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Supplementary Information

Indium Triflate-Catalyzed Stereoselective Tandem Intramolecular Conjugate Addition of Secondary Amines to α,β-Bisenones

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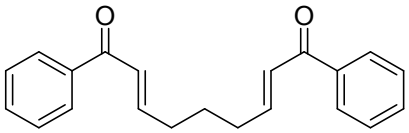
1. Experimental Part

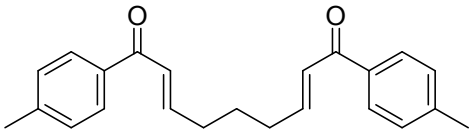
A. General Methods.

Air and/or moisture sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. All compounds were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled (1,4-dioxane and toluene over sodium) or dried by passing through an alumina column. Thin layer chromatography was carried out on glass plates coated with silica gel SiO_2 60 F_{254} from Merck; visualization with a UV lamp (254 nm) or by staining with a *p*-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO_2 60 (0.040–0.063 μm, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL ECP-400 spectrometer at 400 MHz (^1H) or 100 MHz (^{13}C) at 294 K. Chemical shifts are reported in ppm relative to the residual protiated solvent ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). All ^{13}C NMR spectra are proton decoupled. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), and br (broad). Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectrometry (HRMS) was measured on a JEOL JMS-700 spectrometer. Mass peaks are reported in *m*/*z* units.

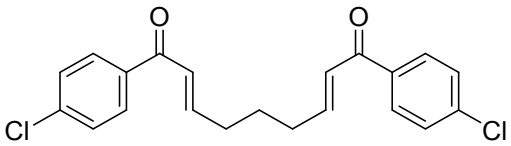
B. Substrate Syntheses



(2*E*,7*E*)-1,9-Diphenylnona-2,7-diene-1,9-dione (1a). Spectral data matched literature references.[S1, S2, S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 7.3 Hz, 4H), 7.56 (t 7.4 Hz, 2H), 7.46 (t, 7.3 Hz, 4H), 7.06 (td, 6.5, 15.3 Hz, 2H), 6.92 (d, 15.3 Hz, 2H), 2.40 (q, 7.3 Hz, 4H), 1.75-1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 148.3, 137.6, 132.5, 128.4, 128.3, 126.3, 32.0, 26.5.

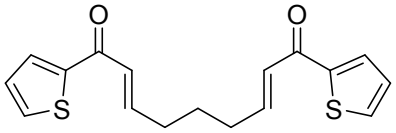


(2*E*,7*E*)-1,9-Di-*p*-tolylnona-2,7-diene-1,9-dione (1b). Spectral data matched literature references.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 8.0 Hz, 4H), 7.26 (d, 8.0 Hz, 4H), 7.05 (td, 6.5, 15.3 Hz, 2H), 6.91 (d, 15.3 Hz, 2H), 2.41 (s, 6H), 2.39, (q, 7.3 Hz, 4H), 1.74-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 147.9, 143.4, 135.1, 129.1, 128.5, 126.3, 32.0, 26.6, 21.5.



(2*E*,7*E*)-1,9-Bis(4-chlorophenyl)nona-2,7-diene-1,9-dione (1c). Spectral data matched literature references.[S2, S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 8.4 Hz, 4H), 7.43 (d, 8.4 Hz,

4H), 7.06 (td, 6.9, 15.3 Hz, 2H), 6.87 (d, 15.3 Hz, 2H), 2.39, (q, 7.3 Hz, 4H), 1.73-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 148.9, 139.0, 135.9, 129.8, 128.7, 125.8, 32.0, 26.5.

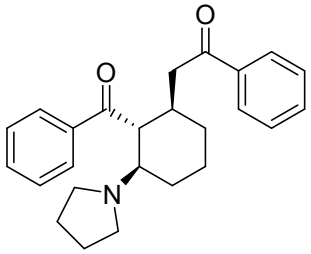


(2*E*,7*E*)-1,9-Di(thiophen-2-yl)nona-2,7-diene-1,9-dione (1d). Spectral data matched literature references.[S4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, 1.1, 4.0 Hz, 2H), 7.64 (dd, 1.1, 4.7 Hz, 2H), 7.14 (dd, 3.6, 4.7 Hz, 2H), 7.10 (td, 6.9, 15.7 Hz, 2H), 6.87 (td, 1.4, 15.3 Hz, 2H), 2.38, (q, 8.4 Hz, 4H), 1.73-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.8, 147.5, 144.8, 133.7, 131.7, 128.0, 125.7, 31.7, 26.4.

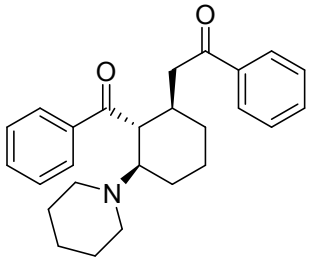
C. General procedure for Tandem Conjugate Addition and Intramolecular Michael Cyclization:

To a mixture of α,β-bisenone (**1**) (1.0 mmol), LiCl (2.0 mmol) and $In(OTf)_3$ (5 mol %)) in THF (3 mL) was added secondary amine (**2**) (1.1 mmol). The resulting mixture was allowed to stir at room temperature for the specified time (Table 2). After completion of the reaction (indicated by TLC), the mixture was quenched with a H_2O (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined, washed with brine (8 mL), dried over anhydrous $MgSO_4$. Then the solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography using ethyl acetate/hexane gradients to afford pure product **3** (Table 2).

D. Product Characterization

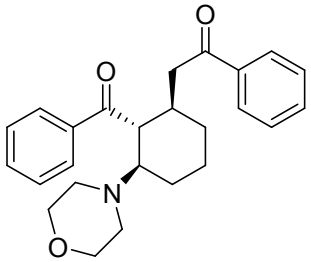


2-(2-Benzoyl-3-(pyrrolidin-1-yl)cyclohexyl)-1-phenylethanone (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 7.3 Hz, 2H), 7.83 (d, 7.3 Hz, 2H), 7.39-7.53 (m, 6H), 3.45(t, 10.2 Hz, 1H), 3.11 (dt, 3.3, 10.9 Hz, 1H), 2.97 (d, 10.9 Hz, 1H), 2.43-2.56 (m, 5H), 1.77- 1.88 (m, 2H), 1.38-1.46 (m, 2H), 1.25-1.34 (m, 5H), 0.80-0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 199.2, 139.8, 136.6, 132.9, 132.1, 128.5, 128.3, 128.2, 127.4, 62.9, 54.5, 47.6, 43.9, 38.1, 31.2, 29.6, 24.2, 23.8, 23.4; IR (neat, cm^{-1}): 3065, 2926, 1688, 1666, 1596, 1579, 1446, 1267, 1217; HRMS-EI(m/z): [M^+] calcd. for $C_{25}H_{29}NO_2$, 375.2198; found, 375.2197.

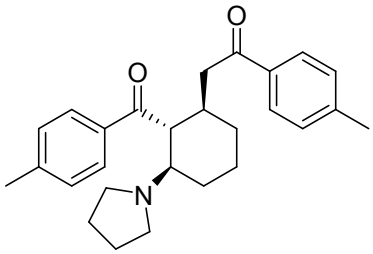


2-(2-Benzoyl-3-(piperidin-1-yl)cyclohexyl)-1-phenylethanone (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 7.3 Hz, 2H), 7.85 (d, 7.3 Hz, 2H), 7.40-7.53 (m, 6H), 3.52(t, 10.2 Hz, 1H), 2.99 (d, 10.9 Hz, 1H), 2.81 (dt, 3.3, 10.9 Hz, 1H), 2.48-2.56 (m, 4H), 2.22 (t, 10.2 Hz, 2H), 1.75-1.85 (m, 3H), 1.24-1.30 (m, 2H), 1.04-1.15 (m, 5H), 0.80 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 199.3, 140.3, 136.6, 132.9, 132.0, 128.5, 128.3, 128.2, 127.5, 69.4, 52.8, 50.1,

44.0, 37.8, 31.0, 25.8, 24.6, 24.4, 23.9; HRMS-EI(m/z): [M^+] calcd. for $C_{26}H_{31}NO_2$, 389.5355; found, 389.5354.

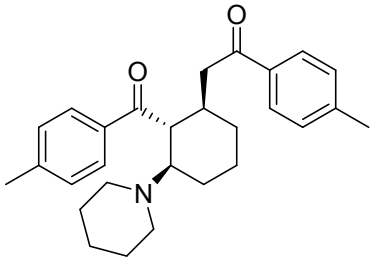


2-(2-Benzoyl-3-morpholinocyclohexyl)-1-phenylethanone (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 7.3 Hz, 2H), 7.84 (d, 7.3 Hz, 2H), 7.40-7.55 (m, 6H), 3.54(t, 10.2 Hz, 1H), 3.25-3.29 (m, 2H), 2.96-3.03 (m, 3H), 2.83 (dt, 3.3, 10.9 Hz, 1H), 2.50-2.61 (m, 4H), 2.28-2.33 (m, 2H), 1.78-1.89 (m, 3H), 1.22-1.34 (m, 2H), 1.06-1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 199.1, 140.2, 136.6, 132.9, 132.3, 128.5, 128.4, 128.2, 127.4, 68.8, 66.8, 52.5, 49.0, 43.7, 37.7, 30.9, 24.3, 24.0; HRMS-EI(m/z): [M^+] calcd. for $C_{25}H_{29}NO_3$, 391.2147; found, 391.2147.

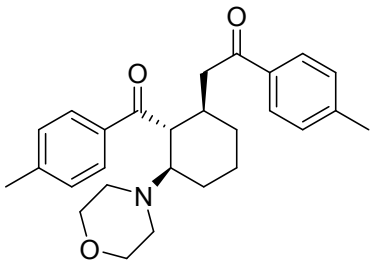


2-(2-(4-Methylbenzoyl)-3-(pyrrolidin-1-yl)cyclohexyl)-1-p-tolylethanone (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 8.0 Hz, 2H), 7.71 (d, 8.0 Hz, 2H), 7.19-7.26 (m, 4H), 3.42 (t, 10.6 Hz, 1H), 3.11 (dt, 3.3, 10.6 Hz, 1H), 2.91 (d, 10.6 Hz, 1H), 2.42-2.51 (m, 6H), 2.39 (s, 3H), 2.37 (s, 3H), 1.70- 1.89 (m, 3H), 1.40-1.48 (m, 2H), 1.25-1.36 (m, 4H), 1.05-1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 199.0, 143.6, 142.9, 137.2, 134.1, 129.1, 129.0, 128.3, 127.7, 62.7,

54.3, 47.7, 43.9, 38.5, 31.2, 24.2, 23.9, 23.5, 21.5, 21.4; HRMS-EI(m/z): [M^+] calcd. for $C_{27}H_{33}NO_2$, 403.2511; found, 403.2510.

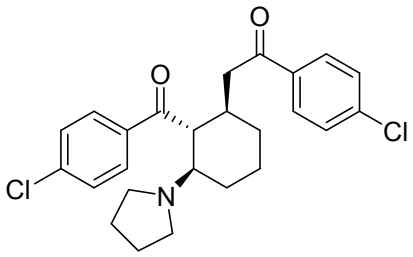


2-(2-(4-Methylbenzoyl)-3-(piperidin-1-yl)cyclohexyl)-1-p-tolylethanone (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, 8.0 Hz, 2H), 7.74 (d, 8.0 Hz, 2H), 7.19-7.26 (m, 4H), 3.48 (t, 10.2 Hz, 1H), 2.94 (d, 11.3 Hz, 1H), 3.11 (dt, 3.3, 11.3 Hz, 1H), 2.44-2.54 (m, 4H), 2.40 (s, 3H), 2.37 (s, 3H), 2.22 (t, 10.2 Hz, 2H), 1.68-1.84 (m, 3H), 1.23-1.28 (m, 2H), 1.01-1.15 (m, 5H), 0.85 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 199.0, 143.6, 142.6, 137.7, 134.1, 129.1, 128.9, 128.4, 127.6, 69.1, 52.6, 50.1, 44.0, 38.1, 31.0, 25.9, 24.6, 24.4, 23.9, 21.5, 21.4; HRMS-EI(m/z): [M^+] calcd. for $C_{28}H_{35}NO_2$, 417.2668; found, 417.2665.

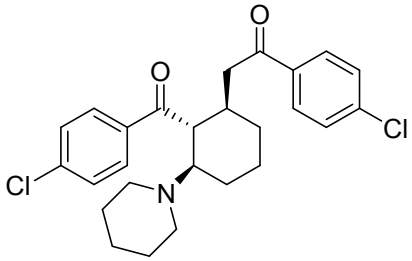


2-(2-(4-Methylbenzoyl)-3-morpholinocyclohexyl)-1-p-tolylethanone (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 8.0 Hz, 2H), 7.73 (d, 8.0 Hz, 2H), 7.20- 7.26 (m, 4H) 3.49 (t, 10.2 Hz, 1H), 3.26-3.32 (m, 2H), 2.96-3.04 (m, 2H), 2.95 (d, 11.3, 1H) 2.82 (dt, 3.3, 10.9 Hz, 1H), 2.46-2.59 (m, 4H), 2.40 (s, 3H), 2.37 (s, 3H), 2.29-2.34 (m, 2H), 1.75-1.88 (m, 3H), 1.25-1.31 (m, 2H),

1.05-1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.6, 198.8, 143.6, 143.0, 137.6, 134.1, 129.15, 129.12, 128.3, 127.6, 68.5, 66.8, 52.2, 49.0, 43.7, 37.9, 30.9, 24.3, 24.0, 21.5, 21.4; HRMS-EI(m/z): [M^+] calcd. for $C_{27}H_{33}NO_3$, 419.2460; found, 419.2457.

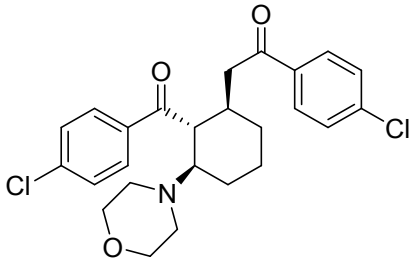


2-(2-(4-Chlorobenzoyl)-3-(pyrrolidin-1-yl)cyclohexyl)-1-(4chlorophenyl)ethanone (3g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, 8.7 Hz, 2H), 7.75 (d, 8.7 Hz, 2H), 7.37-7.41 (m, 4H), 3.40 (t, 10.2 Hz, 1H), 3.08 (dt, 3.3, 10.9 Hz, 1H), 2.87 (d, 11.3 Hz, 1H), 2.41-2.53 (m, 6H), 1.73-1.87 (m, 3H), 1.36-1.46 (m, 2H), 1.24-1.33 (m, 4H), 1.07-1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2, 197.9, 139.4, 138.6, 138.0, 134.9, 129.6, 128.9, 128.8, 128.6, 63.1, 54.4, 47.7, 43.6, 38.1, 31.1, 29.6, 24.1, 23.8, 23.5; HRMS-EI(m/z): [M^+] calcd. for $C_{25}H_{27}Cl_2NO_2$, 443.1419; found, 443.1418.

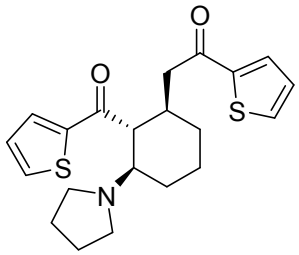


2-(2-(4-Chlorobenzoyl)-3-(piperidin-1-yl)cyclohexyl)-1-(4-chlorophenyl)ethanone (3h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 8.4 Hz, 2H), 7.77 (d, 8.7 Hz, 2H), 7.38-7.44 (m, 4H), 3.47 (t, 10.2 Hz, 1H), 2.89 (d, 10.9 Hz, 1H), 2.78 (dt, 3.3, 10.9 Hz, 1H), 2.45-2.53 (m, 4H), 2.22 (t, 9.1

Hz, 2H), 1.72-1.85 (m, 3H), 1.22-1.29 (m, 2H), 1.03-1.18 (m, 5H), 0.833 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5, 198.0, 139.4, 138.5, 134.9, 129.6, 128.9, 128.8, 128.6, 69.6, 52.6, 50.1, 43.8, 37.8, 31.0, 25.9, 24.5, 24.4, 23.9; HRMS-EI(m/z): [M^+] calcd. for $C_{26}H_{29}Cl_2NO_2$, 457.1575; found, 457.1576.

