| 2 | 22.69 | n.a. | 37.196 | 37.384 | 49.79 | n.a. | BMB* |
| Total: | | | 110.304 | 75.083 | 100.00 | 0.000 | |

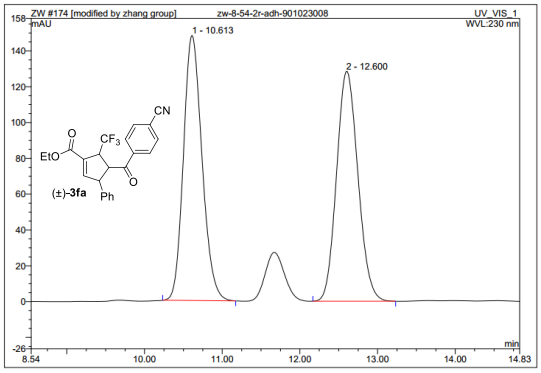


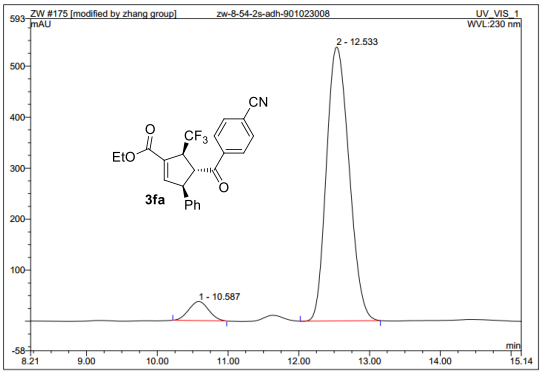

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 19.11 | n.a. | 105.037 | 54.745 | 95.29 | n.a. | BMB* |
| 2 | 22.65 | n.a. | 3.092 | 2.704 | 4.71 | n.a. | BMB* |
| Total: | | | 108.129 | 57.450 | 100.00 | 0.000 | |




**3fa**; colorless oil; $[\alpha]_D^{20}$ = + 82.8 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.00 Hz, 2H), 7.66 (d, *J* = 8.50 Hz, 2H), 7.36–7.35 (m, 3H), 7.09–7.08 (m,

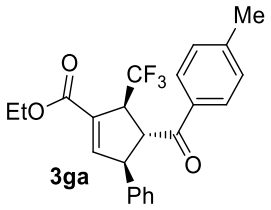
2H), 6.81 (s, 1H), 4.62–4.56 (m, 1H), 4.38–4.21 (m, 3H), 3.98–3.97 (m, 1H), 1.35 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 196.96, 163.05, 146.98, 139.69, 138.23, 132.40, 131.82, 129.42, 129.23, 128.26, 127.88, 126.07 (q, $J$ = 278.13 Hz), 117.60, 117.07, 61.21, 55.30, 54.75 (d, $J$ = 1.25 Hz), 51.32 (q, $J$ = 29.38 Hz), 14.06; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.51 ppm; Enantiomeric excess: 88%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.58 min, second peak: $t_R$ = 12.53 min; HRMS (ESI) m/z calcd. for $C_{23}H_{18}F_3NNaO_3$ $[M+Na]^+$ = 436.1131, found = 436.1131.



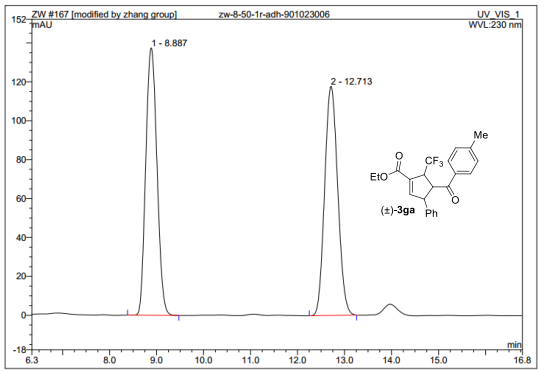

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.61 | n.a. | 147.938 | 41.076 | 50.08 | n.a. | BMB* |
| 2 | 12.60 | n.a. | 128.339 | 40.949 | 49.92 | n.a. | BMB* |
| Total: | | | 276.277 | 82.025 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.59 | n.a. | 37.365 | 12.153 | 5.76 | n.a. | BMB* |
| 2 | 12.53 | n.a. | 536.718 | 198.660 | 94.24 | n.a. | BMB* |
| Total: | | | 574.084 | 210.813 | 100.00 | 0.000 | |

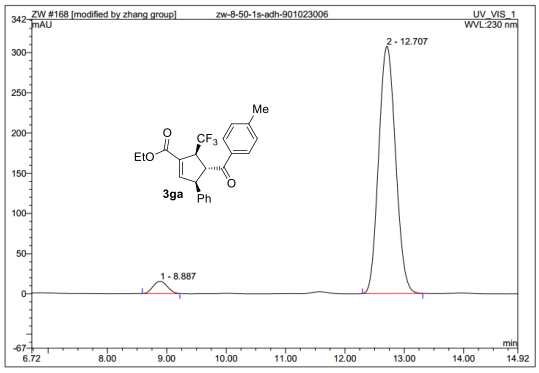



**3ga**; colorless oil; $[\alpha]_D^{20}$ = + 76.5 ($c$ = 0.33, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, $J$ = 8.40 Hz, 2H), 7.35–7.30 (m, 3H), 7.15 (d, $J$ = 8.00 Hz, 2H), 7.11–7.09 (m, 2H), 6.82 (s, 1H), 4.59–4.51 (m, 1H), 4.37–4.20 (m, 3H), 3.99–3.98 (m, 1H), 2.38 (s, 3H), 1.33 (t, $J$ = 7.20 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.78, 163.30, 147.52, 144.88, 140.27, 132.66, 131.91, 129.31, 129.27, 128.93, 128.04, 127.79, 126.31 (q, $J$ = 278.00 Hz), 61.02, 55.53, 53.86, 51.42 (q, $J$ = 28.80 Hz), 21.62, 14.07; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.47 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.6 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 8.88 min, second peak: $t_R$ = 12.70 min; HRMS (ESI) m/z calcd.

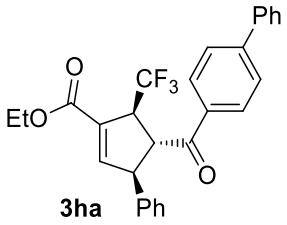
for $C_{23}H_{21}F_3NaO_3$ $[M+Na]^+$ = 425.1335, found = 425.1343.



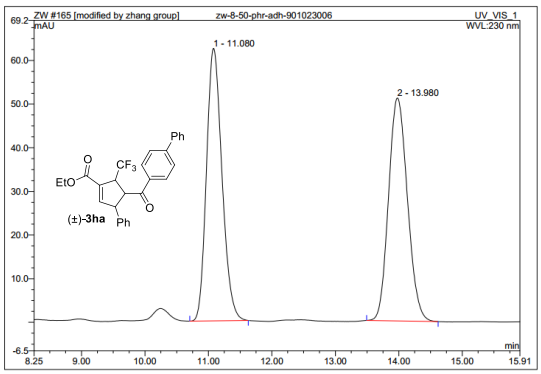

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.89 | n.a. | 137.406 | 37.902 | 50.01 | n.a. | BMB* |
| 2 | 12.71 | n.a. | 117.814 | 37.883 | 49.99 | n.a. | BMB* |
| Total: | | | 255.220 | 75.785 | 100.00 | 0.000 | |

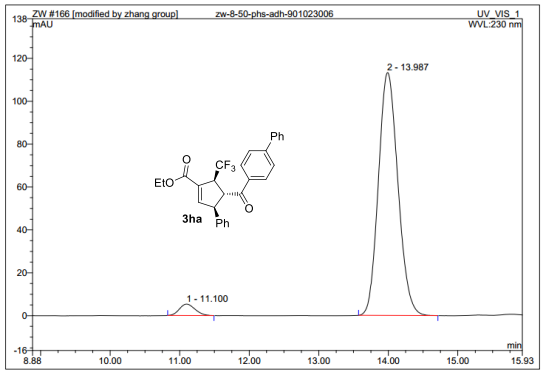



| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.89 | n.a. | 15.245 | 4.216 | 3.99 | n.a. | BMB* |
| 2 | 12.71 | n.a. | 307.460 | 101.468 | 96.01 | n.a. | BMB* |
| Total: | | | 322.706 | 105.684 | 100.00 | 0.000 | |



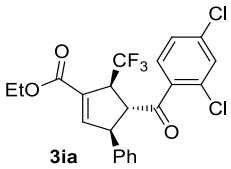

**3jd**; colorless oil; $[\alpha]_D^{20}$ = + 109.3 (*c* = 0.33, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.40 Hz, 2H), 7.59–7.56 (m, 4H), 7.47–7.29 (m, 6H), 7.14–7.11 (m, 2H), 6.83 (s, 1H), 4.64–4.56 (m, 1H), 4.37–4.21 (m, 3H), 4.03–4.02 (m, 1H), 1.33 (t, *J* = 7.20 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.71, 163.27, 147.44, 146.50, 140.23, 139.49, 133.85, 131.93, 129.74, 129.00, 128.95, 128.41, 128.06, 127.88, 127.22, 127.19, 126.32 (q, *J* = 278.10 Hz), 61.05, 55.56, 54.12, 51.44 (q, *J* = 28.90 Hz), 14.07; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.40 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.6 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 11.10 min, second peak: $t_R$ = 13.98 min; HRMS (ESI) m/z calcd. for $C_{28}H_{23}F_3NaO_3$ $[M+Na]^+$ = 487.1491, found = 487.1497.



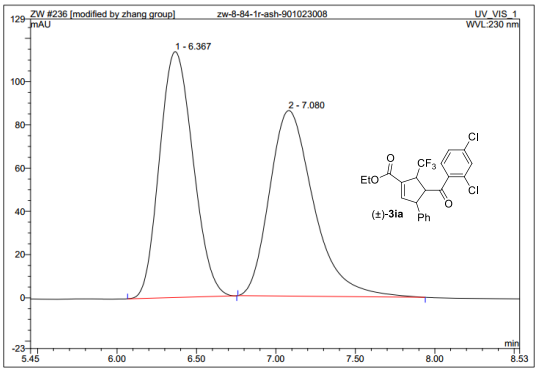



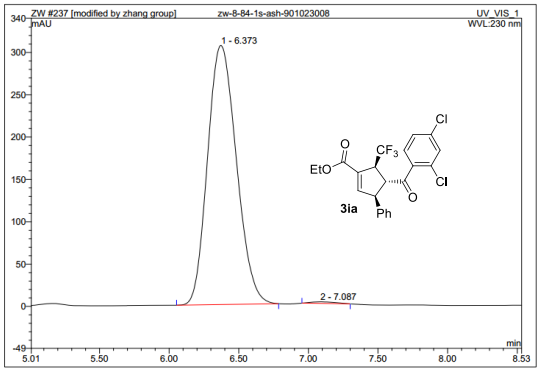

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.08 | n.a. | 62.449 | 17.611 | 49.99 | n.a. | BMB* |
| 2 | 13.98 | n.a. | 51.084 | 17.619 | 50.01 | n.a. | BMB* |
| Total: | | | 113.533 | 35.230 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.10 | n.a. | 5.341 | 1.382 | 3.62 | n.a. | BMB* |
| 2 | 13.99 | n.a. | 113.226 | 36.767 | 96.38 | n.a. | BMB* |
| Total: | | | 118.568 | 38.149 | 100.00 | 0.000 | |



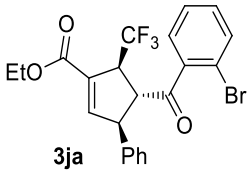

**3ia**; colorless oil; $[\alpha]_D^{20}$ = + 102.0 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 5.60 Hz, 1H), 7.26–7.17 (m, 5H), 6.93–6.90 (m, 2H), 6.81 (s, 1H), 4.52–4.44 (m, 1H), 4.36–4.21 (m, 2H), 4.15–4.11 (m, 2H), 1.33 (t, *J* = 6.80 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.48, 163.07, 147.02, 140.05, 137.91, 135.99, 132.54, 131.76 (q, *J* = 2.00 Hz), 130.60, 130.10, 128.90, 127.78, 127.41, 127.18, 126.02 (q, *J* = 276.30 Hz), 61.14, 58.27, 53.68, 50.12 (q, *J* = 29.30 Hz), 14.06; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.96 ppm; Enantiomeric excess: 99%, determined by HPLC (Chiralpak AS-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 6.37 min, second peak: $t_R$ = 7.08 min; HRMS (ESI) m/z calcd. for $C_{22}H_{17}Cl_2F_3NaO_3$ $[M+Na]^+$ = 479.0399, found = 479.0399.



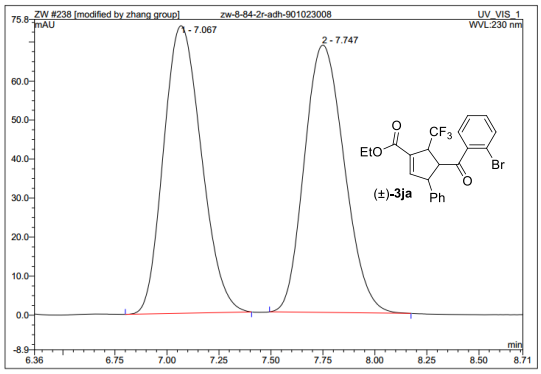




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.37 | n.a. | 113.726 | 27.785 | 50.04 | n.a. | BMB* |
| 2 | 7.08 | n.a. | 85.790 | 27.739 | 49.96 | n.a. | BMB* |
| Total: | | | 199.517 | 55.525 | 100.00 | 0.000 | |

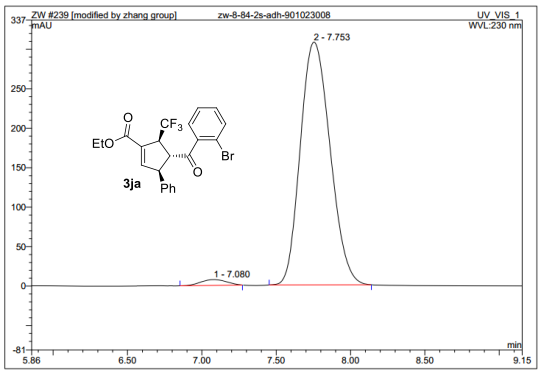
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.37 | n.a. | 306.181 | 73.539 | 99.48 | n.a. | BMB* |
| 2 | 7.09 | n.a. | 1.854 | 0.388 | 0.52 | n.a. | BMB* |
| Total: | | | 308.035 | 73.926 | 100.00 | 0.000 | |



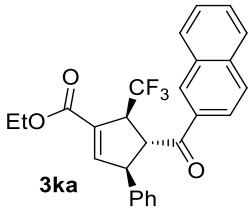

**3ja**; colorless oil; $[\alpha]_D^{20}$ = + 69.1 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.63–7.61 (m, 1H), 7.33–7.26 (m, 2H), 7.21–7.19 (m, 4H), 6.89–6.83 (m, 3H), 4.57–4.49 (m, 1H), 4.37–4.20 (m, 3H), 4.14–4.12 (m, 1H), 1.34 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 199.85, 163.15, 147.14, 140.29, 139.82, 133.86, 132.15, 131.85 (d, *J* = 2.10 Hz), 129.00, 128.77, 127.59, 127.42, 127.31, 126.13 (q, *J* = 278.10 Hz), 119.57, 61.11, 58.29, 53.20, 49.80 (q, *J* = 29.20 Hz), 14.08; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.97 ppm; Enantiomeric excess: 96%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.08 min, second peak: $t_R$ = 7.75 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}BrF_3NaO_3$ $[M+Na]^+$ = 489.0284, found = 489.0288.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.07 | n.a. | 73.701 | 15.543 | 50.42 | n.a. | BMB* |
| 2 | 7.75 | n.a. | 68.497 | 15.283 | 49.58 | n.a. | BMB* |
| Total: | | | 142.198 | 30.825 | 100.00 | 0.000 | |

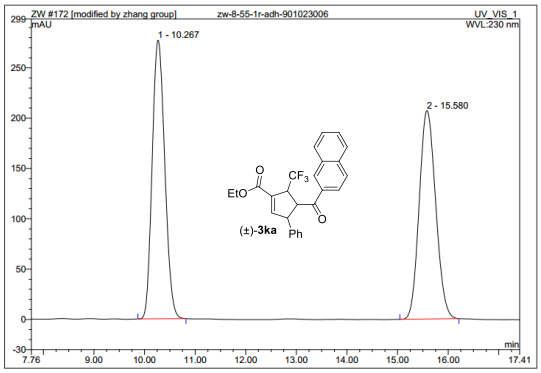



| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.08 | n.a. | 7.438 | 1.495 | 2.05 | n.a. | BMB* |
| 2 | 7.75 | n.a. | 307.709 | 71.568 | 97.95 | n.a. | BMB* |
| Total: | | | 315.147 | 73.062 | 100.00 | 0.000 | |

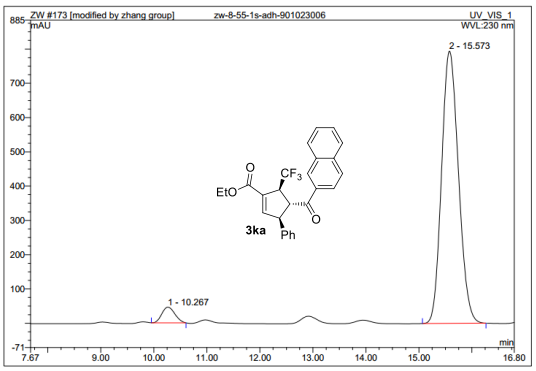



**3ka**; colorless oil; $[\alpha]_D^{20}$ = - 28.0 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.96–7.94 (m, 1H), 7.90 (s, 1H), 7.84 (d, *J* = 8.40 Hz, 2H), 7.60–7.54 (m, 2H), 7.50–7.46 (m, 1H), 7.35–7.29 (m, 3H), 7.13–7.11 (m, 2H), 6.83 (s, 1H), 4.74–4.68 (m, 1H), 4.41–4.24 (m, 3H), 4.02–4.00 (m, 1H), 1.34 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100

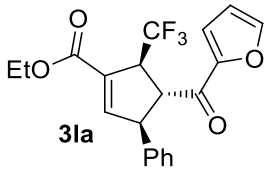
MHz, $CDCl_3$): δ 197.61, 163.37, 147.35, 140.41, 135.88, 132.34, 132.14, 132.03, 131.75, 129.67, 129.10, 128.99, 128.63, 128.30, 128.00, 127.72, 126.89, 126.44 (q, *J* = 278.00 Hz), 124.37, 61.12, 55.73, 54.57, 51.22 (q, *J* = 28.90 Hz), 14.13; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.39 ppm; Enantiomeric excess: 91%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.6 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.26 min, second peak: $t_R$ = 15.57 min; HRMS (ESI) m/z calcd. for $C_{26}H_{21}F_3NaO_3$ $[M+Na]^+$ = 461.1335, found = 461.1344.



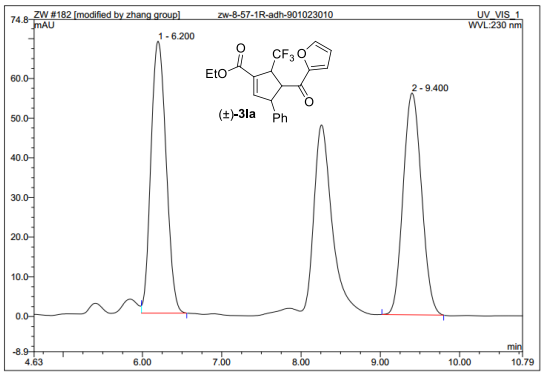

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.27 | n.a. | 276.883 | 79.781 | 50.54 | n.a. | BMB* |
| 2 | 15.58 | n.a. | 207.102 | 78.089 | 49.46 | n.a. | BMB* |
| Total: | | | 483.985 | 157.870 | 100.00 | 0.000 | |

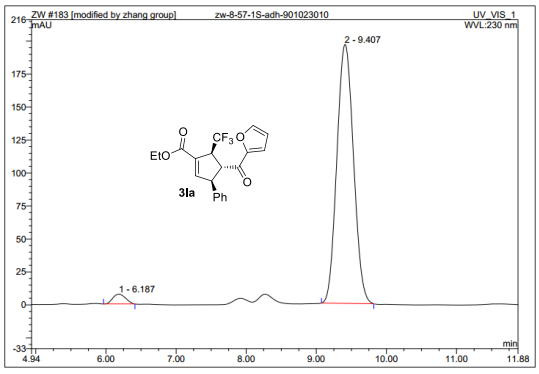



| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.27 | n.a. | 45.944 | 13.055 | 4.27 | n.a. | MB* |
| 2 | 15.57 | n.a. | 793.997 | 293.026 | 95.73 | n.a. | BMB* |
| Total: | | | 839.942 | 306.081 | 100.00 | 0.000 | |



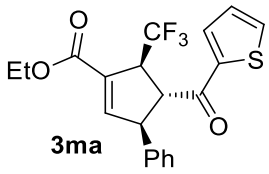

**3la**; colorless oil; $[\alpha]_D^{20}$ = + 104.0 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 1.0 Hz, 1H), 7.37–7.30 (m, 3H), 7.16–7.15 (m, 2H), 6.94 (d, *J* = 3.50 Hz, 1H), 6.87 (s, 1H), 6.50–6.49 (m, 1H), 4.49–4.43 (m, 1H), 4.37–4.23 (m, 2H), 4.15–4.14 (m, 1H), 4.02–4.00 (m, 1H), 1.34 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 186.43, 163.16, 151.15, 147.79, 147.63, 140.34, 131.82, 128.88, 127.82, 127.74, 126.08 (q, *J* = 278.13 Hz), 119.79, 112.55, 61.05, 55.20, 54.68, 51.17 (q, *J* = 29.13 Hz), 14.04; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.74 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 6.18 min, second peak: $t_R$ = 9.40 min; HRMS (ESI) m/z calcd. for $C_{20}H_{17}F_3NaO_4$ $[M+Na]^+$ = 401.0971, found = 401.0974.



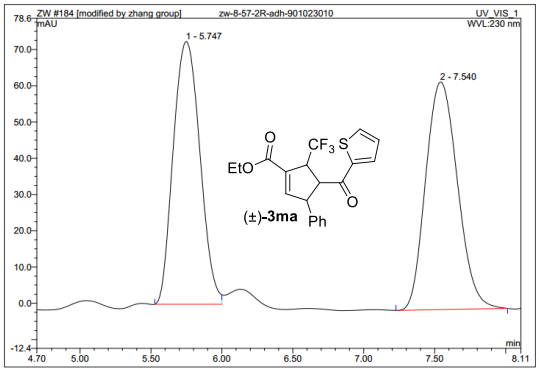



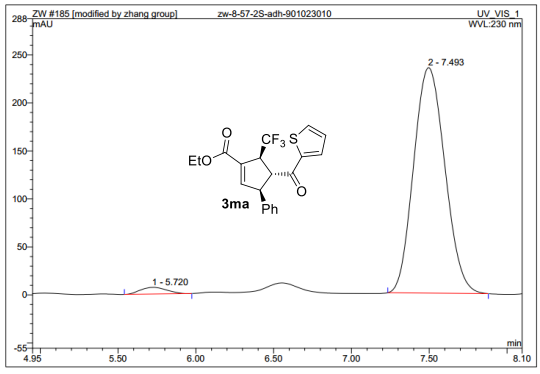

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.20 | n.a. | 68.487 | 15.204 | 50.29 | n.a. | MB* |
| 2 | 9.40 | n.a. | 55.899 | 15.031 | 49.71 | n.a. | BMB* |
| Total: | | | 124.386 | 30.235 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.19 | n.a. | 7.459 | 1.565 | 2.83 | n.a. | BMB* |
| 2 | 9.41 | n.a. | 196.351 | 53.763 | 97.17 | n.a. | BMB* |
| Total: | | | 203.810 | 55.328 | 100.00 | 0.000 | |



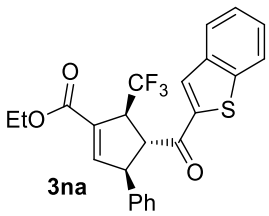

**3ma**; colorless oil; $[\alpha]_D^{20}$ = + 90.7 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.71–7.70 (m, 1H), 7.38–7.33 (m, 3H), 7.20–7.19 (m, 1H), 7.17–7.15 (m, 2H), 7.02–7.00 (m, 1H), 6.87 (s, 1H), 4.55–4.49 (m, 1H), 4.38–4.24 (m, 2H), 4.13–4.11 (m, 1H), 4.07–4.05 (m, 1H), 1.35 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 190.90, 163.16, 147.55, 142.77, 140.25, 135.64, 133.57, 131.82, 128.97, 128.24, 127.92, 127.87, 126.13 (q, *J* = 278.13 Hz), 61.05, 55.68, 55.50, 51.65 (q, *J* = 29.13 Hz), 14.04; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.58 ppm; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 5.72 min, second peak: $t_R$ = 7.49 min; HRMS (ESI) m/z calcd. for $C_{20}H_{17}F_3NaO_3S$ $[M+Na]^+$ = 417.0743, found = 417.0748.



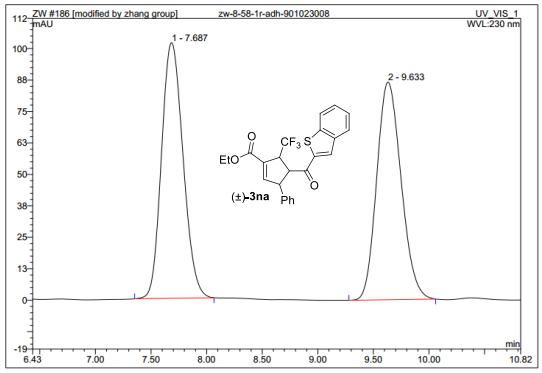




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 5.75 | n.a. | 72.437 | 15.807 | 49.16 | n.a. | BM * |
| 2 | 7.54 | n.a. | 62.809 | 16.347 | 50.84 | n.a. | BMB* |
| Total: | | | 135.246 | 32.154 | 100.00 | 0.000 | |

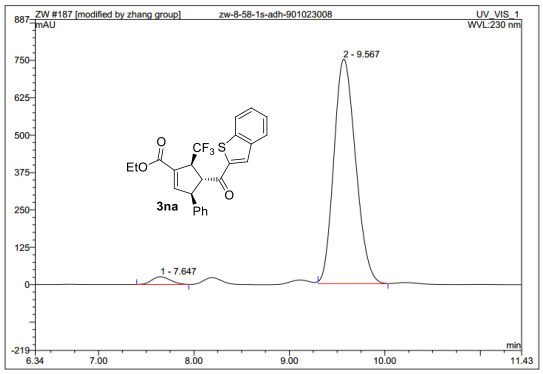
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 5.72 | n.a. | 7.008 | 1.368 | 2.44 | n.a. | BMB* |
| 2 | 7.49 | n.a. | 234.839 | 54.744 | 97.56 | n.a. | BMB* |
| Total: | | | 241.847 | 56.112 | 100.00 | 0.000 | |



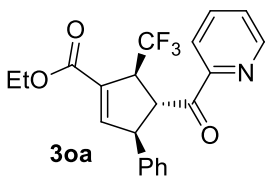

**3na**; colorless oil; $[\alpha]_D^{20}$ = + 46.3 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.85–7.83 (m, 1H), 7.64 (d, *J* = 8.00 Hz, 1H), 7.47–7.43 (m, 1H), 7.37–7.30 (m, 5H), 7.17–7.14 (m, 2H), 6.86 (s, 1H), 4.61–4.53 (m, 1H), 4.37–4.26 (m, 2H), 4.18–4.15 (m, 1H), 4.12–4.10 (m, 1H), 1.33 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 192.26, 163.13, 147.34, 143.13, 142.04, 140.25, 138.74, 131.91, 131.22, 129.04, 128.04, 127.96, 127.93, 126.20, 126.14 (q, *J* = 278.00 Hz), 125.07, 122.86, 61.08, 55.72, 55.52, 51.53 (q, *J* = 29.10 Hz), 14.04; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.55 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.64 min, second peak: $t_R$ = 9.56 min; HRMS (ESI) m/z calcd. for $C_{24}H_{19}F_3NaO_3S$ $[M+Na]^+$ = 467.0899, found = 467.0900.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.69 | n.a. | 101.581 | 22.857 | 50.96 | n.a. | BMB* |
| 2 | 9.63 | n.a. | 86.490 | 21.993 | 49.04 | n.a. | BMB* |
| Total: | | | 188.071 | 44.850 | 100.00 | 0.000 | |

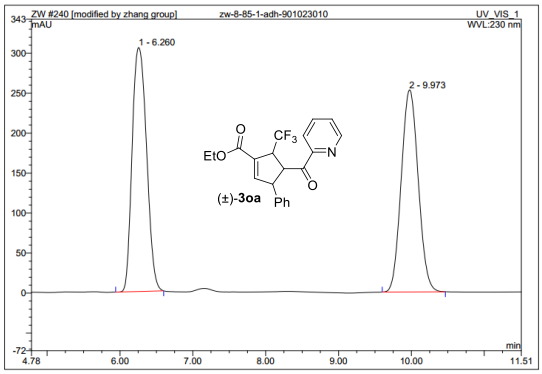


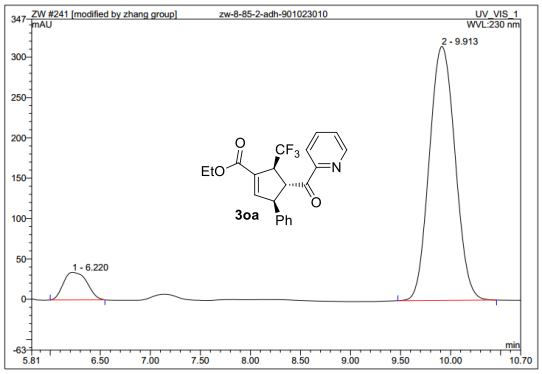

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.65 | n.a. | 25.897 | 5.813 | 2.85 | n.a. | BMB* |
| 2 | 9.57 | n.a. | 750.026 | 198.071 | 97.15 | n.a. | MB* |
| Total: | | | 775.923 | 203.884 | 100.00 | 0.000 | |




**3oa**; colorless oil; $[\alpha]_D^{20}$ = + 50.7 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.50 (d, *J* = 4.00 Hz, 1H), 8.13 (d, *J* = 8.00 Hz, 1H), 7.89–7.86 (m, 1H), 7.49–7.46 (m, 1H), 7.33–7.28 (m, 3H), 7.18–7.16 (m, 2H), 6.91 (s, 1H), 5.01–4.99 (m, 1H),

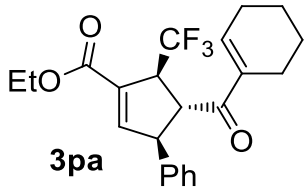
4.54–4.47 (m, 1H), 4.39–4.25 (m, 2H), 4.07 (br, 1H), 1.36 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 199.28, 163.40, 151.56, 148.89, 147.76, 140.44, 136.93, 132.07, 128.40, 128.10, 127.52, 127.26, 126.24 (q, $J$ = 278.25 Hz), 123.14, 60.98, 54.87, 52.42, 50.55 (q, $J$ = 29.00 Hz), 14.09; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.38 ppm; Enantiomeric excess: 82%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 6.22 min, second peak: $t_R$ = 9.91 min; HRMS (ESI) m/z calcd. for $C_{21}H_{19}F_3NO_3$ [M+Na] $^+$ = 390.1312, found = 390.1318.



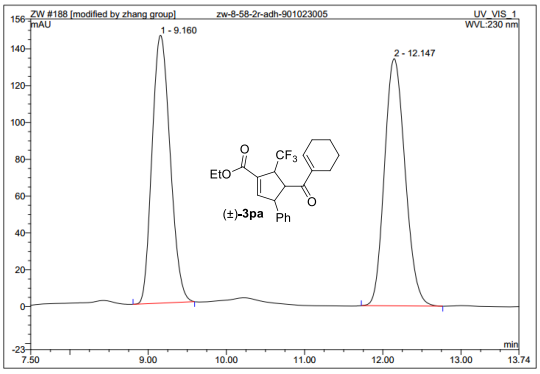



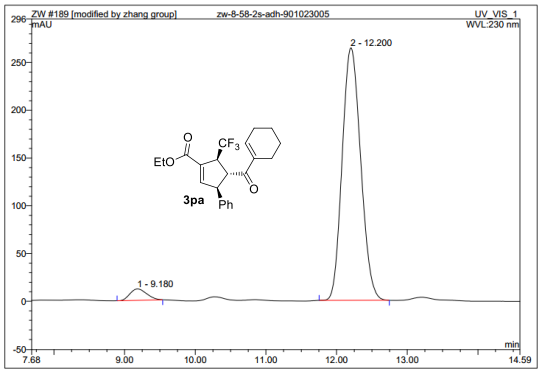

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.26 | n.a. | 304.956 | 70.028 | 50.64 | n.a. | BMB* |
| 2 | 9.97 | n.a. | 252.791 | 68.270 | 49.36 | n.a. | BMB* |
| Total: | | | 557.747 | 138.298 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.22 | n.a. | 34.265 | 9.319 | 9.01 | n.a. | BMB* |
| 2 | 9.91 | n.a. | 314.708 | 94.063 | 90.99 | n.a. | BMB* |
| Total: | | | 348.973 | 103.382 | 100.00 | 0.000 | |



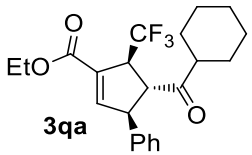

**3pa**; colorless oil; $[\alpha]_D^{20}$ = + 54.5 ($c$ = 0.33, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.37–7.27 (m, 3H), 7.16–7.14 (m, 2H), 6.77 (s, 1H), 6.33–6.31 (m, 1H), 4.47–4.38 (m, 1H), 4.35–4.19 (m, 2H), 3.93–3.90 (m, 1H), 3.84–3.81 (m, 1H), 2.33–1.93 (m, 4H), 1.65–1.54 (m, 4H), 1.32 (t, $J$ = 6.80 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.57, 163.37, 147.38, 143.51, 140.60, 137.88, 132.04, 128.85, 128.00, 126.33 (q, $J$ = 277.00 Hz), 60.95, 55.71, 52.81, 51.25 (q, $J$ = 28.70 Hz), 26.11, 23.55, 21.79, 21.32, 14.05; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.65 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 9.18 min, second peak: $t_R$ = 12.20 min; HRMS (ESI) m/z calcd. for $C_{22}H_{23}F_3NaO_3$ [M+Na] $^+$ = 415.1491, found = 415.1496.



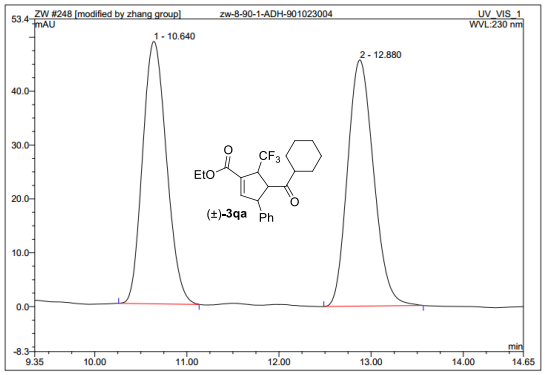



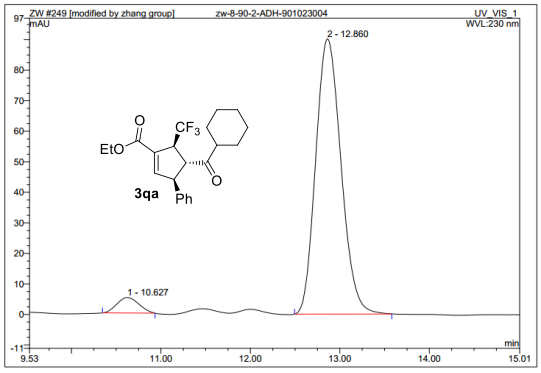

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.16 | n.a. | 145.469 | 39.026 | 48.69 | n.a. | BMB* |
| 2 | 12.15 | n.a. | 134.260 | 41.117 | 51.31 | n.a. | BMB* |
| Total: | | | 279.729 | 80.143 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.18 | n.a. | 11.985 | 3.293 | 3.95 | n.a. | BMB* |
| 2 | 12.20 | n.a. | 264.321 | 80.019 | 96.05 | n.a. | BMB* |
| Total: | | | 276.306 | 83.312 | 100.00 | 0.000 | |



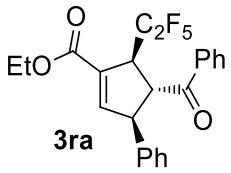

**3qa**; colorless oil; $[\alpha]_D^{20}$ = + 116.8 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.41–7.38 (m, 2H), 7.35–7.32 (m, 1H), 7.23–7.21 (m, 2H), 6.79 (s, 1H), 4.35–4.21 (m, 3H), 4.06–4.04 (m, 1H), 3.55–3.53 (m, 1H), 2.42–2.36 (m, 1H), 1.79–1.72 (m, 4H), 1.46–1.16 (m, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 210.89, 163.23, 147.67, 140.83, 131.54, 129.09, 127.80, 127.62, 126.17 (q, *J* = 278.00 Hz), 61.01, 57.01, 53.94, 50.70 (q, *J* = 28.88 Hz), 50.10, 28.57, 28.02, 25.59, 25.49, 25.35, 14.06; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -68.02 ppm; Enantiomeric excess: 91%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.4 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.63 min, second peak: $t_R$ = 12.86 min; HRMS (ESI) m/z calcd. for $C_{22}H_{25}F_3NaO_3$ $[M+Na]^+$ = 417.1648, found = 417.1653.



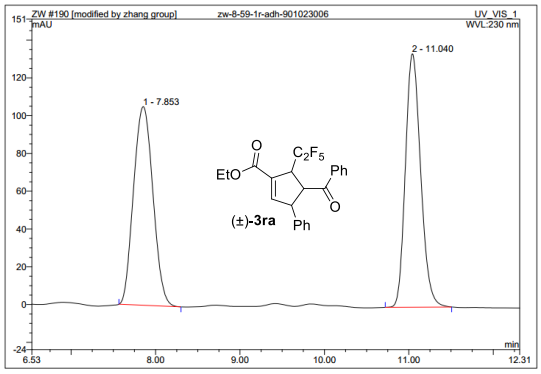




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.64 | n.a. | 48.712 | 14.676 | 49.50 | n.a. | BMB* |
| 2 | 12.88 | n.a. | 45.688 | 14.975 | 50.50 | n.a. | BMB* |
| Total: | | | 94.399 | 29.651 | 100.00 | 0.000 | |

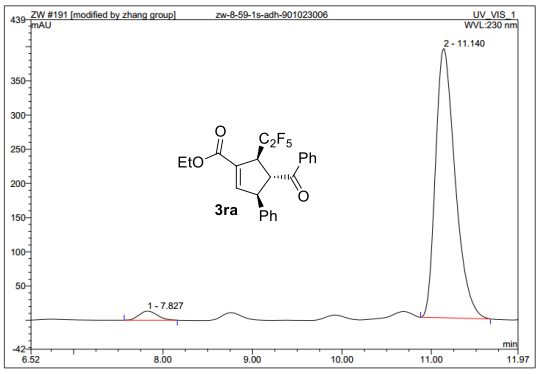
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.63 | n.a. | 5.072 | 1.432 | 4.63 | n.a. | BMB* |
| 2 | 12.86 | n.a. | 90.168 | 29.537 | 95.37 | n.a. | BMB* |
| Total: | | | 95.241 | 30.970 | 100.00 | 0.000 | |



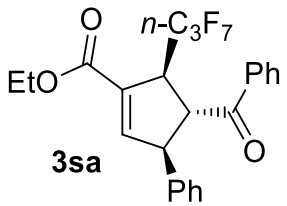

**3ra**; colorless oil; $[\alpha]_D^{20}$ = + 33.9 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.61–7.58 (m, 1H), 7.41–7.38 (m, 2H), 7.35–7.33 (m, 3H), 7.10–7.08 (m, 2H), 6.77–6.76 (m, 1H), 4.84–4.77 (m, 1H), 4.38–4.26 (m, 3H), 3.92–3.91 (m, 1H), 1.36 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 197.87, 163.78, 146.36, 139.96, 135.00, 133.87, 132.20, 129.18, 128.91, 128.64, 128.18, 127.92, 122.47 (t, *J* = 36.25 Hz), 120.19 (t, *J* = 36.50 Hz), 118.20–116.58 (m), 115.63–114.55 (m), 112.94 (t, *J* = 36.75 Hz), 61.11, 56.17, 53.47, 48.33 (t, *J* = 20.50 Hz), 14.02; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -82.94, -116.11 (q) ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.6 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.82 min, second peak: $t_R$ = 11.14 min; HRMS (ESI) m/z calcd. for $C_{23}H_{19}F_5NaO_3$ $[M+Na]^+$ = 461.1147, found = 461.1154.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.85 | n.a. | 105.141 | 27.970 | 49.84 | n.a. | BMB* |
| 2 | 11.04 | n.a. | 134.095 | 28.150 | 50.16 | n.a. | BMB* |
| Total: | | | 239.236 | 56.120 | 100.00 | 0.000 | |

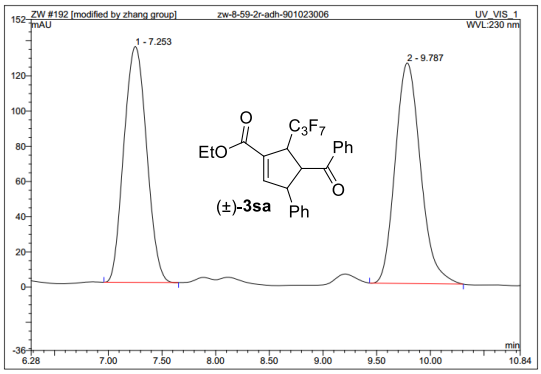



| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.83 | n.a. | 13.230 | 3.105 | 3.00 | n.a. | BMB* |
| 2 | 11.14 | n.a. | 393.574 | 100.313 | 97.00 | n.a. | BMB* |
| Total: | | | 406.804 | 103.418 | 100.00 | 0.000 | |

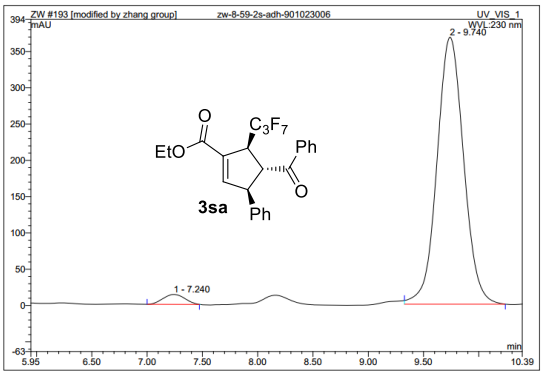



**3sa**; colorless oil; $[\alpha]_D^{20}$ = + 18.8 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ

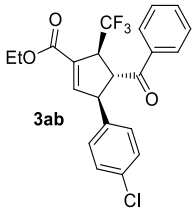
7.73 (d, $J$ = 7.50 Hz, 2H), 7.62–7.59 (m, 1H), 7.42–7.39 (m, 2H), 7.35–7.33 (m, 3H), 7.10–7.08 (m, 2H), 6.77–6.76 (m, 1H), 4.95–4.90 (m, 1H), 4.39–4.25 (m, 3H), 3.90 (br, 1H), 1.36 (t, $J$ = 7.50 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 197.72, 163.83, 146.17, 139.93, 134.96, 133.88, 132.32, 129.18, 128.92, 128.67, 128.21, 127.93, 121.08, 119.24–118.52 (m), 117.19–116.23 (m), 115.14–114.21 (m), 111.80–110.90 (m), 109.70–108.80 (m), 107.59–106.69 (m), 61.08, 56.49, 53.39, 48.39 (t, $J$ = 20.63 Hz), 14.00; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -80.38 (t), -111.06–-115.15 (m), -124.53–-126.91 (m) ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.6 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.24 min, second peak: $t_R$ = 9.74 min; HRMS (ESI) m/z calcd. for $C_{24}H_{19}F_7NaO_3$ $[M+Na]^+$ = 511.1115, found = 511.1125.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.25 | n.a. | 133.988 | 32.976 | 49.09 | n.a. | BMB* |
| 2 | 9.79 | n.a. | 125.257 | 34.205 | 50.91 | n.a. | BMB* |
| Total: | | | 259.246 | 67.181 | 100.00 | 0.000 | |

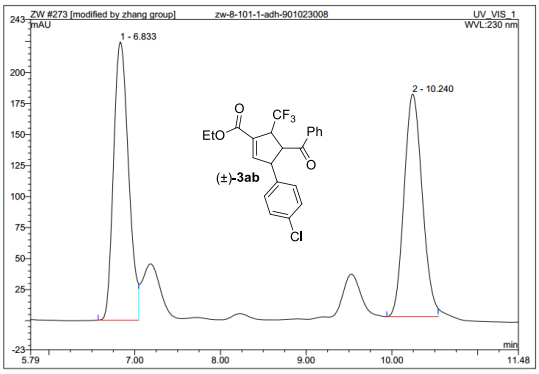


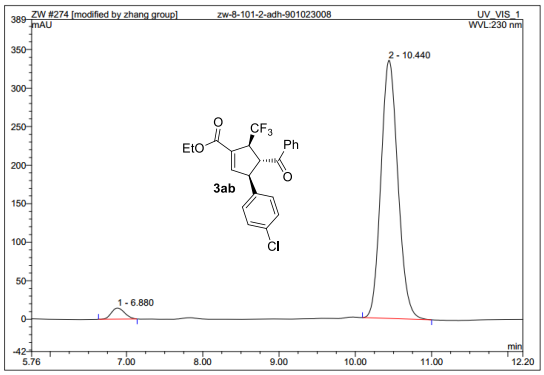

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.24 | n.a. | 13.696 | 3.124 | 2.95 | n.a. | BMB* |
| 2 | 9.74 | n.a. | 368.014 | 102.761 | 97.05 | n.a. | MB* |
| Total: | | | 381.709 | 105.885 | 100.00 | 0.000 | |




**3ab**; colorless oil; $[\alpha]_D^{20}$ = + 137.4 ($c$ = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.62–7.59 (m, 1H), 7.43–7.40 (m, 2H), 7.32–7.30 (m, 2H), 7.04–7.02 (m, 2H), 6.80 (s, 1H), 4.59–4.53 (m, 1H), 4.38–4.32 (m, 1H), 4.30–4.25 (m, 1H), 4.21–4.19 (m, 1H), 4.02–4.01 (m, 1H), 1.35 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 197.85, 163.08, 146.74, 138.68, 135.09, 133.99, 133.77, 132.39, 129.35, 129.10, 129.05, 128.73, 126.18 (q, $J$ = 278.00 Hz), 61.15, 54.61, 54.84, 51.25

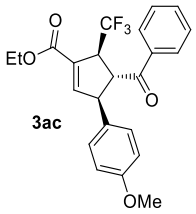
(q, $J$ = 28.88 Hz), 14.05; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.53 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 6.88 min, second peak: $t_R$ = 10.44 min; HRMS (ESI) m/z calcd. for $C_{22}H_{18}ClF_3NaO_3$ $[M+Na]^+$ = 445.0789, found = 445.0792.



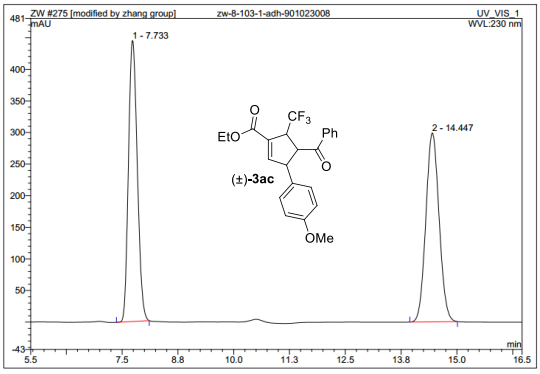



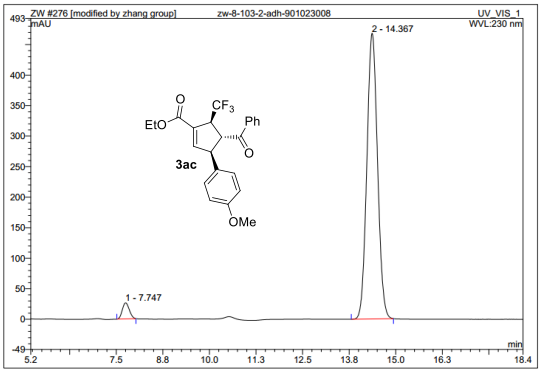

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.83 | n.a. | 224.092 | 45.257 | 50.74 | n.a. | BM * |
| 2 | 10.24 | n.a. | 179.301 | 43.945 | 49.26 | n.a. | BM * |
| Total: | | | 403.393 | 89.202 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 6.88 | n.a. | 14.392 | 2.895 | 3.24 | n.a. | BMB* |
| 2 | 10.44 | n.a. | 335.048 | 86.353 | 96.76 | n.a. | BMB* |
| Total: | | | 349.440 | 89.248 | 100.00 | 0.000 | |



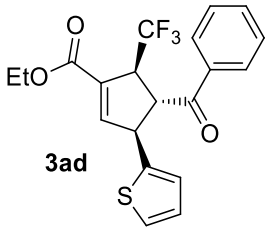

**3ac**; colorless oil; $[\alpha]_D^{20}$ = + 121.6 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, $J$ = 7.50 Hz, 2H), 7.60–7.57 (m, 1H), 7.41–7.38 (m, 2H), 7.02 (d, $J$ = 8.50 Hz, 2H), 6.87 (d, $J$ = 8.50 Hz, 2H), 6.80 (s, 1H), 4.63–4.57 (m, 1H), 4.38–4.31 (m, 1H), 4.30–4.25 (m, 1H), 4.24–4.21 (m, 1H), 3.96–3.95 (m, 1H), 3.83 (s, 3H), 1.35 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 198.19, 163.32, 159.18, 147.69, 135.20, 133.79, 132.18, 131.53, 129.15, 128.61, 126.32 (q, $J$ = 278.00 Hz), 114.26, 61.01, 55.26, 54.83, 54.25, 51.07 (q, $J$ = 28.88 Hz), 14.06; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.50 ppm; Enantiomeric excess: 93%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.74 min, second peak: $t_R$ = 14.36 min; HRMS (ESI) m/z calcd. for $C_{23}H_{21}F_3NaO_4$ $[M+Na]^+$ = 441.1284, found = 441.1289.



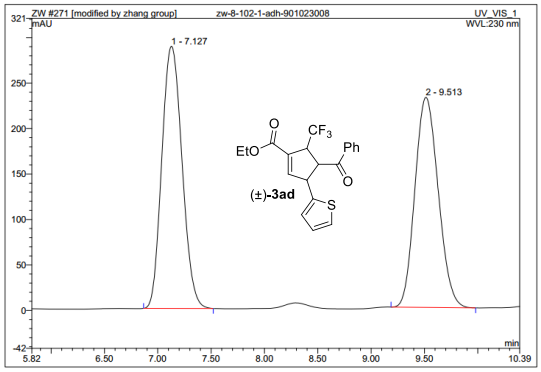



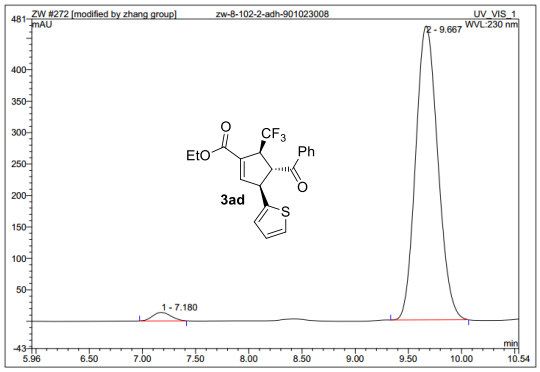

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.73 | n.a. | 444.424 | 102.157 | 49.85 | n.a. | BMB* |
| 2 | 14.45 | n.a. | 298.874 | 102.790 | 50.15 | n.a. | BMB* |
| Total: | | | 743.298 | 204.948 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.75 | n.a. | 26.271 | 5.700 | 3.54 | n.a. | BMB* |
| 2 | 14.37 | n.a. | 468.067 | 155.284 | 96.46 | n.a. | BMB* |
| Total: | | | 494.338 | 160.984 | 100.00 | 0.000 | |



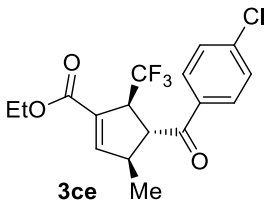

**3ad**; colorless oil; $[\alpha]_D^{20}$ = + 52.5 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.87–7.85 (m, 2H), 7.64–7.61 (m, 1H), 7.47–7.44 (m, 2H), 7.29–7.28 (m, 1H), 7.00–6.98 (m, 1H), 6.86–6.84 (m, 2H), 4.55–4.49 (m, 1H), 4.38–4.33 (m, 3H), 4.29–4.24 (m, 1H), 1.35 (t, *J* = 7.50 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 197.62, 163.07, 146.57, 142.68, 134.96, 133.98, 131.56, 129.14, 128.75, 127.17, 126.07, 126.06 (q, *J* = 276.75 Hz), 125.33, 61.13, 54.10, 51.01 (q, *J* = 29.00 Hz), 49.98, 14.06; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.53 ppm; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.18 min, second peak: $t_R$ = 9.66 min; HRMS (ESI) m/z calcd. for $C_{20}H_{17}F_3NaO_3S$ $[M+Na]^+$ = 417.0743, found = 417.0745.



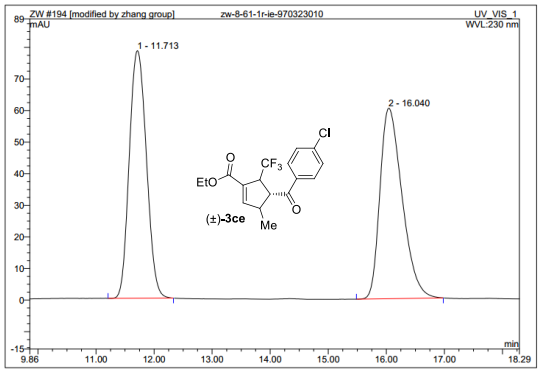



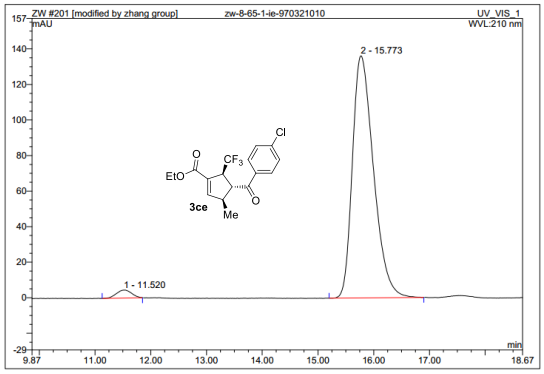

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.13 | n.a. | 288.314 | 63.366 | 52.01 | n.a. | BMB* |
| 2 | 9.51 | n.a. | 231.090 | 58.470 | 47.99 | n.a. | BMB* |
| Total: | | | 519.404 | 121.836 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.18 | n.a. | 13.437 | 2.653 | 2.30 | n.a. | BMB* |
| 2 | 9.67 | n.a. | 467.211 | 112.793 | 97.70 | n.a. | BMB* |
| Total: | | | 480.647 | 115.446 | 100.00 | 0.000 | |



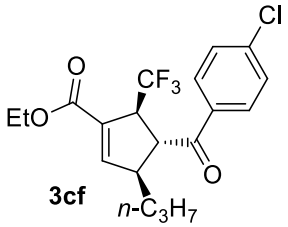

**3ce**; colorless oil; $[\alpha]_D^{20}$ = - 63.7 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.53–7.50 (m, 2H), 6.80 (s, 1H), 4.40–4.20 (m, 3H), 3.84–3.83 (m, 1H), 2.99–2.94 (m, 1H), 1.37 (d, *J* = 7.00 Hz, 3H), 1.33 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 196.67, 163.24, 150.32, 140.35, 133.60, 130.24, 130.00, 129.29, 126.21 (q, *J* = 277.88 Hz), 60.94, 52.38, 50.36 (q, *J* = 29.00 Hz), 44.68, 19.07, 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -68.10 ppm; Enantiomeric excess: 95%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 11.52 min, second peak: $t_R$ = 15.77 min; HRMS (ESI) m/z calcd. for $C_{17}H_{16}ClF_3NaO_3$ $[M+Na]^+$ = 383.0632, found = 383.0633.



