

Supporting Information

Nickel-Catalyzed Asymmetric Intramolecular Reductive Heck- Reaction of Unactivated Alkenes

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General Methods and Materials

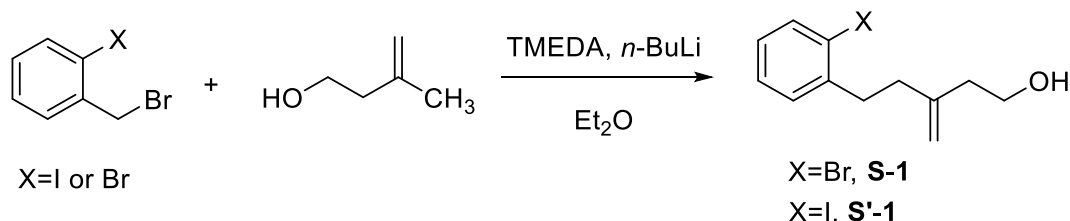
¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in CDCl₃ at 400 and 101 MHz. The chemical shifts are given in ppm relative to tetramethylsilane [¹H: (SiMe₄)= 0.00 ppm] as an internal standard or relative to the resonance of the solvent [¹H: δ(CDCl₃)= 7.26, ¹³C: δ(CDCl₃)= 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on ThermoUltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

All the reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification. Compounds **1ae**,¹ **2ae**,² **2ae-1**,² **2ae-2**² and **2ae-3**² are known compounds and their NMR-data are consistent with these reported in the literature.

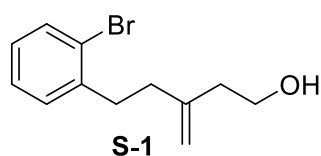
General Procedure for the Synthesis of Alkenes with Tethered Aryl Halides

(1) Preparation of alkenes 1a-1h

Procedure for Synthesis of S-1 and S'-1³

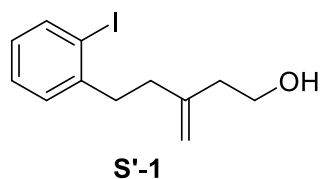


To an ice-cooled solution of tetramethylethylenediamine (8 mL, 53 mmol, 5.3 equiv) in Et₂O (30 mL) was added *n*-BuLi (2.5M in hexanes, 16 mL, 40 mmol, 4 equiv). After stirring at room temperature for 1 h, the solution was then cooled to 0 °C, 3-methyl-3-buten-1-ol (2 mL, 20 mmol, 2 equiv) and benzyl bromides (10 mmol, 1 equiv) in Et₂O (5 mL) were added dropwise, successively. The reaction mixture was allowed to warm up to room temperature and stirred for 6 h, before it was quenched with saturated aq. NH₄Cl and diluted with H₂O. The aqueous phase extracted three times by Et₂O and the combined organic layers was washed successively with 1 M aq. HCl and brine, dried over MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (hexane/ethyl acetate= 4:1 to 2:1) gave the pure product **S-1** or **S'-1**.



5-(2-Bromophenyl)-3-methylenepentan-1-ol (S-1) was isolated as a yellow oil (1.21 g, 48 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.56-7.50 (m, 1H), 7.25-7.20 (m, 2H), 7.10-7.02 (m, 1H), 4.95 (d, *J* = 1.5 Hz, 1H), 4.89 (d, *J* = 1.6 Hz, 1H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.90-2.83 (m, 2H), 2.39-2.29 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 145.3, 141.1, 132.8, 130.3, 127.7, 127.5, 124.4, 112.3, 60.4, 39.3, 35.9, 34.9 ppm. HRMS (ESI): calcd. For C₁₂H₁₆BrO

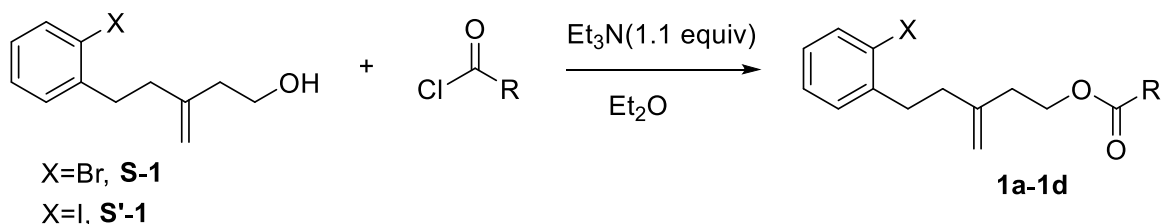
[M+H]⁺: 255.0379, found: 255.0382.



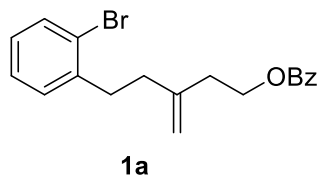
5-(2-Iodophenyl)-3-methylenepentan-1-ol (S'-1) was isolated as a yellow oil (1.51 g, 50% yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.81 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.30-7.24 (m, 1H), 7.22 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.95-6.86 (m, 1H), 4.97 (d, *J* = 1.5 Hz, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 3.77 (t, *J* = 6.3 Hz, 2H), 2.89-2.80 (m, 2H), 2.42-2.36 (m, 2H), 2.33-2.26 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 145.1, 144.3, 139.5, 129.4, 128.4, 127.9, 112.4, 100.4,

60.4, 39.5, 39.3, 36.3 ppm. HRMS (ESI): calcd. For C₁₂H₁₆IO [M+H]⁺: 303.0240, found: 303.0238.

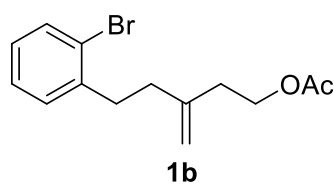
Procedure for Synthesis of Alkenes 1a-d



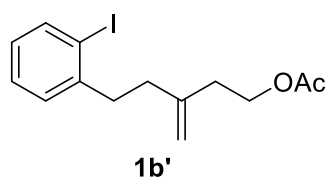
To a stirred solution of **S-1** or **S'-1** (5.0 mmol, 1 equiv) and Et₃N (0.80 mL, 5.5 mmol, 1.1 equiv) in Et₂O (10 mL) were added acyl chlorides (5.0 mmol, 1.0 equiv) at 0 °C. After stirring at this temperature for 1 h and then at room temperature for 8.5 h, the reaction mixture was quenched with water and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The crude residue was purified by column chromatography (hexane/ethyl acetate= 20:1) on silica gel to give the products **1a-1d**.



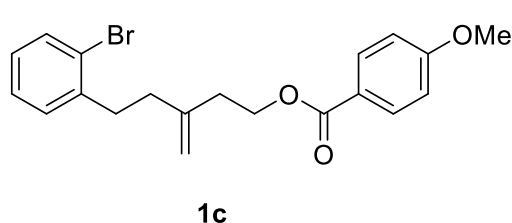
5-(2-Bromophenyl)-3-methylenepentyl benzoate (1a) was isolated as a yellow oil (1.53 g, 85% yield). ¹H NMR (400 MHz, CDCl₃) δ= 8.06-8.04 (m, 1H), 8.04-8.01 (m, 1H), 7.57-7.51 (m, 2H), 7.46-7.39 (m, 2H), 7.24-7.20 (m, 2H), 7.08-7.02 (m, 1H), 4.93 (m, 2H), 4.47 (t, *J*= 6.8 Hz, 2H), 3.03-2.80 (m, 2H), 2.56 (t, *J*= 6.8 Hz, 2H), 2.46-2.25 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 166.6, 144.8, 141.1, 132.9, 132.8, 130.34, 130.30, 129.6(2C), 128.4(2C), 127.7, 127.5, 124.4, 112.1, 63.3, 36.3, 35.2, 34.9 ppm. HRMS (EI): calcd. For C₁₉H₁₉BrO₂ [M]⁺: 358.0562, found: 358.0560.



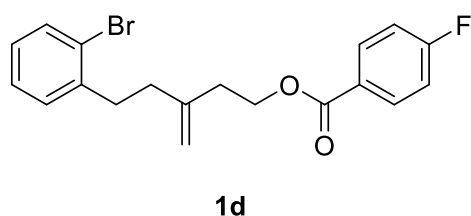
5-(2-Bromophenyl)-3-methylenepentyl acetate (1b) was isolated as a yellow oil (1.12 g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.53 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.26-7.19 (m, 2H), 7.10-7.01 (m, 1H), 4.89 (d, *J* = 1.5 Hz, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.21 (t, *J* = 7.0 Hz, 2H), 2.92-2.82 (m, 2H), 2.48-2.37 (m, 2H), 2.38-2.25 (m, 2H), 2.05 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 171.1, 144.7, 141.1, 132.8, 130.3, 127.7, 127.5, 124.4, 111.9, 62.9, 36.3, 35.0, 34.8, 21.1 ppm. HRMS (ESI): calcd. For C₁₄H₁₈BrO₂ [M+H]⁺: 297.0485, found: 297.0489.



5-(2-Iodophenyl)-3-methylenepentyl acetate (1b') was isolated as a yellow oil (1.38g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.81 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.28-7.25 (m, 1H), 7.21 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.92-6.84 (m, 1H), 4.91 (d, *J* = 1.5 Hz, 1H), 4.85 (d, *J* = 1.5 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 2H), 2.88-2.81 (m, 2H), 2.43 (m, 2H), 2.34-2.26 (m, 2H), 2.06 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 171.1, 144.6, 144.3, 139.5, 129.4, 128.4, 127.9, 111.9, 100.4, 62.9, 39.5, 36.7, 35.1, 21.1 ppm. HRMS (ESI): calcd. For C₁₄H₁₈IO₂ [M+H]⁺: 345.0346, found: 345.0343.

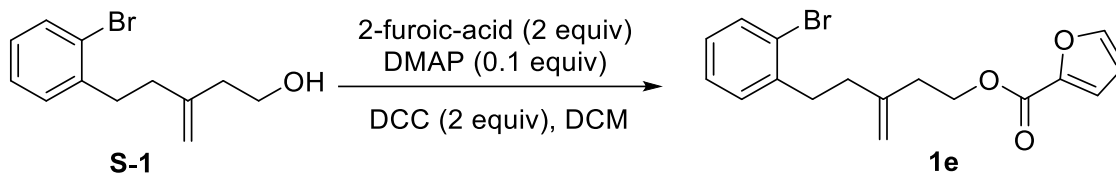


5-(2-Bromophenyl)-3-methylenepentyl 4-methoxybenzoate (1c) was isolated as a colorless oil (1.67 g, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ= 8.02-7.96 (m, 2H), 7.55-7.49 (m, 1H), 7.24-7.20 (m, 2H), 7.08-7.01 (m, 1H), 6.95-6.83 (m, 2H), 4.96-4.87 (m, 2H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 2.94-2.81 (m, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.46-2.32 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 166.3, 163.3, 144.9, 141.1, 132.8, 131.6 (2C), 130.3, 127.7, 127.5, 124.4, 122.8, 113.6 (2C), 112.0, 63.1, 55.4, 36.3, 35.3, 34.9 ppm. HRMS (ESI): calcd. For C₂₀H₂₂BrO₃ [M+H]⁺: 389.0747, found: 389.0750.



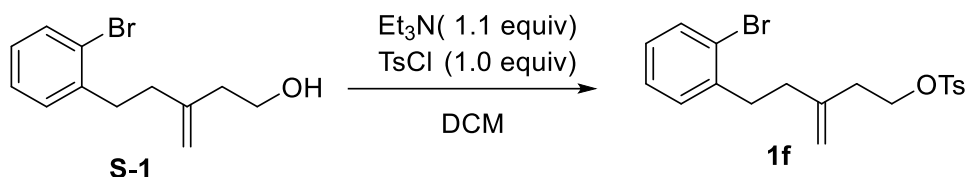
5-(2-Bromophenyl)-3-methylenepentyl 4-fluorobenzoate (1d) was isolated as a colorless oil (1.32 g, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ=8.09-8.00 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 4.3 Hz, 2H), 7.12-7.00 (m, 3H), 4.93 (d, *J* = 1.6 Hz, 1H), 4.92 (d, *J* = 1.6 Hz, 1H), 4.46 (t, *J* = 6.8 Hz, 2H), 2.96-2.80 (m, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 2.39 (dd, *J* = 9.9, 6.5 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 165.7 (d, *J* = 253.7 Hz), 165.6, 144.7, 141.0, 132.8, 132.1 (d, *J* = 9.3 Hz, 2C), 130.3, 127.7, 127.5, 126.6 (d, *J* = 3.0 Hz), 124.4, 115.5 (d, *J* = 22.0 Hz, 2C), 112.1, 63.4, 36.3, 35.2, 34.9 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -105.69--105.91 (m, 1F) ppm. HRMS (EI): calcd. For C₁₉H₁₈BrFO₂ [M]⁺: 376.0468, found: 376.0462.

Procedure for Synthesis of 5-(2-Bromophenyl)-3-methylenepentyl furan-2-carboxylate (**1e**)



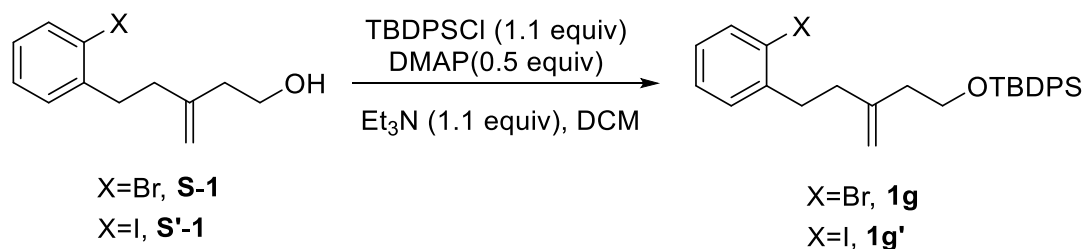
To a solution of the homoallylic alcohol **S1** (1.3g, 5.0 mmol, 1 equiv), 2-furoic acid (1.1 g, 10.0 mmol, 2 equiv) and DMAP (61 mg, 0.5 mmol, 10 mol%) in CH_2Cl_2 (35 mL) was added a solution of DCC (2.0 g, 10.0 mmol, 2 equiv) in CH_2Cl_2 (15 mL). After stirring at room temperature for 12 h, the reaction mixture was filtered through a pad of silica gel. The filtrate was concentrated, and the crude residue was purified by column chromatography (hexane/ethyl acetate= 10:1) on silica gel to give the title product **1e** as a colorless oil (1.40 g, 80 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.61-7.56 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 4.4 Hz, 2H), 7.17 (d, J = 3.5 Hz, 1H), 7.05 (m, 1H), 6.50 (dd, J = 3.5, 1.7 Hz, 1H), 4.92-4.89 (m, 2H), 4.45 (t, J = 7.0 Hz, 2H), 2.96-2.82 (m, 2H), 2.54 (t, J = 7.0 Hz, 2H), 2.42-2.31 (m, 2H) ppm; ^{13}C NMR (101MHz, CDCl_3) δ = 158.7, 146.3, 144.7, 144.5, 141.0, 132.8, 130.3, 127.7, 127.5, 124.4, 117.9, 112.2, 111.8, 63.4, 36.4, 35.1, 34.8 ppm. HRMS (ESI): calcd. For $\text{C}_{17}\text{H}_{18}\text{BrO}_3$ [$\text{M}+\text{H}$] $^+$: 349.0434, found: 349.0435.

Procedure for Synthesis of 5-(2-Bromophenyl)-3-methylenepentyl 4-methylbenzenesulfonate (**1f**)

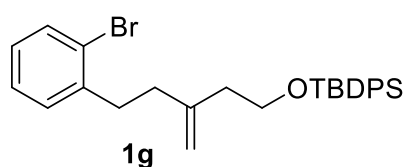


To a stirred solution of the homoallylic alcohol **S1** (1.3 g, 5.0 mmol, 1 equiv) and Et_3N (0.56 g, 5.5 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added tosyl chloride (0.95 g, 5.0 mmol, 1 equiv) at 0 °C dropwise. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The resulting suspension was passed through a pad of Celite and the filtrate was concentrated. The residue was purified by column chromatography (hexane/ethyl acetate= 20:1) on silica gel to give the product **1f** as a colorless oil (1.94 g, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.83-7.76 (m, 2H), 7.51 (dd, J = 8.0, 1.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25-7.19 (m, 1H), 7.17 (d, J = 1.9 Hz, 1H), 7.05 (m, 1H), 4.87 (d, J = 1.5 Hz, 1H), 4.78 (d, J = 1.4 Hz, 1H), 4.15 (t, J = 6.9 Hz, 2H), 2.81-2.73 (m, 2H), 2.49-2.38 (m, 2H), 2.43 (s, 3H), 2.27-2.17 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 144.8, 143.2, 140.8, 133.1, 132.8, 130.3, 129.9(2C), 127.9(2C), 127.8, 127.5, 124.3, 112.8, 68.7, 36.1, 35.2, 34.7, 21.7 ppm. HRMS (ESI): calcd. For $\text{C}_{19}\text{H}_{22}\text{BrO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$: 409.0468, found: 409.0466.

Procedure for Synthesis of Alkenes **1g** and **1g'**

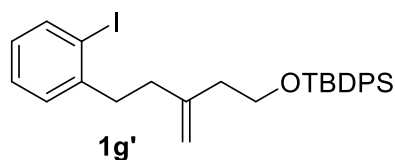


To a stirred solution of the homoallylic alcohols **S-1** or **S'-1** (8.0 mmol, 1 equiv), Et₃N (1.3 mL, 8.8 mmol, 1.1 equiv) and DMAP (50 mg, 0.4 mmol, 5 mol/%) in CH₂Cl₂ (25 mL), TBDPSCl (1.32 g, 8.8 mmol, 1.1 equiv) was added at room temperature. After stirring for 12 h, water was added (30 mL), and the aqueous layer was extracted twice with CH₂Cl₂. The combine organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The crude residue was purified by column chromatography (hexane/ethyl acetate= 20:1) on silica gel to give the product **1g** or **1g'**.



((5-(2-Bromophenyl)-3-methylenepentyl)oxy)(tert-butyl)diphenylsilane (**1g**) was isolated as a colorless oil (1.97g, 50 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.71-7.64 (m, 4H), 7.50 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42-7.30 (m, 6H), 7.23-7.08 (m, 2H), 7.07-6.98 (m, 1H), 4.81 (d, *J* = 1.7 Hz, 1H), 4.78 (d, *J* = 1.6 Hz, 1H), 3.87-3.70 (m, 2H), 2.90-2.74 (m, 2H), 2.47-2.31 (m, 2H), 2.29-2.18 (m, 2H), 1.05 (s, 9H) ppm; ¹³C

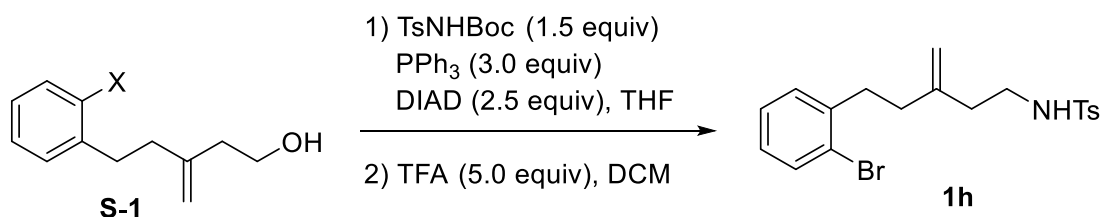
NMR (101MHz, CDCl₃) δ= 145.9, 141.3, 135.6 (4C), 133.9 (2C), 132.8, 130.3, 129.6 (2C), 127.7(4C), 127.6, 127.4, 124.4, 111.5, 63.0, 39.3, 36.5, 34.9, 26.9 (3C), 19.3 ppm. HRMS (ESI): calcd. For C₂₈H₃₄BrOSi [M+H]⁺: 493.1557, found: 493.1555.



((5-(2-Iodophenyl)-3-methylenepentyl)oxy)(tert-butyl)diphenylsilane (**1g'**) was isolated as a colorless oil (2.16 g, 50 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.73-7.64 (m, 4H), 7.44-7.32 (m, 6H), 7.26-7.21 (m, 1H), 7.13 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.86 (d, *J* = 1.7 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.79 (d, *J* = 1.6 Hz, 1H), 3.80 (t, *J* = 7.0 Hz, 2H), 2.83-2.68 (m, 2H), 2.44-2.28 (m, 2H), 2.27-2.10 (m, 2H),

1.05 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 145.8, 144.6, 139.4 (2C), 135.6(4C), 134.0, 129.6 (2C), 129.4, 128.3, 127.71, 127.66 (4C), 111.5, 100.5, 63.0, 39.6, 39.3, 36.8, 26.9 (3C), 19.3 ppm. HRMS (ESI): calcd. For C₂₈H₃₄IOSi [M+H]⁺: 541.1418, found: 541.1419.

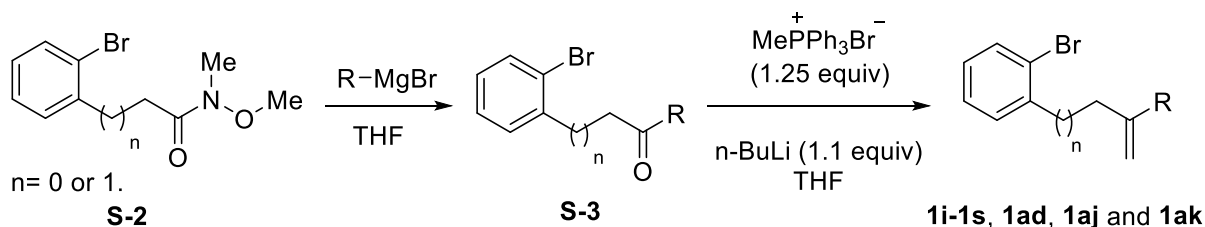
Procedure for Synthesis of *N*-(5-(2-bromophenyl)-3-methylenepentyl)-4-methylbenzenesulfonamide (**1h**)



To a stirred solution of *tert*-butyl tosylcarbamate (6.1 g, 22.5 mmol, 1.5 equiv), the homoallylic alcohol **S-1** (3.81g, 15.0 mmol, 1 equiv), and triphenylphosphine (11.8 g, 45 mmol, 3 equiv) in THF (75 mL), DIAD (7.6 g, 37.5 mmol, 2.5 equiv) was added at 0 °C. After stirring at room temperature overnight, the mixture was quenched with water and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. The residue was dissolved in DCM and then trifluoroacetic acid (8.55 g, 75 mmol, 5 equiv) was added in one portion at room temperature. After stirring at room temperature for 2 h, the mixture was concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate= 5:1) on silica gel to give the alkene **1h** as a yellow oil (4.9 g, 80 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.78-7.72 (m, 2H), 7.50 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.32-7.28 (m, 2H), 7.24-7.19 (m, 1H), 7.17-7.11 (m, 1H), 7.09-7.01 (m, 1H), 4.88 (d, *J* = 1.5 Hz, 1H), 4.75 (d, *J* = 1.5 Hz, 1H),

4.50 (m, 1H), 3.09 (q, $J = 6.5$ Hz, 2H), 2.81-2.68 (m, 2H), 2.40 (s, 3H), 2.23 (t, $J = 6.7$ Hz, 2H), 2.20-2.08 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 144.6, 143.5, 140.7, 136.8, 132.8, 130.2, 129.7$ (2C), 127.8, 127.5, 127.1 (2C), 124.3, 112.8, 40.7, 35.7, 35.4, 34.7, 21.5 ppm. HRMS (ESI): calcd. For $\text{C}_{19}\text{H}_{23}\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 408.0627, found: 408.0629.

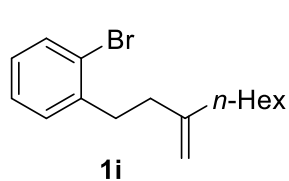
(2) Preparation of alkenes **1i-1s**, **1ad** and **1aj**



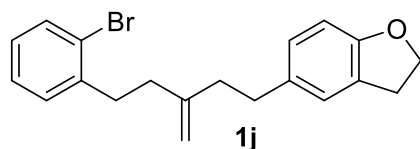
Step 1: A solution of alkyl bromides (15 mmol, 1 equiv) in dry tetrahydrofuran (30 mL) was added dropwise to a mixture of magnesium turnings (0.72 g, 30 mmol, 1 equiv), dry tetrahydrofuran (10 mL) and a crystal of iodine under nitrogen. The mixture was stirred at room temperature for about 2 h, which was then added dropwise at 0 °C into the solution of the Weinreb-amide **S-2**⁴ (7.5 mmol, 1 equiv) in dry tetrahydrofuran (15 mL). After stirring at room temperature for 10 h, the mixture was quenched with water and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated to give the crude ketones **S-3**.

Step 2: To a dry tetrahydrofuran (15 mL) solution of methyltriphenylphosphonium bromide (3.35 g, 9.4 mmol, 1.25 equiv)^a was added *n*-butyllithium (2.5M in hexane, 3.4 mL, 8.3 mmol, 1.1 equiv) at 0°C. After the mixture was stirred at room temperature for 30 min, a tetrahydrofuransolution of the crude ketones **S-3** (7.5 mmol, 1equiv) was added dropwise at 0°C. After stirring at room temperature for 14 h, the mixture was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=50:1) on silica gel to give the alkenes **1i-s** and **1ac**.

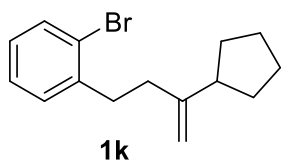
^aIn the case of **1ac** d_3 -methyltriphenylphosphonium bromide was used instead.



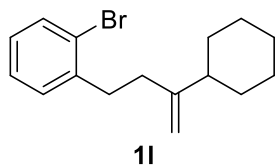
1-Bromo-2-(3-methylenenonyl)benzene (**1i**) was isolated as a colorless oil (1.78 g, 80 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.52$ (d, $J = 8.0$ Hz, 1H), 7.23-7.17 (m, 2H), 7.08-6.99 (m, 1H), 4.77 (s, 2H), 2.90-2.77 (m, 2H), 2.32-2.23 (m, 2H), 2.08 (t, $J = 7.7$ Hz, 2H), 1.49-1.41 (m, 2H), 1.35-1.26 (m, 6H), 0.91-0.86 (m, 3H) ppm; ^{13}C NMR (101MHz, CDCl_3) $\delta = 149.3, 141.6, 132.8, 130.3, 127.5, 127.4, 124.4, 109.3, 36.3, 36.2, 35.0, 31.8, 29.1, 27.8, 22.7, 14.2$ ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{23}\text{Br}$ $[\text{M}]^+$: 294.0977, found: 294.0978.



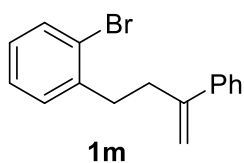
5-(5-(2-Bromophenyl)-3-methylenepentyl)-2,3-dihydrobenzofuran (**1j**) was isolated as a white solid (2.01 g, 75% yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.53$ (dd, $J = 7.8, 1.1$ Hz, 1H), 7.24-7.17 (m, 2H), 7.10-7.02 (m, 2H), 6.93 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 4.82 (s, 2H), 4.54 (t, $J = 8.6$ Hz, 2H), 3.18 (t, $J = 8.6$ Hz, 2H), 3.02-2.80 (m, 2H), 2.75-2.63 (m, 2H), 2.47-2.21 (m, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 158.3, 148.6, 141.4, 134.2, 132.8, 130.4, 127.7, 127.6, 127.5, 126.9, 124.9, 124.4, 109.9, 108.9, 71.2, 38.7, 36.5, 35.1, 33.9, 29.9$ ppm. HRMS (ESI): calcd. For $\text{C}_{20}\text{H}_{22}\text{BrO}$ $[\text{M}+\text{H}]^+$: 357.0849, found: 357.0846.



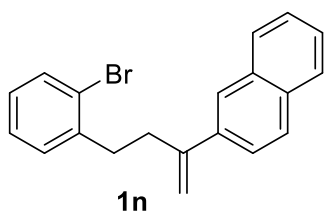
1-Bromo-2-(3-cyclopentylbut-3-en-1-yl)benzene (1k) was isolated as a colorless oil (1.36 g, 65 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.52 (d, J = 7.8 Hz, 1H), 7.24-7.21 (m, 2H), 7.11-6.94 (m, 1H), 4.83 (m, 1H), 4.78 (m, 1H), 2.99-2.80 (m, 2H), 2.57-2.41 (m, 1H), 2.38-2.28 (m, 2H), 1.89-1.80 (m, 2H), 1.74-1.63 (m, 2H), 1.63-1.52 (m, 2H), 1.47-1.33 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 152.5, 141.7, 132.8, 130.3, 127.5, 127.4, 124.4, 107.2, 46.3, 35.6, 35.4, 31.6 (2C), 25.0 (2C) ppm. HRMS (EI): calcd. For $\text{C}_{15}\text{H}_{19}\text{Br}$ $[\text{M}]^+$: 278.0665, found: 278.0664.



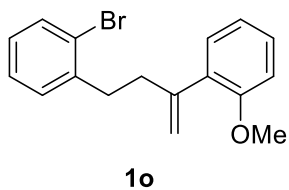
1-Bromo-2-(3-cyclohexylbut-3-en-1-yl)benzene (1l) was isolated as a colorless oil (1.23 g, 56 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.52 (d, J = 7.9 Hz, 1H), 7.22 (d, J = 4.4 Hz, 2H), 7.08-7.00 (m, 1H), 4.79 (s, 1H), 4.77 (s, 1H), 2.89-2.80 (m, 2H), 2.33-2.27 (m, 2H), 1.95-1.86 (m, 1H), 1.83-1.74 (m, 4H), 1.72-1.63 (m, 1H), 1.30-1.13 (m, 5H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 154.6, 141.7, 132.8, 130.3, 127.5, 127.4, 124.4, 107.3, 44.4, 35.4, 35.0, 32.5 (2C), 26.7 (2C), 26.4 ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{21}\text{Br}$ $[\text{M}]^+$: 292.0821, found: 292.0823.



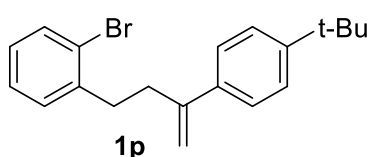
1-Bromo-2-(3-phenylbut-3-en-1-yl)benzene (1m) was isolated as a colorless oil (1.51 g, 70 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.53 (dd, J = 7.9, 1.3 Hz, 1H), 7.50-7.44 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.26 (m, 1H), 7.25-7.18 (m, 1H), 7.19-7.14 (m, 1H), 7.08-7.00 (m, 1H), 5.32 (d, J = 1.3 Hz, 1H), 5.09 (d, J = 1.3 Hz, 1H), 2.92-2.84 (m, 2H), 2.84-2.75 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 147.6, 141.2, 140.9, 132.8, 130.5, 128.4 (2C), 127.7, 127.5, 127.4, 126.2 (2C), 124.4, 112.9, 35.5, 35.4 ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{15}\text{Br}$ $[\text{M}]^+$: 286.0351, found: 286.0351.



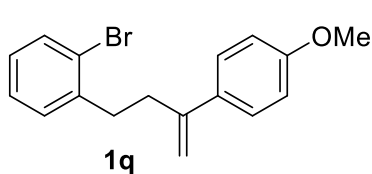
2-(4-(2-bromophenyl)but-1-en-2-yl)naphthalene (1n) was isolated as a white solid (1.77 g, 70 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.91 (d, J = 1.7 Hz, 1H), 7.84-7.75 (m, 3H), 7.65-7.58 (m, 1H), 7.56-7.50 (m, 1H), 7.50-7.38 (m, 2H), 7.22-7.12 (m, 2H), 7.07-6.97 (m, 1H), 5.47 (d, J = 1.2 Hz, 1H), 5.19 (d, J = 1.2 Hz, 1H), 2.96-2.86 (m, 4H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 147.3, 141.2, 138.0, 133.5, 132.92, 132.88, 130.7, 128.3, 128.0, 127.8, 127.6, 127.5, 126.2, 125.9, 124.9, 124.7, 124.4, 113.5, 35.6 (2C) ppm. HRMS (EI): calcd. For $\text{C}_{20}\text{H}_{17}\text{Br}$ $[\text{M}]^+$: 336.0508, found: 336.0504.



1-Bromo-2-(3-(2-methoxyphenyl)but-3-en-1-yl)benzene (1o) was isolated as a colorless oil (2.02 g, 85 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.49 (dd, J = 7.9, 1.2 Hz, 1H), 7.29-7.22 (m, 1H), 7.21-7.13 (m, 3H), 7.05-6.99 (m, 1H), 6.97-6.90 (m, 1H), 6.87 (dd, J = 8.3, 1.0 Hz, 1H), 5.18 (d, J = 1.6 Hz, 1H), 5.07 (d, J = 1.9 Hz, 1H), 3.82 (s, 3H), 2.79 (s, 4H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 156.6, 148.3, 141.5, 132.7, 131.7, 130.4, 130.3, 128.6, 127.5, 127.3, 124.5, 120.6, 114.7, 110.6, 55.4, 36.3, 35.3 ppm. HRMS (ESI): calcd. For $\text{C}_{17}\text{H}_{18}\text{BrO}$ $[\text{M}+\text{H}]^+$: 317.0536, found: 317.0535.

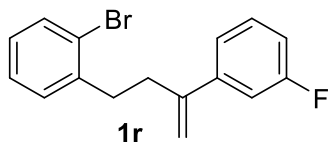


1-Bromo-2-(3-(4-(tert-butyl)phenyl)but-3-en-1-yl)benzene (1p) was isolated as a colorless oil (1.6 g, 80 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.53 (dd, J = 7.9, 1.2 Hz, 1H), 7.46-7.39 (m, 2H), 7.40-7.33 (m, 2H), 7.24-7.14 (m, 2H), 7.09-7.00 (m, 1H), 5.33 (d, J = 1.3 Hz, 1H), 5.05 (d, J = 1.5 Hz, 1H), 3.00-2.85 (m, 2H), 2.84-2.72 (m, 2H), 1.33 (s, 9H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 150.5, 147.2, 141.3, 137.8, 132.8, 130.6, 127.7, 127.4, 125.8 (2C), 125.3 (2C), 124.4, 112.2, 35.6, 35.4, 34.6, 31.4 (3C) ppm. HRMS (EI): calcd. For $\text{C}_{20}\text{H}_{23}\text{Br}$ $[\text{M}]^+$: 342.0977, found: 342.0976.



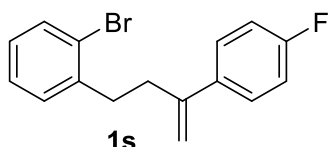
1-Bromo-2-(3-(4-methoxyphenyl)but-3-en-1-yl)benzene (1q) was isolated as a white solid (2.02 g, 85 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ =7.52 (d, J = 1.2 Hz, 1H), 7.46-7.36 (m, 2H), 7.17 (d, J = 1.9 Hz, 2H), 7.08-7.01 (m, 1H), 6.93-6.83 (m, 2H), 5.25 (d, J = 1.3 Hz, 1H), 5.00 (d, J = 1.6 Hz, 1H), 3.83 (s, 3H), 2.92-2.85 (m, 2H), 2.82-2.71 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 153.8, 141.5, 135.9, 127.9, 127.5, 125.3,

122.4, 122.1, 122.0 (2C), 119.1, 108.4 (2C), 106.0, 50.0, 30.3, 30.2 ppm. HRMS (ESI): calcd. For $\text{C}_{17}\text{H}_{18}\text{BrO}$ $[\text{M}+\text{H}]^+$: 317.0536, found: 317.0539.



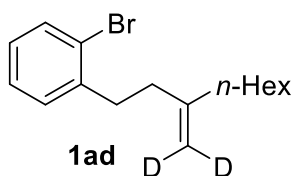
1-Bromo-2-(3-(3-fluorophenyl)but-3-en-1-yl)benzene (1r) was isolated as a colorless oil (1.83 g, 80 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.52 (dd, J = 7.9, 1.3 Hz, 1H), 7.32-7.26 (m, 1H), 7.25-7.18 (m, 2H), 7.18-7.12 (m, 2H), 7.08-7.02 (m, 1H), 7.01-6.94 (m, 1H), 5.34 (d, J = 1.1 Hz, 1H), 5.12 (d, J = 1.3 Hz, 1H), 2.91-2.84 (m, 2H), 2.81-2.72 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 163.0 (d, J = 245.0 Hz), 146.5 (d, J = 2.2 Hz), 143.2

(d, J = 7.4 Hz), 140.9, 132.9, 130.6, 129.8 (d, J = 8.4 Hz), 127.8, 127.5, 124.4, 121.8 (d, J = 2.8 Hz), 114.3 (d, J = 21.2 Hz), 114.0, 113.2 (d, J = 21.7 Hz), 35.4 (2C) ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ = -113.51 - -113.52 (m, 1F) ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{14}\text{BrF}$ $[\text{M}]^+$: 304.0257, found: 304.0262.



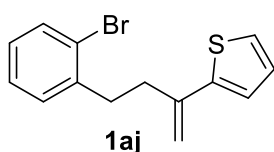
1-Bromo-2-(3-(4-fluorophenyl)but-3-en-1-yl)benzene (1s) was isolated as a colorless oil (1.83 g, 80 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.52 (dd, J = 8.0, 1.3 Hz, 1H), 7.45-7.39 (m, 2H), 7.24-7.18 (m, 1H), 7.14 (dd, J = 7.6, 1.9 Hz, 1H), 7.07-6.98 (m, 3H), 5.26 (d, J = 1.1 Hz, 1H), 5.07 (d, J = 1.3 Hz, 1H), 2.89-2.83 (m, 2H), 2.80-2.73 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 162.4 (d, J = 246.3 Hz), 146.6, 141.0, 136.9 (d, J = 3.4 Hz),

132.9, 130.5, 127.8, 127.7 (d, J = 7.6 Hz, 2C), 127.4, 124.4, 115.2 (d, J = 21.3 Hz, 2C), 112.9 (d, J = 1.4 Hz), 35.6, 35.4 ppm. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ = -115.04 - -115.22 (m, 1F) ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{14}\text{BrF}$ $[\text{M}]^+$: 304.0257, found: 304.0258.



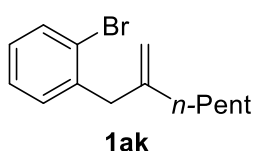
1-Bromo-2-(9-chloro-3-(methylene- d_2)nonyl)benzene (1ad) was isolated as a colorless oil (1.98 g, 80 % yield, 93% D_2); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.55-7.50 (m, 1H), 7.24-7.20 (m, 2H), 7.08-7.01 (m, 1H), 2.89-2.79 (m, 2H), 2.35-2.23 (m, 2H), 2.13-2.01 (m, 2H), 1.51-1.41 (m, 2H), 1.36-1.22 (m, 6H), 0.94-0.84 (m, 3H). ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 149.1, 141.6, 132.8, 130.3, 127.5, 127.4, 124.4, 108.7 (quintet, J = 23.2 Hz), 36.2, 36.1, 35.0,

31.8, 29.1, 27.8, 22.7, 14.1 ppm. HRMS (EI): calcd. For $\text{C}_{16}\text{H}_{21}\text{D}_2\text{Br}$ $[\text{M}]^+$: 296.1102, found: 296.1101.



2-(4-(2-Bromophenyl)but-1-en-2-yl)thiophene (1aj) was isolated as a yellow oil (2.0 g, 92% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ =7.54 (d, J = 8.0 Hz, 1H), 7.26-16 (m, 3H), 7.13 (d, J = 3.6 Hz, 1H), 7.10-03 (m, 1H), 7.02-97 (m, 1H), 5.42 (s, 1H), 4.97 (s, 1H), 3.05-92 (m, 2H), 2.82-59 (m, 2H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ =145.0, 140.9, 140.8, 132.8, 130.6, 127.8, 127.5, 127.4, 124.4, 124.3, 123.5, 111.5, 35.74, 35.66 ppm. HRMS (ESI): calcd. For $\text{C}_{14}\text{H}_{14}\text{BrS}^+$

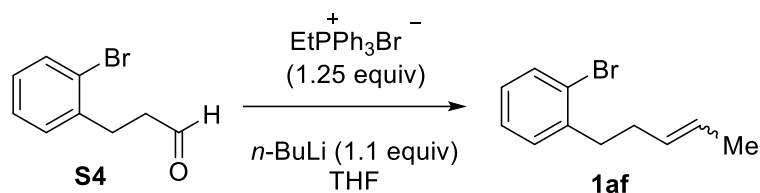
$[\text{M}+\text{H}]^+$: 292.9994, found: 292.9989.



1-Bromo-2-(2-methyleneheptyl)benzene (1ak) was isolated as a yellow oil (1.44 g, 70% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.54 (dd, J = 7.9, 1.1 Hz, 1H), 7.27-7.20 (m, 2H), 7.11-7.03 (m, 1H),

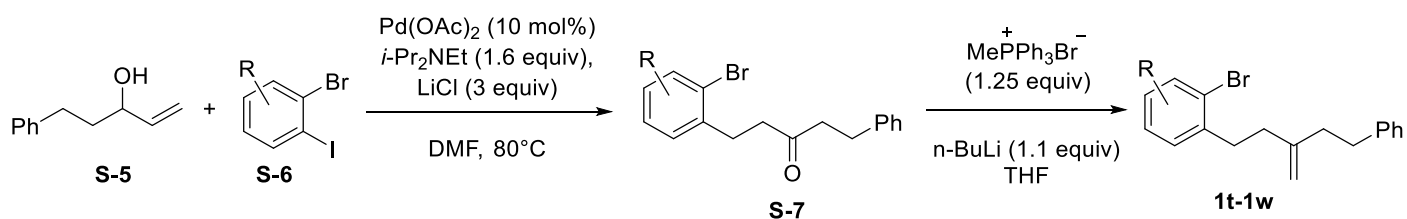
4.85 (s, 1H), 4.53 (s, 1H), 3.45 (s, 2H), 2.04 (t, $J = 7.7$ Hz, 2H), 1.57-1.41 (m, 2H), 1.36-1.21 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 147.7, 139.3, 132.8, 131.1, 127.8, 127.3, 125.2, 111.3, 42.4, 36.2, 31.6, 27.5, 22.6, 14.1$ ppm. HRMS (EI): calcd. For $\text{C}_{14}\text{H}_{19}\text{Br}$ $[\text{M}]^+$: 266.0664, found: 266.0665.

(3) Preparation of alkene **1af**



To a dry tetrahydrofuran (15 mL) solution of ethyltriphenylphosphonium bromide (3.48 g, 9.4 mmol, 1.25 equiv) was added *n*-butyllithium (2.5M in hexane, 3.4 mL, 8.3 mmol, 1.1 equiv) at 0°C. After the mixture was stirred at room temperature for 30 min, a tetrahydrofuransolution of 3-(2-bromophenyl)propanal **S-4**⁵ (1.58 g, 7.5 mmol, 1 equiv) was added dropwise at 0°C. After stirring at room temperature for 14 h, the mixture was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=50:1) on silica gel to give *1-bromo-2-(pent-3-en-1-yl)benzene* (**1af**) as a colorless oil (1.43 g, 85 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.54\text{-}7.50$ (m, 1H), 7.24-7.18 (m, 2H), 7.08-7.01 (m, 1H), 5.54 -5.35 (m, 2H), 2.83-2.71 (m, 2H), 2.40-2.33 (m, 1.56H) [2.32-2.23 (m, 0.57H)], 1.68-1.64 (m, 0.83H) [1.59-1.53 (m, 2.5H)] ppm; Inside the brackets are the chemical shifts of the minor isomer; ^{13}C NMR (101 MHz, CDCl_3) δ (mixture of two isomers)= 141.4, 141.3, 132.74, 132.73, 130.5, 130.4, 130.2, 129.1, 127.53, 127.47, 127.3, 125.7, 125.0, 124.5, 36.3, 36.1, 32.8, 27.2, 17.9, 12.7 ppm. HRMS (EI): calcd. For $\text{C}_{11}\text{H}_{13}\text{Br}$ $[\text{M}]^+$: 224.0196, found: 224.0195.

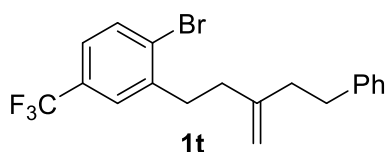
(4) Preparation of alkene **1t-1w**



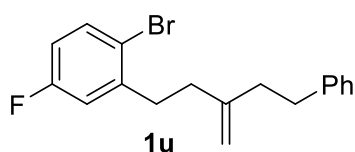
Step 1⁶: In a round bottle were placed Pd(OAc)_2 (157 mg, 0.7 mmol, 10 mol%), LiCl (0.9 g, 21 mmol, 3 equiv) and dried DMF (20 mL). The solution was stirred to afford a yellow suspension, before the successive addition of diisopropylethylamine (1.9 mL, 11.2 mmol, 1.6 equiv), the allylic alcohol **S-5** (1.13g, 7 mmol, 1 equiv) and 2-bromoiodobenzenes **S-6** (7.0 mmol, 1 equiv). The reaction mixture was heated at 80 °C for 18 h, before it was poured into H_2O . The aqueous phase was extracted with EA and the combined organic extracts were washed successively with aq. HCl (1M), H_2O and brine, dried over MgSO_4 , filtered and evaporated. The residue was passed through a pad of silica gel to give the crude products **S-7**.

Step 2: To the THF (20 mL) solution of methyltriphenylphosphonium bromide (3.13 g, 8.75 mmol, 1.25 equiv) was added *n*-butyllithium (2.5M in hexanes, 3 mL, 1.1 equiv) at 0 °C. After the mixture was stirred for 30 min, a THF (10 mL) solution of the crude ketones **S-7** was added at this temperature. After warming up to room temperature and stirring for 14 h, the mixture was quenched with water. The aqueous layer was extracted with ethyl acetate and the combined organic layers were

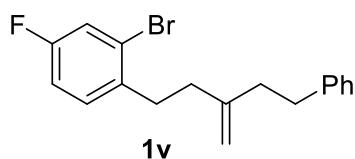
washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=50:1) on silica gel to give the alkenes **1t-1w**.



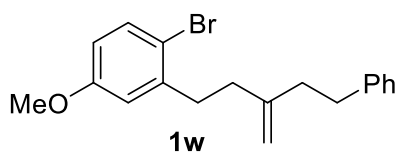
1-Bromo-2-(3-methylene-5-phenylpentyl)-4-(trifluoromethyl)benzene (1t) was isolated as a colorless oil (1.88 g, 70% yield); ¹H NMR (400 MHz, CDCl₃) δ= 7.64 (d, *J* = 8.3 Hz, 1H), 7.46-7.42 (m, 1H), 7.34-7.25 (m, 3H), 7.23-7.16 (m, 3H), 4.85 (s, 1H), 4.83 (s, 1H), 2.96-2.88 (m, 2H), 2.83-2.74 (m, 2H), 2.44-2.30 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 147.8, 142.4, 142.1, 133.4, 130.0 (q, *J* = 32.7 Hz), 128.5 (2C), 128.4 (2C), 128.3 (d, *J* = 1.7 Hz), 127.0 (d, *J* = 3.7 Hz), 126.0, 124.4 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 273.2 Hz), 110.5, 38.0, 36.2, 35.0, 34.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -62.58 (s, 3F) ppm. HRMS (EI): calcd. For C₁₉H₁₈BrF₃ [M]⁺: 382.0539, found: 382.0537.



1-Bromo-4-fluoro-2-(3-methylene-5-phenylpentyl)benzene (1u) was isolated as a colorless oil (1.64 g, 70 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.51-7.41 (m, 1H), 7.32-7.25 (m, 2H), 7.25-7.16 (m, 3H), 6.92 (dd, *J* = 9.4, 3.0 Hz, 1H), 6.84-6.67 (m, 1H), 4.88-4.76 (m, 2H), 2.91-2.68 (m, 4H), 2.41-2.26 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 162.0 (d, *J* = 246.3 Hz), 148.0, 143.5 (d, *J* = 7.3 Hz), 142.1, 133.9 (d, *J* = 8.1 Hz), 128.4 (4C), 125.9, 118.5 (d, *J* = 3.0 Hz), 117.1 (d, *J* = 22.4 Hz), 114.8 (d, *J* = 22.4 Hz), 110.4, 38.1, 36.1, 35.1, 34.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -115.13--115.23 (m, 1F) ppm. HRMS (EI): calcd. For C₁₈H₁₈BrF [M]⁺: 332.0570, found: 332.0572.

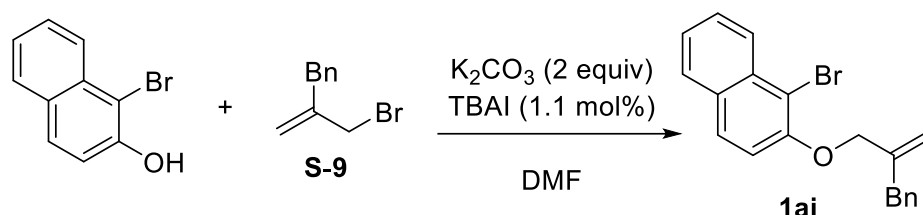
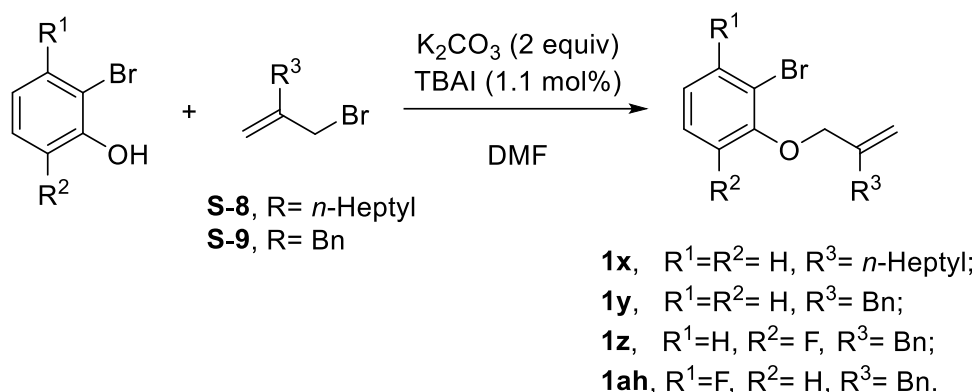


2-Bromo-4-fluoro-1-(3-methylene-5-phenylpentyl)benzene (1v) was isolated as a colorless oil (1.63 g, 70 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.32-7.25 (m, 3H), 7.22-7.11 (m, 4H), 6.98-6.90 (m, 1H), 4.83 (d, *J* = 1.5 Hz, 1H), 4.81 (d, *J* = 1.6 Hz, 1H), 2.88-2.70 (m, 4H), 2.41-2.28 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 160.8 (d, *J* = 248.3 Hz), 148.1, 142.1, 137.2 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.2 Hz), 128.41 (2C), 128.40 (2C), 125.9, 124.1 (d, *J* = 9.3 Hz), 119.9 (d, *J* = 24.1 Hz), 114.5 (d, *J* = 20.6 Hz), 110.2, 38.1, 36.5, 34.5, 34.2 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -115.20 - -115.29 (m, 1F) ppm. HRMS (EI): calcd. For C₁₈H₁₈BrF [M]⁺: 332.0570, found: 332.0570.

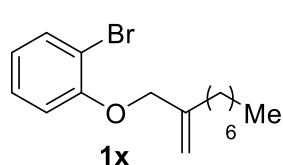


1-Bromo-4-methoxy-2-(3-methylene-5-phenylpentyl)benzene (1w) was isolated as a yellow oil (0.89 g, 70 % yield); ¹H NMR (400 MHz, CDCl₃) δ= 7.41 (d, *J* = 8.7 Hz, 1H), 7.31-7.25 (m, 2H), 7.23-7.17 (m, 3H), 6.77 (d, *J* = 3.1 Hz, 1H), 6.63 (dd, *J* = 8.8, 3.1 Hz, 1H), 4.84-4.83 (m, 2H), 3.77 (s, 3H), 2.86-2.70 (m, 4H), 2.50-2.15 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 159.0, 148.4, 142.4, 142.2, 133.3, 128.39 (2C), 128.35 (2C), 125.8, 116.0, 114.9, 113.2, 110.0, 55.5, 38.1, 36.4, 35.3, 34.5 ppm. HRMS (ESI): calcd. For C₁₉H₂₂BrO [M+H]⁺: 345.0849, found: 345.0848.

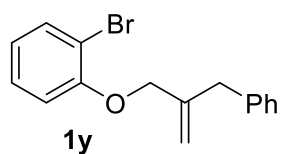
(5) Preparation of alkenes **1x-z**, **1ah** and **1ai**



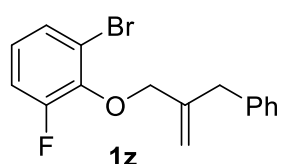
To a suspension of K_2CO_3 (1.38 g, 10 mmol, 2 equiv) in DMF (20 mL) was added the solution of the 2-bromophenol (5 mmol, 1 equiv), 2-(bromomethyl)non-1-ene **S-8**⁷ or 2-(bromomethyl)allylbenzene **S-9**⁸ (5.5 mmol, 1.1 equiv) and TBAI (10 mg, 0.055 mmol, 1.1 mol/%) in DMF (1mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight, before it was quenched with water. The aqueous layer was extracted three times by EtOAc and the combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=50:1) on silica gel to give the products **1x-z**, **1ah** or **1ai**.



1-Bromo-2-((2-methylenenonyl)oxy)benzene (**1x**) was isolated as a colorless oil (1.34 g, 86 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.57-7.49 (m, 1H), 7.27-7.16 (m, 1H), 6.92-6.86 (m, 1H), 6.86-6.75 (m, 1H), 5.19 (d, J = 1.8 Hz, 1H), 5.01 (d, J = 1.5 Hz, 1H), 4.52 (s, 2H), 2.16 (t, J = 7.8 Hz, 2H), 1.58-1.46 (m, 2H), 1.38-1.17 (m, 8H), 0.88 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 155.1, 144.4, 133.3, 128.3, 121.8, 113.4, 112.3, 111.9, 71.6, 33.1, 31.8, 29.4, 29.2, 27.6, 22.7, 14.1 ppm. HRMS (ESI): calcd. For $\text{C}_{16}\text{H}_{24}\text{BrO}$ $[\text{M}+\text{H}]^+$: 311.1005, found: 311.1009.

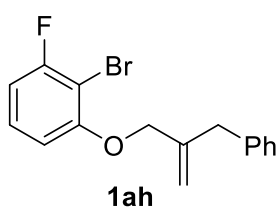


1-((2-Benzylallyl)oxy)-2-bromobenzene (**1y**) was isolated as a colorless oil (1.44 g, 95 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.53 (dd, J = 7.9, 1.6 Hz, 1H), 7.34-7.12 (m, 6H), 6.86-6.72 (m, 2H), 5.28 (d, J = 1.7 Hz, 1H), 5.07 (d, J = 1.3 Hz, 1H), 4.44 (d, J = 1.4 Hz, 2H), 3.52 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 154.9, 143.6, 138.7, 133.4, 129.1 (2C), 128.5 (2C), 128.3, 126.4, 121.9, 114.2, 113.4, 112.3, 70.7, 40.0 ppm. HRMS (ESI): calcd. For $\text{C}_{16}\text{H}_{16}\text{BrO}$ $[\text{M}+\text{H}]^+$: 303.0379, found: 303.0374.

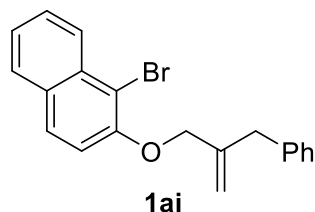


2-((2-Benzylallyl)oxy)-1-bromo-3-fluorobenzene (**1z**) was isolated as a colorless oil (1.20 g, 75 % yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.33-7.27 (m, 3H), 7.27-7.18 (m, 3H), 7.06-6.97 (m, 1H), 6.93-6.83 (m, 1H), 5.30-5.18 (m, 1H), 5.05-4.91 (m, 1H), 4.51 (s, 2H), 3.60 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 155.9 (d, J = 250.2 Hz), 144.2, 144.1, 138.9, 129.2 (2C), 128.5 (d, J

= 3.3 Hz), 128.4 (2C), 126.3, 124.4 (d, $J = 8.2$ Hz), 117.7 (d, $J = 3.1$ Hz), 116.2 (d, $J = 19.9$ Hz), 115.8, 75.9 (d, $J = 5.5$ Hz), 39.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) $\delta = -125.62 - -125.72$ (m, 1F) ppm. HRMS (ESI): calcd. For $\text{C}_{16}\text{H}_{15}\text{BrFO}$ $[\text{M}+\text{H}]^+$: 321.0285, found: 321.0288.

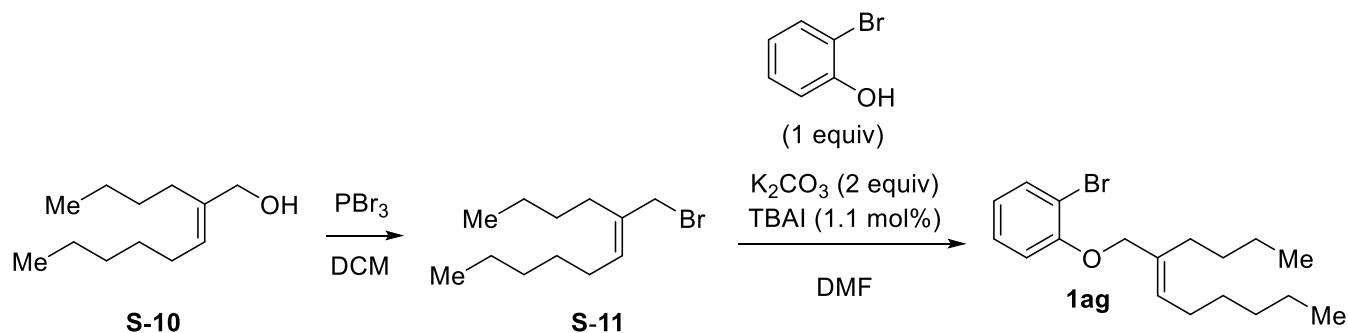


1-((2-Benzylallyl)oxy)-2-bromo-3-fluorobenzene (1ah) was isolated as a colorless oil (1.28 g, 80 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.32-7.26$ (m, 2H), 7.26-7.20 (m, 3H), 7.18-7.09 (m, 1H), 6.77-6.70 (m, 1H), 6.57-6.54 (m, 1H), 5.33-5.23 (m, 1H), 5.19-5.04 (m, 1H), 4.45 (s, 2H), 3.52 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 160.2$ (d, $J = 245.9$ Hz), 156.5 (d, $J = 4.0$ Hz), 143.3, 138.5, 129.0(2C), 128.5(2C), 128.3 (d, $J = 9.8$ Hz), 126.4, 114.4, 108.8 (d, $J = 22.7$ Hz), 108.5 (d, $J = 3.0$ Hz), 99.7, 71.1, 39.9 ppm; ^{19}F NMR (376 MHz, CDCl_3) $\delta = -105.24 - -105.34$ (m, 1F) ppm. HRMS (ESI): calcd. For $\text{C}_{16}\text{H}_{15}\text{BrFO}$ $[\text{M}+\text{H}]^+$: 321.0285, found: 321.0280.



2-((2-Benzylallyl)oxy)-1-bromonaphthalene (1ai) was isolated as white solid (1.11g, 63 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 8.23$ (dd, $J = 8.6, 1.1$ Hz, 1H), 7.78-7.65 (m, 2H), 7.59-7.50 (m, 1H), 7.41-7.35 (m, 1H), 7.33-7.16 (m, 5H), 7.10 (d, $J = 9.0$ Hz, 1H), 5.32 (d, $J = 1.7$ Hz, 1H), 5.09 (q, $J = 1.2$ Hz, 1H), 4.59 (s, 2H), 3.57 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 152.8, 143.8, 138.7, 133.2, 129.9, 129.1$ (2C), 128.7, 128.5 (2C), 128.0, 127.7, 126.4, 126.2, 124.4, 115.0, 114.5, 109.4, 71.5, 40.0 ppm. HRMS (ESI): calcd. For $\text{C}_{20}\text{H}_{18}\text{BrO}$ $[\text{M}+\text{H}]^+$: 353.0536, found: 353.0535.

(6) Preparation of alkene 1ag

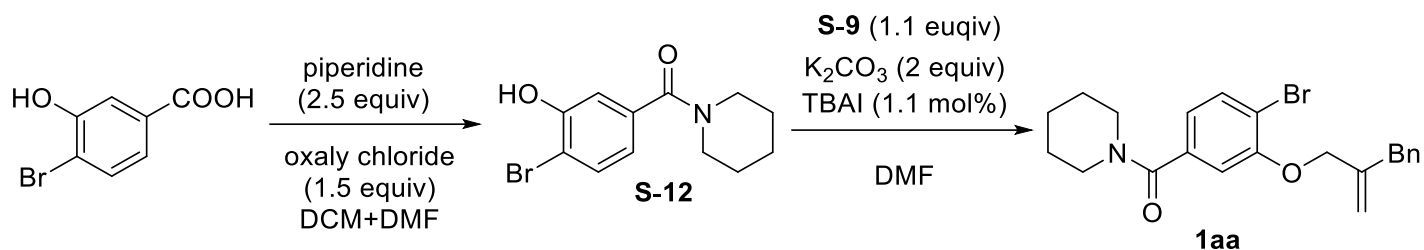


Step 1: (*E*)-2-butyloct-2-en-1-ol **S-10**⁹ (0.92 g, 5 mmol, 1 equiv) was dissolved in DCM (10 mL), and the solution was cooled to 0 °C. PBr_3 (1.49 g, 5.5 mmol, 1.1 equiv) was then dropwise added into it. After stirring at room temperature for 30 min, the mixture was quenched with water. The aqueous layer was extracted with ethyl acetate, and the combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo to give the crude (*E*)-5-(bromomethyl)undec-5-ene **S-11**.

Step 2: To a suspension of K_2CO_3 (1.38 g, 10 mmol, 2 equiv) in DMF (20 mL) was added the solution of 2-bromophenol (0.86 g, 5 mmol, 1 equiv), the crude allylic bromide **S-11** (5 mmol, 1 equiv) and TBAI (10 mg, 0.055 mmol, 1.1 mol%) in DMF (1mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight, before it was quenched with water. The aqueous layer was extracted three times by EtOAc and the combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=50:1) on silica gel to give (*E*)-1-bromo-2-((2-butyloct-2-en-1-yl)oxy)benzene (**1ag**) as a colorless oil (1.22 g, 72 % yield). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.31-7.24$ (m, 1H), 6.97-6.88 (m, 3H), 5.53 (t, $J = 7.2$ Hz, 1H), 4.41 (q, $J = 1.0$ Hz, 2H), 2.16 (t, $J = 8.0$ Hz, 2H), 2.07 (q, $J = 7.3$ Hz, 2H), 1.46-1.25 (m, 10H), 0.95-0.84 (m, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) $\delta = 159.1, 135.1, 129.8, 129.3$ (2C), 120.5, 114.9(2C), 72.3, 31.6, 30.6, 29.3, 27.9, 27.6, 22.9, 22.6, 14.1, 14.0 ppm.

HRMS (ESI): calcd. For C₁₈H₂₈BrO [M+H]⁺: 339.1318, found: 339.1316.

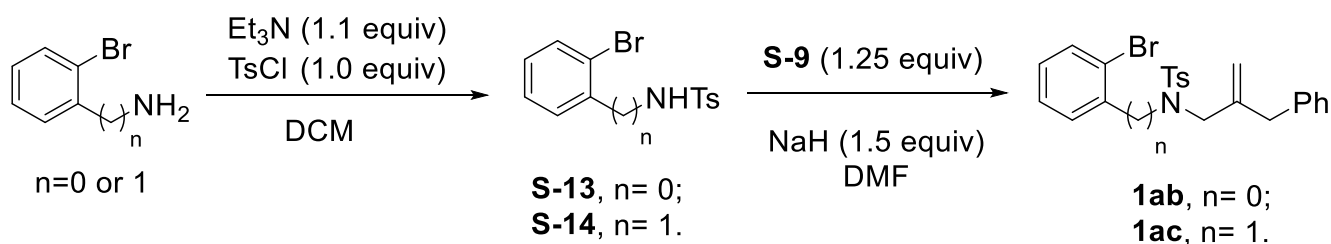
(7) Preparation of alkene 1aa



Step 1: The solution of 4-bromo-3-hydroxybenzoic acid (1.09 g, 5 mmol, 1 equiv) in a mixture of DCM (11 mL) and DMF (7 mL) was cooled at 0 °C, to which oxalyl chloride (0.95 g, 7.5 mmol, 1.5 equiv) was added dropwise. The resultant mixture was warmed to room temperature and stirred at this temperature for 1.5 h, before it was diluted with water. The aqueous layer was extracted three times by EtOAc and the combined organic layers were washed successively with 1 M HCl and brine, dried over MgSO₄, filtered and concentrated in vacuo, to give the crude product **S-12**, which was used in the next step without purification.

Step 2: To a suspension of K₂CO₃ (1.4 g, 10 mmol, 2 equiv) in DMF (20 mL) was added the solution of crude **S-12**, the bromide **S-9** (1.2 g, 5.5 mmol, 1.1 equiv) and TBAI (10 mg, 0.06 mmol, 1.1 mol%) in DMF (1 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight, before it was quenched with water. The aqueous layer was extracted three times by EtOAc and the combined organic phases were concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate=5:1) on silica gel to give the product **1aa** as a yellow oil (1.97 g, 95 % yield). ¹H NMR (400 MHz, CDCl₃) δ = 7.55 (d, *J* = 8.5 Hz, 1H), 7.30-7.18 (m, 5H), 6.87-6.77 (m, 2H), 5.29 (d, *J* = 1.7 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 4.46 (s, 2H), 3.78-3.57 (m, 2H), 3.51 (s, 2H), 3.27 (s, 2H), 1.72-1.56 (m, 4H), 1.52-1.36 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ = 169.1, 154.9, 143.2, 138.5, 136.8, 133.3, 129.0 (2C), 128.5 (2C), 126.4, 120.0, 114.4, 113.4, 111.9, 70.8, 48.7, 43.2, 39.9, 26.6, 25.6, 24.6 ppm. HRMS (ESI): calcd. For C₂₂H₂₄BrNNaO₂ [M+Na]⁺: 436.0883, found: 436.0885.

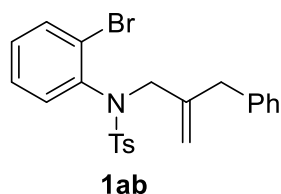
(8) Preparation of alkenes 1ab and 1ac



Step 1: To a solution of the amines (8.0 mmol, 1 equiv) in DCM (20 mL) at room temperature, TsCl (2.3 g, 12.0 mmol, 1.5 equiv) and a solution of triethylamine (1.7 mL, 12 mmol, 1.5 equiv) in 10 mL DCM were added dropwise under vigorous stirring. The mixture was stirred at room temperature overnight and then washed three times with DCM. The organic layer was dried over Na₂SO₄, filtered and concentrated to afford the crude sulfonamide **S-13** or **S-14**, which were used in the next step without further purification.

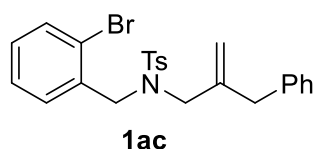
Step 2: To the suspension of NaH (0.48 g, 60 %, 12 mmol, 1.5 equiv) in DMF (20 mL) was added the solution of the crude

sulfonamide **S-13** or **S-14** in DMF (10 mL), followed by the bromide **S-9** (2.11 g, 10 mmol, 1.25 equiv) at the ambient temperature. After stirring at room temperature for 14 h, the mixture was quenched with water. The aqueous layer was extracted with ethyl acetate and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate= 5:1) on silica gel to give the alkenes **1ab** or **1ac**.



N-(2-Benzylallyl)-*N*-(2-bromophenyl)-4-methylbenzenesulfonamide (**1ab**) was isolated as a yellow solid (1.96 g, 86 % yield). ¹H NMR (400 MHz, CDCl₃) δ= 7.62-7.56 (m, 3H), 7.27-7.23 (m, 5H), 7.21-7.16 (m, 2H), 7.15-7.12 (m, 2H), 7.11-7.08 (m, 1H), 4.76 (s, 1H), 4.71 (d, *J* = 1.5 Hz, 1H), 4.25-4.14 (m, 1H), 4.06-3.91 (m, 1H), 3.47 (s, 2H), 2.43 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 143.7, 143.1, 138.8, 137.8, 136.1, 134.1, 131.9, 129.6, 129.5 (2C), 129.3 (2C), 128.3 (2C), 128.1 (2C), 127.8, 126.2, 125.7, 117.3, 55.2, 40.2, 21.6 ppm. HRMS (ESI): calcd.

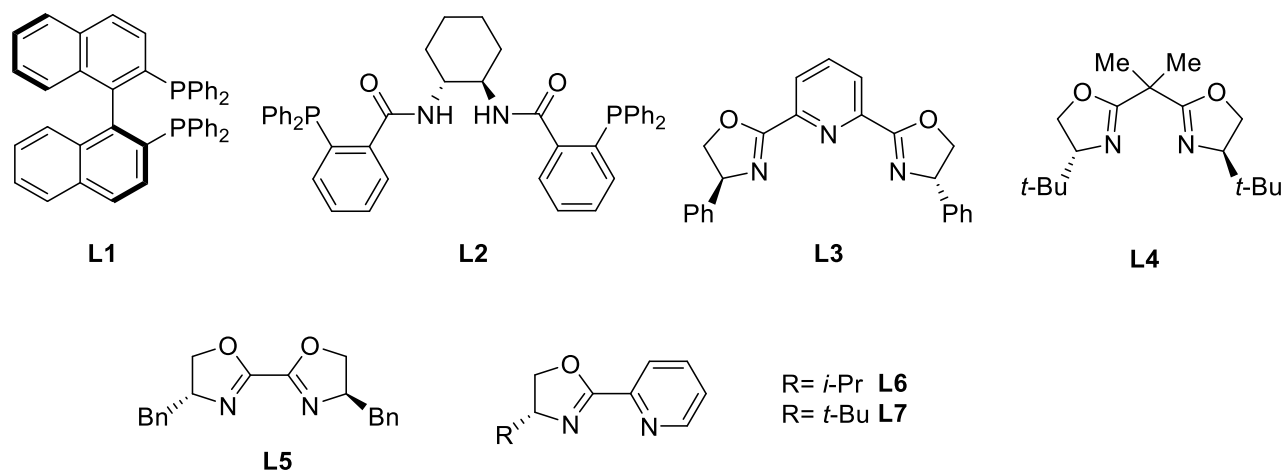
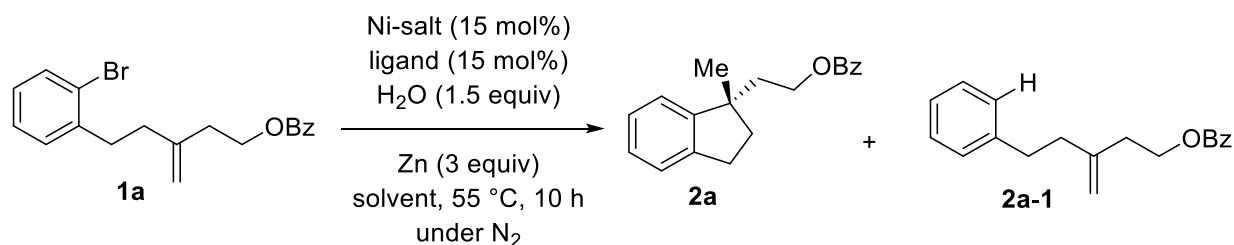
For C₂₃H₂₃BrNO₂S [M+H]⁺: 456.0627, found: 456.0628.



N-(2-Benzylallyl)-*N*-(2-bromobenzyl)-4-methylbenzenesulfonamide (**1ac**) was isolated as a yellow oil (2.0 g, 86 % yield); ¹H NMR (400 MHz, CDCl₃) δ= 7.71 (d, *J* = 8.3 Hz, 2H), 7.57-7.54 (m, 1H), 7.50-7.43 (m, 1H), 7.34-7.27 (m, 3H), 7.25-7.20 (m, 2H), 7.20-7.16 (m, 1H), 7.15-7.09 (m, 1H), 7.00-6.92 (m, 2H), 4.84 (d, *J* = 1.2 Hz, 1H), 4.63 (d, *J* = 1.5 Hz, 1H), 4.45 (s, 2H), 3.73 (s, 2H), 3.16 (s, 2H), 2.44 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 143.5,

142.9, 138.5, 136.4, 135.7, 132.6, 130.1, 129.8 (2C), 129.1 (2C), 128.9, 128.3 (2C), 127.6, 127.4, 126.2(2C), 123.1, 115.8, 53.8, 51.7, 39.9, 21.6 ppm. HRMS (ESI): calcd. For C₂₄H₂₅BrNO₂S [M+H]⁺: 470.0784, found: 470.0782.

Optimization of the Reaction Conditions

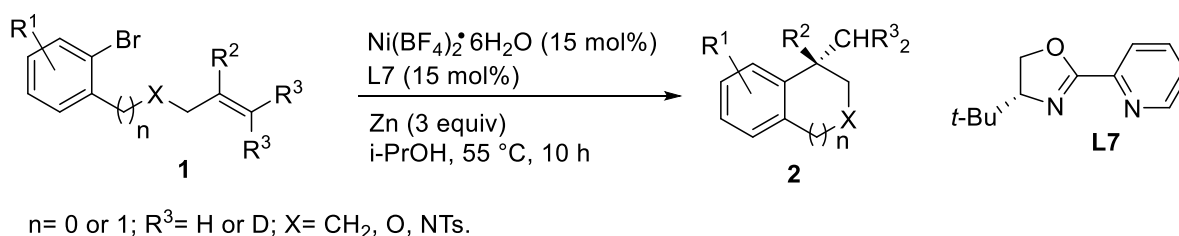


entry	metal	ligand	solvent	Recovered 1a (%) ^b	2a-1 (%) ^b	yield 2a (%) ^b	<i>ee</i> (%) ^c
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1	NiBr ₂	L1	DMA	63	34	trace	n.d. ^d
2	NiBr ₂	L2	DMA	77	21	trace	n.d. ^d
3	NiBr ₂	L3	DMA	98	0	trace	n.d. ^d
4	NiBr ₂	L4	DMA	98	0	trace	n.d. ^d
5	NiBr ₂	L5	DMA	80	0	20	92
6	NiBr ₂	L6	DMA	90	0	10	60
7	NiBr ₂	L7	DMA	75	0	25	94
8	Ni(acac) ₂	L7	DMA	100	0	0	-
9	Ni(dme)Br ₂	L7	DMA	70	0	30	90
10	Ni(BF ₄) ₂ •6H ₂ O	L7	DMA	49	0	51	94
11	Ni(BF ₄) ₂ •6H ₂ O	L7	DMF	46	0	54	92
12	Ni(BF ₄) ₂ •6H ₂ O	L7	THF	98	0	trace	n.d. ^d
13	Ni(BF ₄) ₂ •6H ₂ O	L7	MeOH	50	0	50	94
14	Ni(BF ₄) ₂ •6H ₂ O	L7	<i>i</i> PrOH	2	0	98	94
15 ^e	Ni(BF ₄) ₂ •6H ₂ O	L7	<i>i</i> PrOH	29	0	71	88
16^f	Ni(BF₄)₂•6H₂O	L7	<i>i</i>PrOH	2	0	98	94
17 ^{f,g}	Ni(BF ₄) ₂ •6H ₂ O	L7	<i>i</i> PrOH	10	0	90	94
18 ^{f,h}	Ni(BF ₄) ₂ •6H ₂ O	L7	<i>i</i> PrOH	18	0	82	94

^a Unless otherwise specified, reactions were performed on a 0.2 mmol scale of the aryl bromide **1a** using 1.5 equiv H₂O, 15 mol% Ni-salt, 15 mol% ligand and 3 equiv Zn at 55 °C in 0.5 mL solvent for 10 h under N₂ atmosphere (Set-up in glove-box). ^b Yields of the isolated product after flash chromatography. ^c Determined by HPLC-analysis on chiral stationary phase. ^d Not Determined. ^e Mn was used as reductant instead of Zn. ^f Reaction was performed without H₂O. ^g Reaction was performed with 10 mol% catalyst loading. ^h Reaction was performed with 5 mol% catalyst loading.

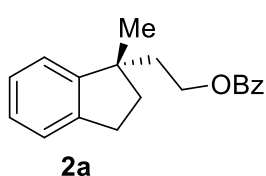
General Procedure for the Ni-Catalyzed Asymmetric Intramolecular Reductive Heck Reaction of Unactivated Alkenes



A sealed test tube charged with ligand **L7** (6.0 mg, 0.03 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles), and then NiBF₄•6H₂O (10.2 mg, 0.03 mmol, 15 mol%) and Zn-powder (39 mg, 0.6 mmol, 3.0 equiv) were added in the glovebox. Subsequently, *i*-PrOH (0.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 55 °C, before alkenes **1** (0.2 mmol, 1.0 equiv) were added and the resulting mixture was stirred at this temperature for 10 h. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding products **2**.

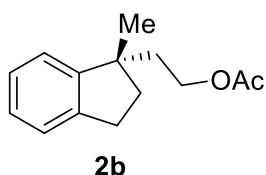
Analytical Data for the Products 2

The products **2l**,^{2b} **2m**,¹⁰ **2q**,¹¹ **2y**¹² and **2aa**¹² are known compounds and their NMR-data are consistent with these reported in the literature.

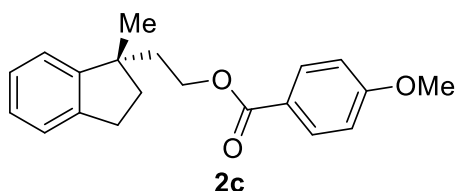


(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl benzoate (**2a**) was isolated through column

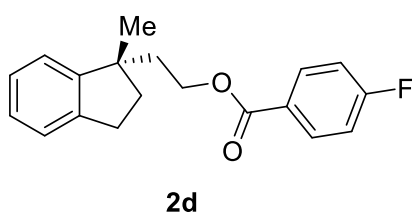
chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a colorless oil (55 mg, 98% yield, 94 %*ee*). ¹H NMR (400 MHz, CDCl₃) δ= 8.01-7.94 (m, 2H), 7.58-7.50 (m, 1H), 7.45-7.38 (m, 2H), 7.23-7.12 (m, 4H), 4.43-4.27 (m, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.21-2.01 (m, 3H), 2.00-1.88 (m, 1H), 1.34 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 166.6, 150.4, 142.9, 132.1, 130.4, 129.5 (2C), 128.3 (2C), 126.6, 126.4, 124.7, 122.5, 62.8, 46.2, 39.4, 38.9, 30.3, 27.1 ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ= 225 nm, hexane/isopropanol= 98/2, flow rate= 0.5 mL/min): t_R(minor)= 14.7 min, t_R(major)= 15.6min; HRMS (EI): calcd. for C₁₉H₂₀O₂ [M]⁺: 280.1458, found: 280.1459.



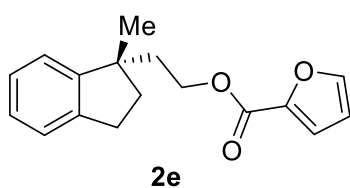
(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl acetate (**2b**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (20:1) as a yellow oil (40 mg, 92 % yield, 95 %*ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.24-7.07 (m, 4H), 4.19-3.97 (m, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.15-2.03 (m, 1H), 1.99 (s, 3H), 1.98-1.83 (m, 3H), 1.28 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 171.1, 150.3, 142.9, 126.6, 126.4, 124.7, 122.5, 62.2, 46.0, 39.2, 38.8, 30.2, 27.0, 21.0 ppm. The *ee* was determined by HPLC analysis (Chiral MD column, λ= 210 nm, hexane/isopropanol= 97/3, flow rate= 0.5 mL/min): t_R(minor)= 11.3 min, t_R(major)=17.3 min; HRMS (ESI): calcd. for C₁₄H₁₉O₂ [M+H]⁺:219.1380, found: 219.1383.



(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl 4-methoxybenzoate (**2c**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a colorless oil (51 mg, 81 % yield, 94 %*ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.96-7.90 (m, 2H), 7.21-7.12 (m, 4H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.38-4.23 (m, 2H), 3.84 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.20-2.11 (m, 1H), 2.10-1.99 (m, 2H), 1.98-1.87 (m, 1H), 1.33 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 166.4, 163.3, 150.5, 142.9, 131.5 (2C), 126.6, 126.4, 124.7, 122.9, 122.6, 113.6 (2C), 62.4, 55.4, 46.2, 39.5, 38.9, 30.3, 27.1 ppm; The *ee* was determined by HPLC analysis (Chiral MD column, λ= 254 nm, hexane/isopropanol= 97/3, flow rate= 0.5 mL/min): t_R(minor)= 23.4 min, t_R(major)= 28.2 min; HRMS (EI): calcd. for C₂₀H₂₂O₃ [M]⁺: 310.1564, found: 310.1565.

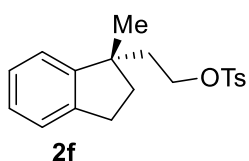


(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl 4-fluorobenzoate (**2d**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (45 mg, 75 % yield, 93 %*ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.99-7.93 (m, 2H), 7.22-7.12 (m, 4H), 7.08 (t, *J* = 8.7 Hz, 2H), 4.41-4.26 (m, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.21-2.01 (m, 3H), 1.99-1.87 (m, 1H), 1.34 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 165.70 (d, *J* = 253.6 Hz), 165.65, 150.4, 142.9, 132.1 (d, *J* = 9.3 Hz, 2C), 126.63 (d, *J* = 2.8 Hz), 126.60, 126.5, 124.7, 122.5, 115.4 (d, *J* = 22.0 Hz, 2C), 62.9, 46.1, 39.4, 38.9, 30.3, 27.2 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= -105.92 - -106.02 (m, 1F) ppm; The *ee* was determined by HPLC analysis (Chiral MD column, λ= 225 nm, hexane/isopropanol= 97/3, flow rate= 0.5 mL/min): t_R(major) = 11.1min, t_R(minor)= 11.9min; HRMS (EI): calcd. for C₁₉H₁₉FO₂ [M]⁺: 298.1364, found: 298.1360.

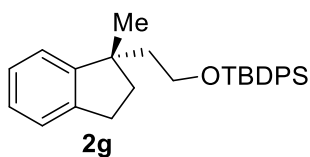


(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl furan-2-carboxylate (**2e**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a yellow oil (45 mg, 83 % yield, 93 %*ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.56 (m, 1H), 7.22-7.13 (m, 4H), 7.10 (d, *J* = 3.5 Hz, 1H), 7.12-7.08 (m, 1H), 4.38-4.24 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.09 (m, 3H), 1.93 (m, 1H), 1.32 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 158.7, 150.3, 146.2, 144.8, 142.9, 126.6, 126.4, 124.7, 122.5, 117.7, 111.8, 62.7, 46.1, 39.3, 38.8, 30.2, 27.1 ppm. The *ee* was determined by HPLC analysis

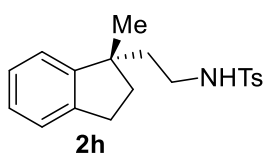
(Chiral MD column, λ = 254 nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): $t_R(\text{minor})$ = 16.0 min, $t_R(\text{major})$ = 17.9 min; HRMS (ESI): calcd. for $C_{17}H_{19}O_3 [M+H]^+$: 271.1329, found: 271.1339.



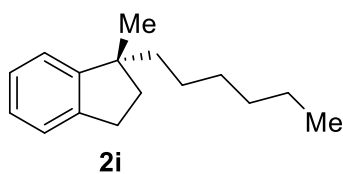
(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl 4-methylbenzenesulfonate (**2f**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a yellow oil (50 mg, 76 % yield, 94 % *ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.78-7.73 (m, 1H), 7.73-7.71 (m, 1H), 7.34-7.28 (m, 2H), 7.18-7.11 (m, 3H), 7.01-6.95 (m, 1H), 4.09-3.96 (m, 2H), 2.87-2.73 (m, 2H), 2.45 (s, 3H), 2.01-1.88 (m, 3H), 1.89-1.74 (m, 1H), 1.21 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.6, 144.7, 142.8, 133.1, 129.8 (2C), 127.8 (2C), 126.7, 126.4, 124.8, 122.4, 68.3, 45.9, 39.3, 38.8, 30.1, 26.9, 21.7 ppm; The *ee* was determined by HPLC analysis (Chiral MD column, λ = 210 nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): $t_R(\text{minor})$ = 23.0 min, $t_R(\text{major})$ = 23.6 min; HRMS (ESI): calcd. for $C_{19}H_{23}O_3S [M+H]^+$: 331.1362, found: 331.1368.



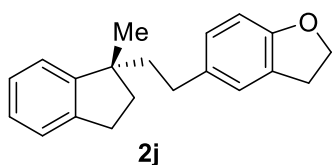
(*S*)-*tert*-Butyl(2-(1-methyl-2,3-dihydro-1H-inden-1-yl)ethoxy)diphenylsilane (**2g**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a colorless oil (75 mg, 90 % yield, 93 % *ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.69-7.56 (m, 4H), 7.43-7.32 (m, 6H), 7.18-7.13 (m, 1H), 7.12-7.08 (m, 2H), 7.03-6.97 (m, 1H), 3.79-3.62 (m, 2H), 2.87-2.75 (m, 2H), 2.05-1.95 (m, 1H), 1.94-1.81 (m, 2H), 1.80-1.72 (m, 1H), 1.18 (s, 3H), 1.03 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.3, 142.9, 135.63 (2C), 135.58 (2C), 133.99, 133.98, 129.59, 129.57, 127.68 (2C), 127.65 (2C), 126.3, 126.2, 124.5, 122.5, 61.5, 46.1, 43.2, 38.8, 30.3, 27.0, 26.9 (3C), 19.2 ppm. The *ee* was determined by HPLC analysis (Chiral MD column, λ = 210 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.7 mL/min): $t_R(\text{major})$ = 9.2 min, $t_R(\text{minor})$ = 9.7 min; HRMS (ESI): calcd. for $C_{28}H_{35}OSi [M+H]^+$: 415.2452, found: 415.2453.



(*S*)-4-Methyl-*N*-(2-(1-methyl-2,3-dihydro-1H-inden-1-yl)ethyl)benzenesulfonamide (**2h**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc = 5:1) as a colorless oil (46 mg, 70 % yield, 88 % *ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.79-7.60 (m, 2H), 7.33-7.23 (m, 2H), 7.21-7.07 (m, 3H), 7.04-6.92 (m, 1H), 4.30 (t, J = 6.1 Hz, 1H), 3.07-2.65 (m, 4H), 2.42 (s, 3H), 1.97-1.86 (m, 1H), 1.82-1.64 (m, 3H), 1.19 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.8, 143.3, 142.9, 136.9, 129.7 (2C), 127.1 (2C), 126.8, 126.5, 124.8, 122.4, 46.2, 40.8, 40.2, 38.6, 30.2, 27.0, 21.5 ppm; The *ee* was determined by HPLC analysis (Chiralpak AD-H column, λ = 225 nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R(\text{major})$ = 16.5 min, $t_R(\text{minor})$ = 17.5 min; HRMS (ESI): calcd. for $C_{19}H_{24}NO_2S [M+H]^+$: 330.1522, found: 330.1529.

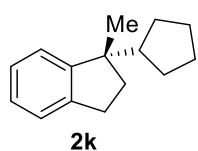


(*S*)-1-(6-Chlorohexyl)-1-methyl-2,3-dihydro-1H-indene (**2i**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (36 mg, 72 % yield, 93 % *ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.22-7.04 (m, 4H), 2.87 (t, J = 7.3 Hz, 2H), 2.07-1.97 (m, 1H), 1.86-1.76 (m, 1H), 1.66-1.42 (m, 2H), 1.36-1.12 (m, 8H), 1.22 (s, 3H), 0.86 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.8, 143.2, 126.12, 126.09, 124.5, 122.7, 47.4, 41.5, 38.6, 31.9, 30.3, 30.1, 26.8, 24.9, 22.7, 14.1 ppm; The *ee* was determined by HPLC analysis (Chiralcel OD-H column, λ = 254 nm, n-Hexane, flow rate = 0.25 mL/min): $t_R(\text{major})$ = 17.4 min, $t_R(\text{minor})$ = 18.9 min; HRMS (ESI): calcd. for $C_{16}H_{25} [M+H]^+$: 216.1873, found: 216.1873.



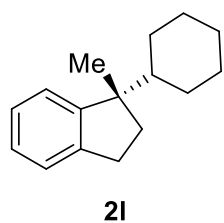
(*S*)-5-(2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)ethyl)-2,3-dihydrobenzofuran (**2j**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a colorless oil (45 mg, 80 % yield, 85 %

ee). ^1H NMR (400 MHz, CDCl_3) δ = 7.24-7.11 (m, 4H), 7.01-6.95 (m, 1H), 6.91-6.83 (m, 1H), 6.67 (d, J = 8.1 Hz, 1H), 4.52 (t, J = 8.6 Hz, 2H), 3.15 (t, J = 8.7 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 2.59 – 2.47 (m, 1H), 2.46-2.36 (m, 1H), 2.15-2.06 (m, 1H), 1.93-1.83 (m, 2H), 1.84-1.73 (m, 1H), 1.30 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 158.1, 151.2, 143.2, 135.0, 127.6, 126.9, 126.3, 126.2, 124.8, 124.6, 122.7, 108.9, 71.1, 47.5, 44.2, 38.5, 30.9, 30.3, 29.8, 26.9 ppm; The *ee* was determined by HPLC analysis (Chiralpak AD-H column, λ = 225 nm, hexane/isopropanol= 97/3, flow rate= 0.3 mL/min): t_{R} (minor)= 15.7min, t_{R} (major)= 16.4min; HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: 279.1743, found: 279.1740.



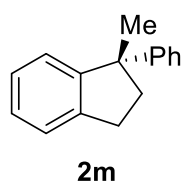
(*S*)-1-Cyclopentyl-1-methyl-2,3-dihydro-1H-indene (**2k**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (25 mg, 63 % yield, 92 %*ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.13-6.95 (m, 4H), 2.88 (t, J = 7.5 Hz, 2H), 2.25-2.01 (m, 2H), 1.83-1.70 (m, 2H), 1.65-1.43 (m, 6H), 1.24 (s, 3H), 1.20 – 1.11 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 151.5, 143.4, 126.1, 126.0, 124.4, 123.2, 49.8, 49.4, 35.9, 30.5, 28.2, 28.1, 26.7, 25.8, 25.6 ppm; The *ee* was determined by

HPLC analysis (Chiral MD column, λ = 254 nm, hexane/isopropanol= 99/1, flow rate= 0.5 mL/min): t_{R} (major) = 10.0 min, t_{R} (minor) = 10.6 min; HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{20}$ $[\text{M}]^+$: 200.1560, found: 200.1558.



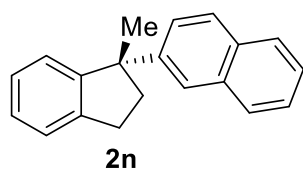
(*S*)-1-Cyclohexyl-1-methyl-2,3-dihydro-1H-indene (**2l**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (27mg, 62 % yield, 95 %*ee*); ^1H NMR (400 MHz, CDCl_3) δ = 7.13-6.95 (m, 4H), 2.78 (t, J = 7.5 Hz, 2H), 2.12-2.01 (m, 1H), 1.81-1.74 (m, 1H), 1.73-1.66 (m, 1H), 1.64-1.52 (m, 3H), 1.44-1.31 (m, 2H), 1.15 (s, 3H), 1.13-0.95 (m, 3H), 0.94-0.81 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 151.1, 143.6, 126.0, 125.8, 124.3, 123.5, 50.8, 46.6, 35.0, 30.9, 28.3, 27.9, 27.04, 26.98, 26.7, 26.2 ppm. The *ee* was determined by HPLC analysis (Chiral MD

column, λ = 254 nm, n-Hexane, flow rate= 0.25 mL/min): t_{R} (major)= 16.6 min, t_{R} (minor)= 17.5 min.



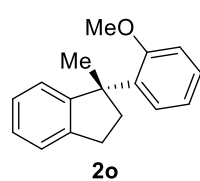
(*S*)-1-Methyl-1-phenyl-2,3-dihydro-1H-indene (**2m**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (30 mg, 72 % yield, 97 %*ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.29-7.13 (m, 8H), 7.09-7.00 (m, 1H), 2.96-2.80 (m, 2H), 2.48-2.32 (m, 1H), 2.29-2.13 (m, 1H), 1.68 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 151.0, 149.0, 143.7, 128.0 (2C), 126.64 (2C), 126.60, 126.5, 125.7, 124.5, 124.2, 52.1, 44.2, 30.5, 27.5 ppm; The *ee* was determined by HPLC analysis

(Chiralcel OD-H column, λ = 254nm, n-Hexane, flow rate= 0.5 mL/min): t_{R} (minor)= 19.6 min, t_{R} (major)= 20.6 min.



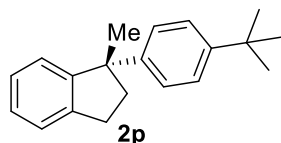
(*S*)-2-(1-Methyl-2,3-dihydro-1H-inden-1-yl)naphthalene (**2n**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (32 mg, 62% yield, 93 %*ee*); ^1H NMR (400 MHz, CDCl_3) δ = 7.79-7.69 (m, 3H), 7.57 (d, J = 1.9 Hz, 1H), 7.45-7.40 (m, 2H), 7.36 (dd, J = 8.7, 2.0 Hz, 1H), 7.33-7.28 (m, 1H), 7.24-7.19 (m, 2H), 7.09-7.03 (m, 1H), 3.03-2.87 (m, 2H), 2.53-2.45 (m, 1H), 2.32-2.19 (m, 1H), 1.77 (s, 3H) ppm; ^{13}C

NMR (101 MHz, CDCl_3) δ = 151.0, 146.4, 143.7, 133.1, 131.8, 128.0, 127.7, 127.4, 126.7, 126.6, 126.0, 125.9, 125.4, 124.6, 124.5, 124.3, 52.3, 43.8, 30.6, 27.4 ppm. The *ee* was determined by HPLC analysis (Chiralcel OJ-H column, λ = 225 nm, hexane/isopropanol= 98/2, flow rate= 0.5 mL/min): t_{R} (major)= 26.3 min, t_{R} (minor)= 32.2 min; HRMS (EI): calcd. for $\text{C}_{20}\text{H}_{18}$ $[\text{M}]^+$: 258.1403, found: 258.1403.



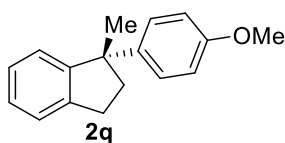
(*S*)-1-(2-Methoxyphenyl)-1-methyl-2,3-dihydro-1H-indene (**2o**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a colorless oil (15 mg, 30 % yield, 95 %*ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.30-7.24 (m, 1H), 7.22-7.14 (m, 3H), 7.13-7.04 (m, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.81-6.69 (m, 2H), 3.72 (s, 3H), 2.91-2.59 (m, 3H), 2.14-1.92 (m, 1H), 1.72 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 158.0,

151.3, 144.0, 136.3, 128.1, 127.4, 126.2, 126.0, 124.5, 124.3, 119.9, 111.8, 55.1, 51.4, 40.5, 30.8, 26.9 ppm. The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 254 nm, n-Hexane, flow rate= 0.5 mL/min): t_R (major)= 9.8min, t_R (minor)= 10.5min; HRMS (ESI): calcd. for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found:239.1434.



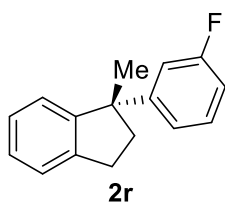
(*S*)-1-(4-(*tert*-Butyl)phenyl)-1-methyl-2,3-dihydro-1*H*-indene (**2p**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (28 mg, 53 % yield, 96 %*ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.24 (m, 3H), 7.22-7.16 (m, 2H), 7.14-7.05 (m, 3H), 2.96-2.83 (m, 2H), 2.48-2.34 (m, 1H), 2.25-2.09 (m, 1H), 1.66 (s, 3H), 1.29 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.1, 148.3, 145.9, 143.7, 126.5, 126.4, 126.2 (2C), 124.8

(2C), 124.5, 124.2, 51.7, 44.0, 34.3, 31.4 (3C), 30.5, 27.5 ppm. The *ee* was determined by HPLC analysis (Chiralcel OD-H column, λ = 210 nm, hexane, flow rate= 0.5 mL/min): t_R (minor)= 13.8min, t_R (major)= 14.5min; HRMS (EI): calcd. for $C_{20}H_{24}$ $[M]^+$:264.1873, found: 264.1873.



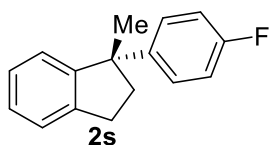
(*S*)-1-(4-Methoxyphenyl)-1-methyl-2,3-dihydro-1*H*-indene (**2q**) was isolated through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1) as a white solid (20 mg, 42 % yield, 90 %*ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.23 (m, 1H), 7.23-7.16 (m, 2H), 7.14-7.08 (m, 2H), 7.07-7.01 (m, 1H), 6.83-6.75 (m, 2H), 3.77 (s, 3H), 2.98-2.79 (m, 2H), 2.43-2.29 (m, 1H), 2.25-2.11 (m, 1H), 1.64 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.6, 151.2, 143.6, 141.2, 127.7 (2C), 126.6, 126.5, 124.5, 124.1, 113.3 (2C), 55.2, 51.5, 44.2, 30.4, 27.6 ppm; The *ee*

was determined by HPLC analysis (Chiralpak IB column, λ = 225 nm, hexane/isopropanol= 98/2, flow rate= 0.3mL/min): t_R (minor)= 15.7min, t_R (major)= 16.3min.



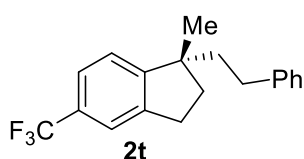
(*S*)-1-(3-Fluorophenyl)-1-methyl-2,3-dihydro-1*H*-indene (**2r**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (28 mg, 60 % yield, 95 %*ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.26 (m, 1H), 7.24-7.17 (m, 3H), 7.08-7.03 (m, 1H), 6.98-6.93 (m, 1H), 6.91-6.81 (m, 2H), 2.97-2.81 (m, 2H), 2.44-2.29 (m, 1H), 2.27-2.14 (m, 1H), 1.66 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.8 (d, J = 244.6 Hz), 152.0 (d, J = 6.4 Hz), 150.3, 143.6, 129.3 (d, J = 8.2 Hz), 126.9, 126.6, 124.7, 124.1, 122.3 (d, J = 2.7 Hz), 113.8 (d, J = 21.7 Hz), 112.6 (d, J =

21.2 Hz), 52.1, 44.0, 30.4, 27.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -118.02 - -118.14 (m, 1F) ppm; The *ee* was determined by HPLC analysis (Chiralcel OD-H column, λ = 225nm, hexane, flow rate= 0.5 mL/min): t_R (major) = 16.7 min, t_R (minor)= 18.7 min; HRMS (EI): calcd. for $C_{16}H_{15}F$ $[M]^+$: 226.1152, found: 226.1147.



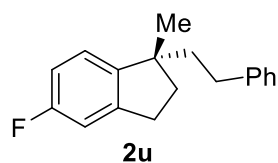
(*S*)-1-(4-Fluorophenyl)-1-methyl-2,3-dihydro-1*H*-indene (**2s**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (30 mg, 66 % yield, 97 %*ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.17 (m, 1H), 7.16-7.09 (m, 2H), 7.09-7.02 (m, 2H), 6.99-6.93 (m, 1H), 6.91-6.79 (m, 2H), 2.98-2.67 (m, 2H), 2.35-2.20 (m, 1H), 2.22-2.03 (m, 1H), 1.58

(s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.1 (d, J = 244.0 Hz), 150.8, 144.8 (d, J = 3.1 Hz), 143.5, 128.2 (d, J = 7.8 Hz, 2C), 126.8, 126.6, 124.6, 124.1, 114.6 (d, J = 20.9 Hz, 2C), 51.6, 44.3, 30.4, 27.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -117.89 - -118.31 (m, 1F) ppm; The *ee* was determined by HPLC analysis (ChiralcelOD-H column, λ = 210 nm, hexane, flow rate= 0.5 mL/min): t_R (major)= 12.3min, t_R (minor)= 13.6 min;HRMS (EI): calcd. for $C_{16}H_{15}F$ $[M]^+$: 226.1152, found: 226.1151.



