Electronic Supporting Information of the paper: "Sulfolefin": A Mixed Sulfinamido-Olefin Ligand in Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to Trifluoromethyl Ketones.

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Contribution from:

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General Methods

All reactions were run under an atmosphere of dry argon using oven-dried glassware and freshly distilled and dried solvents. Toluene, CH_2Cl_2 and diethyl ether were dried on an Innovative technology drying system. The metallic precursors were purchased from Strem Chemicals and the rest of the chemicals were obtained from Sigma-Aldrich and used without further purification. TLC was performed on Silica Gel GF254 (Merck) with detection by charring with phosphomolybdic acid/EtOH. For flash chromatography, silica Gel (Merck 230-400 mesh) was used. Chromatographic columns were eluted with positive air pressure and eluents are given as volume to volume ratios (v/v). NMR spectra were recorded with a Bruker Avance DPX400 (^{1}H, 400 MHz) and Bruker Avance DRX500 (^{1}H, 500 MHz), spectrometers. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Routine spectra were referenced to the residual proton or carbon signals of the solvent. High Resolution mass spectra (HRMS) were recorded in “Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla” with a Kratos MS-80RFA 241-MC apparatus. Optical rotations were determined with a Perkin-Elmer 341 polarimeter. Elemental analysis were measured in a LECO TruSpec® CHNS-932 apparatus. Melting points were measured in STUART SMP3 apparatus in open end capillary tubes. Enantiomeric excesses were measured on a Waters alliance 2695 and Agilent Technologies 1200 series apparatus with stationary chiral phase columns (Chiralcel® AD-H, OJ-H, OD-H).

General procedure for asymmetric addition to trifluoromethyl ketones

To a mixture of the arylboronic acid (0.6 mmol, 2 equiv), K_2CO_3 (0.75 mmol, 3 equiv), ligand **I** (3.6 mg, 0.015 mmol, 5 mol %) and [Rh(C2H4)2Cl]2 (3 mg, 0.0075 mmol, 2.5 mol %) was added the solvent (1.5 mL) and the trifluoromethyl ketone (0.30 mmol, 1 equiv). After stirred at 60 ° C for the corresponding time, the reaction mixture was directly purified by column chromatography [silica gel, (Hexane:CH_2Cl_2, 3:2)] as eluent to afford the desired alcohol product. The enantioselectivity was determined by chiral HPLC on a chiralcel OD-H®, OJ-H® or AD-H®.

(*S*)-2,2,2-trifluoro-1-phenyl-1-(*p*-tolyl)ethan-1-ol, (4a): Following the typical procedure, the reaction of the 2,2,2-trifluoroacetophenone **2a** (42 µL, 0.3 mmol) and *p*-tolyl boronic acid **3a** (81.5 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4a** as a colorless oil. Yield: 58.4mg, 73% $[\alpha]^{D}_{20}$= - 4.5 (*c* 0.8, CH_2Cl_2). HPLC: 68 % *ee*, Chiralcel OJ-H® column (*n*-hexane/2-propanol, 95:5, 1 mL/min); t_R: 20.89 min (mayor), 22.42 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.43-7.37 (m, 5H), 7.22-7.19 (m, 2H), 2.87 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.47, 138.59, 136.53, 129.00, 128.60, 128.23, 127.42, 127.32, 125.38 (q, *J* = 284 Hz), 79.39 (q, *J* = 29 Hz) 21.10. ^{19}F (376 MHz, $CDCl_3$) δ -74.33. HRMS *m/z* calcd for $C_{15}H_{13}F_3O$ 266.0918, found 266.0919.

(*S*)-2,2,2-trifluoro-1-(4-methoxyphenyl)-1-phenylethan-1-ol, (4b): Following the typical procedure , the reaction of the 2,2,2-trifluoroacetophenone **2a** (42 µL, 0.3 mmol) and 4-methoxyphenyl boronic acid **3b** (91.2 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4b** as a colorless oil. Yield: 53 mg, 63% $[\alpha]^{D}_{20}$= - 3.0 (*c* 0.9, CH_2Cl_2). HPLC: 70 % *ee*, Chiralcel OD-H® column (*n*-hexane/2-propanol, 97:3, 1 mL/min); t_R: 10.20 min (major), 11.35 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.44-7.38 (m, 5H), 6.92-6.89 (m, 2H), 3.83 (s, 3H), 2.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.64, 139.54, 131.55, 128.82, 128.59, 128.22, 127.42, 125.40 (q, *J* = 284 Hz), 113.59, 79.23 (q, *J* = 29 Hz), 55.28. ^{19}F (376 MHz, $CDCl_3$) δ -74.42. HRMS *m/z* calcd for $C_{15}H_{13}F_3O_2$ 282.0868, found 282.0863.

(*S*)-2,2,2-trifluoro-1-phenyl-1-(*m*-tolyl)ethan-1-ol, (4c): Following the typical procedure , the reaction of the 2,2,2-trifluoroacetophenone **2a** (42 µL, 0.3 mmol) and *m*-tolyl boronic acid **3c** (81.5 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4c** as a colorless oil. Yield: 28 mg, 35% $[\alpha]^{D}_{20}$= - 9.0 (*c* 0.9, CH_2Cl_2). HPLC: 56 % *ee*, Chiralcel OJ-H® column (*n*-hexane/2-propanol, 95:5, 1 mL/min); t_R: 13.32 min (major), 16.86 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.41-7.38 (m, 3H, 7.35-7.28 (m, 3H), 7.21-7.19 (m, 1H), 2.89 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.37, 129.32, 138.05, 129.44, 128.61, 128.24, 128.15, 127.93, 127.41, 125.33 (q, *J* = 284 Hz), 124.46, 79.44 (q, *J* = 29 Hz), 21.59. ^{19}F (376 MHz, $CDCl_3$) δ -74.20. HRMS *m/z* calcd for $C_{15}H_{13}F_3O$ 266.0918, found 266.0917.

(*R*)-2,2,2-trifluoro-1-(4-fluorophenyl)-1-(*p*-tolyl)ethan-1-ol, (4d): Following the typical procedure , the reaction of the 2,2,2,4'-tetrafluoroacetophenone **2b** (42 µL, 0.3 mmol) and *p*-tolyl boronic acid **3a** (81.5 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4d** as a colorless oil. Yield: 73 mg, 86% $[\alpha]^{D}_{20}$= - 9.0 (*c* 0.9, CH_2Cl_2). HPLC: 78% *ee*, Chiralcel OD-H® column (*n*-hexane/2-propanol, 98:2, 1 mL/min); t_R: 14.52 min (major), 16.68 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.40-7.38 (m, 2H), 7.22-7.20 (m, 2H), 7.09-7.04 (m, 2H), 3.00 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.83 (d, *J* = 247 Hz), 138.82, 136.41, 135.19, 129.55, 129.47, 129.12, 127.20, 125.24 (q, *J* = 286 Hz), 115.19, 114.98, 79.05 (q, *J* = 28 Hz), 21.07. ^{19}F (376 MHz, $CDCl_3$) δ -74.8, -113.3. HRMS *m/z* calcd for $C_{15}H_{12}F_4O$ 284.0824, found 284.0825.

(*R*)-2,2,2-trifluoro-1-(4-fluorophenyl)-1-(*p*-methoxyphenyl)ethan-1-ol, (4e): Following the typical procedure , the reaction of the 2,2,2,4'-tetrafluoroacetophenone **2b** (42 µL, 0.3 mmol) and *p*-methoxyphenyl boronic acid **3b** (91.2 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4e** as a colorless oil. Yield: 81.1 mg, 90% $[\alpha]^{D}_{20}$= - 11.57 (*c* 0.8, CH_2Cl_2). HPLC: 76 % *ee*, Chiralcel AD-H® column (*n*-hexane/2-propanol, 97:3, 1 mL/min); t_R: 9.84 min (major), 12.67 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.42-7.40 (m, 2H), 7.08-7.04 (m, 2H), 6.92-6.90 (m, 2H), 3.83 (s, 3H), 3.06 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.70 (d, *J* = 247 Hz), 159.73, 135.29, 131.43, 129.56, 129.48, 128.73, 125.28 (q, *J* = 29 Hz), 115.18,

114.97, 113.71, 78.92 (q, *J* = 29 Hz), 55.29. ^{19}F (376 MHz, $CDCl_3$) δ -74.65, -113.32. HRMS *m/z* calcd for $C_{15}H_{12}F_4O_2$ 300.0773, found 300.0770.

(*S*)-2,2,2-trifluoro-1-(4-fluorophenyl)-1-(*m*-tolyl)ethan-1-ol, (4f): Following the typical procedure , the reaction of the 2,2,2,4'-tetrafluoroacetophenone **2b** (42 µL, 0.3 mmol) and *m*-tolyl boronic acid **3c** (81.5 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4f** as a colorless oil. Yield: 24.4 mg, 29% $[\alpha]^D_{20}$= - 14.37(*c* 0.7, CH_2Cl_2). HPLC: 66 % *ee*, Chiralcel OJ-H® column (*n*-hexane/2-propanol, 95.5:0.5, 0.5 mL/min); t_R: 78.91 min (minor), 92.18 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H, 7.32-7.29 (m, 3H), 7.22-7.21 (m, 1H), 7.09-7.05 (m, 2H), 2.89 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.71 (d, *J* = 247 Hz), 139.22, 138.23, 135.07, 129.61, 129.54, 129.46, 128.28, 127.84, 125.20 (q, *J* = 284 Hz), 124.31, 115.21, 115.00, 79.14 (q, *J* = 24 Hz), 21.58. . ^{19}F (376 MHz, $CDCl_3$) δ -74.42, -113.26. HRMS *m/z* calcd for $C_{15}H_{12}F_4O$ 284.0824, found 284.0826.

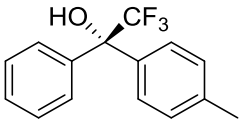
(*S*)-2,2,2-trifluoro-1-(4-fluorophenyl)-1-(naphthalen-2-yl)ethan-1-ol, (4g): Following the typical procedure , the reaction of the 2,2,2,4'-tetrafluoroacetophenone **2b** (42 µL, 0.3 mmol) and 2-naphthyl boronic acid **3d** (103.2 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4g** as a colorless oil. Yield: 123 mg, 99% $[\alpha]^D_{20}$= - 13.61(*c* 0.8, CH_2Cl_2). HPLC: 44 % *ee*, Chiralcel OD-H® column (*n*-hexane/2-propanol, 90:10, 1 mL/min); t_R: 7.20 min (major), 10.18 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.13 (m, 1H), 7.94-7.85 (m, 3H), 7.60-7.48 (m, 5H), 7.11-7.07 (m, 2H), 3.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.81 (d, *J* = 247 Hz), 136.37, 134.94, 133.08, 132.60, 129.71, 129.63, 128.70, 128.40, 127.59, 127.11, 126.70, 125.72 (q, *J* = 145 Hz), 115.34, 115.13, 79.38 (q, *J* = 29 Hz). ^{19}F (376 MHz, $CDCl_3$) δ -74.11, -112.94. HRMS *m/z* calcd for $C_{18}H_{12}F_4O$ 320.0824, found 320.0829.

