

Palladium-catalyzed enantioselective alkenylation of alkenylbenzene derivatives

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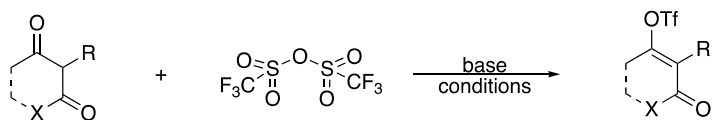
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General Considerations:

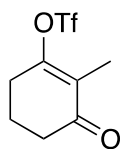
All reactions were performed using oven-dried or flame-dried glassware equipped with a magnetic stir bar under an atmosphere of nitrogen unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification. Dichloromethane, tetrahydrofuran (THF), and acetonitrile were passed through a column of activated alumina immediately prior to use. Methanol was distilled from calcium hydride. The ligand was synthesized according to the literature procedure.¹ ^1H NMR spectra were obtained in CDCl_3 at 300 MHz, 400 MHz or 500 MHz. Chemical shifts are reported in ppm and referenced to the CHCl_3 singlet at 7.26 ppm. ^{13}C NMR spectra were obtained in CDCl_3 at 75 MHz, 100 MHz or 125 MHz and referenced to the center peak of the CDCl_3 triplet at 77.16 ppm. ^{19}F NMR spectra were obtained at 282 MHz (CFCl_3 as the outside standard and low field is positive). The abbreviations s, d, t, quint, sext, sept, dd, ddd, dt, and m stand for the resonance multiplicities singlet, doublet, triplet, quintet, sextet, septet, doublet of doublets, doublet of doublet of doublets, doublet of triplets, and multiplet, respectively. Thin-layer chromatography was performed with EMD silica gel 60 F₂₅₄ plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). GC separations were performed with an HP6890 GC with a flame ionization detector equipped with a DB-5 column using a 50:1 split. IR spectra were recorded using a Thermo Nicolet FT-IR. HRMS data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. LRGC-MS data were obtained on an Agilent Technologies 5975c VL MSD instrument. SFC (supercritical fluid chromatography) analysis was performed at 40 °C, using a Thar instrument fitted with AD-H and OD columns.

Synthesis of Triflates and Substrates

Synthesis of Triflates: 2a-2h

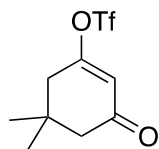


2a: 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate



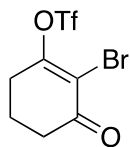
This triflate was prepared according to the literature procedure.² Analytical data matches with the literature.

2b: 5,5-dimethyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate



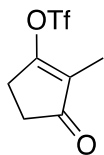
This triflate was prepared according to the literature procedure.² Analytical data matches with the literature.

2c: 2-bromo-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate



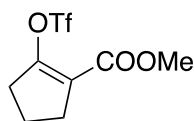
This triflate was prepared according to the literature procedure.³ Analytical data matches with the literature.

2d: 2-methyl-3-oxocyclopent-1-en-1-yl trifluoromethanesulfonate



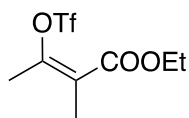
This triflate was prepared according to the literature procedure.⁴ Analytical data matches with the literature.

2e: methyl 2-(((trifluoromethyl)sulfonyl)oxy)cyclopent-1-ene-1-carboxylate



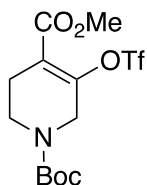
This triflate was prepared according to the literature procedure.⁵ Analytical data matches with the literature.

2f: ethyl (Z)-2-methyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-enoate



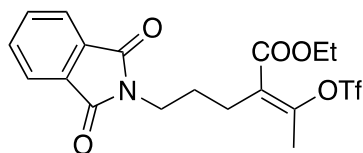
This triflate was prepared according to the literature procedure.⁶ Analytical data matches with the literature.

2g: 1-(*tert*-butyl) 4-methyl 5-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1,4(2*H*)-dicarboxylate



This triflate was prepared according to the literature procedure.⁷ Analytical data matches with the literature.

2h: ethyl (Z)-5-(1,3-dioxoisindolin-2-yl)-2-(1-(((trifluoromethyl)sulfonyl)oxy)ethylidene)-pentanoate

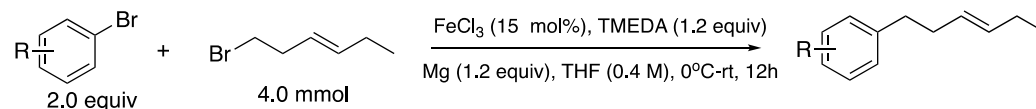


This triflate was prepared according to the literature procedure.⁸ Analytical data matches with the literature.

Synthesis of Alkene Substrates: 1a-1dd

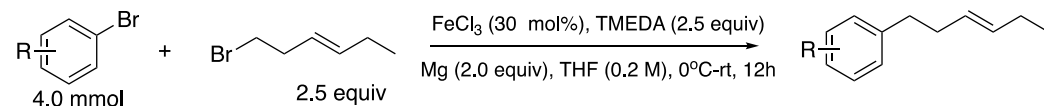
(Prepared according to a modified literature procedure)⁹

General Procedure A:



A 50 mL flask was placed in a water bath (rt), charged with magnesium turnings (116 mg, 4.8 mmol), fitted with a rubber septum, and purged with argon. A solution of FeCl_3 (97.2 mg, 0.6 mmol, 15 mol%) in dry THF (10 mL) was added via syringe followed by TMEDA (724 μL , 4.8 mmol). The mixture was stirred at rt for 20 min. Then, the reaction was cooled to 0 °C, and arylbromide (8.0 mmol) and alkylbromide (4.0 mmol) were added. After 12 h at rt, the reaction was quenched with saturated aqueous NH_4Cl (10 mL) and aqueous HCl (10 %, 4 mL) and extracted with ethyl acetate (3×20 mL). The combined organic phases were dried (Na_2SO_4), concentrated in vacuo, and subjected to flash chromatography (SiO_2 /cyclohexane/ethyl acetate).

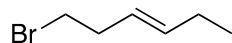
General Procedure B:



A 50 mL flask was placed in a water bath (rt), charged with magnesium turnings (192 mg, 8.0 mmol), fitted with a rubber septum, and purged with argon. A solution of FeCl_3 (194 mg, 1.2 mmol, 30 mol%) in dry THF (20 mL) was added via syringe followed by TMEDA (1.5 mL, 10.0

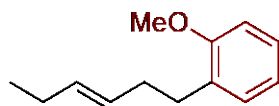
mmol). The mixture was stirred at rt for 20 min. Then, the reaction was cooled to 0 °C, and arylbromide (4 mmol) and alkylbromide (10.0 mmol) were added. After 12 h at rt, the reaction was quenched with saturated aqueous NH₄Cl (10 mL) and aqueous HCl (10 %, 4 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried (Na₂SO₄), concentrated in vacuo, and subjected to flash chromatography (SiO₂/hexane/CH₂Cl₂).

(*E*)-1-bromohex-3-ene (**1ba**)



To a solution of *trans*-3-hexene-1-ol (9.0 g, 90.0 mmol) in CH₂Cl₂ (90 mL) was added PPh₃ (triphenylphosphine, 24.6 g, 93.6 mmol). NBS (*N*-bromo-succinimide, 16.8 g, 93.6 mmol) was added in batches to the colorless mixture over 40 minutes. The yellow solution was stirred for 24 h at rt. After this time, the solution was passed through a short silica plug to remove any solid and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (gradient elution: hexanes), and concentrated in vacuo carefully to afford product **1ba** as a colorless oil (10.4 g, 71% yield): *R_f* = 0.70 (hexanes). NMR data match the one reported in the literature.¹⁰ ¹H NMR (500 MHz, CDCl₃) δ 5.59 (dt, *J* = 15.3, 6.3 Hz, 1 H), 5.39 (dt, *J* = 15.3, 6.7 Hz, 1 H), 3.37 (t, *J* = 7.2 Hz, 2 H), 2.55 (q, *J* = 6.8 Hz, 2 H), 2.03 (quintet, *J* = 6.7 Hz, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 135.4, 125.4, 36.0, 32.9, 25.5, 13.6.

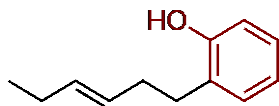
(*E*)-1-(hex-3-en-1-yl)-2-methoxybenzene (**1e**):



The general procedure A was followed using 1-bromo-2-methoxybenzene (**1se**, 14.96 g, 80 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 6.480 g, 40 mmol) in 40 mmol scale. Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1e** as a colorless oil (3.75 g, 49% yield): *R_f* = 0.50 (25% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.12 (m, 2H), 6.98-6.82 (m, 2H), 5.59 – 5.42 (m, 2H), 3.84 (s, 3H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.35 – 2.24 (m, 2H), 2.08 – 1.96 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.4, 132.2, 130.6, 129.8, 128.9, 126.9, 120.2, 110.2, 55.2, 32.7, 30.5, 25.6, 13.9; **IR** (neat) 2960, 2835, 1601, 1493, 1463, 1240, 1179, 1051, 1032, 965, 748

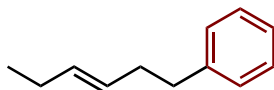
cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₃H₁₉O (M+H)⁺: 191.1436, found 191.1439.

(*E*)-4-(hex-3-en-1-yl)phenol(**1a**)¹¹



Under a nitrogen atmosphere, a 60% dispersion of NaH (0.93 g, 23.3 mmol) in oil was washed with dry hexanes (20 mL) and dry ether (20 mL), and then the NaH was suspended in dry DMF (20 mL). A solution of ethanethiol (2.0 mL, 27 mmol) in DMF (20 mL) was added and when gas evolution had ceased, **1e** (1.92 g, 10 mmol) in DMF (10 mL) was added. The mixture was heated at reflux for 2 h, cooled in an ice bath, and carefully neutralized with aqueous 10% HCl. The neutralized solution was extracted with ether (5 X 100 mL) and the ethereal extracts were washed with water (150 mL) and brine (3 X 100 mL). The resulting pale yellow solution was dried and evaporated to leave an orange oil, which was purified by chromatography on silica gel (gradient elution: 10~35% CH₂Cl₂/hexanes) afforded product **1a** as a colorless oil (1.40 g, 78% yield): R_f = 0.40 (50% CH₂Cl₂/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.20-7.00 (m, 2H), 6.88 (t, J = 6.0 Hz, 1H), 6.78 (d, J = 9.0 Hz, 1H), 5.60 – 5.40 (m, 2H), 4.63 (br, 1H), 2.68 (t, J = 7.5 Hz, 2H), 2.38 – 2.23 (m, 2H), 2.09 – 1.94 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 153.4, 133.1, 130.3, 128.4, 128.0, 127.1, 120.8, 115.3, 32.7, 30.4, 25.6, 13.8; **IR** (neat) 3436, 2961, 2930, 1613, 1591, 1454, 1232, 1094, 965, 748 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₂H₁₇O (M+H)⁺: 177.1279, found 177.1285.

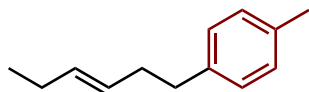
(*E*)-hex-3-en-1-ylbenzene (**1b**):



The general procedure A was followed using bromobenzene (**1sb**, 1256 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1b** as a colorless oil (332 mg, 52% yield): R_f = 0.50 (hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.35– 7.16 (m, 5H), 5.56 – 5.42 (m, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.38 – 2.29 (m, 2H), 2.08 – 1.96 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 142.2, 132.6, 128.4, 128.3, 128.2, 125.7, 36.2, 34.4, 25.6, 13.9; **IR**

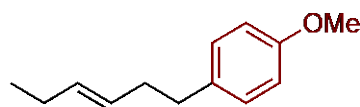
(neat) 2958, 2923, 1454, 965, ¹³C NMR (125 MHz, CDCl₃) δ 139.2, 135.0, 132.5, 128.9, 128.5, 128.3, 35.7, 34.6, 25.6, 21.0, 13.9; **IR** (neat) 2961, 2922, 1515, 1453, 965, 804 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₇ (M+H)⁺: 161.1330, found 161.1331.

(*E*)-1-(hex-3-en-1-yl)-4-methylbenzene (**1c**):



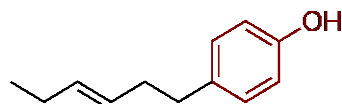
The general procedure A was followed using 1-bromo-4-methylbenzene (**1sc**, 1368 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1c** as a colorless oil (418 mg, 60% yield): *R_f* = 0.50 (hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.24 – 7.05 (m, 4H), 5.56 – 5.35 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.35 – 2.22 (m, 5H), 2.08 – 1.96 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.2, 135.0, 132.5, 128.9, 128.5, 128.3, 35.7, 34.6, 25.6, 21.0, 13.9; **IR** (neat) 2961, 2922, 1515, 1453, 965, 804 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₉ (M+H)⁺: 175.1487, found 175.1501.

(*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**):



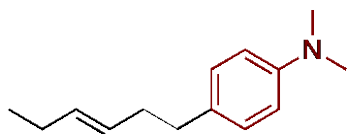
The general procedure A was followed using 1-bromo-4-methoxybenzene (**1sd**, 1496 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1d** as a colorless oil (395 mg, 52% yield): *R_f* = 0.40 (25% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, *J* = 5.0 Hz, 2H), 6.84 (d, *J* = 5.0 Hz, 2H), 5.59 – 5.35 (m, 2H), 3.80 (s, 3H), 2.63 (t, *J* = 10.0 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.08 – 1.96 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.7, 134.3, 132.6, 129.3, 128.4, 113.6, 55.2, 35.2, 34.7, 25.6, 13.9; **IR** (neat) 2962, 2930, 1601, 1509, 1454, 1221, 1157, 965, 823 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₉O (M+H)⁺: 191.1436, found 191.1437.

(*E*)-4-(hex-3-en-1-yl)phenol(**1f**)¹¹



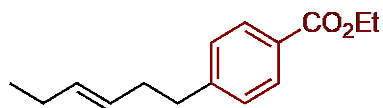
Under a nitrogen atmosphere, a 60% dispersion of NaH (0.933 g, 23.3 mmol) in oil was washed with dry hexanes (10 mL) and dry ether (10 mL), and then the NaH was suspended in dry DMF (16 mL). A solution of ethanethiol (1.95 mL, 27 mmol) in DMF (23 mL) was added and when gas evolution had ceased, **1d** (1.92 g, 10.0 mmol) in DMF (13 mL) was added. The mixture was heated at reflux for 2 h, cooled in an ice bath, and carefully neutralized with aqueous 10% HCl. The neutralized solution was extracted with ether (5 X 50 mL) and the ethereal extracts were washed with water (150 mL) and brine (3 X 50 mL). The resulting pale yellow solution was dried and evaporated to leave an orange oil, which was purified by chromatography on silica gel (gradient elution: 10~35% CH₂Cl₂/hexanes) afforded product **1f** as a colorless oil (1.43 g, 80% yield): *R_f* = 0.30 (50% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.05 (d, *J* = 5.0 Hz, 2H), 6.75 (d, *J* = 10.0 Hz, 2H), 5.52 – 5.32 (m, 2H), 4.65 (br, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.20 (m, 2H), 2.03 – 1.91 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 153.4, 134.5, 132.6, 129.5, 128.4, 115.0, 35.2, 34.6, 25.6, 13.9; IR (neat) 3369, 2961, 2929, 1701, 1613, 1513, 1441, 1359, 1221, 1171, 966, 827 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₇O (M+H)⁺: 177.1279, found 177.1282.

(*E*)-4-(hex-3-en-1-yl)-*N,N*-dimethylaniline (**1g**):



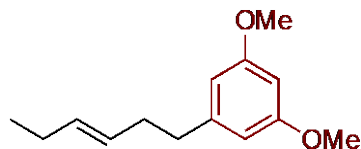
The general procedure A was followed using 4-bromo-*N,N*-dimethylaniline (**1sg**, 1592 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1g** as a colorless oil (503 mg, 62% yield): *R_f* = 0.30 (25% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, *J* = 10.0 Hz, 1H), 6.74 (d, *J* = 10.0 Hz, 1H), 5.60 – 5.42 (m, 2H), 2.95 (s, 6H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.35 – 2.24 (m, 2H), 2.12 – 1.98 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 149.0, 132.3, 130.5, 129.0, 128.8, 113.0, 40.9, 35.2, 34.8, 25.6, 13.9; IR (neat) 2960, 2917, 2846, 1615, 1519, 1443, 1341, 1223, 1162, 965, 947, 803 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₁₄H₂₂N (M+H)⁺: 204.1752, found 204.1757.

ethyl (*E*)-4-(hex-3-en-1-yl)benzoate (**1h**)



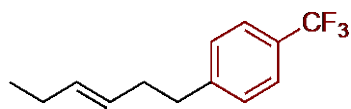
A 50 mL flask was placed in a water bath (rt), charged with magnesium turnings (144 mg, 6.0 mmol), fitted with a rubber septum, and purged with argon. A solution of FeCl₃ (146 mg, 0.9 mmol, 30 mol %) in dry THF (15 mL) was added via syringe followed by TMEDA (280 mg, 2.4 mmol). The mixture was stirred at rt for 20 min. Then, the reaction was cooled to 0 °C, and ethyl 4-bromobenzoate (**1sh**, 687 mg, 3 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1215 mg, 7.5 mmol) were added. After 12 h at rt, the reaction was quenched with saturated aqueous NH₄Cl (10 mL) and aqueous HCl (10 %, 4 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried (Na₂SO₄), concentrated in vacuo, and subjected to flash chromatography (SiO₂/hexane/CH₂Cl₂) to afford product **1h** as a colorless oil (341 mg, 49% yield): *R*_f = 0.35 (50% CH₂Cl₂/hexanes); **¹H NMR** (300 MHz, CDCl₃) δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 6.0 Hz, 2H), 5.55 – 5.32 (m, 2H), 4.36 (q, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.38 – 2.24 (m, 2H), 2.08 – 1.90 (m, 2H), 1.38 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 166.7, 147.5, 133.1, 129.5, 128.4, 128.0, 127.7, 60.7, 36.1, 34.0, 25.5, 14.3, 13.8; **IR** (neat) 2962, 2932, 1714, 1270, 1176, 1100, 1022, 967, 764, 711 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₂₁O₂ (M+H)⁺: 233.1542, found 233.1547.

(*E*)-1-(hex-3-en-1-yl)-3,5-dimethoxybenzene (**1i**)



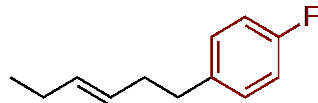
The general procedure B was followed using 1-bromo-3,5-dimethoxybenzene (**1si**, 864 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: CH₂Cl₂/hexanes) afforded product **1i** as a colorless oil (616 mg, 70% yield): *R*_f = 0.25 (25% CH₂Cl₂/hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 6.35 (s, 2H), 6.30 (s, 1H), 5.55 – 5.36 (m, 2H), 3.78 (s, 6H), 2.61 (t, *J* = 10.0 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.08 – 1.92 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 160.7, 144.6, 132.7, 128.3, 106.5, 97.8, 55.2, 36.5, 34.2, 25.6, 13.9; **IR** (neat) 2962, 2932, 1714, 1270, 1176, 1100, 1022, 967, 764, 711 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₂₁O₂ (M+H)⁺: 221.1542, found 221.1549.

(*E*)-1-(hex-3-en-1-yl)-4-(trifluoromethyl)benzene (**1j**)



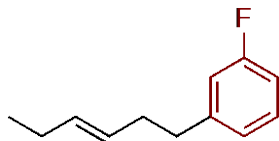
The general procedure B was followed using 1-bromo-4-(trifluoromethyl)benzene (**1sj**, 900 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1j** as a colorless oil (483 mg, 53% yield): R_f = 0.50 (hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.53 (d, J = 10.0 Hz, 2H), 7.28 (d, J = 5.0 Hz, 1H), 5.55 – 5.36 (m, 2H), 2.73 (t, J = 10.0 Hz, 2H), 2.38 – 2.26 (m, 2H), 2.08 – 1.92 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.3, 133.3, 128.8, 128.2 (q, J = 32.5 Hz), 127.6, 125.1, 124.4 (q, J = 270.00 Hz), 36.0, 34.0, 25.6, 13.8; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 62.7 (s, 3F); **IR** (neat) 2964, 2933, 1619, 1322, 1162, 1119, 1066, 1019, 966, 844, 827 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{Ag}$ ($\text{M}+\text{Ag}$) $^+$: 335.0177, found 335.0219.

(*E*)-1-fluoro-4-(hex-3-en-1-yl)benzene (**1k**)



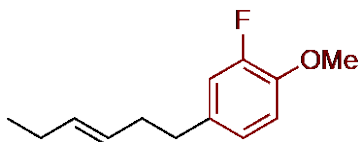
The general procedure B was followed using 1-bromo-4-fluorobenzene (**1sk**, 696 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes/ CH_2Cl_2) afforded product **1k** as a colorless oil (292 mg, 41% yield): R_f = 0.50 (hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.16 – 7.09 (m, 2H), 7.00 – 6.93 (m, 2H), 5.53 – 5.37 (m, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.08 – 1.95 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 161.2 (d, J = 241.25 Hz), 137.7 (d, J = 3.75 Hz), 132.9, 129.7 (d, J = 7.50 Hz), 128.0, 114.9 (d, J = 21.25 Hz), 35.3, 34.5, 25.6, 13.9; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 118.4 (m, 1F); **IR** (neat) 2962, 2931, 1601, 1509, 1455, 1221, 1157, 966, 850, 823 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{F}$ ($\text{M}+\text{H}$) $^+$: 179.1236, found 179.1222.

(*E*)-1-fluoro-3-(hex-3-en-1-yl)benzene (**1l**)



The general procedure B was followed using 1-bromo-3-fluorobenzene (**1sl**, 696 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1l** as a colorless oil (356 mg, 50% yield): R_f = 0.50 (hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.26 – 7.16 (m, 1H), 6.98 – 6.82 (m, 3H), 5.55 – 5.34 (m, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.08 – 1.92 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 162.9 (d, J = 243.75 Hz), 144.8 (d, J = 6.25 Hz), 133.0, 129.5 (d, J = 8.75 Hz), 127.8, 124.1 (d, J = 2.50 Hz), 115.3 (d, J = 21.25 Hz), 112.5 (d, J = 21.25 Hz), 35.9 (d, J = 1.25 Hz), 34.1, 25.5, 13.9; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 114.6 (m, 1F); **IR** (neat) 2962, 2931, 1615, 1589, 1487, 1255, 1140, 966, 864, 779, 690 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{F}$ ($\text{M}+\text{H}$) $^+$: 179.1236, found 179.1241.

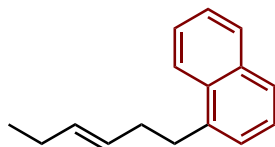
(*E*)-2-fluoro-4-(hex-3-en-1-yl)-1-methoxybenzene (**1m**)



A 50 mL flask was placed in a water bath (rt), charged with magnesium turnings (192 mg, 8.0 mmol), fitted with a rubber septum, and purged with argon. A solution of FeCl_3 (194 mg, 1.2 mmol, 30 mol%) in dry THF (20 mL) was added via syringe followed by TMEDA (1.5 mL, 10.0 mmol). The mixture was stirred at rt for 20 min. Then, the reaction was cooled to 0 °C, and 4-bromo-2-fluoro-1-methoxybenzene (**1sm**, 816 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol) were added. After 12 h at rt, the reaction was quenched with saturated aqueous NH_4Cl (10 mL) and aqueous HCl (10 %, 4 mL) and extracted with ethyl acetate (3×20 mL). The combined organic phases were dried (Na_2SO_4), concentrated in vacuo, and subjected to flash chromatography ($\text{SiO}_2/\text{hexane}/\text{CH}_2\text{Cl}_2$) to afford product **1m** as a colorless oil (333 mg, 40% yield): R_f = 0.50 (25% $\text{CH}_2\text{Cl}_2/\text{hexanes}$); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.95 – 6.85 (m, 3H), 5.55 – 5.34 (m, 2H), 3.87 (s, 3H), 2.60 (t, J = 7.5 Hz, 2H), 2.35 – 2.22 (m, 2H), 2.05 – 1.96 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.2 (d, J = 245.00 Hz), 145.6 (d, J = 11.25 Hz), 135.4 (d, J = 5.00 Hz), 132.9, 127.9, 123.8 (d, J = 3.75 Hz), 116.1 (d, J = 18.75 Hz), 113.4, 56.4, 35.1, 34.3, 25.5, 13.8; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 136.4 (m, 1F); **IR** (neat)

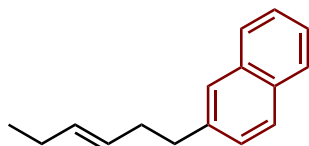
2961, 2932, 1585, 1515, 1442, 1272, 1222, 1125, 1030, 966, 868, 804, 760 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{OF}$ ($\text{M}+\text{H}$) $^{+}$: 209.1342, found 209.1344.

(*E*)-1-(hex-3-en-1-yl)naphthalene (**1n**):



The general procedure B was followed using 1-bromonaphthalene (**1sn**, 828 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1n** as a colorless oil (442 mg, 53% yield): R_f = 0.50 (hexanes); ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, J = 5.0 Hz, 1H), 7.86 (d, J = 5.0 Hz, 1H), 7.72 (d, J = 5.0 Hz, 1H), 7.60 – 7.28 (m, 4H), 5.64 – 5.42 (m, 2H), 3.14 (t, J = 7.5 Hz, 2H), 2.52 – 2.38 (m, 2H), 2.08 – 1.96 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 138.3, 133.9, 132.7, 131.9, 128.7, 128.5, 126.5, 125.9, 125.6, 125.5, 125.4, 123.8, 33.7, 33.3, 25.6, 13.9; **IR** (neat) 2960, 2931, 1596, 1510, 1459, 964, 792, 773, 731 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{19}$ ($\text{M}+\text{H}$) $^{+}$: 211.1487, found 211.1486.

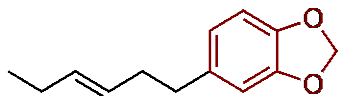
(*E*)-2-(hex-3-en-1-yl)naphthalene (**1o**):



The general procedure B was followed using 2-bromonaphthalene (**1so**, 828 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1o** as a colorless oil (435 mg, 52% yield): R_f = 0.50 (hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.72 (m, 3H), 7.62 (s, 1H), 7.47 – 7.37 (m, 2H), 7.34 (d, J = 5.0 Hz, 1H), 5.55 – 5.40 (m, 2H), 2.84 (t, J = 7.5 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.08 – 1.92 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.7, 133.6, 132.8, 132.0, 128.3, 127.7, 127.6, 127.5, 127.4, 126.4, 125.8, 125.0, 36.3, 34.3, 25.6, 13.9; **IR** (neat) 2960, 2930, 1600, 1508, 1453, 964, 851, 813, 742 cm^{-1} ; **HRMS**

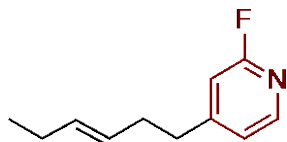
(ESI-TOF) m/z calcd for $C_{16}H_{19}$ ($M+H$)⁺: 211.1487, found 211.1488.

(*E*)-5-(hex-3-en-1-yl)benzo[*d*][1,3]dioxole (**1p**):

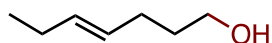


The general procedure A was followed using 5-bromobenzo[*d*][1,3]dioxole (**1sp**, 1600 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH_2Cl_2 /hexanes) afforded product **1p** as a colorless oil (490 mg, 60% yield): R_f = 0.20 (25% CH_2Cl_2 /hexanes); ¹H NMR (300 MHz, $CDCl_3$) δ 6.92-6.52 (m, 3H), 5.91 (s, 2H), 5.52 – 5.32 (m, 2H), 2.59 (t, J = 6.0 Hz, 2H), 2.32 – 2.20 (m, 2H), 2.06 – 1.94 (m, 2H), 0.96 (t, J = 6.0 Hz, 3H); ¹³C NMR (125 MHz, $CDCl_3$) δ 147.4, 145.5, 136.1, 132.7, 128.2, 121.1, 108.9, 108.0, 100.7, 35.9, 34.7, 25.6, 13.9; IR (neat) 2961, 2929, 1502, 1487, 1440, 1242, 1186, 1039, 966, 938, 806, 634 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{17}O_2$ ($M+H$)⁺: 205.1229, found 205.1228.

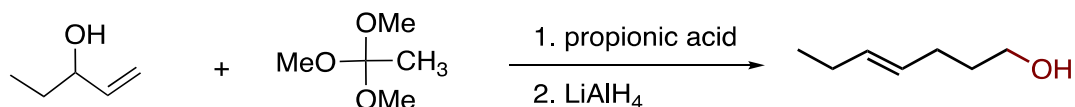
(*E*)-2-fluoro-4-(hex-3-en-1-yl)pyridine (**1q**)



The general procedure B was followed using 4-bromo-2-fluoropyridine (**1sq**, 700 mg, 4.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 1620 mg, 10.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes/) afforded product **1q** as a colorless oil (308 mg, 43% yield): R_f = 0.25 (50% CH_2Cl_2 /hexanes); ¹H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 3.0 Hz, 1H), 7.02-6.90 (m, 1H), 6.73 (s, 1H), 5.52 – 5.30 (m, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.37 – 2.24 (m, 2H), 2.04 – 1.90 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 164.0 (d, J = 236.25 Hz), 157.0 (d, J = 8.25 Hz), 147.1 (d, J = 15.75 Hz), 133.8, 126.7, 121.7 (d, J = 3.75 Hz), 109.1 (d, J = 36.00 Hz), 35.1, 32.8, 25.4, 13.7; ¹⁹F NMR (282 MHz, $CDCl_3$) δ 69.8 (s, 1F); IR (neat) 2962, 2933, 1611, 1566, 1409, 1277, 1147, 967, 837, 652, 562 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{15}NF$ ($M+H$)⁺: 180.1189, found 180.1193.

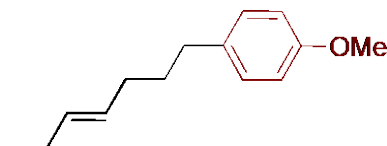


(*E*)-hept-4-en-1-ol



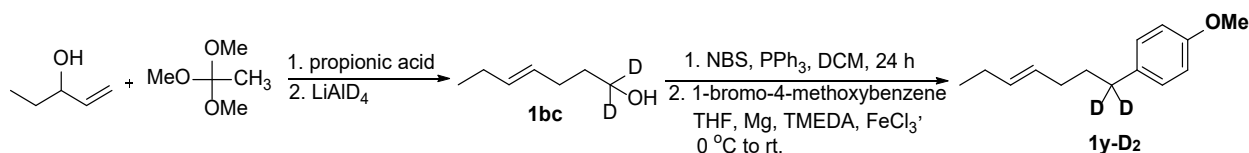
1-Penten-3-ol (2.5 g, 29 mmol, 1.0 equiv), propionic acid (0.1 mL, 1.45 mmol, 0.05 equiv), and trimethyl orthoacetate (10.5 g, 87 mmol, 3.0 equiv) were added to a high-pressure sealed tube. The reaction vessel was then sealed and heated at 120 °C for 12 h. Upon completion, the reaction contents were cooled to 25 °C, the cap was removed, and the reaction contents were reheated to 120 °C for 2 h, open to the atmosphere, to distill off the methanol byproduct. The resultant yellow oil was then dissolved in Et₂O (20 mL) and cannulated dropwise into a suspension of lithium aluminium hydride (1.1 g, 29 mmol, 1.0 equiv) in Et₂O (100 mL) at 0 °C. The resultant slurry was stirred at 0 °C for 60 min and then quenched by careful dropwise addition of saturated aqueous ammonium chloride (20 mL). The resultant biphasic mixture was stirred vigorously for 16 h at 25 °C. The layers were then allowed to separate and the aqueous layer was extracted with additional diethyl ether (2 × 200 mL). The combined organic layers were washed with brine (200 mL), dried over sodium sulphate, and concentrated. The resultant crude oil was purified by flash column chromatography (silica gel, 0-20% ethyl acetate in hexane) to afford (*E*)-hept-4-en-1-ol (2.1g, 64%) as a moderately volatile colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 5.49 (m, 1 H), 5.41 (m, 1 H), 3.65 (t, *J* = 6.4 Hz, 2 H), 2.12–1.96 (m, 4 H), 1.64 (quintet, *J* = 6.8 Hz, 2 H), 1.40 (br s, 1 H), 0.97 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 132.9, 128.6, 62.8, 32.6, 29.0, 25.7, 14.0. Analytical data matches with the literature.¹²

(*E*)-1-(hept-4-en-1-yl)-4-methoxybenzene (**1y**)

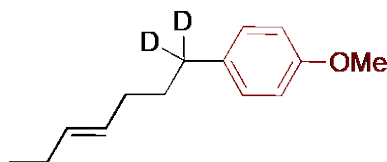


To a solution of (*E*)-hept-4-en-1-ol (1.026 g, 9.0 mmol) in CH₂Cl₂ (9 mL) was added PPh₃ (triphenylphosphine, 2.46 g, 9.36 mmol). NBS (*N*-bromo-succinimide, 1.68 g, 9.36 mmol) was added in batches to the colorless mixture over 15 minutes. The yellow solution was stirred for 24 h at rt. After this time, the solution was passed through a short silica plug to remove any solid

and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (gradient elution: hexanes), and concentrated in vacuo carefully to afford product a colorless oil **1bb** (1.188 g, 75% yield): $R_f = 0.65$ (hexanes). Using **1bb** (704 mg, 4.0 mmol) and 1-bromo-4-methoxybenzene (**1sd**, 1496 mg, 8.0 mmol) by the general procedure A. Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1y** as a colorless oil (449 mg, 55% yield): $R_f = 0.50$ (25% CH₂Cl₂/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.13 (d, $J = 6.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 5.59 – 5.33 (m, 2H), 3.81 (s, 3H), 2.58 (t, $J = 9.0$ Hz, 2H), 2.10 – 1.90 (m, 4H), 1.80 – 1.53 (m, 2H), 1.01 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.6, 134.7, 132.4, 129.3, 128.8, 113.6, 55.2, 34.4, 32.0, 31.6, 25.6, 14.0; IR (neat) 2960, 2929, 2834, 1612, 1511, 1461, 1242, 1175, 1038, 965, 818, 805 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₄H₂₁O (M+H)⁺: 205.1592, found 205.1591.



(*E*)-1-(hept-4-en-1-yl-1,1-*d*₂)-4-methoxybenzene (**1y-D₂**)

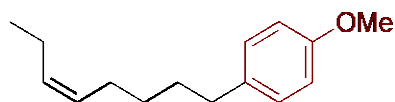


Using the same procedure of synthesis (*E*)-hept-4-en-1-ol to afford a moderately volatile colorless oil **1bc** (lithium aluminium deuteride instead of lithium aluminium hydride). To a solution of **1bc** (1.026 g, 9.0 mmol) in CH₂Cl₂ (9 mL) was added PPh₃ (triphenylphosphine, 2.46 g, 9.36 mmol). NBS (*N*-bromo-succinimide, 1.68 g, 9.36 mmol) was added in batches to the colorless mixture over 15 minutes. The yellow solution was stirred for 24 h at rt. After this time, the solution was passed through a short silica plug to remove any solid and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (gradient elution: hexanes), and concentrated in vacuo carefully to afford product a colorless oil **1bd** (1.188 g, 75% yield): $R_f = 0.65$ (hexanes).

Using this colorless oil (**1bd**, 704 mg, 4.0 mmol) and 1-bromo-4-methoxybenzene (**1sd**, 1496 mg, 8.0 mmol) by the general procedure A. Purification of this material by chromatography on

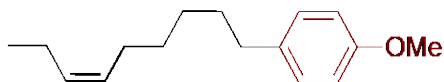
silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1y-D₂** as a colorless oil (449 mg, 55% yield): *R_f* = 0.50 (25% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, *J* = 10.0 Hz, 2H), 6.83 (d, *J* = 10.0 Hz, 2H), 5.59 – 5.33 (m, 2H), 3.79 (s, 3H), 2.10 – 1.90 (m, 4H), 1.75 – 1.53 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); HRMS (ESI-TOF) *m/z* calcd for C₁₄H₁₉D₂O (M+H)⁺: 207.1718, found 207.1719.

(*Z*)-1-methoxy-4-(oct-5-en-1-yl)benzene (**1z**)



To a solution of (*Z*)-oct-5-en-1-ol (1.152 g, 9.0 mmol) in CH₂Cl₂ (9 mL) was added PPh₃ (triphenylphosphine, 2.46 g, 9.36 mmol). NBS (*N*-bromo-succinimide, 1.68 g, 9.36 mmol) was added in batches to the colorless mixture over 15 minutes. The yellow solution was stirred for 24 h at rt. After this time, the solution was passed through a short silica plug to remove any solid and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (gradient elution: hexanes), and concentrated in vacuo carefully to afford product **1be** as a colorless oil (1.231 g, 72% yield): *R_f* = 0.65 (hexanes). **The general procedure A** was followed using 1-bromo-4-methoxybenzene (**1sz**, 1496 mg, 8.0 mmol) and **1be** (760 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1z** as a colorless oil (523 mg, 60% yield): *R_f* = 0.50 (25% CH₂Cl₂/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, *J* = 10.0 Hz, 2H), 6.83 (d, *J* = 10.0 Hz, 2H), 5.45 – 5.25 (m, 2H), 3.79 (s, 3H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.10 – 1.99 (m, 4H), 1.68 – 1.50 (m, 2H), 1.47 – 1.33 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.6, 134.8, 131.7, 129.2, 129.0, 113.6, 55.2, 34.9, 31.3, 29.3, 26.9, 20.5, 14.4; IR (neat) 2929, 2854, 1611, 1511, 1462, 1299, 1243, 1175, 1036, 821, 698 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₁₅H₂₃O (M+H)⁺: 219.1749, found 219.1753.

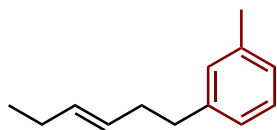
(*Z*)-1-methoxy-4-(non-6-en-1-yl)benzene (**1aa**)



To a solution of (*Z*)-non-6-en-1-ol (1.278 g, 9.0 mmol) in CH₂Cl₂ (9 mL) was added PPh₃ (triphenylphosphine, 2.46 g, 9.36 mmol). NBS (*N*-bromo-succinimide, 1.68 g, 9.36 mmol) was

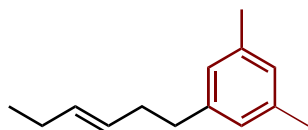
added in batches to the colorless mixture over 15 minutes. The yellow solution was stirred for 24 h at rt. After this time, the solution was passed through a short silica plug to remove any solid and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (gradient elution: hexanes), and concentrated in vacuo carefully to afford product **1bf** as a colorless oil (1.377 g, 75% yield): $R_f = 0.65$ (hexanes). The general procedure A was followed using 1-bromo-4-methoxybenzene (**1saa**, 1496 mg, 8.0 mmol) and **1bf** (816 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: 2~20% CH₂Cl₂/hexanes) afforded product **1aa** as a colorless oil (575 mg, 62% yield): $R_f = 0.50$ (25% CH₂Cl₂/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.13 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 5.45 – 5.28 (m, 2H), 3.81 (s, 3H), 2.58 (t, $J = 7.5$ Hz, 2H), 2.15 – 1.95 (m, 4H), 1.72 – 1.50 (m, 2H), 1.49 – 1.25 (m, 4H), 1.00 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 157.5, 134.9, 131.6, 129.2, 129.1, 113.6, 55.2, 35.0, 31.7, 29.6, 28.9, 27.0, 20.5, 14.4; IR (neat) 2928, 2854, 1612, 1511, 1462, 1243, 1175, 1037, 826, cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₆H₂₅O (M+H)⁺: 233.1905, found 233.1912.

(*E*)-1-(hex-3-en-1-yl)-3-methylbenzene (**1bb**)



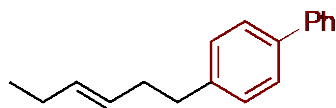
The general procedure A was followed using 1-bromo-3-methylbenzene (**1sbb**, 1368 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1bb** as a colorless oil (418 mg, 60% yield): $R_f = 0.60$ (hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.24 – 7.15 (m, 1H), 7.10 – 6.95 (m, 3H), 5.56 – 5.35 (m, 2H), 2.69 (t, $J = 7.5$ Hz, 2H), 2.45 – 2.25 (m, 5H), 2.15 – 1.95 (m, 2H), 1.02 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.1, 137.7, 132.5, 129.3, 128.4, 128.1, 126.4, 125.4, 36.1, 34.5, 25.6, 21.4, 13.9; IR (neat) 2928, 2869, 1661, 1614, 1454, 1348, 1300, 1248, 1104, 965, 774, 694 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₃H₁₉ (M+H)⁺: 175.1487, found 175.1495.

(*E*)-1-(hex-3-en-1-yl)-3,5-dimethylbenzene (**1cc**)



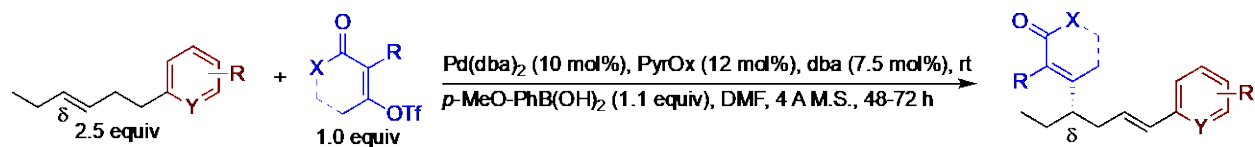
The general procedure A was followed using 1-bromo-3,5-dimethylbenzene (**1scc**, 1368 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1cc** as a colorless oil (452 mg, 60% yield): R_f = 0.60 (hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.95 – 6.75 (m, 3H), 5.56 – 5.35 (m, 2H), 2.62 (t, J = 7.5 Hz, 2H), 2.45 – 2.25 (m, 8H), 2.15 – 1.95 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 142.2, 137.6, 132.4, 128.6, 127.3, 126.3, 36.0, 34.6, 25.6, 21.3, 13.9; **IR** (neat) 2929, 2866, 1662, 1604, 1455, 1300, 1033, 966, ^[1]_{SEP}848, 693 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{21}$ ($\text{M}+\text{H}$) $^+$: 189.1643, found 189.1649.

(*E*)-4-(hex-3-en-1-yl)-1,1'-biphenyl (**1dd**)



The general procedure A was followed using 4-bromo-1,1'-biphenyl (**1sdd**, 1856 mg, 8.0 mmol) and (*E*)-1-bromohex-3-ene (**1ba**, 648 mg, 4.0 mmol). Purification of this material by chromatography on silica gel (gradient elution: hexanes) afforded product **1bb** as a colorless oil (472 mg, 50% yield): R_f = 0.50 (hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61 (d, J = 10.0 Hz, 2H), 7.54 (d, J = 10.0 Hz, 2H), 7.45 (t, J = 10.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 10.0 Hz, 2H), 5.75 – 5.35 (m, 2H), 2.74 (t, J = 7.5 Hz, 2H), 2.45 – 2.25 (m, 2H), 2.15 – 1.95 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 141.3, 141.1, 138.6, 132.7, 128.9, 128.7, 128.3, 127.0, 126.9, 35.8, 34.4, 25.6, 13.9; **IR** (neat) 3027, 2930, 2859, 1662, 1486, 1456, 1302, 763, 698 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{21}$ ($\text{M}+\text{H}$) $^+$: 237.1643, found 237.1628.

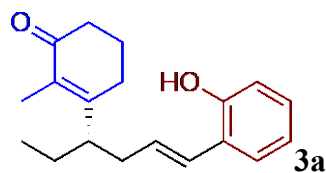
Enantioselective Relay Heck Reaction (General Procedure C):



To a 10 mL Schlenk flask was added Pd(dba)₂ (11.5 mg, 0.02 mmol, 0.10 equiv), PyrOx (6.5 mg, 0.024 mmol, 0.12 equiv), 4 Å MS (100 mg, 500 mg/1.0 mmol **2**), and DMF (1.0 mL). A three-way adapter fitted with a balloon of N₂ was then added to the Schlenk flask and evacuated via house vacuum and refilled with N₂ three times while stirring. The resulting mixture was stirred under an N₂ atmosphere for 20 min. A solution of alkene **1** (0.50 mmol, 2.5 equiv), dba (3.5 mg, 0.015 mmol, 0.075 equiv), (4-methoxyphenyl)boronic acid (34 mg, 0.22 mmol, 1.1 equiv) and triflate reagent **2** (0.20 mmol, 1.0 equiv) in DMF (1.0 mL) was then added in a single portion. The resulting mixture was stirred for another 48 h to 72 h at ambient temperature (23 °C). The reaction progress was monitored by TLC, and upon complete consumption of triflate reagent **2** the reaction was extracted with Et₂O (3X20 mL) and washed with NaHCO₃ (20 mL). The combined solvent was dried over Na₂SO₄, and the filtrate was concentrated to afford a yellow oil. The oil was purified by chromatography on silica gel (first using 1:2 hexanes:CH₂Cl₂ to remove dba ~ yellow on the gel, then gradient elution: 5–10% Acetone/hexanes), and concentrated in vacuo carefully to afford product **3** as a colorless oil.

Product Purification/Characterization Data

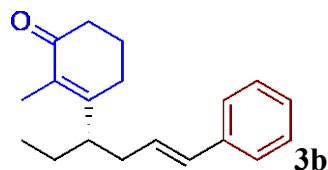
(*S,E*)-3-(6-(2-hydroxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3a**):



The general procedure C was followed using (*E*)-4-(hex-3-en-1-yl)phenol (**1a**, 88 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3a** as a colorless oil (39.2 mg, 69% yield): *R*_f = 0.25 (25% Acetone/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 10.0 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 10.0 Hz, 1H), 6.57 (d, *J* = 20.0 Hz, 1H), 6.18-5.90 (m, 1H), 5.02 (br, 1H), 2.90 (br, 1H), 2.50-2.10 (m, 6H), 2.00-1.85 (m, 2H), 1.82 (s, 3H), 1.70-1.30 (m, 2H), 0.86 (t, *J* =

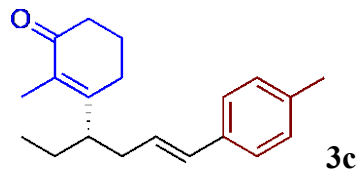
7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.9, 161.0, 152.6, 132.4, 129.7, 128.2, 127.2, 125.9, 124.6, 120.8, 115.7, 44.9, 38.1, 37.1, 25.9, 24.9, 22.5, 12.1, 10.9; IR (neat) 3310, 2957, 2929, 2870, 1639, 1602, 1454, 1365, 1300, 1244, 1191, 1093, 1039, 977, 751 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 285.1855, found 285.1859; $[\alpha]_{\text{D}}^{20} = -6^\circ$ ($c = 0.2$, CHCl_3).

(*S,E*)-2-methyl-3-(6-phenylhex-5-en-3-yl)cyclohex-2-en-1-one (**3b**):



The general procedure C was followed using (*E*)-4-(hex-3-en-1-yl)phenol (**1b**, 80 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3a** as a colorless oil (34.3 mg, 64% yield): $R_f = 0.35$ (25% Acetone/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.10 (m, 5H), 6.37 (d, $J = 18.0$ Hz, 1H), 6.05 (m, 1H), 3.00-2.75 (m, 1H), 2.50-2.10 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.4, 160.4, 137.4, 132.4, 131.4, 128.5, 128.0, 127.1, 126.0, 44.9, 38.2, 36.8, 25.8, 25.0, 22.6, 12.1, 10.8; IR (neat) 2928, 2869, 1661, 1616, 1454, 1379, 1301, 1190, 1104, 964, 743, 693 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{25}\text{O}$ ($\text{M}+\text{H}$) $^+$: 269.1905, found 269.1909; $[\alpha]_{\text{D}}^{20} = -8^\circ$ ($c = 0.1$, CHCl_3).

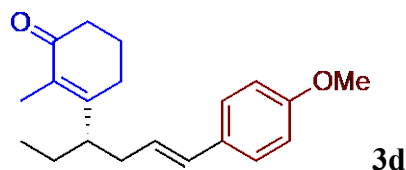
(*S,E*)-2-methyl-3-(6-(*p*-tolyl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3c**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methylbenzene (**1c**, 87 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3c** as a colorless oil (31.6 mg, 56% yield): $R_f = 0.35$ (25% Acetone/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.17 (d, $J = 10.0$ Hz, 2H), 7.09 (d, $J = 10.0$ Hz, 2H), 6.34 (d, $J = 15.0$ Hz, 1H), 6.10-5.90 (m, 1H), 3.00-2.80 (m, 1H), 2.50-2.20 (m, 9H), 2.00-

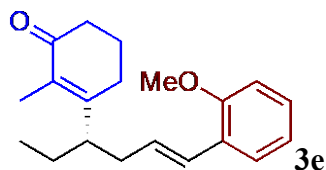
1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.4, 160.4, 136.9, 134.6, 132.3, 131.2, 129.2, 126.9, 125.9, 44.9, 38.2, 36.8, 25.8, 25.0, 22.6, 21.1, 12.1, 10.8; **IR** (neat) 2929, 2869, 1660, 1616, 1512, 1454, 1378, 1300, 1189, 1105, 1039, 965, 812, 794 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{27}\text{O}$ ($\text{M}+\text{H}$) $^+$: 283.2062, found 283.2063; $[\alpha]_{\text{D}}^{20} = +2.1^\circ$ ($c = 0.4$, CHCl_3).

(*S,E*)-3-(6-(4-methoxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3d**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3d** as a colorless oil (37.0 mg, 62% yield): $R_f = 0.30$ (25% Acetone/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.21 (d, $J = 10.0$ Hz, 2H), 6.82 (d, $J = 10.0$ Hz, 2H), 6.32 (d, $J = 15.0$ Hz, 1H), 5.90 (dt, $J = 15.0$ Hz, $J = 7.5$ Hz, 1H), 3.79 (s, 3H), 2.95-2.80 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.5, 160.6, 158.9, 132.3, 130.7, 130.2, 127.0, 125.8, 114.0, 55.3, 45.0, 38.2, 36.8, 25.8, 24.9, 22.6, 12.1, 10.8; **IR** (neat) 2930, 2870, 1659, 1607, 1504, 1456, 1364, 1299, 1174, 1105, 1033, 965, 840, 821 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 299.2011, found 299.2002; $[\alpha]_{\text{D}}^{20} = +5.5^\circ$ ($c = 0.4$, CHCl_3).

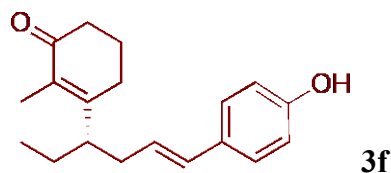
(*S,E*)-3-(6-(2-methoxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3e**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-2-methoxybenzene (**1e**, 95 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3e** as a colorless oil (28.0 mg, 47% yield): $R_f = 0.30$ (25%

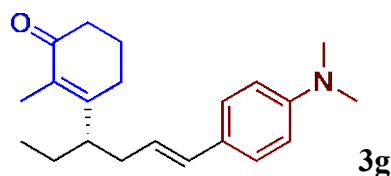
Acetone/hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.30-7.26 (m, 1H), 7.20-7.08 (m, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 6.68 (d, *J* = 15.0 Hz, 1H), 6.03 (dt, *J* = 15.0 Hz, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.00-2.80 (m, 1H), 2.50-2.10 (m, 6H), 2.00-1.85 (m, 2H), 1.82 (s, 3H), 1.70-1.30 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 199.5, 160.6, 156.4, 132.4, 128.6, 128.1, 126.6, 126.5, 126.1, 120.7, 110.8, 55.4, 44.9, 38.2, 37.1, 25.9, 25.0, 22.6, 12.1, 10.8; **IR** (neat) 2930, 2870, 1660, 1616, 1488, 1326, 1242, 1177, 1103, 1029, 971, 750 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₇O₂ (M+H)⁺: 299.2011, found 299.2007; [α]_D²⁰ = -10.5° (c = 0.5, CHCl₃).

(*S,E*)-3-(6-(4-hydroxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3f**):



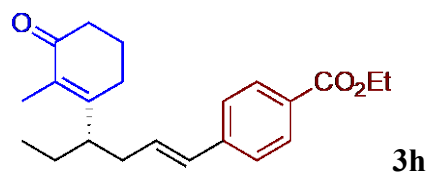
The general procedure C was followed using (*E*)-4-(hex-3-en-1-yl)phenol (**1f**, 88 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3f** as a colorless oil (23.8 mg, 42% yield): *R_f* = 0.15 (25% Acetone/hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.15 (d, *J* = 10.0 Hz, 2H), 6.77 (d, *J* = 10.0 Hz, 2H), 6.30 (d, *J* = 15.0 Hz, 1H), 5.95-5.75 (m, 1H), 5.69 (br, 1H), 2.95-2.75 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.82 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, *J* = 5.0 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 200.0, 161.3, 155.2, 132.3, 130.8, 130.1, 127.2, 125.6, 115.5, 45.0, 38.1, 36.7, 25.8, 25.0, 22.6, 12.1, 10.8; **IR** (neat) 2927, 2869, 1660, 1608, 1510, 1456, 1326, 1299, 1246, 1174, 1035, 965, 840, 822 cm⁻¹; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₅O₂ (M+H)⁺: 285.1855, found 285.1859; [α]_D²⁰ = +2° (c = 0.2, CHCl₃).

(*S,E*)-3-(6-(4-(dimethylamino)phenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3g**):



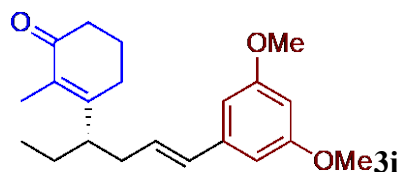
The general procedure C was followed using (*E*)-4-(hex-3-en-1-yl)-*N,N*-dimethylaniline (**1g**, 102 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) without adding (4-methoxyphenyl)boronic acid to afford product **3g** as a colorless oil (28.0 mg, 44% yield): $R_f = 0.30$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.17 (d, $J = 10.0$ Hz, 2H), 6.65 (d, $J = 5.0$ Hz, 2H), 6.28 (d, $J = 15.0$ Hz, 1H), 5.84 (dt, $J = 15.0$ Hz, $J = 7.5$ Hz, 1H), 3.00-2.80 (m, 7H), 2.45-2.15 (m, 6H), 1.95-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.5, 160.8, 149.9, 132.2, 131.1, 126.8, 126.1, 123.7, 112.6, 45.2, 40.6, 38.2, 36.8, 25.7, 25.0, 22.6, 12.1, 10.8; **IR** (neat) 2931, 2870, 1661, 1610, 1521, 1445, 1350, 1326, 1187, 1166, 963, 947, 815 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{30}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 312.2327, found 312.2329; $[\alpha]_{\text{D}}^{20} = +13.5^\circ$ ($c = 0.4$, CHCl_3).

(*S,E*)-2-methyl-3-(6-(*p*-tolyl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3h**):



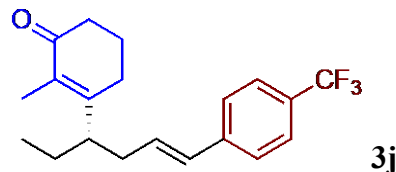
The general procedure C was followed using ethyl (*E*)-4-(hex-3-en-1-yl)benzoate (**1h**, 116 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3h** as a colorless oil (36.0 mg, 53% yield): $R_f = 0.25$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (d, $J = 10.0$ Hz, 2H), 7.32 (d, $J = 5.0$ Hz, 2H), 6.40 (d, $J = 15.0$ Hz, 1H), 6.25-6.10 (m, 1H), 4.36 (q, $J = 5.0$ Hz, 2H), 2.95-2.80 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.42 (m, 2H), 1.38 (t, $J = 7.5$ Hz, 3H), 0.86 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.3, 166.4, 159.9, 141.7, 132.4, 130.8, 130.7, 129.9, 129.0, 125.8, 60.8, 44.7, 38.1, 36.8, 25.8, 25.0, 22.6, 14.3, 12.1, 10.8; **IR** (neat) 2932, 2870, 1712, 1660, 1606, 1270, 1176, 1100, 1019, 969, 855, 758, 698 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{29}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 341.2117, found 341.2119; $[\alpha]_{\text{D}}^{20} = +3.5^\circ$ ($c = 0.5$, CHCl_3).

(*S,E*)-3-(6-(3,5-dimethoxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3i**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-3,5-dimethoxybenzene (**1i**, 87 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3i** as a colorless oil (37.4 mg, 57% yield): R_f = 0.15 (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.43 (s, 2H), 6.33 (s, 1H), 6.30 (d, J = 15.0 Hz, 1H), 6.10-5.95 (m, 1H), 3.78 (s, 6H), 2.95-2.75 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, J = 5.0 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.3, 160.9, 160.2, 139.4, 132.3, 131.4, 128.6, 104.2, 99.3, 55.3, 44.8, 38.1, 36.7, 25.7, 25.0, 22.6, 12.1, 10.8; **IR** (neat) 2934, 1710, 1660, 1591, 1456, 1425, 1356, 1219, 1205, 1152, 1064, 966, 826, 757 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 329.2117, found 329.2121; $[\alpha]_{\text{D}}^{20}$ = +5.8° (c = 0.5, CHCl_3).

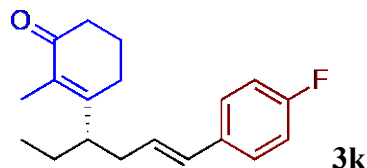
(*S,E*)-2-methyl-3-(6-(*p*-tolyl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3j**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-(trifluoromethyl)benzene (**1j**, 114 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3j** as a colorless oil (31.6 mg, 47% yield): R_f = 0.35 (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 (d, J = 5.0 Hz, 2H), 7.36 (d, J = 10.0 Hz, 2H), 6.40 (d, J = 20.0 Hz, 1H), 6.25-6.05 (m, 1H), 2.95-2.80 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.35 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.3, 159.9, 140.8, 132.5, 130.9, 130.2, 129.0 (q, J = 31.25 Hz), 126.1, 125.5 (q, J = 3.75 Hz), 124.2 (q, J = 271.25 Hz), 44.7, 38.1, 36.8, 25.8, 24.9, 22.6, 12.1, 10.8; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 62.9 (s, 3F); **IR** (neat) 2931, 1643, 1613, 1515, 1453, 1323, 1265, 1222, 1162, 1066, 967, 825 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{OF}_3$ ($\text{M}+\text{H}$) $^+$: 337.1779, found

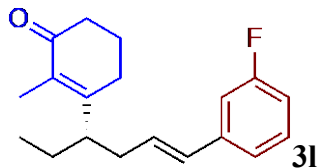
337.1784; $[\alpha]_D^{20} = -17.0^\circ$ ($c = 1.0$, CHCl_3).

(*S,E*)-3-(6-(4-fluorophenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3k**):



The general procedure C was followed using (*E*)-1-fluoro-4-(hex-3-en-1-yl)benzene (**1k**, 89 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) without adding (4-methoxyphenyl)boronic acid to afford product **3c** as a colorless oil (22.9 mg, 40% yield): $R_f = 0.35$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.22 (dd, $J = 10.0$ Hz, 5.0 Hz, 2H), 6.96 (t, $J = 7.5$ Hz, 2H), 6.33 (d, $J = 20.0$ Hz, 1H), 6.05-5.85 (m, 1H), 2.95-2.75 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.4, 162.1 (d, $J = 245.0$ Hz), 160.2, 133.5 (d, $J = 2.5$ Hz), 132.4, 130.2, 127.8 (d, $J = 2.5$ Hz), 127.4 (d, $J = 7.5$ Hz), 115.4 (d, $J = 22.5$ Hz), 44.9, 38.2, 36.7, 25.8, 25.0, 22.6, 12.1, 10.8; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 115.6 (m, 1F); **IR** (neat) 2930, 2970, 1660, 1616, 1507, 1455, 1344, 1300, 1157, 1094, 965, 812, 844, 821, 767 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{24}\text{OF}$ ($\text{M}+\text{H}$) $^+$: 287.1811, found 287.1810; $[\alpha]_D^{20} = -4^\circ$ ($c = 0.2$, CHCl_3).

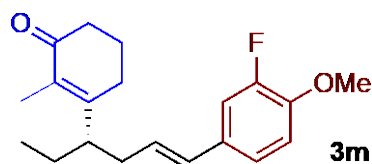
(*S,E*)-3-(6-(3-fluorophenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3l**):



The general procedure C was followed using (*E*)-1-fluoro-3-(hex-3-en-1-yl)benzene (**1l**, 89 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) without adding (4-methoxyphenyl)boronic acid to afford product **3l** as a colorless oil (34.9 mg, 61% yield): $R_f = 0.35$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30-7.15 (m, 1H), 7.10-6.85 (m, 3H), 6.33 (d, $J = 20.0$ Hz, 1H), 6.15-5.85 (m, 1H), 2.95-2.75 (m, 1H),

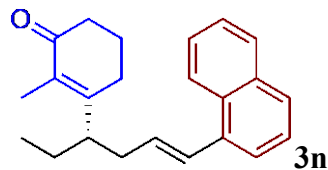
2.50-2.05 (m, 6H), 2.00-1.82 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.4, 163.1 (d, $J = 243.8$ Hz), 160.0, 139.7 (d, $J = 7.5$ Hz), 132.4, 130.4 (d, $J = 2.5$ Hz), 130.0 (d, $J = 8.8$ Hz), 129.5, 121.8 (d, $J = 3.8$ Hz), 113.9 (d, $J = 21.2$ Hz), 112.4 (d, $J = 21.2$ Hz), 44.8, 38.1, 36.7, 25.8, 24.9, 22.6, 12.1, 10.8; ^{19}F NMR (282 MHz, CDCl_3) δ 114.0 (m, 1F); IR (neat) 2933, 2971, 1660, 1611, 1582, 1445, 1344, 1301, 1142, 965, 874, 778, 684 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{24}\text{OF}$ ($\text{M}+\text{H}$) $^+$: 287.1811, found 287.1817; $[\alpha]_{\text{D}}^{20} = -0.8^\circ$ ($c = 0.4$, CHCl_3).

(*S,E*)-3-(6-(3-fluoro-4-methoxyphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3m**):



The general procedure C was followed using (*E*)-2-fluoro-4-(hex-3-en-1-yl)-1-methoxybenzene (**1c**, 104 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3m** as a colorless oil (32.2 mg, 51% yield): $R_f = 0.30$ (25% Acetone/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.15-6.75 (m, 3H), 6.26 (d, $J = 20.0$ Hz, 1H), 6.00-5.80 (m, 1H), 3.87 (s, 3H), 2.95-2.75 (m, 2H), 2.50-2.15 (m, 6H), 2.00-1.85 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.4, 160.2, 152.5 (d, $J = 243.8$ Hz), 146.9, 132.4, 131.1, 129.9 (d, $J = 1.2$ Hz), 127.3, 122.0 (d, $J = 2.5$ Hz), 113.5 (d, $J = 2.5$ Hz), 113.2 (d, $J = 18.8$ Hz), 56.4, 44.9, 38.1, 36.6, 25.8, 25.0, 22.6, 12.1, 10.8; ^{19}F NMR (282 MHz, CDCl_3) δ 135.9 (m, 1F); IR (neat) 2933, 2871, 1658 1616, 1514, 1455, 1326, 1300, 1119, 963, 874, 811, 760 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{F}$ ($\text{M}+\text{H}$) $^+$: 317.1917, found 317.1919; $[\alpha]_{\text{D}}^{20} = +4.7^\circ$ ($c = 0.5$, CHCl_3).

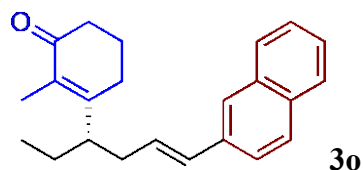
(*S,E*)-2-methyl-3-(6-(naphthalen-1-yl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3n**):



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)naphthalene (**1n**, 105 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20

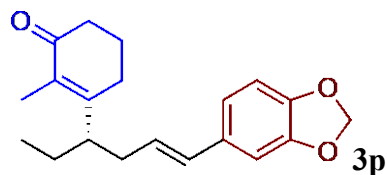
mmol) to afford product **3n** as a colorless oil (36.2 mg, 57% yield): $R_f = 0.35$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (t, $J = 5.0$ Hz, 1H), 7.84 (d, $J = 5.0$ Hz, 1H), 7.74 (d, $J = 5.0$ Hz, 1H), 7.55-7.35 (m, 4H), 7.10 (d, $J = 15.0$ Hz, 1H), 6.15-6.00 (m, 1H), 3.05-2.85 (m, 1H), 2.65-2.20 (m, 6H), 2.00-1.88 (m, 2H), 1.87 (s, 3H), 1.75-1.45 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.4, 160.3, 135.3, 133.6, 132.5, 131.4, 131.0, 128.7, 128.5, 127.5, 125.9, 125.7, 125.6, 123.74, 123.69, 44.8, 38.2, 37.1, 26.0, 25.0, 22.6, 12.1, 10.9; **IR** (neat) 2931, 2869, 1658, 1615, 1454, 1378, 1301, 1104, 966, 775, 753 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{O}$ ($\text{M}+\text{H}$) $^+$: 319.2062, found 319.2065; $[\alpha]_{\text{D}}^{20} = -24.9^\circ$ ($c = 0.4$, CHCl_3).

(*S,E*)-2-methyl-3-(6-(naphthalen-2-yl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3o**):



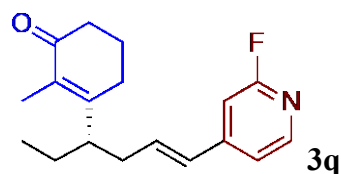
The general procedure C was followed using (*E*)-2-(hex-3-en-1-yl)naphthalene (**1o**, 105 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3n** as a colorless oil (28.0 mg, 44% yield): $R_f = 0.35$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80-7.70 (m, 3H), 7.63 (s, 1H), 7.55-7.35 (m, 3H), 6.54 (d, $J = 15.0$ Hz, 1H), 6.25-6.10 (m, 1H), 3.00-2.80 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.86 (m, 2H), 1.85 (s, 3H), 1.75-1.45 (m, 2H), 0.88 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.4, 160.3, 134.8, 133.6, 132.8, 132.4, 131.5, 128.4, 128.2, 127.8, 127.6, 126.2, 125.6, 125.5, 123.4, 44.9, 38.2, 36.9, 25.8, 25.0, 22.6, 12.1, 10.9; **IR** (neat) 2933, 2870, 1661, 1616, 1454, 1379, 1326, 1301, 963, 816, 745 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{O}$ ($\text{M}+\text{H}$) $^+$: 319.2062, found 319.2060; $[\alpha]_{\text{D}}^{20} = +2.5^\circ$ ($c = 0.5$, CHCl_3).

(*S,E*) -3-(6-(benzo[*d*][1,3]dioxol-5-yl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3p**):



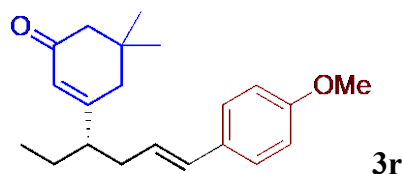
The general procedure C was followed using (*E*)-5-(hex-3-en-1-yl)benzo[*d*][1,3]dioxole (**1p**, 102 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3p** as a colorless oil (26.2 mg, 42% yield): $R_f = 0.20$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.81 (s, 1H), 6.75-6.65 (m, 2H), 6.28 (d, $J = 15.0$ Hz, 1H), 6.00-5.80 (m, 3H), 2.90-2.80 (m, 1H), 2.45-2.15 (m, 6H), 2.00-1.82 (m, 2H), 1.81 (s, 3H), 1.70-1.30 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.4, 160.4, 148.0, 146.8, 132.3, 131.9, 130.9, 126.2, 120.3, 108.2, 105.4, 101.0, 44.9, 38.2, 36.7, 25.8, 25.0, 22.6, 12.1, 10.8; **IR** (neat) 2931, 2871, 1658, 1615, 1502, 1488, 1444, 1358, 1302, 1246, 1190, 1036, 963, 856, 812, 794 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 313.1804, found 313.1805; $[\alpha]_{\text{D}}^{20} = +10^\circ$ ($c = 0.2$, CHCl_3).

(*S,E*)-3-(6-(2-fluoropyridin-4-yl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3q**):



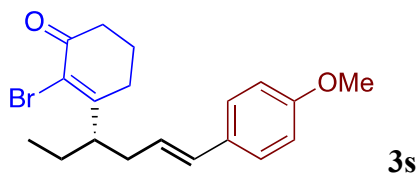
The general procedure C was followed using (*E*)-2-fluoro-4-(hex-3-en-1-yl)pyridine (**1q**, 89.5 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3q** as a colorless oil (37.9 mg, 66% yield): $R_f = 0.20$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.09 (d, $J = 10.0$ Hz, 1H), 7.04 (d, $J = 5.0$ Hz, 1H), 6.74 (s, 1H), 6.35-5.30 (m, 2H), 3.00-2.80 (m, 1H), 2.50-2.20 (m, 6H), 2.00-1.85 (m, 2H), 1.80 (s, 3H), 1.70-1.30 (m, 2H), 0.86 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 199.2, 164.5 (d, $J = 236.2$ Hz), 159.2, 150.2, 147.7 (d, $J = 16.2$ Hz), 134.8, 132.6, 128.4 (d, $J = 3.8$ Hz), 118.3 (d, $J = 3.8$ Hz), 105.9 (d, $J = 38.8$ Hz), 44.4, 38.1, 36.6, 25.8, 24.9, 22.6, 12.0, 10.8; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 69.2 (s, 1F); **IR** (neat) 2933, 2871, 1657, 1607, 1548, 1405, 1346, 1298, 1154, 1111, 968, 875, 824 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{NOF}$ ($\text{M}+\text{H}$) $^+$: 288.1764, found 288.1768; $[\alpha]_{\text{D}}^{20} = -9.0^\circ$ ($c = 0.4$, CHCl_3).

(*S,E*)-3-(6-(4-methoxyphenyl)hex-5-en-3-yl)-5,5-dimethylcyclohex-2-en-1-one (**3r**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and 5,5-dimethyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2b**, 55 mg, 0.20 mmol) to afford product **3r** as a colorless oil (25.6 mg, 41% yield): R_f = 0.30 (25% Acetone/hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.26 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.36 (d, J = 15.0 Hz, 1H), 6.03-5.86 (m, 2H), 3.83 (s, 3H), 2.50-2.10 (m, 7H), 1.80-1.40 (m, 2H), 1.06 (s, 6H), 0.90 (t, J = 6.0 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 200.0, 160.0, 158.9, 131.1, 130.1, 127.1, 125.8, 125.4, 113.9, 55.3, 51.4, 49.6, 41.2, 36.6, 33.5, 28.5, 28.4, 25.5, 11.9; **IR** (neat) 2957, 2928, 2871, 1662, 1607, 1510, 1463, 1368, 1299, 1280, 1174, 1033, 966, 838, 806 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 313.2168, found 313.2169; $[\alpha]_D^{20}$ = +36.6° (c = 0.4, CHCl_3).

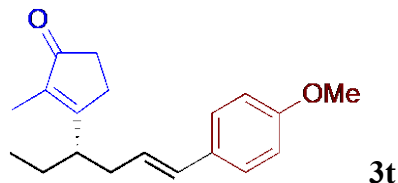
(*S,E*)-2-bromo-3-(6-(4-methoxyphenyl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3s**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and 2-bromo-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2c**, 64 mg, 0.20 mmol) to afford product **3s** as a colorless oil (21.7 mg, 30% yield): R_f = 0.30 (25% Acetone/hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.22 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 6.32 (d, J = 15.0 Hz, 1H), 6.05-5.80 (m, 1H), 3.79 (s, 3H), 3.50-2.75 (m, 1H), 2.65-2.10 (m, 5H), 2.00-1.80 (m, 2H), 1.75-1.30 (m, 3H), 0.91 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 191.3, 165.6, 158.9, 131.0, 130.0, 127.2, 125.0, 124.7, 113.9, 55.3, 49.0, 38.4, 36.5, 27.5, 25.6, 22.0, 12.0; **IR** (neat) 2958, 2922, 2854, 1694, 1637, 1510, 1441, 1298, 1244, 1174, 1032, 966,

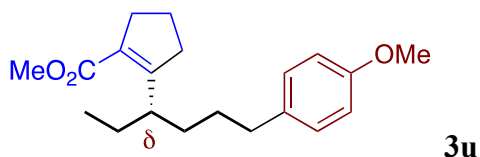
827, 802 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Br}$ ($\text{M}+\text{H}$) $^+$: 363.0960, found 363.0957; $[\alpha]_{\text{D}}^{20} = -70.5^\circ$ ($c = 0.5$, CHCl_3).

(*S,E*)-3-(6-(4-methoxyphenyl)hex-5-en-3-yl)-2-methylcyclopent-2-en-1-one (**3t**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and 2-methyl-3-oxocyclopent-1-en-1-yl trifluoromethanesulfonate (**2d**, 49 mg, 0.20 mmol) to afford product **3t** as a colorless oil (25.6 mg, 45% yield): $R_f = 0.20$ (25% Acetone/hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.22 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 6.32 (d, $J = 15.0$ Hz, 1H), 6.00-5.80 (m, 1H), 3.79 (s, 3H), 2.95-2.80 (m, 1H), 2.50-2.10 (m, 6H), 1.80-1.50 (m, 5H), 0.84 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 210.5, 175.8, 158.9, 137.4, 130.9, 130.0, 127.0, 125.4, 113.9, 55.3, 43.0, 36.9, 33.9, 26.1, 25.0, 12.1, 8.4; **IR** (neat) 2958, 2922, 2854, 1694, 1637, 1510, 1441, 1298, 1174, 1032, 966, 827, 802 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 285.1855, found 285.1852; $[\alpha]_{\text{D}}^{20} = +28.9^\circ$ ($c = 0.4$, CHCl_3).

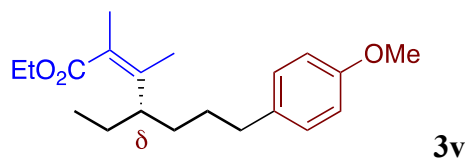
methyl (*S*)-2-(6-(4-methoxyphenyl)hexan-3-yl)cyclopent-1-ene-1-carboxylate (**3u**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and methyl 2-(((trifluoromethyl)sulfonyl)oxy)cyclopent-1-ene-1-carboxylate (**2e**, 55 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H_2 . After stirring for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3u** as a colorless oil (32.9 mg, 52% yield, $\delta:\gamma = 2.8$): $R_f = 0.45$ (25% Acetone/hexanes), data bellow belongs to the major product (δ position); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.06 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 3.65-3.45 (m, 1H), 2.70-2.25 (m, 6H), 1.90-1.65 (m, 2H), 1.55-1.10 (m, 6H), 0.79 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.8, 162.6, 157.5, 134.7, 129.2,

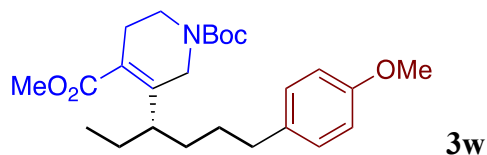
128.8, 113.6, 55.2, 50.8, 39.7, 35.0, 33.6, 33.2, 32.4, 29.6, 26.9, 21.7, 12.1; **IR** (neat) 2928, 2856, 1710, 1630, 1512, 1462, 1434, 1245, 1178, 1120, 1038, 818, 770 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 317.2117, found 317.2120; $[\alpha]_{\text{D}}^{20} = -4.8^\circ$ ($c = 0.5$, CHCl_3).

ethyl (*S,Z*)-4-ethyl-7-(4-methoxyphenyl)-2,3-dimethylhept-2-enoate (**3v**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and ethyl (*Z*)-2-methyl-3-(((trifluoromethyl)sulfonyl)oxy)but-2-enoate (**2f**, 55 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H_2 . After stirring for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3v** as a colorless oil (38.2 mg, 60% yield, $\delta:\gamma = 4.3$): $R_f = 0.45$ (25% Acetone/hexanes), data bellow belongs to the major product (δ position); **^1H NMR** (300 MHz, CDCl_3) δ 7.07 (d, $J = 6.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 4.17 (q, $J = 7.0$ Hz, 2H), 3.78 (s, 3H), 2.95-2.75 (m, 1H), 2.70-2.30 (m, 2H), 1.84 (s, 3H), 1.52 (s, 3H), 1.45-1.15 (m, 9H), 0.77 (t, $J = 7.5$ Hz, 3H); **^{13}C NMR** (75 MHz, CDCl_3) δ 170.6, 157.5, 144.5, 134.8, 129.2, 125.0, 113.5, 60.0, 55.2, 44.1, 35.0, 32.7, 29.5, 26.3, 16.0, 14.3, 12.6, 12.0; **IR** (neat) 2957, 2930, 1712, 1612, 1512, 1462, 1380, 1299, 1243, 1175, 1037, 819, 775 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{31}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 319.2273, found 319.2275; $[\alpha]_{\text{D}}^{20} = -7.6^\circ$ ($c = 0.5$, CHCl_3).

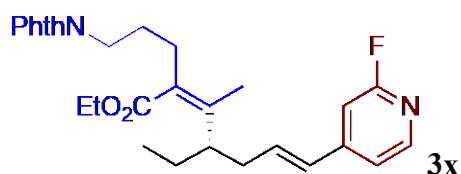
1-(*tert*-butyl) 4-methyl (*S*)-5-(6-(4-methoxyphenyl)hexan-3-yl)-3,6-dihydropyridine-1,4(2*H*)-dicarboxylate (**3w**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and 1-(*tert*-butyl) 4-methyl 5-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1,4(2*H*)-dicarboxylate (**2g**, 78 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H_2 . After stirring

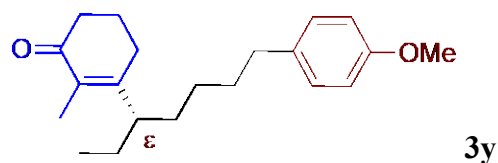
for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3w** as a colorless oil (52.6 mg, 61% yield): $R_f = 0.30$ (25% Acetone/hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.06 (d, $J = 9.0$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 4.09 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.39 (br, 3H), 2.70-2.30 (m, 2H), 2.07 (br, 2H), 1.70-1.15 (m, 15H), 0.79 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 167.2, 157.6, 154.6, 150.2, 134.5, 129.2, 129.1, 113.6, 79.8, 55.2, 51.3, 43.9, 42.3, 39.1, 34.9, 32.4, 29.5, 28.4, 26.2, 23.7, 12.0; **IR** (neat) 2929, 2857, 1694, 1512, 1455, 1419, 1295, 1164, 1116, 1037, 952, 830, 768 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{37}\text{NO}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 454.2569, found 454.2576; $[\alpha]_{\text{D}}^{20} = -6.0^\circ$ ($c = 0.5$, CHCl_3).

ethyl (S,2Z,6E)-2-(3-(1,3-dioxoisindolin-2-yl)propyl)-4-ethyl-7-(2-fluoropyridin-4-yl)-3-methylhepta-2,6-dienoate (**3x**)



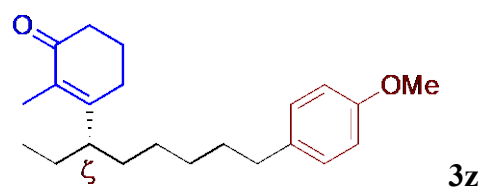
The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-4-methoxybenzene (**1d**, 95 mg, 0.50 mmol) and ethyl (*Z*)-5-(1,3-dioxoisindolin-2-yl)-2-(1-(((trifluoromethyl)sulfonyl)-oxy)ethylidene)-pentanoate (**2h**, 90 mg, 0.20 mmol) to afford product **3x** as a colorless oil (48.8 mg, 51% yield, using 2% Acetone/toluene for column): $R_f = 0.20$ (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 (d, $J = 5.0$ Hz, 1H), 7.82 (t, $J = 5.0$ Hz, 2H), 7.70 (d, $J = 5.0$ Hz, 2H), 7.06 (d, $J = 5.0$ Hz, 1H), 6.75 (s, 1H), 6.50-6.32 (m, 1H), 6.26 (d, $J = 20.0$ Hz, 1H), 4.20-4.10 (m, 2H), 3.63 (t, $J = 7.5$ Hz, 2H), 3.00-2.80 (m, 1H), 2.40-2.20 (m, 4H), 1.85-1.70 (m, 2H), 1.61 (s, 3H), 1.50-1.30 (m, 2H), 1.24 (t, $J = 7.5$ Hz, 3H), 0.81 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 170.0, 168.2, 164.5 (d, $J = 236.2$ Hz), 150.9, 147.4 (d, $J = 16.2$ Hz), 142.6, 136.4, 133.9, 132.1, 130.3, 127.3 (d, $J = 3.8$ Hz), 123.2, 118.4 (d, $J = 3.8$ Hz), 105.9 (d, $J = 37.5$ Hz), 60.3, 44.8, 37.7, 36.9, 27.6, 27.4, 25.8, 14.2, 12.2, 11.9; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ 69.7 (s, 1F); **IR** (neat) 2929, 1710, 1609, 1396, 1206, 1088, 1038, 720 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_4\text{F}$ ($\text{M}+\text{H}$) $^+$: 479.2346, found 479.2355; $[\alpha]_{\text{D}}^{20} = -22.6^\circ$ ($c = 0.4$, CHCl_3).

(*S*)-3-(7-(4-methoxyphenyl)heptan-3-yl)-2-methylcyclohex-2-en-1-one (**3y**)



The general procedure C was followed using (*E*)-1-(hept-4-en-1-yl)-4-methoxybenzene (**1y**, 102 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H₂. After stirring for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3y** as a colorless oil (39.3 mg, 63% yield, ϵ : δ = 2.6): **R_f** = 0.30 (25% Acetone/hexanes), data bellow belongs to the major product (ϵ position); **¹H NMR** (300 MHz, CDCl₃) δ 7.06 (d, J = 5.0 Hz, 2H), 6.81 (d, J = 10.0 Hz, 2H), 3.78 (s, 3H), 2.75-2.58 (m, 1H), 2.56-2.28 (m, 4H), 2.25-2.00 (m, 2H), 1.98-1.72 (m, 5H), 1.70-1.05 (m, 8H), 0.80 (t, J = 7.5 Hz, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 199.5, 161.4, 157.6, 134.5, 132.2, 129.2, 113.6, 55.2, 44.4, 38.2, 34.8, 33.1, 31.8, 27.1, 26.4, 24.5, 22.6, 12.1, 10.9; **IR** (neat) 2930, 2856, 1661, 1612, 1512, 1456, 1344, 1300, 1244, 1177, 1036, 818 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₂₁H₃₀O₂Na (M+Na)⁺: 337.2143, found 337.2141; $[\alpha]_D^{20}$ = -0.3° (c = 0.5, CHCl₃).

