Electronic Supplementary Material (ESI) for RSC Advances.

Hydrogen Bond Donor-Acceptor-Donor Organocatalysis for Conjugate Addition of Benzylidene Barbiturates via Complementary DAD-ADA Hydrogen Bonding

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Supporting Information

General Methods

Chemicals purchased from commercial sources were used without further purification. Flash column chromatography was performed using silica gel 60 (230-400 mesh ASTM) with ethyl acetate/n-hexane as eluent. Melting points were recorded by Bamstead Electrothermal 9100. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian AS-400 or Varian AS-500 or Bruker DPX-400 spectrometers. Chemical shifts (ppm) were referenced to TMS and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; dd, double doublet; br d, broad doublet; t, triplet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR Nicolet-380 spectrometer. Low resolution mass spectra (MS) and high resolution mass spectra (HR-MS) were measured on Waters Q-TOF 2^{TM} with a positive ESI source. X-ray crystal structures were obtained by Bruker CCD area detector diffractometer. UV/Vis. titration experiments were monitored by Hewlett Packard 8453 Photo-diode Array UV-Visible spectrometer.

General Procedure for Synthesis of HB-DAD Organocatalysts 1a and 3a: A mixture of 2,6-diamino-N-heterocyclic compounds (1.0 mmol) and trifluoroacetic anhydride (3.0 mmol) in CH_2Cl_2 (10 mL) was stirred under nitrogen atmosphere at room temperature for 24 h. The reaction mixture was added with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent to give **1a** (58% yield) and **3a** (68% yield).

General Procedure for Synthesis of HB-DAD Organocatalysts 1b, **1c**, **3b and 3c:** A mixture of 2,6-diamino-N-heterocyclic compounds (1.0 mmol), acid chloride (2.5 mmol), 4-dimethylaminopyridine (0.2 mmol) and triethylamine (2.5 mmol) in CH_2Cl_2 (10 mL) was stirred under nitrogen atmosphere at room temperature for 24 h. The reaction mixture was treated with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent to give **1b** (15% yield), **1c** (62% yield), **3b** (58% yield) and **3c** (62% yield).

General Procedure for Synthesis of Benzylidene Barbiturates: A mixture of barbiturate acid (2.0 mmol) and benzaldehyde (2.0 mmol) in EtOH (10 mL) was refluxed for 2-12 h. The reaction mixture was allowed to cool to room temperature and filtered to obtain solid /

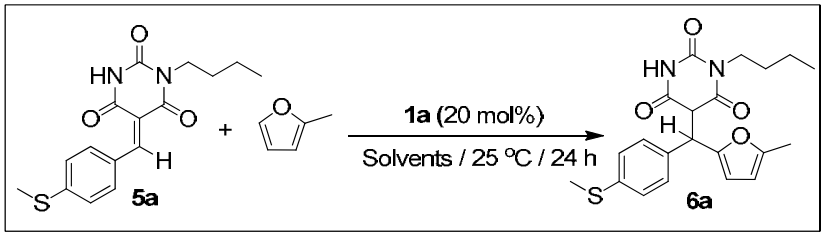
crystalline crude products. The residue was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent to give benzylidene barbiturates in 24-95% yield.

Procedure for Catalytic Conjugate Addition of Benzylidene Barbiturates: A mixture of benzylidene barbiturates **5** (0.05 mmol), 2-methylfuran (0.05 mmol) and HB-DAD organocatalyst (0.01 mmol) in CH_2Cl_2 (1 mL) was stirred at 25 ^oC for 24 h. The product yield was determined by crude ^1H NMR with toluene (0.02 mmol) as internal standard. The reaction mixture was concentrated. The residue was purified by flash column chromatography on silica gel using ethyl acetate-hexane as eluent to obtain isolated yield.

Optimization of Reaction Conditions of 1a-Catalyzed Conjugate Addition of 5a with 2-Methylfuran

As depicted in Table S1, a series of polar aprotic solvents gave good yield (entries 1-3). Particularly, the **1a**-catalyzed conjugate addition of **5a** in CH_2Cl_2 gave 61% yield (entry 1). The yield was further improved in the conjugate addition of **5a** using dried CH_2Cl_2 as solvent (3.0; entry 4). However, no yield increase of the reaction was observed in 48 h (2.0; entry 5). In addition, no yield increase in the reaction was observed using acetone and toluene as solvents (entries 6 and 7). In this connection, CH_2Cl_2 was selected as solvent system for subsequent studies.

Table S1. Effect of solvent in **1a**-catalyzed conjugate addition of **5a**[a]

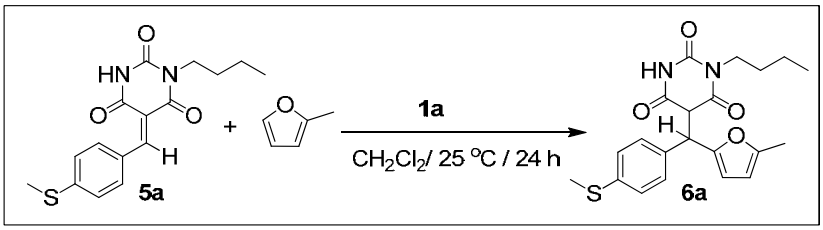


Entry[a]	Solvent	NMR Yield (%)[b]	Background NMR Yield (%)[b, c]
1	CH_2Cl_2	61	28
2	$CHCl_3$	51	24
3	CH_3CN	21	16
4[d]	CH_2Cl_2	69	23
5[e]	CH_2Cl_2	60	30
6	Acetone	14	14
7 [f]	Toluene	trace	trace

[a] Reaction conditions: **5a** (0.05 mmol), 2-methylfuran (0.05 mmol), **1a** (0.01 mmol), solvents (1 mL), 25 °C, 24 h. [b] Yields were determined by ^{1}H NMR of the crude product using toluene as the internal standard. [c] Without addition of **1a**. [d] Dried CH_2Cl_2. [e] For 48 h. [f] Ethyl acetate as the internal standard.

The conjugate addition of **5a**, using 50 mol% and 20 mol% of **1a**, gave 62% and 61% yield (Table S2; entries 1-2). A lower yield (49%) was observed in using of 10 mol% of **1a** (entry 3). No yield increase was observed in using 5 mol% of **1a** (entry 4). In this connection, using 20 mol% of **1a** in catalyzed conjugate addition of **5a** is more effective than using 50 mol% of **1a** in the reaction because of the same yield obtained in using of a lower quantity of **1a**.