(*R*)-1-(4-chlorophenyl)-2,2,2-trifluoro-1-(*p*-methoxyphenyl)ethan-1-ol, (4h): Following the typical procedure , the reaction of the 4'-chloro-2,2,2-trifluoroacetophenone **2c** (45 µL, 0.3 mmol) and *p*-methoxyphenyl boronic acid **3b** (91.2 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4h** as a colorless oil. Yield: 55 mg, 58 % $[\alpha]^D_{20}$= - 12.80 (*c* 0.8, CH_2Cl_2). HPLC: 66 % *ee*, Chiralcel OD-H® column (*n*-hexane/2-propanol, 90:10, 1 mL/min); t_R: 5.73 min (major), 6.29 min (minor). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.47-7.35 (m, 6H), 6.92-6.90 (m, 2H), 3.84 (s, 3H), 2.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.79, 137.92, 134.71, 131.20, 129.00, 128.72, 128.36, 125.19 (q, *J* = 284 Hz), 113.77, 78.93 (q, *J* = 29 Hz), 55.31. ^{19}F (376 MHz, $CDCl_3$) δ -74.57. HRMS *m/z* calcd for $C_{15}H_{12}ClF_3O_2$ 316.0478, found 316.0471.

(*R*)-1-(4-chlorophenyl)-2,2,2-trifluoro-1-(*p*-tolyl)ethan-1-ol, (4i): Following the typical procedure , the reaction of the 4'-chloro-2,2,2-trifluoroacetophenone **2c** (45 µL, 0.3 mmol) and *p*-tolyl boronic acid **3a** (81.5 mg, 0.6 mmol) gave, after flash chromatography (Hexane:CH_2Cl_2, 3:2) the product **4i** as a colorless oil. Yield: 55 mg, 61 % $[\alpha]^{D}_{20}$= - 13.02 (*c* 0.8, CH_2Cl_2). HPLC: 74 % *ee*, Chiralcel AD-H® column (*n*-hexane/2-propanol, 95:5, 1 mL/min); t_R: 8.79 min (major), 9.50 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.40-7.35 (m, 4H), 7.23-7.21 (m, 2H), 2.92 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.91, 137.83, 136.19, 134.72, 129.17, 128.99, 128.37, 127.18, 125.17 (q, *J* = 285 Hz), 79.08 (q, *J* = 29 Hz), 21.09. ^{19}F (376 MHz, $CDCl_3$) δ -74.49. HRMS *m/z* calcd for $C_{15}H_{12}ClF_3O$ 300.0529, found 300.0528.

HPLC Chromatograms



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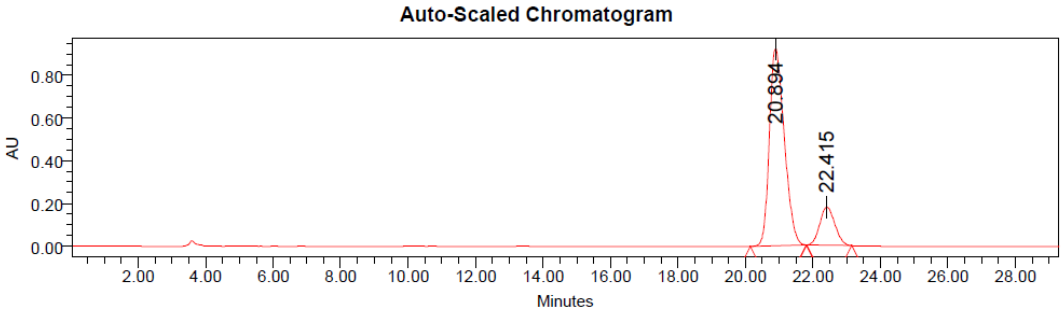

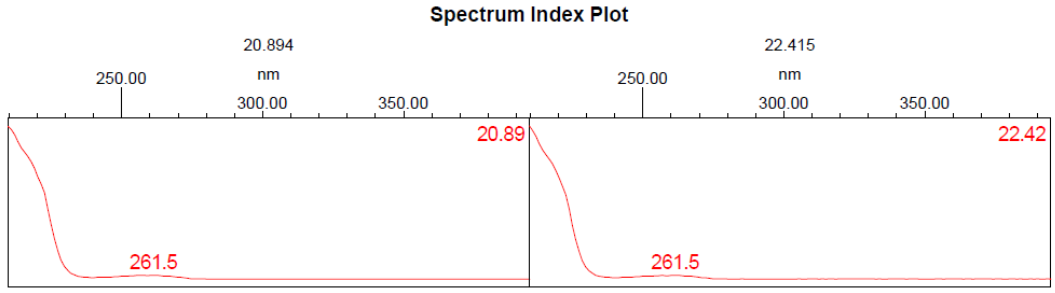

Peak Results

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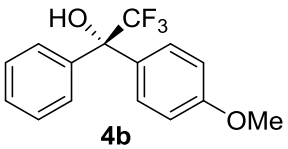
2		22.415	16.46



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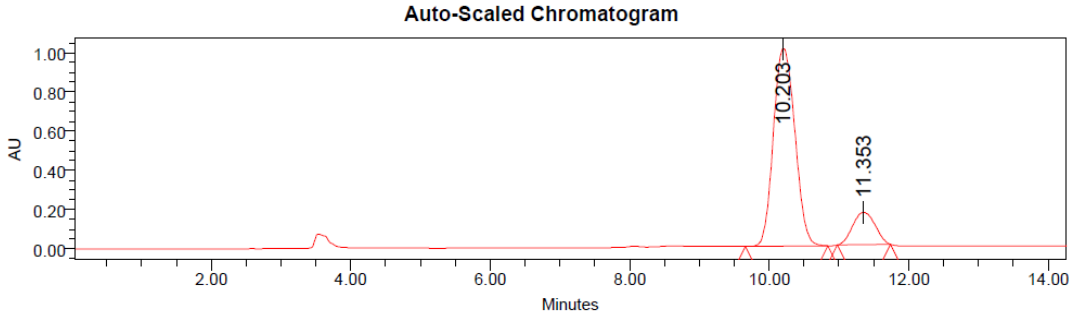

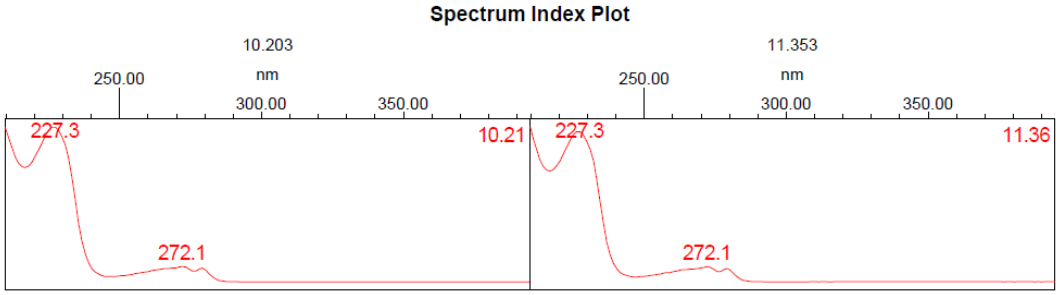

Peak Results

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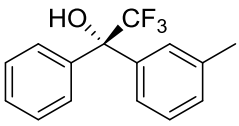

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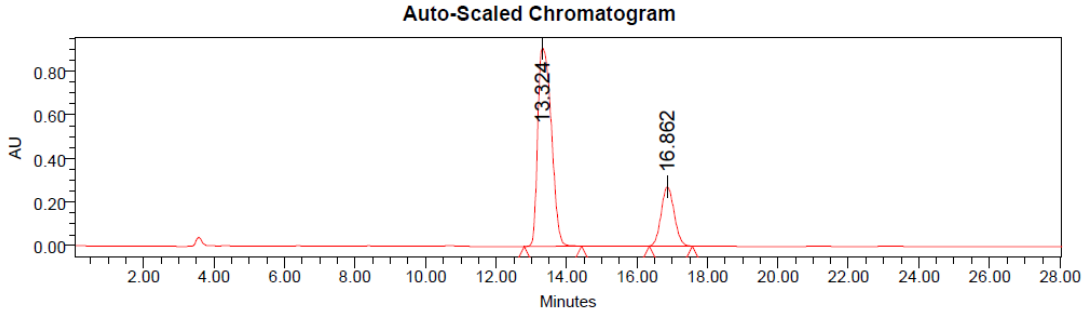

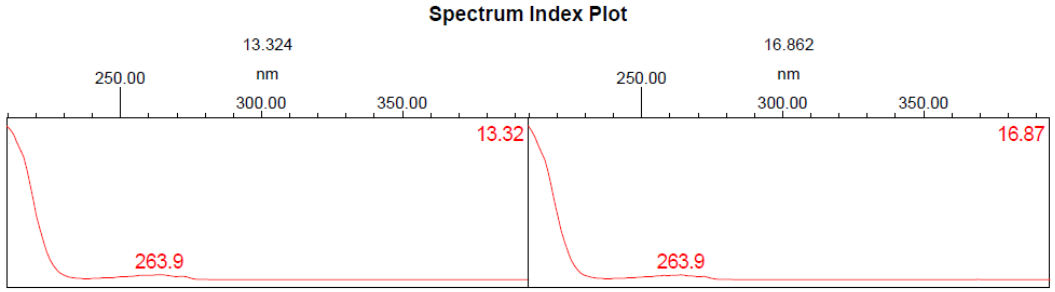

Peak Results

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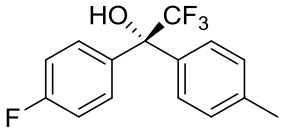

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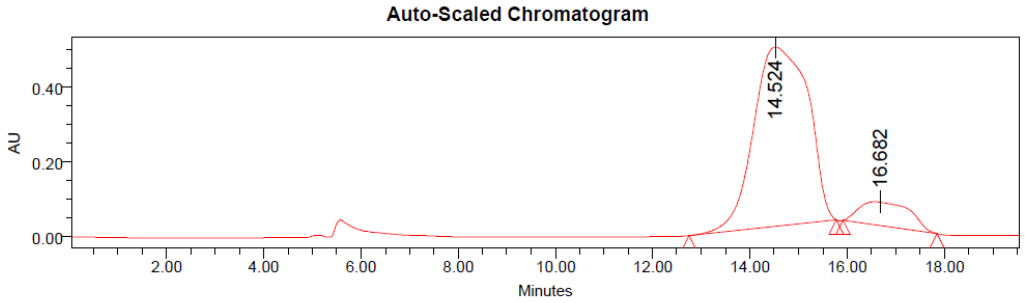

