

Chiral *N*-*tert*-Butanesulfinyl α,β-Unsaturated Ketimine: A Simple and Highly Effective Olefin/Sulfinimide Hybrid Ligand for Asymmetric 1,4-Additions

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General procedure for the synthesis of chiral olefin/sulfinimide ligands 4. To a solution of (*R*)-*tert*-butanesulfinamide (0.727 g, 6.0 mmol) in THF (12.0 mL) under argon was added α,β -unsaturated ketone or aldehyde (6.6 mmol), and then Ti(OEt)₄ (2.5 mL, 12.0 mmol) was added. The resulting mixture was heated at 80 °C overnight before cooled to room temperature. Brine (12.0 mL) was then added and the mixture was stirred at room temperature for 5 min before filtered through celite. The filter cake was washed with ethyl acetate and the aqueous layer was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated under vacuum to give the crude product. The residue was then purified by flash chromatography on silica gel (hexanes/ethyl acetate = 10/1 to 5/1, v/v) to afford the corresponding products 4.

(R)-N-[(E)-1,3-diphenylprop-2-enylidene]-*tert*-butanesulfinamide (4a): 71% yield, yellow solid; $[\alpha]_D^{20} = -378.3$ (*c* 0.95, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, *J* = 16.0 Hz, 1H), 7.75-7.57 (m, 2H), 7.56-7.41 (m, 5H), 7.40-7.31 (m, 3H), 6.90 (d, *J* = 16.0 Hz, 1H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.1, 143.6, 138.5, 135.0, 130.5, 129.9, 129.0, 128.6, 128.1, 127.8, 122.2, 58.1, 22.6.

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(R)-N-[(E)-1,3-bis(*p*-tolyl)prop-2-enylidene]-*tert*-butanesulfinamide (4b): 57% yield, yellow oil; $[\alpha]_D^{20} = -390.7$ (*c* 0.89, CHCl₃); IR (film): 1538, 1088 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 13.6 Hz, 1H), 7.66-7.45 (m, 2H), 7.29-7.17 (m, 2H), 7.16-7.06 (m, 2H), 6.89 (d, *J* = 16.0 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.8, 143.9, 141.1, 140.4, 136.1, 132.6, 129.6, 129.4, 129.0, 128.1, 121.6, 58.0, 22.7, 21.5, 21.5; HRMS (EI) calcd for C₂₁H₂₅NOS (M): 339.1657; Found: 339.1661.

(R)-N-[(E)-1,3-bis(3-chlorophenyl)prop-2-enylidene]-*tert*-butanesulfinamide (4c): 89% yield, yellow oil; $[\alpha]_D^{20} = -300.7$ (*c* 1.00, CHCl₃); IR (film): 1473, 1275, 1074 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 14.4 Hz, 1H), 7.73-7.08 (m, 8H), 6.78 (d, *J* = 16.4 Hz, 1H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 142.1, 140.1, 136.8, 134.8, 134.4, 130.6, 130.0, 129.9, 129.6, 128.9, 127.8, 127.2, 126.1, 123.2, 58.8, 22.8; HRMS (EI) calcd for C₁₉H₁₉NOSCl₂ (M): 379.0564; Found: 379.0569.

(R)-N-[(E)-1-phenyl-3-(*p*-tolyl)prop-2-enylidene]-*tert*-butanesulfinamide (4d): 63% yield, yellow solid; mp 79-81 °C; $[\alpha]_D^{20} = -395.7$ (*c* 1.00, CHCl₃); IR (film): 1540, 1069 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, *J* = 15.2 Hz, 1H), 7.74-7.33 (m, 7H), 7.17 (d, *J* = 17.6 Hz, 2H), 6.88 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 144.4, 140.7, 139.0, 132.6, 130.7, 129.8, 129.4, 128.4, 128.3, 121.6, 58.3, 22.9, 21.6; Anal. Calcd for C₂₀H₂₃NOS: C, 73.81; H, 7.12; N, 4.30. Found: C, 73.88; H, 7.16; N, 4.21.

(R)-N-[(E)-3-(4-nitrophenyl)-1-phenylprop-2-enylidene]-*tert*-butanesulfinamide (4e): 83% yield, orange solid; mp 42-45 °C; $[\alpha]_D^{20} = -388.7$ (*c* 1.00, CHCl₃); IR (film): 1519, 1344, 1089 cm⁻¹; ¹H NMR

(400 MHz, CDCl₃): δ 8.29 (d, *J* = 16.0 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 4H), 7.57-7.42 (m, 3H), 6.90 (d, *J* = 16.0 Hz, 1H), 1.36 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 148.3, 141.7, 140.0, 138.4, 131.1, 129.2, 128.6, 126.7, 124.2, 59.2, 23.0; HRMS (EI) calcd for C₁₉H₂₀N₂O₃S (M): 356.1195; Found: 356.1190.

(R)-N-[(E)-3-(naphthalen-1-yl)-1-phenylprop-2-enylidene]-tert-butanesulfinamide (4f): 77% yield, yellow solid; mp 99-101 °C; [α]_D²⁰ = -332.2 (*c* 1.00, CHCl₃); IR (film): 1607, 1540, 1069 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 14.8 Hz, 1H), 7.95-7.64 (m, 7H), 7.61-7.43 (m, 6H), 1.37 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.7, 140.8, 133.9, 132.7, 131.6, 131.1, 130.5, 129.6, 129.0, 128.6, 127.0, 126.3, 125.9, 125.5, 123.2, 58.5, 23.0; Anal. Calcd for C₂₃H₂₃NOS: C, 76.42; H, 6.41; N, 3.87. Found: C, 76.52; H, 6.48; N, 3.68.

(R)-N-[(E)-3-phenylprop-2-enylidene]-tert-butanesulfinamide (4g): 98% yield, light yellow solid; [α]_D²⁰ = -333.5 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 9.2 Hz, 1H), 7.59-7.48 (m, 2H), 7.45-7.33 (m, 3H), 7.24 (d, *J* = 16.0 Hz, 1H), 7.08 (dd, *J* = 16.0, 9.2 Hz, 1H), 1.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.0, 146.5, 135.3, 130.4, 129.2, 128.1, 125.8, 57.8, 22.7.

H. K. Chang, D. Y. Jung, M. K. Kim and Y. H. Kim, *Synlett*, 2005, 304.

(R)-N-[(E)-1-methyl-3-phenylprop-2-enylidene]-tert-butanesulfinamide (4h): 85% yield, orange solid; [α]_D²⁰ = -173.6 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 16.4 Hz, 0.3H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.39-7.27 (m, 3H), 7.23 (d, *J* = 16.4 Hz, 0.7 H), 7.12 (d, *J* = 16.4 Hz, 0.3H), 6.80 (d, *J* = 16.4 Hz, 0.7H), 2.50 (s, 2.1H), 2.37 (s, 0.9H), 1.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 173.6, 140.6, 138.8, 134.7, 134.6, 129.7, 129.6, 129.4, 128.4, 127.6, 127.4, 121.7, 57.1, 56.5, 23.9, 22.1, 18.4.

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(R)-N-[(E)-1-phenylprop-2-enylidene]-tert-butanesulfinamide (4i): 53% yield, orange oil; [α]_D²⁰ = -123.2 (*c* 0.94, CHCl₃); IR (film): 1550, 1075 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.76-7.33 (m, 6H), 5.92 (d, *J* = 11.2 Hz, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 175.5, 137.9, 131.7, 131.1, 129.3, 128.9, 128.3, 58.2, 22.7; HRMS (EI) calcd for C₁₃H₁₇NOS (M): 235.1031; Found: 235.1034.

(R)-N-[(IE,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene]-tert-butanesulfinamide (4j): 67% yield, yellow solid; mp 135-138 °C; [α]_D²⁰ = -296.6 (*c* 0.90, CHCl₃); IR (film): 1559, 1067 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, *J* = 13.2 Hz, 1H), 7.65-7.45 (m, 5H), 7.45-7.32 (m, 6H), 7.32-7.07 (m, 2H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 170.8, 140.3, 135.6, 130.0, 129.1, 128.2, 124.8, 58.7, 23.0; Anal. Calcd for C₂₁H₂₃NOS: C, 74.74; H, 6.87; N, 4.15. Found: C, 74.58; H, 7.00; N, 4.10.

(R)-N-[(E)-2-benzylidene cyclohexylidene]-tert-butanesulfinamide (4k): 63% yield, yellow oil; $[\alpha]_D^{20} = +118.4$ (c 1.06, CHCl_3); IR (film): 1261, 1275, 1066 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.21 (m, 6H), 3.16-3.01 (m, 1H), 2.98-2.86 (m, 1H), 2.85-2.64 (m, 2H), 1.94-1.74 (m, 2H), 1.74-1.59 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 183.1, 138.4, 136.4, 132.9, 130.1, 128.4, 128.1, 57.0, 34.4, 29.2, 24.1, 22.6; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NOS}$: C, 70.54; H, 8.01; N, 4.84. Found: C, 70.37; H, 7.96; N, 4.63.

(R)-N-(cyclohex-2-en-ylidene)-tert-butanesulfinamide (4l): 65% yield, yellow oil; $[\alpha]_D^{20} = -331.9$ (c 0.75, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.07 (d, $J = 10.0$ Hz, 0.4H), 6.68-6.55 (m, 1H), 6.18 (d, $J = 10.0$ Hz, 0.6H), 3.09-2.93 (m, 0.6H), 2.87-2.73 (m, 0.6H), 2.58-2.51 (m, 0.8H), 2.34-2.19 (m, 2H), 1.99-1.75 (m, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 177.9, 175.7, 146.0, 144.9, 130.4, 123.1, 56.9, 56.5, 36.1, 30.9, 26.0, 25.2, 22.5, 22.3, 22.2, 21.9.

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General procedure for 4a/Rh-catalyzed asymmetric 1,4-additions (Table 2): To a dried Schlenk flask charged with $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (0.0023 g, 0.006 mmol, 1.5 mol %), and ligand **4a** (0.0045 g, 0.0144 mmol, 3.6 mol %) was added CH_3OH (0.50 mL) under argon. The resulting mixture was stirred at room temperature for 15 min before heated to 30 °C. Then $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (0.030 mmol, 0.008 g, 7.5 mol %), arylboronic acid **6** (0.60 mmol), enone **5** (0.4 mmol) and CH_3OH (1.0 mL) was added sequentially. After stirring at 30 °C for 5 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel (hexanes/ethyl ether) to afford the desired product **7**.

(S)-3-Phenylcyclohexanone (Table 2, entry 1): light yellow oil; $[\alpha]_D^{20} = -21.8$ (c 0.89, CHCl_3) (96% ee) [lit.: $[\alpha]_D^{20} = -21.0$ (c 0.96, CHCl_3) (97% ee) for S-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.29 (m, 2H), 7.27-7.19 (m, 3H), 3.08-2.94 (m, 1H), 2.66-2.31 (m, 4H), 2.20-2.04 (m, 2H), 1.93-1.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.2, 144.5, 128.9, 126.9, 126.8, 49.1, 44.9, 41.4, 33.0, 25.7.

Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

(S)-3-p-Tolylcyclohexanone (Table 2, entry 2): light yellow solid; $[\alpha]_D^{20} = -17.8$ (c 0.85, CHCl_3) (96% ee) [lit.: $[\alpha]_D^{20} = -17.0$ (c 0.95, CHCl_3) (97% ee) for S-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.15 (d, $J = 13.2$ Hz, 2H), 7.13 (d, $J = 13.2$ Hz, 2H), 3.04-2.92 (m, 1H), 2.63-2.36 (m, 4H), 2.34 (s, 1H), 2.20-2.03 (m, 2H), 1.90-1.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.2, 141.6, 136.4, 129.5, 126.6, 49.2, 44.5, 41.3, 33.1, 25.7, 21.1.

Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

(S)-3-(Biphenyl-4-yl)cyclohexanone (Table 2, entry 3): white solid; $[\alpha]_D^{20} = -8.8$ (*c* 1.00, CHCl₃) (98% ee) [lit.: $[\alpha]_D^{25} = -5.5$ (*c* 0.50, CHCl₃) (93% ee) for *S*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (t, *J* = 8.0 Hz, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.36-7.27 (m, 3H), 3.13-2.97 (m, 1H), 2.68-2.33 (m, 4H), 2.21-2.08 (m, 2H), 1.93-1.73 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 211.1, 143.6, 141.0, 139.9, 129.0, 127.6, 127.4, 127.2, 49.1, 44.6, 41.4, 33.0, 25.7.

T. Zhang and M. Shi, *Chem.-Eur. J.*, 2008, **14**, 3759.

(S)-3-(4-Fluorophenyl)cyclohexanone (Table 2, entry 4): colorless oil; $[\alpha]_D^{20} = -17.5$ (*c* 0.61, CHCl₃) (96% ee) [lit.: $[\alpha]_D^{20} = +14.3$ (*c* 1.20, CHCl₃) (98% ee) for *R*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.13 (m, 2H), 7.05-6.95 (m, 2H), 3.06-2.92 (m, 1H), 2.61-2.30 (m, 4H), 2.18-2.02 (m, 2H), 1.88-1.70 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 210.7, 161.7 (d, *J*_{C-F} = 243.4 Hz), 140.2 (d, *J*_{C-F} = 3.1 Hz), 128.1 (d, *J*_{C-F} = 7.8 Hz), 115.6 (d, *J*_{C-F} = 20.9 Hz), 49.2, 44.1, 41.2, 33.1, 25.5.

M. Pucheault, S. Darses and J. P. Genêt, *Eur. J. Org. Chem.*, 2002, 3552.

(S)-3-[4-(Trifluoromethyl)phenyl]cyclohexanone (Table 2, entry 5): light yellow solid; $[\alpha]_D^{20} = -25.7$ (*c* 0.98, CHCl₃) (96% ee) [lit.: $[\alpha]_D^{20} = -11.0$ (*c* 0.97, CHCl₃) (99% ee) for *S*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 3.12-3.02 (m, 1H), 2.64-2.31 (m, 4H), 2.19-2.03 (m, 2H), 1.93-1.69 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 210.3, 148.4, 129.2 (q, *J*_{C-F} = 32.4 Hz), 127.2, 125.8 (q, *J*_{C-F} = 3.9 Hz), 124.3 (q, *J*_{C-F} = 270.4 Hz), 123.0, 48.7, 44.7, 41.3, 32.7, 25.6.

Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

(S)-3-(4-Acetylphenyl)cyclohexanone (Table 2, entry 6): white solid; $[\alpha]_D^{20} = -7.3$ (*c* 0.74, CHCl₃) (94% ee) [lit.: $[\alpha]_D^{32} = -7.8$ (*c* 1.02, CHCl₃) (97% ee) for *S*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.11-2.98 (m, 1H), 2.60-2.32 (m, 6H), 2.58 (s, 3H), 2.19-2.03 (m, 2H), 1.92-1.78 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 210.4, 197.7, 149.8, 135.9, 129.0, 127.0, 48.5, 44.8, 41.2, 32.6, 26.7, 25.5.

C. Defieber, J.-F. Paquin, S. Serna and E. M. Carreira, *Org. Lett.*, 2004, **6**, 3873.

(S)-3-[4-(Hydroxymethyl)phenyl]cyclohexanone (Table 2, entry 7): colorless oil; $[\alpha]_D^{20} = -11.4$ (*c* 0.86, CHCl₃) (95% ee) [lit.: $[\alpha]_D^{20} = -18.8$ (*c* 0.97, CHCl₃) (92% ee) for *S*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 2H), 3.05-2.94 (m, 1H), 2.60-2.31 (m, 4H), 2.17-2.03 (m, 3H), 1.90-1.67 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 211.4, 143.9, 139.6, 127.6, 126.9, 65.1, 49.1, 44.6, 41.3, 32.9, 25.7.

Q. Li, Z. Dong and Z.-X. Yu, *Org. Lett.*, 2011, **13**, 1122.

(S)-3-(1-Naphthyl)cyclohexanone (Table 2, entry 8): white solid; $[\alpha]_D^{20} = -56.0$ (*c* 1.00, CHCl₃) (95% ee) [lit.: $[\alpha]_D = +45.8$ (*c* 1.5, CHCl₃) (98% ee) for *R*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* =

8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.58-7.44 (m, 3H), 7.40 (d, J = 7.2 Hz, 1H), 3.93-3.80 (m, 1H), 2.83-2.41 (m, 4H), 2.30-2.14 (m, 2H), 2.08-1.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.3, 140.2, 134.2, 131.1, 129.3, 127.4, 126.4, 125.8, 125.7, 122.9, 122.6, 48.7, 41.6, 39.6, 32.5, 25.8.

C. S. Cho, S. Motofusa, K. Ohe, S. Uemura and S. C. Shim, *J. Org. Chem.*, 1995, **60**, 883.

(S)-3-(2-Naphthyl)cyclohexanone (Table 2, entry 9): white solid; $[\alpha]_D^{20} = -8.1$ (c 1.08, CHCl_3) (92% ee) [lit.: $[\alpha]_D^{20} = -8.3$ (c 0.89, CHCl_3) (99% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.87-7.78 (m, 3H), 7.65 (s, 1H), 7.52-7.41 (m, 2H), 7.37 (dd, J = 8.4, 1.6 Hz, 1H), 3.25-3.12 (m, 1H), 2.74-2.59 (m, 2H), 2.55-2.36 (m, 2H), 2.24-2.12 (m, 2H), 2.04-1.76 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.0, 141.9, 133.7, 132.6, 128.5, 127.9, 127.8, 126.4, 125.8, 125.5, 124.9, 49.0, 45.0, 41.4, 32.9, 25.7.

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(S)-3-*o*-Methoxyphenylcyclohexanone (Table 2, entry 10): colorless oil; $[\alpha]_D^{20} = -37.8$ (c 0.63, CHCl_3) (92% ee) [lit.: $[\alpha]_D^{32} = -36.3$ (c 1.02, CHCl_3) (94% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.25-7.14 (m, 2H), 6.94 (dd, J = 8.0, 7.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 3.49-3.35 (m, 1H), 2.63-2.31 (m, 4H), 2.18-1.98 (m, 2H), 1.94-1.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.8, 156.9, 132.7, 127.7, 126.7, 120.9, 110.8, 55.4, 47.8, 41.6, 38.2, 31.2, 25.8.

C. Defieber, J.-F. Paquin, S. Serna and E. M. Carreira, *Org. Lett.*, 2004, **6**, 3873.

(S)-3-*o*-Tolylcyclohexanone (Table 2, entry 11): colorless oil; $[\alpha]_D^{20} = -40.8$ (c 1.16, CHCl_3) (90% ee) [lit.: $[\alpha]_D = -15.0$ (c 0.87, CHCl_3) (95% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.24-7.07 (m, 4H), 3.24-3.15 (m, 1H), 2.52-2.31 (m, 4H), 2.31 (s, 3H), 2.18-2.11 (m, 1H), 2.03-1.95 (m, 1H), 1.88-1.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.6, 142.4, 135.1, 130.7, 126.5, 126.4, 125.2, 48.4, 41.4, 40.4, 32.1, 25.8, 19.3.

Y. Ma, C. Song, C. Ma, Z. Sun, Q. Chai and M. B. Andrus, *Angew. Chem., Int. Ed.*, 2003, **42**, 5871.

(S)-3-(2-Chlorophenyl)cyclohexanone (Table 2, entry 12): colorless oil; $[\alpha]_D^{20} = -41.4$ (c 1.07, CHCl_3) (94% ee) [lit.: $[\alpha]_D^{20} = -21.5$ (c 1.3, CHCl_3) (64% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.35 (d, J = 8.0 Hz, 1H), 7.30-7.22 (m, 2H), 7.19-7.12 (m, 1H), 3.58-3.43 (m, 1H), 2.65-2.56 (m, 1H), 2.53-2.31 (m, 3H), 2.19-2.01 (m, 2H), 1.91-1.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.5, 141.4, 133.6, 130.0, 127.9, 127.4, 127.1, 47.4, 41.4, 40.7, 31.4, 25.4.

X. Hu, M. Zhuang, Z. Cao and H. Du, *Org. Lett.*, 2009, **11**, 4744.

(S)-3-*m*-Tolylcyclohexanone (Table 2, entry 13): colorless oil; $[\alpha]_D^{20} = -19.6$ (c 1.10, CHCl_3) (96% ee) [lit.: $[\alpha]_D^{20} = -15.6$ (c 0.95, CHCl_3) (82% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.17 (m, 1H), 7.07-6.95 (m, 3H), 3.01-2.88 (m, 1H), 2.62-2.29 (m, 4H), 2.34 (s, 3H), 2.18-2.00 (m, 2H), 1.90-1.68

(m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.1, 144.5, 138.3, 128.7, 127.5, 127.4, 123.7, 49.1, 44.8, 41.3, 32.9, 25.7, 21.6.

X. Hu, M. Zhuang, Z. Cao and H. Du, *Org. Lett.*, 2009, **11**, 4744.

(S)-3-(3-Fluorophenyl)cyclohexanone (Table 2, entry 14): colorless oil; $[\alpha]_D^{20} = -18.9$ (c 0.85, CHCl_3) (96% ee); ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.23 (m, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.96-6.88 (m, 2H), 3.06-2.95 (m, 1H), 2.64-2.31 (m, 4H), 2.19-2.04 (m, 2H), 1.89-1.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.5, 163.2 (d, $J_{\text{C}-\text{F}} = 244.6$ Hz), 140.1 (d, $J_{\text{C}-\text{F}} = 6.8$ Hz), 130.3 (d, $J_{\text{C}-\text{F}} = 8.3$ Hz), 113.8 (d, $J_{\text{C}-\text{F}} = 6.2$ Hz), 113.6 (d, $J_{\text{C}-\text{F}} = 6.7$ Hz), 48.9, 44.6, 41.3, 32.8, 25.6.

J.-G. Boiteau, R. Imbos, A. J. Minnaard and B. L. Feringa, *Org. Lett.*, 2003, **5**, 681.

(S)-3-(3,5-Dimethylphenyl)cyclohexanone (Table 2, entry 15): colorless oil; $[\alpha]_D^{20} = -17.5$ (c 1.10, CHCl_3) (97% ee) [lit.: $[\alpha]_D^{25} = +14.3$ (c 1.60, CHCl_3) (96% ee) for *R*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 6.88 (s, 1H), 6.84 (s, 2H), 2.99-2.86 (m, 1H), 2.61-2.33 (m, 4H), 2.31 (s, 6H), 2.20-2.01 (m, 2H), 1.91-1.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 211.3, 144.6, 138.4, 128.5, 124.6, 49.2, 44.9, 41.4, 33.1, 25.8, 21.5.

F. Lang, D. Li, J. Chen, J. Chen, L. Li, L. Cun, J. Zhu, J. Deng and J. Liao, *Adv. Synth. Catal.*, 2010, **352**, 843.

(S)-3-(2,4-Dimethoxyphenyl)cyclohexanone (Table 2, entry 16): colorless oil; $[\alpha]_D^{20} = -40.7$ (c 0.55, CHCl_3) (90% ee) [lit.: $[\alpha]_D^{20} = -25.4$ (c 0.97, CHCl_3) (87% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.06 (d, $J = 9.2$ Hz, 1H), 6.46 (d, $J = 9.6$ Hz, 1H), 6.45 (s, 1H), 3.79 (s, 6H), 3.36-3.25 (m, 1H), 2.59-2.30 (m, 4H), 2.14-1.96 (m, 2H), 1.89-1.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 212.0, 157.9, 127.1, 125.3, 104.2, 98.9, 55.5, 55.4, 48.0, 41.6, 37.8, 31.4, 25.7.

Q. Li, Z. Dong and Z.-X. Yu, *Org. Lett.*, 2011, **13**, 1122.

(S)-3-Phenylcyclopentanone (Table 2, entry 17): colorless oil; $[\alpha]_D^{20} = -86.6$ (c 0.94, CHCl_3) (91% ee) [lit.: $[\alpha]_D^{20} = -73.8$ (c 0.82, CHCl_3) (97% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.30 (m, 2H), 7.29-7.21 (m, 3H), 3.48-3.34 (m, 1H), 2.66 (dd, $J = 18.4, 8.0$ Hz, 1H), 2.52-2.39 (m, 2H), 2.39-2.23 (m, 2H), 2.06-1.92 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 218.5, 143.2, 128.9, 126.9, 46.0, 42.4, 39.0, 31.4.

Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

(S)-3-p-Tolylcyclopentanone (Table 2, entry 18): colorless oil; $[\alpha]_D^{20} = -78.6$ (c 1.03, CHCl_3) (89% ee) [lit.: $[\alpha]_D^{24} = -81.0$ (c 1.16, CHCl_3) (93% ee) for *S*-isomer]; ^1H NMR (400 MHz, CDCl_3): δ 7.16 (s, 4H), 3.46-3.31 (m, 1H), 2.66 (dd, $J = 18.4, 7.6$ Hz, 1H), 2.52-2.23 (m, 4H), 2.35 (s, 3H), 2.04-1.89 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 218.7, 140.2, 136.5, 129.5, 126.8, 46.1, 42.0, 39.0, 31.5, 21.1.

Y. Takaya, M. Ogasawara, and T. Hayashi, *Tetrahedron Lett.*, 1999, **40**, 6957.

(S)-4-Phenyltetrahydro-2H-pyran-2-one (Table 2, entry 19): colorless oil; $[\alpha]_D^{20} = -4.2$ (c 0.90, CHCl₃) (97% ee) [lit.: $[\alpha]_D^{25} = +4.0$ (c 2.70, CHCl₃) (98% ee) for *S*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.32 (m, 2H), 7.31-7.24 (m, 1H), 7.23-7.17 (m, 2H), 4.56-4.46 (m, 1H), 4.44-4.34 (m, 1H), 3.30-3.18 (m, 1H), 2.98-2.86 (m, 1H), 2.64 (dd, $J = 17.6, 10.4$ Hz, 1H), 2.24-2.13 (m, 1H), 2.11-1.97 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.9, 143.0, 129.2, 127.4, 126.7, 68.8, 37.7, 37.6, 30.5.

Y. Takaya, T. Senda, H. Kurushima, M. Ogasawara and T. Hayashi, *Tetrahedron: Asymmetry*, 1999, **10**, 4047.

(S)-4-Phenylheptan-2-one (Table 2, entry 20): colorless oil; $[\alpha]_D^{20} = +21.2$ (c 1.20, CHCl₃) (60% ee) [lit.: $[\alpha]_D^{23} = -37.0$ (c 1.01, CHCl₃) (75% ee) for *R*-isomer]; ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.23 (m, 2H), 7.21-7.14 (m, 3H), 3.16-3.09 (m, 1H), 2.73-2.67 (m, 2H), 2.00 (s, 3H), 1.62-1.51 (m, 2H), 1.21-1.11 (m, 2H), 0.84 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 208.1, 144.8, 128.6, 127.7, 126.5, 51.1, 41.3, 38.9, 30.8, 20.7, 14.1.

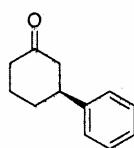
S. Oi, A. Taira, Y. Honma and Y. Inoue, *Org. Lett.*, 2003, **5**, 97.

(S)-4-Phenylnonan-2-one (Table 2, entry 21): colorless oil; $[\alpha]_D^{20} = -79.5$ (c 0.79, CHCl₃) (60% ee) [lit.: $[\alpha]_D = -17.0$ (c 1.26, CHCl₃) (92% ee)]; ¹H NMR (400 MHz, CDCl₃): δ 7.28 (t, $J = 8.0$ Hz, 2H), 7.22-7.12 (m, 3H), 3.16-3.05 (m, 1H), 2.78-2.63 (m, 2H), 2.00 (s, 3H), 1.67-1.58 (m, 2H), 1.27-1.05 (m, 6H), 0.89-0.75 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 208.2, 144.8, 128.6, 127.6, 126.5, 51.1, 41.5, 36.6, 31.9, 30.8, 27.2, 22.7, 14.2.

Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

The chromatograms for determination of the enantiomeric excess

Table 2, entry 1



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV 210 nm

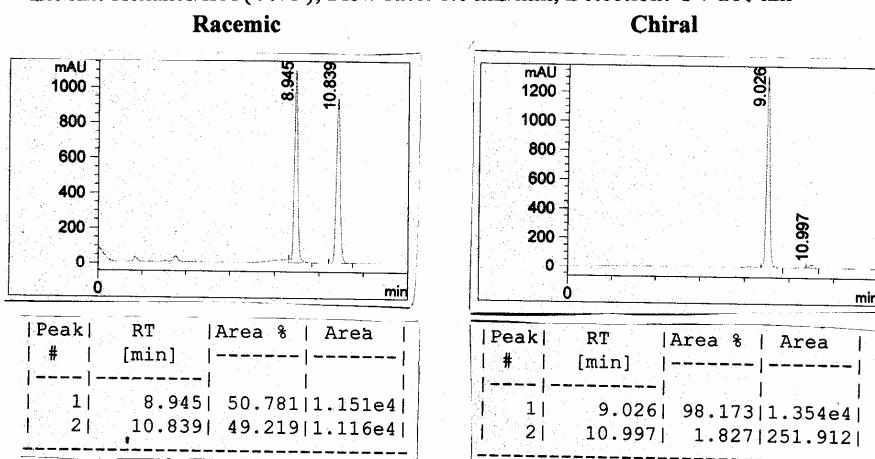
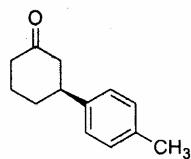


Table 2, entry 2



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (97/3); **Flow rate:** 1.0 mL/min; **Detection:** UV 214 nm

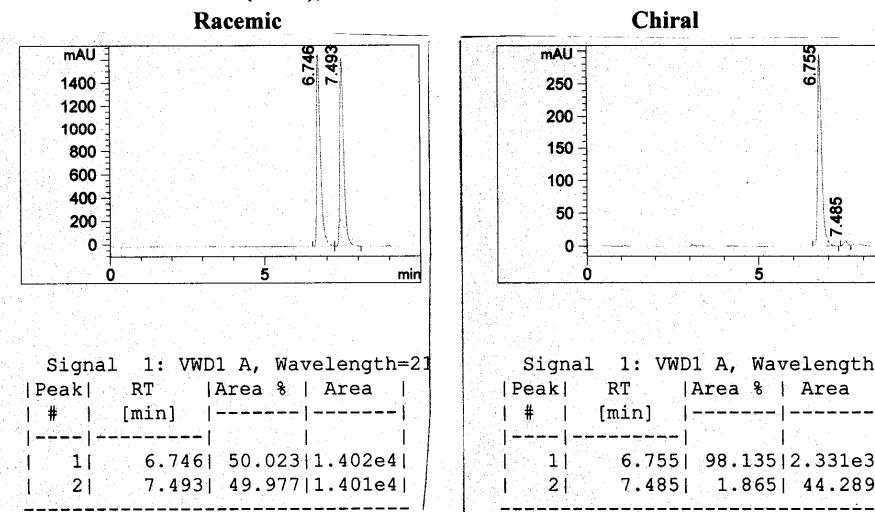
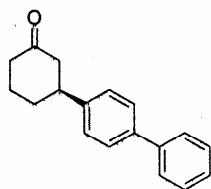


Table 2, entry 3



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV 211 nm

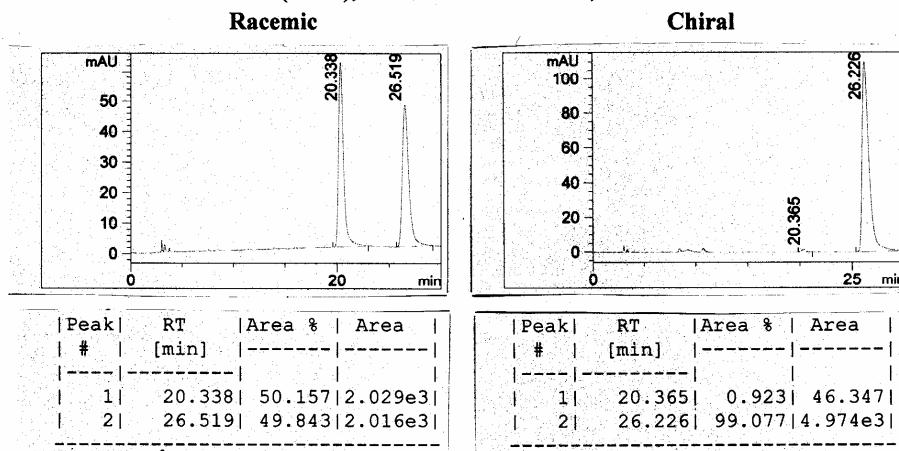
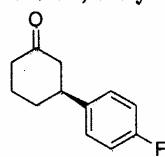


Table 2, entry 4



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (97/3); **Flow rate:** 1.0 mL/min; **Detection:** UV 214 nm

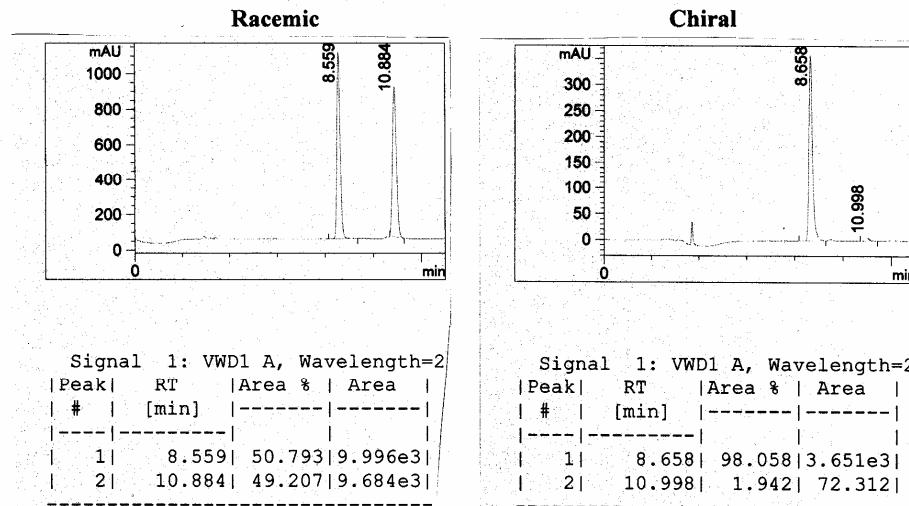
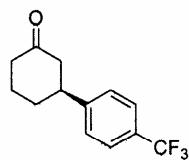


Table 2, entry 5



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV 218 nm

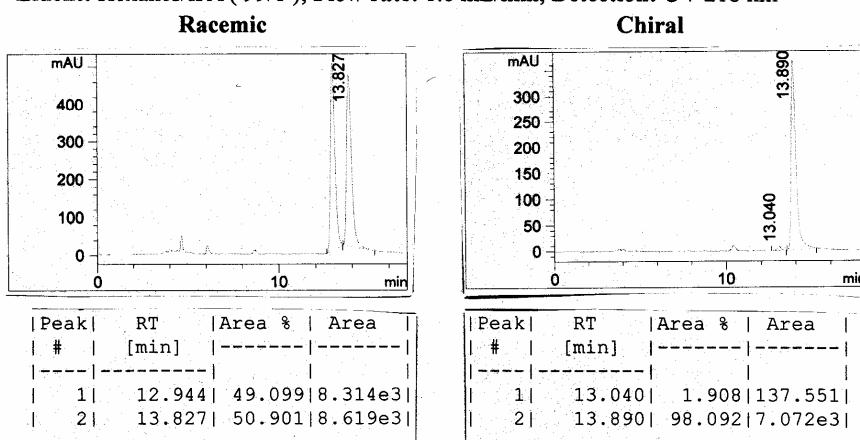
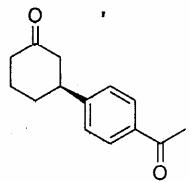