Table S2. Effect of catalyst loading in **1a**-catalyzed conjugate addition of **5a**[a]

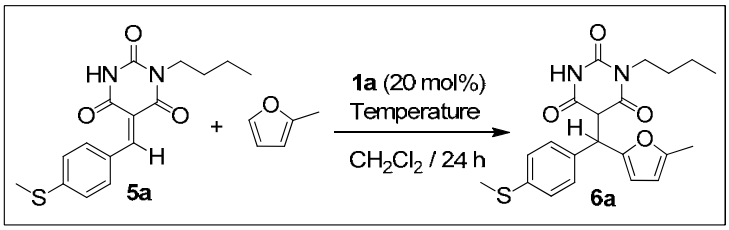


Entry[a]	Catalyst Loading (mol%)	NMR Yield (%)[b]
1	50	62
2	20	61
3	10	49
4	5	28
5	0	28

[a] Reaction conditions: **5a** (0.05 mmol), 2-methylfuran (0.05 mmol), **1a** (0.05-0.5 equiv.), CH_2Cl_2 (1 mL), 25 °C, 24 h. [b] Yields were determined by ^1H NMR of the crude product using toluene as the internal standard.

Only trace amount of **5a** was obtained in -20 ^{o}C of the conjugate addition of **5a** (Table S3; entry 1). 25% yield was afford when the present reaction was conducted in 0 ^{o}C (entry 2). The **1a**-catalyzed conjugate addition of **5a** worked smoothly in 25 ^{o}C to give good yield of adduct **6a** (entry 3). However, the no significant yield increase in the reaction carried at 40 ^{o}C (entry 4) and the background NMR yield (49%) increased observably. In balancing the yield of conjugate addition of **5a**, the subsequent studies of HB-DAD catalyzed conjugate addition could be performed in 25 ^{o}C.

Table S3. Effect of reaction temperature in **1a**-catalyzed conjugate addition of **5a**[a]



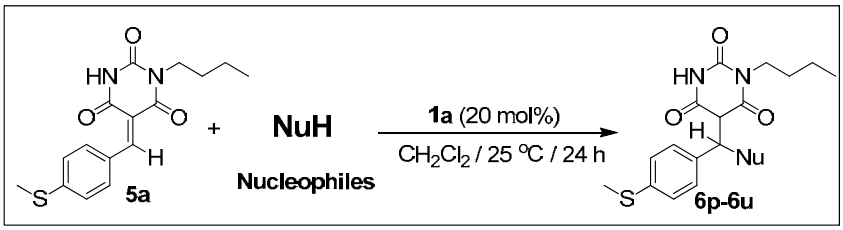
Entry[a]	Temperature (^{o}C)	NMR Yield (%)[b]	Background NMR Yield (%)[b, c]
1	-20	trace	trace
2	0	25	10
3	25	61	28
4	40	62	49

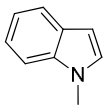
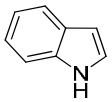
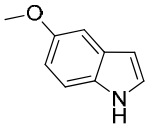
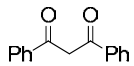
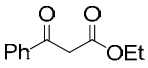
[a] Reaction conditions: **5a** (0.05 mmol), 2-methyfuran (0.05 mmol), **1a** (0.01 mmol), CH_2Cl_2 (1 mL), 24 h. [b] Yields were determined by ^{1}H NMR of the crude product using toluene as the internal standard. [c] Without addition of **1a.**

Substrate Scope - Conjugate Additions of Benylidene Barbiturate with other Nucleophiles

We attempted to extend the substrate scope of **1a**-catalyzed conjugate addition of **5a** with different nucleophiles (Table S4). Using **5a** and nucleophiles including 1-methylindole, indole and 5-methoxylindole, the corresponding adducts (**6p**-**6r**) were obtained with lower yield in the presence of **1a** than without **1a** (entries 1-3). However, the conjugate additions of **5a** with thiophene, dibenzoylmethane and ethylbenzyolacetate gave no conversion of starting materials (entries 4-6).

Table S4. Substrate scope of **1a**-catalyzed conjugate addition of **5a** with other nucleophiles

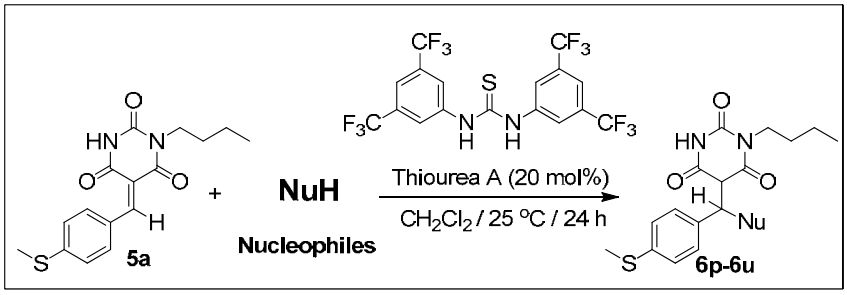


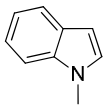
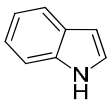
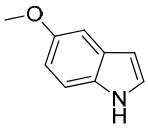
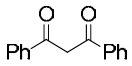
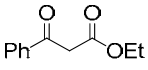
Entry[a]	Nucleophiles	Product	NMR Yield (%)[b]	Background NMR Yield (%)[b, c]
1		**6p**	62	72
2		**6q**	63	76
3		**6r**	39	45
4		**6s**	0	0
5		**6t**	0	0
6		**6u**	0	0

[a] Reaction conditions: **5a** (0.05 mmol), Nucleophile (0.05 mmol), **1a** (0.01 mmol), CH_2Cl_2 (1 mL), 25 °C, 24 h. [b] Yields were determined by ^1H NMR of the crude product using toluene as the internal standard. [c] Without addition of **1a**

We studied the substrate scope of thiourea A-catalyzed conjugate addition of **5a** with different nucleophiles (Table S5). Using **5a** and nucleophiles including 1-methylindole, indole and 5-methoxylindole, the corresponding adducts (**6p**-**6r**) were obtained were also obtained with lower yield in the presence of thiourea A than without thiourea A (entries 1-3). However, the conjugate additions of **5a** with thiophene, dibenzoylmethane and ethylbenzyolacetate gave no conversion of starting materials (entries 4-6).

