

Triflimide-Catalyzed Allylsilane Annulations of Benzylic Alcohols for the Divergent Synthesis of Indanes and Tetralins

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Supporting Information

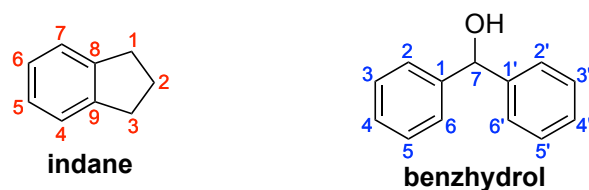
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1. General Information. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. Methanol, THF and DCM were purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Armarego and Chai.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and *p*-anisaldehyde stain. Germanium ATR infrared spectra were recorded using a Bruker Tensor 37. ¹H-NMR spectra were recorded on a Varian Inova 500 (500 MHz), Inova 400 (400 MHz) or Bruker Advance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm) or tetramethylsilane (0.00 ppm). Two-

¹ A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometal.* **1996**, *15*, 1518–1520.

² D. D. Perrin, W. L. Armarego, *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford, 1988.

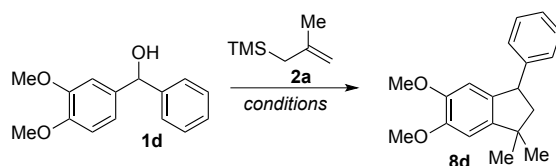
dimensional NMR experiments were run on a Bruker Advance III 500 (500 MHz). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; integration; coupling constant(s) in Hz. Proton-decoupled ^{13}C -NMR spectra were recorded on a Varian Inova 500 (125 MHz) or Bruker Advance III 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl_3 at 77.00 ppm). Mass spectra data were obtained on an Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.



Scheme S1: Numbering systems for indane and benzhydryl compounds

2. Reaction Development

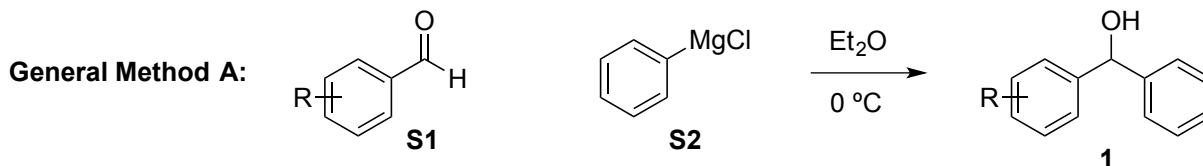
Table S1: Benzhydryl Optimization Studies^[a]



entry	catalyst (mol %)	Silane equiv	solvent	temp (°C)	yield (%) ^[b]
1	HNTf ₂ (20)	1.5	MeNO ₂	23	78
2	TMSOTf (20)	1.5	MeNO ₂	23	55
3	FeCl ₃ (15)	1.5	MeNO ₂	23	70
4	TFA (50)	1.5	MeNO ₂	23	NR ^[c]
5	HNTf ₂ (10)	1.5	DCM	23	42
6	HNTf ₂ (10)	1.5	DCE	23	23
7	HNTf ₂ (10)	1.5	PhMe	23	19
8	HNTf ₂ (10)	1.5	PhCF ₃	23	trace
9	HNTf ₂ (10)	1.5	EtOAc	23	trace
10	HNTf ₂ (10)	1.5	MeNO ₂	0	68
11	HNTf ₂ (10)	1.5	MeNO ₂	23	74
12	HNTf ₂ (10)	1.5	MeNO ₂	80	19
13	HNTf ₂ (10)	1.2	MeNO ₂	23	62

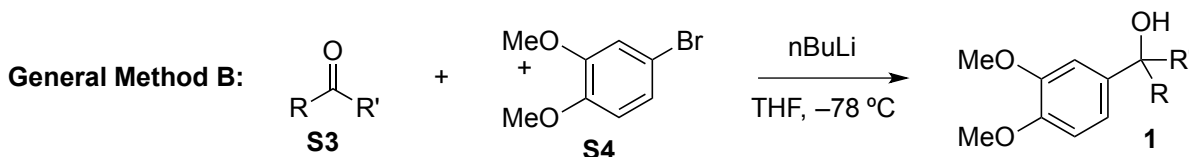
[a] Reaction conditions: 1.5 equiv **2a**, 0.1 M, 2 h. [b] Yields by NMR with durene internal standard. [c] Only uncyclized homoallylic benzhydryl **8d** is observed.

3. Starting Material Experimental Procedures and Characterization Data



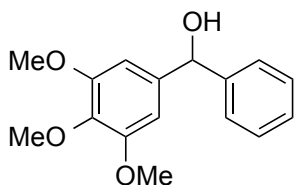
Scheme S2: General method A for synthesis of starting materials through a Grignard reaction

General Method A: Aryl aldehyde **S1** (1 equiv) was dissolved in dry Et₂O (0.33 M soln), cooled to 0 °C and allowed to stir under N₂ atmosphere. Phenylmagnesium chloride (1.8 equiv) was then added dropwise to the stirred solution. The reaction mixture was allowed to stir at 0 °C until all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH₄Cl solution and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with EtOAc in hexanes solvent systems.



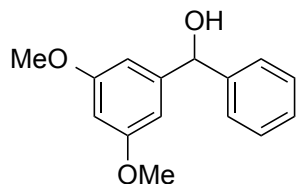
Scheme S3: General method B for synthesis of starting materials through a lithium-halogen exchange reaction

General Method B: 4-Bromoveratrol (1.6 equiv) was dissolved in dry THF (0.33 M soln) and cooled to -78 °C. A solution of nBuLi in hexanes (1.5 equiv) was added dropwise and the solution was allowed to stir at -78 °C under N₂ atmosphere for two hours. Aryl aldehyde or ketone **S3** (1 equiv) was dissolved in dry THF (1 mL/ mmol **S3**) and added dropwise via cannula to the stirred solution (1 mL/ mmol **S3** rinse). The solution was allowed to come to room temperature and stir for 1 hour. At this time, all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH₄Cl solution and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with EtOAc in hexanes solvent systems.

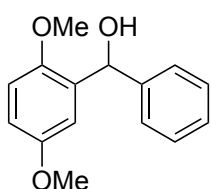


3,4,5-Trimethoxybenzhydryl alcohol (1a): Synthesized from 3,4,5-trimethoxy benzaldehyde (4.74 mmol) via General Method A (1.15 g, 88% yield): ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.24 (m, 5H), 6.61 (s, 2H), 5.78 (d, *J* = 3.1 Hz, 1H), 3.83 (s, 9H), 2.27 (d, *J* = 3.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 153.4, 143.7, 139.6, 137.4, 128.7, 127.9, 126.6, 103.6, 76.5, 61.0, 56.2. All spectroscopic data for this compound agrees with previously reported values.³

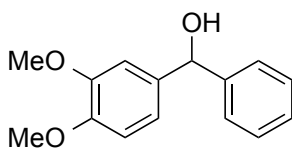
³ a) R. P. Tanpure, A. R. Harkrider, T. E. Strecker, E. Hamel, M. L. Trawick, K. G. Pinney, *Bioorg. Med. Chem.* **2009**, *17*, 6993–7001; b) A. Krasovskiy, B. F. Straub, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 159–162.



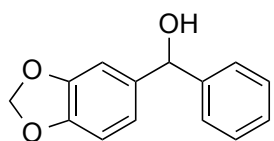
3,5-Dimethoxybenzhydrol (1b): Synthesized from 3,5-dimethoxy benzaldehyde (1.84 mmol) via General Method A (440 mg, 98% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.26 (m, 5H), 6.58 (d, $J = 2.3$ Hz, 2H), 6.39 (t, $J = 2.3$ Hz, 1H), 5.79 (d, $J = 3.5$ Hz, 1H), 3.79 (s, 6H), 2.25 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.0, 146.4, 143.6, 128.7, 127.8, 126.7, 104.7, 99.6, 76.4, 55.5. All spectroscopic data for this compound agrees with previously reported values.⁴



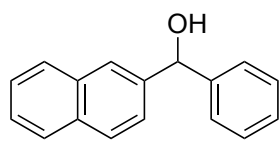
2,5-Dimethoxybenzhydrol (1c): Synthesized from 2,5-dimethoxybenzaldehyde (5.06 mmol) via General Method A (1.2 g, 97% yield): IR (Germanium ATR): 3418, 2934, 1591, 1492, 1213, 1038, 830 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.19 (m, 5H), 6.83 (d, $J = 3.0$ Hz, 1H), 6.79 (d, $J = 8.8$ Hz, 1H), 6.75 (dd, $J = 8.8, 3.0$ Hz, 1H), 5.99 (d, $J = 5.4$ Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.04 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9, 151.1, 143.2, 133.2, 128.3, 127.4, 126.6, 114.2, 112.9, 112.0, 72.4, 56.1, 55.8; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 267.0992. Found 267.1000.



3,4-Dimethoxybenzhydrol (1d): Synthesized from veratraldehyde (5.11 mmol) via General Method A (1.2 g, 99% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.25 (m, 5H), 6.93 (d, $J = 2.0$ Hz, 1H), 6.89 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 5.81 (d, $J = 3.5$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.18 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.6, 144.0, 136.7, 128.6, 127.7, 126.6, 119.1, 111.1, 109.9, 76.2, 56.1, 56.0. All spectroscopic data for this compound agrees with previously reported values.⁵



3,4-Methylenedioxybenzhydrol (1e): Synthesized from piperonal (2.18 mmol) via General Method A (497 mg, 99% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.26 (m, 5H), 6.91 – 6.85 (m, 2H), 6.79 (d, $J = 8.4$ Hz, 1H), 5.95 (q, $J = 1.4$ Hz, 2H), 5.79 (d, $J = 3.4$ Hz, 1H), 2.20 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.0, 147.2, 143.9, 138.1, 128.6, 127.7, 126.5, 120.2, 108.2, 107.3, 101.2, 76.2. All spectroscopic data for this compound agrees with previously reported values.⁶

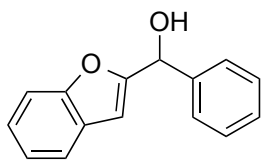


2-Naphthyl(phenyl)methanol (1f): Synthesized from 2-naphthaldehyde (4.95 mmol) via General Method A (1.2 g, 99% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.90 (s, 1H), 7.87 – 7.78 (m, 3H), 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 3H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.01 (d, $J = 3.5$ Hz, 1H), 2.32 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.8, 141.3, 133.4, 133.0, 128.7, 128.5, 128.2, 127.8, 127.8, 126.9, 126.3, 126.1, 125.2, 124.9, 76.5. All spectroscopic data for this compound agrees with previously reported values.⁶

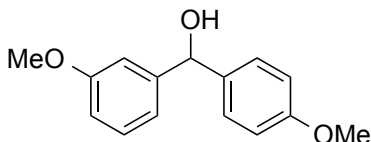
⁴ G. W. Muller, F. Payvandi, L. H. Zhang, M. J. Robarge, R. Chen, H.-W. Man, A. L. Ruchelman (Celgene Corp), US2005107339 A1, **2005**.

⁵ B. Lantaño, J. M. Aguirre, L. Finkielstein, E. N. Alesso, E. Brunet, G. Y. Moltrasio, *Synth. Commun.* **2004**, *34*, 625–641.

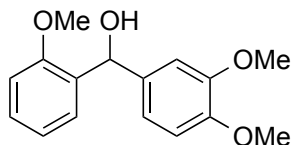
⁶ M. Kuriyama, N. Ishiyama, R. Shimazawa, O. Onomura, *Tetrahedron* **2010**, *66*, 6814–6819.



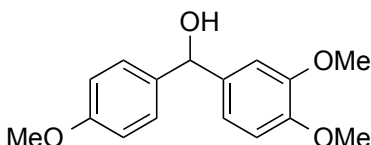
2-(1-Hydroxyphenylmethyl)benzofuran (1g): Synthesized from 2-benzofurancarboxaldehyde (4.0 mmol) via General Method A (870 mg, 97% yield): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 – 7.47 (m, 3H), 7.45 (dq, $J = 8.3, 0.9$ Hz, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.26 (td, $J = 7.7, 1.4$ Hz, 1H), 7.20 (td, $J = 7.5, 1.0$ Hz, 1H), 6.53 (s, 1H), 5.96 (d, $J = 4.5$ Hz, 1H), 2.49 (d, $J = 4.5$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.6, 155.2, 140.4, 128.8, 128.6, 128.2, 126.9, 124.5, 123.0, 121.3, 111.5, 104.2, 70.9. All spectroscopic data for this compound agrees with previously reported values.⁶



3,4'-Dimethoxybenzhydrol (1h): 4-bromoanisole (8 mmol) was dissolved in dry THF (15 mL) and cooled to -78 °C. A solution of $n\text{BuLi}$ in hexanes (7.5 mmol) was added dropwise and the solution was allowed to stir at -78 °C under N_2 atmosphere for two hours. 3-anisaldehyde (5 mmol) was dissolved in dry THF (5 mL) and added dropwise via cannula to the stirred solution (5 mL rinse). The solution was allowed to come to room temperature and stir for 1 hour. At this time, all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (1.2 g, 98% yield): melting point: 33.5 – 35.8 °C; IR (Germanium ATR): 3415, 3001, 2835, 1609, 1510, 1244, 1029, 833, 694 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 (s, 3H), 6.98 – 6.91 (m, 2H), 6.89 – 6.84 (m, 2H), 6.80 (ddd, $J = 8.3, 2.7, 1.0$ Hz, 1H), 5.77 (d, $J = 3.5$ Hz, 1H), 3.79 (s, 6H), 2.17 (d, $J = 3.5$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 159.9, 159.2, 145.8, 136.2, 129.6, 128.0, 118.9, 114.0, 113.0, 112.1, 75.9, 55.4, 55.4; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 267.0992. Found 267.0998.

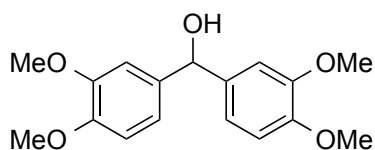


2,3',4'-Trimethoxybenzhydrol (1i): Synthesized from 2-anisaldehyde (1.0 mmol) via General Method B (274 mg, 99% yield): melting point: 60.5 – 68.1 °C; IR (Germanium ATR): 3198, 3009, 2835, 1504, 1243, 1153, 1020, 802, 760 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.27 (td, $J = 8.2, 1.7$ Hz, 1H), 7.20 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.00 (d, $J = 2.0$ Hz, 1H), 6.94 (td, $J = 7.5, 1.1$ Hz, 1H), 6.90 (dd, $J = 8.2, 1.1$ Hz, 1H), 6.86 (dd, $J = 8.3, 2.0$ Hz, 1H), 6.81 (d, $J = 8.3$ Hz, 1H), 6.02 (d, $J = 5.2$ Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.02 (d, $J = 5.2$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 156.9, 148.9, 148.3, 135.9, 132.2, 128.9, 127.9, 121.0, 119.0, 110.9, 110.9, 110.1, 72.2, 56.0, 56.0, 55.6; HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$ $[\text{M}+\text{H}]^+$, 275.1278. Found 275.1285.

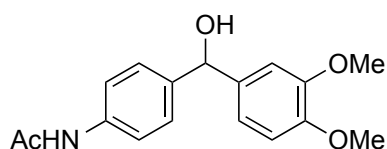


3,4,4'-Trimethoxybenzhydrol (1j): Synthesized from 4-anisaldehyde (5.0 mmol) via General Method B (961 mg, 70% yield): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.28 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 2.0$ Hz, 1H), 6.89 – 6.85 (m, 3H), 6.82 (d, $J = 8.2$ Hz, 1H), 5.76 (d, $J = 3.1$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 2.18 (d, $J = 3.1$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 159.13, 149.13, 148.49, 136.87, 136.34, 127.91, 118.89, 113.96, 111.03, 109.77, 75.68, 56.05, 55.98, 55.41. All spectroscopic data for this compound agrees with previously reported values.⁷

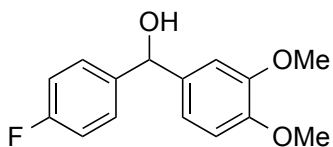
⁷ A. S. Kumar, S. Ghosh, K. Bhima, G. N. Mehta, *J. Chem. Res.* **2009**, 2009, 482–484.



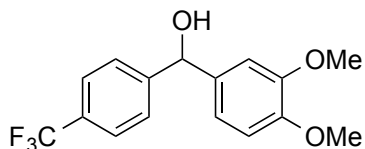
3,3',4,4'-Tetramethoxybenzhydrol (1k and 15): Synthesized from veratraldehyde (5.0 mmol) via General Method B (1.46 g, 96% yield): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.92 (d, $J = 1.9$ Hz, 2H), 6.88 (dd, $J = 8.2, 1.9$ Hz, 2H), 6.83 (d, $J = 8.2$ Hz, 2H), 5.75 (d, $J = 3.5$ Hz, 1H), 3.87 (s, 6H), 3.85 (s, 6H), 2.19 (d, $J = 3.5$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.1, 148.6, 136.7, 119.0, 111.0, 109.8, 75.9, 56.1, 56.0. All spectroscopic data for this compound agrees with previously reported values.⁸



4-(N-Acetamide)-3',4'-dimethoxybenzhydrol (1l): *N*-(4-bromophenyl)acetamide (8 mmol) was dissolved in dry THF (15 mL) and cooled to -78 °C. A solution of *n*BuLi in hexanes (15 mmol) was added dropwise and the solution was allowed to stir at -78 °C under N_2 atmosphere for 20 min. Veratraldehyde (5 mmol) was dissolved in dry THF (5 mL) and added dropwise via cannula to the stirred solution (5 mL rinse). The solution was allowed to come to room temperature and stir for 30 min. At this time, all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% to 50% EtOAc in hexanes gradient solvent system (393 mg, 27% yield): IR (Germanium ATR): 3333, 3197, 3066, 2959, 2935, 1602, 1512, 1232, 1137 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 (d, $J = 8.6$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.20 (s, 1H), 6.90 (d, $J = 2.0$ Hz, 1H), 6.87 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 5.77 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.22 (s, 1H), 2.16 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.4, 149.2, 148.6, 140.0, 137.3, 136.6, 127.3, 120.0, 119.1, 111.1, 109.8, 75.7, 56.1, 56.0, 24.8; HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$, 302.1387. Found 302.1399.

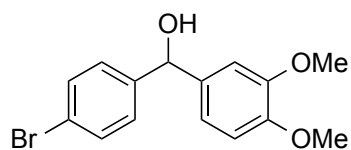


4-fluoro-3',4'-dimethoxybenzhydrol (1m): Synthesized from 4-fluoro benzaldehyde (6.18 mmol) via General Method A (1.4 g, 86% yield): IR (Germanium ATR): 3464, 3005, 1603, 1507, 1464, 1419, 1260, 1223, 1138, 1030, 841, 747 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 – 7.31 (m, 2H), 7.05 – 6.99 (m, 2H), 6.90 – 6.81 (m, 3H), 5.78 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.22 (s, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.3 (d, $J = 245.7$ Hz), 149.3, 148.7, 139.7 (d, $J = 3.1$ Hz), 136.5, 128.2 (d, $J = 8.0$ Hz), 119.0, 115.4 (d, $J = 21.4$ Hz), 111.1, 109.8, 75.5, 56.1, 56.0; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{15}\text{FO}_3$ $[\text{M}+\text{Na}]^+$, 285.0884. Found 285.0899.

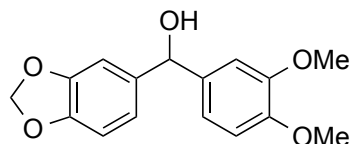


4-Trifluoromethyl-3',4'-dimethoxybenzhydrol (1n): Synthesized from 4-trifluoromethylbenzaldehyde (5.0 mmol) via General Method A (1.0 g, 66% yield): melting point: 77.6–81.3 °C; IR (Germanium ATR): 3549, 3187, 3003, 2842, 1517, 1328, 1103, 1068, 1016, 812 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 8.2$ Hz, 2H), 6.90 – 6.85 (m, 2H), 6.85 – 6.82 (m, 1H), 5.84 (d, $J = 3.1$ Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.26 (d, $J = 3.2$ Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.4, 149.0, 147.7, 136.0, 129.7 (q, $J_{\text{CF}} = 32.3$ Hz), 126.7 (2C), 125.5 (q, $J_{\text{CF}} = 3.9$ Hz, 2C), 124.3 (q, $J_{\text{CF}} = 272.0$ Hz), 119.3, 111.2, 109.8, 75.7, 56.1, 56.0; HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$, 335.0866. Found 335.0877.

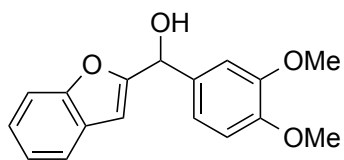
⁸ Y. Peng, Z.-B. Luo, J.-J. Zhang, L. Luo, Y.-W. Wang, *Org. Biomol. Chem.* **2013**, *11*, 7574–7586.



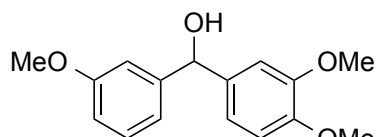
4-Bromo-3',4'-dimethoxybenzhydrol (1o): Synthesized from 4-bromo benzaldehyde (5.0 mmol) via General Method A (1.0 g, 62% yield): IR (Germanium ATR): 3456, 3000, 2834, 1592, 1511, 1256, 1136, 1008, 800, 600 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 6.90 – 6.86 (m, 2H), 6.84 (d, $J = 8.1$ Hz, 1H), 5.77 (d, $J = 3.4$ Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.22 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.3, 148.9, 142.9, 136.2, 131.6, 128.3, 121.5, 119.1, 111.1, 109.8, 75.6, 56.1, 56.0; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{15}\text{BrO}_3$ $[\text{M}+\text{Na}]^+$, 345.0097. Found 345.0107.



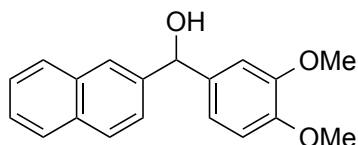
3,4-Methylenedioxy-3',4'-dimethoxybenzhydrol (1p): Synthesized from piperonal (1.0 mmol) via General Method B (242 mg, 84% yield): melting point: 101.5–103.5 $^{\circ}\text{C}$; IR (Germanium ATR): 3338, 2992, 2837, 1594, 1505, 1235, 1140, 1021, 874, 810 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.91 (d, $J = 1.8$ Hz, 1H), 6.88 (dd, $J = 8.3, 1.8$ Hz, 2H), 6.86 – 6.84 (m, 2H), 6.83 (d, $J = 8.3$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 5.94 (s, 2H), 5.72 (d, $J = 3.3$ Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 2.14 (d, $J = 3.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.6, 147.9, 147.1, 138.2, 136.6, 120.0, 118.8, 111.1, 109.7, 108.2, 107.3, 101.2, 75.9, 56.1, 56.0; HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{16}\text{O}_5$ $[\text{M}+\text{Na}]^+$, 311.0890. Found 311.0899.



Benzo[b]furan-2-yl-(3,4-dimethoxyphenyl)carbinol (1q): Synthesized from 2-benzofurancarboxaldehyde (2.0 mmol) via General Method B (475 mg, 83% yield): IR (Germanium ATR): 3453, 3002, 2836, 1512, 1453, 1254, 1136, 1024, 809, 742 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.52 (ddd, $J = 7.8, 1.3, 0.6$ Hz, 1H), 7.47 – 7.43 (m, 1H), 7.26 (ddd, $J = 8.3, 7.2, 1.4$ Hz, 1H), 7.21 (ddd, $J = 7.5, 7.2, 0.9$ Hz, 1H), 7.06 (d, $J = 2.0$ Hz, 1H), 7.01 (ddd, $J = 8.3, 2.0, 0.4$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 6.54 (t, $J = 0.9$ Hz, 1H), 5.91 (d, $J = 4.3$ Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.51 (d, $J = 4.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.8, 155.2, 149.3, 149.3, 133.0, 128.2, 124.4, 123.0, 121.3, 119.4, 111.5, 111.1, 110.0, 104.0, 70.7, 56.1, 56.1; HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 307.0941. Found 307.0951.

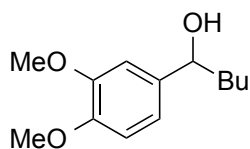


3,3',4-Trimethoxybenzhydrol (1r): Synthesized from 3-anisaldehyde (5.0 mmol) via General Method B (1.0 g, 74% yield): melting point: 113.5–115.2 $^{\circ}\text{C}$; IR (Germanium ATR): 3392, 3089, 2841, 1520, 1261, 1134, 1025, 798, 754 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.23 (m, 1H), 6.98 – 6.92 (m, 3H), 6.89 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.85 – 6.79 (m, 2H), 5.77 (d, $J = 3.4$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 2.18 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.9, 149.2, 148.7, 145.7, 136.5, 129.6, 119.1, 118.9, 113.0, 112.2, 111.1, 109.9, 76.1, 56.1, 56.0, 55.4; HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 297.1097. Found 297.1107.

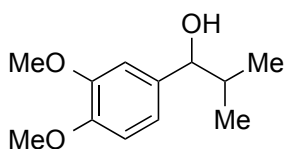


(3,4-Dimethoxyphenyl)(2-naphthyl)methanol (1s): Synthesized from 2-naphthaldehyde (3.0 mmol) via General Method B (608 mg, 69% yield): melting point: 84.9–86.1 $^{\circ}\text{C}$; IR (Germanium ATR): 3334, 3053, 2837, 1591, 1511, 1232, 1135, 1021, 725 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.89 (s, 1H), 7.87 – 7.81 (m, 2H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.51 – 7.45 (m, 2H), 7.43 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.96 (d, $J = 1.8$ Hz, 1H), 6.93 (dd, $J = 8.2, 1.8$ Hz,

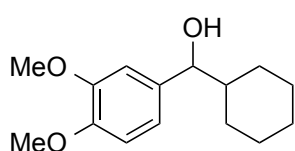
1H), 6.83 (d, $J = 8.2$ Hz, 1H), 5.95 (d, $J = 3.3$ Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.36 (d, $J = 3.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.7, 141.3, 136.5, 133.4, 133.0, 128.4, 128.2, 127.8, 126.3, 126.1, 125.0, 124.9, 119.3, 111.1, 110.0, 76.2, 56.0, 56.0; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 317.1148. Found 317.1158.



1-(3,4-Dimethoxyphenyl)pentan-1-ol (1t): Veratraldehyde (3 mmol) was dissolved in dry Et_2O (6 mL) and cooled to -78 °C under N_2 atmosphere. A solution of $n\text{BuLi}$ in hexanes (3.0 mmol) was added dropwise. The solution was slowly allowed to warm to room temperature and stir for 12 hours. At this time, all starting material was consumed as determined by TLC and the solution was cooled to 0 °C. The reaction was then quenched with sat. NH_4Cl solution and extracted with Et_2O (3 x 6 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting oil was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (673 mg, 67% yield): IR (Germanium ATR): 3403, 3003, 2932, 1516, 1463, 1259, 1138, 1027, 808 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.91 (d, $J = 1.9$ Hz, 1H), 6.86 (dd, $J = 8.2$, 1.9 Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 4.61 (dd, $J = 7.4$, 6.0 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.85 – 1.76 (m, 2H), 1.73 – 1.64 (m, 1H), 1.44 – 1.31 (m, 3H), 1.31 – 1.17 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.5, 137.8, 118.3, 111.0, 109.1, 74.7, 56.1, 56.0, 38.9, 28.2, 22.8, 14.2; HRMS (ESI): Exact mass calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 247.1305. Found 247.1315.

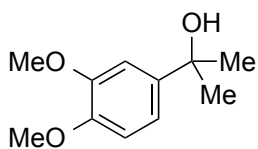


1-(3,4-Dimethoxyphenyl)-2-methyl-1-propanol (1u): Veratraldehyde (2 mmol) was dissolved in dry Et_2O (9 mL), cooled to 0 °C and allowed to stir under N_2 atmosphere. A solution of isopropylmagnesium chloride (3 mmol) was then added dropwise to the stirred solution. The reaction mixture was allowed to stir at 0 °C for 30 min, at which point all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (383 mg, 91% yield): ^1H NMR (500 MHz, CDCl_3) δ 6.88 (s, 1H), 6.83 (s, 2H), 4.29 (d, $J = 7.2$ Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.00 – 1.87 (m, 1H), 1.78 (s, 1H), 1.02 (d, $J = 6.6$ Hz, 3H), 0.78 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.0, 148.5, 136.5, 119.1, 110.8, 109.6, 80.2, 56.1, 56.0, 35.5, 19.2, 18.7. All spectroscopic data for this compound agrees with previously reported values.⁹

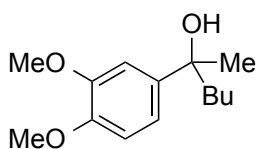


1-Cyclohexyl-1-(3,4-dimethoxyphenyl)methanol (1v): Synthesized from cyclohexanecarboxaldehyde (1.0 mmol) via General Method B (186 mg, 74% yield): melting point: 91.7–93.2 °C; IR (Germanium ATR): 3497, 3002, 2922, 2850, 1593, 1258, 1138, 1026 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.87 (d, $J = 1.4$ Hz, 1H), 6.85 – 6.78 (m, 2H), 4.29 (d, $J = 7.5$ Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.01 (dtd, $J = 12.9$, 4.5, 4.1, 2.3 Hz, 1H), 1.85 – 1.73 (m, 2H), 1.70 – 1.53 (m, 3H), 1.36 (ddq, $J = 12.6$, 3.8, 2.0 Hz, 1H), 1.30 – 1.10 (m, 3H), 1.04 (tdd, $J = 12.7$, 11.3, 3.5 Hz, 1H), 0.90 (qd, $J = 12.4$, 3.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.0, 148.5, 136.5, 119.1, 110.8, 109.7, 79.5, 56.1, 56.0, 45.1, 29.5, 29.3, 26.6, 26.2, 26.2; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 273.1461. Found 273.1473.

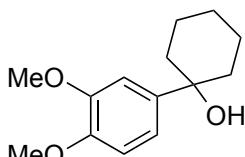
⁹ S. A. Zacchino, S. N. López, G. D. Pezzenati, R. L. Furlán, C. B. Santecchia, L. Muñoz, F. A. Giannini, A. M. Rodríguez, R. D. Enriz, *J. Nat. Prod.* **1999**, 62, 1353–1357.



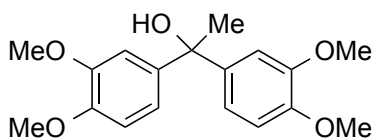
3,4-Dimethoxy-(1'-hydroxy-1'-methylethyl)benzene (1w): Synthesized from acetone (5.0 mmol) via General Method B (721 mg, 73% yield): $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.09 (d, $J = 2.2$ Hz, 1H), 6.98 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.83 (d, $J = 8.4$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 1.70 (s, 1H), 1.58 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.8, 147.9, 142.1, 116.5, 110.9, 108.4, 72.5, 56.1, 56.0, 32.0. All spectroscopic data for this compound agrees with previously reported values.¹⁰



2-(3,4-Dimethoxyphenyl)hexan-2-ol (1x): Synthesized from 2-hexanone (5.0 mmol) via General Method B (1.0 g, 85% yield): IR (Germanium ATR): 3499, 2933, 1591, 1509, 1463, 1255, 1140, 1026, 806 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.02 (d, $J = 2.2$ Hz, 1H), 6.91 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.82 (d, $J = 8.3$ Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.84 – 1.72 (m, 2H), 1.54 (s, 3H), 1.31 – 1.09 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.7, 147.7, 141.1, 117.0, 110.8, 108.7, 74.7, 56.0, 56.0, 44.1, 30.2, 26.4, 23.2, 14.2; HRMS (ESI): Exact mass calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 261.1461. Found 261.1474.

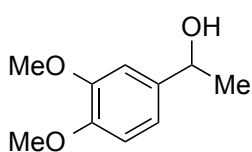


1-(3,4-Dimethoxyphenyl)cyclohexanol (1y): Synthesized from cyclohexanone (5.0 mmol) via General Method B (1.2 g, 85% yield): melting point: 92.1–94.0 $^\circ\text{C}$; IR (Germanium ATR): 3518, 2997, 2928, 2833, 1583, 1515, 1463, 1256, 1143, 1026, 975, 799, 764 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.11 (d, $J = 2.2$ Hz, 1H), 7.00 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 1.87 – 1.70 (m, 7H), 1.67 – 1.61 (m, 2H), 1.55 (s, 1H), 1.37 – 1.22 (m, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.8, 147.9, 142.5, 116.7, 110.9, 108.6, 73.1, 56.1, 56.0, 39.1, 25.7, 22.4; HRMS (ESI): Exact mass calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 259.1305. Found 259.1314.

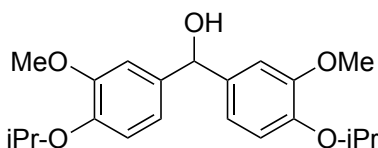


3,3',4,4'-Tetramethoxy-7-methylbenzhydrol (1z): 3,3',4,4'-tetramethoxybenzhydrol (**15**) (0.617 mmol) was dissolved in dry THF (3 mL) at room temperature. Manganese (IV) oxide (4.01 mmol) was then added portionwise. Starting material was consumed after 36 h, as determined by TLC. The solution was filtered through a pad of Celite and concentrated. A portion of the resulting benzhydryl ketone (0.474 mmol) was dissolved in dry THF (5 mL), cooled to 0 $^\circ\text{C}$ and allowed to stir under N_2 atmosphere. A solution of methylmagnesium bromide (0.947 mmol) was then added dropwise to the stirred solution. The reaction mixture was allowed to stir at 0 $^\circ\text{C}$ for 1 hour, at which point all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 50% EtOAc in hexanes solvent system (139 mg, 92% yield over two steps): melting point: 129.3–130.3 $^\circ\text{C}$; IR (Germanium ATR): 3513, 3001, 2934, 1596, 1511, 1462, 1253, 1138, 1024, 811 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.98 (d, $J = 2.2$ Hz, 2H), 6.90 (dd, $J = 8.4, 2.2$ Hz, 2H), 6.80 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 6H), 3.83 (s, 6H), 2.11 (s, 1H), 1.92 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.7, 148.1, 141.0, 118.2, 110.6, 109.7, 76.2, 56.0, 56.0, 31.5; HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{O}_5$ $[\text{M}+\text{Na}]^+$, 341.1359. Found 341.1372.

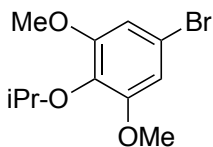
¹⁰ C. Lambertucci, M. Sundukova, D. D. Kachare, D. S. Panmand, D. Dal Ben, M. Buccioni, G. Marucci, A. Marchenkova, A. Thomas, A. Nistri, G. Cristalli, R. Volpini, *Eur. J. Med. Chem.* **2013**, *65*, 41–50.



1-(3,4-Dimethoxyphenyl)ethanol (1aa): Veratraldehyde (5 mmol) was dissolved in dry Et₂O (15 mL), cooled to 0 °C and allowed to stir under N₂ atmosphere. A solution of methylmagnesium bromide (7.5 mmol) was then added dropwise to the stirred solution. The reaction mixture was allowed to stir at 0 °C for 15 min, at which point all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH₄Cl solution and extracted with Et₂O (3 x 15 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (659 mg, 72% yield): ¹H NMR (500 MHz, CDCl₃) δ 6.95 (d, *J* = 1.9 Hz, 1H), 6.89 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.86 (q, *J* = 6.4 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 1.76 (bs, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 149.2, 148.5, 138.7, 117.7, 111.1, 108.8, 70.4, 56.1, 56.0, 25.2. All spectroscopic data for this compound agrees with previously reported values.¹¹

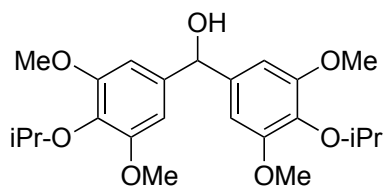


4,4'-Diisopropoxy-3,3'-dimethoxybenzhydrol (16): 4-bromo-1-isopropoxy-2-methoxy-benzene (10.0 mmol) was dissolved in dry THF (20 mL) and cooled to -78 °C. A solution of nBuLi in hexanes (10.0 mmol) was added dropwise and the solution was allowed to stir at -78 °C under N₂ atmosphere for one hour. Freshly distilled ethyl formate (5.0 mmol) was added dropwise to the stirred solution. The solution was allowed to come to room temperature and stir for 5 hours. At this time, all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH₄Cl solution and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (1.21 g, 67% yield): IR (Germanium ATR): 3511, 2981, 1605, 1506, 1465, 1419, 1260, 1225, 1136, 1036, 953 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 1.2 Hz, 2H), 6.87 – 6.84 (m, 4H), 5.74 (d, *J* = 2.9 Hz, 1H), 4.50 (hept, *J* = 6.1 Hz, 2H), 3.82 (s, 6H), 2.15 (d, *J* = 3.4 Hz, 1H), 1.36 (d, *J* = 6.1 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 150.5, 146.9, 137.0, 119.1, 115.6, 110.7, 76.0, 71.6, 56.1, 22.3; HRMS (ESI): Exact mass calcd for C₂₁H₂₈O₅ [M+Na]⁺, 383.1829. Found 383.1832.



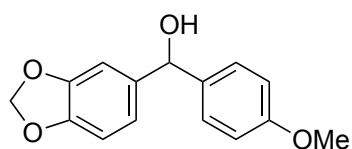
5-bromo-1,3-dimethoxy-2-isopropoxybenzene (S5): 4-bromo-2,6-dimethoxyphenol (17.16 mmol) was dissolved in dry DMF (20 mL) followed by the addition of 2-bromopropane (34.32 mmol) and K₂CO₃ (25.74 mmol). The solution was heated to 90 °C and allowed to stir under N₂ atmosphere for 6 hours. The reaction was then cooled down to room temperature and allowed to stir overnight. Starting material was still present as determined by TLC, therefore more 2-bromopropane (34.32 mmol) was added and the reaction was stirred overnight. At this time, all starting material was consumed and the reaction was diluted with H₂O (100 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with HCl (0.5 M, 100 mL) and H₂O (100 mL), then dried over Na₂SO₄ and concentrated under reduced pressure to afford the product (4.63 g, 98% yield). IR (Germanium ATR): 2972, 2933, 1585, 1491, 1404, 1303, 1224, 1124, 930 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.70 (s, 2H), 4.31 (hept, *J* = 6.2 Hz, 1H), 3.80 (s, 6H), 1.27 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 154.6, 135.5, 115.8, 109.0, 75.5, 56.4, 22.5; HRMS (ESI): Exact mass calcd for C₁₁H₁₅BrO₃ [M+Na]⁺, 297.0097. Found 297.0097.

¹¹ K. Zhu, M. P. Shaver, S. P. Thomas, *Eur. J. Org. Chem.* **2015**, 2015, 2119–2123.



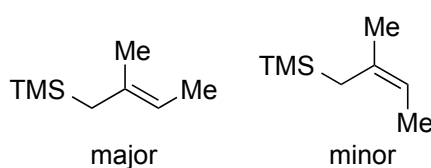
4,4'-Diisopropoxy-3,3'-dimethoxy-5,5'-dimethoxybenzhydrol (19):

5-bromo-1,3-dimethoxy-2-isopropoxybenzene (**S5**, 2.49 mmol) was dissolved in dry THF (4 mL) and cooled to $-78\text{ }^{\circ}\text{C}$. A solution of *n*BuLi in hexanes (2.49 mmol) was added dropwise and the solution was allowed to stir at $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere for one hour. Freshly distilled ethyl formate (1.24 mmol) was added dropwise to the stirred solution. The solution was allowed to come to room temperature and stir overnight. At this time, all starting material was consumed as determined by TLC. The reaction was quenched with sat. NH_4Cl solution and extracted with Et_2O . The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting material was purified by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system (210.7 mg, 40% yield): IR (Germanium ATR): 3449, 2974, 2935, 1593, 1462, 1418, 1325, 1228, 1123, 930 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.59 (s, 4H), 5.71 (d, $J = 3.3$ Hz, 1H), 4.34 (hept, $J = 6.3$ Hz, 2H), 3.80 (s, 12H), 2.21 (d, $J = 3.6$ Hz, 1H), 1.29 (d, $J = 6.2$ Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.0, 138.8, 135.7, 104.0, 76.6, 75.4, 56.3, 22.6; HRMS (ESI): Exact mass calcd for $\text{C}_{23}\text{H}_{32}\text{O}_7$ $[\text{M}+\text{Na}]^+$, 443.204. Found 443.2054.



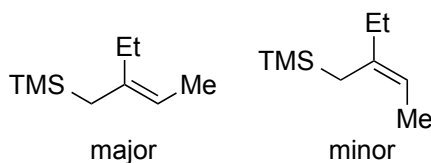
3,4-Methylenedioxy-4'-methoxybenzhydrol (22):

Synthesized from piperonal (8.2 mmol) with 4-bromoanisole (9.6 mmol) rather than 4-bromoveratrol via General Method B (2.34 g, 99% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2H), 6.90 – 6.82 (m, 4H), 6.78 – 6.74 (m, 1H), 5.93 (s, 2H), 5.72 (d, $J = 3.4$ Hz, 1H), 3.79 (s, 3H), 2.14 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.2, 147.9, 147.0, 138.4, 136.3, 127.8, 120.0, 114.0, 108.2, 107.2, 101.2, 77.2, 75.7, 55.4. All spectroscopic data for this compound agrees with previously reported values.¹²



1-(Trimethylsilyl)-2-methyl-2-butene (2b):

Followed same procedure as Yamamoto and co workers¹³ (185 mmol scale, 11.7 g, 44% yield after distillation, 3.3:1 d.r.): Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 5.00 (qq, $J = 6.6, 1.2$ Hz, 1H), 1.59 (q, $J = 1.1$ Hz, 3H), 1.56 (dq, $J = 6.7, 1.1$ Hz, 3H), 1.46 (t, $J = 1.1$ Hz, 2H), -0.01 (s, 9H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 133.5, 116.9, 30.0, 18.5, 13.7, -1.1; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 5.12 – 5.06 (m, 1H), 1.67 (p, $J = 1.5$ Hz, 3H), 1.52 – 1.49 (m, 5H), 0.03 (s, 9H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 134.1, 115.9, 26.4, 23.0, 14.1, -0.5. All spectroscopic data for this compound agrees with previously reported values.¹³



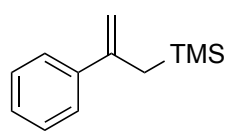
1-(Trimethylsilyl)-2-ethyl-2-butene (2c):

Followed same procedure as Yamamoto and co workers¹³ (46 mmol scale, 10.22 g, 33% yield after distillation, 4:1 d.r.): Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 4.97 (q, $J = 6.7$ Hz, 1H), 1.97 (q, $J = 7.7$ Hz,

¹² C. Qin, H. Wu, J. Cheng, X. a. Chen, M. Liu, W. Zhang, W. Su, J. Ding, *J. Org. Chem.* **2007**, 72, 4102–4107.

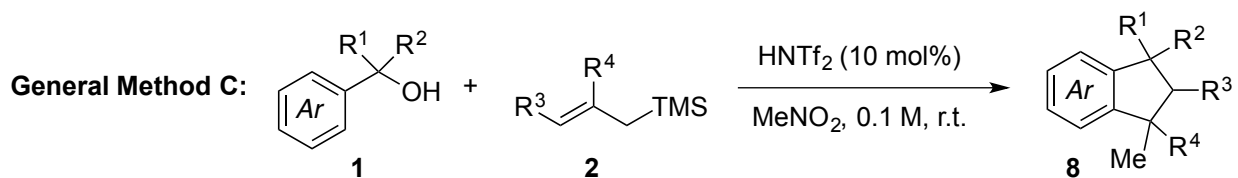
¹³ D. Ferraris, B. Young, C. Cox, T. Dudding, W. J. Drury, L. Ryzhkov, A. E. Taggi, T. Lectka, *J. Am. Chem. Soc.* **2002**, 124, 67–77.

2H), 1.57 (d, $J = 6.7$ Hz, 3H), 1.45 (s, 2H), 0.95 (t, $J = 7.6$ Hz, 3H), -0.01 (s, 9H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 139.5, 115.8, 26.5, 25.0, 13.3, 12.8, -1.0; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 5.09 (q, $J = 6.9$ Hz, 1H), 1.94 (q, $J = 6.0$ Hz, 2H), 1.55 – 1.50 (m, 5H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.02 (s, 9H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 139.8, 113.9, 32.0, 21.2, 14.1, 13.0, -0.5. All spectroscopic data for this compound agrees with previously reported values.¹³



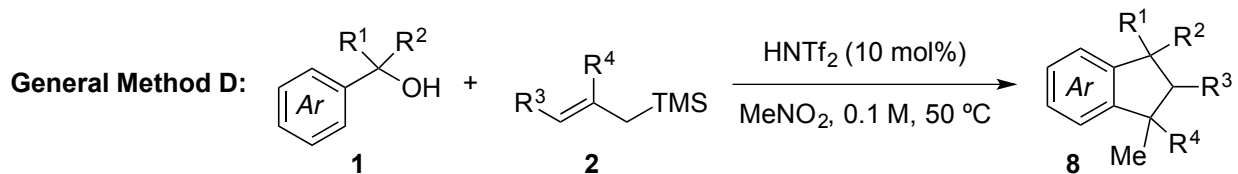
2-Phenyl-3-(trimethylsilyl)-1-propene (2d): Followed same procedure as Ferraris and co workers¹³ (40 mmol scale, 2.47 g, 31% yield): ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.38 (m, 2H), 7.30 (tt, $J = 6.7, 0.9$ Hz, 2H), 7.26 – 7.22 (m, 1H), 5.13 (d, $J = 1.7$ Hz, 1H), 4.87 (dd, $J = 1.2$ Hz, 1H), 2.03 (d, $J = 1.1$ Hz, 2H), -0.10 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.8, 142.9, 128.2, 127.3, 126.5, 110.2, 26.3, -1.3. All spectroscopic data for this compound agrees with previously reported values.¹⁴

4. Indane Experimental Procedures and Characterization Data



Scheme S4: General method for synthesis of indanes

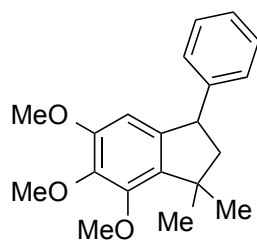
General Method C (standard indane reaction): Benzhydryl or benzyl alcohol **1** (1 equiv) was dissolved in MeNO₂ (0.1 M soln) and allowed to stir under N₂ atmosphere. Alkyl silane **2** (1.5 equiv) was added, followed by a solution of triflimide in DCM (10 mol%). The reaction was allowed to stir at room temperature for 2 hours before being quenched with sat. NaHCO₃ solution. The biphasic solution was extracted with DCM and the combined organic layers were dried over Na₂SO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with EtOAc in hexanes solvent systems afforded the desired indane.



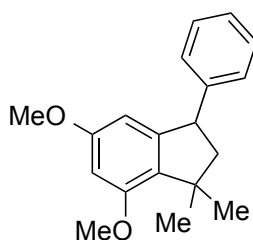
Scheme S5: General method for synthesis of indanes at elevated temperature

General Method D (indane reaction at elevated temperature): Benzhydryl or benzyl alcohol **1** (1 equiv) was dissolved in MeNO₂ (0.1 M soln) and allowed to stir while warming to 50 °C under N₂ atmosphere. Alkyl silane **2** (1.5 equiv) was added, followed by a solution of triflimide in DCM (10 mol%). The reaction was allowed to stir at 50 °C for 2 hours before being quenched with sat. NaHCO₃ solution. The biphasic solution was extracted with DCM and the combined organic layers were dried over Na₂SO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with EtOAc in hexanes solvent systems afforded the desired indane.

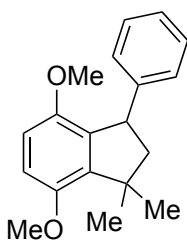
¹⁴ H. Zhang, W. Pu, T. Xiong, Y. Li, X. Zhou, K. Sun, Q. Liu, Q. Zhang, *Angew. Chem. Int. Ed.* **2013**, 52, 2529–2533.



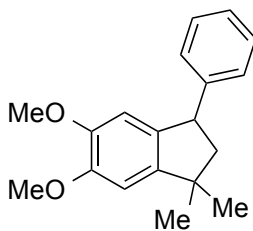
5,6,7-Trimethoxy-1,1-dimethyl-3-phenylindane (8a): Synthesized from 3,4,5-trimethoxybenzhydrol (**1a**, 0.200 mmol) and silane **2a** via General Method C (50 mg, 80% yield): IR (Germanium ATR): (Germanium ATR): 2937, 1605, 1479, 1411, 1327, 1226, 1201, 1104, 1029, 933 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 6.16 (d, J = 1.0 Hz, 1H), 4.29 (ddd, J = 10.3, 7.8, 1.1 Hz, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.69 (s, 3H), 2.31 (dd, J = 12.5, 7.7 Hz, 1H), 1.94 (dd, J = 12.5, 10.2 Hz, 1H), 1.51 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.2, 150.4, 145.2, 141.4, 141.2, 136.4, 128.6, 128.5, 126.5, 103.9, 61.0, 60.8, 56.3, 53.9, 49.8, 44.1, 29.1, 27.7; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$, 313.1798. Found 313.1811.



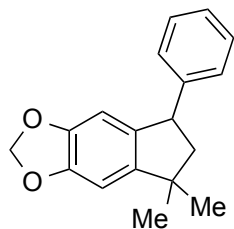
5,7-Dimethoxy-1,1-dimethyl-3-phenylindane (8b): Synthesized from 3,5-dimethoxybenzhydrol (**1b**, 0.308 mmol) and silane **2a** via General Method D (58 mg, 66% yield): IR (Germanium ATR): 2999, 2834, 1597, 1486, 1454, 1300, 1203, 1155, 1074, 1045, 933, 752, 717 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 6.32 (dd, J = 2.2, 0.8 Hz, 1H), 5.99 (dd, J = 2.2, 1.0 Hz, 1H), 4.33 – 4.28 (m, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 2.34 (dd, J = 12.6, 7.9 Hz, 1H), 1.95 (dd, J = 12.6, 10.0 Hz, 1H), 1.48 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.5, 157.3, 148.1, 145.4, 131.6, 128.6, 126.4, 101.0, 97.7, 55.6, 55.2, 53.8, 50.0, 43.6, 28.8, 26.7; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$, 283.1693. Found 283.1701.



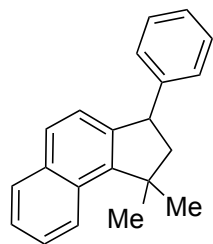
4,7-Dimethoxy-1,1-dimethyl-3-phenylindane (8c): Synthesized from 2,5-dimethoxybenzhydrol (**1c**, 0.620 mmol) and silane **2a** via General Method D (105 mg, 60% yield): IR (Germanium ATR): 3029, 1601, 1491, 1462, 1358, 1255, 1215, 1064, 842, 760 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.20 (m, 2H), 7.17 – 7.12 (m, 1H), 7.11 – 7.06 (m, 2H), 6.74 (d, J = 8.6 Hz, 1H), 6.65 (d, J = 8.6 Hz, 1H), 4.46 (dd, J = 9.2, 5.9 Hz, 1H), 3.82 (s, 3H), 3.51 (s, 3H), 2.46 (dd, J = 13.0, 9.2 Hz, 1H), 1.92 (dd, J = 13.0, 5.9 Hz, 1H), 1.36 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.1, 150.9, 146.8, 141.4, 133.9, 128.1, 127.5, 125.6, 110.5, 110.0, 55.9, 55.7, 53.0, 47.2, 45.1, 28.5, 28.3; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$, 283.1693. Found 283.1678.



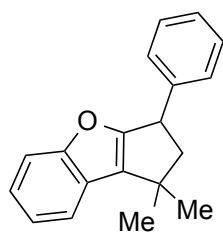
5,6-Dimethoxy-1,1-dimethyl-3-phenylindane (8d): Synthesized from 3,4-dimethoxybenzhydrol (**1d**, 0.368 mmol) and silane **2a** via General Method C (86 mg, 82% yield): IR (Germanium ATR): 2951, 2859, 1605, 1500, 1464, 1453, 1291, 1212, 1069, 1029, 995, 855, 748 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 6.72 (s, 1H), 6.41 (s, 1H), 4.38 – 4.32 (m, 1H), 3.91 (s, 3H), 3.72 (s, 3H), 2.40 (dd, J = 12.4, 7.5 Hz, 1H), 1.93 (dd, J = 12.4, 9.8 Hz, 1H), 1.39 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.8, 148.4, 145.7, 144.9, 136.7, 128.6, 128.4, 126.4, 108.1, 105.1, 56.2, 56.2, 53.5, 49.1, 43.3, 29.3, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$, 283.1693. Found 283.1702.



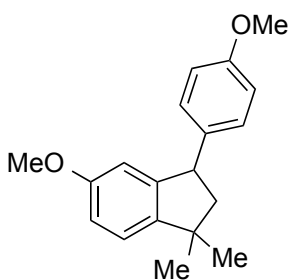
5,6-Methylenedioxy-1,1-dimethyl-3-phenylindane (8e): Synthesized from 3,4-methylenedioxybenzhydrol (**1e**, 0.189 mmol) and silane **2a** via General Method C (39 mg, 77% yield): IR (Germanium ATR): 2954, 1603, 1495, 1476, 1357, 1268, 1234, 1072, 1042, 979 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 6.67 (s, 1H), 6.32 (s, 1H), 5.92 (d, $J = 1.4$ Hz, 1H), 5.89 (d, $J = 1.4$ Hz, 1H), 4.29 (dd, $J = 10.0, 7.5$ Hz, 1H), 2.39 (dd, $J = 12.5, 7.5$ Hz, 1H), 1.96 (dd, $J = 12.4, 10.0$ Hz, 1H), 1.36 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.1, 146.7, 146.2, 145.4, 138.2, 128.6, 128.4, 126.5, 105.6, 102.6, 101.1, 53.2, 48.9, 43.1, 29.2, 29.0; HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{H}]^+$, 267.138. Found 267.1369.



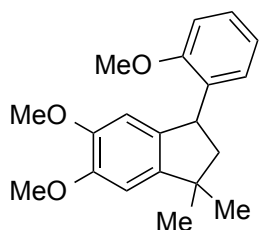
1,1-Dimethyl-3-phenyl-2,3-dihydro-1H-cyclopenta[a]naphthalene (8f): Synthesized from 2-naphthyl(phenyl)methanol (**1f**, 0.560 mmol) silane **2a** via General Method C (95 mg, 62% yield): IR (Germanium ATR): 3052, 3025, 2958, 2863, 1601, 1513, 1495, 1363, 1029, 817, 762 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.25 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.88 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.66 (d, $J = 8.3$ Hz, 1H), 7.51 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1H), 7.45 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 7.38 – 7.30 (m, 2H), 7.30 – 7.23 (m, 3H), 7.03 (d, $J = 8.3$ Hz, 1H), 4.49 (t, $J = 8.9$ Hz, 1H), 2.57 (dd, $J = 12.7, 8.1$ Hz, 1H), 2.15 (dd, $J = 12.7, 9.7$ Hz, 1H), 1.78 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.2, 145.8, 142.9, 134.0, 130.0, 129.4, 128.6, 128.6, 128.0, 126.5, 125.7, 124.8, 124.1, 123.8, 54.6, 49.4, 45.4, 30.3, 27.8; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{20}$ $[\text{M}+\text{H}]^+$, 273.1638. Found 273.1644.



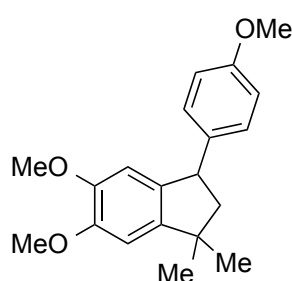
1,1-Dimethyl-3-phenyl-2,3-dihydro-1H-cyclopenta[b]benzofuran (8g): Synthesized from 2-(1-Hydroxyphenylmethyl)benzofuran (**1g**, 0.259 mmol) and silane **2a** via General Method C (49 mg, 72% yield): IR (Germanium ATR): 3061, 3028, 2955, 2864, 1630, 1604, 1497, 1444, 1363, 1205, 1054, 1009, 826 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.56 – 7.51 (m, 1H), 7.47 – 7.41 (m, 1H), 7.37 – 7.31 (m, 2H), 7.26 (m, 5H), 4.52 (dd, $J = 8.5, 6.6$ Hz, 1H), 2.88 (dd, $J = 13.0, 8.5$ Hz, 1H), 2.32 (dd, $J = 13.0, 6.6$ Hz, 1H), 1.52 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.6, 160.5, 143.0, 130.8, 128.8, 127.6, 126.9, 125.6, 123.1, 122.6, 118.9, 112.3, 56.0, 44.0, 37.9, 29.7, 28.9; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{18}\text{O}$ $[\text{M}+\text{H}]^+$, 263.143. Found 263.1424.



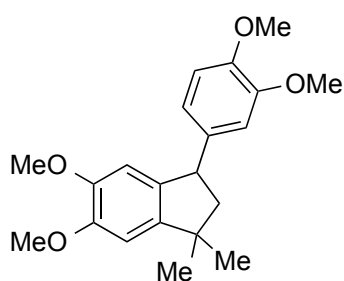
5-Methoxy-3-(4-methoxyphenyl)-1,1-dimethylindane (8h): Synthesized from 3,4'-dimethoxybenzhydrol (**1h**, 0.650 mmol) and silane **2a** via General Method C (111 mg, 60% yield): IR (Germanium ATR): 2997, 2952, 2861, 1609, 1584, 1512, 1487, 1249, 1034 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.17 – 7.11 (m, 2H), 7.09 (d, $J = 8.3$ Hz, 1H), 6.90 – 6.83 (m, 2H), 6.77 (ddd, $J = 8.3, 2.5, 0.9$ Hz, 1H), 6.40 (dd, $J = 2.5, 1.1$ Hz, 1H), 4.31 (dd, $J = 10.3, 7.5$ Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 2.36 (dd, $J = 12.4, 7.5$ Hz, 1H), 1.93 (dd, $J = 12.4, 10.3$ Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.0, 158.3, 147.3, 145.1, 137.1, 129.5, 122.6, 114.0, 113.1, 110.1, 55.6, 55.4, 53.4, 48.4, 42.5, 29.3, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$, 283.1693. Found 283.1712.



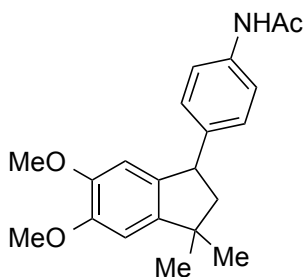
5,6-Dimethoxy-3-(2-methoxyphenyl)-1,1-dimethylindane (8i): Synthesized from 2,3',4'-trimethoxybenzhydrol (**1i**, 0.187 mmol) and silane **2a** via General Method C (42 mg, 72% yield): IR (Germanium ATR): 2950, 1599, 1491, 1238, 1211, 1068, 1029, 855, 752 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.21 (ddd, $J = 8.2, 7.4, 1.8$ Hz, 1H), 7.03 (dd, $J = 7.6, 1.8$ Hz, 1H), 6.92 (dd, $J = 8.2, 1.0$ Hz, 1H), 6.88 (td, $J = 7.5, 1.0$ Hz, 1H), 6.72 (s, 1H), 6.48 (s, 1H), 4.80 (t, $J = 8.8, 7.9$ Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 2.43 (dd, $J = 12.4, 7.9$ Hz, 1H), 1.84 (dd, $J = 12.4, 8.8$ Hz, 1H), 1.33 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.7, 148.6, 148.3, 145.1, 136.3, 134.3, 128.4, 127.2, 120.8, 110.5, 108.3, 105.3, 56.2, 56.2, 55.6, 51.4, 43.3, 41.4, 29.6, 29.6; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$, 313.1798. Found 313.1806.



5,6-Dimethoxy-3-(4-methoxyphenyl)-1,1-dimethylindane (8j): Synthesized from 3,4,4'-trimethoxybenzhydrol (**1j**, 0.295 mmol) and silane **2a** via General Method C (60 mg, 65% yield): IR (Germanium ATR): 3005, 2948, 2833, 1604, 1499, 1462, 1178, 1038, 997, 870, 821 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.14 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.71 (s, 1H), 6.39 (s, 1H), 4.29 (ddd, $J = 9.8, 7.5, 1.0$ Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 2.37 (dd, $J = 12.4, 7.5$ Hz, 1H), 1.89 (dd, $J = 12.4, 9.8$ Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.2, 148.7, 148.4, 144.7, 137.6, 137.0, 129.3, 114.0, 108.1, 105.1, 56.2, 56.2, 55.4, 53.6, 48.2, 43.2, 29.2, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$, 313.1798. Found 313.1803.

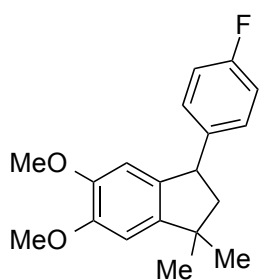


5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1,1-dimethylindane (8k): Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**1k**, 0.302 mmol) and silane **2a** via General Method C (88 mg, 85% yield): IR (Germanium ATR): 2996, 2950, 2860, 1500, 1211, 1138, 1028 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.83 (d, $J = 8.1$ Hz, 1H), 6.78 (dd, $J = 8.1, 2.0$ Hz, 1H), 6.72 (m, 2H), 6.42 (s, 1H), 4.29 (dd, $J = 9.8, 7.4$ Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 2.38 (dd, $J = 12.4, 7.4$ Hz, 1H), 1.90 (dd, $J = 12.4, 9.8$ Hz, 1H), 1.39 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 148.7, 148.4, 147.6, 144.7, 138.1, 136.8, 120.4, 111.4, 111.3, 108.0, 105.1, 56.2, 56.2, 56.0, 56.0, 53.5, 48.7, 43.1, 29.1, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{26}\text{O}_4$ $[\text{M}+\text{H}]^+$, 343.1904. Found 343.1904.

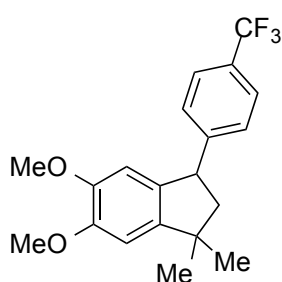


N-(4-(5,6-Dimethoxy-3,3-dimethylindan-1-yl)phenyl)acetamide (8l): 4-(*N*-acetamide)-3',4'-dimethoxybenzhydrol (**1l**, 0.201 mmol) was dissolved in MeNO_2 (0.1 M soln) and allowed to stir while warming to 80 $^\circ\text{C}$ under N_2 atmosphere. Silane **2a** (1.5 equiv) was added, followed by a solution of triflimide in DCM (10 mol%). The reaction was allowed to stir at 80 $^\circ\text{C}$ for 2 hours before being quenched with sat. NaHCO_3 solution. The biphasic solution was extracted with DCM and the combined organic layers were dried over Na_2SO_4 . Concentration under reduced pressure followed by flash column chromatography on silica gel with EtOAc in hexanes solvent systems afforded the desired indane (64 mg, 95% yield): IR (Germanium ATR): 3310, 3000, 2953, 1666, 1602, 1513, 1500, 1210, 1068, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.41 (m, 2H), 7.19 – 7.15 (m, 2H), 6.71 (s, 1H), 6.37 (d, $J = 0.9$ Hz, 1H), 4.31 (dd, $J = 9.7, 7.5$ Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 2.37 (dd, $J = 12.4,$

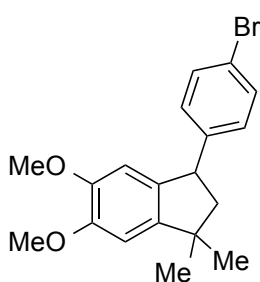
7.5 Hz, 1H), 2.18 (s, 3H), 1.89 (dd, $J = 12.5, 9.8$ Hz, 1H), 1.71 – 1.62 (m, 1H), 1.37 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.4, 148.8, 148.4, 144.8, 141.8, 136.7, 136.1, 129.0, 120.3, 108.0, 105.2, 56.2, 56.2, 53.4, 48.5, 43.3, 29.2, 29.1, 24.7; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_3$ $[\text{M}+\text{H}]^+$, 340.1907. Found 340.1919.



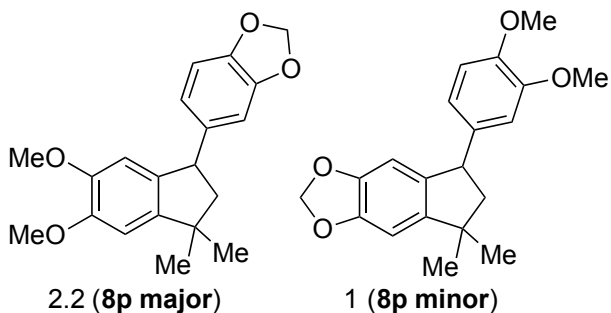
3-(4-Fluorophenyl)-5,6-dimethoxy-1,1-dimethylindane (8m): Synthesized from 4-fluoro-3',4'-dimethoxybenzhydrol (**1m**, 0.320 mmol) and silane **2a** via General Method C (65 mg, 67% yield): IR (Germanium ATR): 2952, 2861, 1604, 1502, 1290, 1212, 1068, 856, 832 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.20 – 7.14 (m, 2H), 7.03 – 6.97 (m, 2H), 6.71 (s, 1H), 6.36 (s, 1H), 4.32 (dd, $J = 9.8, 7.5$ Hz, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 2.39 (dd, $J = 12.5, 7.5$ Hz, 1H), 1.88 (dd, $J = 12.5, 9.8$ Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.7 (d, $J_{\text{CF}} = 243.9$ Hz), 148.9, 148.5, 144.8, 141.3 (d, $J_{\text{CF}} = 3.1$ Hz), 136.6, 129.8 (d, $J_{\text{CF}} = 7.8$ Hz, 2C), 115.4 (d, $J_{\text{CF}} = 21.1$ Hz, 2C), 108.0, 105.2, 56.2, 56.2, 53.6, 48.3, 43.3, 29.2, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{21}\text{FO}_2$ $[\text{M}+\text{Na}]^+$, 323.1418. Found 323.1422.



5,6-Dimethoxy-1,1-dimethyl-3-(4-(trifluoromethyl)phenyl)indane (8n): Synthesized from 4-trifluoromethyl-3',4'-dimethoxybenzhydrol (**1n**, 0.570 mmol) and silane **2a** via General Method C (164 mg, 82% yield): IR (Germanium ATR): 2953, 2863, 1618, 1500, 1461, 1322, 1128, 1068, 858, 840 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.72 (s, 1H), 6.36 (s, 1H), 4.40 (dd, $J = 9.6, 7.6$ Hz, 1H), 3.92 (s, 3H), 3.73 (s, 3H), 2.42 (dd, $J = 12.5, 7.6$ Hz, 1H), 1.90 (dd, $J = 12.5, 9.6$ Hz, 1H), 1.39 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.0, 149.0, 148.6, 145.0, 135.7, 128.7 (2C), 128.7 (q, $J_{\text{CF}} = 32.3$ Hz), 125.6 (q, $J_{\text{CF}} = 3.9$ Hz, 2C), 124.5 (q, $J_{\text{CF}} = 272.1$ Hz), 107.9, 105.2, 56.2 (2C), 53.4, 49.0, 43.5, 29.3, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$, 351.1566. Found 351.1572.

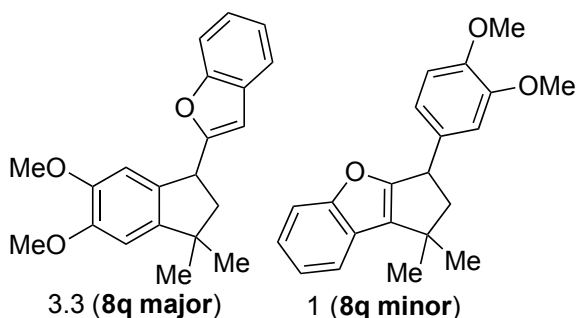


3-(4-Bromophenyl)-5,6-dimethoxy-1,1-dimethylindane (8o): Synthesized from 4-bromo-3',4'-dimethoxybenzhydrol (**1o**, 0.400 mmol) and silane **2a** via General Method C (119 mg, 82% yield): IR (Germanium ATR): 3019, 2952, 1604, 1500, 1292, 1211, 1069, 1009, 855, 821 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.71 (s, 1H), 6.36 (s, 1H), 4.30 (dd, $J = 9.7, 7.5$ Hz, 1H), 3.91 (s, 3H), 3.73 (s, 3H), 2.39 (dd, $J = 12.5, 7.5$ Hz, 1H), 1.87 (dd, $J = 12.5, 9.7$ Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.9, 148.5, 144.9, 144.8, 136.1, 131.7, 130.2, 120.1, 107.9, 105.2, 56.2, 56.2, 53.4, 48.6, 43.4, 29.2, 29.1; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{21}\text{BrO}_2$ $[\text{M}+\text{Na}]^+$, 383.0617. Found 383.0617.



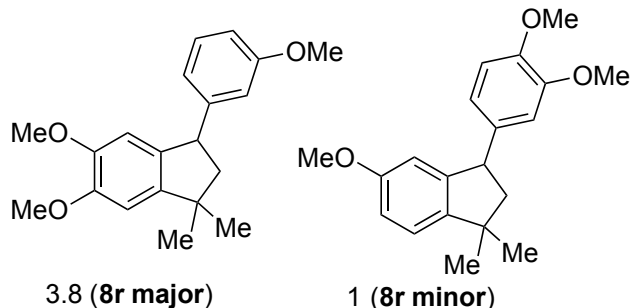
5,6-Dimethoxy-3-(3,4-methylenedioxyphenyl)-1,1-dimethylindane (8p major) and **5,6-Methylenedioxy-3-(3,4-dimethoxyphenyl)-1,1-dimethylindane (8p minor)**: Synthesized from 3,4-methylenedioxy-3',4'-dimethoxy benzhydrol (**1p**, 0.507 mmol) and silane **2a** via General Method C (124 mg, 2.2:1 cyclization isomer ratio, 75% yield): IR (Germanium ATR): 2999, 2862, 1605, 1501, 1487, 1440, 1294, 1231, 1140, 1069, 1038 cm^{-1} ;

Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.76 (d, $J = 7.9$ Hz, 1H), 6.72 – 6.69 (m, 2H), 6.66 (s, 1H), 6.41 (s, 1H), 5.94 (dd, $J = 5.5, 1.3$ Hz, 2H), 4.27 (dd, $J = 9.6, 7.4$ Hz, 1H), 3.90 (s, 3H), 3.75 (s, 3H), 2.36 (dd, $J = 12.5, 7.5$ Hz, 1H), 1.87 (dd, $J = 12.4, 9.8$ Hz, 1H), 1.38 (s, 3H), 1.22 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.8, 148.4, 147.9, 146.1, 144.8, 139.6, 136.7, 121.5, 108.6, 108.2, 108.0, 105.1, 101.0, 56.2, 56.2, 53.5, 48.8, 43.2, 29.3, 29.1; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.82 (d, $J = 8.1$ Hz, 1H), 6.76 (d, $J = 7.9$ Hz, 1H), 6.72 – 6.69 (m, 1H), 6.66 (s, 1H), 6.34 (s, 1H), 5.90 (dd, $J = 15.7, 1.5$ Hz, 2H), 4.23 (dd, $J = 10.2, 7.5$ Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.36 (dd, $J = 12.5, 7.5$ Hz, 1H), 1.93 (dd, $J = 12.5, 10.2$ Hz, 1H), 1.36 (s, 3H), 1.21 (s, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 147.7, 147.1, 146.7, 146.1, 138.3, 137.8, 120.4, 111.5, 111.3, 105.5, 102.6, 101.1, 56.1, 56.1, 53.3, 48.6, 43.0, 29.1, 29.0; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 349.141. Found 349.142.



2-(5,6-Dimethoxy-3,3-dimethylindan-1-yl)benzofuran (8q major) and **3-(3,4-Dimethoxyphenyl)-1,1-dimethyl-2,3-dihydro-1H-cyclopenta[b]benzofuran (8q minor)**: Synthesized from benzo[b]furan-2-yl-(3,4-dimethoxyphenyl) carbinol (**1q**, 0.30 mmol) and silane **2a** via General Method C (50 mg, 3.3:1 cyclization isomer ratio, 51% yield): IR (Germanium ATR): 3059, 2996, 2862, 1605, 1502, 1454, 1295, 1254, 1214, 1070, 1028, 855, 755 cm^{-1} ;

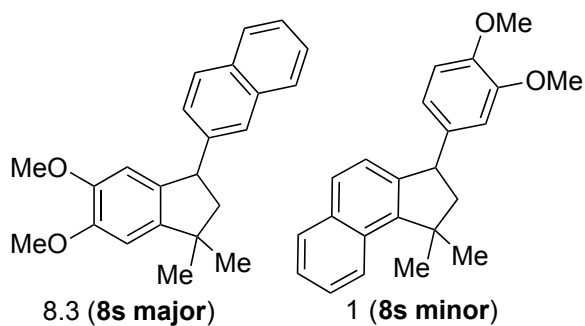
Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 7.52 – 7.49 (m, 1H), 7.46 – 7.42 (m, 1H), 7.25 – 7.17 (m, 2H), 6.73 (s, 1H), 6.71 (d, $J = 0.9$ Hz, 1H), 6.47 (d, $J = 0.9$ Hz, 1H), 4.56 (t, $J = 8.1$ Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 2.41 (dd, $J = 12.5, 7.9$ Hz, 1H), 2.28 (dd, $J = 12.5, 8.5$ Hz, 1H), 1.40 (s, 3H), 1.27 (s, 3H); Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 1H), 7.26 – 7.16 (m, 2H), 6.83 (d, $J = 8.2$ Hz, 1H), 6.80 – 6.76 (m, 2H), 4.46 (dd, $J = 8.4, 6.7$ Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.85 (dd, $J = 12.9, 8.5$ Hz, 1H), 2.32 – 2.27 (m, 1H), 1.52 (s, 3H), 1.42 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 161.4, 155.1, 149.3, 148.5, 144.4, 133.2, 128.9, 123.5, 122.6, 120.6, 111.2, 107.8, 105.5, 102.5, 56.3, 56.2, 48.3, 43.5, 42.5, 29.4, 29.4; Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 160.7, 160.6, 149.3, 148.0, 135.5, 130.6, 125.6, 123.1, 122.7, 119.5, 118.9, 112.4, 111.5, 110.8, 56.1, 56.1, 56.0, 43.7, 37.8, 29.8, 28.8; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3$ $[\text{M}+\text{H}]^+$, 323.1462. Found 323.1653.



5,6-Dimethoxy-3-(3-methoxyphenyl)-1,1-dimethylindane (8r major**) and 5-Methoxy-3-(3,4-dimethoxyphenyl)-1,1-dimethylindane (**8r minor**):**

Synthesized from 3,3',4-trimethoxybenzhydrol (**1r**, 0.322 mmol) and silane **2a** via General Method C (56 mg, 3.8:1 cyclization isomer ratio, 55% yield): IR (Germanium ATR): 2998, 2950, 2860, 2832, 1607, 1500, 1464, 1314, 1236, 1212, 1139, 1069, 1030, 996, 855, 767 cm^{-1} ;

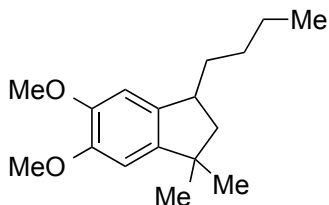
Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 7.24 (td, $J = 7.7, 0.8$ Hz, 1H), 6.83 – 6.76 (m, 3H), 6.71 (s, 1H), 6.43 (d, $J = 1.0$ Hz, 1H), 4.32 (dd, $J = 9.1, 7.8$ Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 2.39 (dd, $J = 12.4, 7.5$ Hz, 1H), 1.93 (dd, $J = 12.4, 9.7$ Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 159.9, 148.8, 148.4, 147.4, 144.9, 136.5, 129.5, 120.9, 114.2, 111.6, 108.1, 105.1, 56.2 (2C), 55.3, 53.3, 49.1, 43.3, 29.3, 29.1; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 7.10 (d, $J = 8.3$ Hz, 1H), 6.86 – 6.76 (m, 3H), 6.73 (d, $J = 2.0$ Hz, 1H), 6.44 (s, 1H), 4.35 – 4.28 (m, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H), 2.44 – 2.33 (m, 1H), 1.99 – 1.89 (m, 1H), 1.40 (s, 3H), 1.23 (s, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 159.0, 149.1, 147.7, 147.1, 145.1, 137.5, 122.6, 120.6, 113.2, 111.6, 111.3, 110.1, 56.1, 56.1, 55.6, 53.3, 48.9, 42.5, 29.2, 29.0; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$, 313.1798. Found 313.1805.



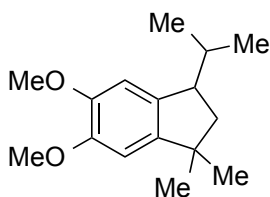
2-(5,6-Dimethoxy-3,3-dimethylindan-1-yl)naphthalene (8s major**) and 3-(3,4-Dimethoxyphenyl)-1,1-dimethyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalene (**8s minor**):**

Synthesized from (3,4-dimethoxyphenyl)(2-naphthyl)methanol (**1s**, 0.418 mmol) and silane **2a** via General Method C (96 mg, 8.3:1 cyclization isomer ratio, 69% yield): IR (Germanium ATR): 2999, 2955, 2859, 2829, 1603, 1500, 1463, 1236, 1213, 1139, 1029, 889, 819, 754 cm^{-1} ;

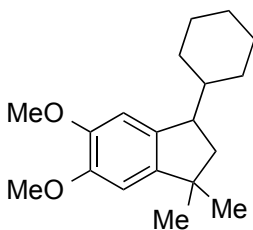
Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.78 (m, 3H), 7.72 (s, 1H), 7.54 – 7.41 (m, 2H), 7.31 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.76 (s, 1H), 6.41 (s, 1H), 4.52 (dd, $J = 9.6, 7.7$ Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H), 2.46 (dd, $J = 12.5, 7.5$ Hz, 1H), 2.04 (dd, $J = 12.5, 9.8$ Hz, 1H), 1.43 (s, 3H), 1.28 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.8, 148.5, 144.9, 143.0, 136.7, 133.7, 132.5, 128.3, 127.8, 127.7, 126.9 (2C), 126.1, 125.5, 108.1, 105.2, 56.2, 56.7, 53.3, 49.3, 43.4, 29.4, 29.2; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 8.23 (dd, $J = 8.5, 1.1$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.49 – 7.40 (m, 2H), 7.04 (d, $J = 8.3$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.80 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.74 (d, $J = 2.0$ Hz, 1H), 4.42 (dd, $J = 9.8, 8.0$ Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 2.53 (dd, $J = 12.6, 7.9$ Hz, 1H), 2.11 (dd, $J = 12.6, 9.9$ Hz, 1H), 1.77 (s, 3H), 1.54 (s, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 147.7, 146.1, 143.0, 138.3, 134.0, 130.0, 129.4, 128.0, 125.7, 124.8, 124.1, 123.8, 120.6, 111.6, 111.3, 56.1, 56.0, 54.7, 49.0, 45.3, 30.3, 27.7; HRMS (ESI): Exact mass calcd for $\text{C}_{23}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{H}]^+$, 333.1849. Found 333.1855.



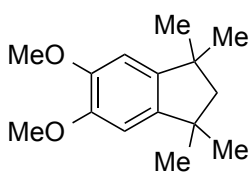
3-Butyl-5,6-dimethoxy-1,1-dimethylindane (8t): Synthesized from 1-(3,4-dimethoxyphenyl)pentan-1-ol (**1t**, 0.156 mmol) and silane **2a** via General Method C (33 mg, 84% yield): IR (Germanium ATR): 2952, 2856, 1606, 1499, 1464, 1212, 1065 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.70 (s, 1H), 6.66 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.14 – 3.02 (m, 1H), 2.14 (dd, $J = 12.2, 7.3$ Hz, 1H), 1.99 – 1.88 (m, 1H), 1.52 (dd, $J = 12.3, 8.9$ Hz, 1H), 1.46 – 1.34 (m, 5H), 1.33 (s, 3H), 1.15 (s, 3H), 0.98 – 0.92 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.4, 148.2, 144.3, 138.0, 106.8, 105.5, 56.2, 56.2, 49.1, 42.9, 42.0, 35.3, 30.2, 29.7, 29.5, 23.1, 14.3; HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 285.1825. Found 285.1842.



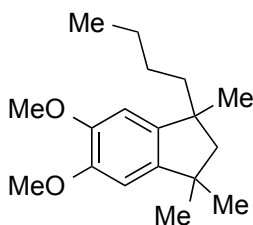
3-Isopropyl-5,6-dimethoxy-1,1-dimethylindane (8u): Synthesized from 1-(3,4-dimethoxyphenyl)-2-methyl-1-propanol (**1u**, 0.209 mmol) and silane **2a** via General Method C (39 mg, 76% yield): IR (Germanium ATR): 2951, 1605, 1499, 1463, 1289, 1211, 1073, 852 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.67 (d, $J = 1.1$ Hz, 1H), 6.64 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.16 (dddd, $J = 9.1, 7.7, 4.6, 1.1$ Hz, 1H), 2.21 (pd, $J = 6.9, 4.6$ Hz, 1H), 1.87 (dd, $J = 12.5, 7.7$ Hz, 1H), 1.66 (dd, $J = 12.5, 9.1$ Hz, 1H), 1.32 (s, 3H), 1.15 (s, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 0.75 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.3, 148.1, 145.0, 136.5, 107.3, 105.4, 56.3, 56.1, 48.0, 42.5, 42.3, 30.1, 29.4, 29.4, 21.6, 17.2; HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 271.1669. Found 271.1683.



3-Cyclohexyl-5,6-dimethoxy-1,1-dimethylindane (8v): Synthesized from 1-cyclohexyl-1-(3,4-dimethoxyphenyl)methanol (**1v**, 0.408 mmol) and silane **2a** via General Method C (86 mg, 73% yield): IR (Germanium ATR): 2993, 2922, 2849, 1605, 1500, 1448, 1317, 1288, 1212, 1070, 993 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.67 (s, 1H), 6.63 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.11 (td, $J = 8.4, 4.6$ Hz, 1H), 1.88 (dd, $J = 12.5, 7.8$ Hz, 1H), 1.84 – 1.66 (m, 6H), 1.50 – 1.42 (m, 1H), 1.38 – 1.08 (m, 10H), 1.02 – 0.88 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.4, 148.0, 145.0, 136.1, 107.5, 105.5, 56.4, 56.1, 47.6, 43.5, 42.6, 40.3, 32.3, 30.1, 29.5, 27.8, 27.2, 26.9, 26.8; HRMS (ESI): Exact mass calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 311.1982. Found 311.1996.