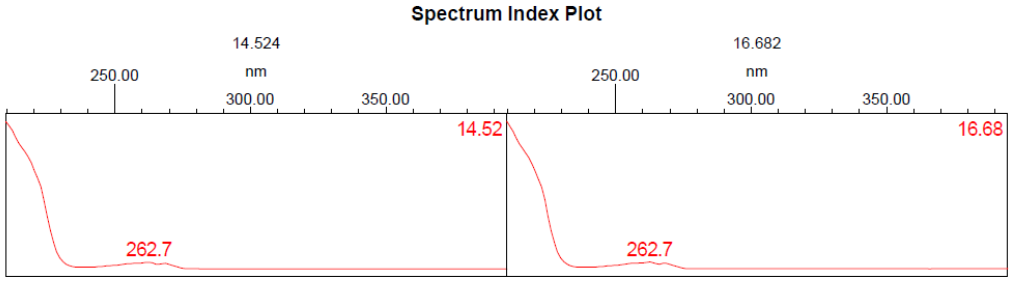

Peak Results

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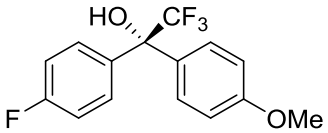
2		16.682	11.18



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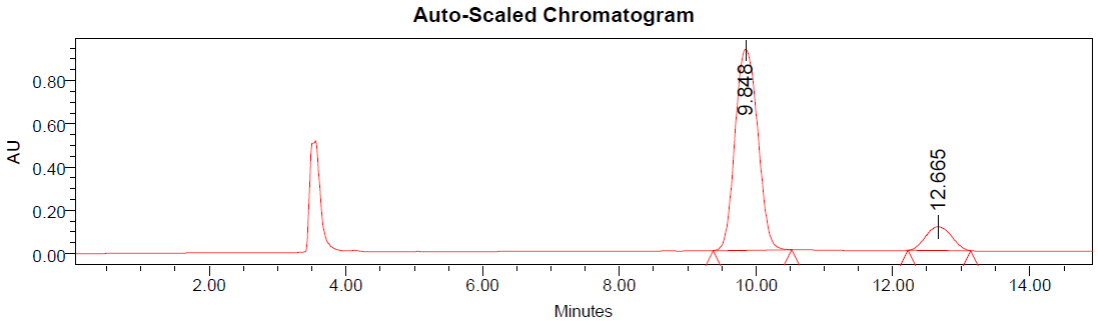

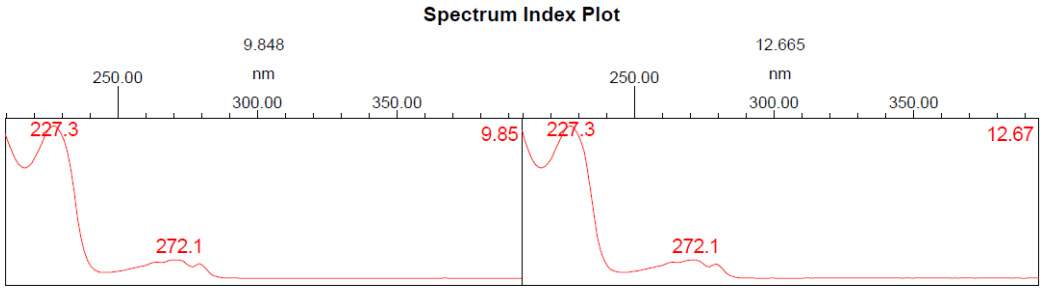

Peak Results

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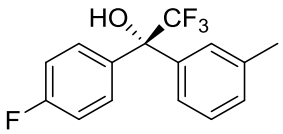

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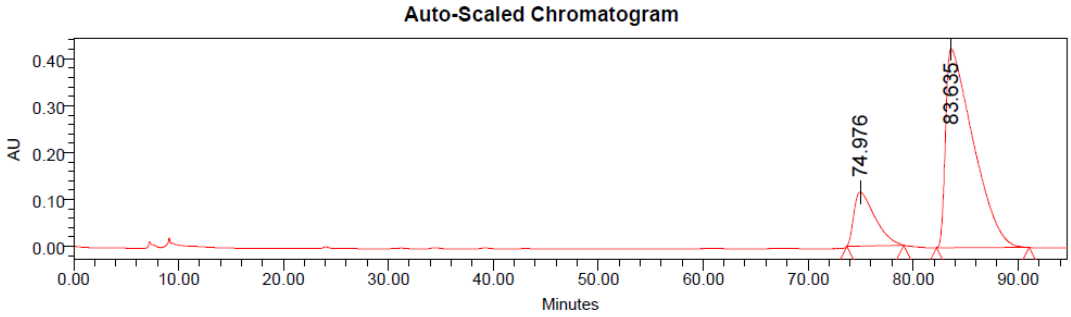

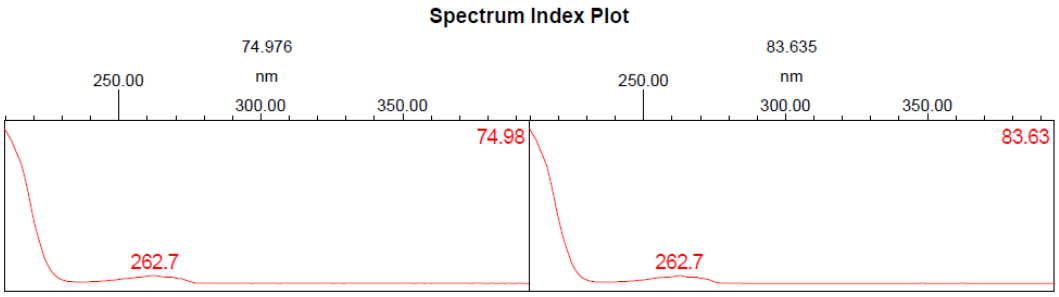

Peak Results

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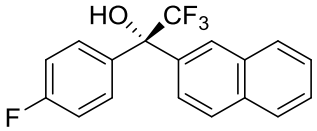

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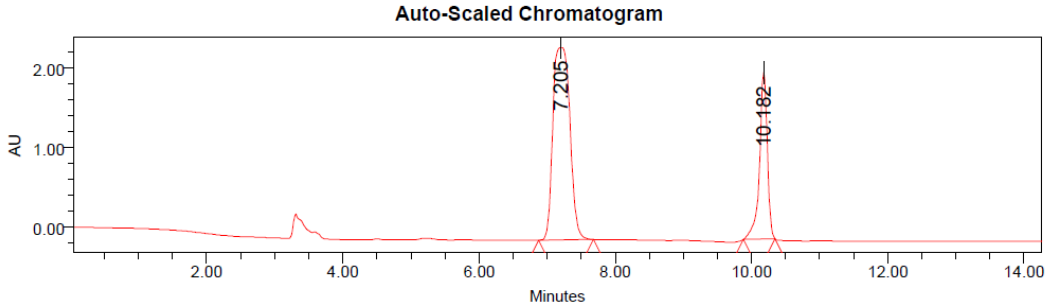

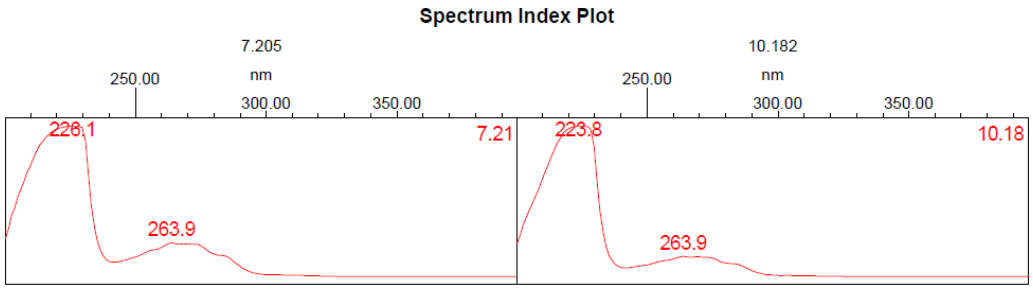

Peak Results

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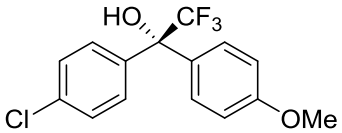

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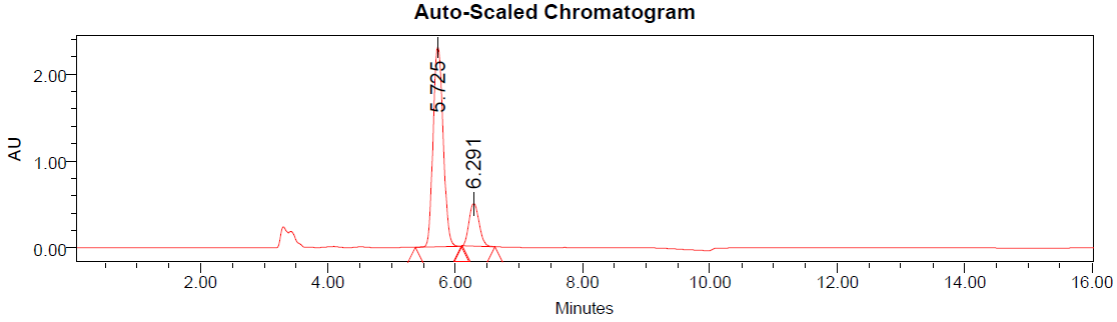
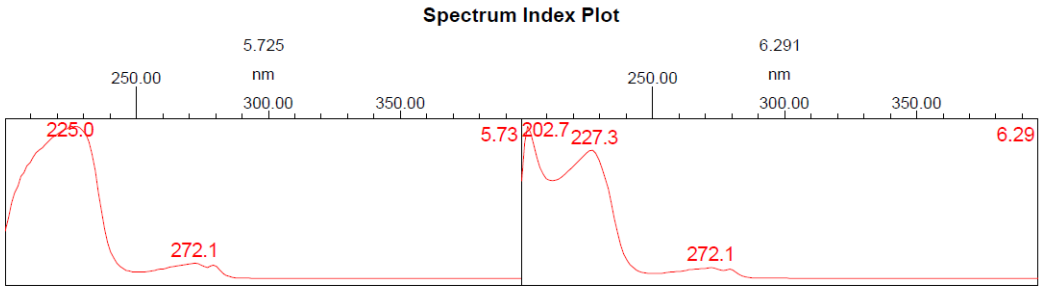
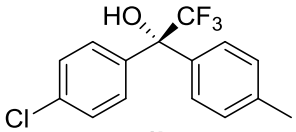