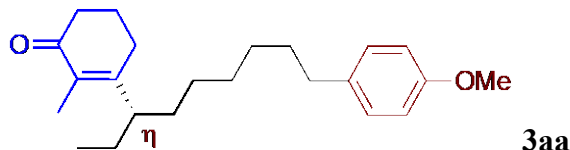
(*S*)-3-(8-(4-methoxyphenyl)octan-3-yl)-2-methylcyclohex-2-en-1-one (**3z**)



The general procedure C was followed using (*Z*)-1-methoxy-4-(oct-5-en-1-yl)benzen (**1z**, 109 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H₂. After stirring for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3z** as a colorless oil (38.5 mg, 59% yield, ζ : ϵ = 2.6): **R_f** = 0.30 (25% Acetone/hexanes), data bellow belongs to the major product (ζ position); **¹H NMR** (500 MHz, CDCl₃) δ 7.07 (d, J = 10.0 Hz, 2H), 6.82 (d, J = 5.0 Hz, 2H), 3.78 (s, 3H), 2.75-2.58 (m, 1H), 2.52 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 5.0 Hz, 2H), 2.17 (t, J = 5.0 Hz, 2H), 1.98-1.80 (m, 2H), 1.78 (s, 3H), 1.65-1.10 (m, 10H), 0.80 (t, J = 7.5 Hz, 3H); **¹³C NMR** (75

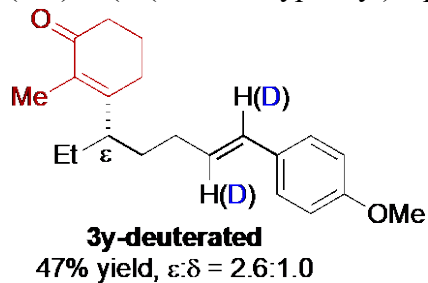
MHz, CDCl₃) δ 199.6, 161.5, 157.6, 134.7, 132.2, 129.2, 113.6, 55.2, 44.5, 38.2, 34.9, 33.2, 31.5, 29.4, 27.5, 26.4, 24.5, 22.6, 12.1, 10.8; **IR** (neat) 2928, 2855, 1662, 1612, 1511, 1456, 1344, 1300, 1244, 1176, 1036, 830 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₂₂H₃₃O₂ (M+H)⁺: 329.2481, found 329.2488; $[\alpha]_D^{20} = +3.5^\circ$ (c = 0.5, CHCl₃).

(S)-3-(9-(4-methoxyphenyl)nonan-3-yl)-2-methylcyclohex-2-en-1-one (**3aa**)

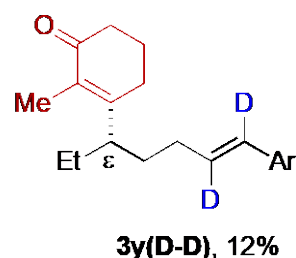
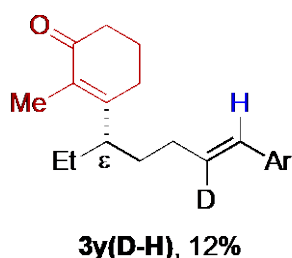
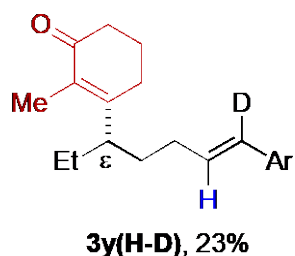


The general procedure C was followed using (Z)-1-methoxy-4-(non-6-en-1-yl)benzene (**1aa**, 116 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H₂. After stirring for 1 h at rt, the solution was passed through a short silica plug remove any solid to give product **3aa** as a colorless oil (38.8 mg, 57% yield, $\eta:\zeta = 2.0$): **R_f** = 0.30 (25% Acetone/hexanes), data bellow belongs to the major product (η position); **¹H NMR** (300 MHz, CDCl₃) δ 7.08 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 3.78 (s, 3H), 2.75-2.58 (m, 1H), 2.52 (t, $J = 6.0$ Hz, 2H), 2.40 (t, $J = 6.0$ Hz, 2H), 2.17 (m, 2H), 1.98-1.80 (m, 2H), 1.79 (s, 3H), 1.65-1.10 (m, 12H), 0.80 (t, $J = 7.5$ Hz, 3H); **¹³C NMR** (75 MHz, CDCl₃) δ 199.6, 161.6, 157.5, 134.8, 132.2, 129.2, 113.6, 55.2, 44.5, 38.2, 34.9, 33.3, 31.7, 29.7, 29.1, 27.6, 26.4, 24.5, 22.6, 12.1, 10.8; **IR** (neat) 2927, 2854, 1661, 1612, 1511, 1456, 1300, 1243, 1176, 1036, 828 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₂₃H₃₅O₂ (M+H)⁺: 343.2637, found 343.2638; $[\alpha]_D^{20} = +2.5^\circ$ (c = 0.4, CHCl₃).

(S,E)-3-(7-(4-methoxyphenyl)hept-6-en-3-yl)-2-methylcyclohex-2-en-1-one (**3y-deuterated**)

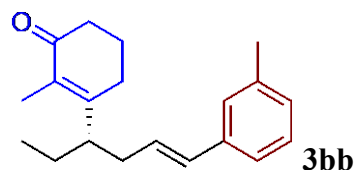


Product Distribution



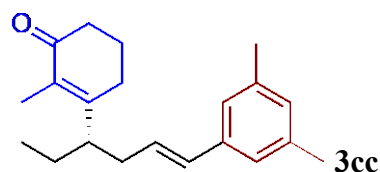
The general procedure C was followed using (*E*)-1-(hept-4-en-1-yl-1,1-*d*₂)-4-methoxybenzene (**1y-D₂**, 107 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product (*S,E*)-3-(7-(4-methoxyphenyl)hept-6-en-3-yl)-2-methylcyclohex-2-en-1-one as a colorless oil (29.7 mg, 47% yield; 63% yield with byproduct **4y**): *R_f* = 0.30 (25% Acetone/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 10.0 Hz, 1.48H), 7.13-6.95 (m, 0.56 H), 6.88-6.78 (m, 2H), 6.27 (s, 0.19H, **3y(D-H)**), 6.01 (t, *J* = 7.5 Hz, 0.36H, **3y(H-D)**), 5.65-5.05 (m, 0.54H, byproduct **4y**).

(*S,E*)-2-methyl-3-(6-(*m*-tolyl)hex-5-en-3-yl)cyclohex-2-en-1-one (**3bb**)



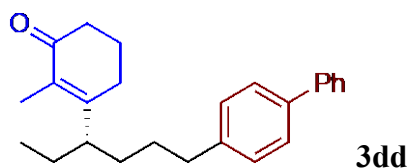
The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-3-methylbenzene (**1bb**, 87 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3bb** as a colorless oil (31.6 mg, 56% yield): *R_f* = 0.30 (25% Acetone/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.25-6.82 (m, 4H), 6.34 (d, *J* = 15.0 Hz, 1H), 6.12-5.90 (m, 1H), 2.95-2.75 (m, 1H), 2.50-2.20 (m, 9H), 2.00-1.84 (m, 2H), 1.82 (s, 3H), 1.80-1.40 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 199.6, 160.5, 138.0, 137.2, 132.3, 131.4, 128.4, 127.9, 127.7, 126.7, 123.1, 44.8, 38.1, 36.8, 25.8, 24.9, 22.6, 21.4, 12.1, 10.8; IR (neat) 2928, 2869, 1661, 1614, 1454, 1348, 1300, 1177, 1104, 1038, 965, 774, 694 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₂₀H₂₇O (M+H)⁺: 283.2062, found 283.2070.

(*S,E*)-3-(6-(3,5-dimethylphenyl)hex-5-en-3-yl)-2-methylcyclohex-2-en-1-one (**3cc**)



The general procedure C was followed using (*E*)-1-(hex-3-en-1-yl)-3,5-dimethylbenzene (**1cc**, 94 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford product **3cc** as a colorless oil (35.5 mg, 60% yield): R_f = 0.30 (25% Acetone/hexanes); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.90 (s, 2H), 6.84 (s, 1H), 6.30 (d, J = 15.0 Hz, 1H), 6.12-5.90 (m, 1H), 2.95-2.75 (m, 1H), 2.50-2.20 (m, 12H), 2.00-1.84 (m, 2H), 1.82 (s, 3H), 1.75-1.50 (m, 2H), 0.84 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 199.6, 160.6, 138.0, 132.2, 131.5, 128.9, 127.5, 126.2, 123.8, 44.8, 38.2, 36.8, 25.8, 24.9, 22.6, 21.3, 12.1, 10.8; **IR** (neat) 2929, 2866, 1662, 1604, 1455, 1300, 1033, 966, 848, 693 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{O}$ ($\text{M}+\text{H}$) $^+$: 297.2218, found 297.2225.

(*S,E*)-3-(6-(4-methoxyphenyl)hex-5-en-3-yl)-5,5-dimethylcyclohex-2-en-1-one (**3dd**)

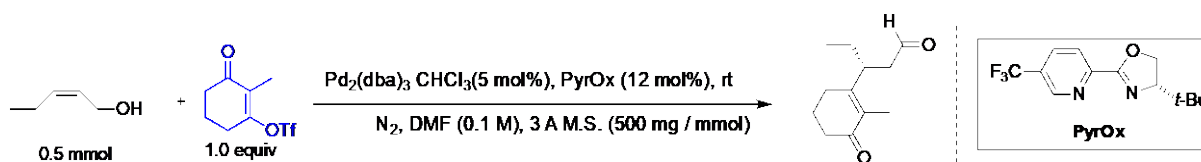


The general procedure C was followed using (*E*)-4-(hex-3-en-1-yl)-1,1'-biphenyl (**1dd**, 118 mg, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford a colorless oil. Then 10 mol % of Pd/C was added to this oil with 0.5 mL methanol under a balloon of H_2 . After stirring for 1h at rt, the solution was passed through a short silica plug remove any solid to give product **3dd** as a colorless oil (48.4 mg, 70% yield): R_f = 0.30 (25% Acetone/hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 (d, J = 10.0 Hz, 2H), 7.51 (d, J = 10.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 10.0 Hz, 2H), 2.95-2.50 (m, 3H), 2.48-2.30 (m, 2H), 2.30-2.05 (m, 2H), 2.00-1.70 (m, 5H), 1.65-1.40 (m, 4H), 1.35-1.20 (m, 2H), 0.81 (t, J = 5.0 Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 199.5, 161.2, 141.2, 141.0, 138.8, 132.4, 128.73, 128.69, 127.04, 127.95, 44.4, 38.2, 35.6, 32.8, 29.4, 26.4, 24.5, 22.6, 12.1, 11.0; **IR** (neat) 3027, 2930, 2859, 1662, 1486, 1456, 1302, 763, 698 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{30}\text{ONa}$ ($\text{M}+\text{Na}$) $^+$: 369.2194, found 369.2194.

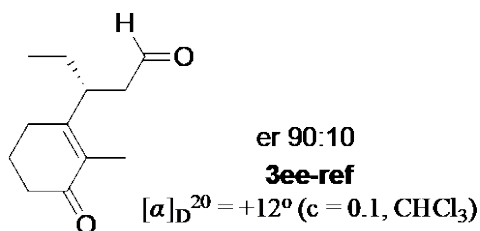
Correlation byproduct **4**.

The general procedure C was followed using (**1**, 0.50 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 52 mg, 0.20 mmol) to afford mixture including product **3** and byproduct **4** as a colorless oil. The ratio of **3** to **4** was obtained by the integration of ^1H NMR.

Determination of absolute configuration

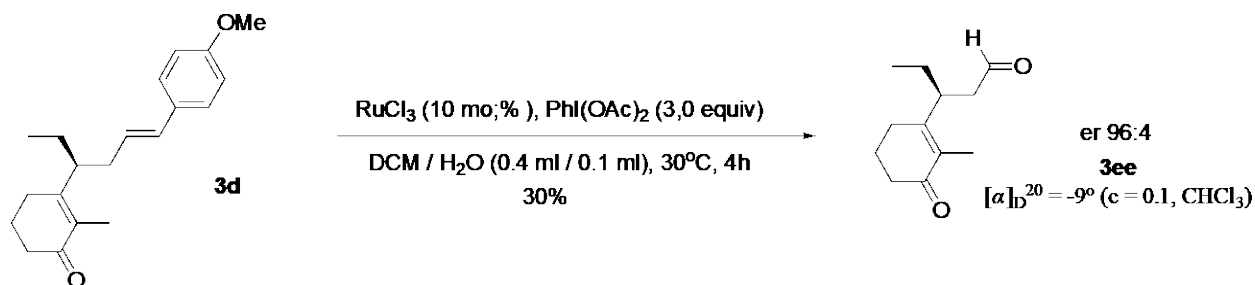


Prepared according to a modified literature procedure.¹³ To a dry 20 mL scintillation vial, equipped with a stir bar was added, $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (26 mg, 0.025 mmol, 5 mol %), magic ligand (PyrOx, 16.5 mg, 0.06 mmol, 12 mol %), 3 Å MS (250mg, 50mg/mmol) and sealed using a rubber septum. The reaction vial was evacuated and refilled with N_2 three times. To this, 3 mL dimethyl formamide (DMF) was added under nitrogen and the resulting mixture was stirred for 10 min at room temperature and for another 10 min at rt. To this, a DMF solution (3 mL) of (*Z*)-pent-2-en-1-ol (43 mg, 0.5 mmol) and 2-methyl-3-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (**2a**, 130 mg, 0.50 mmol) were added via syringe. After that, the resulting mixture was stirred at rt for 16 h. The mixture was diluted with ethyl acetate (150 mL) and water (100 mL). The aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic layers were washed with water (2 x 50 mL), brine (1 x 50 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel flash chromatography using 0 to 30% ethyl acetate in hexanes, to give the corresponding products **3ee-ref** as a colorless oil (48.4 mg, 70% yield): R_f = 0.30 (25% Acetone/hexanes);



(R)-3-(2-methyl-3-oxocyclohex-1-en-1-yl)pentanal

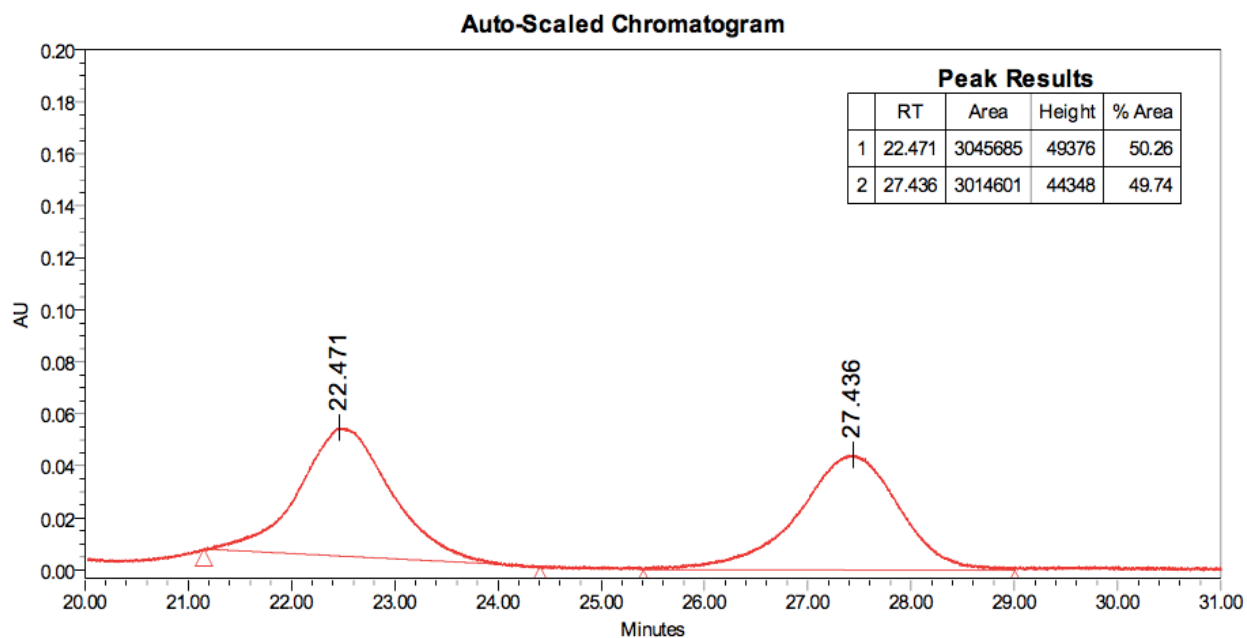
¹H NMR (500 MHz, CDCl₃) δ 9.67 (t, *J* = 3.0 Hz, 1H), 3.35-3.20 (m, 1H), 2.62-2.26 (m, 4H), 2.25-2.10 (m, 2H), 2.00-1.85 (m, 2H), 1.83 (s, 3H), 1.65-1.40 (m, 2H), 0.85 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.6, 199.2, 157.9, 132.5, 47.0, 38.6, 37.9, 25.9, 25.0, 22.5, 11.8, 10.8; IR (neat) 2932, 2873, 1721, 1658, 1616, 1457, 1380, 1327, 1301, 1125, 1051, 1028, 877 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₉O₂ (M+H)⁺: 195.1385, found 195.1383; $[\alpha]_D^{20} = +12^\circ$ (c = 0.1, CHCl₃).



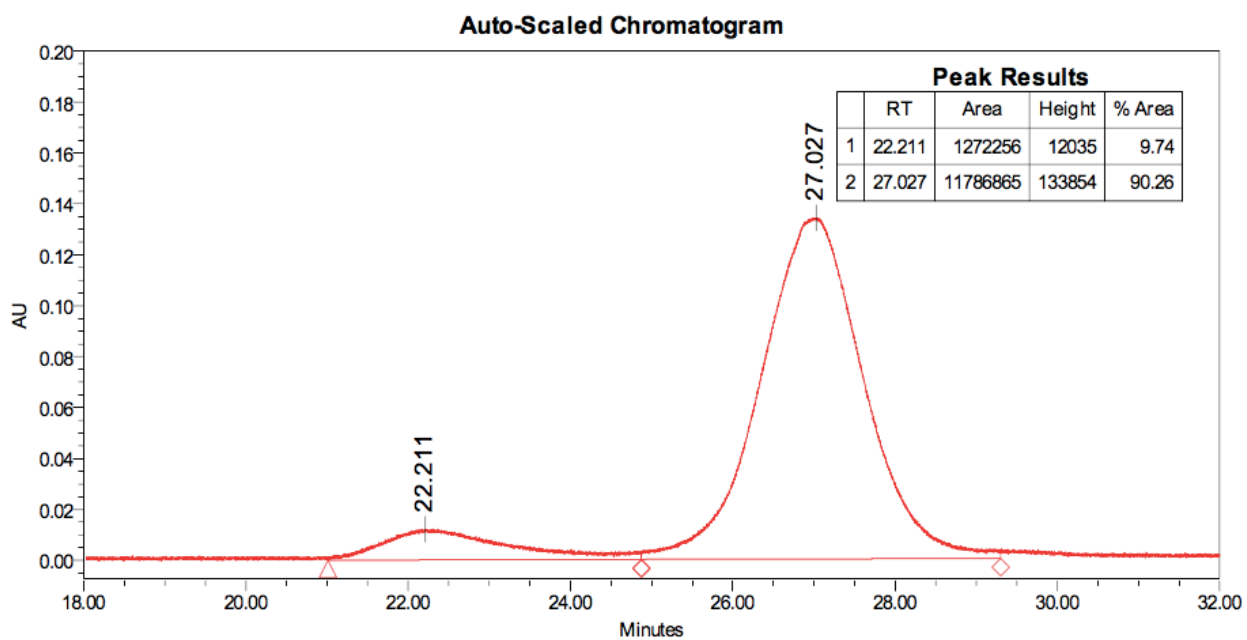
Prepared according to a modified literature procedure.¹⁴ The typical solution containing 0.2 mmol of **3d**, 1 mol % RuCl₃ and 3 equiv of PhI(OAc)₂, was heated to 30 °C. After Reaction for 4 h at the same temperature, the mixture was then separated with separatory funnel and the DCM phase was dried over anhydrous Na₂SO₄, filtered and the solvent removed under vacuum. The crude product was purified via a standard silica gel chromatography using hexanes/ethyl acetate as eluent to give the desired aldehyde **3ee** ($[\alpha]_D^{20} = -9^\circ$ (c = 0.1, CHCl₃)).

SFC Analysis of **3ee** and **3ee-ref**:

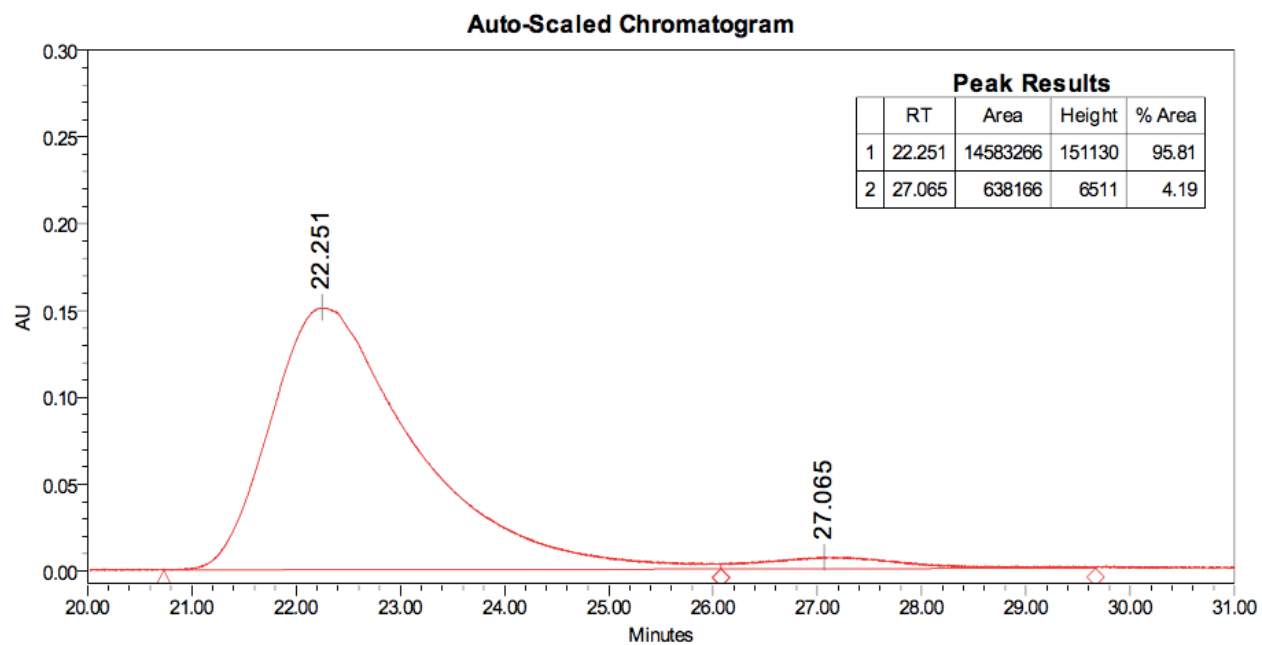
The SFC trace of **3ee** was compared to **3ee-ref**.



3ee-Rac sample (Conditions): OZ-H column, 40.0 °C, *i*-PrOH: CO₂ = 4:96, 2 mL/min, 138 bar, 40 min; $t_1 = 22.471$ min, $t_2 = 27.436$ min.



3ee-ref sample (Conditions): OZ-H column, 40.0 °C, *i*-PrOH: CO₂ = 4:96, 2 mL/min, 138 bar, 40 min; $t_1 = 22.211$ min, $t_2 = 27.027$ min, er = 10:90.



3ee sample (Conditions): OZ-H column, 40.0 °C, *i*-PrOH: CO₂ = 4:96, 2 mL/min, 138 bar, 40 min; $t_1 = 22.251$ min, $t_2 = 27.065$ min, er = 96:4.

Computational Analysis of Side Product Formation

Apart from the energy of the unfilled π^* orbital, the energy of the filled π orbital at the same position, which is highly collinear with $E(\pi^*_{\text{ortho}})$ ($R^2 = 0.95$), unavoidably has a similar correlation with the product selectivity (**Figure S1A**). However, evaluation of non-covalent interactions utilizing symmetry-adapted perturbation theory¹⁵ (SAPT) revealed a positive correlation of side product formation and the π interaction with anion (model system: Br^-), while interaction with cation (model system: B^+) is inversely correlated (**Figure S1B**), which suggests that despite the cationic nature of the organopalladium intermediates, the terminal aryl group of the substrate effects product selectivity by allowing back-bonding into the empty orbital.

Intermediate calculation demonstrated the structural viability for the proposed E2 elimination (**Figure S1C**. **int-1a**: $\text{dist}(\text{C}_\alpha\text{-H}_{a1}) = 1.1015 \text{ \AA}$, $\text{dist}(\text{C}_\alpha\text{-H}_{a2}) = 1.095 \text{ \AA}$, $\varphi(\text{H}_{a1}\text{-C}_\alpha\text{-C-Pd}) = 160.8^\circ$. **int-1b**: $\text{dist}(\text{C}_\alpha\text{-H}_{a1}) = 1.093 \text{ \AA}$, $\text{dist}(\text{C}_\alpha\text{-H}_{a2}) = 1.101 \text{ \AA}$, $\varphi(\text{H}_{a2}\text{-C}_\alpha\text{-C-Pd}) = 178.5^\circ$. It is hypothesized that DMF will act as the deprotonating base. The activated electron-deficient hydrogen is accessible in both cases). Additionally, it is confirmed that the alkenyl-Pd interaction is the main stabilizing force of the γ -Pd intermediate.

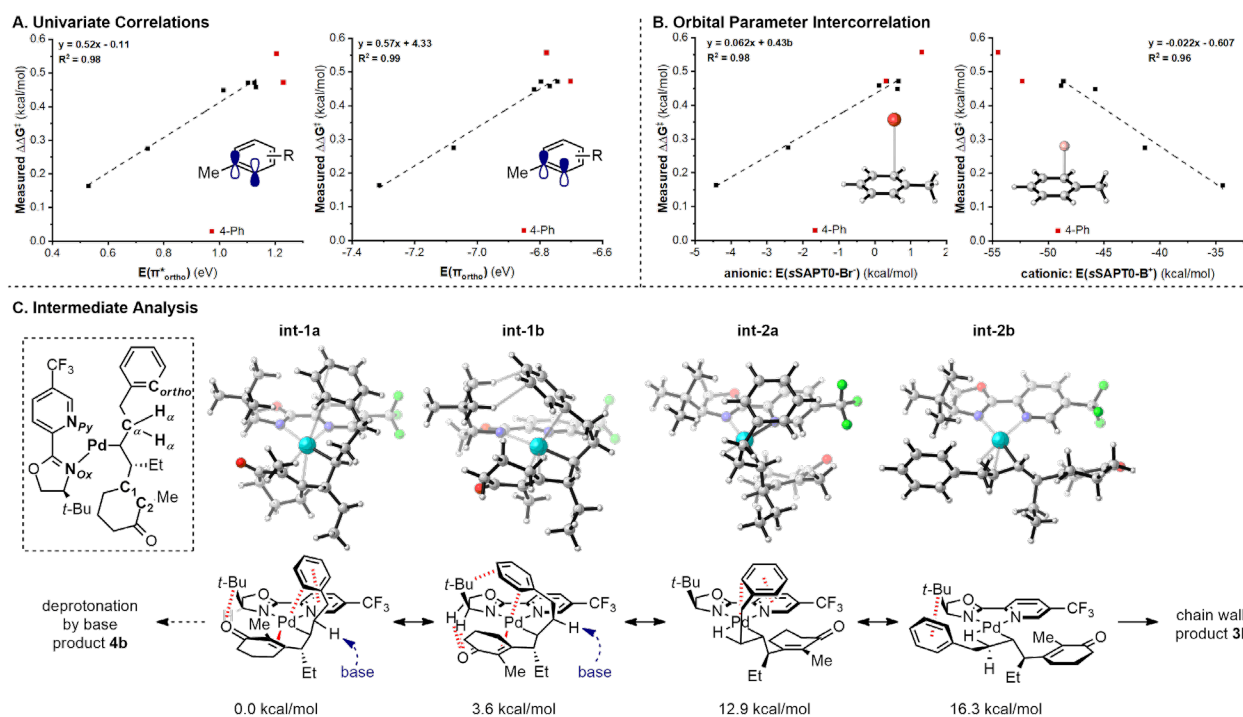


Figure S1. Additional analysis on the chemoselectivity.

On the other hand, through examination of intermediate structural changes during optimization, it was revealed that the alkenyl-Pd interaction is mutually exclusive with the Pd-H α interaction leading up to β -hydride elimination. Furthermore, the stabilizing Pd- π_{Ar} interaction also disfavors, is not prohibits, the β -hydride elimination (**int-2a**: dist(C α -H α_2) = 1.168 Å, dist(Pd-H α_2) = 1.965 Å, ϕ (H α_2 -C α -C-Pd) = 19.4°. **int-2b**: dist(C α -H α_2) = 1.2125 Å, dist(Pd-H α_2) = 1.755 Å, ϕ (H α_2 -C α -C-Pd) = 1.7°).

Computational Methods

All geometry optimizations were performed under ideal gas phase approximation and ultrafine integration grid using the Gaussian 16¹⁶ software. Toluene derivatives were optimized in the gas phase with the functional B3LYP-D3(BJ)¹⁷ and the basis set 6-31+G(d,p).¹⁸ Single-point energies and molecular descriptors were acquired from the optimized structures using the functional M06¹⁹ and a triple- ζ basis set def2-TZVP.²⁰ NBO^{21a, 18c, 21b} partial charges and orbitals were computed using NBO 3.1²² (accessed through Gaussian 16). SAPT calculations were performed with the optimized structures using PSI4,²³ with the benchmarked error-cancelling computational level *s*SAPT0/jun-cc-pVDZ.^{15d} Boltzmann averages were taken for molecules with multiple conformers. The intermediate complexes were optimized with the functional B3LYP-D3(BJ), the basis set LanL2DZ and its corresponding effective core potential²⁴ (ECP) for Pd, and the basis set 6-31G(d,p) for all other atoms. Geometry information was extracted from the optimized structures. Single-point energies were acquired from these structures utilizing the functional M06,^{19b} the basis set SDD and its ECP for Pd, and the basis set def2TZVP for all other atoms.

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Table of Descriptors

entry	E(π^* _{ortho}) (eV)	E(π _{ortho}) (eV)	E(sSAPT0-Br ⁻) (kcal/mol)	E(sSAPT0-B ⁺) (kcal/mol)	$\Delta\Delta G^\ddagger$ (kcal/mol)
4-OMe-C ₆ H ₄	1.126	-6.796	0.329	-48.608	0.472

4-Me-C ₆ H ₄	1.103	-6.743	0.664	-48.684	0.472
3-Me-C ₆ H ₄	1.131	-6.768	0.120	-48.840	0.459
C ₆ H ₅	1.014	-6.819	0.635	-45.779	0.448
4-CO ₂ Et-C ₆ H ₄	0.743	-7.076	-2.413	-41.335	0.275
4-CF ₃ -C ₆ H ₄	0.528	-7.314	-4.420	-34.373	0.164
3,5-OMe-C ₆ H ₃	1.205	-6.780	1.304	-54.554	0.558
3,5-Me-C ₆ H ₃	1.229	-6.703	0.299	-52.360	0.473
4-Ph-C ₆ H ₄	0.971	-6.851	-1.669	-49.157	0.03

Cartesians

4-CO₂Et-C₆H₄ conf1				C	-1.422148	0.001656	-0.013831	C	4.036071	-0.002923	0.004134
C	-4.411207	-0.674149	0.016856	C	-0.697373	-1.198279	-0.007876	H	3.872105	2.023426	-0.716844
H	-4.803172	-0.630479	1.040630	C	0.697392	-1.198257	0.007820	H	3.865138	-2.028983	0.724366
H	-5.000093	0.022853	-0.587316	C	1.422160	0.001691	0.013792	H	5.121795	-0.004207	0.005724
H	-4.584973	-1.686021	-0.359867	C	0.698348	1.199921	0.007767	C₆H₅			
C	-2.945276	-0.320274	-0.009408	C	-0.698391	1.199909	-0.007820	C	-2.424697	0.000965	0.009465
C	-1.961436	-1.319135	-0.011650	H	-1.232040	-2.145118	-0.013683	H	-2.803014	-0.136707	1.029994
C	-0.605948	-0.995253	-0.006818	H	1.232064	-2.145097	0.013597	H	-2.829327	0.944991	-0.367045
C	-0.205954	0.347600	-0.002003	H	1.232600	2.146818	0.013371	H	-2.831555	-0.811149	-0.601404
C	-1.180981	1.354672	-0.003388	H	-1.232680	2.146787	-0.013465	C	-0.914727	0.002211	-0.011664
C	-2.531667	1.021112	-0.008203	C	2.931938	-0.001715	-0.005080	C	-0.196902	-1.202316	-0.008887
H	-2.261711	-2.363420	-0.018997	H	3.336734	-0.825336	0.591728	C	1.199270	-1.207281	0.002023
H	0.144592	-1.776837	-0.010112	H	3.314234	-0.120394	-1.026698	C	1.905781	-0.001675	0.008354
H	-0.860084	2.390671	-0.003849	H	3.337350	0.934429	0.390294	C	1.203072	1.205229	0.001966
H	-3.278853	1.810236	-0.012972	3-Me-C₆H₄				C	-0.193976	1.203999	-0.008801
C	1.224276	0.753391	0.000925	C	-2.527668	-1.035051	0.000212	H	-0.738043	-2.145303	-0.017351
O	1.613404	1.908399	0.004036	H	-3.133448	-0.781482	-0.877489	H	1.734960	-2.152157	0.002128
O	2.064805	-0.305865	0.000423	H	-2.361145	-2.115991	-0.008000	H	2.991531	-0.003218	0.014153
C	3.478479	0.002214	0.003815	H	-3.125570	-0.793962	0.886920	H	1.741322	2.148637	0.001770
H	3.705420	0.608021	-0.878524	C	-1.221313	-0.276846	-0.000240	H	-0.732799	2.148105	-0.016978
H	3.701905	0.604786	0.889258	C	0.003784	-0.949885	-0.000399	4-OMe-C₆H₄			
C	4.229133	-1.314530	0.002886	C	1.228773	-0.264568	-0.000127	C	-3.330991	-0.299383	0.000192
H	3.985536	-1.903357	-0.886551	C	1.208944	1.133516	-0.000027	H	-3.794122	0.158579	0.882089
H	5.307238	-1.123992	0.005382	C	-0.006928	1.824824	0.000131	H	-3.793975	0.157009	-0.882607
H	3.981998	-1.906621	0.889176	C	-1.212717	1.126885	-0.000051	H	-3.591808	-1.361617	0.001105
4-CO₂Et-C₆H₄ conf2				H	0.007914	-2.038176	-0.000614	C	-1.833690	-0.104162	0.000116
C	-4.445894	-0.379919	-0.182231	H	2.145640	1.684384	-0.000041	C	-0.953701	-1.187257	-0.000176
H	-4.915695	-0.229665	0.797731	H	-0.010331	2.911091	0.000150	C	0.436753	-1.012066	-0.000408
H	-4.906318	0.329956	-0.876302	H	-2.154498	1.669891	-0.000168	C	0.966777	0.280759	-0.000318
H	-4.691803	-1.392540	-0.514047	C	2.530433	-1.030481	0.000185	C	0.099443	1.383351	-0.000010
C	-2.954148	-0.174894	-0.096491	H	3.389852	-0.354190	-0.005930	C	-1.275667	1.186459	0.000196
C	-2.082627	-1.264056	0.044335	H	2.613408	-1.671094	0.885822	H	-1.351750	-2.198729	-0.000217
C	-0.706007	-1.075939	0.152712	H	2.608337	-1.680835	-0.878753	H	1.080543	-1.883068	-0.000682
C	-0.170404	0.218419	0.119181	4-Ph-C₆H₄				H	0.526266	2.380873	0.000077
C	-1.032119	1.314653	-0.025303	C	-4.620507	-0.007329	0.016218	H	-1.932936	2.052591	0.000425
C	-2.404957	1.116477	-0.132327	H	-4.995927	-0.478249	0.933385	O	2.304252	0.573213	-0.000677
H	-2.488144	-2.271896	0.067891	H	-5.027892	1.007162	-0.022908	C	3.223558	-0.508944	0.000730
H	-0.042950	-1.926212	0.259761	H	-5.028583	-0.570409	-0.829200	H	4.216544	-0.058171	0.001507
H	-0.606391	2.311716	-0.054300	C	-3.111435	0.004560	-0.008064	H	3.105237	-1.132443	0.896147
H	-3.063158	1.973538	-0.247462	C	-2.387142	-1.126555	-0.409490	H	3.107089	-1.133273	-0.894360
C	1.288838	0.480764	0.226966	C	-0.993650	-1.130185	-0.406762	4-CF₃-C₆H₄			
O	1.790305	1.591472	0.201021	C	-0.267509	0.001917	-0.001632	C	3.922793	-0.004580	0.004076
O	2.010057	-0.656246	0.362499	C	-0.992769	1.135410	0.397462	H	4.304979	-0.129616	-1.016464
C	3.448256	-0.508587	0.454321	H	-2.387321	1.134997	0.391686	H	4.327690	0.932767	0.395584
H	3.672286	0.372892	1.059388	C	-2.921759	-2.013524	-0.740352	H	4.321158	-0.827482	0.605308
H	3.774128	-1.407665	0.981749	H	-0.460738	-2.011740	-0.749939	C	2.414368	0.001348	0.012715
C	4.080135	-0.408779	-0.924866	H	-0.460072	2.018852	0.736053	C	1.692930	-1.201539	0.003272
H	3.748277	0.497742	-1.436892	H	-2.921862	2.025855	0.711521	C	0.300362	-1.205806	-0.020487
H	5.170690	-0.369501	-0.828336	C	1.215100	0.000476	-0.000019	C	-0.397613	0.005798	-0.035319
H	3.819730	-1.279001	-1.535115	C	1.938419	1.136831	-0.399996	C	0.303002	1.213890	-0.020191
4-Me-C₆H₄				C	1.934536	-1.137724	0.401780	C	1.697292	1.204907	0.003244
C	-2.931919	-0.001731	0.005180	C	3.333481	1.136437	-0.396394	H	2.228742	-2.146610	0.013778
H	-3.314131	-0.117573	1.027172	H	1.401822	2.017558	-0.739140	H	-0.242559	-2.144621	-0.030138
H	-3.337410	0.933325	-0.392716	C	3.329591	-1.140653	0.402477	H	-0.236590	2.154288	-0.029360
H	-3.336762	-0.827008	-0.589304	H	1.394771	-2.017305	0.738928				

H	2.235729	2.148305	0.013666
C	-1.898756	0.001250	-0.004643
F	-2.424433	-1.047357	-0.688200
F	-2.431472	1.130277	-0.535062
F	-2.382474	-0.091658	1.266776

3,5-diMe-C₆H₃

C	0.102120	2.918327	-0.000052
H	-0.403481	3.330312	0.880968
H	1.132245	3.285399	0.002003
H	-0.399798	3.330021	-0.883318
C	0.056396	1.408701	0.000070
C	-1.177673	0.738092	-0.000056
C	-1.248185	-0.655519	-0.000081
C	-0.050386	-1.388950	0.000021
C	1.191788	-0.753196	0.000081
C	1.228058	0.650835	0.000167
H	-2.098045	1.318348	-0.000128
H	-0.092689	-2.476139	0.000008
H	2.190756	1.157783	0.000212
C	-2.578438	-1.370712	0.000025
H	-2.683799	-2.011792	0.882916
H	-3.411370	-0.662098	-0.001346
H	-2.682697	-2.014027	-0.881351
C	2.476315	-1.547599	-0.000090
H	3.085254	-1.316830	0.881666
H	2.279161	-2.623246	0.000446
H	3.084491	-1.317603	-0.882595

3,5-diOMe-C₆H₃_conf1

C	-1.037942	3.076645	0.000037
H	-1.662199	3.257743	0.882662
H	-0.231907	3.814926	-0.000026
H	-1.662418	3.257792	-0.882416
C	-0.492946	1.668232	-0.000039
C	-1.387128	0.579340	-0.000172
C	-0.885337	-0.721042	-0.000195
C	0.498984	-0.963665	-0.000094
C	1.371202	0.120892	0.000003
C	0.877209	1.437693	0.000039
H	-2.453277	0.770406	-0.000299
H	0.837833	-1.990882	-0.000100
H	1.586469	2.258311	0.000119
O	-1.663139	-1.847041	-0.000374
C	-3.074558	-1.686944	0.000390
H	-3.489098	-2.695625	0.000750
H	-3.414608	-1.151618	0.895700
H	-3.415624	-1.151874	-0.894692
O	2.732828	0.004240	0.000103
C	3.293591	-1.301327	0.000075
H	4.375071	-1.161607	0.000164
H	2.996829	-1.862105	0.895148
H	2.996962	-1.862005	-0.895106

3,5-diOMe-C₆H₃_conf2

C	-3.455542	-0.000033	0.013431
H	-3.825553	-0.001719	1.046081
H	-3.862313	0.887451	-0.480153
H	-3.862428	-0.885846	-0.483055
C	-1.945557	-0.000044	-0.013517
C	-1.241753	-1.208007	-0.011143
C	0.155641	-1.204081	-0.000505
C	0.873630	0.000007	0.004865
C	0.155580	1.204111	-0.000735
C	-1.241772	1.207991	-0.011366
H	-1.759808	-2.611117	-0.018693
H	1.953062	0.000051	0.008886
H	-1.759967	2.161014	-0.019079
O	0.753055	-2.435564	0.000540
C	2.170956	-2.501930	0.002590
H	2.419912	-3.563667	0.001395
H	2.595358	-2.028144	-0.891795
H	2.592796	-2.030964	0.899685
O	0.753009	2.435587	-0.000015
C	2.170905	2.501963	0.003159
H	2.419840	3.563706	0.002251
H	2.592032	2.030914	0.900541
H	2.596030	2.028283	-0.890941

int-1a

C	-1.086755	-1.426044	-1.365009
C	-2.131944	-2.060747	-2.029675
C	-3.398030	-1.480953	-1.989702
C	-3.558425	-0.286394	-1.296874
C	-2.454743	0.294674	-0.670416
N	-1.245099	-0.259980	-0.697202
C	1.963708	-3.283114	-1.981683
H	2.144812	-4.349636	-1.870770
H	2.385162	-2.931029	-2.926985
O	0.510868	-3.087444	-2.060521
N	1.239027	-1.473114	-0.668947
C	0.270941	-1.984598	-1.343726
H	-1.943732	-2.986462	-2.558600
Pd	0.636361	0.568290	0.125874
C	2.382984	-2.421879	-0.771785
C	2.601064	-3.223190	0.545619
H	3.295830	-1.863765	-0.978714
C	2.767343	-2.241150	1.716593
H	3.617787	-1.577702	1.546312
H	1.872632	-1.628302	1.848721
C	2.942551	-2.793601	2.644682
C	1.425342	-4.175274	0.822039
H	1.347924	-4.970843	0.075216
H	1.564659	-4.661364	1.792097
H	0.472050	-3.642751	0.854055
C	3.901985	-4.029365	0.385034
C	4.101294	-4.602712	1.294769
H	3.848714	-4.744522	-0.442764
H	4.755454	-3.366641	0.211137
H	-4.240857	-1.944700	-2.489294
H	-2.556185	1.230661	-0.139613
C	-4.918794	0.340386	-1.128924
F	-4.822099	1.672746	-0.951685
F	-5.701820	0.105313	-2.192423
F	-5.539247	-0.168657	-0.040535
C	-0.155742	2.353854	0.855298
H	-1.023925	2.506022	0.206046
C	-0.514507	2.314213	2.334531
H	-0.574876	3.365447	2.658002
H	0.314931	1.893170	2.912493
C	-1.829824	1.634329	2.723805
H	-2.655307	2.102530	2.173400
H	-2.019746	1.863392	3.780592
C	-1.890011	0.136366	2.532933
C	-0.781546	-0.684875	2.776304
C	-3.088096	-0.466356	2.131550
C	-0.871819	-2.068381	2.615324
H	0.151285	-0.254546	3.127102
C	-3.174118	-1.844839	1.941598
H	-3.963334	0.151375	1.954676
C	-2.061142	-2.652845	2.180101
H	-0.012825	-2.688318	2.841174
H	-4.111641	-2.282447	1.613382
H	-2.125955	-3.728650	2.051778
C	0.944085	3.359765	0.524991
H	1.490403	3.616145	1.437339
C	0.432672	4.672235	-0.075605
C	1.835155	2.471544	-0.341873
H	-0.357616	5.043410	0.587990
H	-0.053587	4.485016	-1.040318
C	1.518084	5.744153	-0.207544
C	2.687843	1.547251	0.290303
C	1.833439	2.676825	-1.850356
H	1.938691	5.991041	0.772539
H	1.111897	6.663223	-0.637537
H	2.346994	5.418790	-0.844846
C	3.596687	0.700174	-0.563023
C	3.096238	1.591810	1.747861
C	3.117772	2.187078	-2.518560
H	0.964230	2.178485	-2.295872
H	1.697857	3.740900	-2.051618
C	3.441083	0.764898	-2.069412
O	4.436440	-0.017596	-0.041438
H	2.357599	2.062770	2.390729
H	3.289277	0.584614	2.113894
H	4.036352	2.147594	1.842384
H	3.016523	2.238006	-3.606032
H	3.945596	2.852201	-2.245025
H	4.361583	0.380029	-2.513670
H	2.621866	0.091887	-2.356880

int-1b

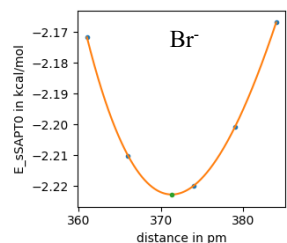
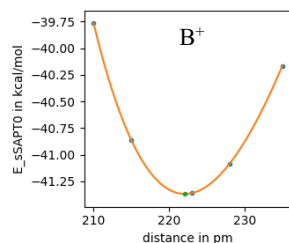
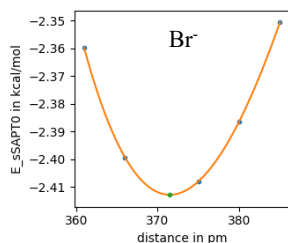
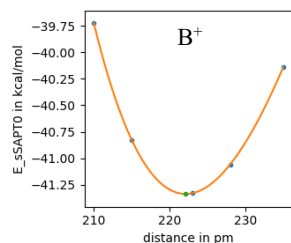
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C	-4.098223	-0.853588	-0.424786
C	-2.960891	-0.115305	-0.098942
N	-1.724095	-0.571973	-0.301035
C	1.393360	-3.467004	-2.053665
H	1.660722	-4.513340	-1.925248
H	1.574155	-3.155358	-3.084901
O	-0.043857	-3.352128	-1.810666
N	0.859406	-1.633349	-0.654539
C	-0.191141	-2.233802	-1.089830
H	-2.480537	-3.546037	-1.698161
Pd	0.208617	0.575379	-0.076773
C	2.020594	-2.502955	-1.023806
C	2.659590	-3.200273	0.209281
H	2.777110	-1.887915	-1.509709
C	3.276479	-2.127930	1.113874
H	4.086321	-1.602884	0.597782
H	2.528151	-1.401705	1.429871
H	3.700528	-2.583705	2.013493
C	1.614770	-4.008698	0.994023
H	1.133824	-4.771976	0.373805
H	2.092085	-4.524872	1.831992
H	0.839444	-3.355965	1.402951
C	3.785808	-4.126851	-0.284902
H	4.334858	-4.528579	0.571478
H	3.412166	-4.981930	-0.855423
H	4.500392	-3.584592	-0.913570
H	-4.816635	-2.698478	-1.274732
H	-3.056698	0.876330	0.322881
C	-5.460245	-0.290637	-0.099385
F	-5.469162	1.050498	-0.243048
F	-6.405665	-0.810501	-0.897553
F	-5.792641	-0.564854	1.176456
C	-0.713574	2.423311	0.108261
H	-1.486127	2.359832	-0.664976
C	-1.319203	2.646705	1.486094
H	-2.168762	1.978296	1.649851
H	-1.751552	3.659316	1.478142
C	-0.361078	2.538077	2.676792
H	-0.906893	2.853767	3.574891
H	0.459368	3.254670	2.571358
C	0.213387	1.159651	2.927696
C	1.513575	1.025120	3.439080
C	-0.568137	0.000099	2.794155
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H	2.129105	1.911693	3.563987
C	-0.073180	-1.247921	3.813398
H	-1.593066	0.073543	2.449848
C	1.208571	-1.357781	3.713351
H	3.007388	-0.294218	4.242481
H	-0.703185	-2.127093	3.089373
H	1.589076	-2.324113	4.026051
C	0.408193	3.383264	-0.278739
H	0.722808	3.932953	0.613143
C	0.068117	4.444653	-1.338503
C	1.542746	2.409393	-0.595393
H	-0.674260	5.119620	-0.896149
H	-0.414009	3.988687	-2.205912
C	1.294253	5.241968	-1.786656
C	1.501299	1.558295	-1.702907
C	2.773603	2.549361	0.267991
H	1.782355	5.733893	-0.938562
H	1.015570	6.017085	-2.504783
C	2.034291	4.595377	-2.270905
H	2.708959	0.696673	-2.000837
C	0.533202	1.625256	-2.866105
C	3.688345	1.334974	0.252836
H	3.304607	3.441719	-0.100716
H	2.470266	2.783167	1.291191
C	3.965858	0.897599	-1.183411
O	2.669436	-0.106505	-2.920331
H	-0.459804	1.969443	-2.592120
H	0.933895	2.302307	-3.630841
H	0.459919	0.638560	-3.323175
H	4.626154	1.556287	0.770370
H	3.200491	0.527216	0.803313

H	4.562219	-0.015926	-1.244743	H	-2.283433	-1.102601	3.618633	H	-6.276653	-2.566217	-0.749625
H	4.541833	1.679840	-1.700900	H	-0.491915	-2.786870	3.316228	H	-5.580306	-3.804597	0.290622
int-2a				C	-0.978389	3.076452	-0.584395	H	-5.955400	-2.202386	0.949750
C	0.397832	-1.917692	-0.885508	H	-0.116507	3.599119	-1.020871	H	3.251343	-4.497302	-0.237706
C	-0.159086	-3.179443	-1.056832	C	-2.006521	4.186487	-0.234487	H	2.318820	-0.311340	-0.545288
C	-1.435498	-3.417448	-0.546586	C	-1.464734	2.077520	-1.637331	C	4.393450	-2.050921	-0.748723
C	-2.094262	-2.386309	0.112512	H	-2.863983	3.758791	0.286915	F	5.048540	-1.705604	0.369753
C	-1.492221	-1.130272	0.192851	H	-2.386959	4.573724	-1.186619	F	5.019774	-3.102841	-1.298172
N	-0.279844	-0.898171	-0.306547	C	-1.433457	5.338203	0.592495	F	4.467639	-1.013792	-1.612234
C	3.824449	-1.921503	-2.117972	C	-2.595110	1.338489	-1.527280	C	0.097833	1.778209	0.001134
H	4.551878	-2.632591	-1.728513	C	-0.527168	1.957460	-2.823336	H	0.334171	1.881261	-1.057186
H	3.969690	-1.799881	-3.192040	H	-1.171991	5.025677	1.608301	C	-1.279575	2.193232	0.329840
O	2.497567	-2.512284	-1.922259	H	-2.169665	6.141126	0.684649	H	-1.375668	2.663394	1.308355
N	2.362782	-0.509480	-0.903898	H	-0.538744	5.765393	0.125726	H	-1.950599	1.206003	0.542673
C	1.786646	-1.604609	-1.249902	C	-2.872510	0.268107	-2.537504	C	-2.088813	2.908089	-0.762889
H	0.410162	-3.954455	-1.554797	C	-3.623136	1.422020	-0.423431	H	-1.798106	2.506419	-1.738384
Pd	0.890342	0.894062	0.034901	C	-0.686774	0.679949	-3.644798	H	-1.776373	3.960356	-0.753215
C	3.771700	-0.572383	-1.344168	H	-0.691523	2.839779	-3.461874	C	-3.589038	2.800873	-0.600249
C	4.765494	-0.446168	-0.157125	H	0.508835	2.043730	-2.469972	C	-4.202120	2.960908	0.649296
H	3.954326	0.266099	-2.024793	C	-2.167051	0.366882	-3.871935	C	-4.393591	2.536178	-1.713464
C	4.602408	0.941976	0.484550	O	-3.613251	-0.669073	-2.268527	C	-5.585768	2.845422	0.329840
H	4.746580	1.741071	-0.250721	H	-3.206757	1.677914	0.551742	H	-3.604360	3.189557	1.527372
H	3.609604	1.057959	0.926552	H	-4.378660	2.178680	-0.661817	C	-5.778165	2.429421	-1.584849
H	5.342240	1.080707	1.278224	H	-4.138470	0.465891	-0.344339	H	-3.931595	2.410877	-2.688993
C	4.495837	-1.531860	0.896158	H	-0.158060	0.772151	-4.598226	C	-6.377831	2.577885	-0.334342
H	4.627058	-2.542145	0.495303	H	-0.225324	-0.154353	-3.102720	H	-6.045122	2.974566	1.757754
H	5.192042	-1.424960	1.732654	H	-2.320570	-0.567206	-4.415901	H	-6.386628	2.227341	-2.460636
H	3.478825	-1.450284	1.289500	H	-2.632888	1.176690	-4.450213	H	-7.454654	2.492897	-0.231457
C	6.196213	-0.573134	-0.708514	int-2b				C	1.278661	2.009436	0.949550
H	6.921820	-0.434619	0.097701	C	0.346818	-2.820671	0.233138	H	1.293075	1.182985	1.668139
H	6.387711	-1.556496	-1.149058	C	1.211409	-3.906059	0.170328	C	1.135983	3.286587	1.834580
H	6.397249	0.186252	-1.471669	C	2.543980	-3.678594	-0.173722	C	2.617953	2.020416	0.224710
H	-1.901589	-4.391057	-0.646199	C	2.950918	-2.375666	-0.437907	H	1.988344	3.297895	2.520460
H	-1.995135	-0.304094	0.667349	C	2.022196	-1.334744	-0.359761	H	0.248909	3.166002	2.467139
C	-3.395776	-2.641794	0.829341	N	0.746671	-1.550415	-0.029719	C	1.067933	4.621115	1.091779
F	-4.077963	-1.503458	1.054421	C	-2.964413	-3.919375	1.266608	C	3.717923	1.482395	0.808896
F	-4.176969	-3.488432	0.148417	H	-3.581632	-4.638882	0.732382	C	2.689215	2.692447	-1.132273
F	-3.141089	-3.197369	2.039965	H	-3.020087	-4.108144	2.340309	H	2.007511	4.846991	0.581571
C	-0.470646	2.312196	0.634690	O	-1.572535	-4.156322	0.859661	H	0.877242	5.434897	1.796541
H	-1.254430	1.829300	1.212656	N	-1.861826	-1.939386	0.621919	H	0.267218	4.639538	0.344879
C	0.655034	2.864516	1.439760	C	-1.073374	-2.952238	0.582951	C	5.055653	1.548431	0.132999
H	0.825902	3.931898	1.265102	H	0.839152	-4.899374	0.388693	C	3.705624	0.780402	2.145464
H	1.642739	2.443166	0.980721	Pd	-0.786577	-0.072788	0.243105	C	4.067442	3.293267	-1.408169
C	0.653174	2.483457	2.939059	C	-3.228802	-2.436116	0.888969	H	2.458002	1.954843	-1.918249
H	-0.101058	3.099005	3.439584	C	-4.176983	-2.220373	-0.324356	H	1.915597	3.460858	-1.213294
H	1.621370	2.746962	3.374829	H	-3.635950	-1.885006	1.741733	C	5.143582	2.227856	-1.220869
C	0.351369	1.016914	3.147519	C	-4.264967	-0.720097	-0.639748	O	6.041119	1.045564	0.649041
C	1.360790	0.053346	3.003789	H	-4.556968	-0.130347	0.234879	H	3.001786	-0.060560	2.158145
C	-0.958296	0.580441	3.389876	H	-3.311765	-0.332127	-1.008547	H	4.703531	0.394311	2.350961
C	1.062350	-1.308963	3.070512	H	-5.011079	-0.539792	-1.417233	H	3.423341	1.452407	2.961811
H	2.388814	0.371385	2.855074	C	-3.664123	-2.968613	-1.565257	H	4.105249	3.710371	-2.418713
C	-1.261750	-0.780570	3.446694	H	-3.604007	-4.050414	-1.410145	H	4.242485	4.121689	-0.710968
H	-1.747099	1.313639	3.536083	H	-4.342976	-2.801362	-2.405838	H	6.156024	2.622425	-1.332578
C	-0.252166	-1.729564	3.275224	H	-2.674952	-2.608030	-1.864827	H	5.024796	1.439609	-1.977479
H	1.858808	-2.039844	2.971963	C	-5.573233	-2.732197	0.070821				

SAPT Energies

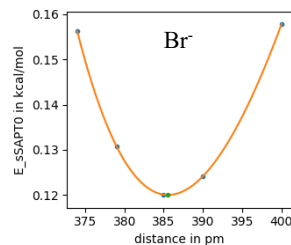
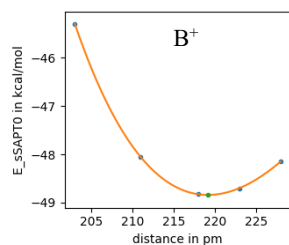
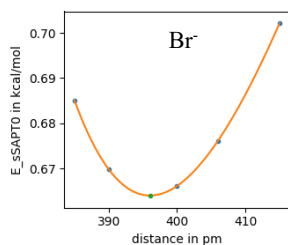
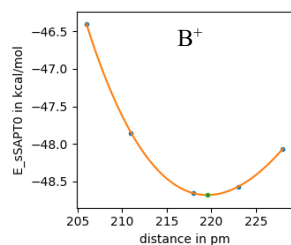
4-CO₂Et-C₆H₄_conf1

4-CO₂Et-C₆H₄_conf2



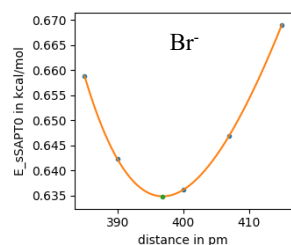
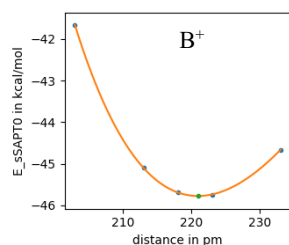
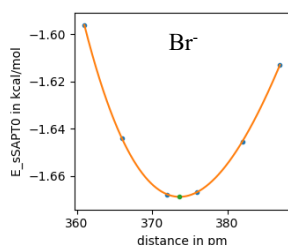
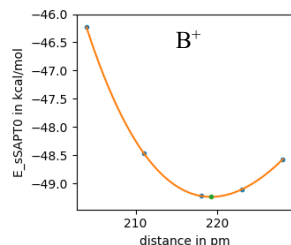
4-Me-C₆H₄

3-Me-C₆H₄



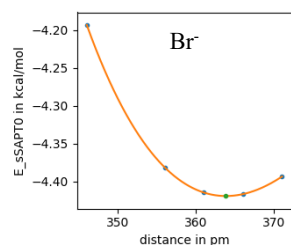
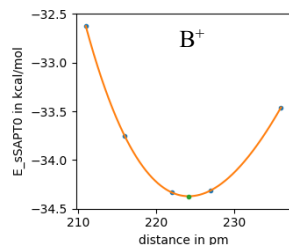
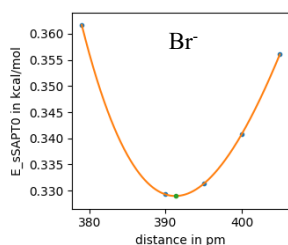
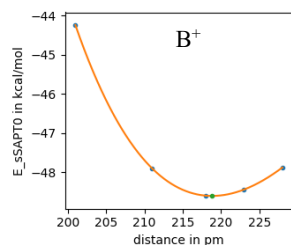
4-Ph-C₆H₄

C₆H₅



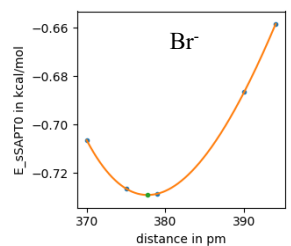
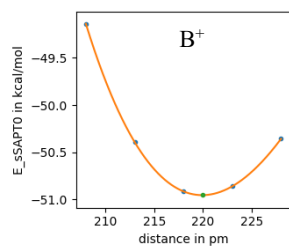
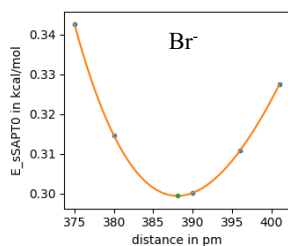
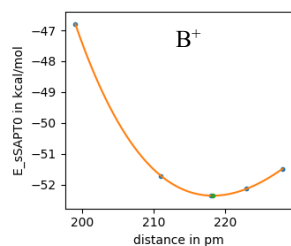
4-OMe-C₆H₄

4-CF₃-C₆H₄

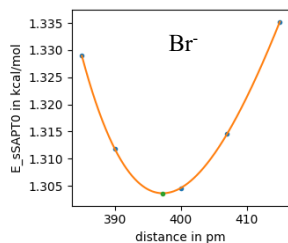
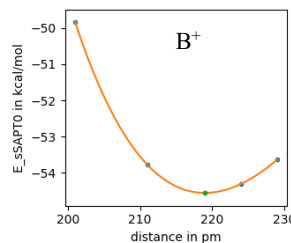


3,5-diMe-C₆H₃

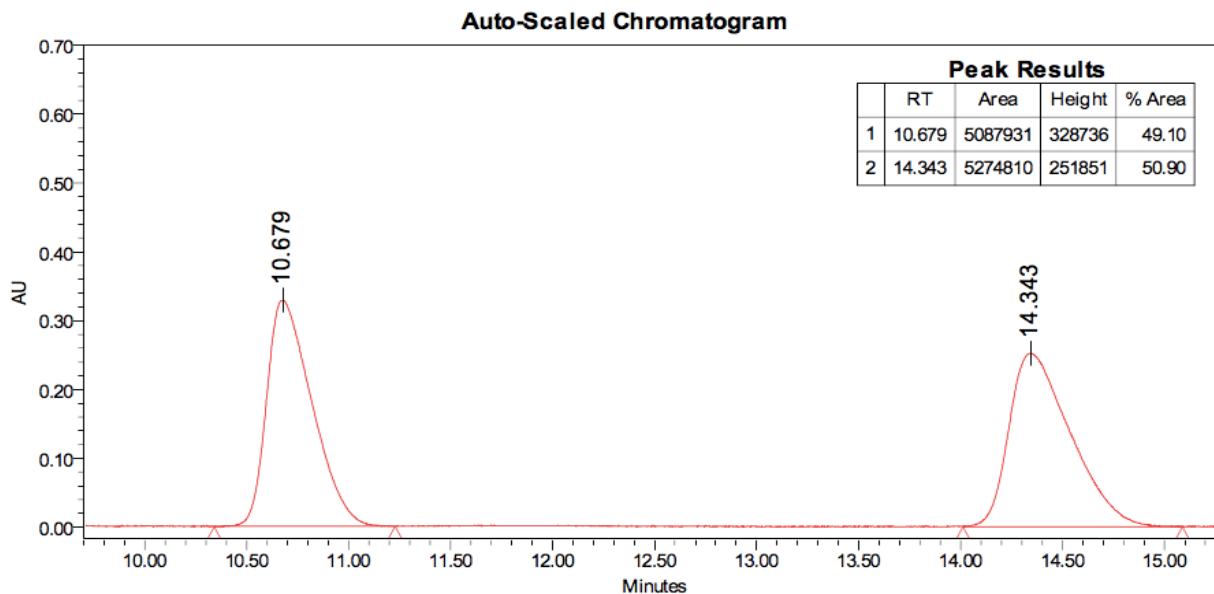
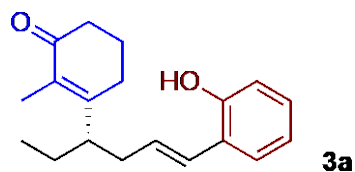
3,5-diOMe-C₆H₃-confI



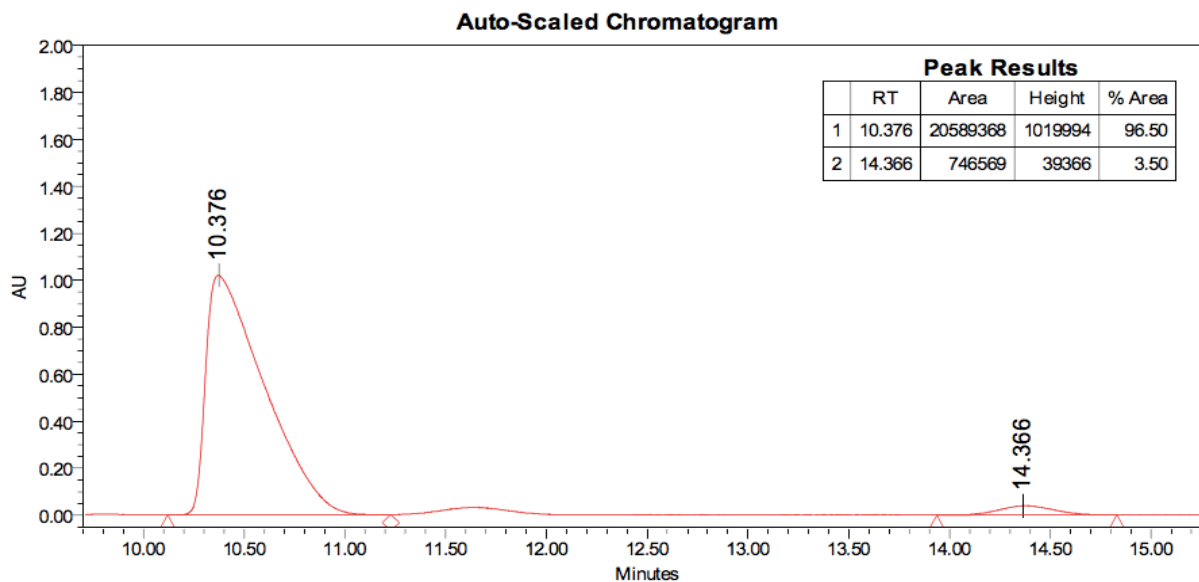
3,5-diOMe-C₆H₃-conf2



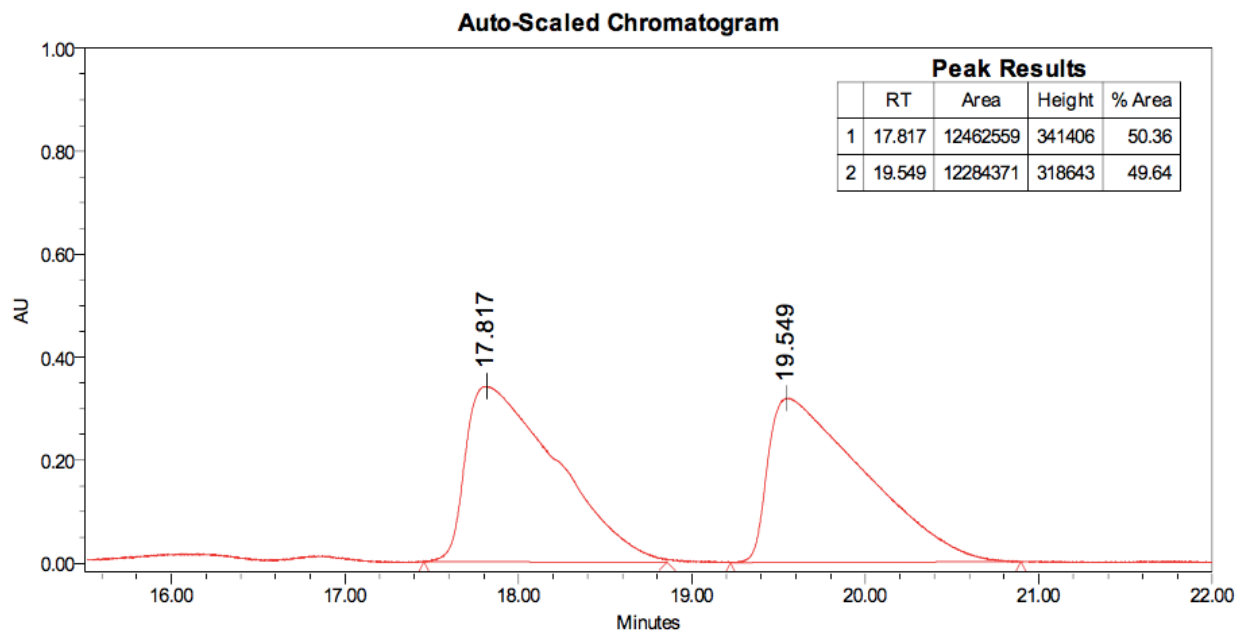
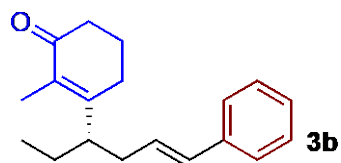
Determination of enantiomeric ratios and SFC traces



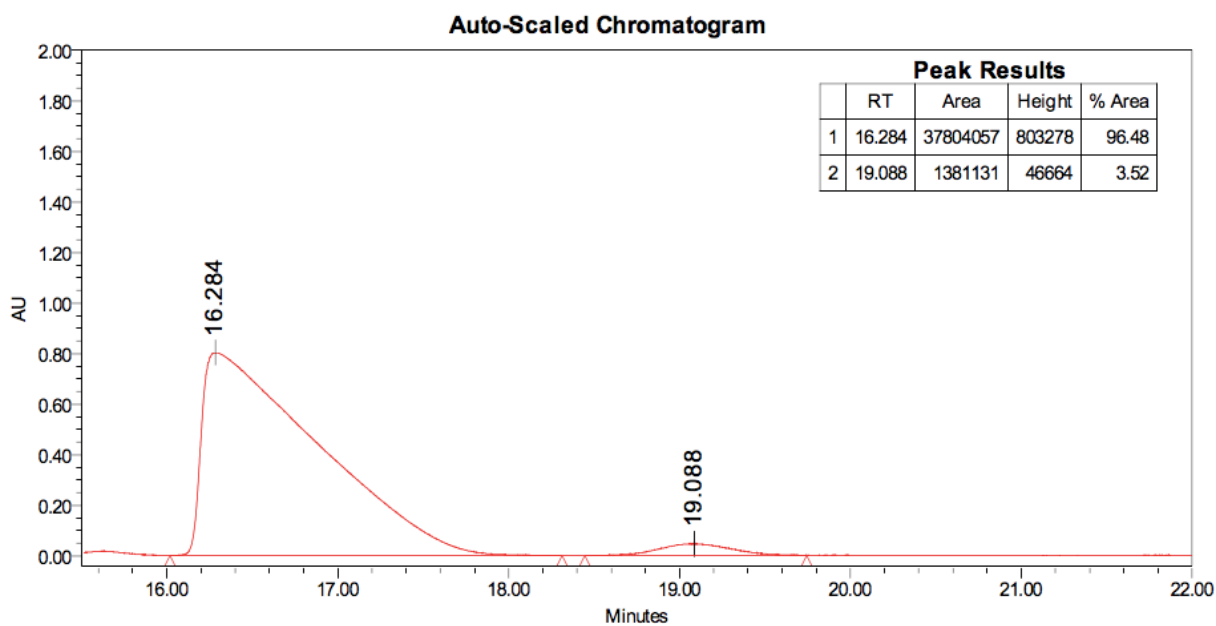
Separation by SFC, Chiralcel® **3a**-Rac sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 5:95, 2 mL/min, 138 bar, 40 min; *t*₁ = 10.679 min, *t*₂ = 14.343 min.



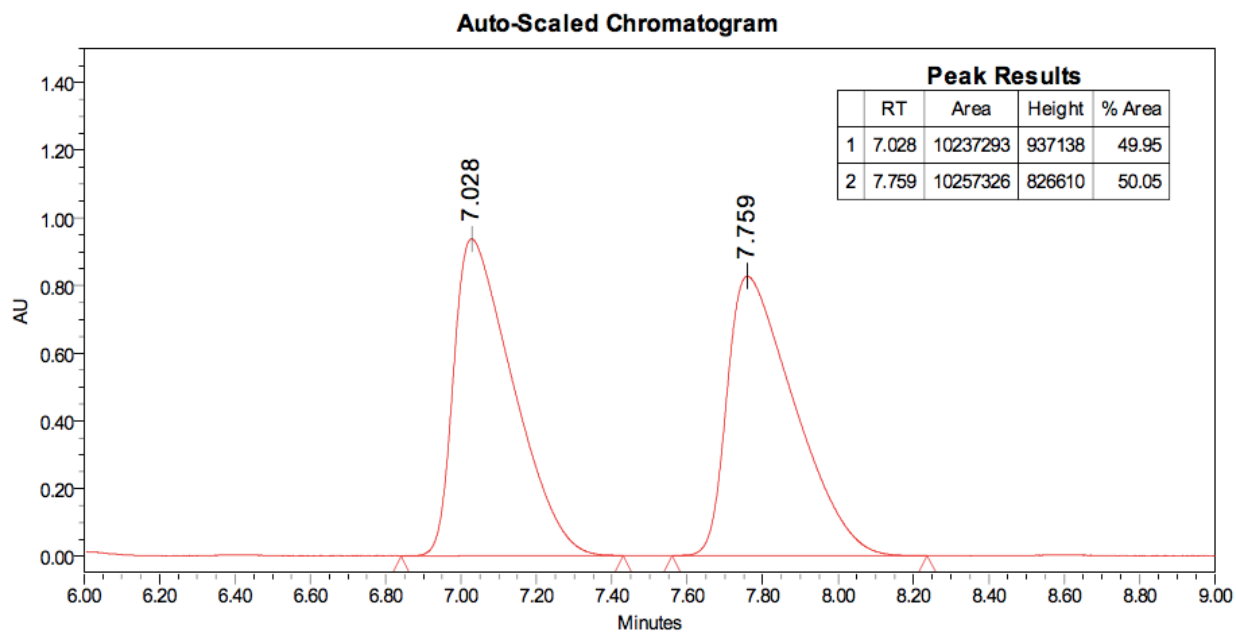
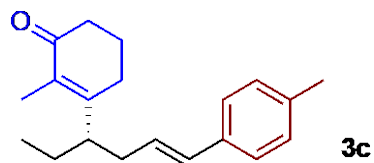
3a sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 5:95, 2 mL/min, 138 bar, 40 min; *t*₁ = 10.376 min, *t*₂ = 14.366 min, er = 96.5:3.5.



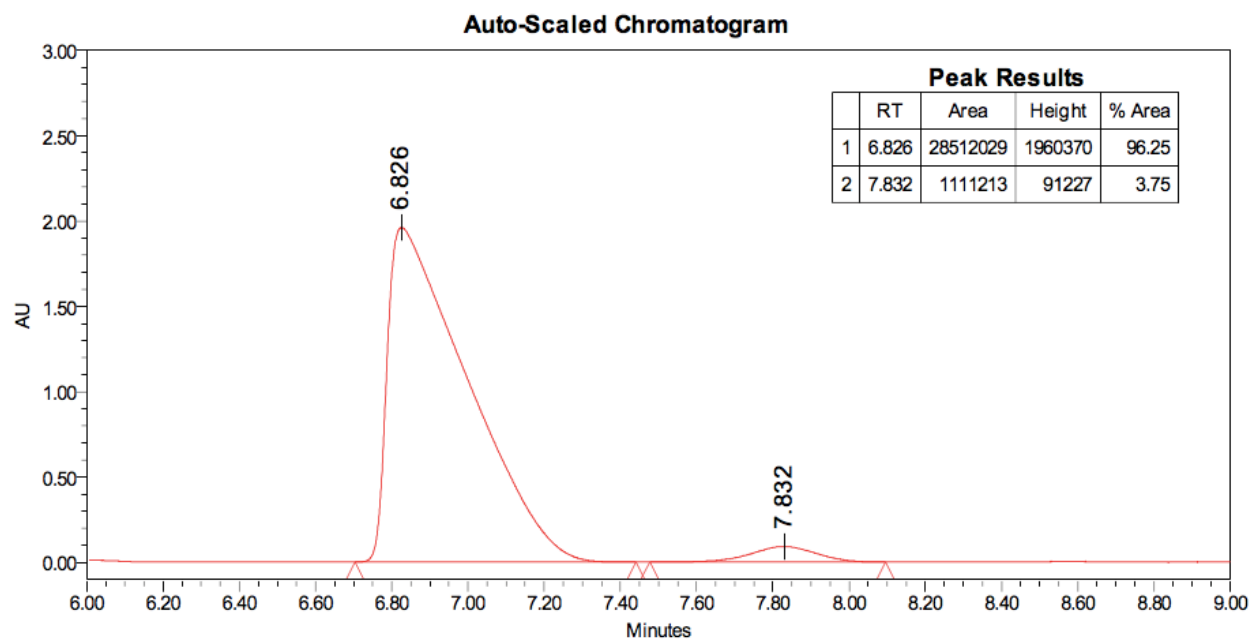
Separation by SFC, Chiralcel® **3b**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 2 mL/min, 138 bar, 40 min; $t_1 = 17.817$ min, $t_2 = 19.549$ min.



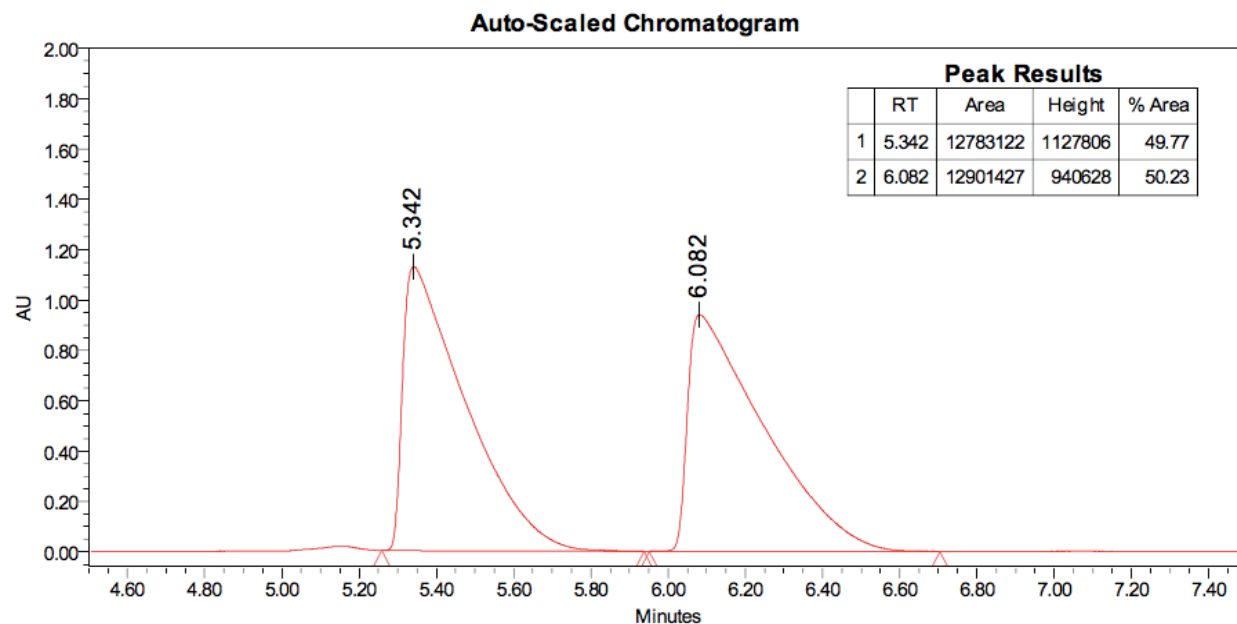
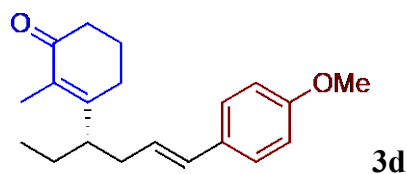
3b sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 2 mL/min, 138 bar, 40 min; $t_1 = 16.284$ min, $t_2 = 19.088$ min, er = 96.5:3.5.



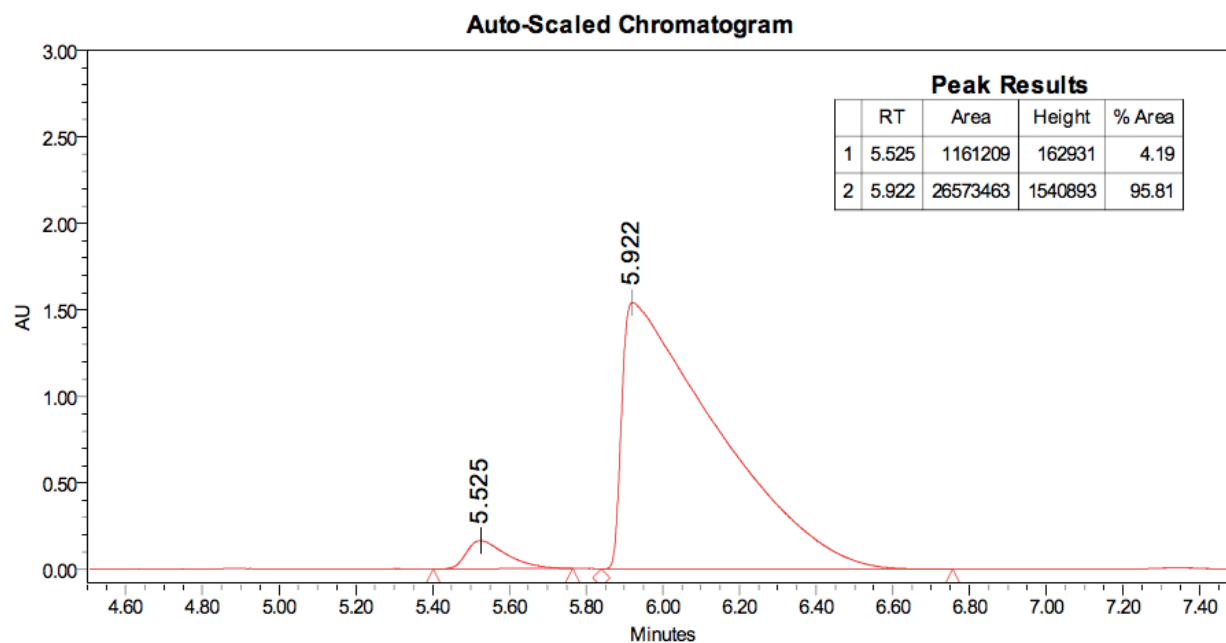
Separation by SFC, Chiralcel® **3c**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 20 min; $t_1 = 7.028$ min, $t_2 = 7.759$ min.