Table 2, entry 6



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (90/10); **Flow rate:** 0.8 mL/min; **Detection:** UV 210 nm

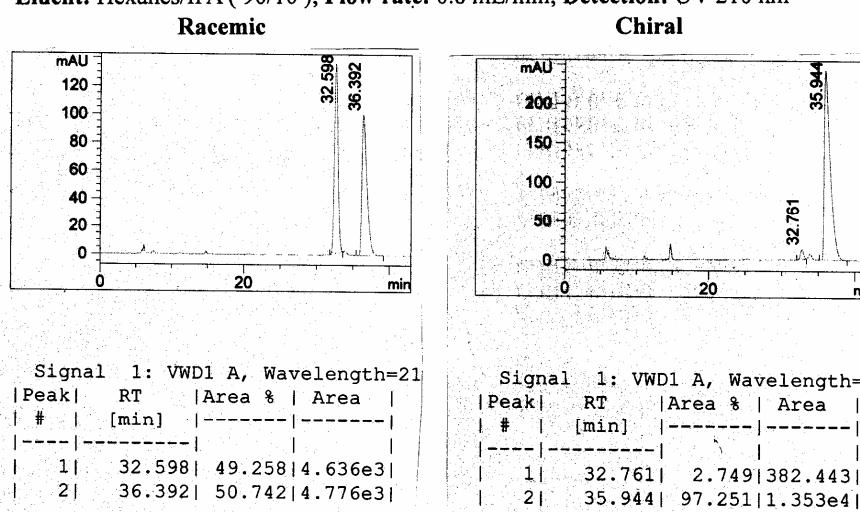
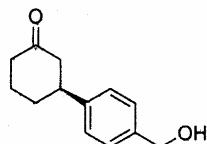
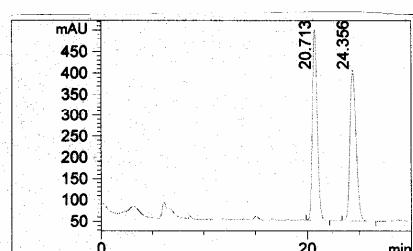


Table 2, entry 7



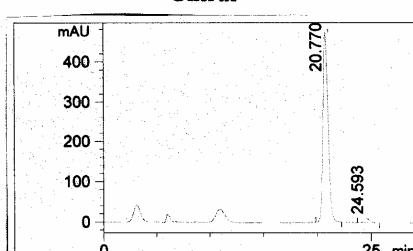
HPLC Conditions: Column: Chiraldak AS-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (60/40); **Flow rate:** 0.5 mL/min; **Detection:** UV 210 nm

Racemic



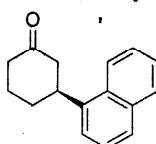
Peak	RT [min]	Area %	Area
1	20.713	50.005	1.443e4
2	24.356	49.995	1.443e4

Chiral



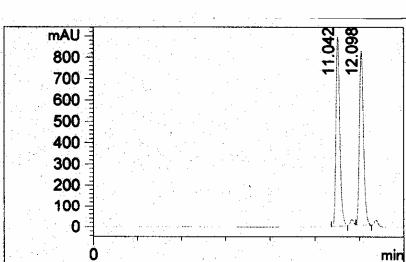
Peak	RT [min]	Area %	Area
1	20.770	97.703	1.555e4
2	24.593	2.297	365.480

Table 2, entry 8



HPLC Conditions: Column: Chiraldak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (95/5); **Flow rate:** 0.7 mL/min; **Detection:** UV 222 nm

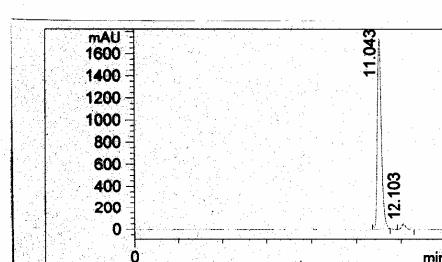
Racemic



Signal 1: VWD1 A, Wavelength=222 nm

Peak	RT [min]	Area %	Area
1	11.042	50.293	1.070e4
2	12.098	49.707	1.058e4

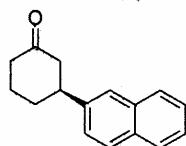
Chiral



Signal 1: VWD1 A, Wavelength=222 nm

Peak	RT [min]	Area %	Area
1	11.043	97.198	2.159e4
2	12.103	2.802	622.485

Table 2, entry 9



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (85/15); **Flow rate:** 0.5 mL/min; **Detection:** UV 221 nm

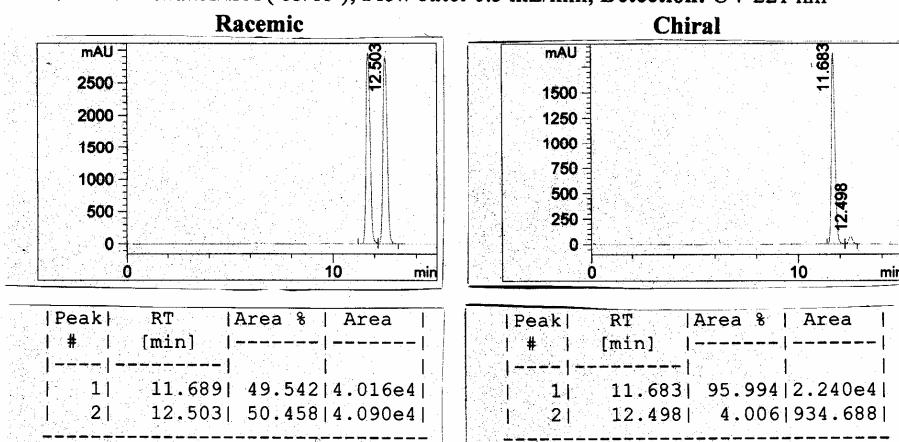
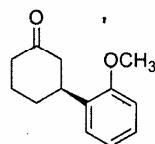


Table 2, entry 10



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); **Flow rate:** 0.7 mL/min; **Detection:** UV 217 nm

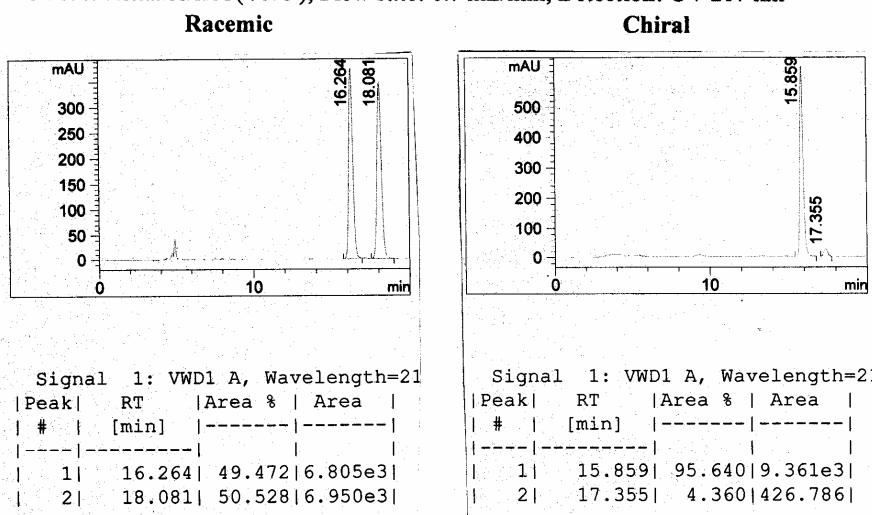
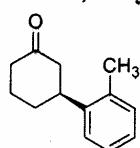
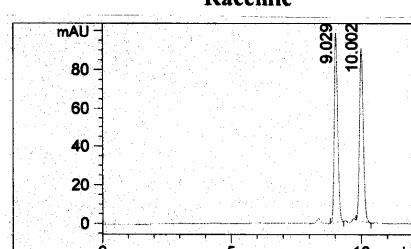


Table 2, entry 11



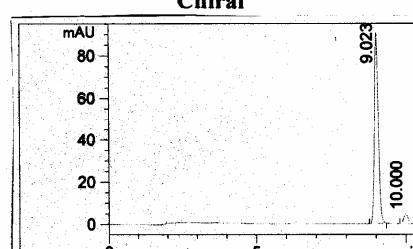
HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (85/15); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

Racemic



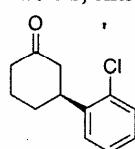
Peak	RT	Area %	Area
#	[min]	-----	-----
1	9.029	49.693	885.172
2	10.002	50.307	896.126

Chiral



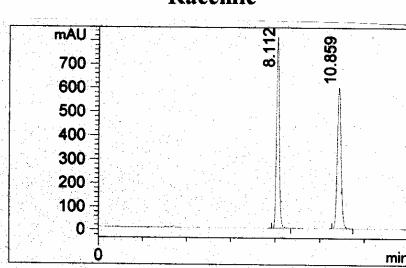
Peak	RT	Area %	Area
#	[min]	-----	-----
1	9.023	94.381	812.544
2	10.000	5.619	48.376

Table 2, entry 12



HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (97/3); **Flow rate:** 1.0 mL/min; **Detection:** UV 214 nm

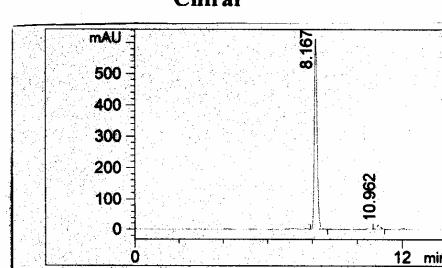
Racemic



Signal 1: VWD1 A, Wavelength=214 nm

Peak	RT	Area %	Area
#	[min]	-----	-----
1	8.112	49.970	1.031e3
2	10.859	50.030	1.040e3

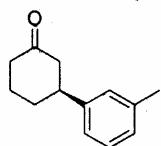
Chiral



Signal 1: VWD1 A, Wavelength=214 nm

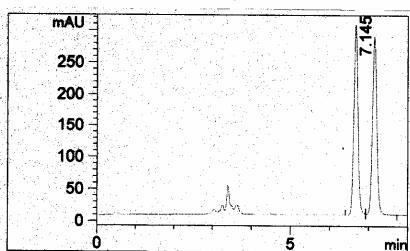
Peak	RT	Area %	Area
#	[min]	-----	-----
1	8.167	97.171	5.341e3
2	10.962	2.829	155.495

Table 2, entry 13

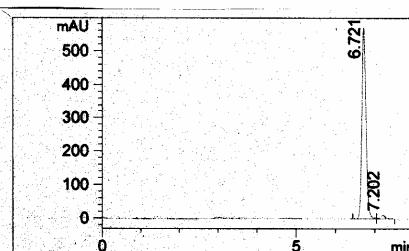


HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (97/3); **Flow rate:** 1.0 mL/min; **Detection:** UV 212 nm

Racemic



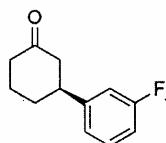
Chiral



Signal 1: VWD1 A, Wavelength=21			
Peak	RT [min]	Area %	Area
1	6.666	49.668	2.182e3
2	7.145	50.332	2.212e3

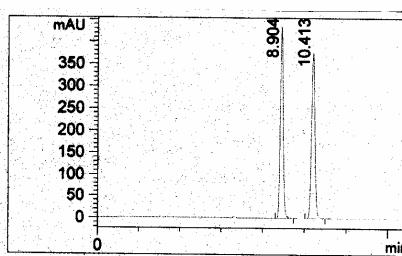
Signal 1: VWD1 A, Wavelength=21			
Peak	RT [min]	Area %	Area
1	6.721	97.964	4.163e3
2	7.202	2.036	86.533

Table 2, entry 14

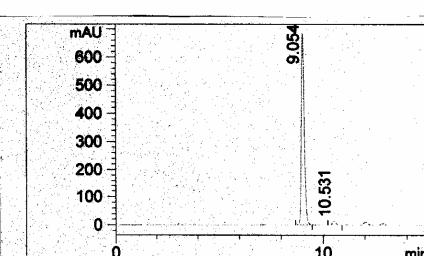


HPLC Conditions: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (97/3); **Flow rate:** 1.0 mL/min; **Detection:** UV 214 nm

Racemic



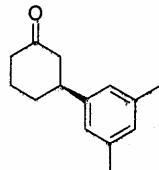
Chiral



Signal 1: VWD1 A, Wavelength=21			
Peak	RT [min]	Area %	Area
1	8.904	49.860	4.258e3
2	10.413	50.140	4.282e3

Signal 1: VWD1 A, Wavelength=21			
Peak	RT [min]	Area %	Area
1	9.054	97.873	6.710e3
2	10.531	2.127	145.841

Table 2, entry 15



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV 208 nm

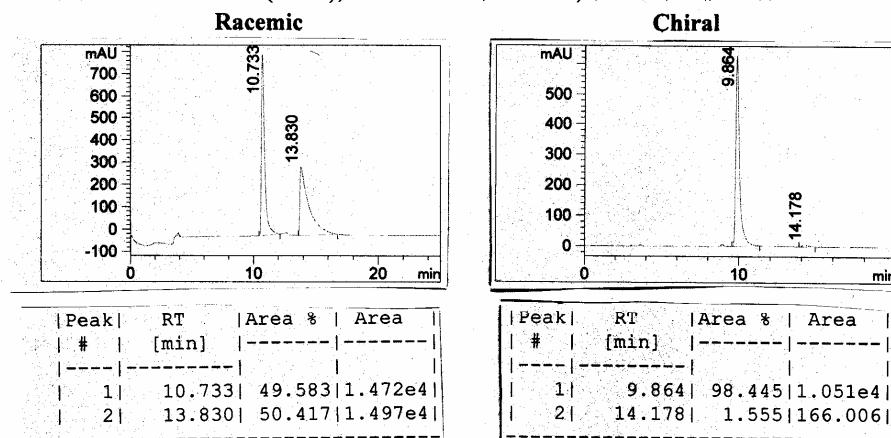
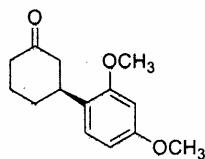


Table 2, entry 16



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (95/5); **Flow rate:** 1.0 mL/min; **Detection:** UV 228 nm

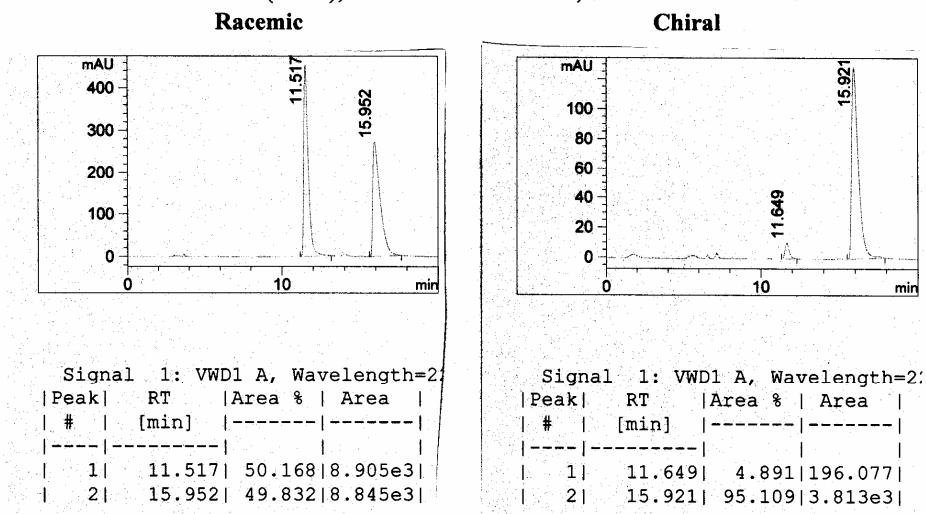
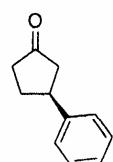
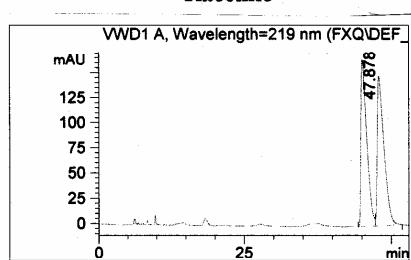


Table 2, entry 17



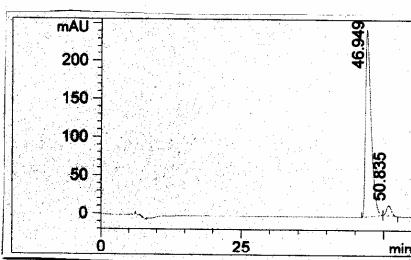
HPLC Conditions: Column: Chiralcel OB-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); **Flow rate:** 0.5 mL/min; **Detection:** UV 219 nm

Racemic



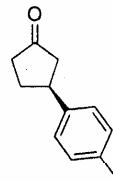
Peak	RT [min]	Area %	Area
1	45.057	49.343	1.150e4
2	47.878	50.657	1.181e4

Chiral



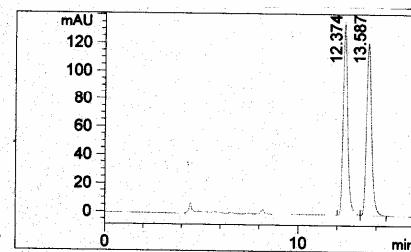
Peak	RT [min]	Area %	Area
1	46.949	95.282	1.652e4
2	50.835	4.718	818.266

Table 2, entry 18



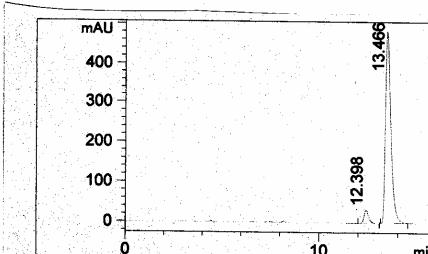
HPLC Conditions: Column: Chiralcel OB-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (90/10); **Flow rate:** 0.7 mL/min; **Detection:** UV 219 nm

Racemic



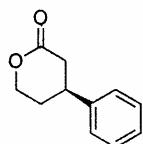
Peak	RT [min]	Area %	Area
1	12.374	49.730	2.191e3
2	13.587	50.270	2.215e3

Chiral



Peak	RT [min]	Area %	Area
1	12.398	5.400	521.603
2	13.466	94.600	9.138e3

Table 2, entry 19



HPLC Conditions: Column: Chiralpak AS-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (60/40); **Flow rate:** 0.6 mL/min; **Detection:** UV 214 nm

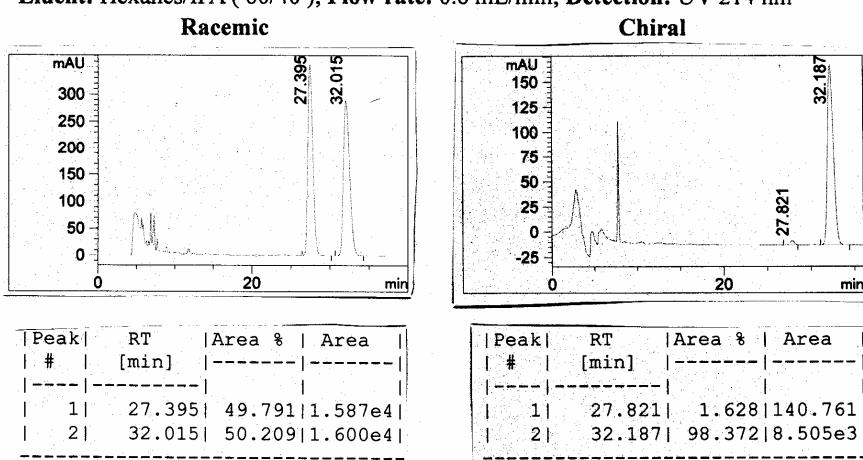
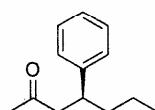


Table 2, entry 20



HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99.5/0.5); **Flow rate:** 0.5 mL/min; **Detection:** UV 216 nm

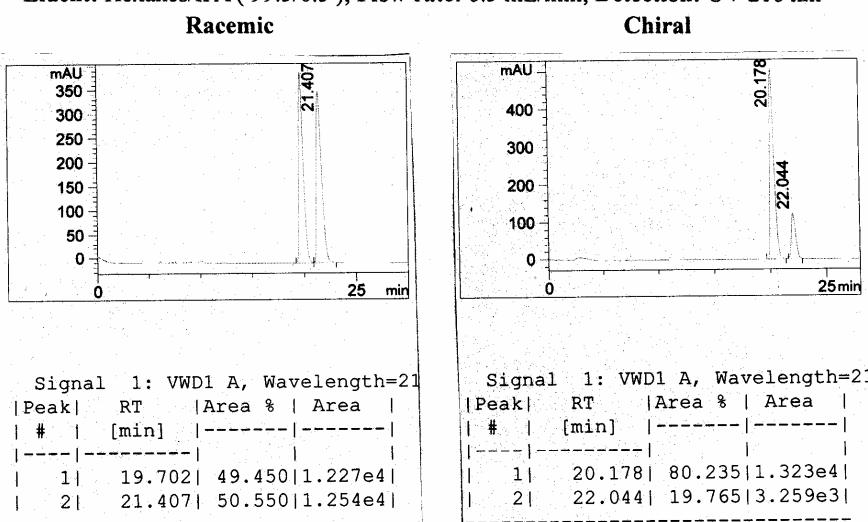
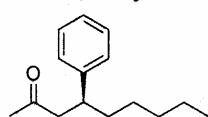
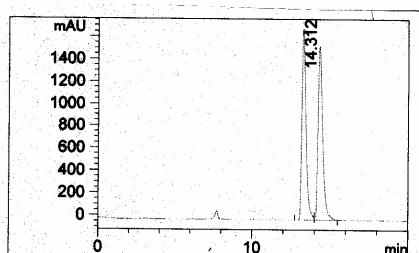


Table 2, entry 21

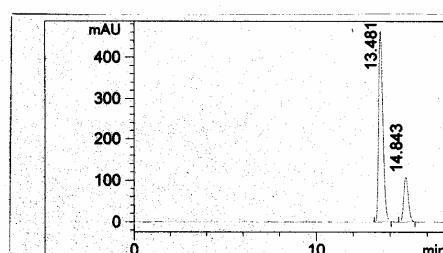


HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.,
Eluent: Hexanes/IPA (99/1); Flow rate: 0.5 mL/min; Detection: UV 211 nm

Racemic



Chiral

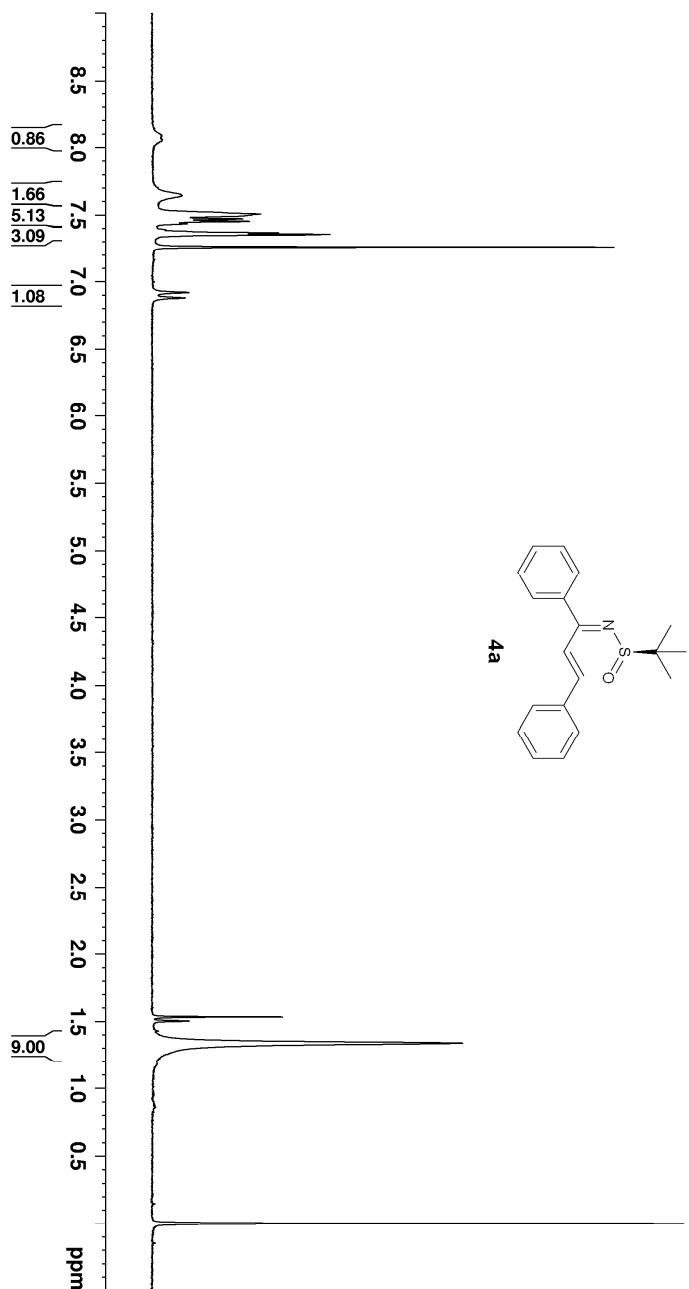


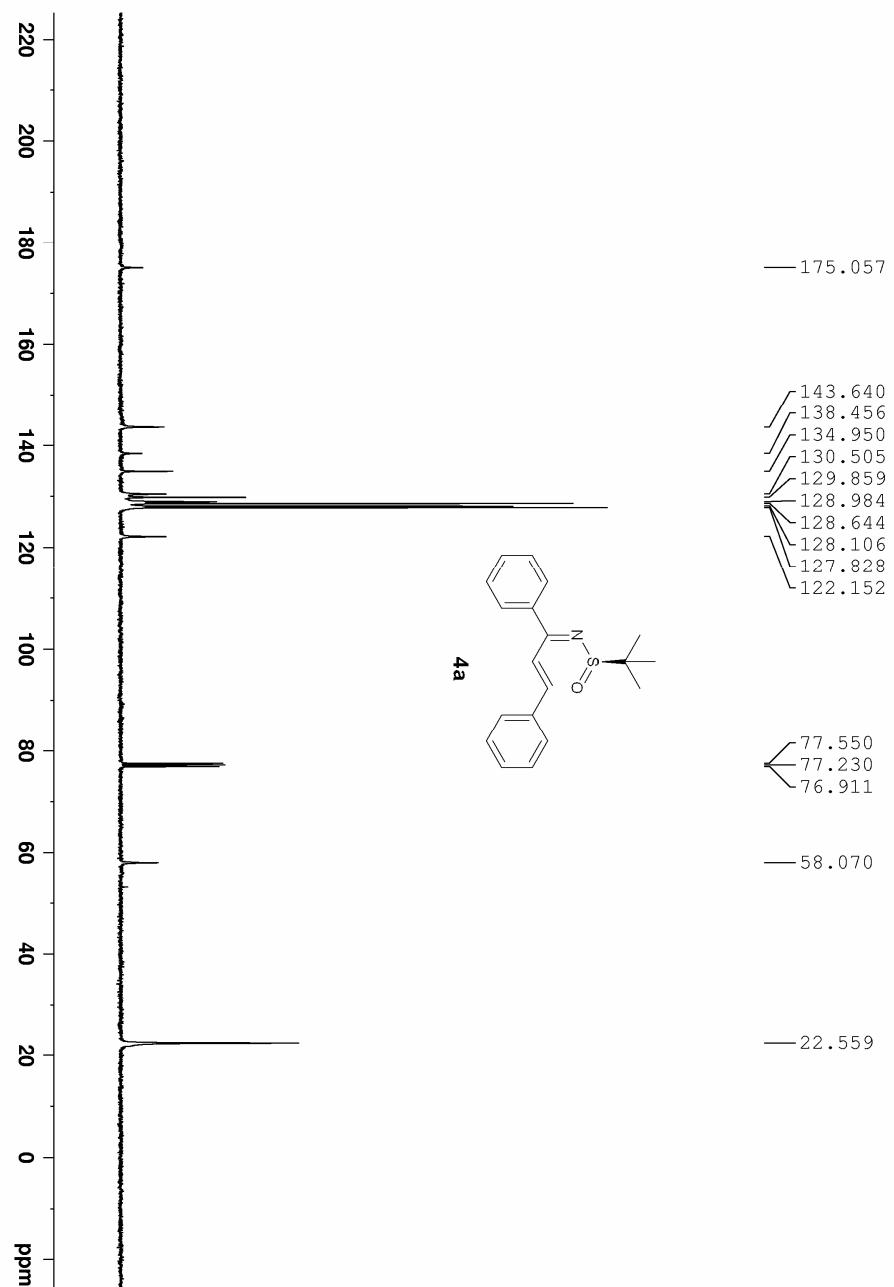
Signal 1: VWD1 A, Wavelength=21

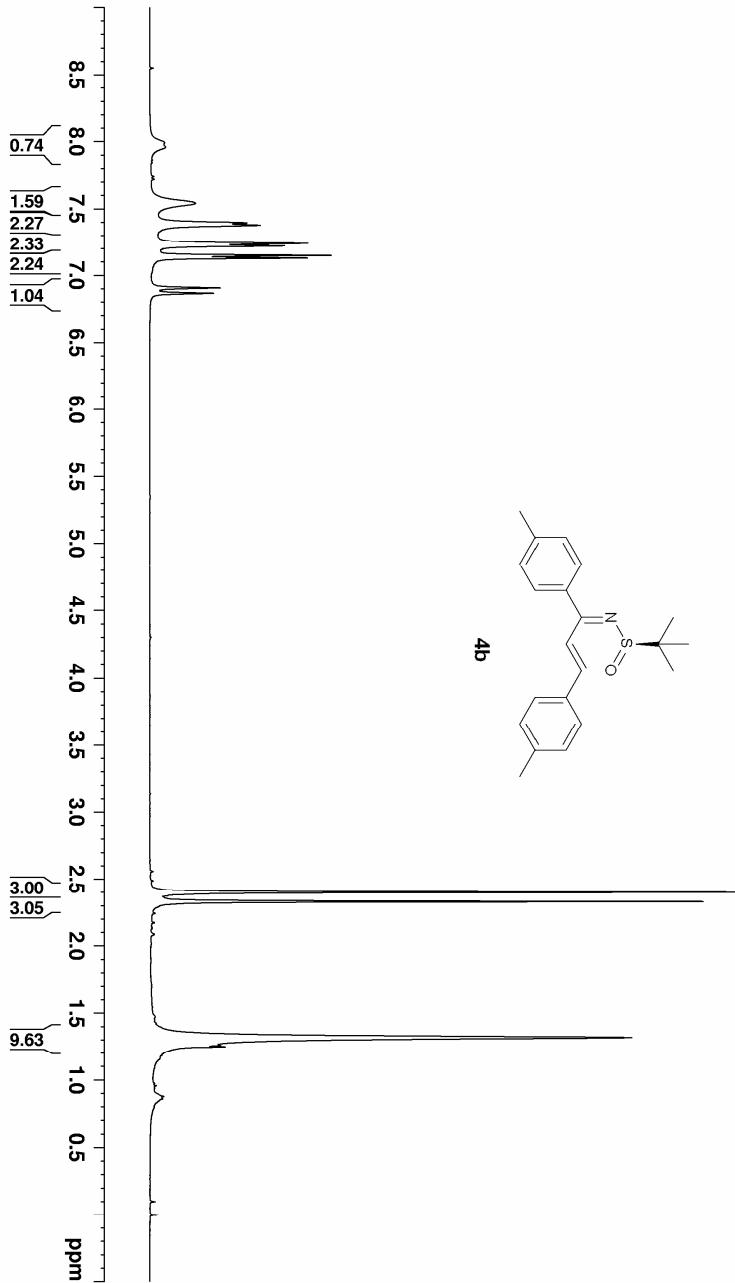
Peak	RT [min]	Area %	Area
1	13.267	49.507	3.131e4
2	14.312	50.493	3.193e4