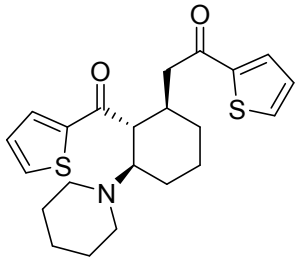


2-(2-(4-Chlorobenzoyl)-3-morpholinocyclohexyl)-1-(4-chlorophenyl)ethanone (3i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 8.7 Hz, 2H), 7.76 (d, 8.7 Hz, 2H), 7.44 (d, 8.7 Hz, 2H) 7.39 (d, 8.4 Hz, 2H), 3.49 (t, 10.2 Hz, 1H), 3.27-3.32 (m, 2H), 3.01 (brs, 2H), 2.90 (d, 11.3 Hz, 1H), 2.80 (dt, 3.3, 11.3 Hz, 1H), 2.47-2.57 (m, 4H), 2.29-2.34 (m, 2H), 1.74-1.90 (m, 3H), 1.23-1.33 (m, 2H), 1.06-1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.9, 197.8, 139.5, 138.8, 138.3, 134.9, 129.5, 128.9, 128.87, 128.80, 68.9, 66.8, 52.3, 49.0, 43.4, 37.7, 30.9, 24.3, 24.0; HRMS-EI(m/z): [M^+] calcd. for $C_{25}H_{27}Cl_2NO_3$, 459.1368; found, 459.1370.

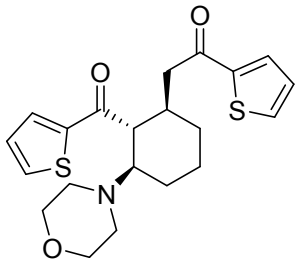


2-(3-(Pyrrolidin-1-yl)-2-(thiophene-2-carbonyl)cyclohexyl)-1-(thiophen-2-yl)ethanone (3j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 3.6 Hz, 1H), 7.60 (d, 5.1 Hz, 1H), 7.56-7.58 (m, 2H),

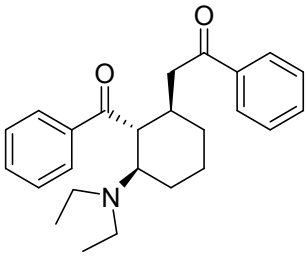
7.10 (t, 4.0 Hz, 1H), 7.07 (t, 4.0 Hz, 1H), 3.14-3.25 (m, 2H), 2.89 (d, 10.9 Hz, 1H), 2.44-2.62 (m, 6H), 1.79-1.91 (m, 3H), 1.46-1.55 (m, 2H), 1.30-1.43 (m, 4H), 1.11-1.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 192.1, 144.3, 133.6, 133.3, 132.3, 131.1, 128.1, 127.9, 62.2, 47.7, 44.4, 38.8, 31.1, 24.1, 23.7, 23.6; HRMS-EI(m/z): [M^+] calcd. for $C_{21}H_{25}NO_2S_2$, 387.1327; found, 387.1330.



2-(3-(Piperidin-1-yl)-2-(thiophene-2-carbonyl)cyclohexyl)-1-(thiophen-2-yl)ethanone (3k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 3.6 Hz, 1H), 7.60 (dd, 1.1, 5.1 Hz, 2H), 7.57 (dd, 1.1, 5.1 Hz, 1H), 7.11 (dd, 3.6, 5.1 Hz, 1H), 7.07 (dd, 4.0, 4.7 Hz, 1H), 3.33 (brt, 9.8 Hz, 1H), 2.92 (d, 10.9 Hz, 1H), 2.85 (brt, 10.6 Hz, 1H), 2.58-2.63 (m, 2H), 2.41-2.49, (m, 2H), 2.25-2.29, (m, 2H), 1.78-1.88 (m, 3H), 1.09-1.32 (m, 7H), 0.97 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 192.2, 144.3, 133.6, 132.9, 132.4, 130.7, 128.1, 127.8, 68.6, 54.7, 50.1, 44.4, 38.4, 30.9, 26.1, 24.7, 24.3, 23.9; HRMS-EI(m/z): [M^+] calcd. for $C_{22}H_{27}NO_2S_2$, 401.1483; found, 401.1487.

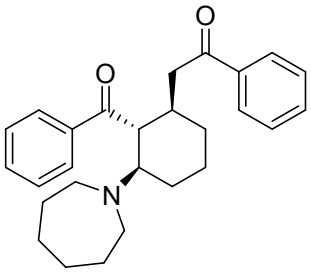


2-(3-Morpholino-2-(thiophene-2-carbonyl)cyclohexyl)-1-(thiophen-2-yl)ethanone (3l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 3.6 Hz, 1H), 7.62 (dd, 1.1, 5.1 Hz, 1H), 7.57-7.59 (m, 2H), 7.11 (dd, 3.6, 4.7 Hz, 1H), 7.06 (dd, 3.6, 4.7 Hz, 1H), 3.36-3.41 (m, 3H), 3.14 (brs, 2H), 2.92 (d, 10.9 Hz, 1H), 2.84-2.89 (m, 1H), 2.63- 2.68 (m, 2H), 2.45-2.52 (m, 2H), 2.35-2.39 (m, 2H), 1.80-1.92 (m, 3H), 1.09-1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 192.0, 144.3, 133.7, 133.3, 132.3, 130.9, 128.1, 128.0, 67.9, 67.1, 54.4, 49.1, 44.1, 38.3, 30.8, 24.2, 24.0; HRMS-EI(m/z): [M^+] calcd. for $C_{21}H_{25}NO_3S_2$, 403.1276; found, 403.1279.



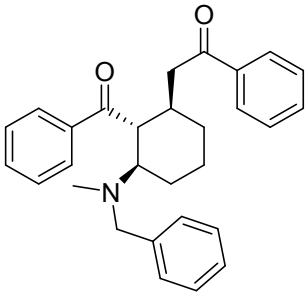
2-(2-benzoyl-3-(diethylamino) cyclohexyl)-1-phenylethanone (3m):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 6.9 Hz, 2H), 7.84 (d, 6.9 Hz, 2H), 7.40-7.53 (m, 6H), 3.54 (t, 10.2 Hz, 1H), 2.95-3.04 (m, 2H), 2.48-2.55 (m, 2H), 2.34-2.43 (m, 2H), 2.16-2.24 (m, 2H), 1.72- 1.84 (m, 3H), 1.20-1.30 (m, 2H), 1.04-1.15 (m, 1H), 0.57 (t, 6.9 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 199.3, 140.3, 136.6, 132.9, 132.1, 128.5, 128.4, 128.3, 127.6, 63.9, 44.3, 43.1, 38.1, 31.1, 24.6, 24.3, 13.4; HRMS-EI (m/z): [M^+] calcd. for $C_{25}H_{31}NO_2$, 377.2355; found, 377.2357.



2-(3-(azepan-1-yl)-2-benzoylcyclohexyl)-1-phenylethanone (3n):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 6.9 Hz, 2H), 7.83 (d, 6.9 Hz, 2H), 7.39-7.55 (m, 6H), 3.49 (t, 10.2 Hz, 1H), 2.90-3.00 (m, 2H), 2.49-2.64 (m, 4H), 2.37-2.43 (m, 2H), 1.73- 1.83 (m, 3H), 1.23-1.34 (m, 4H), 1.04-1.19 (m, 5H), 0.89-0.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 199.3, 139.9, 136.6, 132.9, 132.3, 128.5, 128.4, 128.2, 127.8, 70.4, 52.2, 44.1, 38.3, 31.1, 28.9, 26.2, 24.7, 24.5; HRMS-EI (m/z): [M^+] calcd. for $C_{27}H_{33}NO_2$, 403.2511; found, 403.2513.



2-(2-benzoyl-3-(benzyl (methyl) amino) cyclohexyl)-1-phenylethanone (3o):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 7.3 Hz, 2H), 7.82 (d, 7.3 Hz, 2H), 7.39-7.55 (m, 6H), 7.05-7.10 (m, 3H), 6.80-6.82 (m, 2H), 3.64 (t, 10.2 Hz, 1H), 3.60 (d, 13.1 Hz, 1H), 3.43 (d, 13.1 Hz, 1H), 3.13 (dt, 3.3, 11.3 Hz, 1H), 2.98 (d, 11.3 Hz, 1H), 2.51-2.61 (m, 2H), 1.94-1.98 (m, 1H), 1.96 (s, 3H), 1.78- 1.86 (m, 2H), 1.33-1.45 (m, 2H), 1.10-1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 199.1, 139.4, 139.3, 136.6, 132.9, 132.5, 128.5, 128.4, 128.1, 127.8, 127.7, 126.4, 67.5, 58.4, 43.8, 38.3, 36.5, 31.1, 24.3, 23.4; HRMS-EI (m/z): [M^+] calcd. for $C_{29}H_{31}NO_2$, 425.2355; found, 425.2356.

2. References

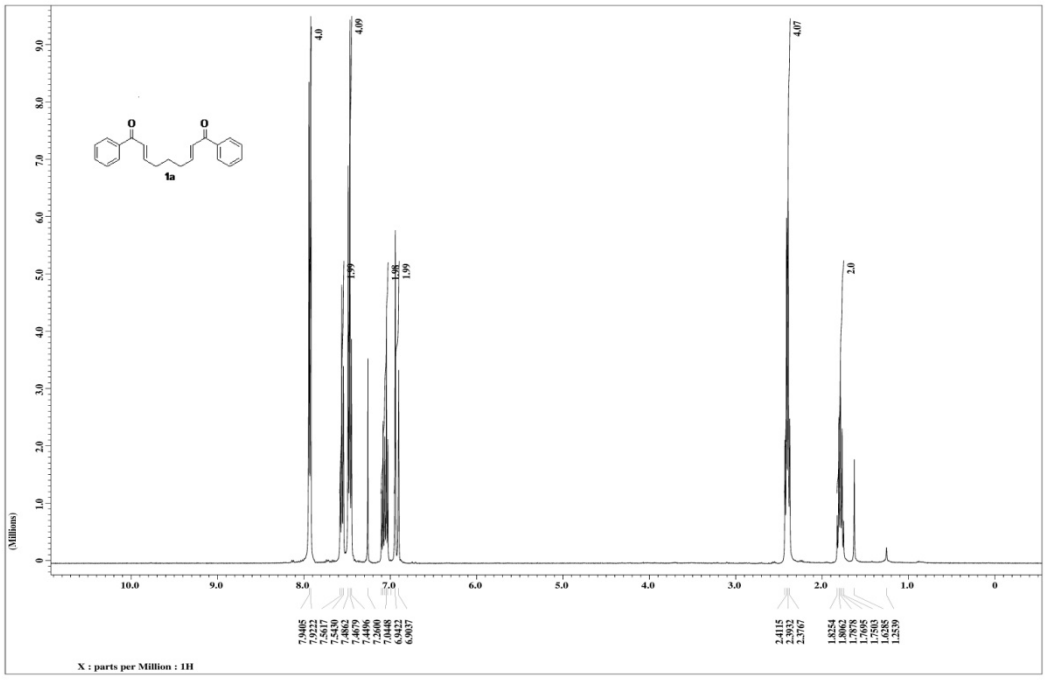
[S1] P. M. Brown, N. Käppel, P. J. Murphy, S. J. Coles, M. B. Hursthouse, *Tetrahedron* **2007**, *63,* 1100-1106.

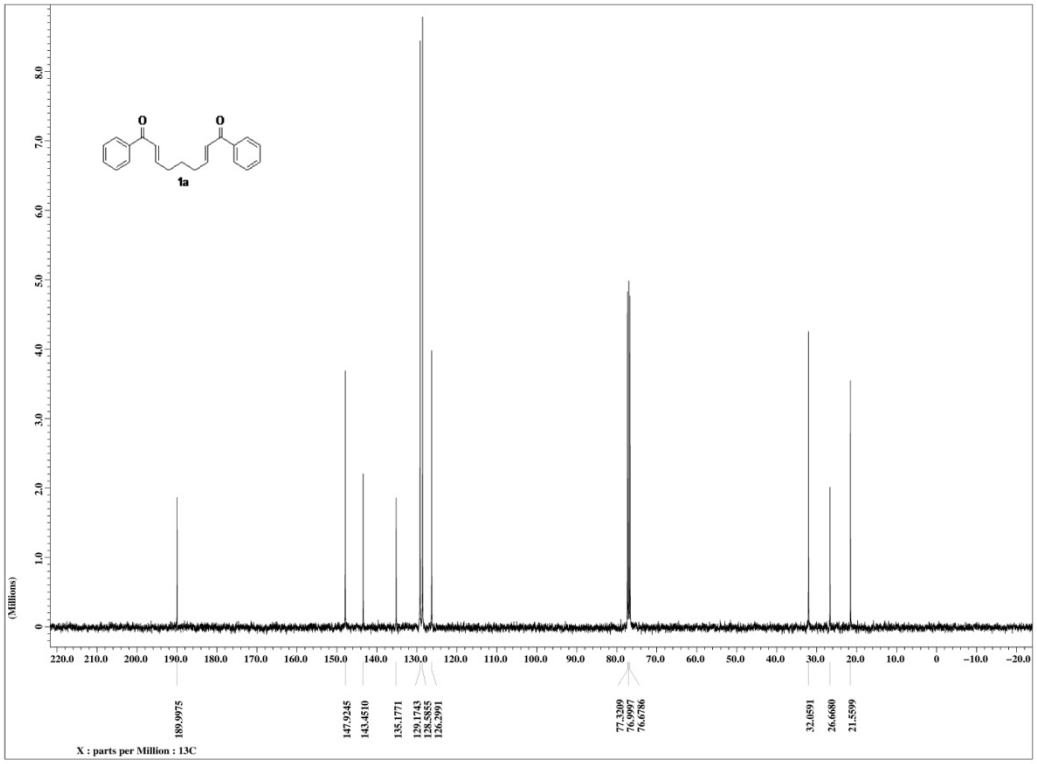
[S2] J. Yang, D. F.Cauble, A. J. Berro, N. L. Bauld, M. J. Krische, *J. Org. Chem.* **2004**, *69*, 7979-7984.

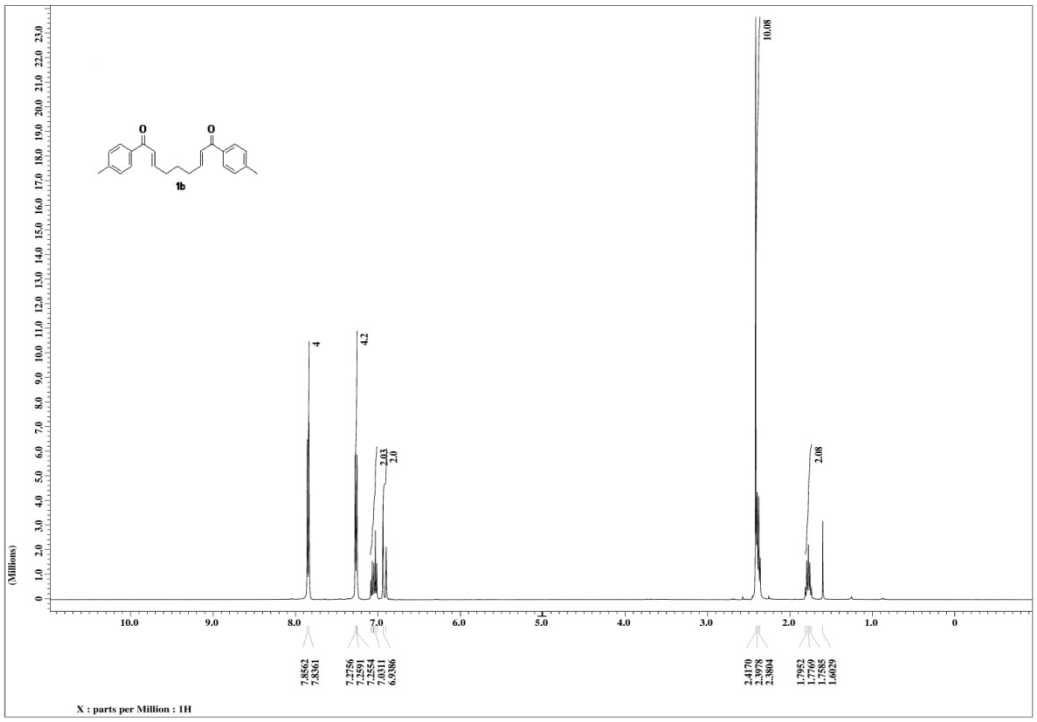
[S3] a) W. J. Chung, S. Higashiya, J. T. Welch, *Tetrahedron Lett.* **2002**, *43*, 5801–5803; b) H. Tsuji, K-i. Yamagata, Y. Itoh, K. Endo, M. Nakamura, E. Nakamura, *Angew. Chem., Int. Ed.* **2007**, *46*, 8060-8062; c) K. Endo, T. Hatakeyama, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 5264-5271; d) Y. Nishimoto, M. Yasuda, A. Baba, *Org. Lett.* **2007**, *9*, 4931-4934; e) H. Tsuji, T. Fujimoto, K. Endo, M. Nakamura, E. Nakamura, *Org. Lett.* **2008**, *10,* 1219-1221; f) J-I. Matsuo, R. Okuno, H. Ishibashi, *Tetrahedron Lett.* **2012**, *53*, 2257-2259.