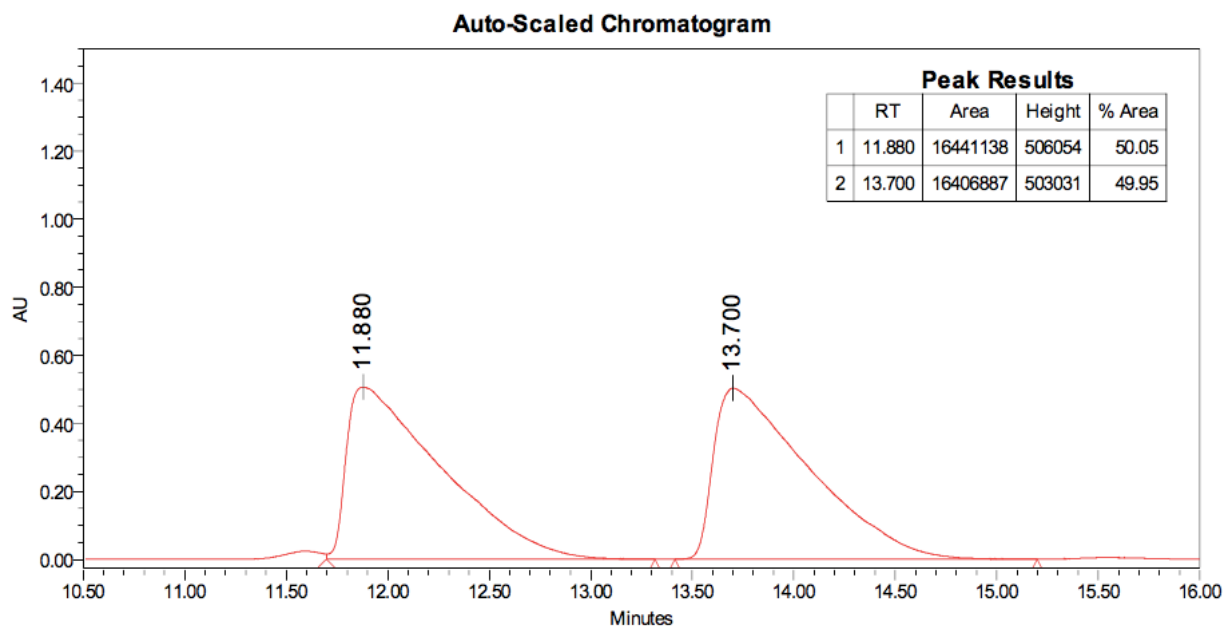
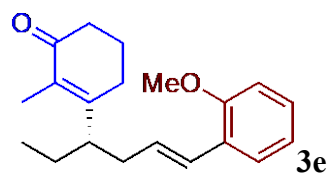
3c sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; $t_1 = 6.826$ min, $t_2 = 7.832$ min, er = 96:4.



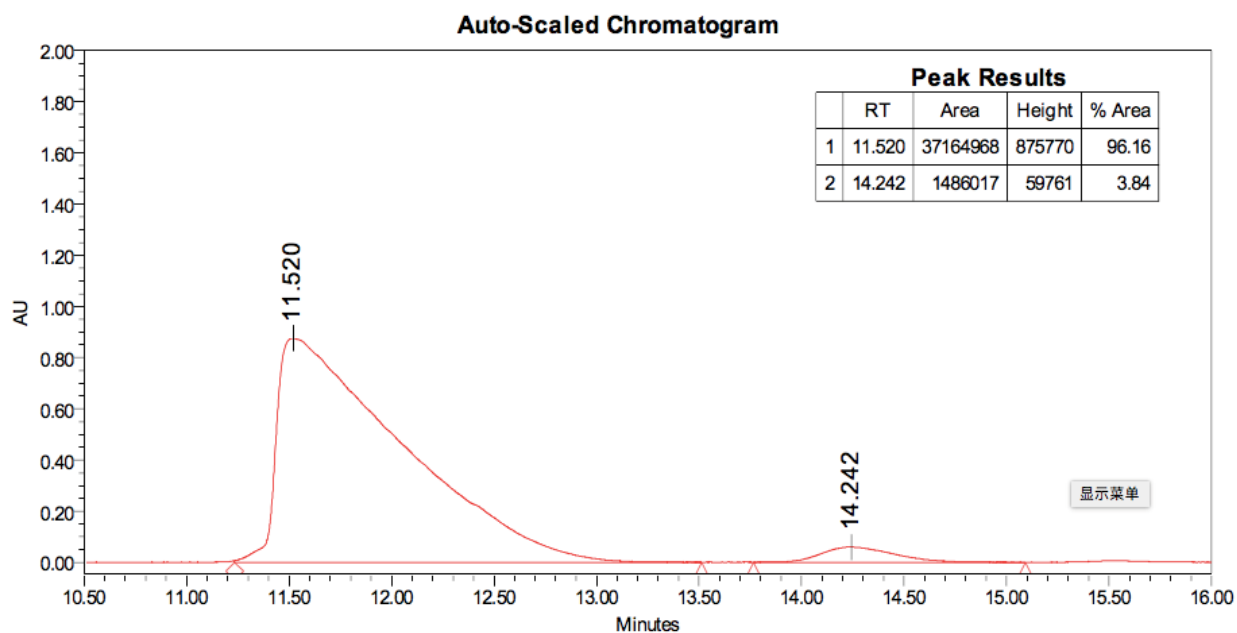
Separation by SFC, Chiralcel® **3d**-Rac sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 5.342 min, *t*₂ = 6.082 min.



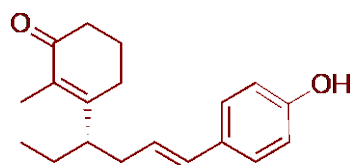
3d sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 5.525 min, *t*₂ = 5.922 min, er = 4:96.



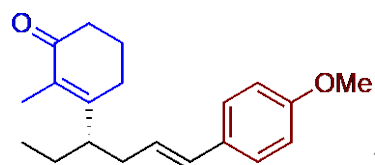
Separation by SFC, Chiralcel® **3e**-Rac sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 11.880 min, *t*₂ = 13.700 min.



3e sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 11.520 min, *t*₂ = 14.242 min, er = 96:4.

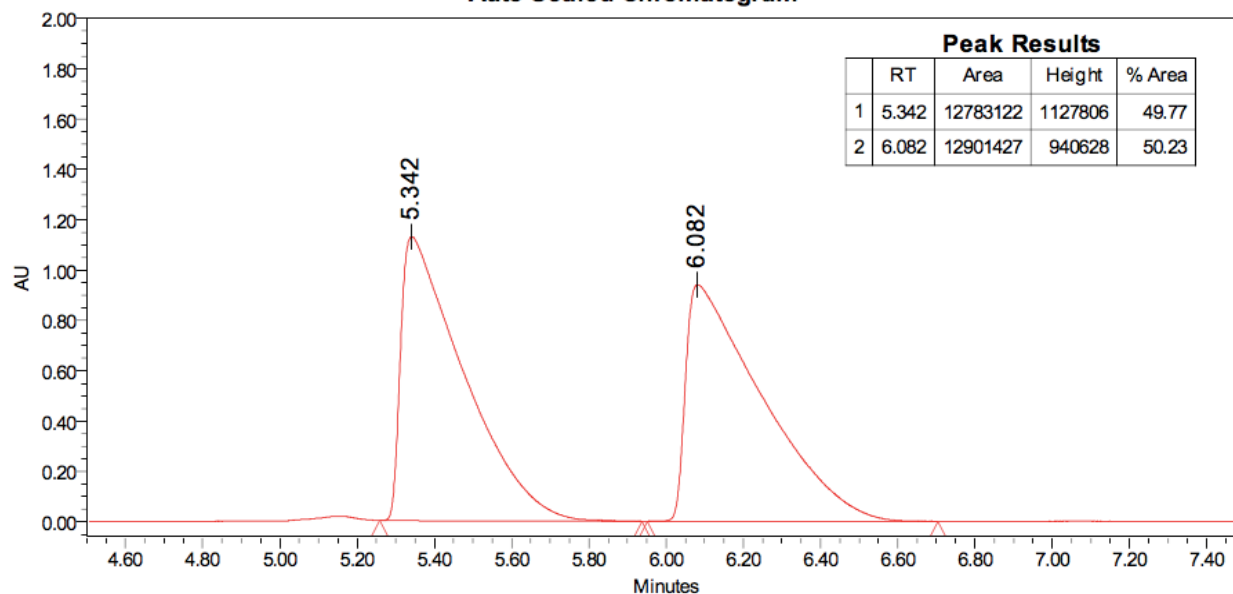


3f er was got after methylation



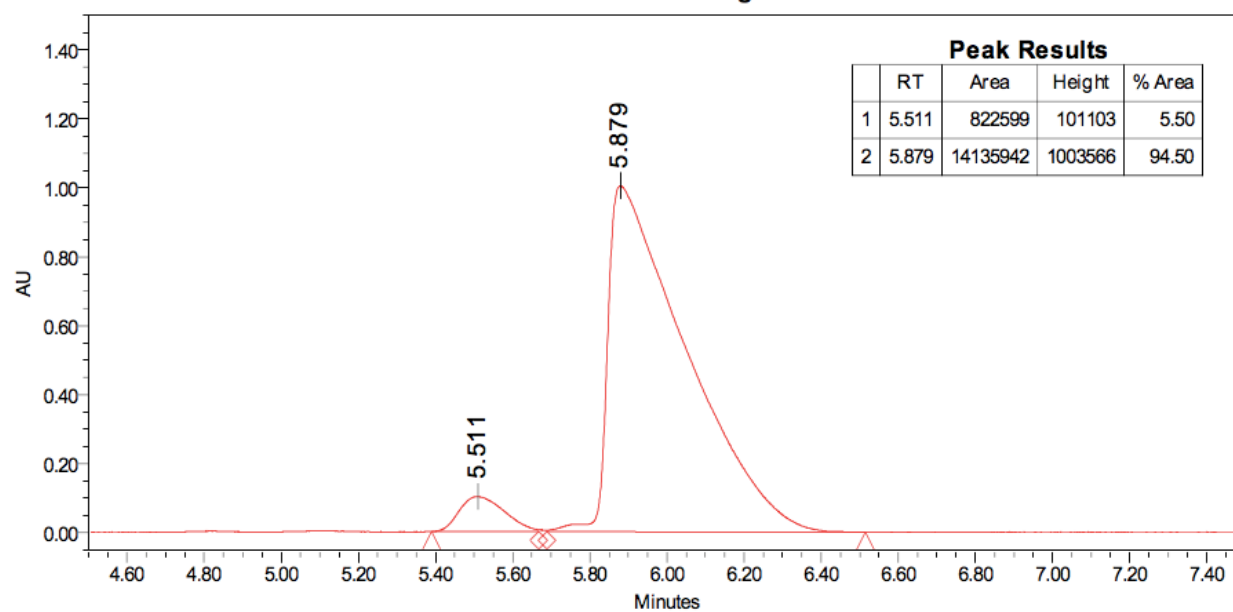
3d

Auto-Scaled Chromatogram

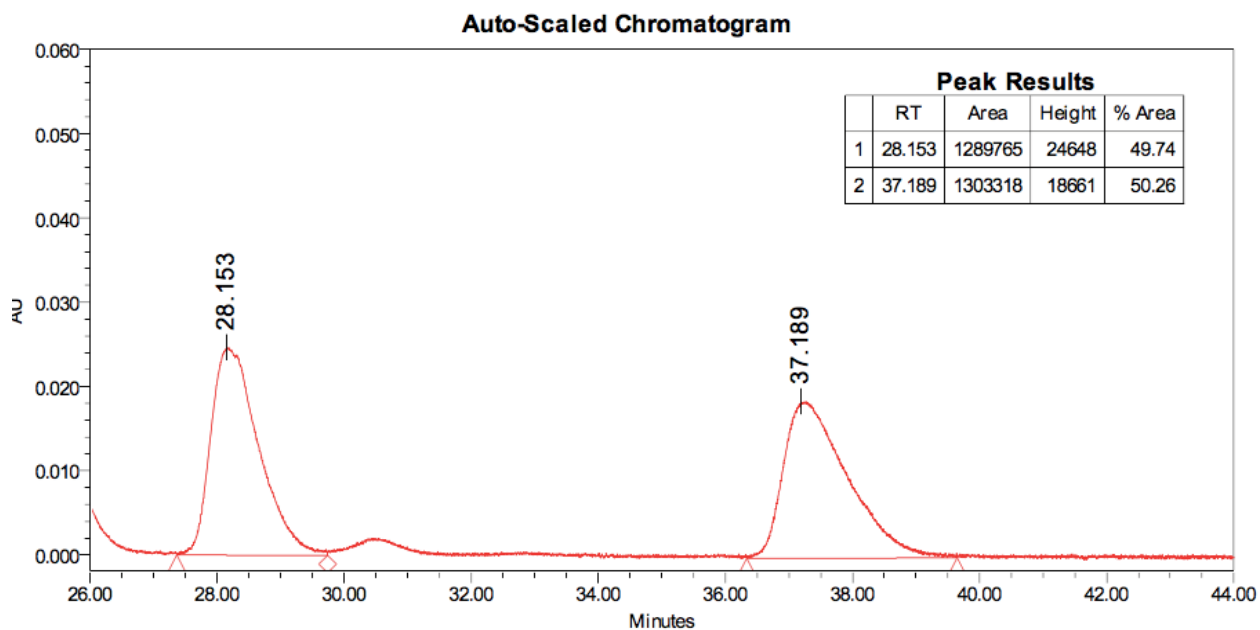
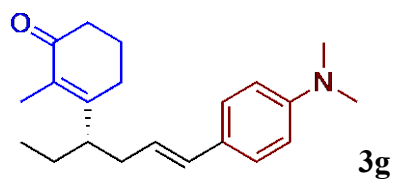


Separation by SFC, Chiralcel® **3d**-Rac sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 5.342 min, *t*₂ = 6.082 min.

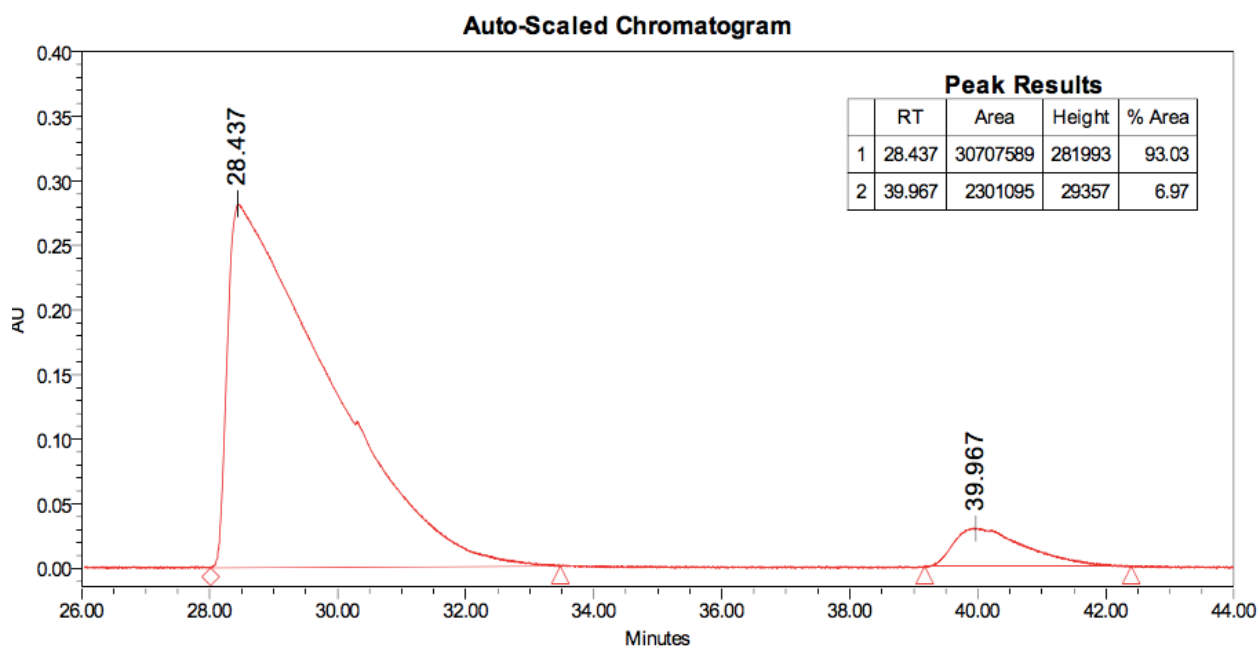
Auto-Scaled Chromatogram



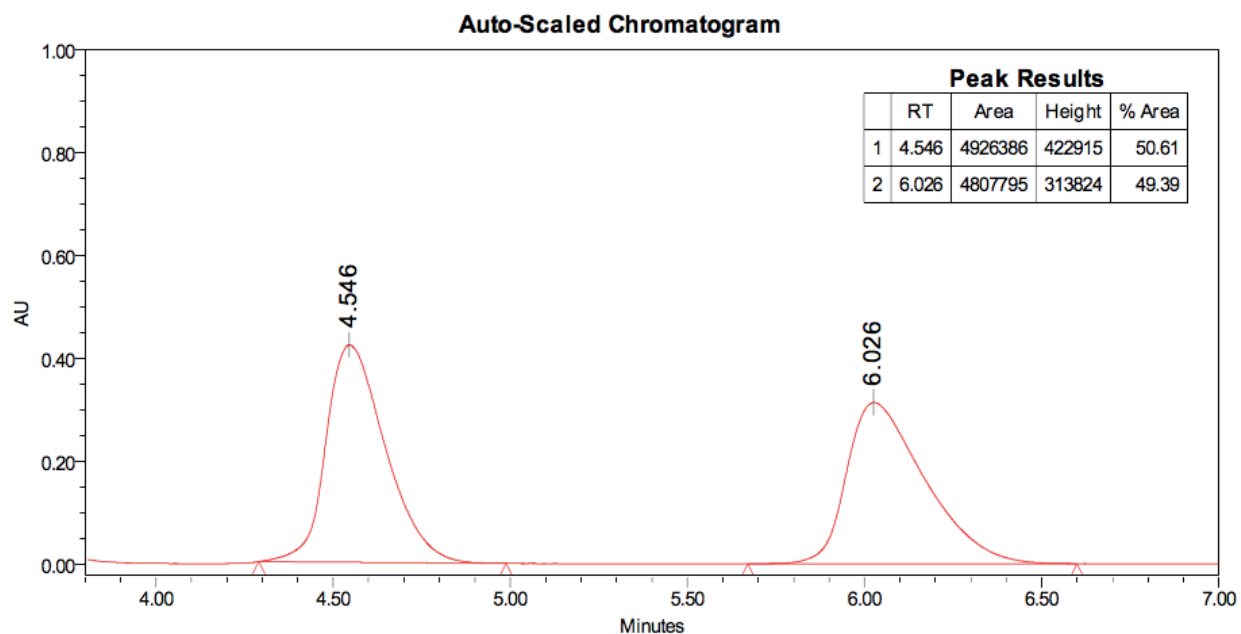
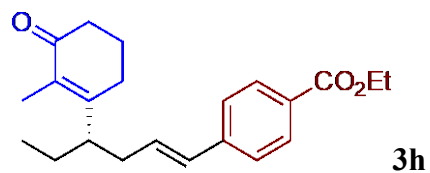
3d sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 5.511min, *t*₂ = 5.879 min, er = 5.5:94.5.



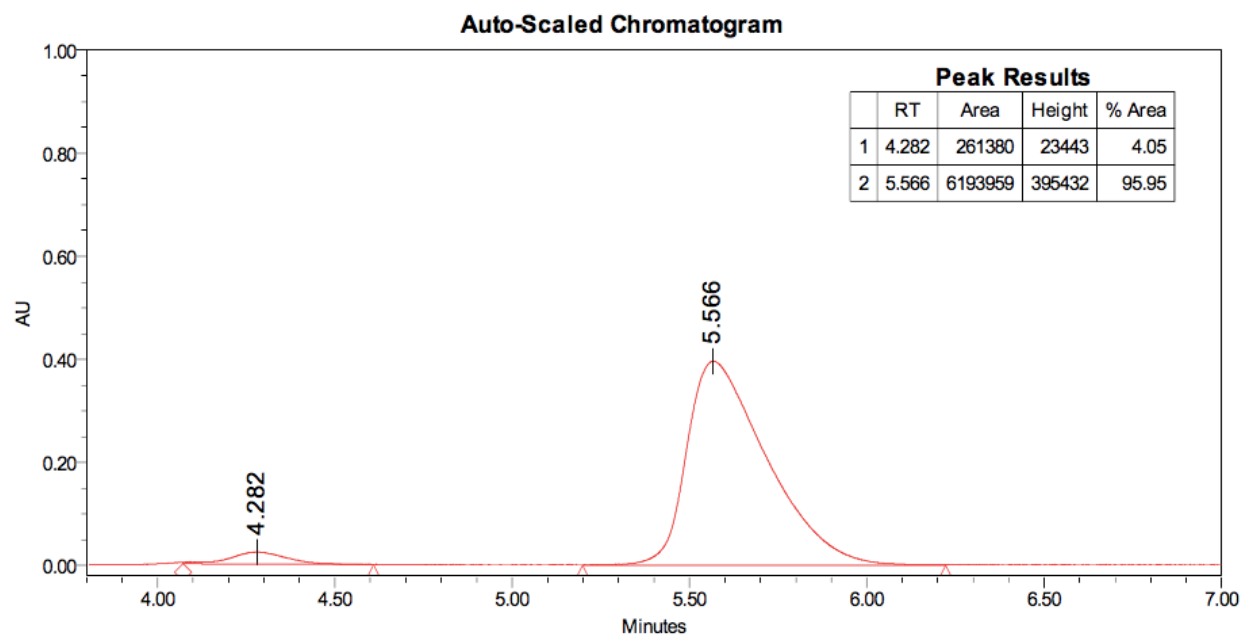
Separation by SFC, Chiralcel® **3g**-Rac sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 28.153 min, *t*₂ = 37.189 min.



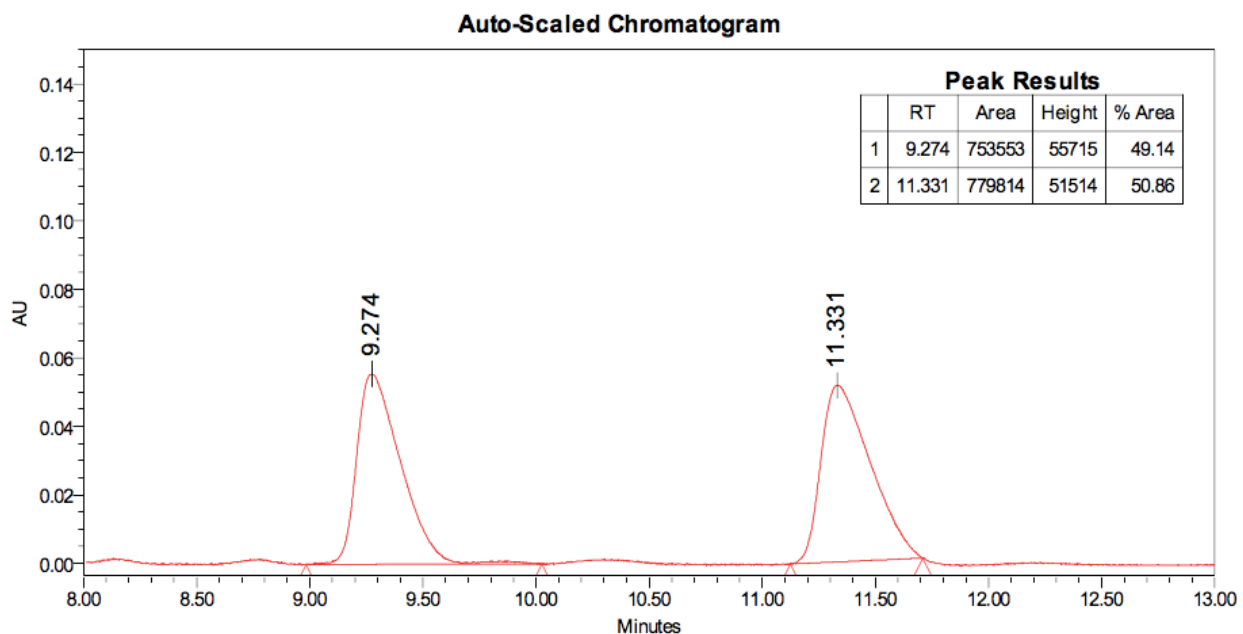
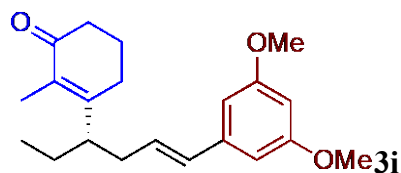
3g sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 28.437 min, *t*₂ = 39.967 min, er = 93:7.



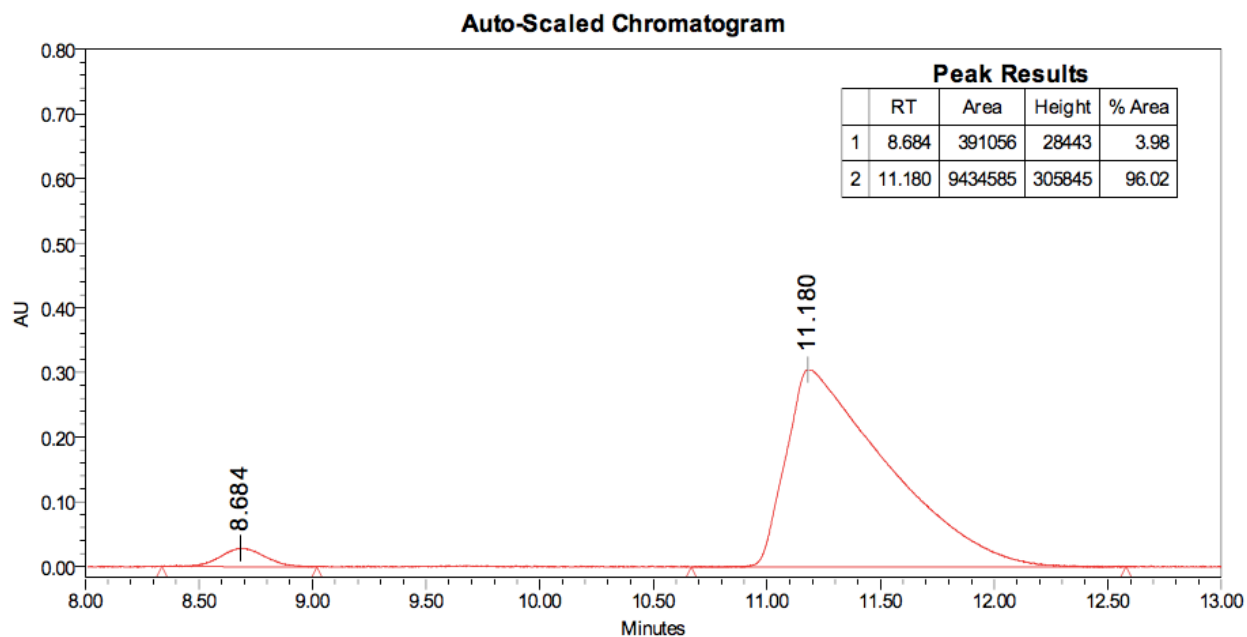
Separation by SFC, Chiralcel® **3h**-Rac sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 8:92, 2 mL/min, 138 bar, 20 min; t_1 = 4.546 min, t_2 = 6.026 min.



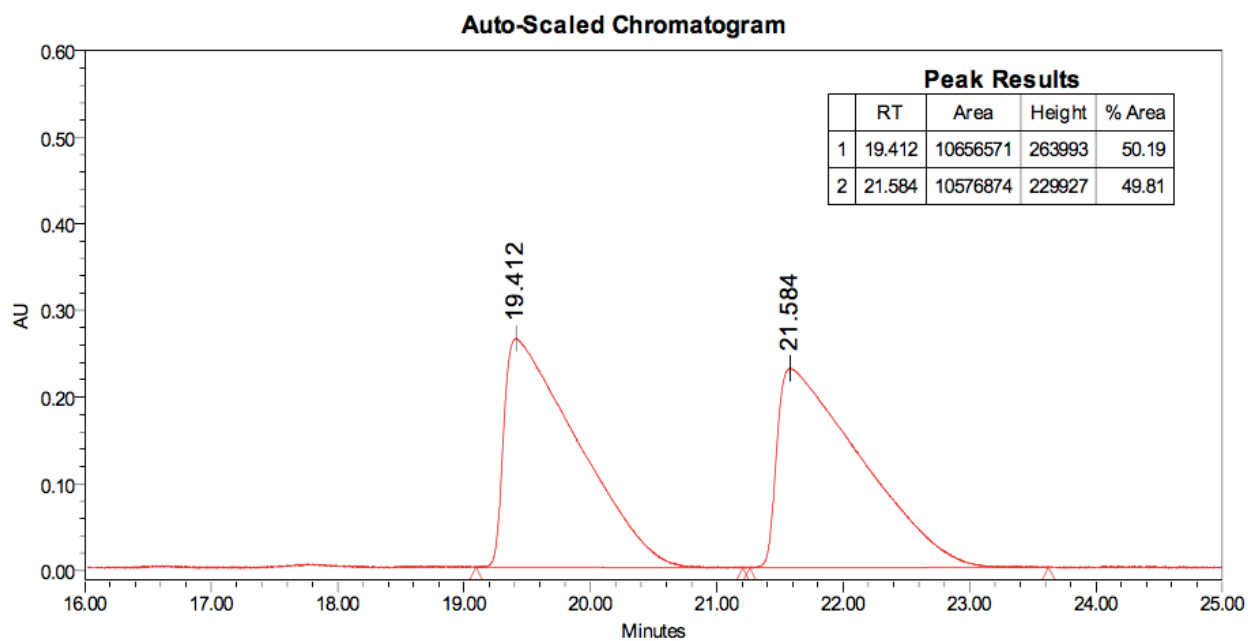
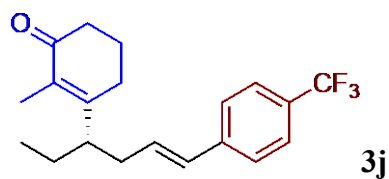
3h sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 8:92, 2 mL/min, 138 bar, 20 min; t_1 = 4.282 min, t_2 = 5.566 min, er = 4:96.



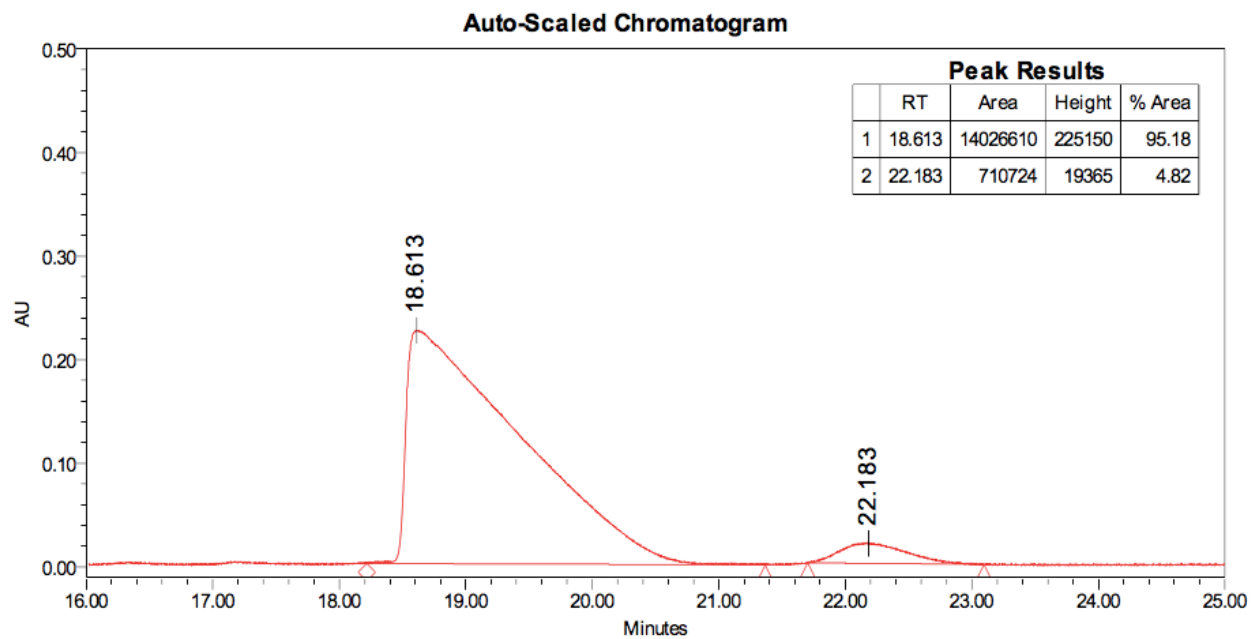
Separation by SFC, Chiralcel® **3i**-Rac sample (Conditions): Cel1 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; $t_1 = 9.274$ min, $t_2 = 11.331$ min.



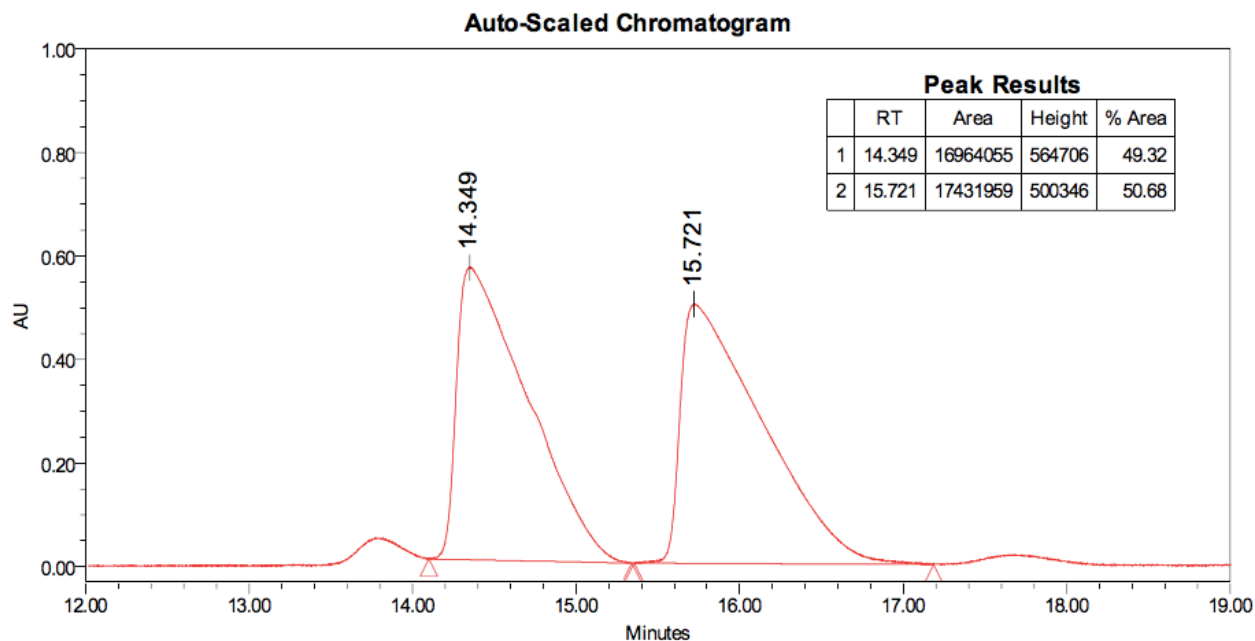
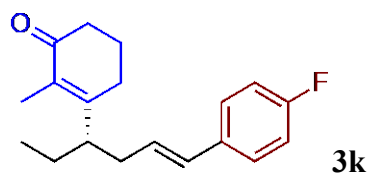
3i sample (Conditions): Cel1 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; $t_1 = 8.684$ min, $t_2 = 11.180$ min, er = 4:96.



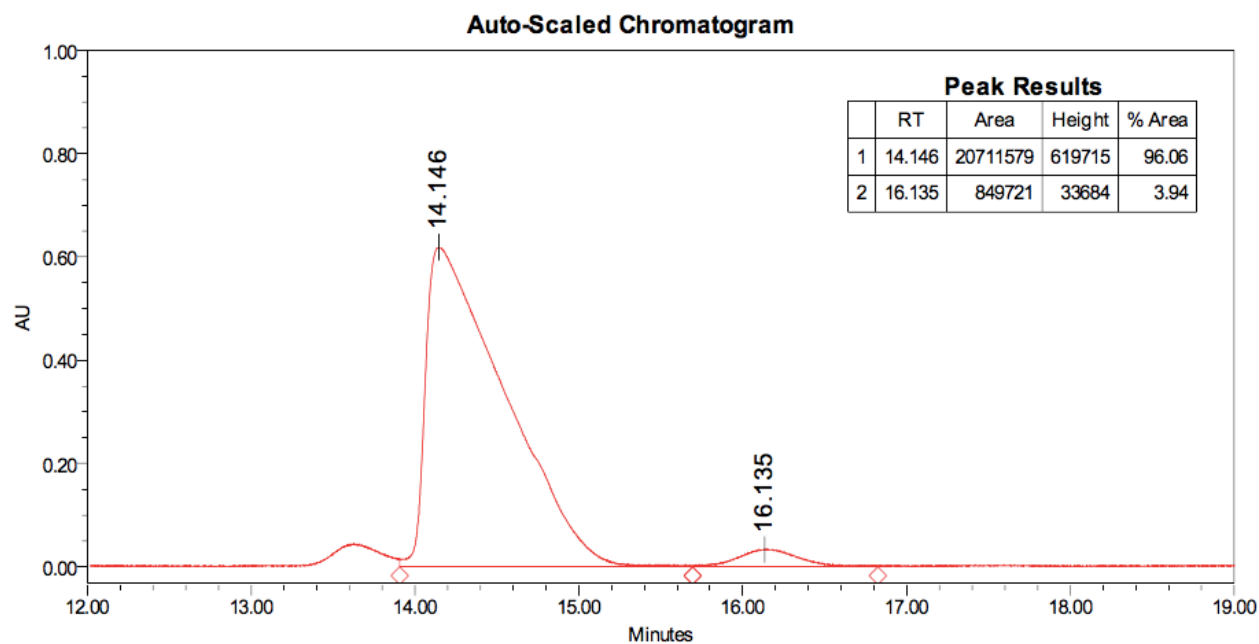
Separation by SFC, Chiralcel® **3j**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 1 mL/min, 138 bar, 40 min; t_1 = 19.412 min, t_2 = 21.584 min.



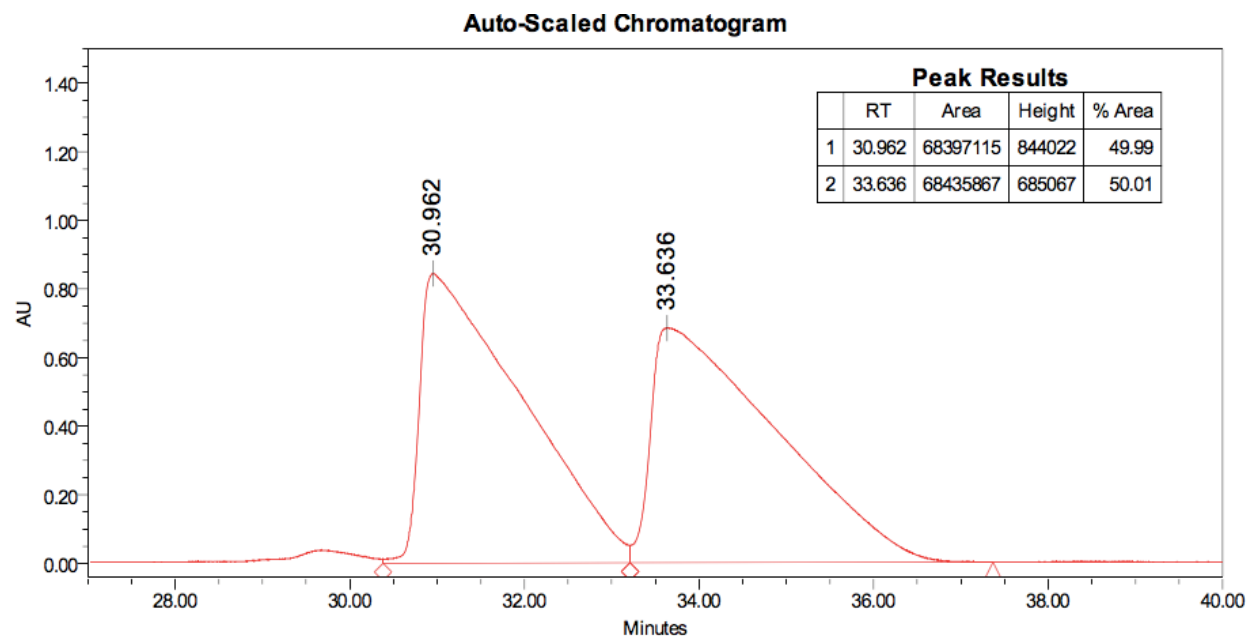
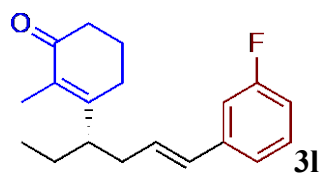
3j sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 1 mL/min, 138 bar, 40 min; t_1 = 18.613 min, t_2 = 22.183 min, er = 95:5.



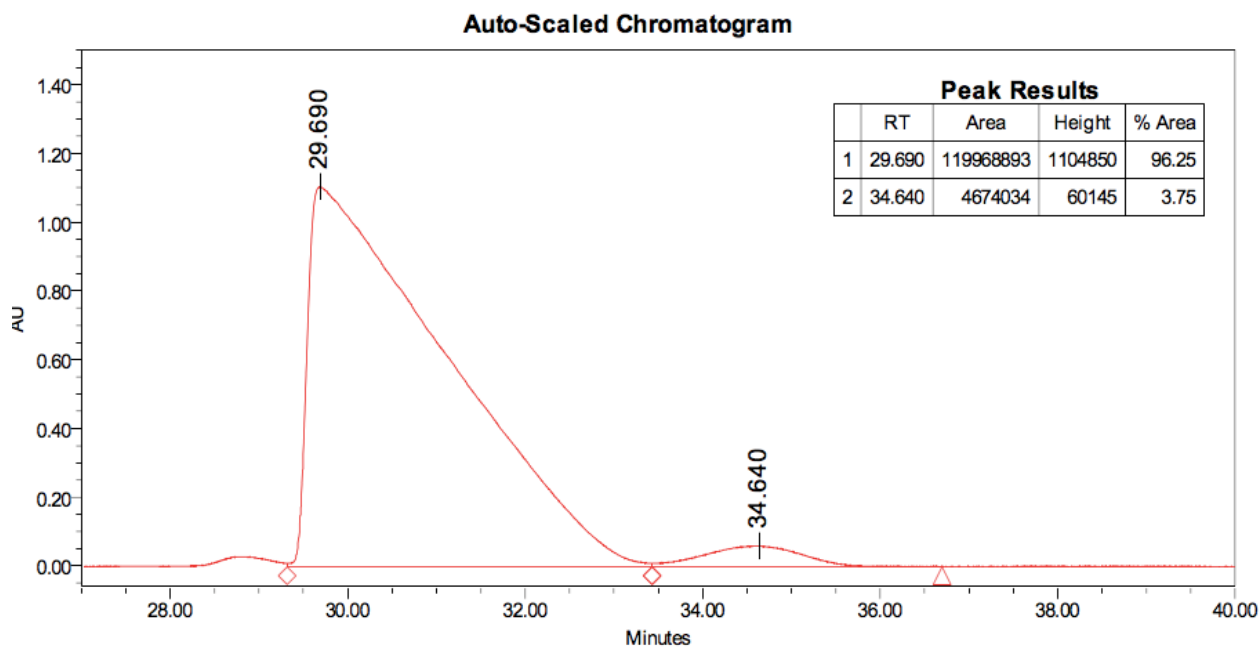
Separation by SFC, Chiralcel® **3k**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 2 mL/min, 138 bar, 40 min; t_1 = 14.349 min, t_2 = 15.721 min.



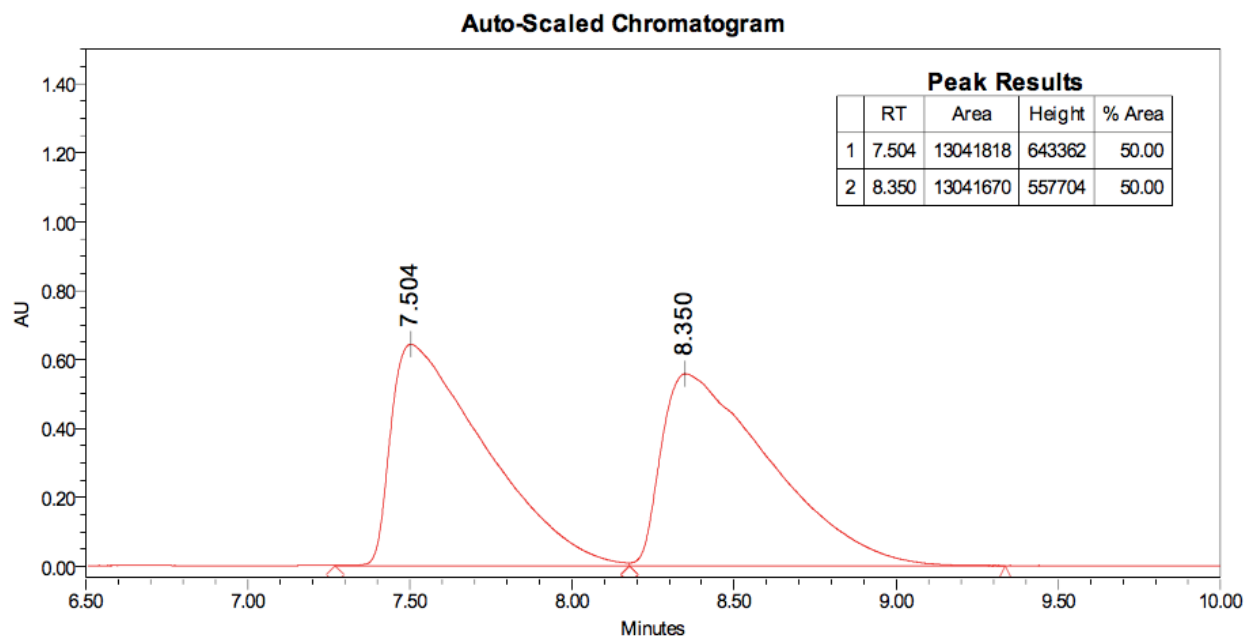
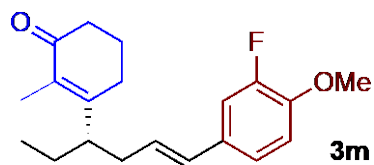
3k sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 2 mL/min, 138 bar, 40 min; t_1 = 14.146 min, t_2 = 16.135 min, er = 96:4.



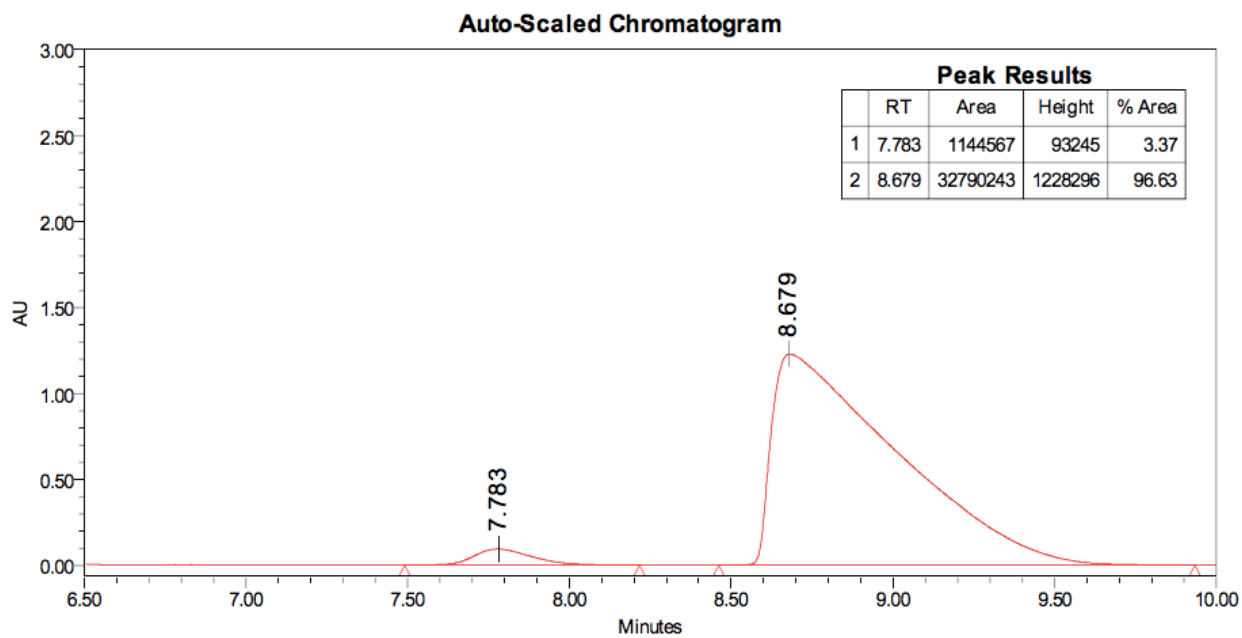
Separation by SFC, Chiralcel® **31**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 1 mL/min, 138 bar, 40 min; t_1 = 30.962 min, t_2 = 33.636 min.



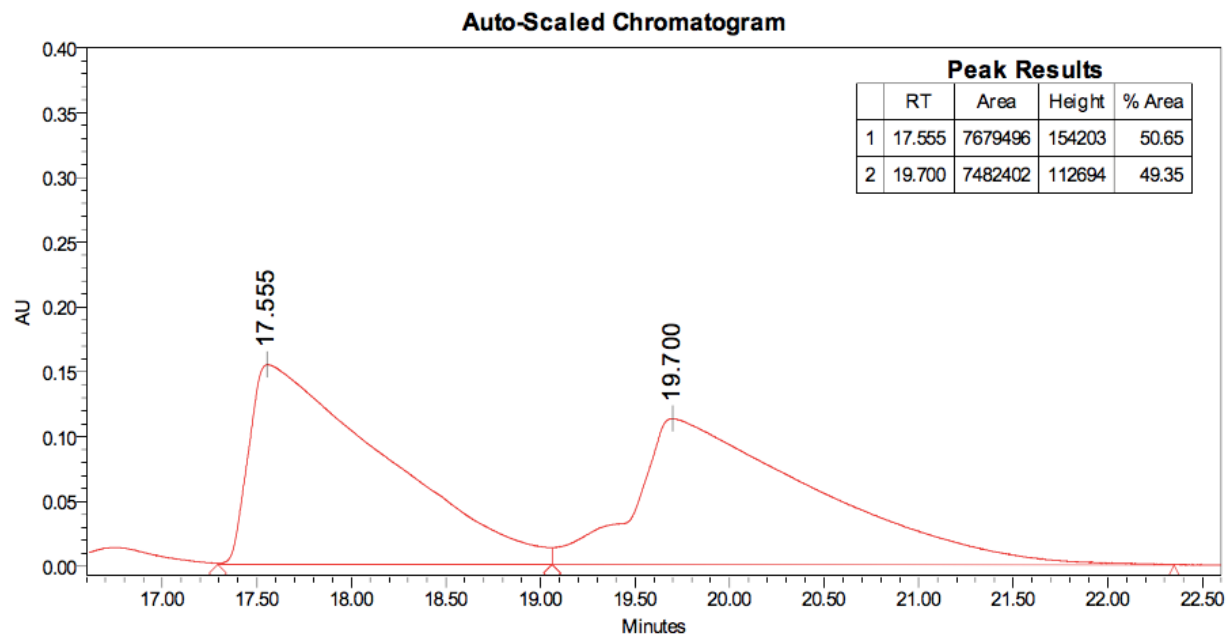
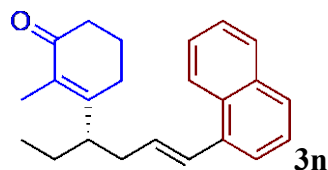
31 sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 1:99, 1 mL/min, 138 bar, 40 min; t_1 = 29.690 min, t_2 = 34.640 min, er = 96:4.



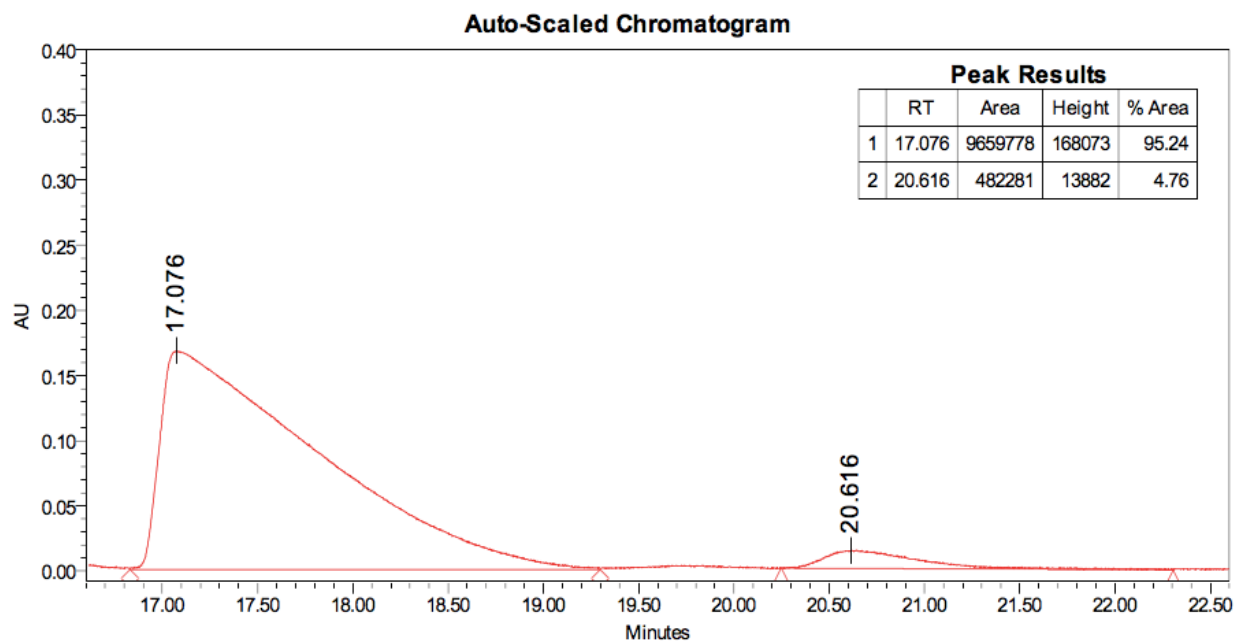
Separation by SFC, Chiralcel® **3m**-Rac sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 7.504 min, *t*₂ = 8.350 min.



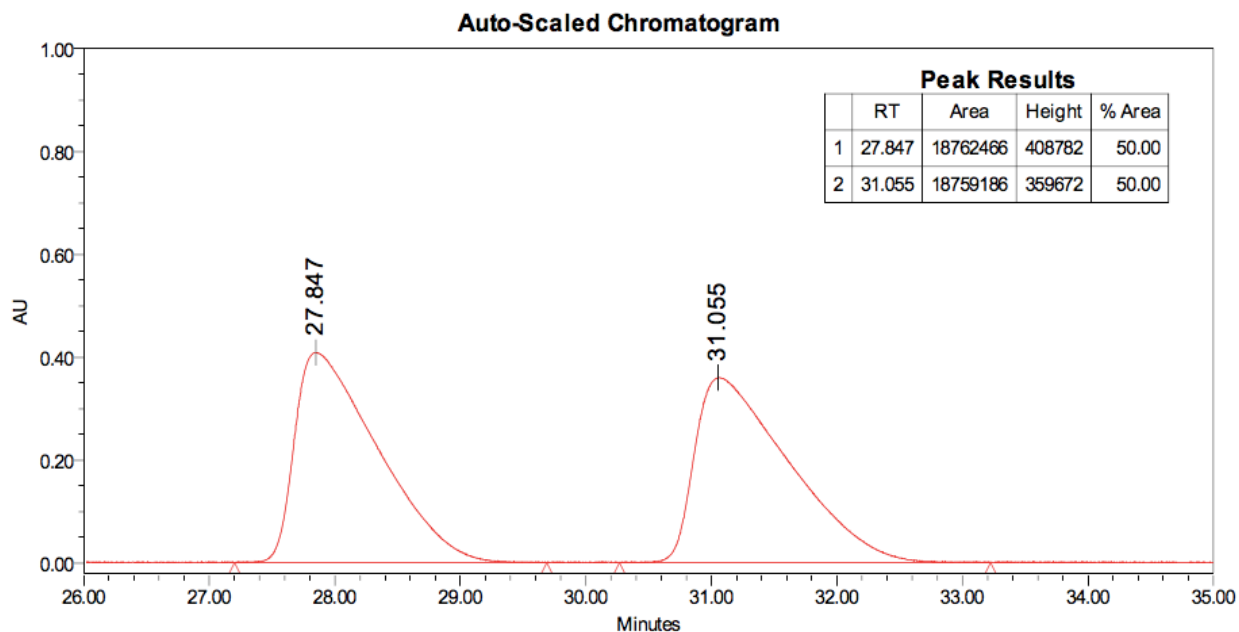
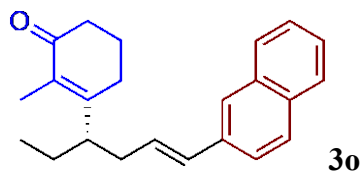
3m sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; *t*₁ = 7.783 min, *t*₂ = 8.679 min, er = 3.5:96.5.



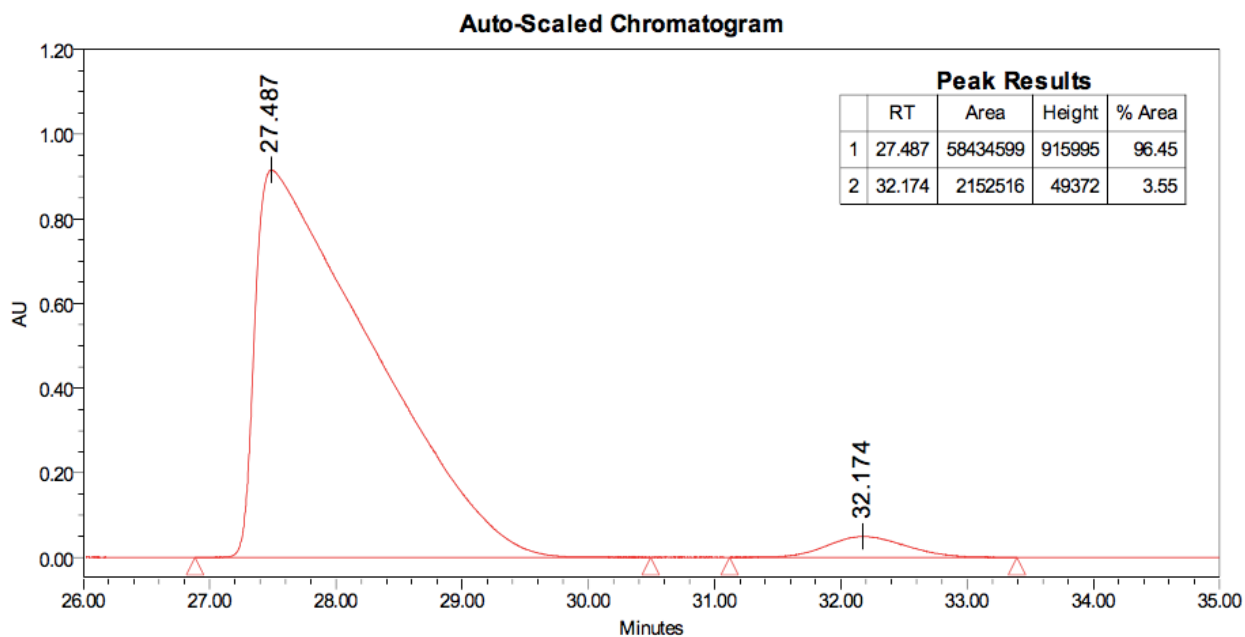
Separation by SFC, Chiralcel® **3n**-Rac sample (Conditions): Cell1 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; $t_1 = 17.555$ min, $t_2 = 19.700$ min.



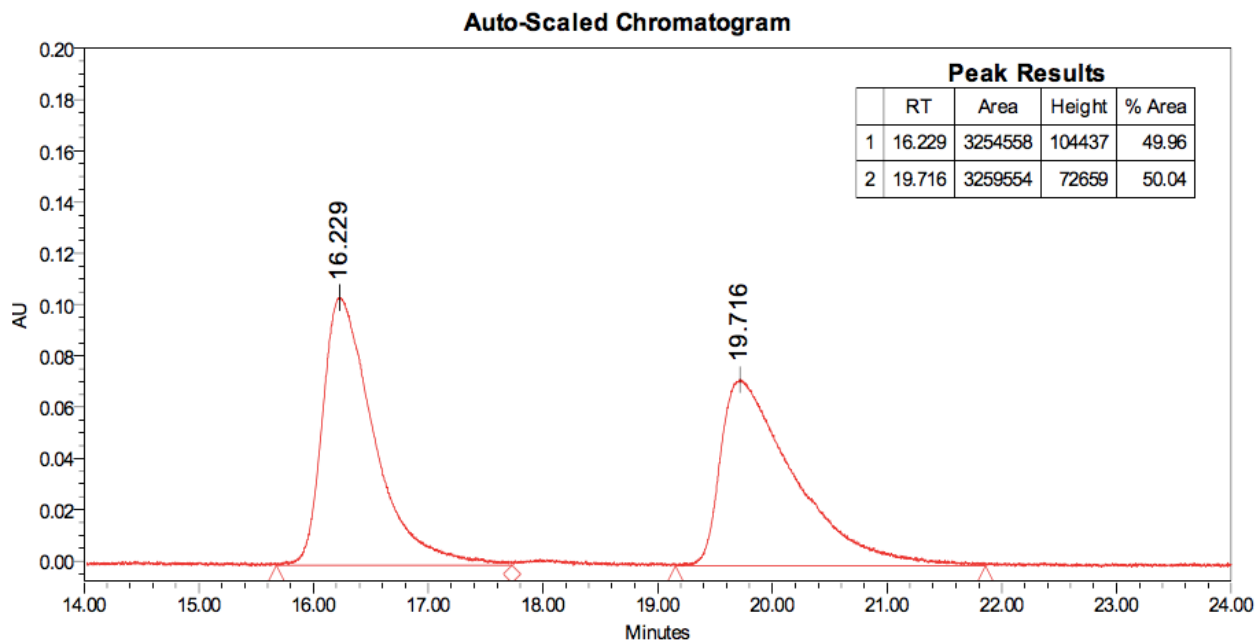
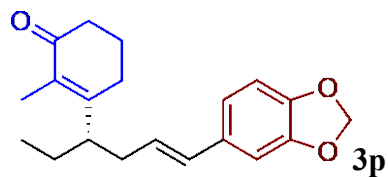
3n sample (Conditions): Cell1 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; $t_1 = 17.076$ min, $t_2 = 20.616$ min, er = 95:5.



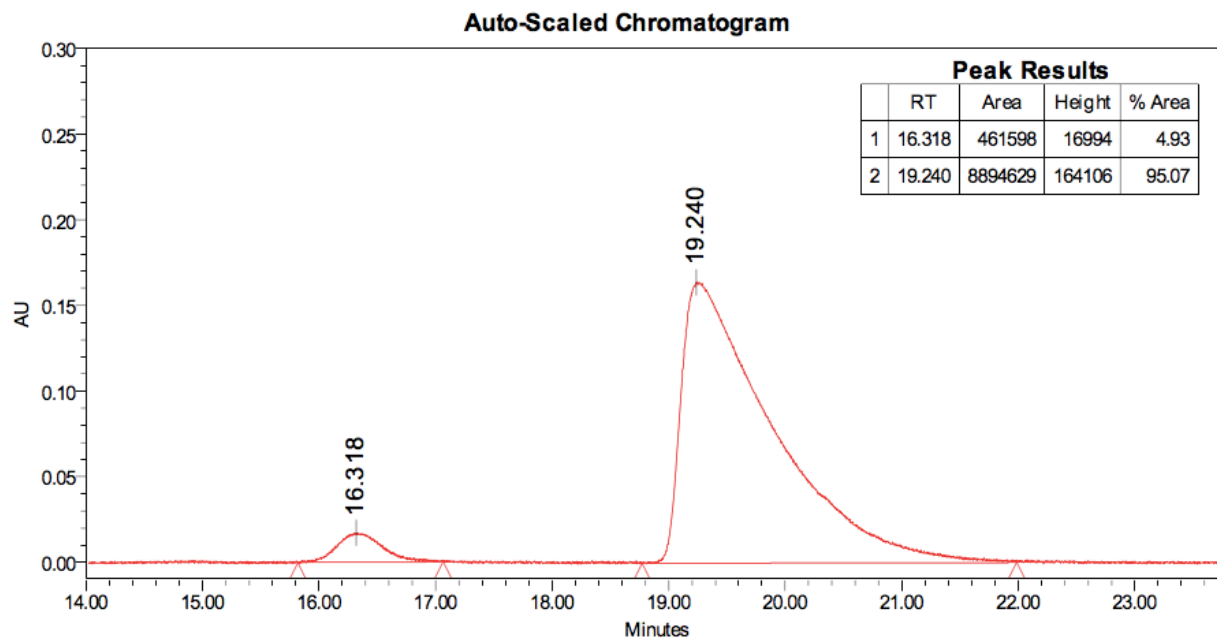
Separation by SFC, Chiralcel® **30**-Rac sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; t_1 = 27.847 min, t_2 = 31.055 min.



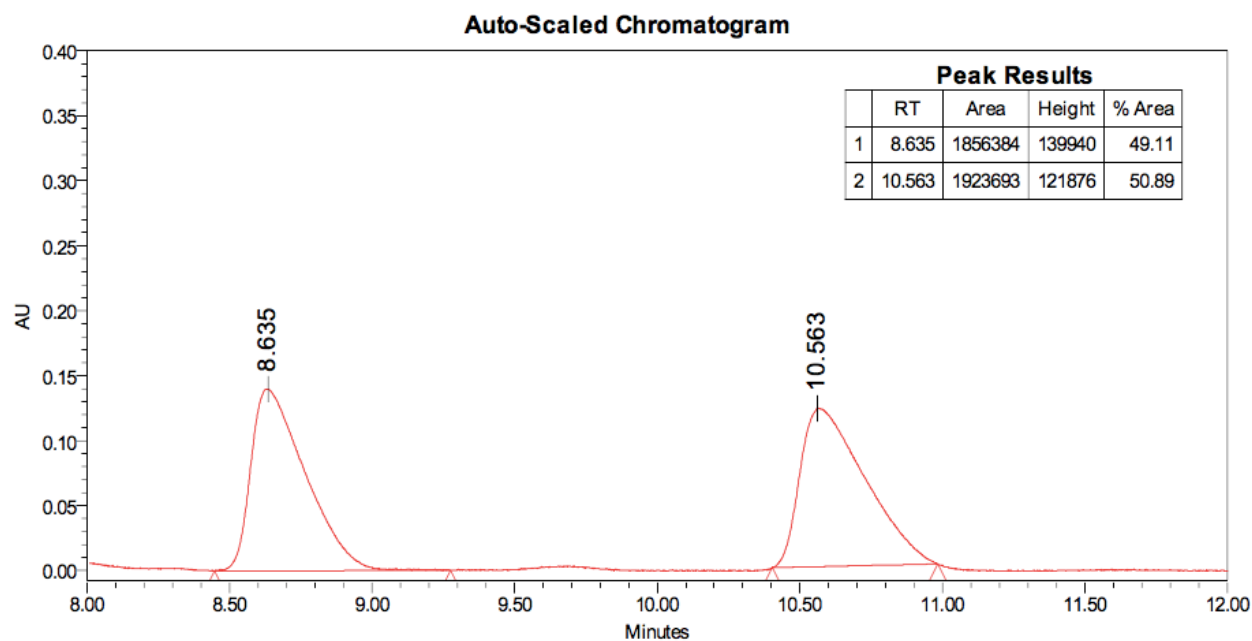
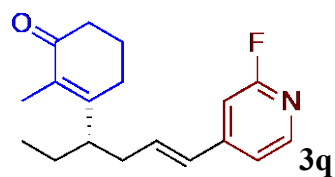
30 sample (Conditions): Cel2 column, 40.0 °C, MeOH: CO₂ = 2:98, 2 mL/min, 138 bar, 40 min; t_1 = 27.487 min, t_2 = 32.174 min, er = 96:4.



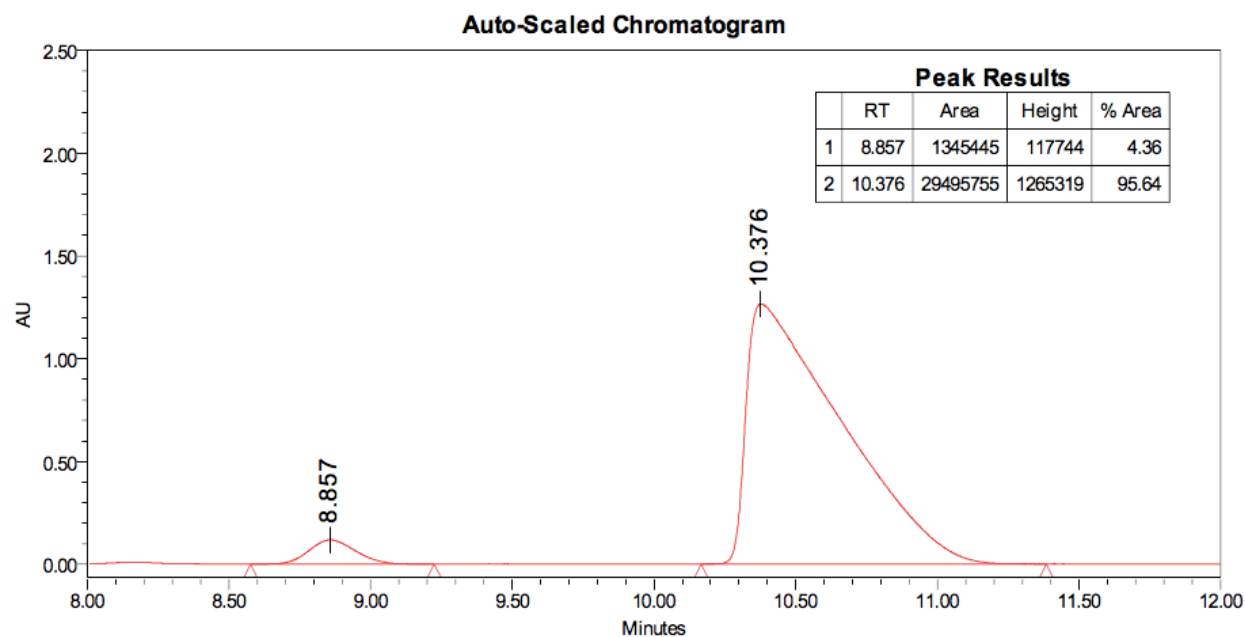
Separation by SFC, Chiralcel® **3p**-Rac sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 16.229 min, t_2 = 19.716 min.



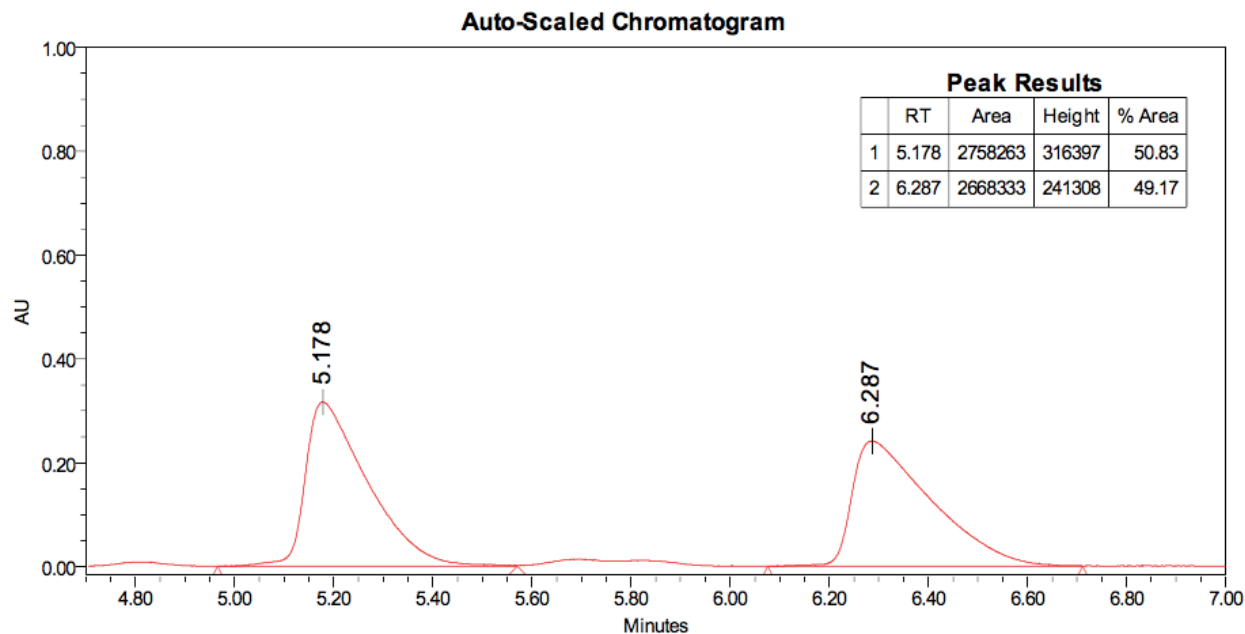
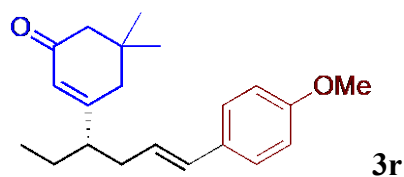
3p sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 16.318 min, t_2 = 19.240 min, er = 5:95.



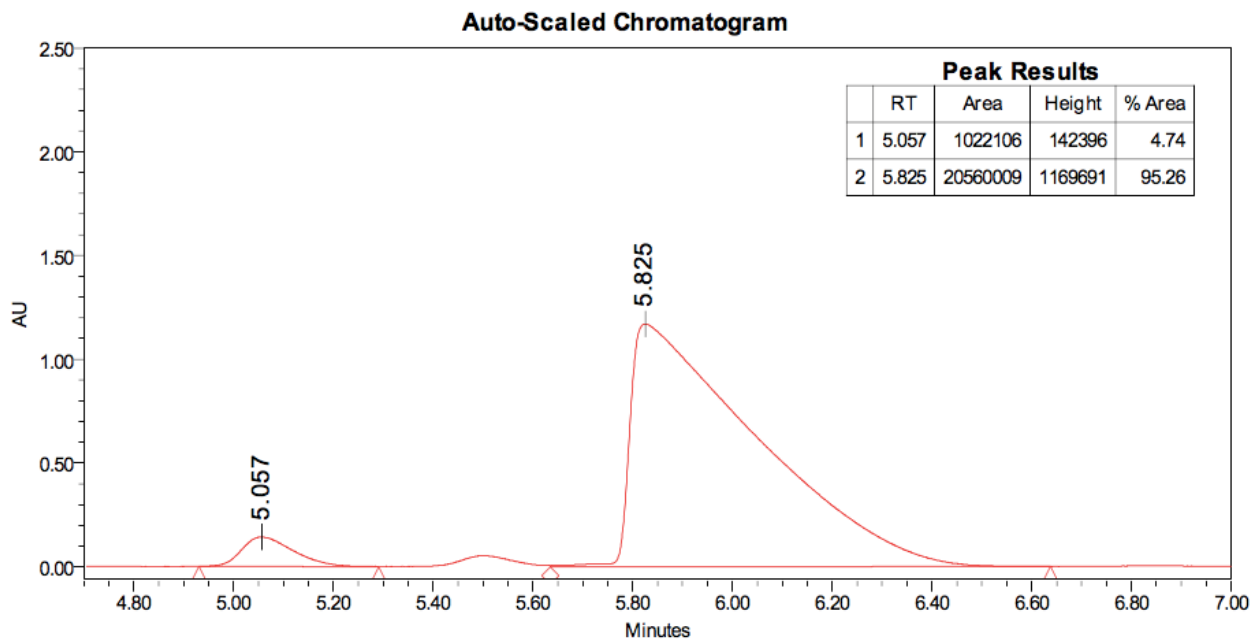
Separation by SFC, Chiralcel® **3q**-Rac sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 5:95, 2 mL/min, 138 bar, 40 min; t_1 = 8.635 min, t_2 = 10.563 min.



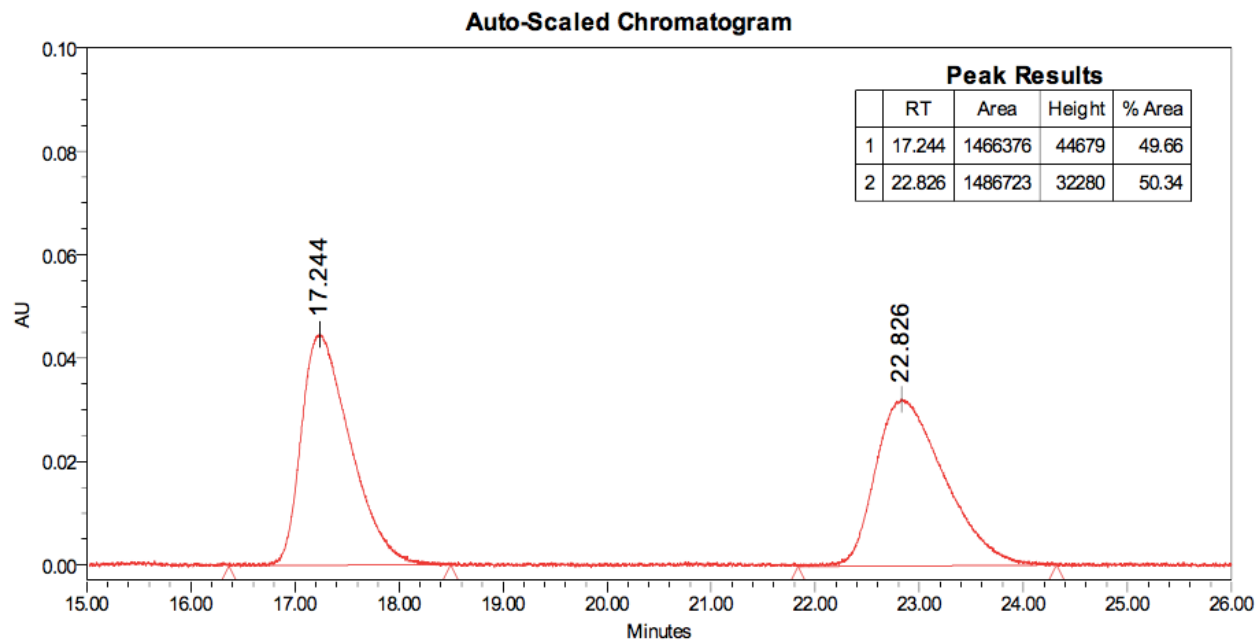
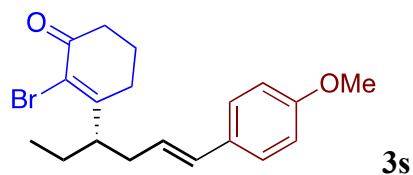
3q sample (Conditions): Cel2 column, 40.0 °C, *i*-PrOH: CO₂ = 5:95, 2 mL/min, 138 bar, 40 min; t_1 = 8.857 min, t_2 = 10.376 min, er = 4.5:95.5.



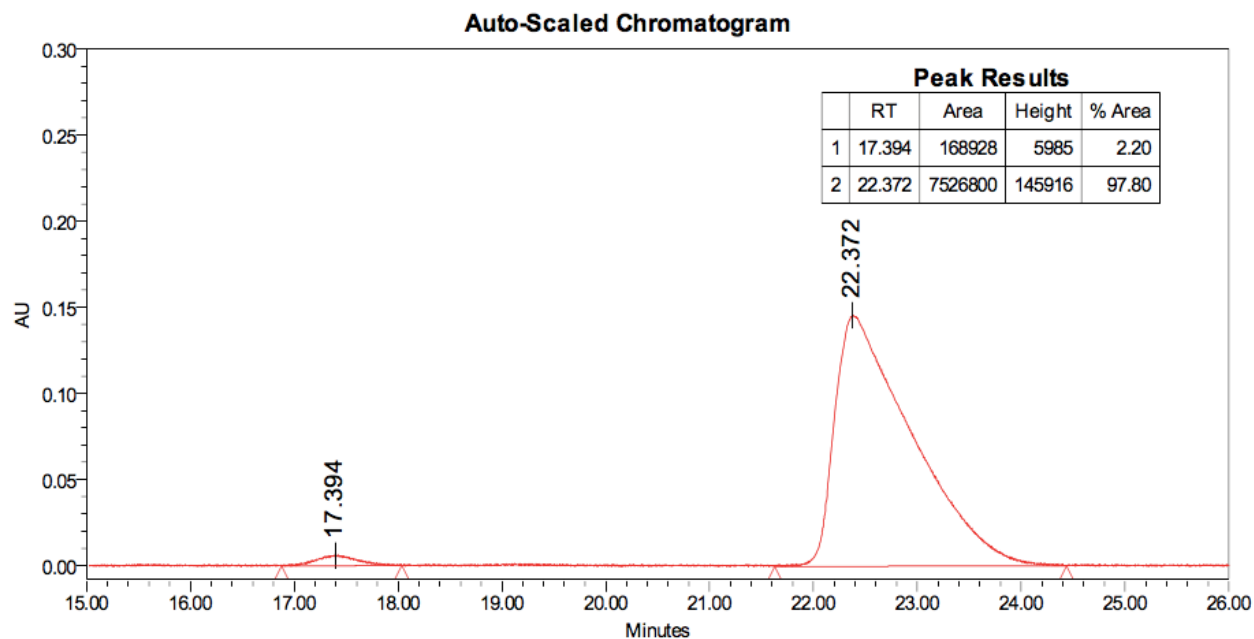
Separation by SFC, Chiralcel® **3r**-Rac sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 5.178 min, t_2 = 6.287 min.



