

**A Palladium-Catalyzed Enantioselective Hydroesterification of
Alkenylphenols with Phenyl Formate. A Facile Approach to Optically
Active Dihydrocoumarins****

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Supporting Information

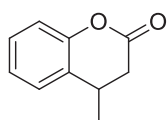
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General Methods. All commercially available reagents were used without further purification. Solvents were purified with solvent purification systems. Column chromatography was performed on silica gel (200-300 mesh). ¹H NMR spectra were recorded on a 400 MHz NMR spectrometer and ¹³C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. All ligands were purchased from commercial suppliers. Olefins **1a-d**, **f**, **g** were prepared according to the reported procedures.¹ Olefin **1e** was prepared from 5'-bromo-2'-hydroxyacetophenone via Suzuki coupling,² and Wittig olefination.¹ Olefins **1h-m** were prepared from 2'-hydroxy-5'-methylacetophenone via bromination,³ Suzuki coupling,² and Wittig olefination.¹ Olefins **1n-p** were prepared from 2'-hydroxyacetophenone via dibromination,³ Suzuki coupling,² and Wittig olefination.¹ Phenyl formate and formate **3a** were prepared from the corresponding phenols according to the reported procedures.⁴

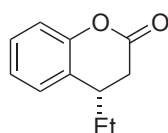
- 1) Konishi, H.; Ueda, T.; Muto, T.; Manabe, K. *Org. Lett.* **2012**, *14*, 4722.
- 2) Bartoszek, M.; Beller, M.; Deutsch, J.; Klawonn, M.; Köckritz, A.; Nemati, N.; Pews-Davtyan, A. *Tetrahedron* **2008**, *64*, 1316.
- 3) Tillu, V. H.; Shinde, P. D.; Bedekar, A. V.; Wakharkar, R. D. *Synth. Commun.* **2003**, *33*, 1399.
- 4) Katafuchi, Y.; Fujihara, T.; Iwai, T.; Terao, J.; Tsuji, Y. *Adv. Synth. Catal.* **2011**, *353*, 475.

Representative procedure for hydroesterification (Table 2, 2j). A mixture of Pd(OAc)₂ (0.0056 g, 0.025 mmol), (*R*)-(-)-DTBM-SEGPHOS (0.059 g, 0.050 mmol), and THF (0.50 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added olefin **1j** (0.1262 g, 0.50 mmol), phenyl formate (0.0733 g, 0.60 mmol), and HCOOH (0.023 g, 0.50 mmol) successively via syringe. After the vial was sealed with a septum cap, the reaction mixture was stirred at 55 °C for 24 h and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50/1) to give lactone **2j** as a white solid (0.1276 g, 91% yield, 91% ee).

Table 2, 2a

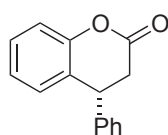
Colorless oil; $[\alpha]_{20}^D = -16.8$ (c 1.00, CHCl_3) (76% ee); IR (film) 1767, 1486 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.21 (m, 2H), 7.13 (td, $J = 7.5, 1.2$ Hz, 1H), 7.06 (dd, $J = 8.1, 1.2$ Hz, 1H), 3.24-3.13 (m, 1H), 2.84 (dd, $J = 15.8, 5.5$ Hz, 1H), 2.59 (dd, $J = 15.8, 7.2$ Hz, 1H), 1.34 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 151.4, 128.4, 128.0, 126.7, 124.8, 117.1, 37.0, 29.6, 20.1.

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Table 2, 2b

Light yellow oil; $[\alpha]_{20}^D = -28.2$ (c 1.00, CHCl_3) (62% ee); [lit.¹ for (R)-**2b**; $[\alpha]_{20}^D = +53.6$ (c 1.0, CHCl_3) (95% ee)]; IR (film) 1771, 1487 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (td, $J = 7.7, 1.6$ Hz, 1H), 7.19 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.11 (t, $J = 7.3$ Hz, 1H), 7.06 (d, $J = 8.1$ Hz, 1H), 2.95-2.87 (m, 1H), 2.84 (dd, $J = 15.7, 5.6$ Hz, 1H), 2.76 (dd, $J = 15.7, 4.0$ Hz, 1H), 1.73-1.54 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 151.5, 128.5, 128.1, 126.7, 124.5, 117.3, 36.8, 34.6, 27.8, 11.4; HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{13}\text{O}_2$ (M+H): 177.0910; Found: 177.0911.

1) Teichert, J. F.; Feringa, B. L. *Chem. Commun.* **2011**, *47*, 2679.

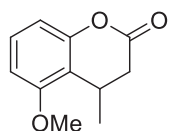
Table 2, 2c

White solid; mp. 80-81 $^{\circ}\text{C}$; $[\alpha]_{20}^D = -12.6$ (c 0.70, CHCl_3) (56% ee); [lit.¹ for (R)-**2c**; $[\alpha]_{20}^D$

= -45.1 (*c* 0.98, CHCl₃) (>99% ee)]; IR (film) 1762, 1486 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.27 (m, 4H), 7.19-7.12 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 4.35 (t, *J* = 7.0 Hz, 1H), 3.09 (dd, *J* = 15.9, 6.1 Hz, 1H), 3.03 (dd, *J* = 15.9, 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 151.9, 140.5, 129.3, 129.0, 128.5, 127.9, 127.8, 126.0, 124.9, 117.3, 40.9, 37.2; HRMS (ESI) Calcd for C₁₅H₁₂NaO₂ (M+Na): 247.0730; Found: 247.0735.

1) Chen, G.; Tokunaga, N.; Hayashi, T. *Org. Lett.* **2005**, *7*, 2285.

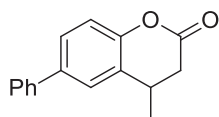
Table 2, 2d



White solid; mp. 97-99 °C; [α]₂₀^D = -16.4 (*c* 0.95, CHCl₃) (73% ee); IR (film) 1760, 1462 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (t, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.55-3.45 (m, 1H), 2.76 (dd, *J* = 15.8, 6.0 Hz, 1H), 2.70 (dd, *J* = 15.8, 2.3 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 156.6, 152.1, 128.5, 116.6, 109.8, 106.5, 56.0, 36.4, 24.7, 19.8; HRMS (ESI) Calcd for C₁₁H₁₃O₃ (M+H): 193.0859; Found: 193.0859.

Dong, C.; Alper, H. *J. Org. Chem.* **2004**, *69*, 5011.

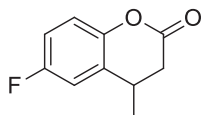
Table 2, 2e



White solid; mp. 65-67 °C; [α]₂₀^D = 8.7 (*c* 0.92, CHCl₃) (73% ee); IR (film) 1764, 1481 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.53 (m, 2H), 7.50-7.42 (m, 4H), 7.39-7.33 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 3.30-3.20 (m, 1H), 2.89 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.63 (dd, *J* = 15.8, 7.1 Hz, 1H), 1.40 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 150.9, 140.5, 138.1, 129.1, 128.4, 127.6, 127.2, 125.5, 117.6, 37.0, 29.9, 20.2; HRMS (ESI) Calcd for C₁₆H₁₅O₂

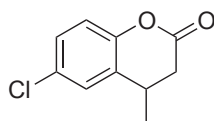
(M+H): 239.1067; Found: 239.1063.

Table 2, 2f



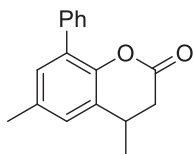
White solid; mp. 70-71 °C; $[\alpha]_{20}^D = -13.6$ (*c* 1.25, CHCl₃) (73% ee); IR (film) 1770, 1492 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.05-6.99 (m, 1H), 6.99-6.91 (m, 2H), 3.22-3.11 (m, 1H), 2.84 (dd, *J* = 15.9, 5.4 Hz, 1H), 2.56 (dd, *J* = 15.9, 7.7 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 159.4 (d, *J* = 242 Hz), 147.4 (d, *J* = 2 Hz), 129.8 (d, *J* = 7 Hz), 118.4 (d, *J* = 8 Hz), 115.0 (d, *J* = 24 Hz), 113.4 (d, *J* = 24 Hz), 36.6, 29.7, 19.7; HRMS (ESI) Calcd for C₁₀H₁₀O₂F (M+H): 181.0659; Found: 181.0654.

Table 2, 2g

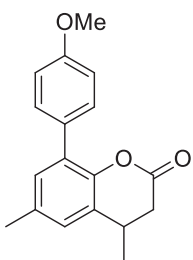


White solid; mp. 57-59 °C; $[\alpha]_{20}^D = -2.9$ (*c* 1.09, CHCl₃) (75% ee); IR (film) 1773, 1482 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.18 (m, 2H), 6.99 (d, *J* = 9.1 Hz, 1H), 3.21-3.09 (m, 1H), 2.83 (dd, *J* = 15.9, 5.5 Hz, 1H), 2.57 (dd, *J* = 15.9, 7.4 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 150.0, 129.9, 129.7, 128.5, 126.7, 118.5, 36.6, 29.6, 19.8.

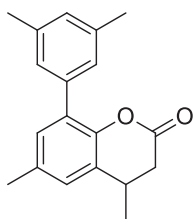
Wang, H.; Dong, B.; Li, J.; Shi, Y. *Org. Lett.* **2014**, *16*, 186.

Table 2, 2h

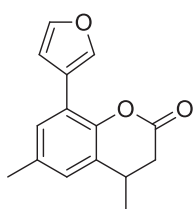
Colorless oil; $[\alpha]_{20}^D = -21.2$ (*c* 0.50, CHCl_3) (90% ee); IR (film) 1769, 1468 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.48 (m, 2H), 7.46-7.39 (m, 2H), 7.38-7.31 (m, 1H), 7.12 (d, *J* = 1.8 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 3.25-3.13 (m, 1H), 2.84 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.60 (dd, *J* = 15.7, 6.7 Hz, 1H), 2.38 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 146.1, 136.9, 134.2, 130.6, 130.4, 129.7, 128.5, 128.4, 127.7, 126.5, 37.0, 30.2, 21.0, 20.3; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_2$ (*M*+*Na*): 275.1043; Found: 275.1043.

Table 2, 2i

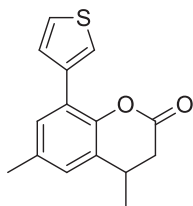
White solid; mp. 100-101 $^{\circ}\text{C}$; $[\alpha]_{20}^D = -22.2$ (*c* 1.00, CHCl_3) (89% ee); IR (film) 1770, 1511 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.42 (m, 2H), 7.10 (d, *J* = 1.7 Hz, 1H), 7.00-6.93 (m, 3H), 3.84 (s, 3H), 3.23-3.11 (m, 1H), 2.83 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.59 (dd, *J* = 15.7, 6.7 Hz, 1H), 2.37 (s, 3H), 1.36 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 159.3, 146.0, 134.2, 130.8, 130.3, 129.9, 129.2, 128.5, 126.0, 113.9, 55.5, 37.0, 30.2, 21.0, 20.3; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{18}\text{NaO}_3$ (*M*+*Na*): 305.1148; Found: 305.1148.

Table 2, 2j

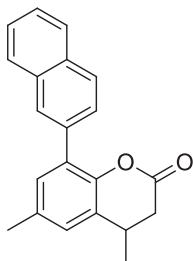
White solid; mp. 120-121 °C; $[\alpha]_{20}^D = -24.8$ (*c* 0.50, CHCl₃) (91% ee); IR (film) 1770, 1468 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.10 (s, 3H), 7.00 (s, 2H), 3.23-3.13 (m, 1H), 2.83 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.59 (dd, *J* = 15.6, 6.7 Hz, 1H), 2.37 (s, 9H), 1.36 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 146.1, 137.8, 136.8, 134.0, 130.7, 130.6, 129.4, 128.4, 127.5, 126.2, 37.0, 30.2, 21.6, 21.0, 20.3; HRMS (ESI) Calcd for C₁₉H₂₁O₂ (M+H): 281.1536; Found: 281.1538.

Table 2, 2k

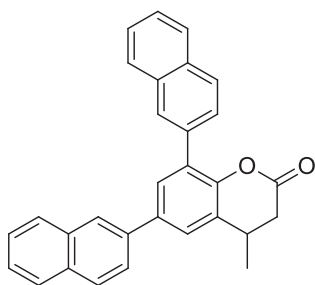
Light yellow solid; mp. 88-89 °C; $[\alpha]_{20}^D = -25.6$ (*c* 0.50, CHCl₃) (86% ee); IR (film) 1767, 1460 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 6.80 (d, *J* = 1.1 Hz, 1H), 3.22-3.10 (m, 1H), 2.84 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.61 (dd, *J* = 15.7, 6.6 Hz, 1H), 2.36 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 146.0, 142.8, 142.2, 134.1, 128.5, 127.4, 125.6, 120.8, 120.6, 109.6, 36.7, 30.0, 21.0, 20.1; HRMS (ESI) Calcd for C₁₅H₁₅O₃ (M+H): 243.1016; Found: 243.1016.

Table 2, 2l

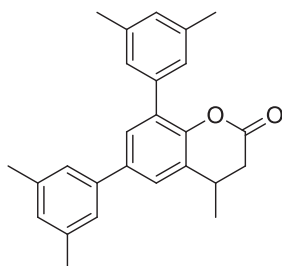
White solid; mp. 106-107 °C; $[\alpha]_{20}^D = -26.4$ (*c* 0.50, CHCl₃) (88% ee); IR (film) 3103, 1762, 1445 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.36 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.29-7.24 (m, 1H), 6.97 (d, *J* = 1.9 Hz, 1H), 3.24-3.11 (m, 1H), 2.84 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.61 (dd, *J* = 15.7, 6.6 Hz, 1H), 2.37 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 146.0, 136.6, 134.2, 129.2, 128.7, 128.5, 126.2, 125.2, 124.6, 124.3, 36.8, 30.1, 21.0, 20.2; HRMS (ESI) Calcd for C₁₅H₁₅O₂S (M+H): 259.0787; Found: 259.0789.

Table 2, 2m

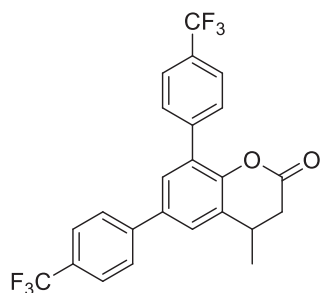
White solid; mp. 59-61 °C; $[\alpha]_{20}^D = -21.6$ (*c* 1.00, CHCl₃) (87% ee); IR (film) 1767, 1457 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 1.0 Hz, 1H), 7.92-7.83 (m, 3H), 7.66 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 1H), 3.27-3.16 (m, 1H), 2.87 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.63 (dd, *J* = 15.7, 6.7 Hz, 1H), 2.41 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 146.4, 134.6, 134.3, 133.6, 132.9, 130.8, 130.4, 128.6, 128.5, 127.9, 127.84, 127.81, 126.6, 126.30, 126.27, 37.0, 30.3, 21.1, 20.3; HRMS (ESI) Calcd for C₂₁H₁₉O₂ (M+H): 303.1380; Found: 303.1384.

Table 2, 2n

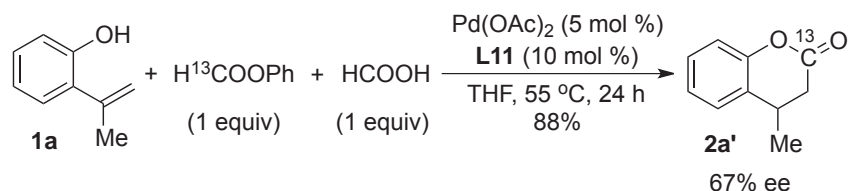
White solid; mp. 161-163 °C; $[\alpha]_{20}^D = 3.4$ (*c* 1.00, CHCl₃) (89% ee); IR (film) 1770, 1448 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 8.05 (s, 1H), 7.97-7.86 (m, 6H), 7.81-7.73 (m, 3H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.56-7.48 (m, 4H), 3.42-3.31 (m, 1H), 2.96 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.72 (dd, *J* = 15.7, 6.6 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 148.0, 137.9, 137.6, 134.4, 133.9, 133.6, 133.0, 132.9, 131.2, 129.33, 129.31, 128.9, 128.8, 128.5, 128.4, 128.0, 127.9, 127.87, 127.84, 126.7, 126.5, 126.4, 126.37, 125.9, 125.5, 125.0, 37.0, 30.5, 20.5; HRMS (ESI) Calcd for C₃₀H₂₃O₂ (M+H): 415.1693; Found: 415.1696.

Table 2, 2o

White solid; mp. 67-69 °C; $[\alpha]_{20}^D = 5.2$ (*c* 0.50, CHCl₃) (91% ee); IR (film) 1771, 1456 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.22 (s, 2H), 7.17 (s, 2H), 7.02 (s, 2H), 3.34-3.24 (m, 1H), 2.90 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.66 (dd, *J* = 15.7, 6.6 Hz, 1H), 2.40 (s, 6H), 2.39 (s, 6H), 1.44 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 147.6, 140.4, 138.6, 138.0, 137.9, 136.8, 131.3, 129.6, 129.3, 128.9, 127.6, 125.1, 124.4, 37.0, 30.5, 21.6, 21.59, 20.4; HRMS (ESI) Calcd for C₂₆H₂₇O₂ (M+H): 371.2006; Found: 371.2008.

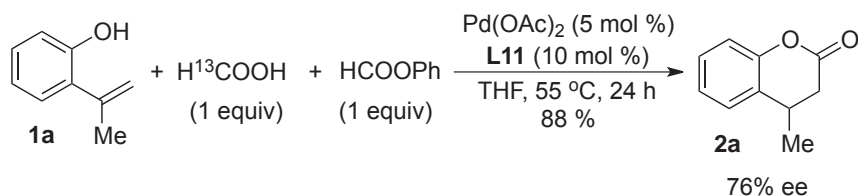
Table 2, 2p

White solid; mp. 88-90 °C; $[\alpha]_{20}^D = 4.6$ (c 1.00, CHCl_3) (71% ee); IR (film) 1779, 1465 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.64 (m, 8 H), 7.52 (d, $J = 2.2$ Hz, 1H), 7.49 (d, $J = 2.0$ Hz, 1H), 3.40-3.28 (m, 1 H), 2.93 (dd, $J = 15.8, 5.4$ Hz, 1 H), 2.70 (dd, $J = 15.8, 6.7$ Hz, 1 H), 1.46 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 148.2, 143.5, 140.2, 136.6, 130.1, 129.9 (q, $J = 32$ Hz), 129.8 (q, $J = 32$ Hz), 129.7, 128.6, 127.5, 126.0 (q, $J = 3$ Hz), 125.6, 125.4 (q, $J = 3$ Hz), 124.4 (q, $J = 270$ Hz), 124.35 (q, $J = 270$ Hz), 36.5, 30.3, 20.1; HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{16}\text{F}_6\text{NaO}_2$ ($\text{M}+\text{Na}$): 473.0947; Found: 473.0947.