[S4] L.-C. Wang, A. L. Luis, K. Agapiou, H.-Y. Jang, M. J. Krische, *J. Am. Chem. Soc.* **2002**, *124*, 2402-2403.

3. ^{1}H and ^{13}C NMR Spectra



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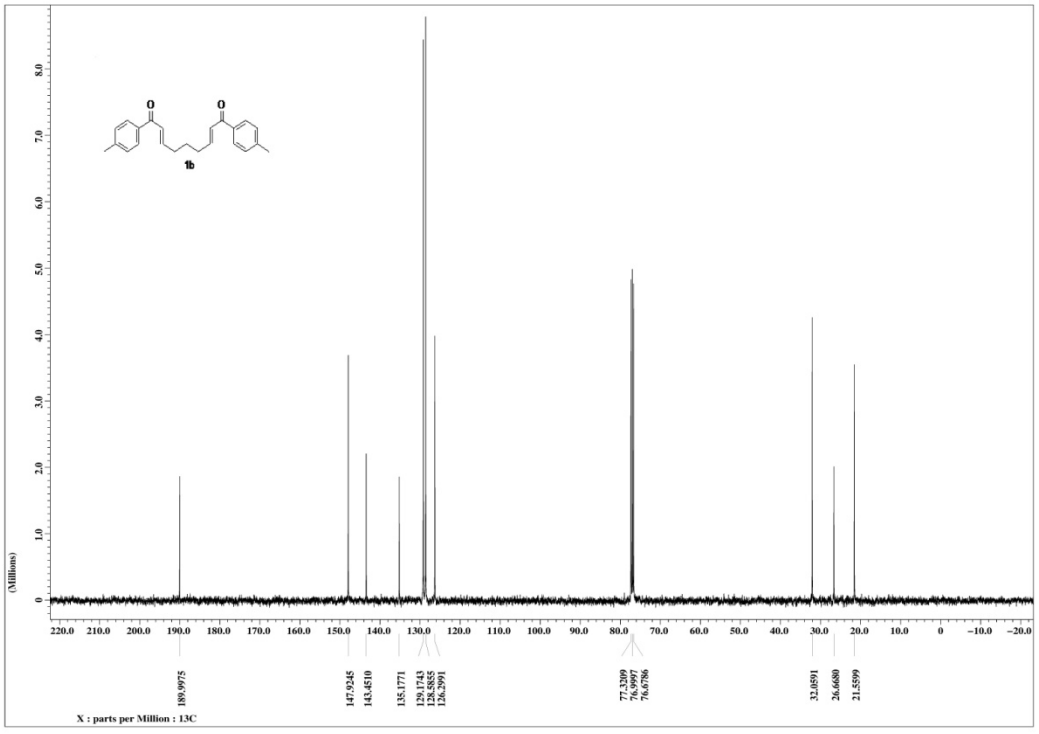
10.08
4
4.2
2.03
2.0
2.08
(Millions)
X : parts per Million : 1H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(Millions)
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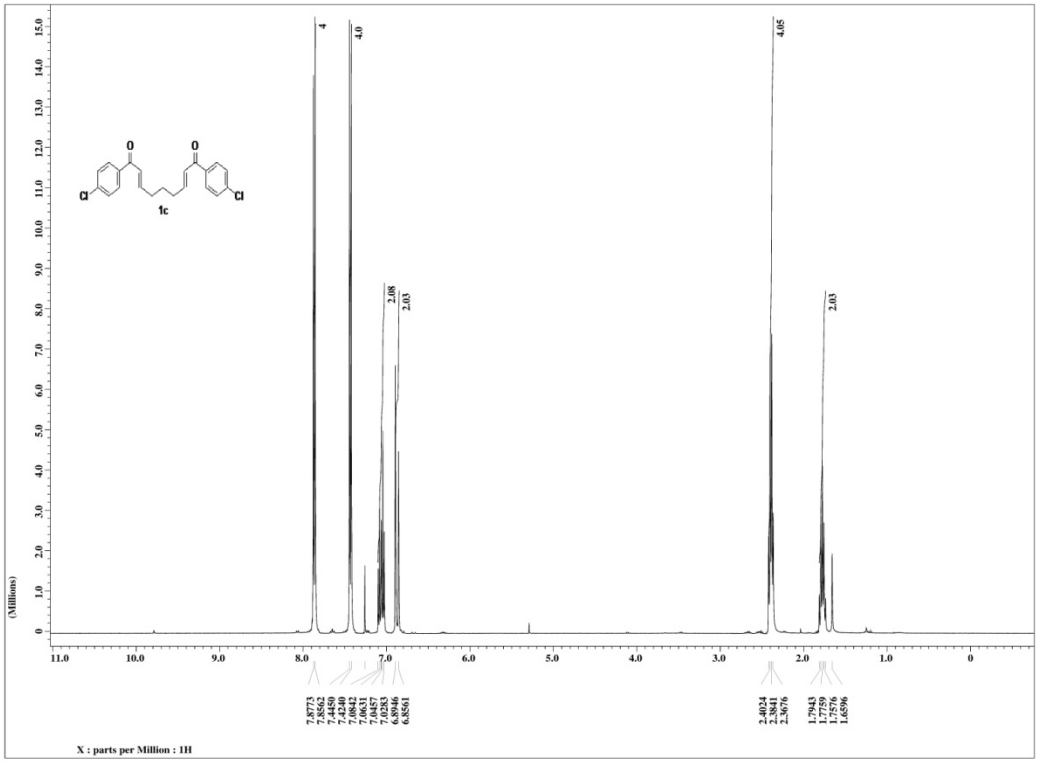
1c
4
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4.05
2.08
2.03
2.03
(Millions)
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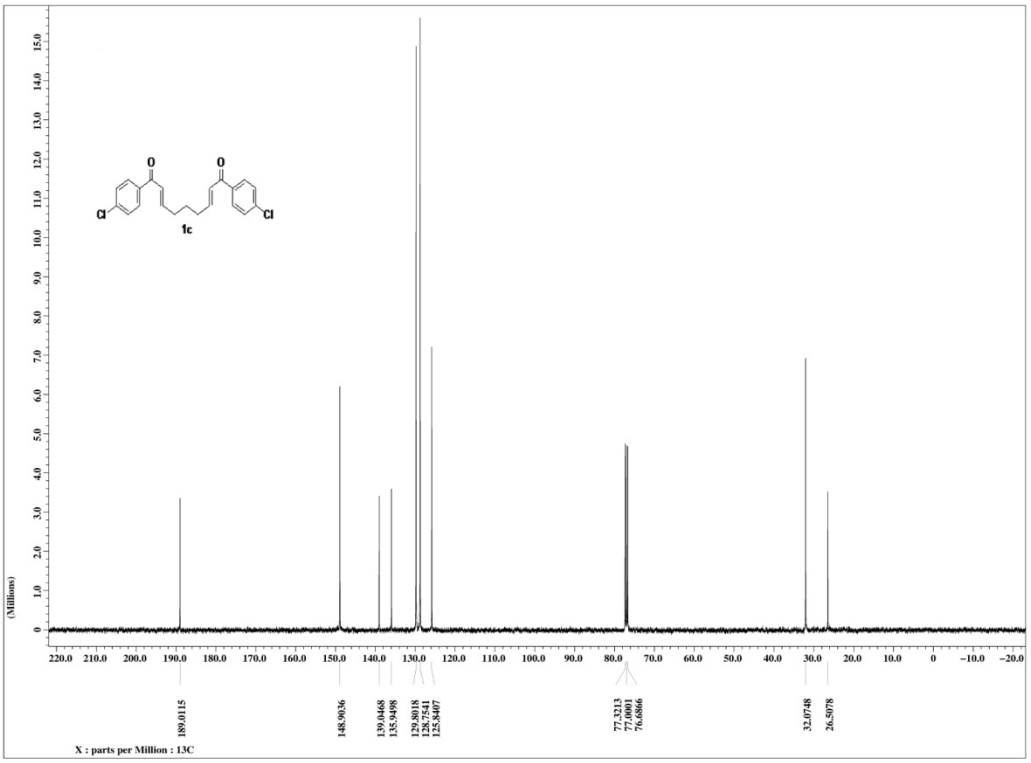
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(Millions)
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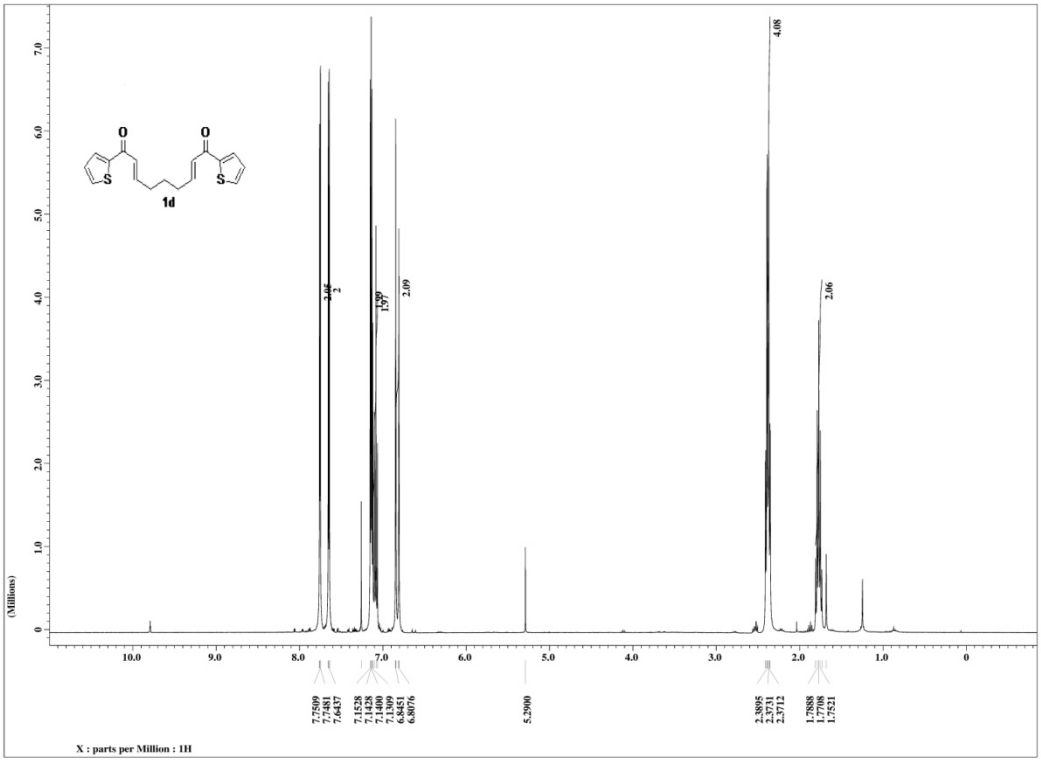
32.0748
26.5078
X : parts per Million : 13C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(Millions)