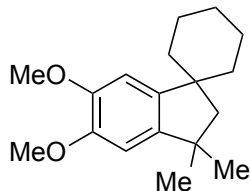


5,6-Dimethoxy-1,1,3,3-tetramethylindane (8w): Synthesized from 3,4-dimethoxy-(1'-hydroxy-1'-methylethyl)benzene (**1w**, 0.400 mmol) and silane **2a** via General Method C (75 mg, 79% yield): IR (Germanium ATR): 3008, 2860, 1602, 1502, 1464, 1290, 1213, 1059, 852 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.62 (s, 2H), 3.88 (s, 6H), 1.91 (s, 2H), 1.29 (s, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.6, 142.8, 105.6, 57.1, 56.2, 42.6, 31.7; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 257.1512. Found 257.1532.



1-Butyl-5,6-dimethoxy-1,3,3-trimethylindane (8x): Synthesized from 2-(3,4-dimethoxyphenyl)hexan-2-ol (**1x**, 0.600 mmol) and silane **2a** via General Method C (157 mg, 94% yield): IR (Germanium ATR): 2952, 2859, 1605, 1502, 1464, 1288, 1212, 1149, 1057, 852 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.61 (s, 1H), 6.58 (s, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 2.01 (d, $J = 13.2$ Hz, 1H), 1.76 (d, J

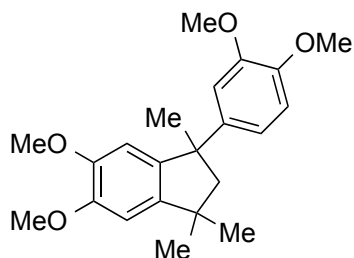
= 13.2 Hz, 1H), 1.64 – 1.56 (m, 1H), 1.55 – 1.45 (m, 1H), 1.35 – 1.27 (m, 3H), 1.29 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H), 1.21 – 1.12 (m, 1H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.5, 148.4, 143.1, 142.3, 105.9, 105.5, 56.2, 56.1, 53.8, 45.9, 43.3, 42.5, 32.3, 31.5, 29.8, 27.5, 23.6, 14.2; HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{NH}_4]^+$, 294.2428. Found 294.2441.



5',6'-Dimethoxy-3',3'-dimethylspiro[cyclohexane-1,1'-indane] (8y):

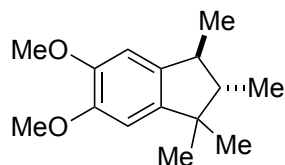
(8y):

Synthesized from 1-(3,4-dimethoxyphenyl)cyclohexanol (**1y**, 0.301 mmol) and silane **2a** via General Method C (62 mg, 85% yield): IR (Germanium ATR): 2952, 2852, 1604, 1503, 1464, 1289, 1214, 1032, 974, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.64 (s, 1H), 6.63 (s, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 1.95 (s, 2H), 1.76 – 1.66 (m, 3H), 1.61 – 1.53 (m, 4H), 1.51 – 1.40 (m, 2H), 1.29 (s, 6H), 1.33 – 1.22 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.7, 148.5, 143.0, 143.0, 105.8, 105.6, 56.1, 56.1, 51.6, 46.9, 42.7, 40.2, 32.2, 26.1, 23.6; HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{NH}_4]^+$, 292.2271. Found 292.2273.

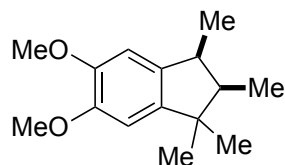


1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1,3,3-trimethylindane (8z):

Synthesized from 3,3',4,4'-tetramethoxy-7-methylbenzhydrol (**1z**, 0.102 mmol) and silane **2a** via General Method C (21 mg, 58% yield): IR (Germanium ATR): 2995, 2953, 1604, 1502, 1463, 1253, 1145, 1028 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.74 (d, $J = 8.4$ Hz, 1H), 6.72 (d, $J = 2.2$ Hz, 1H), 6.70 – 6.66 (m, 2H), 6.60 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 2.34 (d, $J = 12.9$ Hz, 1H), 2.17 (d, $J = 12.9$ Hz, 1H), 1.66 (s, 3H), 1.32 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.0, 148.5, 148.5, 147.0, 144.2, 144.1, 140.4, 118.8, 110.6, 110.6, 107.6, 105.3, 59.9, 56.3, 56.1, 56.0, 55.9, 50.5, 42.9, 31.0, 31.0, 30.6; HRMS (ESI): Exact mass calcd for $\text{C}_{22}\text{H}_{28}\text{O}_4$ $[\text{M}+\text{NH}_4]^+$, 374.2326. Found 374.2336.



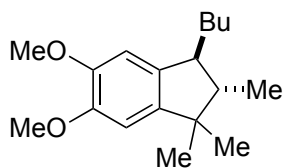
3.2 (8aa major)



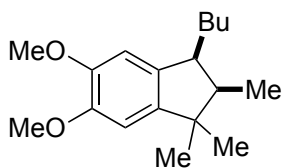
1 (8aa minor)

anti-5,6-Dimethoxy-1,1,2,3-tetramethylindane (8aa major) and syn-5,6-Dimethoxy-1,1,2,3-tetramethylindane (8aa minor):

Synthesized from 1-(3,4-dimethoxyphenyl)ethanol (**1aa**, 0.268 mmol) and silane **2b** via General Method C (56 mg, 3.2:1 d.r., 89% yield): IR (Germanium ATR): 2954, 2867, 1608, 1501, 1464, 1405, 1288, 1212, 1049, 853, 766 cm^{-1} ; Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.69 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 2.64 (ddt, $J = 10.1, 7.4, 6.2$ Hz, 1H), 1.63 – 1.52 (m, 1H), 1.28 (d, $J = 6.7$ Hz, 3H), 1.26 (s, 3H), 1.05 (d, $J = 6.9$ Hz, 3H), 0.93 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.3, 148.2, 144.7, 138.1, 106.5, 105.7, 56.3, 56.2, 54.6, 44.7, 43.2, 26.9, 23.7, 17.3, 11.9; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.69 (s, 1H), 6.65 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.14 (p, $J = 7.5$ Hz, 1H), 2.20 (p, $J = 7.5$ Hz, 1H), 1.20 (s, 3H), 1.12 (d, $J = 7.4$ Hz, 3H), 1.08 (s, 3H), 0.92 (d, $J = 7.5$ Hz, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.4, 148.2, 143.8, 138.9, 107.3, 105.9, 56.2, 56.2, 47.7, 45.6, 41.2, 28.9, 26.3, 17.1, 10.6; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 257.1512. Found 257.1512.



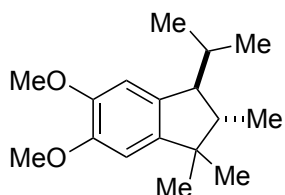
2.8 (8bb major)



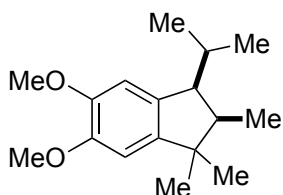
1 (8bb minor)

anti-3-Butyl-5,6-dimethoxy-1,1,2-trimethylindane (8bb major) and **syn-3-Butyl-5,6-dimethoxy-1,1,2-trimethylindane (8bb minor)**: Synthesized from 1-(3,4-dimethoxyphenyl)pentan-1-ol (**1t**, 0.143 mmol) and silane **2b** via General Method C (34 mg, 2.9:1 d.r., 87% yield): IR (Germanium ATR): 2953, 2927,

2858, 1606, 1498, 1209, 1058, 982 cm^{-1} ; Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.72 (s, 1H), 6.68 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.72 – 2.57 (m, 1H), 1.82 – 1.65 (m, 2H), 1.62 – 1.33 (m, 5H), 1.26 (s, 3H), 1.06 (d, $J = 6.9$ Hz, 3H), 0.97 – 0.94 (m, 3H), 0.93 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.3, 148.0, 144.9, 137.0, 107.0, 105.6, 56.3, 56.2, 51.0, 48.4, 44.7, 31.8, 29.3, 27.2, 23.9, 23.5, 14.3, 12.8; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.73 (s, 1H), 6.68 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.02 (q, $J = 7.3$ Hz, 1H), 2.23 (p, $J = 7.3$ Hz, 1H), 1.82 – 1.65 (m, 1H), 1.62 – 1.33 (m, 5H), 1.20 (s, 3H), 1.14 (s, 3H), 0.97 – 0.94 (m, 3H), 0.90 (d, $J = 7.3$ Hz, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.3, 147.7, 144.0, 137.5, 108.1, 106.0, 56.2, 56.2, 48.0, 46.3, 45.3, 30.9, 30.3, 28.8, 25.5, 23.3, 14.3, 10.6; HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{Na}]^+$, 299.1982. Found 299.1991.



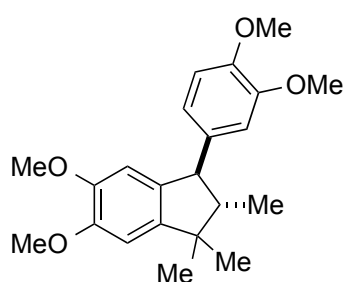
2.2 (8cc major)



1 (8cc minor)

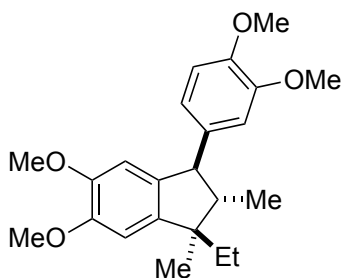
anti-3-Isopropyl-5,6-dimethoxy-1,1,2-trimethylindane (8cc major) and **syn-3-Isopropyl-5,6-dimethoxy-1,1,2-trimethylindane (8cc minor)**: Synthesized from 1-(3,4-dimethoxyphenyl)-2-methyl-1-propanol (**1u**, 0.216 mmol) and silane **2b** via General Method C (51 mg, 2.2:1 d.r., 90% yield): IR (Germanium ATR): 2954, 2870, 1605,

1499, 1464, 1211, 1060, 987, 851, 773 cm^{-1} ; Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.81 (d, $J = 0.9$ Hz, 1H), 6.65 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.91 (ddd, $J = 7.3, 7.3, 0.8$ Hz, 1H), 2.27 (dq, $J = 7.4, 7.4$ Hz, 1H), 2.05 – 1.91 (m, 1H), 1.19 (s, 3H), 1.12 (s, 3H), 1.09 (d, $J = 6.7$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 7.3$ Hz, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.2, 147.3, 144.8, 135.9, 109.5, 105.8, 56.3, 56.1, 53.0, 48.7, 45.2, 29.0, 28.1, 25.1, 24.1, 22.1, 11.3; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.72 (d, $J = 1.1$ Hz, 1H), 6.65 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.68 (ddd, $J = 9.6, 2.9, 1.0$ Hz, 1H), 2.20 (pd, $J = 7.0, 2.9$ Hz, 1H), 1.86 (dq, $J = 9.7, 6.9$ Hz, 1H), 1.25 (s, 3H), 1.06 (d, $J = 7.0$ Hz, 3H), 1.02 (d, $J = 7.1$ Hz, 3H), 0.99 (d, $J = 7.1$ Hz, 3H), 0.93 (s, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 148.2, 147.8, 145.3, 135.3, 107.6, 105.5, 56.3, 56.1, 54.9, 47.0, 44.8, 29.0, 27.5, 24.4, 20.3, 20.1, 14.4; HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{H}]^+$, 263.2006. Found 263.2008.



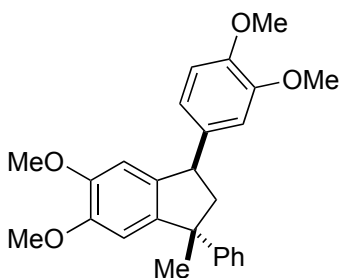
anti-3-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1,1,2-trimethylindane (8dd): Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.204 mmol) and silane **2b** via General Method C (69 mg, 95% yield): IR (Germanium ATR): 2999, 2955, 2869, 2831, 1605, 1514, 1499, 1463, 1247, 1208, 1030, 986 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.85 (d, $J = 8.1$ Hz, 1H), 6.79 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.75 (s, 1H), 6.69 (d, $J = 2.0$ Hz, 1H), 6.39 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 3.69 (d, $J = 10.6$ Hz, 1H), 1.97 (dq, $J = 10.6, 6.9$ Hz, 1H), 1.34 (s,

3H), 1.02 (s, 3H), 0.98 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 148.6, 148.2, 147.8, 145.1, 136.5, 136.4, 121.2, 111.6, 111.1, 108.0, 105.3, 56.6, 56.2 (3C), 56.1, 56.0, 44.7, 26.8, 23.6, 11.7; HRMS (ESI): Exact mass calcd for $\text{C}_{22}\text{H}_{28}\text{O}_4$ $[\text{M}+\text{H}]^+$, 357.206. Found 357.2059.



(1R,2SR,3RS)-3-(3,4-Dimethoxyphenyl)-1-ethyl-5,6-dimethoxy-1,2-dimethylindane (8ee): Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.174 mmol) and silane **2c** via General Method C (71 mg, 1.8:1 d.r., 97% yield): IR (Germanium ATR): 2995, 2956, 2831, 1605, 1512, 1503, 1464, 1249, 1205, 1069, 1030, 853, 762 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.85 (d, $J = 8.2$ Hz, 1H), 6.78 (dd, $J = 8.1, 2.0$ Hz, 1H), 6.68 (d, $J = 2.0$ Hz, 1H), 6.66 (s, 1H), 6.38 (s, 1H), 3.90 (s, 3H), 3.90 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 3.68 (d, $J = 10.2$ Hz,

1H), 2.15 (dq, $J = 10.3, 6.8$ Hz, 1H), 1.78 (dq, $J = 14.9, 7.5$ Hz, 1H), 1.68 (dq, $J = 14.6, 7.4$ Hz, 1H), 1.02 (s, 3H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.85 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.0, 148.6, 148.2, 147.8, 143.3, 137.1, 137.1, 121.1, 111.7, 111.2, 107.9, 105.7, 56.4, 56.3, 56.1, 56.0, 56.0, 51.0, 48.3, 31.0, 23.6, 12.4, 9.3; HRMS (ESI): Exact mass calcd for $\text{C}_{23}\text{H}_{30}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 393.2036. Found 393.2045.



anti-3-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1-methyl-1-phenylindane (8ff): Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.234 mmol) and silane **2d** (0.217 mmol, 0.9 equiv) via General Method C (94 mg, 2.5:1 d.r., 99% yield): IR (Germanium ATR): 2999, 2830, 1605, 1514, 1463, 1282, 1210, 1139, 1077, 1029, 855 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 – 7.08 (m, 2H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.78 (s, 1H), 6.75 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.48 (s, 1H), 4.06 (dd, $J = 10.6, 6.8$

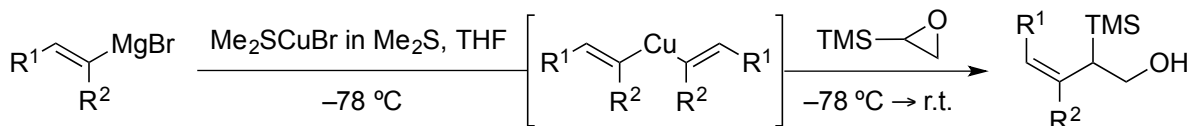
Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 2.76 (dd, $J = 12.3, 6.8$ Hz, 1H), 2.21 (dd, $J = 12.3, 10.6$ Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 149.0, 148.8, 148.7, 147.7, 141.9, 138.7, 137.2, 128.3 (2C), 126.6 (2C), 126.0, 120.5, 111.6, 111.4, 107.8, 107.0, 56.2 (2C), 56.1 (2C), 56.0, 51.1, 48.6, 28.7; HRMS (ESI): Exact mass calcd for $\text{C}_{26}\text{H}_{28}\text{O}_4$ $[\text{M}+\text{NH}_4]^+$, 422.2326. Found 422.2335.

5. Type B Allylsilane Experimental Procedures and Characterization Data

(Trimethylsilyl)ethylene oxide (14): A modified version of Croudace's procedure was used¹⁵: A solution of *m*CPBA (77%, 50.3 g, 224 mmol) in chloroform (370 mL) was added dropwise to a solution of vinyltrimethylsilane (15 g, 150 mmol) in chloroform (40 mL) at 0 °C. The mixture was then gradually warmed to room temperature and allowed to stir overnight. The cloudy white reaction was neutralized by careful treatment with 5% aqueous NaHCO_3 at 0 °C. The organic layer was washed repetitively with 5% NaHCO_3 (2 L) until *m*CPBA was no longer present as monitored by TLC. The organic layer was then dried over magnesium sulfate and concentrated under reduced pressure. The crude material was distilled at atmospheric pressure and 110 °C to afford the title compound as a clear oil (74% yield): ^1H NMR (500 MHz, CDCl_3) δ 2.91 (dd, $J = 5.8, 5.6$ Hz, 1H), 2.56 (dd, $J = 5.8, 4.1$ Hz, 1H), 2.20 (dd, $J = 5.5, 4.1$ Hz, 1H), 0.06 (s, 9H); ^{13}C NMR (126 MHz,

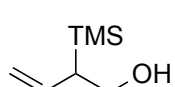
¹⁵ Croudace, M. C.; Schore, N. E., *J. Org. Chem.* **1981**, *46*, 5357–5363.

CDCl₃) δ 44.8, 44.3, -3.7. All spectroscopic data for this compound agrees with previously reported values.¹⁶

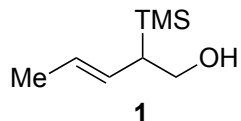
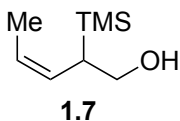


Scheme S6: General method for the synthesis of **3a** and **3b** allylsilanes

General Method E: A solution of vinyl bromide Grignard in THF (0.5 M, 2 equiv) was charged in a round bottom flask with dry THF (0.1 M total solution volume) and cooled to $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere. A solution of copper(I) bromide dimethyl sulfide complex (1 equiv) in dimethyl sulfide (0.5 M soln) was added dropwise to the suspension. The mixture was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 1 hr. (Trimethylsilyl)ethylene oxide (1 equiv) was added dropwise to the reaction. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 hr then warmed up to room temperature and stirred overnight. The reaction was quenched by addition of saturated aqueous NH_4Cl soln and stirred for 20 min before being filtered through Celite. The organic layer was washed with additional NH_4Cl soln. The aqueous layer was extracted with diethyl ether three times, dried over magnesium sulfate and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel with 30% ether/pentanes solvent system to afford the desired allylsilane.



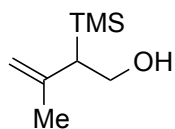
2-(Trimethylsilyl)but-3-en-1-ol (3a): Synthesized from vinyl cuprate via General Method E (10.5 mmol scale, 64% yield): IR (Germanium ATR): 3379, 3077, 2953, 1628, 1248, 837 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.70 (ddd, $J = 17.1, 10.3, 9.6$ Hz, 1H), 5.07 (ddd, $J = 10.4, 1.8, 0.6$ Hz, 1H), 5.01 (ddd, $J = 17.2, 1.9, 1.0$ Hz, 1H), 3.80 – 3.74 (m, 1H), 3.74 – 3.68 (m, 1H), 1.92 (ddd, $J = 10.7, 9.7, 4.2$ Hz, 1H), 1.48 – 1.43 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 137.2, 115.2, 62.4, 40.2, -2.9; HRMS (ESI): Exact mass calcd for $\text{C}_7\text{H}_{16}\text{OSi}$ [$\text{M}+\text{Na}$]⁺, 167.0863. Found 167.0869.



2-(Trimethylsilyl)pent-3-en-1-ol (3b): Synthesized from 1-propenyl cuprate via General Method E (15.0 mmol scale, 1.7:1 *Z:E* ratio, 73% yield): IR (Germanium ATR): 3354, 3008, 2954, 1648, 1251, 1095, 1049, 965, 861, 833, 749 cm^{-1} ; Major Isomer

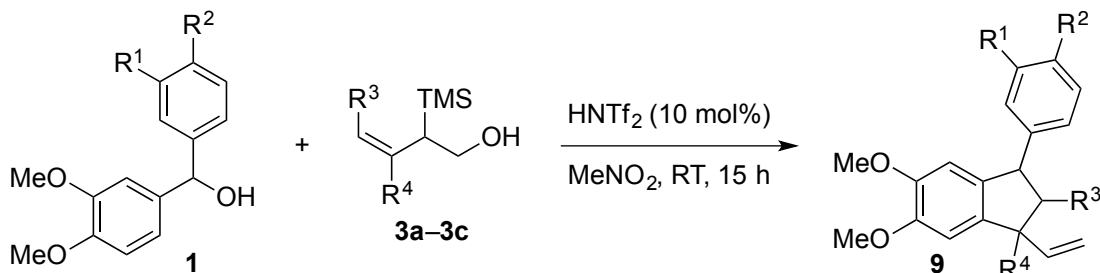
^1H NMR (500 MHz, CDCl_3) δ 5.64 (dq, $J = 10.8, 6.8, 0.9$ Hz, 1H), 5.32 – 5.21 (m, 1H), 3.77 (ddd, $J = 10.6, 8.1, 3.9$ Hz, 1H), 3.65 – 3.57 (m, 1H), 2.27 (tdd, $J = 11.2, 4.0, 0.9$ Hz, 1H), 1.62 (dd, $J = 6.8, 1.8$ Hz, 3H), 1.38 (d, $J = 8.2$ Hz, 1H), 0.00 (s, 9H); Major Isomer ^{13}C NMR (101 MHz, CDCl_3) δ 129.0, 125.8, 63.5, 33.7, 13.5, -2.7; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 5.44 (dq, $J = 15.2, 6.3, 0.7$ Hz, 1H), 5.32 – 5.21 (m, 1H), 3.71 (ddd, $J = 10.7, 8.2, 4.0$ Hz, 1H), 3.65 – 3.57 (m, 1H), 1.81 (td, $J = 10.4, 4.1$ Hz, 1H), 1.71 (dd, $J = 6.3, 1.5$ Hz, 3H), 1.48 (d, $J = 8.3$ Hz, 1H), -0.01 (s, 9H); Minor Isomer ^{13}C NMR (101 MHz, CDCl_3) δ 129.1, 126.6, 62.7, 38.6, 18.4, -2.8; HRMS (ESI): Exact mass calcd for $\text{C}_8\text{H}_{18}\text{OSi}$ [$\text{M}+\text{Na}$]⁺, 181.1019. Found 181.102.

¹⁶ Jankowski, P.; Masnyk, M.; Wicha, J., *Synth. Commun.* **1989**, *19*, 873–880.



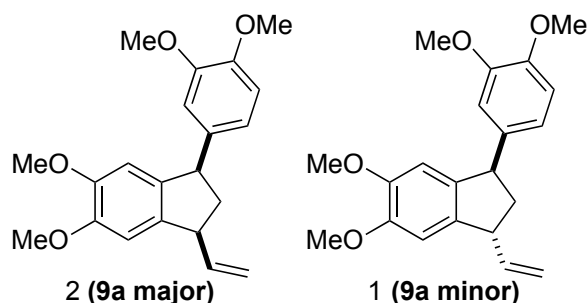
3-methyl-2-(Trimethylsilyl)but-3-en-1-ol (3c): A solution of copper(I) bromide dimethyl sulfide complex (1 equiv) in dimethyl sulfide (0.5 M soln) was charged in a round bottom flask with dry THF (0.1 M total solution volume) and cooled to $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere. A solution of vinyl bromide Grignard in THF (0.5 M, 2 equiv) was added dropwise to the suspension. The mixture was slowly warmed up to $-30\text{ }^{\circ}\text{C}$ and stirred for 10 min, then cooled back to $-78\text{ }^{\circ}\text{C}$. (Trimethylsilyl)ethylene oxide (1 equiv) was added dropwise to the reaction. The mixture was then warmed up to room temperature and allowed to stir overnight. The reaction was quenched by addition of saturated aqueous NH_4Cl soln and stirred for 20 min before being filtered through Celite. The organic layer was washed with additional NH_4Cl soln. The aqueous layer was extracted with diethyl ether, dried over magnesium sulfate and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel with 30% ether/pentanes solvent system to afford the desired allylsilane (5.0 mmol scale, 51% yield): IR (Germanium ATR): 3329, 3008, 2955, 2880, 1437, 1248, 1095, 1049, 862, 834 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.87 (d, $J = 1.5$ Hz, 1H), 4.66 (d, $J = 1.5$ Hz, 1H), 3.84 (td, $J = 11.3, 2.2$ Hz, 1H), 3.72 (ddd, $J = 11.4, 8.0, 4.4$ Hz, 1H), 1.94 (dd, $J = 11.8, 4.4$ Hz, 1H), 1.75 (s, 3H), 1.60 – 1.59 (m, 1H), 0.03 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.4, 110.2, 61.8, 43.0, 23.8, -2.2; HRMS (ESI): Exact mass calcd for $\text{C}_8\text{H}_{18}\text{OSi}$ $[\text{M}+\text{Na}]^+$, 181.1019. Found 181.1022.

6. Type B Indane Experimental Procedures and Characterization Data



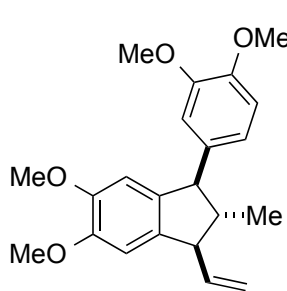
Scheme S7: General method for synthesis of indanes with Type B allylsilanes

General Method F: Benzhydrol **1** (1 equiv) was dissolved in MeNO_2 (0.1 M) and allowed to stir under N_2 atmosphere. Alkyl silane **3** (1.5 equiv) was added, followed by a solution of triflimide in DCM (10 mol%). The reaction was allowed to stir at room temperature for 15 hours before being quenched with saturated aqueous NaHCO_3 solution. The biphasic solution was extracted with DCM and the combined organic layers were dried over MgSO_4 . Concentration under reduced pressure followed by flash column chromatography on silica gel with EtOAc in hexanes solvent systems afforded the desired indane.



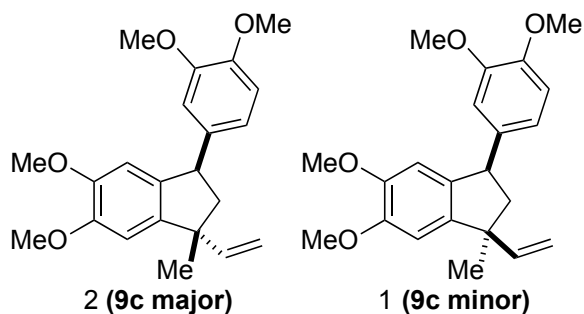
***syn*-1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-3-vinylindane (9a major) and *anti*-1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-3-vinylindane (9a minor):** Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.291 mmol) and 2-(trimethylsilyl)but-3-en-1-ol (**3a**) via General Method F (54 mg, 2:1 d.r., 54% yield): IR (Germanium ATR): 3072, 2950, 1639, 1604, 1501, 1463, 1211, 1028, 915, 855 cm^{-1} ; Major Isomer ^1H NMR (500 MHz, CDCl_3) δ

6.84 (s, 1H), 6.82 (d, $J = 1.9$ Hz, 1H), 6.73 (d, $J = 2.0$ Hz, 1H), 6.72 (s, 1H), 6.45 (s, 1H), 5.97 – 5.83 (m, 1H), 5.25 (dd, $J = 16.7, 1.6$ Hz, 1H), 5.16 (dd, $J = 10.0, 1.9$ Hz, 1H), 4.18 (dd, $J = 10.5, 7.1$ Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 3.74 (s, 3H), 3.73 – 3.68 (m, 1H), 2.72 (dt, $J = 12.5, 7.1$ Hz, 1H), 1.81 (dt, $J = 12.4, 10.2$ Hz, 1H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.7, 148.6, 147.8, 141.2, 138.5, 137.8, 137.5, 120.6, 115.7, 111.4, 111.3, 108.0, 107.1, 56.3, 56.2, 56.1, 56.1, 50.5, 49.0, 45.3; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.85 (s, 1H), 6.80 (d, $J = 1.8$ Hz, 1H), 6.74 (s, 1H), 6.64 (d, $J = 2.0$ Hz, 1H), 6.57 (s, 1H), 5.97 – 5.83 (m, 1H), 5.09 (dd, $J = 17.1, 1.5$ Hz, 1H), 5.05 (dd, $J = 9.9, 1.9$ Hz, 1H), 4.34 (dd, $J = 8.1, 5.9$ Hz, 1H), 3.89 (s, 6H), 3.81 (s, 3H), 3.78 (s, 3H), 3.73 – 3.68 (m, 1H), 2.39 (ddd, $J = 12.7, 8.1, 5.6$ Hz, 1H), 2.29 (ddd, $J = 12.8, 7.9, 5.9$ Hz, 1H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 148.8, 148.7, 147.6, 141.4, 138.4, 138.0, 137.5, 119.8, 114.5, 111.3, 111.1, 108.1, 107.5, 56.3, 56.2, 56.1, 56.0, 49.6, 48.4, 44.0; HRMS (ESI): Exact mass calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 363.1567. Found 363.158.



1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-2-methyl-3-vinylindane (9b):

Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.197 mmol) and (*E*)-2-(trimethylsilyl)pent-3-en-1-ol (**3b**) via General Method F (40 mg, 4:1 d.r., 57% yield): IR (Germanium ATR): 3016, 2953, 1639, 1503, 1463, 1212, 1027, 913 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.86 (d, $J = 8.2$ Hz, 1H), 6.80 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.69 (d, $J = 1.0$ Hz, 1H), 6.42 (d, $J = 1.0$ Hz, 1H), 5.81 (ddd, $J = 17.0, 10.0, 9.0$ Hz, 1H), 5.30 – 5.21 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 3.68 (d, $J = 10.1$ Hz, 1H), 3.25 (t, $J = 9.3$ Hz, 1H), 2.03 (tq, $J = 10.0, 6.6$ Hz, 1H), 1.12 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.7, 148.5, 147.9, 140.1, 138.0, 137.4, 136.2, 121.2, 117.2, 111.5, 111.2, 108.0, 107.1, 58.3, 56.9, 56.3, 56.2, 56.1, 56.0, 53.7, 15.8; HRMS (ESI): Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$ $[\text{M}+\text{NH}_4]^+$, 372.2169. Found 372.2179.

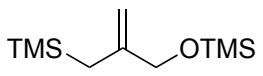


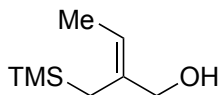
***anti*-3-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1-methyl-1-vinylindane (9c major) and *syn*-3-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1-methyl-1-vinylindane (9c minor):**

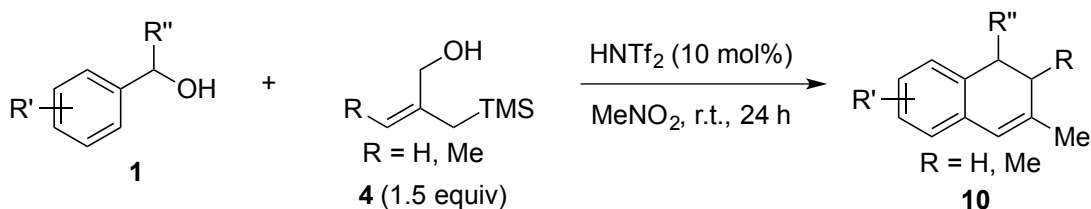
Synthesized from 3,3',4,4'-tetramethoxybenzhydrol (**15**, 0.184 mmol) and 3-methyl-2-(trimethylsilyl)but-3-en-1-ol (**3c**) via General Method F (42 mg, 2:1 d.r., 55% yield): IR (Germanium ATR): 2997, 2953, 1634, 1499, 1463, 1208, 1027, 911 cm^{-1} ; Major Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.83 (s, 1H), 6.81 – 6.77 (m, 1H), 6.73 – 6.71 (m, 1H), 6.69 (s, 1H), 6.44 (s, 1H), 6.00 (dd, $J = 17.2, 10.4$ Hz, 1H), 4.91 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.70 (dd, $J = 17.2, 1.5$ Hz, 1H), 4.19 (dd, $J = 10.2, 7.1$ Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 2.52 (dd, $J = 12.4, 7.1$ Hz, 1H), 1.94 (dd, $J = 12.4, 10.3$ Hz, 1H), 1.47 (s, 3H); Major Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.1, 148.7, 147.7, 146.9, 145.9, 140.9, 138.1, 137.5, 120.5, 111.5, 111.3, 111.1, 108.0, 106.4, 56.2, 56.2, 56.1, 56.1, 52.4, 49.6, 49.1, 26.3; Minor Isomer ^1H NMR (500 MHz, CDCl_3) δ 6.84 (s, 1H), 6.81 – 6.77 (m, 1H), 6.73 – 6.71 (m, 1H), 6.63 (s, 1H), 6.44 (s, 1H), 6.09 (dd, $J = 17.4, 10.5$ Hz, 1H), 5.17 (dd, $J = 17.4, 1.3$ Hz, 1H), 5.11 (dd, $J = 10.6, 1.3$ Hz, 1H), 4.34 (dd, $J = 9.8, 7.4$ Hz, 1H), 3.88 (s, 6H), 3.82 (s, 3H), 3.74 (s, 3H), 2.38 (dd, $J = 12.6, 7.4$ Hz, 1H), 2.08 (dd, $J = 12.6, 9.8$ Hz, 1H), 1.34 (s, 3H); Minor Isomer ^{13}C NMR (126 MHz, CDCl_3) δ 149.2, 148.7, 148.7, 148.6, 145.9, 142.4, 137.7, 137.1, 120.5, 112.0, 111.5,

111.3, 108.0, 106.2, 56.2, 45.2, 56.1, 56.1, 52.3, 49.5, 48.5, 24.9; HRMS (ESI): Exact mass calcd for C₂₂H₂₆O₄ [M+NH₄]⁺, 372.2169. Found 372.2175.

7. Type C Allylsilanes and Tetralins Experimental Procedures and Characterization Data

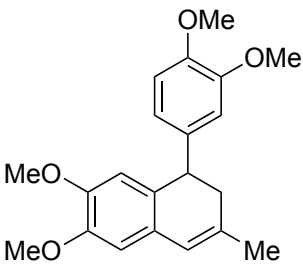
 **2-Trimethylsilylmethyl-3-trimethylsiloxy-1-propene (4a):** Followed same procedure as Trost and co-workers¹⁷ (60 mmol scale, 3.5 g, 26% yield after distillation): ¹H NMR (400 MHz, CDCl₃) δ 4.91 (m, 1H), 4.63 (m, 1H), 3.94 (d, *J* = 1.6 Hz, 2H), 1.49 (d, *J* = 1.3 Hz, 2H), 0.13 (s, 9H), 0.02 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 106.8, 66.7, 23.0, -0.3, -1.2. All spectroscopic data for this compound agrees with previously reported values.¹⁷

 **(Z)-2-Trimethylsilylmethyl-2-buten-1-ol (4b):** Followed same procedure as Trost and co-workers¹⁸ (60 mmol scale, 3.5 g, 26% yield after distillation): ¹H NMR (500 MHz, CDCl₃) δ 5.40 (q, *J* = 6.9 Hz, 1H), 3.97 – 3.93 (m, 2H), 1.64 – 1.53 (m, 5H), 1.25 (brs, 1H), 0.03 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 138.1, 117.6, 68.9, 18.7, 13.9, -0.5. All spectroscopic data for this compound agrees with previously reported values.¹⁸



Scheme S8: General method for synthesis of tetralins with Type C allylsilanes

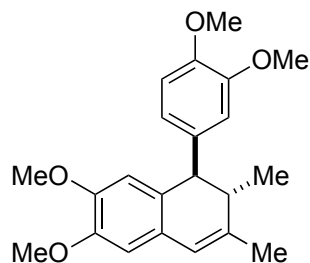
General Method G: Benzhydryl **1** (1 equiv) was dissolved in MeNO₂ (0.1 M) and allowed to stir under N₂ atmosphere. Alkyl silane **4** (1.5 equiv) was added, followed by a solution of triflimide in DCM (10 mol%). The reaction was allowed to stir at room temperature for 24 hours before being quenched with saturated aqueous NaHCO₃ solution. The biphasic solution was extracted with DCM and the combined organic layers were dried over MgSO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with EtOAc in hexanes solvent systems afforded the desired tetralin.

 **4-(3,4-Dimethoxyphenyl)-3,4-dihydro-6,7-dimethoxy-2-methylnaphthalene (10a):** Synthesized from 3,3',4,4'-tetramethoxybenzhydryl (**15**, 0.251 mmol) and 2-trimethylsilylmethyl-3-trimethylsiloxy-1-propene (**4a**) via General Method G (40 mg, 46% yield): IR (Germanium ATR): 2998, 2956, 2831, 1603, 1512, 1463, 1260, 1231, 1111, 1028, 994, 864, 768 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.81 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.62 (s, 1H), 6.40 (s, 1H), 6.20 (d, *J* = 1.5 Hz, 1H), 4.01 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.87 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.69 (s, 3H), 2.56 – 2.41 (m, 2H), 1.87 (d, *J* = 1.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 147.7, 147.7, 147.4, 137.6, 134.9, 129.2, 128.2, 122.3, 120.5, 111.7, 111.4, 111.2, 109.2, 56.1

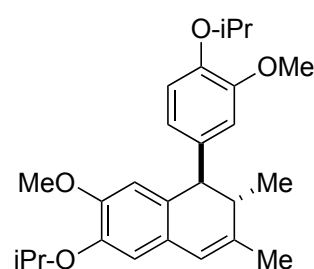
¹⁷ B. M. Trost, P. Renaut, *J. Am. Chem. Soc.* **1982**, *104*, 6668–6672.

¹⁸ B. M. Trost, M. C. Matelich, *Synthesis* **1992**, 151–156.

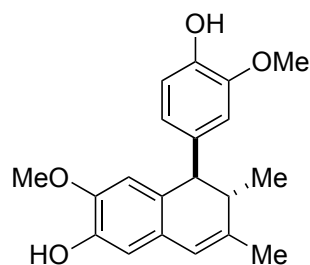
(2C), 56.0, 56.0, 44.1, 38.1, 23.5; HRMS (ESI): Exact mass calcd for C₂₁H₂₄O₄ [M+H]⁺, 341.1747. Found 341.1751.



(±)-Cyclogalgravin (13): Synthesized from 3,3',4,4'-tetramethoxy benzhydrol (**15**, 0.259 mmol) and (*Z*)-2-trimethylsilylmethyl-2-buten-1-ol (**4b**) via General Method G (72 mg, 78% yield): IR (Germanium ATR): 2956, 1604, 1508, 1463, 1226, 1140, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.71 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 6.62 (s, 1H), 6.55 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.55 (s, 1H), 6.14 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.78 (s, 6H), 3.68 (d, *J* = 3.2 Hz, 1H), 2.39 (qd, *J* = 7.0, 3.0 Hz, 1H), 1.80 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 148.8, 147.7, 147.6, 147.4, 139.0, 138.3, 127.4, 127.2, 121.2, 119.7, 113.0, 111.1, 111.0, 109.0, 56.1 (2C), 55.9, 55.9, 51.0, 42.1, 22.3, 18.8; HRMS (ESI): Exact mass calcd for C₂₂H₂₆O₄ [M+H]⁺, 355.1904. Found 355.1913. All spectroscopic data for this compound agrees with previously reported values.¹⁹



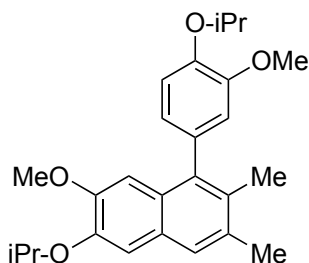
***trans*-4-(4-Isopropoxy-3-methoxyphenyl)-3,4-dihydro-7-isopropoxy-6-methoxy-2,3-dimethylnaphthalene (10b):** Synthesized from 4,4'-diisopropoxy-3,3'-dimethoxybenzhydrol (**16**, 0.112 mmol) and (*Z*)-2-trimethylsilylmethyl-2-buten-1-ol (**4b**) via General Method G (23 mg, 49% yield): IR (Germanium ATR): 2973, 2928, 1603, 1508, 1465, 1264, 1224, 1138, 1112, 1036, 941, 889 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.73 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 6.63 (s, 1H), 6.54 (s, 1H), 6.53 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.11 (d, *J* = 1.6 Hz, 1H), 4.50 (p, *J* = 6.1 Hz, 1H), 4.44 (p, *J* = 6.1 Hz, 1H), 3.74 (d, *J* = 0.9 Hz, 6H), 3.66 (d, *J* = 3.5 Hz, 1H), 2.39 (qd, *J* = 7.0, 3.5 Hz, 1H), 1.79 (d, *J* = 1.4 Hz, 3H), 1.36 (dd, *J* = 6.1, 3.5 Hz, 6H), 1.33 (dd, *J* = 6.1, 1.8 Hz, 6H), 1.08 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 150.1, 149.2, 145.9, 145.7, 138.7, 138.7, 128.2, 127.3, 121.3, 119.8, 115.5, 113.8, 113.7, 111.9, 71.7, 71.4, 56.2, 56.0, 51.1, 42.0, 22.4, 22.4, 22.3, 18.8; HRMS (ESI): Exact mass calcd for C₂₆H₃₄O₄ [M+H]⁺, 411.253. Found 411.2536.



(±)-4',5-O-Didemethylcyclogalgravin (17): *trans*-4-(4-Isopropoxy-3-methoxyphenyl)-3,4-dihydro-7-isopropoxy-6-methoxy-2,3-dimethylnaphthalene (**10b**, 0.151 mmol) was dissolved in DCM (12 mL) and cooled to 0 °C. BCl₃ (1.0 M in DCM, 0.453 mmol, 0.453 μL) was added and the reaction was allowed to stir for 50 min before being quenched with MeOH. The solution was washed with brine, and the aqueous layer was extracted with DCM (3 x 3 mL). The combined organic layers were dried over MgSO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system afforded the desired product (40 mg, 81% yield): IR (Germanium ATR): 3511, 2962, 2841, 1611, 1507, 1463, 1449, 1357, 1265, 1219, 1092, 1031, 879 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.76 (d, *J* = 8.1 Hz, 1H), 6.67 (s, 1H), 6.58 (d, *J* = 2.0 Hz, 1H), 6.56 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.52 (s, 1H), 6.11 (d, *J* = 1.7 Hz, 1H), 5.45 (s, 1H), 5.43 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.65 (d, *J* = 3.3 Hz, 1H), 2.35 (qd, *J* = 7.0, 3.2 Hz, 1H), 1.78 (d, *J* = 1.6 Hz, 3H), 1.07 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.3,

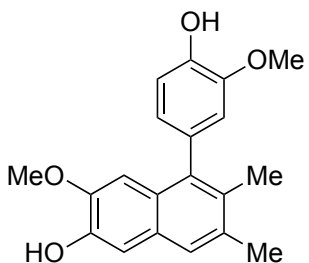
¹⁹ a) Fonseca, S. F.; Nielsen, L. T.; Rúveda, E. A. *Phytochemistry* **1979**, *18*, 1703–1708; b) Reddel, J. C. T.; Lutz, K. E.; Diagne, A. B.; Thomson, R. J., *Angew. Chem. Int. Ed.* **2014**, *53*, 1395–1398

145.2, 144.3, 144.0, 139.0, 137.9, 127.9, 127.0, 121.2, 120.5, 114.1, 112.2, 111.8, 110.2, 56.1, 55.9, 51.2, 42.3, 22.3, 18.9; HRMS (ESI): Exact mass calcd for C₂₀H₂₂O₄ [M+Na]⁺, 349.141. Found 349.1428. All spectroscopic data for this compound agrees with previously reported values.²⁰



4-(4-Isopropoxy-3-methoxyphenyl)-7-isopropoxy-6-methoxy-2,3-dimethylnaphthalene (S6): *trans*-4-(4-Isopropoxy-3-methoxyphenyl)-3,4-dihydro-7-isopropoxy-6-methoxy-2,3-dimethylnaphthalene (**10b**, 0.083 mmol) was dissolved in dry DCM (6 mL) and DDQ (0.08 mmol, 18.1 mg) was added in one portion. The reaction was allowed to stir at room temperature for 30 min before being quenched with H₂O (10 mL). The aqueous layer was extracted with DCM (3 x 3 mL) and the combined organic layers were dried over MgSO₄. Concentration under reduced

pressure followed by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system afforded the title compound (31 mg, 90% yield): IR (Germanium ATR): 2975, 2934, 1604, 1503, 1466, 1248, 1109, 1038, 955, 877 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.48 (s, 1H), 7.09 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.79 – 6.76 (m, 2H), 6.69 (s, 1H), 4.72 – 4.59 (m, 2H), 3.82 (s, 3H), 3.67 (s, 3H), 2.44 (s, 3H), 2.13 (s, 3H), 1.48 – 1.40 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 150.3, 149.8, 147.0, 146.1, 137.2, 133.8, 133.5, 131.5, 127.7, 127.6, 125.8, 122.4, 115.8, 114.1, 109.4, 106.1, 71.5, 71.0, 56.1, 55.8, 22.4, 22.3, 22.1, 21.2, 17.6; HRMS (ESI): Exact mass calcd for C₂₆H₃₂O₄ [M+H]⁺, 409.2373. Found 409.238.

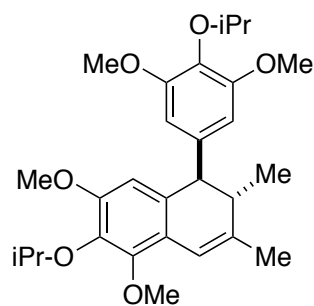


Cinnamophilin A (18): 4-(4-Isopropoxy-3-methoxyphenyl)-7-isopropoxy-6-methoxy-2,3-dimethylnaphthalene (**S6**, 0.054 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. BCl₃ (1.0 M in DCM, 0.162 mmol, 162 μL) was added and the reaction was allowed to stir for 1 hour before being quenched with MeOH. Concentration under reduced pressure followed by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system afforded the desired product (16 mg, 90% yield): IR (Germanium ATR): 3419, 2923, 1609, 1050, 1457, 1417, 1249, 1201, 1033,

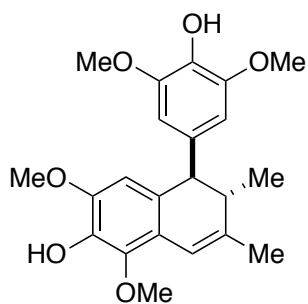
880 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (s, 1H), 7.18 (s, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.75 (d, *J* = 1.8 Hz, 1H), 6.66 (s, 1H), 5.78 (s, 1H), 5.66 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H), 2.11 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.7, 146.6, 145.0, 144.5, 137.3, 133.9, 133.0, 131.4, 128.2, 127.5, 125.9, 123.2, 114.5, 112.8, 108.7, 104.9, 56.2, 55.8, 21.2, 17.6; HRMS (ESI): Exact mass calcd for C₂₀H₂₀O₄ [M+Na]⁺, 347.1254. Found 347.1263. All spectroscopic data for this compound agrees with previously reported values.²¹

²⁰ Messiano, G. B.; Wijeratne, E. M. K.; Lopes, L. M. X.; Gunatilaka, A. A. L., *J. Nat. Prod.* **2010**, 73, 1933–1937

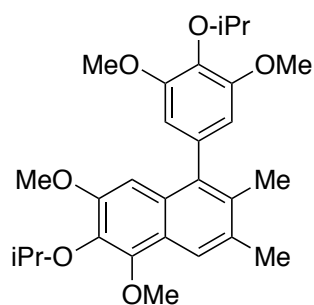
²¹ a) Rangkaew, N.; Suttisri, R.; Moriyasu, M.; Kawanishi, K., *Fitoterapia*, **2009**, 80, 377–379; b) Chen, C.-Y.; Yeh, Y.-T.; Hsui, Y.-R. *Chem. Nat. Compd.* **2011**, 47, 519



***trans*-4-(4-Isopropoxy-2,3-dimethoxyphenyl)-7-isopropoxy-6,8-dimethoxy-2,3-dimethylnaphthalene (10c):** Synthesized from 4,4'-diisopropoxy-3,3'-dimethoxy-5,5'-dimethoxybenzhydrol (**19**, 0.197 mmol) and (*Z*)-2-trimethylsilylmethyl-2-buten-1-ol (**4b**) via General Method G (63 mg, 68% yield): IR (Germanium ATR): 2971, 2933, 1635, 1589, 1487, 1464, 1415, 1334, 1232, 1127, 937 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.44 (d, $J = 1.7$ Hz, 1H), 6.34 (s, 1H), 6.27 (s, 2H), 4.40 (hept, $J = 6.2$ Hz, 1H), 4.28 (hept, $J = 6.2$ Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 3.71 (s, 6H), 3.63 (d, $J = 3.8$ Hz, 1H), 2.41 (qd, $J = 7.0, 3.8$ Hz, 1H), 1.82 (d, $J = 1.5$ Hz, 3H), 1.30 (d, $J = 6.2$ Hz, 6H), 1.26 (d, $J = 6.2$ Hz, 6H), 1.08 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.5, 152.5, 149.5, 140.5, 138.8, 138.6, 134.5, 130.9, 121.2, 115.3, 109.0, 105.0, 75.5, 75.2, 61.2, 56.0, 56.0, 52.3, 41.7, 22.7, 22.7, 22.6, 18.8; HRMS (ESI): Exact mass calcd for $\text{C}_{28}\text{H}_{38}\text{O}_6$ $[\text{M}+\text{H}]^+$, 471.2741. Found 471.2751.



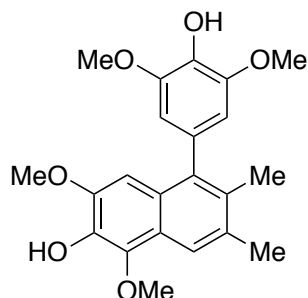
(±)-Sacidumlignan B (20): *trans*-4-(4-Isopropoxy-2,3-dimethoxyphenyl)-7-isopropoxy-6,8-dimethoxy-2,3-dimethylnaphthalene (**10c**, 0.066 mmol) was dissolved in DCM (4 mL) and cooled to 0 °C. BCl_3 (1.0 M in DCM, 0.199 mmol, 199 μL) was added and the reaction was allowed to stir for 1 hour before being quenched with MeOH. The solution was washed with brine, and the aqueous layer was extracted with DCM (3 x 3 mL). The combined organic layers were dried over MgSO_4 . Concentration under reduced pressure followed by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system afforded the desired product (22 mg, 87% yield): IR (Germanium ATR): 3439, 2958, 2934, 2839, 1612, 1517, 1456, 1320, 1215, 1114, 759 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.45 (s, 1H), 6.35 (s, 1H), 6.30 (s, 2H), 5.43 (s, 1H), 5.34 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H), 3.60 (d, $J = 3.5$ Hz, 1H), 2.37 (qd, $J = 7.1, 3.5$ Hz, 1H), 1.82 (d, $J = 1.5$ Hz, 3H), 1.07 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.8, 146.0, 142.5, 139.3, 137.2, 136.7, 133.1, 126.9, 121.0, 115.0, 108.2, 104.5, 61.4, 56.3 (3C), 51.9, 42.1, 22.7, 18.8; HRMS (ESI): Exact mass calcd for $\text{C}_{22}\text{H}_{26}\text{O}_6$ $[\text{M}+\text{Na}]^+$, 409.1622. Found 409.1629. All spectroscopic data for this compound agrees with previously reported values.²²



4-(4-Isopropoxy-2,3-dimethoxyphenyl)-7-isopropoxy-6,8-dimethoxy-2,3-dimethylnaphthalene (S7): *trans*-4-(4-Isopropoxy-2,3-dimethoxyphenyl)-7-isopropoxy-6,8-dimethoxy-2,3-dimethylnaphthalene (**10c**, 0.029 mmol) was dissolved in dry DCM (4 mL) and the reaction was cooled to 0 °C. DDQ (0.028 mmol, 6.3 mg) was added in one portion. The reaction was allowed to stir at 0 °C for 30 min before being quenched with H_2O (10 mL). The aqueous layer was extracted with DCM (3 x 3 mL) and the combined organic layers were dried over MgSO_4 . Concentration under reduced pressure followed by flash column chromatography on silica gel with a 15% EtOAc in hexanes solvent system afforded the title compound (6 mg, 44% yield): IR (Germanium ATR): 2972, 2033, 1577, 1462, 1399, 1336, 1257, 1236, 1124, 1089, 981, 755 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.86 (s, 1H), 6.48 (s, 3H), 4.50 (hept, $J = 6.2$ Hz, 1H), 4.49 (hept, $J = 6.2$ Hz, 1H), 4.04 (s, 3H), 3.80 (s, 6H), 3.63 (s, 3H), 2.48 (s, 3H), 2.16 (s, 3H), 1.37 (d, $J = 6.2$ Hz, 6H), 1.33 (d, $J =$

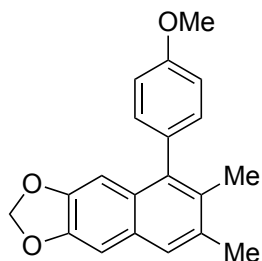
²² Rout, J. K.; Ramana, C. V. *J. Org. Chem.* **2012**, *77*, 1566.

6.2 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.0, 152.8, 148.0, 138.2, 137.5, 136.1, 134.8, 133.3, 132.9, 129.0, 122.9, 120.8, 107.2, 101.5, 75.9, 75.2, 61.2, 56.3, 55.6, 29.9, 22.7, 22.6, 21.4, 17.8; HRMS (ESI): Exact mass calcd for $\text{C}_{28}\text{H}_{36}\text{O}_6$ $[\text{M}+\text{Na}]^+$, 491.2404. Found 491.2411.



Sacidumlignan A (21): 4-(4-Isopropoxy-2,3-dimethoxyphenyl)-7-isopropoxy-6,8-dimethoxy-2,3-dimethylnaphthalene (**S7**, 0.011 mmol) was dissolved in DCM (2 mL) and cooled to 0 °C. BCl_3 (1.0 M in DCM, 0.011 mmol, 11 μL) was added and the reaction was allowed to stir for 30 min before being quenched with MeOH. Concentration under reduced pressure followed by flash column chromatography on silica gel with a 30% EtOAc in hexanes solvent system afforded the desired product (4 mg, 98% yield): IR (Germanium ATR): 3490, 3437, 3001, 2935, 1609, 1518, 1463, 1414, 1336, 1286, 1209, 1114, 1083, 913, 758 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.82 (s, 1H), 6.50 (s, 1H), 6.48 (s, 2H), 5.73 (s, 1H), 5.59 (s, 1H), 4.04 (s,

3H), 3.86 (s, 6H), 3.75 (s, 3H), 2.48 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 147.3, 147.3, 139.5, 137.7, 136.5, 133.8, 133.5, 132.0, 132.0, 126.8, 122.8, 120.2, 106.8, 101.0, 61.2, 56.5, 56.1, 21.5, 17.6; HRMS (ESI): Exact mass calcd for $\text{C}_{22}\text{H}_{24}\text{O}_6$ $[\text{M}+\text{Na}]^+$, 407.1465. Found 407.1471. All spectroscopic data for this compound agrees with previously reported values.²²

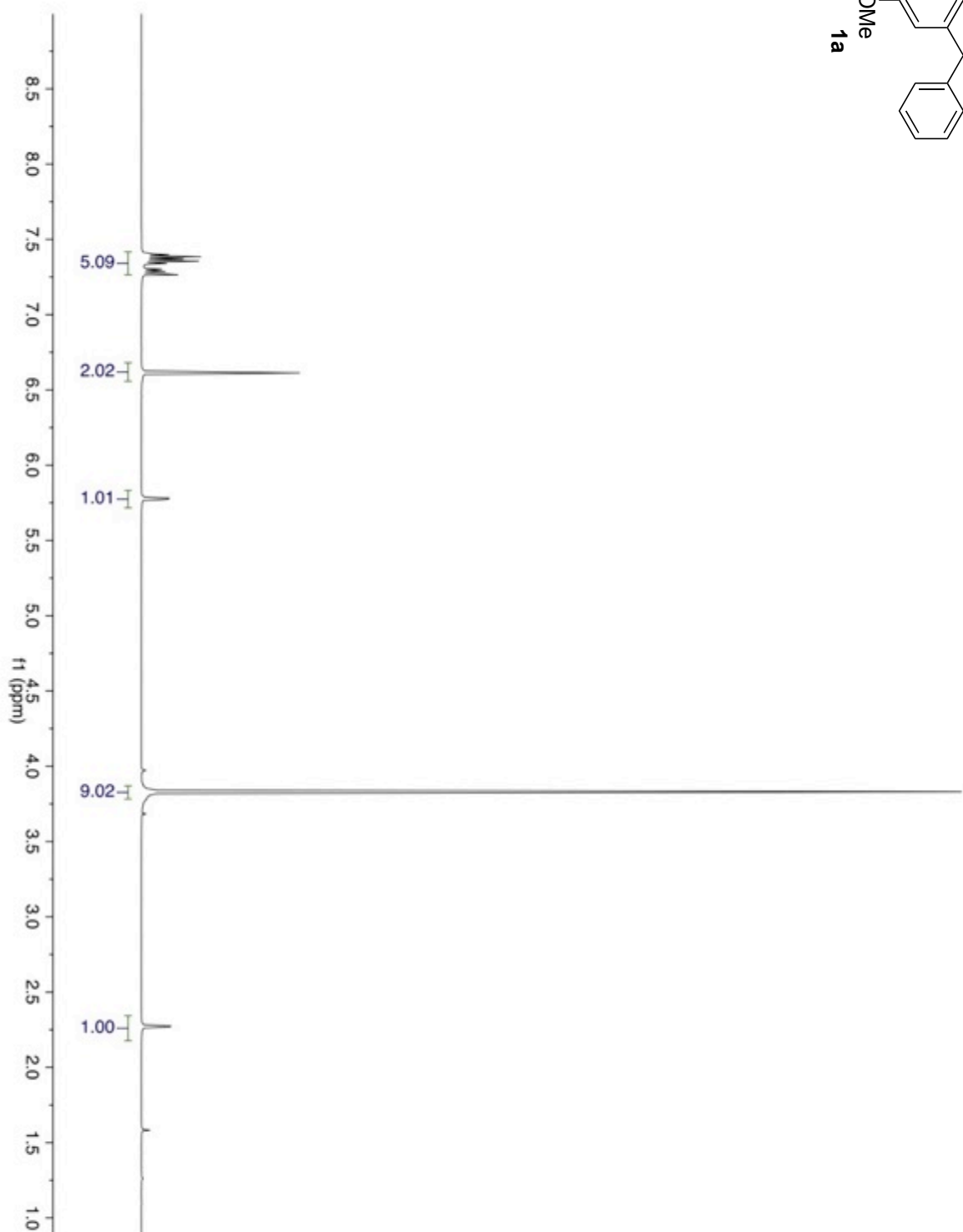
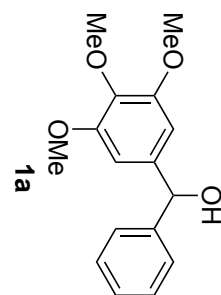


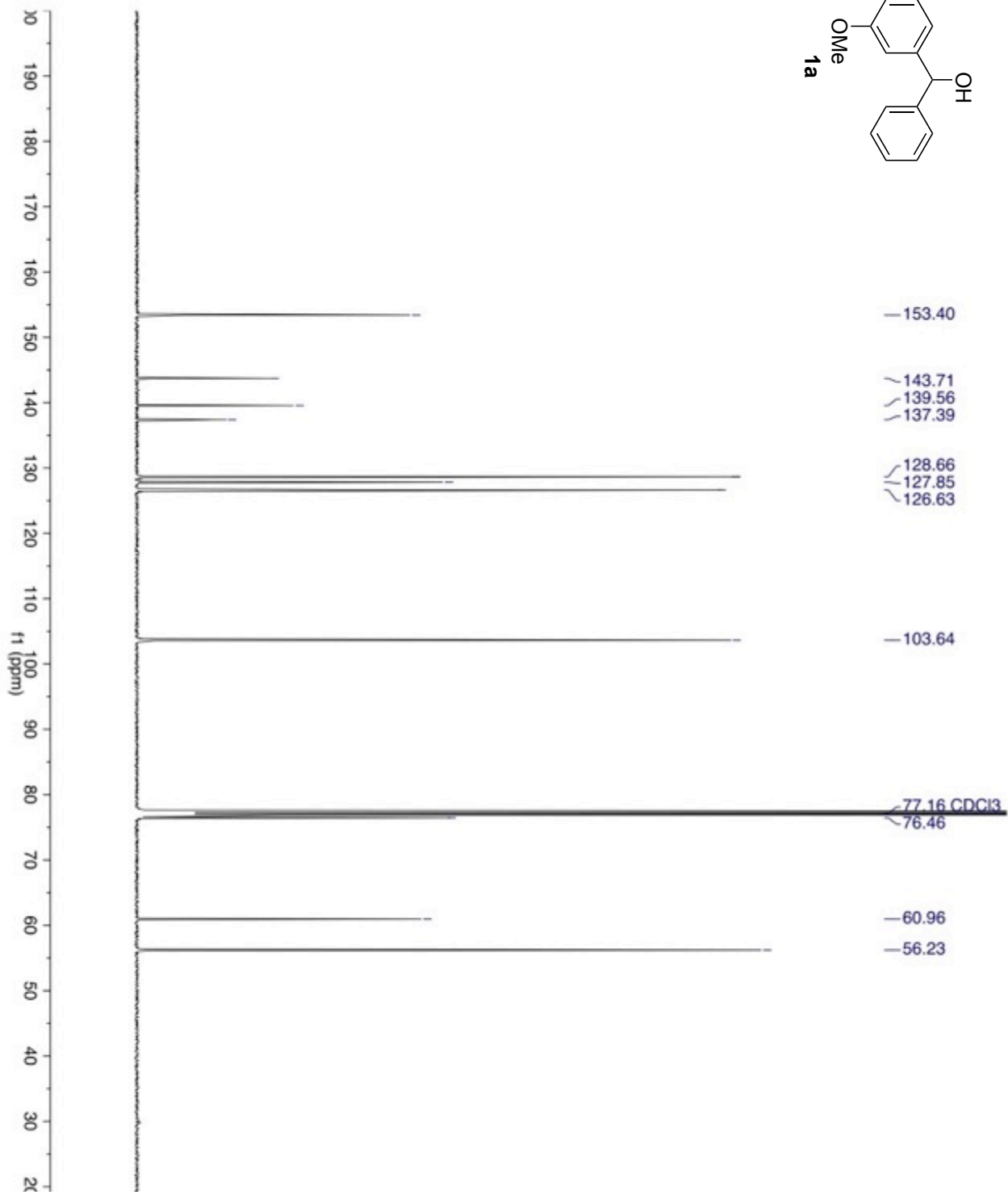
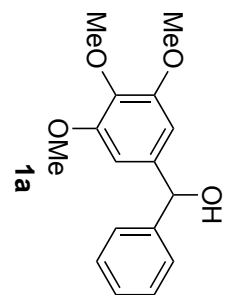
Pycnanthuligene C (23): A mixture of *cis*- and *trans*-dihydronaphthalene isomers (**10d**) was synthesized from 3,4-methylenedioxy-4'-methoxybenzhydrol (**22**, 0.173 mmol) and (*Z*)-2-trimethylsilylmethyl-2-buten-1-ol (**4b**) via General Method G. The crude reaction mixture was then re-dissolved in dry DCM (10 mL) and DDQ (0.200 mmol, 45 mg) was added in one portion. The reaction was allowed to stir at room temperature for 30 min before being quenched with H_2O (10 mL). The organic layer was separated and dried over Na_2SO_4 . Concentration

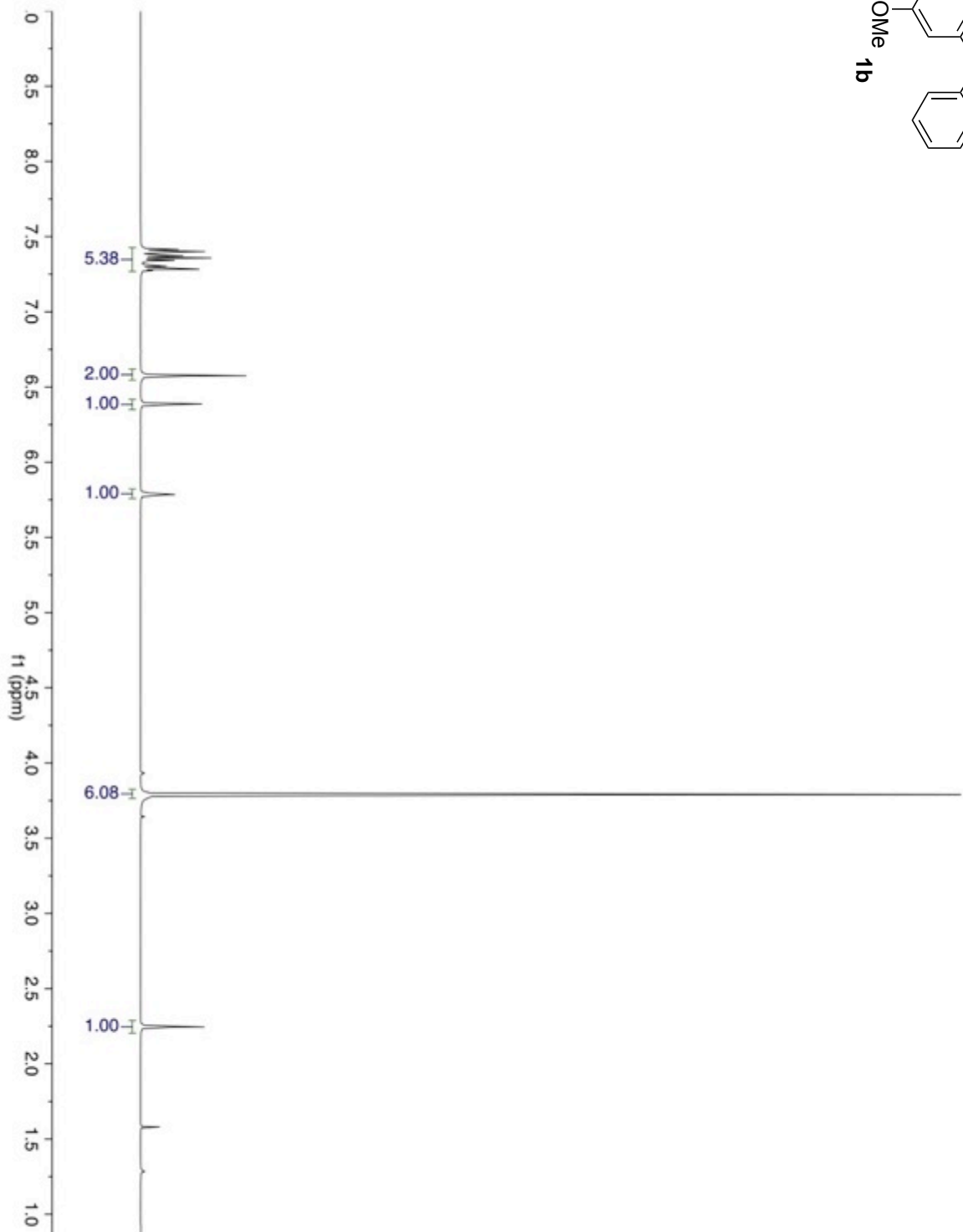
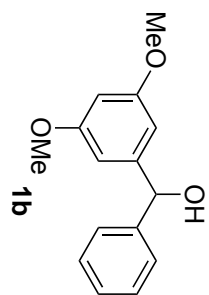
under reduced pressure followed by flash column chromatography on silica gel with a 10% EtOAc in hexanes solvent system afforded the title compound (34 mg, 73% yield over two steps): IR (Germanium ATR): 2994, 2898, 1610, 1515, 1497, 1461, 1285, 1236, 1175, 1039, 1039, 900 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.47 (s, 1H), 7.15 – 7.12 (m, 2H), 7.06 – 7.01 (m, 3H), 6.64 (s, 1H), 5.94 (s, 2H), 3.90 (s, 3H), 2.43 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 146.9, 146.7, 137.7, 133.8, 133.1, 132.0, 131.3, 129.0, 128.9, 126.6, 114.0, 103.2, 103.2, 100.9, 55.5, 21.1, 17.6; HRMS (ESI): Exact mass calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$ $[\text{M}+\text{H}]^+$, 307.1329. Found 307.133. All spectroscopic data for this compound agrees with previously reported values.²³

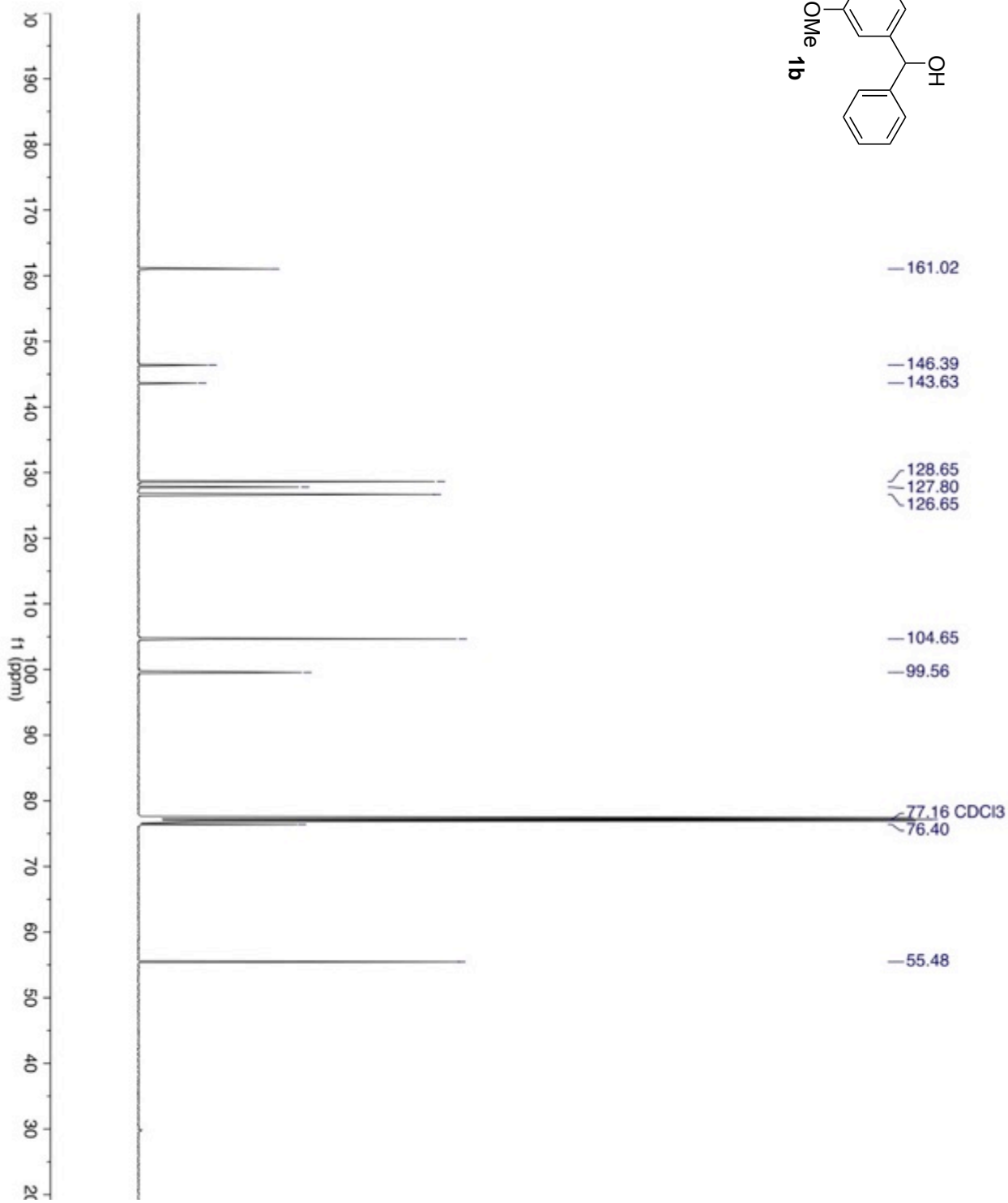
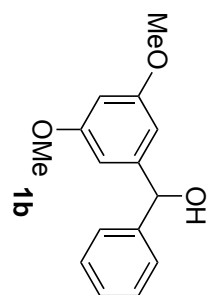
²³ E. C. N. Nono, P. Mkounga, V. Kuete, K. Marat, P. G. Hultin, A. E. Nkengfack, *J. Nat. Prod.* **2010**, 73, 213–216.