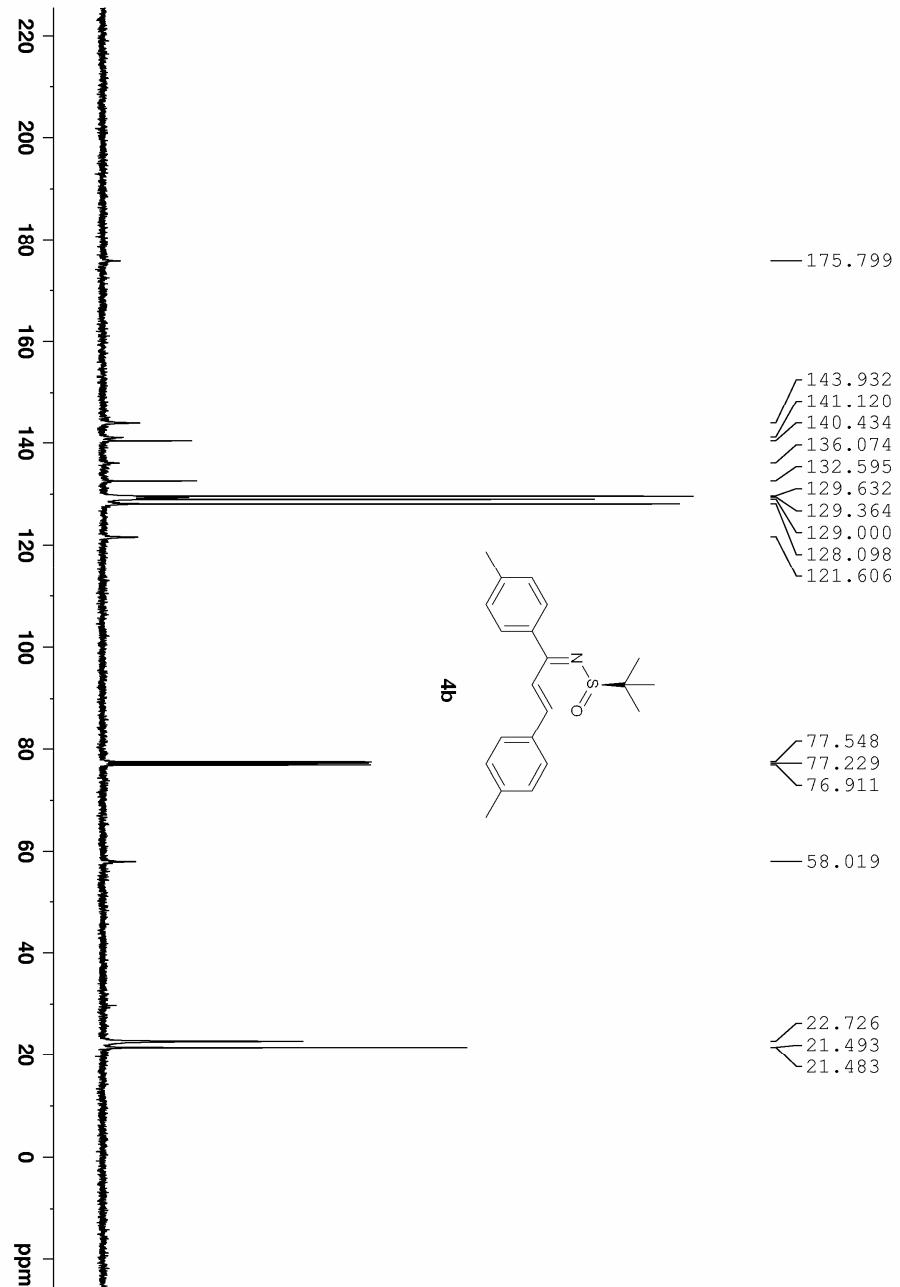
Signal 1: VWD1 A, Wavelength=21

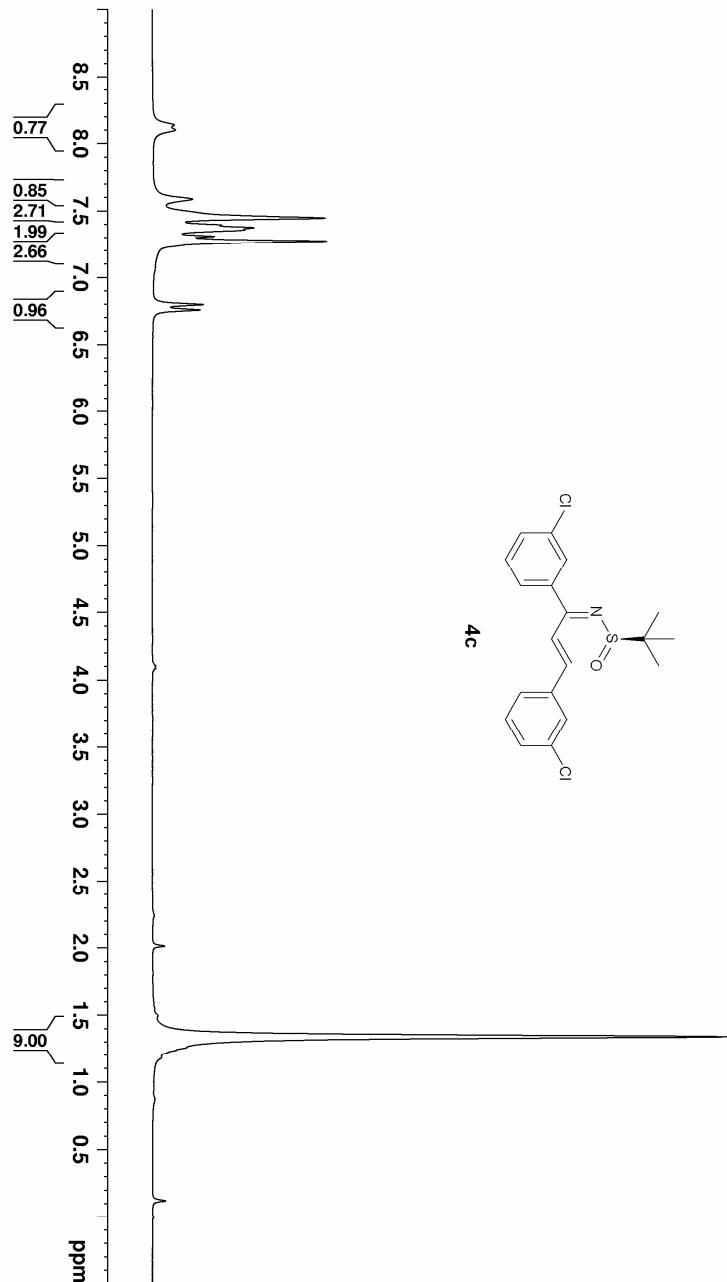
Peak	RT [min]	Area %	Area
1	13.481	79.998	7.320e3
2	14.843	20.002	1.830e3