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2.09
2.06
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7.7481
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7.1528
7.1428
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7.1369
6.8451
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2.3895
2.3711
2.3712
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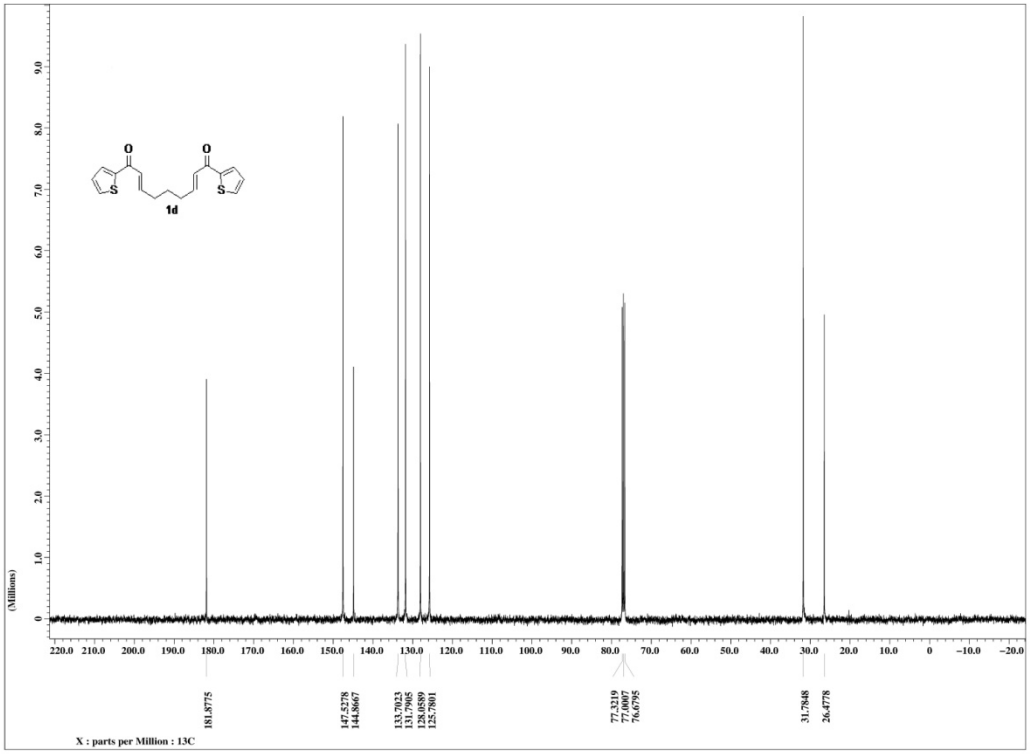
1.7708
1.7521
X : parts per Million : 1H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(Millions)
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144.8667
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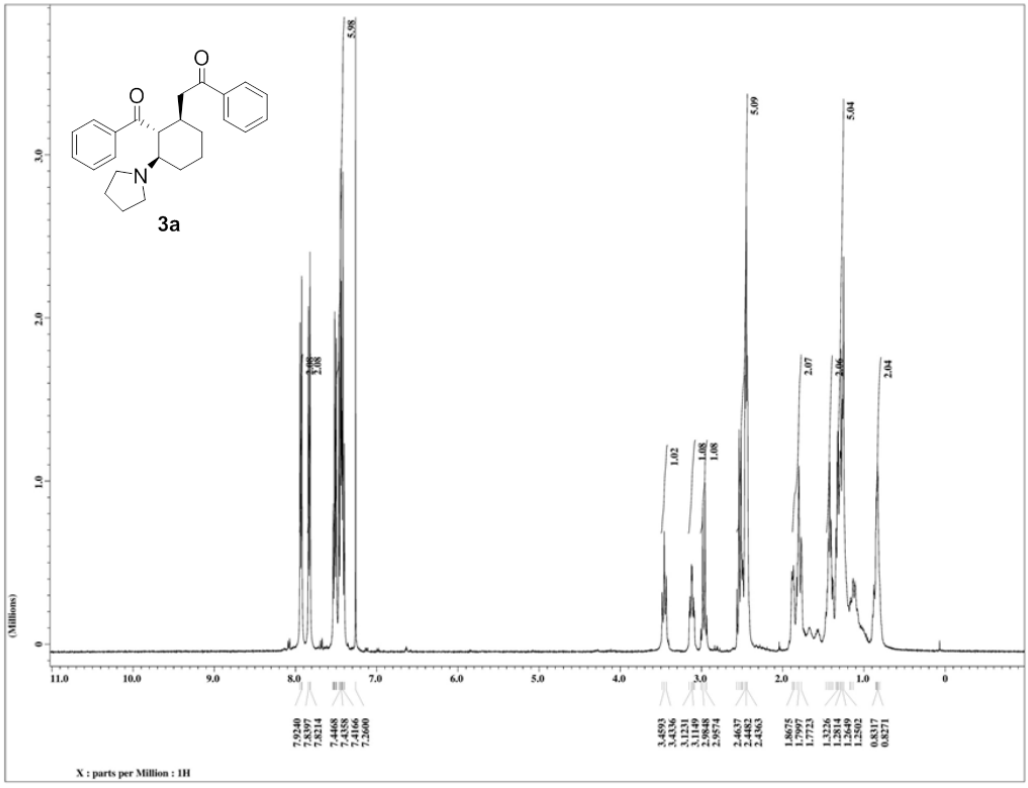
X : parts per Million : 13C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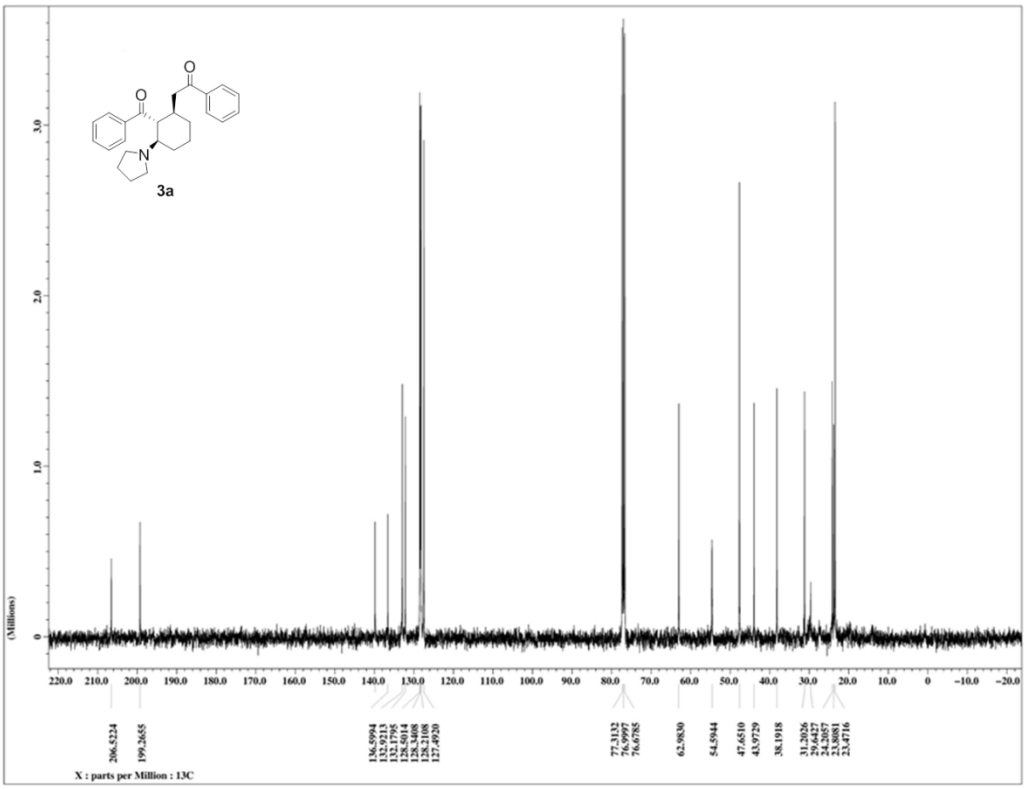
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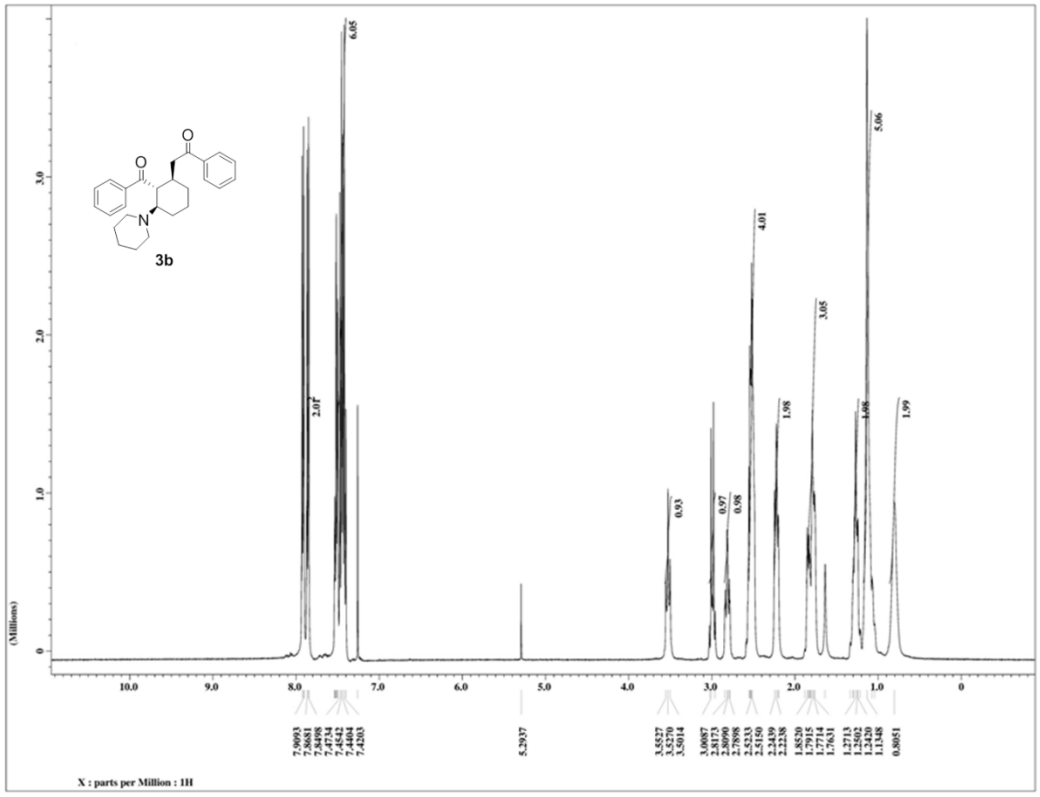
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(Millions)