Peak Results

	Name	RT	% Area
1		5.725	82.67
2		6.291	17.33



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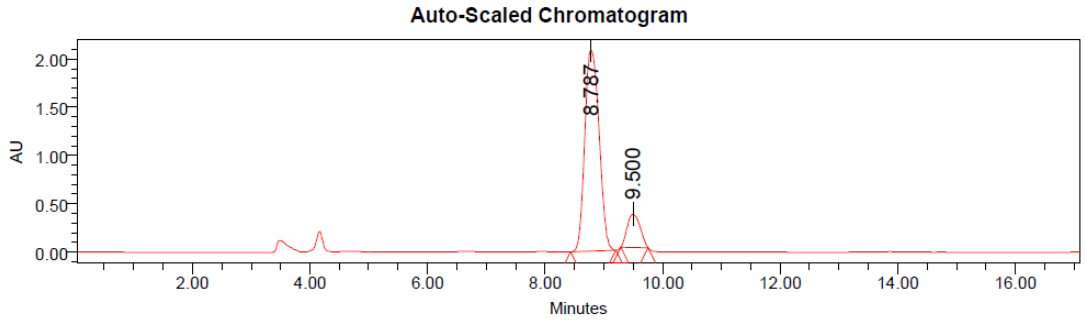
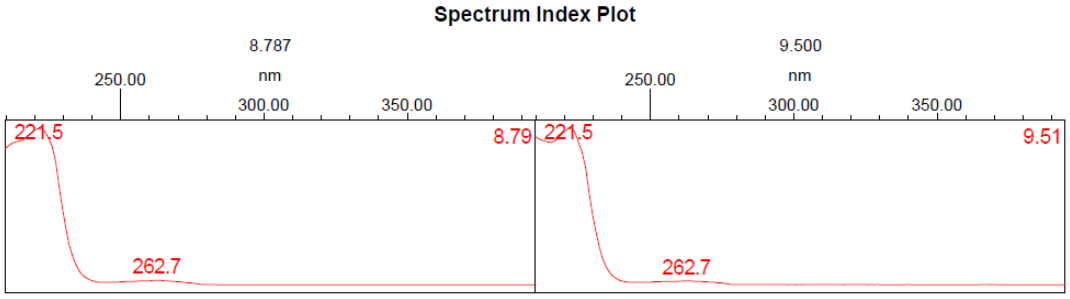
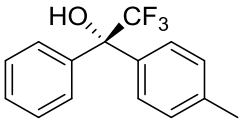




Peak Results

	Name	RT	% Area
1		8.787	87.04
2		9.500	12.96

NMR Spectra collection



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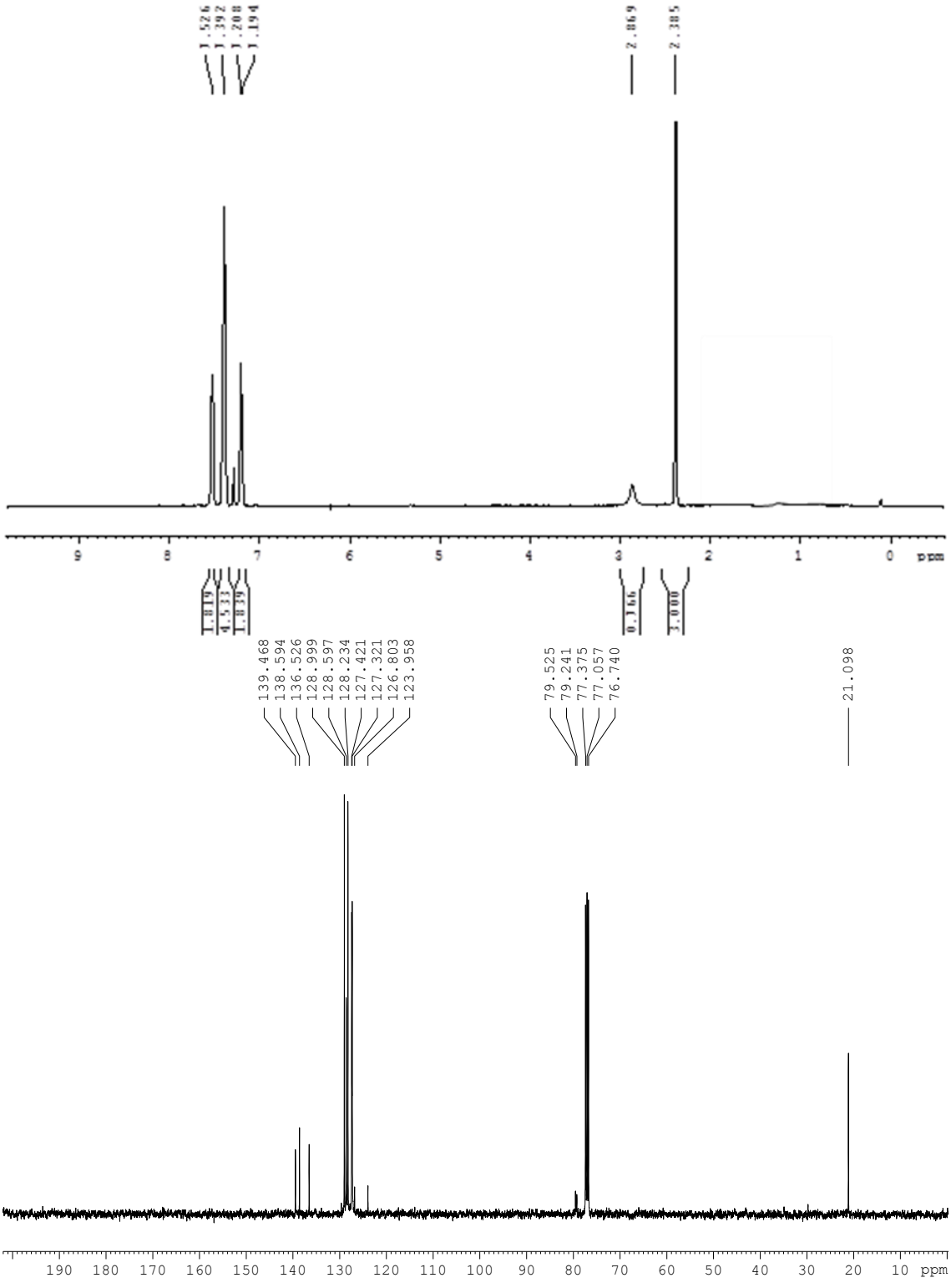

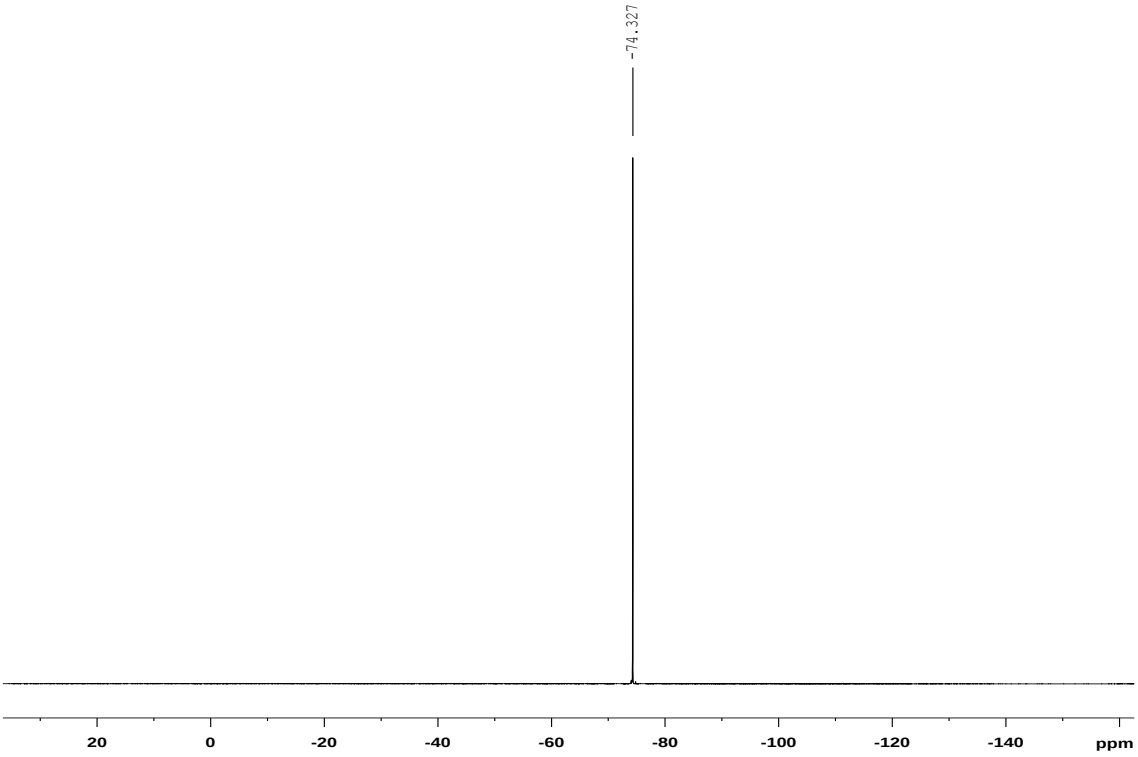

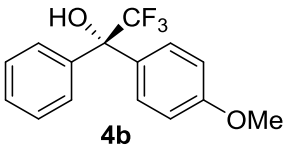

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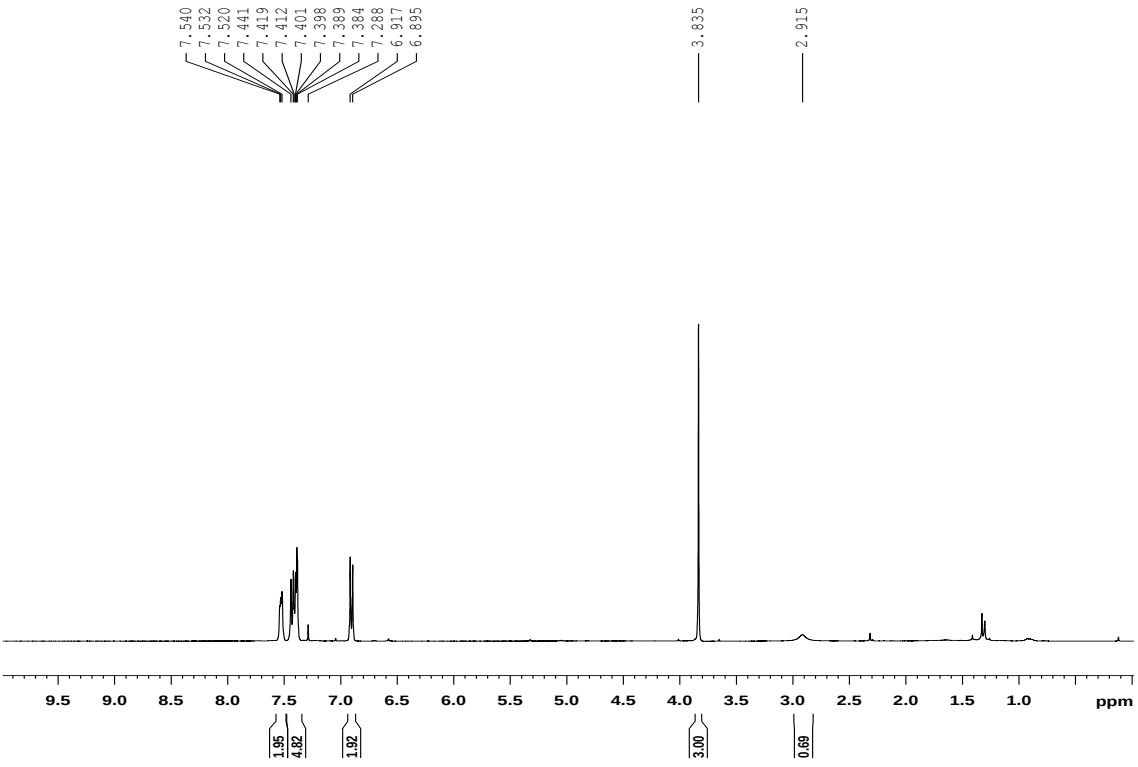

