

Extending the Substrate Scope in the Hydrogenation of Unfunctionalized Tetrasubstituted Olefins with Ir/P-stereogenic Aminophosphine-Oxazoline Catalysts

Maria Biosca,[†] Ernest Salomó,[§] Pol de la Cruz Sánchez,[†] Antoni Riera,^{§,‡} Xavier Verdaguer,^{*,§,‡} Oscar Pàmies,^{*,†} Montserrat Diéguez^{*,†}

[†] Universitat Rovira i Virgili. Departament de Química Física i Inorgànica. C/ Marcel·lí Domingo, 1. 43007 Tarragona (Spain).

[§] Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology (BIST), C/ Baldiri Reixac, 10. 08028 Barcelona (Spain).

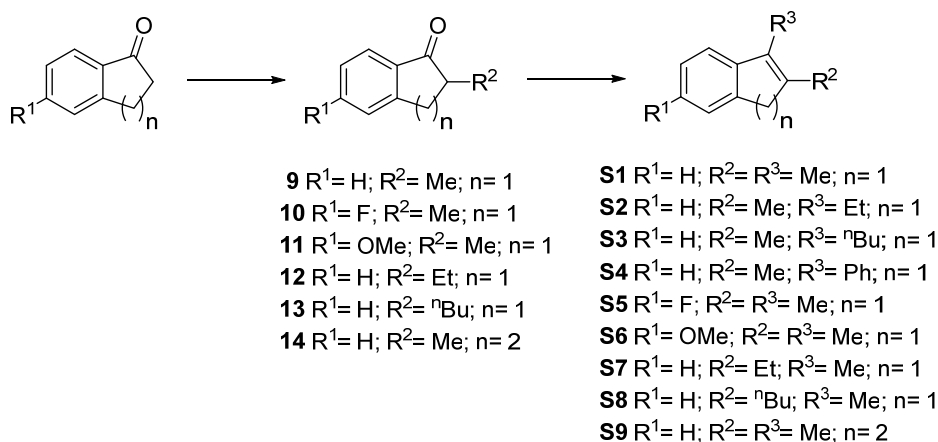
[‡] Dept. Química Inorgànica i Orgànica. Secció Orgànica, Universitat de Barcelona. C/ Martí i Franquès, 1. 08028 Barcelona (Spain).

SI.1. General considerations	SI-2
SI.2. Preparation of bicyclic tetrasubstituted olefins S1–S9	SI-2
SI.3. Preparation of acyclic tetrasubstituted olefins S10–S18	SI-5
SI.4. Preparation of fluorinated tetrasubstituted olefins S19–S23	SI-7
SI.5. Typical procedure for the hydrogenation product	SI-8
SI.6. Optimization of the reaction conditions for the hydrogenation of acyclic vinyl fluorides	SI-9
SI.7. Characterization and ee determination details of hydrogenated compounds	SI-10
SI.8. ¹ H and ¹³ C-NMR spectra of new compounds	SI-33
SI.9. References	SI-44

SI.1. General considerations

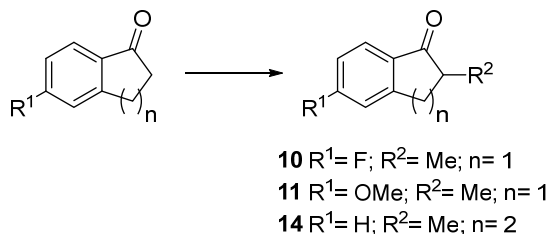
All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. All reagents were used as received. Ir-catalyst precursors **5–8a–c** were prepared as previously reported.¹ ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of SiMe_4 (^1H and ^{13}C). ^1H and ^{13}C assignments were made based on ^1H - ^1H gCOSY and ^1H - ^{13}C gHSQC.

SI.2. Preparation of bicyclic tetrasubstituted olefins S1-S9



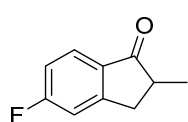
Compounds **9**, **12** and **13** were purchased from commercial sources.

Preparation of methylated ketones **10**, **11** and **14**



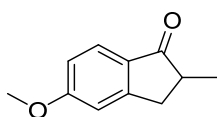
To a solution of ketone (1.0 mmol) in anhydrous THF (10 mL) at $-40\text{ }^\circ\text{C}$ was added a solution of $\text{LiN}(\text{SiMe}_3)_2$ (1.3 mmol, 1 M in THF, 1.3 mL) dropwise. The reaction mixture was stirred at $-40\text{ }^\circ\text{C}$ for 2 h, after which methyl iodide (1.4 mmol, 0.09 mL) was added dropwise and the reaction mixture brought to $0\text{ }^\circ\text{C}$ and stirred overnight. The reaction mixture was diluted with an aqueous solution of NH_4Cl (20 mL) and the volatiles removed under reduced pressure. The residue was extracted into toluene ($3 \times 50\text{ mL}$). The organic phases were combined, washed successively with water (25 mL) and brine (25 mL), dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography.

5-Fluoro-2-methyl-2,3-dihydro-1H-inden-1-one (10)²: Colorless oil (152 mg, 36%).



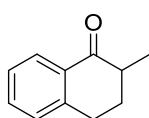
SiO₂-chromatography (petroleum ether/Et₂O = 10:1). ¹H NMR (400 MHz, CDCl₃): δ = 1.31 (d, 3H, Me, *J* = 7.2 Hz), 2.70-2.78 (m, 2H, CH₂), 3.38 (dd, 1H, CH, *J* = 7.2 Hz, *J* = 16.8 Hz), 7.05-7.10 (m, 2H, CH=), 7.75 (m, 1H, CH=).

5-Methoxy-2-methyl-2,3-dihydro-1H-inden-1-one (11)³: Colorless oil (250 mg, 52%).



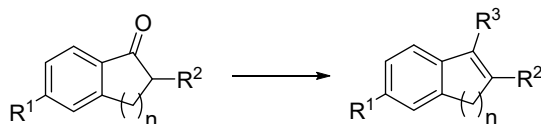
SiO₂-chromatography (petroleum ether/EtOAc = 8:1). ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (d, 3H, CH₃, Me, *J* = 7.3 Hz), 2.62-2.72 (m, 2H, CH₂), 3.27-3.40 (m, 1H, CH), 3.87 (s, 3H, CH₃-O), 6.85-6.90 (m, 2H, CH=), 7.67 (d, 1H, CH=, *J* = 8.4 Hz).

2-Methyl-3,4-dihydronaphthalen-1(2H)-one (14)⁴: Colorless oil (542 mg, 70%). SiO₂-



chromatography (petroleum ether/EtOAc = 50:1). ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (d, 3H, Me, *J* = 6.8 Hz), 1.86-1.91 (m, 1H, CH₂), 2.16-2.23 (m, 1H, CH₂), 2.54-2.62 (m, 1H, CH), 2.93-3.06 (m, 2H, CH₂), 7.20-7.30 (m, 2H, CH=), 7.44 (t, 1H, CH=, *J* = 8.4 Hz), 8.02 (d, 1H, CH=, *J* = 7.8 Hz).

Preparation of bicyclic tetrasubstituted olefins S1-S9



9 R¹ = H; R² = Me; n = 1
10 R¹ = F; R² = Me; n = 1
11 R¹ = OMe; R² = Me; n = 1
12 R¹ = H; R² = Et; n = 1
13 R¹ = H; R² = ⁿBu; n = 1
14 R¹ = H; R² = Me; n = 2

S1 R¹ = H; R² = R³ = Me; n = 1
S2 R¹ = H; R² = Me; R³ = Et; n = 1
S3 R¹ = H; R² = Me; R³ = ⁿBu; n = 1
S4 R¹ = H; R² = Me; R³ = Ph; n = 1
S5 R¹ = F; R² = R³ = Me; n = 1
S6 R¹ = OMe; R² = R³ = Me; n = 1
S7 R¹ = H; R² = Et; R³ = Me; n = 1
S8 R¹ = H; R² = ⁿBu; R³ = Me; n = 1
S9 R¹ = H; R² = R³ = Me; n = 2

Olefins **S1-S9** were prepared by using the addition/dehydration protocol reported by Buchwald.⁵ In this way, a solution of the corresponding ketone (1.4 mmol) in THF (2 mL) was added dropwise via syringe to a solution of the corresponding organometallic (for **S1**, **S5-S9**, MeLi·LiBr 1.5 M in diethyl ether (1.4 mL, 2.1 mmol); for **S2**, EtMgBr 3.0 M in diethyl ether (0.7 mL, 2.1 mmol); for **S3**, ⁿBuLi 1.6M in hexane (1.31 mL, 2.1 mmol); for **S4**, PhMgBr 3.0 M in diethyl ether (0.7 mL, 2.1 mmol)) under argon at 0 °C. The mixture was stirred at room temperature for 3.5 h for **S1**, **S5-S9** or 5 h for **S2-S4**. A saturated aqueous solution of NH₄Cl was then added dropwise to quench the reaction,

followed by the addition of diethyl ether and water. The aqueous phase was separated and extracted with diethyl ether. The combined organic phases were washed with saturated aqueous NaCl solution, dried over MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was dissolved in toluene (5 mL). *p*-Toluenesulfonic acid (2 mg) was added and the mixture was refluxed overnight. It was allowed to cool to room temperature, and diethyl ether and saturated aqueous NaHCO₃ solution were added. The organic phase was separated and washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography (petroleum ether for **S1–S5** and **S7–S9** and 9:1 petroleum ether: EtOAc for **S6**) afforded the corresponding product.

2,3-Dimethyl-1*H*-indene (S1)⁵: Light yellow oil (430 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ = 2.03 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 3.26 (s, 2H, CH₂), 7.13–7.20 (m, 1H, CH=), 7.25–7.29 (m, 1H, CH=), 7.29–7.35 (m, 1H, CH=), 7.38–7.44 (m, 1H, CH=).

3-Ethyl-2-methyl-1*H*-indene (S2)⁵: Yellow oil (561 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (t, 3H, CH₃, Et, *J* = 7.6 Hz), 2.06 (s, 3H, CH₃), 2.53 (q, 2H, CH₂, Et, *J* = 7.6 Hz), 3.26 (s, 2H, CH₂), 7.07–7.12 (m, 1H, CH=), 7.23–7.25 (m, 2H, CH=), 7.36 (dd, 1H, CH=, *J* = 7.3 Hz, *J* = 0.7 Hz).

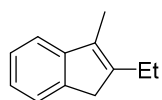
3-Butyl-2-methyl-1*H*-indene (S3)⁶: Yellow oil (0.167 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ = 0.93 (t, 3H, CH₃, ⁿBu, *J* = 7.2 Hz), 1.37 (m, 2H, CH₂, ⁿBu), 1.53 (m, 2H, CH₂, ⁿBu), 2.06 (s, 3H, CH₃), 2.51 (t, 2H, CH₂, ⁿBu, *J* = 7.5 Hz), 3.26 (s, 2H, CH₂), 7.10 (m, 1H, CH=), 7.24 (m, 2H, CH=), 7.36 (m, 1H, CH=).

2-Methyl-3-phenyl-1*H*-indene (S4)⁵: White solid (270 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ = 2.14 (s, 3H, CH₃), 3.44 (s, 2H, CH₂), 7.12–7.23 (m, 3H, CH=), 7.32–7.48 (m, 6H, CH=).

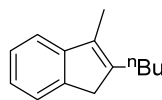
6-Fluoro-2,3-dimethyl-1*H*-indene (S5)³: Colorless oil (54 mg, 45%). ¹H NMR (400 MHz, CDCl₃): δ = 2.02 (s, 3H, CH₃), 2.05 (s, 3H, CH₃), 3.24 (s, 2H, CH₂), 6.93–7.02 (m, 1H, CH=), 7.06–7.14 (m, 2H, CH=).

6-Methoxy-2,3-dimethyl-1*H*-indene (S6)³: Yellow oil (71 mg, 30%). ¹H NMR (400 MHz, CDCl₃): δ = 2.00 (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 3.23 (s, 2H, CH₂), 3.82 (s, 3H, CH₃-O), 6.84 (dd, 1H, CH=, *J* = 8.2, *J* = 2.4 Hz), 7.00 (d, 1H, CH=, *J* = 2.4 Hz), 7.08 (d, 1H, CH=, *J* = 8.2 Hz).

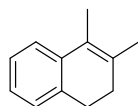
2-Ethyl-3-methyl-1*H*-indene (S7)⁷: Colorless oil (223 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (t, 3H, CH₃, Et, *J* = 7.6 Hz), 2.04 (s, 3H, CH₃), 2.48 (q, 2H, CH₂, Et, *J* = 7.6 Hz), 3.29 (s, 2H, CH₂), 7.10-7.14 (m, 1H, CH=), 7.22-7.29 (m, 2H, CH=), 7.37-7.39 (m, 1H, CH=).



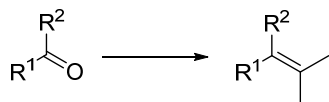
2-Butyl-3-methyl-1*H*-indene (S8)⁵: Colorless oil (215 mg, 52%). ¹H NMR (400 MHz, CDCl₃): δ = 0.92 (t, 3H, CH₃, ⁿBu, *J* = 7.4 Hz), 1.28-1.41 (m, 2H, CH₂, ⁿBu), 1.46-1.56 (m, 2H, CH₂, ⁿBu), 2.03 (s, 3H, CH₃), 2.45 (t, 2H, CH₂, ⁿBu, *J* = 7.5 Hz), 3.27 (s, 2H, CH₂), 7.11 (td, 1H, CH=, *J* = 1.5 Hz, *J* = 7.1 Hz), 7.21-7.29 (m, 2H, CH=), 7.37 (d, 1H, CH=, *J* = 7.5 Hz).



3,4-Dimethyl-1,2-dihydronaphthalene (S9)⁵: Colorless oil (168 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ = 1.90 (s, 3H, CH₃), 2.01 (s, 3H, CH₃), 2.21 (t, 2H, CH₂, *J* = 7.8 Hz), 2.72 (t, 2H, CH₂, *J* = 7.8 Hz), 7.06-7.08 (m, 2H, CH=), 7.14-7.21 (m, 2H, CH=).



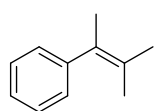
SI.3. Preparation of acyclic tetrasubstituted olefins S10-S18



- S10** R¹ = Ph; R² = Me
S11 R¹ = 4-Me-C₆H₄; R² = Me
S12 R¹ = 4-OMe-C₆H₄; R² = Me
S13 R¹ = 3-Me-C₆H₄; R² = Me
S14 R¹ = 2-OMe-C₆H₄; R² = Me
S15 R¹ = 4-OMe-C₆H₄; R² = Et
S16 R¹ = 4-OMe-C₆H₄; R² = ⁿPr
S17 R¹ = 2,5-Me₂-furan; R² = Me
S18 R¹ = 2,5-Me₂-thiophene; R² = Me

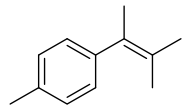
A flame-dried Schlenk flask was charged with potassium *tert*-butoxide (4 mmol, 0.43 g) and stir bar. Dry DMSO (4 mL) was added, followed by isopropyltriphenylphosphonium iodide (4 mmol, 0.43 g). This mixture was added dropwise with a syringe to a solution of the corresponding ketone (1 mmol) in toluene (3.5 mL). The reaction was heated to reflux overnight. It was allowed to cool to room temperature, and petroleum ether and water were added. The organic phase was separated and washed with water (2x25 mL) and brine (25 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. Compounds **S10**, **S11** and **S13** were purified by flash column chromatography (petroleum ether), while compounds **S12** and **S14-S18** were purified by distillation *in vacuo* at 130-170 °C.

(3-Methylbut-2-en-2-yl)benzene (S10)⁸: Colorless oil (300 mg, 80%). ¹H NMR (400



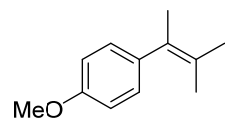
MHz, CDCl₃): δ = 1.62 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 1.99 (s, 3H, CH₃), 7.13-7.36 (m, 5H, CH=).

1-Methyl-4-(3-methylbut-2-en-2-yl)benzene (S11)⁹: Colorless oil (236 mg, 86%). ¹H



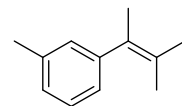
NMR (400 MHz, CDCl₃): δ = 1.60 (s, 3H, CH₃), 1.80 (s, 3H, CH₃), 1.94 (s, 3H, CH₃), 2.33 (s, 3H, CH₃, Me-Ar), 7.03 (m, 2H, CH=), 7.11 (m, 2H, CH=).

1-Methoxy-4-(3-methylbut-2-en-2-yl)benzene (S12)⁷: Colorless oil (210 mg, 81%). ¹H



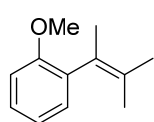
NMR (400 MHz, CDCl₃): δ = 1.60 (s, 3H, CH₃), 1.80 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 3.80 (s, 3H, CH₃-O), 6.85 (m, 2H, CH=), 7.05 (m, 2H, CH=).

1-Methyl-3-(3-methylbut-2-en-2-yl)benzene (S13): Colorless oil (222 mg, 84%). ¹H



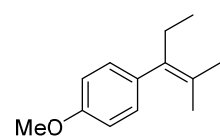
NMR (400 MHz, CDCl₃): δ = 1.61 (s, 3H, CH₃), 1.82 (s, 3H, CH₃), 1.96 (s, 3H, CH₃), 2.36 (s, 3H, CH₃, Me-Ar), 6.93-7.03 (m, 3H, CH=), 7.20 (td, 1H, CH=, Ar, J = 7.5 Hz, J = 1.1 Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ = 20.7 (CH₃), 21.0 (CH₃), 21.6 (CH₃), 22.2 (CH₃), 125.6 (CH=), 126.6 (CH=), 127.1 (C=), 127.9 (CH=), 129.2 (CH=), 130.2 (C=), 137.7 (C=), 145.4 (C=). MS HR-ESI [found 183.1142 C₁₂H₁₆ (M+Na)⁺ requires 183.1144].

1-Methoxy-2-(3-methylbut-2-en-2-yl)benzene (S14)¹⁰: Colorless oil (135 mg, 52%). ¹H



NMR (400 MHz, CDCl₃): δ = 1.53 (s, 3H, CH₃), 1.85 (s, 3H, CH₃), 1.93 (s, 3H, CH₃), 3.82 (s, 3H, CH₃-O), 6.71-6.75 (m, 3H, CH=), 7.22 (m, 1H, CH=).

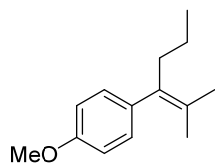
1-Methoxy-4-(2-methylpent-2-en-3-yl)benzene (S15): Colorless oil (57 mg, 30%). ¹H



NMR (400 MHz, CDCl₃): δ = 0.9 (t, 3H, CH₃, Et, J = 7.5 Hz), 1.56 (s, 3H, CH₃), 1.82 (s, 3H, CH₃), 2.34-2.39 (m, 1H, CH₂, Et), 3.84 (s, 3H, CH₃, OMe), 6.88 (d, 2H, CH=, J = 8.6 Hz), 7.04 (d, 2H, CH=, J = 8.6

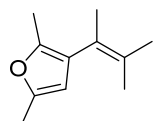
Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ = 12.9 (CH₃, Et), 19.9 (CH₃), 22.2 (CH₃), 27.6 (CH₂, Et), 55.2 (CH₃, MeO), 113.2 (CH=), 126.4 (C=), 129.9 (CH=), 136.3 (C=), 157.6 (C=). MS HR-ESI [found 213.1246 C₁₃H₁₈O (M+Na)⁺ requires 213.1250].

1-Methoxy-4-(2-methylhex-2-en-3-yl)benzene (S16): Colorless oil (51 mg, 25%). ¹H



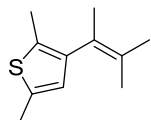
NMR (400 MHz, CDCl₃): δ= 0.77 (t, 3H, CH₃, ⁿPr, *J*= 7.3 Hz), 1.14-1.24 (m, 2H, CH₂, ⁿPr), 1.47 (s, 3H, CH₃); 1.72 (s, 3H, CH₃), 2.20-2.24 (m, 2H, CH₂, ⁿPr), 3.73 (s, 3H, CH₃, OMe), 6.77 (d, 2H, CH=, *J*= 8.6 Hz), 6.93 (d, 2H, CH=, *J*= 8.6 Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ= 14.1 (CH₃, ⁿPr), 20.2 (CH₃), 21.4 (CH₂, ⁿPr), 22.2 (CH₃), 36.8 (CH₂, ⁿPr), 55.2 (CH₃, OMe), 114.0 (CH=), 127.2 (C=), 129.9 (CH=), 134.8 (C=), 136.7 (C=), 157.2 (C=). MS HR-ESI [found 227.1405 C₁₄H₂₀O (M+Na)⁺ requires 227.1406].

2,5-Dimethyl-3-(3-methylbut-2-en-2-yl)furan (S17): Colorless oil (59 mg, 36%). ¹H



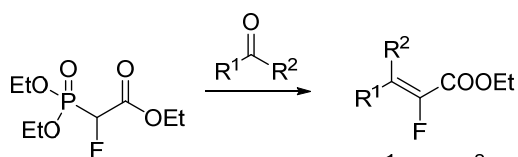
NMR (400 MHz, CDCl₃): δ= 1.57 (s, 3H, CH₃), 1.74 (s, 3H, CH₃), 1.80 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 5.74 (s, 1H, CH=). ¹³C NMR (100.6 MHz, CDCl₃): δ= 12.5 (CH₃), 13.5 (CH₃), 19.8 (CH₃), 20.2 (CH₃), 22.0 (CH₃), 107.5 (CH=), 121.6 (C=), 123.5 (C=), 128.1 (C=), 144.7 (C=), 148.9 (C=). MS HR-ESI [found 187.1090 C₁₁H₁₆O (M+Na)⁺ requires 187.1093].

2,5-Dimethyl-3-(3-methylbutan-2-yl)thiophene (S18): Colorless oil (72 mg, 40%). ¹H



NMR (400 MHz, CDCl₃): δ= 1.54 (s, 3H, CH₃), 1.80 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 2.19 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 6.39 (s, 1H, CH=). ¹³C NMR (100.6 MHz, CDCl₃): δ= 13.5 (CH₃), 15.2 (CH₃), 19.8 (CH₃), 20.0 (CH₃), 21.8 (CH₃), 124.7 (C=), 126.4 (CH=), 128.6 (C=), 130.3 (C=), 135.0 (C=), 141.4 (C=). MS HR-ESI [found 203.0865 C₁₁H₁₆S (M+Na)⁺ requires 203.0865].

SI.4. Preparation of fluorinated tetrasubstituted olefins S19-S23

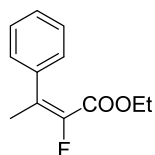


- S19** R¹= Me; R²= Ph
S20 R¹= Ph; R²= Me
S21 R¹= R²= tetrahydronaphthalene
S22 R¹= Cyc; R²= Me
S23 R¹= ⁱPr; R²= Me

Substrates **S19-S22** were prepared following a reported procedure.¹¹ To a stirred suspension of NaH (4.1 mmol, 60 % mineral dispersion, 164 mg) in anhydrous THF (2 mL) at 0 °C, 2-fluoro-2-phosphonoacetic acid triethyl ester (4.1 mmol, 1 g) was added dropwise. The reaction mixture was then heated to 40 °C and stirred for 1 h. After cooling again to 0 °C, a suitable ketone (4 mmol) was added dropwise and the resulting mixture was stirred at 40 °C for another 12 h. After completion of the reaction, monitored by TLC,

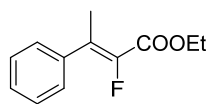
the reaction was quenched with water. The reaction mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography using n-pentane, Et₂O mixture to afford the desired tetra-substituted vinylfluorides.