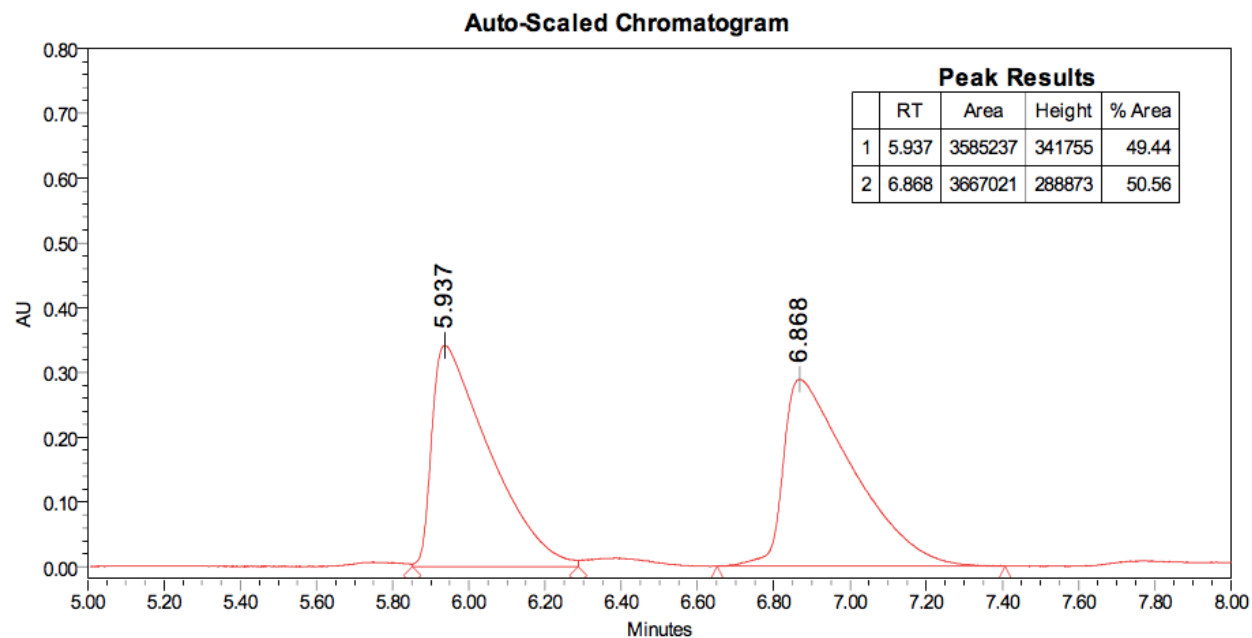
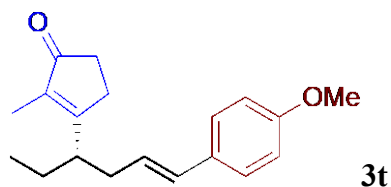
3r sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 5.057 min, t_2 = 5.825 min, er = 5:95.



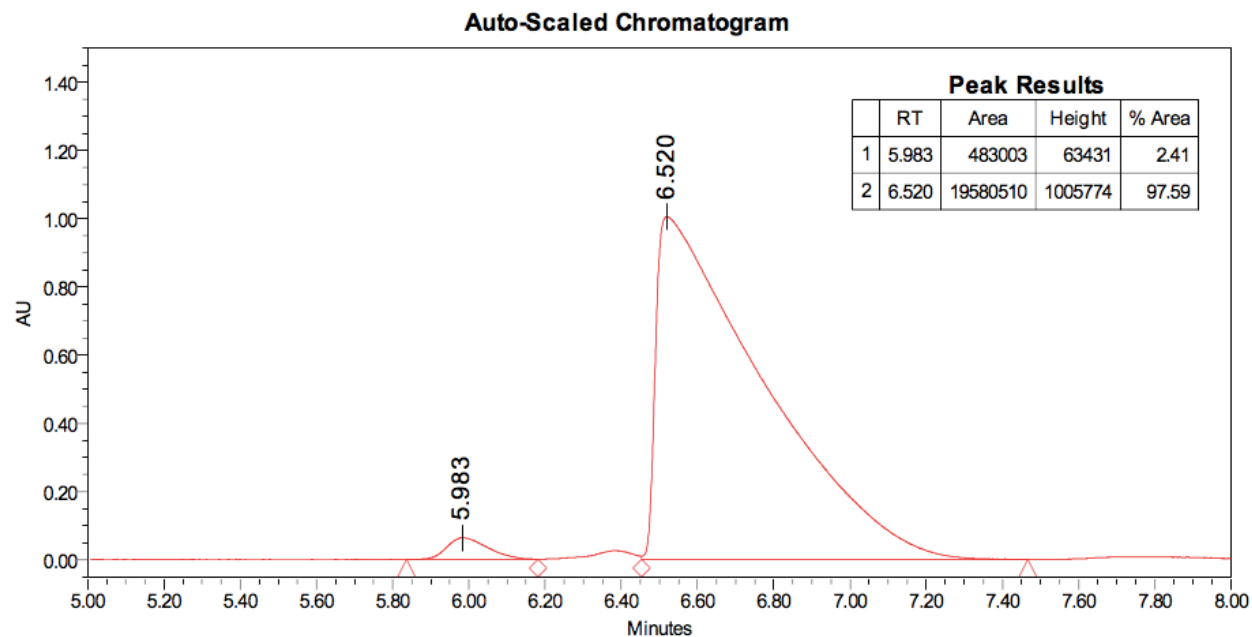
Separation by SFC, Chiralcel® **3s**-Rac sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 17.244 min, t_2 = 22.826 min.



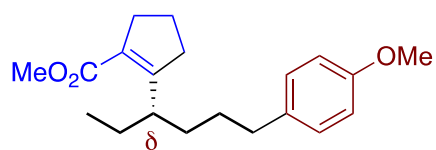
3s sample (Conditions): Amyl column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 17.394 min, t_2 = 22.826 min, er = 2:98.



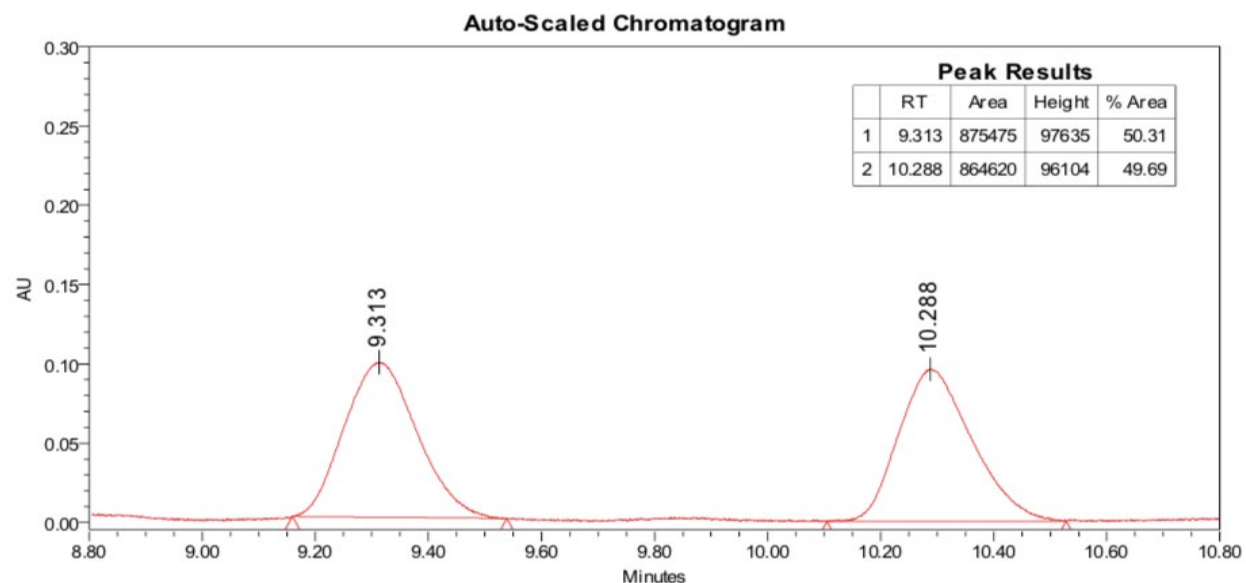
Separation by SFC, Chiralcel® **3t**-Rac sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 5.937 min, t_2 = 6.868 min.



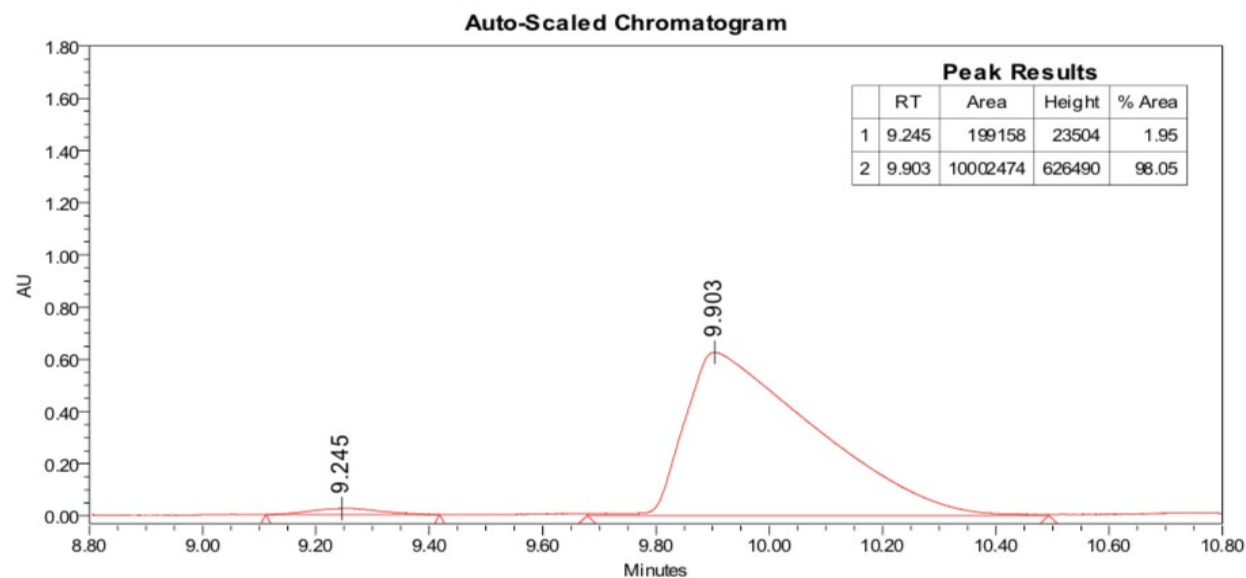
3t sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 5.983 min, t_2 = 6.520 min, er = 2.5:97.5.



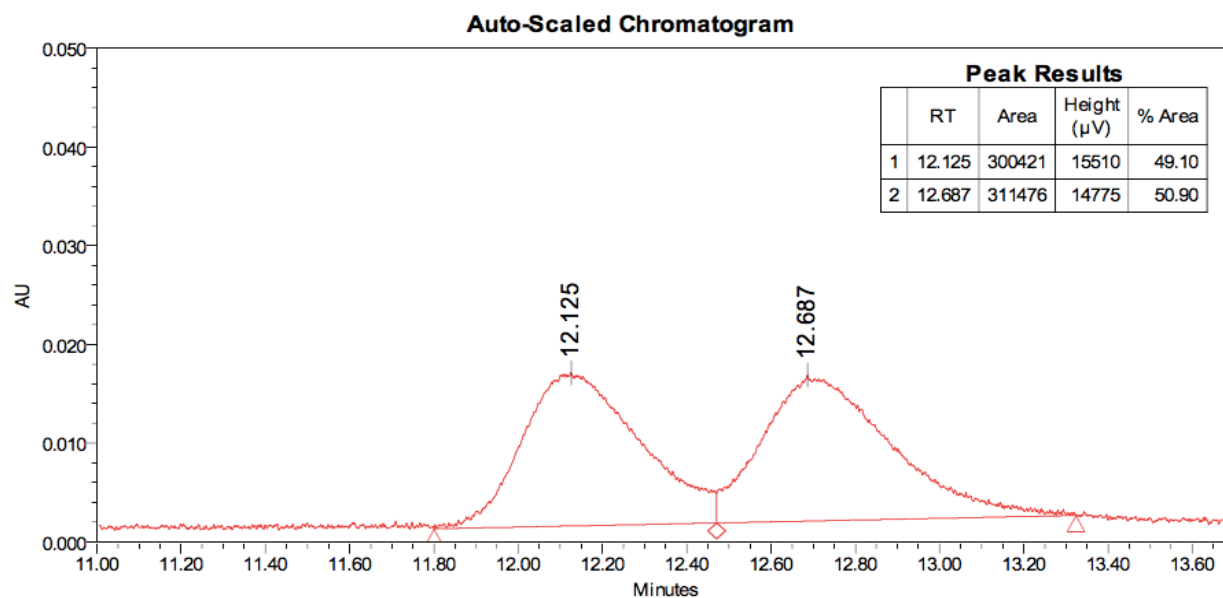
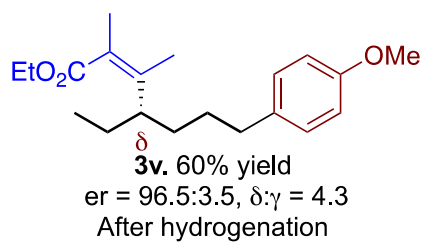
3u. 52% yield
 er = 98:2, δ : γ = 2.8
 After hydrogenation



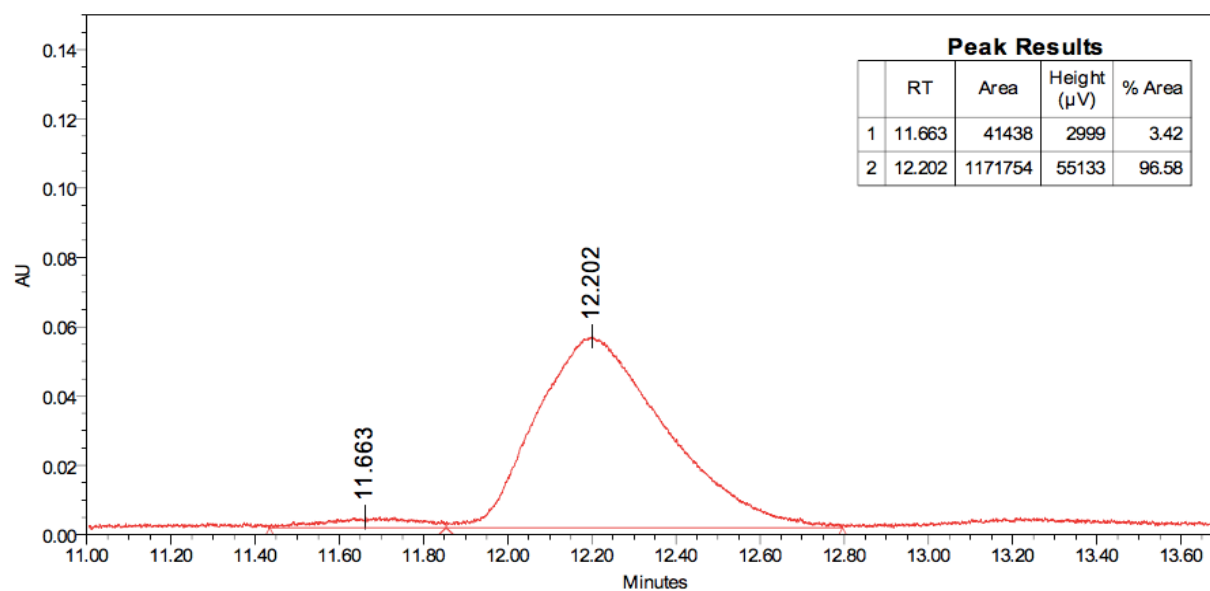
Separation by SFC, Chiralcel® **3u**-Rac sample (Conditions): Cell1 column, 40.0 °C,
 Heptane: CO₂ = 6:94, 1 mL/min, 138 bar, 40 min; t_1 = 9.313 min, t_2 = 10.288 min.



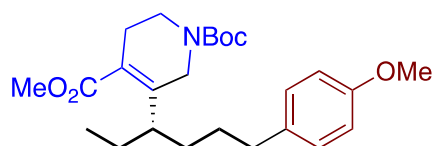
3u sample (Conditions): Cell1 column, 40.0 °C, Heptane: CO₂ = 6:94, 1 mL/min,
 138 bar, 40 min; t_1 = 9.245 min, t_2 = 9.903 min, er = 2:98.



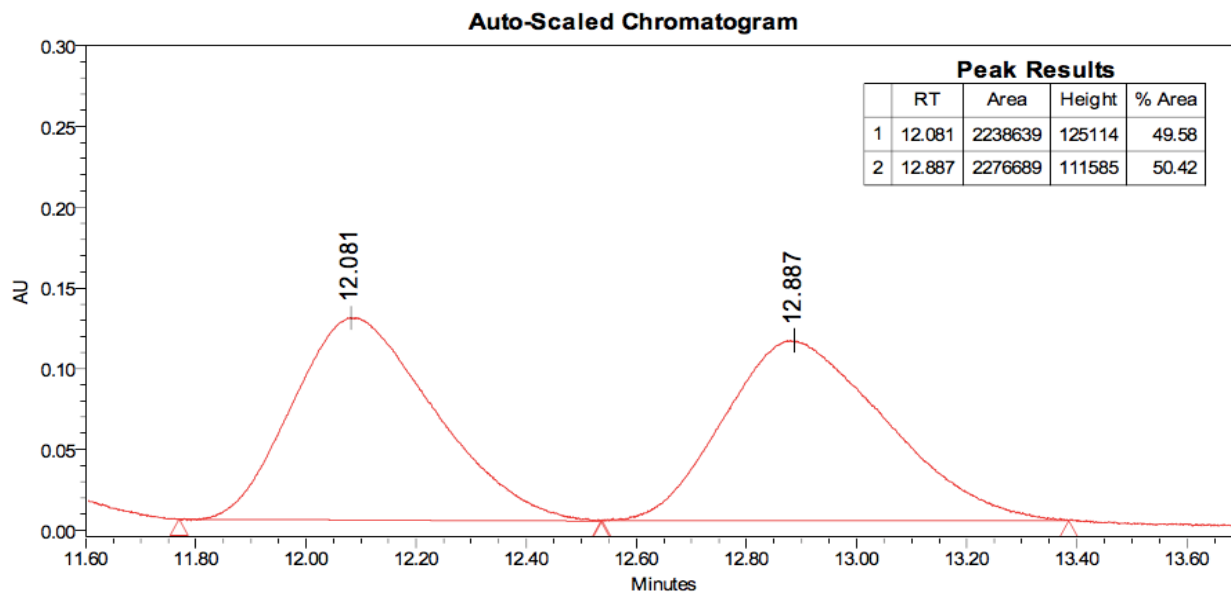
Separation by SFC, Chiralcel® **3v**-Rac sample (Conditions): Cell column, 40.0 °C,
 Heptane: CO₂ = 1:99, 1 mL/min, 138 bar, 40 min; t_1 = 12.125 min, t_2 = 12.687 min.



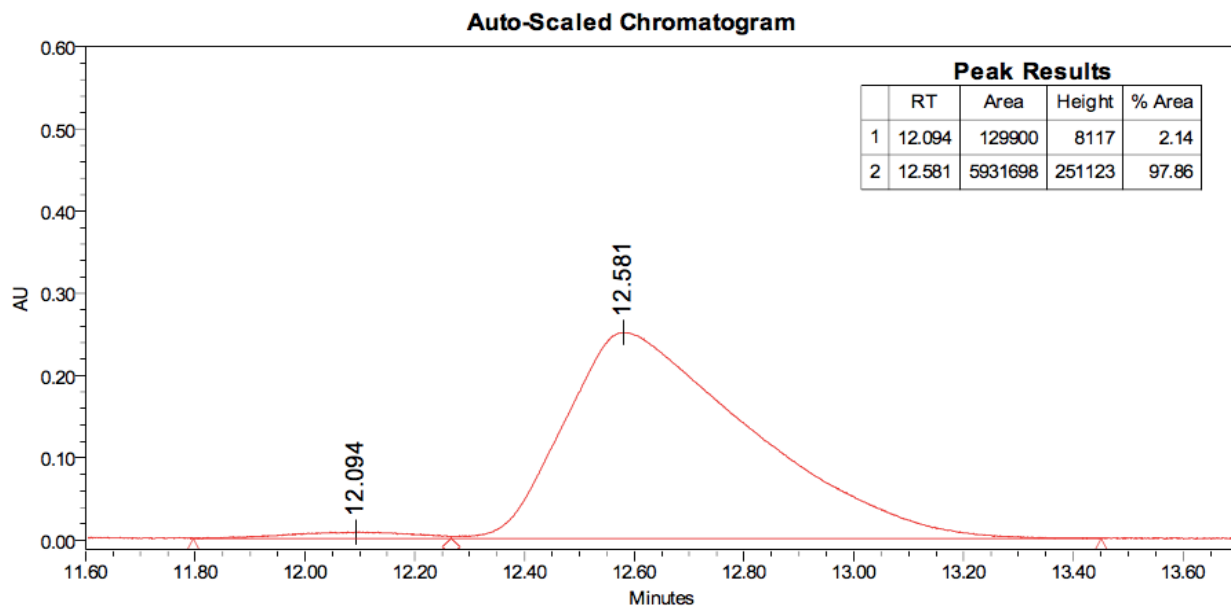
3v sample (Conditions): Cell column, 40.0 °C, Heptane: CO₂ = 1:99, 1 mL/min,
 138 bar, 40 min; t_1 = 11.663 min, t_2 = 12.202 min, er = 96.5:3.5.



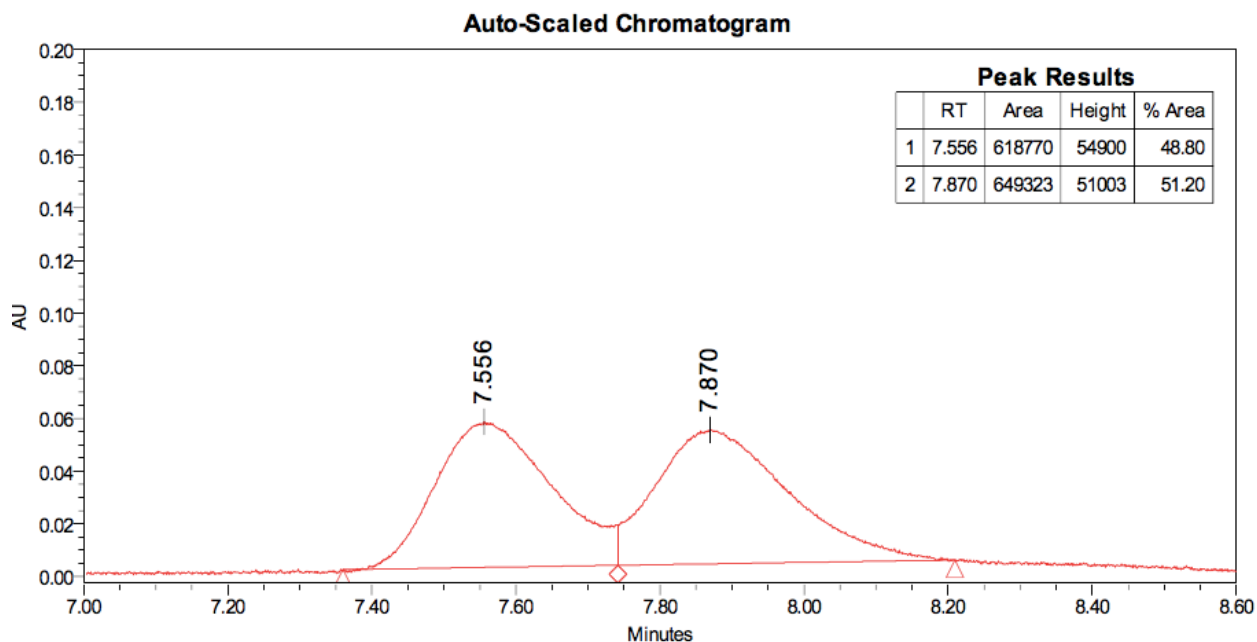
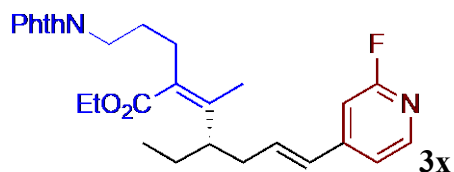
3w. 61% yield
er = 98:2
After hydrogenation



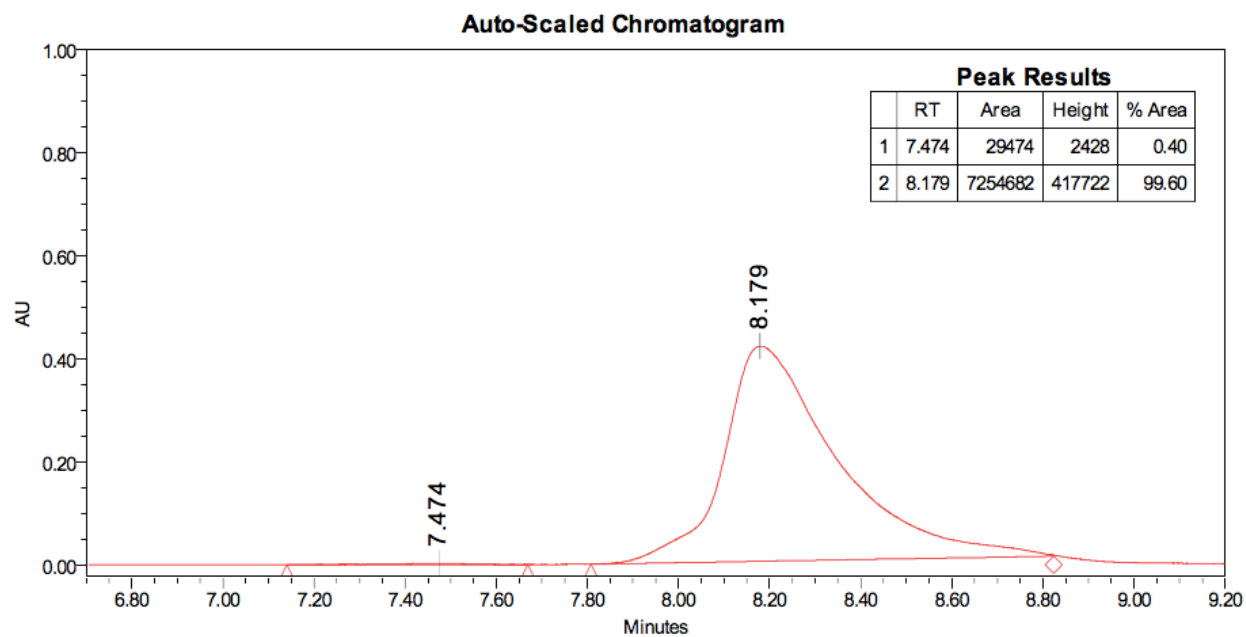
Separation by SFC, Chiralcel® **3w**-Rac sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 1 mL/min, 138 bar, 40 min; *t*₁ = 12.081 min, *t*₂ = 12.887 min.



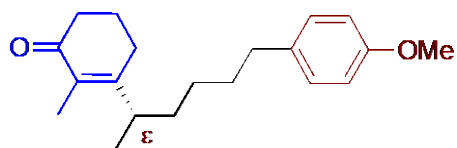
3w sample (Conditions): Cell1 column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 1 mL/min, 138 bar, 40 min; *t*₁ = 12.094 min, *t*₂ = 12.581 min, er = 2:98.



Separation by SFC, Chiralcel® **3x**-Rac sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 4:96, 2 mL/min, 138 bar, 40 min; t_1 = 7.556 min, t_2 = 7.870 min.



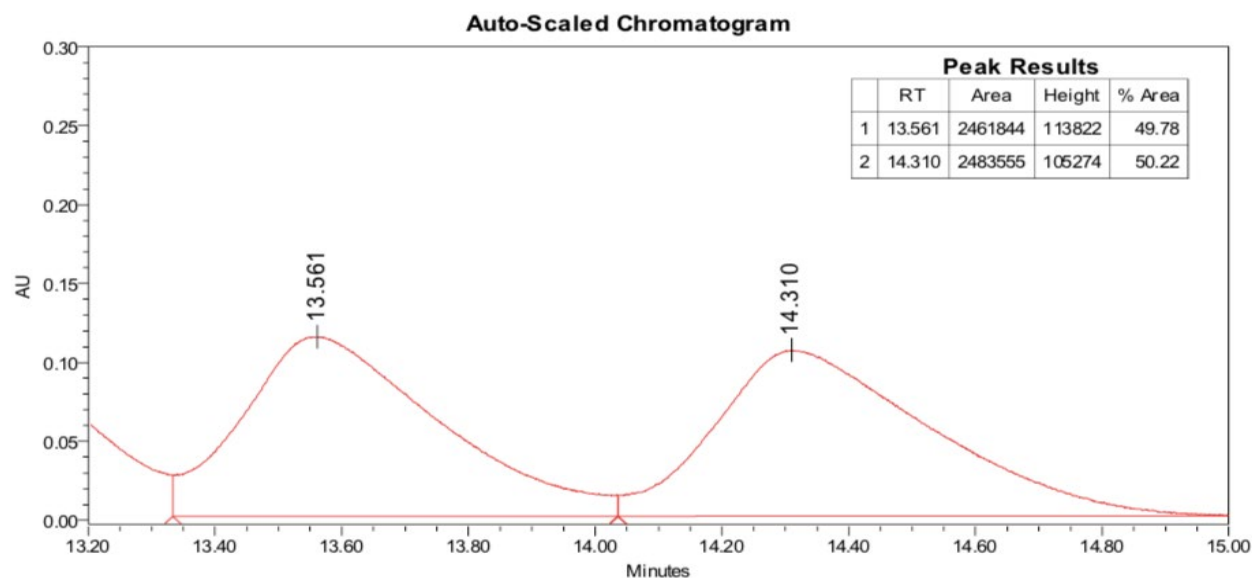
3x sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 4:96, 2 mL/min, 138 bar, 40 min; t_1 = 7.474 min, t_2 = 8.179 min, er = 0.4:99.6.



from *E*-alkene

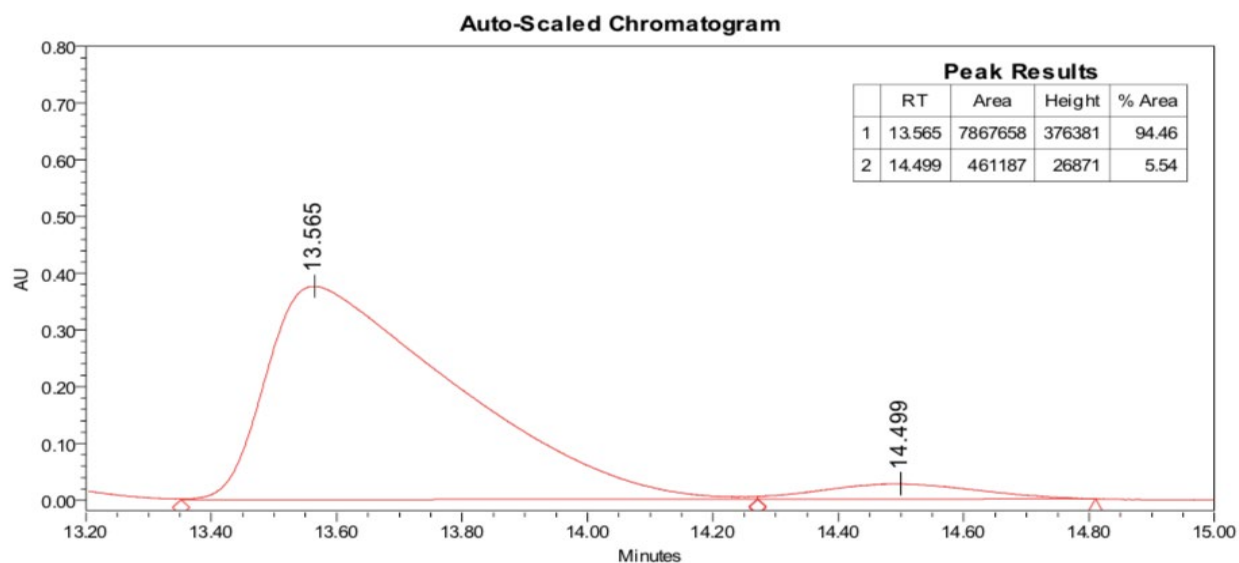
63% yield, er = 94.5:5.5, $\epsilon:\delta$ = 2.6

After hydrogenation



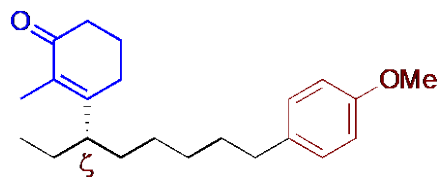
Separation by SFC, Chiralcel® **3y**-Rac sample (Conditions): Cell column, 40.0 °C,

i-PrOH: CO₂ = 3:97, 1 mL/min, 138 bar, 40 min; t_1 = 13.561 min, t_2 = 14.310 min.

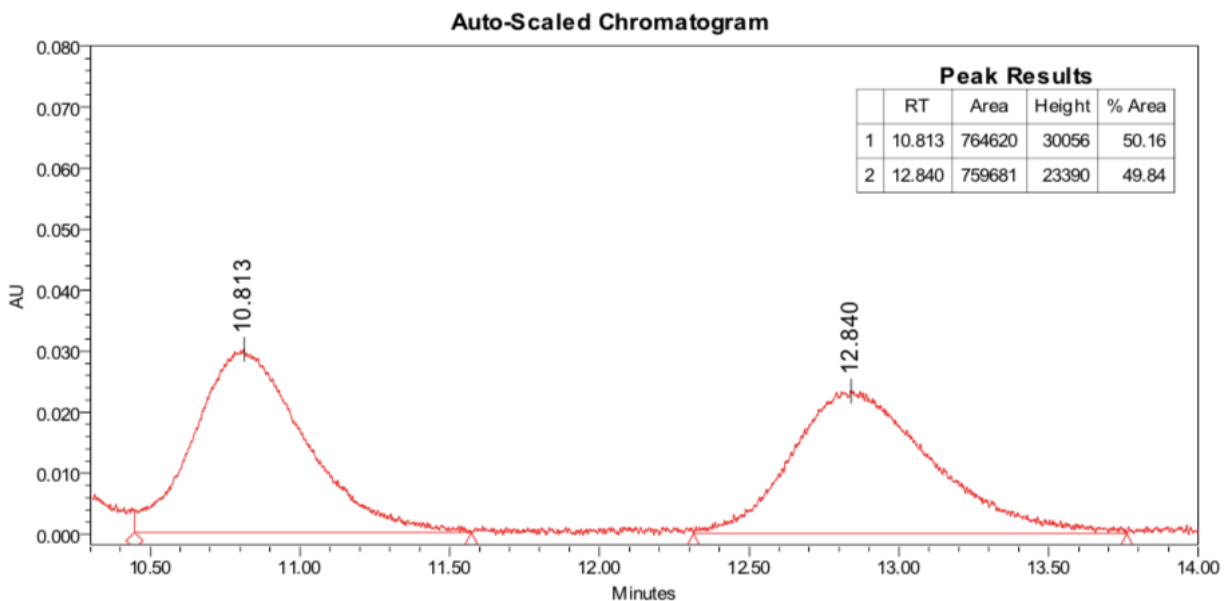


3y sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 1 mL/min,

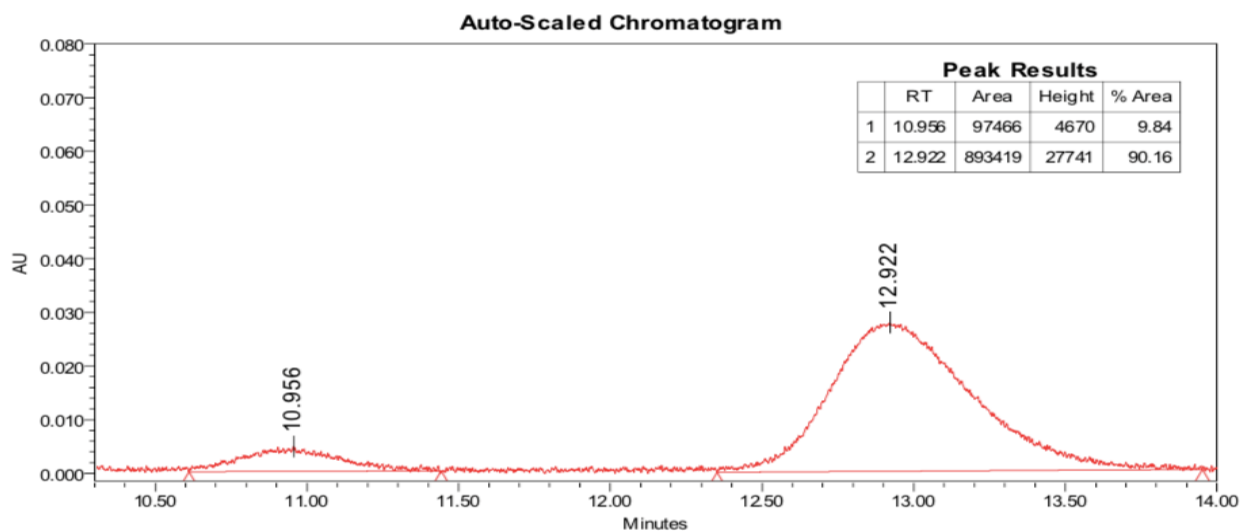
138 bar, 40 min; t_1 = 13.565 min, t_2 = 14.499 min, er = 94.5:5.5.



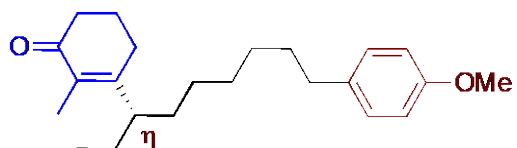
from Z-alkene
 59% yield, er = 10:90, $\zeta:\epsilon$ = 2.6
 After hydrogenation



Separation by SFC, Chiralcel® **3z**-Rac sample (Conditions): AD-H column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 10.813 min, t_2 = 12.840 min.

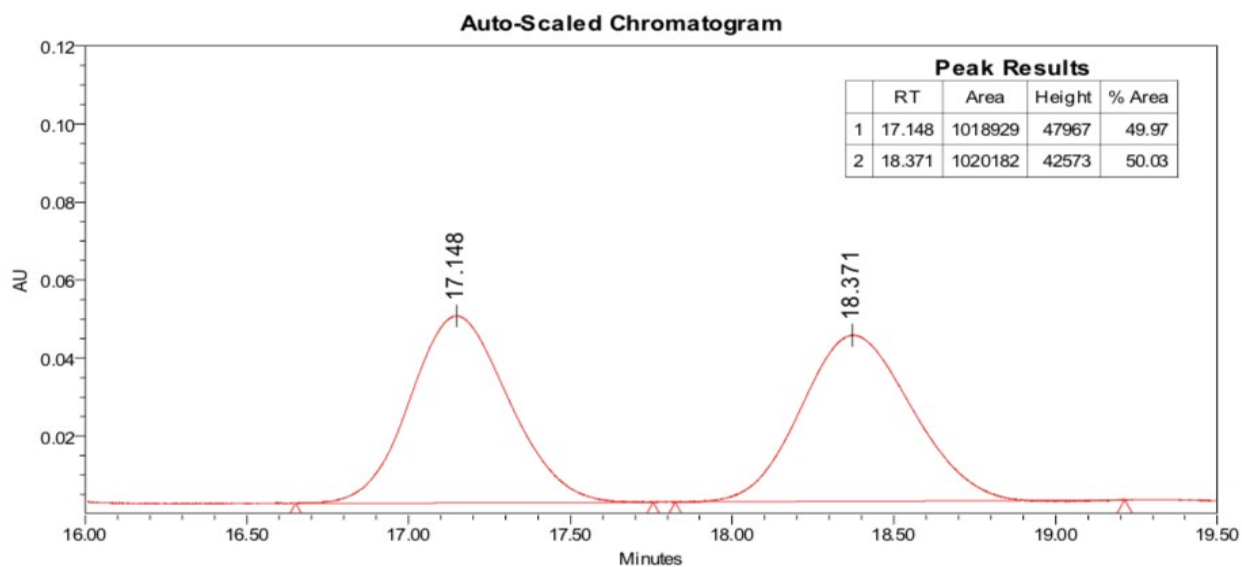


3z sample (Conditions): AD-H column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 2 mL/min, 138 bar, 40 min; t_1 = 10.956 min, t_2 = 12.922 min, er = 10:90.

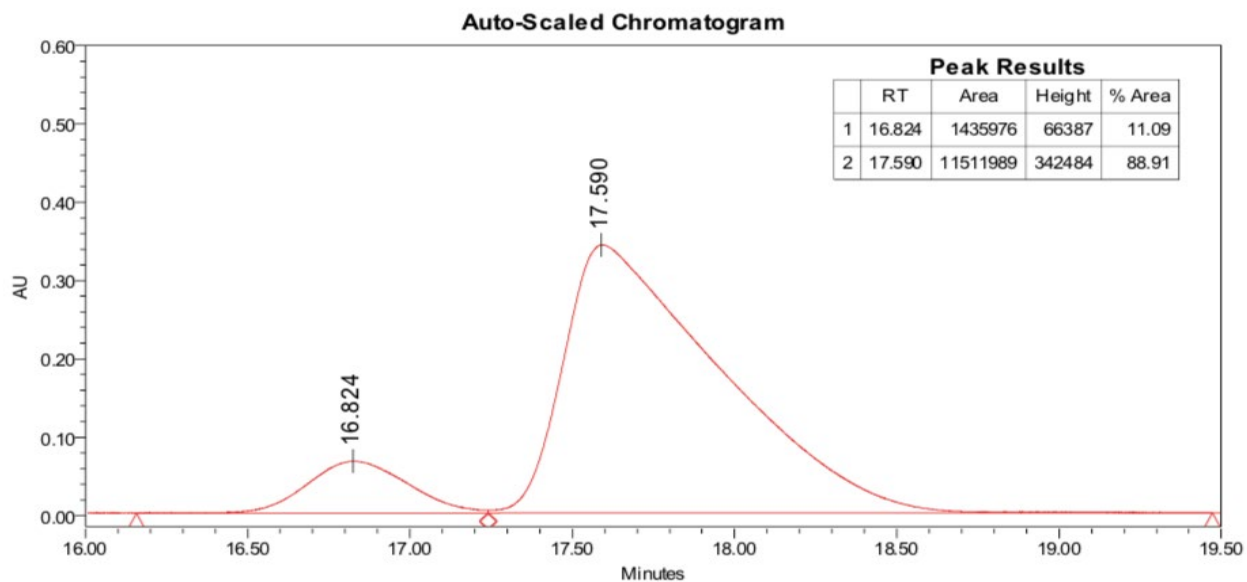


from Z-alkene
 57% yield, er = 11:89, η : ζ = 2.0
 After hydrogenation

3aa

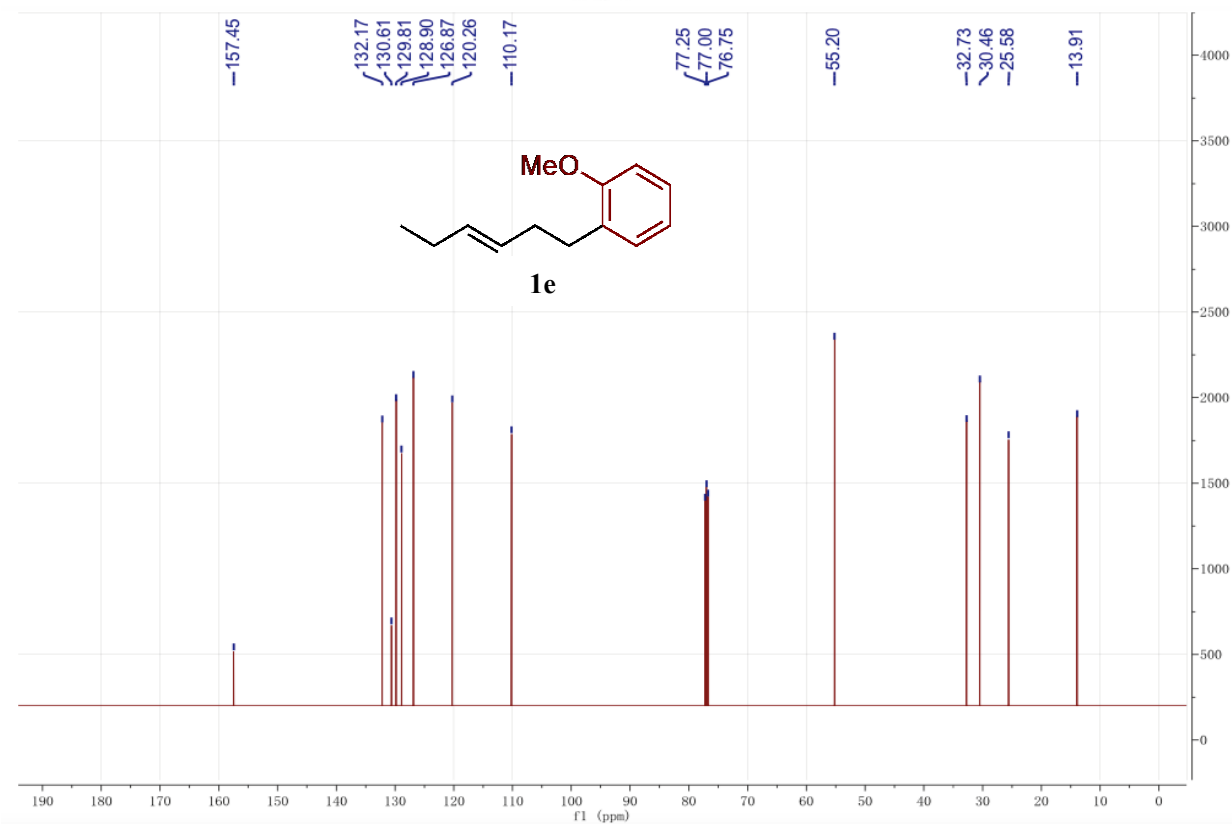
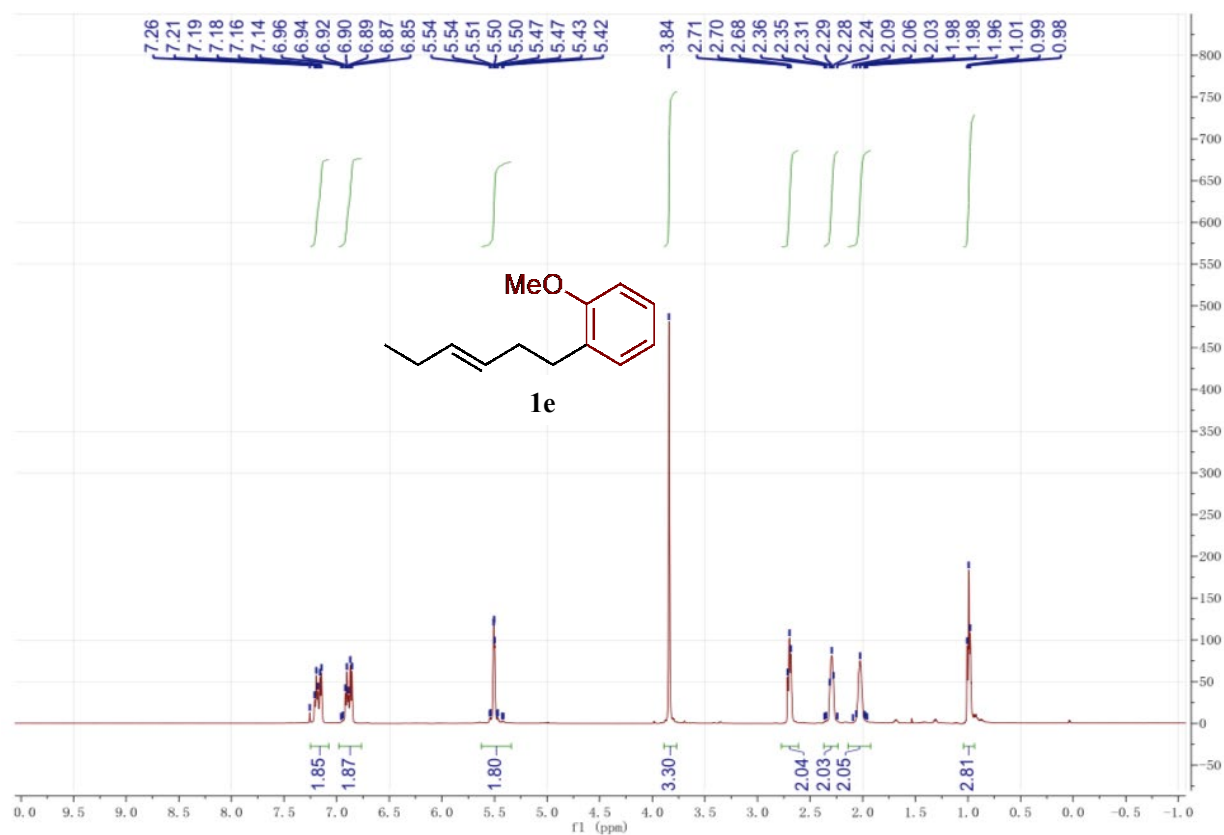


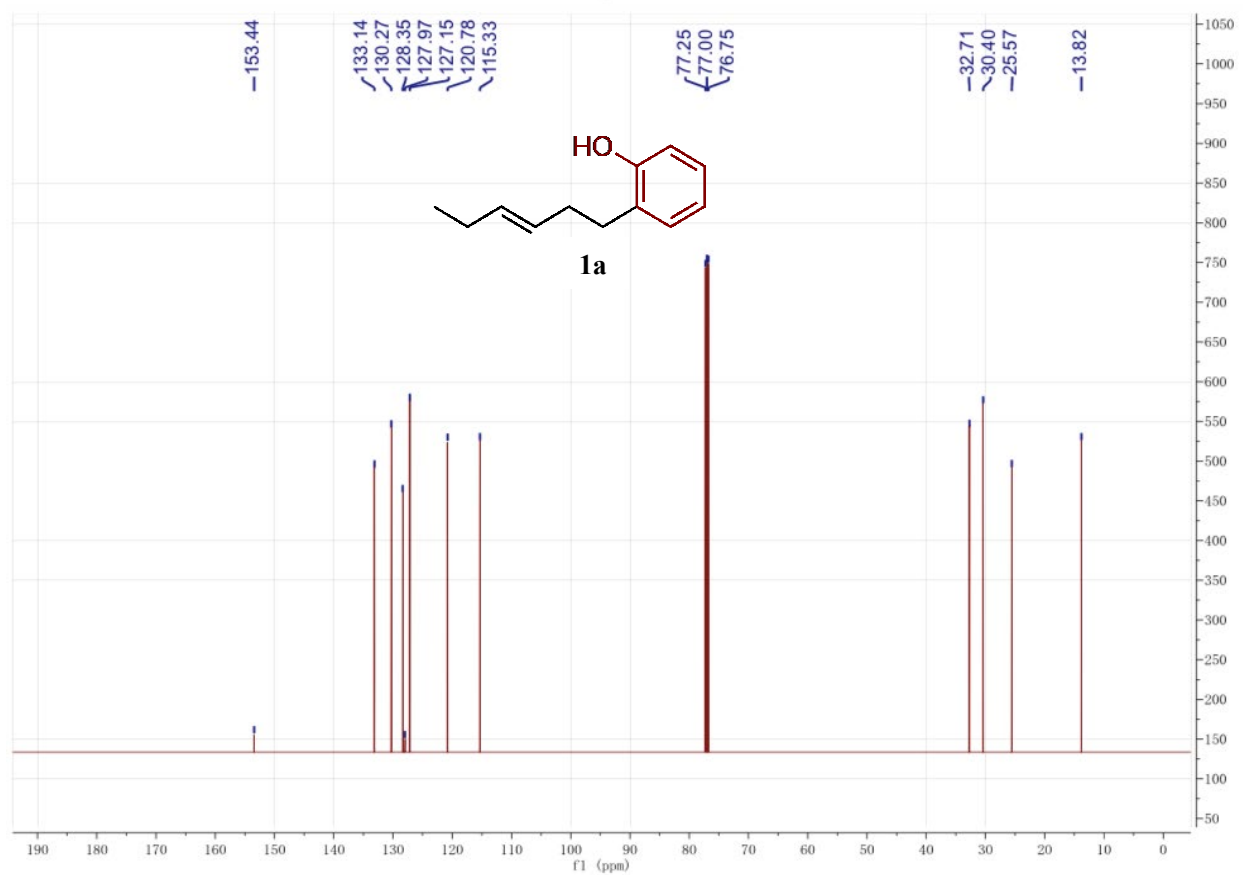
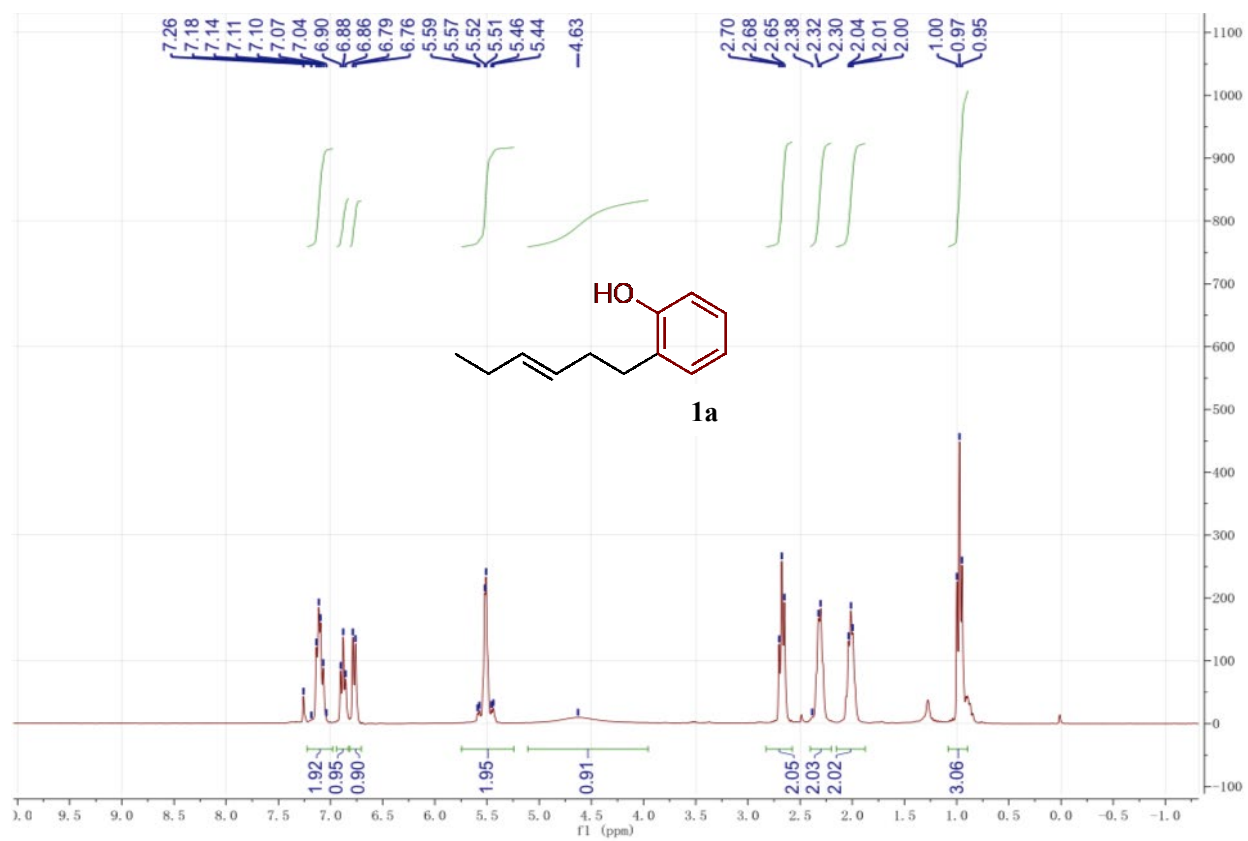
Separation by SFC, Chiralcel® **3z**-Rac sample (Conditions): Cell column, 40.0 °C,
i-PrOH: CO₂ = 3:97, 1 mL/min, 138 bar, 40 min; t_1 = 17.148 min, t_2 = 18.371 min.

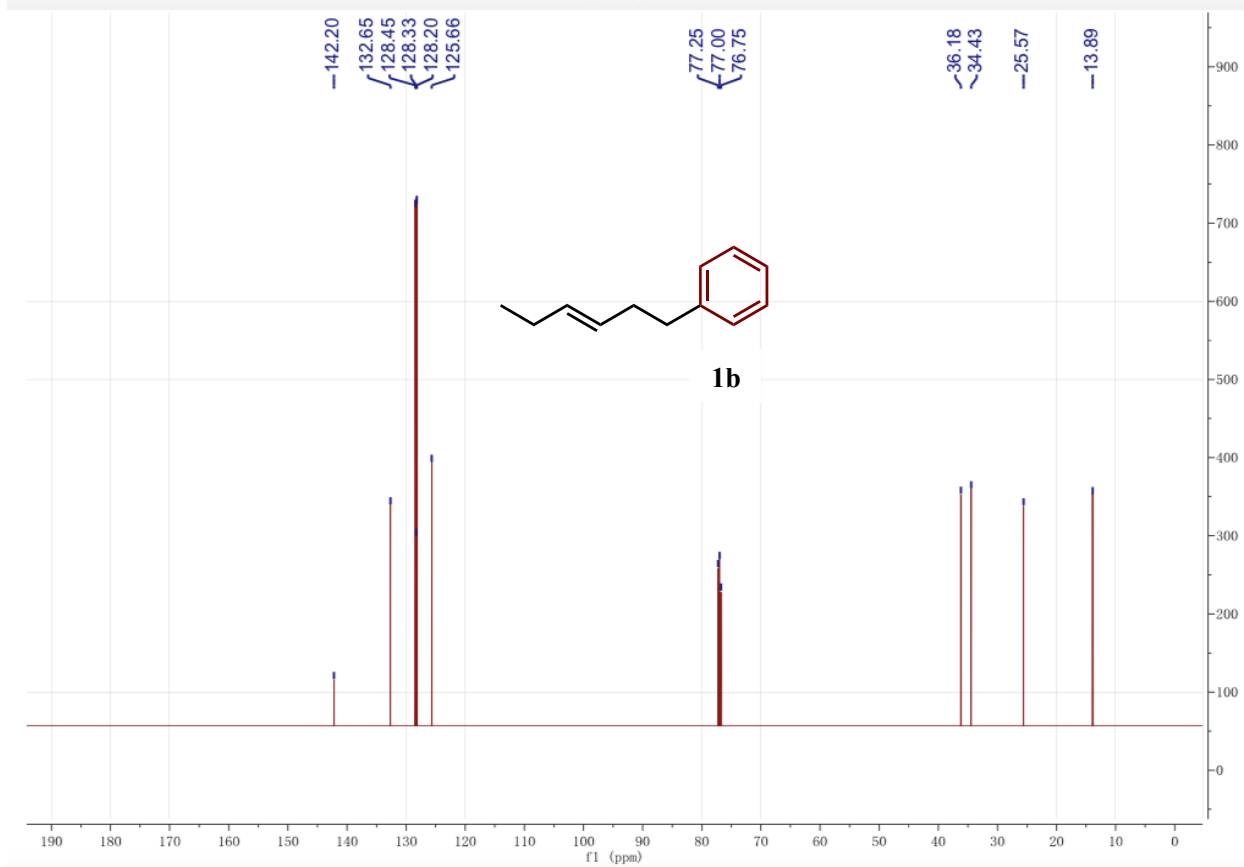
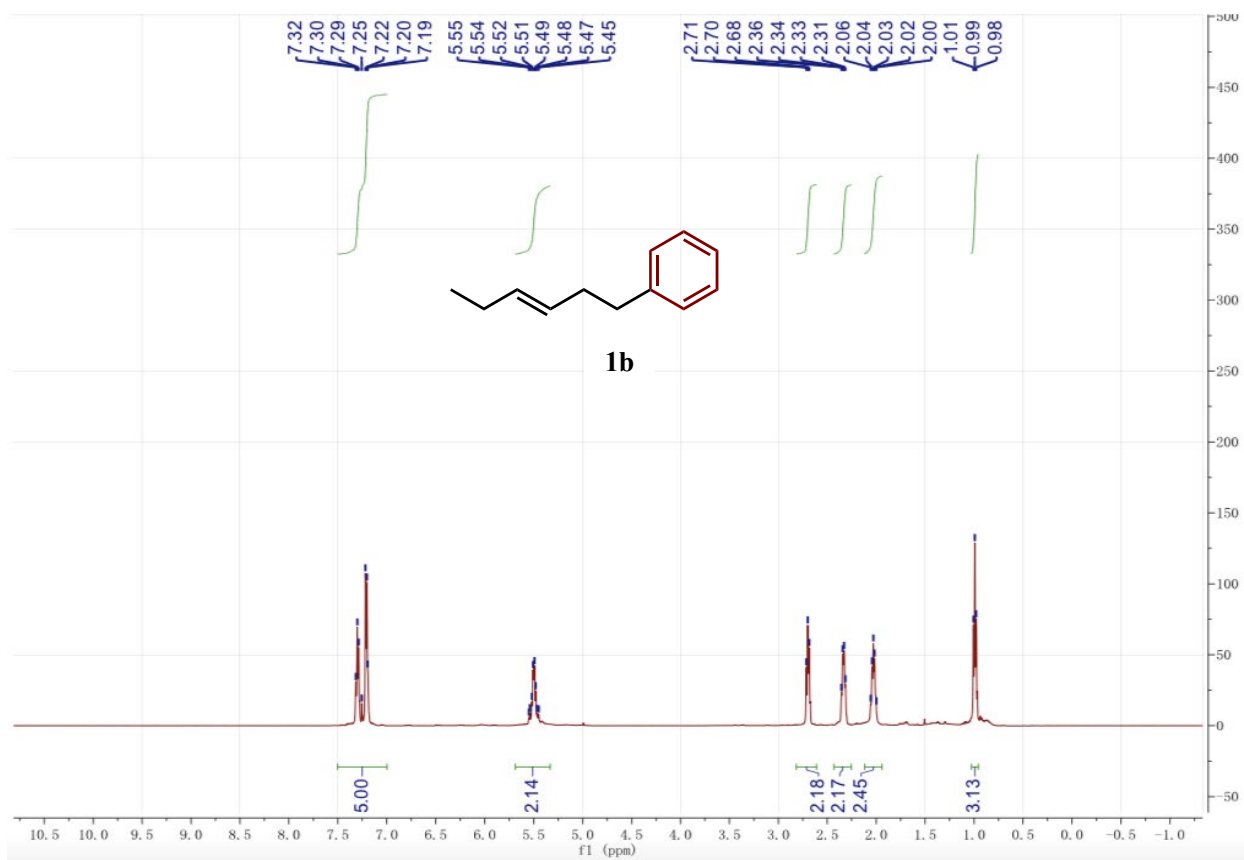


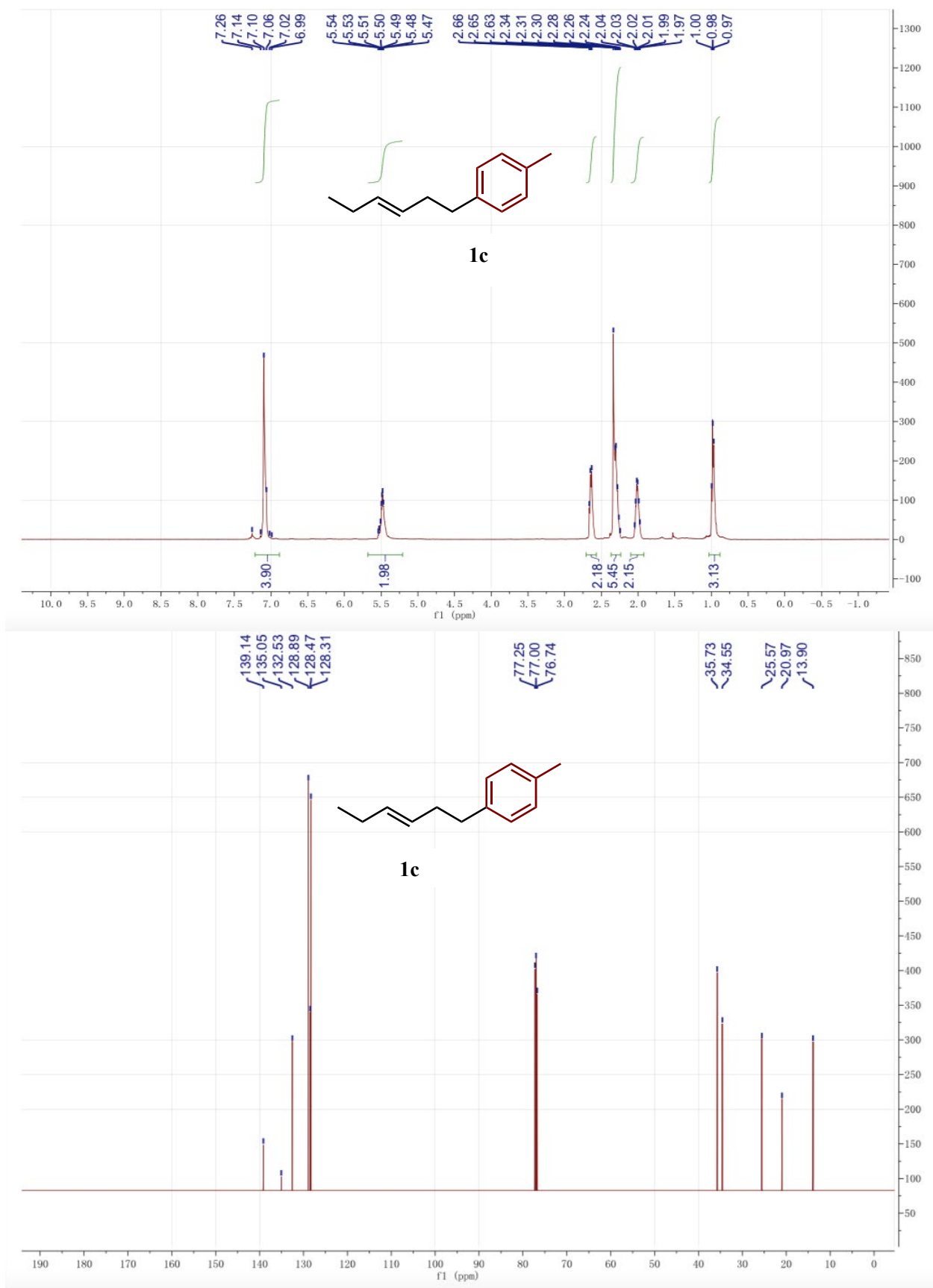
3z sample (Conditions): Cell column, 40.0 °C, *i*-PrOH: CO₂ = 3:97, 1 mL/min,
 138 bar, 40 min; t_1 = 16.824 min, t_2 = 17.590 min, er = 11:89.

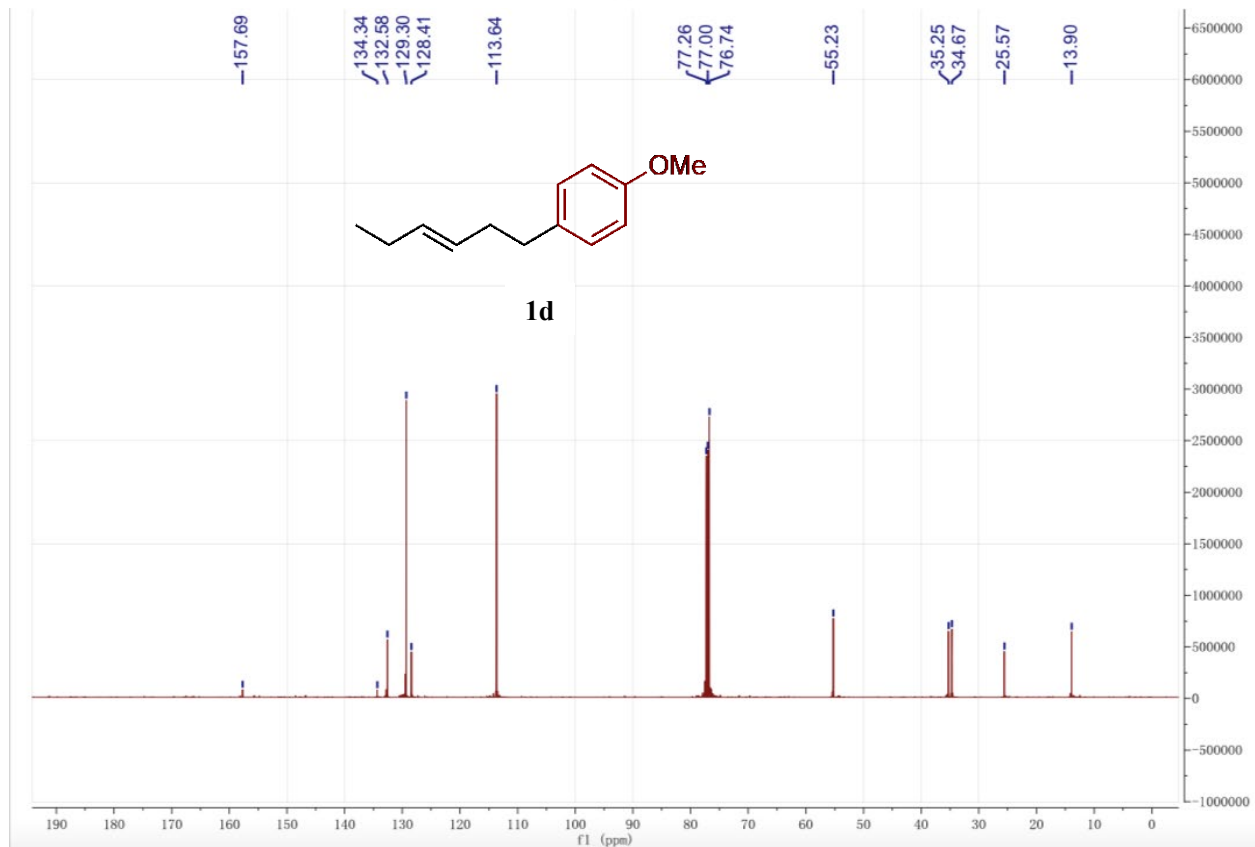
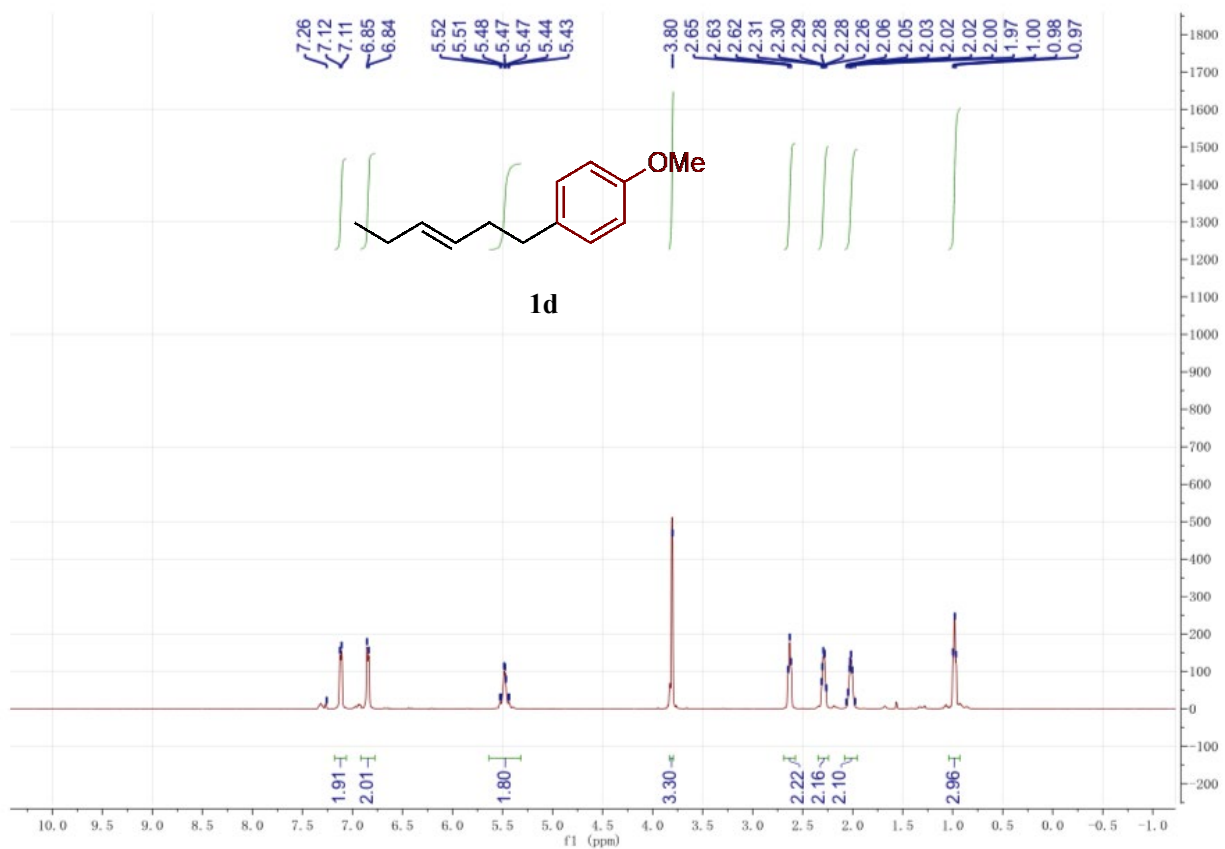
¹H and ¹³C NMR Spectra (Substrates):

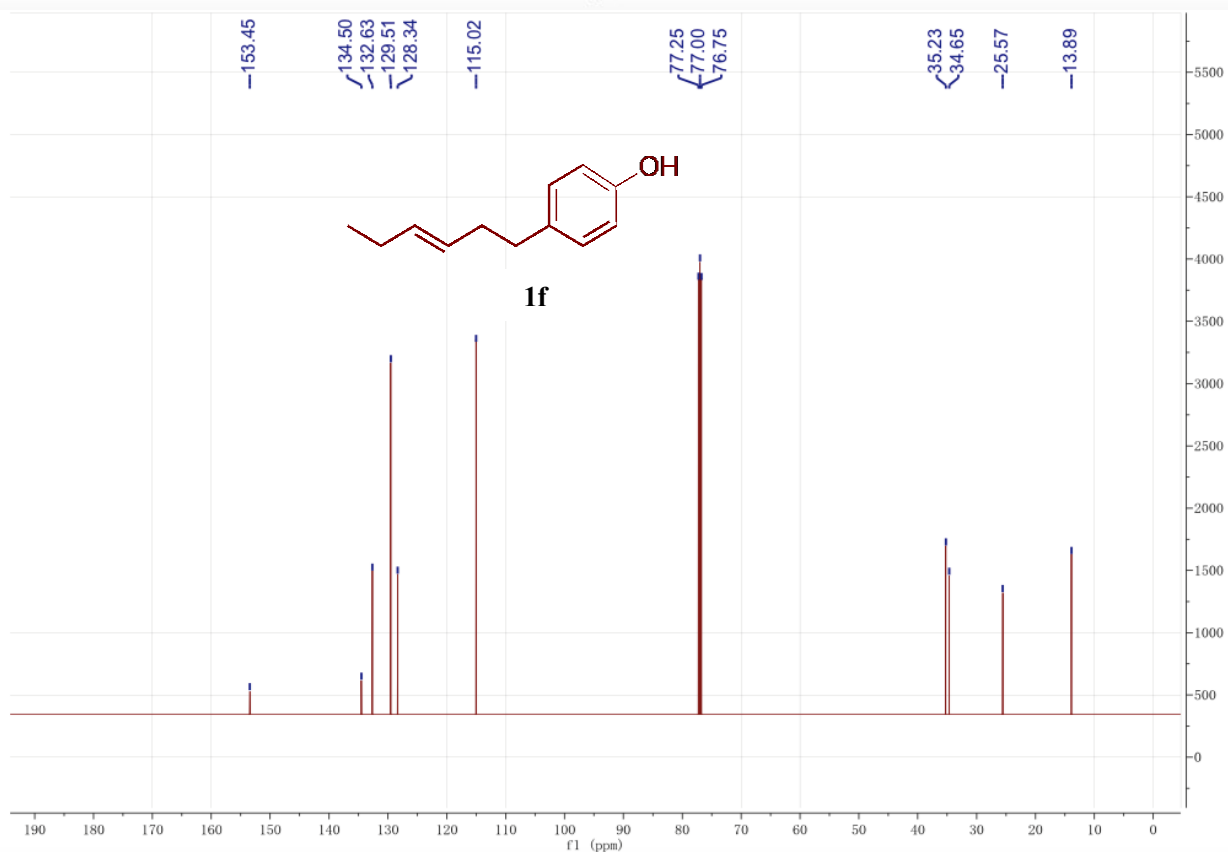
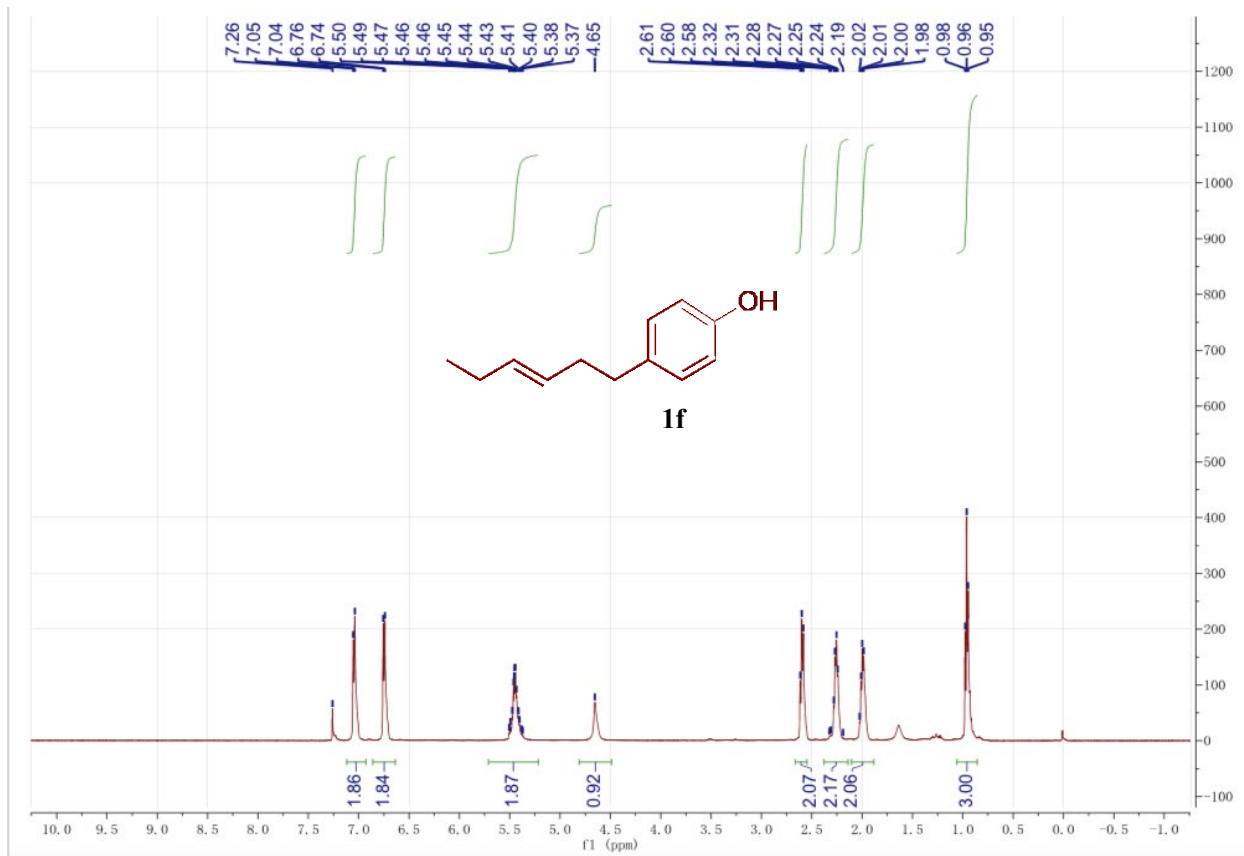