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4.01
3.05
2.07
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1.99
1.68
0.93
0.97
0.98
7.9093
7.8681
7.8498
7.4734
7.4542
7.4464
7.4203
5.2937
3.5527
3.5270
3.5014
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2.2238
1.8520
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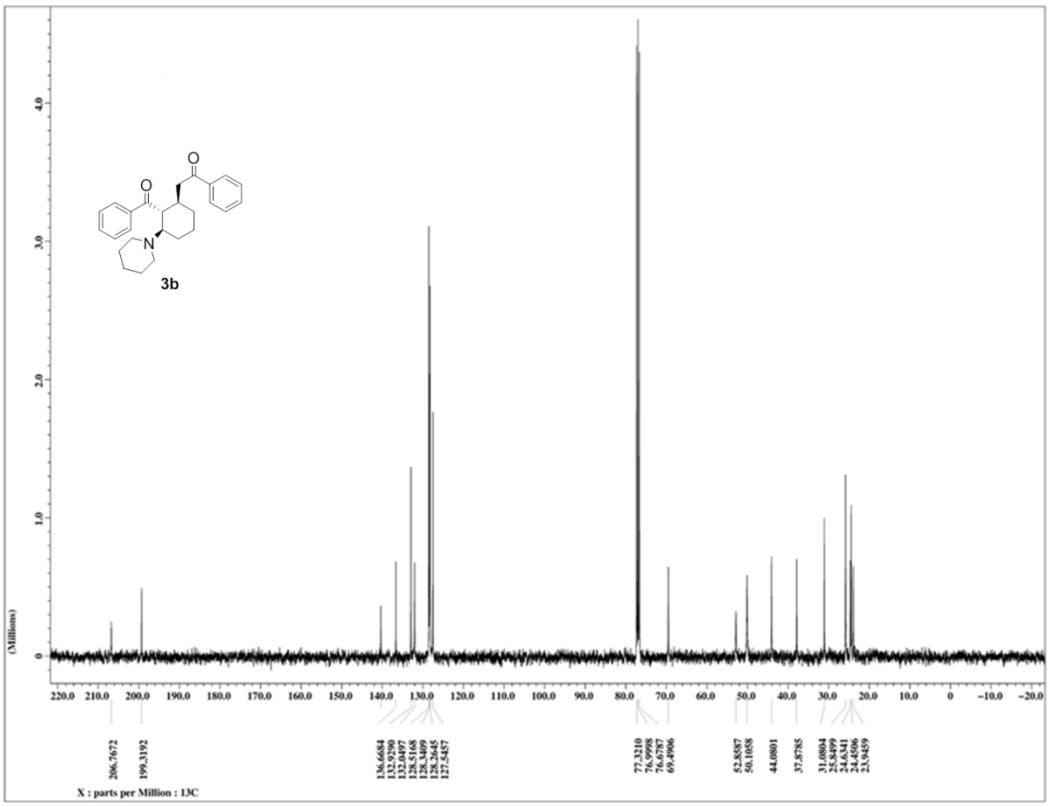
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128.3449
128.2445
127.5457
77.3210
76.9998
76.6787
69.4986
52.8887
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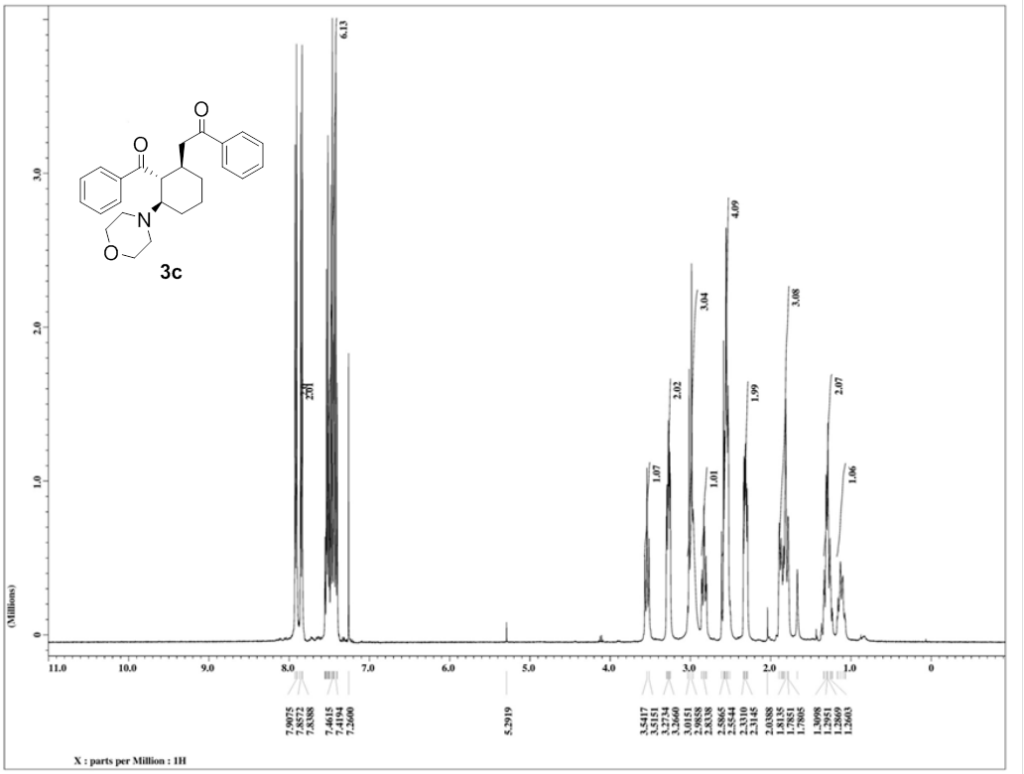
X : parts per Million : 13C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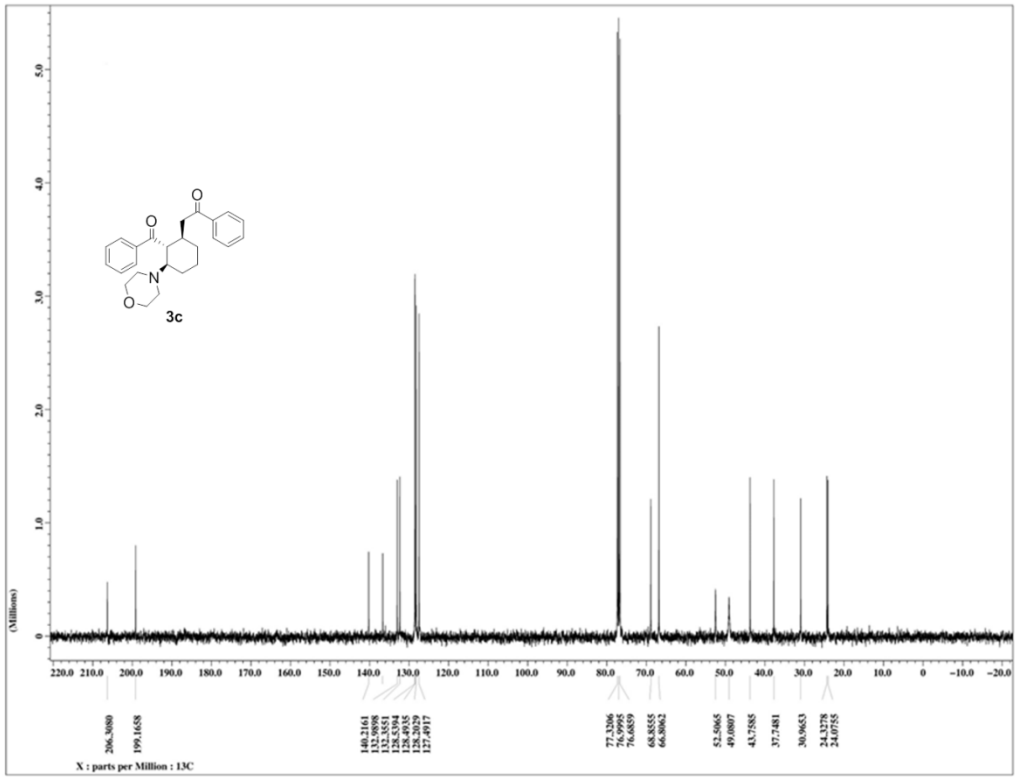
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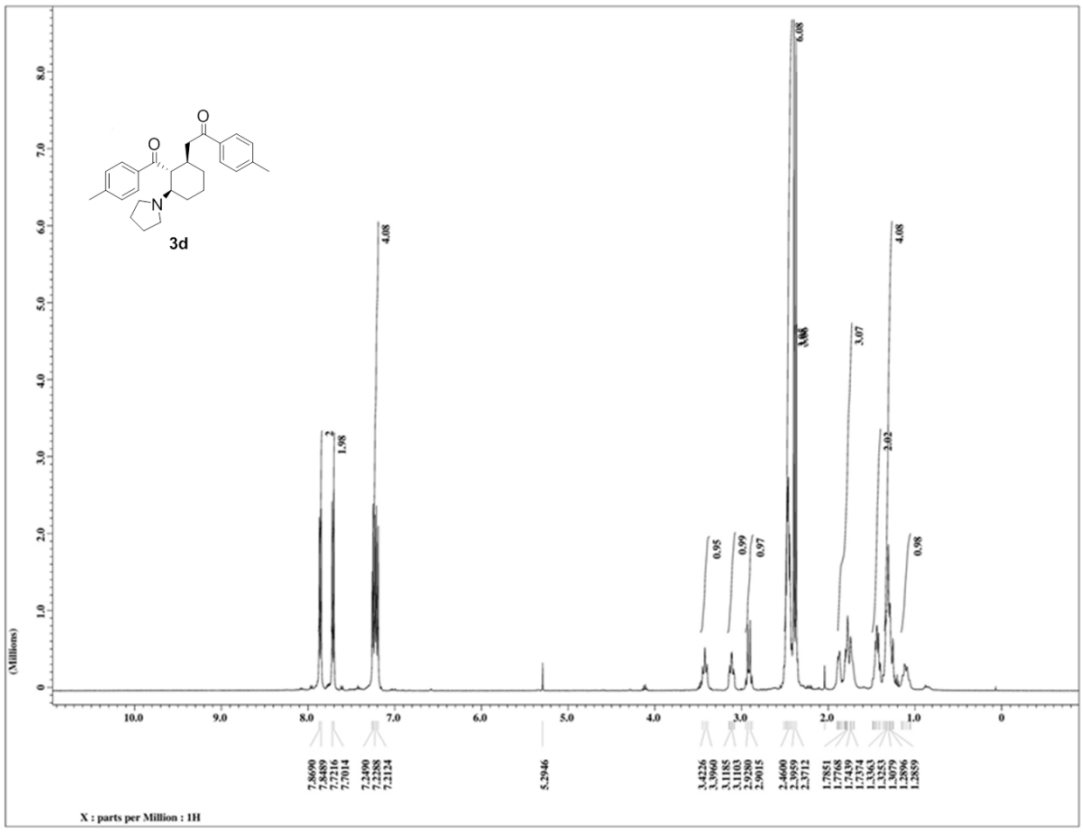
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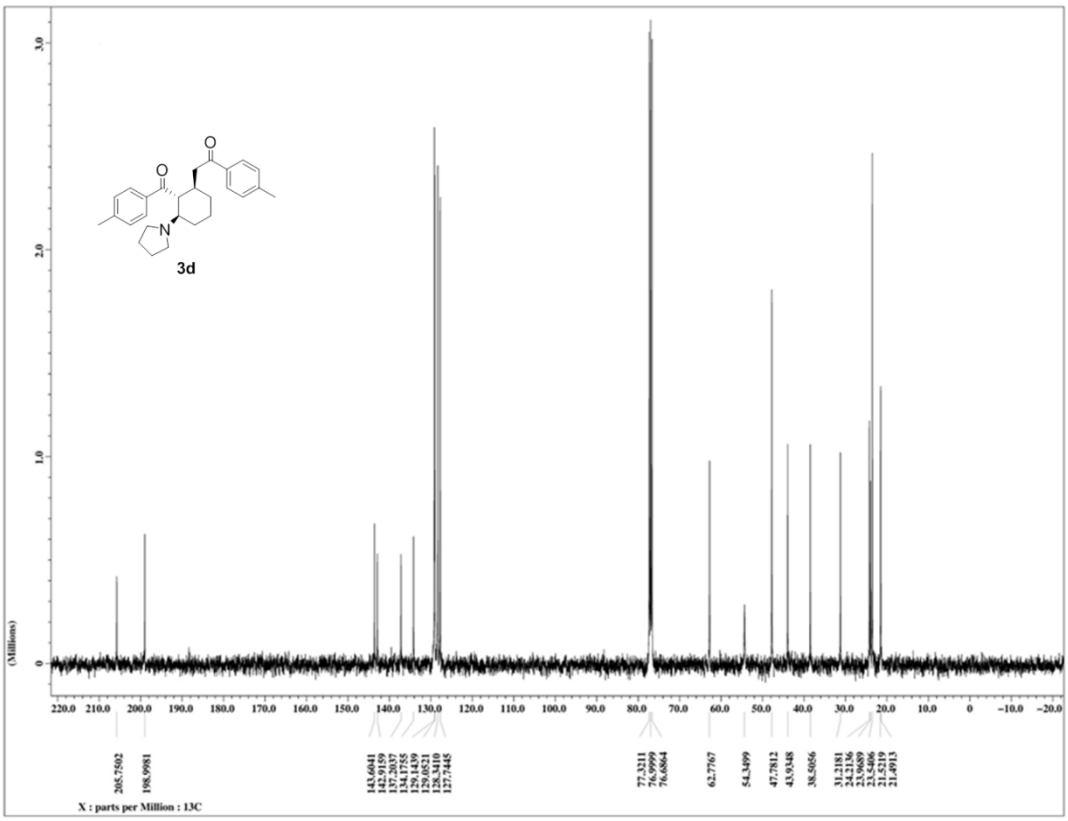