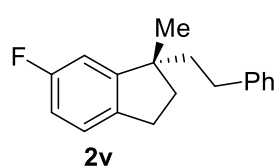
(*S*)-1-Methyl-1-phenethyl-5-(trifluoromethyl)-2,3-dihydro-1*H*-indene (**2t**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (50 mg, 82 %, 94 %*ee*). 1H NMR (400 MHz, $CDCl_3$) δ = 7.49-7.41 (m, 2H), 7.28-7.20 (m, 3H), 7.18-7.09 (m, 3H), 2.96 (t, J = 7.4 Hz, 2H), 2.67-2.56 (m, 1H), 2.53-2.35 (m, 1H), 2.23-2.11 (m, 1H), 2.00-

1.74 (m, 3H), 1.32 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 155.2, 144.0, 142.6, 128.8 (q, J = 31.8 Hz), 128.4 (2C), 128.3 (2C), 125.8, 124.6 (q, J = 272.9 Hz), 123.6 (q, J = 4.0 Hz), 122.9, 121.6 (q, J = 3.7 Hz), 47.7, 43.3, 38.4, 31.5, 30.2, 26.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -61.82 (s, 3F) ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 210nm, hexane/isopropanol= 99.5/0.5, flow rate= 0.5 mL/min): t_{R} (minor)= 11.5 min, t_{R} (major)= 12.0 min; HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_3$ $[\text{M}]^+$: 304.1433, found: 304.1434.



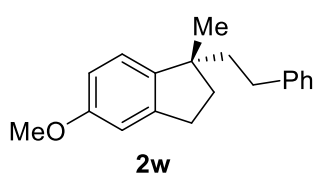
(*S*)-5-Fluoro-1-methyl-1-phenethyl-2,3-dihydro-1H-indene (**2u**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (49 mg, 96 % yield, 92 % *ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.28-7.20 (m, 2H), 7.19-7.10 (m, 3H), 7.08-7.01 (m, 1H), 6.91-6.80 (m, 2H), 2.89 (t, J = 7.3 Hz, 2H), 2.66-2.55 (m, 1H), 2.53-2.39 (m, 1H), 2.21-2.04 (m, 1H), 1.98-1.87 (m, 2H), 1.87-1.73 (m, 1H), 1.29 (s, 3H) ppm; ^{13}C NMR (101 MHz,

CDCl_3) δ = 162.1 (d, J = 242.7 Hz), 146.6 (d, J = 2.4 Hz), 145.3 (d, J = 7.9 Hz), 142.9, 128.4 (2C), 128.3 (2C), 125.7, 123.5 (d, J = 8.9 Hz), 113.1 (d, J = 22.4 Hz), 111.5 (d, J = 21.6 Hz), 46.9, 43.7, 38.9, 31.6, 30.3, 27.1 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -117.54 - -117.84 (m, 1F) ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 225nm, hexane/isopropanol= 99.5/0.5, flow rate= 0.5 mL/min): t_{R} (minor)= 10.2 min, t_{R} (major)= 10.6 min; HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{19}\text{F}[\text{M}]^+$: 254.1465, found: 254.1466.



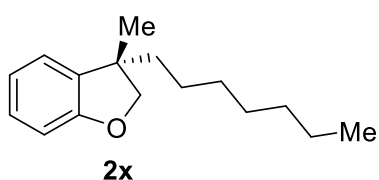
(*S*)-6-Fluoro-1-methyl-1-phenethyl-2,3-dihydro-1H-indene (**2v**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (48 mg, 94 % yield, 90 % *ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.28-7.22 (m, 2H), 7.19-7.07 (m, 4H), 6.90-6.77 (m, 2H), 2.87 (t, J = 7.3 Hz, 2H), 2.73-2.54 (m, 1H), 2.54-2.40 (m, 1H), 2.21-2.08 (m, 1H), 2.03-1.74 (m, 3H), 1.29 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 162.2 (d, J = 242.5 Hz), 153.4

(d, J = 6.8 Hz), 142.7, 138.4 (d, J = 2.4 Hz), 128.4(2C), 128.3(2C), 125.7, 125.39 (d, J = 8.6 Hz), 113.2 (d, J = 22.4 Hz), 109.7 (d, J = 21.7 Hz), 47.8, 43.4, 39.0, 31.4, 29.7, 26.8 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ = -117.29- -117.45 (m, 1F) ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 254nm, hexane/isopropanol= 99.5/0.5, flow rate= 0.7 mL/min): t_{R} (minor)= 7.7 min, t_{R} (major)= 8.3 min; HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{19}\text{F}[\text{M}]^+$: 254.1465, found: 254.1465.



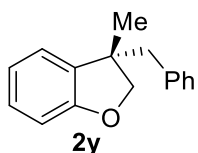
(*S*)-5-Methoxy-1-methyl-1-phenethyl-2,3-dihydro-1H-indene (**2w**) was isolated through column chromatography on silica gel (petroleum ether: EtOAc= 50:1) as a colorless oil (28 mg, 52 % yield, 95 % *ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.28-7.22 (m, 2H), 7.17-7.11 (m, 3H), 7.04 (d, J = 8.1 Hz, 1H), 6.80-6.71 (m, 2H), 3.79 (s, 3H), 2.89 (t, J = 7.3 Hz, 2H), 2.64-2.55 (m, 1H), 2.53-2.44 (m, 1H), 2.16-2.07 (m, 1H), 1.96-1.85 (m, 2H), 1.84-1.74 (m, 1H),

1.29 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ = 158.7, 144.7, 143.3, 143.1, 128.30 (2C), 128.28 (2C), 125.6, 123.2, 112.2, 109.9, 55.4, 46.8, 43.8, 38.9, 31.6, 30.5, 27.2 ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 225 nm, hexane/isopropanol= 98/2, flow rate= 0.5 mL/min): t_{R} (minor) = 9.0 min, t_{R} (major) = 10.1 min; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{23}\text{O}[\text{M}+\text{H}]^+$: 266.1665, found: 266.1670.

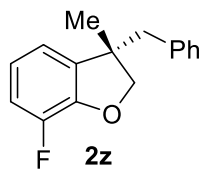


(*S*)-3-Heptyl-3-methyl-2,3-dihydrobenzofuran (**2x**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (20 mg, 45 % yield, 93 % *ee*). ^1H NMR (400 MHz, CDCl_3) δ = 7.15-7.03 (m, 2H), 6.91-6.83 (m, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.35 (d, J = 8.6 Hz, 1H), 4.15 (d, J = 8.6 Hz, 1H), 1.65-1.53 (m, 3H), 1.32 (s, 3H), 1.13-1.02 (m, 1H), 1.30-1.19 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H) ppm; ^{13}C

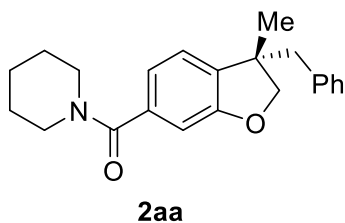
NMR (101 MHz, CDCl_3) δ = 159.5, 135.5, 127.9, 122.8, 120.4, 109.5, 82.6, 45.3, 40.9, 31.8, 30.1, 29.2, 25.6, 24.6, 22.7, 14.1 ppm; The *ee* was determined by HPLC analysis (Chiralpak IA column, λ = 225 nm, hexane, flow rate= 0.5 mL/min): t_{R} (minor)= 10.5 min, t_{R} (major)= 11.3 min; HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{25}\text{O}[\text{M}+\text{H}]^+$: 233.1900 found: 233.1905.



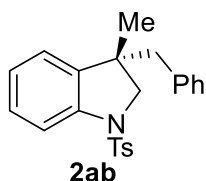
(*S*)-3-Benzyl-3-methyl-2,3-dihydrobenzofuran (**2y**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (23 mg, 50 % yield, 96 % *ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.26-7.20 (m, 3H), 7.17-7.08 (m, 1H), 7.03-6.97 (m, 2H), 6.96-6.89 (m, 1H), 6.89-6.83 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 8.7 Hz, 1H), 2.94-2.79 (m, 2H), 1.36 (s, 3H).ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 159.5, 137.6, 134.8, 130.4 (2C), 128.2, 128.0 (2C), 126.5, 123.4, 120.3, 109.7, 81.9, 46.6, 46.3, 24.6 ppm; The *ee* was determined by HPLC analysis (Chiral MD column, λ= 225 nm, hexane/isopropanol= 95/5, flow rate= 0.75 mL/min): t_R(major)= 11.2min, t_R(minor) = 11.6 min.



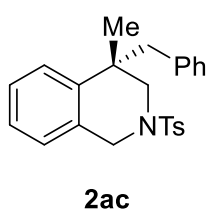
(*S*)-3-Benzyl-7-fluoro-3-methyl-2,3-dihydrobenzofuran (**2z**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (30 mg, 62 % yield, 97 % *ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.27-7.20 (m, 3H), 7.03-6.95 (m, 2H), 6.96-6.87 (m, 1H), 6.82-6.75 (m, 1H), 6.71 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.01-2.75 (m, 2H), 1.37 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 147.7 (d, *J* = 245.6 Hz), 146.0 (d, *J* = 10.4 Hz), 138.5, 137.1, 130.3(2C), 128.0(2C), 126.6, 120.9 (d, *J* = 5.5 Hz), 118.7 (d, *J* = 3.4 Hz), 115.3 (d, *J* = 16.8 Hz), 83.1, 47.0 (d, *J* = 1.8 Hz), 46.4, 24.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ= - 137.00- - 143.83 (m,1F) ppm; The *ee* was determined by HPLC analysis (ChiralMD column, λ= 225 nm, hexane/isopropanol= 95/5, flow rate= 0.5 mL/min): t_R(minor)= 20.3 min, t_R(major)= 21.4 min. HRMS (ESI): calcd. for C₁₆H₁₆FO [M+H]⁺: 243.1180 found: 243.1185.



(*S*)-(3-Benzyl-3-methyl-2,3-dihydrobenzofuran-6-yl)(piperidin-1-yl)methanone (**2aa**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (36 mg, 54 % yield, 98 % *ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.23 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.03-6.98 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.89 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.75 (d, *J* = 1.3 Hz, 1H), 4.53 (d, *J* = 8.8 Hz, 1H), 4.09 (d, *J* = 8.7 Hz, 1H), 3.69 (s, 2H), 3.34 (s, 2H), 2.88 (d, *J* = 4.5 Hz, 2H), 1.78-1.63 (m, 4H), 1.58-1.46 (m, 2H), 1.36 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 170.2, 159.5, 137.3, 136.7, 136.2, 130.4 (2C), 128.0 (2C), 126.6, 123.4, 119.1, 108.2, 82.3, 48.9, 46.6, 46.2, 43.1, 27.2, 26.6, 24.64, 24.55. The *ee* was determined by HPLC analysis (Chiralpak IB column, λ= 210 nm, hexane/isopropanol= 90/10, flow rate= 0.5 mL/min): t_R(minor)= 33.4 min, t_R(major)= 35.3 min.

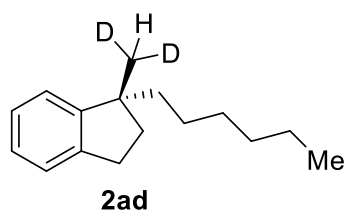


(*S*)-3-Benzyl-3-methyl-1-tosylindoline (**2ab**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (52 mg, 69 % yield, 80 % *ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.69-7.66 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.25-7.18 (m, 6H), 6.99-6.94 (m, 1H), 6.90 (dd, *J* = 6.6, 3.1 Hz, 2H), 6.87-6.82 (m, 1H), 3.94 (d, *J* = 10.1 Hz, 1H), 3.36 (d, *J* = 10.2 Hz, 1H), 2.74 (d, *J* = 13.3 Hz, 1H), 2.65 (d, *J* = 13.3 Hz, 1H), 2.36 (s, 3H), 1.16 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 144.0, 141.1, 138.7, 137.0, 134.0, 130.4 (2C), 129.6 (2C), 128.1, 128.0 (2C), 127.3 (2C), 126.5, 123.5, 123.2, 114.2, 61.1, 46.4, 44.4, 25.3, 21.5 ppm; The *ee* was determined by HPLC analysis (Chiralpak IB column, λ= 254 nm, hexane/isopropanol= 80/20, flow rate = 0.75 mL/min): t_R(minor)=7.9 min, t_R(major)= 8.6 min; HRMS (ESI): calcd. for C₂₃H₂₄NO₂S [M+H]⁺: 378.1522, found: 378.1529.



(*S*)-4-Benzyl-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (**2ac**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (59 mg, 75 % yield, 44 % *ee*). ¹H NMR (400 MHz, CDCl₃) δ= 7.77-7.69 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31-7.23 (m, 3H), 7.20-7.12 (m, 4H), 7.10-7.06 (m, 1H), 7.05-6.99 (m, 1H), 4.53 (d, *J* = 14.6 Hz, 1H), 3.89 (d, *J* = 14.7 Hz, 1H), 3.56 (dd, *J* = 11.6, 1.3 Hz, 1H), 3.09 (d, *J* = 13.4 Hz, 1H), 2.93 (d, *J* = 13.4 Hz, 1H), 2.48-2.39 (m, 1H), 2.43 (s, 3H), 1.18 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ= 143.8, 141.3, 137.5, 132.3, 131.2 (2C), 130.6, 129.7 (2C), 128.0 (2C), 127.9 (2C), 126.8, 126.7, 126.4, 126.3, 126.2, 53.3, 48.7, 46.8, 39.2, 24.5, 21.6 ppm; The *ee*

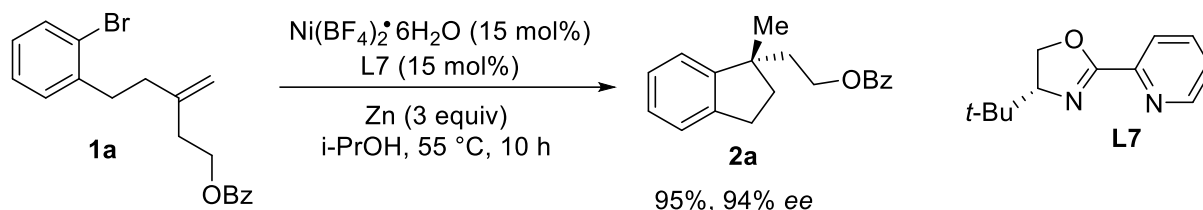
was determined by HPLC analysis (Chiralpak IB column, $\lambda=254$ nm, hexane/isopropanol= 80/20, flow rate= 0.75 mL/min): $t_R(\text{major})=9.8$ min, $t_R(\text{minor})=11.7$ min; HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$ $[M+H]^+$: 392.1679 found: 392.1683



(*S*)-1-(6-Chlorohexyl)-1-(methyl-*d*2)-2,3-dihydro-1*H*-indene (**2ad**) was isolated through column chromatography on silica gel with petroleum ether as a colorless oil (31 mg, 72% yield, 94 %*ee*). 1H NMR (400 MHz, $CDCl_3$) $\delta=7.21-7.06$ (m, 4H), 2.91-2.82 (m, 2H), 2.06-1.94 (m, 1H), 1.87-1.76 (m, 1H), 1.61-1.42 (m, 2H), 1.32-1.21 (m, 9H), 0.86 (t, $J=6.6$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) $\delta=151.8, 143.2, 126.11, 126.08, 124.4, 122.6, 47.2, 41.4, 38.5, 31.9, 30.3, 30.1, 26.2$ (quintet, $J=18.9$ Hz), 24.9, 22.7, 14.1 ppm; The *ee*

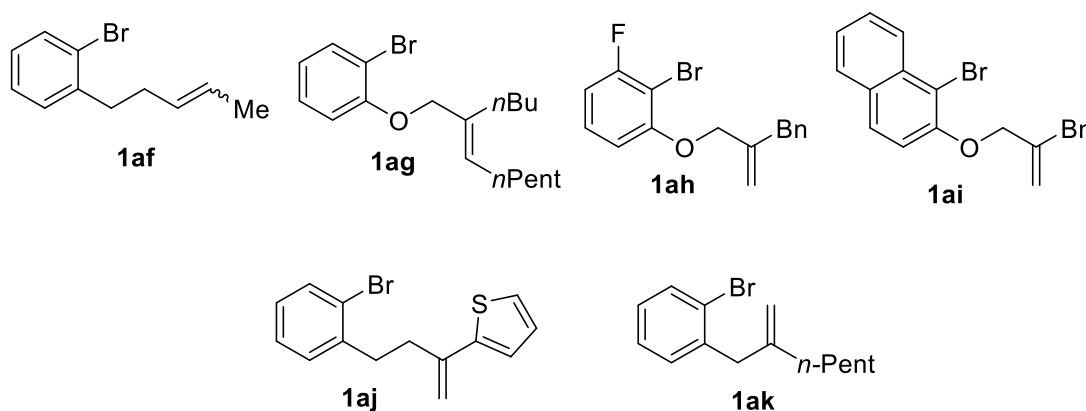
was determined by HPLC analysis (Chiralcel OD-H column, $\lambda=254$ nm, *n*-Hexane, flow rate= 0.25 mL/min): $t_R(\text{major})=17.7$ min, $t_R(\text{minor})=19.1$ min; HRMS (ESI): calcd. for $C_{16}H_{23}D_2$ $[M+H]^+$: 218.1998, found: 218.1998.

Procedure for the Ni-Catalyzed Asymmetric Reductive Heck of **1a** on 5-mmol Scale



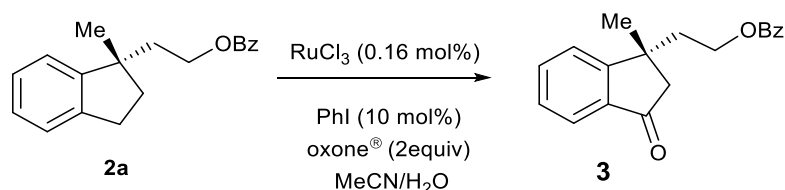
A sealed test tube charged with ligand **L7** (150 mg, 0.75 mmol, 15 mol%) and a stir bar was evacuated and filled with nitrogen (three cycles), and then $NiBF_4 \cdot 6H_2O$ (255 mg, 0.75 mmol, 15 mol%) and Zn-powder (975 mg, 15 mmol, 3.0 equiv) were added in the glovebox. Subsequently, *i*-PrOH (12.5 mL) was added to the mixture under nitrogen atmosphere. Then the reaction mixture was heated to 55 °C, before the alkene **1a** (1.79 g, 5 mmol, 1.0 equiv) was added and the resulting mixture was stirred at this temperature for 10 h. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel with petroleum ether to the mixture eluent of petroleum ether and ethyl acetate (50:1), affording the product **2a** as a colorless oil (1.33 g, 95% yield, 94 %*ee*).

Unsuccessful Substrates



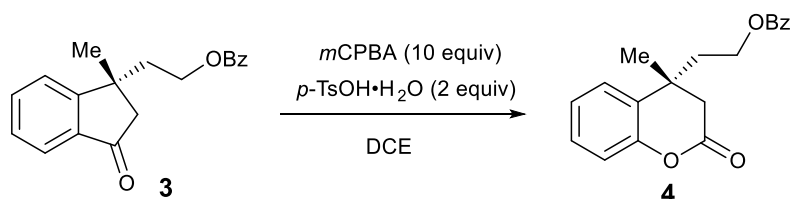
Derivatizations of the Reductive Heck Product 2a

(1) Oxidation 2a to the Indanone 3¹³



To a mixture of **2a** (1.47 g, 5.24 mmol, 1 equiv), PhI (109 mg, 0.53 mmol, 10 mol%), and Oxone[®] (6.52 g, 10.6 mmol, 2 equiv) in 16 mL of acetonitrile and 16 mL of water, RuCl_3 (1.75 mg, 0.0084 mmol, 0.16 mol%) was added under stirring at room temperature. After stirring for 10 h, 20 mL of ethyl acetate and 20 mL of water were added, and the mixture was stirred for another 5 min. The aqueous phase was extracted with EtOAc (3×20 mL) and the combined organic phases were washed with water and aqueous saturated NaCl solution, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel with the mixture eluent of petroleum ether and ethyl acetate (10:1) to give the (*S*)-2-(1-methyl-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl benzoate (**3**) as a yellow oil (1.32 g, 90 % yield, 95 % *ee*); ¹H NMR (400 MHz, CDCl_3) δ = 7.93-7.86 (m, 2H), 7.74-7.69 (m, 1H), 7.65-7.59 (m, 1H), 7.58-7.49 (m, 2H), 7.46-7.36 (m, 3H), 4.35-4.19 (m, 2H), 2.91 (d, *J* = 18.9 Hz, 1H), 2.57 (d, *J* = 18.9 Hz, 1H), 2.30-2.14 (m, 2H), 1.50 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl_3) δ = 205.2, 166.4, 161.7, 135.8, 135.2, 133.0, 129.9, 129.5 (2C), 128.4 (2C), 127.9, 123.9, 123.6, 62.1, 50.4, 40.8, 40.1, 28.9 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_3$ [M+H]⁺:295.1329, found: 295.1335. The *ee* was determined by HPLC analysis (Chiralpak IB column, λ = 225 nm, hexane/isopropanol= 70/30, flow rate= 0.5 mL/min): t_{R} (minor)=11.1 min, t_{R} (major)= 11.7 min.

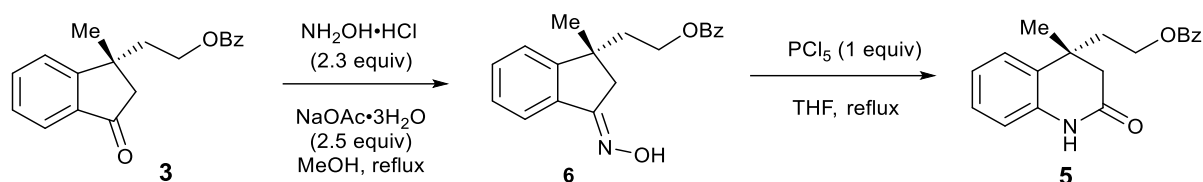
(2) *m*-CPBA-Mediated Baeyer-Villiger Oxidation of the Indanone 3



A mixture of the indanone **3** (59 mg, 0.2 mmol, 1 equiv), *m*-CPBA (85%, 404 mg, 2.0 mmol, 10 equiv), and *p*-TsOH·H₂O (77 mg, 0.4 mmol, 2 equiv) in dichloroethane (4.0 mL) was stirred at 60 °C for 5 h. After diluting with EtOAc, the mixture was washed with saturated aqueous Na_2SO_3 solution, saturated aqueous NaHCO_3 solution, and brine. The organic phase was dried over Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by preparative thin-layer chromatography (petroleum ether:EtOAc= 5:1) to afford (*S*)-2-(4-methyl-2-oxochroman-4-yl)ethyl benzoate (**4**) as a colorless oil (47 mg, 75% yield, 96 % *ee*). ¹H NMR (400 MHz, CDCl_3) δ = 7.98-7.89 (m, 2H), 7.59-7.52 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.30-7.24 (m, 1H), 7.18-7.12 (m, 1H), 7.09 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.45-4.34 (m, 1H), 4.34-4.22 (m, 1H), 2.85 (d, *J* = 15.7 Hz, 1H), 2.68 (d, *J* = 15.7 Hz, 1H), 2.22-1.95 (m, 2H), 1.49 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl_3) δ = 167.8, 166.4, 150.9, 133.1, 129.8, 129.6 (2C), 129.5, 128.7, 128.4 (2C), 125.2, 124.9, 117.5, 61.2, 42.2, 38.0, 35.5, 25.3 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_4$ [M+H]⁺:311.1278, found: 311.1284. The *ee* was

determined by HPLC analysis (Chiralpak AD-H column, $\lambda = 225$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R(\text{minor}) = 13.7$ min, $t_R(\text{major}) = 14.4$ min.

(3) Beckmann Rearrangement the Indanone 3



Step 1: To a solution of the indanone **3** (147 mg, 0.5 mmol, 1 equiv) and hydroxylamin hydrochloride (74.8 mg, 1.15 mmol, 2.3 equiv) in 0.6 mL of MeOH, sodium acetate trihydrate (102.5 mg, 1.25 mmol, 2.5 equiv) in 0.3 mL of water was added at room temperature. The mixture was refluxed for 1 h, before it was neutralized by adding saturated aqueous NaHCO_3 . The aqueous phase was extracted with diethyl ether and the organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered and removed in vacuo. The residue was purified by preparative thin-layer chromatography (petroleum ether:AcOEt = 2:1) to afford (*S,E*)-2-(3-(hydroxyimino)-1-methyl-2,3-dihydro-1H-inden-1-yl)ethyl benzoate (**6**) as a colorless oil (131 mg, 85 % yield); $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 10.38$ - 10.11 (brs, 1H), 8.04 - 7.88 (m, 2H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 3H), 7.32 - 7.23 (m, 2H), 4.27 (t, $J = 7.0$ Hz, 2H), 3.22 (d, $J = 18.8$ Hz, 1H), 2.84 (d, $J = 18.8$ Hz, 1H), 2.22 - 2.03 (m, 2H), 1.41 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 166.6$, 161.7 , 154.9 , 134.8 , 132.9 , 130.9 , 130.1 , 129.6 (2C), 128.3 (2C), 127.7 , 123.4 , 121.8 , 62.3 , 43.4 , 40.5 , 40.3 , 29.2 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 310.1438, found: 310.1439

Step 2: Phosphorus pentachloride (41.6 mg, 0.2 mmol, 1.0 equiv) was added in one portion to a solution of **3** (62 mg, 0.2 mmol, 1.0 equiv) in THF (4 mL). The reaction mixture was then heated under reflux for 1.5 h, before it was quenched with sat. aq. NH_4Cl solution (10 mL). The aqueous phase was extracted with EtOAc (2 \times 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over NaSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether:EtOAc = 2:1) to give (*R*)-2-(4-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-4-yl)ethyl benzoate (**5**) as a colorless oil (32 mg, 52 % yield, 96 % *ee*). $^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 8.10$ - 8.05 (brs, 1H), 7.99 - 7.93 (m, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.22 - 7.18 (m, 1H), 7.09 - 7.03 (m, 1H), 6.77 (dd, $J = 7.9$, 1.2 Hz, 1H), 4.41 - 4.32 (m, 1H), 4.27 - 4.20 (m, 1H), 2.66 (d, $J = 16.0$ Hz, 1H), 2.57 (d, $J = 16.1$ Hz, 1H), 2.12 (t, $J = 6.8$ Hz, 2H), 1.47 (s, 3H) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 170.0$, 166.5 , 136.0 , 133.0 , 129.98 , 129.95 , 129.6 (2C), 128.3 (2C), 128.0 , 125.5 , 123.7 , 115.9 , 61.6 , 43.9 , 37.6 , 36.2 , 25.6 ppm; HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 310.1438, found: 310.1441. The *ee* was determined by HPLC analysis (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.5 mL/min): $t_R(\text{major}) = 16.5$ min, $t_R(\text{minor}) = 18.5$ min.

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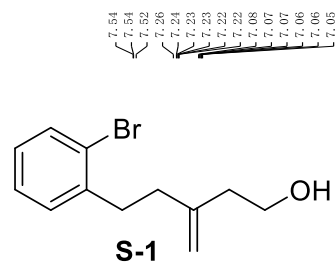
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NMR-Spectra

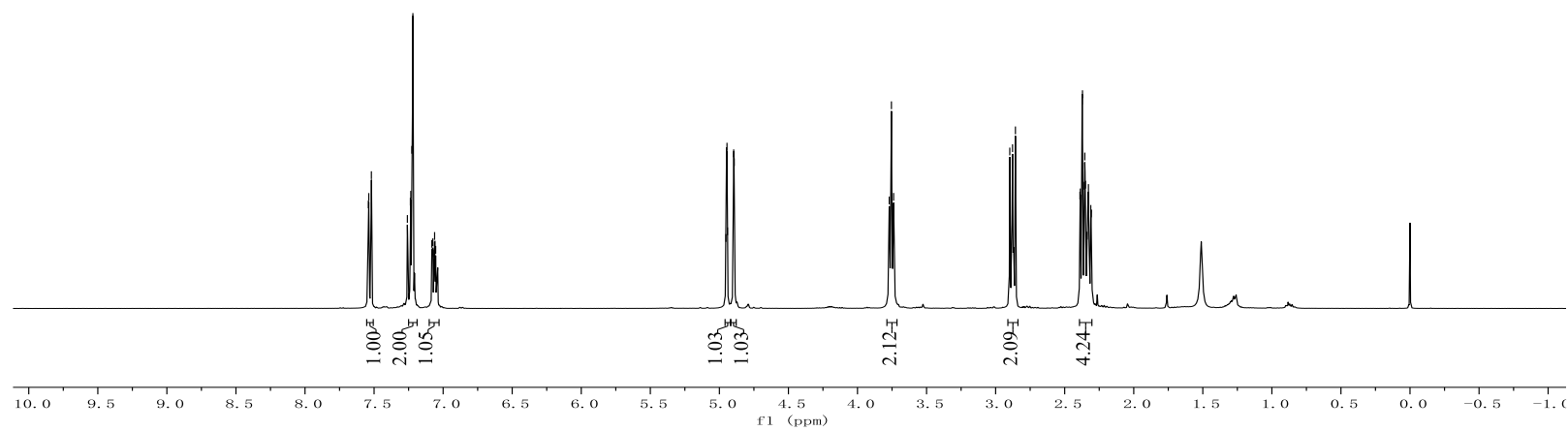


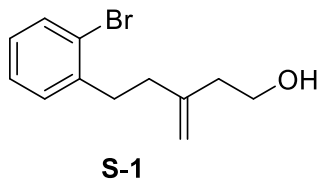
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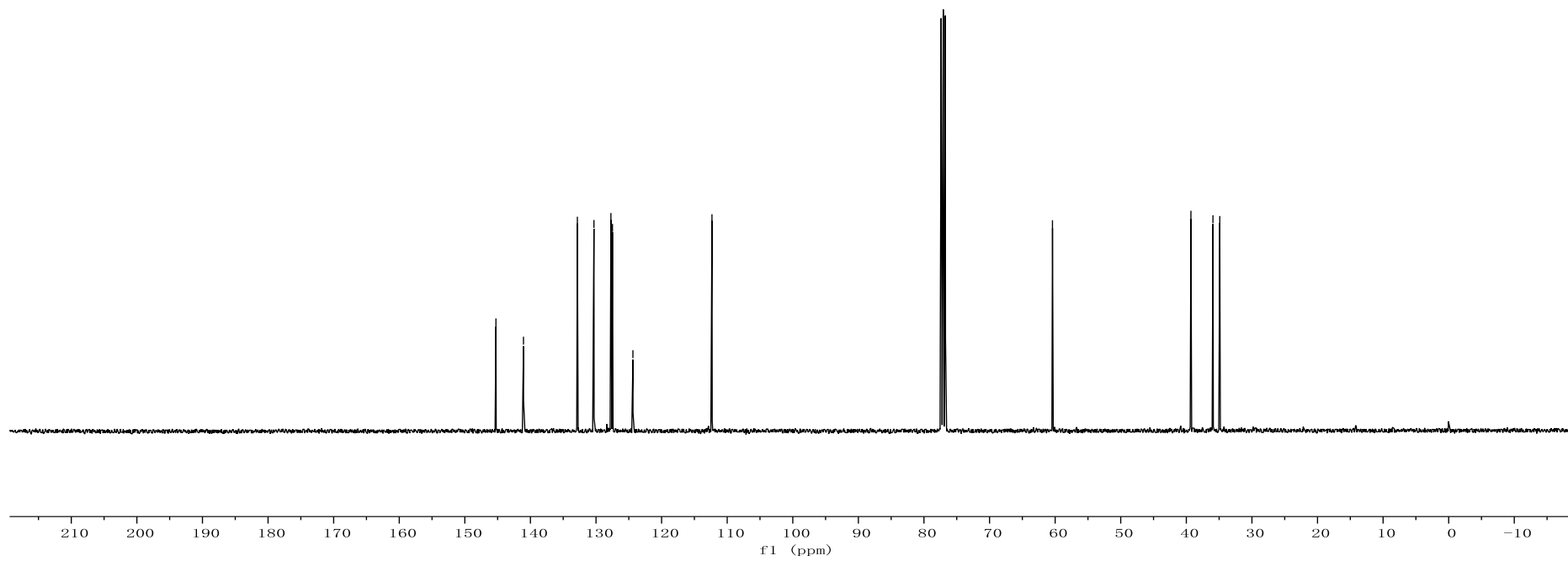




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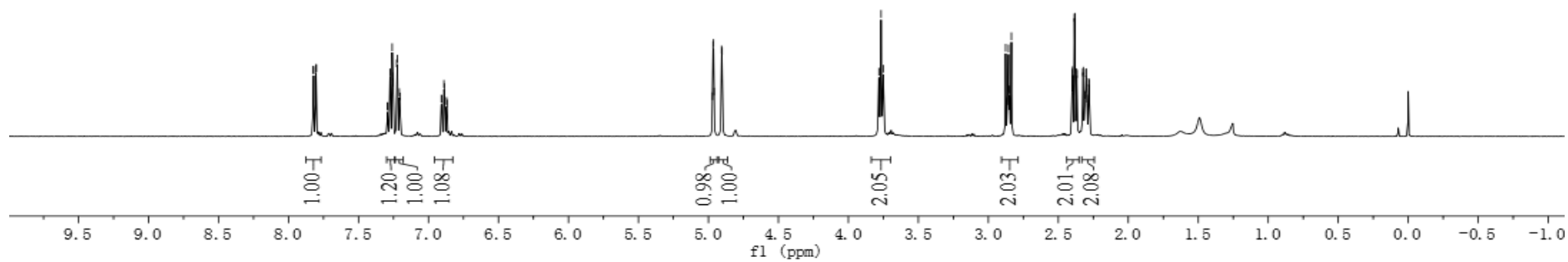
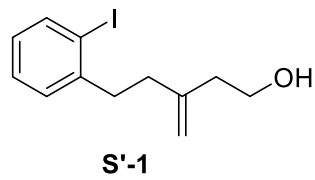


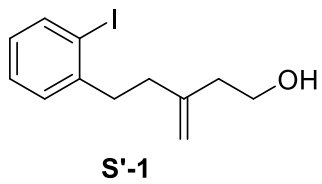
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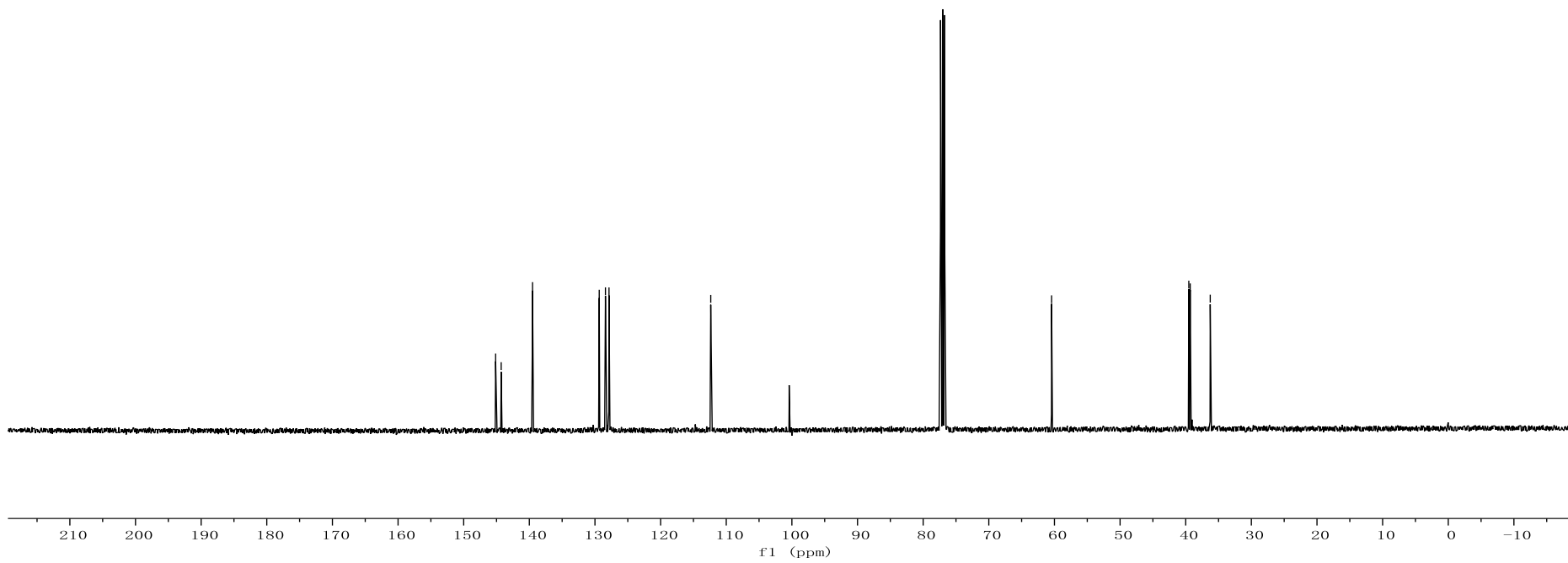
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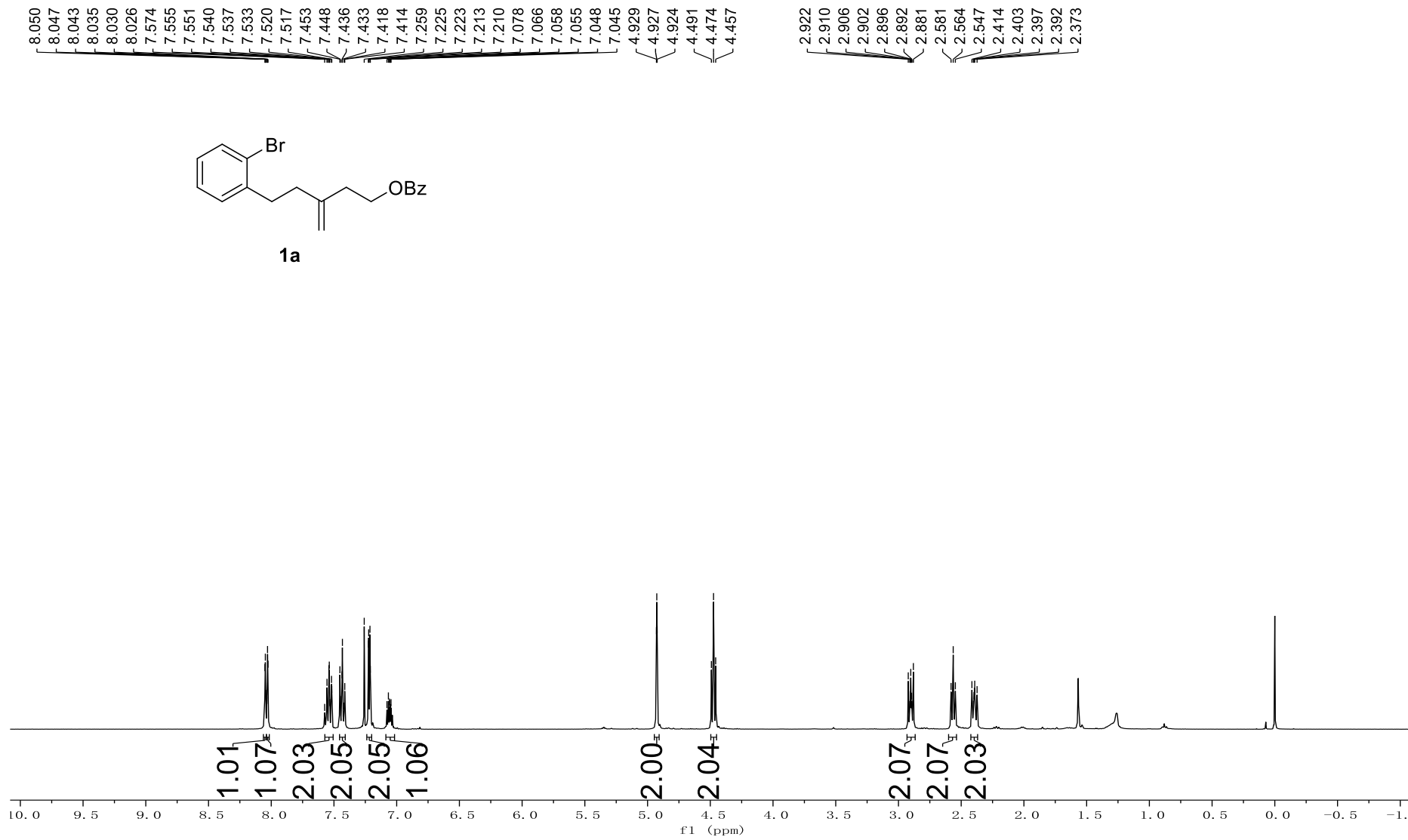
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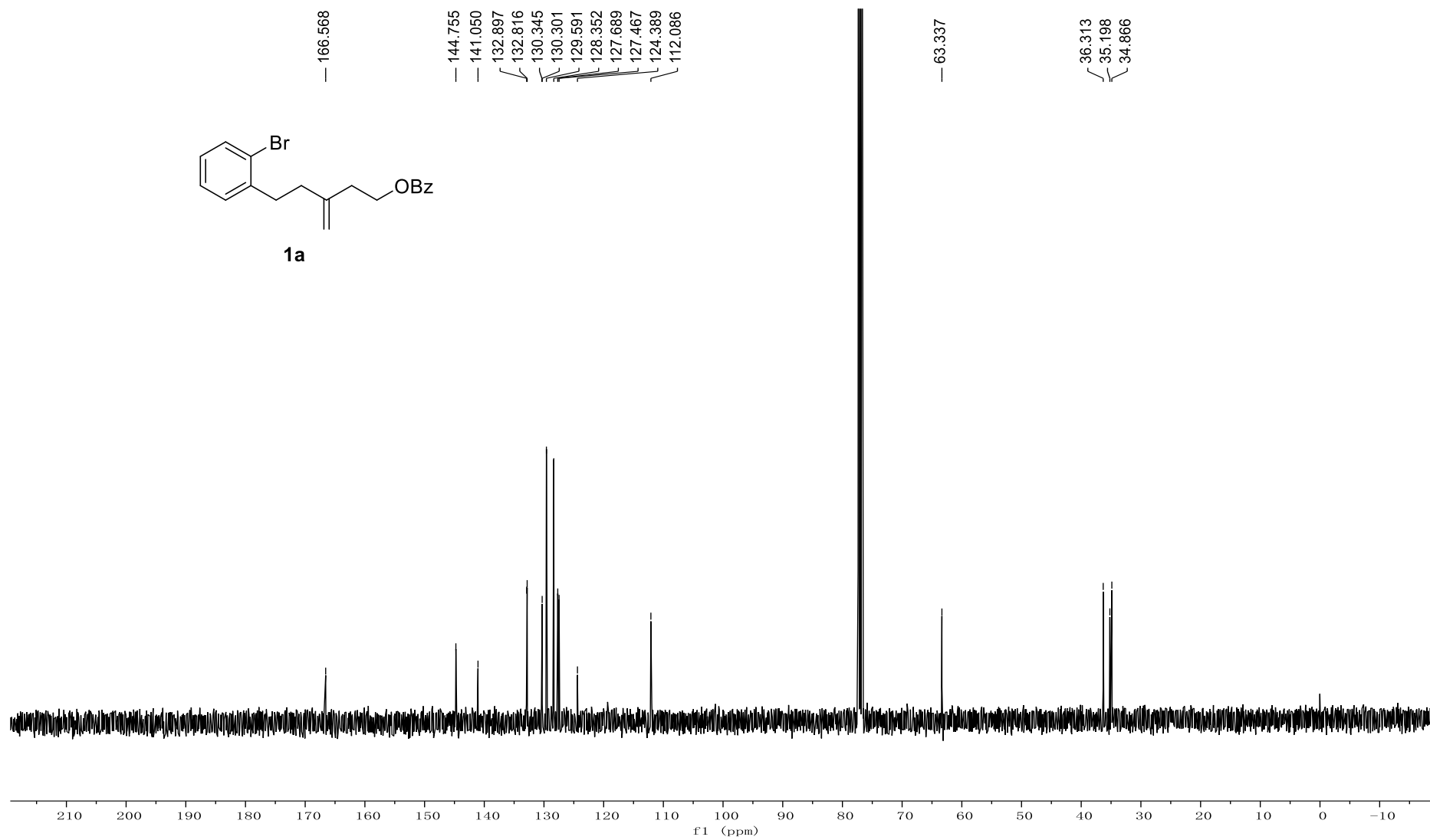
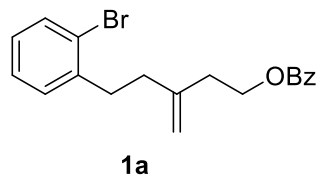
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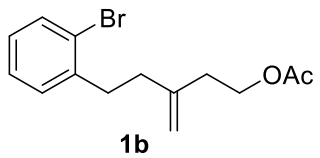
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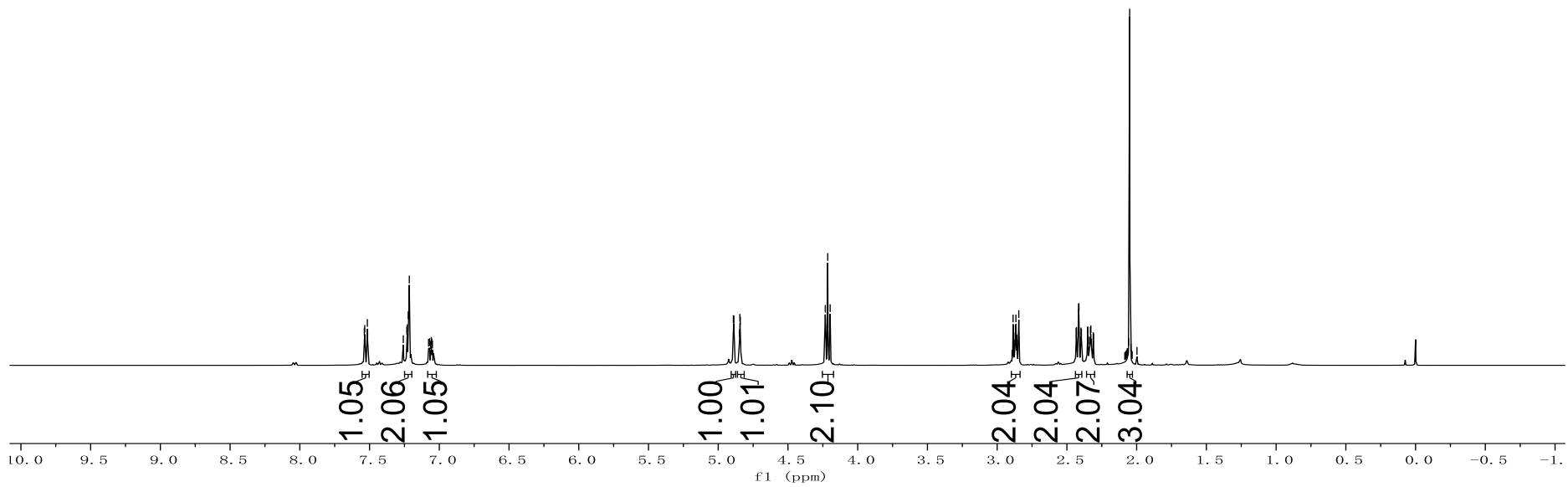


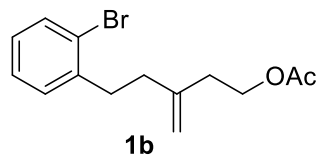


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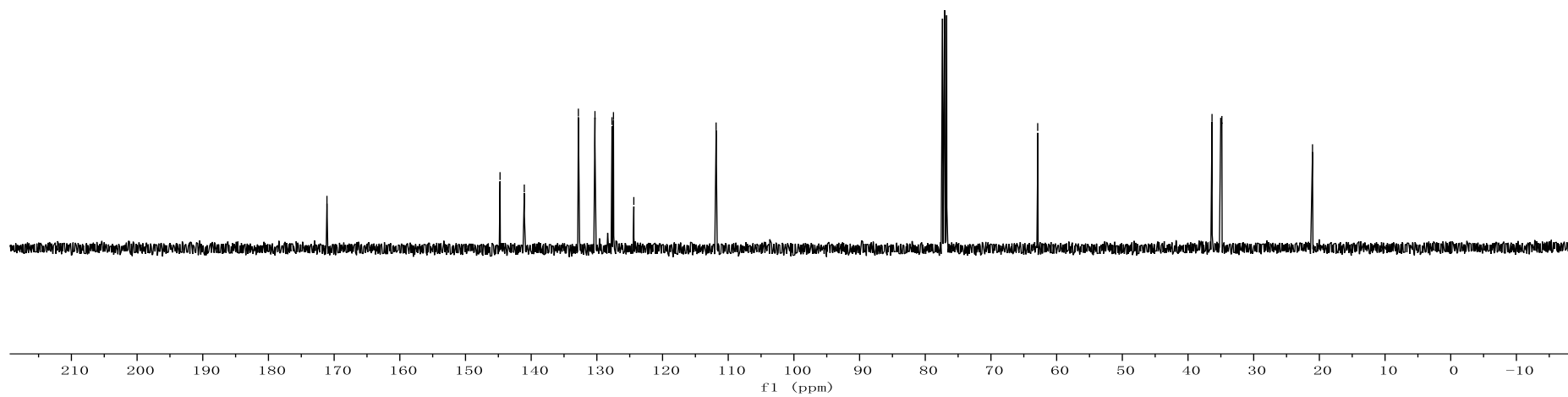
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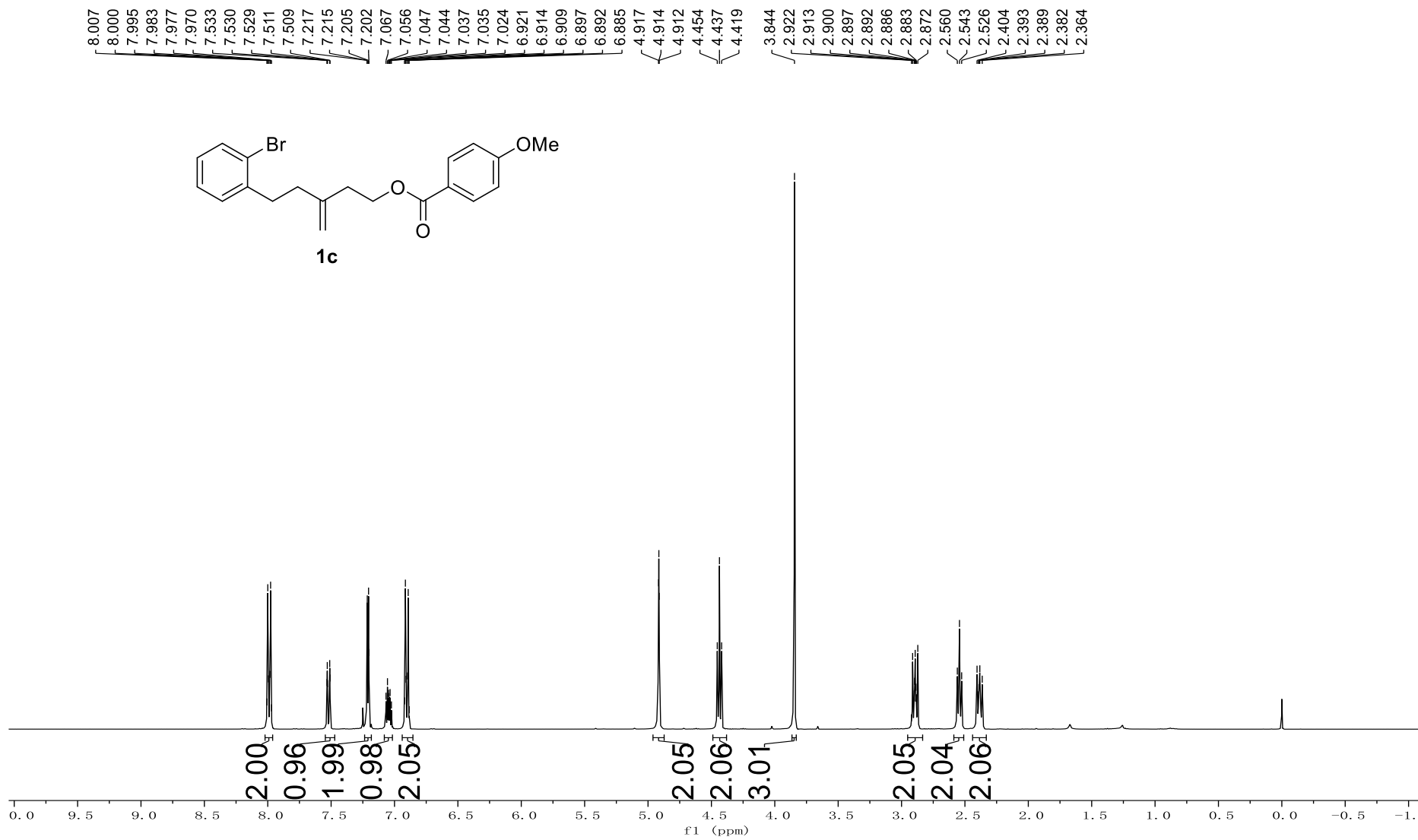
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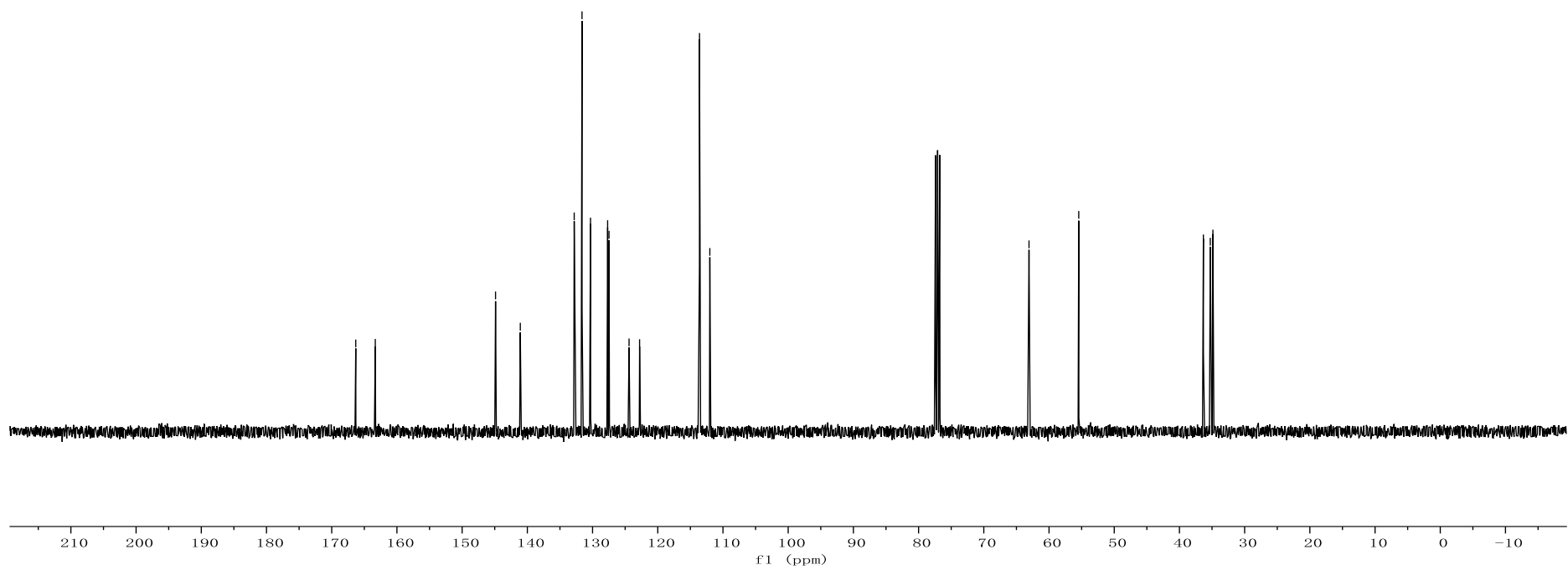
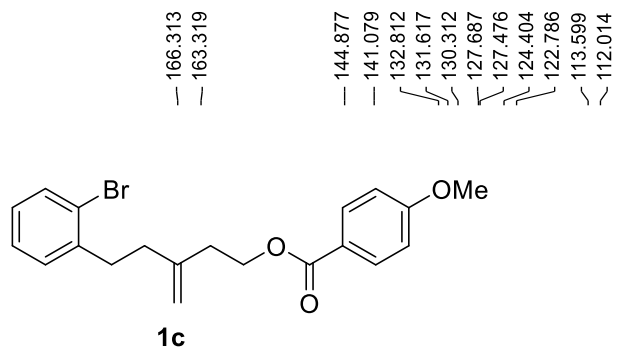
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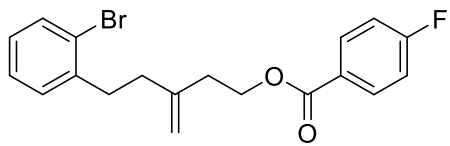
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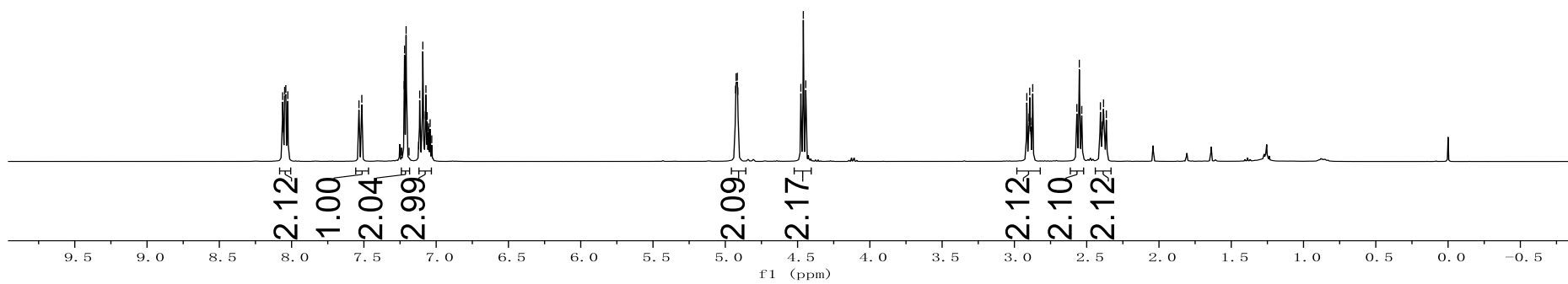


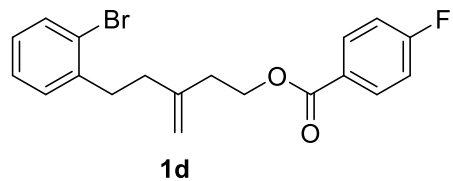


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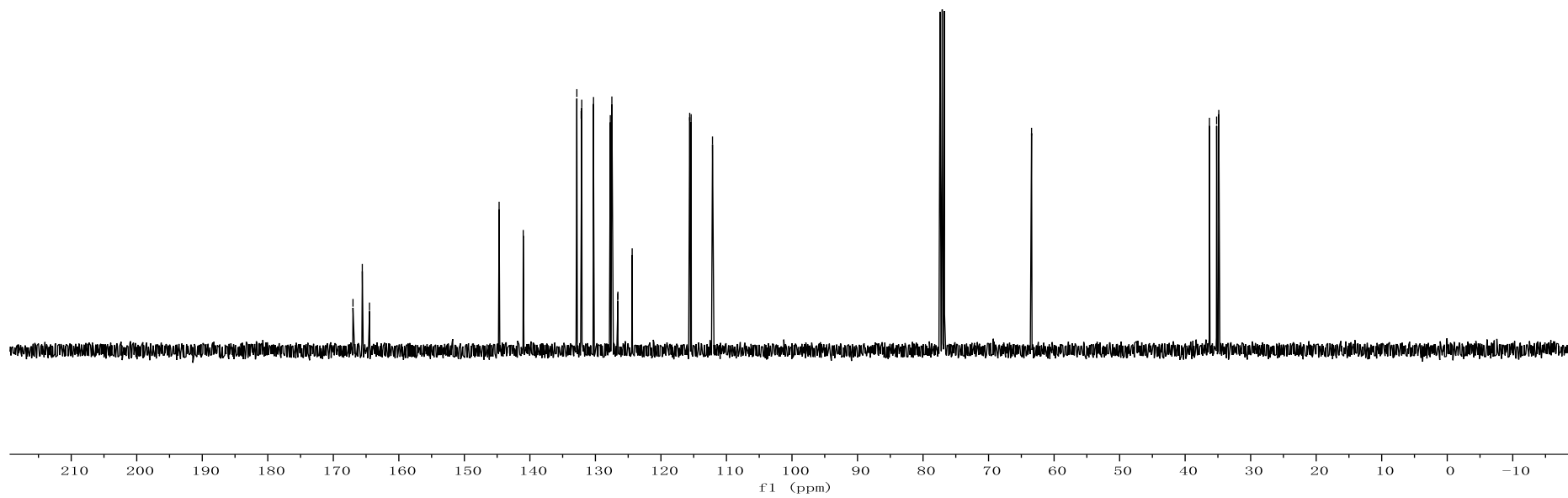


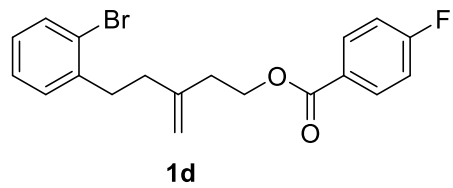
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115.391
112.133

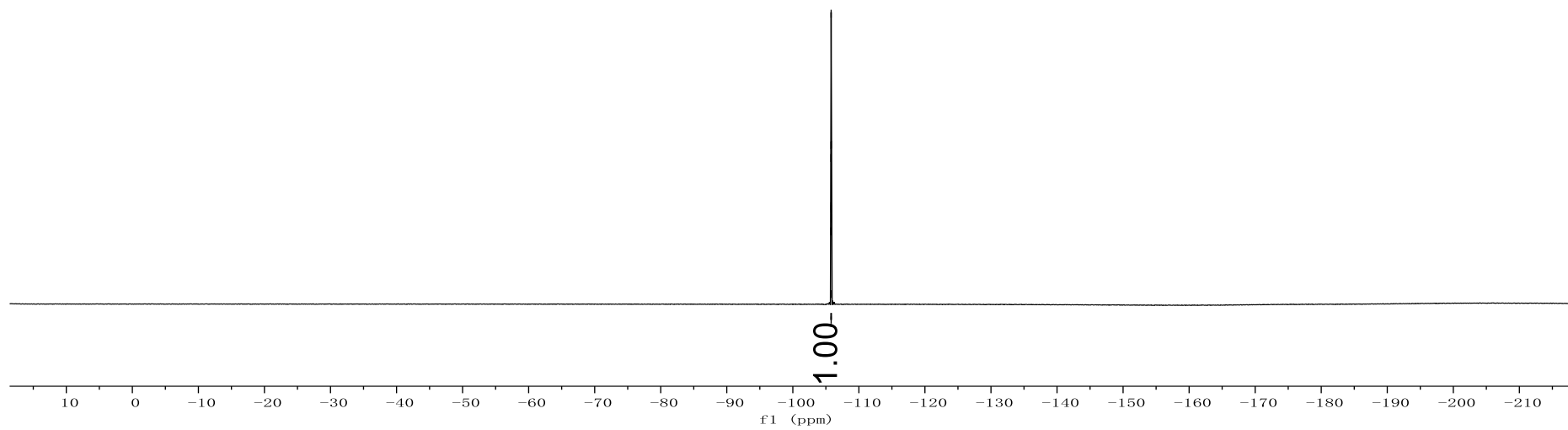
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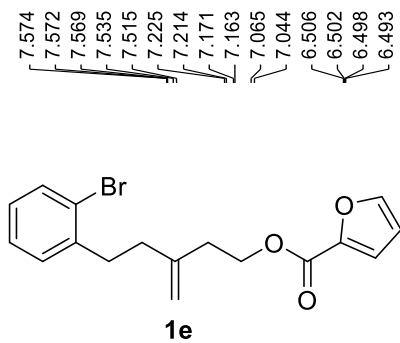
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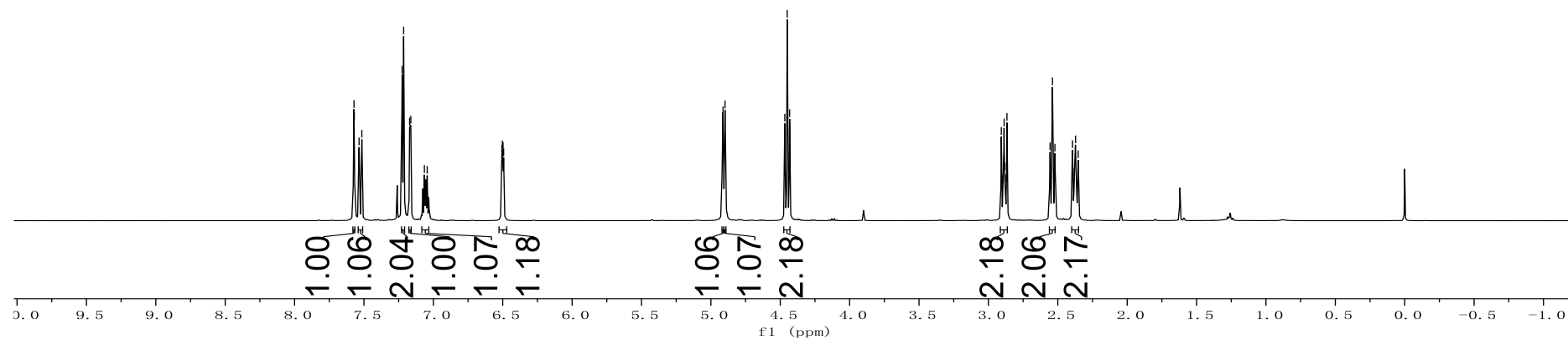
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-105.785
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-105.823
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-105.868

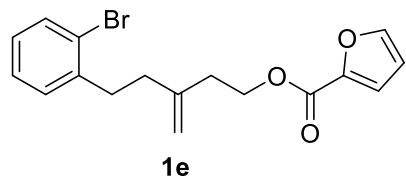




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 4.432

2.907
 2.895
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 2.353

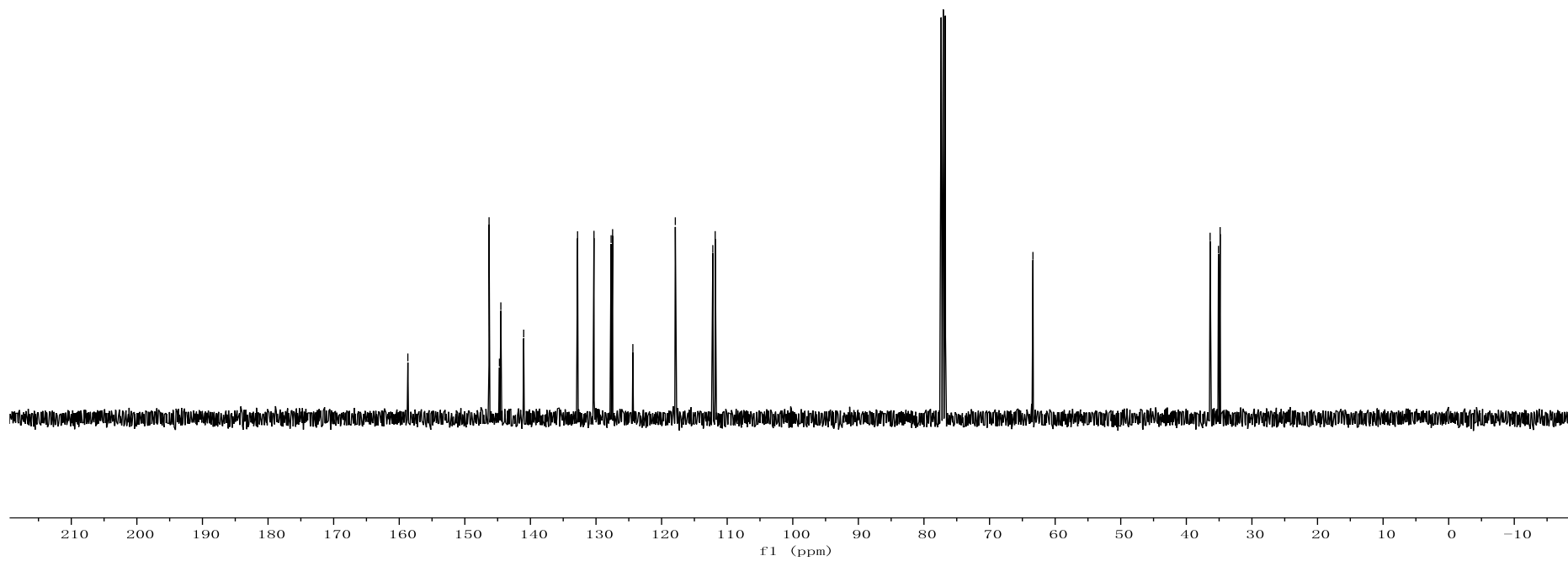




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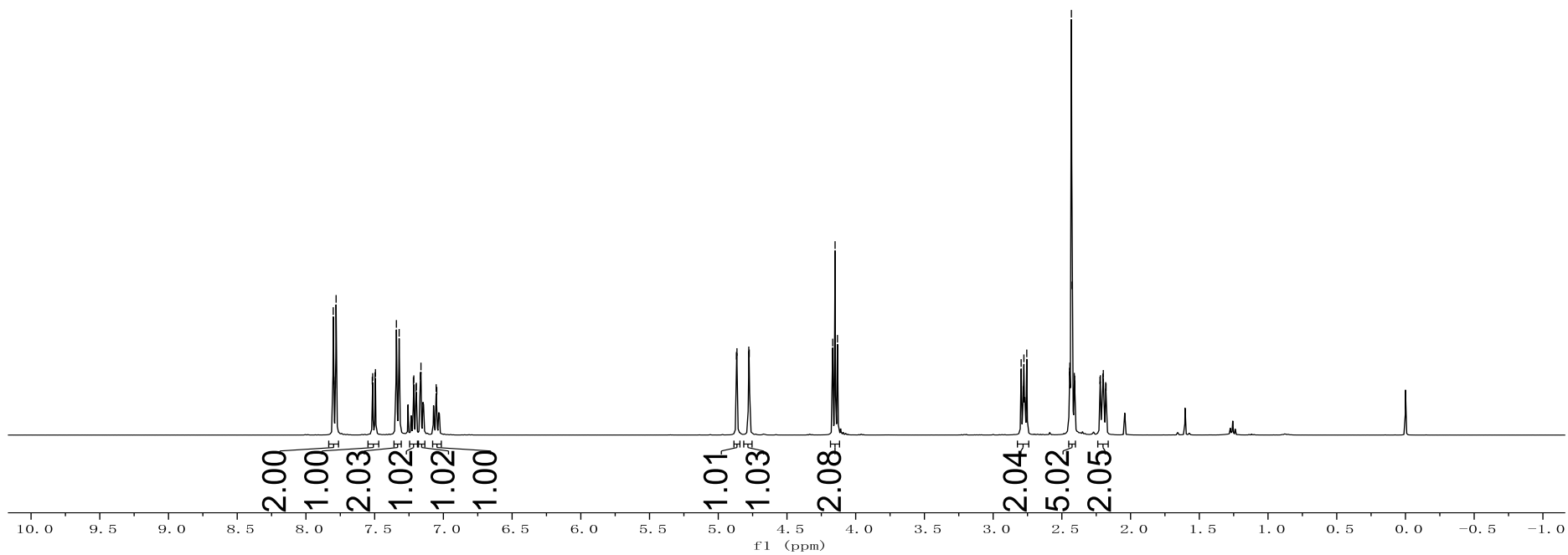
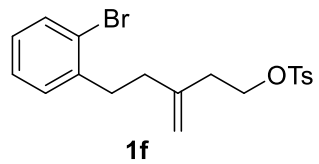
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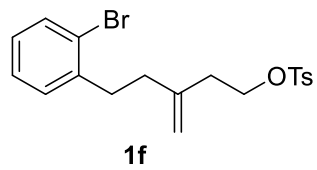


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2.178



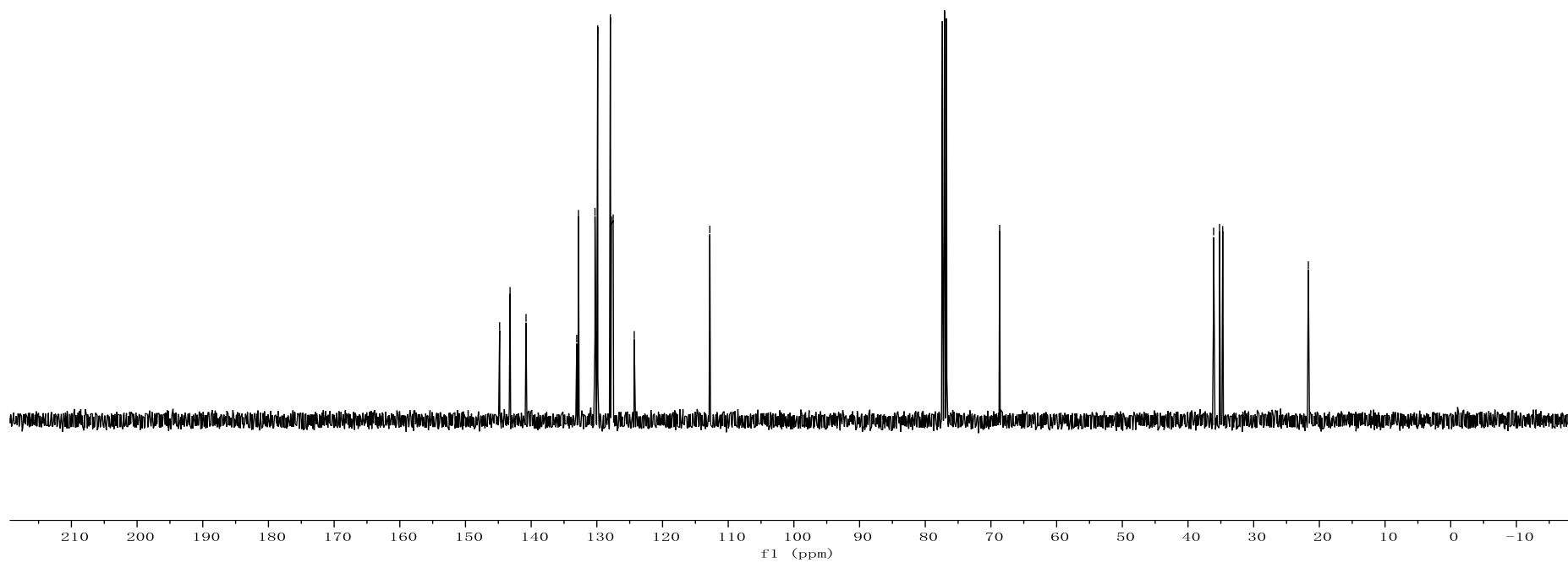


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127.951
127.770
127.517
124.308
112.798

— 68.676

36.100
35.199
34.716

— 21.679



7.690
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7.683
7.676
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7.511
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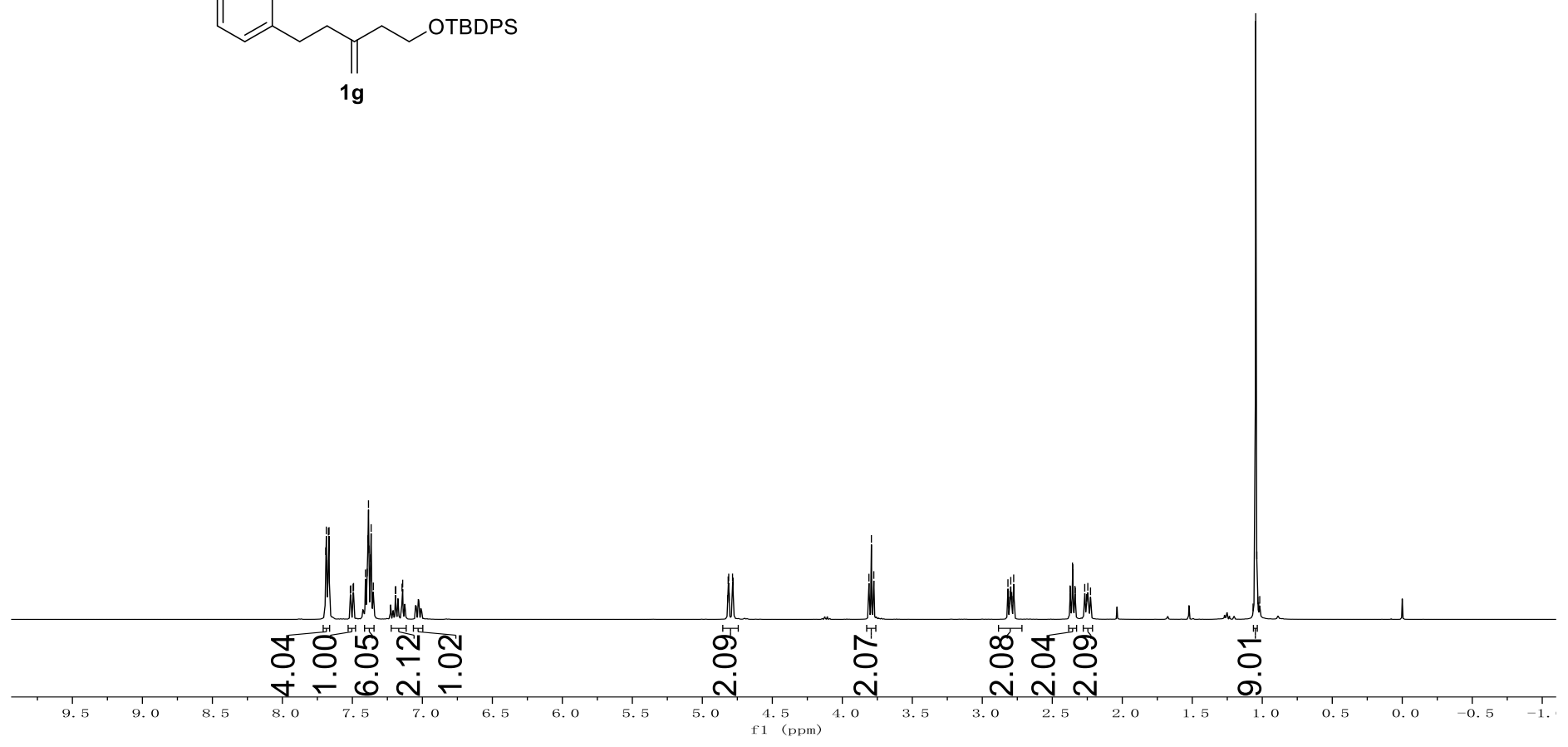
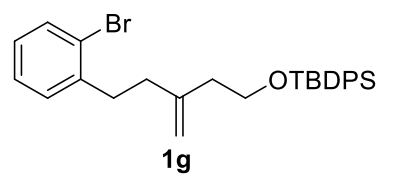
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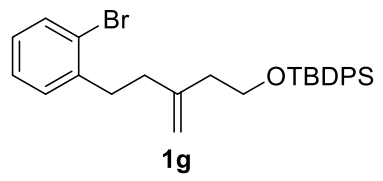
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2.255
2.246
2.227

1.066
1.047
1.039
1.032
1.025
1.018





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124.429
— 111.497

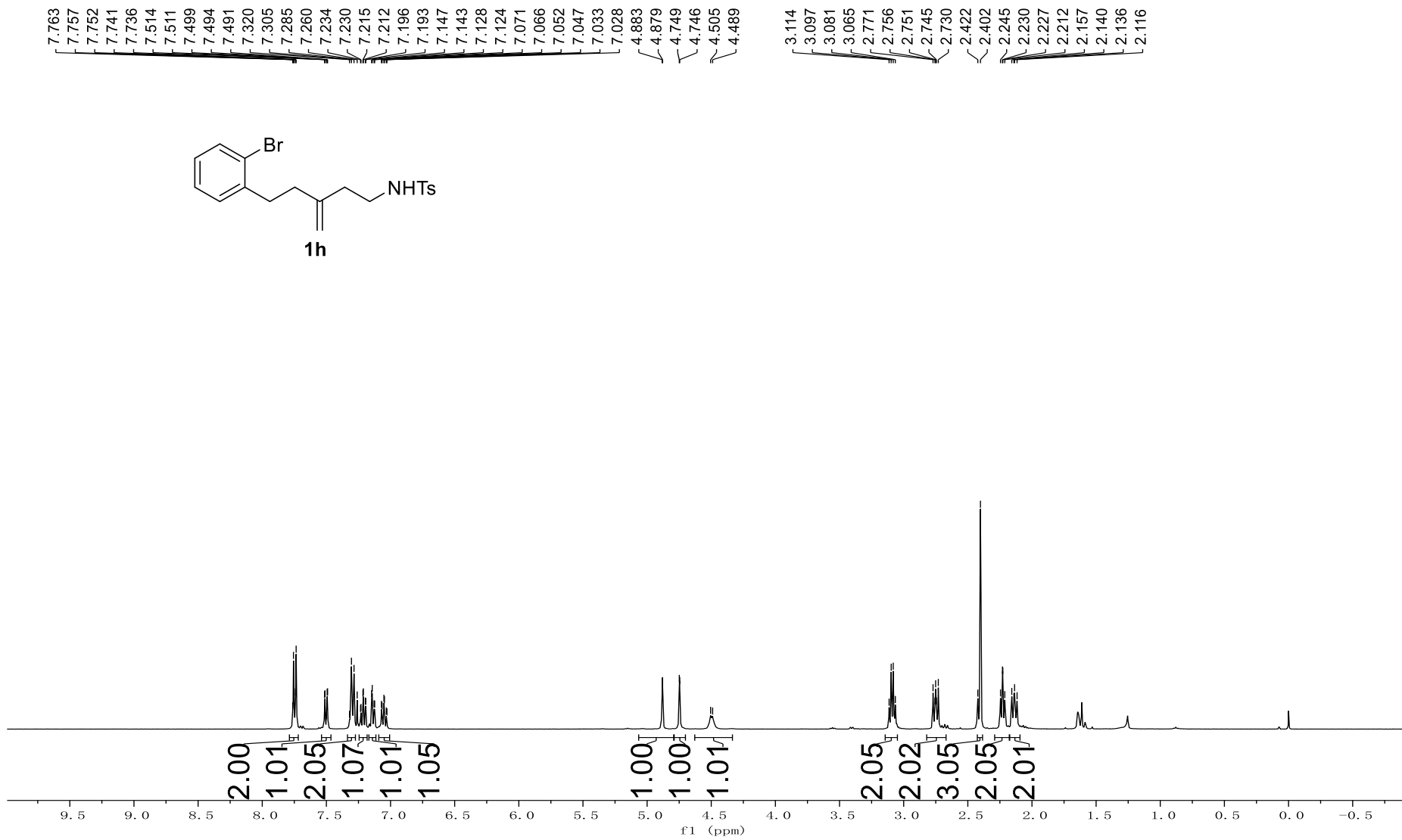
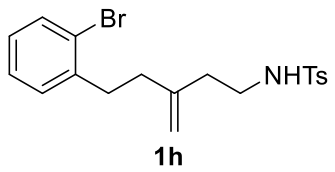
— 63.004

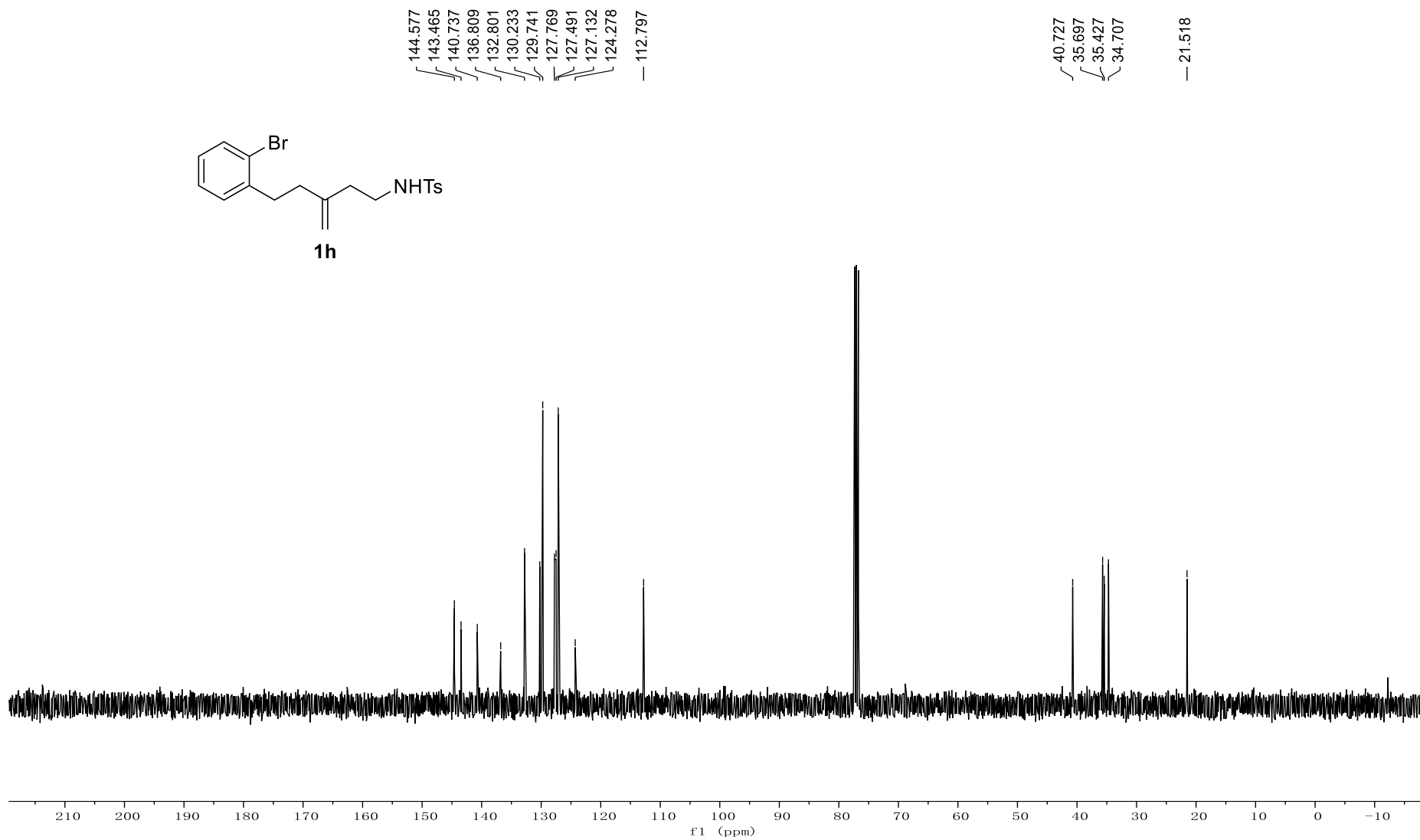
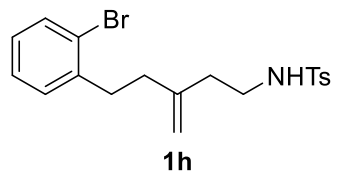
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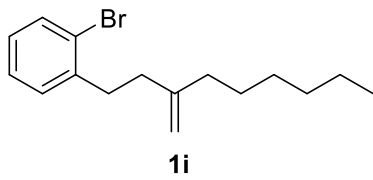
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— 19.258





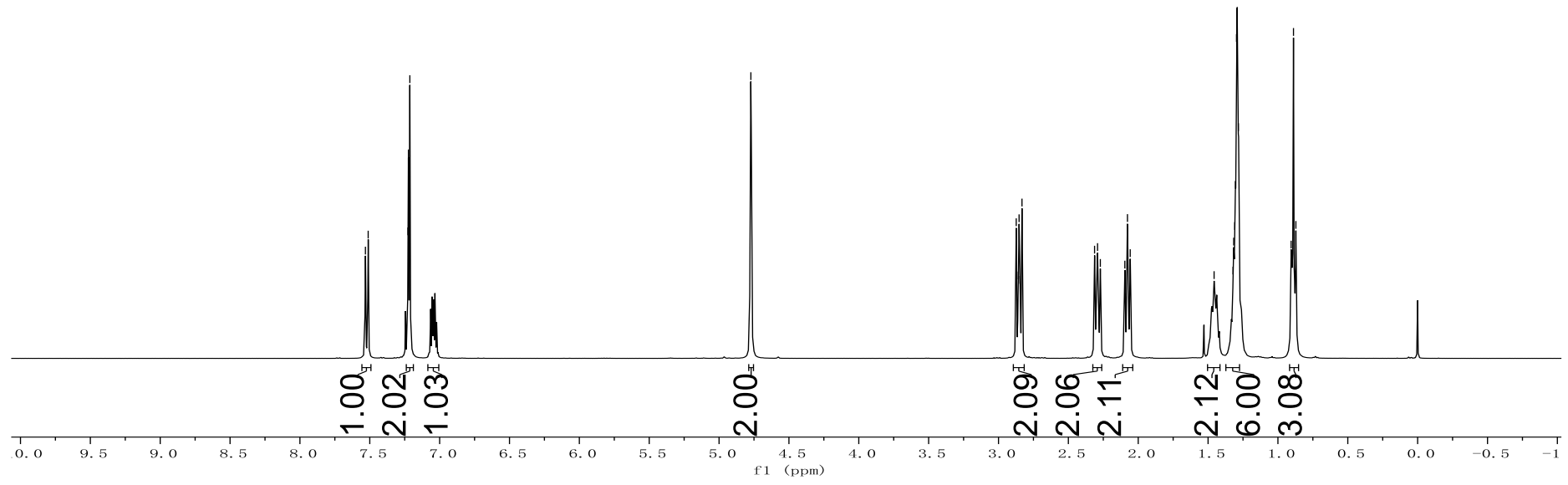


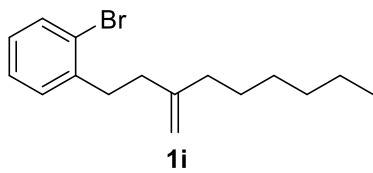


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 2.077
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 0.871

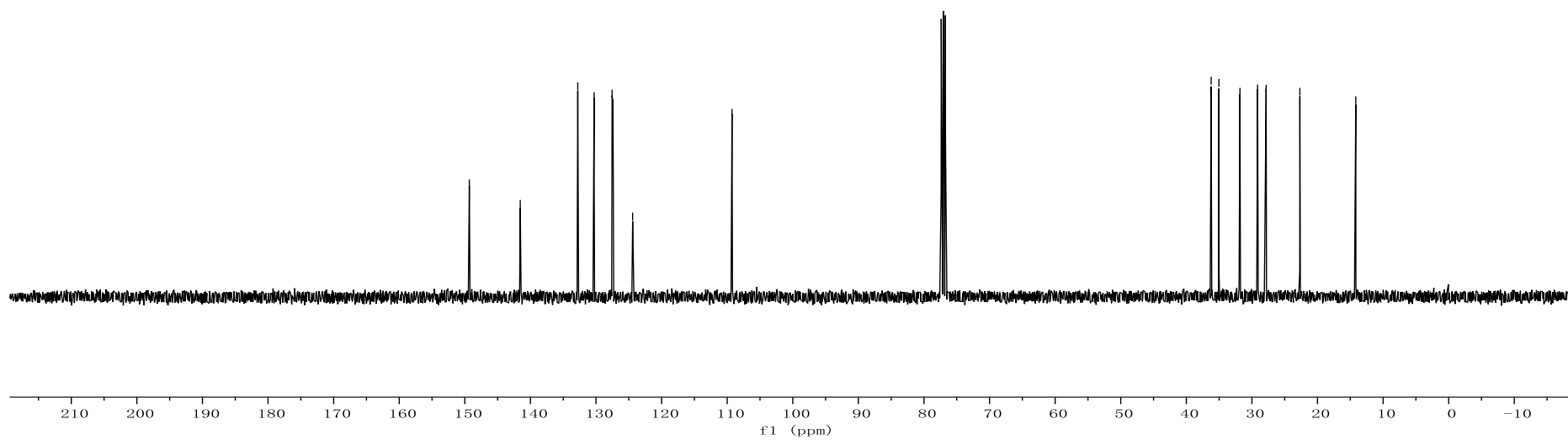


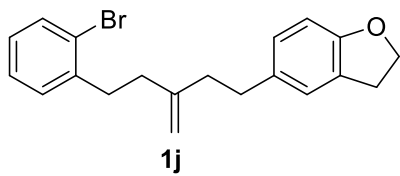


— 149.318
— 141.550
/ 132.780
/ 130.291
/ 127.545
/ 127.412
/ 124.415

— 109.267

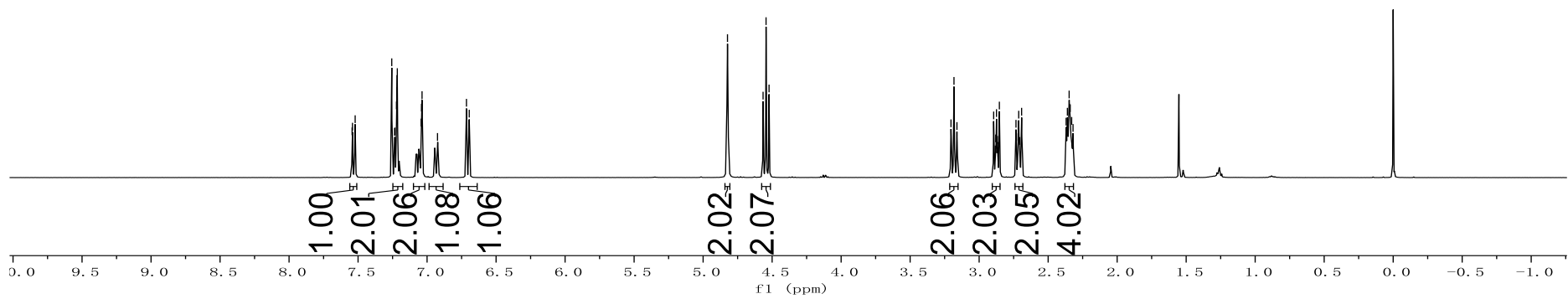
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/ 36.215
/ 35.030
/ 31.824
/ 29.132
/ 27.831
/ 22.691
— 14.166

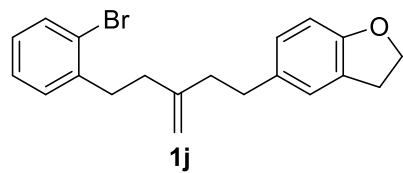




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7.222
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7.216
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7.036
6.924
6.715
6.695

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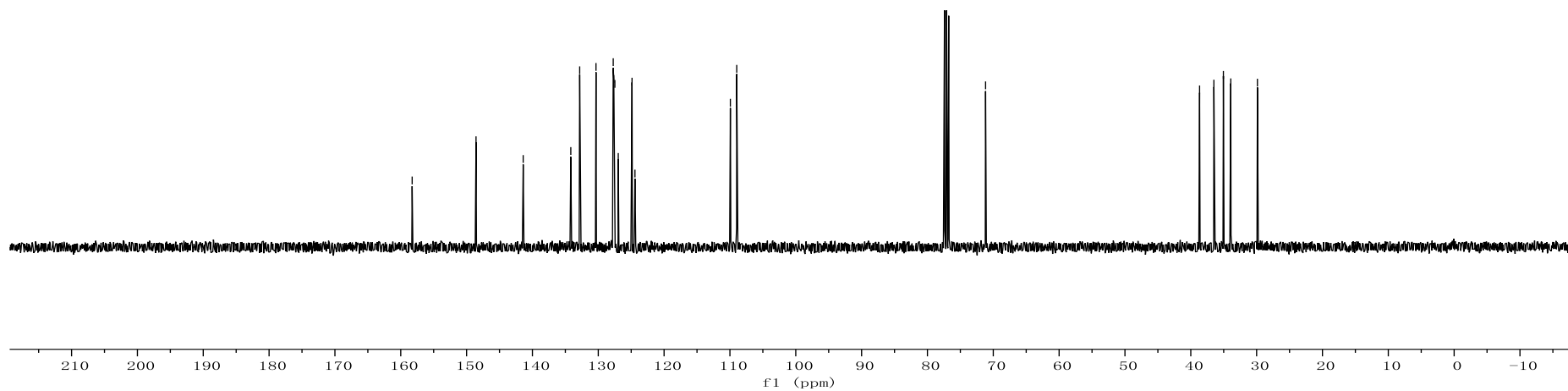


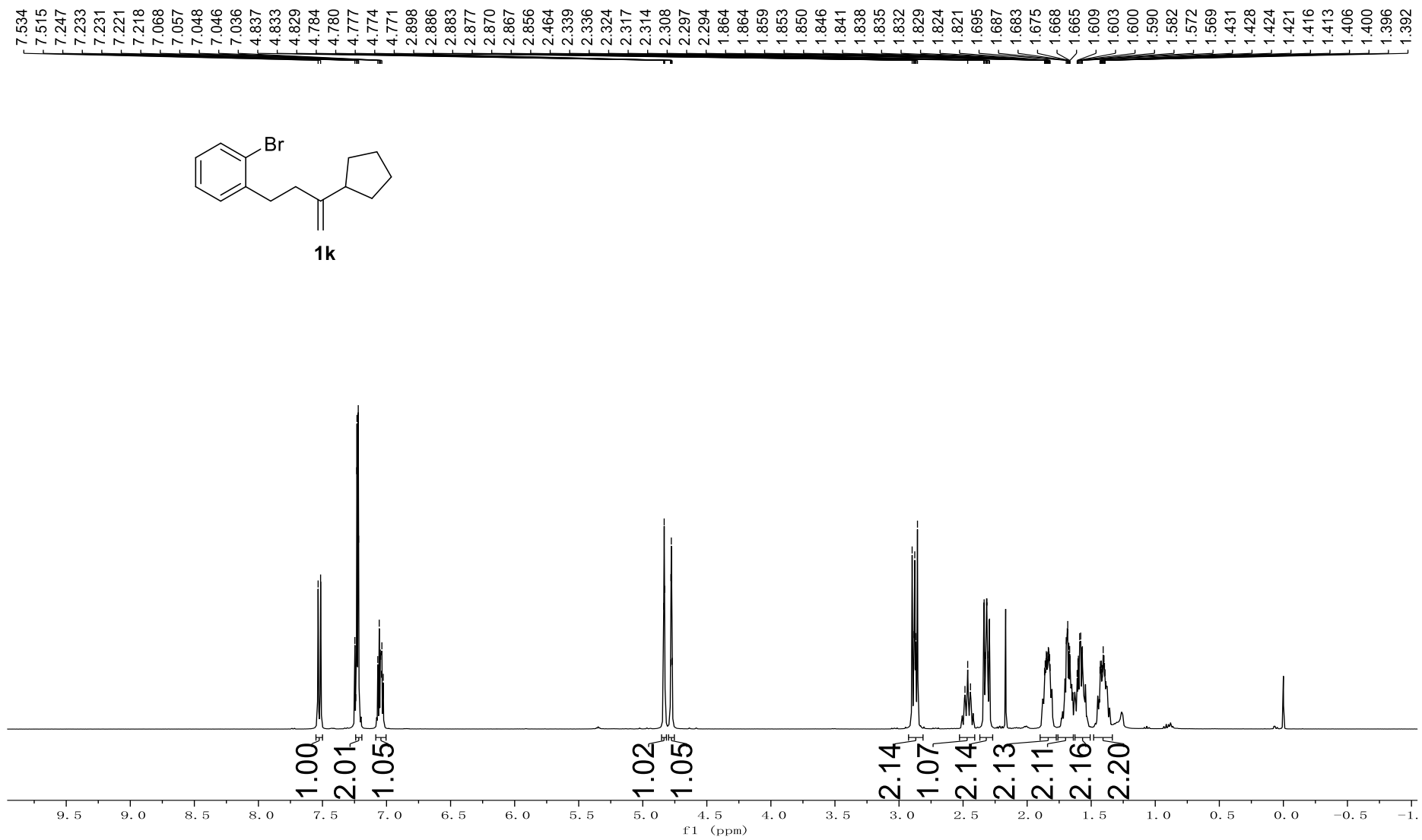


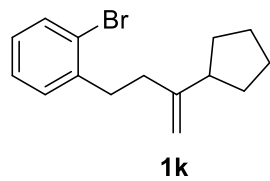
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— 148.566
— 141.402
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127.478
126.964
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124.426
109.932
108.966