Procedures for Schemes 2-4**Scheme 2**

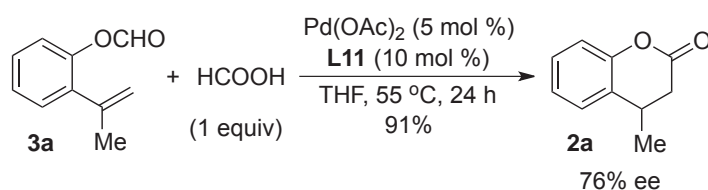
A mixture of $\text{Pd}(\text{OAc})_2$ (0.0056 g, 0.025 mmol), (*R*)-(-)-DTBM-SEGPHOS (0.059 g, 0.050 mmol), and THF (0.50 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added olefin **1a** (0.0671 g, 0.50 mmol), $\text{H}^{13}\text{COOPh}$ (0.0616 g, 0.50 mmol), and HCOOH (0.023 g, 0.50 mmol) successively via syringe. After the vial was sealed with a septum cap, the reaction mixture was stirred at 55 °C for 24 h and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50/1) to give lactone **2a'** as a colorless oil (0.0718 g, 88% yield, 67% ee). $[\alpha]_{20}^D = -15.8$ (c 1.00, CHCl_3); IR (film) 1725, 1487, 1216 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.21 (m, 2H), 7.13 (td, $J = 7.5, 1.2$ Hz, 1H), 7.06 (dd, $J = 8.1, 1.0$ Hz, 1H), 3.25-3.12 (m, 1H), 2.85 (ddd, $J = 15.8, 6.8, 5.5$

Hz, 1H), 2.59 (ddd, $J = 15.8, 7.1, 6.4$ Hz, 1H), 1.35 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 151.4 (d, $J = 1.0$ Hz), 128.4, 128.0 (d, $J = 4.0$ Hz), 126.7, 124.8, 117.1 (d, $J = 2.0$ Hz), 37.0 (d, $J = 53.0$ Hz), 29.6 (d, $J = 3.0$ Hz), 20.1 (d, $J = 3.0$ Hz); HRMS (ESI) Calcd for $\text{C}_9^{13}\text{CH}_{11}\text{O}_2$ (M+H): 164.0787; Found: 164.0788.



Scheme 3

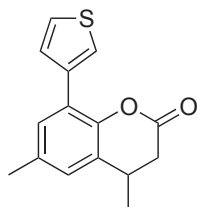
A mixture of $\text{Pd}(\text{OAc})_2$ (0.0056 g, 0.025 mmol), (*R*)-(-)-DTBM-SEGPHOS (0.059 g, 0.050 mmol), and THF (0.50 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added olefin **1a** (0.0671 g, 0.50 mmol), HCOOPh (0.0611 g, 0.50 mmol), and H^{13}COOH (0.0235 g, 0.50 mmol) successively via syringe. After the vial was sealed with a septum cap, the reaction mixture was stirred at 55 °C for 24 h and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50/1) to give lactone **2a** as a colorless oil (0.0714 g, 88% yield, 76% ee).



Scheme 4

A mixture of $\text{Pd}(\text{OAc})_2$ (0.0056 g, 0.025 mmol), (*R*)-(-)-DTBM-SEGPHOS (0.059 g, 0.050 mmol), and THF (0.50 mL) in a vial (4.0 mL) was sonicated for 30 seconds. To the resulting solution were added olefin **3a** (0.0811 g, 0.50 mmol) and HCOOH (0.023 g, 0.50 mmol) successively via syringe. After the vial was sealed with a septum cap, the reaction mixture was stirred at 55 °C for 24 h and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50/1) to give lactone **2a** as a colorless oil (0.0738 g, 91% yield, 76% ee).

The X-ray structure of compound **21**



21

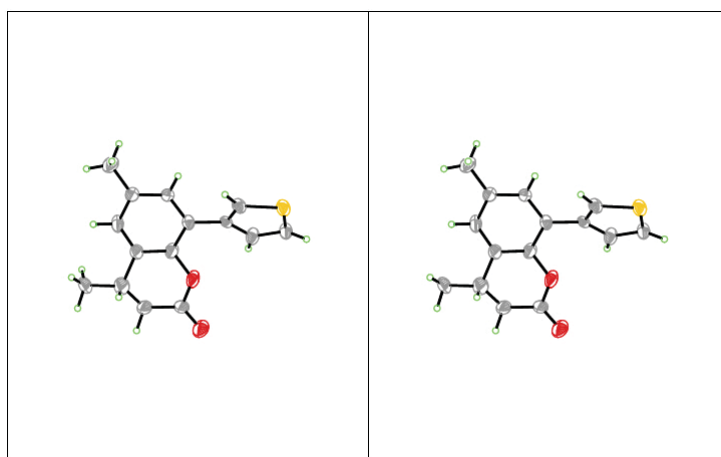
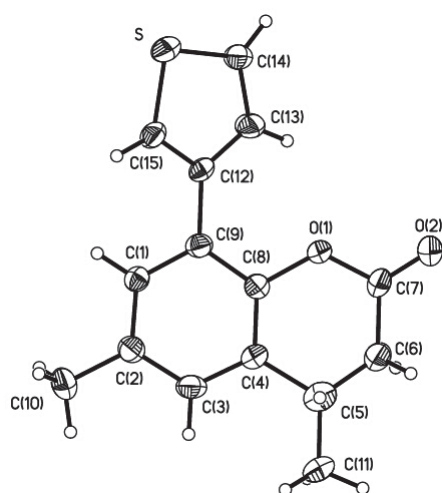


Table S1 - Crystal Data and Details of the Structure Determination for: **21**

Identification code	21
Empirical formula	C ₁₅ H ₁₄ O ₂ S
Formula weight	258.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/C
Unit cell dimensions	a = 8.1040(16) Å alpha = 90 deg. b = 17.252(4) Å beta = 106.24(3) deg. c = 9.4860(19) Å gamma = 90 deg.
Volume	1273.3(4) Å ³
Z, Calculated density	4, 1.348 Mg/m ³
Absorption coefficient	0.244 mm ⁻¹
F(000)	544
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	2.36 to 25.43 deg.
Limiting indices	-9<=h<=9, 0<=k<=20, 0<=l<=11
Reflections collected / unique	2339 / 2339 [R(int) = 0.0000]
Completeness to theta = 25.43	99.5 %
Absorption correction	Psi-scan
Max. and min. transmission	0.9760 and 0.9527
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2339 / 2 / 163
Goodness-of-fit on F ²	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0987, wR2 = 0.2268
R indices (all data)	R1 = 0.1371, wR2 = 0.2481
Largest diff. peak and hole	0.535 and -0.399 e.Å ⁻³

Table S2 - Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2l**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S	4050(2)	3204(1)	9680(2)	61(1)
C(1)	1390(6)	3662(3)	4765(5)	41(1)
O(1)	3457(8)	5472(2)	6236(4)	109(2)
C(2)	791(7)	3810(3)	3269(5)	50(1)
O(2)	4456(9)	6634(3)	6811(5)	110(2)
C(3)	1140(8)	4535(3)	2779(6)	61(2)
C(4)	1981(9)	5105(3)	3724(6)	67(2)
C(5)	2558(13)	5866(4)	3204(7)	104(3)
C(6)	3148(9)	6393(3)	4337(6)	71(2)
C(7)	3744(8)	6193(3)	5889(6)	63(2)
C(8)	2512(8)	4932(3)	5207(6)	62(2)
C(9)	2197(7)	4222(3)	5774(5)	45(1)
C(10)	-107(9)	3205(3)	2216(7)	72(2)
C(11)	1836(9)	6086(4)	1685(6)	71(2)
C(12)	2863(5)	4018(3)	7371(5)	37(1)
C(13)	2969(8)	4503(3)	8563(6)	59(2)
C(14)	3608(8)	4146(3)	9929(6)	56(1)
C(15)	3425(8)	3294(3)	7816(6)	52(1)

Table S3 - Bond lengths [Å] and angles [deg] for **2l**.

S-C(14)	1.694(6)
S-C(15)	1.705(5)
C(1)-C(9)	1.388(7)
C(1)-C(2)	1.389(7)
C(1)-H(1A)	0.93
O(1)-C(7)	1.325(7)
O(1)-C(8)	1.410(7)
C(2)-C(3)	1.390(8)
C(2)-C(10)	1.487(7)
O(2)-C(7)	1.180(7)
C(3)-C(4)	1.376(8)
C(3)-H(3A)	0.93
C(4)-C(8)	1.383(7)
C(4)-C(5)	1.522(8)
C(5)-C(6)	1.387(7)
C(5)-C(11)	1.446(8)
C(5)-H(5)	0.98
C(6)-C(7)	1.457(8)
C(6)-H(6A)	0.97
C(6)-H(6B)	0.97
C(8)-C(9)	1.391(7)
C(9)-C(12)	1.501(6)
C(10)-H(10A)	0.96
C(10)-H(10B)	0.96
C(10)-H(10C)	0.96
C(11)-H(11A)	0.96
C(11)-H(11B)	0.96
C(11)-H(11C)	0.96
C(12)-C(15)	1.357(7)
C(12)-C(13)	1.390(7)
C(13)-C(14)	1.397(7)
C(13)-H(13A)	0.93
C(14)-H(14A)	0.93
C(15)-H(15B)	0.93
C(14)-S-C(15)	92.5(2)
C(9)-C(1)-C(2)	122.6(5)
C(9)-C(1)-H(1A)	118.7
C(2)-C(1)-H(1A)	118.7
C(7)-O(1)-C(8)	123.2(4)
C(3)-C(2)-C(1)	117.5(5)
C(3)-C(2)-C(10)	120.9(5)
C(1)-C(2)-C(10)	121.5(5)
C(4)-C(3)-C(2)	122.3(5)
C(4)-C(3)-H(3A)	118.8

C(2)-C(3)-H(3A)	118.8
C(3)-C(4)-C(8)	117.7(5)
C(3)-C(4)-C(5)	123.1(5)
C(8)-C(4)-C(5)	118.6(5)
C(6)-C(5)-C(11)	123.8(6)
C(6)-C(5)-C(4)	112.6(6)
C(11)-C(5)-C(4)	118.3(6)
C(6)-C(5)-H(5)	97.7
C(11)-C(5)-H(5)	97.7
C(4)-C(5)-H(5)	97.7
C(5)-C(6)-C(7)	125.0(6)
C(5)-C(6)-H(6A)	106.1
C(7)-C(6)-H(6A)	106.1
C(5)-C(6)-H(6B)	106.1
C(7)-C(6)-H(6B)	106.1
H(6A)-C(6)-H(6B)	106.3
O(2)-C(7)-O(1)	120.3(5)
O(2)-C(7)-C(6)	123.5(5)
O(1)-C(7)-C(6)	116.2(5)
C(4)-C(8)-C(9)	123.0(5)
C(4)-C(8)-O(1)	121.1(5)
C(9)-C(8)-O(1)	115.9(4)
C(8)-C(9)-C(1)	116.7(4)
C(8)-C(9)-C(12)	122.9(4)
C(1)-C(9)-C(12)	120.0(4)
C(2)-C(10)-H(10A)	109.5
C(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(5)-C(11)-H(11A)	109.5
C(5)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(5)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(15)-C(12)-C(13)	111.2(4)
C(15)-C(12)-C(9)	121.7(4)
C(13)-C(12)-C(9)	127.1(4)
C(12)-C(13)-C(14)	114.3(5)
C(12)-C(13)-H(13A)	122.9
C(14)-C(13)-H(13A)	122.9
C(13)-C(14)-S	109.4(4)
C(13)-C(14)-H(14A)	125.3
S-C(14)-H(14A)	125.3

C(12)-C(15)-S	112.5(4)
C(12)-C(15)-H(15B)	123.7
S-C(15)-H(15B)	123.7

Symmetry transformations used to generate equivalent atoms:

Table S4 - Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2I**. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S	82(1)	50(1)	49(1)	14(1)	14(1)	5(1)
C(1)	37(3)	39(3)	44(3)	4(2)	10(2)	2(2)
O(1)	200(6)	56(3)	39(2)	13(2)	-15(3)	-54(3)
C(2)	53(3)	48(3)	47(3)	-1(2)	10(2)	2(2)
O(2)	182(6)	59(3)	62(3)	4(2)	-9(3)	-48(3)
C(3)	88(4)	56(3)	37(3)	4(3)	15(3)	7(3)
C(4)	97(5)	51(3)	45(3)	11(3)	5(3)	-17(3)
C(5)	148(8)	87(5)	64(4)	16(4)	10(5)	-37(5)
C(6)	82(4)	57(4)	60(4)	13(3)	-2(3)	-21(3)
C(7)	77(4)	45(3)	60(4)	8(3)	8(3)	-19(3)
C(8)	93(5)	40(3)	42(3)	2(2)	0(3)	-5(3)
C(9)	54(3)	43(3)	39(3)	4(2)	14(2)	7(2)
C(10)	95(5)	48(3)	63(4)	-13(3)	7(3)	-8(3)
C(11)	101(5)	63(4)	53(3)	18(3)	25(3)	-9(4)
C(12)	29(2)	41(3)	43(3)	10(2)	14(2)	0(2)
C(13)	75(4)	49(3)	43(3)	7(2)	1(3)	13(3)
C(14)	77(4)	48(3)	41(3)	2(2)	15(3)	6(3)
C(15)	73(4)	36(3)	50(3)	6(2)	23(3)	4(3)

Table S5 - Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2I**.

	x	y	z	U(eq)
H(1A)	1244	3168	5105	49
H(3A)	792	4638	1777	73
H(5)	3680	5691	3128	125
H(6A)	2230	6767	4246	85
H(6B)	4087	6670	4116	85
H(10A)	-434	3416	1240	108
H(10B)	-1116	3037	2472	108
H(10C)	647	2772	2256	108
H(11A)	2344	6564	1499	107
H(11B)	616	6152	1488	107
H(11C)	2067	5688	1060	107
H(13A)	2642	5021	8461	70
H(14A)	3766	4387	10834	67
H(15B)	3464	2891	7175	62

Table S6 - Torsion angles [deg] for **2l**.

C(9)-C(1)-C(2)-C(3)	4.7(8)
C(9)-C(1)-C(2)-C(10)	-178.5(5)
C(1)-C(2)-C(3)-C(4)	-2.6(9)
C(10)-C(2)-C(3)-C(4)	-179.5(6)
C(2)-C(3)-C(4)-C(8)	1.1(10)
C(2)-C(3)-C(4)-C(5)	172.7(7)
C(3)-C(4)-C(5)-C(6)	171.1(7)
C(8)-C(4)-C(5)-C(6)	-17.3(12)
C(3)-C(4)-C(5)-C(11)	15.8(13)
C(8)-C(4)-C(5)-C(11)	-172.7(7)
C(11)-C(5)-C(6)-C(7)	174.4(7)
C(4)-C(5)-C(6)-C(7)	20.7(13)
C(8)-O(1)-C(7)-O(2)	175.5(7)
C(8)-O(1)-C(7)-C(6)	-5.0(11)
C(5)-C(6)-C(7)-O(2)	169.2(9)
C(5)-C(6)-C(7)-O(1)	-10.3(12)
C(3)-C(4)-C(8)-C(9)	-1.5(11)
C(5)-C(4)-C(8)-C(9)	-173.5(7)
C(3)-C(4)-C(8)-O(1)	176.8(7)
C(5)-C(4)-C(8)-O(1)	4.8(11)
C(7)-O(1)-C(8)-C(4)	7.1(12)
C(7)-O(1)-C(8)-C(9)	-174.4(6)
C(4)-C(8)-C(9)-C(1)	3.4(9)
O(1)-C(8)-C(9)-C(1)	-175.0(5)
C(4)-C(8)-C(9)-C(12)	176.2(6)
O(1)-C(8)-C(9)-C(12)	-2.2(9)
C(2)-C(1)-C(9)-C(8)	-5.1(8)
C(2)-C(1)-C(9)-C(12)	-178.1(4)
C(8)-C(9)-C(12)-C(15)	-142.3(6)
C(1)-C(9)-C(12)-C(15)	30.2(7)
C(8)-C(9)-C(12)-C(13)	39.1(8)
C(1)-C(9)-C(12)-C(13)	-148.4(5)
C(15)-C(12)-C(13)-C(14)	-0.3(7)
C(9)-C(12)-C(13)-C(14)	178.4(5)
C(12)-C(13)-C(14)-S	-0.4(7)
C(15)-S-C(14)-C(13)	0.7(5)
C(13)-C(12)-C(15)-S	0.8(6)
C(9)-C(12)-C(15)-S	-178.0(4)
C(14)-S-C(15)-C(12)	-0.9(5)

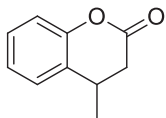
Symmetry transformations used to generate equivalent atoms:

Table S7 - Hydrogen bonds for **2I** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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The chromatograms for determination of enantioselectivity

Table 2, 2a



HPLC Condition: Column: Chiralpak OJ-H, Daicel Chemical Industries, Ltd.;
Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV238 nm.

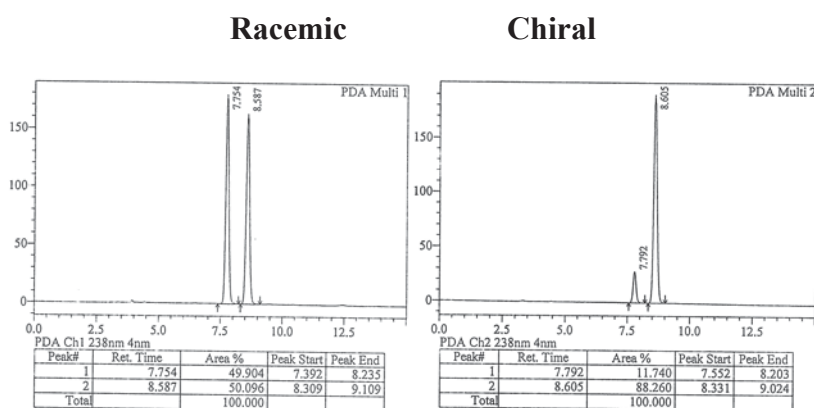
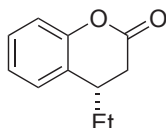


Table 2, 2b



HPLC Condition: Column: Chiralpak OJ-H, Daicel Chemical Industries, Ltd.;
Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV224 nm.

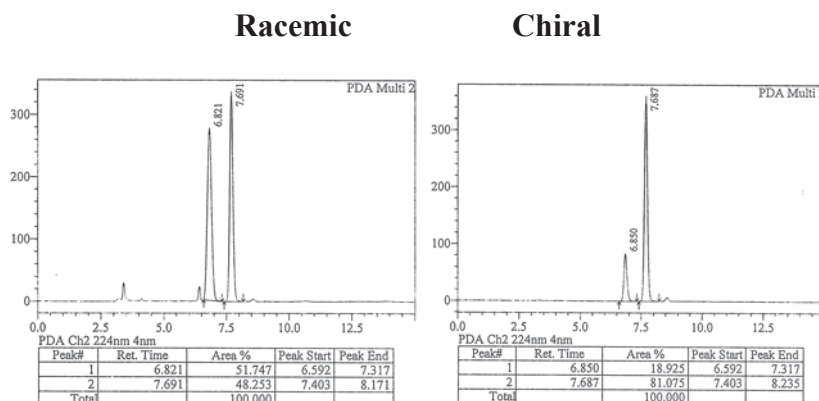
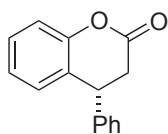


Table 2, 2c



HPLC Condition: Column: Chiralpak OB-H, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV218 nm.