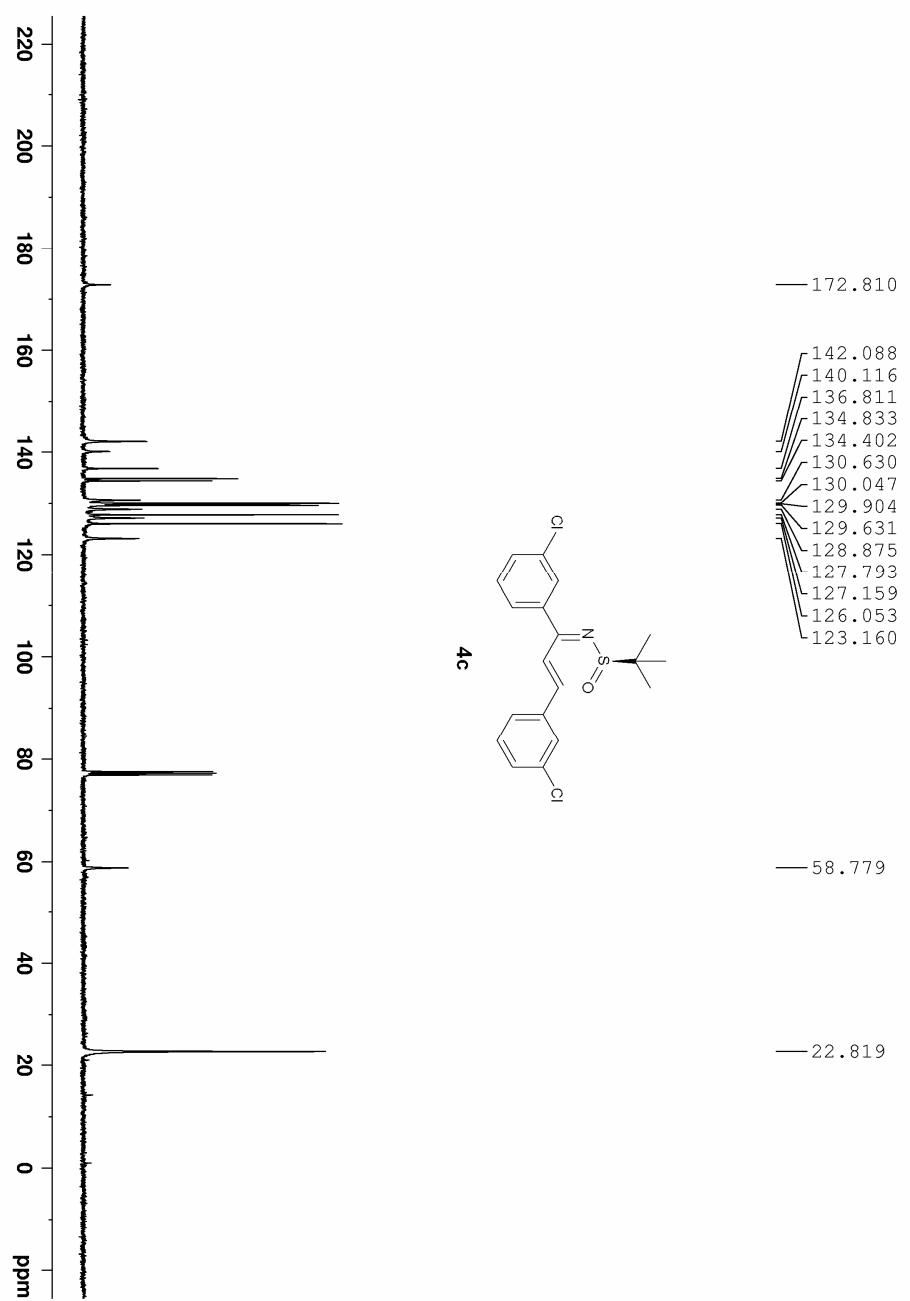


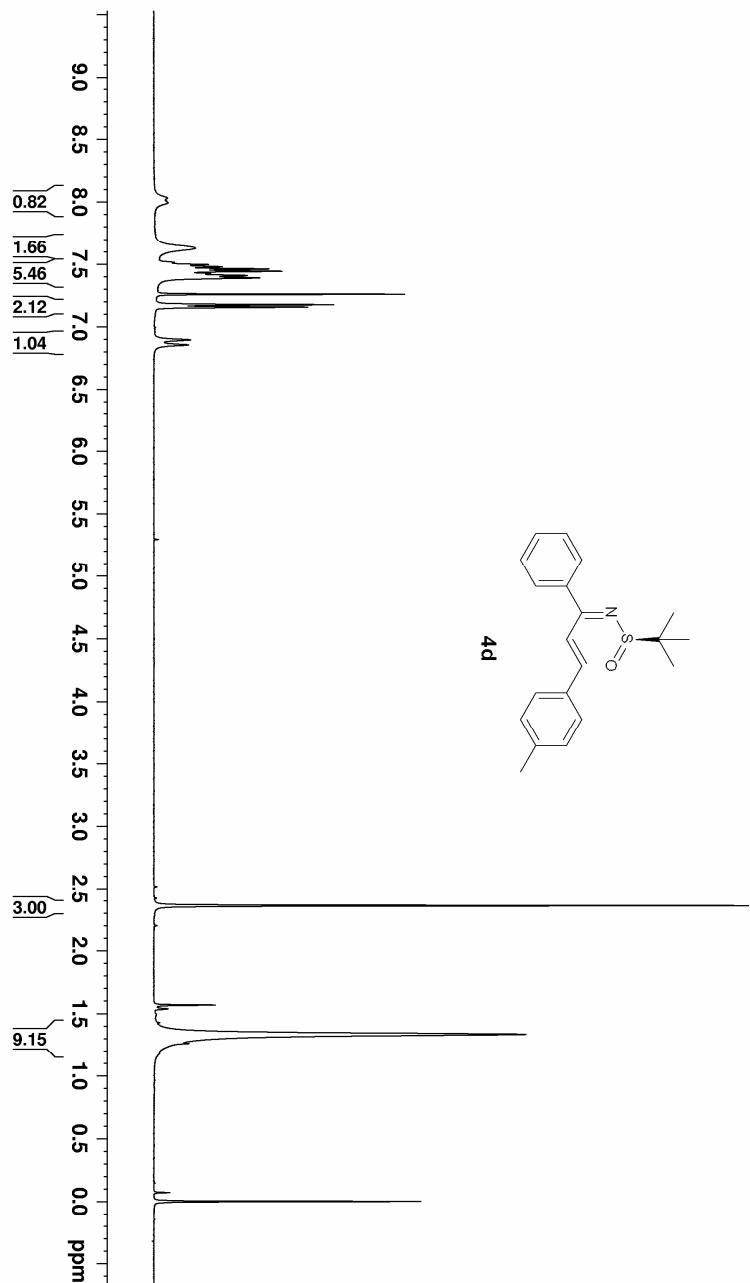


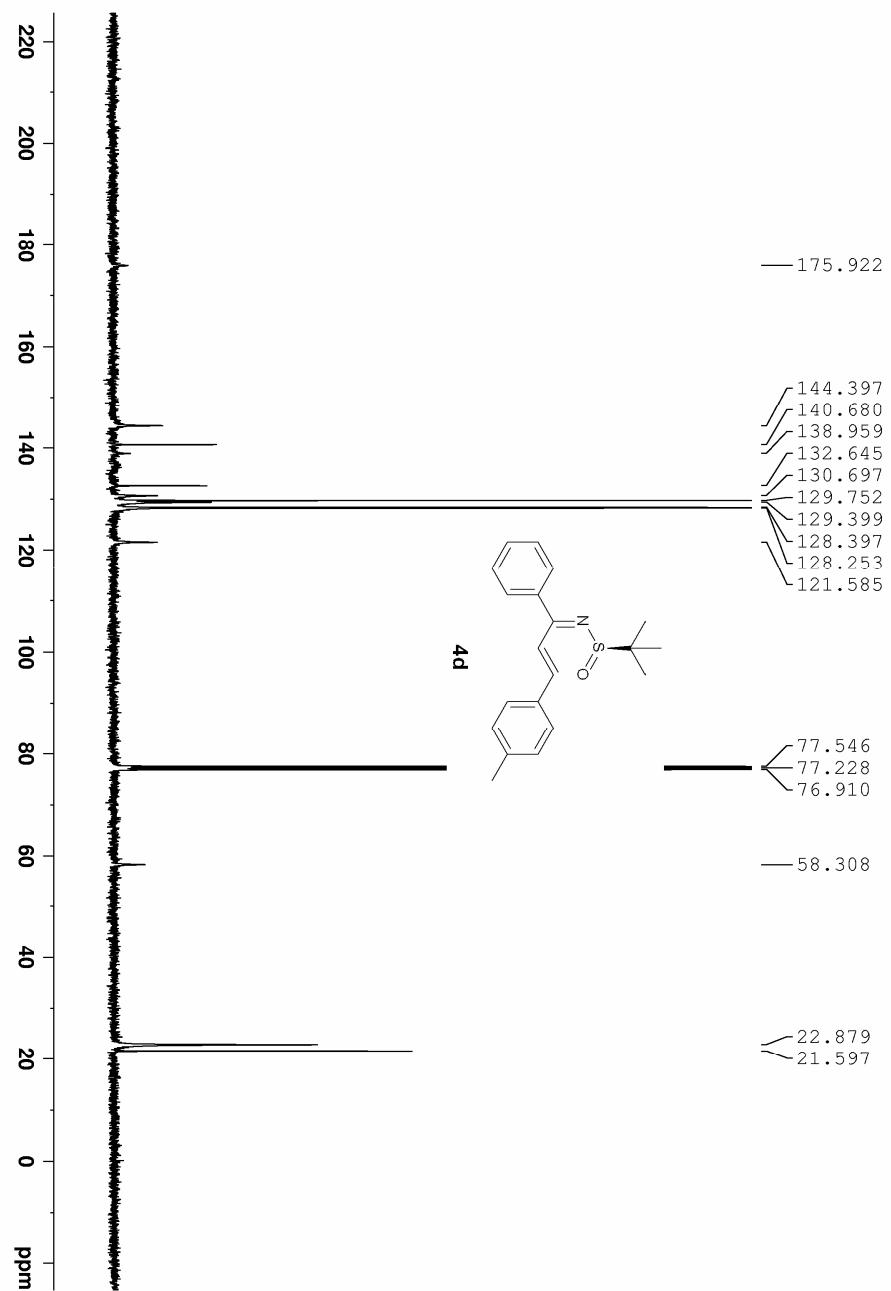


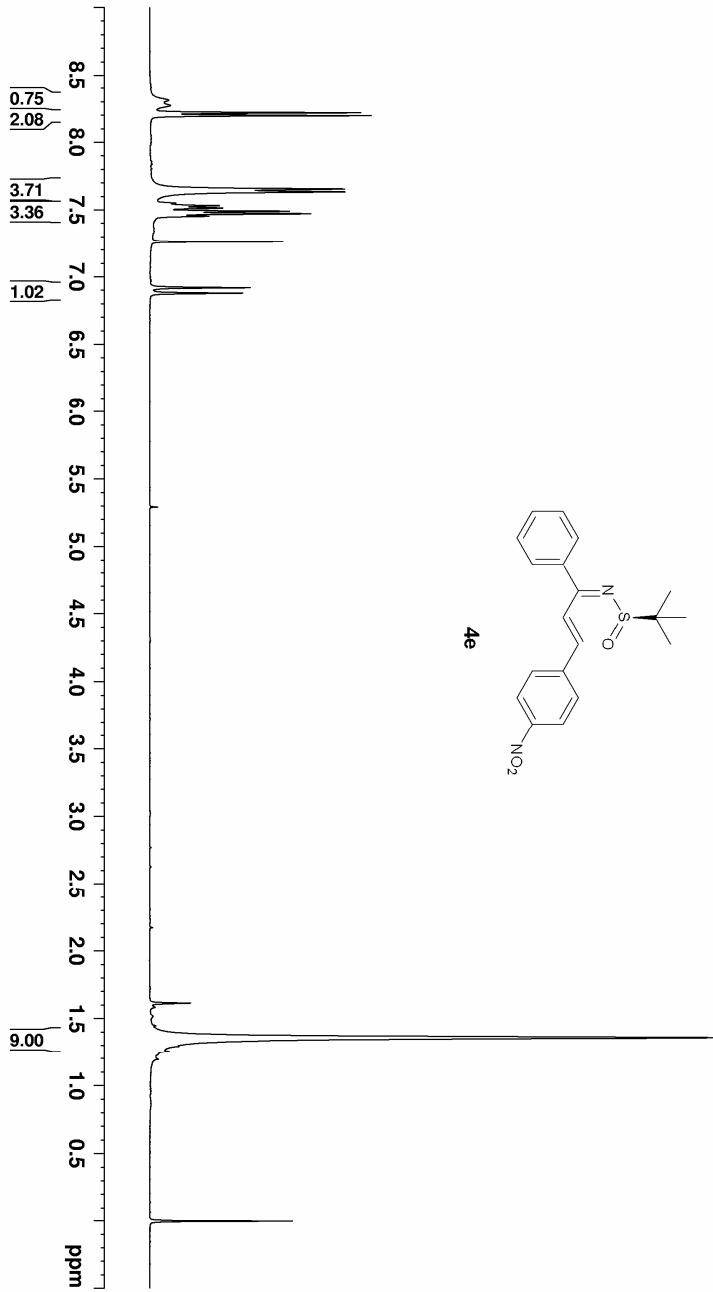


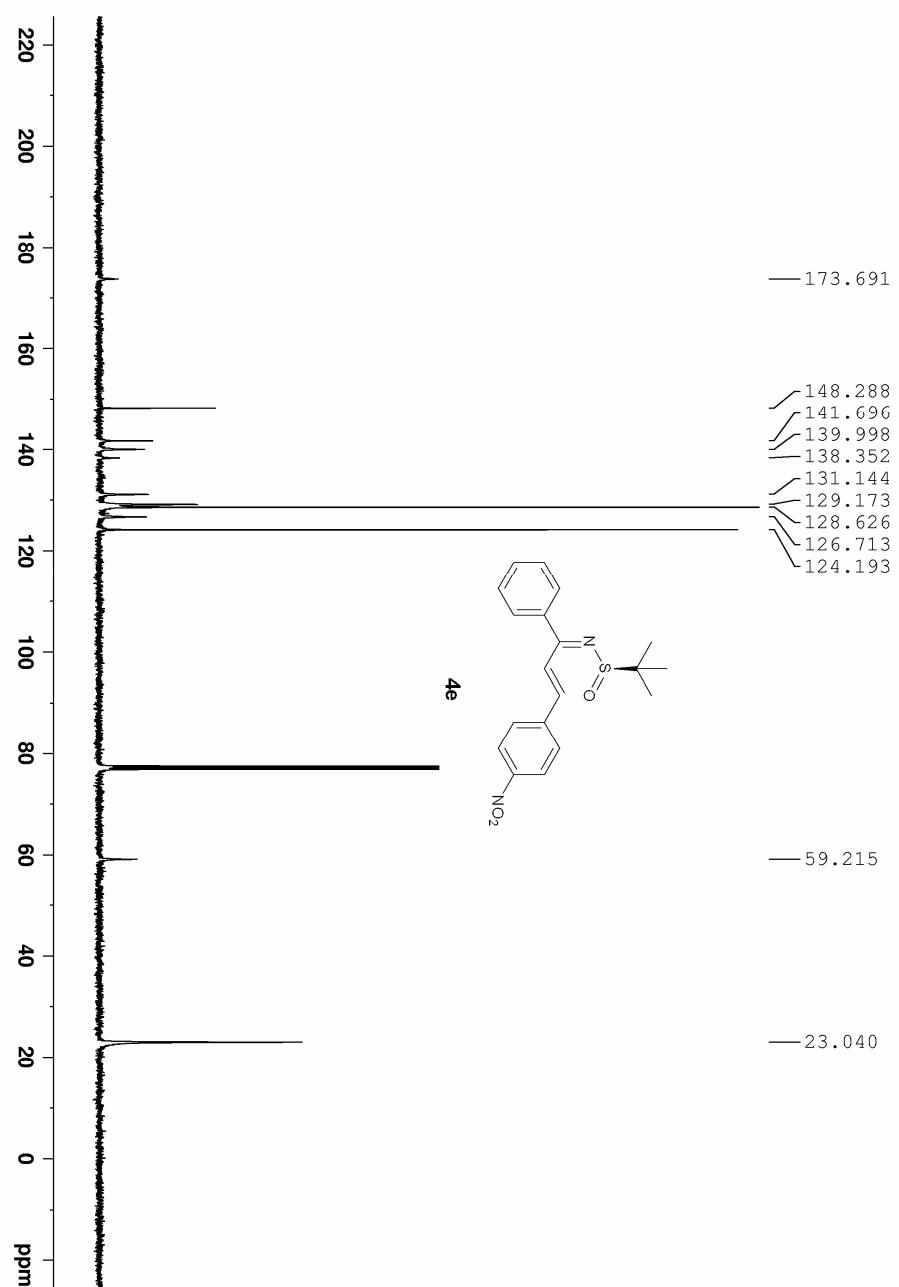


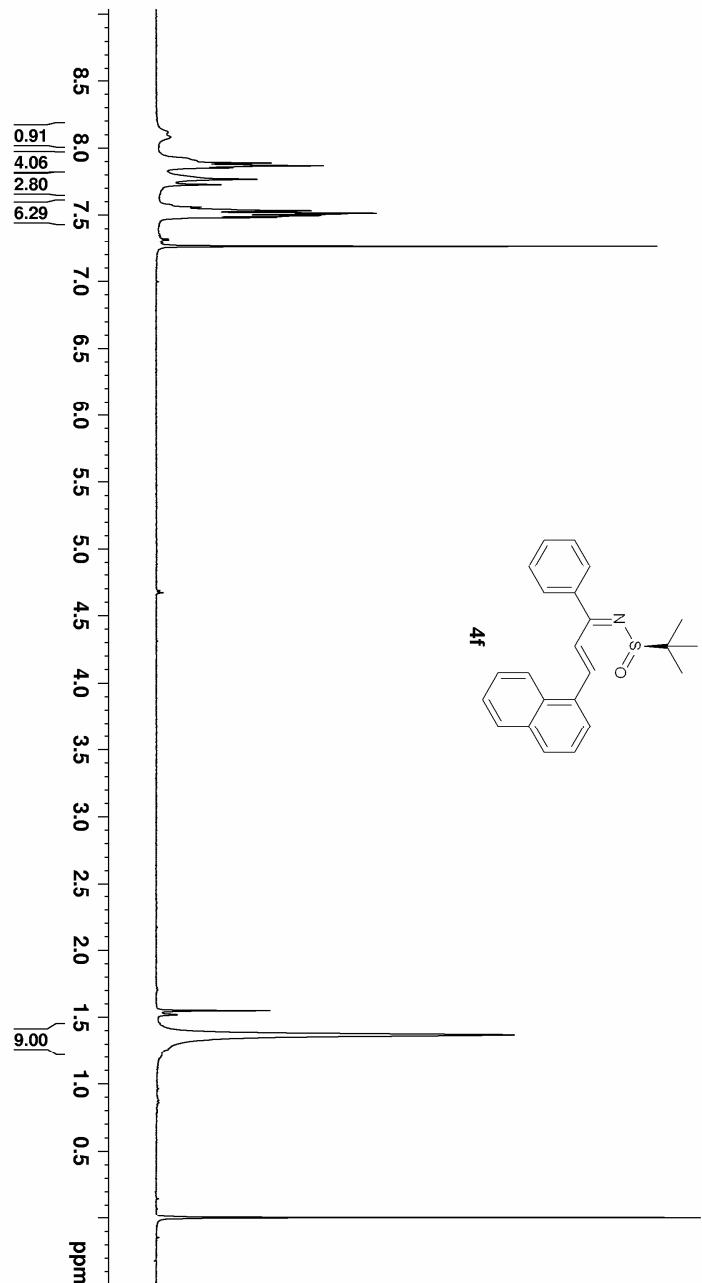


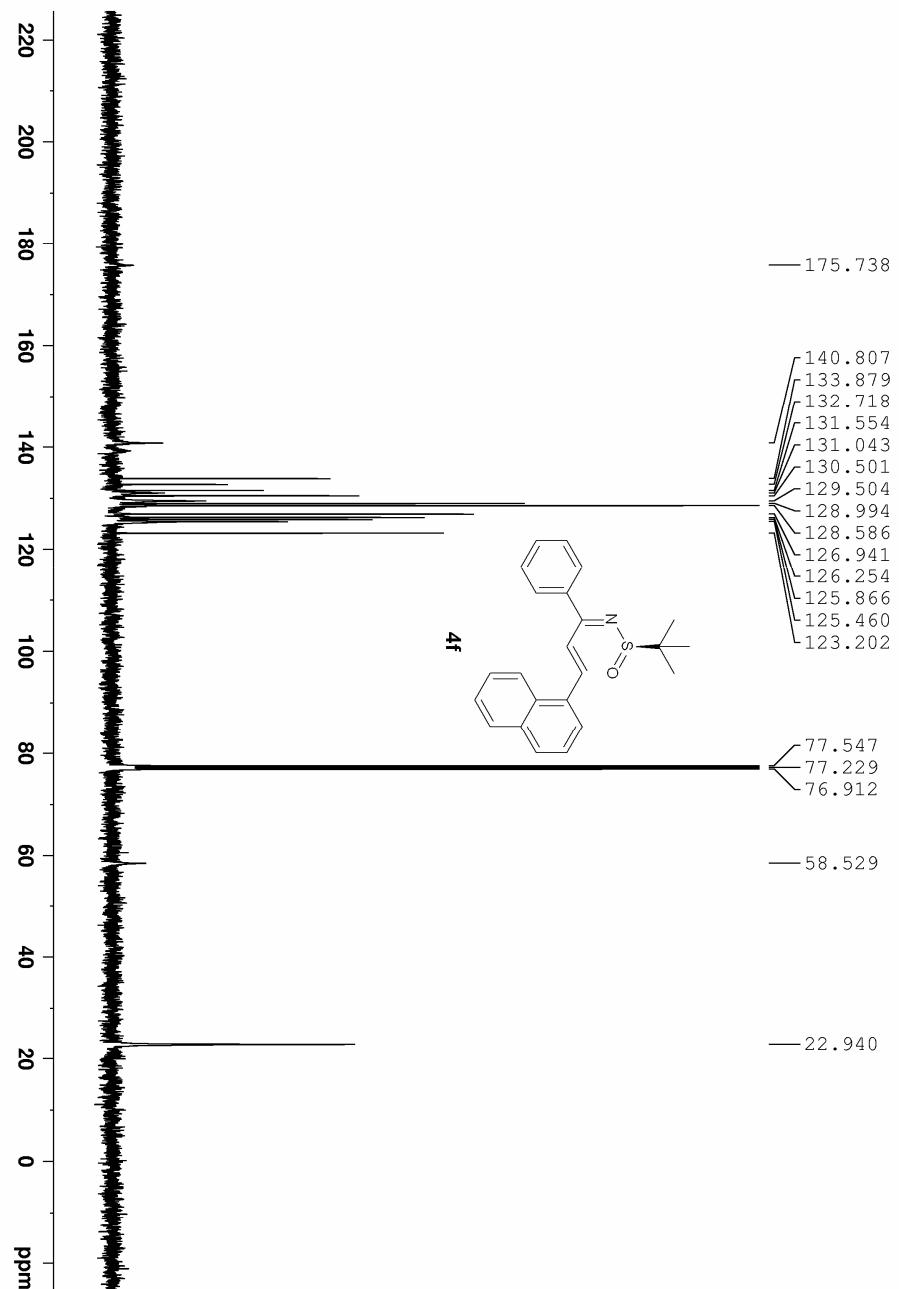


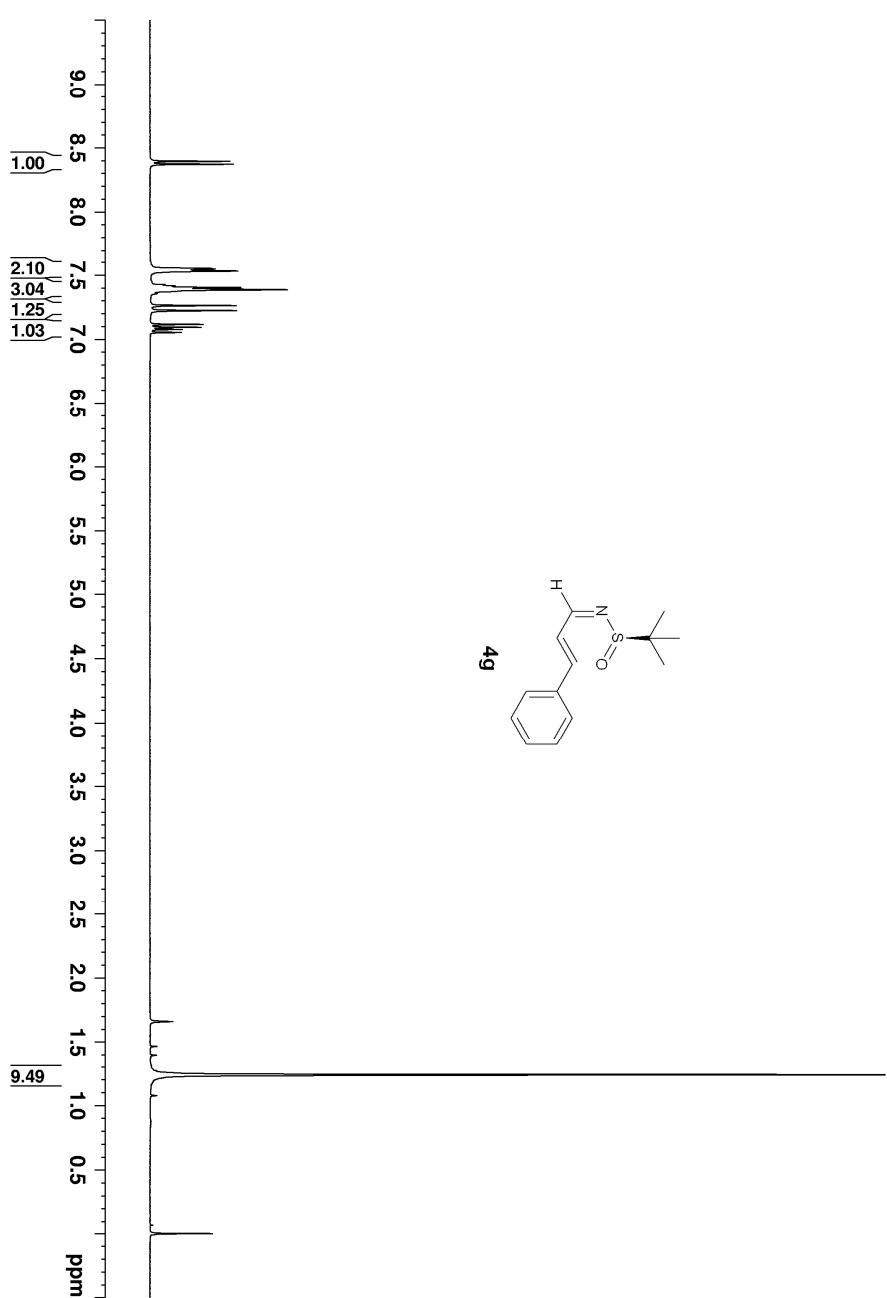


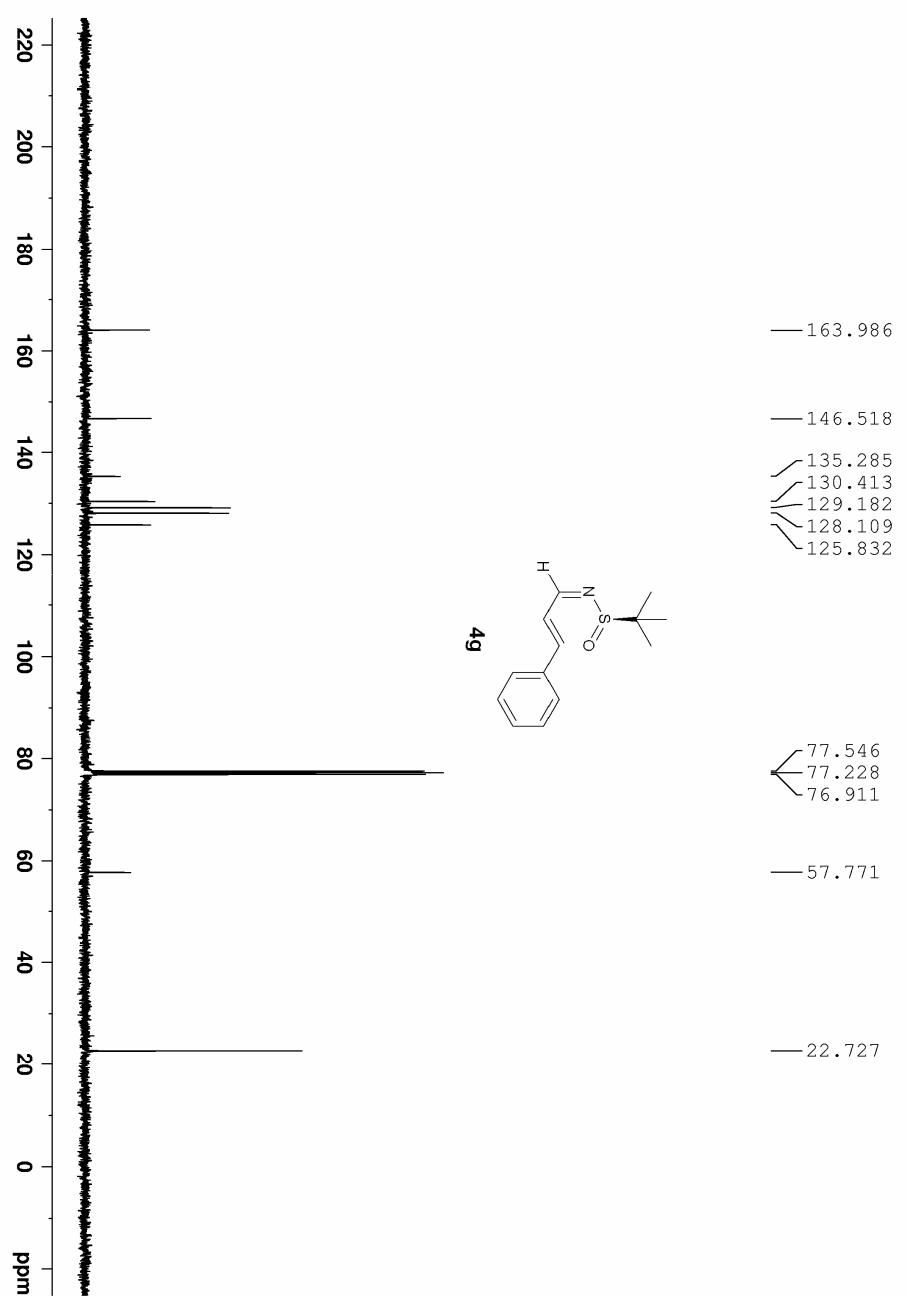


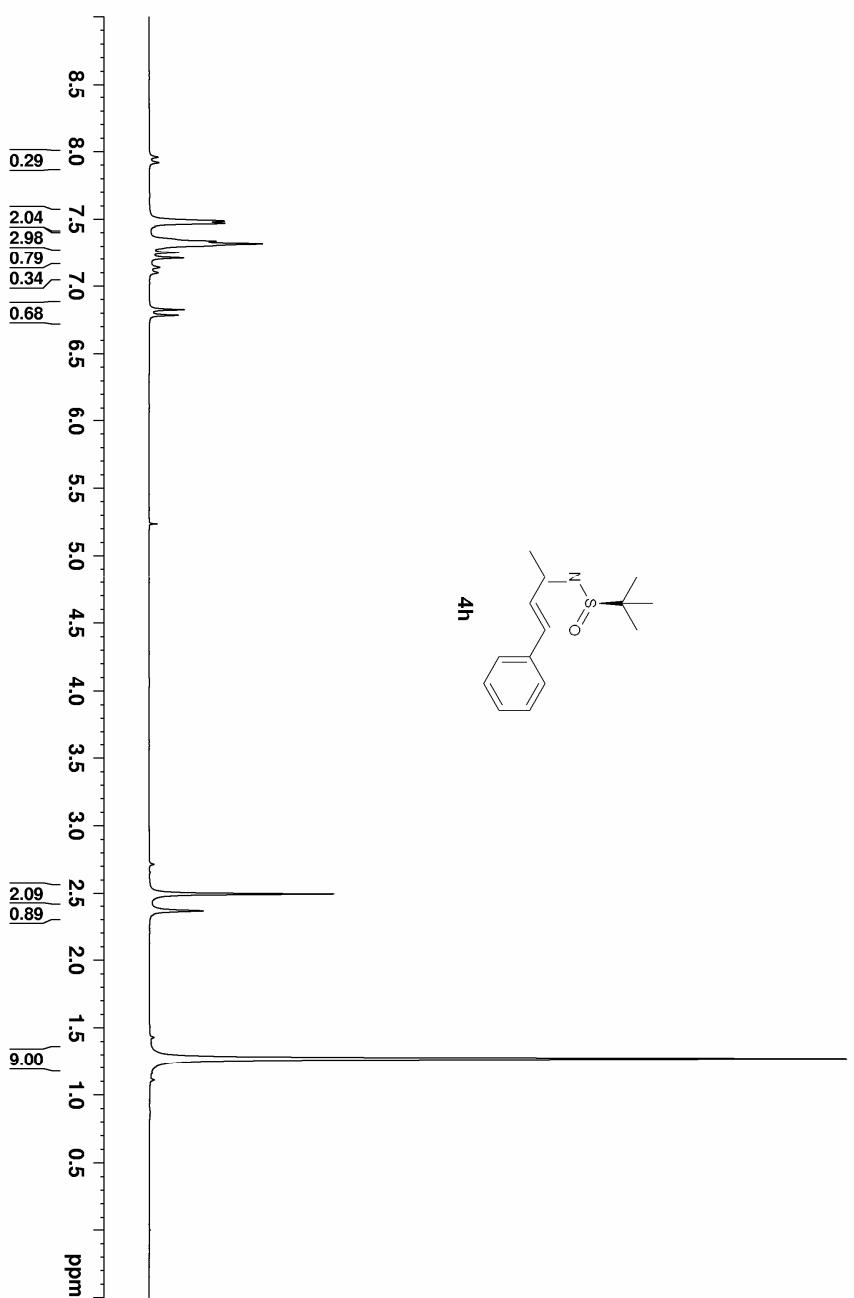


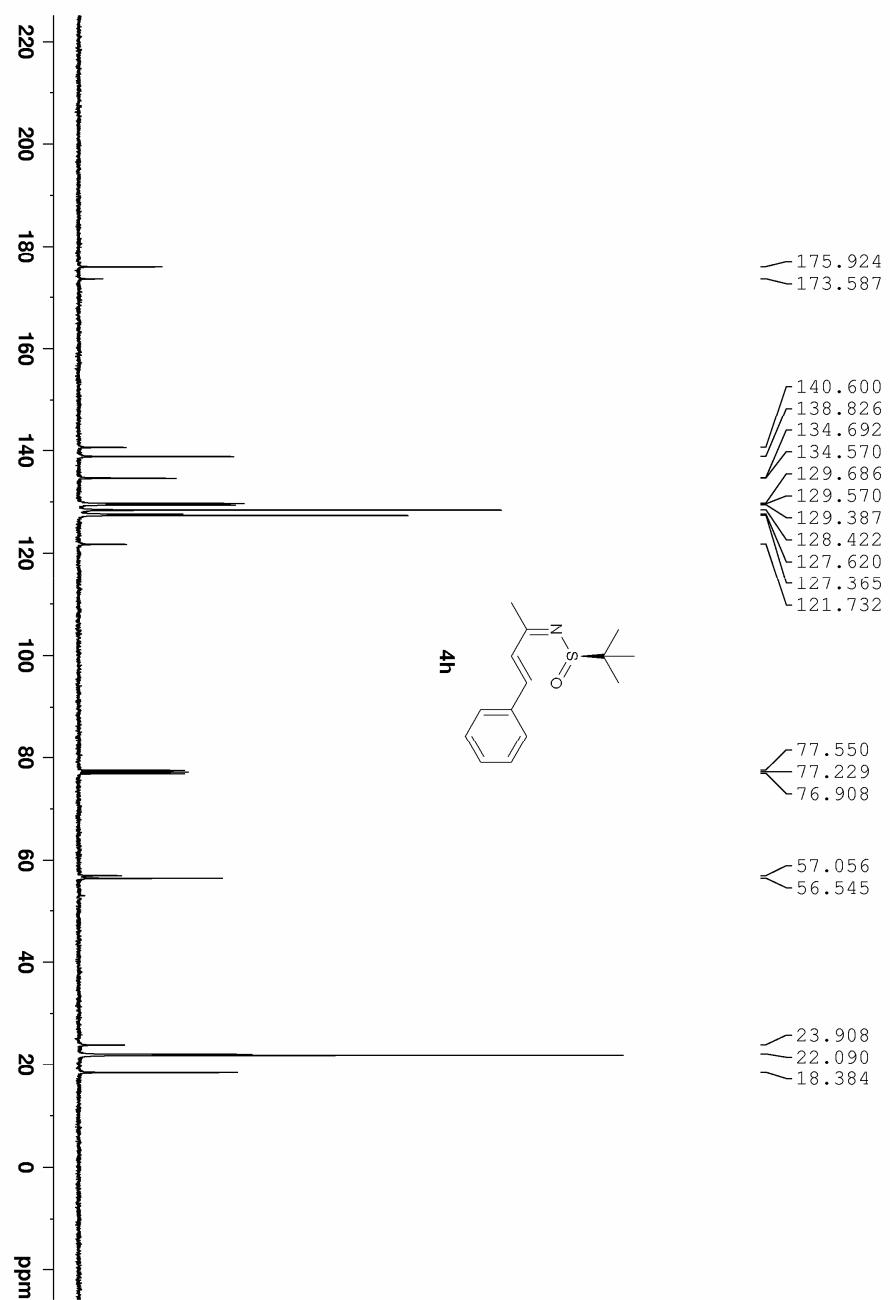


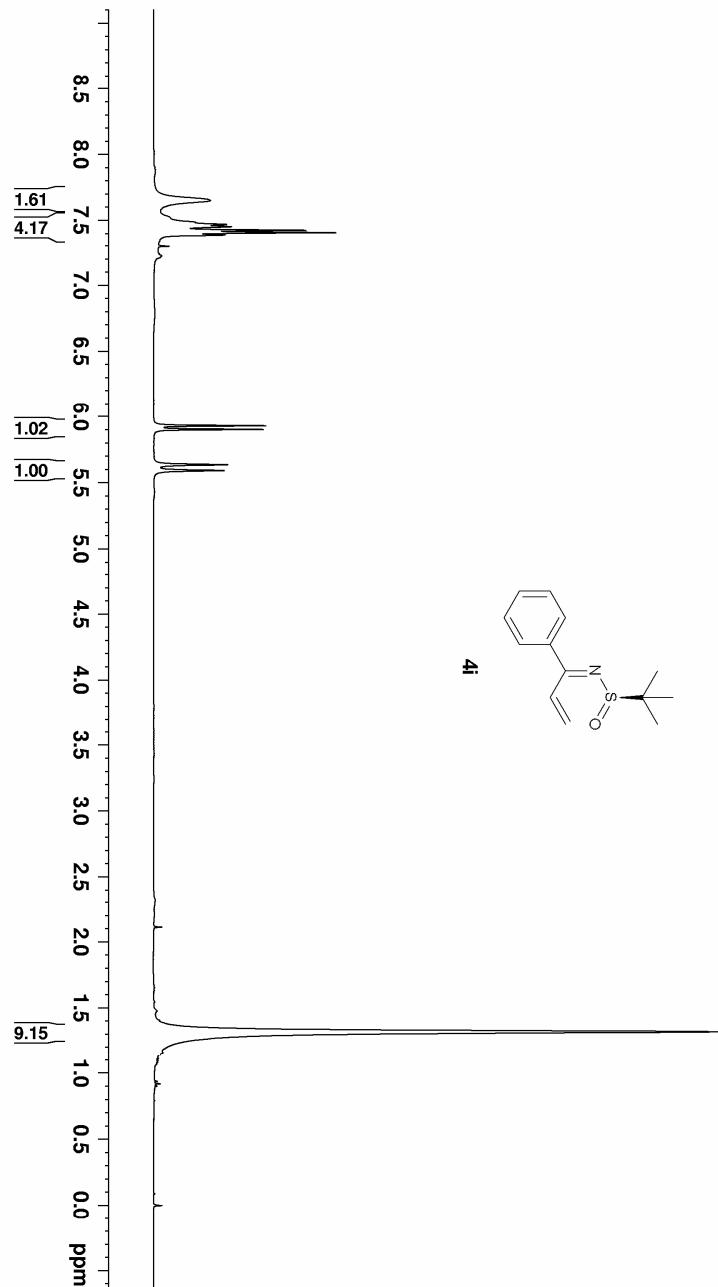


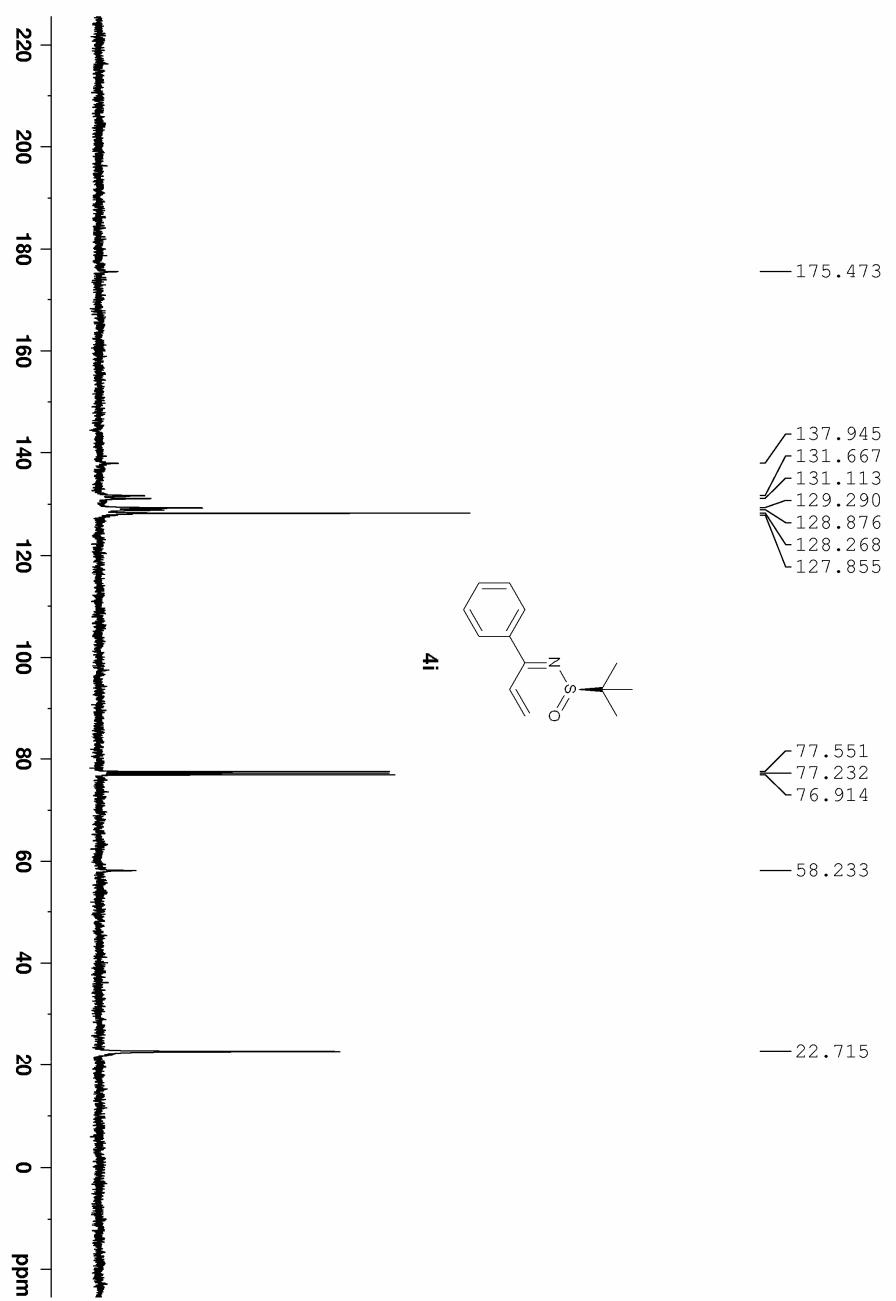


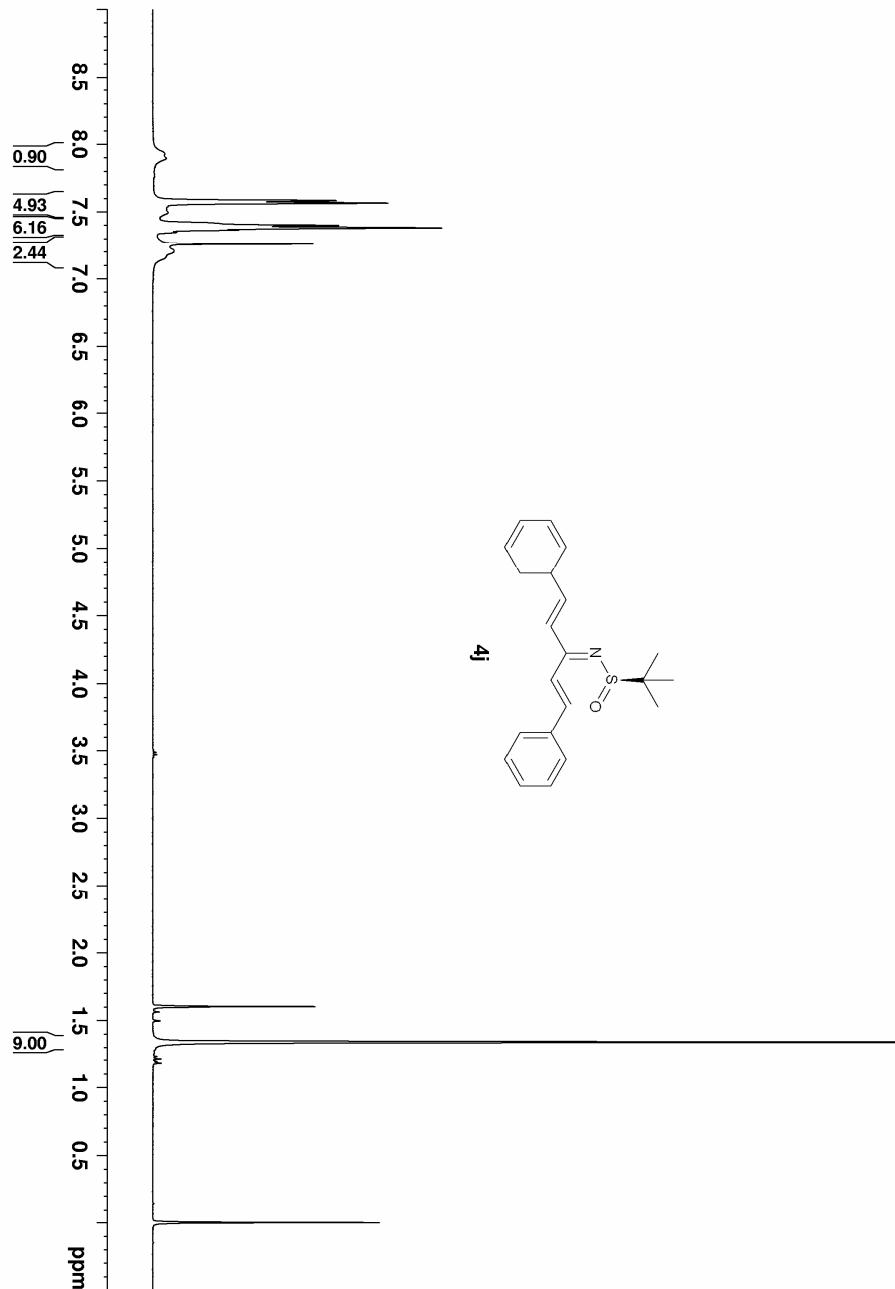


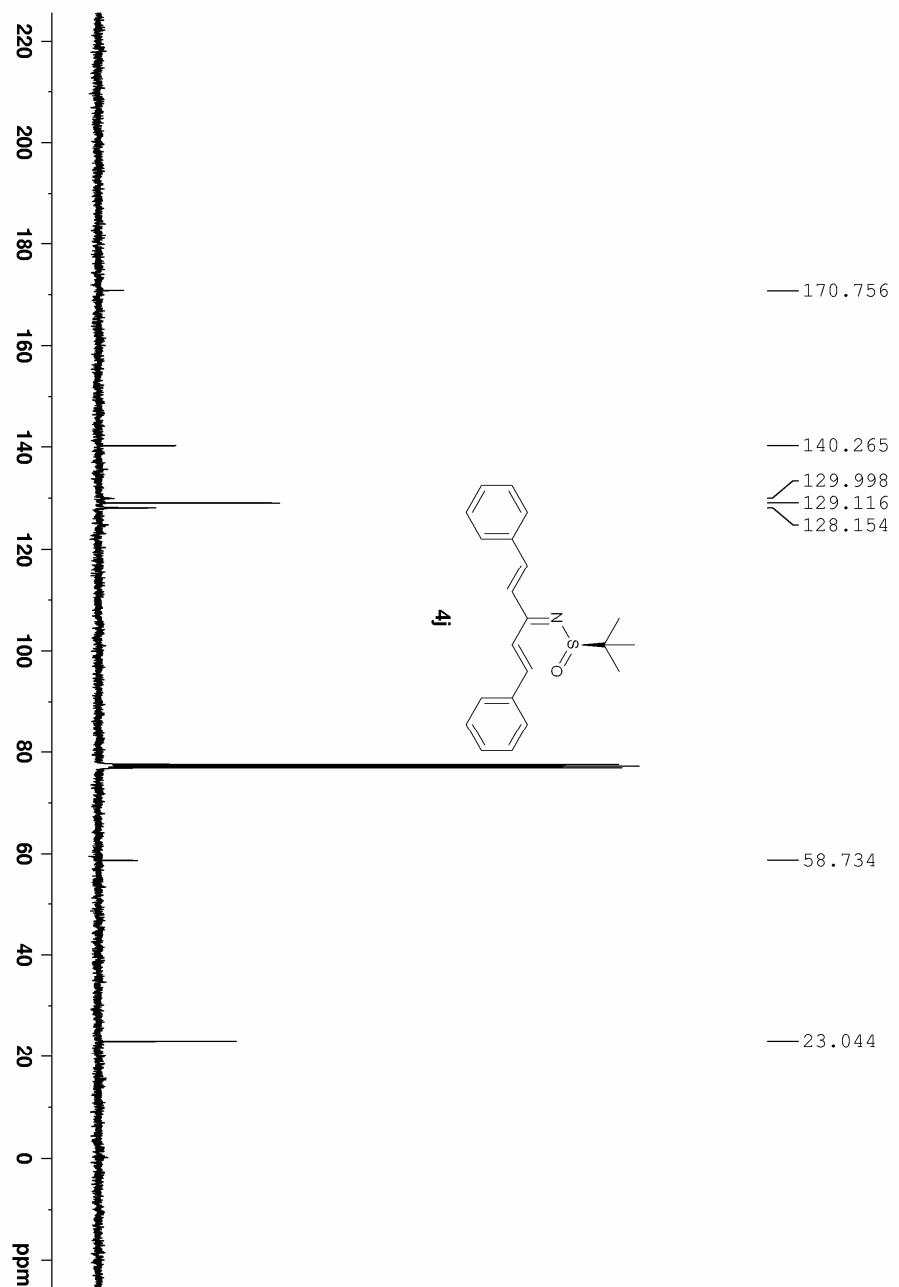


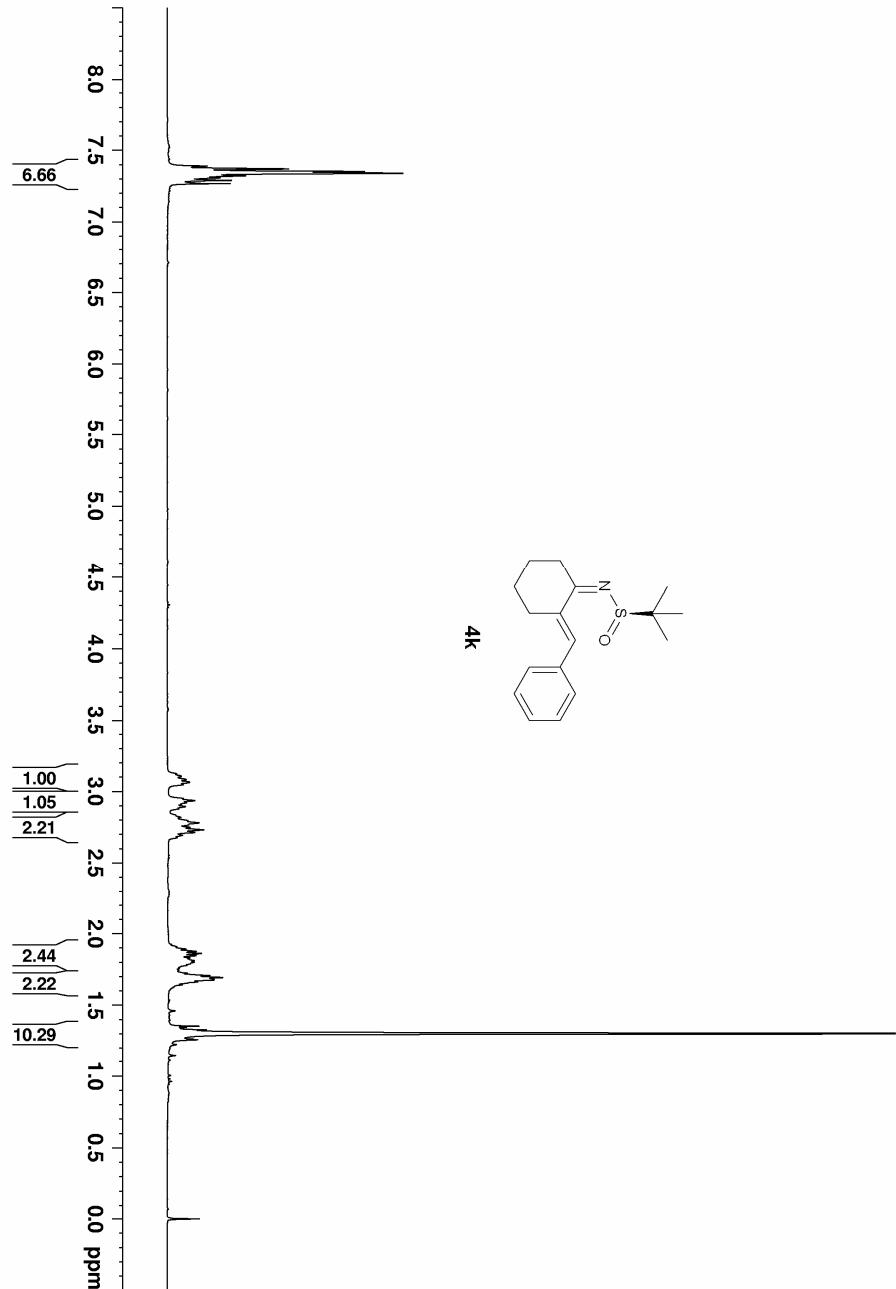