— 71.168

38.664
36.489
35.047
33.924
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— 152.528

— 141.671

✓ 132.773

✓ 130.316

✓ 127.539

✓ 127.425

✓ 124.412

— 107.167

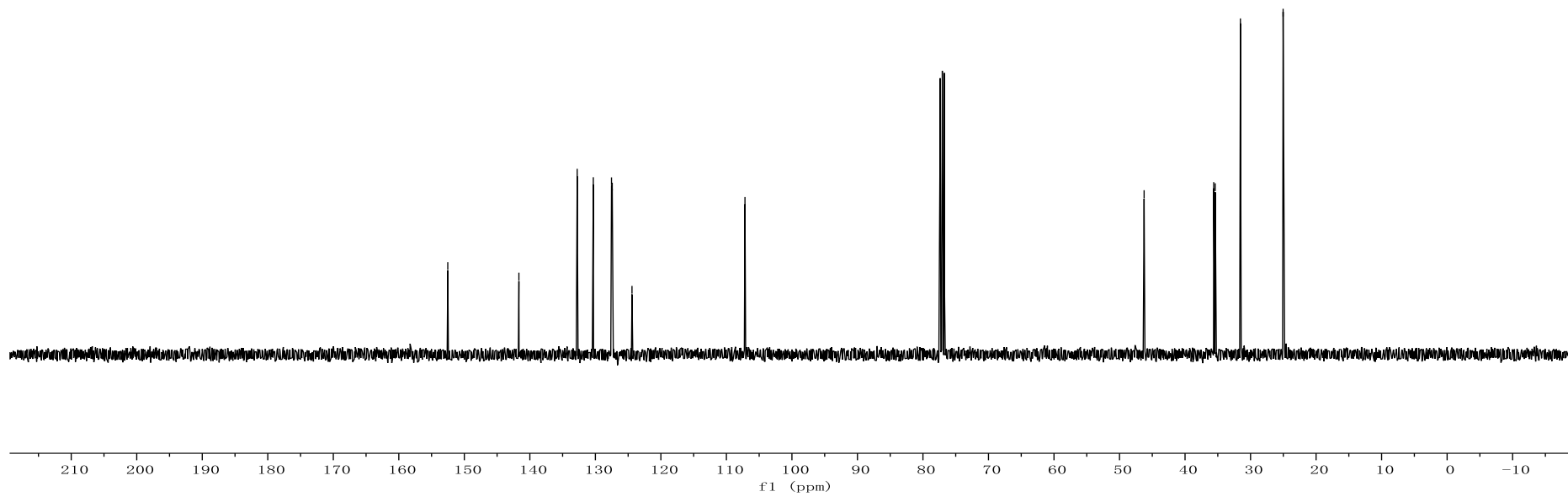
— 46.247

✓ 35.621

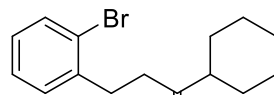
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✓ 31.547

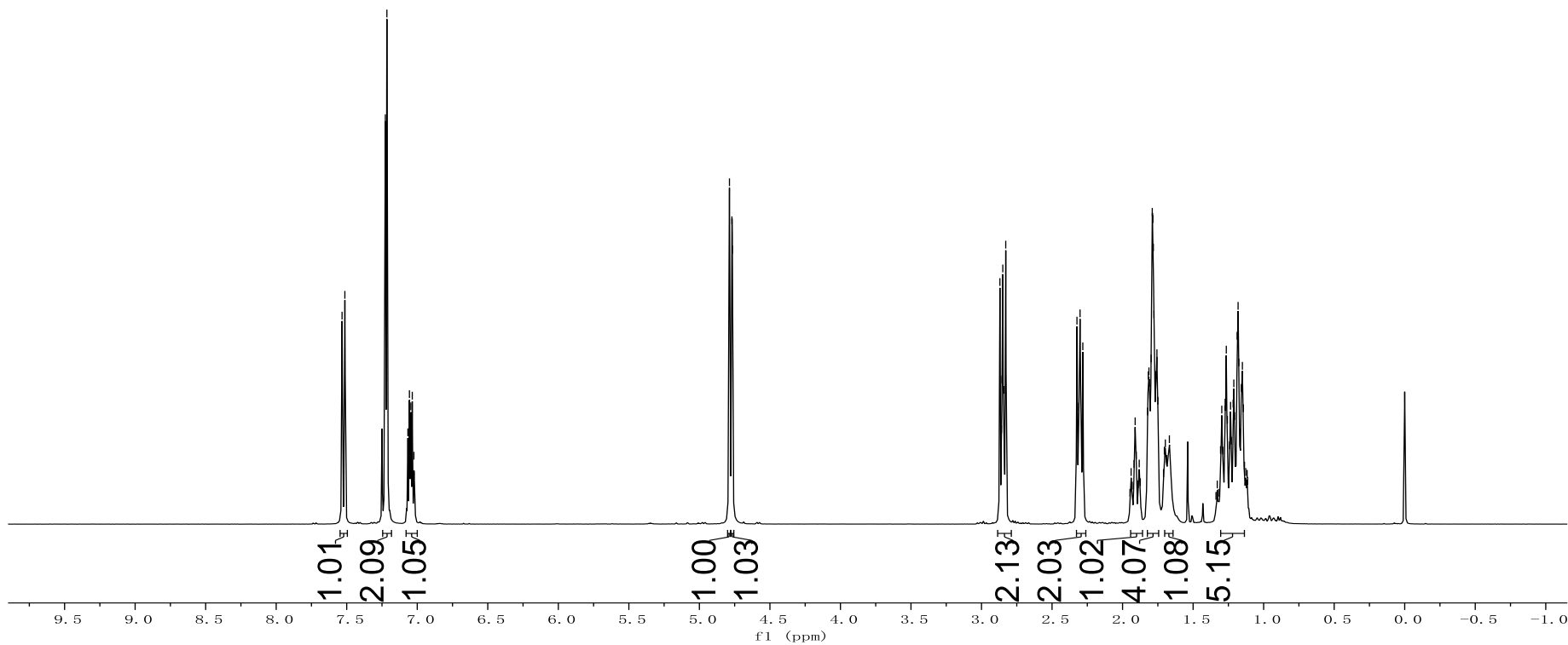
✓ 25.031

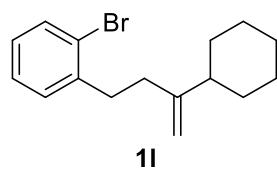


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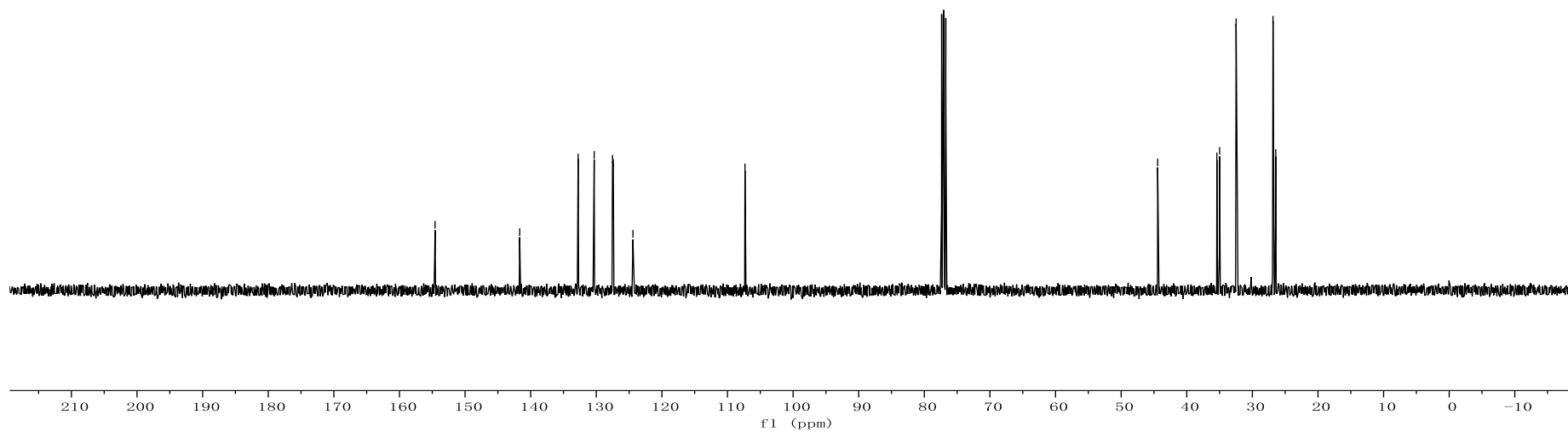


11



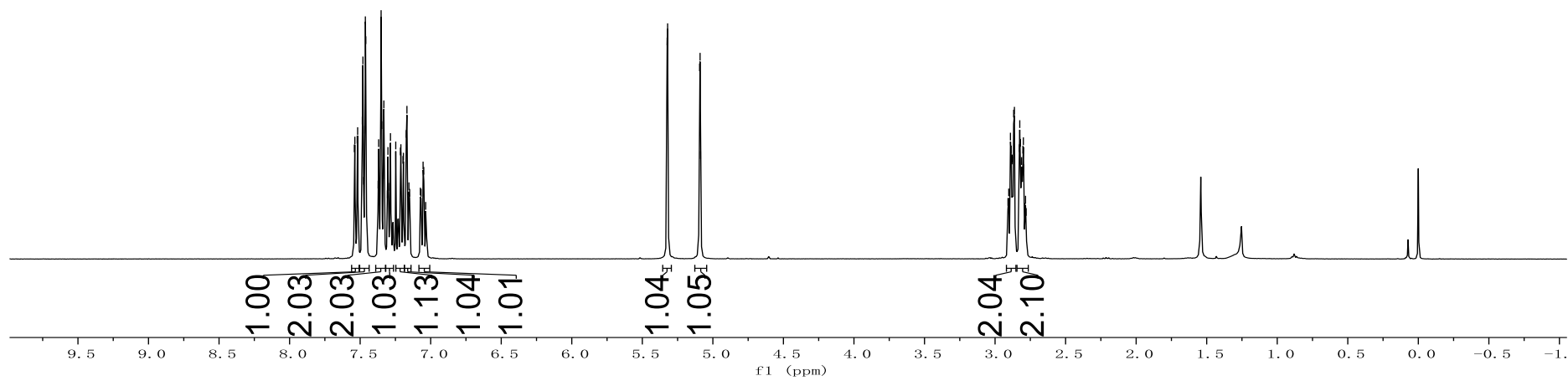
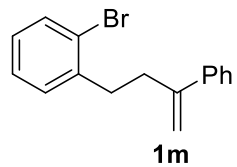


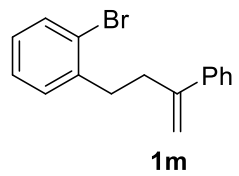
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124.415
— 107.336
— 44.434
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32.478
26.856
26.437



7.541
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7.518
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7.480
7.475
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5.091
5.087

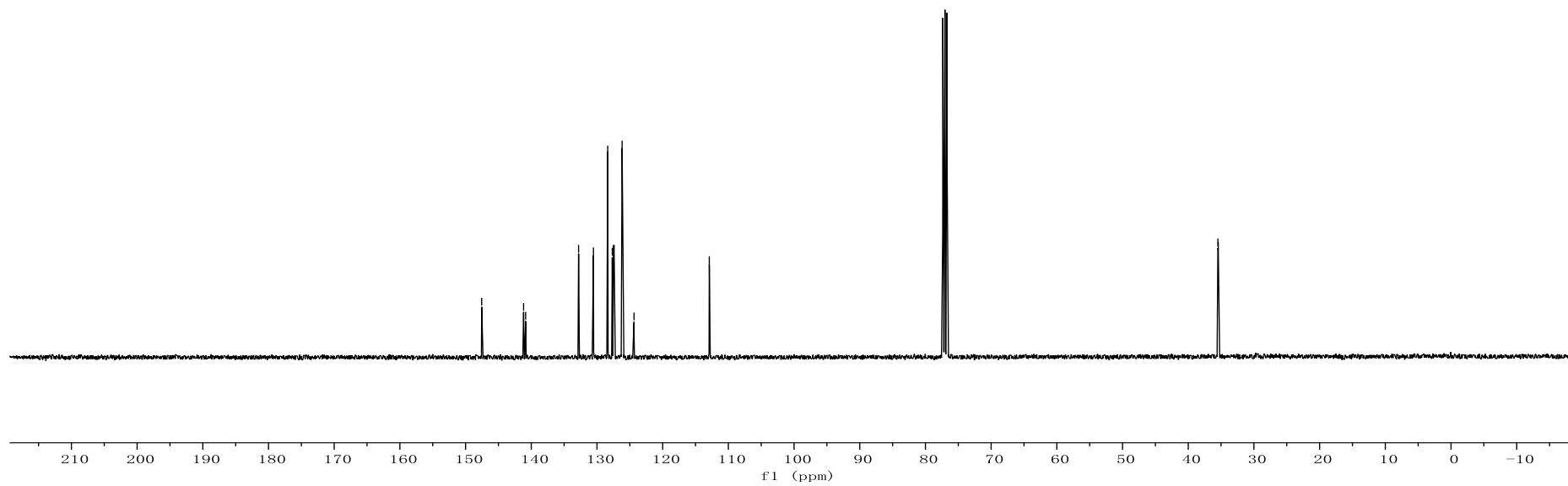
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2.784
2.780



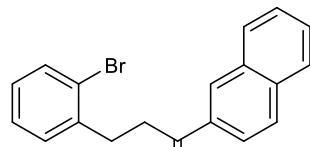


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112.902

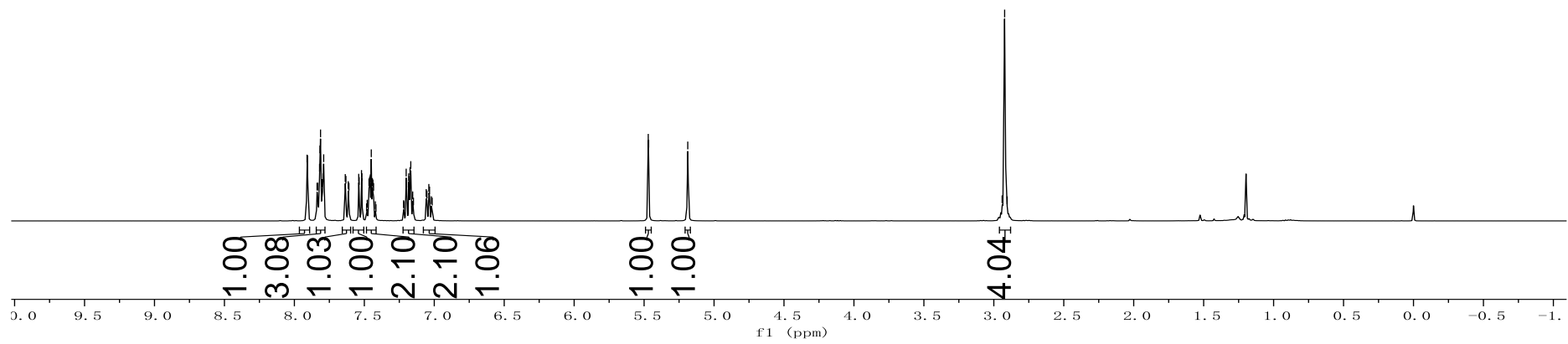
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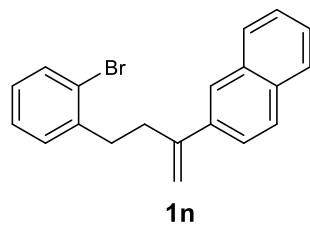


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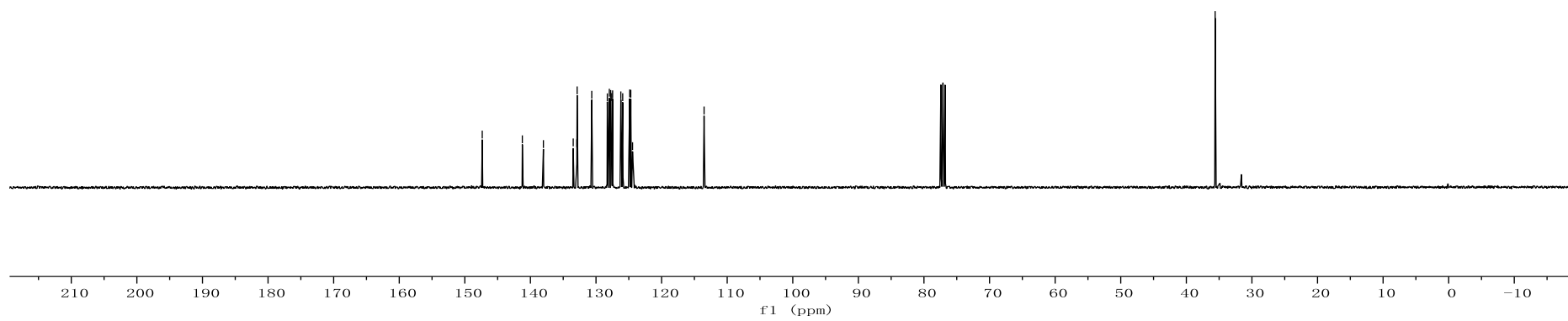
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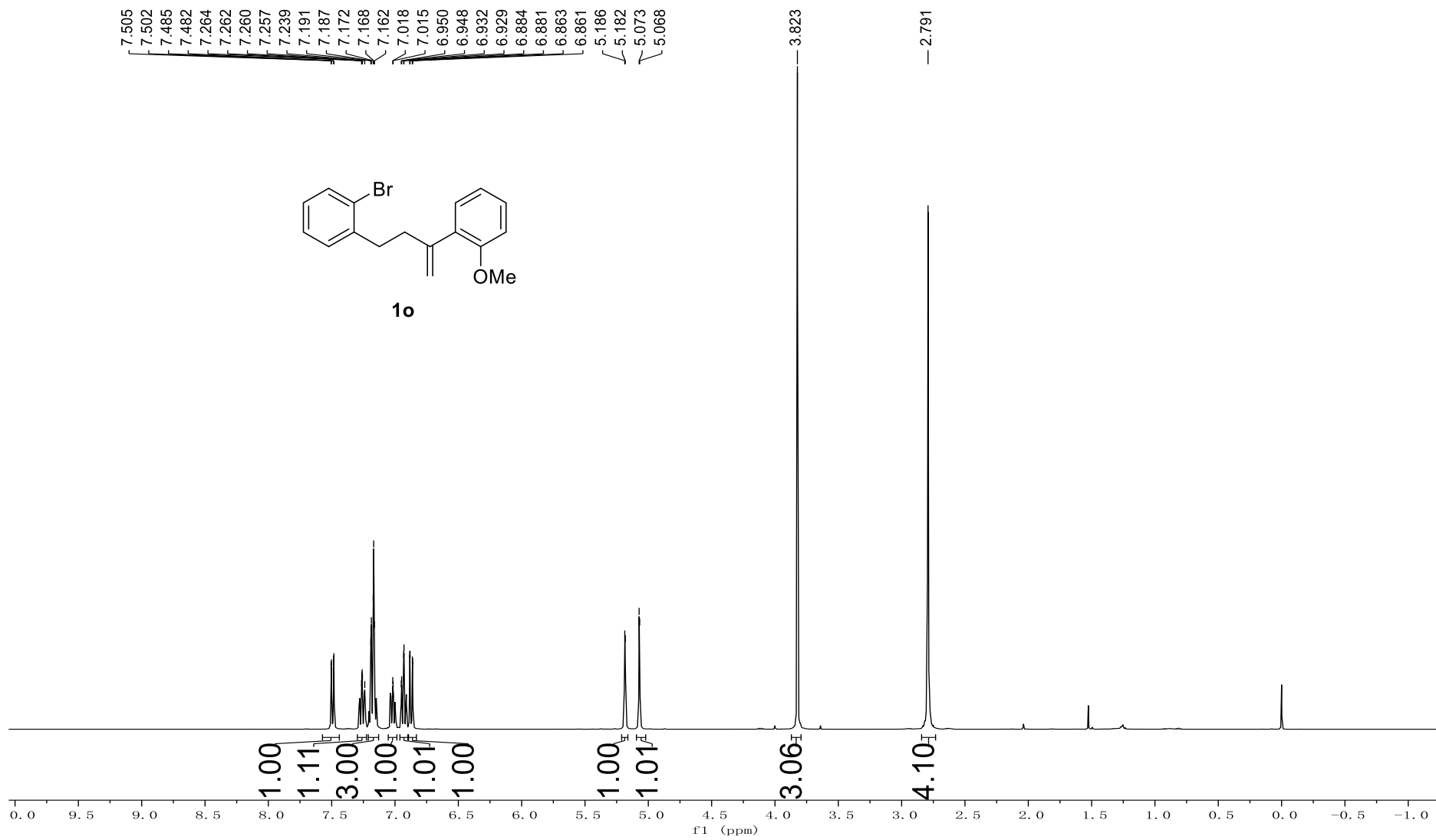


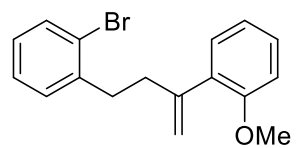


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124.699
124.430
— 113.522

— 35.604





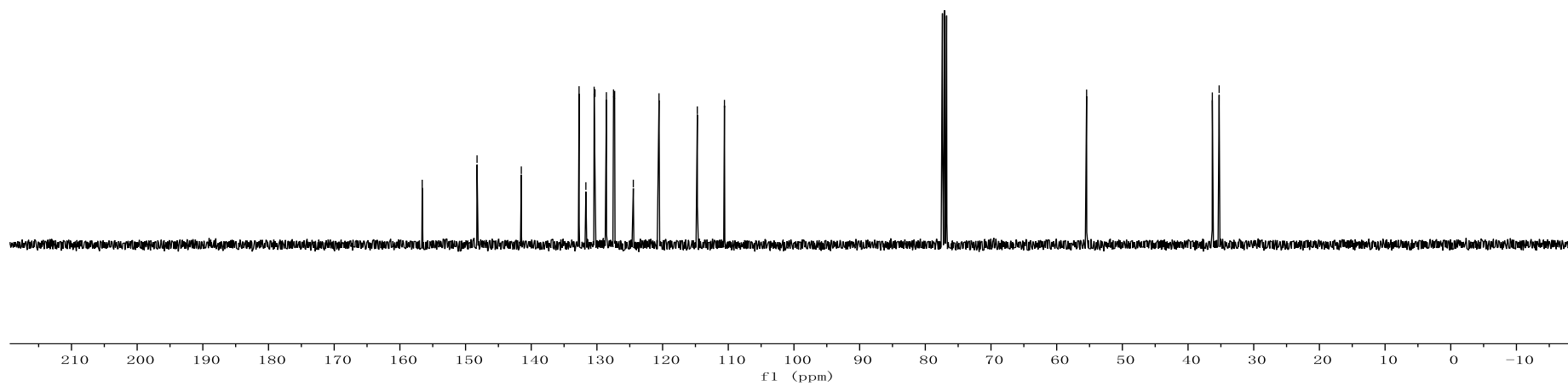


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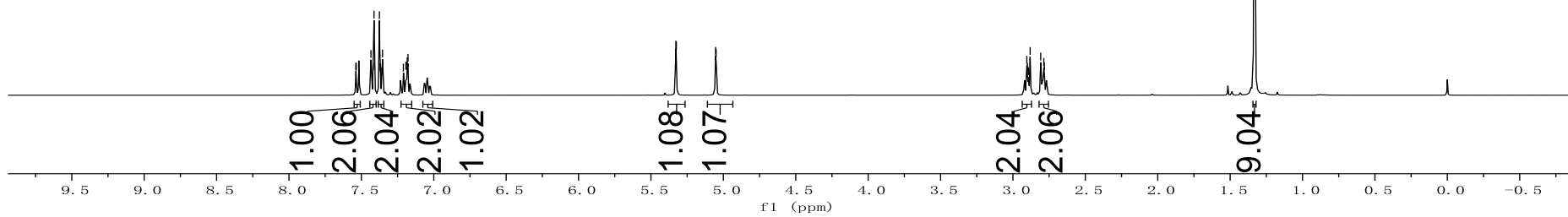
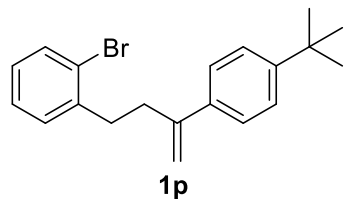


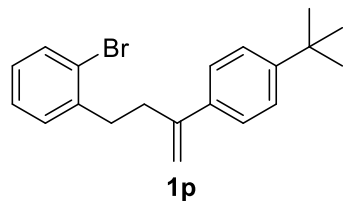
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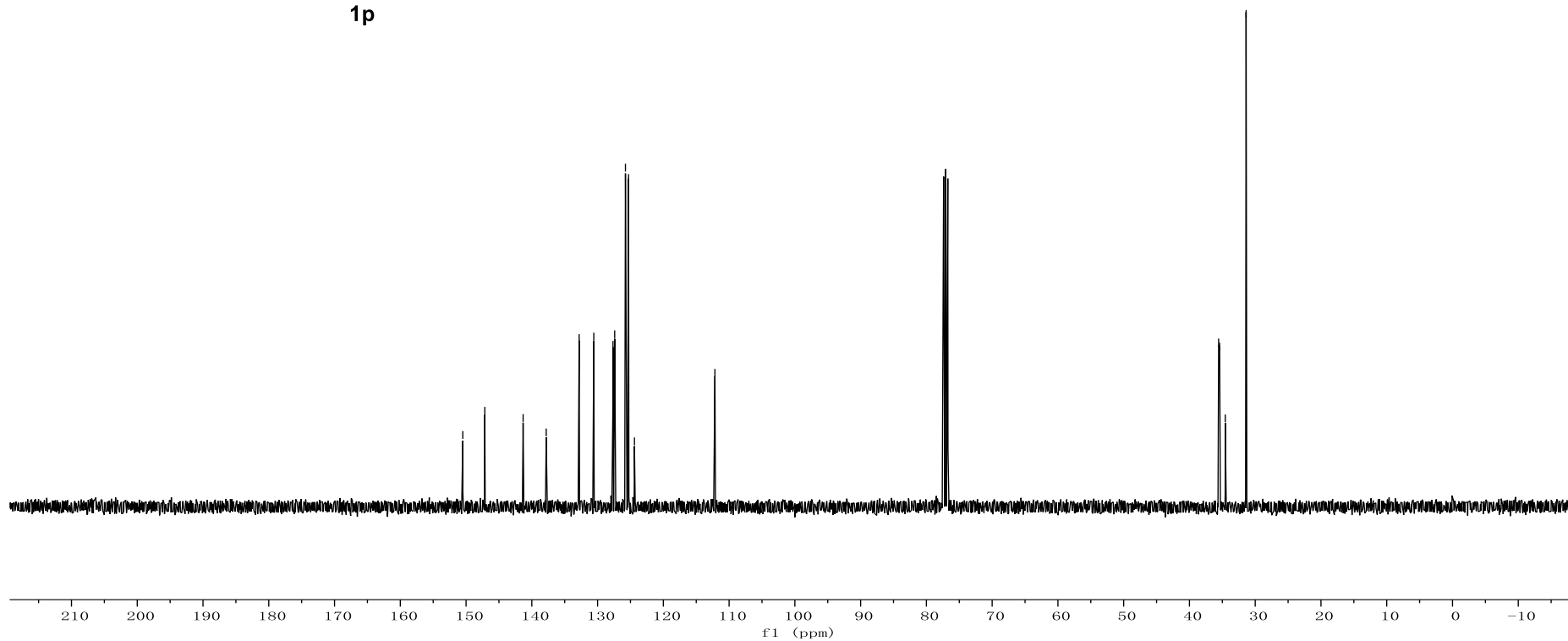
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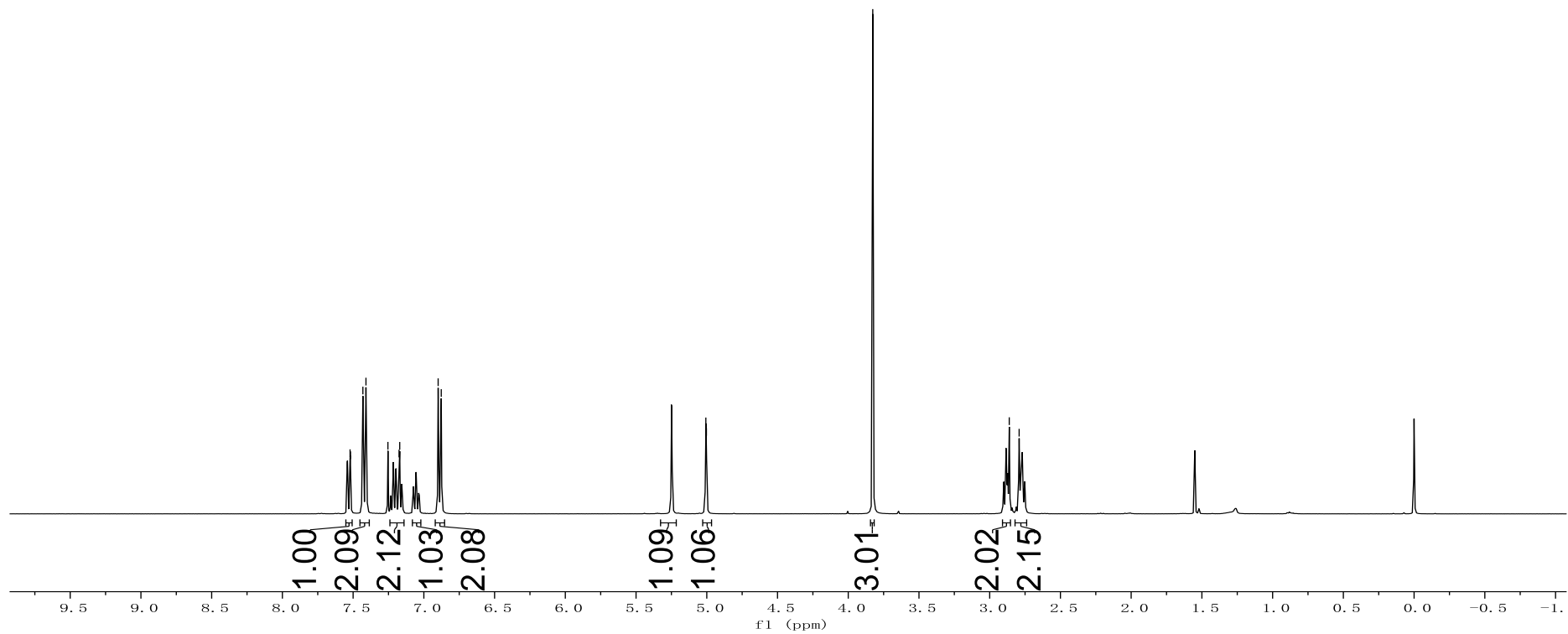
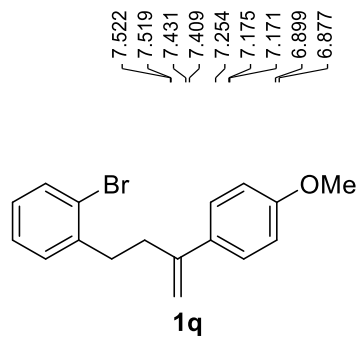


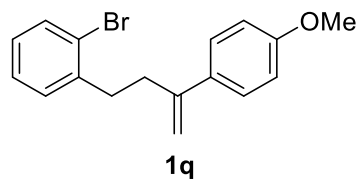


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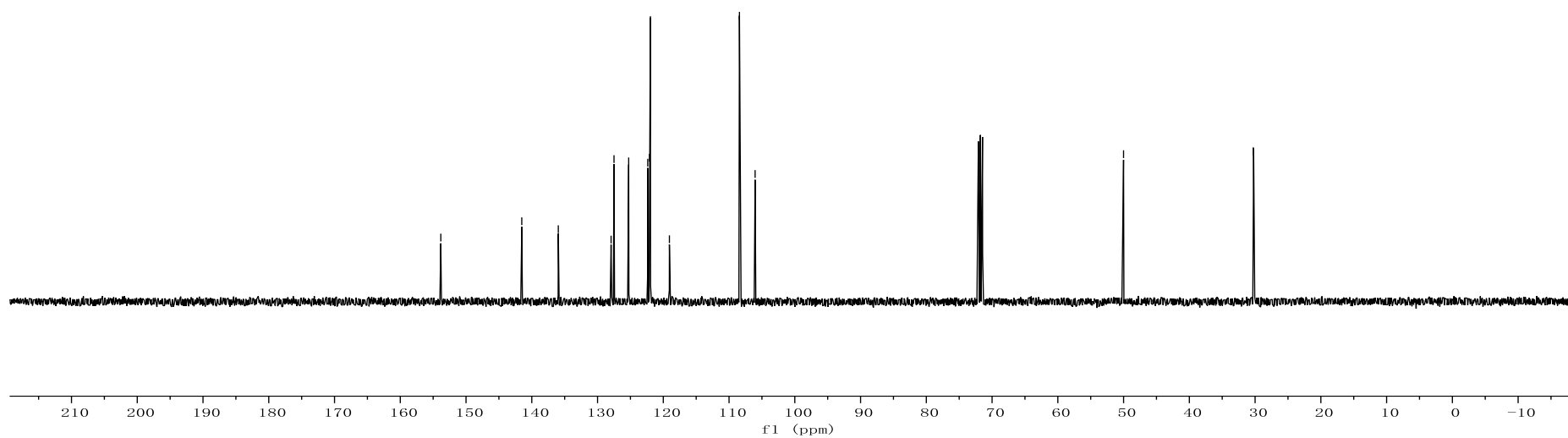
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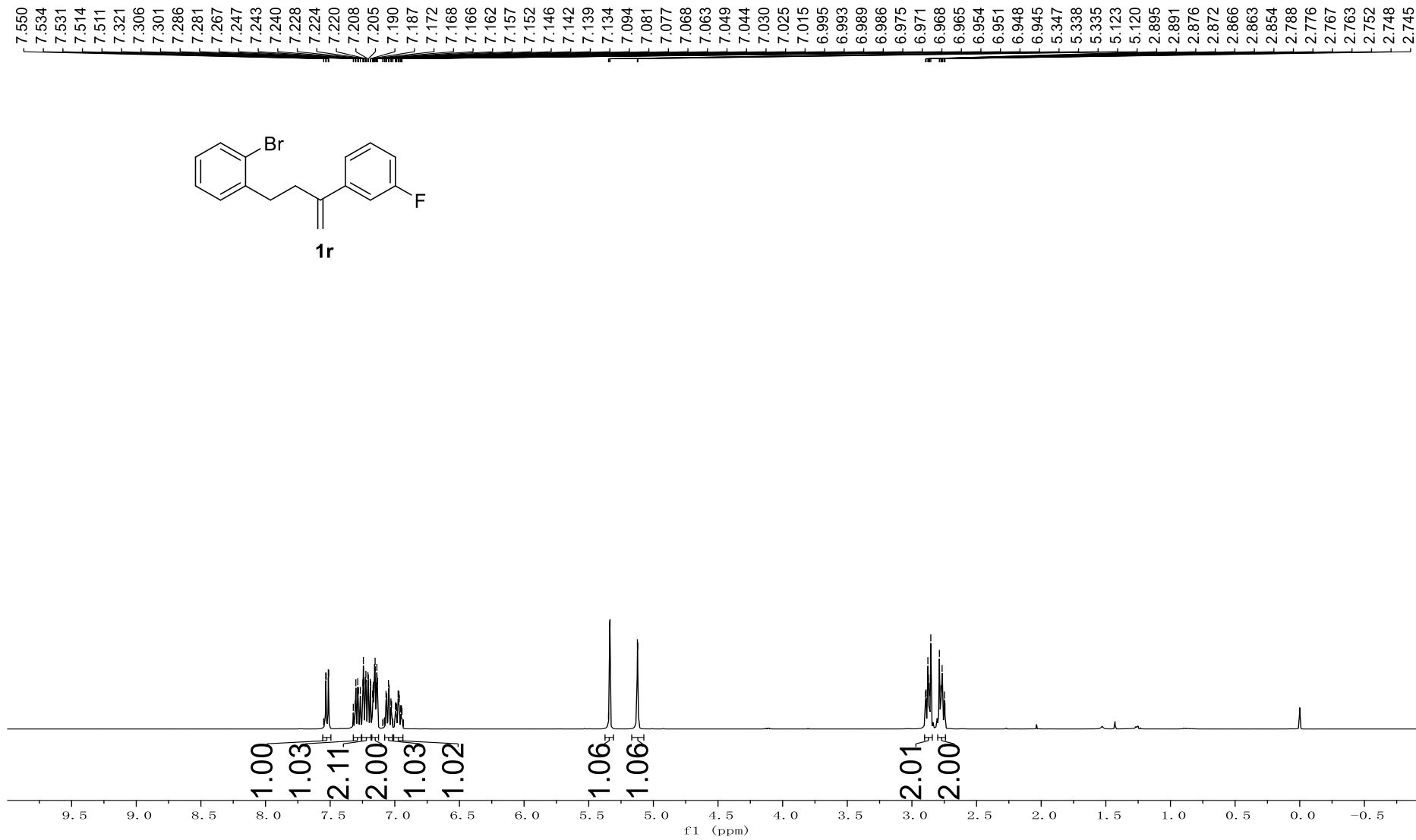


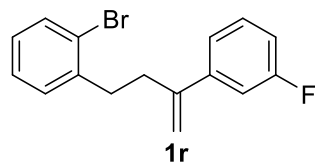




— 153.836
— 141.522
— 135.968
— 127.941
— 127.497
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— 122.099
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— 106.035
— 50.005
— 30.283
— 30.222

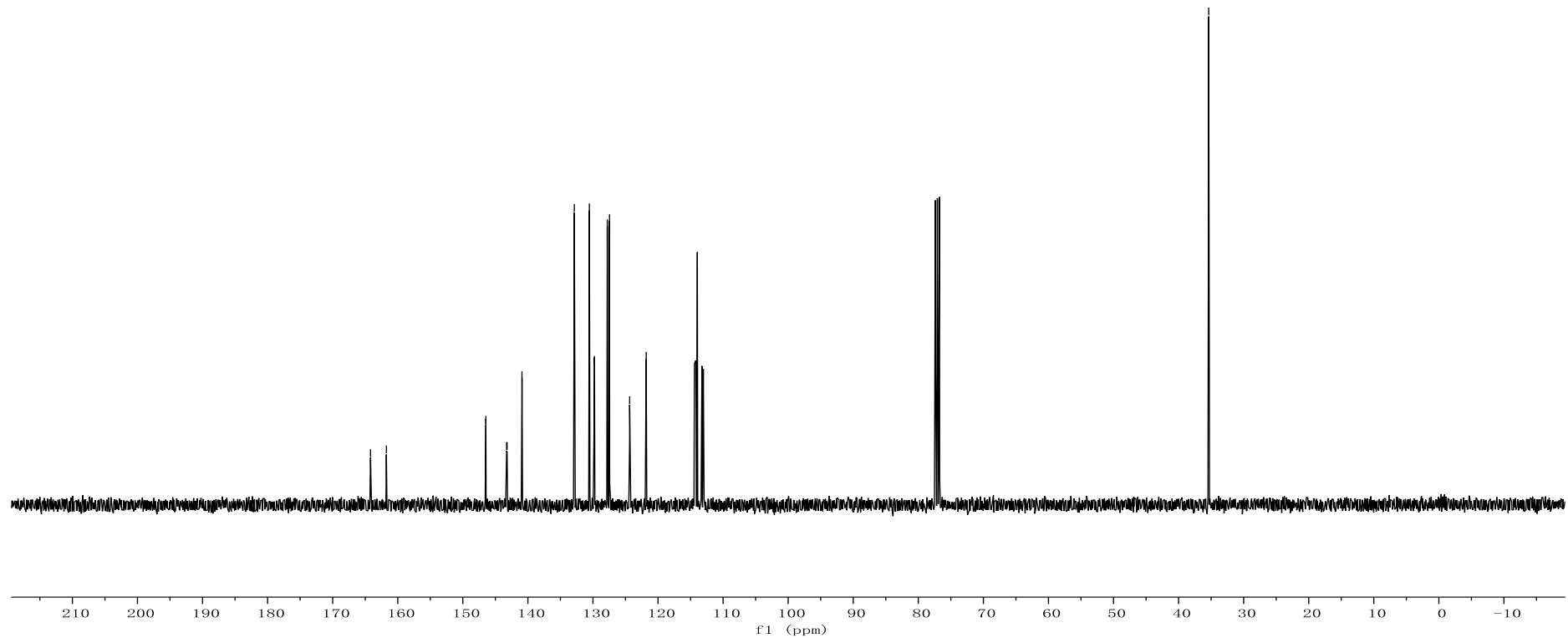


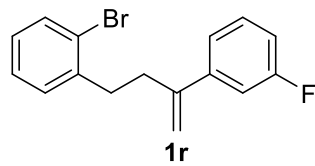




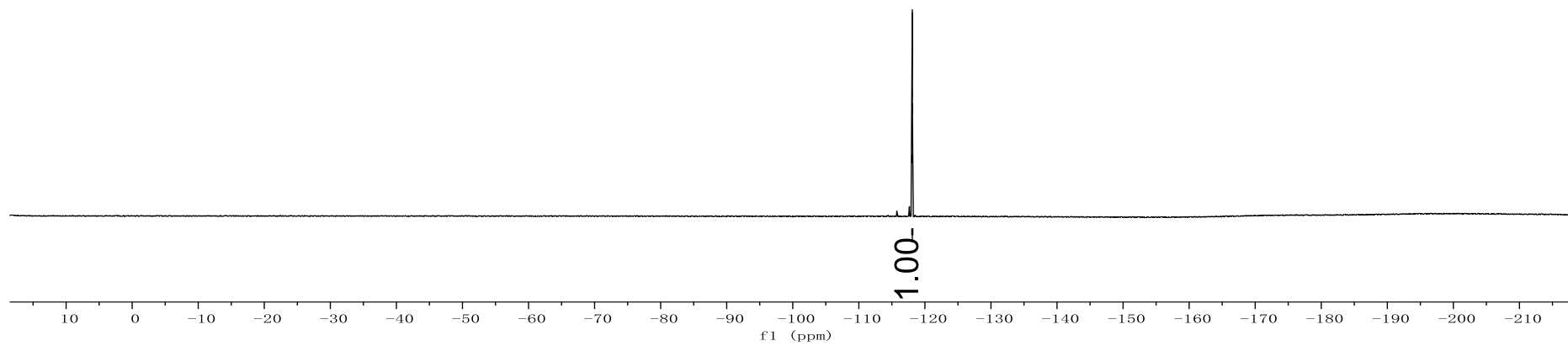
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35.373





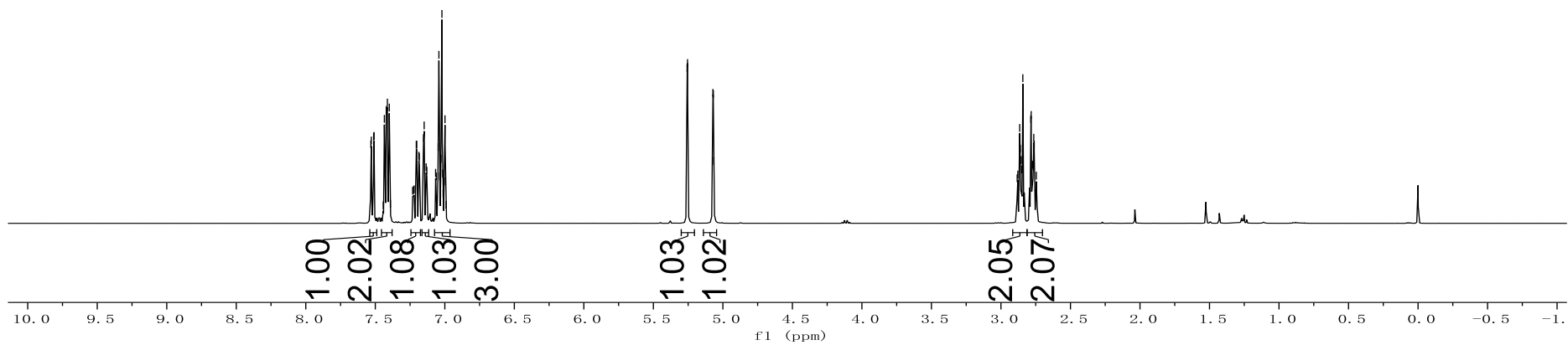
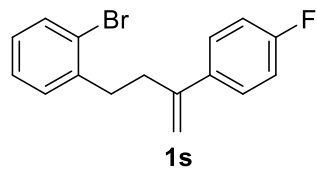
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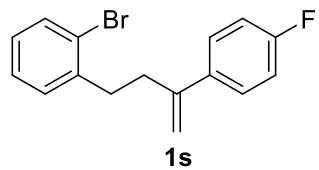


S68

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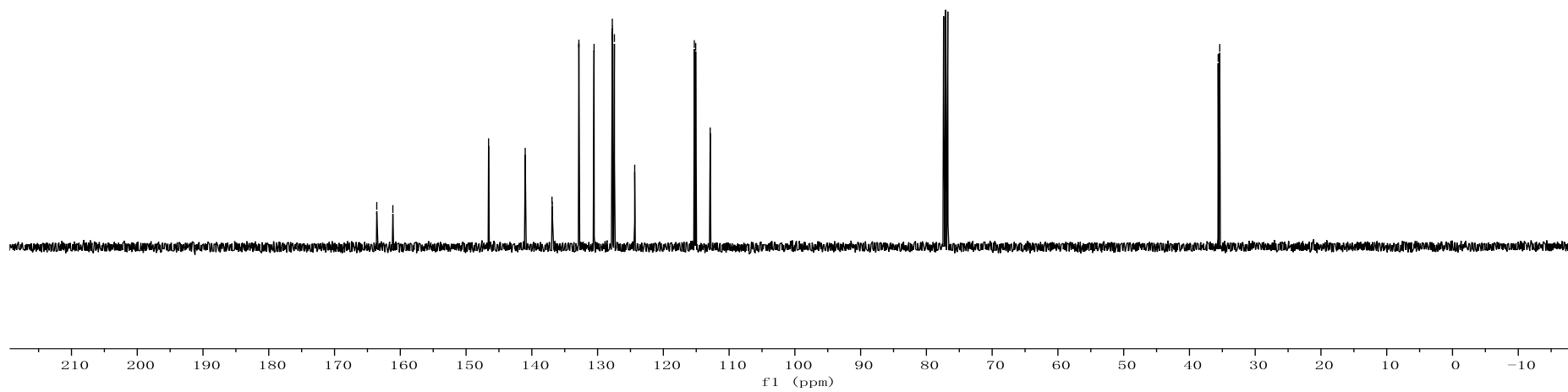
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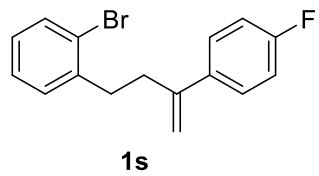




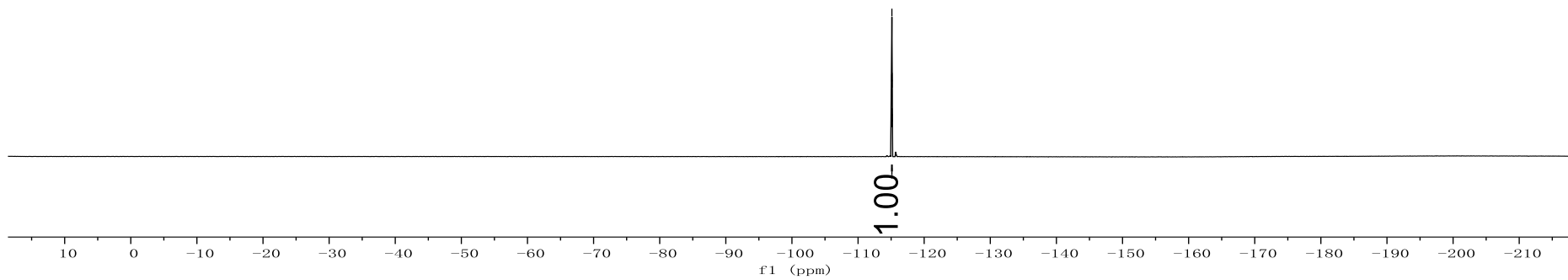
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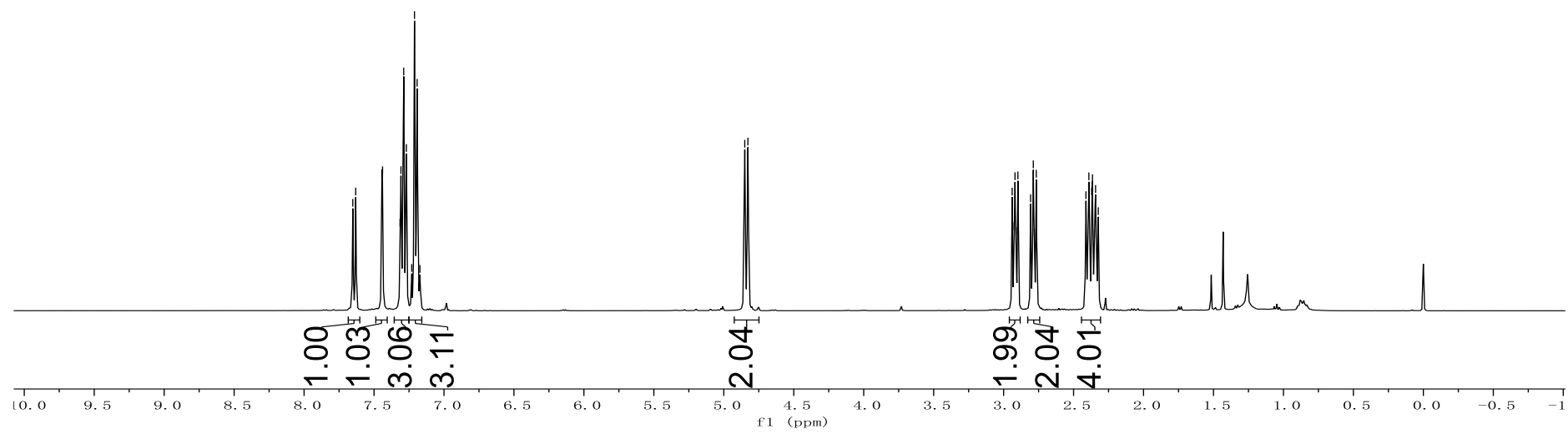
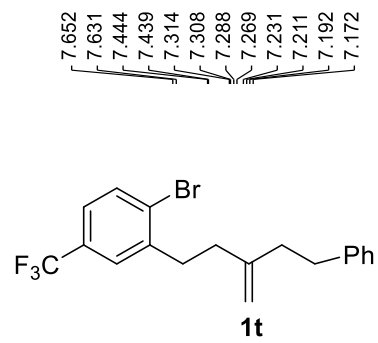


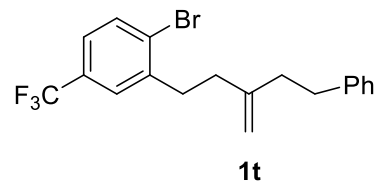


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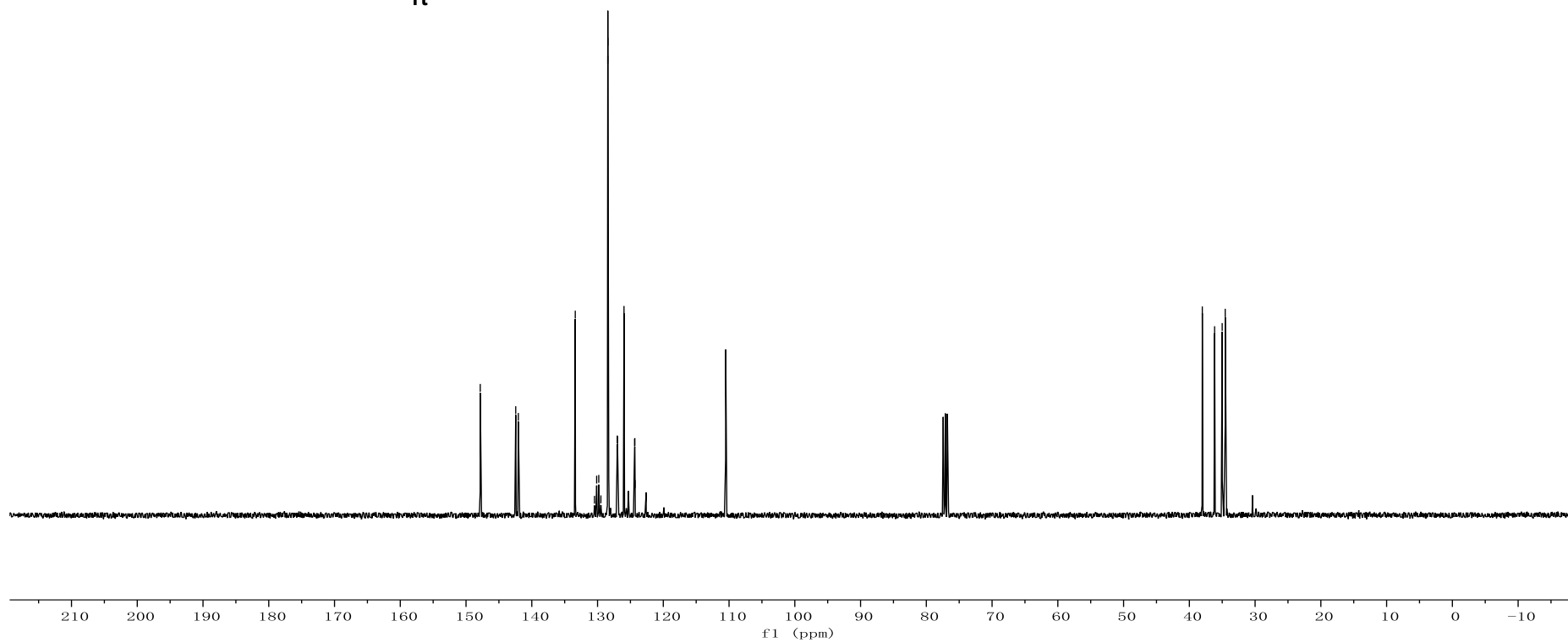
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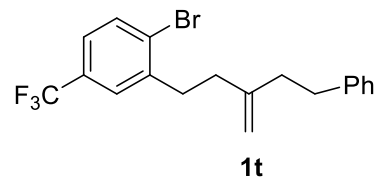




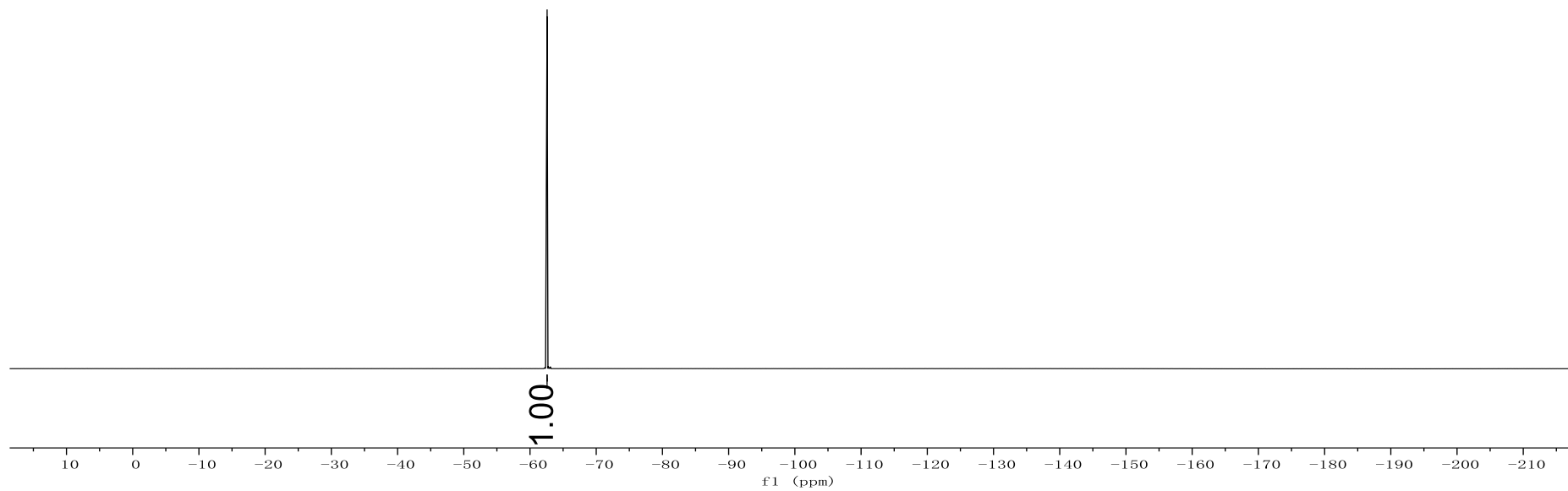
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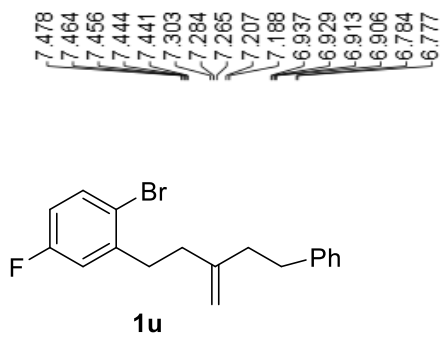




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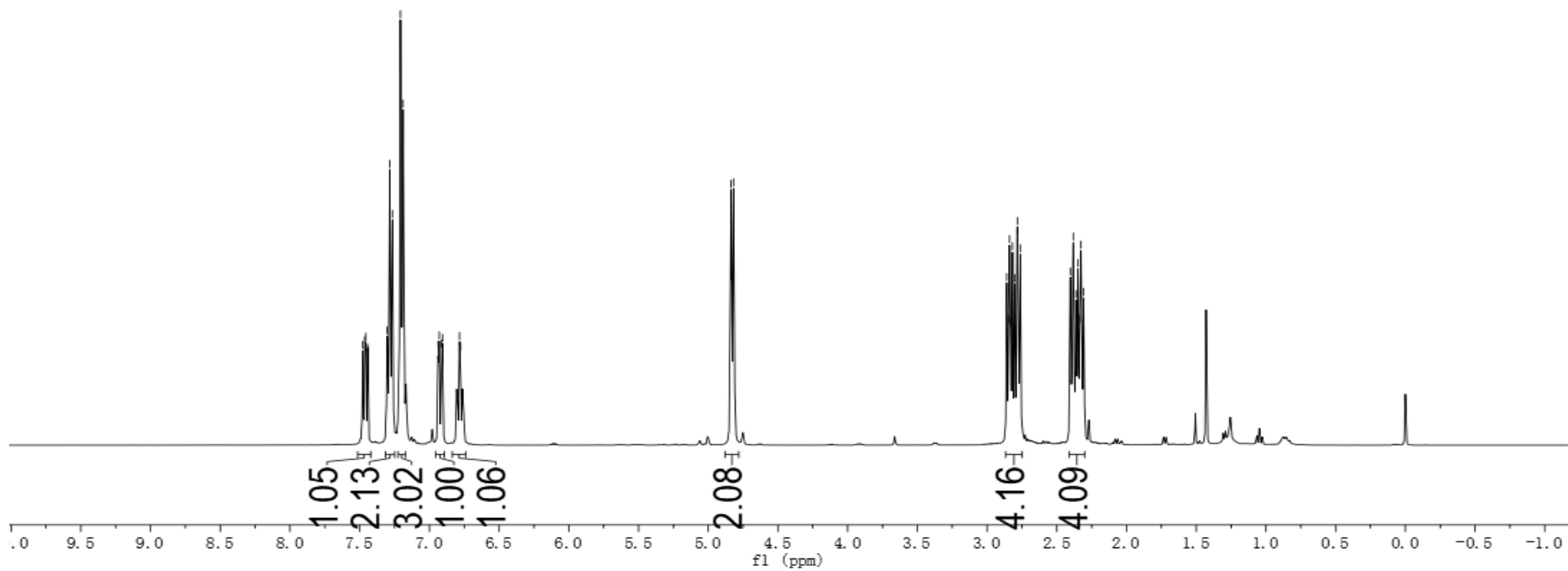
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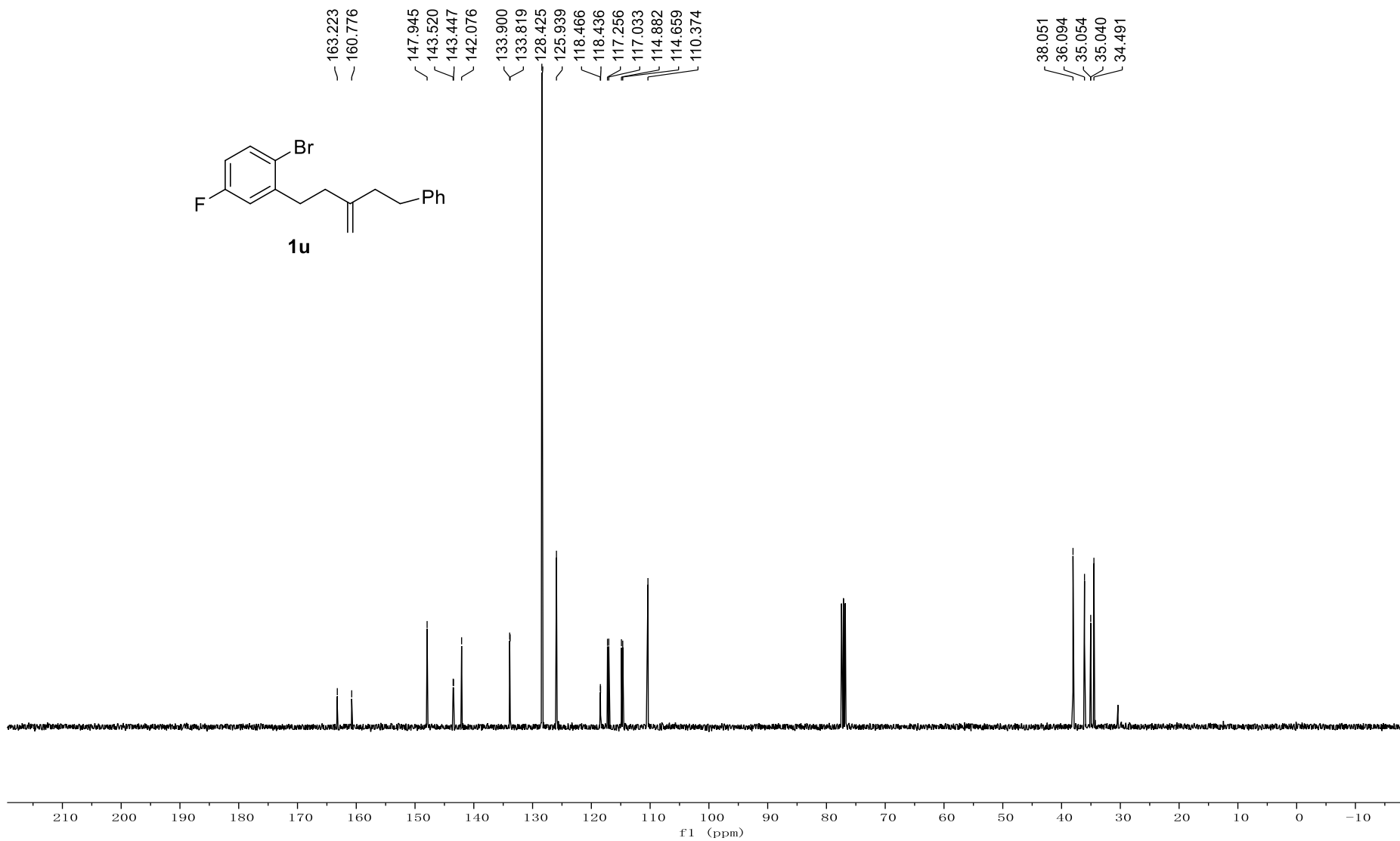
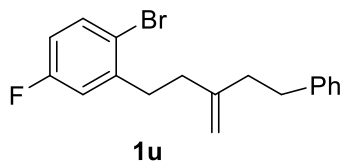


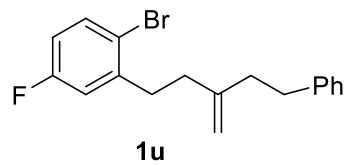
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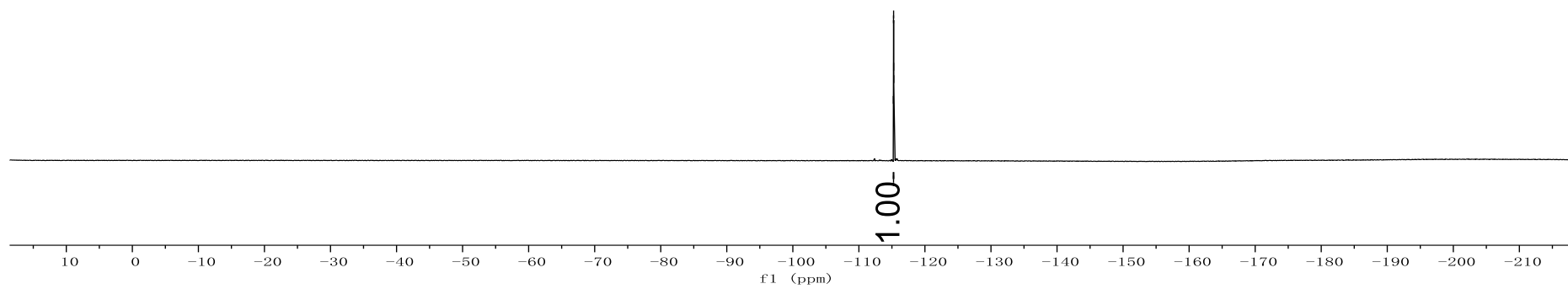
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2.326
2.307







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-115.264
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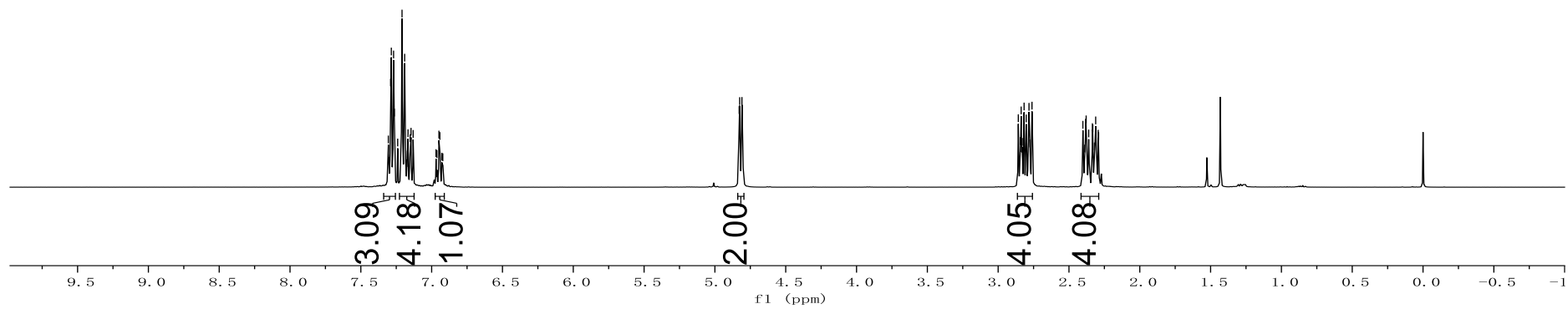
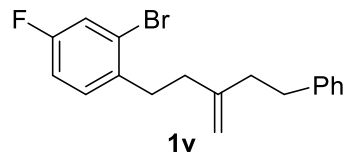


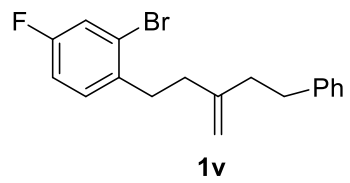
S77

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7.146
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4.805

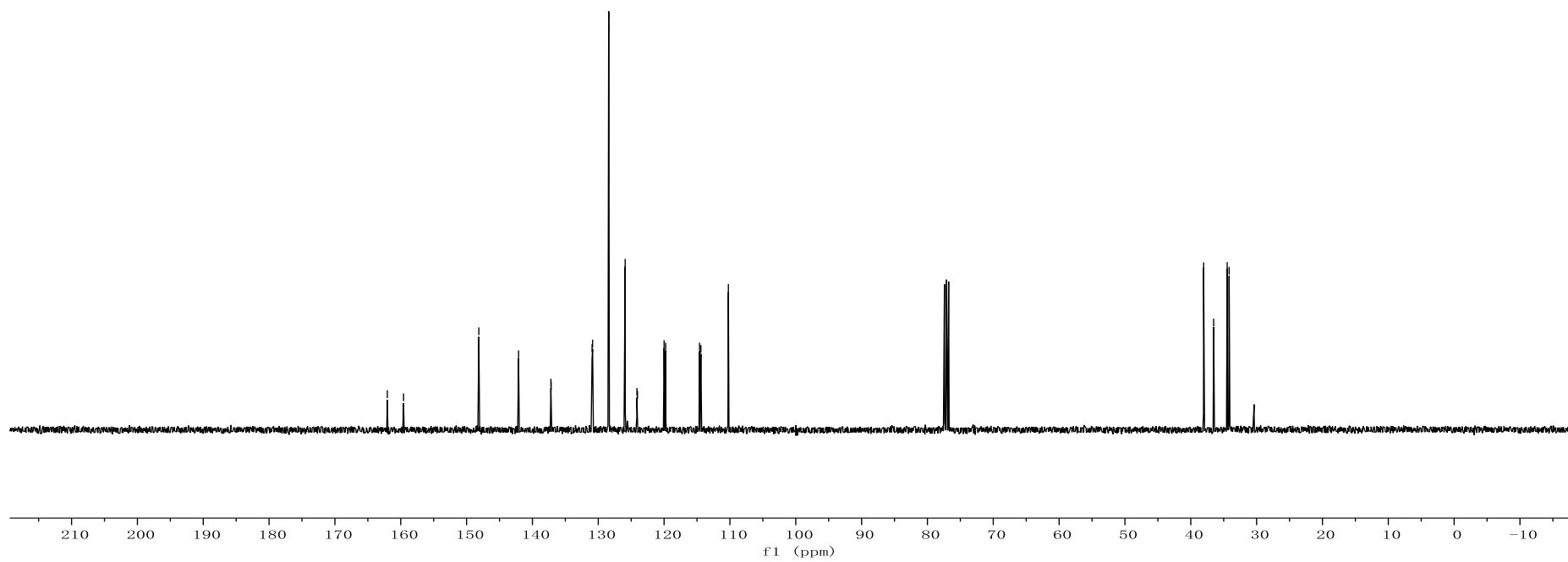
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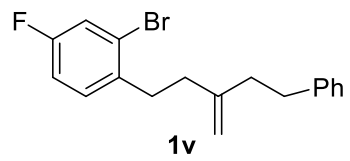




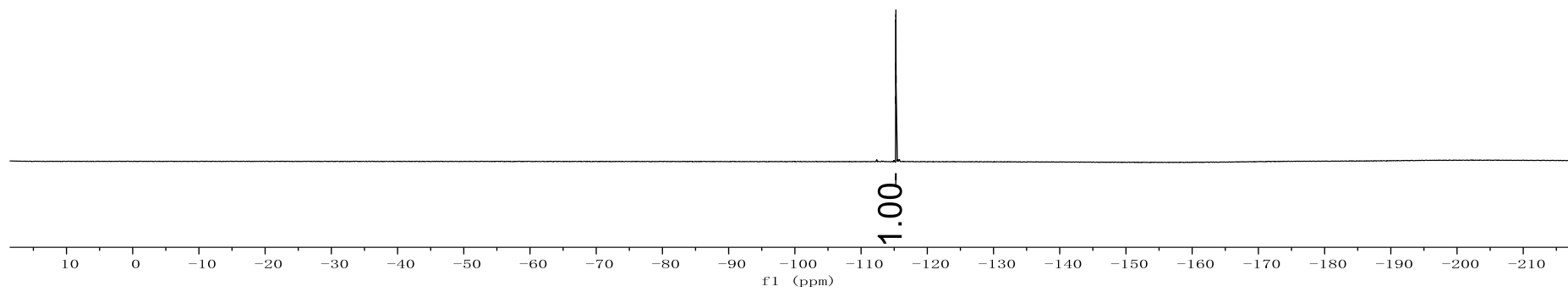
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34.472
34.173

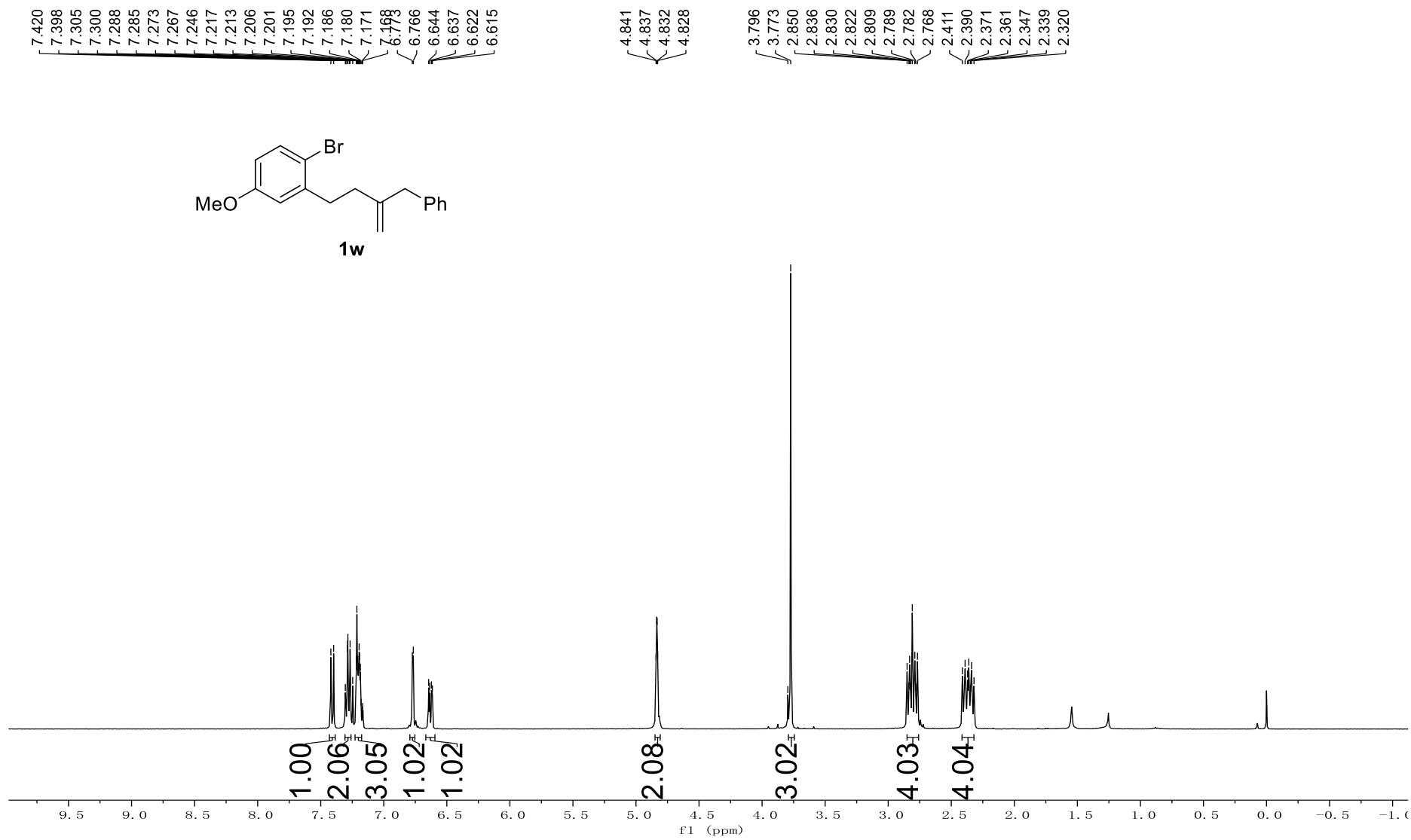
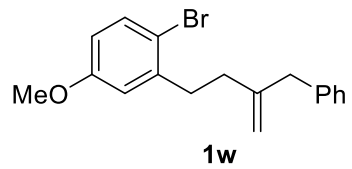


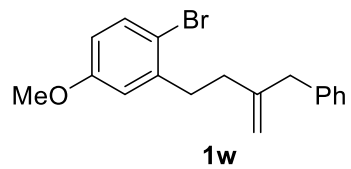


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-115.280

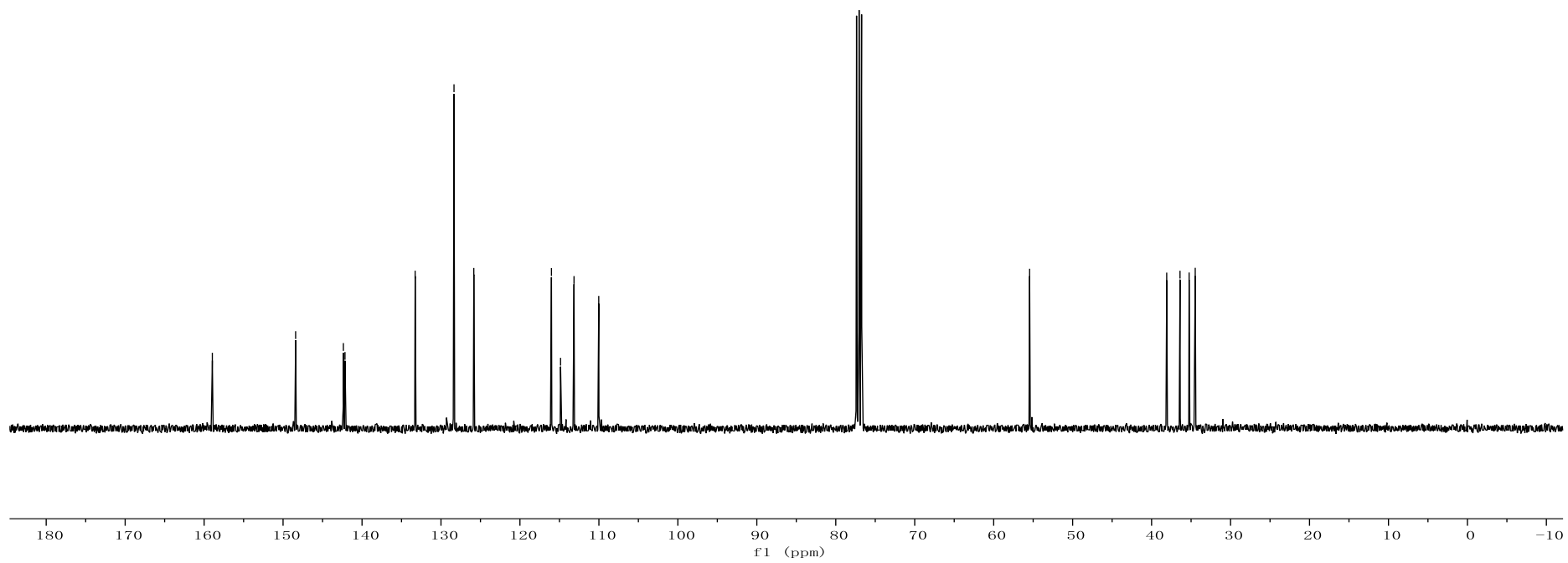


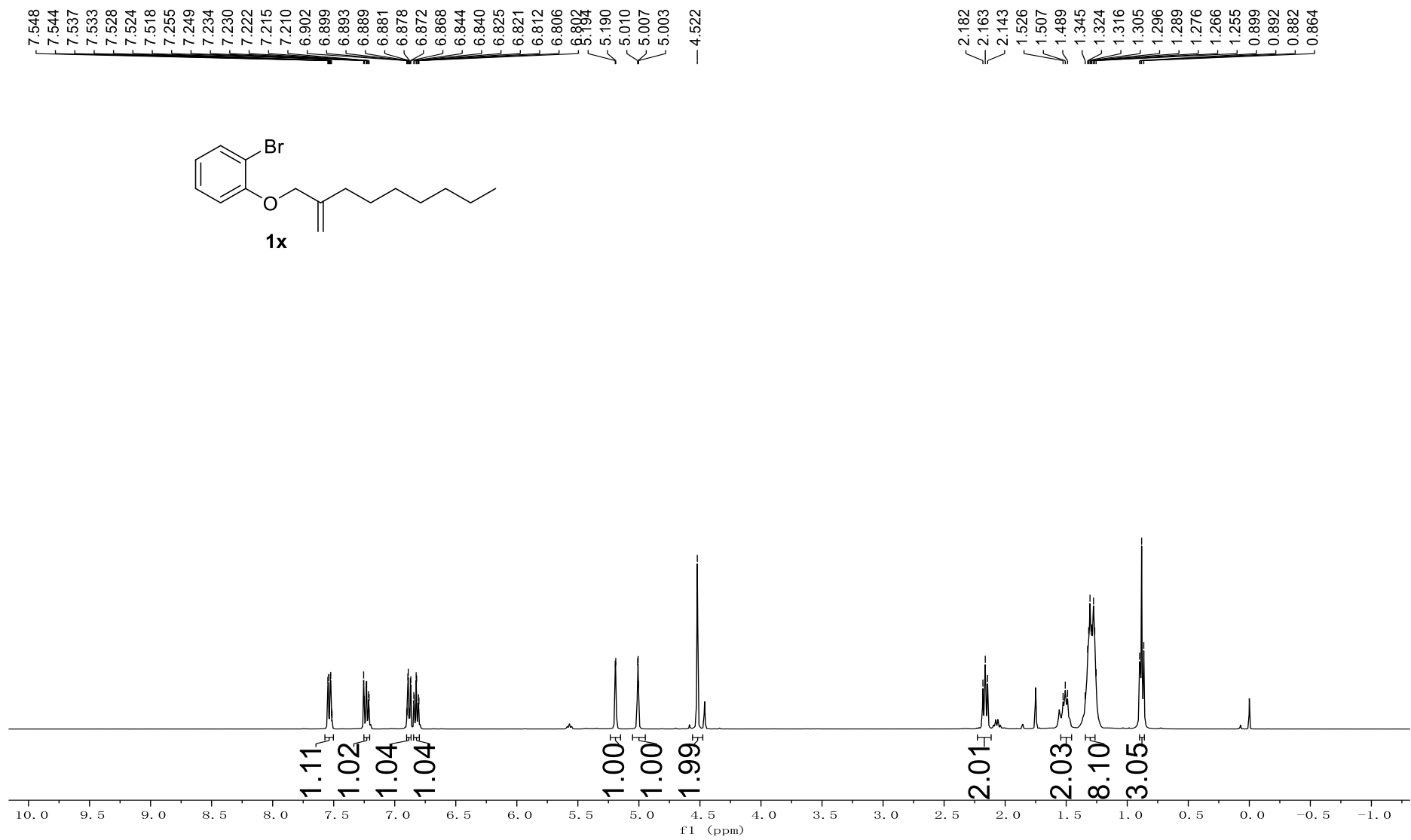
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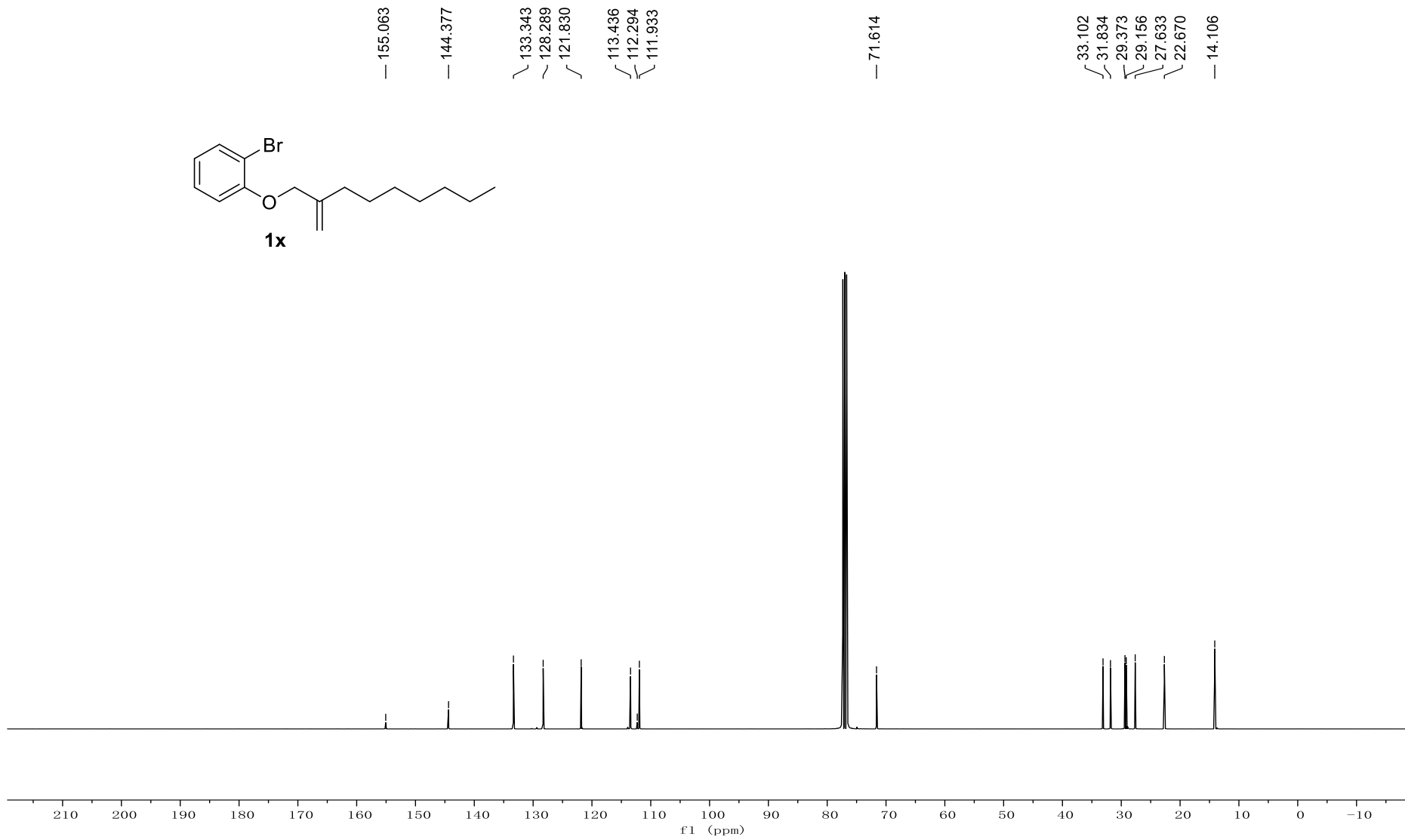
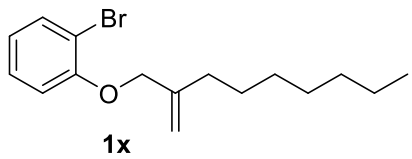




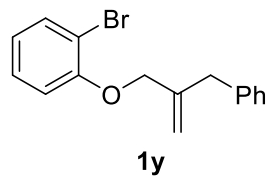
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142.362
142.158
133.273
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114.854
113.151
110.018
— 55.447
38.086
36.401
35.249
34.473



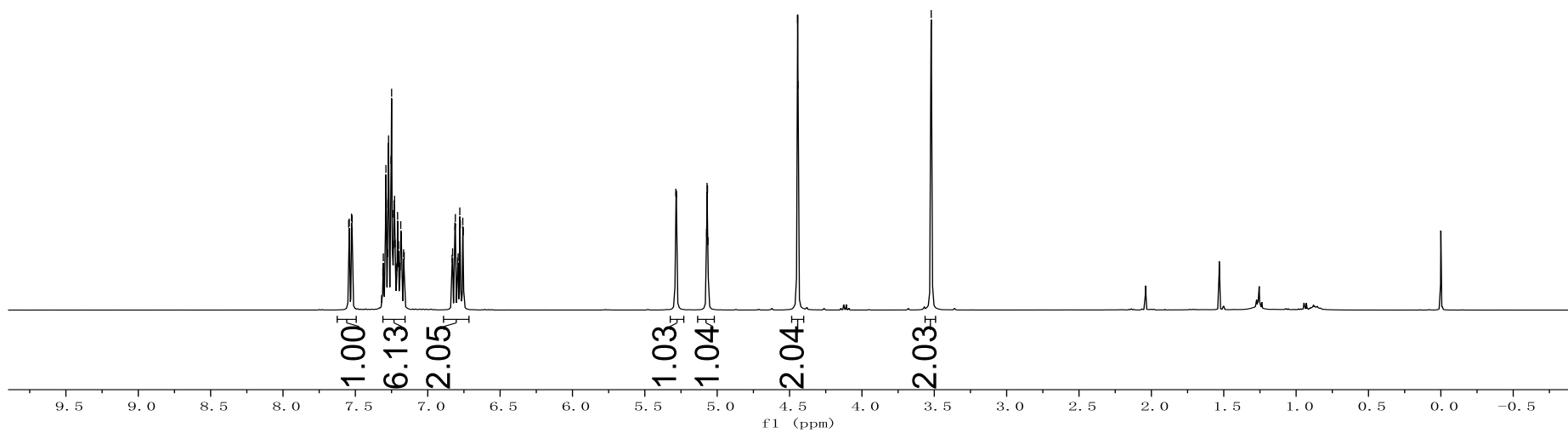


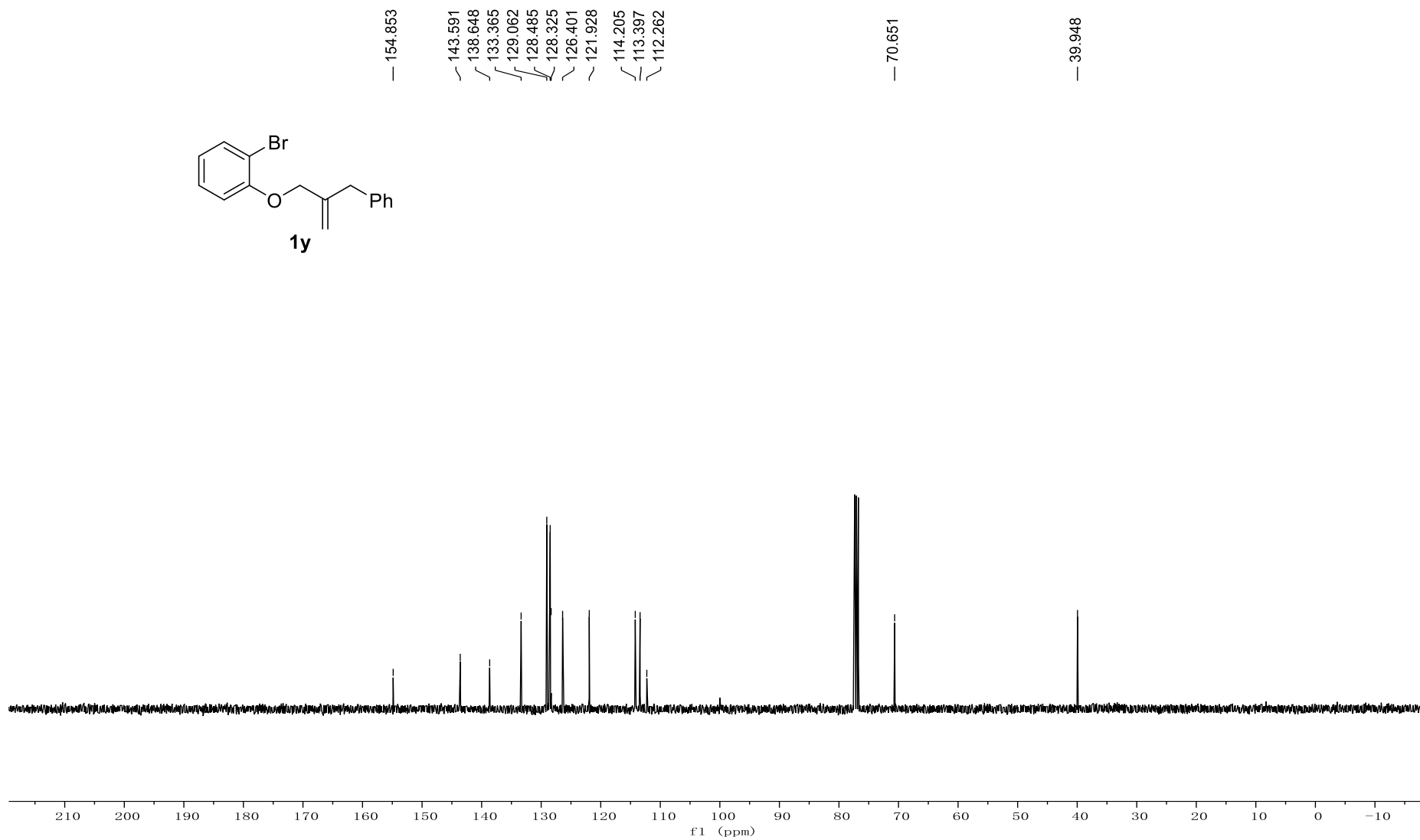
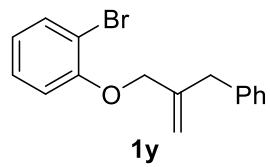


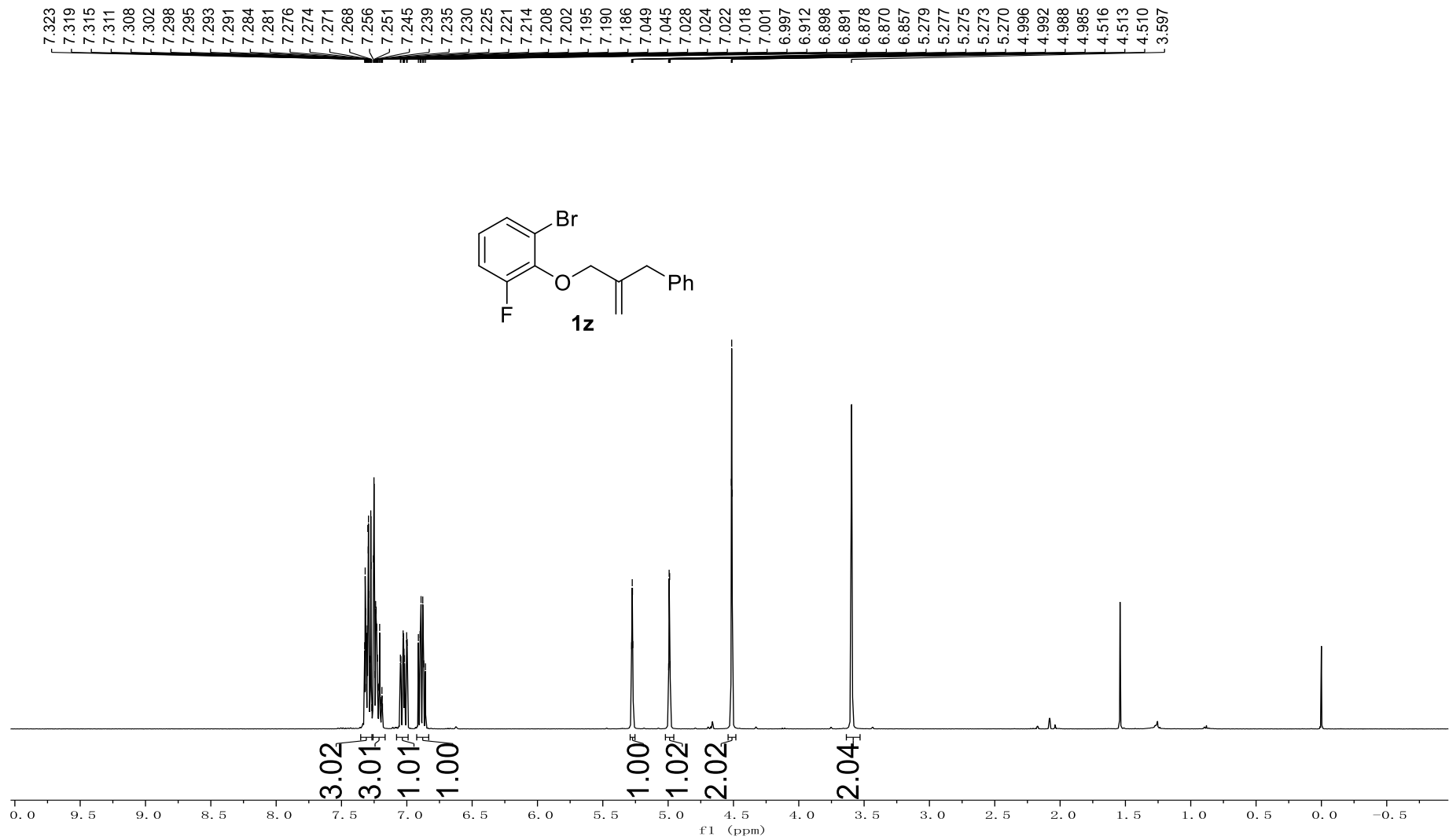
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7.229
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6.813
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4.442



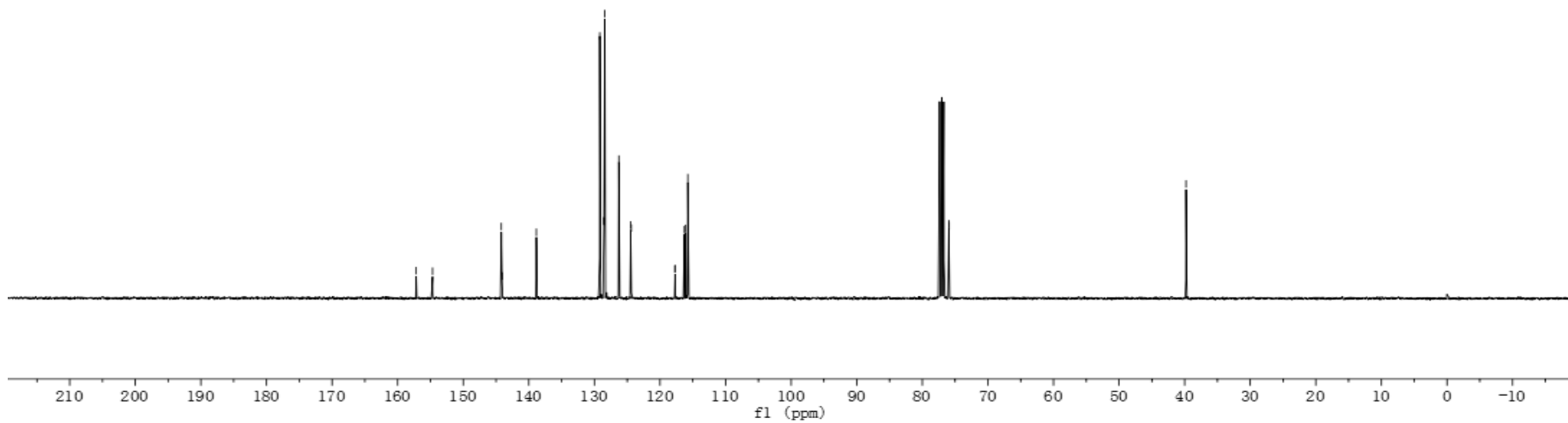
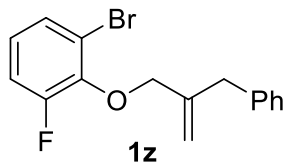
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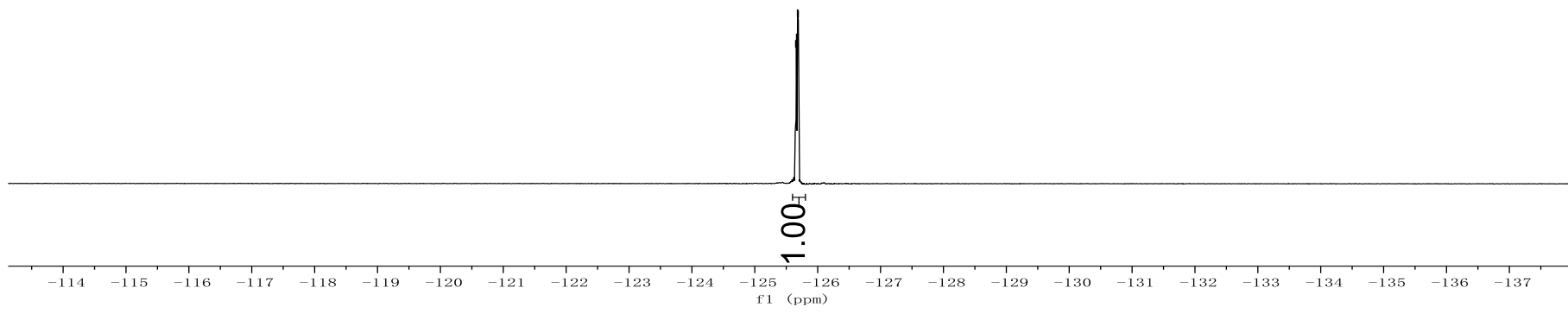
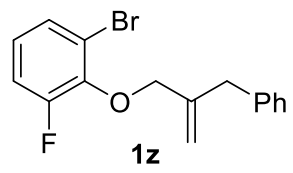