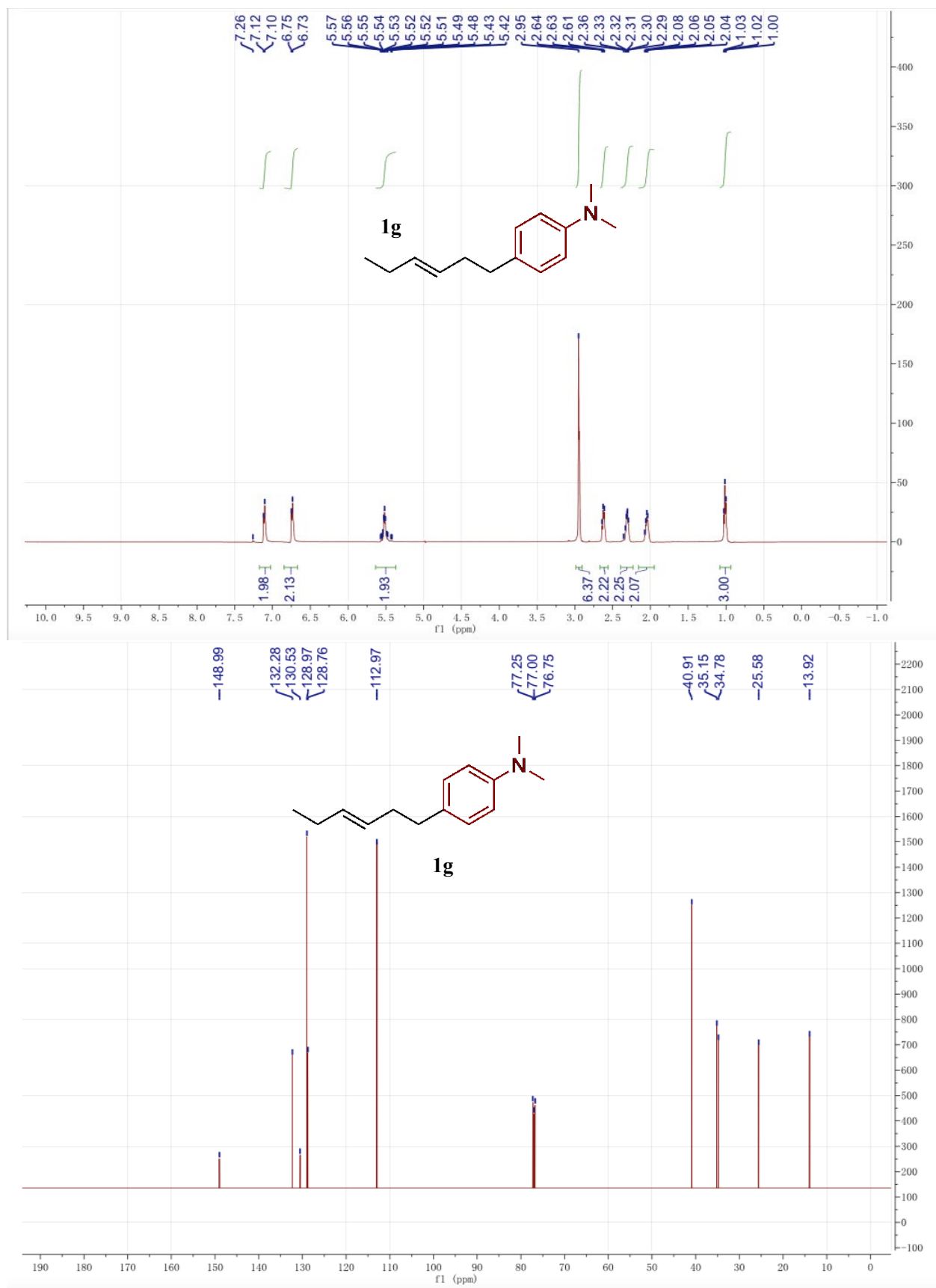


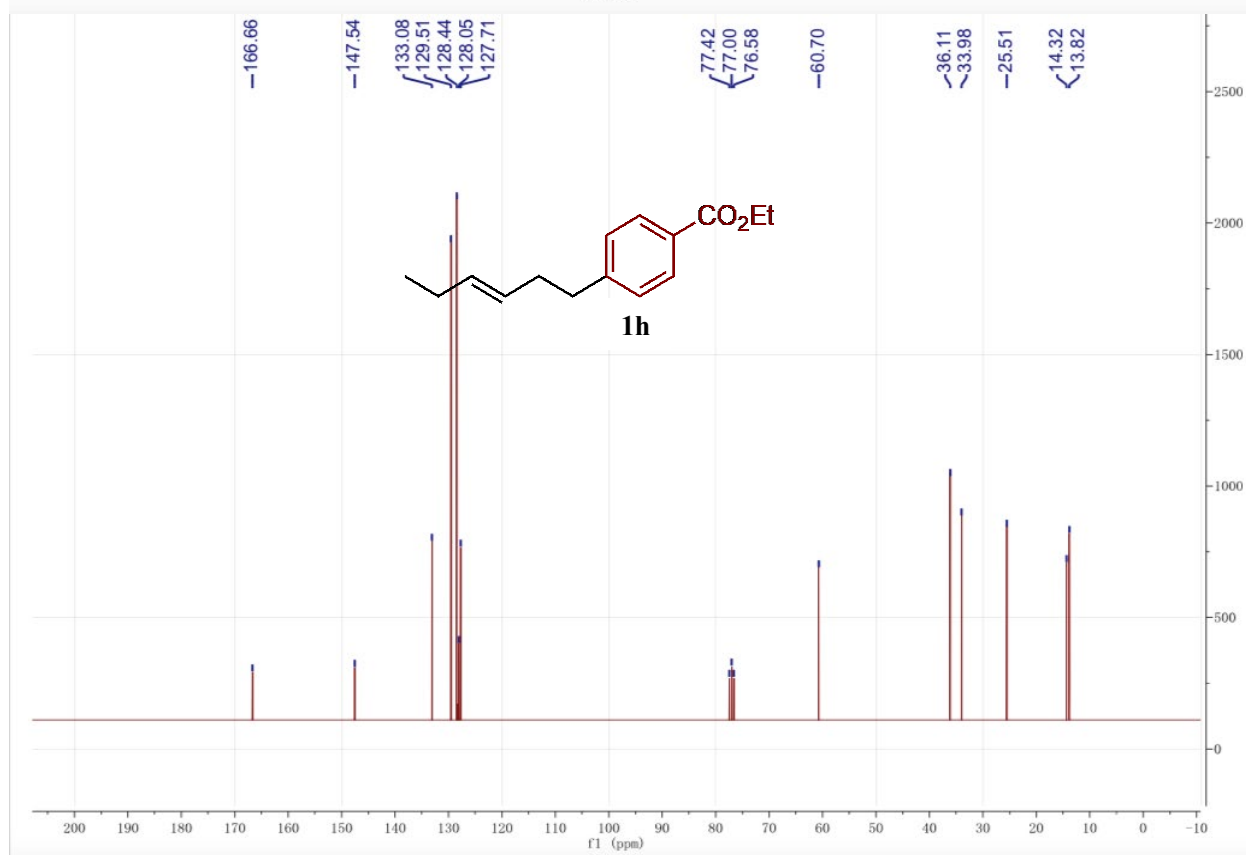
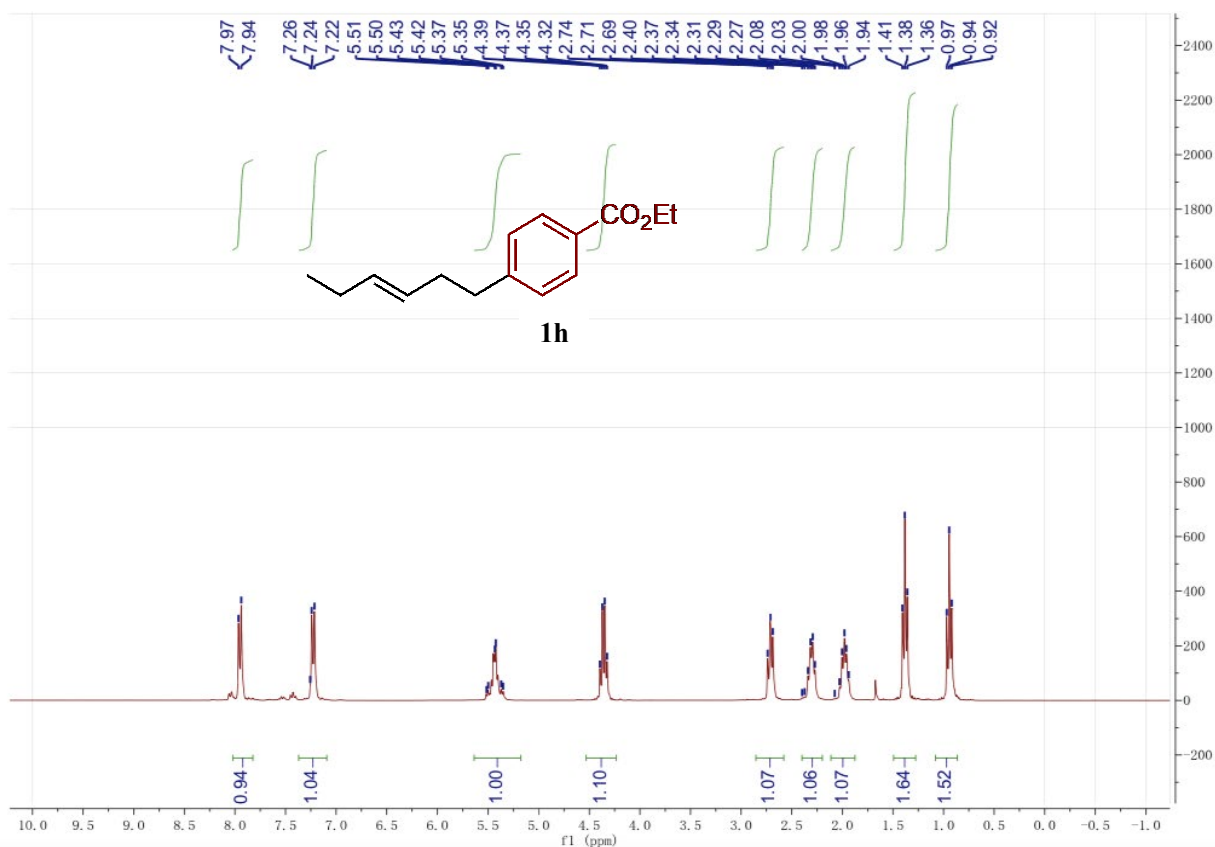


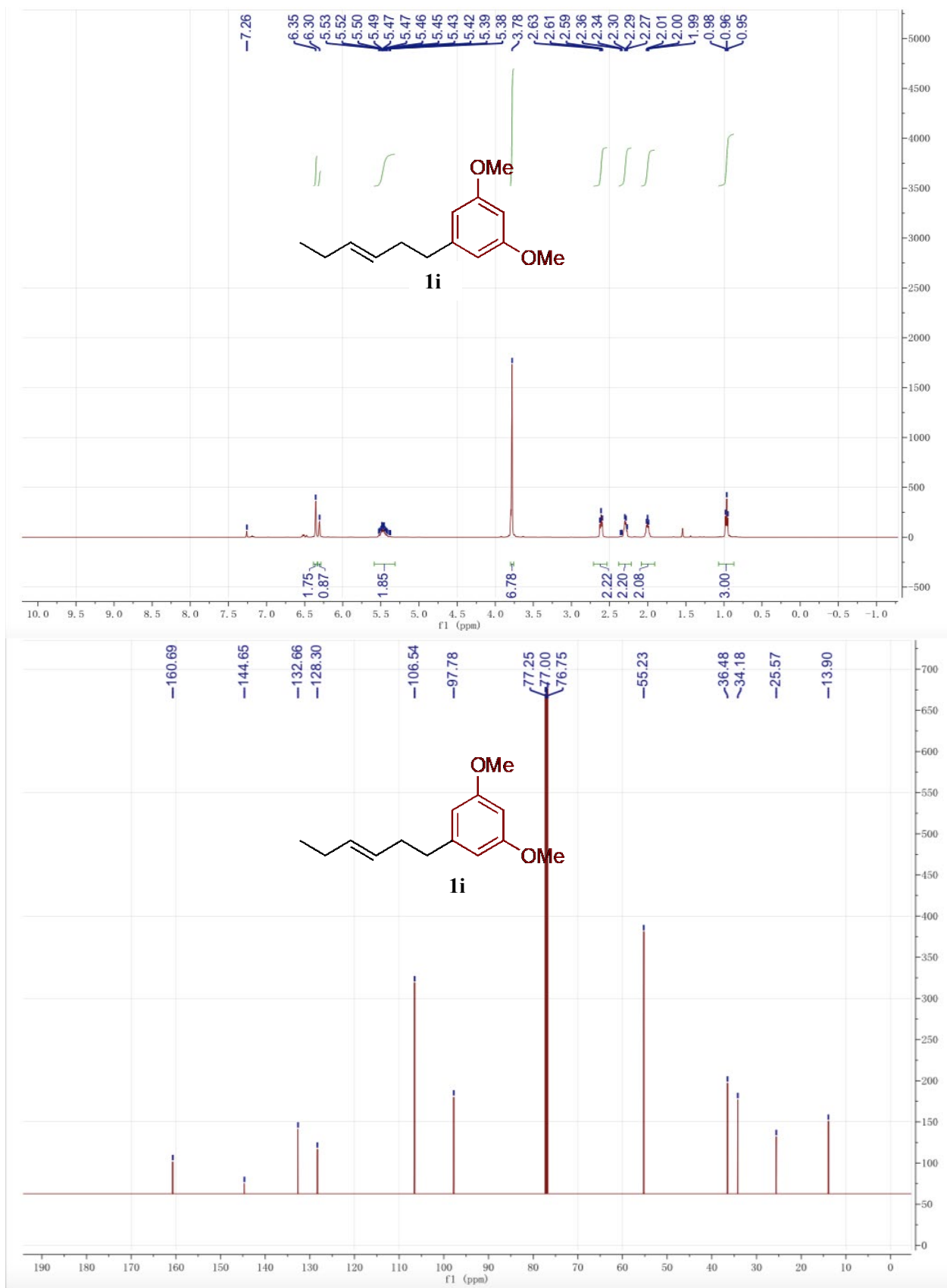


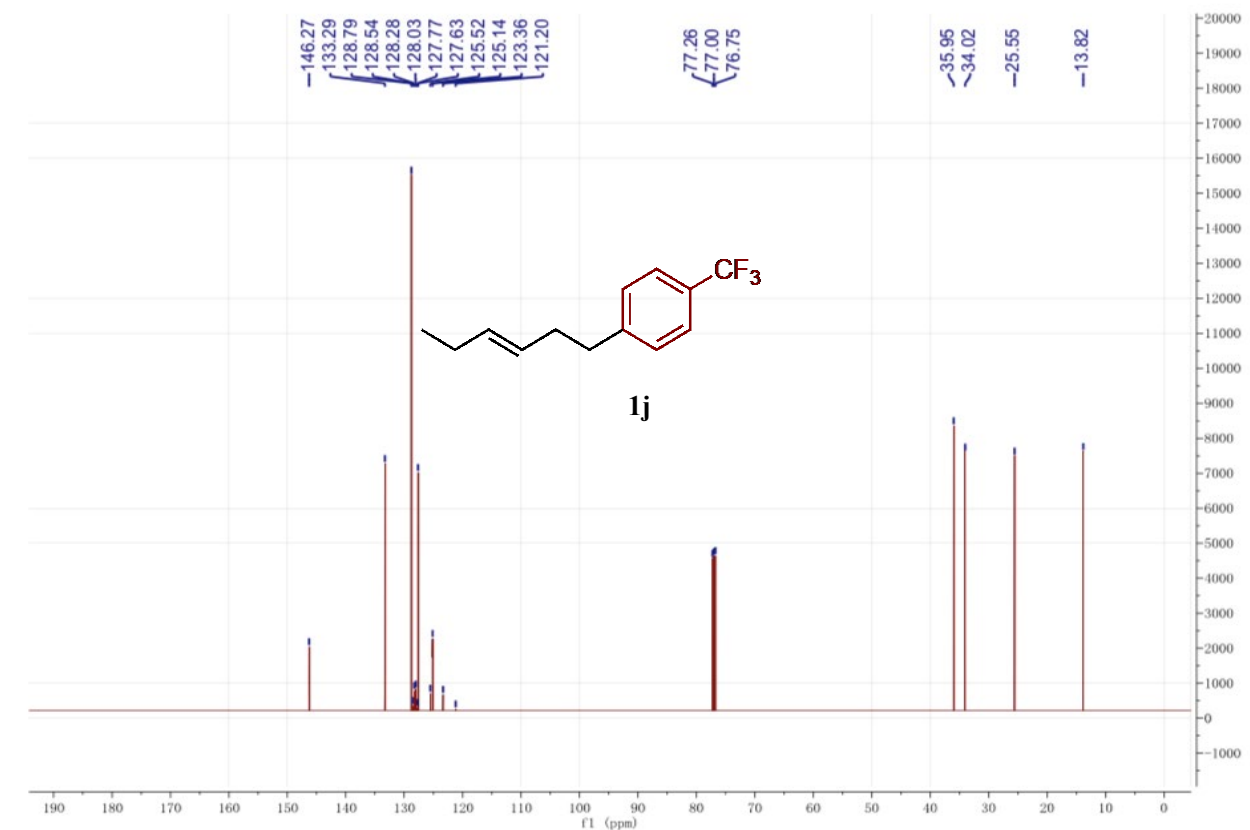
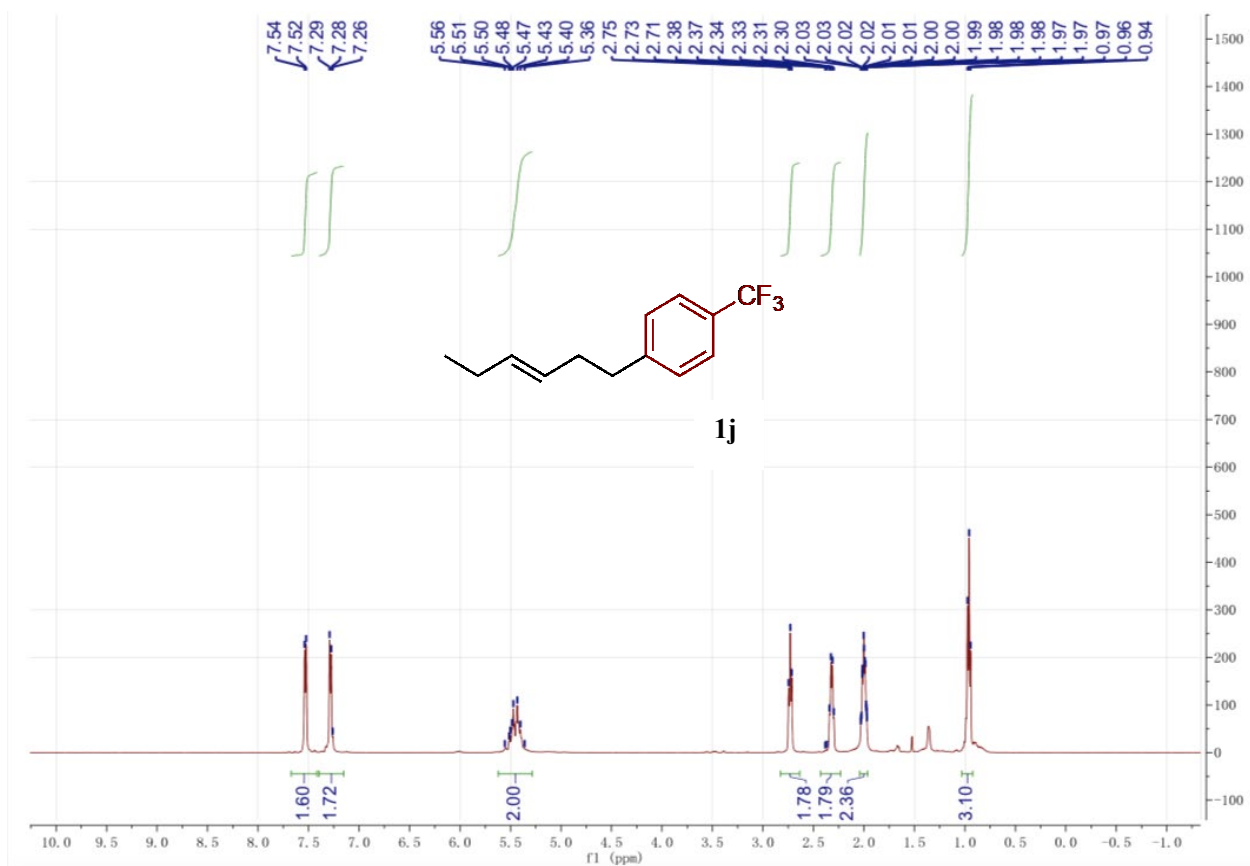


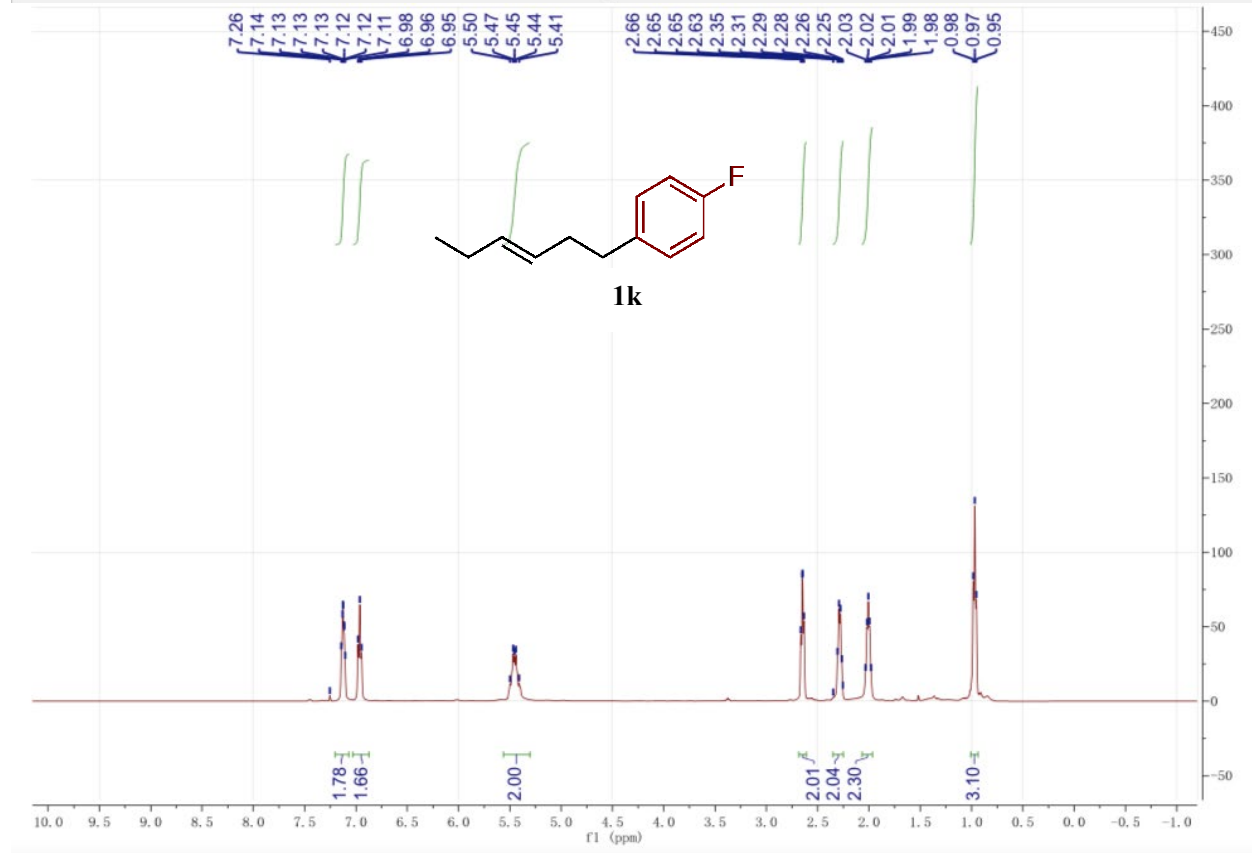
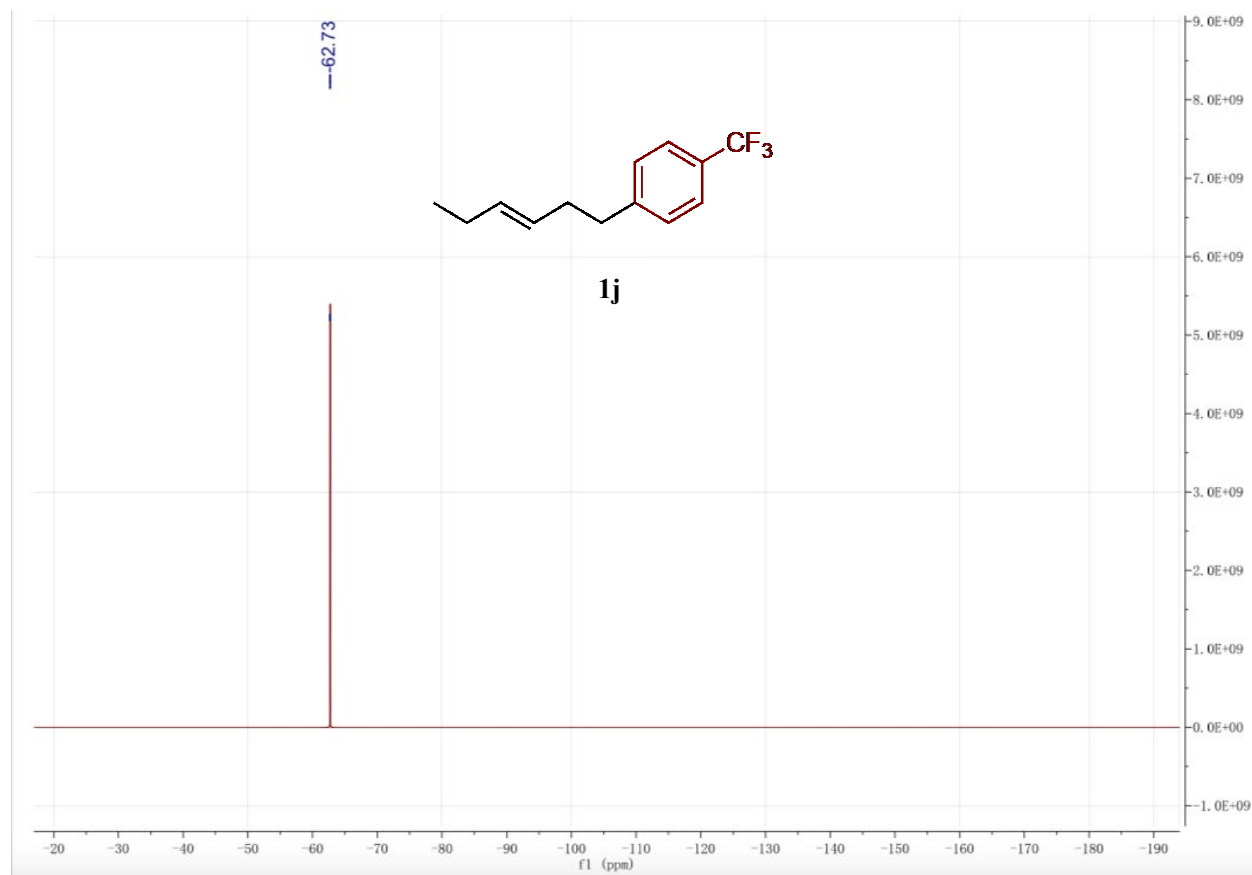


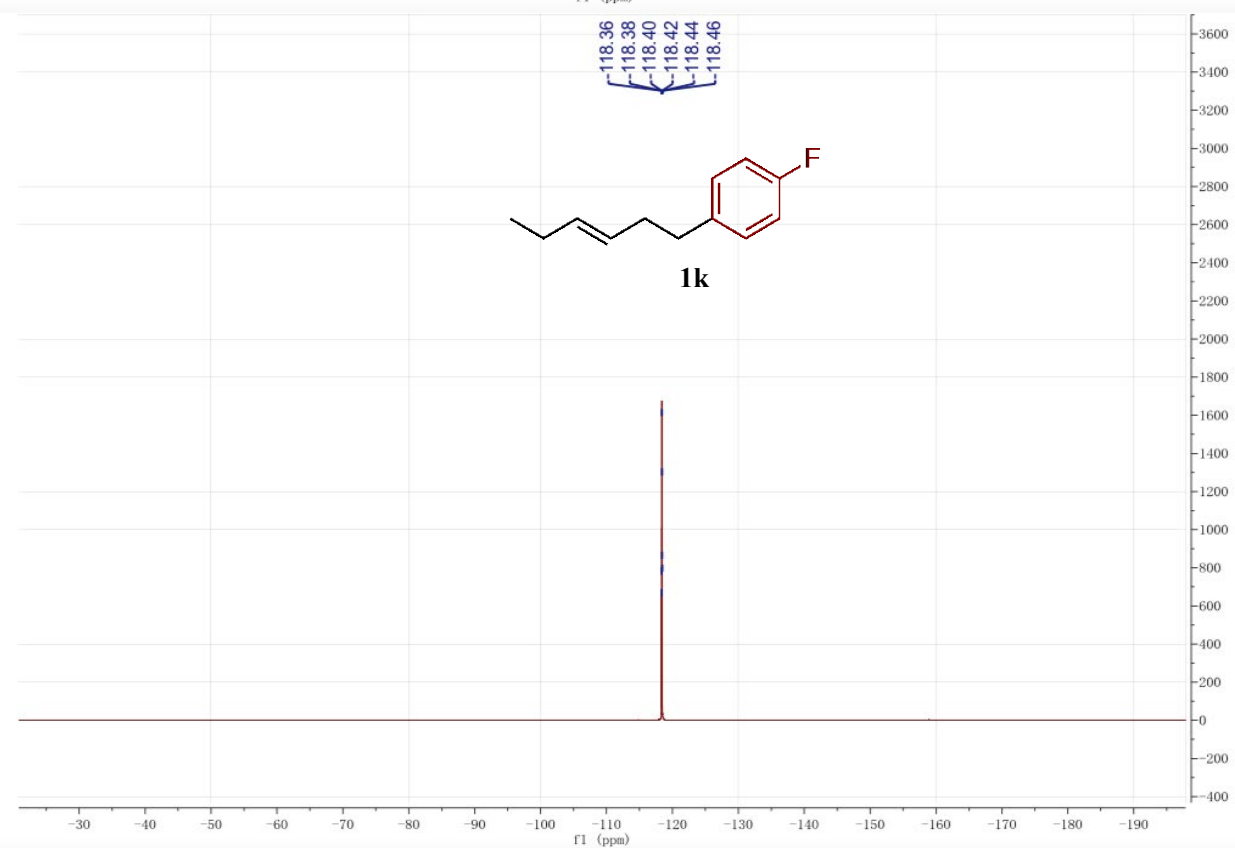
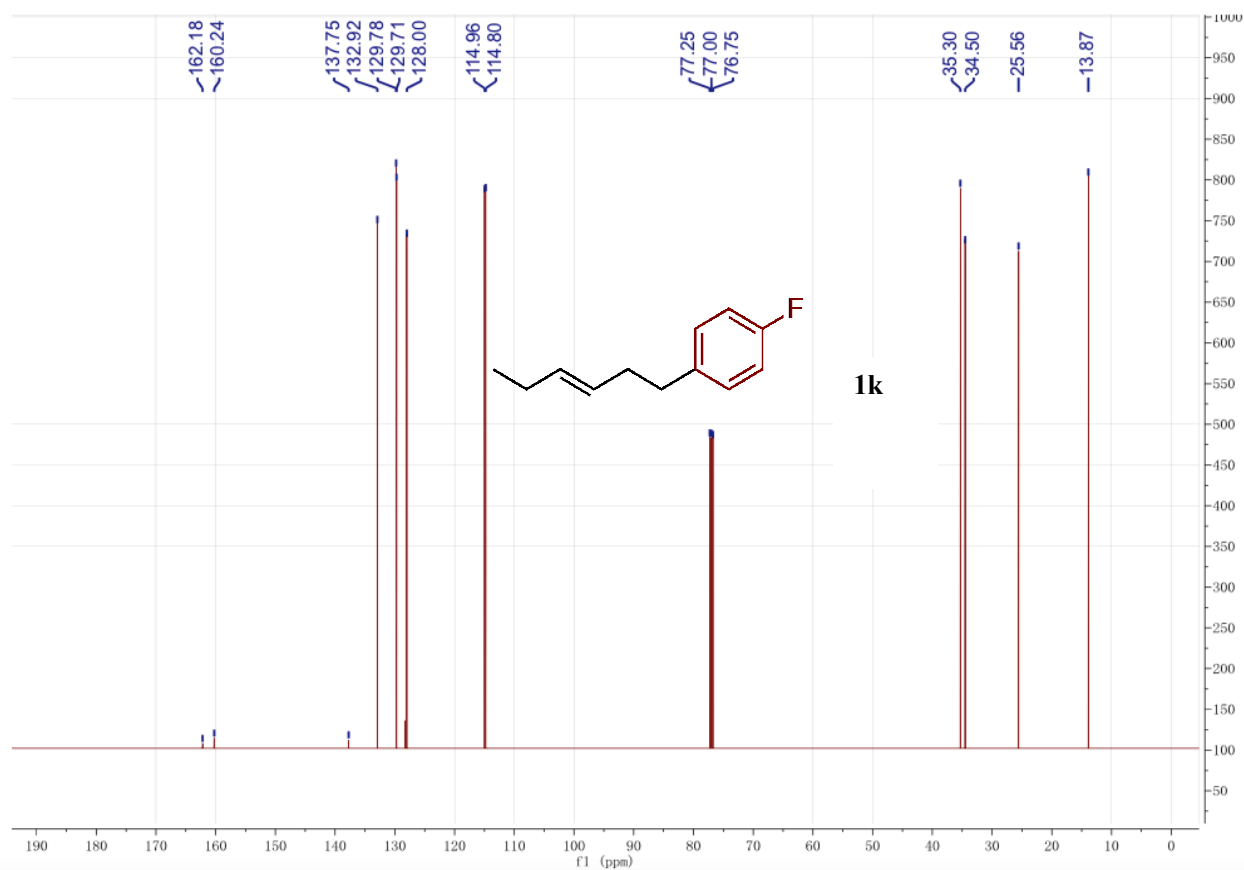


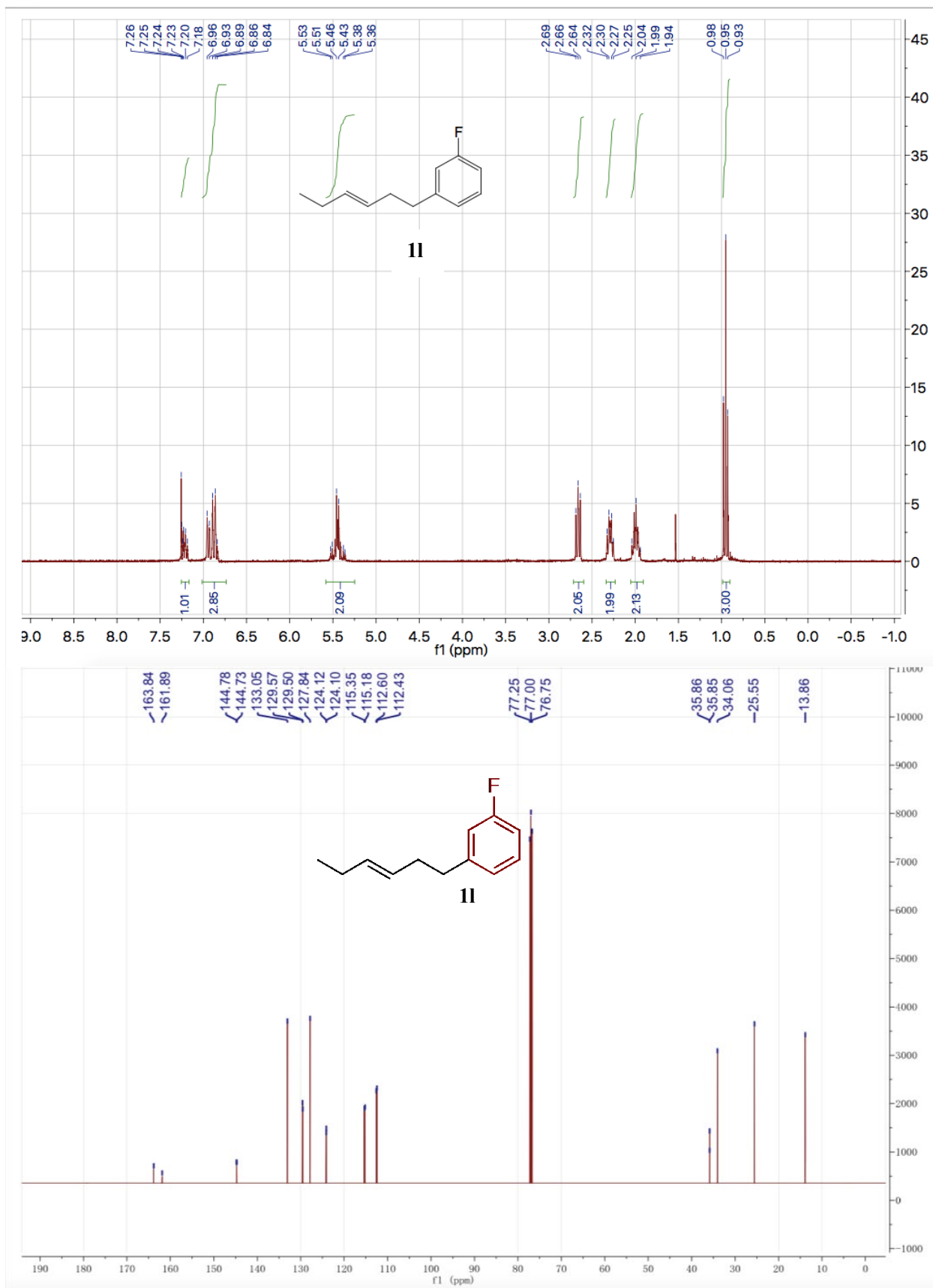


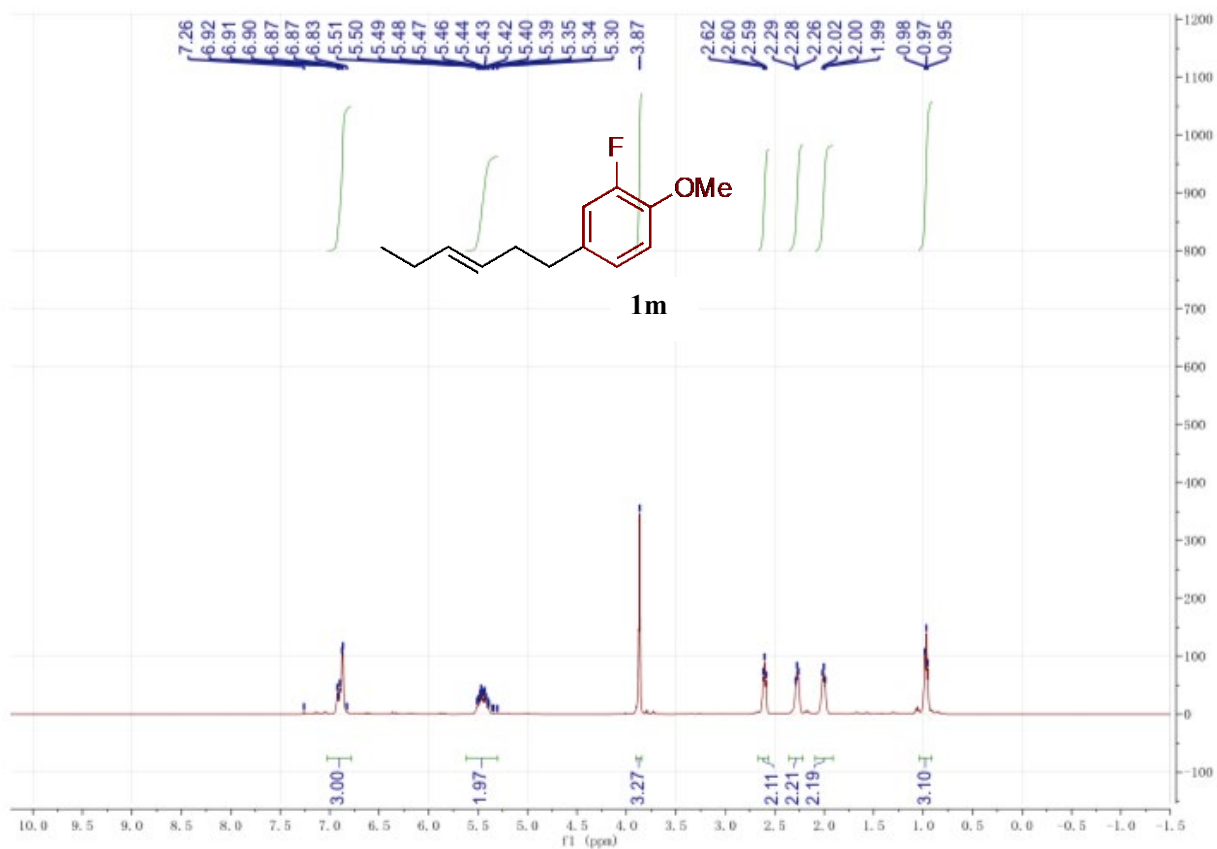
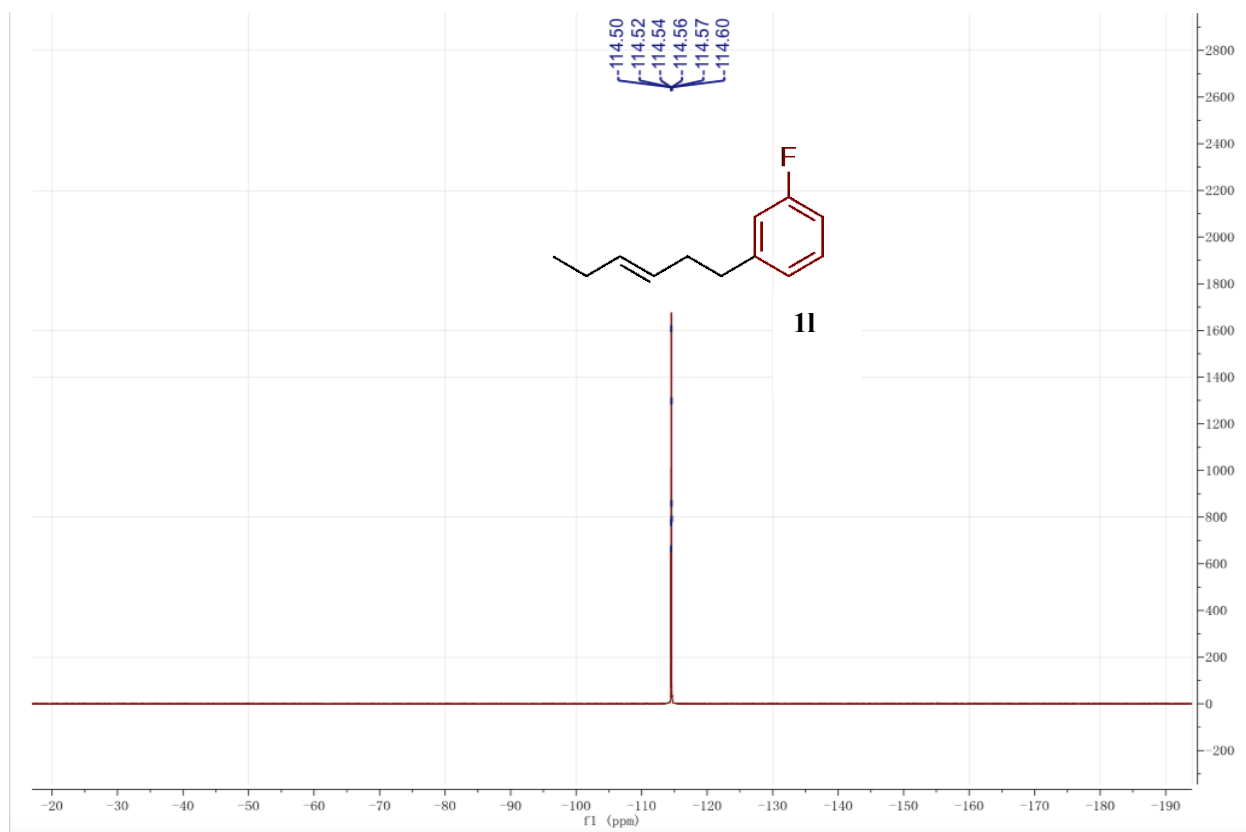


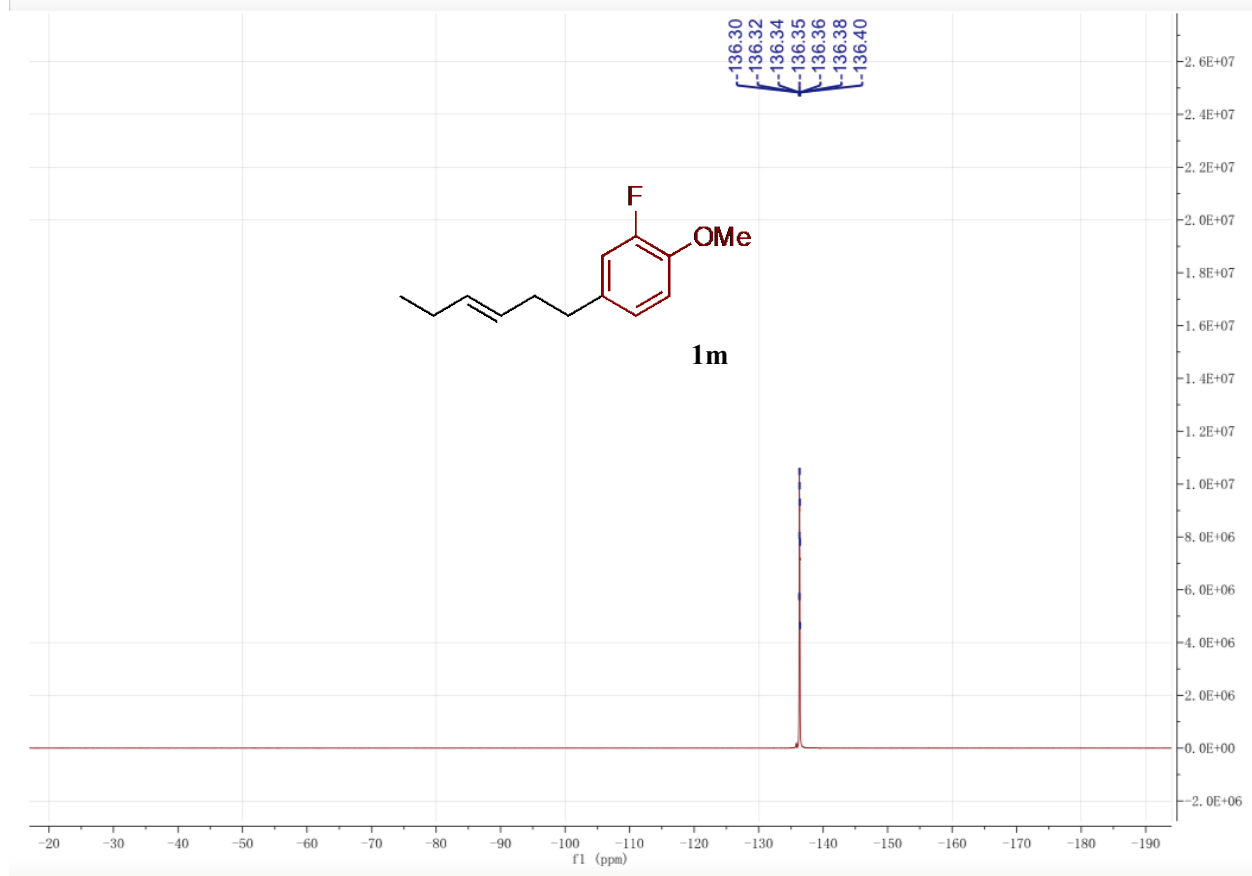
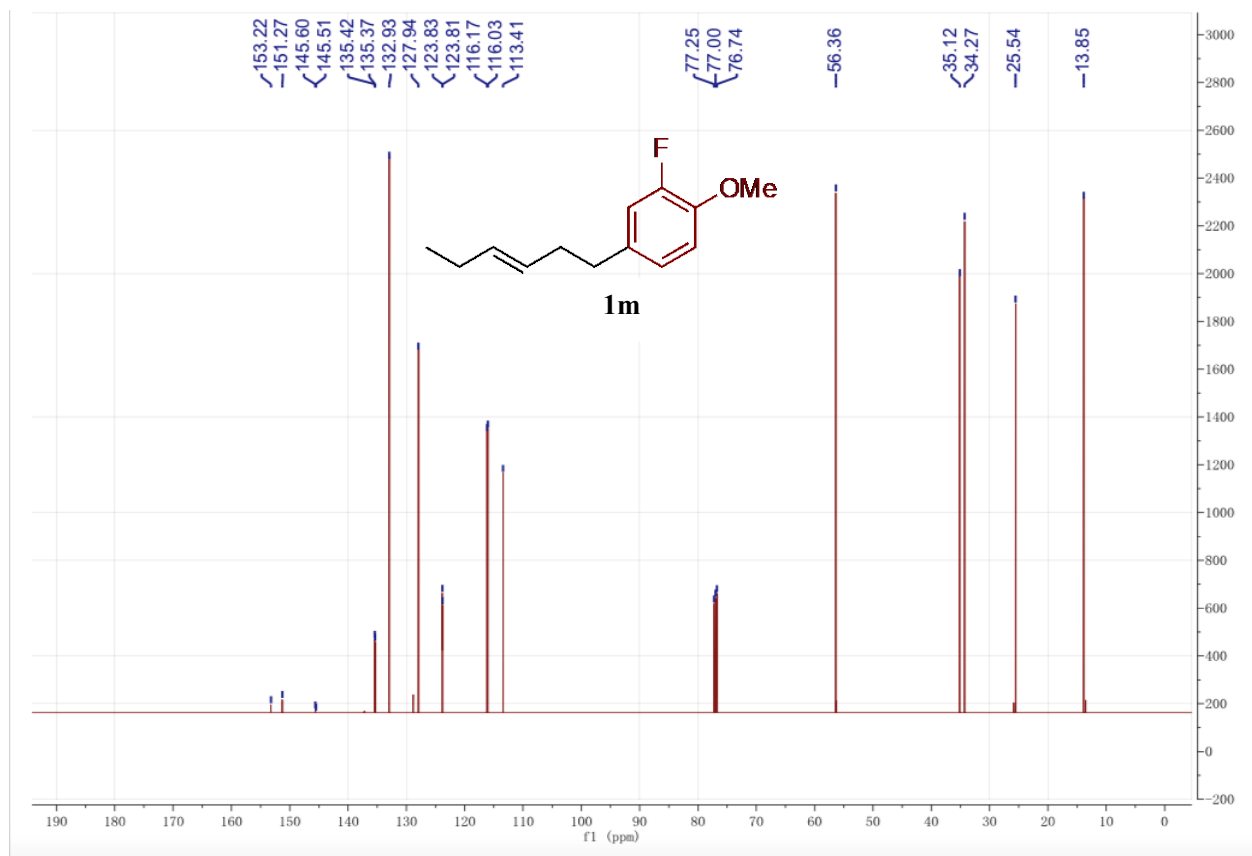


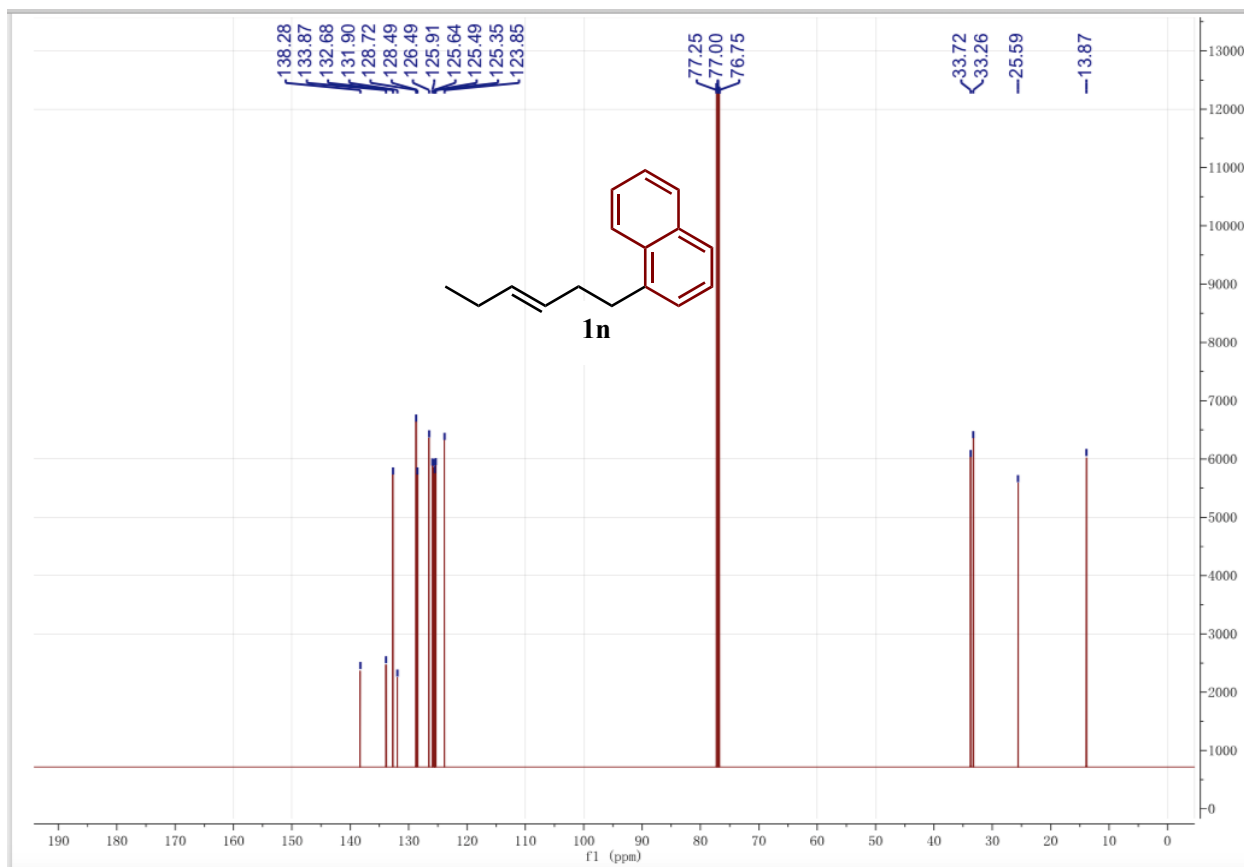
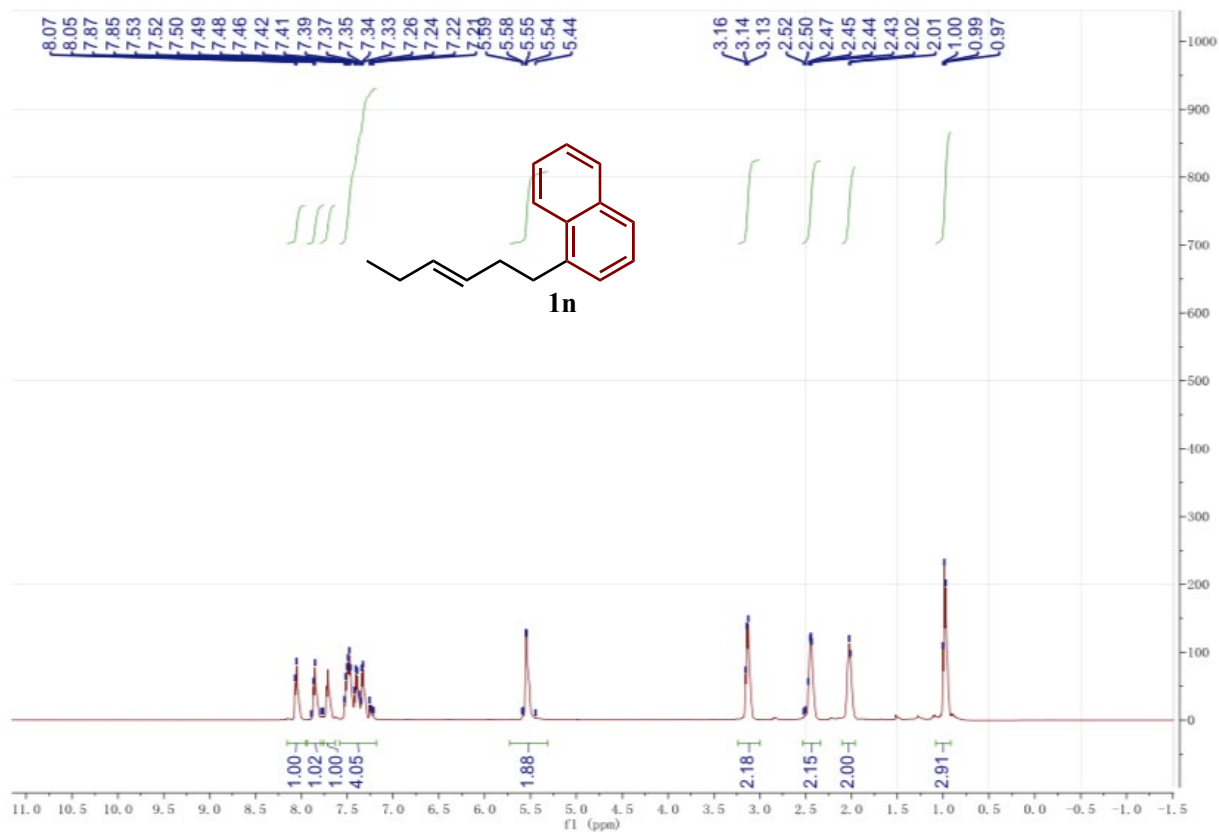


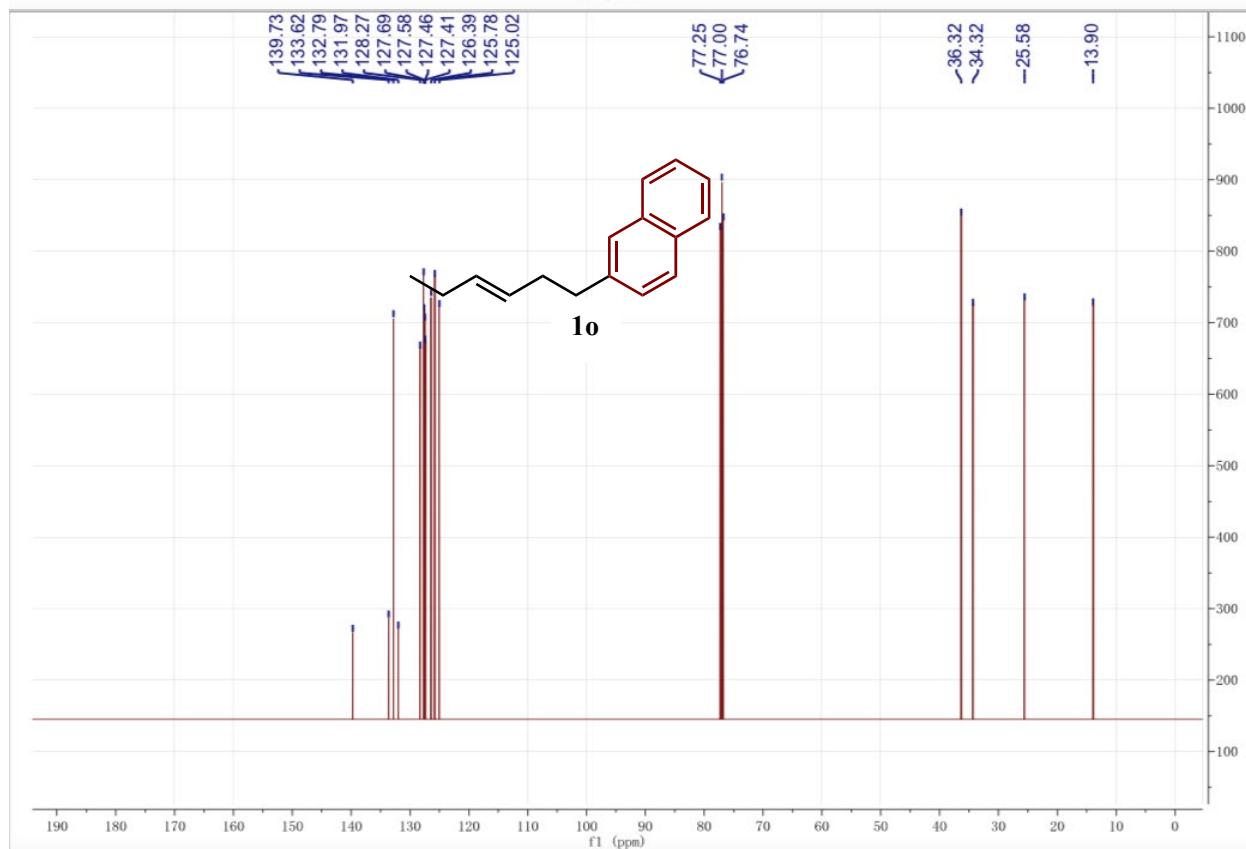
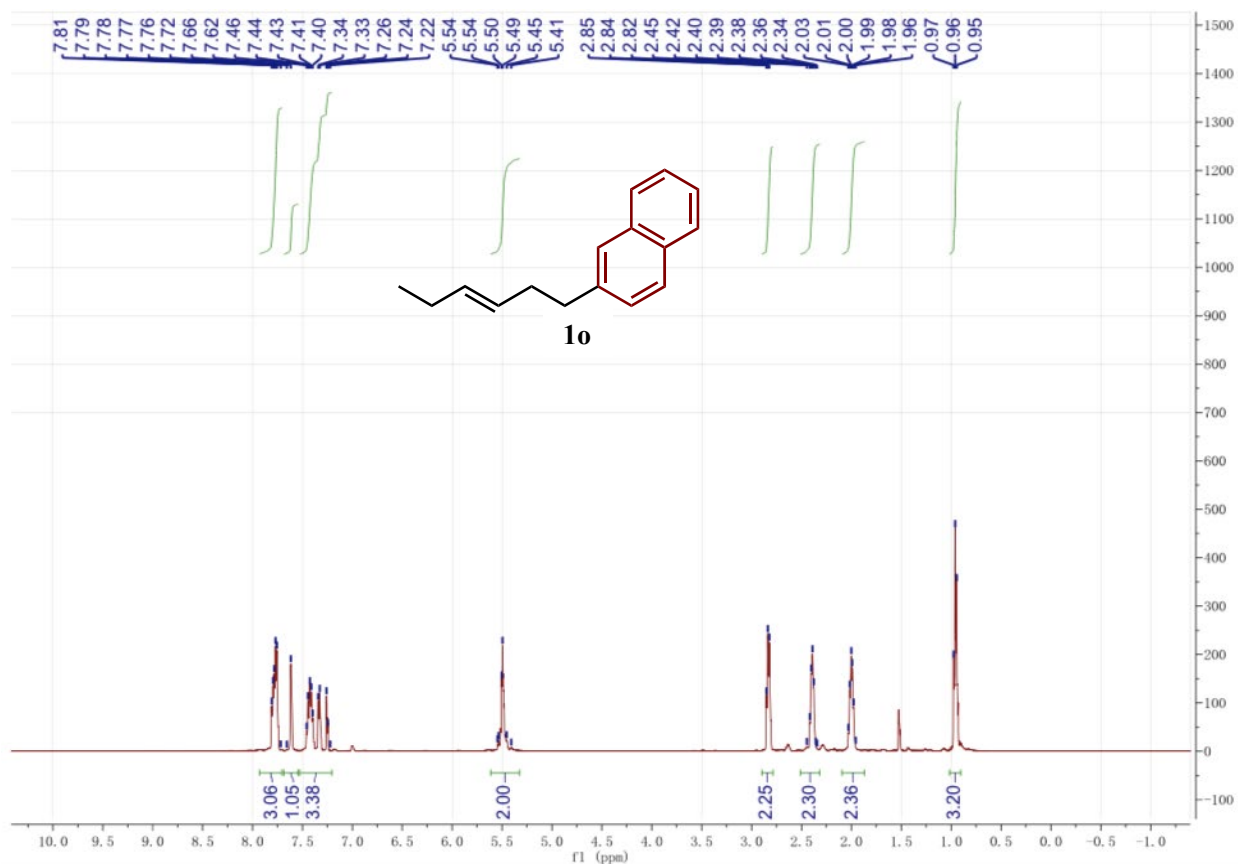


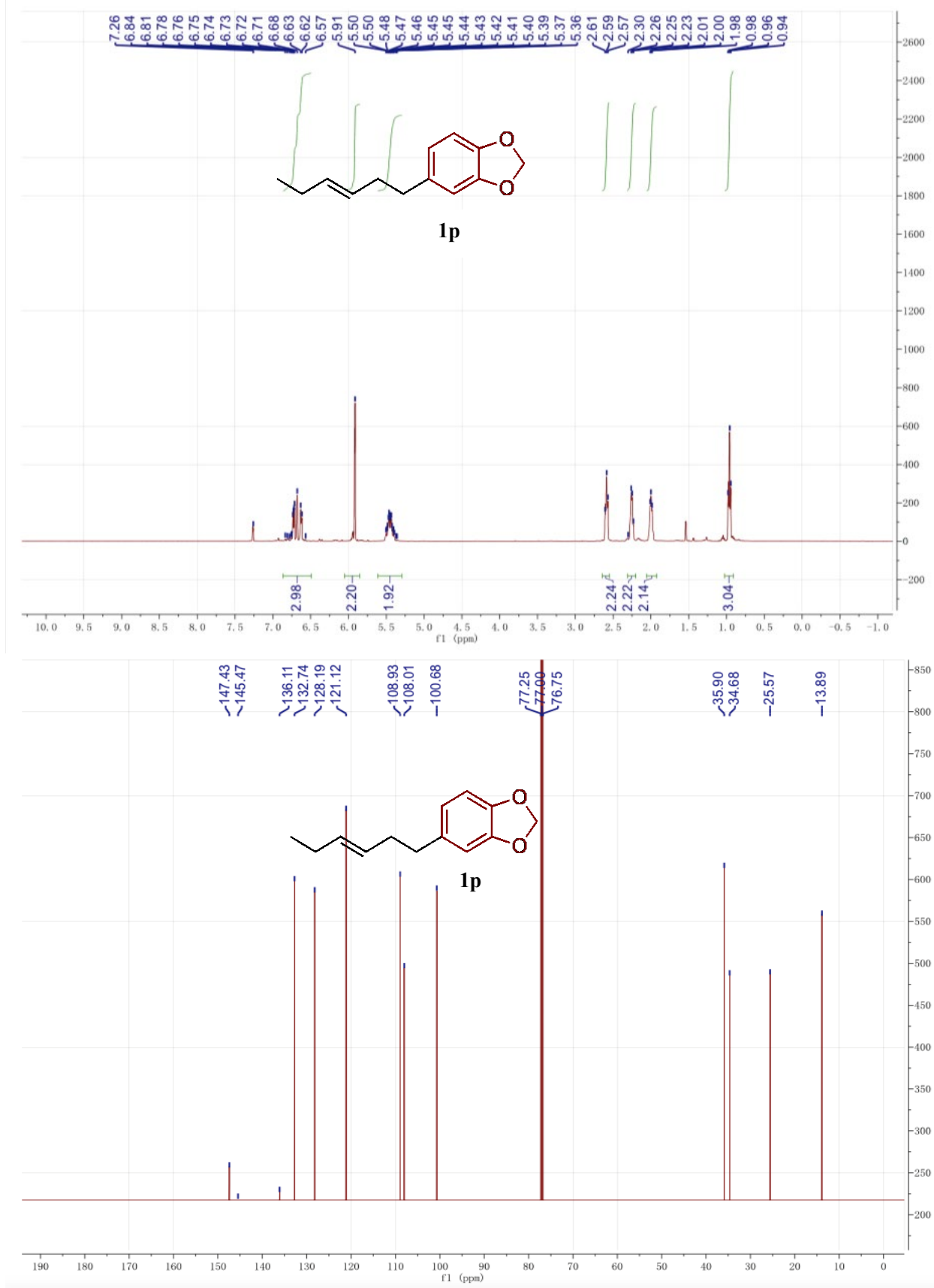


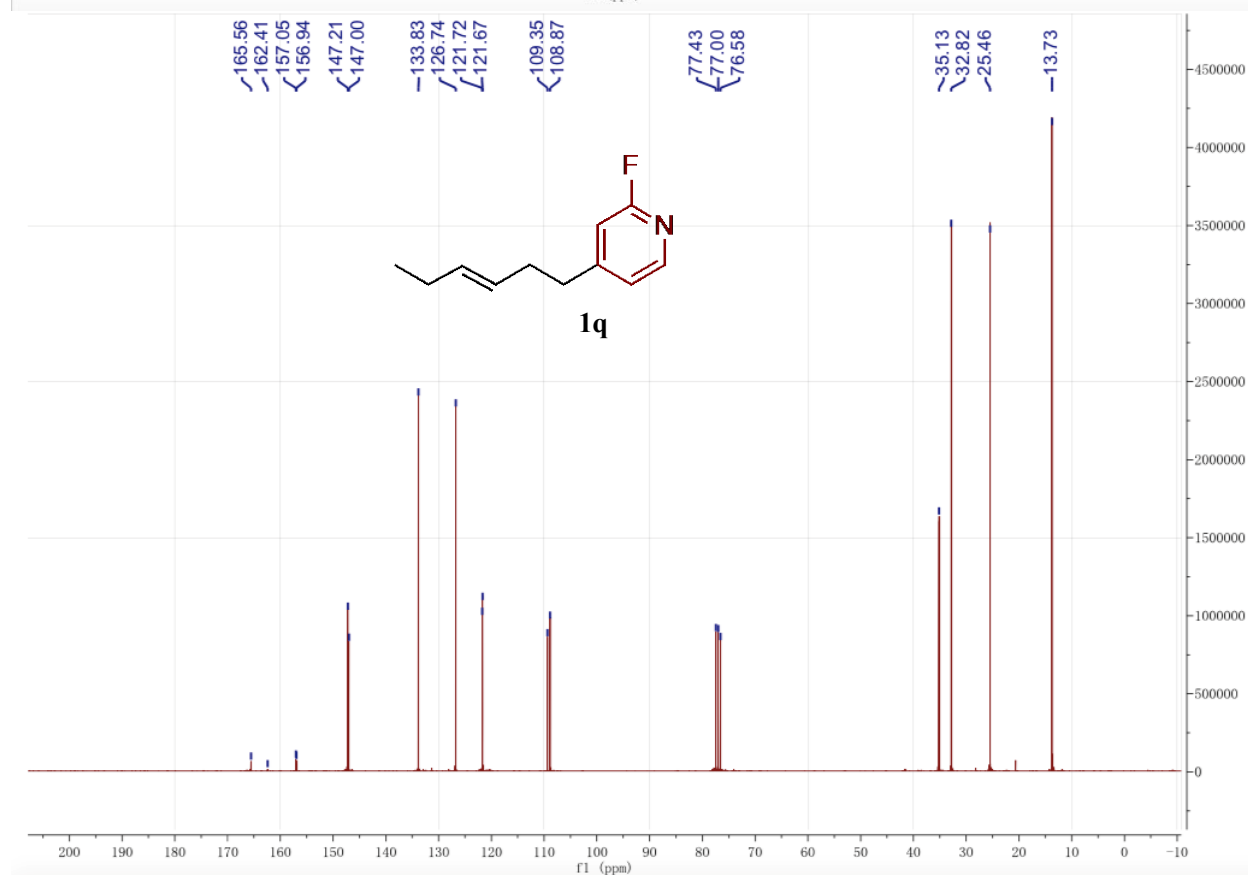
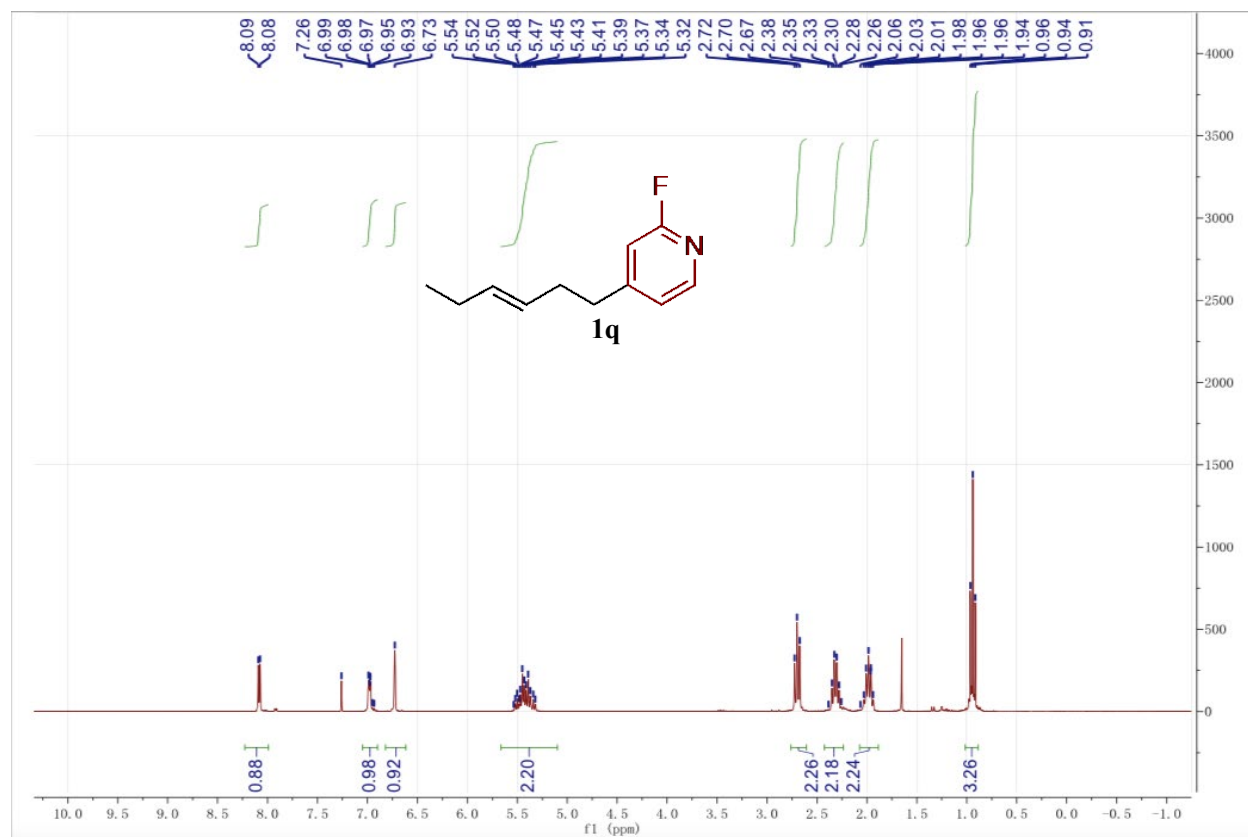


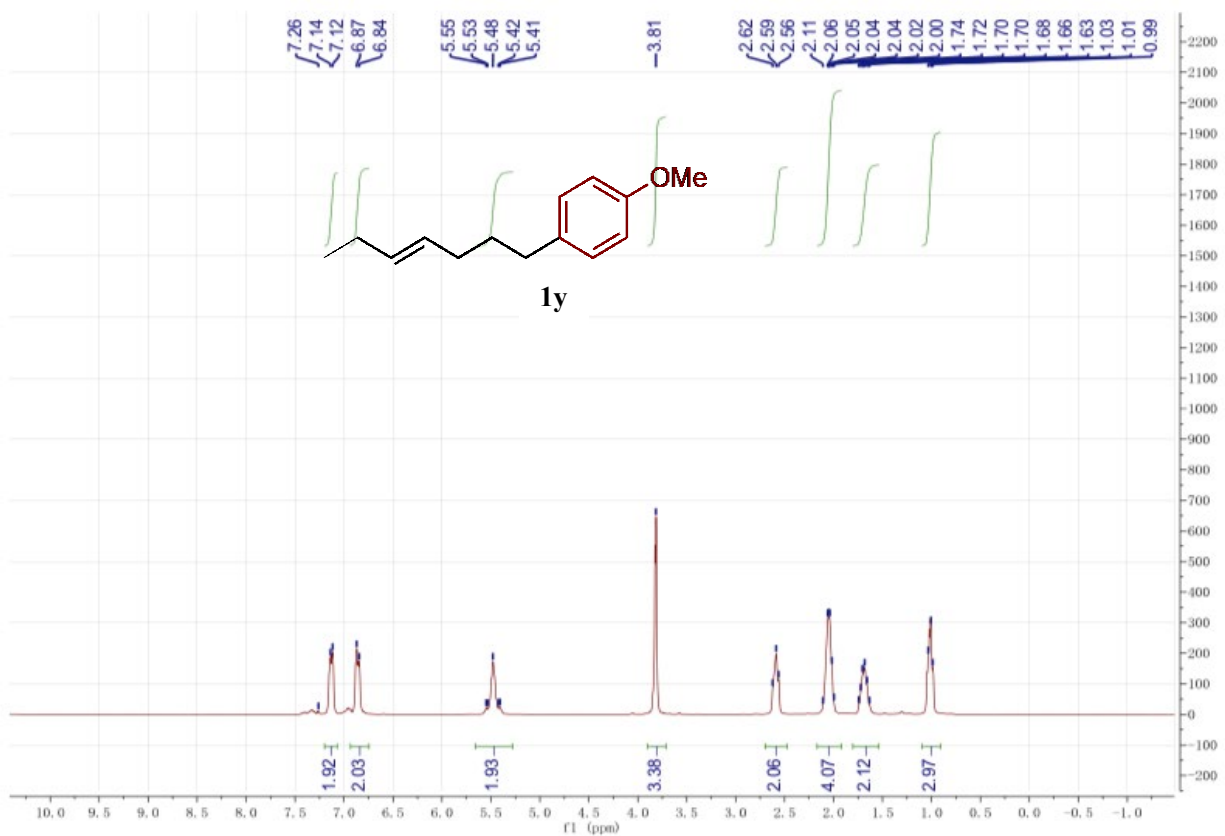
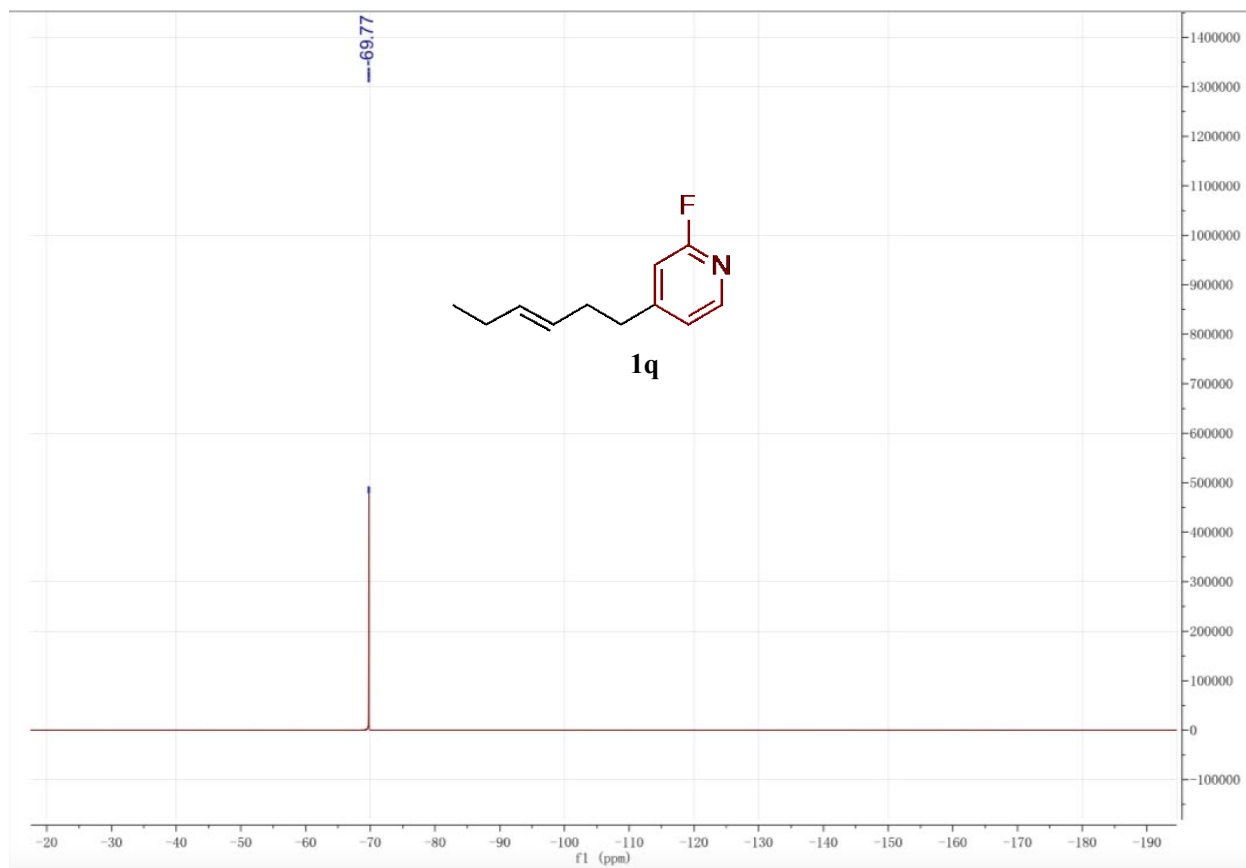