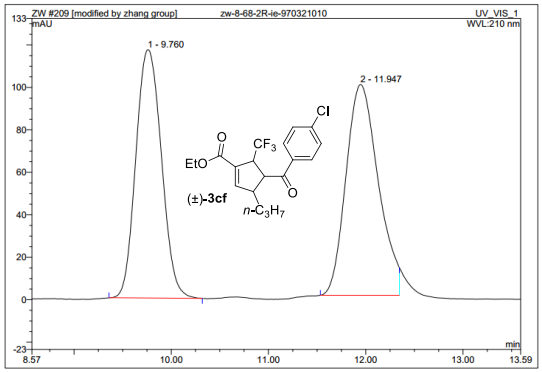




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.71 | n.a. | 78.409 | 26.789 | 50.07 | n.a. | BMB* |
| 2 | 16.04 | n.a. | 60.317 | 26.713 | 49.93 | n.a. | BMB* |
| Total: | | | 138.726 | 53.502 | 100.00 | 0.000 | |

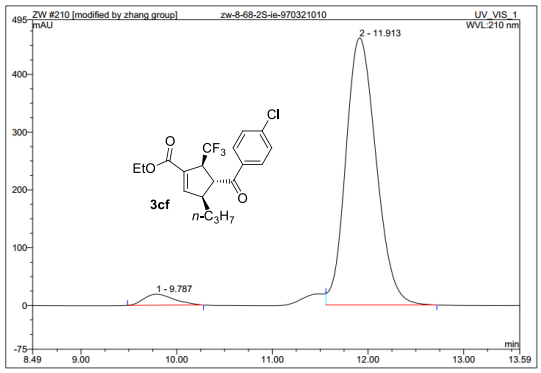
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.52 | n.a. | 4.501 | 1.423 | 2.33 | n.a. | BMB* |
| 2 | 15.77 | n.a. | 136.232 | 59.712 | 97.67 | n.a. | BMB* |
| Total: | | | 140.732 | 61.135 | 100.00 | 0.000 | |



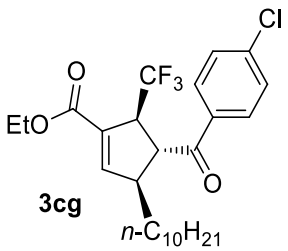

**3cf**; colorless oil; $[\alpha]_D^{20}$ = - 31.4 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.52–7.50 (m, 2H), 6.93 (s, 1H), 4.33–4.27 (m, 1H), 4.24–4.20 (m, 2H), 3.89–3.88 (m, 1H), 2.95–2.91 (m, 1H), 1.72–1.65 (m, 2H), 1.48–1.39 (m, 1H), 1.37–1.31 (m, 4H), 0.90 (t, *J* = 7.50 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 197.47, 163.23, 149.52, 140.33, 133.72, 130.41, 130.01, 129.25, 126.19 (q, *J* = 278.00 Hz), 60.90, 50.94, 50.85 (q, *J* = 28.50 Hz), 49.87, 36.52, 20.96, 14.07, 13.87; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.88 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 9.78 min, second peak: $t_R$ = 11.91 min; HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClF_3NaO_3$ $[M+Na]^+$ = 411.0945, found = 411.0946.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.76 | n.a. | 116.986 | 35.680 | 48.35 | n.a. | BMB* |
| 2 | 11.95 | n.a. | 99.336 | 38.119 | 51.65 | n.a. | BM * |
| Total: | | | 216.322 | 73.799 | 100.00 | 0.000 | |

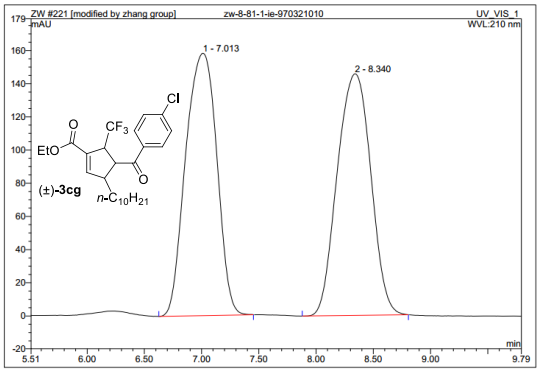


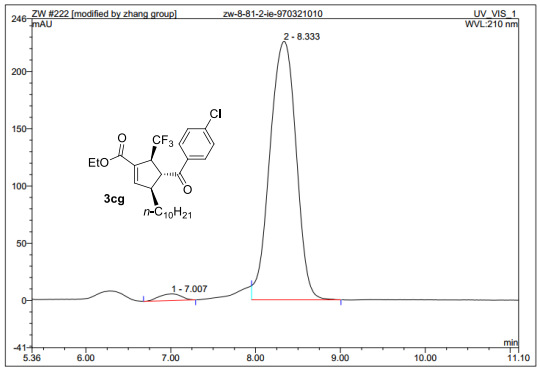

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.79 | n.a. | 18.986 | 6.966 | 3.95 | n.a. | BMB* |
| 2 | 11.91 | n.a. | 462.060 | 169.430 | 96.05 | n.a. | MB* |
| Total: | | | 481.046 | 176.396 | 100.00 | 0.000 | |




**3cg**; colorless oil; $[\alpha]_D^{20}$ = - 27.2 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.40 Hz, 2H), 7.49 (d, *J* = 8.80 Hz, 2H), 6.92 (s, 1H), 4.32–4.16 (m, 3H), 3.88–3.86 (m, 1H), 2.90–2.87 (m, 1H), 1.71–1.64 (m, 2H), 1.33–1.22 (m, 19H), 0.88

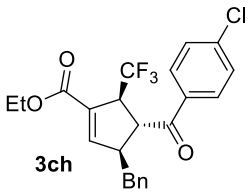
(t, $J$ = 6.80 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.50, 163.25, 149.57, 140.33, 133.74, 130.40, 130.01, 129.24, 126.20 (q, $J$ = 277.90 Hz), 60.90, 50.96, 50.82 (q, $J$ = 28.80 Hz), 50.10, 34.36, 31.84, 29.51, 29.46, 29.33, 29.26, 27.72, 22.64, 14.07; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.87 ppm; Enantiomeric excess: 96%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.00 min, second peak: $t_R$ = 8.33 min; HRMS (ESI) m/z calcd. for $C_{26}H_{34}ClF_3NaO_3$ [M+Na] $^+$ = 509.2041, found = 509.2044.



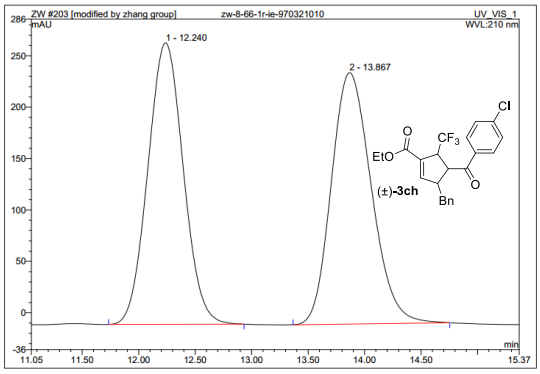



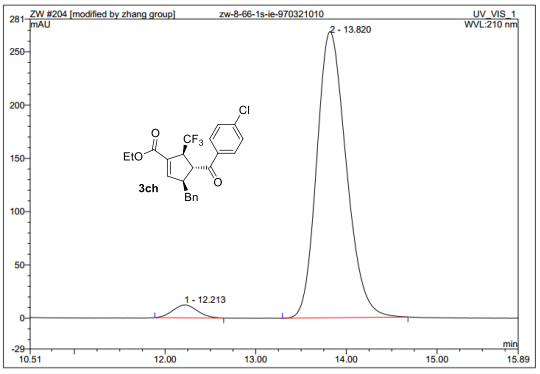

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.01 | n.a. | 158.132 | 49.998 | 50.21 | n.a. | BMB* |
| 2 | 8.34 | n.a. | 145.611 | 49.571 | 49.79 | n.a. | BMB* |
| Total: | | | 303.743 | 99.570 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.01 | n.a. | 5.827 | 1.737 | 2.10 | n.a. | BMB* |
| 2 | 8.33 | n.a. | 225.800 | 80.810 | 97.90 | n.a. | MB* |
| Total: | | | 231.627 | 82.547 | 100.00 | 0.000 | |



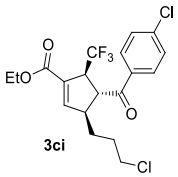

**3ch**; colorless oil; $[\alpha]_D^{20}$ = - 101.3 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, $J$ = 9.0 Hz, 2H),7.33–7.27 (m, 5H), 7.17–7.15 (m, 2H), 6.89 (s, 1H), 4.35–4.20 (m, 3H), 3.97–3.96 (m, 1H), 3.24–3.20 (m, 1H), 3.07–3.03 (m, 1H), 2.88–2.83 (m, 1H), 1.34 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 197.36, 163.13, 149.03, 139.93, 138.38, 133.14, 131.10, 129.87, 129.06, 129.03, 128.99, 126.97, 126.23 (q, $J$ = 278.13 Hz), 61.01, 51.98,50.69 (q, $J$ = 29.00 Hz), 49.10, 39.89, 14.09; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.32 ppm; Enantiomeric excess: 93%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 12.21 min, second peak: $t_R$ = 13.82 min; HRMS (ESI) m/z calcd. for $C_{23}H_{20}ClF_3NaO_3$ [M+Na] $^+$ = 459.0945, found = 459.0958.



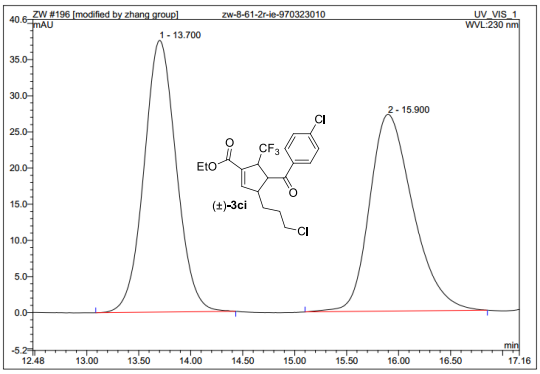



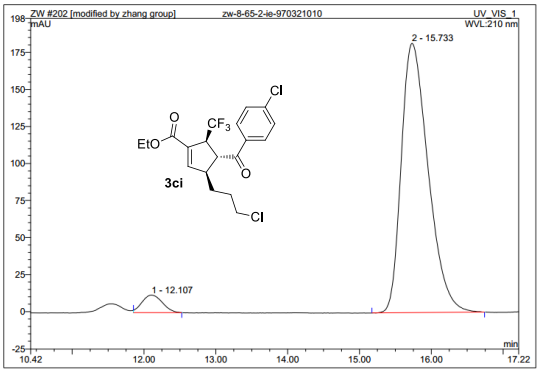

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 12.24 | n.a. | 273.775 | 99.522 | 49.83 | n.a. | BMB* |
| 2 | 13.87 | n.a. | 244.529 | 100.211 | 50.17 | n.a. | BMB* |
| Total: | | | 518.305 | 199.734 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 12.21 | n.a. | 12.131 | 3.808 | 3.63 | n.a. | BMB* |
| 2 | 13.82 | n.a. | 268.486 | 101.241 | 96.37 | n.a. | BMB* |
| Total: | | | 280.617 | 105.049 | 100.00 | 0.000 | |



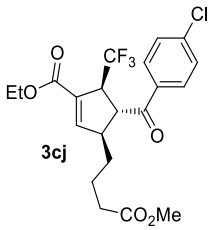

**3ci**; colorless oil; $[\alpha]_D^{20}$ = + 8.7 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.54–7.51 (m, 2H), 6.91 (s, 1H), 4.34–4.19 (m, 3H), 3.92–3.90 (m, 1H), 3.54–3.52 (m, 2H), 2.99–2.96 (m, 1H), 1.97–1.75 (m, 4H), 1.33 (t, *J* = 7.50 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 197.09, 163.06, 148.55, 140.55, 133.50, 131.09 (d, *J* = 1.50 Hz), 130.04, 129.36, 126.11 (q, *J* = 278.00 Hz), 61.05, 50.91 (q, *J* = 28.88 Hz), 50.83, 49.12, 44.22, 31.37, 30.38, 14.08; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.84 ppm; Enantiomeric excess: 91%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 12.10 min, second peak: $t_R$ = 15.73 min; HRMS (ESI) m/z calcd. for $C_{19}H_{19}Cl_2F_3NaO_3$ $[M+Na]^+$ = 445.0556, found = 445.0560.



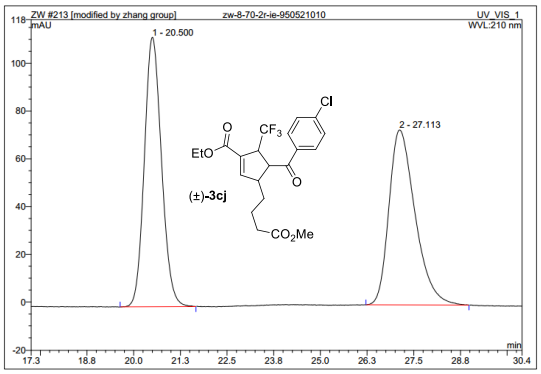




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 13.70 | n.a. | 37.576 | 13.509 | 50.63 | n.a. | BMB* |
| 2 | 15.90 | n.a. | 27.205 | 13.171 | 49.37 | n.a. | BMB* |
| Total: | | | 64.781 | 26.680 | 100.00 | 0.000 | |

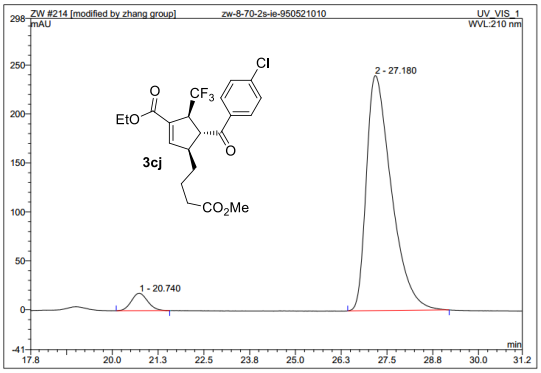
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 12.11 | n.a. | 11.815 | 3.886 | 4.70 | n.a. | MB* |
| 2 | 15.73 | n.a. | 181.824 | 78.836 | 95.30 | n.a. | BMB* |
| Total: | | | 193.639 | 82.723 | 100.00 | 0.000 | |



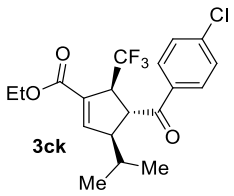

**3cj**; colorless oil; $[\alpha]_D^{20}$ = - 18.6 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.40 Hz, 2H), 7.50 (d, *J* = 8.40 Hz, 2H), 6.92 (s, 1H), 4.32–4.18 (m, 3H), 3.91–3.89 (m, 1H), 3.66 (s, 3H), 2.94–2.93 (m, 1H), 2.32–2.29 (m, 2H), 1.80–1.70 (m, 4H), 1.31 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 197.25, 173.30, 163.09, 148.90, 140.42, 133.58, 130.79, 130.06, 129.30, 126.12 (q, *J* = 278.00 Hz), 60.96, , 51.60, 50.67, 50.90 (q, *J* = 29.00 Hz), 49.59, 33.50, 22.91, 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.86 ppm; Enantiomeric excess: 91%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 95/05; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 20.74 min, second peak: $t_R$ = 27.18 min; HRMS (ESI) m/z calcd. for $C_{21}H_{22}ClF_3NaO_5$ $[M+Na]^+$ = 469.1000, found = 469.1008.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 20.50 | n.a. | 112.885 | 60.247 | 50.34 | n.a. | BMB* |
| 2 | 27.11 | n.a. | 73.246 | 59.429 | 49.66 | n.a. | BMB* |
| Total: | | | 186.131 | 119.676 | 100.00 | 0.000 | |

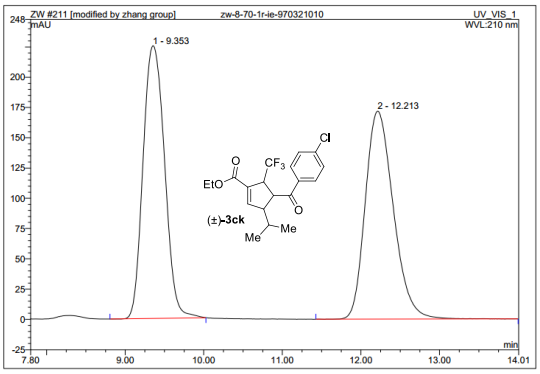


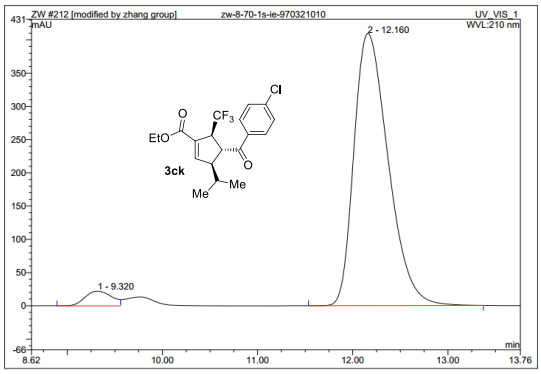

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 20.74 | n.a. | 17.852 | 9.163 | 4.59 | n.a. | BMB* |
| 2 | 27.18 | n.a. | 240.139 | 190.323 | 95.41 | n.a. | BMB* |
| Total: | | | 257.991 | 199.486 | 100.00 | 0.000 | |




**3ck**; colorless oil; $[\alpha]_D^{20}$ = + 20.6 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.40 Hz, 2H), 7.49 (d, *J* = 8.80 Hz, 2H), 6.96 (s, 1H), 4.32–4.16 (m, 2H), 4.07–3.99 (m, 2H), 2.89–2.86 (m, 1H), 1.87–1.78 (m, 1H), 1.30 (t, *J* = 7.60 Hz, 3H), 0.97 (d, *J* = 6.80 Hz, 3H), 0.93 (d, *J* = 6.80 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ

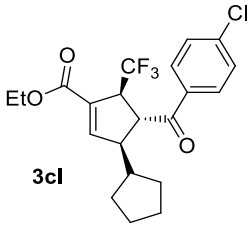
199.30, 163.24, 149.09, 140.39, 134.06, 130.34, 130.08, 129.23, 126.17 (q, $J$ = 278.30 Hz), 60.91, 57.44, 52.61 (q, $J$ = 28.70 Hz), 48.06, 31.52, 21.69, 19.80, 14.07; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.56 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 9.32 min, second peak: $t_R$ = 12.16 min; HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClF_3NaO_3$ $[M+Na]^+$ = 411.0945, found = 411.0948.



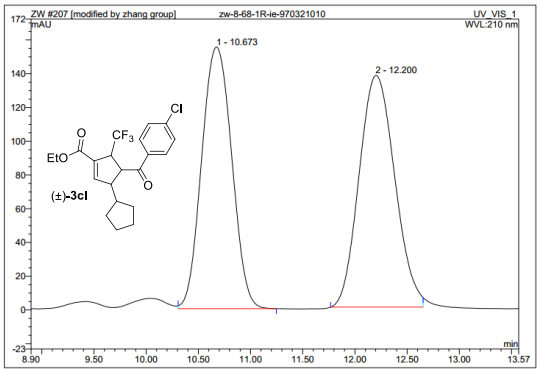



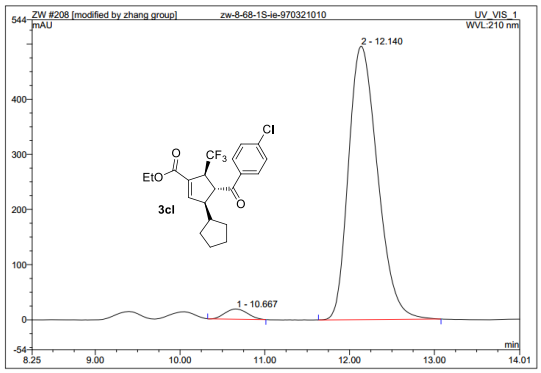

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.35 | n.a. | 225.252 | 71.548 | 50.16 | n.a. | BMB* |
| 2 | 12.21 | n.a. | 171.721 | 71.088 | 49.84 | n.a. | BMB* |
| Total: | | | 396.973 | 142.635 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.32 | n.a. | 22.040 | 7.153 | 4.03 | n.a. | BM * |
| 2 | 12.16 | n.a. | 409.563 | 170.511 | 95.97 | n.a. | BMB* |
| Total: | | | 431.603 | 177.663 | 100.00 | 0.000 | |



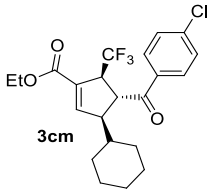

**3cl**; colorless oil; $[\alpha]_D^{20}$ = + 32.4 ($c$ = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.52–7.49 (m, 2H), 6.95 (s, 1H), 4.28–4.18 (m, 2H), 4.05–3.99 (m, 2H), 2.95–2.93 (m, 1H), 2.03–1.78 (m, 3H), 1.67–1.54 (m, 4H), 1.32 (t, $J$ = 7.00 Hz, 3H), 1.28–1.20 (m, 1H), 1.07–0.99 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 199.15, 163.30, 149.95, 140.37, 134.02, 130.11, 130.03, 129.20, 126.18 (q, $J$ = 278.25 Hz), 60.90, 56.05, 52.52 (q, $J$ = 28.75 Hz), 49.54, 44.12, 32.24, 30.68, 25.16, 24.94, 14.08; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.71 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.66 min, second peak: $t_R$ = 12.14 min; HRMS (ESI) m/z calcd. for $C_{21}H_{22}ClF_3NaO_3$ $[M+Na]^+$ = 437.1102, found = 437.1112.



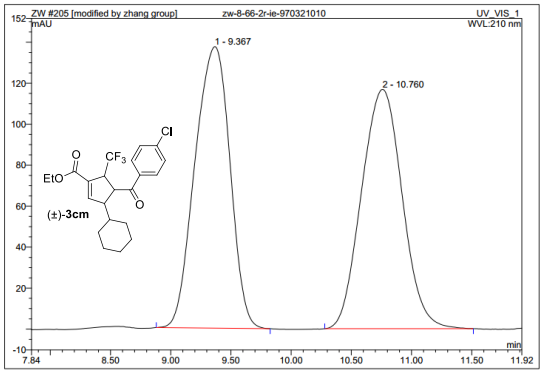



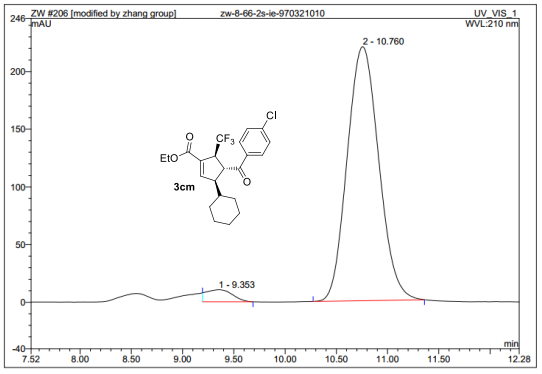

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.67 | n.a. | 155.049 | 51.788 | 48.81 | n.a. | MB* |
| 2 | 12.20 | n.a. | 137.340 | 54.304 | 51.19 | n.a. | BM * |
| Total: | | | 292.389 | 106.092 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.67 | n.a. | 18.479 | 5.618 | 2.78 | n.a. | BMB* |
| 2 | 12.14 | n.a. | 495.720 | 196.750 | 97.22 | n.a. | BMB* |
| Total: | | | 514.199 | 202.368 | 100.00 | 0.000 | |



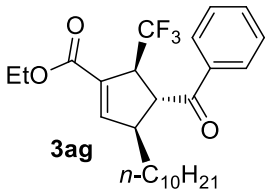

**3cm**; colorless oil; $[\alpha]_D^{20}$ = + 37.4 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.94–7.92 (m, 2H), 7.51–7.49 (m, 2H), 7.01 (s, 1H), 4.32–4.17 (m, 2H), 4.09–4.07 (m, 1H), 4.03–3.97 (m, 1H), 2.92–2.90 (m, 1H), 1.87–1.66 (m, 5H), 1.51–1.45 (m, 1H), 1.31 (t, *J* = 7.00 Hz, 3H), 1.24–1.11 (m, 3H), 1.02–0.93 (m, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 199.24, 163.25, 149.41, 140.35, 133.96, 130.09, 129.94, 129.20, 126.17 (q, *J* = 278.50 Hz), 60.87, 56.34, 52.43 (q, *J* = 28.75 Hz), 47.66, 41.32, 32.21, 30.46, 26.04, 26.03, 25.95, 14.06; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.59 ppm; Enantiomeric excess: 92%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 9.35 min, second peak: $t_R$ = 10.76 min; HRMS (ESI) m/z calcd. for $C_{22}H_{24}ClF_3NaO_3$ $[M+Na]^+$ = 451.1258, found = 451.1266.



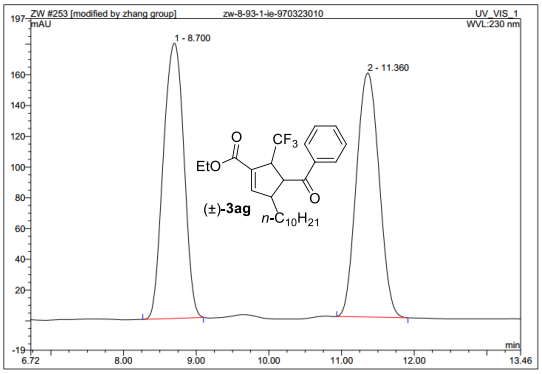



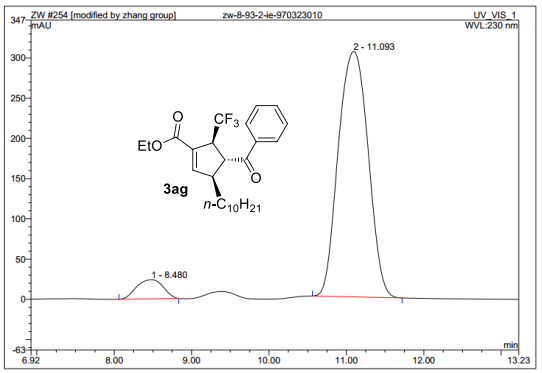

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.37 | n.a. | 137.422 | 46.391 | 50.32 | n.a. | BMB* |
| 2 | 10.76 | n.a. | 116.801 | 45.805 | 49.68 | n.a. | BMB* |
| Total: | | | 254.223 | 92.196 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.35 | n.a. | 10.408 | 3.107 | 3.80 | n.a. | MB* |
| 2 | 10.76 | n.a. | 220.165 | 78.693 | 96.20 | n.a. | BMB* |
| Total: | | | 230.573 | 81.799 | 100.00 | 0.000 | |



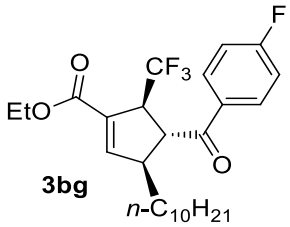

**3ag**; colorless oil; $[\alpha]_D^{20}$ = - 19.6 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.64–7.61 (m, 1H), 7.53–7.50 (m, 2H), 6.92 (s, 1H), 4.33–4.16 (m, 3H), 3.94–3.93 (m, 1H), 2.91–2.88 (m, 1H), 1.74–1.61 (m, 2H), 1.33–1.21 (m, 19H), 0.88 (t, *J* = 6.80 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 198.66, 163.34, 149.67, 135.47, 133.66, 130.47, 128.86, 128.62, 126.19 (q, *J* = 277.90 Hz), 60.84, 51.00, 50.72 (q, *J* = 28.90 Hz), 50.12, 34.35, 31.83, 29.50, 29.44, 29.32, 29.30, 29.24, 27.68, 22.62, 14.05; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.87 ppm; Enantiomeric excess: 87%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 8.48 min, second peak: $t_R$ = 11.09 min; HRMS (ESI) m/z calcd. for $C_{26}H_{35}F_3NaO_3$ $[M+Na]^+$ = 475.2431, found = 475.2435.



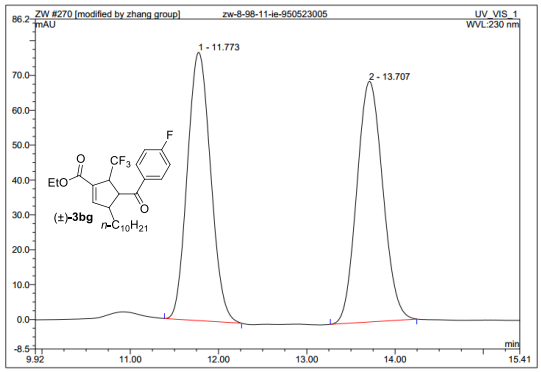




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.70 | n.a. | 179.029 | 58.703 | 50.58 | n.a. | BMB* |
| 2 | 11.36 | n.a. | 158.847 | 57.365 | 49.42 | n.a. | BMB* |
| Total: | | | 337.876 | 116.068 | 100.00 | 0.000 | |

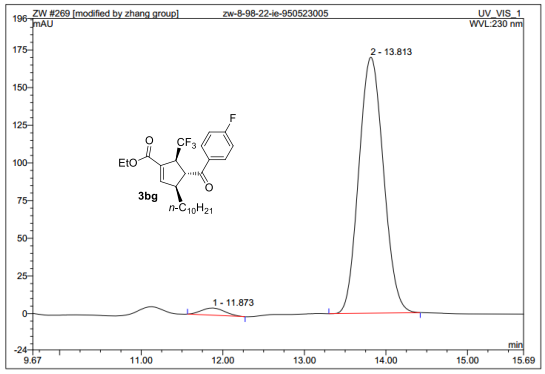
| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.48 | n.a. | 23.773 | 9.485 | 6.50 | n.a. | BMB* |
| 2 | 11.09 | n.a. | 305.037 | 136.542 | 93.50 | n.a. | BMB* |
| Total: | | | 328.810 | 146.028 | 100.00 | 0.000 | |



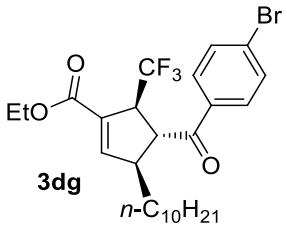

**3bg**; colorless oil; $[\alpha]_D^{20}$ = -7.4 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.02–7.98 (m, 2H), 7.21–7.17 (m, 2H), 6.92 (s, 1H), 4.33–4.16 (m, 3H), 3.89–3.88 (m, 1H), 2.93–2.87 (m, 1H), 1.72–1.65 (m, 2H), 1.33–1.22 (m, 19H), 0.88 (t, *J* = 6.80 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 197.18, 166.13 (d, *J* = 254.60 Hz), 149.62, 131.84 (d, *J* = 2.90 Hz), 131.31 (d, *J* = 9.40 Hz), 130.41, 126.23 (q, *J* = 278.10 Hz), 116.07 (d, *J* = 21.80 Hz), 60.87, 50.94 (q, *J* = 28.80 Hz), 50.91, 50.16, 34.35, 31.83, 29.50, 29.45, 29.33, 29.32, 29.24, 27.72, 22.62, 14.06, 14.04; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.89, -103.91 ppm; Enantiomeric excess: 95%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 95/05; flow rate 0.5 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 11.87 min, second peak: $t_R$ = 13.81 min; HRMS (ESI) m/z calcd. for $C_{26}H_{34}F_4NaO_3$ $[M+Na]^+$ = 493.2336, found = 493.2338.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.77 | n.a. | 76.928 | 23.535 | 50.00 | n.a. | BMB* |
| 2 | 13.71 | n.a. | 69.018 | 23.536 | 50.00 | n.a. | BMB* |
| Total: | | | 145.946 | 47.071 | 100.00 | 0.000 | |

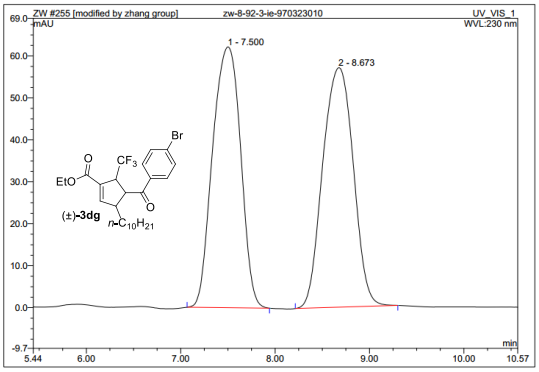



| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 11.87 | n.a. | 4.758 | 1.571 | 2.57 | n.a. | BMB* |
| 2 | 13.81 | n.a. | 169.820 | 59.497 | 97.43 | n.a. | BMB* |
| Total: | | | 174.578 | 61.068 | 100.00 | 0.000 | |

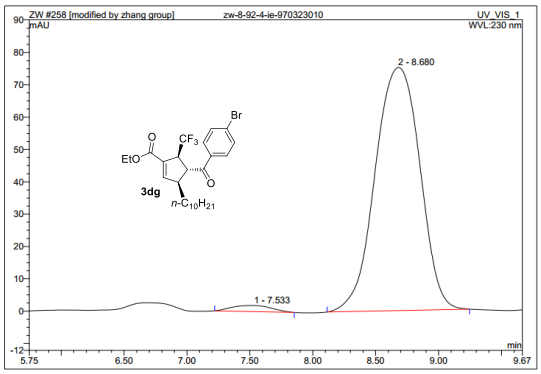



**3dg**; colorless oil; $[\alpha]_D^{20}$ = -30.7 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.40 Hz, 2H), 7.66 (d, *J* = 8.40 Hz, 2H), 6.92 (s, 1H), 4.33–4.16 (m, 3H),

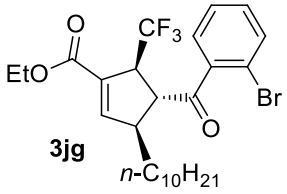
3.87–3.85 (m, 1H), 2.90–2.86 (m, 1H), 1.69–1.64 (m, 2H), 1.33–1.22 (m, 19H), 0.88 (t, $J$ = 6.80 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.70, 163.26, 149.58, 134.13, 132.25, 130.37, 130.10, 129.09, 126.19 (q, $J$ = 278.00 Hz), 60.93, 50.94, 50.78 (q, $J$ = 32.40 Hz), 50.07, 34.38, 31.86, 29.53, 29.48, 29.34, 29.28, 27.73, 22.66, 14.10; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.86 ppm; Enantiomeric excess: 96%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.53 min, second peak: $t_R$ = 8.68 min; HRMS (ESI) m/z calcd. for $C_{26}H_{34}BrF_3NaO_3$ [M+Na] $^+$ = 553.1536, found = 553.1541.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.50 | n.a. | 62.158 | 21.379 | 49.93 | n.a. | BMB* |
| 2 | 8.67 | n.a. | 57.082 | 21.442 | 50.07 | n.a. | BMB* |
| Total: | | | 119.240 | 42.821 | 100.00 | 0.000 | |



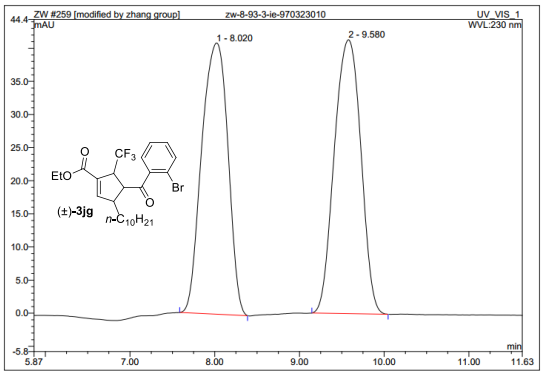

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.53 | n.a. | 1.898 | 0.678 | 2.14 | n.a. | BMB* |
| 2 | 8.68 | n.a. | 75.193 | 31.039 | 97.86 | n.a. | BMB* |
| Total: | | | 77.091 | 31.717 | 100.00 | 0.000 | |

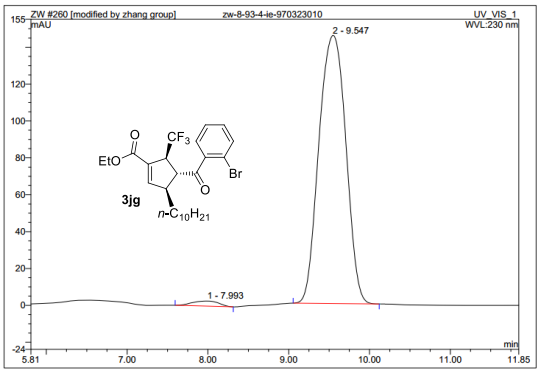



**3jg**; colorless oil; $[\alpha]_D^{20}$ = -11.7 (*c* = 0.33, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.67–7.66 (m, 1H), 7.45–7.41 (m, 1H), 7.38–7.34 (m, 2H), 6.86 (s, 1H), 4.44–4.20 (m, 3H), 3.86–3.85 (m, 1H), 3.02–2.98 (m, 1H), 1.55–1.40 (m, 2H), 1.35–1.12 (m, 19H), 0.90 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 200.67, 163.28, 149.17, 140.

10, 133.77, 131.92, 130.21, 128.65, 127.40, 126.15 (q, $J$ = 277.88 Hz), 119.21, 60.89, 54.87, 49.13 (q, $J$ = 29.00 Hz), 48.52, 34.36, 31.85, 29.50, 29.38, 29.27, 29.25, 29.05, 27.39, 22.64, 14.08; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -68.29 ppm; Enantiomeric excess: 96%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 97/03; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 7.99 min, second peak: $t_R$ = 9.54 min;

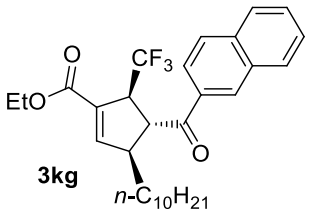
HRMS (ESI) m/z calcd. for $C_{26}H_{34}BrF_3NaO_3$ $[M+Na]^+$ = 553.1536, found = 553.1550.



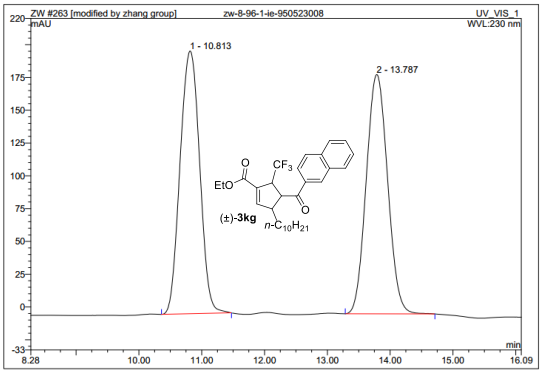



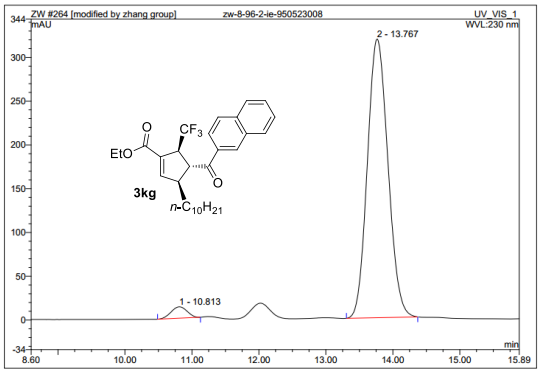

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.02 | n.a. | 40.952 | 14.690 | 49.44 | n.a. | BMB* |
| 2 | 9.58 | n.a. | 41.348 | 15.021 | 50.56 | n.a. | BMB* |
| Total: | | | 82.300 | 29.711 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 7.99 | n.a. | 2.771 | 1.039 | 1.81 | n.a. | BMB* |
| 2 | 9.55 | n.a. | 145.440 | 56.275 | 98.19 | n.a. | BMB* |
| Total: | | | 148.211 | 57.314 | 100.00 | 0.000 | |



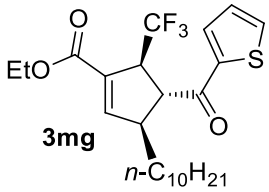

**3kg**; colorless oil; $[\alpha]_D^{20}$ = -52.5 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.06–7.92 (m, 4H), 7.68–7.60 (m, 2H), 6.97 (s, 1H), 4.38–4.21 (m, 3H), 4.13–4.12 (m, 1H), 3.00–2.97 (m, 1H), 1.85–1.69 (m, 2H), 1.36–1.19 (m, 19H), 0.89 (t, *J* = 7.00 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 198.59, 163.39, 149.79, 135.80, 132.74, 132.45, 130.49, 130.34, 129.63, 128.89, 128.86, 127.79, 127.05, 126.37 (q, *J* = 278.00 Hz), 124.23, 60.87, 51.05, 50.84 (q, *J* = 28.63 Hz), 50.28, 34.39, 31.82, 29.48, 29.43, 29.34, 29.30, 29.22, 27.72, 22.62, 14.09, 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -67.74 ppm; Enantiomeric excess: 94%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 95/05; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 10.81 min, second peak: $t_R$ = 13.76 min; HRMS (ESI) m/z calcd. for $C_{30}H_{37}F_3NaO_3$ $[M+Na]^+$ = 525.2587, found = 525.2591.



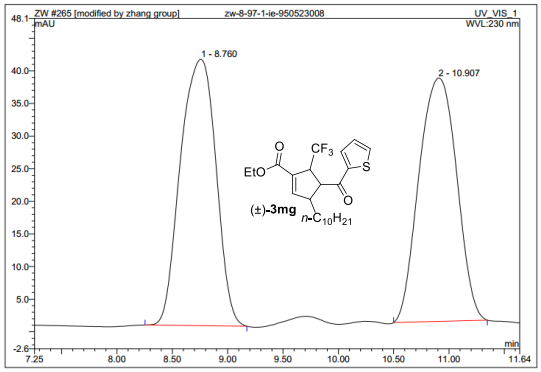



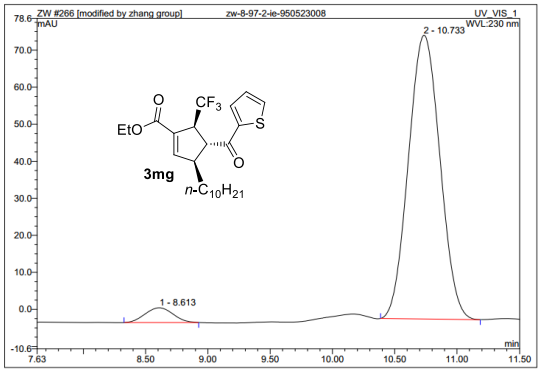

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.81 | n.a. | 200.325 | 72.365 | 50.16 | n.a. | BMB* |
| 2 | 13.79 | n.a. | 182.509 | 71.902 | 49.84 | n.a. | BMB* |
| Total: | | | 382.834 | 144.267 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 10.81 | n.a. | 13.009 | 3.595 | 3.07 | n.a. | BMB* |
| 2 | 13.77 | n.a. | 318.262 | 113.313 | 96.93 | n.a. | BMB* |
| Total: | | | 331.272 | 116.908 | 100.00 | 0.000 | |



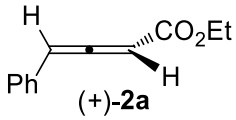

**3mg**; colorless oil; $[\alpha]_D^{20}$ = + 10.7 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 3.50 Hz, 1H), 7.76 (d, *J* = 5.00 Hz, 1H), 7.22–7.20 (m, 1H), 6.96 (s, 1H), 4.33–4.18 (m, 3H), 3.75–3.73 (m, 1H), 3.06–3.03 (m, 1H), 1.77–1.63 (m, 2H), 1.33–1.25 (m, 19H), 0.89 (t, *J* = 6.50 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 191.66, 163.28, 149.98, 142.75, 135.20, 132.58, 130.21, 128.45,126.15 (q, *J* = 278.00 Hz), 60.86, 52.34, 51.48 (q, *J* = 28.88 Hz), 50.42, 34.38, 31.84, 29.46, 29.41, 29.35, 29.25, 27.71, 22.63, 14.07; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ = -68.00 ppm; Enantiomeric excess: 91%, determined by HPLC (Chiralpak IE, hexane/*i*-PrOH = 95/05; flow rate 0.8 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 8.61 min, second peak: $t_R$ = 10.73 min; HRMS (ESI) m/z calcd. for $C_{24}H_{33}F_3NaO_3S$ $[M+Na]^+$ = 481.1995, found = 481.1999.



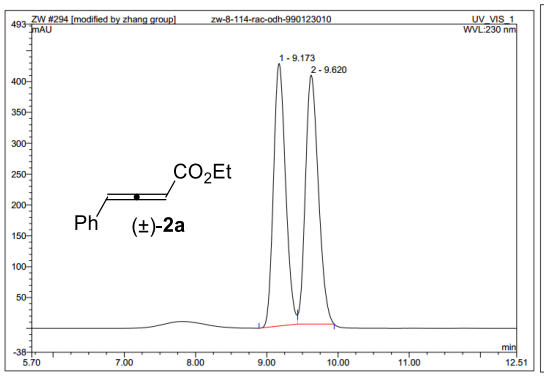



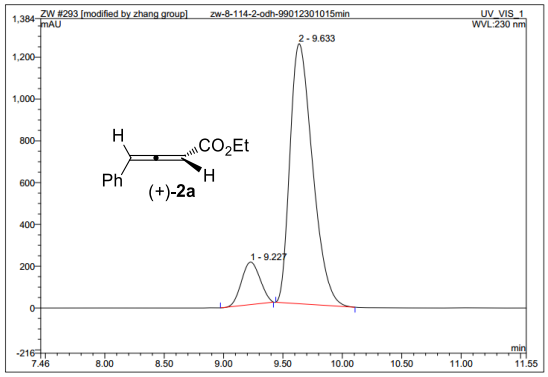

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.76 | n.a. | 40.837 | 15.210 | 50.78 | n.a. | BMB* |
| 2 | 10.91 | n.a. | 37.314 | 14.741 | 49.22 | n.a. | BMB* |
| Total: | | | 78.151 | 29.951 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 8.61 | n.a. | 3.972 | 1.030 | 4.39 | n.a. | BMB* |
| 2 | 10.73 | n.a. | 76.624 | 22.443 | 95.61 | n.a. | BMB* |
| Total: | | | 80.597 | 23.473 | 100.00 | 0.000 | |



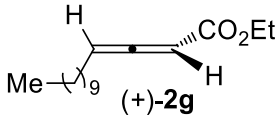

(*S*)-**2a**;[3] colorless oil; $[\alpha]_D^{20}$ = + 239.8.3 (*c* = 0.33, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, 5H), 6.55 (d, *J* = 6.40 Hz, 1H), 5.94 (d, *J* = 6.40 Hz, 1H), 4.15 (q, *J* = 7.20 Hz, 2H), 1.21 (t, *J* = 7.20 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 214.58, 165.07, 131.11, 128.81, 128.06, 127.46, 98.63, 91.91, 61.10, 14.20; Enantiomeric excess: 76%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 99/01; flow rate 1.0 ml/min; 25 °C; 230 nm), first peak: $t_R$ = 9.22 min, second peak: $t_R$ = 9.63 min.



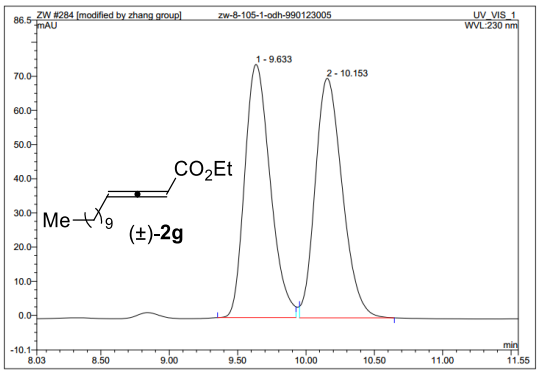

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.17 | n.a. | 425.332 | 83.754 | 49.57 | n.a. | BM * |
| 2 | 9.62 | n.a. | 403.358 | 85.212 | 50.43 | n.a. | MB* |
| Total: | | | 828.690 | 168.966 | 100.00 | 0.000 | |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.23 | n.a. | 203.829 | 36.793 | 11.82 | n.a. | BMB* |
| 2 | 9.63 | n.a. | 1243.632 | 274.504 | 88.18 | n.a. | BMB* |
| Total: | | | 1447.461 | 311.298 | 100.00 | 0.000 | |

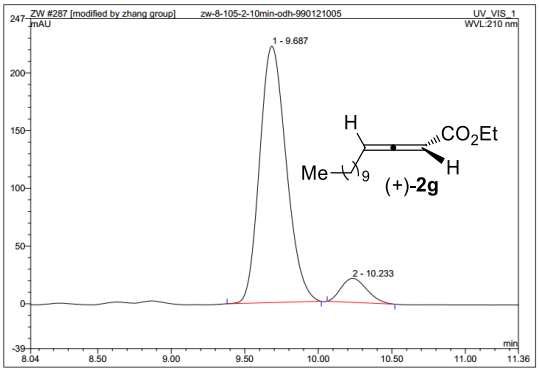



(*S*)-**2g**;[4] colorless oil; $[\alpha]_D^{20}$ = + 306.3 (*c* = 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.63–5.66 (m, 2H), 4.23–4.17 (m, 2H), 2.16–2.11 (m, 2H), 1.49–1.44 (m, 2H),

1.37–1.27 (m, 2H), 0.89 (t, $J$ = 7.00 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 212.26, 166.27, 95.34, 88.17, 60.66, 31.86, 29.56, 29.54, 29.32, 29.28, 28.89, 28.68, 27.46, 22.64, 14.20, 14.06; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -67.50 ppm; Enantiomeric excess: 83%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 99/01; flow rate 0.5 ml/min; 25 °C; 210 nm), first peak: $t_R$ = 9.68 min, second peak: $t_R$ = 10.23 min.




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.63 | n.a. | 74.159 | 16.028 | 49.83 | n.a. | BM * |
| 2 | 10.15 | n.a. | 70.152 | 16.135 | 50.17 | n.a. | MB* |
| Total: | | | 144.311 | 32.163 | 100.00 | 0.000 | |




| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.69 | n.a. | 221.937 | 46.572 | 91.69 | n.a. | BMB* |
| 2 | 10.23 | n.a. | 20.885 | 4.221 | 8.31 | n.a. | BMB* |
| Total: | | | 242.822 | 50.793 | 100.00 | 0.000 | |

## 9. References

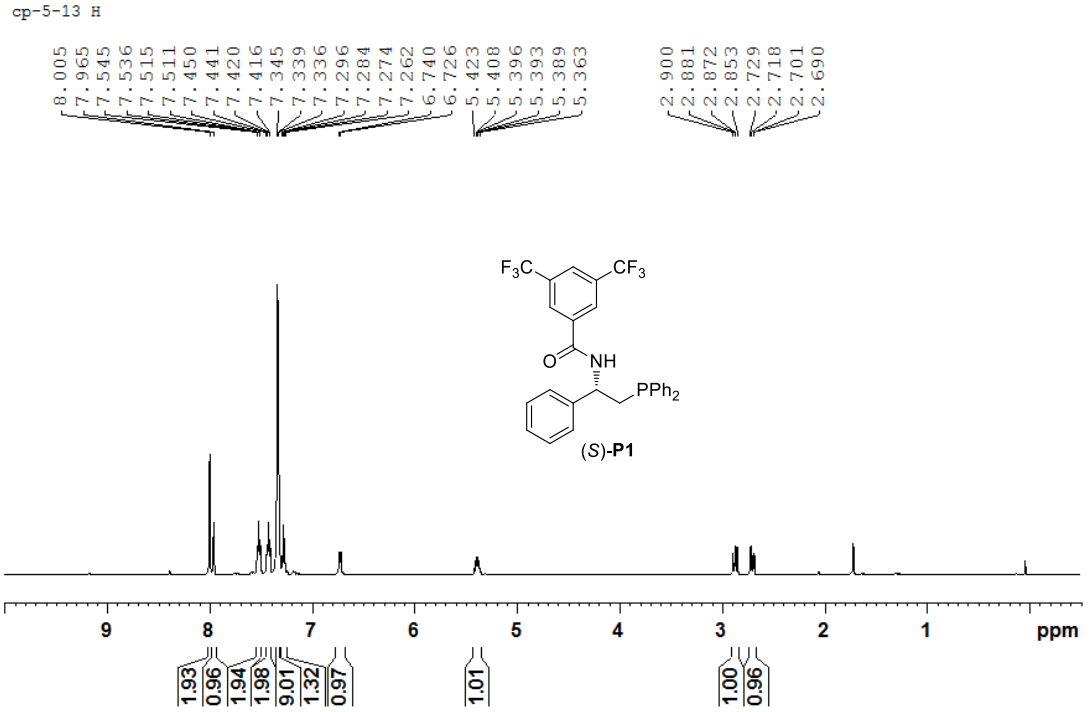

[1] a) X. Su, W. Zhou, Y. Li, J. Zhang, *Angew. Chem. Int. Ed*. **2015**, *54*, 6874; *Angew. Chem.* **2015**, *127*, 6978; b) W. Zhou, X. Su. M. Tao, C. Zhu, Q. Zhao, J. Zhang, *Angew. Chem. Int. Ed*. **2015**, *54*, 14853; *Angew. Chem.* **2015**, *127*, 15066; c) W. Zhou, P. Chen, M. Tao, X. Su, Q. Zhao, J. Zhang, *Chem. Commun*. **2016**, *52*, 7612; d) P. Chen, X. Su, W. Zhou, Y. Xiao, J. Zhang, *Tetrahedron* **2016**, *72*, 2700.

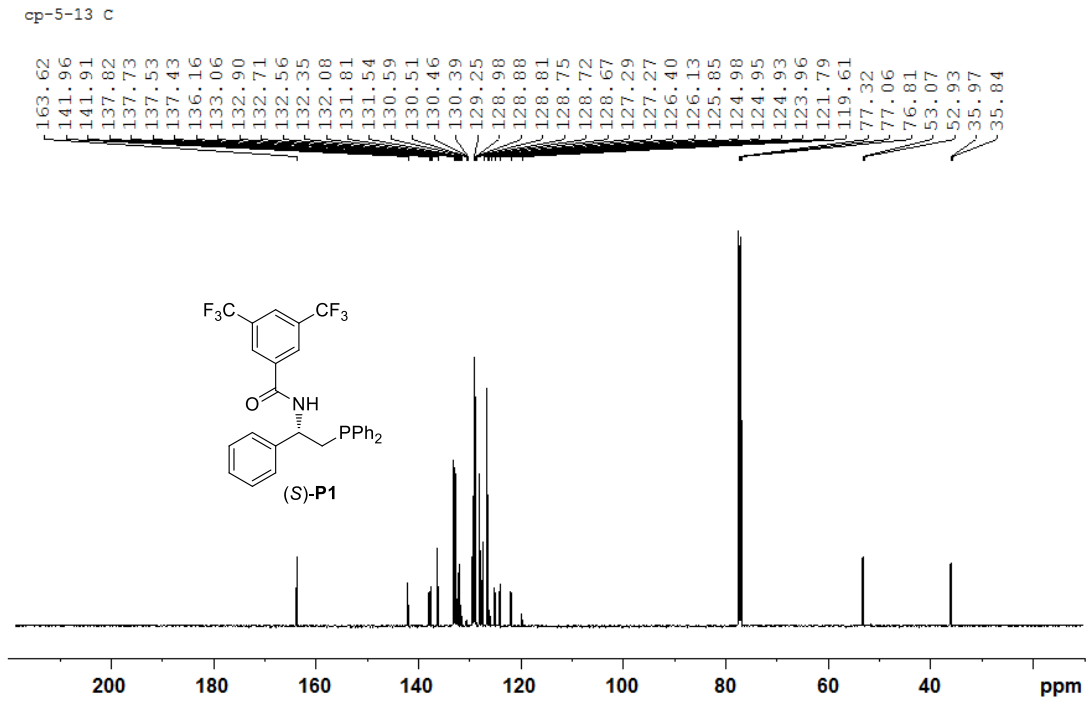
[2] T. Yamazaki, T. Kawasaki-Takasuka, A. Furuta, S. Sakamoto, *Tetrahedron*, **2009**, *65*, 5945.

[3] T. Inokuma, M. Furukawa, T. Uno, Y. Suzuki, K. Yoshida, Y. Yano, K. Matsuzaki, Y. Takemoto, *Chem. Eur. J*. **2011**, *17*, 10470.

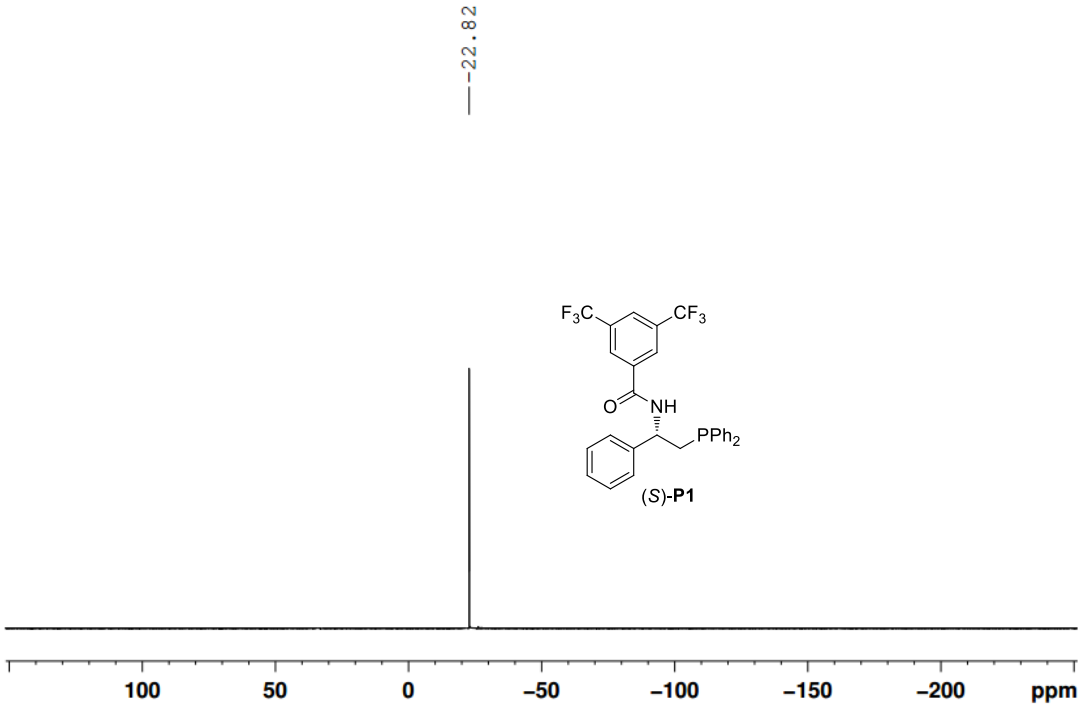
[4] C.-Y. Li, X.-L. Sun, Q. Jing, Y. Tang, *Chem. Commun*. **2006**, 2980.