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39.789



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-125.692



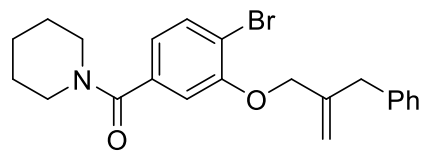
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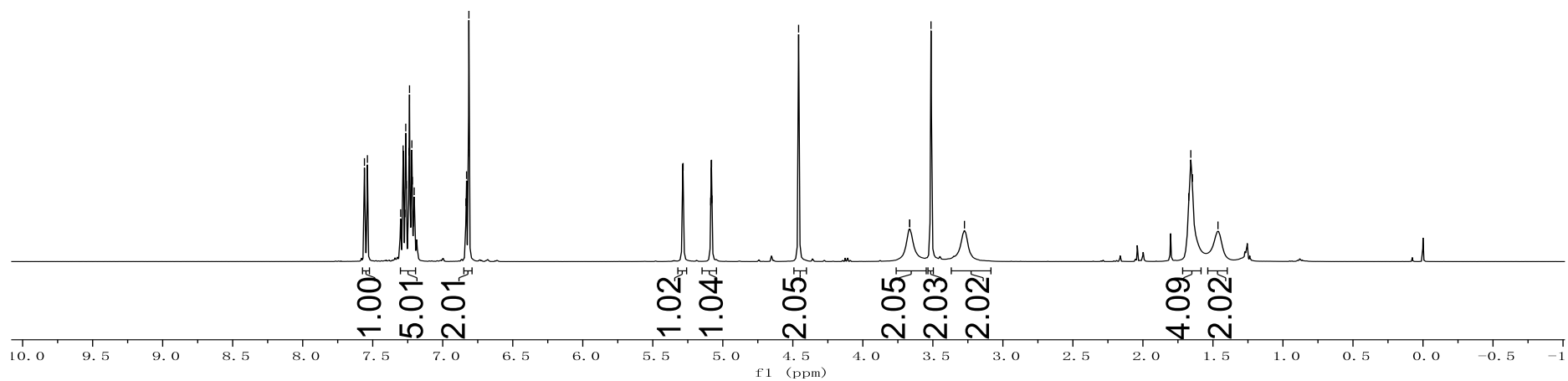
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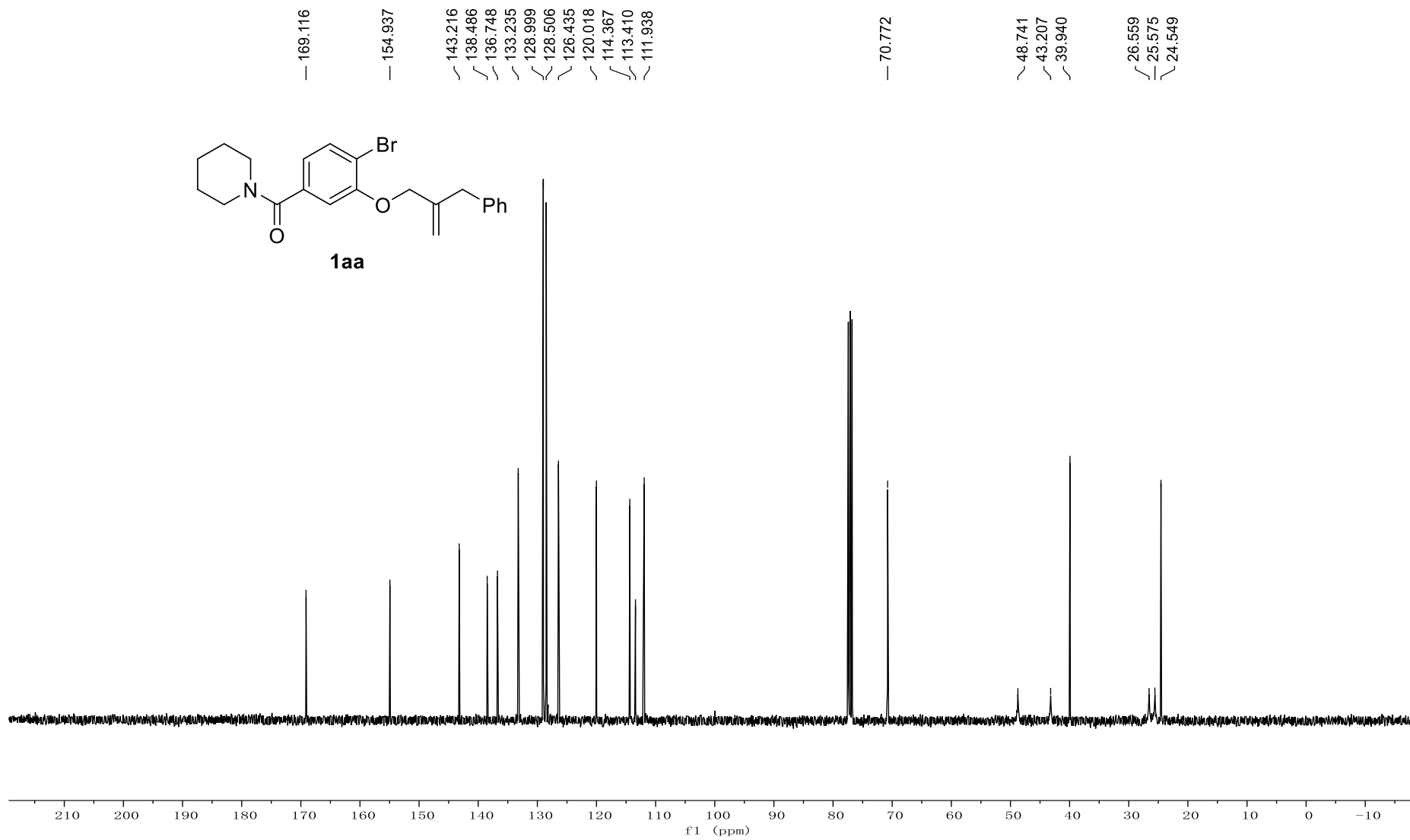
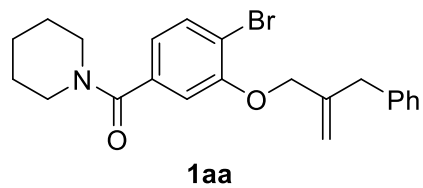
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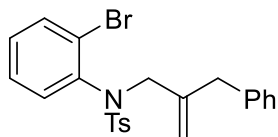


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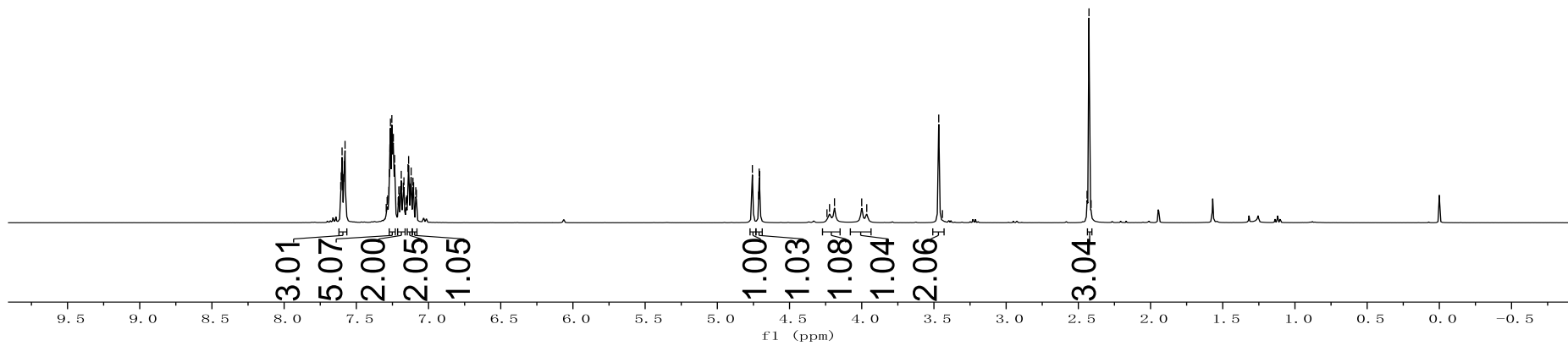


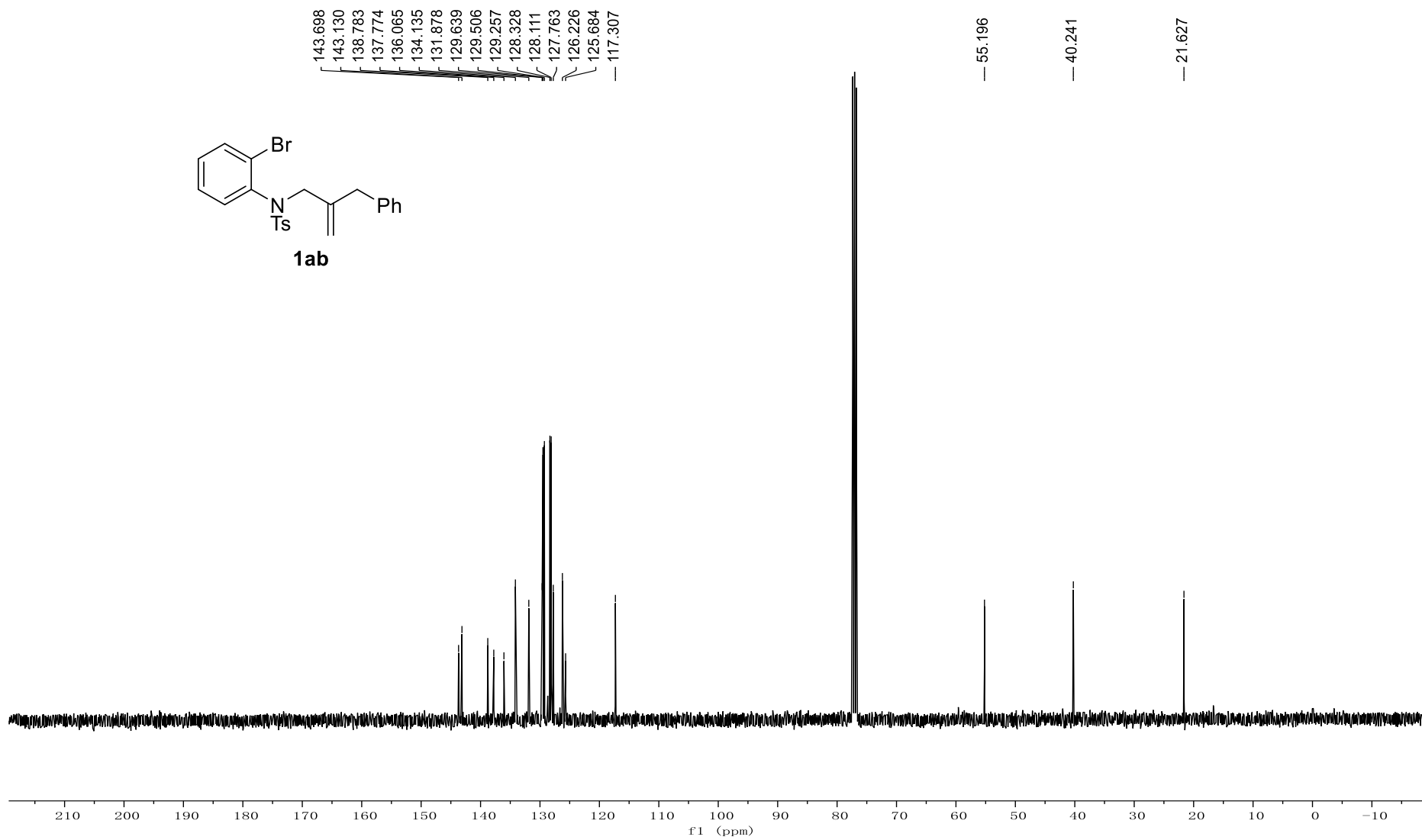
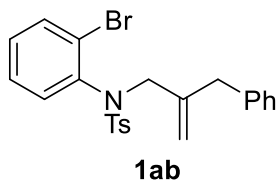


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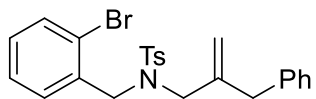
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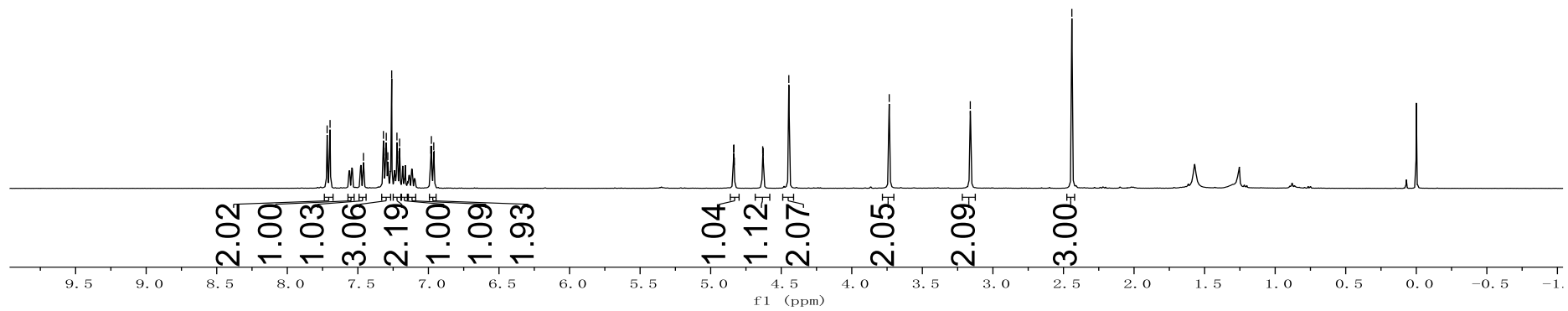
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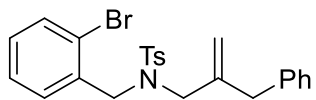
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1ac





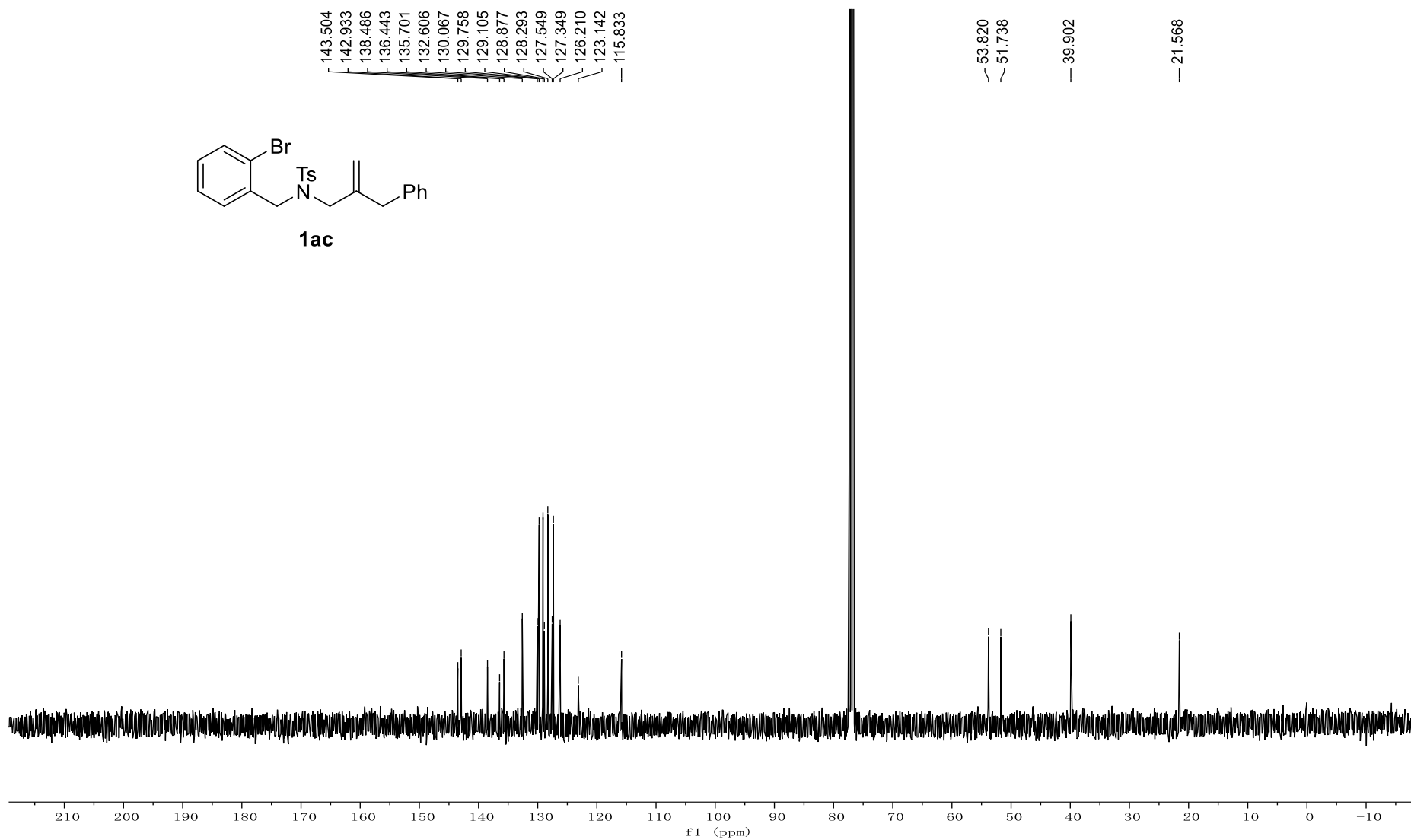
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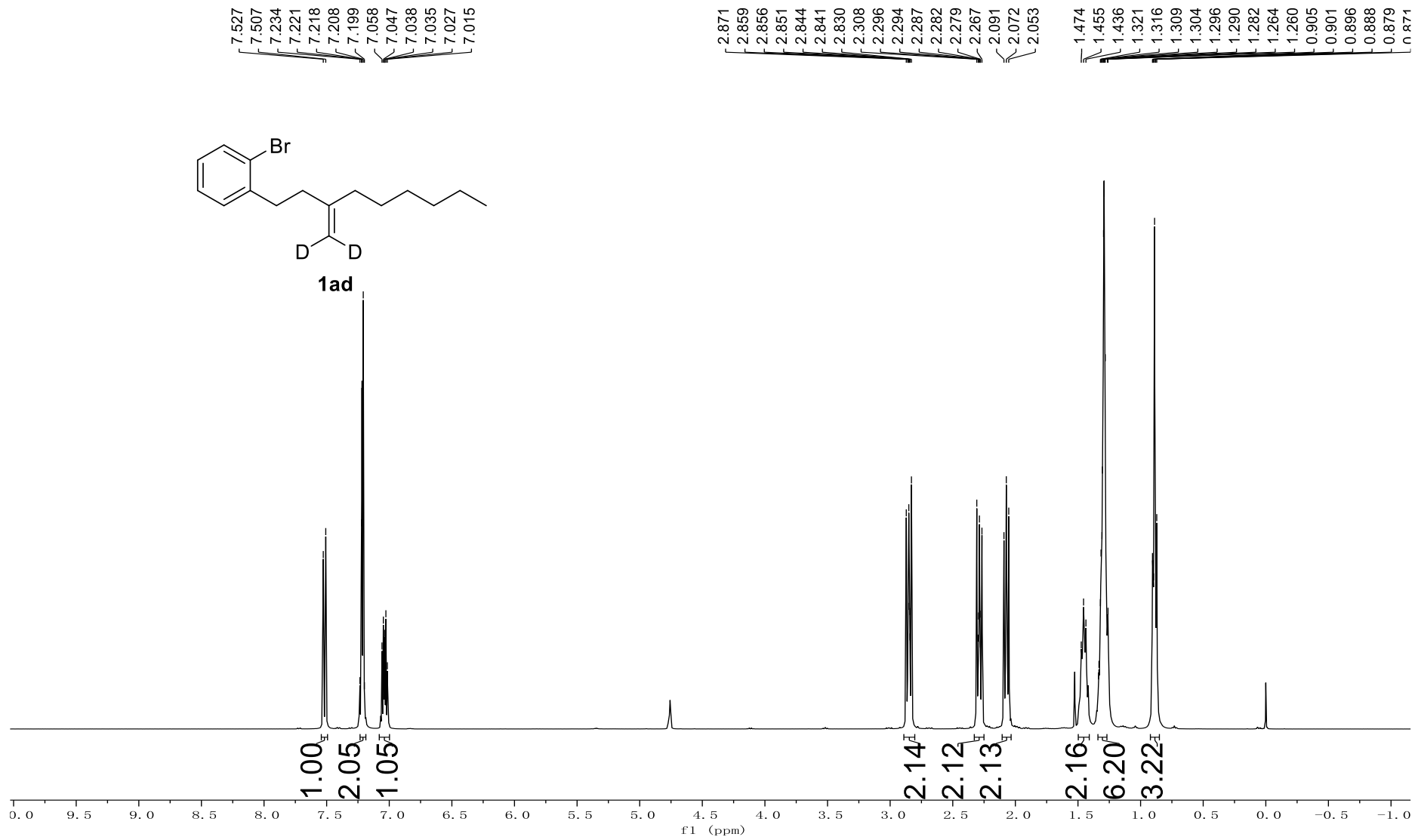
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— 115.833

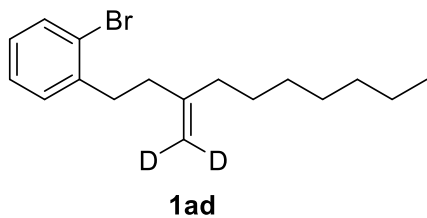
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~ 51.738

— 39.902

— 21.568

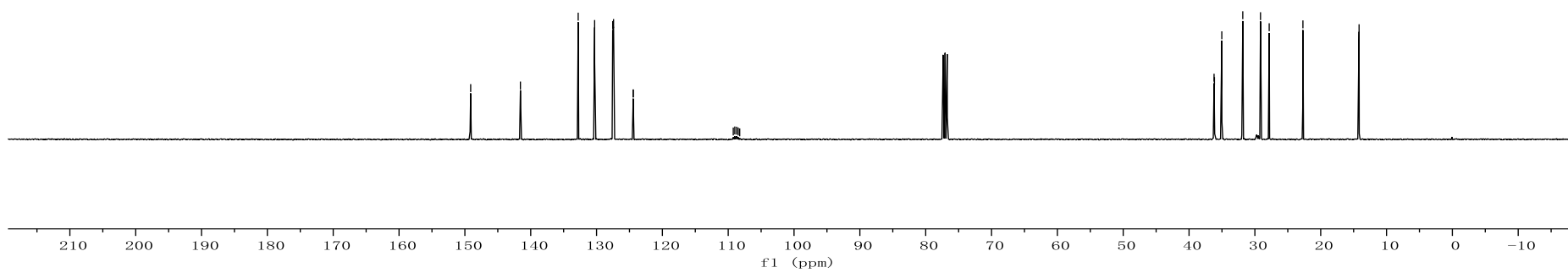


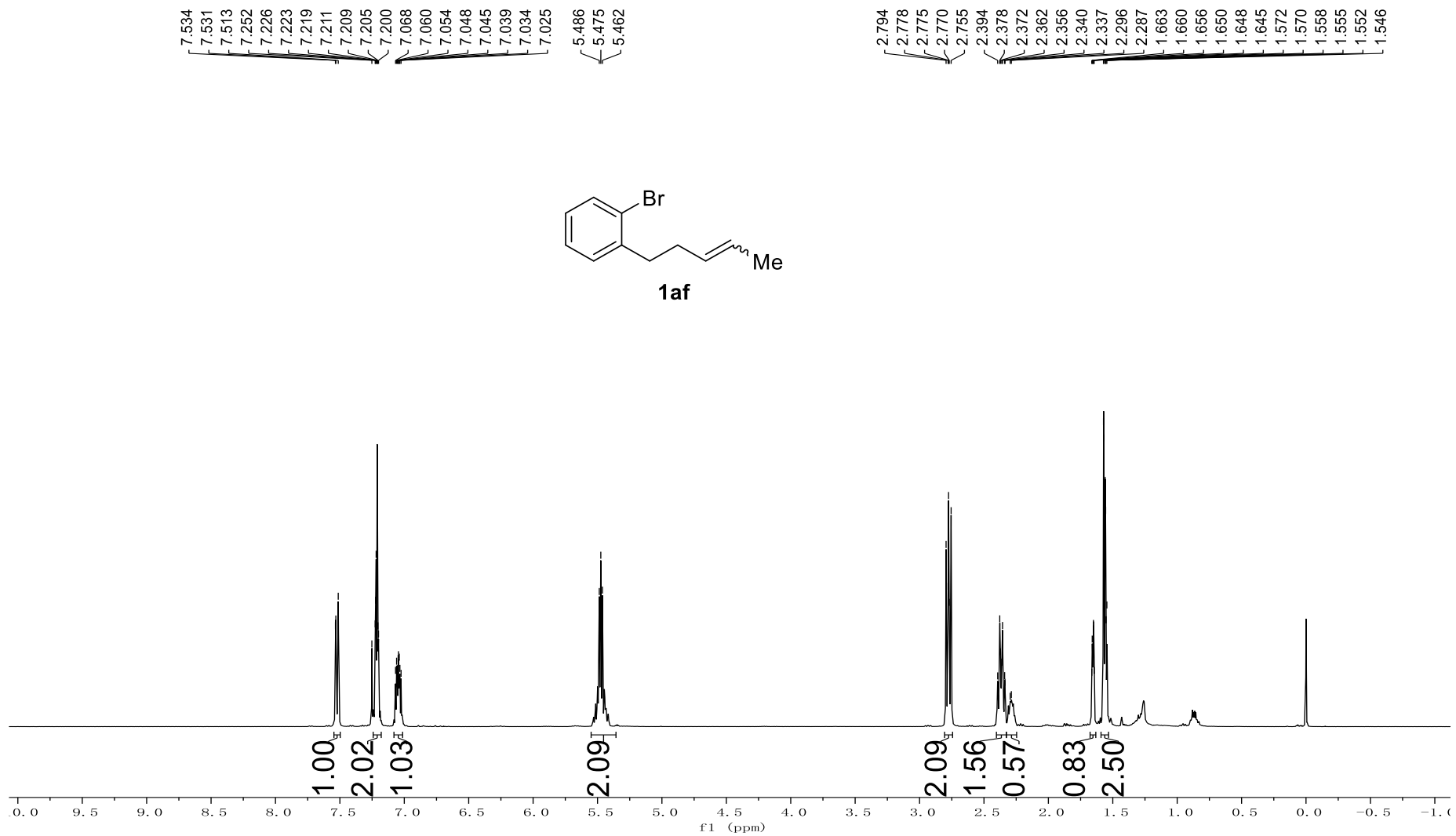




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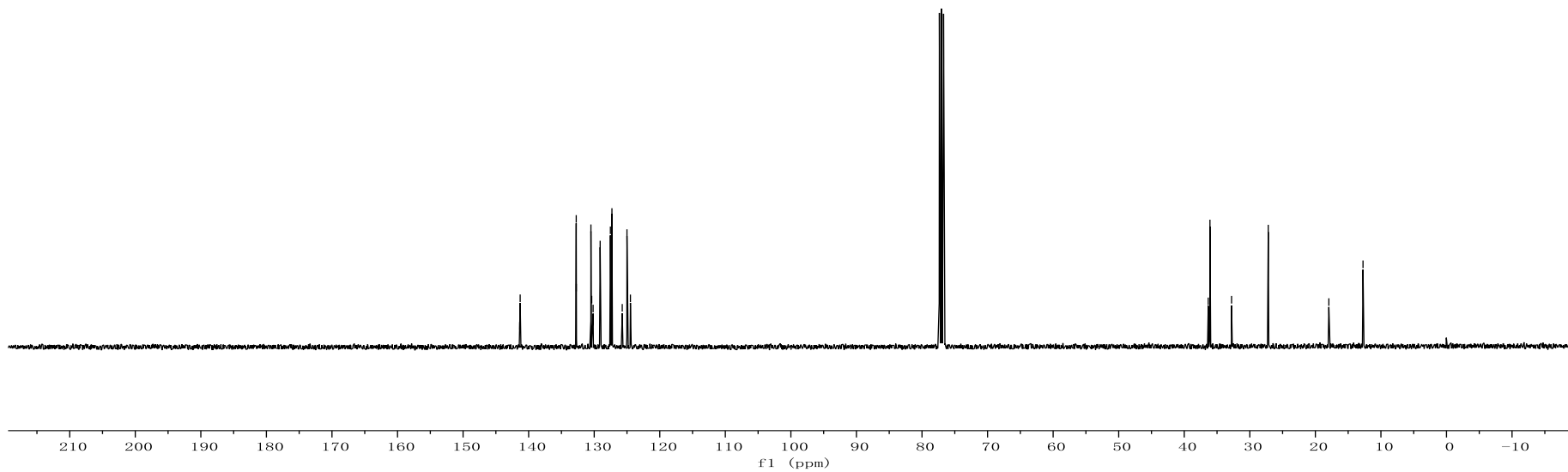
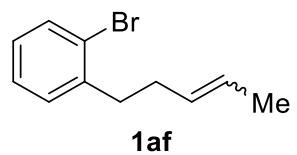
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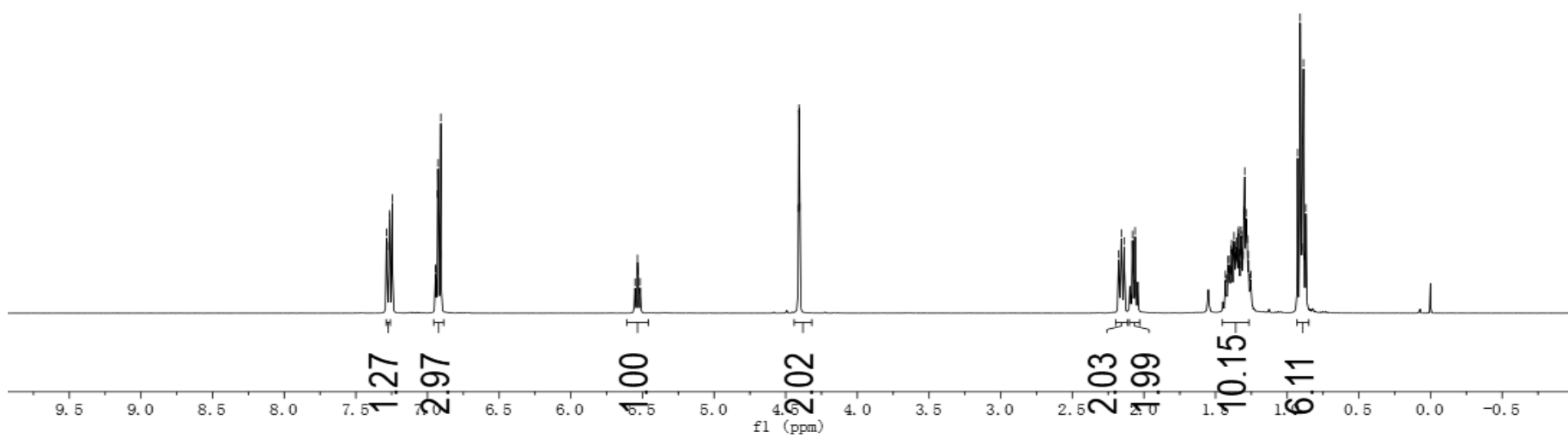
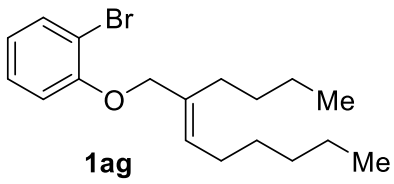


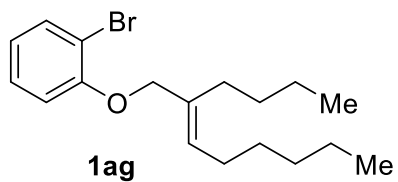
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— 159.052

— 135.104

— 129.780

— 129.314

— 120.532

— 114.861

— 72.316

— 31.596

— 30.626

— 29.330

— 27.881

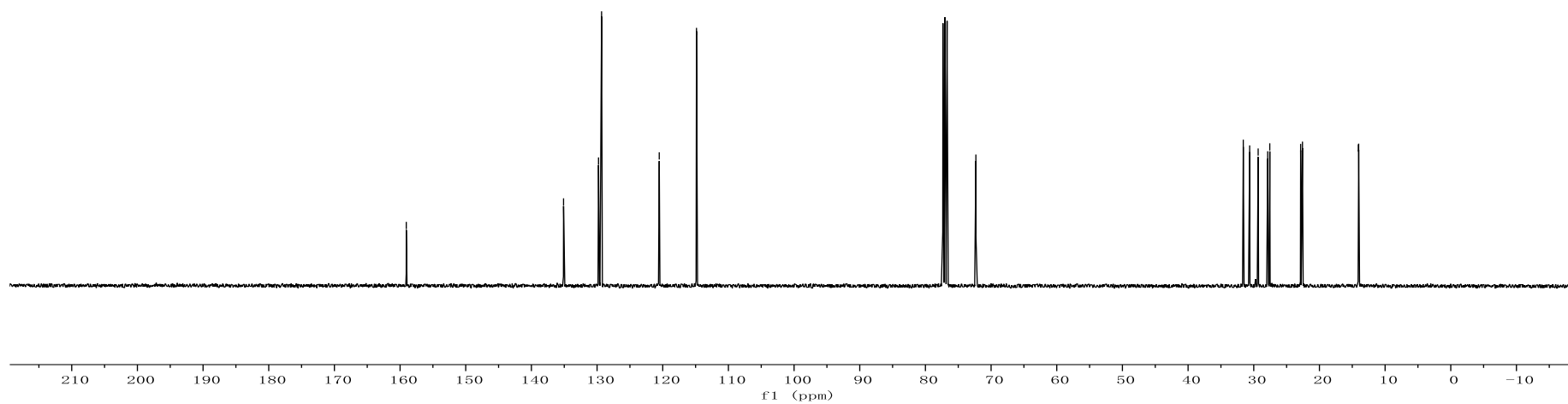
— 27.560

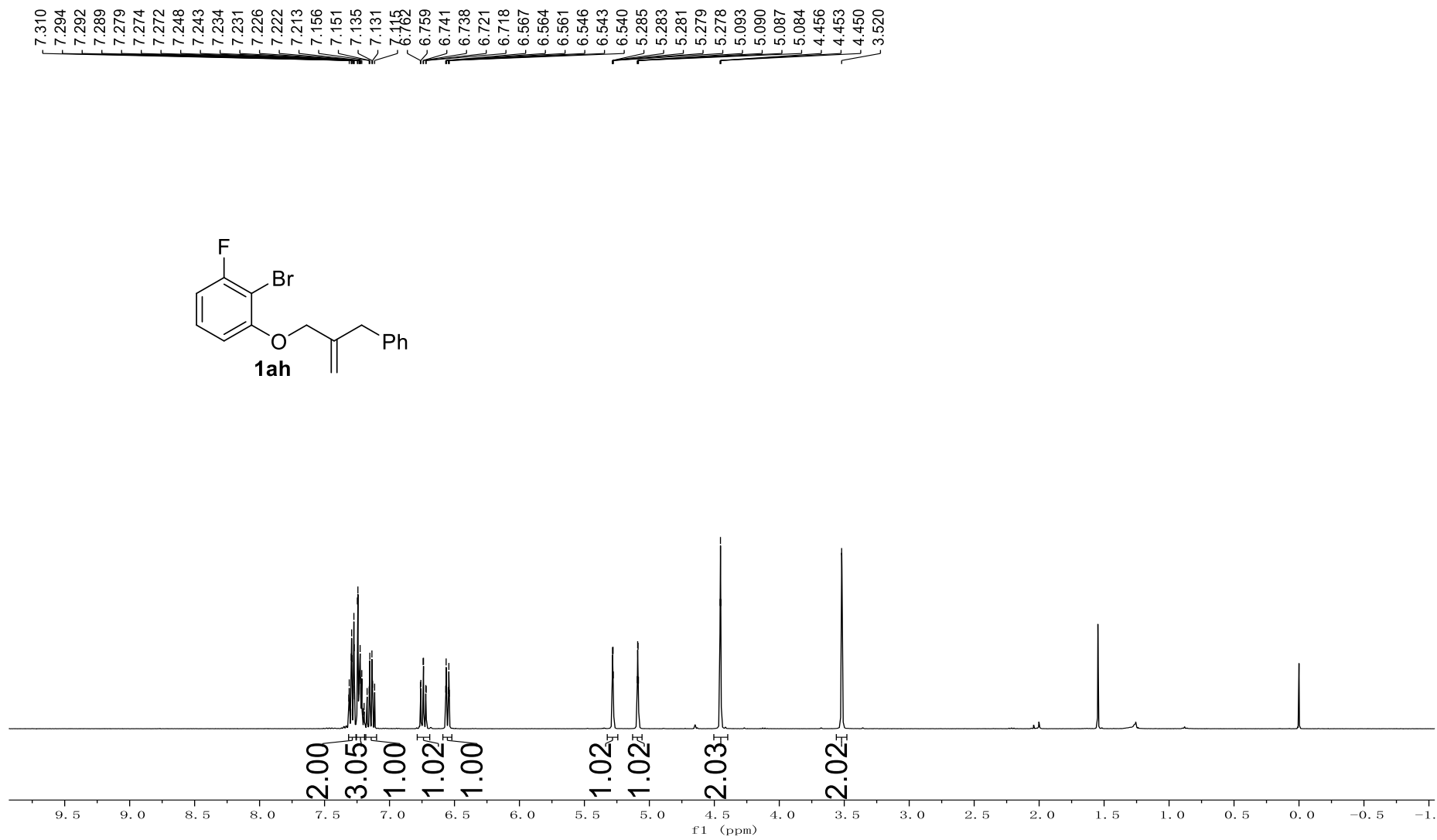
— 22.861

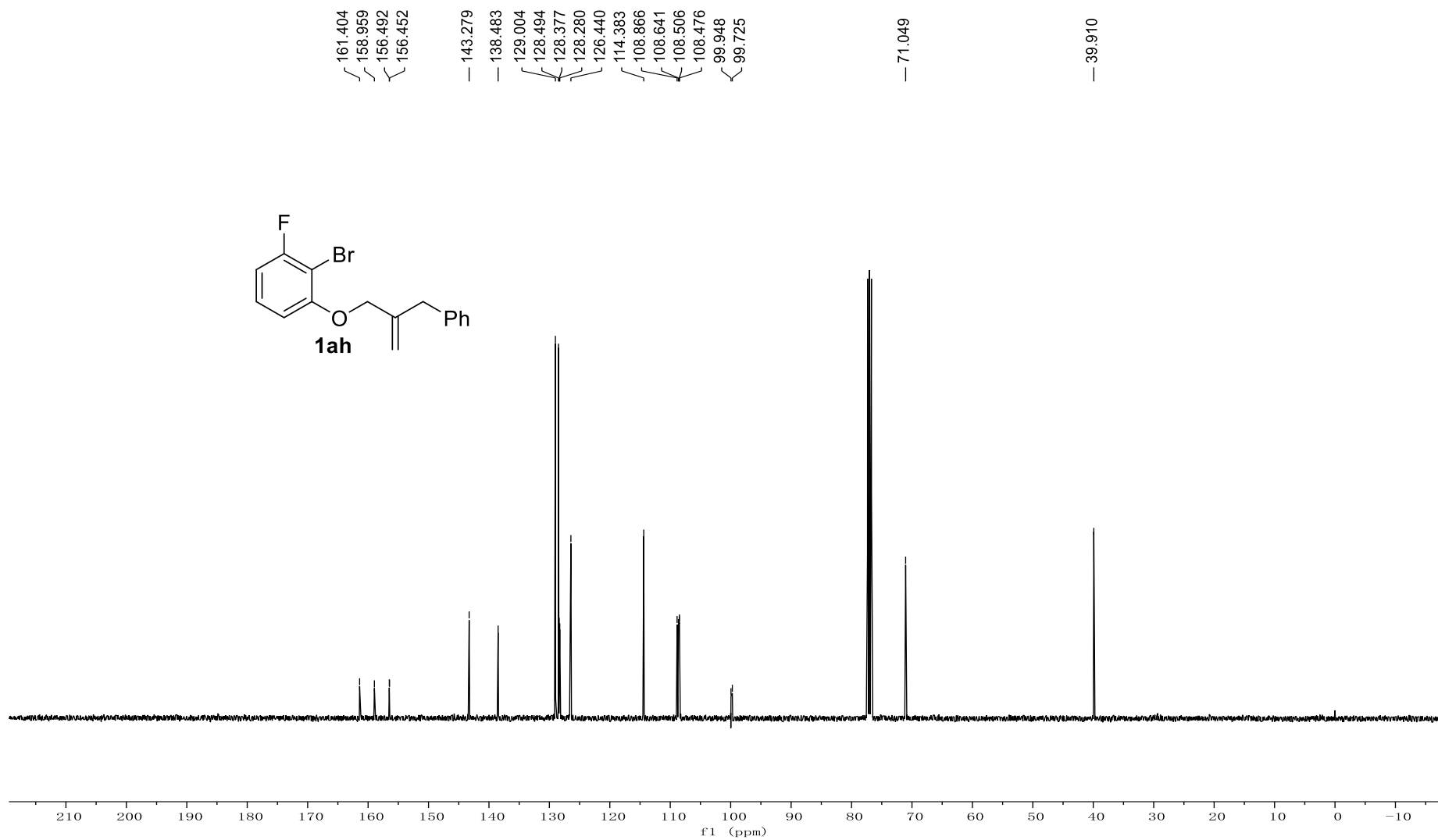
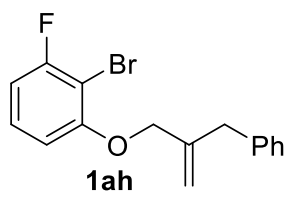
— 22.582

— 14.069

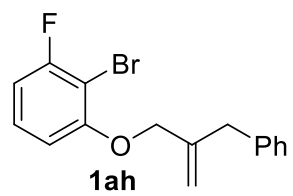
— 14.023



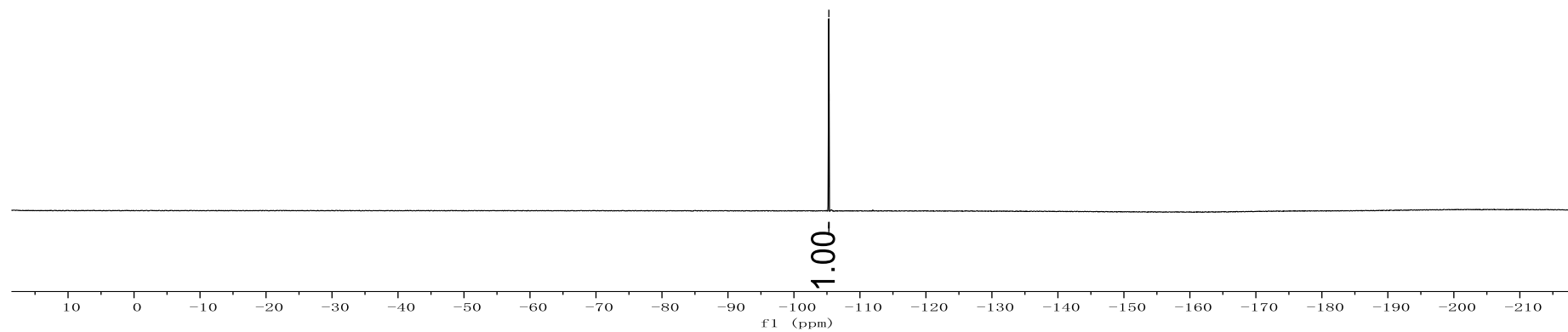




S103

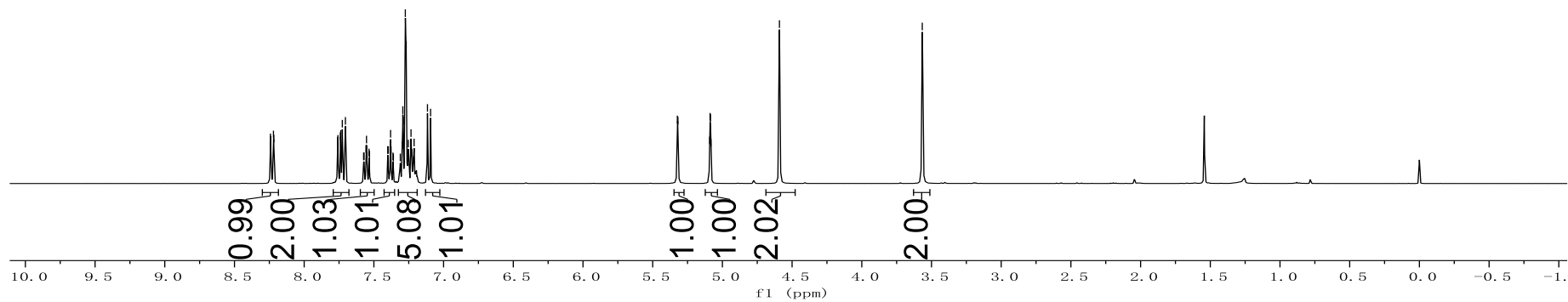
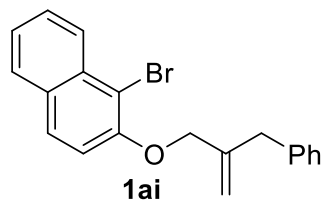


-105.271
-105.278
-105.283
-105.291
-105.294
-105.309



S104

8.242
8.239
8.220
8.218
7.761
7.758
7.740
7.738
7.727
7.704
7.574
7.571
7.557
7.553
7.549
7.535
7.532
7.401
7.398
7.383
7.380
7.377
7.363
7.360
7.311
7.296
7.292
7.290
7.274
7.268
7.253
7.234
7.228
7.218
7.211
7.116
7.093
5.323
5.319
5.091
5.088
5.085
5.082
4.591
3.566

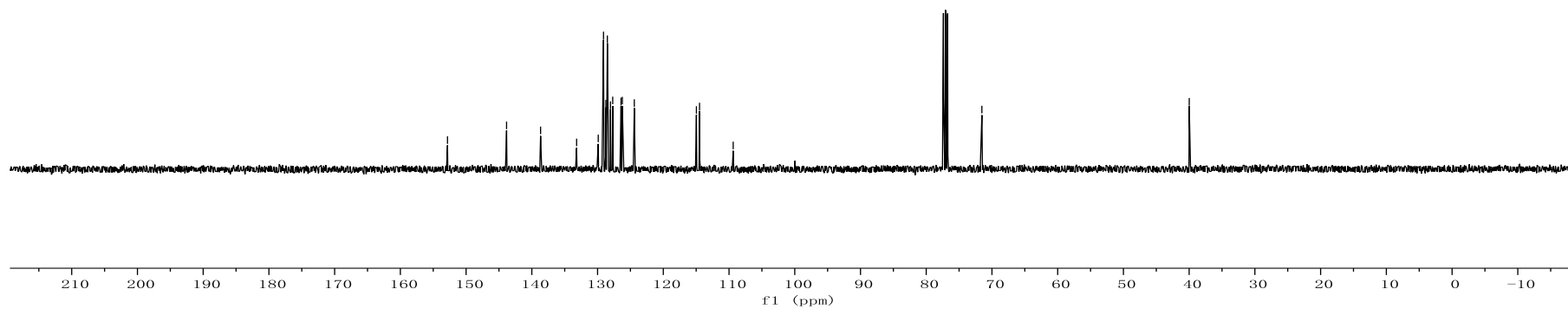
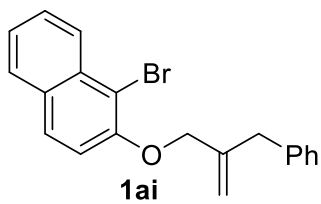


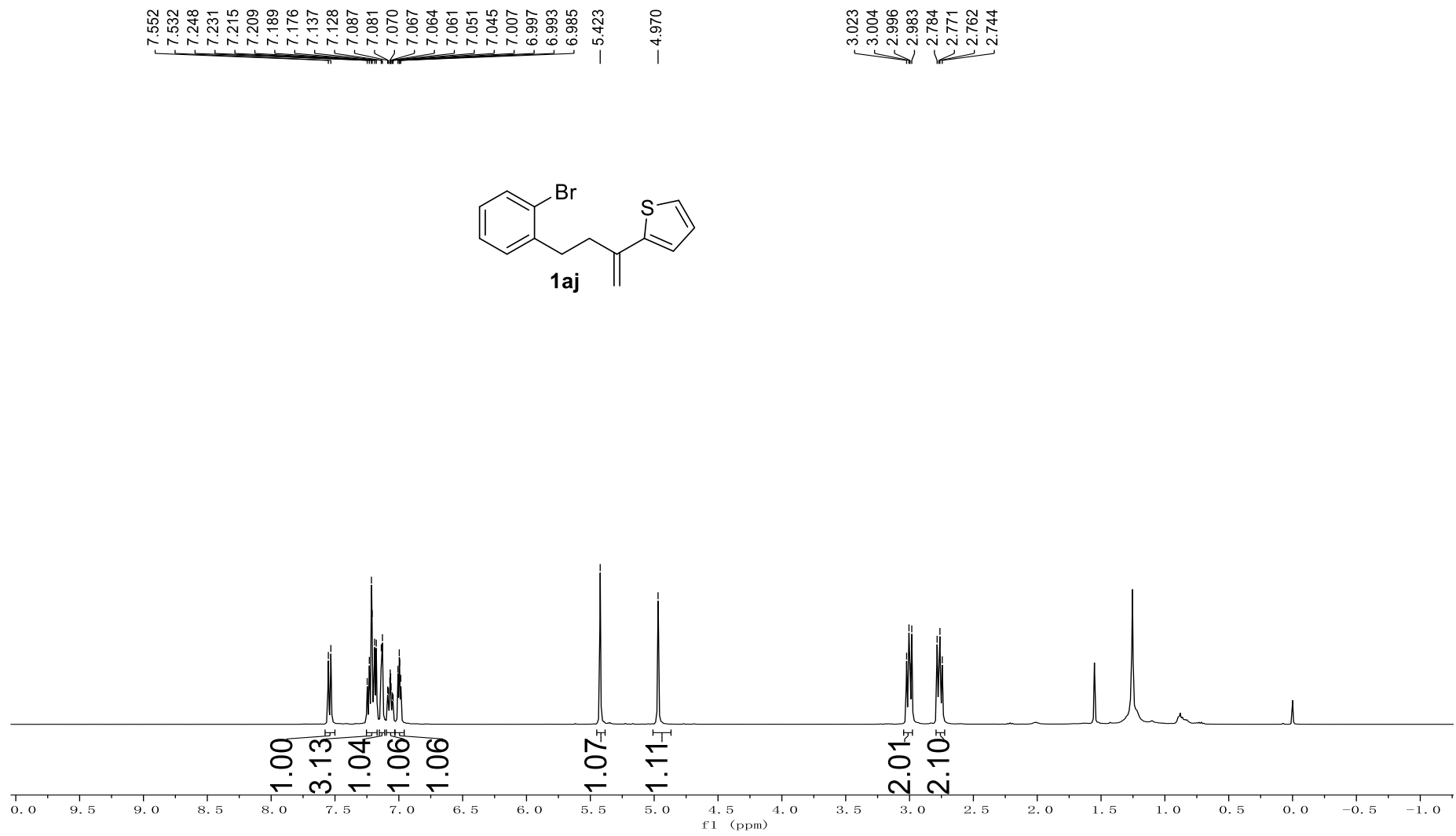
S105

152.830
143.844
138.668
133.188
129.897
129.096
128.736
128.509
128.037
127.696
126.427
126.230
124.411
114.963
114.486
109.366

— 71.531

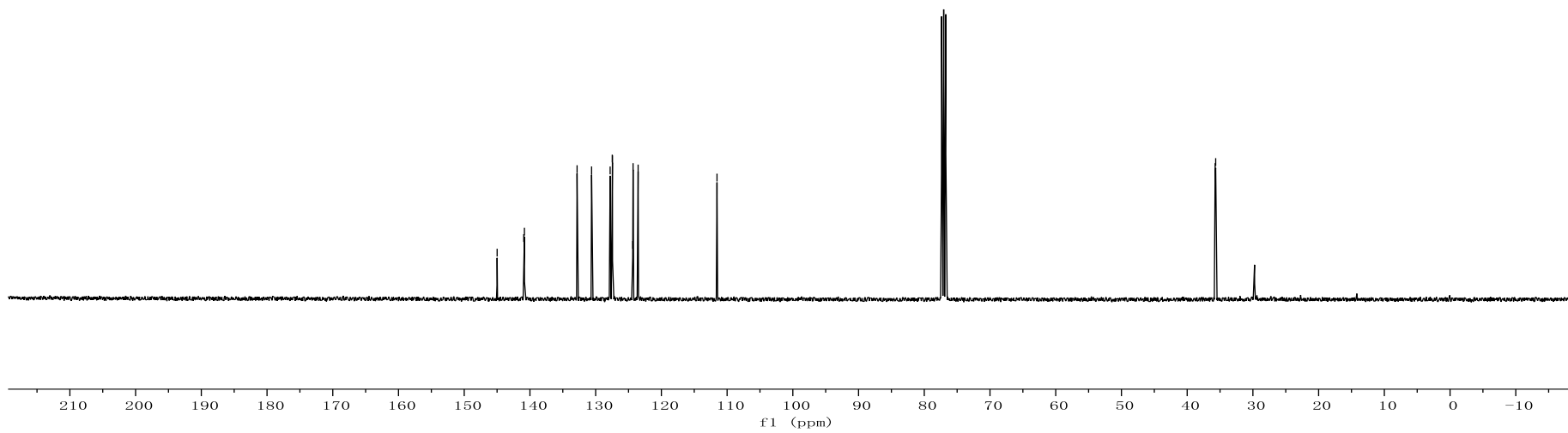
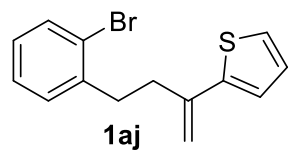
— 39.986

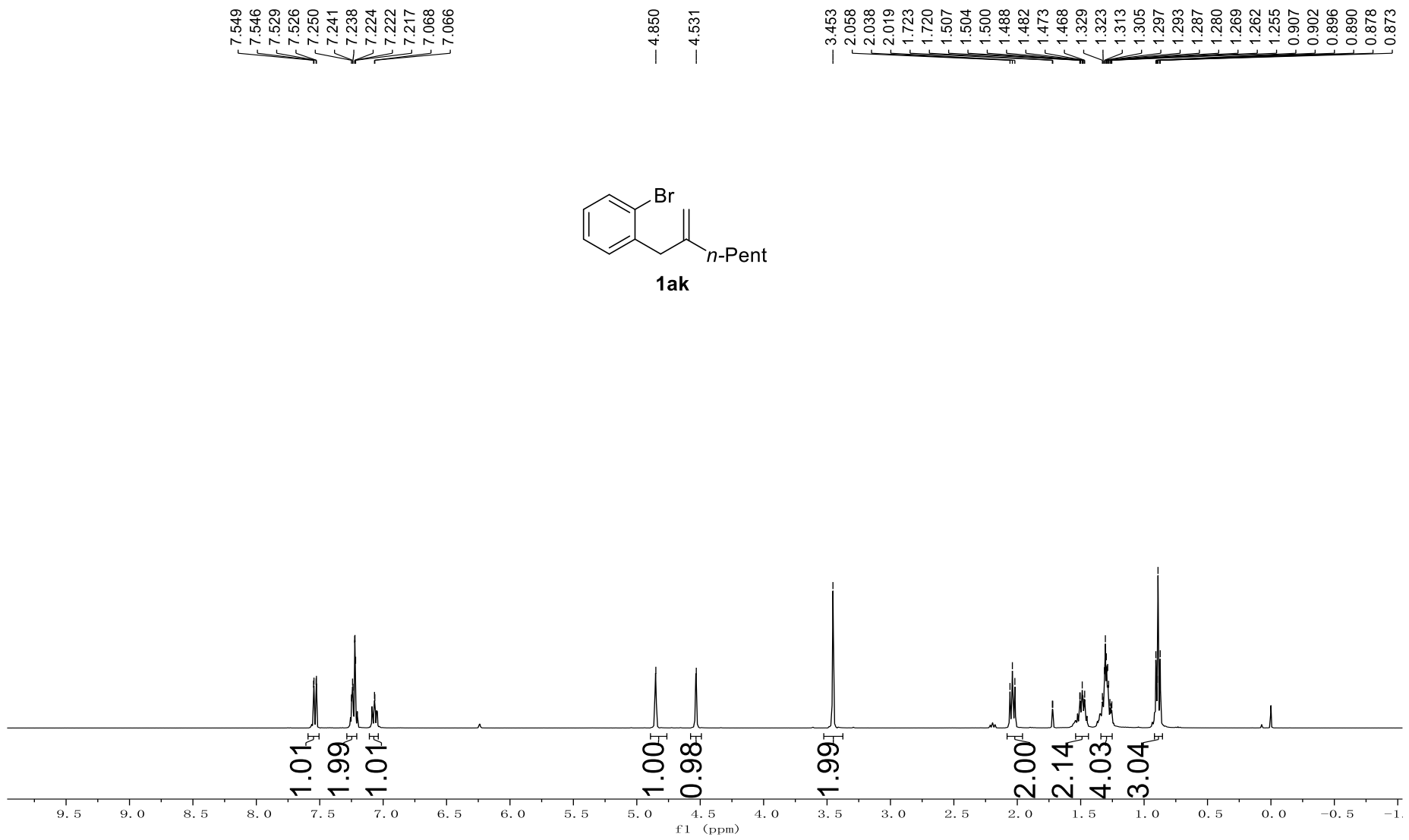




144.991
140.943
140.839
132.828
130.619
127.795
127.472
127.445
124.360
124.308
123.540
111.536

35.744
35.661



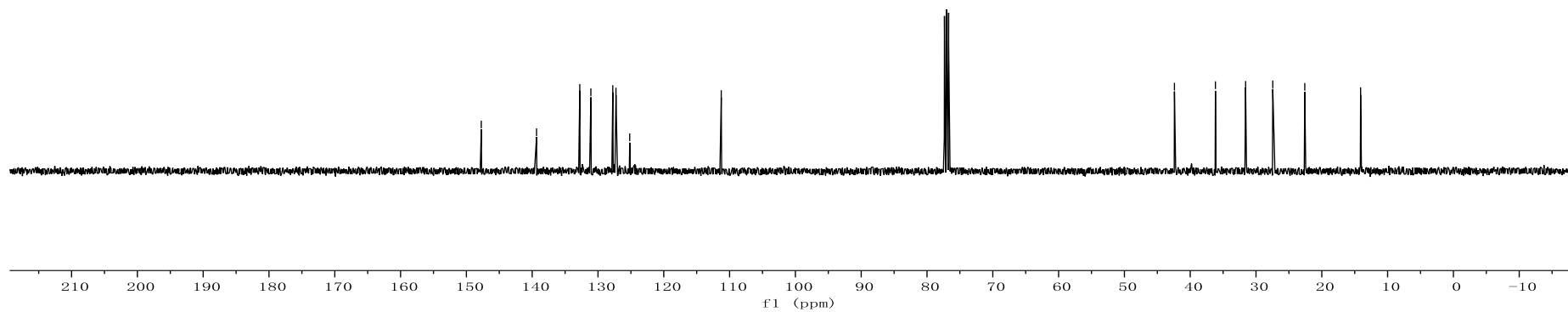
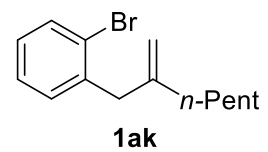


— 147.738
/ 139.337
/ 132.767
/ 131.081
/ 127.752
/ 127.267
/ 125.176

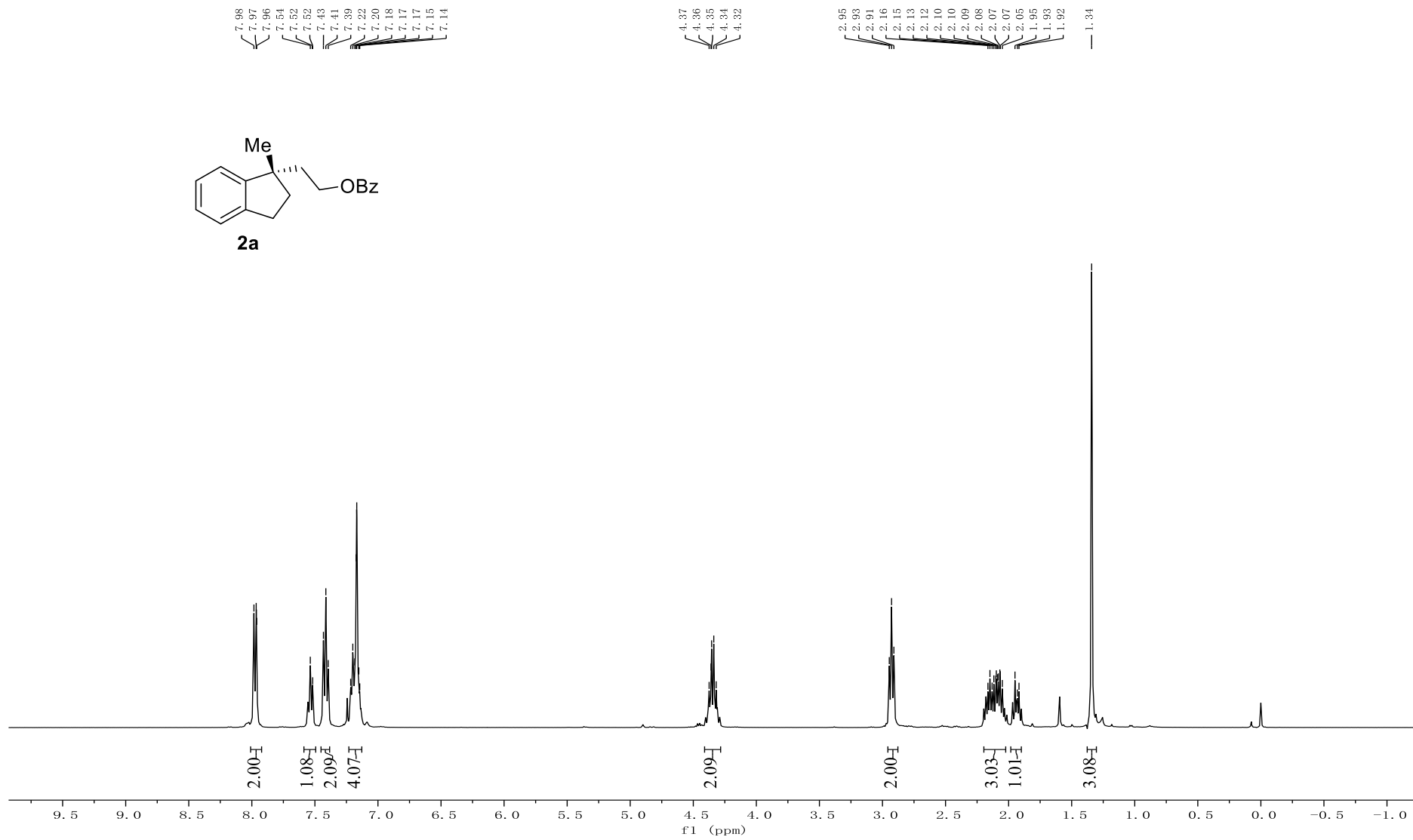
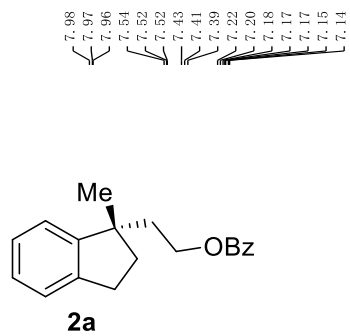
— 111.268

/ 42.397
/ 36.166
/ 31.580
/ 27.450
/ 22.589

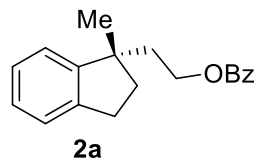
— 14.104



S110



S111

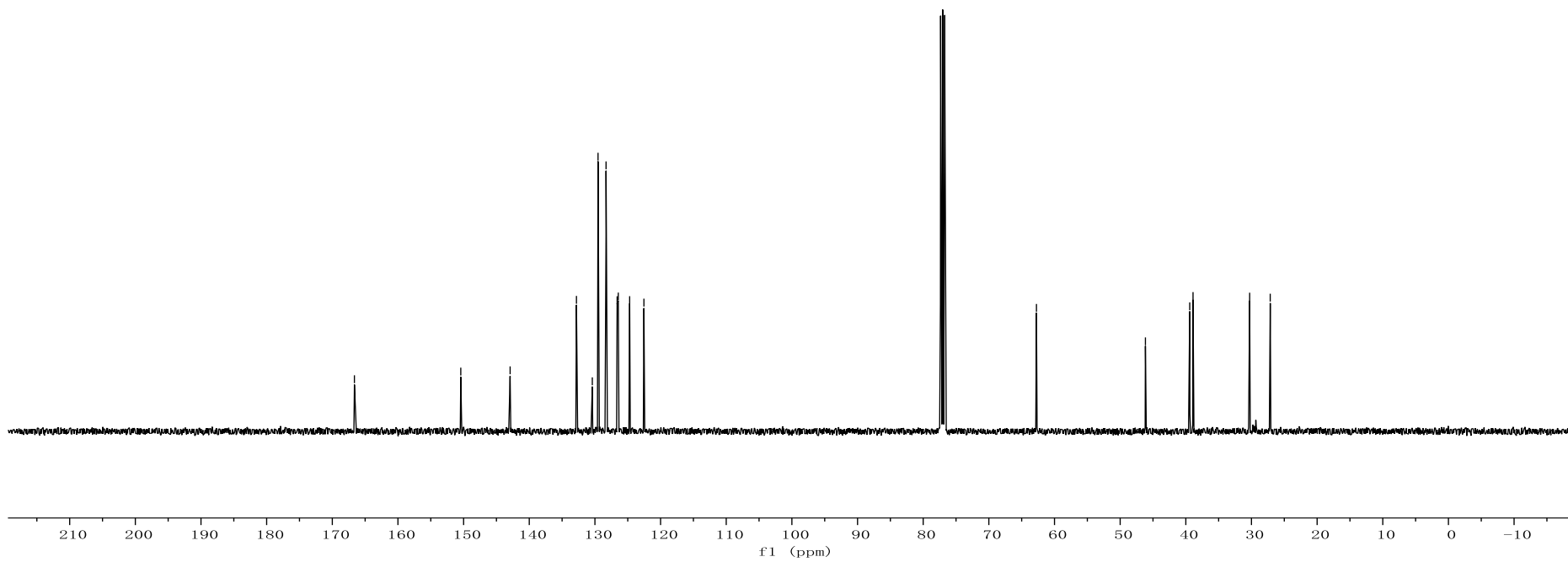


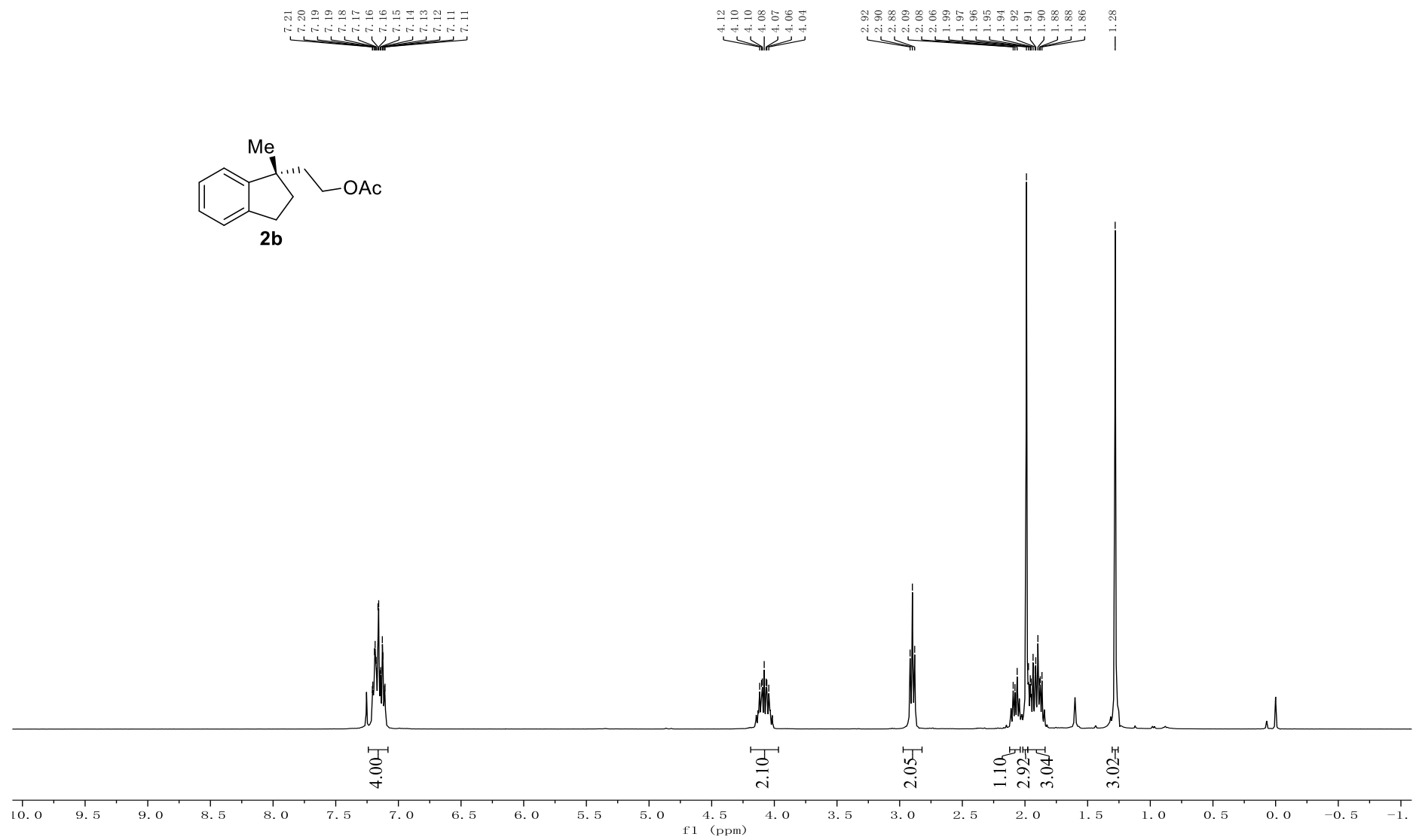
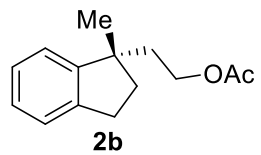
— 166.631
— 150.432
— 142.916
— 132.813
— 130.396
— 129.526
— 128.303
— 126.616
— 126.442
— 124.709
— 122.536

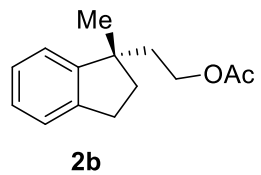
— 62.748

— 46.154
— 39.403
— 38.901

— 30.277
— 27.143







— 171.095

— 150.343

— 142.871

∩ 126.584

∩ 126.369

∩ 124.660

∩ 122.487

— 62.186

— 46.018

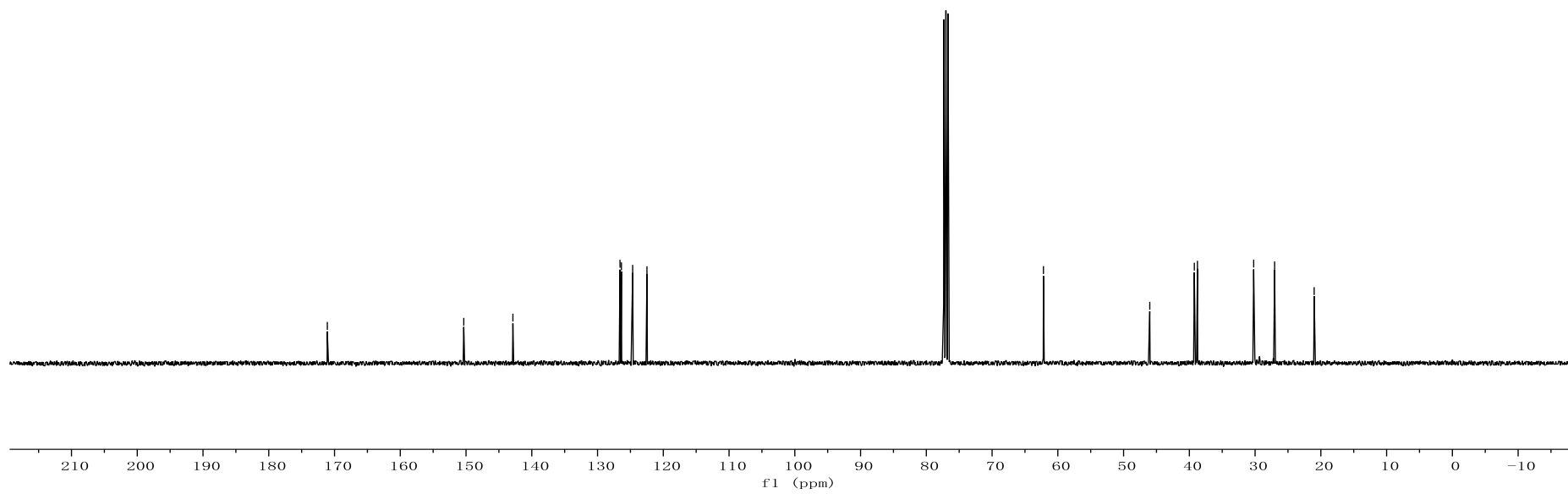
∩ 39.243

∩ 38.770

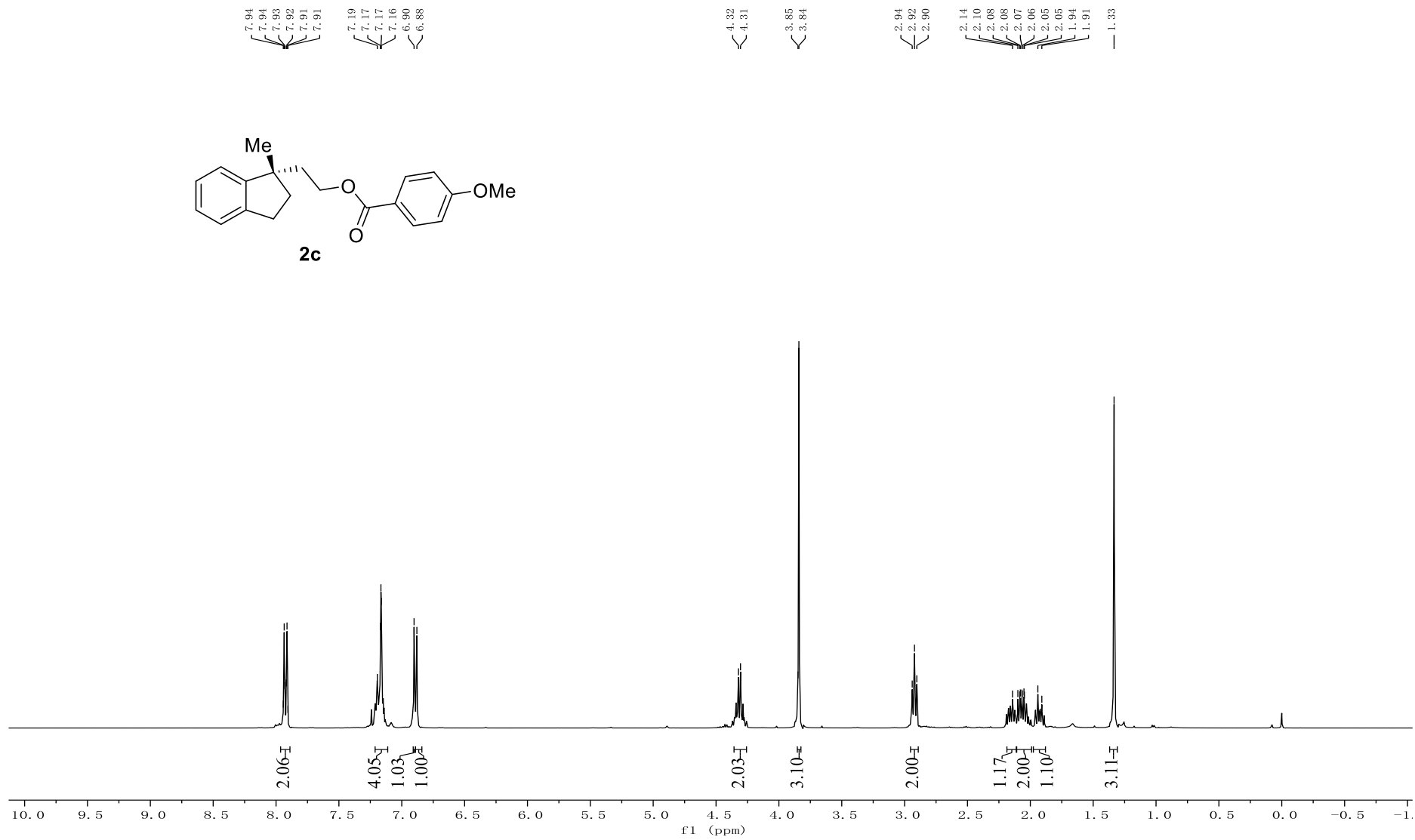
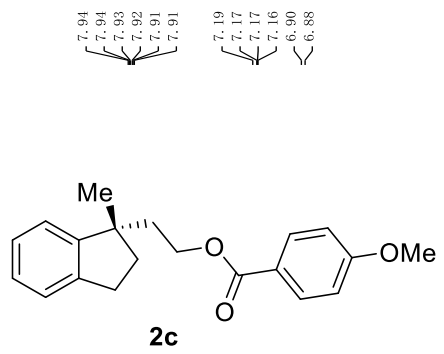
∩ 30.214

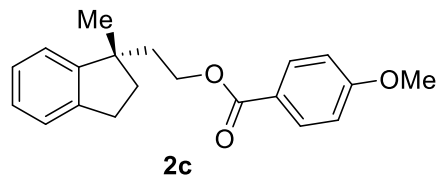
∩ 27.033

∩ 21.015



S114





— 166.386
— 163.280

— 150.522

— 142.925

— 131.543

— 126.590

— 126.431

— 124.698

— 122.858

— 122.552

— 113.563

— 62.438

— 55.414

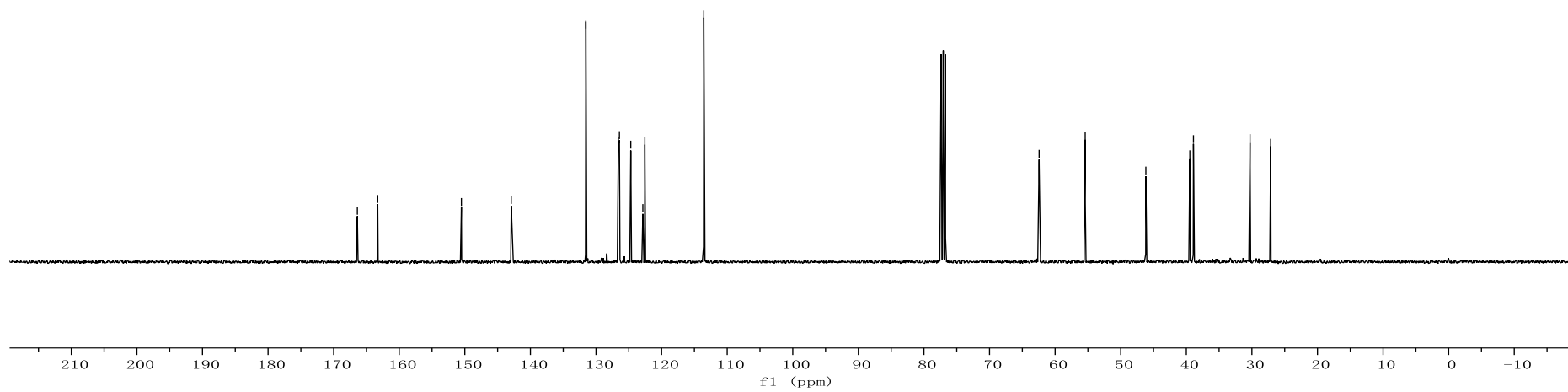
— 46.168

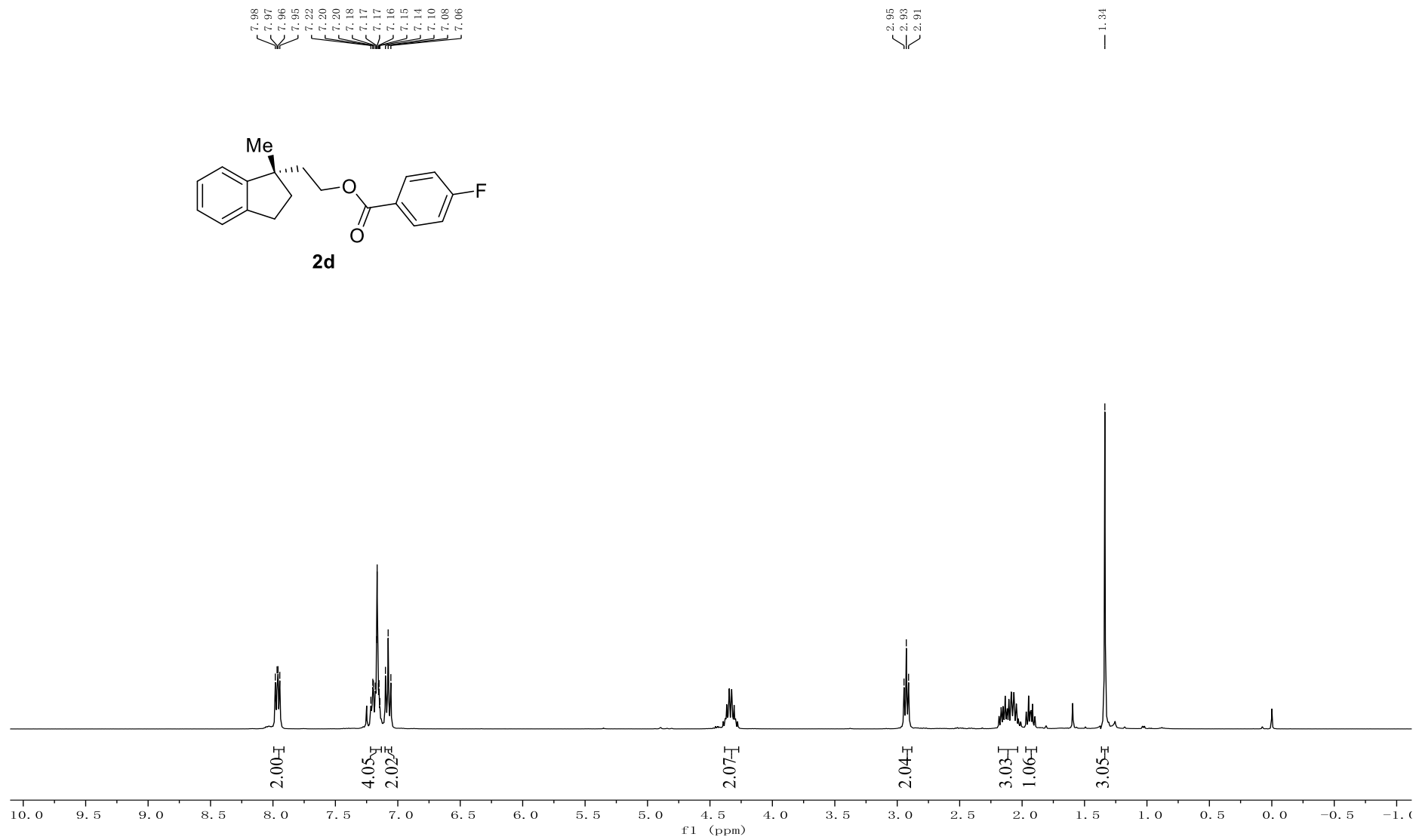
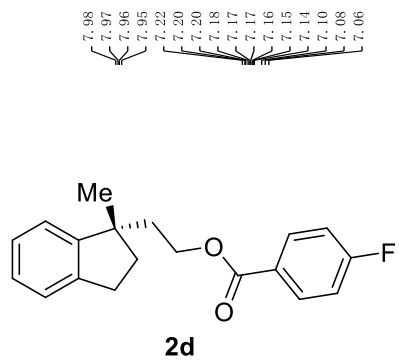
— 39.462

— 38.910

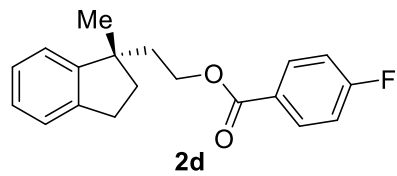
— 30.287

— 27.138





S117



166.955
165.647
164.435

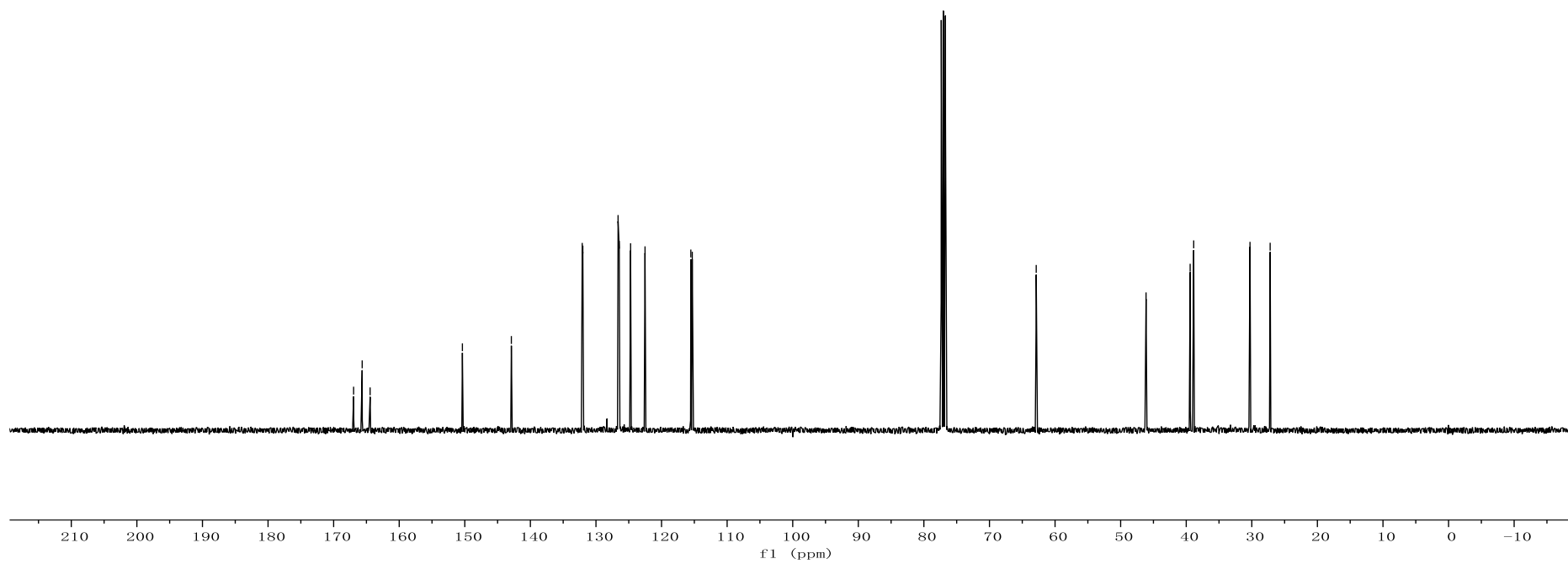
150.365
142.900

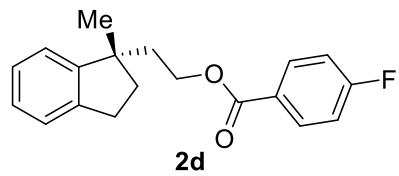
132.095
132.002
126.629
126.448
124.721
122.520
115.535
115.317

62.871

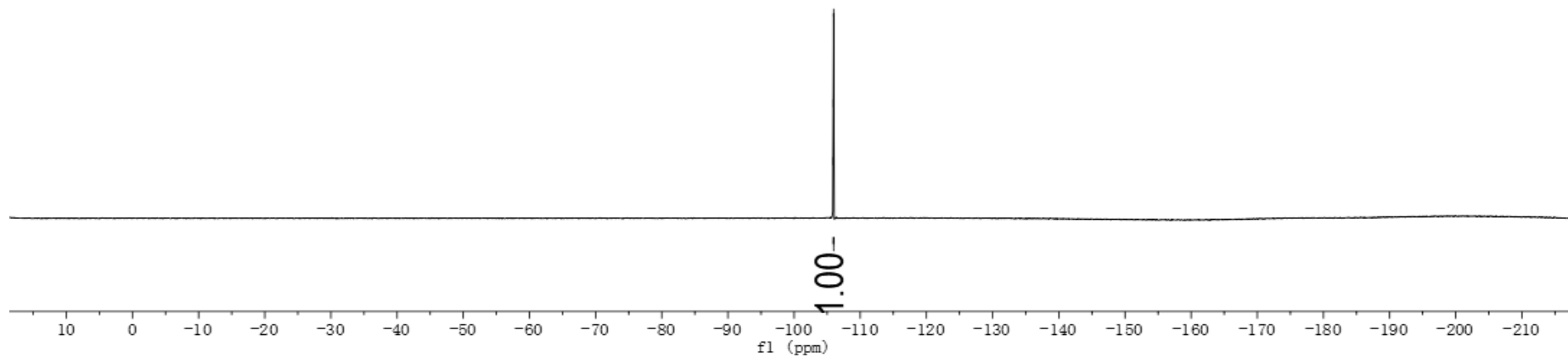
46.126
39.401
38.859

30.277
27.201

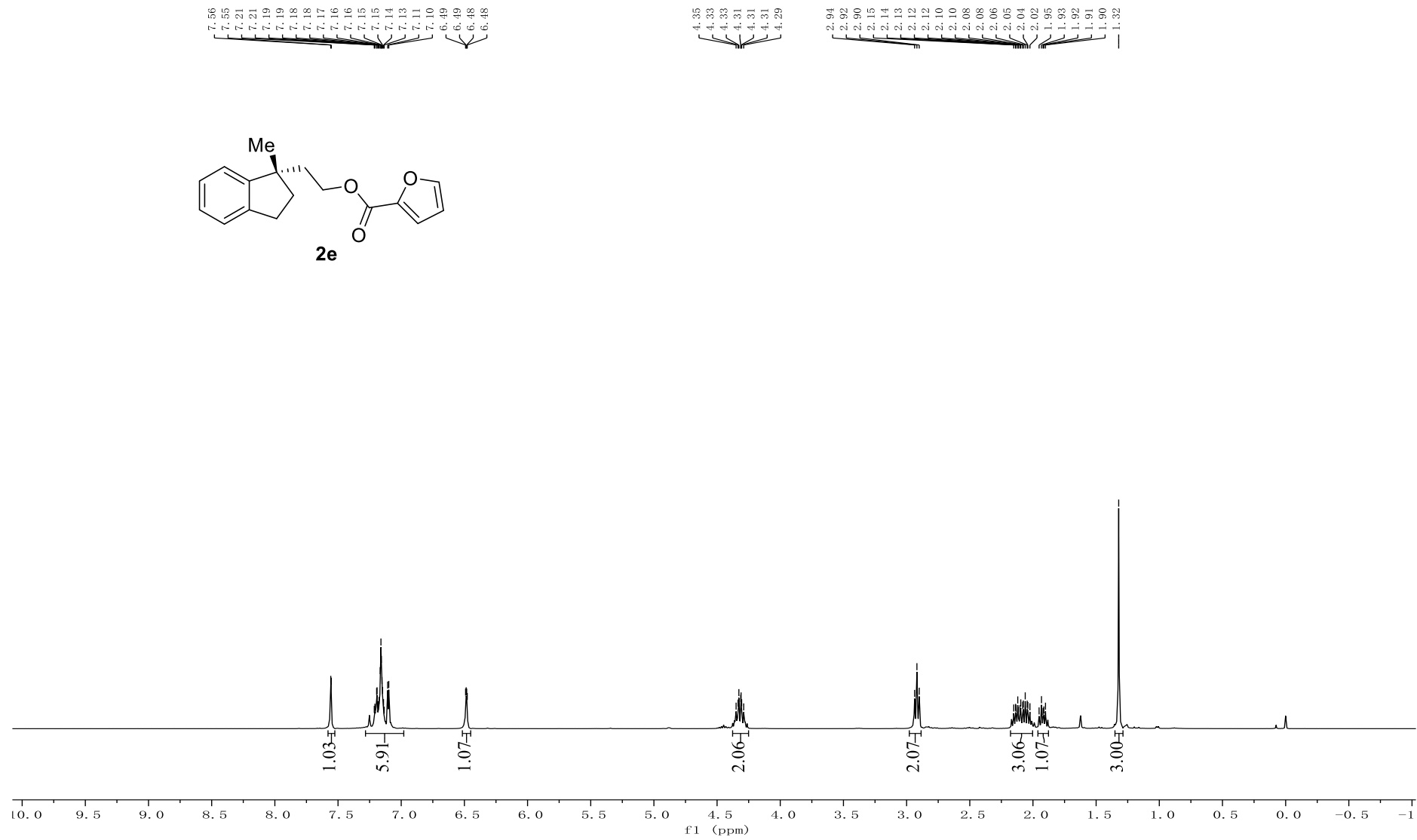
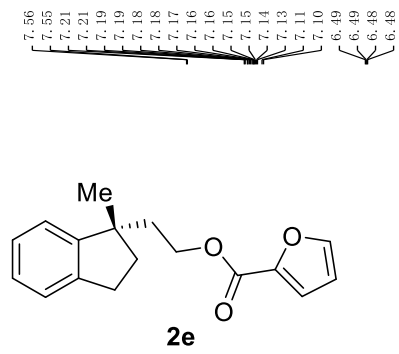




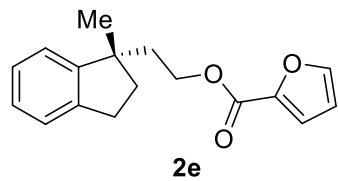
105.928
105.951
105.966
105.980
105.988
106.002



S119



S120



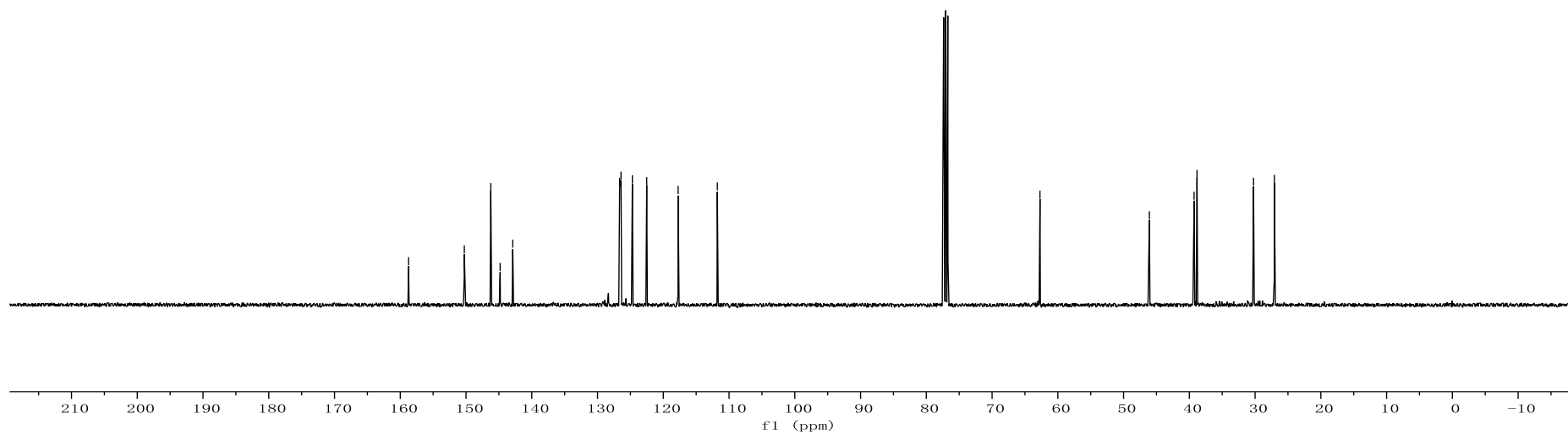
— 158.738
/ 150.261
/ 146.231
— 144.812
/ 142.893

126.641
126.430
124.710
122.523
117.744
111.781

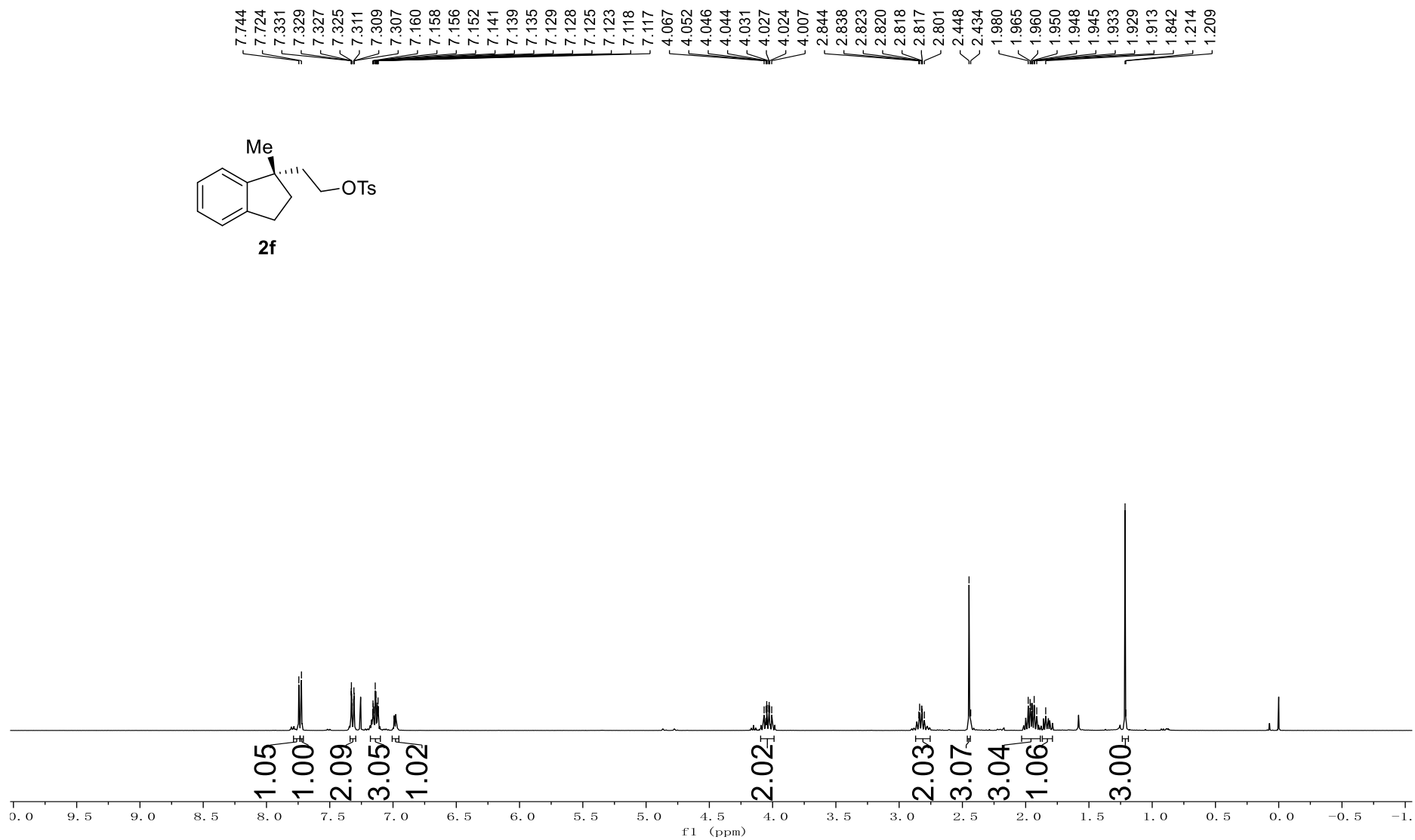
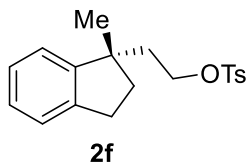
— 62.716