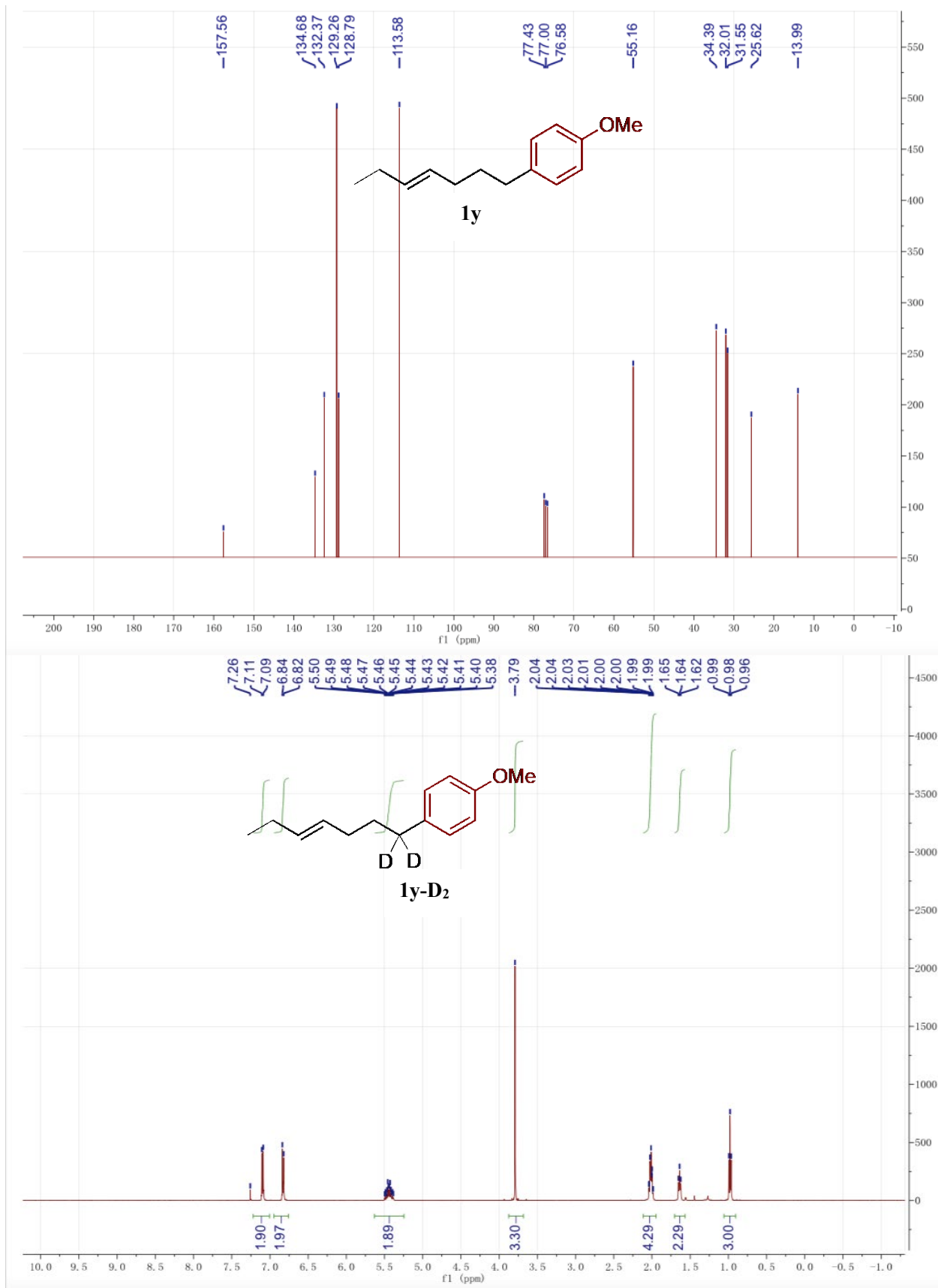


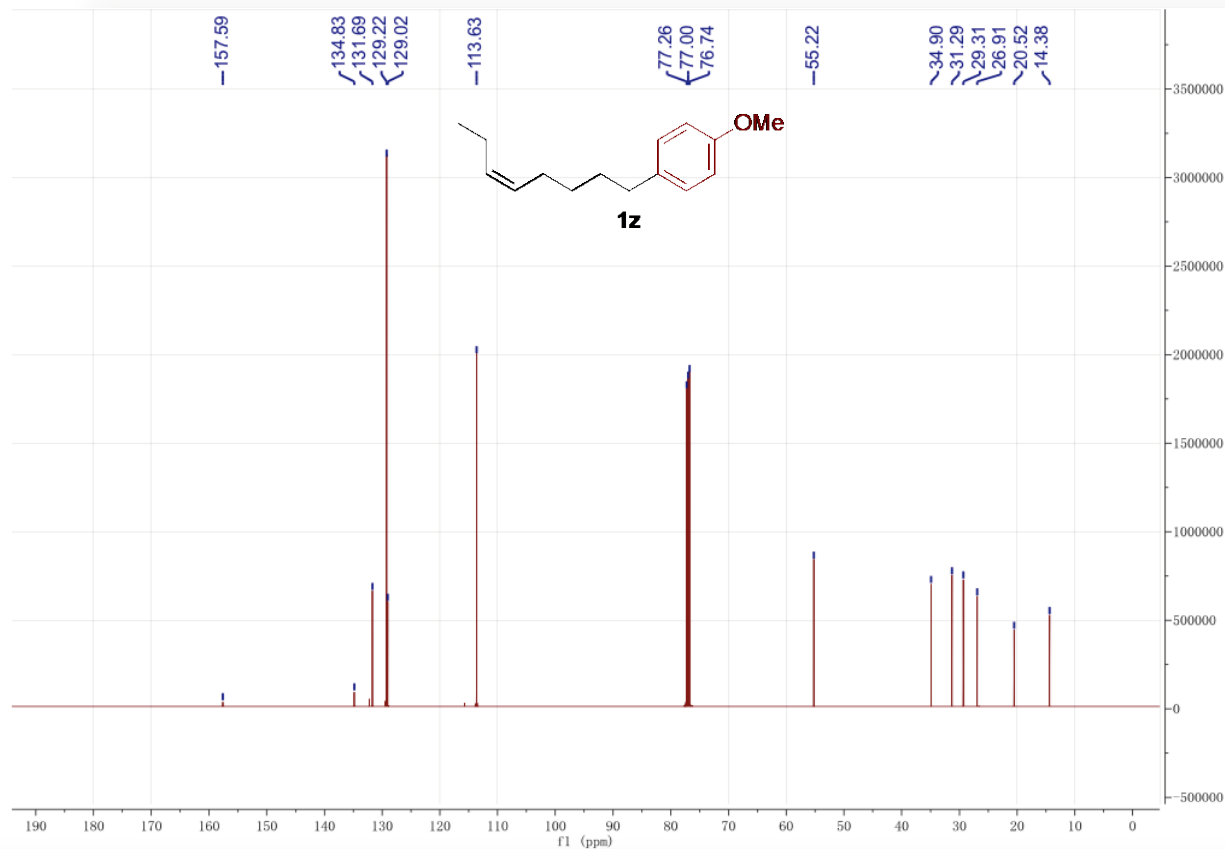
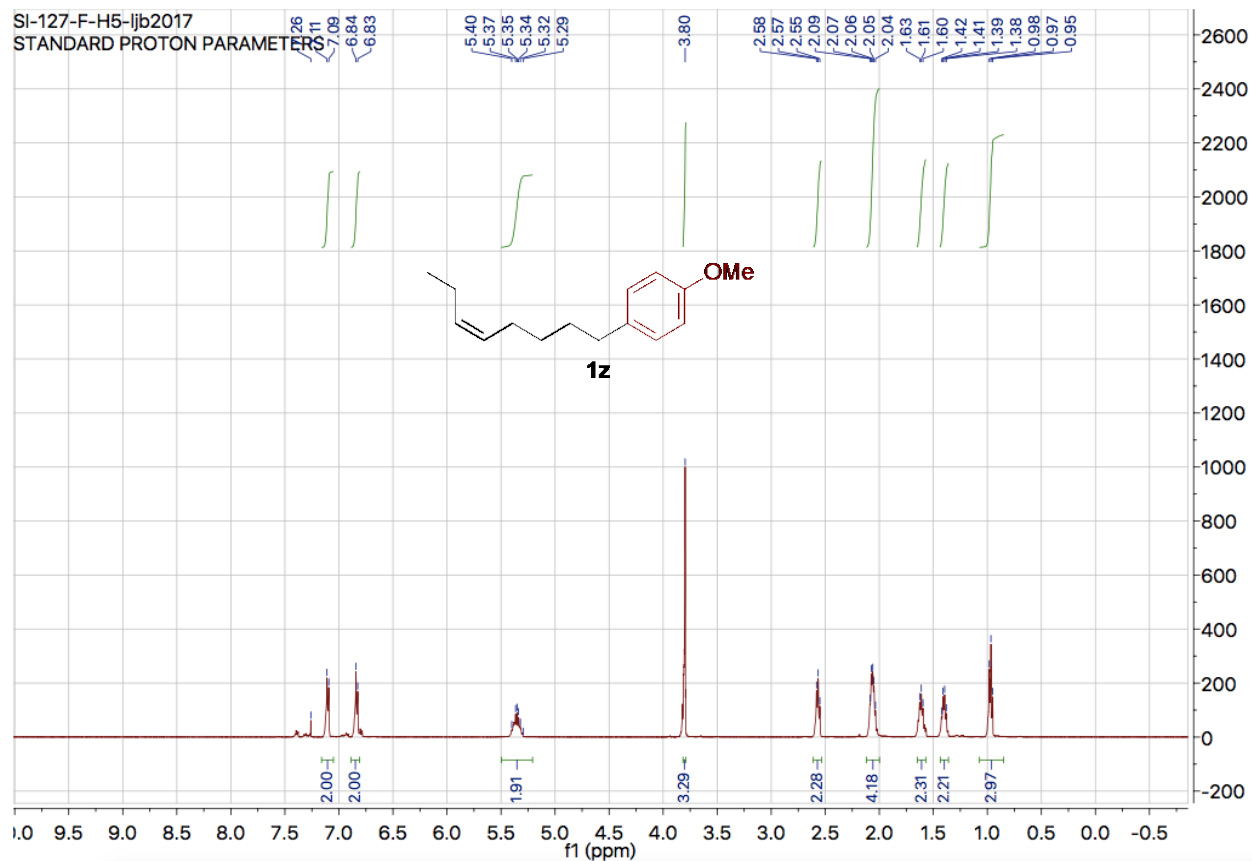




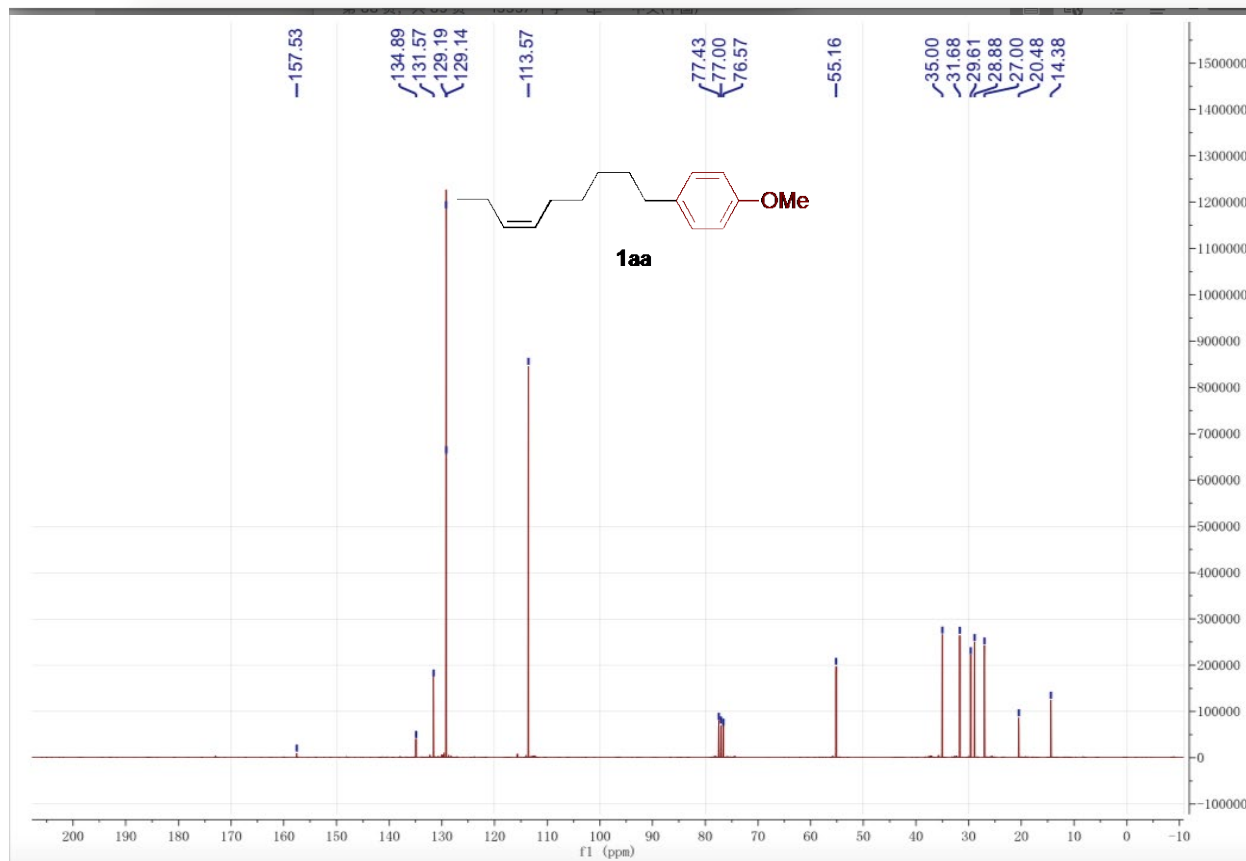
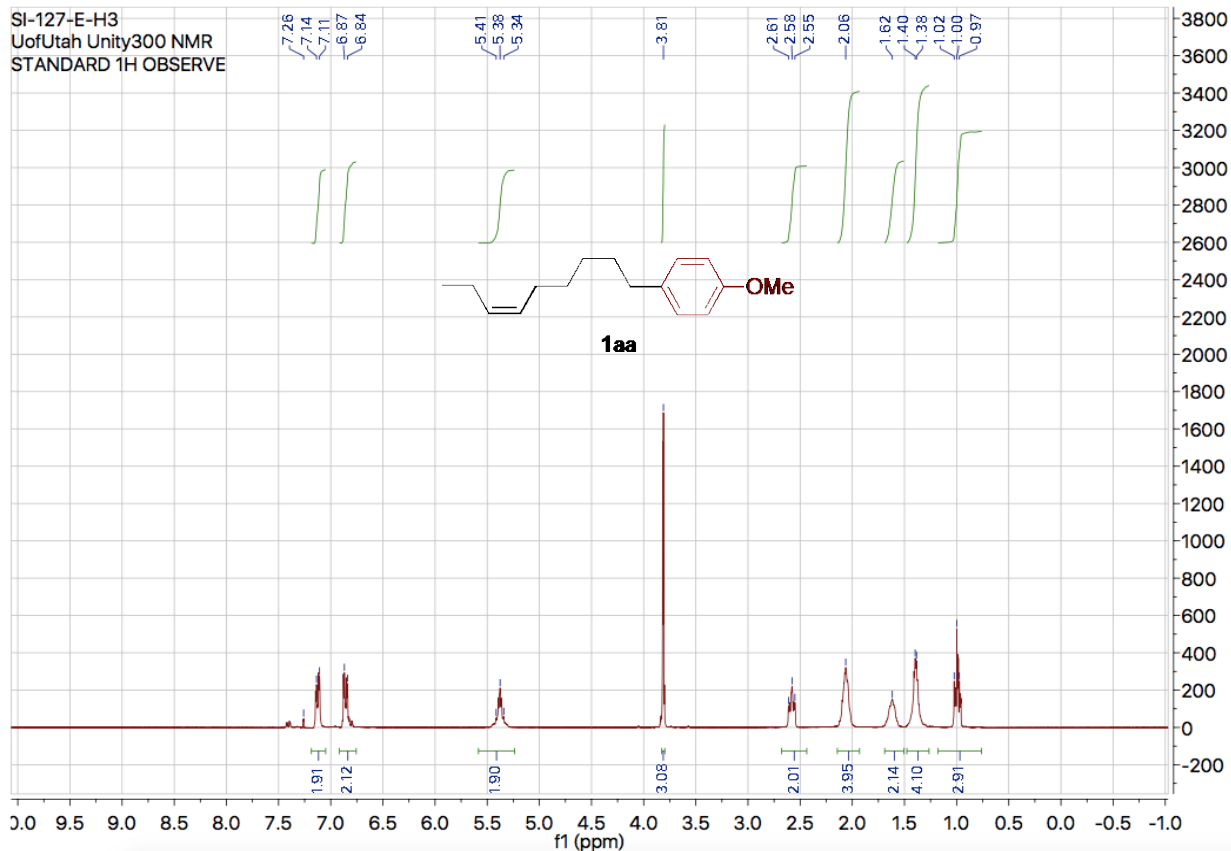


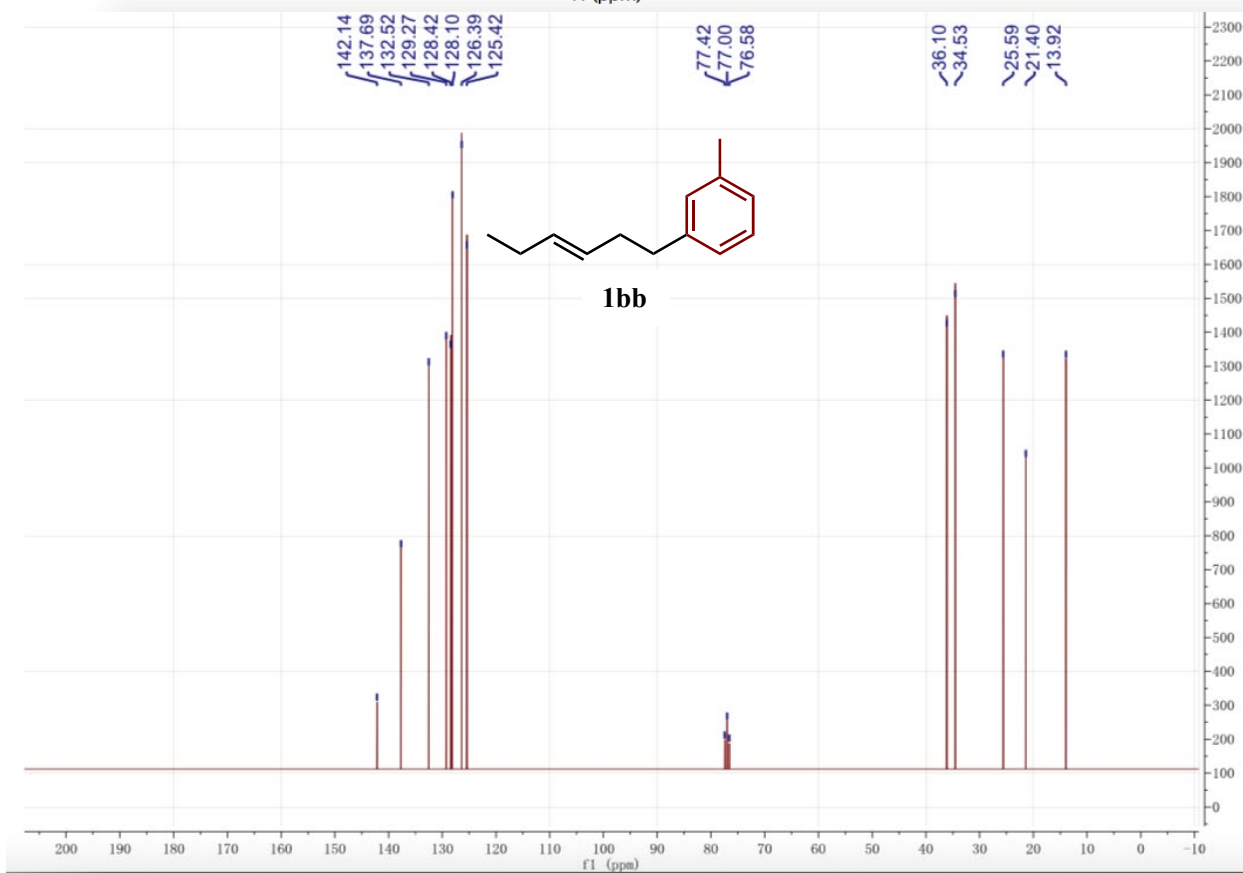
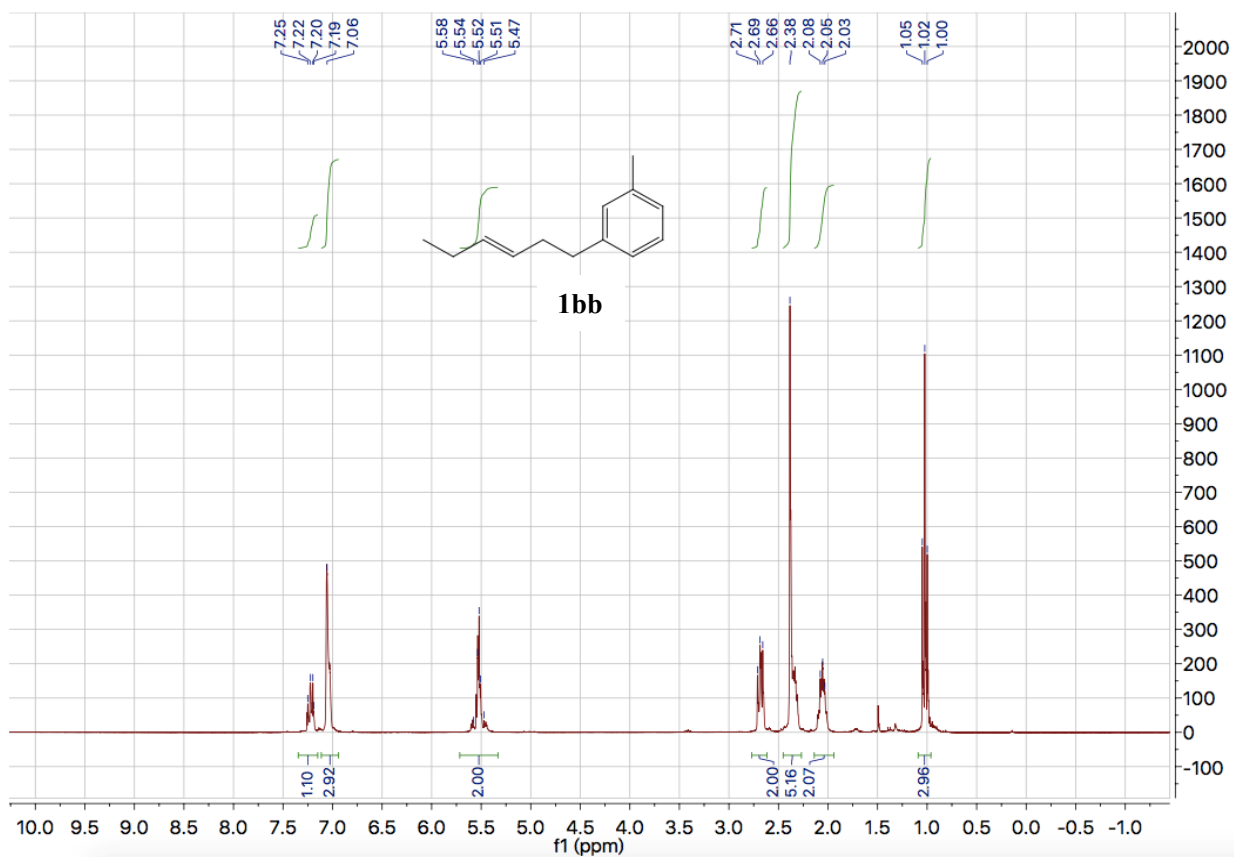


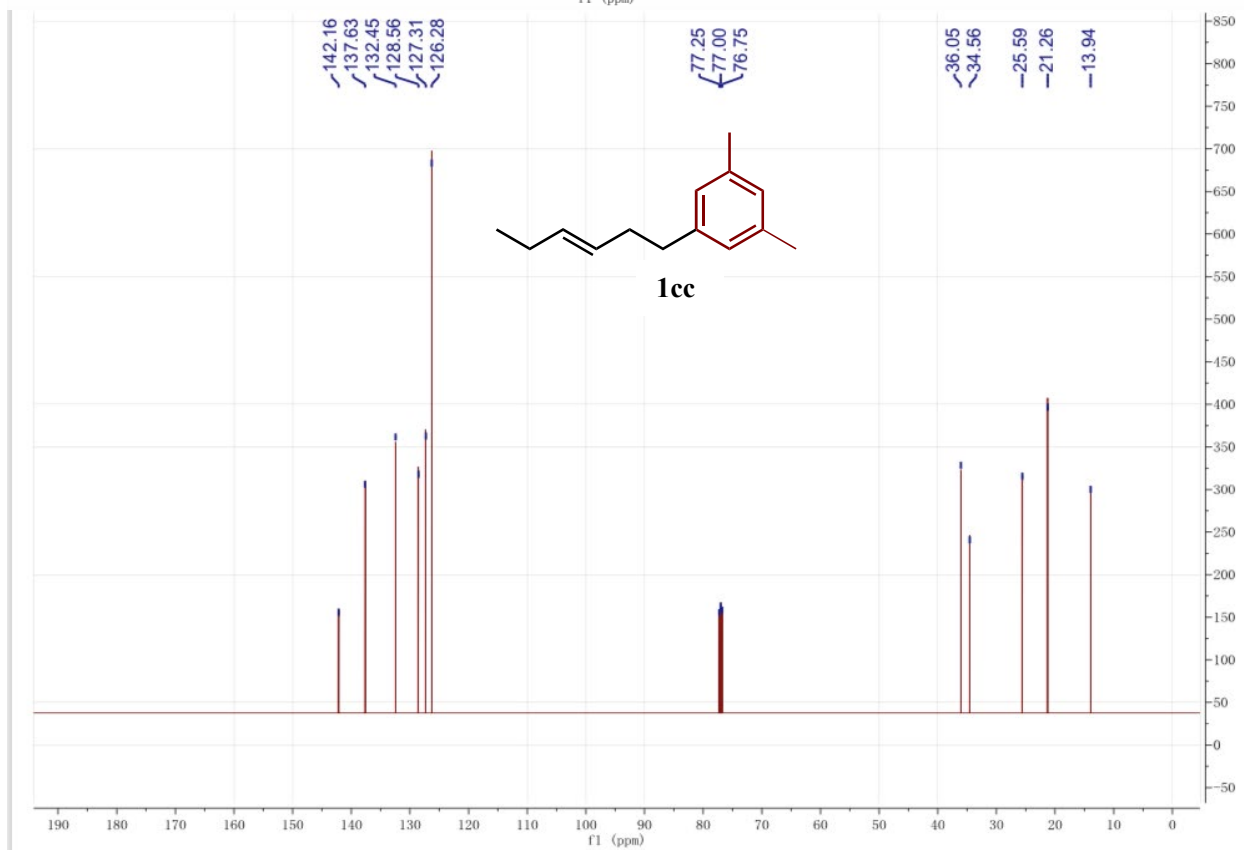
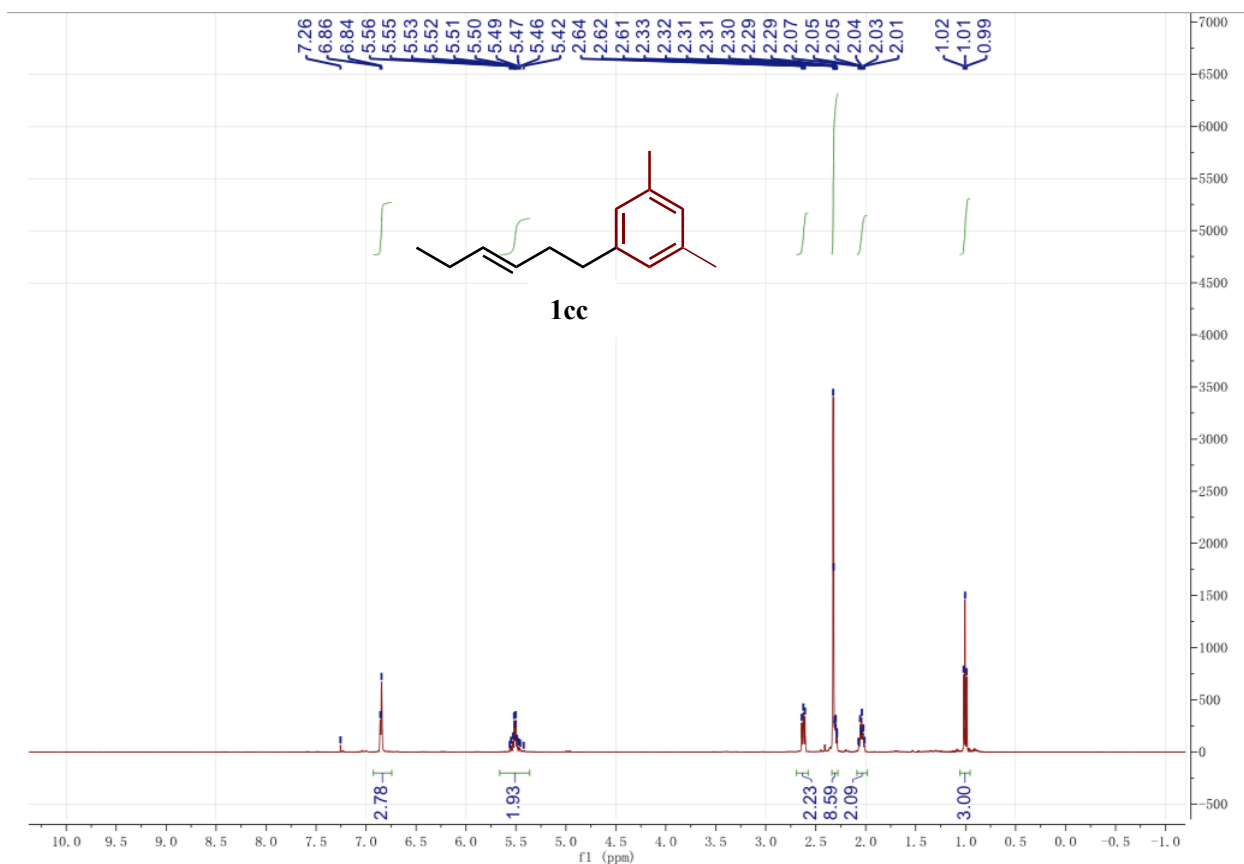


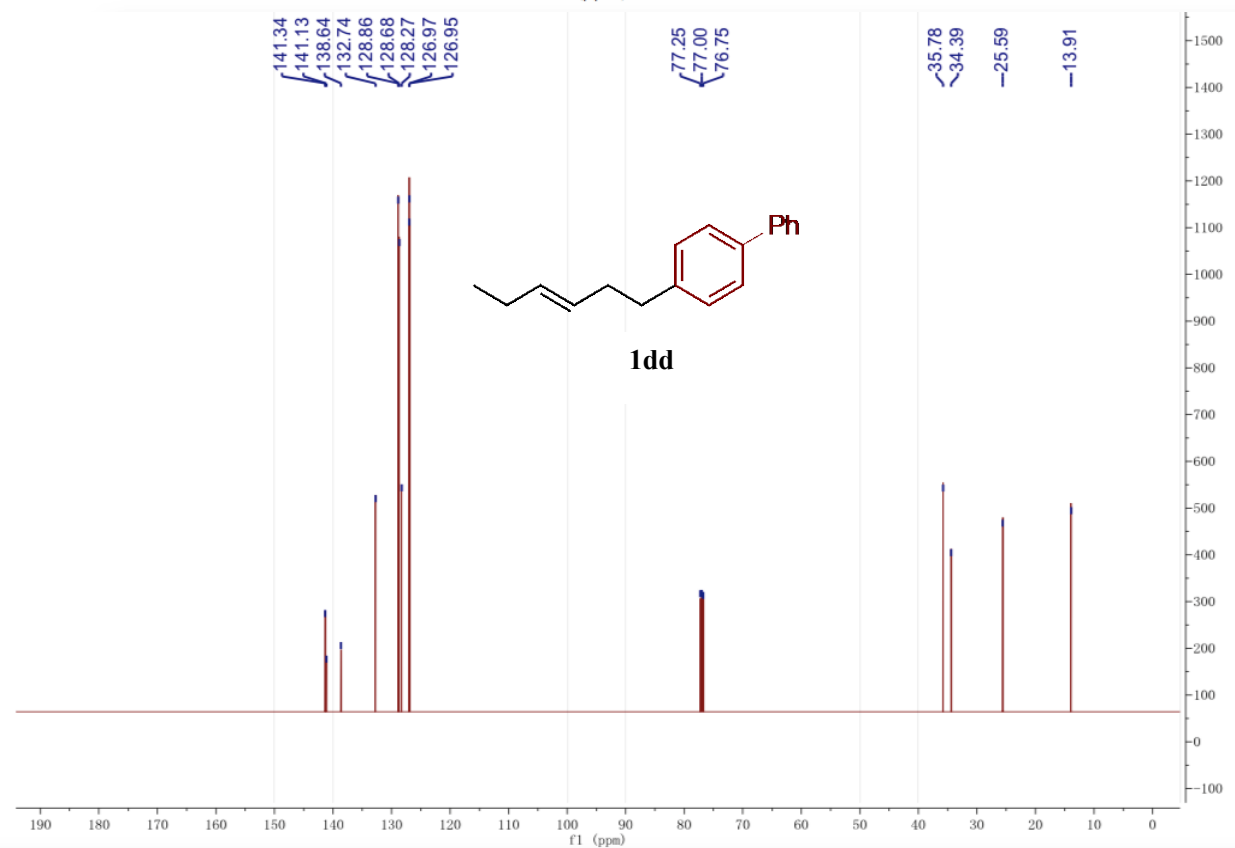
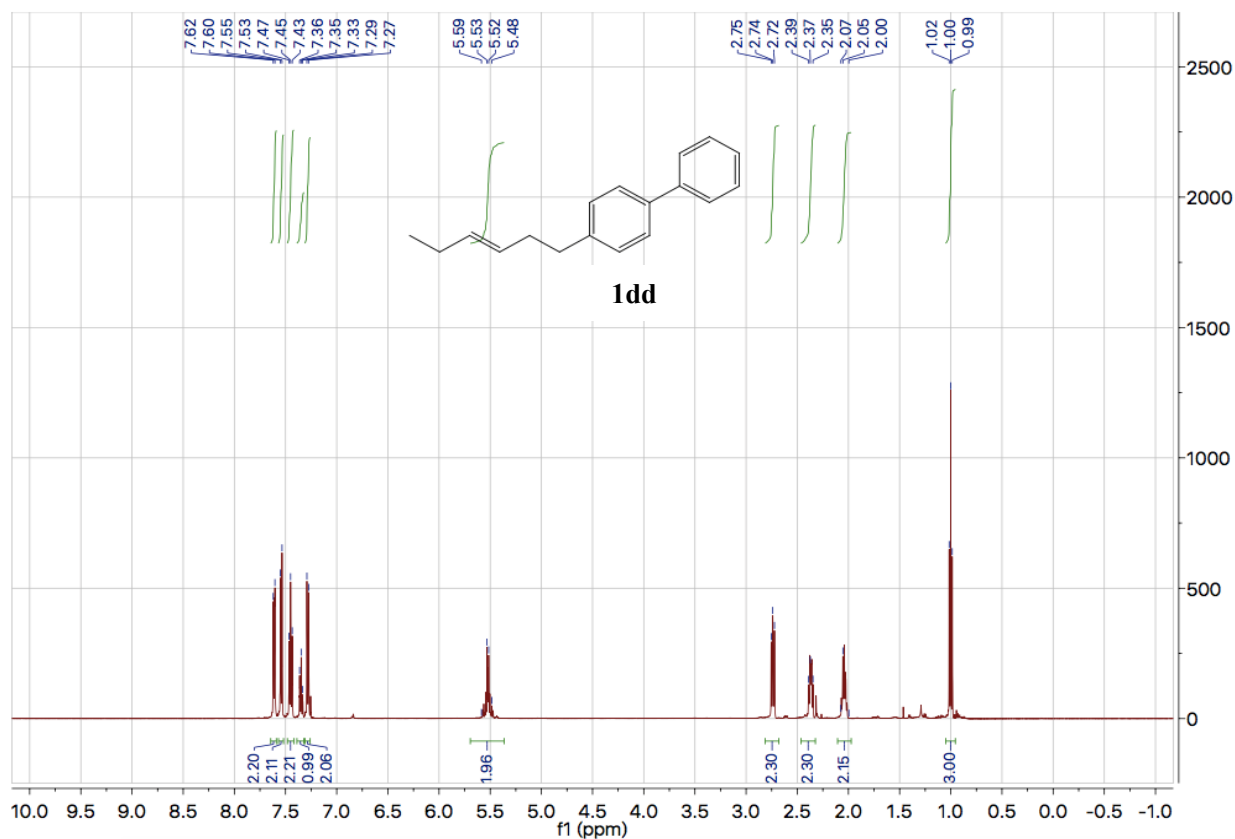


SI-127-E-H3
UofUtah Unity300 NMR
STANDARD 1H OBSERVE

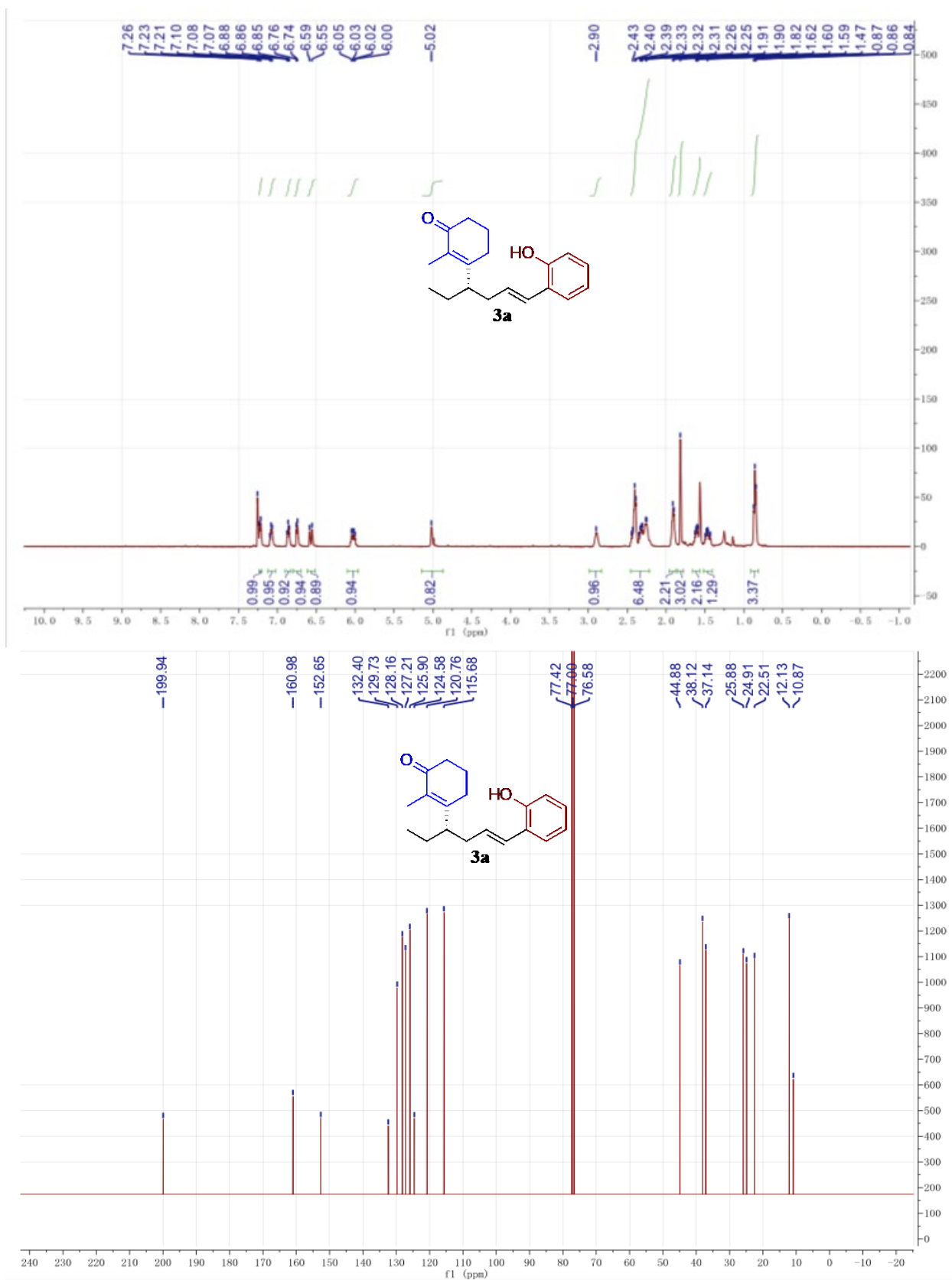


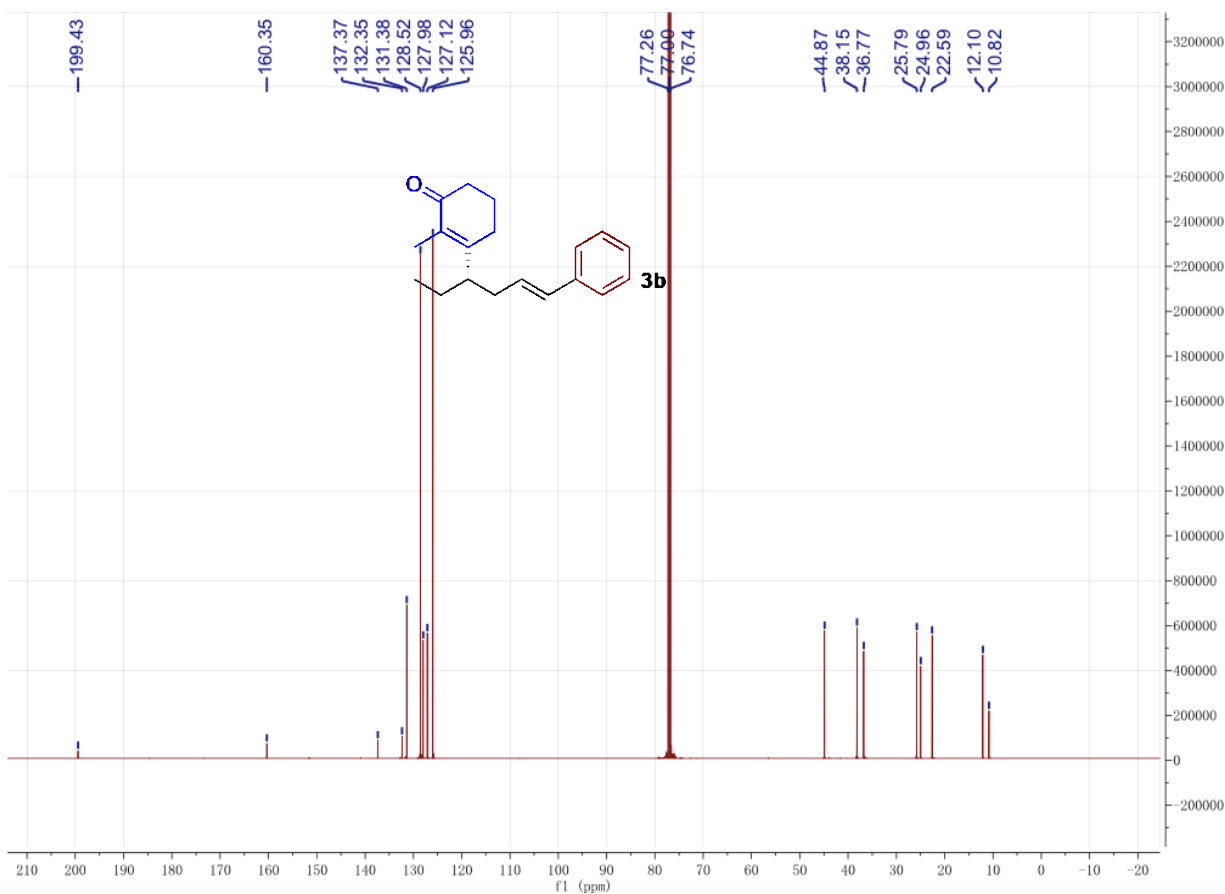
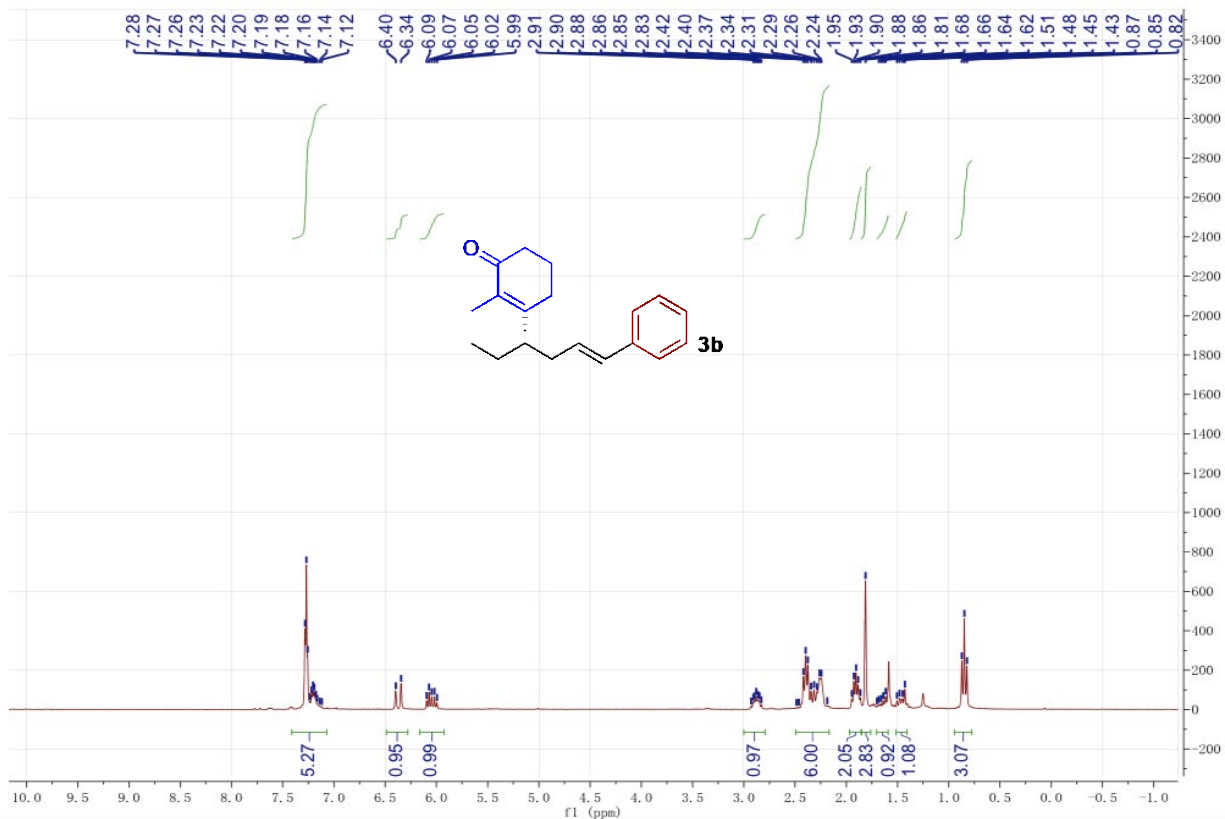


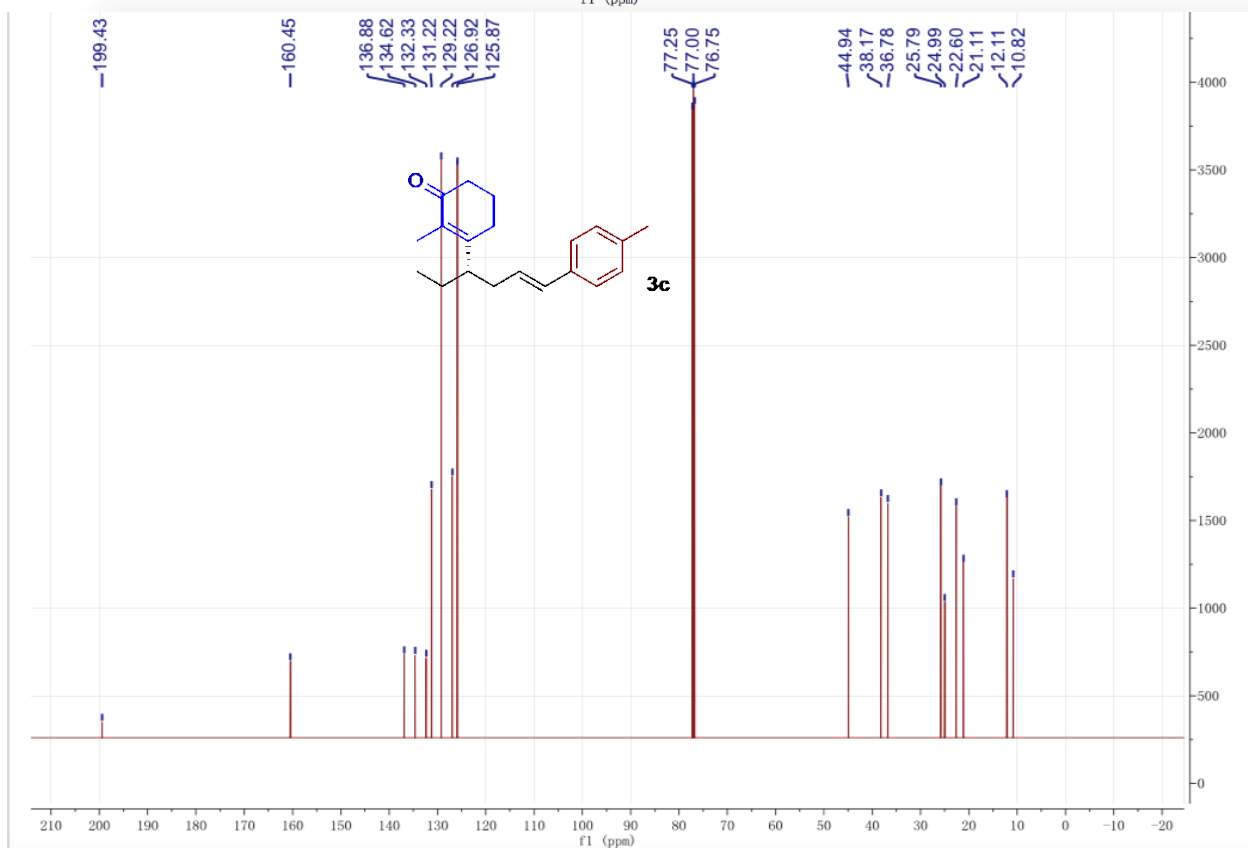
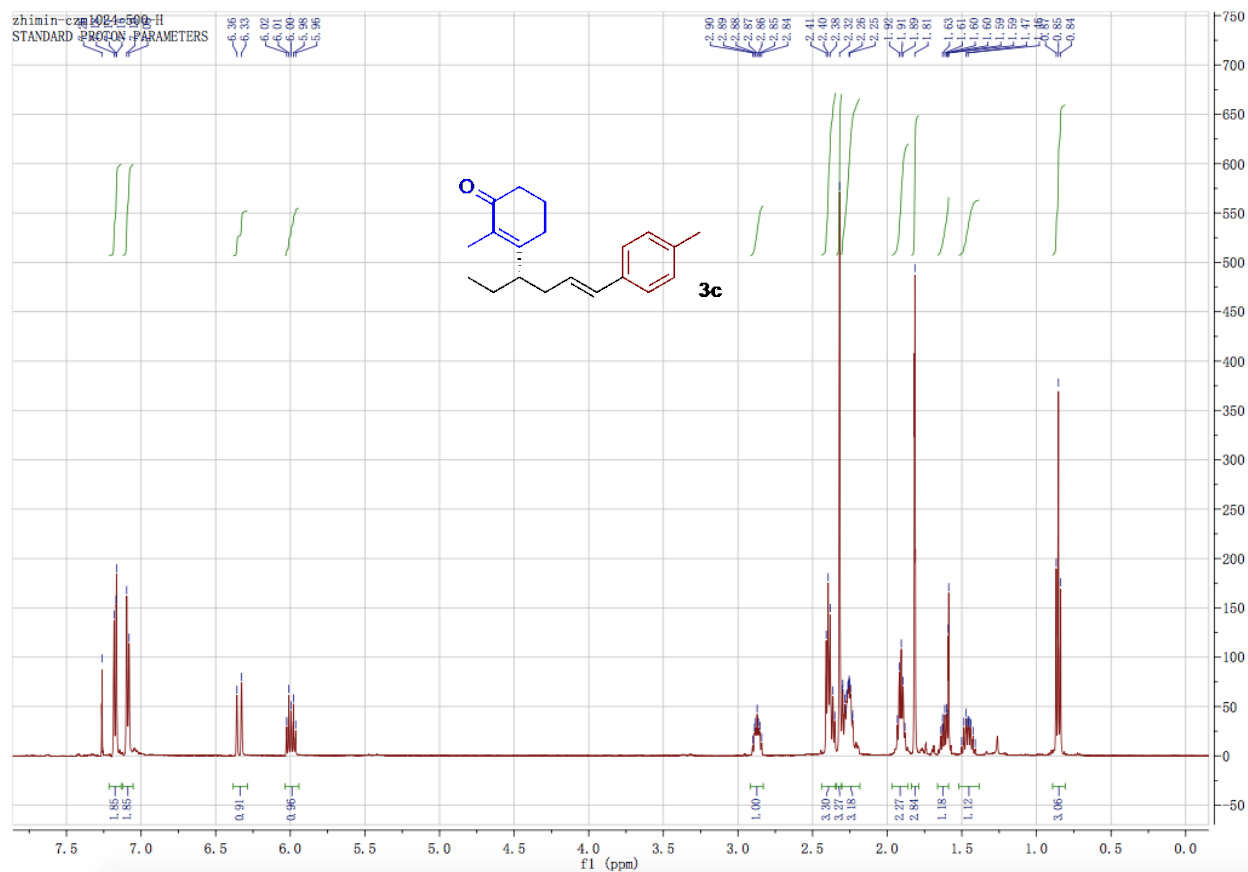


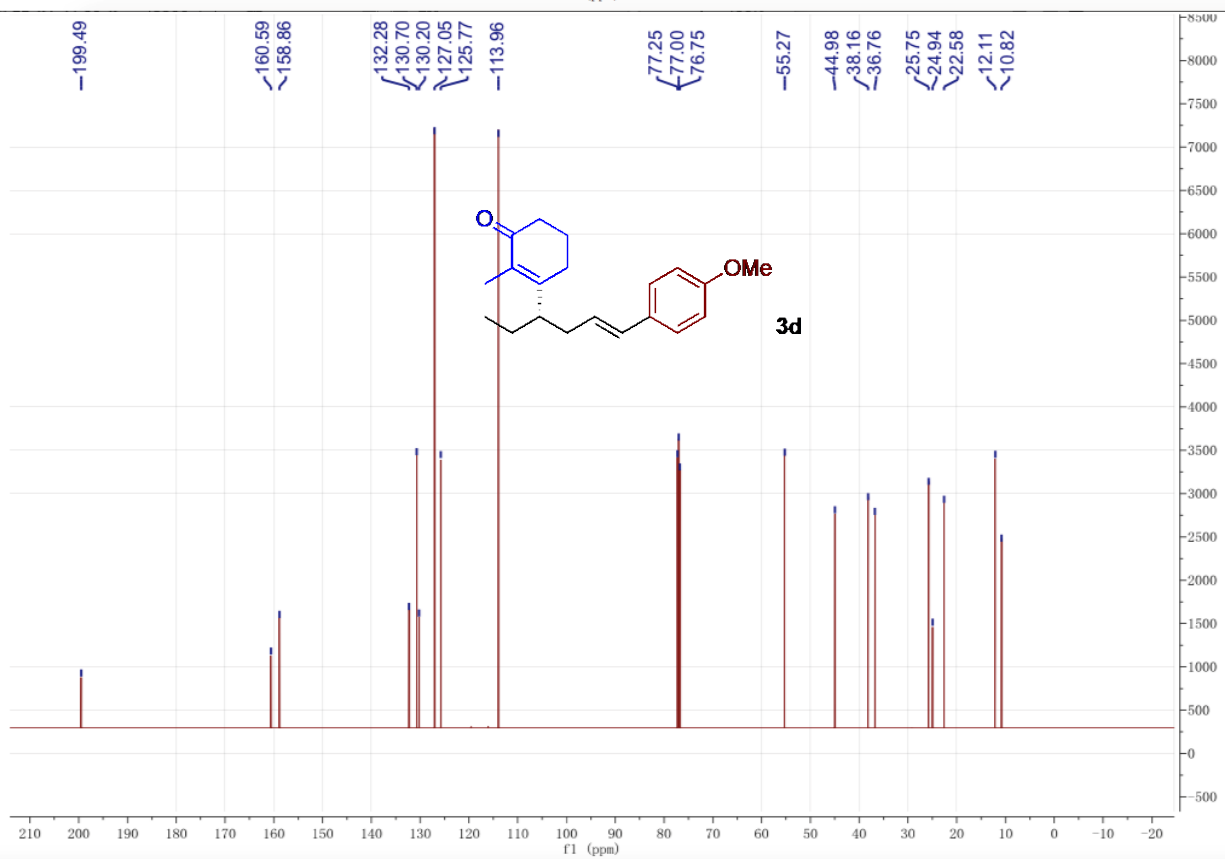
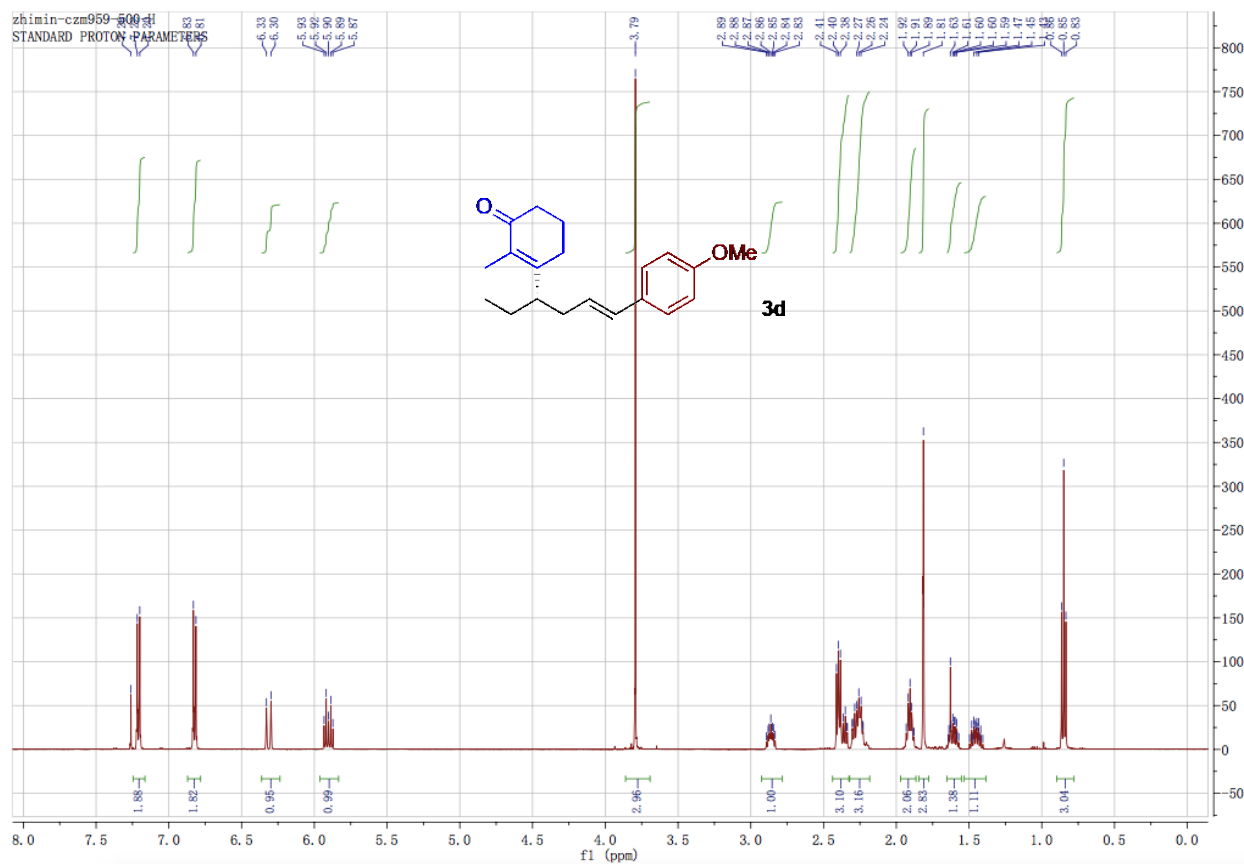


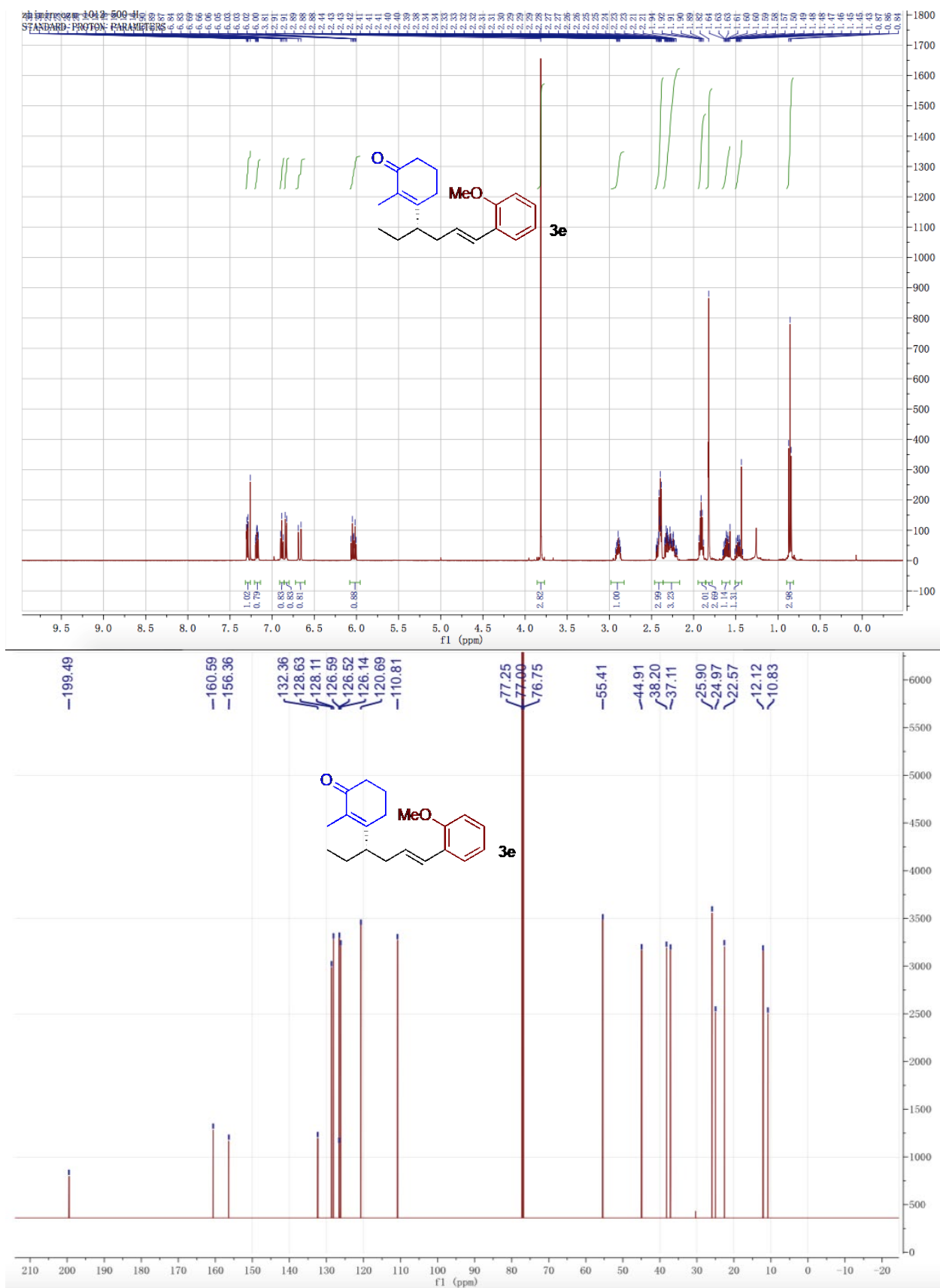
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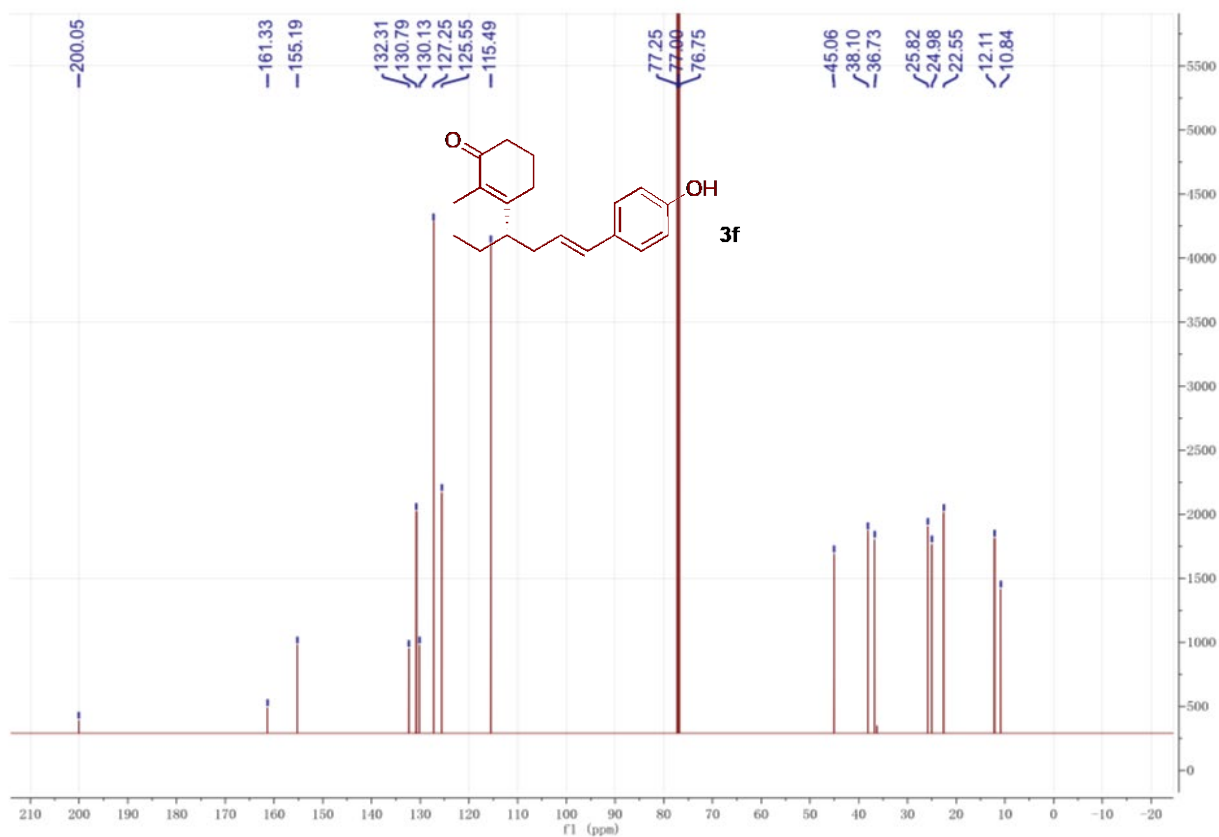
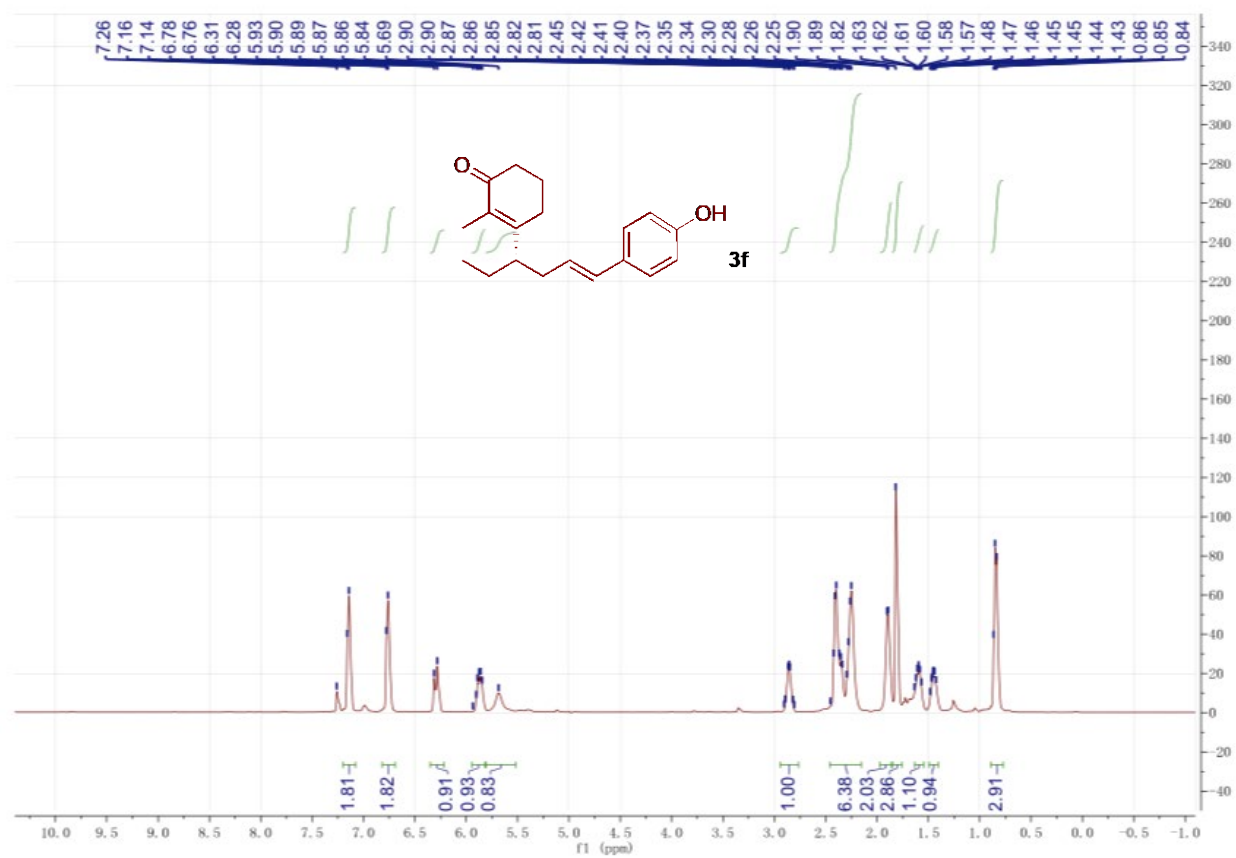


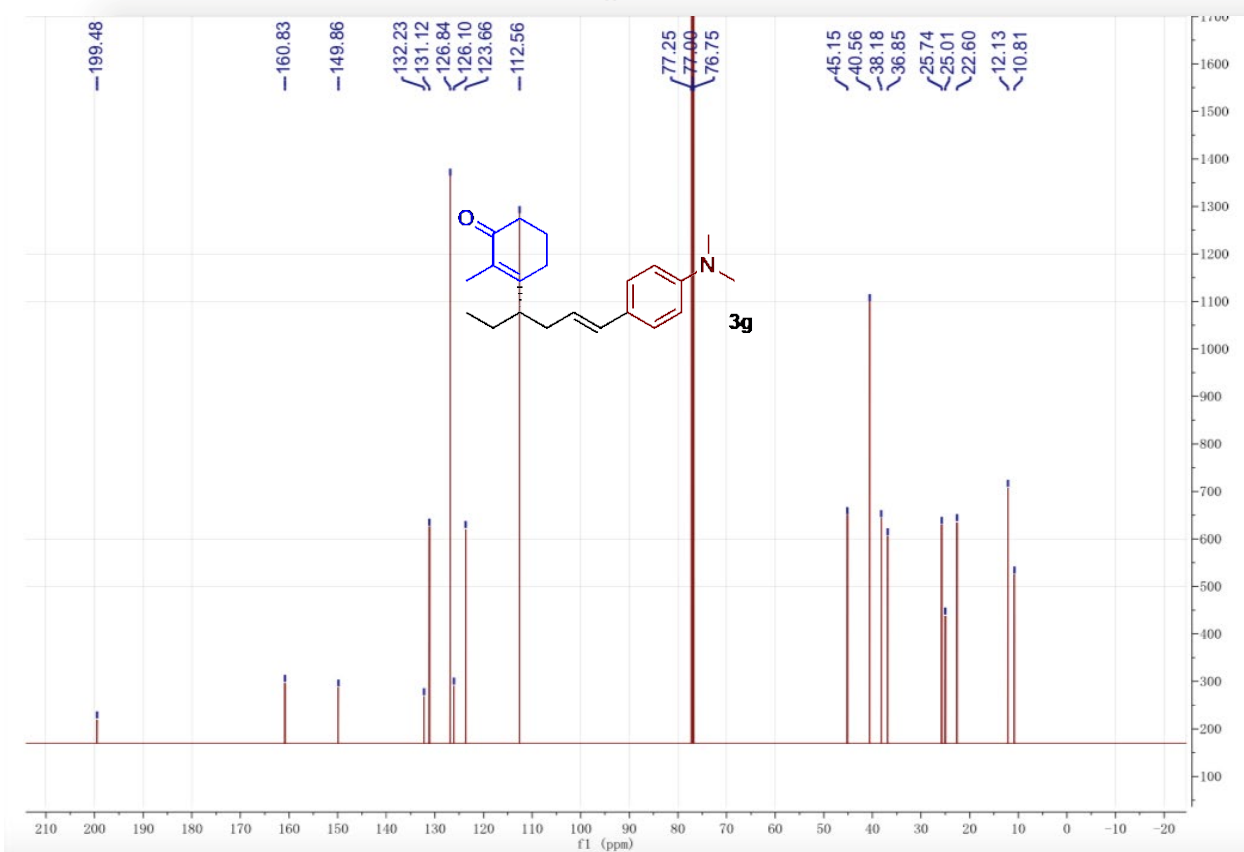
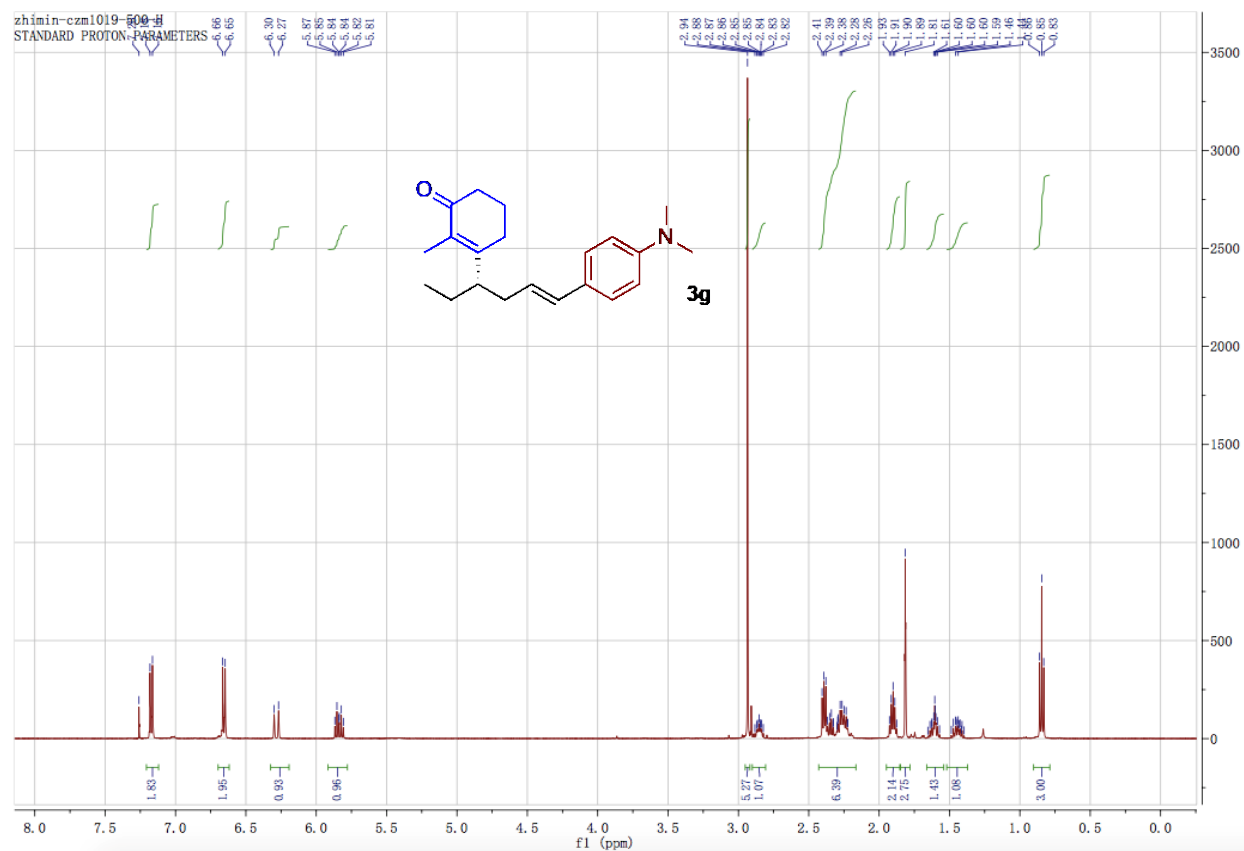


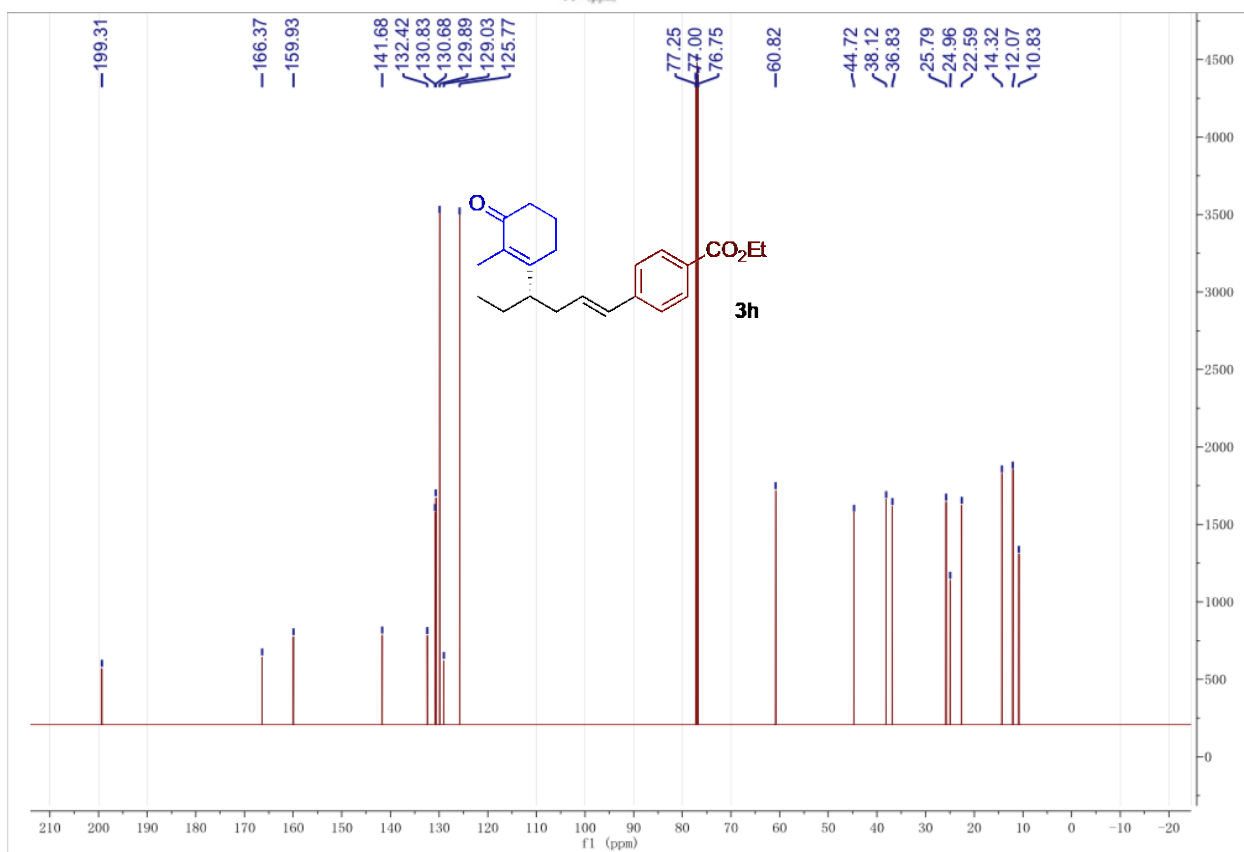
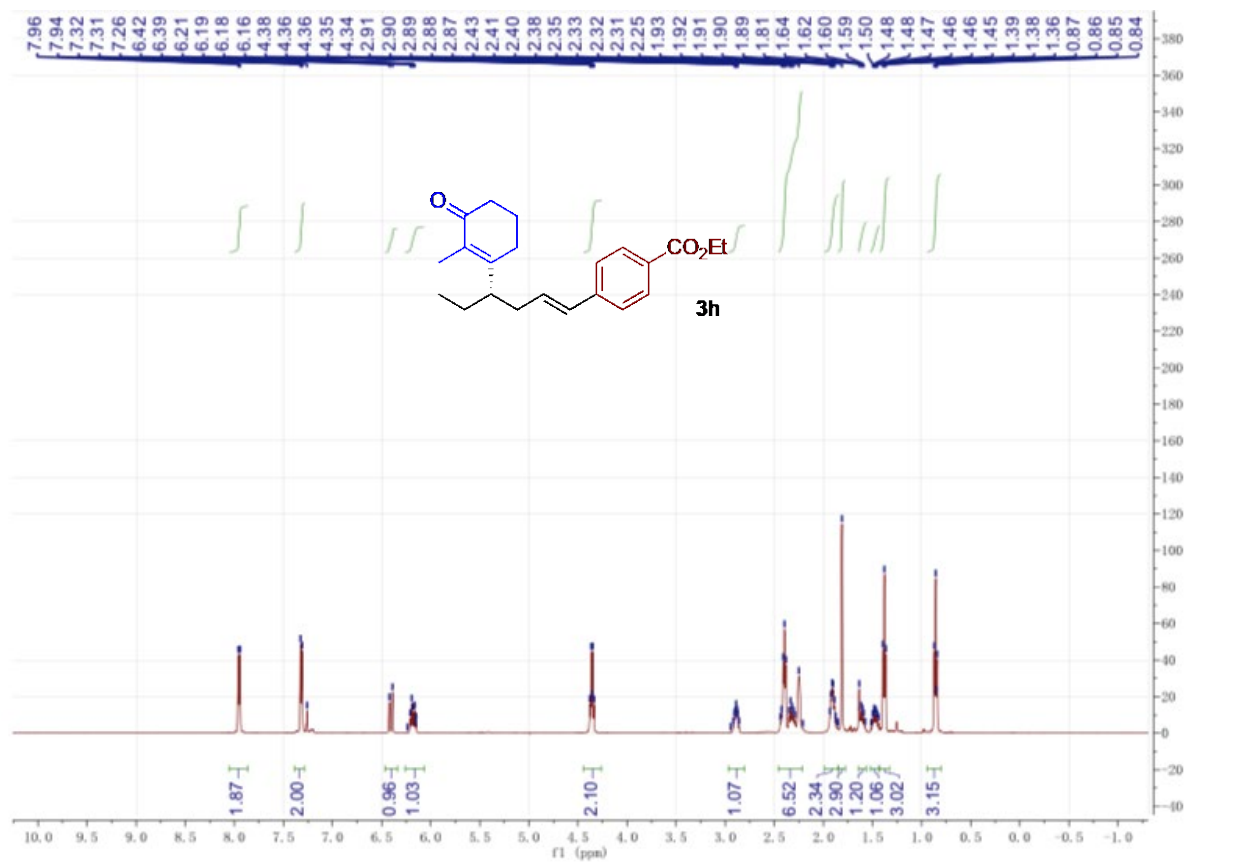