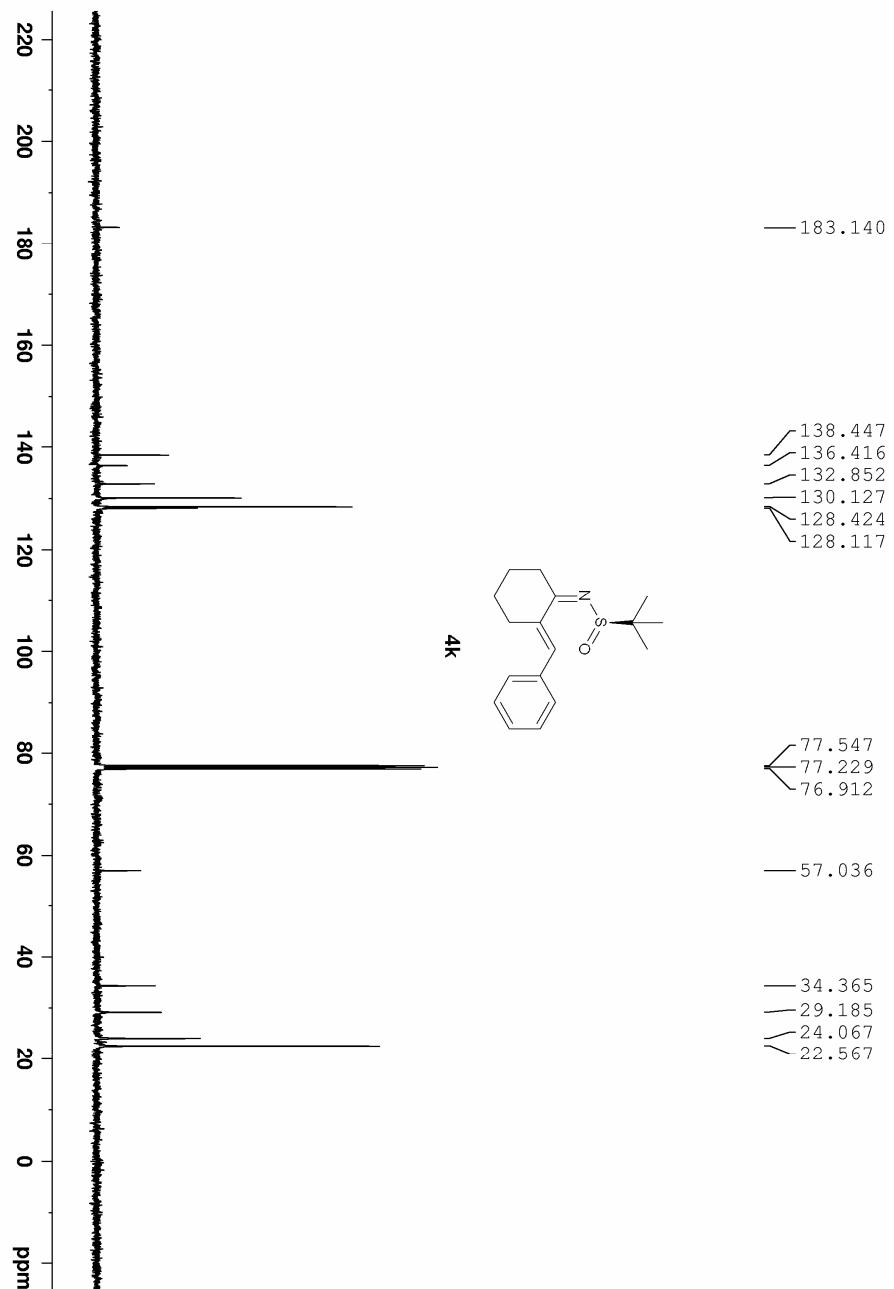


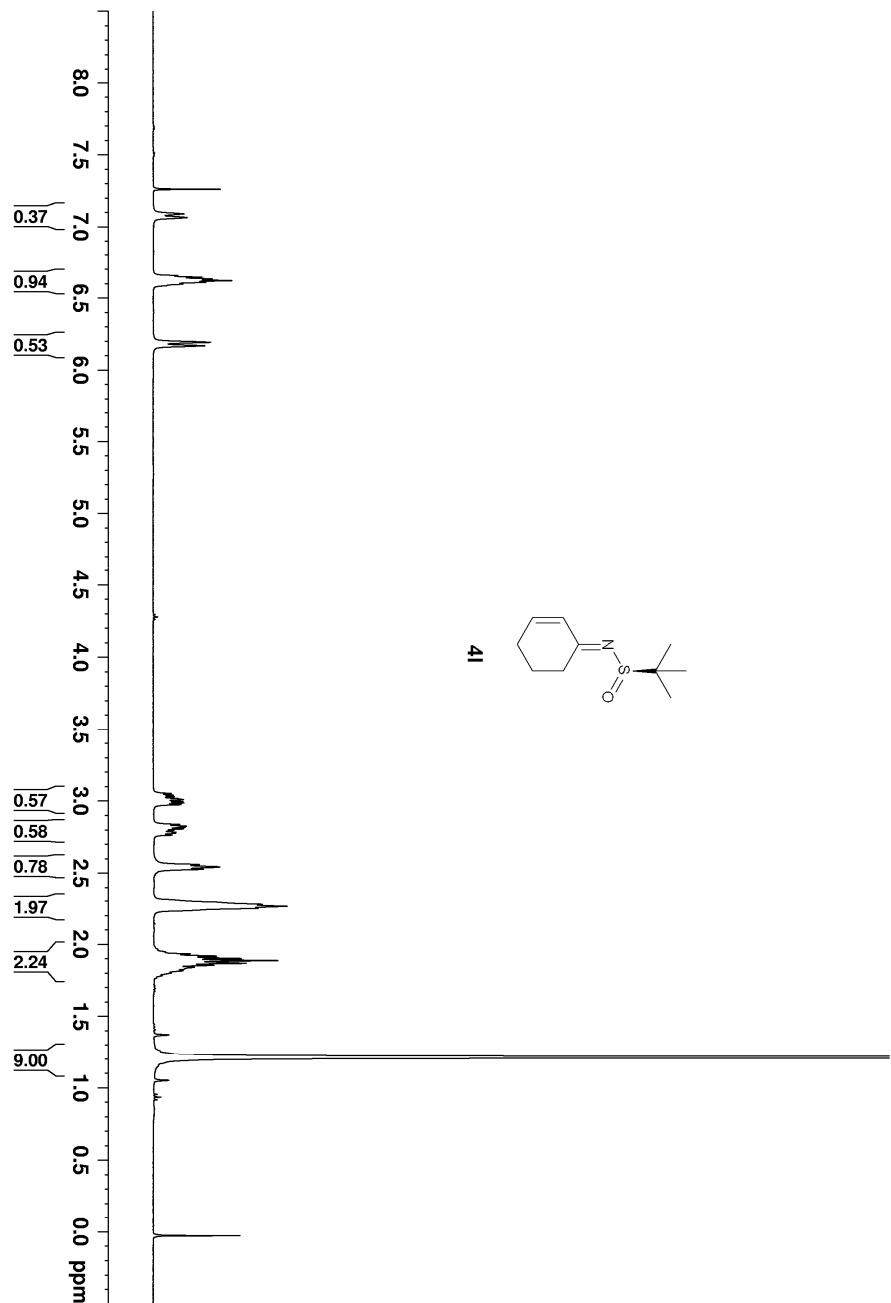


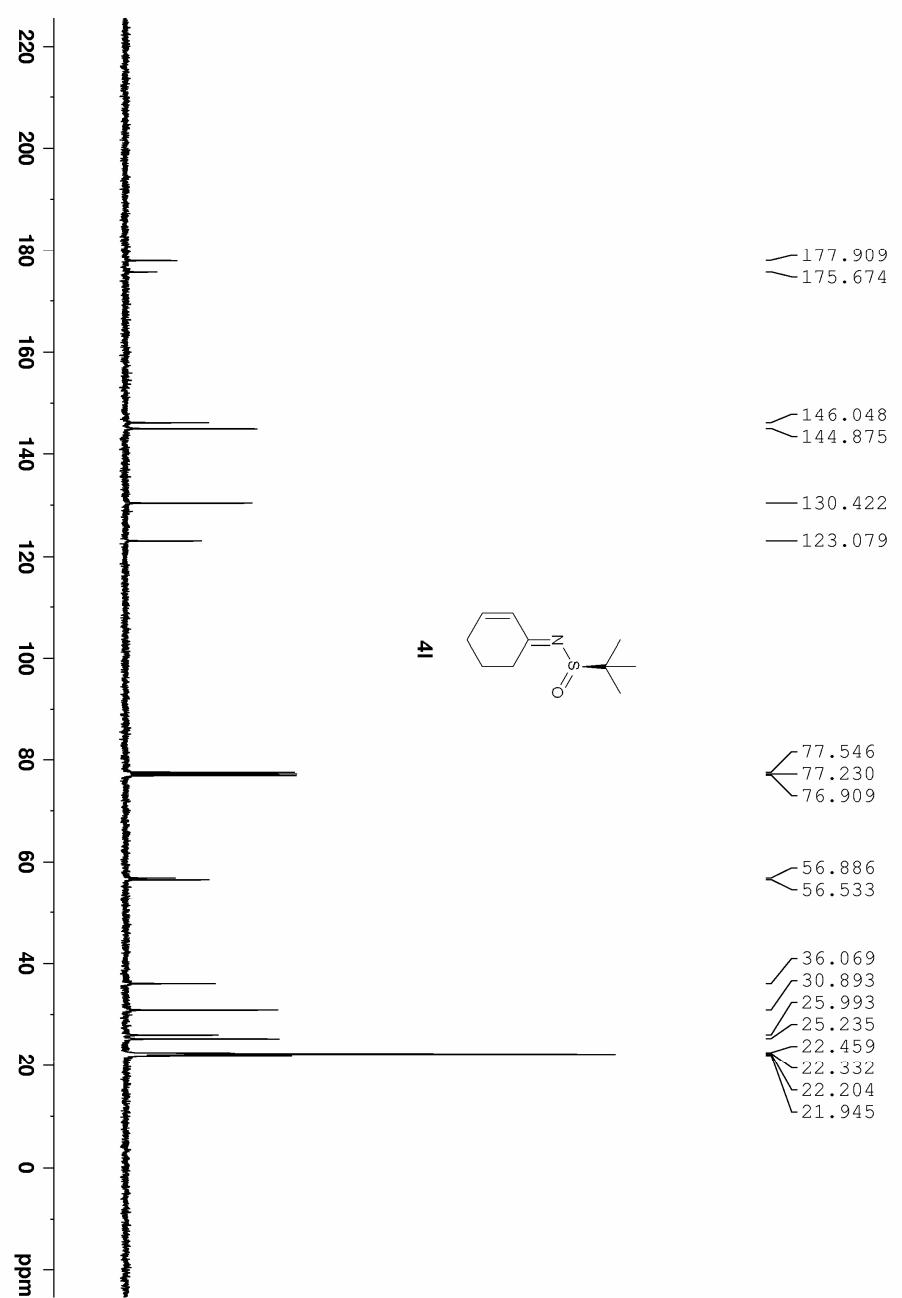


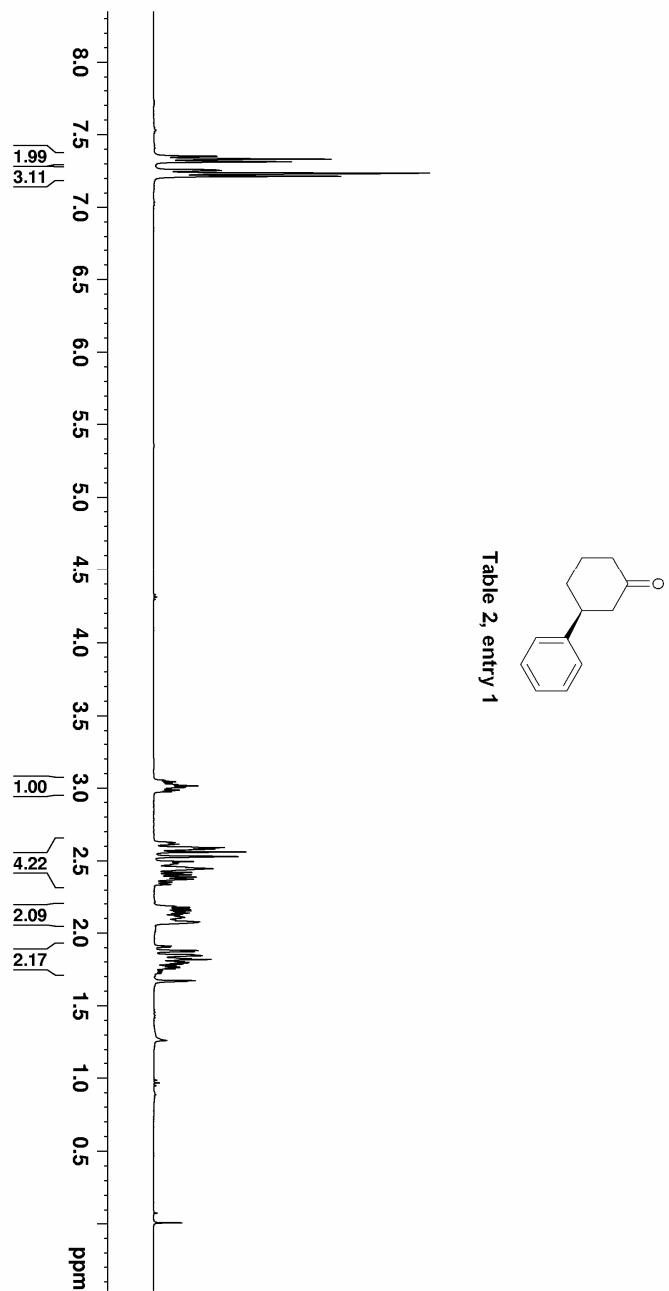


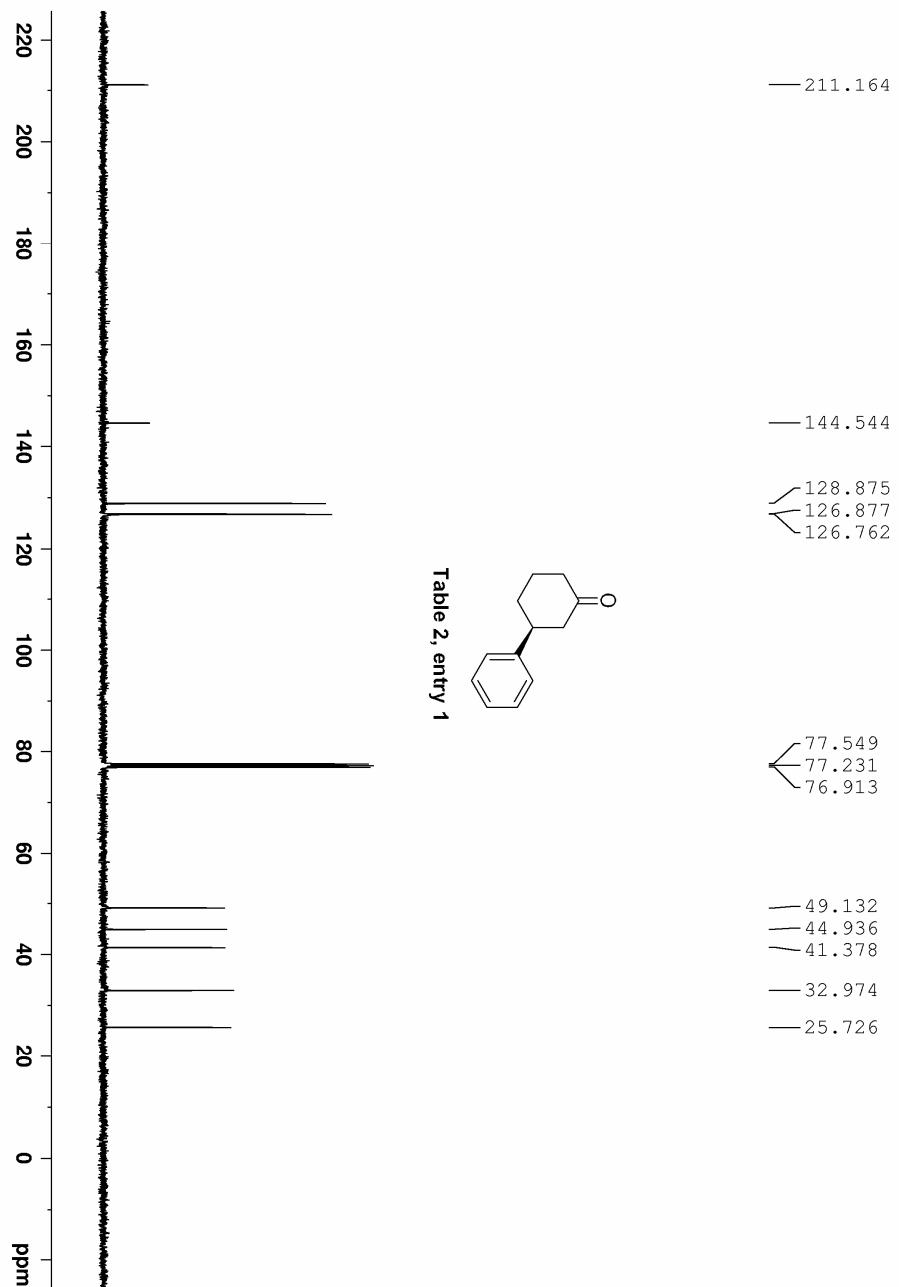


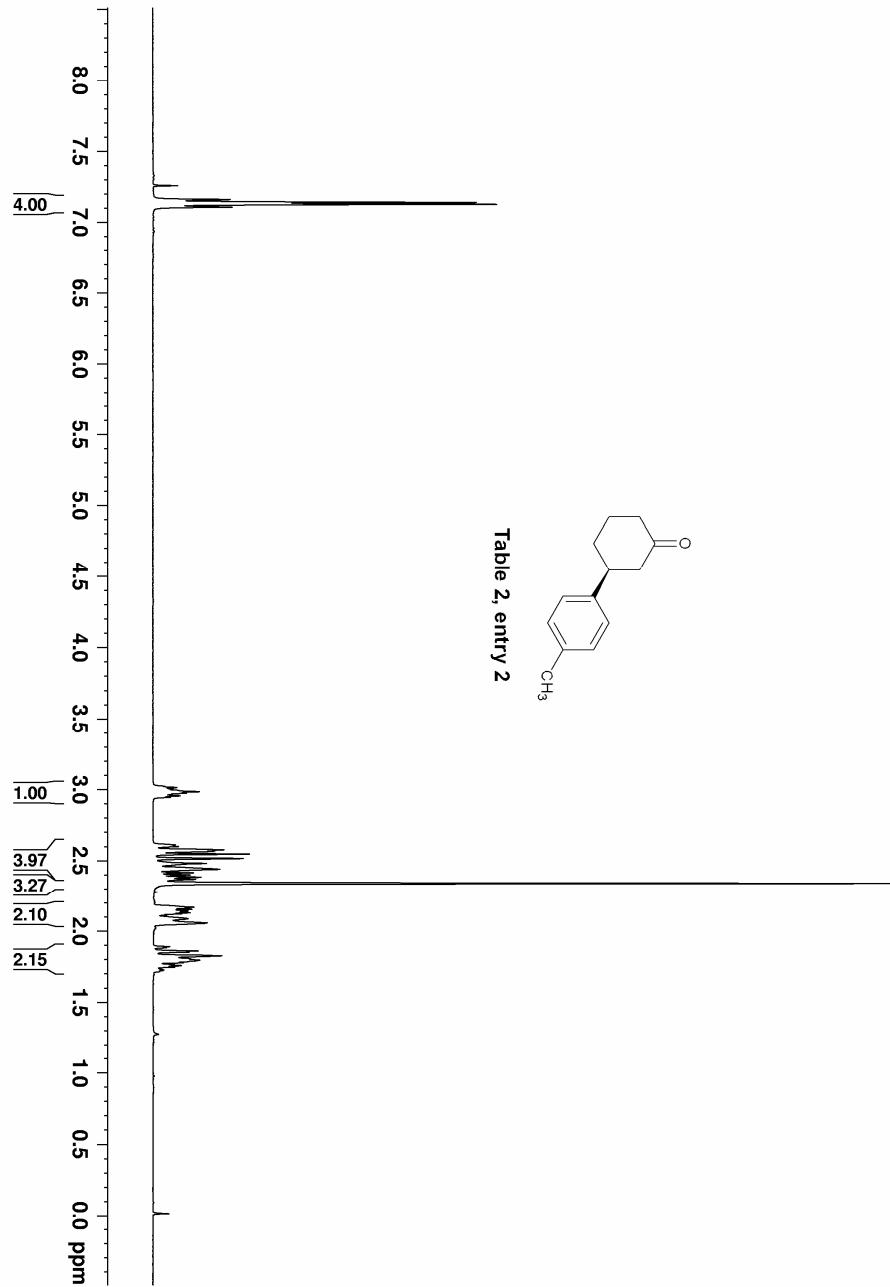












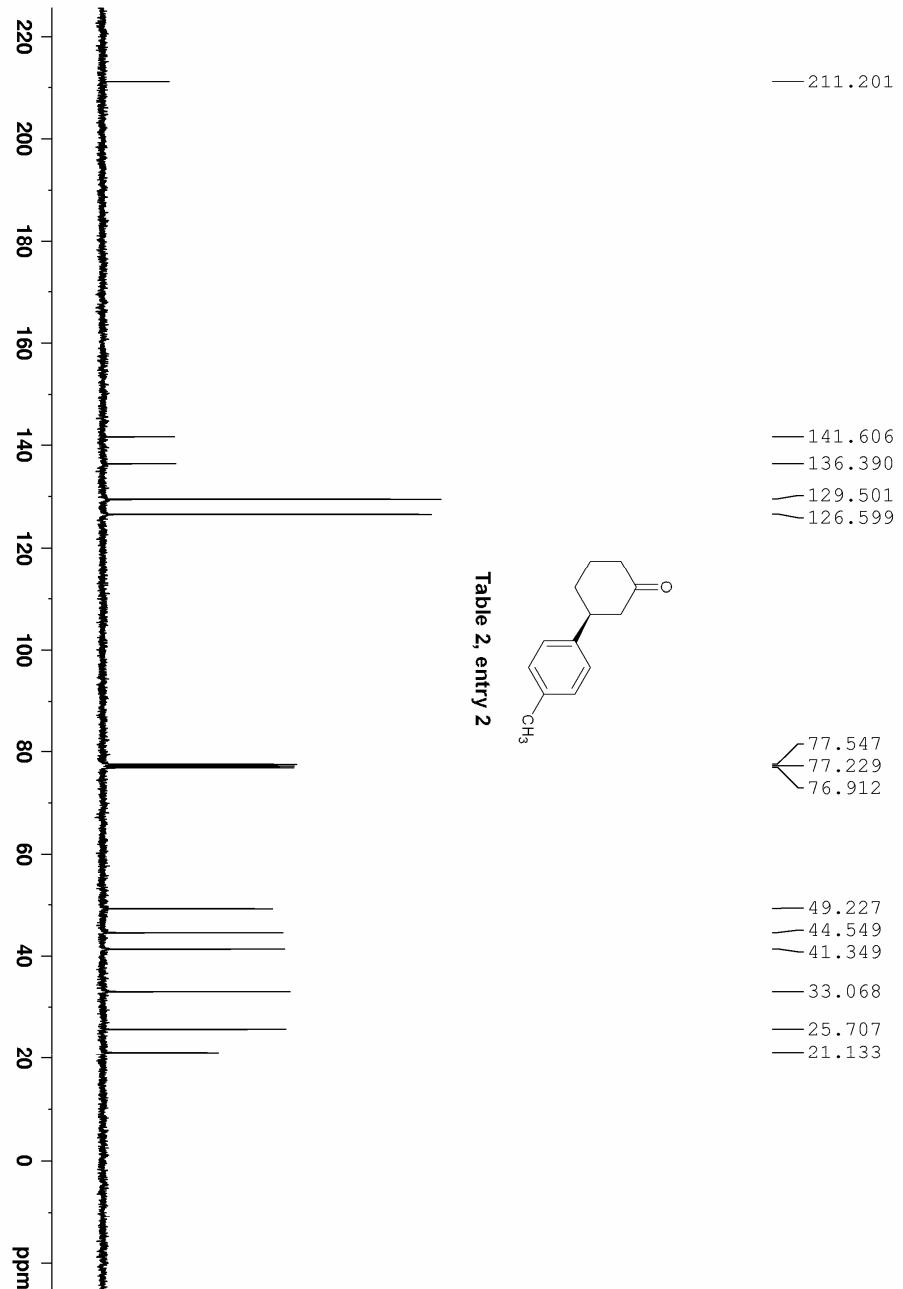


Table 2, entry 2

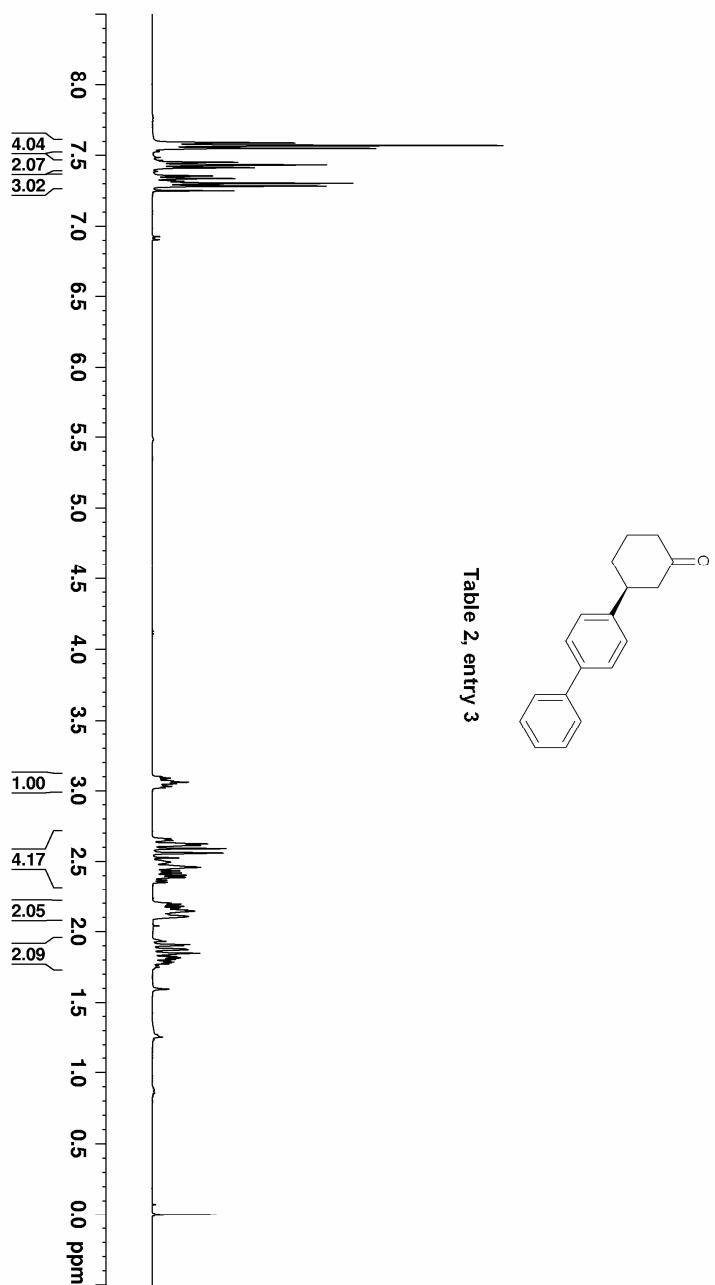
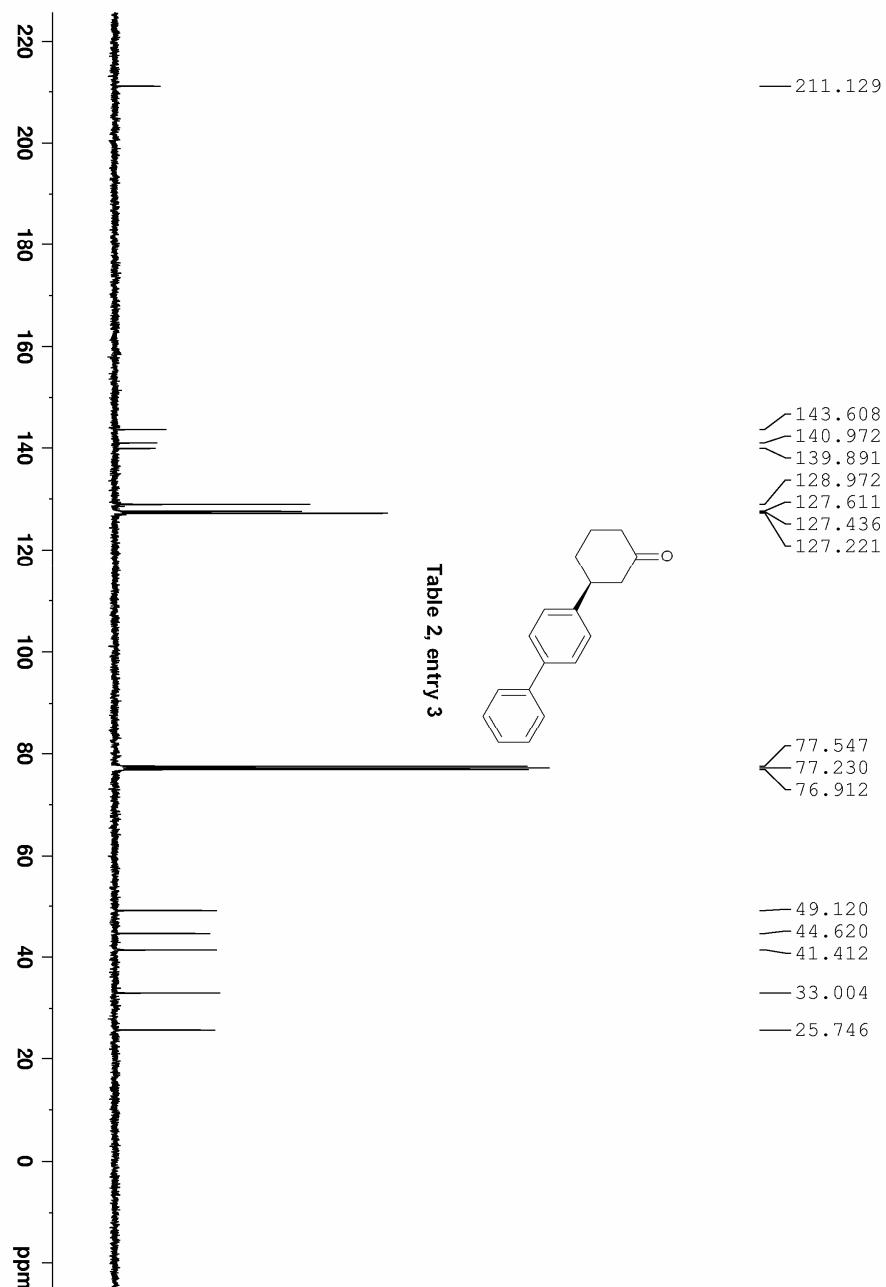


Table 2, entry 3



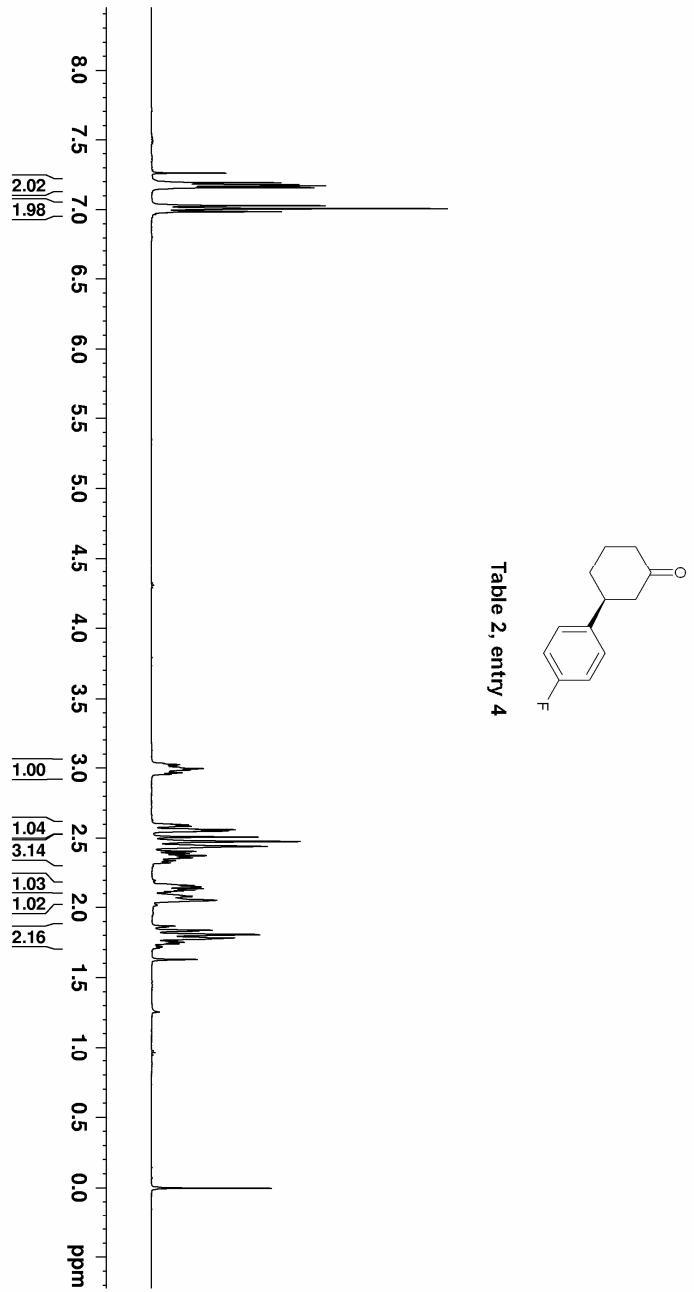


Table 2, entry 4

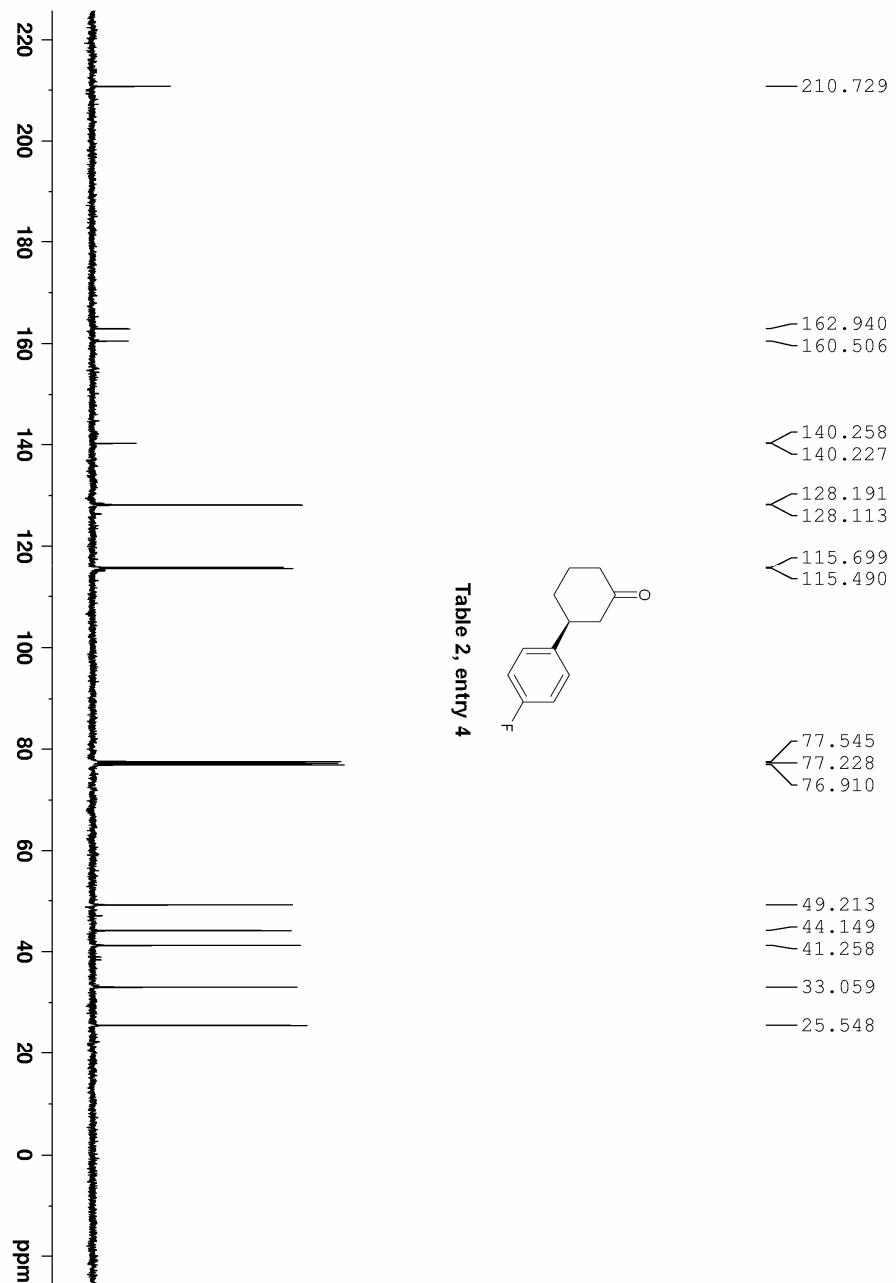
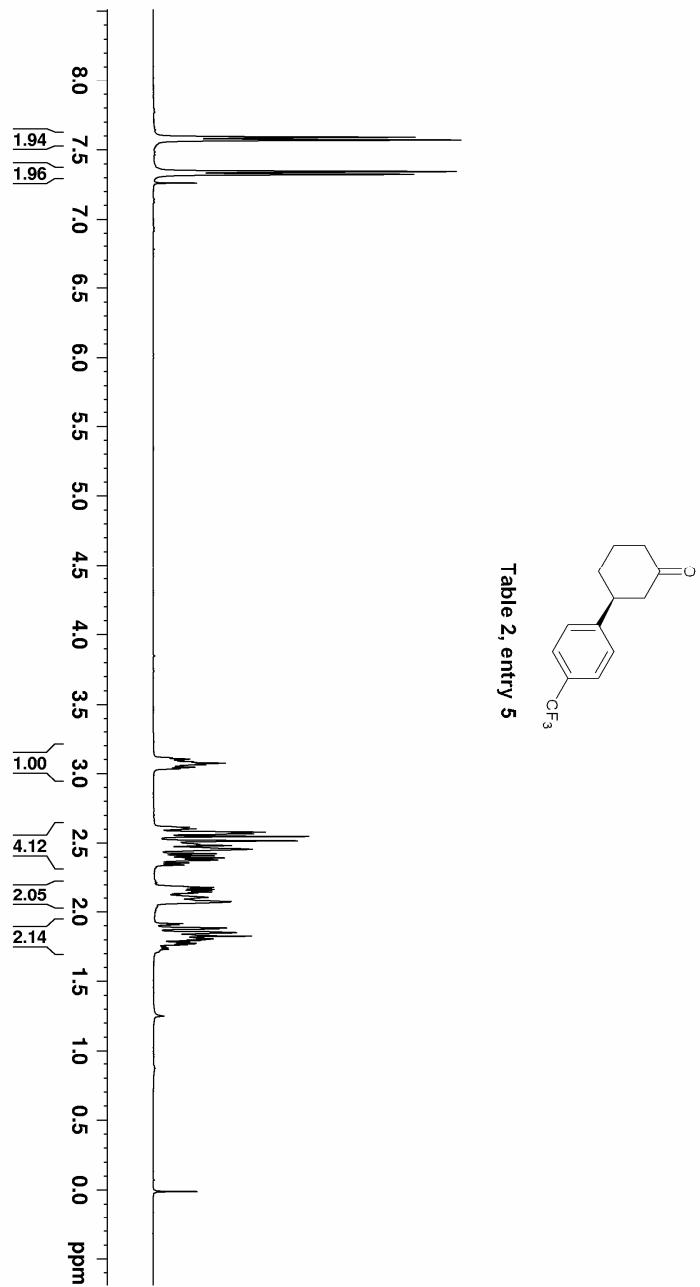
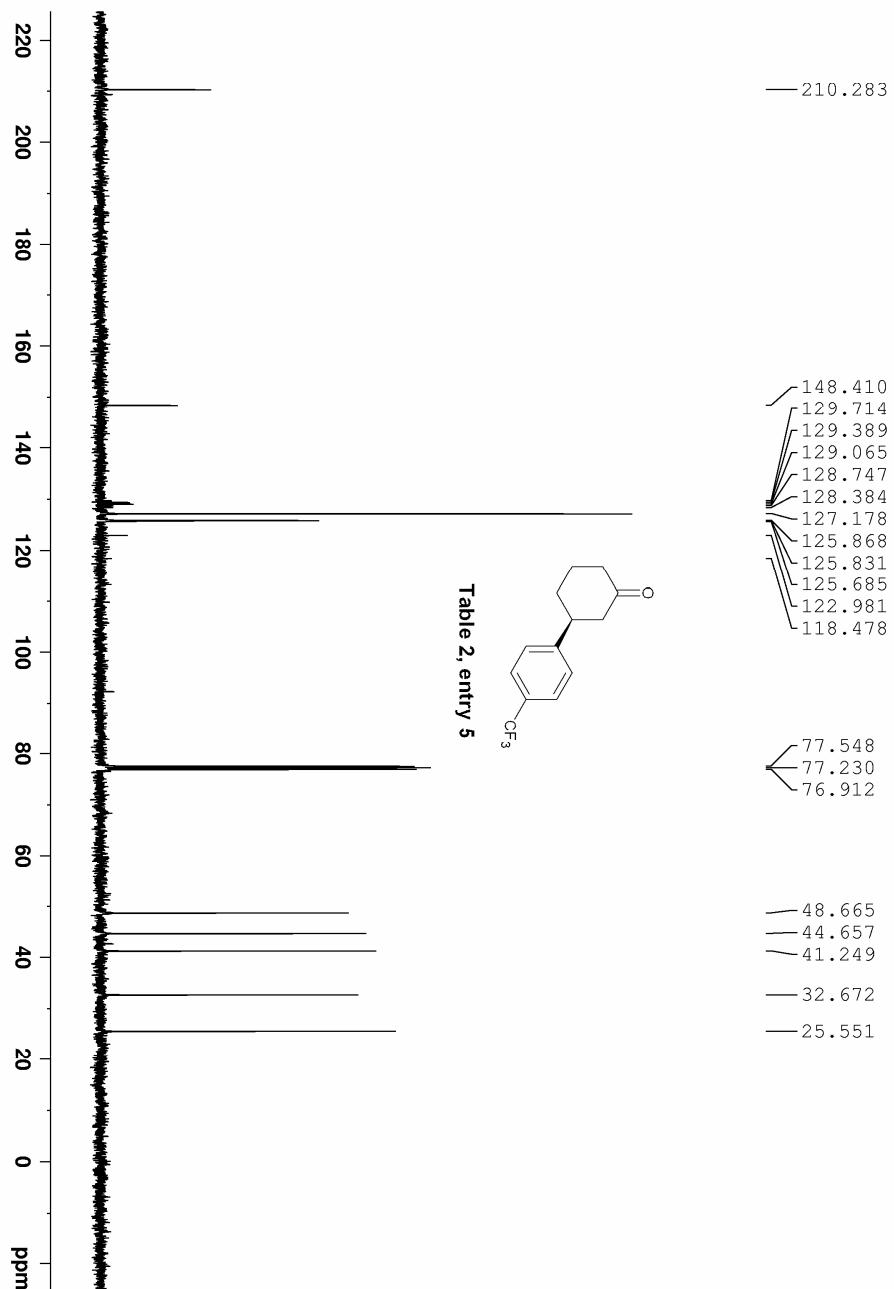
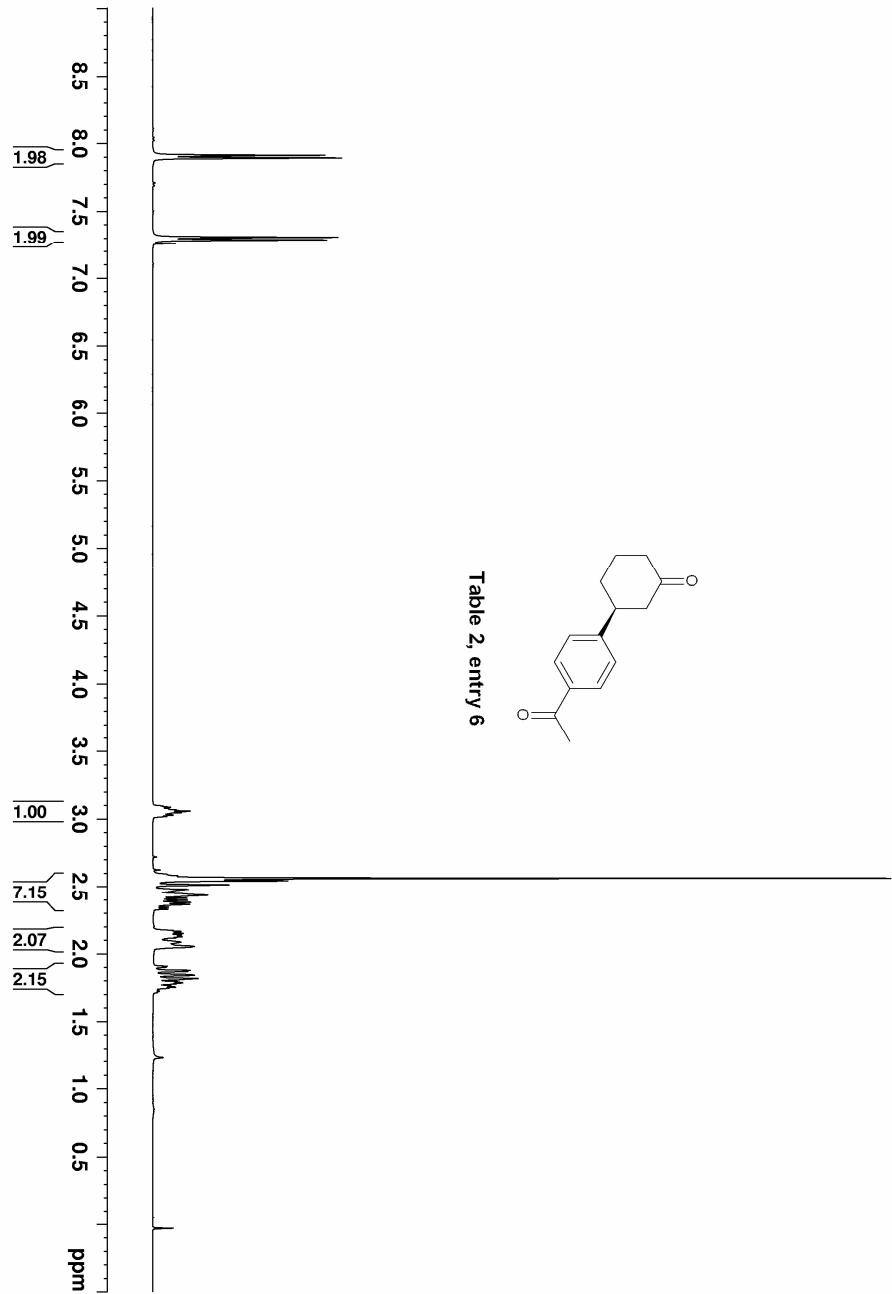
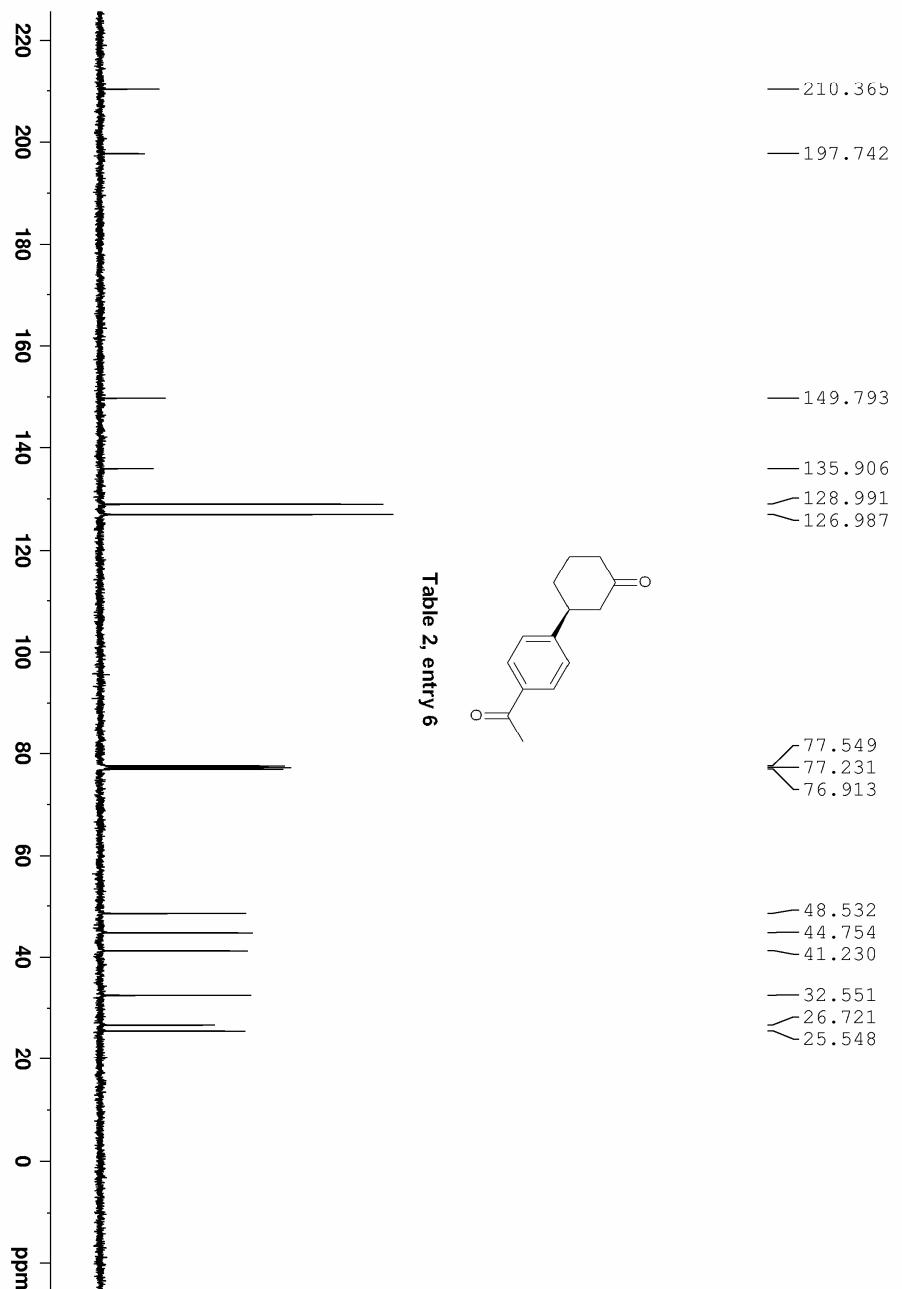