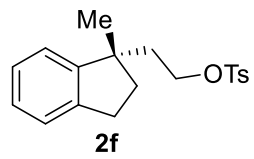
— 46.078
/ 39.278
/ 38.832

— 30.241
— 27.070



S121

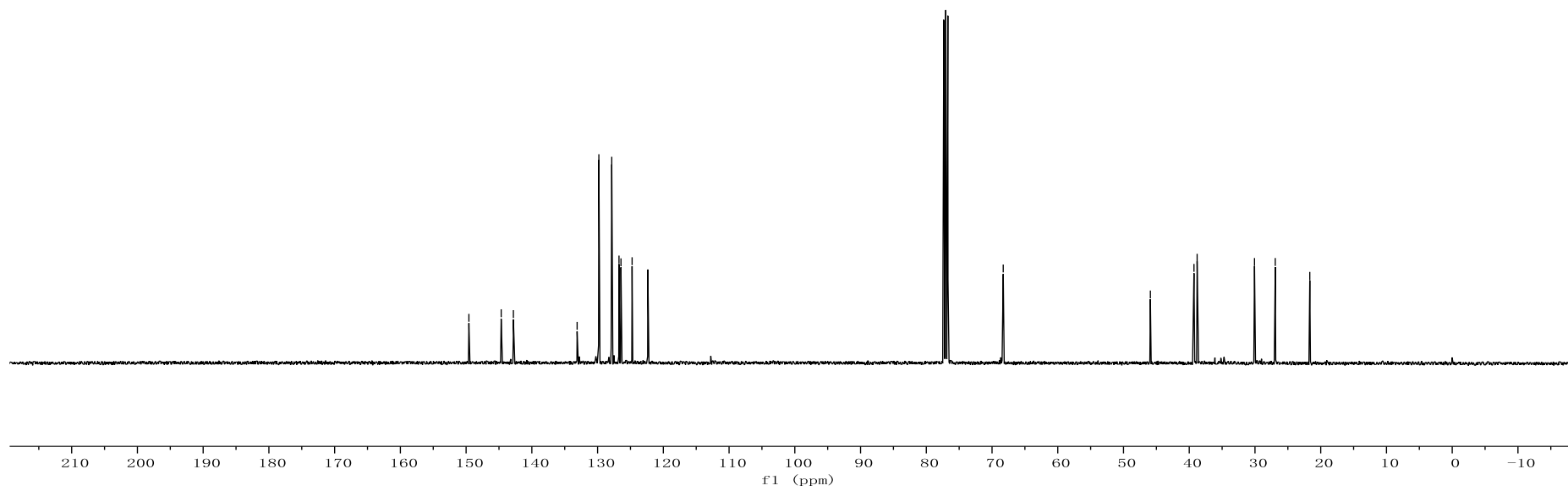




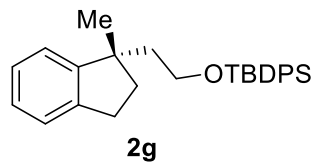
— 149.576
/ 144.664
— 142.808
/ 133.112
/ 129.807
/ 127.844
/ 126.744
/ 126.444
/ 124.749

— 68.297

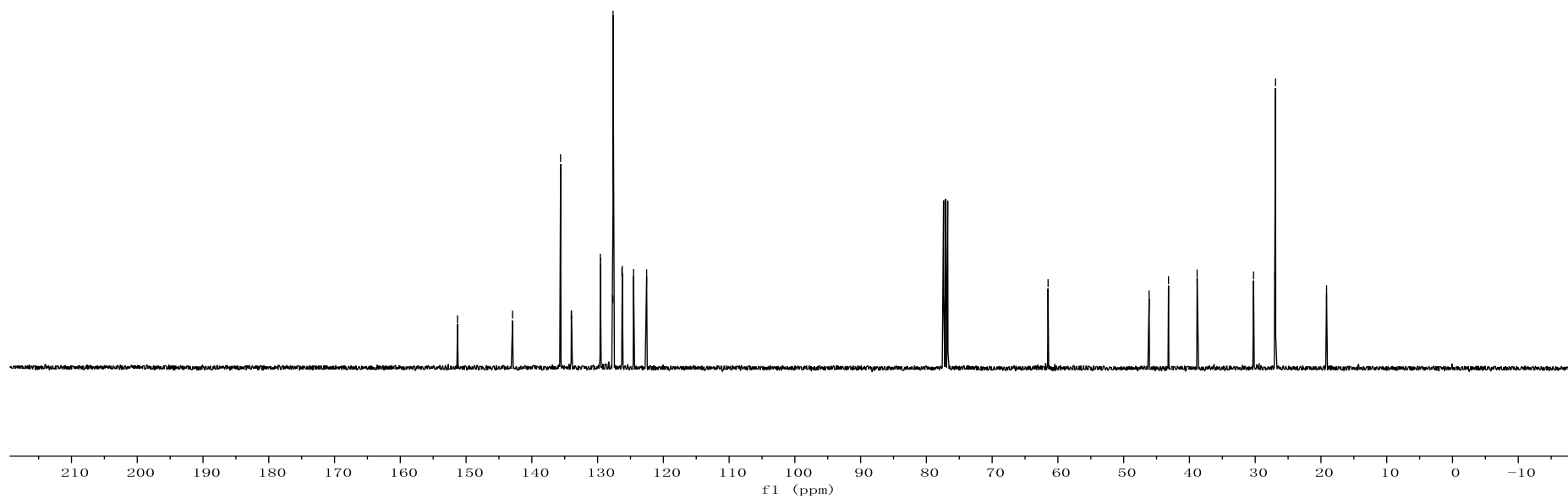
— 45.914
/ 39.281
/ 38.801
/ 30.073
/ 26.915
/ 21.663

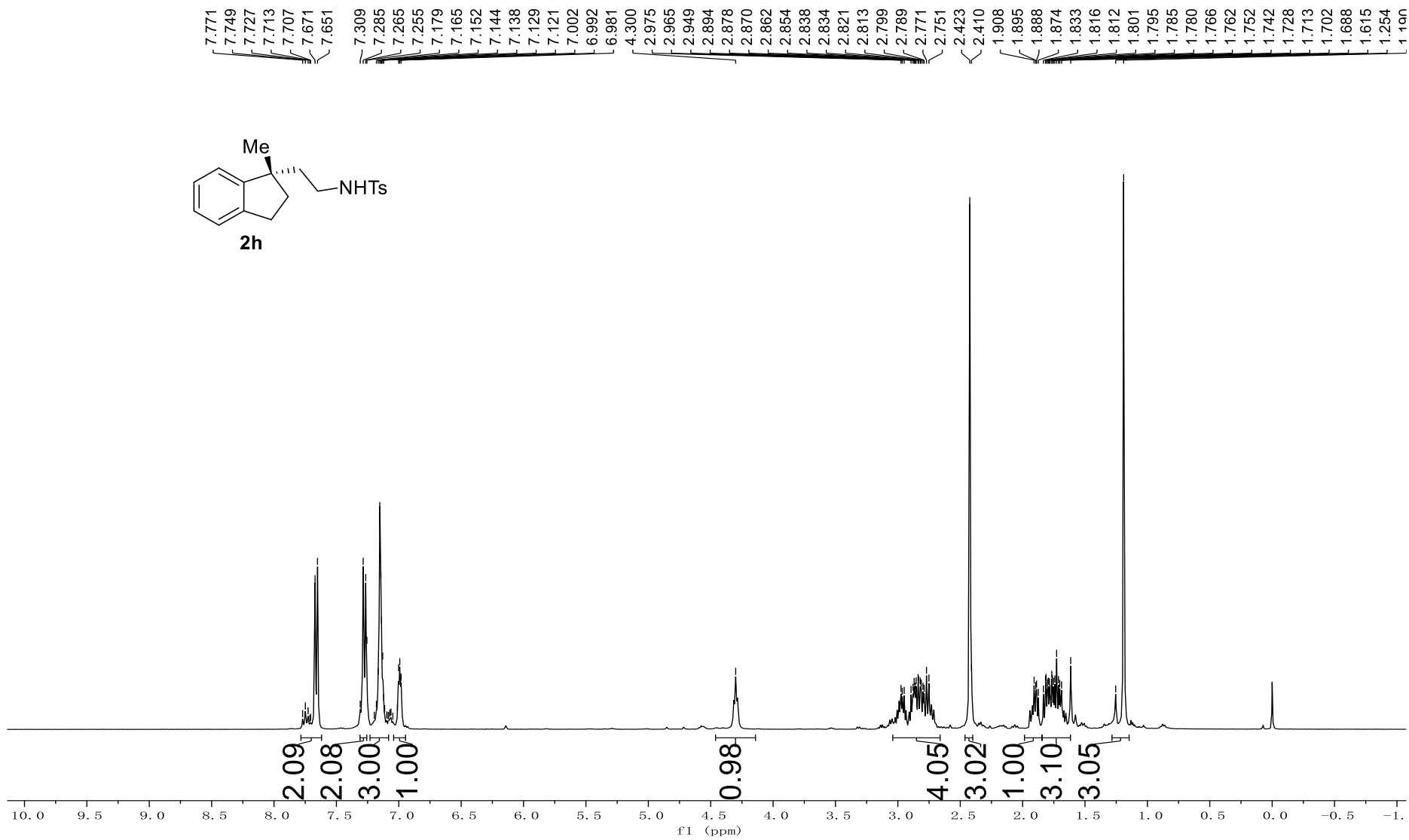
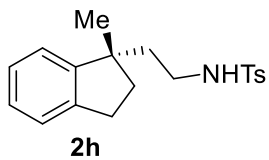


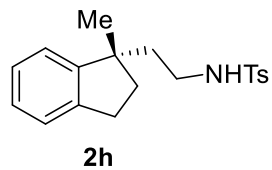
S123



- 151.300
- 142.931
- 135.630
- 135.598
- 133.992
- 133.981
- 129.587
- 129.567
- 127.675
- 127.650
- 126.298
- 126.249
- 124.532
- 122.542
- 61.498
- 46.134
- 43.183
- 38.833
- 30.250
- 27.012
- 26.906
- 19.152

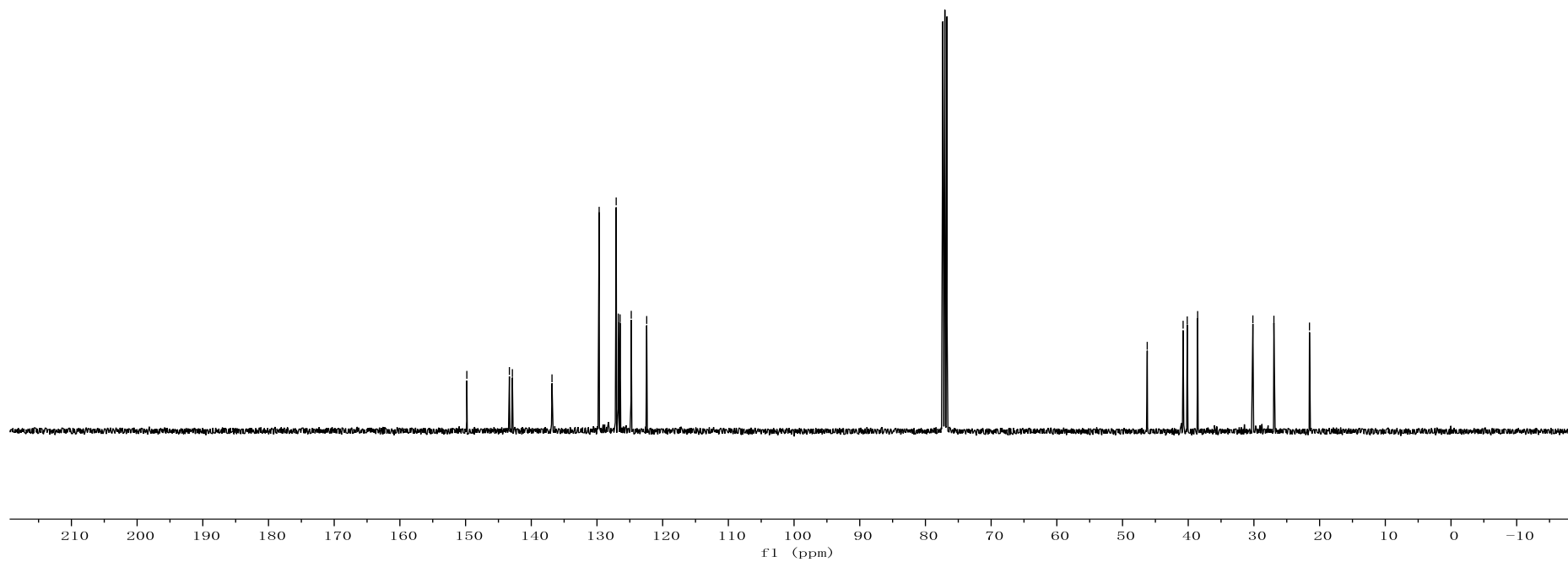


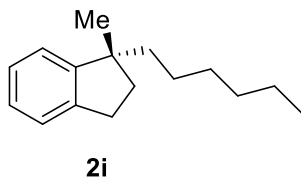




149.812
143.333
142.876
136.846
129.670
127.076
126.753
126.481
124.783
122.427

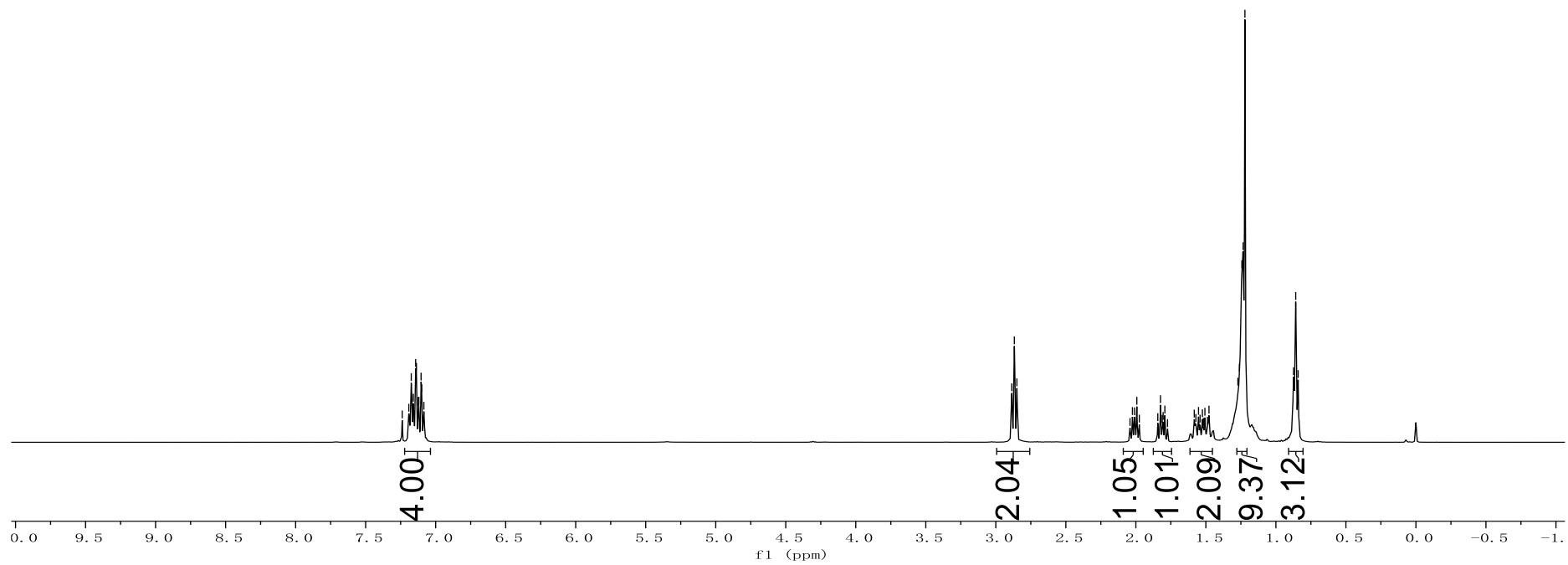
46.240
40.776
40.147
38.564
30.157
26.957
21.544

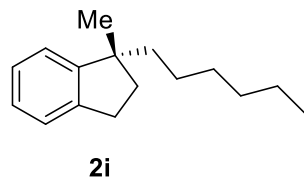




7.239
7.192
7.174
7.159
7.143
7.137
7.124
7.120
7.104
7.100
7.084

2.886
2.868
2.849
2.042
2.024
2.009
1.993
1.975
1.843
1.824
1.812
1.805
1.793
1.774
1.583
1.571
1.552
1.541
1.525
1.517
1.507
1.489
1.478
1.271
1.261
1.243
1.234
1.221
0.874
0.858
0.841





— 151.829

— 143.196

∟ 126.121

∟ 126.087

∟ 124.451

∟ 122.648

∟ 47.355

∟ 41.471

∟ 38.588

∟ 31.898

∟ 30.307

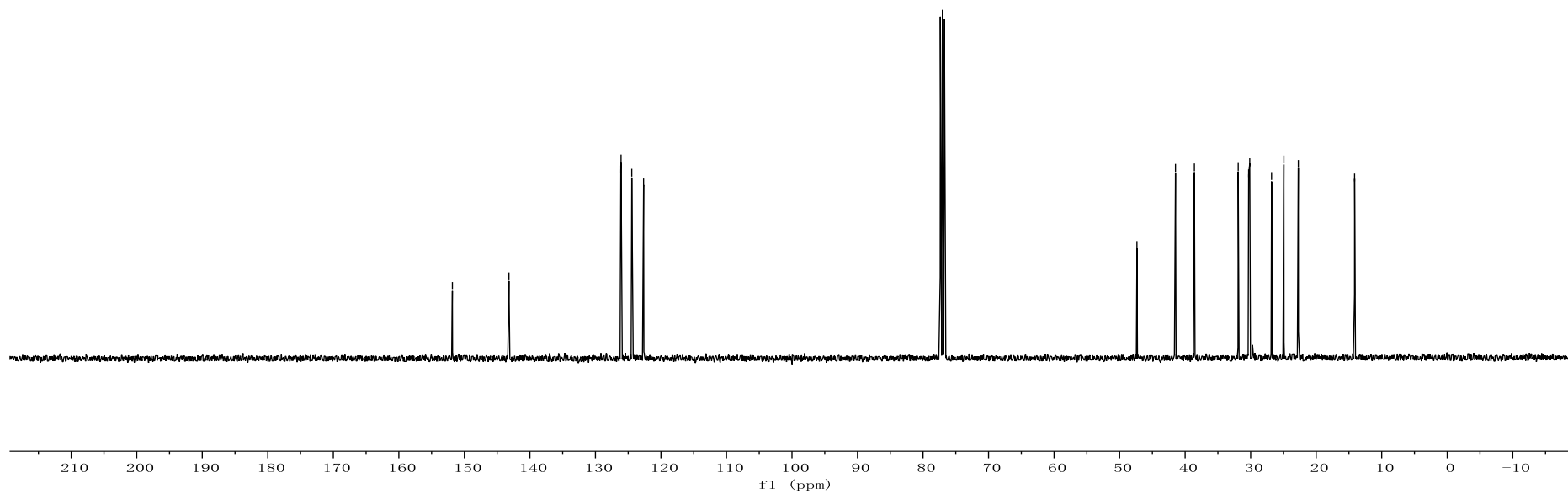
∟ 30.140

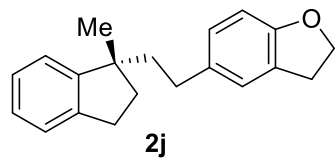
∟ 26.807

∟ 24.930

∟ 22.725

— 14.139

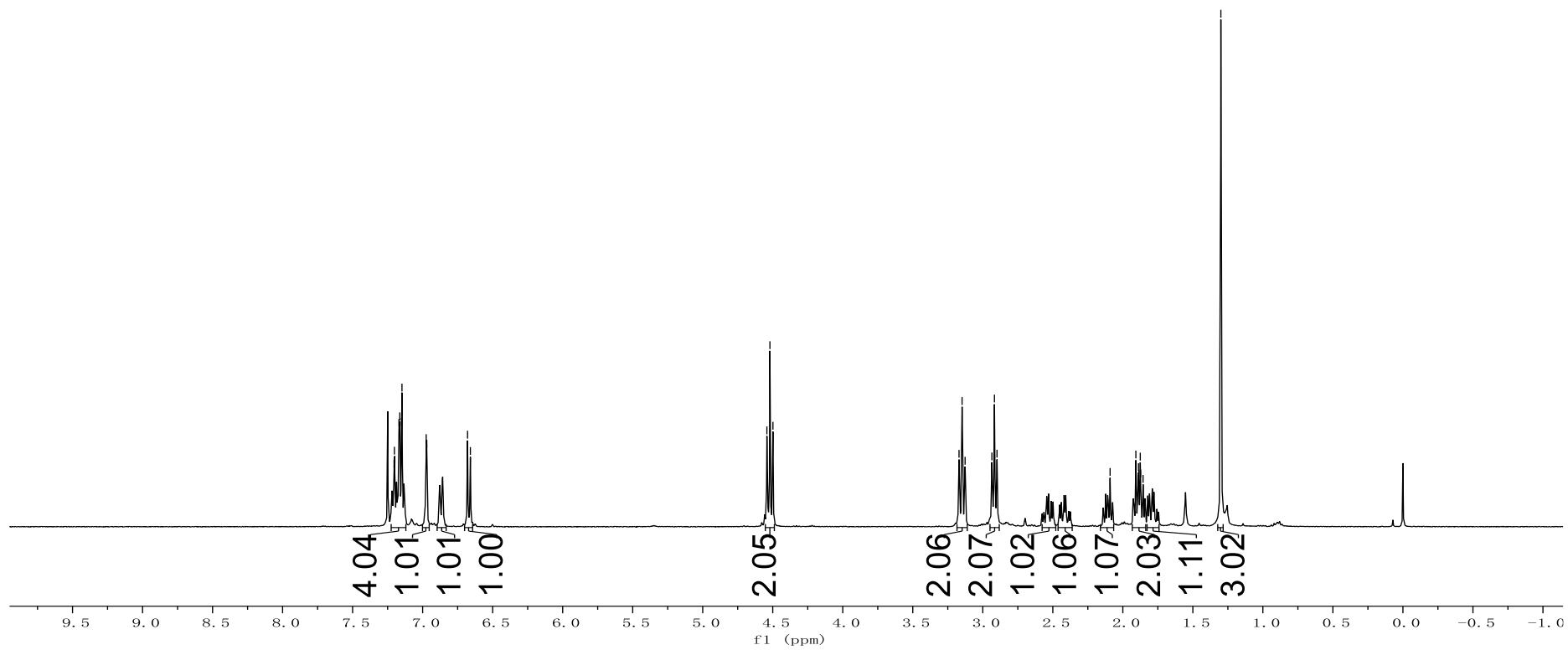




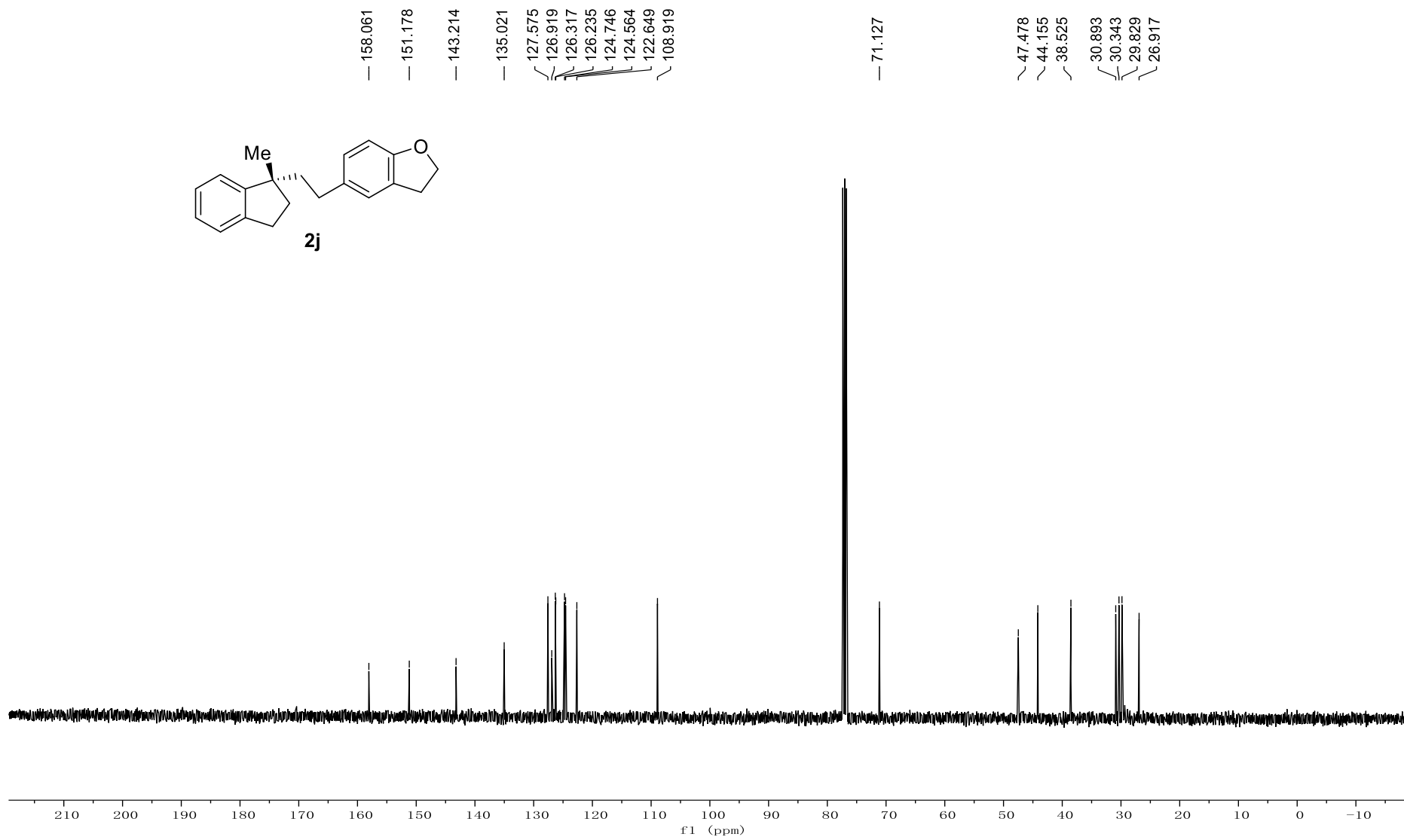
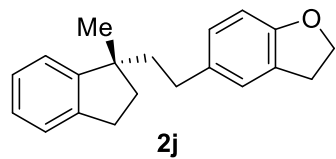
7.204
7.201
7.199
7.169
7.163
7.151
7.148
6.975
6.970
6.679
6.659

4.542
4.520
4.499

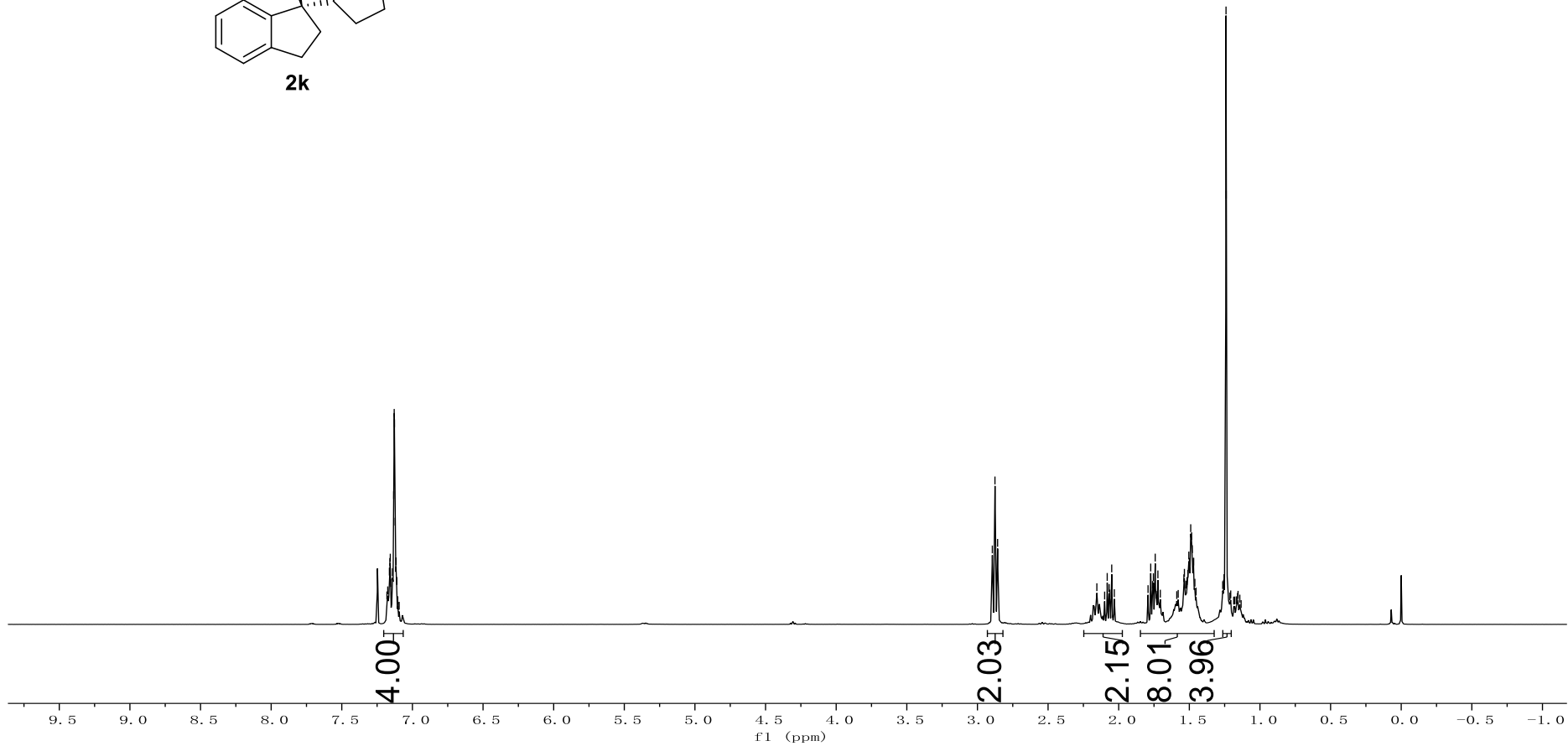
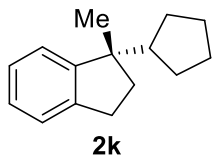
3.170
3.148
3.126
2.935
2.917
2.899
2.091
1.907
1.888
1.886
1.876
1.873
1.856
1.300



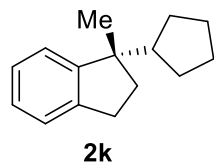
S130



7.181
7.175
7.163
7.160
7.157
7.154
7.148
7.141
7.133
7.129
7.127
7.122
7.116
7.110
7.104
7.100
7.094
2.895
2.876
2.857
2.155
2.100
2.081
2.068
2.063
2.049
2.031
1.792
1.773
1.760
1.754
1.741
1.735
1.730
1.723
1.705
1.589
1.579
1.538
1.535
1.524
1.516
1.510
1.504
1.499
1.490
1.484
1.479
1.472
1.469
1.461
1.452
1.264
1.258
1.254
1.240
1.239
1.213
1.207
1.186
1.179
1.168
1.159
1.155
1.143
1.134



S132



— 151.463

— 143.398

↙ 126.089

↘ 125.956

↙ 124.359

↘ 123.219

↙ 49.784

↘ 49.406

↙ 35.861

↘ 30.518

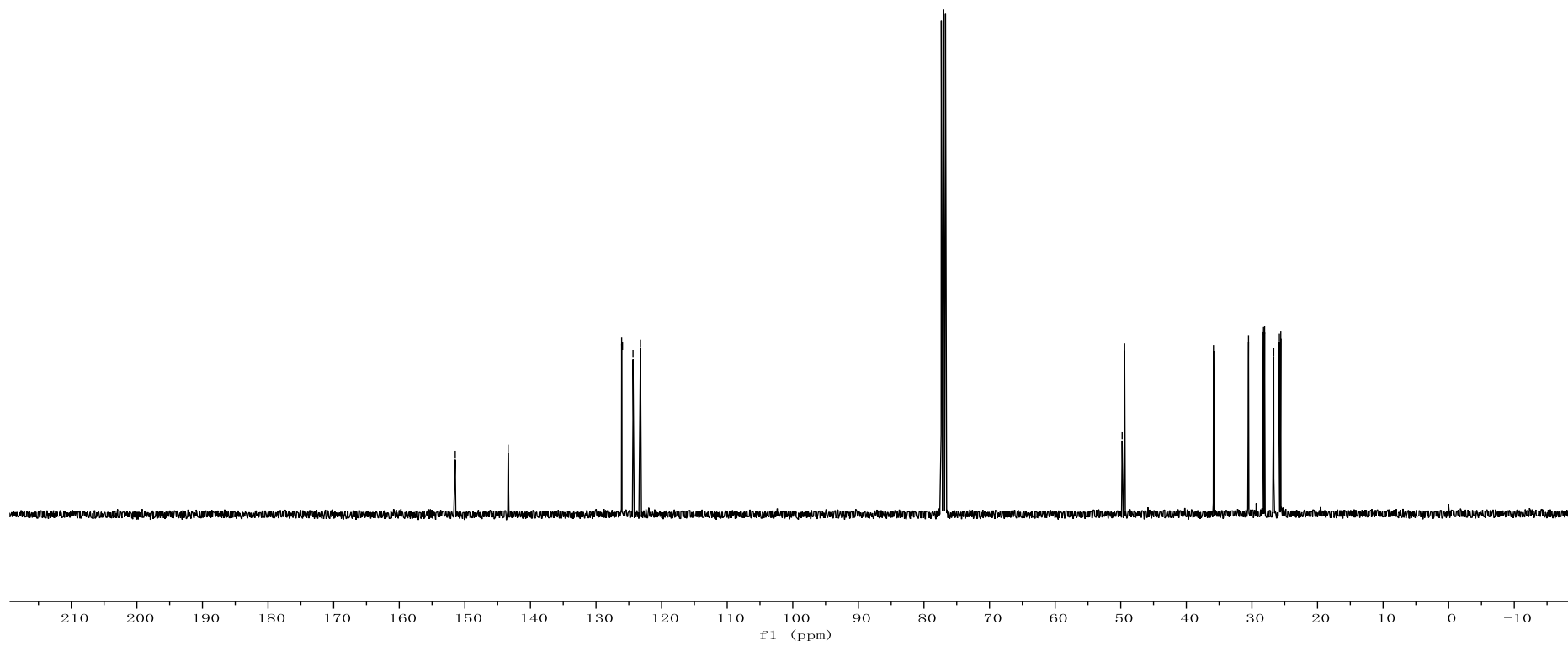
↙ 28.232

↘ 28.065

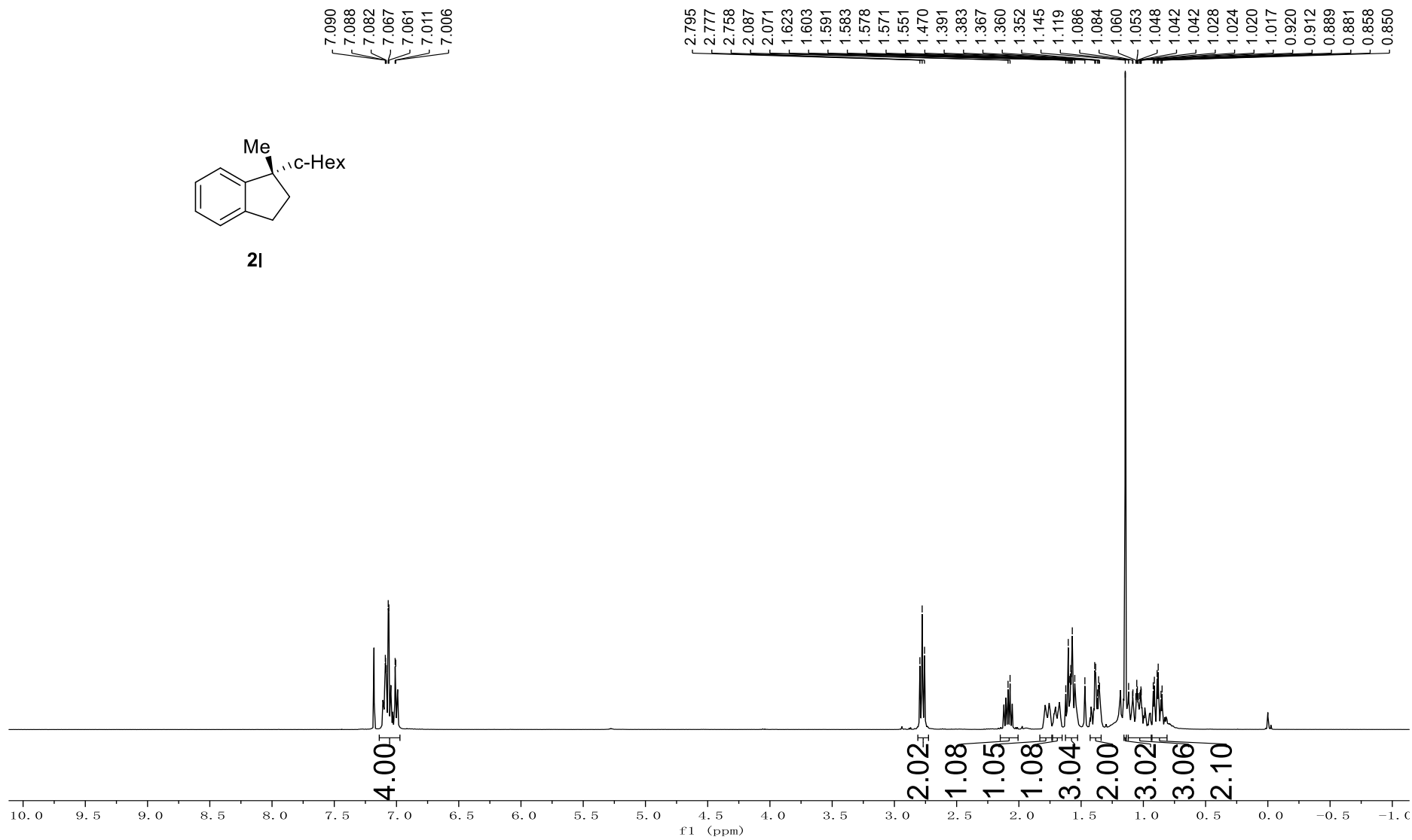
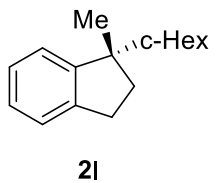
↙ 26.675

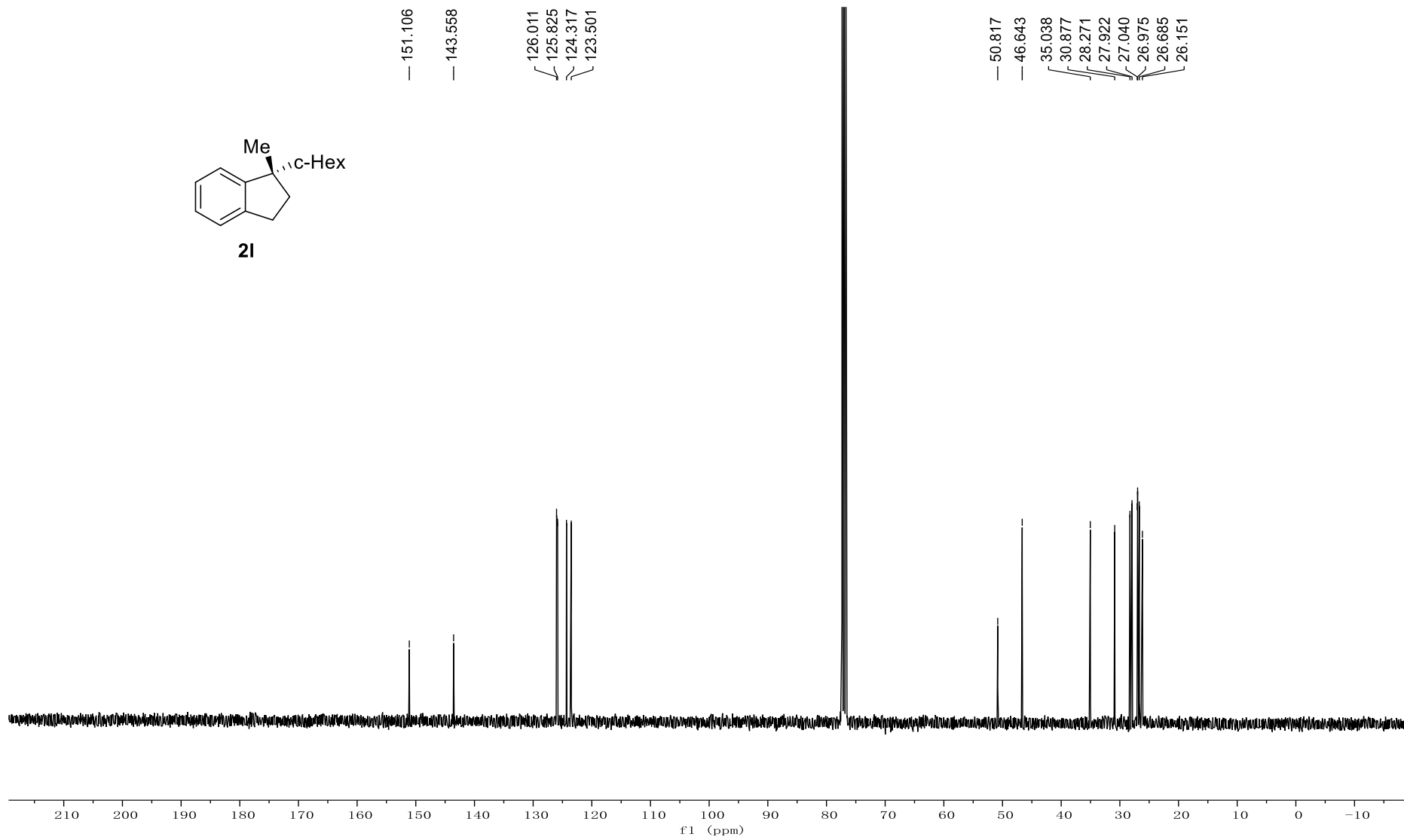
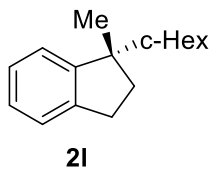
↘ 25.815

↙ 25.598

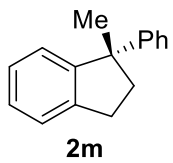


S133



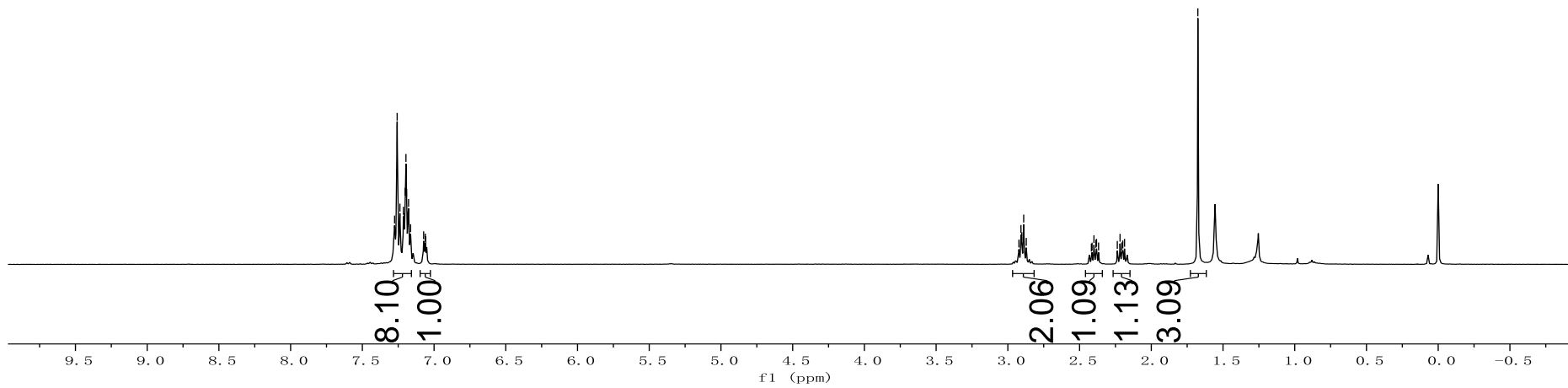


S135

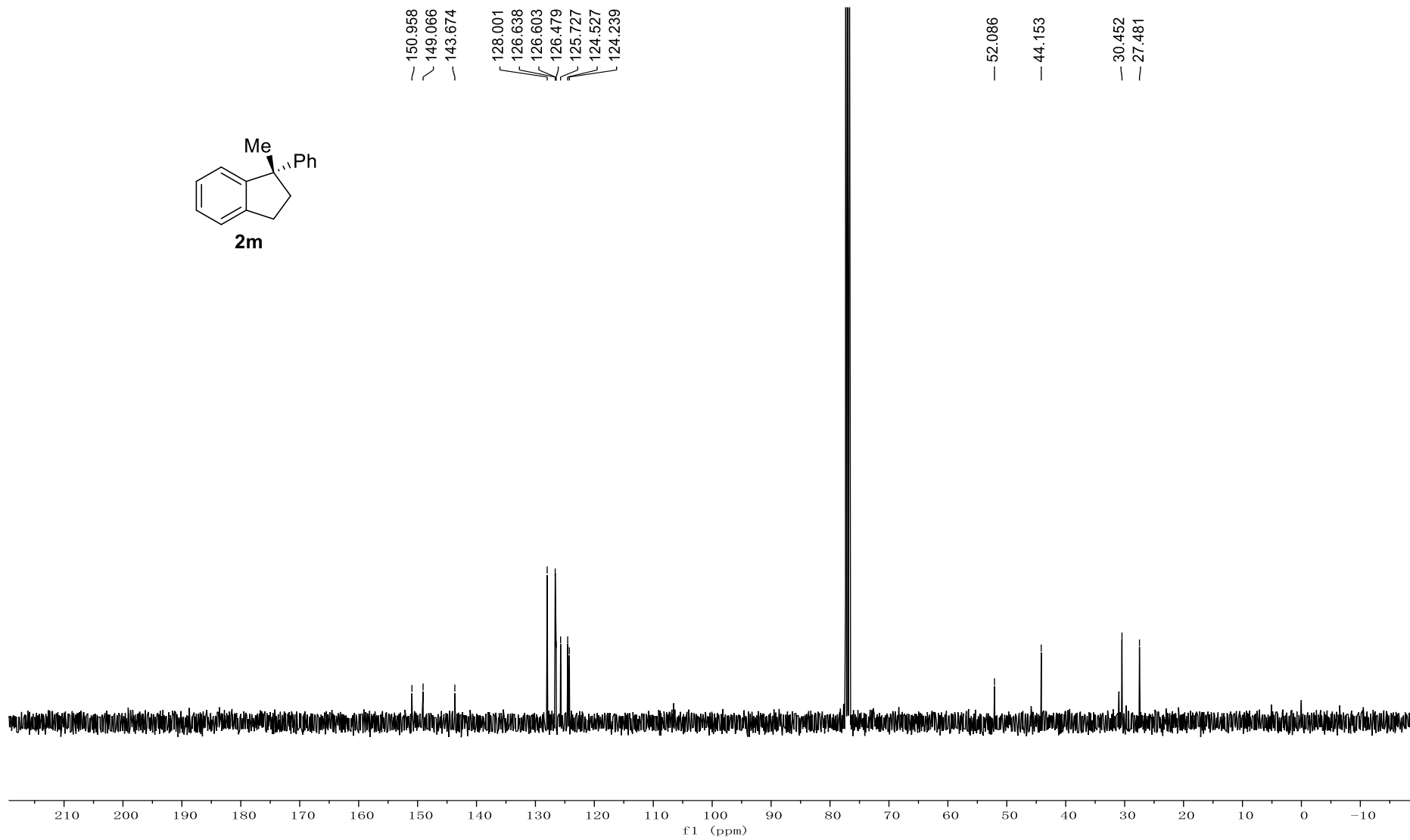
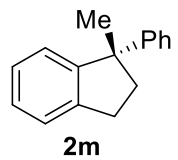


7.275
7.257
7.244
7.238
7.214
7.209
7.202
7.196
7.191
7.183
7.178
7.168
7.163
7.073
7.061
7.058

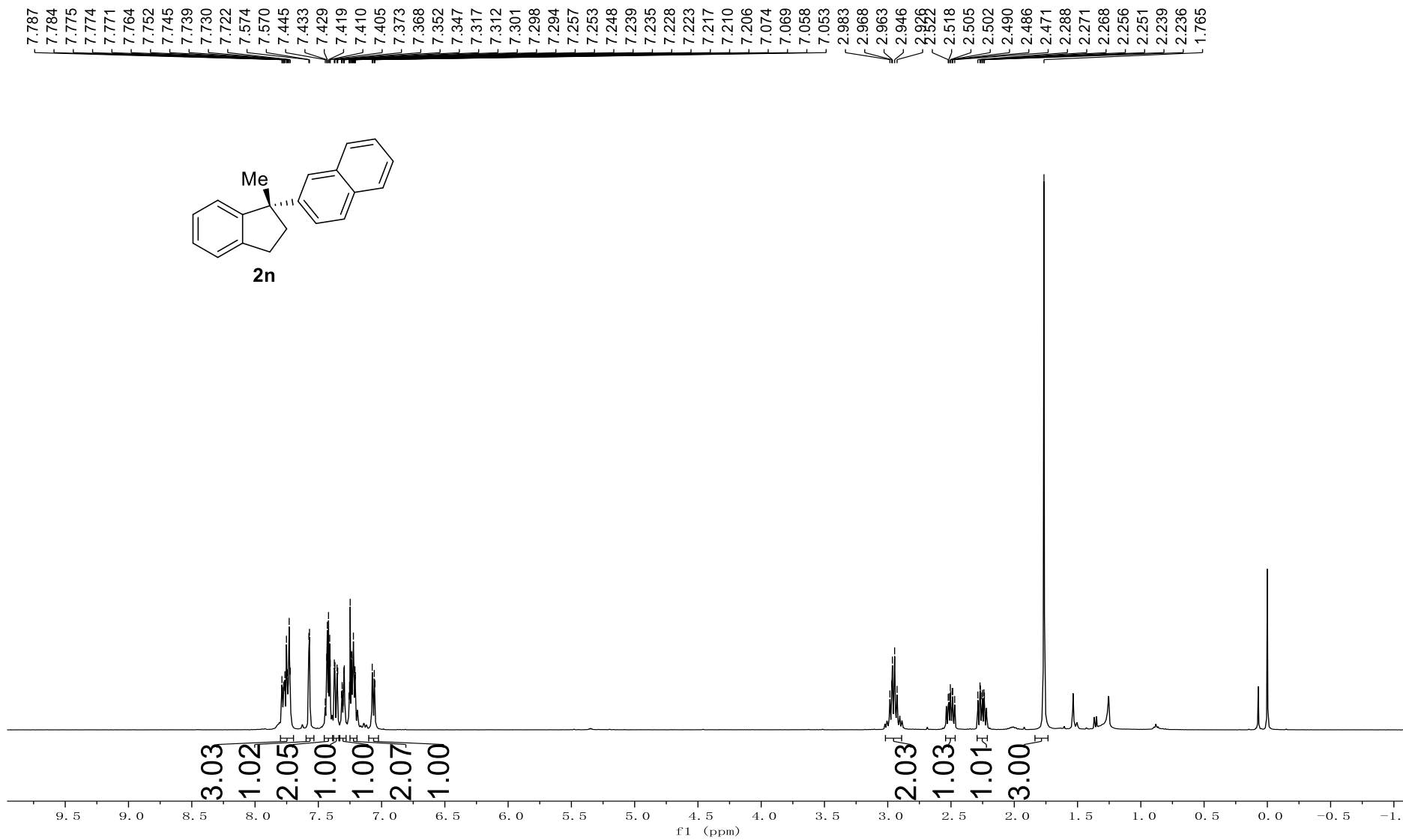
2.923
2.909
2.903
2.890
2.872
2.418
2.413
2.400
2.386
2.382
2.368
2.237
2.218
2.206
2.199
2.187
1.675

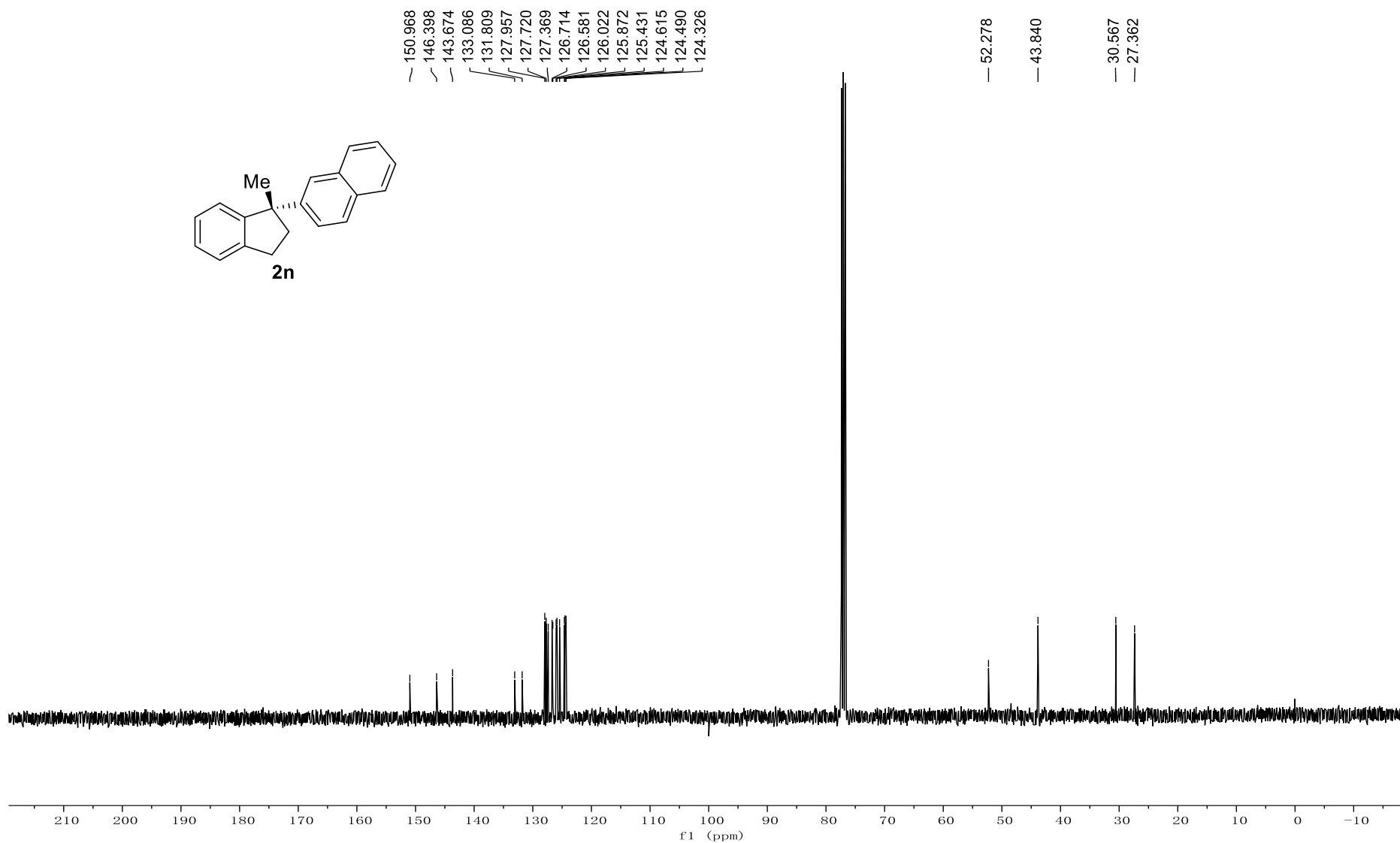
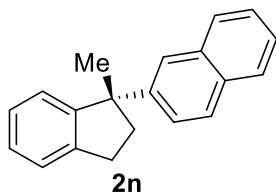


S136

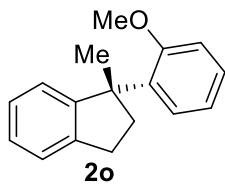


S137



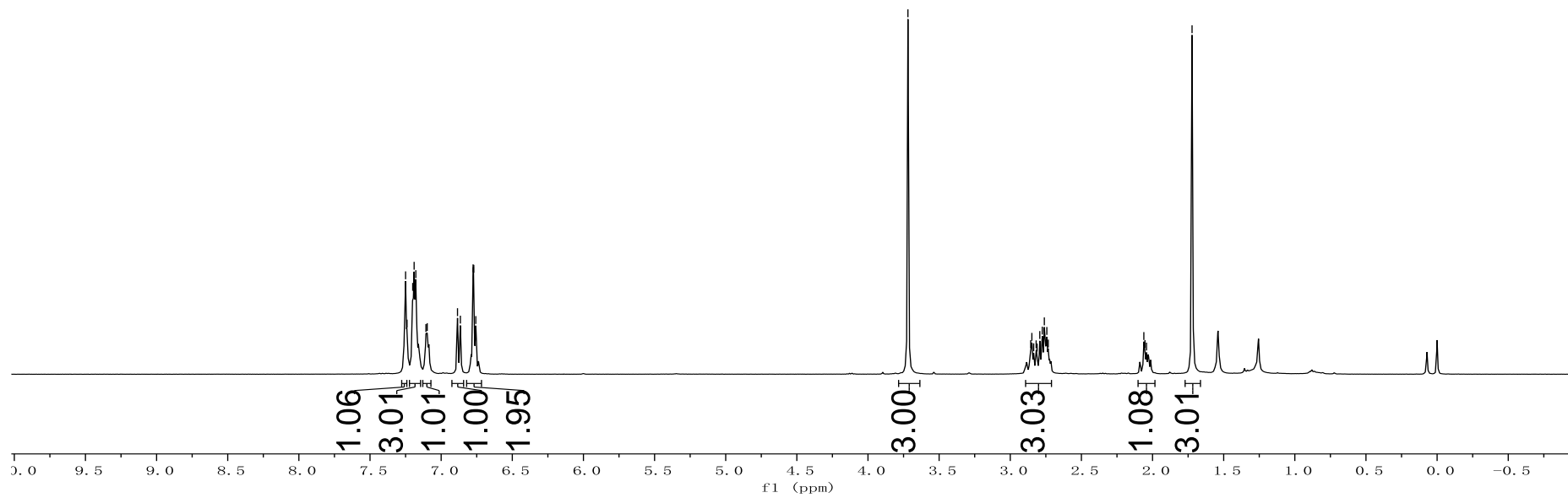


S139

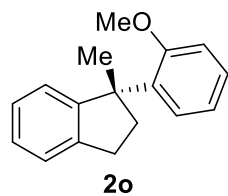


7.250
7.240
7.200
7.190
7.178
7.107
7.098
6.885
6.865
6.776
6.771
6.756

3.719
2.856
2.848
2.835
2.818
2.812
2.792
2.775
2.761
2.743
2.733
2.061
2.053
2.042
1.722

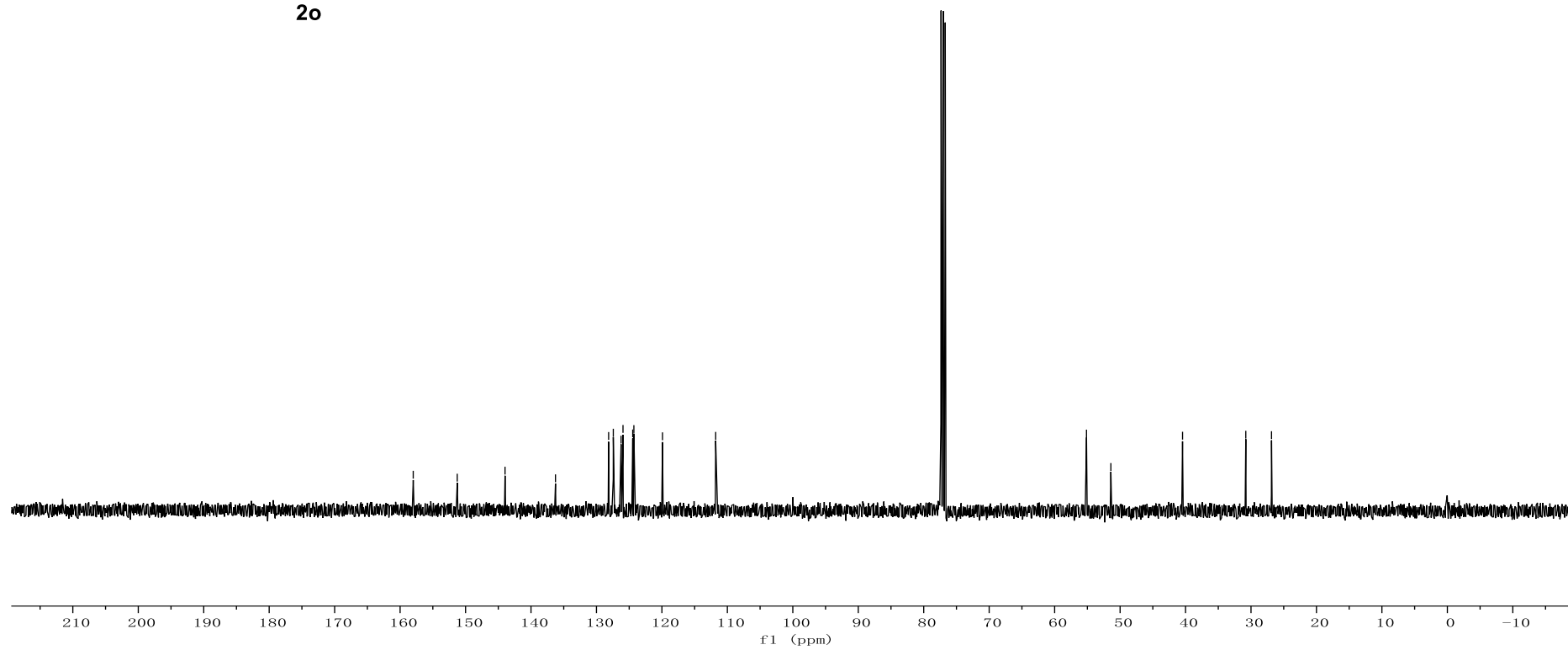


S140

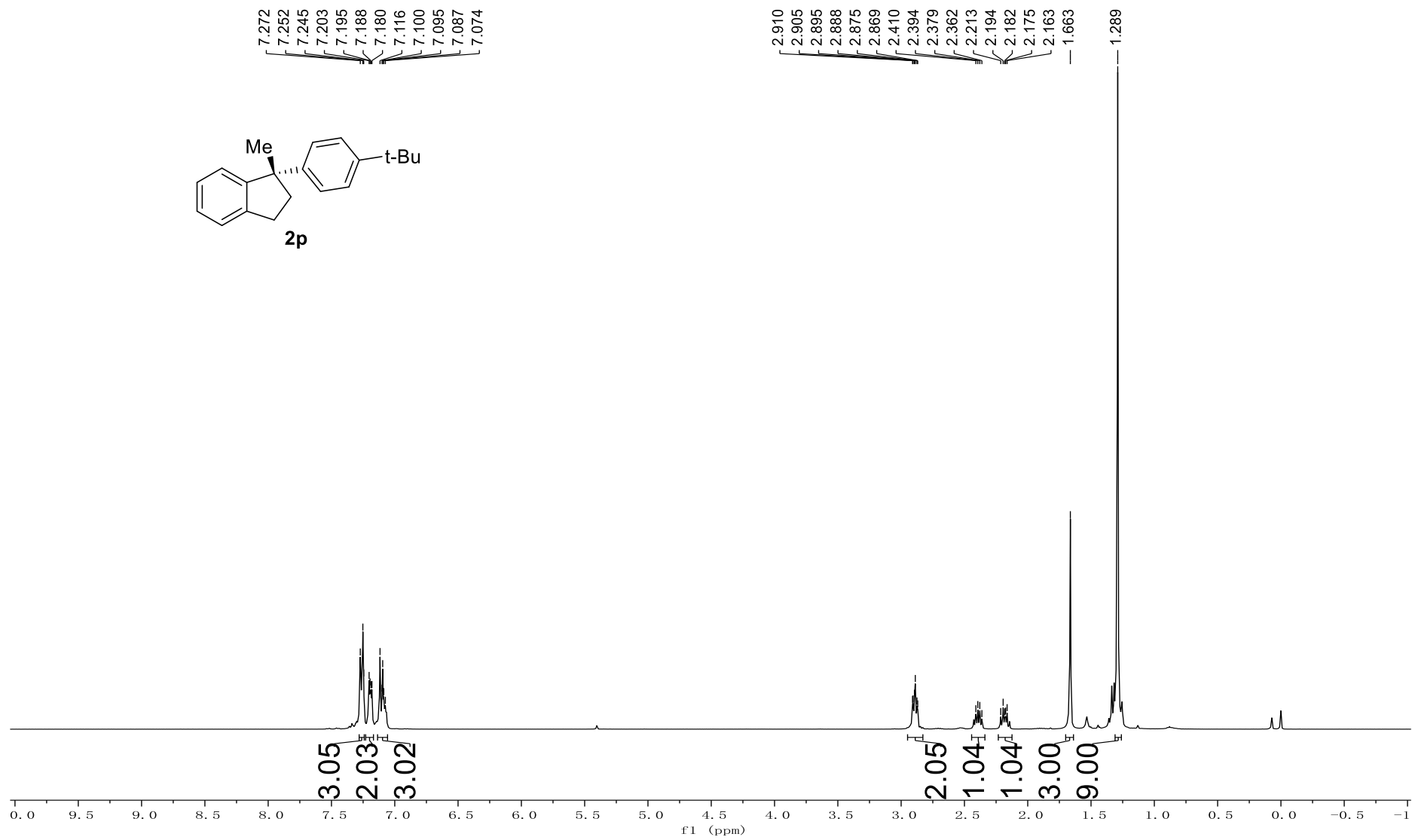
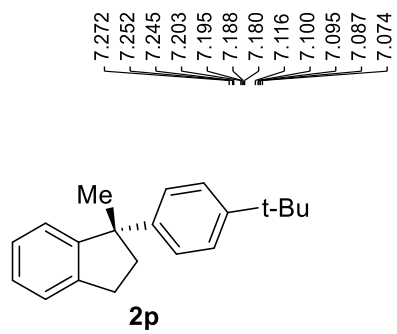


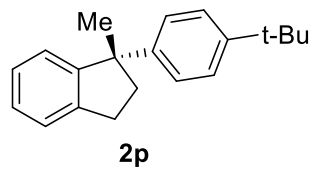
— 157.993
— 151.270
— 143.967
— 136.262
— 128.140
— 127.426
— 126.239
— 125.945
— 124.459
— 124.284
— 119.909
— 111.786

— 55.133
— 51.408
— 40.459
— 30.796
— 26.866



S141





151.139
148.333
145.902
143.650

126.503
126.396
126.209
124.839
124.476
124.215

51.652

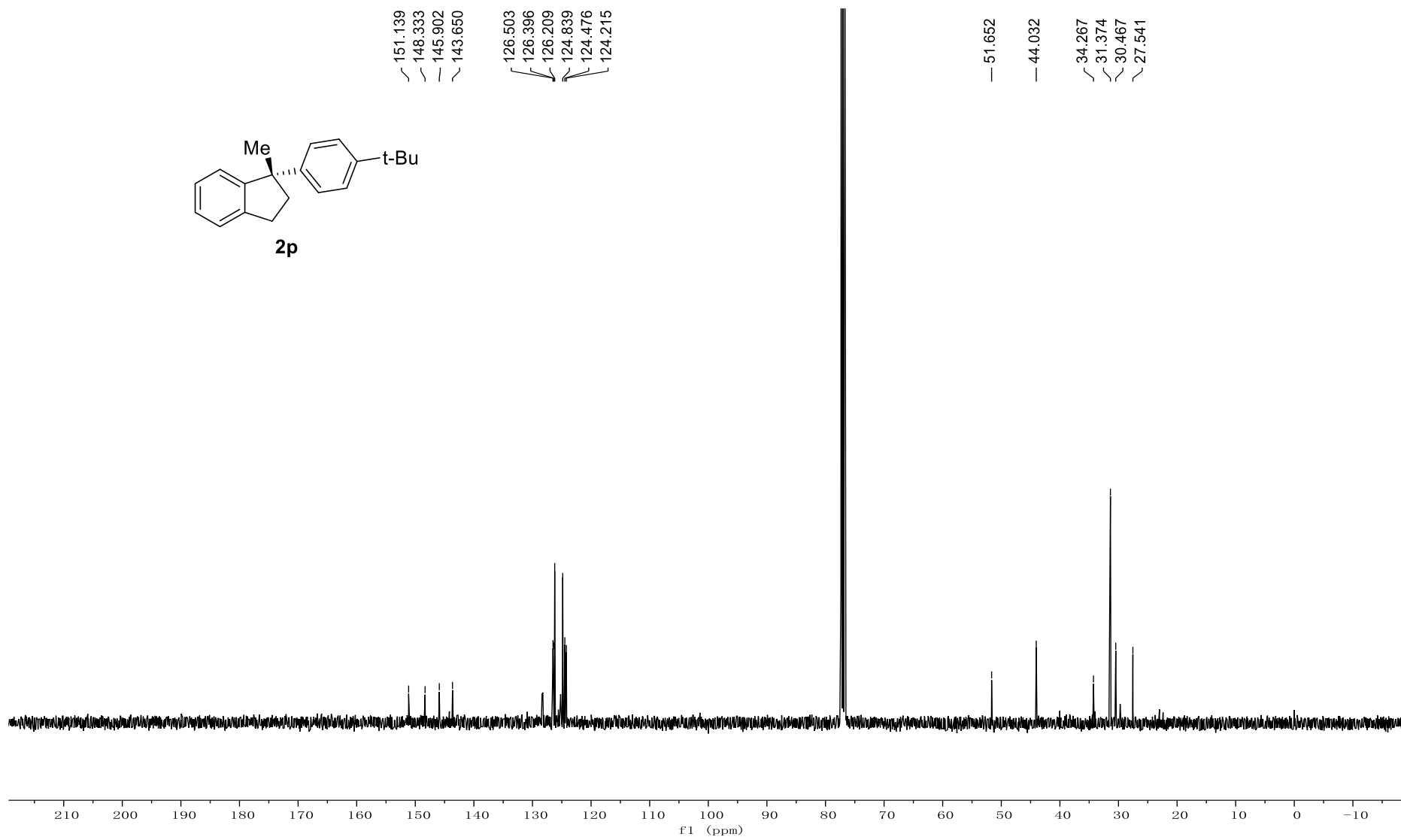
44.032

34.267

31.374

30.467

27.541

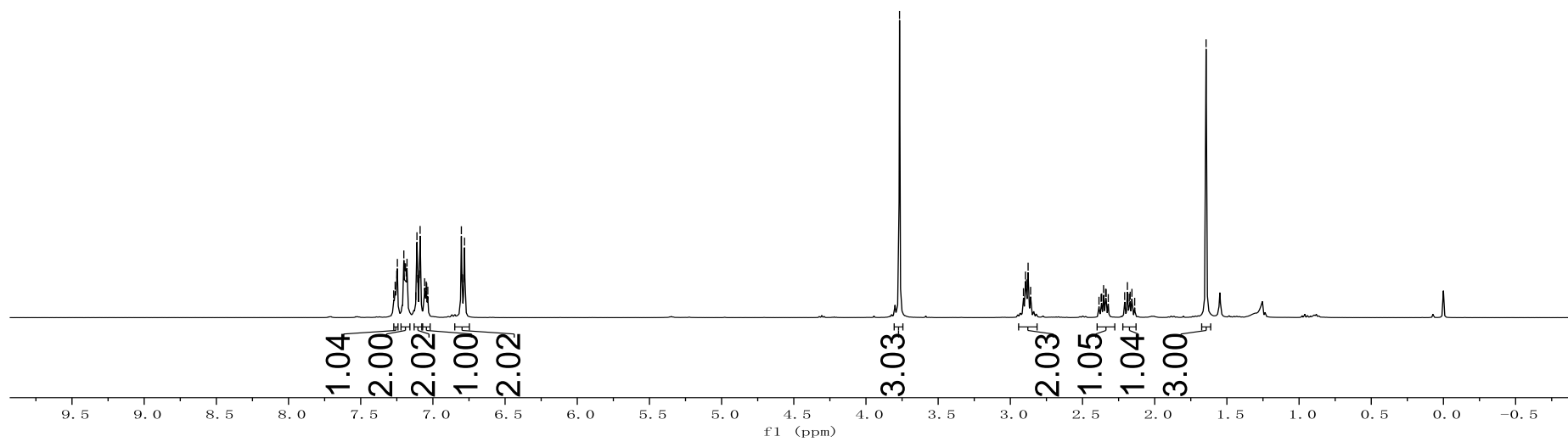
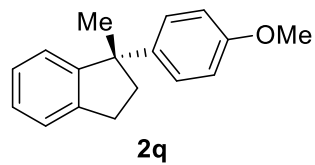


S143

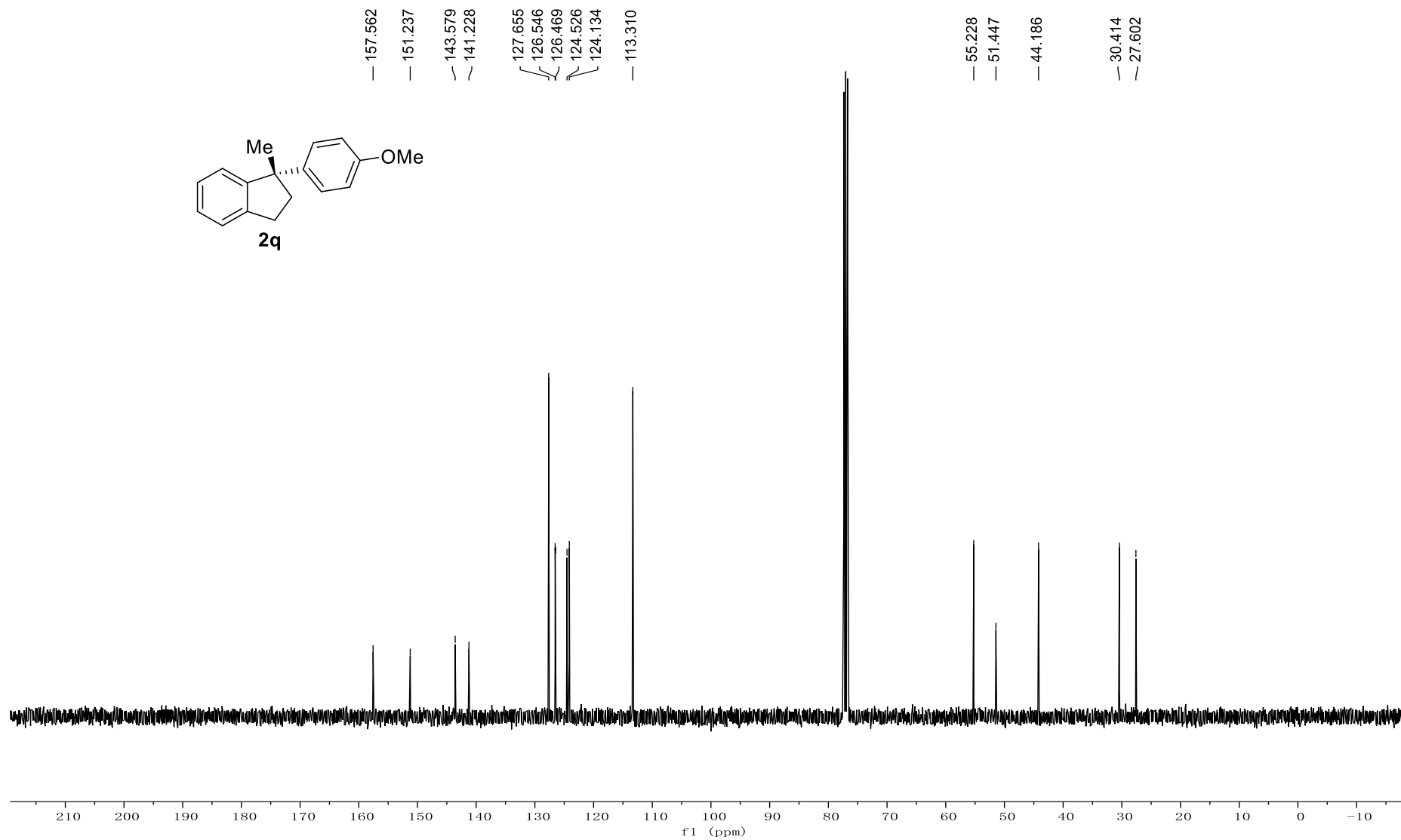
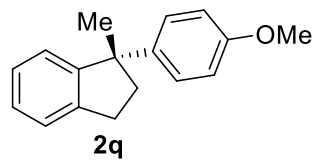
7.271
7.261
7.250
7.246
7.201
7.195
7.189
7.185
7.179
7.119
7.110
7.105
7.094
7.089
7.057
7.052
7.046
7.043
7.035
6.803
6.797
6.786
6.781

— 3.768

2.909
2.895
2.889
2.877
2.860
2.386
2.371
2.367
2.354
2.340
2.336
2.322
2.208
2.189
2.176
2.170
2.158
2.139
1.644

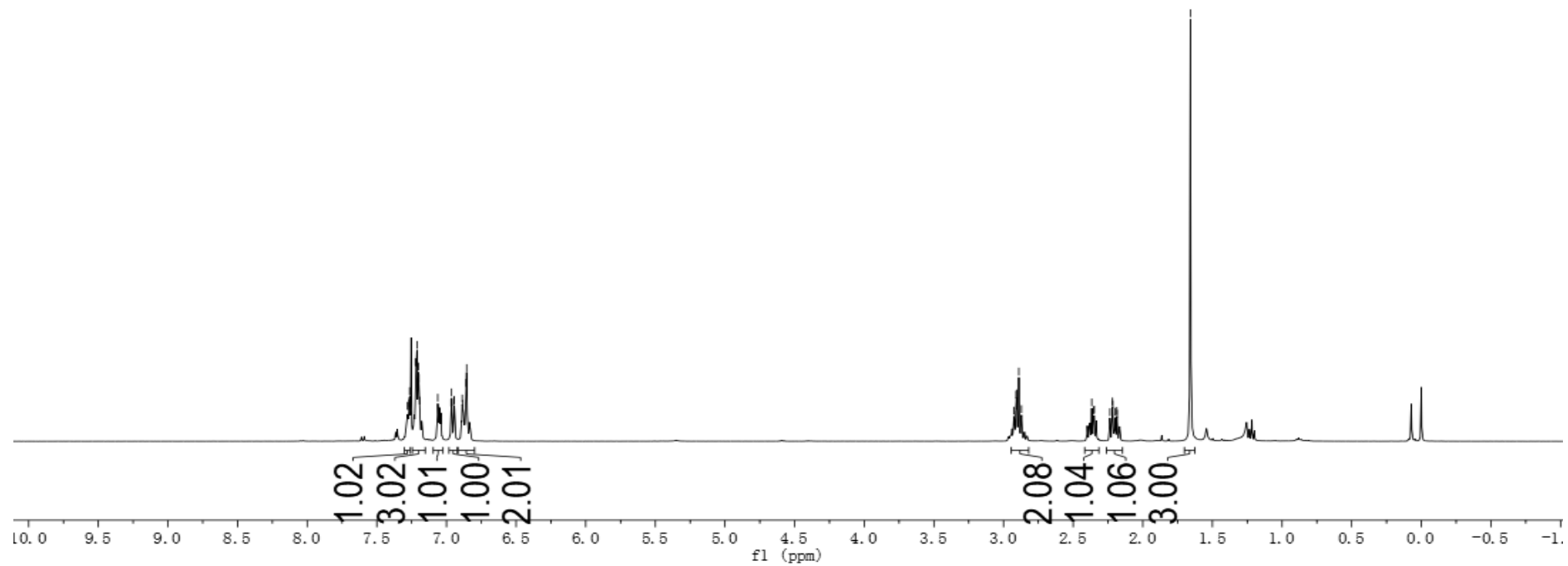
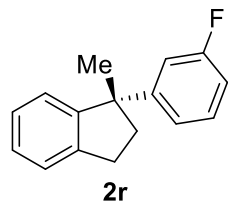


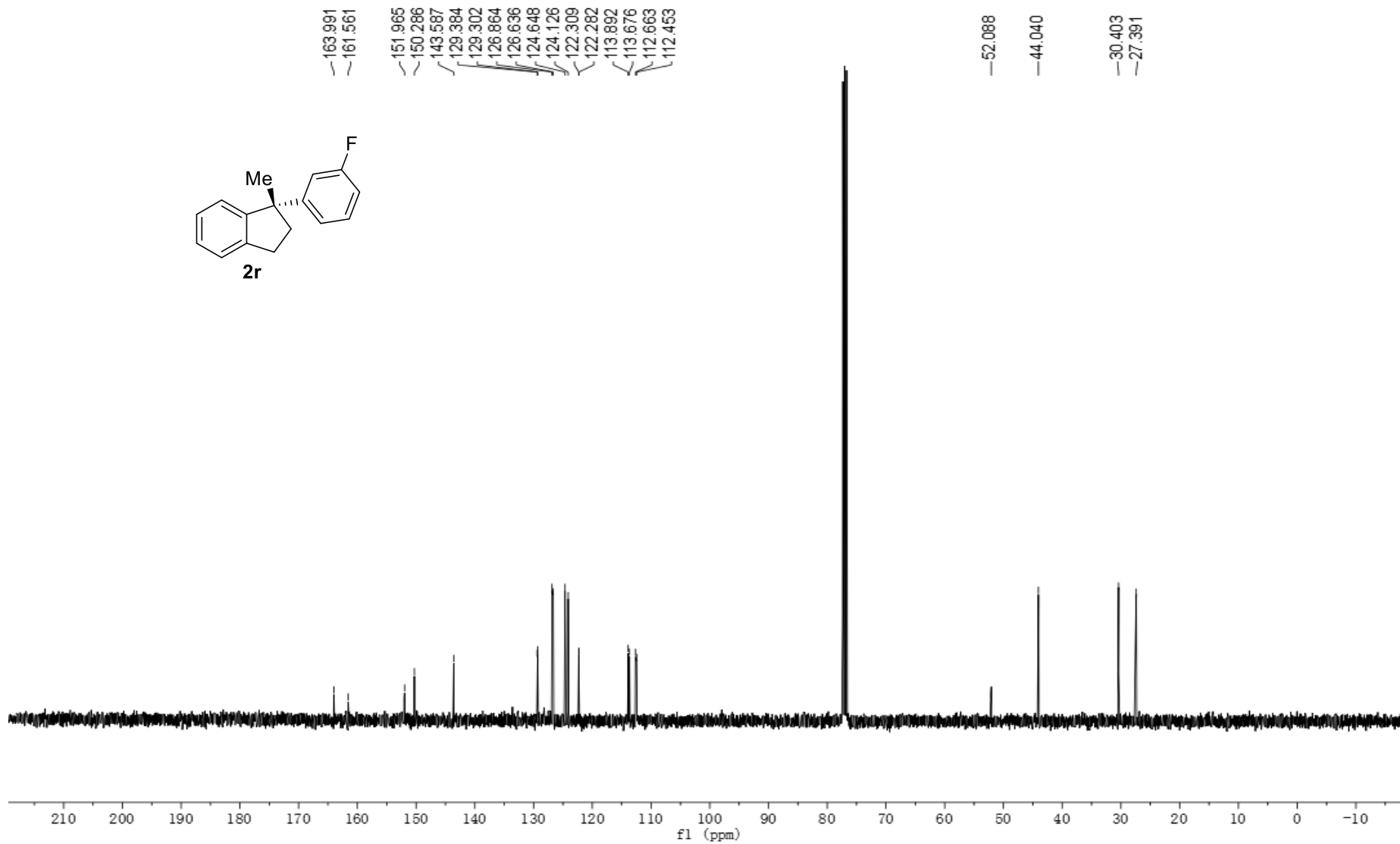
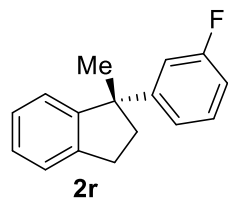
S144

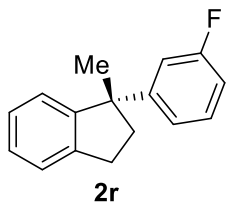


7.279
7.276
7.269
7.265
7.262
7.223
7.218
7.212
7.206
7.202
7.198
7.193
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6.945
6.943
6.887
6.882
6.859
6.855

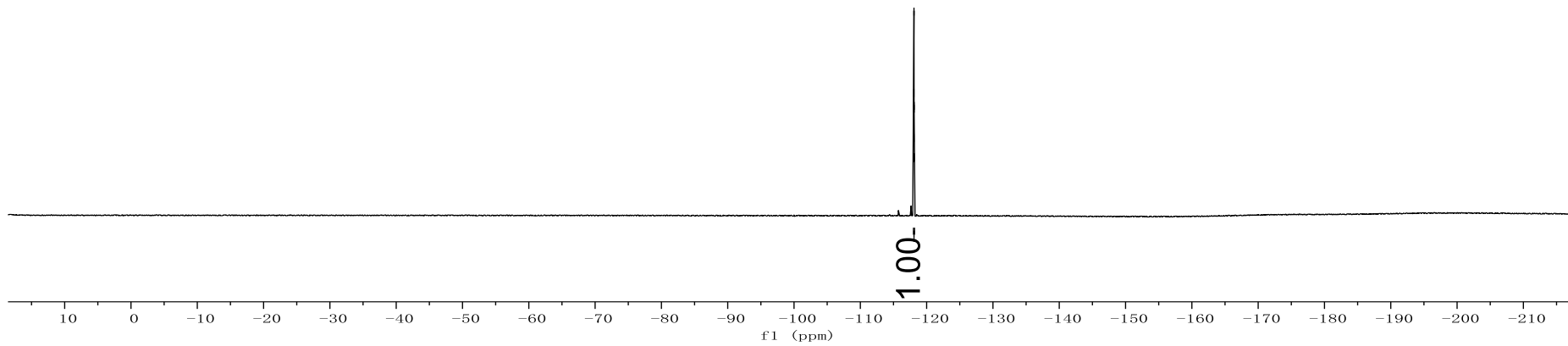
2.925
2.910
2.906
2.890
2.871
2.367
2.353
2.348
2.236
2.218
2.216
2.198
2.186
2.184
-1.658



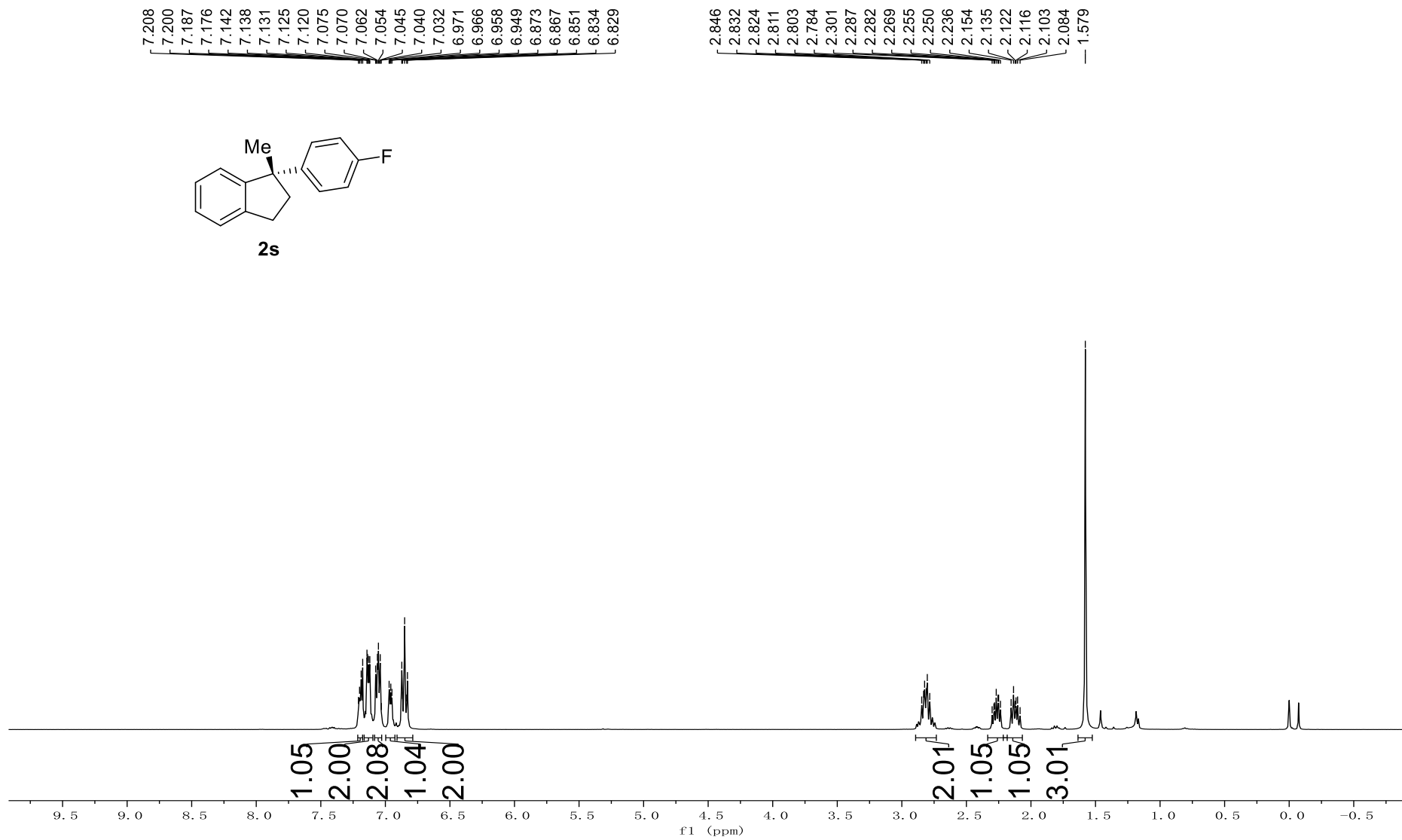
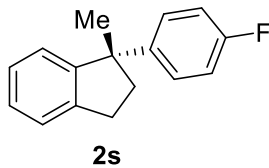


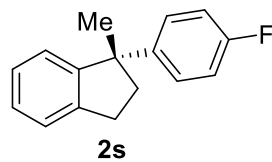


-118.052
-118.066
-118.075
-118.081
-118.089
-118.103
-118.112
-118.126



S148





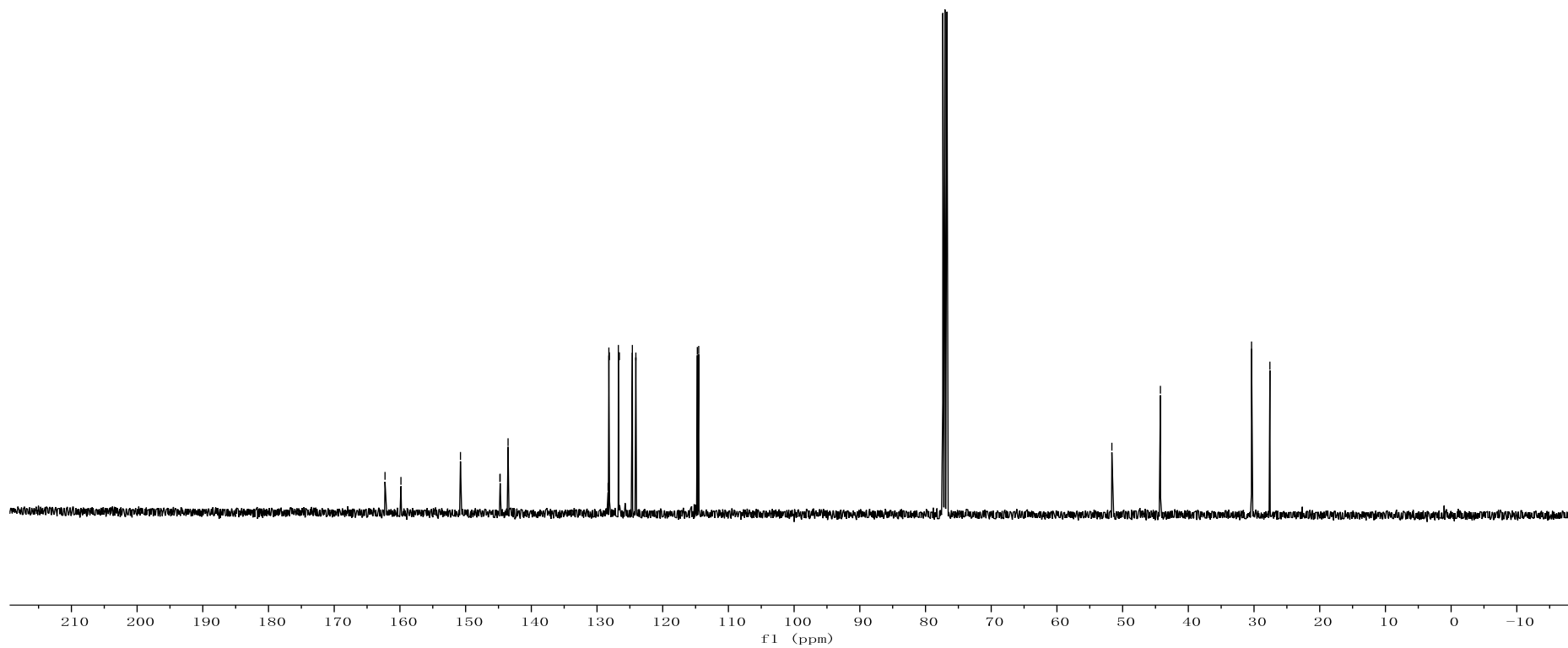
162.267
159.842
150.784
144.778
144.748
143.539
128.314
128.198
128.121
126.751
126.592
124.618
124.086
114.730
114.522

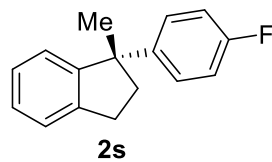
51.637

44.247

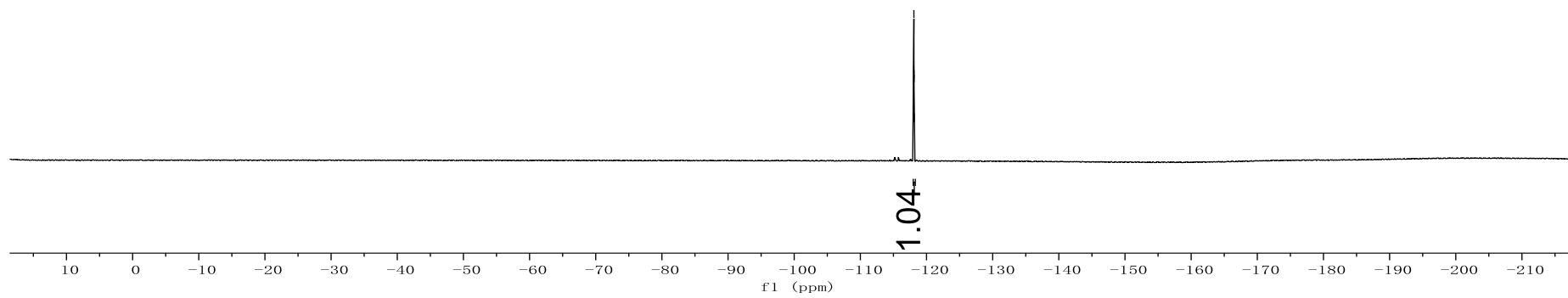
30.376

27.584

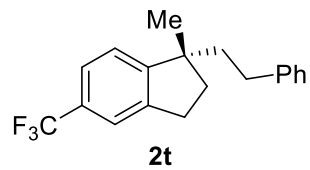




-118.054
-118.069
-118.078
-118.092
-118.107
-118.114
-118.129

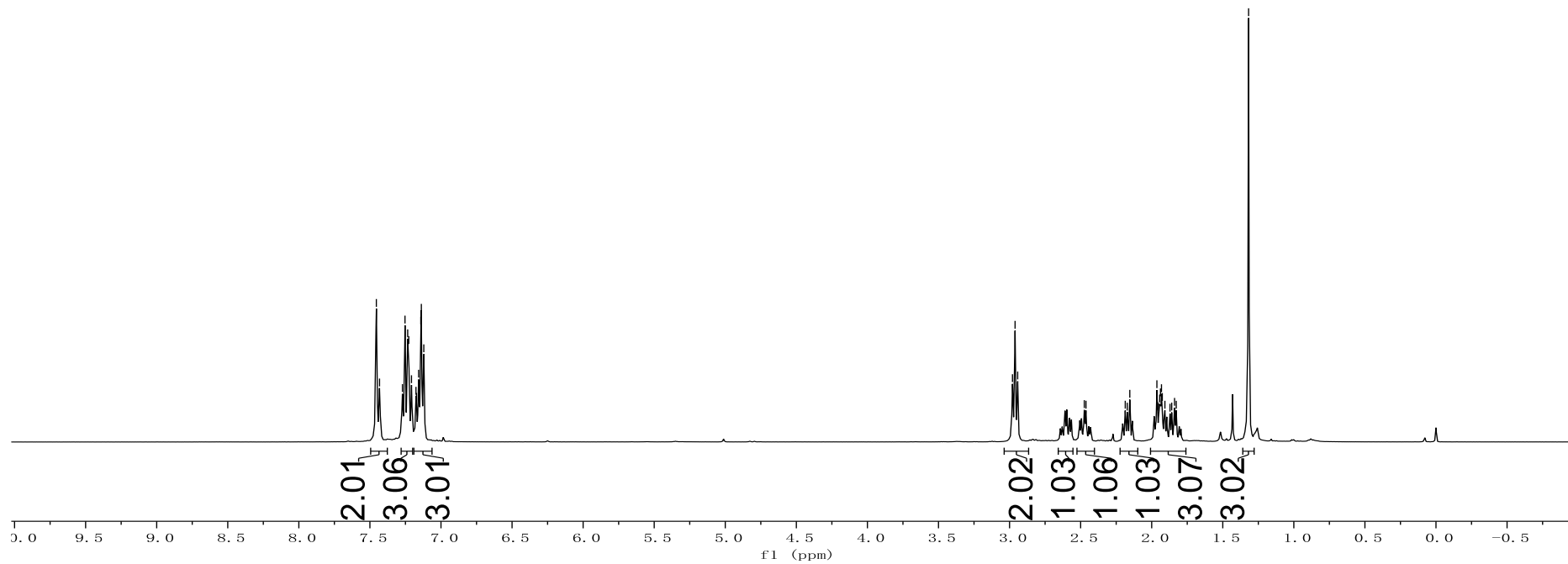


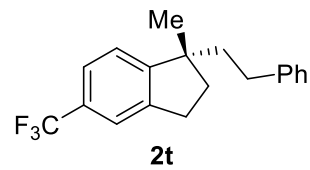
S151



7.455
7.432
7.271
7.253
7.234
7.227
7.208
7.176
7.172
7.157
7.142
7.138
7.121

2.980
2.961
2.943
2.474
2.462
2.186
2.172
2.154
1.963
1.958
1.951
1.944
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1.931
1.925
1.907
1.871
1.859
1.839
1.827
1.318