## 10. $^{1}H$, $^{13}C$, $^{31}P$ and $^{19}F$ NMR Spectra

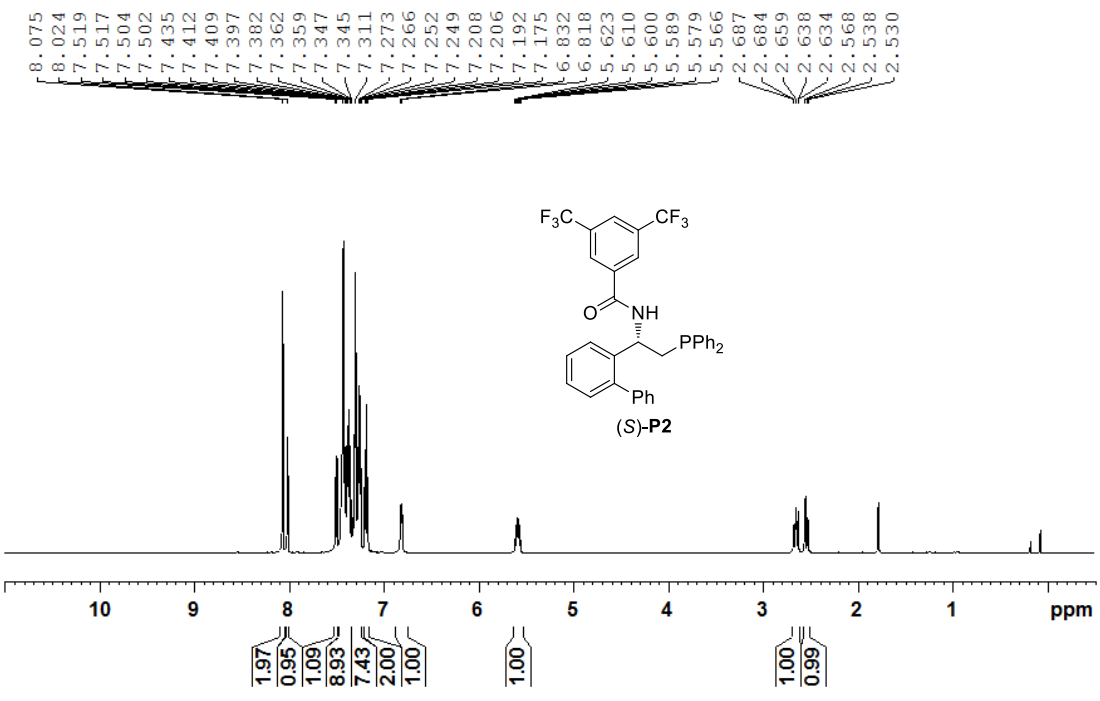


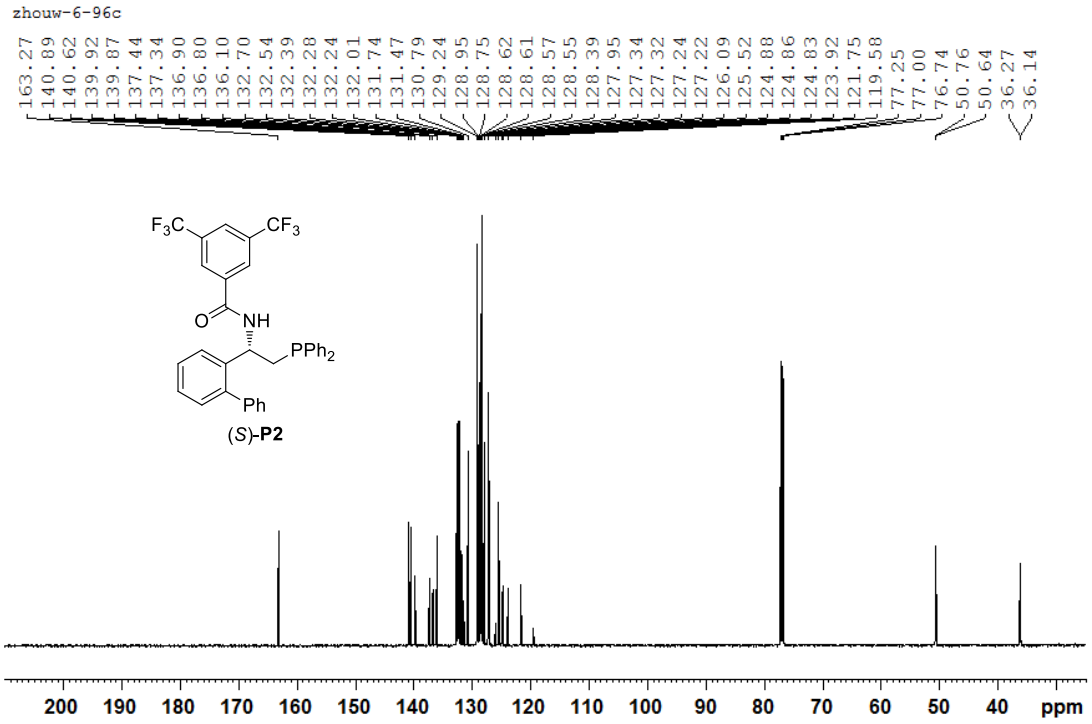



cp-5-13 P




zhouw-6-96

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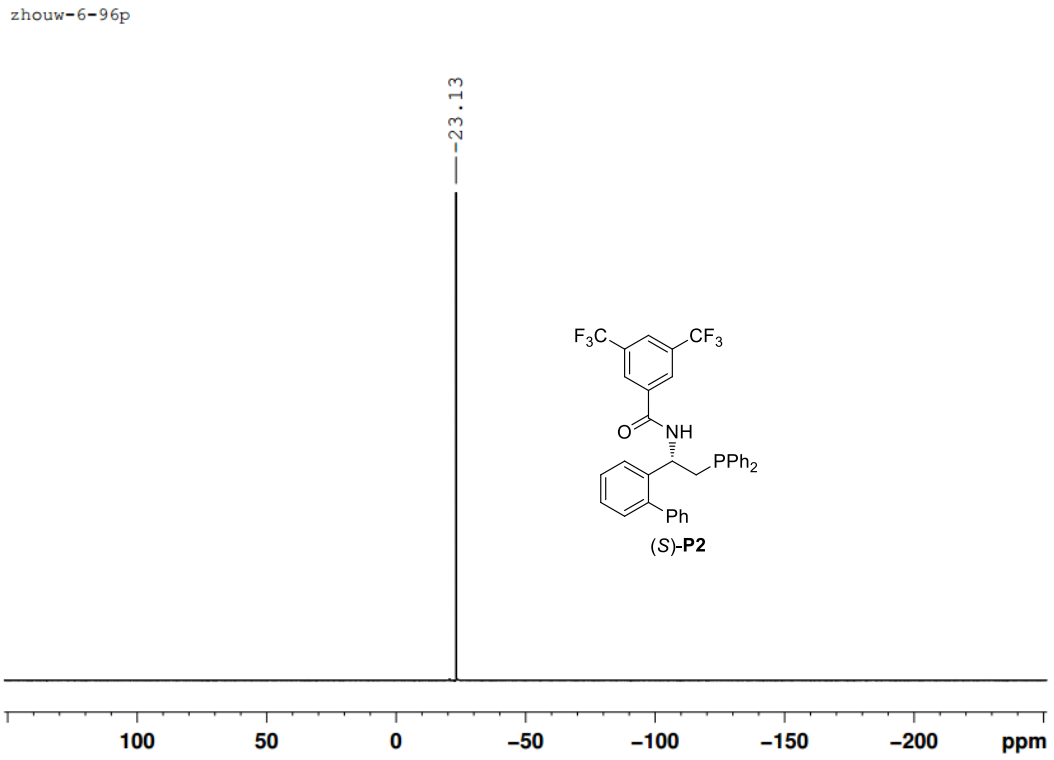
140.62
139.92
139.87
137.44
137.34
136.90
136.80
136.10
132.70
132.54
132.39
132.28
132.24
132.01
131.74
131.47
130.79
129.24
128.95
128.75
128.62
128.61
128.57
128.55
128.39
127.95
127.34
127.32
127.24
127.22
126.09
125.52
124.88
124.86
124.83
123.92
121.75
119.58
77.25
77.00
76.74
50.76
50.64
36.27
36.14
F3C
CF3
O
NH
PPh2
Ph
(S)-P2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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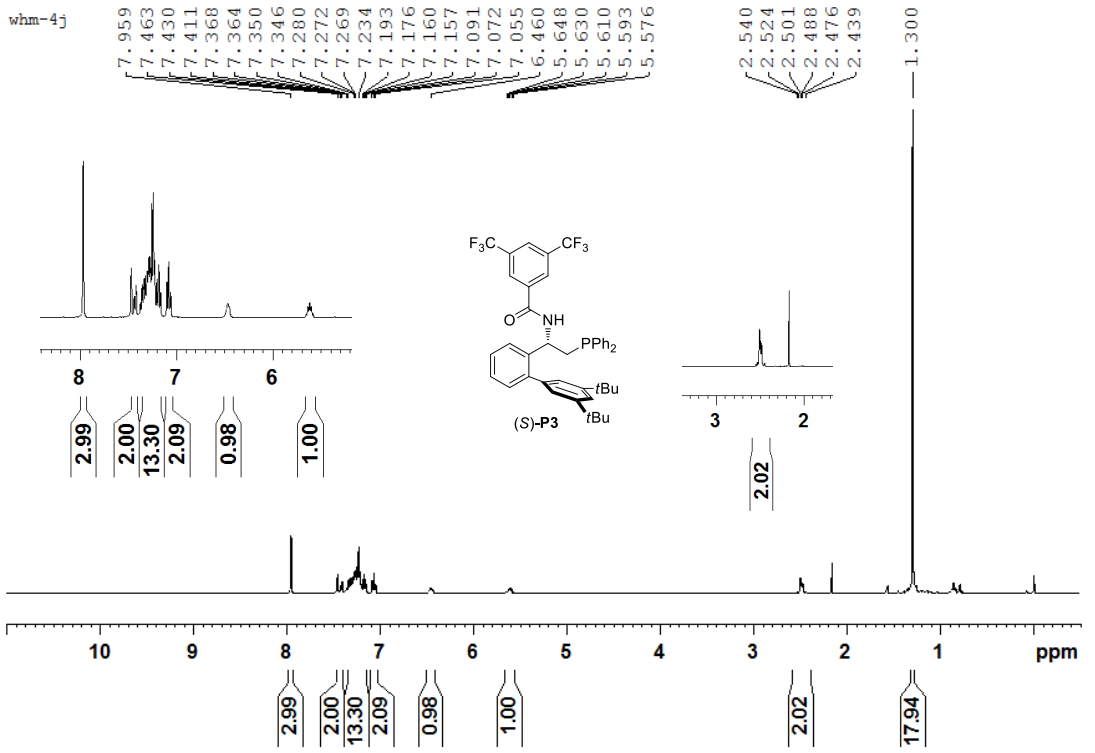
-23.13
F3C
CF3
O
NH
PPh2
Ph
(S)-P2
100
50
0
-50
-100
-150
-200
ppm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7.463
7.430
7.411
7.368
7.364
7.350
7.346
7.280
7.272
7.269
7.234
7.193
7.176
7.160
7.157
7.091
7.072
7.055
6.460
5.648
5.630
5.610
5.593
5.576
2.540
2.524
2.501
2.488
2.476
2.439
1.300
F3C
CF3
O
NH
PPh2
tBu
tBu
(S)-P3
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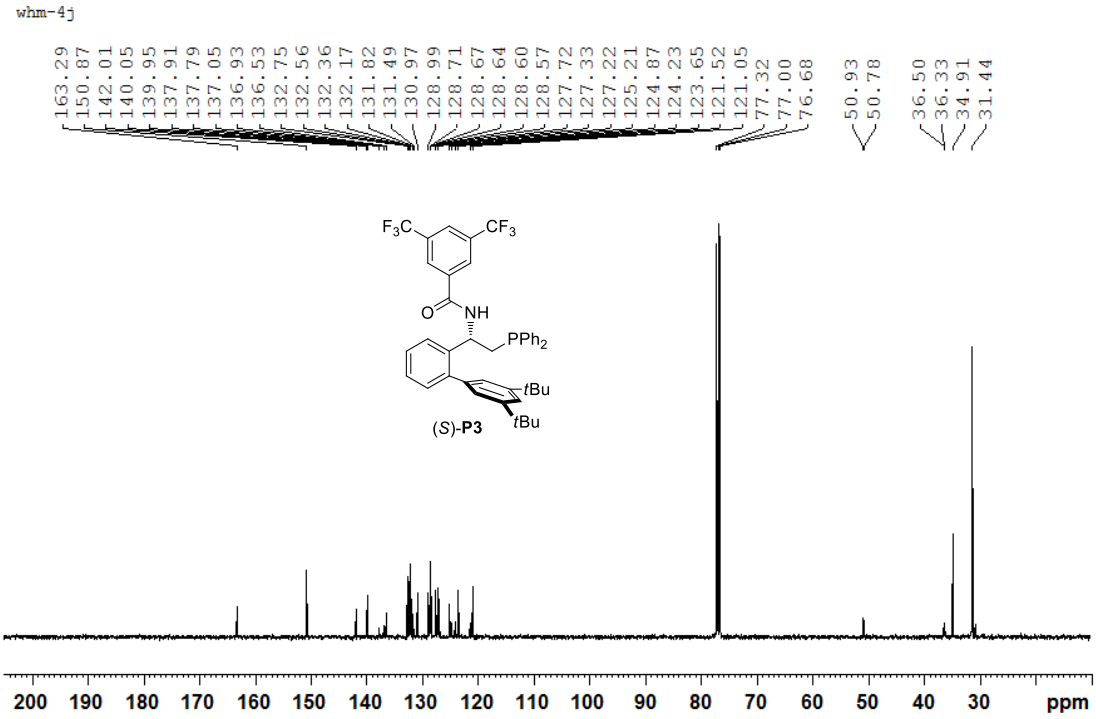
13.30
2.09
0.98
1.00
2.02
17.94
ppm


whm-4j
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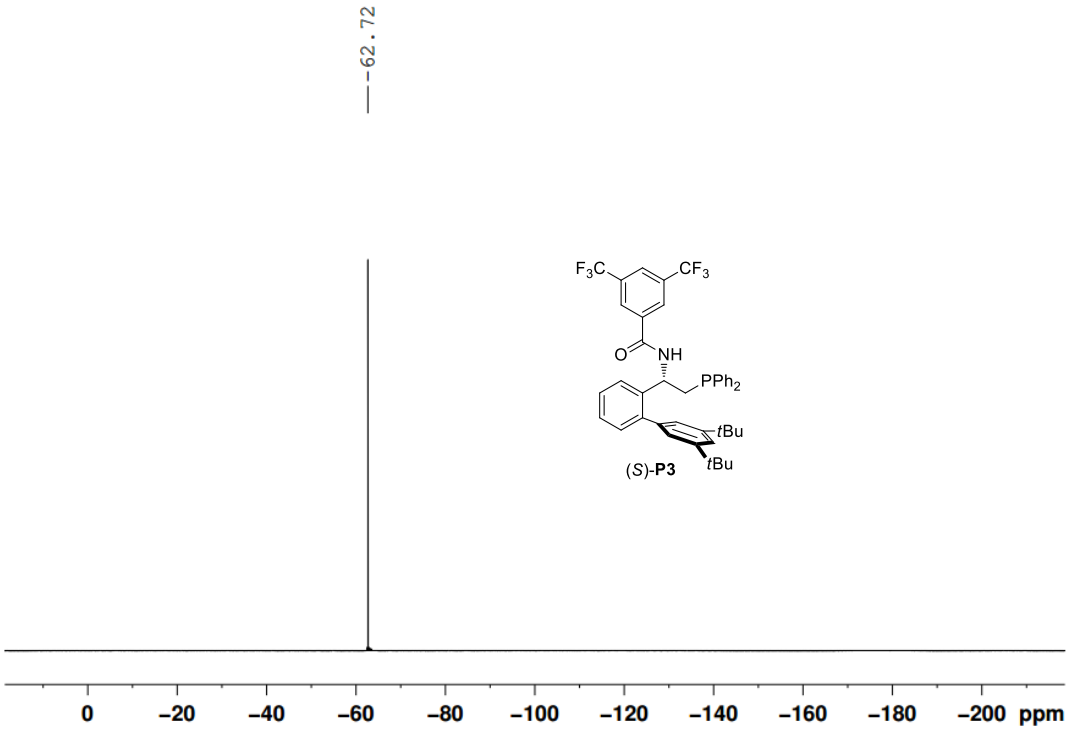
150.87
142.01
140.05
139.95
137.91
137.79
137.05
136.93
136.53
132.75
132.56
132.36
132.17
131.82
131.49
130.97
128.99
128.71
128.67
128.64
128.60
128.57
127.72
127.33
127.22
125.21
124.87
124.23
123.65
121.52
121.05
77.32
77.00
76.68
50.93
50.78
36.50
36.33
34.91
31.44
F3C
CF3
O
NH
PPh2
tBu
tBu
(S)-P3
ppm

whm-4j

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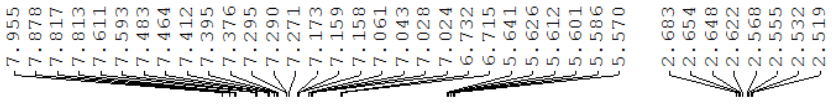
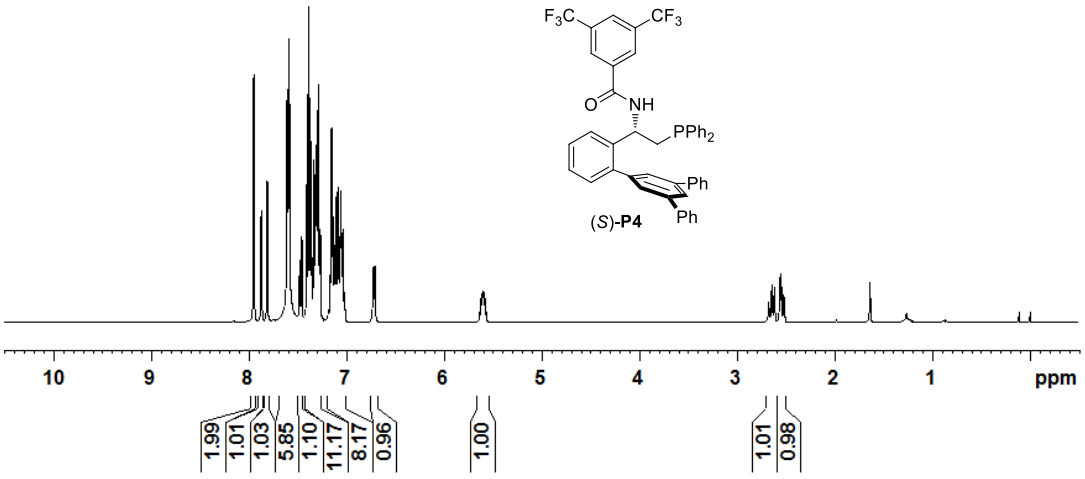
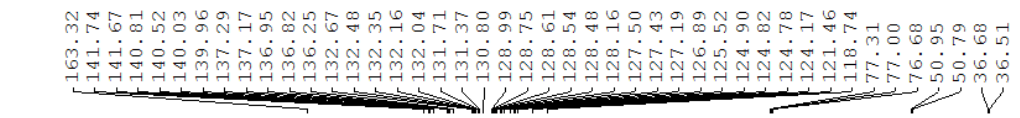
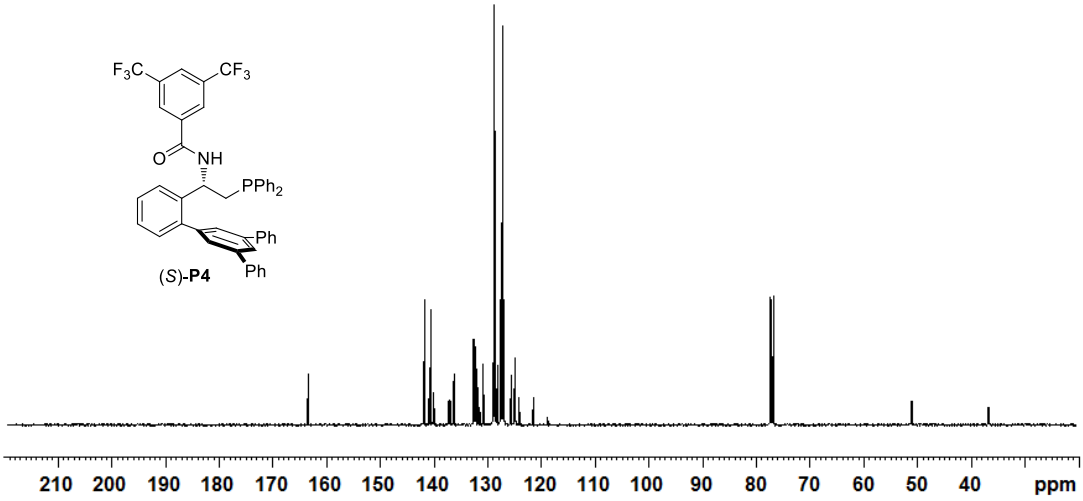


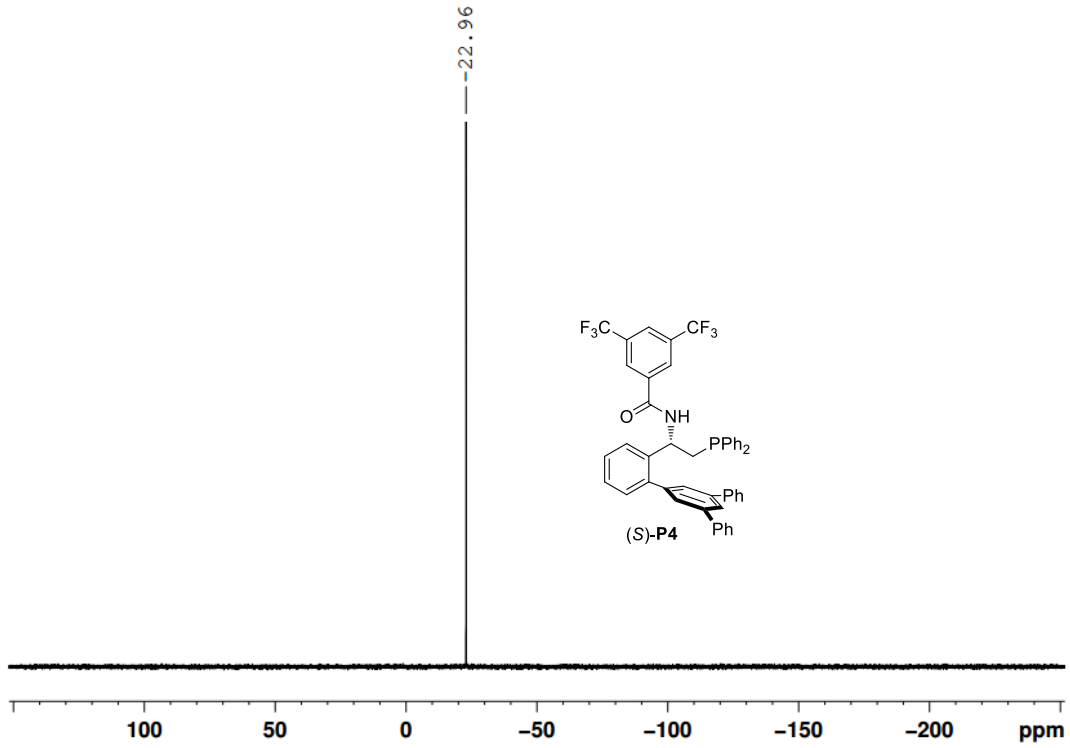



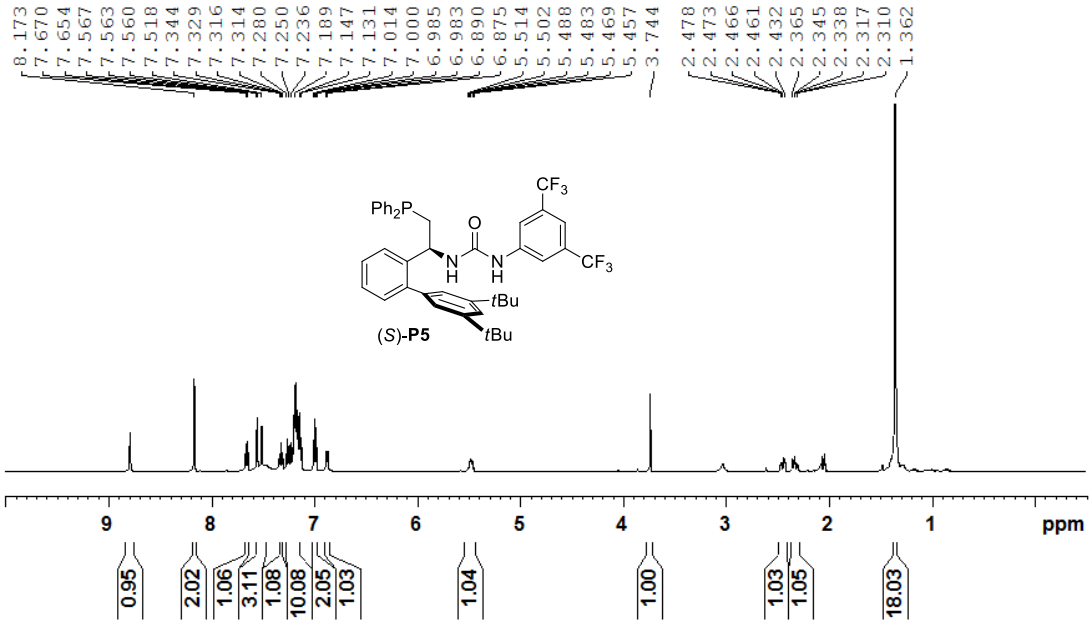
zhouw-6-103c




zhouw-6-103p

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7.250
7.236
7.189
7.147
7.131
7.014
7.000
6.985
6.983
6.890
6.875
5.514
5.502
5.488
5.483
5.469
5.457
3.744
2.478
2.473
2.466
2.461
2.432
2.365
2.345
2.338
2.317
2.310
1.362
Ph2P
O
N
H
N
H
CF3
CF3
tBu
tBu
(S)-P5
9
8
7
6
5
4
3
2
1
ppm
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3.11
1.08
10.08
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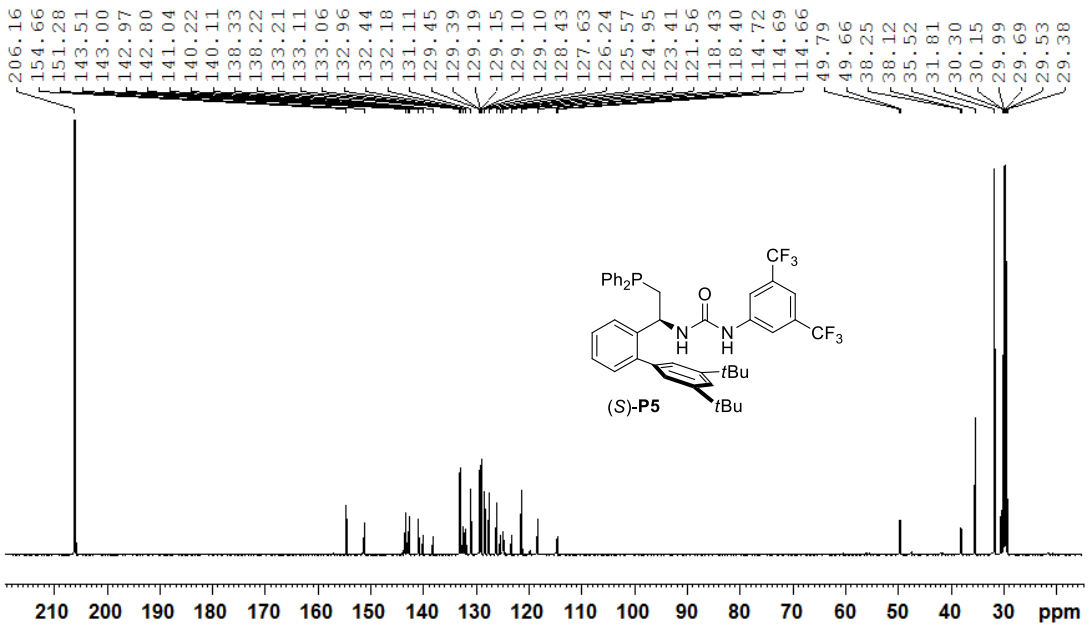
1.03
1.04
1.00
1.03
1.05
18.03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142.80
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140.22
140.11
138.33
138.22
133.21
133.11
133.06
132.96
132.44
132.18
131.11
129.45
129.39
129.19
129.15
129.10
129.10
128.43
127.63
126.24
125.57
124.95
123.41
121.56
118.43
118.40
114.72
114.69
114.66
49.79
49.66
38.25
38.12
35.52
31.81
30.30
30.15
29.99
29.69
29.53
29.38
Ph2P
O
N
H
N
H
CF3
CF3
tBu
tBu
(S)-P5
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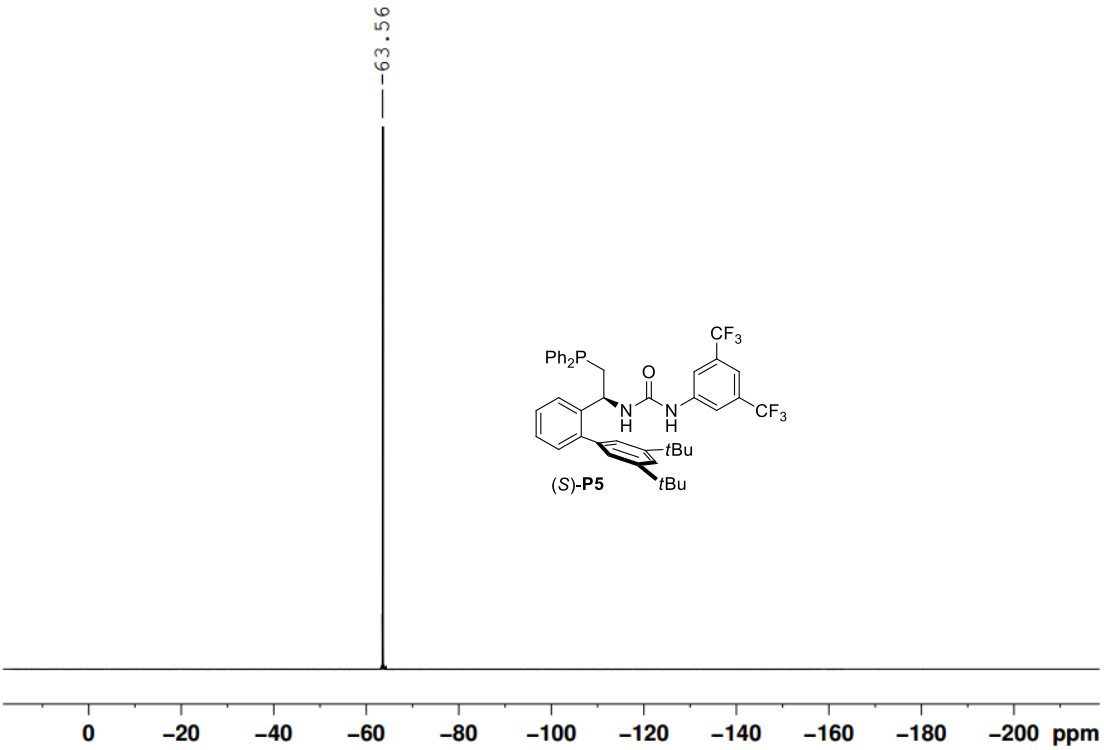
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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N
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-120
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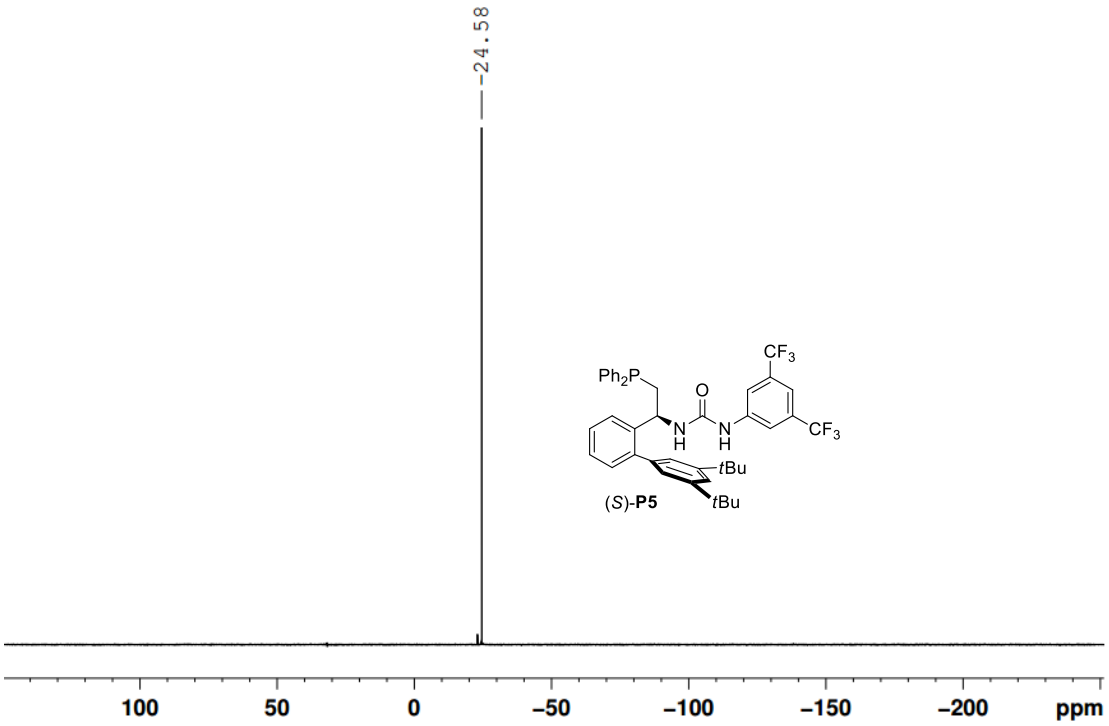
-180
-200
ppm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CF3
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tBu
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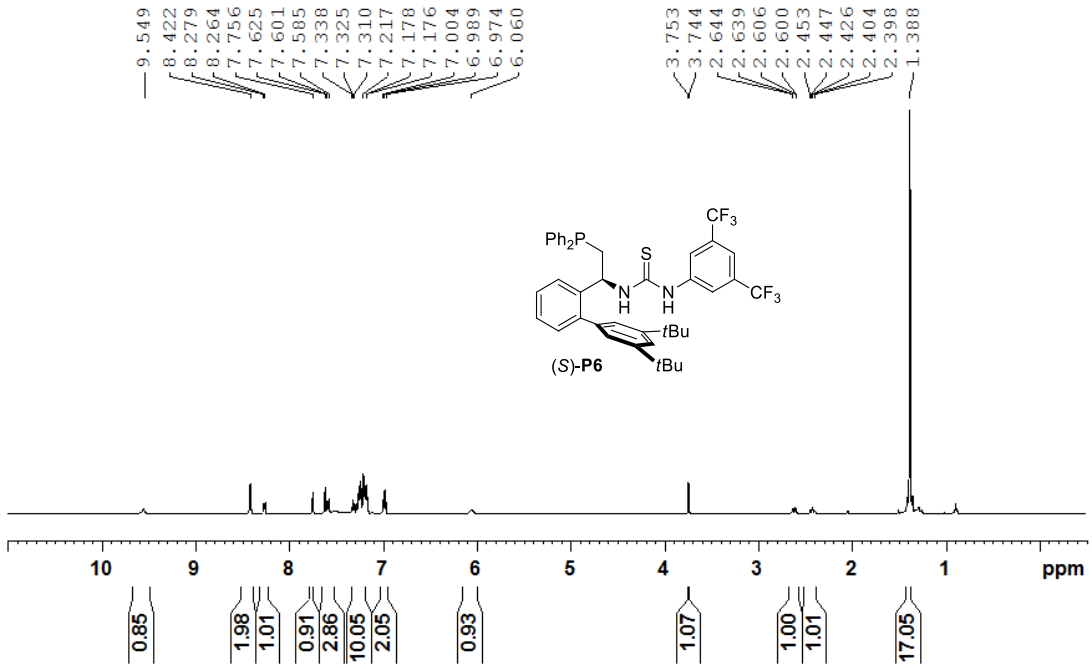
-200
ppm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7.178
7.176
7.004
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6.974
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3.744
2.644
2.639
2.606
2.600
2.453
2.447
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2.404
2.398
1.388
Ph2P
S
N
H
N
H
CF3
CF3
tBu
tBu
(S)-P6
10
9
8
7
6
5
4
3
2
1
ppm
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0.91
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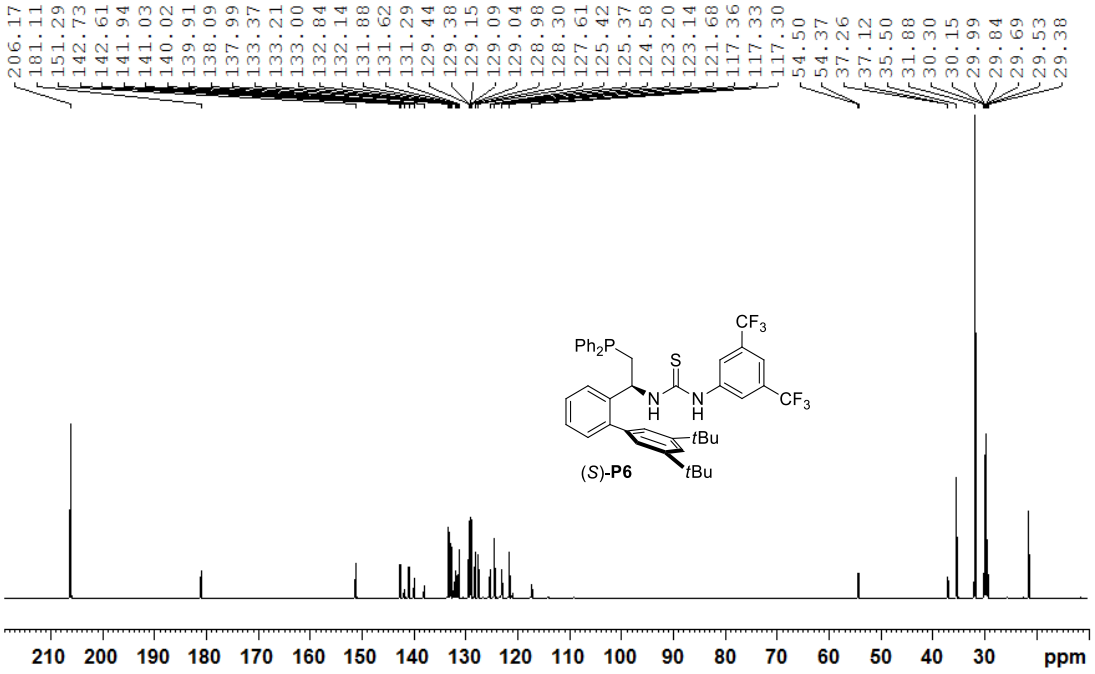
17.05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131.29
129.44
129.38
129.15
129.09
129.04
128.98
128.30
127.61
125.42
125.37
124.58
123.20
123.14
121.68
117.36
117.33
117.30
54.50
54.37
37.26
37.12
35.50
31.88
30.30
30.15
29.99
29.84
29.69
29.53
29.38
Ph2P
S
N
H
N
H
CF3
CF3
tBu
tBu
(S)-P6
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200
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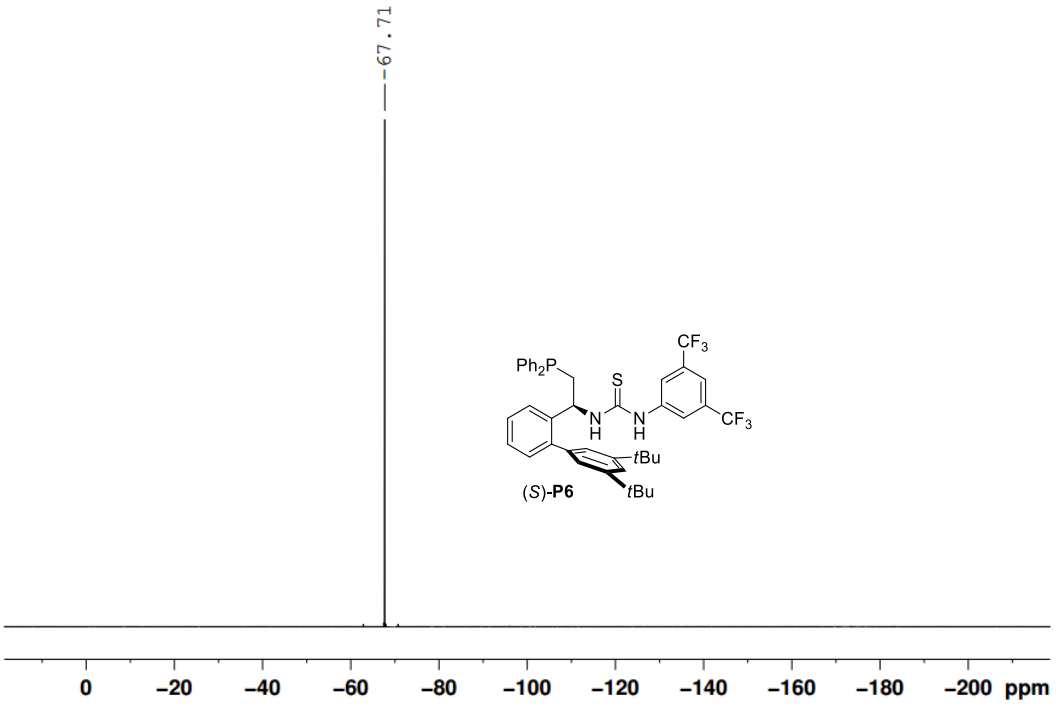
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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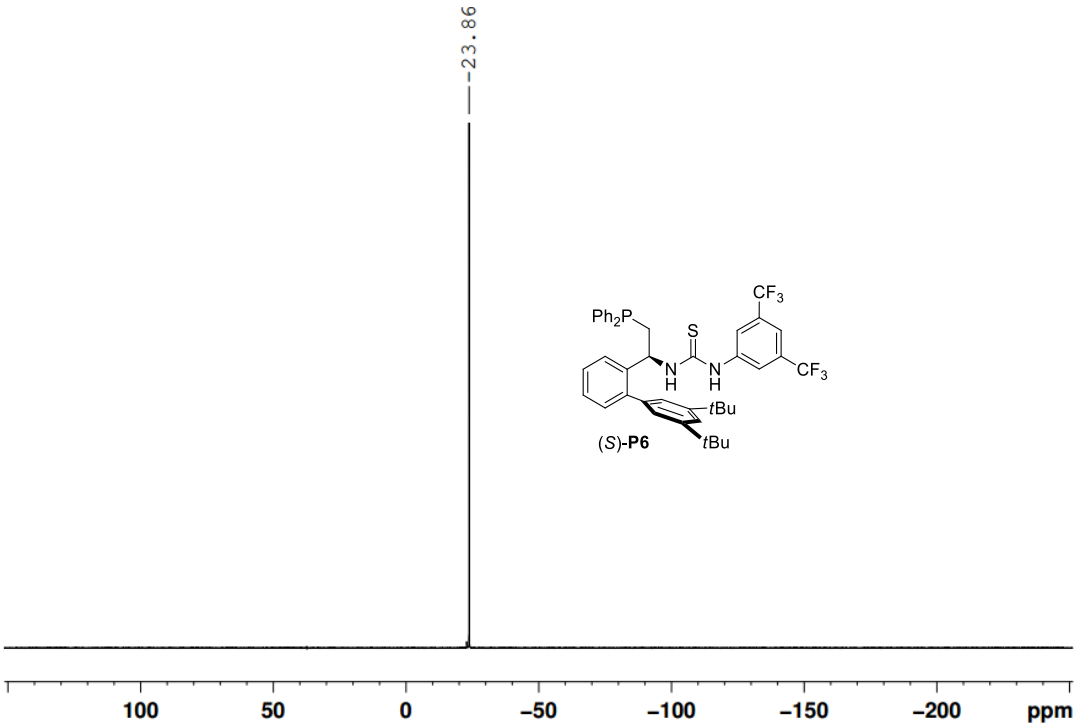
S
N
H
N
H
CF3
CF3
tBu
tBu
(S)-P6
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm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S
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N
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50
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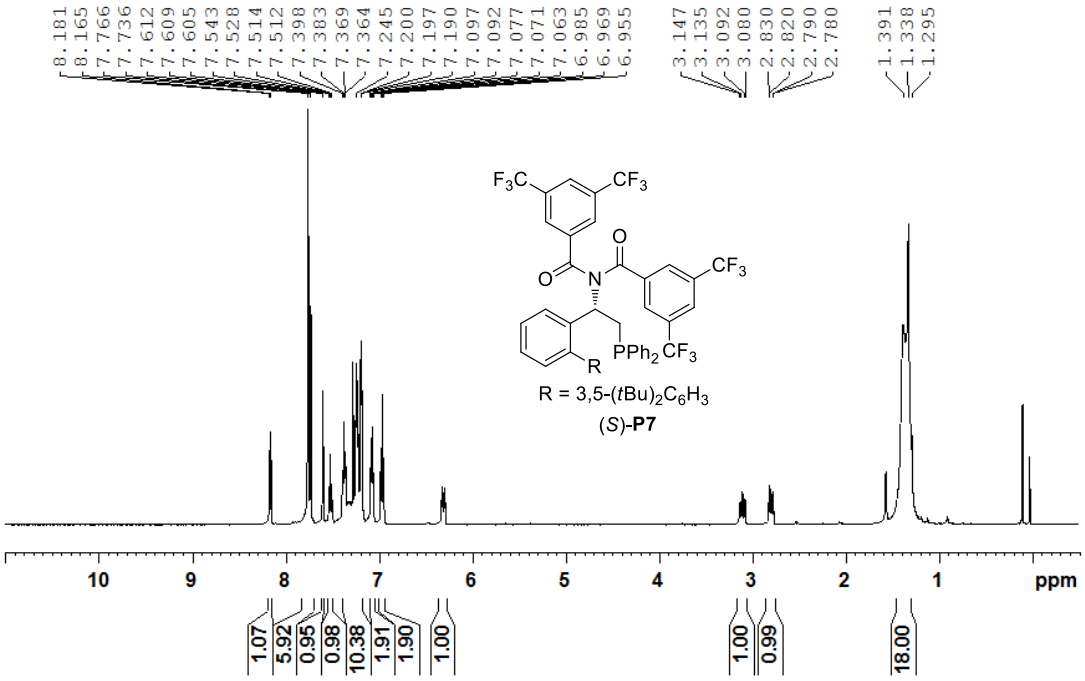
−50
−100
−150
−200
ppm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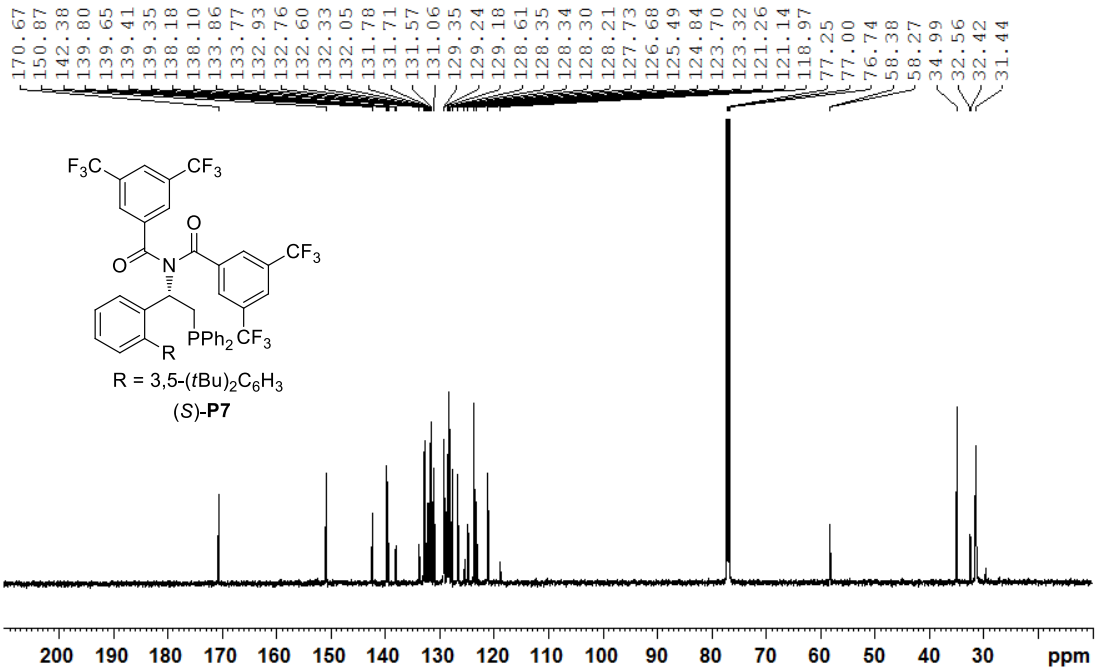
7.609
7.605
7.543
7.528
7.514
7.512
7.398
7.383
7.369
7.364
7.245
7.200
7.197
7.190
7.097
7.092
7.077
7.071
7.063
6.985
6.969
6.955
3.147
3.135
3.092
3.080
2.830
2.820
2.790
2.780
1.391
1.338
1.295
F3C
CF3
O
N
O
CF3
R
PPh2 CF3
R = 3,5-(tBu)2C6H3
(S)-P7
10
9
8
7
6
5
4
3
2
1
ppm
1.07
5.92
0.95
0.98
10.38
1.91
1.90
1.00
1.00
0.99
18.00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132.60
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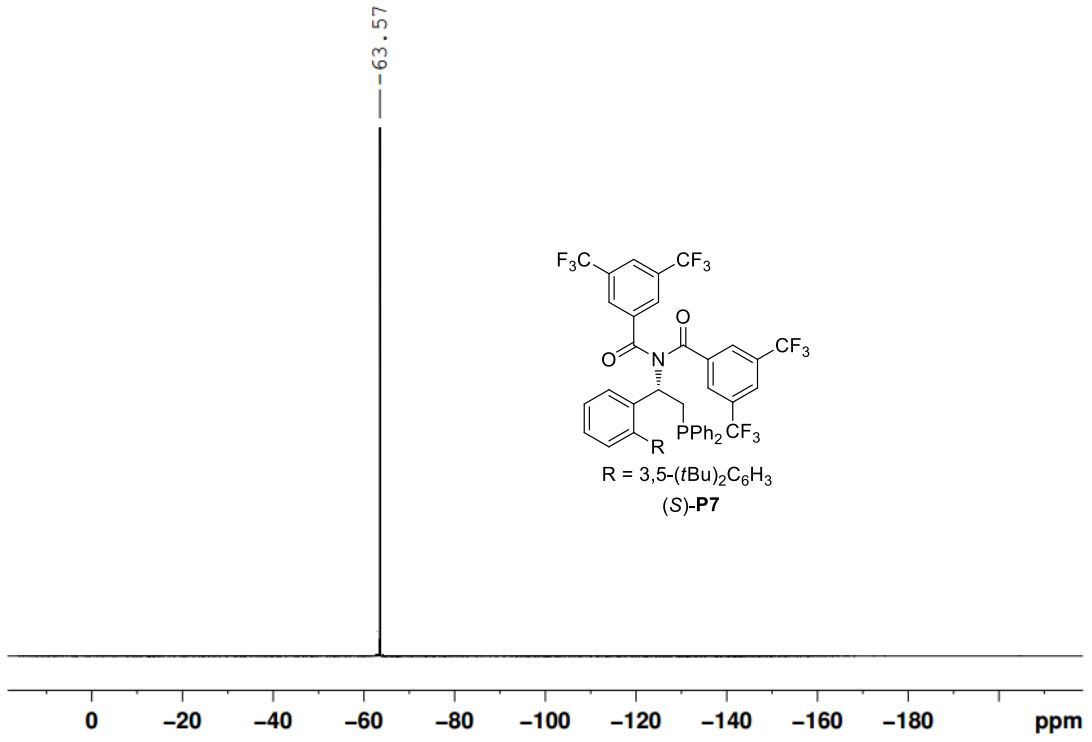
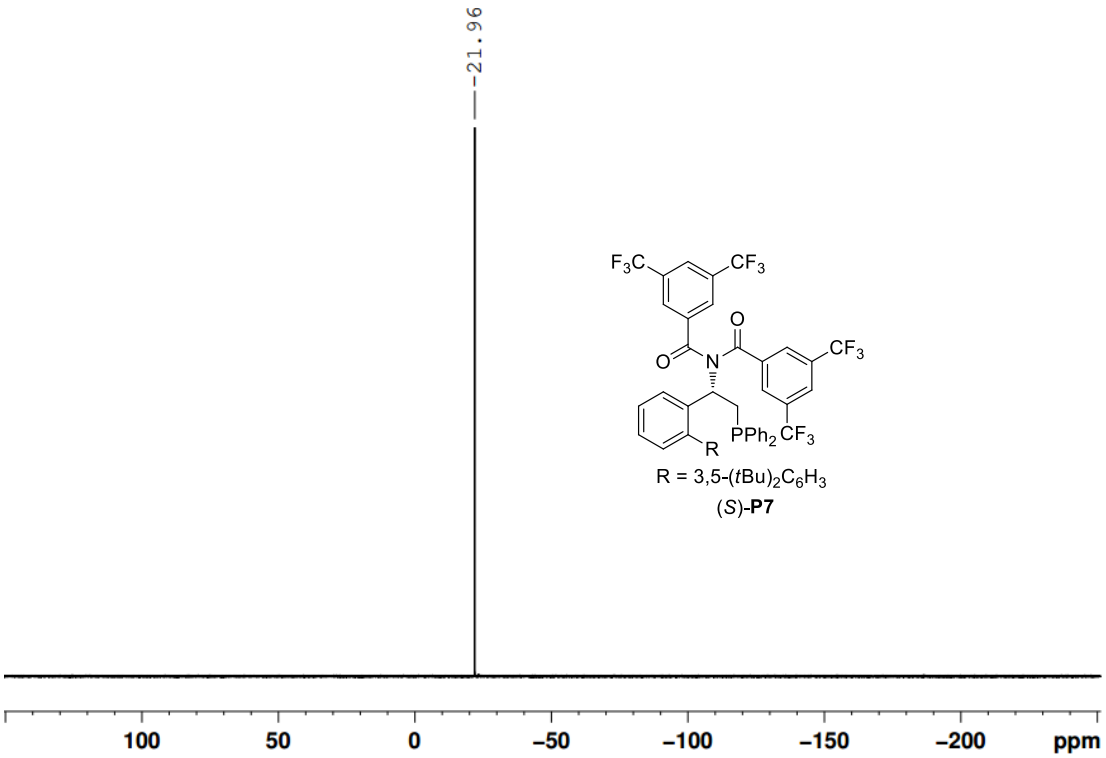
131.78
131.71
131.57
131.06
129.35
129.24
129.18
128.61
128.35
128.34
128.30
128.21
127.73
126.68
125.49
124.84
123.70
123.32
121.26
121.14
118.97
77.25
77.00
76.74
58.38
58.27
34.99
32.56
32.42
31.44
F3C
CF3
O
N
O
CF3
R
PPh2 CF3
R = 3,5-(tBu)2C6H3
(S)-P7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm



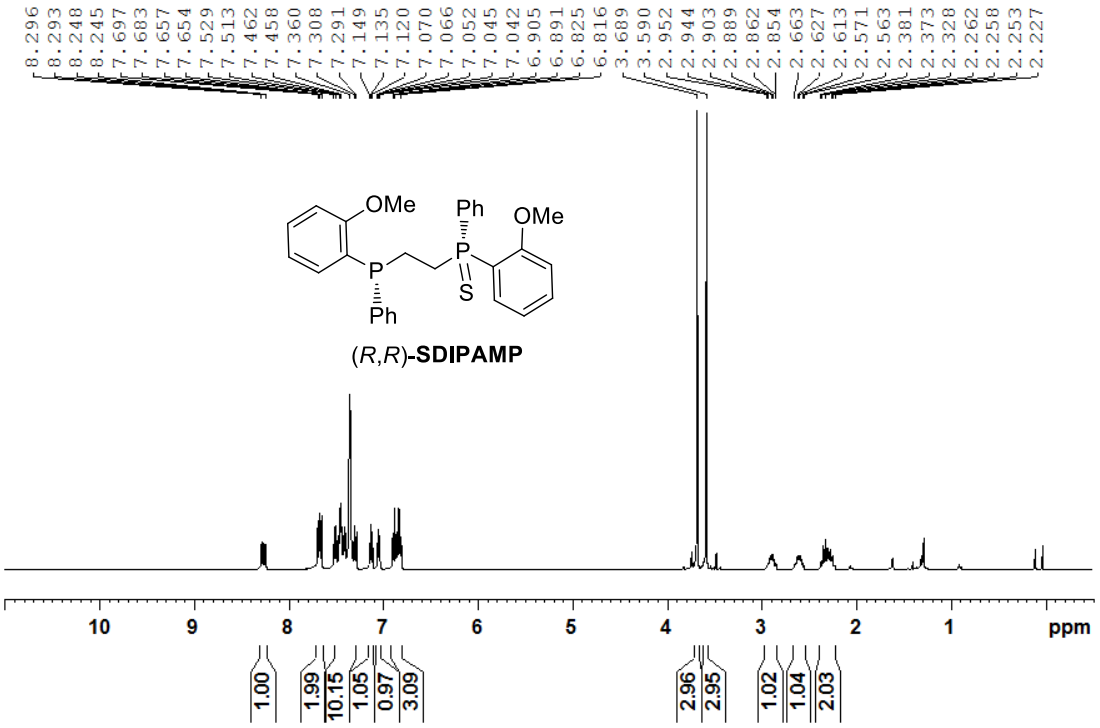

R = 3,5-(*t*Bu)$_2$C$_6$H$_3$

(*S*)-**P7**




R = 3,5-(*t*Bu)$_2$C$_6$H$_3$

(*S*)-**P7**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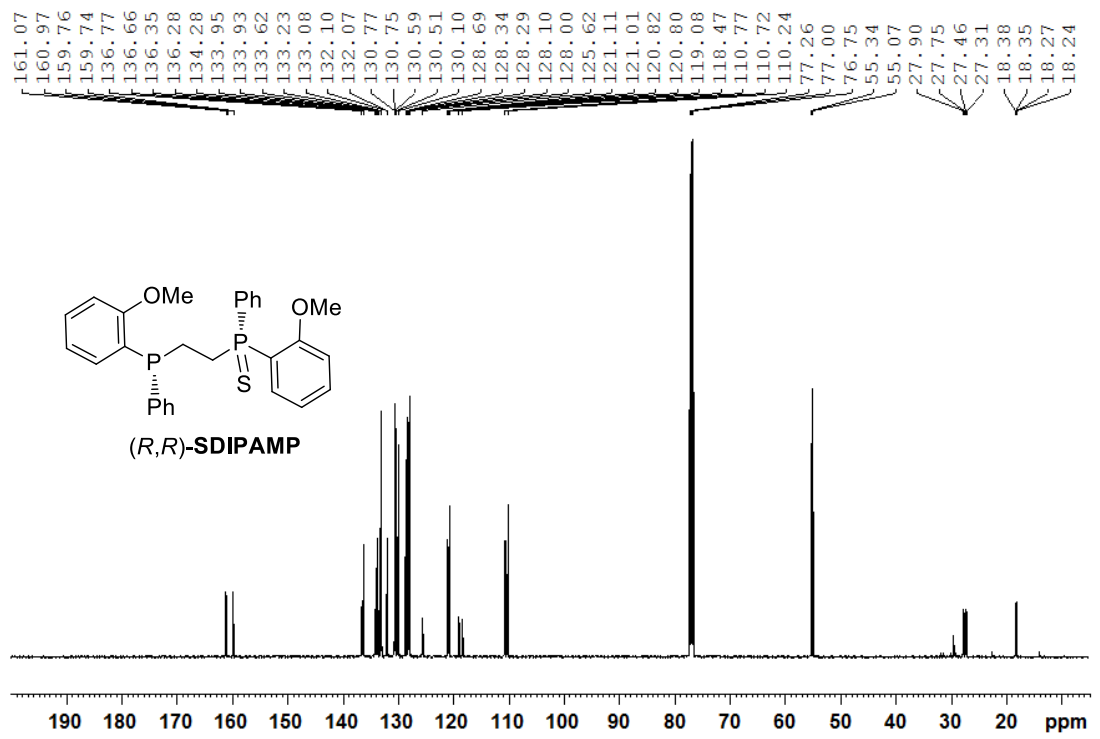
8.293
8.248
8.245
7.697
7.683
7.657
7.654
7.529
7.513
7.462
7.458
7.360
7.308
7.291
7.149
7.135
7.120
7.070
7.066
7.052
7.045
7.042
6.905
6.891
6.825
6.816
3.689
3.590
2.952
2.944
2.903
2.889
2.862
2.854
2.663
2.627
2.613
2.571
2.563
2.381
2.373
2.328
2.262
2.258
2.253
2.227
OMe
Ph
OMe
P
P
S
Ph
(R,R)-SDIPAMP
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
10.15
1.05
0.97
3.09
2.96
2.95
1.02
1.04
2.03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160.97
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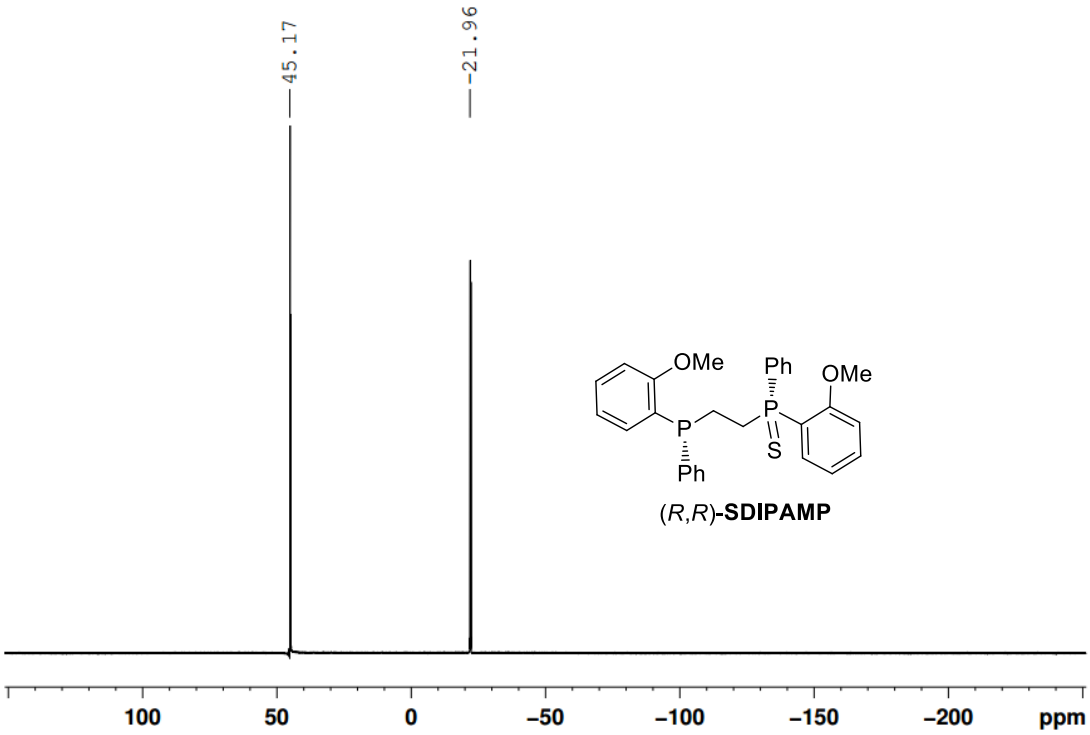
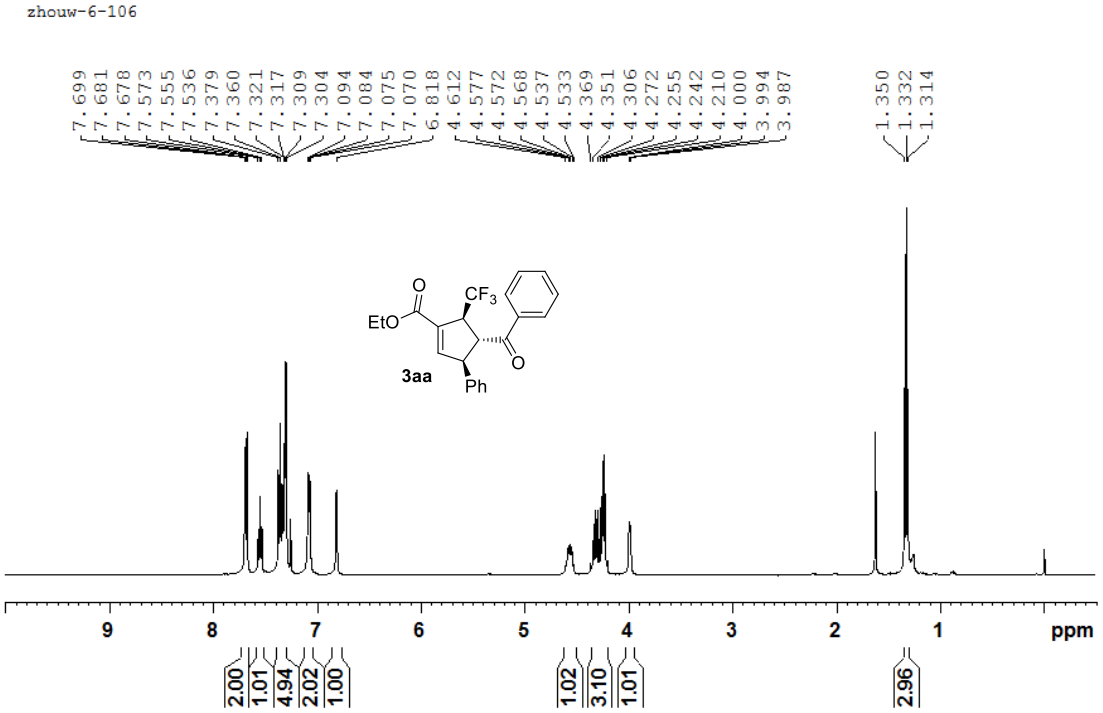
159.74
136.77
136.66
136.35
136.28
134.28
133.95
133.93
133.62
133.23
133.08
132.10
132.07
130.77
130.75
130.59
130.51
130.10
128.69
128.34
128.29
128.10
128.00
125.62
121.11
121.01
120.82
120.80
119.08
118.47
110.77
110.72
110.24
77.26
77.00
76.75
55.34
55.07
27.90
27.75
27.46
27.31
18.38
18.35
18.27
18.24
OMe
Ph
OMe
P
P
S
Ph
(R,R)-SDIPAMP
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


45.17
-21.96
OMe
Ph
OMe
P
P
S
Ph
100
50
0
−50
−100
−150
−200
ppm

(*R*,*R*)-**SDIPAMP**


zhouw-6-106
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7.678
7.573
7.555
7.536
7.379
7.360
7.321
7.317
7.309
7.304
7.094
7.084
7.075
7.070
6.818
4.612
4.577
4.572
4.568
4.537
4.533
4.369
4.351
4.306
4.272
4.255
4.242
4.210
4.000
3.994
3.987
1.350
1.332
1.314
EtO
O
CF3
O
O
Ph
3aa
9
8
7
6
5
4
3
2
1
ppm
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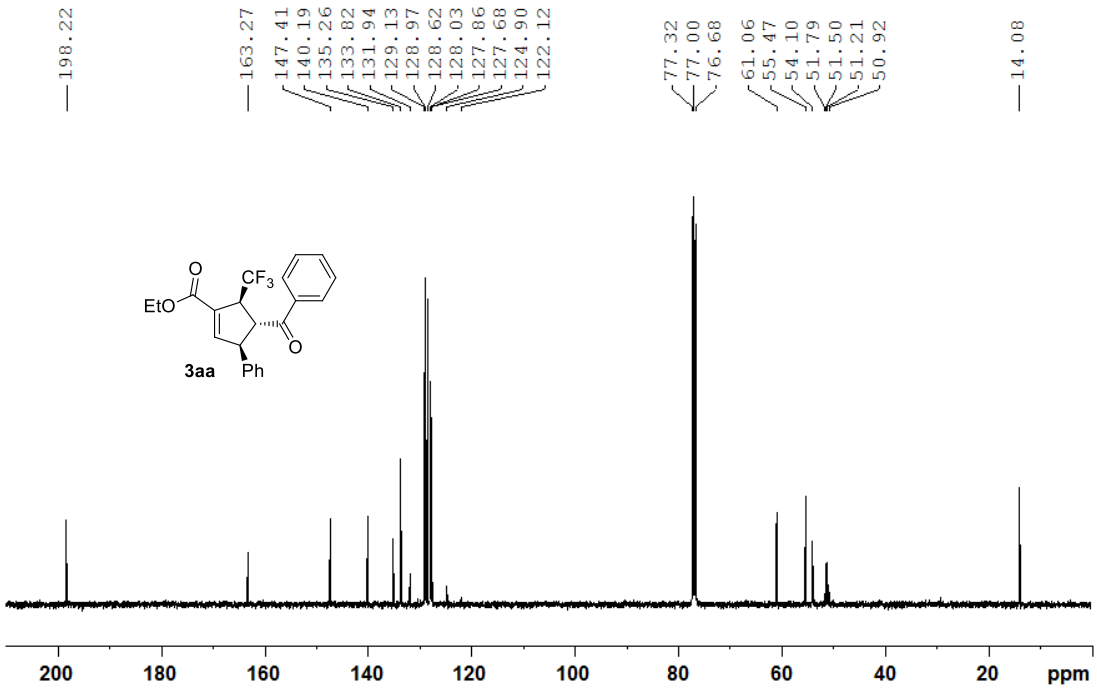
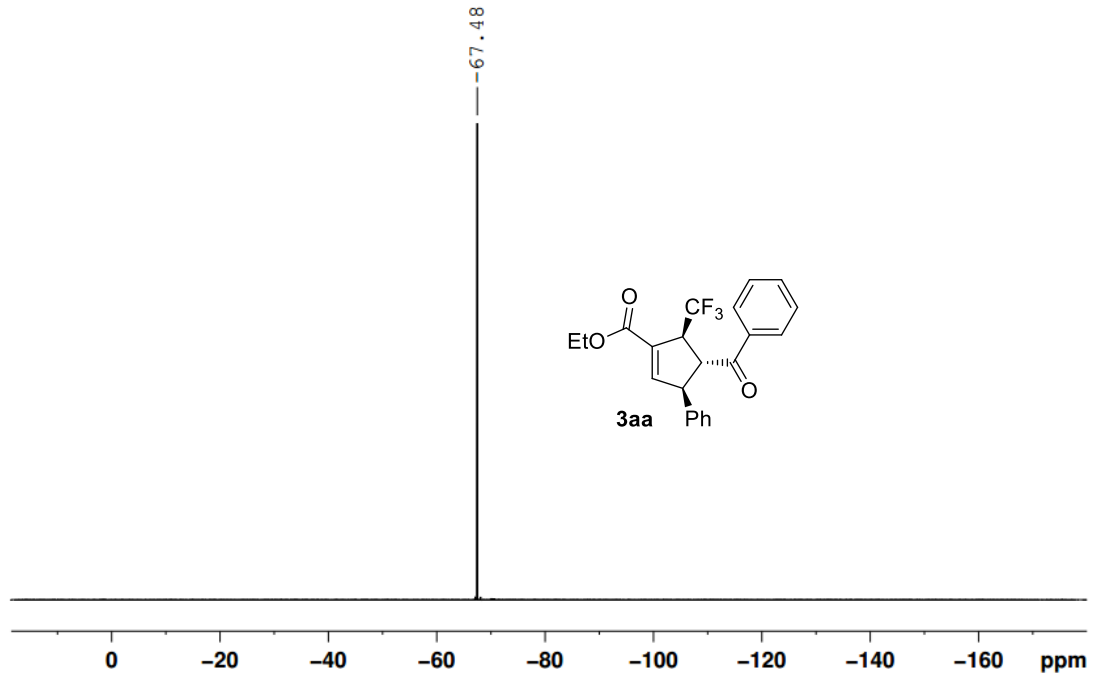
1.01
4.94
2.02
1.00
1.02
3.10
1.01
2.96

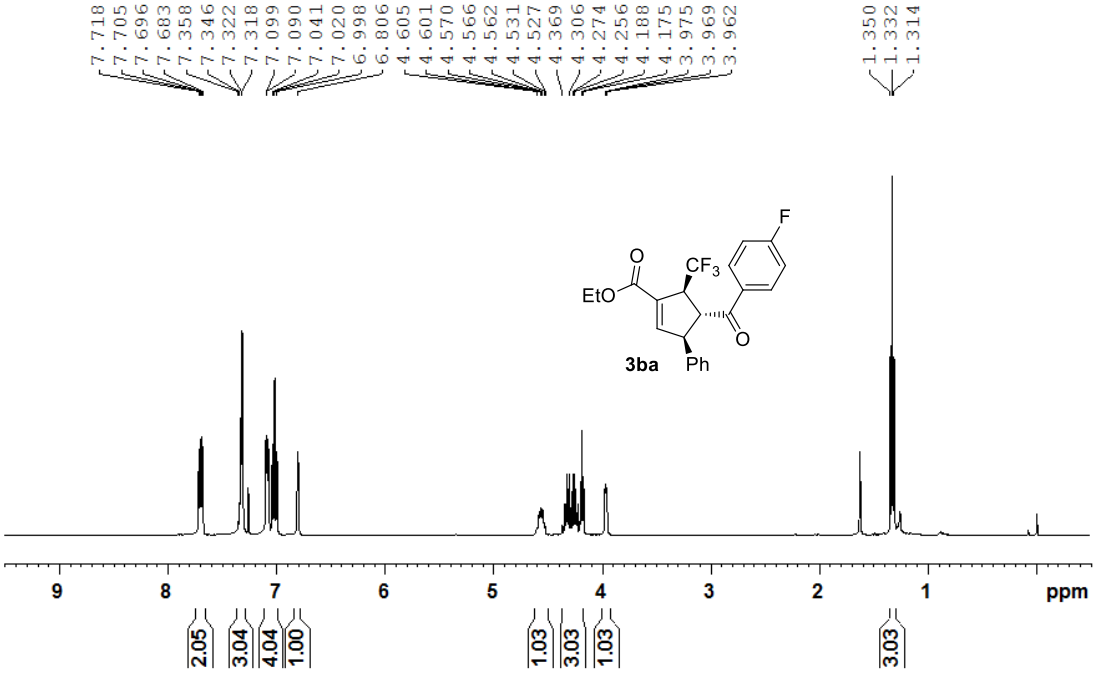
zhouw-6-106c



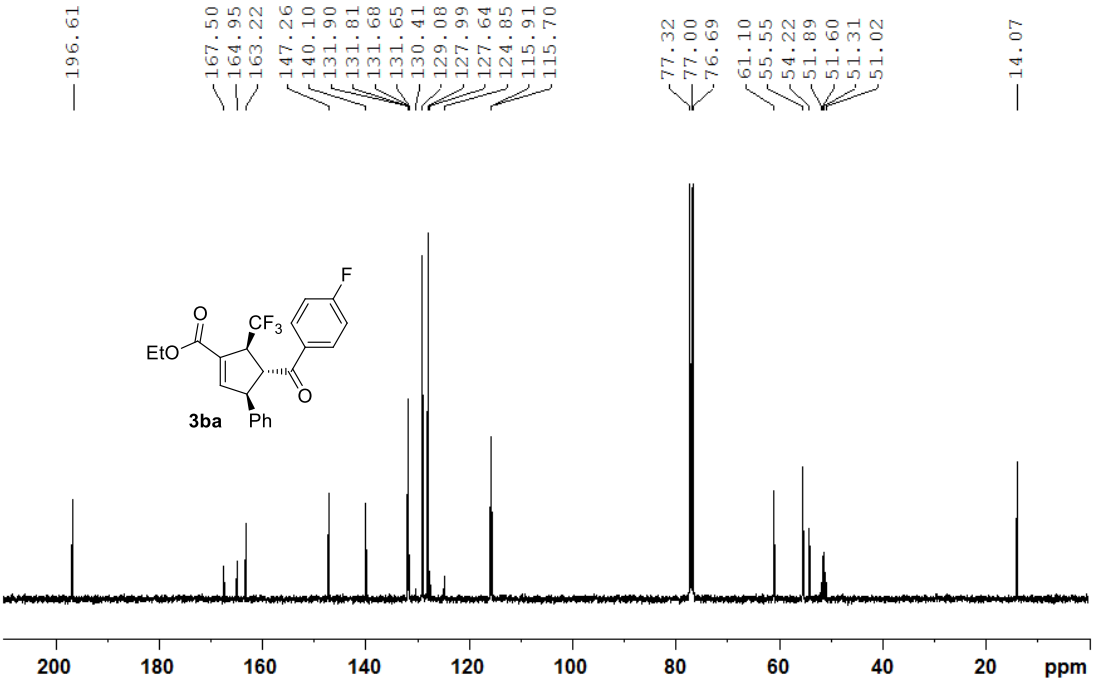

zhouw-6-106f



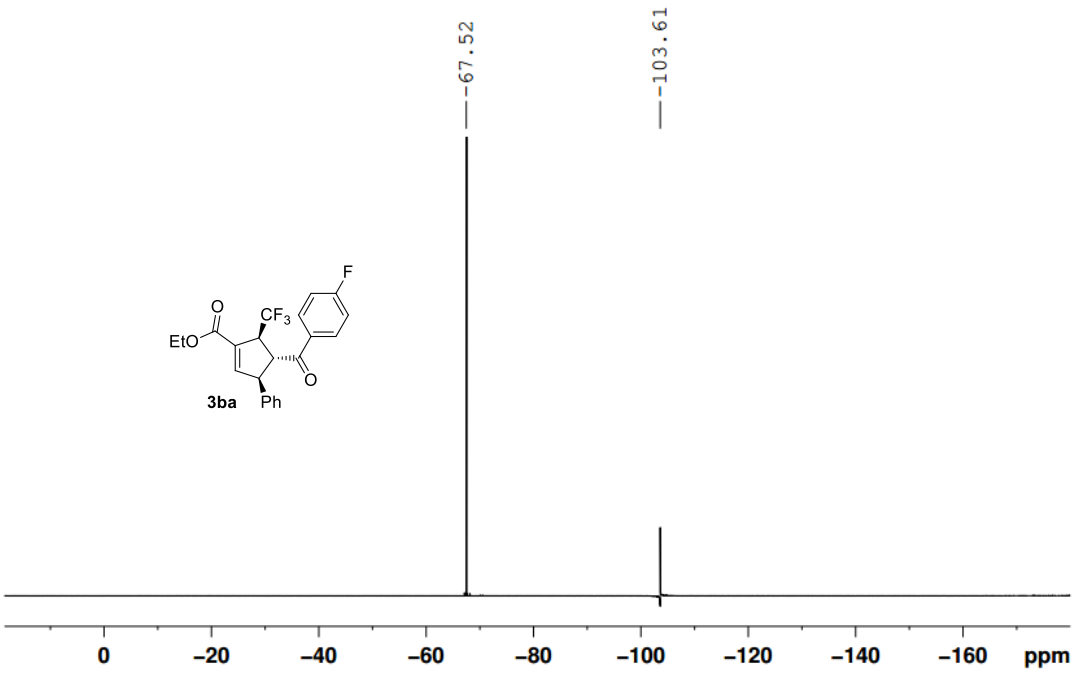
zhouw-6-107



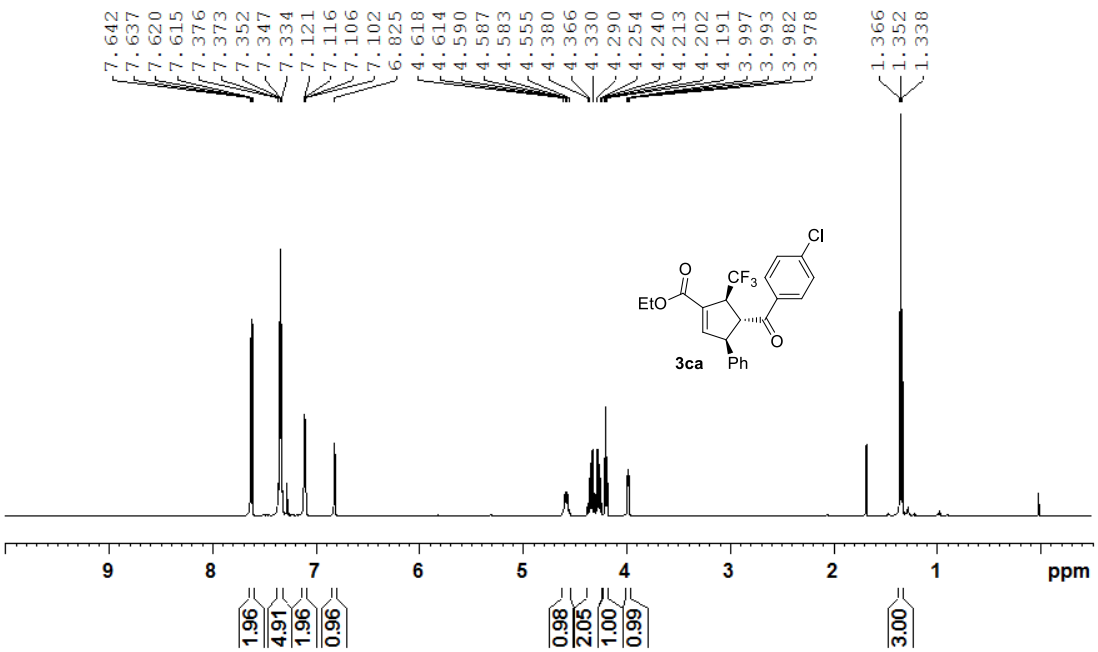

zhouw-6-107c



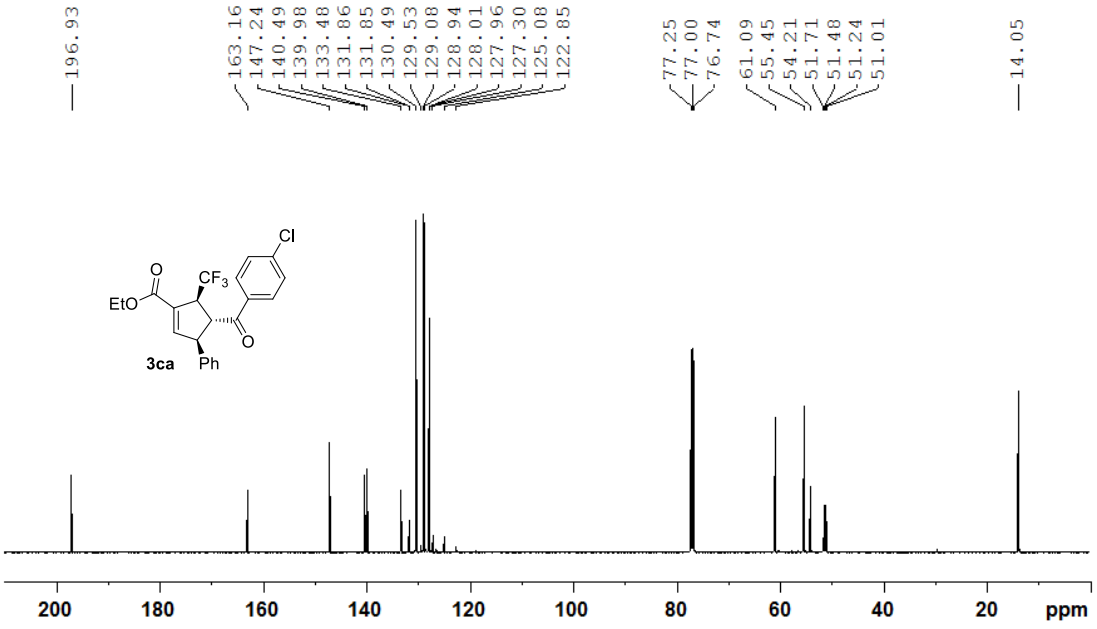
zhouw-6-107f



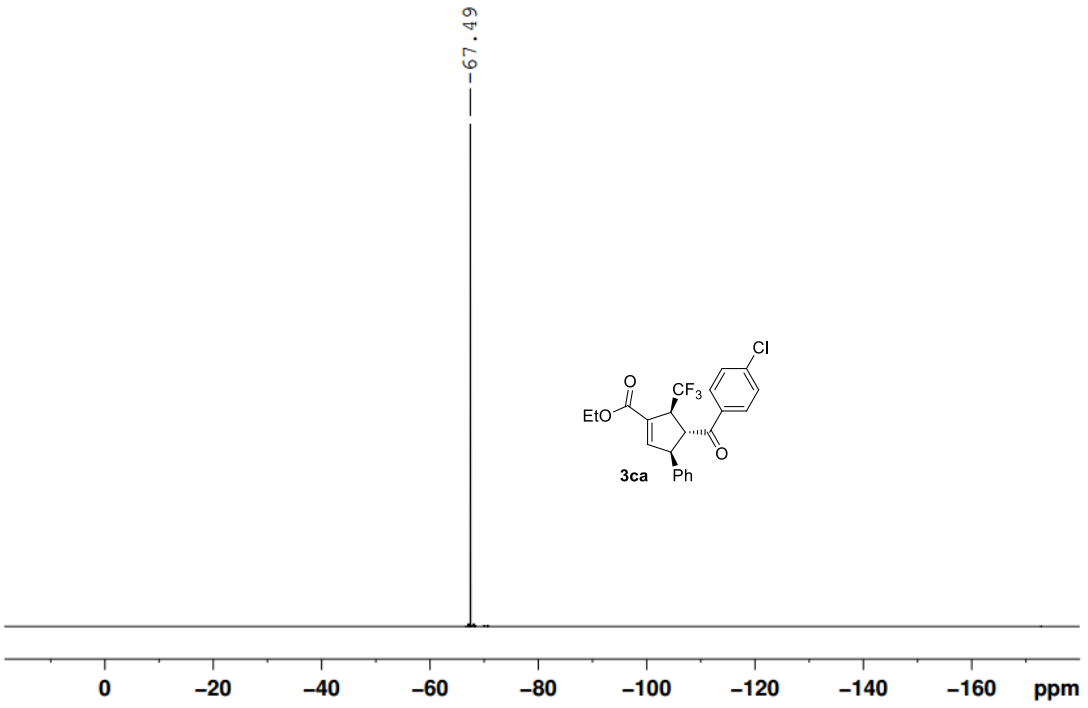

zhouw-6-77



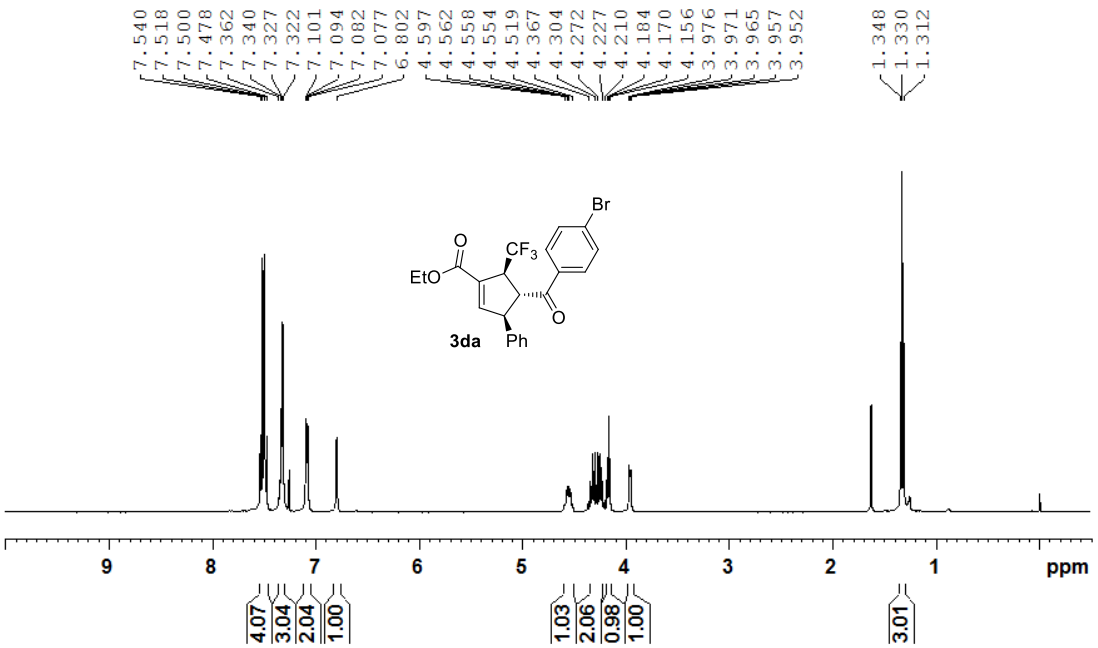
zhouw-6-77c



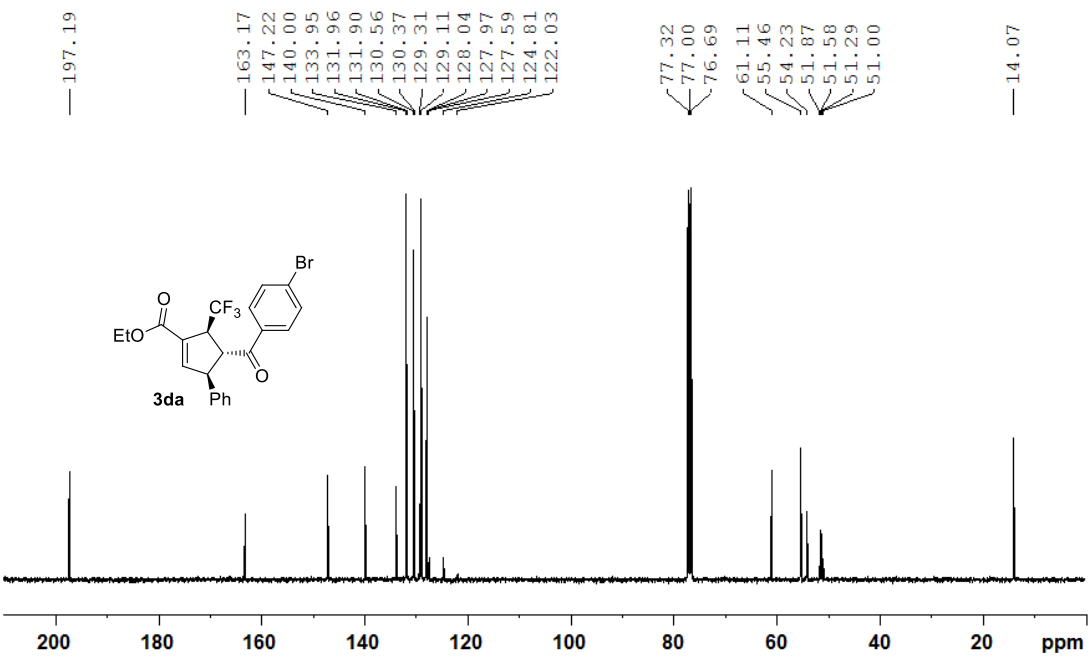

zhouw-6-77f



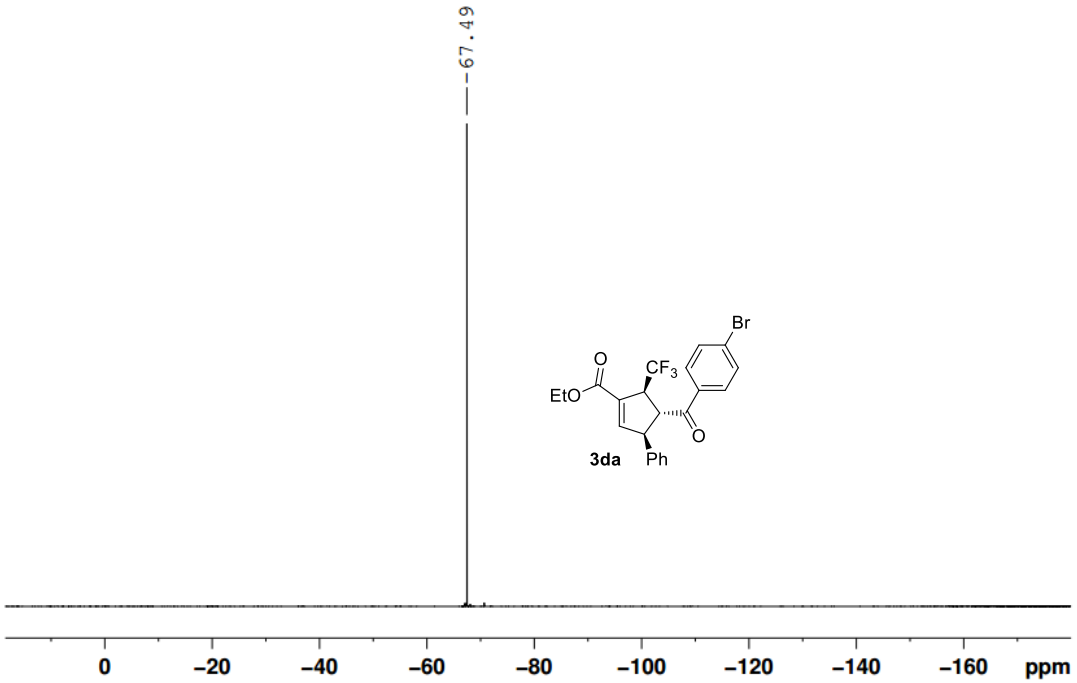
zhouw-6-108



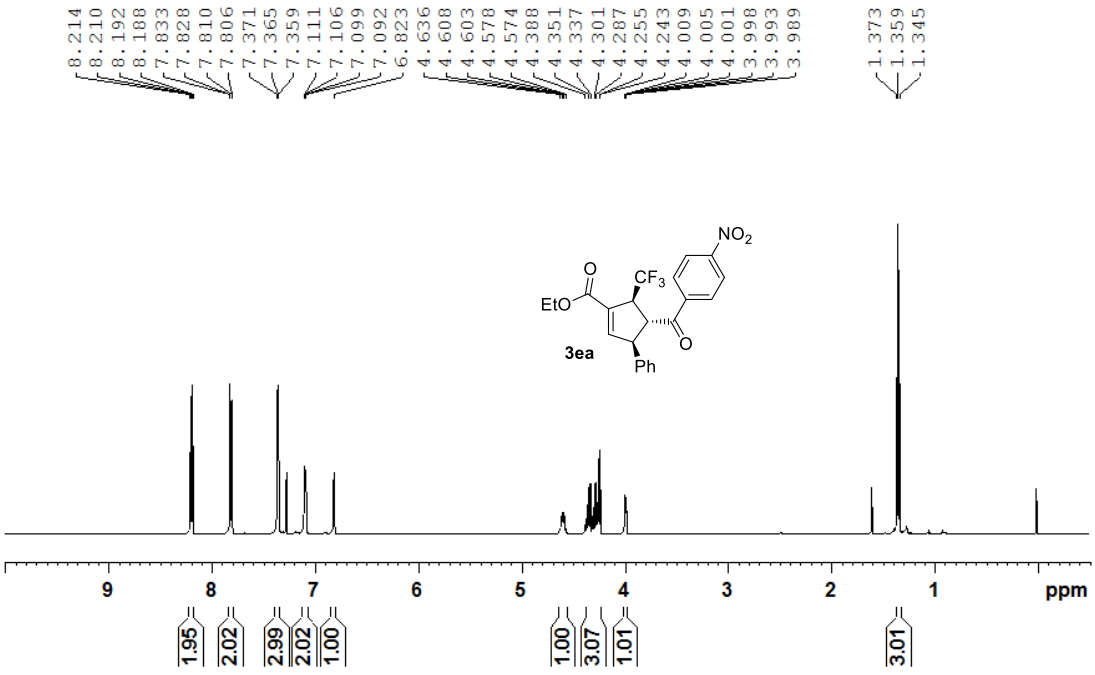

zhouw-6-108c



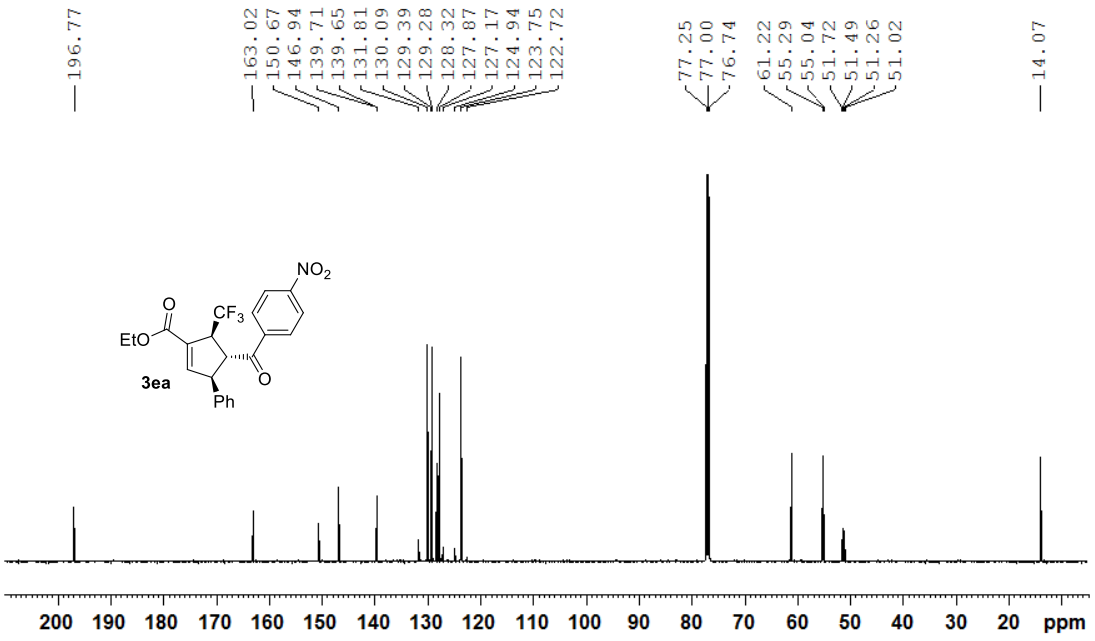
zhouw-6-108f



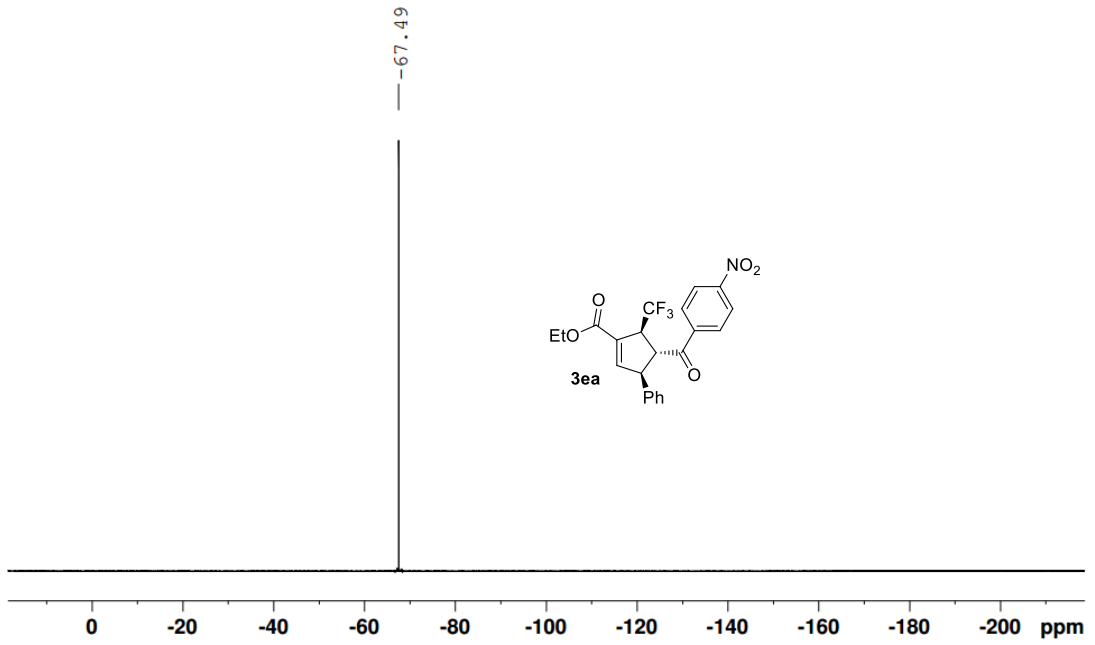

zhouw-7-55



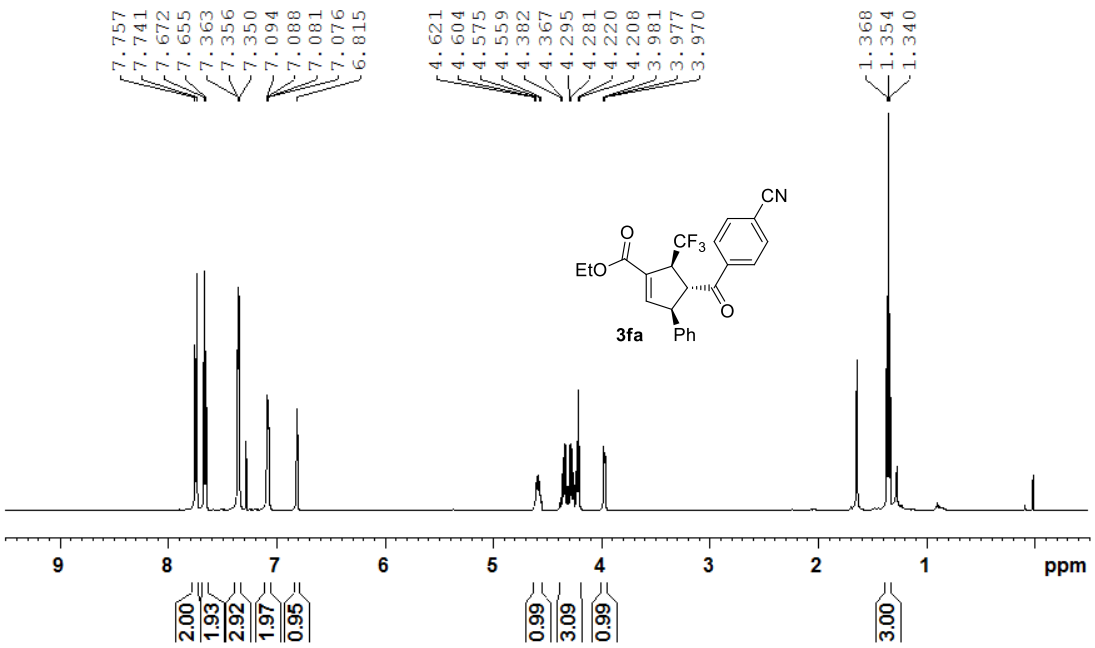
zhouw-7-55c



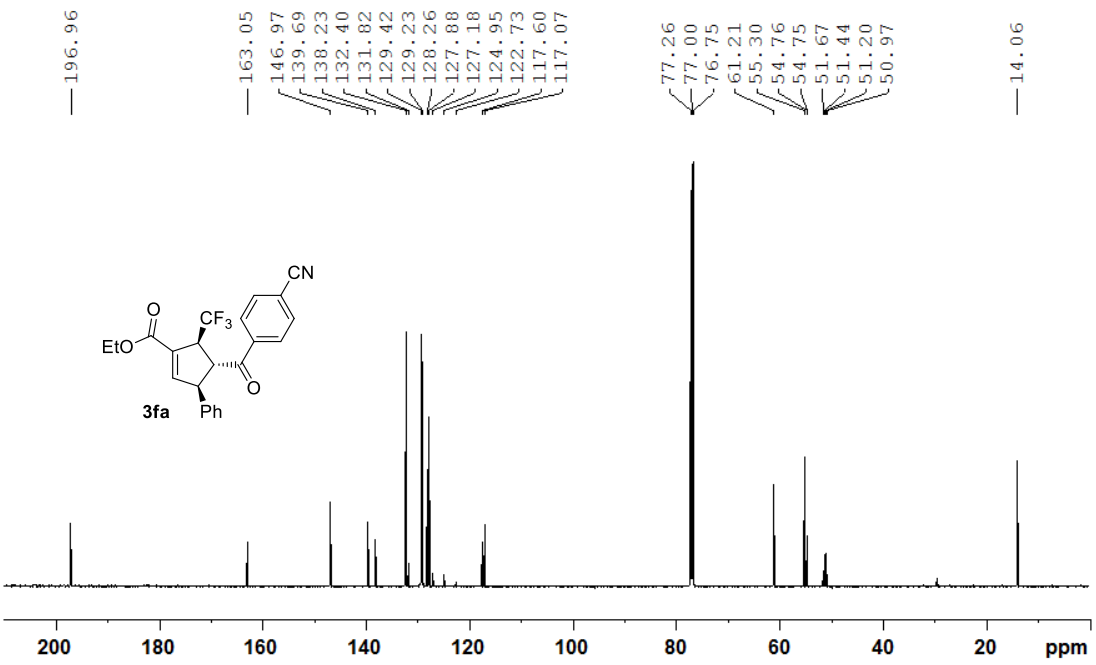

zhouw-7-55f



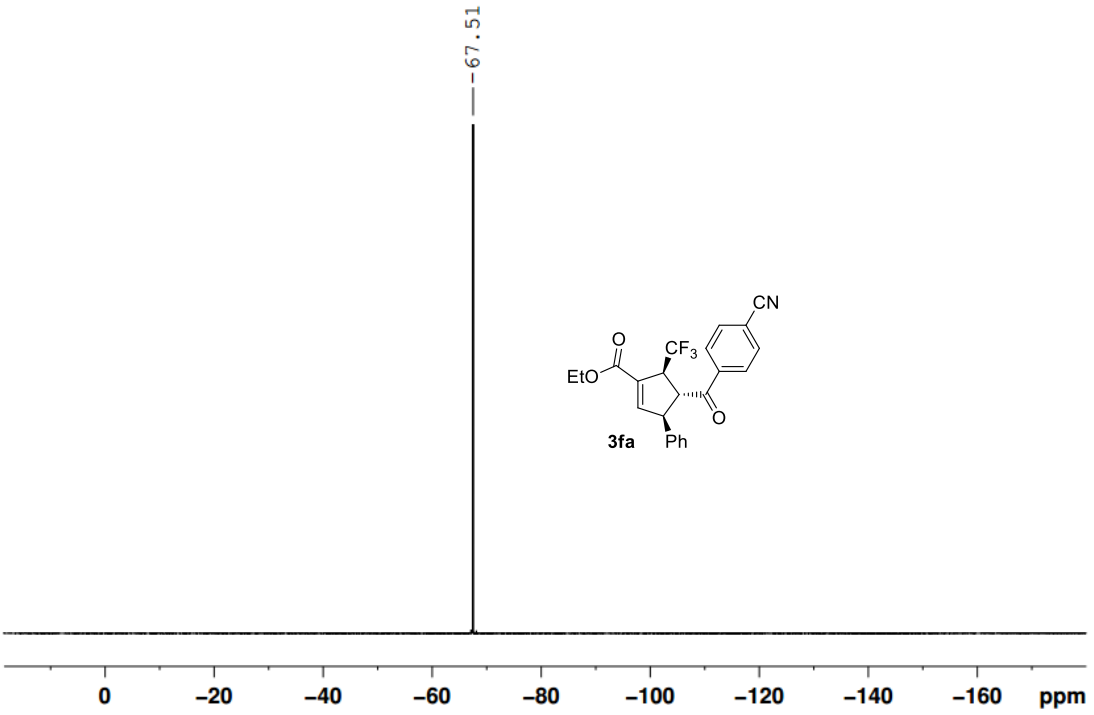
zhouw-6-112



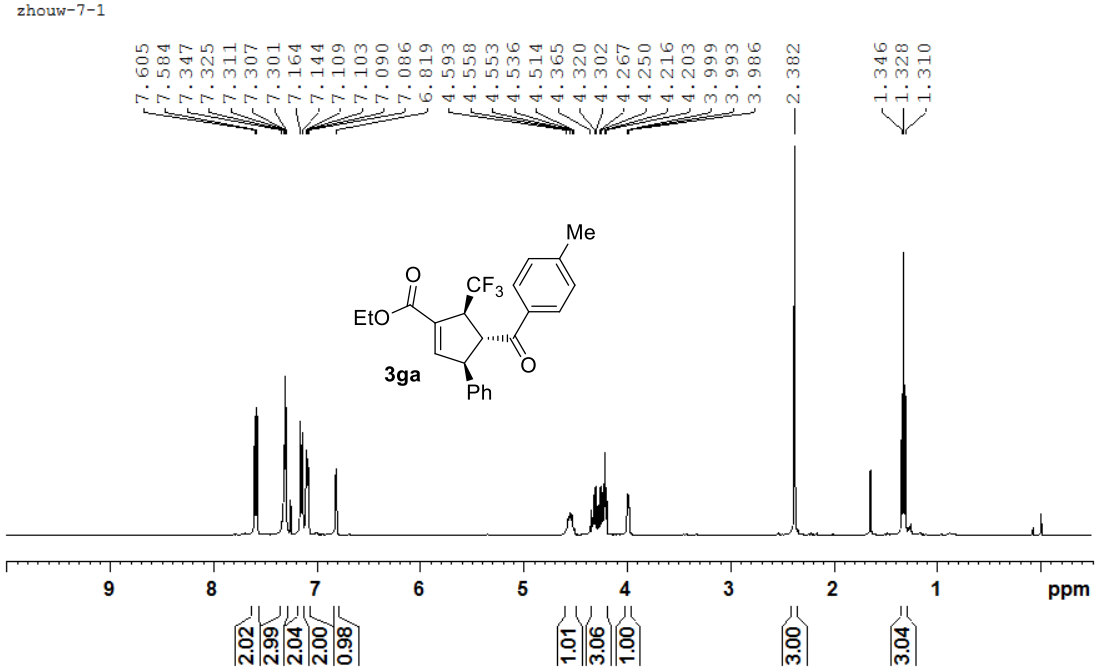

zhouw-6-112c



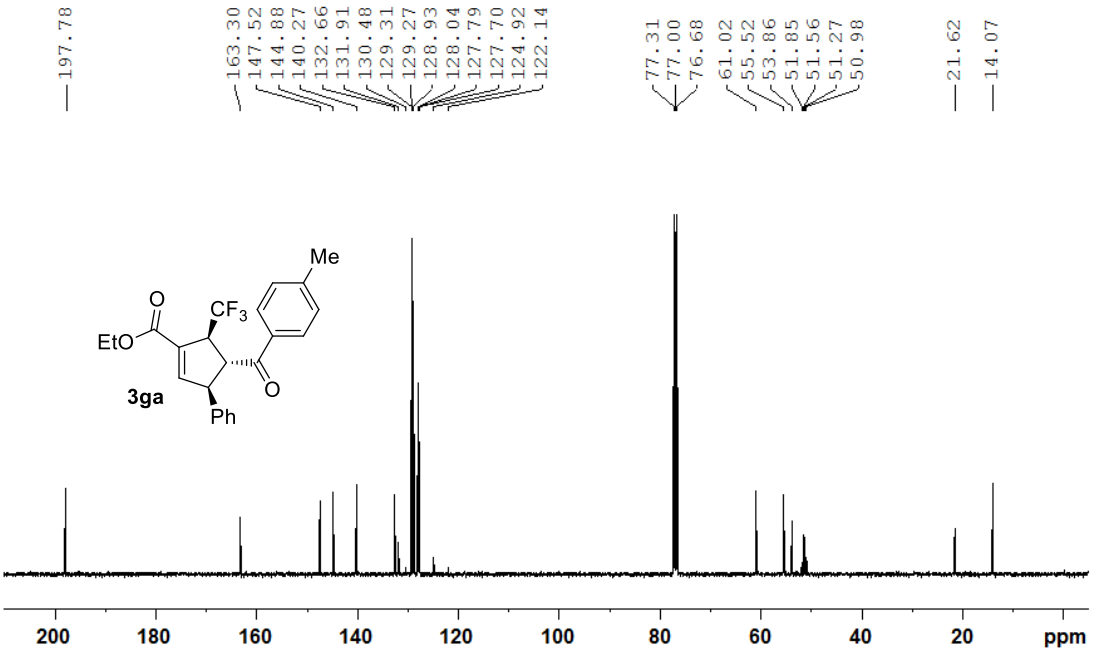
zhouw-6-112f



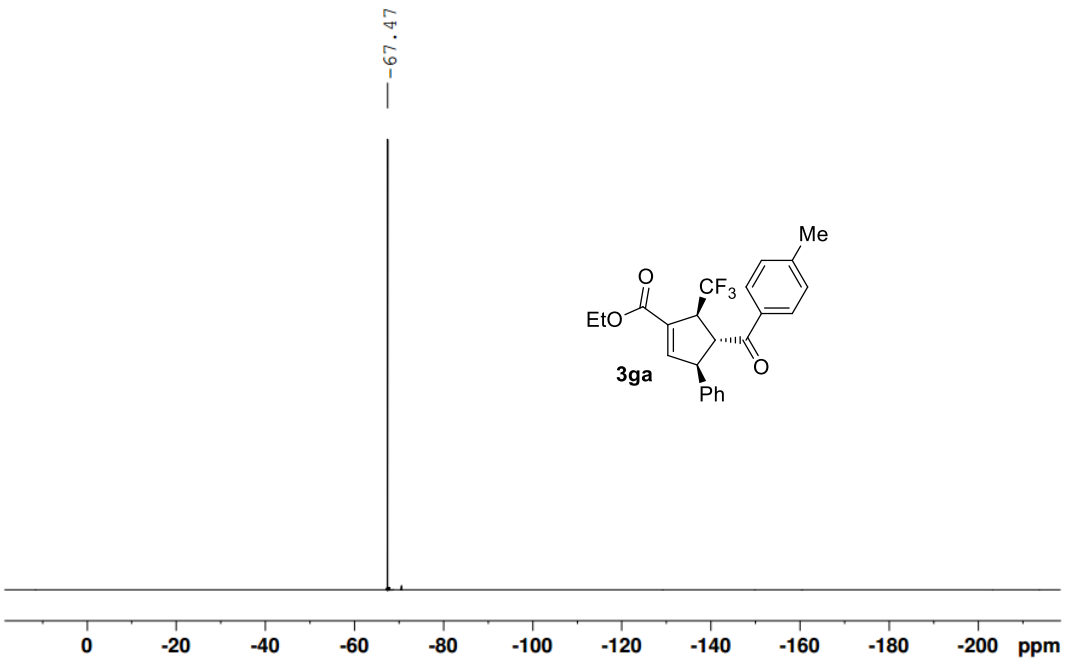

zhouw-7-1

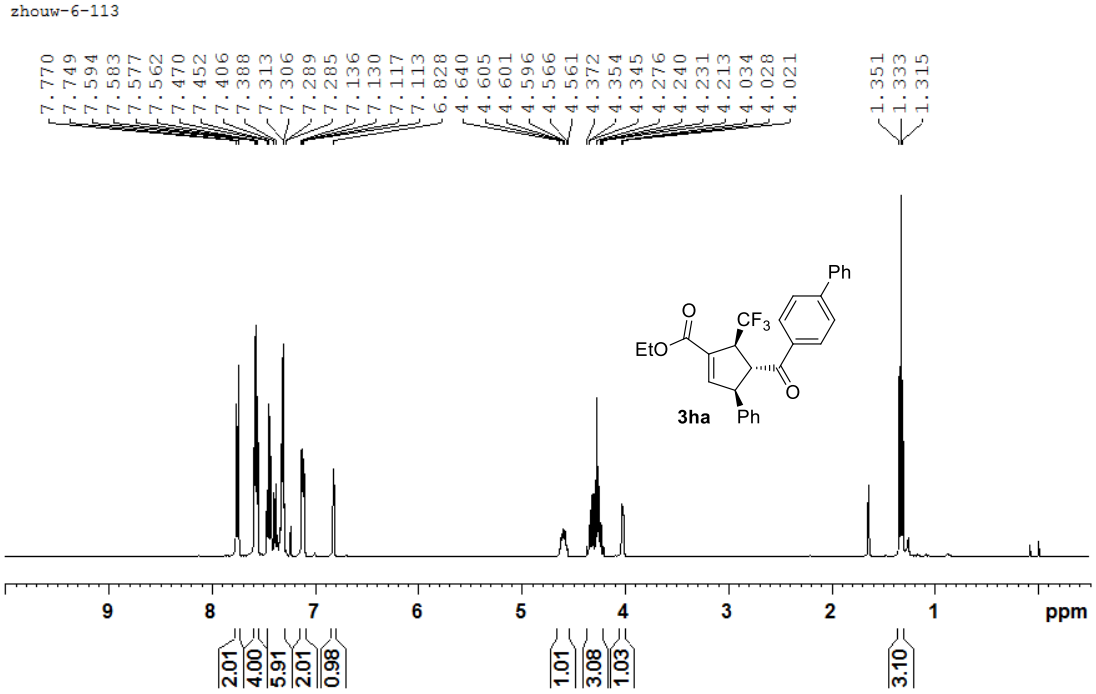


zhouw-7-1c




zhouw-7-1f




zhouw-6-113
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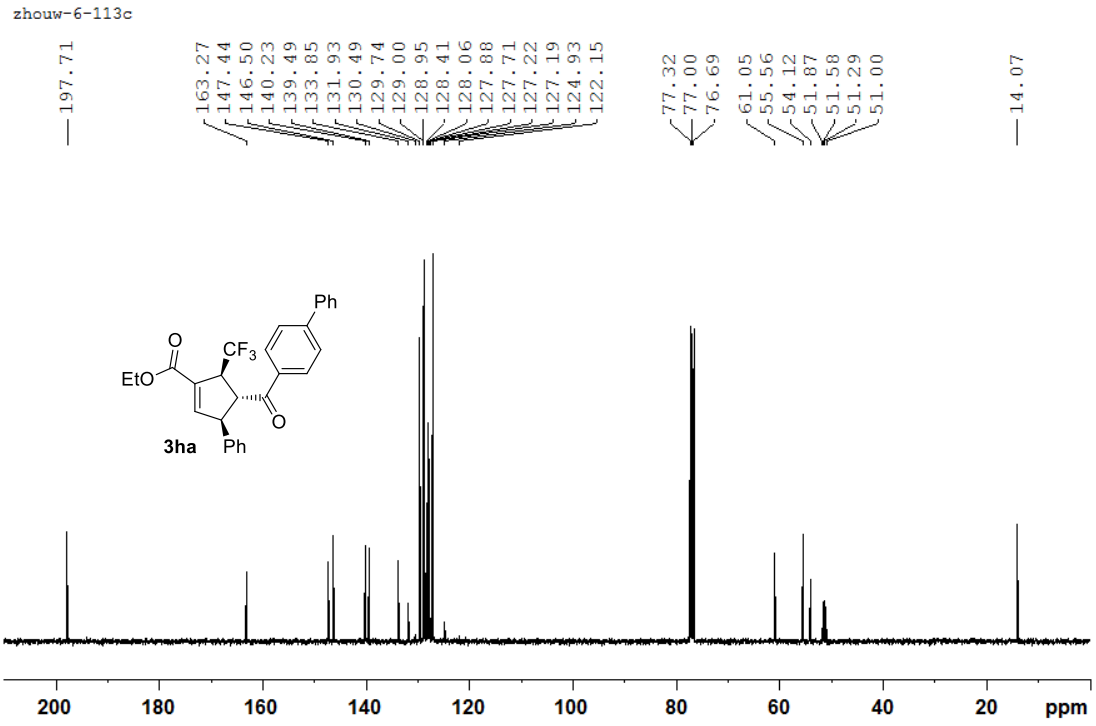
7.583
7.577
7.562
7.470
7.452
7.406
7.388
7.313
7.306
7.289
7.285
7.136
7.130
7.117
7.113
6.828
4.640
4.605
4.601
4.596
4.566
4.561
4.372
4.354
4.345
4.276
4.240
4.231
4.213
4.034
4.028
4.021
1.351
1.333
1.315
Ph
O
CF3
EtO
O
3ha
Ph
9
8
7
6
5
4
3
2
1
ppm
2.01
4.00
5.91
2.01
0.98
1.01
3.08
1.03
3.10