Ethyl (*E*)-2-fluoro-3-phenylbut-2-enoate (S19):¹² Colorless oil (550 mg, 64%). ¹H



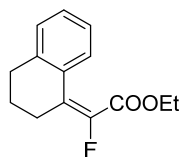
NMR (400 MHz): δ = 1.03 (t, 3H, Me, J = 7.2 Hz), 2.15 (d, 3H, MeC, J = 4.3 Hz), 4.05 (q, 2H, CH₂, J = 6.9 Hz), 7.15-7.21 (m, 2 H, CH=), 7.29-7.39 (m, 3 H, CH=).

Ethyl (*Z*)-2-fluoro-3-phenylbut-2-enoate (S20):¹² Colorless oil (120 mg, 14%). ¹H



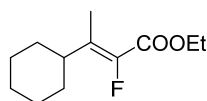
NMR (400 MHz): δ = 1.38 (t, 3H, Me, J = 7.3 Hz), 2.45 (d, 3H, MeC, J = 3.5 Hz), 4.34 (q, 2H, CH₂, J = 7.2 Hz), 7.30-7.41 (m, 5 H, CH=).

Ethyl (*E*)-2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)-2-fluoroacetate (S21):¹²



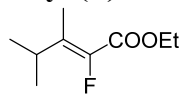
Colorless oil (440 mg, 47%). 1.33 (t, 3H, CH₃, Et, J = 7.2 Hz), 1.65-1.73 (m, 2H), 2.67-2.82 (m, 4H), 4.26 (q, 2H, CH₂, Et, J = 7.2 Hz), 7.7-7.0 (m, 4H, CH=).

Ethyl (*Z*)-3-cyclohexyl-2-fluorobut-2-enoate (S22):¹¹ Colorless oil (40 mg, 5%). ¹H



NMR (CDCl₃, 400 MHz): δ = 1.09-1.19 (m, 1H), 1.21-1.44 (m, 7H), 1.49-1.61 (m, 2H), 1.65-1.72 (m, 1H), 1.73-1.84 (m, 5H), 3.42-3.45 (m, 1H), 4.25 (q, 2H, CH₂, Et, J = 7.1 Hz).

Ethyl (*Z*)-2-fluoro-3,4-dimethylpent-2-enoate (S23):¹¹ Colorless oil (160 mg, 23%). ¹H



NMR (CDCl₃, 400 MHz): δ = 1.02 (dd, 6H, Me, ¹Pr, J = 6.9 Hz, J = 1.1 Hz), 1.33 (t, 3H, Me, Et, J = 7.1 Hz), 1.75 (d, 3H, CH₃, J = 4.4 Hz), 3.78 (pd, 1H, CH, ¹Pr, J = 6.8 Hz, J = 2.8 Hz), 4.26 (q, CH₂, Et, J = 7.1 Hz, 2H).

SI.5. Typical procedure for the hydrogenation product

The alkene (0.5 mmol) and Ir complex (2 mol%) were dissolved in CH₂Cl₂ (2 mL) in a high-pressure autoclave. The autoclave was purged four times with hydrogen. Then, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et₂O (1.5 mL) and filtered through a short plug of celite. Conversions were determined by ¹H NMR and enantiomeric excesses were determined by chiral GC.

SI.6. Optimization of the reaction conditions for the hydrogenation of acyclic vinyl fluorides

Table SI-1. Asymmetric hydrogenation of ethyl (*E*)-2-fluoro-3-phenylbut-2-enoate S19. Optimization of the catalyst and reaction conditions

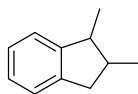
Reaction scheme: **S19** (ethyl (*E*)-2-fluoro-3-phenylbut-2-enoate) reacts with **Ir-complex** (2 mol %) in CH_2Cl_2 (0.25 M) at 23 °C under H_2 to form **27** (ethyl (2*R*,3*S*)-2-fluoro-3-phenylbutanoate).

entry	Ir-complex	P _{H₂} (bar)	% conv (% yield) ^a	dr	% ee ^b
1	5a	50	100 (98)	>99	58 (2 <i>R</i> ,3 <i>S</i>)
2	6a	50	100 (99)	>99	97 (2 <i>R</i> ,3 <i>S</i>)
3	7a	50	100 (97)	>99	48 (2 <i>R</i> ,3 <i>S</i>)
4	8a	50	100 (97)	>99	91 (2 <i>R</i> ,3 <i>S</i>)
5	6b	50	100 (-) ^c	>99	94 (2 <i>R</i> ,3 <i>S</i>)
6	6c	50	100 (-) ^c	>99	92 (2 <i>R</i> ,3 <i>S</i>)
7	6a	100	100 (-) ^c	>99	96 (2 <i>R</i> ,3 <i>S</i>)
8	6a	20	100 (-) ^c	>99	97 (2 <i>R</i> ,3 <i>S</i>)
9	6a	2	100 (99)	>99	97 (2 <i>R</i> ,3 <i>S</i>)

^a Conversions were measured by ¹H NMR spectroscopy after 24 h. ^b Enantiomeric excesses determined by chiral HPLC. ^c Isolated yield not calculated.

SI.7. Characterization and ee determination details of hydrogenated compounds

1,2-Dimethyl-2,3-dihydro-1*H*-indene (9)⁵: Pale yellow oil. Yield: 70 mg (96%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂,

Isotherm at 90 °C). t_R 11.7 (*R,R*); t_R 12.6 (*S,S*). ¹H NMR (400 MHz, CDCl₃):

δ = 0.96 (d, 3H, CH₃, J = 6.8 Hz), 1.12 (d, 3H, CH₃, J = 7.1 Hz), 2.51-2.61 (m, 2H, CH₂), 2.94-2.98 (m, 1H, CH), 3.12-3.16 (m, 1H, CH), 7.10-7.19 (m, 4H, CH=).

Racemic sample

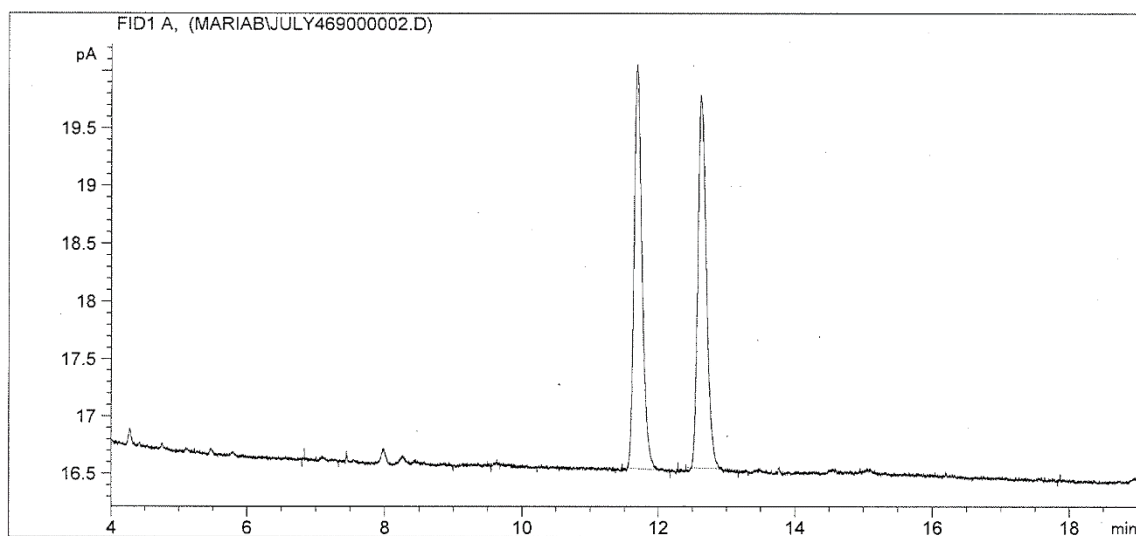
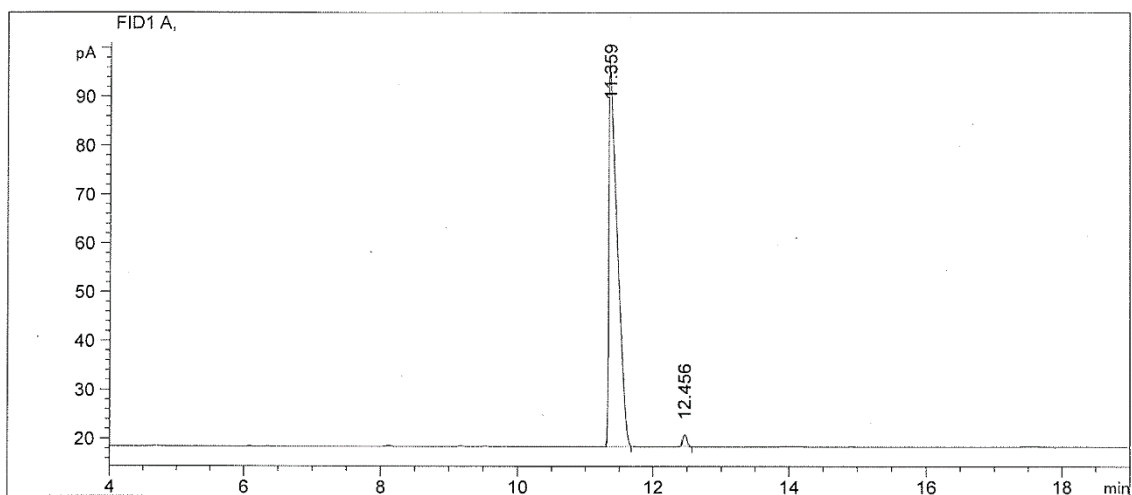
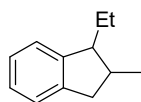


Table 1, entry 8 (95% ee)



1-Ethyl-2-methyl-2,3-dihydro-1H-indene (10)⁵: Pale yellow oil. Yield: 78 mg (98%).



Enantiomeric excess determined by GC using Hydrodex β -3P (100 kPa H₂,

Isotherm at 90 °C). t_R 18.0 (*R,R*); t_R 18.9 (*S,S*). ¹H NMR (400 MHz, CDCl₃):

δ = 0.94 (d, 3H, CH₃, J = 6.9 Hz), 1.01 (t, 3H, CH₃, Et, J = 7.4 Hz), 1.49-1.68 (m, 2H, CH₂, Et), 2.51-2.66 (m, 2H, CH₂), 2.87-2.96 (m, 2H, CH), 7.10-7.20 (m, 4H, CH=).

Racemic sample

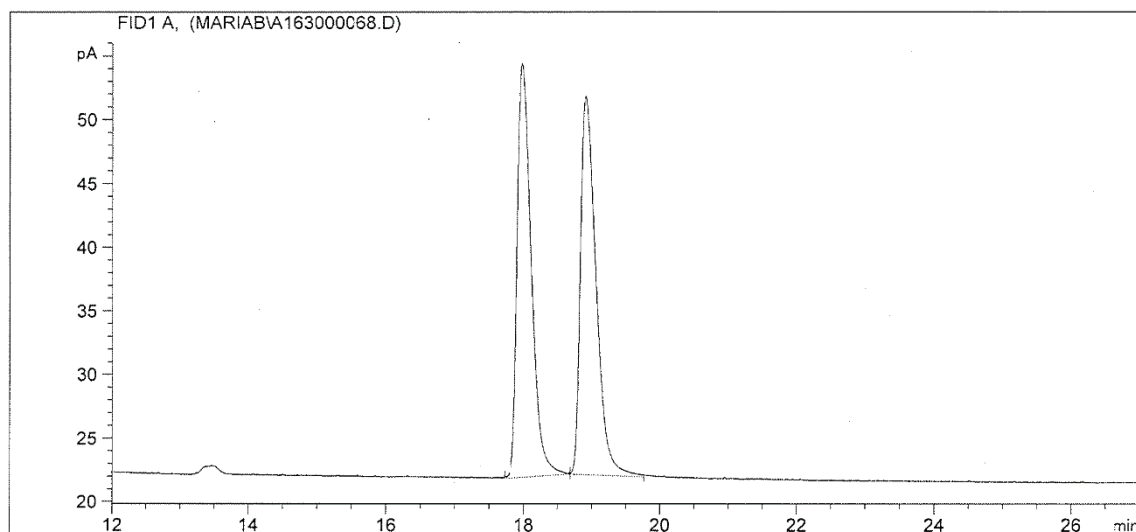
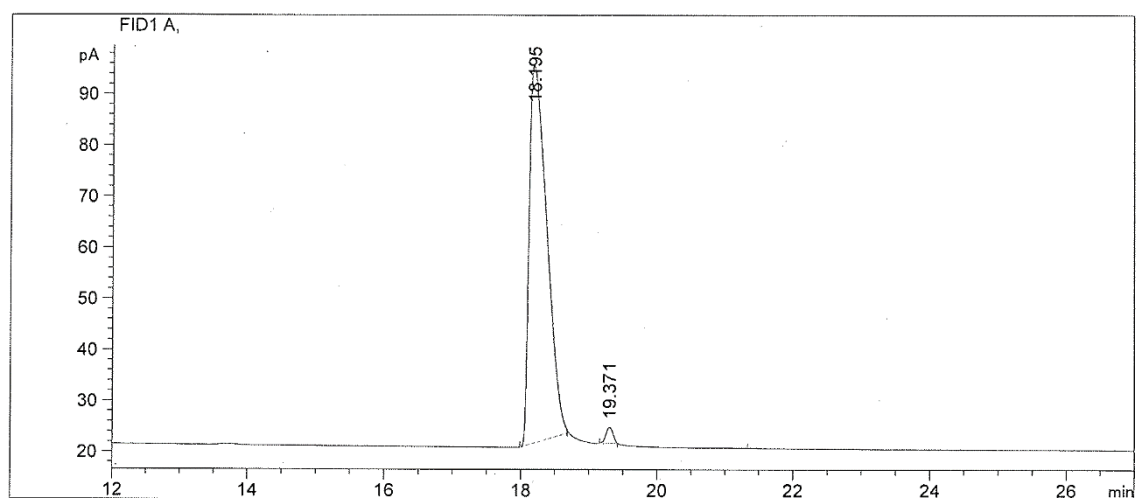
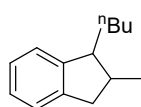


Table 2, entry 1 (95% ee)



1-Butyl-2-methyl-2,3-dihydro-1*H*-indene (11)⁶: Pale yellow oil. Yield: 90 mg (96%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 120 °C). t_R 12.8 (*R,R*); t_R 13.3 (*S,S*). ¹H NMR (400 MHz, CDCl₃):

δ = 0.91 – 0.95 (m, 6H, CH₃), 1.36-1.40 (m, 4H, CH₂, ⁿBu), 1.53-1.57 (m, 2H, CH₂, ⁿBu), 2.51-2.65 (m, 2H, CH₂), 2.90-3.00 (m, 2H, CH), 7.11-7.20 (m, 4H, CH=).

Racemic sample

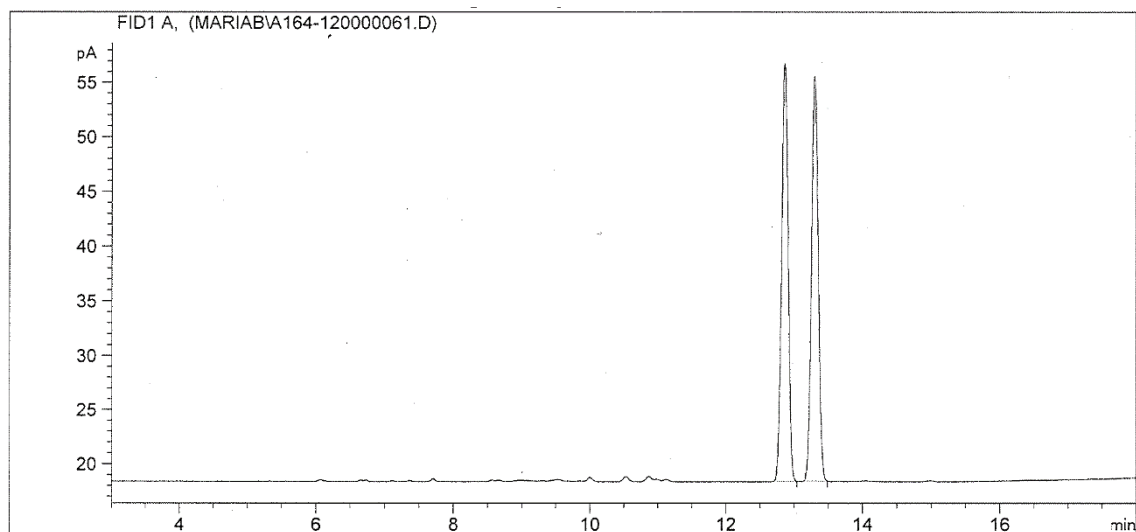
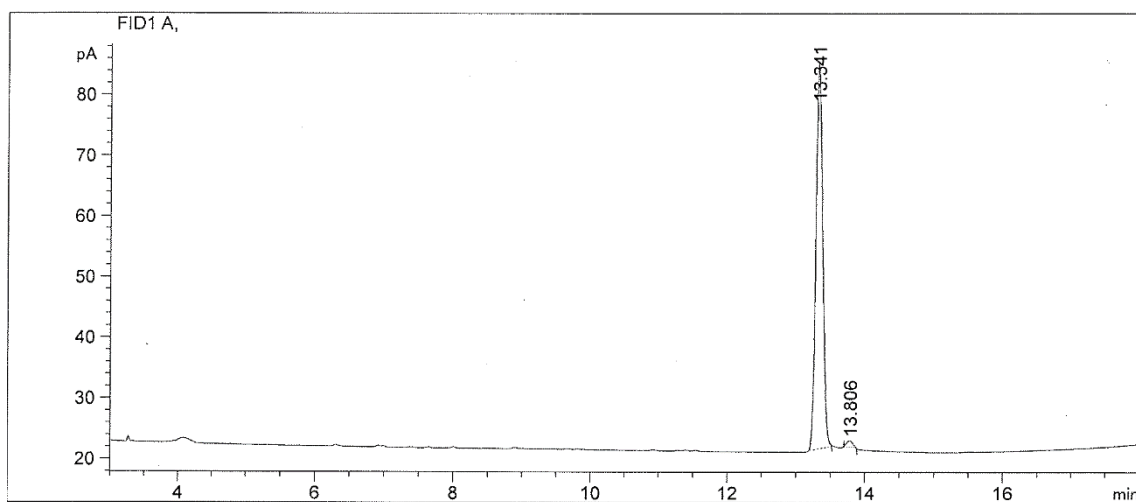
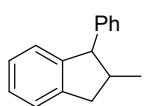


Table 2, entry 2 (96% ee)



2-Methyl-1-phenyl-2,3-dihydro-1*H*-indene (12)⁵: Colorless solid. Enantiomeric excess



determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 150 °C).

t_R 13.6 (*S,R*); t_R 14.6 (*R,S*). ¹H NMR (400 MHz, CDCl₃): δ = 0.70 (d, 3H,

CH₃, J = 7.0 Hz), 2.68 (dd, 1H, CH₂, J = 15.4 Hz, J = 7.4 Hz), 2.83 (m, 1H,

CH), 3.05 (dd, 1H, CH₂, J = 15.4 Hz, J = 7.4 Hz), 4.37 (d, 1H, CH-Ph, J = 7.9 Hz), 6.98

(m, 2H, CH=), 7.14-7.33 (m, 7H, CH=).

Racemic sample

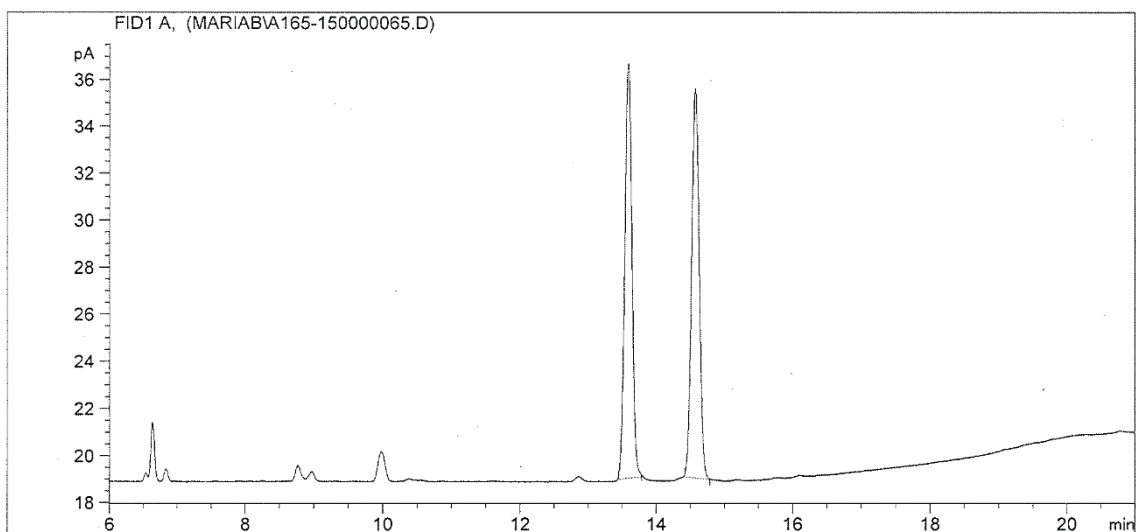
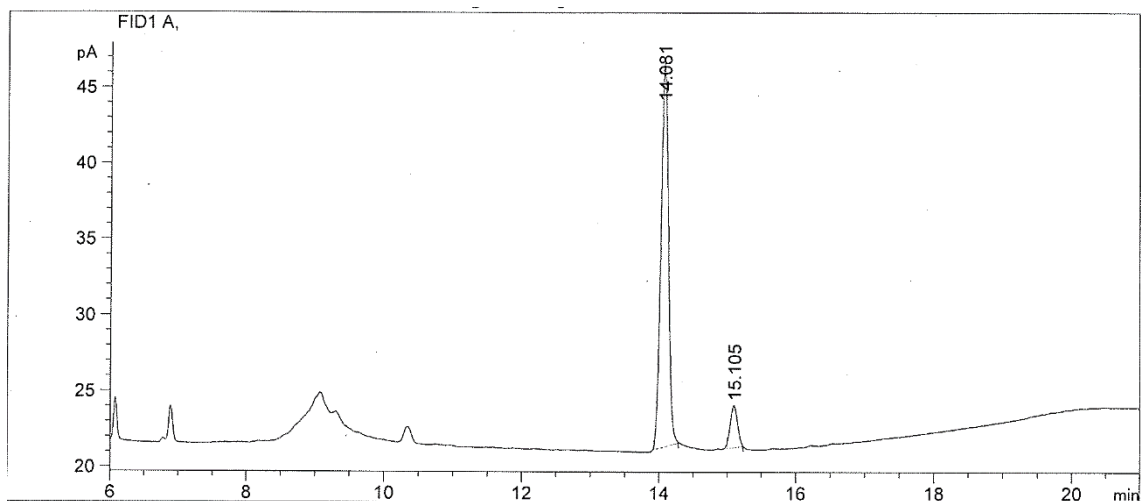
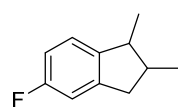


Table 2, entry 3 (82% ee)



5-Fluoro-1,2-dimethyl-2,3-dihydro-1*H*-indene (13)³: Yellow oil. Yield: 77 mg (94%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 90 °C). t_R 15.5 (*R,R*); t_R 17.4 (*S,S*). ¹H NMR (400 MHz, CDCl₃): δ = 0.96 (d, 3H, CH₃, J = 6.9 Hz), 1.10 (d, 3H, CH₃, J = 7.2 Hz), 2.49-2.64 (m, 2H, CH₂), 2.89-3.00 (m, 1H, CH), 3.07-3.14 (m, 1H, CH), 6.81-6.89 (m, 2H, CH=), 7.08 (dd, 1H, CH, J = 8.1 Hz, J = 5.3 Hz).