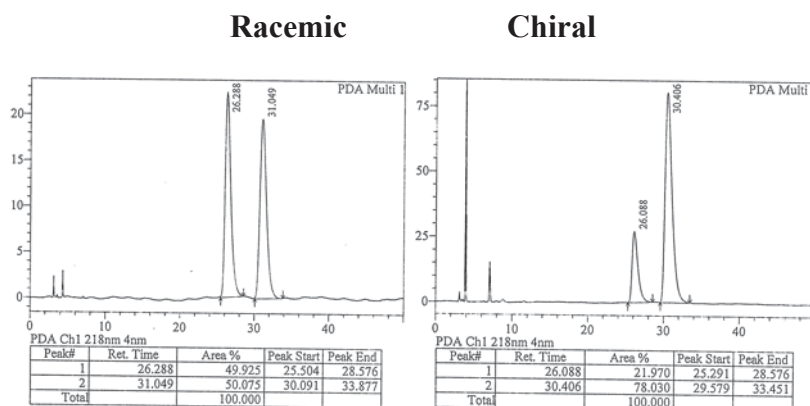
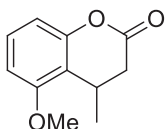


Table 2, 2d



HPLC Condition: Column: Chiralpak OB-H, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV225 nm.

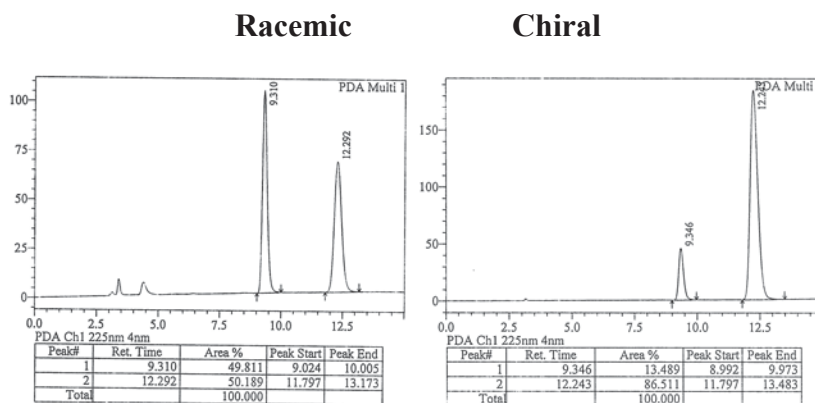
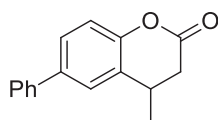
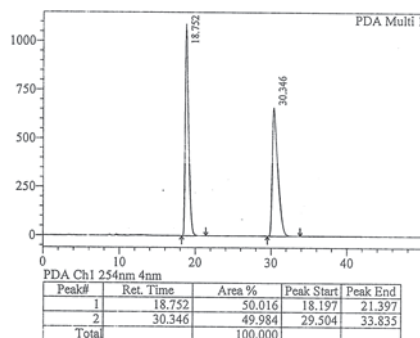


Table 2, 2e



HPLC Condition: Column: Chiralpak OJ-H, Daicel Chemical Industries, Ltd.;
Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

Racemic



Chiral

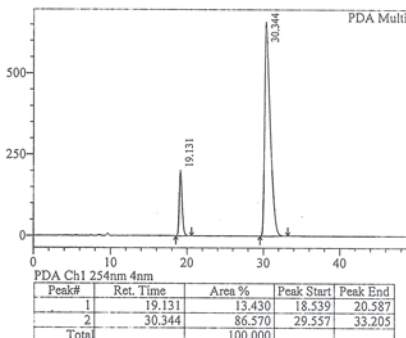
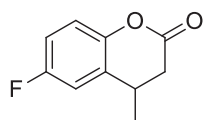
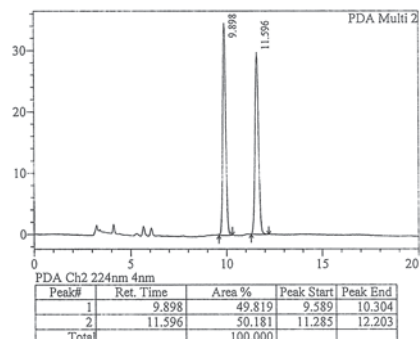


Table 2, 2f



HPLC Condition: Column: Chiralpak OJ-H, Daicel Chemical Industries, Ltd.;
Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV224 nm.

Racemic



Chiral

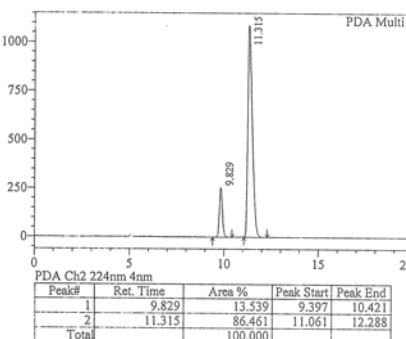
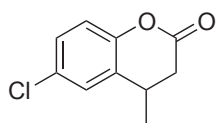


Table 2, 2g



HPLC Condition: Column: Chiralpak OB-H, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV238 nm.

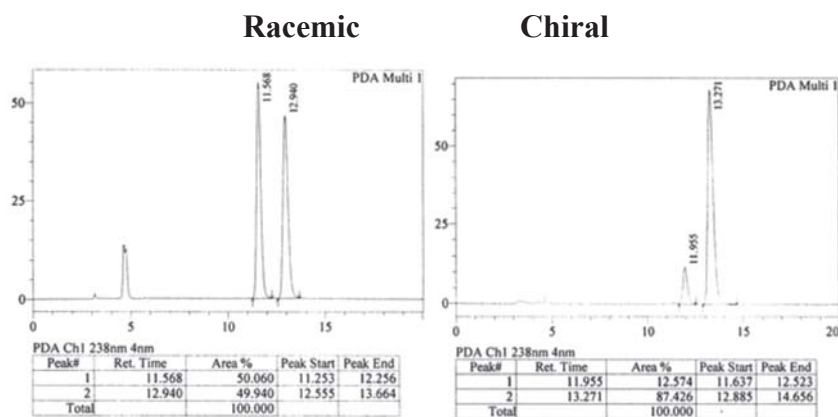
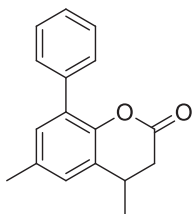


Table 2, 2h



HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99.5/0.5); **Flow rate:** 1.0 mL/min; **Detection:** UV224 nm.

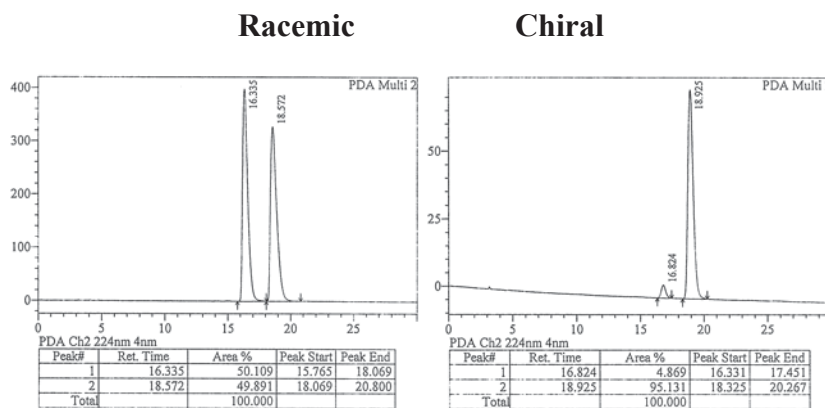
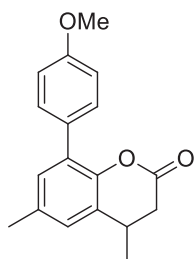


Table 2, 2i



HPLC Condition: Column: Chiralpak IB, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

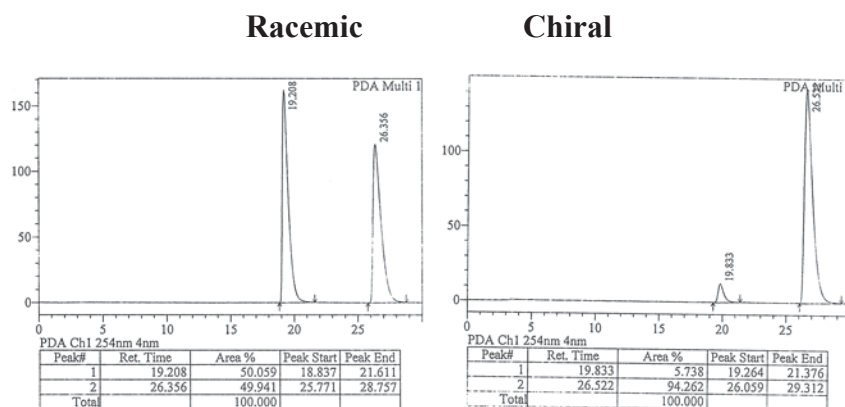
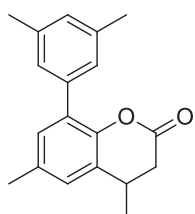


Table 2, 2j



HPLC Condition: Column: Chiralpak IB, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99.5/0.5); **Flow rate:** 1.0 mL/min; **Detection:** UV224 nm.

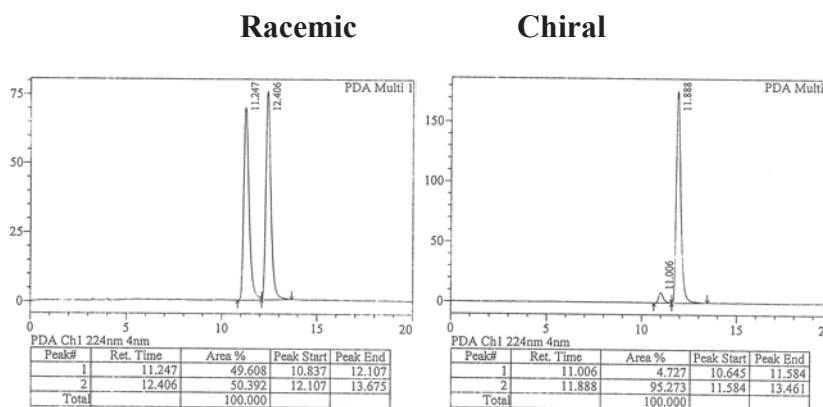
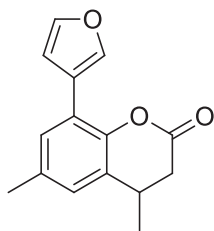


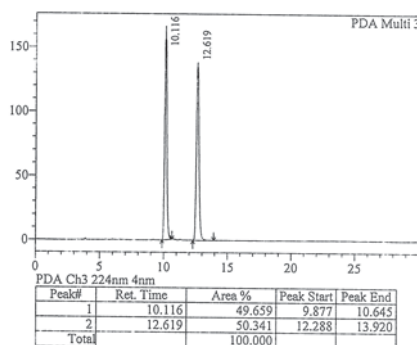
Table 2, 20



HPLC Condition: Column: Chiralpak IB, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99/1); Flow rate: 1.0 mL/min; Detection: UV224 nm.

Racemic



Chiral

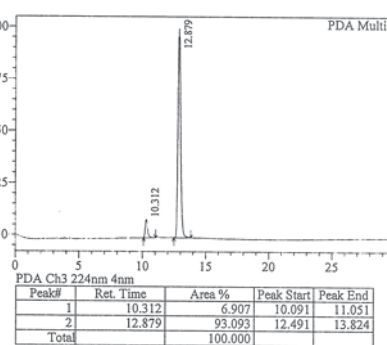
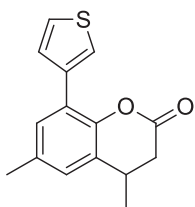


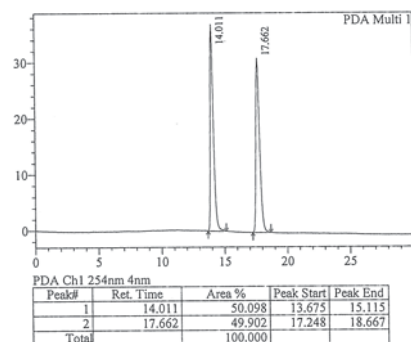
Table 2, 21



HPLC Condition: Column: Chiralpak IB, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99/1); Flow rate: 1.0 mL/min; Detection: UV254 nm.

Racemic



Chiral

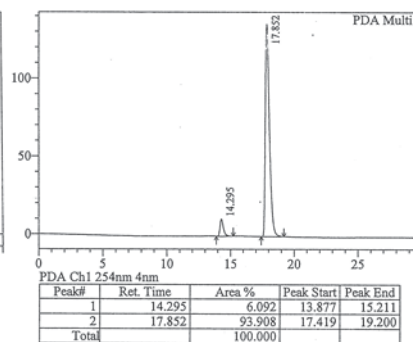
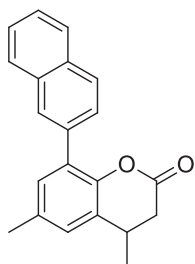


Table 2, 2m



HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

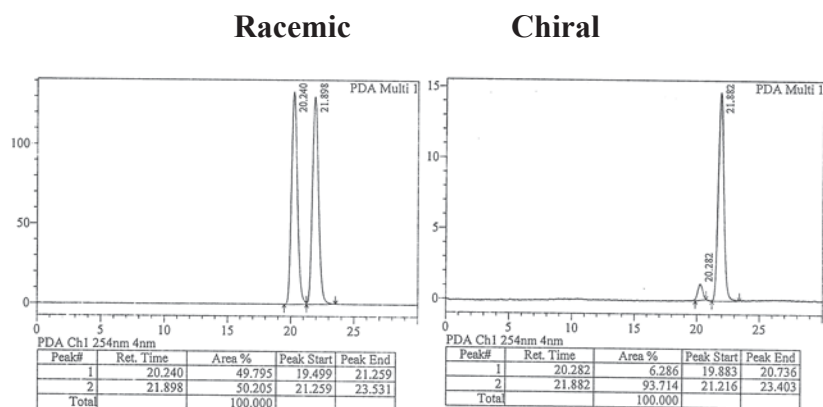
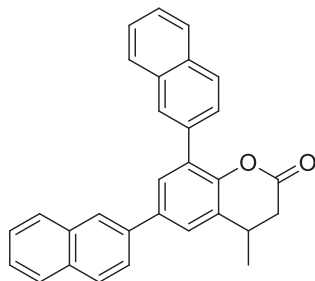


Table 2, 2n



HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

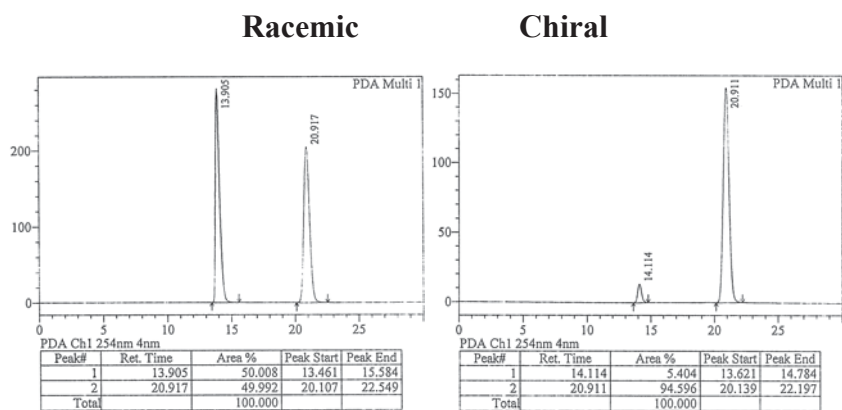
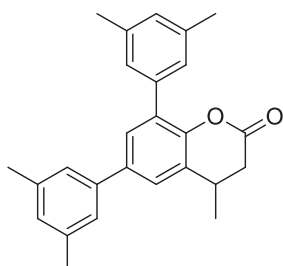


Table 2, 2o



HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

Racemic

Chiral

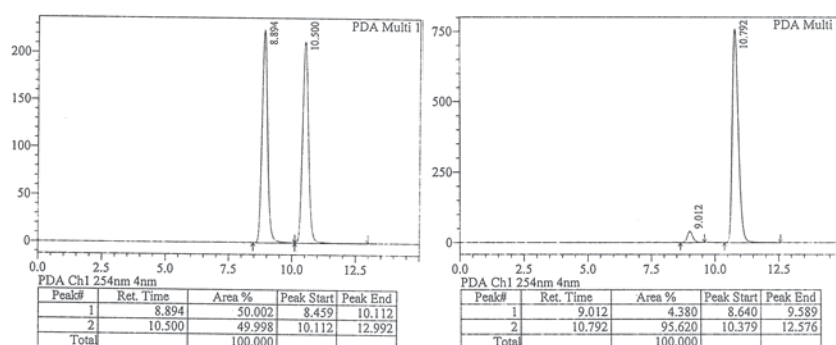
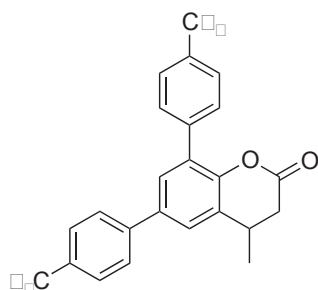


Table 2, 2p

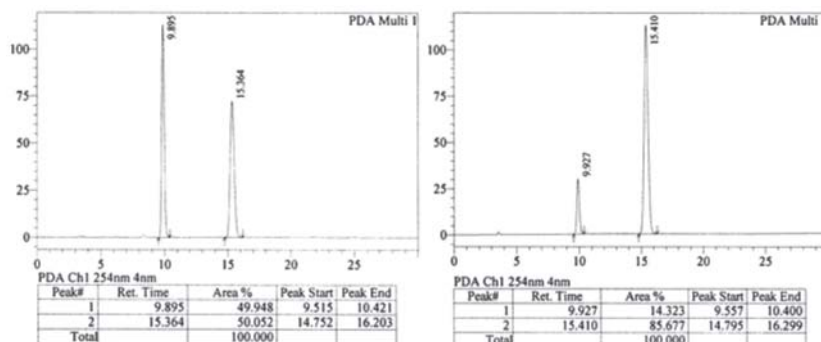


HPLC Condition: Column: Chiralpak IA, Daicel Chemical Industries, Ltd.;

Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV254 nm.