zhouw-6-113c
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140.23
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130.49
129.74
129.00
128.95
128.41
128.06
127.88
127.71
127.22
127.19
124.93
122.15
77.32
77.00
76.69
61.05
55.56
54.12
51.87
51.58
51.29
51.00
14.07
Ph
O
CF3
EtO
O
3ha
Ph
200
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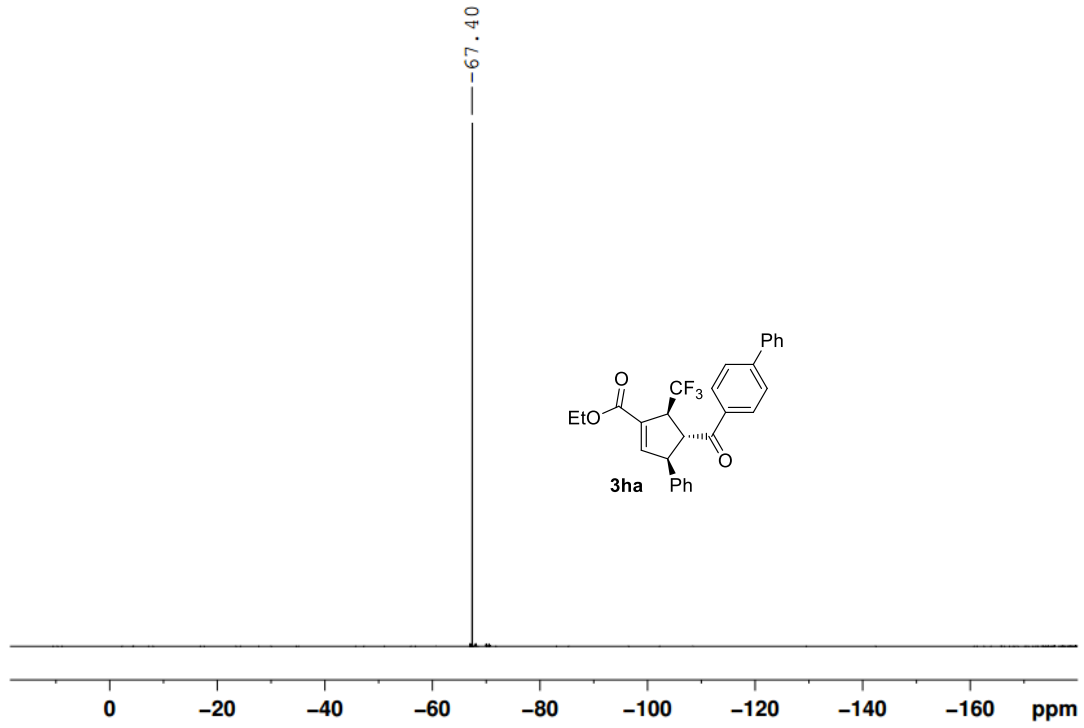
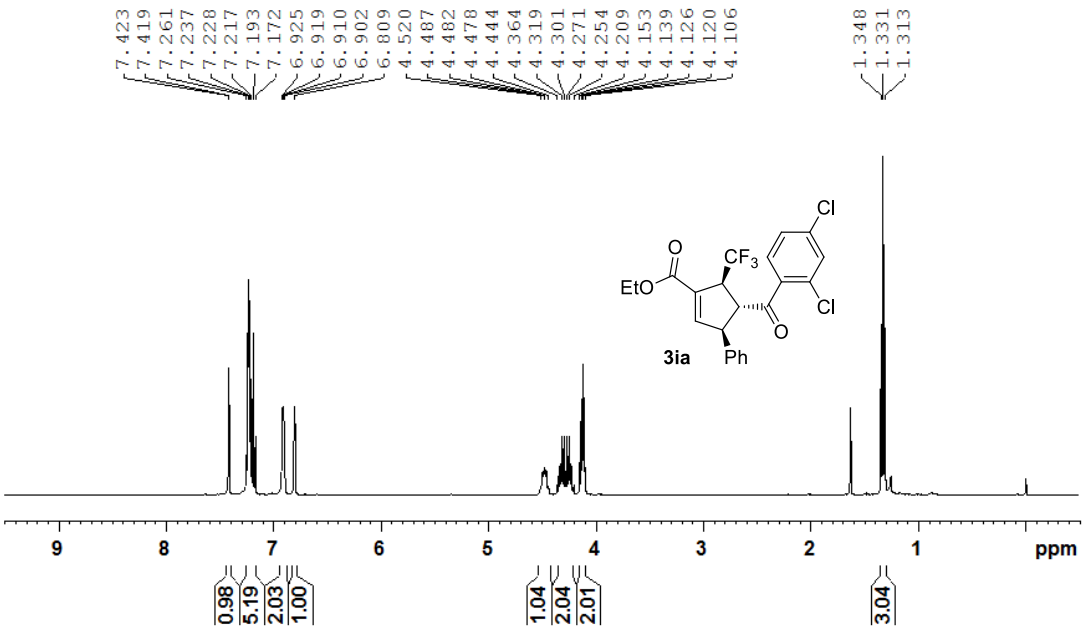
160
140
120
100
80
60
40
20
ppm

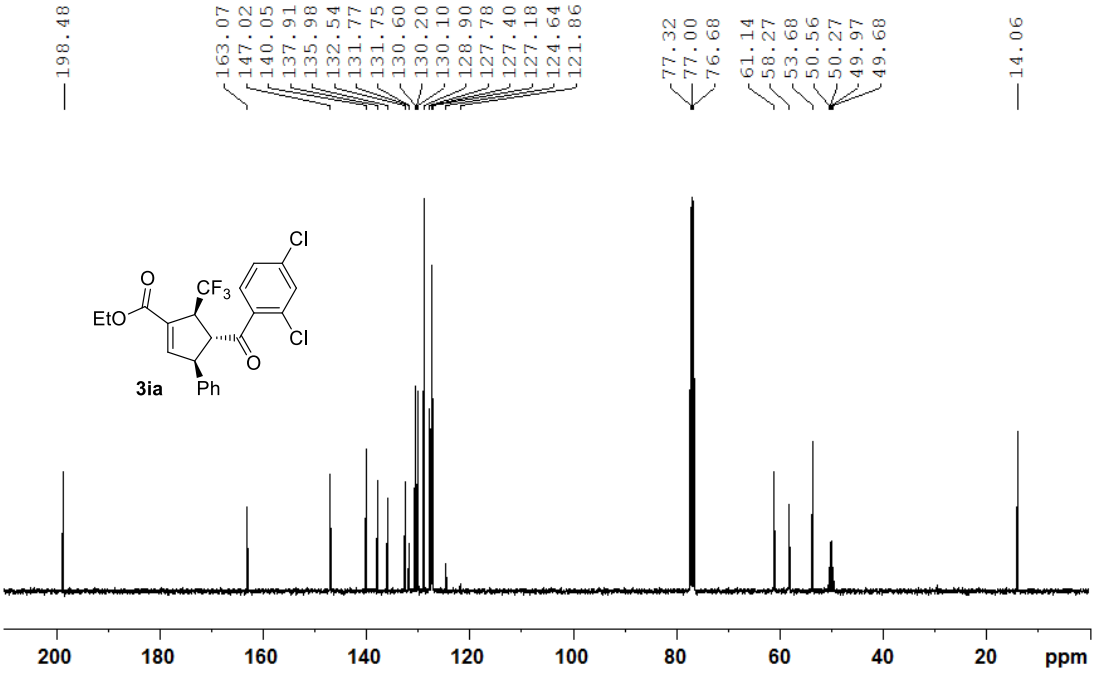
zhouw-6-113f



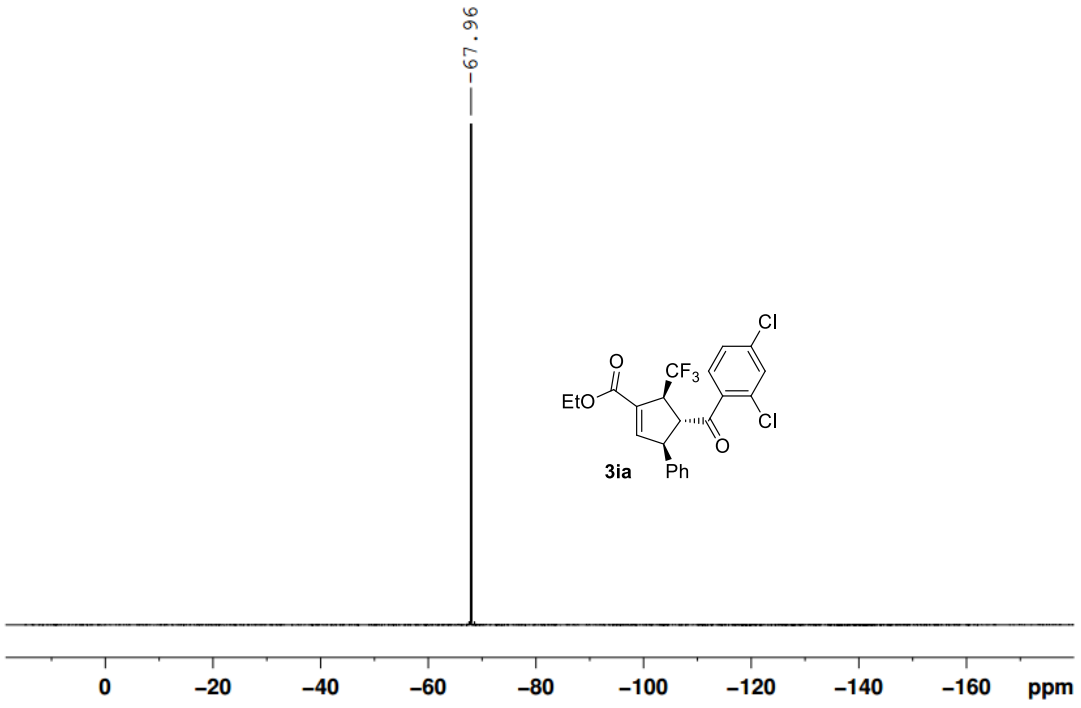

zhouw-6-114

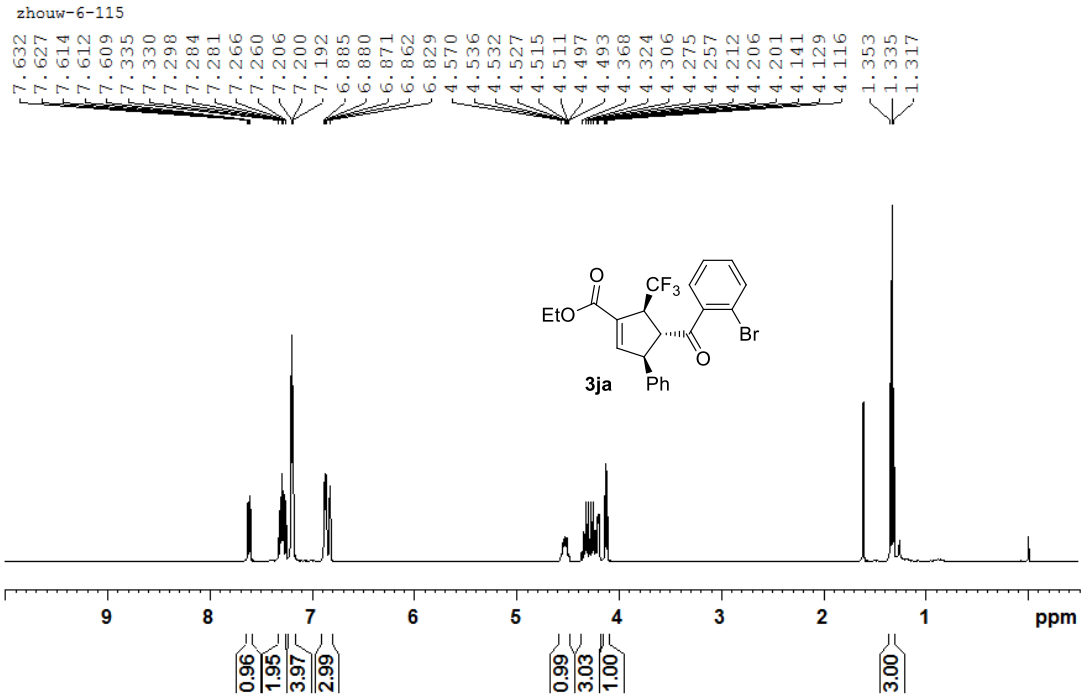


zhouw-6-114c




zhouw-6-114f




zhouw-6-115
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7.612
7.609
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7.330
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7.284
7.281
7.266
7.260
7.206
7.200
7.192
6.885
6.880
6.871
6.862
6.829
4.570
4.536
4.532
4.527
4.515
4.511
4.497
4.493
4.368
4.324
4.306
4.275
4.257
4.212
4.206
4.201
4.141
4.129
4.116
1.353
1.335
1.317
EtO
O
CF3
Br
O
3ja
Ph
9
8
7
6
5
4
3
2
1
ppm
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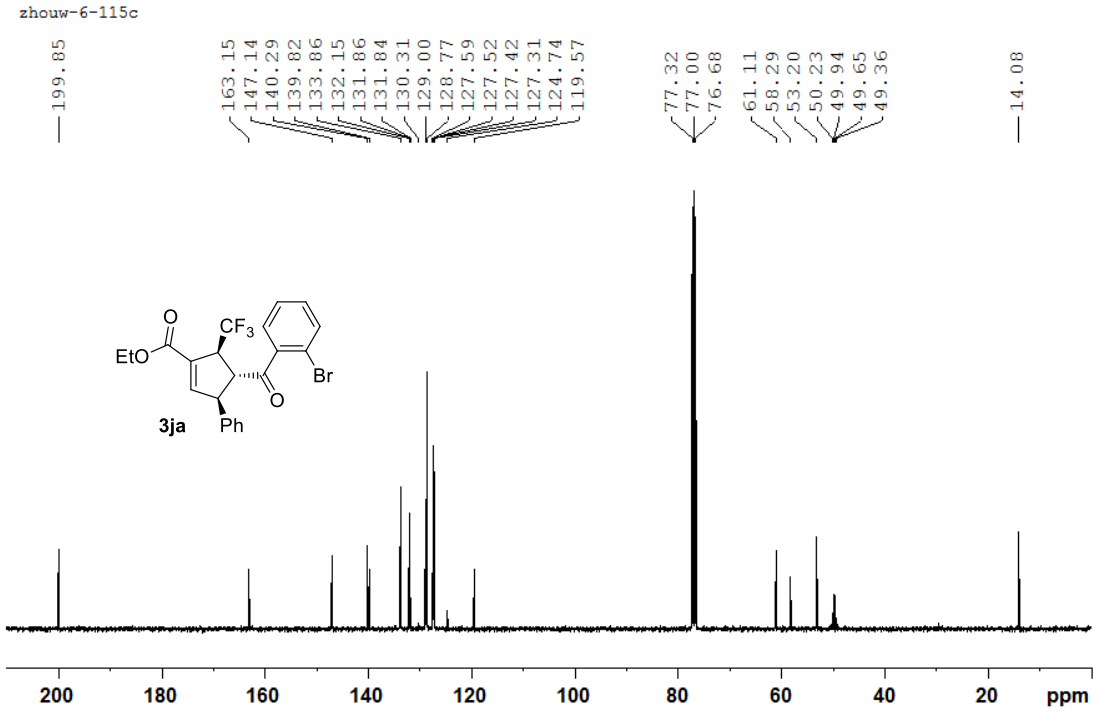
1.95
3.97
2.99
0.99
3.03
1.00
3.00


zhouw-6-115c
199.85
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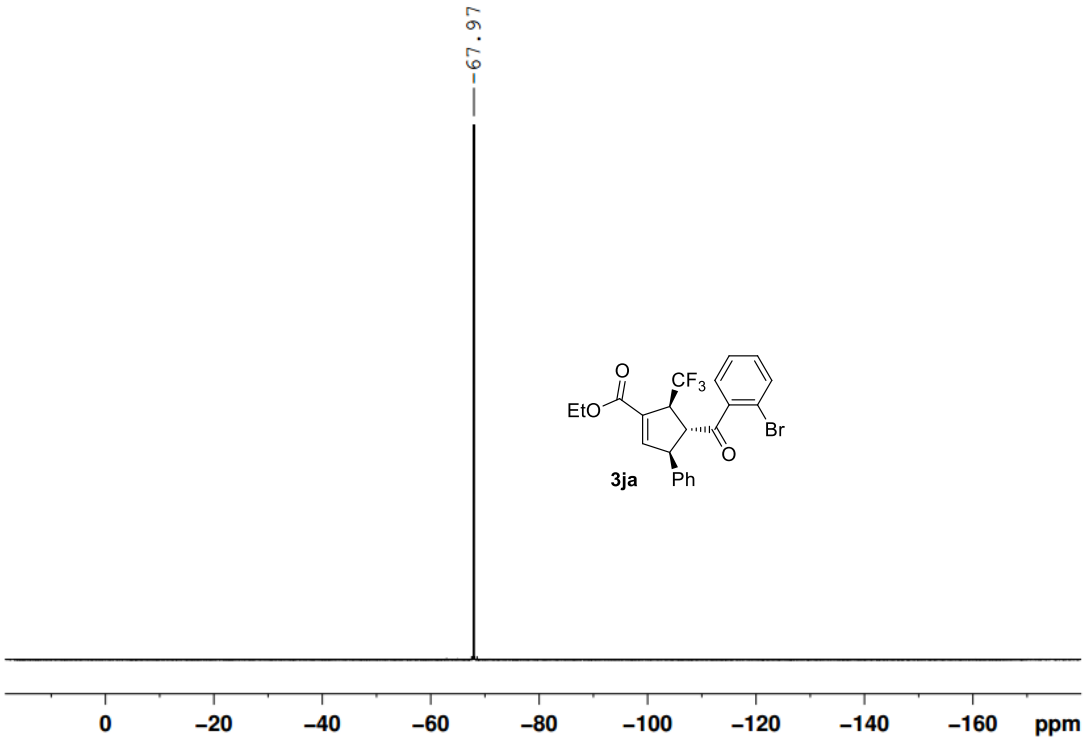
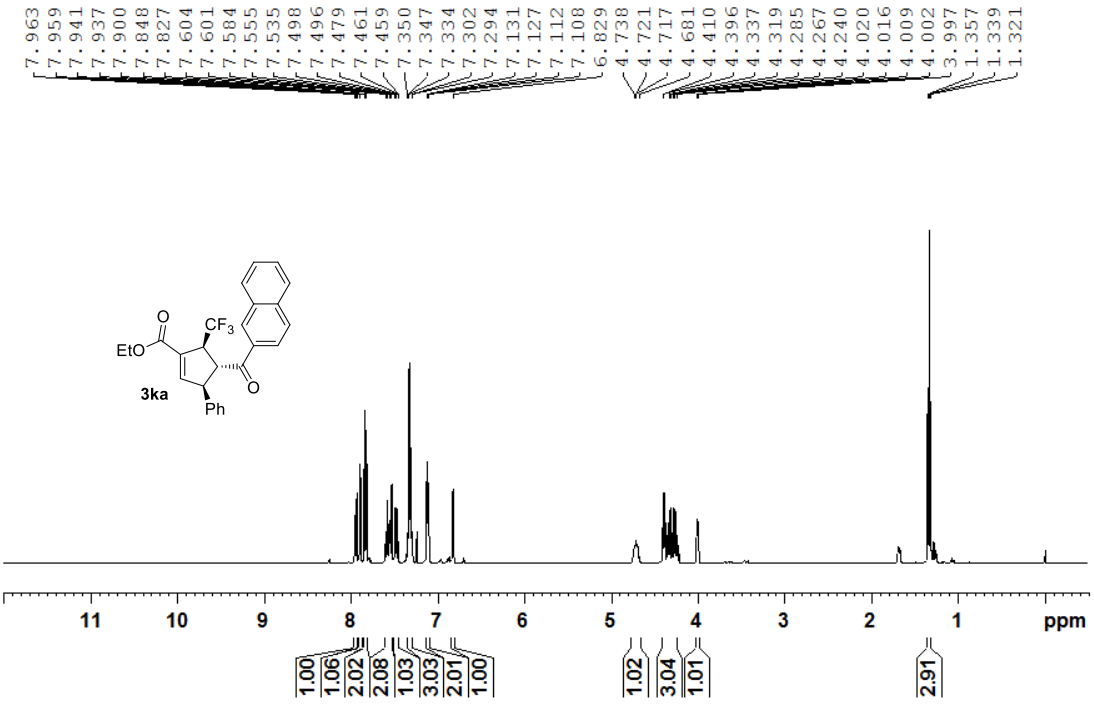
147.14
140.29
139.82
133.86
132.15
131.86
131.84
130.31
129.00
128.77
127.59
127.52
127.42
127.31
124.74
119.57
77.32
77.00
76.68
61.11
58.29
53.20
50.23
49.94
49.65
49.36
14.08
EtO
O
CF3
Br
O
3ja
Ph
200
180
160
140
120
100
80
60
40
20
ppm

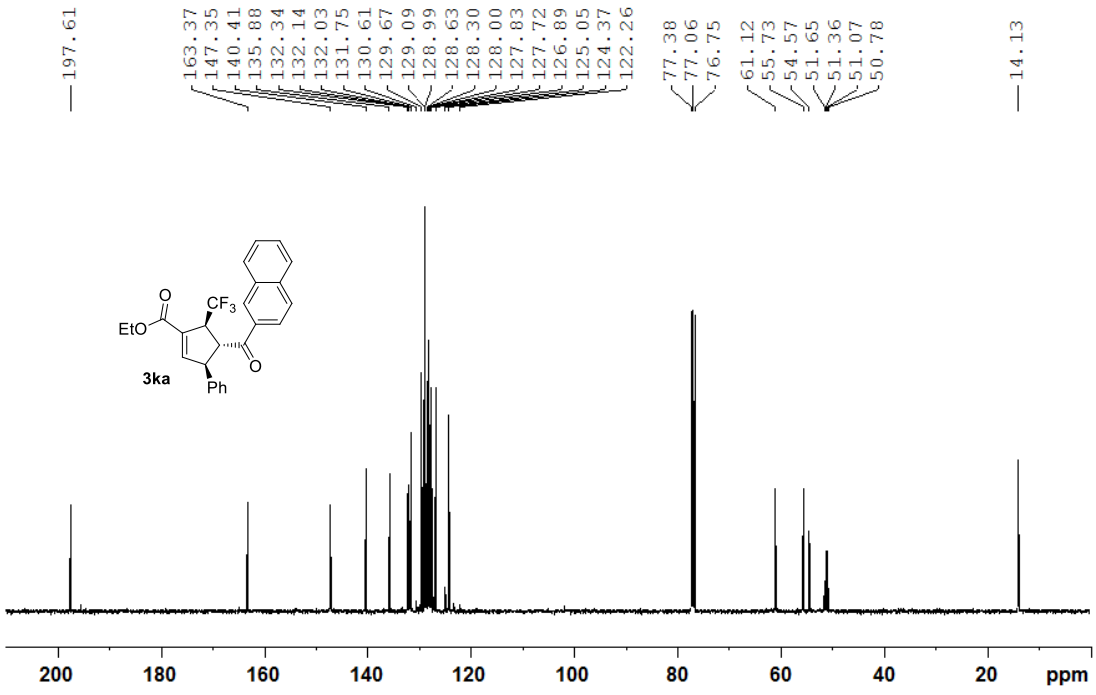
zhouw-6-115f



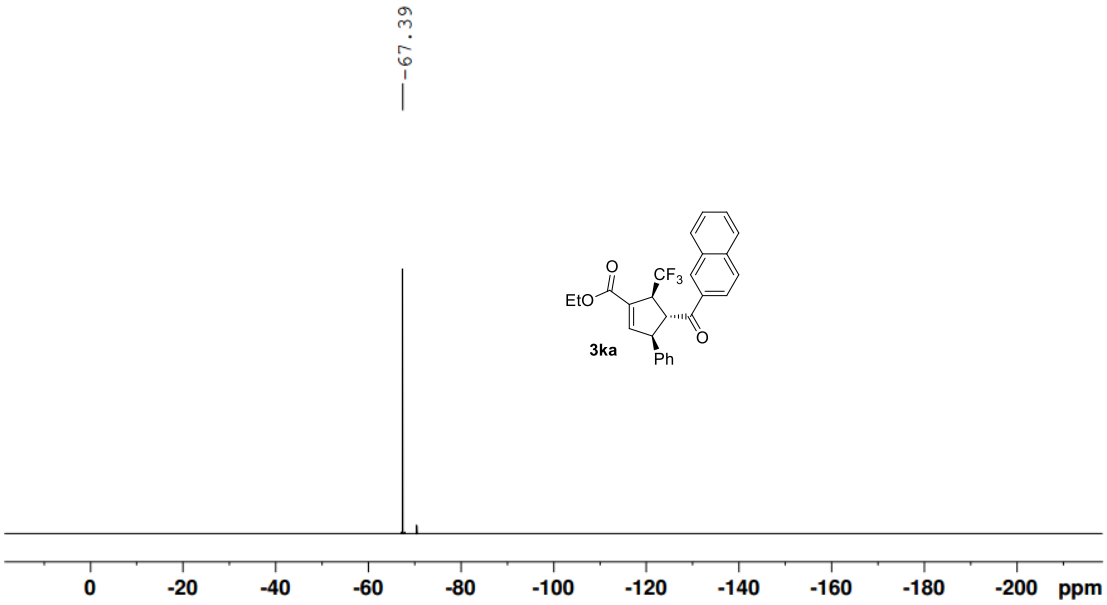

zhouw-7-6

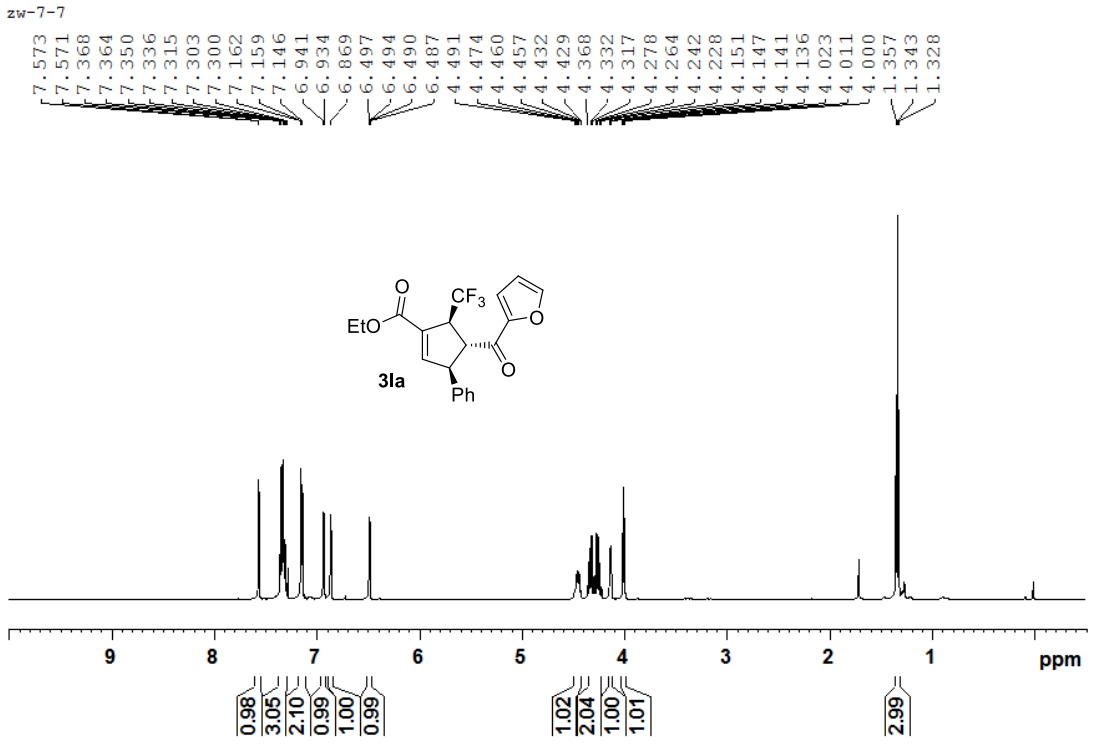


zhouw-7-6c




zhouw-7-6f




zw-7-7
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7.368
7.364
7.350
7.336
7.315
7.303
7.300
7.162
7.159
7.146
6.941
6.934
6.869
6.497
6.494
6.490
6.487
4.491
4.474
4.460
4.457
4.432
4.429
4.368
4.332
4.317
4.278
4.264
4.242
4.228
4.151
4.147
4.141
4.136
4.023
4.011
4.000
1.357
1.343
1.328
EtO
CF3
O
O
O
3la
Ph
9
8
7
6
5
4
3
2
1
ppm
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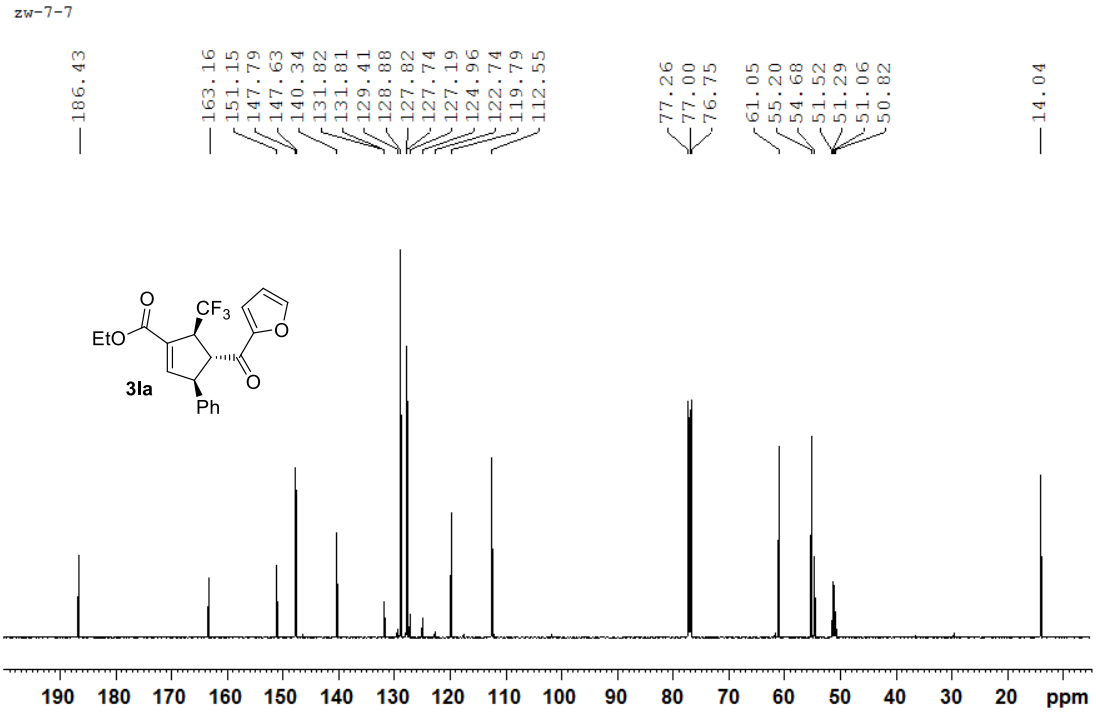
3.05
2.10
0.99
1.00
0.99
1.02
2.04
1.00
1.01
2.99


zw-7-7
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151.15
147.79
147.63
140.34
131.82
131.81
129.41
128.88
127.82
127.74
127.19
124.96
122.74
119.79
112.55
77.26
77.00
76.75
61.05
55.20
54.68
51.52
51.29
51.06
50.82
14.04
EtO
CF3
O
O
O
3la
Ph
190
180
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130
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110
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90
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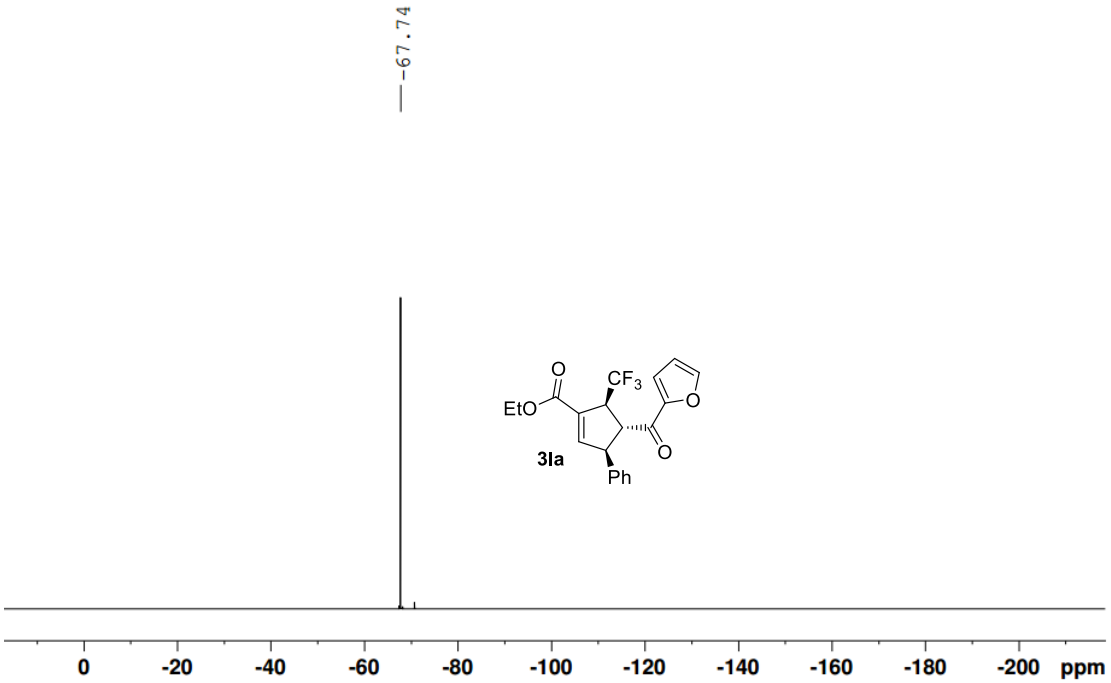
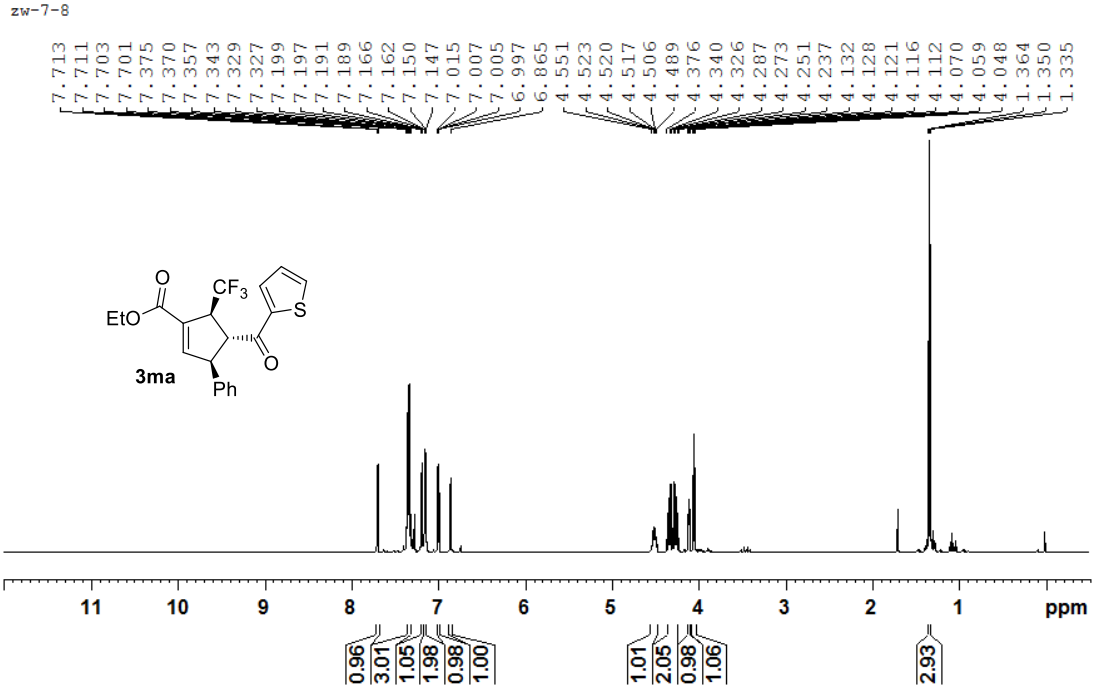
50
40
30
20
ppm

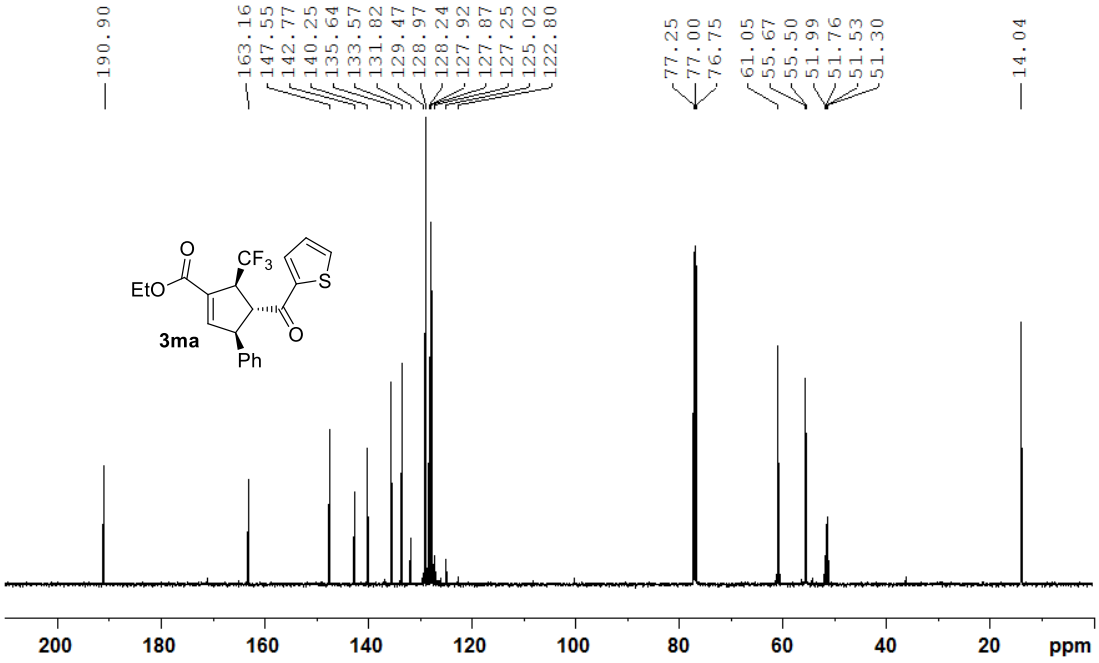
zhouw-7-7f



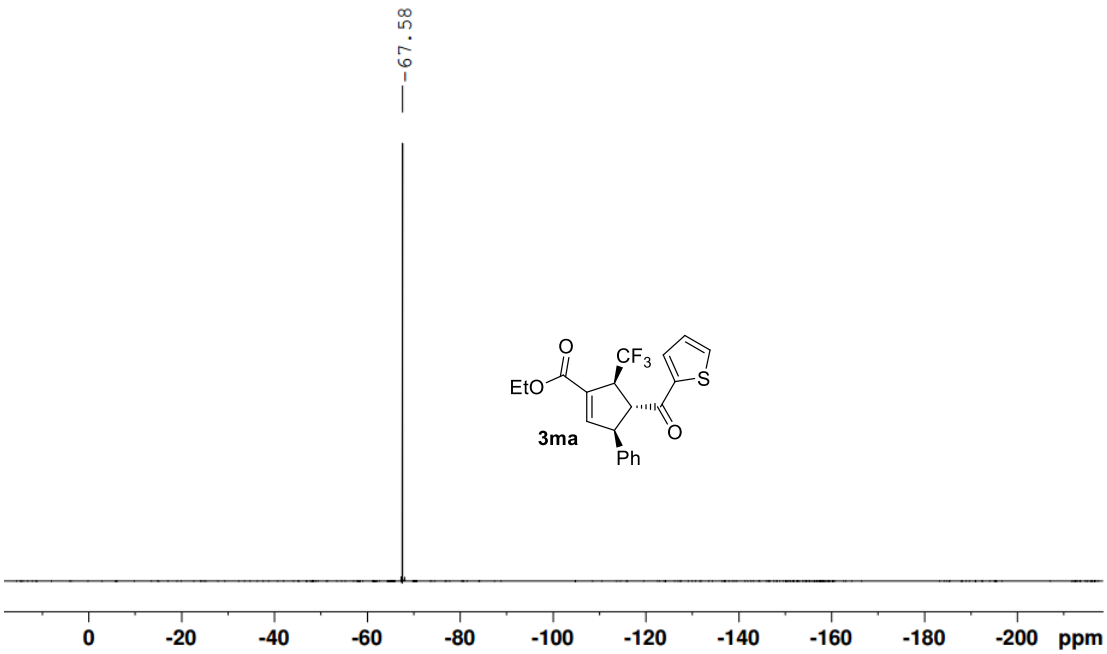

zw-7-8

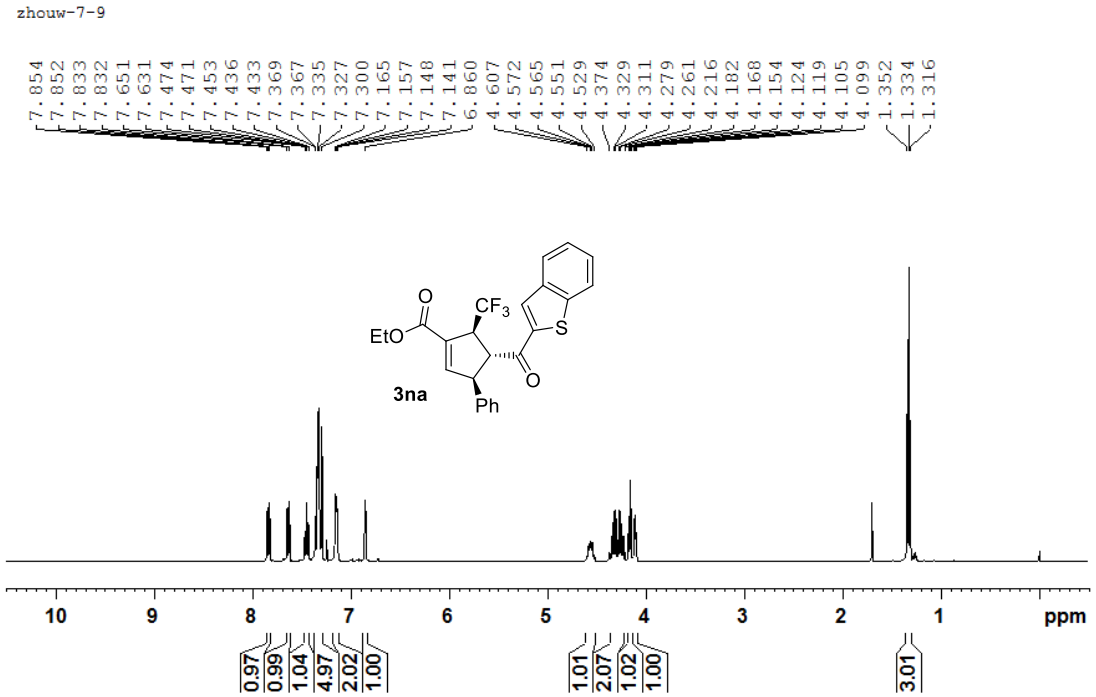


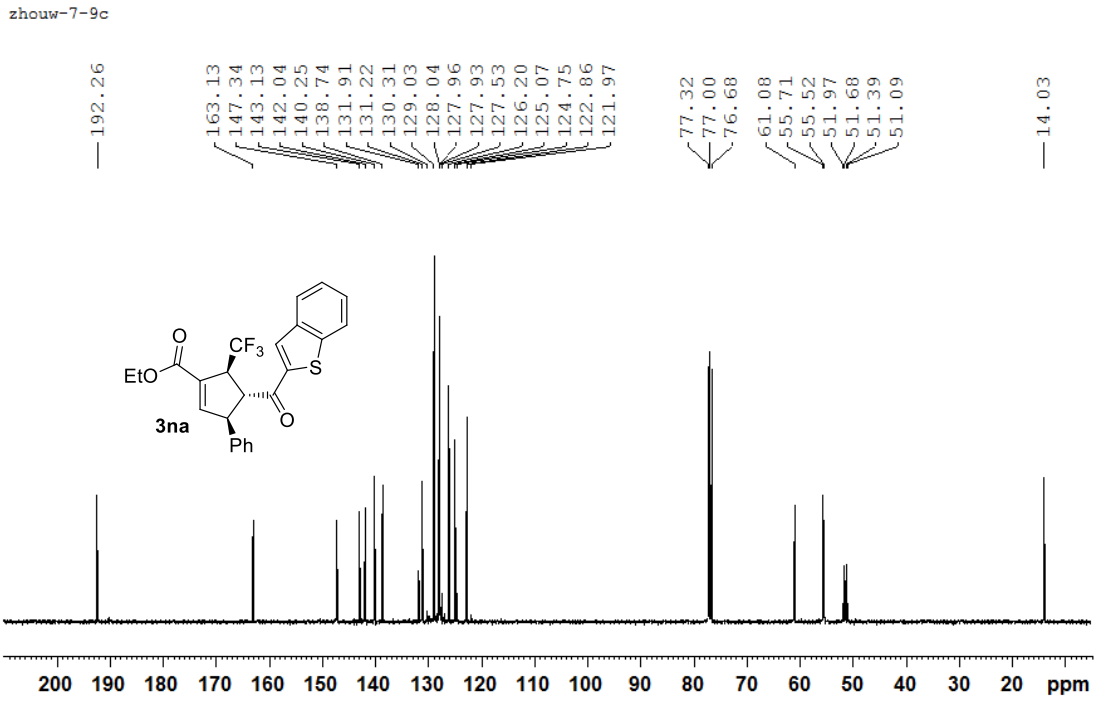
zw-7-8



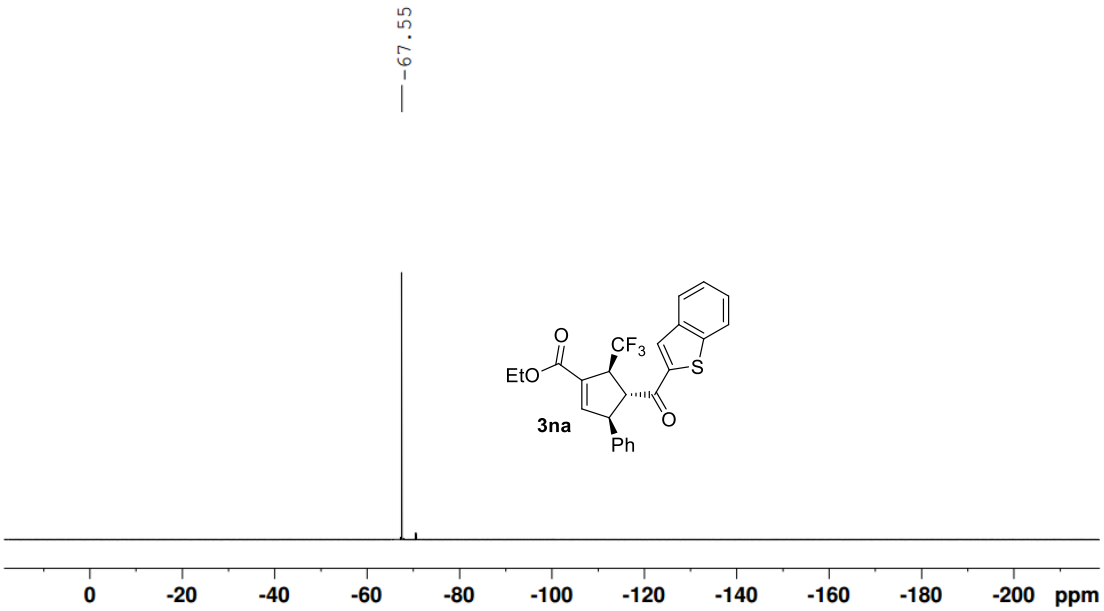

zhouw-7-8f



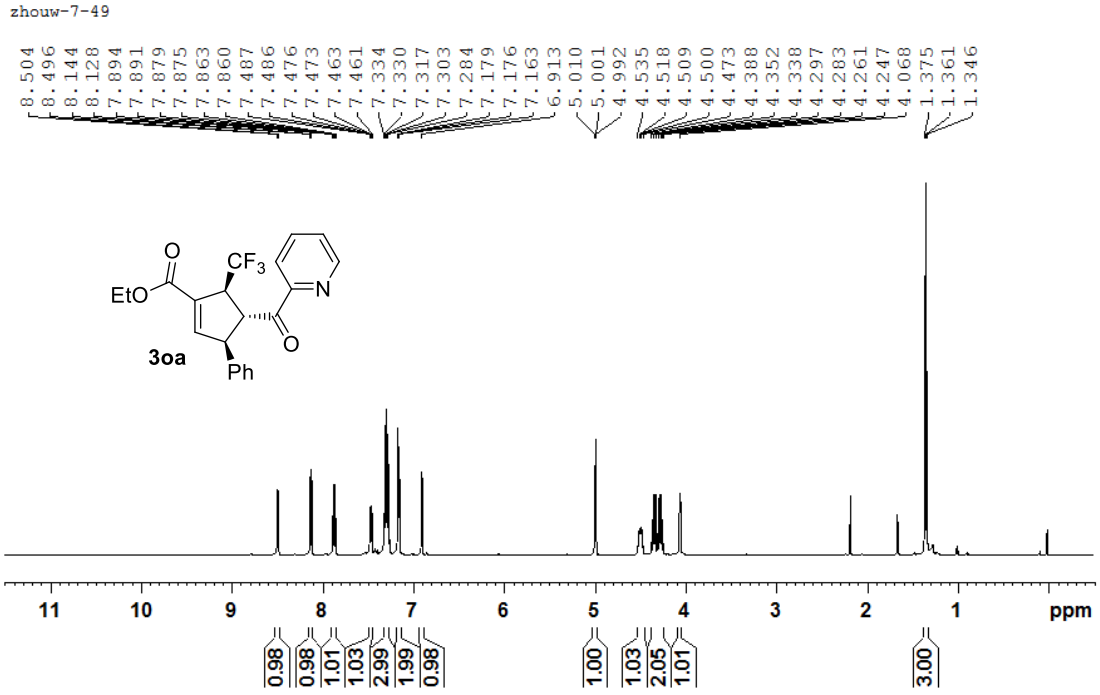

zhouw-7-9
7.854
7.852
7.833
7.832
7.651
7.631
7.474
7.471
7.453
7.436
7.433
7.369
7.367
7.335
7.327
7.300
7.165
7.157
7.148
7.141
6.860
4.607
4.572
4.565
4.551
4.529
4.374
4.329
4.311
4.279
4.261
4.216
4.182
4.168
4.154
4.124
4.119
4.105
4.099
1.352
1.334
1.316
EtO
O
CF3
S
O
Ph
3na
10
9
8
7
6
5
4
3
2
1
ppm
0.97
0.99
1.04
4.97
2.02
1.00
1.01
2.07
1.02
1.00
3.01


zhouw-7-9c
192.26
163.13
147.34
143.13
142.04
140.25
138.74
131.91
131.22
130.31
129.03
128.04
127.96
127.93
127.53
126.20
125.07
124.75
122.86
121.97
77.32
77.00
76.68
61.08
55.71
55.52
51.97
51.68
51.39
51.09
14.03
EtO
O
CF3
S
O
Ph
3na
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