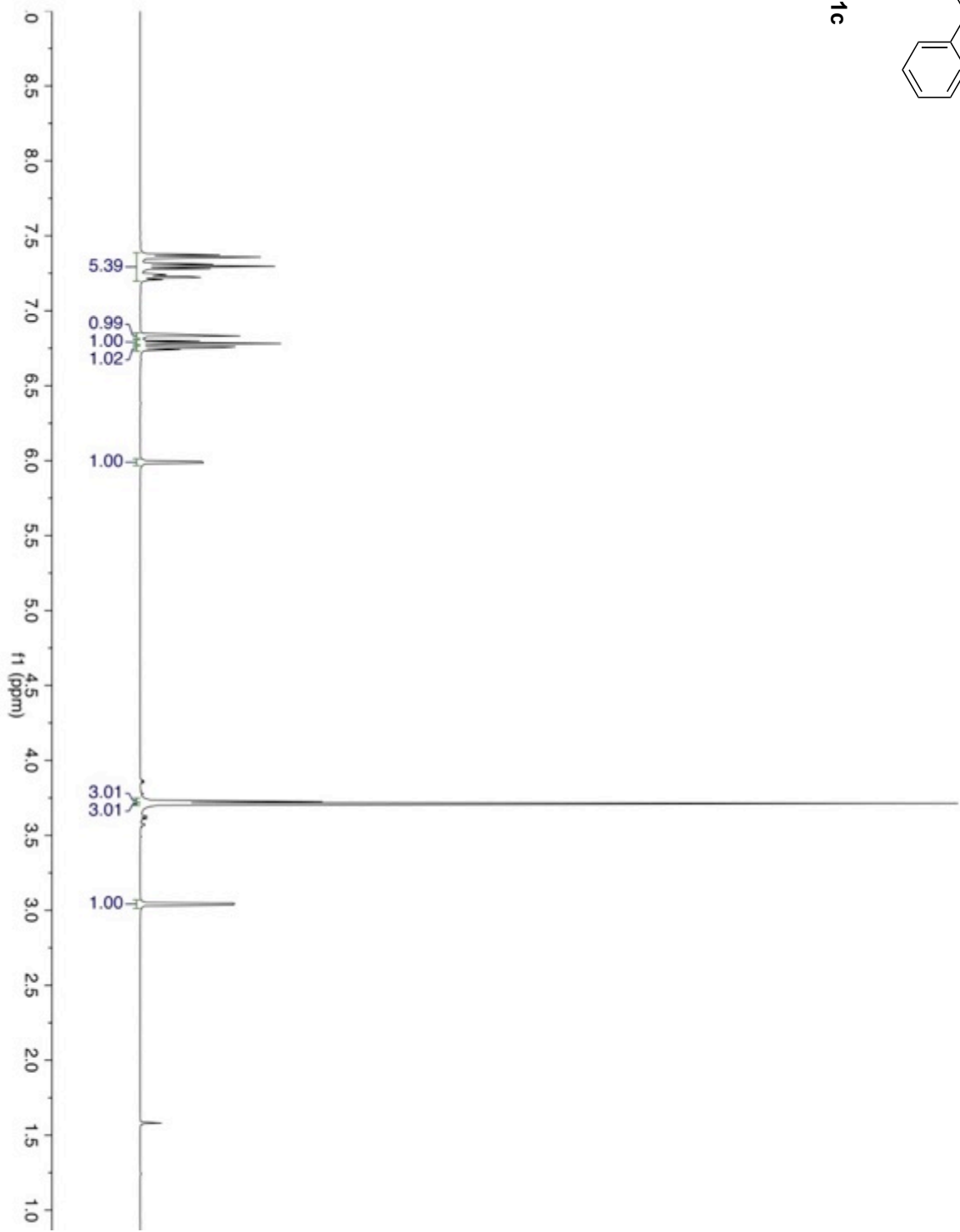
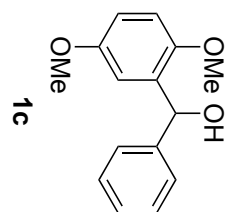
8. ^1H and ^{13}C NMR Spectra

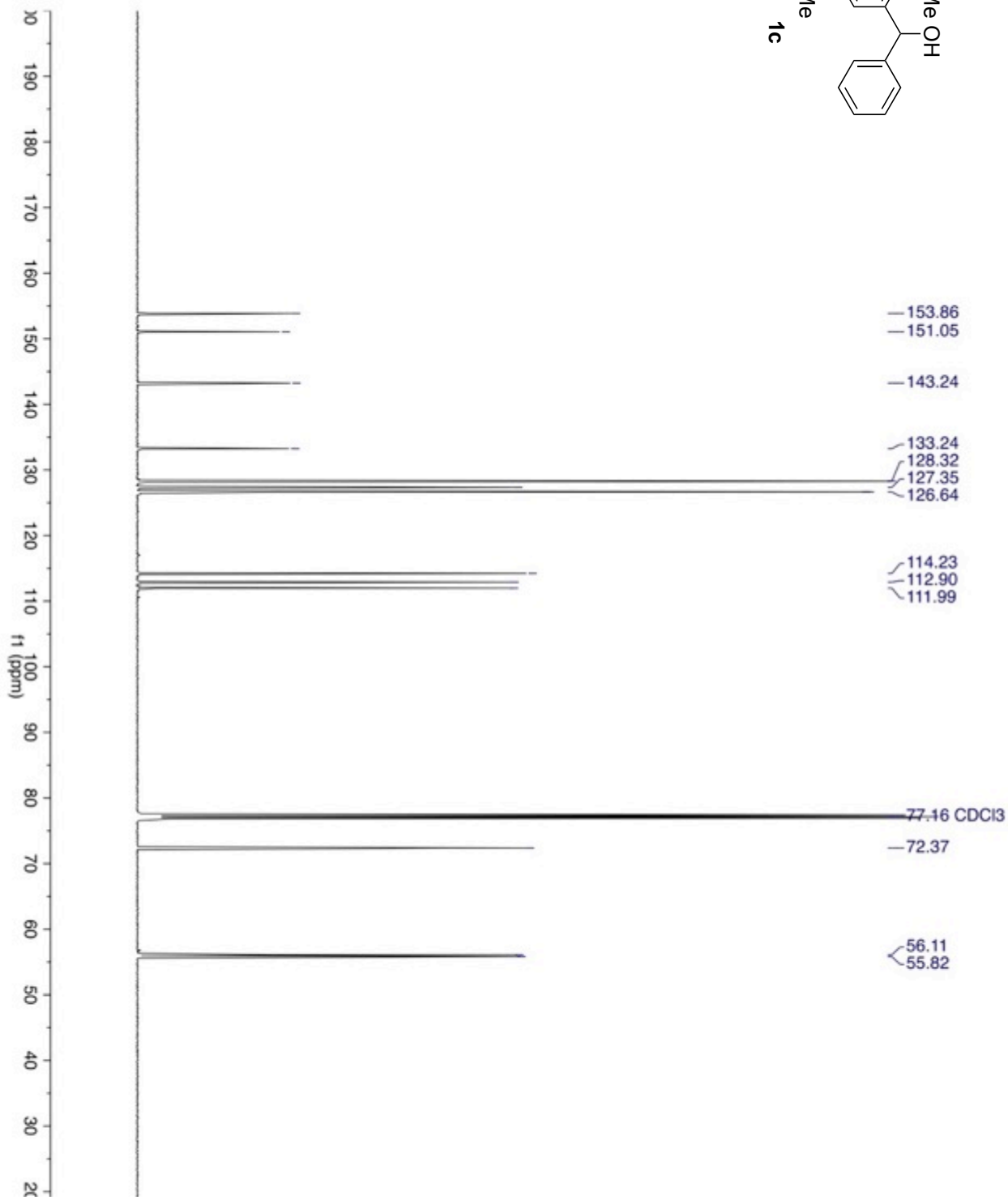
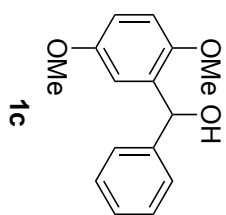


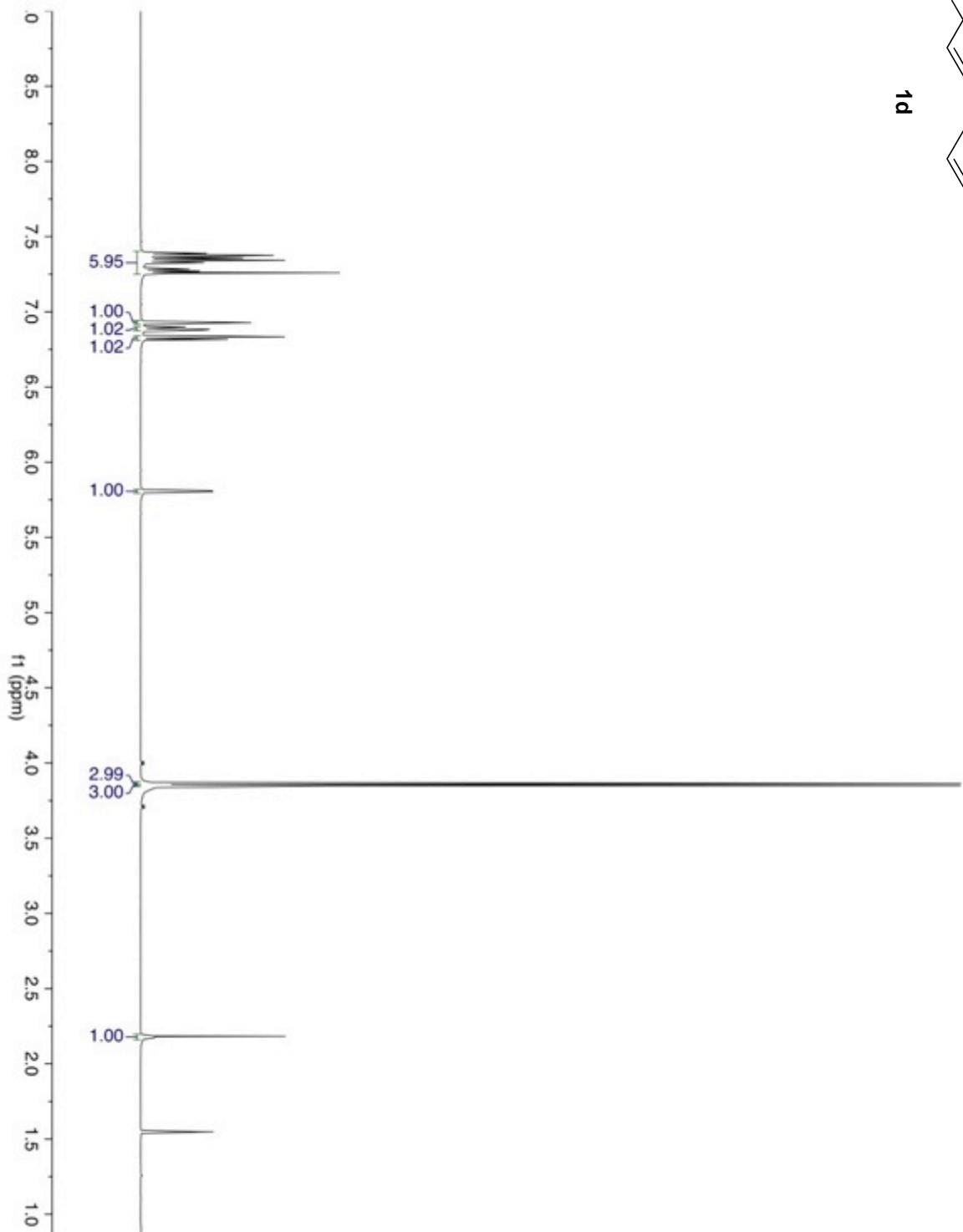
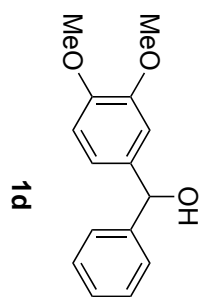


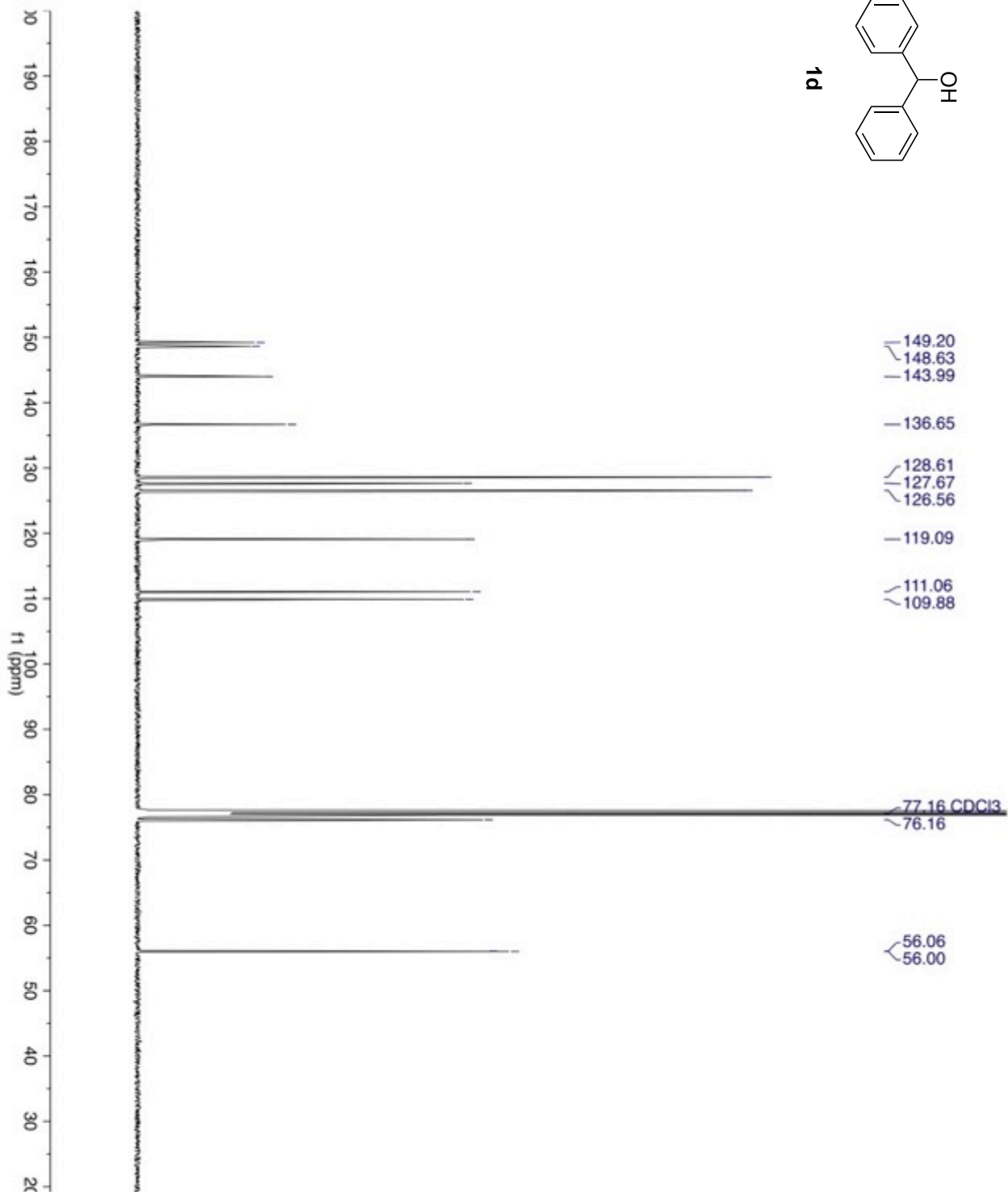
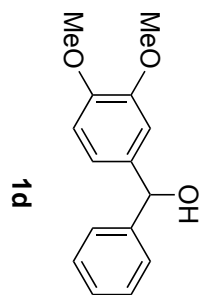


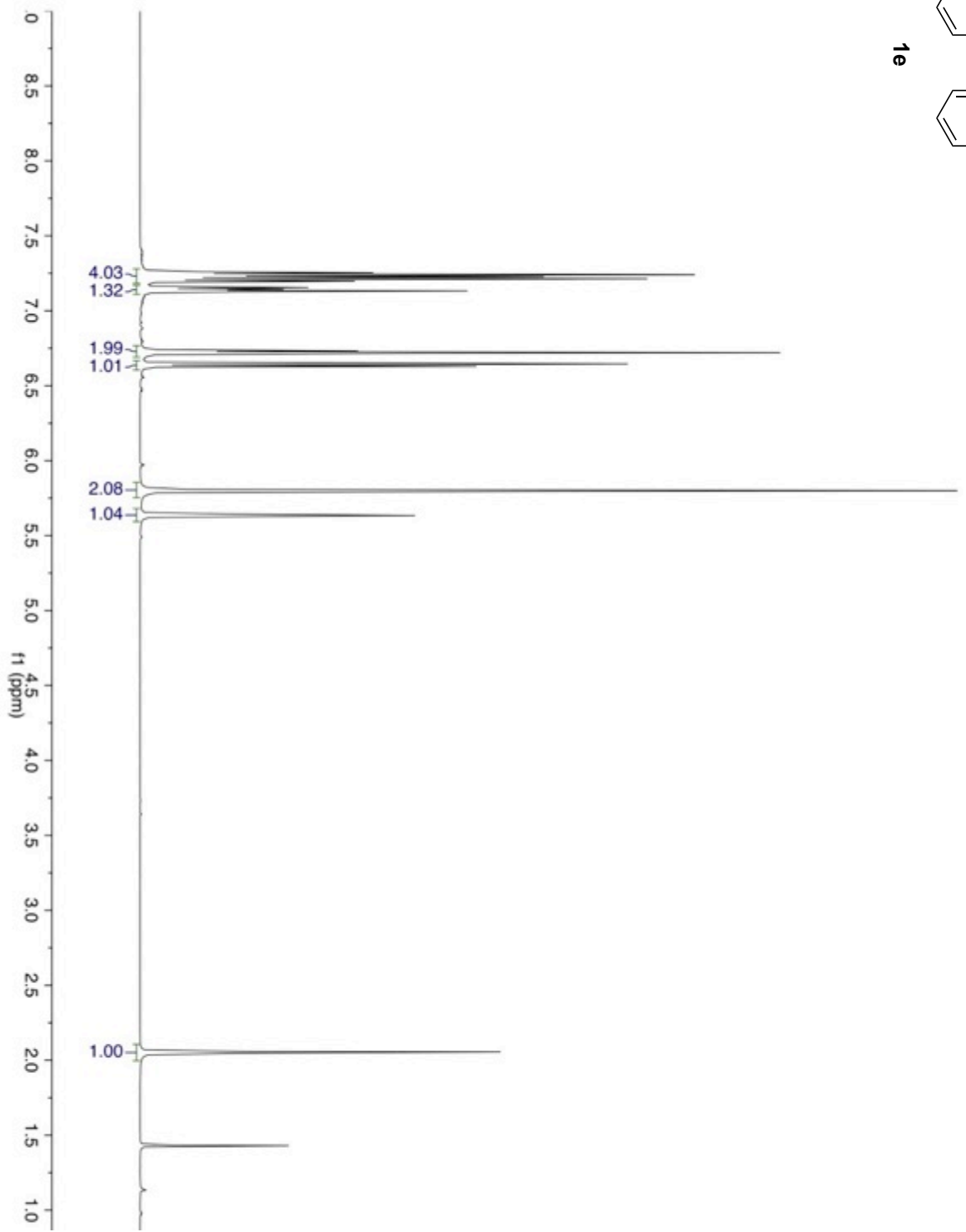
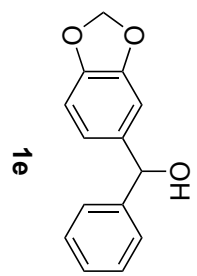


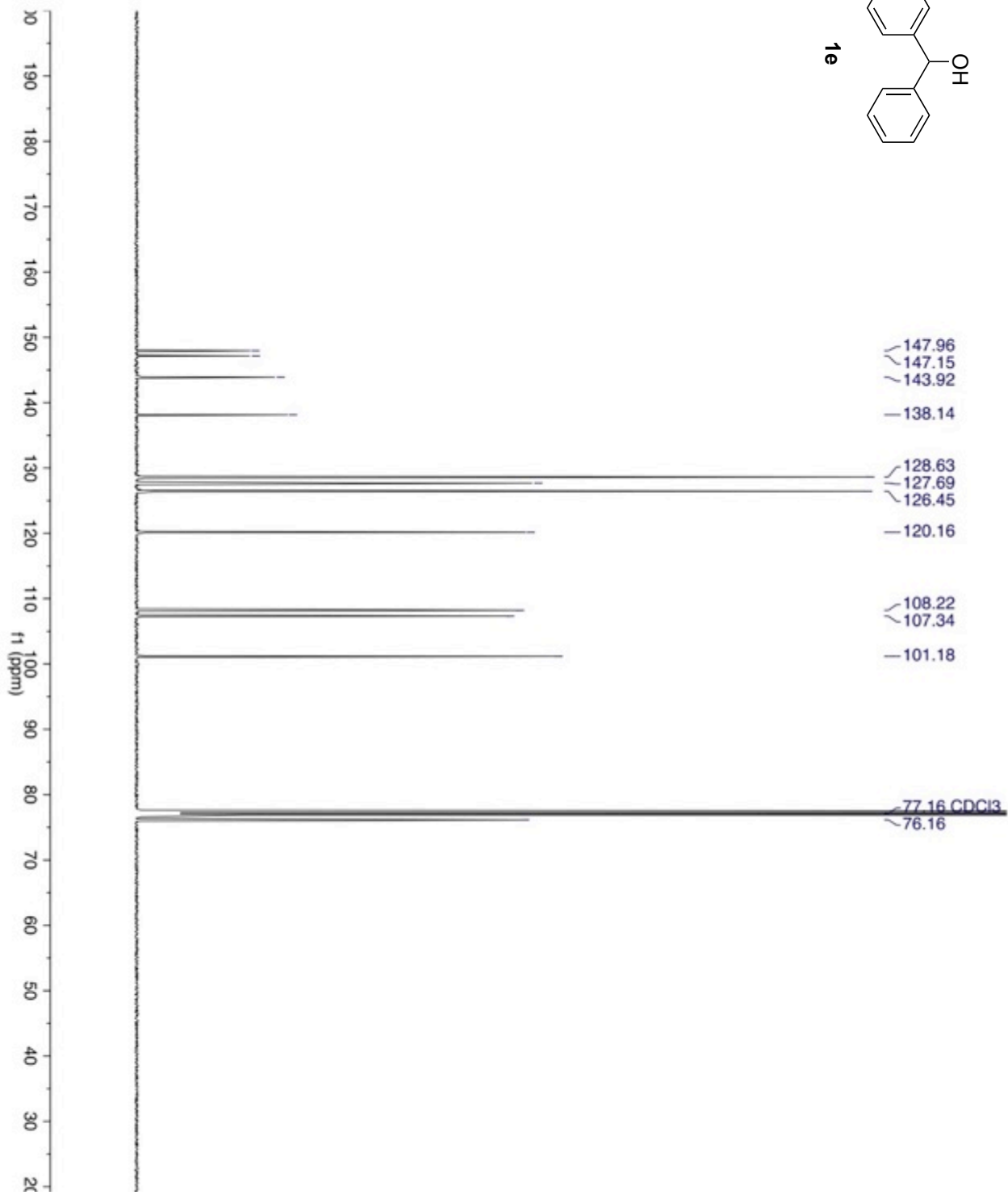
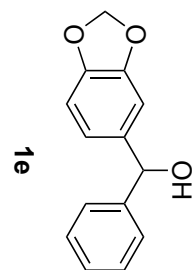


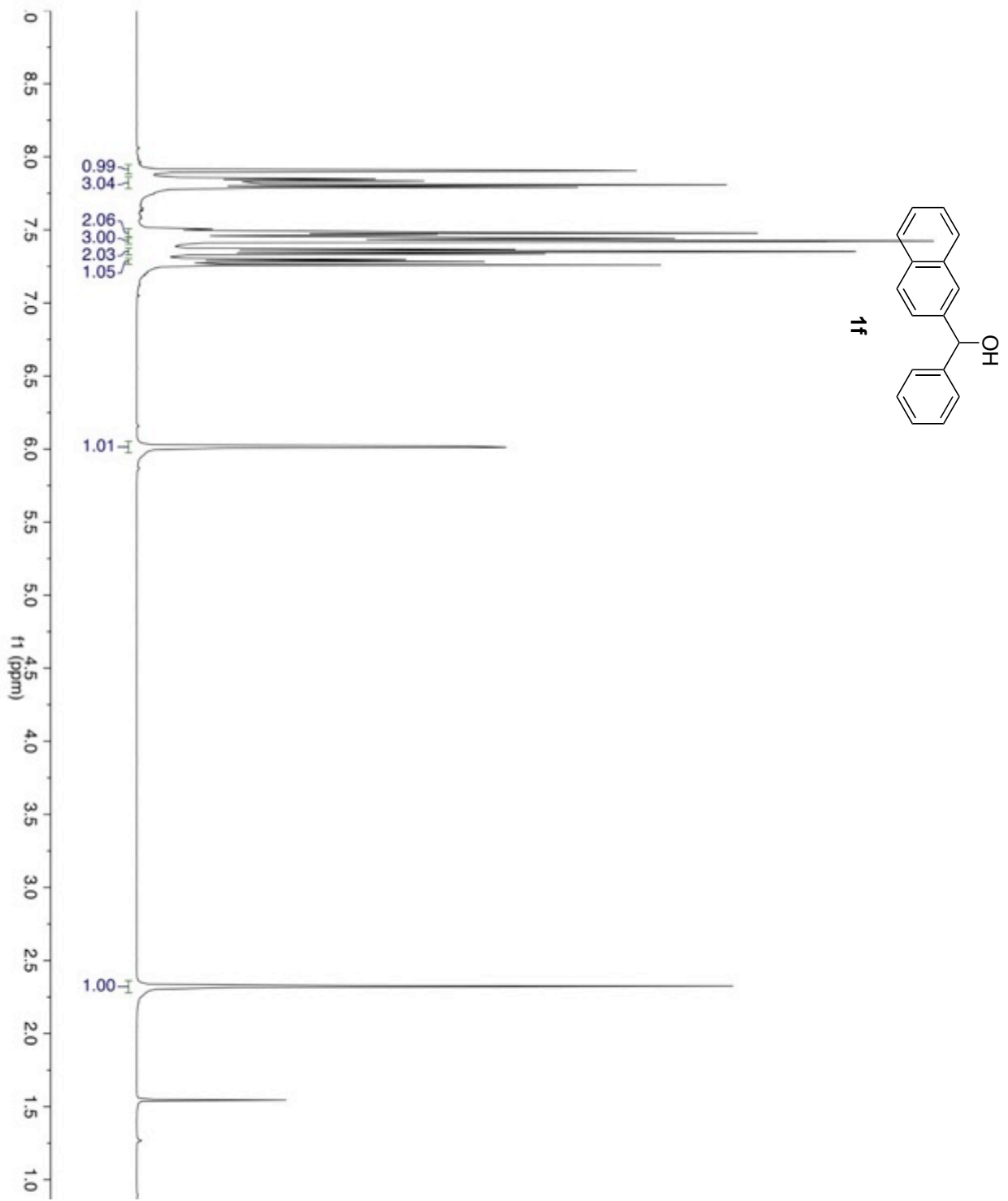


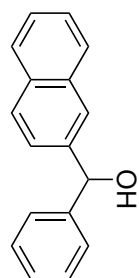




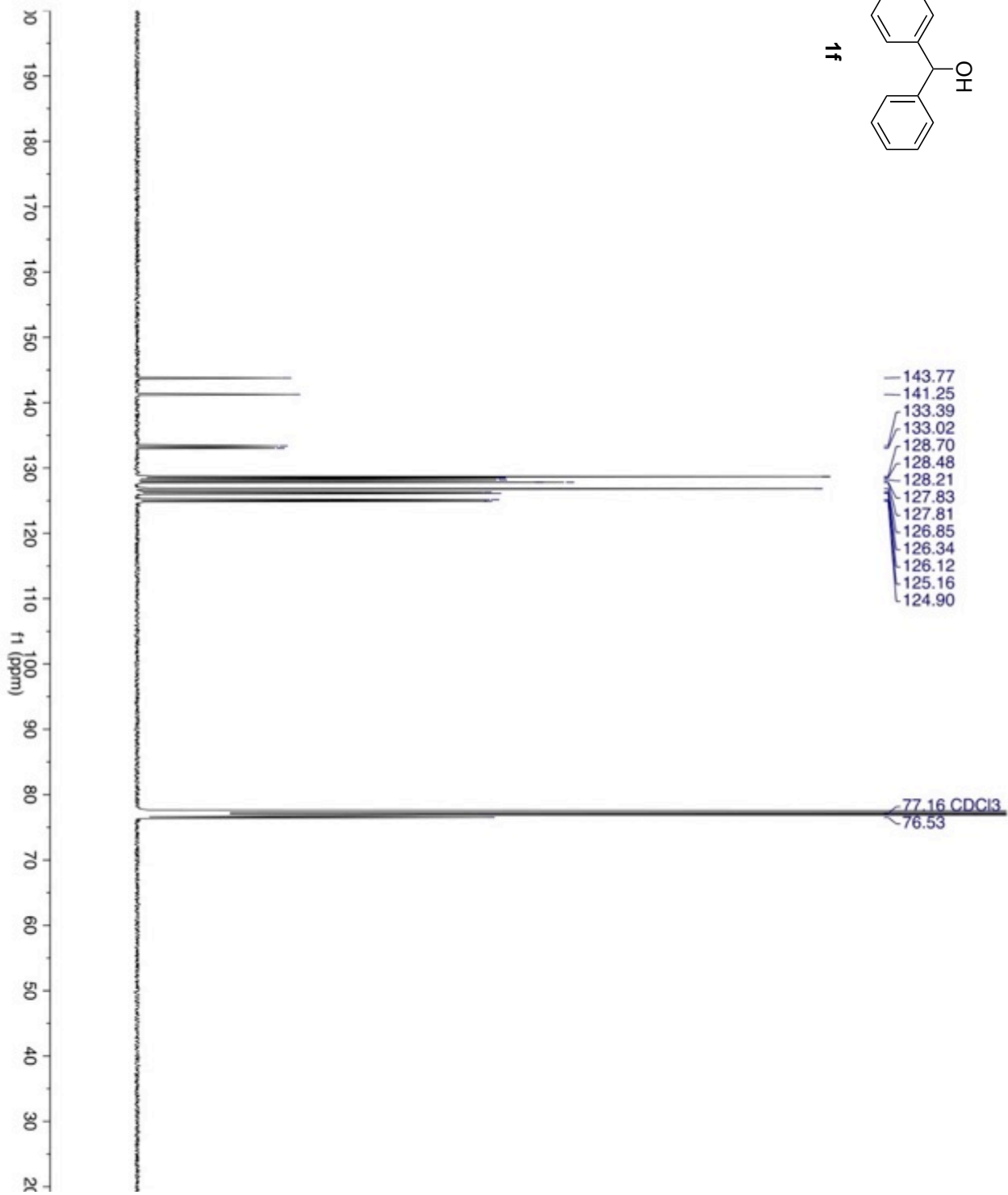


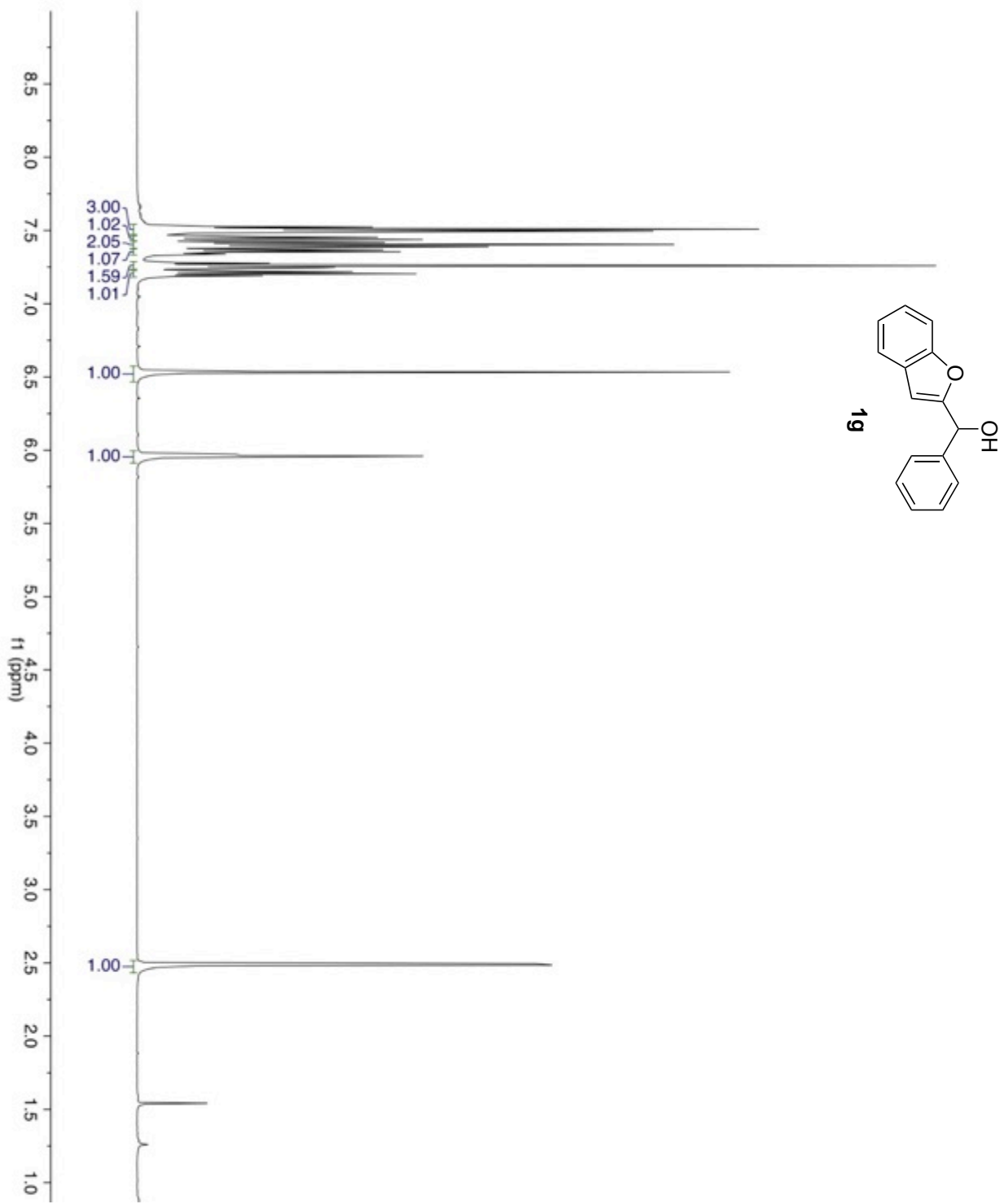


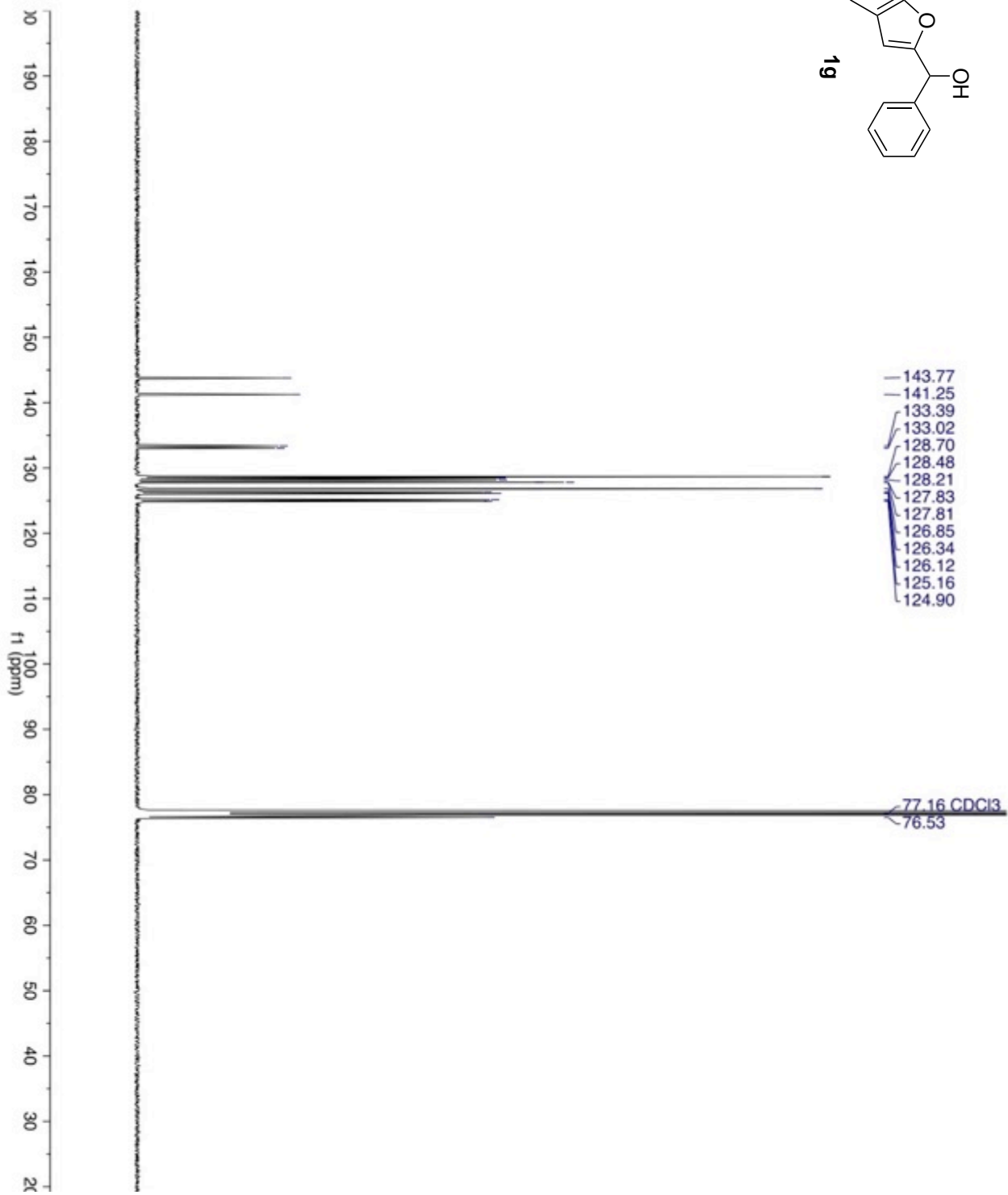
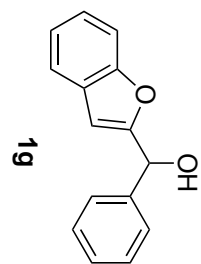


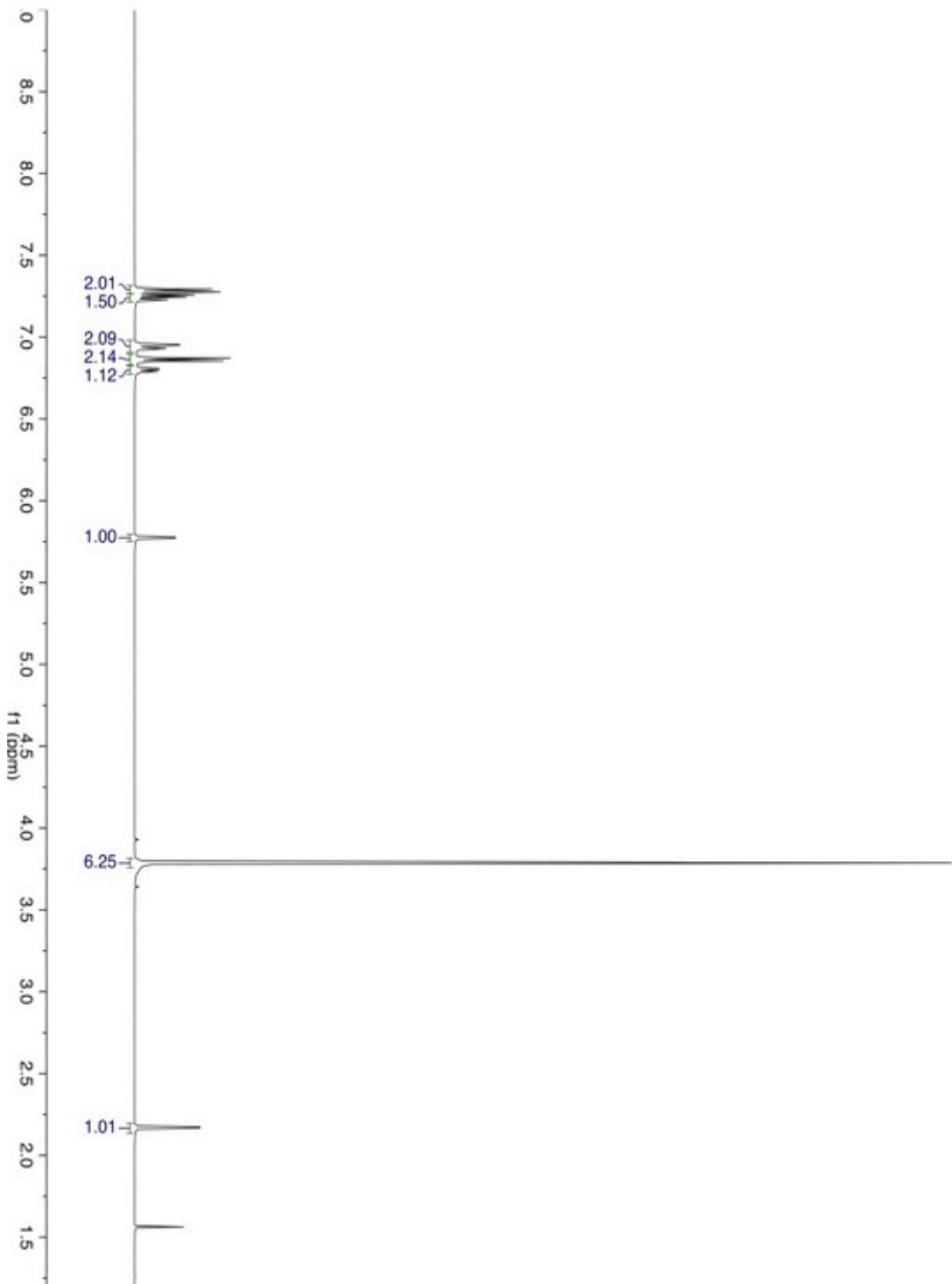
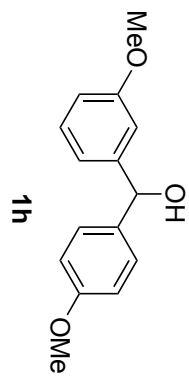


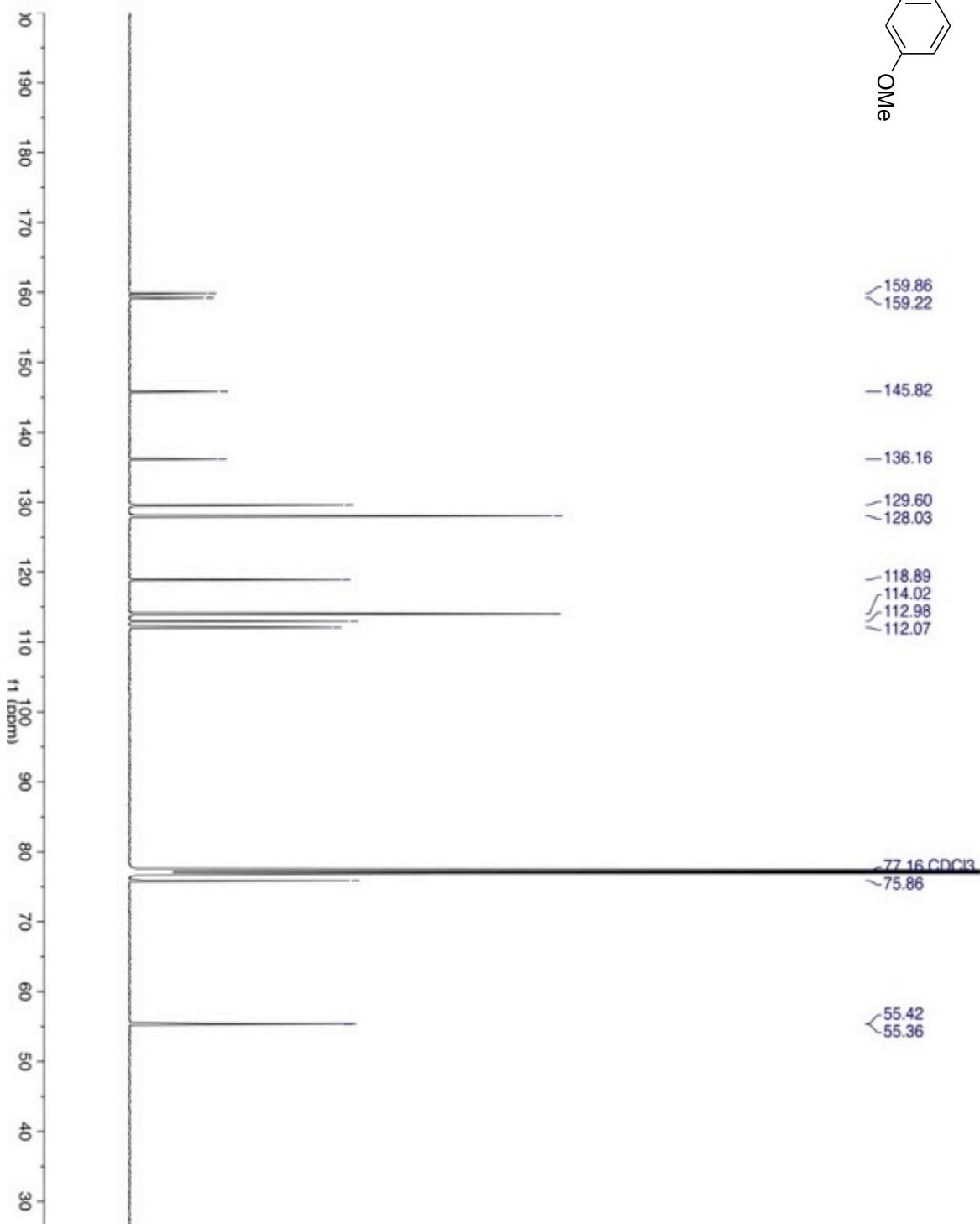
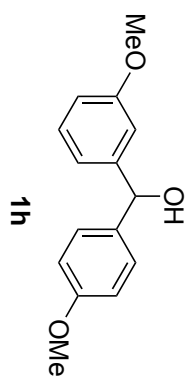
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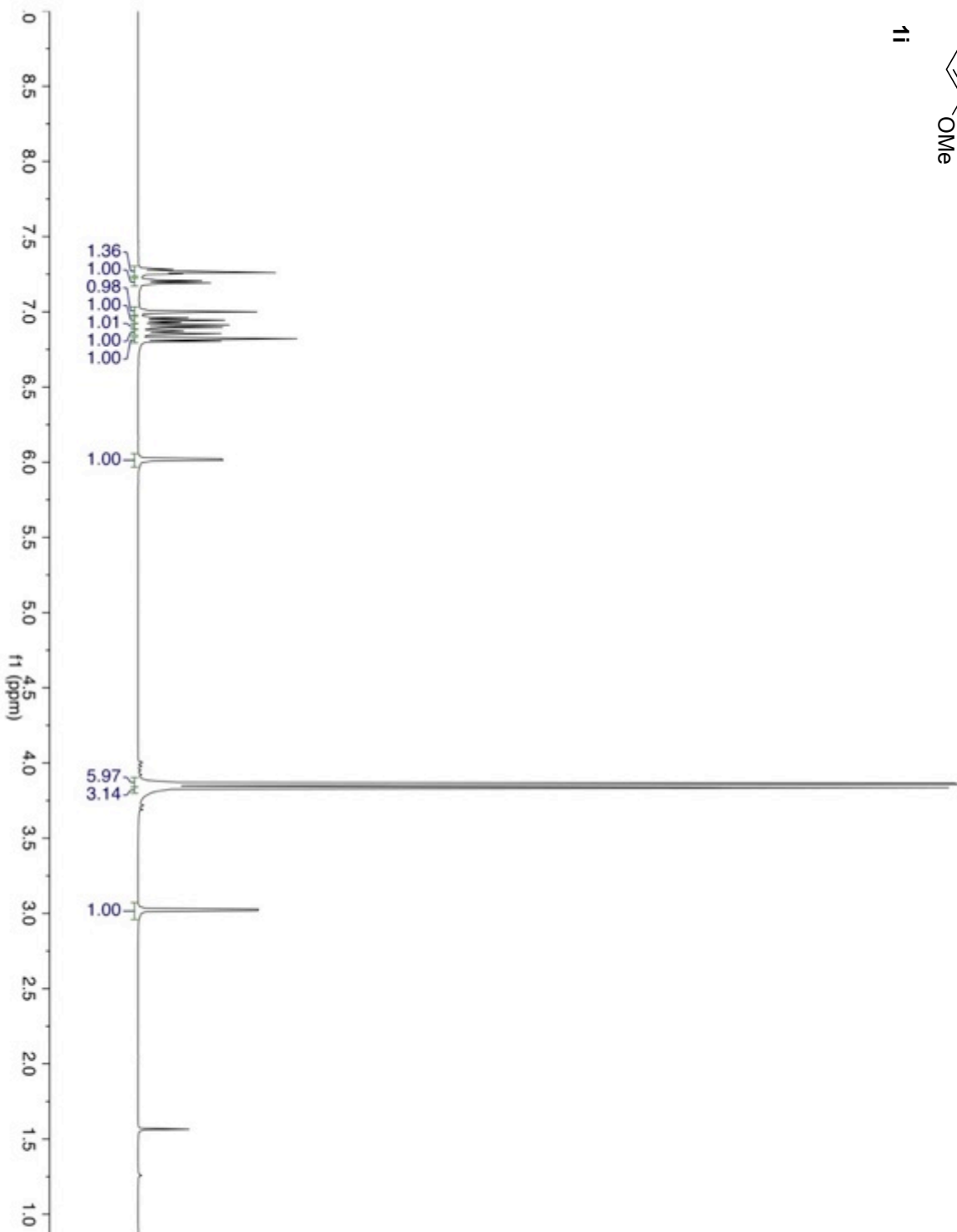
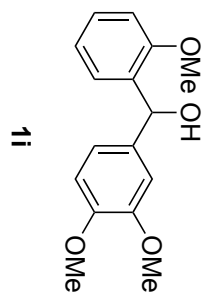


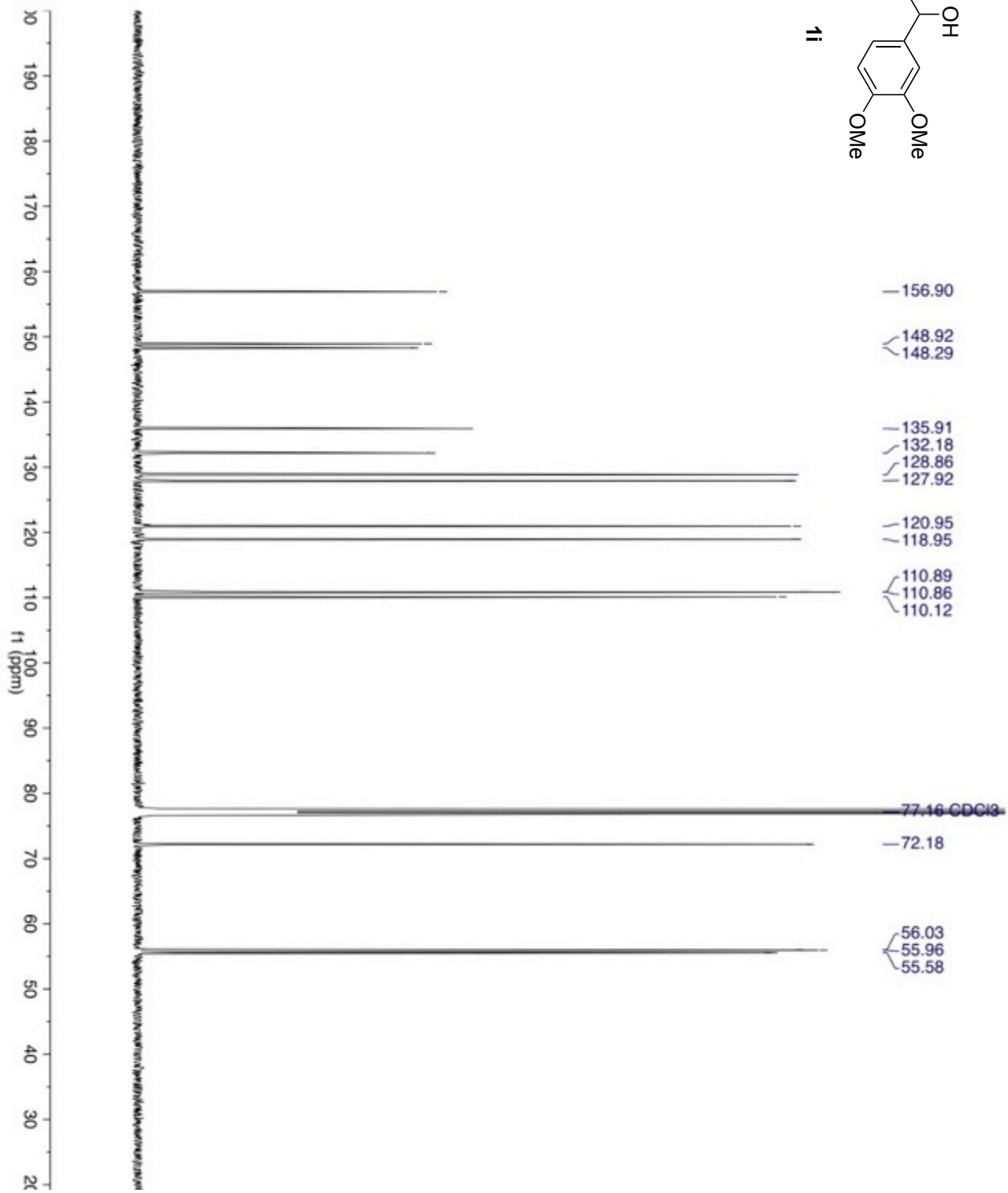
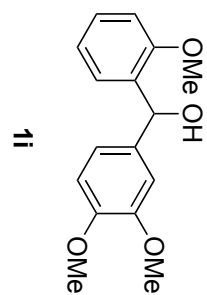


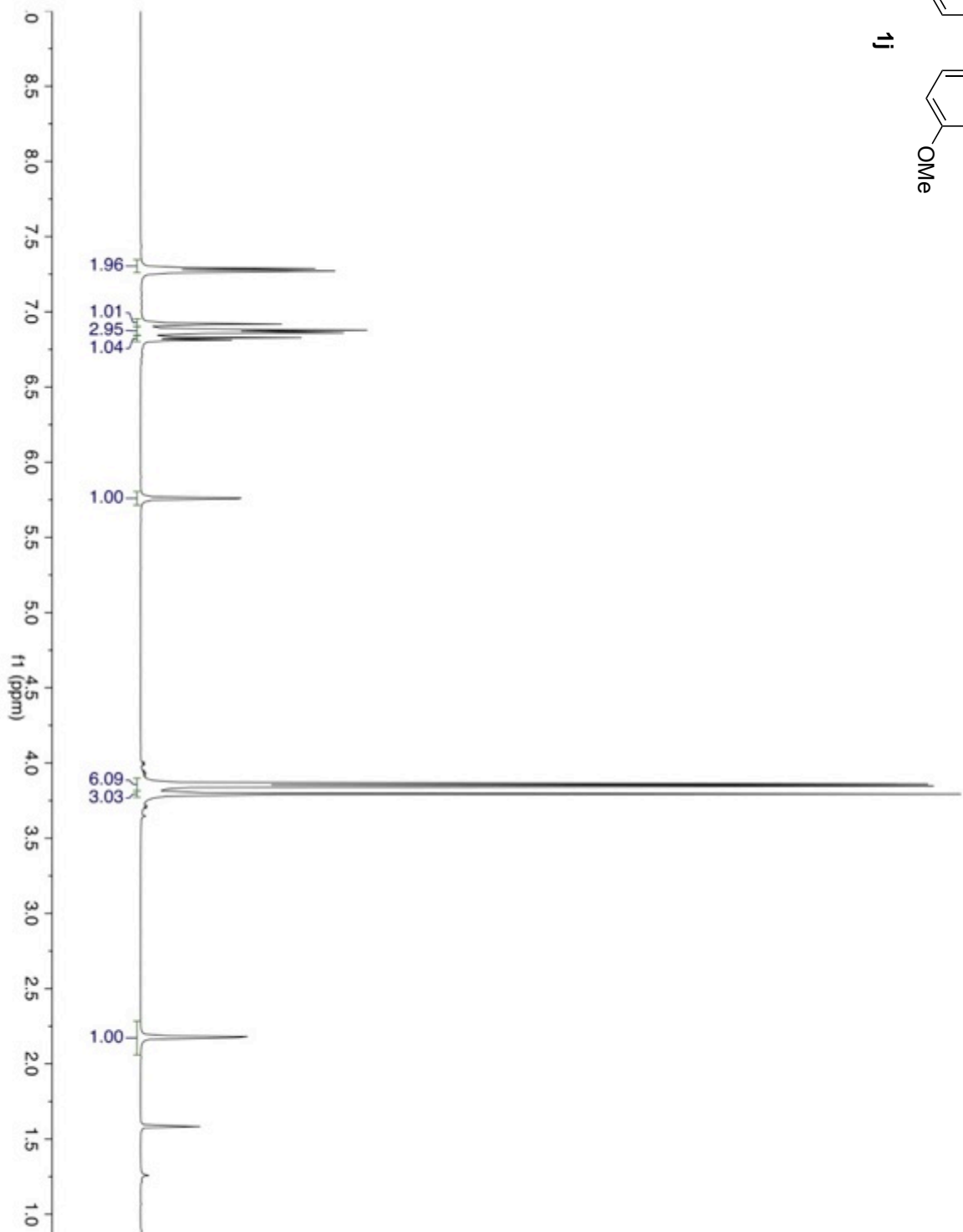
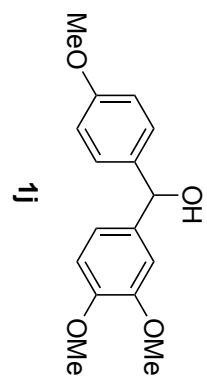


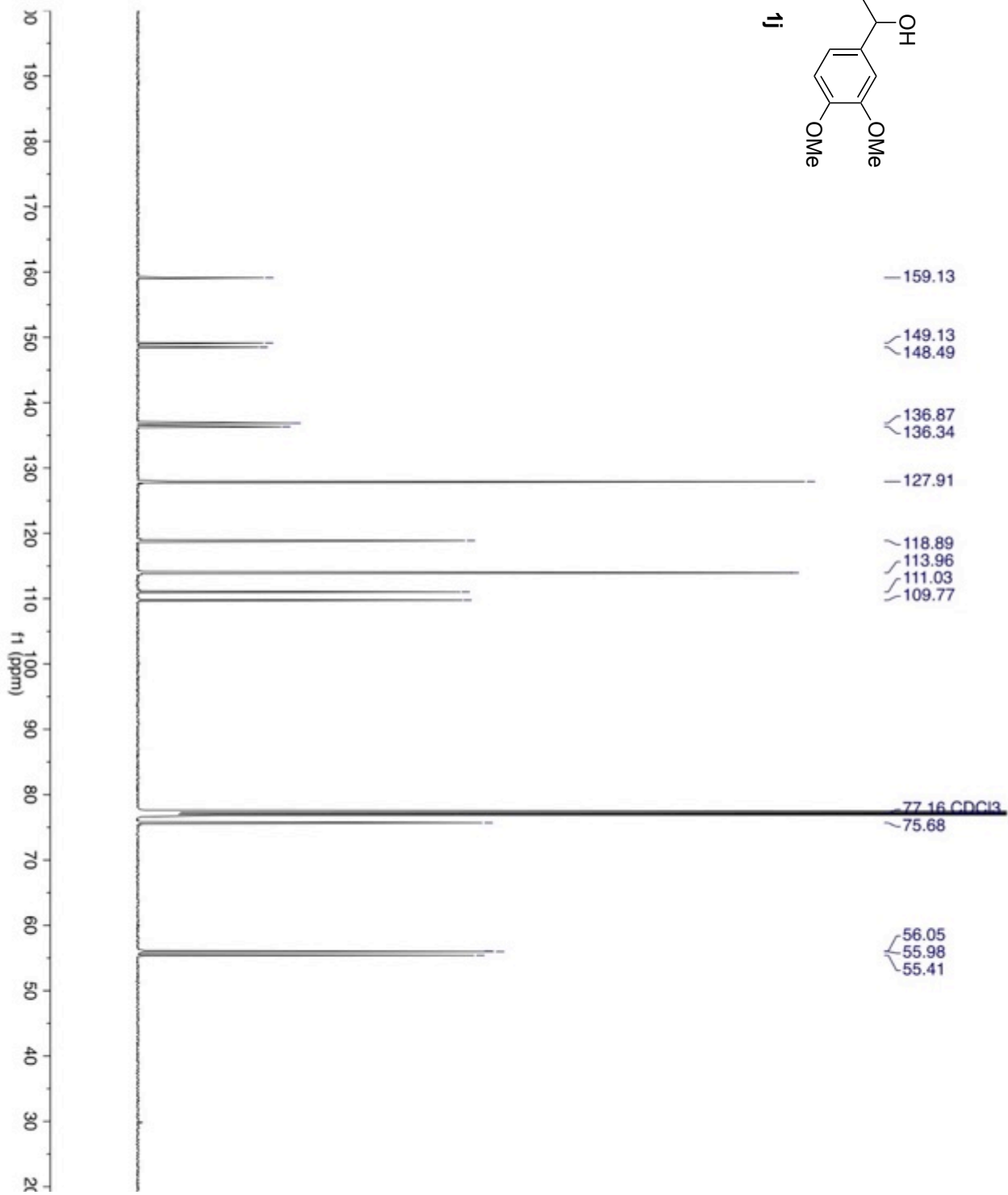
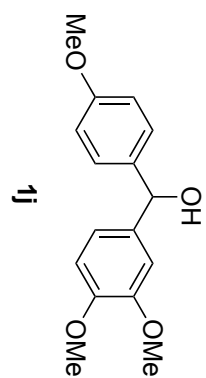


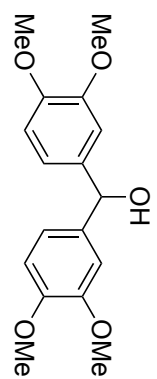




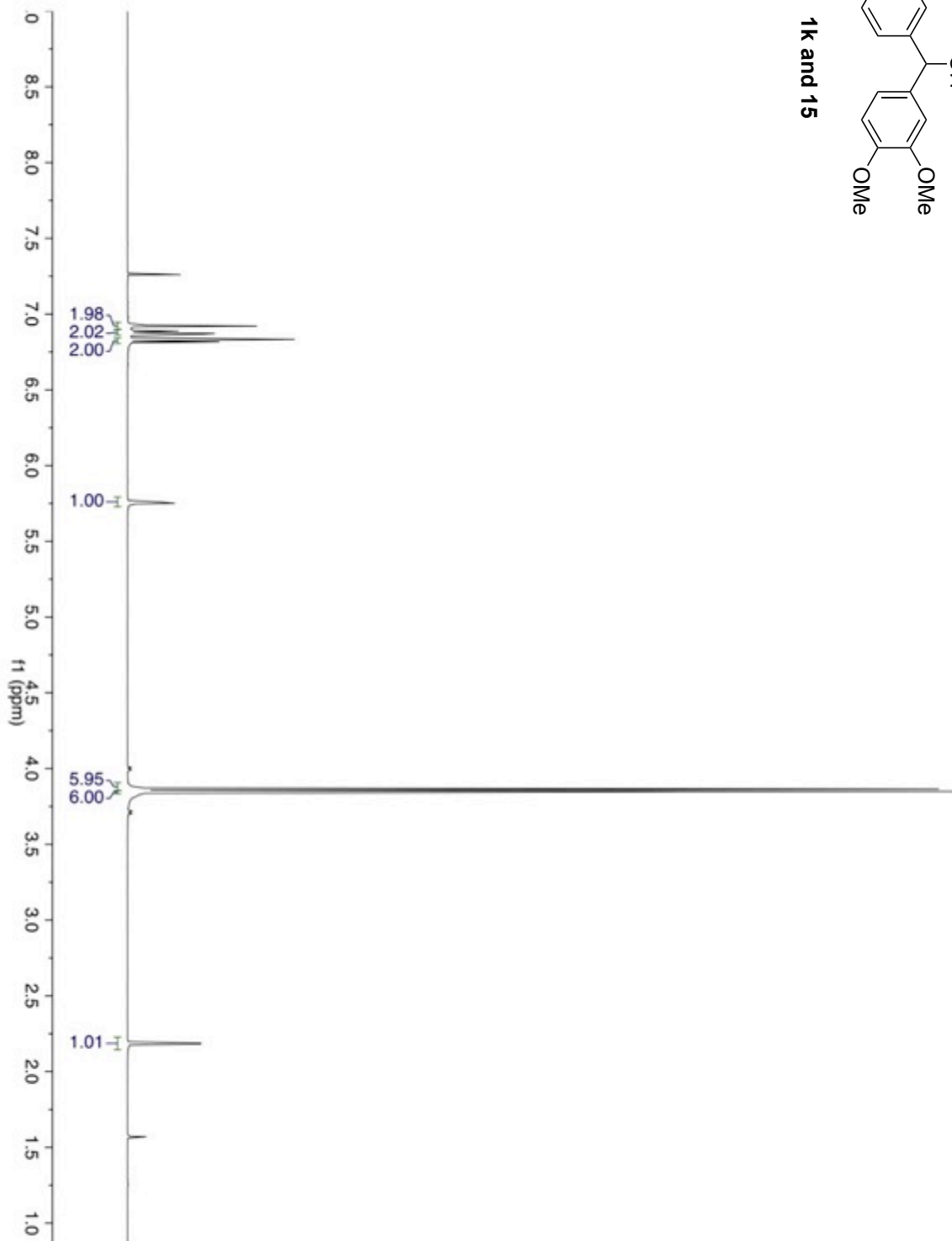


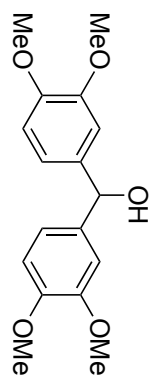




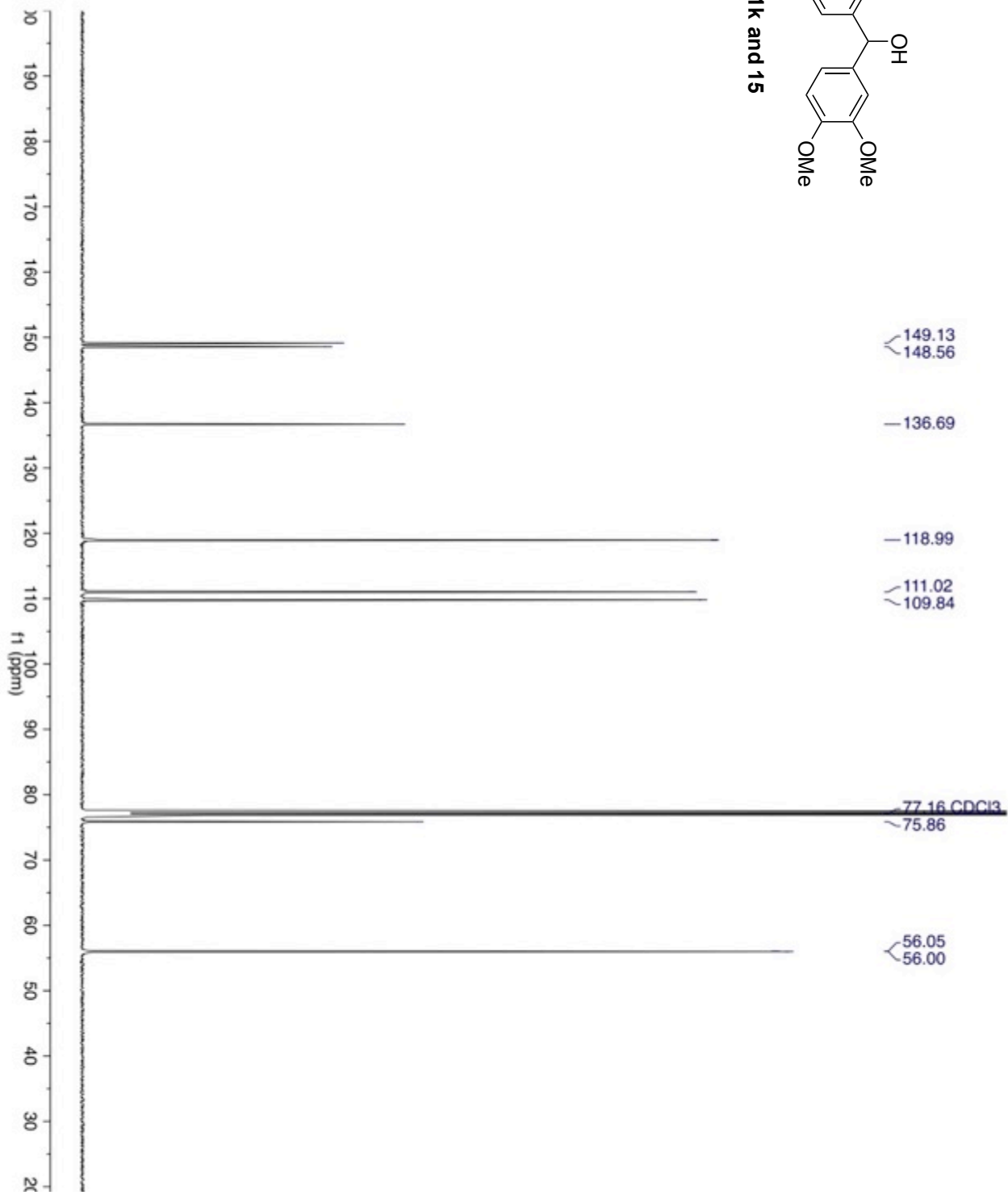


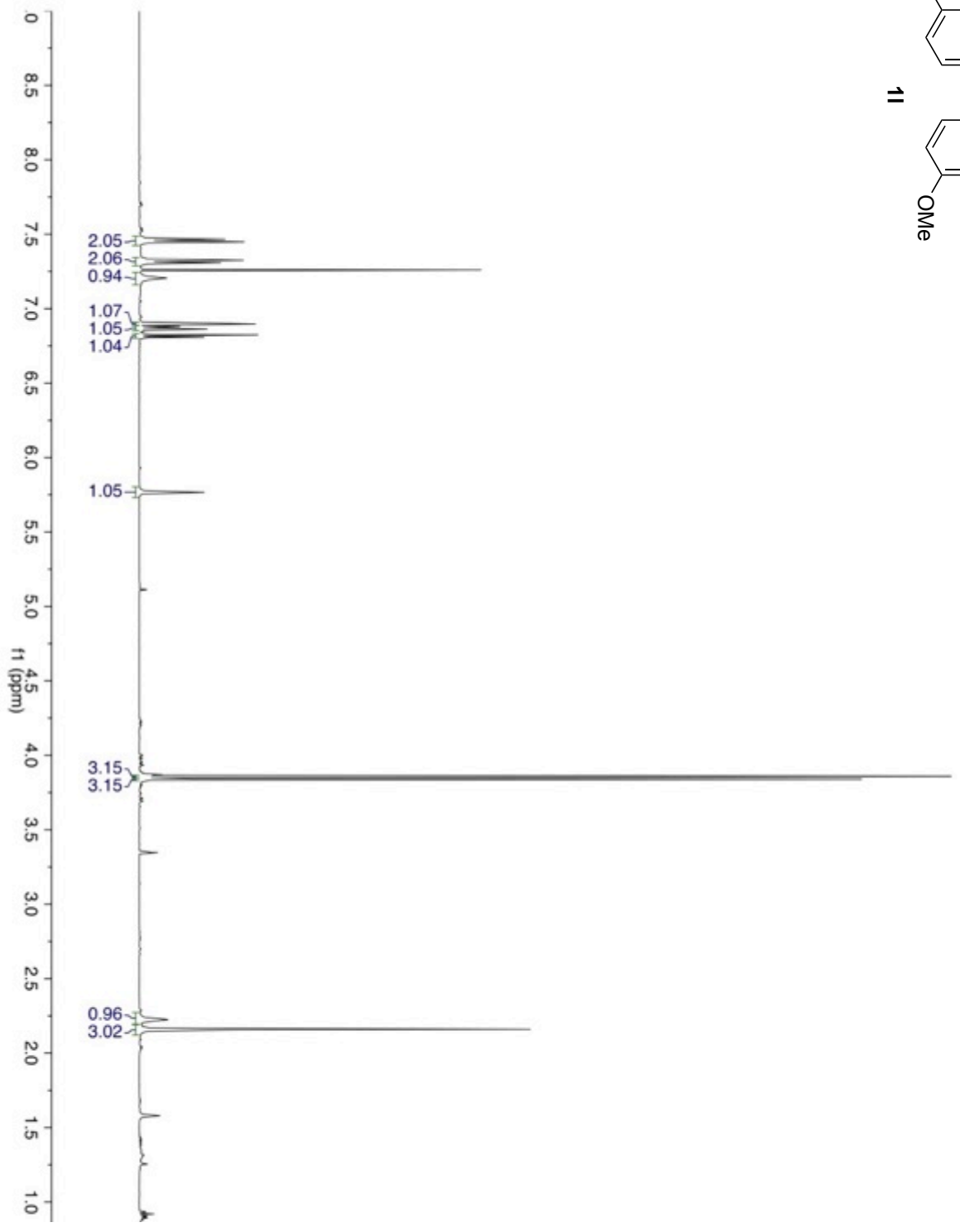
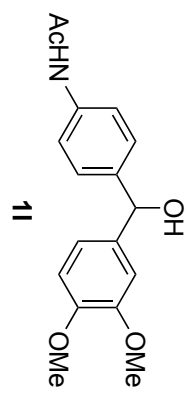
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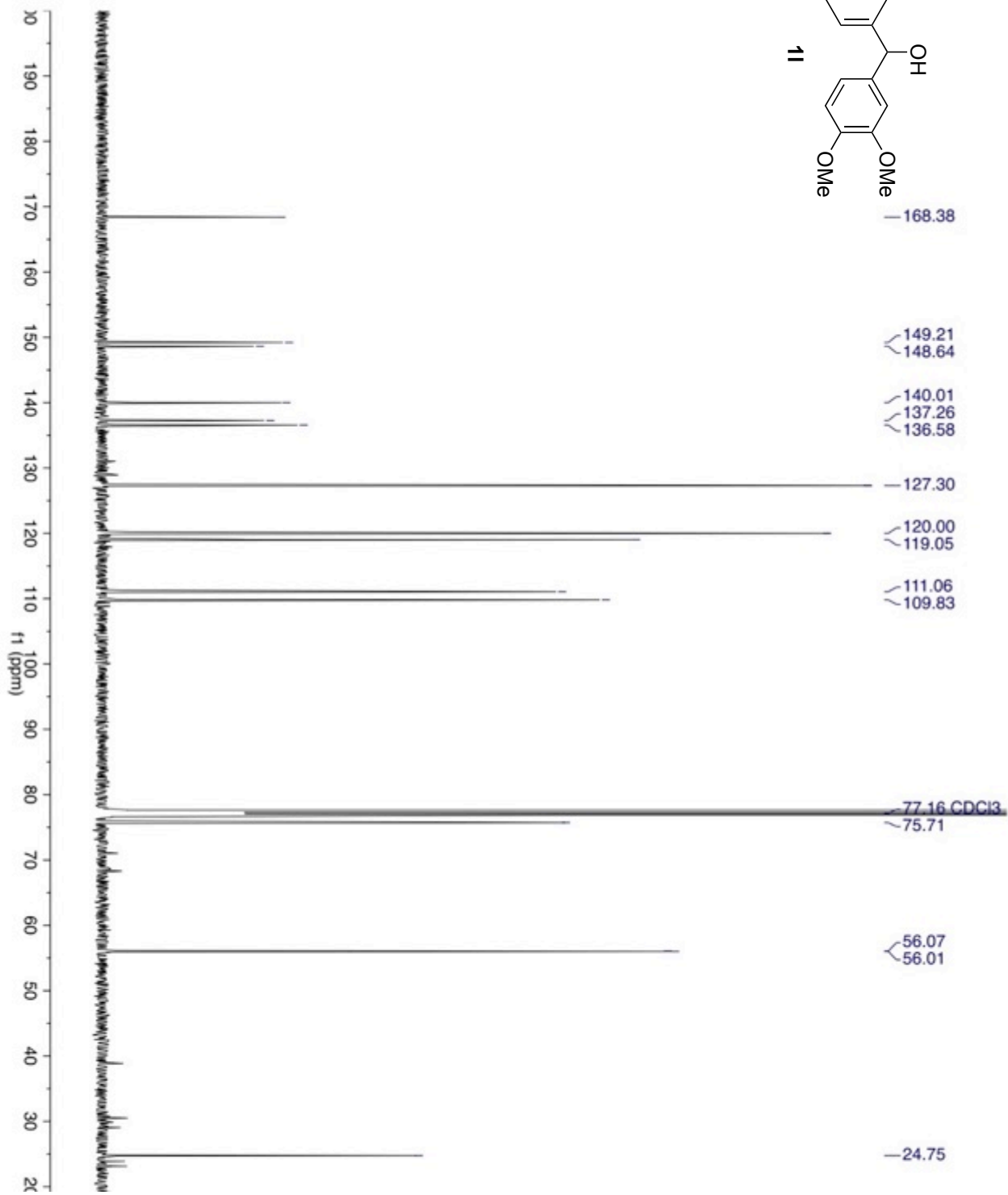
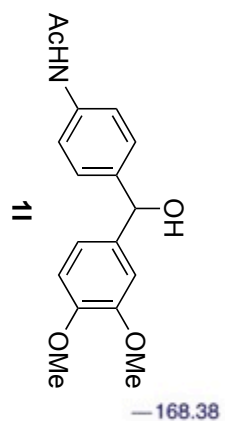


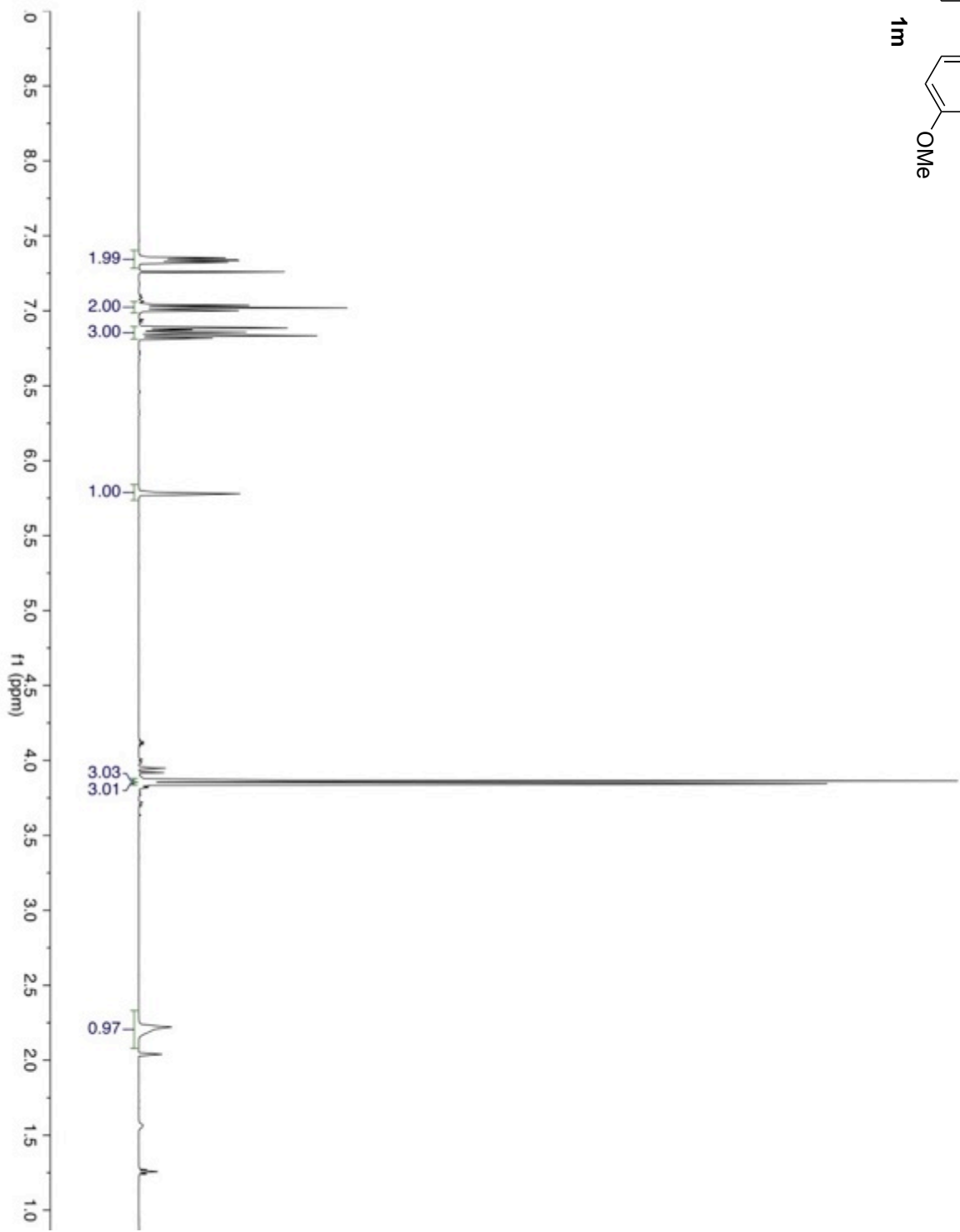
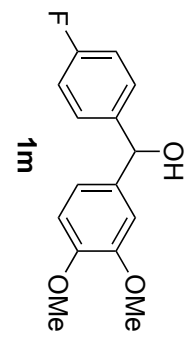


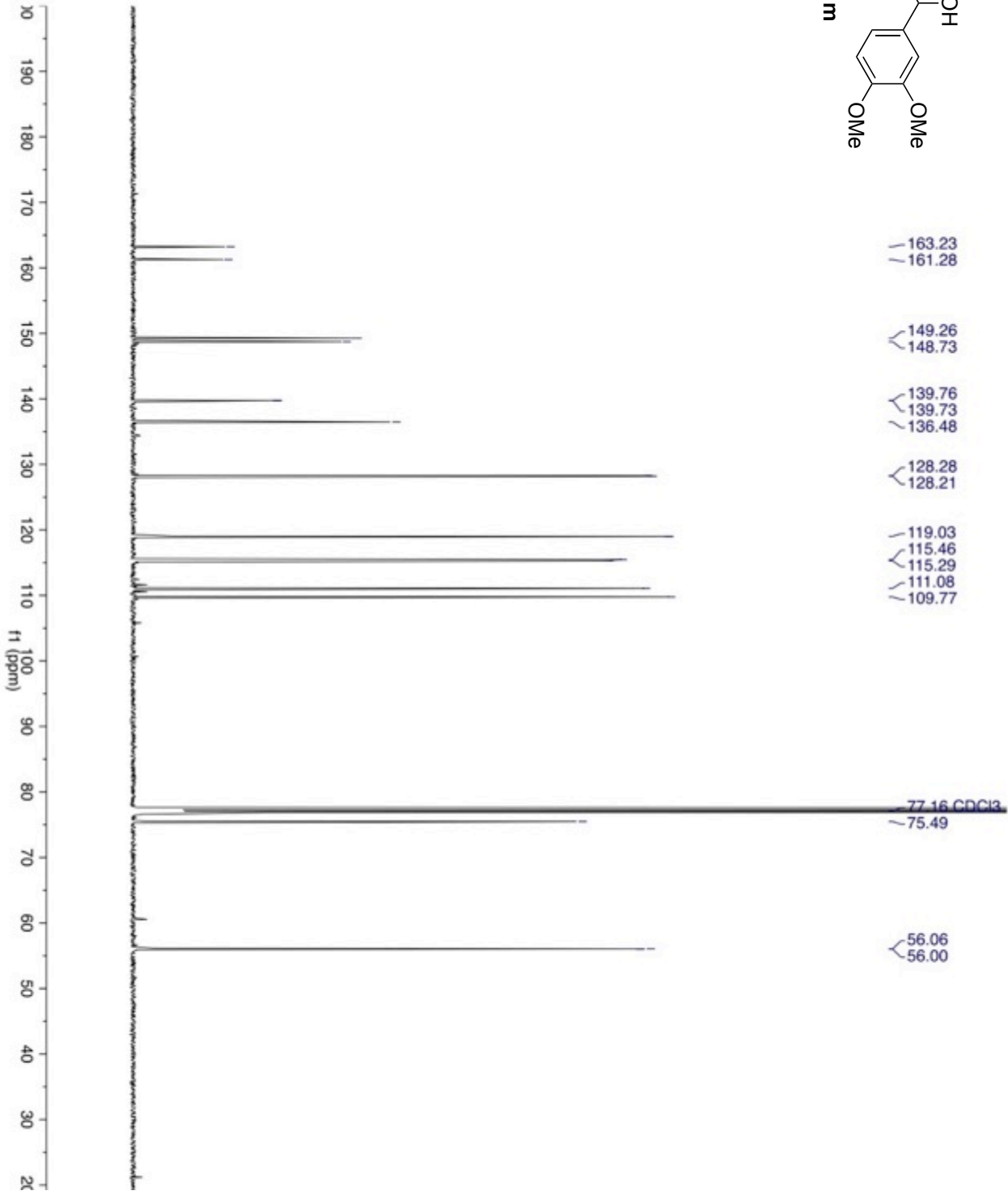
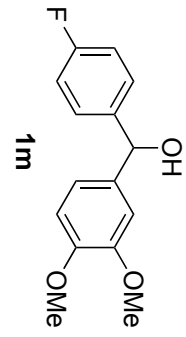
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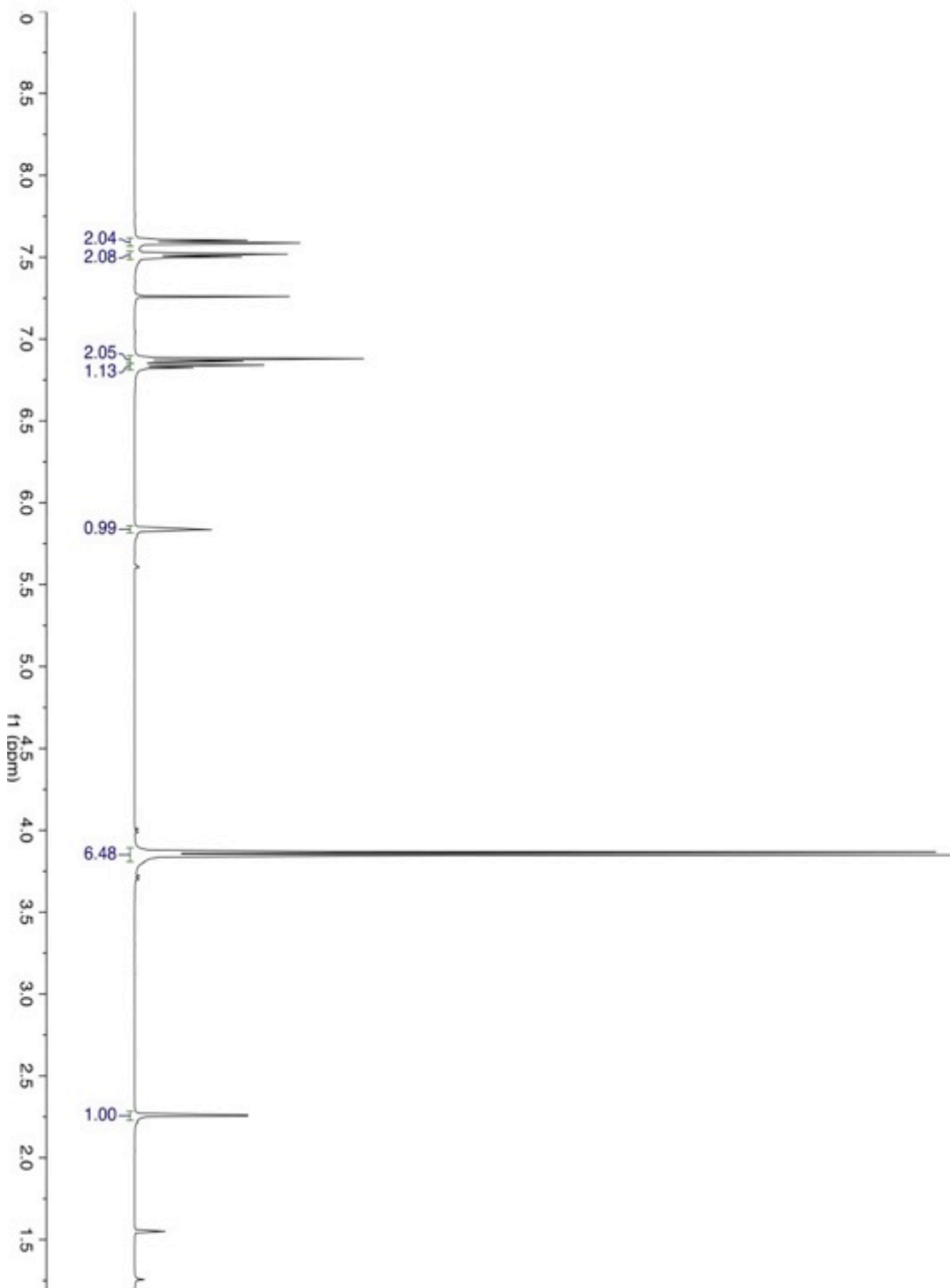
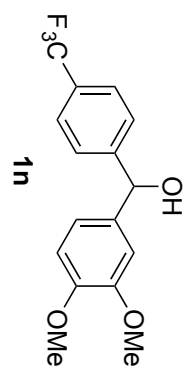


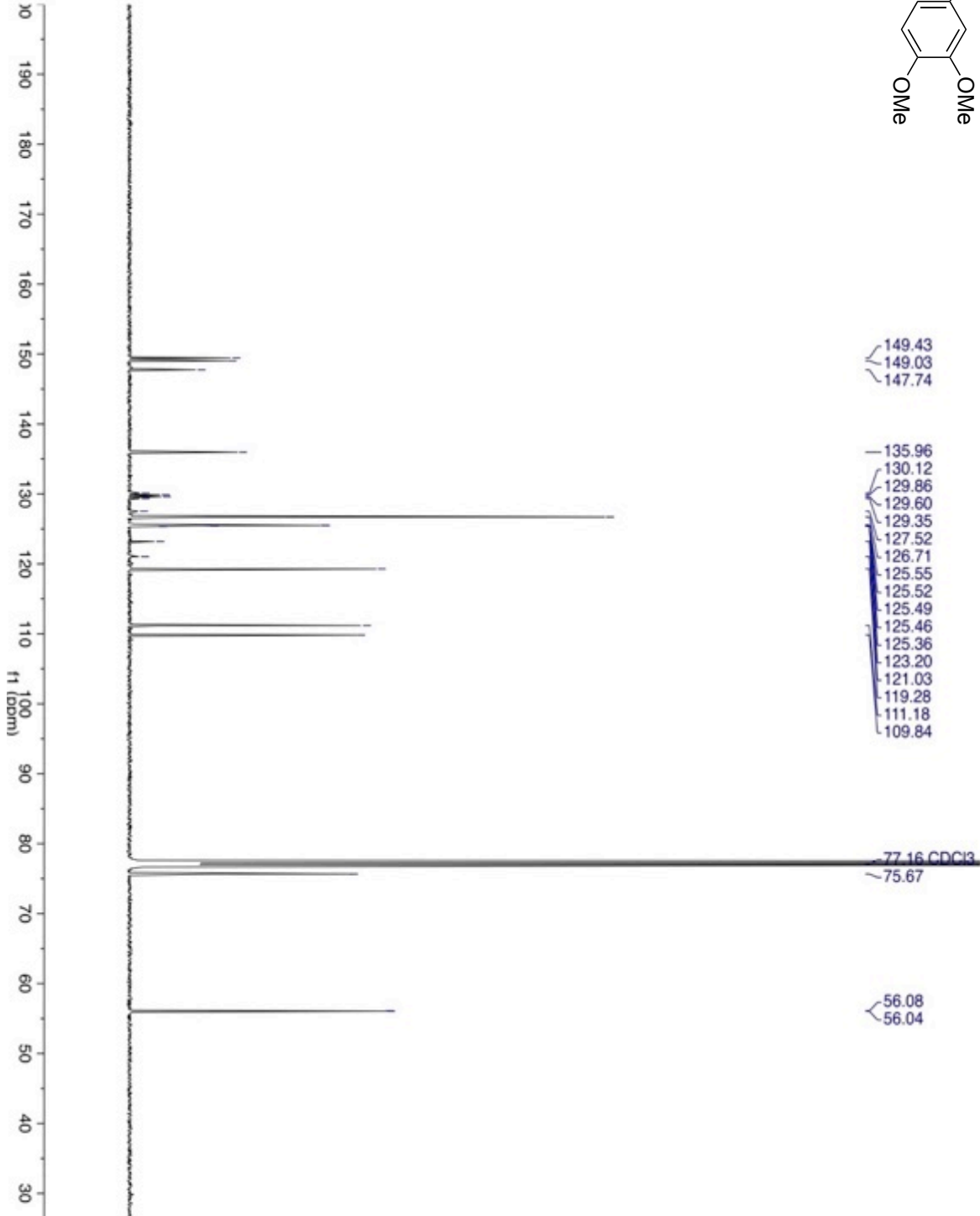
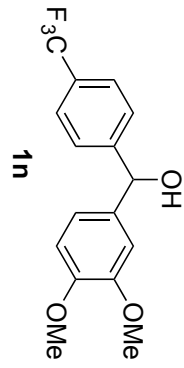