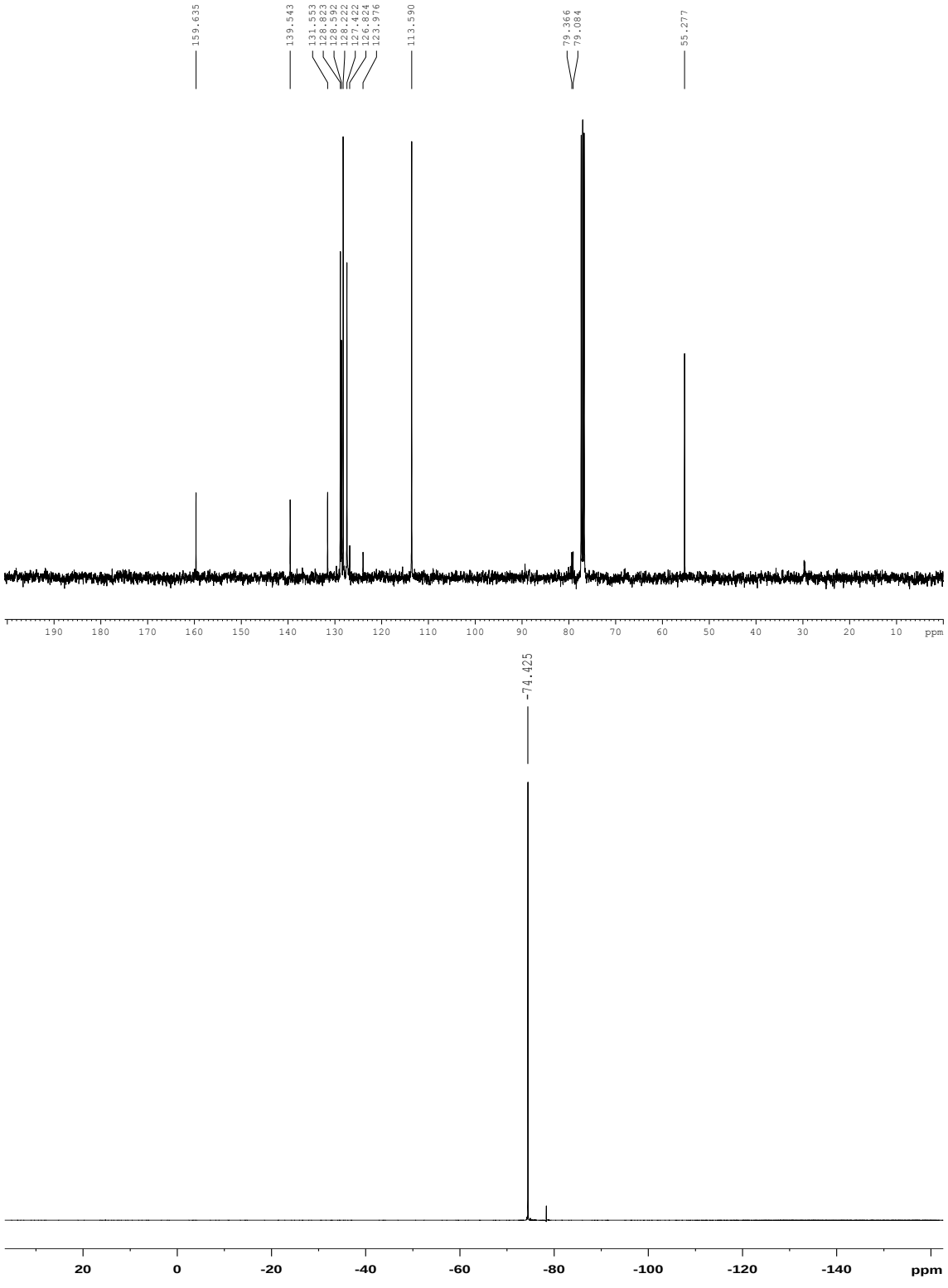

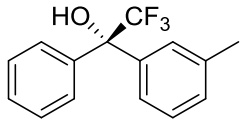

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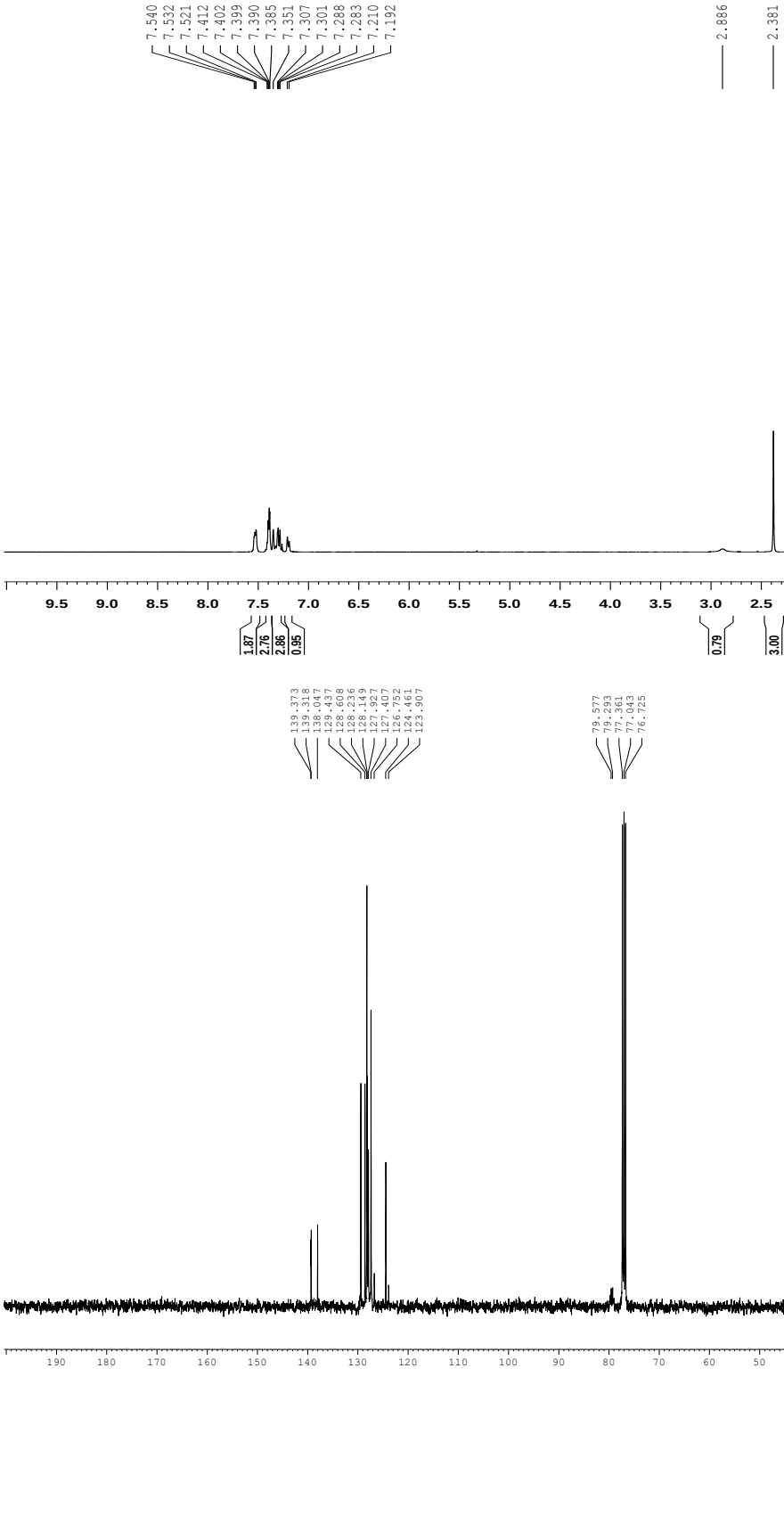