Racemic

Chiral



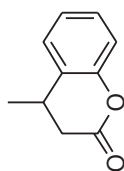
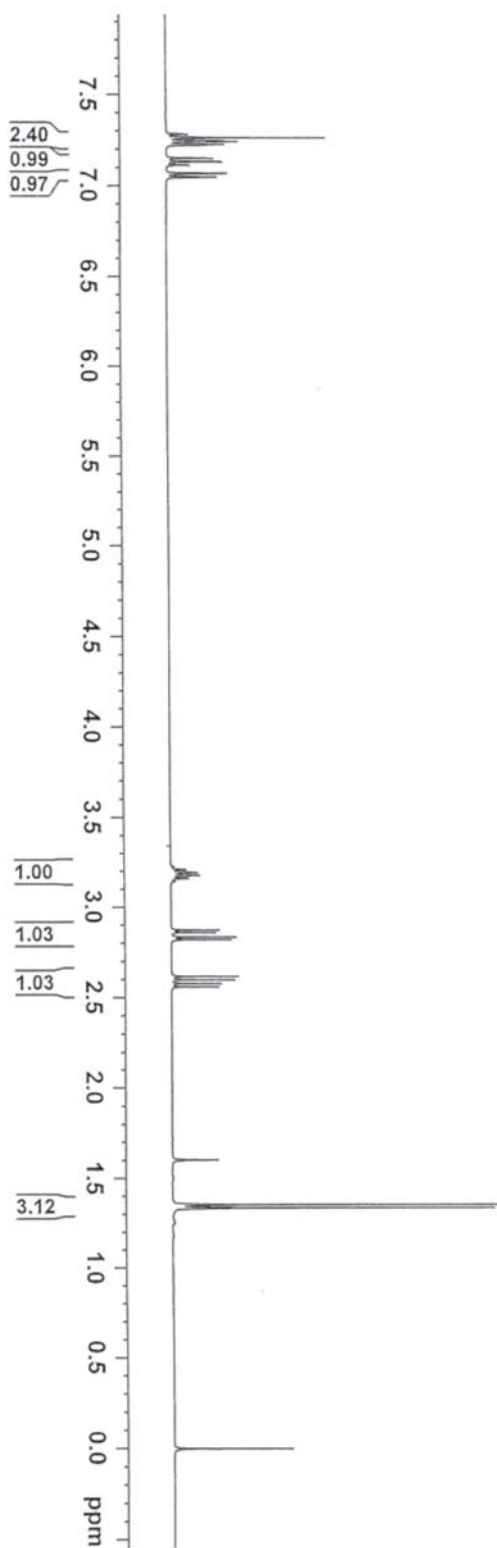
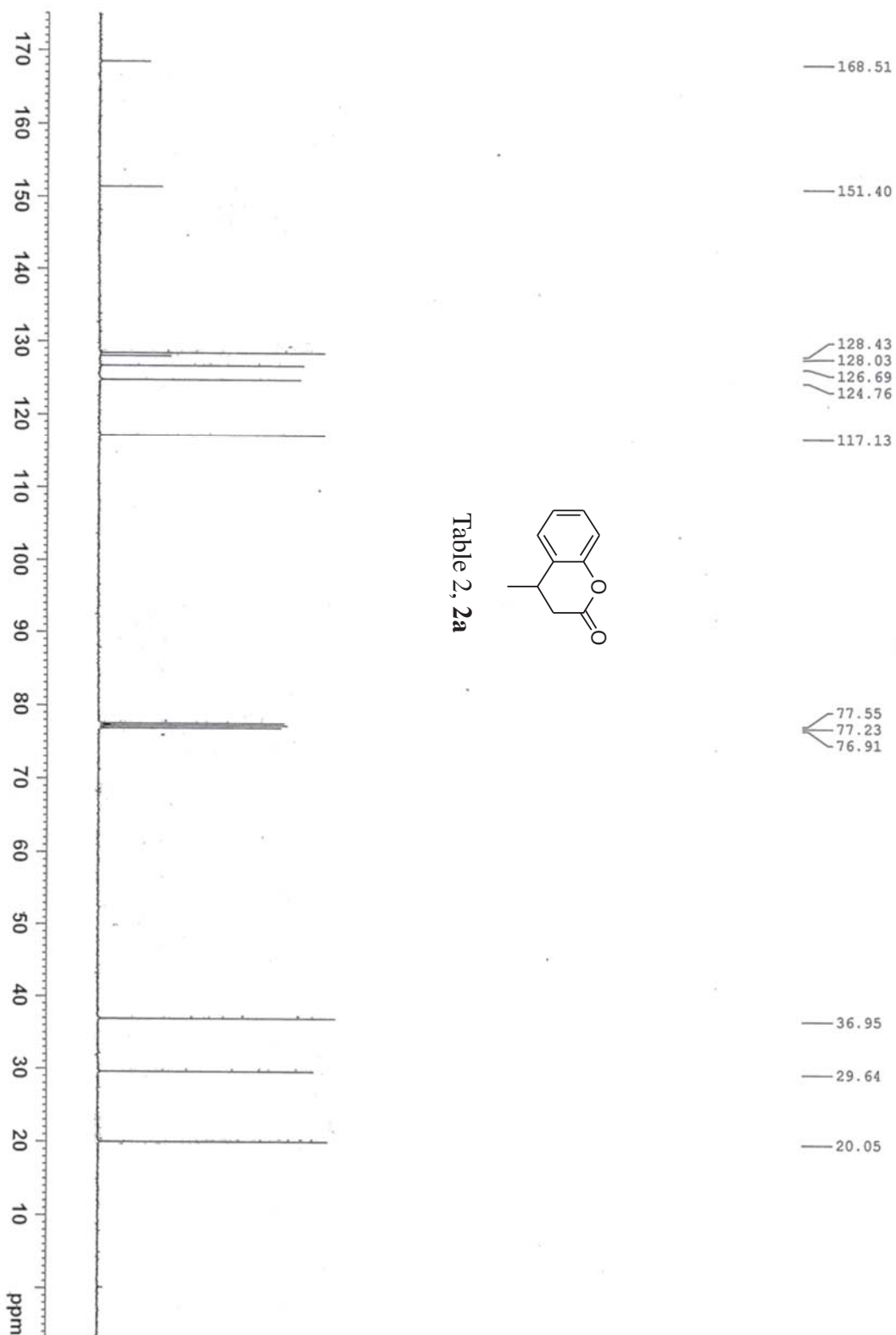


Table 2, 2a





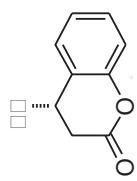
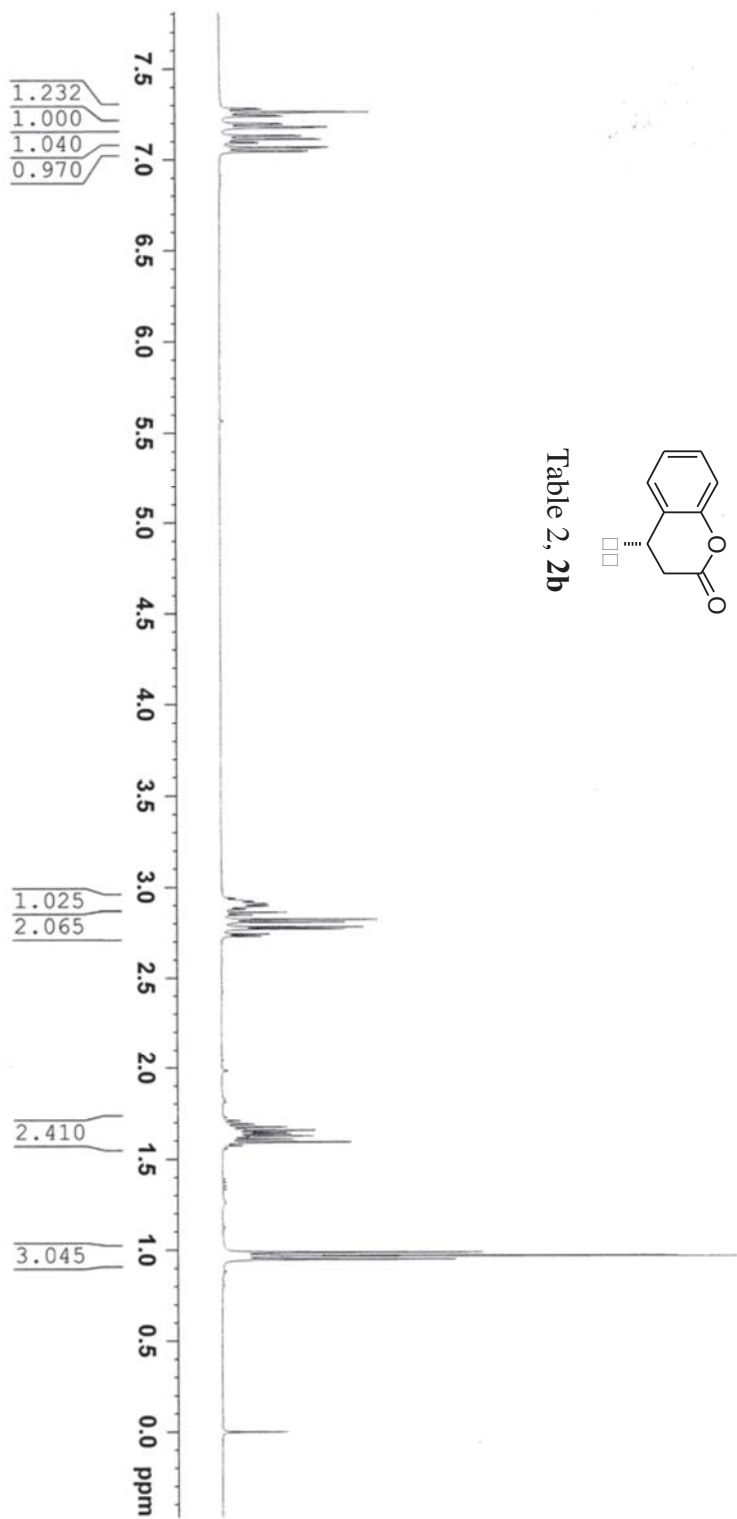
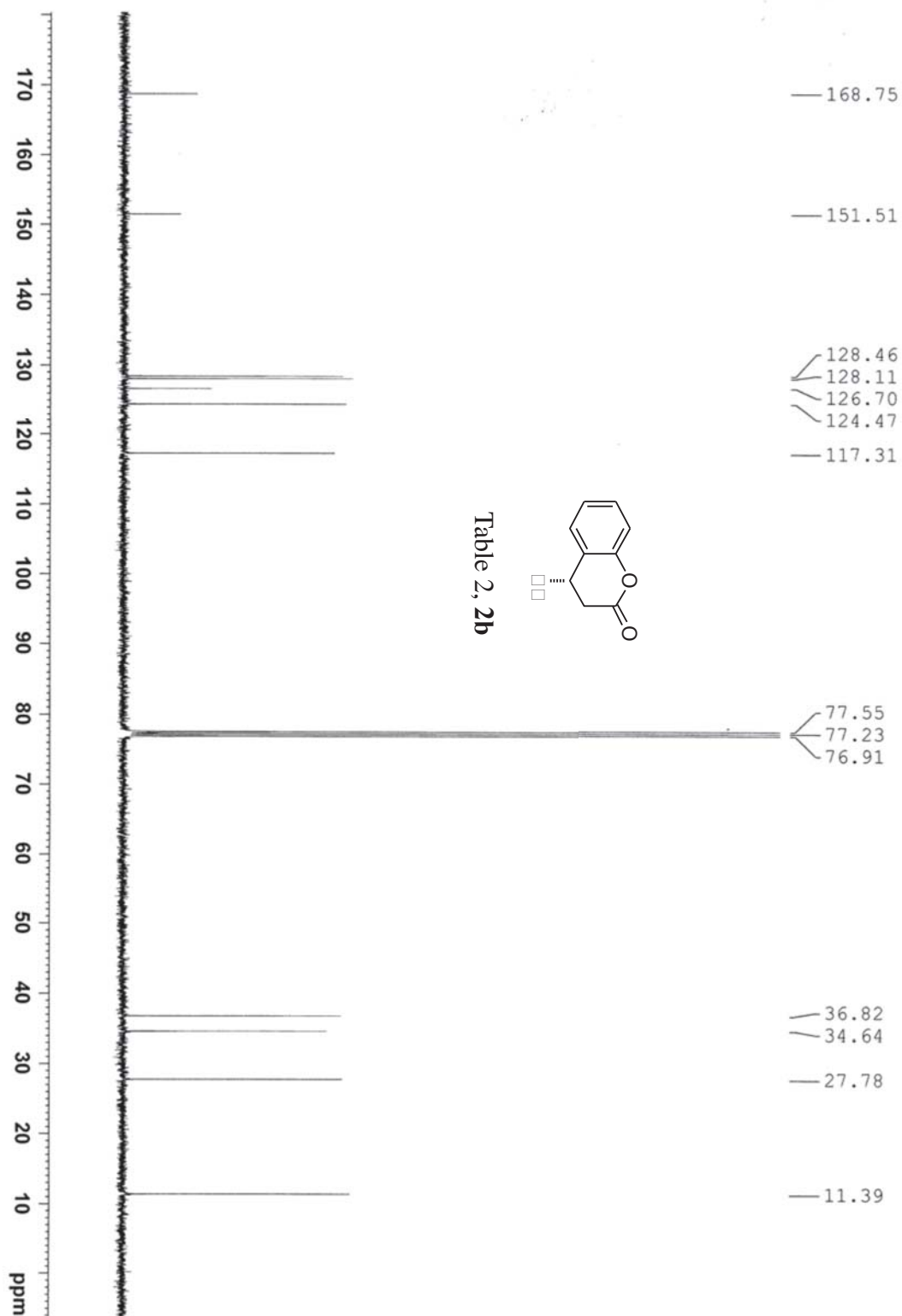
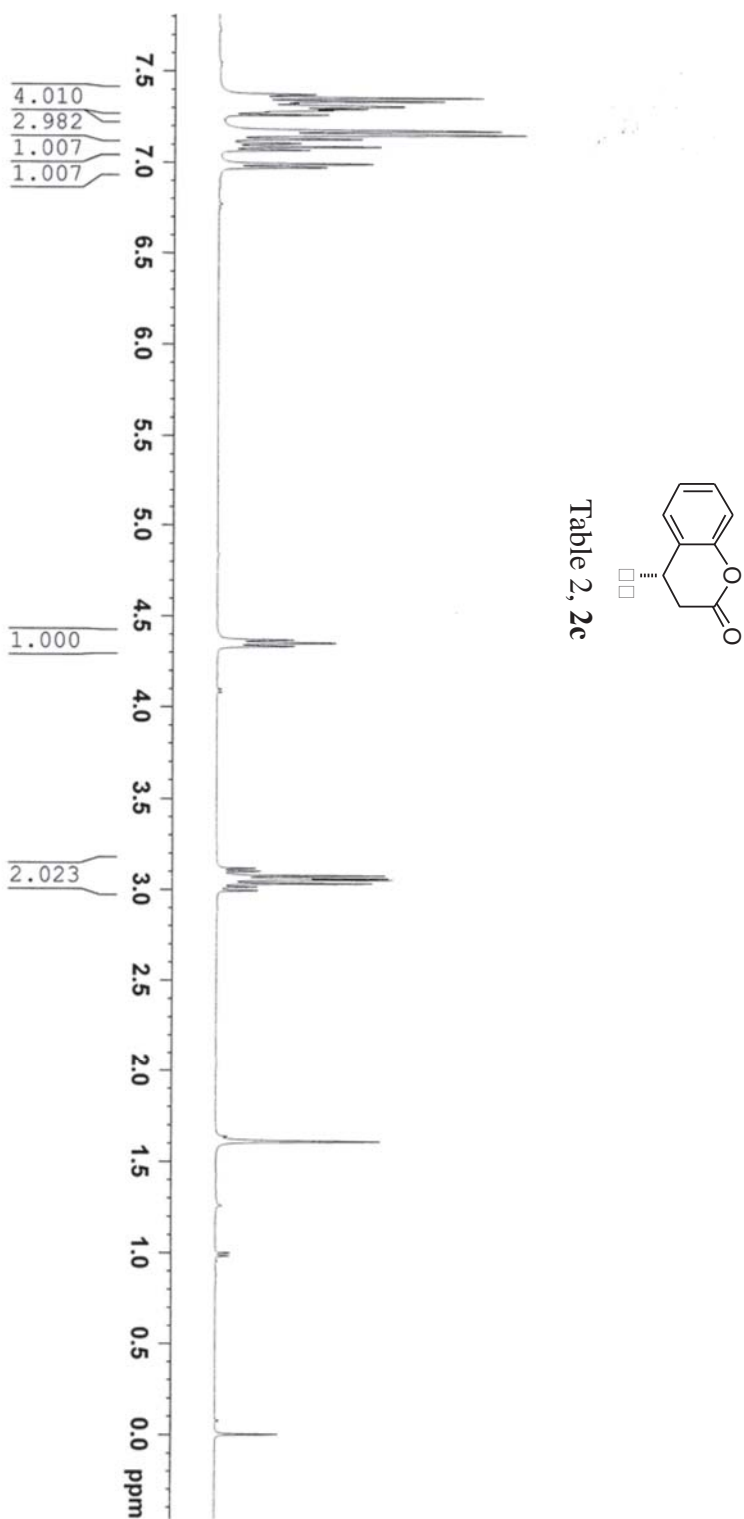
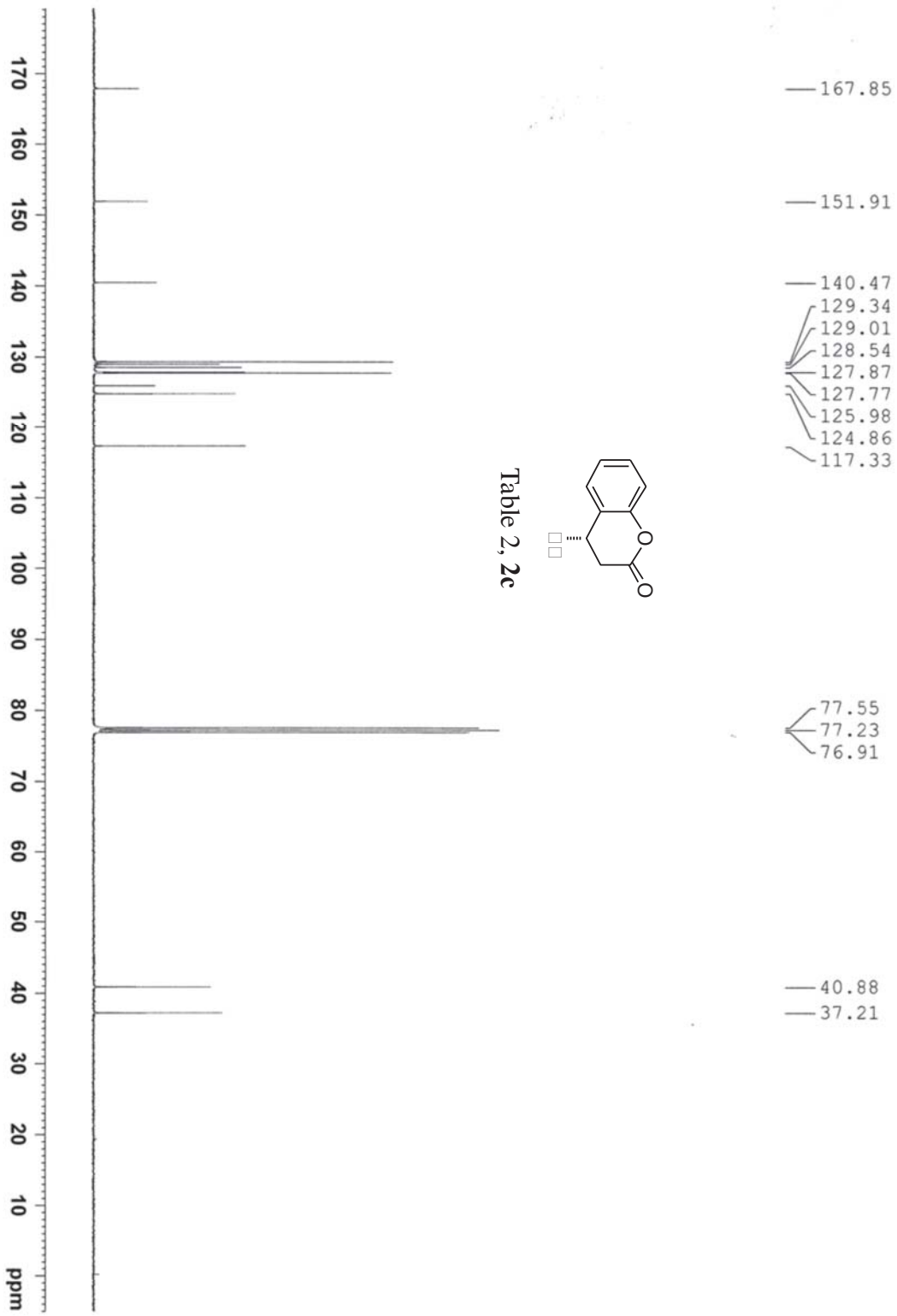
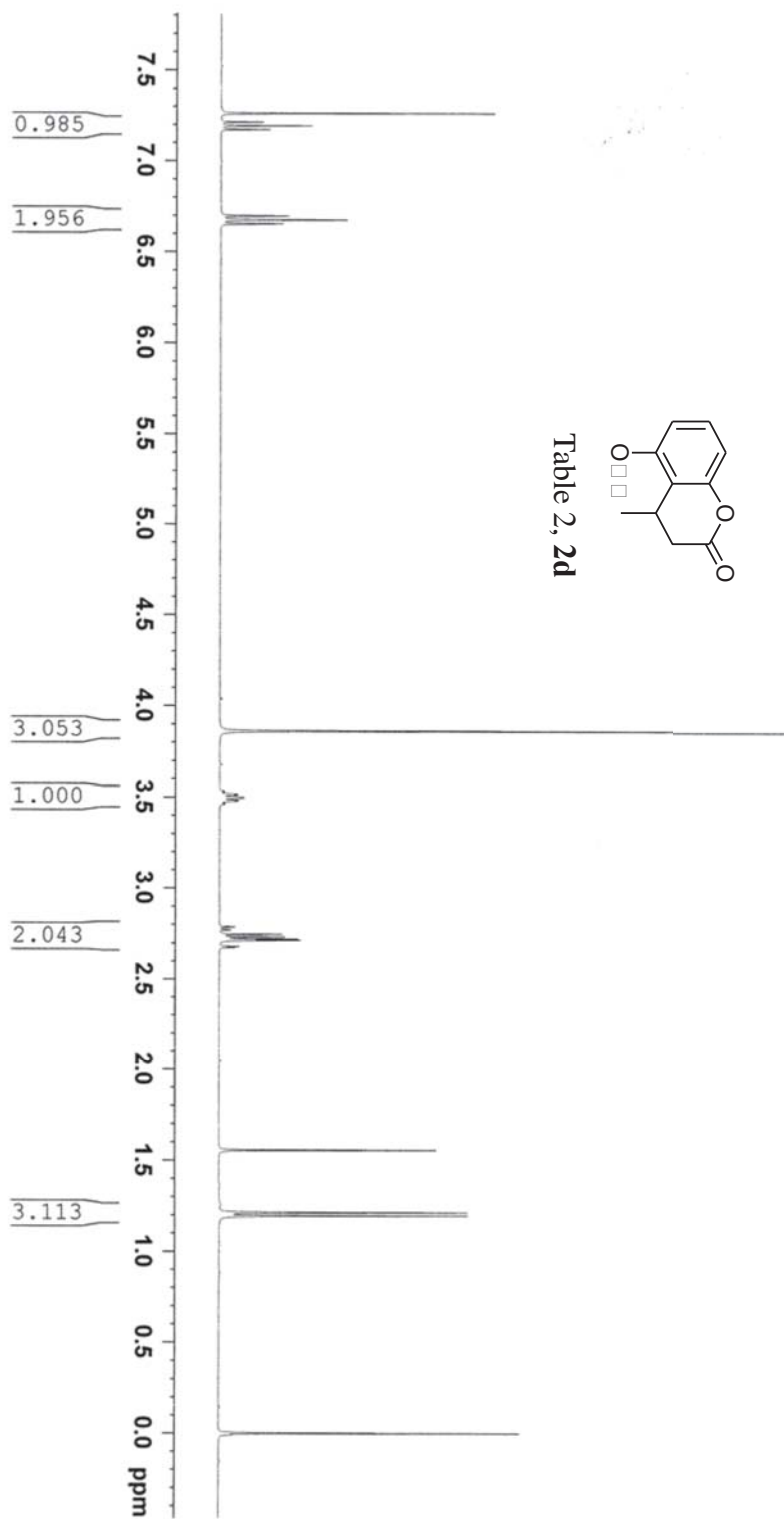