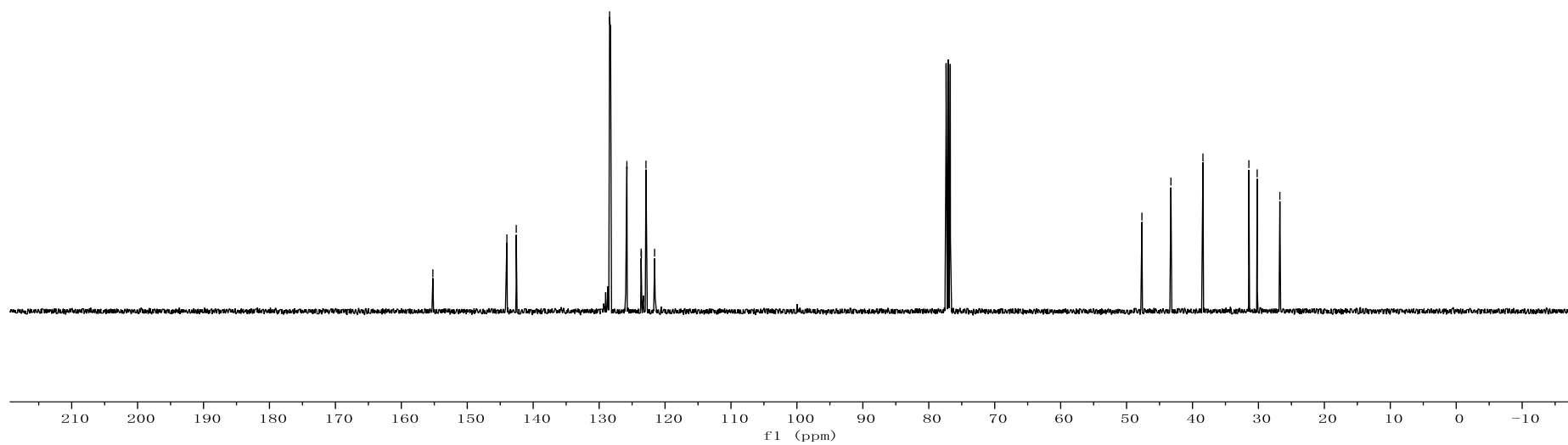
— 155.218

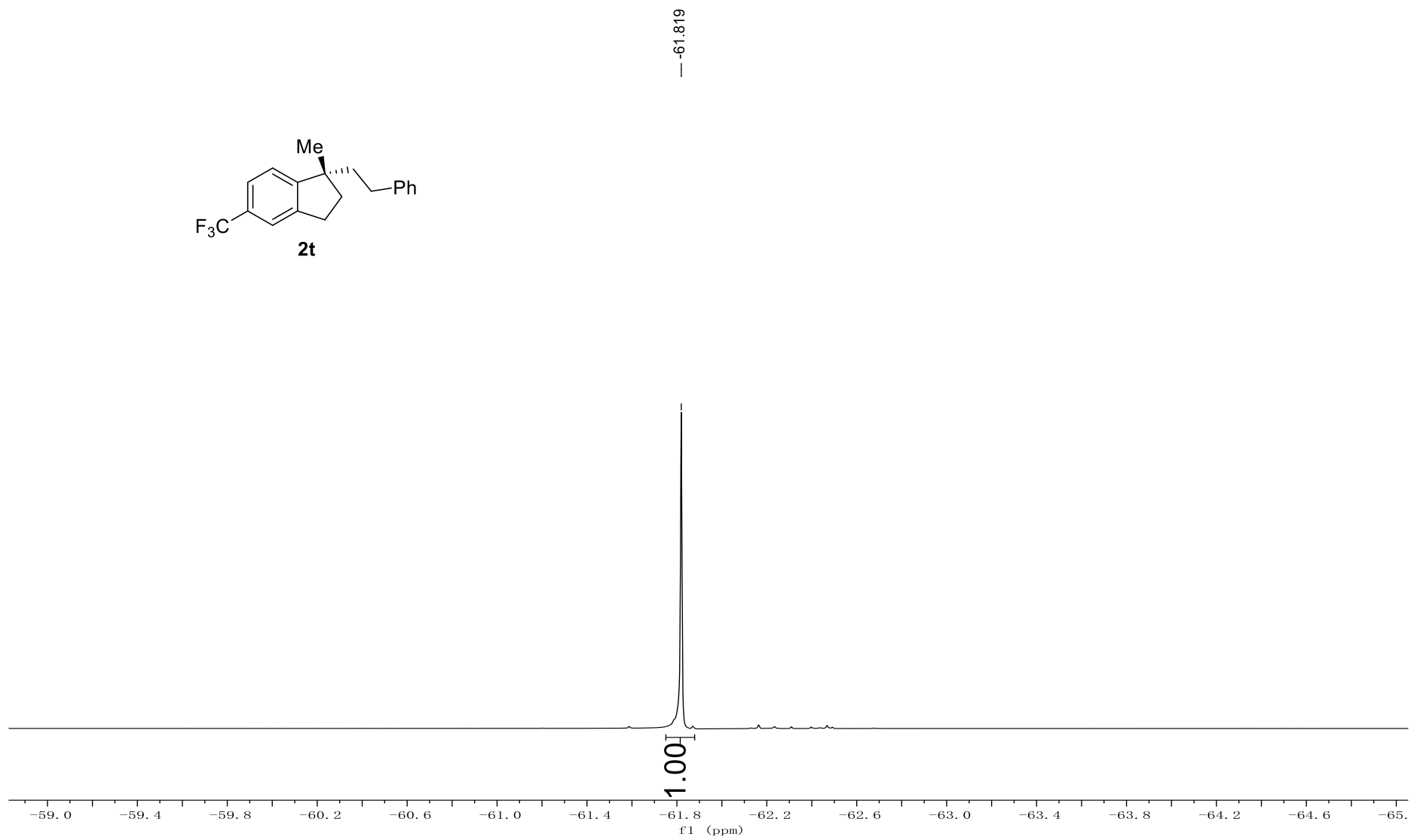
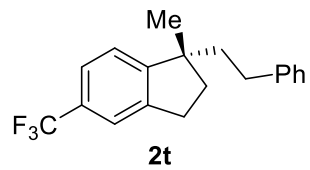
~ 143.993
~ 142.573

~ 128.413
~ 128.266
~ 125.790
~ 123.631
~ 123.591
~ 122.894
~ 121.586

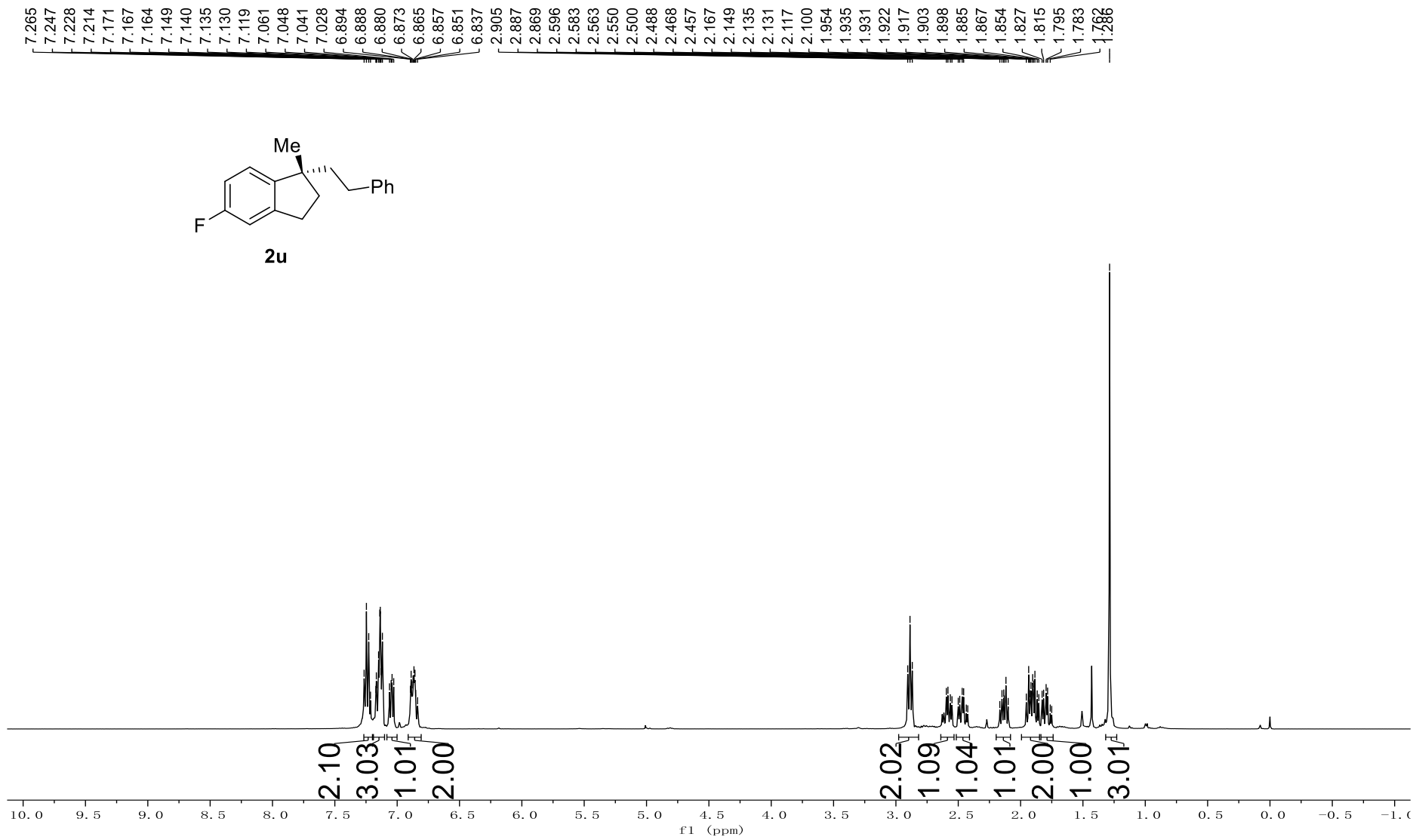
~ 47.674
~ 43.275
~ 38.417

~ 31.451
~ 30.194
~ 26.749

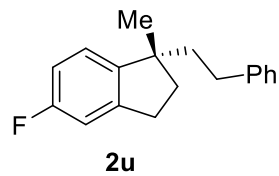




S154

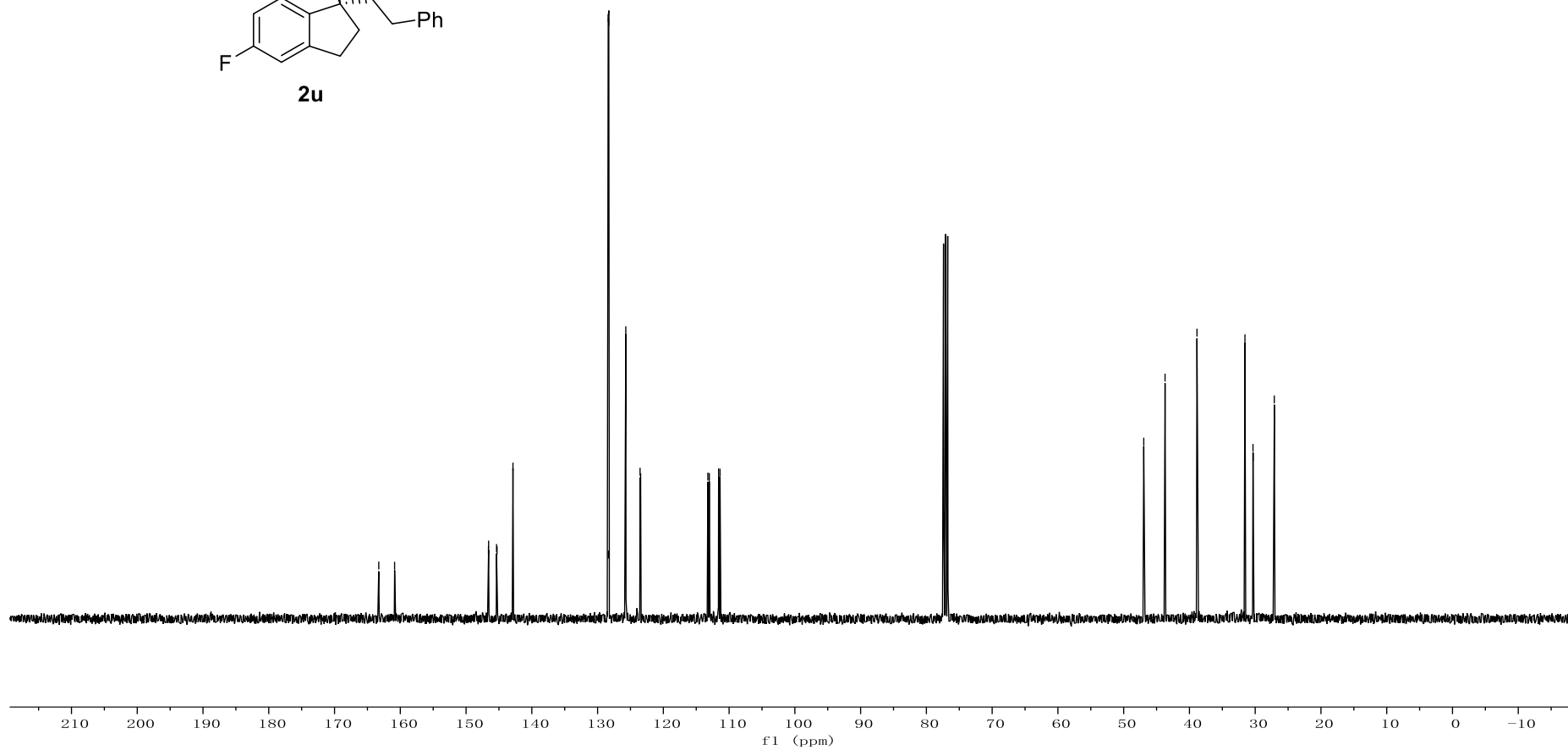


S155

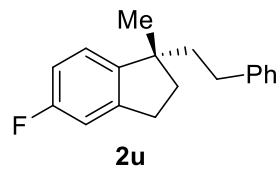


163.276
160.864
146.595
146.572
145.365
145.287
142.869
128.387
128.355
128.297
125.710
123.540
123.451
113.234
113.012
111.599
111.384

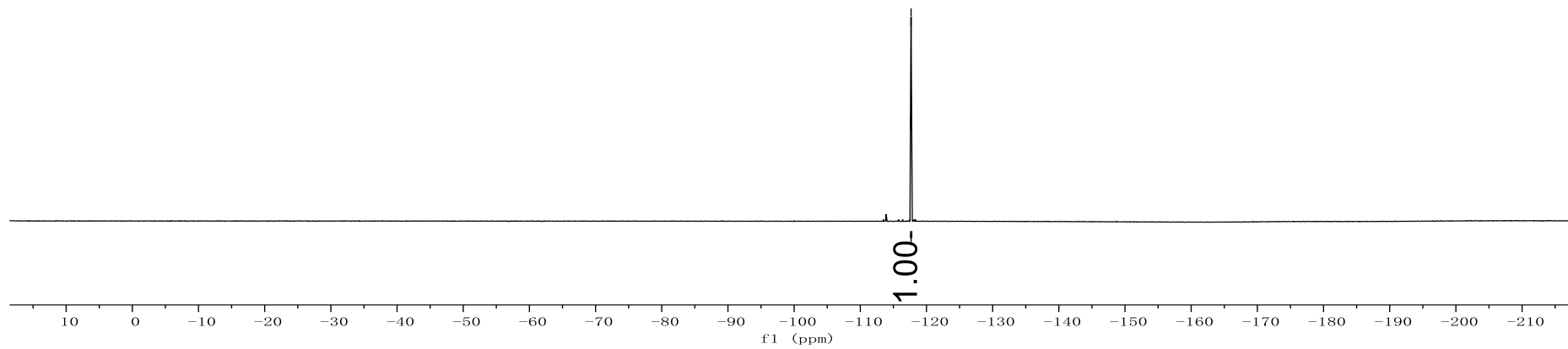
46.945
43.707
38.854
31.559
30.336
30.315
27.099



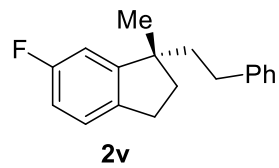
S156



-117.634
-117.648
-117.658
-117.672
-117.683
-117.697

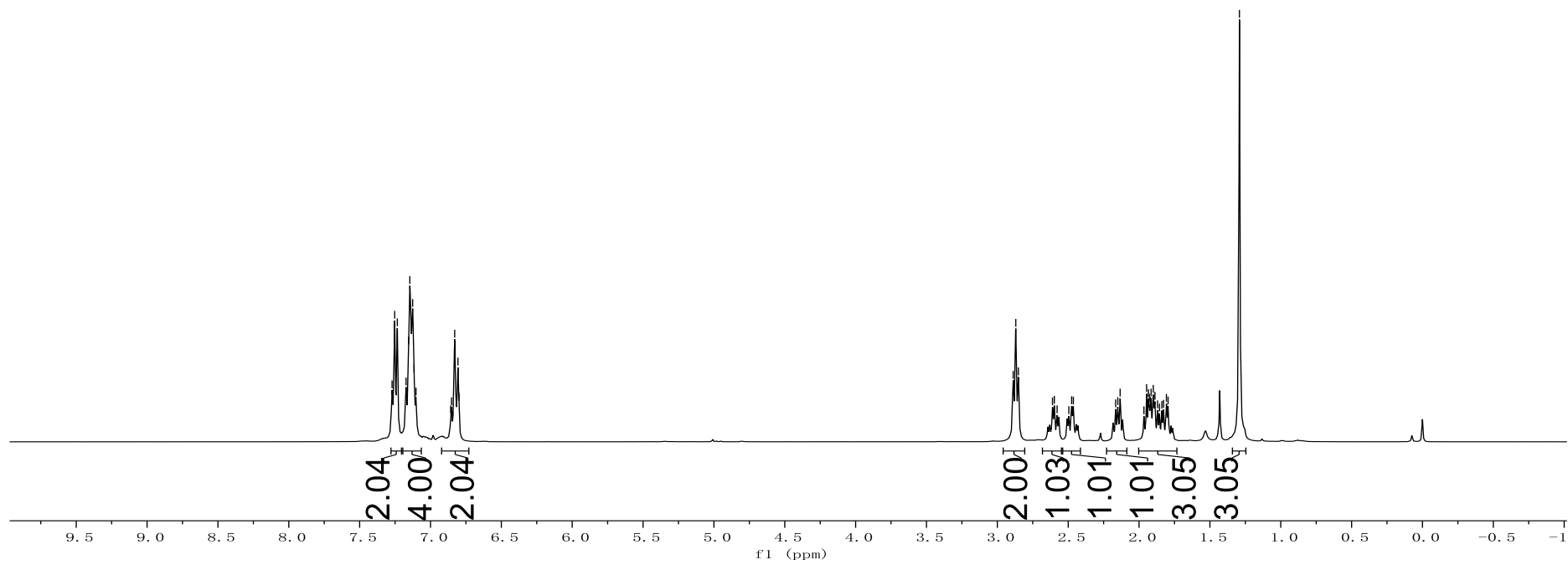


S157

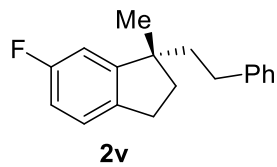


7.271
7.253
7.234
7.172
7.155
7.146
7.136
7.126
7.116
7.102
6.858
6.851
6.829
6.806
6.799

2.888
2.870
2.852
2.611
2.598
2.578
2.495
2.476
2.464
2.165
2.150
2.133
1.966
1.947
1.934
1.928
1.921
1.915
1.900
1.888
1.869
1.856
1.839
1.827
1.807
1.795
1.292

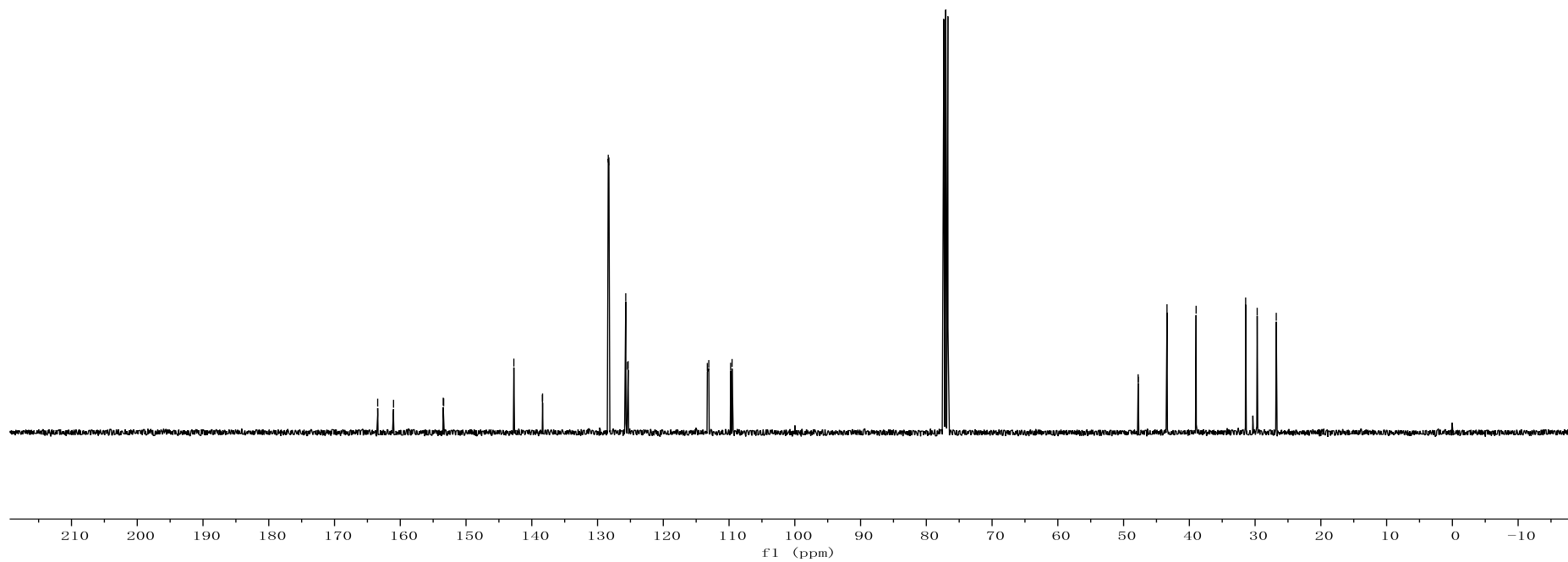


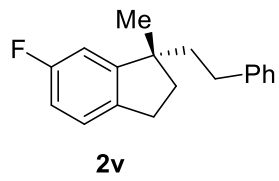
S158



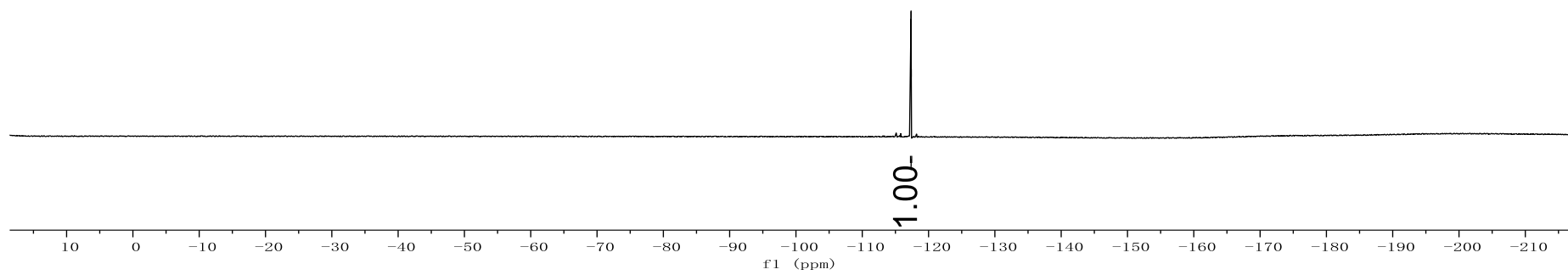
163.437
161.027
153.470
153.402
142.728
138.386
138.362
128.369
128.268
125.709
125.434
125.349
113.302
113.079
109.758
109.542

47.788
47.769
43.399
38.969
31.439
29.683
26.784

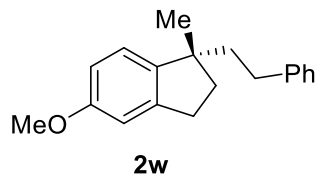




-117.327
-117.341
-117.351
-117.365
-117.376
-117.389

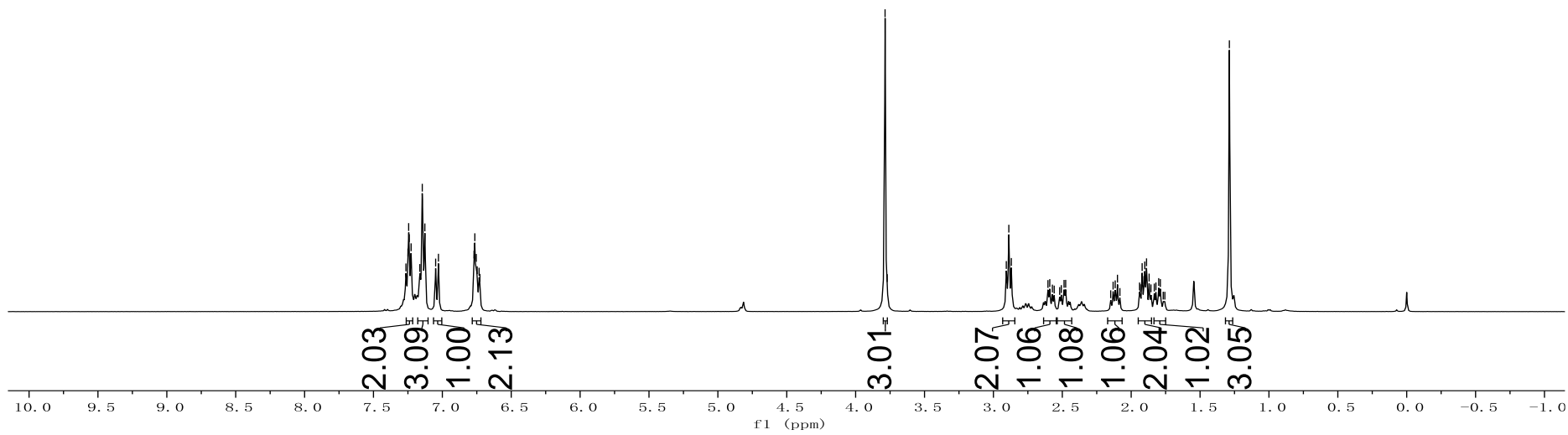


S160

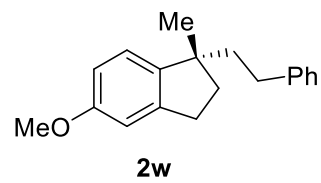


7.264
 7.250
 7.245
 7.240
 7.227
 7.163
 7.146
 7.127
 7.049
 7.028
 6.770
 6.764
 6.754
 6.747
 6.733
 6.727

3.786
 3.771
 2.906
 2.888
 2.870
 2.604
 2.591
 2.572
 2.559
 2.519
 2.507
 2.487
 2.475
 2.149
 2.131
 2.116
 2.100
 2.082
 1.939
 1.934
 1.920
 1.907
 1.901
 1.888
 1.870
 1.857
 1.832
 1.820
 1.800
 1.788
 1.768
 1.756
 1.287



S161



— 158.698

~ 144.721
~ 143.312
~ 143.104

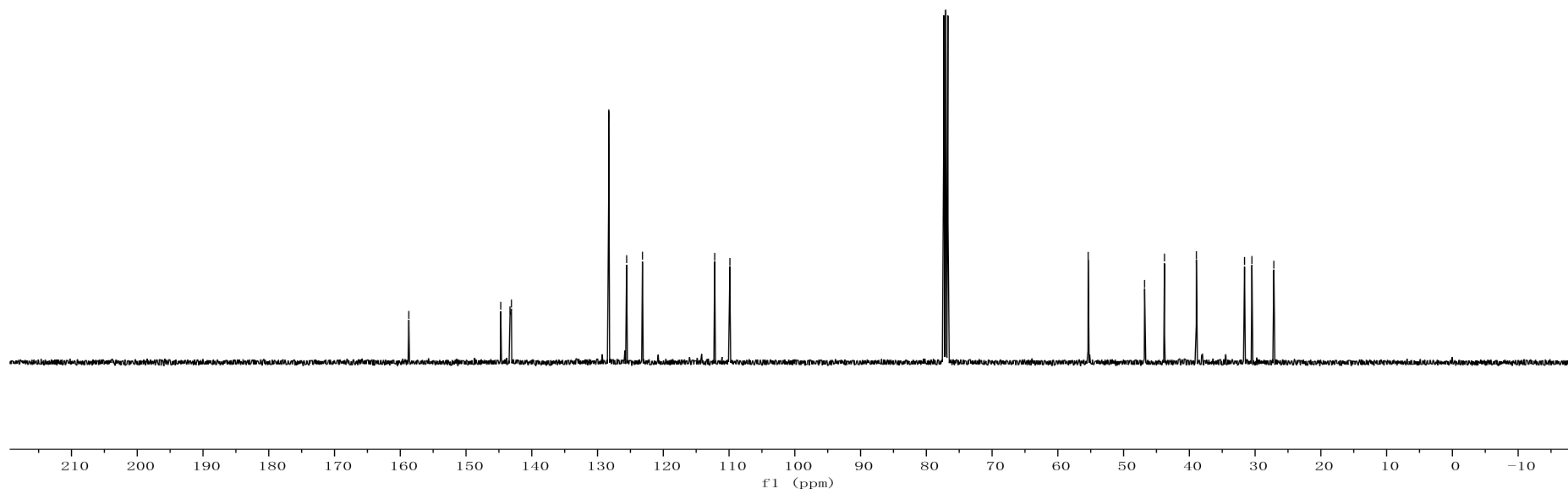
~ 128.303
~ 128.286
~ 125.577
~ 123.172

~ 112.185
~ 109.868

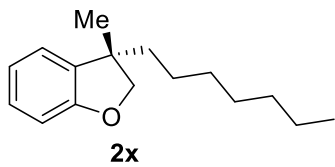
— 55.386

~ 46.802
~ 43.785
~ 38.933

~ 31.606
~ 30.485
~ 27.148

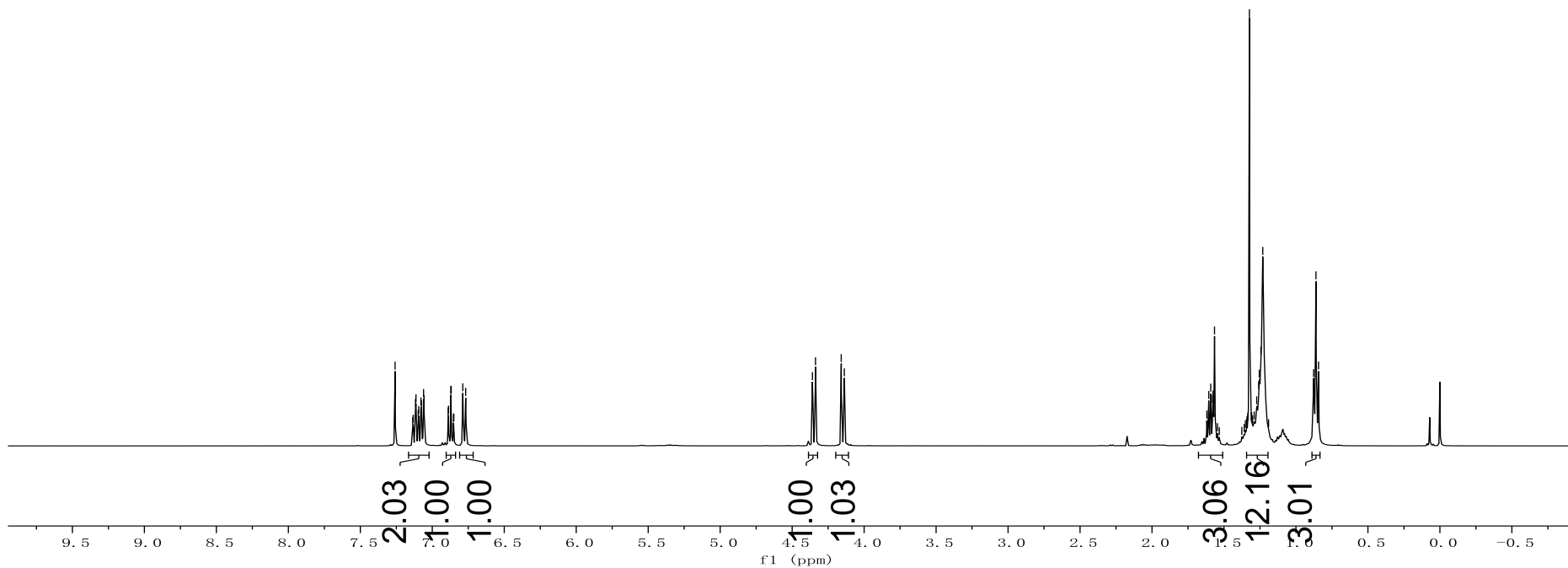


S162

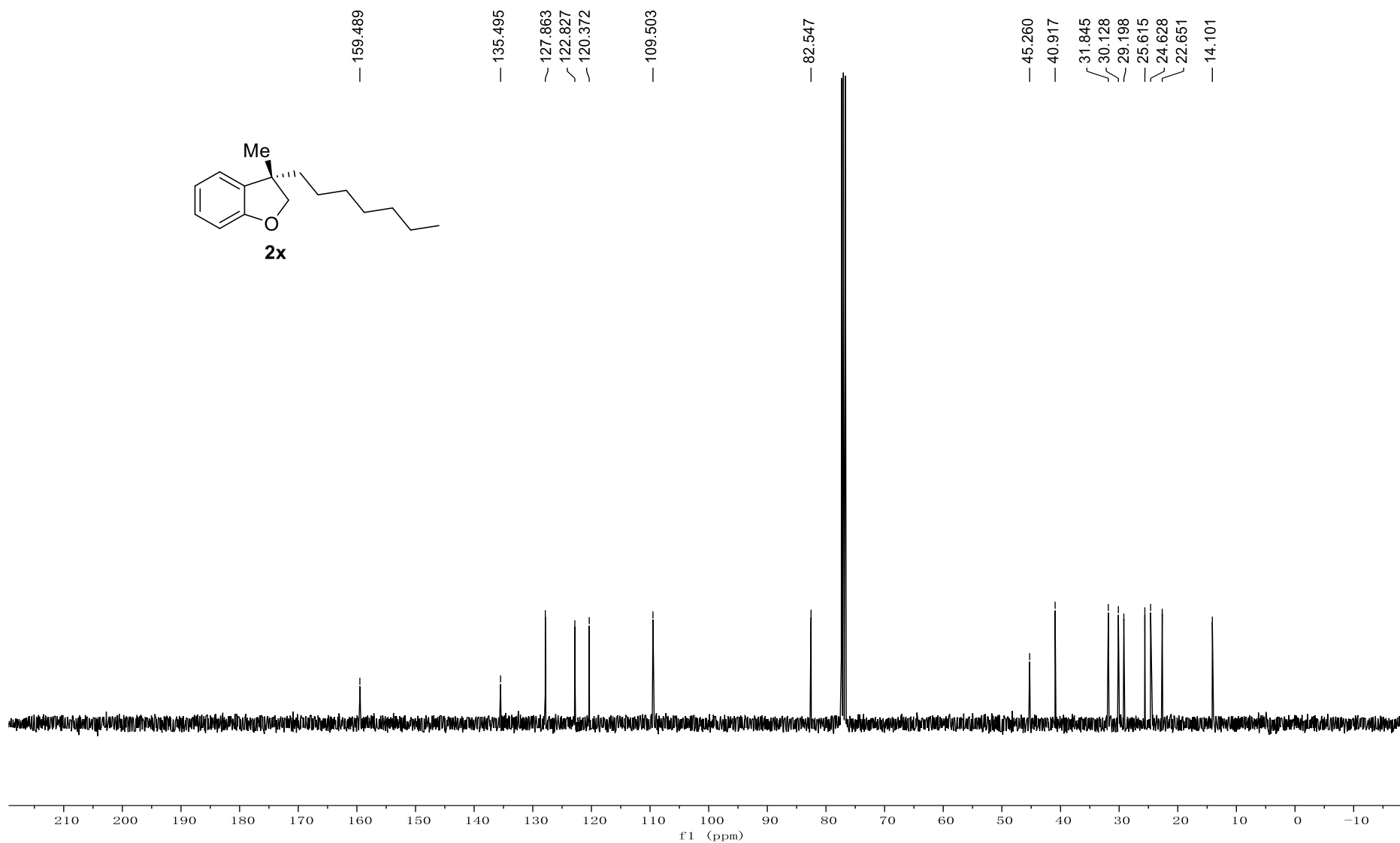
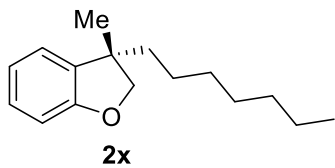


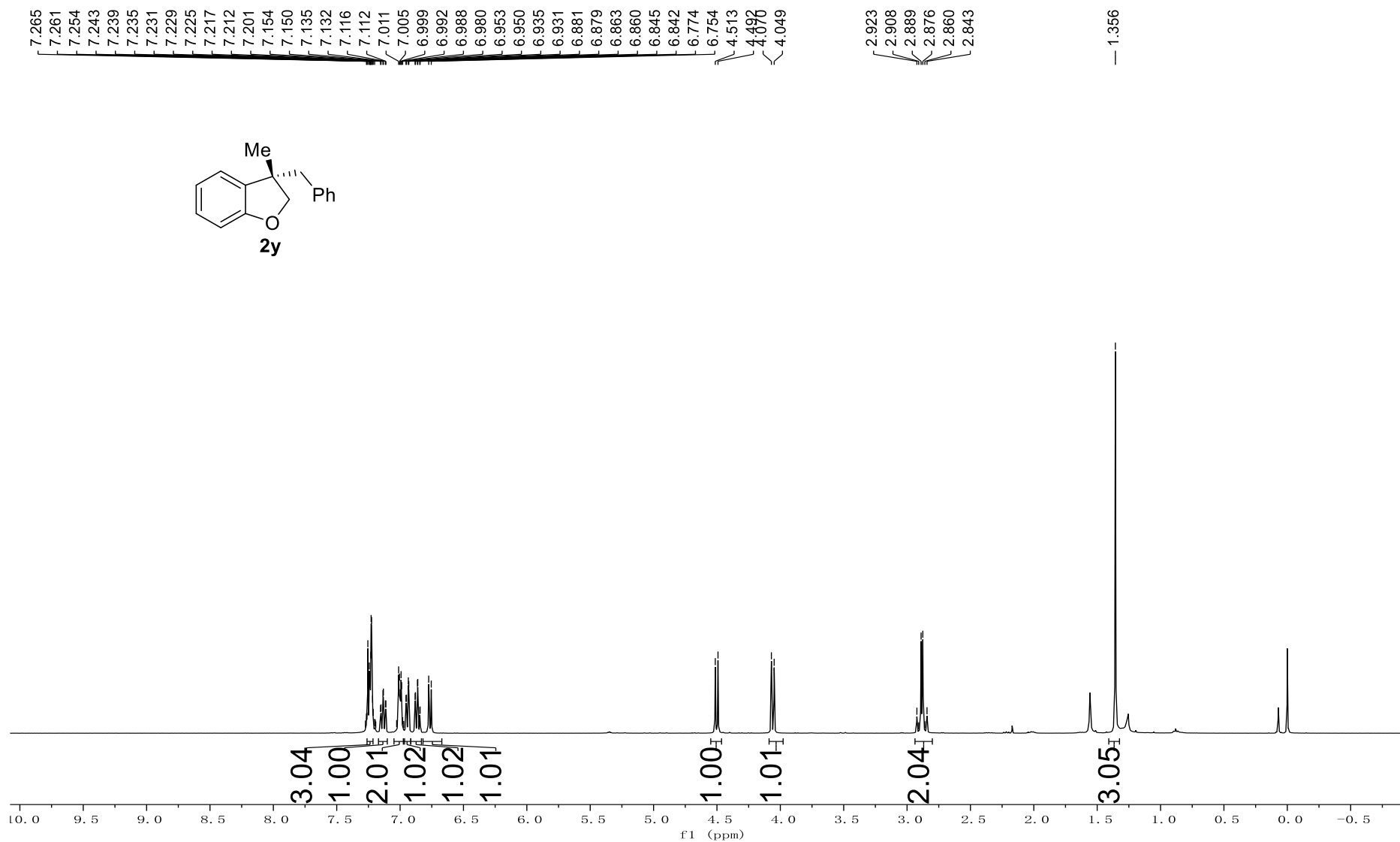
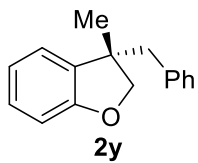
7.258
7.136
7.132
7.117
7.113
7.098
7.094
7.079
7.075
7.061
7.057
6.890
6.887
6.871
6.869
6.853
6.850
6.788
6.768

4.359
4.338
4.159
4.138
1.619
1.610
1.606
1.592
1.579
1.576
1.566
1.545
1.532
1.376
1.359
1.351
1.343
1.340
1.334
1.323
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0.861
0.843

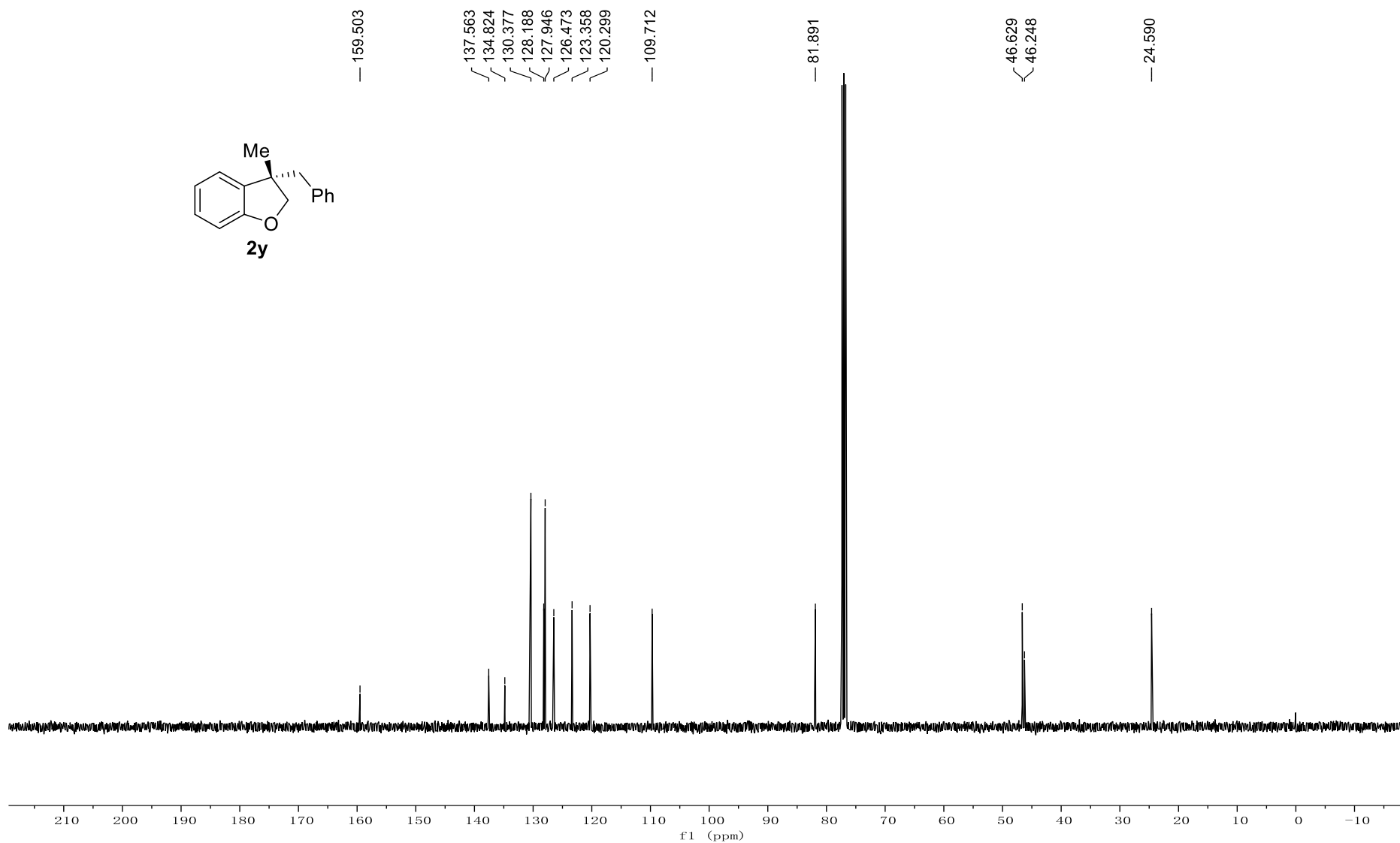
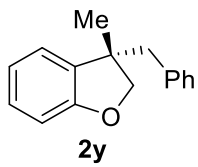


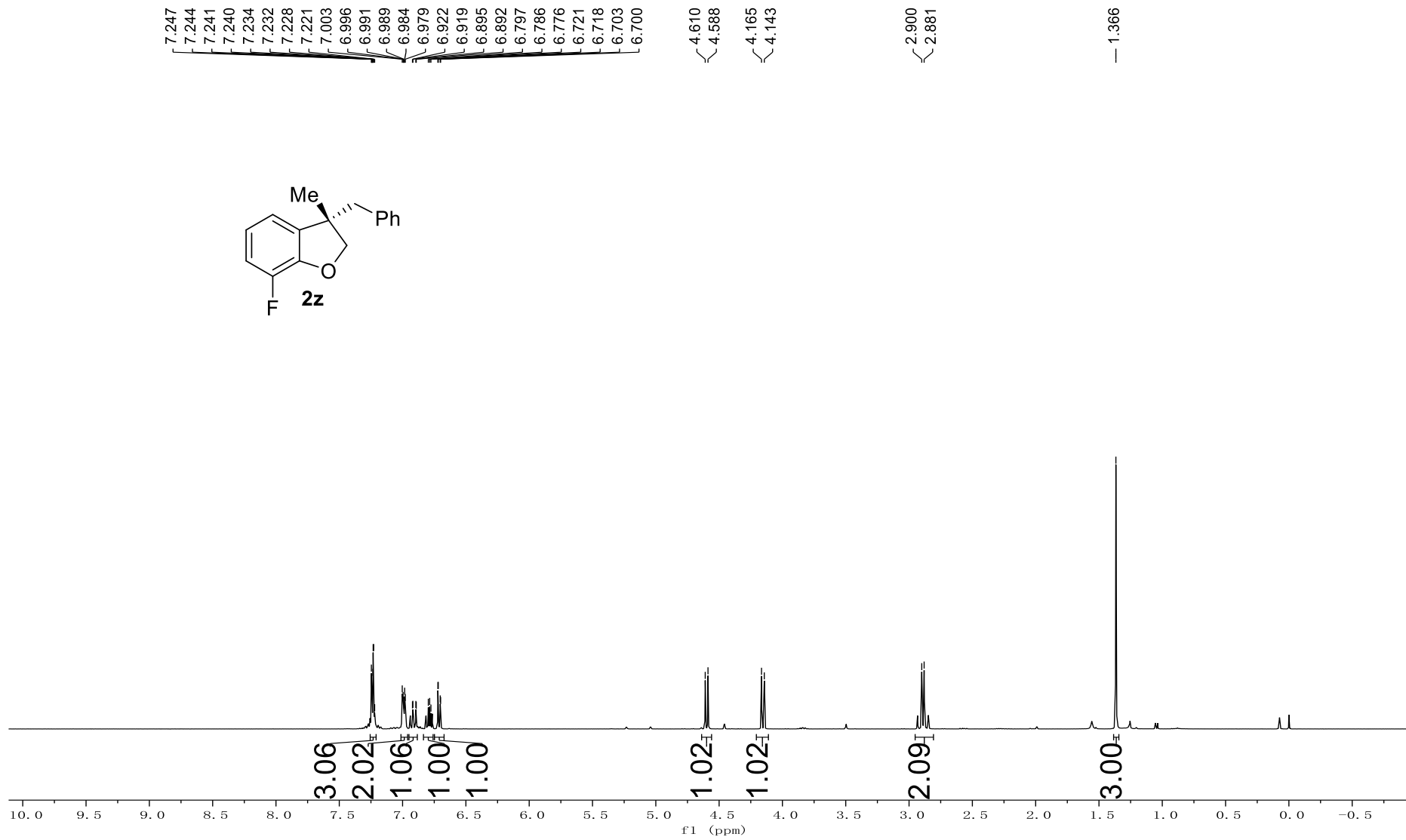
S163



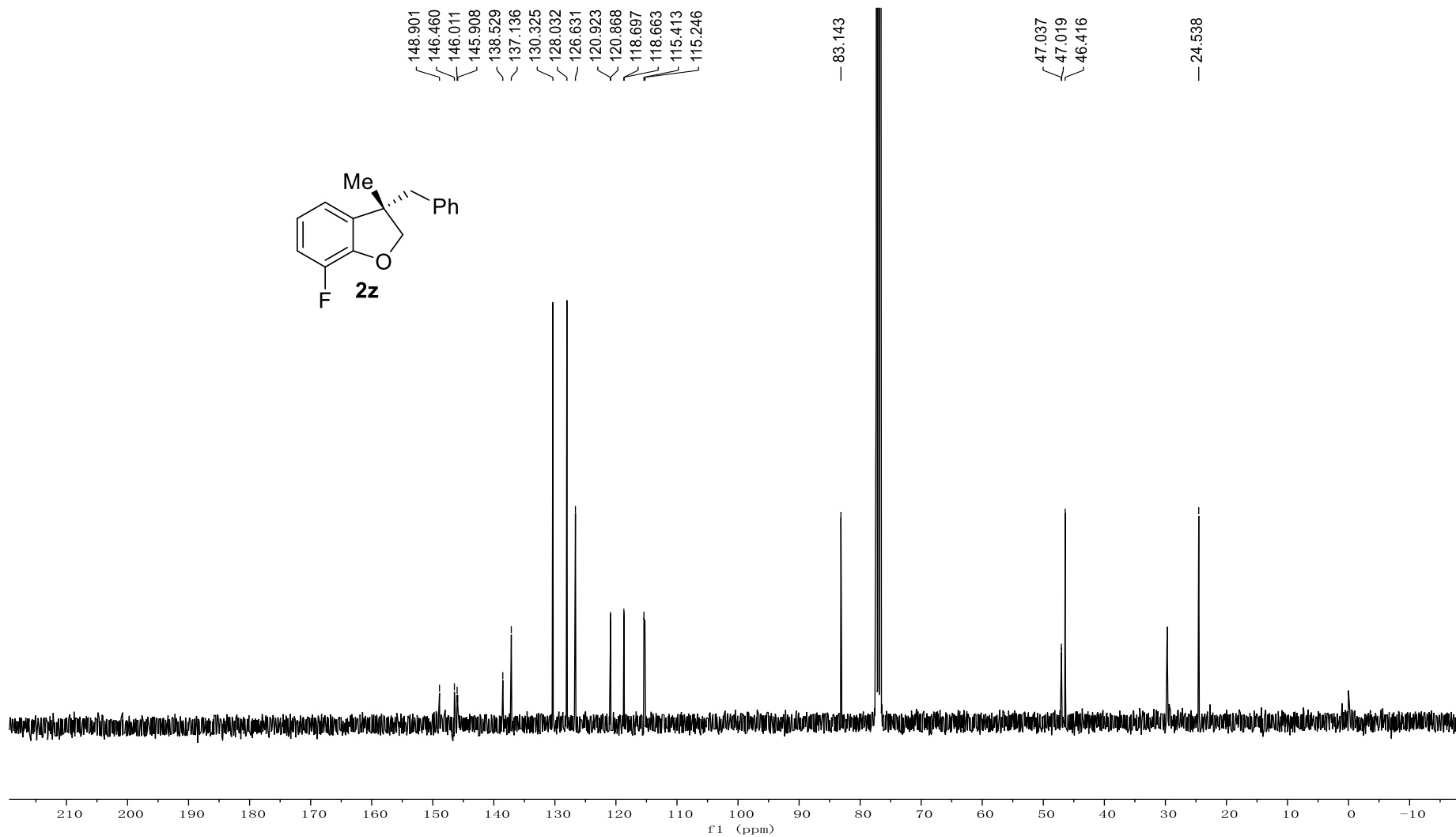


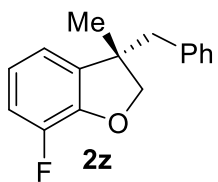
S165



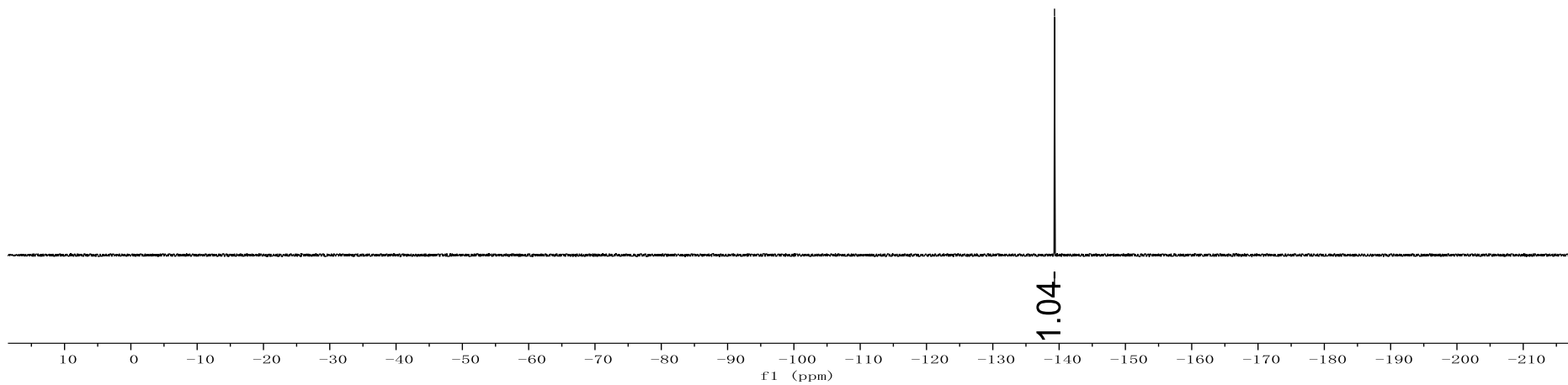


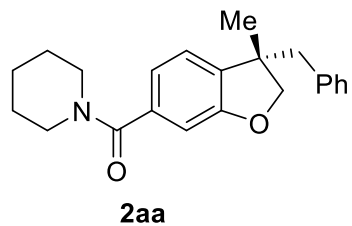
S167





-139.277
-139.289
-139.289
-139.306
-139.317

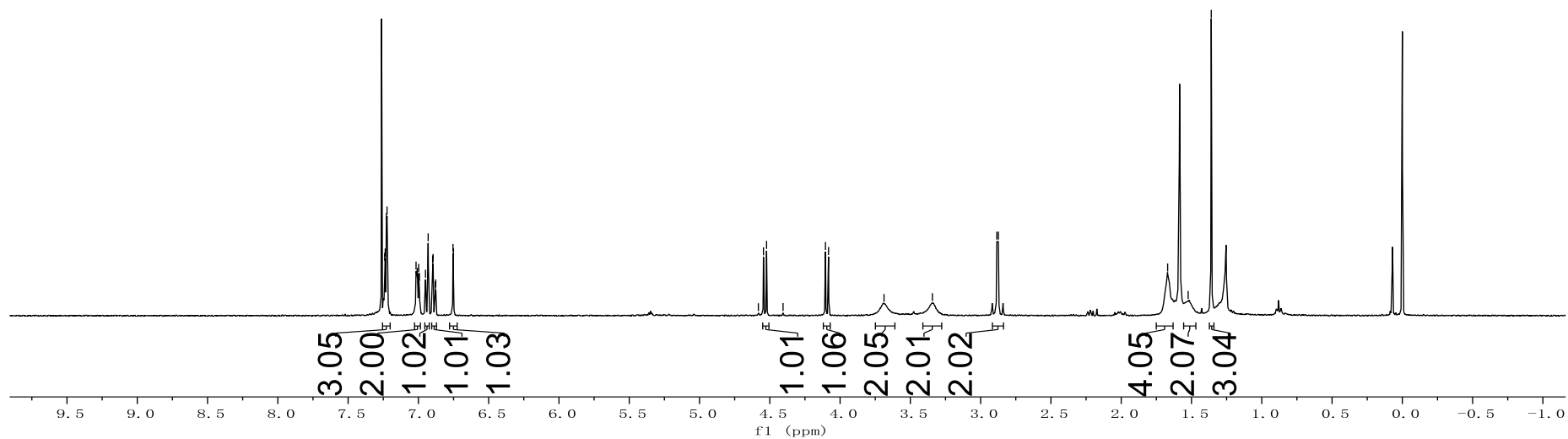




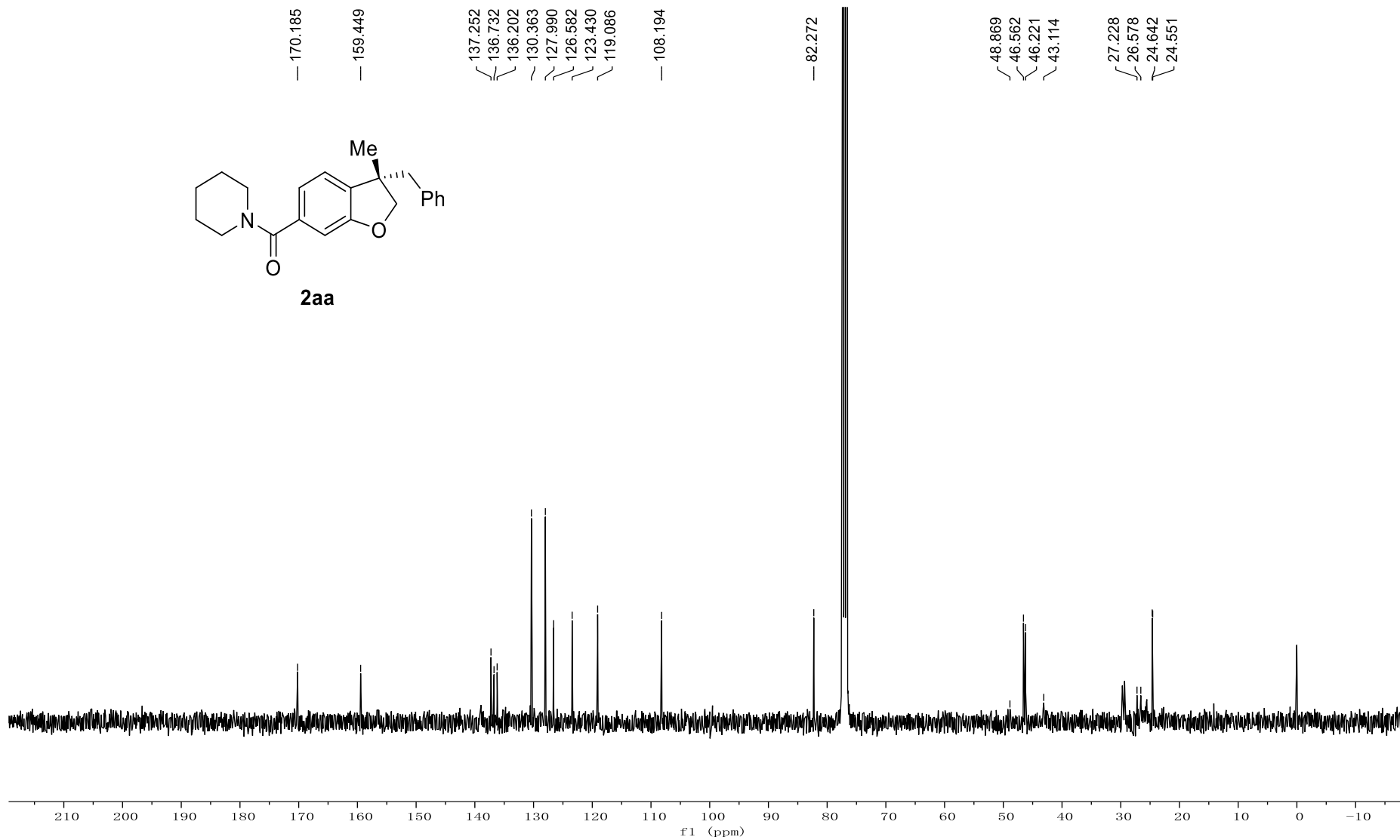
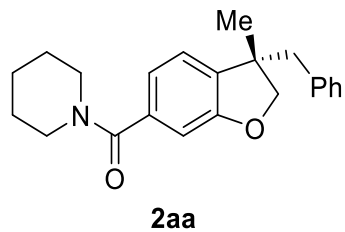
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 6.895
 6.880
 6.876
 6.754
 6.750

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 4.523
 4.406
 4.104
 4.082
 — 3.687
 — 3.343
 2.885
 2.874

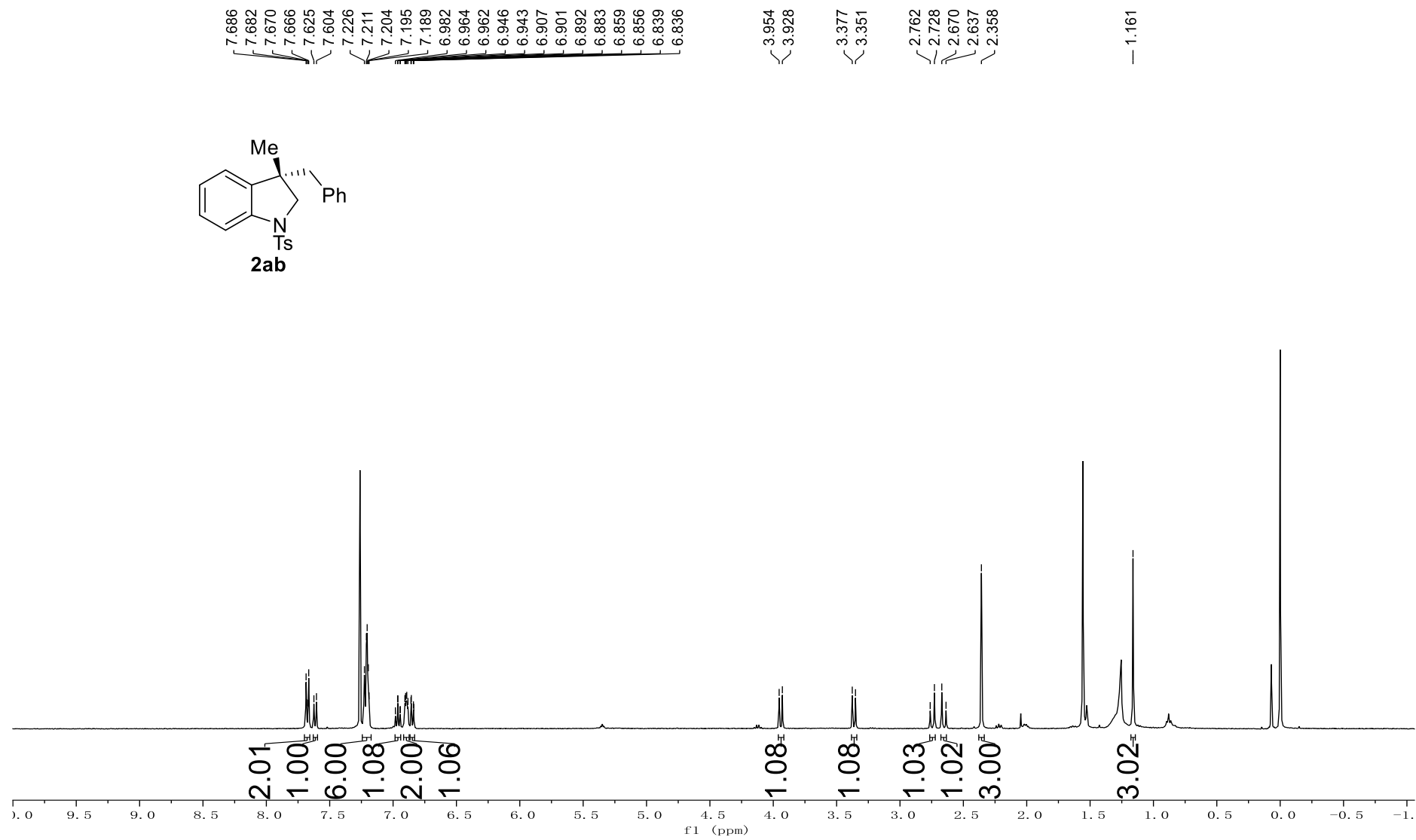
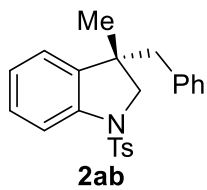
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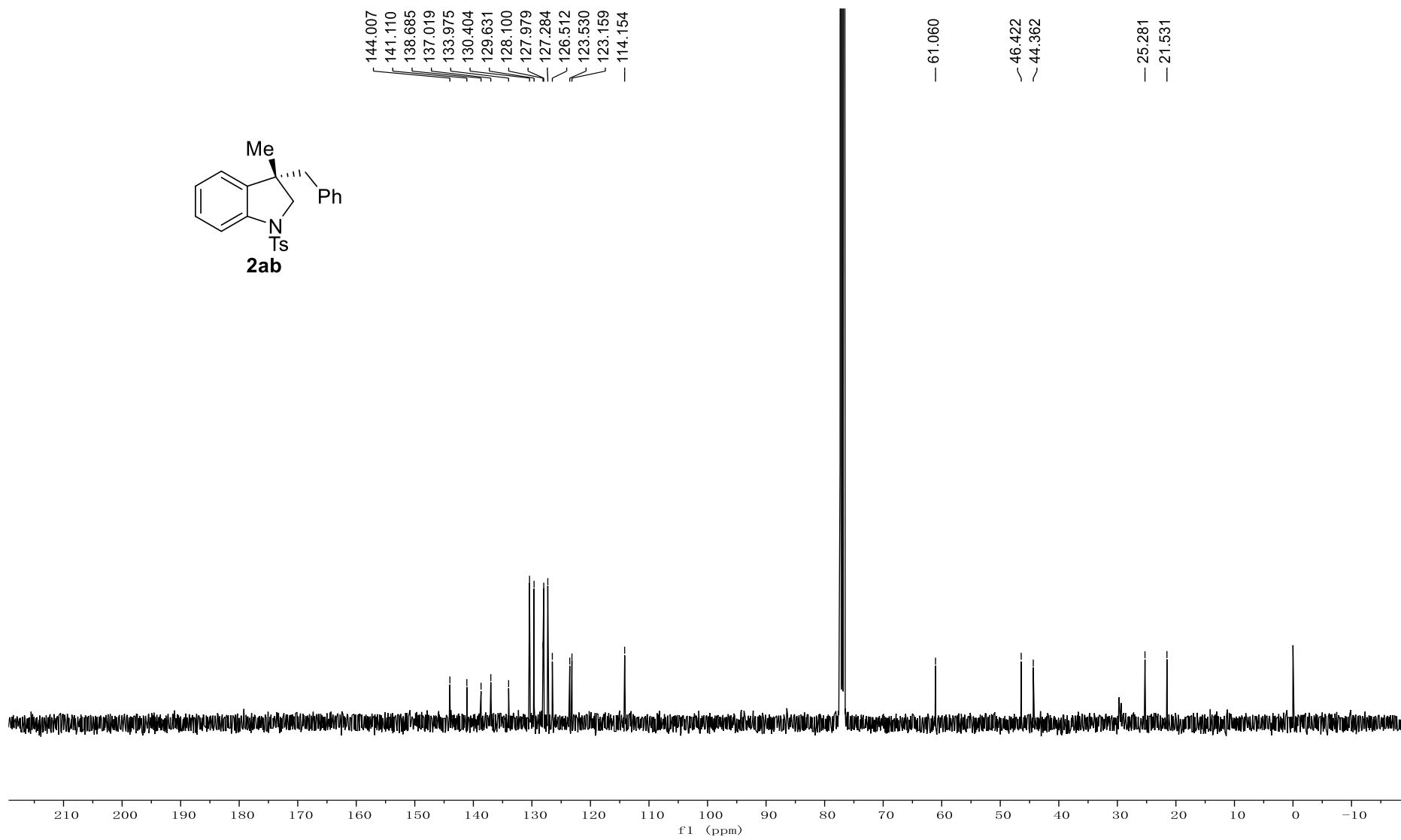
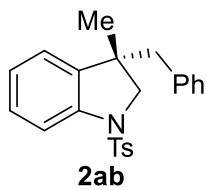


S170

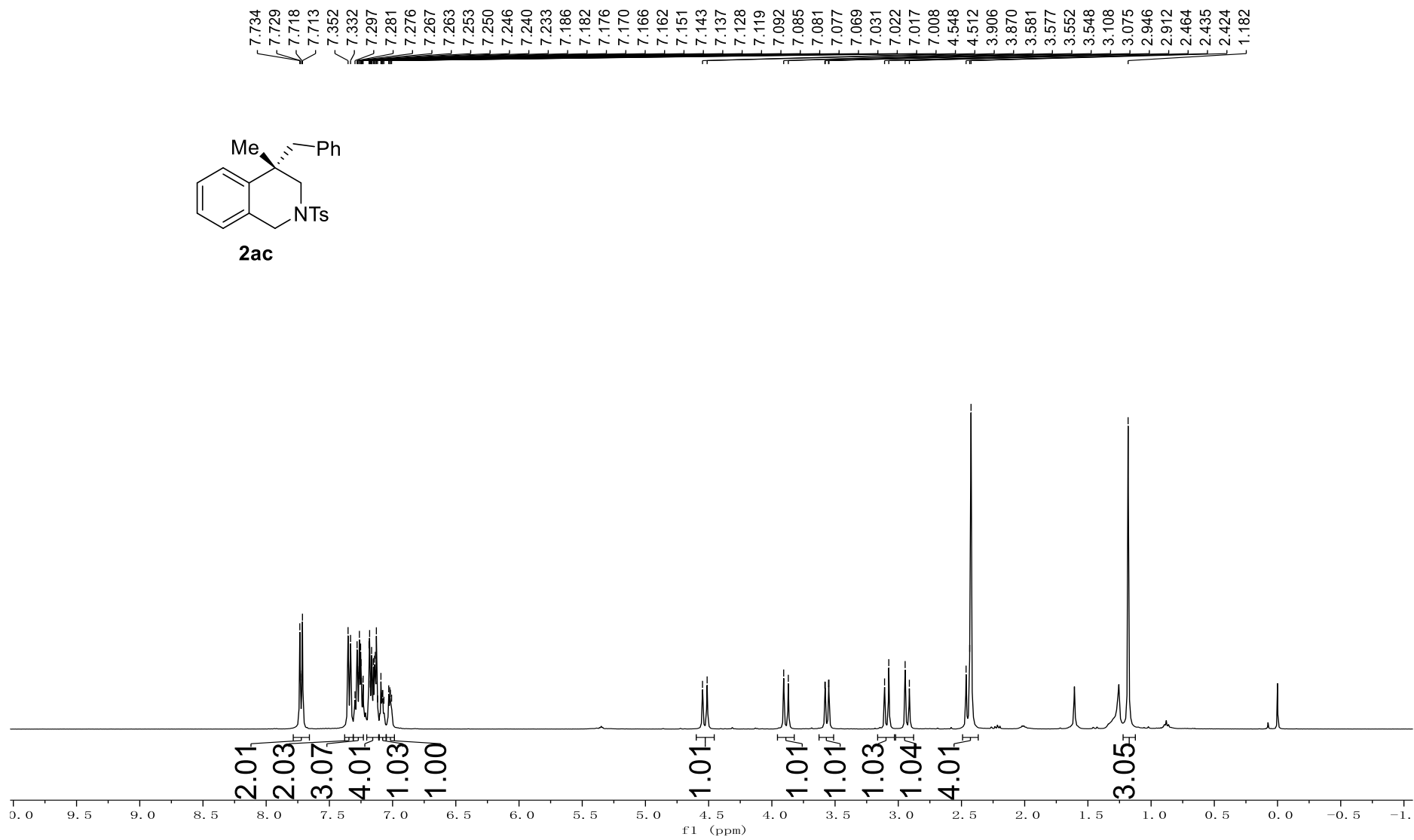
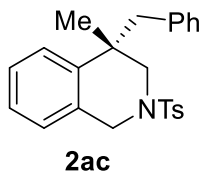


S171

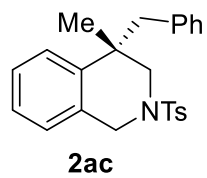




S173



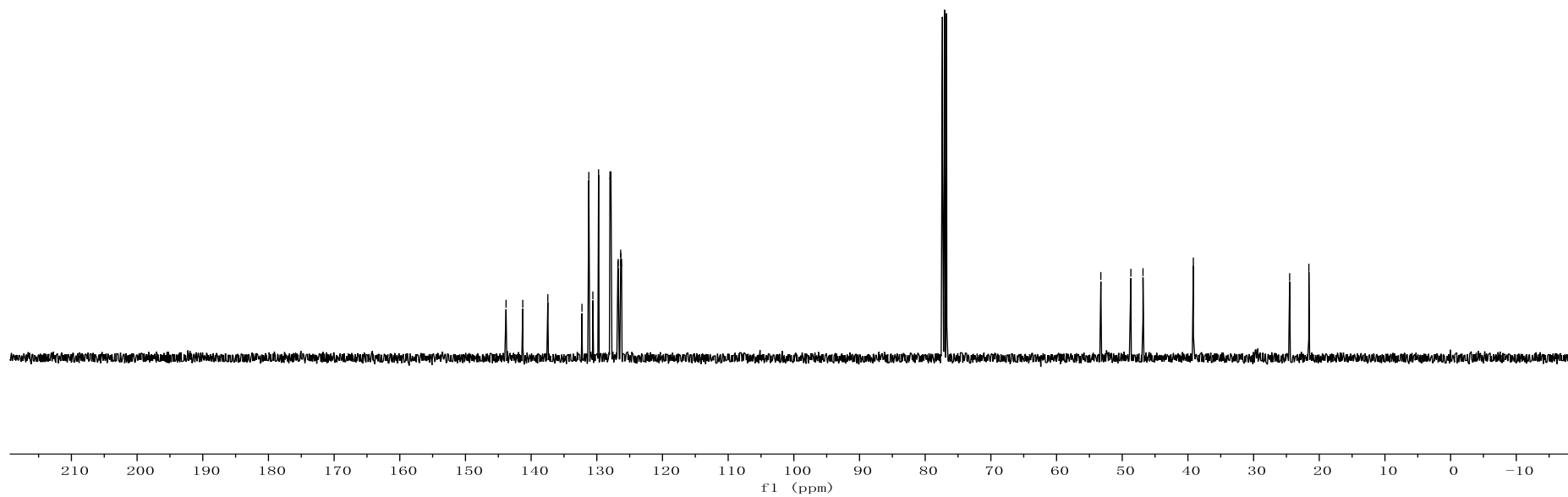
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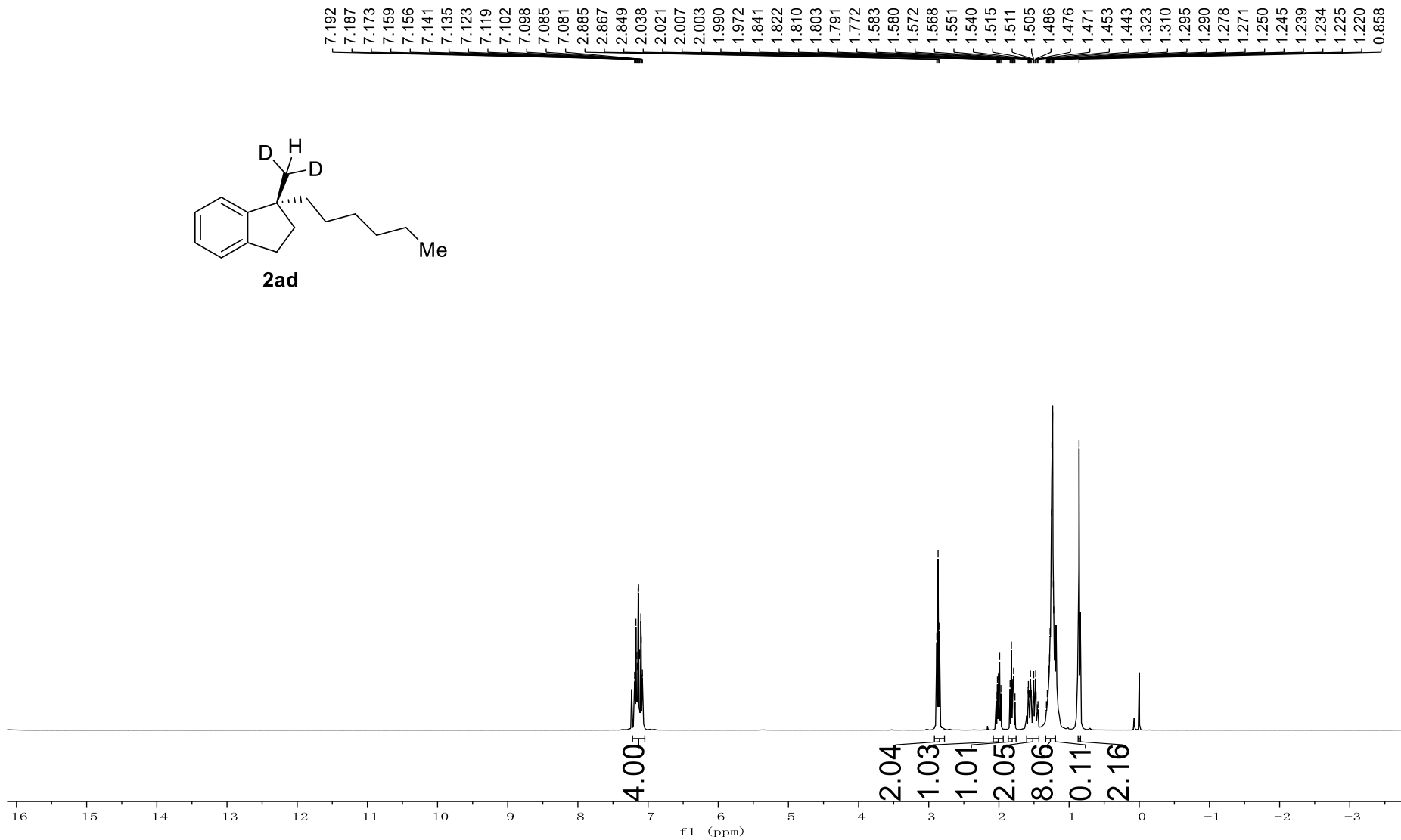
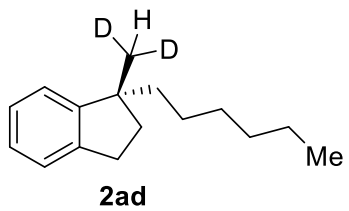


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126.230

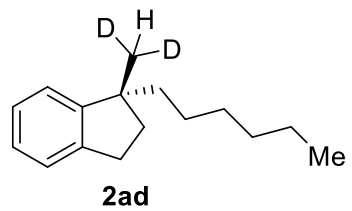
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21.581





S176



— 151.822

— 143.190

└ 126.112

└ 126.082

└ 124.442

└ 122.638

└ 47.219

└ 41.438

└ 38.536

└ 31.889

└ 30.309

└ 30.135

└ 26.502

└ 26.376

└ 26.191

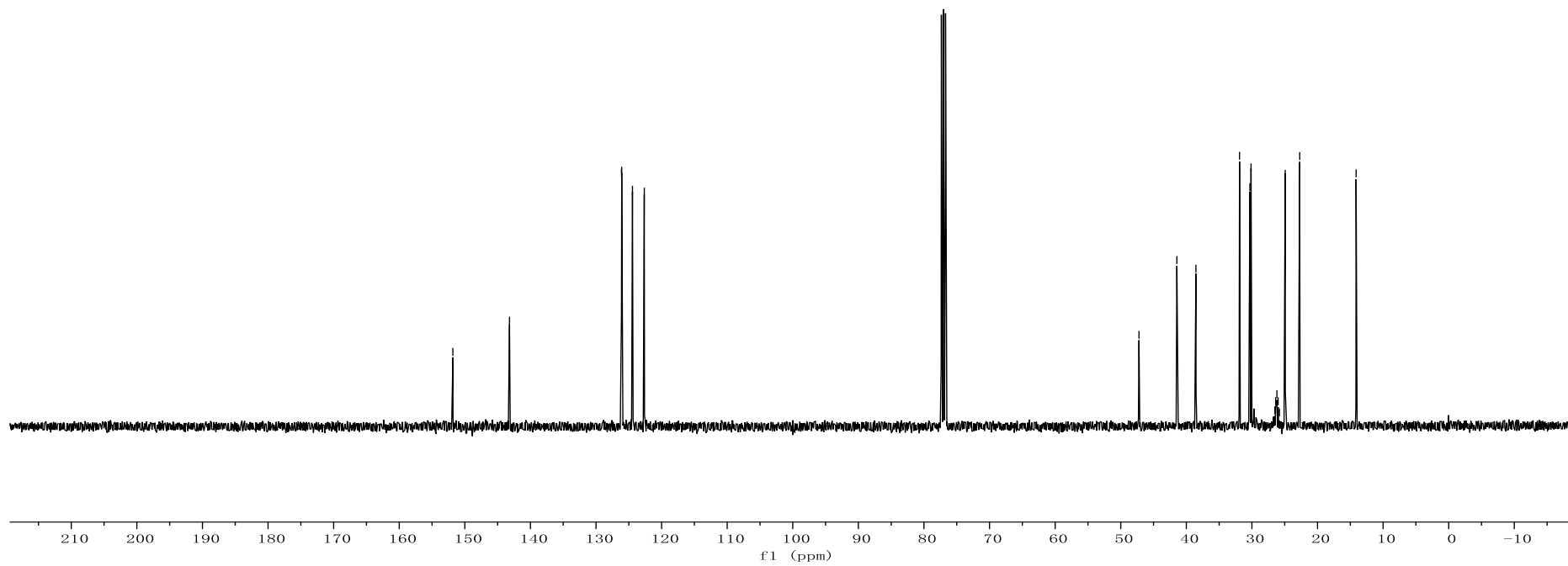
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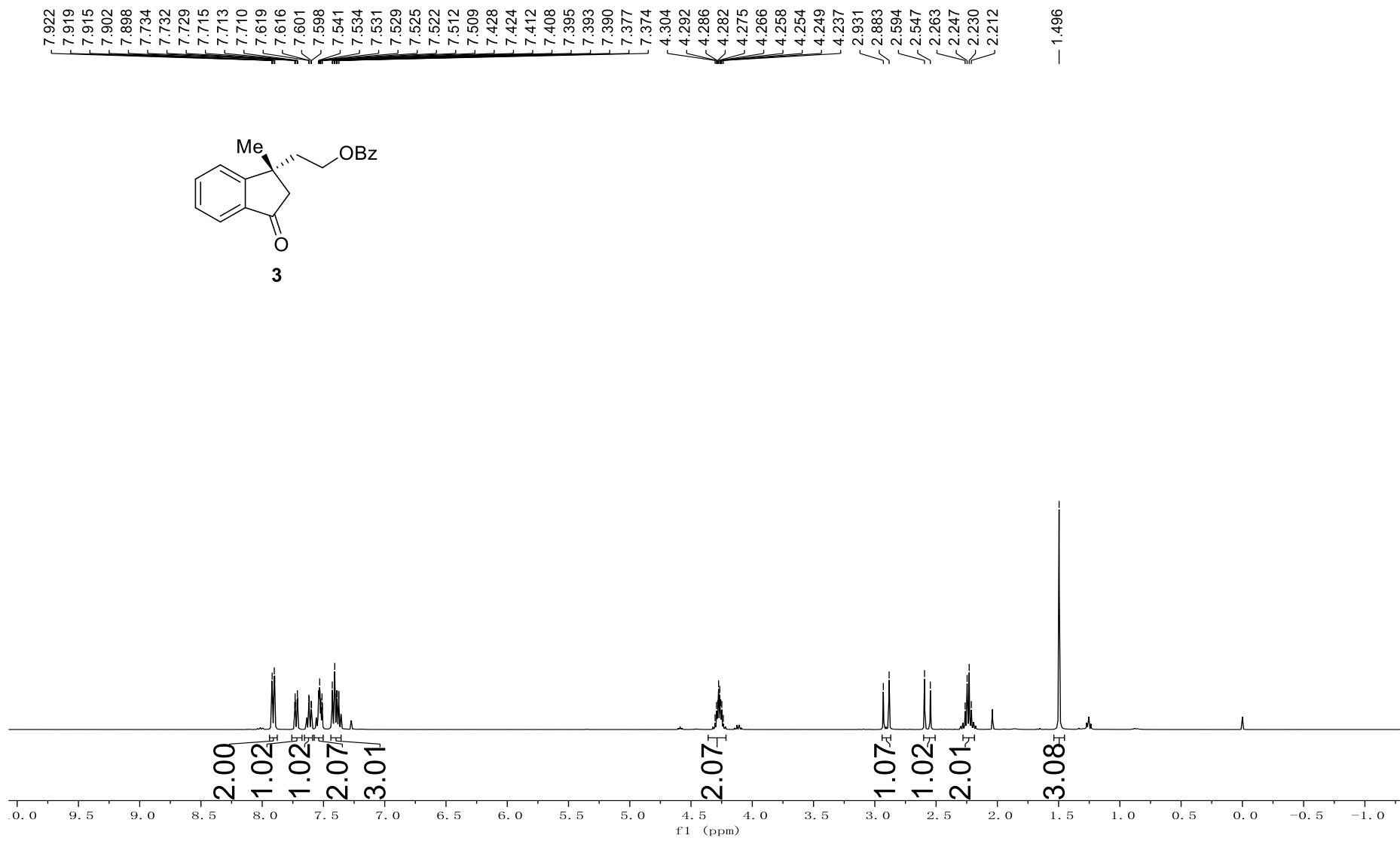
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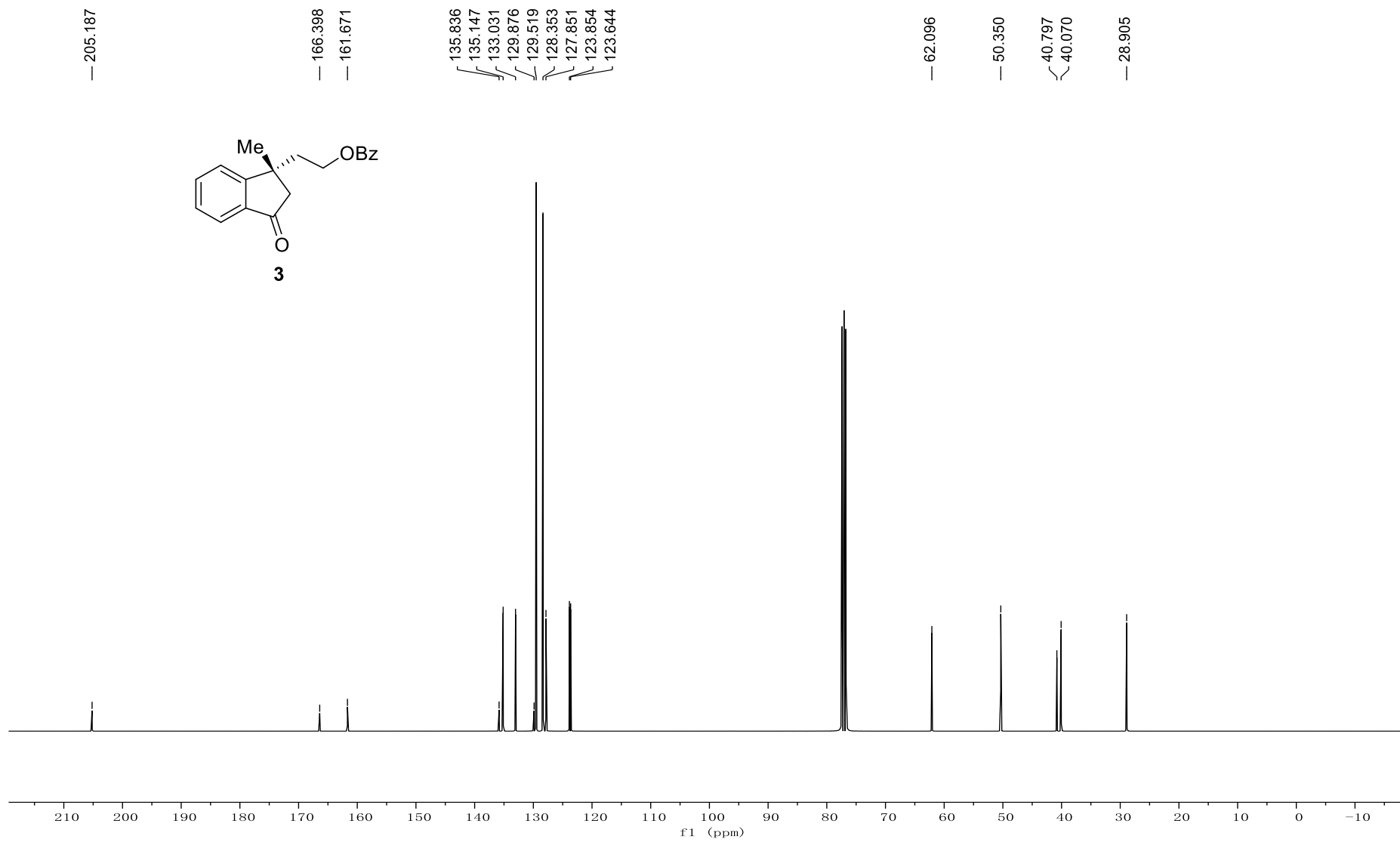
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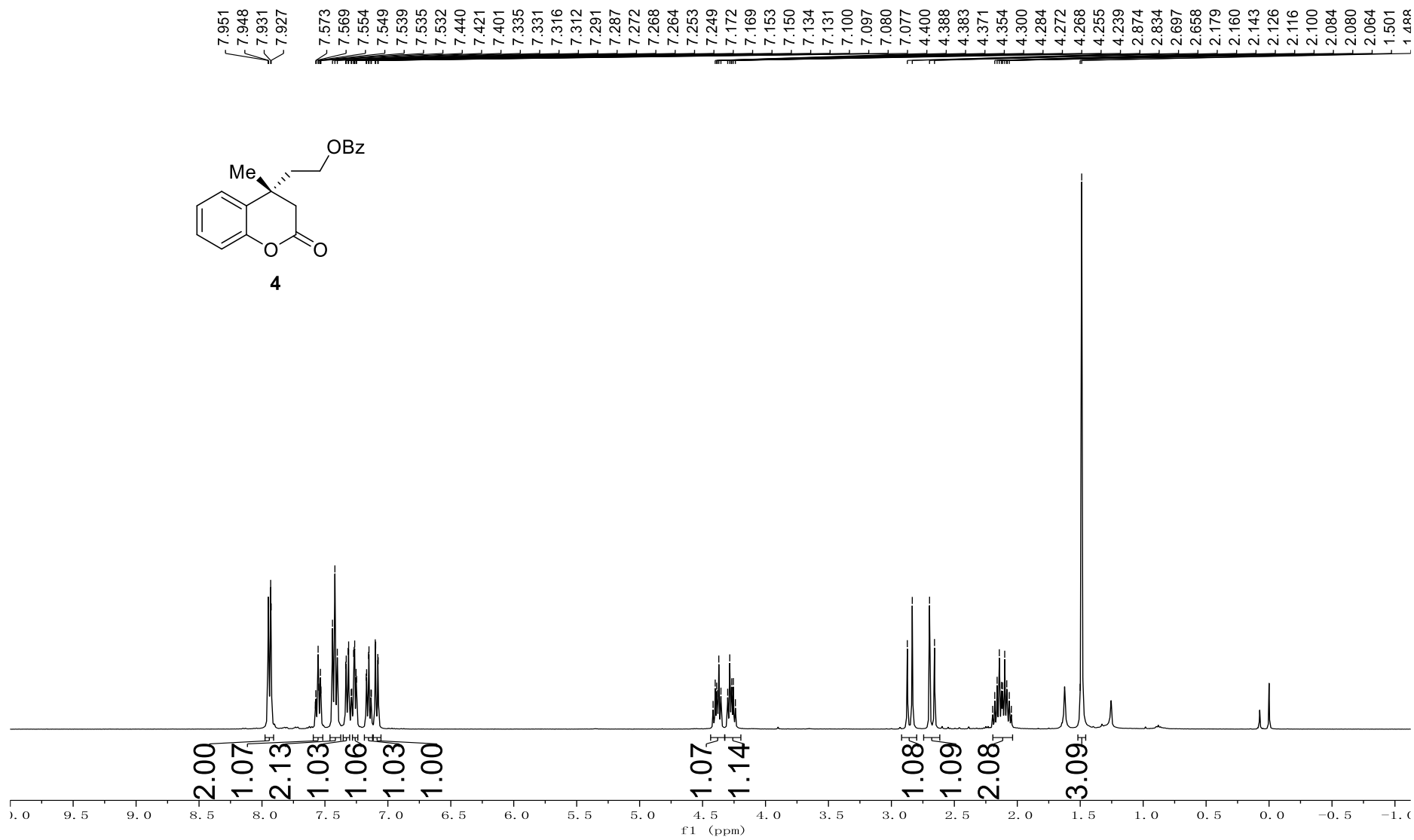
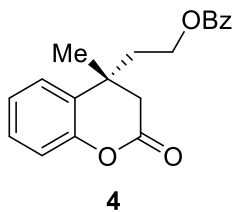


S177

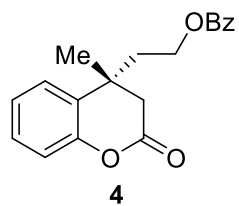


S178





S180



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133.096

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129.573

129.462

128.717

128.373

125.152

124.885

117.471

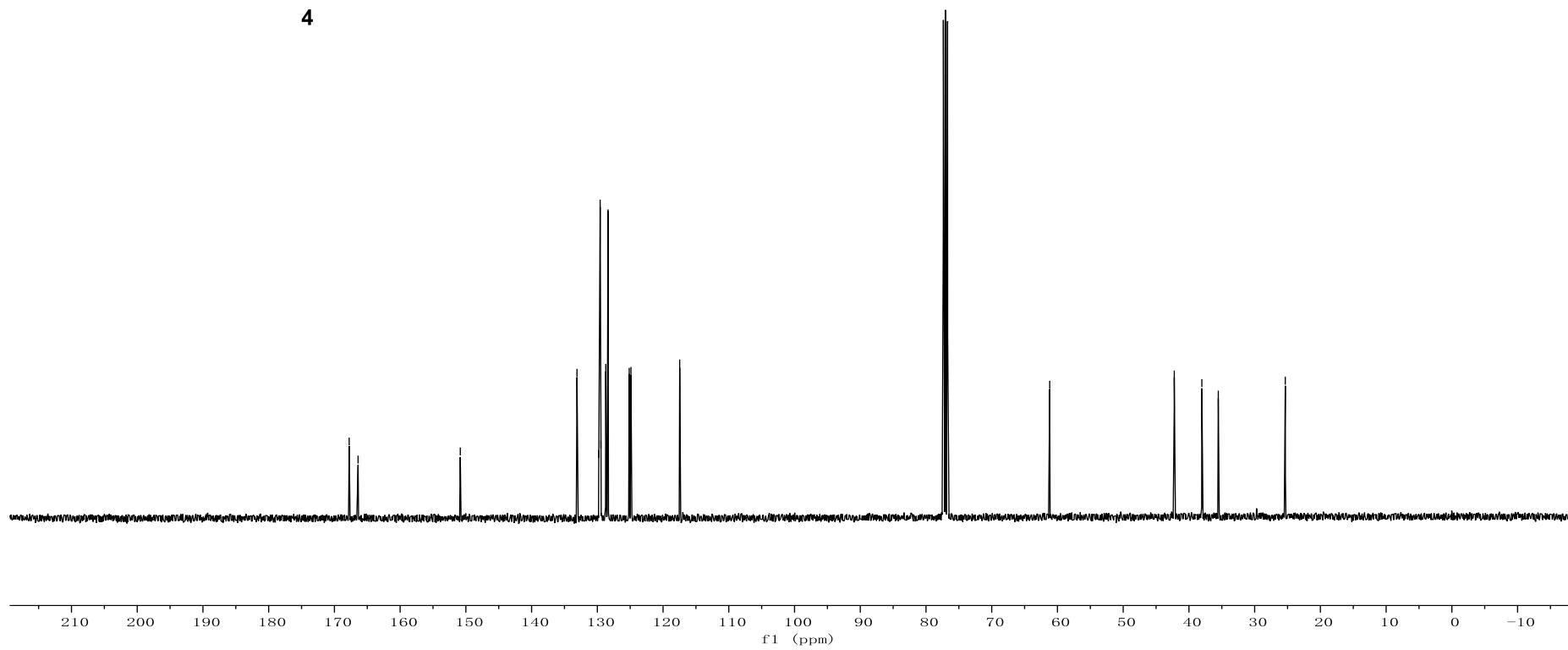
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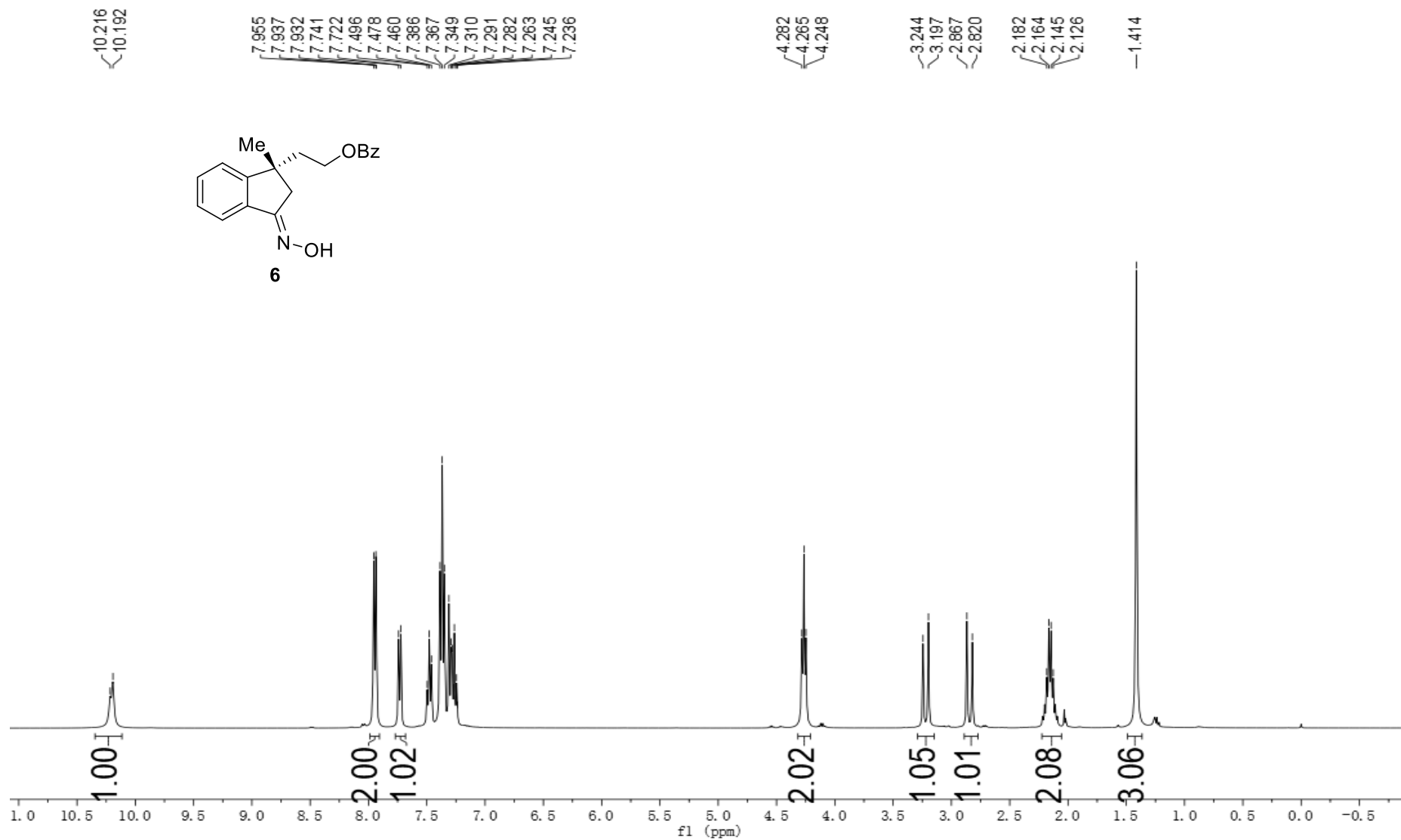
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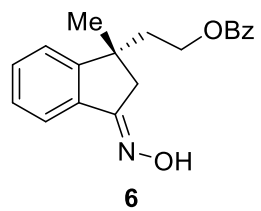
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S181