Table 2, entry 4









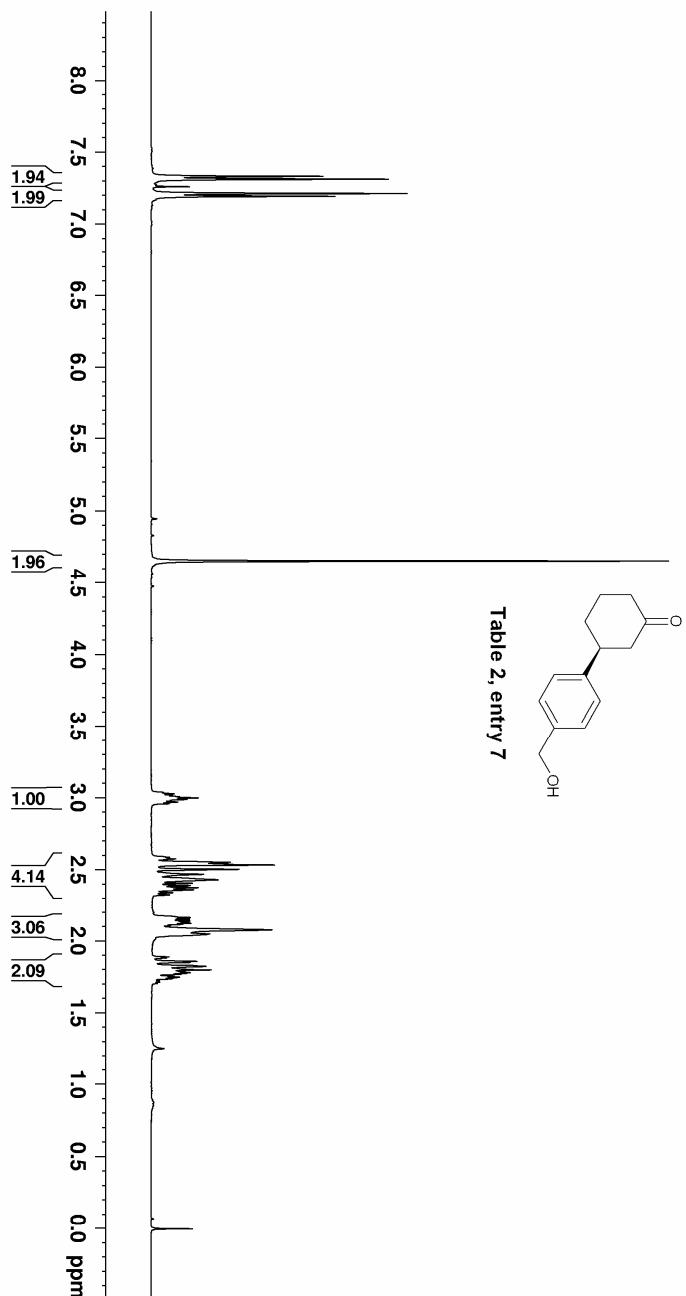


Table 2, entry 7

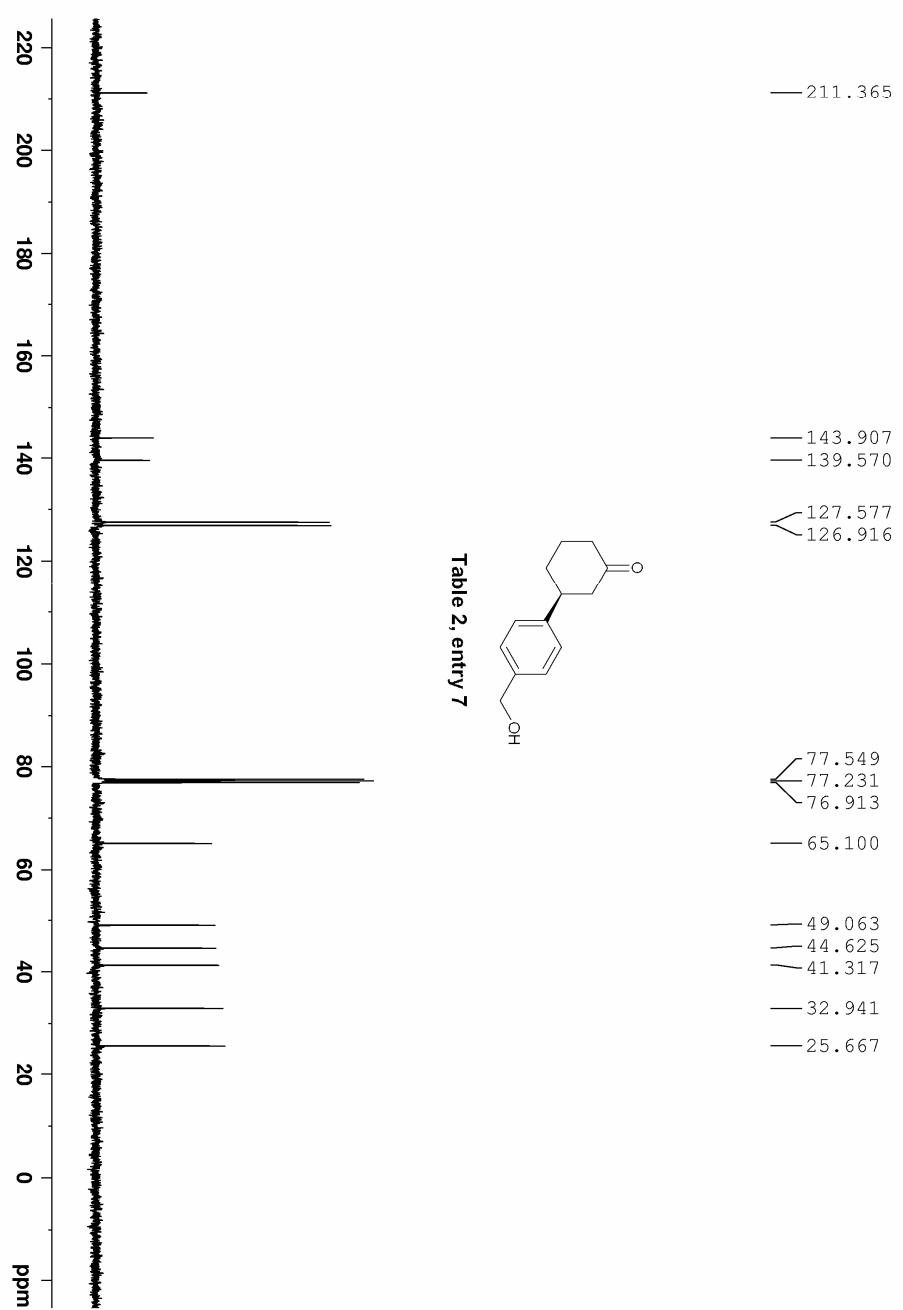


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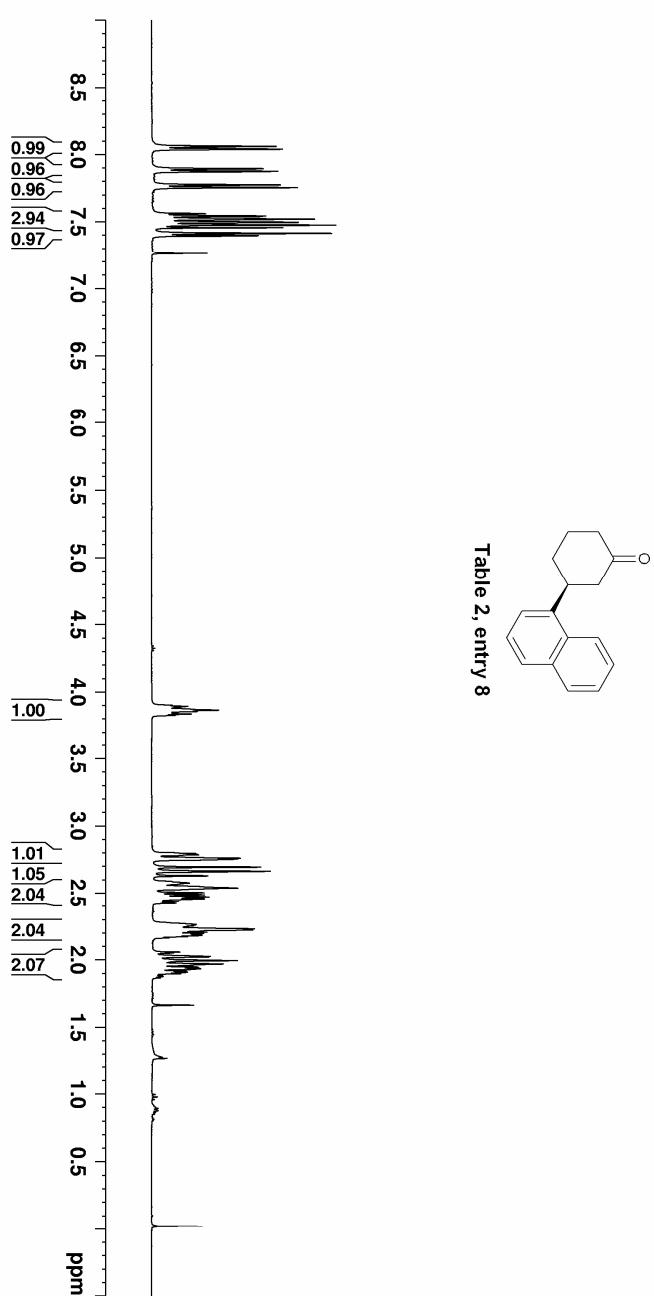


Table 2, entry 8

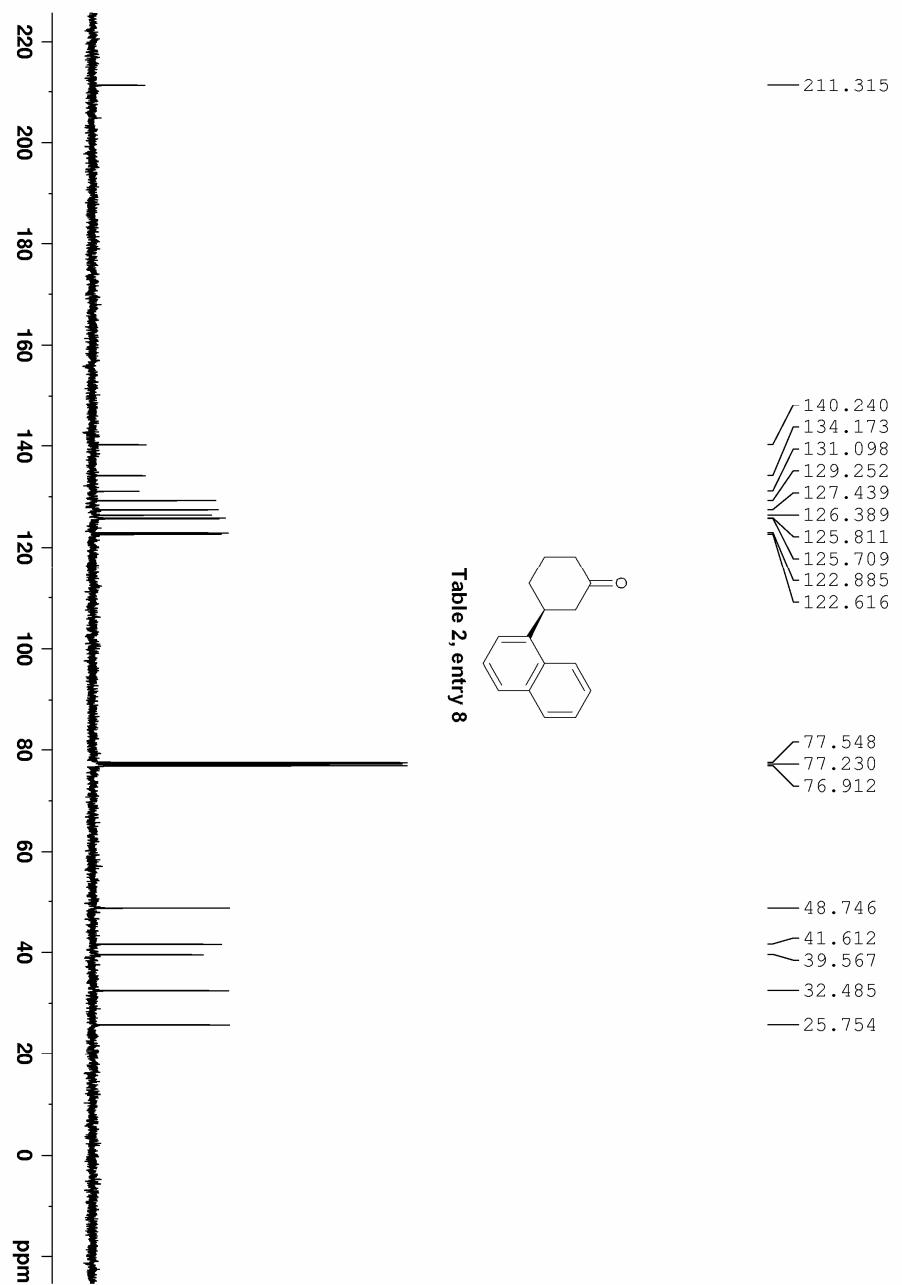


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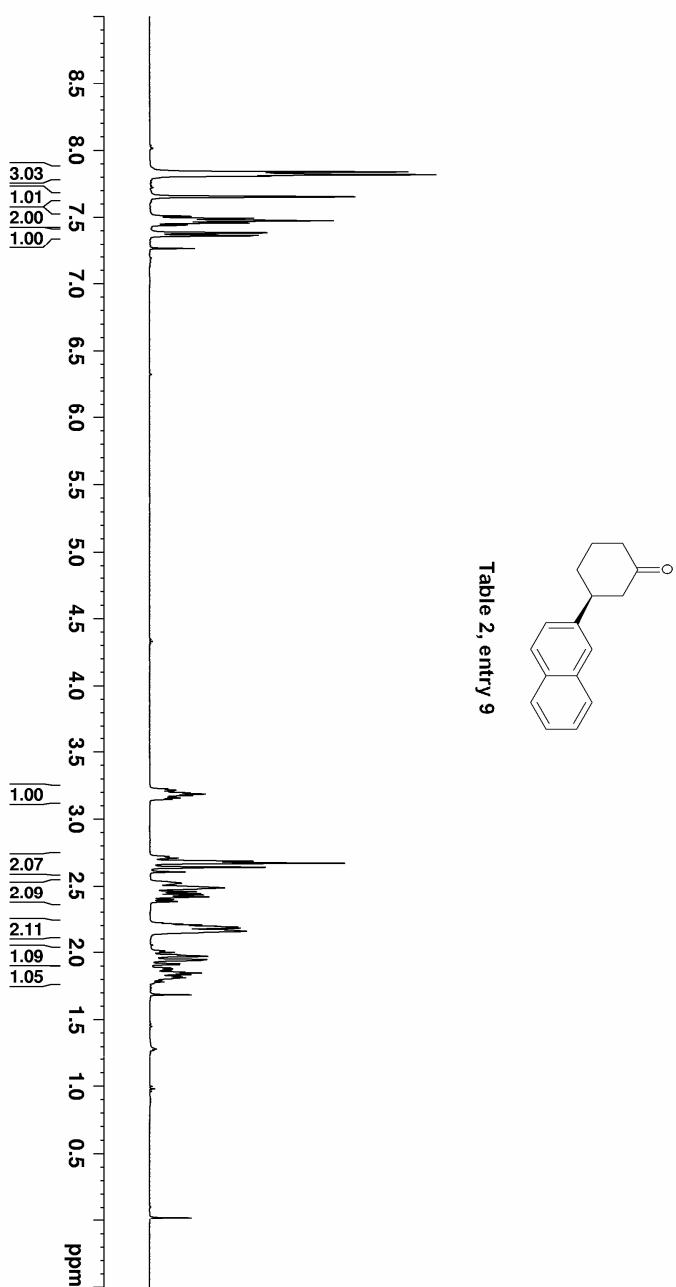


Table 2, entry 9

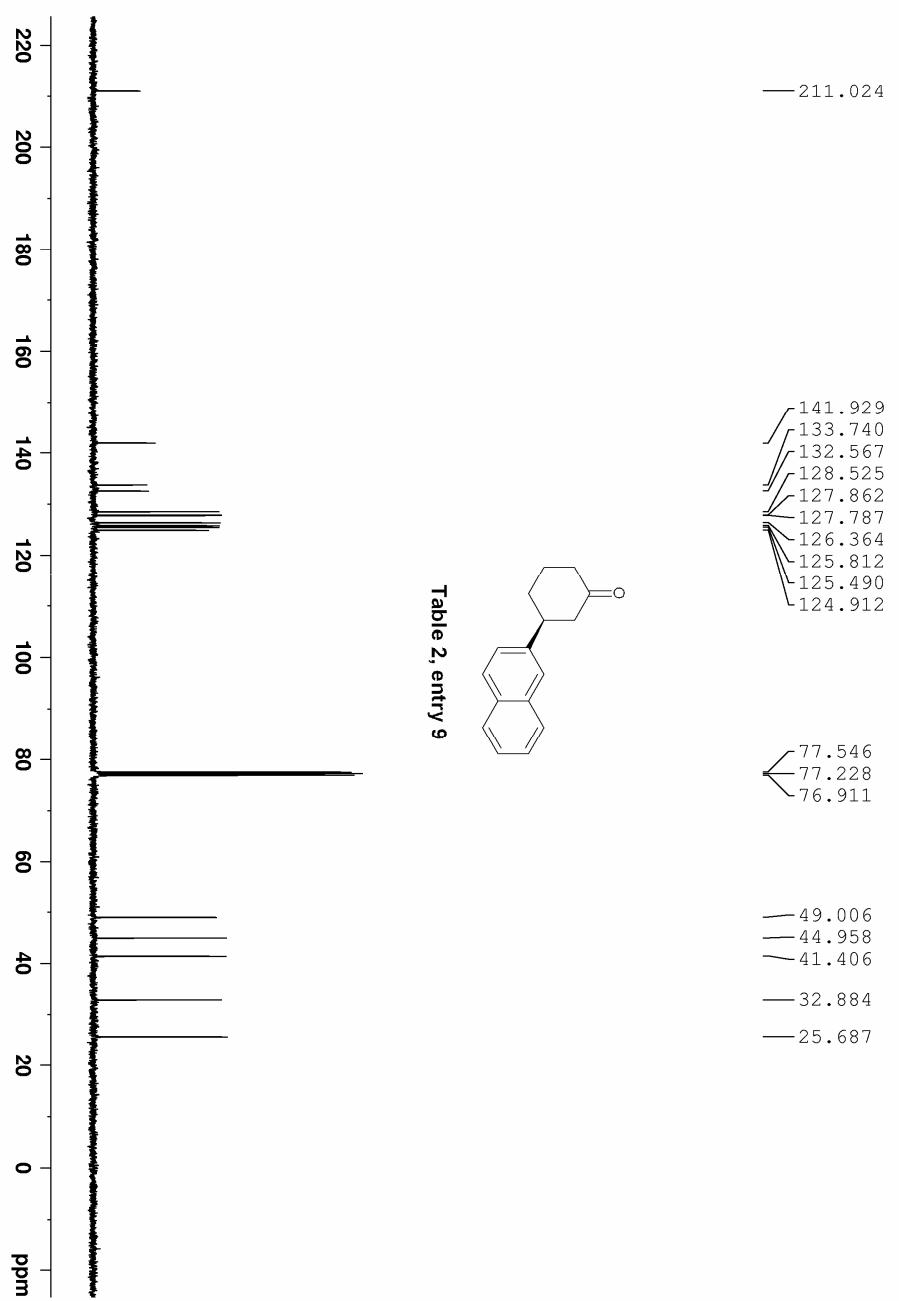
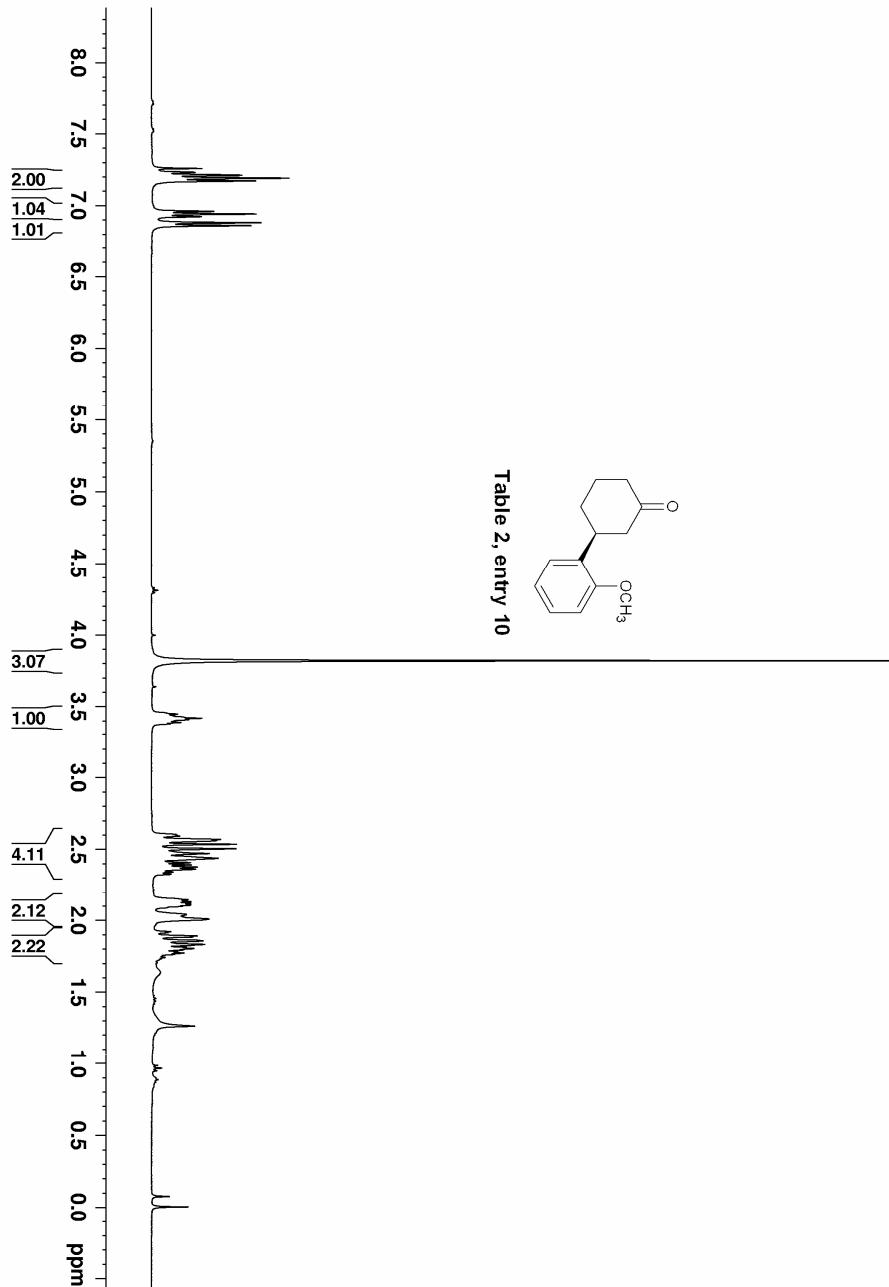
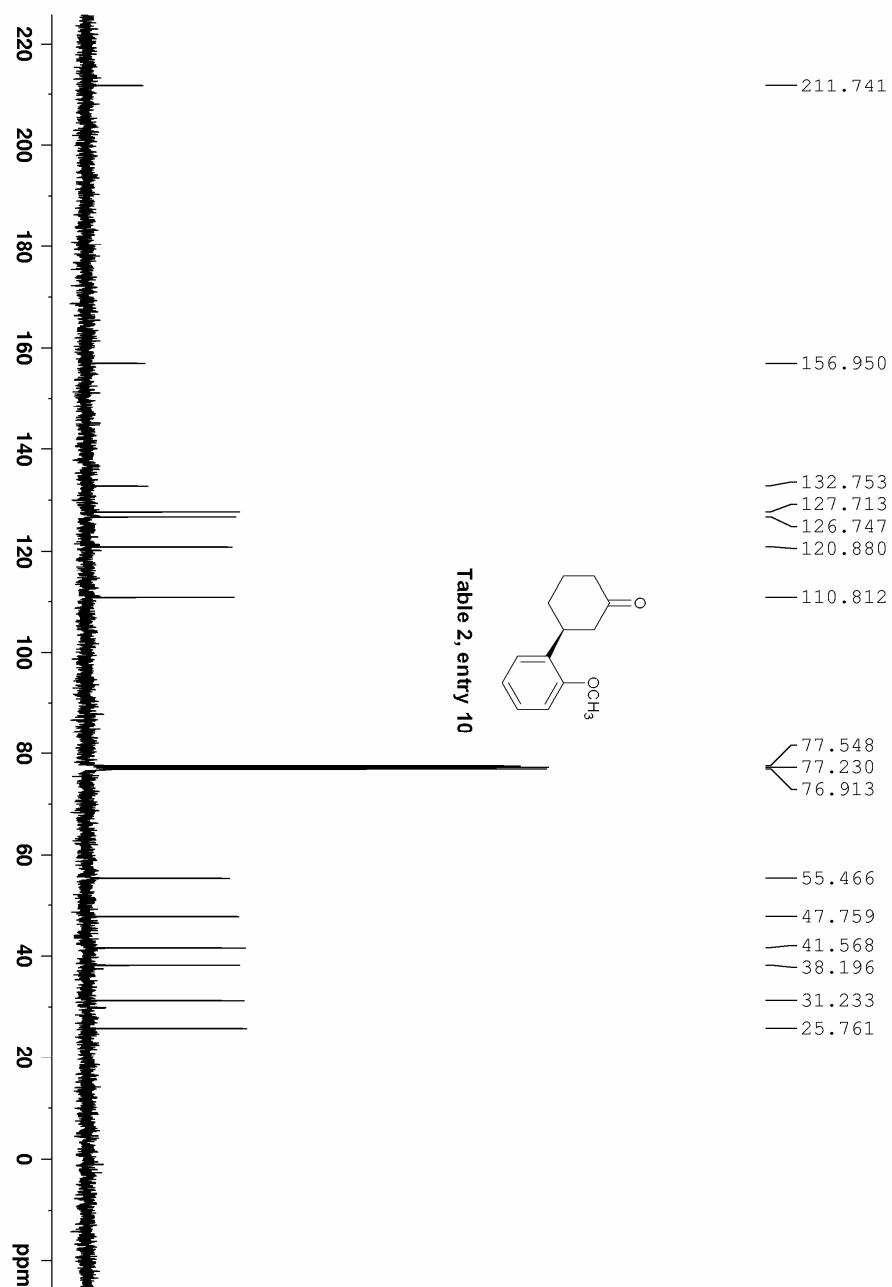
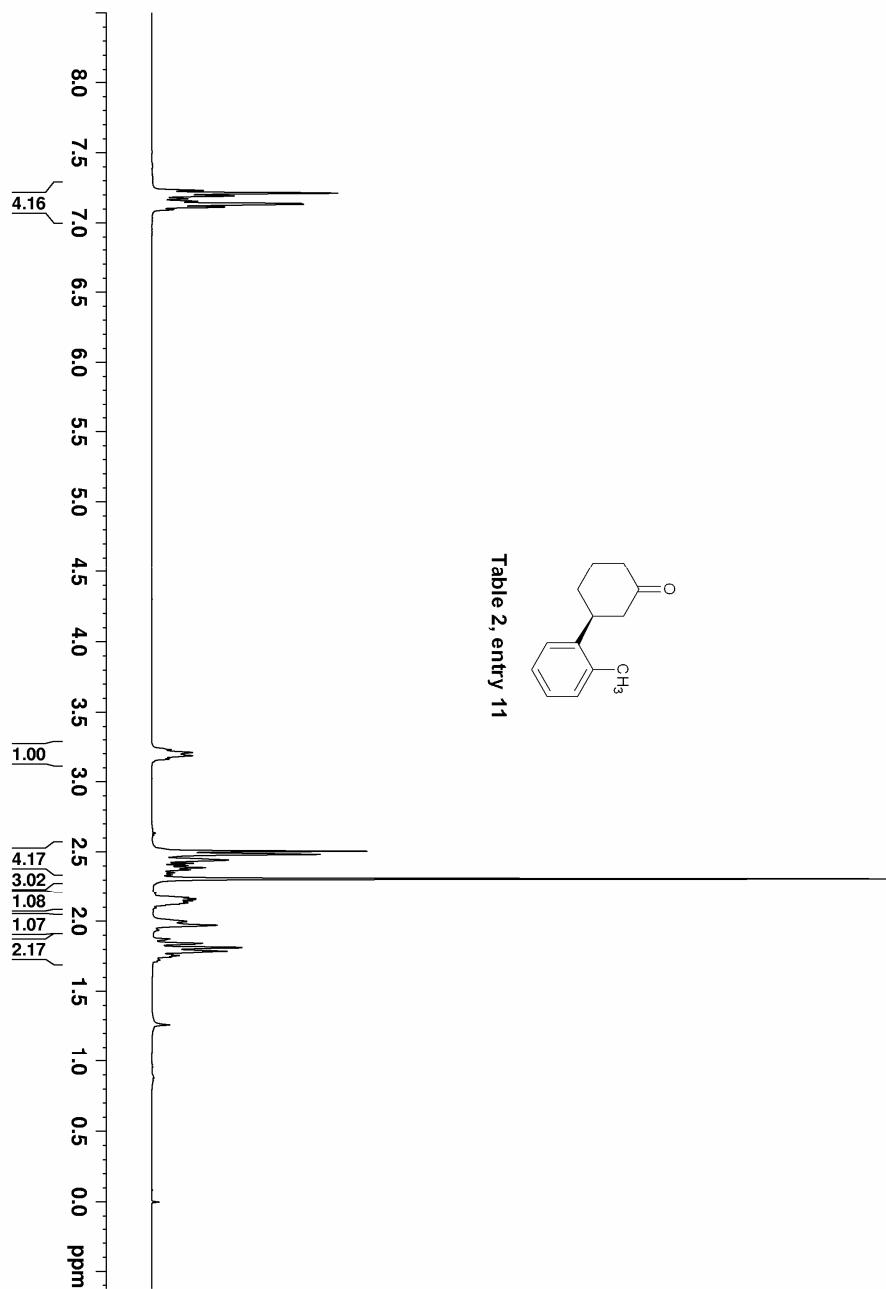
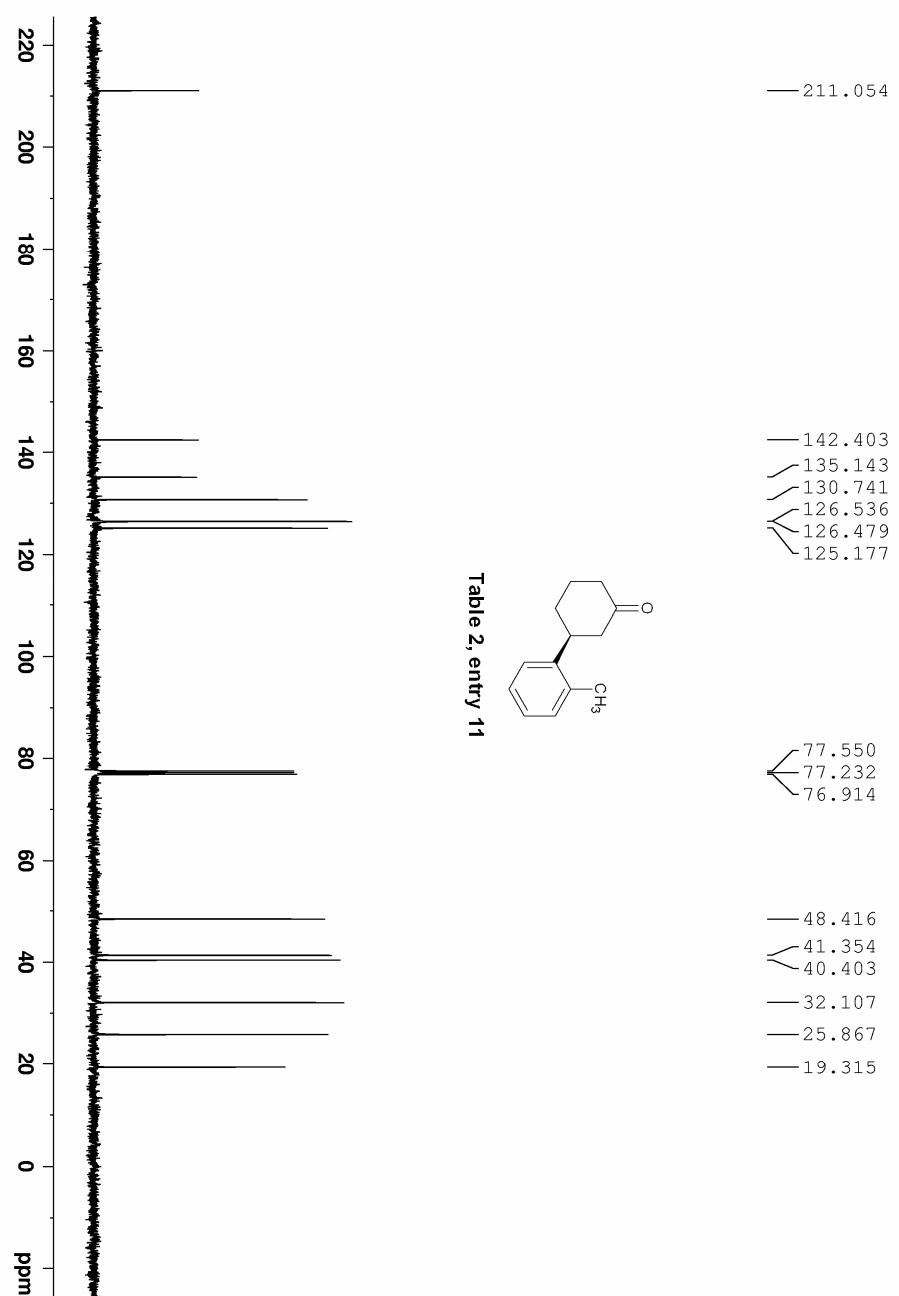