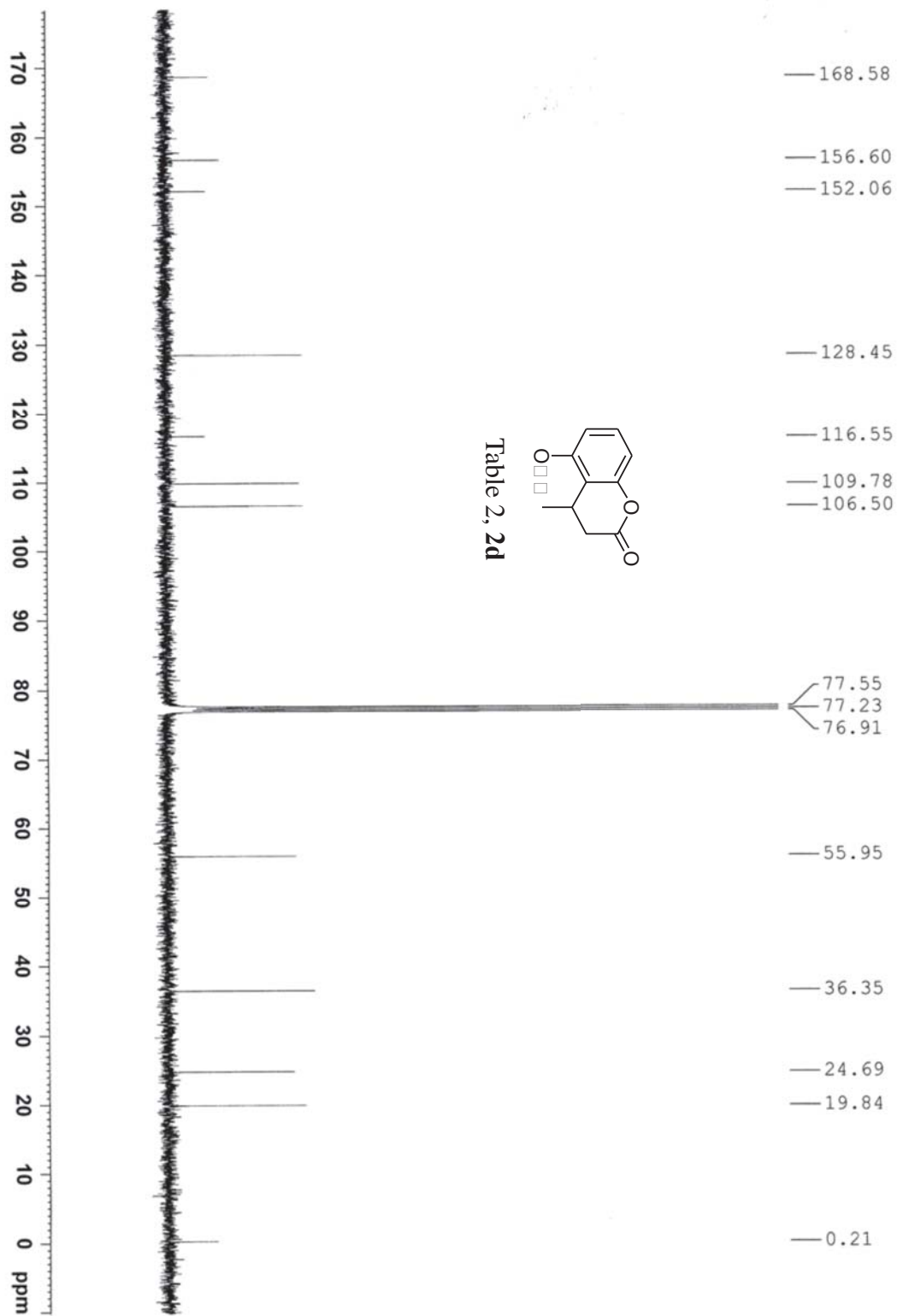
Table 2, 2b

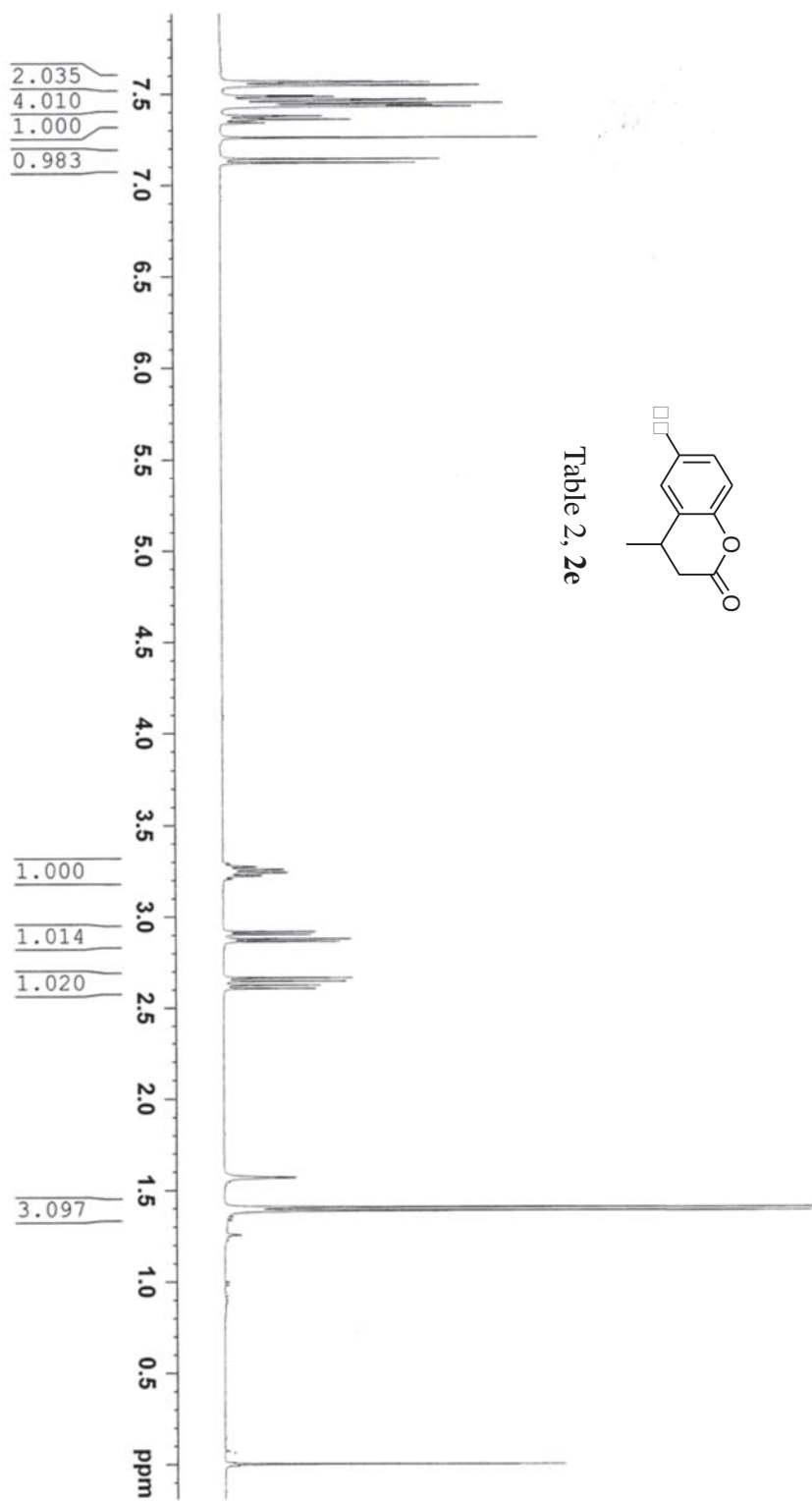


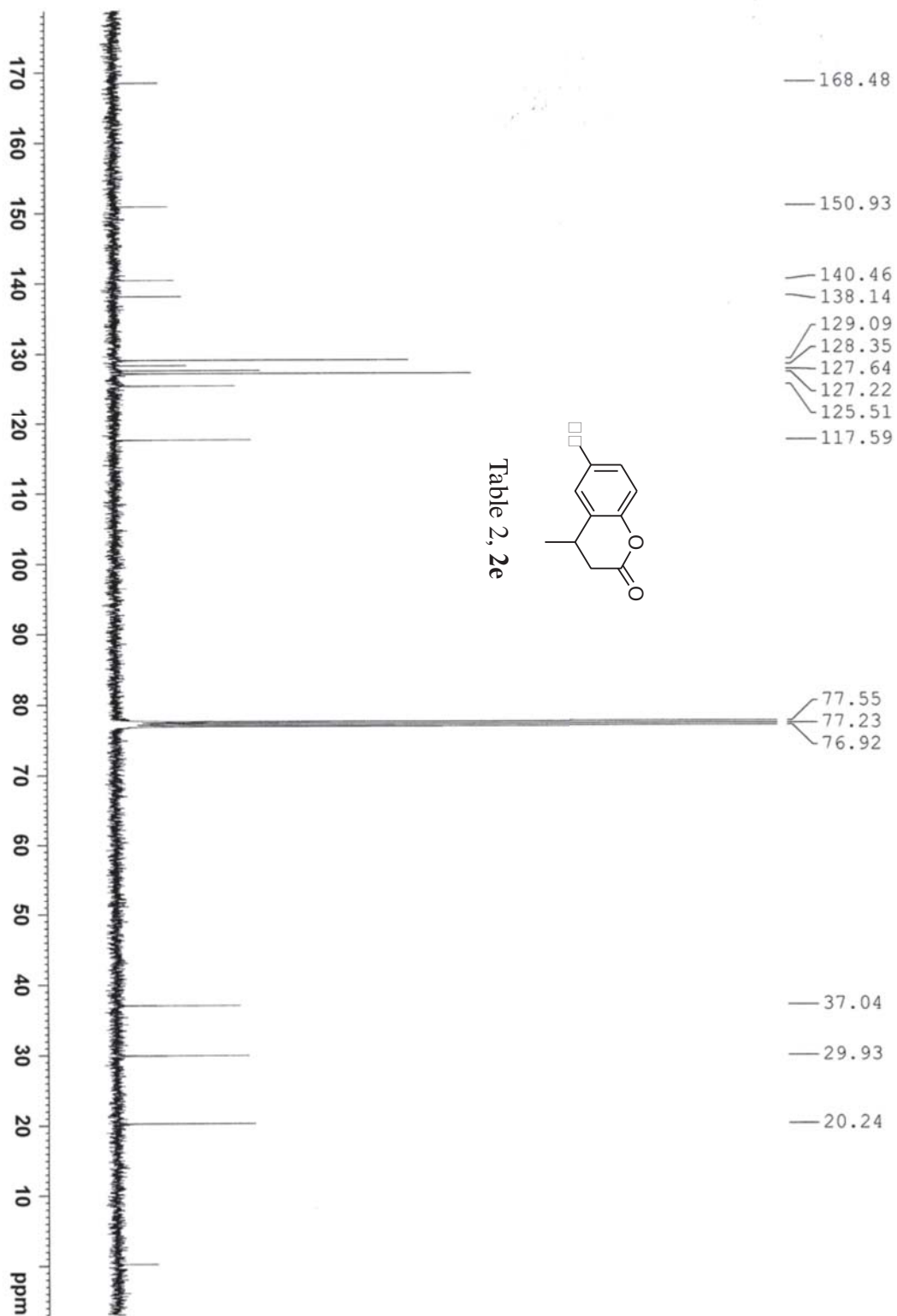












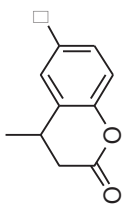
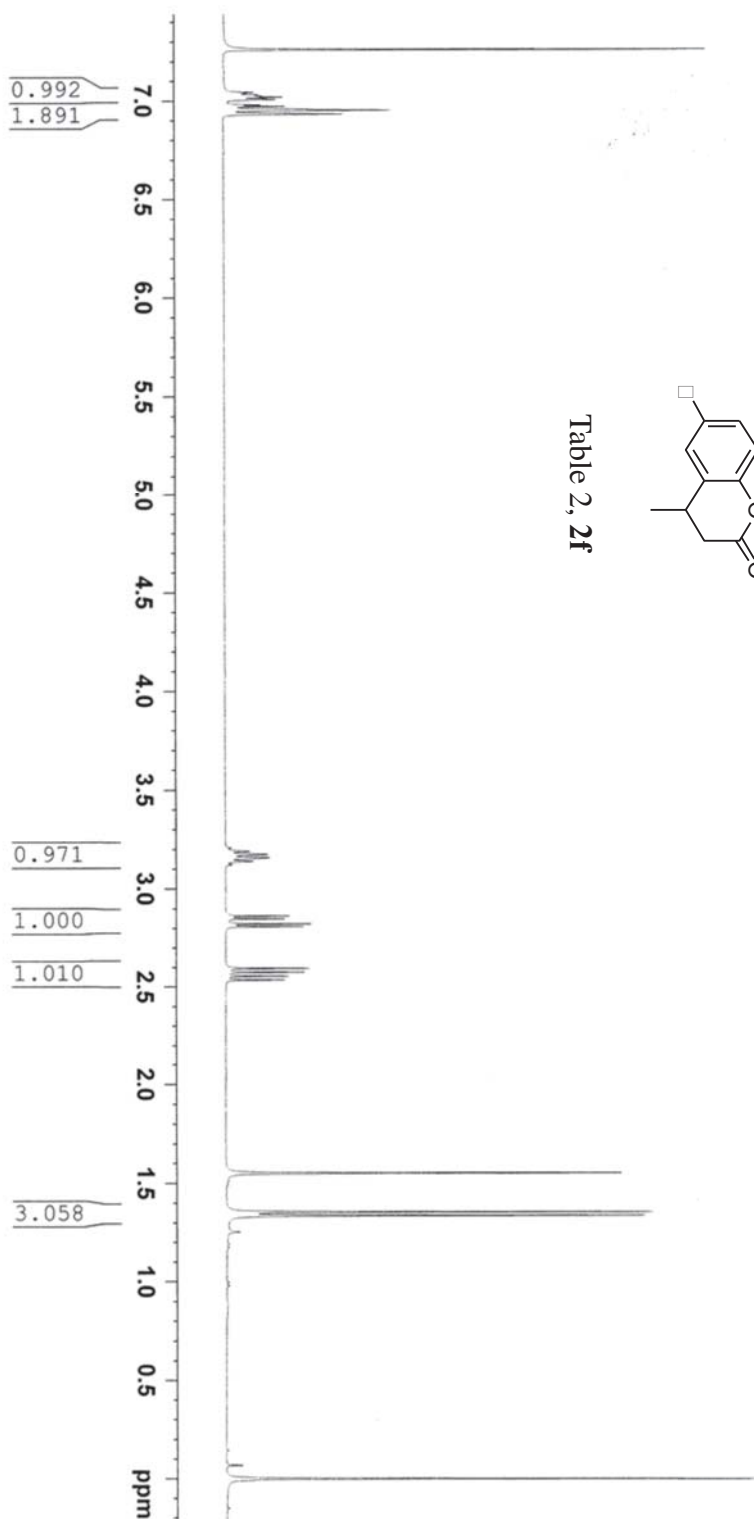
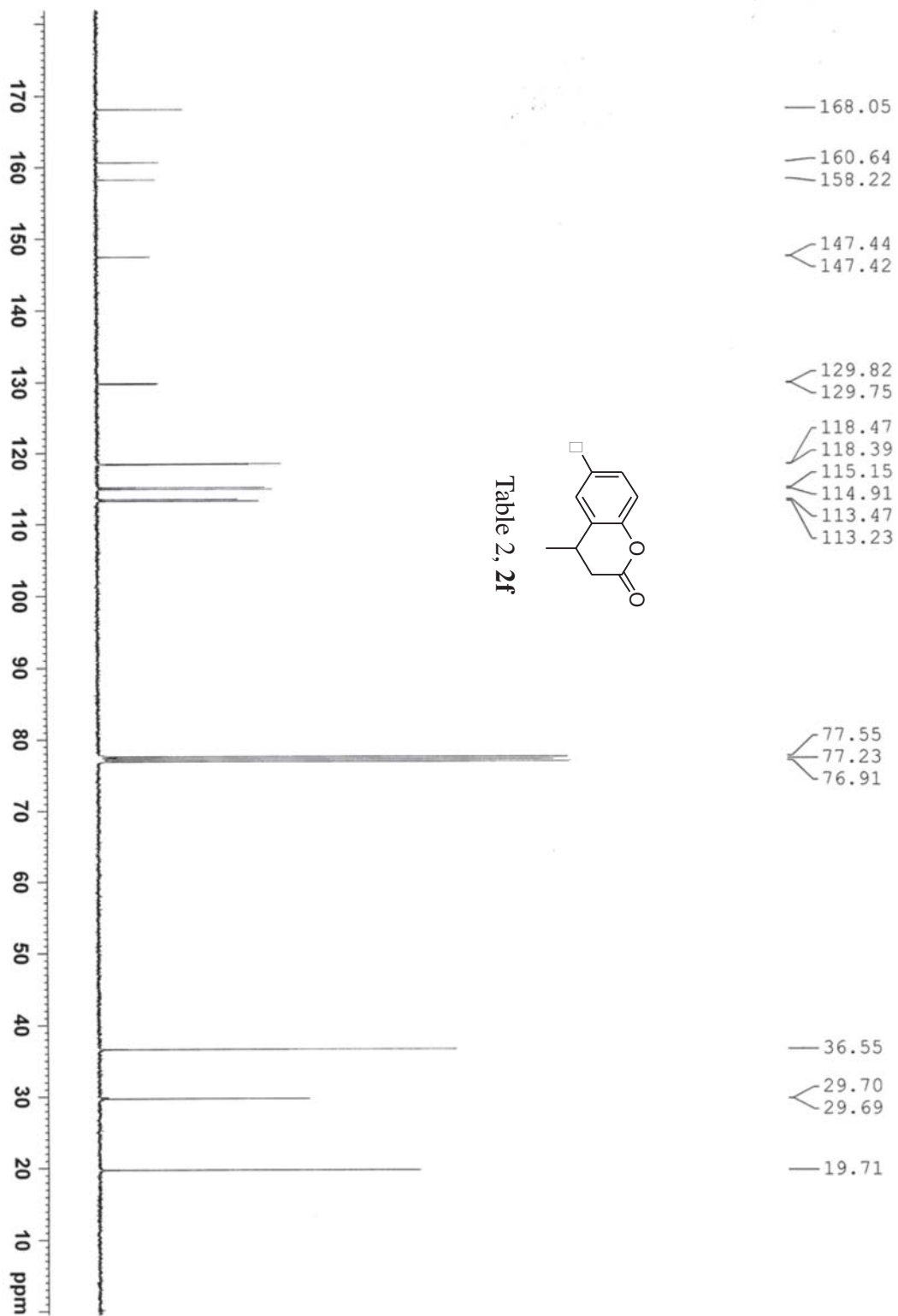