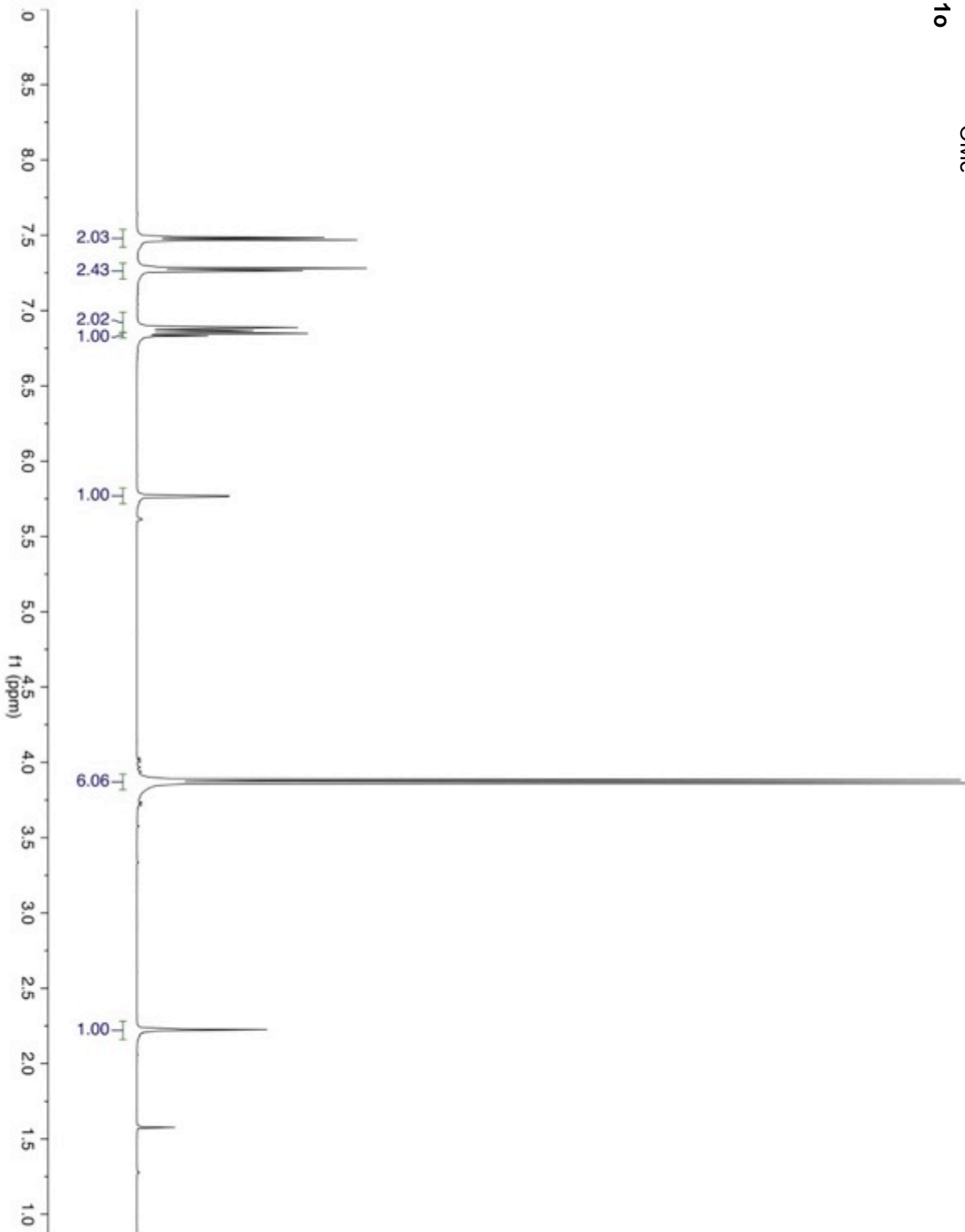
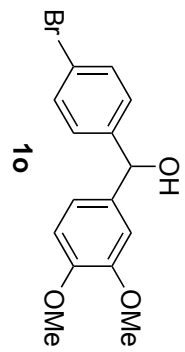


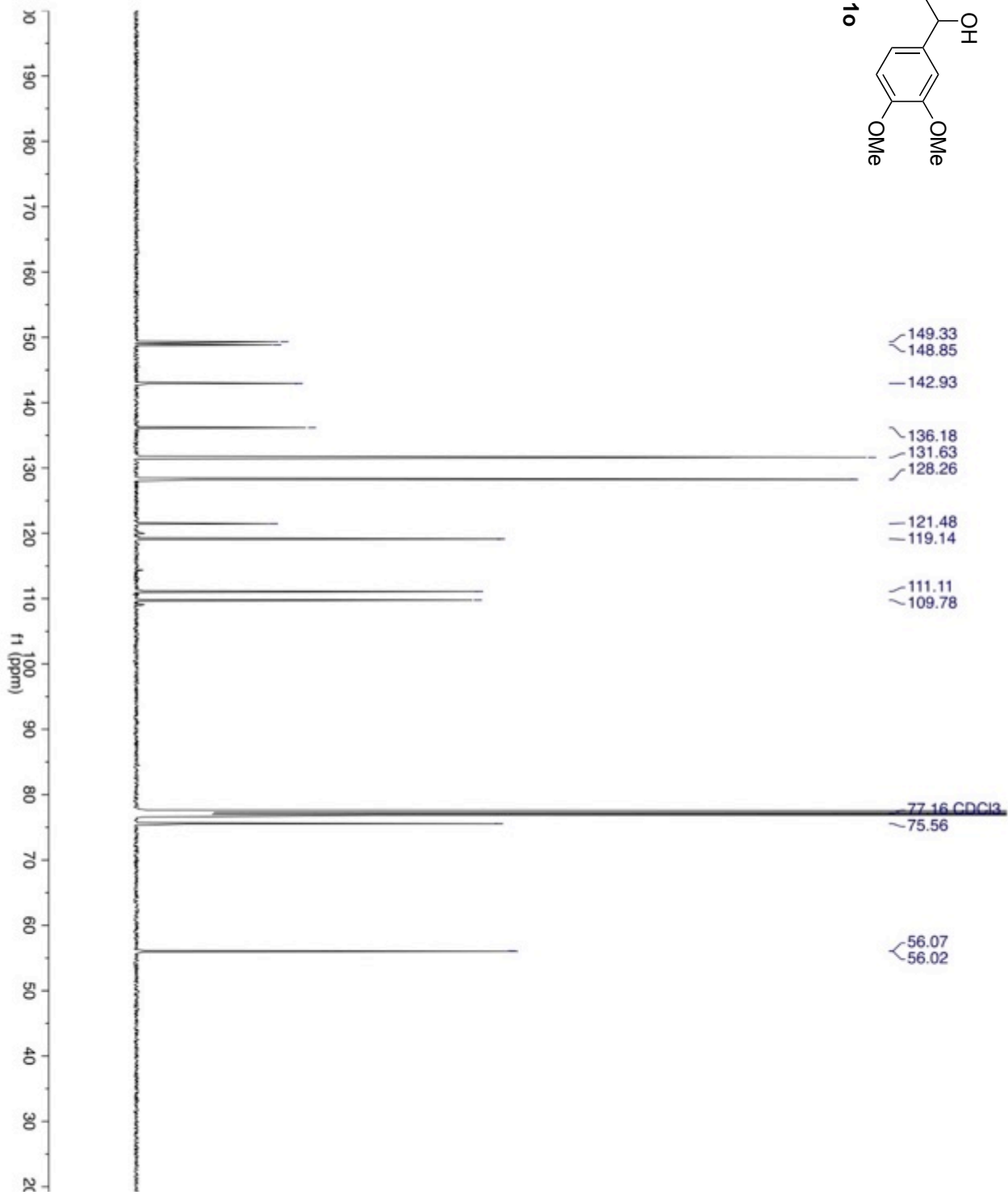
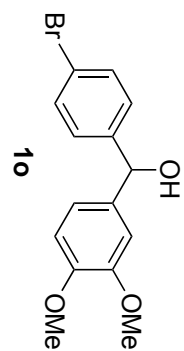


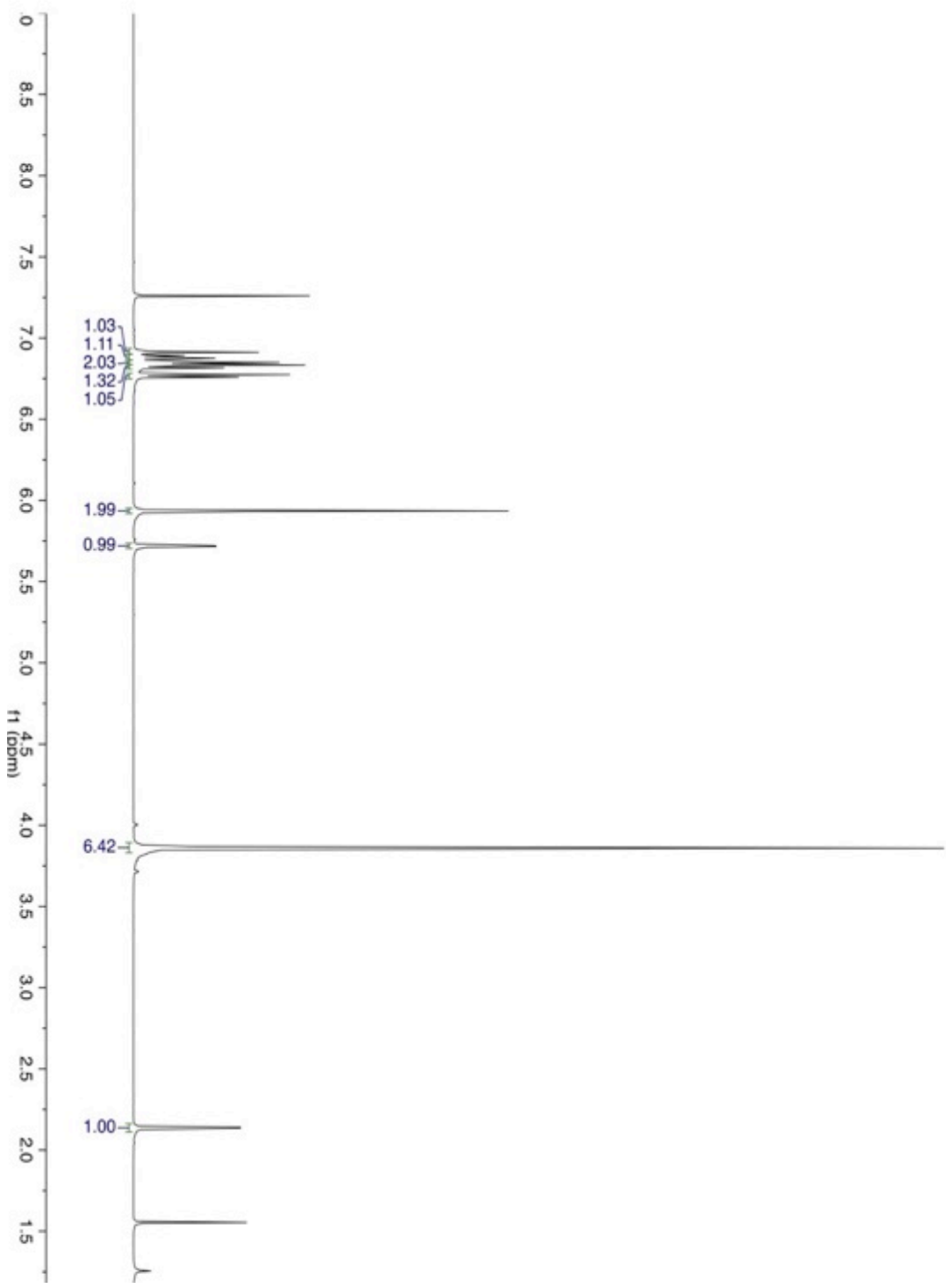
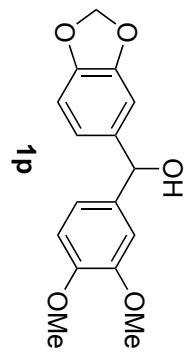


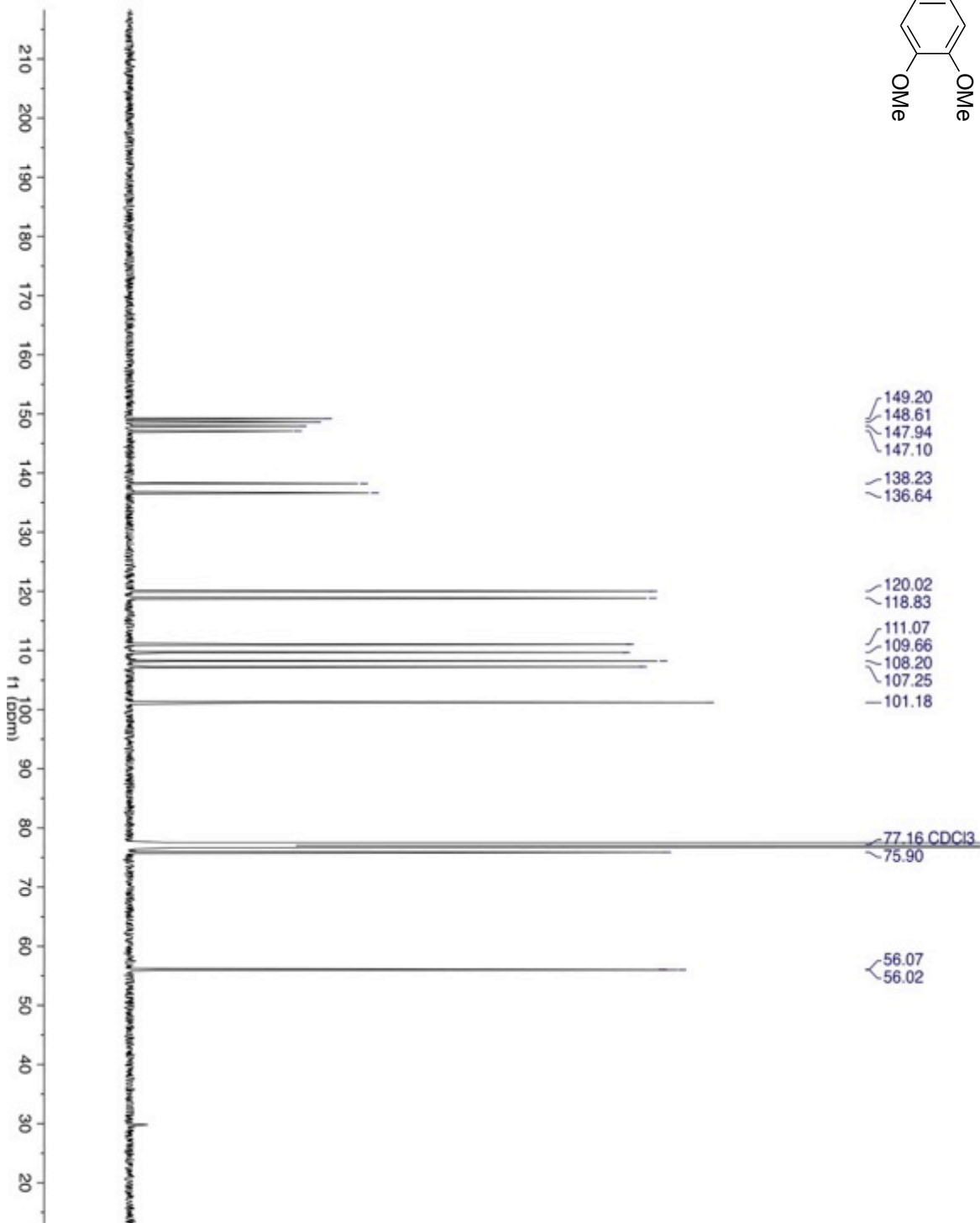
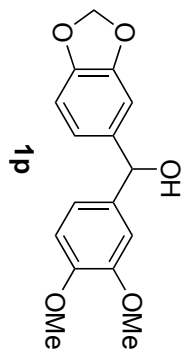


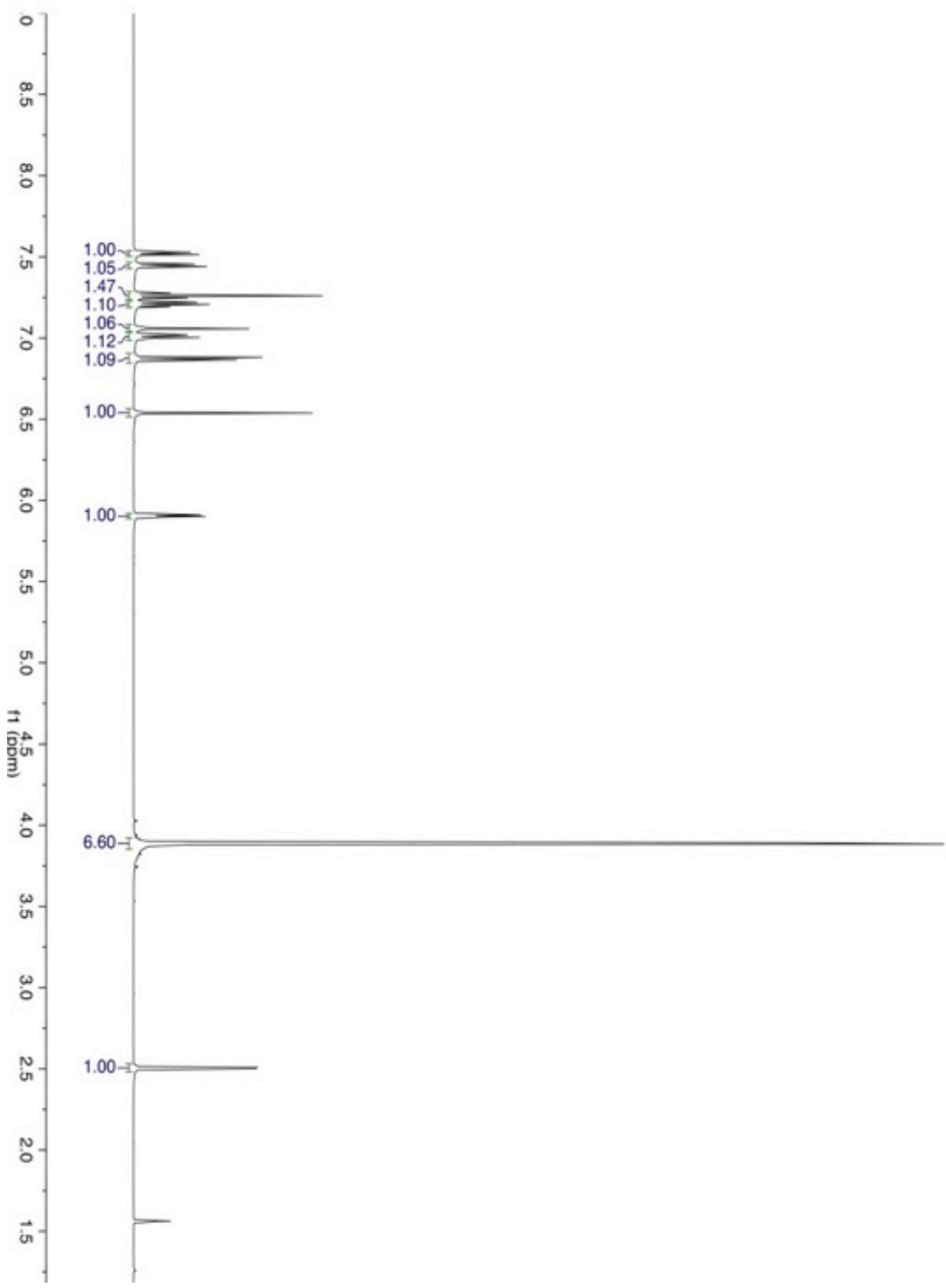
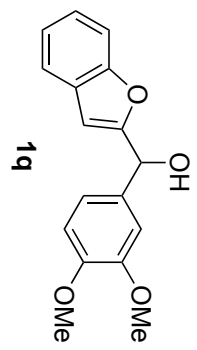


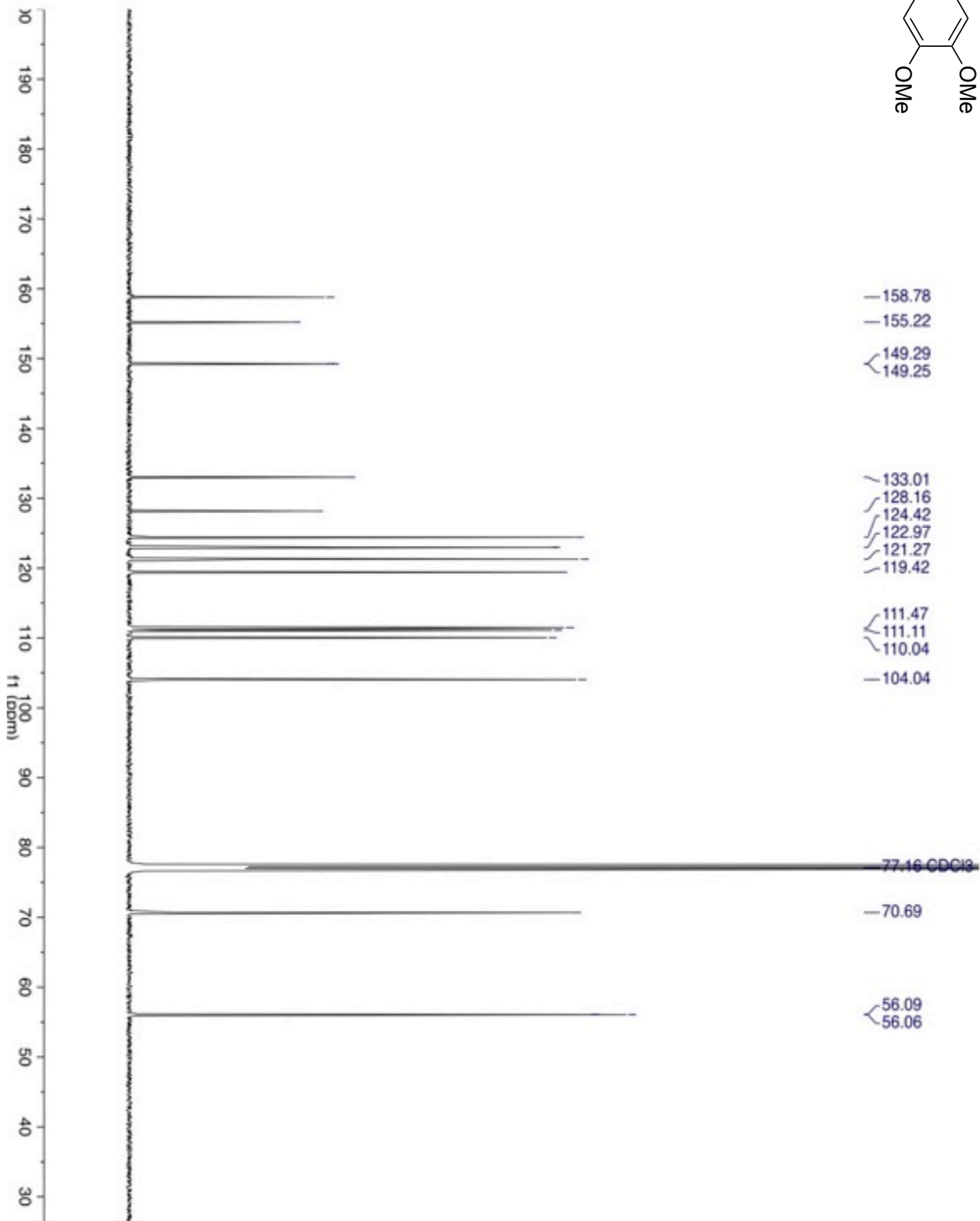
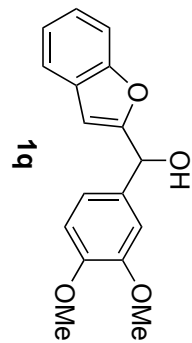


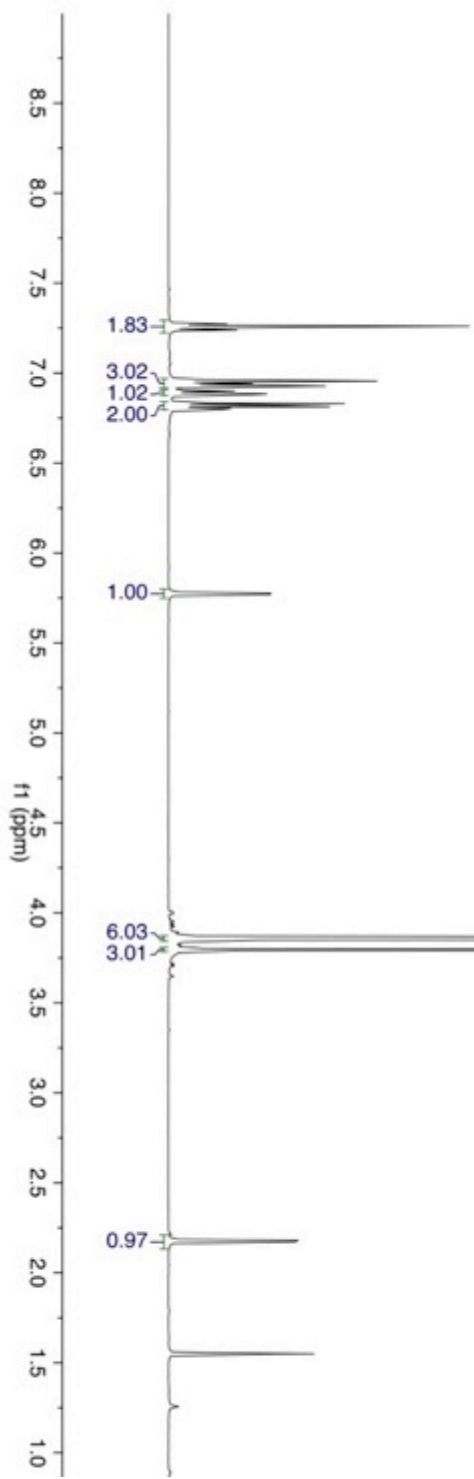
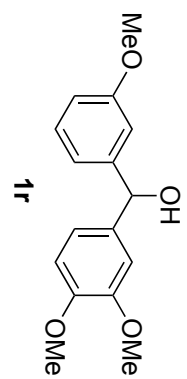


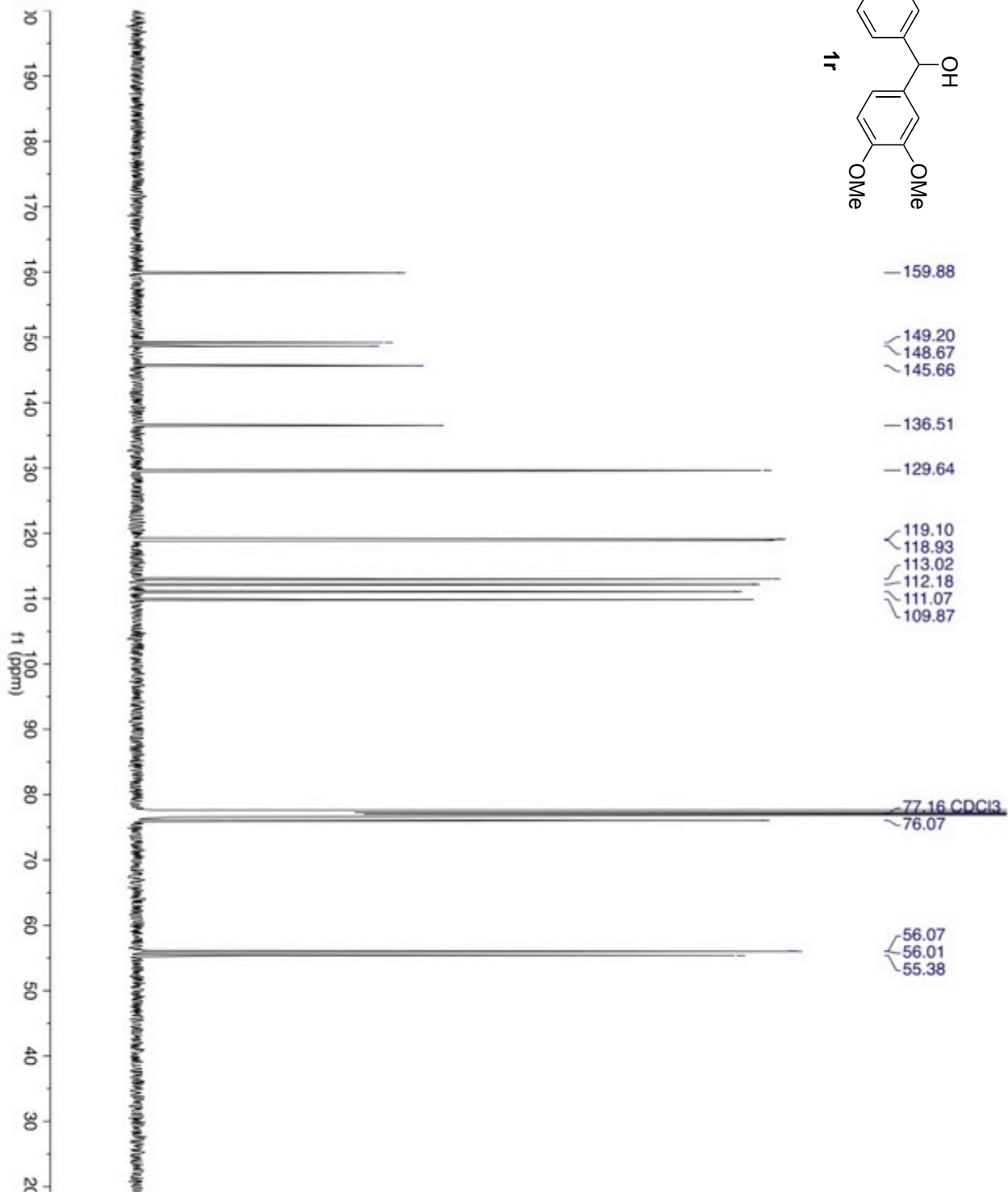
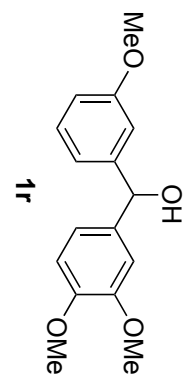


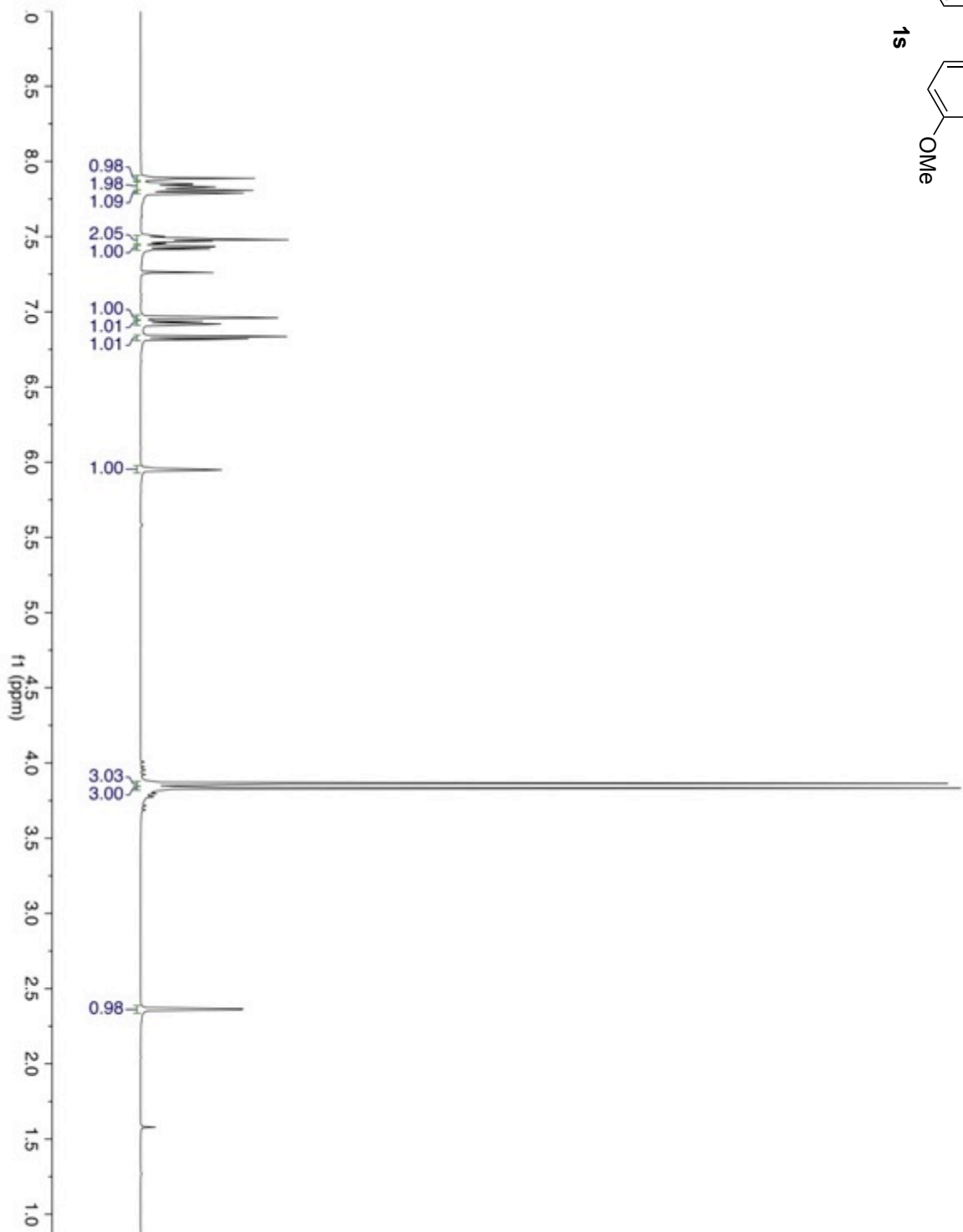
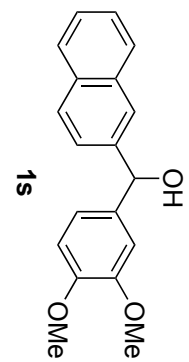


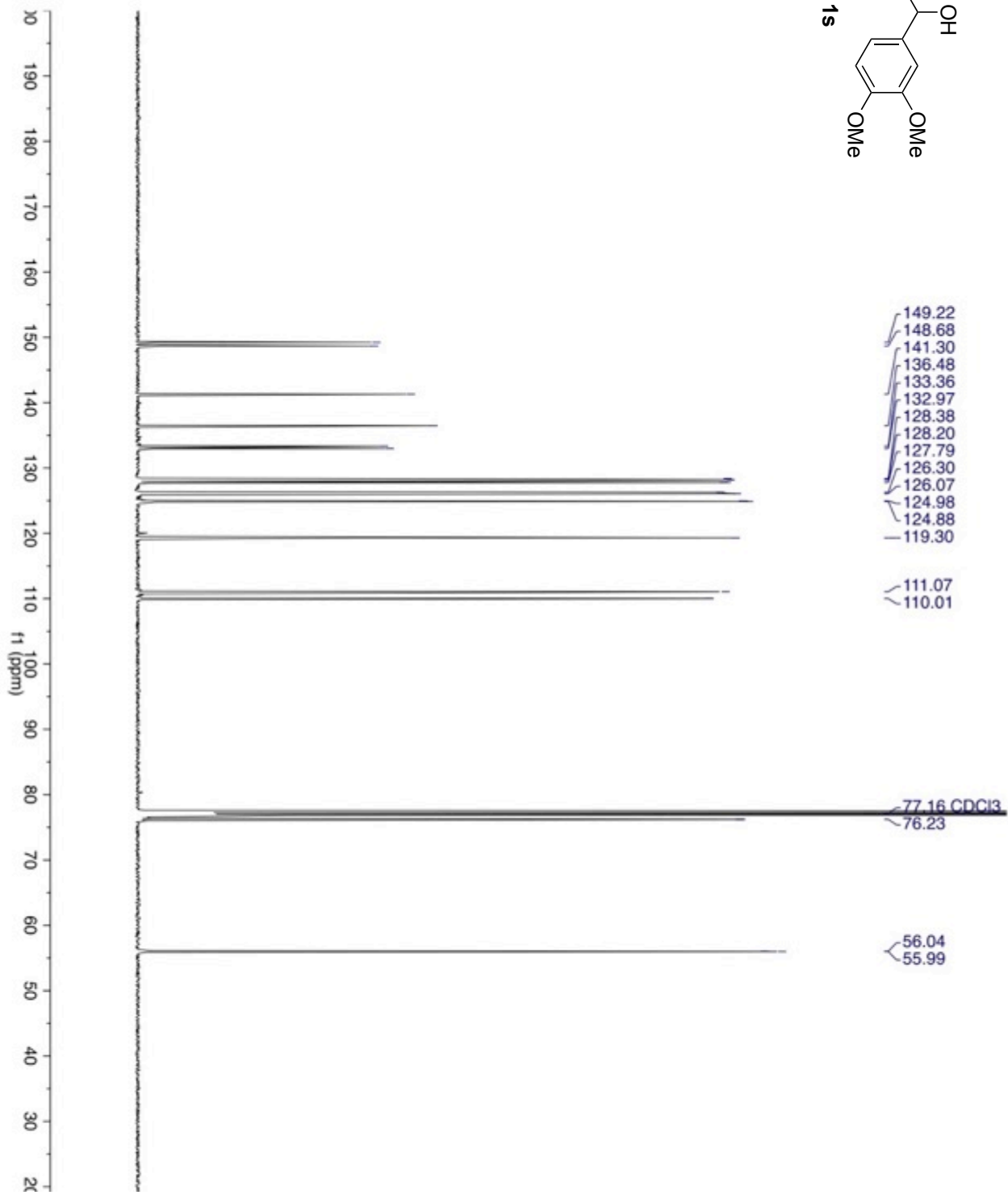
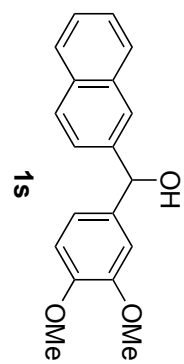


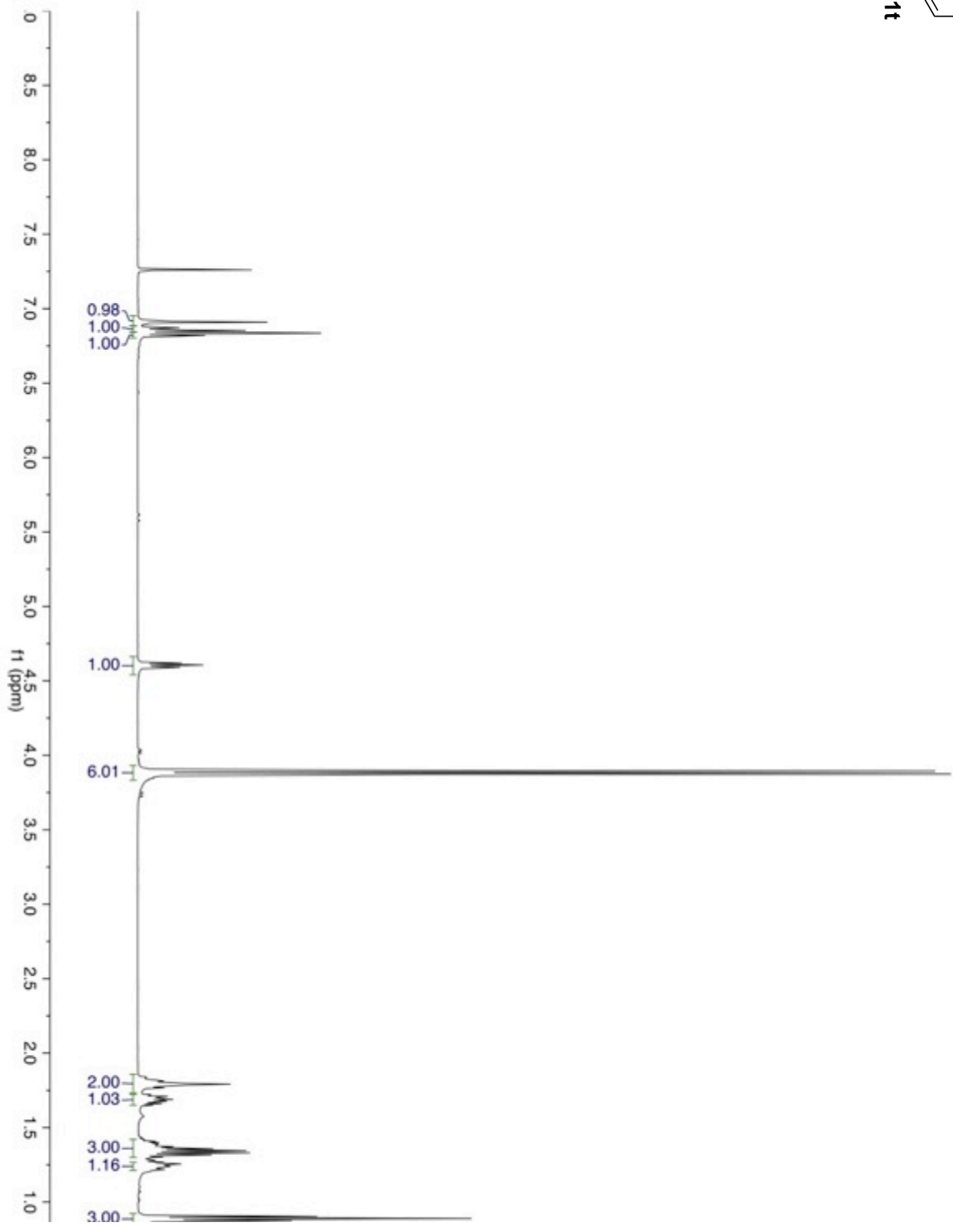
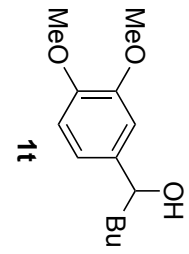


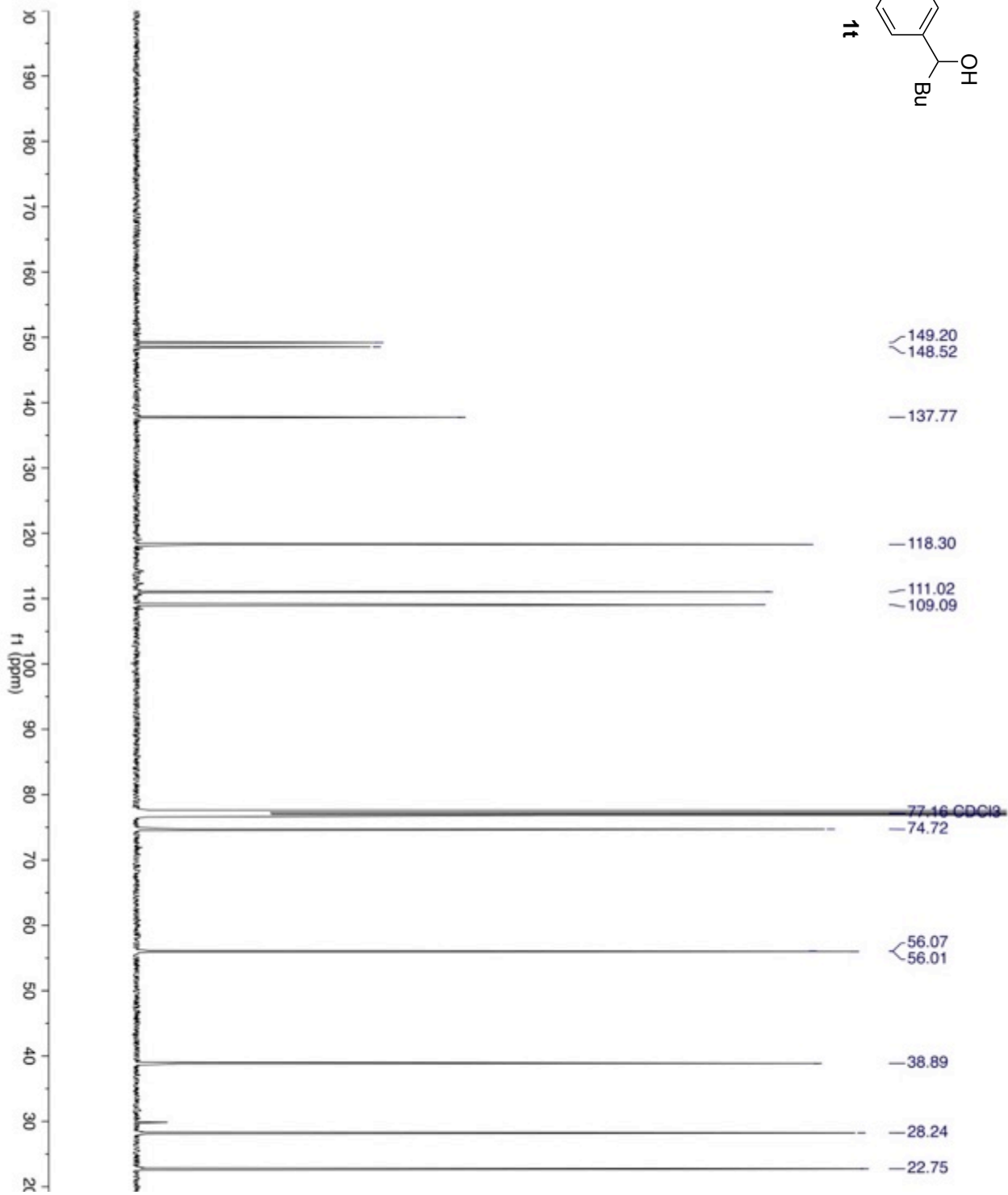
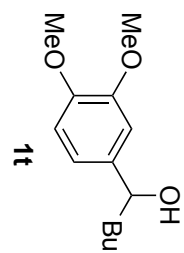


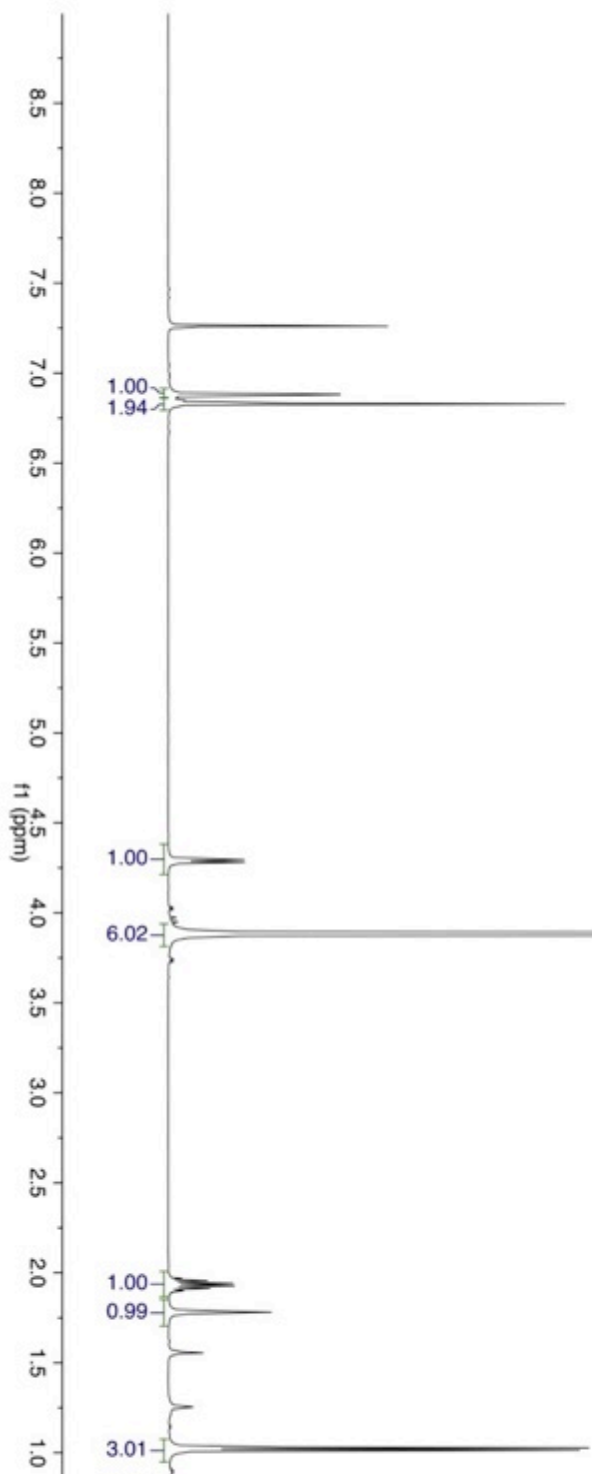
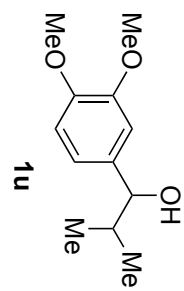


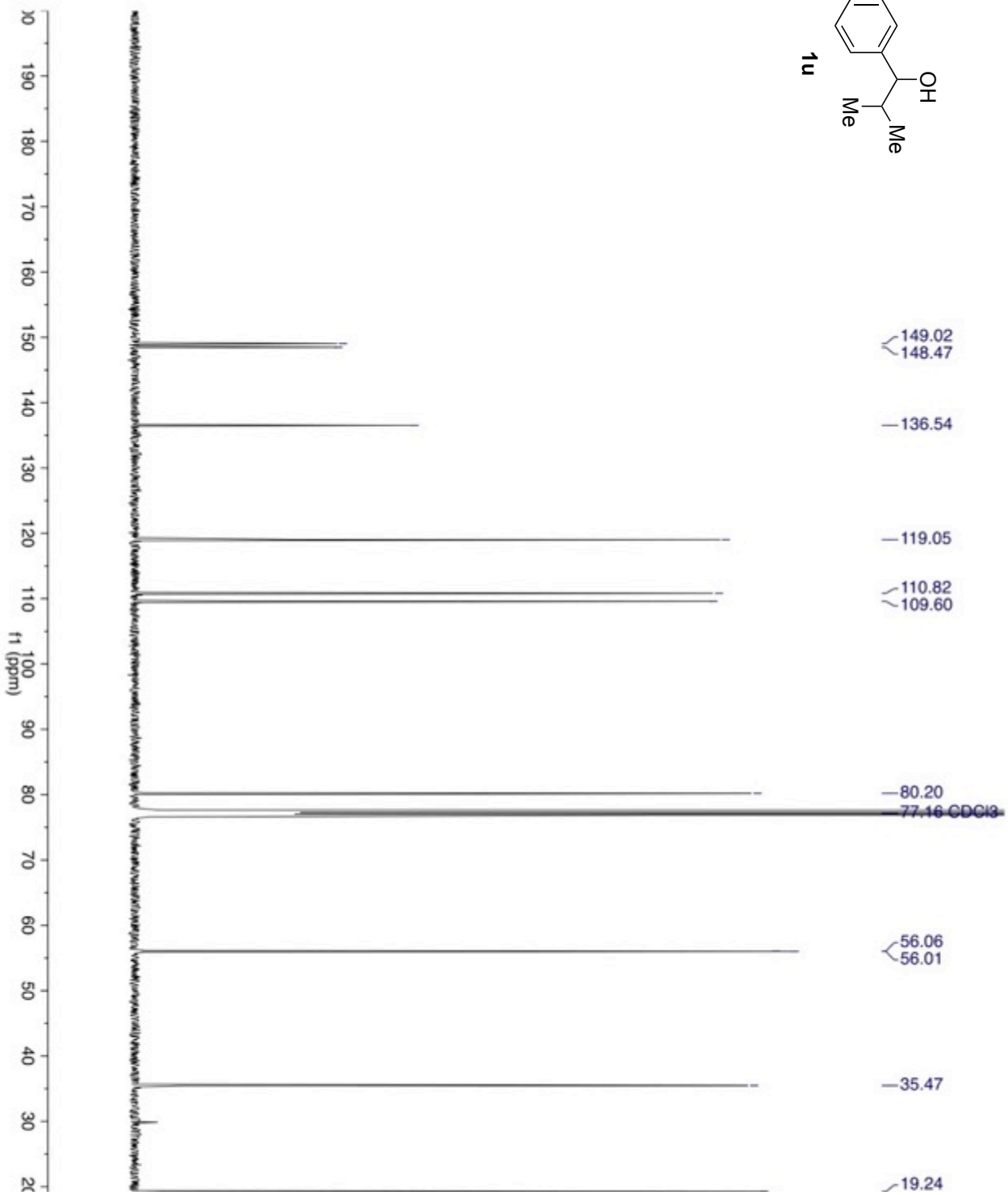
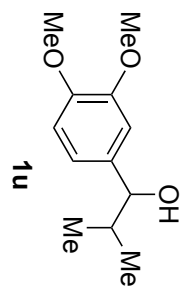


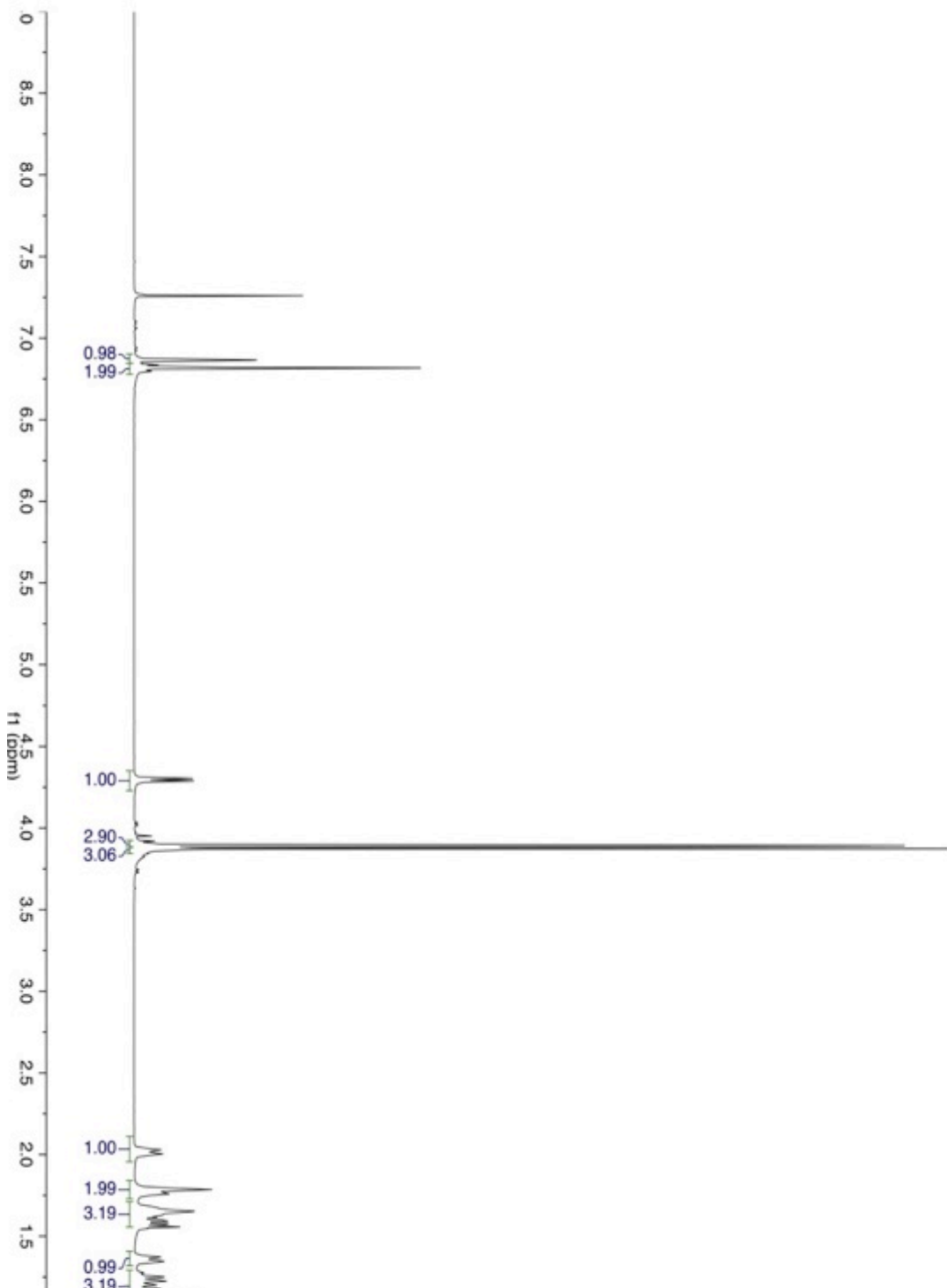
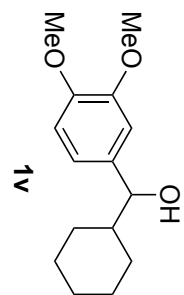


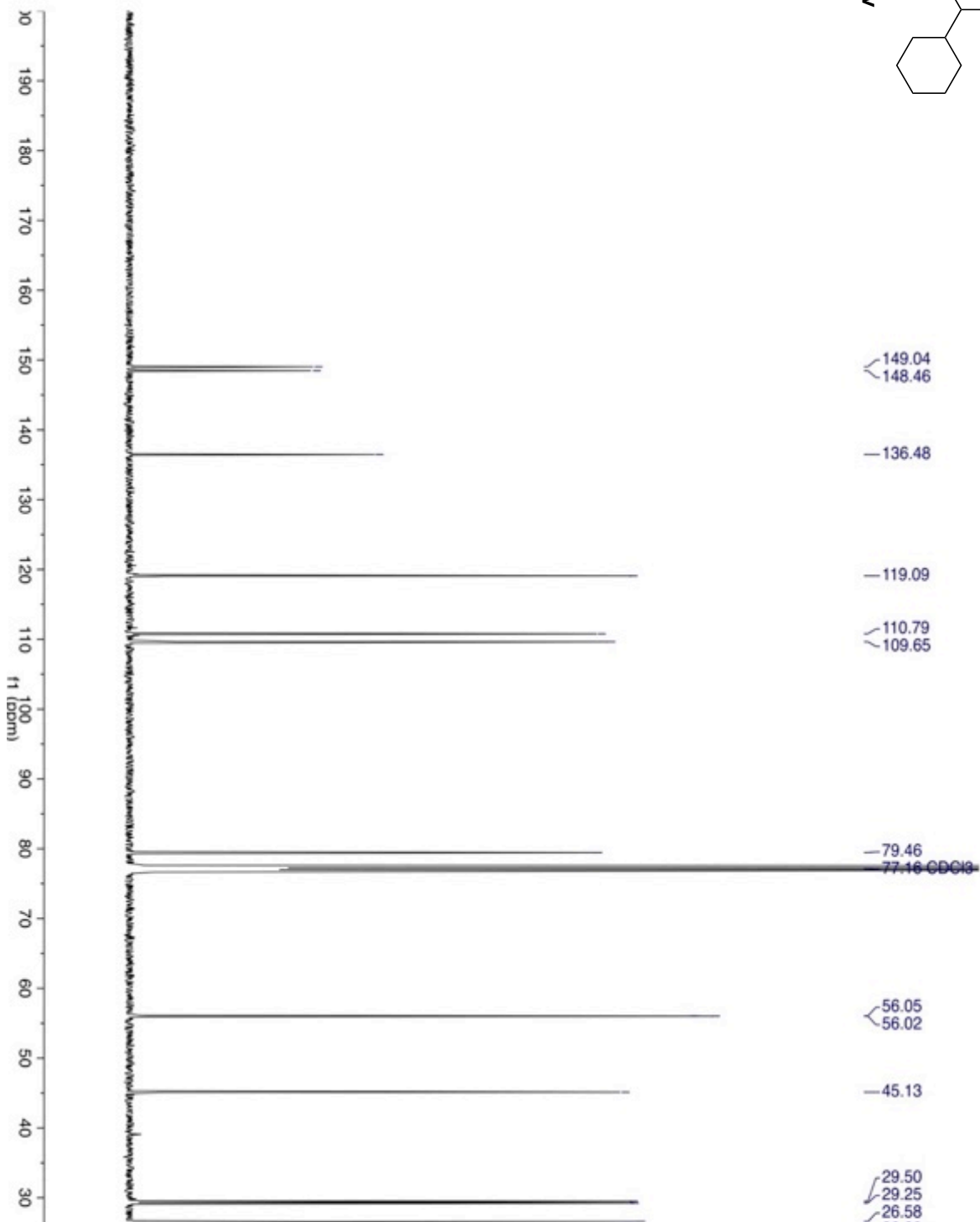
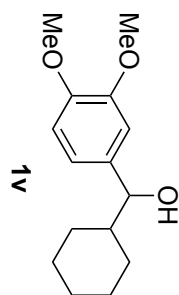


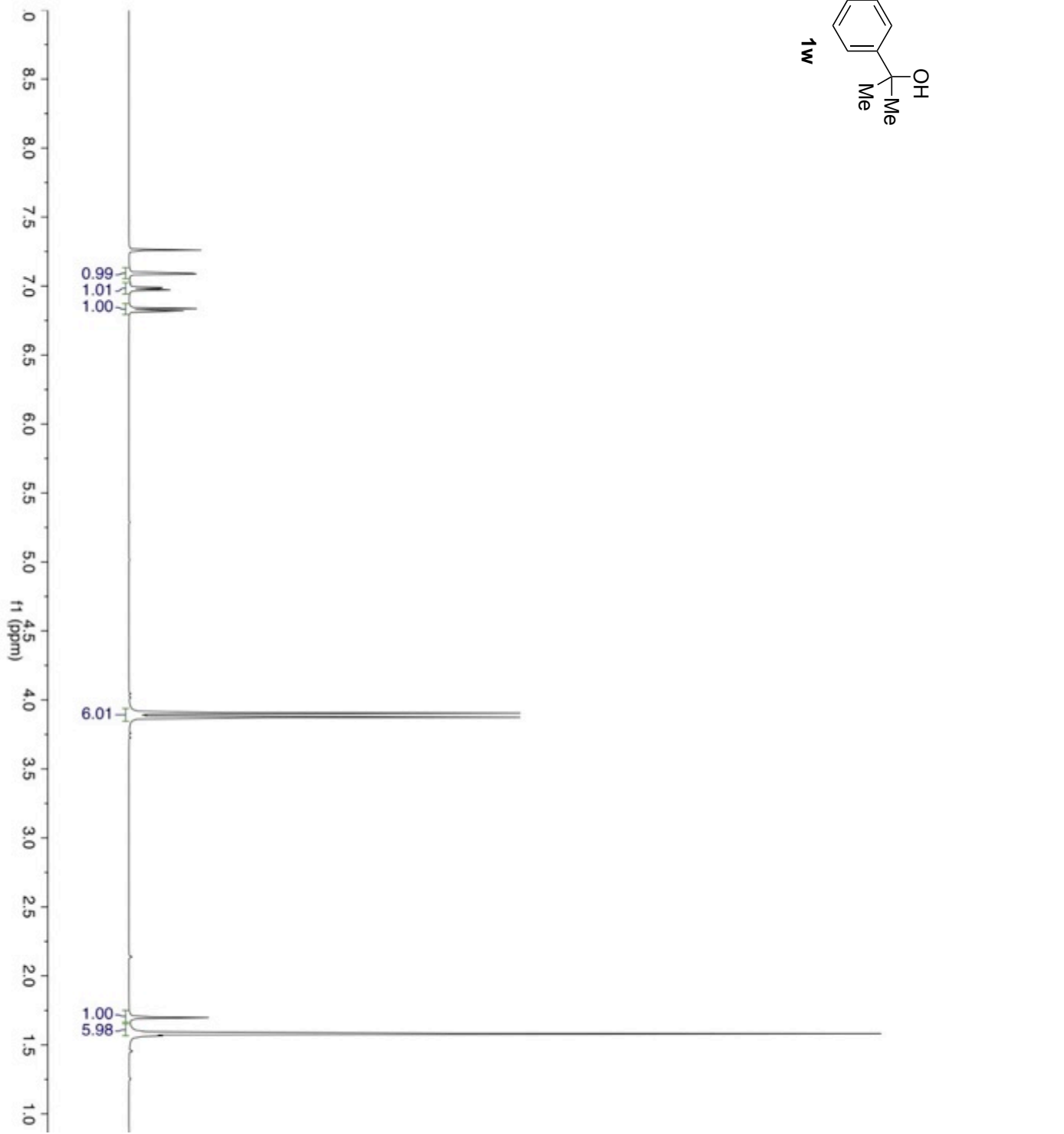
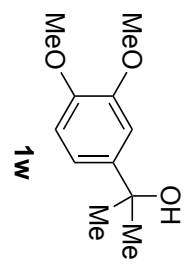


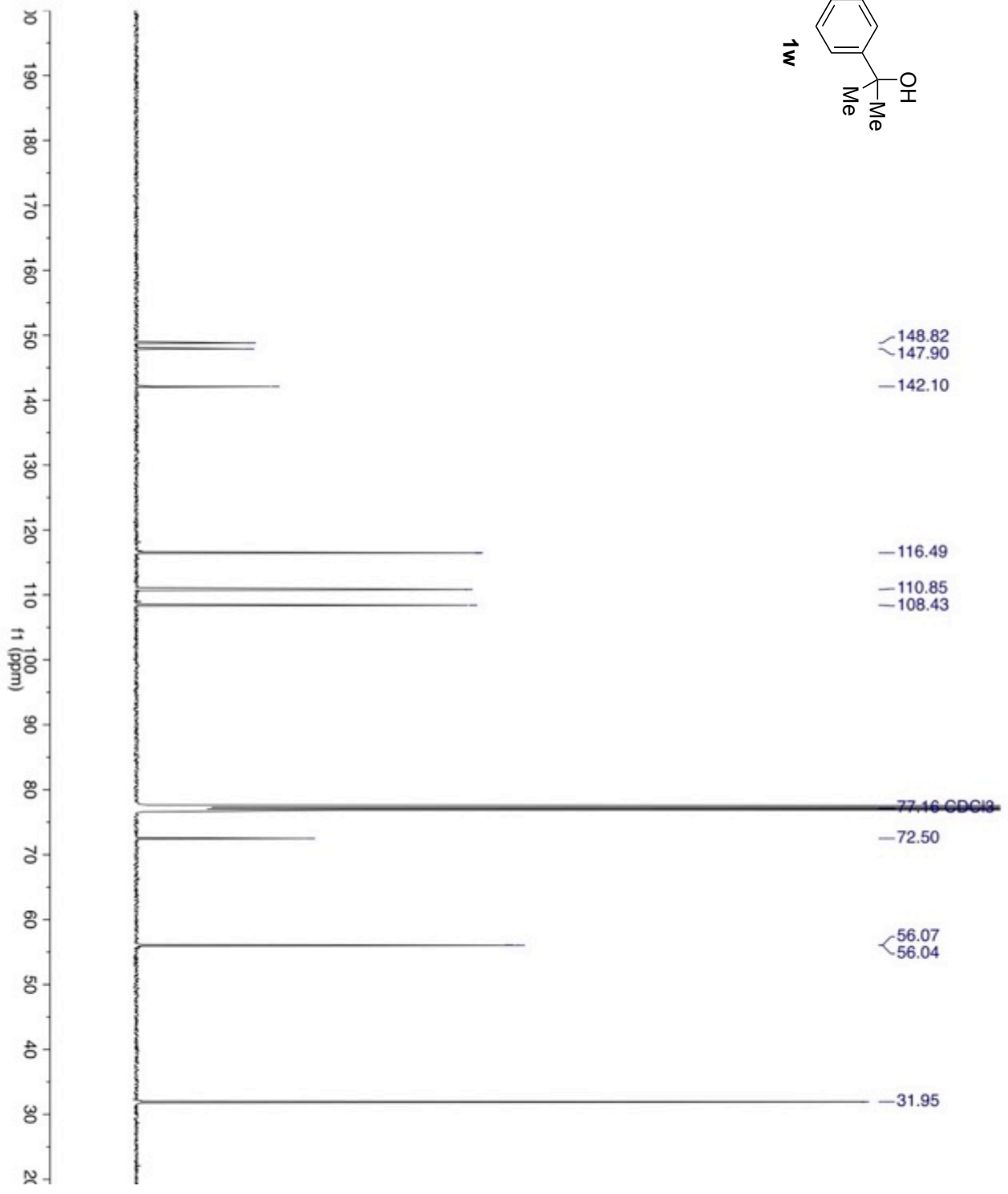
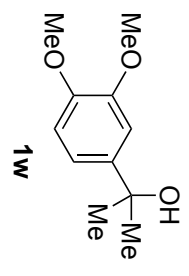


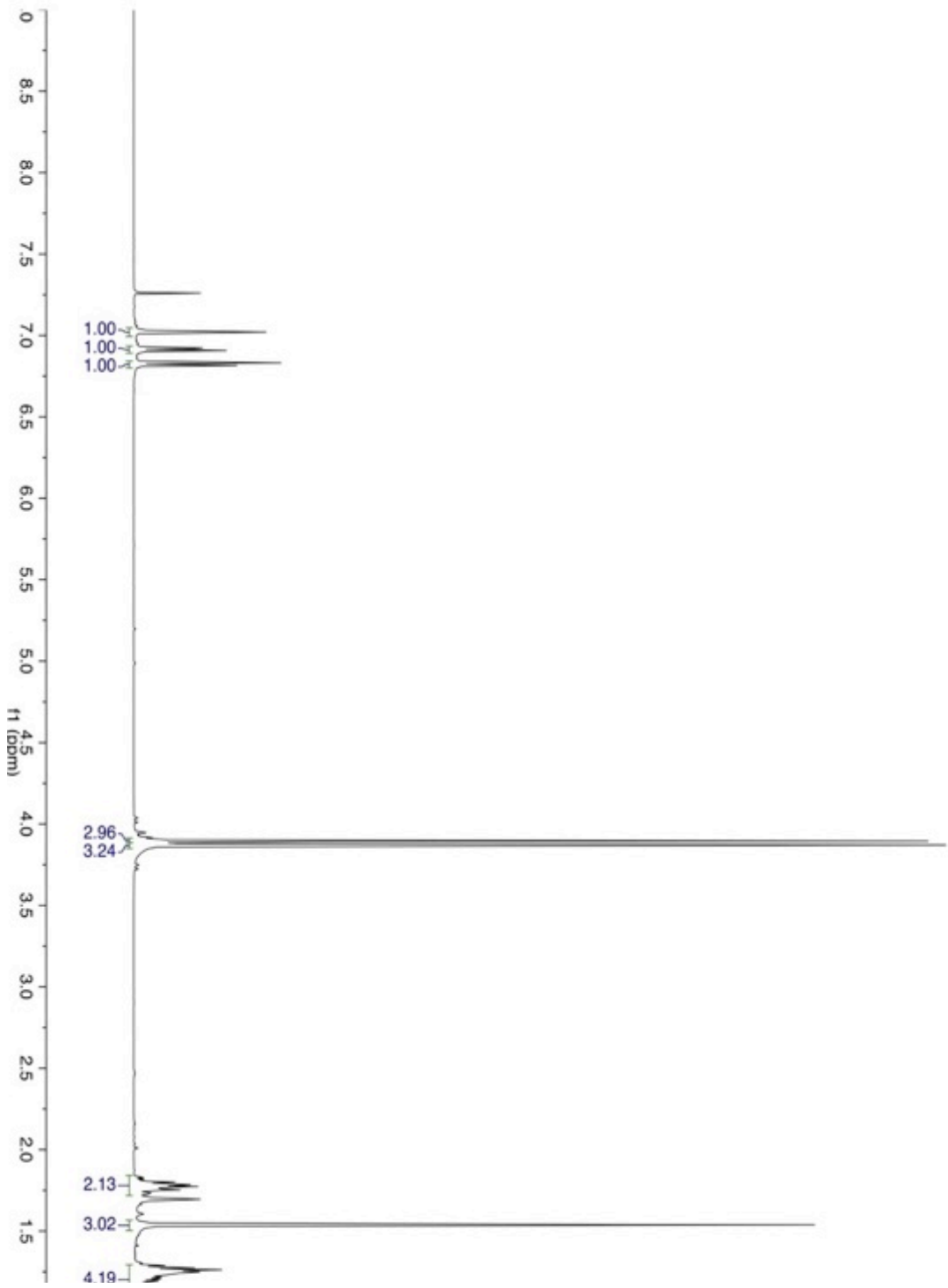
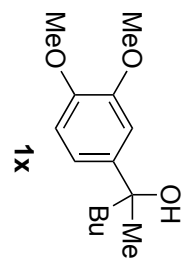


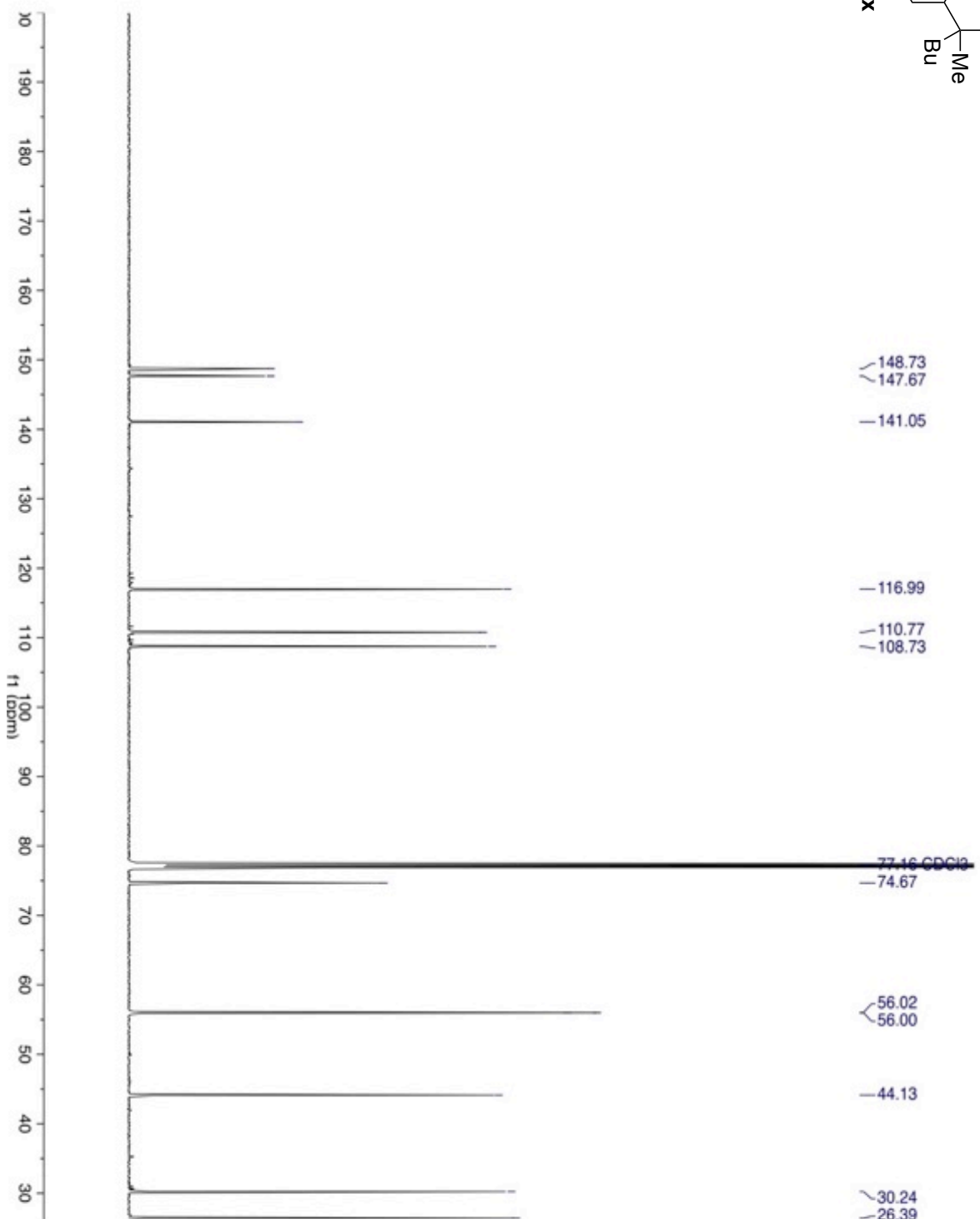
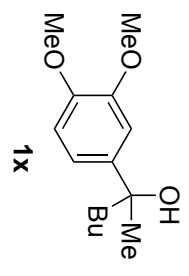


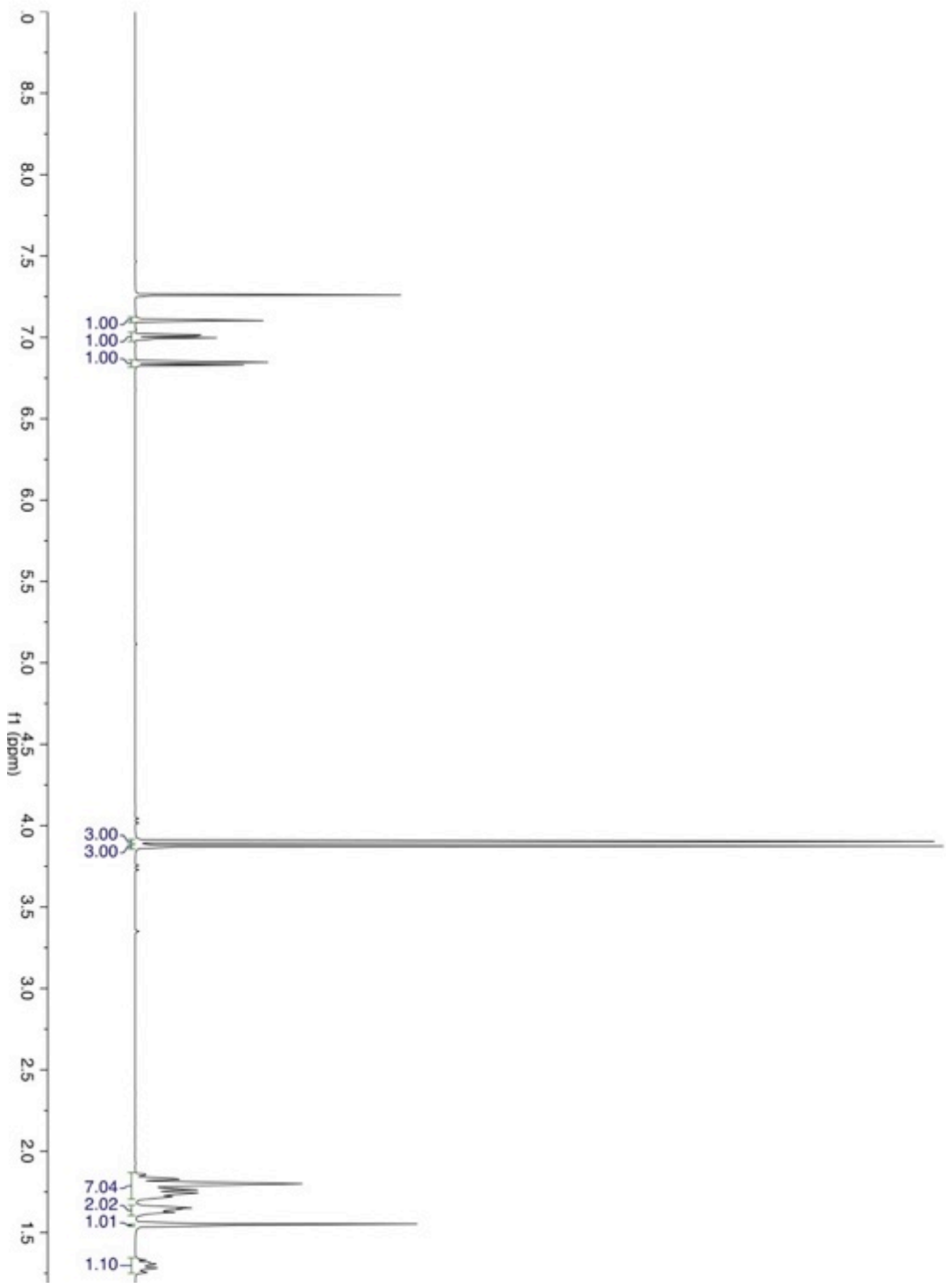
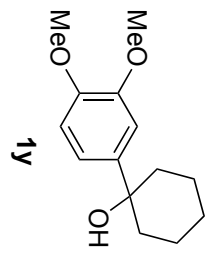


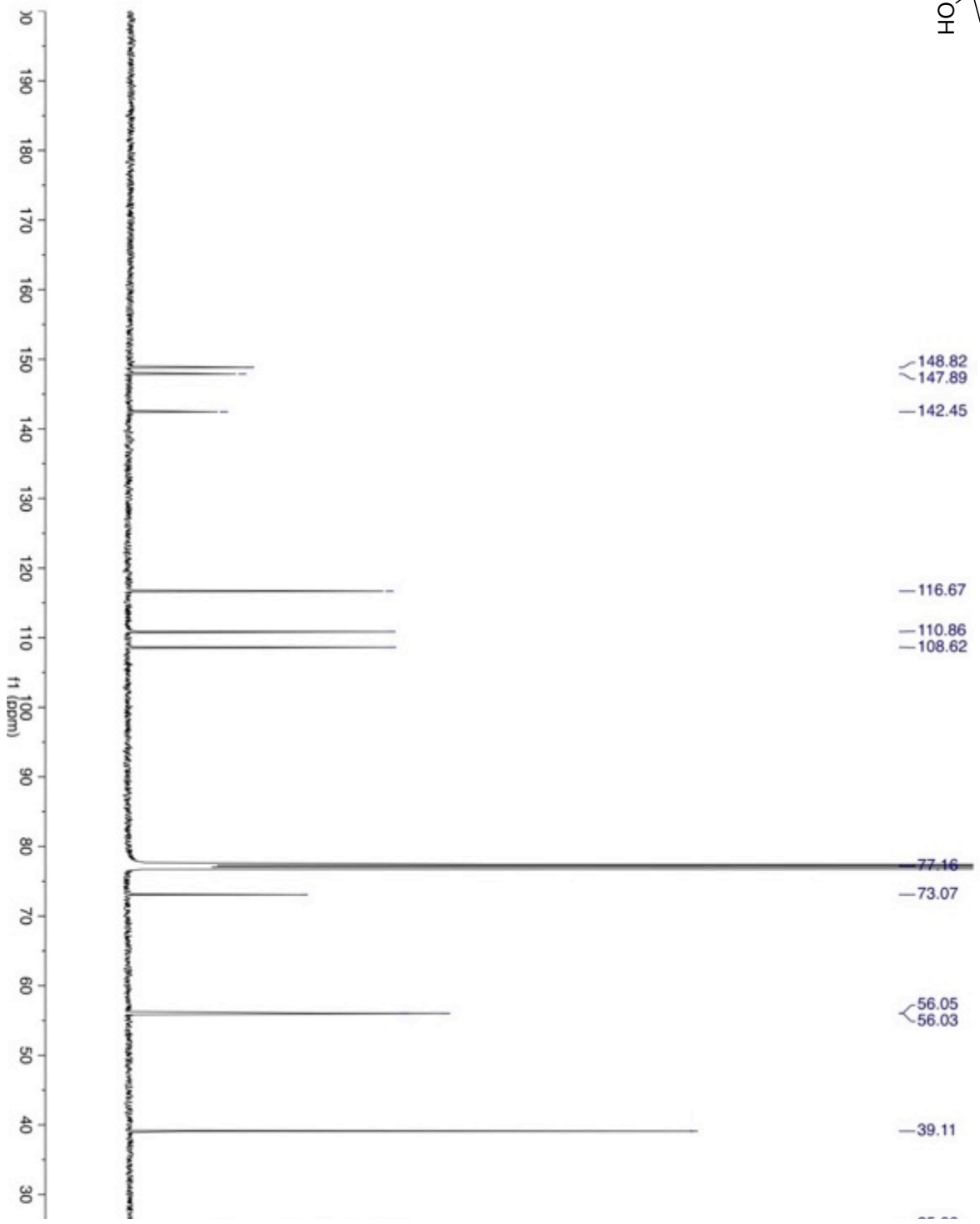
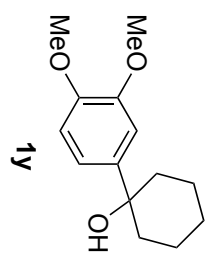