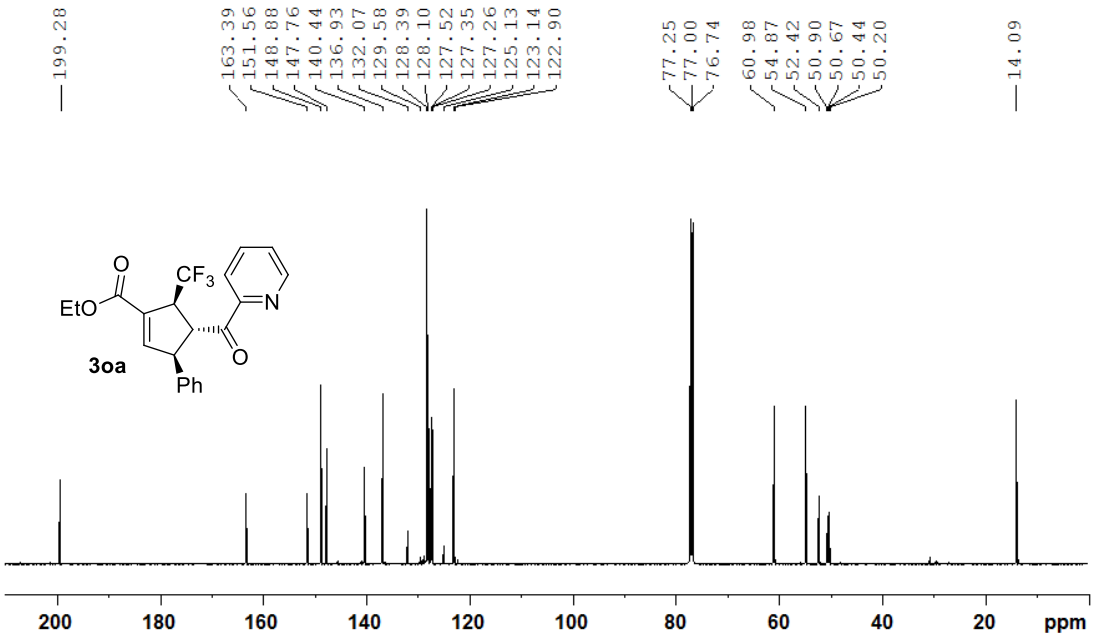
zhouw-7-9



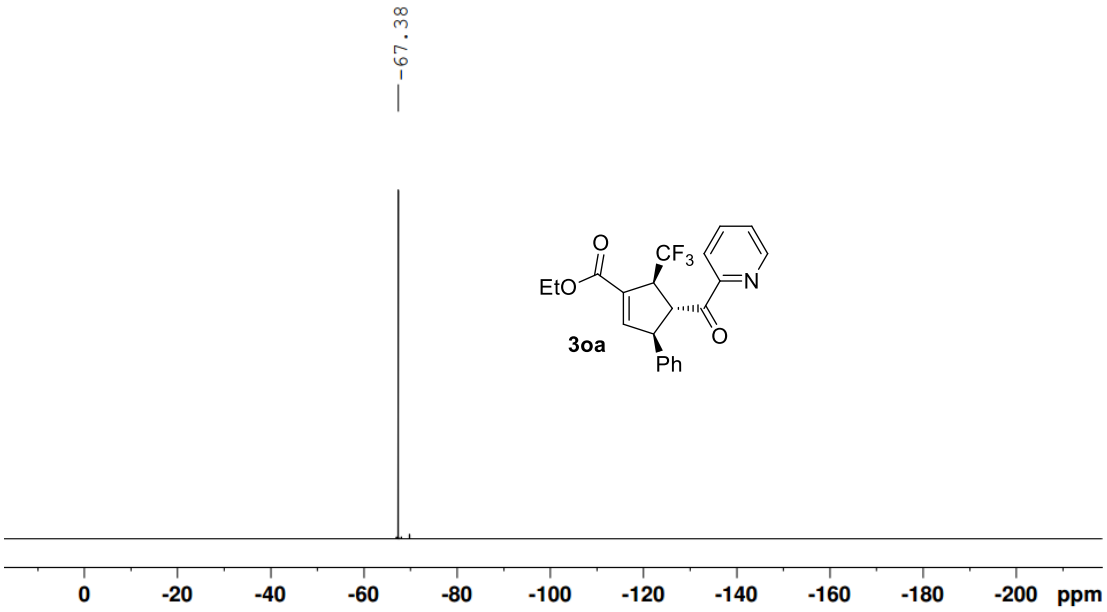

zhouw-7-49

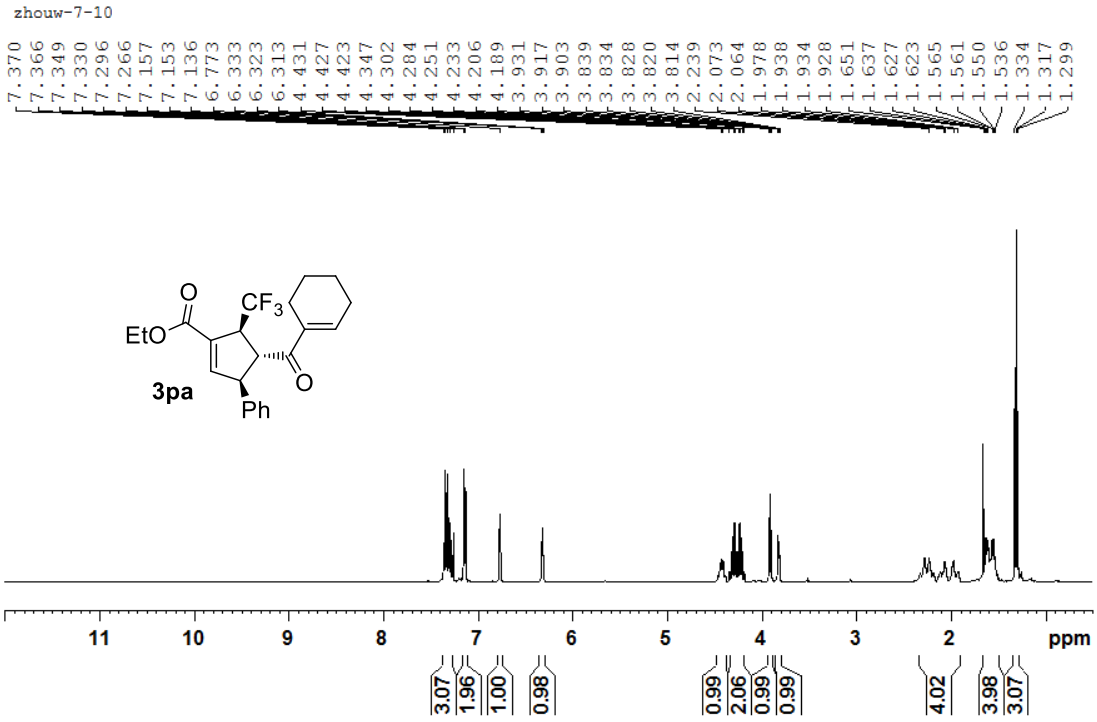


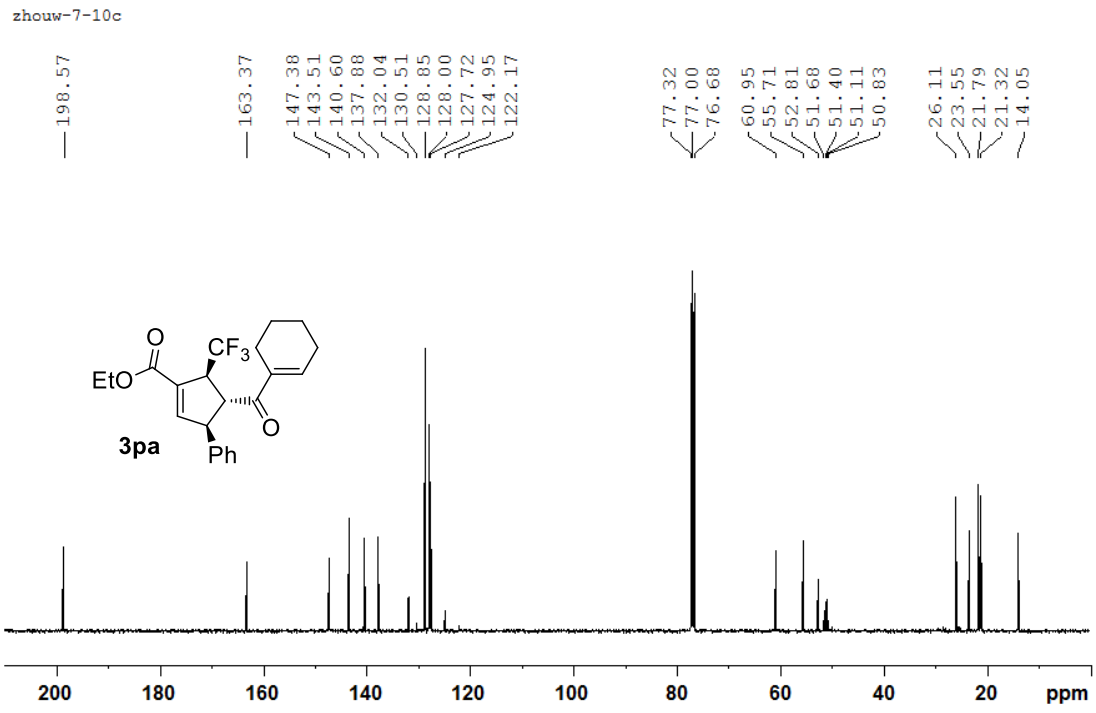
zhouw-7-49c



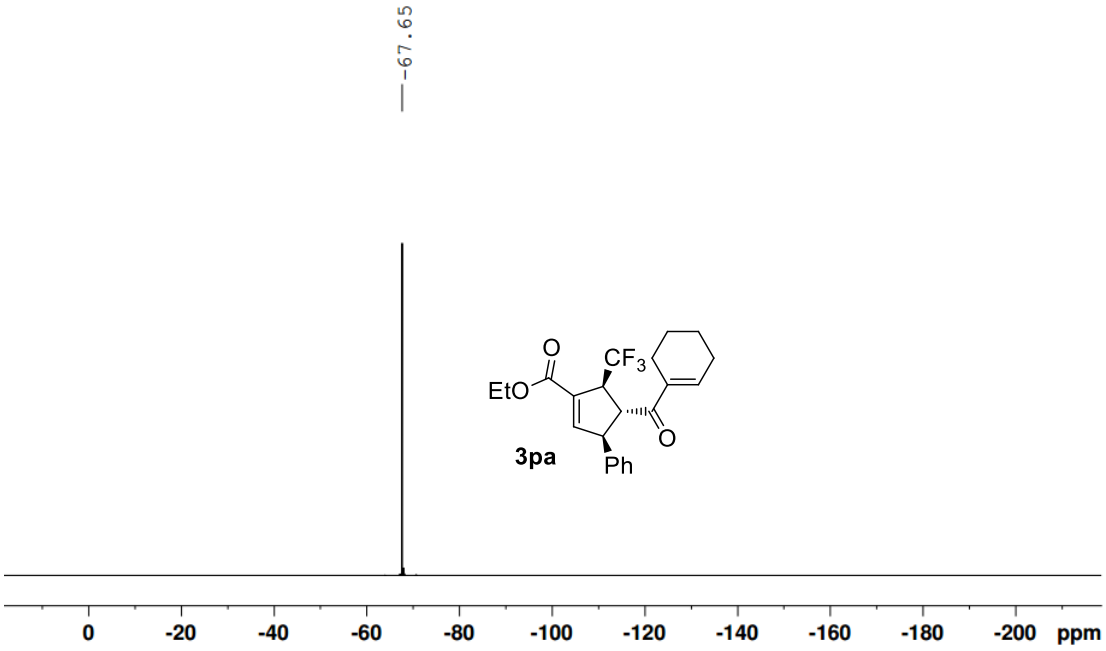

zhouw-7-49f



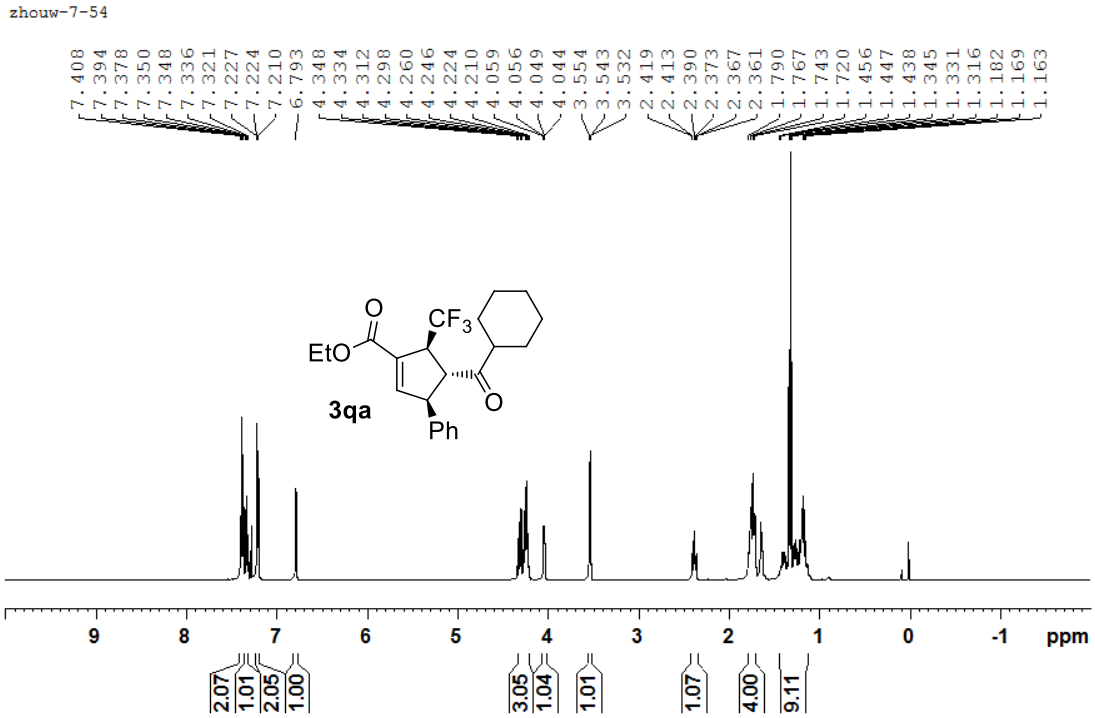

zhouw-7-10
7.370
7.366
7.349
7.330
7.296
7.266
7.157
7.153
7.136
6.773
6.333
6.323
6.313
4.431
4.427
4.423
4.347
4.302
4.284
4.251
4.233
4.206
4.189
3.931
3.917
3.903
3.839
3.834
3.828
3.820
3.814
2.239
2.073
2.064
1.978
1.938
1.934
1.928
1.651
1.637
1.627
1.623
1.565
1.561
1.550
1.536
1.334
1.317
1.299
EtO
O
CF3
O
Ph
3pa
11
10
9
8
7
6
5
4
3
2
ppm
3.07
1.96
1.00
0.98
0.99
2.06
0.99
0.99
4.02
3.98
3.07


zhouw-7-10c
198.57
163.37
147.38
143.51
140.60
137.88
132.04
130.51
128.85
128.00
127.72
124.95
122.17
77.32
77.00
76.68
60.95
55.71
52.81
51.68
51.40
51.11
50.83
26.11
23.55
21.79
21.32
14.05
EtO
O
CF3
O
Ph
3pa
200
180
160
140
120
100
80
60
40
20
ppm

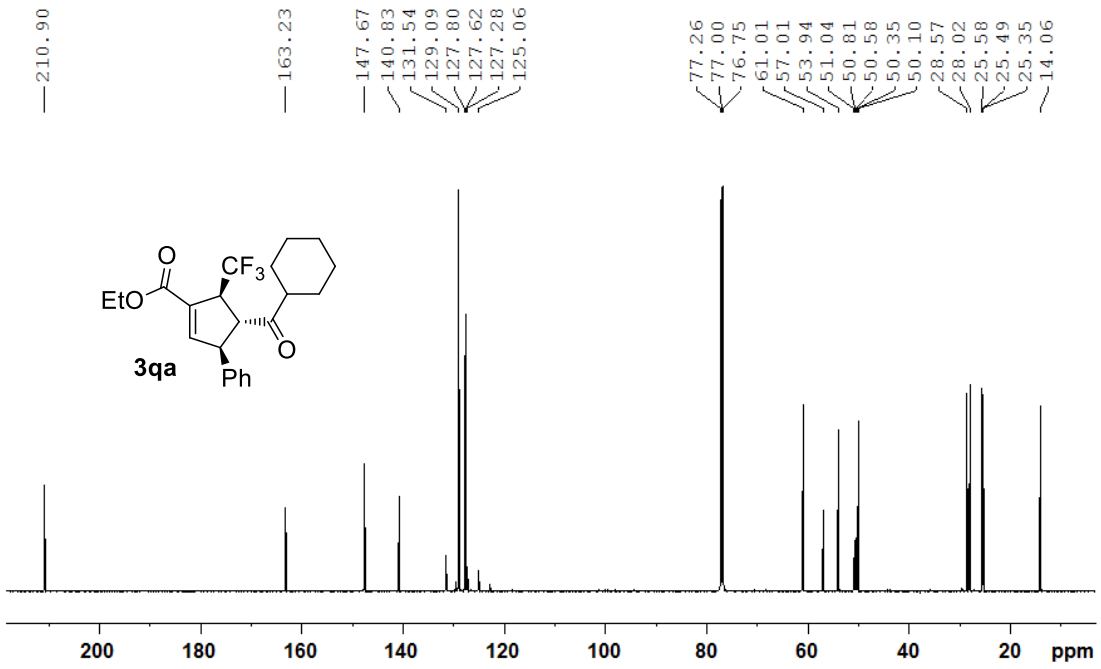
zhouw-7-10f



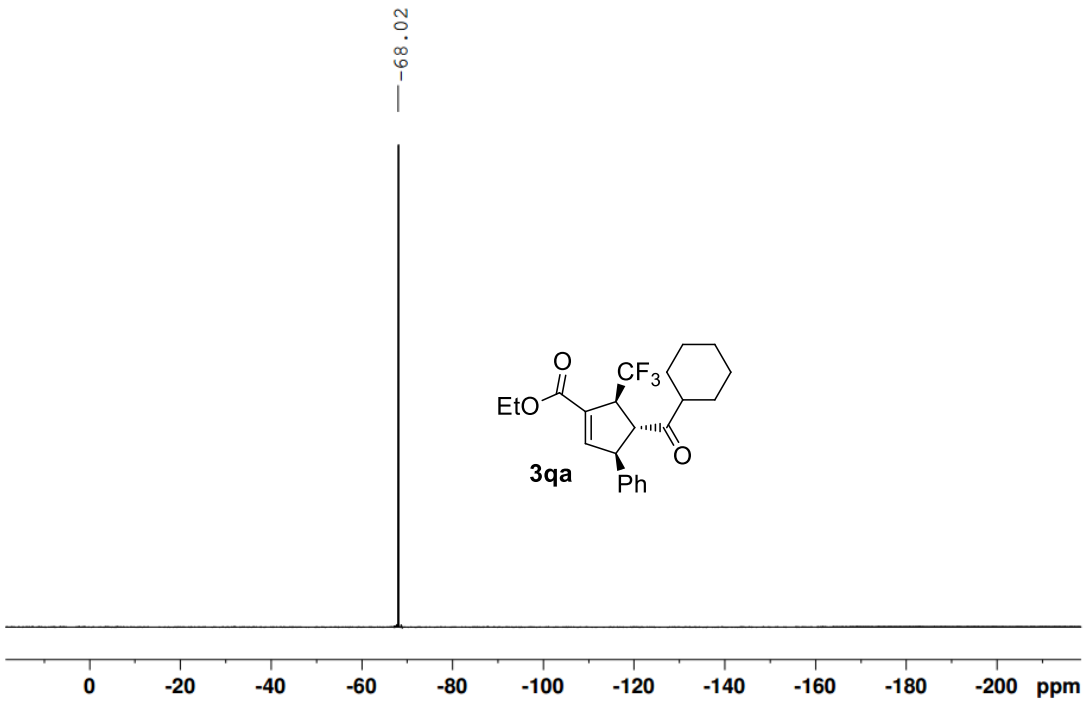

zhouw-7-54



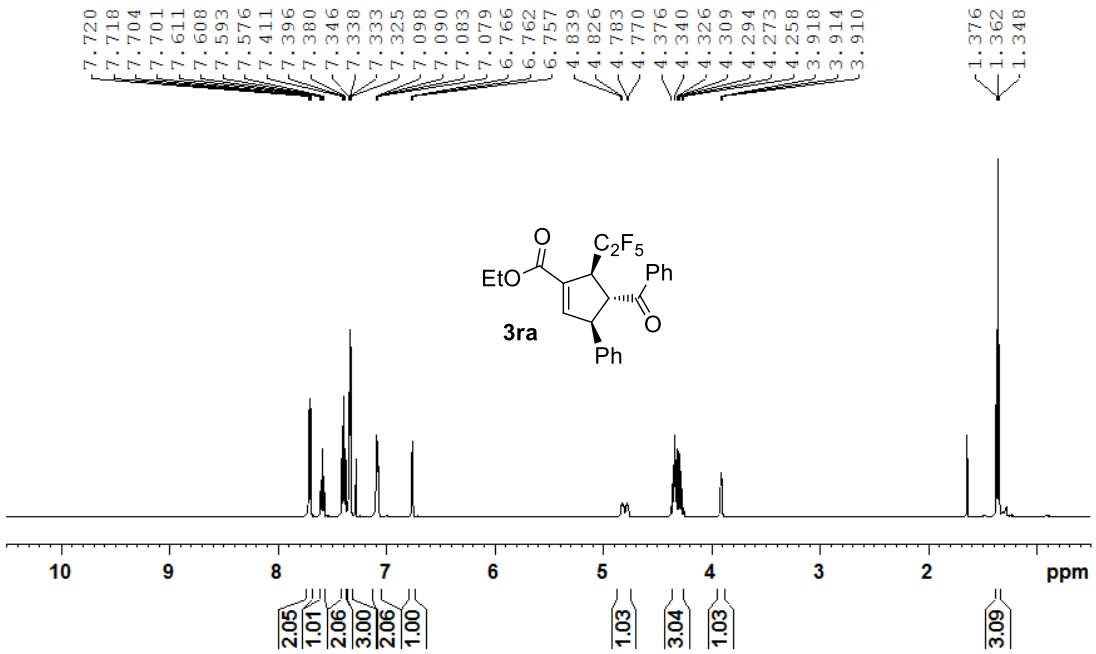
zhouw-7-54c



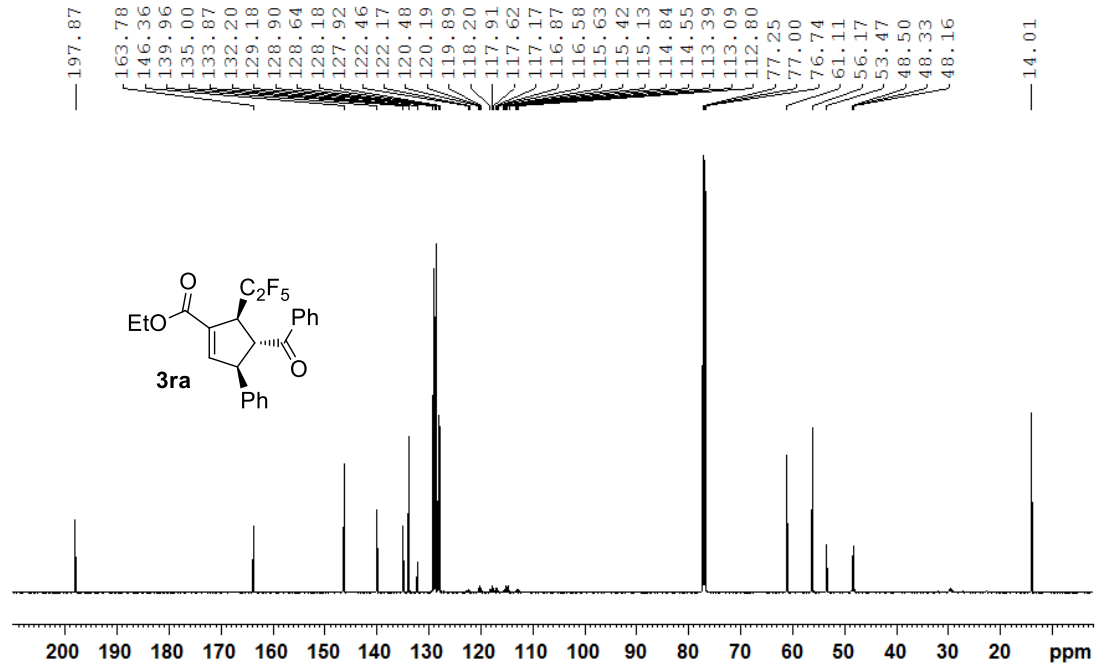

zhouw-7-54f



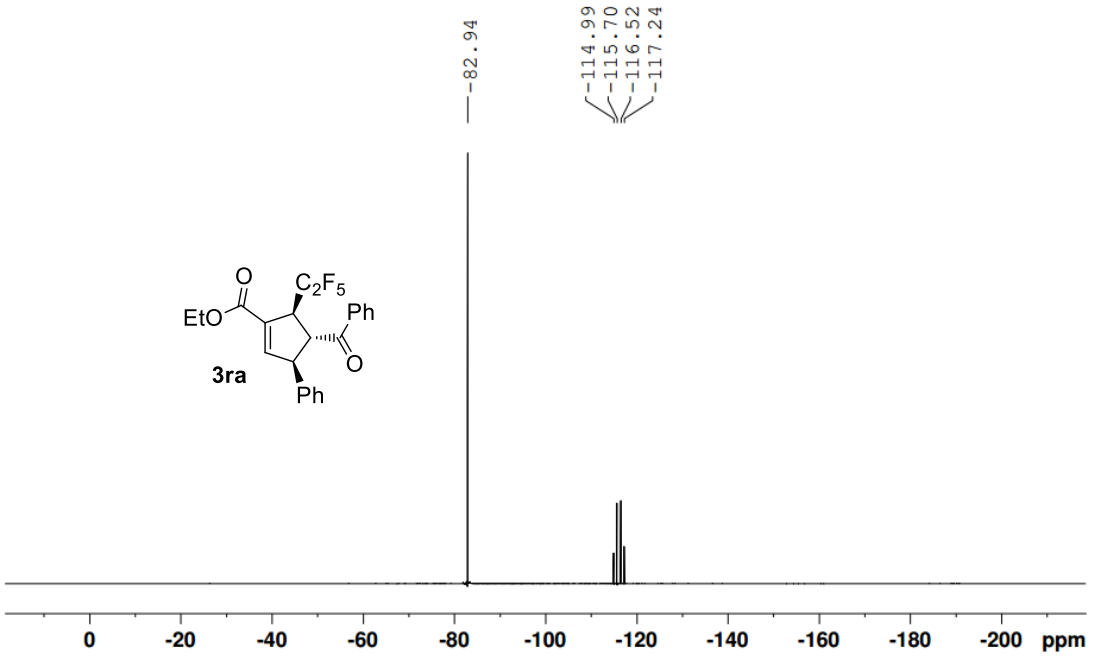
zhouw-7-11



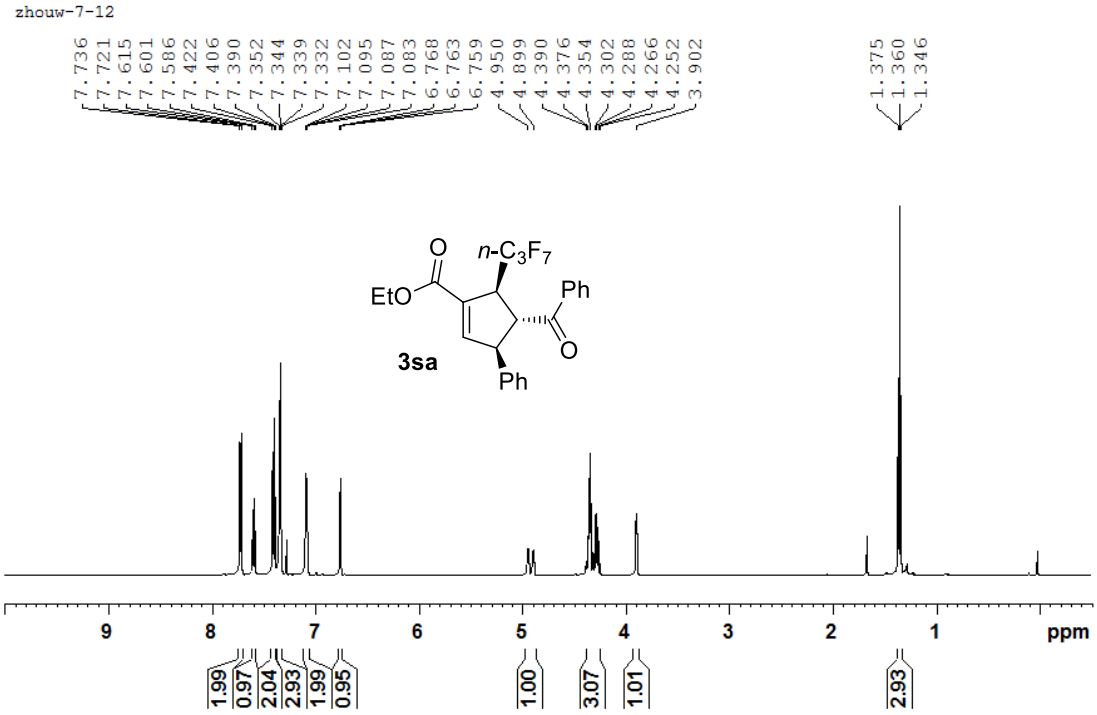

zhouw-7-11c



zhouwei-7-11f

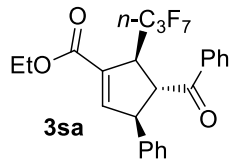



zhouw-7-12



zhouw-7-12c

197.71
163.83
146.17
139.93
134.96
133.88
132.32
129.18
128.92
128.67
128.21
128.19
127.93
121.08
119.24
119.05
118.99
118.79
118.74
118.52
117.19
116.94
116.76
116.69
116.50
116.22
115.14
114.89
114.65
111.80
111.50
111.20
110.90
109.70
109.40
109.10
108.80
107.29
106.99
77.25
77.00
76.75
61.08
56.49
53.39
48.55
48.39
48.22
14.00

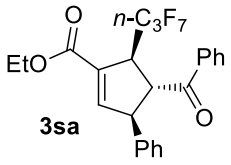




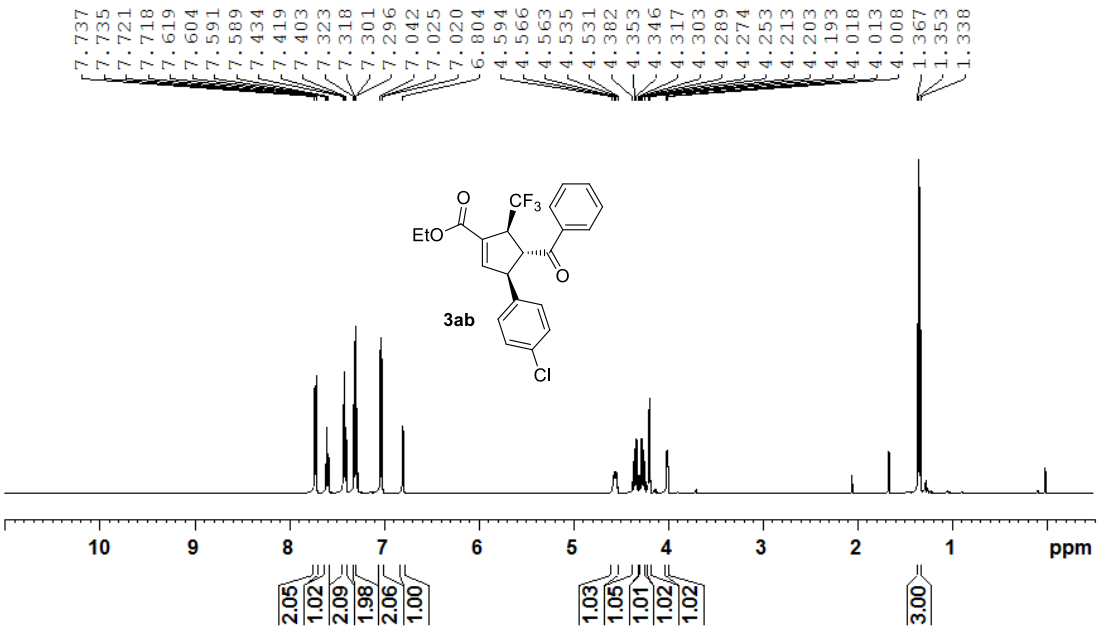


zhouwei-7-12f

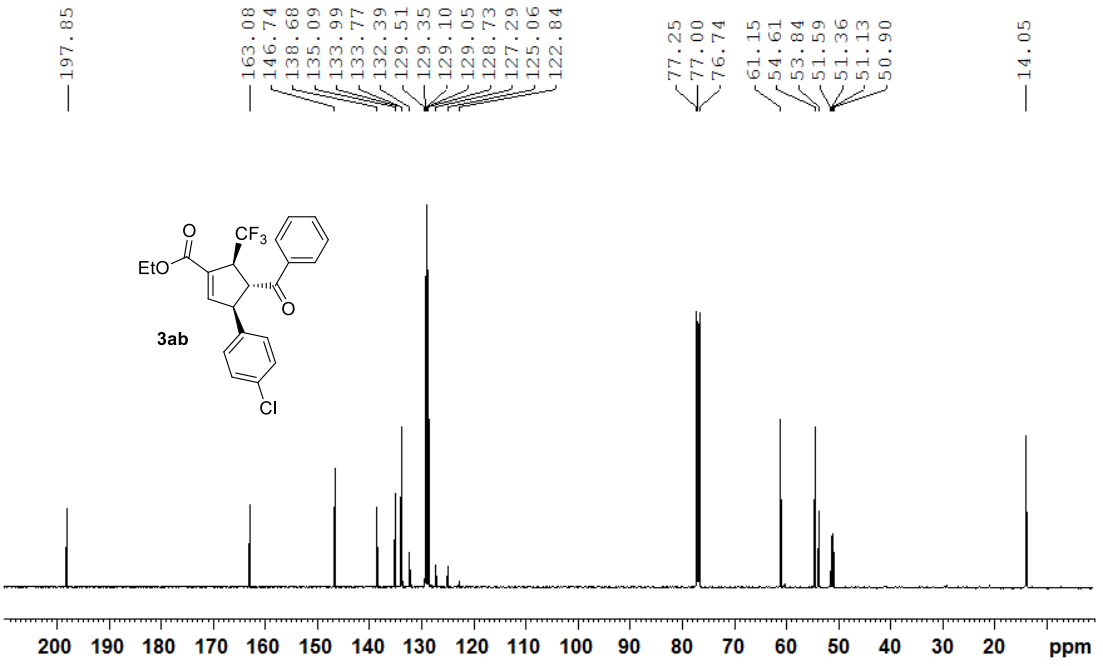
-80.36
-80.38
-80.41
-110.99
-111.05
-111.06
-111.12
-111.72
-111.78
-111.79
-111.84
-111.86
-114.28
-114.36
-114.39
-114.41
-115.02
-115.03
-115.09
-115.12
-115.15
-124.53
-124.54
-124.57
-124.58
-125.31
-125.32
-125.35
-125.36
-126.07
-126.09
-126.11
-126.13
-126.85
-126.87
-126.88
-126.90

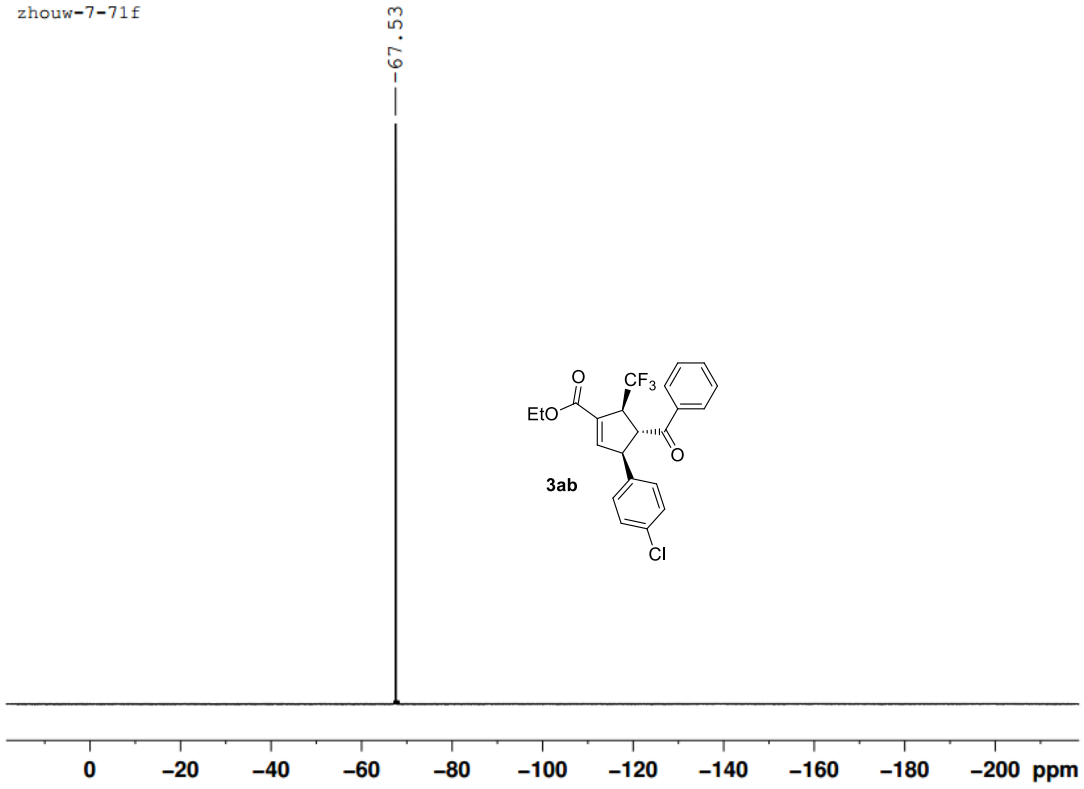


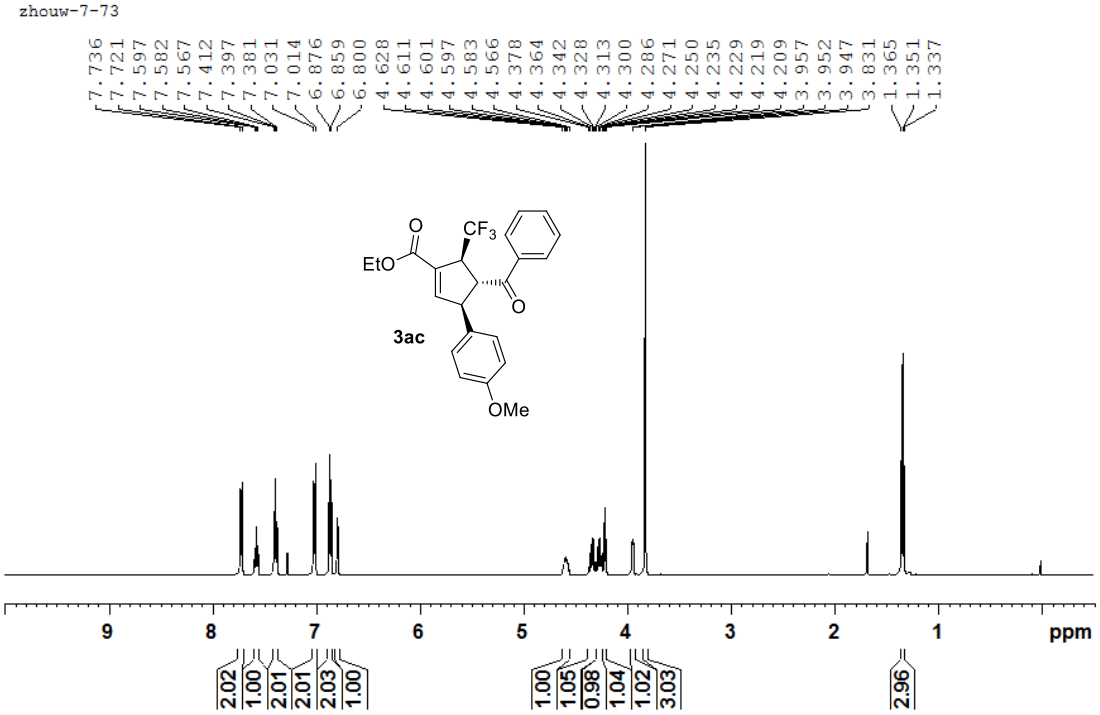
zhouw-7-71

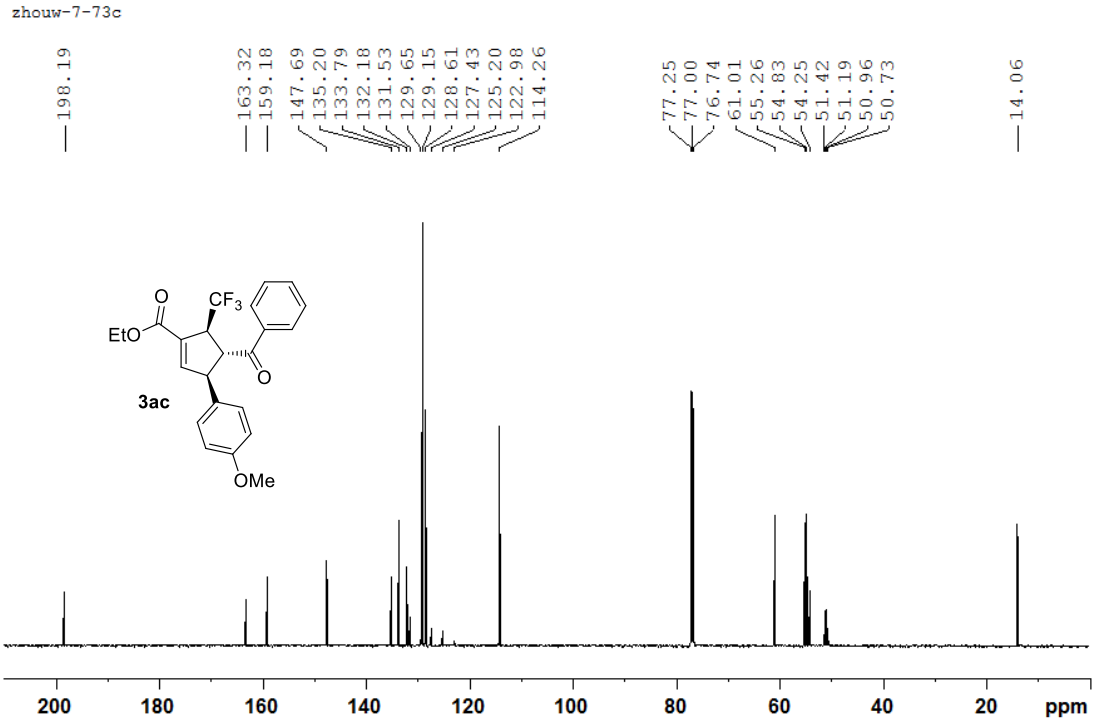


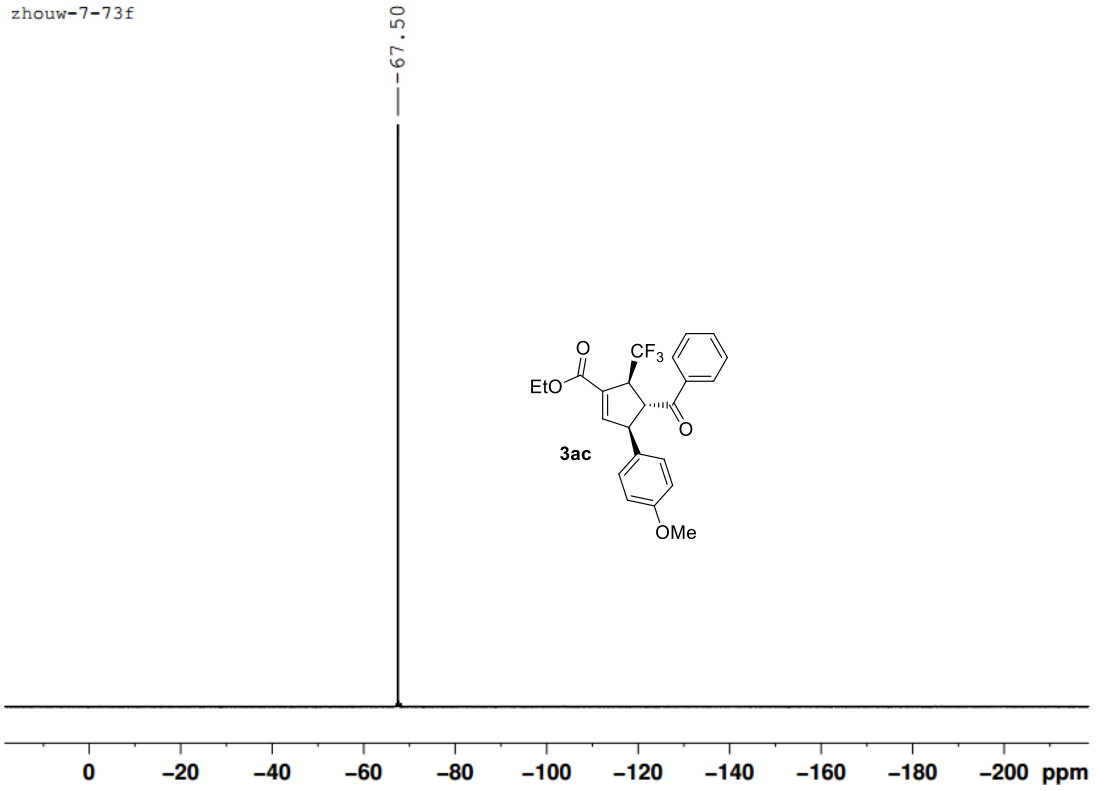

zhouw-7-71c



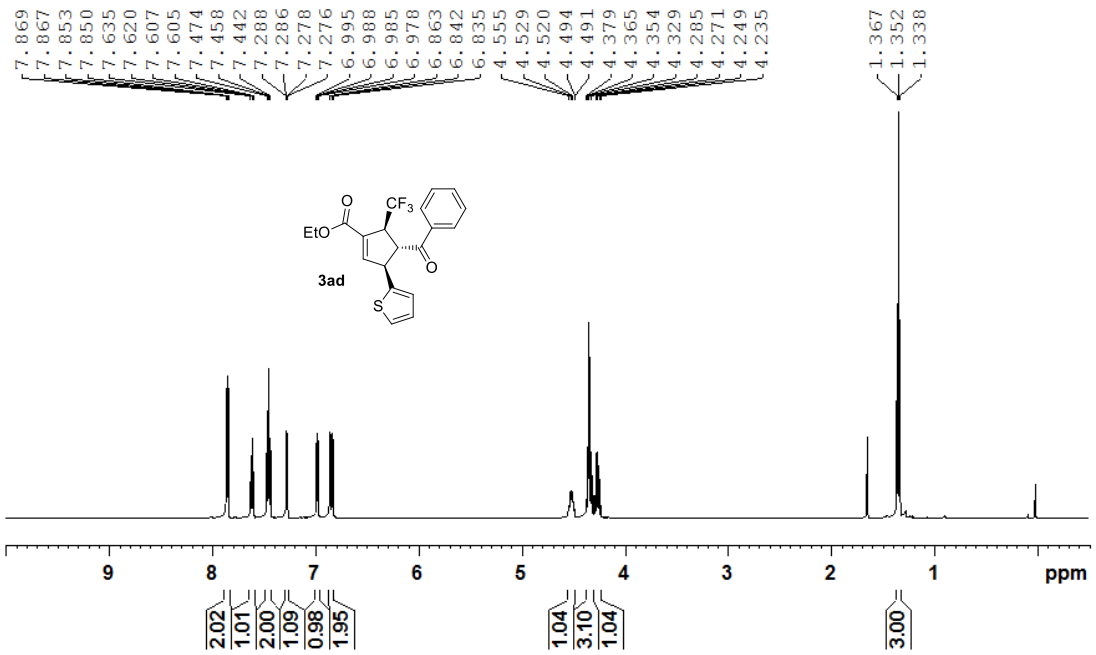

zhouw-7-71f
-67.53
O
CF3
EtO
O
3ab
Cl
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm


zhouw-7-73
7.736
7.721
7.597
7.582
7.567
7.412
7.397
7.381
7.031
7.014
6.876
6.859
6.800
4.628
4.611
4.601
4.597
4.583
4.566
4.378
4.364
4.342
4.328
4.313
4.300
4.286
4.271
4.250
4.235
4.229
4.219
4.209
3.957
3.952
3.947
3.831
1.365
1.351
1.337
O
CF3
EtO
O
3ac
OMe
9
8
7
6
5
4
3
2
1
ppm
2.02
1.00
2.01
2.01
2.03
1.00
1.00
1.05
0.98
1.04
1.02
3.03
2.96

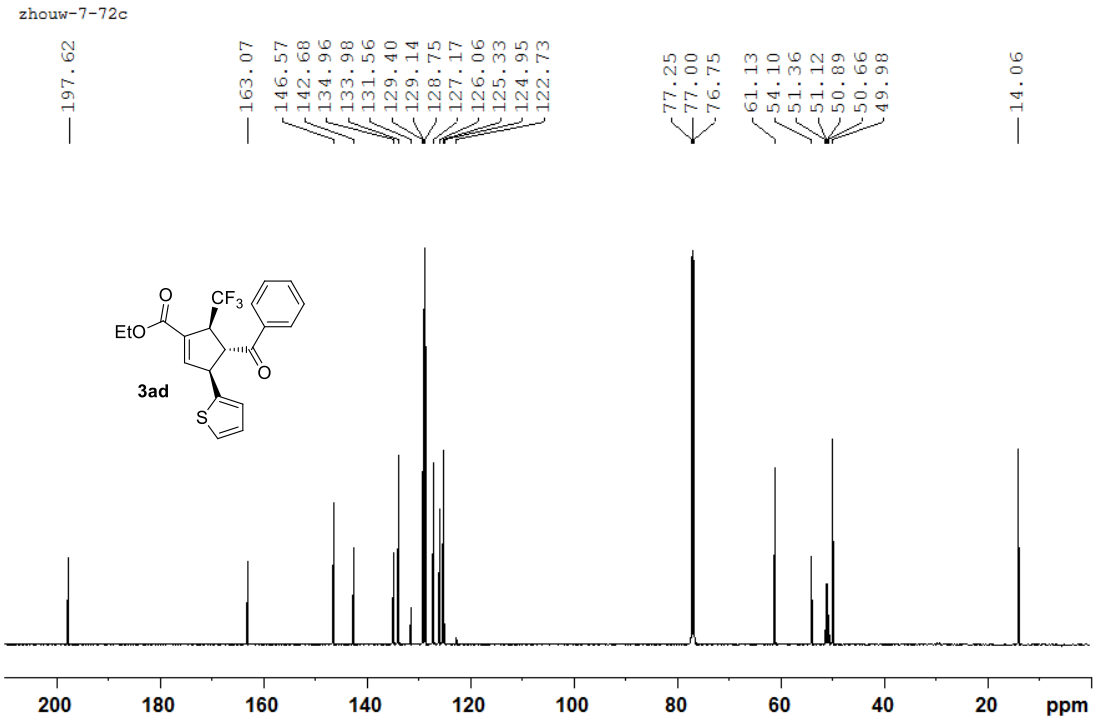

zhouw-7-73c
198.19
163.32
159.18
147.69
135.20
133.79
132.18
131.53
129.65
129.15
128.61
127.43
125.20
122.98
114.26
77.25
77.00
76.74
61.01
55.26
54.83
54.25
51.42
51.19
50.96
50.73
14.06
EtO
O
CF3
O
3ac
OMe
200
180
160
140
120
100
80
60
40
20
ppm

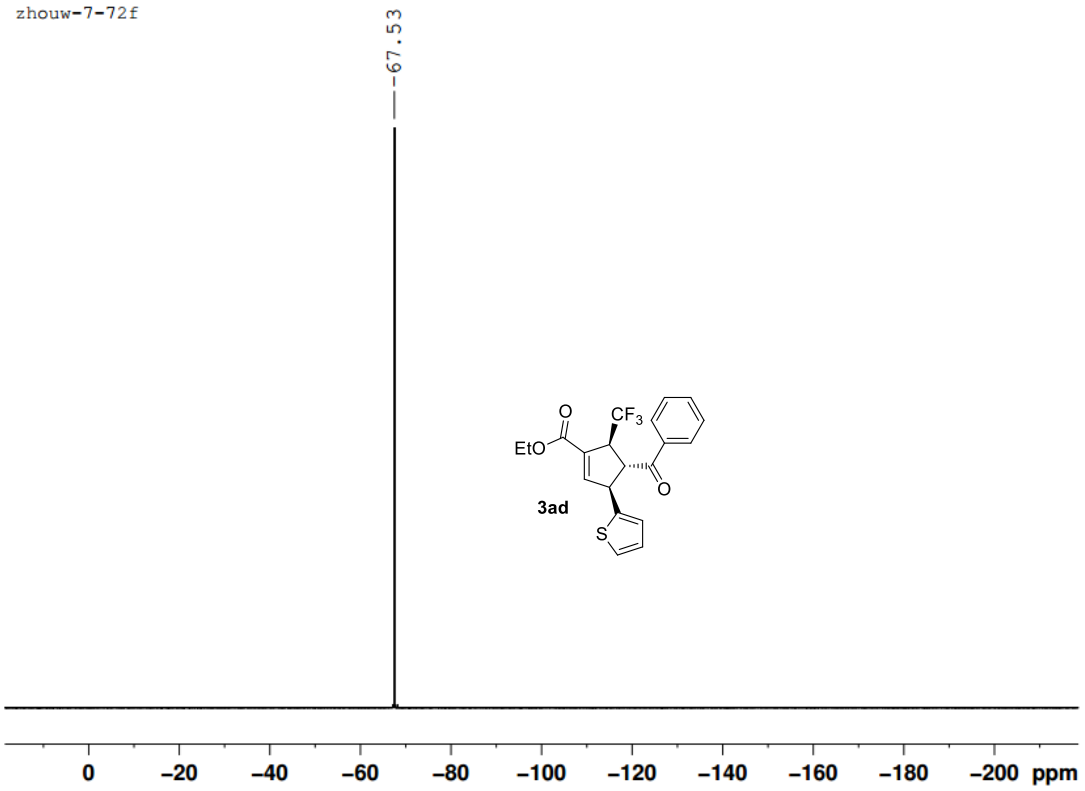

zhouw-7-73f
-67.50
EtO
O
CF3
O
3ac
OMe
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

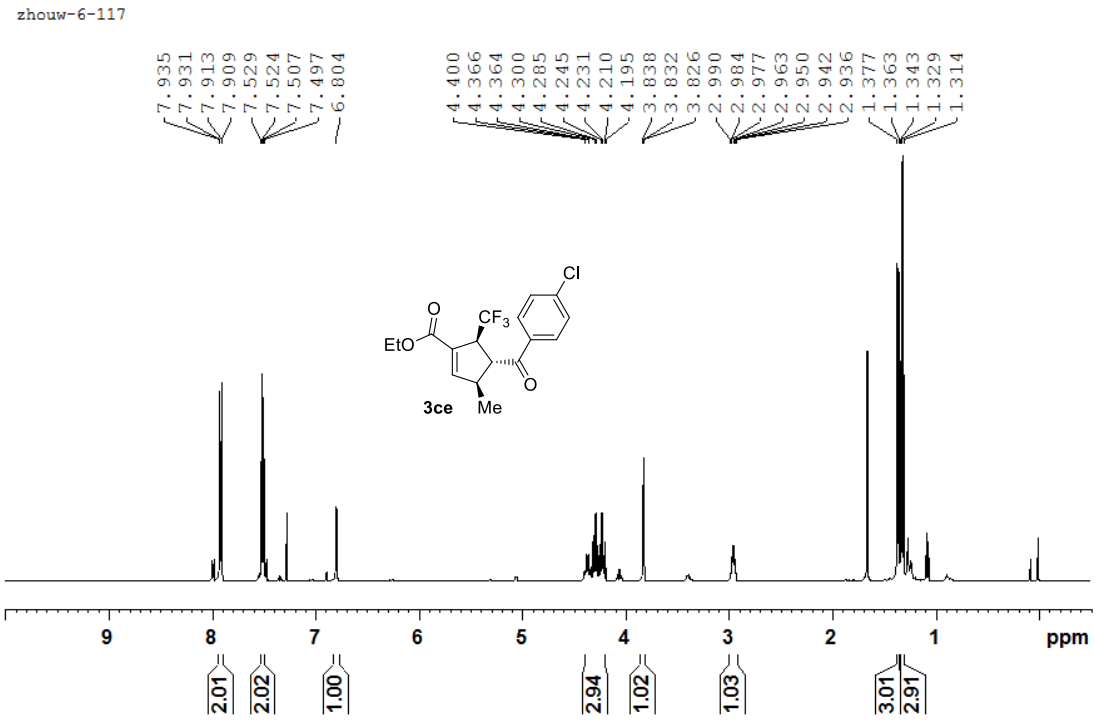
zhouw-7-72



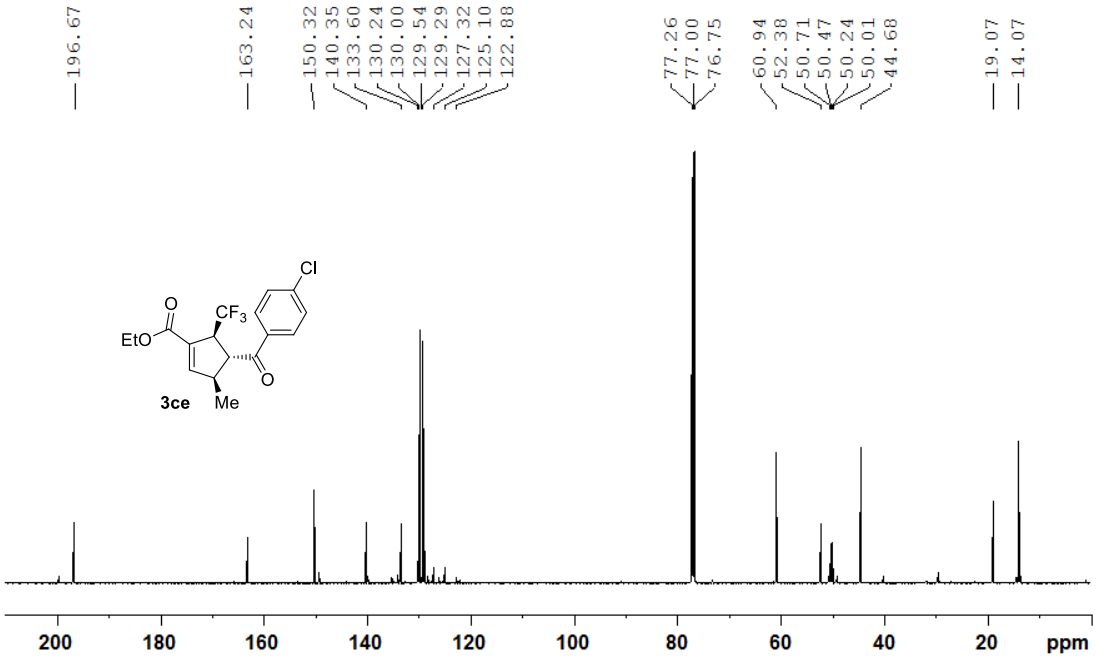

zhouw-7-72c



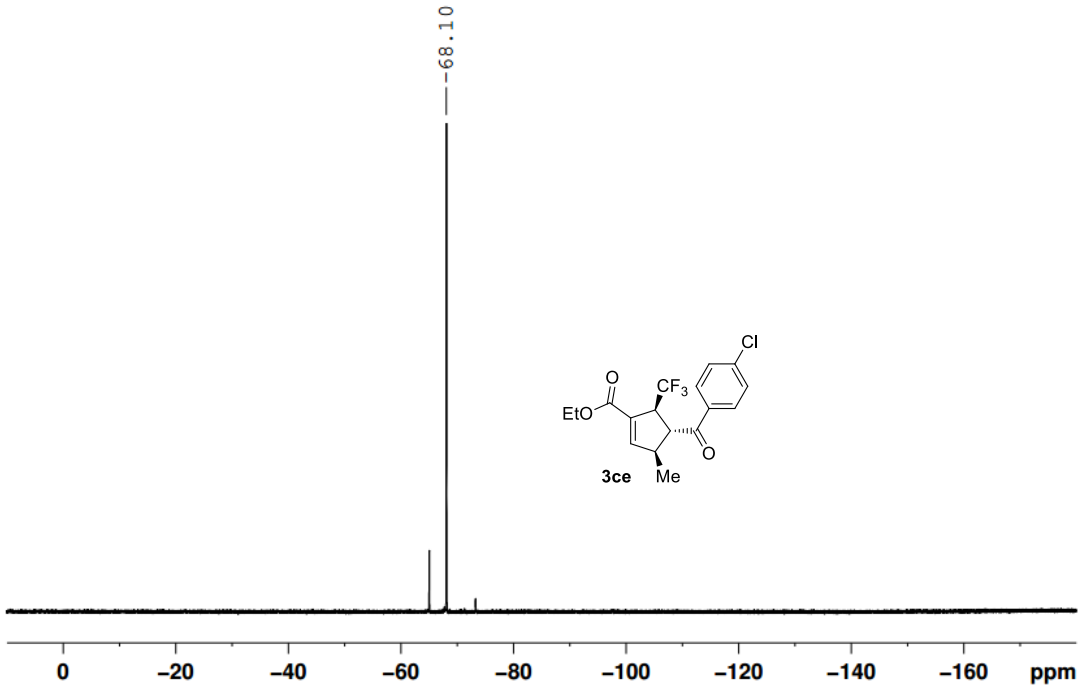

zhouw-7-72f
-67.53
O
CF3
EtO
O
3ad
S
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