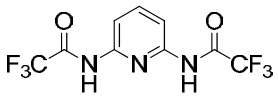
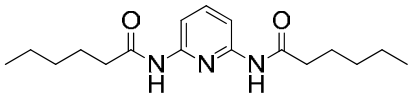
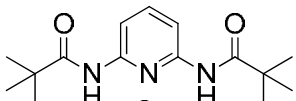
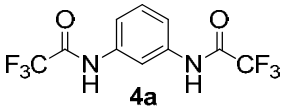
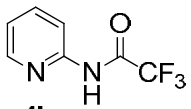
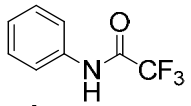
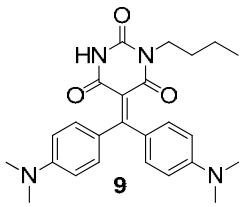
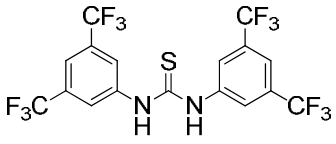
Table S5. Substrate scope of Thiourea A-catalyzed conjugate addition of **5a** with other nucleophiles



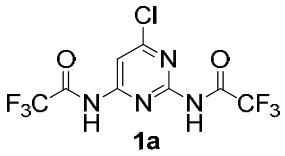
Entry[a]	Nucleophiles	Product	NMR Yield (%)[b]	Background NMR Yield (%)[b, c]
1		**6p**	52	72
2		**6q**	62	76
3		**6r**	35	45
4		**6s**	0	0
5		**6t**	0	0
6		**6u**	0	0

[a] Reaction conditions: **5a** (0.05 mmol), Nucleophile (0.05 mmol), Thiourea A (0.01 mmol), CH_2Cl_2 (1 mL), 25 °C, 24 h. [b] Yields were determined by ^1H NMR of the crude product using toluene as the internal standard. [c] Without addition of **1a**.

Literature Reference of 2a-c, 4a-4c, 9 and Thiourea A

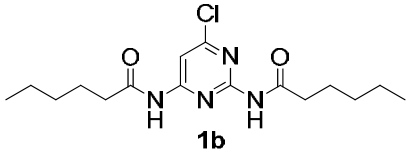
Compounds	Reference
 **2a**	I. Bolz, D. Schaarschmidt, T. Ruffer, H. Lang and S. Spange, *Angew. Chem. Int. Ed.*, 2009, **48**, 7440.
 **2b**	D. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner, M. Pollak, K. Mereiter, J. Kisala and K. Kirchner, *Organometallics*, 2006, **25**, 1900.
 **2c**	Z. Xu, P. Daka, I. Budik, H. Wang, F. Q. Bai and H. X. Zhang, *Eur. J. Org. Chem.*, 2009, 4581.
 **4a**	M. Habel, C. Niederalt, S. Grimme, M. Nieger and F. Vogtle, *Eur. J. Org. Chem.*, 1998, 1471.
 **4b**	J. Barluenga, J. M. Álvarez-Gutiérrez, A. Ballesteros and J. M. González, *Angew. Chem. Int. Ed.*, 2007, **46**, 1281.
 **4c**	J. Barluenga, J. M. Álvarez-Gutiérrez, A. Ballesteros and J. M. González, *Angew. Chem. Int. Ed.*, 2007, **46**, 1281.
 **9**	M. Bauer and S. Spange, *Angew. Chem. Int. Ed.* 2011, **50**, 9727.
 **Thiourea A**	K. M. Lippert, K. Hof, D. Gerbig, D. Ley, H. Hausmann, S. Guenther and P. R. Schreiner, *Eur. J. Org. Chem.* 2012, 5919.

Characterizations



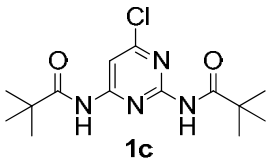
1a

Transparent crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 58% isolated yield; M.p. 80.0-81.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (br s, 1H), 10.94 (br s, 1H), 7.95 (s, 1H); ^{13}C NMR (100 MHz, d^6-Acetone) δ 162.6, 158.80, 156.5 (q, $^{2}J_{CF}$ = 39.4), 155.8, 154.1 (q, $^{2}J_{CF}$ = 38.6), 115.4 (q, $^{1}J_{CF}$ = 286.7), 115.3 (q, $^{1}J_{CF}$ = 285.8), 107.1; IR υ_{max} (cm^{-1}) 3598, 3502, 1732, 1679; ESIMS *m/z* 337 [M+H$^+$]; HRMS (ESI) for $C_8H_4N_4O_2Cl$ $[M+H]^+$ calcd: 336.9927, found: 336.9935; X-ray crystallography obtained.



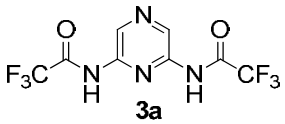
1b

White solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 15% isolated yield; M.p. 198.7-202.5 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (br s, 1H), 9.66 (br s, 1H), 8.08 (s, 1H), 2.98 (br s, 2H), 2.51-5.54 (m, 2H), 1.70-1.74 (m, 4H), 1.36-1.39 (m, 8H), 0.91-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 174.4, 162.6, 160.5, 156.4, 105.1, 37.50, 37.49, 31.62, 31.55, 25.1, 24.7, 22.7, 22.6, 14.13, 14.10; IR υ_{max} (cm^{-1}) 3281, 1716, 1671; ESIMS *m/z* 341 [M+H$^+$]; HRMS (ESI) for $C_{16}H_{26}N_4O_2Cl$ $[M+H]^+$ calcd: 341.1744, found: 341.1740.



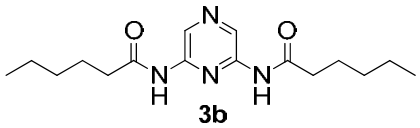
1c

White solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 62% isolated yield; M.p. 128.0-129.9 ^{o}C; ^{1}H NMR (400 MHz, d^6-Acetone) δ 10.11 (br s, 1H), 9.01 (br s, 1H), 7.92 (s, 1H), 1.34 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, d^6-Acetone) δ 178.6, 176.0, 161.6, 160.7, 157.3, 104.0, 40.3, 40.2, 26.6, 26.4; IR υ_{max} (cm^{-1}) 3576, 3479, 1697; ESIMS *m/z* 313 [M+H$^+$]; HRMS (ESI) for $C_{14}H_{21}N_4O_2ClNa$ $[M+Na]^+$ calcd: 335.1251, found: 335.1241.



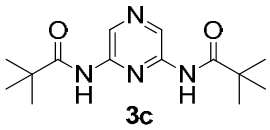
3a

White solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 68% isolated yield; M.p. 194.2-195.8 ^{o}C; ^{1}H NMR (400 MHz, d^6-Acetone) δ 11.00-11.02 (br s, 2H), 9.19 (s, 2H); ^{13}C NMR (100 MHz, d^6-Acetone) δ 155.62 (q, $^{2}J_{CF}$ = 40.8), 145.1, 134.0, 115.9 (q, $^{1}J_{CF}$ = 228.8); IR υ_{max} (cm^{-1}) 3349, 3320, 1752, 1734; ESIMS *m/z* 303 [M+H^{+}].