Racemic sample

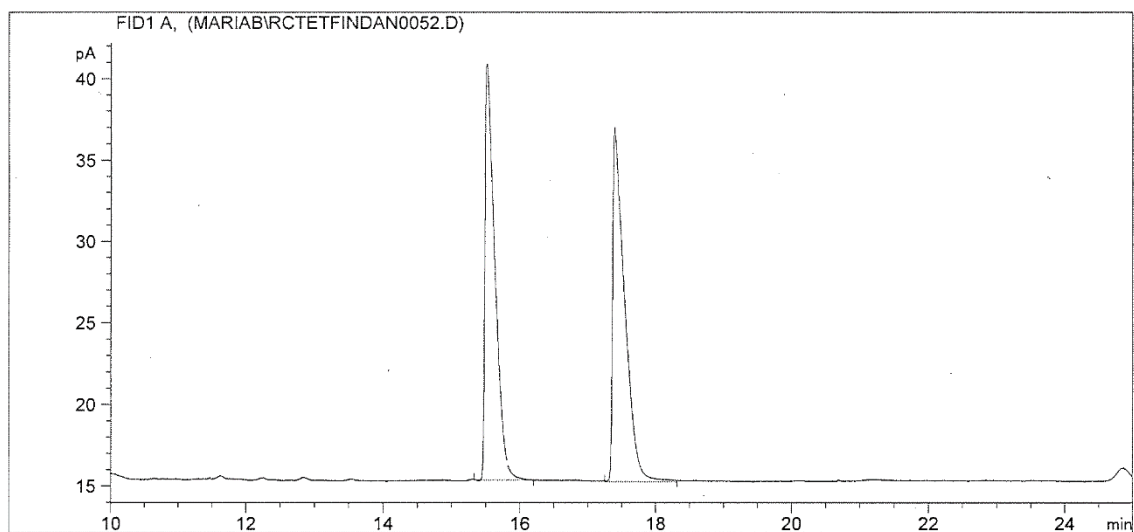
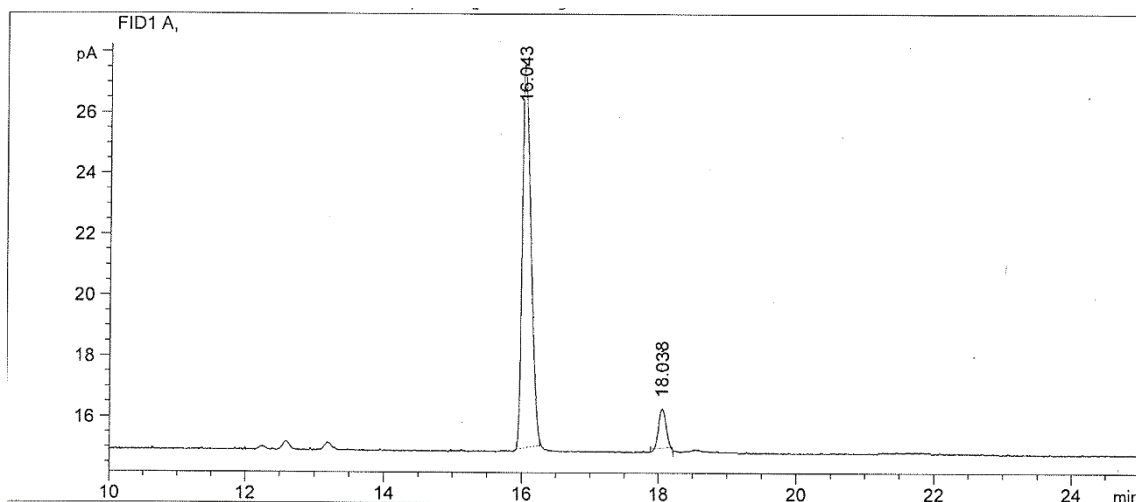
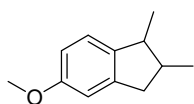


Table 2, entry 4 (85% ee)



5-Methoxy-1,2-dimethyl-2,3-dihydro-1*H*-indene (14)³: Pale yellow oil. Yield: 84 mg (96%). Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 150 °C). *t_R* 5.3 (*R,R*); *t_R* 5.4 (*S,S*). ¹H NMR (400 MHz, CDCl₃): δ = 0.98 (d, 3H, CH₃, *J* = 6.9 Hz), 1.11 (d, 3H, CH₃, *J* = 7.2 Hz), 2.46-2.65 (m, 2H, CH₂), 2.90-3.02 (m, 1H, CH), 3.06-3.17 (m, 1H, CH), 3.80 (s, 3H, CH₃-O), 6.73 (dd, 1H, CH=, *J* = 8.2 Hz, *J* = 2.4 Hz), 6.78 (d, 1H, CH=, *J* = 2.4 Hz), 7.08 (d, 1H, CH=, *J* = 8.2 Hz).



Racemic sample

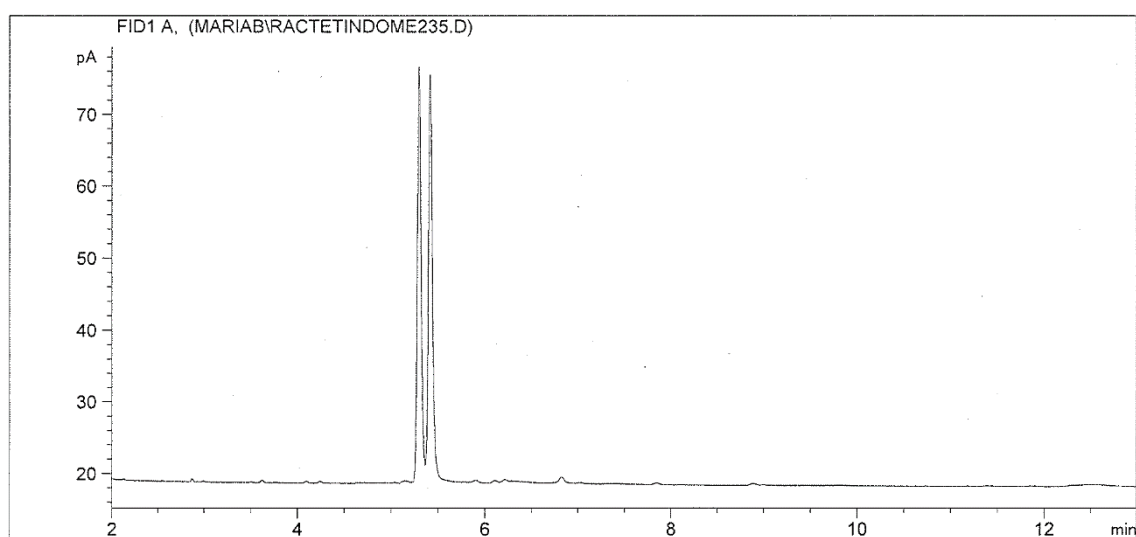
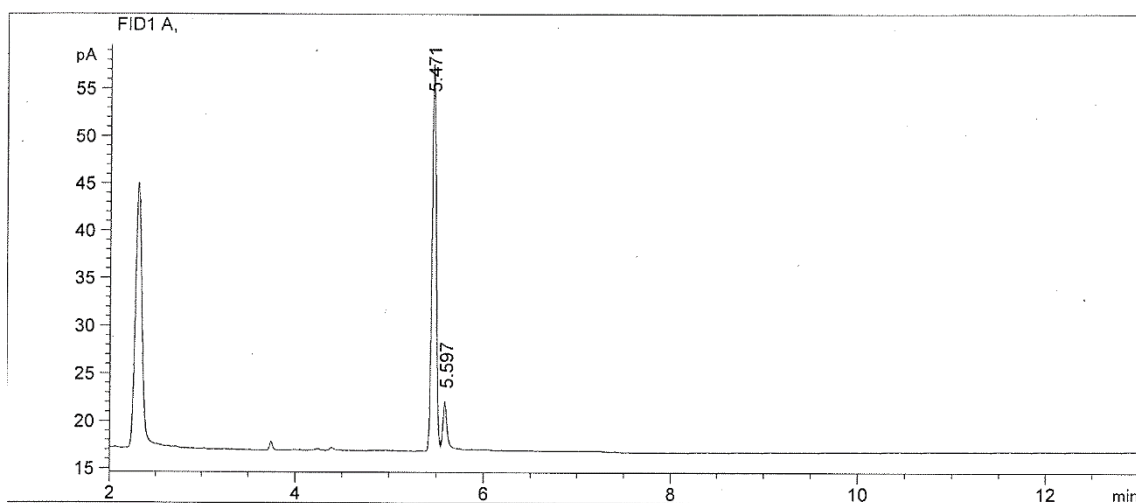
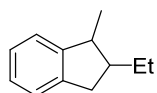


Table 2, entry 5 (91% ee)



2-Ethyl-1-methyl-2,3-dihydro-1H-indene (15)¹³: Colorless oil. Yield: 73 mg (91%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 90 °C). t_R 18.9 (*R,R*); t_R 19.9 (*S,S*). ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, 3H, CH₃, Et, J = 8.0 Hz), 1.04 (d, 3H, CH₃, J = 7.5 Hz), 1.42 (m, 1H, CH₂, Et), 1.53 (m, 1H, CH₂, Et), 2.30 (m, 1H, CH₂), 2.60 (dd, 1H, CH₂, J = 9.4 Hz, J = 15.4 Hz), 2.90 (dd, 1H, CH, J = 7.5 Hz, J = 15.4 Hz), 3.16 (m, 1H, CH), 7.08-7.18 (m, 4H, CH=).

Racemic sample

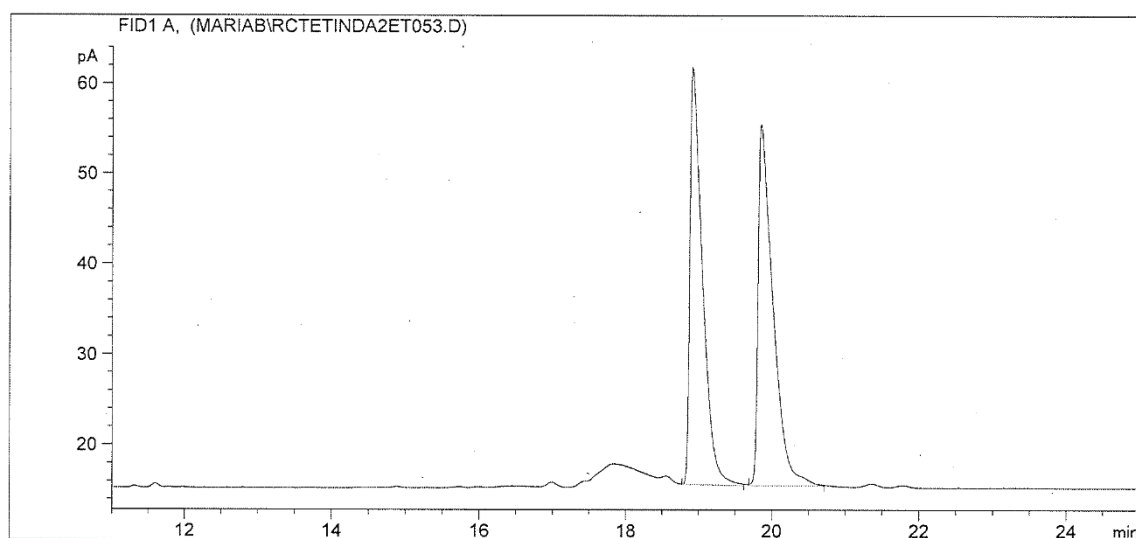
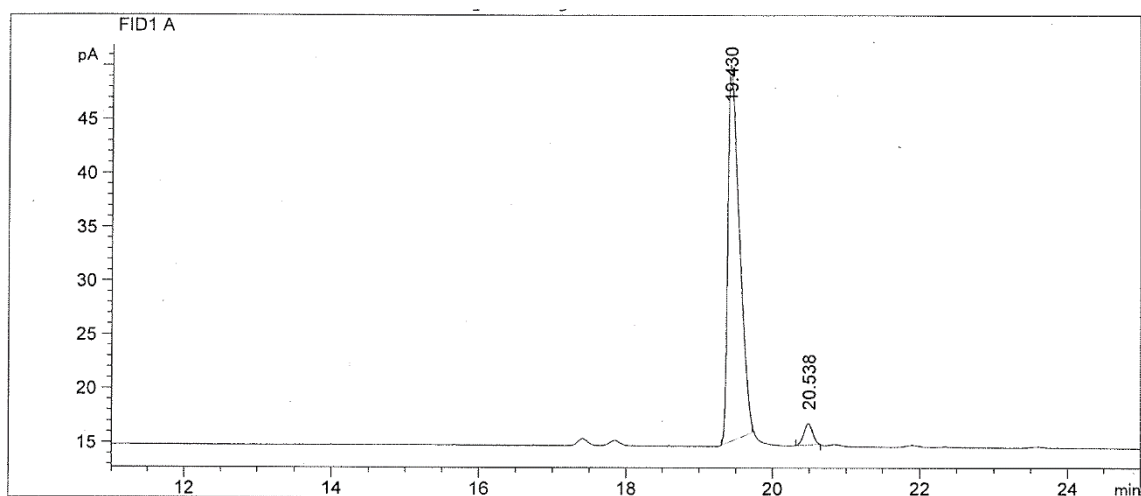
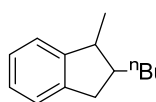


Table 2, entry 6 (92% ee)



2-Butyl-1-methyl-2,3-dihydro-1*H*-indene (16)⁵: Colorless oil. Yield: 87 mg (92%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H_2 , 90 °C, 45 min – 5 °C/min – 175 °C). t_R 53.2 (*R,R*); t_R 53.8 (*S,S*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (m, 3H, CH_3 , nBu), 1.03 (d, 3H, CH_3 , J = 7.0 Hz), 1.30-1.45 (m, 5H, CH_2 , nBu), 1.69-1.74 (1H, m, CH_2 , nBu), 1.85-1.95 (m, 1H, CH_2), 2.51 (dd, 1H, CH_2 , J = 9.2 Hz, J = 15.7 Hz), 2.76 (qd, 1H, CH, J = 6.6 Hz, J = 7.0 Hz), 3.05 (dd, 1H, CH, J = 7.7 Hz, J = 15.6 Hz), 7.11-7.19 (m, 4H, CH=).

Racemic sample

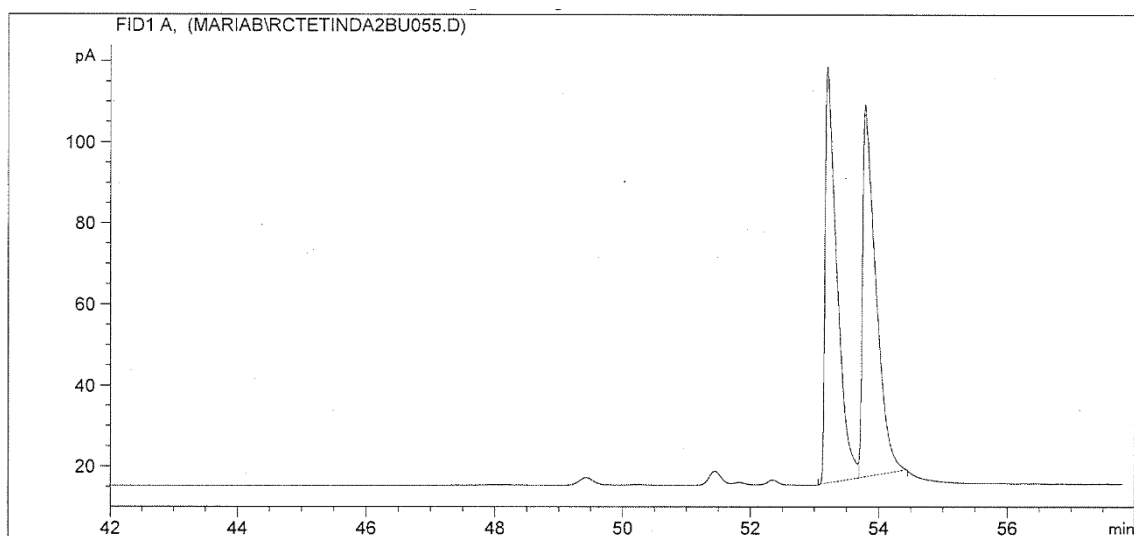
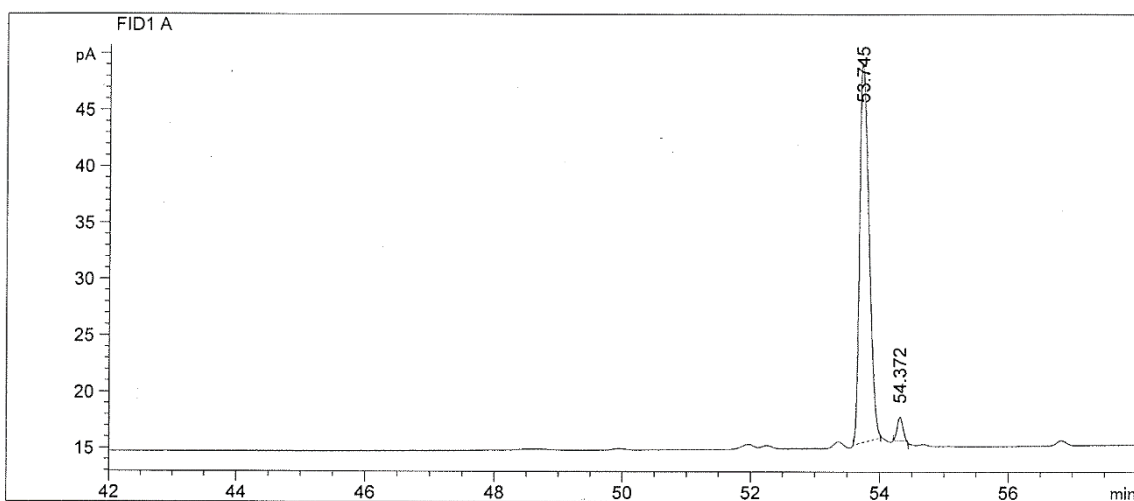
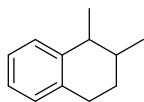


Table 2, entry 7 (91% ee)



1,2-Dimethyl-1,2,3,4-tetrahydronaphthalene (17)⁵: Colorless oil. Yield: 75 mg (93%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂,

Isotherm at 90 °C). t_R 28.1 (*R,R*); t_R 33.7 (*S,S*). ¹H NMR (400 MHz, CDCl₃):

δ = 0.99 (d, 3H, CH₃, J = 6.9 Hz), 1.11 (d, 3H, CH₃, J = 7.2 Hz), 1.64 (dq, 2H, CH₂, J = 6.4 Hz, J = 2.0 Hz), 1.98 (m, 1H, CH), 2.82 (m, 3H, CH, CH₂), 7.08-7.16 (m, 4H, CH=).

Racemic sample

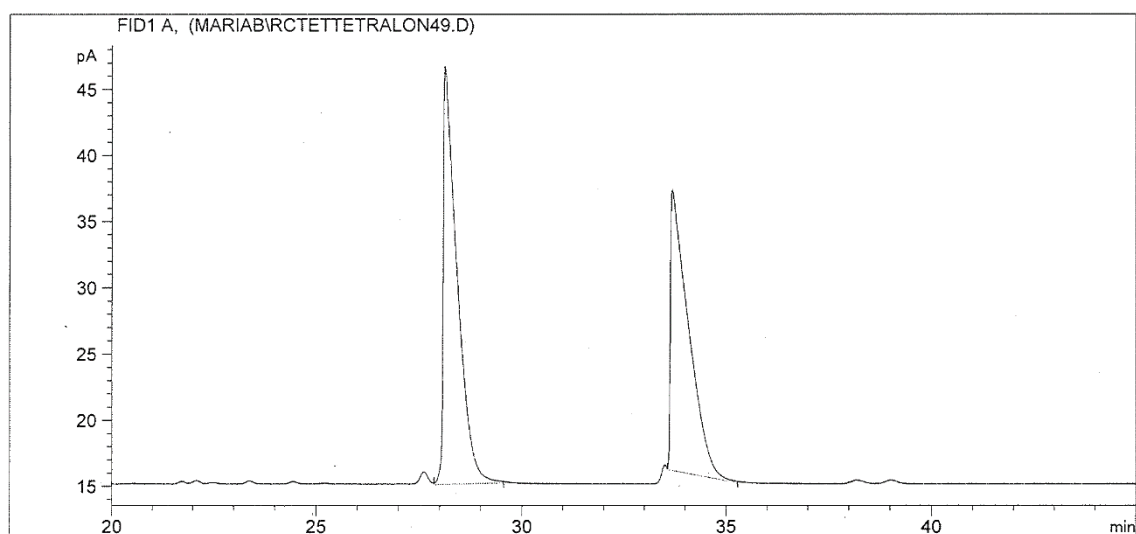
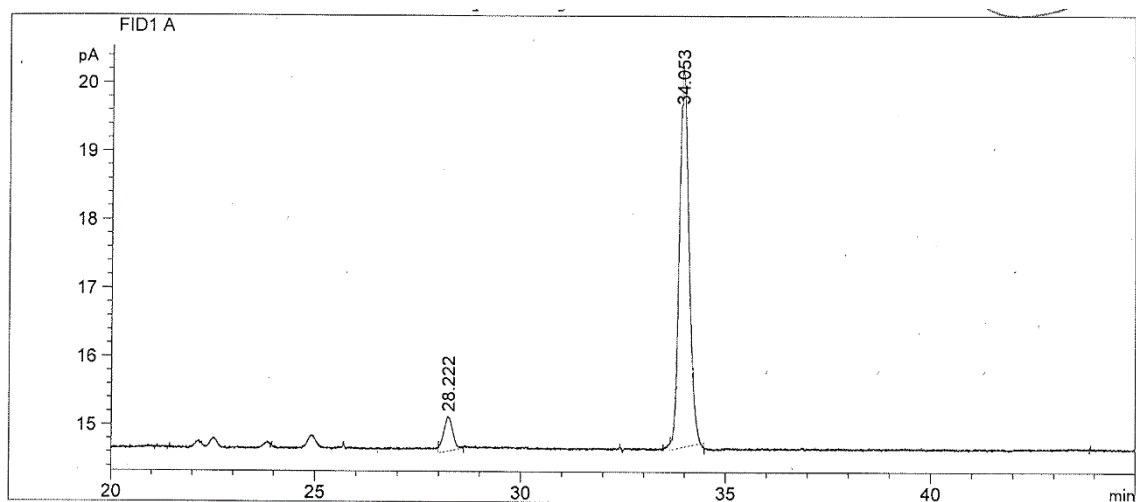
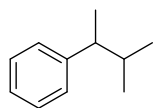


Table 2, entry 8 (89% ee)



(3-Methylbutan-2-yl)benzene (18)⁸: Colorless oil. Yield: 70 mg (95%). Enantiomeric



excess determined by GC using Chiraldex β -DM (100 kPa H₂, Isotherm at 60 °C). t_R 22.5 (*S*); t_R 24.4 (*R*). ¹H NMR (400 MHz, CDCl₃): δ = 0.76 (d, 3H, CH₃, J = 6.7 Hz), 0.94 (d, 3H, CH₃, J = 6.7 Hz), 1.24 (d, 3H, CH₃, J = 7.0 Hz), 1.77 (m, 1H, CH), 2.42 (d, 1H, CH, J = 7.0 Hz), 7.14-7.35 (m, 5H, CH=).