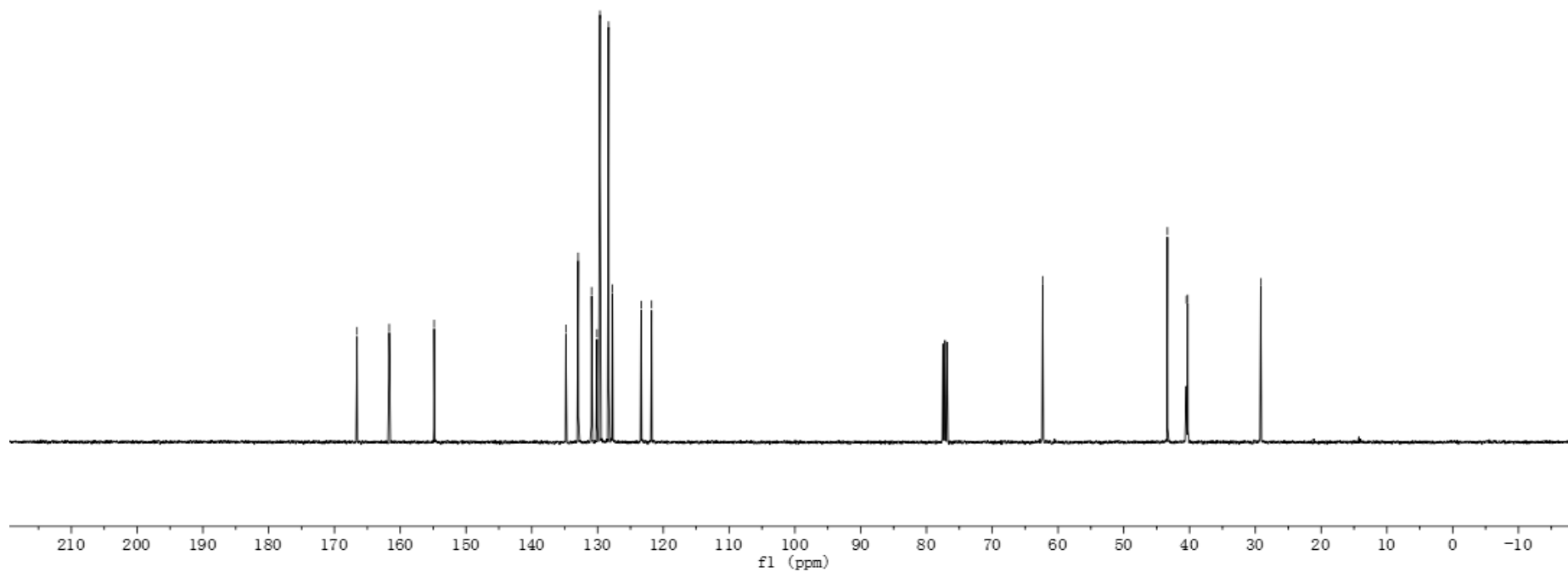
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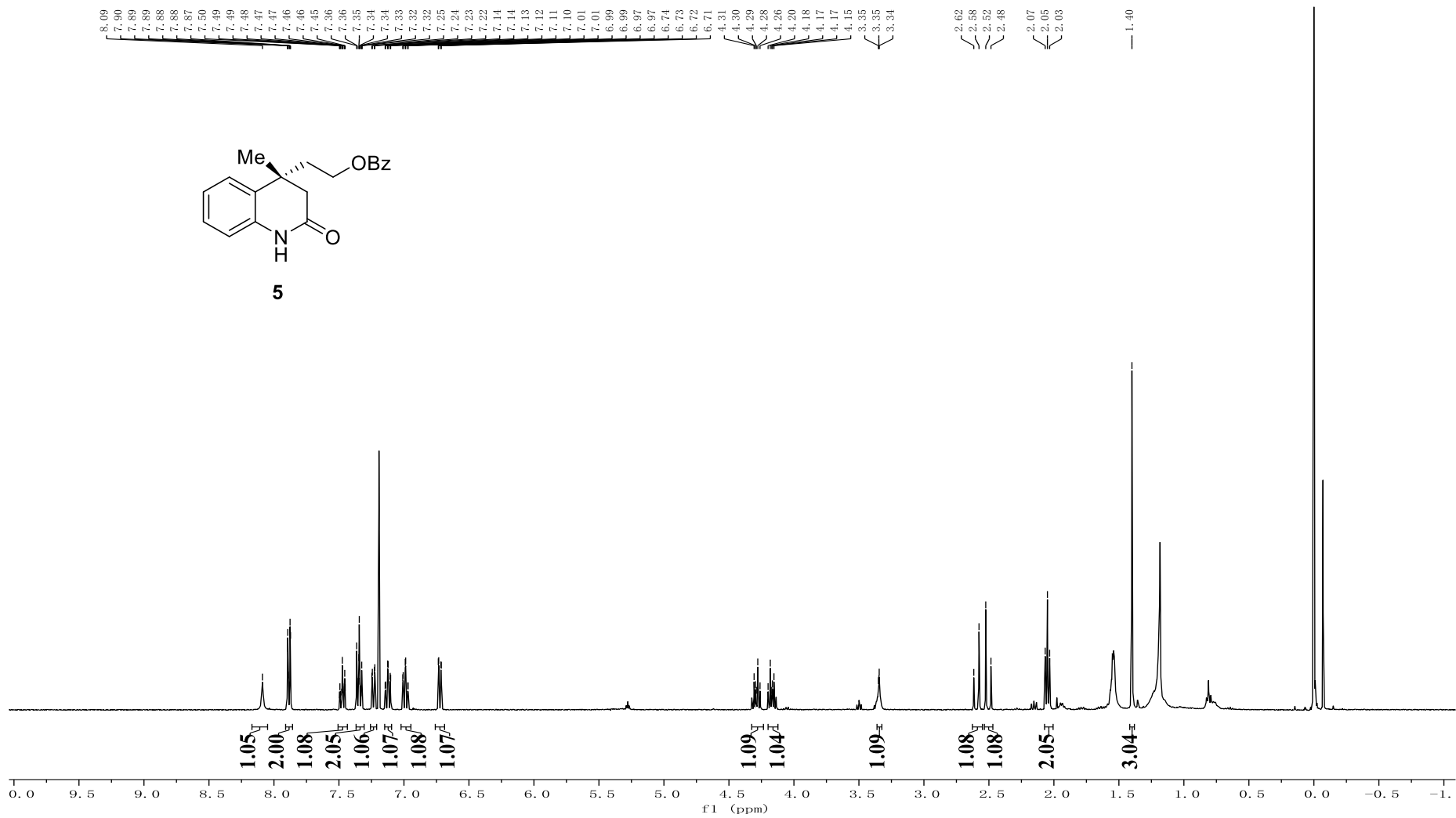
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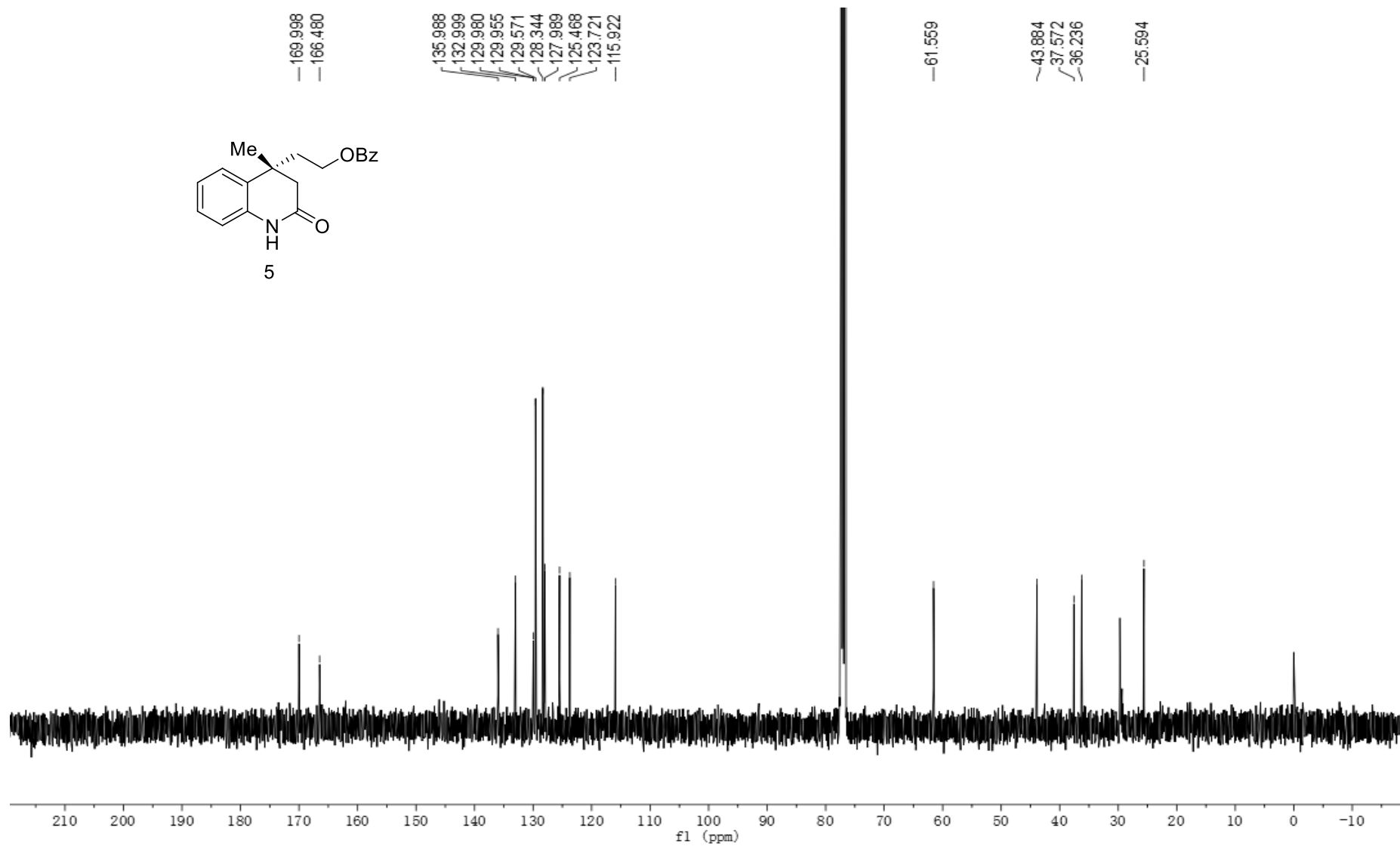
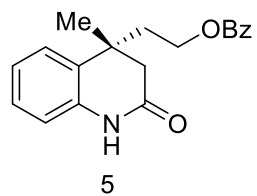
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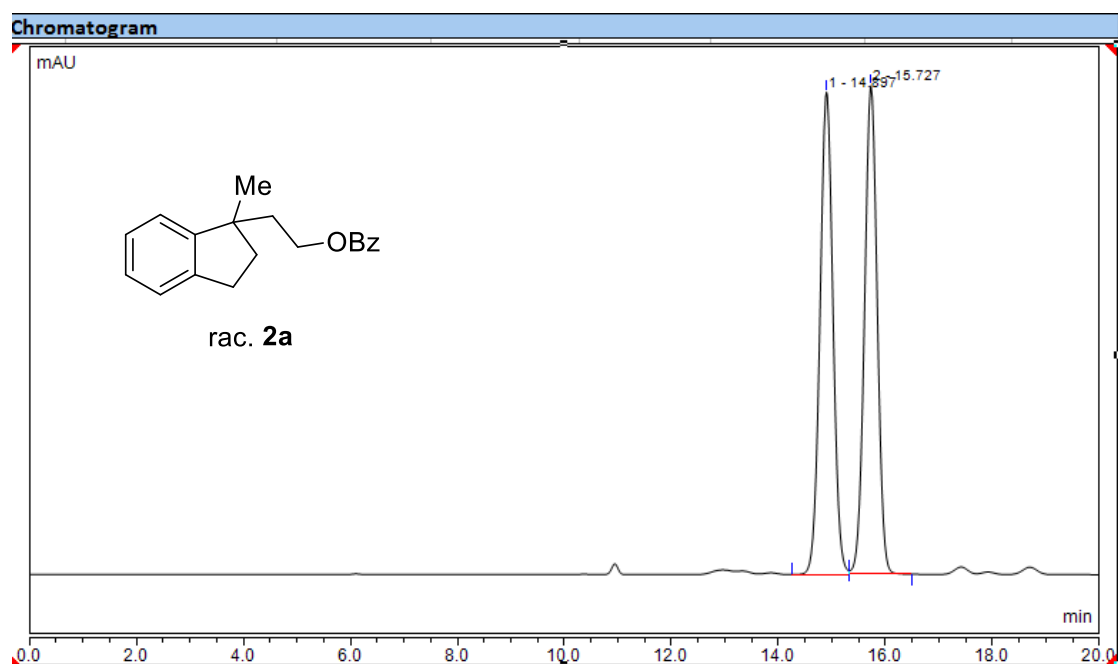
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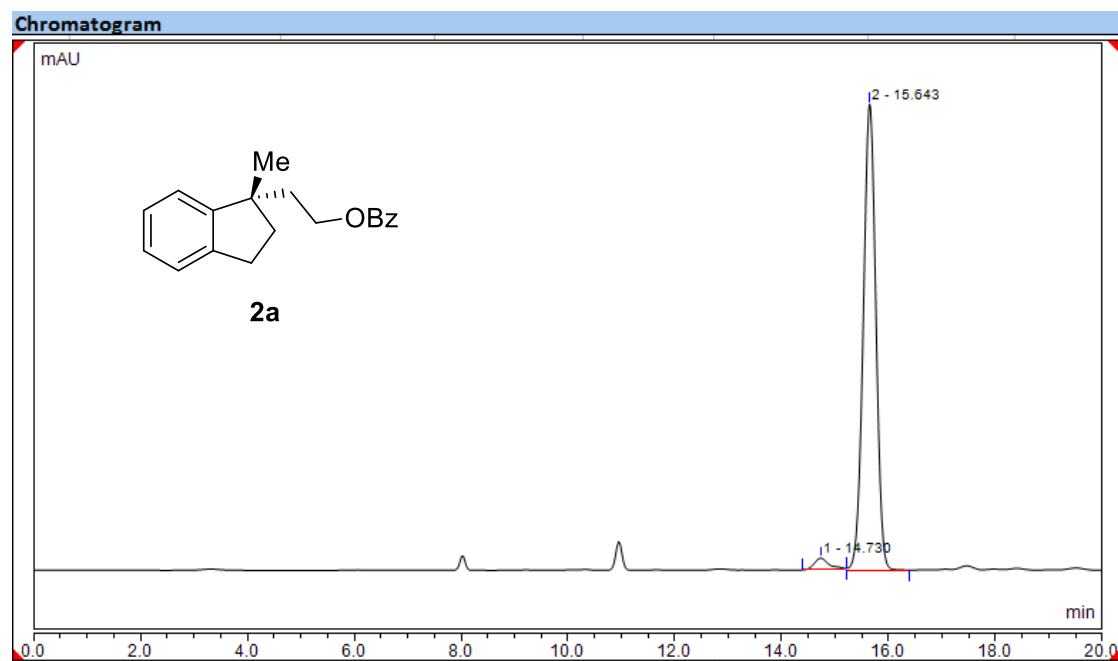


HPLC Data and Chromatograms



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		14.897	115.543	411.373	50.21	49.69	n.a.
2		15.727	114.562	416.565	49.79	50.31	n.a.
Total:			230.105	827.938	100.00	100.00	

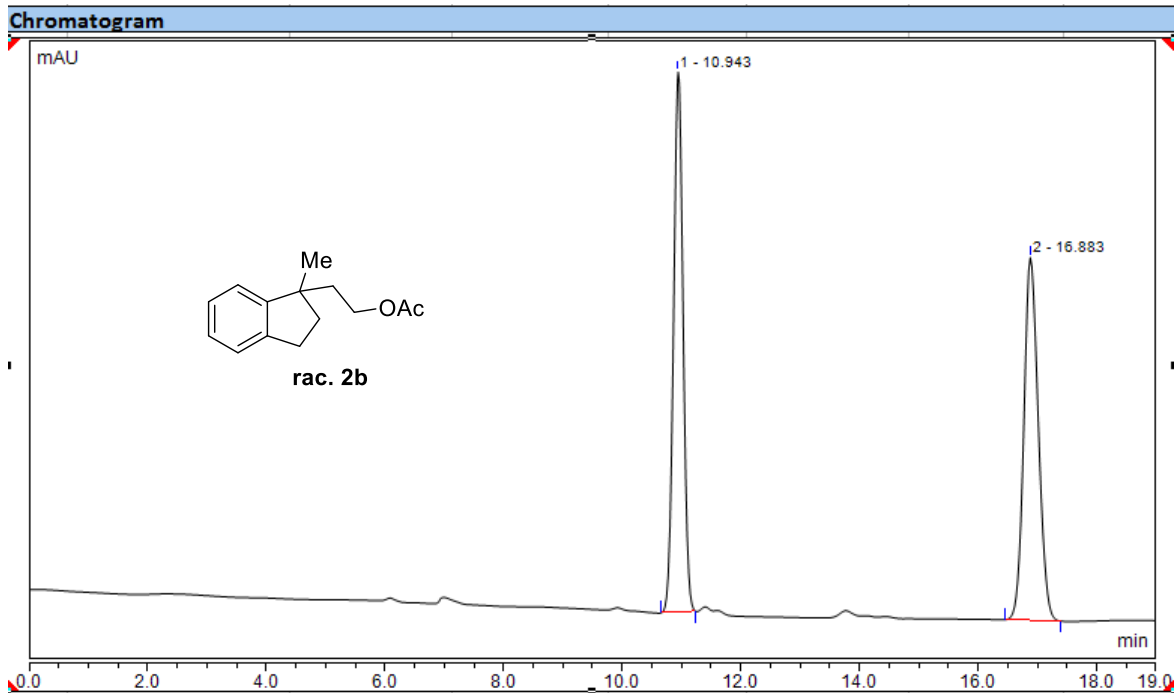


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		14.730	6.906	20.283	3.10	2.48	n.a.
2		15.643	216.205	796.045	96.90	97.52	n.a.
Total:			223.111	816.328	100.00	100.00	

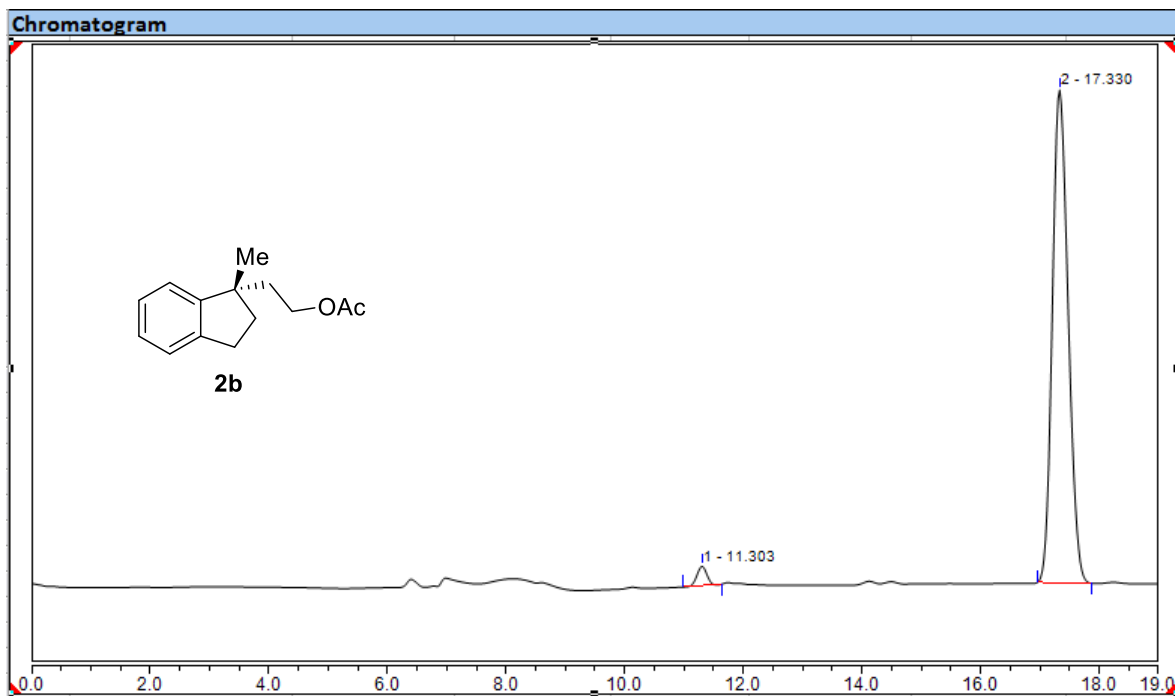
HPLC (Chiral MD): t_R = 14.7 (minor), 15.6 (major)

Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		10.943	145.676	787.289	49.42	59.80	n.a.
2		16.883	149.084	529.149	50.58	40.20	n.a.
Total:			294.760	1316.438	100.00	100.00	

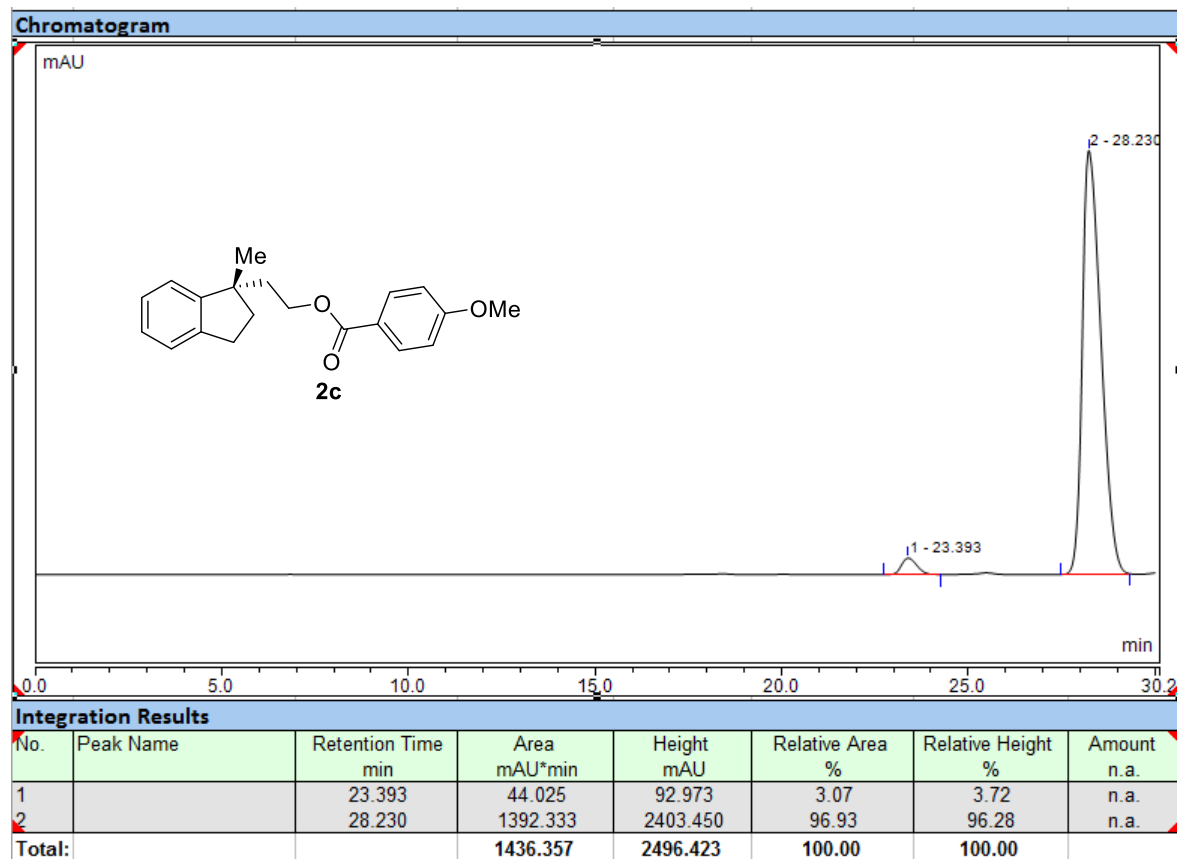
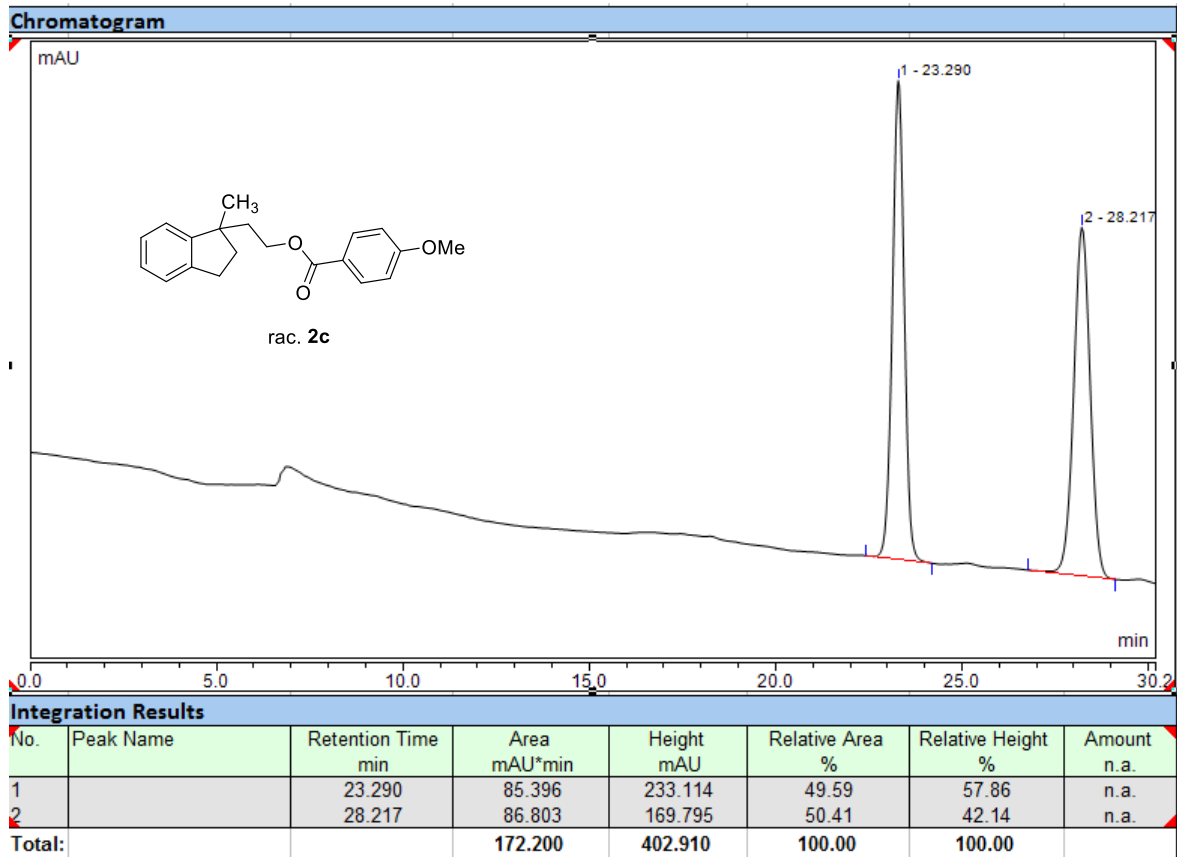


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.303	4.718	25.169	2.34	3.78	n.a.
2		17.330	197.145	640.042	97.66	96.22	n.a.
Total:			201.864	665.211	100.00	100.00	

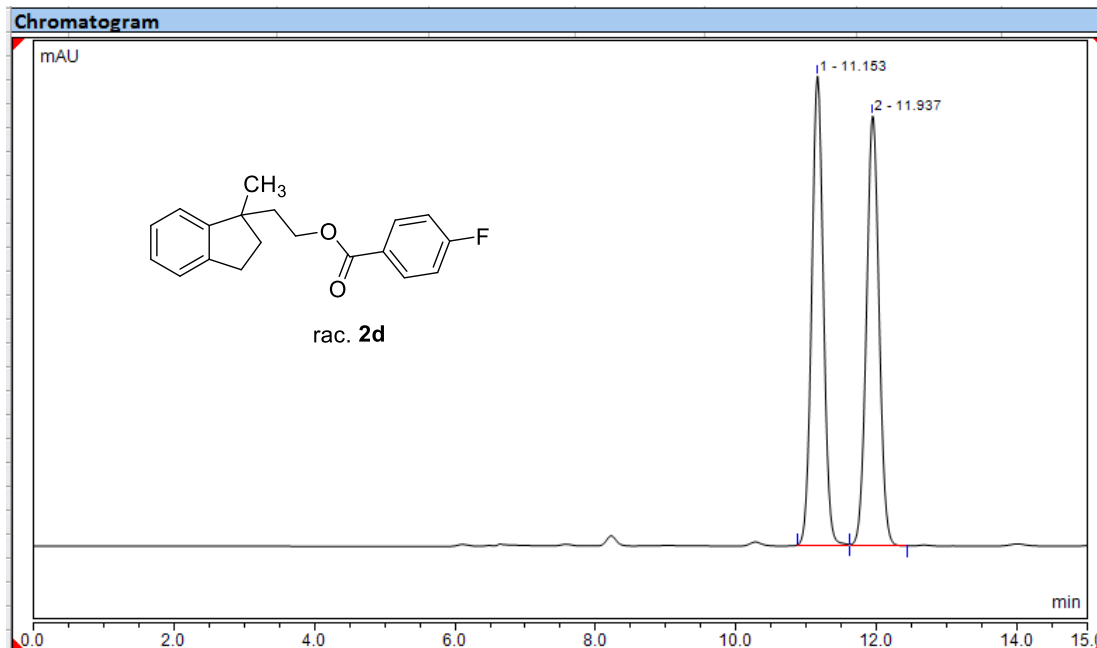
HPLC (Chiral MD): t_R = 11.3 (minor), 17.3 (major)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



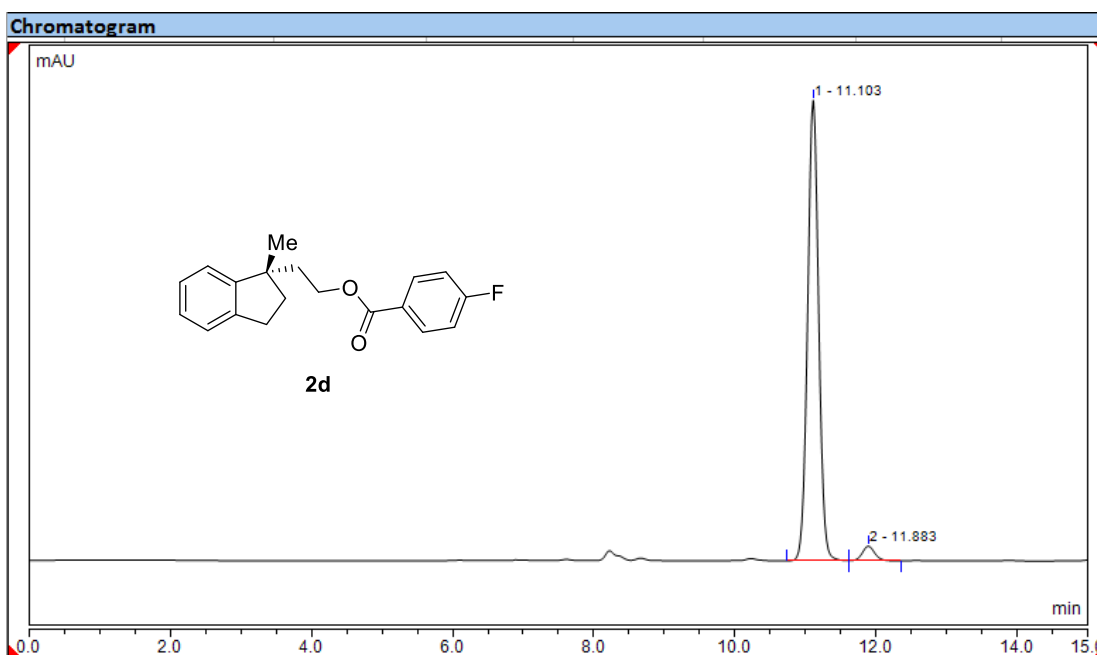
HPLC (Chiral MD): t_R = 23.4 (minor), 28.2 (major)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.153	124.640	649.655	50.19	52.19	n.a.
2		11.937	123.684	595.234	49.81	47.81	n.a.
Total:			248.323	1244.889	100.00	100.00	

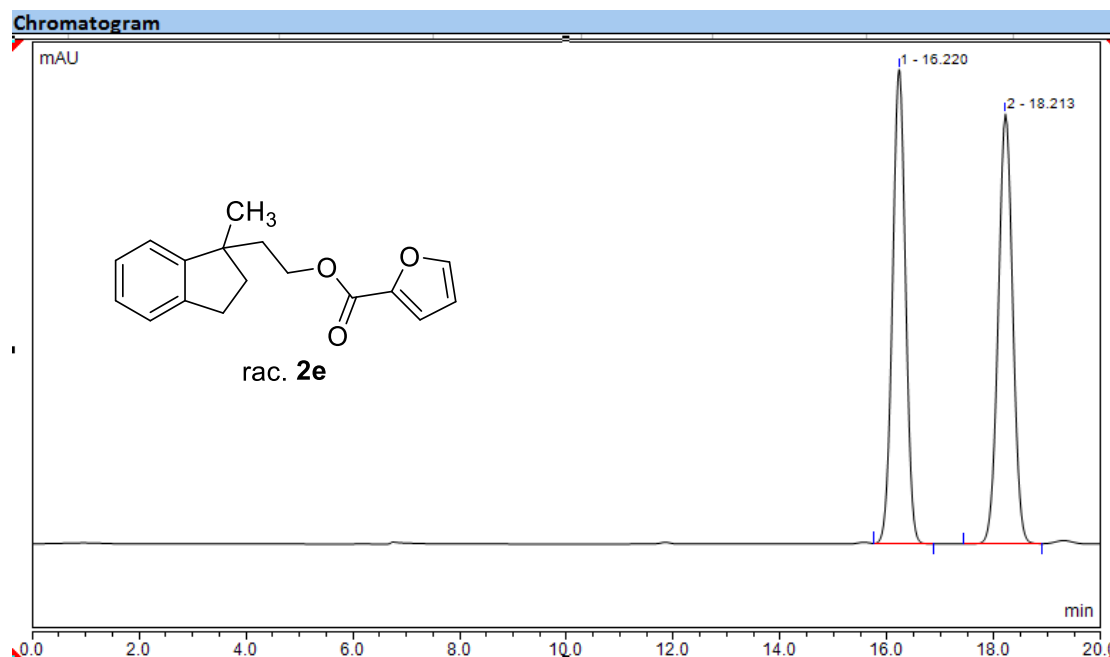


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.103	129.076	715.317	96.53	96.91	n.a.
2		11.883	4.643	22.808	3.47	3.09	n.a.
Total:			133.719	738.125	100.00	100.00	

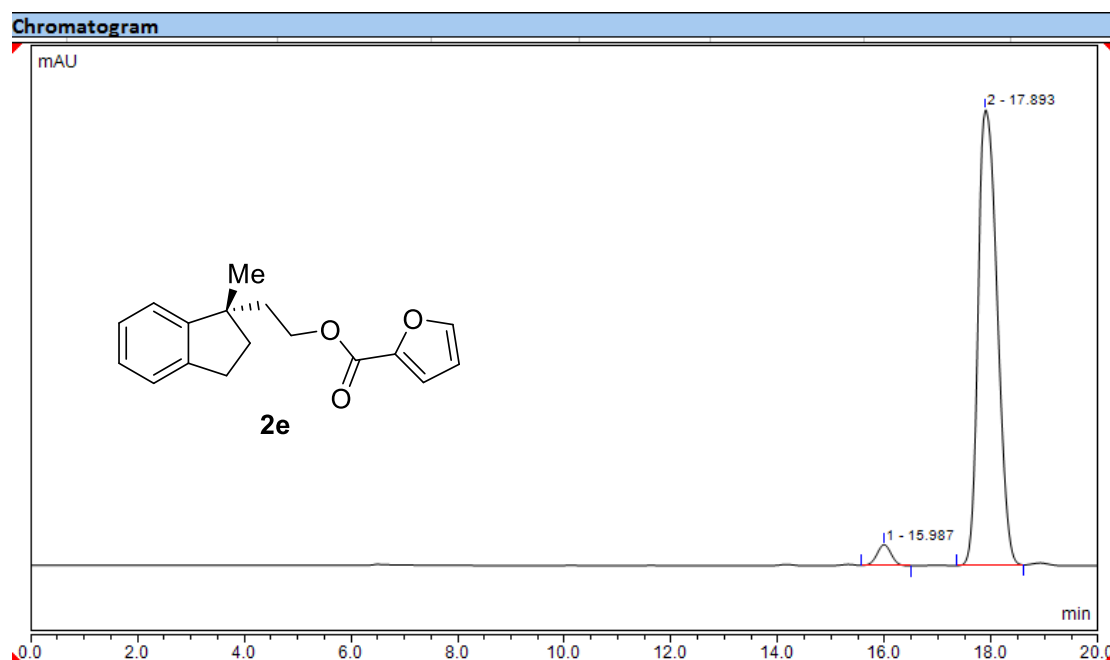
HPLC (Chiral MD): t_R =11.1 (major), 11.9 (minor)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.220	79.845	283.705	49.67	52.45	n.a.
2		18.213	80.901	257.225	50.33	47.55	n.a.
Total:			160.747	540.930	100.00	100.00	

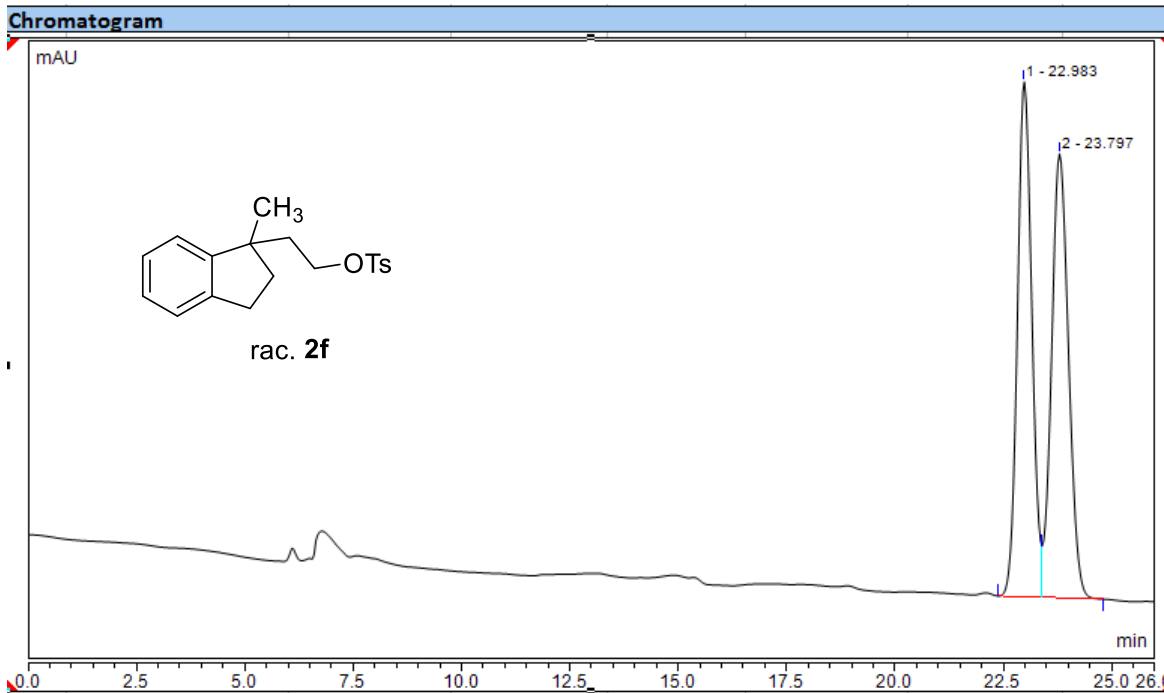


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.987	49.483	160.742	3.30	4.38	n.a.
2		17.893	1450.195	3506.425	96.70	95.62	n.a.
Total:			1499.678	3667.167	100.00	100.00	

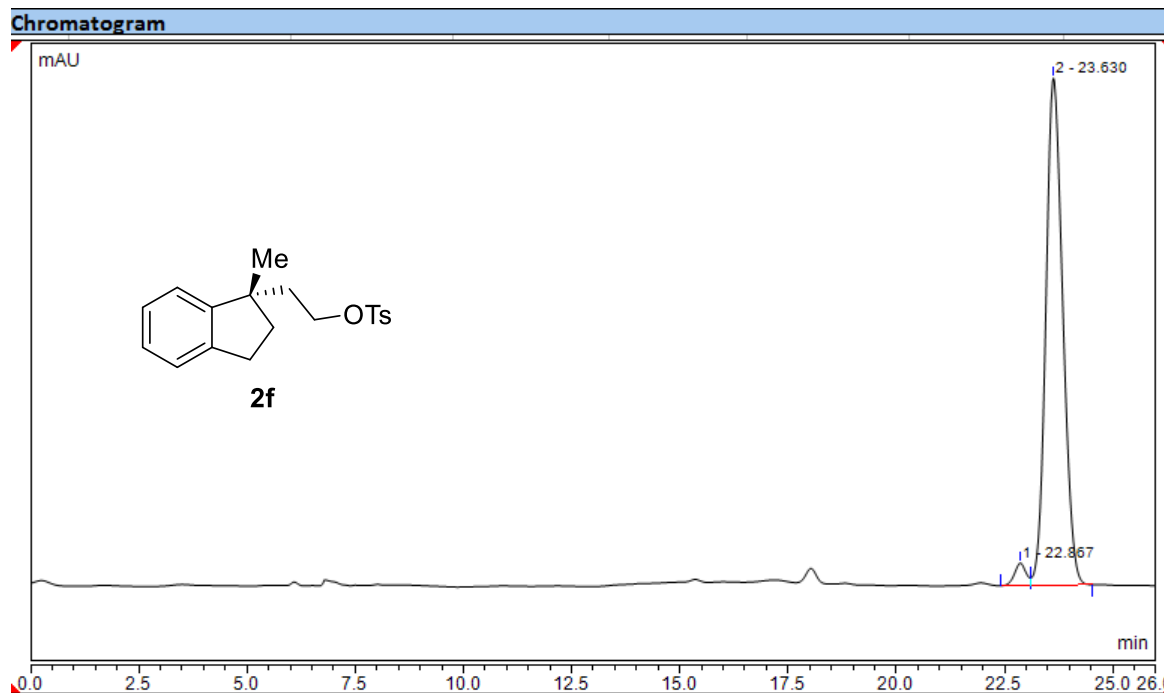
HPLC (Chiral MD): t_R = 16.0 (minor), 17.9 (major)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		22.983	160.449	417.272	49.54	53.70	n.a.
2		23.797	163.426	359.815	50.46	46.30	n.a.
Total:			323.875	777.086	100.00	100.00	

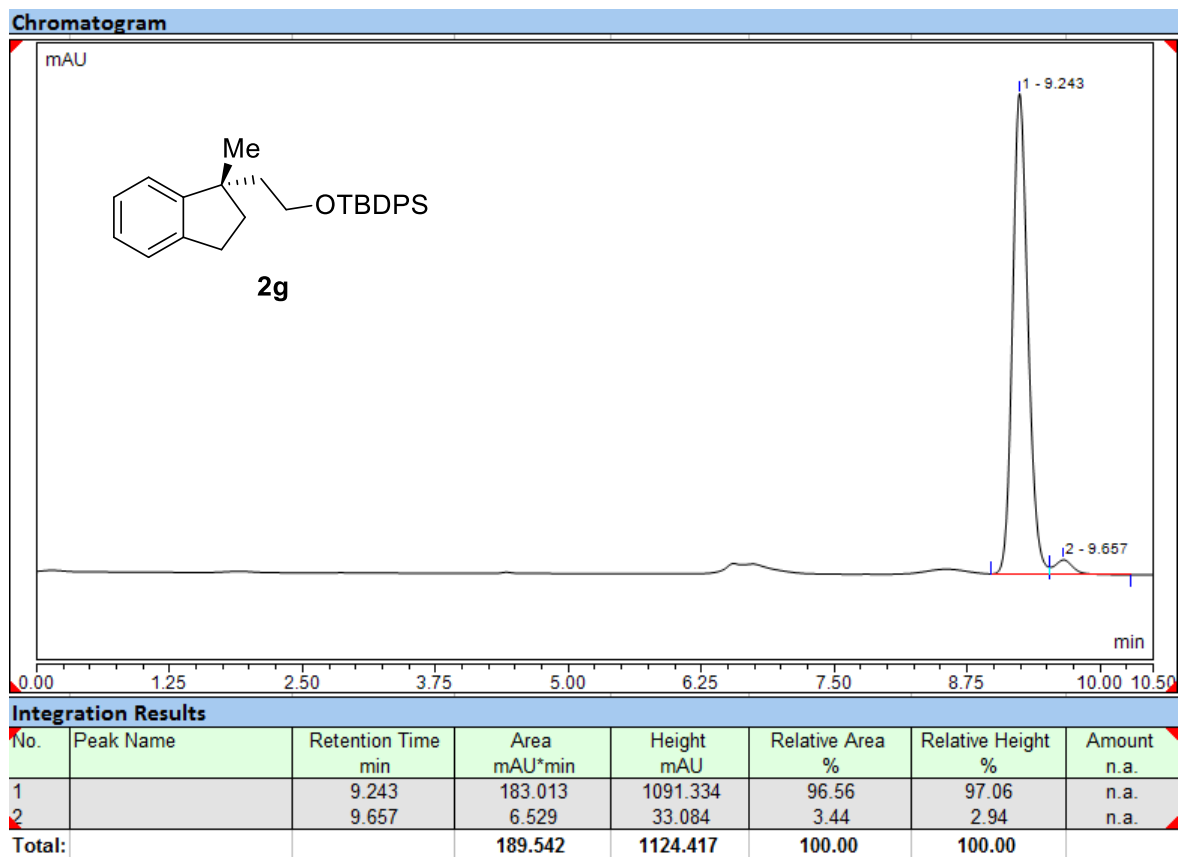
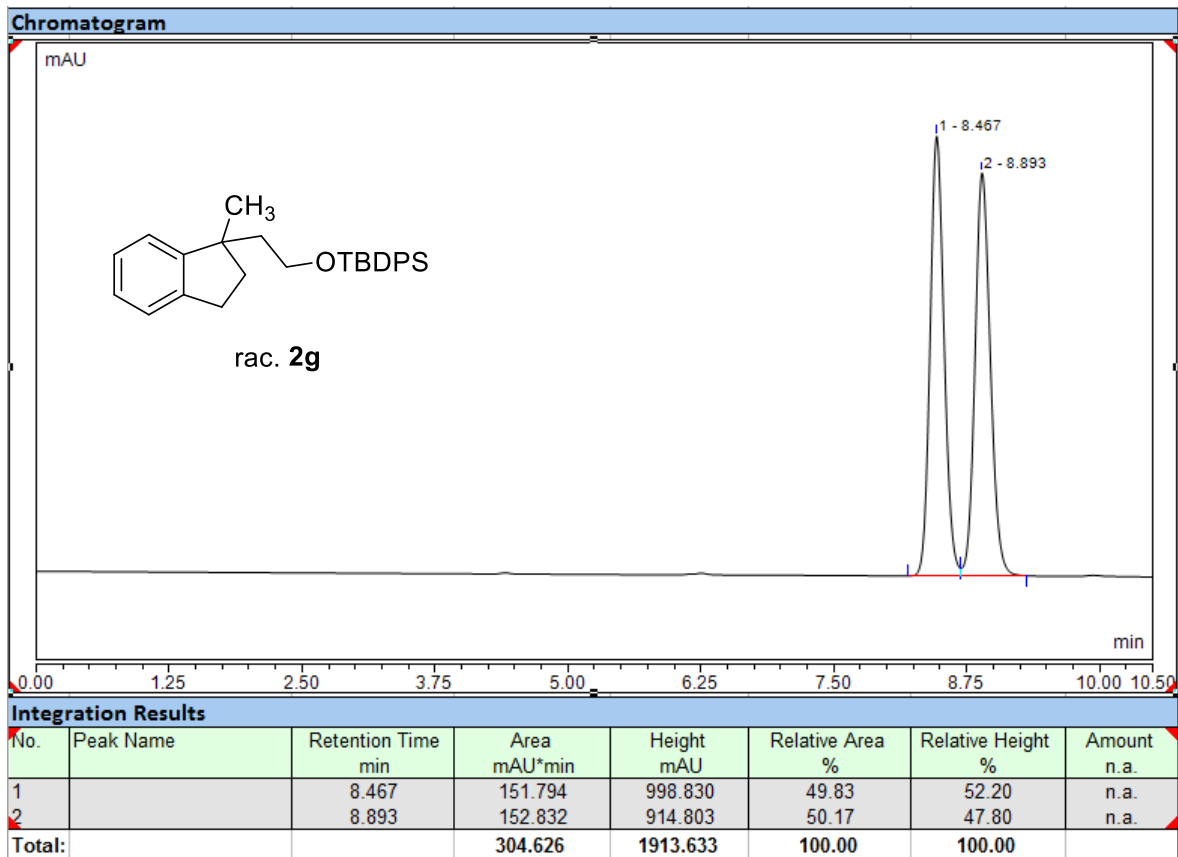


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		22.867	8.947	29.367	2.91	4.27	n.a.
2		23.630	298.107	657.772	97.09	95.73	n.a.
Total:			307.054	687.140	100.00	100.00	

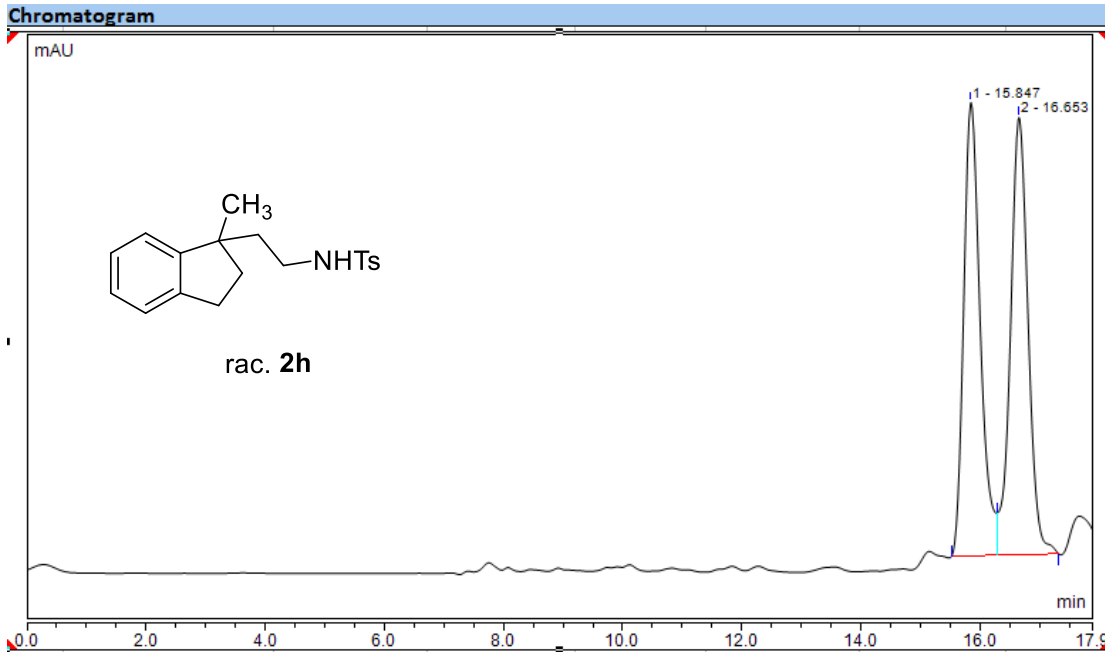
HPLC (Chiral MD): t_R = 22.9 (minor), 23.6 (major)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



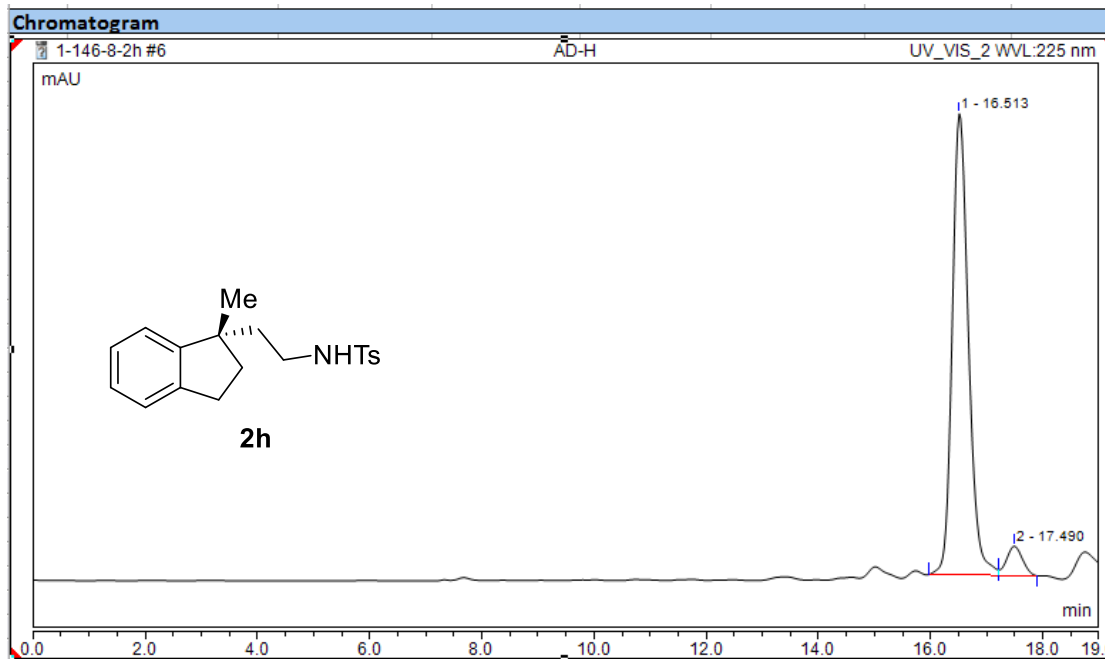
HPLC (Chiral MD): t_R = 9.2 (major), 9.7 (minor)

Condition: 99.5:0.5 n-Hexane:*i*-PrOH, flow rate 0.7 mL/min, 25°C.



Integration Results

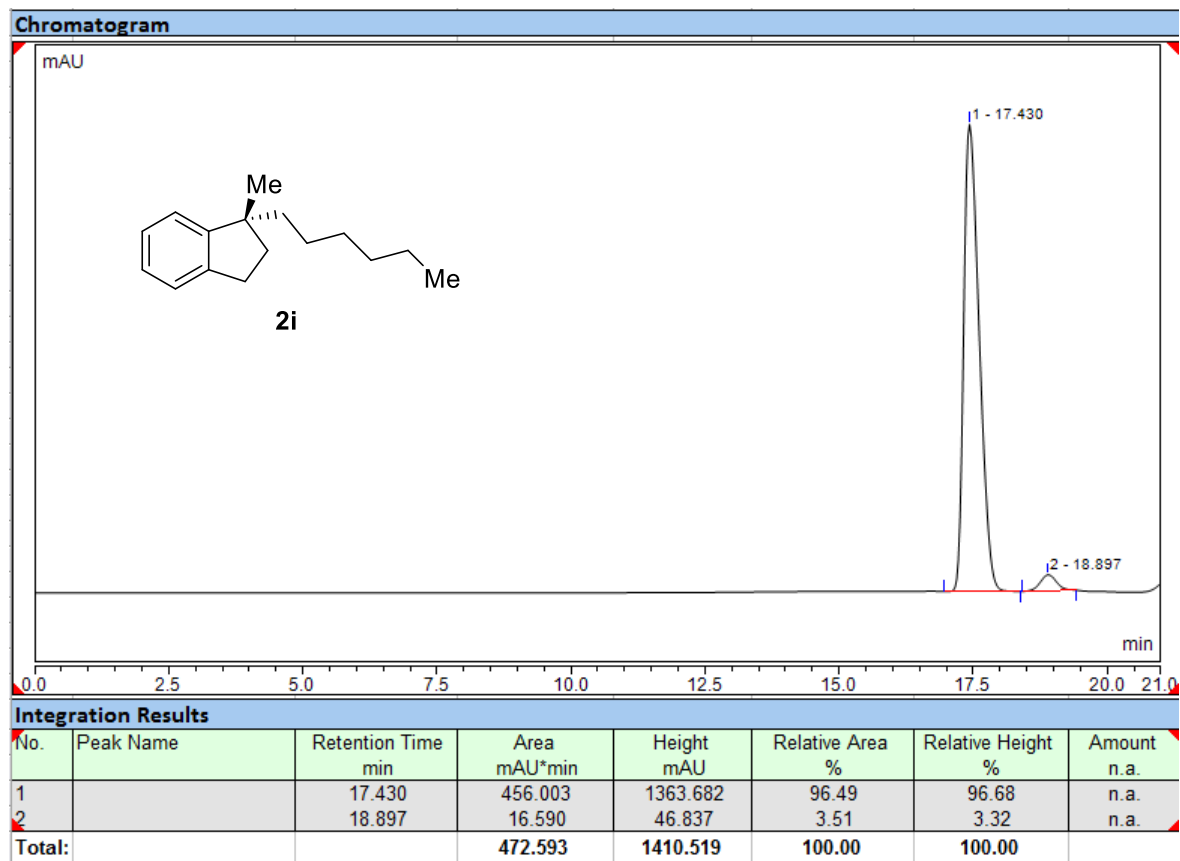
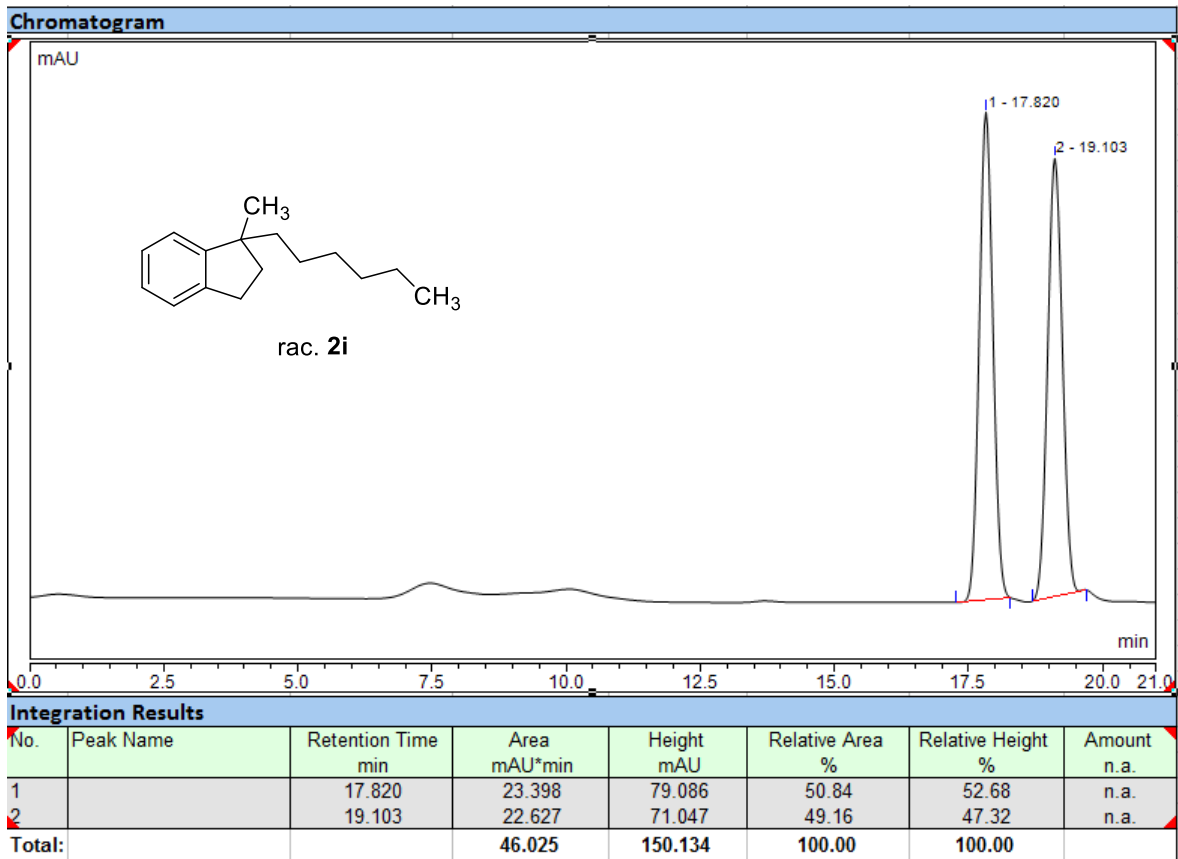
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.847	14.957	46.624	49.18	50.90	n.a.
2		16.653	15.454	44.973	50.82	49.10	n.a.
Total:			30.411	91.597	100.00	100.00	



Integration Results

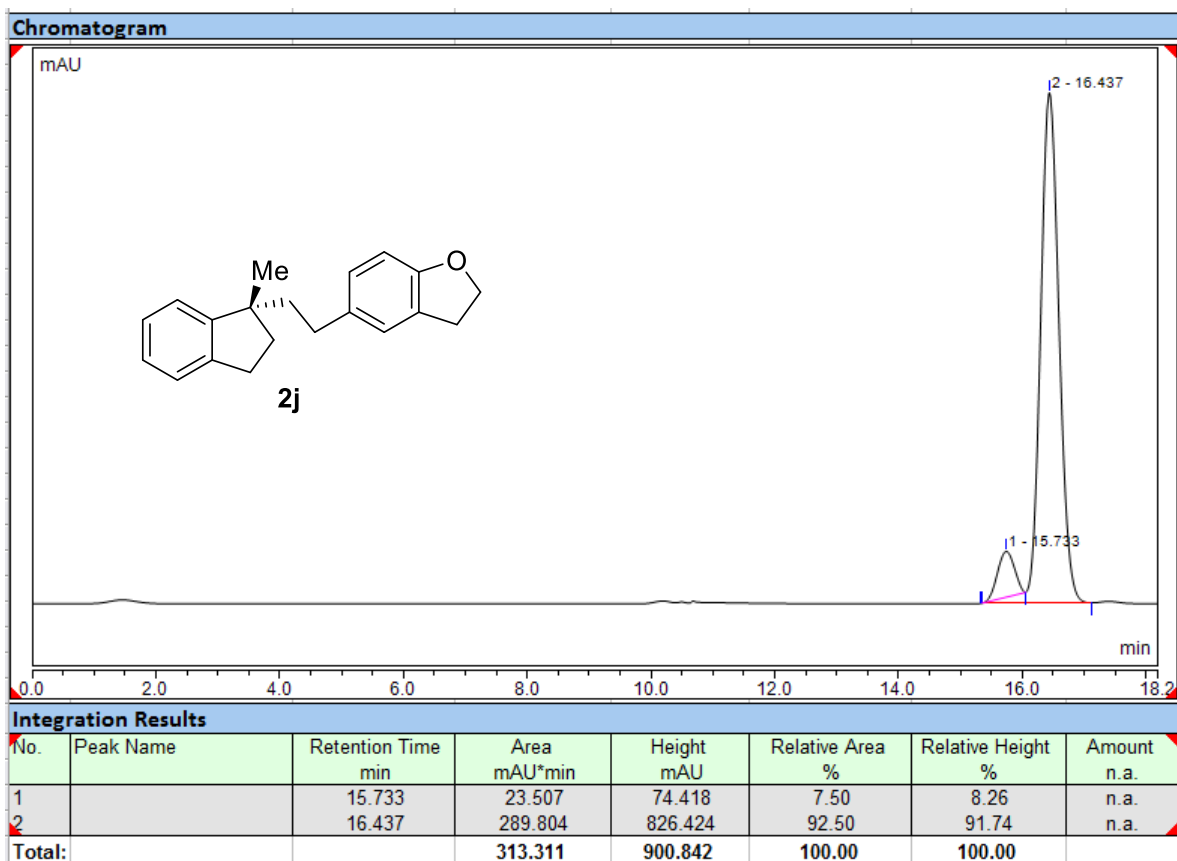
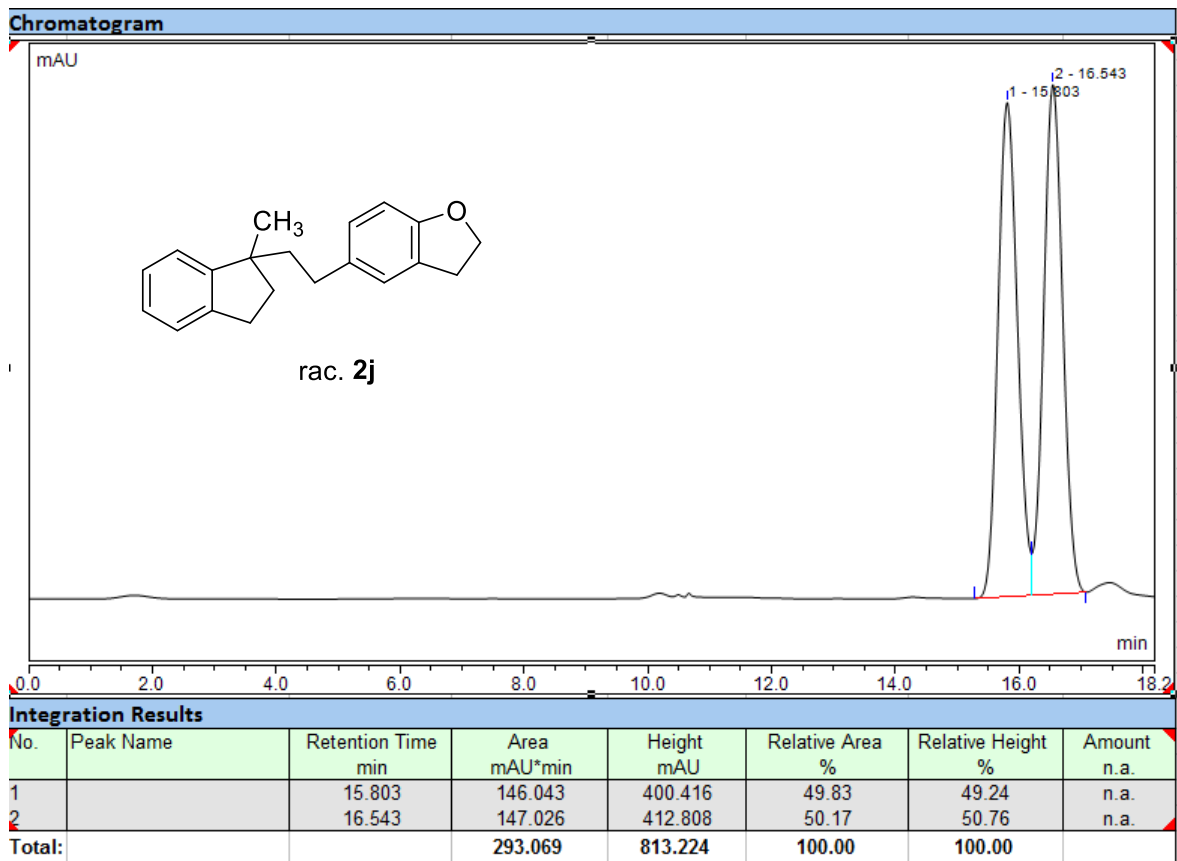
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.513	657.159	1965.937	94.12	94.01	n.a.
2		17.490	41.084	125.292	5.88	5.99	n.a.
Total:			698.243	2091.229	100.00	100.00	

HPLC (Chiralpak AD-H): $t_r = 16.5$ (major), 17.5 (minor)
 Condition: 70:30 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



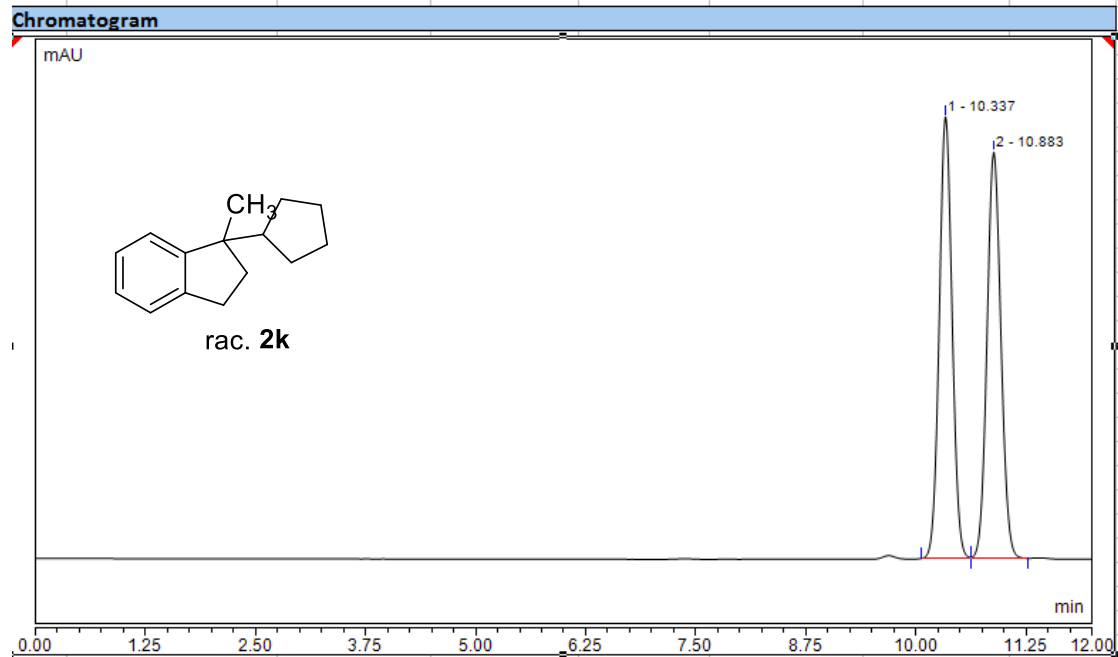
HPLC (Chiralcel OD-H): $t_R=17.4$ (major), 18.9 (minor)

Condition: n-Hexane, flow rate 0.25 mL/min, 25 °C.



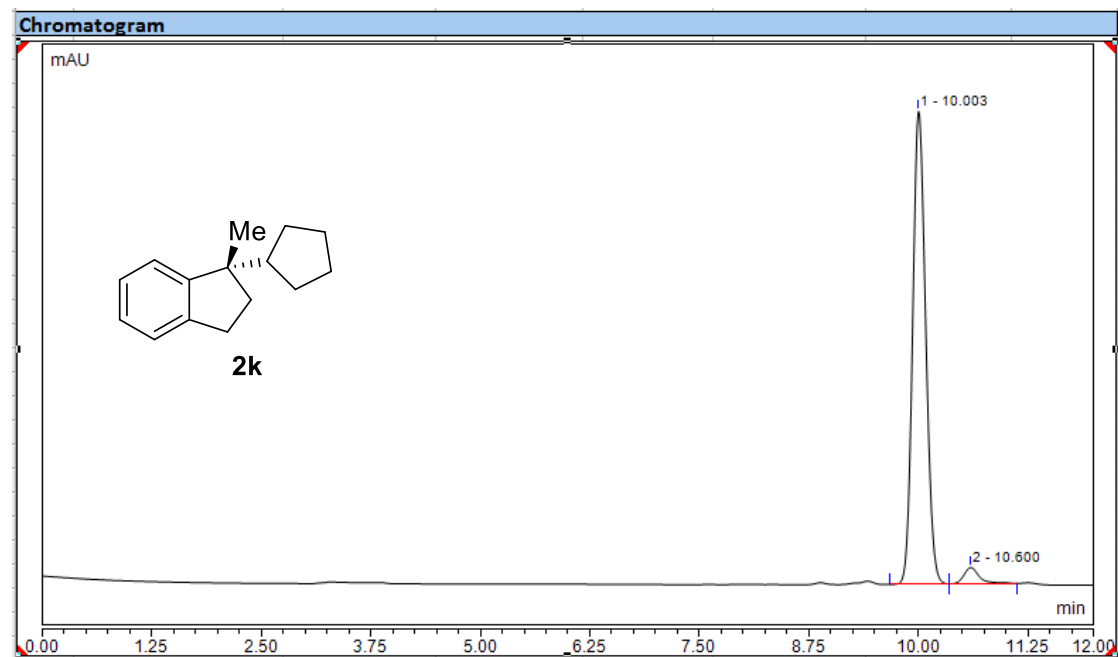
HPLC (Chiralpak AD-H): $t_R = 15.7$ (minor), 16.4 (major)

Condition: 97:3 n-Hexane:*i*-PrOH, flow rate 0.3 mL/min, 25 °C.



Integration Results

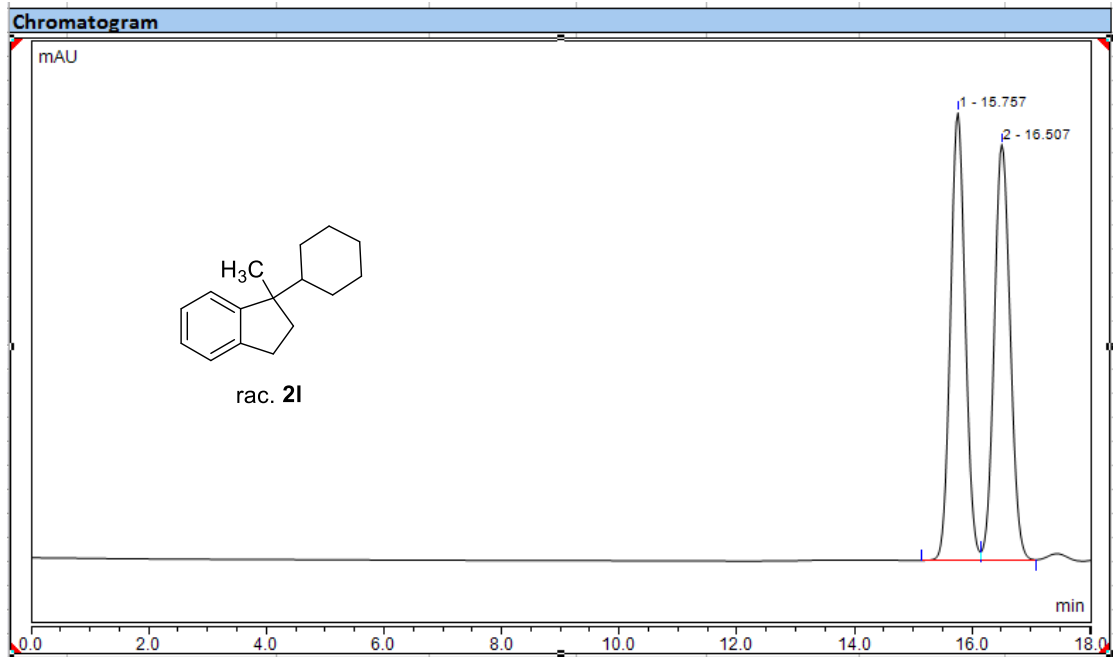
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.337	23.042	136.131	50.14	52.09	n.a.
2		10.883	22.914	125.224	49.86	47.91	n.a.
Total:			45.956	261.355	100.00	100.00	



Integration Results

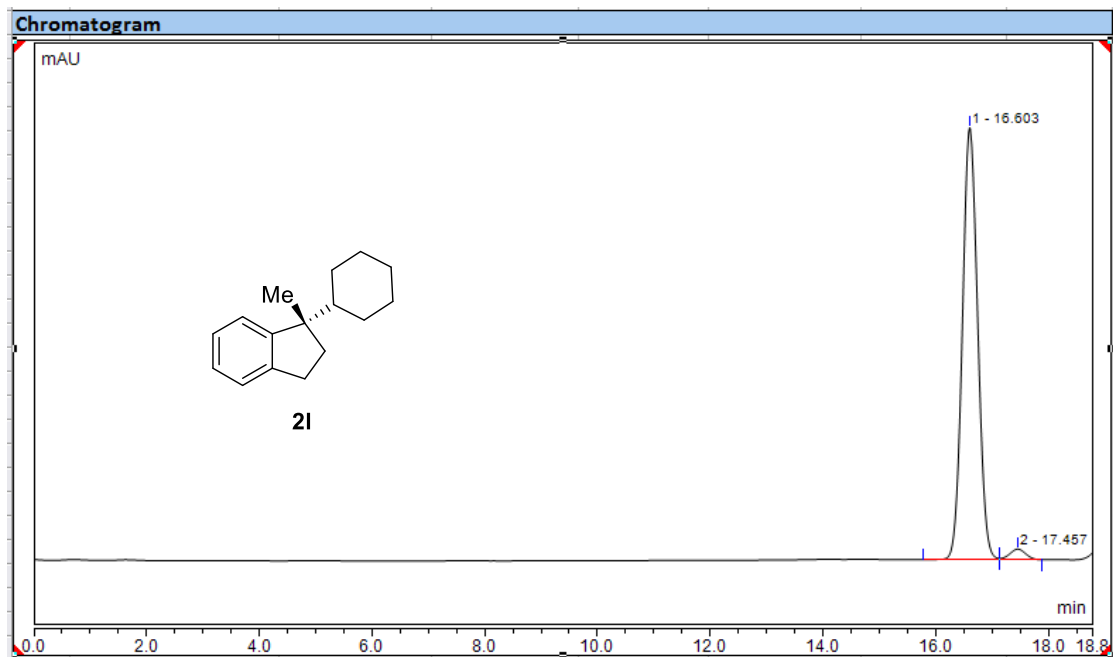
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.003	83.863	489.039	96.02	96.66	n.a.
2		10.600	3.479	16.893	3.98	3.34	n.a.
Total:			87.342	505.932	100.00	100.00	

HPLC (Chiral MD): t_R =10.0 (major), 10.6 (minor)
Condition: 99:1 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

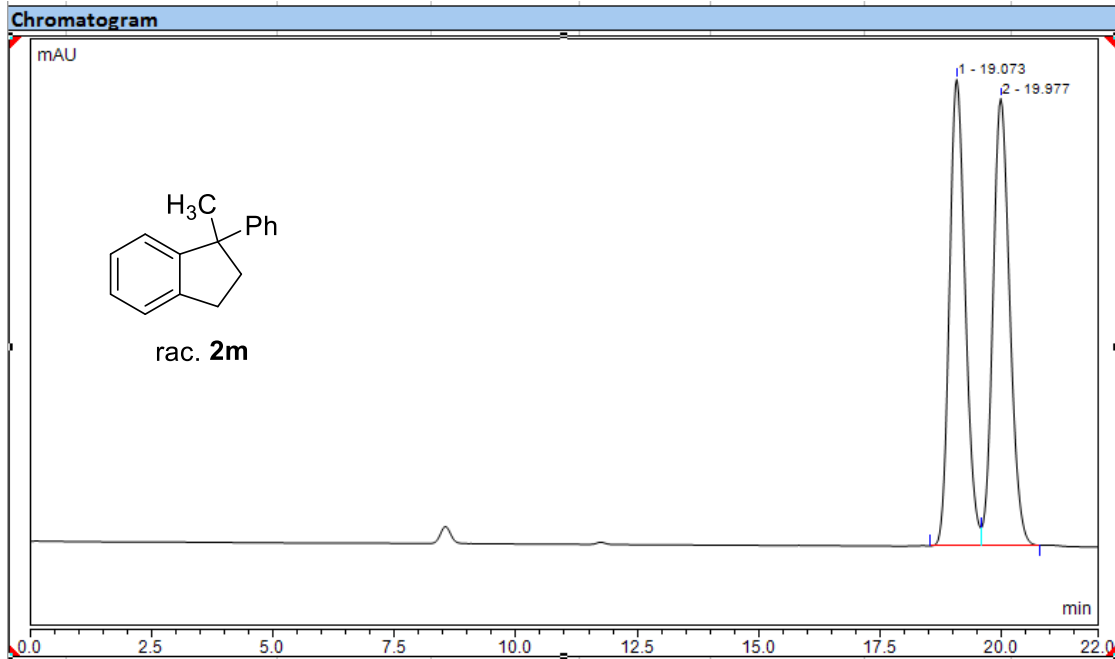
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.757	100.828	346.681	49.90	51.85	n.a.
2		16.507	101.236	321.900	50.10	48.15	n.a.
Total:			202.064	668.581	100.00	100.00	



Integration Results

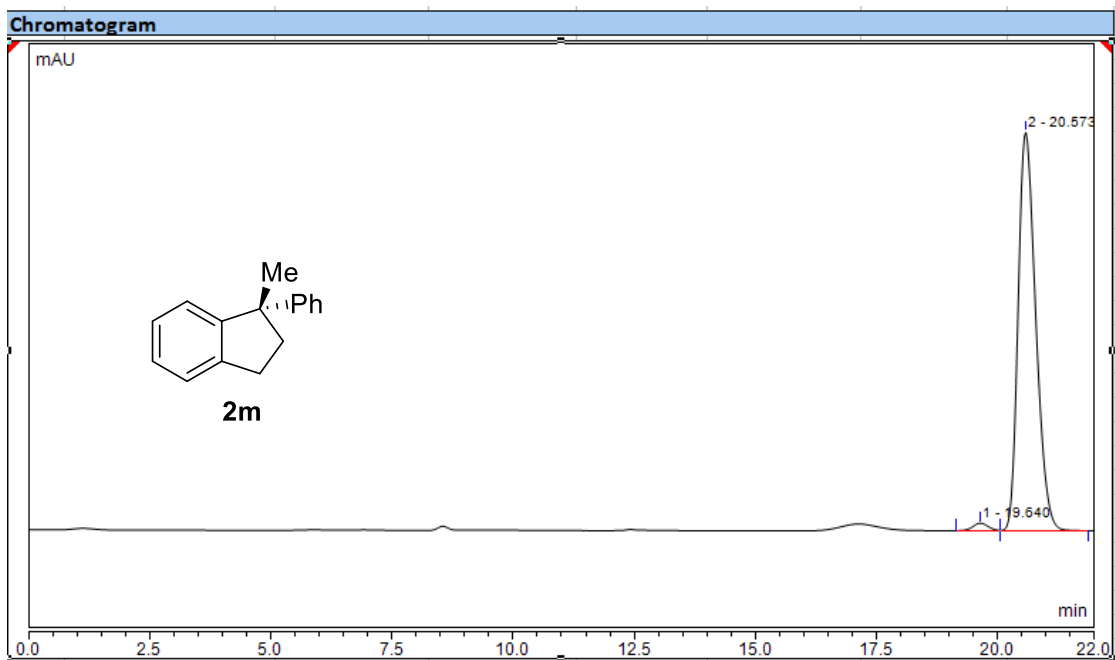
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.603	104.489	334.657	97.49	97.60	n.a.
2		17.457	2.687	8.231	2.51	2.40	n.a.
Total:			107.176	342.888	100.00	100.00	

HPLC (Chiral MD): $t_r = 16.6$ (major), 17.5 (minor)
Condition: n-Hexane, flow rate 0.25 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19.073	20.955	55.740	49.47	51.06	n.a.
2		19.977	21.402	53.434	50.53	48.94	n.a.
Total:			42.357	109.175	100.00	100.00	

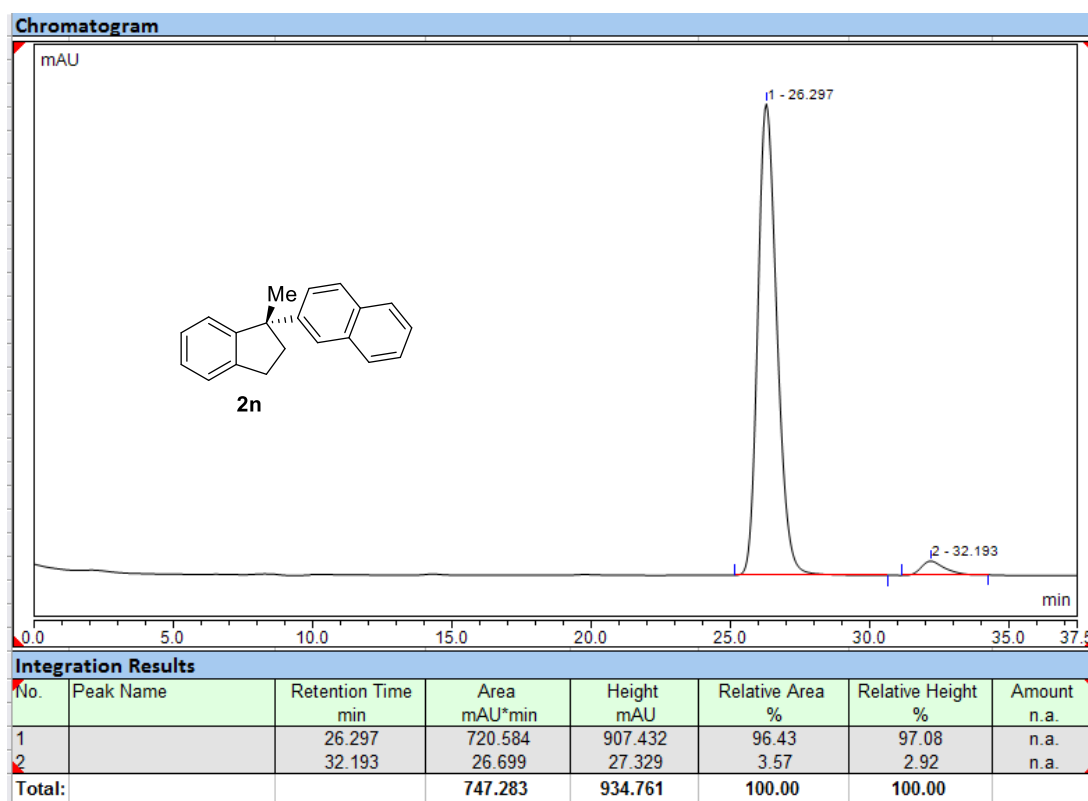
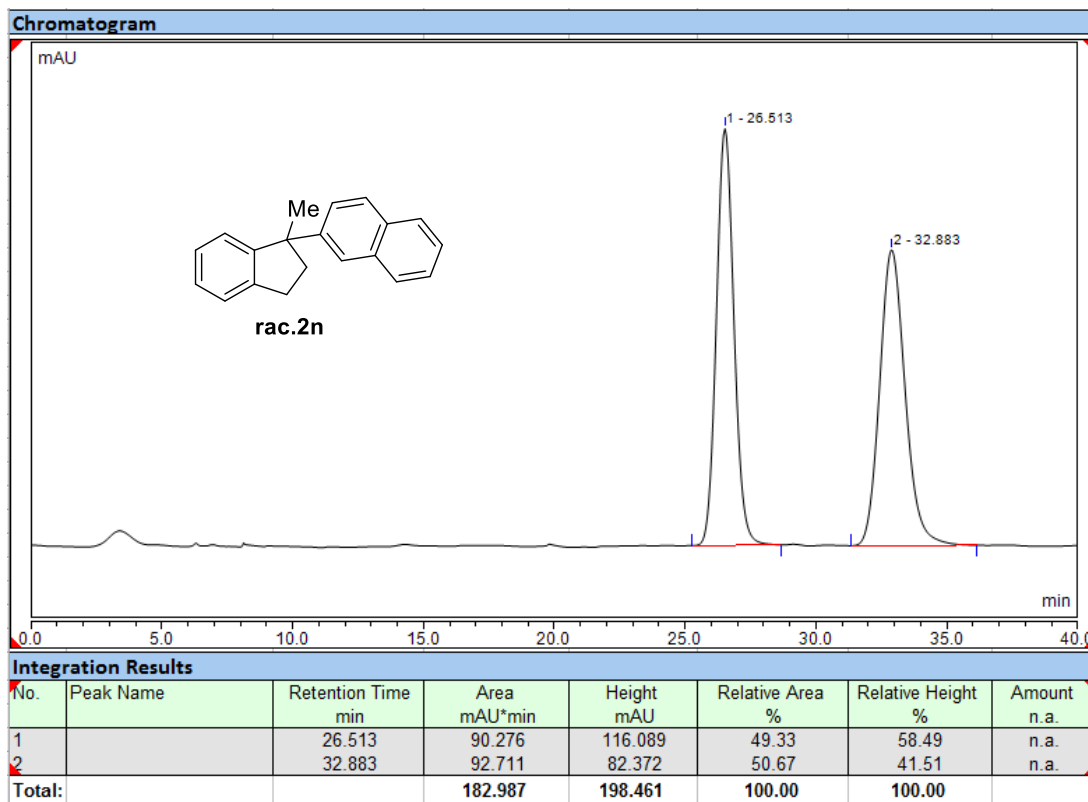


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		19.640	1.430	3.905	1.63	1.87	n.a.
2		20.573	86.152	205.073	98.37	98.13	n.a.
Total:			87.582	208.979	100.00	100.00	

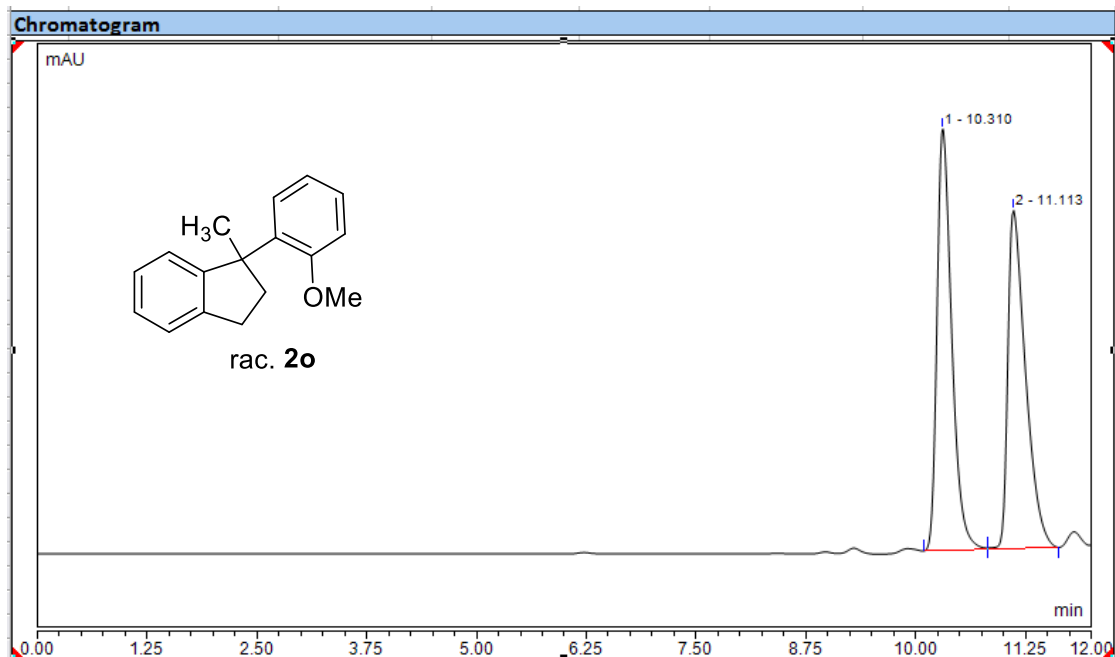
HPLC (Chiralcel OD-H): t_{R} = 19.6 (minor), 20.6 (major)

Condition: n-Hexane, flow rate 0.5 mL/min, 25 °C.



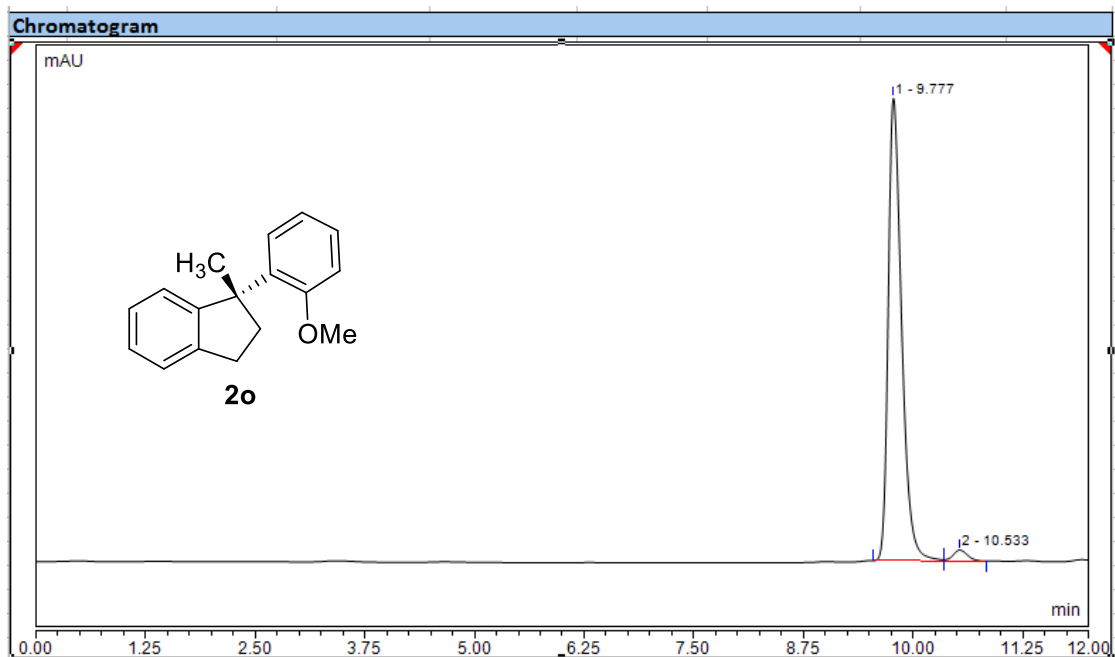
HPLC (Chiralcel OJ-H): t_R =26.3 (major), 32.2 (minor)

Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.5mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.310	224.786	1157.773	50.90	55.46	n.a.
2		11.113	216.810	929.773	49.10	44.54	n.a.
Total:			441.597	2087.546	100.00	100.00	

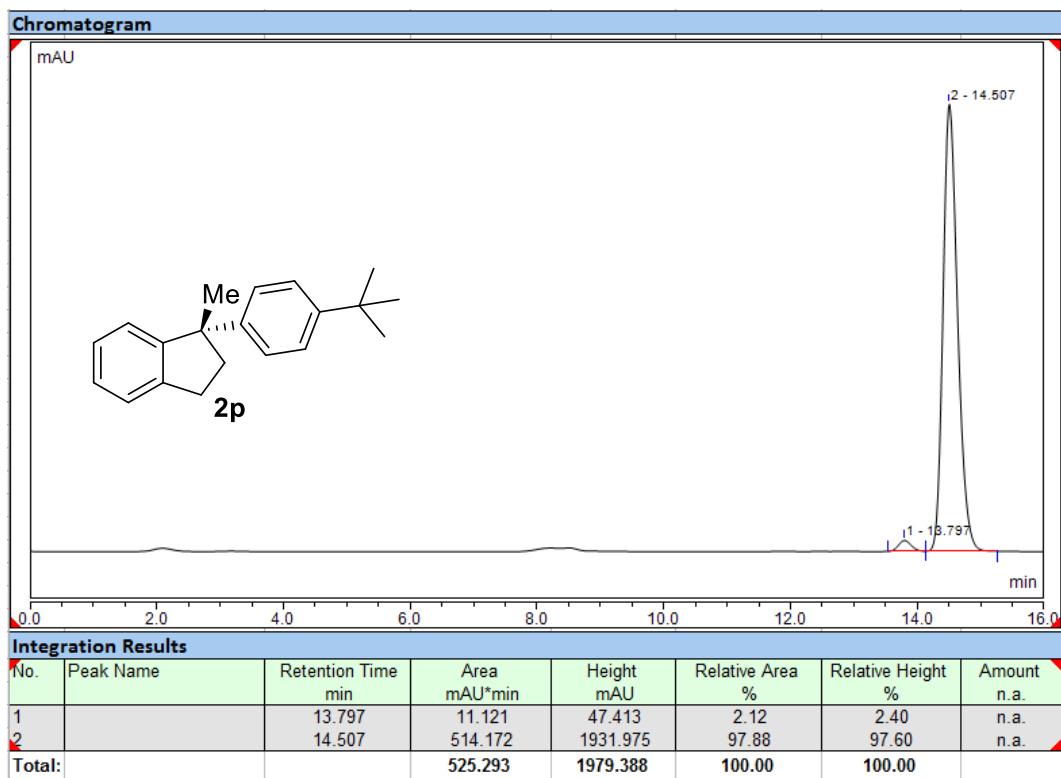
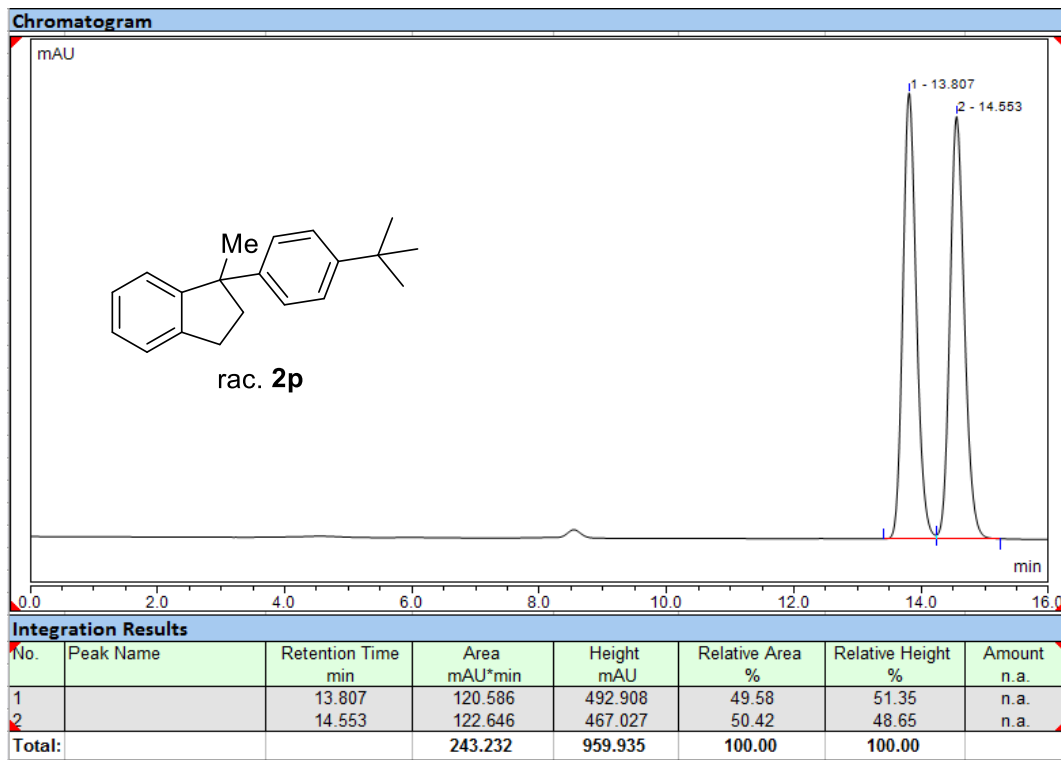


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.777	253.318	1432.508	97.54	97.69	n.a.
2		10.533	6.386	33.839	2.46	2.31	n.a.
Total:			259.704	1466.347	100.00	100.00	

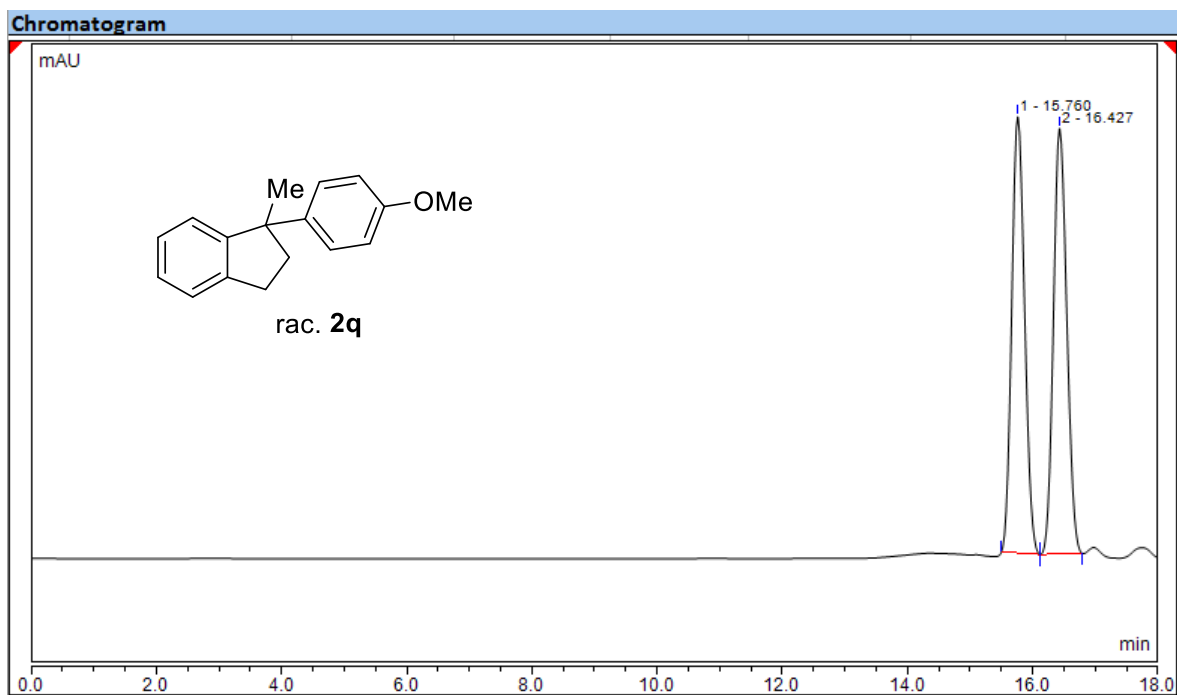
HPLC (Chiralpak IA): $t_R = 9.8$ (major), 10.5 (minor)

Condition: n-Hexane, flow rate 0.5 mL/min, 25 °C.