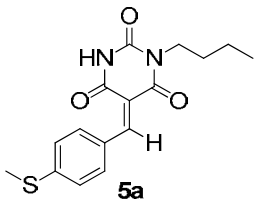
3b

White solid, analytical TLC (silica gel 60) (ethyl acetate) R_f = 0.1; 58% isolated yield; M.p. 273.9-275.7 ^{o}C; ^{1}H NMR (400 MHz, d^6-DMSO) δ 10.35 (br s, 2H), 8.97 (s, 2H), 2.43 (t, *J* = 7.0 Hz, 4H), 1.55-1.62 (m, 4H), 1.26-1.29 (m, 8H), 0.87 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, d^6-DMSO) δ 172.5, 146.6, 130.6, 35.8, 30.8, 24.6, 21.9, 13.9; IR υ_{max} (cm^{-1}) 3336, 1685; ESIMS *m/z* 307 [M+H^{+}]; HRMS (ESI) for $C_{16}H_{27}N_4O_2$ [M+H]$^{+}$ calcd: 307.2134, found: 307.2149.



3c

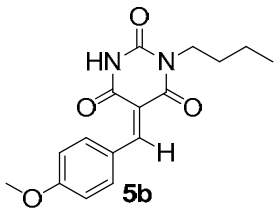
White solid, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 62% isolated yield; M.p. 147.6-149.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 145.8, 131.6, 40.0, 27.6; IR υ_{max} (cm^{-1}) 3420, 1701; ESIMS *m/z* 279 [M+H^{+}]; HRMS (ESI) for $C_{14}H_{23}N_4O_2$ [M+H]$^{+}$ calcd: 279.1821, found: 279.1808.



5a *E* / *Z* mixture

Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 73% isolated yield; M.p. 159.4-160.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (br s, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.94-3.98 (m, 2H), 2.55 (s, 3H), 1.65-1.68 (m, 2H), 1.38-1.40 (m, 2H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 160.4, 159.5, 150.1, 148.5, 135.5, 128.7, 124.7, 115.4, 41.8, 30.2, 20.2, 14.6, 13.8; IR υ_{max} (cm^{-1})

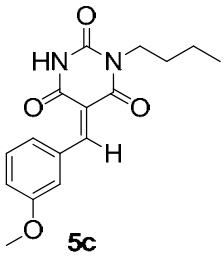
3471, 3416, 1730, 1695; ESIMS *m/z* 319 [M+H$^+$]; HRMS (ESI) for $C_{16}H_{19}N_2O_3S$ [M+H]$^+$ calcd: 319.1116, found: 319.1108.



5b

E / *Z* mixture

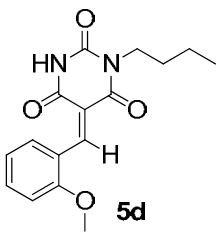
Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 72% isolated yield; M.p. 166.4-167.1 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1H), 8.38 (d, *J* = 9.0 Hz, 2H), 8.33 (br s, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 2H), 3.92 (s, 3H), 1.63-1.66 (m, 2H), 1.37-1.42 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8, 163.9, 161.6, 160.9, 160.8, 160.0, 159.1, 150.4, 150.3, 138.7, 138.5, 125.7, 125.6, 114.34, 114.30, 114.14, 114.07, 55.9, 41.9, 41.3, 30.3, 20.4, 20.3, 15.0, 14.0; IR υ_{max} (cm^{-1}) 3464, 1741, 1689; ESIMS *m/z* 303 [M+H$^+$]; HRMS (ESI) for $C_{16}H_{19}N_2O_4$ [M+H]$^+$ calcd: 303.1345, found: 303.1357.



5c

E / *Z* mixture

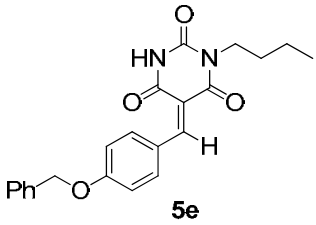
Yellow solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 78% isolated yield; M.p. 149.2-149.6 ^oC;^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.94 (br s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.96 (t, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 1.62-1.68 (m, 2H), 1.36-1.42 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 162.8, 160.9, 160.7, 160.3, 159.5, 150.5, 150.4, 133.8, 129.5, 128.1, 127.2, 120.9, 120.0, 118.2, 117.9, 117.6, 117.4, 55.70, 55.68, 42.0, 41.4, 30.3, 20.33, 20.31, 14.0; IR υ_{max} (cm^{-1}) 3419, 1737, 1698; ESIMS *m/z* 303 [M+H$^+$]; HRMS (ESI) for $C_{16}H_{19}N_2O_4$ [M+H]$^+$ calcd: 303.1345, found: 303.1359.



5d

E / *Z* mixture

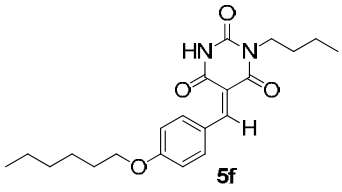
Yellow solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 25% isolated yield; M.p. 163.6-167.3 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.16 (br s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.88-3.91 (m, 5H), 1.59-1.63 (m, 2H), 1.34-1.40 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.9, 160.0, 155.5, 150.3, 135.2, 133.0, 122.1, 120.1, 117.2, 110.7, 56.02, 56.01, 45.0, 41.4, 30.3, 20.4, 14.0; IR υ_{max} (cm^{-1}) 3449, 1698, 1668; ESIMS *m/z* 303 [M+H$^+$]; HRMS (ESI) for $C_{16}H_{19}N_2O_4$ [M+H]$^+$ calcd: 303.1345, found: 303.1337.



5e

E / *Z* mixture

Yellow crystal, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 58% isolated yield; M.p. 168.8-170.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 2H), 7.97 (br s, 1H), 7.36-7.42 (m, 5H), 7.05 (d, *J* = 9.0 Hz, 2H), 5.18 (s, 2H), 3.95 (t, *J* = 7.5 Hz, 2H), 1.63-1.67 (m, 2H), 1.36-1.43 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.00, 163.96, 163.9, 163.2, 161.6, 161.0, 159.9, 159.1, 150.5, 150.4, 138.7, 138.6, 136.0, 129.97, 128.96, 128.6, 127.8, 127.7, 125.9, 125.8, 115.14, 115.12, 114.23, 114.18, 70.6, 45.0, 41.9, 41.4, 30.34, 30.33, 20.39, 20.35, 14.01, 13.99; IR υ_{max} (cm^{-1}) 3449, 1731, 1697, 1653; ESIMS *m/z* 379 [M+H$^+$]; HRMS (ESI) for $C_{22}H_{23}N_2O_4$ [M+H]$^+$ calcd: 379.1658, found: 379.1667.