Racemic sample

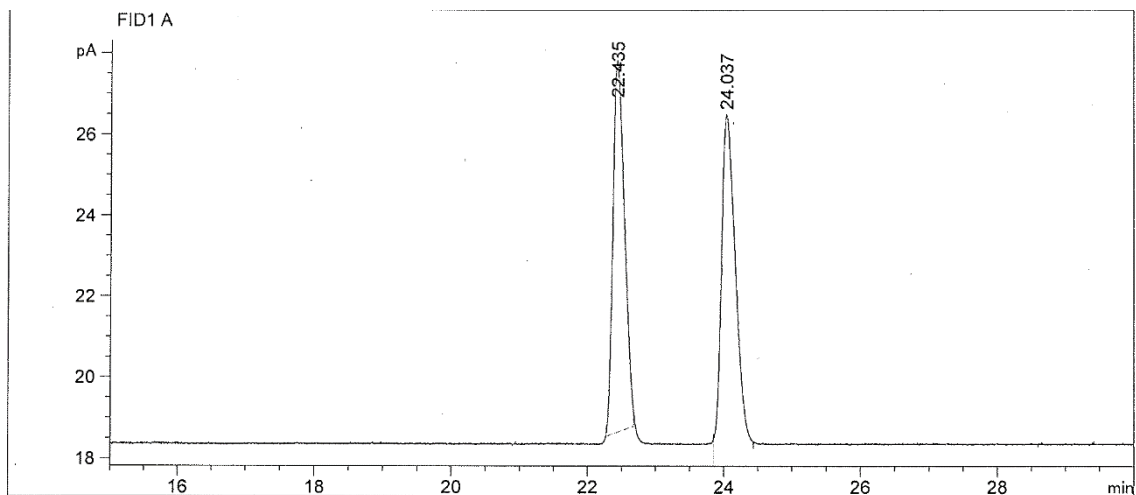
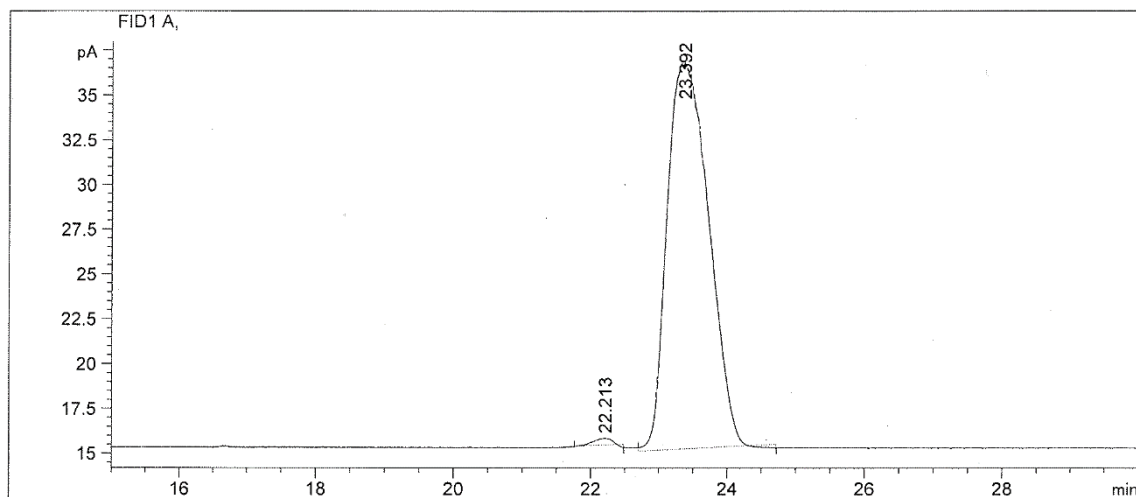
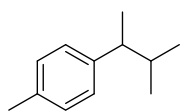


Table 3, entry 9 (98% ee)



1-Methyl-4-(3-methylbutan-2-yl)benzene (19)¹⁴: Colorless oil. Yield: 78 mg (96%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H_2 , 60 °C, 30 min – 3 °C/min – 175 °C). t_R 38.7 (*S*); t_R 40.0 (*R*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, 3H, CH_3 , J = 6.7 Hz), 0.92 (d, 3H, CH_3 , J = 6.7 Hz), 1.21 (d, 3H, CH_3 , J = 7.1 Hz), 1.68 (m, 1H, CH), 2.32 (s, 3H, CH_3), 2.39 (q, 1H, CH, J = 7.2 Hz), 7.05 (d, 2H, CH=, J = 7.9 Hz), 7.09 (d, 2H, CH=, J = 7.9 Hz).

Racemic sample

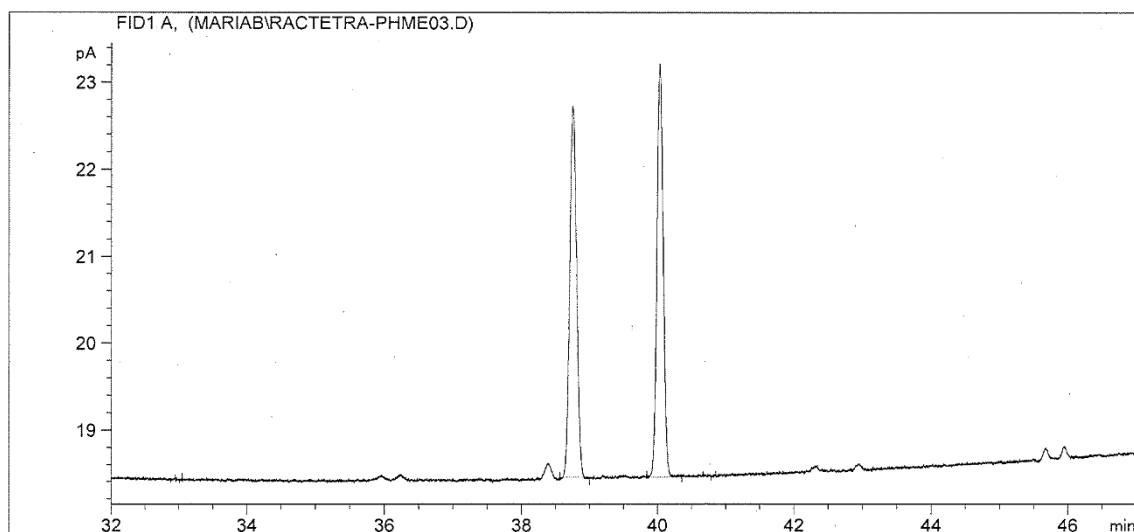
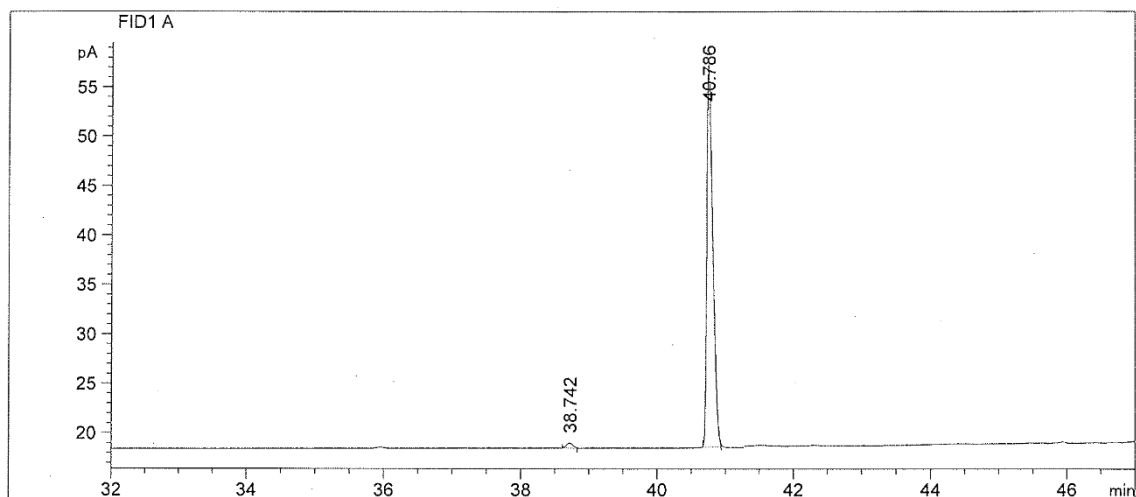
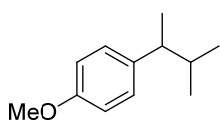


Figure 3 (97% ee)



1-Methoxy-4-(3-methylbutan-2-yl)benzene (20)⁶: Colorless oil. Yield: 86 mg (97%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, 60 °C, 30 min – 3 °C/min – 175 °C). t_R 50.7 (*S*); t_R 51.3 (*R*).

¹H NMR (400 MHz, CDCl₃): δ = 0.74 (d, 3H, CH₃, J = 6.7 Hz), 0.91 (d, 3H, CH₃, J = 6.7 Hz), 1.20 (d, 3H, CH₃, J = 7.1 Hz), 1.71 (m, 1H, CH), 2.38 (m, 1H, CH), 3.78 (s, 3H, CH₃-O), 7.02-7.09 (m, 4H, CH=).

Racemic sample

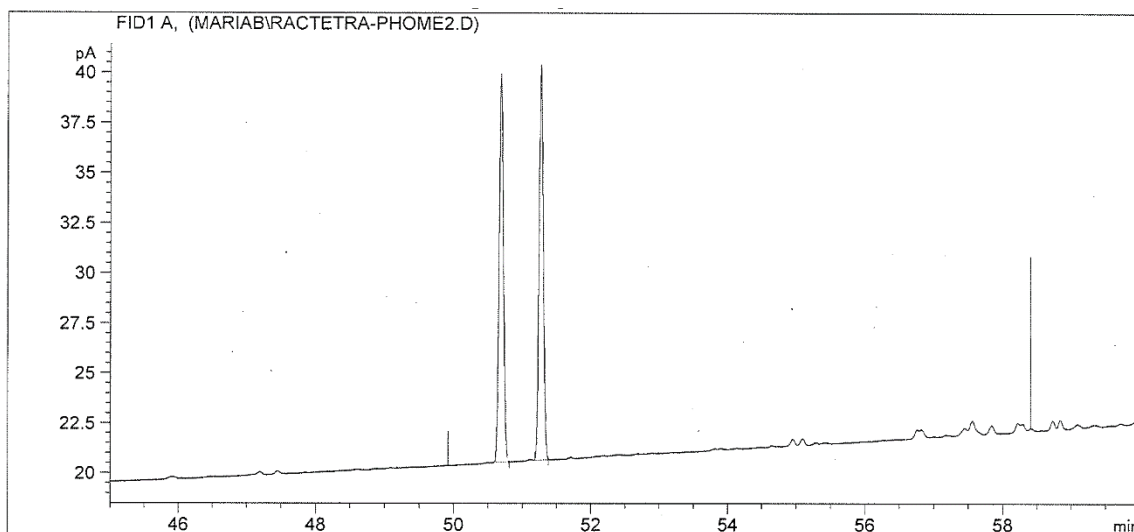
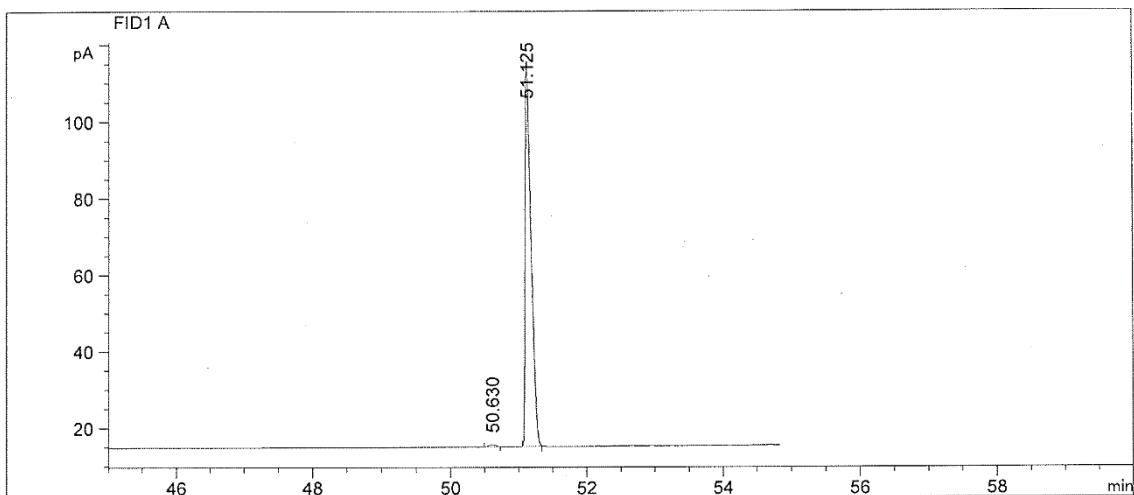
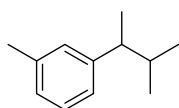


Figure 3 (98% ee)



1-Methyl-3-(3-methylbutan-2-yl)benzene (21): Colorless oil. Yield: 77 mg (95%).



Enantiomeric excess determined by GC using Hydrodex β -3P (100 kPa H_2 , 50 °C, 30 min – 3 °C/min – 170 °C). t_R 43.2 (*S*); t_R 43.5 (*R*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (d, 3H, CH_3 , J = 6.7 Hz), 0.92 (d, 3H, CH_3 , J = 6.7 Hz), 1.23 (d, 3H, CH_3 , J = 7.0 Hz), 1.78 (m, 1H, CH), 2.33 (s, 3H, CH_3), 2.39 (m, 1H, CH), 6.98 (m, 3H, CH=), 7.17 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.9 (CH_3), 20.3 (CH_3), 21.4 (CH_3), 21.7 (CH_3), 34.5 (CH), 47.0 (CH), 124.8 (CH=), 126.5 (CH=), 128.0 (CH=), 128.6 (CH=), 137.5 (C), 147.3 (C). MS HR-ESI [found 185.1298 $C_{12}H_{18}$ ($M+Na$) $^+$ requires 185.1301].

Racemic sample

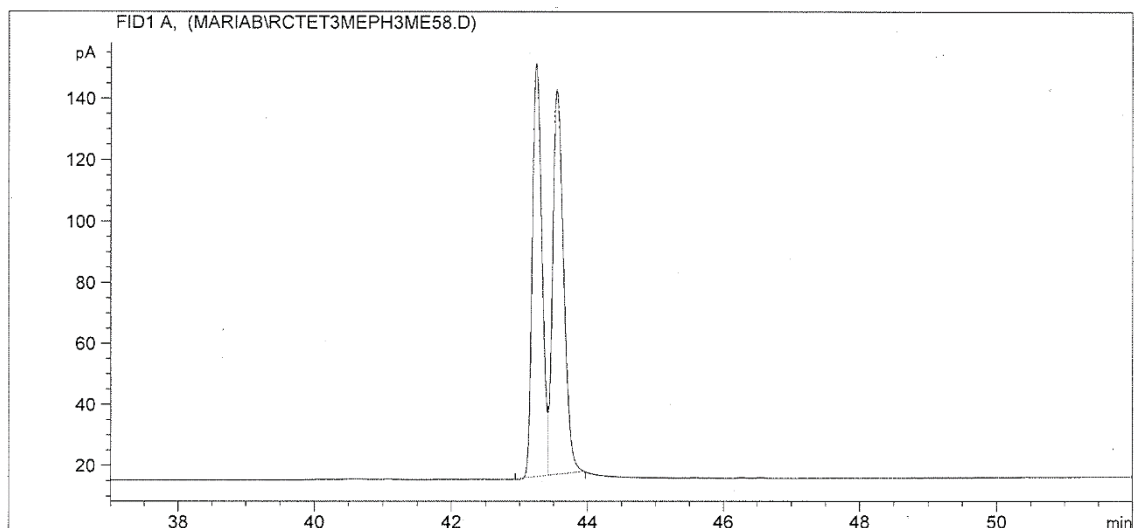
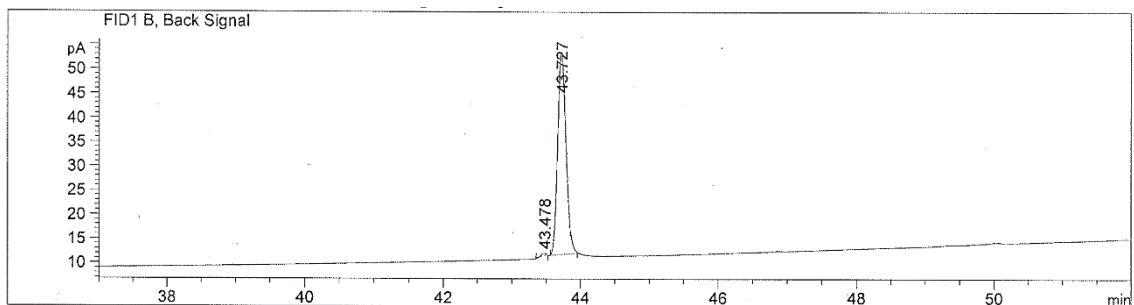
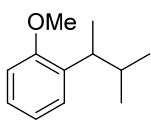


Figure 3 (99% ee)



1-Methoxy-2-(3-methylbutan-2-yl)benzene (22): Colorless oil. Yield: 83 mg (93%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H_2 , 60 °C, 30 min – 3 °C/min – 175 °C). t_R 48.7 (*S*); t_R 49.1 (*R*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.77 (d, 3H, CH_3 , J = 6.7 Hz), 0.92 (d, 3H, CH_3 , J = 6.7 Hz), 1.21 (d, 3H, CH_3 , J = 7.0 Hz), 1.76 (m, 1H, CH), 2.39 (m, 1H, CH), 3.8 (s, 3H, CH_3 -O), 6.72 (m, 3H, CH=), 7.18 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.6 (CH_3), 20.2 (CH_3), 21.1 (CH_3), 34.4 (CH), 46.9 (CH), 55.1 (CH_3 -O), 110.6 (CH=), 113.7 (CH=), 120.2 (CH=), 129.0 (CH=), 148.9 (C), 159.4 (C). MS HR-ESI [found 201.1249 $C_{12}H_{18}O$ ($M+Na$) $^+$ requires 201.1250].

Racemic sample

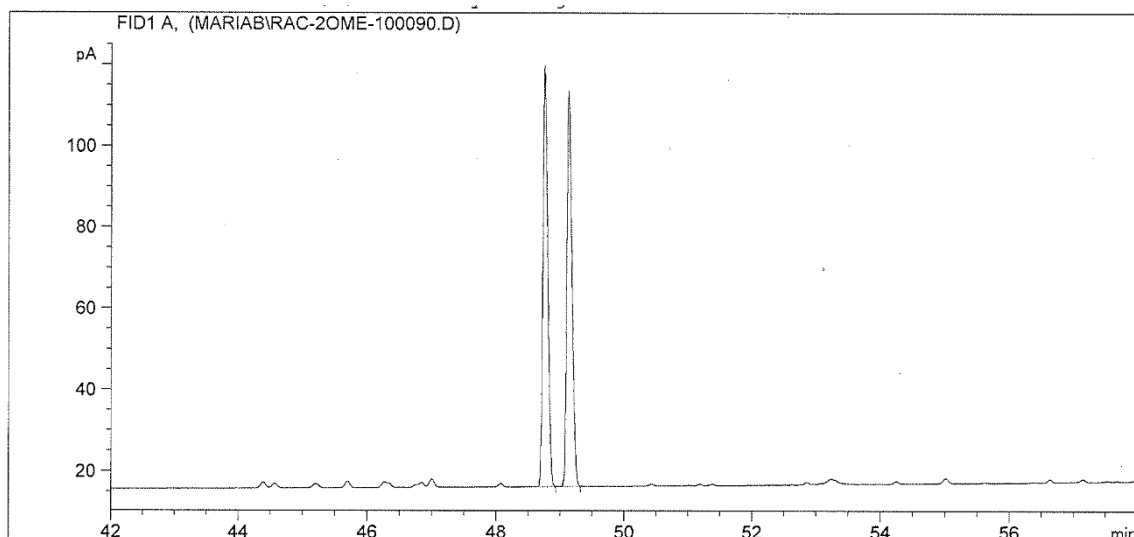
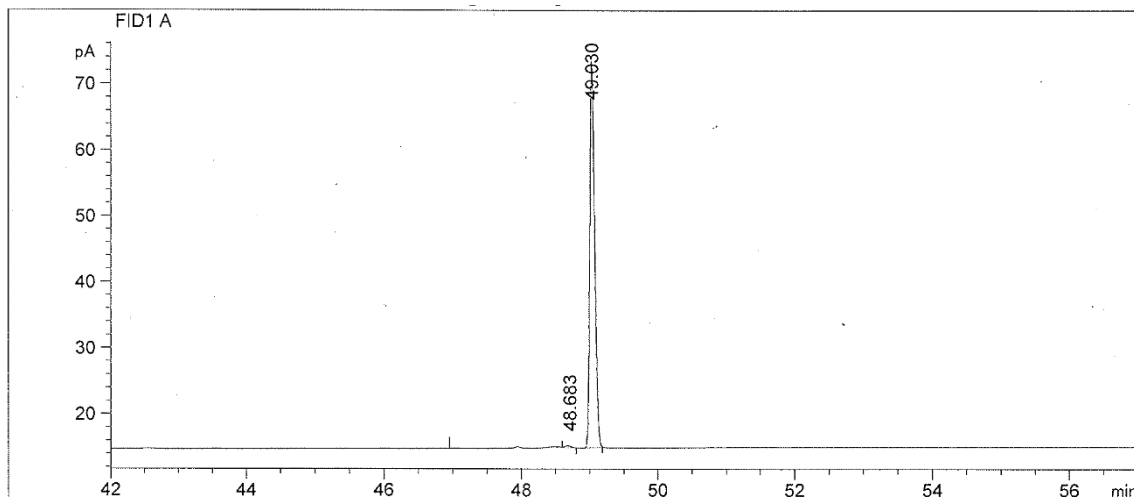
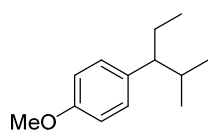


Figure 3 (98% ee)



1-Methoxy-4-(2-methylpentan-3-yl)benzene (23): Colorless oil. Yield: 95 mg (99%).



Enantiomeric excess determined by GC using Chiraldex β -DM (100 kPa H₂, 70 °C, 120 min – 3 °C/min – 175 °C). t_R 108.1 (*S*); t_R 110.5 (*R*). ¹H NMR (400 MHz, CDCl₃): δ = 0.70 (m, 6H, CH₃, Et and CH₃), 0.92 (d, 3H, CH₃, J = 6.7 Hz), 1.45-1.53 (m, 1H, CH), 1.71-1.81 (m, 2H, CH₂, Et), 2.06-2.12 (m, 1H, CH), 3.78 (s, 3H, CH₃, OMe), 6.81 (d, 2H, CH=, J = 8.6 Hz), 7.00 (d, 2H, CH=, J = 8.6 Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ = 12.4 (CH₃, Et), 20.5 (CH₃), 21.0 (CH₃), 25.8 (CH₂, Et), 33.2 (CH), 54.0 (CH), 55.1 (CH₃, MeO), 113.3 (CH=), 129.4 (CH=), 136.4 (C=), 157.5 (C=). MS HR-ESI [found 2015.1404 C₁₃H₂₀O (M+Na)⁺ requires 215.1406].