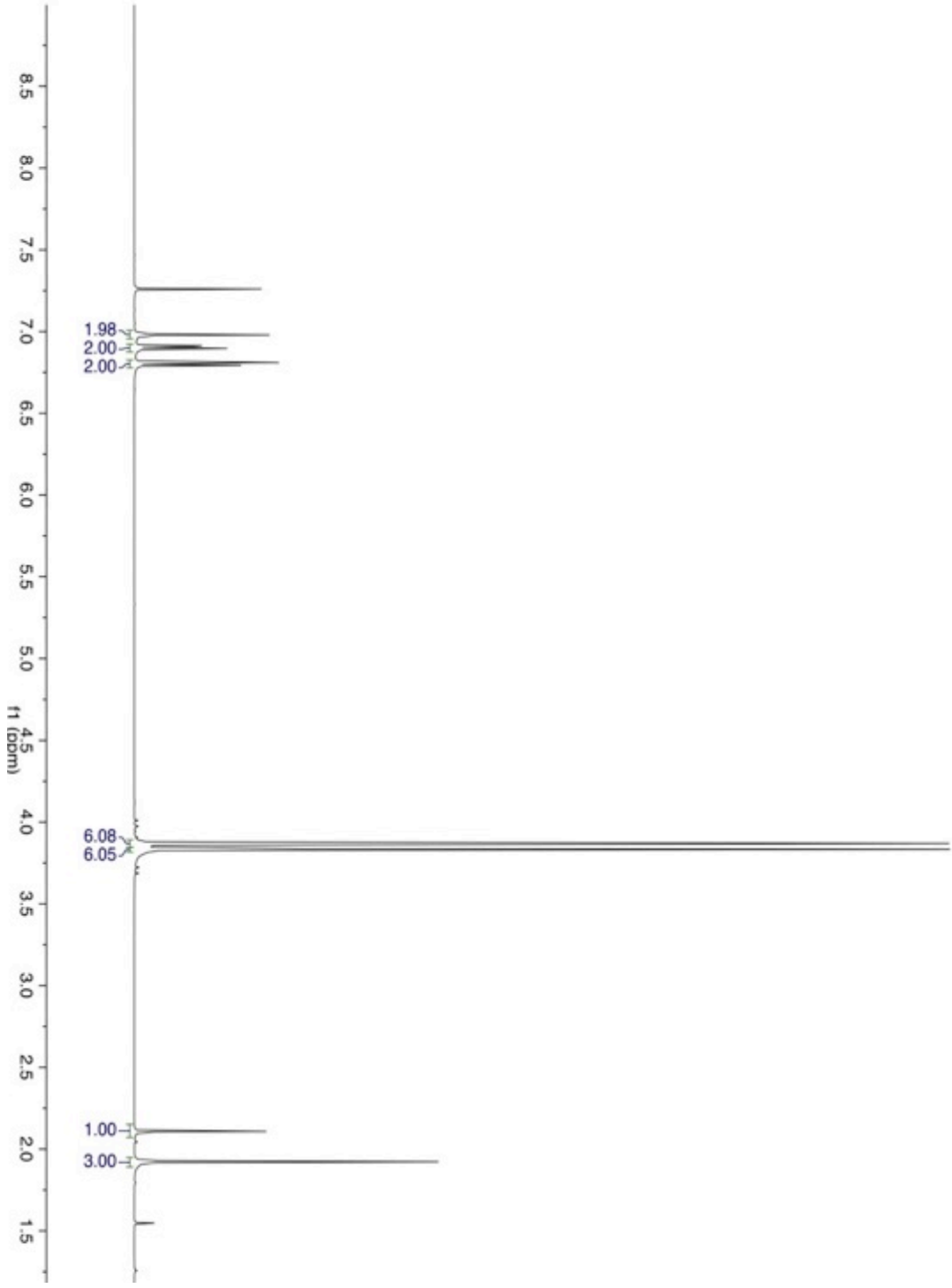
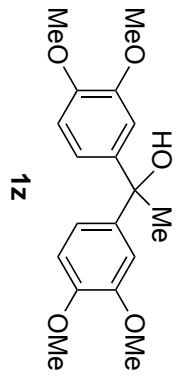


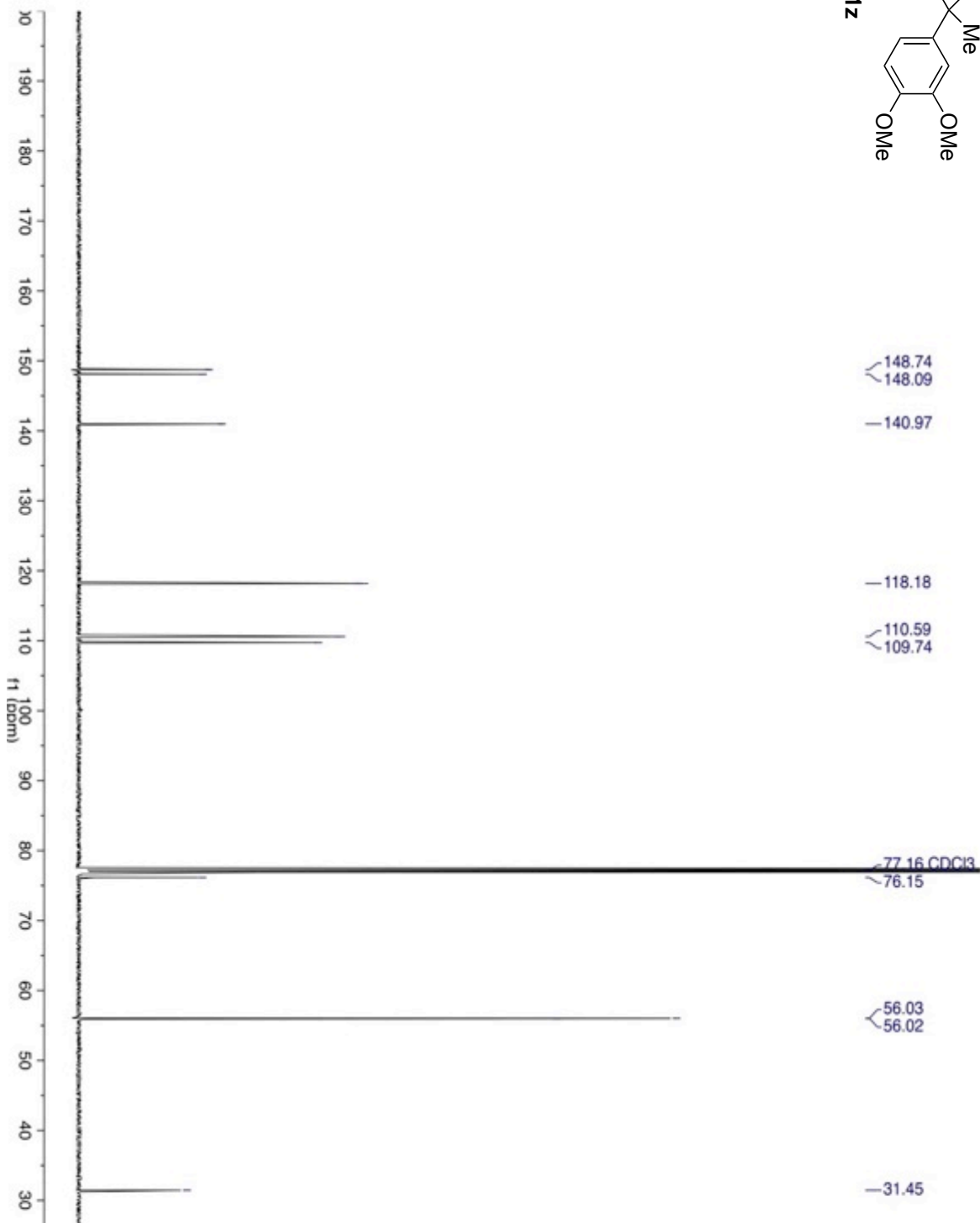
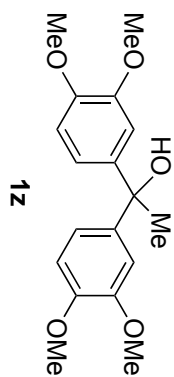


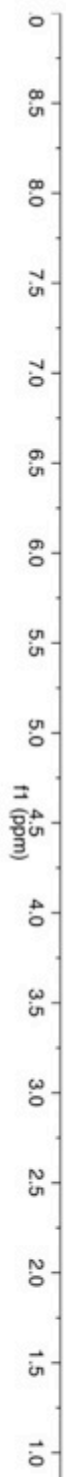
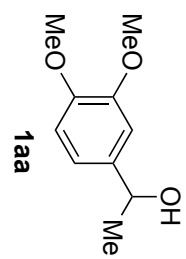


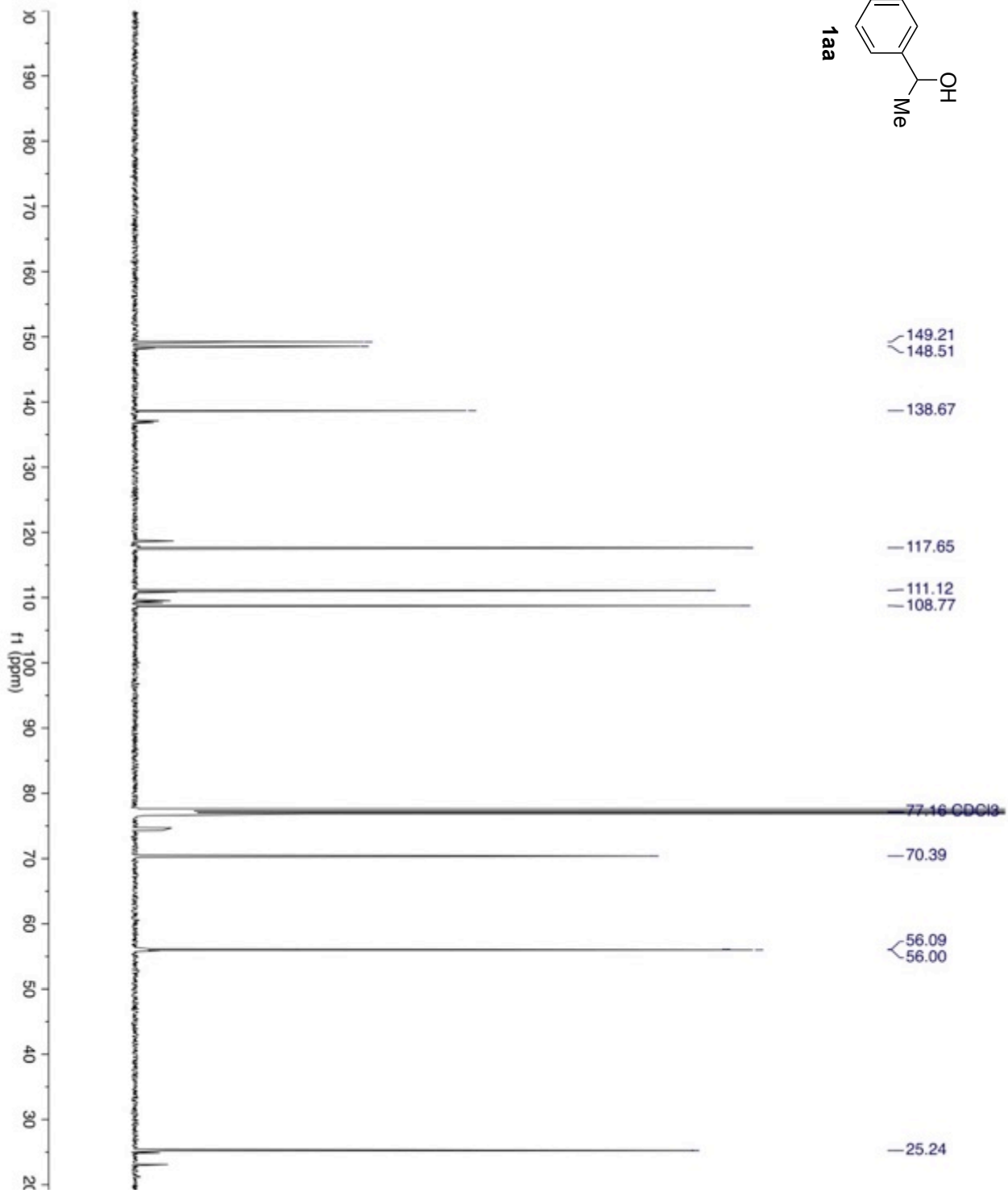
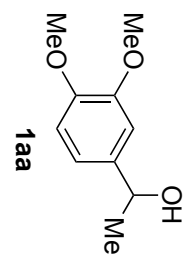


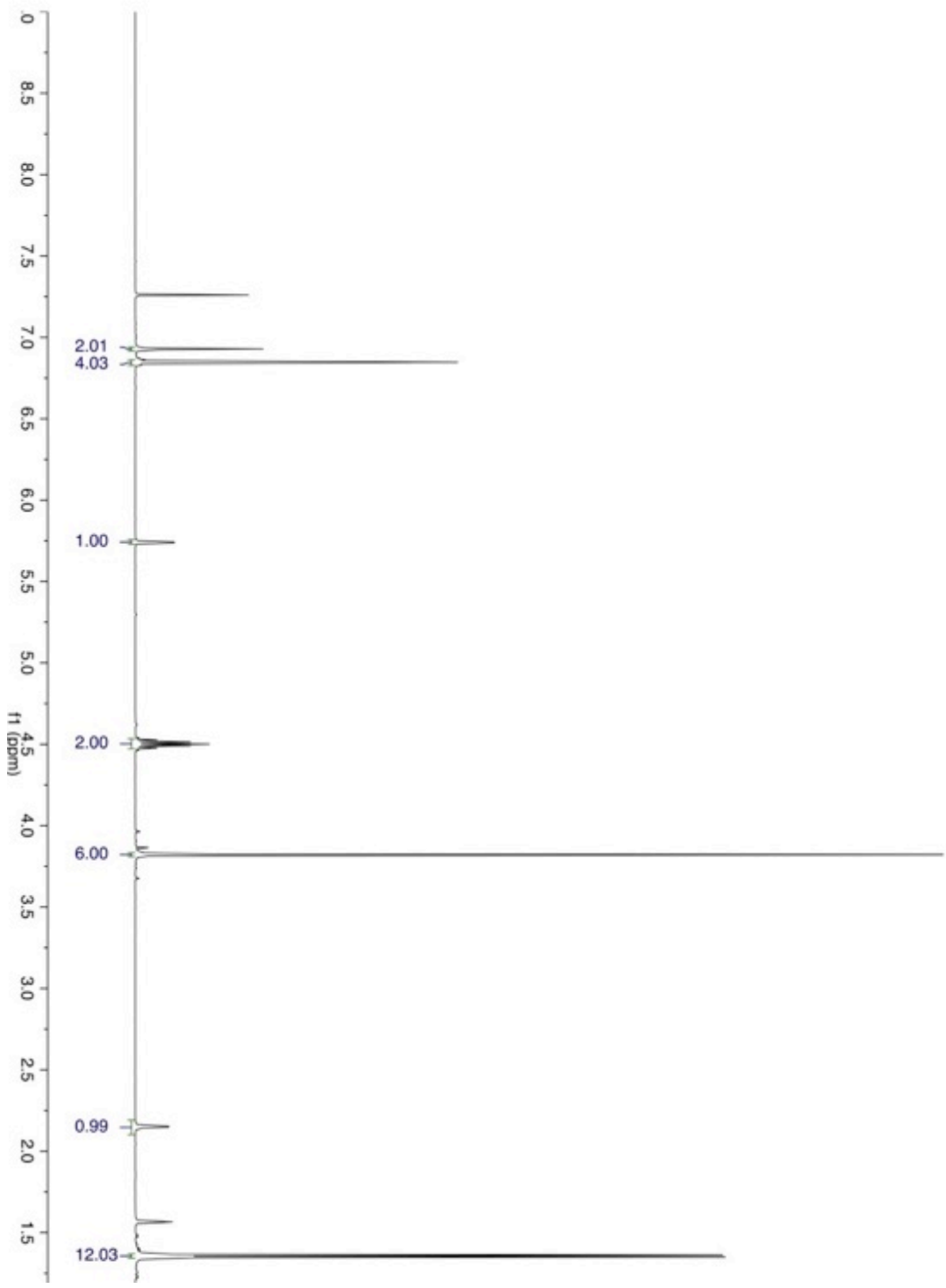
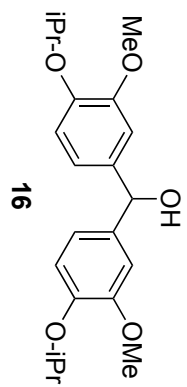


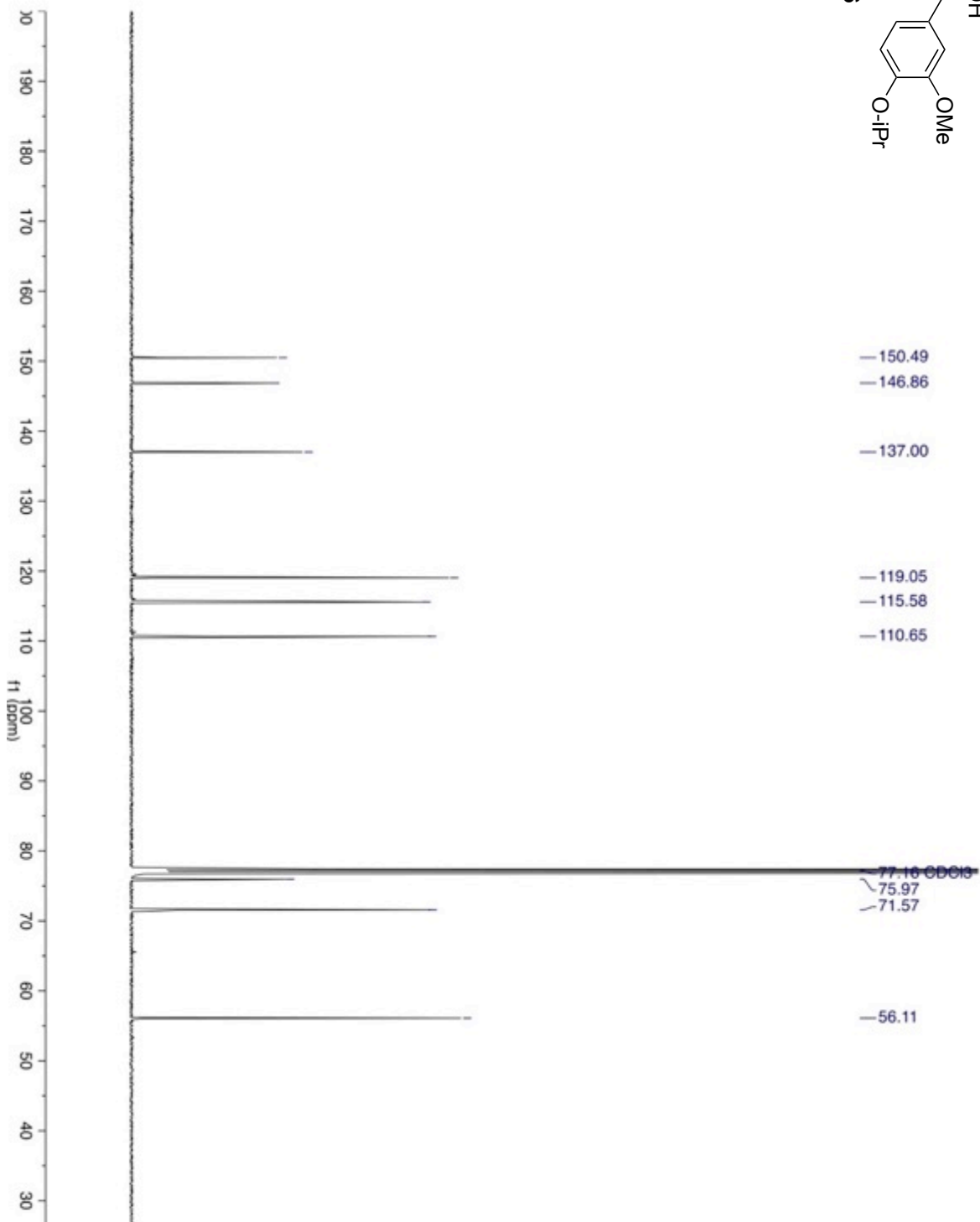
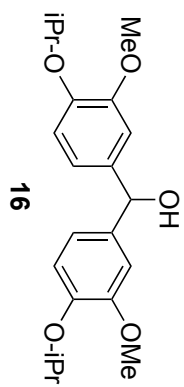


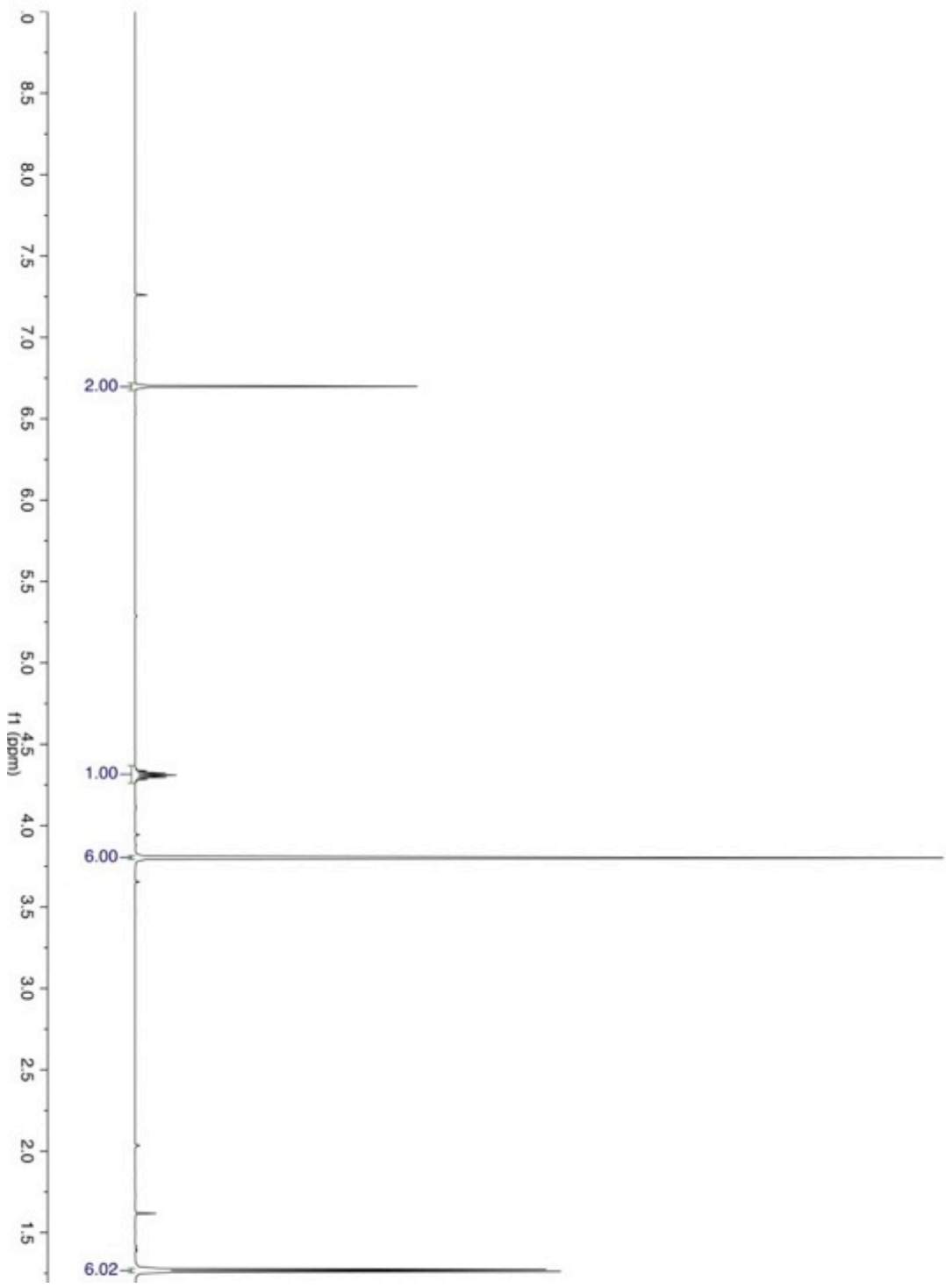
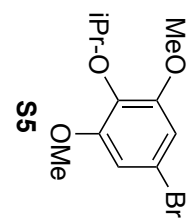


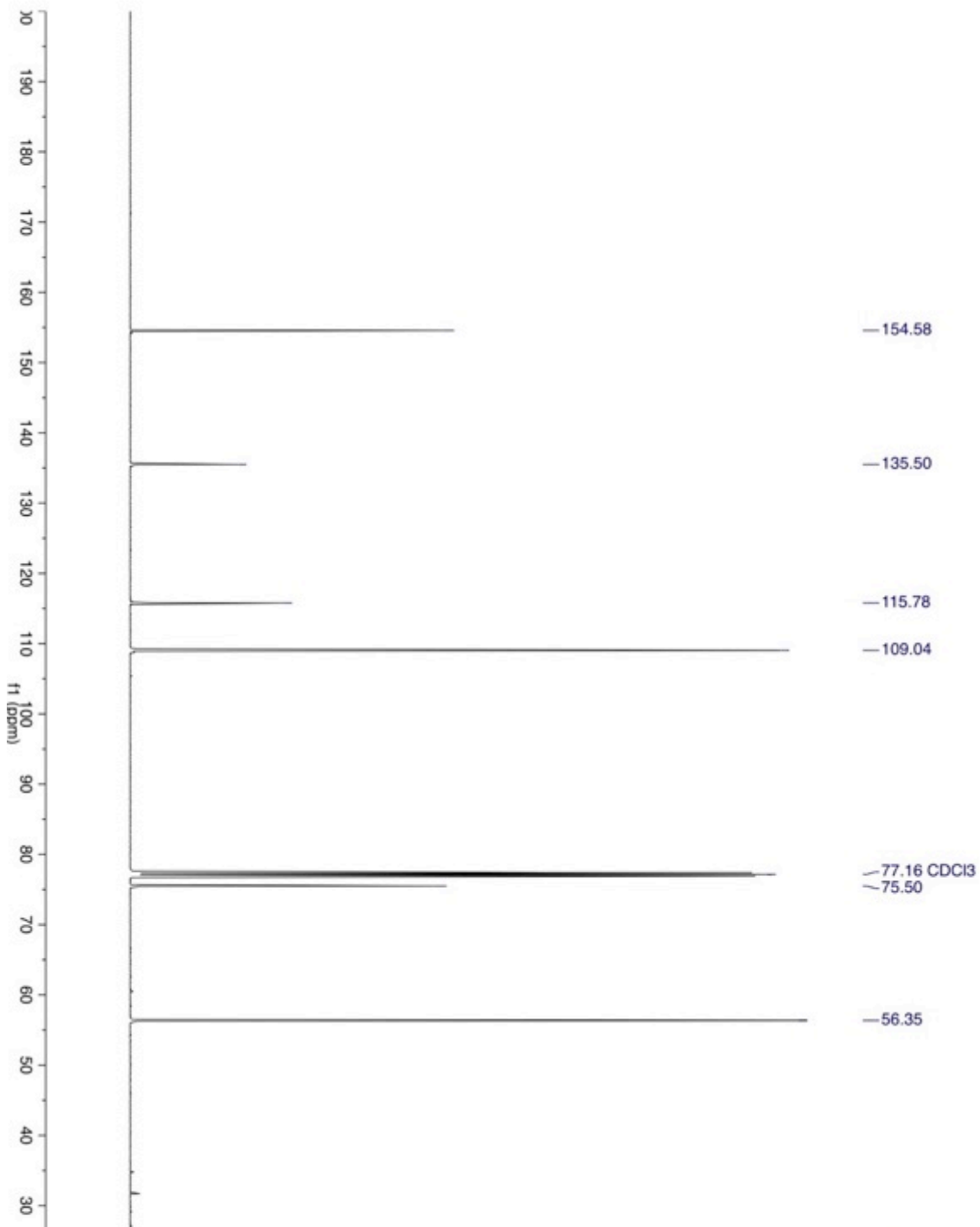
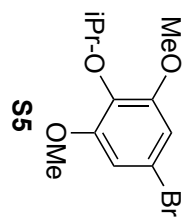


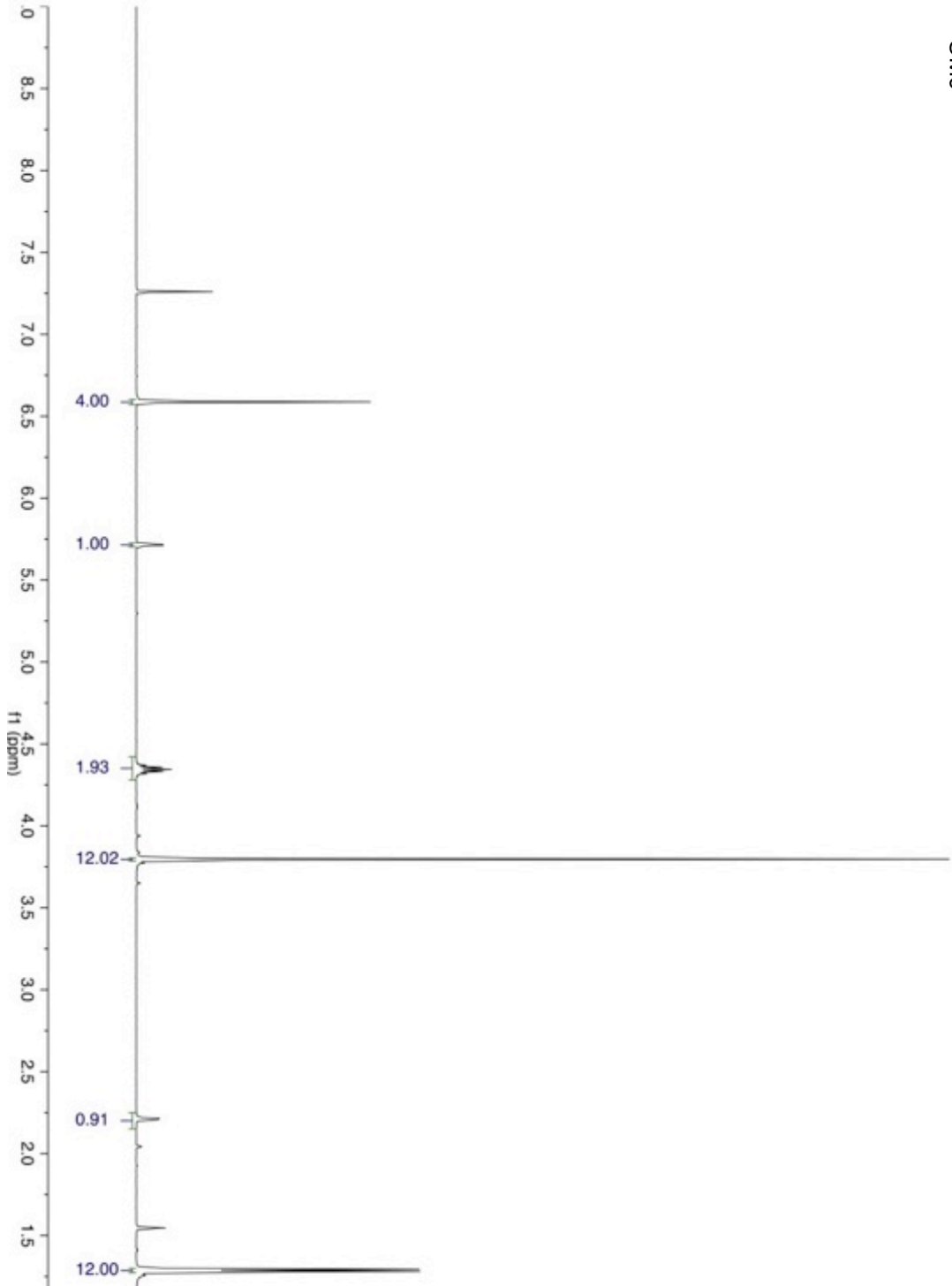
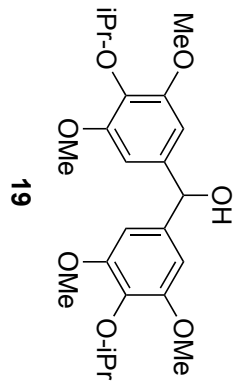


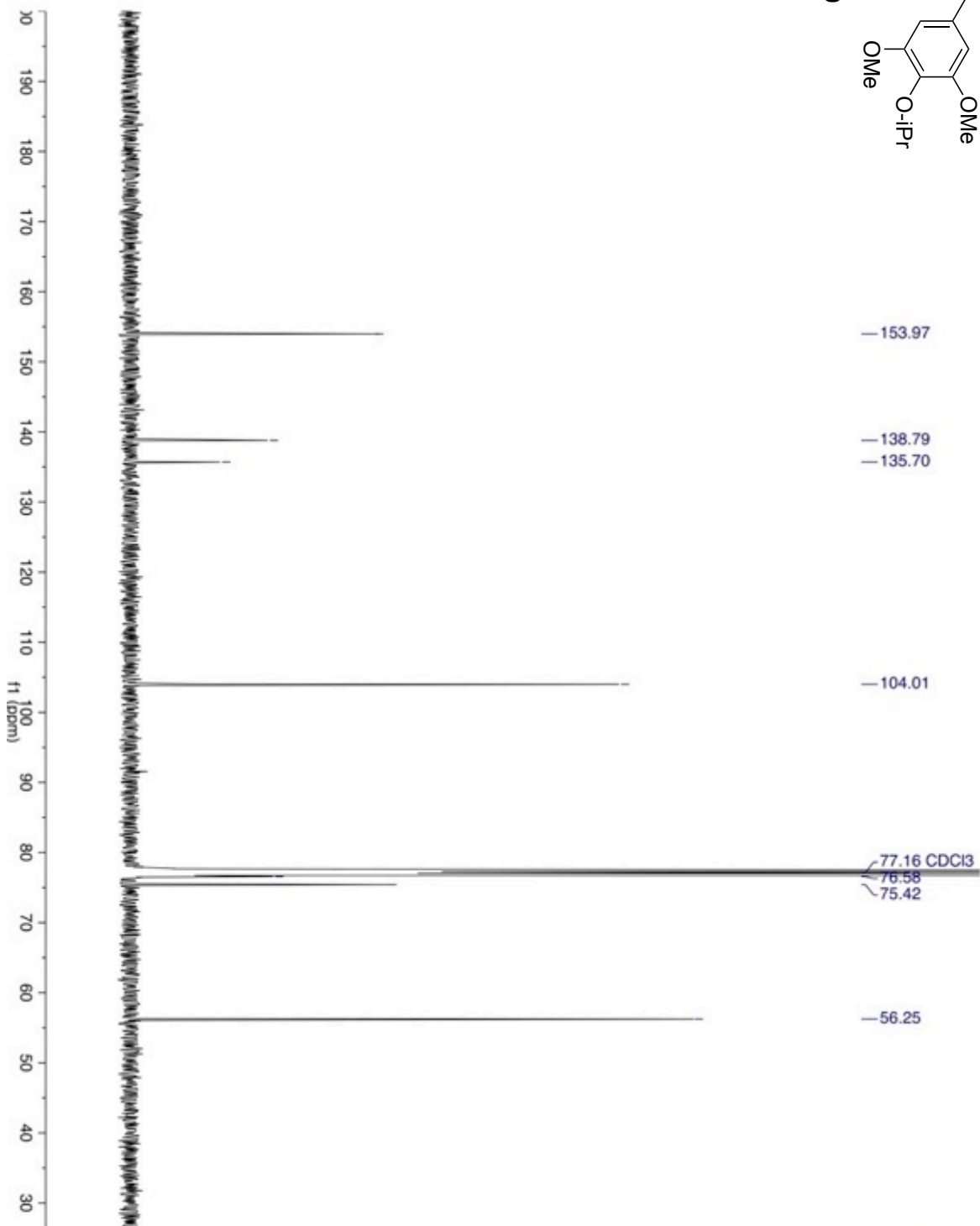
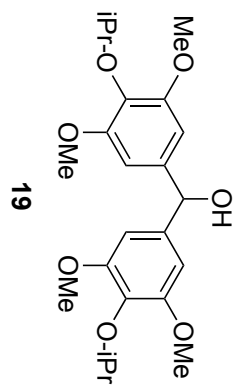


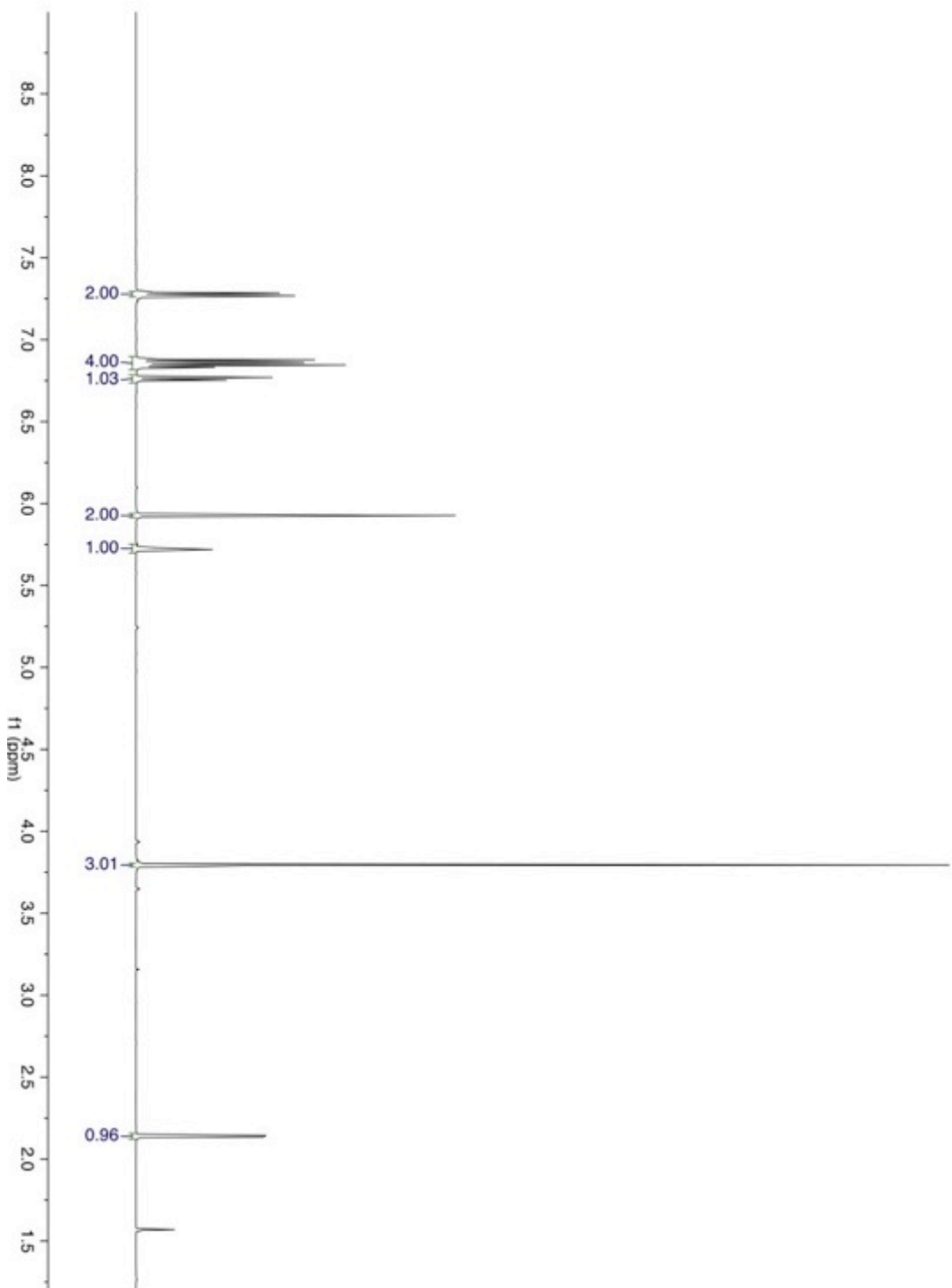
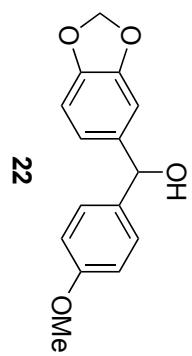


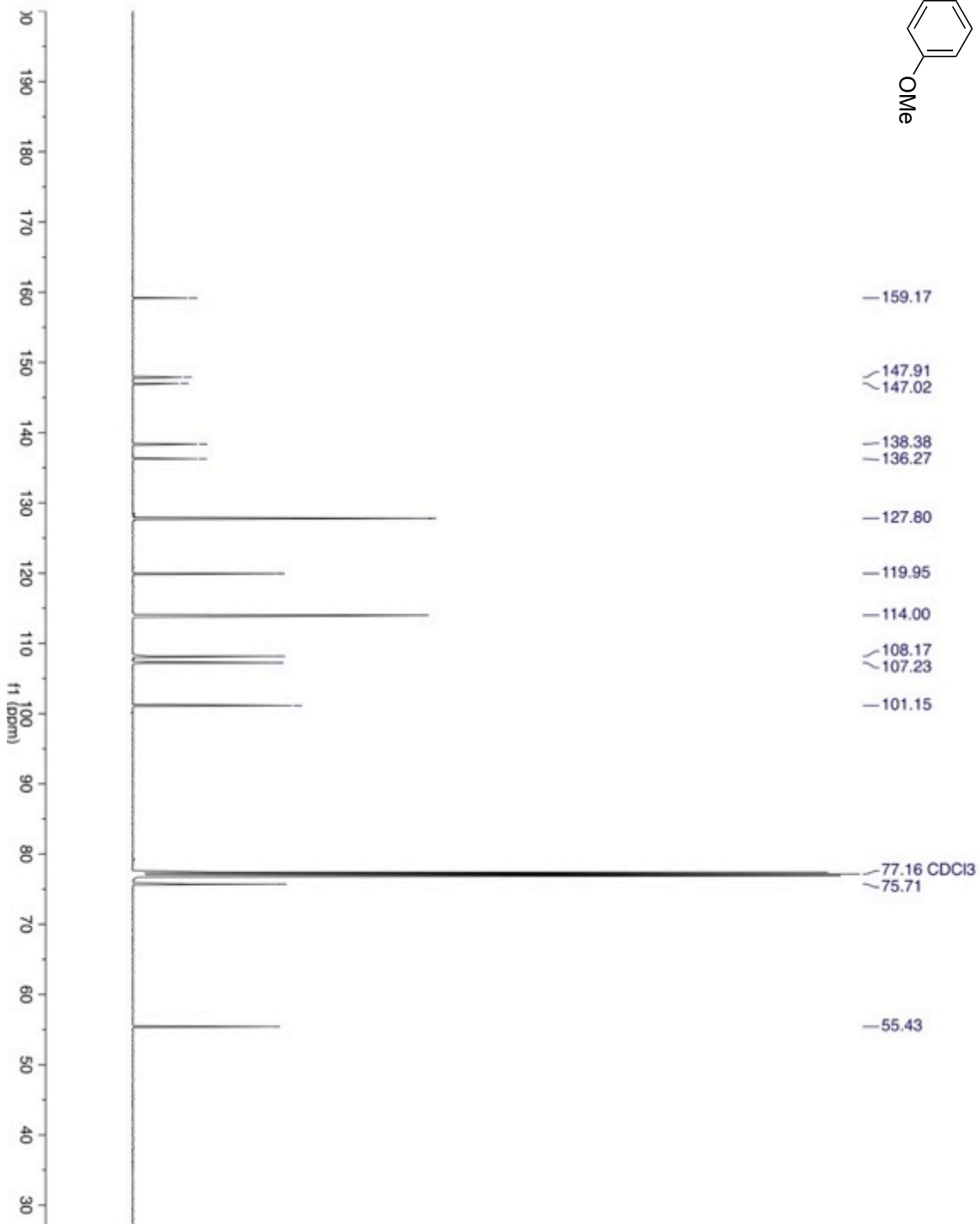
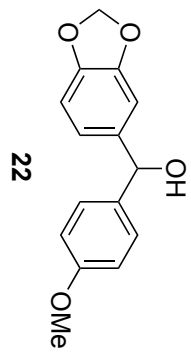


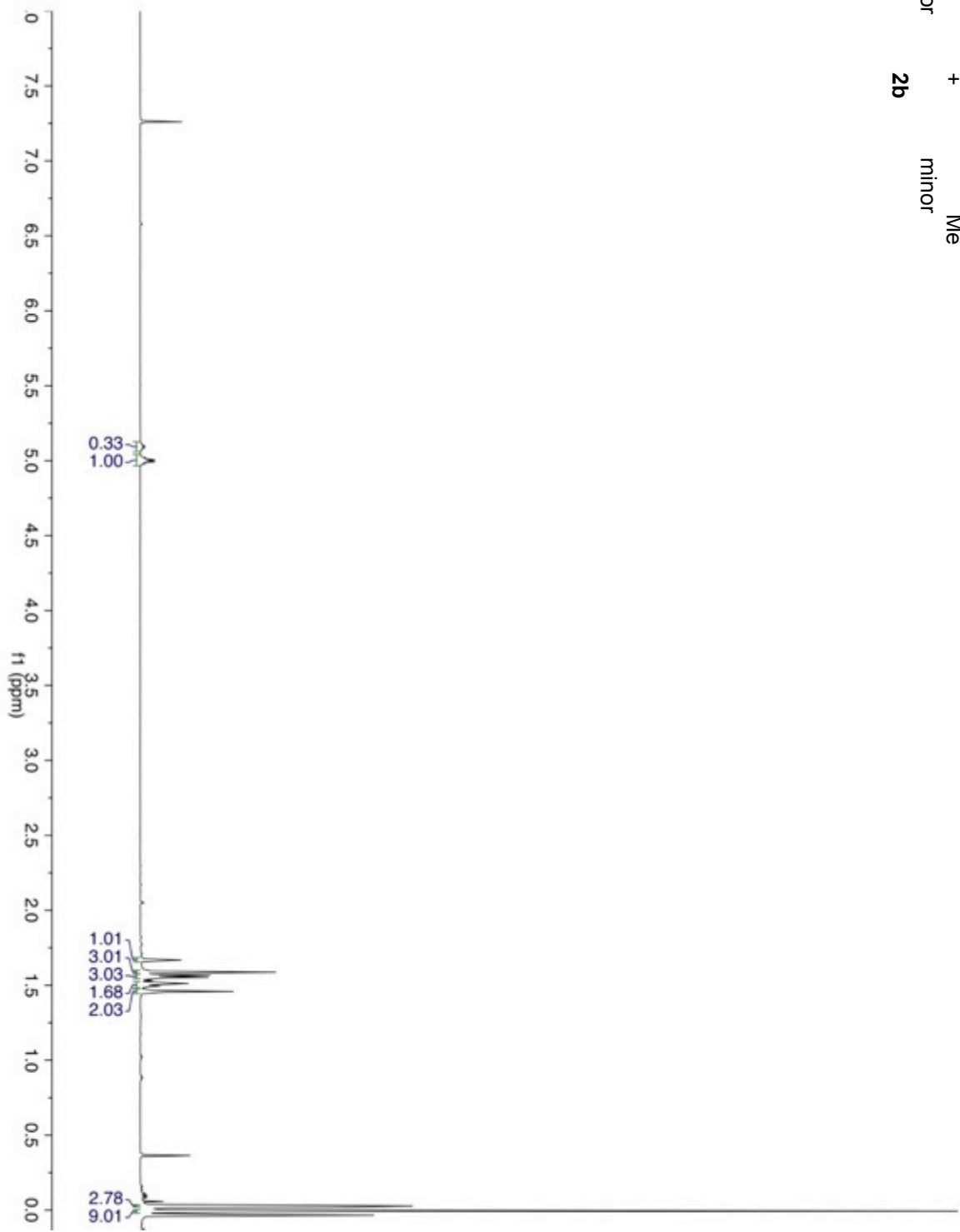
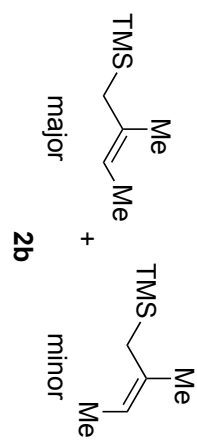


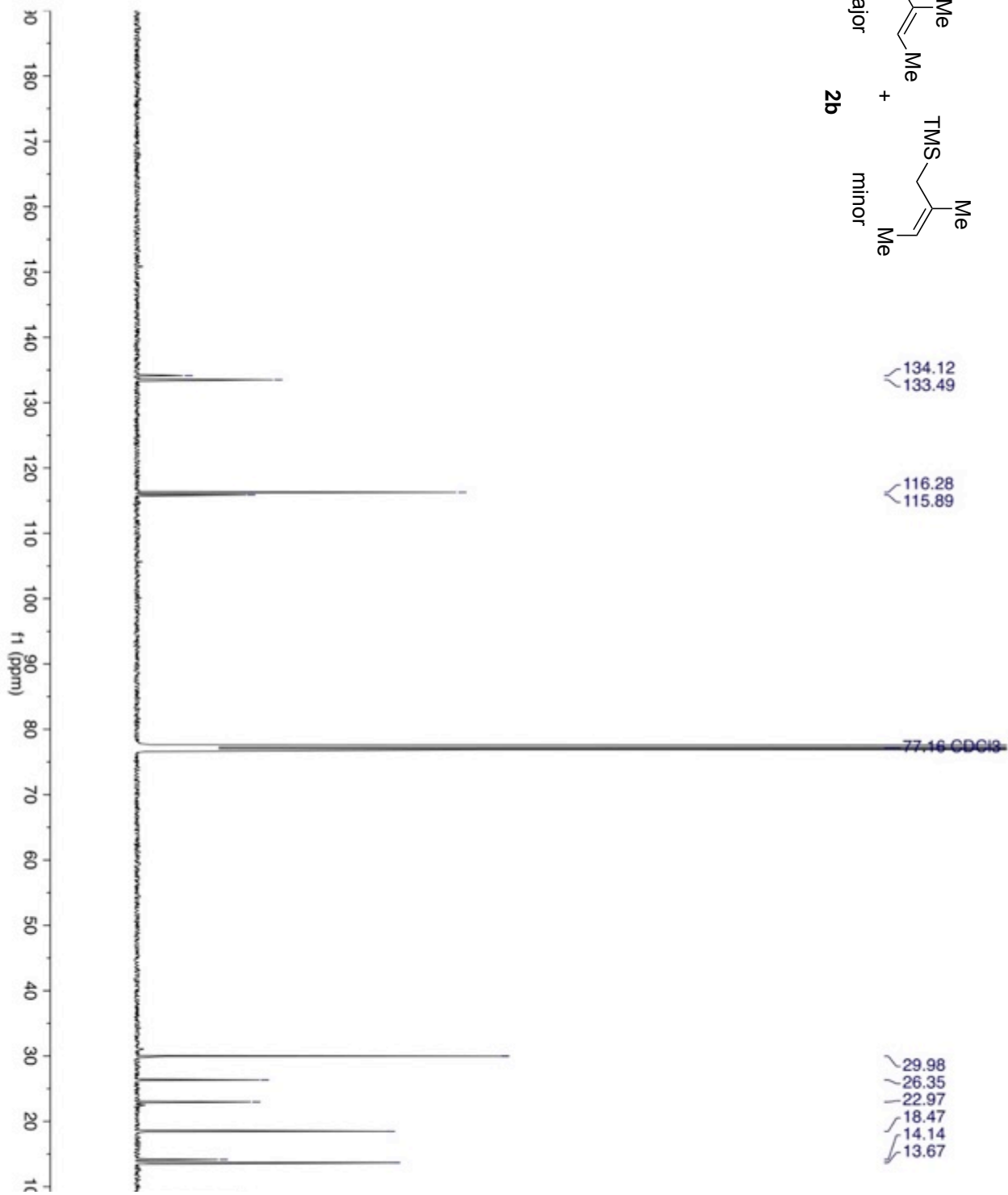
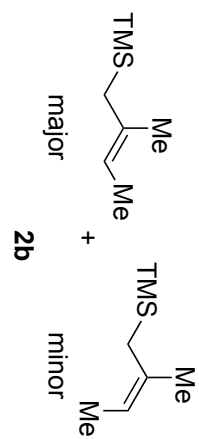


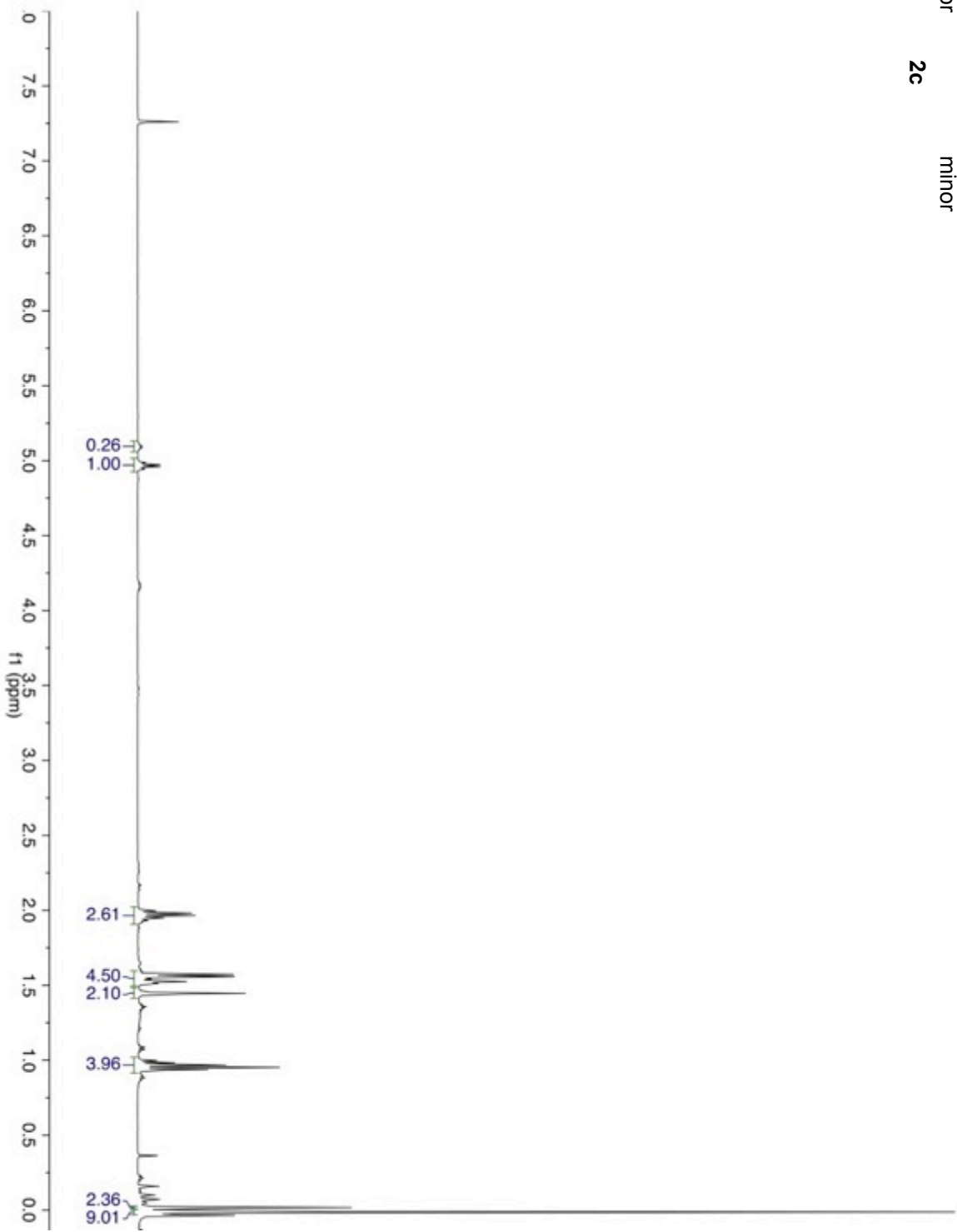
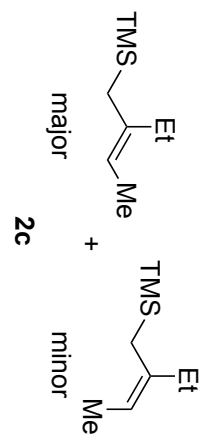


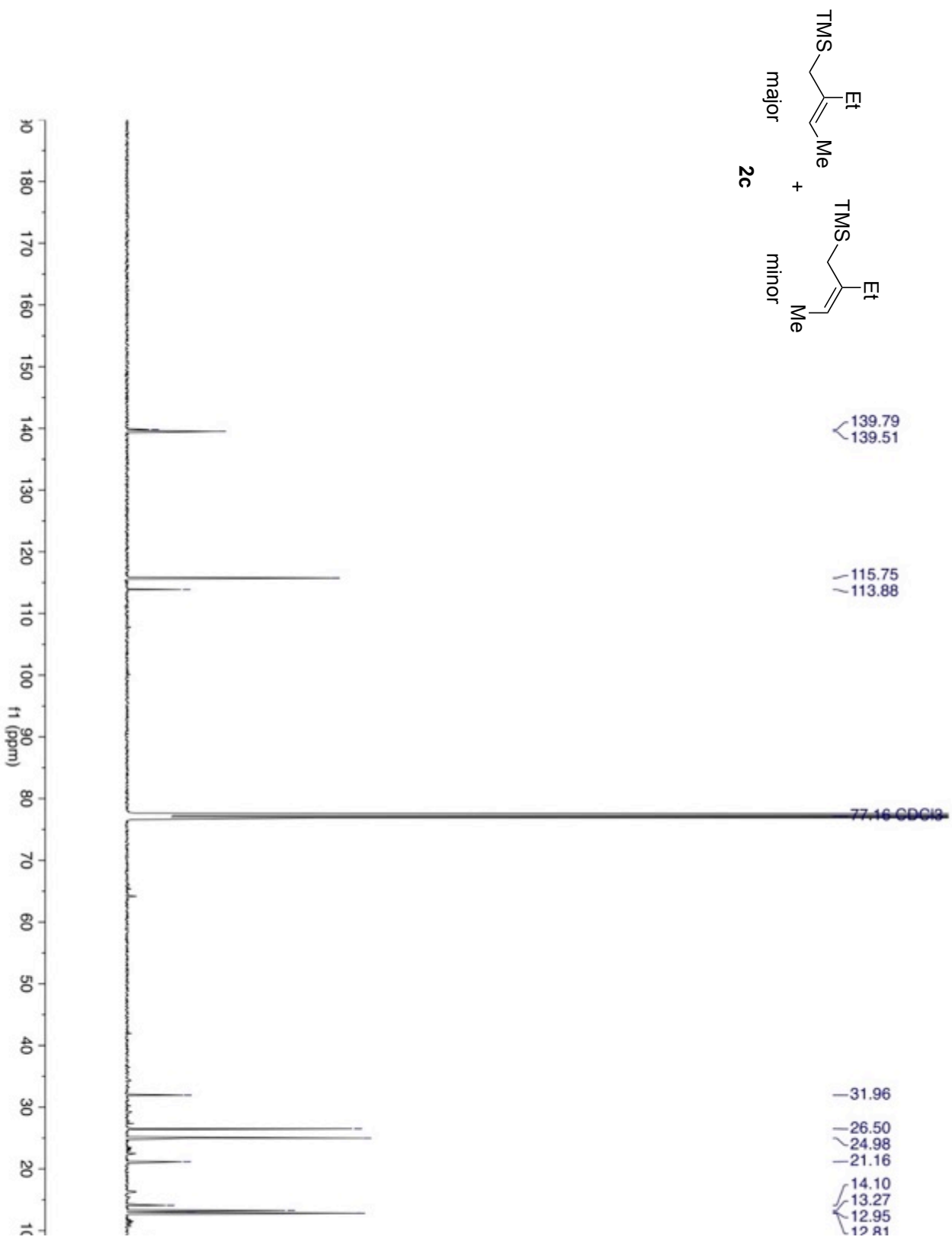


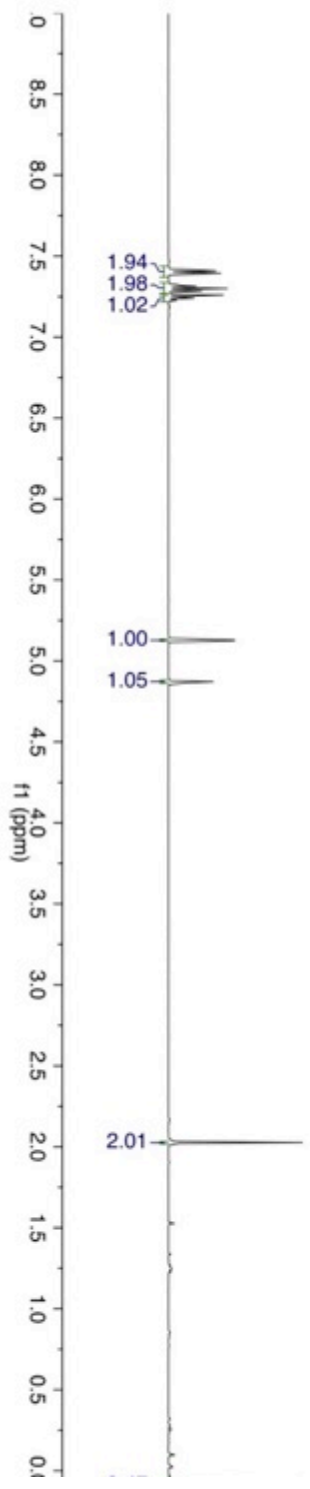
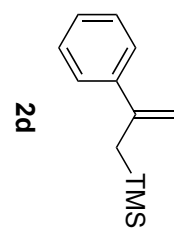


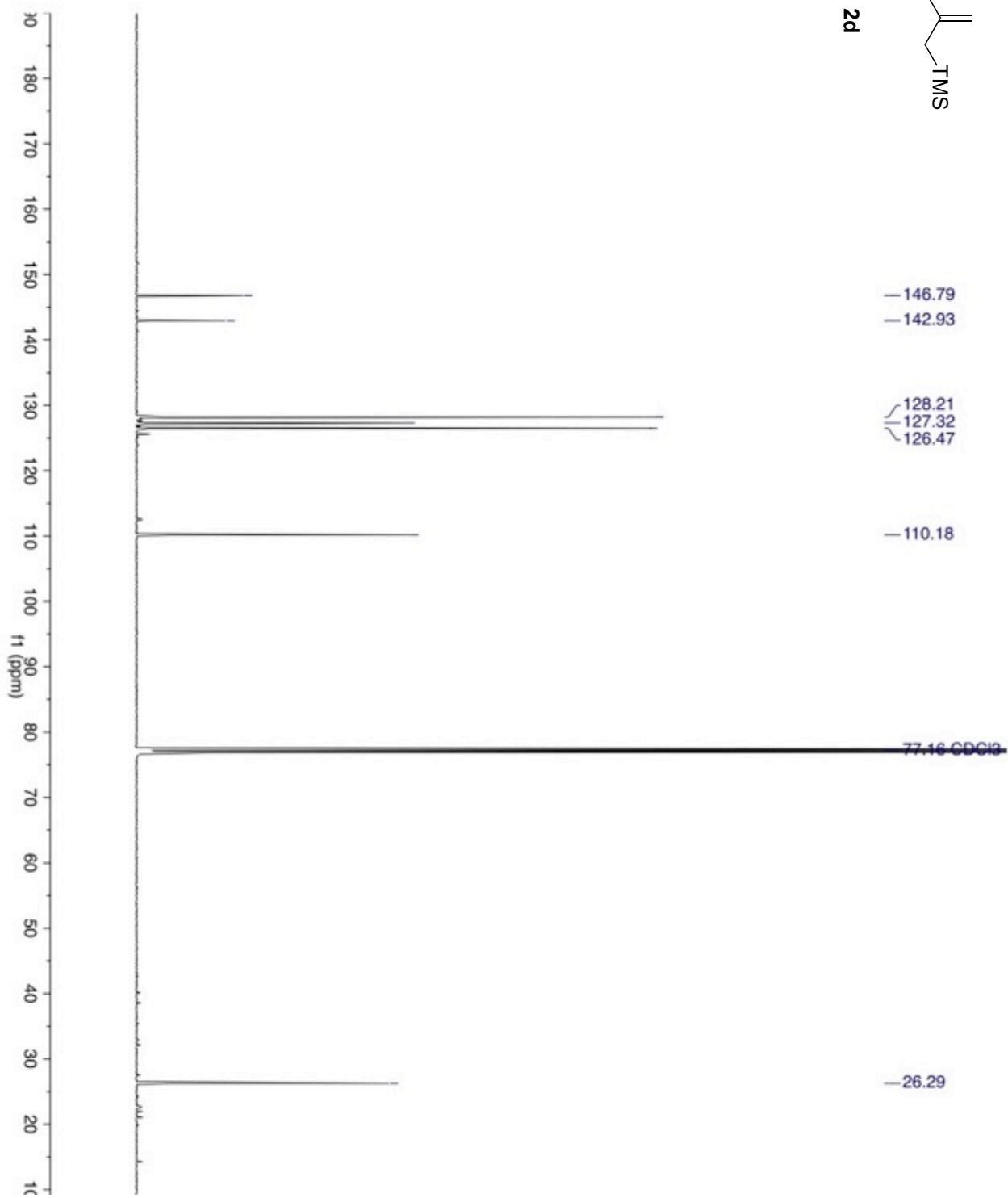
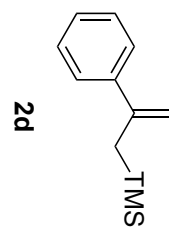


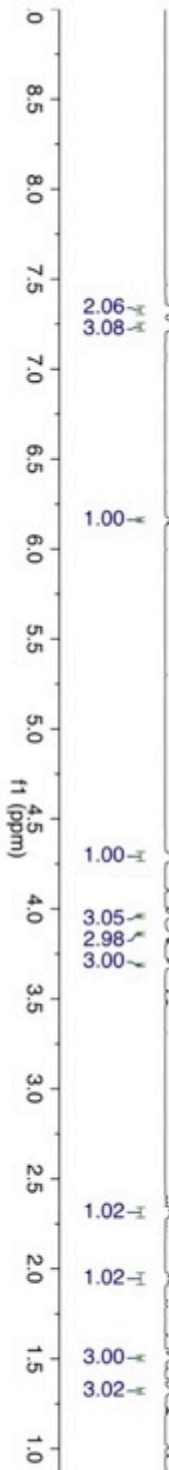
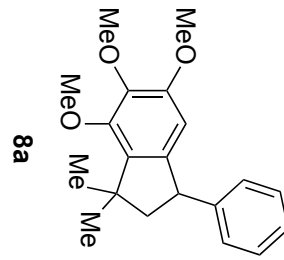


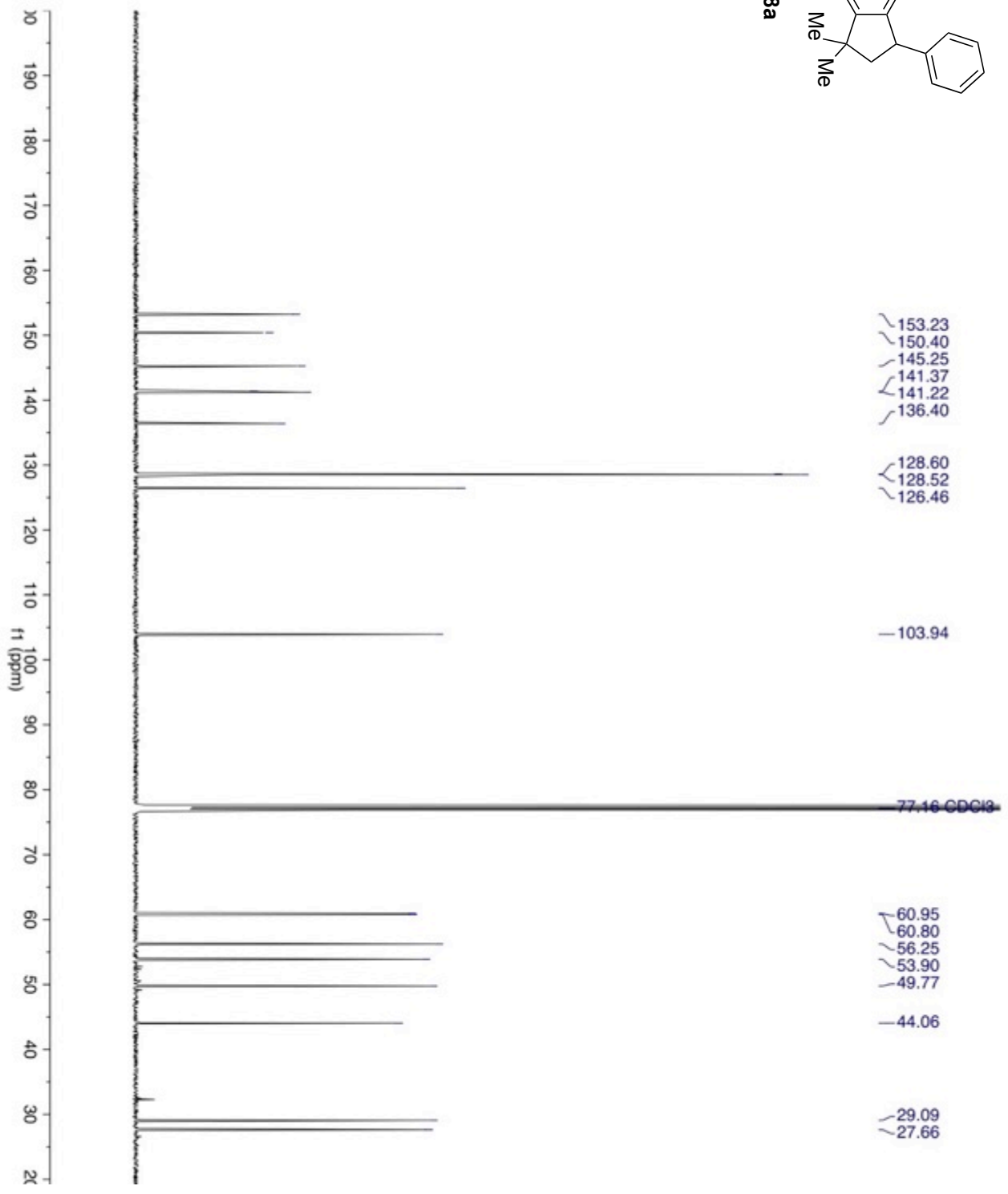
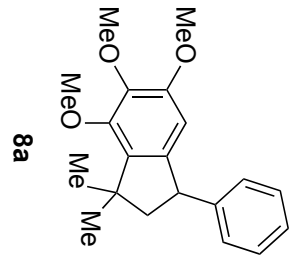


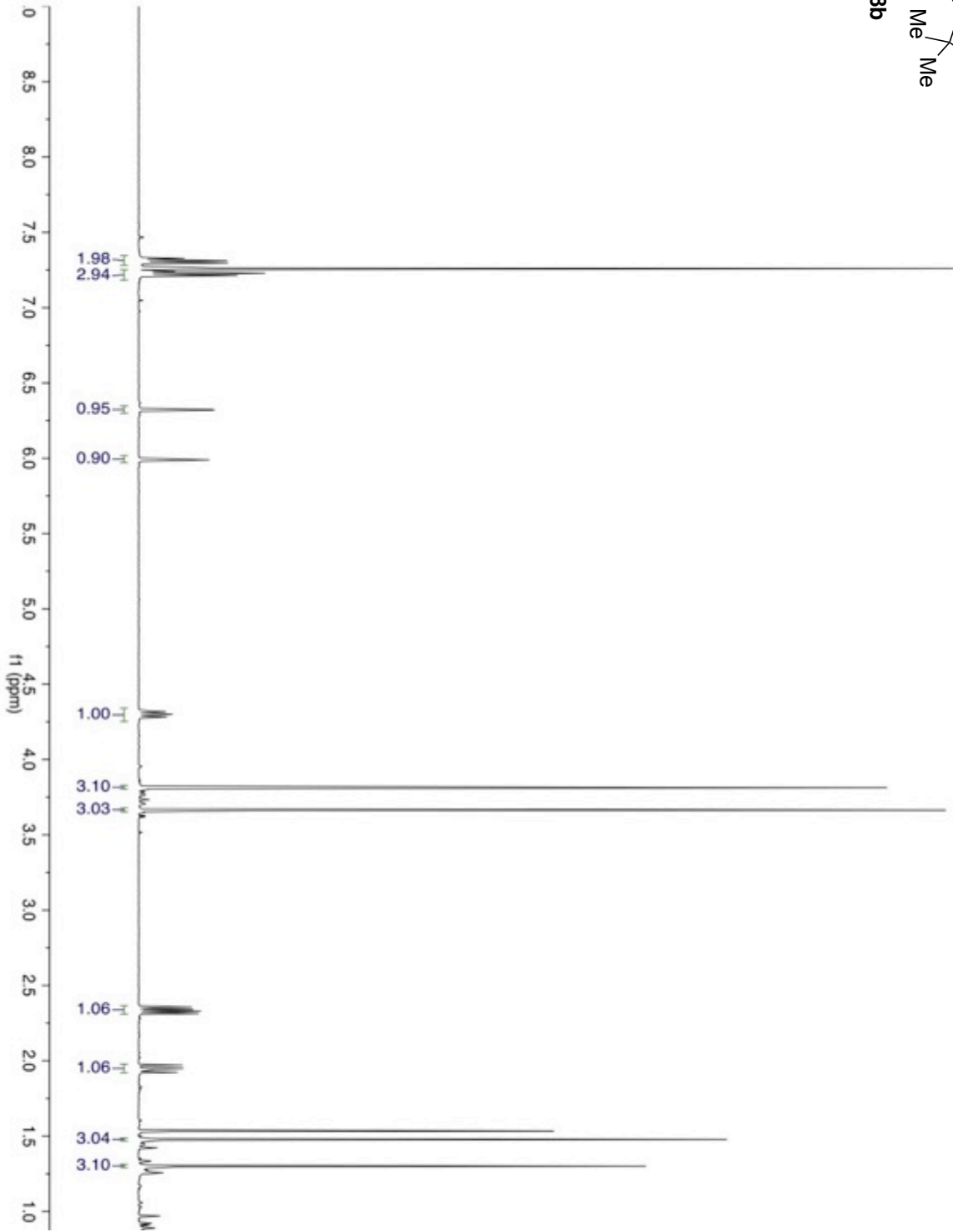
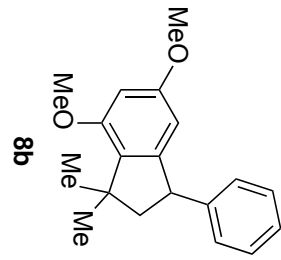


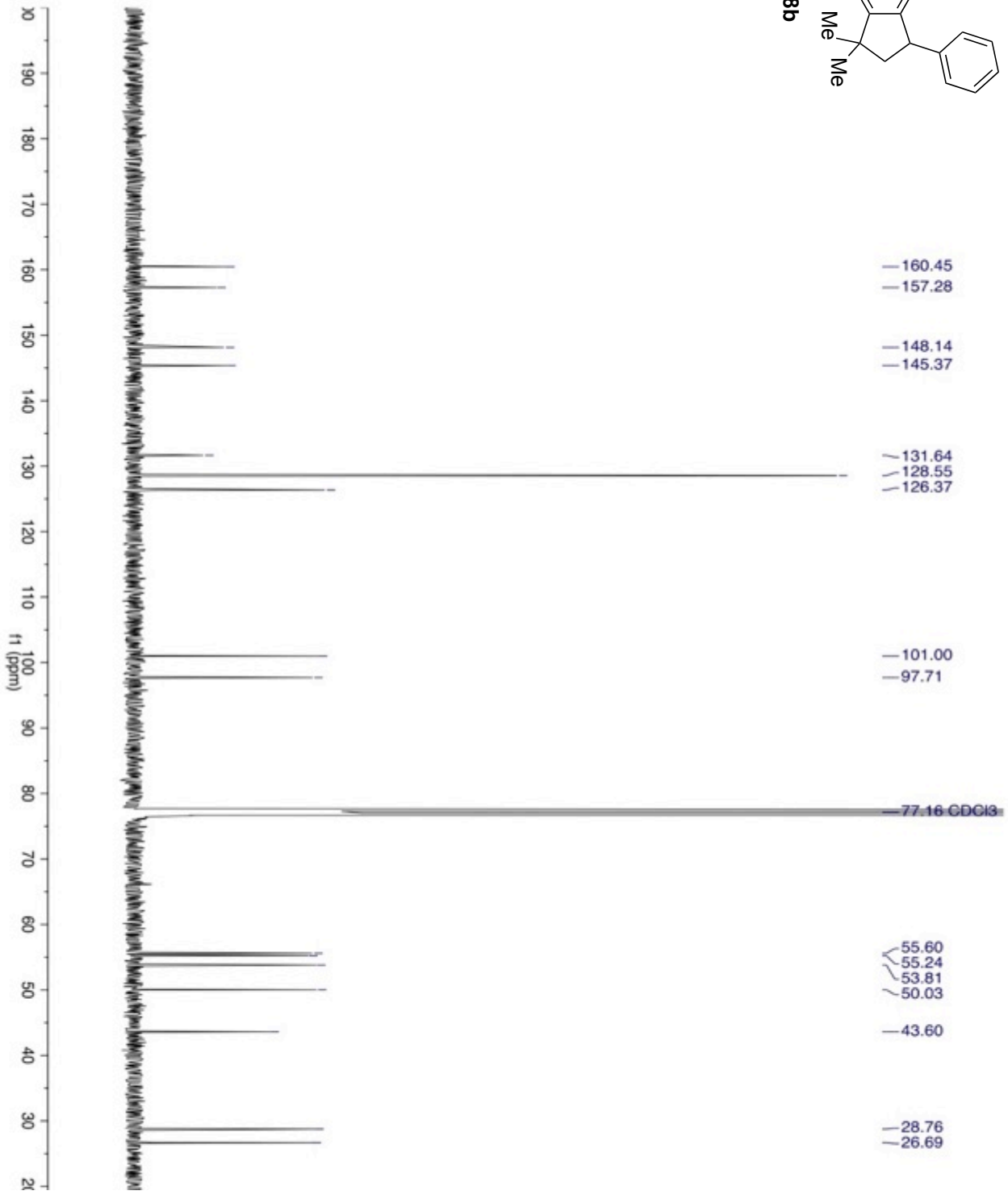
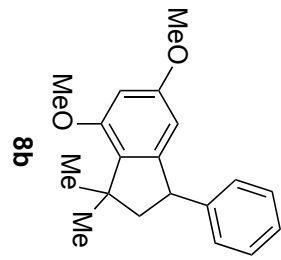


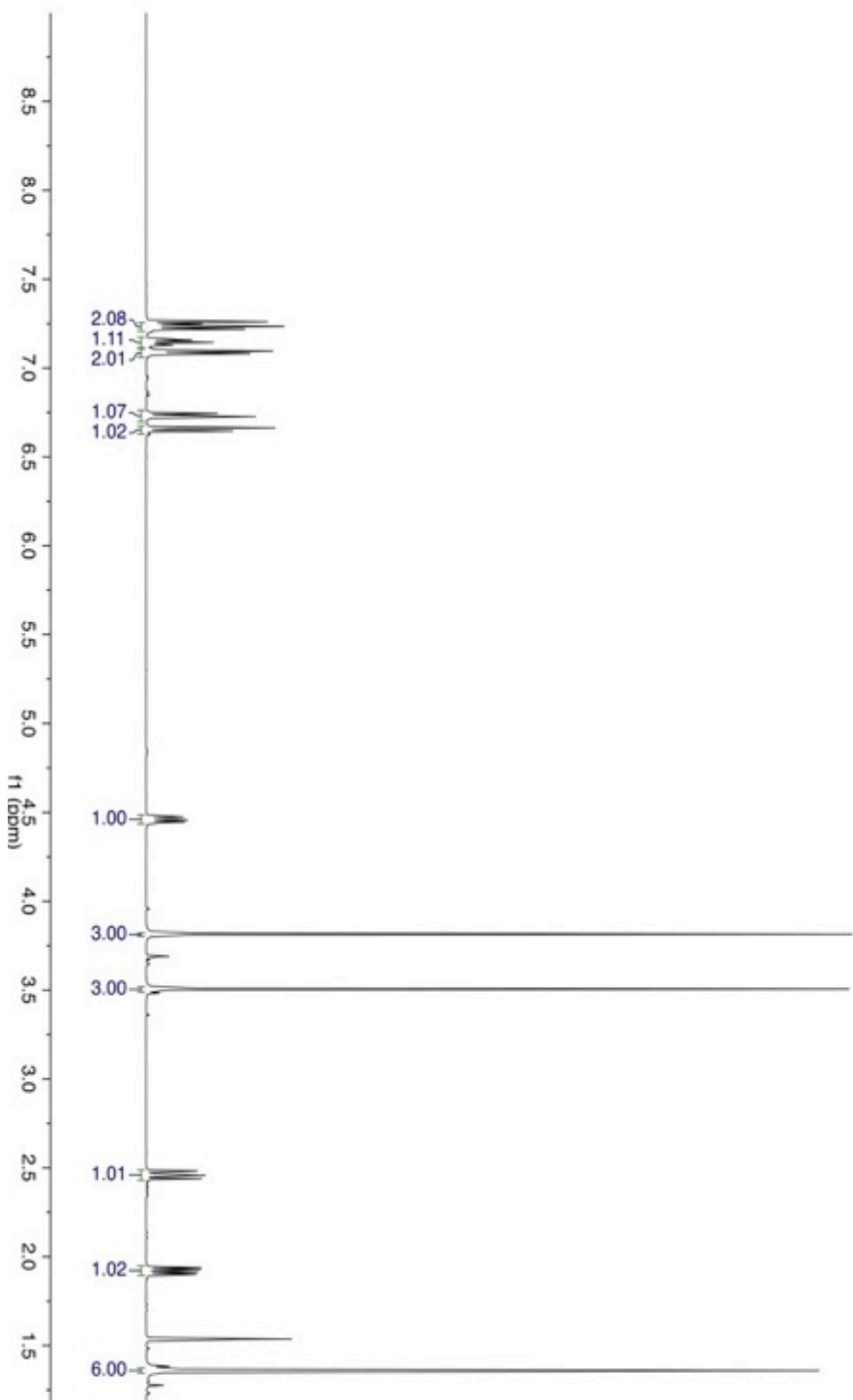
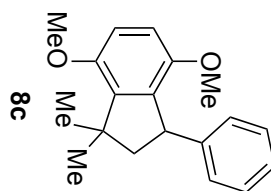