Table 2, 2f





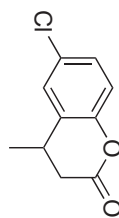
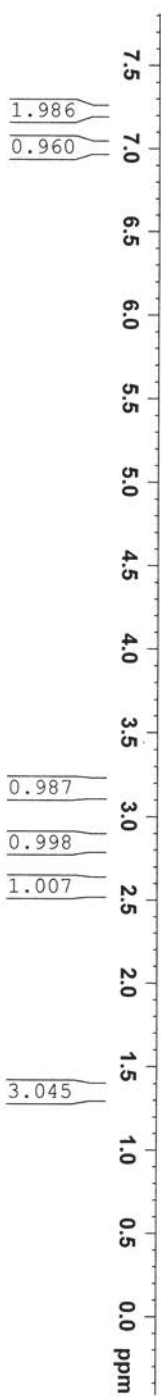
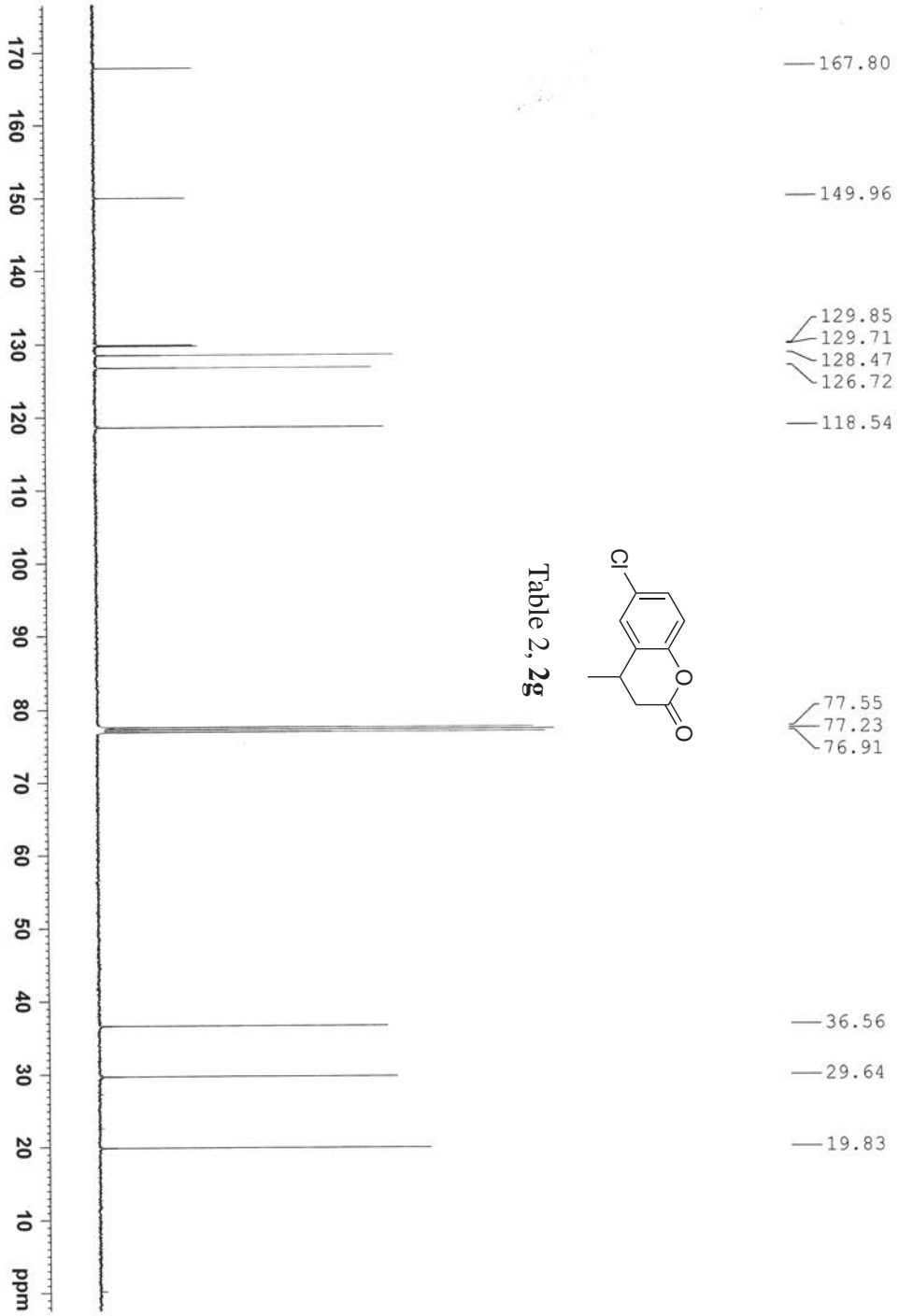


Table 2, **2g**





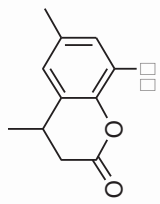
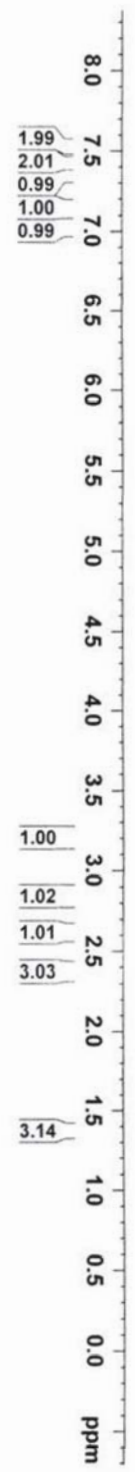
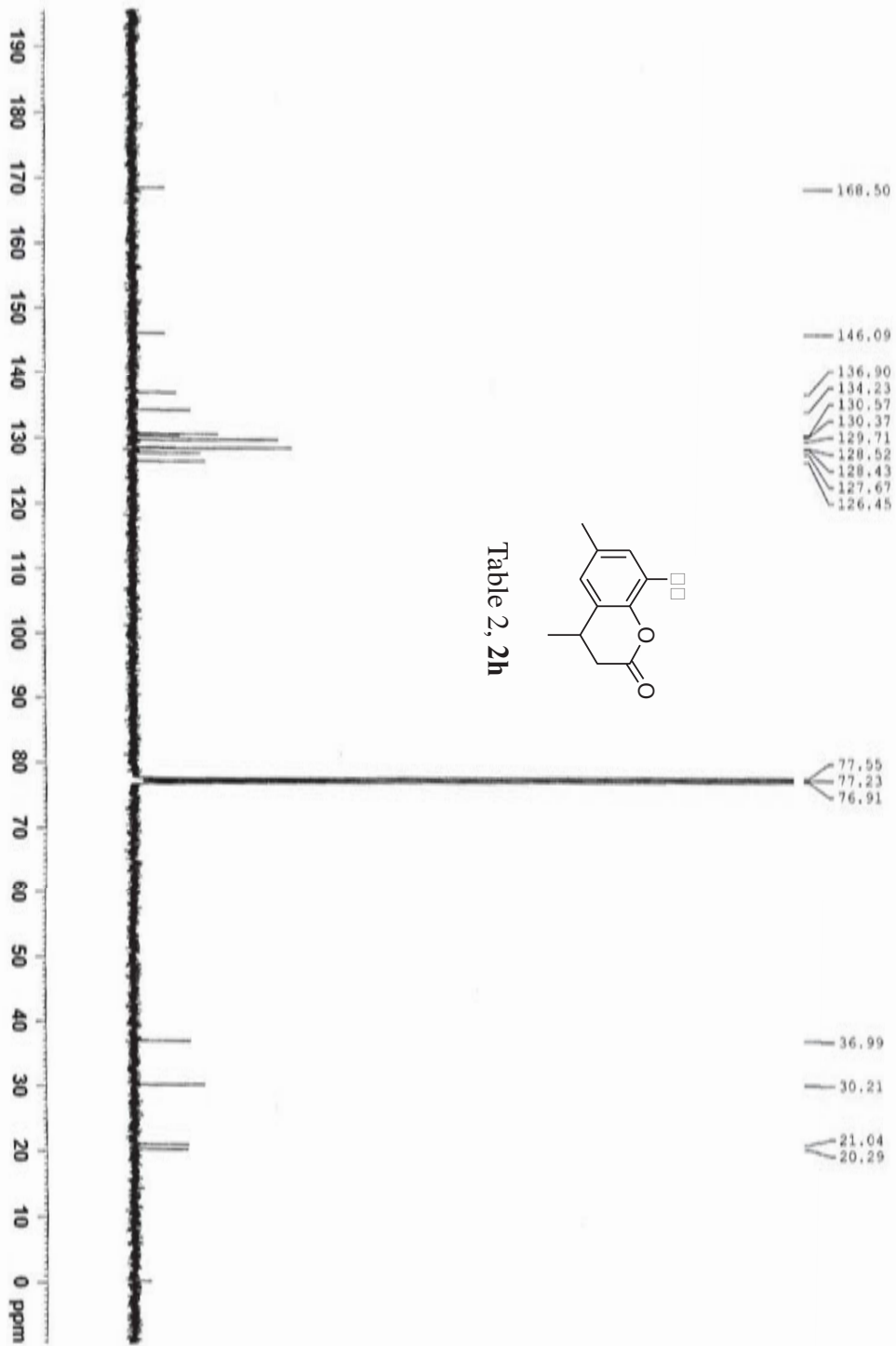