Racemic sample

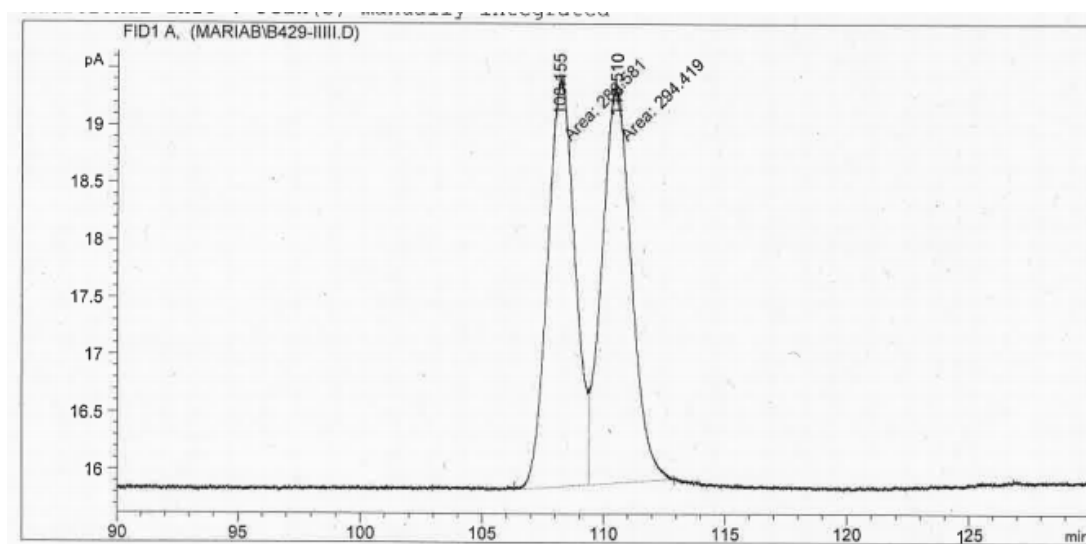
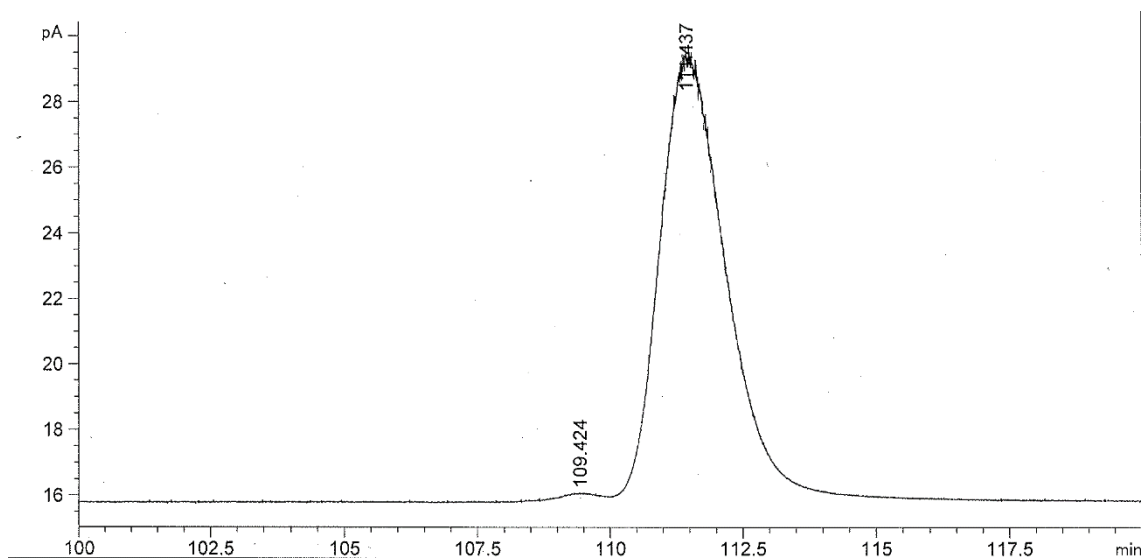
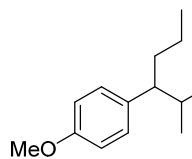


Figure 3 (97% ee)



1-Methoxy-4-(2-methylhexan-3-yl)benzene (24): Colorless oil. Yield: 100 mg (97%).



Enantiomeric excess determined by GC Hydrodex β -3P (100 kPa, 60 °C – 30 min – 1 °C/min – 175 °C). t_R 77.8 (+); t_R 78.3 (-). 1H NMR (400 MHz, $CDCl_3$): δ = 0.69 (d, 3H, CH_3 , J = 7.3 Hz), 0.81 (t, 3H, CH_3 , nPr , J = 6.7 Hz), 0.89 (d, 3H, CH_3 , J = 7.3 Hz), 1.06-1.09 (m, 2H, CH_2 , nPr), 1.45-1.48 (m, 1H, CH), 1.68-1.72 (m, 2H, CH_2 , nPr), 2.17-2.19 (m, 1H, CH), 3.77 (s, 3H, CH_3 , MeO), 6.81-6.85 (m, 2H, CH=), 6.97-6.99 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (CH_3 , nPr), 20.6 (CH_3), 21.0 (CH_2), 21.1 (CH_3), 33.5 (CH), 35.3 (CH_2), 51.9 (CH), 55.2 (CH_3O), 113.2 (CH=), 129.3 (CH=), 136.7 (C=), 157.6 (C=). MS HR-ESI [found 229.1561 $C_{14}H_{22}O$ ($M+Na$) $^+$ requires 229.1563].

Racemic sample

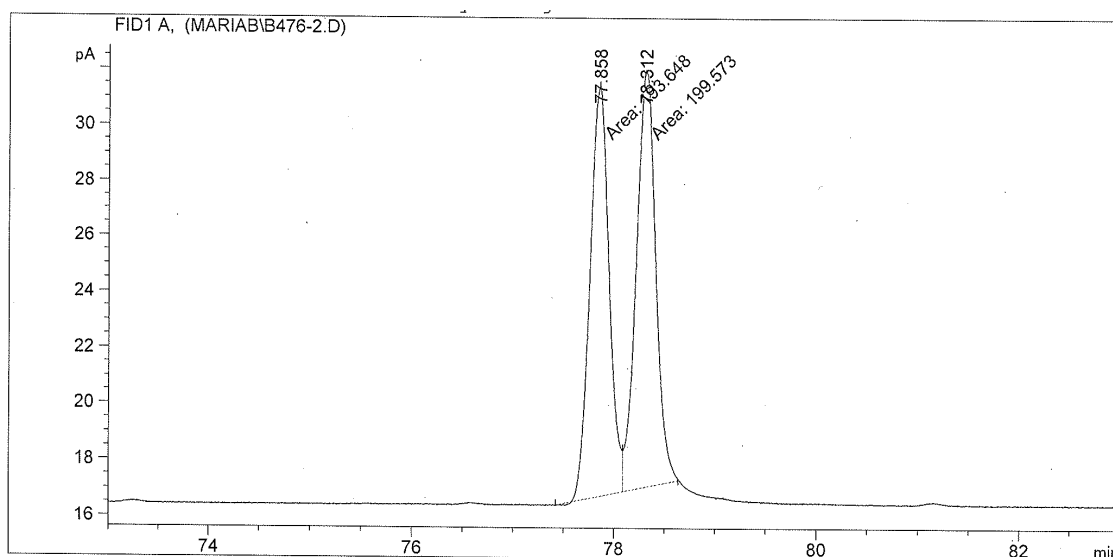
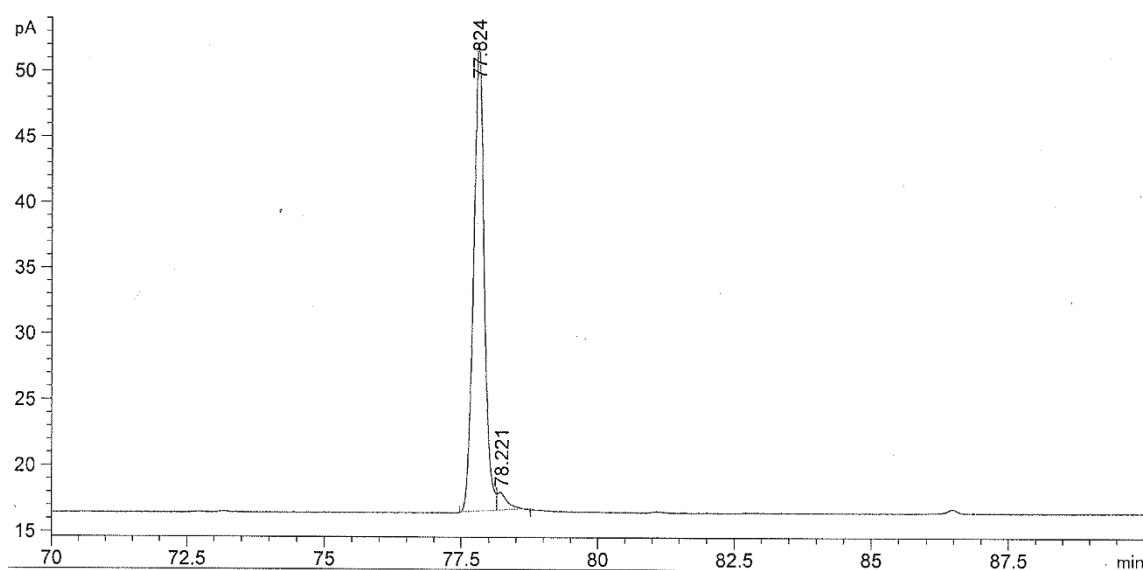
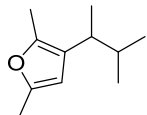


Figure 3 (96% ee)



2,5-Dimethyl-3-(3-methylbutan-2-yl)furan (25): Colorless oil. Yield: 91 mg (96%).



Enantiomeric excess determined by GC ChiralDEX β -DM (100 kPa, 60 °C).

t_R 15.4 (*S*); t_R 16.5 (*R*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (d, 3H, CH_3 , J = 7.0 Hz), 0.88 (d, 3H, CH_3 , J = 6.7 Hz), 1.08 (d, 3H, CH_3 , J = 6.7 Hz), 1.53-1.61 (m, CH, 1H), 2.14 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.19-2.26 (m, 1H, CH), 5.73 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.6 (CH_3), 13.5 (CH_3), 18.8 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 34.4 (CH), 36.8 (CH), 105.7 (CH=), 124.1 (C=), 144.7 (C=), 148.7 (C=). MS HR-ESI [found 189.1248 $C_{11}H_{18}O$ ($M+Na$) $^+$ requires 189.1250].

Racemic sample

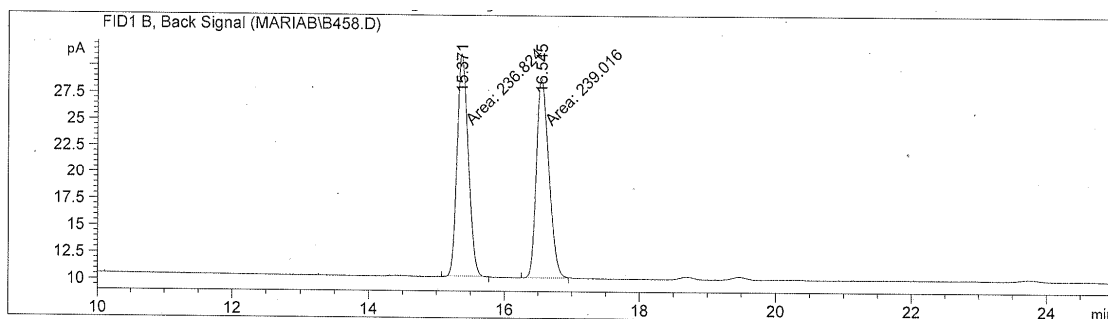
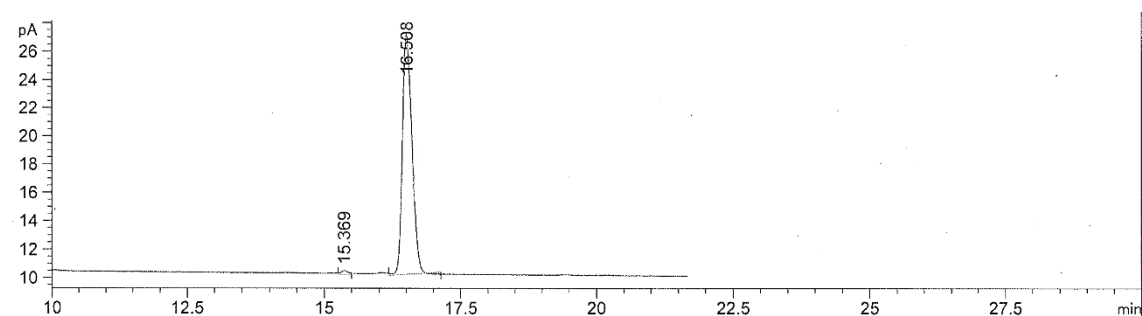
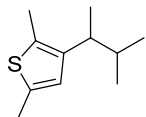


Figure 3 (98% ee)



2,5-Dimethyl-3-(3-methylbutan-2-yl)thiophene (26): Colorless oil. Yield: 61 mg



(67%). Enantiomeric excess determined by GC ChiralDEX B-DM (100 kPa, 60 °C – 30 min – 1 °C/min – 175 °C). t_R 38.9 (*S*); t_R 39.5 (*R*). 1H NMR (400 MHz, $CDCl_3$): δ = 0.72 (d, 3H, CH_3 , J = 7.0 Hz), 0.91 (d, 3H, CH_3 , J = 6.7 Hz), 1.10 (d, 3H, CH_3 , J = 6.7 Hz), 1.54-1.62 (m, CH, 1H), 2.25 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.36-2.40 (m, 1H, CH), 6.43 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.6 (CH_3), 15.4 (CH_3), 18.4 (CH_3), 20.0 (CH_3), 20.8 (CH_3), 34.6 (CH), 38.9 (CH), 108.7 (C=), 125.1 (CH=), 135.6 (C=), 142.7 (C=). MS HR-ESI [found 205.1018 $C_{11}H_{18}S$ ($M+Na$) $^+$ requires 205.1021].

Racemic sample

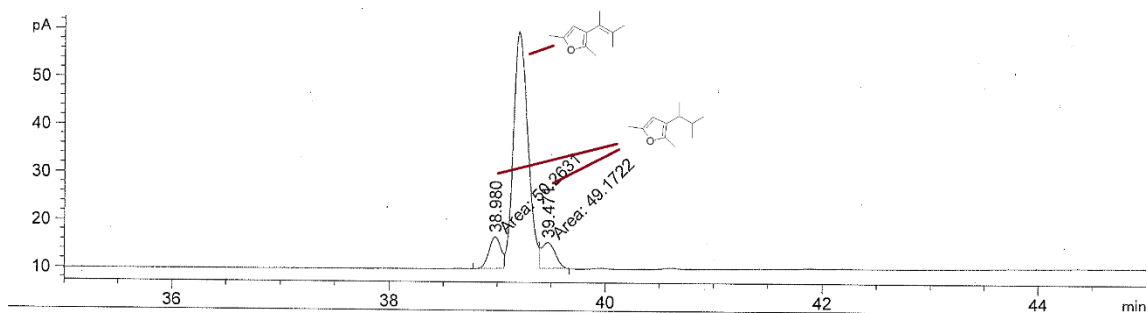
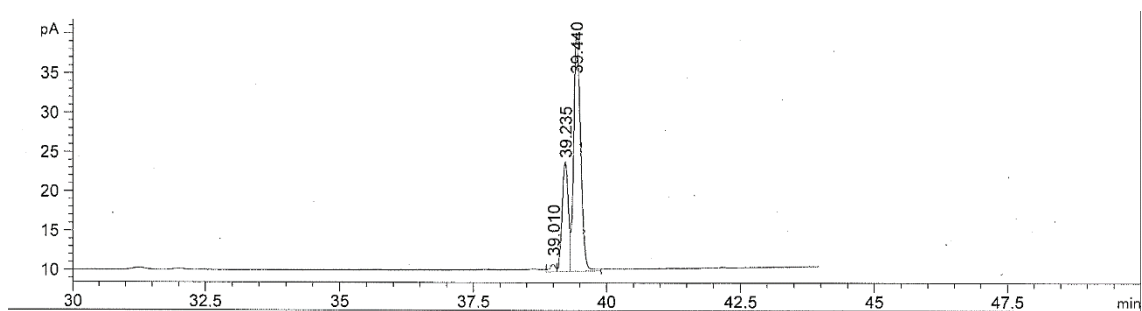
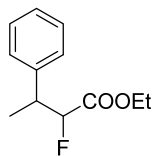


Figure 3 (96% ee)



Ethyl 2-fluoro-3-phenylbutanoate (27):¹¹



From (*E*)-ethyl 2-fluoro-3-phenylbut-2-enoate (S19): Colorless oil.

Yield: 104 mg (99%). Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1mL/min, λ = 210 nm). t_R 10.5 min (*S,S*); t_R 11.7 min (*R,R*). 1H NMR (400 MHz, $CDCl_3$): δ =

1.21 (t, 3H, CH_3 , Et, J = 7.2 Hz), 1.38 (d, 3H, CH_3 , J = 7.2 Hz), 3.35 (ddq, 1H, CH, J = 26.9 Hz, J = 7.2 Hz, J = 4.3 Hz), 4.19 (dq, 1H, CH_2 , Et, J = 7.2, J = 2.8 Hz), 4.95 (dd, 1H, CHF, J = 49.0, J = 4.3 Hz), 7.24-7.40 (m, 5 H, CH=).

Racemic sample

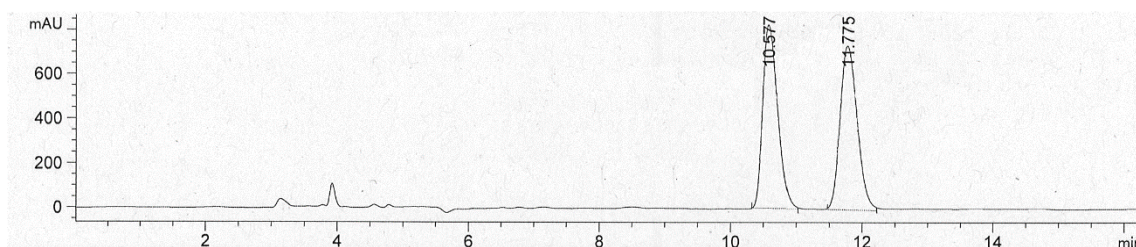
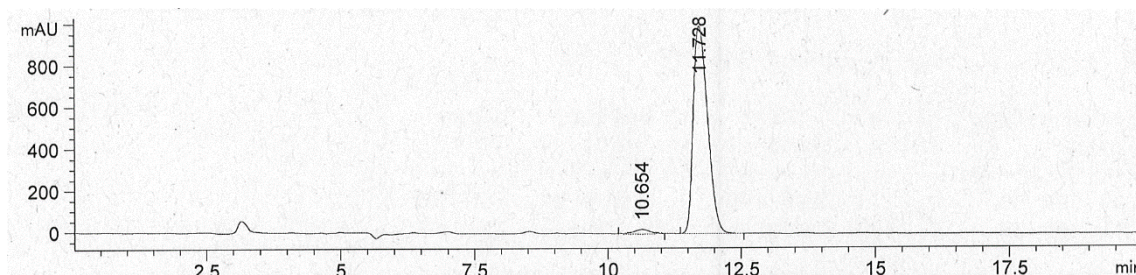


Figure 4 (97% ee (2R, 3R))



From (Z)-ethyl 2-fluoro-3-phenylbut-2-enoate (S20): Colorless oil. Yield: 104 mg (99%). Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1mL/min, λ = 210 nm). t_R 9.0 min (*R,S*); t_R 11.1 min (*S,R*). 1H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, 3H, CH_3 , Et, J = 7.2 Hz), 1.45 (d, 3H, CH_3 , J = 7.3 Hz), 3.36 (ddq, 1H, CH, J = 28.5 Hz, J = 7.3 Hz, J = 4.6 Hz), 4.11 (dq, 2H, CH_2 , Et, J = 7.1 Hz, J = 3.3 Hz), 5.00 (dd, 1H, CHF, J = 48.9 Hz, J = 4.6 Hz), 7.15-7.75 (m, 5 H, CH=).

Racemic sample

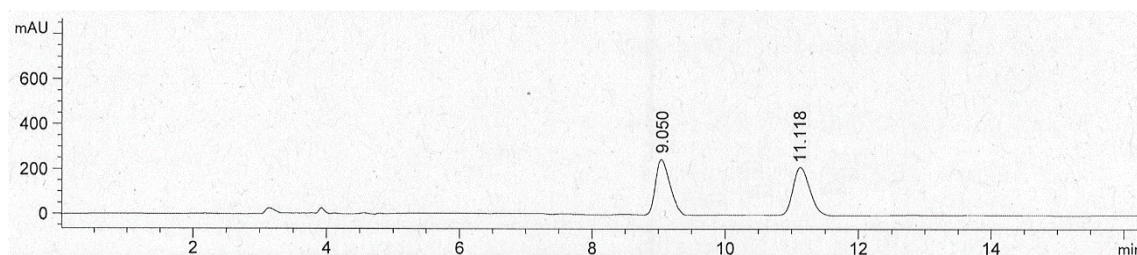
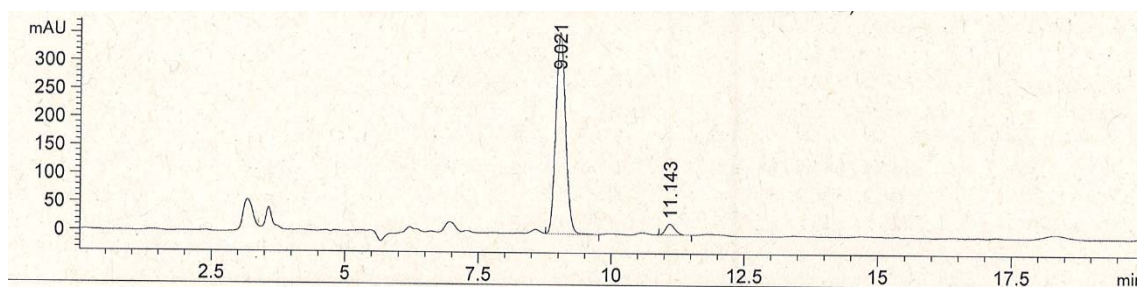
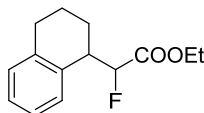


Figure 4 (95% ee (2R, 3S))



Ethyl 2-fluoro-2-(1,2,3,4-tetrahydronaphthalen-1-yl)acetate (28):¹¹ Colorless oil.



Yield: 116.5 mg (99%). Enantiomeric excess determined by GC

Chiraldex β -DM (120 kPa, Isotherm 120 °C). t_R 54.3; t_R 56.9. 1H NMR

(400 MHz, $CDCl_3$): δ = 1.26 (t, 3H, CH_3 , Et, J = 7.1 Hz), 1.77 (dtd, 1H, CH_2 , J = 12.9 Hz, J = 6.1 Hz, J = 4.3 Hz), 1.83-2.02 (m, 3H, CH_2), 2.80 (q, 2H, CH_2 , J = 5.7 Hz), 3.45 (dq, 1H, CH, J = 20.4 Hz, J = 5.5 Hz), 4.25 (qd, 2H, CH_2 , Et, J = 7.2 Hz, J = 3.1 Hz), 5.03 (dd, 1H, CH, J = 48.6 Hz, J = 6.1 Hz), 7.05-7.24 (m, 4H, CH=).