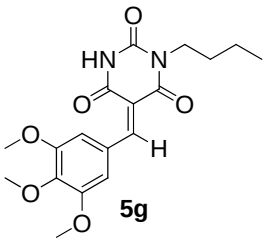


5f

E / *Z* mixture

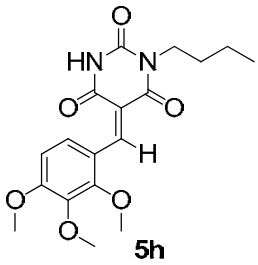
Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 80% isolated yield; M.p. 149.8-152.2 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 2H), 1.79-1.84 (m, 2H), 1.61-1.67 (m, 2H), 1.46-1.48 (m, 2H), 1.34-1.41 (m, 6H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.90-0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.0, 160.0, 138.9, 125.5, 114.8, 113.8, 68.7, 41.87, 41.86, 41.85, 31.7, 30.3, 29.2, 25.8, 22.8, 20.3, 14.2, 14.0; IR υ_{max} (cm^{-1}) 3464, 1697, 1649; ESIMS *m/z* 373 [M+H$^+$]; HRMS (ESI) for $C_{21}H_{29}N_2O_4$ [M+H]$^+$

calcd: 373.2127, found: 373.2122.



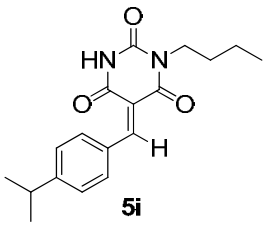
E / *Z* mixture

Yellow solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 42% isolated yield; M.p. 169.0-170.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46-9.60 (br d, 1H), 8.49 (d, *J* = 9.0 Hz, 1H), 7.82 (s, 1H), 7.74 (s, 1H), 3.94-4.01 (m, 11H), 1.62-1.67 (m, 2H), 1.37-1.42 (m, 2H), 0.94-0.99 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.3, 161.30, 161.29, 160.33, 159.26, 152.59, 152.55, 150.3, 144.1, 144.0, 127.5, 127.4, 115.5, 115.4, 113.7, 113.5, 61.3, 56.6, 56.5, 42.0, 41.2, 30.30, 30.26, 20.3, 14.0; IR υ_{max} (cm^{-1}) 3422, 1736, 1697, 1655; ESIMS *m/z* 363 [M+H$^+$]; HRMS (ESI) for $C_{18}H_{23}N_2O_6$ [M+H]$^+$ calcd: 363.1556, found: 363.1557.



E / *Z* mixture

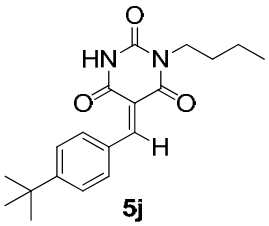
Yellow solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 69% isolated yield; M.p. 155.7-158.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.32-8.35 (m, 2H), 6.76 (d, *J* = 9.0 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H), 3.89-3.93 (m, 2H), 3.86 (s, 3H), 1.58-1.66 (m, 2H), 1.33-1.42 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.3, 159.2, 156.3, 154.2, 150.4, 141.2, 130.0, 120.0, 115.0, 106.4, 62.2, 60.9, 56.2, 41.1, 30.1, 20.2, 13.8; IR υ_{max} (cm^{-1}) 3465, 1745, 1697, 1655; ESIMS *m/z* 363 [M+H$^+$]; HRMS (ESI) for $C_{18}H_{20}N_4O_3Na$ [M+Na]$^+$ calcd: 363.1433, found: 363.1469.



E / *Z* mixture

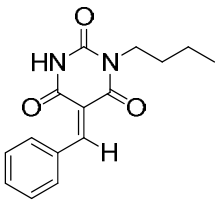
Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.7; 24%

isolated yield; M.p. 149.1-149.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (br s, 1H), 8.60 (s, 1H), 8.20 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.98 (t, J = 7.5 Hz, 2H), 2.97-3.04 (m, 1H), 1.63-1.71 (m, 2H), 1.41-1.46 (m, 2H), 1.30 (d, J = 7.5 Hz, 6H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.4, 160.2, 156.0, 150.1, 135.2, 130.2, 126.7, 116.0, 41.8, 34.5, 30.1, 23.5, 20.1, 13.8; IR υ_{max} (cm^{-1}) 3416, 1735, 1698, 1653; ESIMS *m/z* 315 [M+H$^+$].



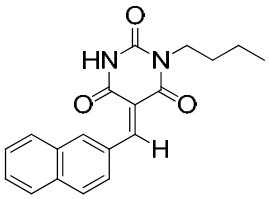
5j *E* / *Z* mixture

Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.7; 52% isolated yield; M.p. 156.3-160.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (br d, 1H), 8.58 (s, 1H), 8.13-8.22 (m, 2H), 7.48-7.51 (m, 2H), 3.92-3.98 (m, 2H), 1.62-1.67 (m, 2H), 1.30-1.42 (m, 11H), 0.94-0.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.2, 161.2, 160.8, 160.3, 159.6, 158.3, 158.1, 150.7, 150.5, 135.1, 134.9, 130.0, 129.9, 125.7, 125.7, 116.3, 41.9, 41.3, 35.6, 31.2, 30.3, 20.3, 20.3, 13.97, 13.96; IR υ_{max} (cm^{-1}) 3464, 1730, 1698, 1653; ESIMS *m/z* 329 [M+H$^+$], HRMS (ESI) for $C_{19}H_{25}N_2O_3$ [M+H]$^+$ calcd: 329.1865, found: 329.1869.



5k *E* / *Z* mixture

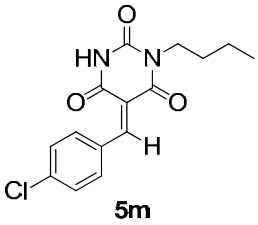
Transparent crystal, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.6; 40% isolated yield; M.p. 155.5-156.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13 (d, J = 8.0 Hz, 2H), 7.46-7.56 (m, 3H), 3.96 (t, J = 7.5 Hz, 2H), 1.62-1.68 (m, 2H), 1.36-1.44 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 160.5, 160.0, 159.8, 150.1, 134.3, 134.0, 133.7, 133.5, 132.6, 128.6, 128.6, 117.4, 45.01, 45.00, 42.1, 30.3, 20.4, 20.3, 14.0; IR υ_{max} (cm^{-1}) 3436, 1731, 1701, 1655; ESIMS *m/z* 273 [M+H$^+$].