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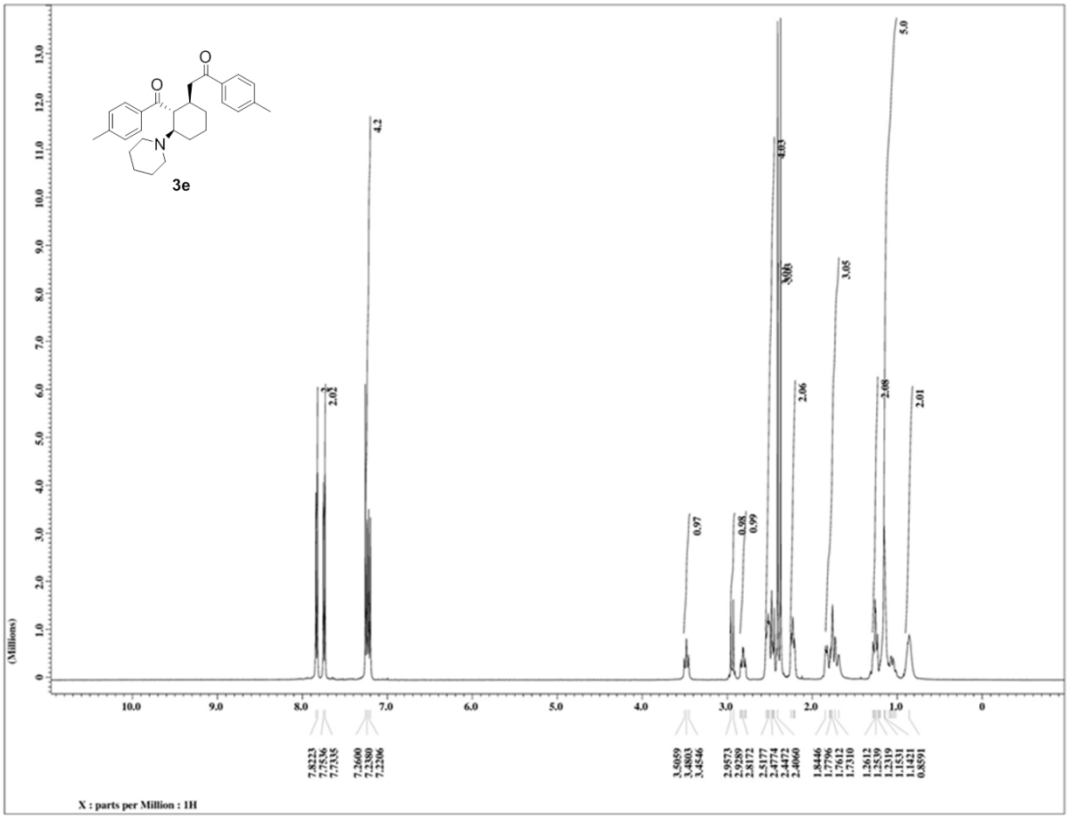
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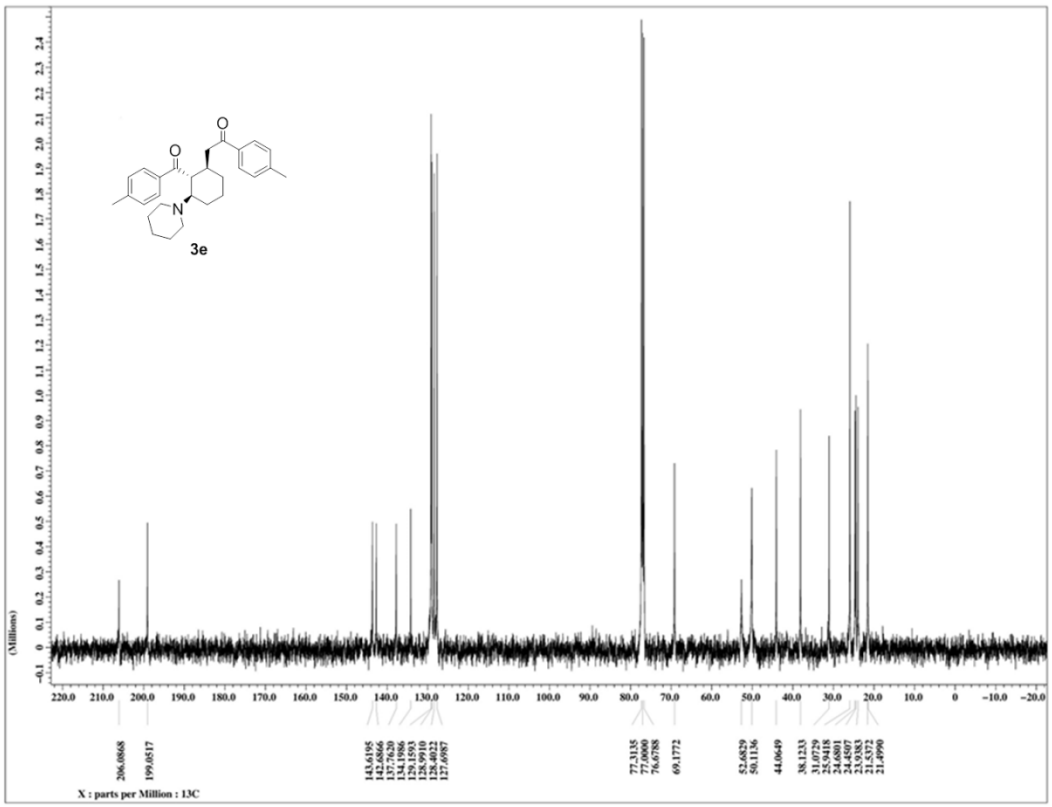
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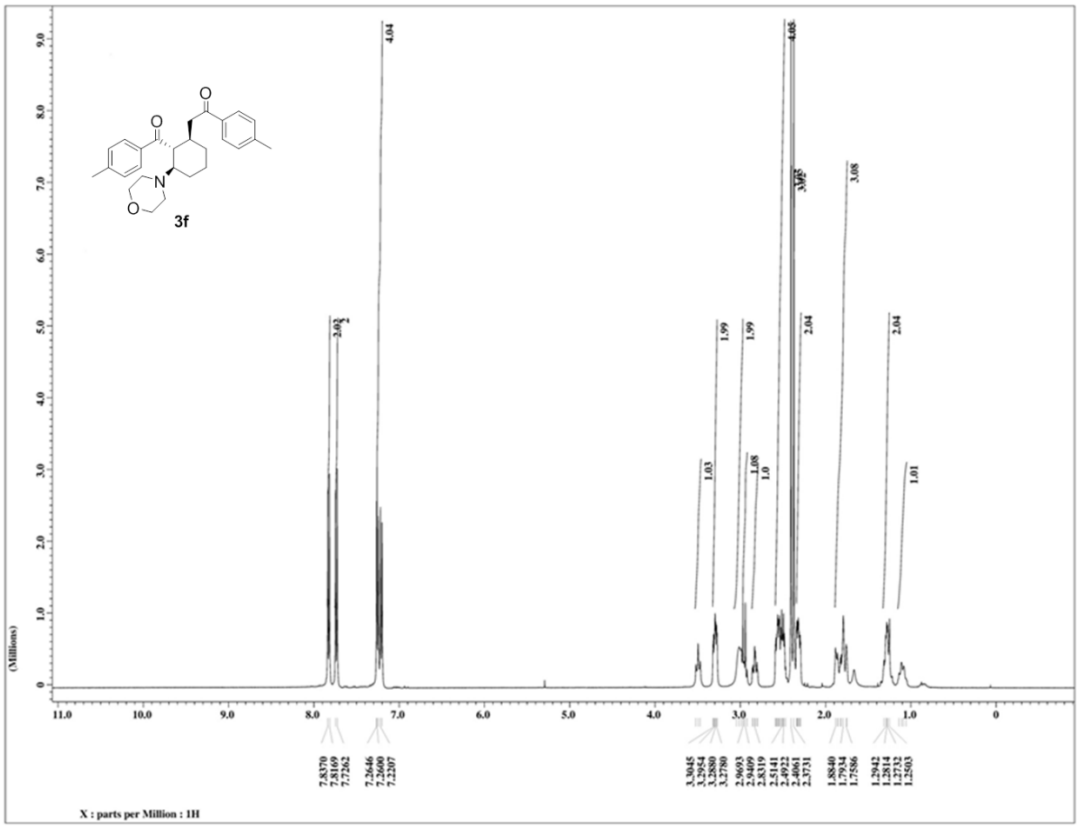
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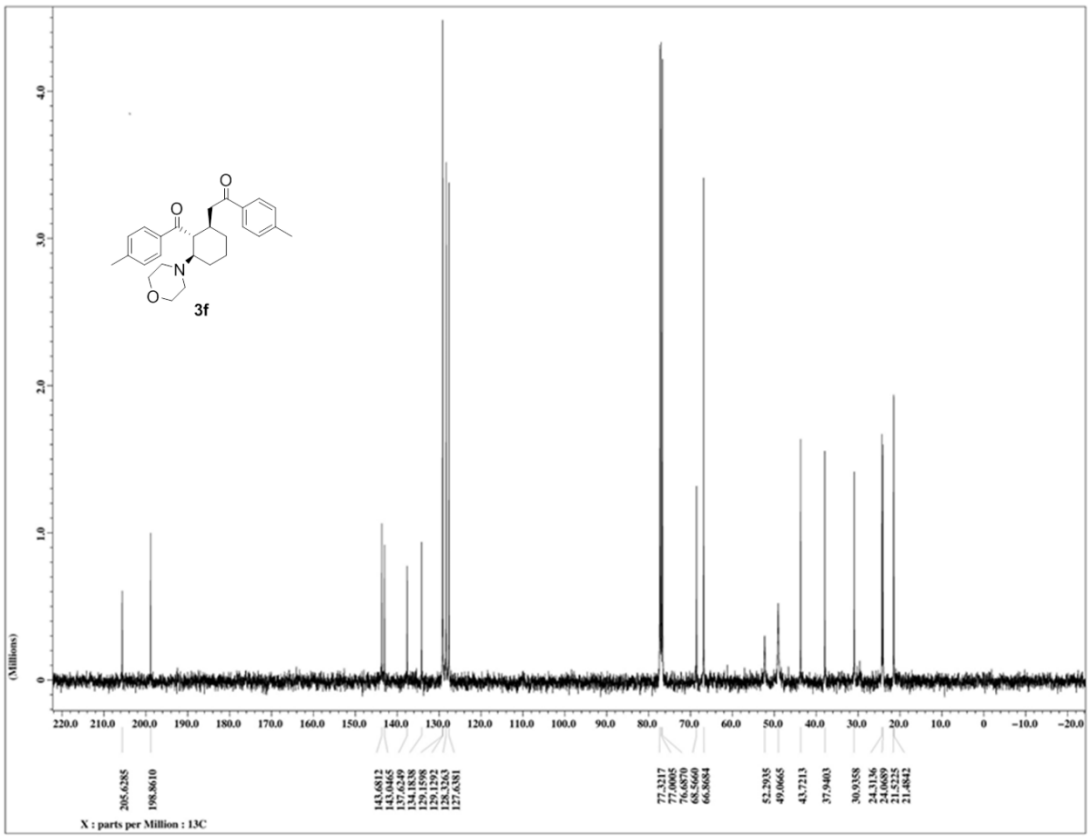
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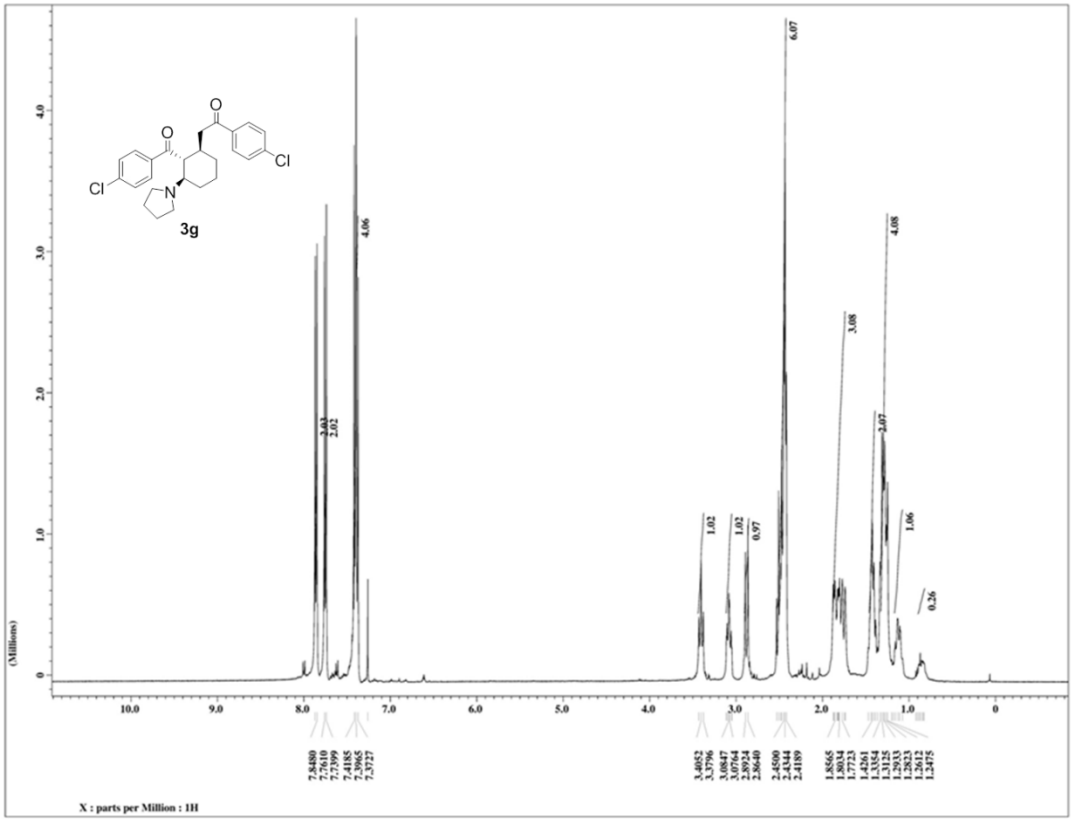
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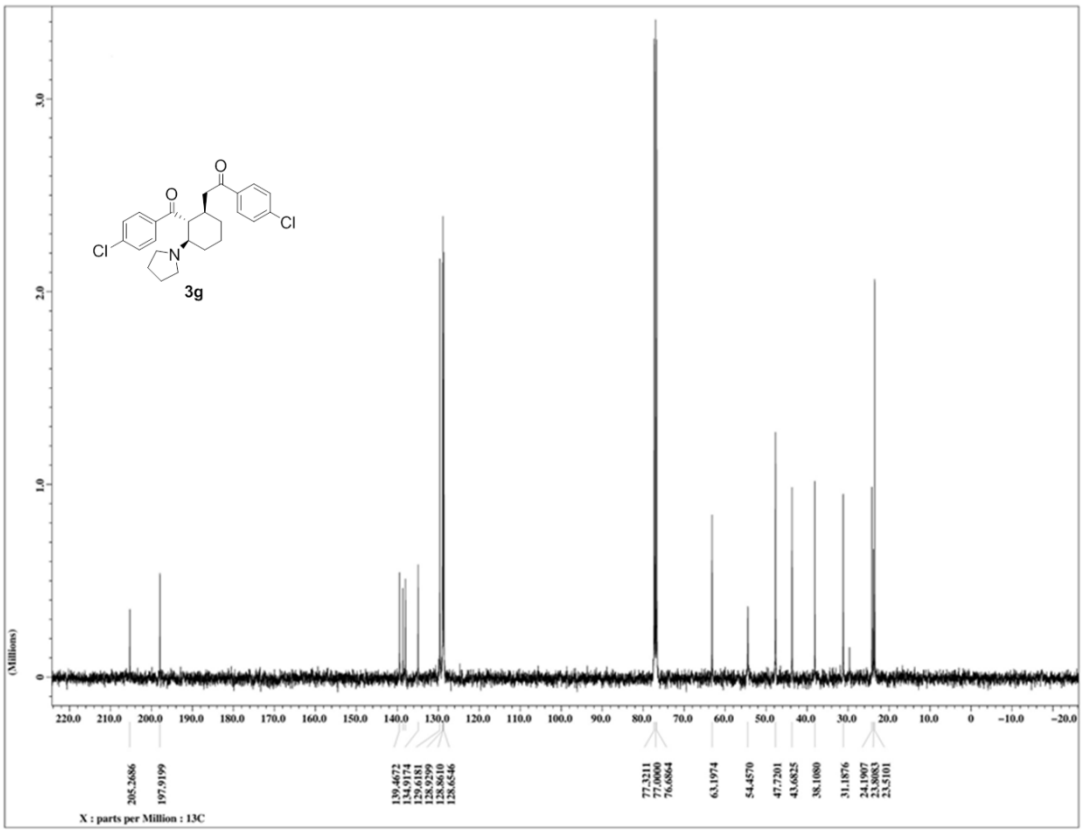
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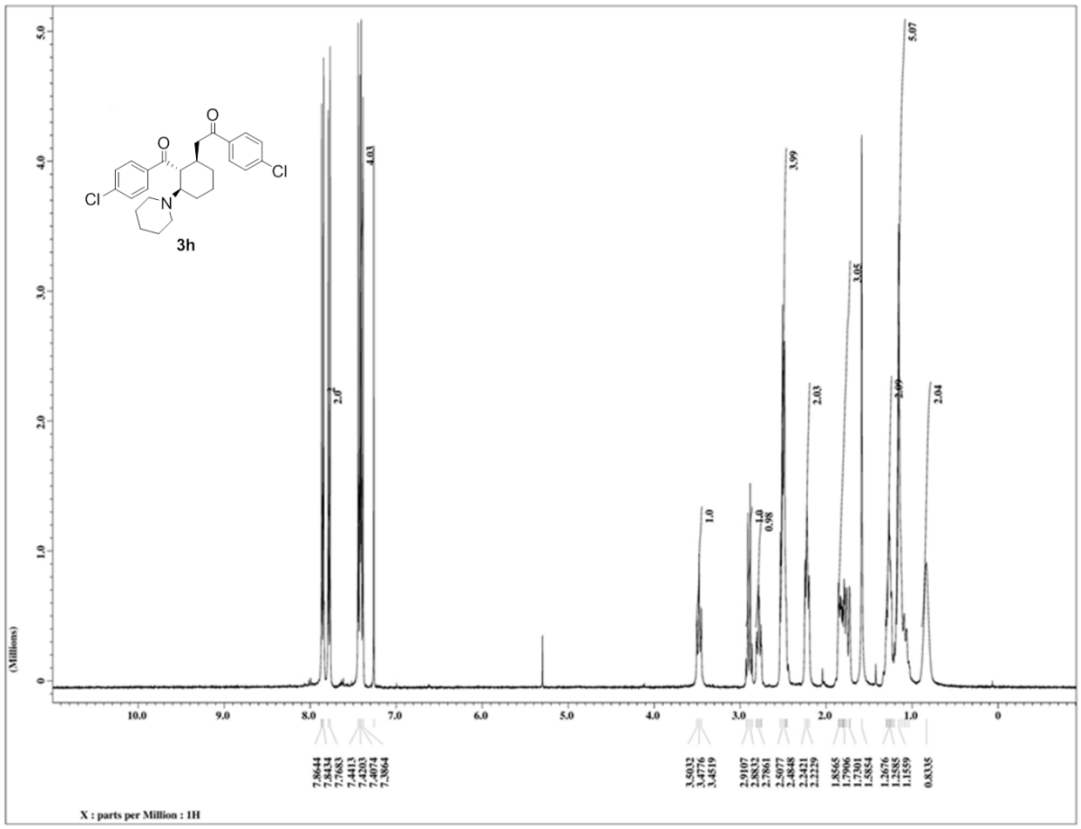
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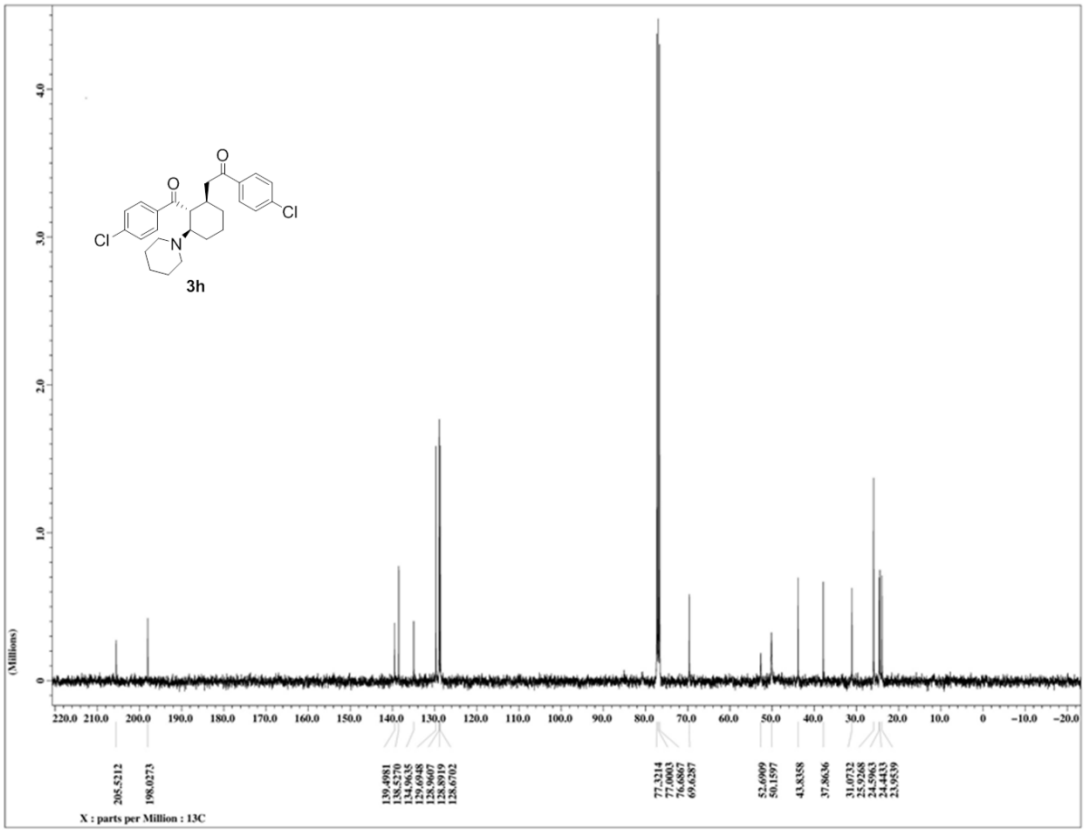
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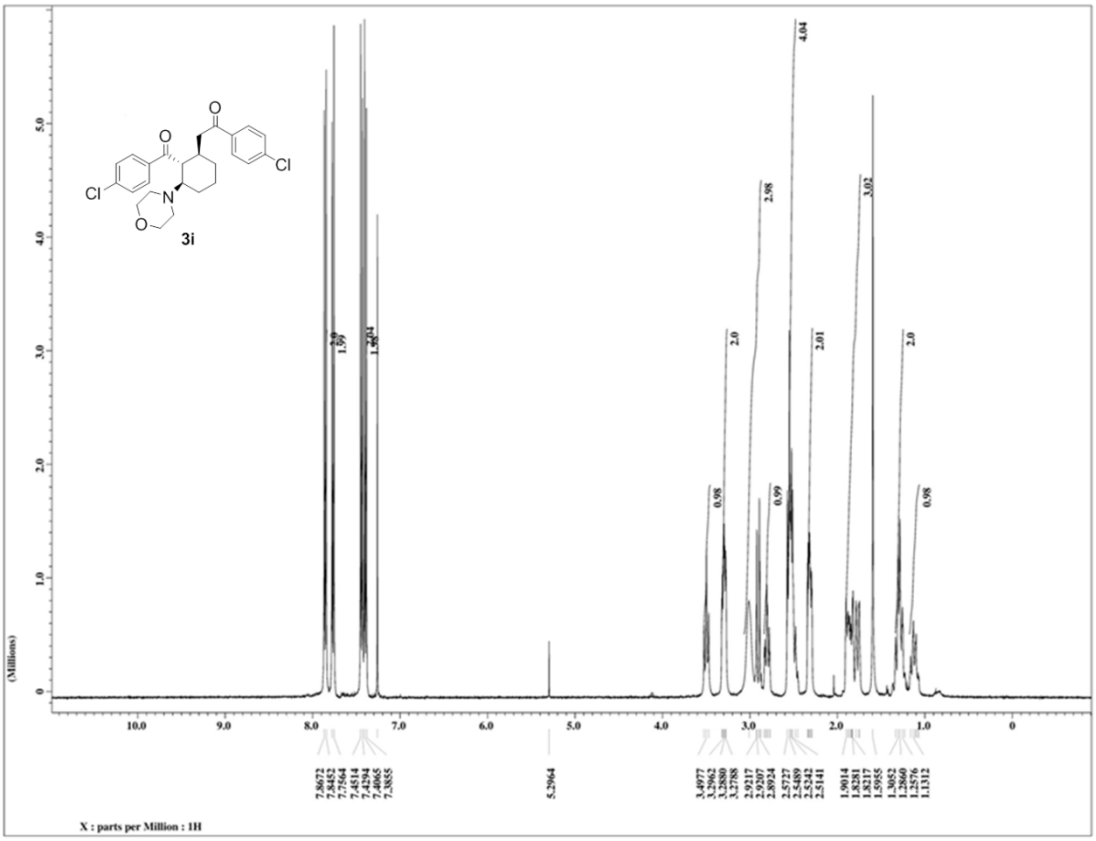
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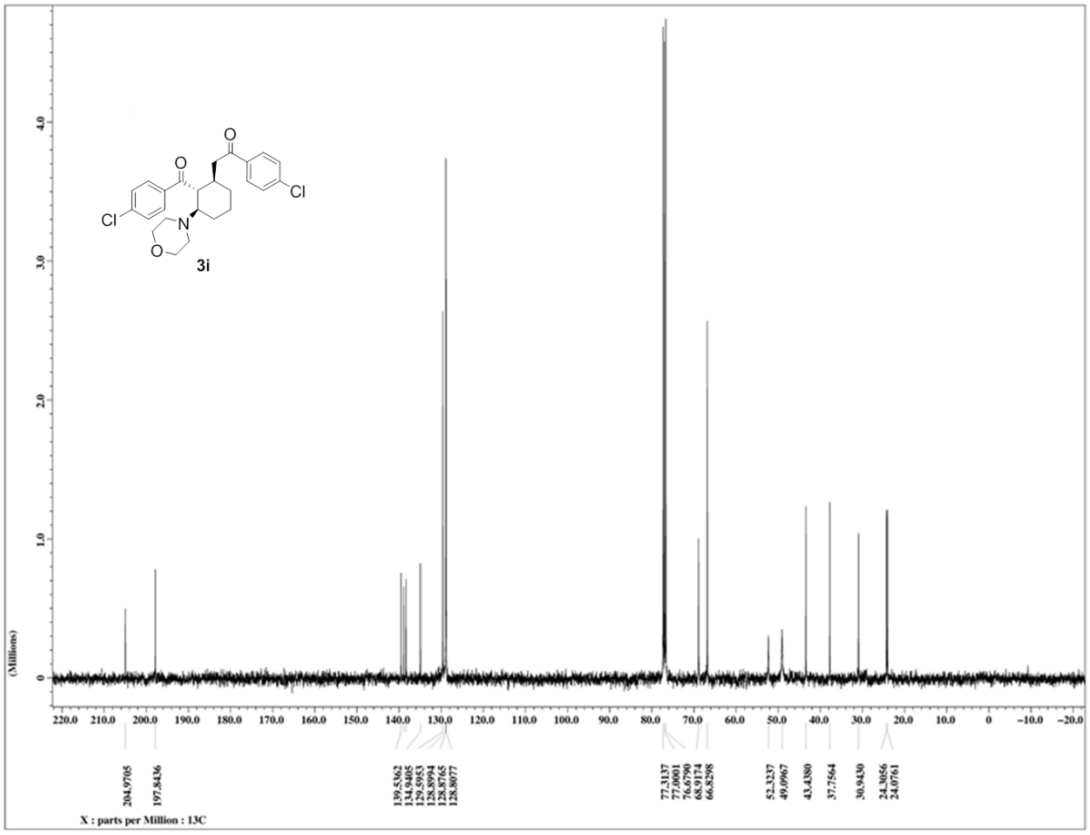