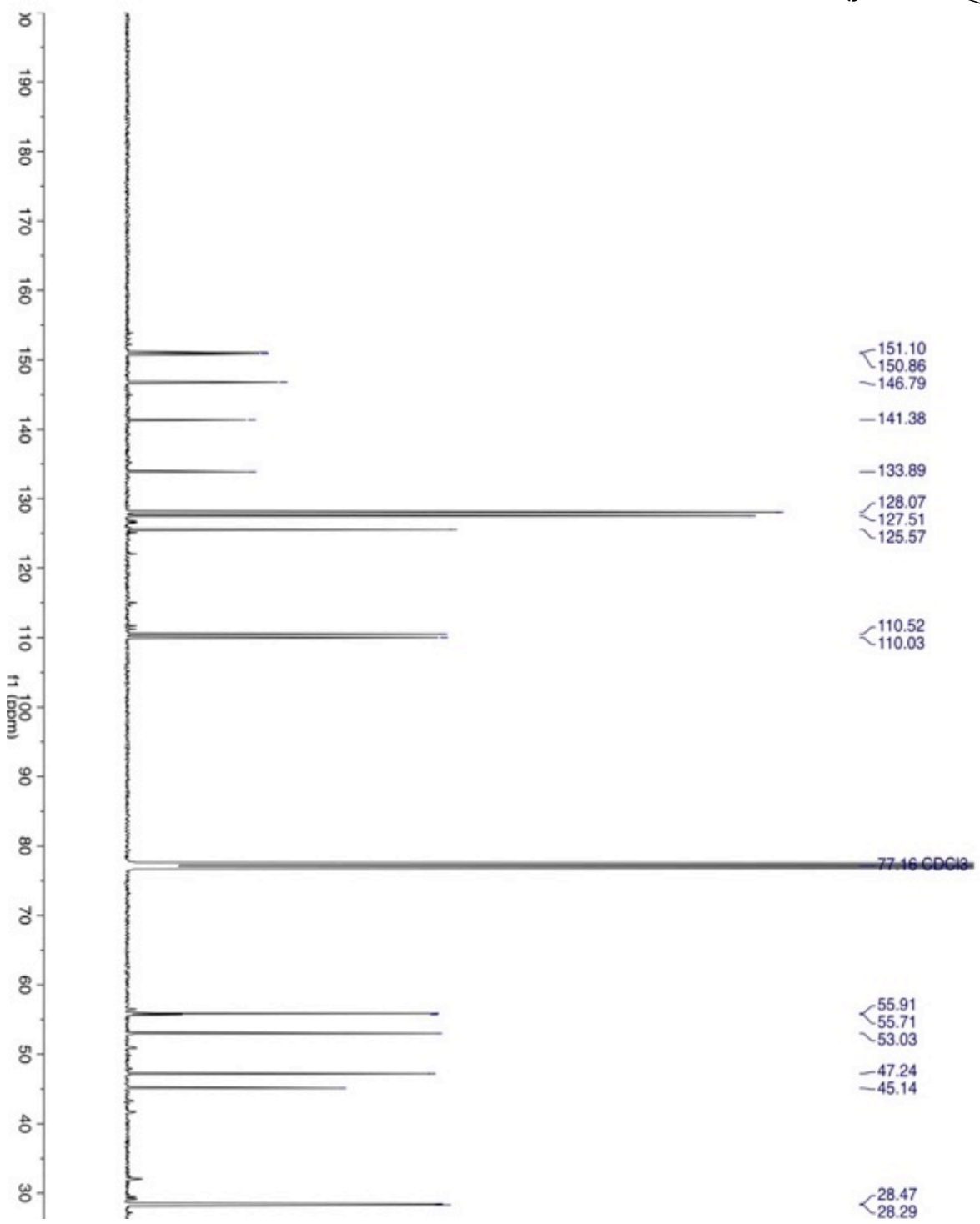
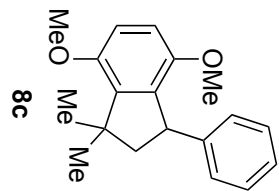


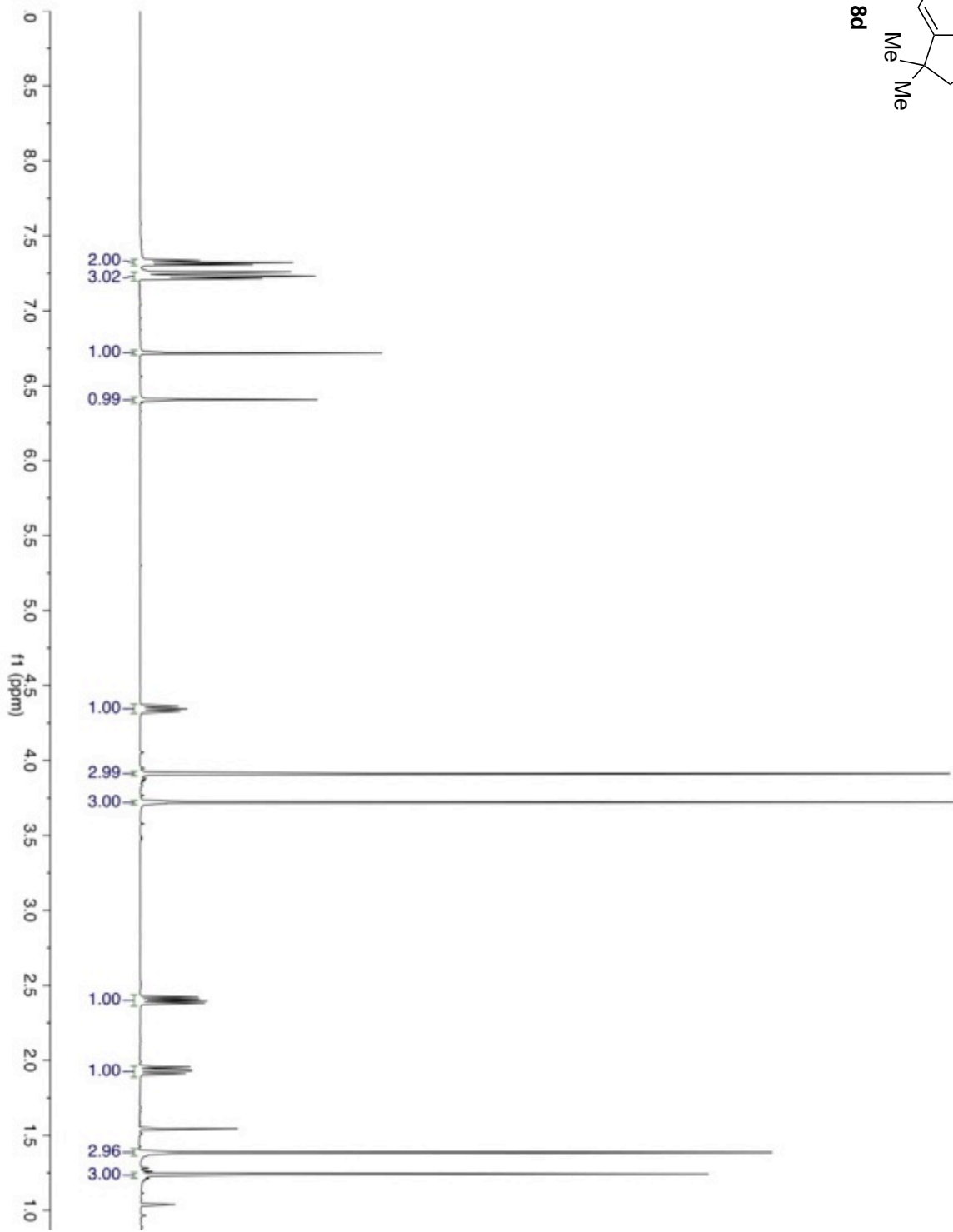
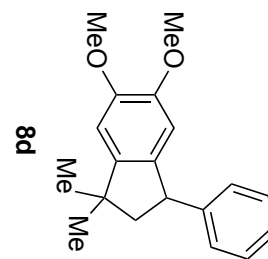


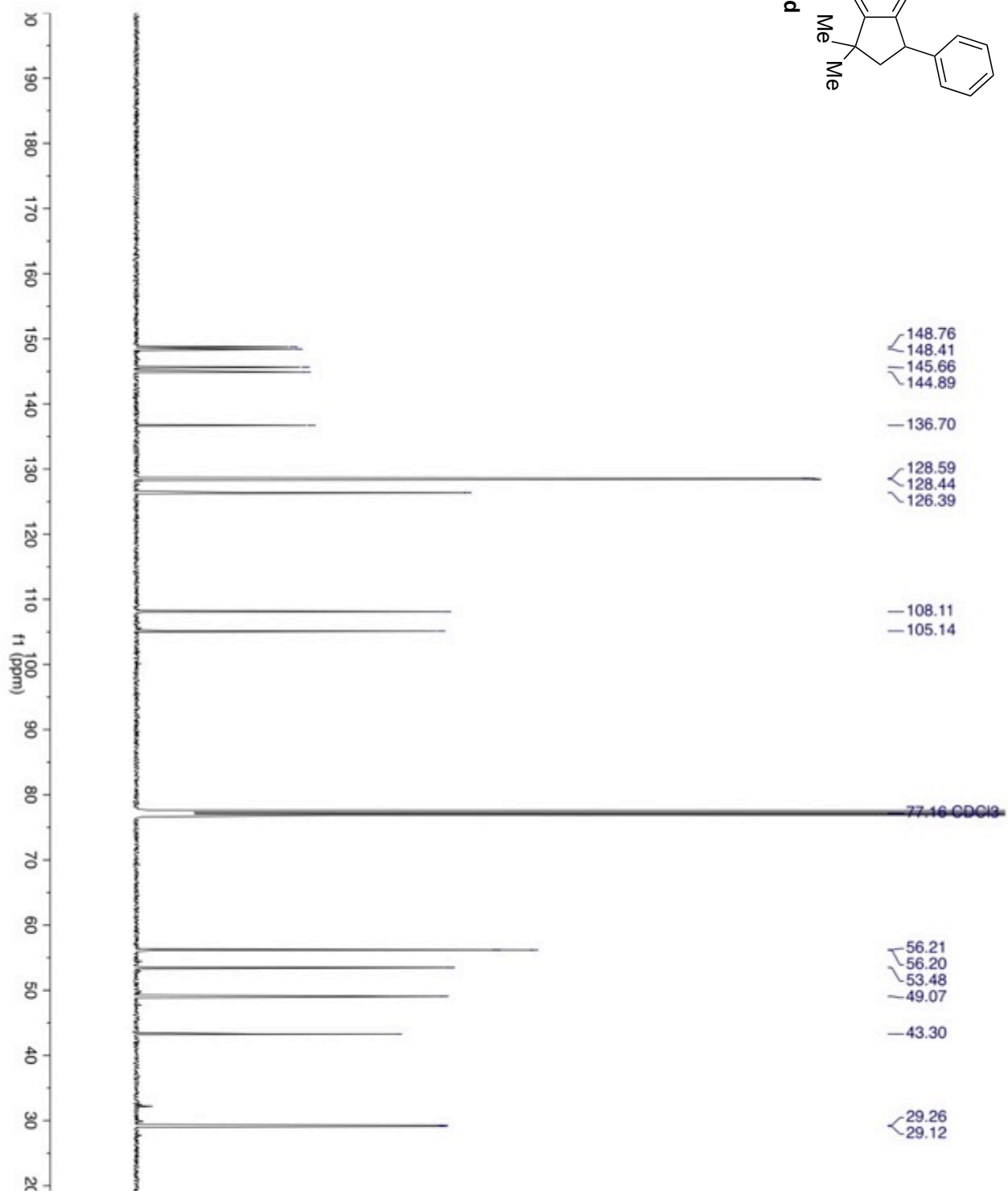
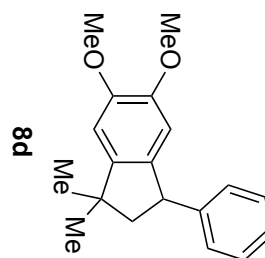


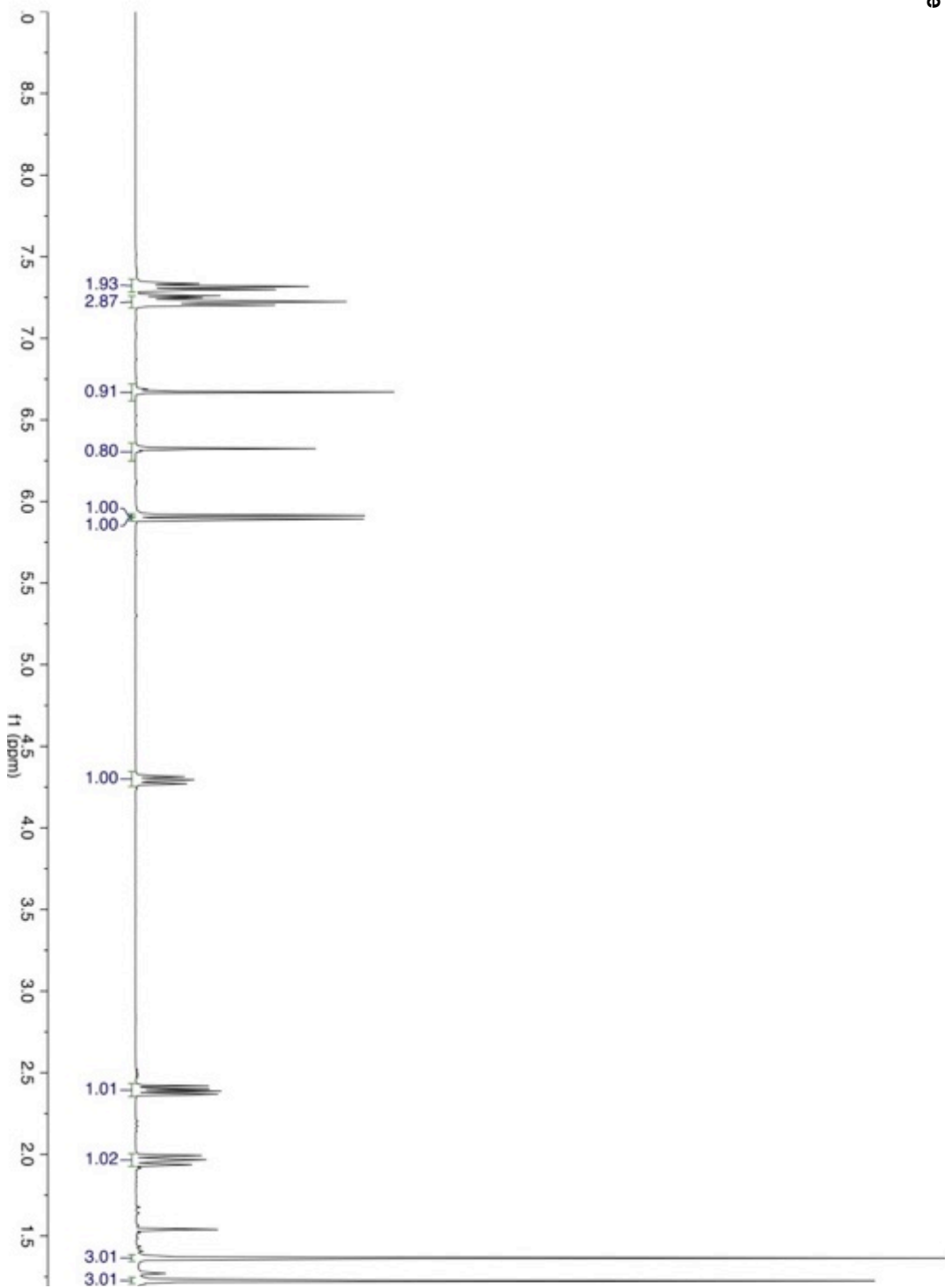
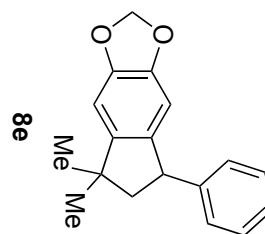


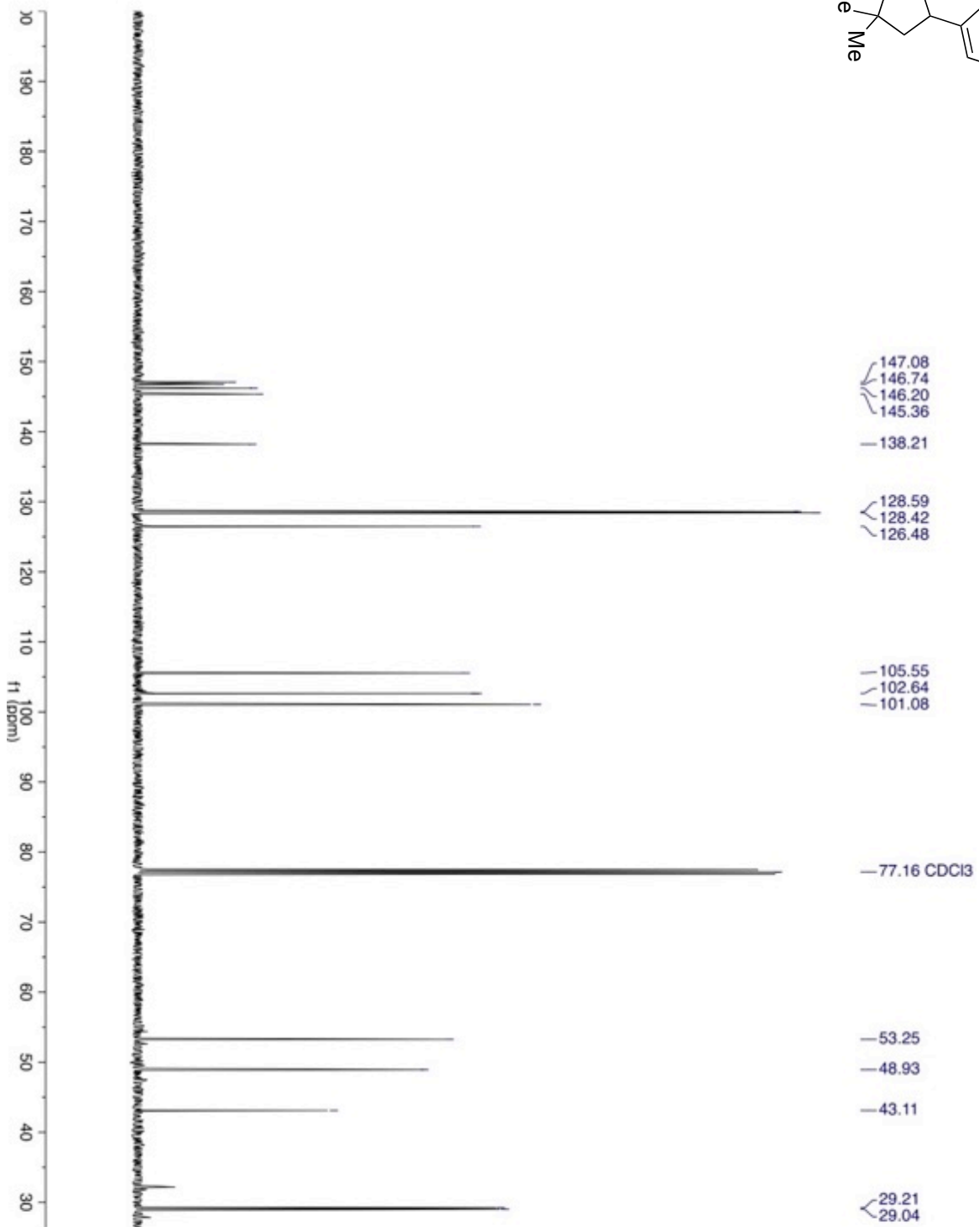
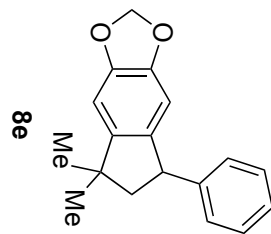


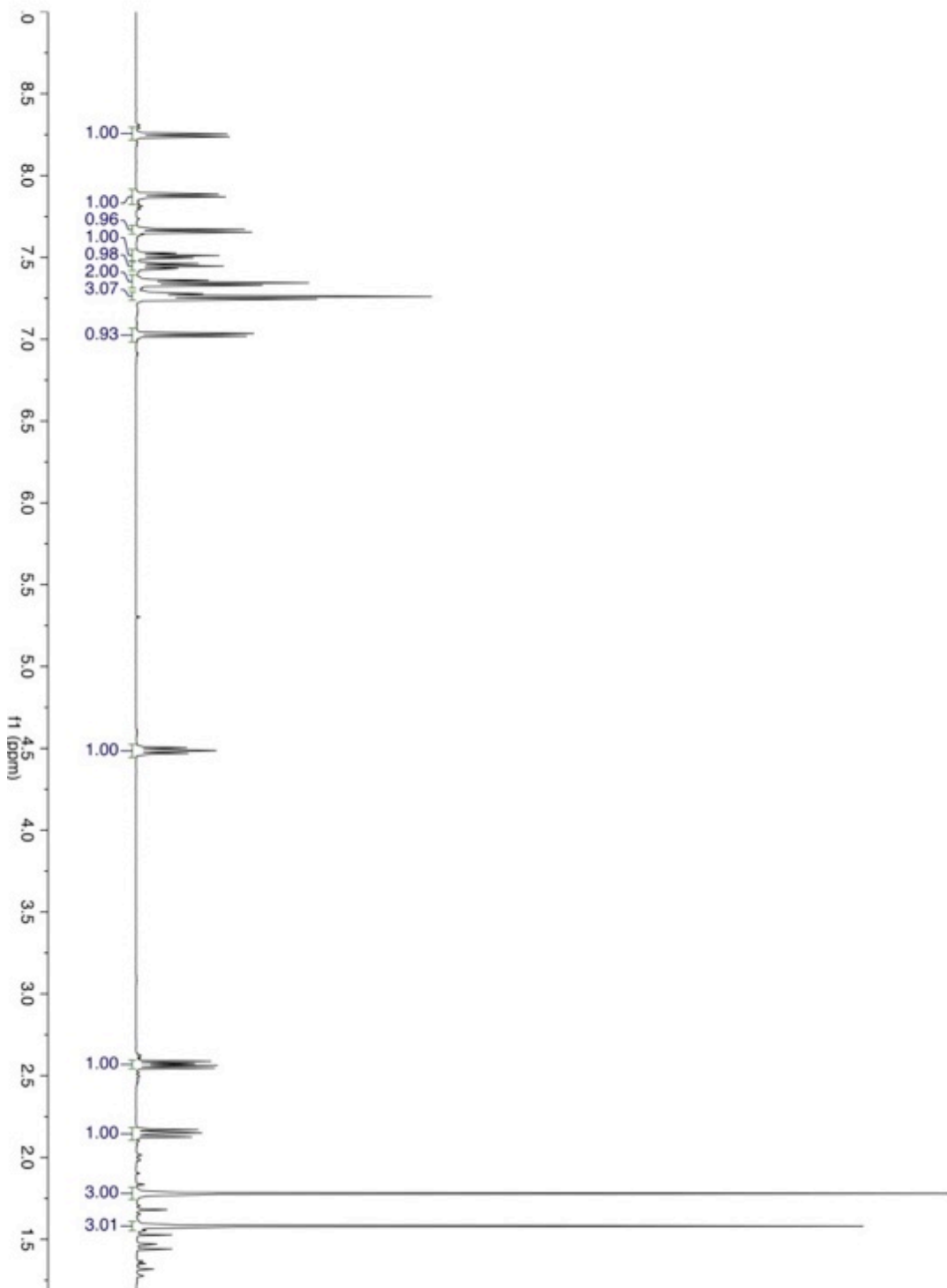
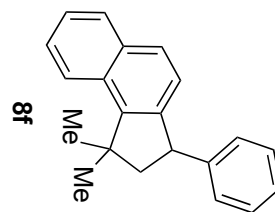


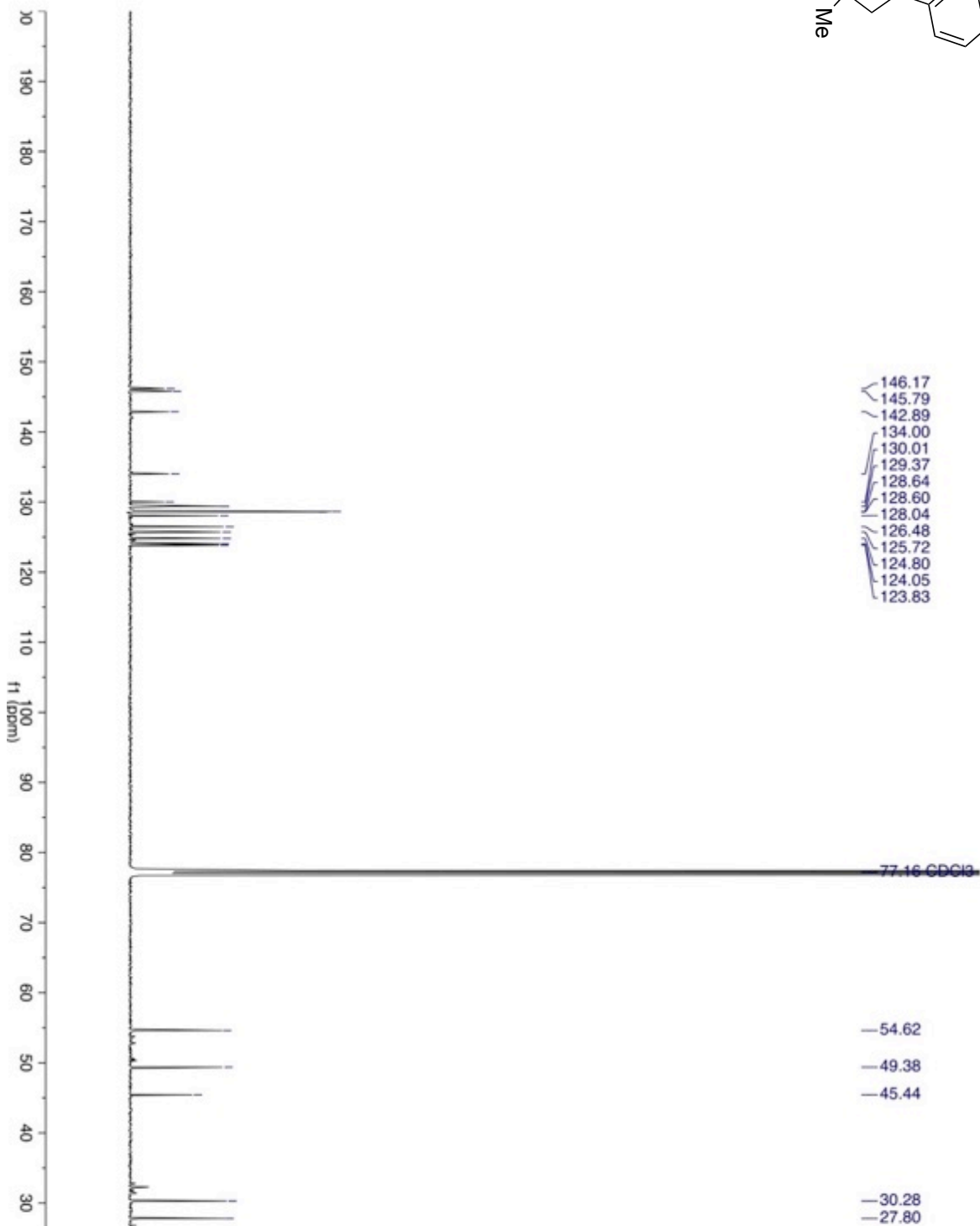
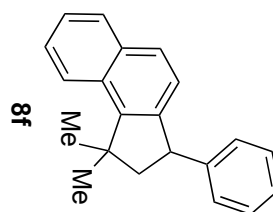


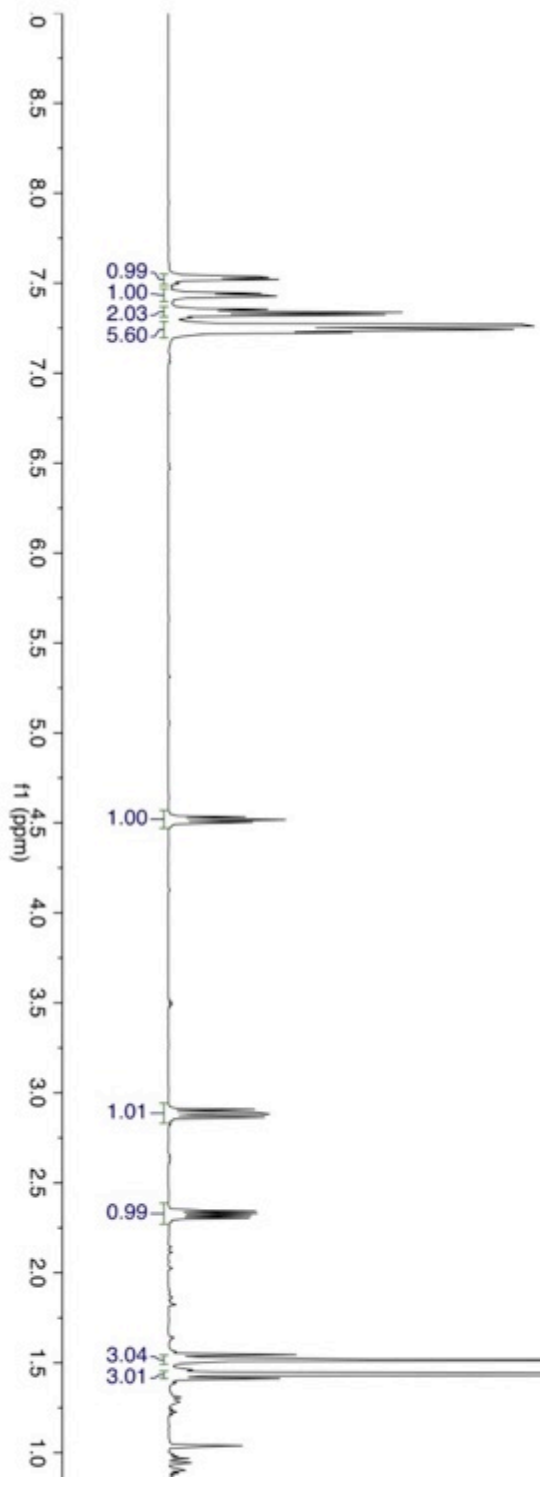
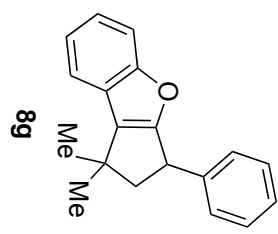


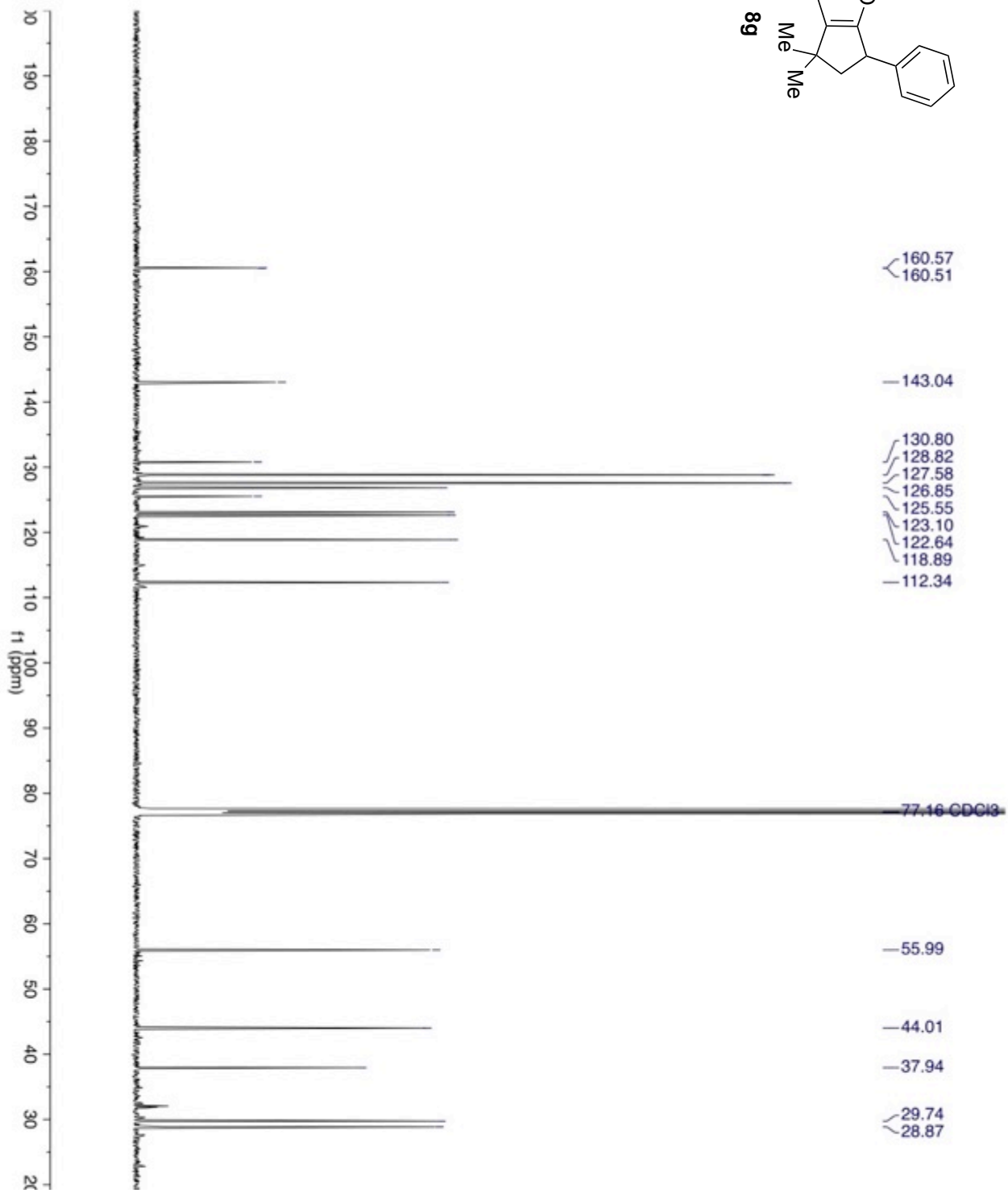
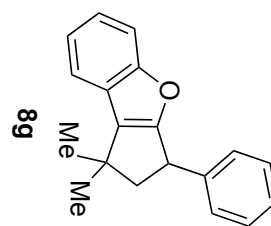


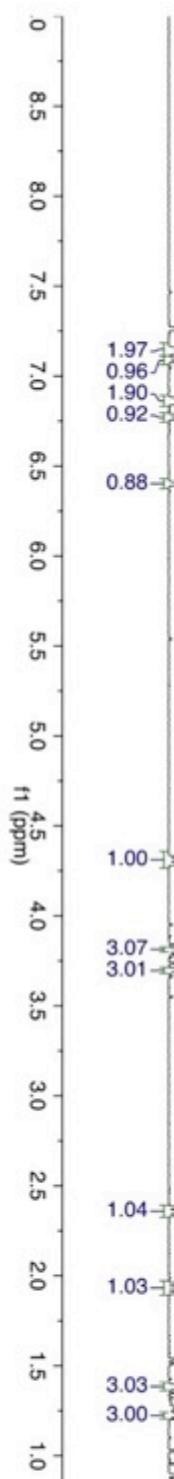
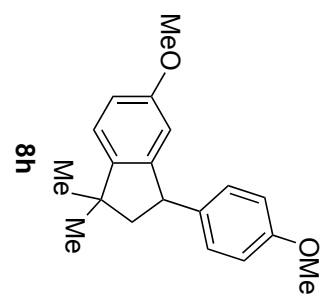


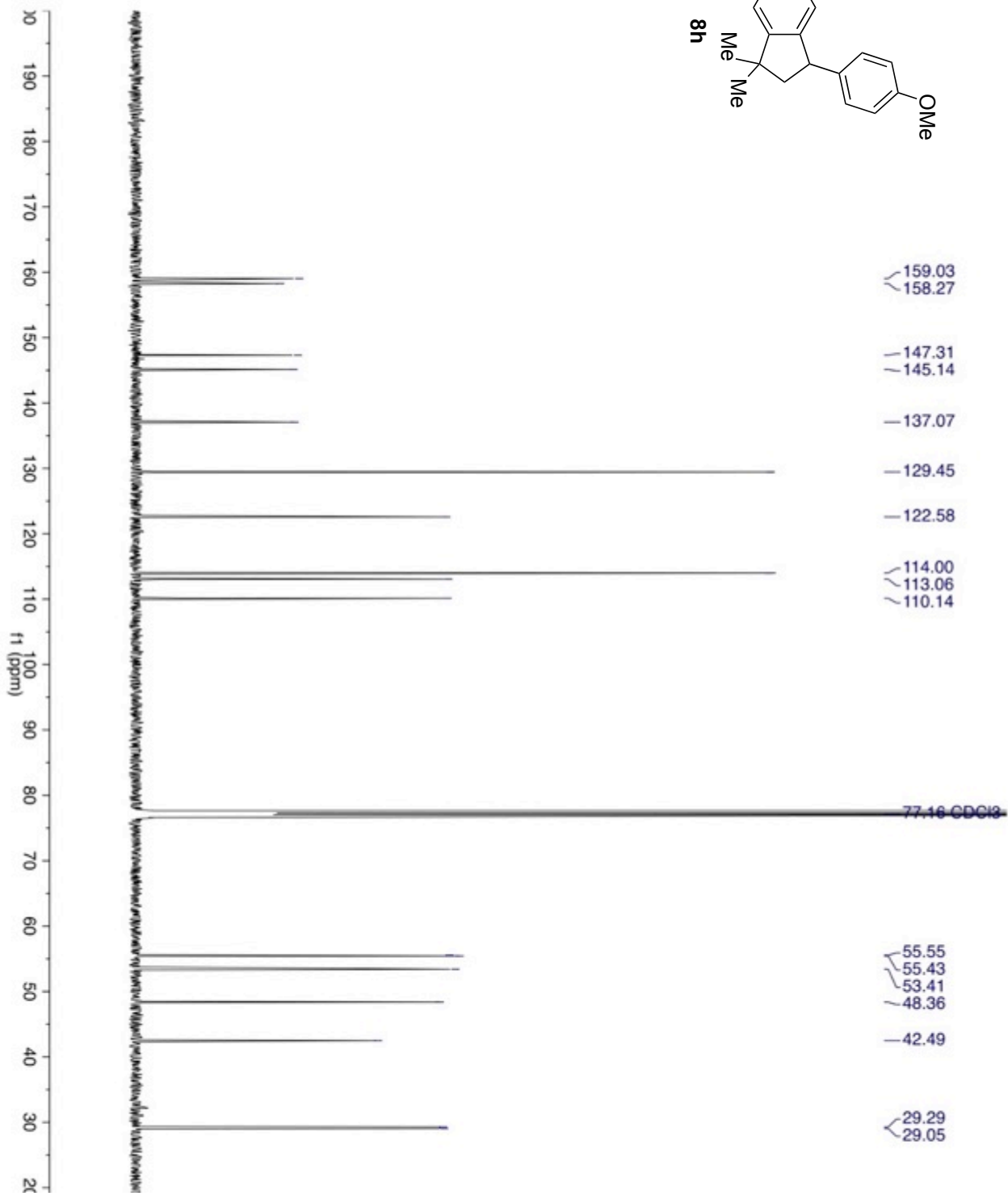
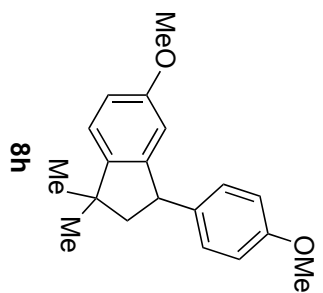


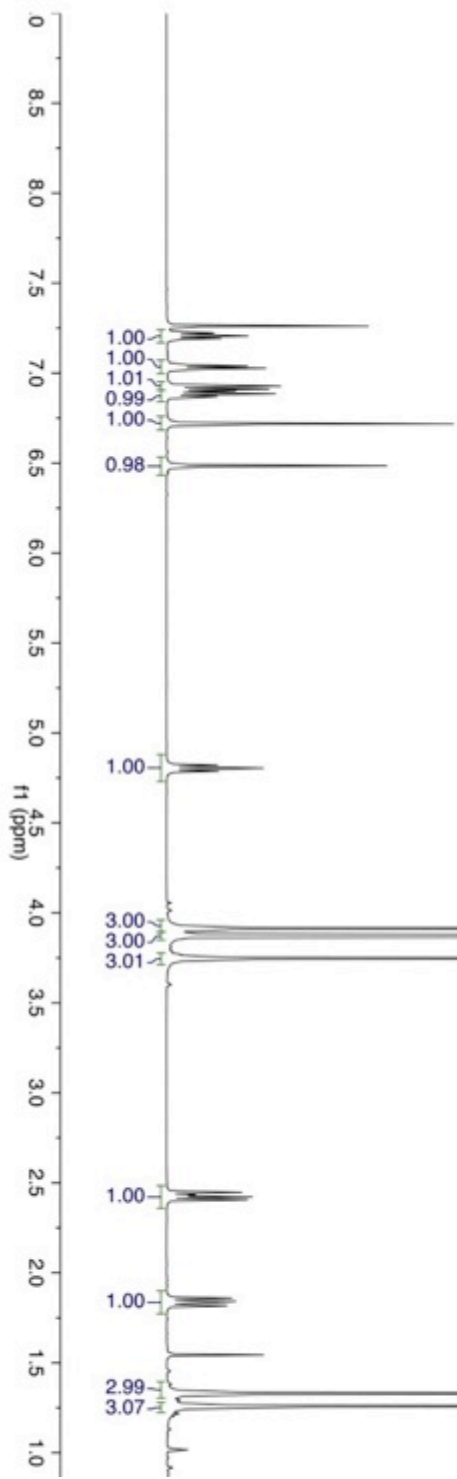
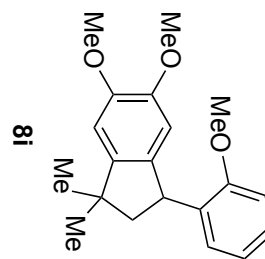


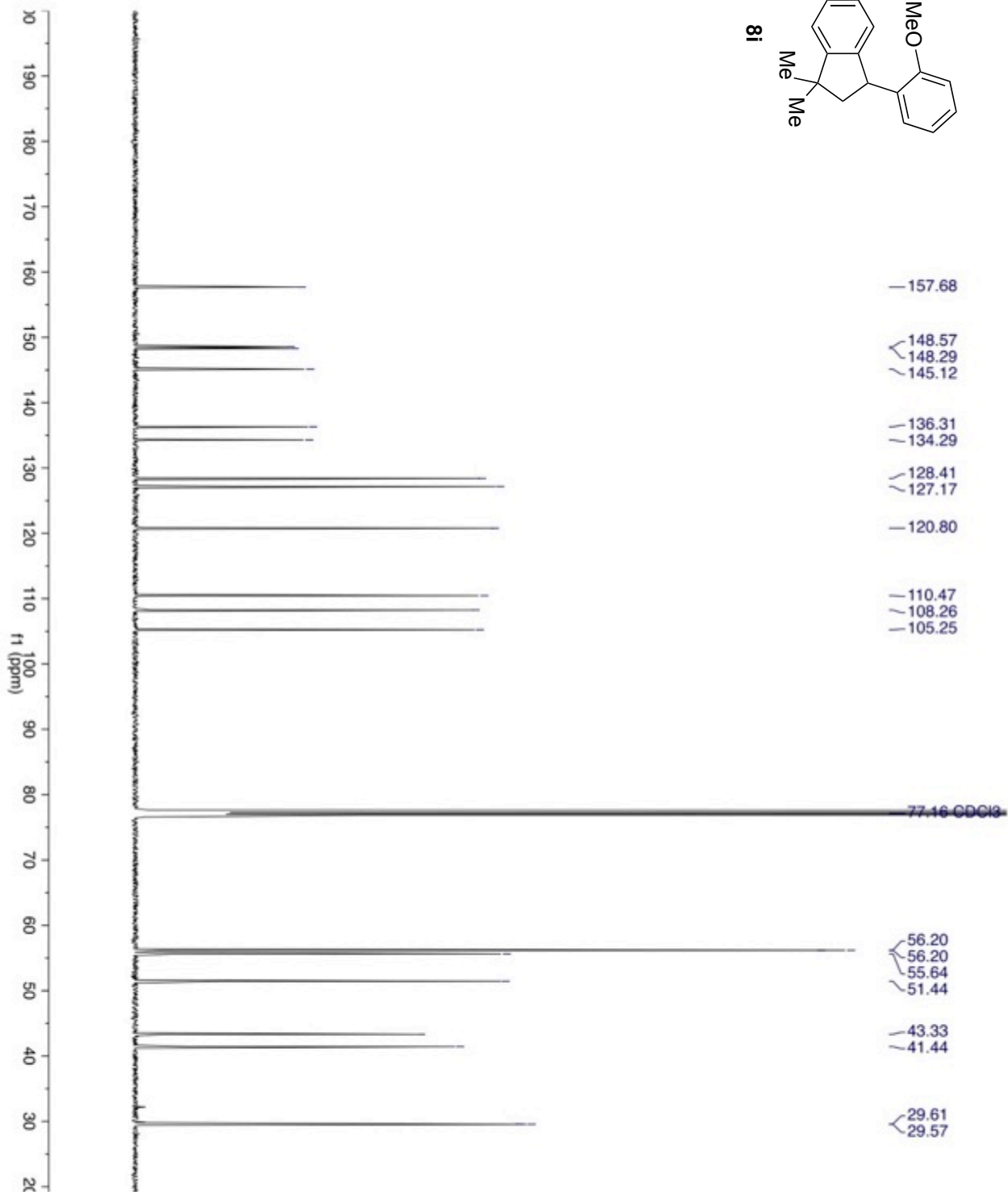
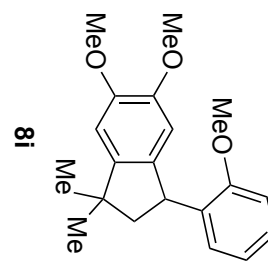


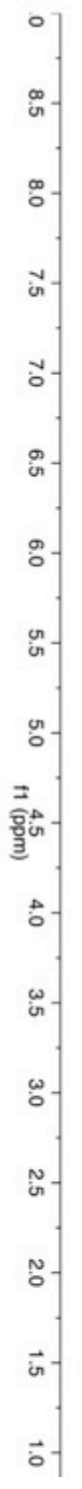
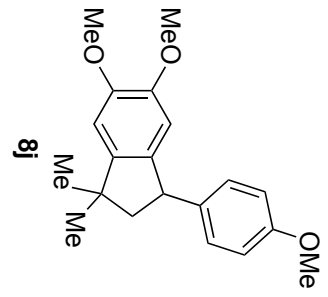


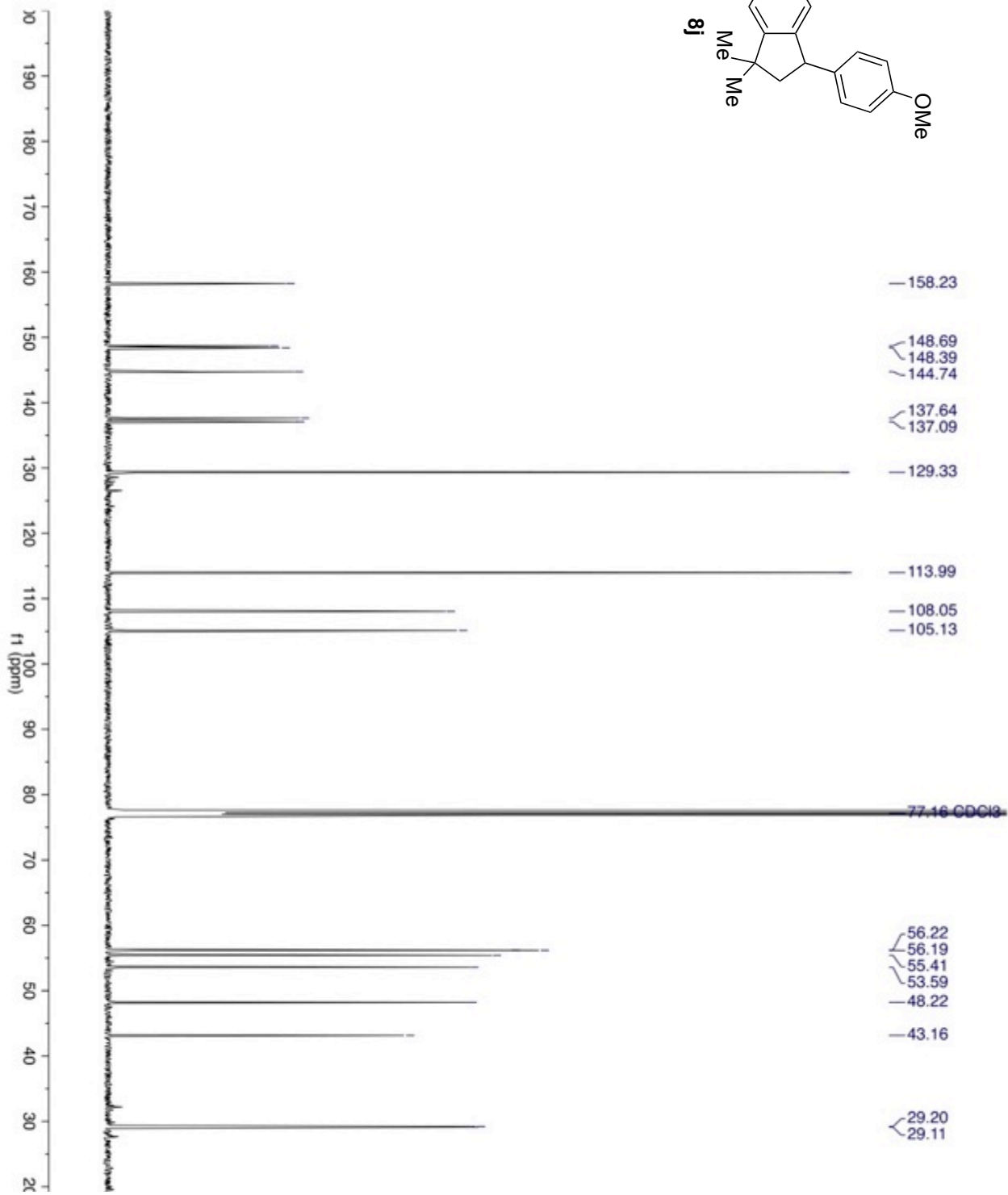
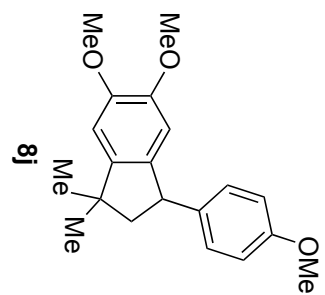


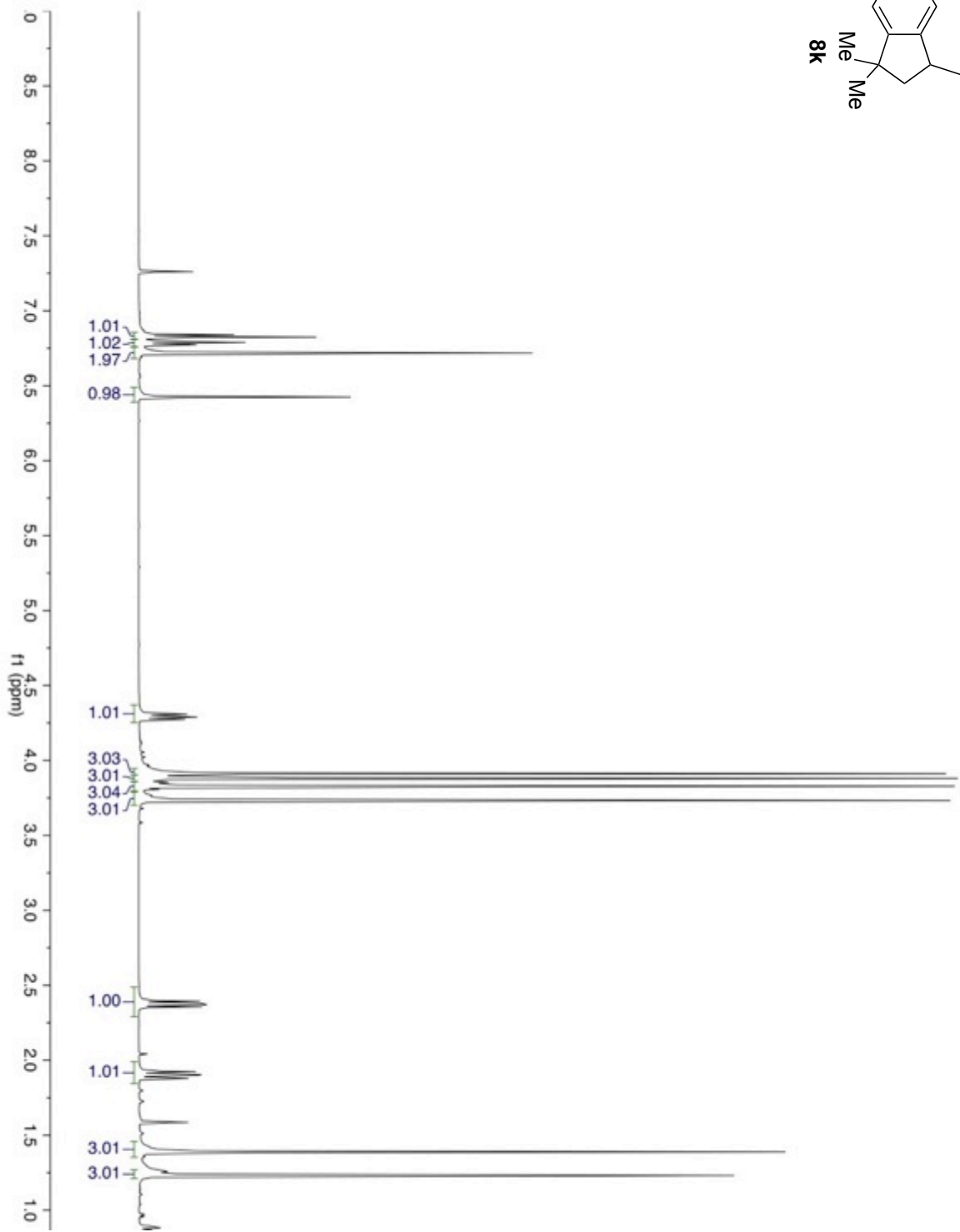
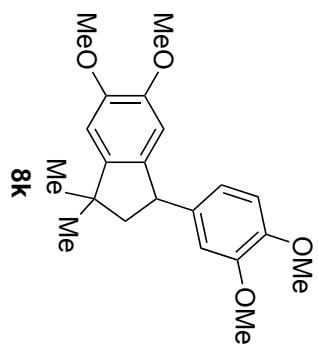


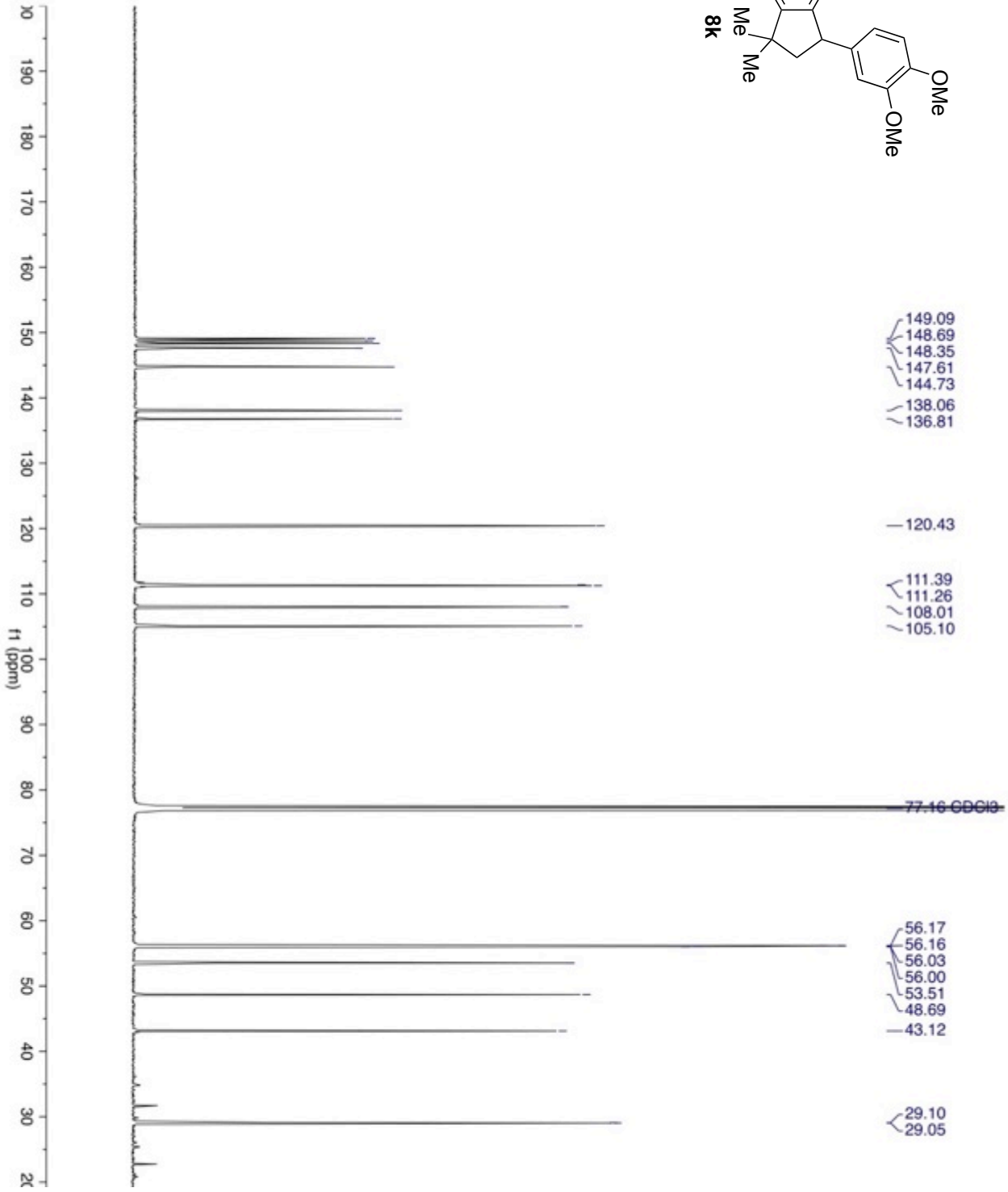
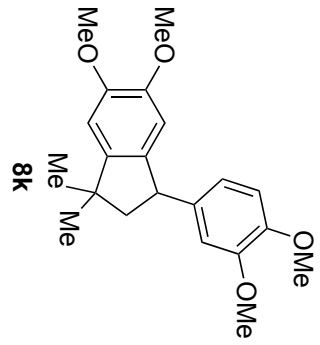


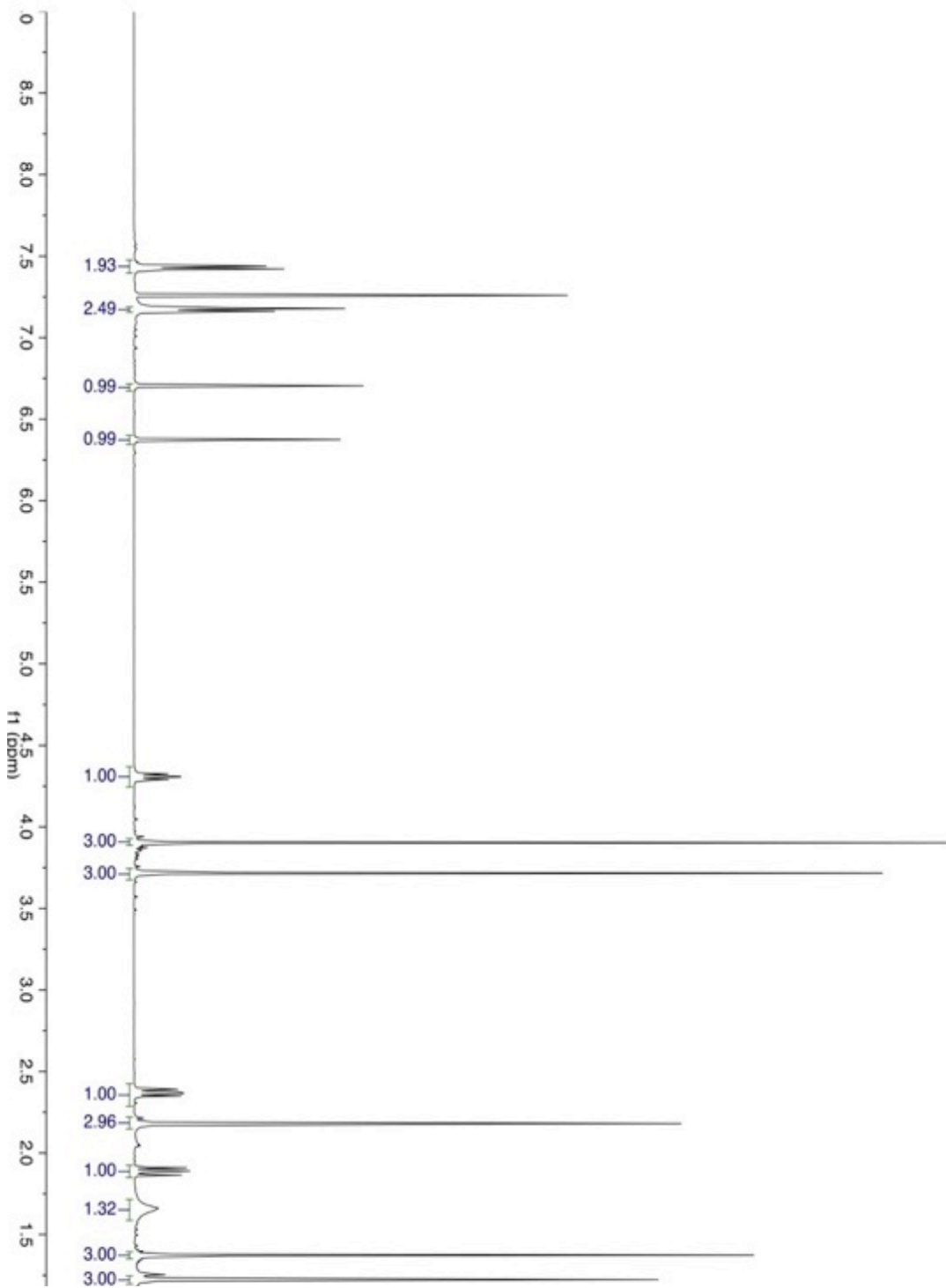
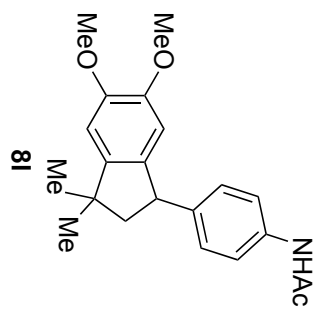


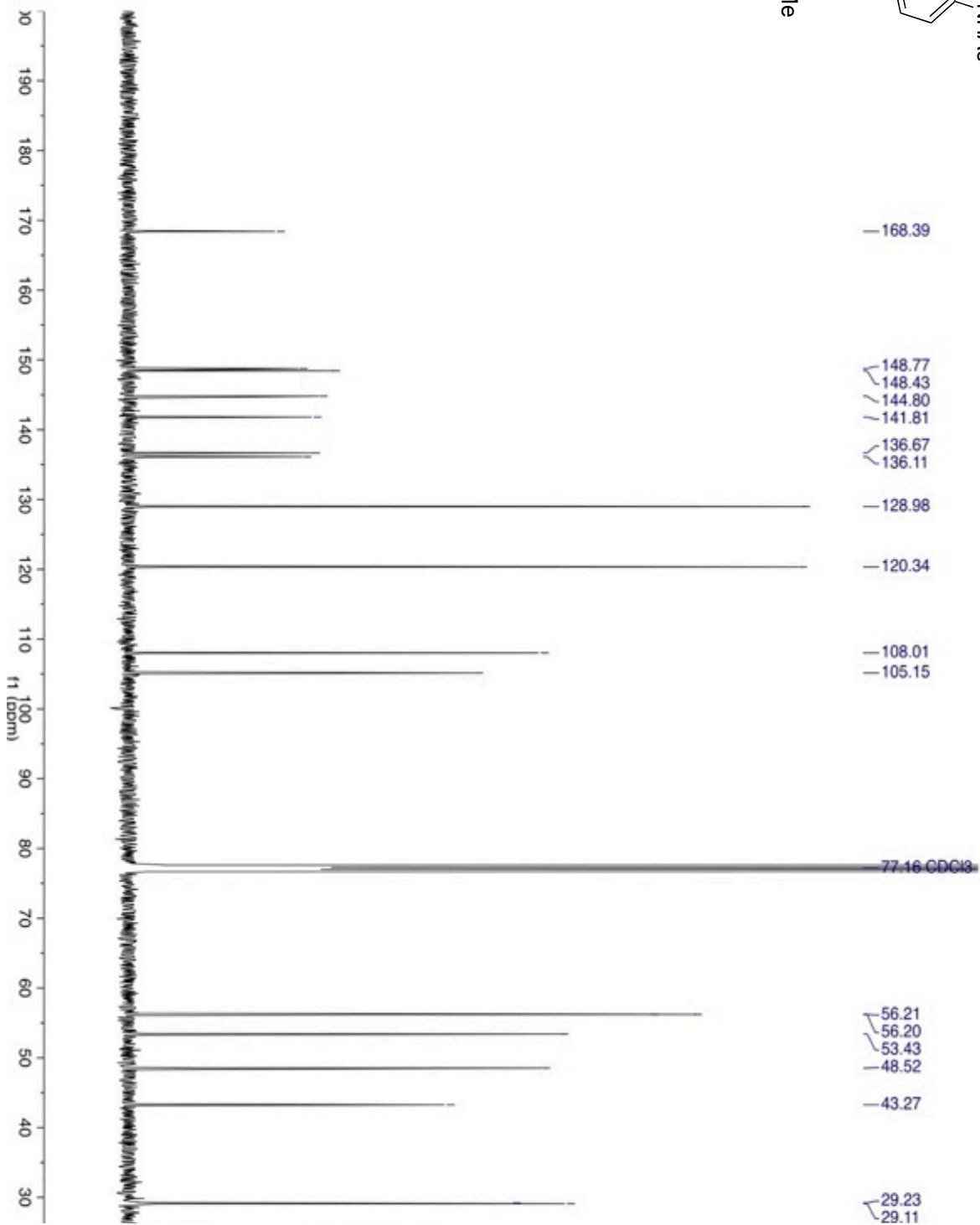
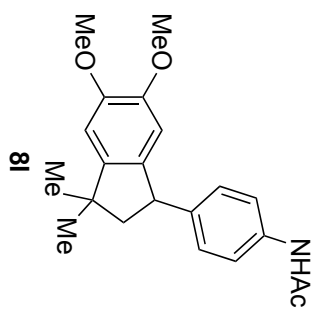


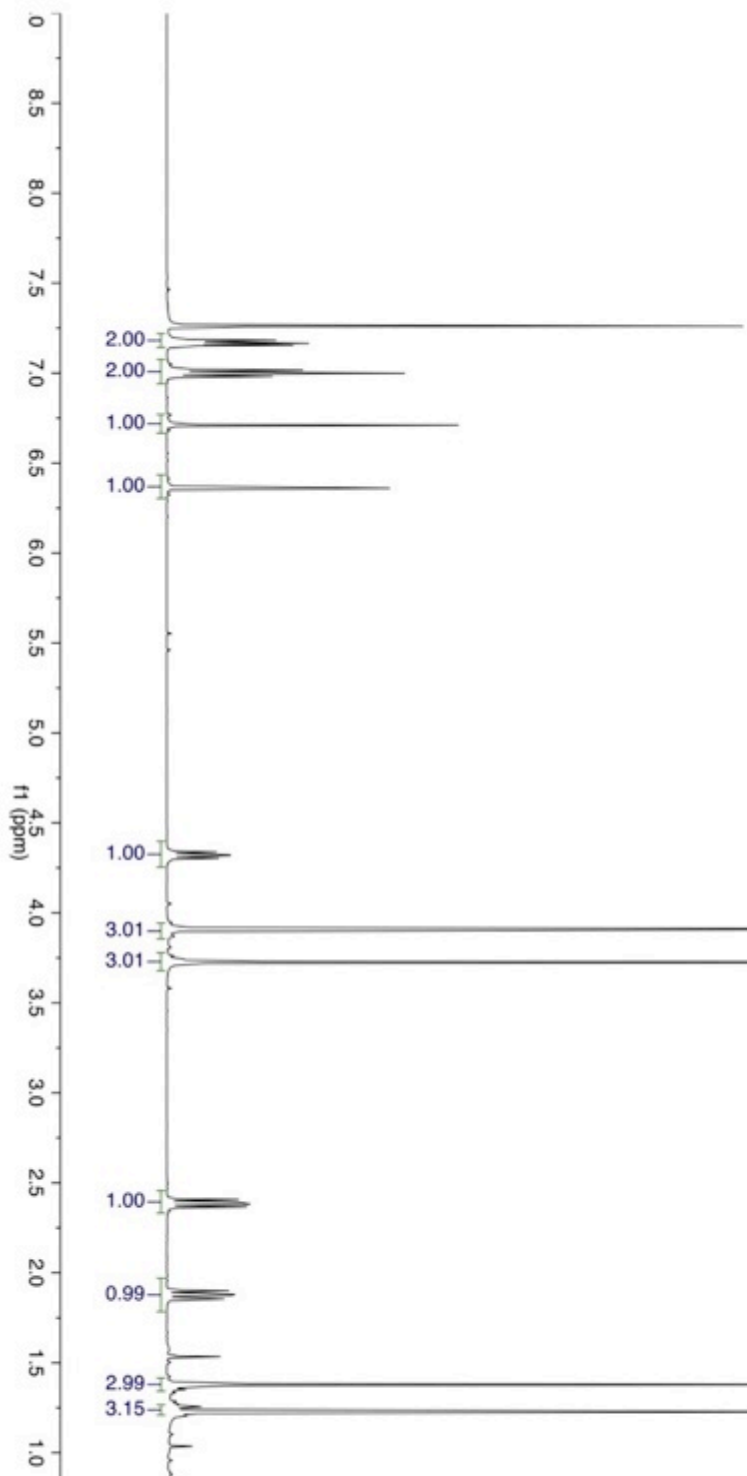
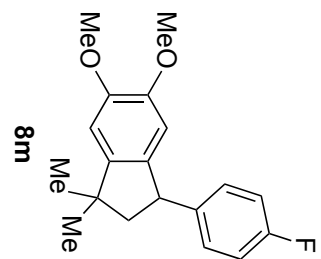


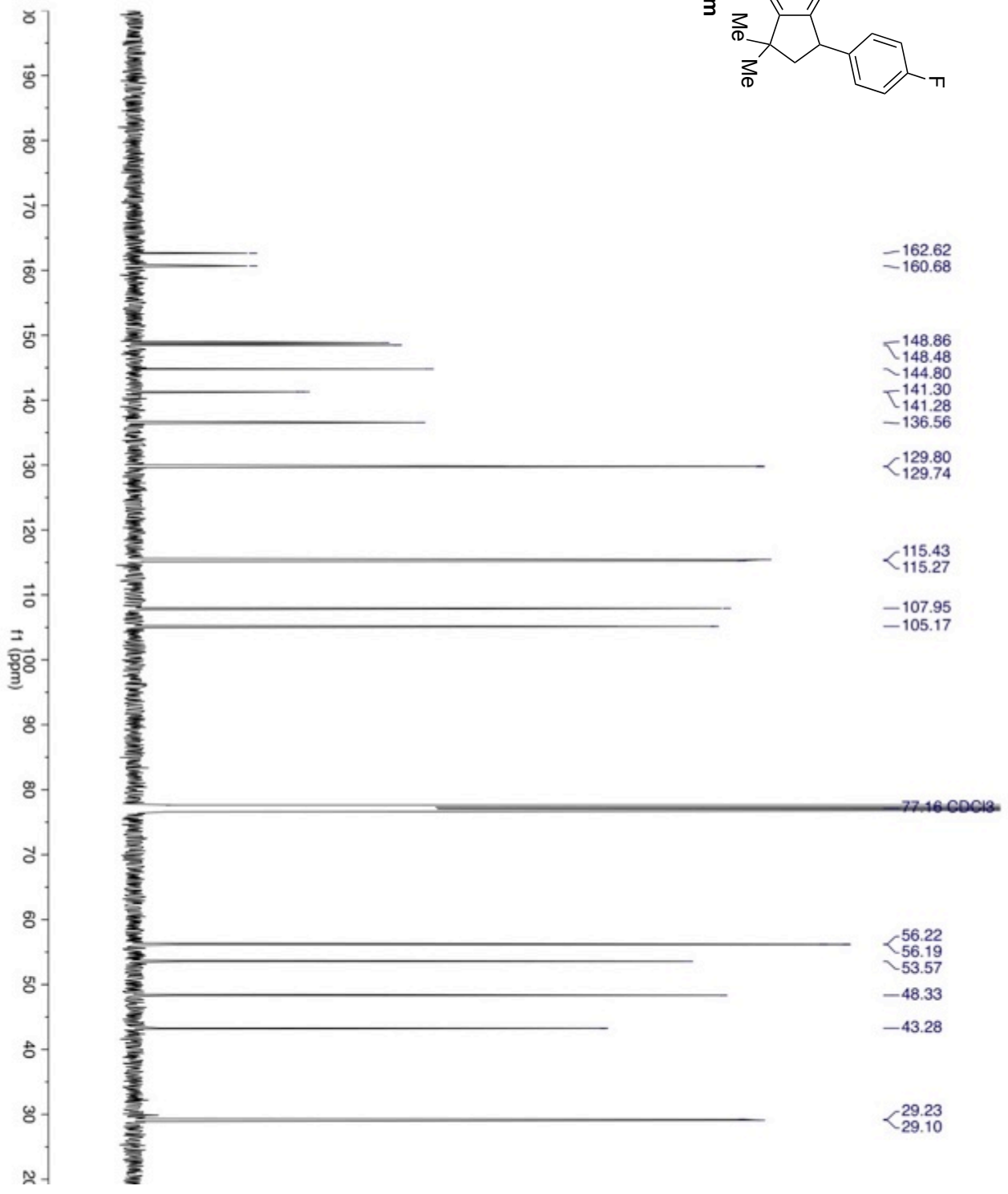
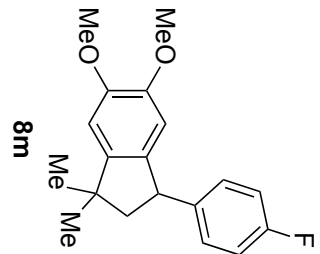


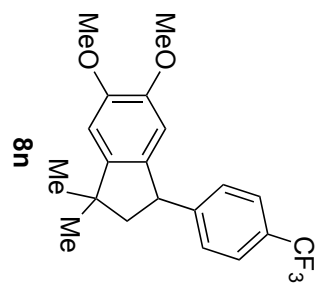








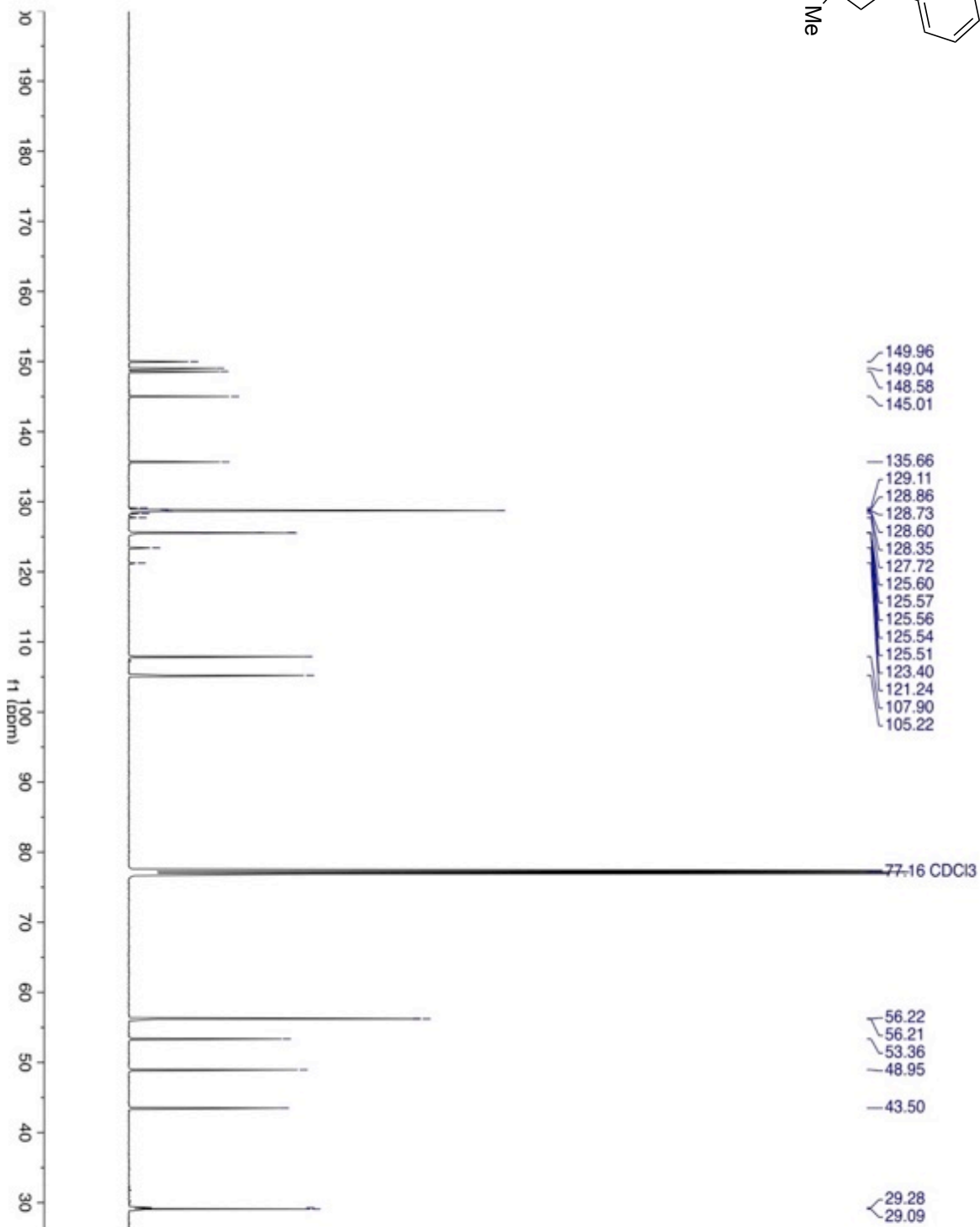
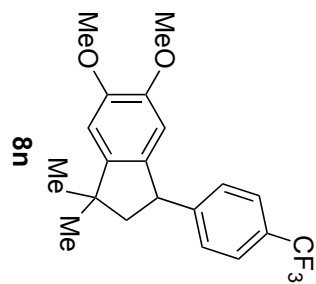


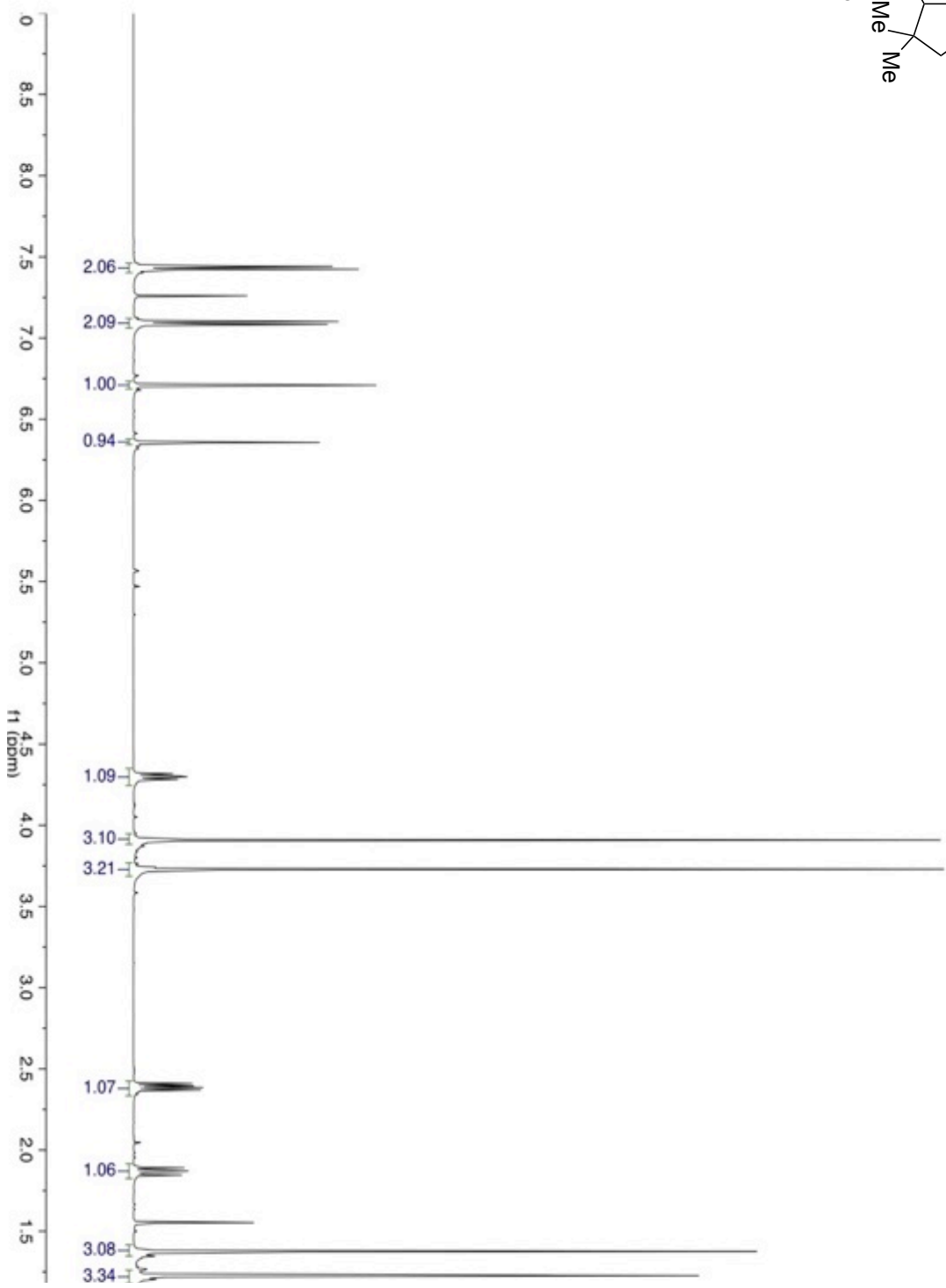
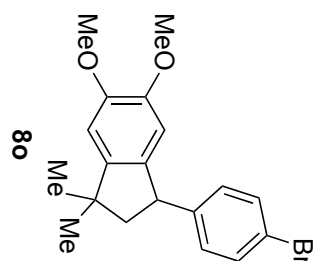