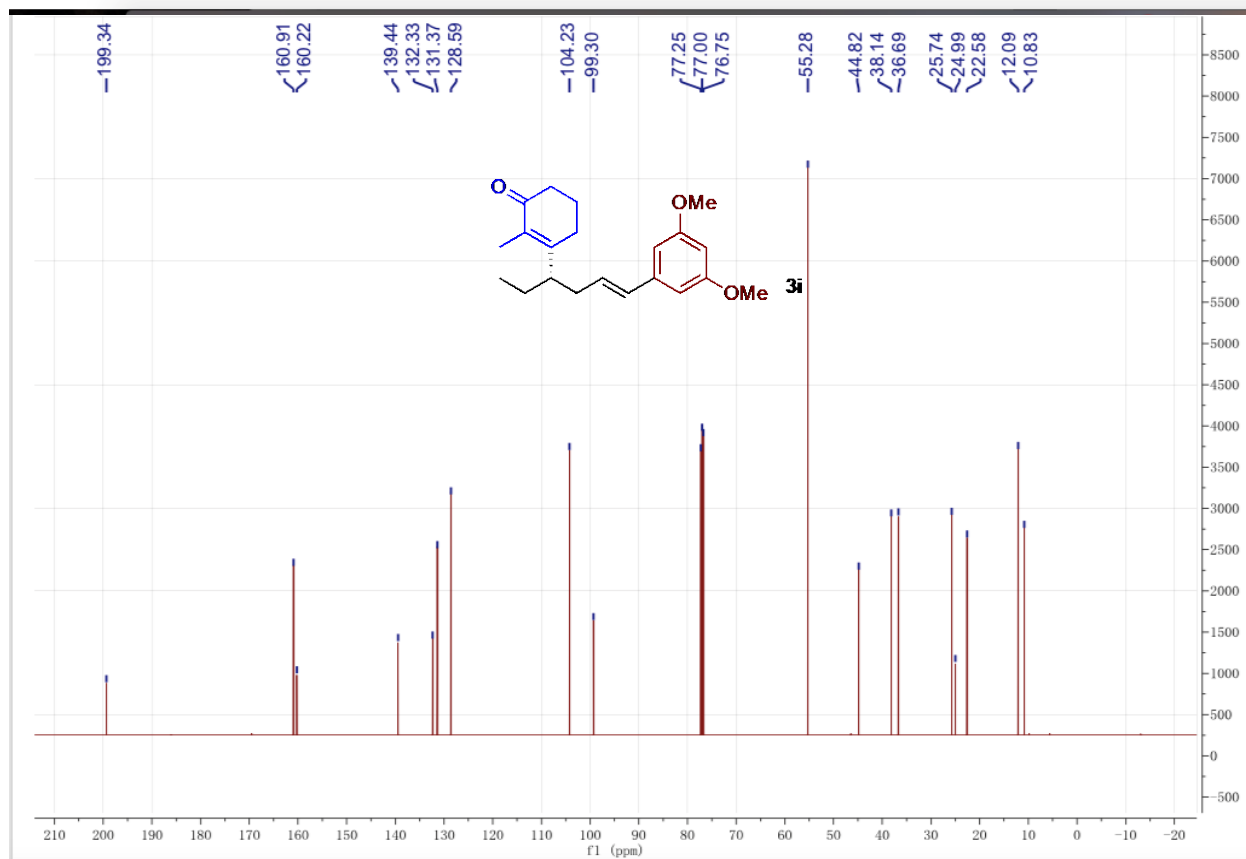
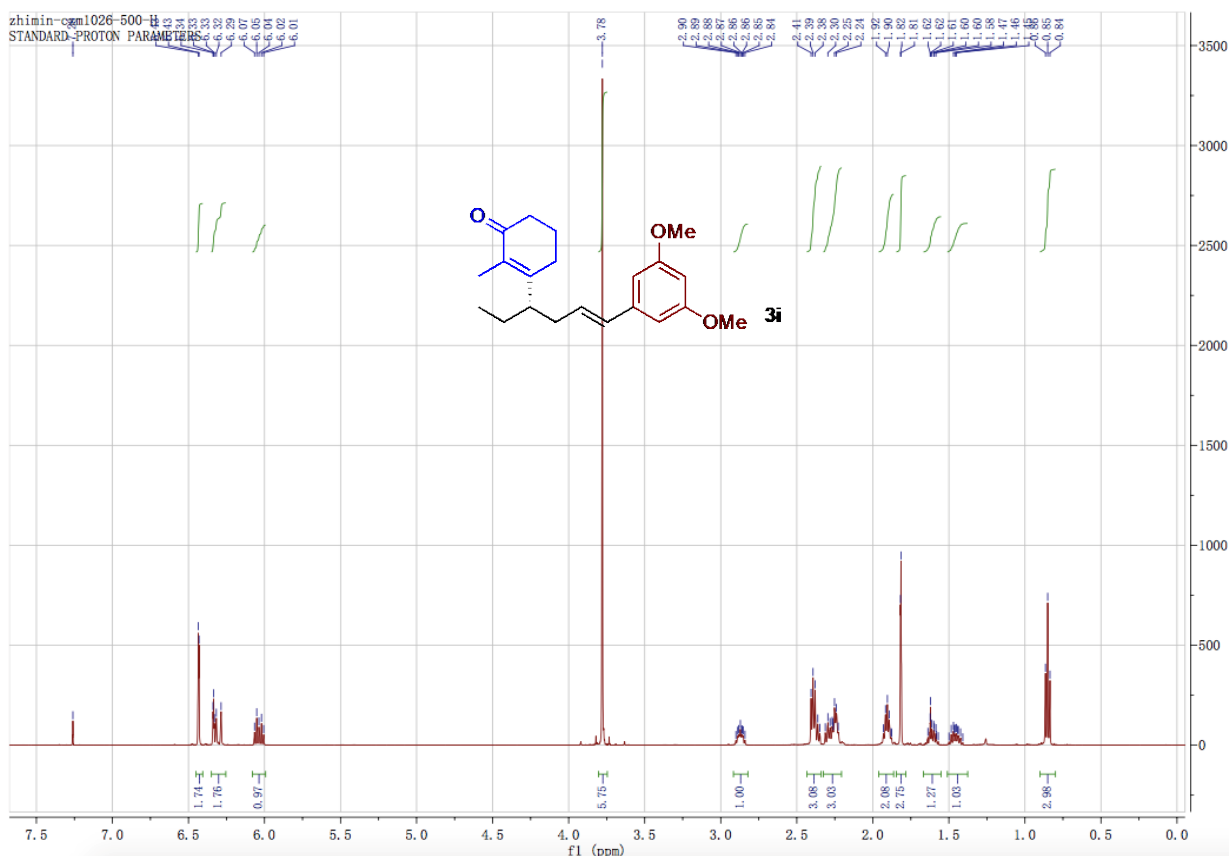


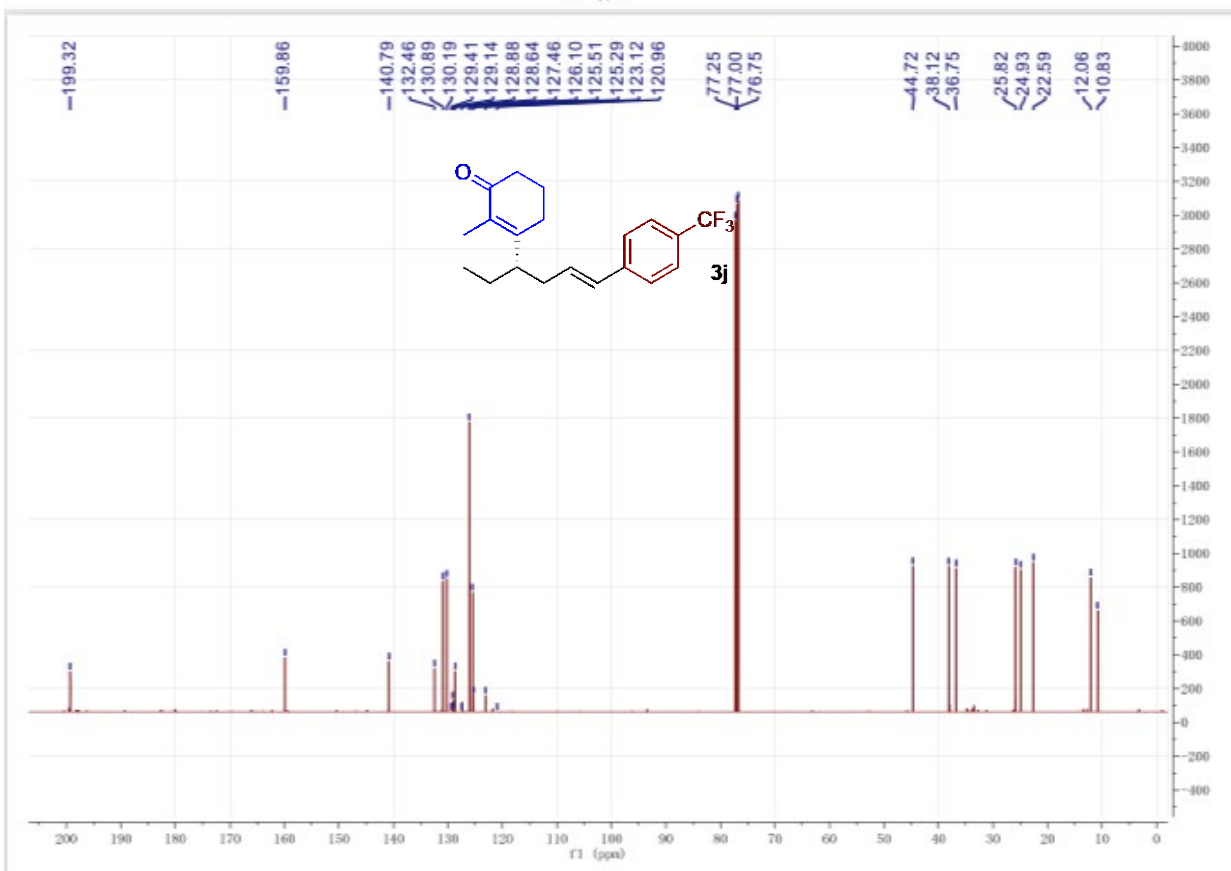
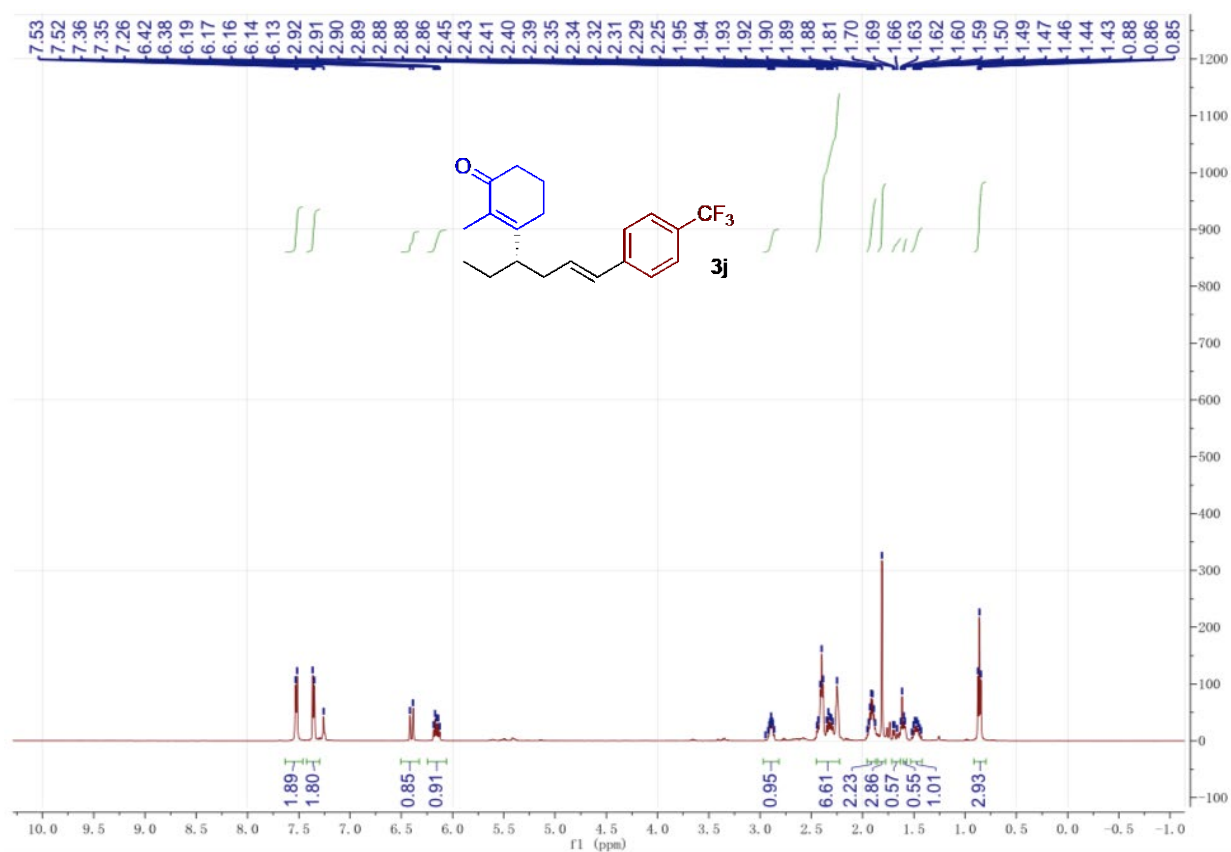


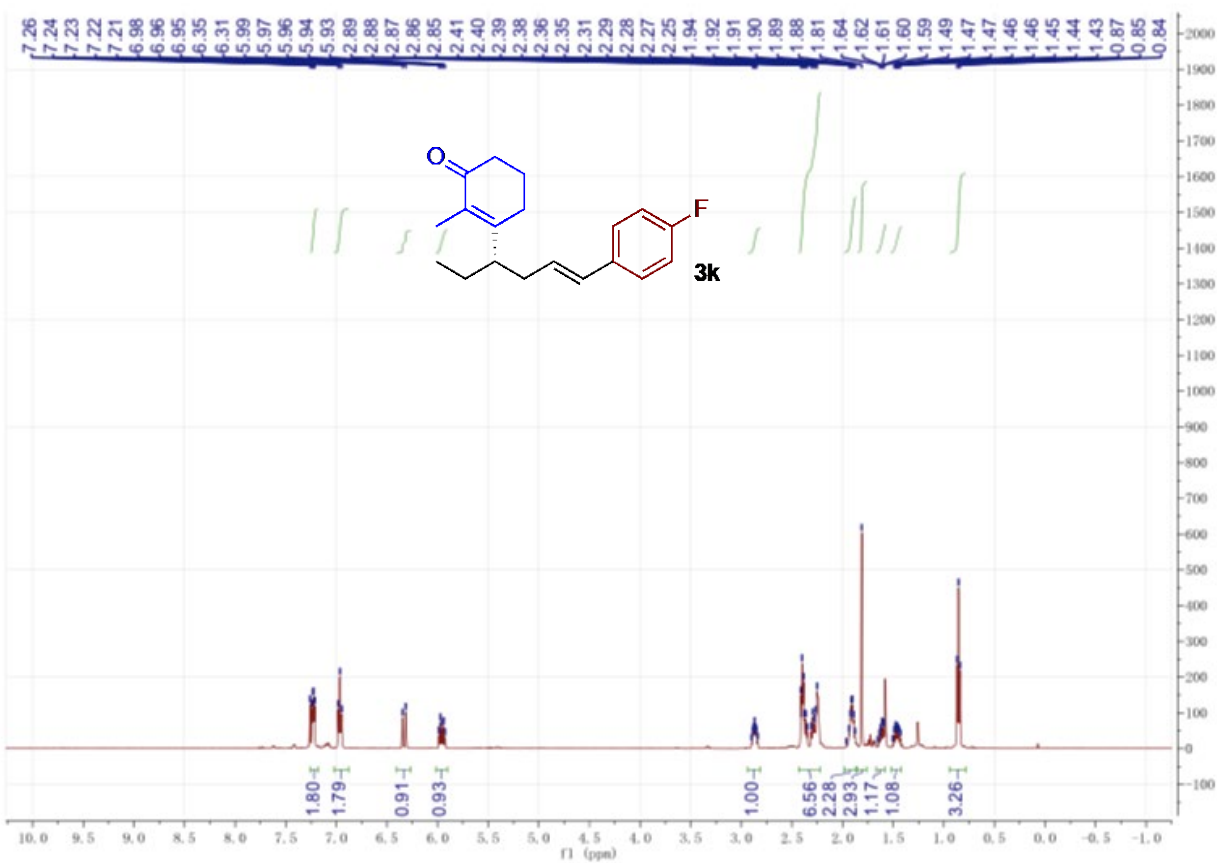
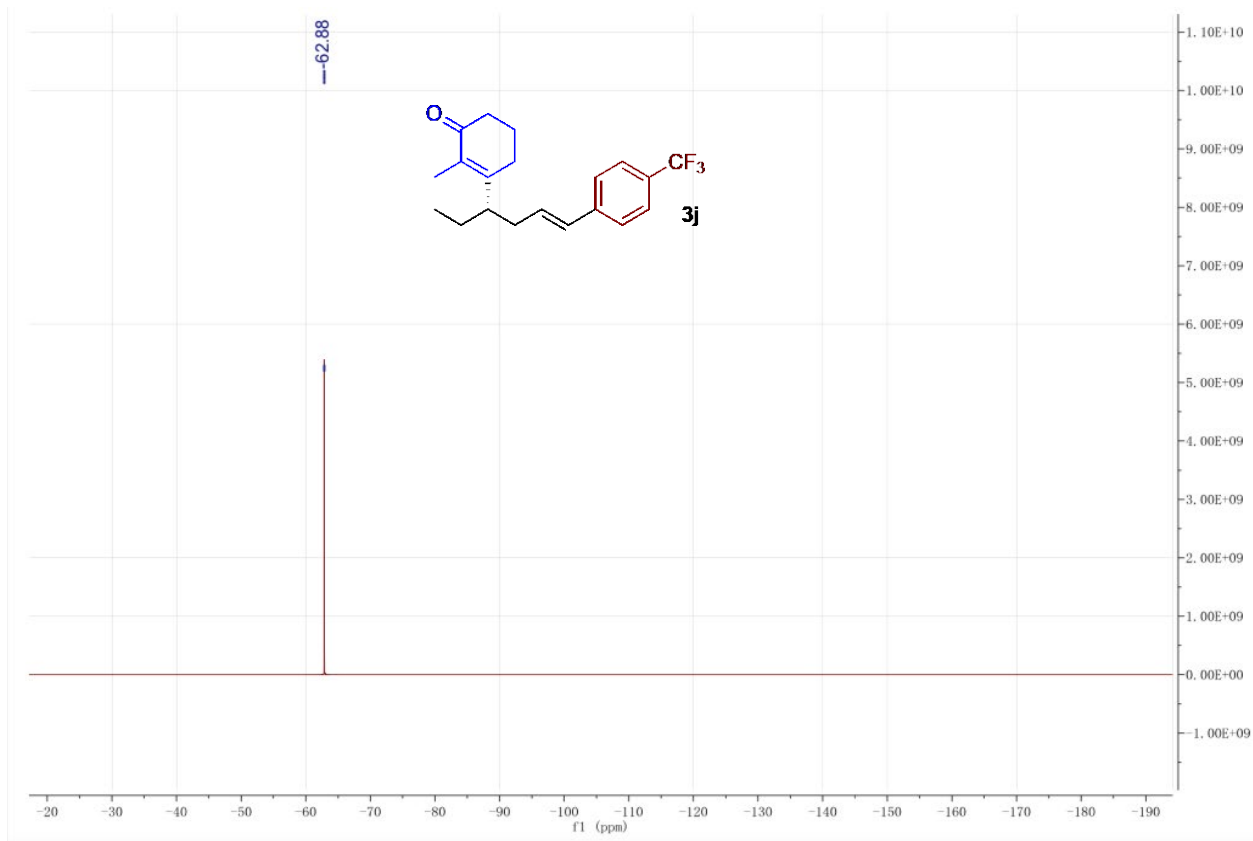


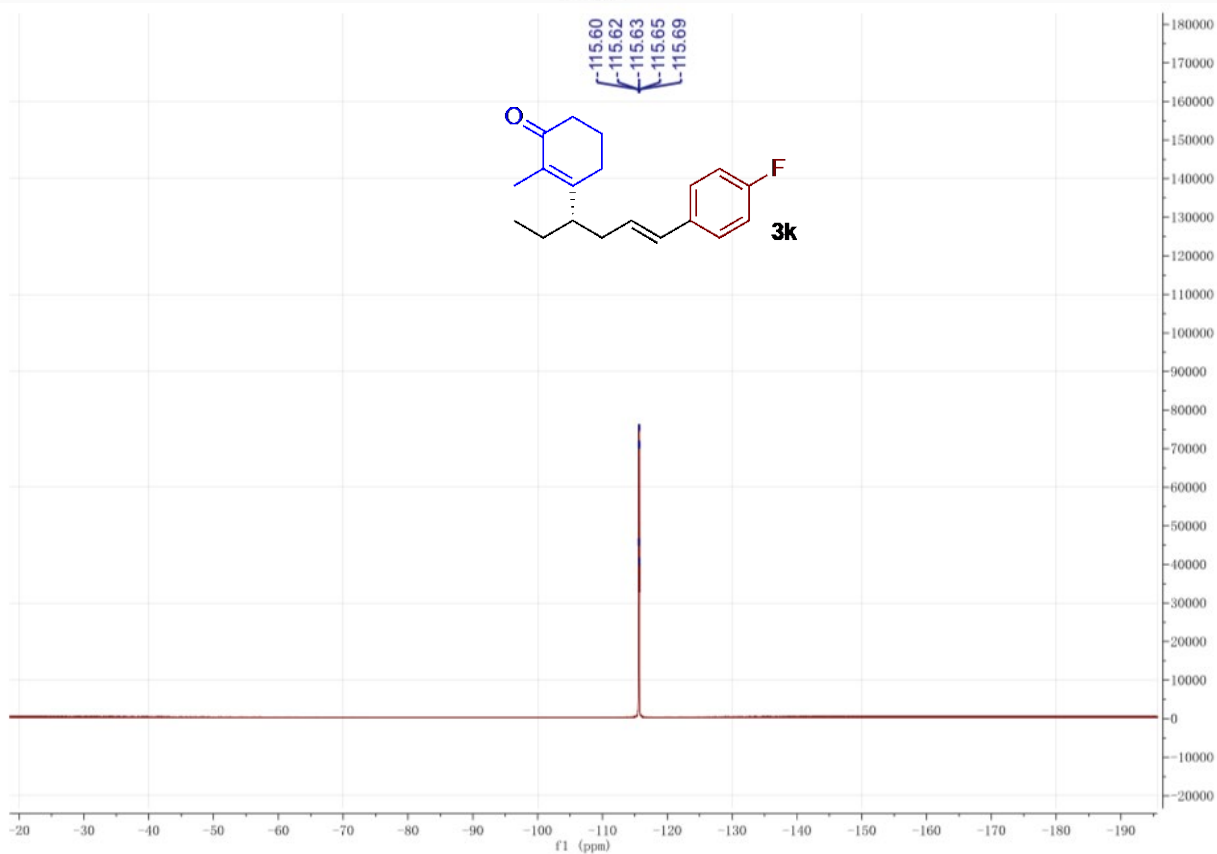
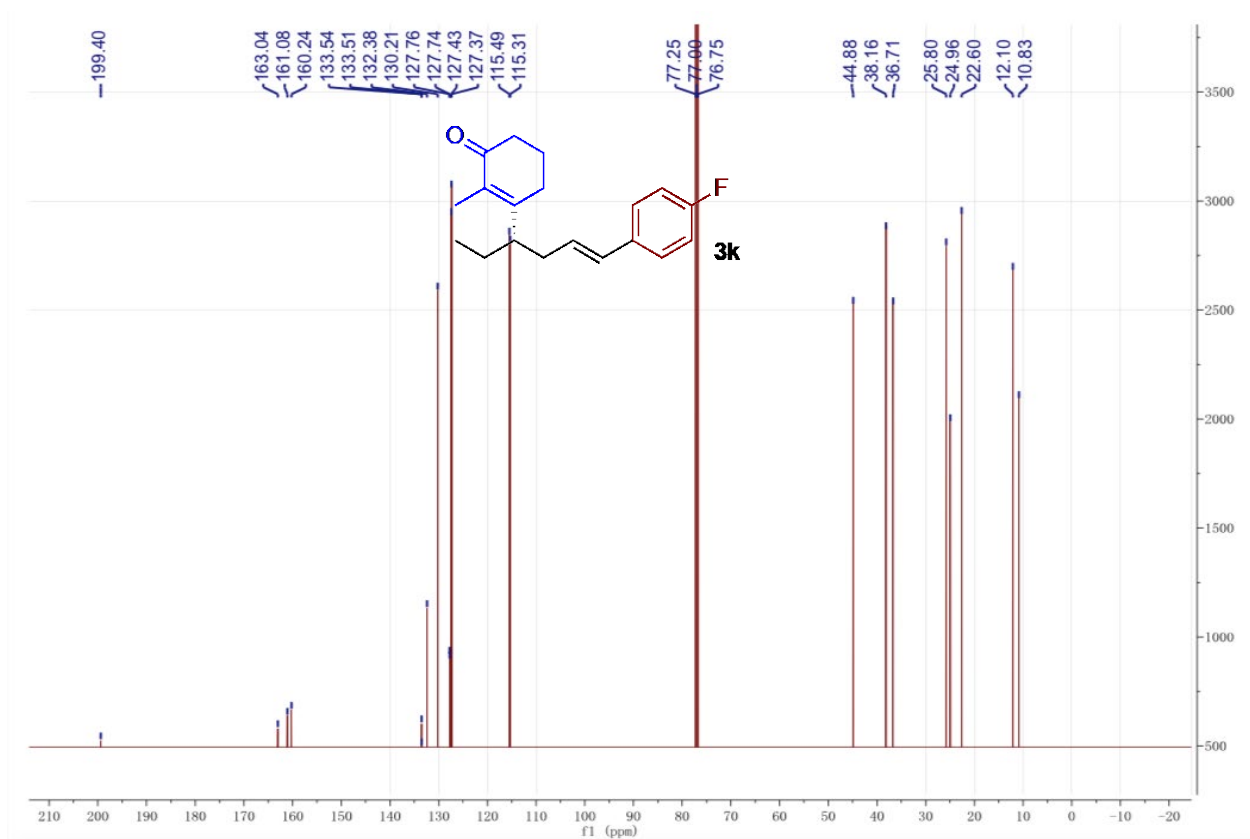


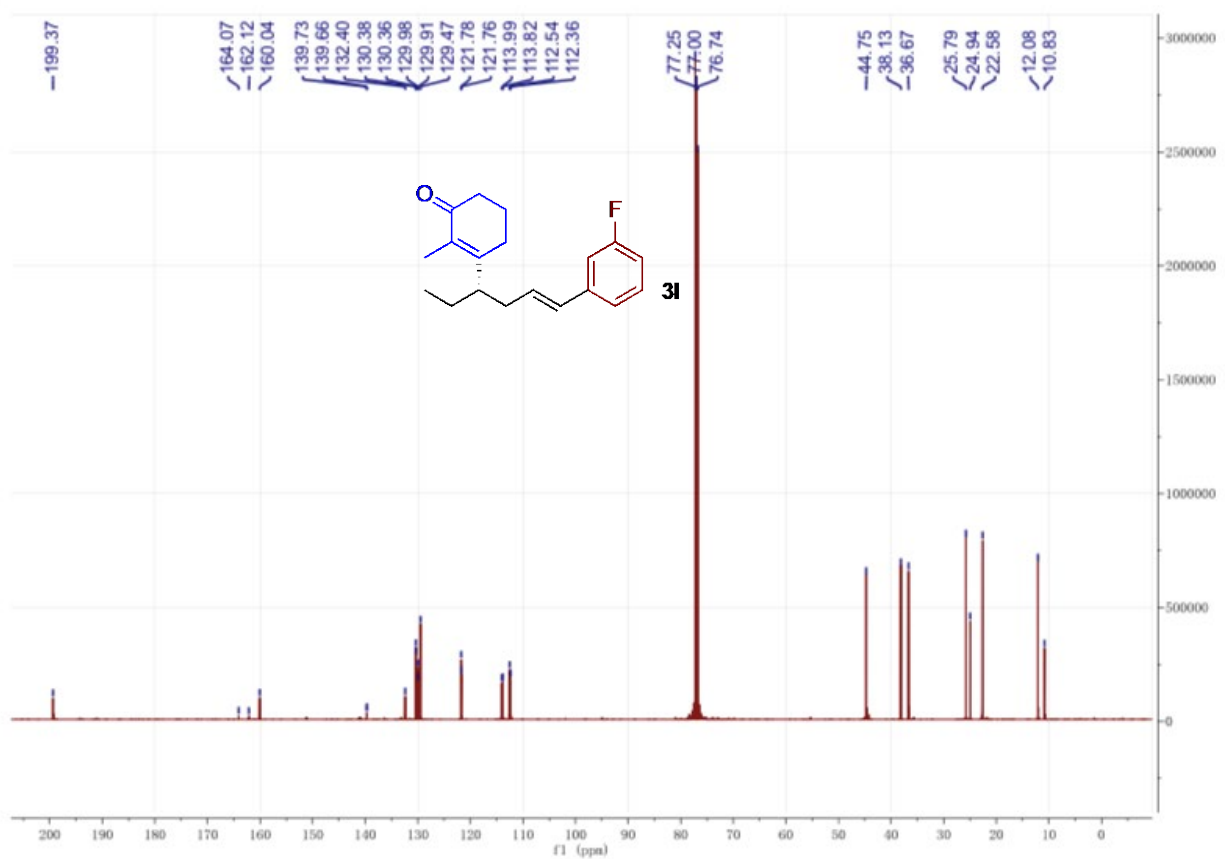
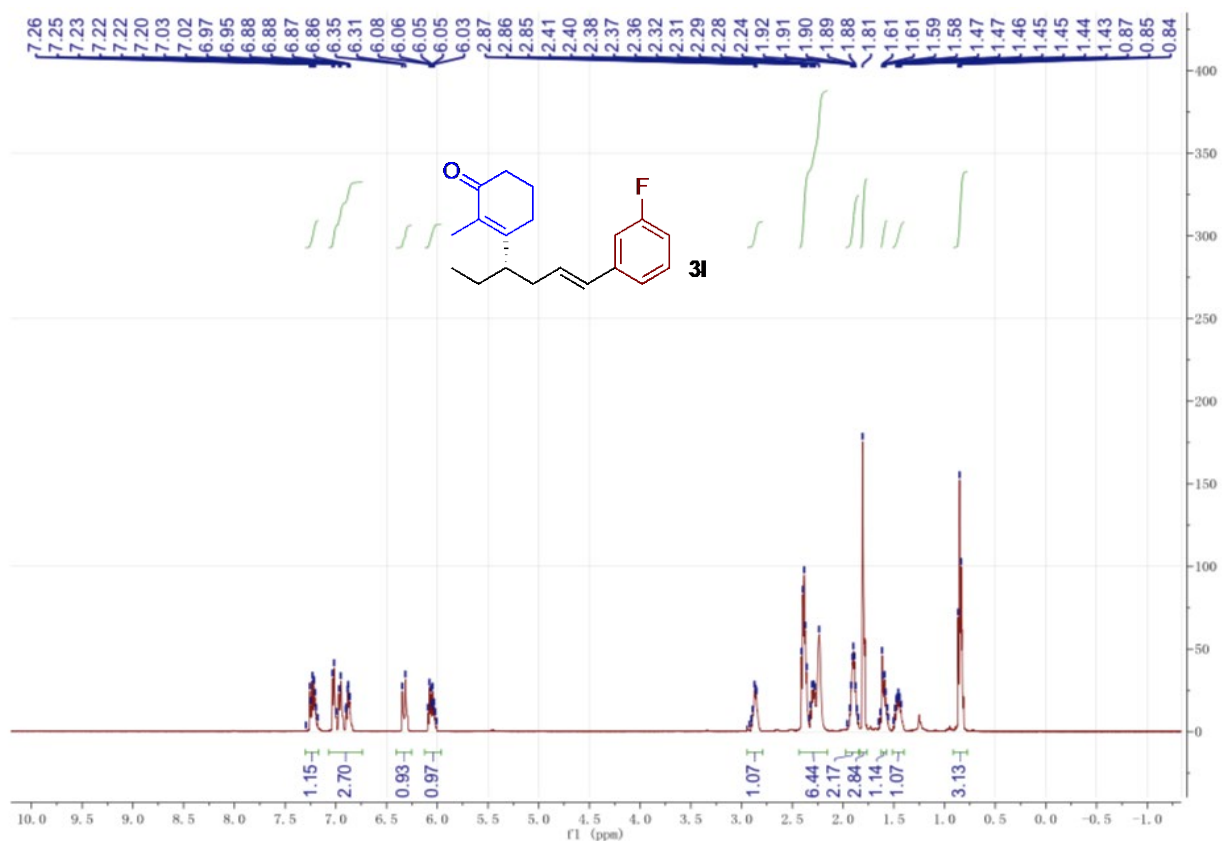


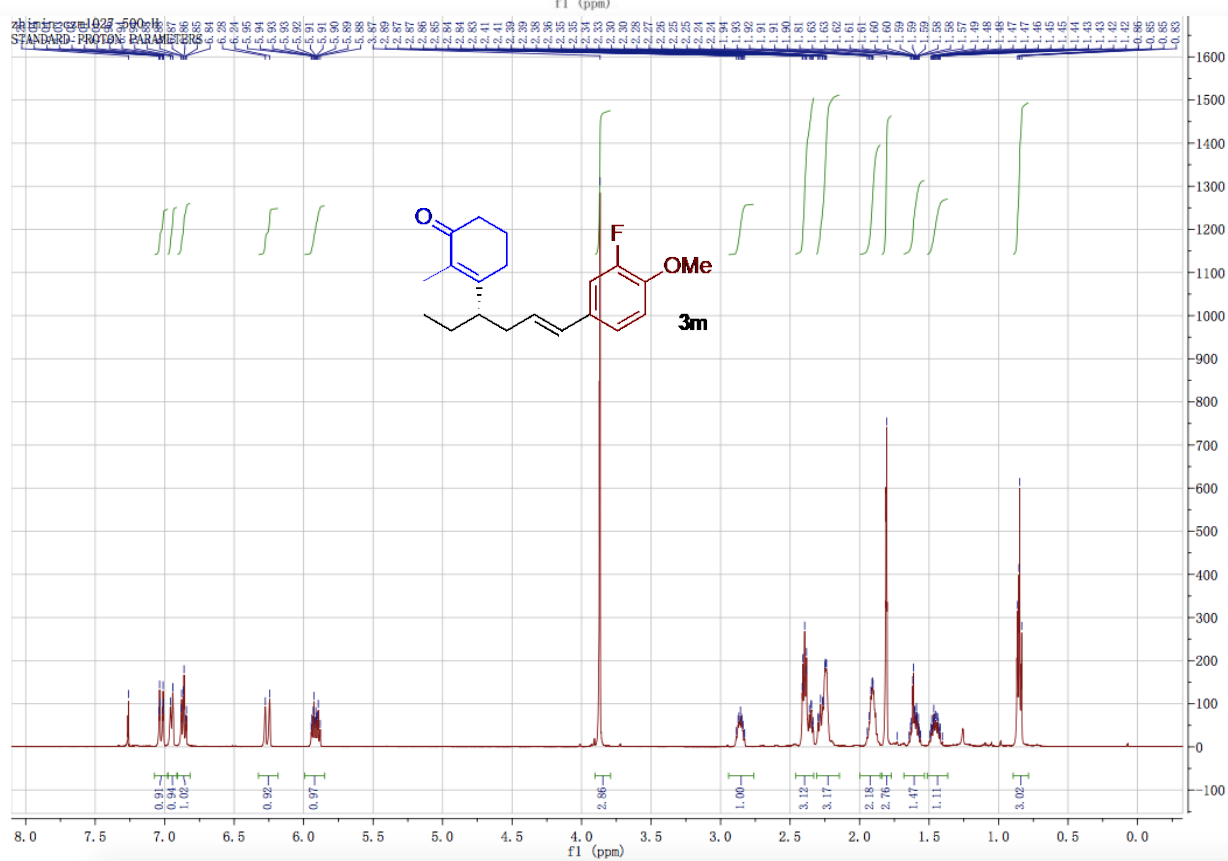
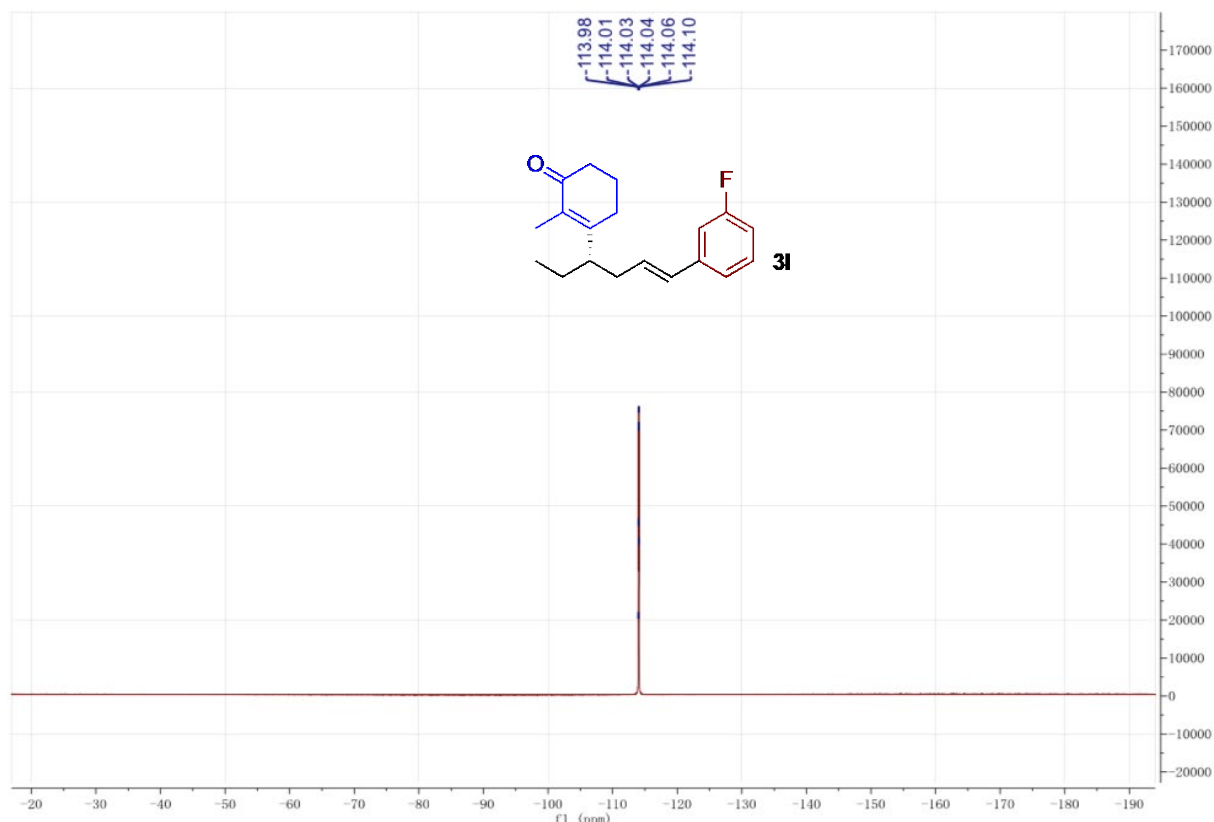


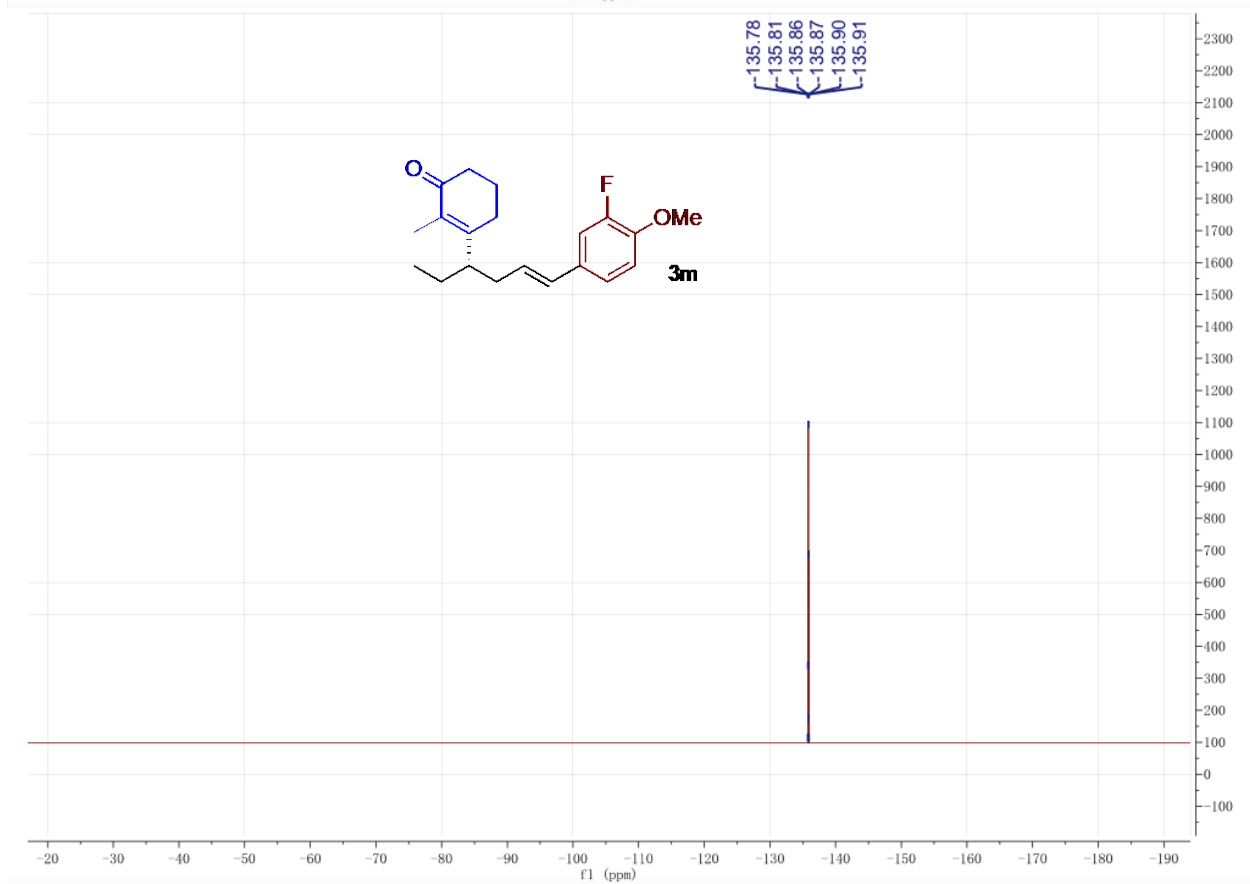
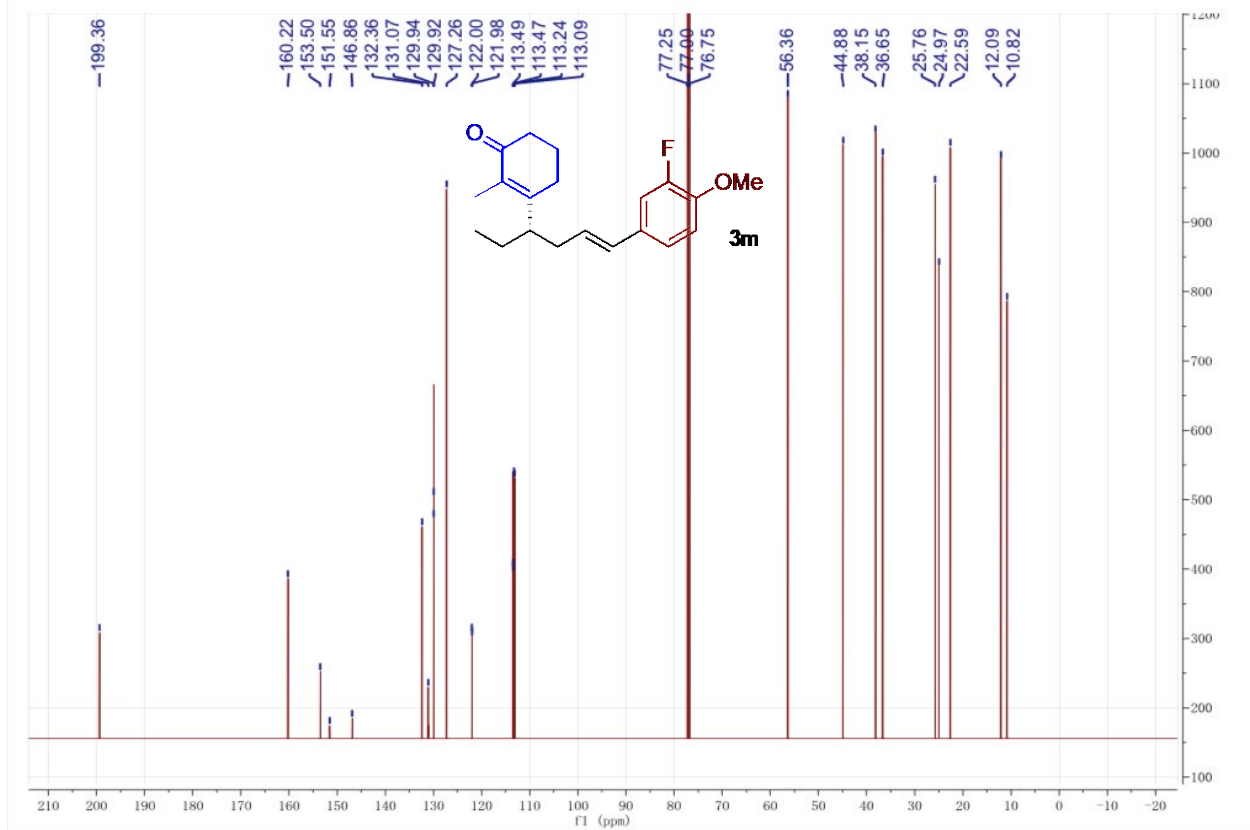


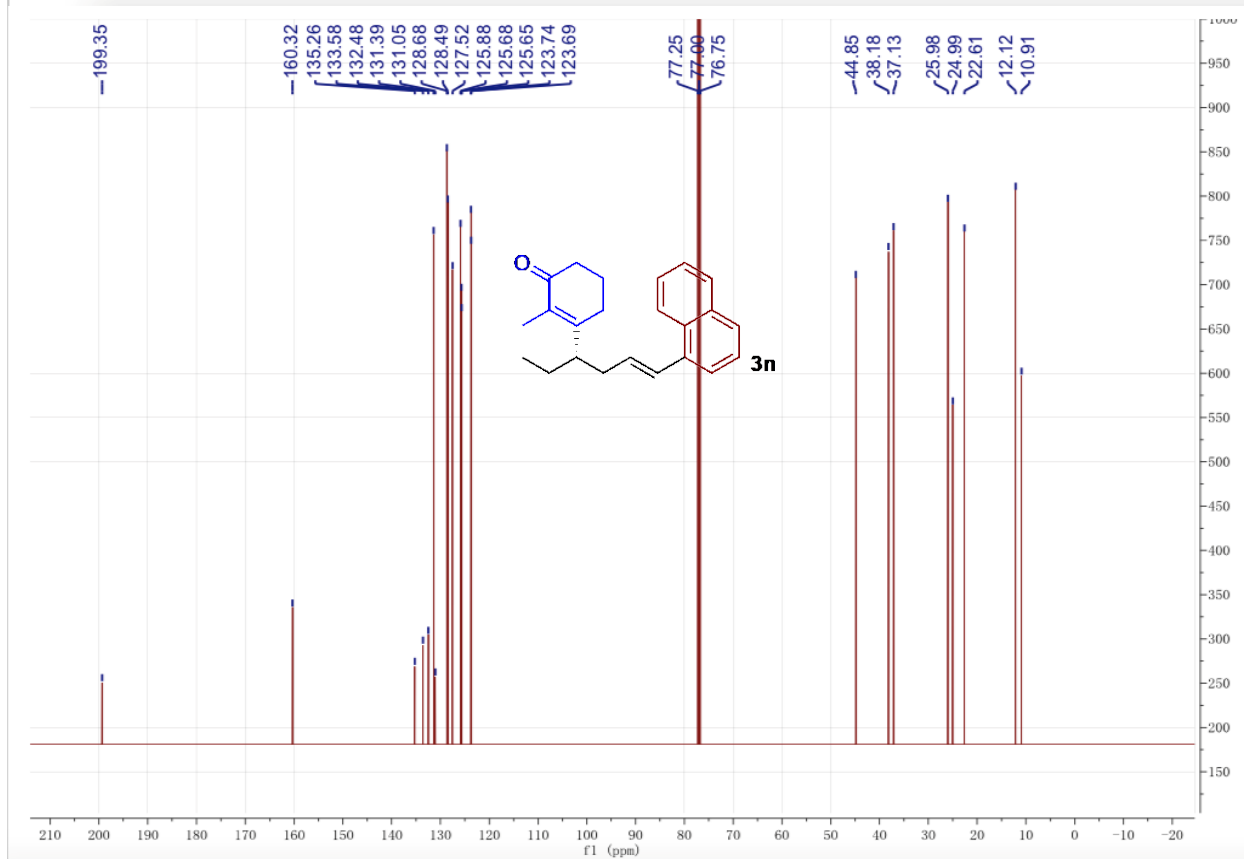
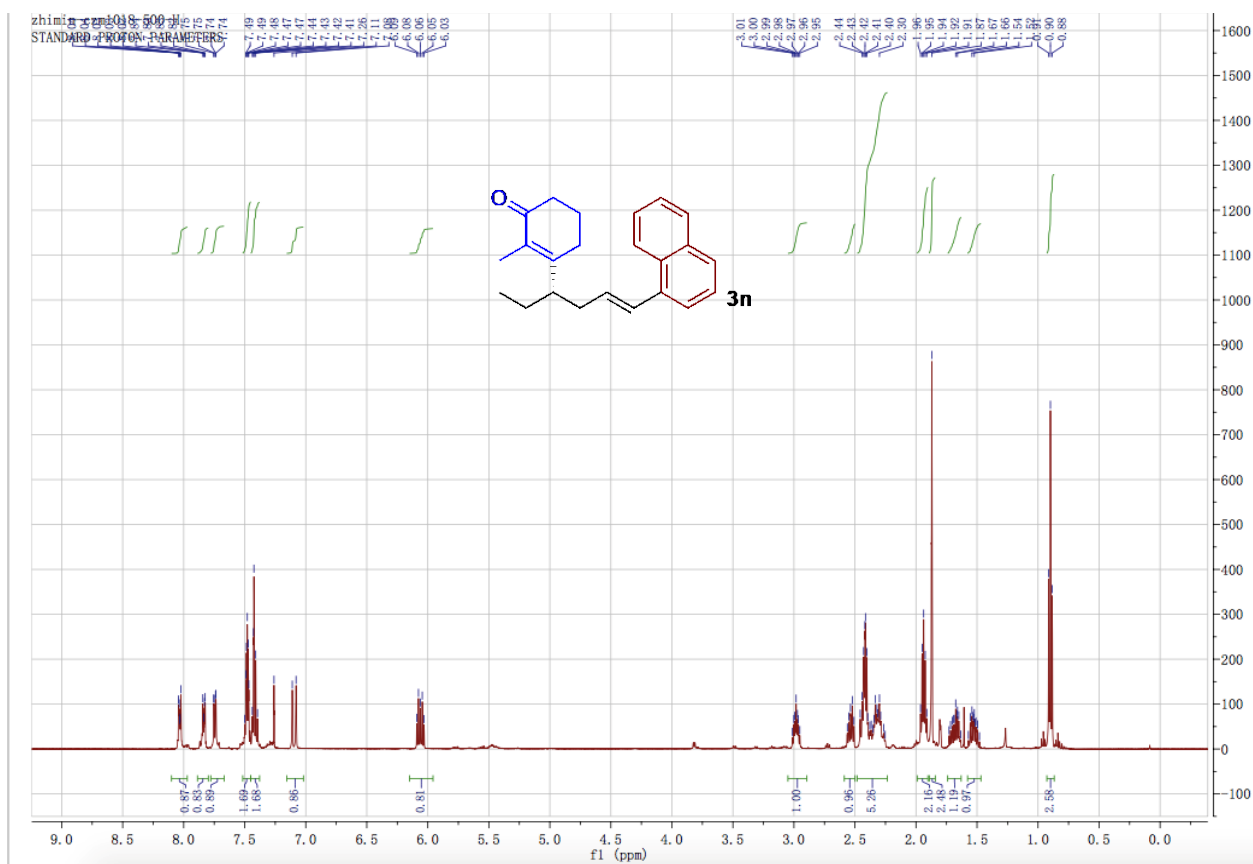


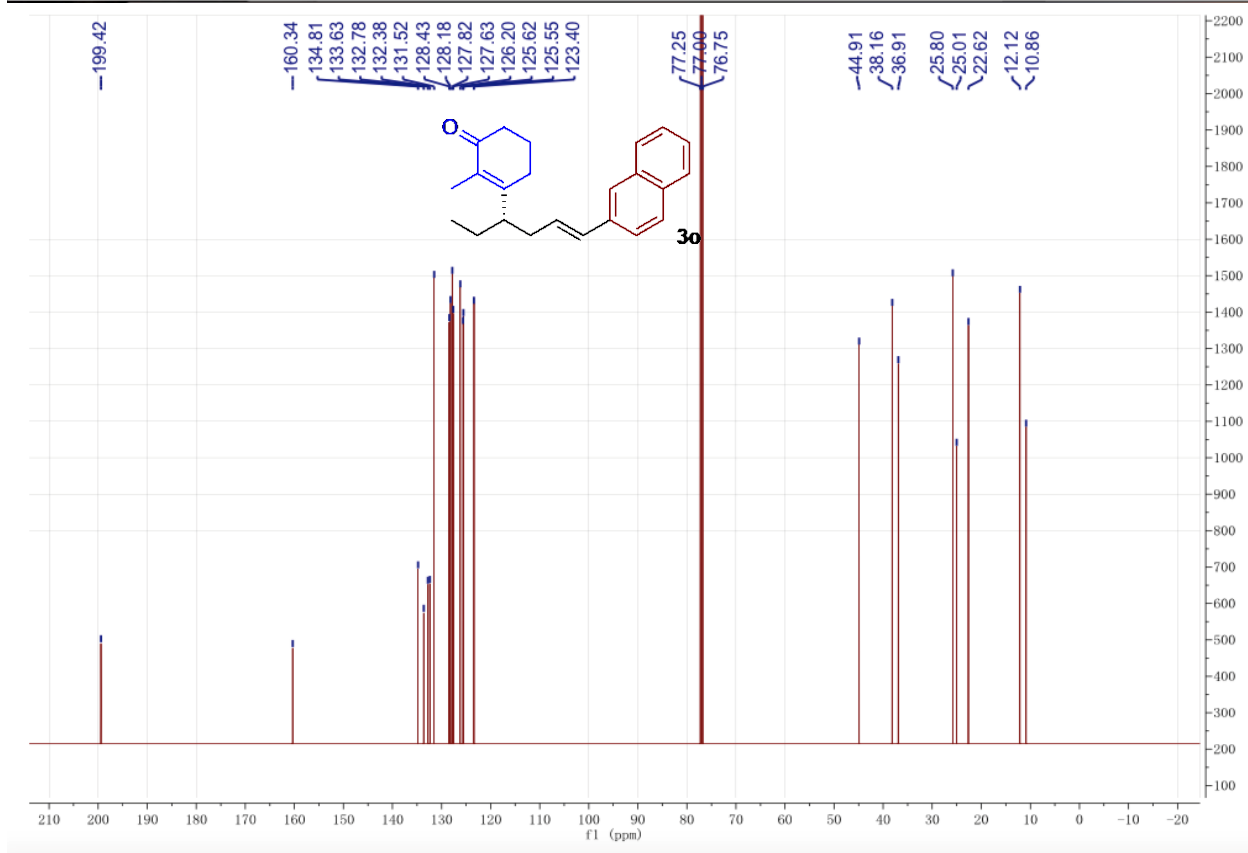
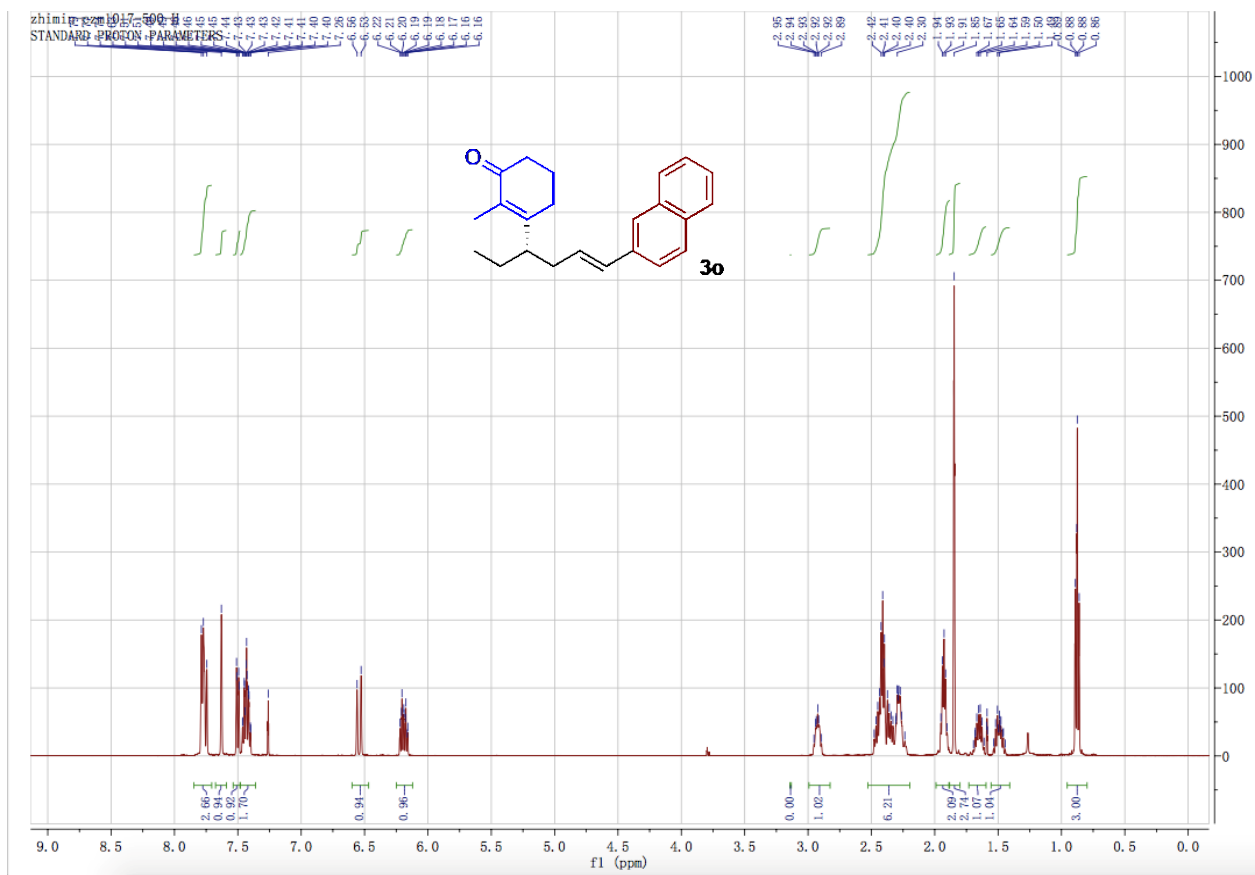


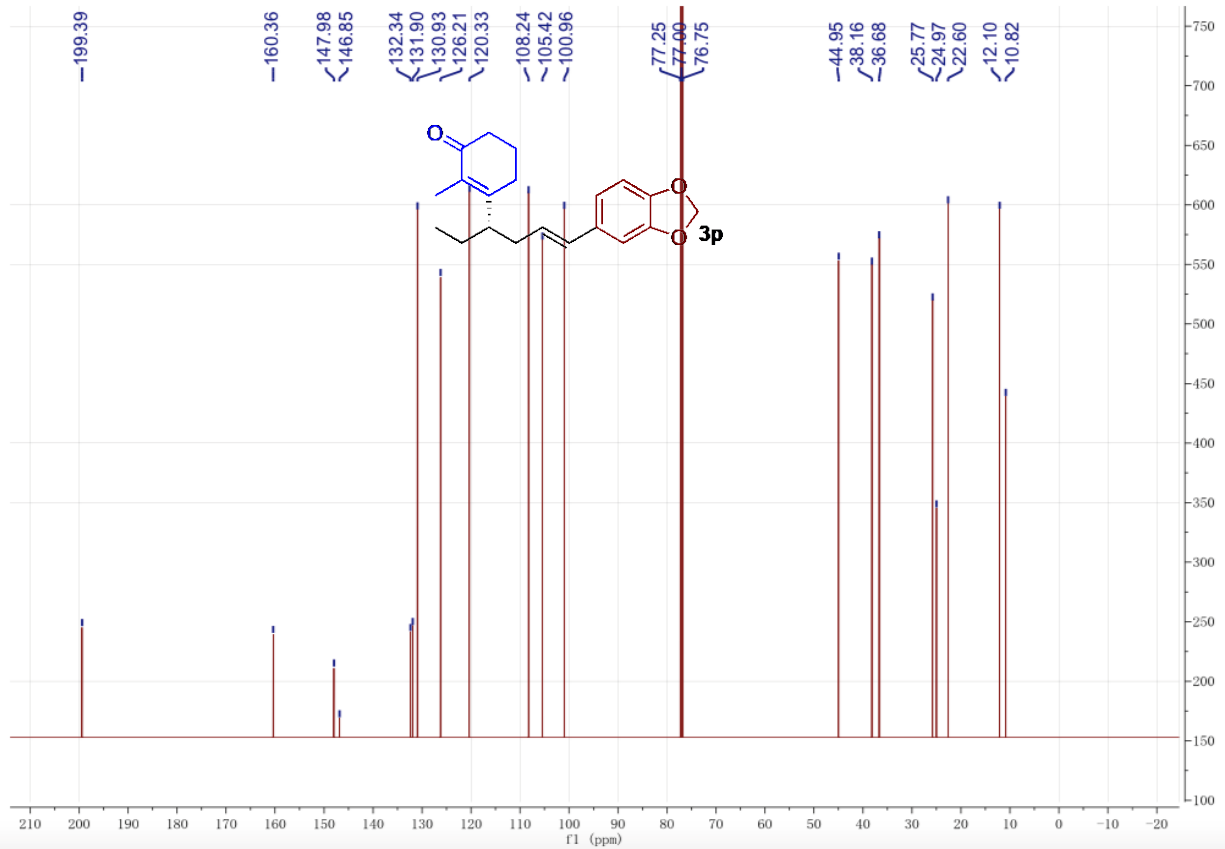
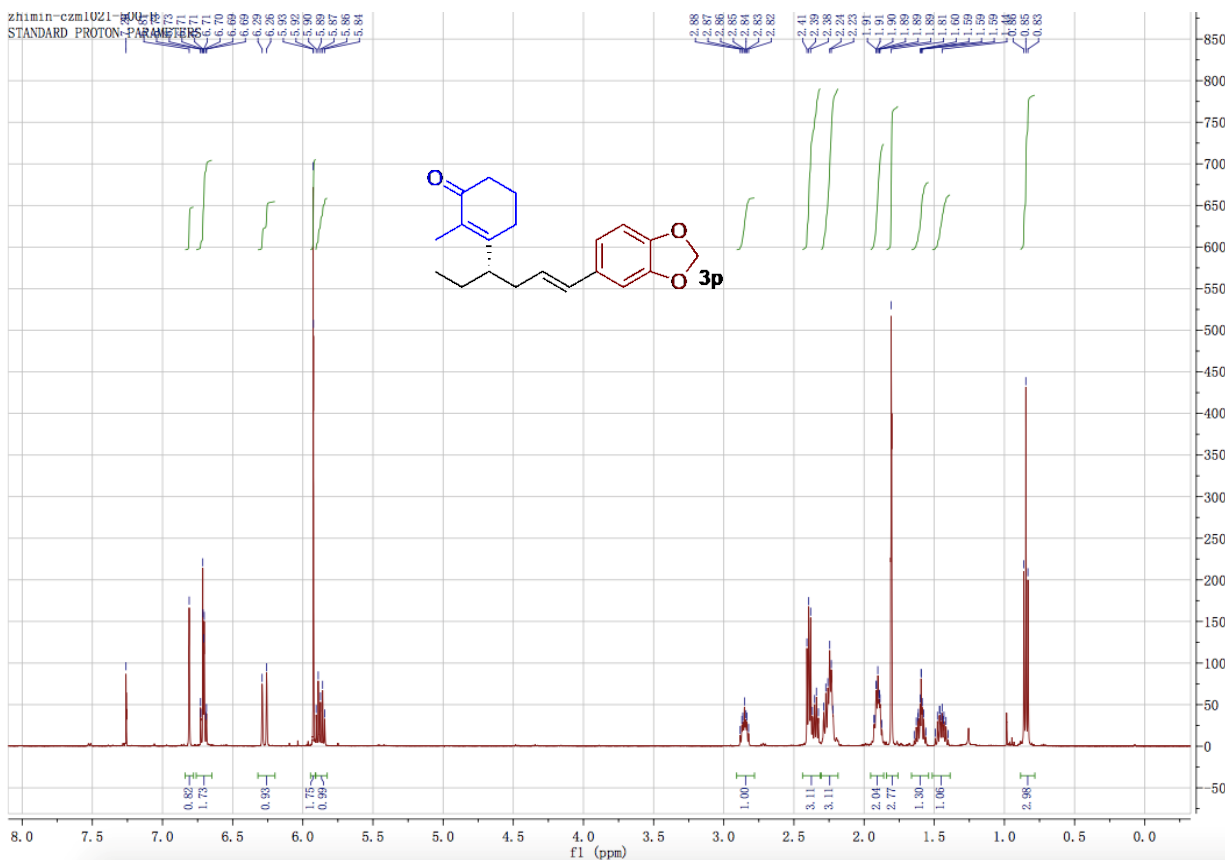


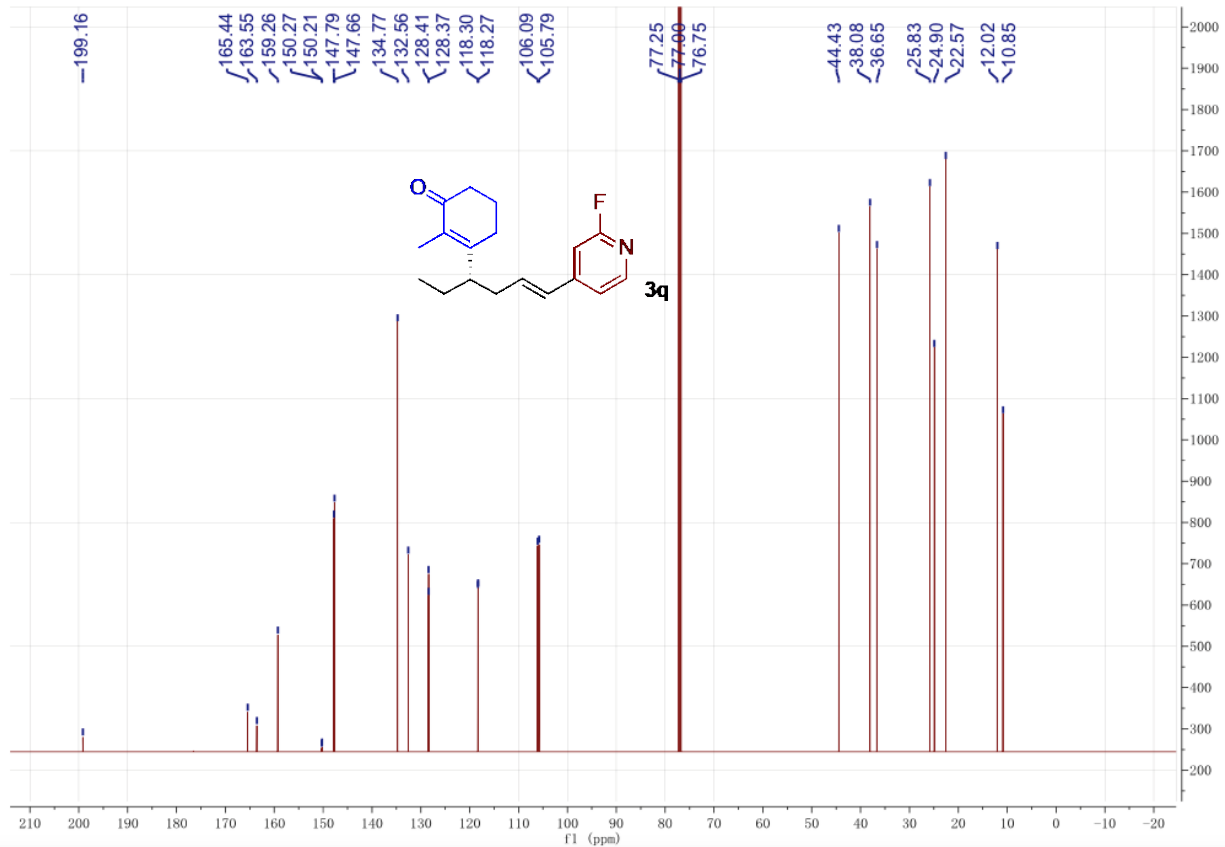
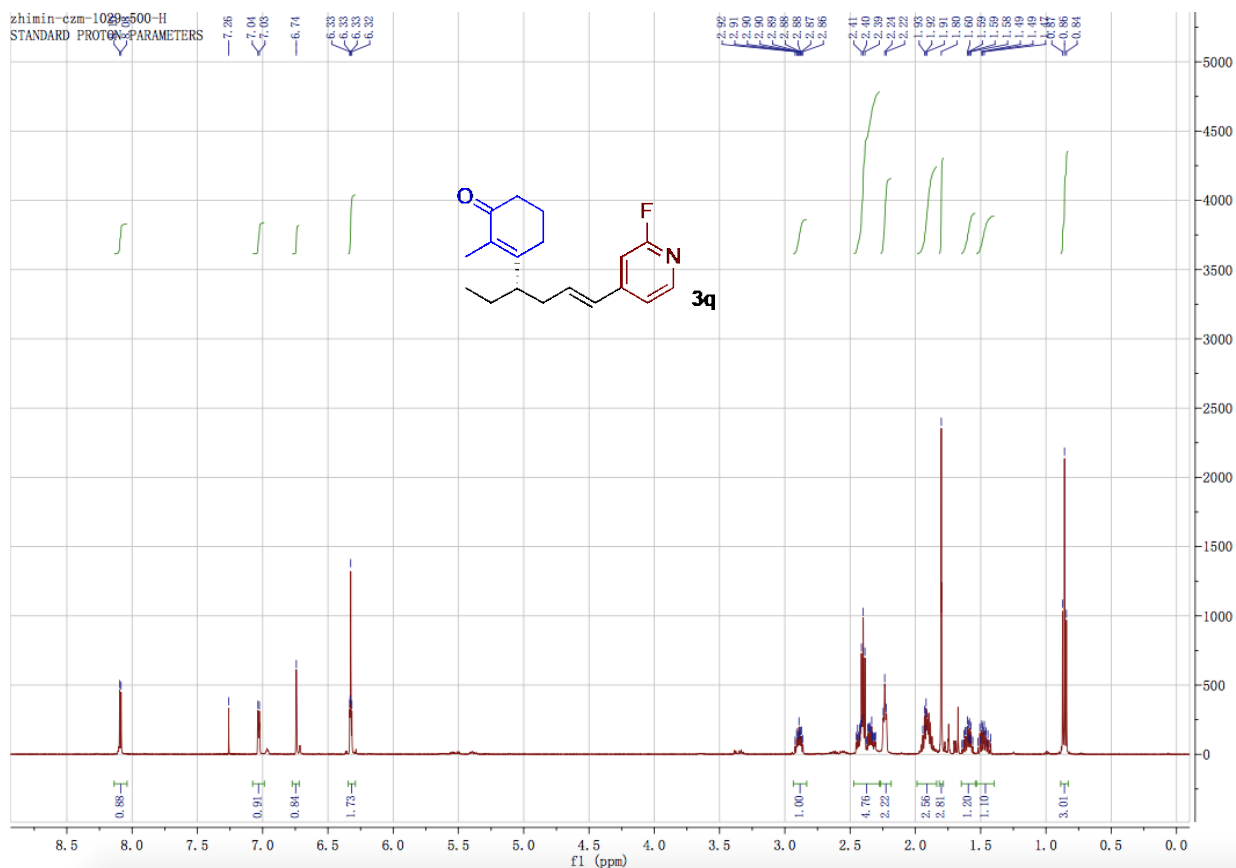


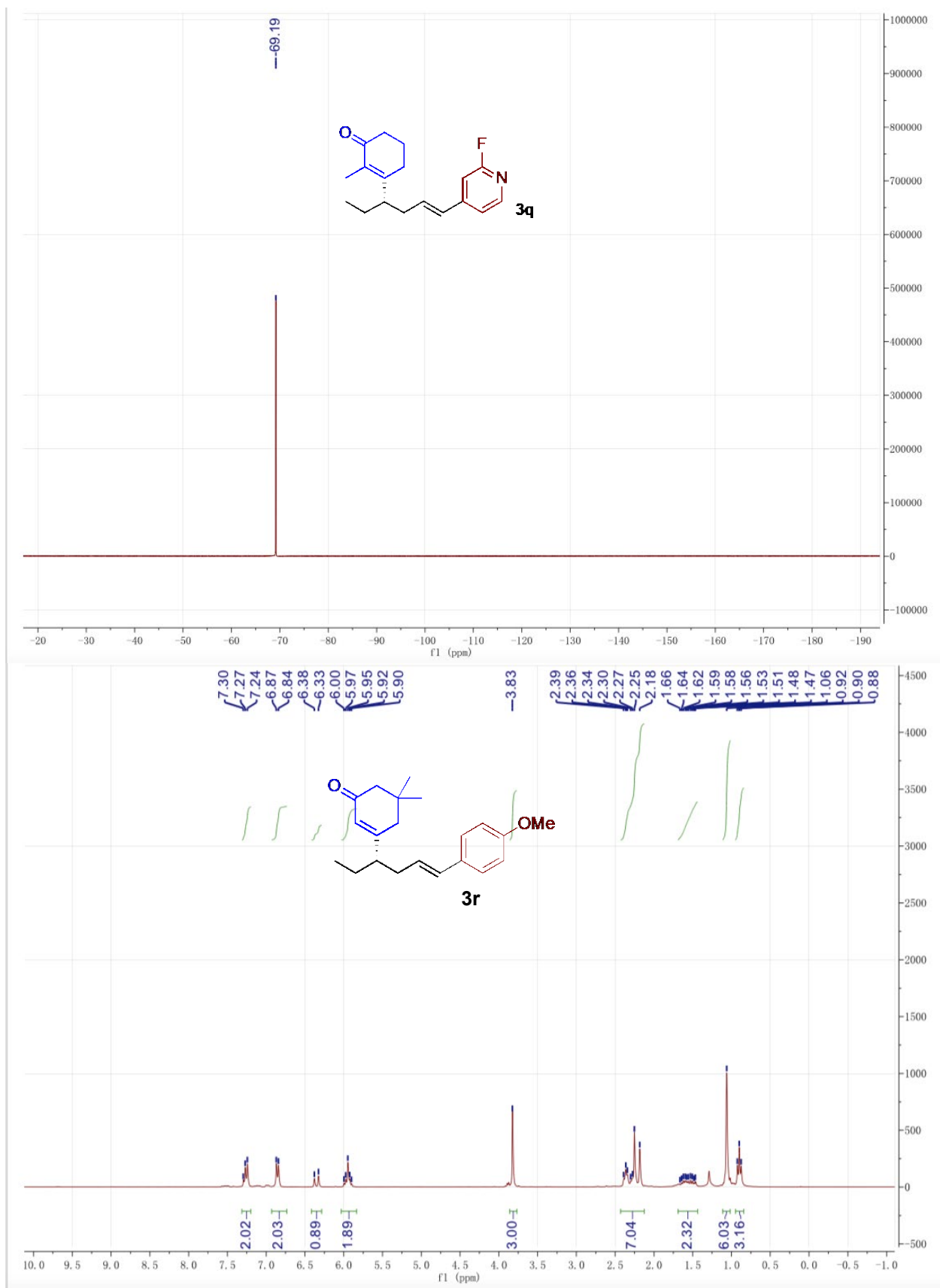


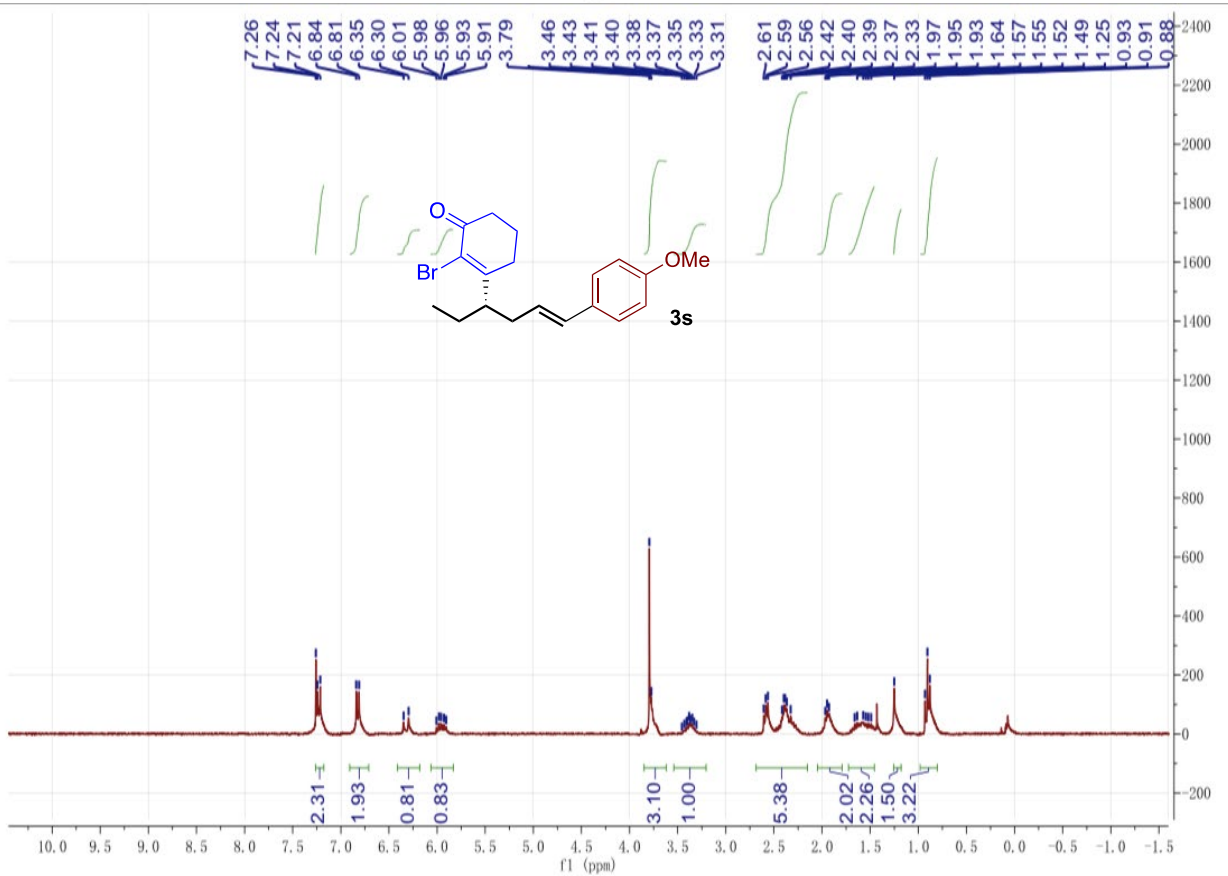
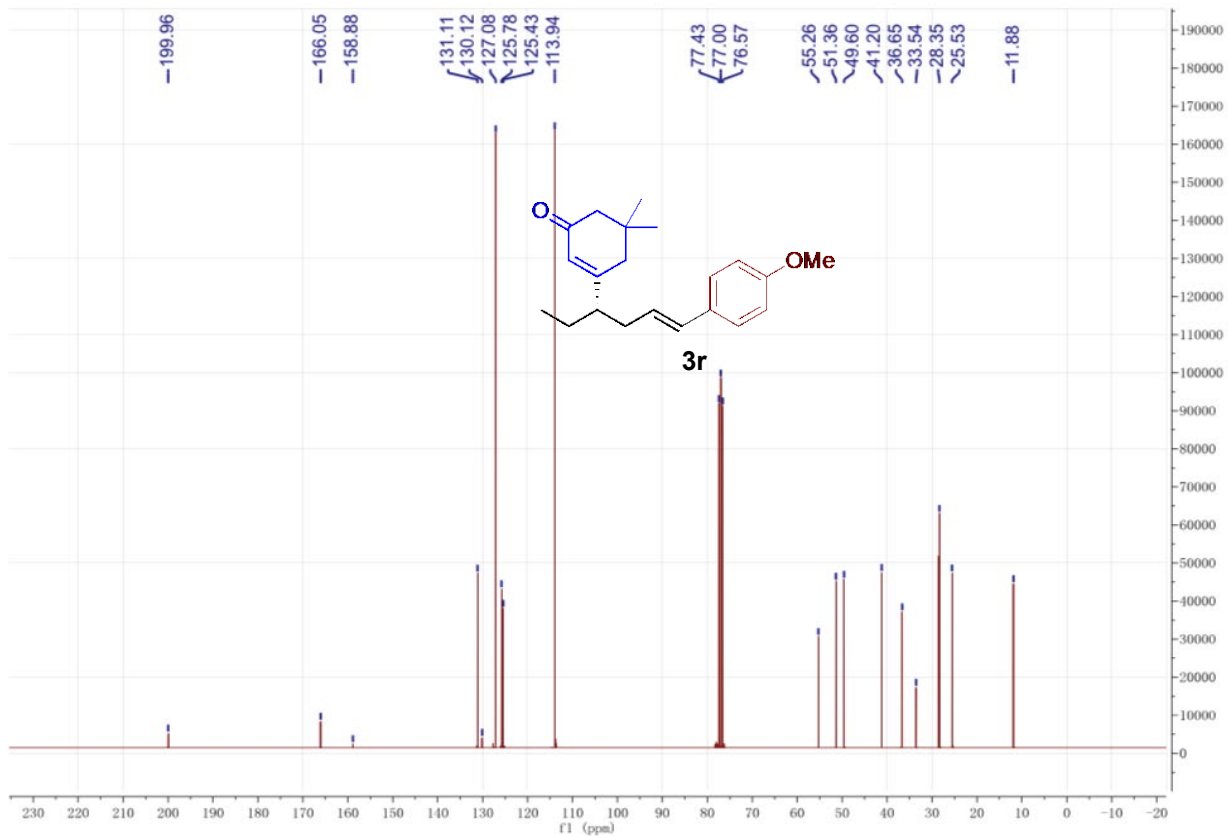