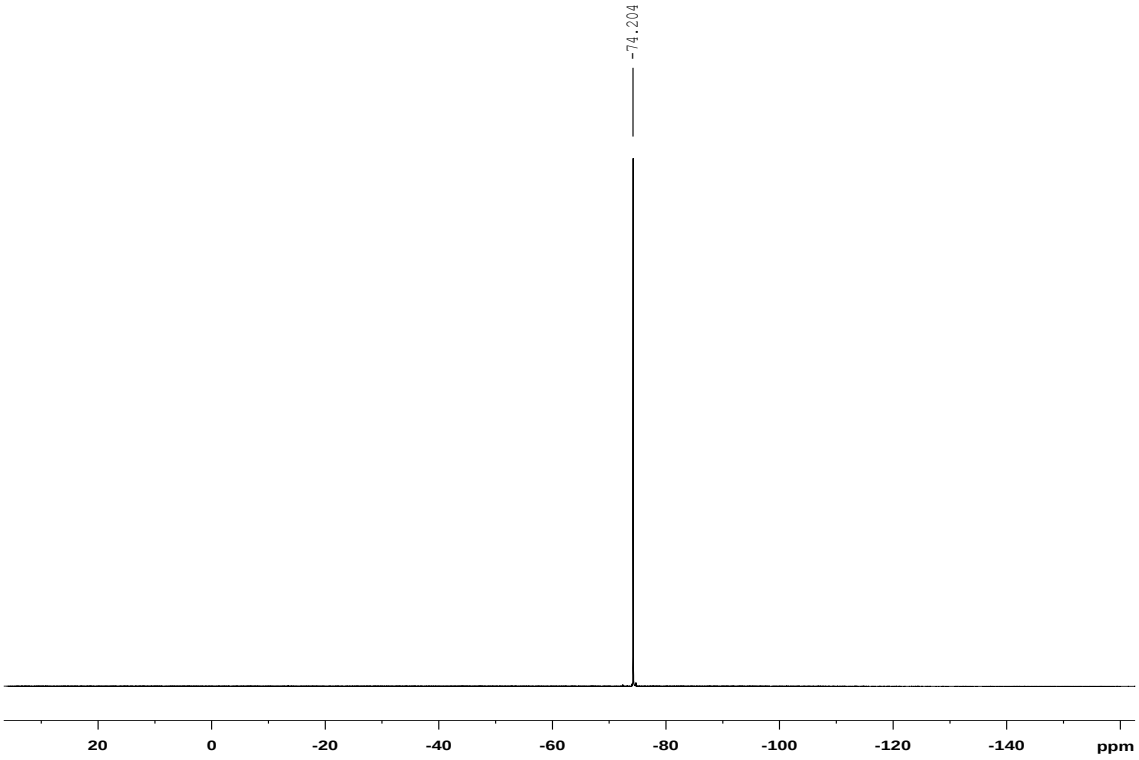

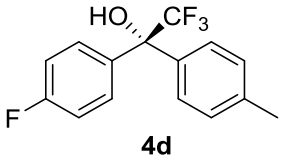

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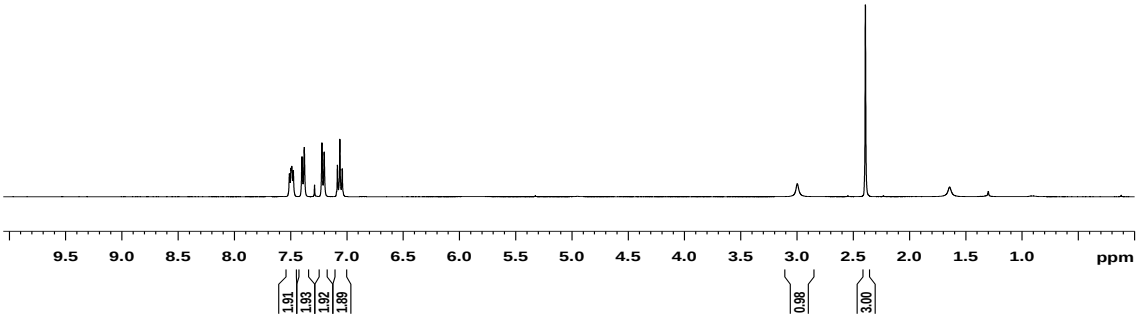

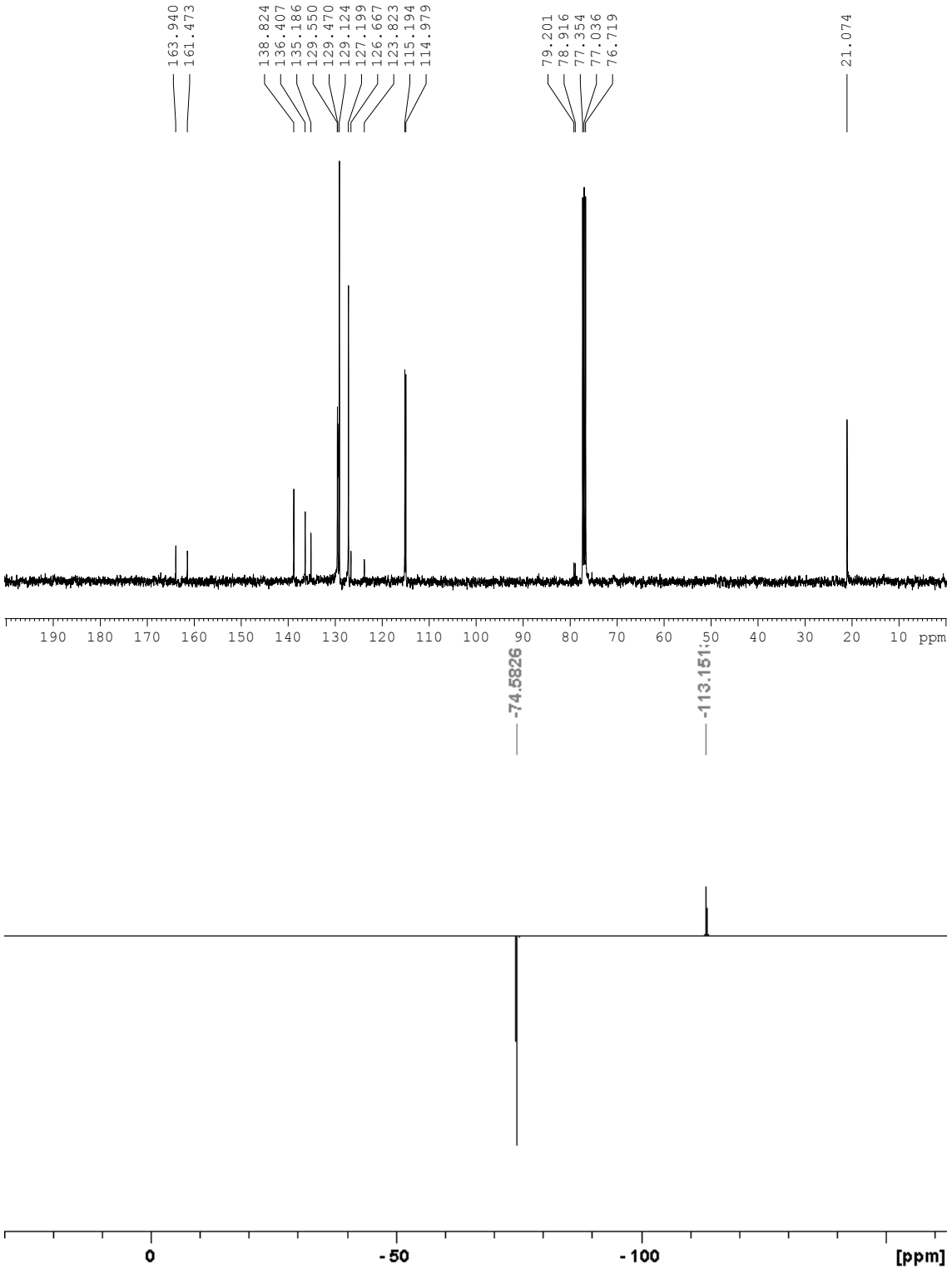

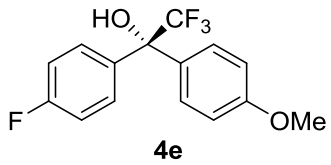

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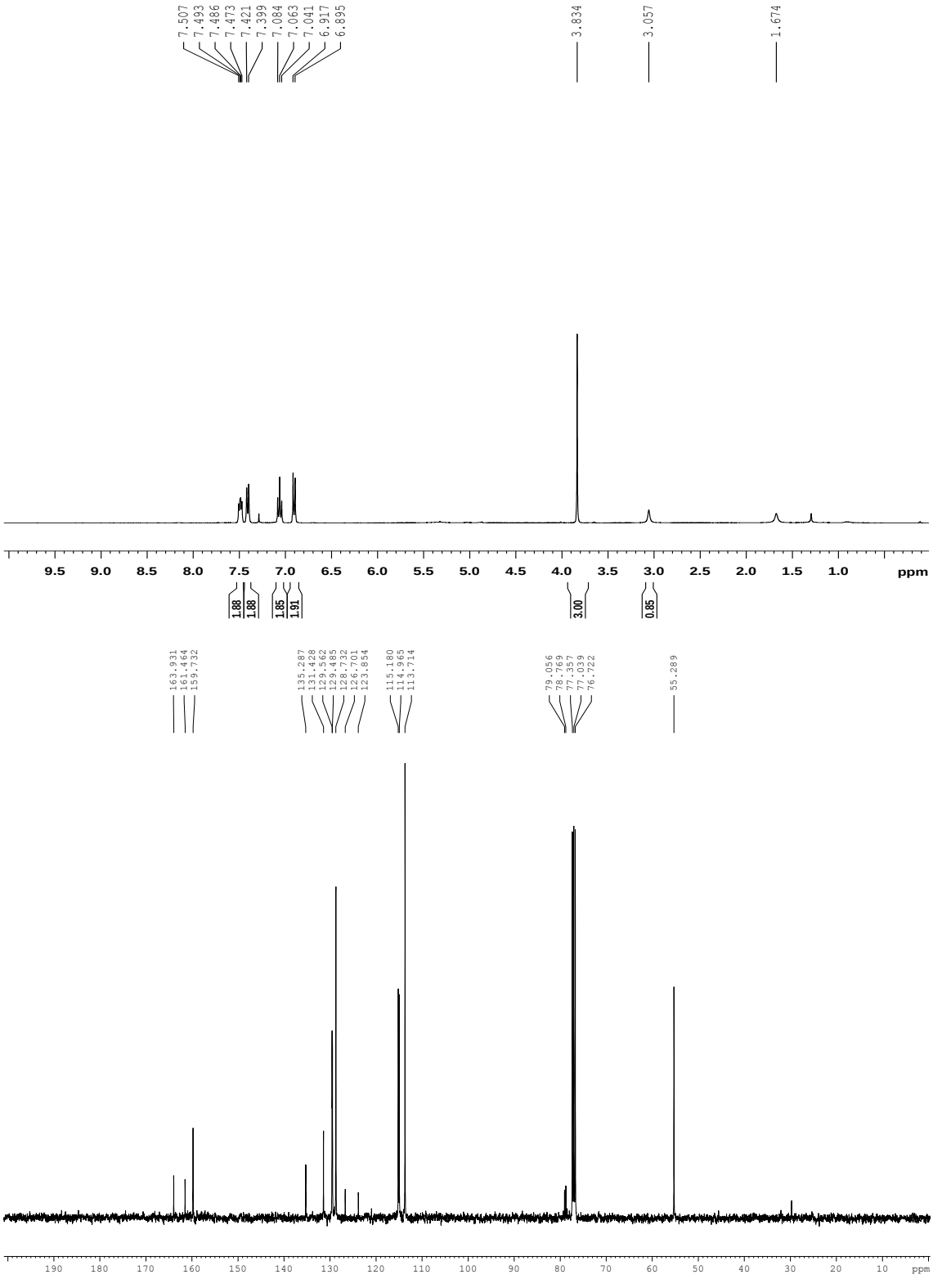