Racemic sample

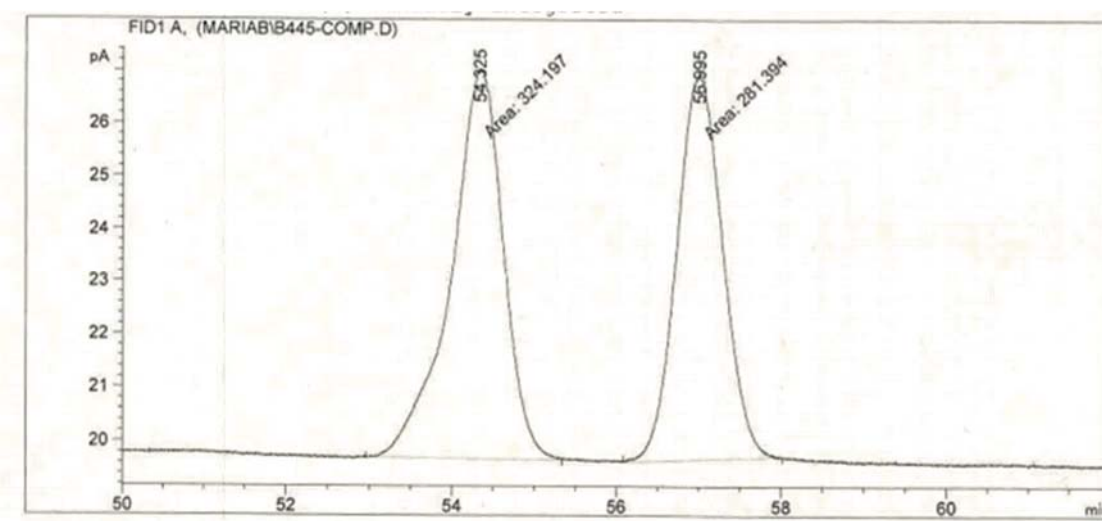
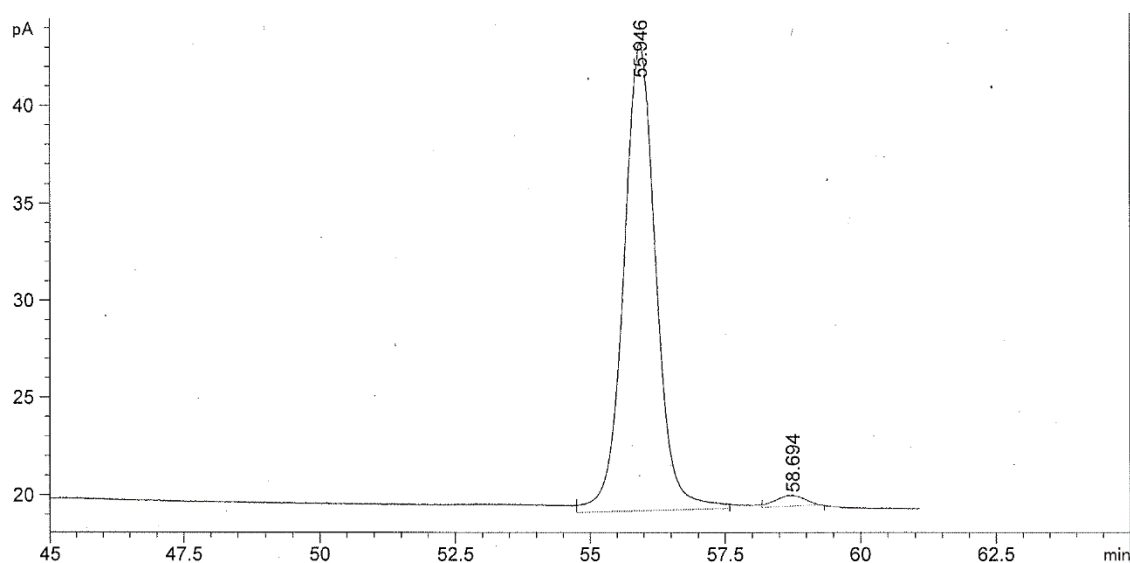
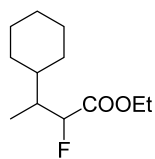


Figure 4 (98% ee)



Ethyl 3-cyclohexyl-2-fluorobutanoate (29):¹¹ Colorless oil. Yield: 107 mg (99%).



Enantiomeric excess determined by GC ChiralDEX β -DM (100 kPa, Isotherm 110 °C). t_R 74.8; t_R 72.1. 1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, 3H, CH_3 , Et, J = 7.1 Hz), 1.77 (dtd, 1H, CH_2 , J = 12.9 Hz, J = 6.1 Hz, J = 4.3 Hz), 1.83-2.02 (m, 3H, CH_2), 2.80 (q, 2H, CH_2 , J = 5.7 Hz), 3.45 (dq, 1H, CH, J = 20.4 Hz, J = 5.5 Hz), 4.25 (qd, 2H, CH_2 , Et, J = 7.2 Hz, J = 3.1 Hz), 5.03 (dd, 1H, CH, J = 48.6 Hz, J = 6.1 Hz), 7.05-7.24 (m, 4H, CH=).

Racemic sample

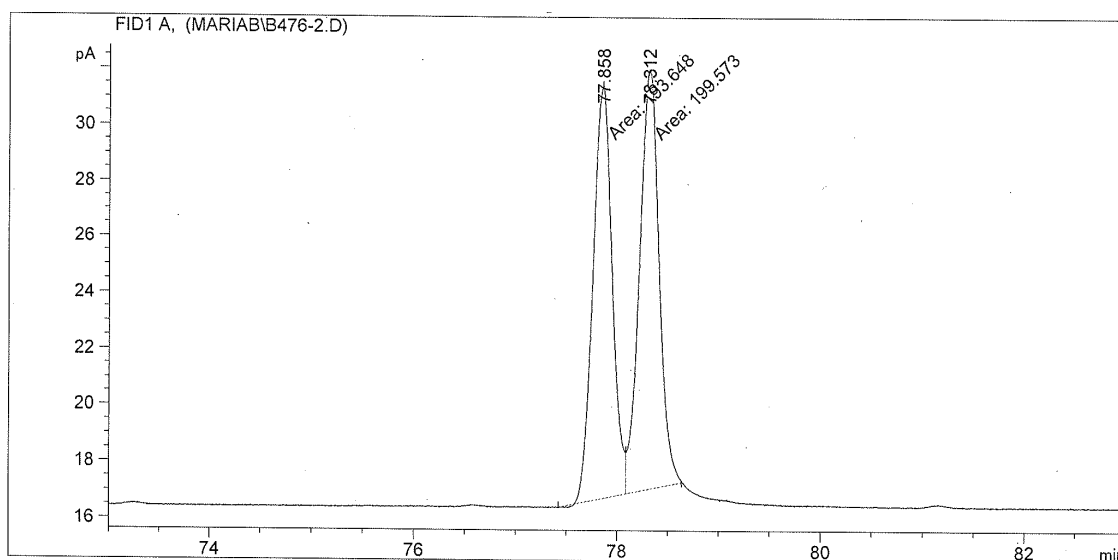
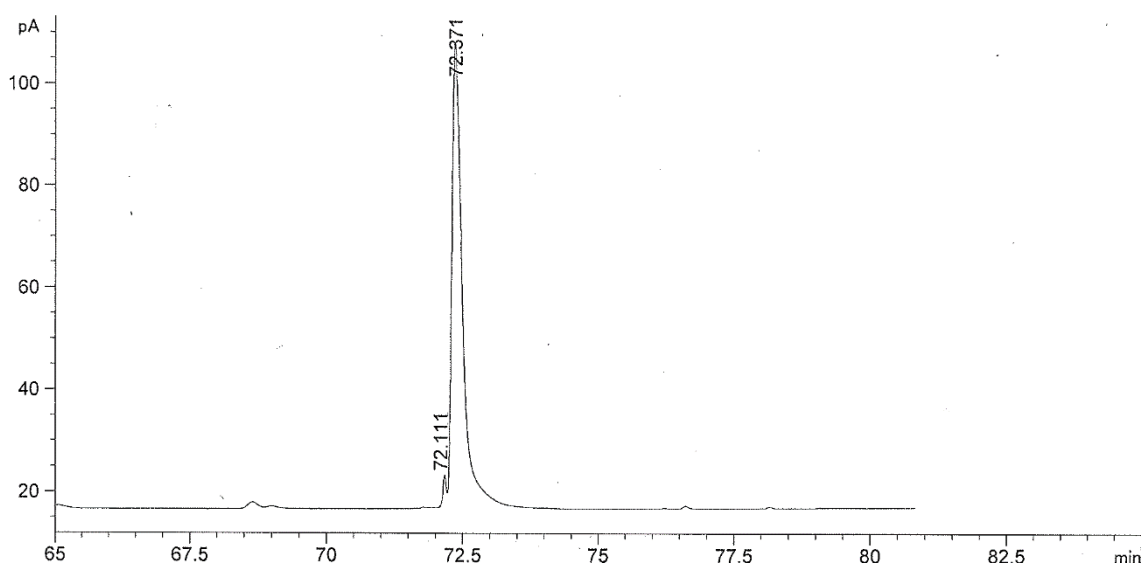
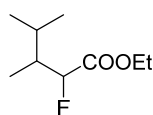


Figure 4 (94% ee)



Ethyl 2-fluoro-3,4-dimethylpentanoate (30):¹¹ Colorless oil. Yield: 87 mg (99%).



Enantiomeric excess determined by GC Hydrodex β -3P (100 kPa,

Isotherm 50 °C). t_R 36.5; t_R 38.9. 1H NMR (400 MHz, $CDCl_3$): δ = 0.89

(td, 6H, CH_3 , iPr , J = 6.7 Hz, J = 0.8 Hz), 0.95 (d, 3H, CH_3 , J = 6.7 Hz),

1.31 (t, CH_3 , Et, J = 7.2 Hz, 3H), 1.84-1.99 (m, 2H, CH), 4.25 (q, 2H, CH_2 , J = 7.1 Hz),

4.76 (dd, 1H, CH, J = 49.1 Hz, J = 6.3 Hz).

Racemic sample

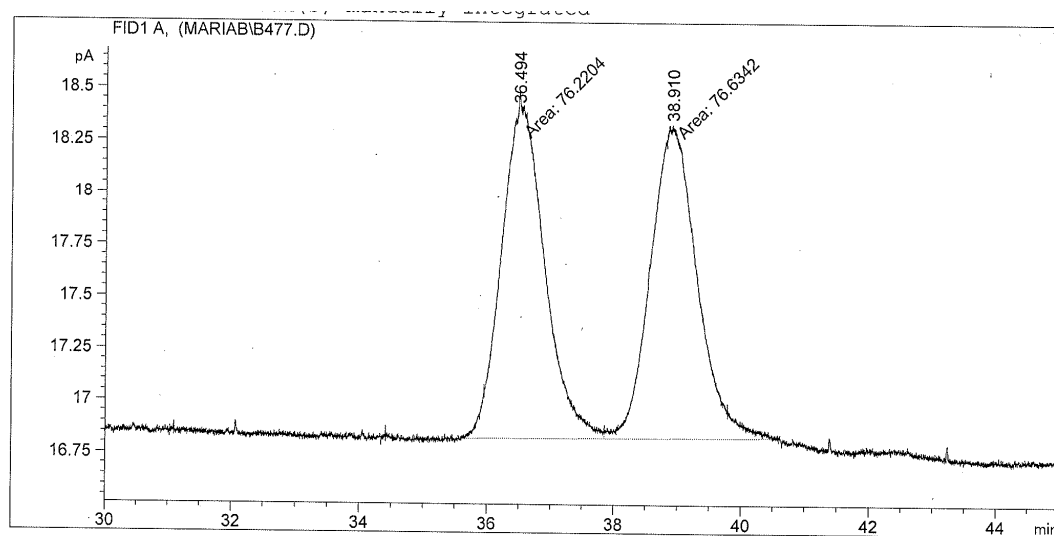
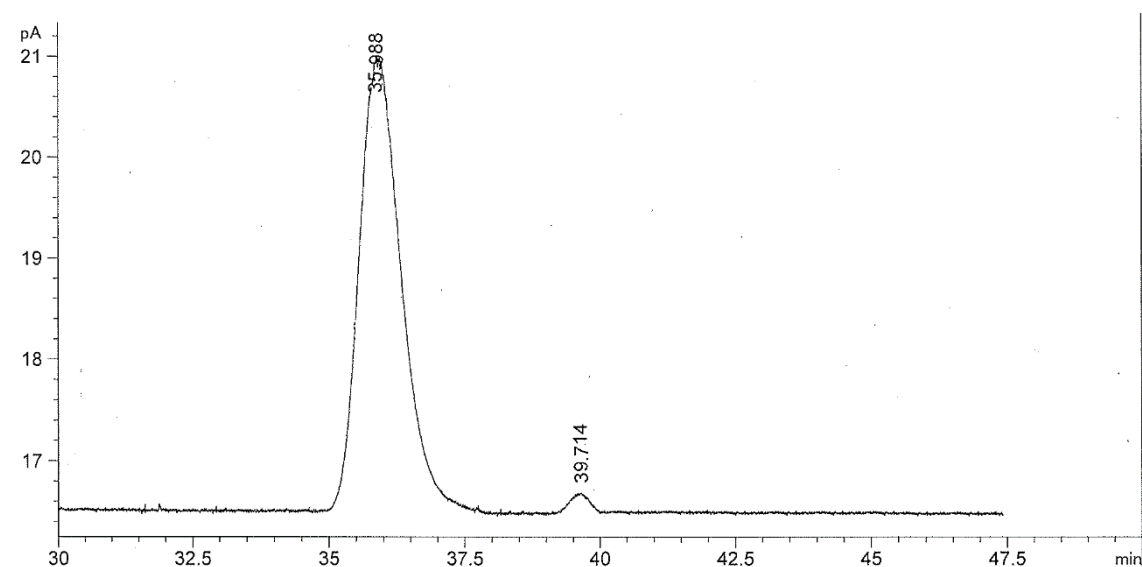
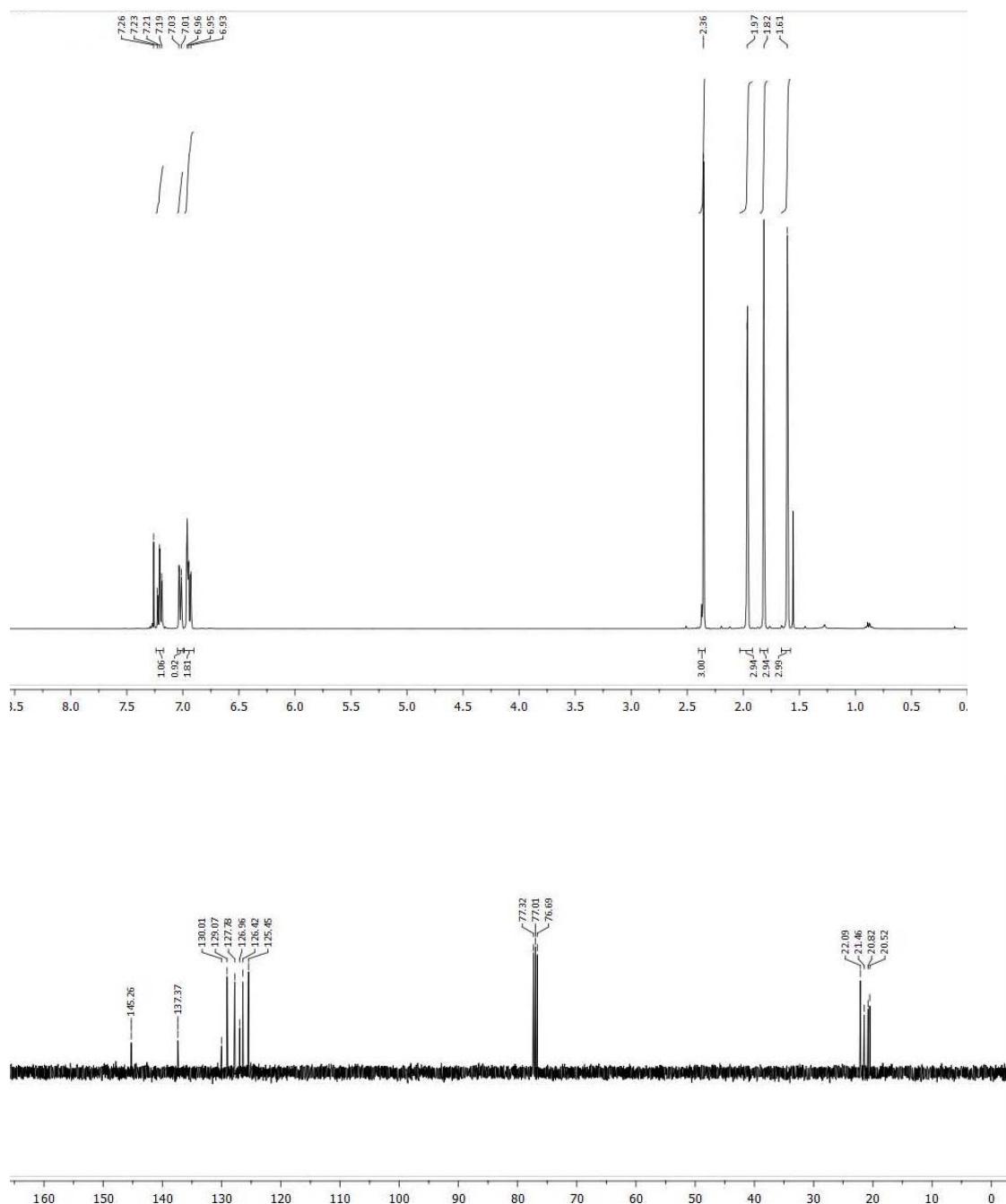
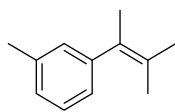


Figure 4 (91% ee)

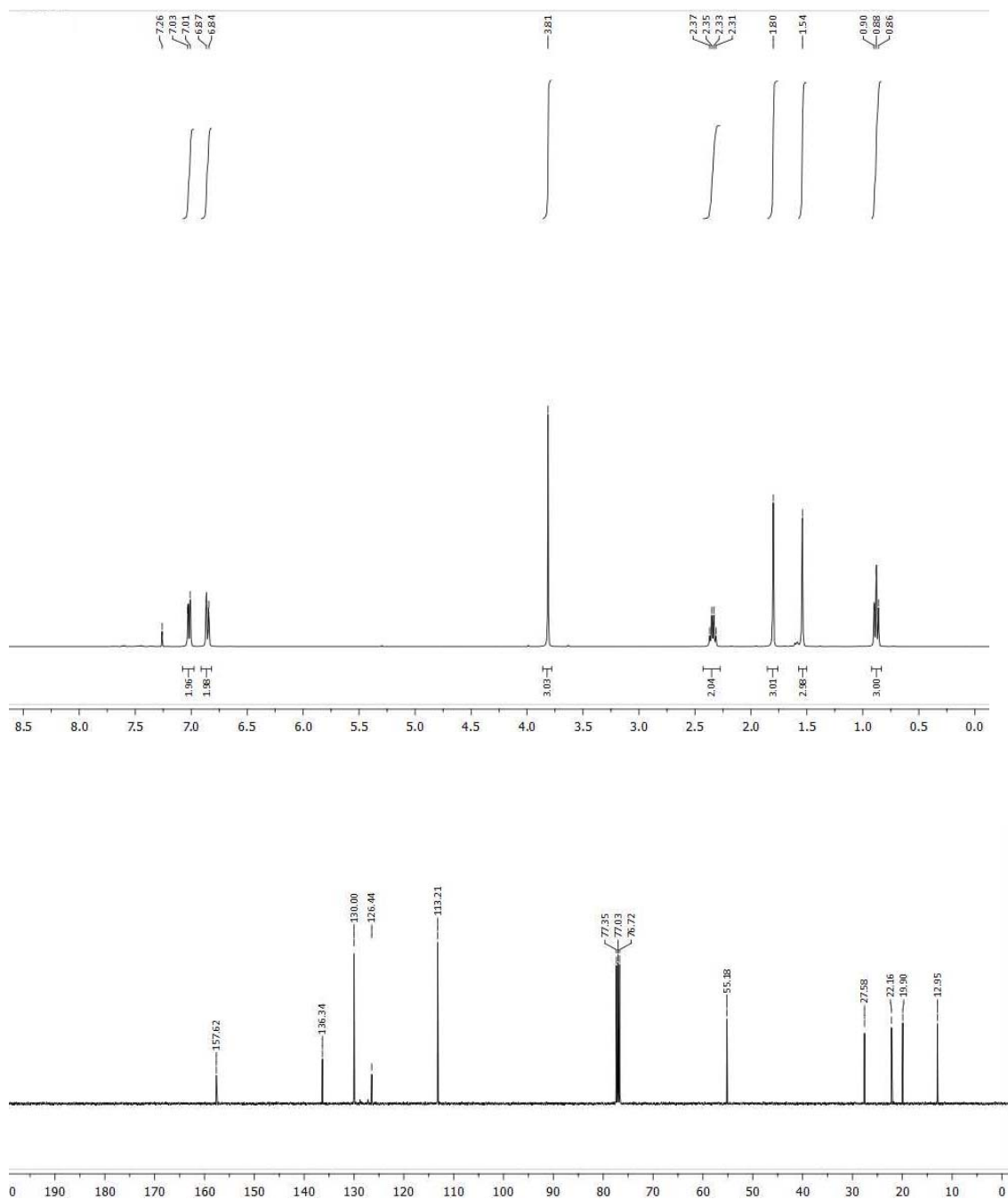
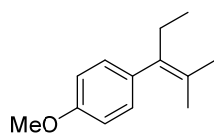