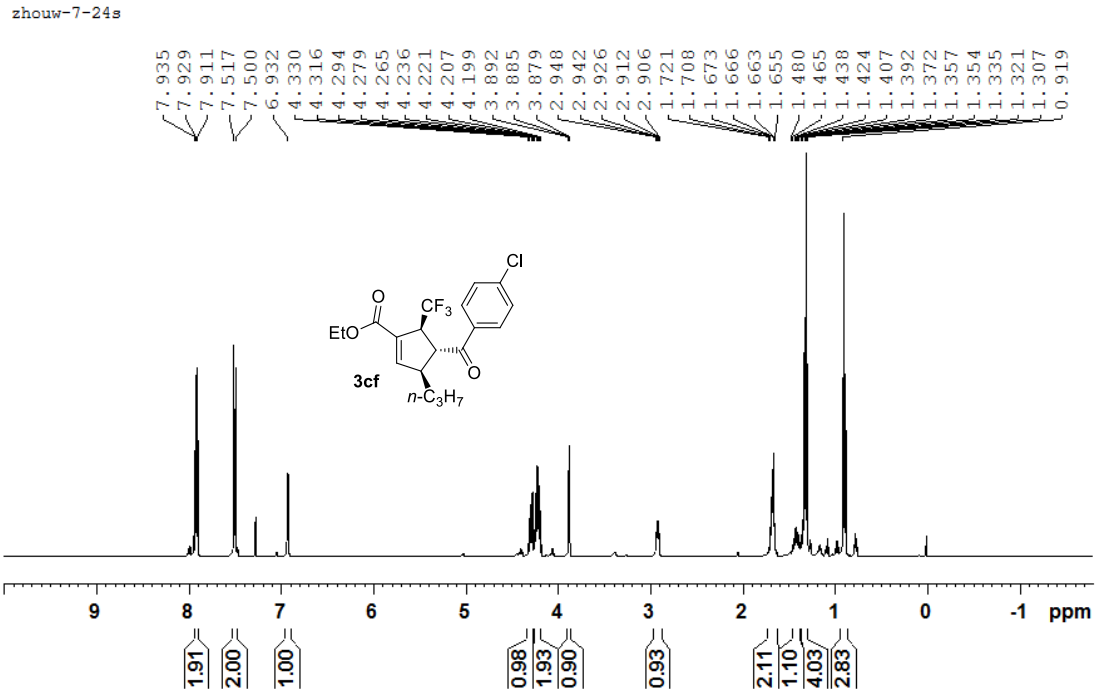

zhouw-6-117
7.935
7.931
7.913
7.909
7.529
7.524
7.507
7.497
6.804
4.400
4.366
4.364
4.300
4.285
4.245
4.231
4.210
4.195
3.838
3.832
3.826
2.990
2.984
2.977
2.963
2.950
2.942
2.936
1.377
1.363
1.343
1.329
1.314
Cl
O
CF3
EtO
O
3ce
Me
9
8
7
6
5
4
3
2
1
ppm
2.01
2.02
1.00
2.94
1.02
1.03
3.01
2.91

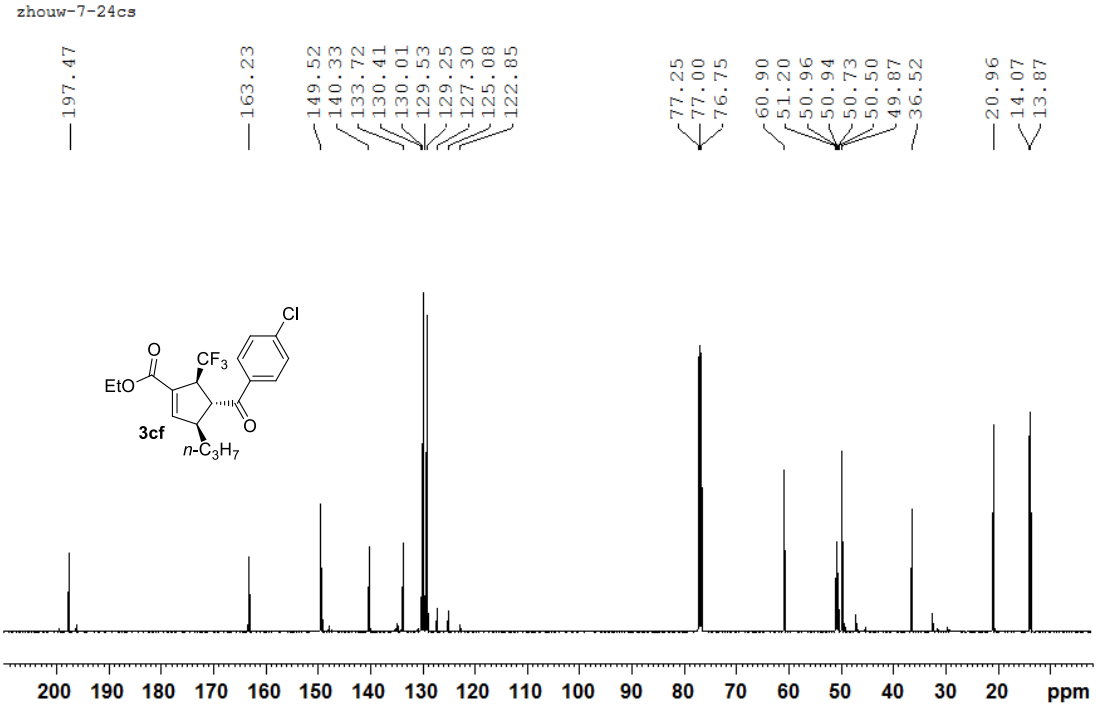
zhouw-6-117c



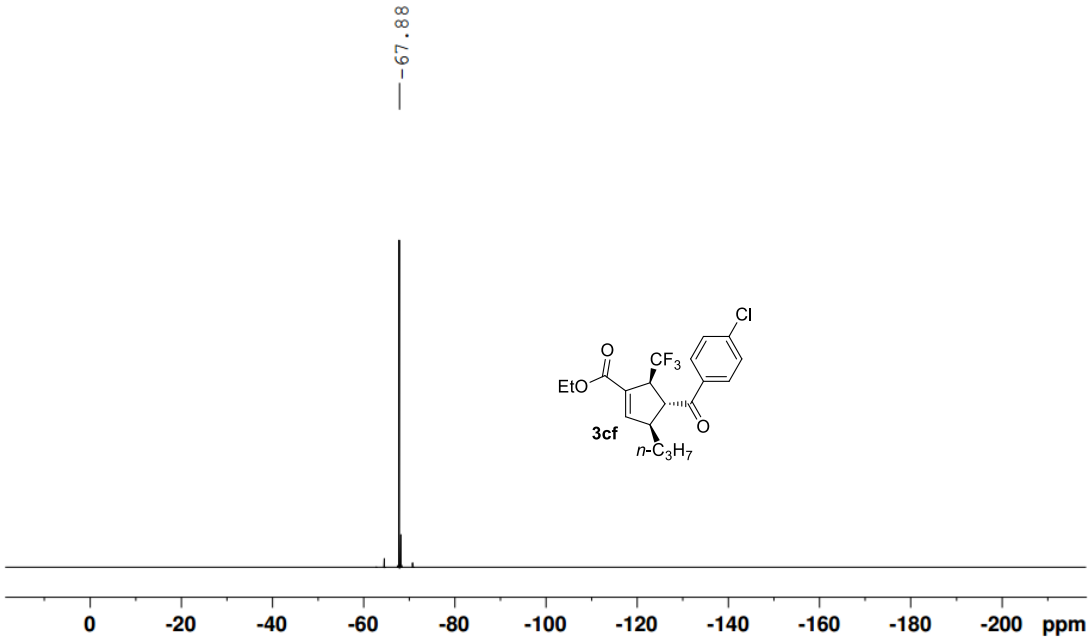

zhouw-6-117f



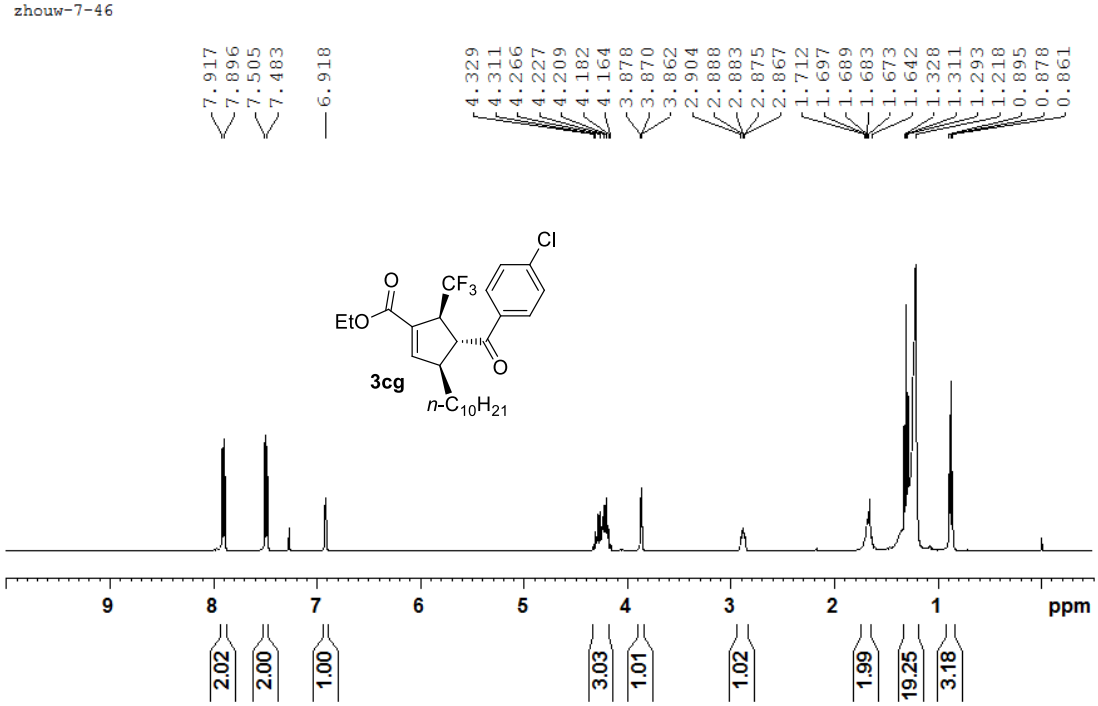

zhouw-7-24s
7.935
7.929
7.911
7.517
7.500
6.932
4.330
4.316
4.294
4.279
4.265
4.236
4.221
4.207
4.199
3.892
3.885
3.879
2.948
2.942
2.926
2.912
2.906
1.721
1.708
1.673
1.666
1.663
1.655
1.480
1.465
1.438
1.424
1.407
1.392
1.372
1.357
1.354
1.335
1.321
1.307
0.919
Cl
O
CF3
EtO
O
3cf
n-C3H7
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.91
2.00
1.00
0.98
1.93
0.90
0.93
2.11
1.10
4.03
2.83

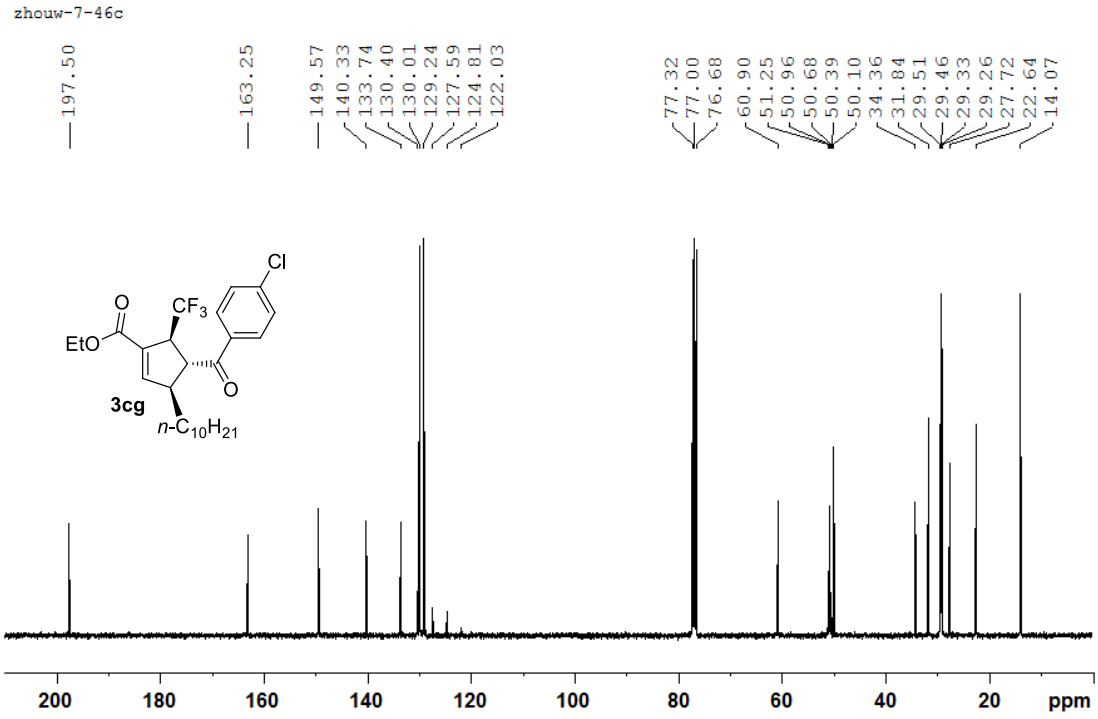

zhouw-7-24cs
197.47
163.23
149.52
140.33
133.72
130.41
130.01
129.53
129.25
127.30
125.08
122.85
77.25
77.00
76.75
60.90
51.20
50.96
50.94
50.73
50.50
49.87
36.52
20.96
14.07
13.87
Cl
O
CF3
EtO
O
3cf
n-C3H7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

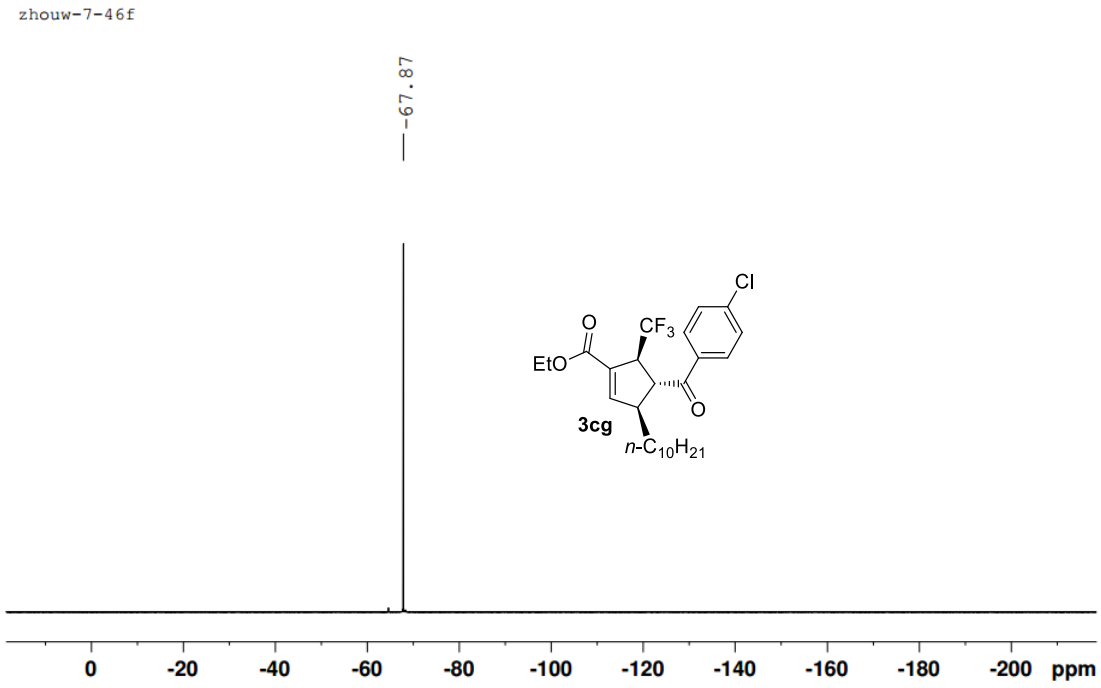
zhouw-7-24f



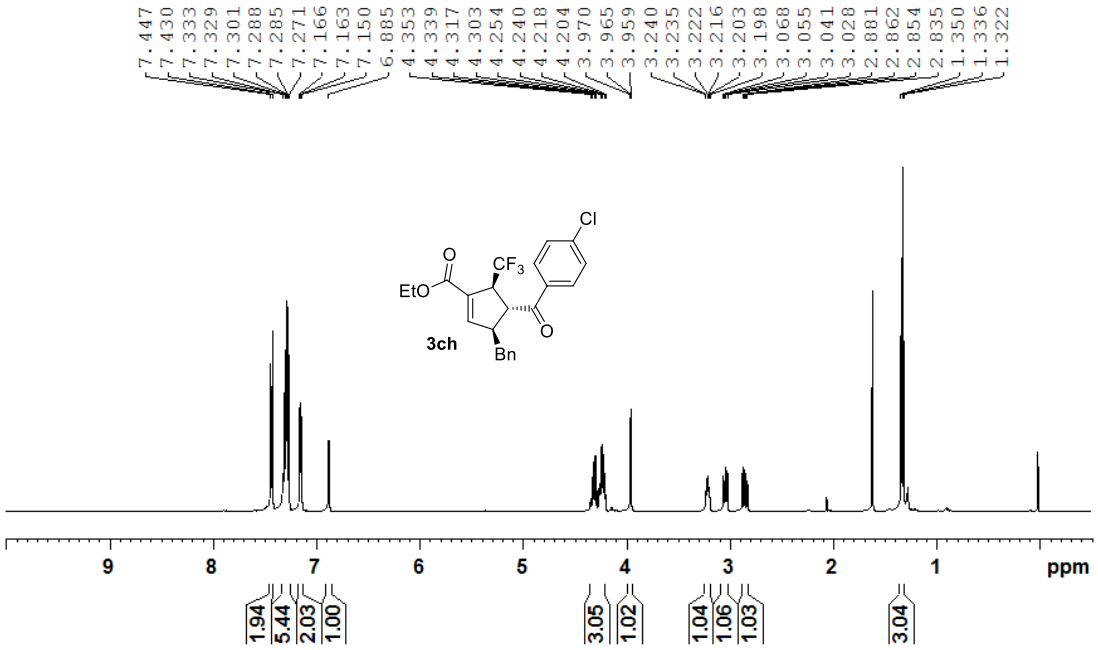

zhouw-7-46



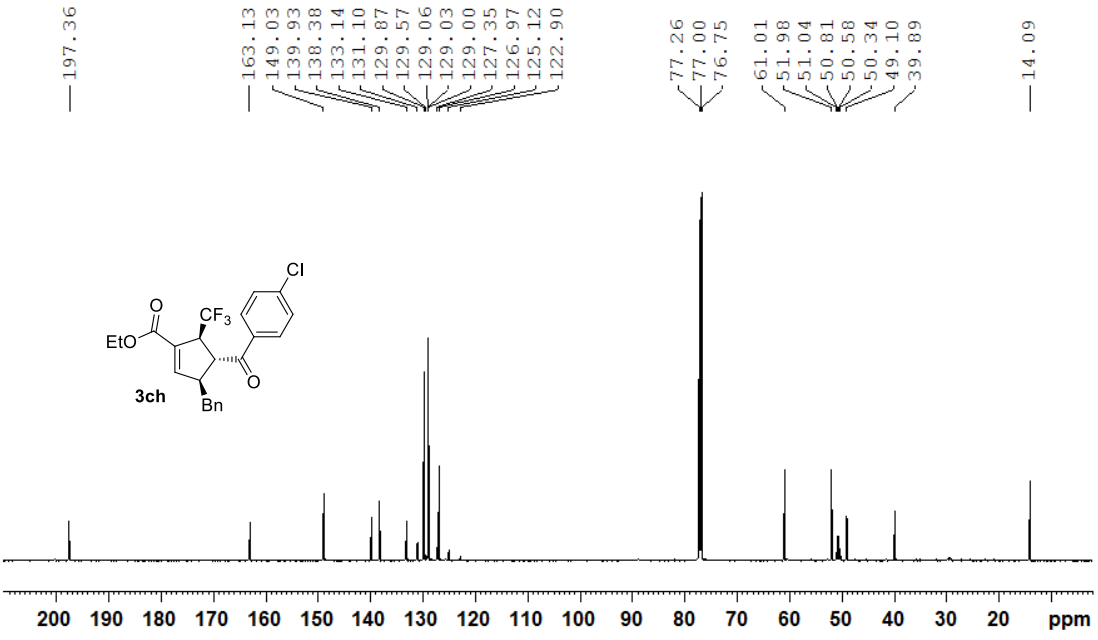

zhouw-7-46c
197.50
163.25
149.57
140.33
133.74
130.40
130.01
129.24
127.59
124.81
122.03
77.32
77.00
76.68
60.90
51.25
50.96
50.68
50.39
50.10
34.36
31.84
29.51
29.46
29.33
29.26
27.72
22.64
14.07
Cl
O
CF3
EtO
O
3cg
n-C10H21
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-7-46f
-67.87
Cl
O
CF3
EtO
O
3cg
n-C10H21
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

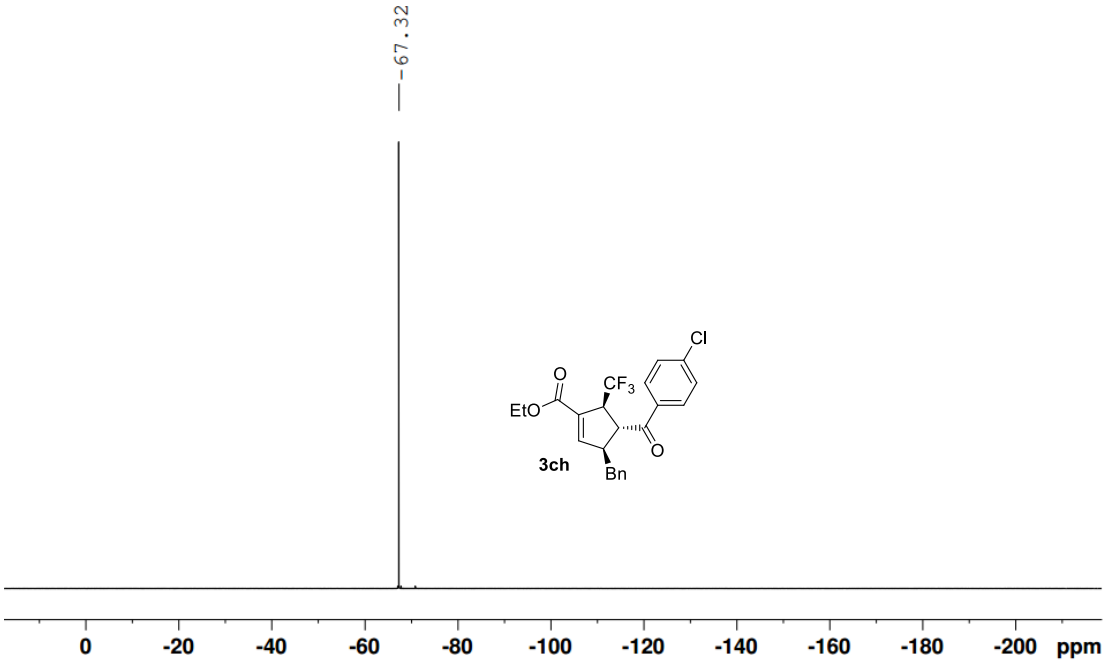
zhouw-7-19



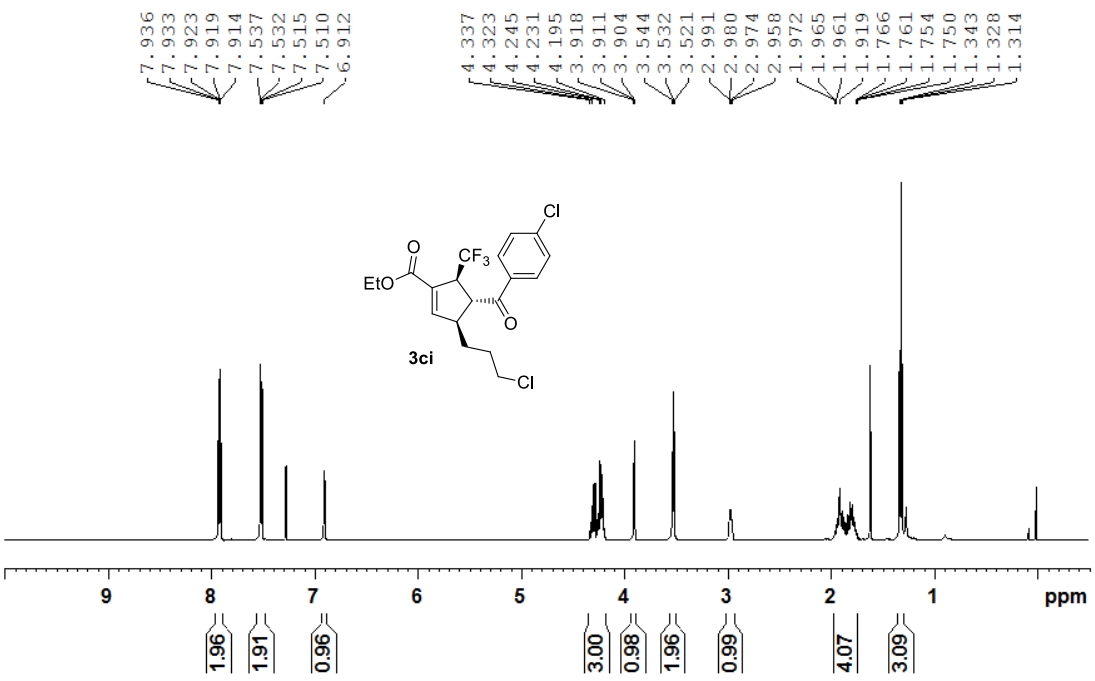

zhouw-7-19c



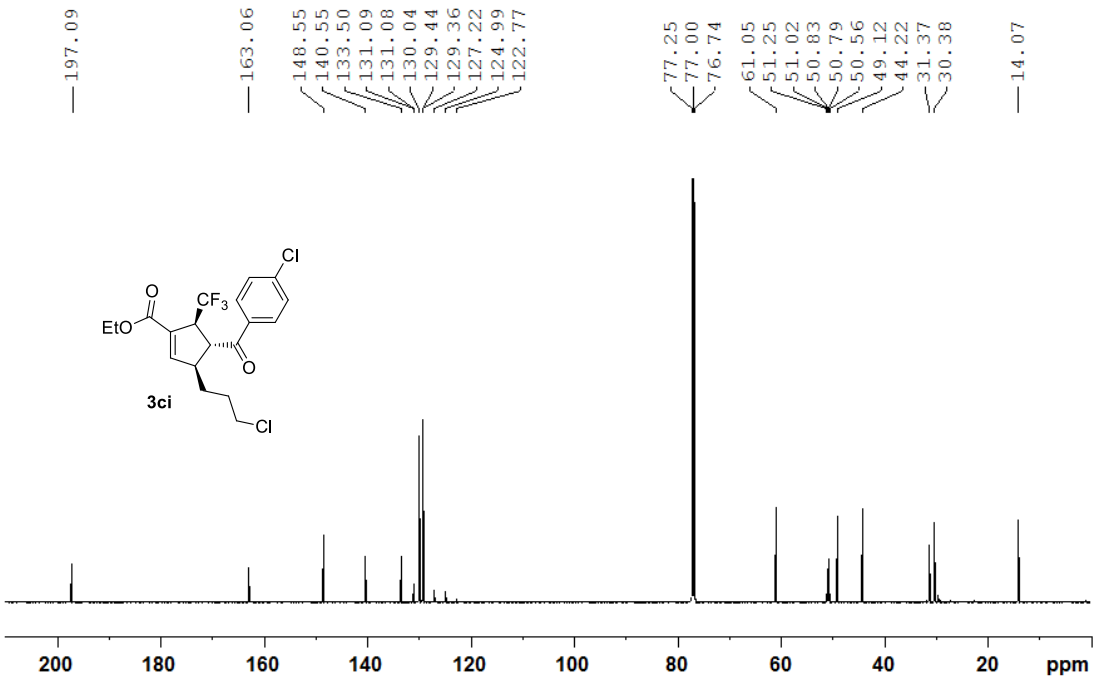
zhouw-7-19f



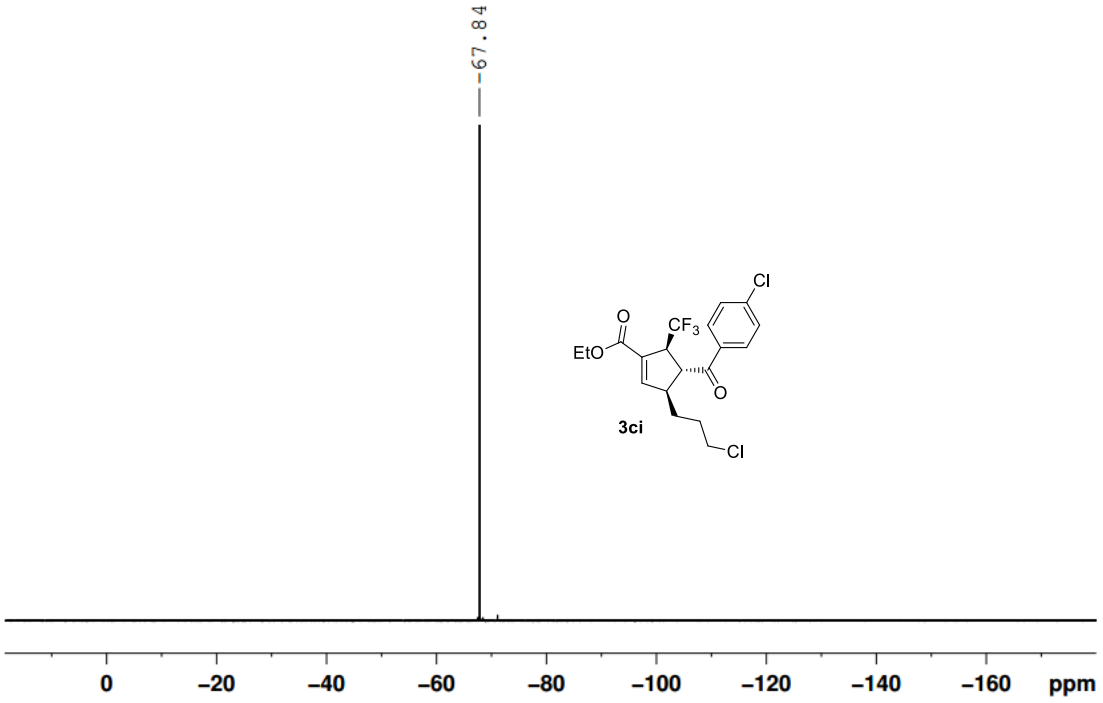

zhouw-6-120



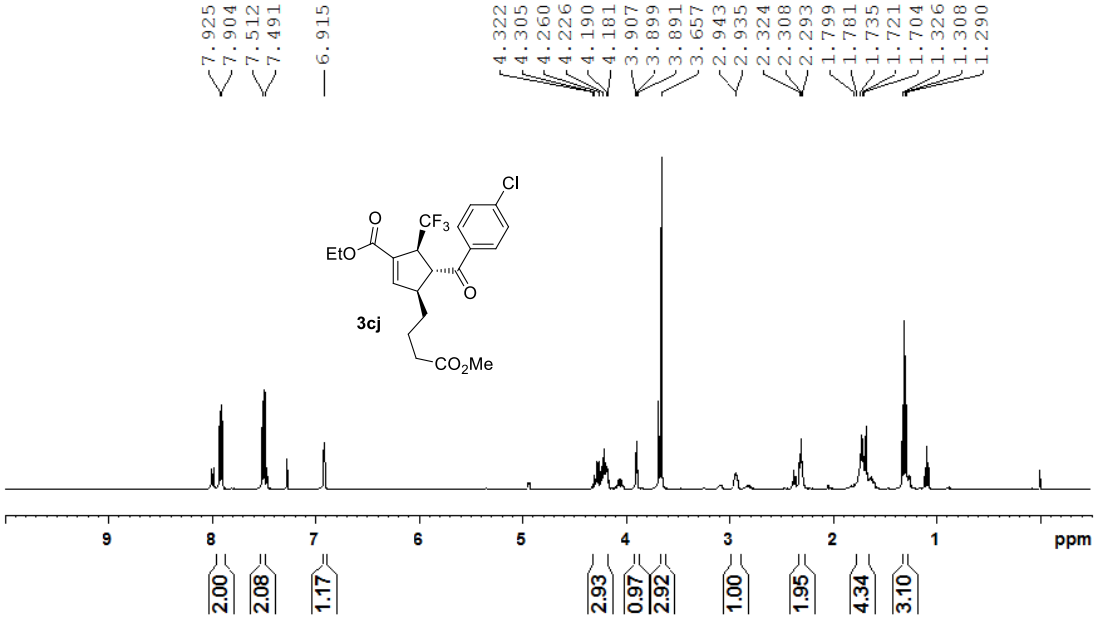
zhouw-6-120c



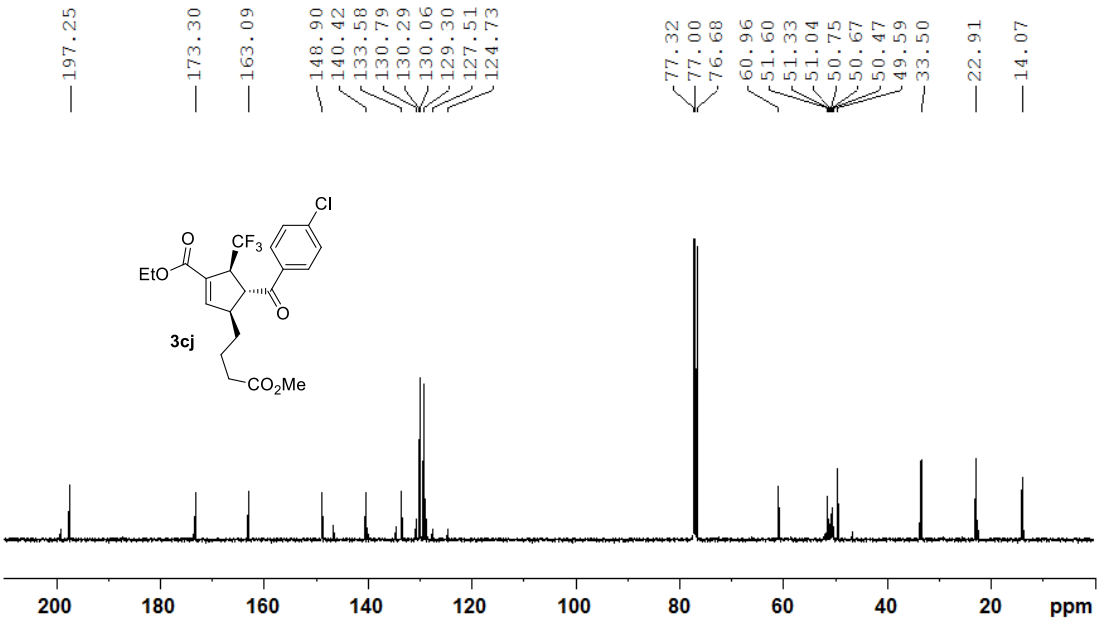

zhouw-6-120f



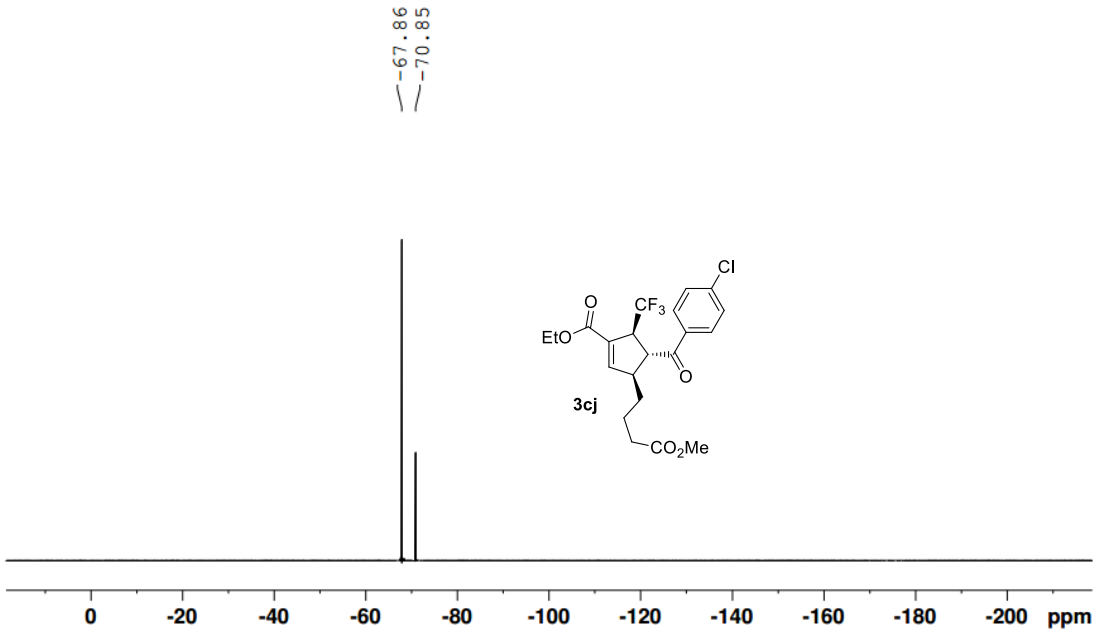
zhouw-7-28



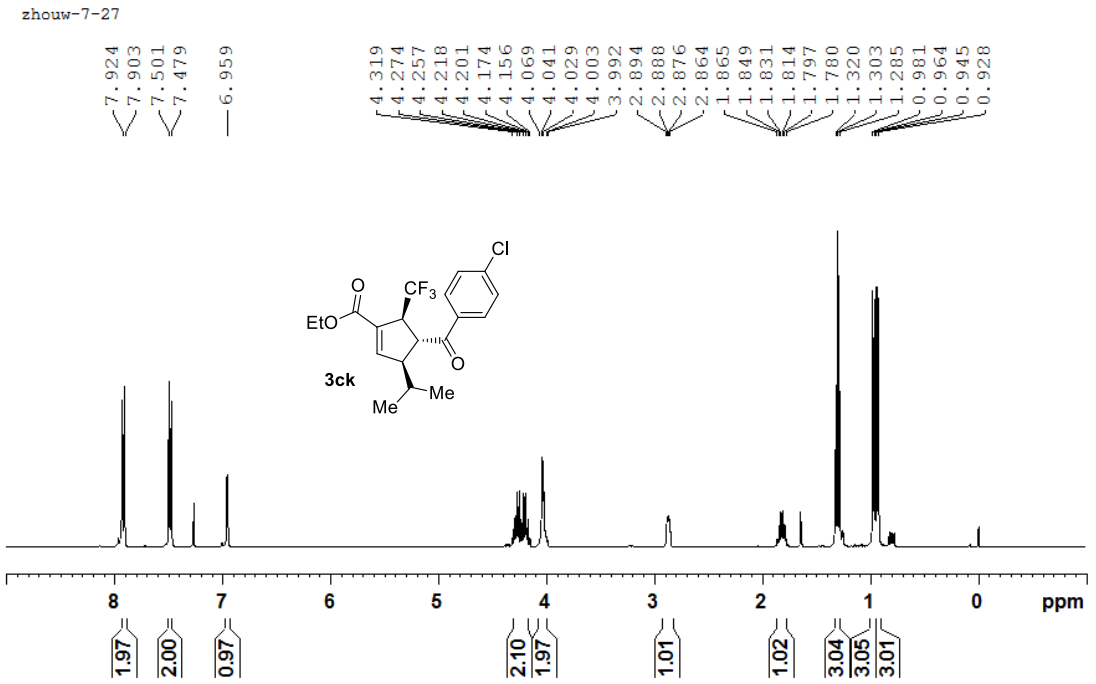

zhouw-7-28c



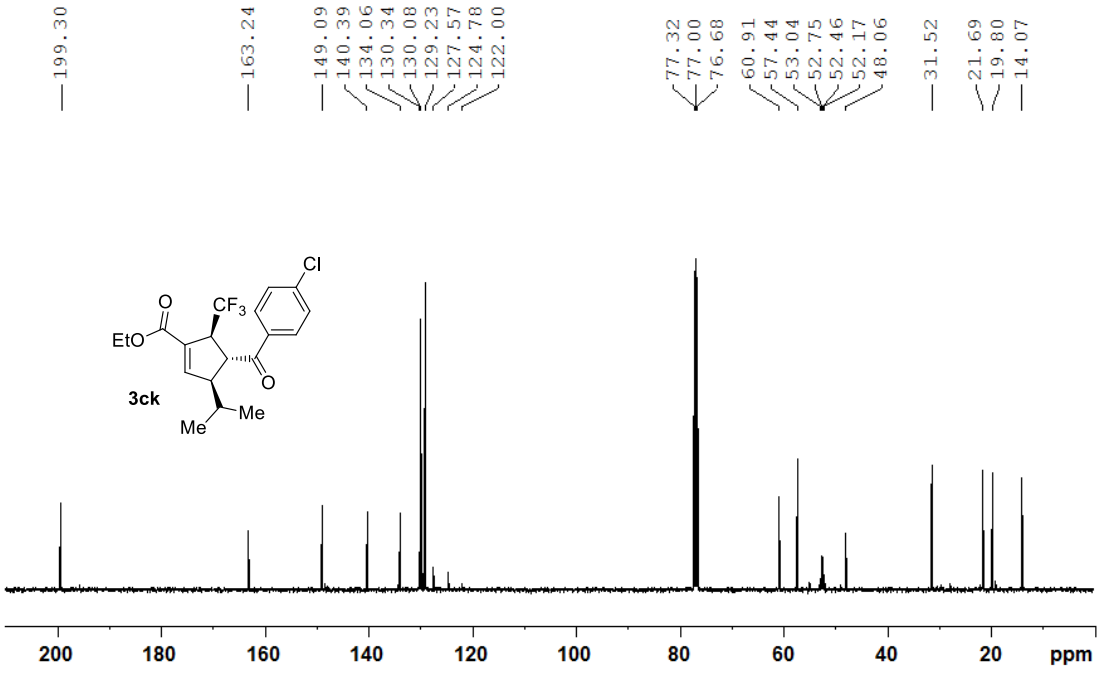
zhouw-7-28f



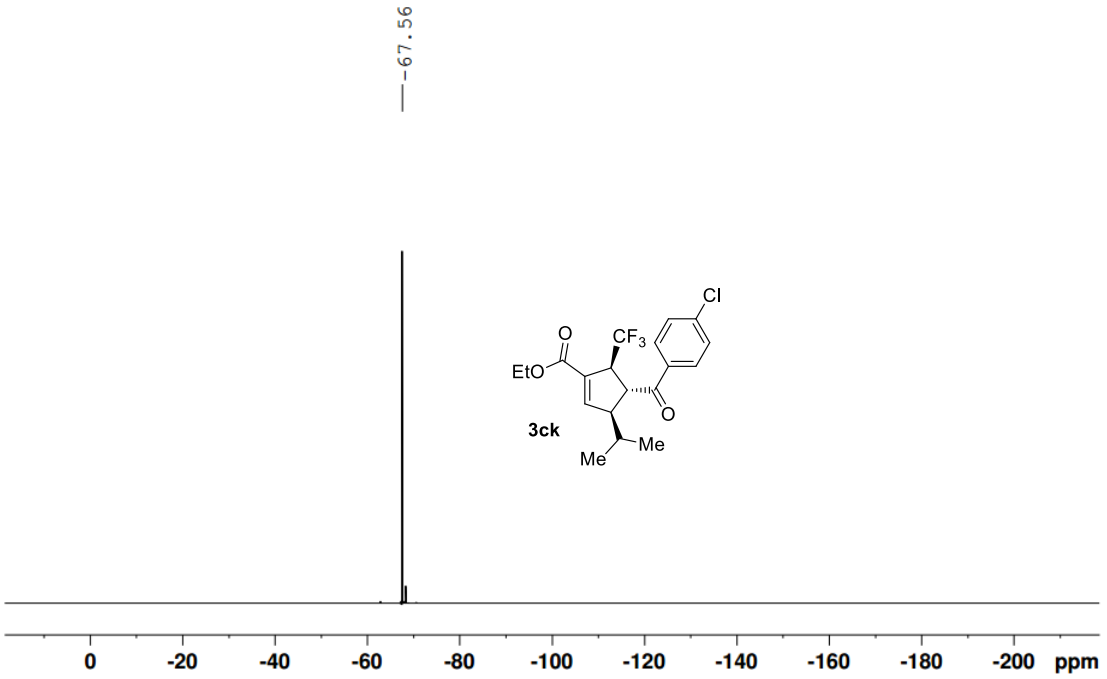

zhouw-7-27

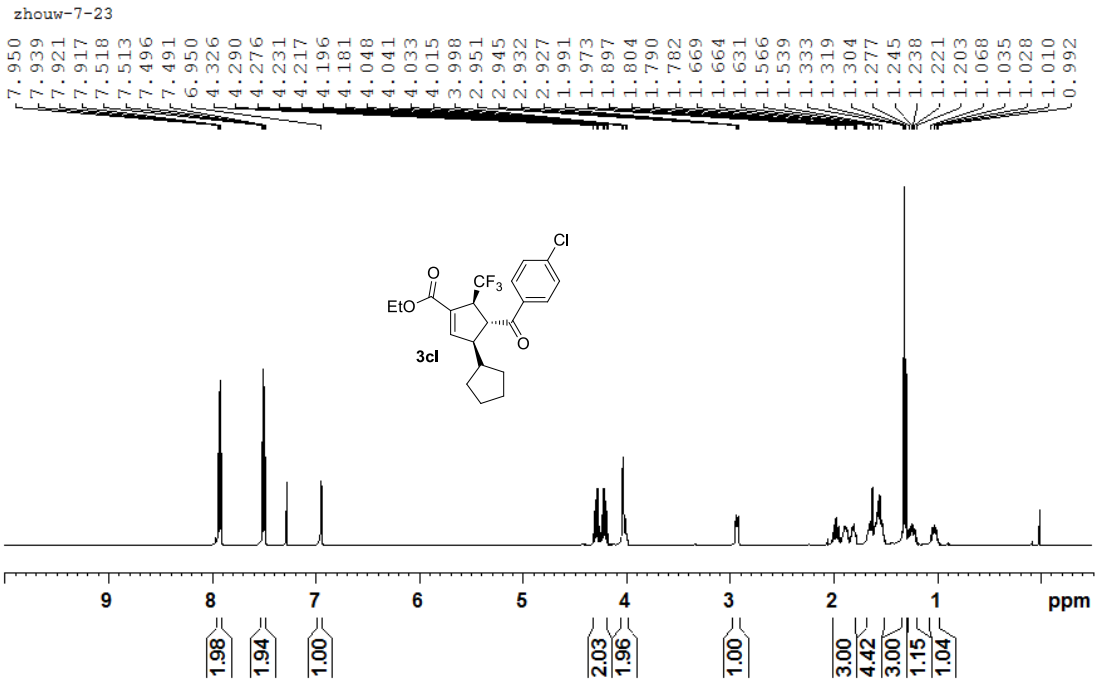


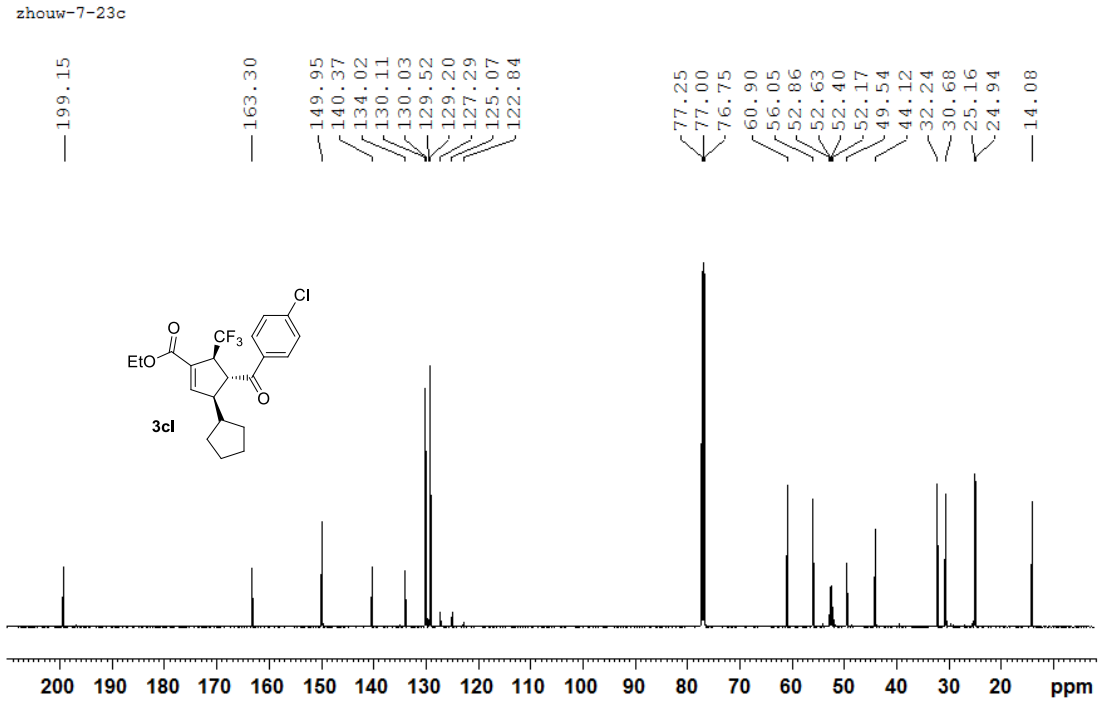
zhouw-7-27c



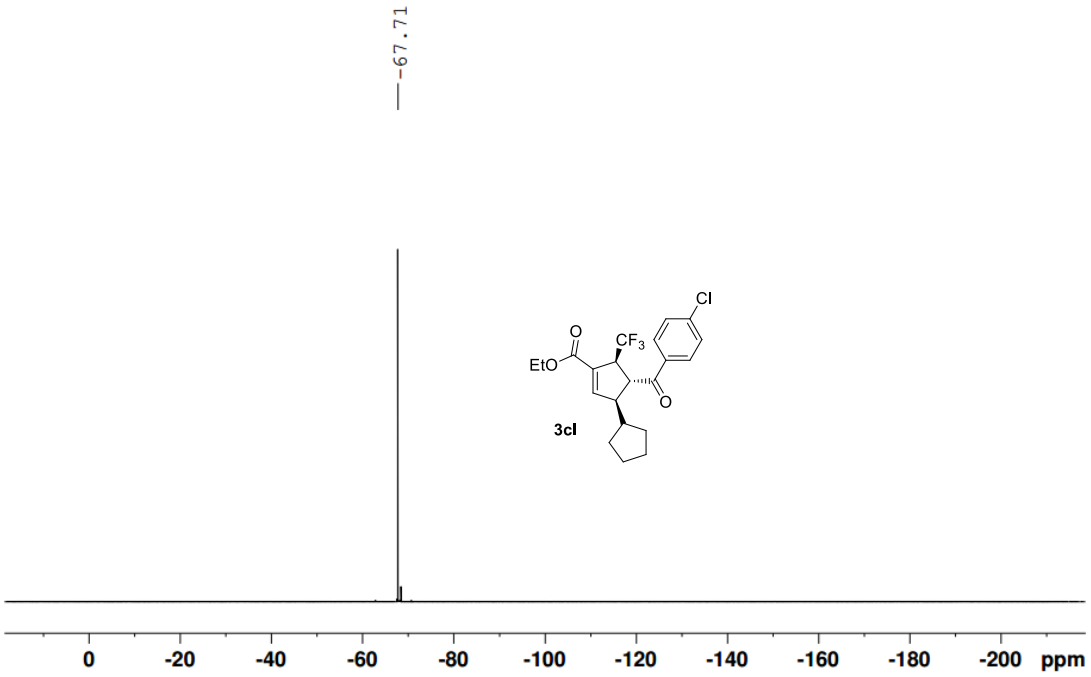

zhouw-7-27f



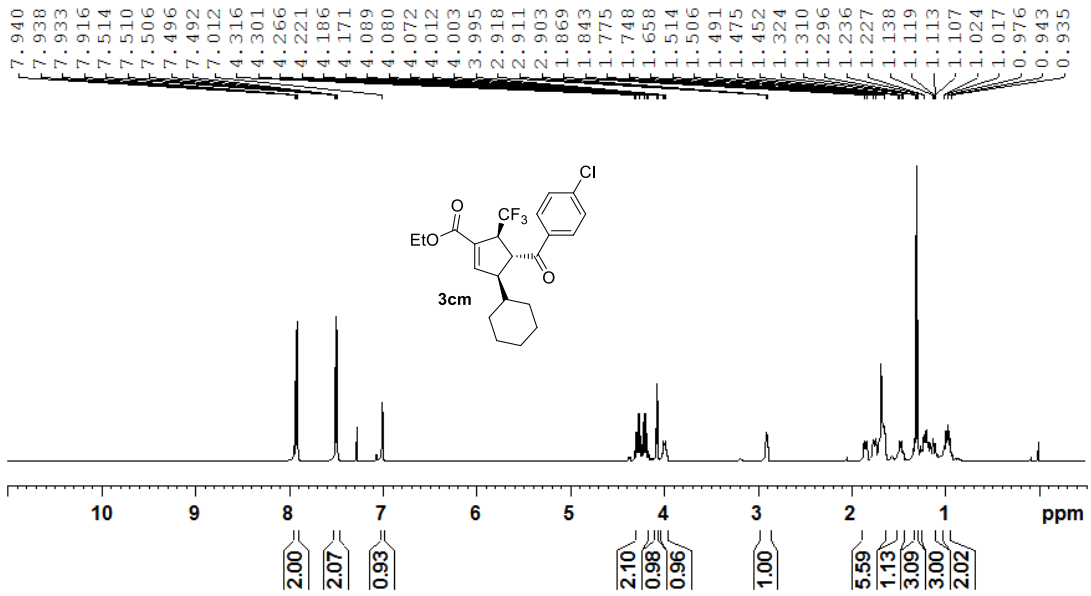

zhouw-7-23
7.950
7.939
7.921
7.917
7.518
7.513
7.496
7.491
6.950
4.326
4.290
4.276
4.231
4.217
4.196
4.181
4.048
4.041
4.033
4.015
3.998
2.951
2.945
2.932
2.927
1.991
1.973
1.897
1.804
1.790
1.782
1.669
1.664
1.631
1.566
1.539
1.333
1.319
1.304
1.277
1.245
1.238
1.221
1.203
1.068
1.035
1.028
1.010
0.992
Cl
O
CF3
EtO
O
3cl
9
8
7
6
5
4
3
2
1
ppm
1.98
1.94
1.00
2.03
1.96
1.00
3.00
4.42
3.00
1.15
1.04


zhouw-7-23c
199.15
163.30
149.95
140.37
134.02
130.11
130.03
129.52
129.20
127.29
125.07
122.84
77.25
77.00
76.75
60.90
56.05
52.86
52.63
52.40
52.17
49.54
44.12
32.24
30.68
25.16
24.94
14.08
Cl
O
CF3
EtO
O
3cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