Table 2, entry 9









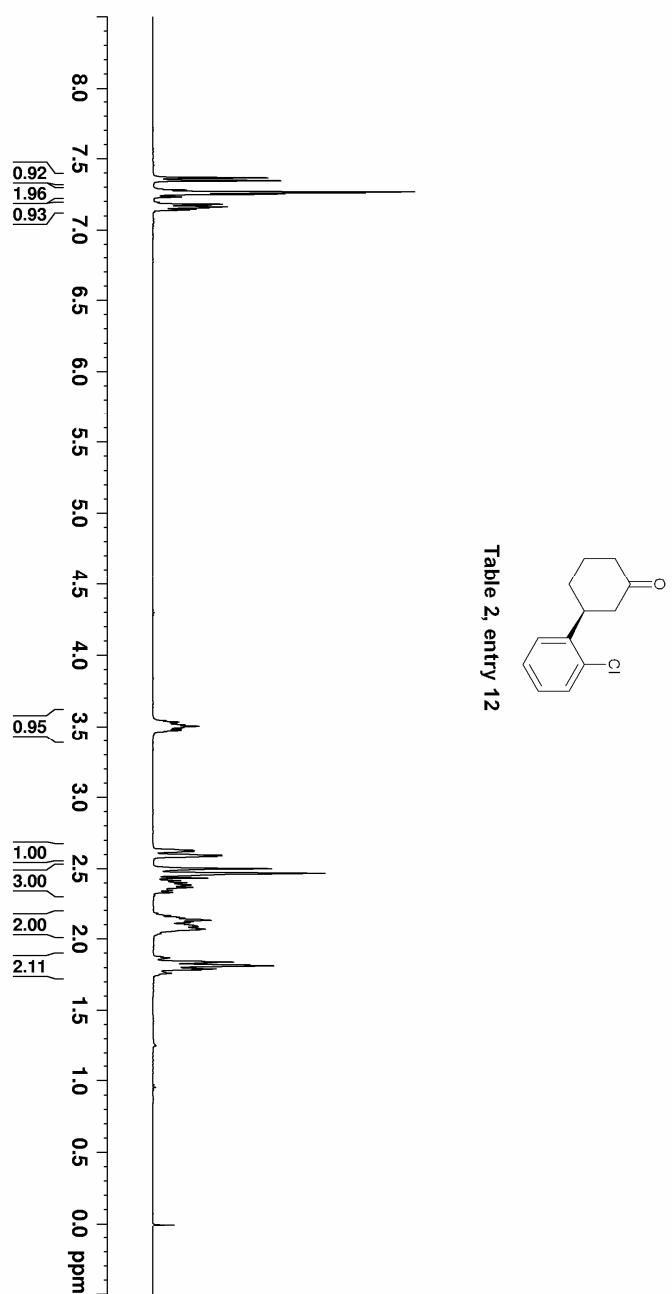
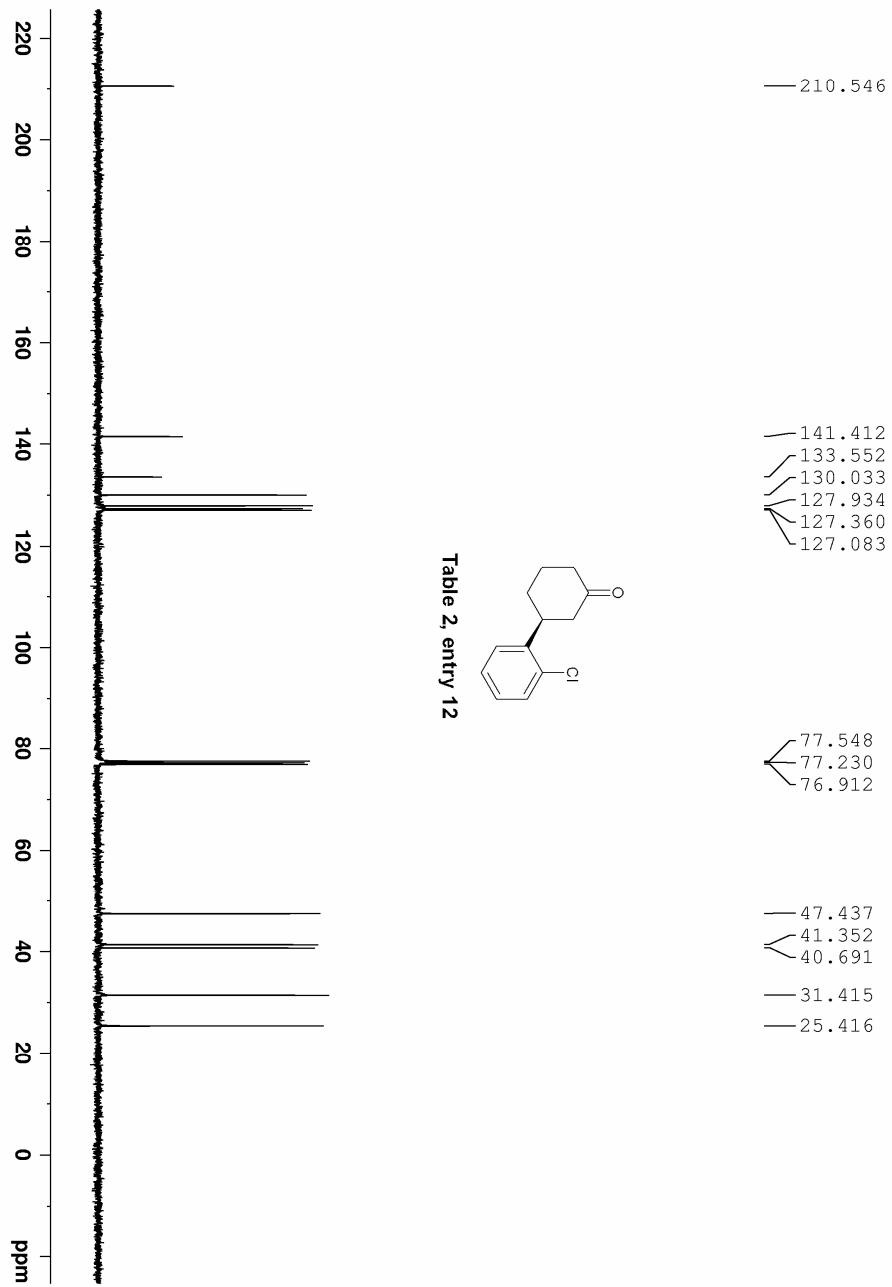
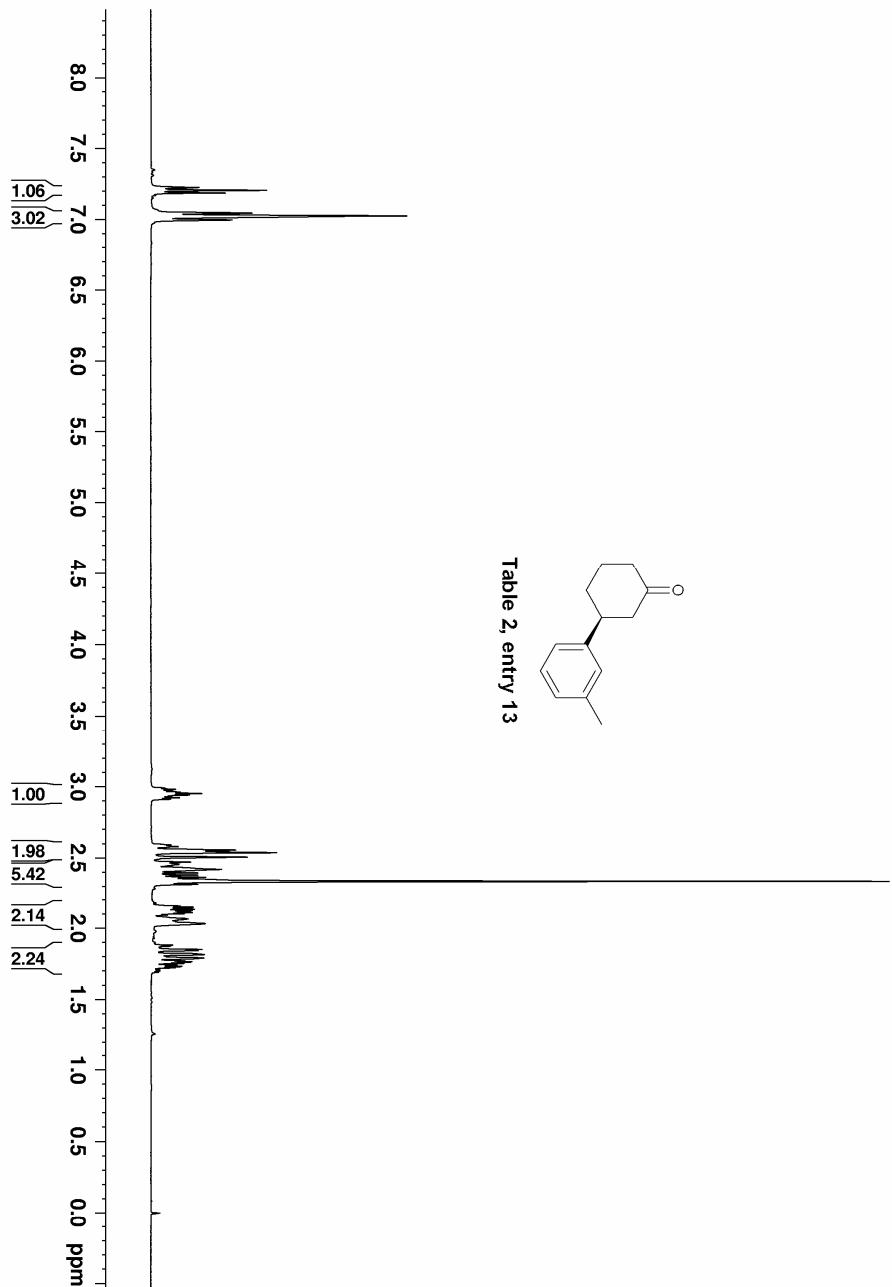


Table 2, entry 12





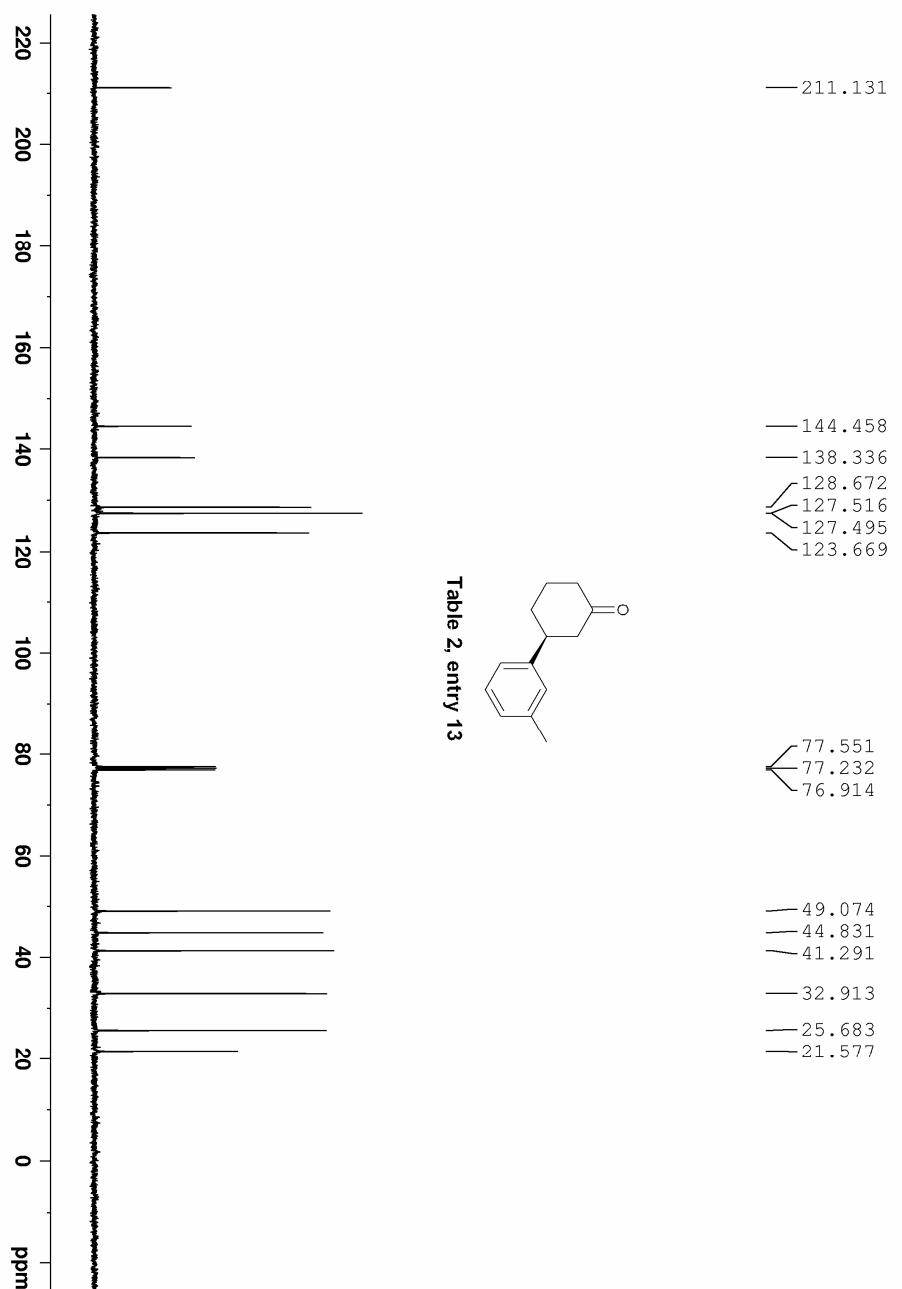


Table 2, entry 13

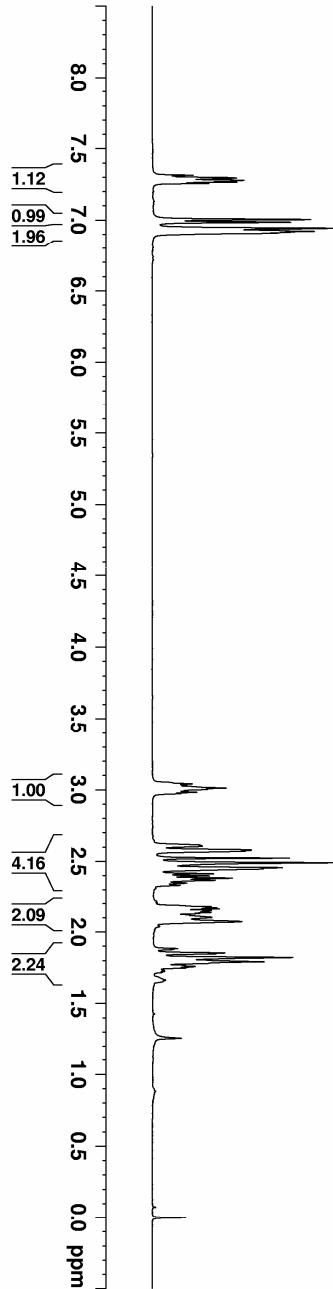
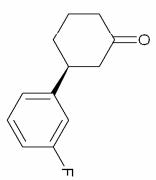
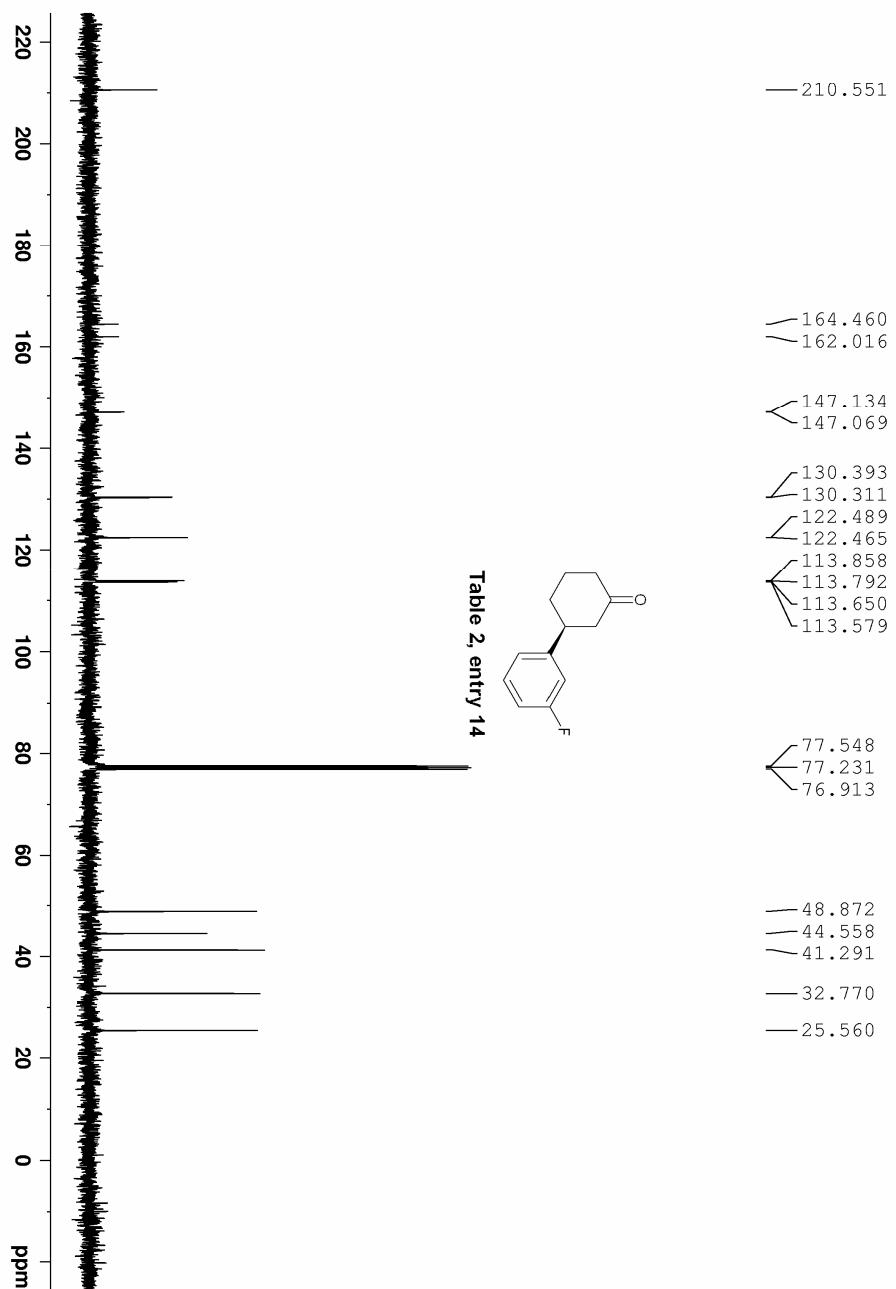
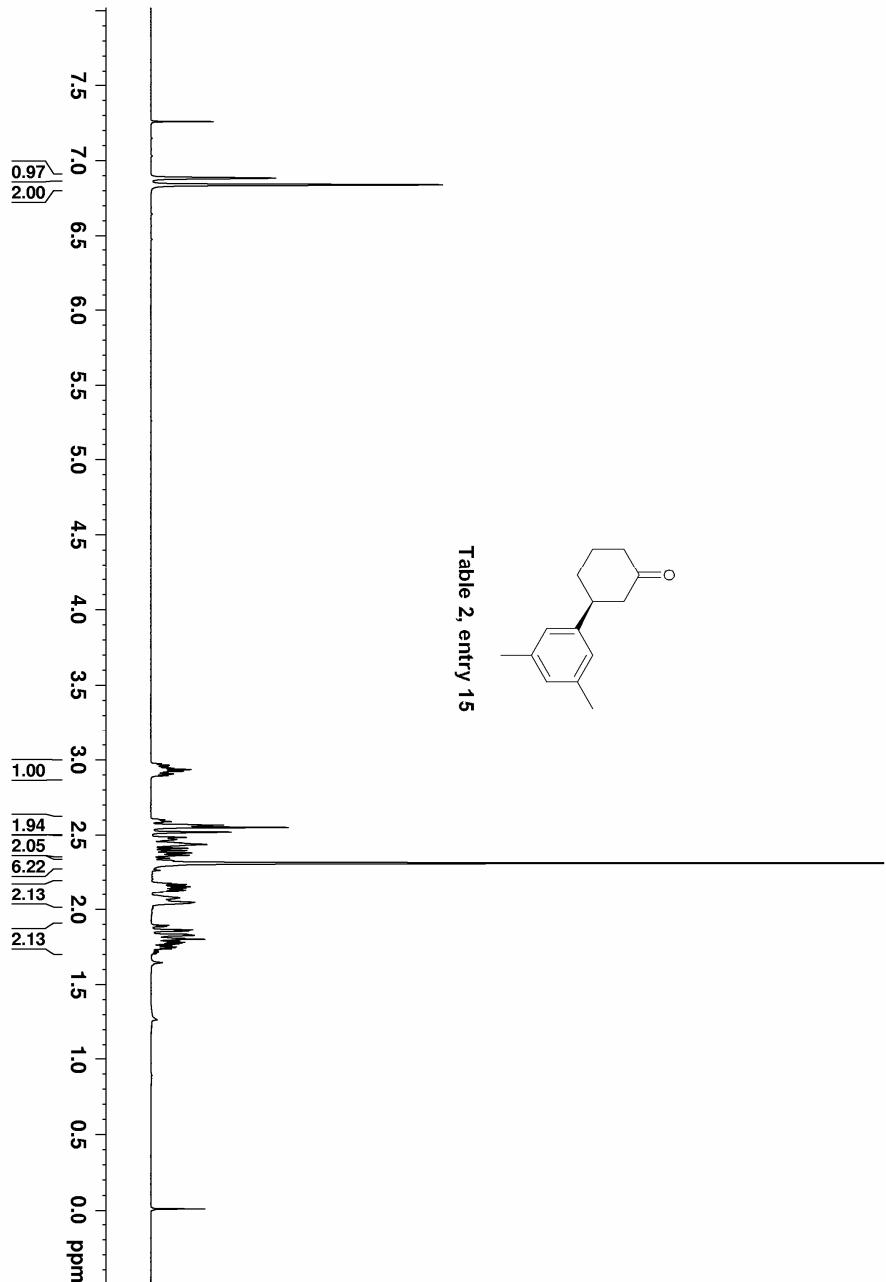
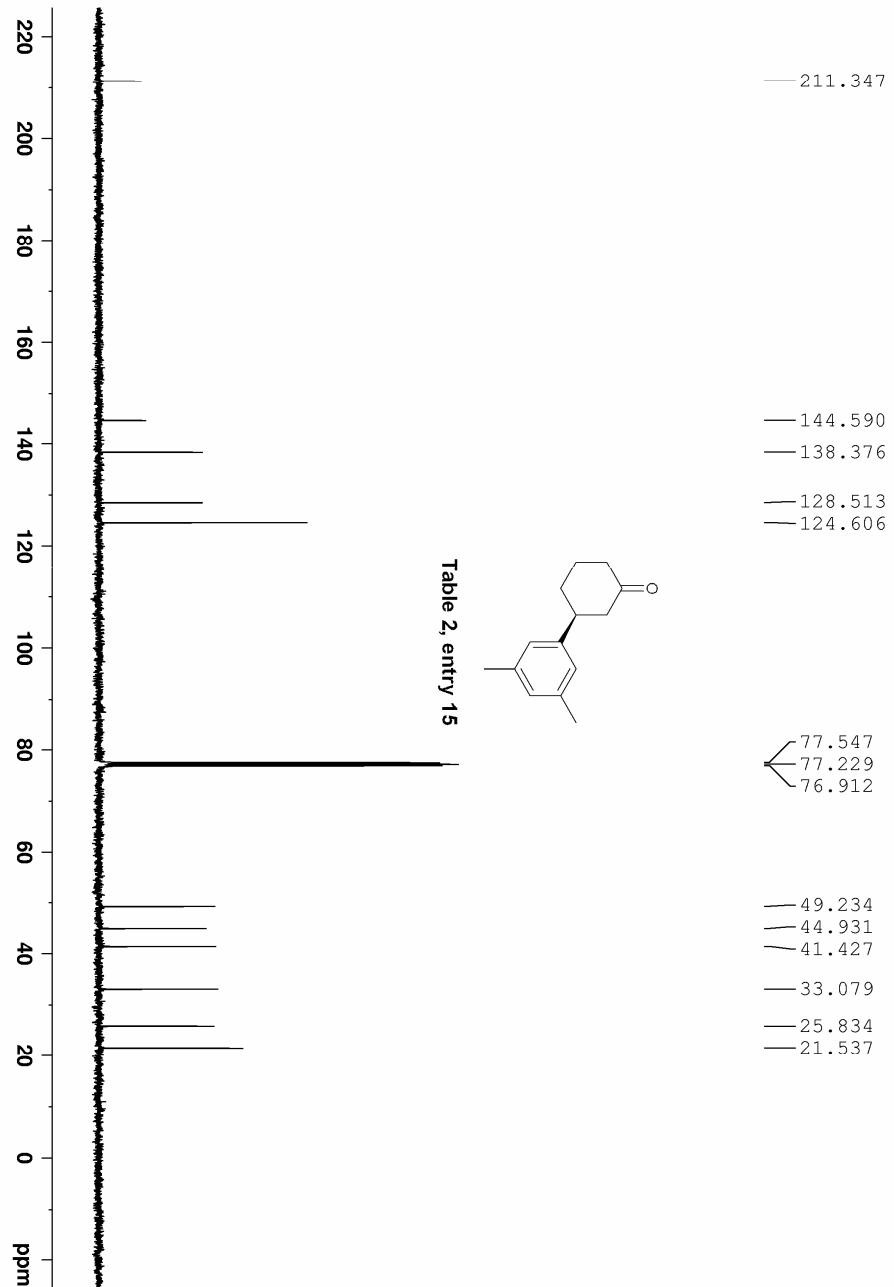