SI.8. ^1H and ^{13}C -NMR spectra of new compounds

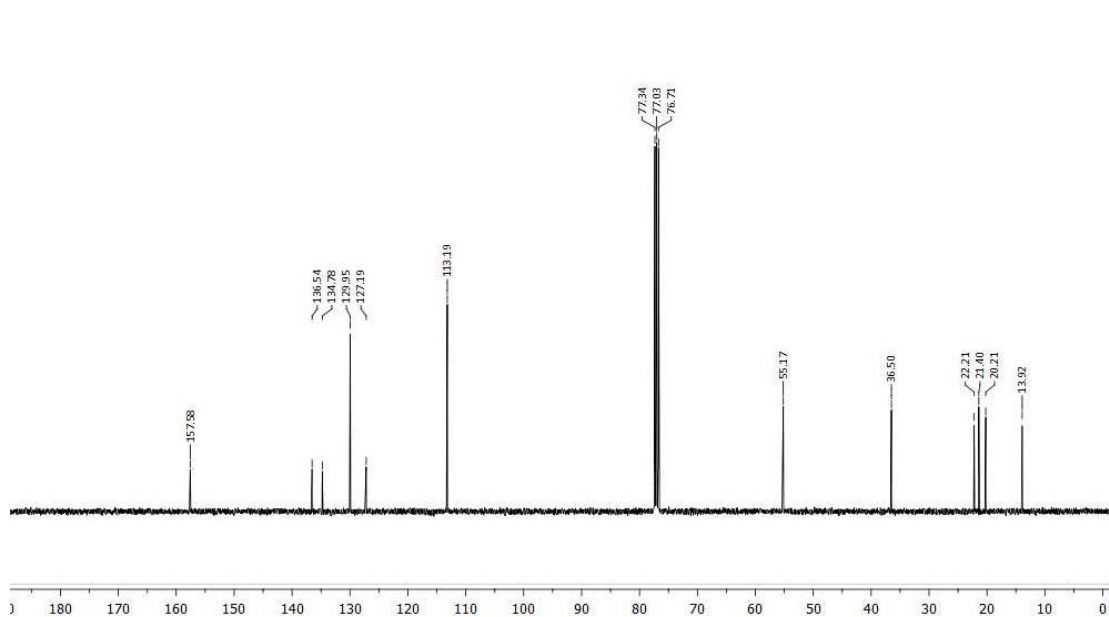
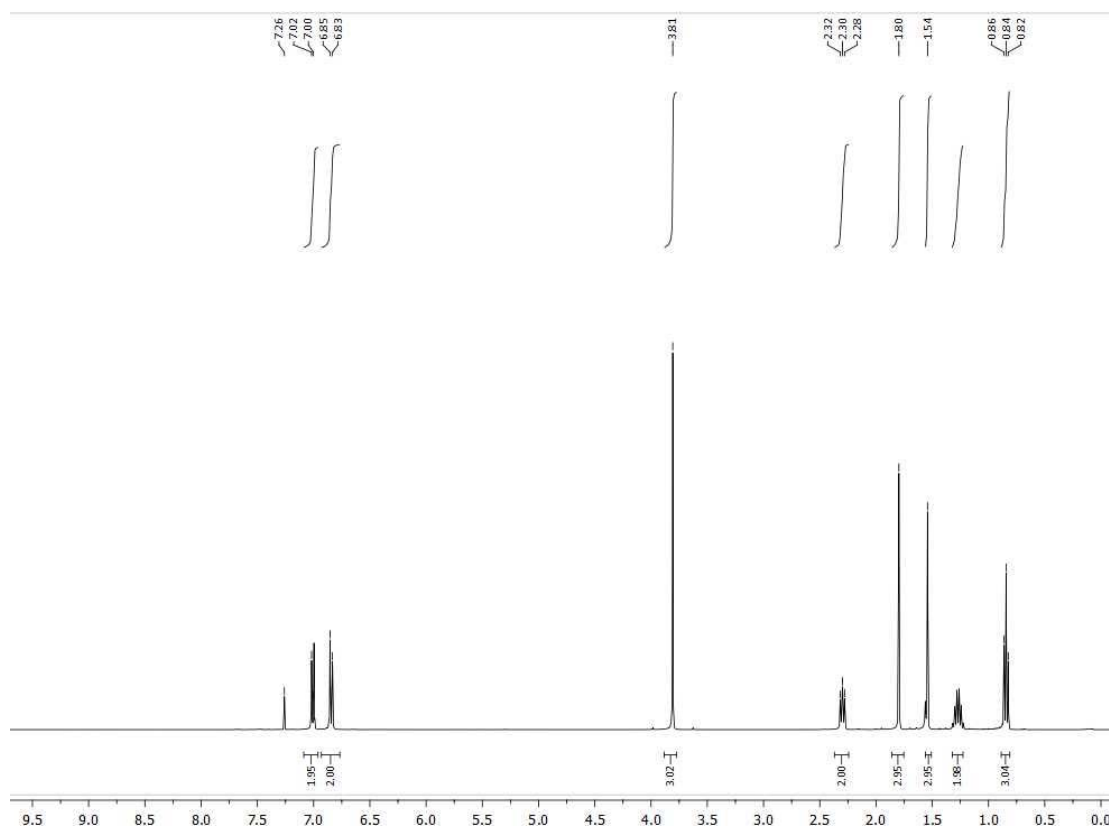
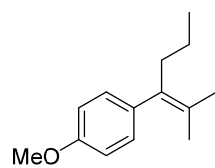
1-Methyl-3-(3-methylbut-2-en-2-yl)benzene (S13)



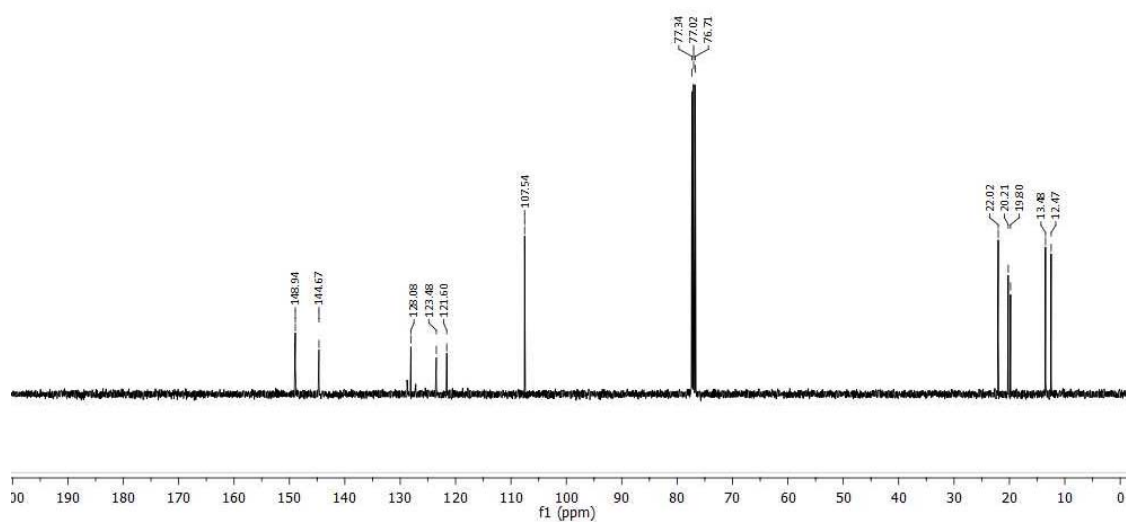
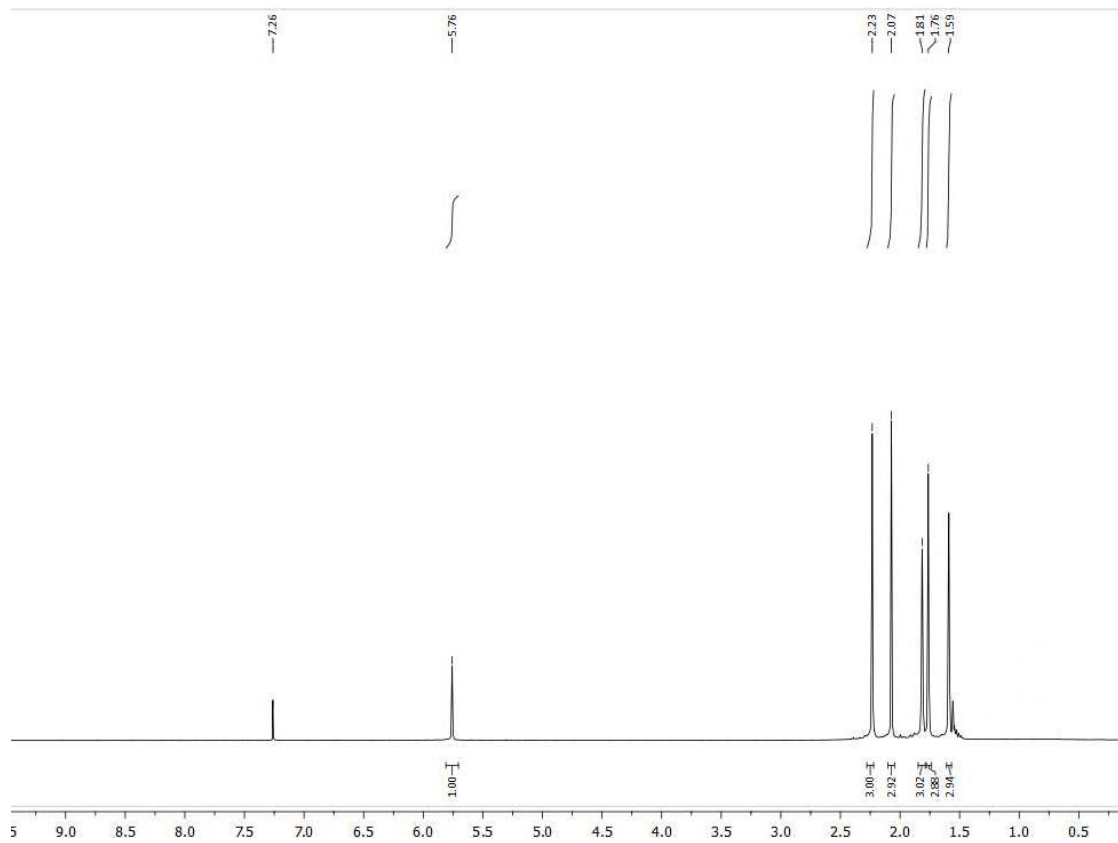
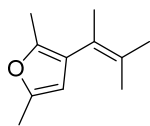
1-Methoxy-4-(2-methylpent-2-en-3-yl)benzene (S15)



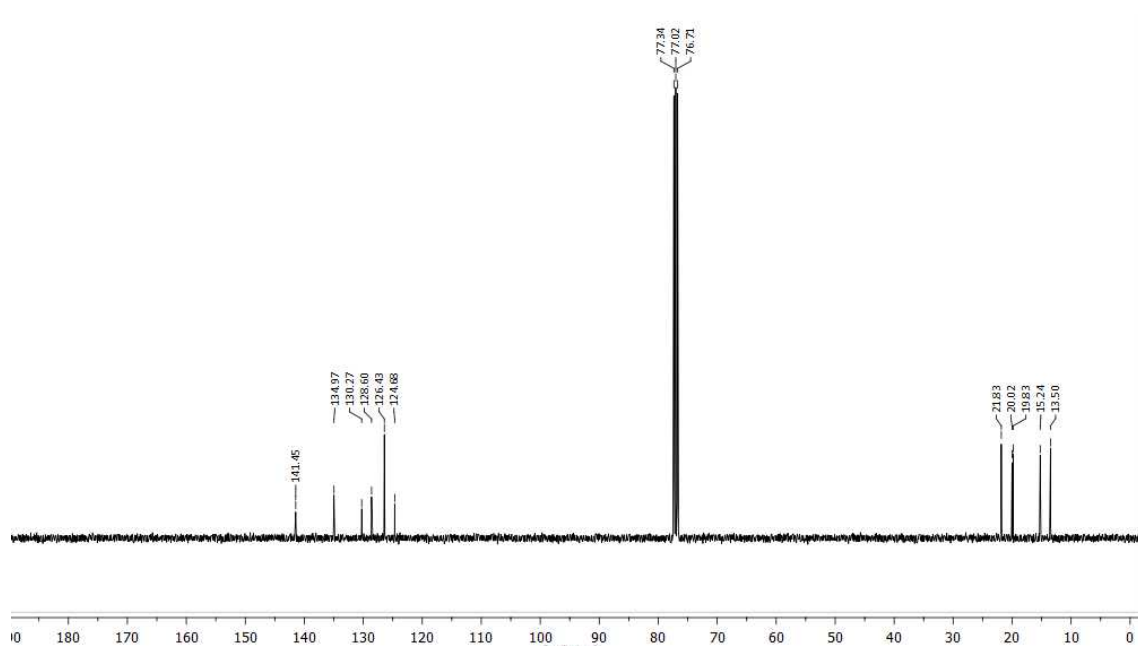
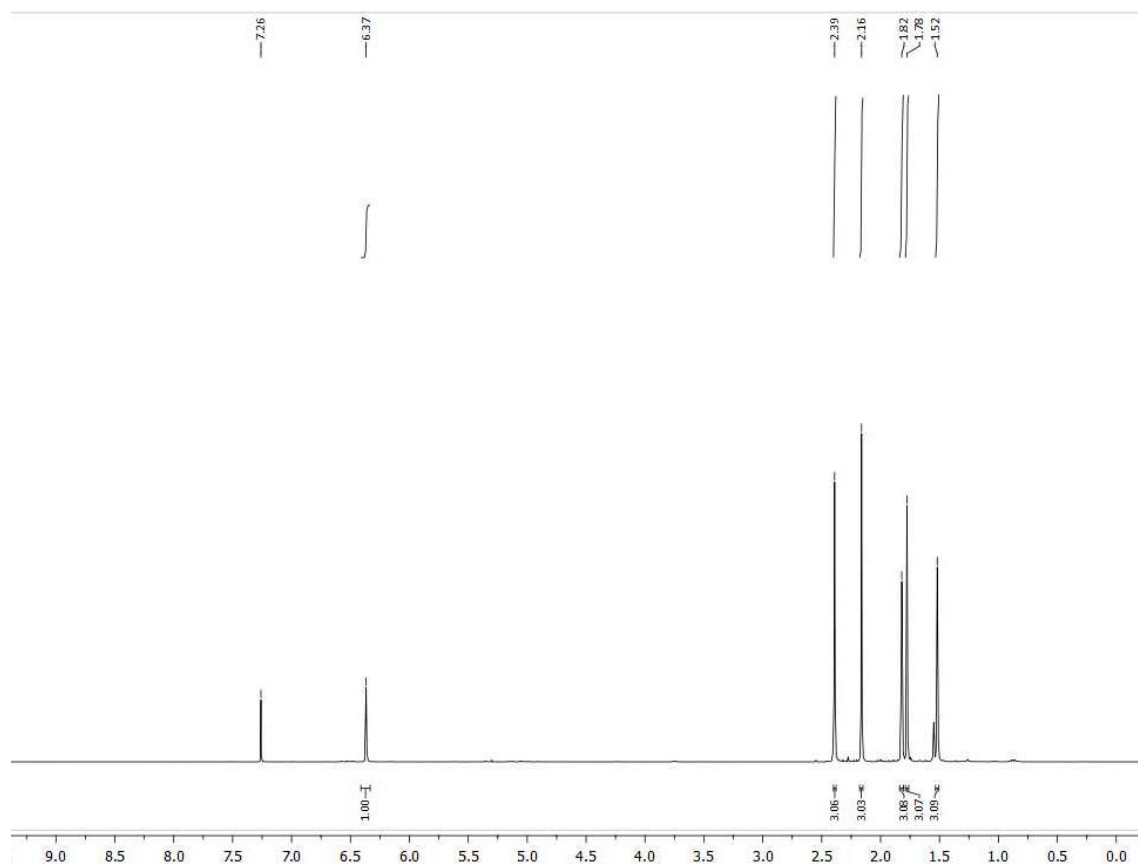
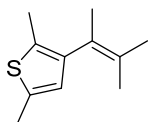
1-Methoxy-4-(2-methylhex-2-en-3-yl)benzene (S16)



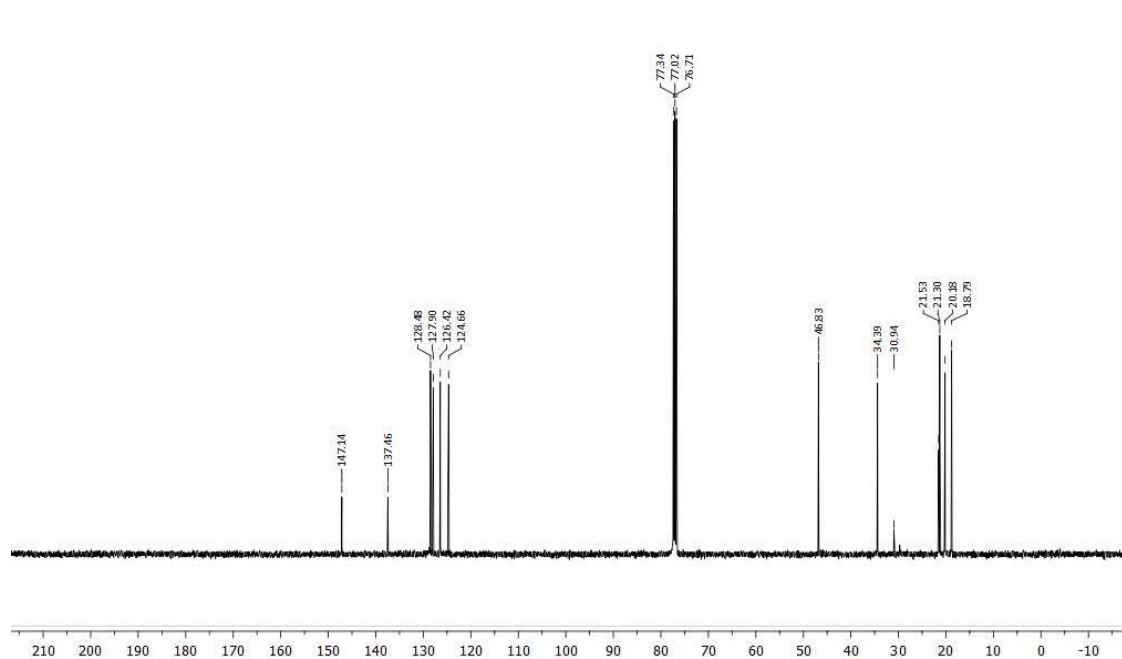
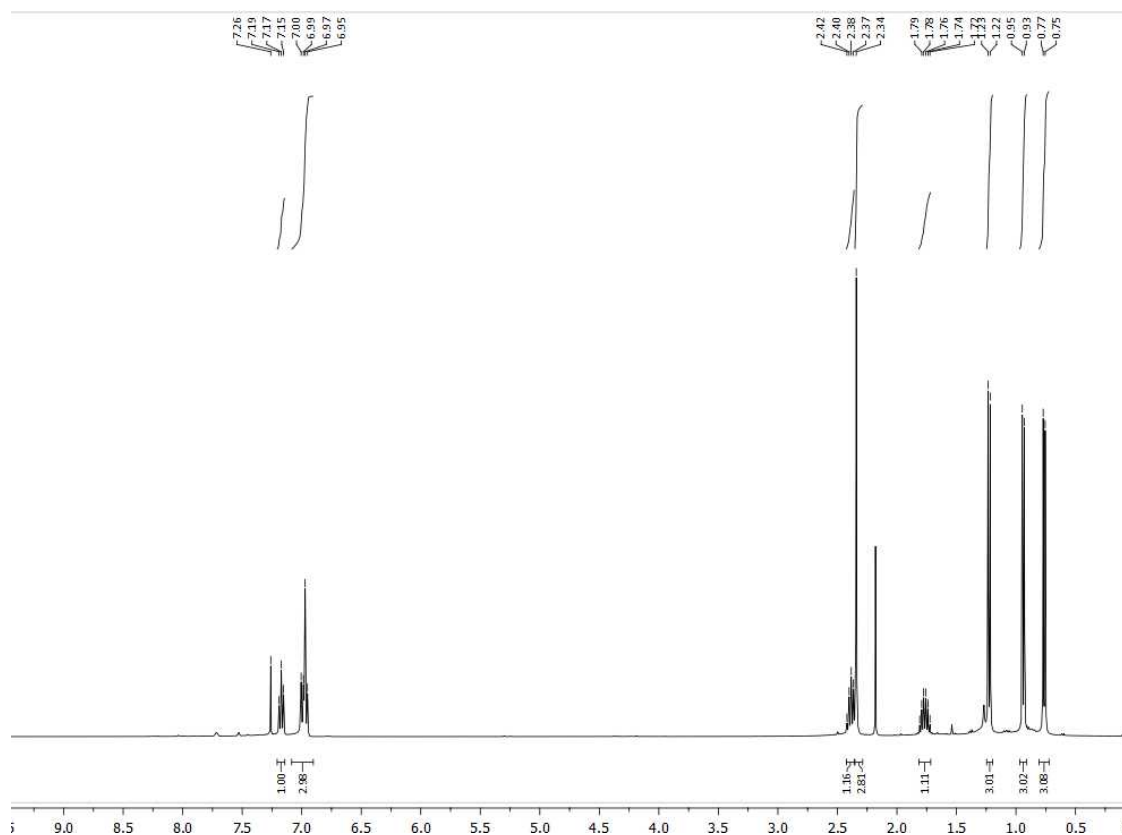
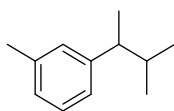
2,5-Dimethyl-3-(3-methylbut-2-en-2-yl)furan (S17)



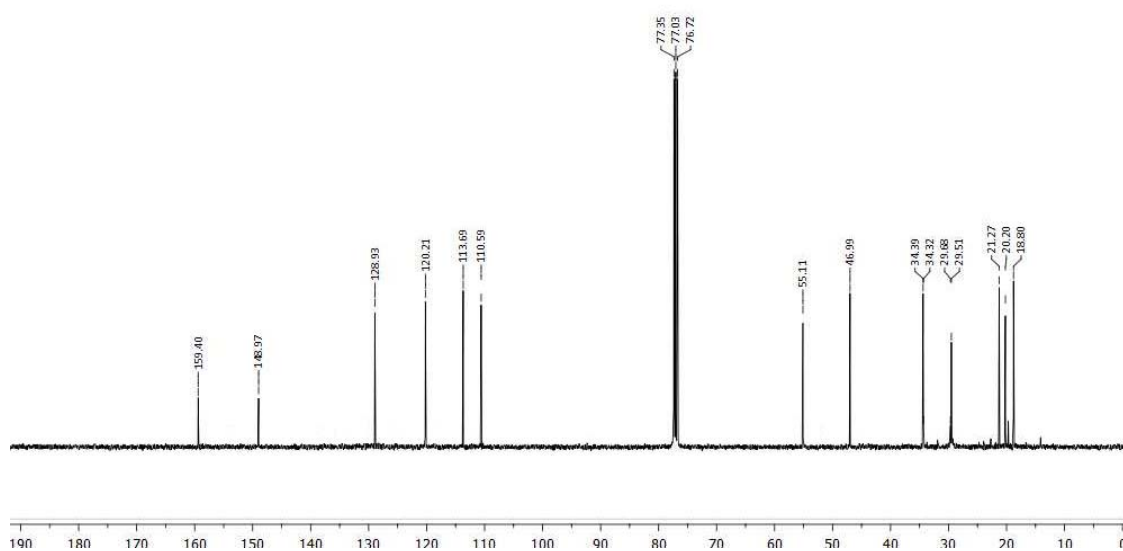
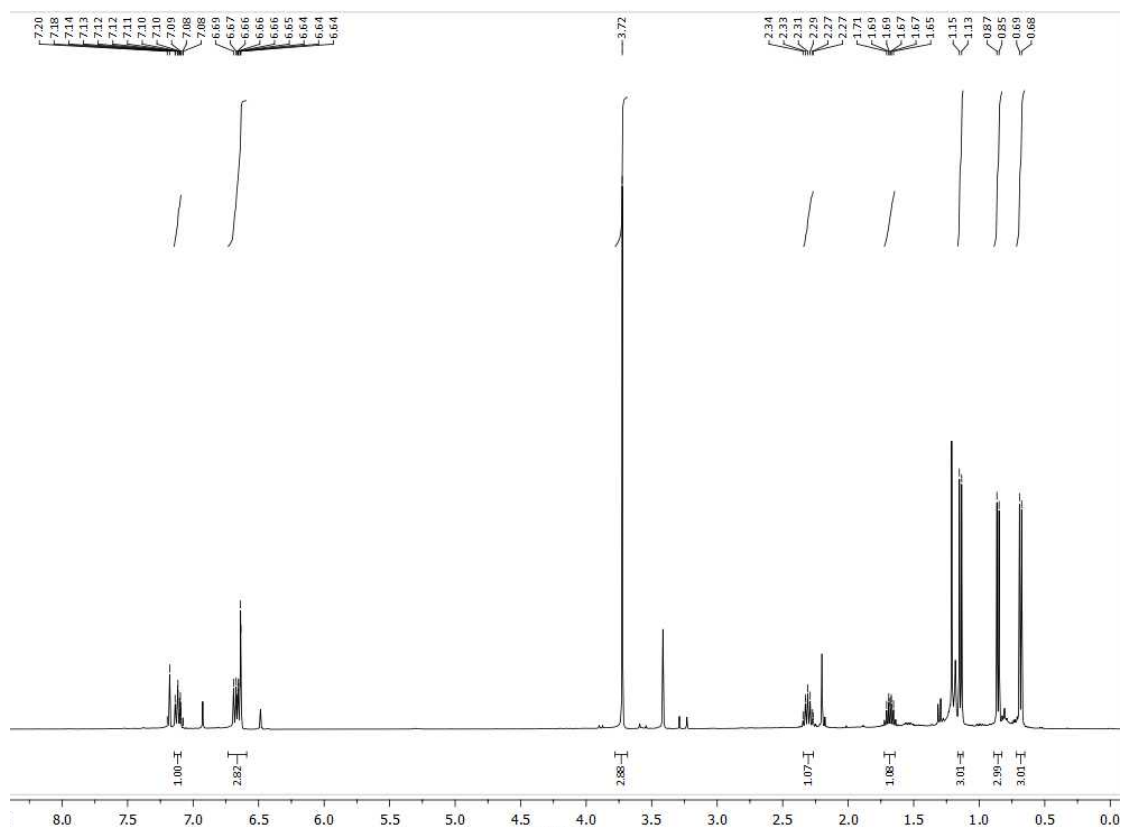
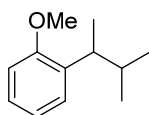
2,5-Dimethyl-3-(3-methylbutan-2-yl)thiophene (S18)