5l

E / *Z* mixture

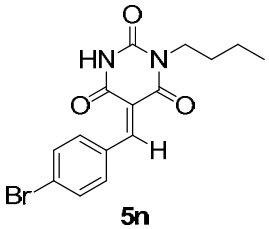
Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 85% isolated yield; M.p. 199.0-202.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.25 (br s, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.88-7.93 (m, 2H), 7.54-7.58 (m, 3H), 3.84-3.88 (m, 2H), 1.54-1.62 (m, 2H), 1.30-1.36 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 161.4, 160.4, 159.3, 158.4, 157.8, 149.8, 133.4, 133.1, 132.9, 132.0, 131.8, 130.4, 130.1, 130.0, 129.9, 127.73, 127.69, 126.7, 125.0, 124.9, 124.23, 124.16, 119.4, 119.3, 45.0, 42.0, 41.5, 30.3, 30.2, 20.4, 20.3, 13.94, 13.89; IR υ_{max} (cm^{-1}) 3415, 1737, 1699, 1666; ESIMS *m/z* 323[$M+H^+$]; HRMS (ESI) for $C_{14}H_{18}N_4O_5Na$ $[M+Na]^+$ calcd: 345.1175, found: 345.1162.



5m

E / *Z* mixture

Transparent crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 80% isolated yield; M.p. 187.4-194.0 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.24 (br s, 1H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 2H), 1.63-1.68 (m, 2H), 1.36-1.43 (m, 2H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.9, 160.1, 158.7, 150.0, 140.1, 135.7, 135.5, 131.0, 129.99, 128.96, 117.6, 45.0, 42.10 30.3, 20.3, 14.0; IR υ_{max} (cm^{-1}) 3416, 1730, 1697, 1655; ESIMS *m/z* 307 [$M+H^+$]; HRMS (ESI) for $C_{15}H_{16}N_2O_3Cl$ $[M+H]^+$ calcd: 307.0849, found: 307.0861.

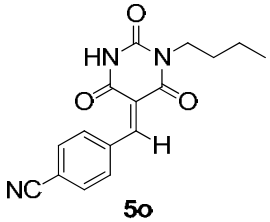


5n

E / *Z* mixture

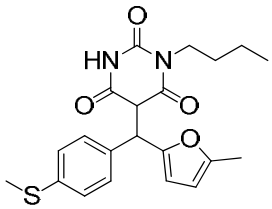
Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.6; 32% isolated yield; M.p. 188.1-188.6 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.26 (br s, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 3.96 (t, *J* = 7.5 Hz, 2H), 1.63-1.68 (m, 2H), 1.36-1.43 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.9,

160.2, 158.8, 158.1, 150.2, 135.6, 135.4, 132.0, 131.9, 131.38, 131.36, 128.9, 128.7, 117.81, 117.78, 45.0, 42.1, 41.5, 30.3, 20.34, 20.31, 14.0; IR υ_{max} (cm^{-1}) 3449, 1728, 1697, 1659; ESIMS *m/z* 351 [M+H^+]; HRMS (ESI) for $C_{15}H_{16}N_2O_3Br$ $[M+H]^+$ calcd: 351.0344, found: 351.0337.



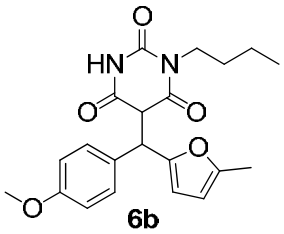
5o *E* / *Z* mixture

Yellow solid, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 85% isolated yield; M.p. 223.5-225.1 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 3.97 (t, *J* = 7.5 Hz, 2H), 1.60-1.68 (m, 2H), 1.34-1.44 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 161.0, 160.3, 159.3, 157.0, 156.3, 149.6, 149.5, 136.9, 136.8, 132.9, 132.6, 132.99, 131.97, 120.2, 118.3, 115.5, 115.4, 45.0, 42.2, 30.23, 30.20, 20.31, 20.29, 13.93, 13.92; IR υ_{max} (cm^{-1}) 3417, 2235, 1727, 1698, 1655; ESIMS *m/z* 298 [M+H^+]; HRMS (ESI) for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ calcd: 298.1192, found: 298.1198.



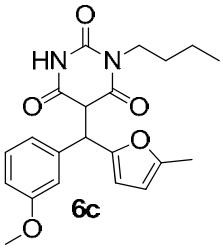
6a

Yellow oil, analytical TLC (silica gel 60) (30% ethyl acetate in *n*-hexane) R_f = 0.6; 55% isolated yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (br s, 1H), 7.18-7.28 (m, 4H), 5.96-5.99 (m, 1H), 5.91-5.92 (m, 1H), 5.00 (d, *J* = 4.0 Hz, 1H), 4.15-4.18 (m, 1H), 3.68-3.80 (m, 2H), 2.48 (s, 3H), 2.28 (s, 3H), 1.42-1.46 (m, 2H), 1.25-1.30 (m, 2H), 0.89-0.949 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.6, 167.1, 166.9, 152.1, 152.0, 150.4, 150.4, 150.1, 138.9, 133.6, 133.5, 129.6, 126.6, 126.6, 109.9, 109.8, 106.7, 53.5, 53.4, 47.8, 41.50, 41.47, 31.8, 30.01, 29.97, 22.9, 20.2, 20.1, 15.8, 14.3, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3461, 1717, 1684; ESIMS *m/z* 401[M+H^+].



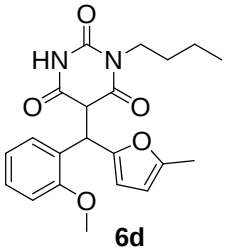
6b

Yellow oil, analytical TLC (silica gel 60) (30% ethyl acetate in *n*-hexane) R_f = 0.6; 52% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (br s, 1H), 7.23-7.26 (m, 2H), 6.82-6.85 (m, 2H), 5.95 (d, *J* = 9.0 Hz, 1H), 5.89-5.90 (m, 1H), 4.97 (d, *J* = 4.0 Hz, 1H), 4.16 (dd, *J* = 4.0, 7.0 Hz, 1H), 3.79 (s, 3H), 3.64-3.75 (m, 2H), 2.27 (s, 3H), 1.35-1.48 (m, 2H), 1.17-1.29 (m, 2H), 0.86-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.6, 167.3, 166.9, 159.6, 151.93, 151.91, 150.9, 150.8, 150.1, 130.3, 128.5, 114.2, 114.2, 109.8, 109.7, 106.67, 106.65, 55.4, 53.7, 53.7, 47.9, 47.8, 41.5, 41.4, 30.01, 29.96, 20.2, 20.1, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3436, 1719, 1690; ESIMS *m/z* 385 [$M+H^+$].