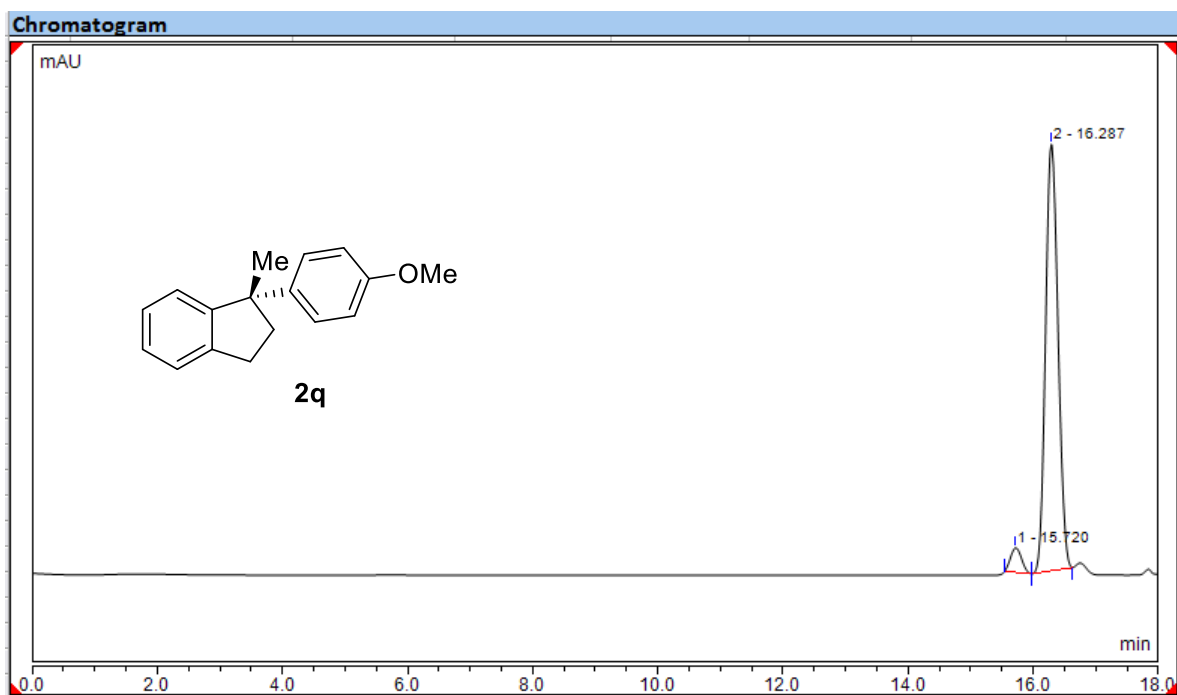
HPLC (Chiralcel OD-H): t_R = 13.8 (minor), 14.5 (major)

Condition: n-Hexane, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		15.760	503.893	2119.427	49.75	50.62	n.a.
2		16.427	509.016	2067.122	50.25	49.38	n.a.
Total:			1012.910	4186.549	100.00	100.00	

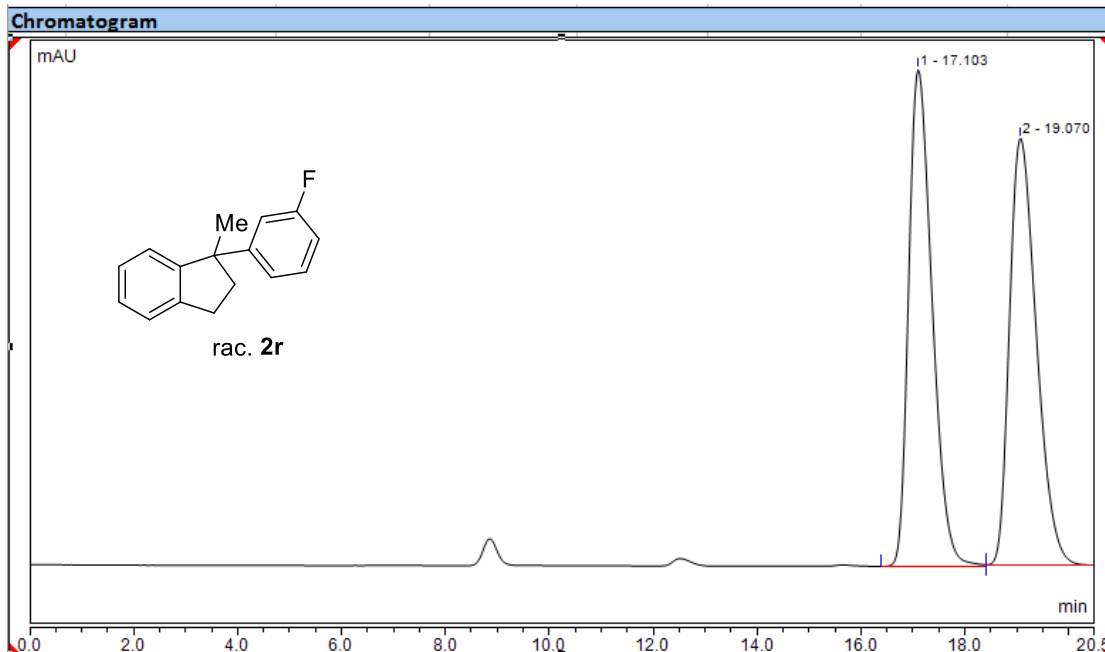


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		15.720	28.604	140.449	4.88	5.48	n.a.
2		16.287	558.040	2423.165	95.12	94.52	n.a.
Total:			586.643	2563.613	100.00	100.00	

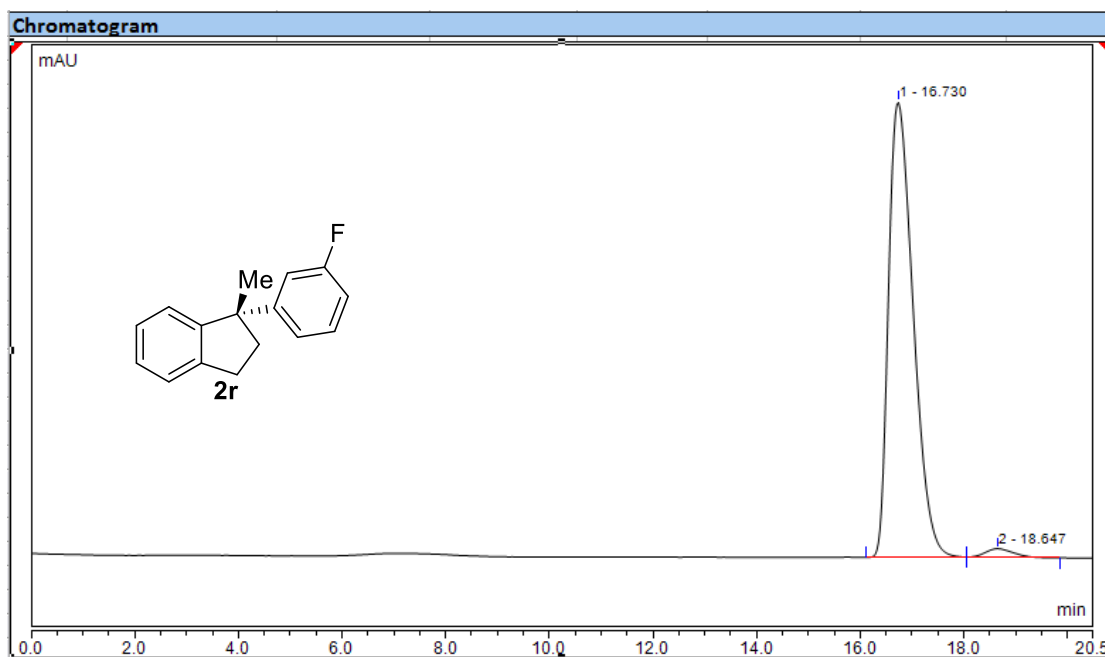
HPLC (Chiralpak IB): $t_R = 15.7$ (minor), 16.3 (major)

Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.3 mL/min, 25 °C.



Integration Results

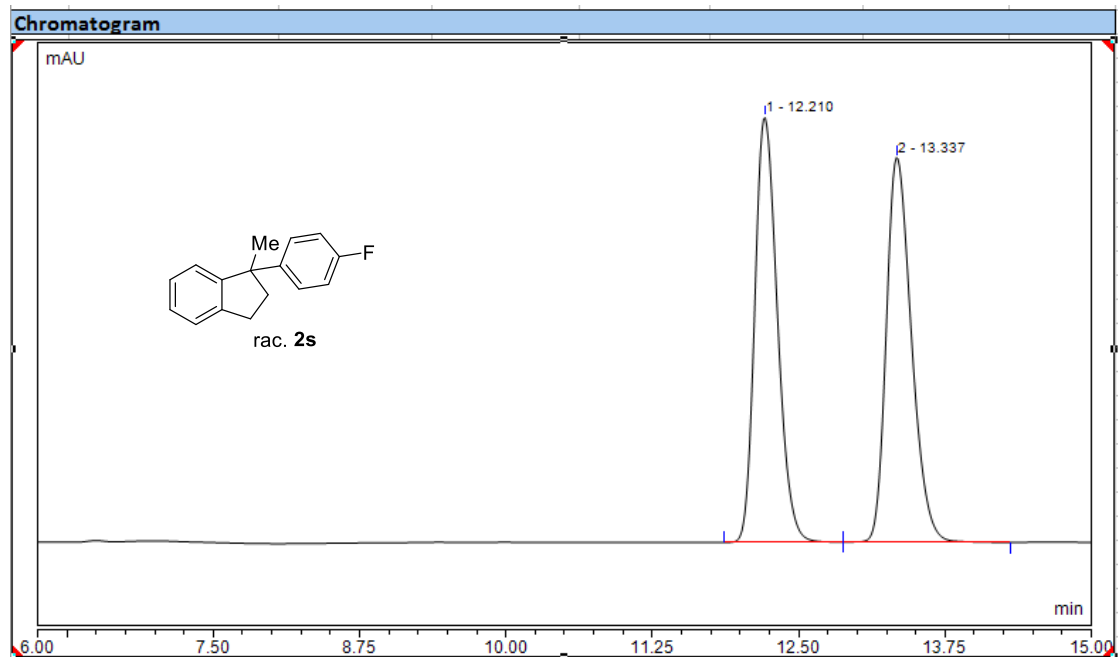
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.103	44.446	85.249	50.21	53.73	n.a.
2		19.070	44.079	73.427	49.79	46.27	n.a.
Total:			88.525	158.676	100.00	100.00	



Integration Results

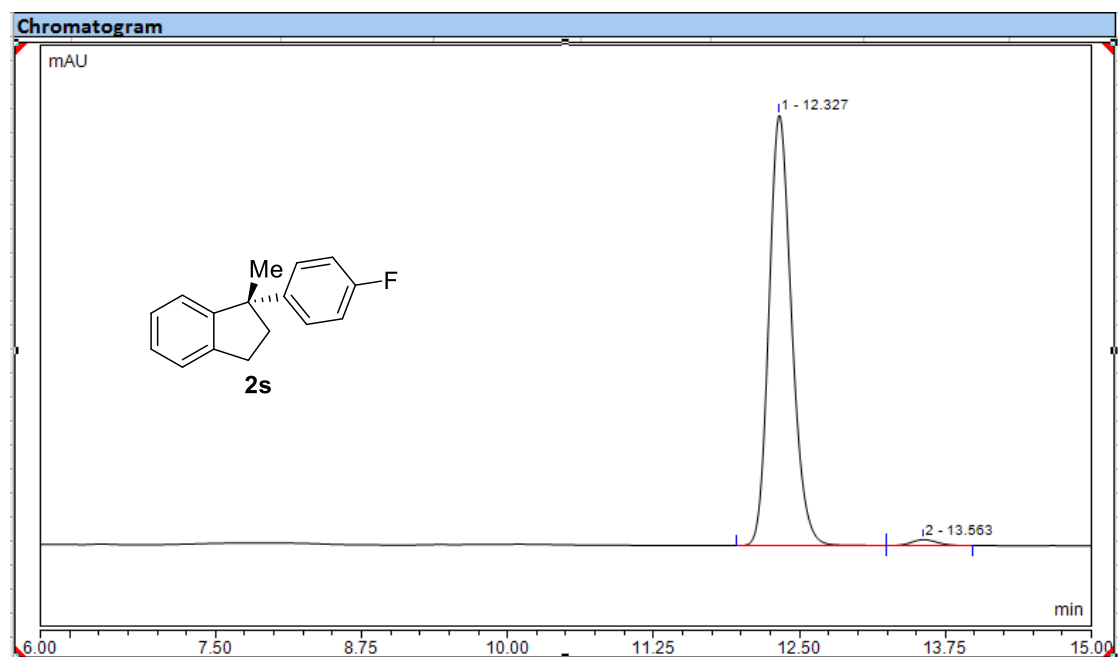
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.730	34.541	62.682	97.70	98.05	n.a.
2		18.647	0.812	1.244	2.30	1.95	n.a.
Total:			35.353	63.926	100.00	100.00	

HPLC (Chiralcel OD-H): $t_R = 16.7$ (major), 18.6 (minor)
Condition: n-Hexane, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.210	571.150	2555.657	49.72	52.48	n.a.
2		13.337	577.654	2314.446	50.28	47.52	n.a.
Total:			1148.804	4870.103	100.00	100.00	

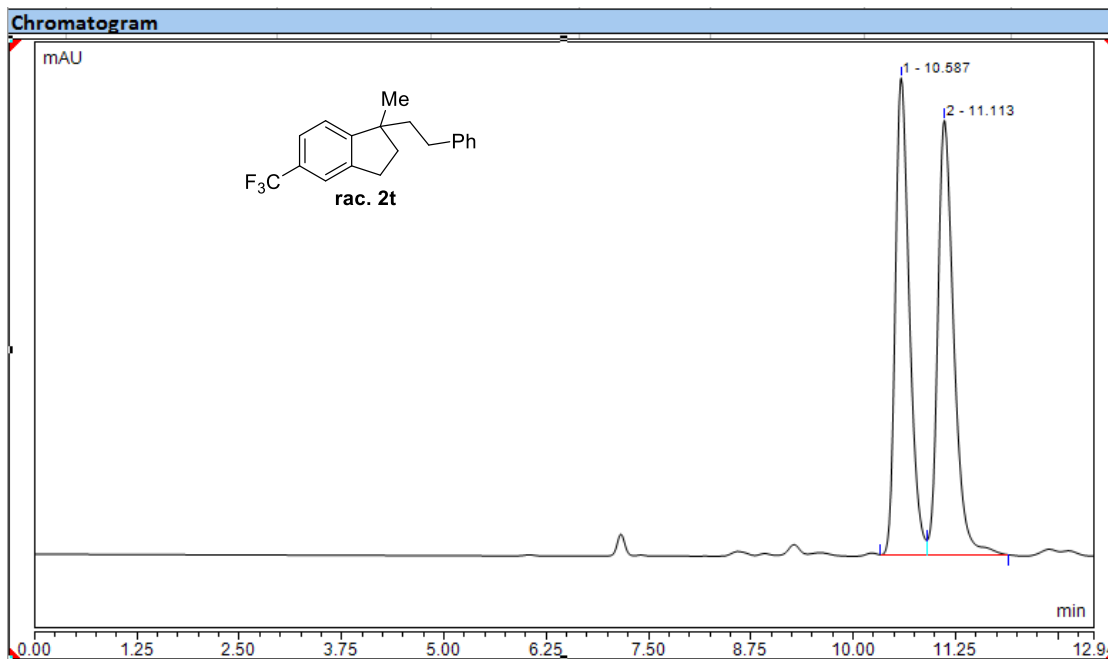


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.327	232.958	1039.664	98.44	98.63	n.a.
2		13.563	3.690	14.422	1.56	1.37	n.a.
Total:			236.648	1054.087	100.00	100.00	

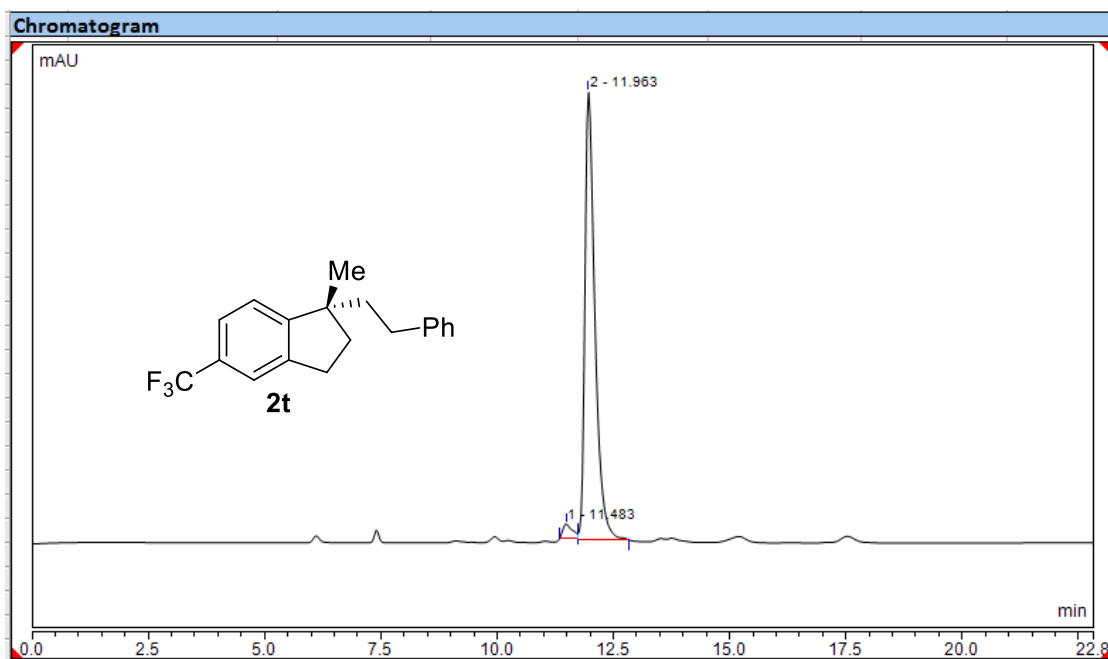
HPLC (Chiralcel OD-H): $t_R = 12.3$ (major), 13.6 (minor)

Condition: n-Hexane, flow rate 0.5 mL/min , 25°C .



Integration Results

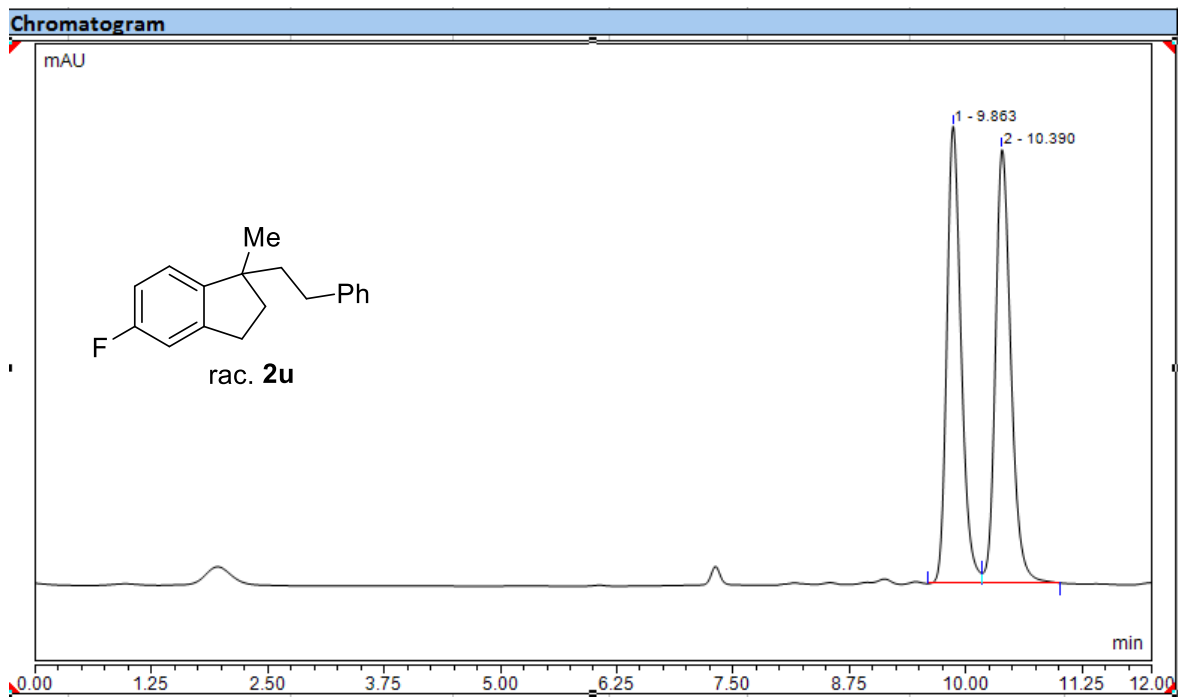
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.587	257.690	1303.936	48.86	52.33	n.a.
2		11.113	269.693	1187.690	51.14	47.67	n.a.
Total:			527.383	2491.626	100.00	100.00	



Integration Results

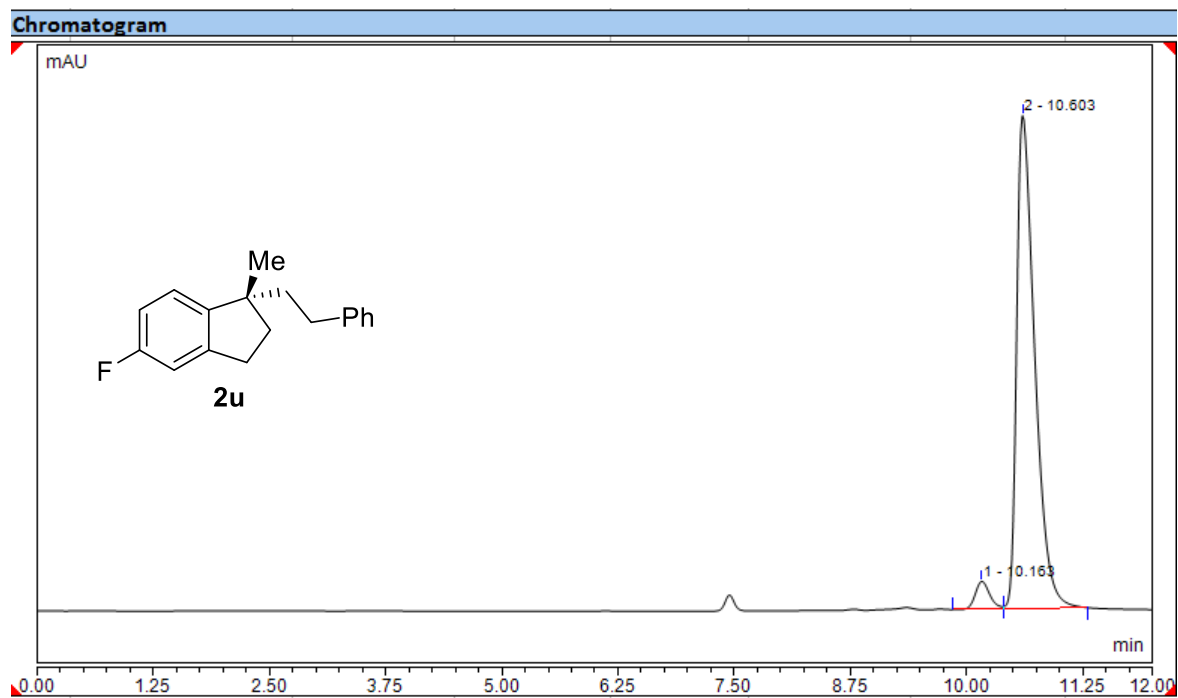
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.483	8.666	35.823	3.14	3.23	n.a.
2		11.963	267.486	1074.421	96.86	96.77	n.a.
Total:			276.152	1110.245	100.00	100.00	

HPLC (Chiralpak IA): $t_R = 11.5$ (minor), 12.0 (major)
 Condition: 99.5:0.5 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.863	52.705	296.736	49.28	51.32	n.a.
2		10.390	54.250	281.464	50.72	48.68	n.a.
Total:			106.955	578.200	100.00	100.00	

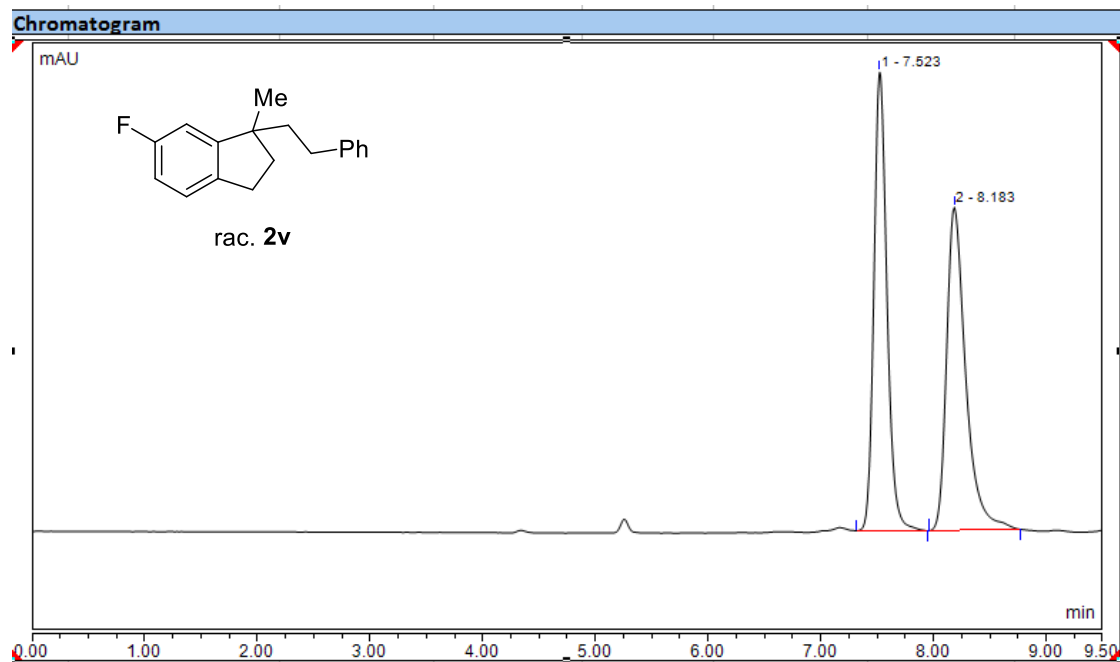


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.163	9.720	54.028	4.32	5.34	n.a.
2		10.603	215.207	958.285	95.68	94.66	n.a.
Total:			224.927	1012.313	100.00	100.00	

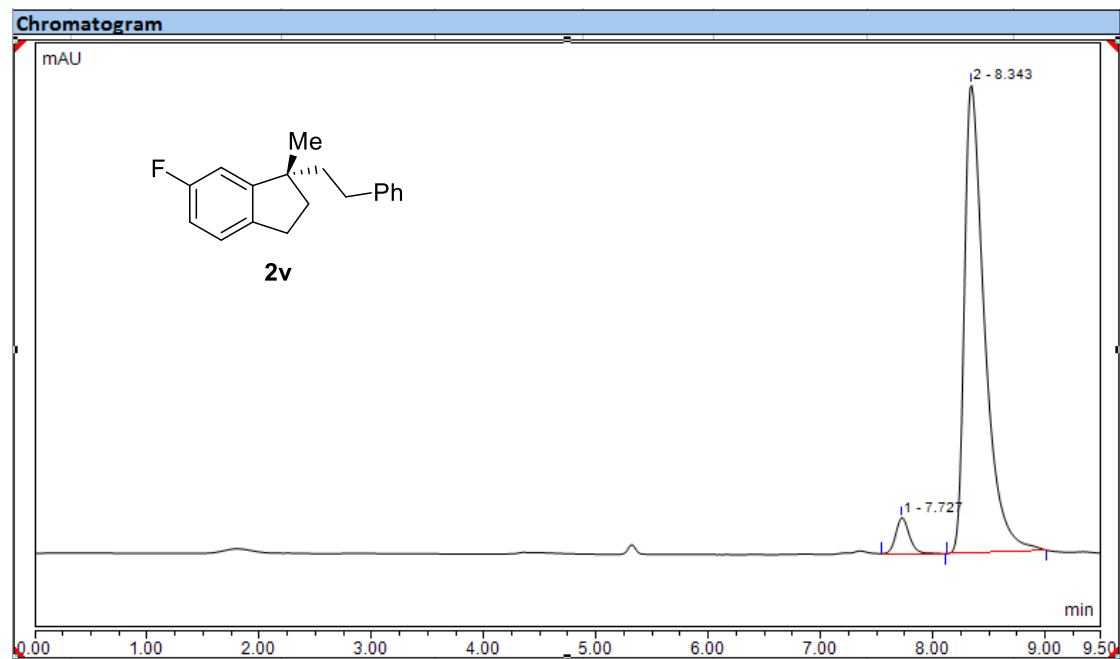
HPLC (Chiralpak IA): t_R = 10.2 (minor), 10.6 (major)

Condition: 99.5:0.5 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25°C.



Integration Results

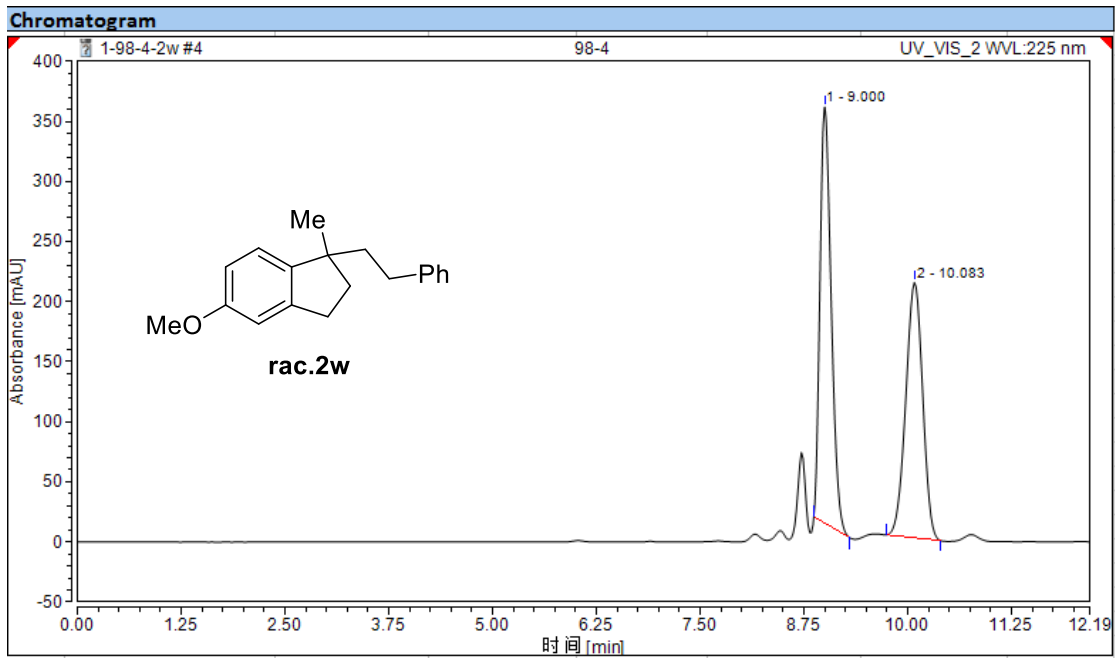
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.523	3.150	23.478	49.22	58.65	n.a.
2		8.183	3.250	16.553	50.78	41.35	n.a.
Total:			6.400	40.031	100.00	100.00	



Integration Results

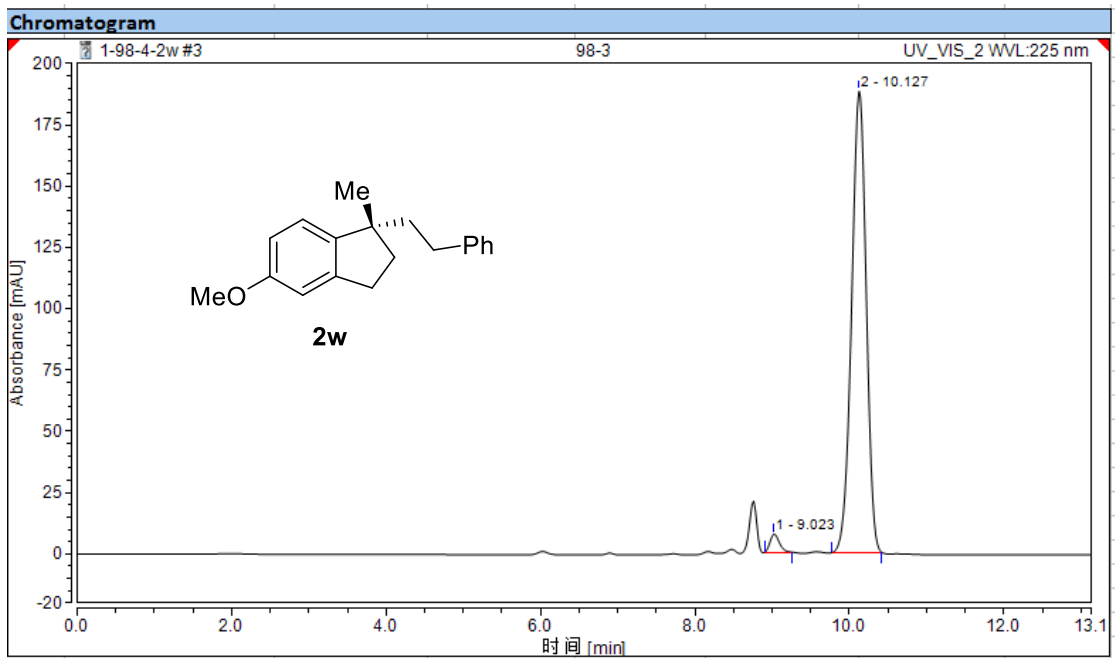
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.727	0.689	4.948	4.91	7.16	n.a.
2		8.343	13.343	64.197	95.09	92.84	n.a.
Total:			14.032	69.145	100.00	100.00	

HPLC (Chiralpak IA): t_R =7.7 (minor), 8.3 (major)
Condition: 99.5:0.5 n-Hexane:*i*-PrOH, flow rate 0.7 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.000	54.033	346.327	51.96	61.95	n.a.
2		10.083	49.967	212.746	48.04	38.05	n.a.
Total:			104.000	559.073	100.00	100.00	

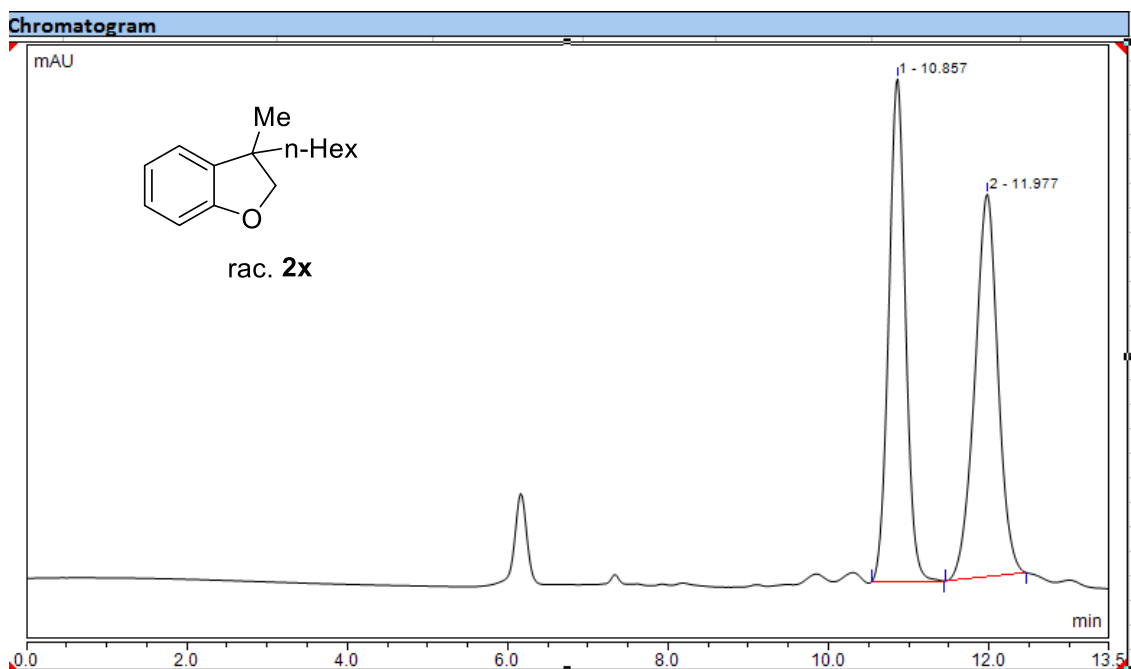


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.023	1.022	7.434	2.43	3.80	n.a.
2		10.127	41.076	188.082	97.57	96.20	n.a.
Total:			42.099	195.516	100.00	100.00	

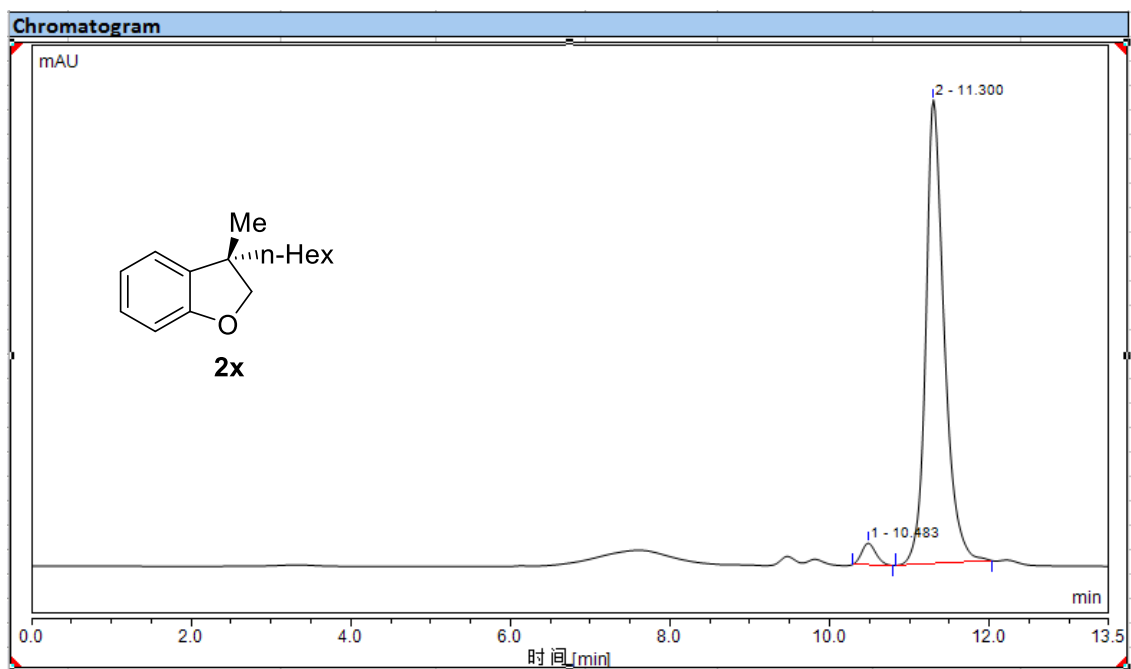
HPLC (Chiralpak IA): $t_R = 9.0$ (minor), 10.1 (major)

Condition: 98:2 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.857	20.427	84.893	48.62	56.77	n.a.
2		11.977	21.584	64.639	51.38	43.23	n.a.
Total:			42.011	149.532	100.00	100.00	

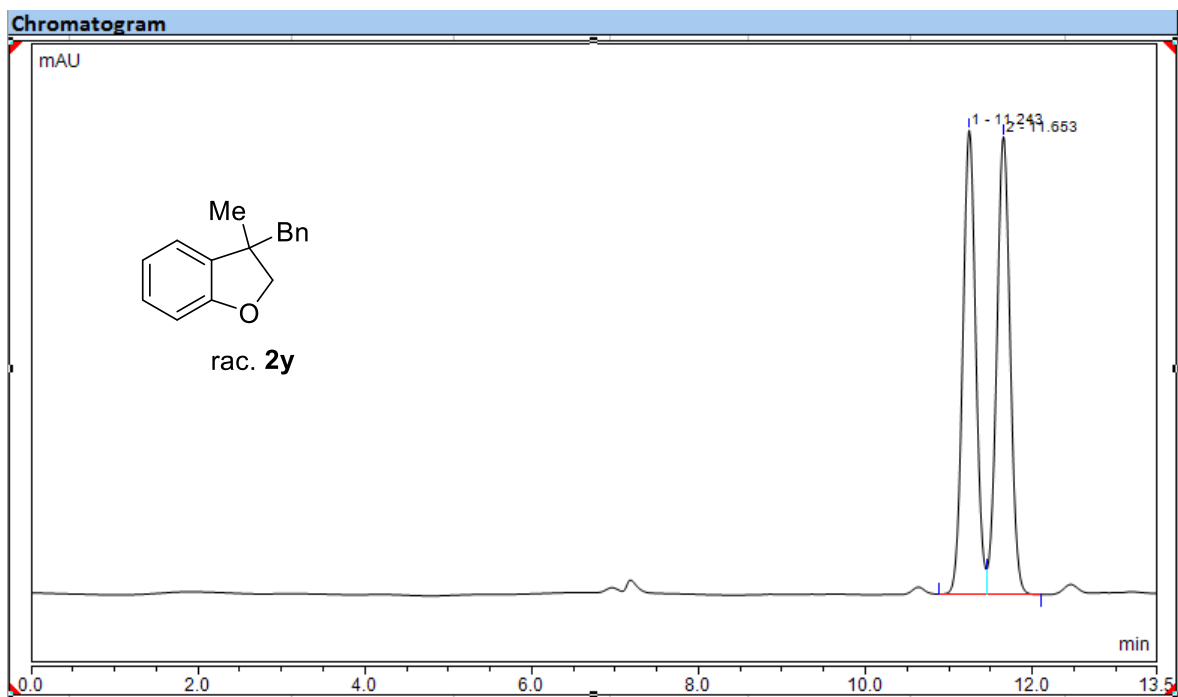


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.483	4.719	22.832	3.47	4.45	n.a.
2		11.300	131.155	489.761	96.53	95.55	n.a.
Total:			135.874	512.593	100.00	100.00	

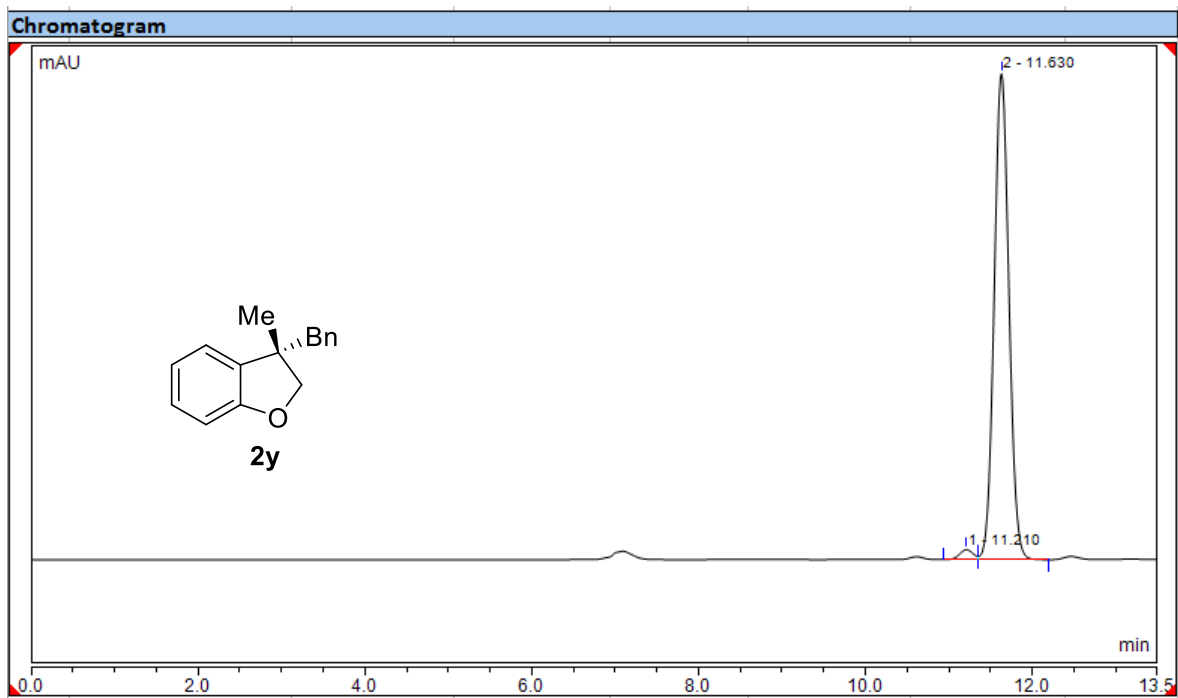
HPLC (Chiralpak IA): t_R = 10.5 (minor), 11.3 (major)

Condition: n-Hexane, flow rate 0.5 mL/min, 25°C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.243	24.292	135.290	49.41	50.34	n.a.
2		11.653	24.873	133.449	50.59	49.66	n.a.
Total:			49.165	268.739	100.00	100.00	

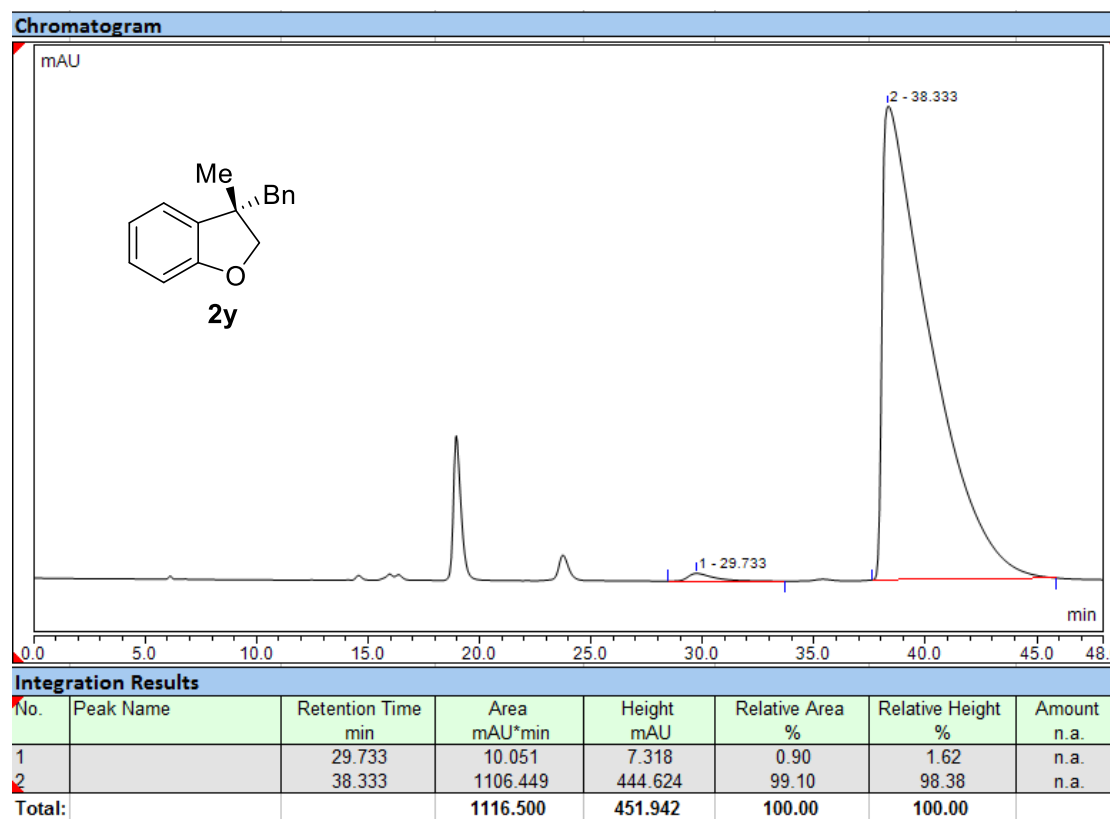
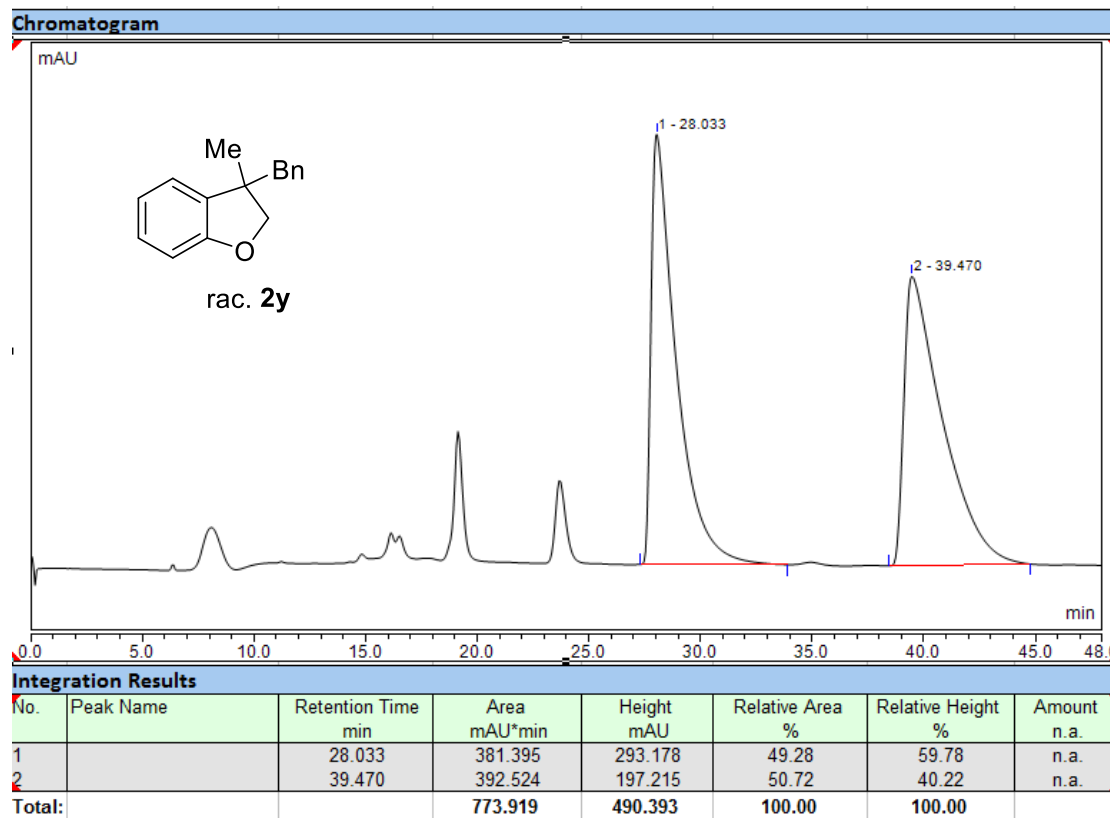


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		11.210	9.089	48.478	1.84	2.01	n.a.
2		11.630	484.270	2365.807	98.16	97.99	n.a.
Total:			493.358	2414.285	100.00	100.00	

HPLC (Chiral MD): t_R = 11.2 (minor), 11.6 (major)

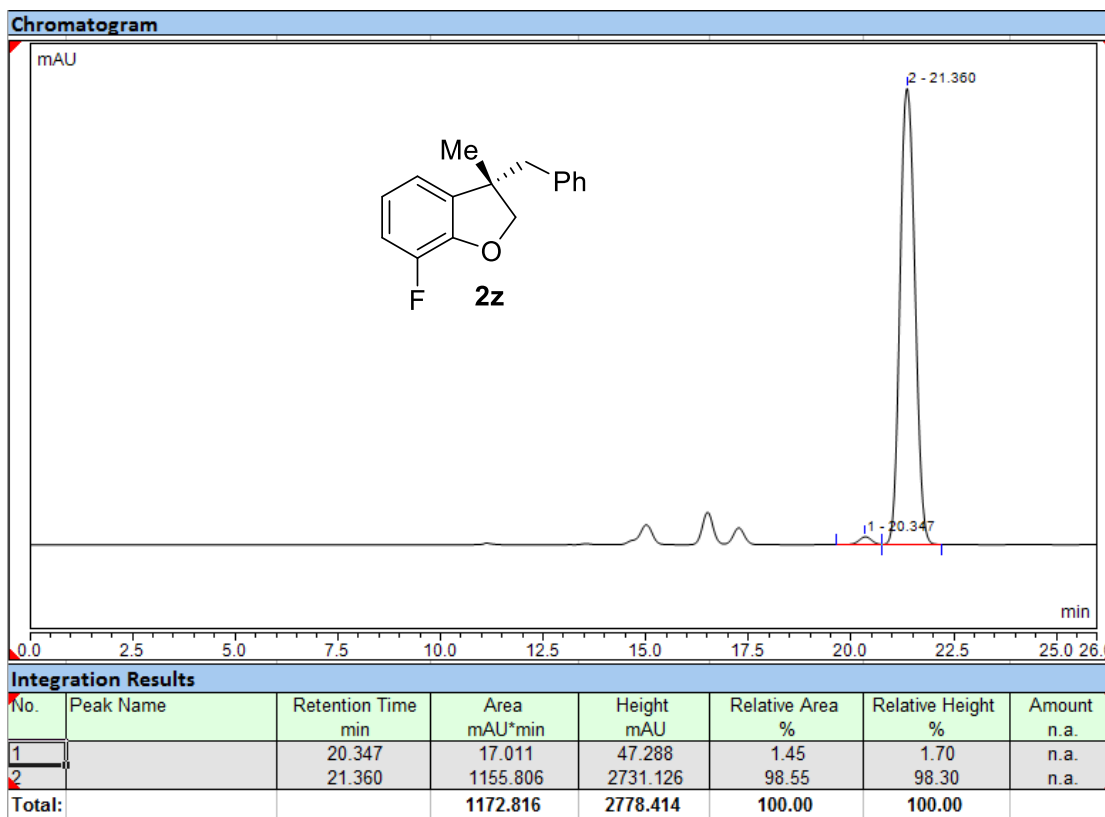
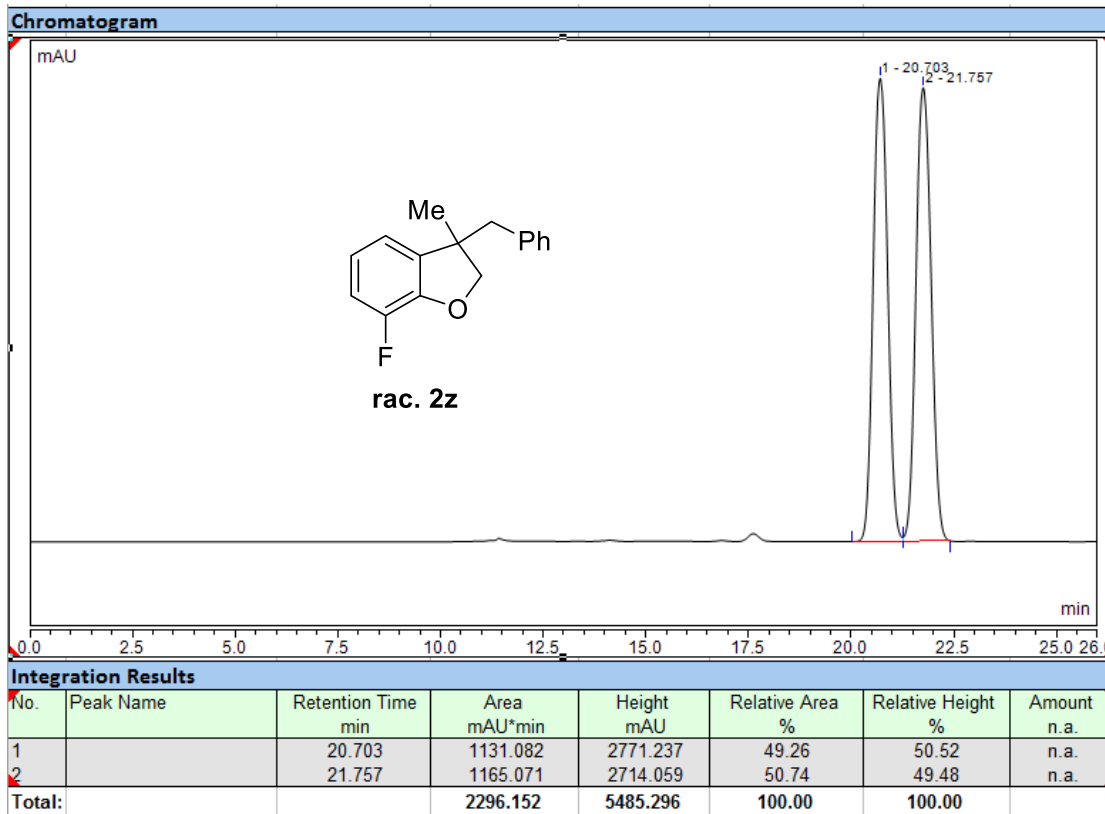
Condition: 95:5 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C



HPLC (Chiralpak IA): t_R = 29.7 (minor), 38.3 (major) Lit.: [t_R = 17.9 (minor), 24.6 (major)]

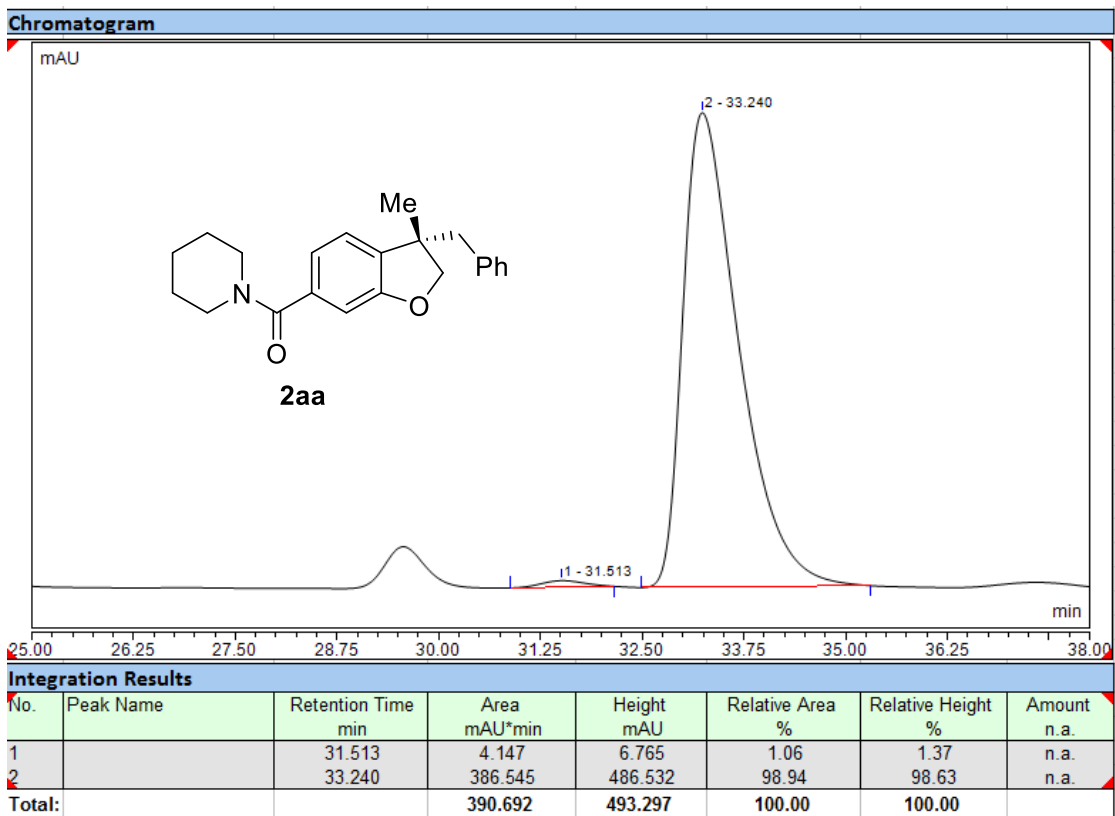
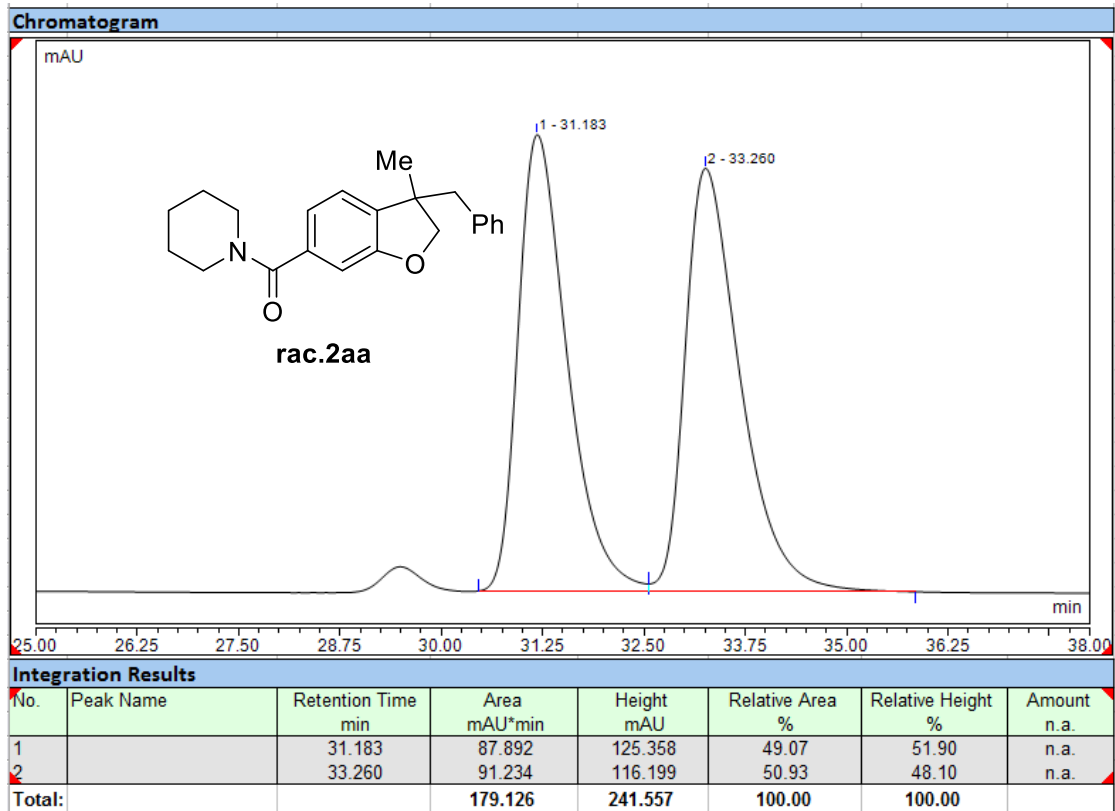
Condition: n-Hexane, flow rate 0.5 mL/min, 25 °C

Lit.: Z.-M. Zhang, B. Xu, Y. Qian, L. Wu, Y. Wu, L. Zhou, Y. Liu, J. Zhang, Palladium-Catalyzed Enantioselective Reductive Heck Reactions: Convenient Access to 3,3-Disubstituted 2,3-Dihydrobenzofuran. *Angew. Chem. Int. Ed.* **2018**, *57*, 10373-10377.

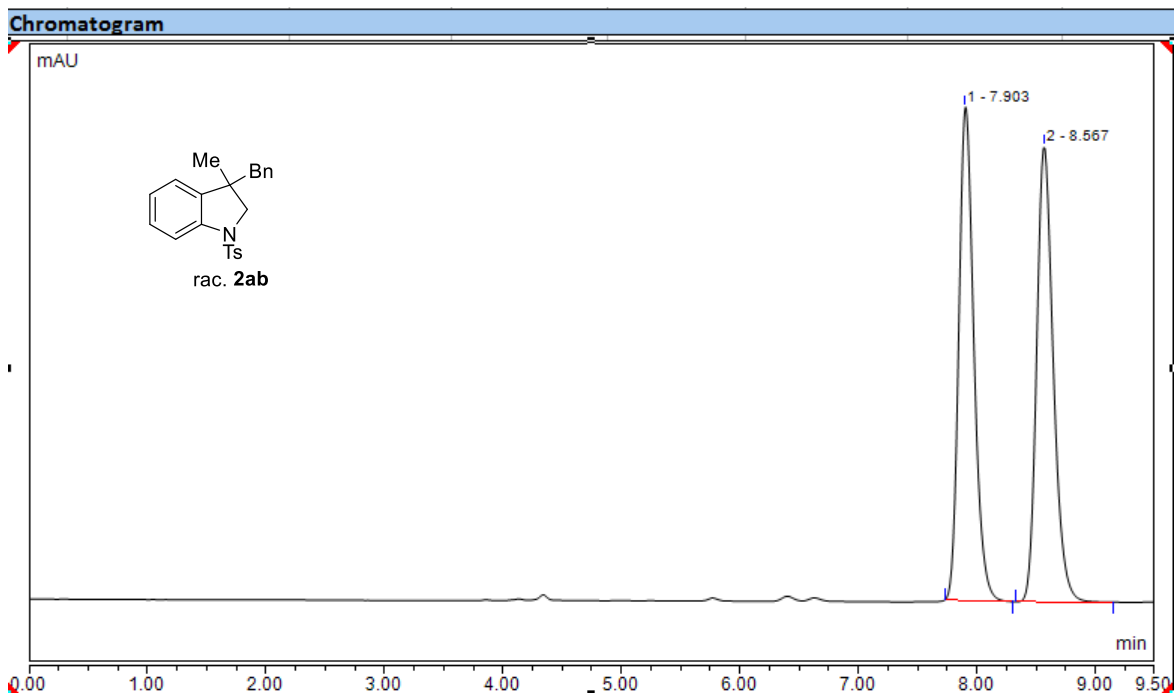


HPLC (Chiral MD): tR= 20.3 (minor), 21.4 (major)

Condition: 95:5 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.

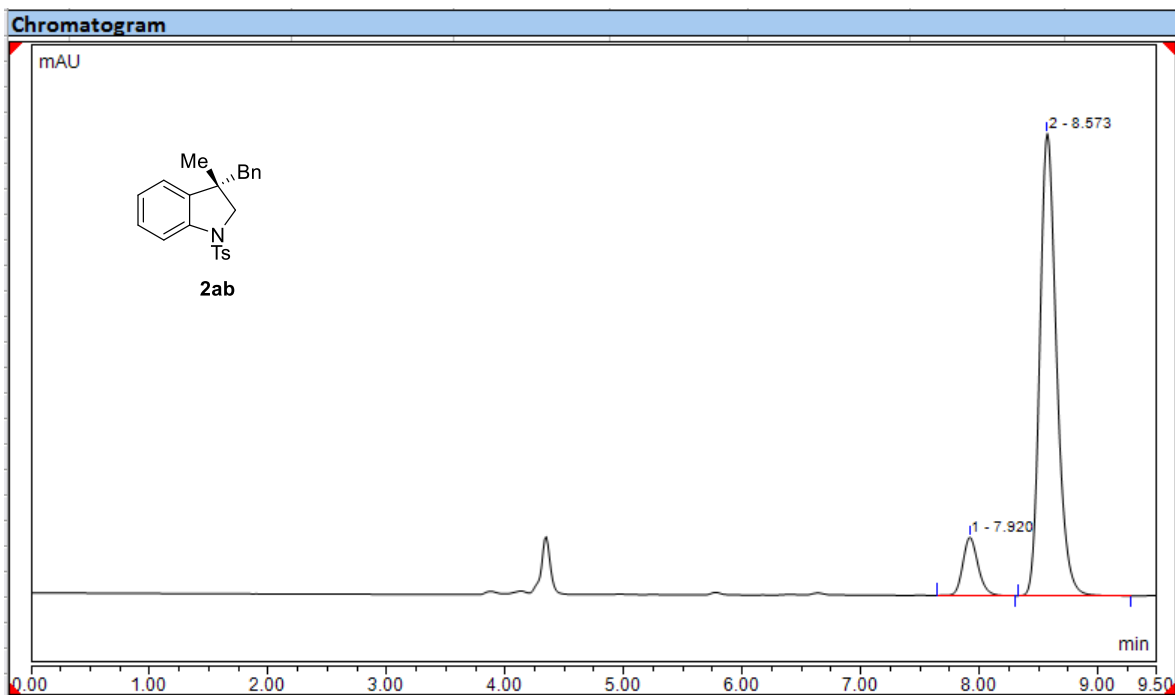


HPLC (Chiralpak IB): t_R = 33.4 (minor), 35.3 (major)
 Condition: 90:10 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.903	11.746	79.984	49.46	52.00	n.a.
2		8.567	12.004	73.819	50.54	48.00	n.a.
Total:			23.750	153.803	100.00	100.00	

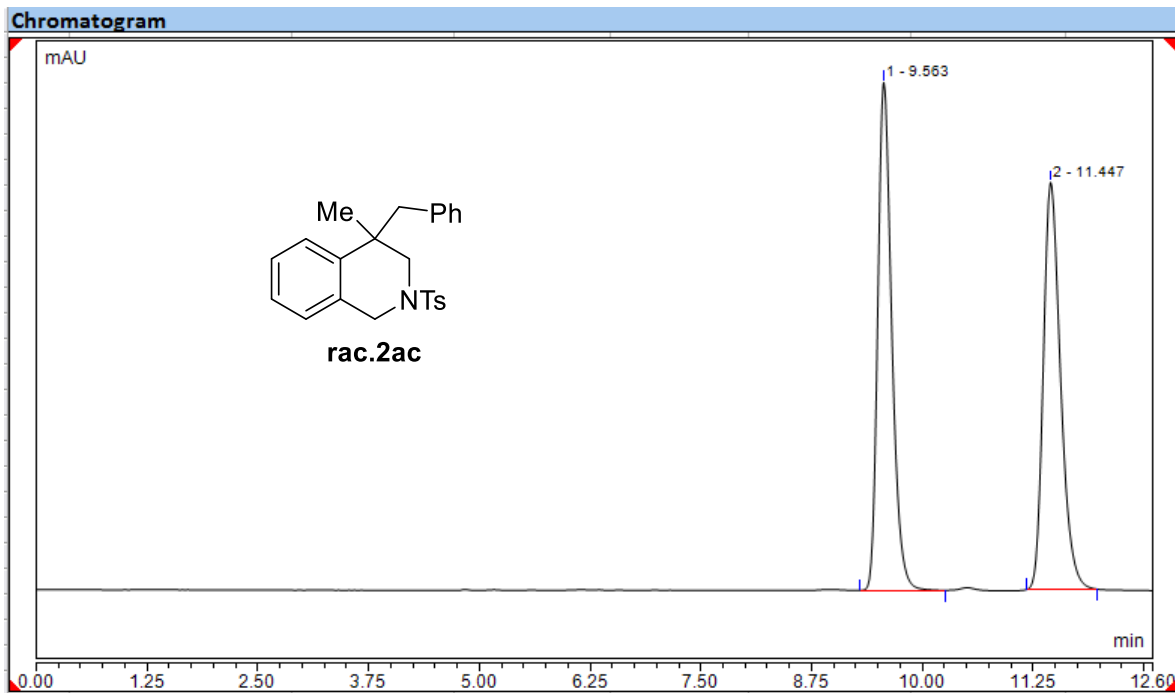


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.920	1.268	8.518	10.30	11.21	n.a.
2		8.573	11.040	67.500	89.70	88.79	n.a.
Total:			12.309	76.018	100.00	100.00	

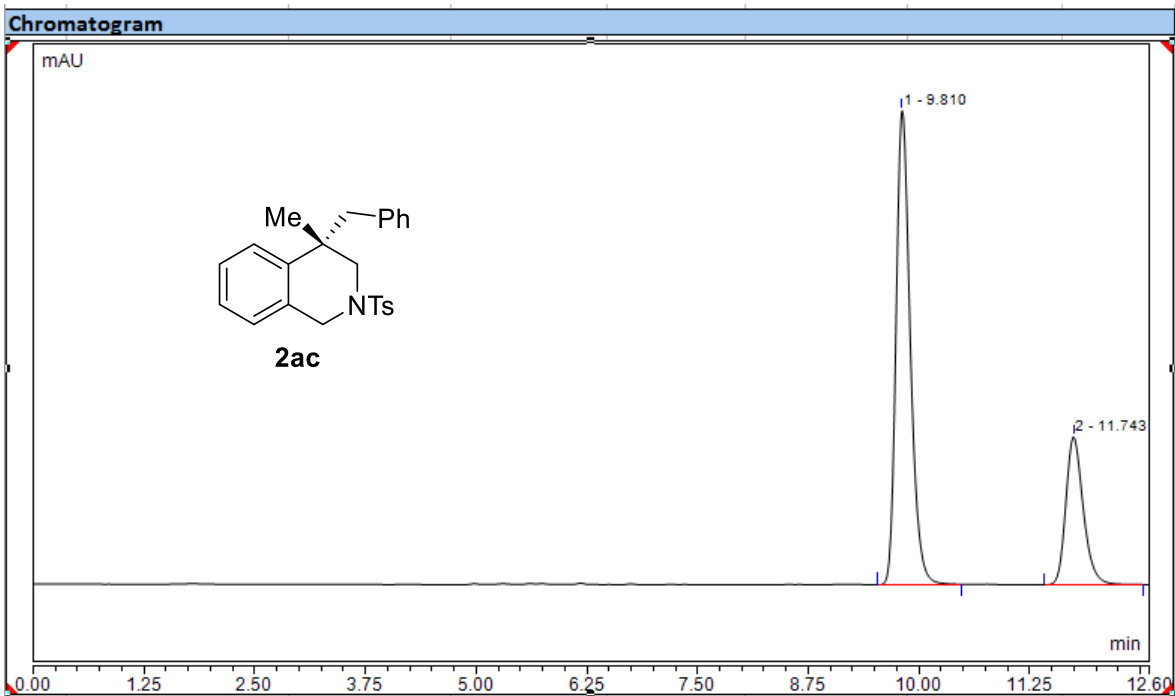
HPLC (Chiralpak IB): $t_R = 7.9$ (minor), 8.6 (major)

Condition: 80:20 n-Hexane:*i*-PrOH, flow rate 0.75 mL/min, 25 °C.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.563	13.527	74.089	50.31	55.52	n.a.
2		11.447	13.360	59.361	49.69	44.48	n.a.
Total:			26.888	133.450	100.00	100.00	

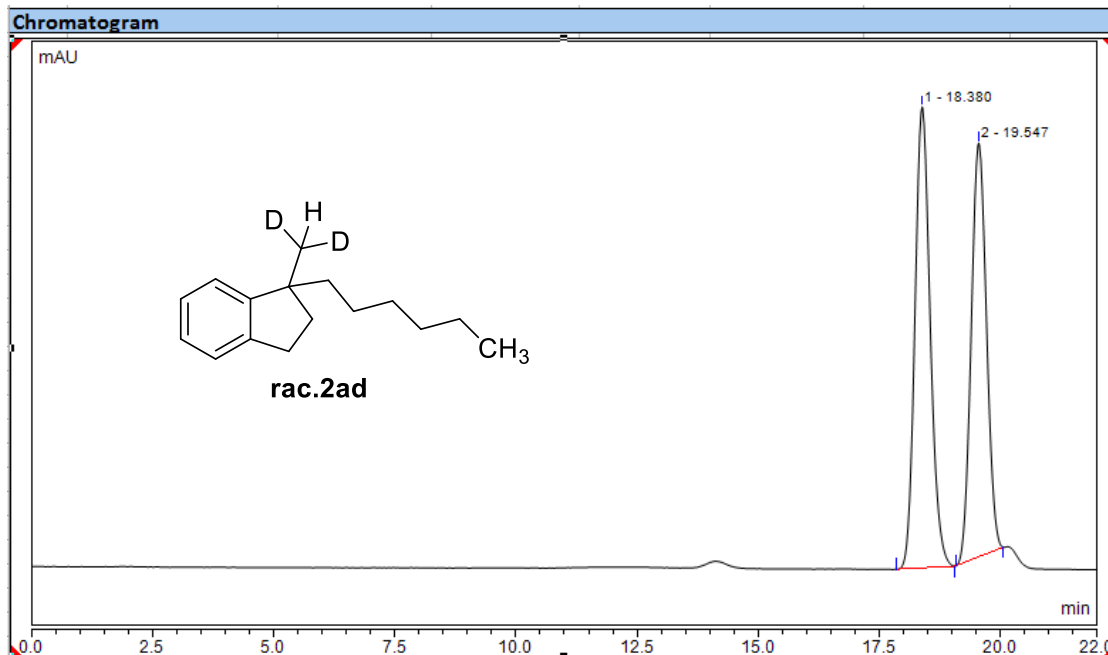


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.810	11.391	61.449	72.22	76.18	n.a.
2		11.743	4.383	19.212	27.78	23.82	n.a.
Total:			15.773	80.661	100.00	100.00	

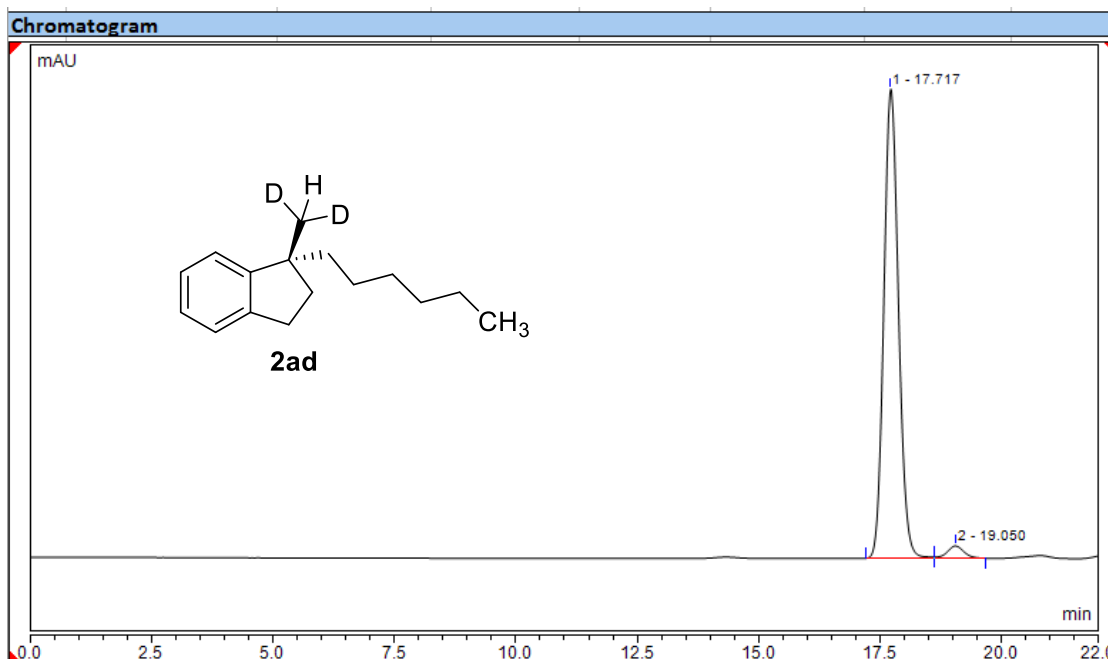
HPLC (Chiralpak IB): $t_R = 9.8$ (major), 11.7 (minor)

Condition: 80:20 n-Hexane:*i*-PrOH, flow rate 0.75 mL/min, 25 °C.



Integration Results

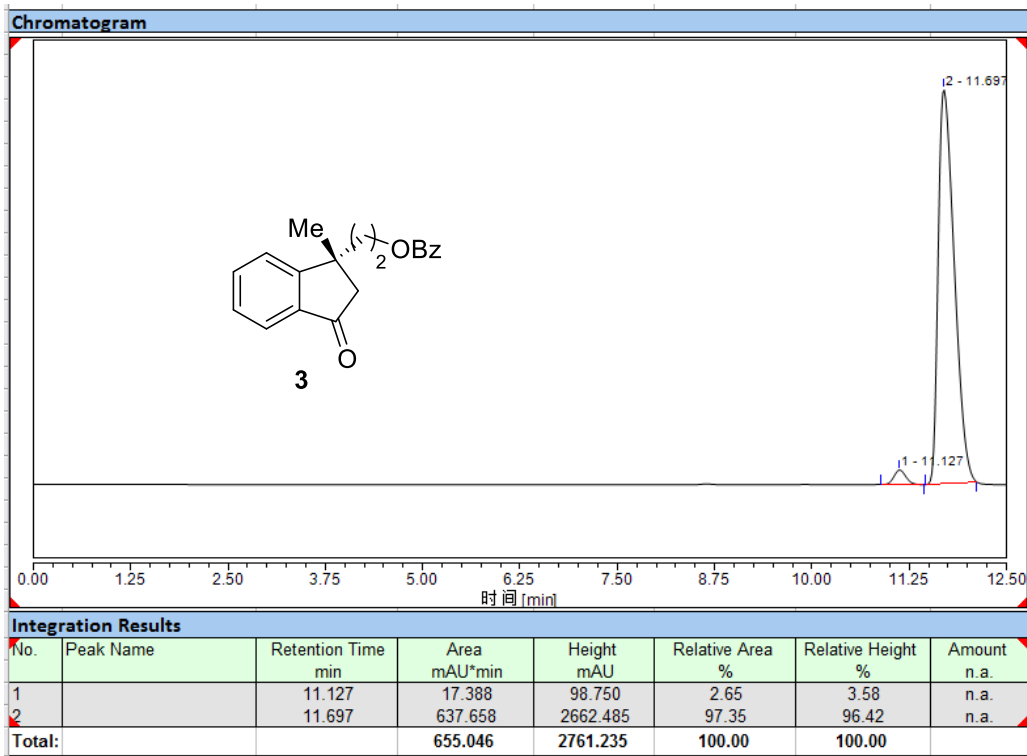
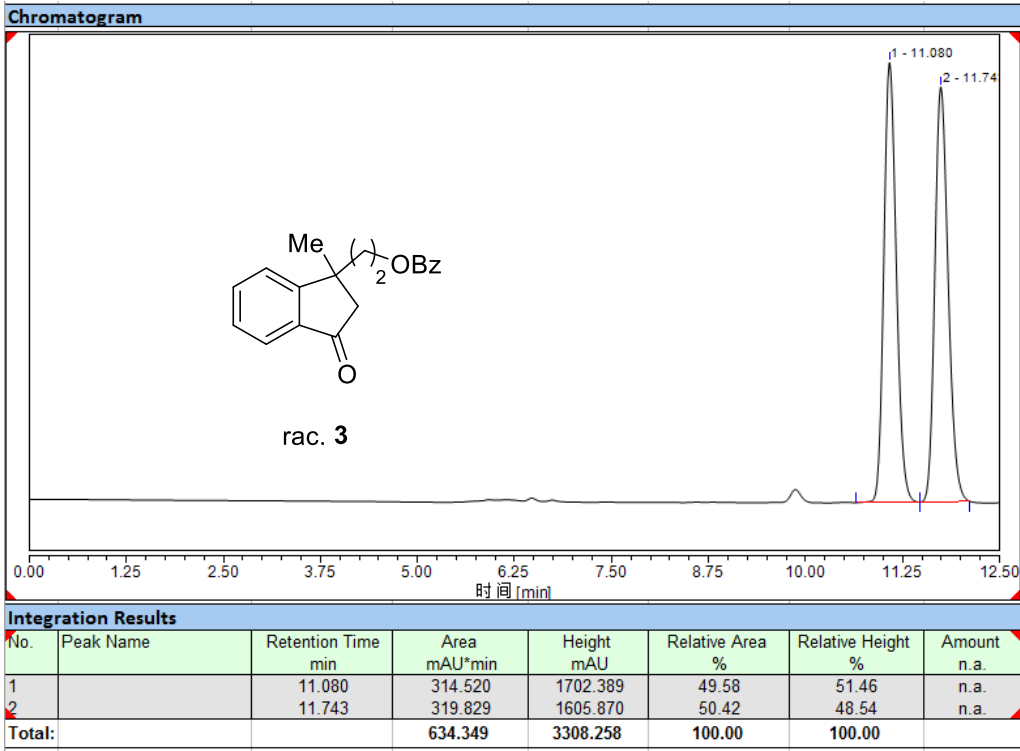
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.380	5.755	15.810	52.74	52.70	n.a.
2		19.547	5.157	14.191	47.26	47.30	n.a.
Total:			10.912	30.000	100.00	100.00	



Integration Results

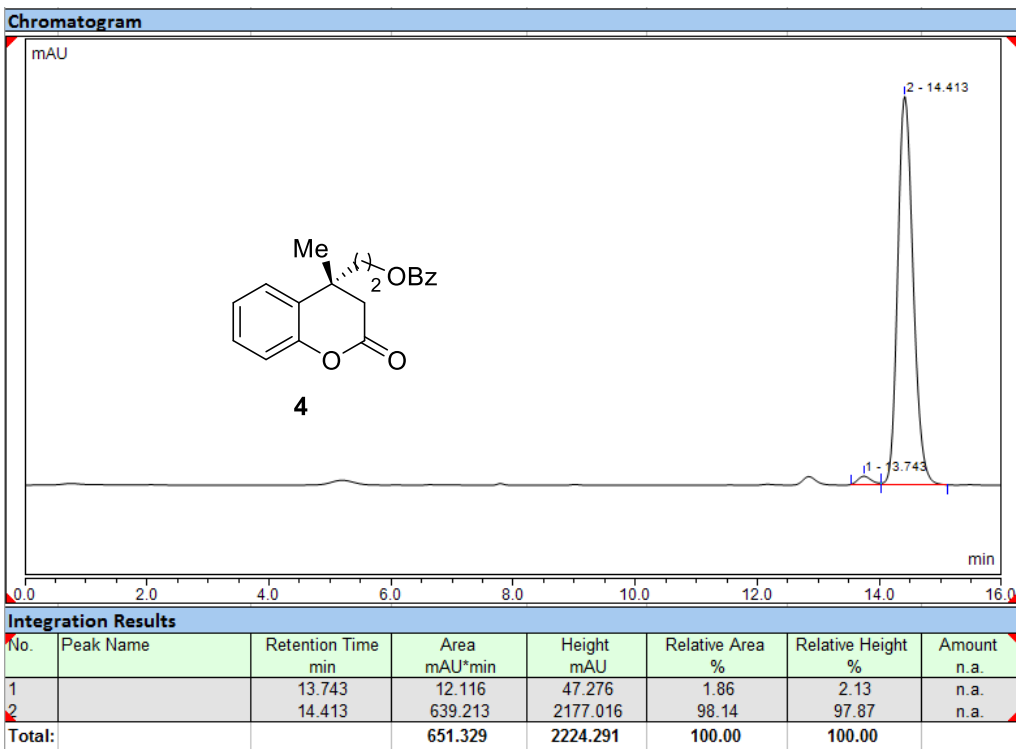
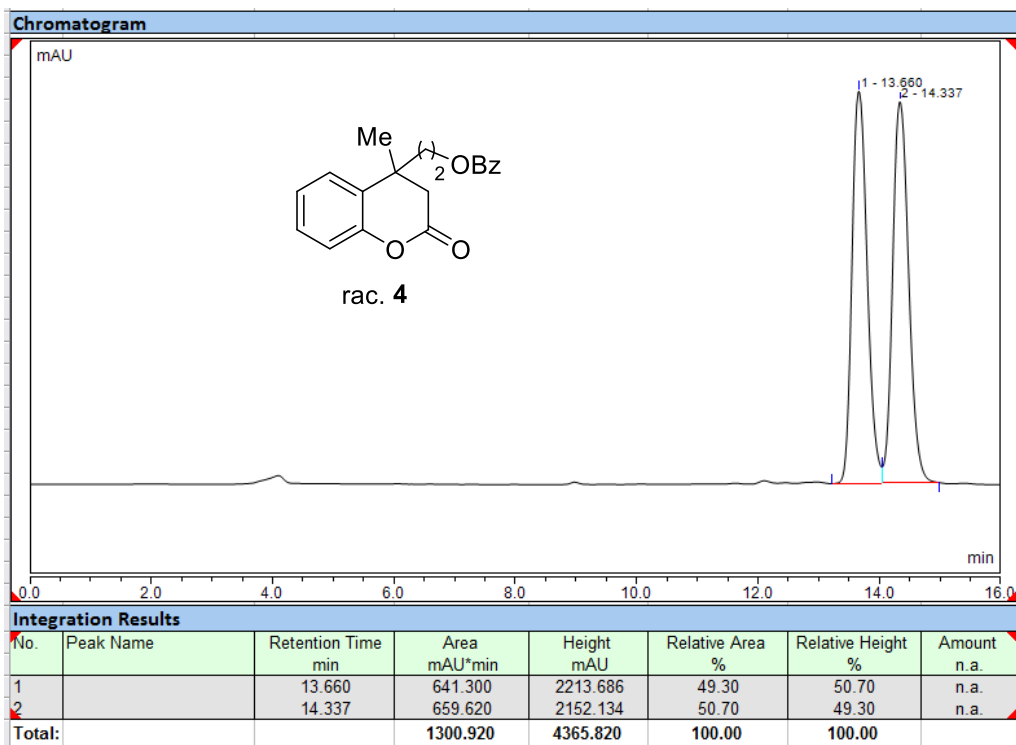
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.717	22.335	64.105	97.05	97.43	n.a.
2		19.050	0.680	1.691	2.95	2.57	n.a.
Total:			23.015	65.795	100.00	100.00	

HPLC (Chiralcel OD-H): $t_R = 17.7$ (major), 19.1 (minor)
 Condition: n-Hexane, flow rate 0.25 mL/min, 25 °C.



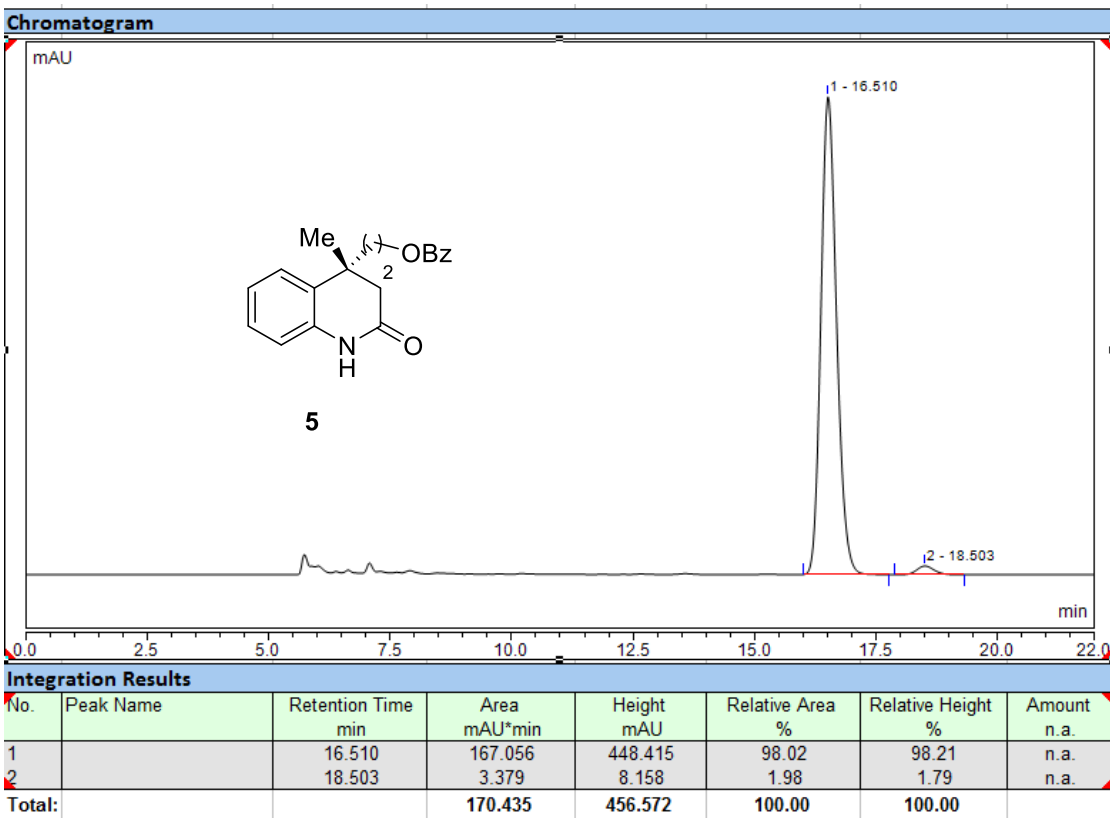
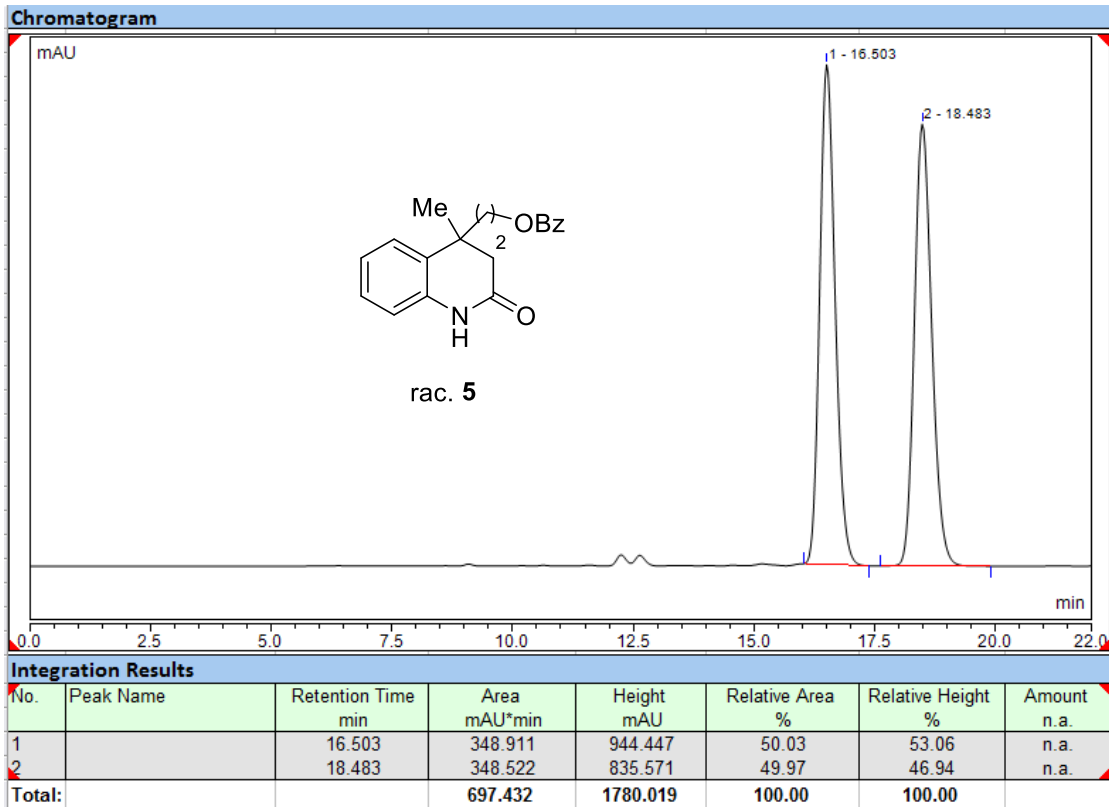
HPLC (Chiralpak IB): tR= 11.1 (minor), 11.7 (major)

Condition: 70:30 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.



HPLC (Chiralpak AD-H): tR= 13.7 (minor), 14.4 (major)

Condition: 70:30 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25°C.



HPLC (Chiralpak AD-H): tR= 16.5 (major), 18.5(minor)

Condition: 70:30 n-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C.