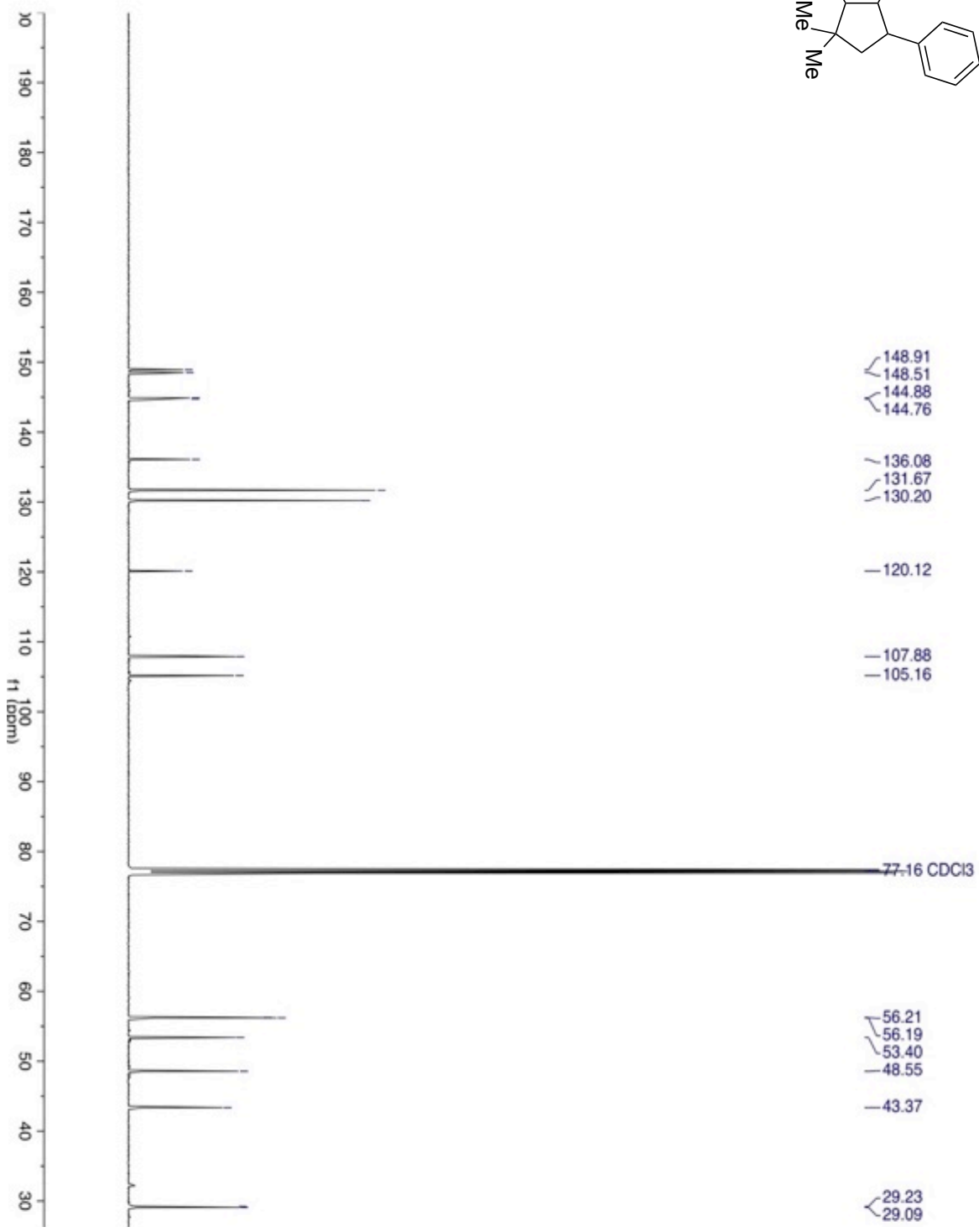
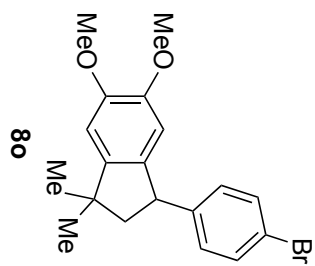
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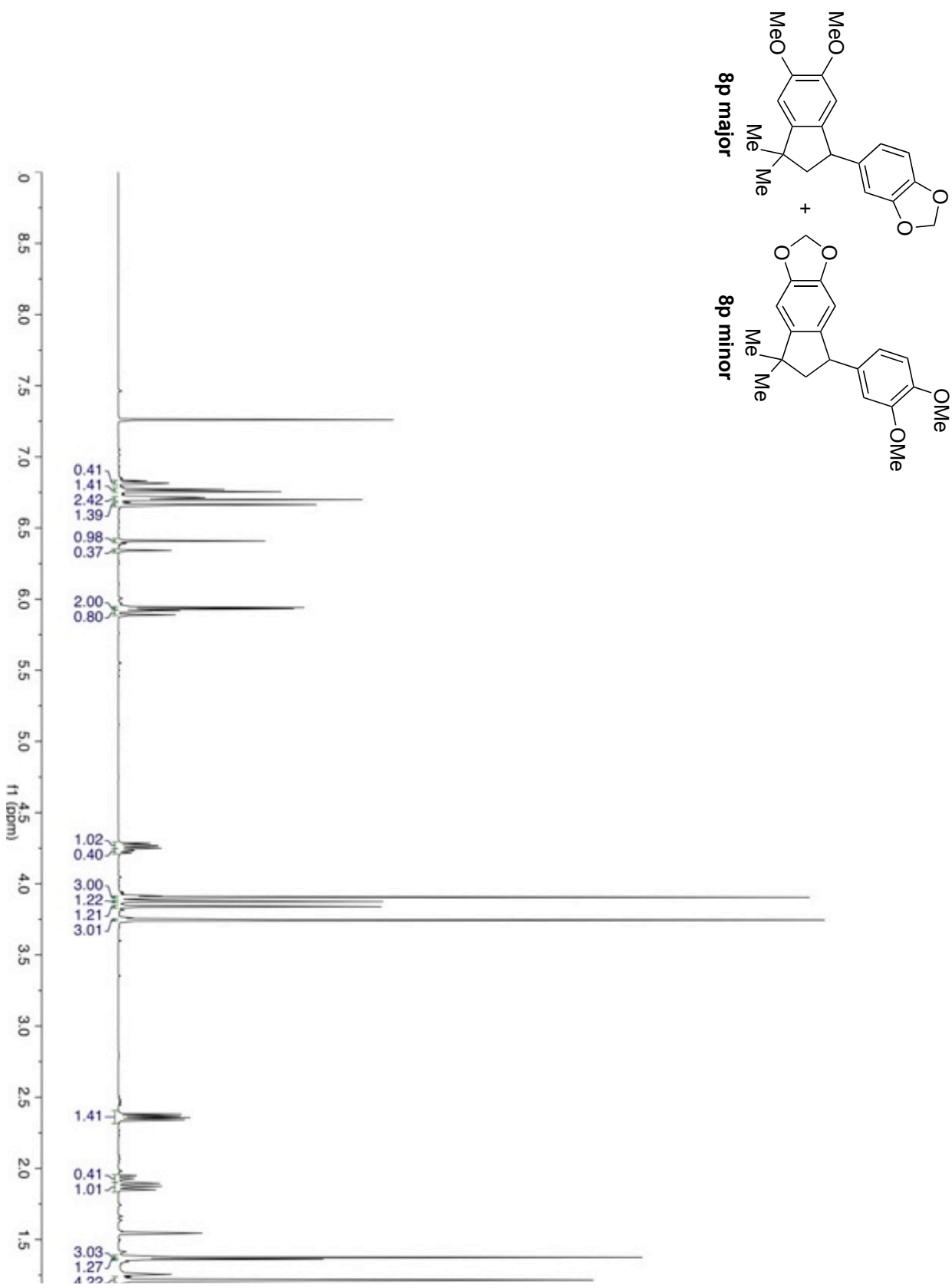
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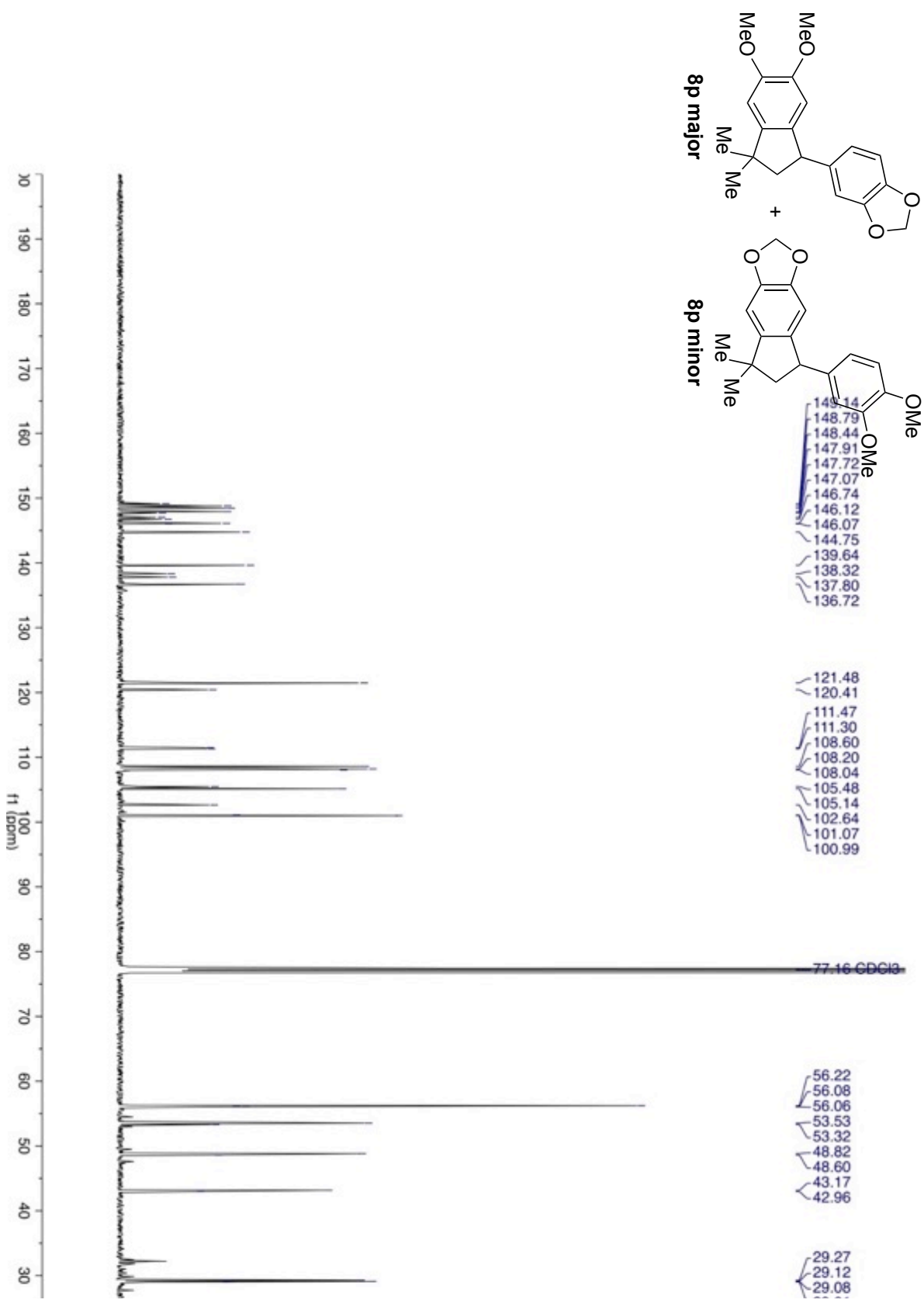


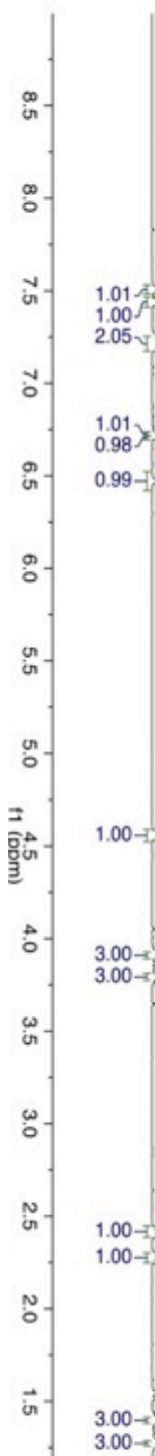
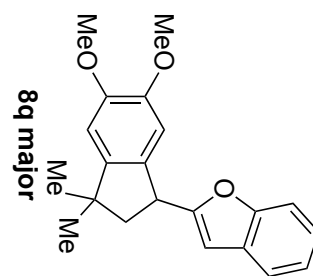


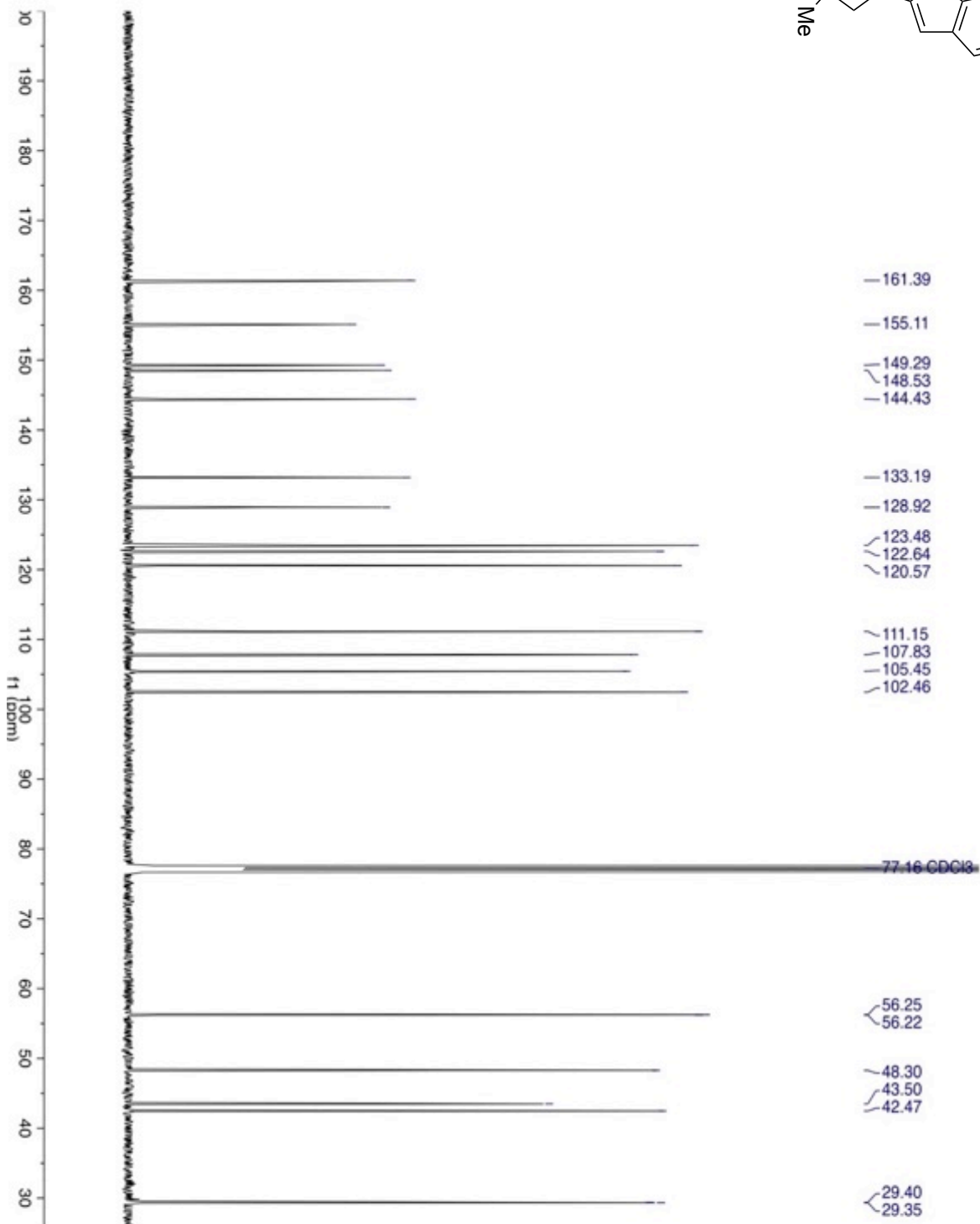
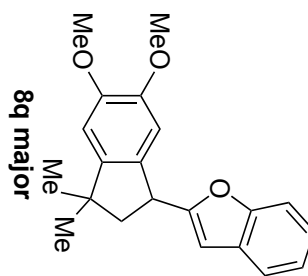


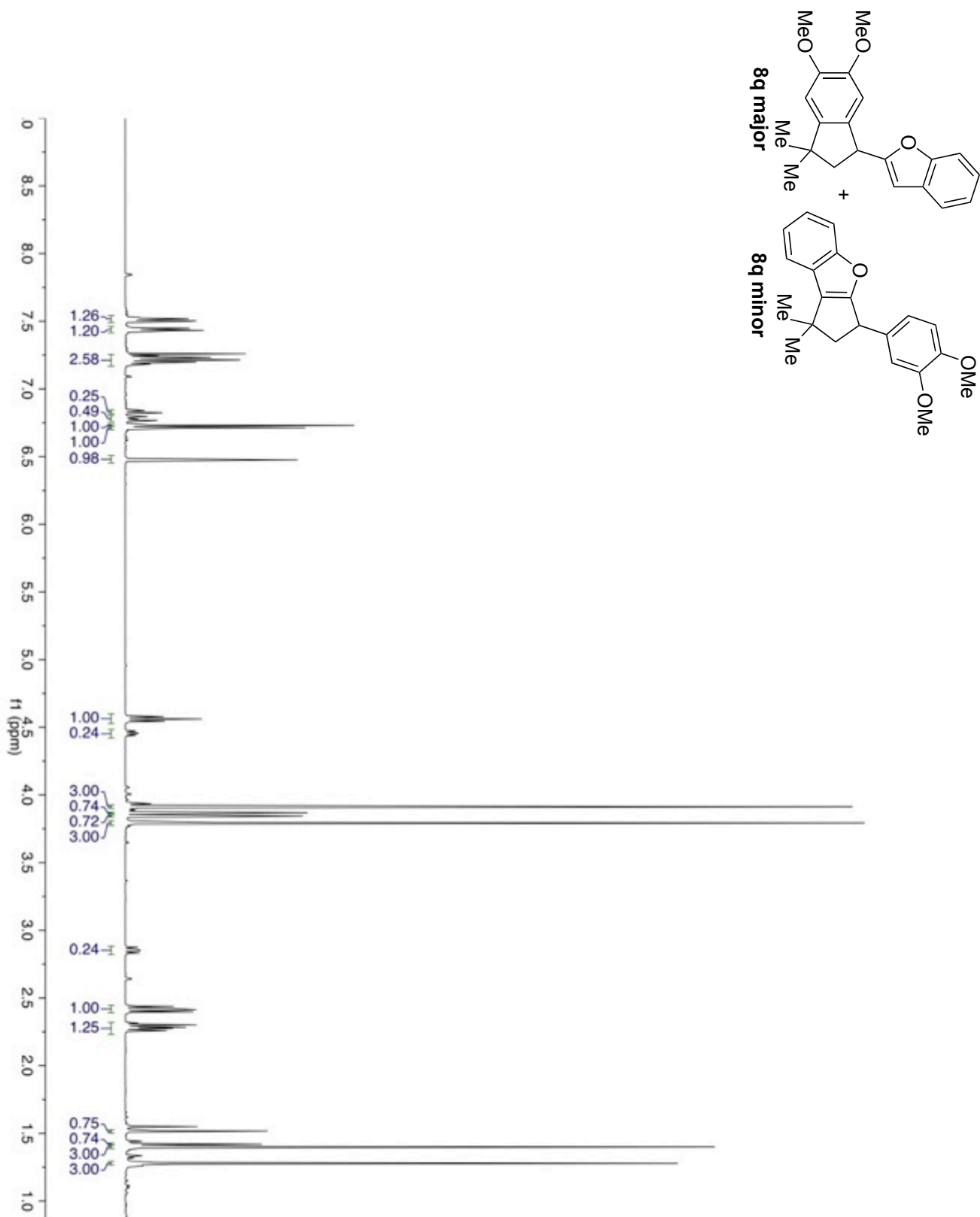


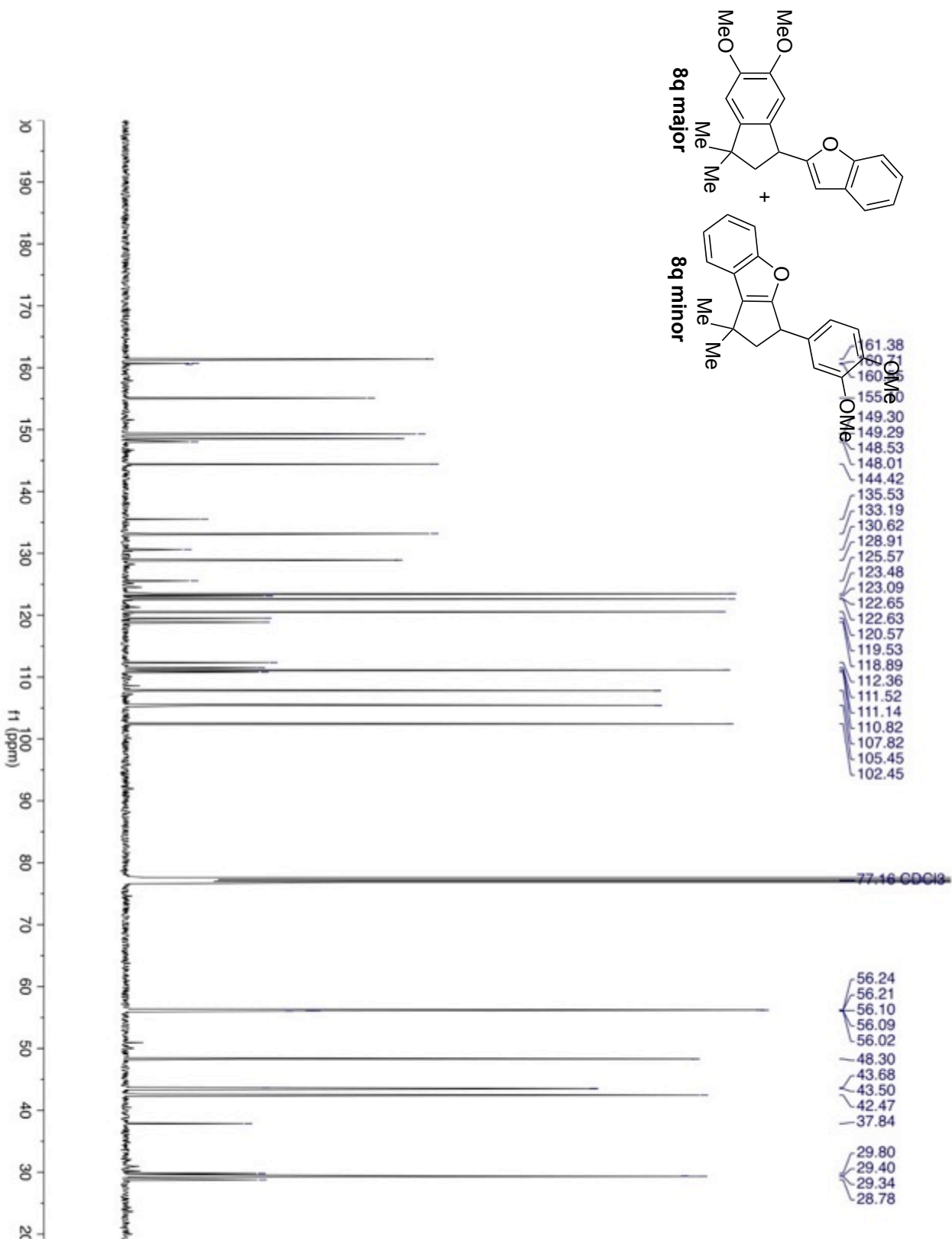


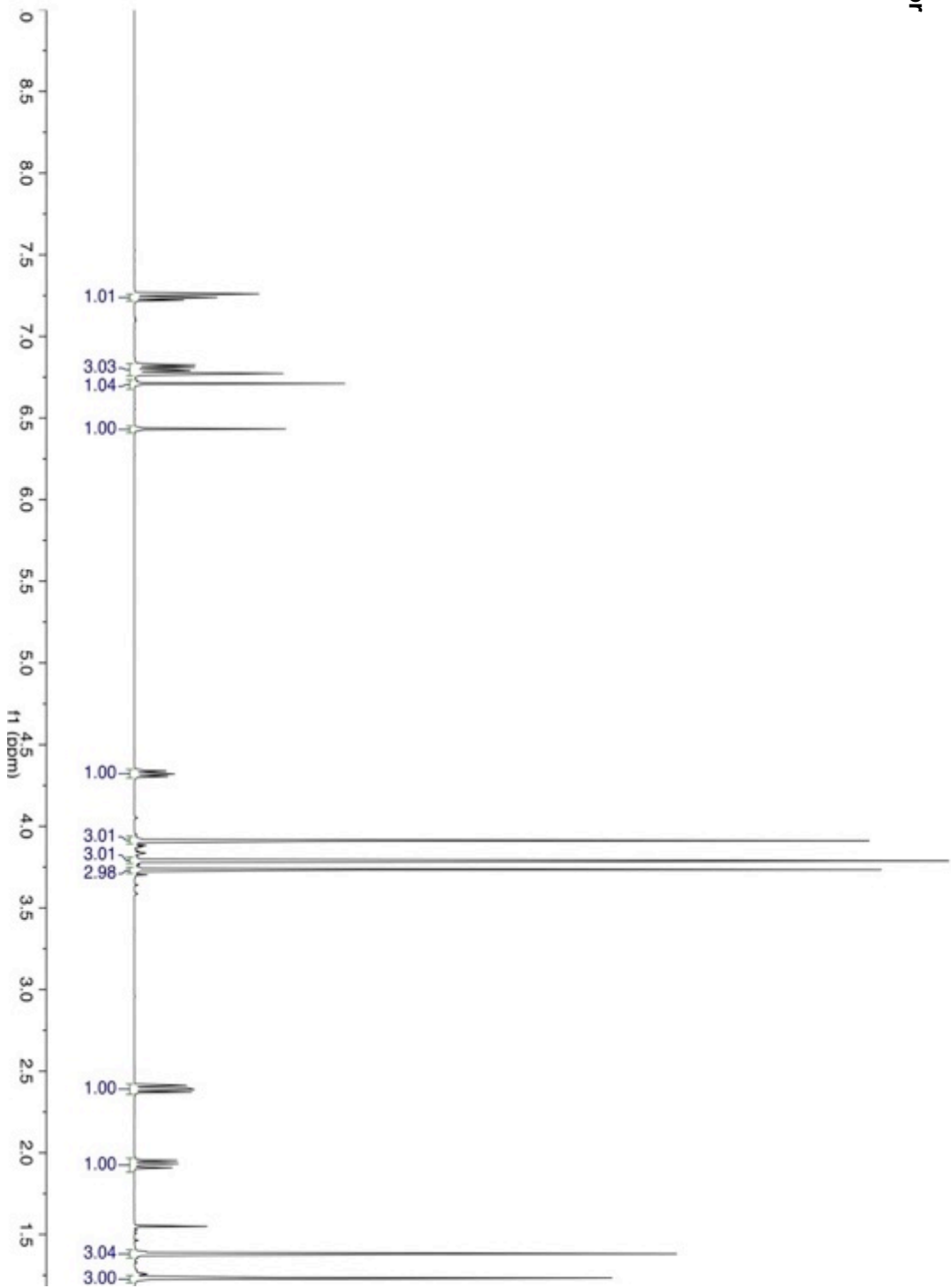
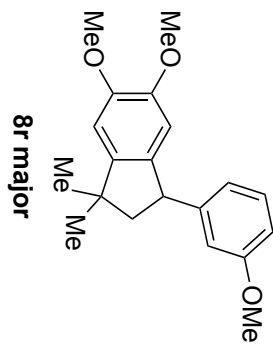


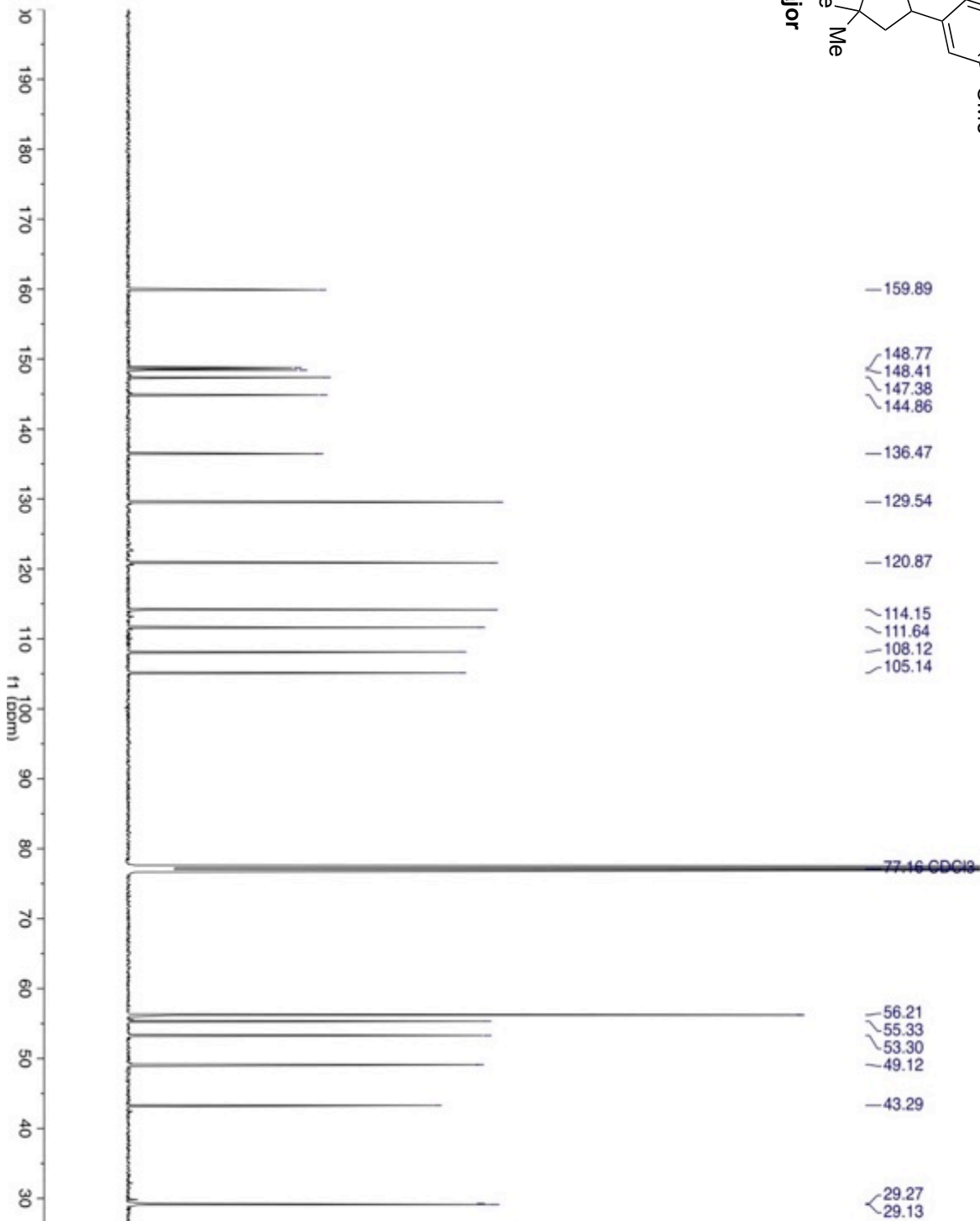
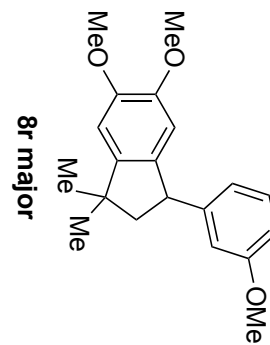


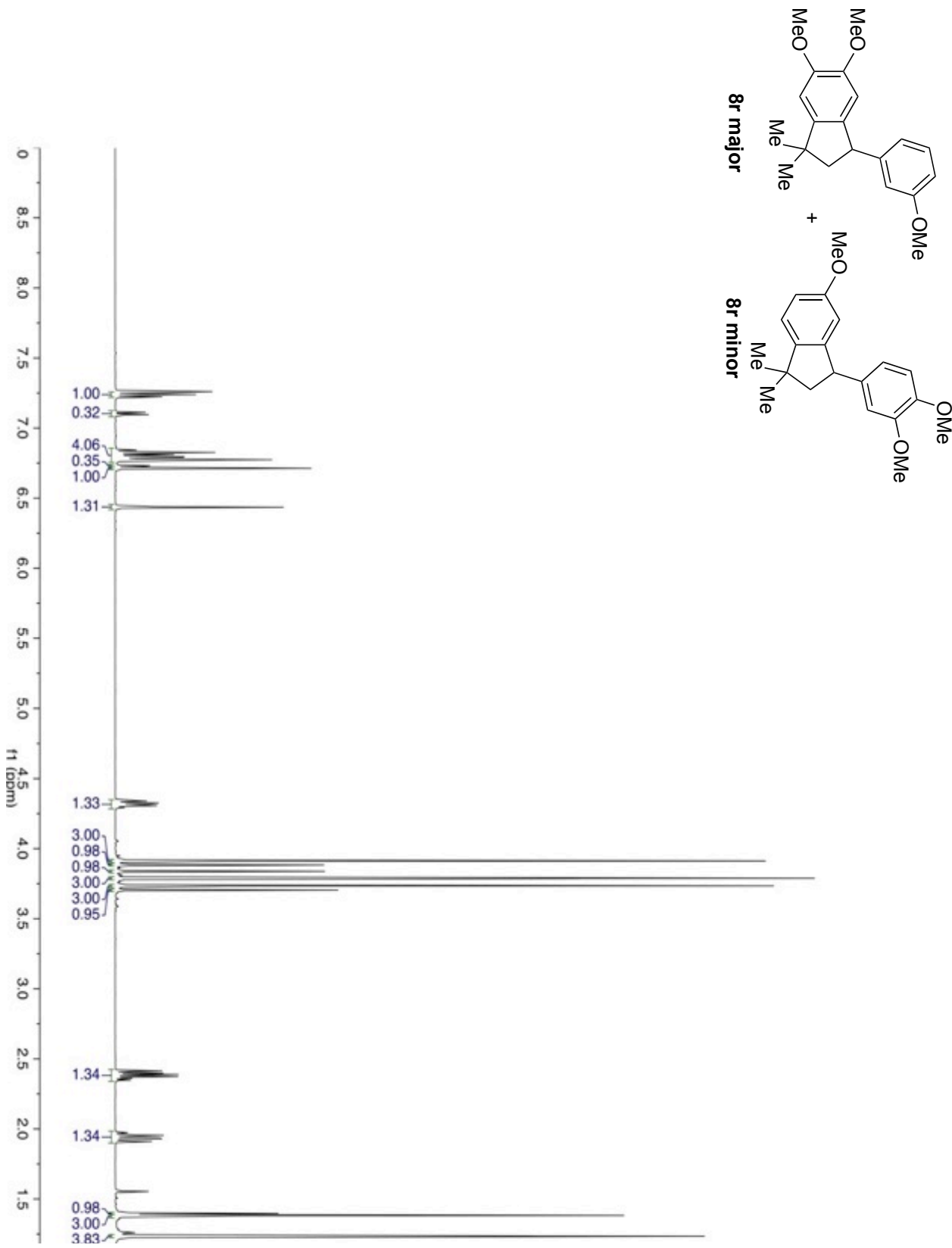


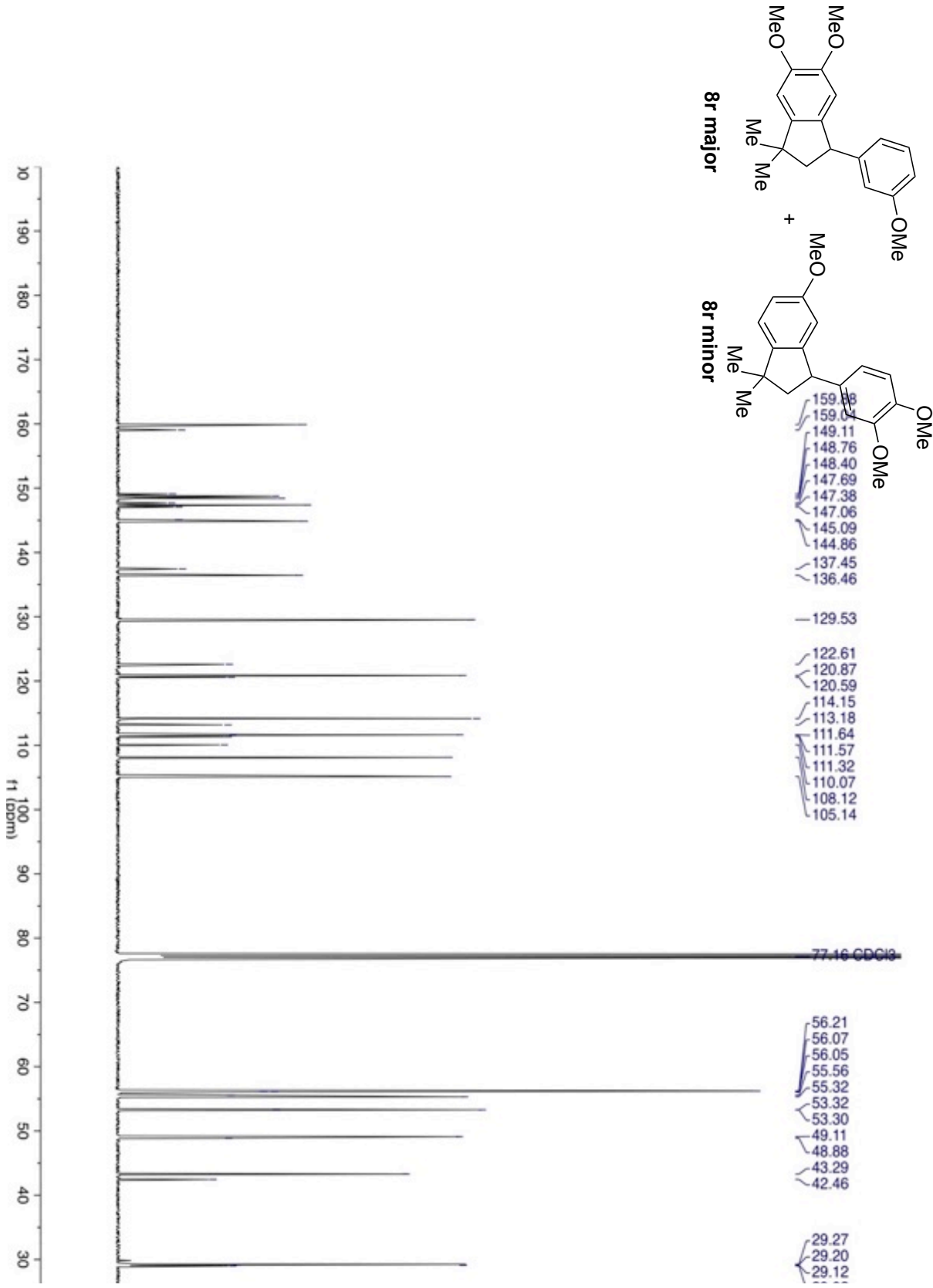


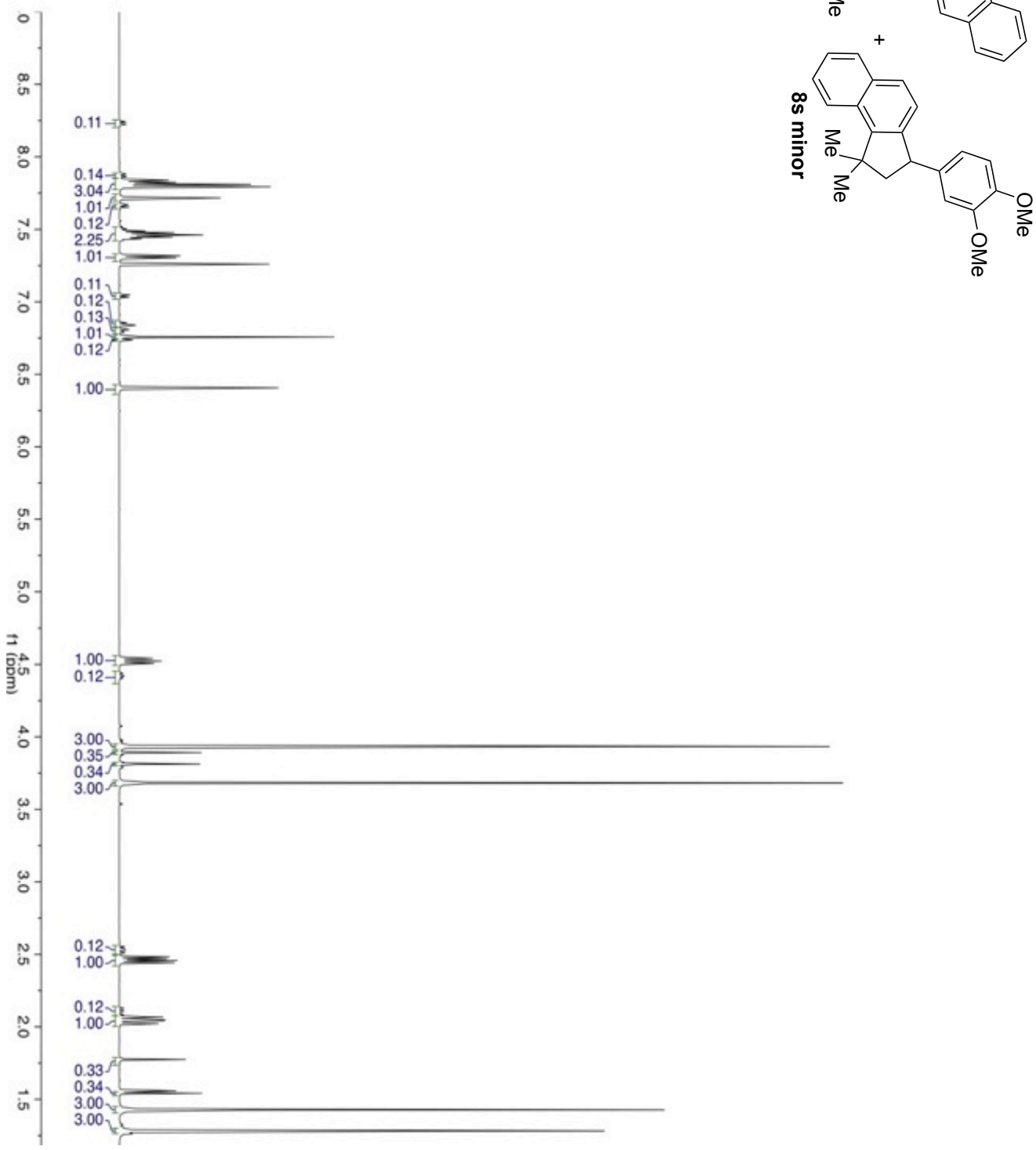


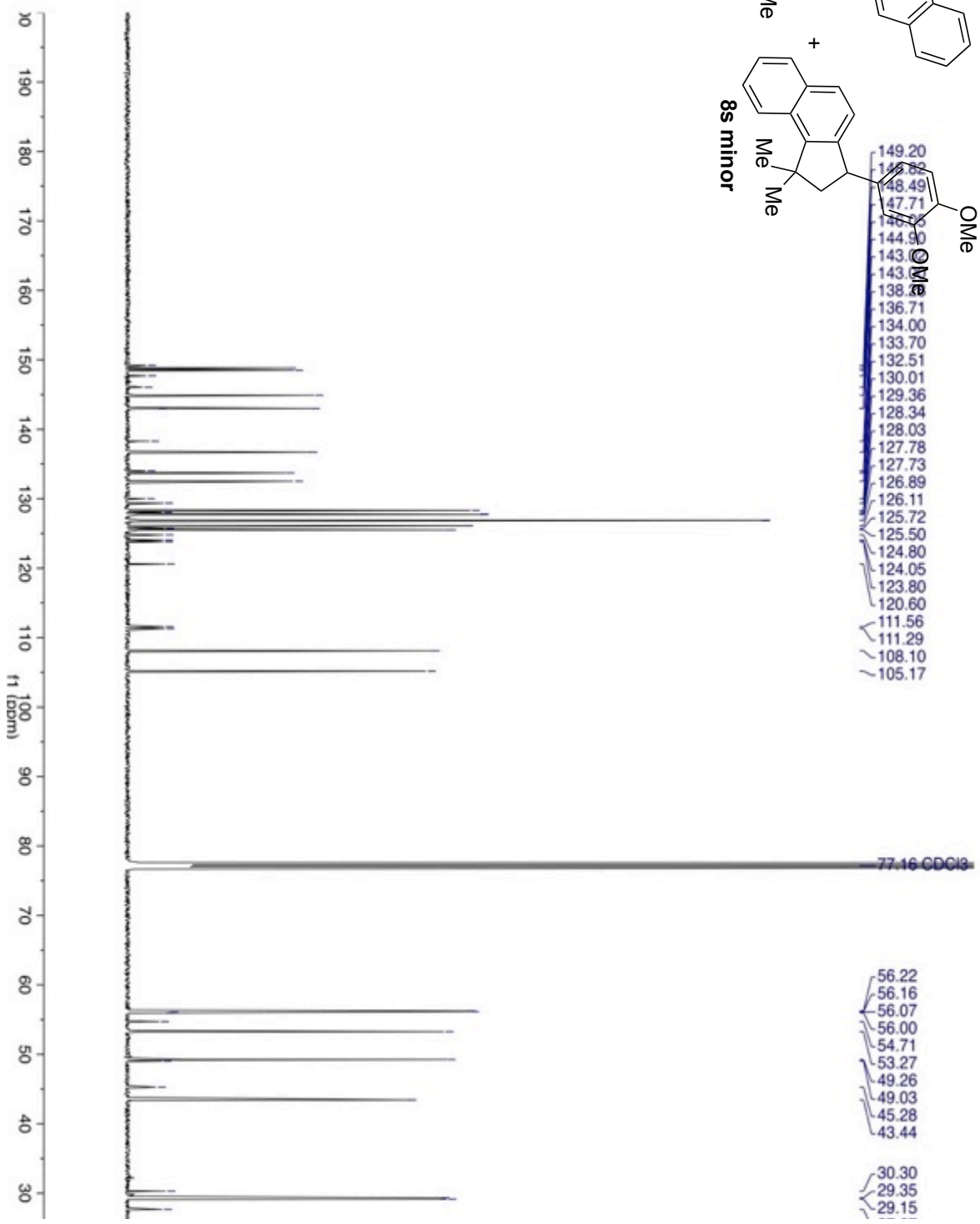


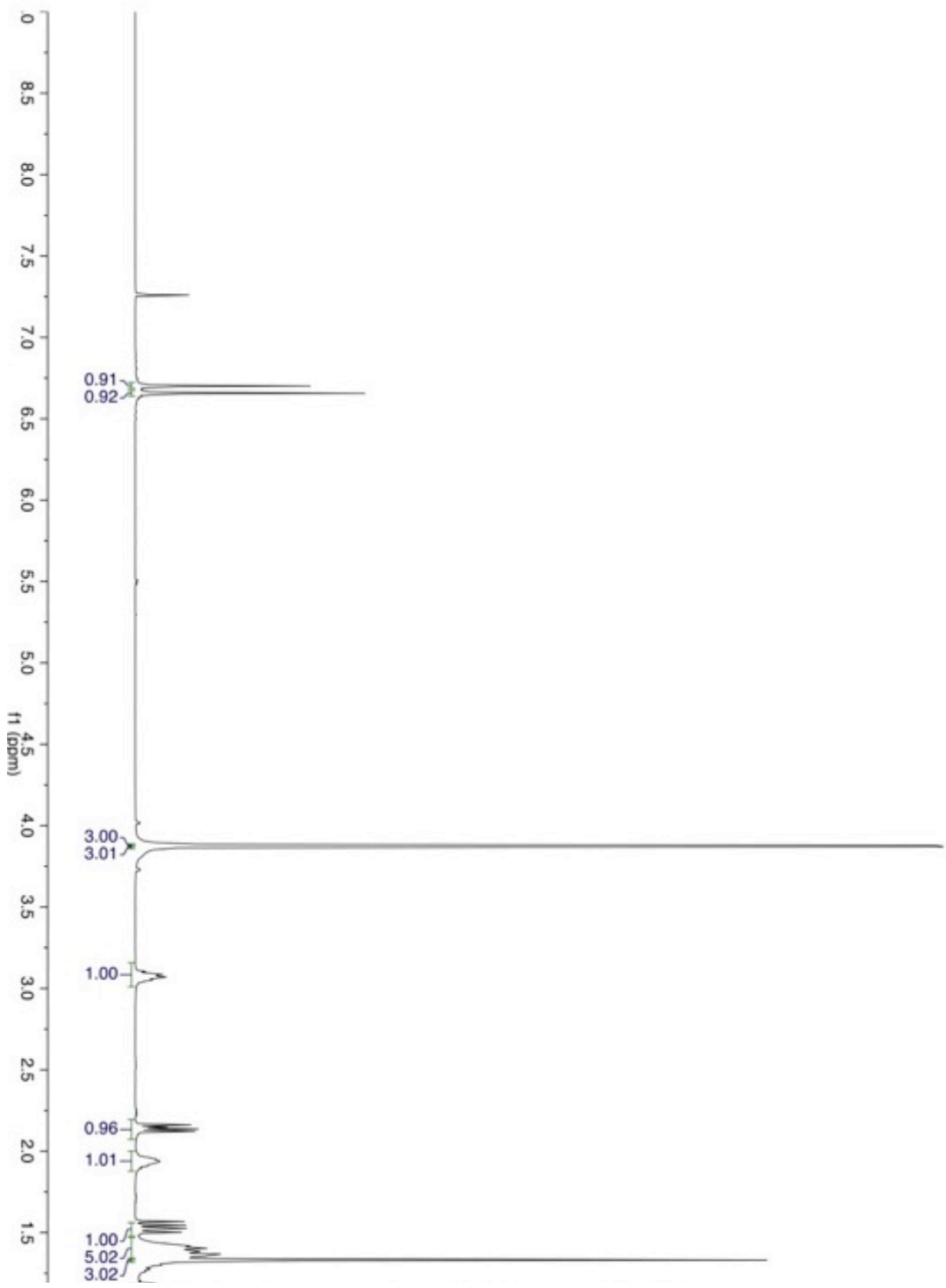
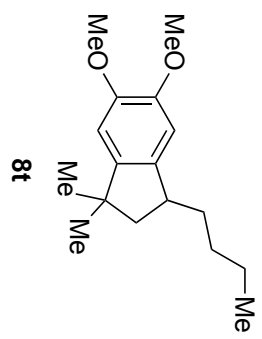


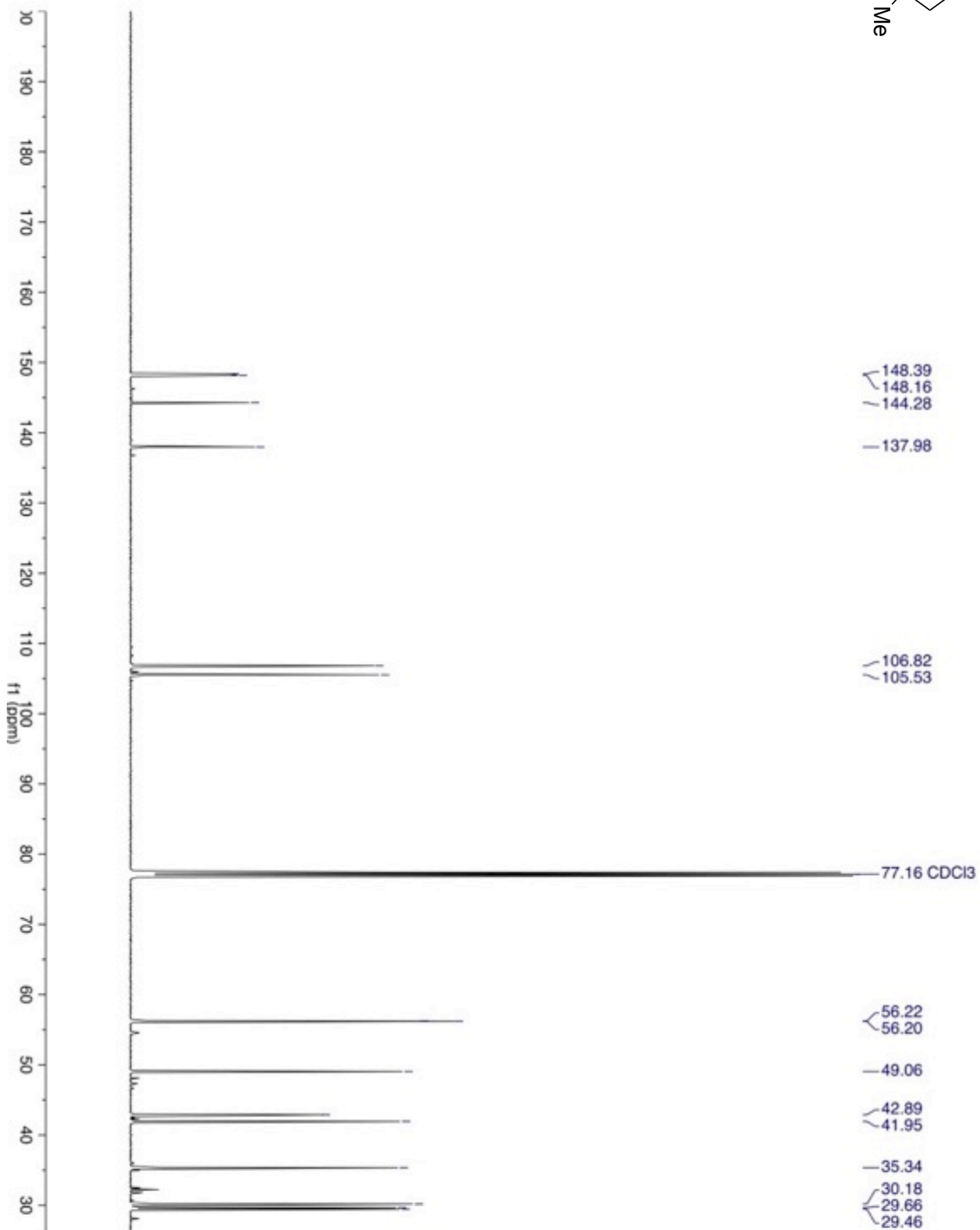
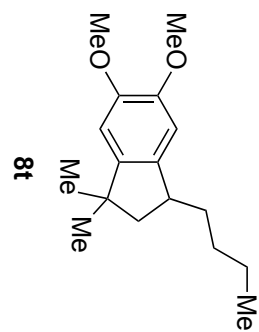


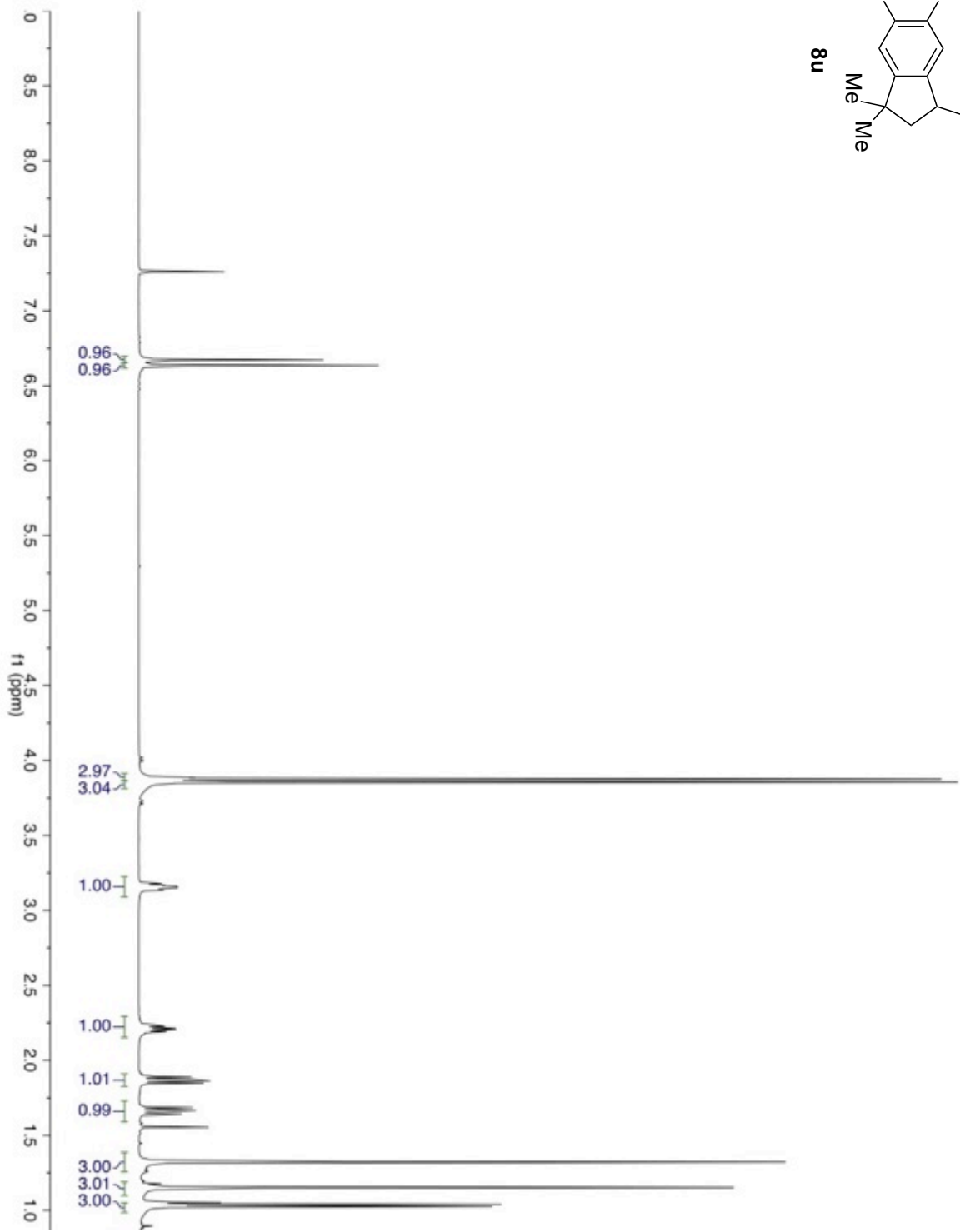
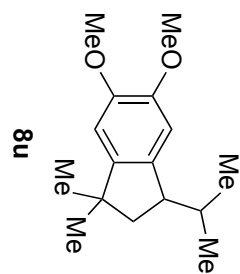


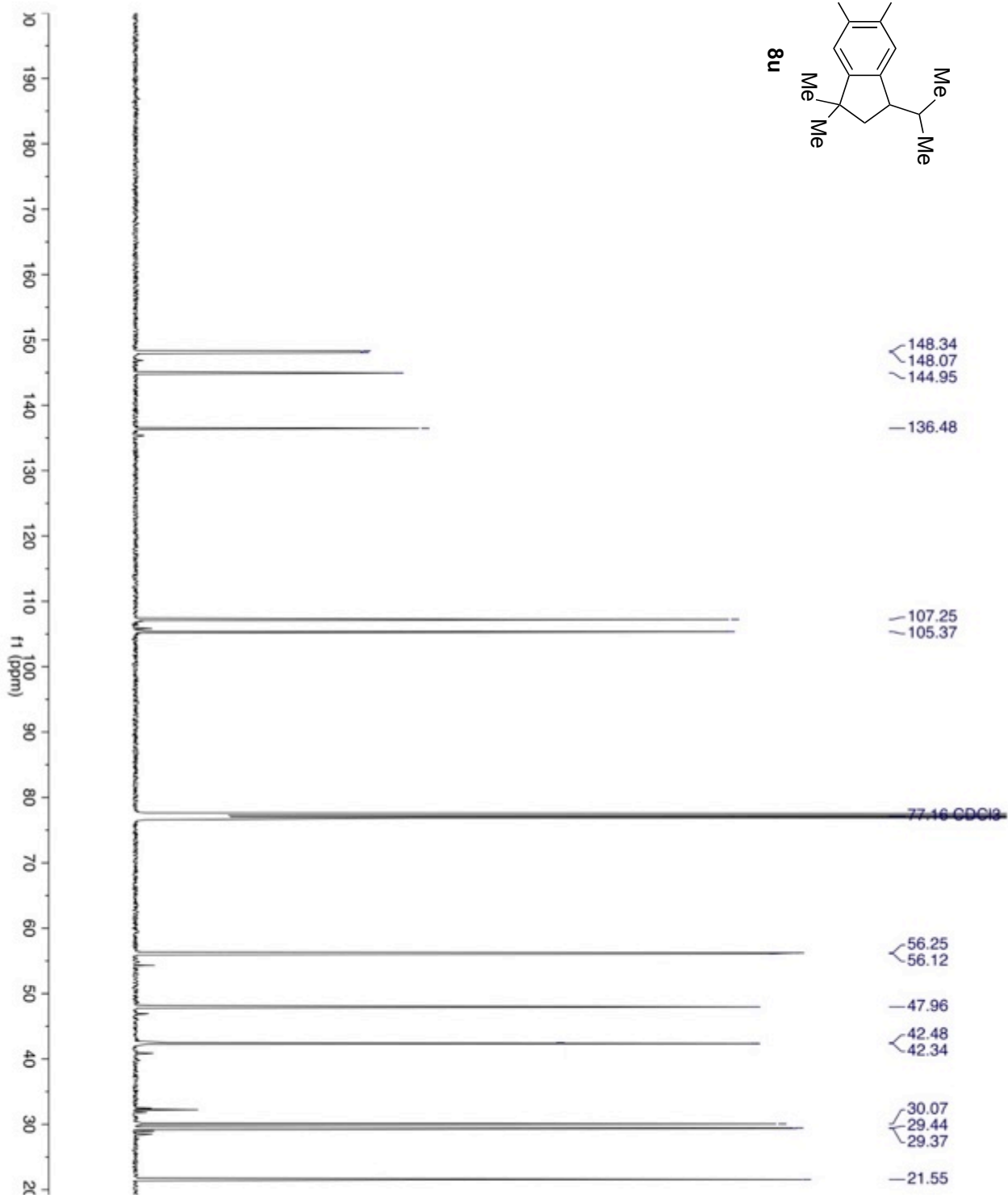
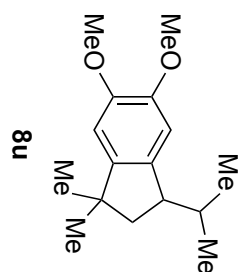


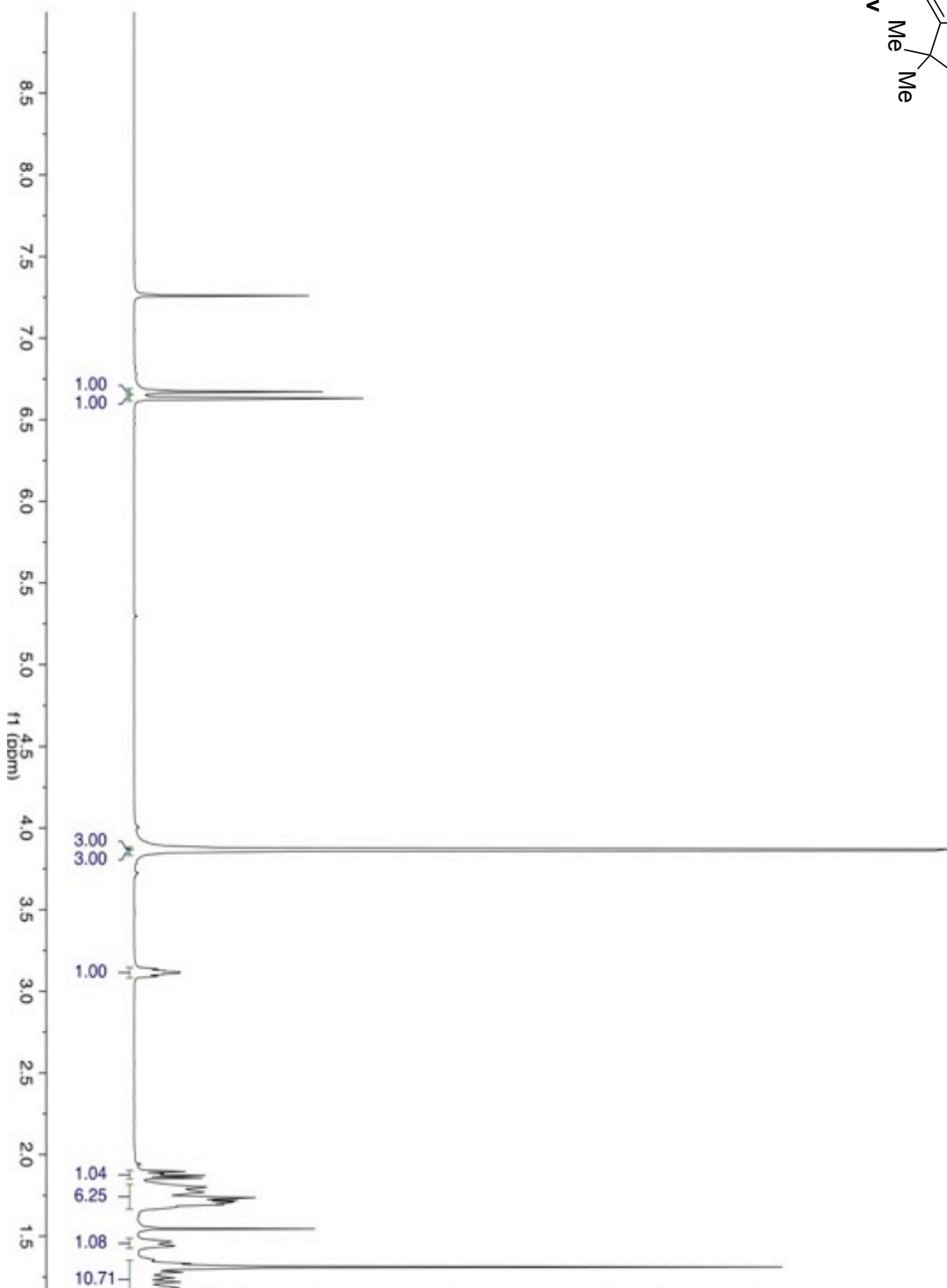
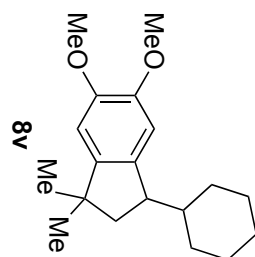


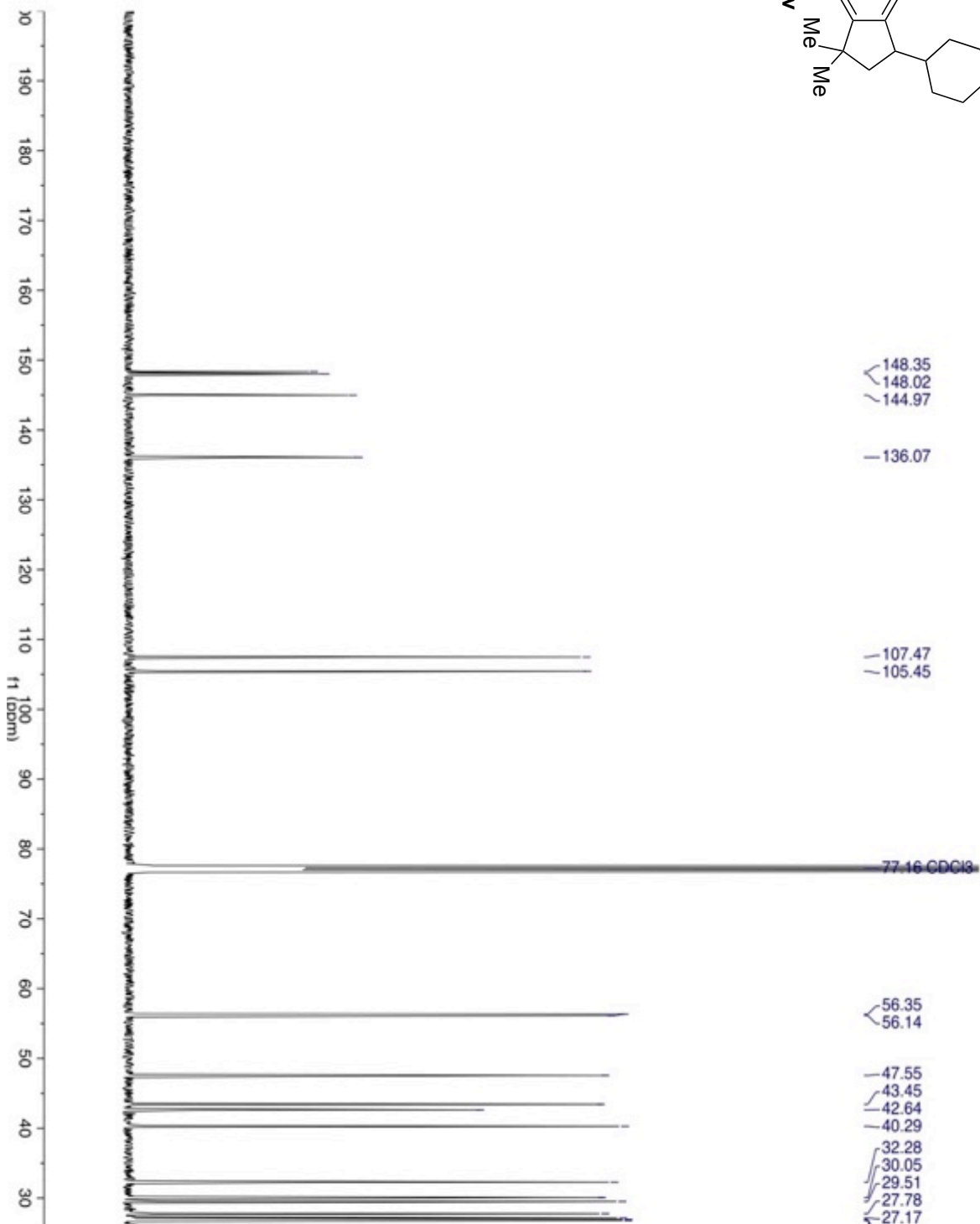
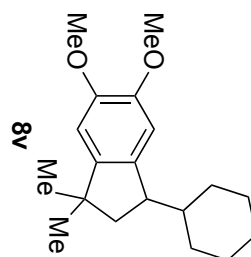


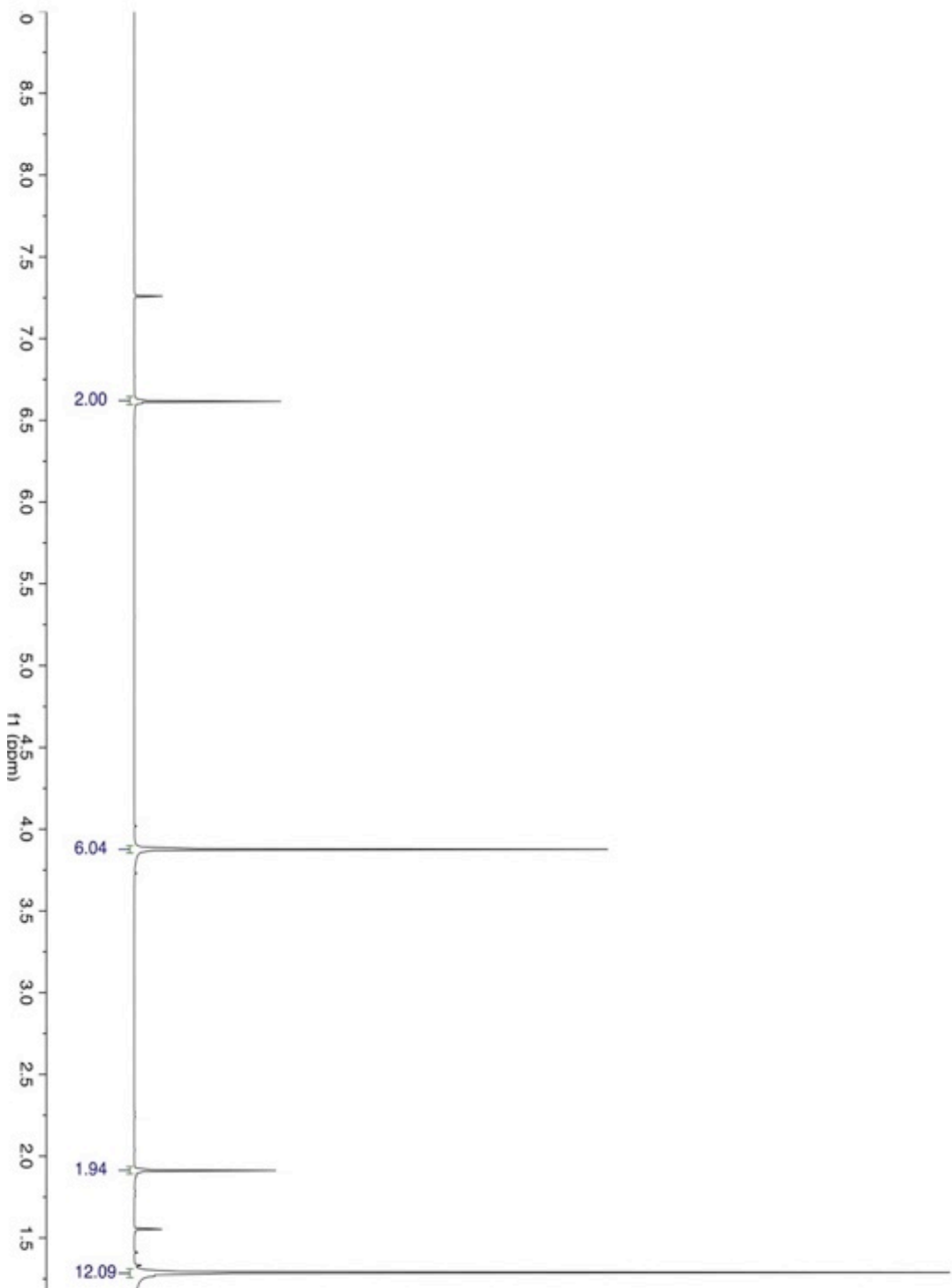
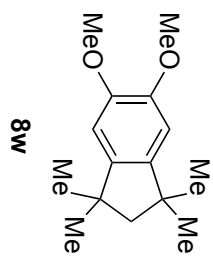


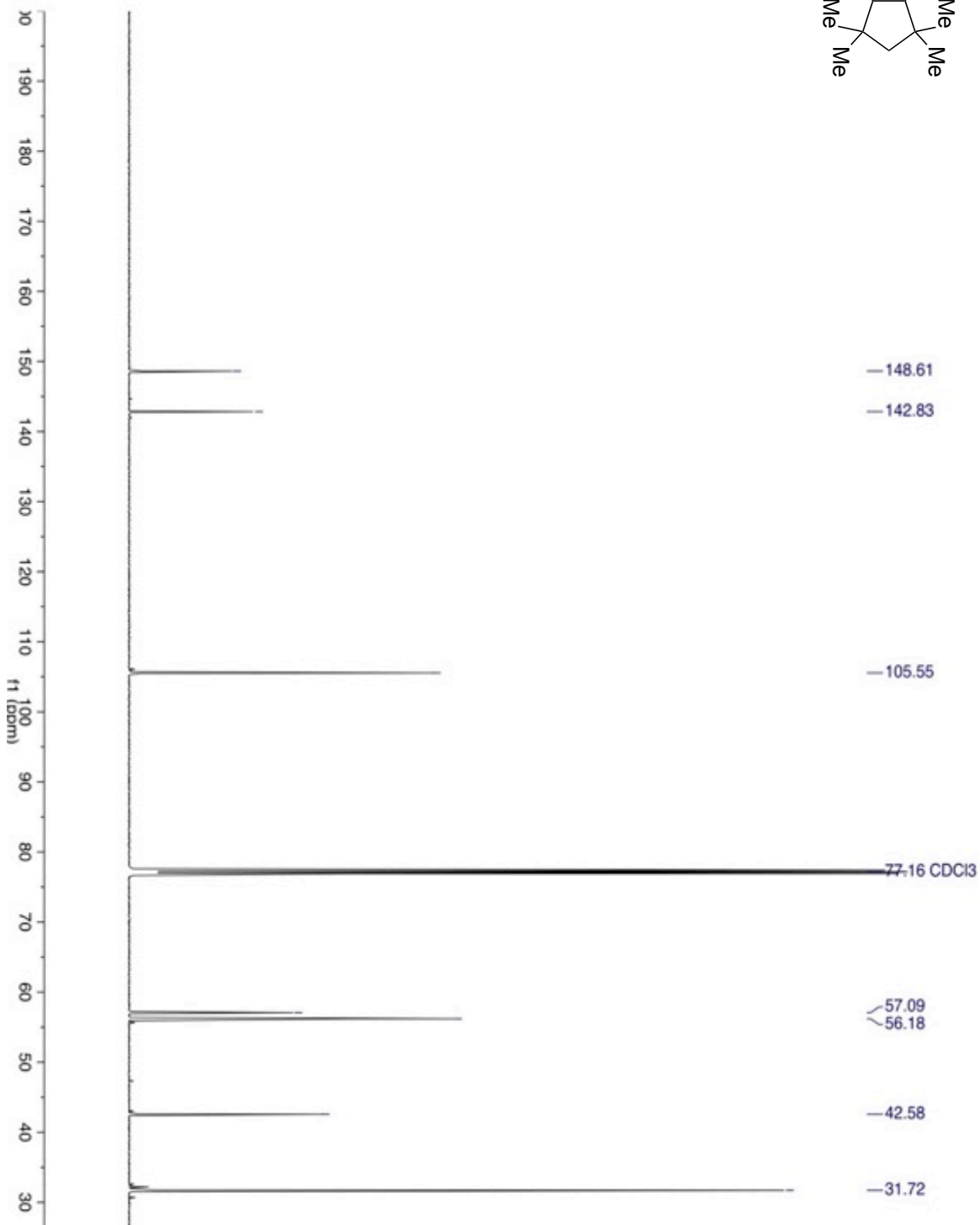
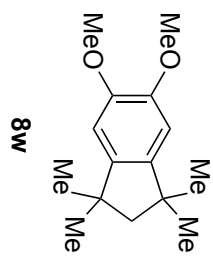


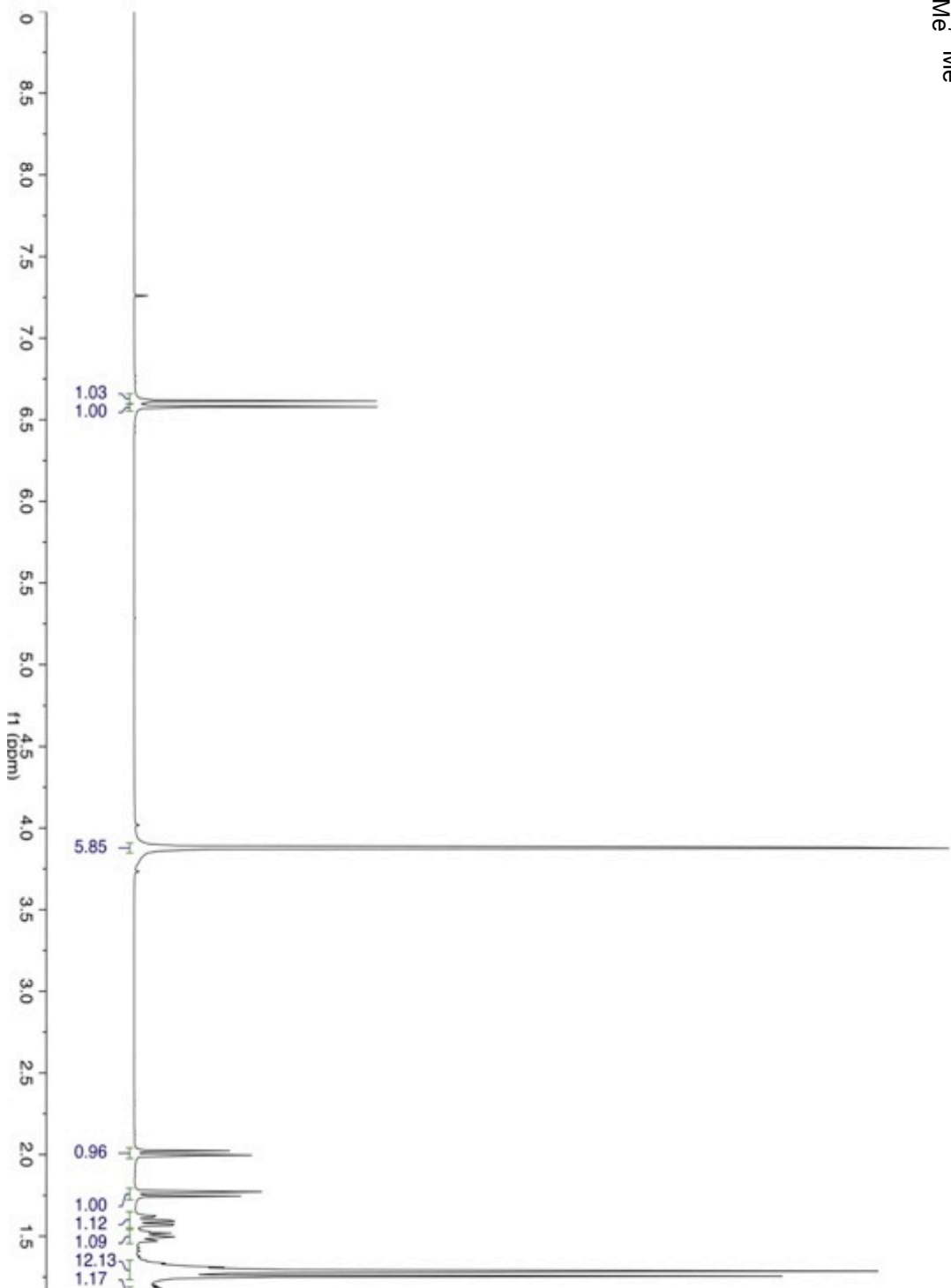
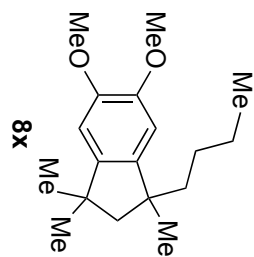