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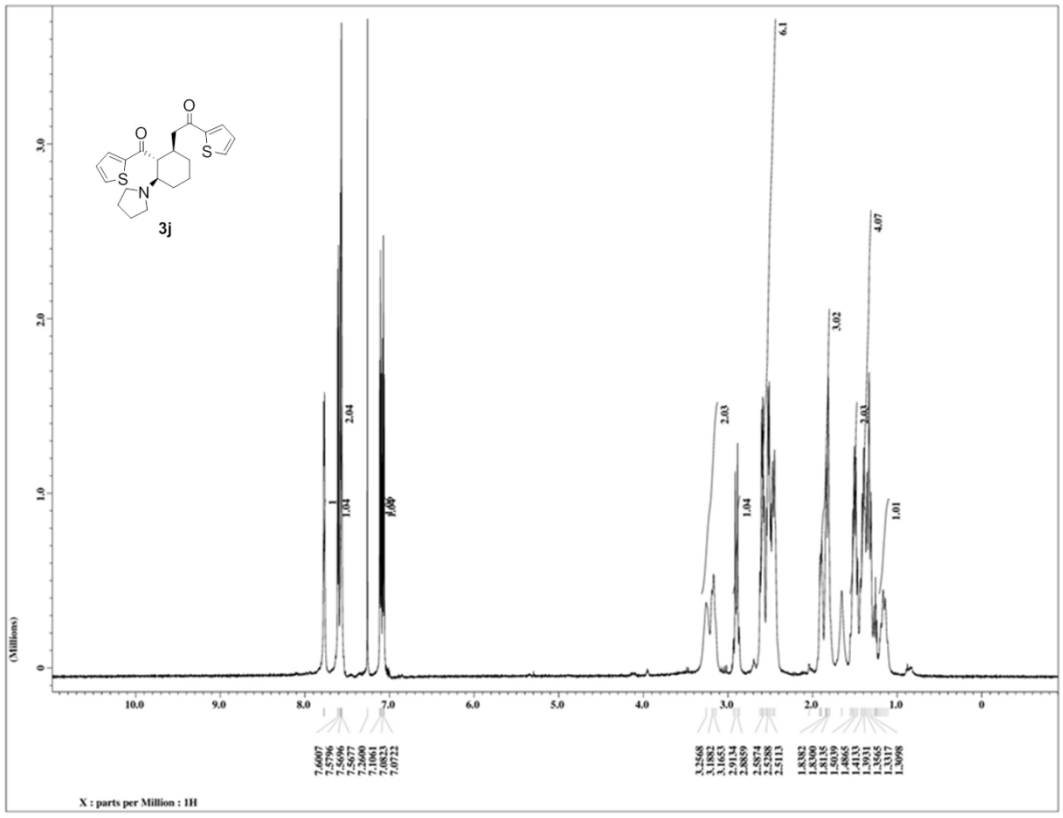
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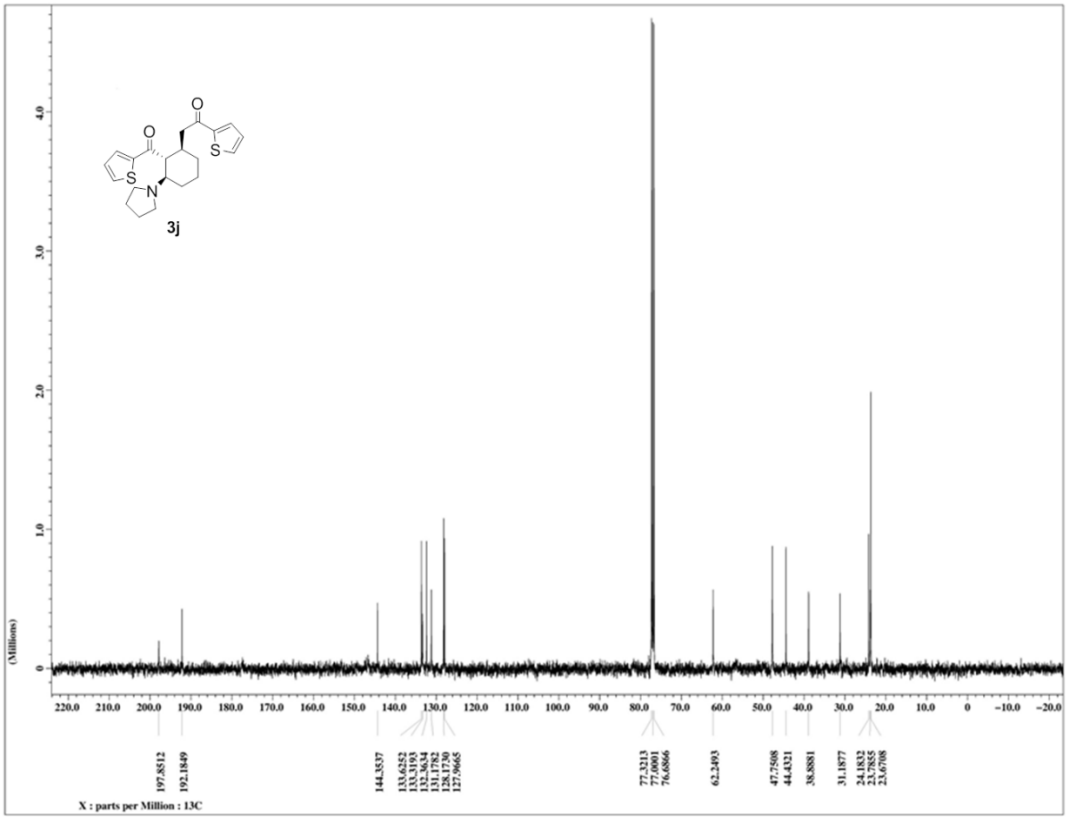
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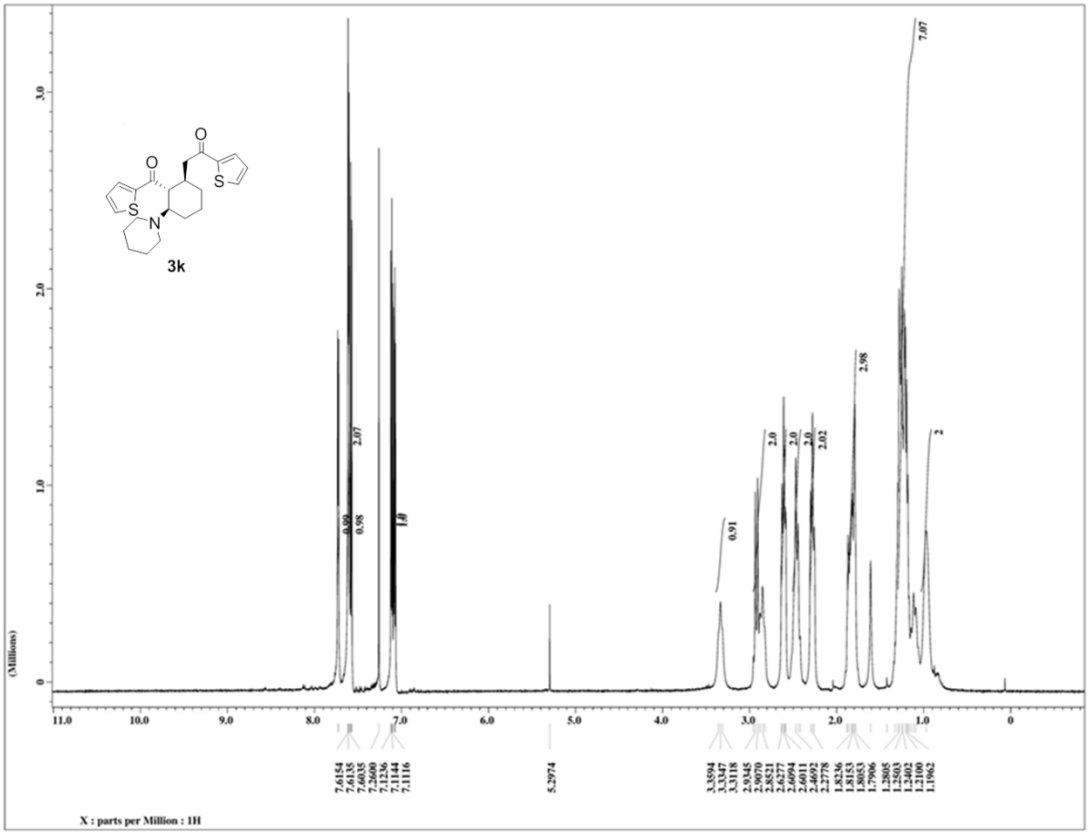
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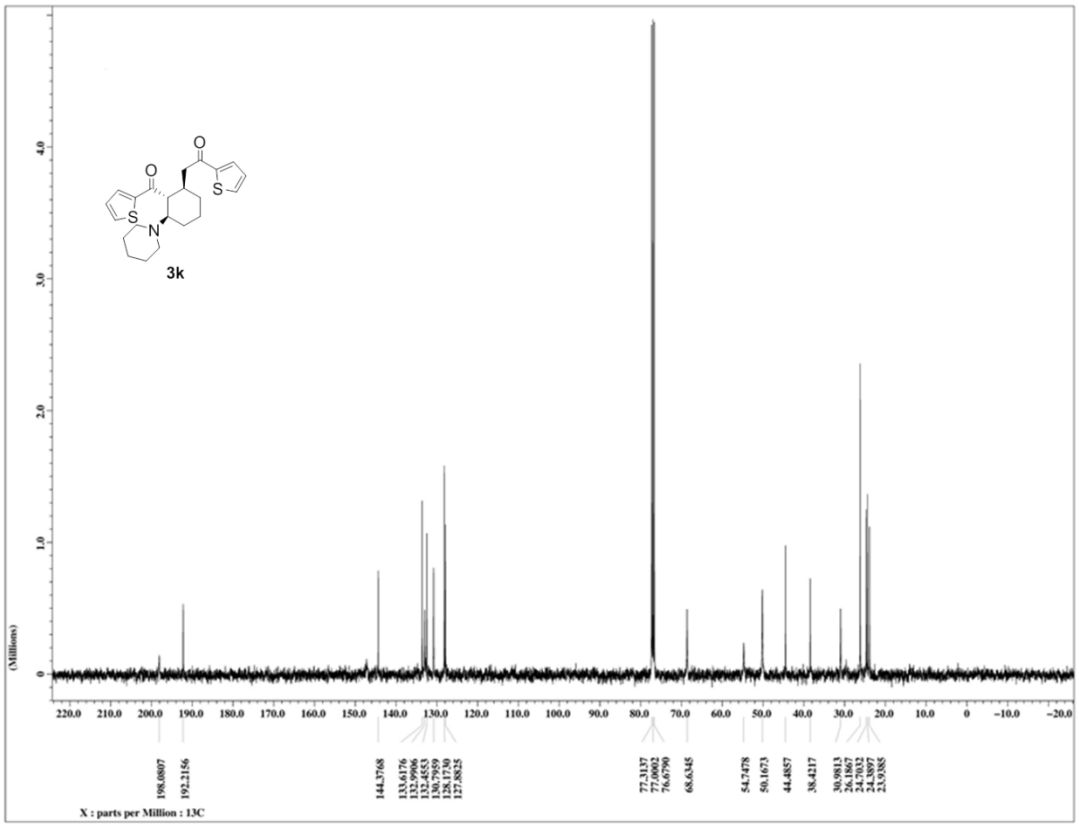
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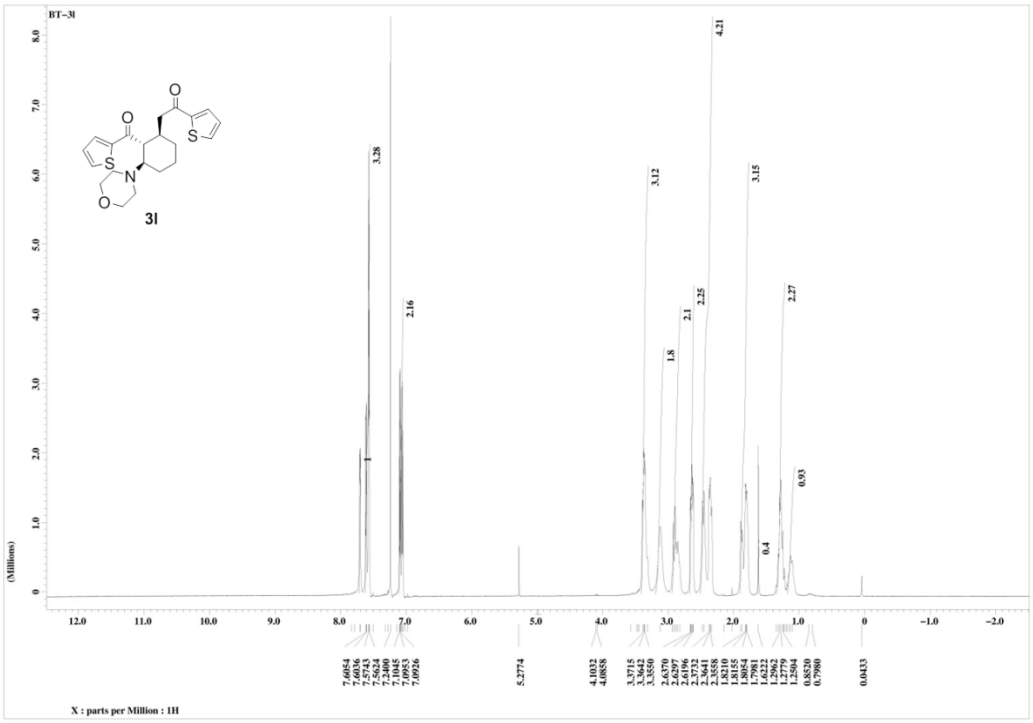
BT-3l
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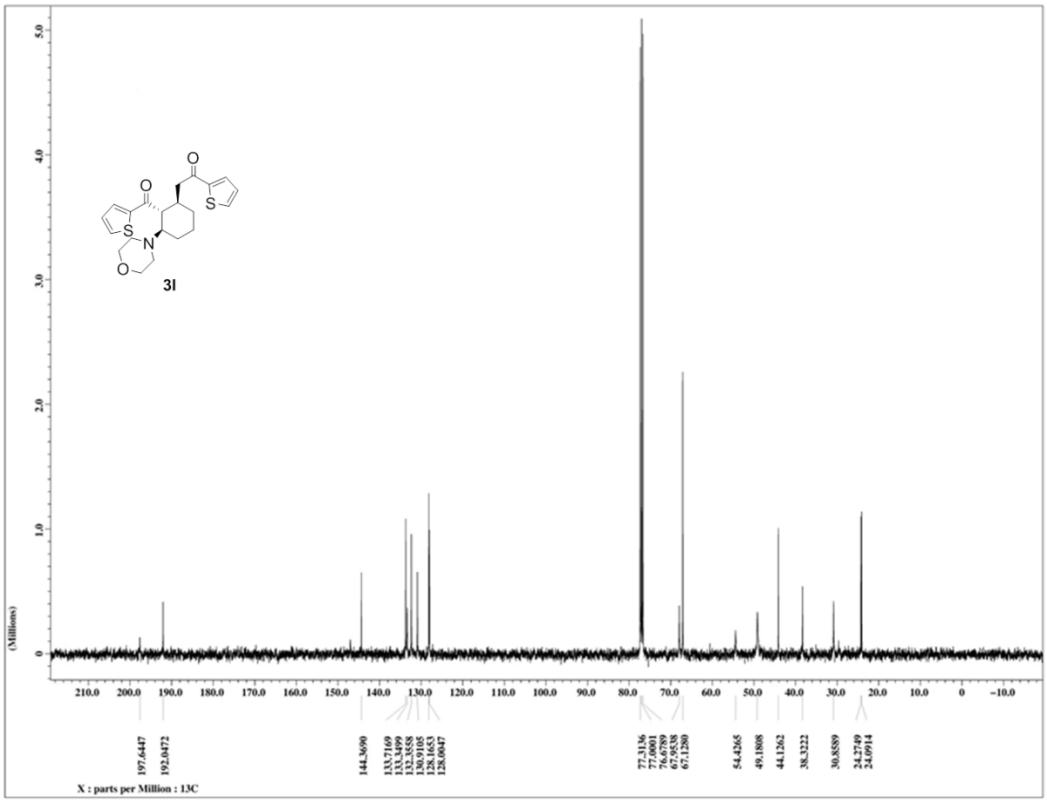
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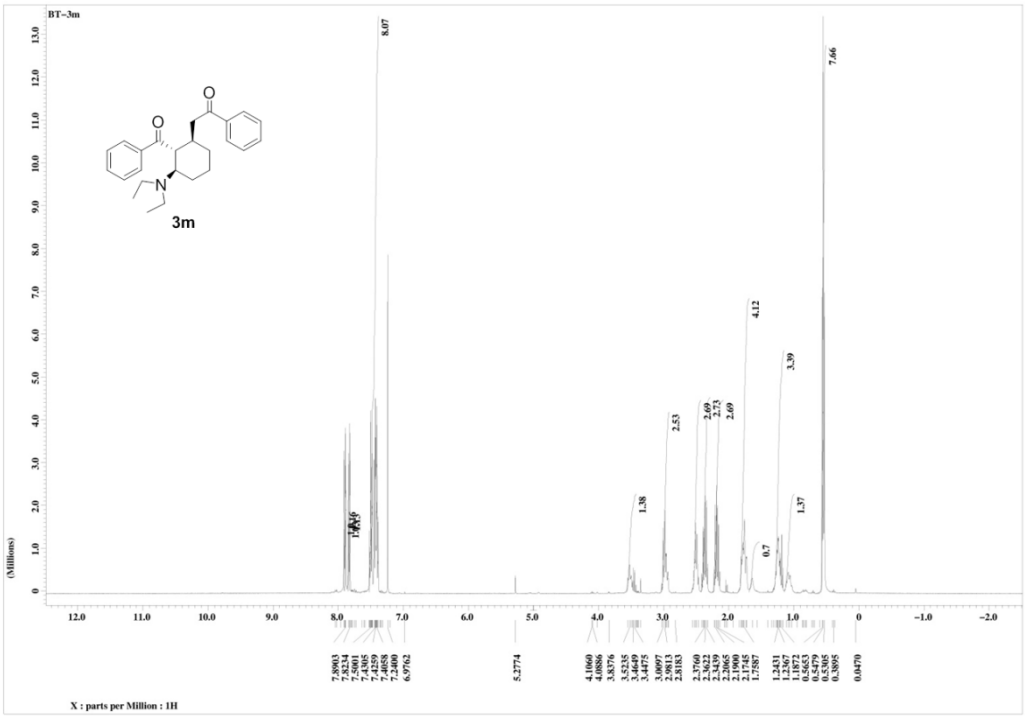
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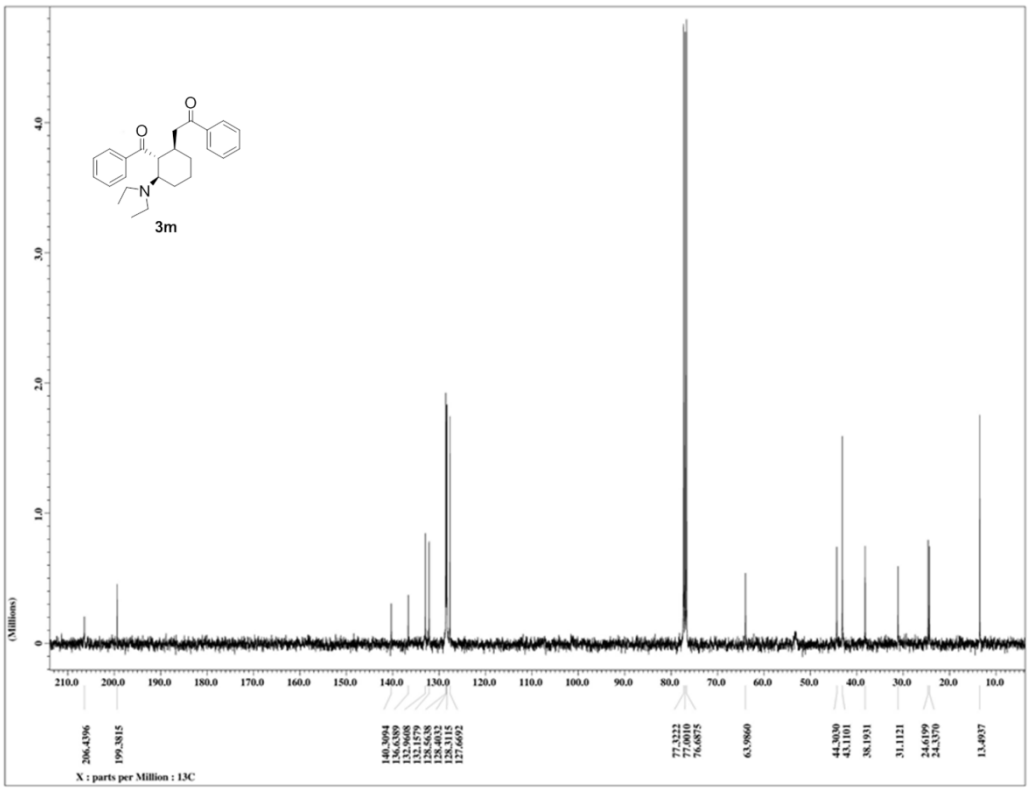
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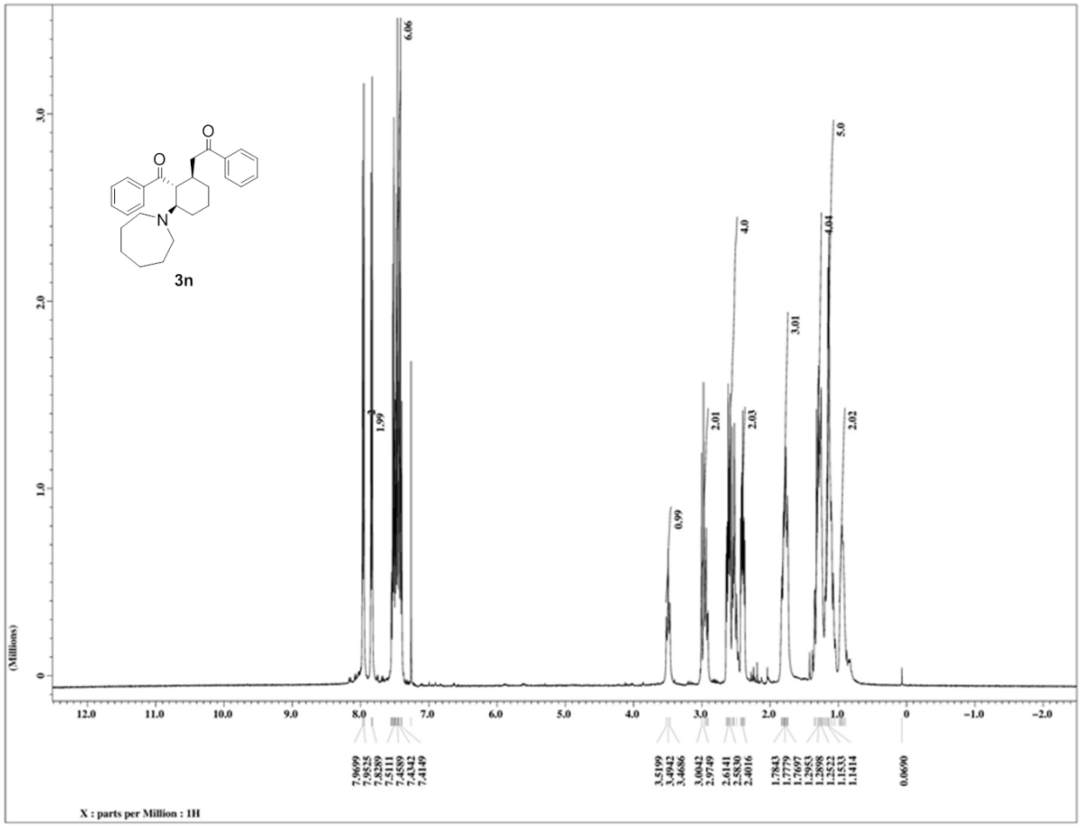
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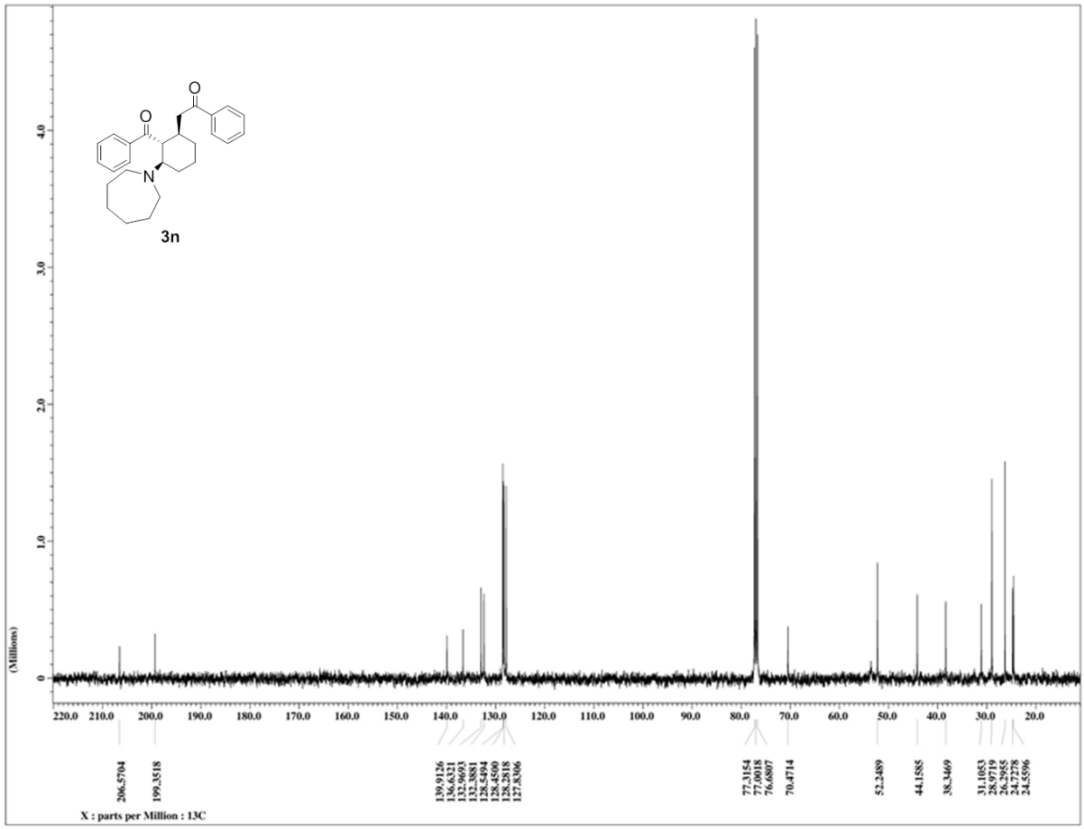
(Millions)
X : parts per Million : 1H