6c

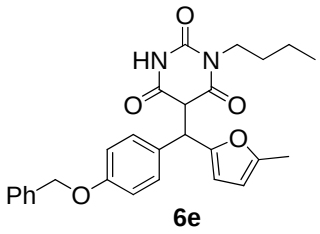
Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.4; 78% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (br s, 1H), 7.19-7.26 (m, 1H), 6.82-6.91 (m, 3H), 6.00 (dd, *J* = 3.5, 15.5 Hz, 1H), 5.89 (dd, *J* = 3.0, 7.5 Hz, 1H), 4.98 (m, 1H), 4.17 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.63-3.76 (m, 5H), 2.26 (s, 3H), 1.37-1.44 (m ,2H), 1.20-1.27 (m, 2H), 0.86-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.84, 167.83, 167.66, 167.57, 152.1, 152.0, 150.50, 150.45, 150.4, 150.3, 136.8, 136.7, 129.1, 128.9, 128.8, 128.42, 128.39, 110.0, 109.9, 106.7, 53.6, 53.5, 48.41, 48.39, 48.38, 41.48, 41.45, 29.99, 29.95, 20.2, 20.1, 13.9, 13.81, 13.75; IR υ_{max} (cm^{-1}) 3421, 1718, 1686; ESIMS *m/z* 385 [$M+H^+$].



6d

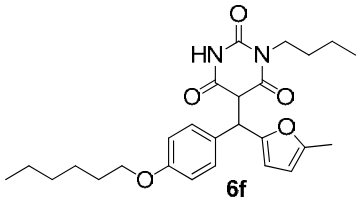
Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.4; 25% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (br d, 1H), 7.24-7.29 (m, 1H), 7.08 (dd, *J* =

7.5, 19.0 Hz, 1H), 6.87-6.92 (m, 2H), 6.07 (dd, *J* = 2.5, 34.5 Hz, 1H), 5.91 (br s, 1H), 5.38, (t, *J* = 5.0 Hz, 1H), 4.26 (dd, *J* = 4.5, 16.5 Hz, 1H), 3.88 (d, *J* = 4.5 Hz, 3H), 3.77 (t, *J* = 9.5 Hz, 1H), 3.60-3.75 (m, 1H), 2.24 (s, 3H), 1.50-1.54 (m, 1H), 1.17-1.32 (m, 4H), 0.85-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.9, 167.6, 167.3, 156.40, 156.37, 152.22, 152.17, 150.73, 150.66, 150.5, 150.3, 130.29, 130.27, 129.1, 129.0, 126.9, 126.7, 120.67, 120.65, 110.3, 110.2, 110.0, 106.8, 106.7, 60.7, 55.64, 55.62, 55.52, 55.51, 51.6, 51.4, 45.0, 42.1, 41.7, 41.4, 41.3, 30.1, 30.0, 21.3, 20.3, 20.1, 14.4, 14.0, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3434, 1720, 1687; ESIMS *m/z* 385 [M+H$^+$].



6e

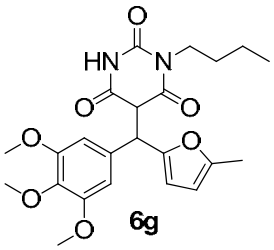
Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.3; 30% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (br s, 1H), 7.32-7.42 (m, 5H), 7.24 (t, *J* = 9.5 Hz, 2H), 6.89-6.92 (m, 2H), 5.95 (dd, *J* = 2.5, 10.0 Hz, 1H), 5.89-5.90 (m, 1H), 5.03 (s, 2H), 4.96 (d, *J* = 3.5 Hz, 1H), 4.14 (dd, *J* = 5.0, 9.0 Hz, 1H), 3.67-3.75 (m, 2H), 2.26 (s, 3H), 1.18-1.45 (m, 4H), 0.87-0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.6, 167.3, 166.9, 158.9, 152.0, 152.0, 150.83, 150.81, 150.10, 150.08, 137.0, 130.3, 128.9, 128.84, 128.83, 128.3., 127.74, 127.73, 115.12, 115.09, 109.8, 109.7, 106.7, 70.2, 53.72, 53.69, 47.91, 47.85, 45.01, 45.00, 41.50, 41.48, 41.47, 30.03, 29.97, 20.22, 20.16, 13.94, 13.93, 13.83, 13.78; IR υ_{max} (cm^{-1}) 3448, 1719, 1686; ESIMS *m/z* 461 [M+H$^+$]; HRMS (ESI) for $C_{27}H_{28}N_2O_5Na$ [M+Na]$^+$ calcd: 483.1896, found: 483.1881.



6f

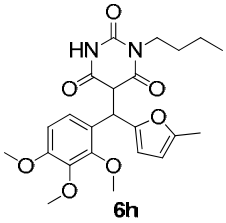
Yellow oil, analytical TLC (silica gel 60) (10% ethyl acetate in *n*-hexane) R_f = 0.6; 16% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 7.23 (t, *J* = 8.5 Hz 2H), 6.82-6.86 (m, 2H), 5.90-5.99 (m, 2H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.18 (dd, *J* = 3.5, 7.0 Hz, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.65-3.79 (m, 2H), 2.29 (s, 3H), 1.75-1.82 (m, 2H), 1.19-1.49 (m, 10H), 0.89-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.6, 167.3, 166.8, 159.2, 151.89, 151.86, 151.82, 150.94, 150.88, 150.00, 149.96, 149.92, 130.2, 130.05, 129.99,

129.97, 128.2, 114.8, 114.7, 114.6, 109.72, 109.66, 109.57, 106.6, 68.2, 53.74, 53.70, 48.98, 47.88, 47.85, 41.46, 41.42, 41.38, 31.8, 30.0, 30.0, 29.9, 25.9, 22.8, 20.2, 20.1, 14.2, 13.86, 13.80, 13.76, 13.72, 13.66; IR υ_{max} (cm^{-1}) 3416, 1719, 1686; ESIMS *m/z* 455 [$M+H^+$].



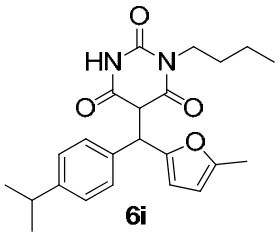
6g

Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.4; 65% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.3 (br d, 1H), 6.60 (d, *J* = 3.5 Hz, 2H), 5.98-6.02 (m, 1H), 5.90-2.92 (m, 1H), 4.96 (d, *J* = 7.0 Hz, 1H), 4.19 (d, *J* = 3.5 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 6H), 3.62-3.77 (m, 2H), 2.27 (s, 3H), 1.34-1.50 (m, 2H), 1.18-1.32 (m, 2H), 0.87-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.7, 167.1, 166.8, 153.38, 153.35, 152.0, 151.9, 150.69, 150.66, 150.0, 149.9, 138.2, 138.1, 132.4, 132.1, 109.83, 109.75, 106.8, 106.7, 106.6, 106.5, 61.0, 56.37, 56.35, 53.5, 48.6, 48.3, 41.5, 41.4, 30.1, 20.2, 20.1, 13.84, 13.76, 13.7; IR υ_{max} (cm^{-1}) 3424, 1719, 1686; ESIMS *m/z* 445 [$M+H^+$].