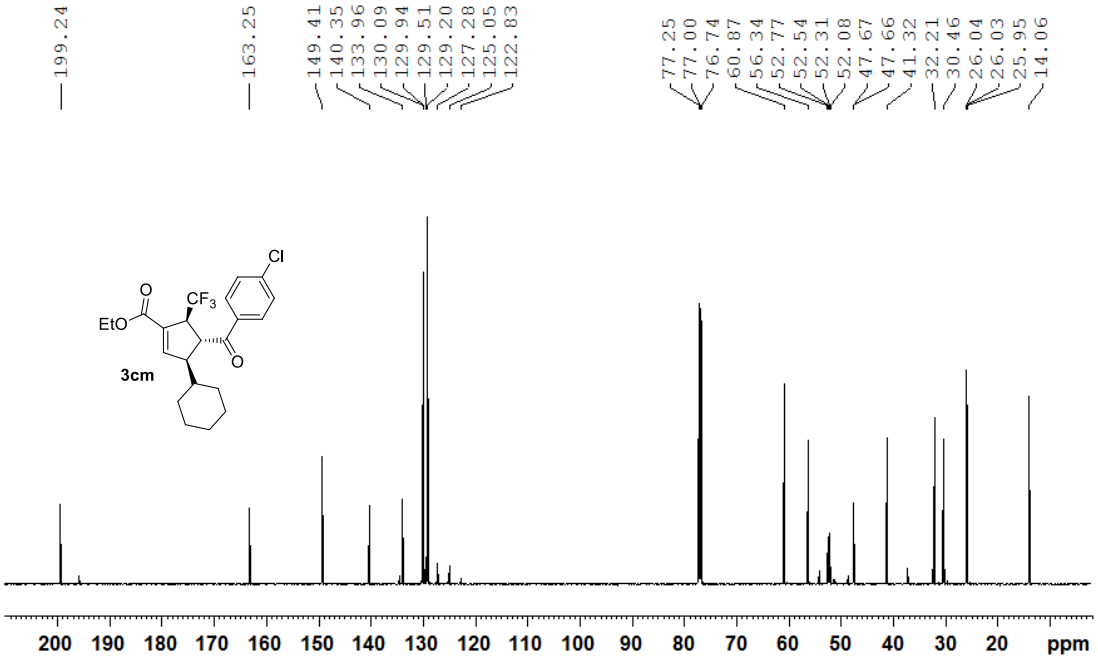
zhouw-7-23f



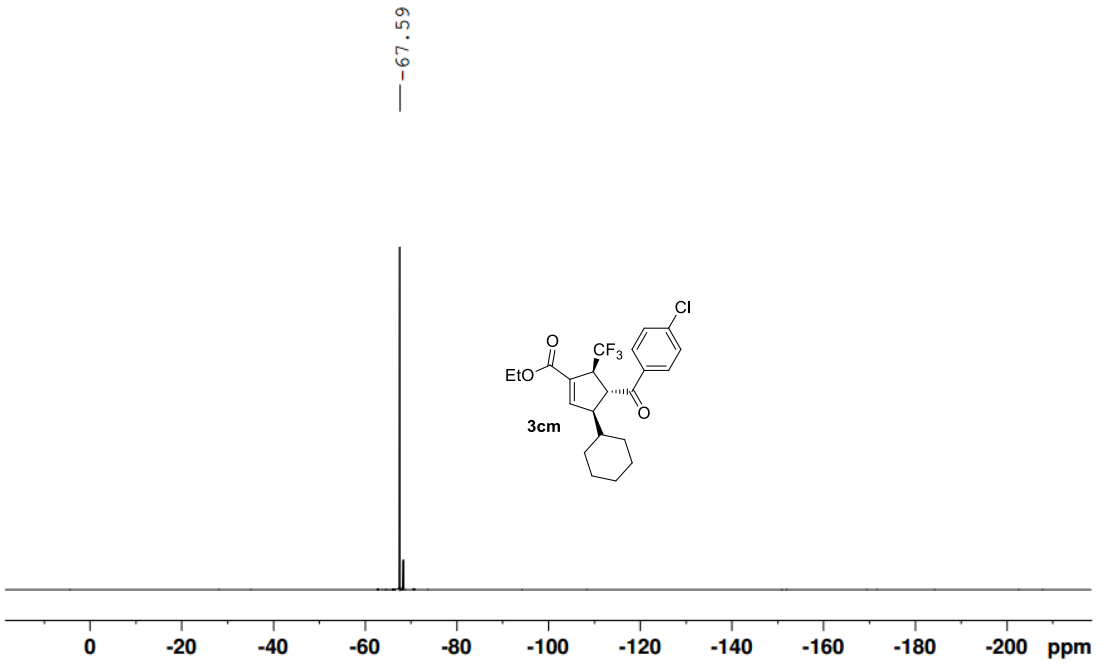

zhouw-7-20



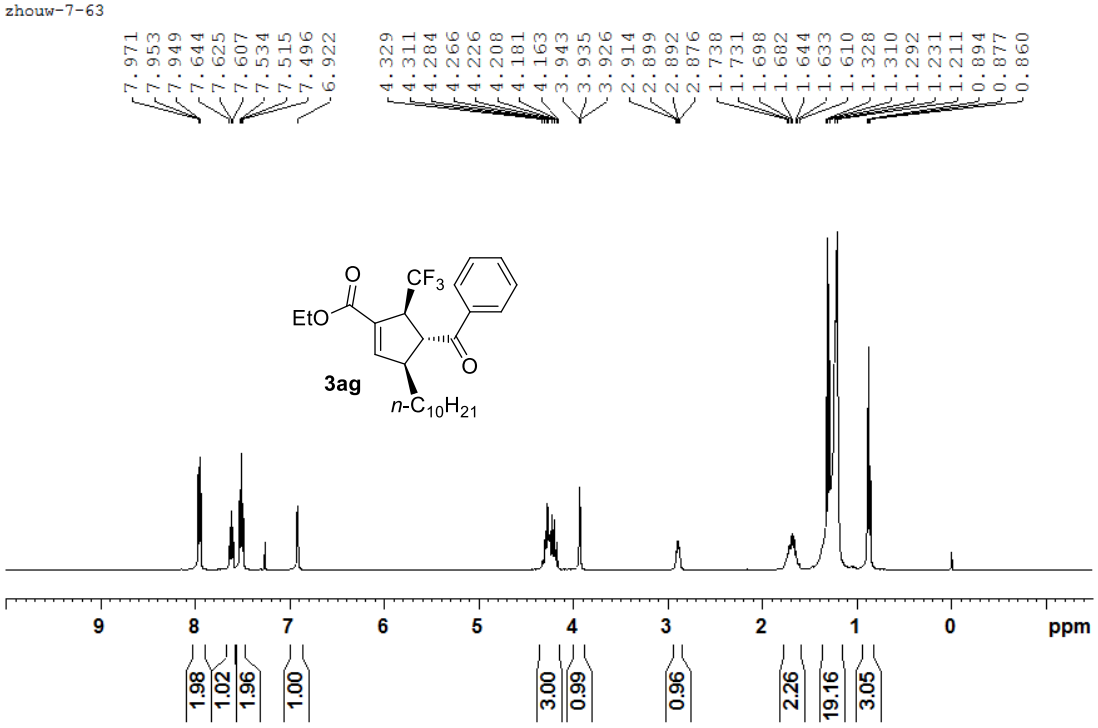
zhouw-7-20c



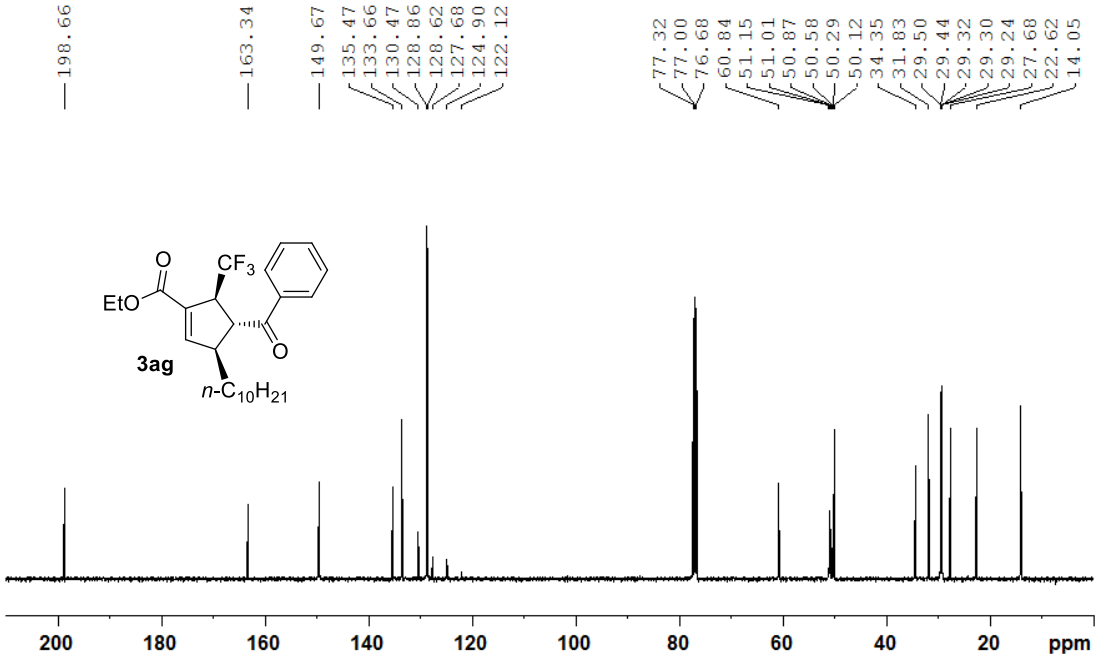

zhouw-7-20f



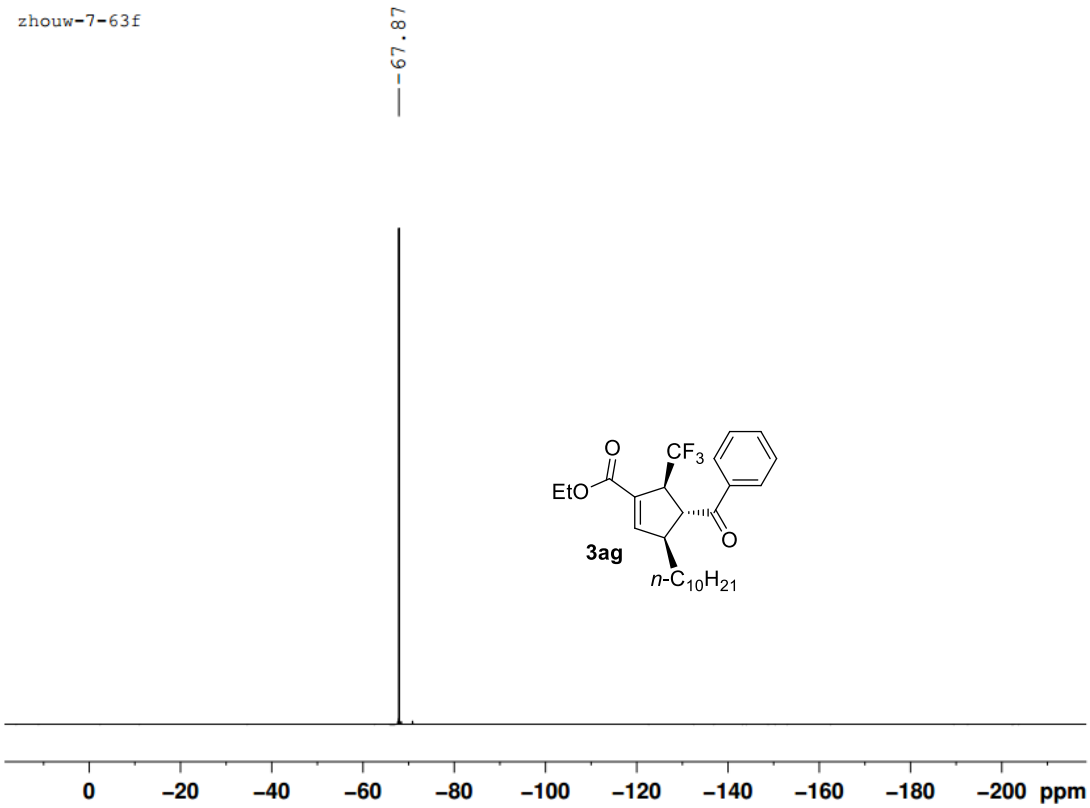
zhouw-7-63



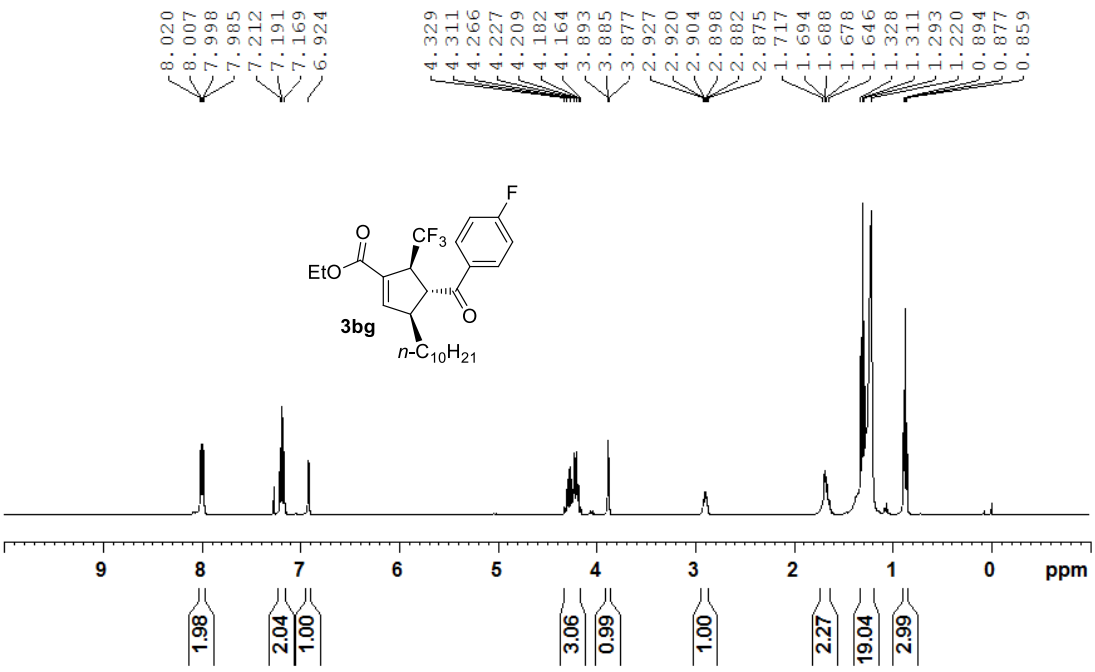

zhouw-7-63c

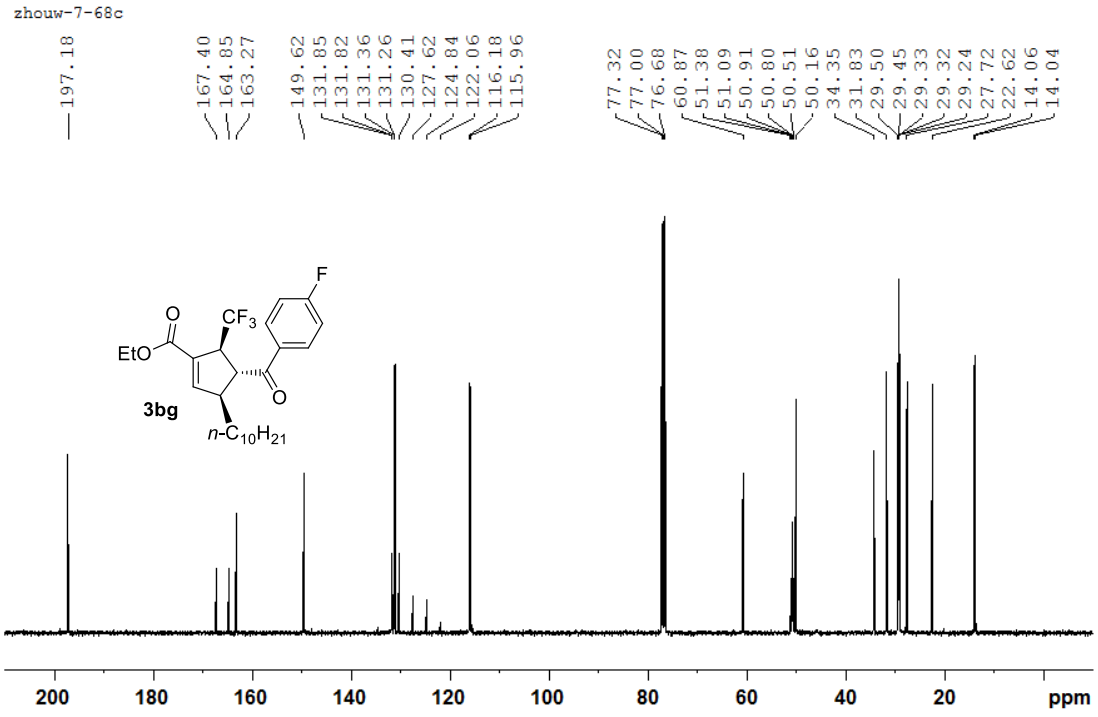


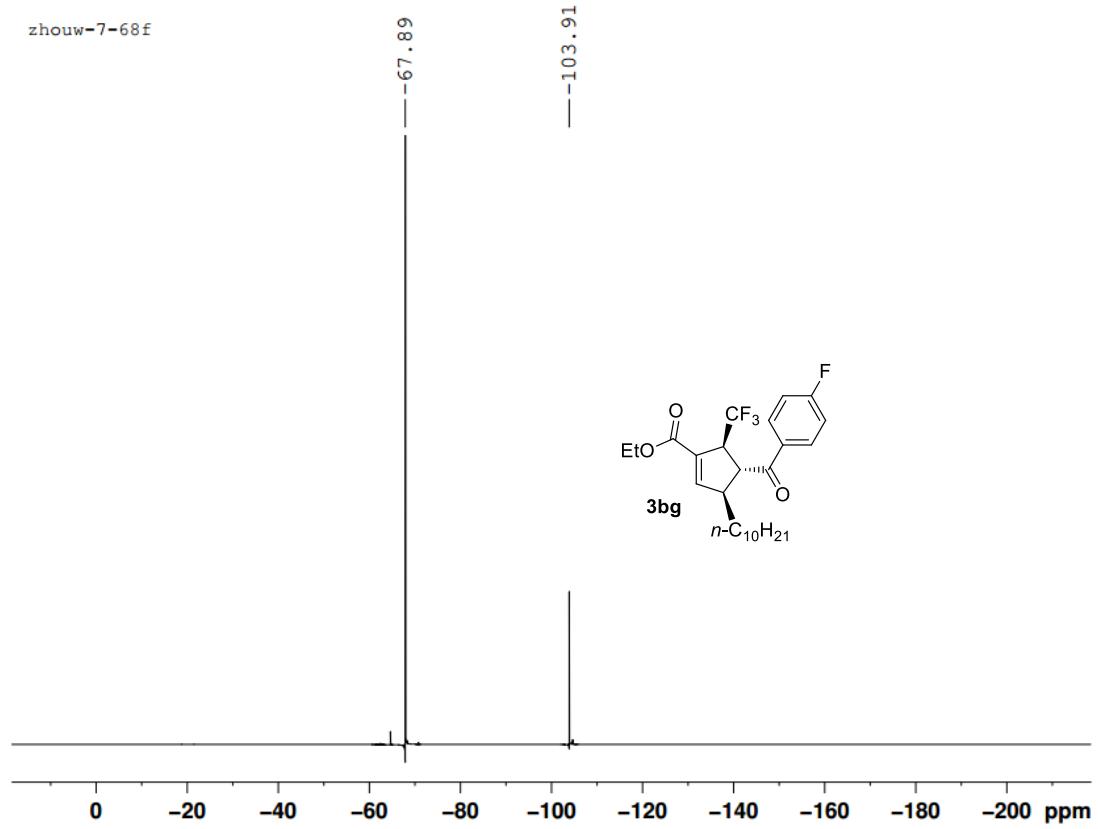
zhouw-7-63f

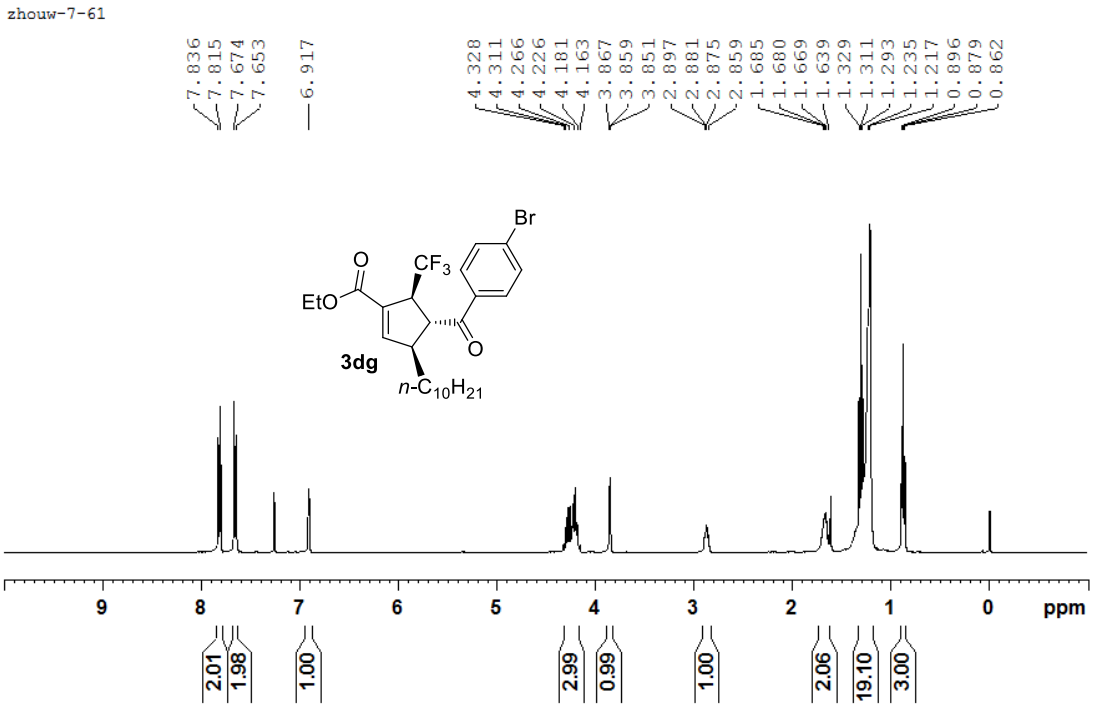


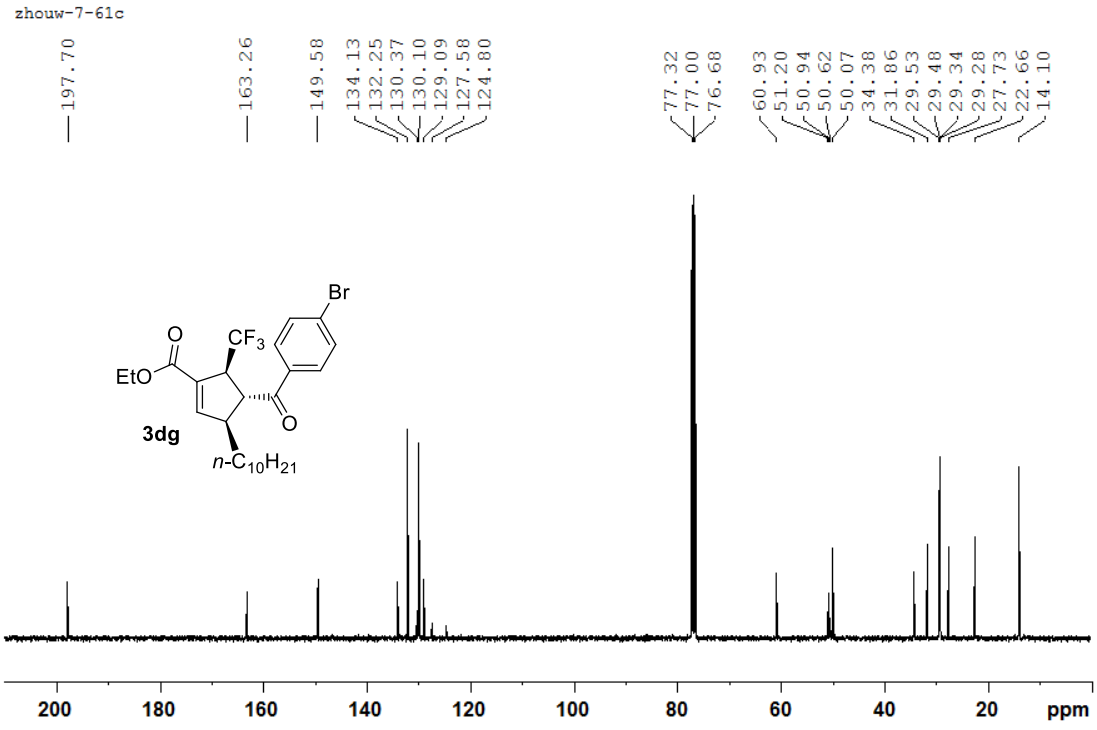

zhouw-7-68



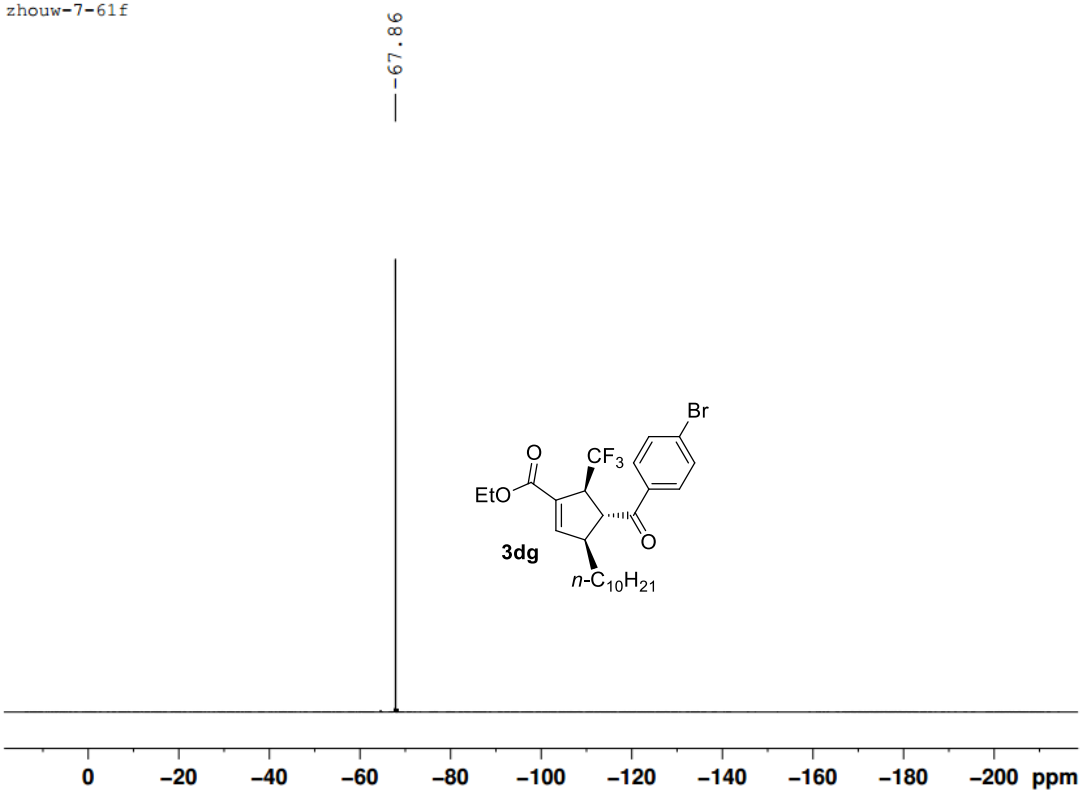

zhouw-7-68c
197.18
167.40
164.85
163.27
149.62
131.85
131.82
131.36
131.26
130.41
127.62
124.84
122.06
116.18
115.96
77.32
77.00
76.68
60.87
51.38
51.09
50.91
50.80
50.51
50.16
34.35
31.83
29.50
29.45
29.33
29.32
29.24
27.72
22.62
14.06
14.04
F
CF3
O
EtO
O
3bg
n-C10H21
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-7-68f
-67.89
-103.91
F
CF3
O
EtO
O
3bg
n-C10H21
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

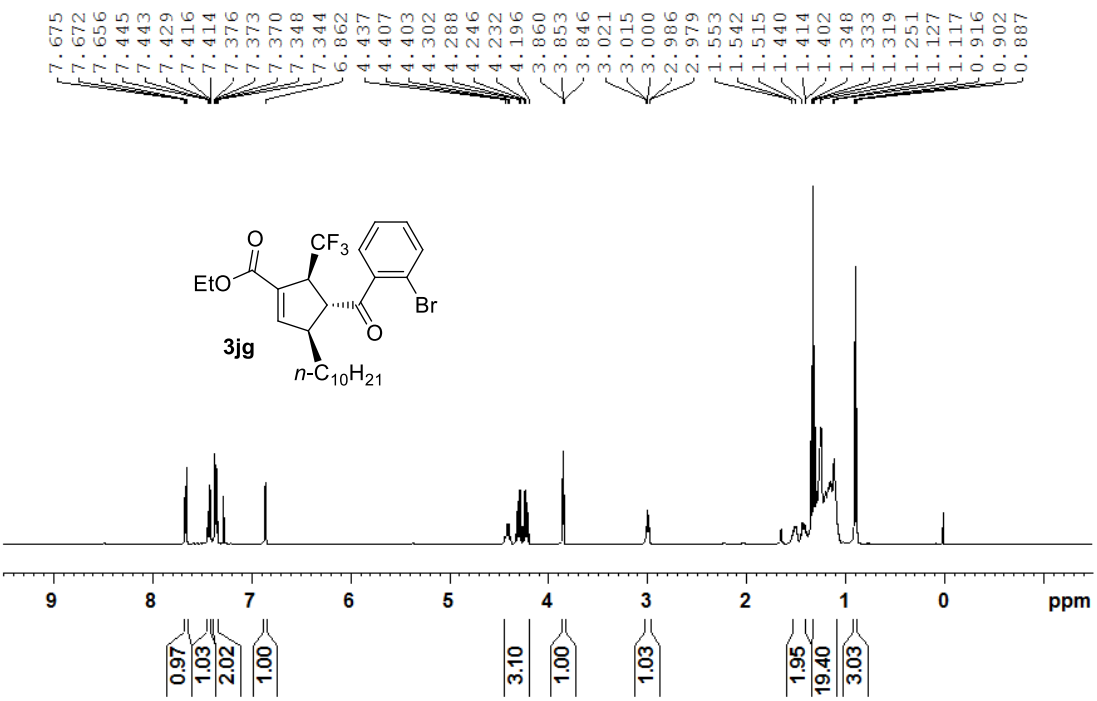

zhouw-7-61
7.836
7.815
7.674
7.653
6.917
4.328
4.311
4.266
4.226
4.181
4.163
3.867
3.859
3.851
2.897
2.881
2.875
2.859
1.685
1.680
1.669
1.639
1.329
1.311
1.293
1.235
1.217
0.896
0.879
0.862
Br
O
CF3
EtO
O
3dg
n-C10H21
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.98
1.00
2.99
0.99
1.00
2.06
19.10
3.00

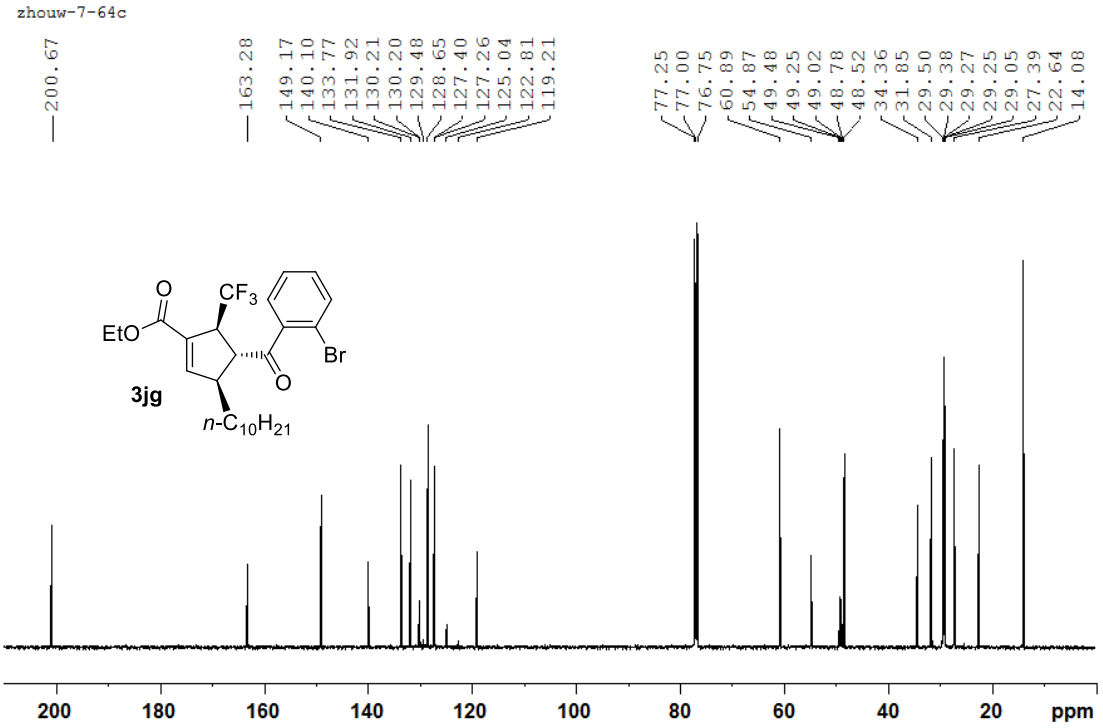

zhouw-7-61c
197.70
163.26
149.58
134.13
132.25
130.37
130.10
129.09
127.58
124.80
77.32
77.00
76.68
60.93
51.20
50.94
50.62
50.07
34.38
31.86
29.53
29.48
29.34
29.28
27.73
22.66
14.10
Br
O
CF3
EtO
O
3dg
n-C10H21
200
180
160
140
120
100
80
60
40
20
ppm

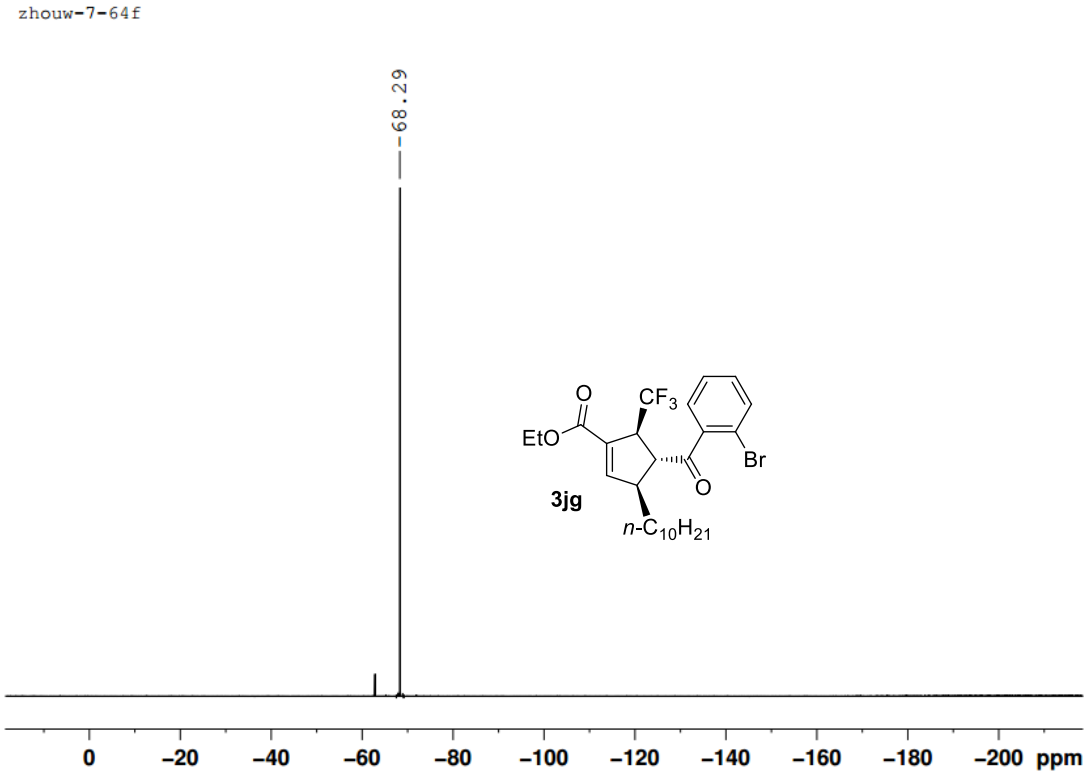
zhouw-7-61f



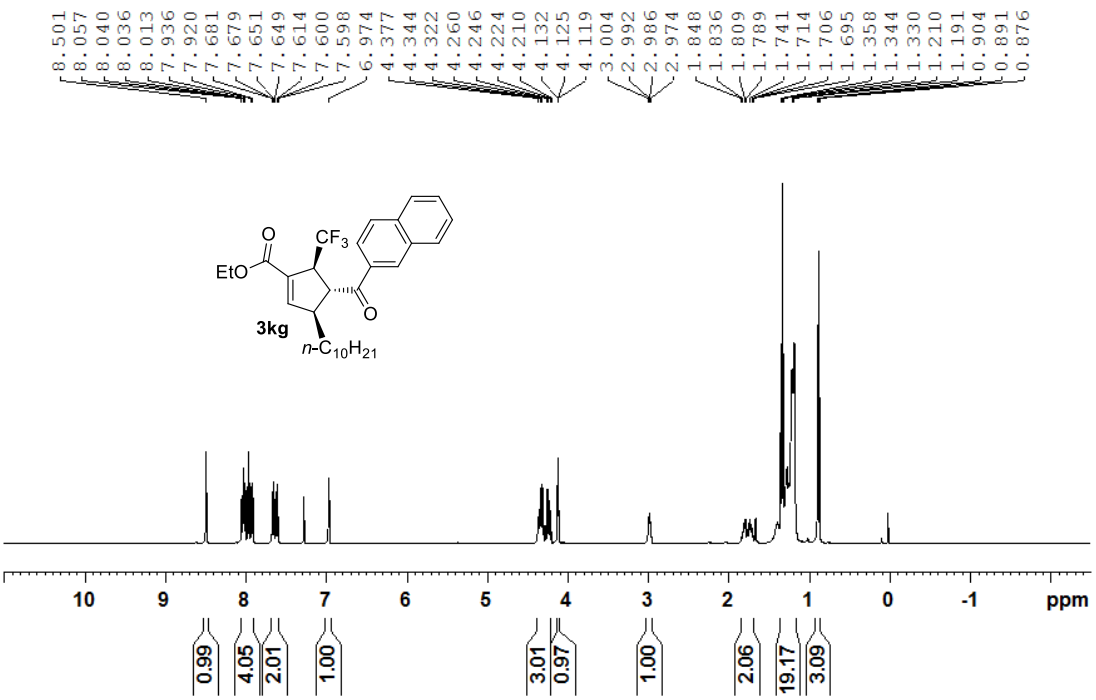

zhouw-7-64



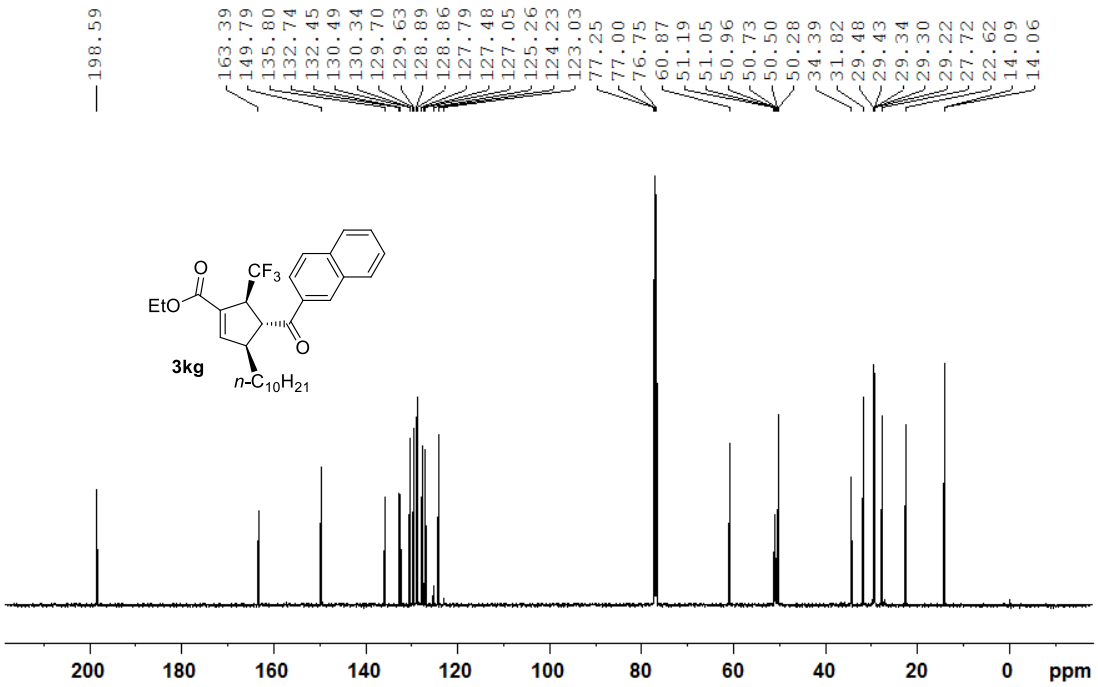

zhouw-7-64c
200.67
163.28
149.17
140.10
133.77
131.92
130.21
130.20
129.48
128.65
127.40
127.26
125.04
122.81
119.21
77.25
77.00
76.75
60.89
54.87
49.48
49.25
49.02
48.78
48.52
34.36
31.85
29.50
29.38
29.27
29.25
29.05
27.39
22.64
14.08
O
CF3
EtO
Br
O
3jg
n-C10H21
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-7-64f
-68.29
O
CF3
EtO
Br
O
3jg
n-C10H21
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

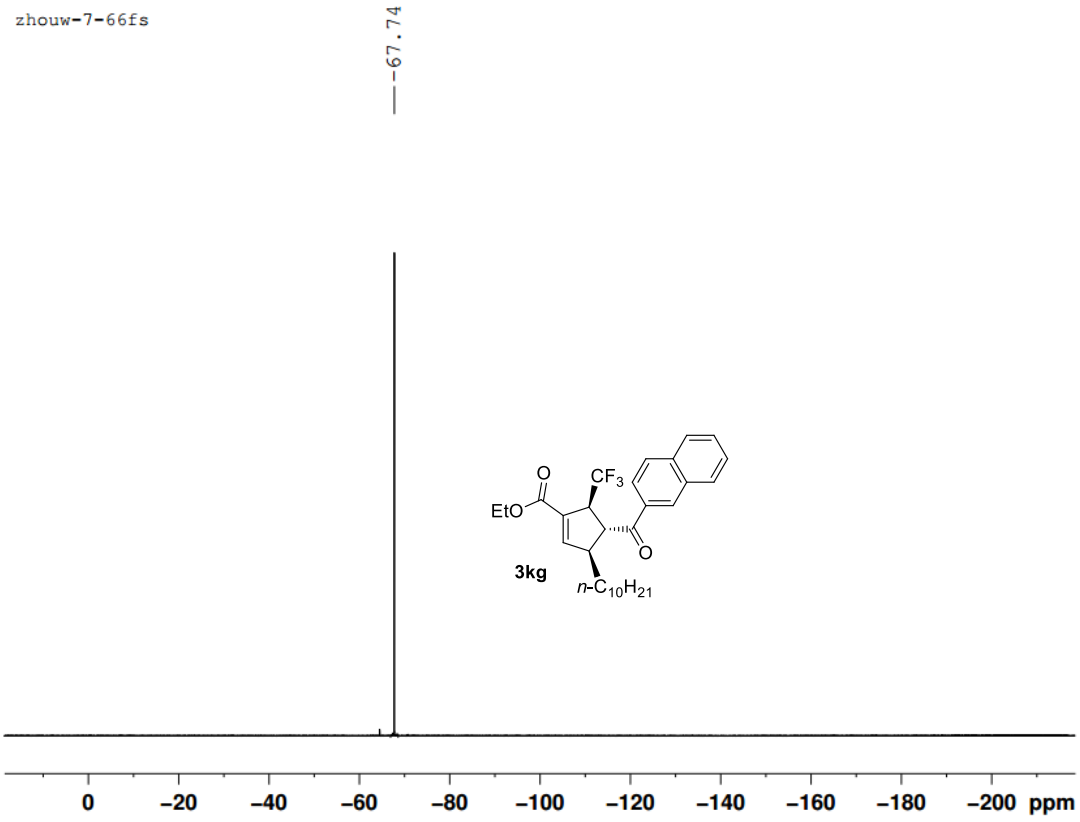
zhouw-7-66



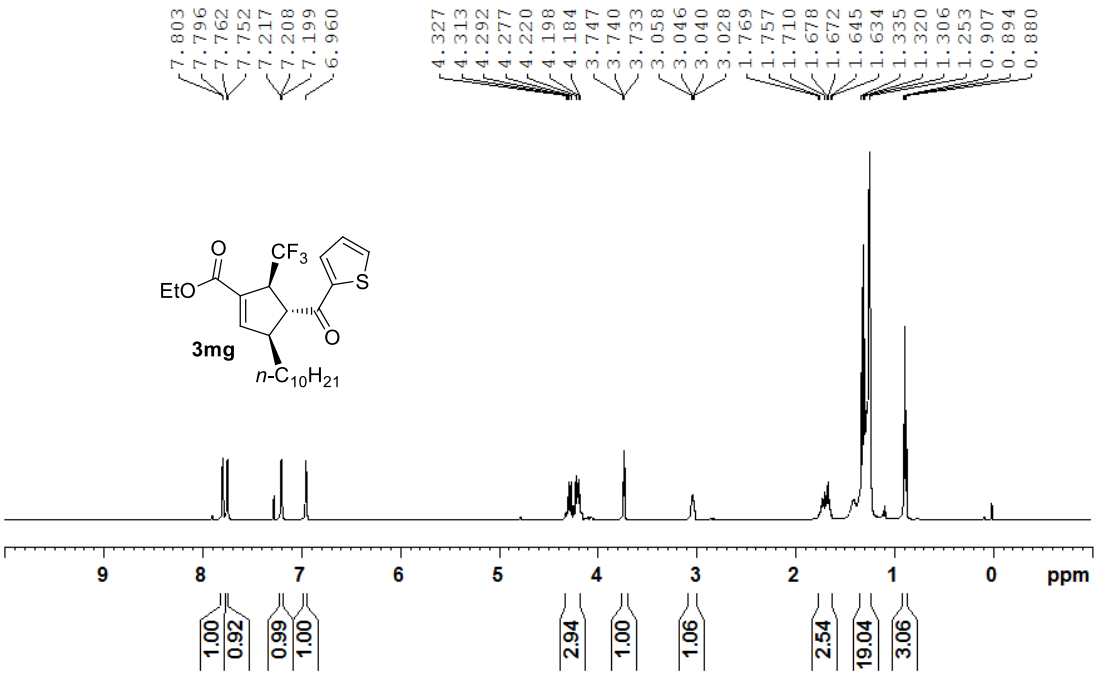

zhouw-7-66c

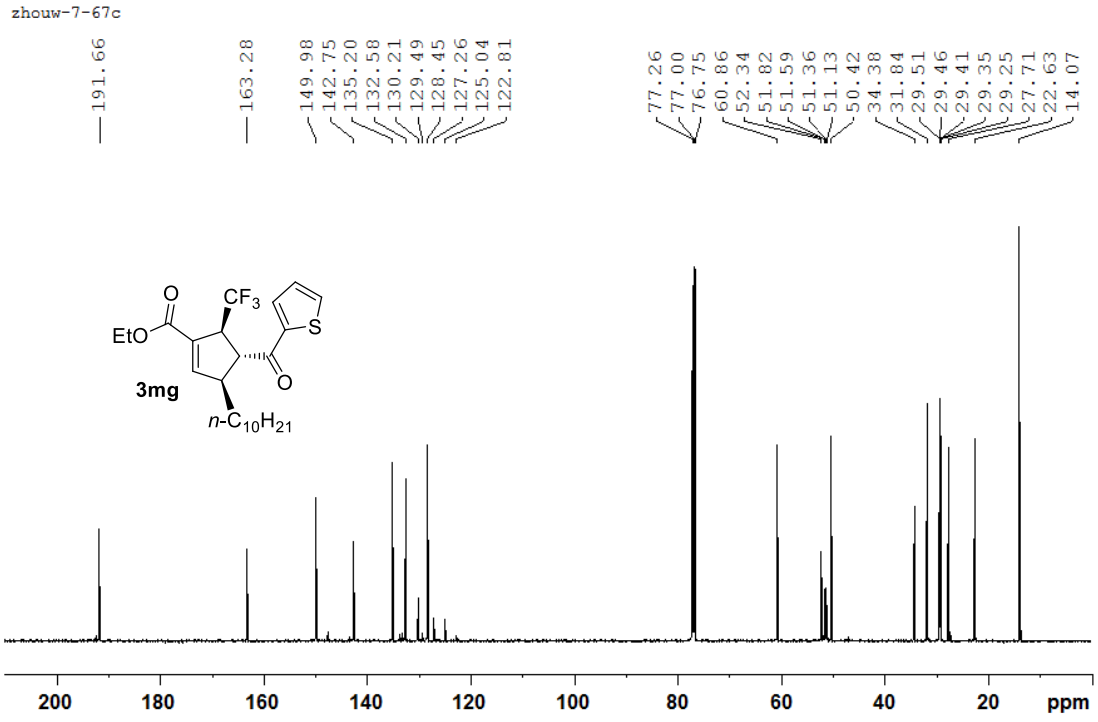


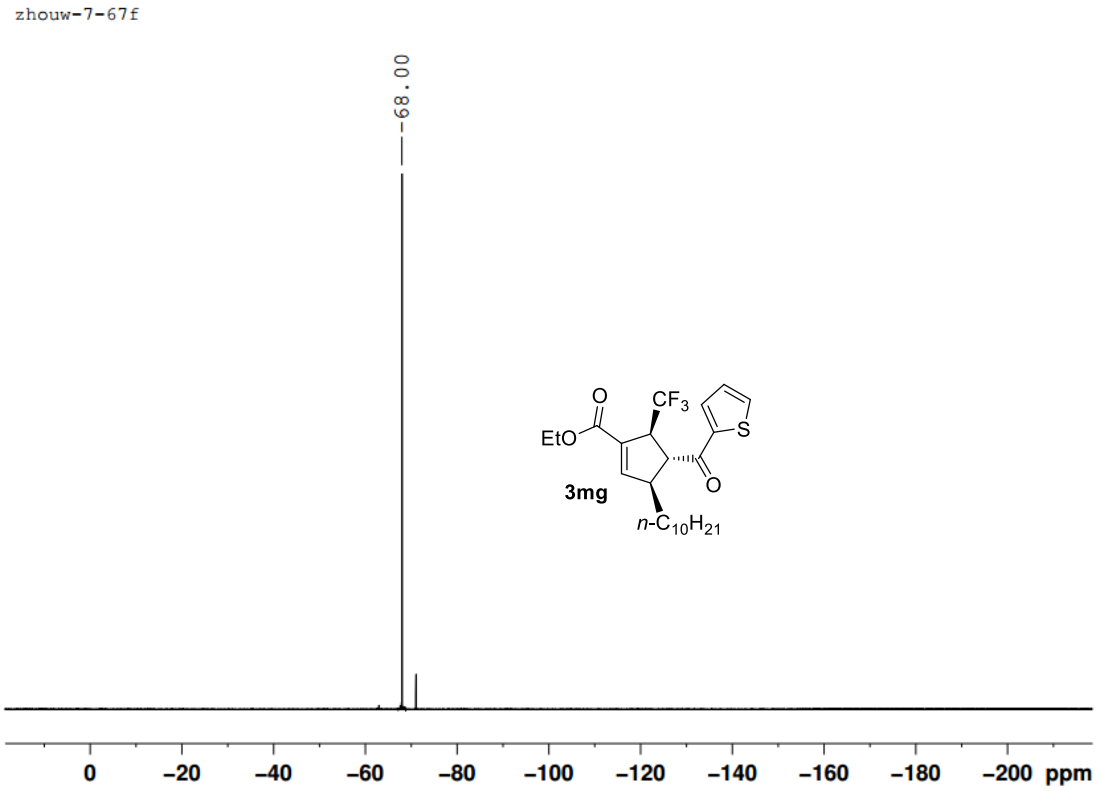
zhouw-7-66fs

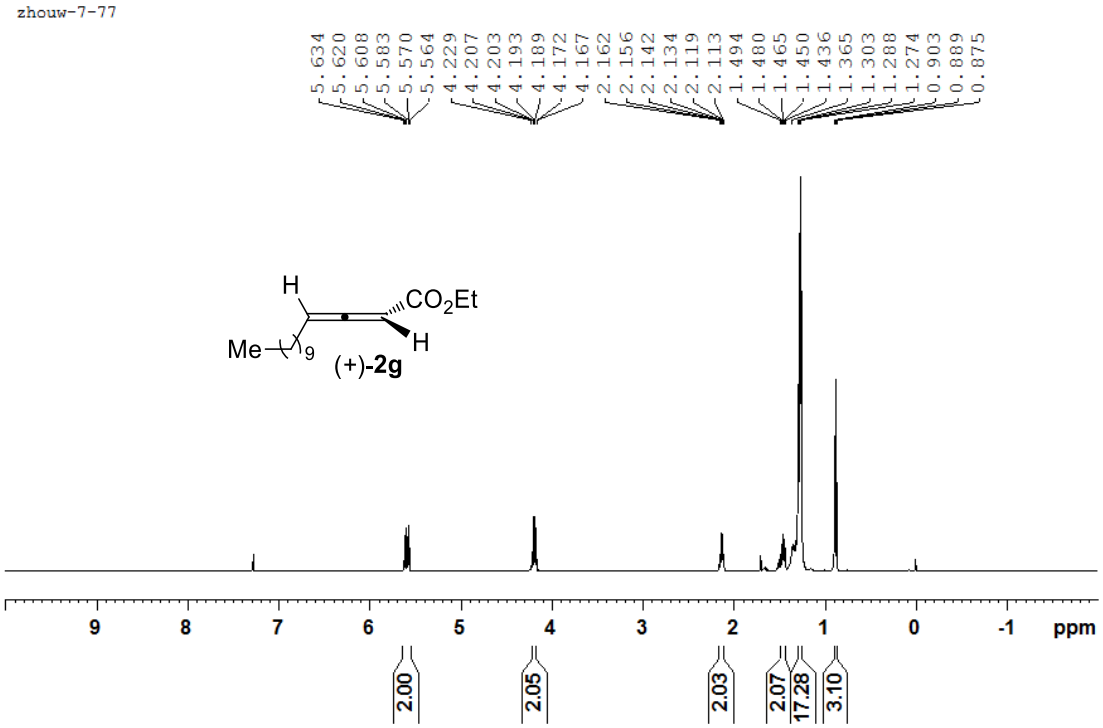


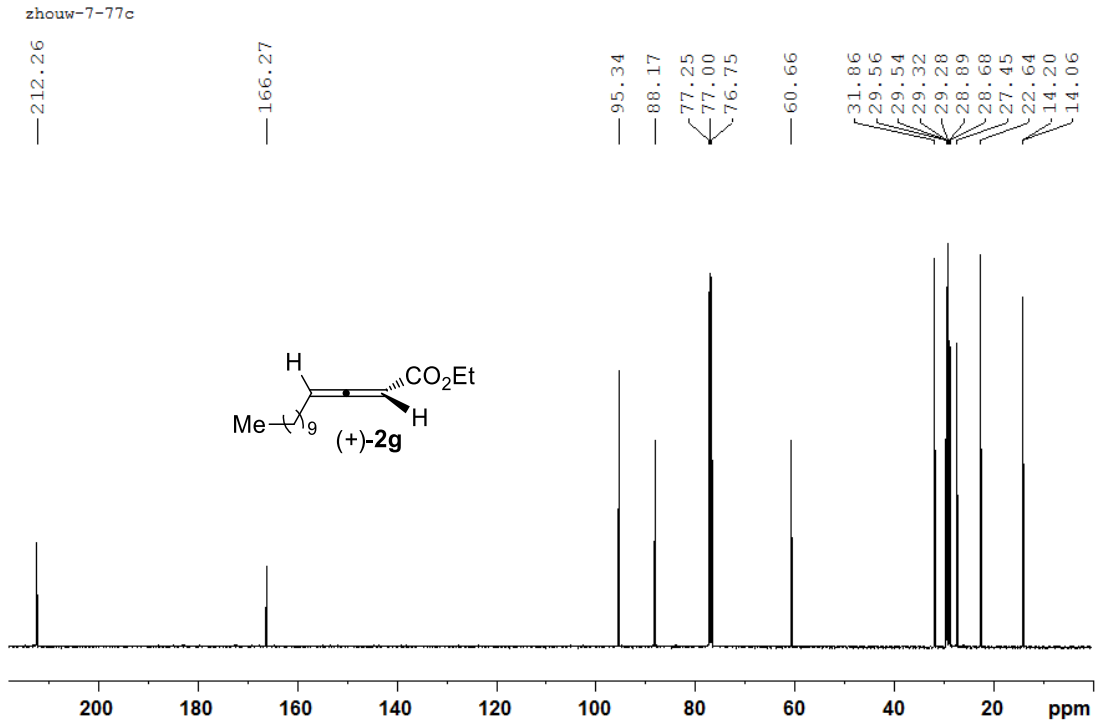

zhouw-7-67




zhouw-7-67c
191.66
163.28
149.98
142.75
135.20
132.58
130.21
129.49
128.45
127.26
125.04
122.81
77.26
77.00
76.75
60.86
52.34
51.82
51.59
51.36
51.13
50.42
34.38
31.84
29.51
29.46
29.41
29.35
29.25
27.71
22.63
14.07
EtO
CF3
S
O
O
3mg
n-C10H21
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-7-67f
-68.00
EtO
CF3
S
O
O
3mg
n-C10H21
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


zhouw-7-77
5.634
5.620
5.608
5.583
5.570
5.564
4.229
4.207
4.203
4.193
4.189
4.172
4.167
2.162
2.156
2.142
2.134
2.119
2.113
1.494
1.480
1.465
1.450
1.436
1.365
1.303
1.288
1.274
0.903
0.889
0.875
H
CO2Et
Me
9
H
(+)-2g
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
2.05
2.03
2.07
17.28
3.10


zhouw-7-77c
212.26
166.27
95.34
88.17
77.25
77.00
76.75
60.66
31.86
29.56
29.54
29.32
29.28
28.89
28.68
27.45
22.64
14.20
14.06
H
CO2Et
Me
9
H
(+)-2g
200
180
160
140
120
100
80
60
40
20
ppm