Table 2, 2h





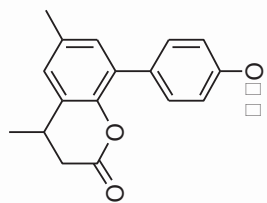
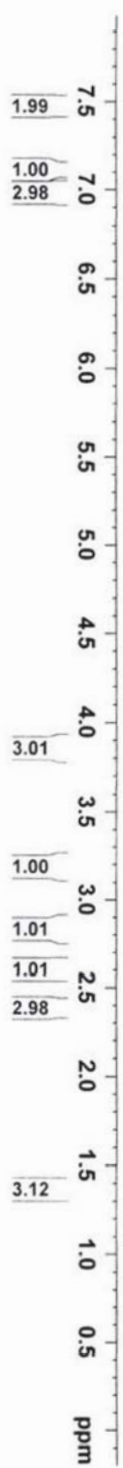
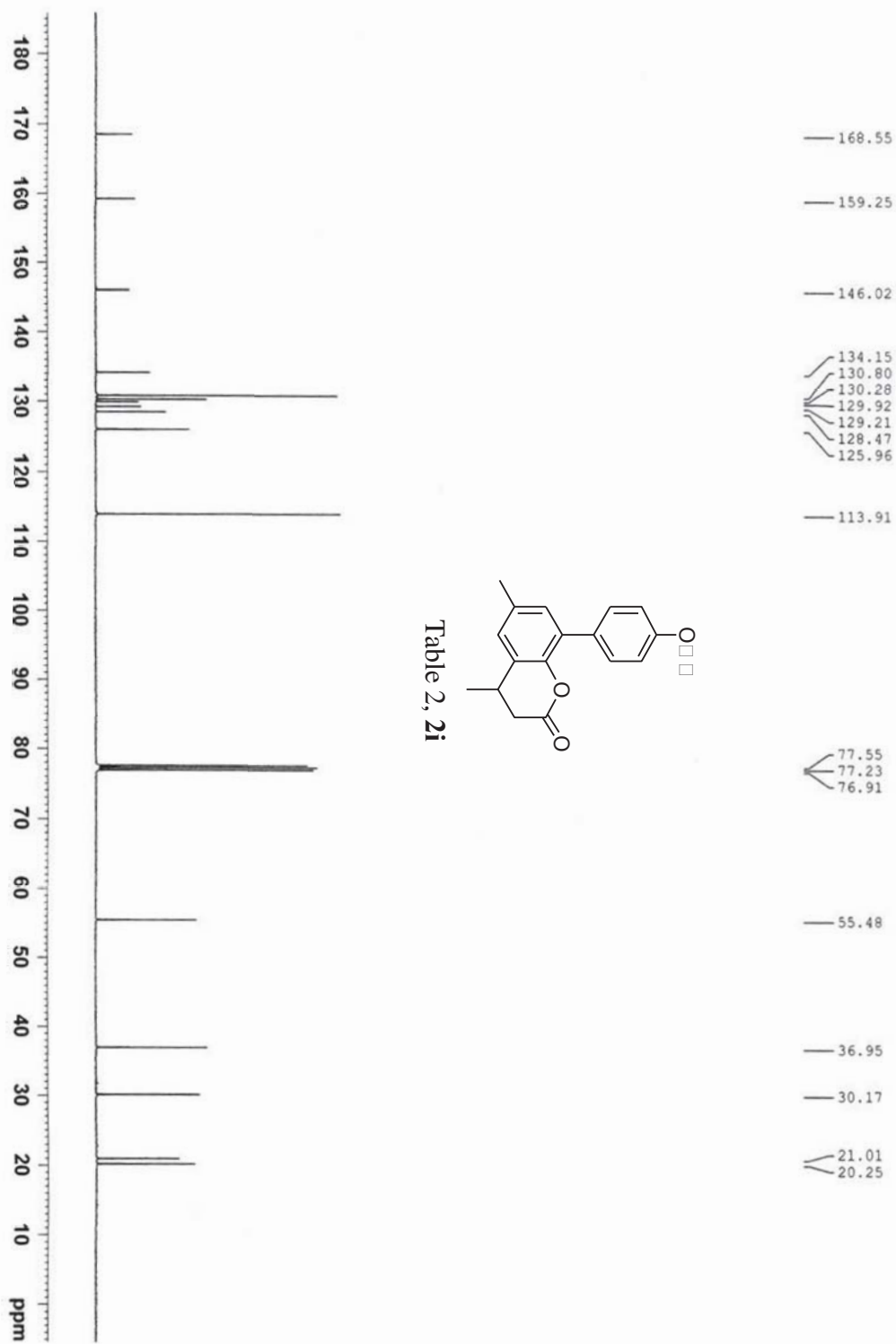
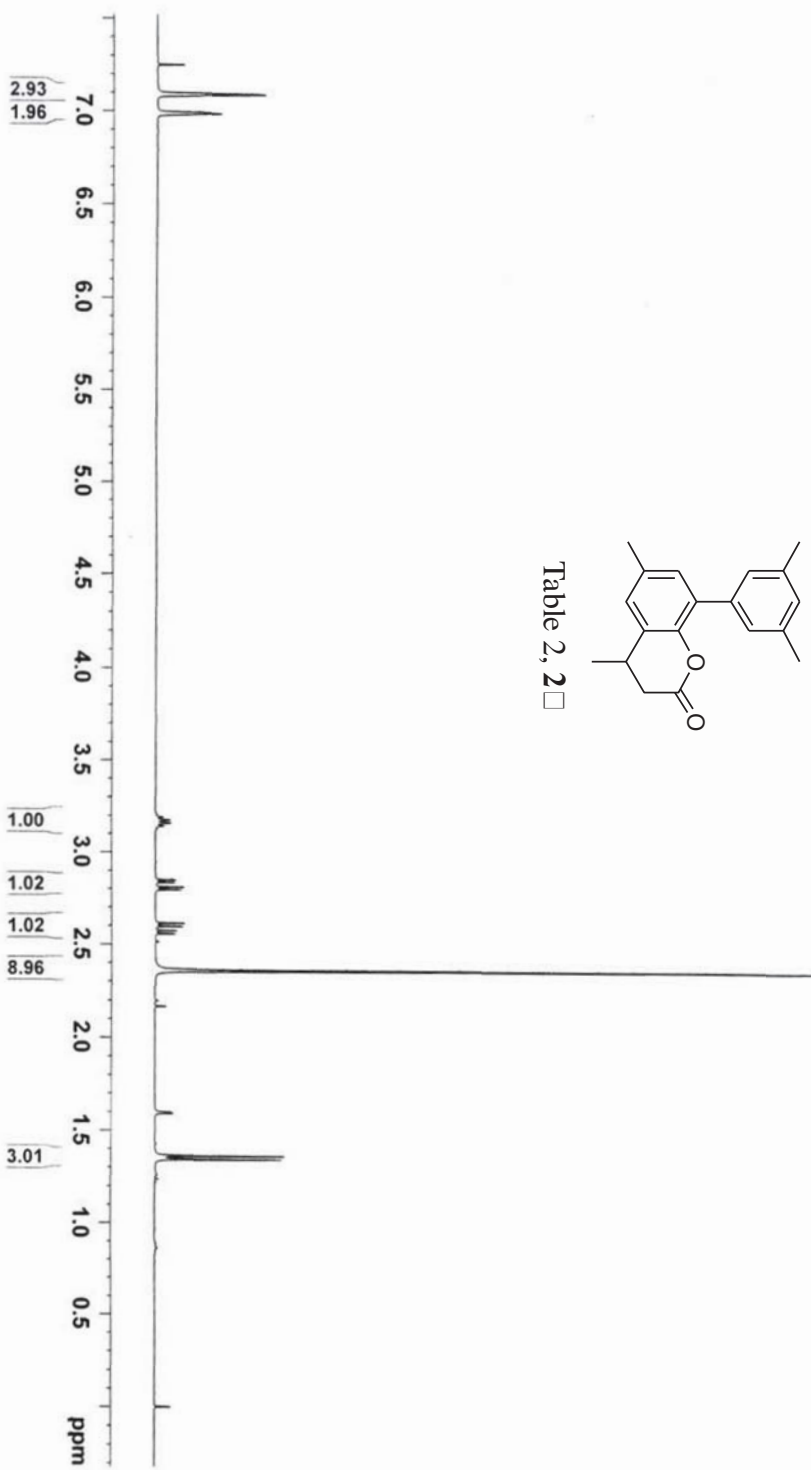


Table 2, 2i







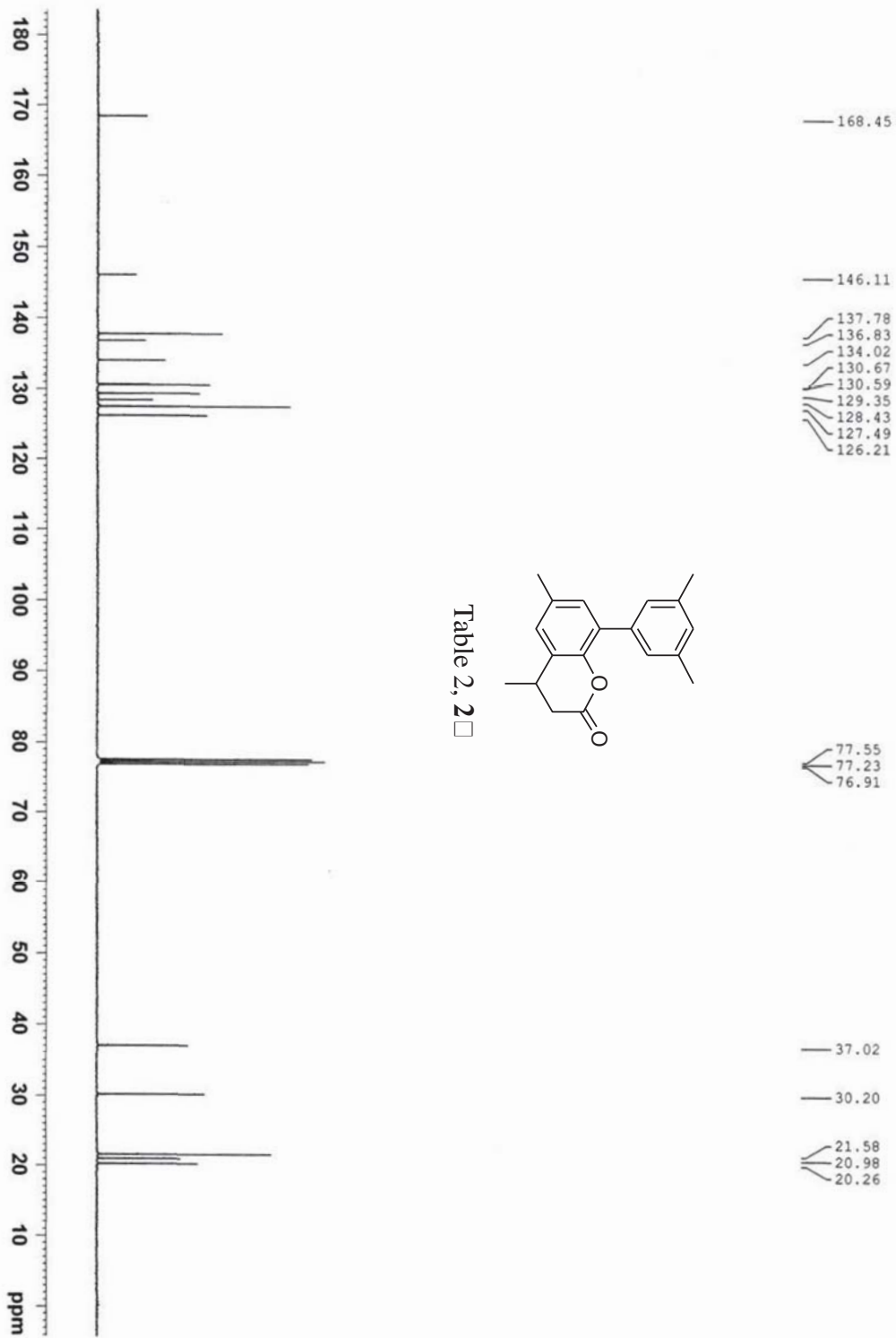
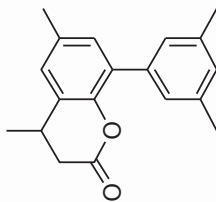


Table 2, 2 □



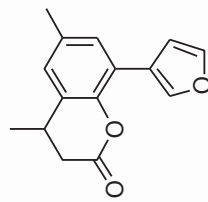
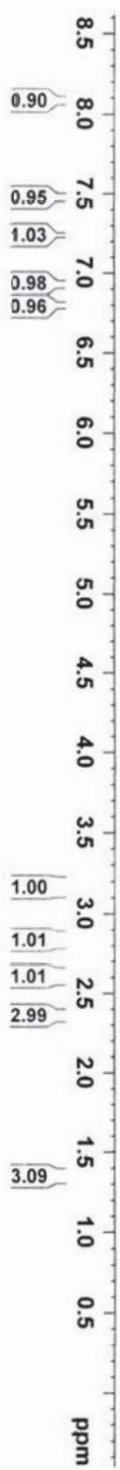


Table 2, 2 □



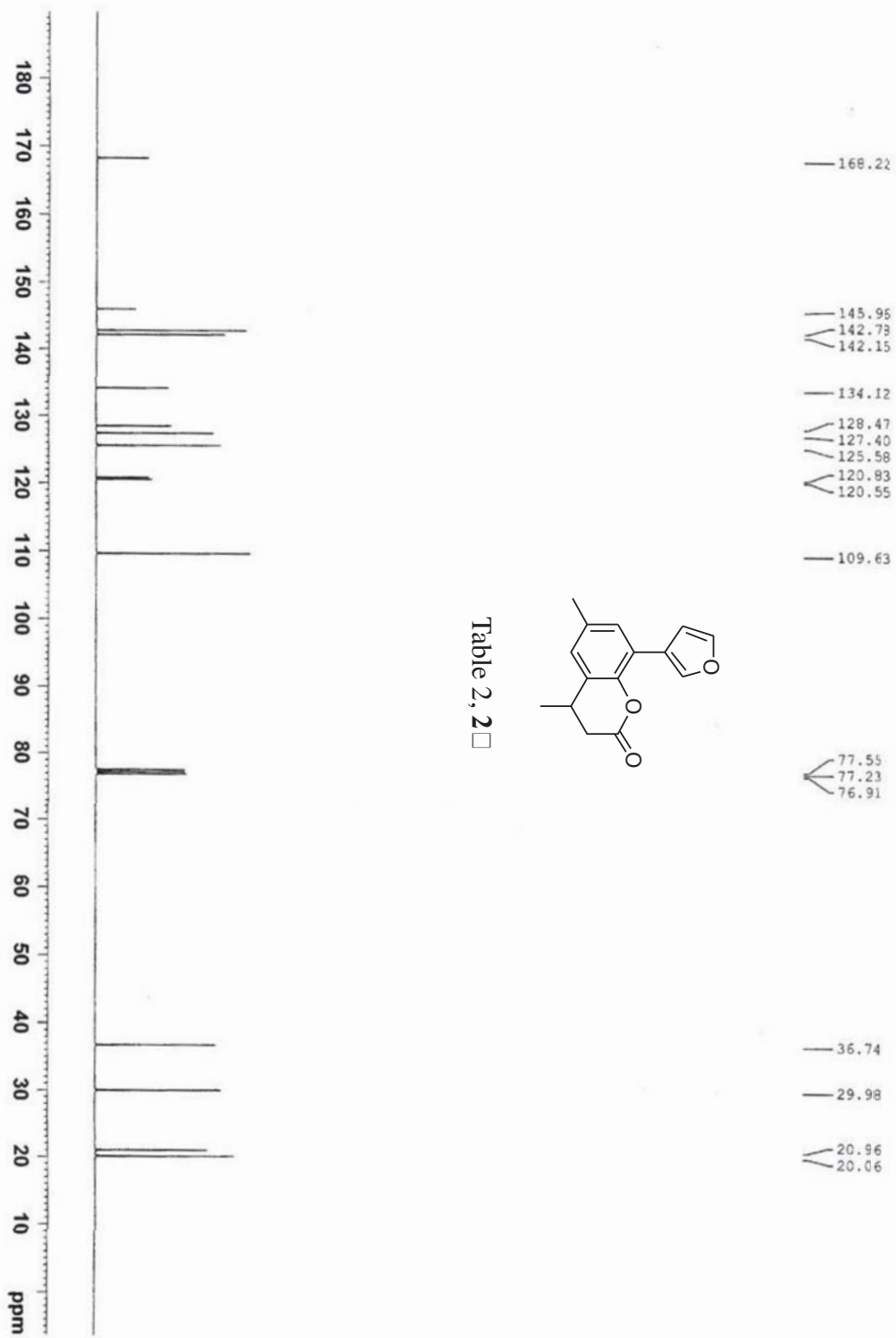
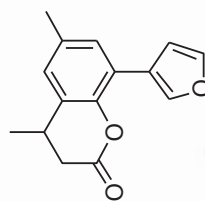


Table 2, 2 □



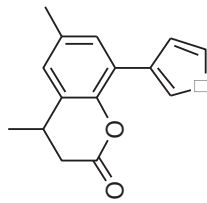
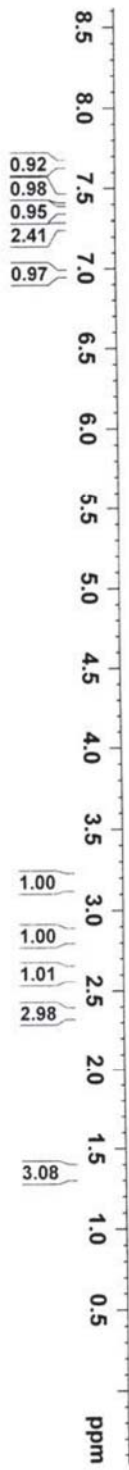
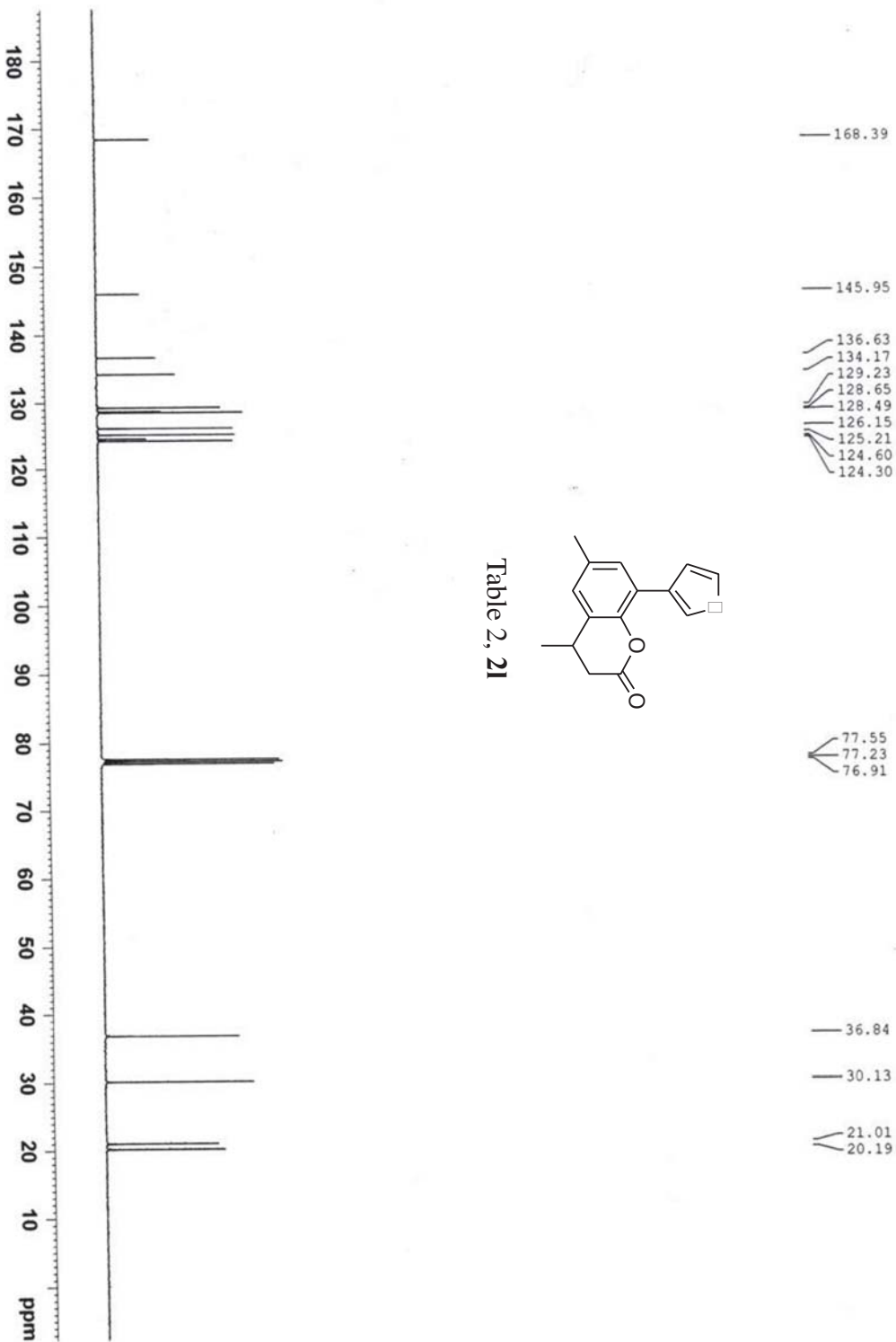