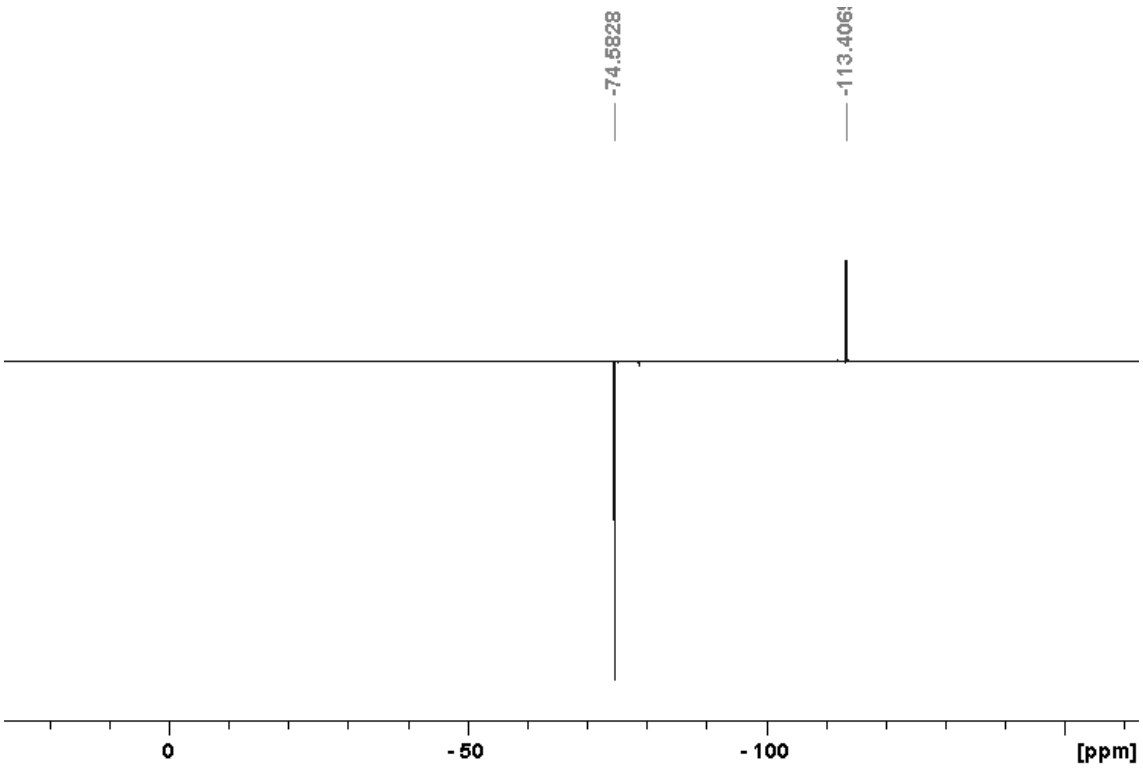

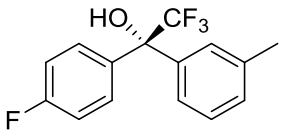

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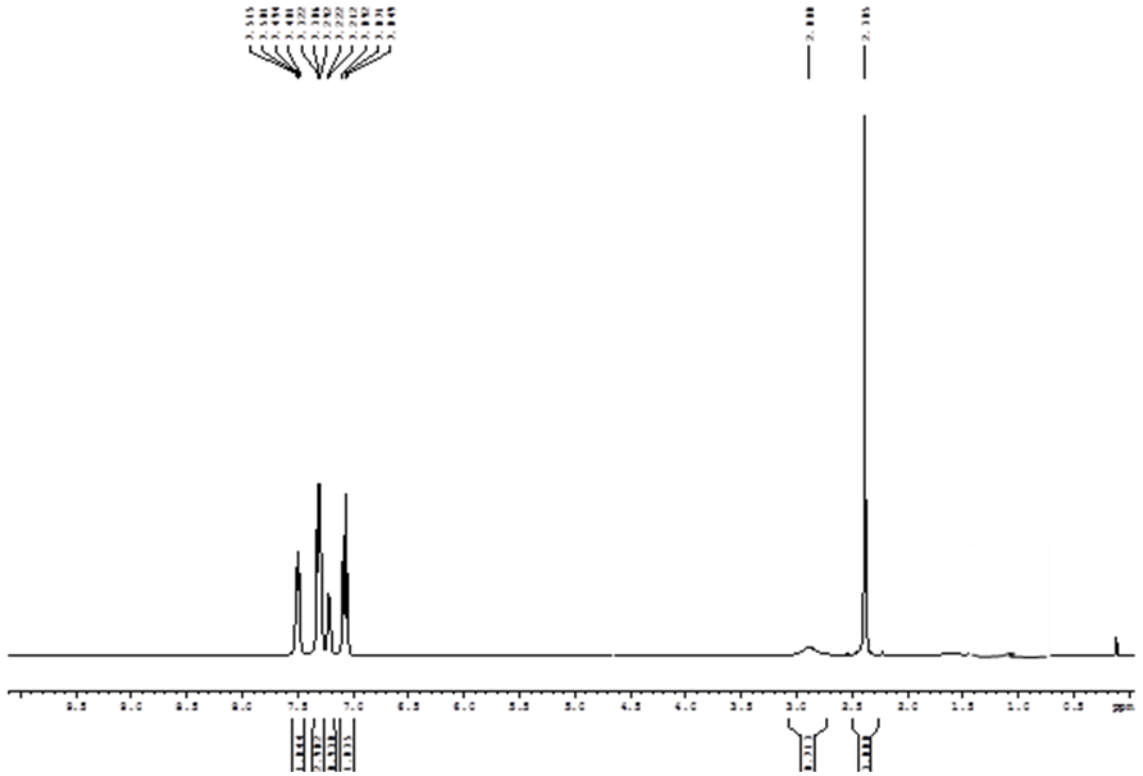

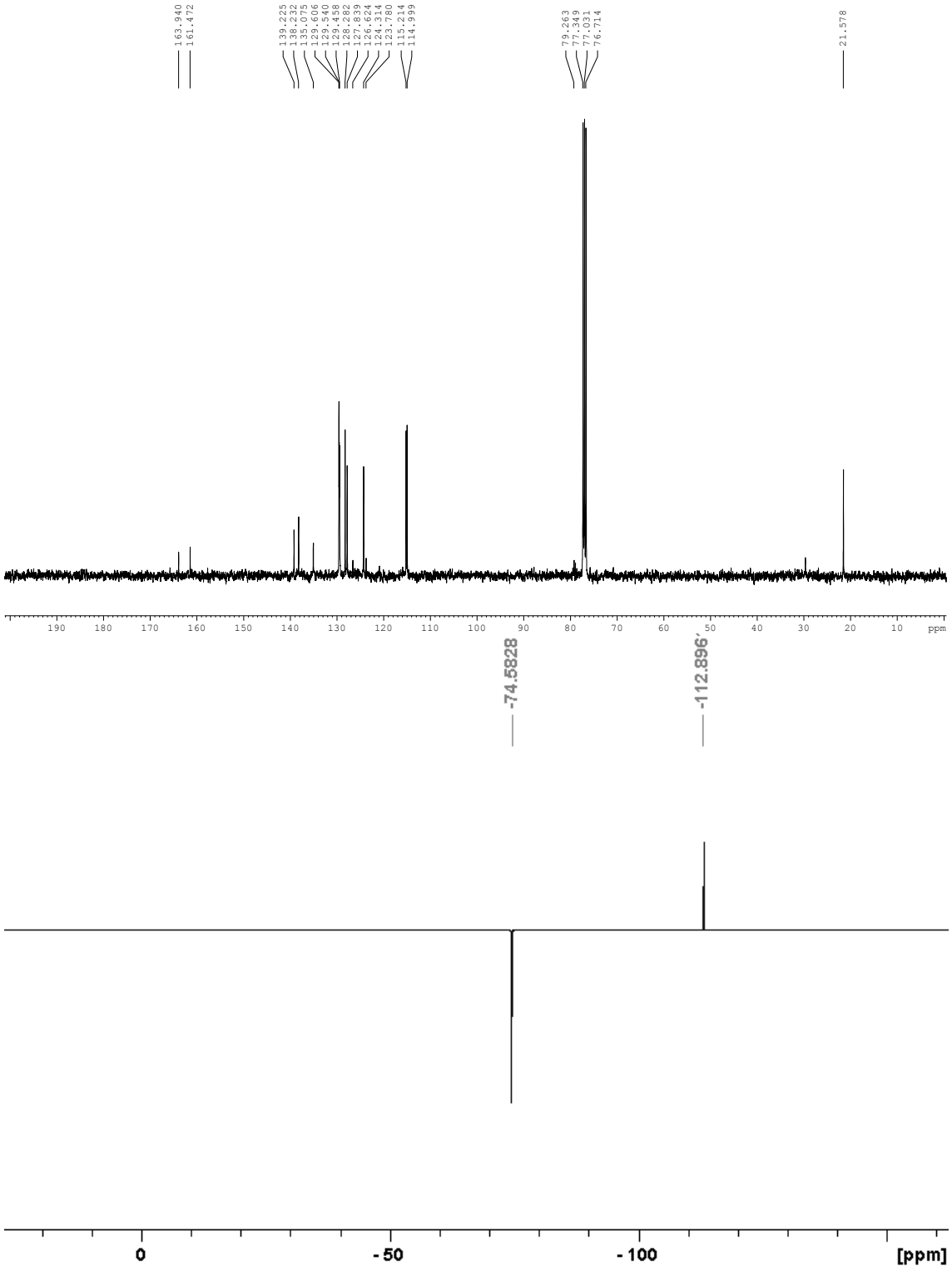

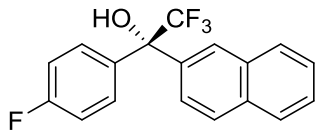

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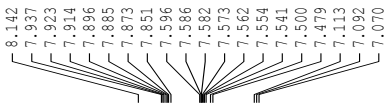