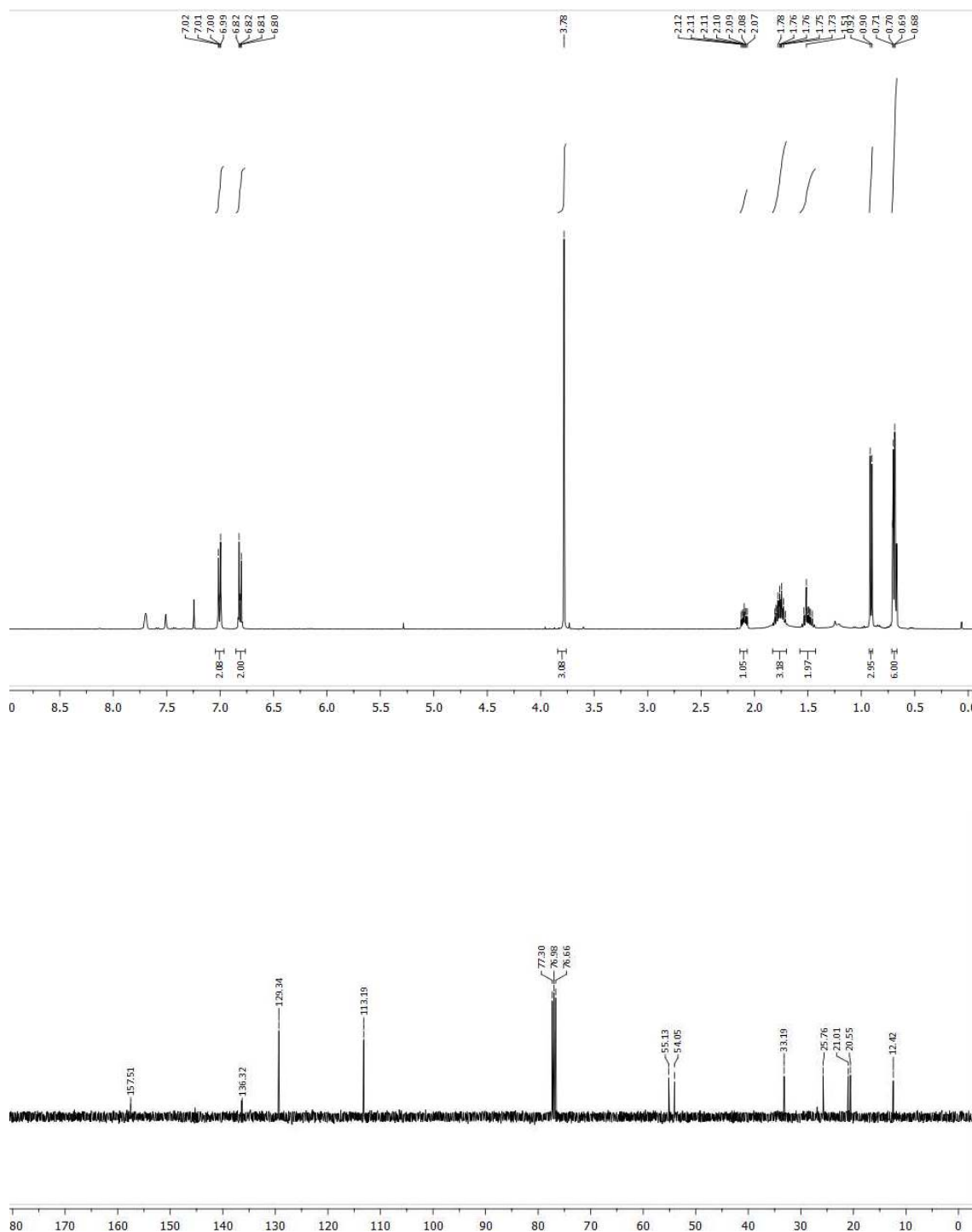
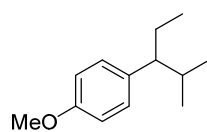
1-Methyl-3-(3-methylbutan-2-yl)benzene (21)



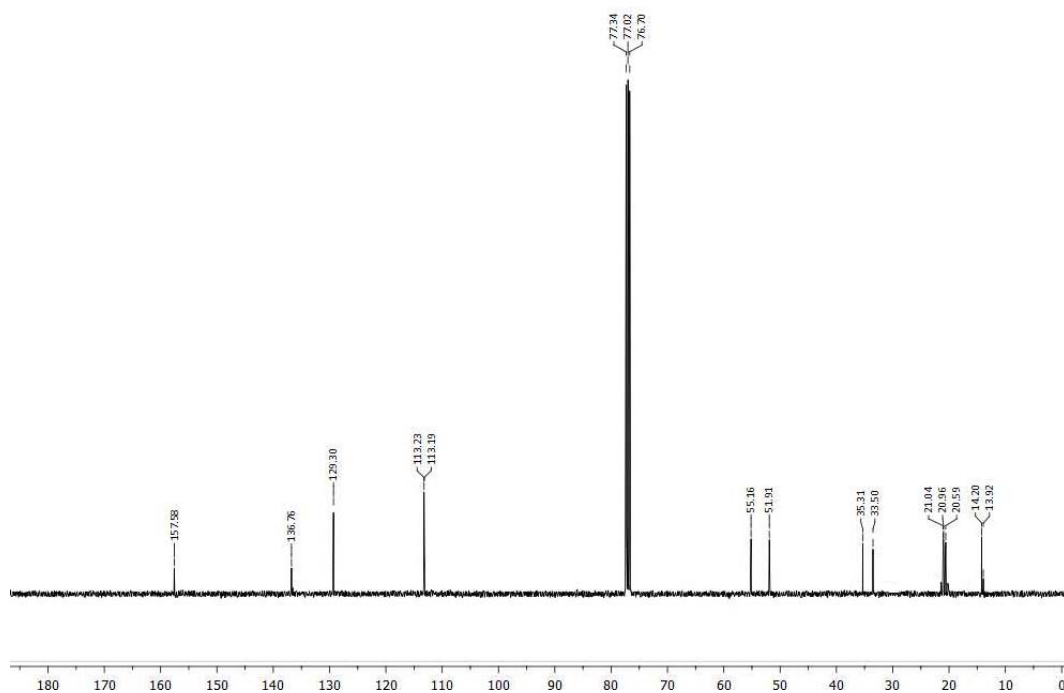
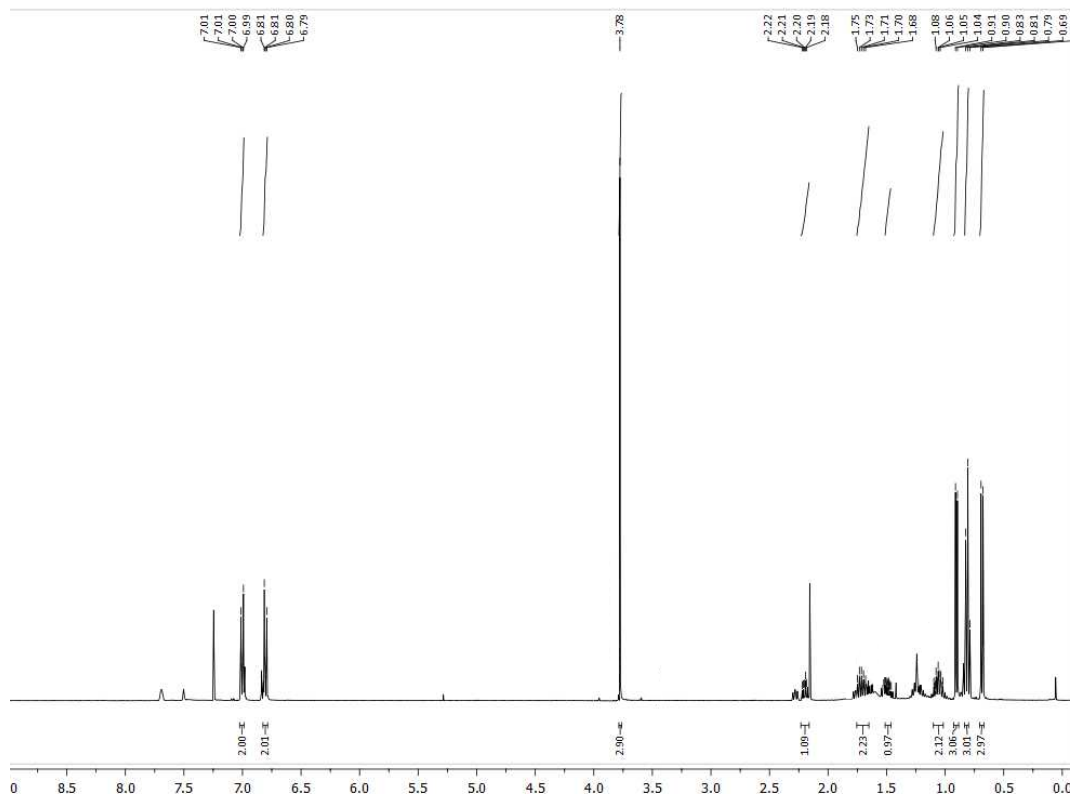
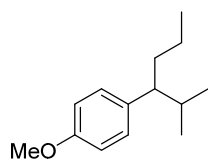
1-Methoxy-2-(3-methylbutan-2-yl)benzene (22)



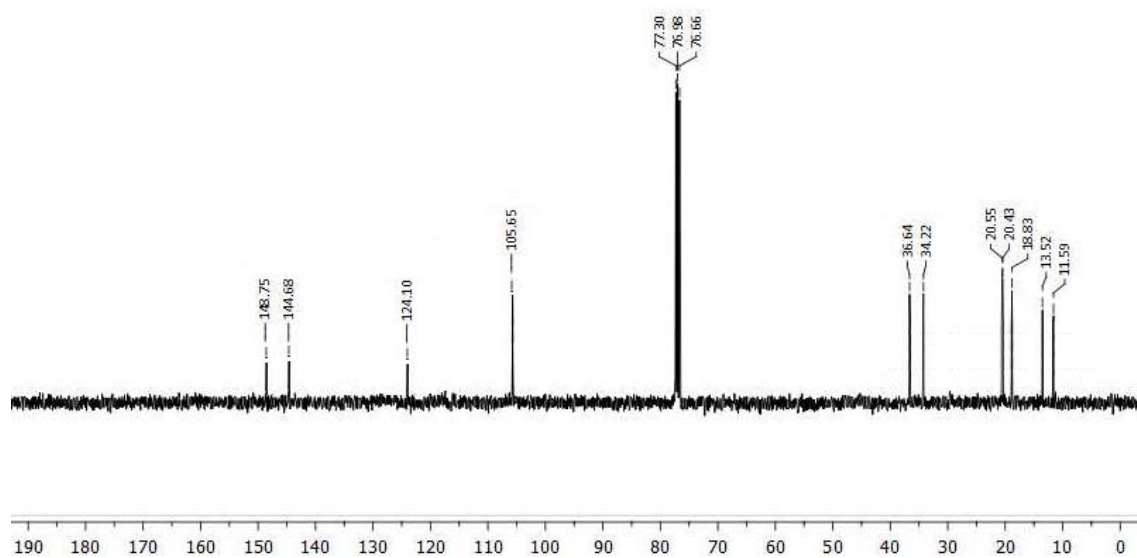
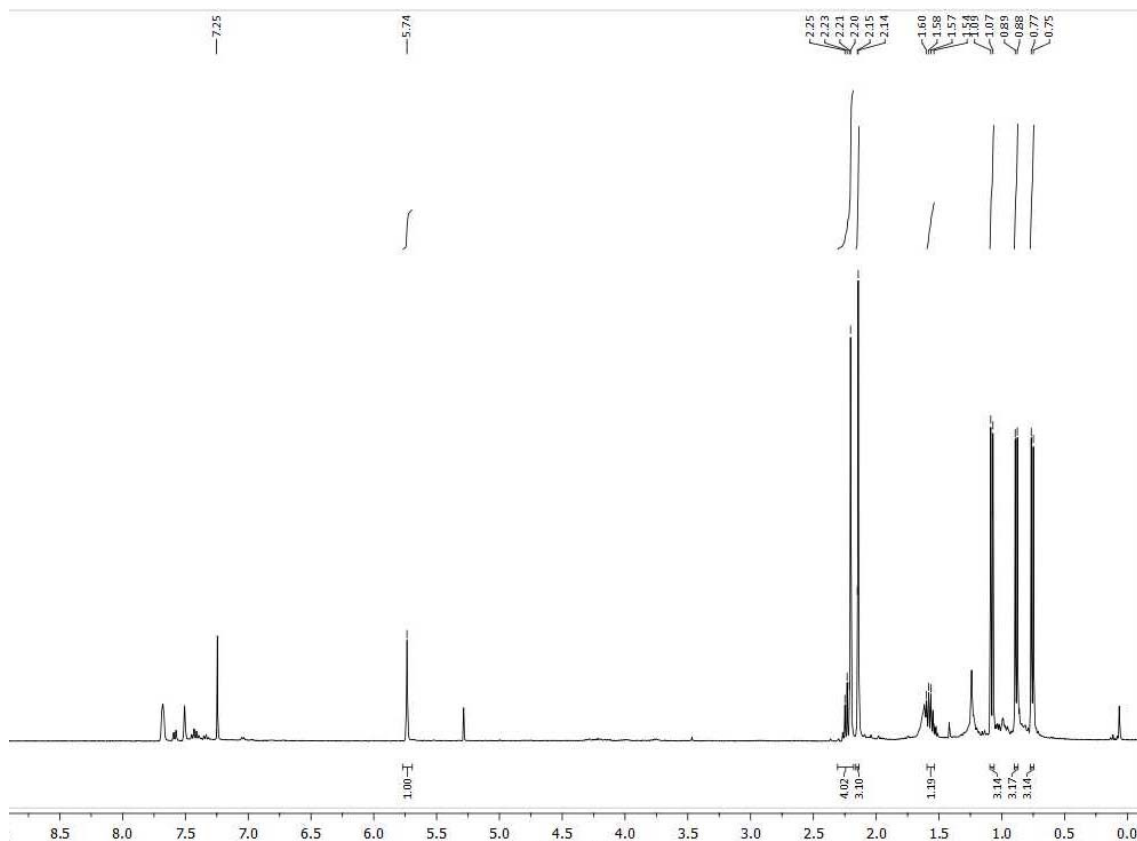
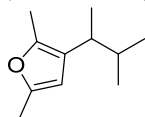
1-Methoxy-4-(2-methylpentan-3-yl)benzene (23)



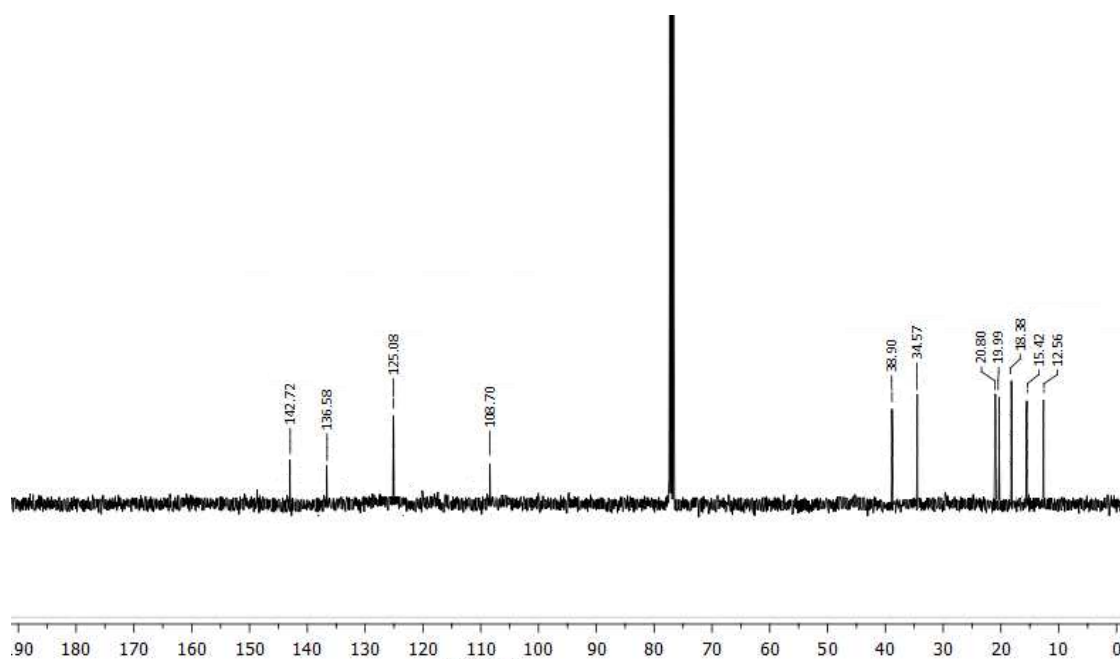
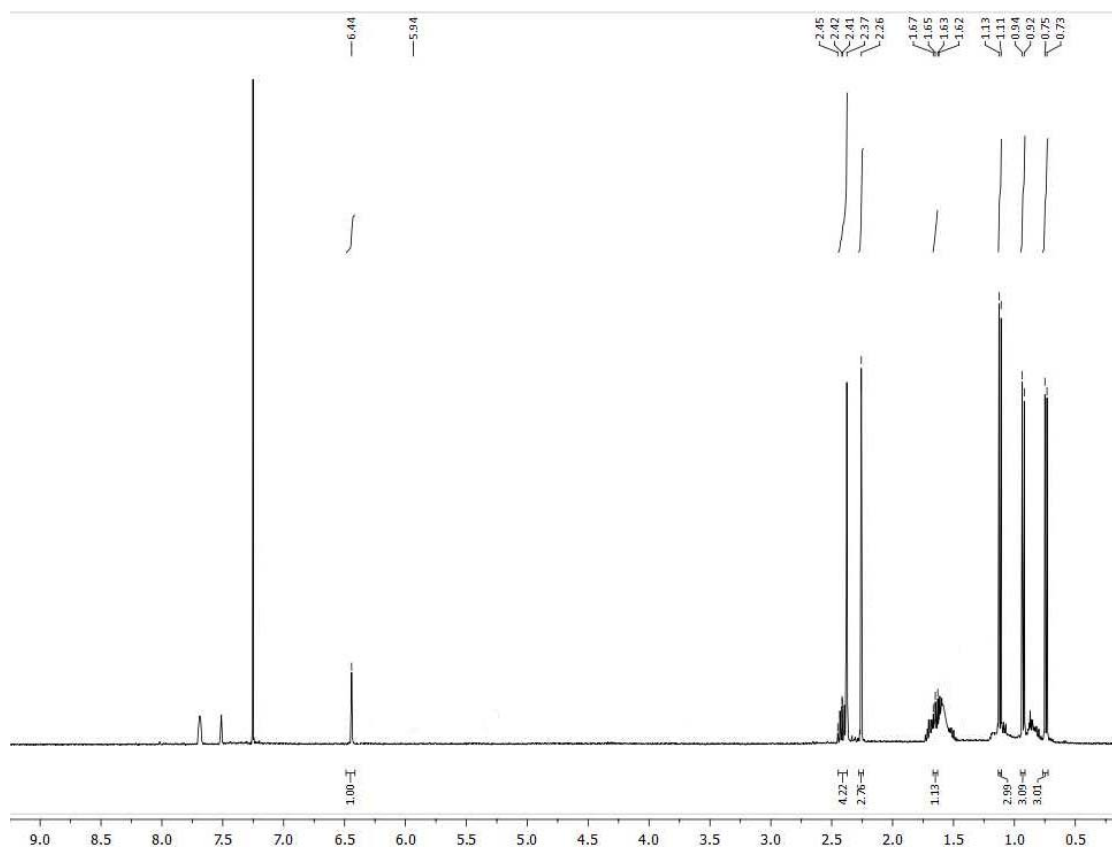
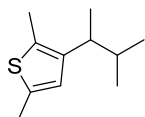
1-Methoxy-4-(2-methylhexan-3-yl)benzene (24)



2,5-Dimethyl-3-(3-methylbutan-2-yl)furan (25)



2,5-Dimethyl-3-(3-methylbutan-2-yl)thiophene (26)



SI.9. References

- ¹ (a) Orgué, S.; Flores, A.; Biosca, M.; Pàmies, O.; Diéguez, M.; Riera, A.; Verdaguer, X. *Chem. Commun.* **2015**, *51*, 17548. (b) Salomó, E.; Orgué, S.; Riera, A.; Verdaguer, X. *Angew Chem. Int. Ed.* **2016**, *55*, 7988.
- ² Tsang, A. S.-K.; Kapat, A.; Schoenebeck, F. *J. Am. Chem. Soc.* **2016**, *138*, 518.
- ³ Zhang, Z.; Wang, J.; Li, J.; Yang, F.; Liu, G.; Tang, W.; He, W.; Fu, J.-J.; Shen, Y.-H.; Li, A.; Zhang, W.-D. *J. Am. Chem. Soc.* **2017**, *139*, 5558.
- ⁴ Chakrabarti, K.; Maji, M.; Panja, D.; Paul, B.; Shee, S.; Das, D.-K.; Kundu, S. *Org. Lett.* **2017**, *19*, 4750.
- ⁵ Troutman, M.V.; Appella, D.H.; Buchwald, S.L. *J. Am. Chem. Soc.* **1999**, *121*, 4916.
- ⁶ Schrems, M. G.; Neumann, E.; Pfaltz, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 8274.
- ⁷ Morrison, H.; Giacherio, D.; Palensky, F.J. *J. Org. Chem.* **1982**, *47*, 1051.
- ⁸ Gieshoff, T. N.; Chakraborty, U.; Villa, M.; Jacobi von Wangelin, A.; *Angew. Chem. Int. Ed.* **2017**, *56*, 3585.
- ⁹ Richardson, W. H.; Stiggal-Estbergm D.L.; Chen, Z.; Baker, J. C. Burns, D.M.; Sherman, D.G. *J. Org. Chem.* **1987**, *52*, 3143.
- ¹⁰ Vila, C.; Cembellín, S.; Hornillos, V.; Giannerini, M.; Fañanás-Mastral, M.; Feringa, B. L. *Chem. Eur. J.* **2015**, *21*, 15520.
- ¹¹ Ponra, S.; Rabten, W.; Yang, J.; Wu, H.; Kerdphon, S.; Andersson, P. G. *J. Am. Chem. Soc.* **2018**, *140*, 13878.
- ¹² Lemonnier, G.; Zoute, L.; Dupas, G.; Quirion, J.-C.; Jubault, P. *J. Org. Chem.* **2009**, *74*, 4124.
- ¹³ Scully, F.; Nylund, T.; Palensky, F.; Morrison, H. *J. Am. Chem. Soc.* **1978**, *23*, 1352.
- ¹⁴ Monfete, S.; Turner, Z.R.; Semproni, S.P.; Chirik, P.J. *J. Am. Chem. Soc.* **2012**, *134*, 4561.