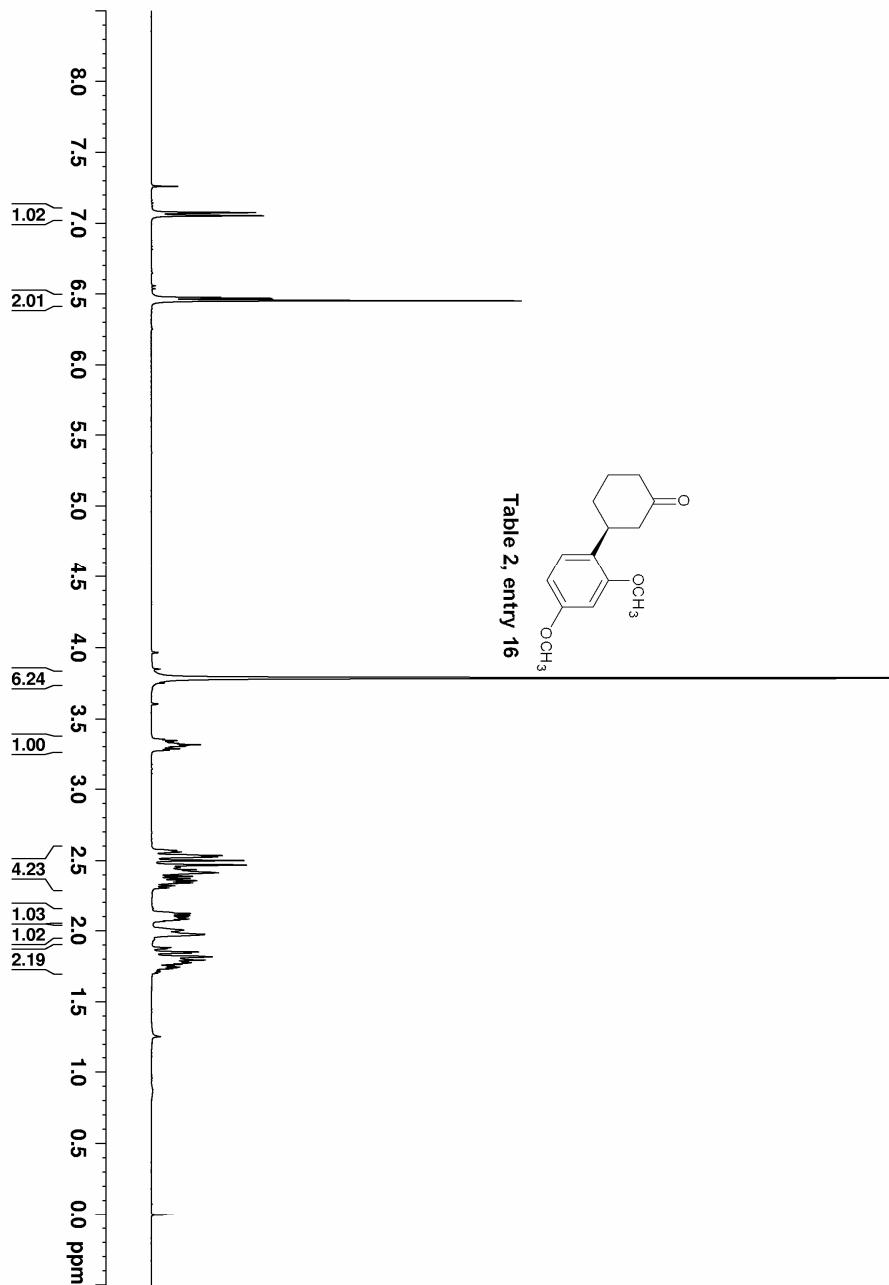
Table 2, entry 14

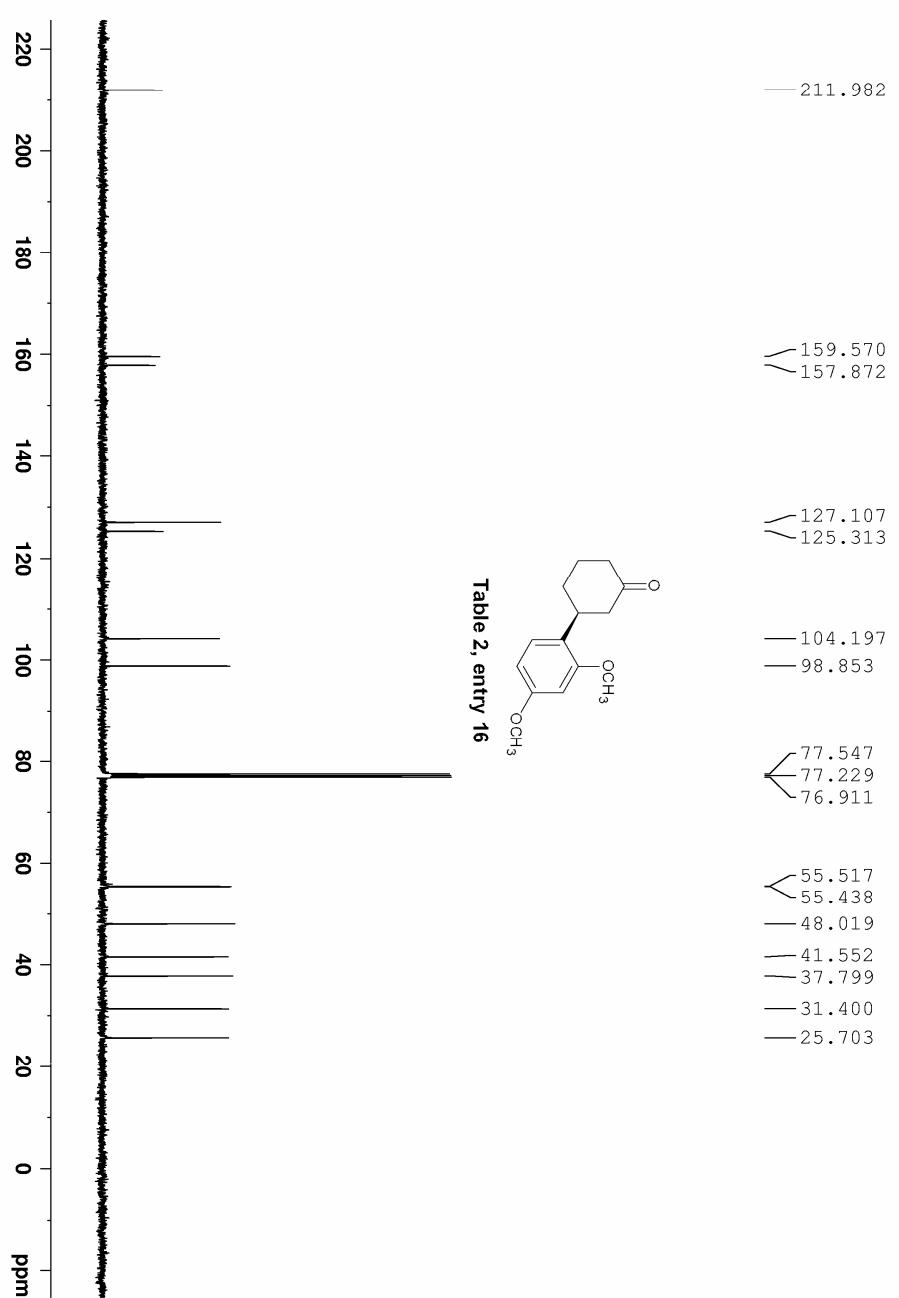












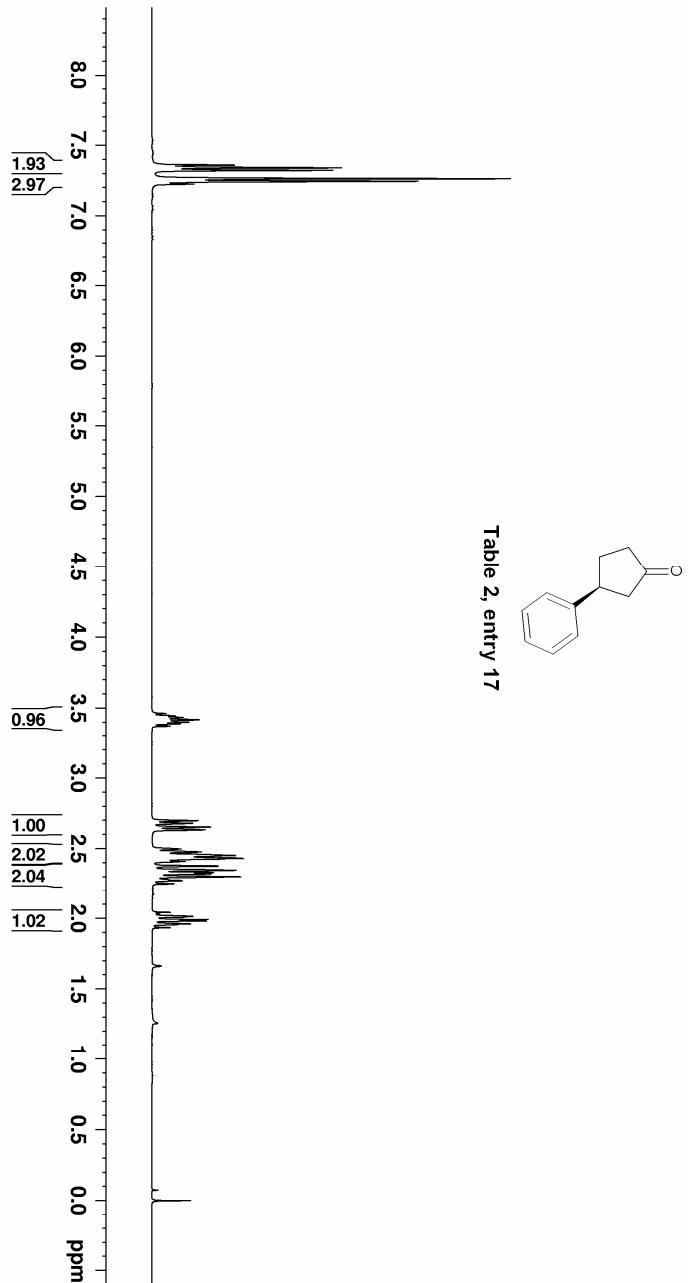
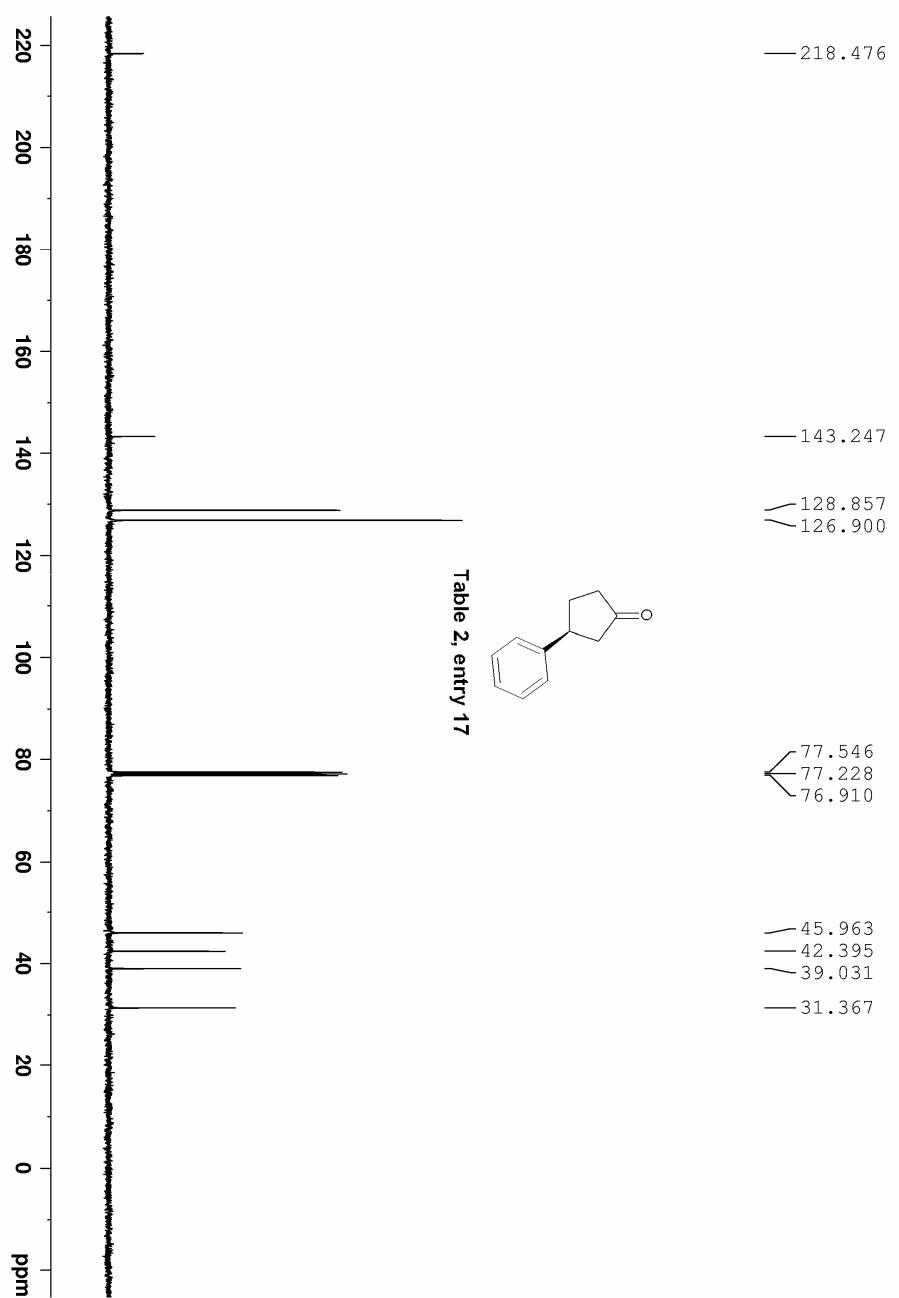
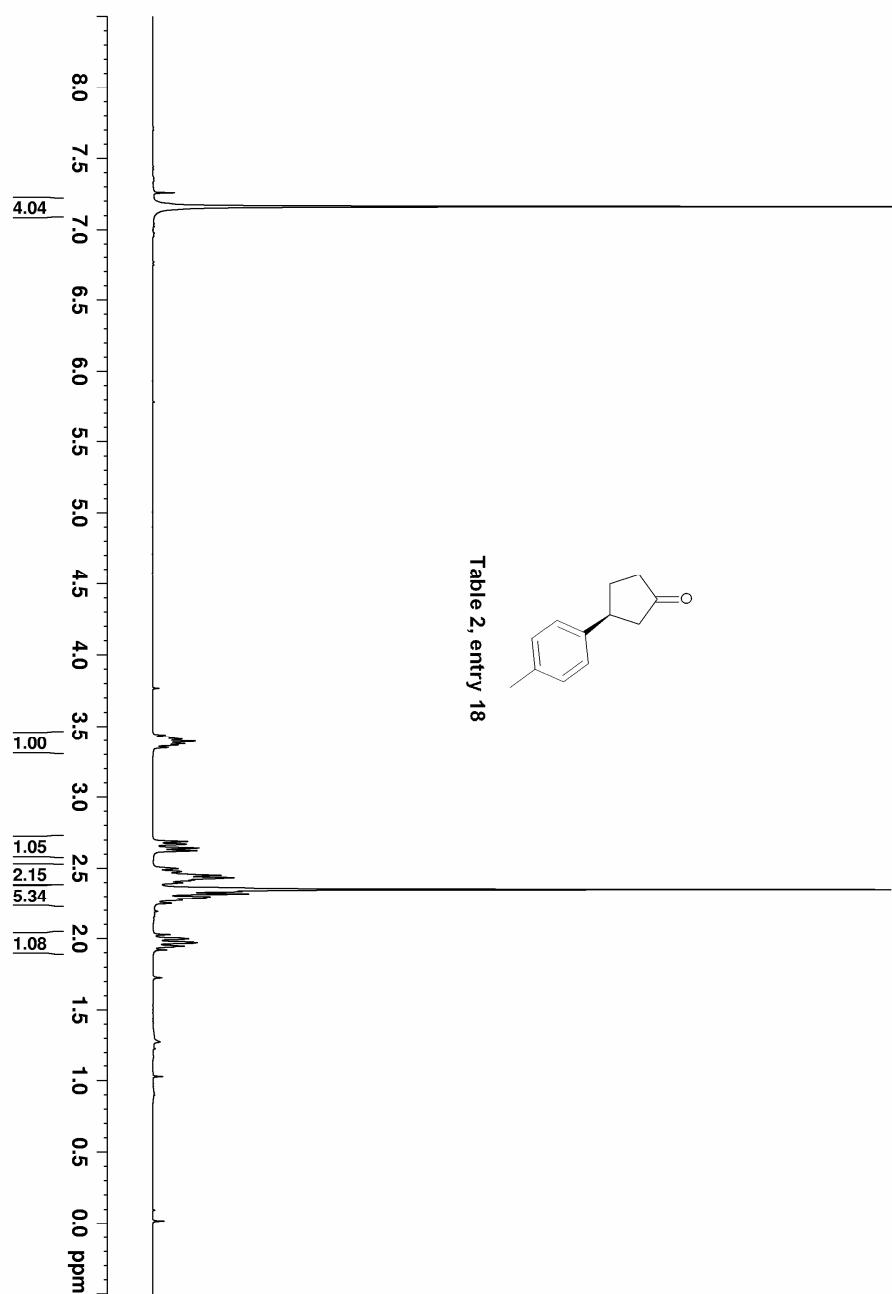
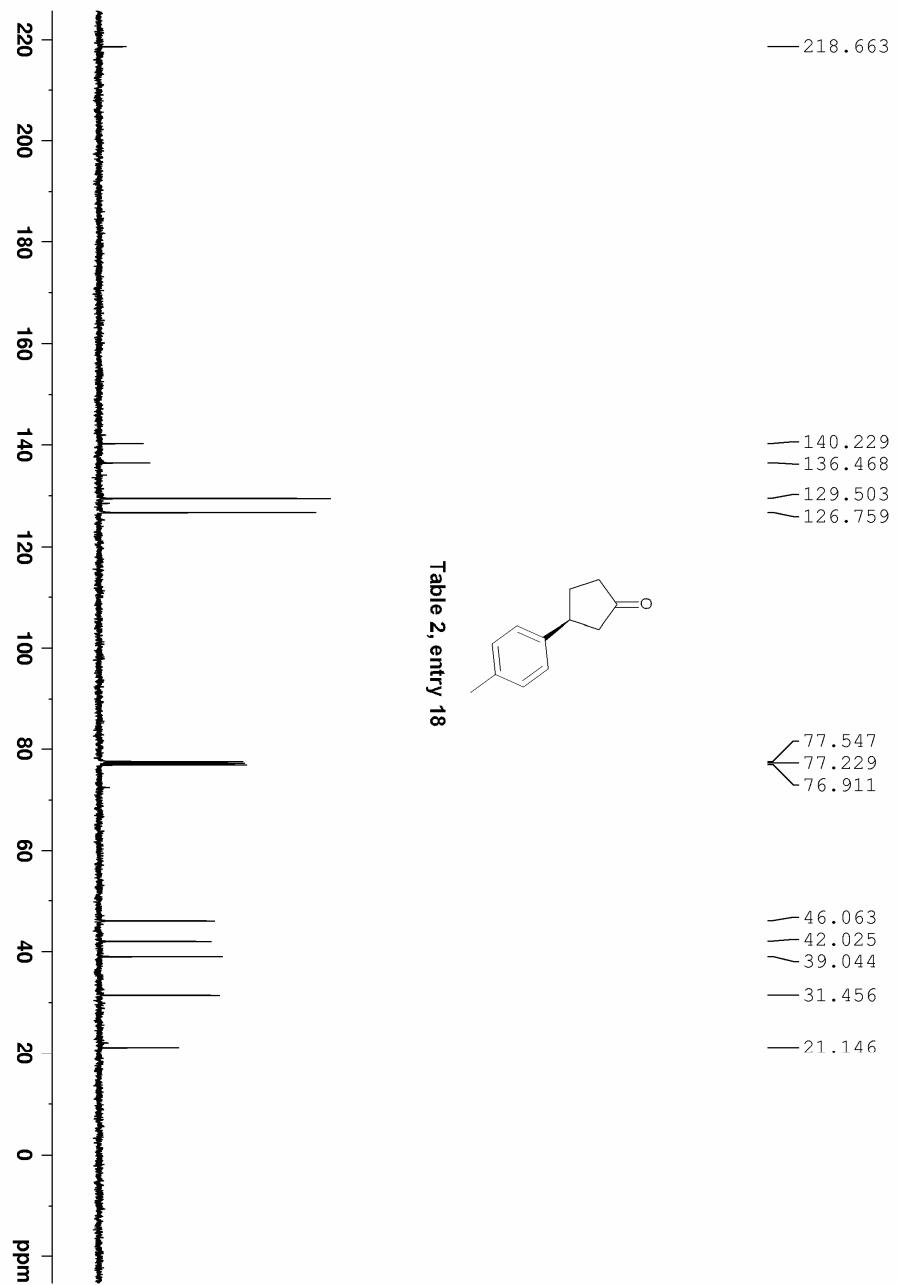


Table 2, entry 17







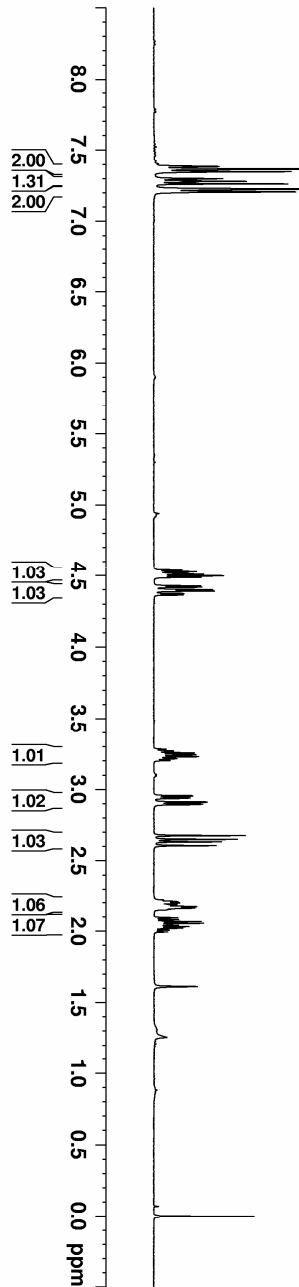
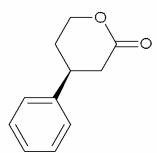
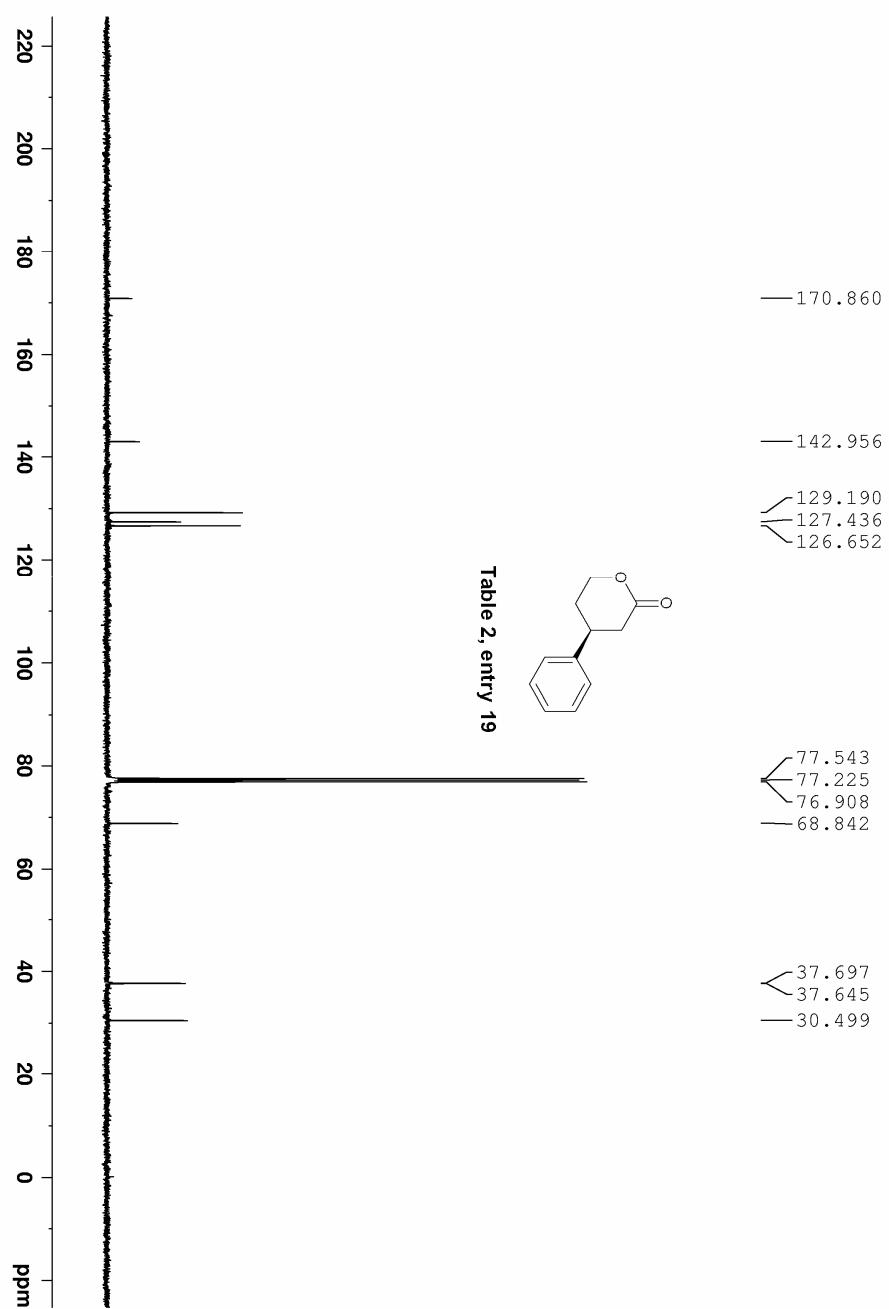
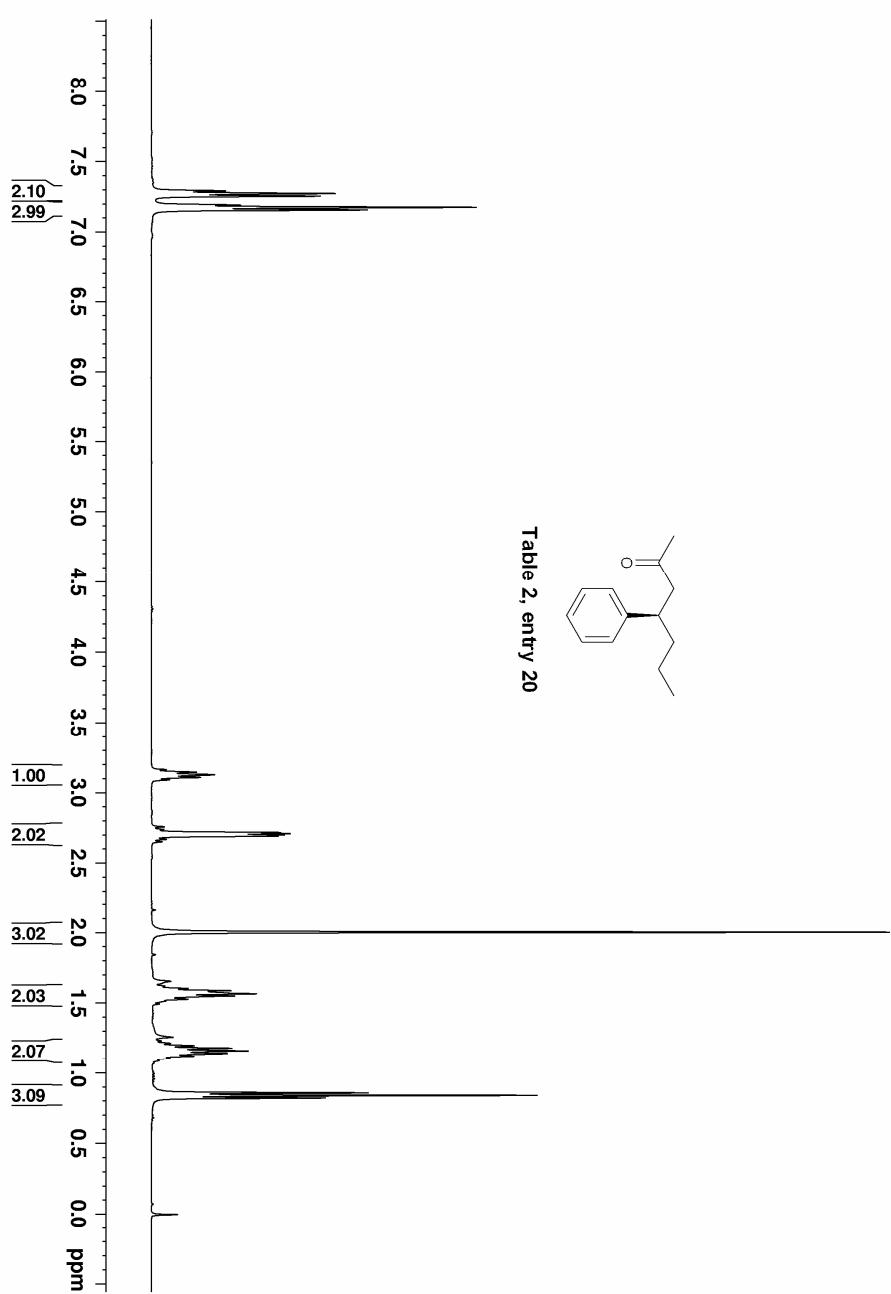
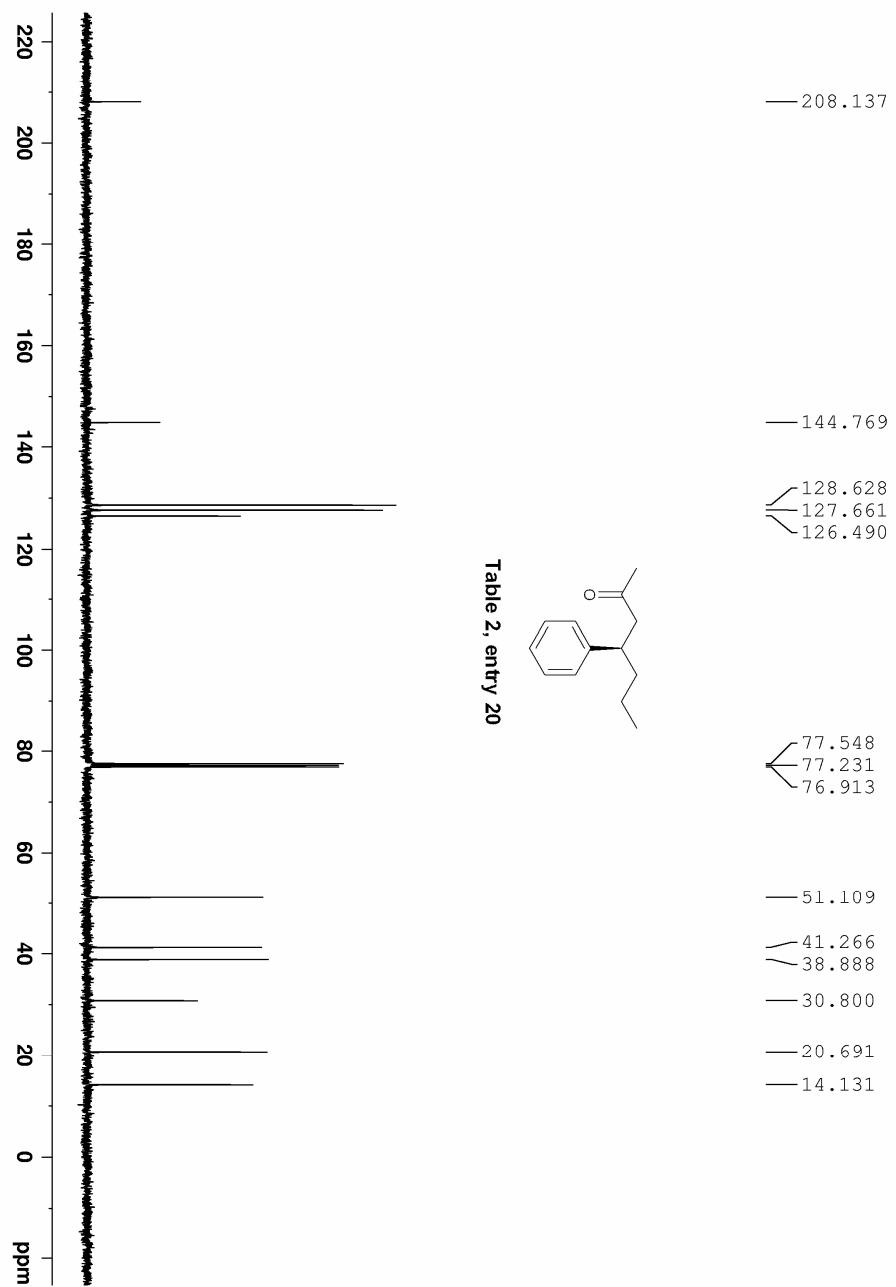


Table 2, entry 19









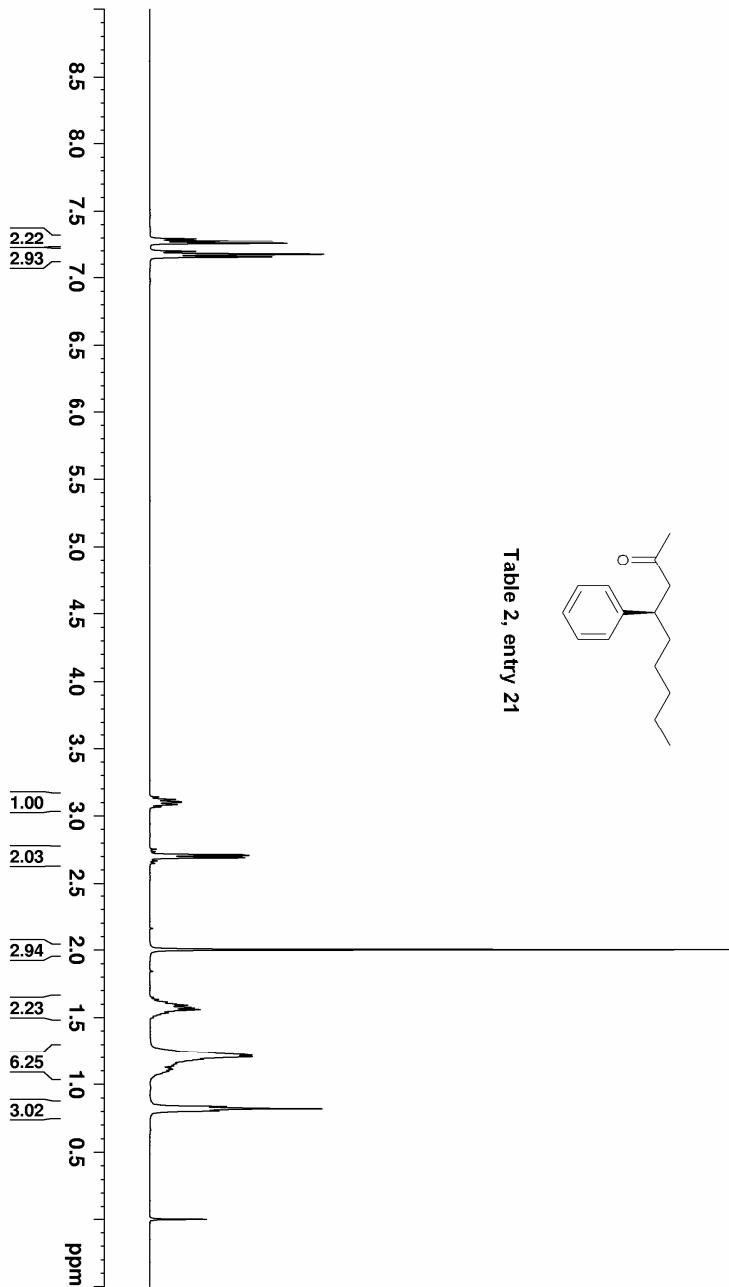


Table 2, entry 21

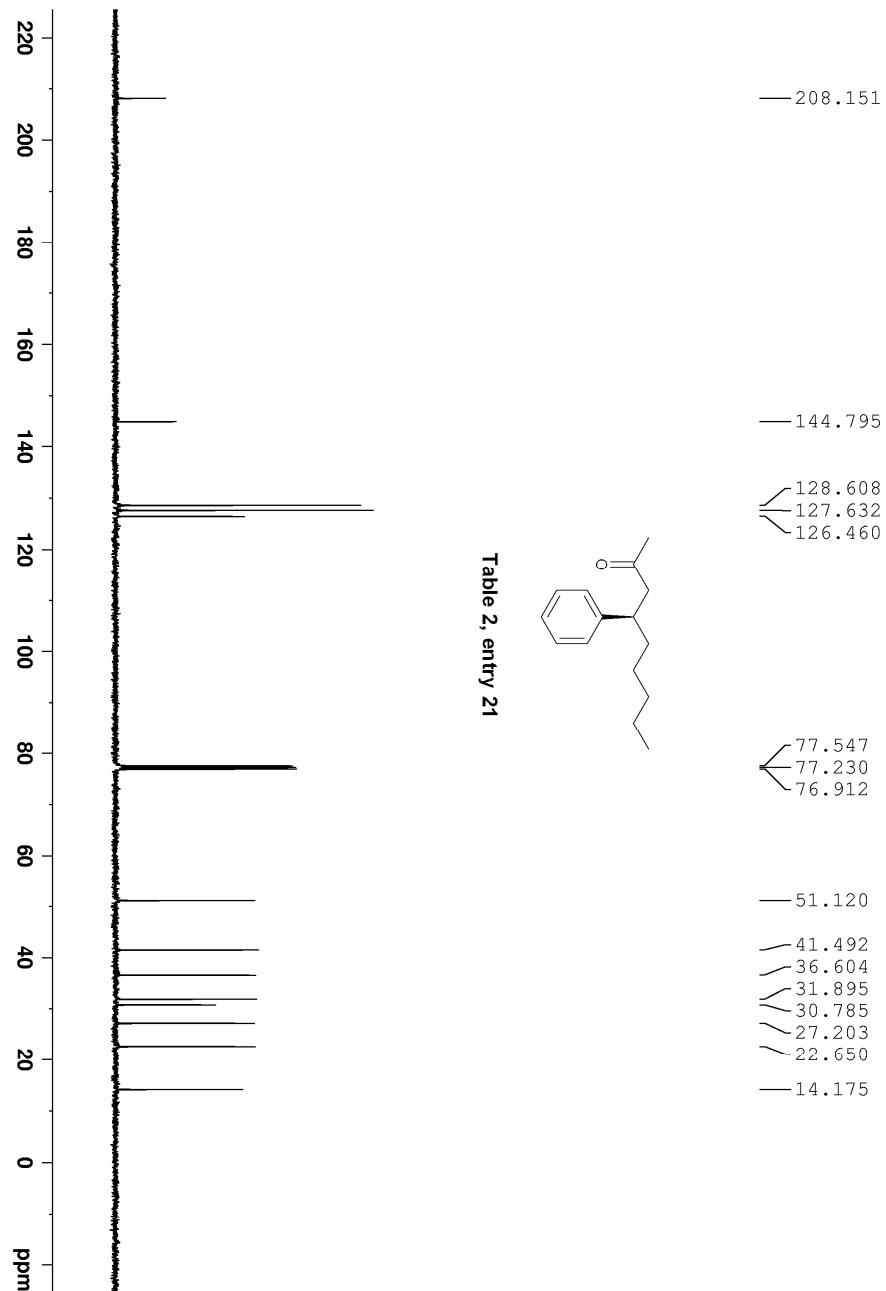


Table 2, entry 21