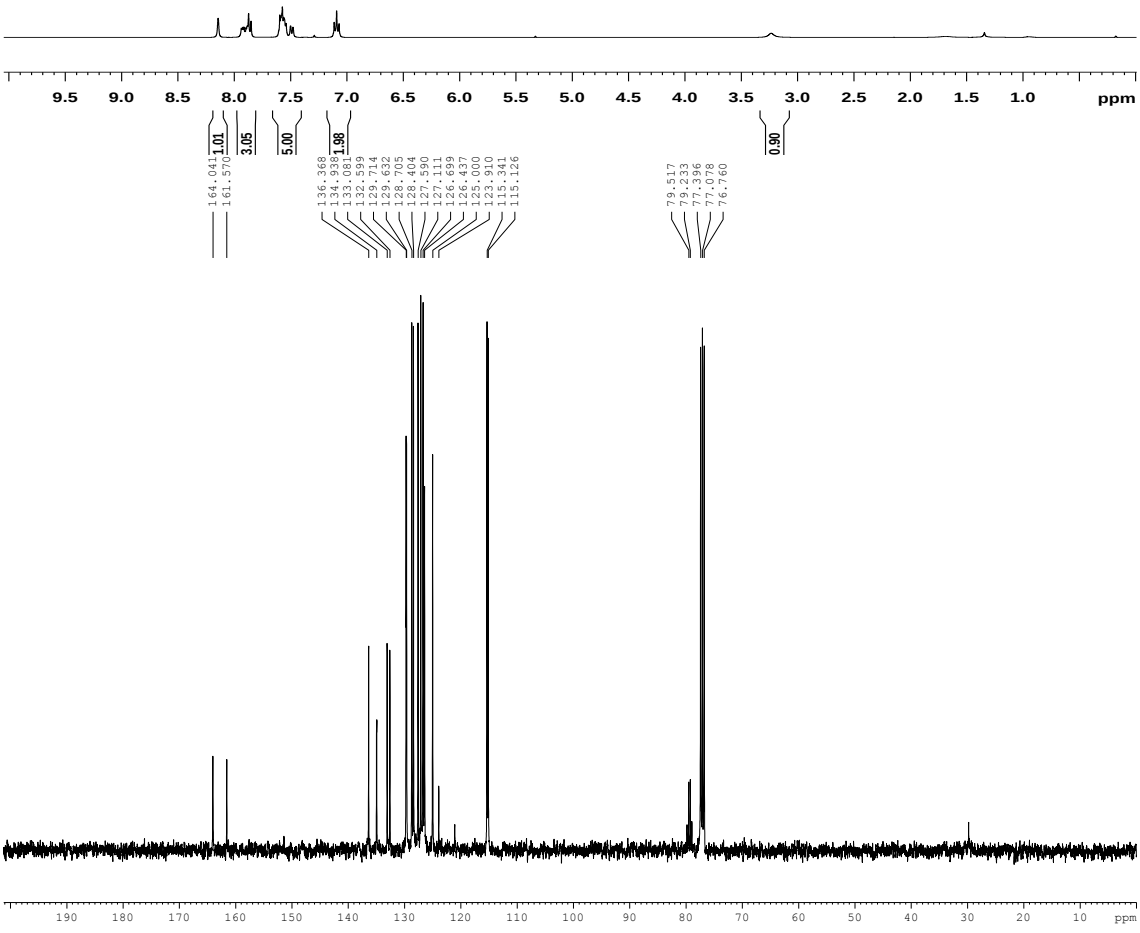

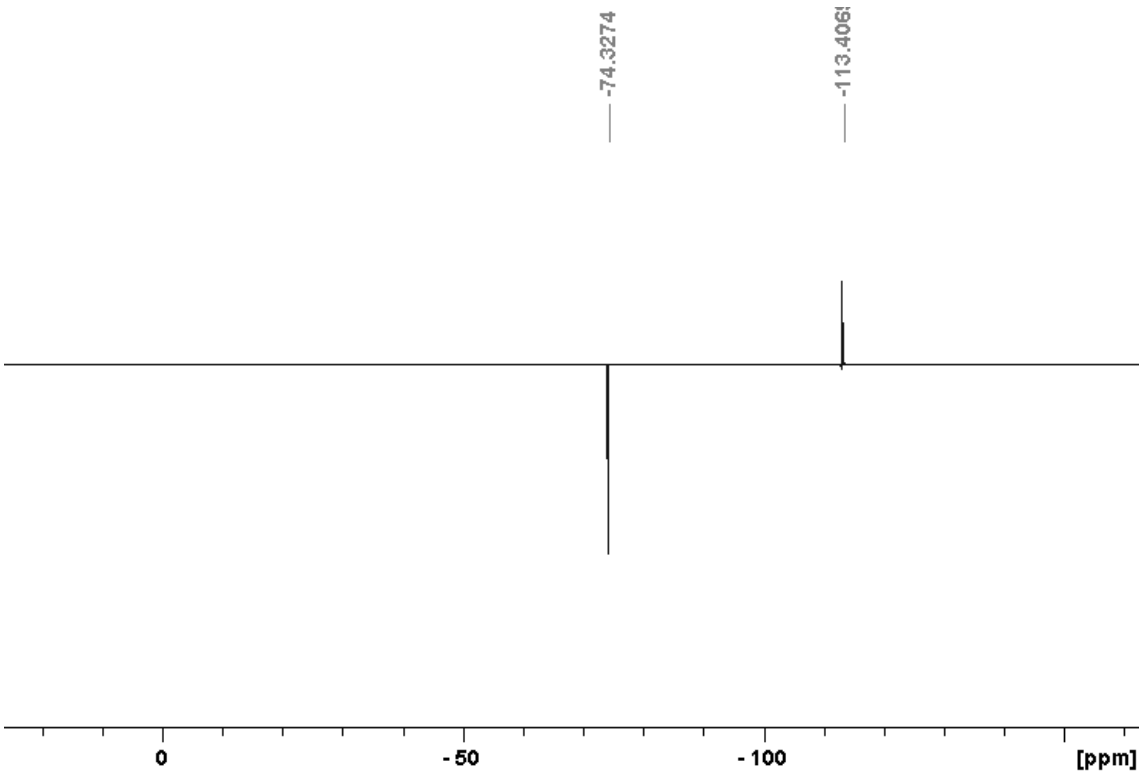

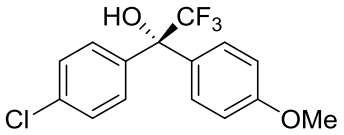

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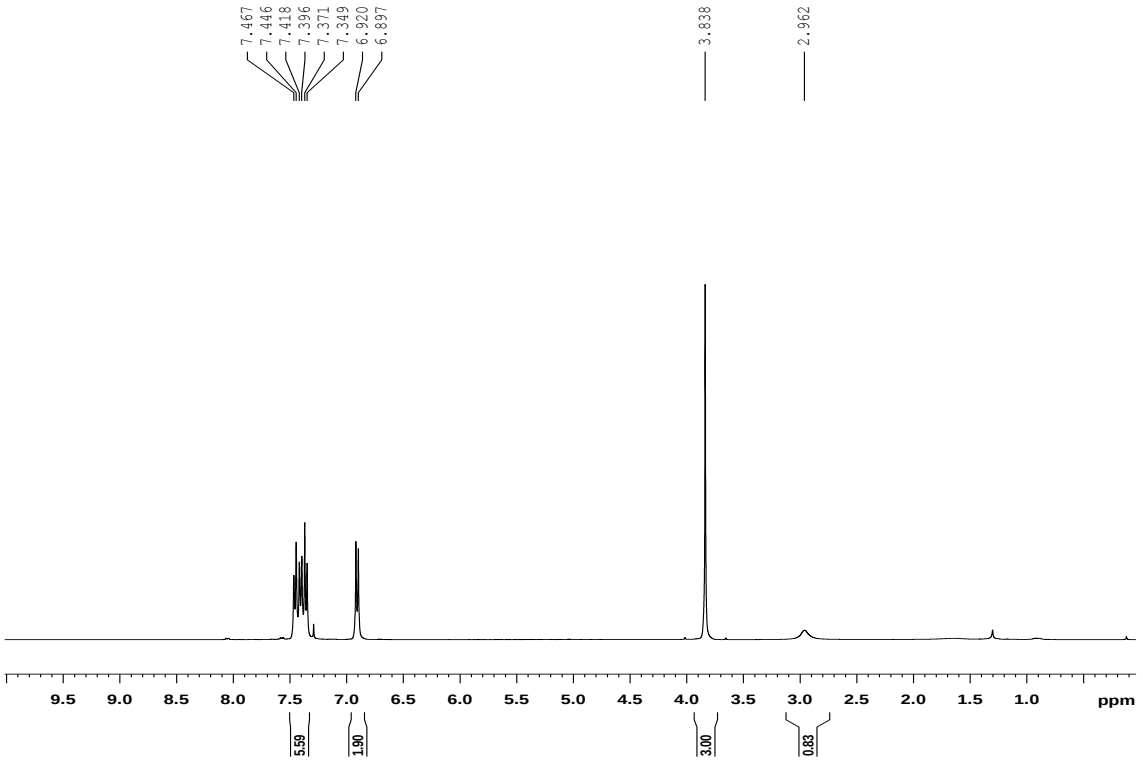

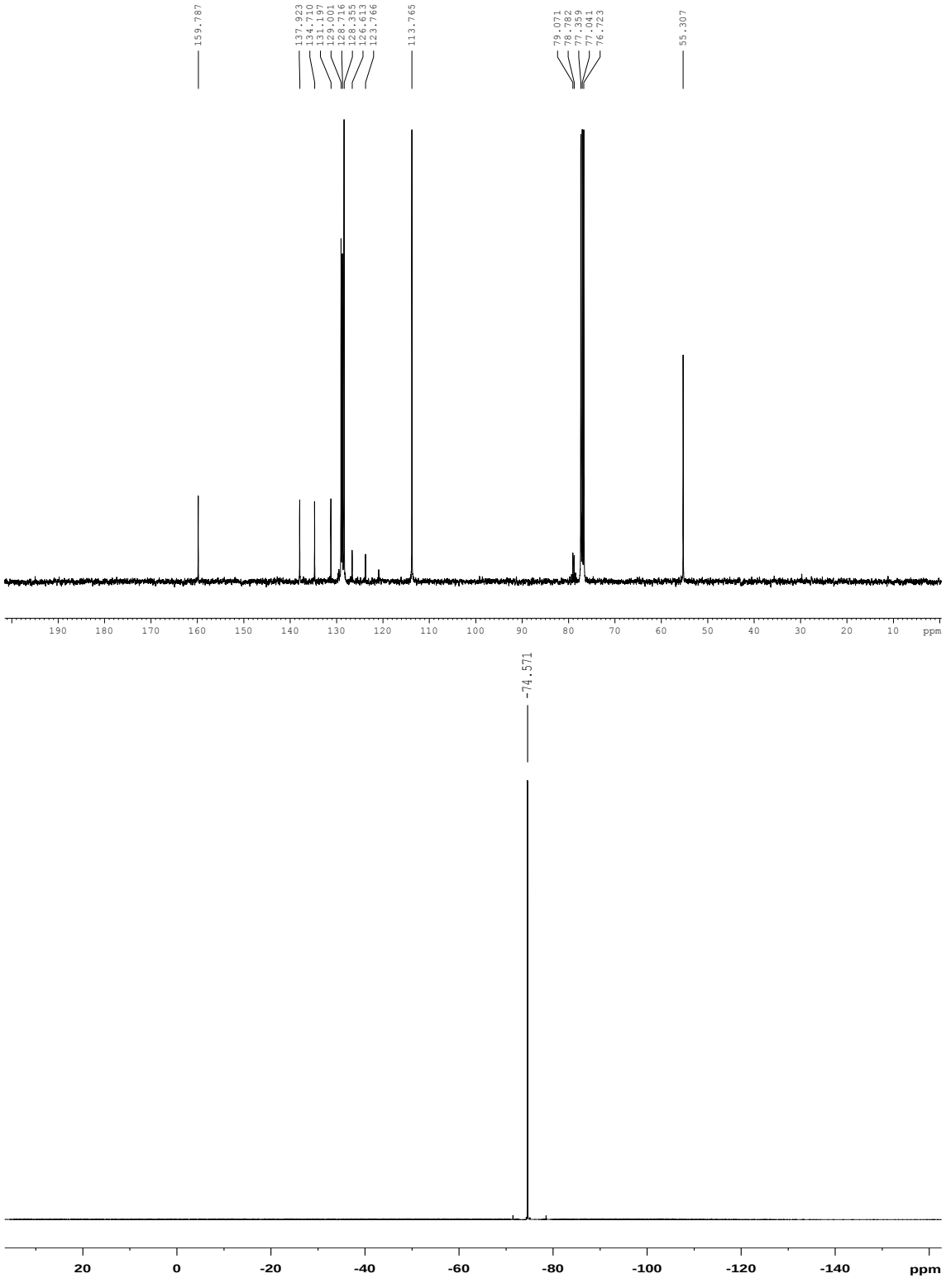

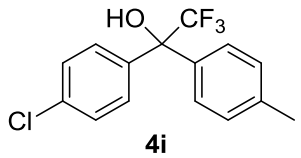

4i