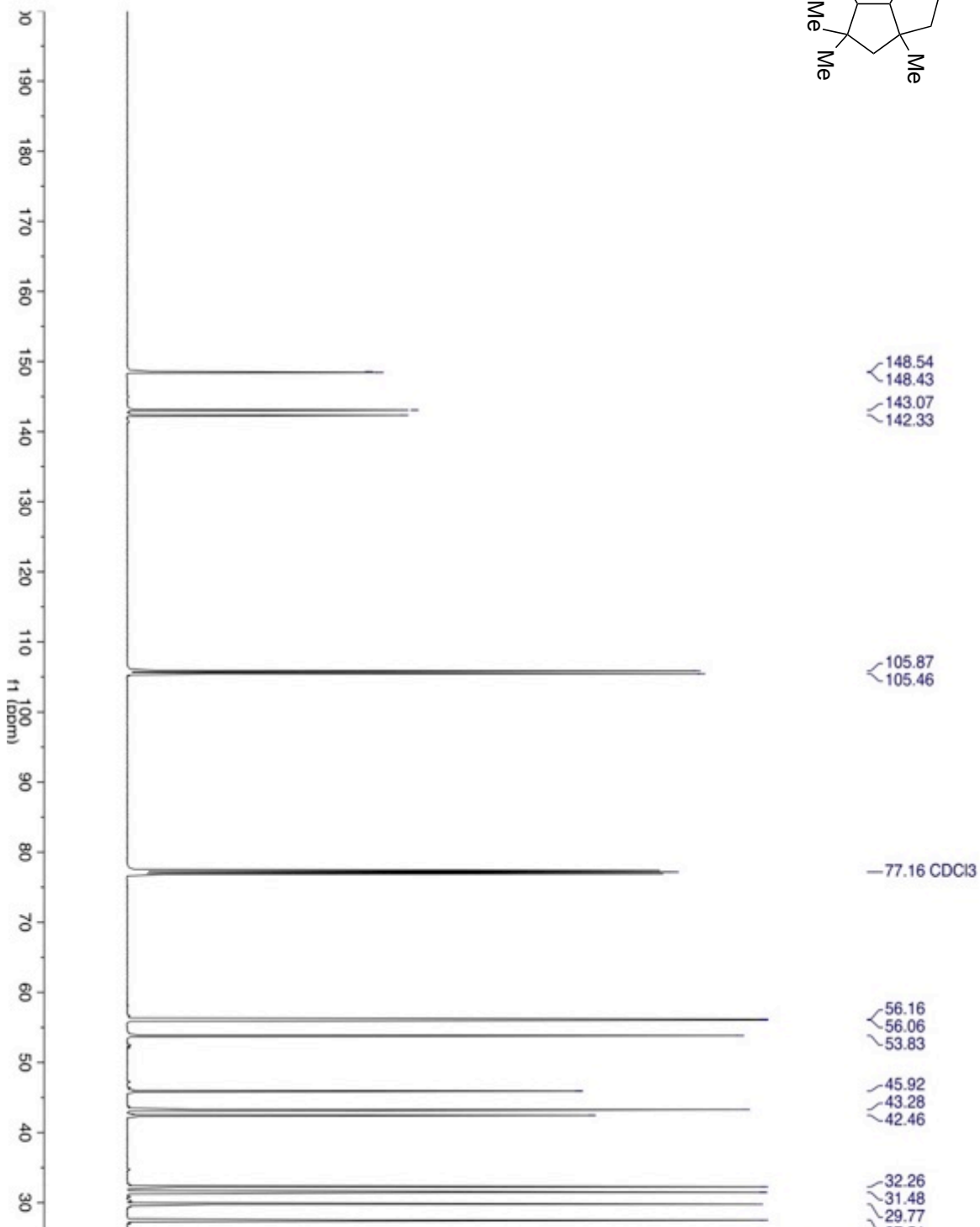
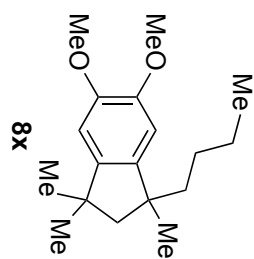


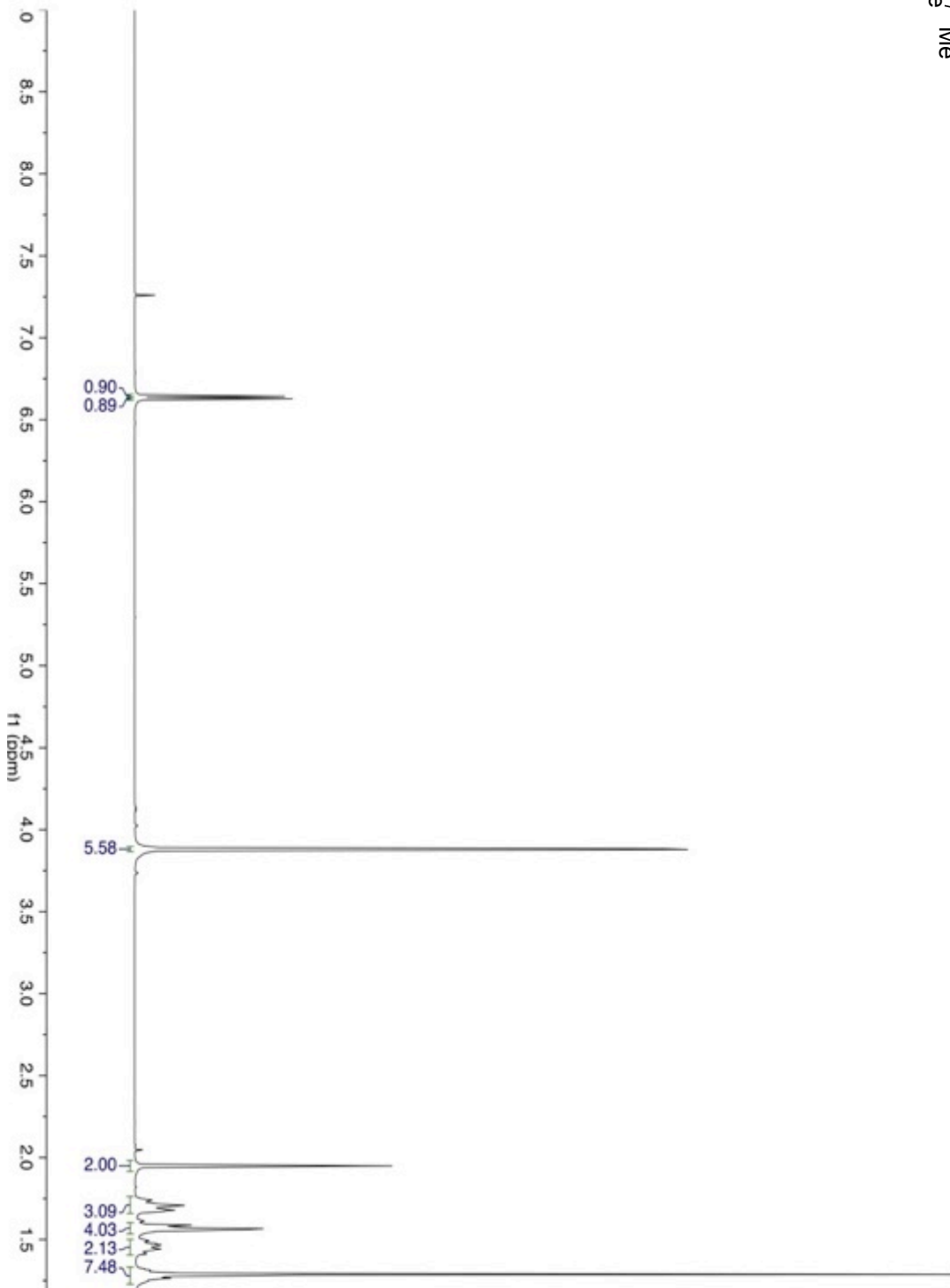
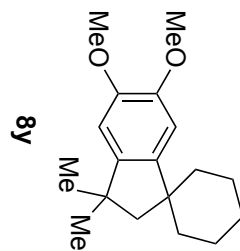


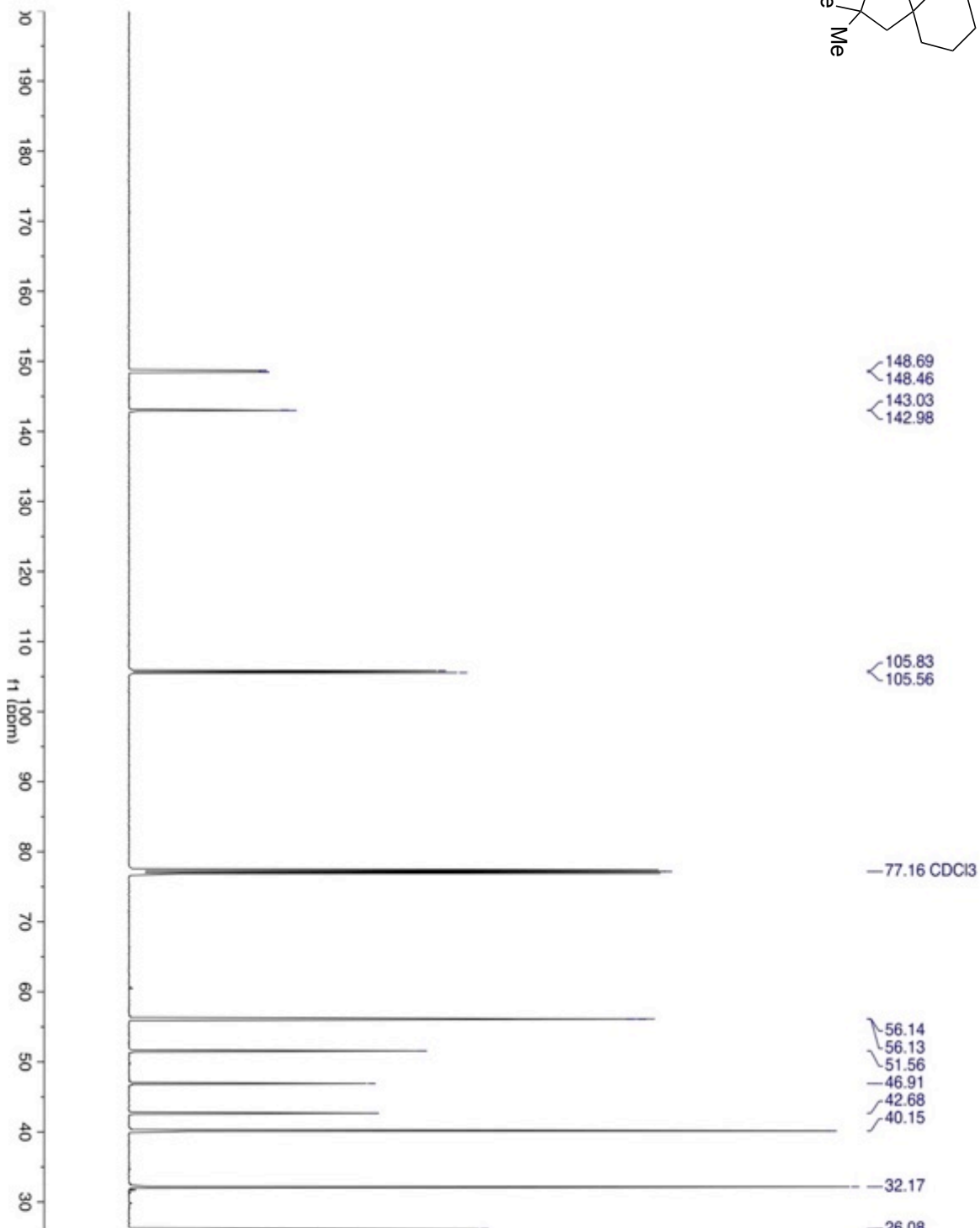
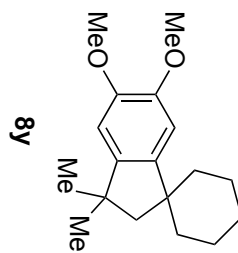


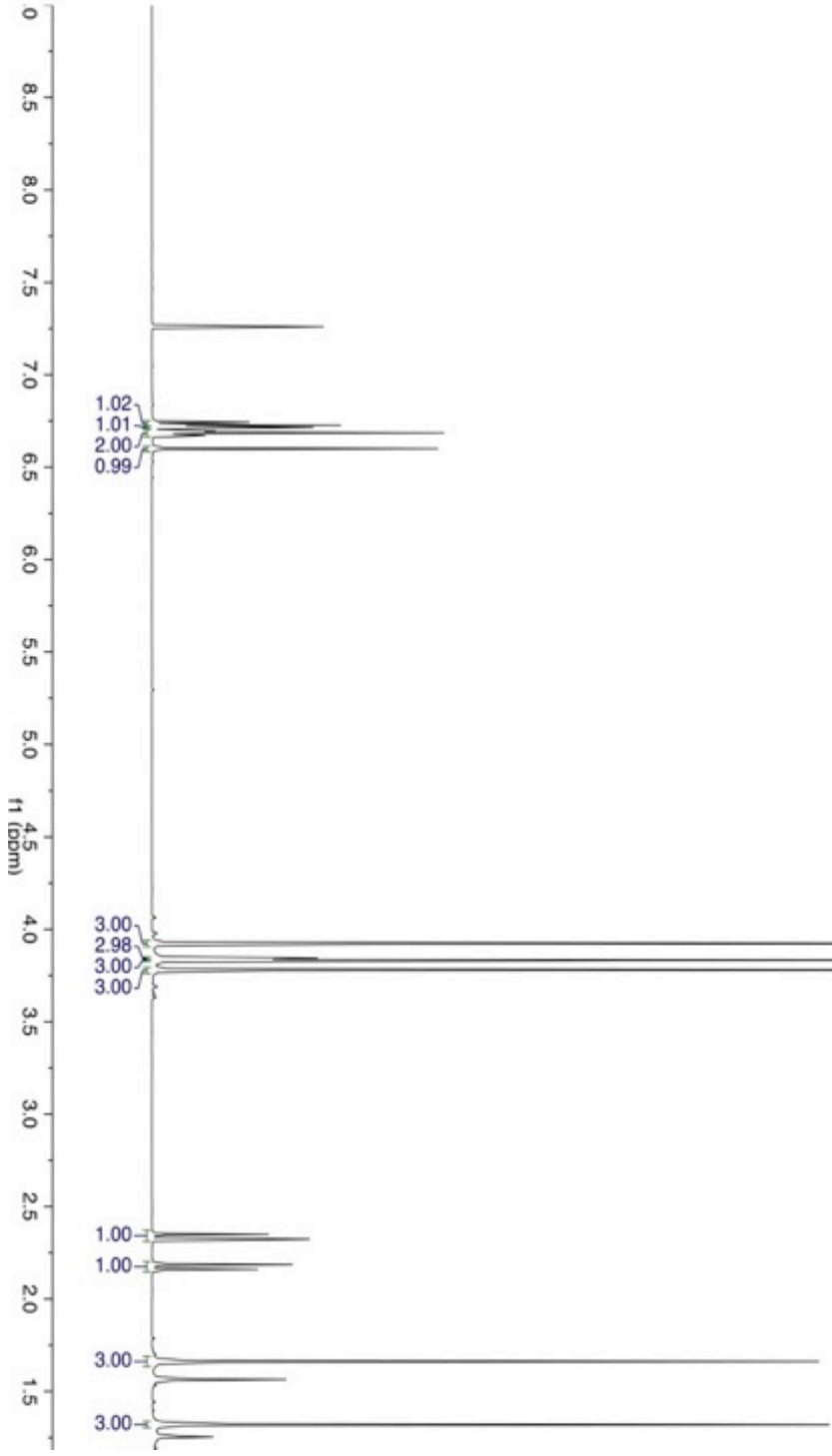
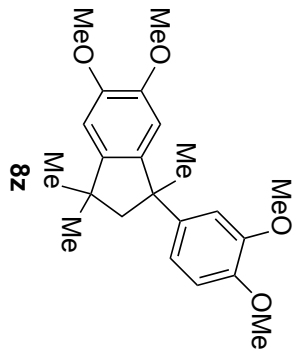


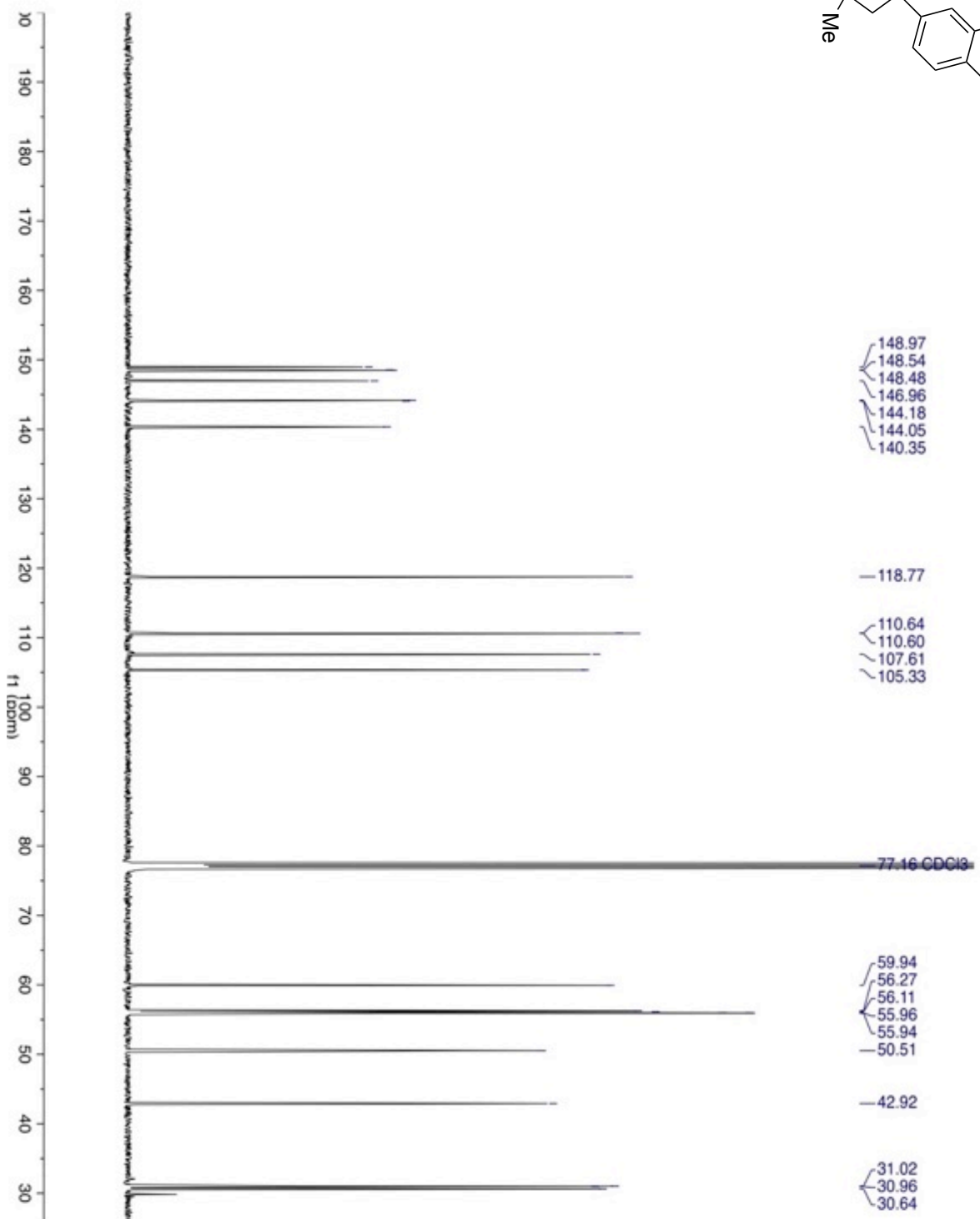
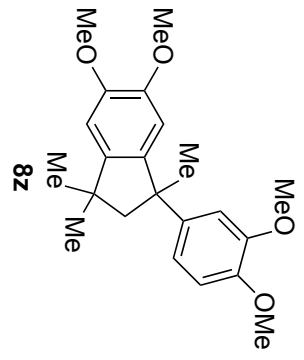


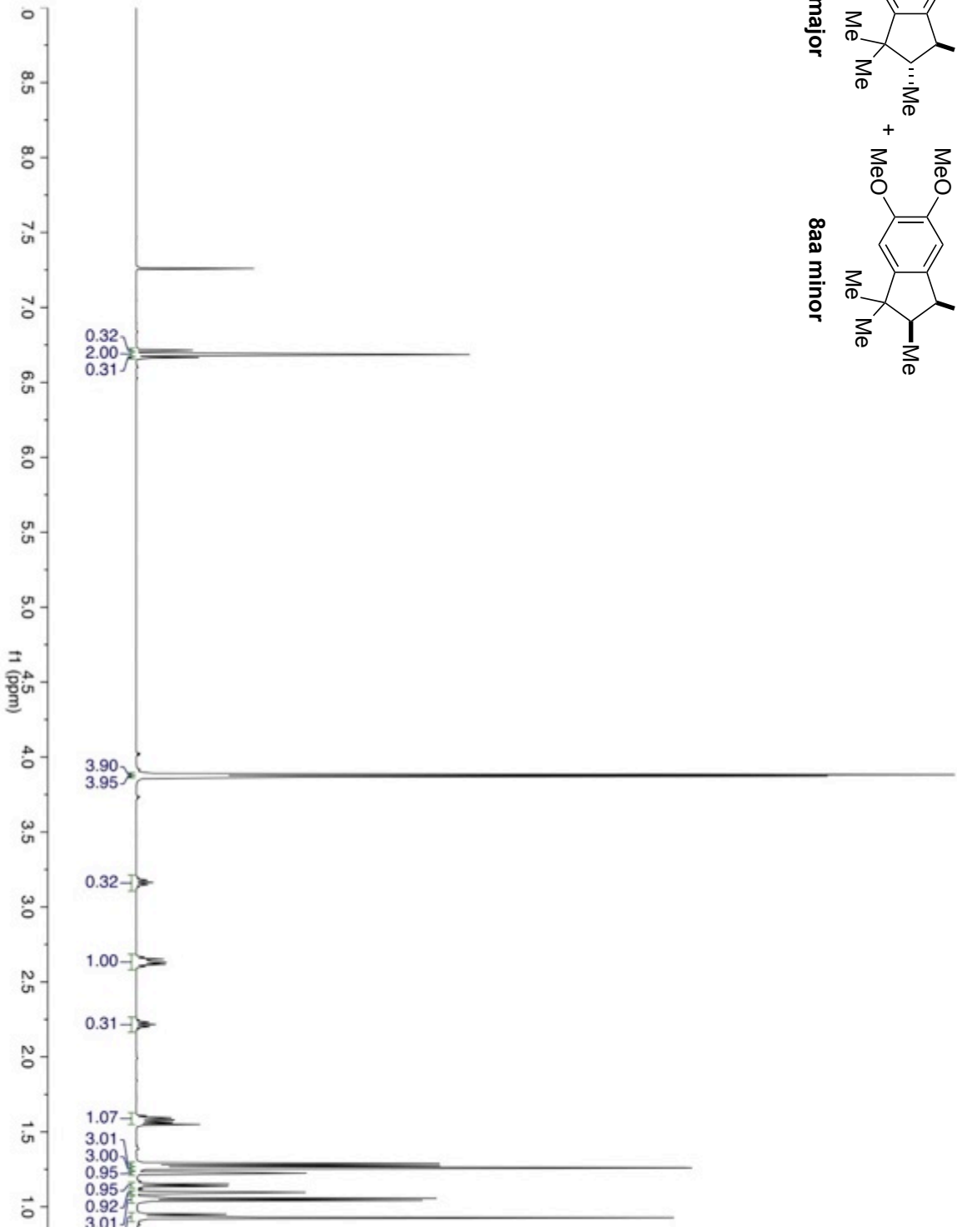
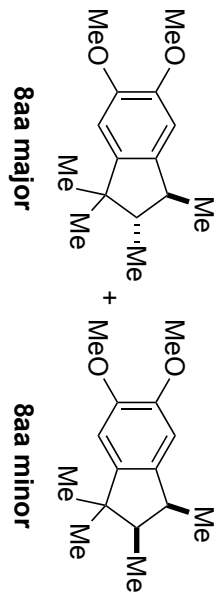


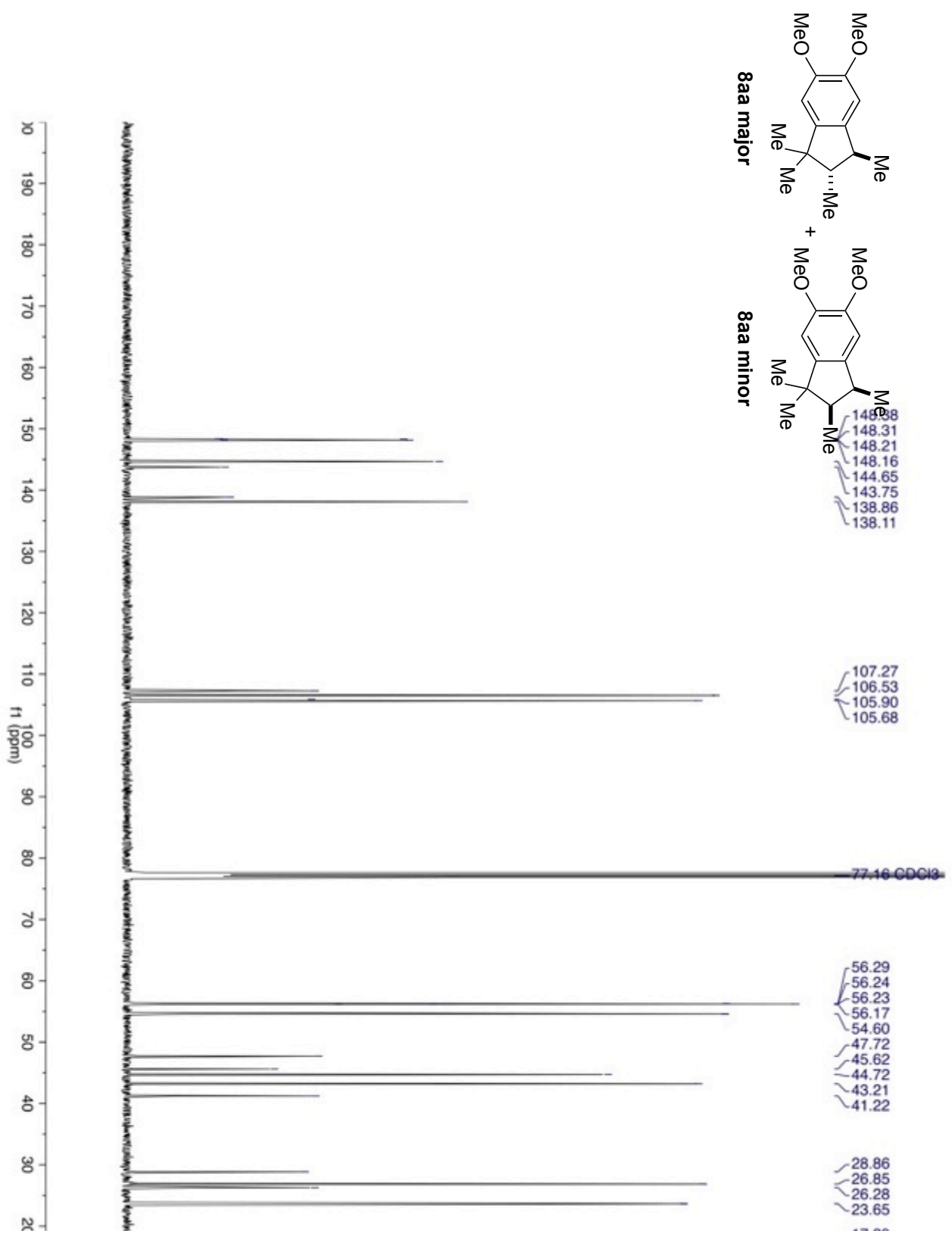


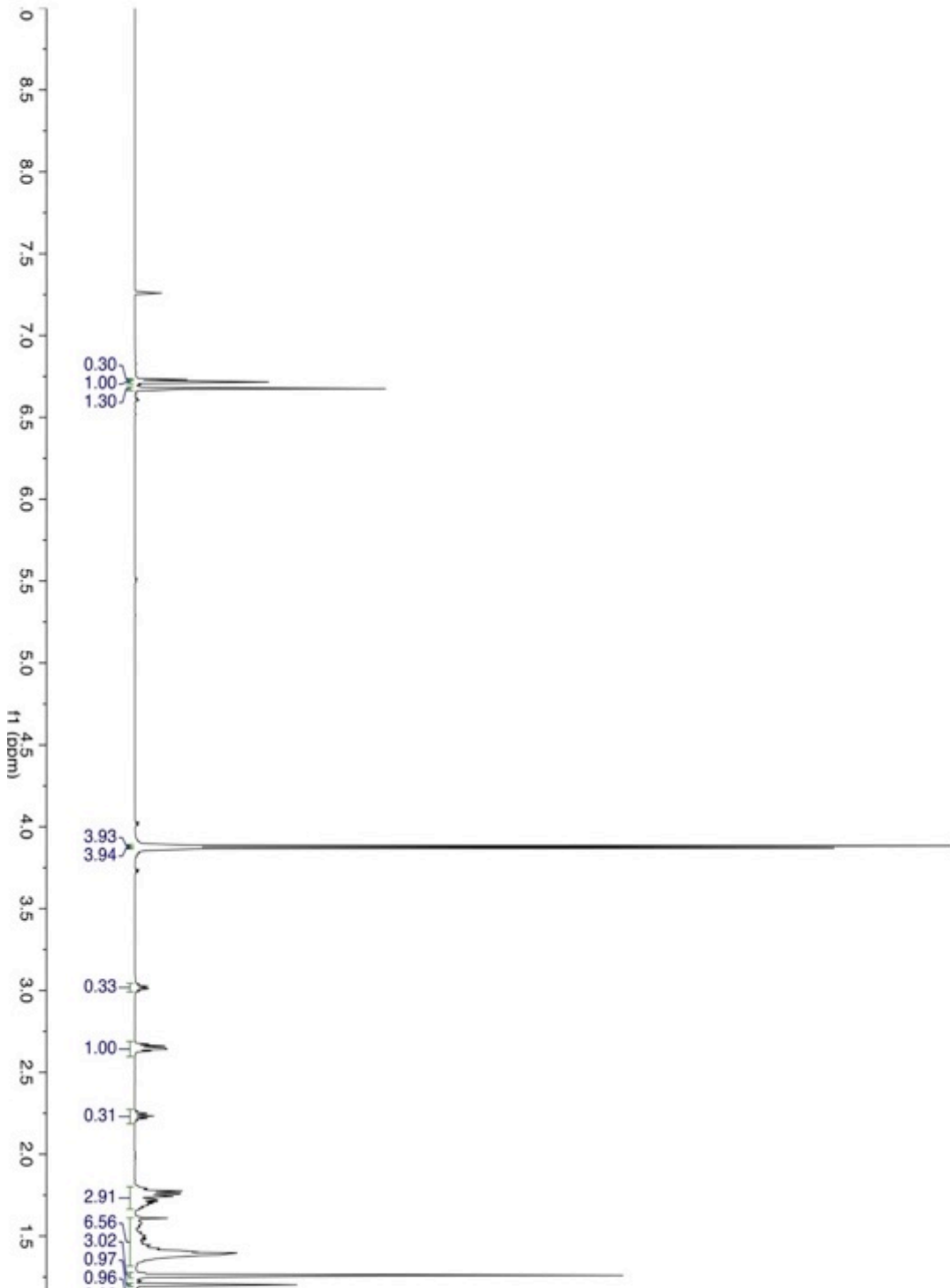
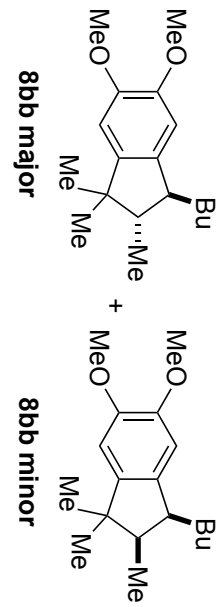


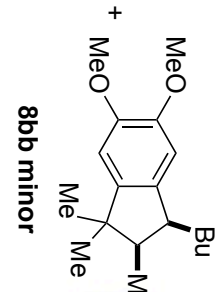
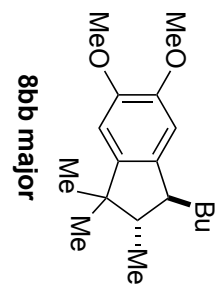






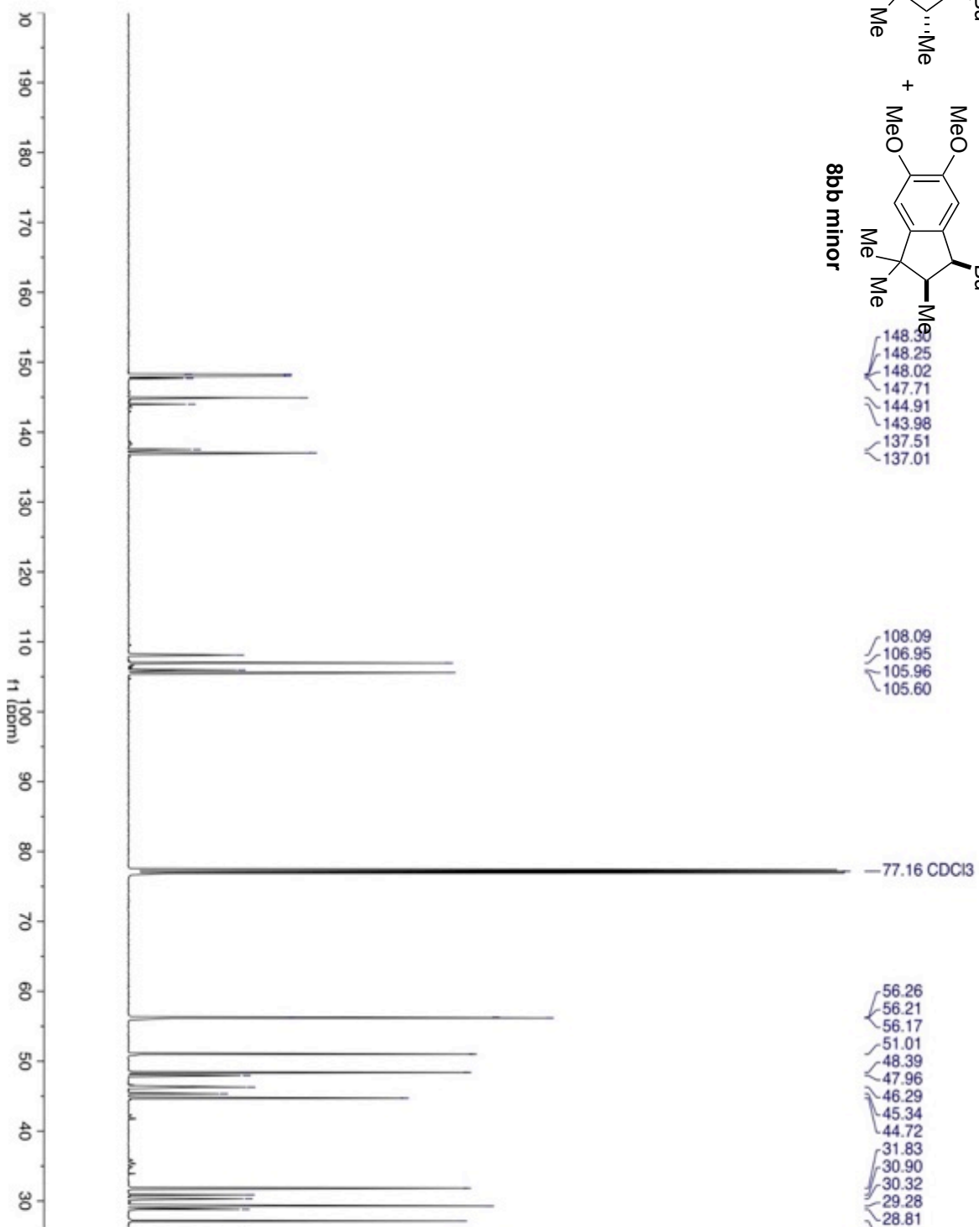


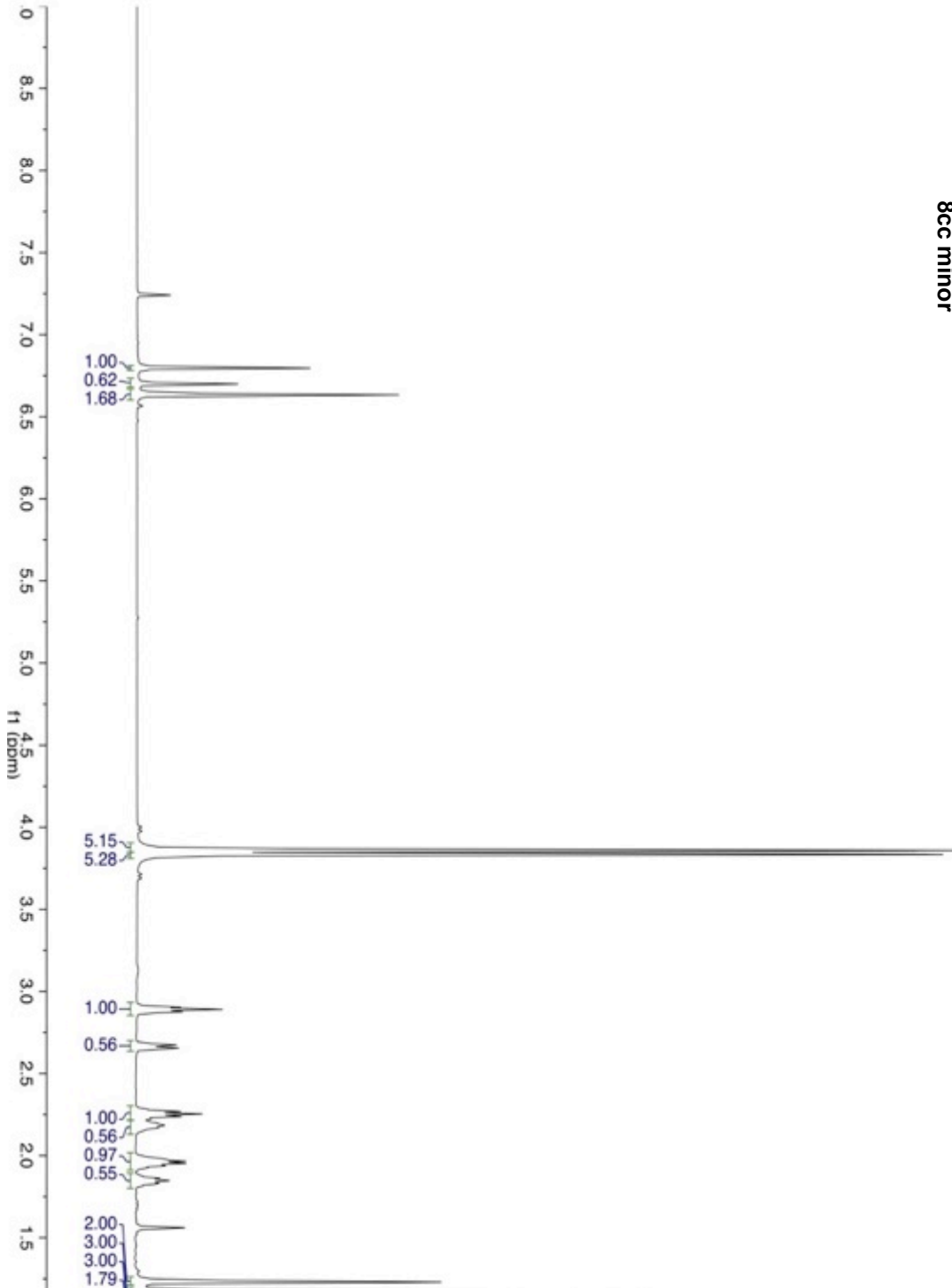
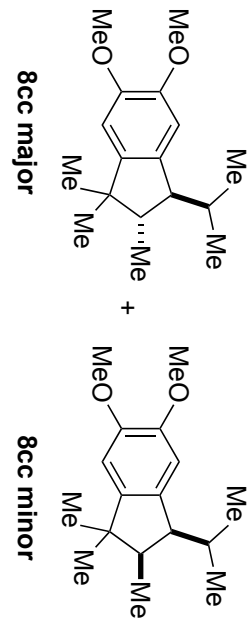


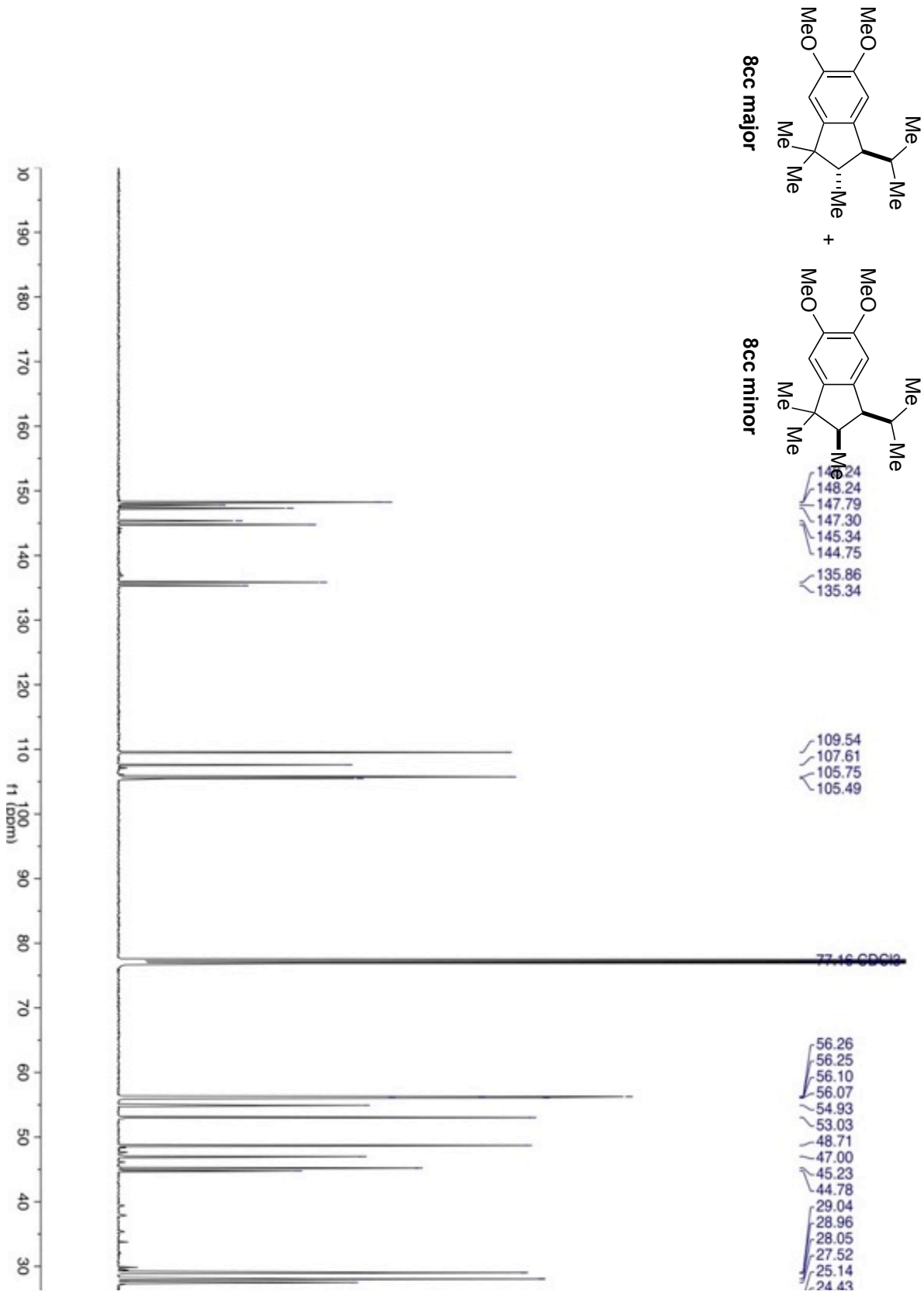


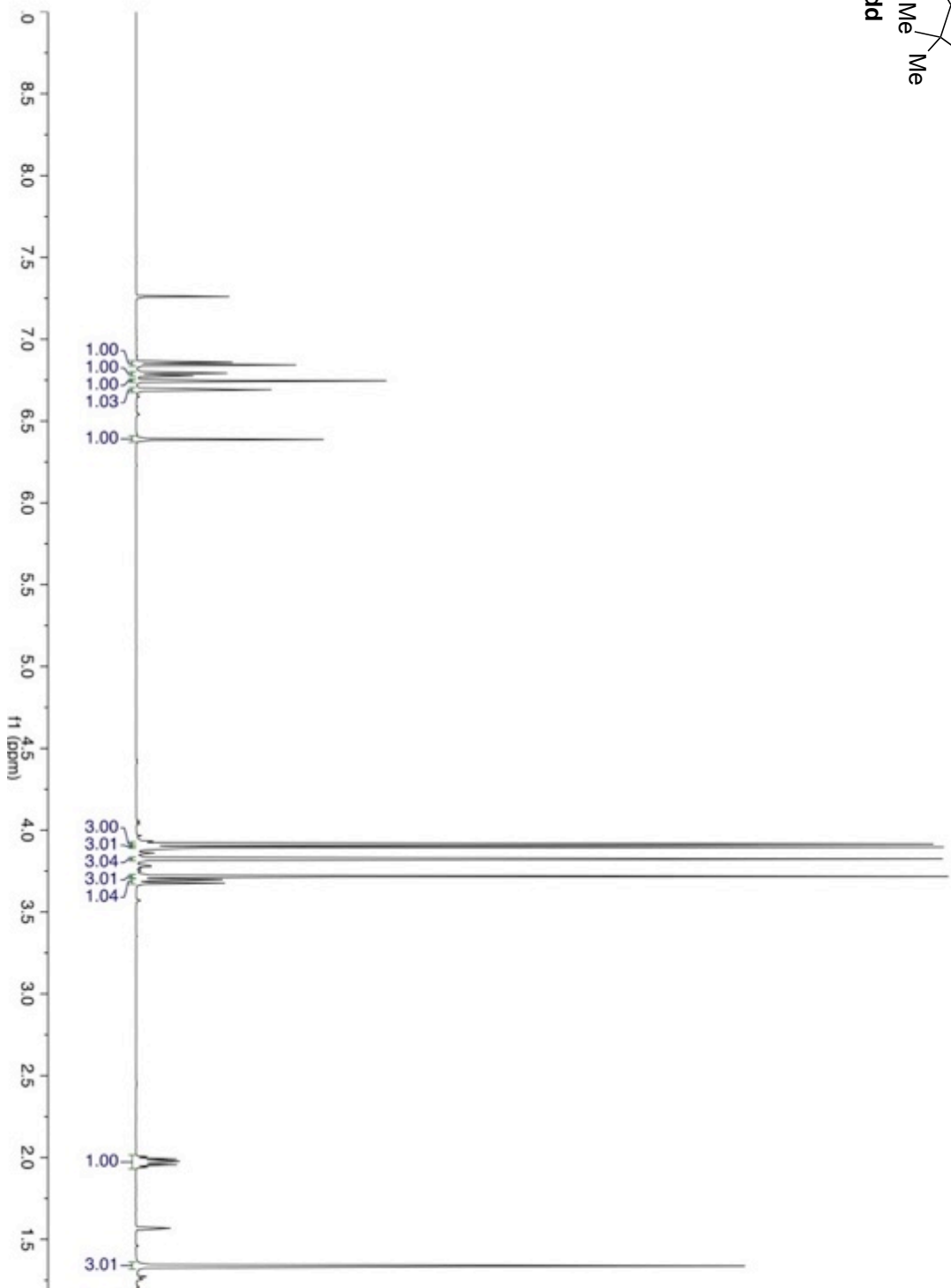
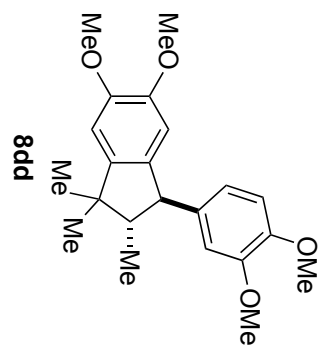
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- 148.25
- 148.02
- 147.71
- 144.91
- 143.98
- 137.51
- 137.01
- 108.09
- 106.95
- 105.96
- 105.60

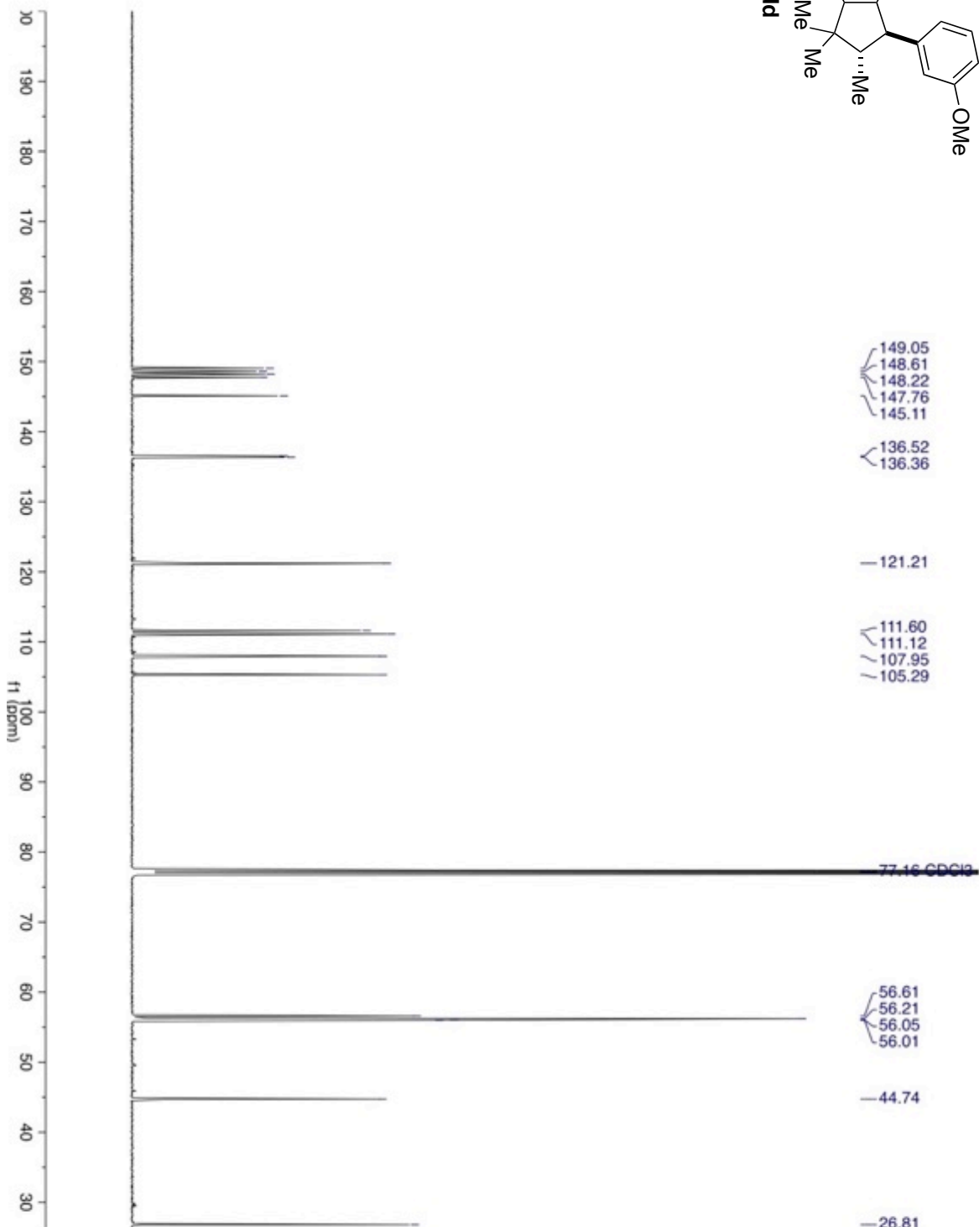
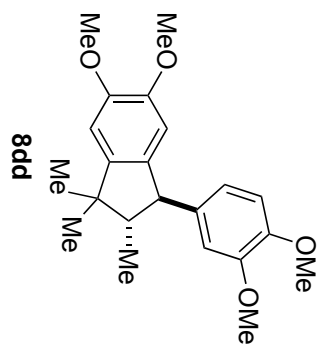
- 56.26
- 56.21
- 56.17
- 51.01
- 48.39
- 47.96
- 46.29
- 45.34
- 44.72
- 31.83
- 30.90
- 30.32
- 29.28
- 28.81

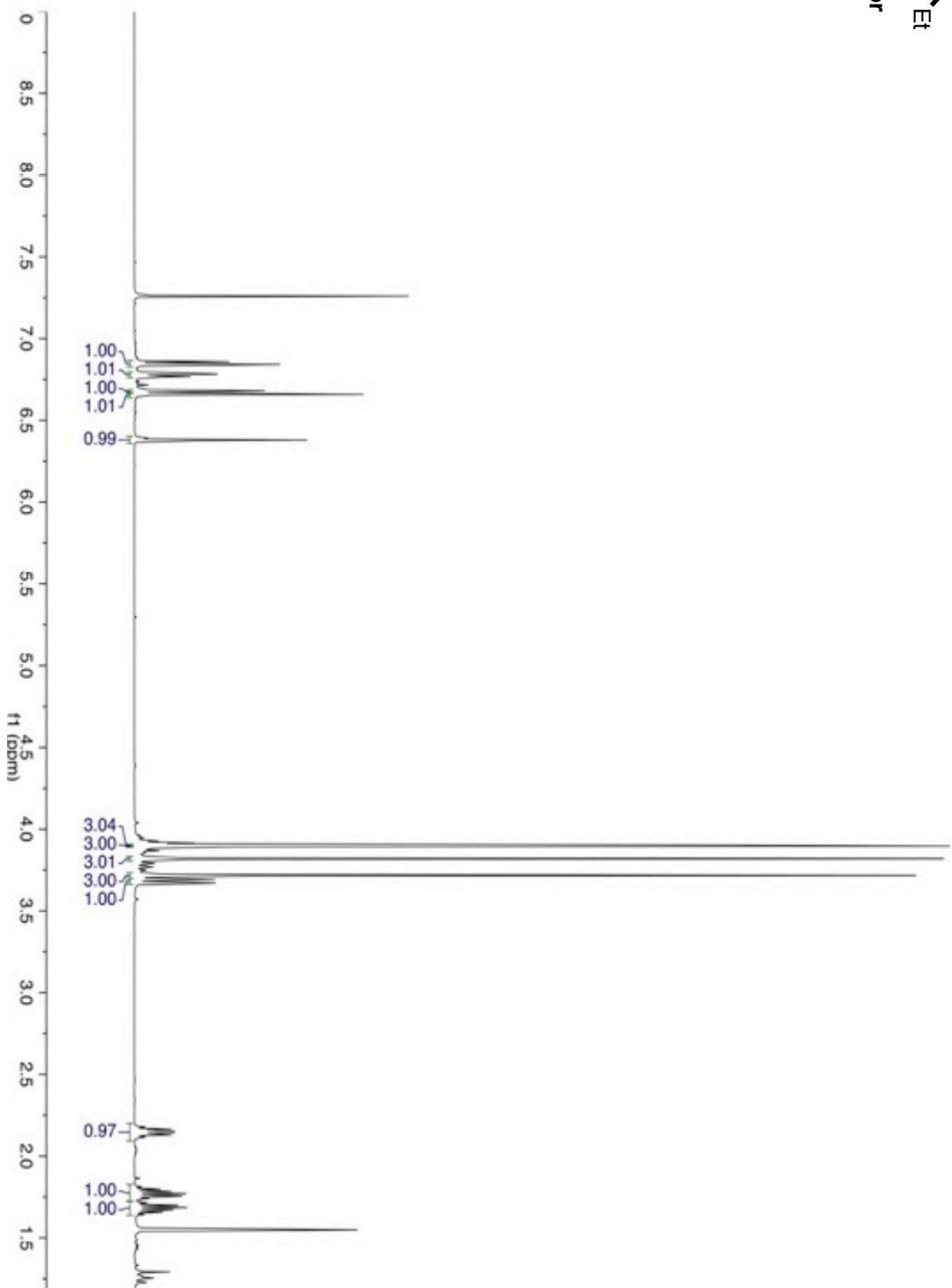
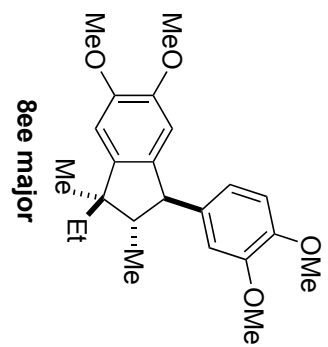


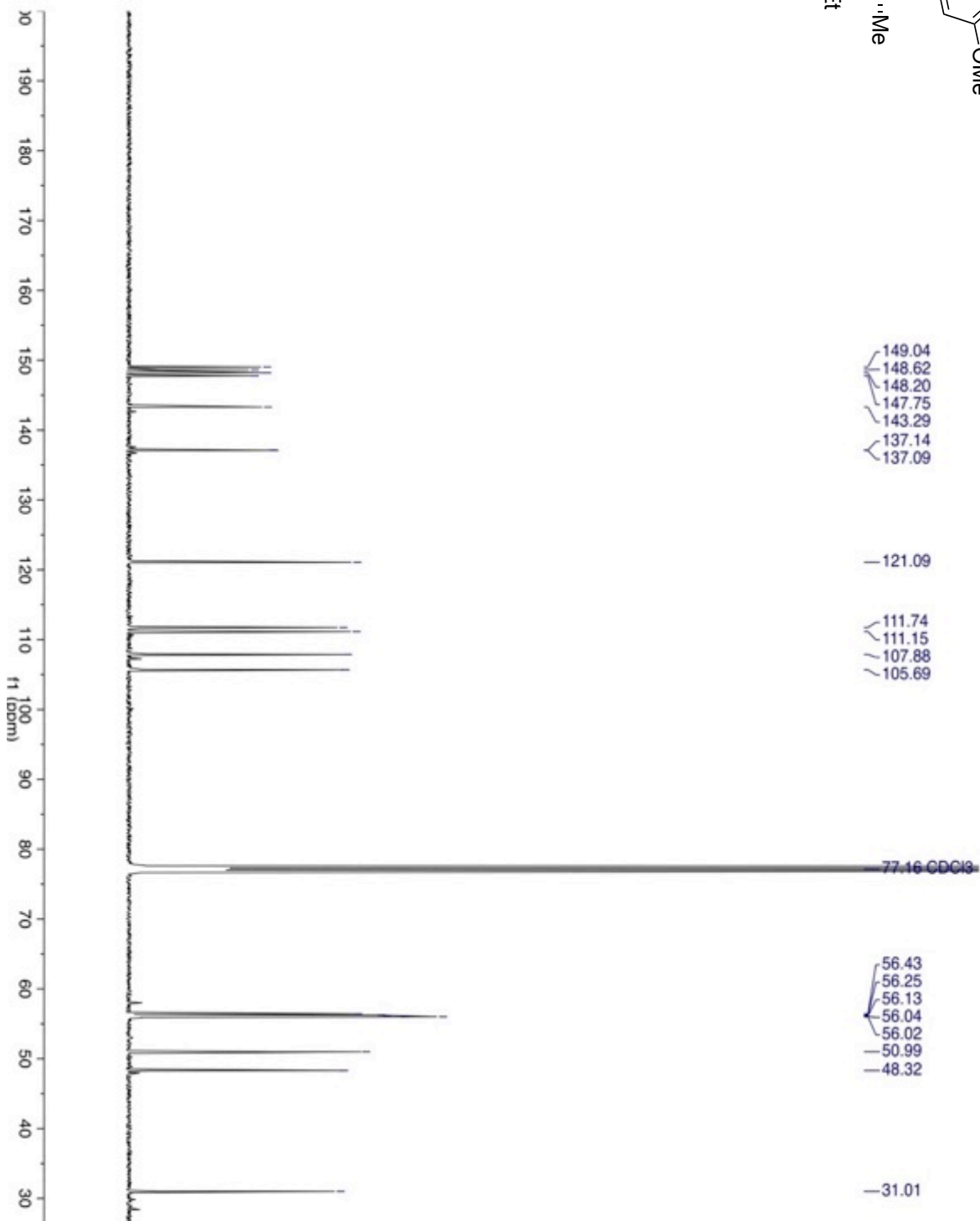
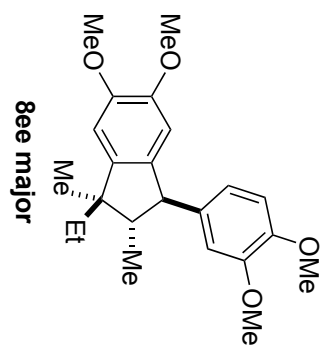


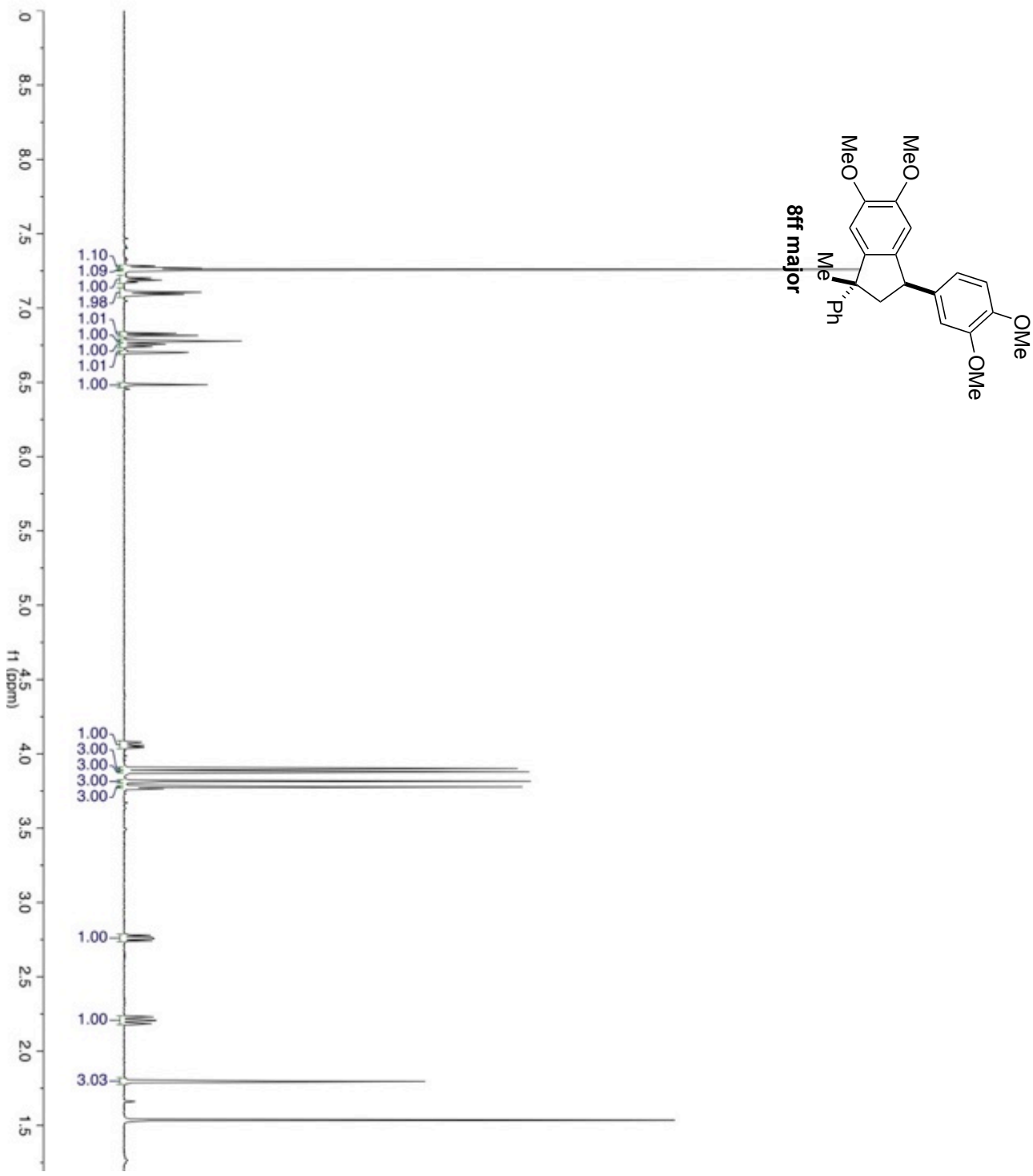


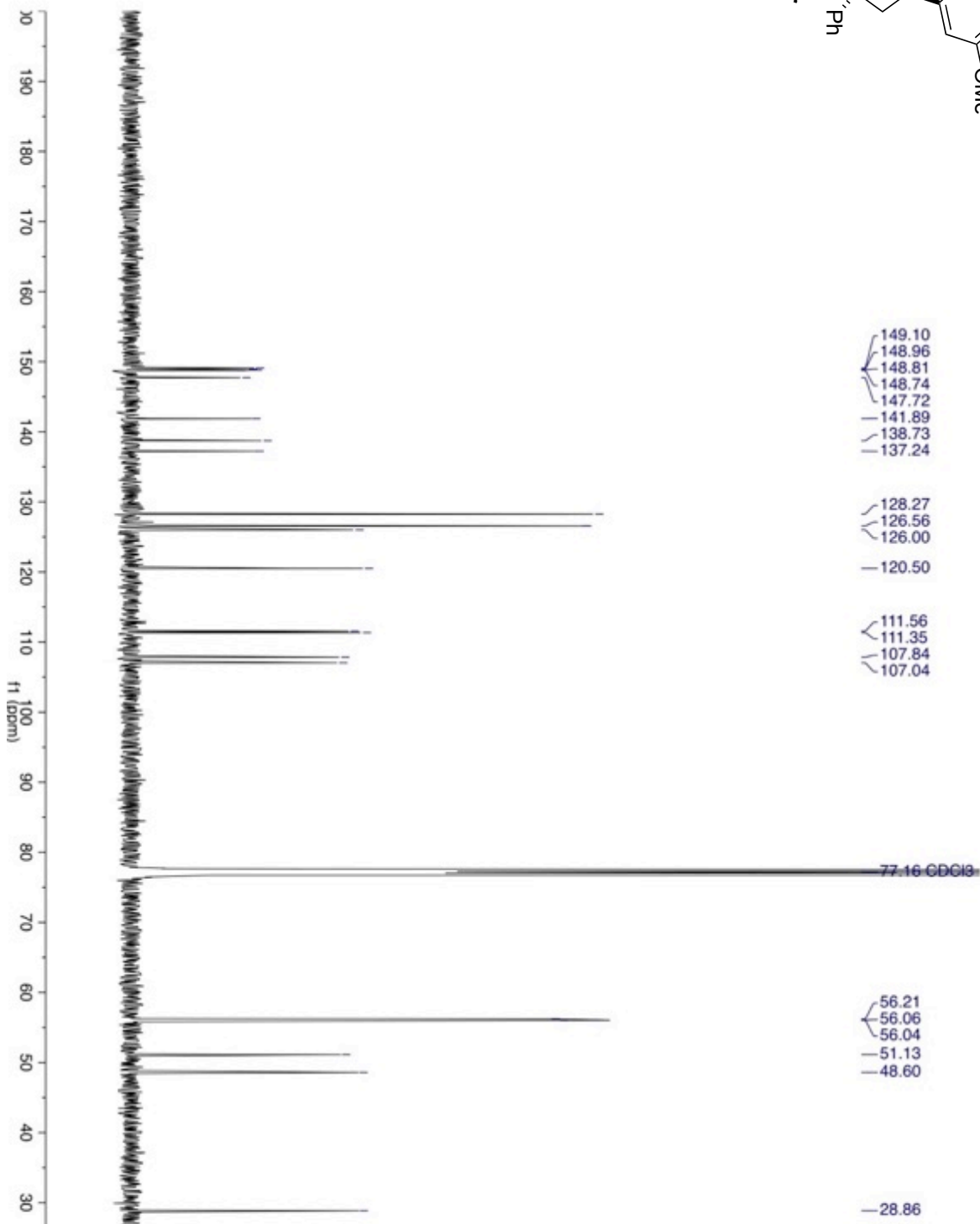
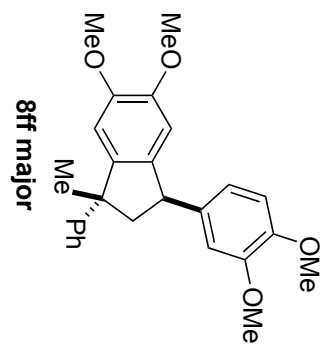






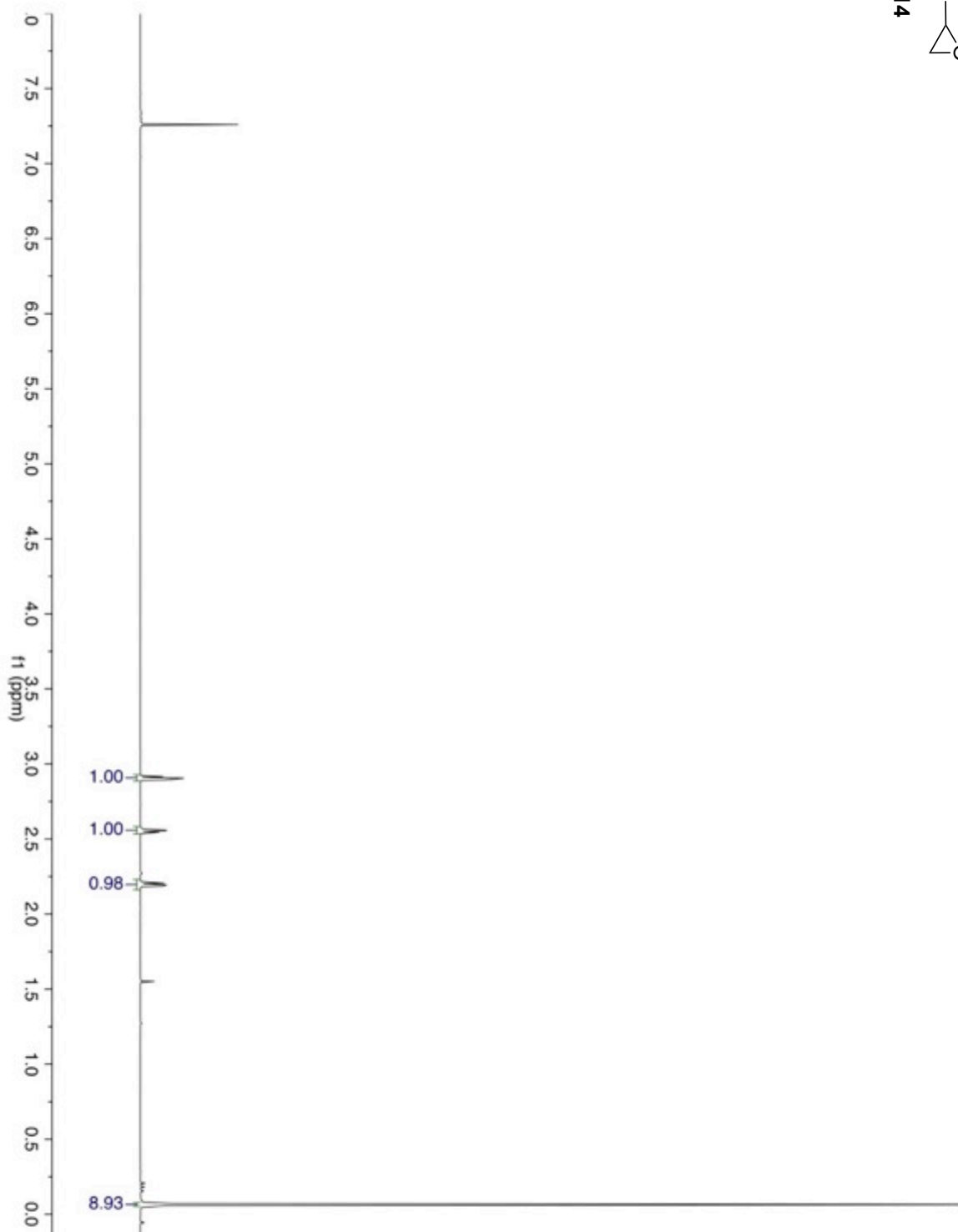


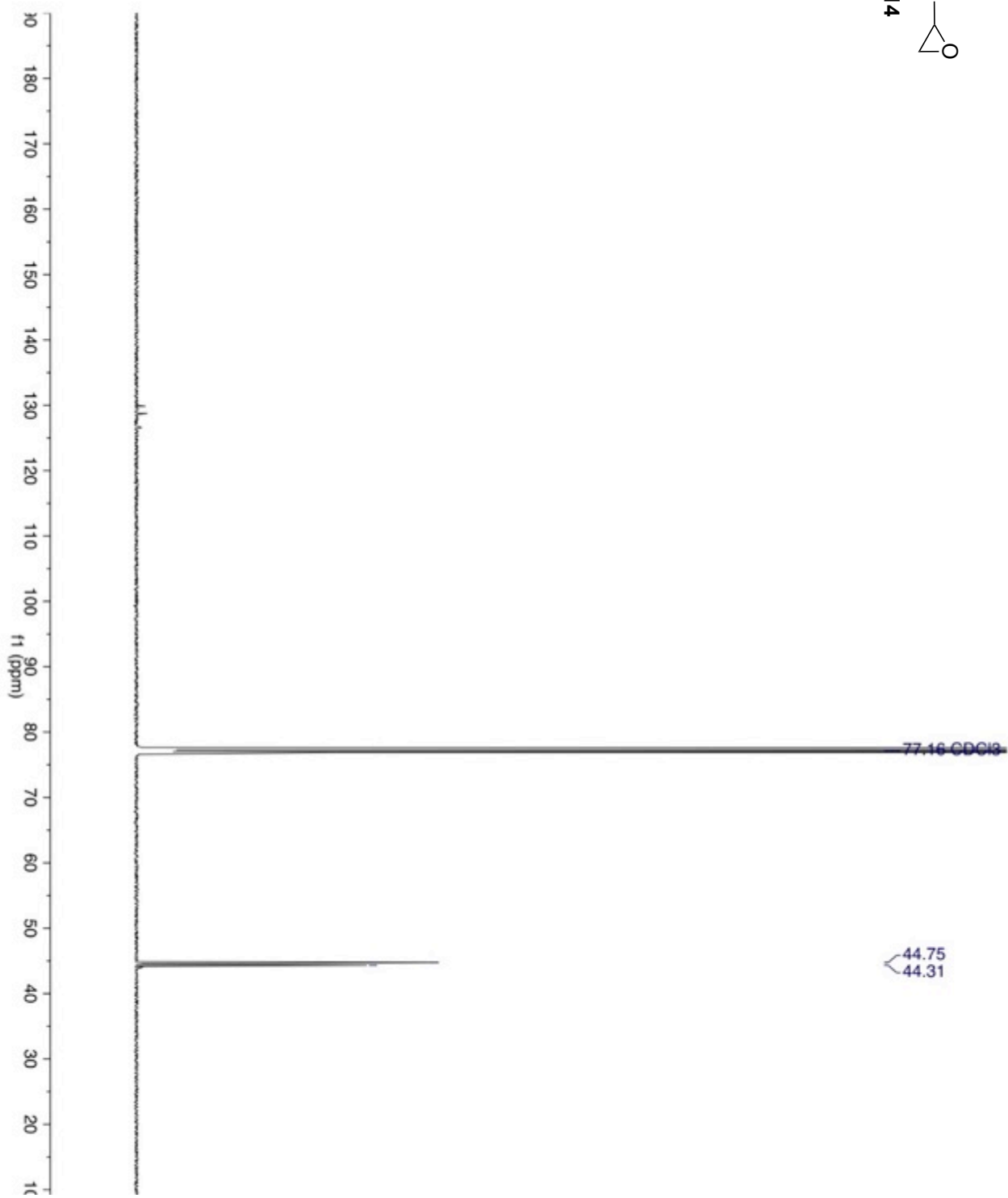
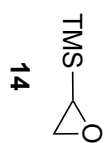


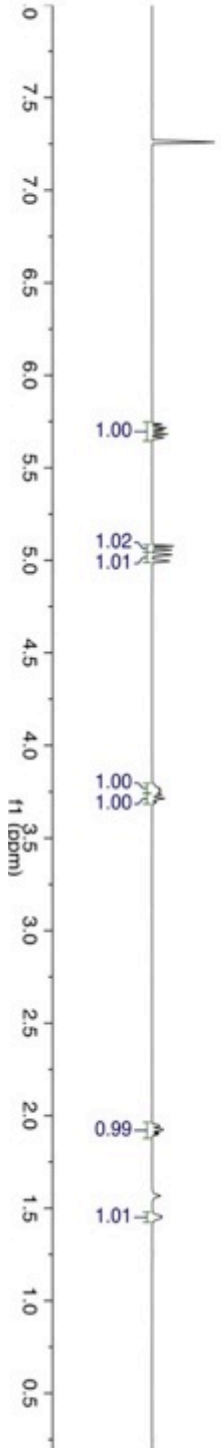
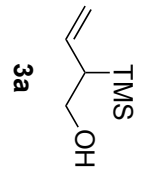


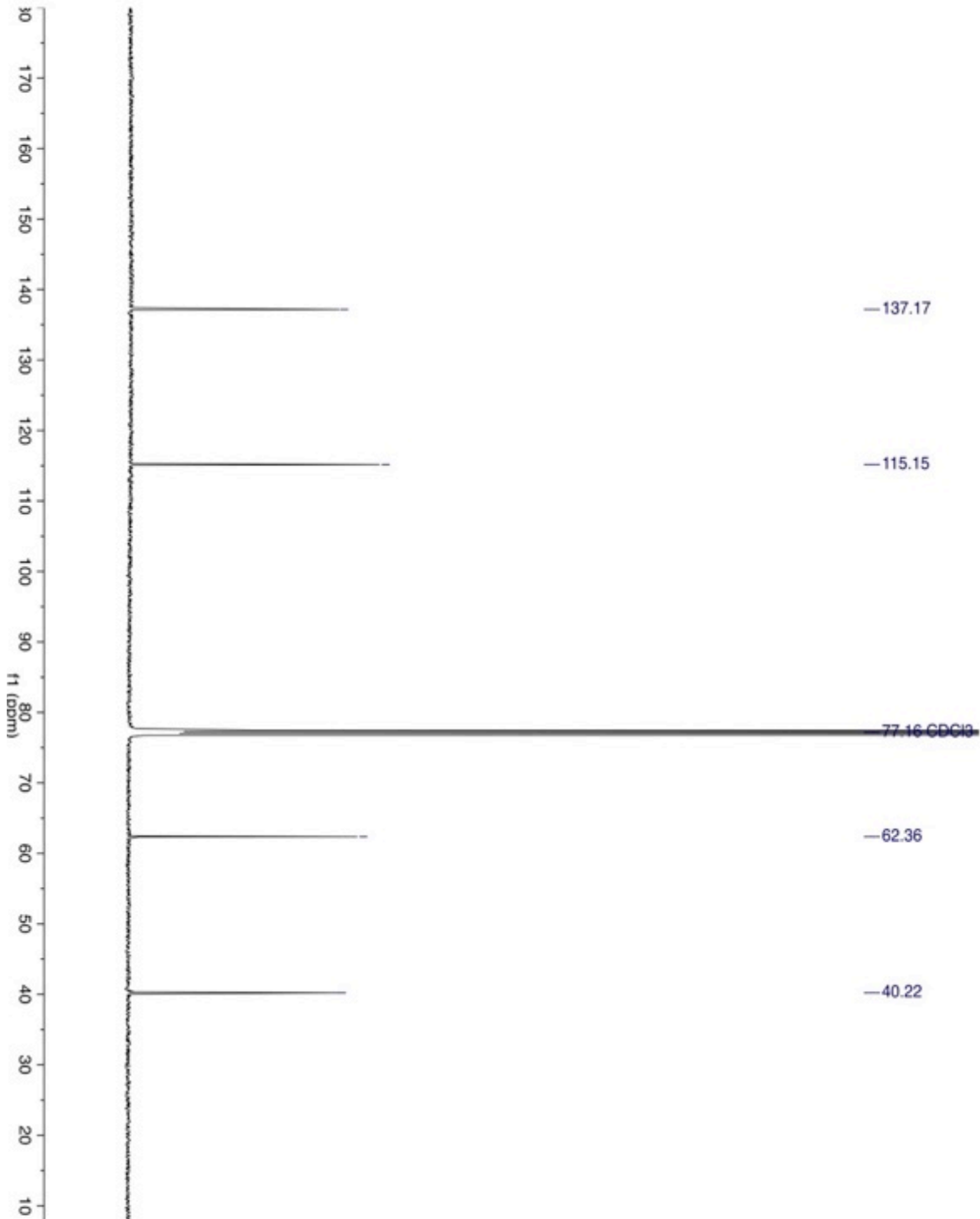
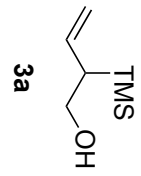


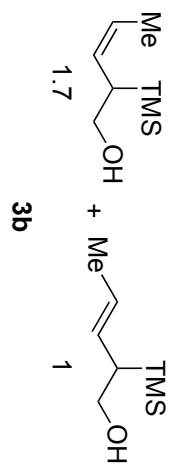
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129.11
128.99
126.55
125.76