3n
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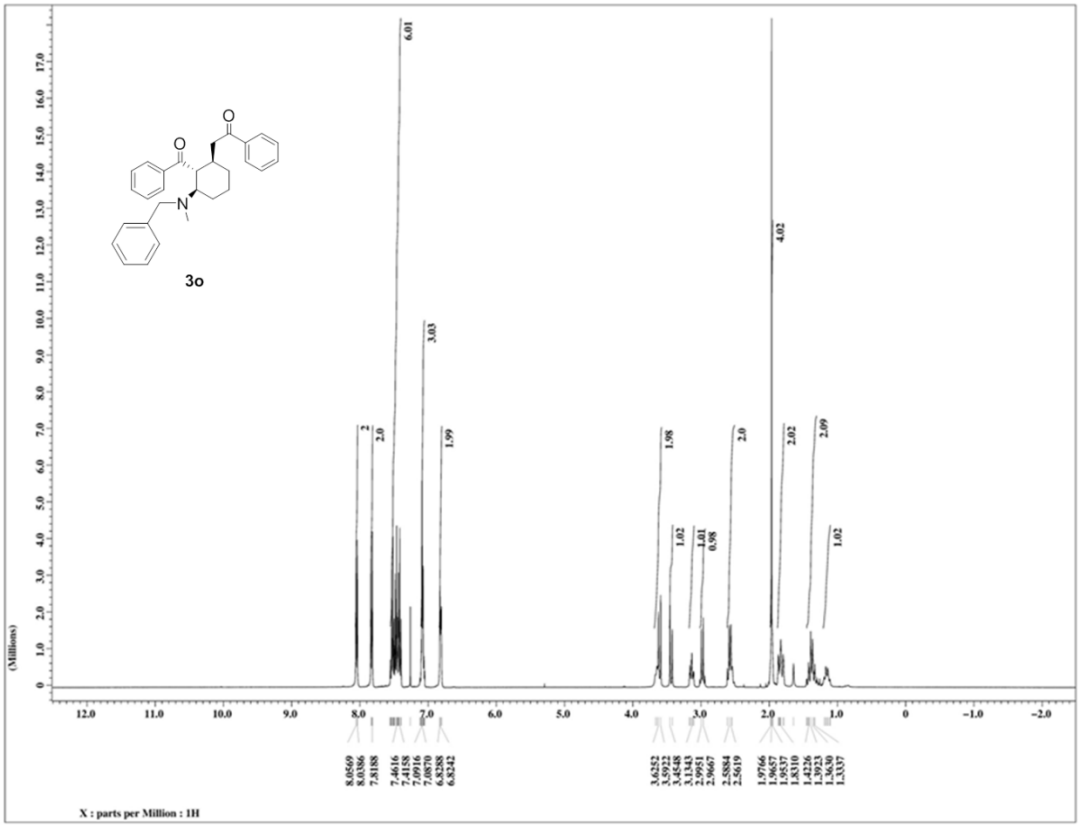
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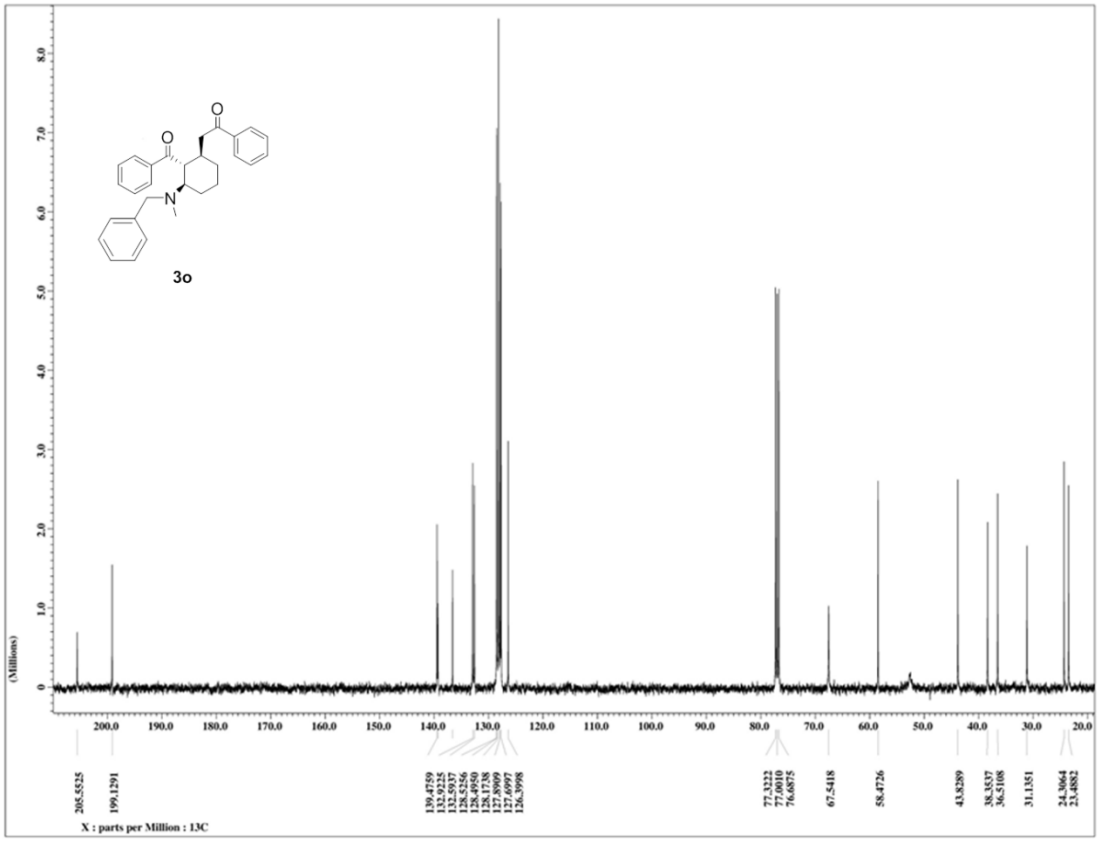
3o
(Millions)
X : parts per Million : 13C