Table 2, 21





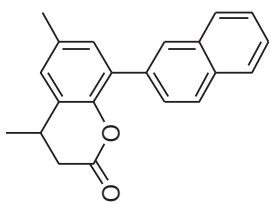
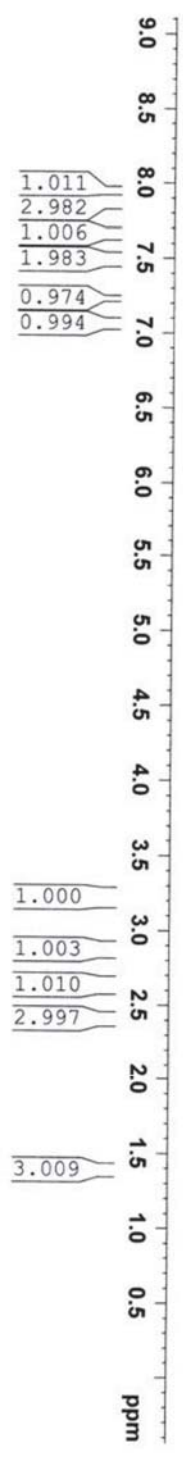
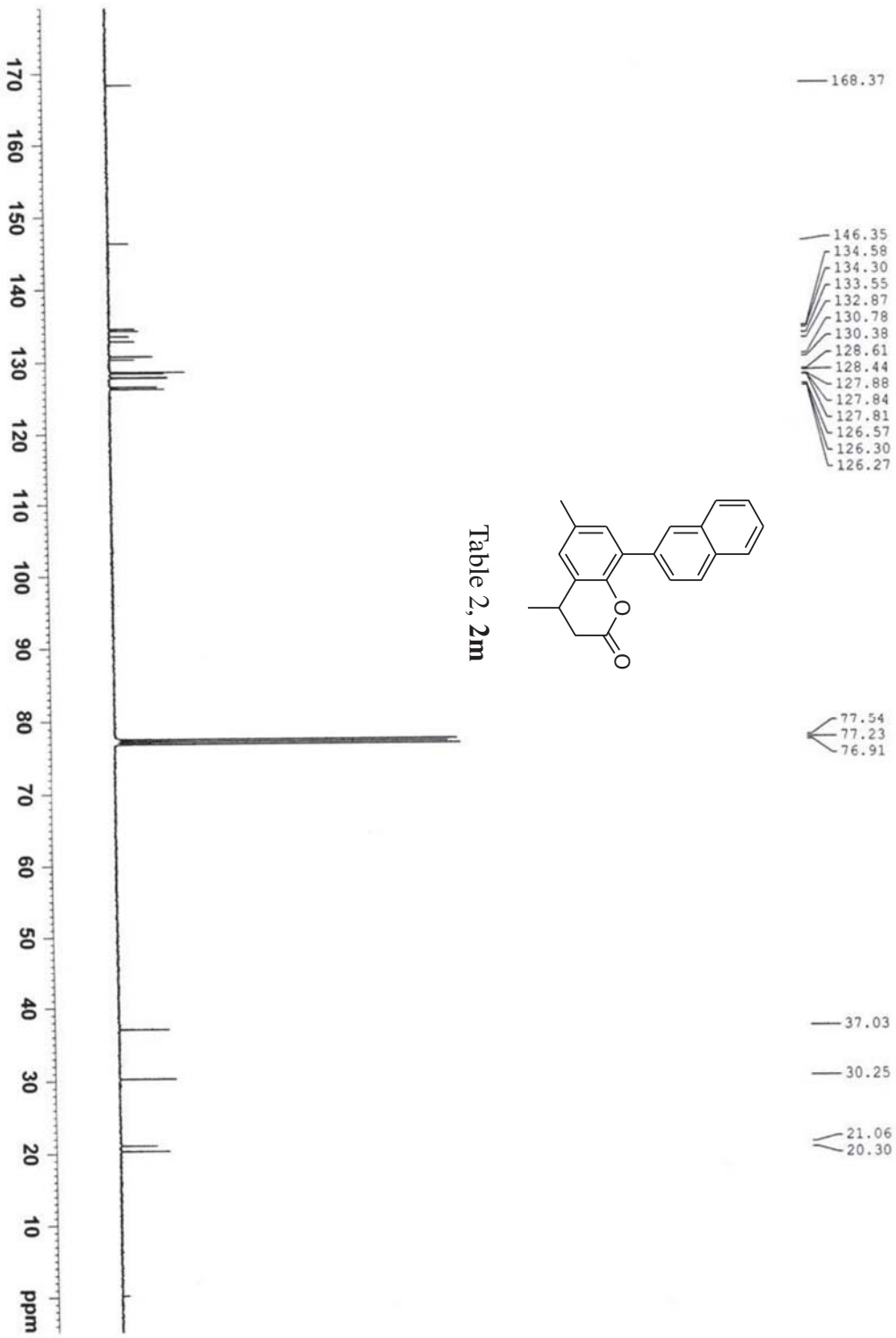


Table 2, 2m





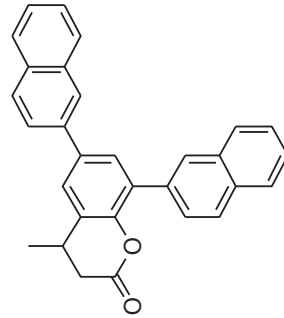
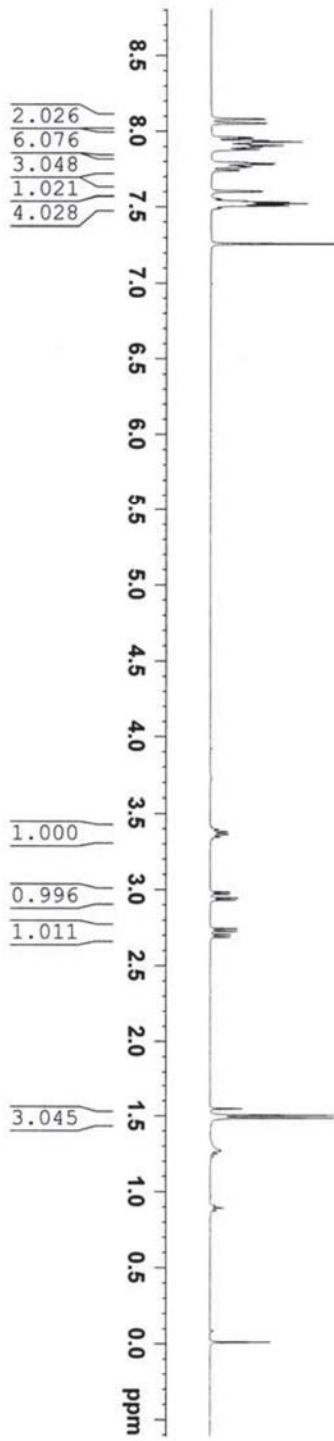


Table 2, 2n



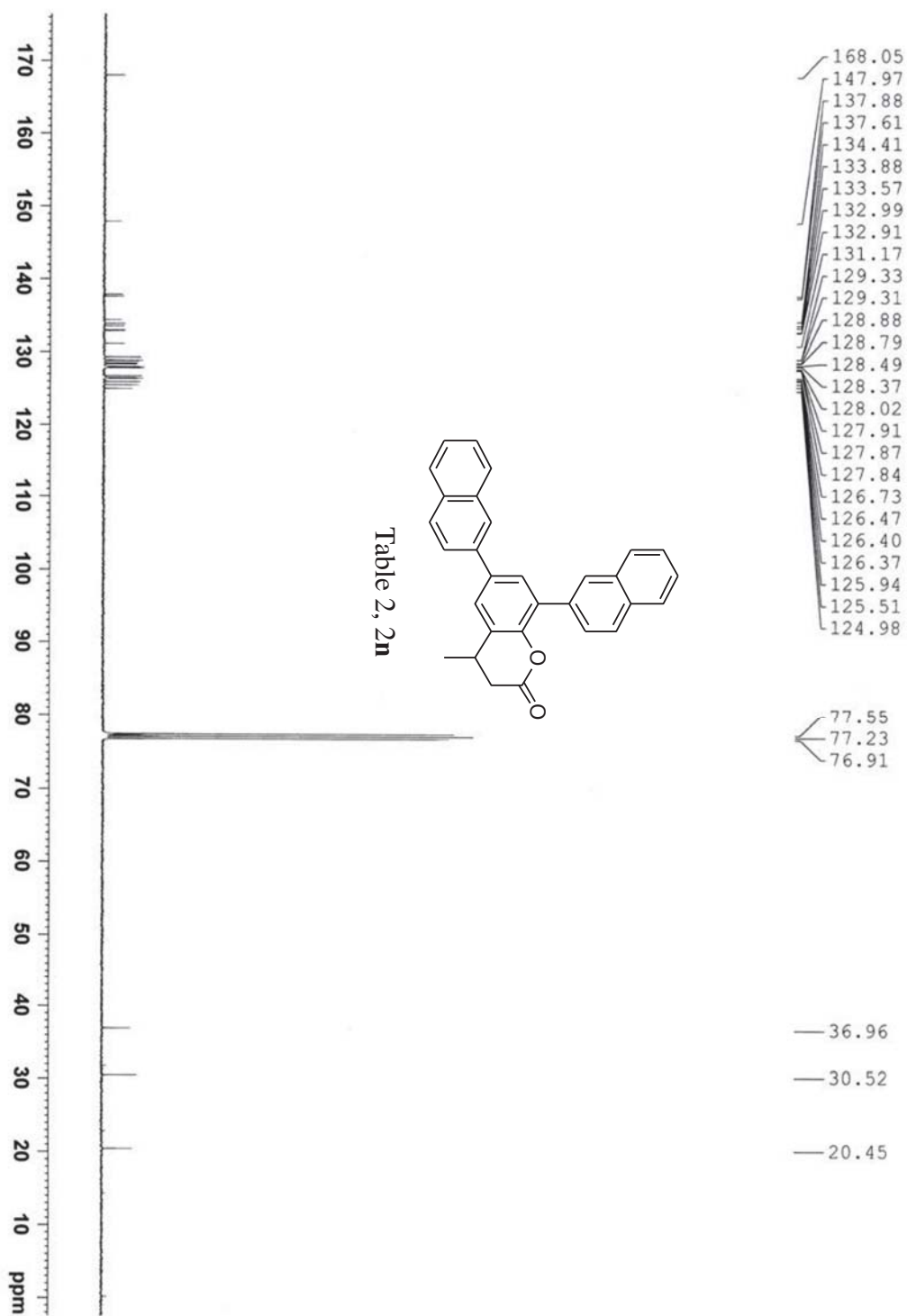
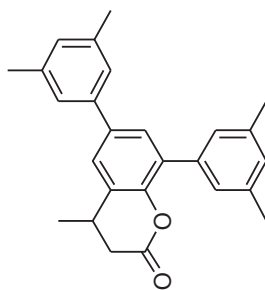




Table 2, 20



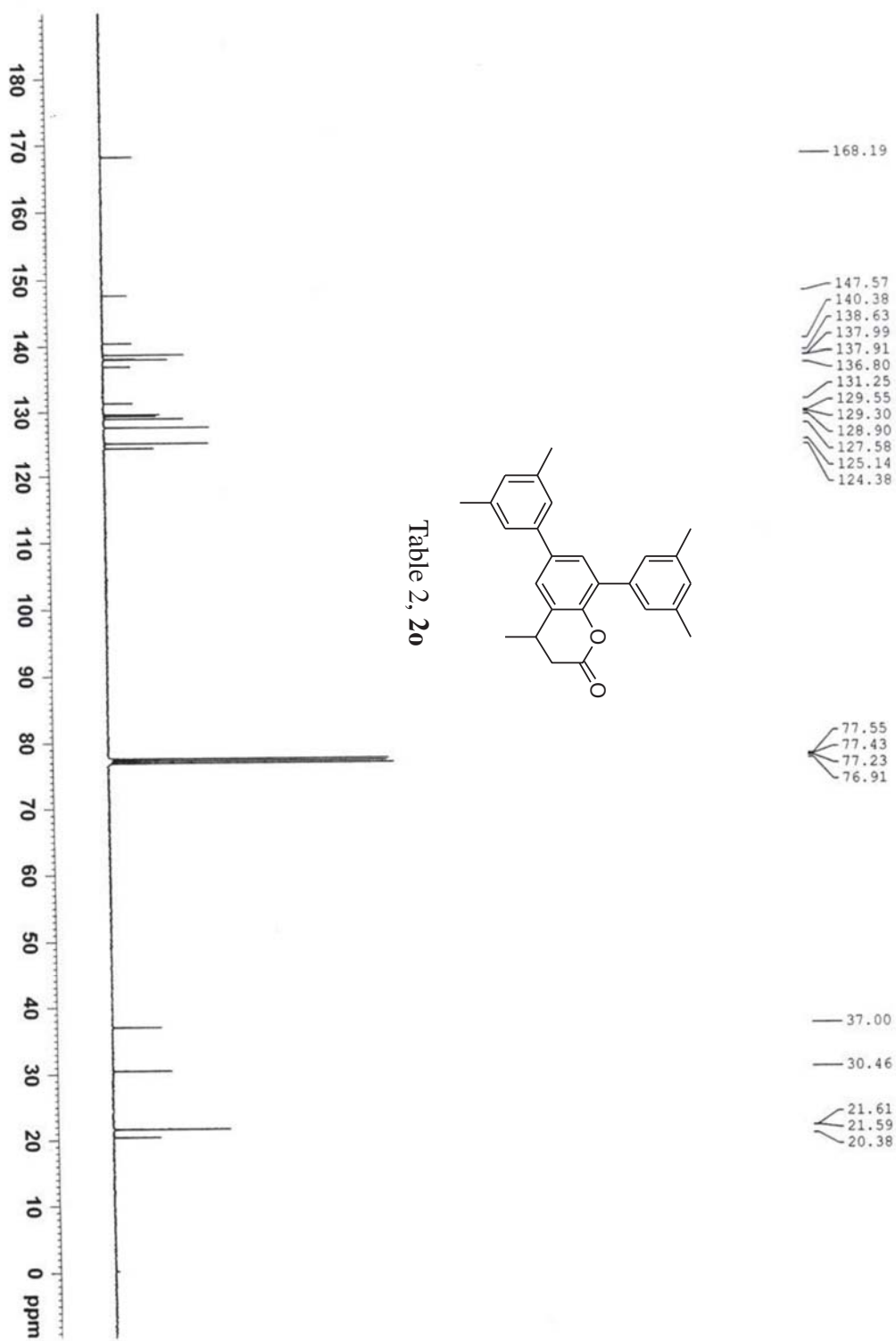
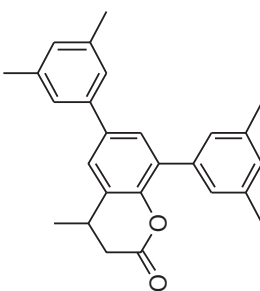


Table 2, 20



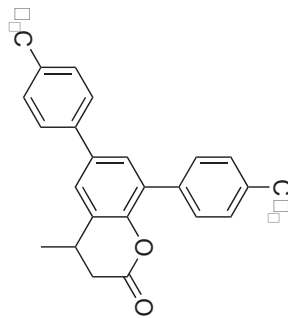
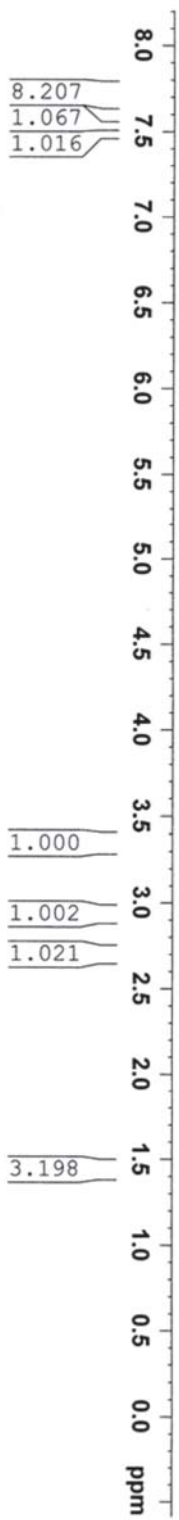
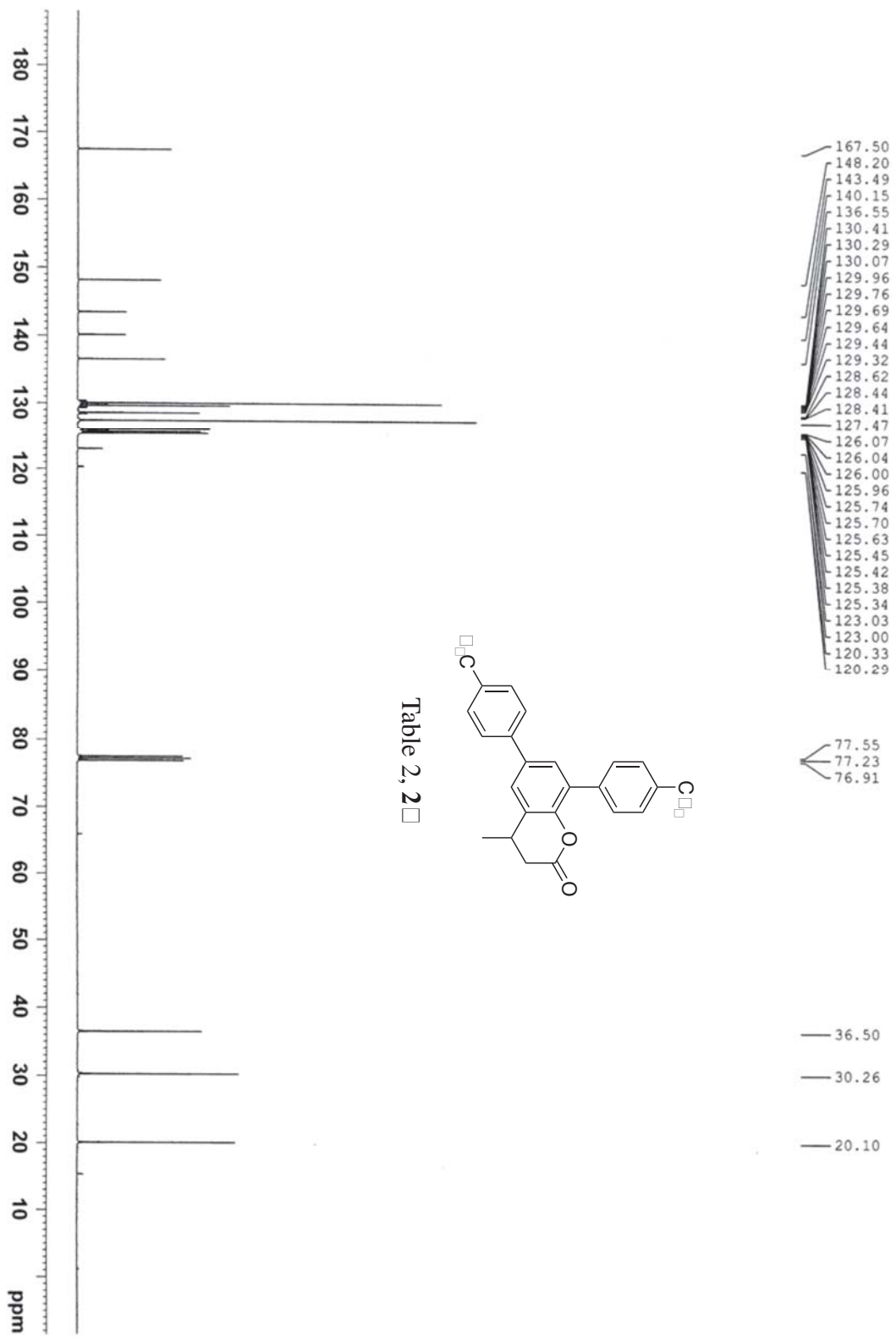
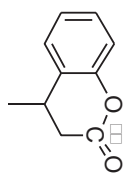


Table 2, 2







Scheme 2, 2a