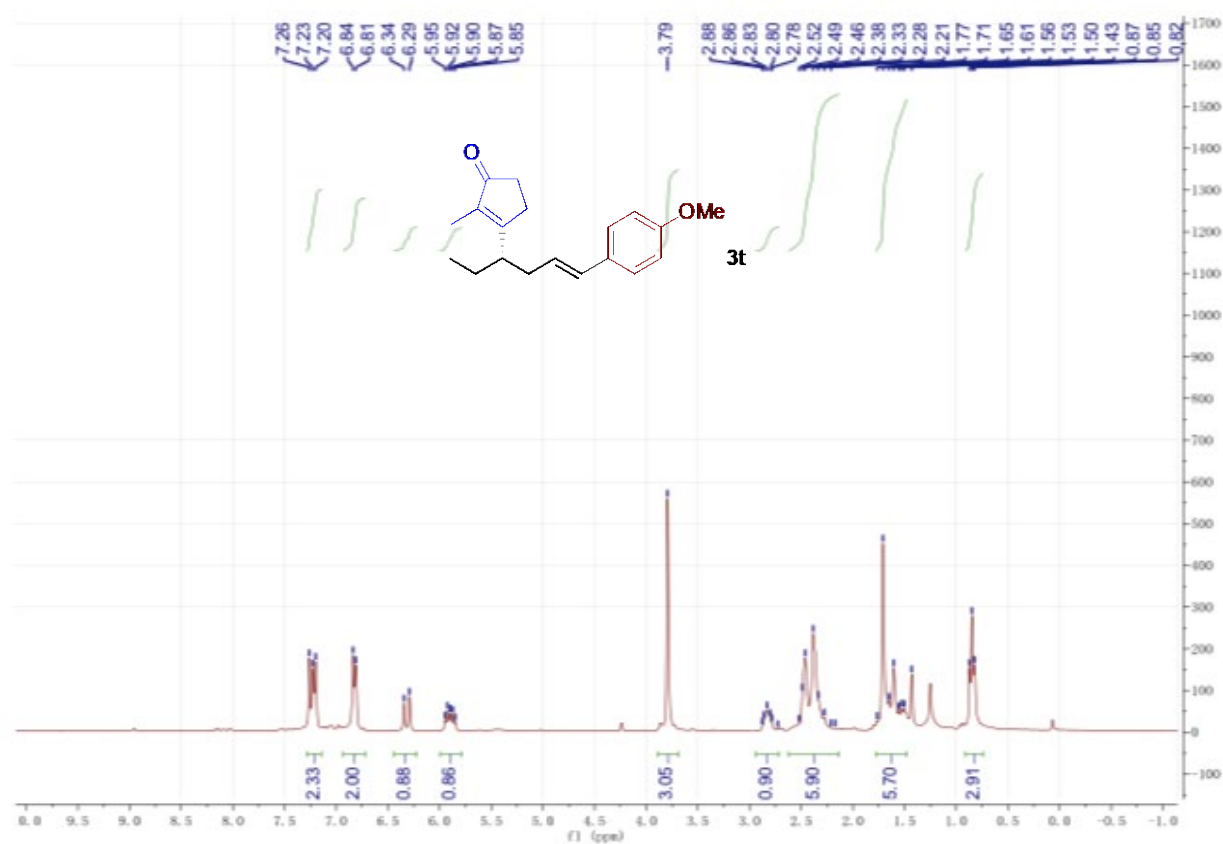
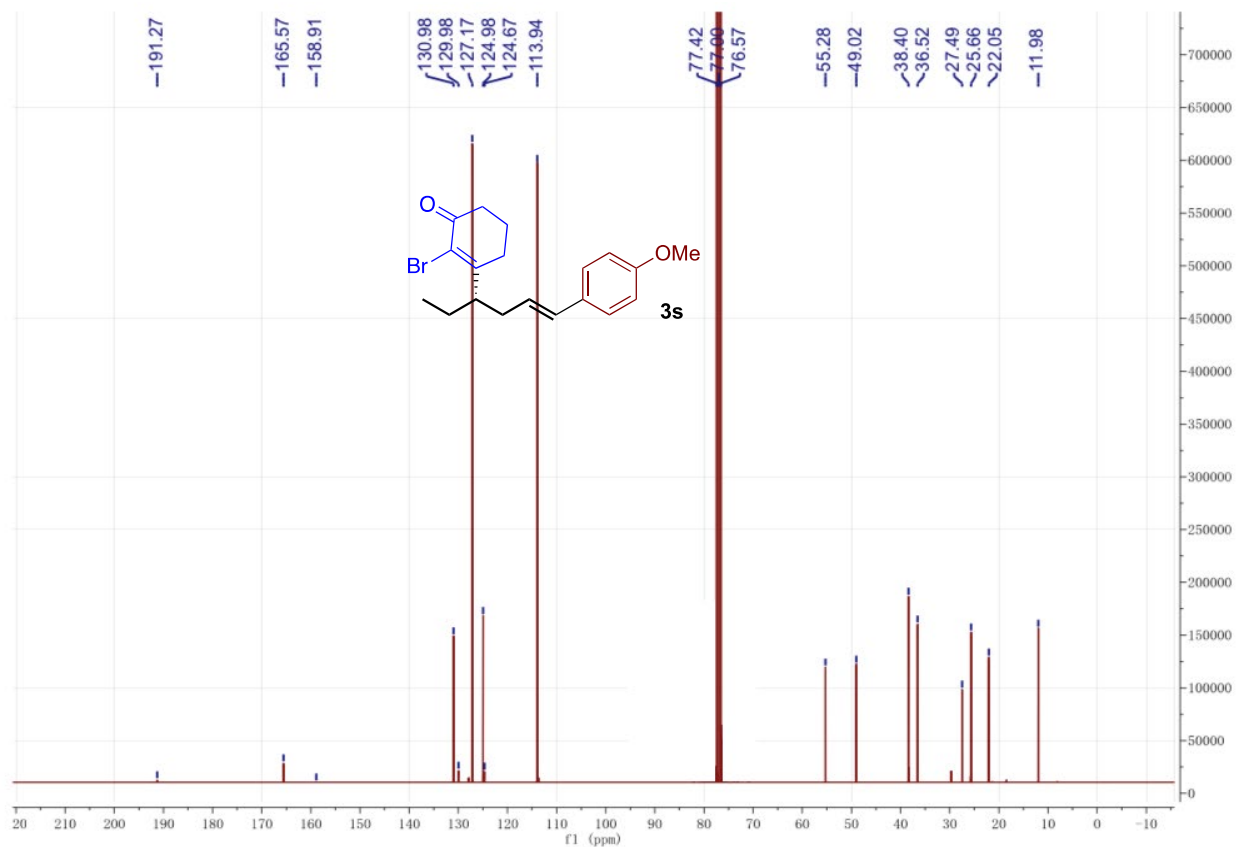


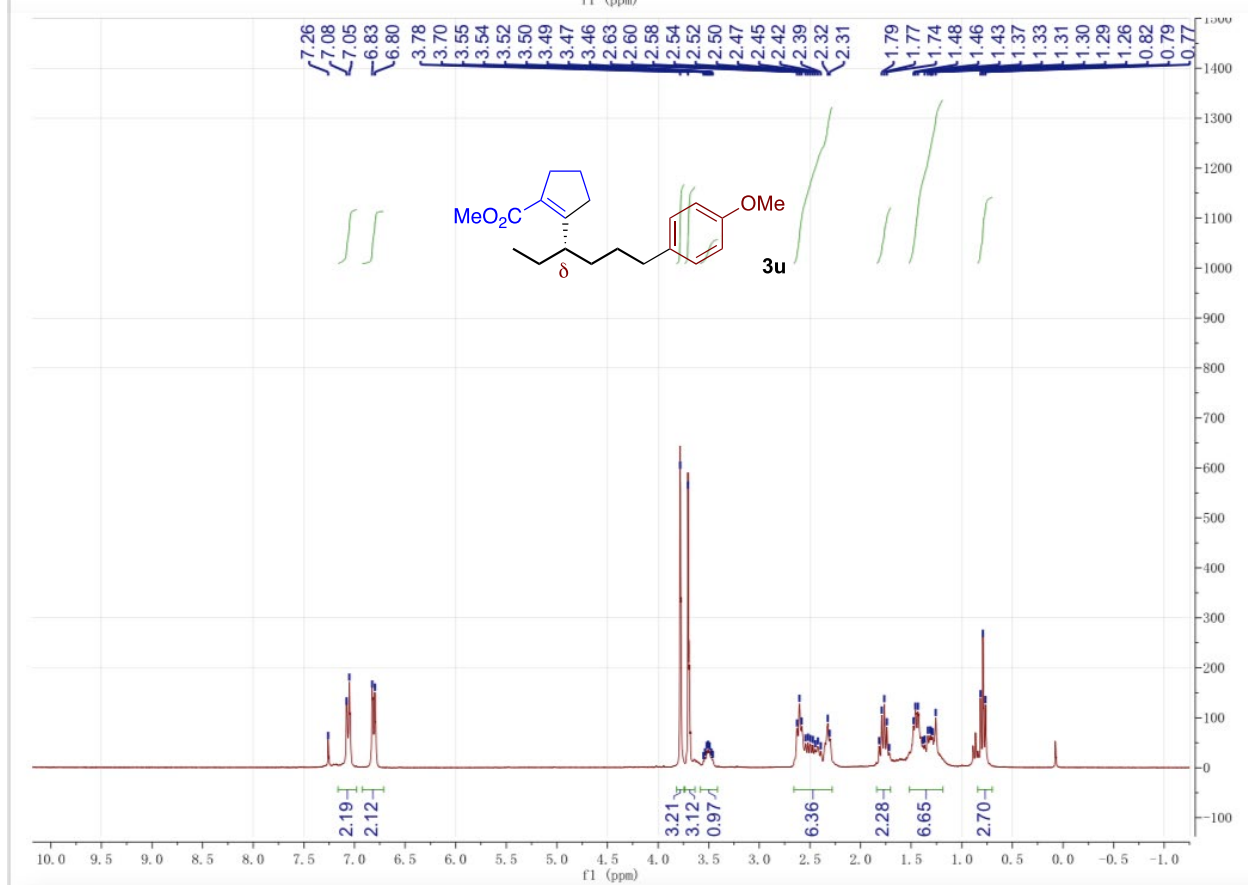
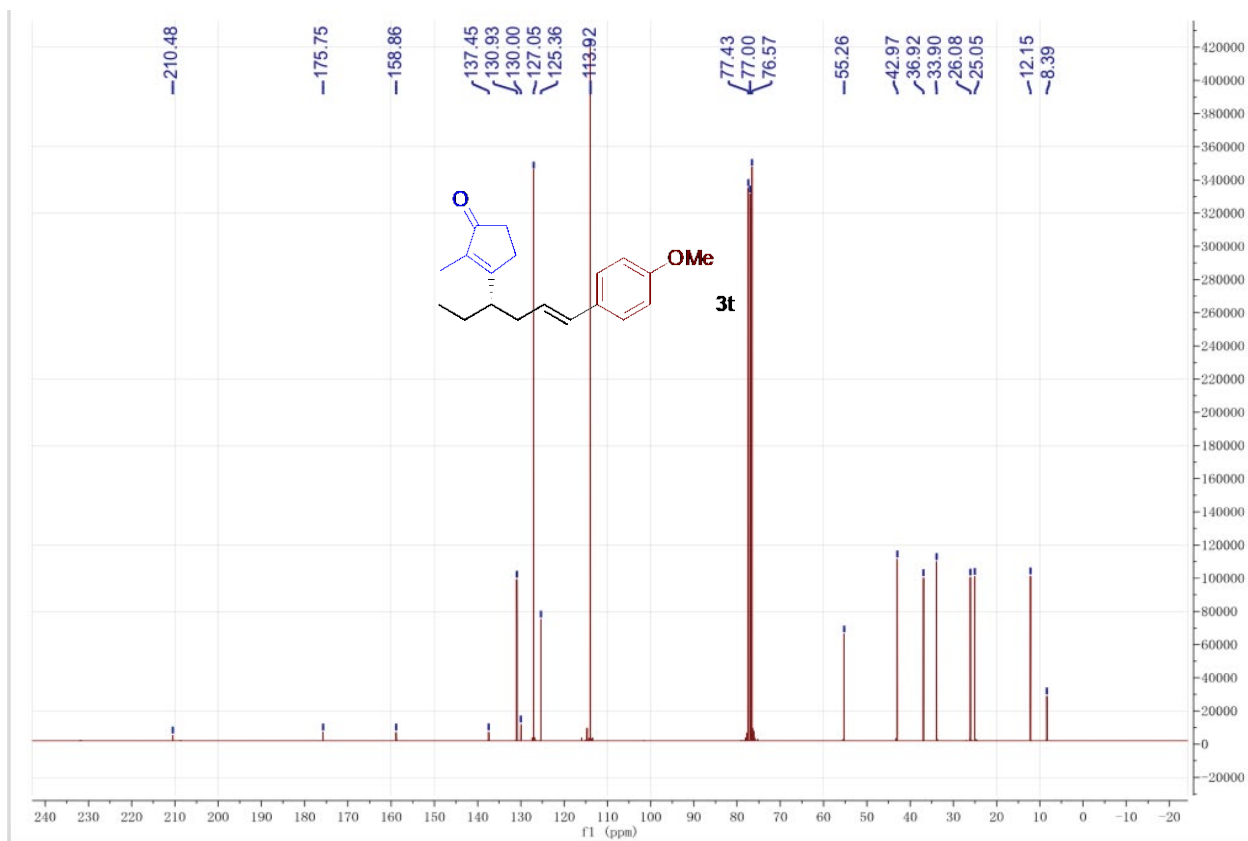


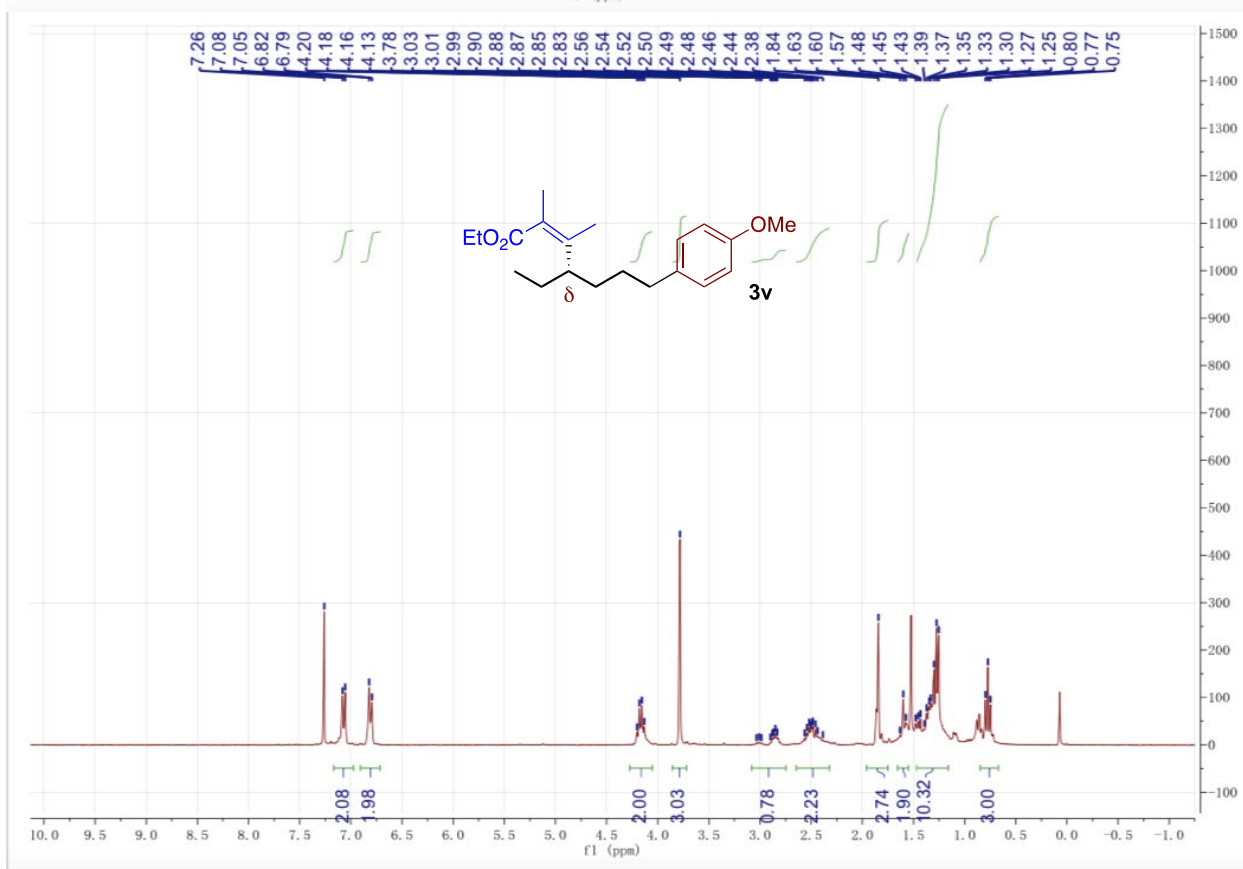
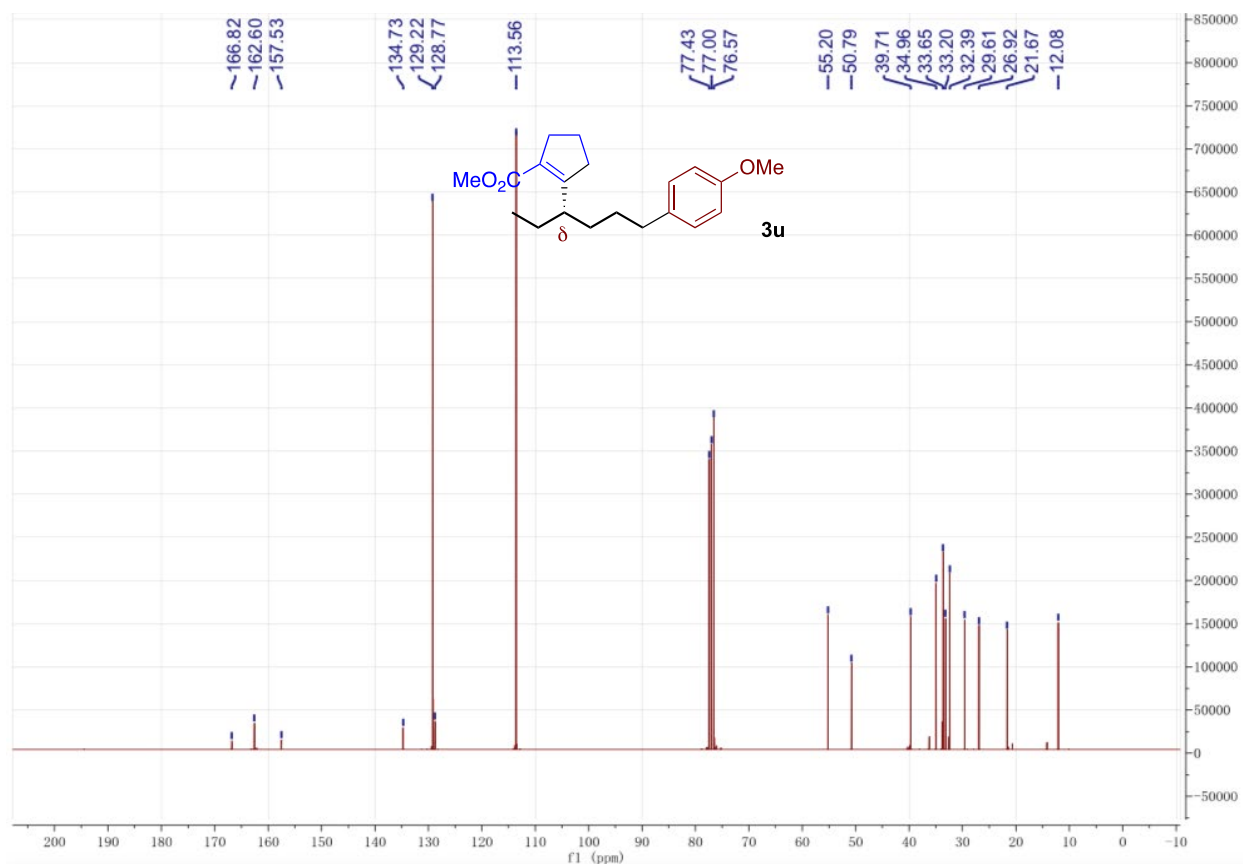


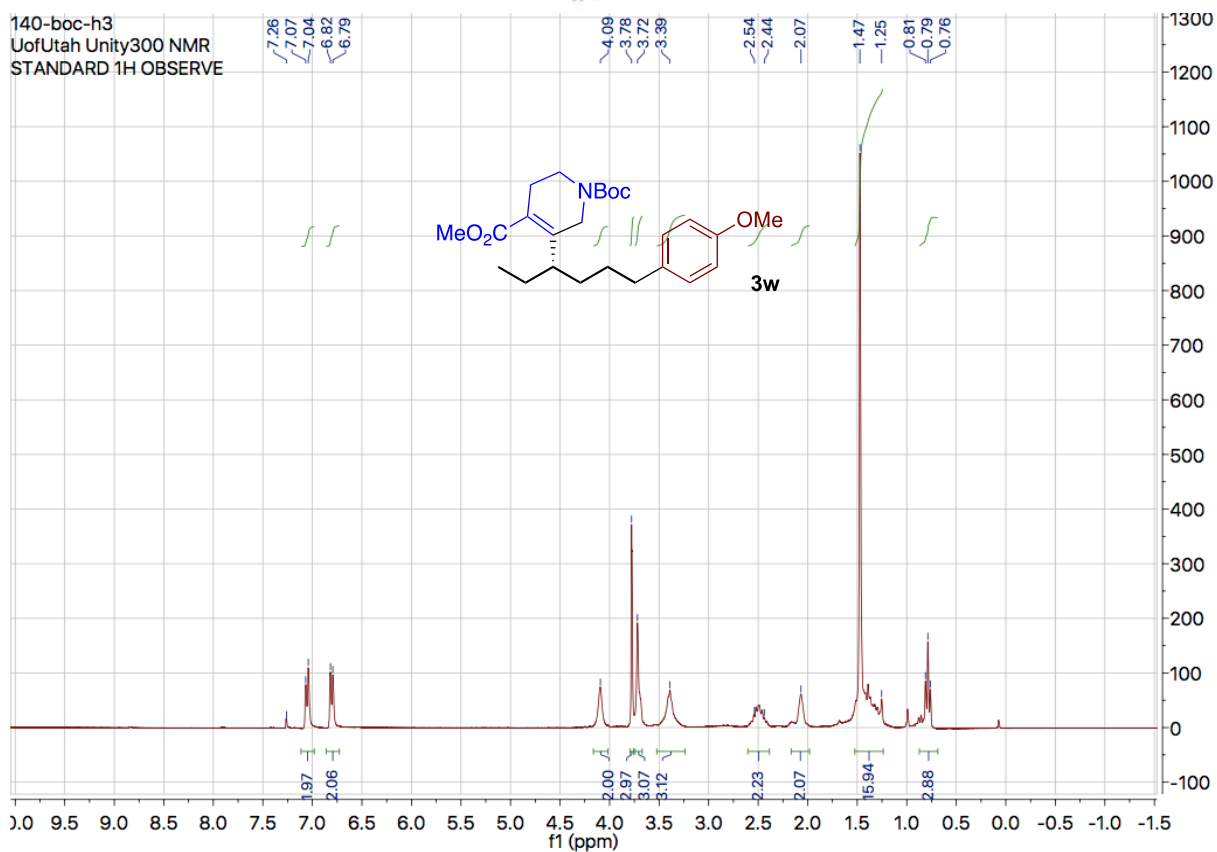
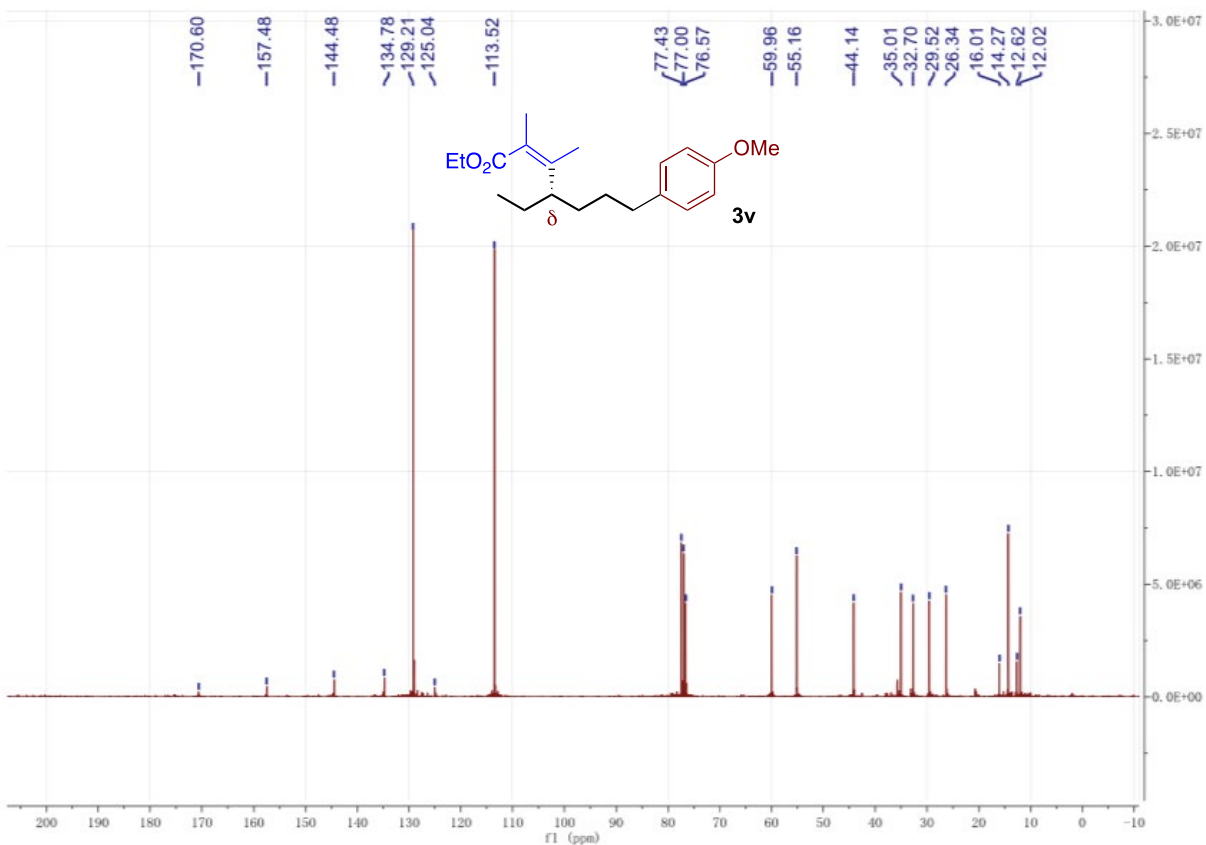


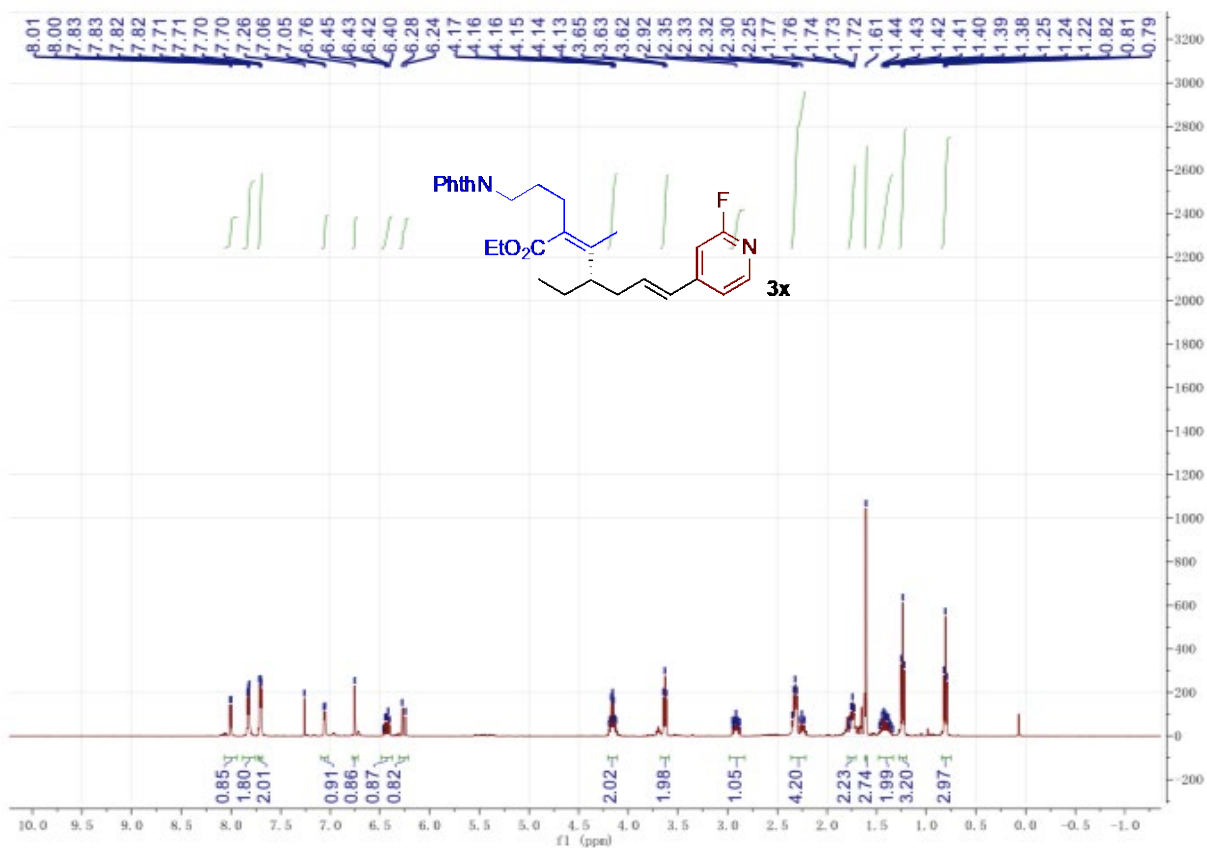
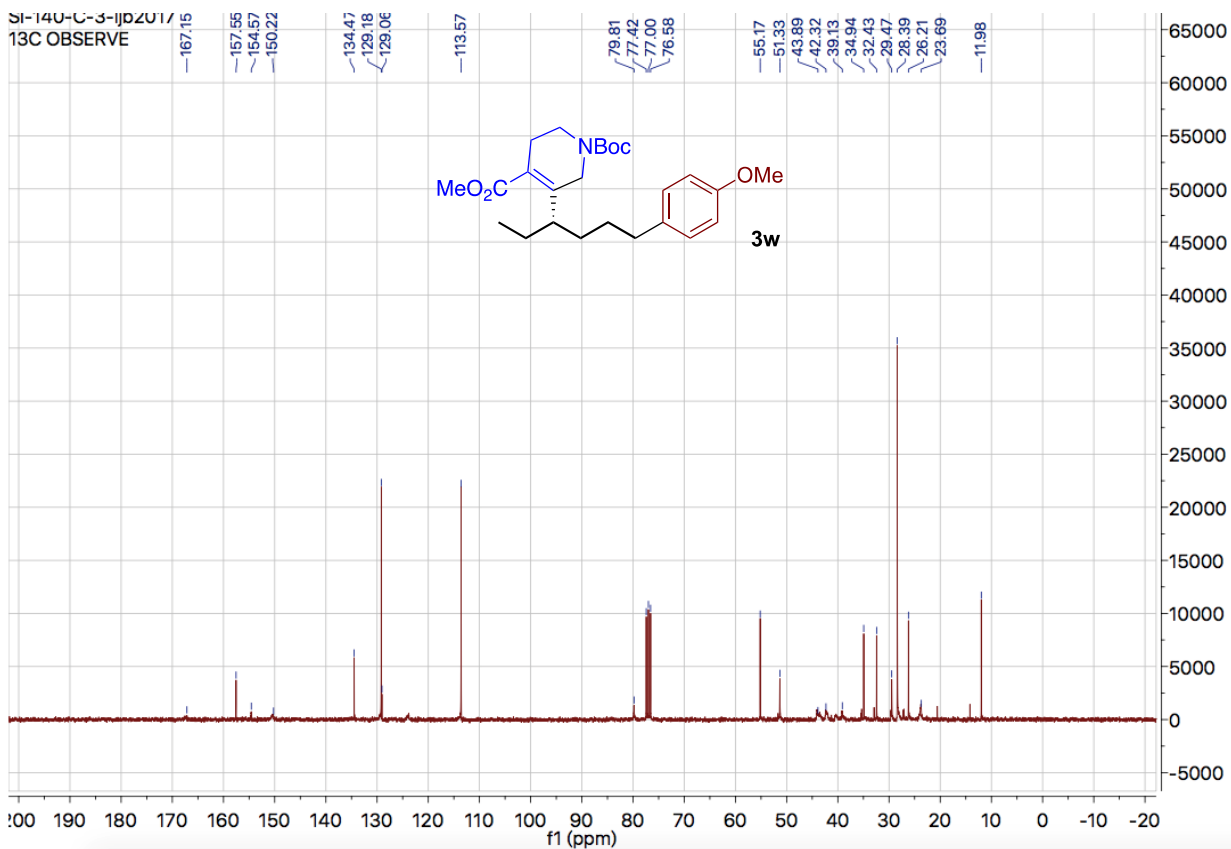


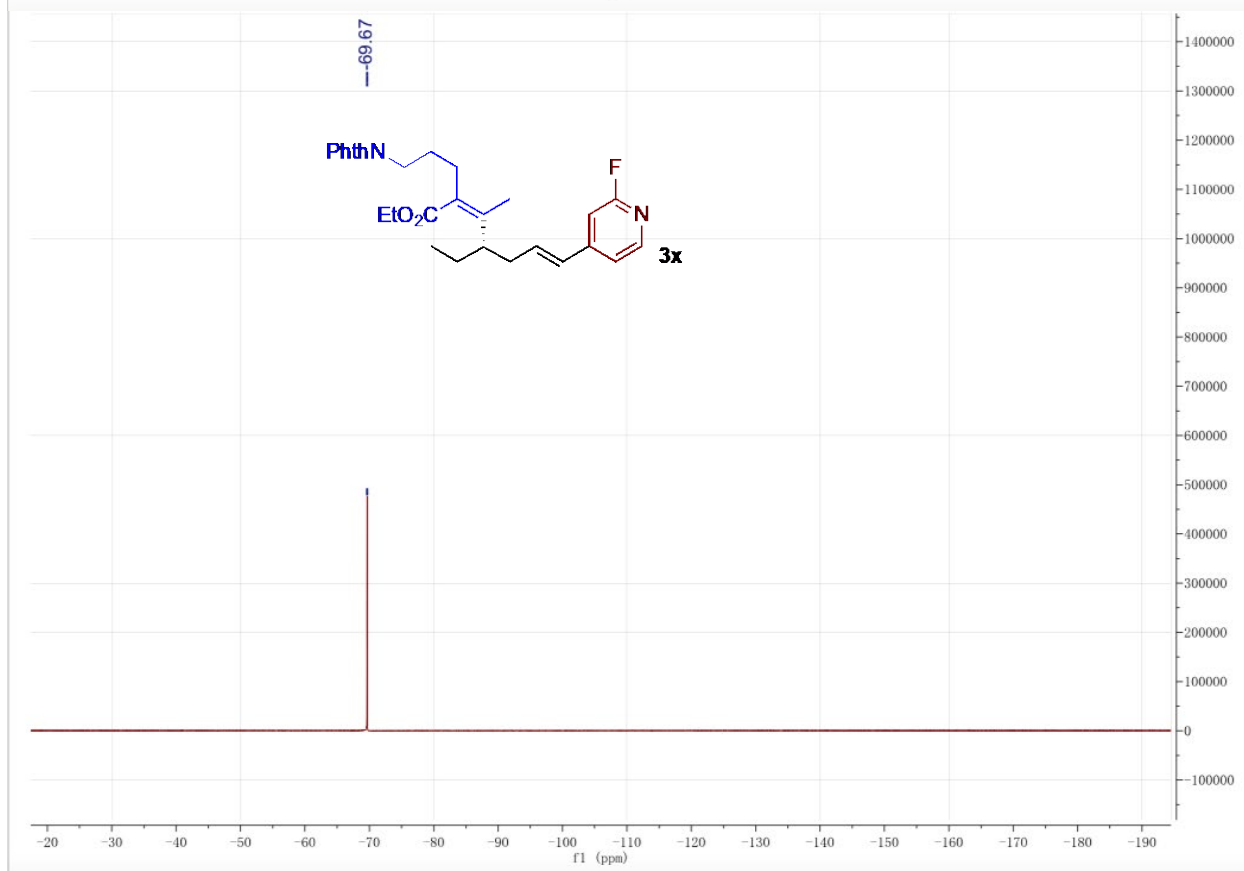
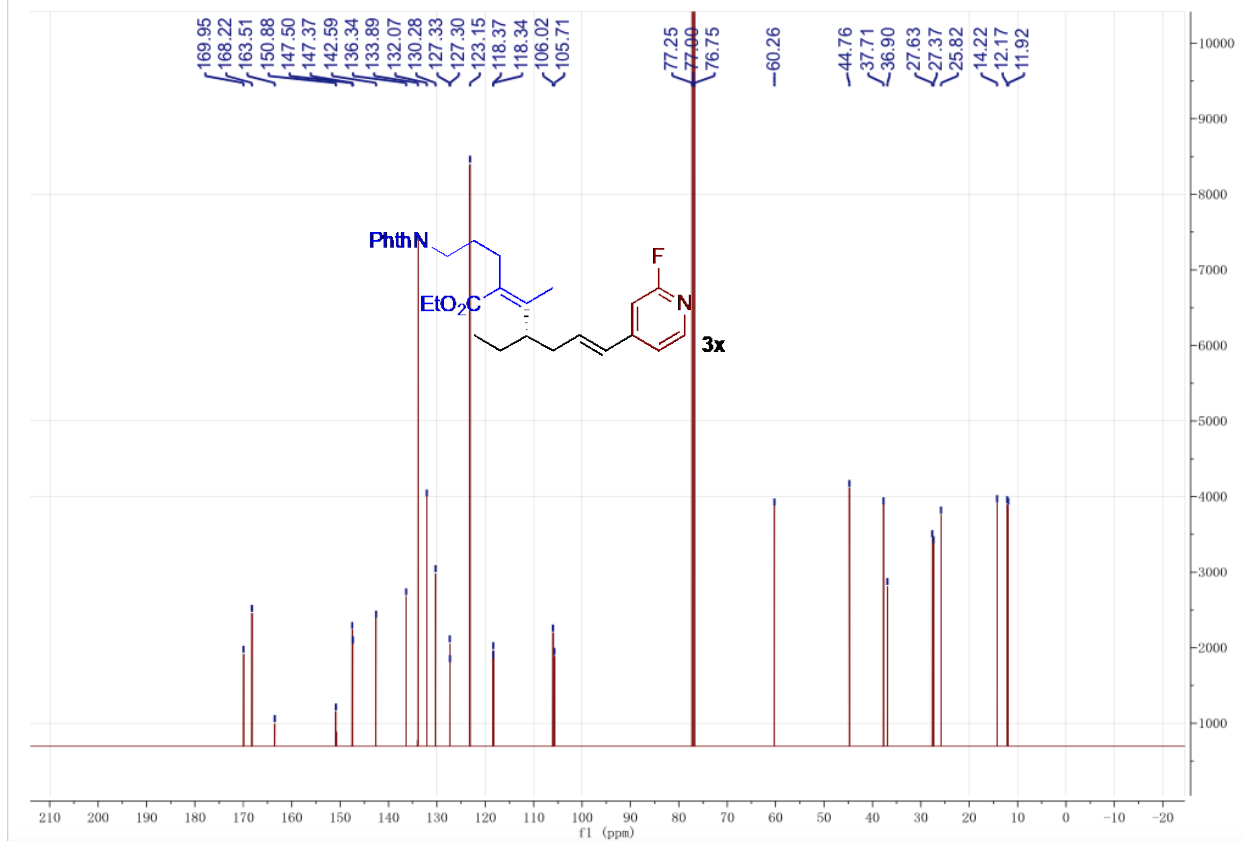


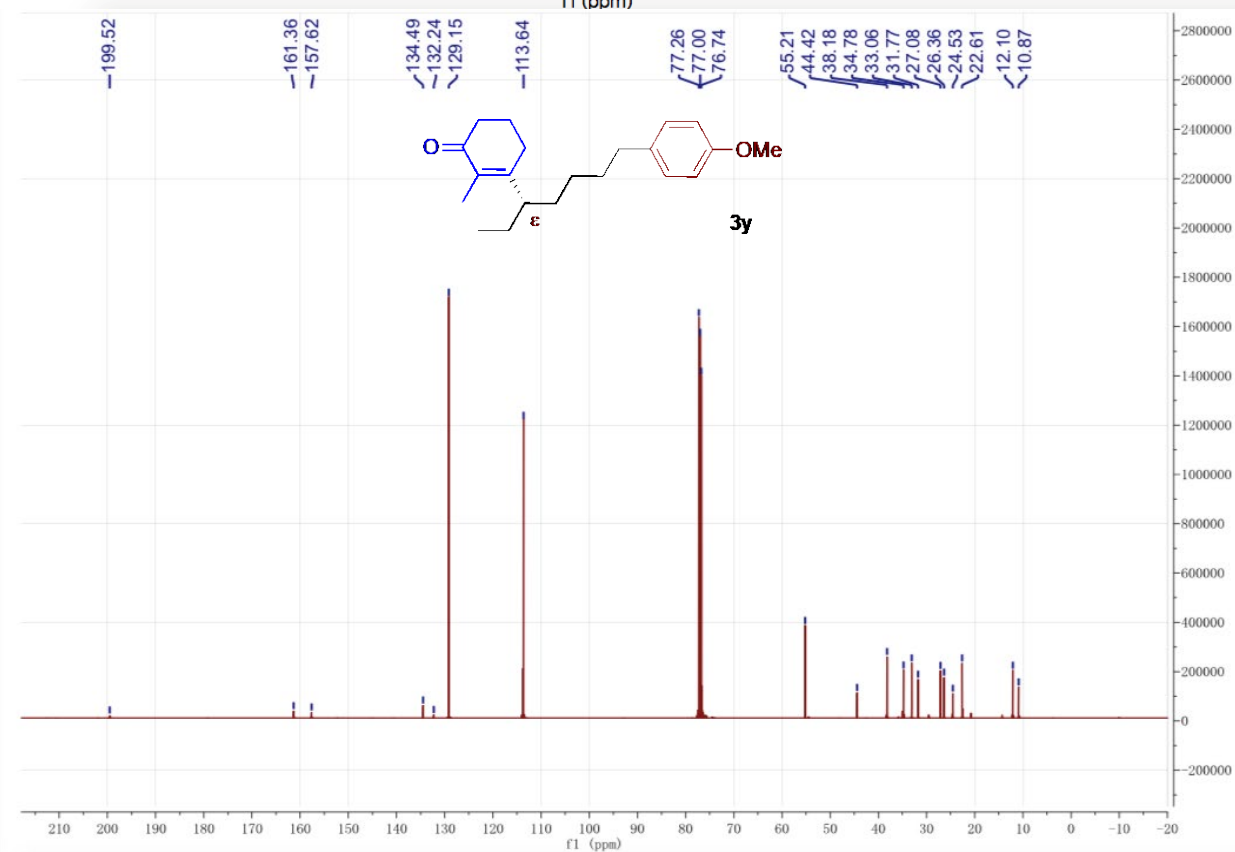
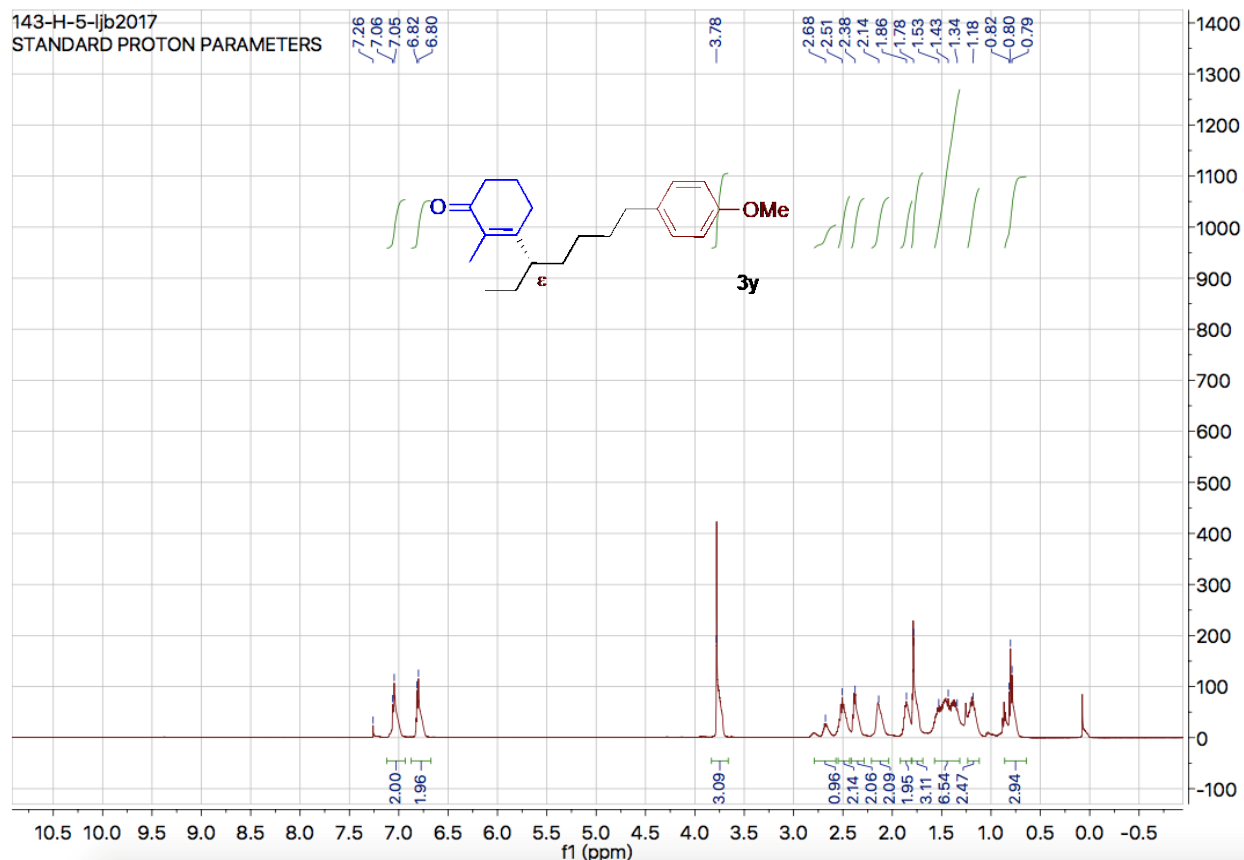






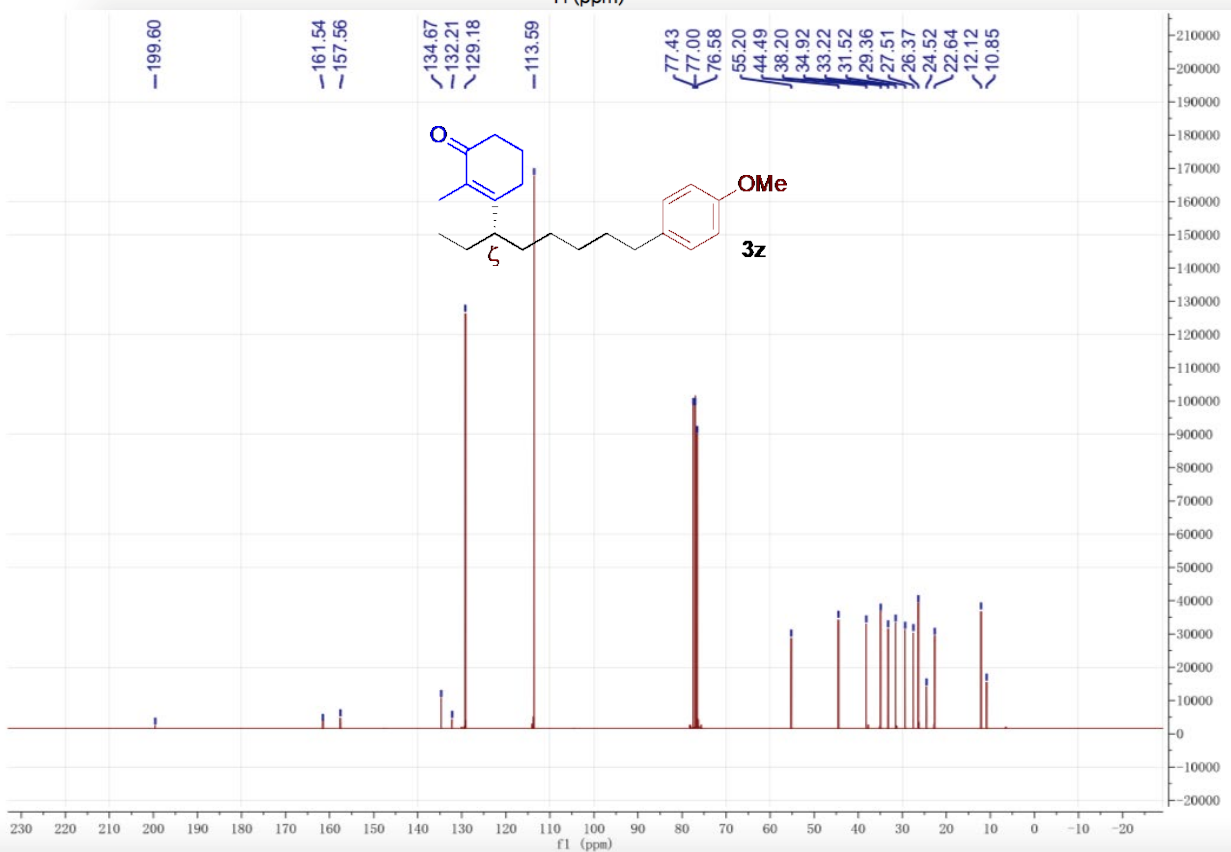
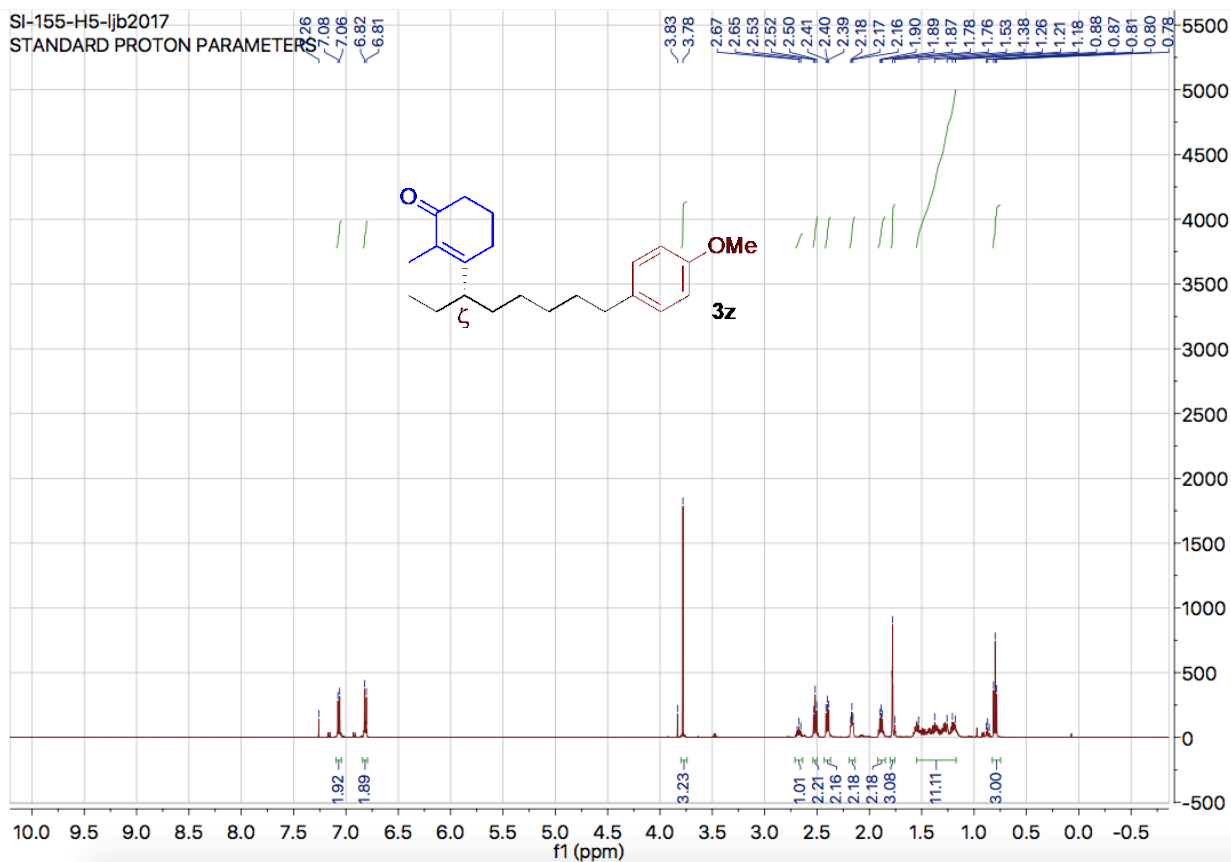


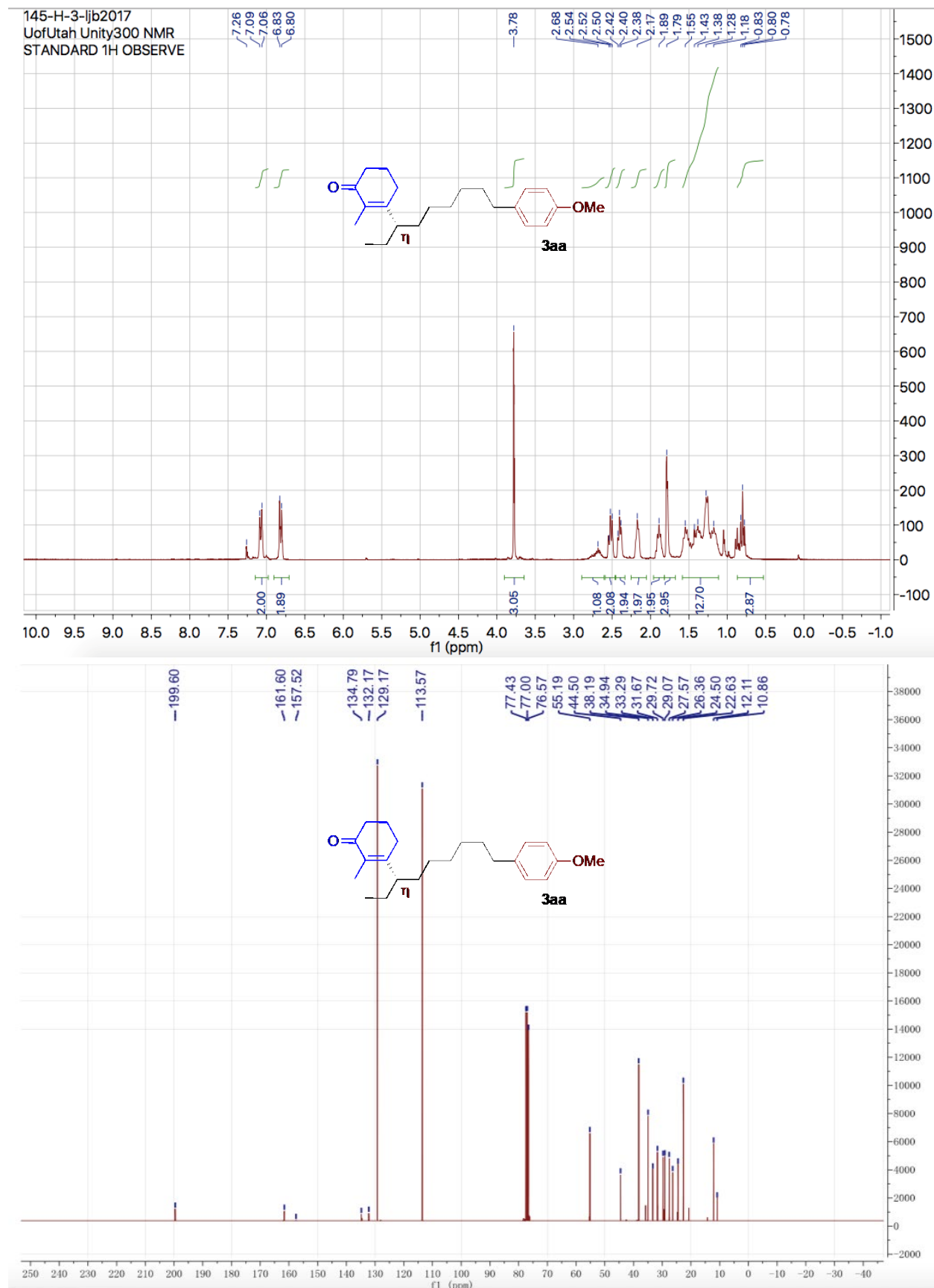




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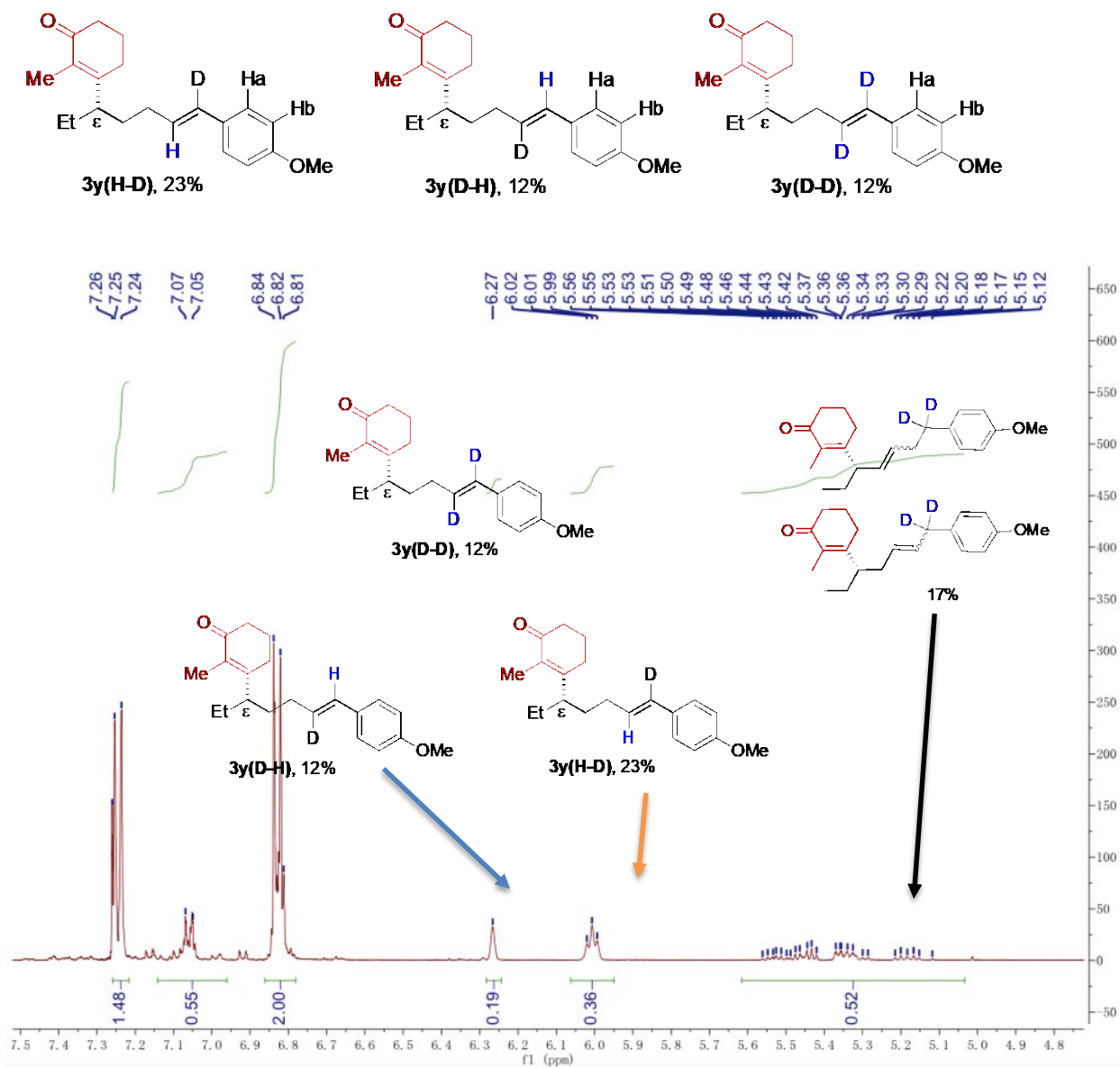
STANDARD PROTON PARAMETERS

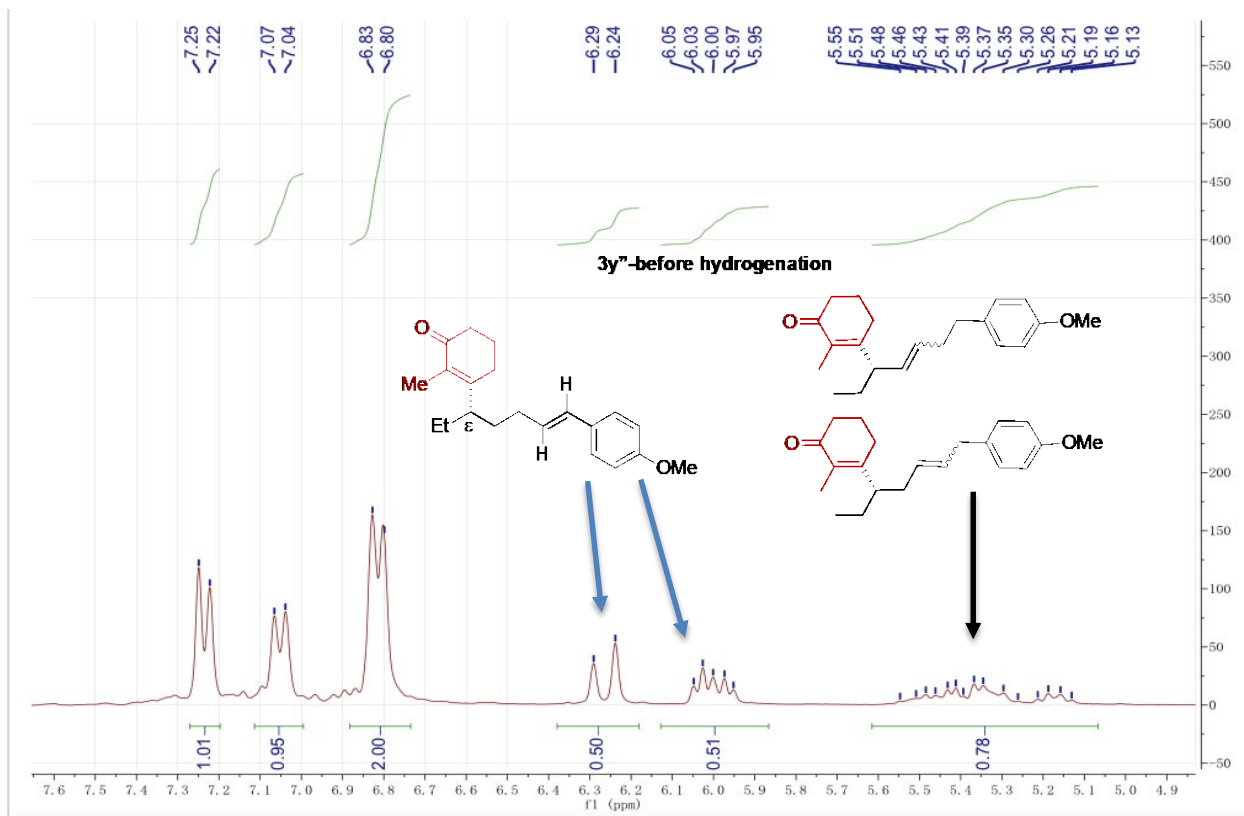


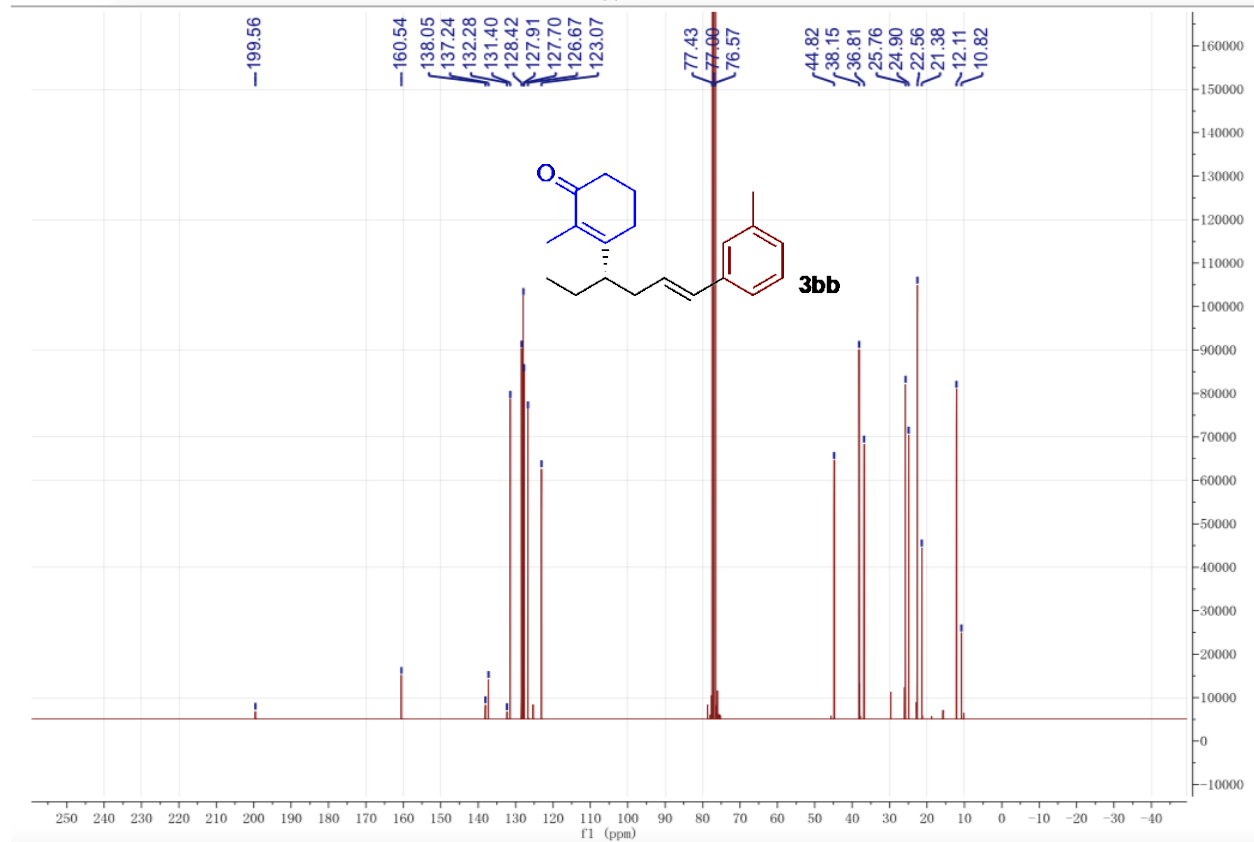
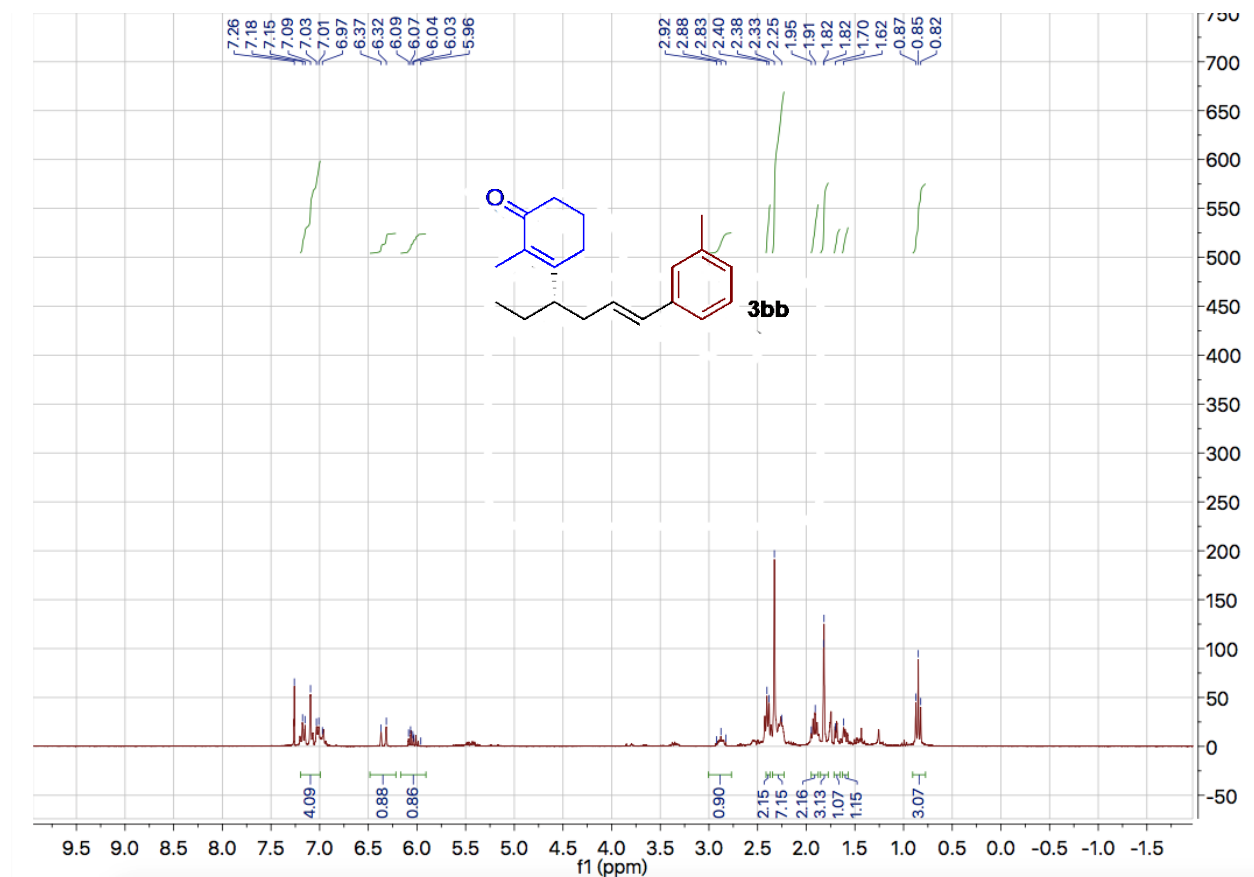


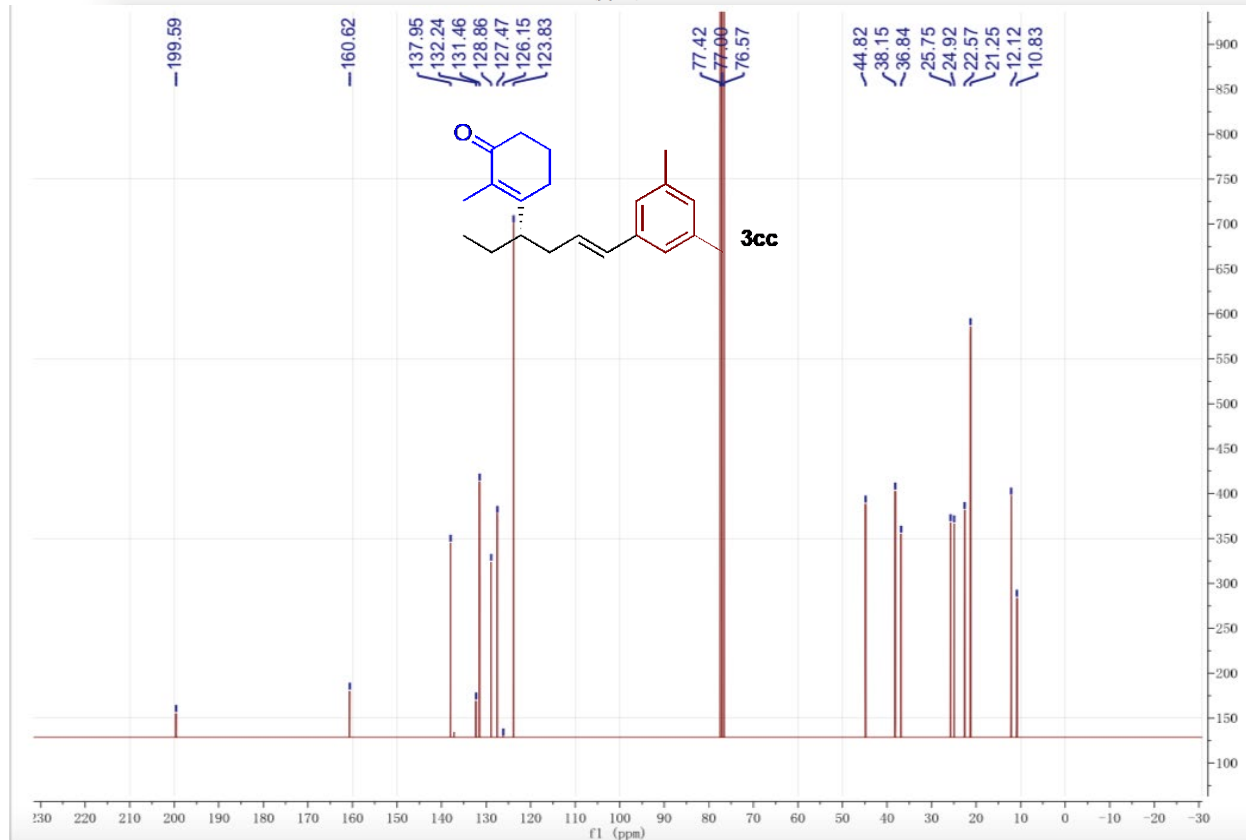
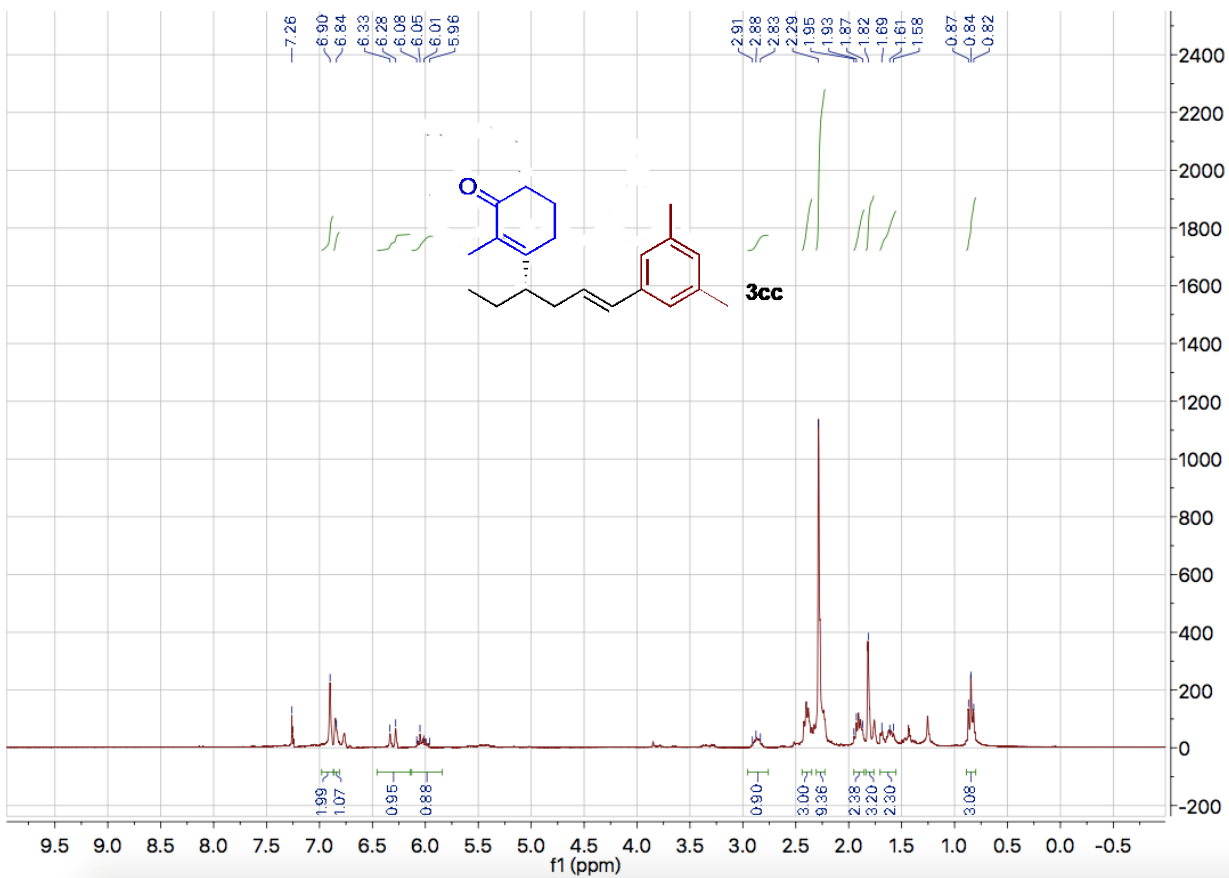
As shown below, protons on the aryl ring of **3y** include Ha and Hb (1:1). Ha has a chemical shift of ~7.24 and Hb has a chemical shift of ~6.82. Similarly, protons on the aryl ring of side products **4y** have a chemical shift of ~7.06 and 6.82. From the $3y$ - ^1H NMR, the total integration of **3y** is 1.48, **3y** (H-D) is 0.72 (0.36×2), and **3y** (D-H) is 0.38 (0.19×2), so the **3y** (D-D) is 0.38 ($1.48 - 0.72 - 0.38$). That is to say the ratio of **3y** (H-D), **3y** (D-H), and **3y** (D-D) is 72:38:38. As the overall yield of **3y** is 47%, we know the yields of every product (such as **3y** (H-D)) is $47\% \times 72/148 = 23\%$.

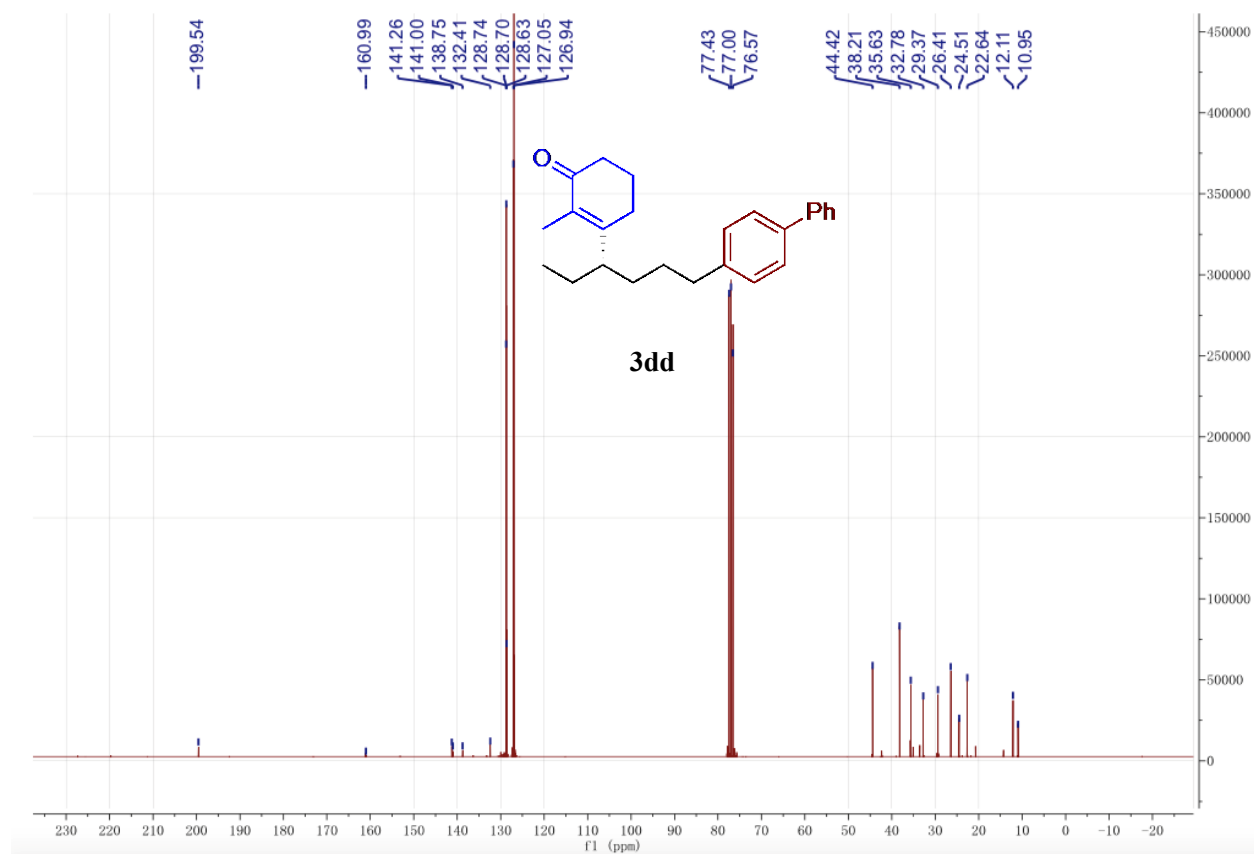
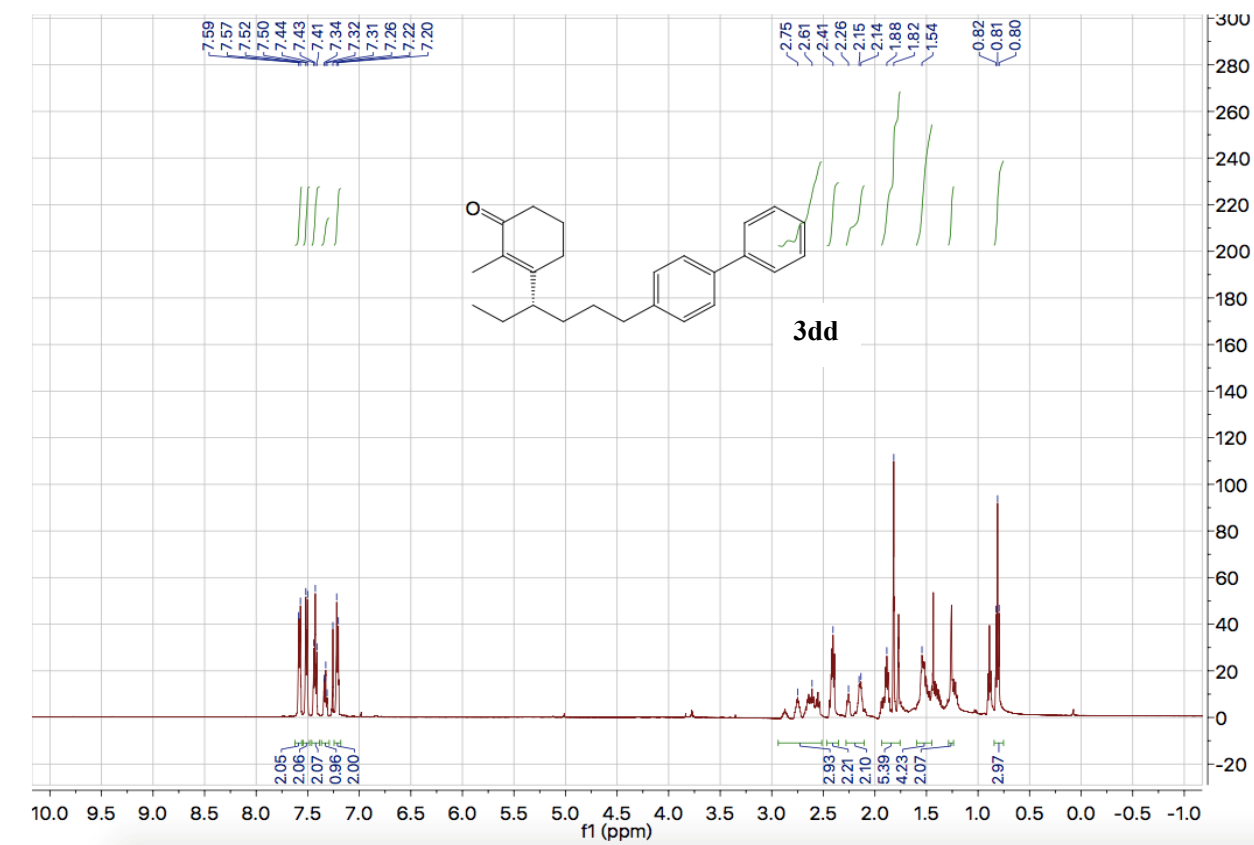
Product Distribution

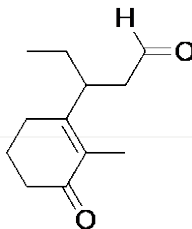
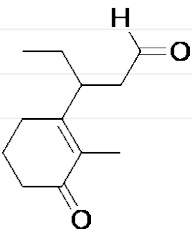












The ^1H NMR of mixture for the correlation analysis describing the formation of alkene byproduct **4**