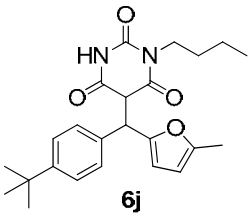
6h

Yellow oil, analytical TLC (silica gel 60) (30% ethyl acetate in *n*-hexane) R_f = 0.5; 47% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66-8.70 (br d, 1H), 6.81-6.91 (m, 1H), 6.57-6.62 (m, 1H), 6.04 (d, *J* = 25.6 Hz, 1H), 5.89 (br s, 1H), 5.29 (br s, 1H), 4.13-4.16 (m, 1H), 3.95 (s, 3H), 3.82-3.83 (m, 6H), 3.61-3.78 (m, 2H), 2.24 (s, 3H), 1.52-1.54 (m, 1H), 1.20-1.37 (m, 3H), 0.86-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.8, 167.7, 167.5, 153.51, 153.50, 152.00, 151.97, 151.4, 150.9, 150.73, 150.68, 150.6, 141.9, 124.5, 124.4, 123.9, 123.7, 109.7, 107.0, 107.0, 106.7, 106.6, 61.3, 61.2, 60.9, 56.1, 56.0, 52.70, 52.66, 41.9, 41.5, 41.4, 41.3, 30.1, 30.0, 20.2, 20.1, 13.89, 13.87, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3421, 1719, 1686; ESIMS *m/z* 445 [$M+H^+$]; HRMS (ESI) for $C_{23}H_{28}N_2O_7Na$ $[M+Na]^+$ calcd: 467.1794, found: 467.1780.



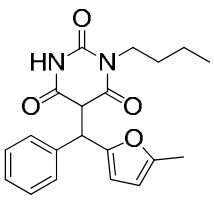
6i

Yellow oil, analytical TLC (silica gel 60) (30% ethyl acetate in *n*-hexane) R_f = 0.6; 66% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 7.15-7.26 (m, 4H), 5.98 (dd, *J* = 3.0, 10.5 Hz, 1H), 5.89-5.90 (m, 1H), 4.98 (br s, 1H), 4.17 (dd, *J* = 3.5, 7.0 Hz, 1H), 3.61-3.76 m, 2H), 2.83-2.93 (m, 1H), 2.26 (s, 3H), 1.30-1.46 (m, 2H), 1.15-1.23 (m, 8H), 0.86-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.7, 167.3, 166.9, 152.0, 151.9, 150.72, 150.67, 150.1, 149.1, 149.0, 133.94, 133.93, 133.8, 129.0, 129.0, 126.9, 126.8, 109.9, 109.8, 106.68, 106.65, 53.64, 53.61, 48.3, 48.2, 41.5, 41.4, 33.9, 29.9, 24.11, 24.08, 24.0, 20.2, 20.1, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3449, 1719, 1686; ESIMS *m/z* 397 [$M+H^+$].



6j

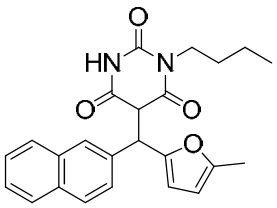
Brown oil, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 73% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (br d, 1H), 7.22-7.34 (m, 4H), 5.98 (dd, *J* = 3.0, 13.0 Hz, 1H), 5.88-5.90 (m, 1H), 4.98-5.00 (m, 1H), 4.16 (dd, *J* = 3.5, 7.0 Hz, 1H), 3.61-3.76 (m, 2H), 2.26 (s, 3H), 1.34-1.44 (m, 2H), 1.33 (s, 9H), 1.14-1.29 (m, 2H), 0.86-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.7, 167.5, 167.2, 151.94, 151.88, 151.33, 151.28, 150.73, 150.66, 150.2, 133.6, 133.5, 128.8, 128.7, 125.73, 125.69, 109.9, 109.8, 106.68, 106.65, 53.62, 53.59, 48.2, 48.0, 41.44, 41.36, 34.7, 31.5, 30.0, 20.2, 20.1, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3414, 1719, 1686; ESIMS *m/z* 410 [$M+H^+$]; HRMS (ESI) for $C_{24}H_{30}N_2O_4Na$ $[M+Na]^+$ calcd: 433.2103, found: 433.2096.



6k

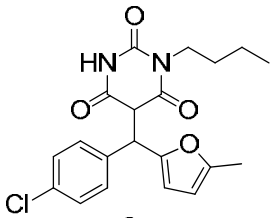
Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 79% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (br s, 1H), 7.31 (m, 5H), 5.98 (dd, *J* = 3.5, 15.5 Hz, 1H), 5.89-5.91 (m, 1H), 5.01 (d, *J* = 4.5 Hz, 1H), 4.17 (dd, *J* = 4.5, 10.5 Hz, 1H),

3.63-3.76 (m, 2H), 2.26 (s, 3H), 1.27-1.45 (m, 2H), 1.15-1.20 (m, 2H), 0.86-0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.6, 167.3, 167.3, 159.84, 159.83, 152.1, 152.0, 150.41, 150.35, 138.22, 138.20, 129.84, 129.81, 121.4, 121.3, 115.2, 115.1, 113.64, 113.57, 110.0, 109.9, 106.73, 106.72, 55.4, 53.5, 53.4, 48.4, 48.3, 41.5, 41.4, 30.01, 29.98, 20.2, 20.1, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3414, 1719, 1685; ESIMS *m/z* 355 [$M+H^+$].



6l

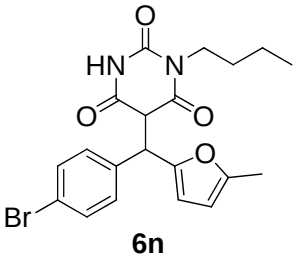
Yellow oil, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.4; 35% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.24 (m, 1H), 7.82-7.91 (m, 2H), 7.41-7.61 (m, 4H), 6.01 (dd, *J* = 3.0, 11.0 Hz, 1H), 5.92-5.94 (m, 2H), 4.17 (dd, *J* = 3.5, 15.0 Hz, 1H), 3.72-3.87 (m, 1H), 3.66 (t, *J* = 7.5 Hz, 1H), 2.27 (s, 3H), 1.44-1.51 (m, 1H), 1.13-1.31 (m, 3H), 0.80-0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 167.8, 167.2, 166.6, 152.23, 152.17, 150.3, 150.2, 150.1, 134.12, 134.10, 133.7, 133.6, 130.92, 130.85, 129.62, 129.58, 128.9, 127.8, 127.7, 127.2, 127.1, 125.94, 125.92, 125.4, 122.3, 122.2, 110.24, 110.18, 107.0, 52.4, 52.3, 43.9, 43.2, 41.6, 41.4, 30.0, 29.9, 20.2, 20.1, 13.9, 13.83, 13.80, 13.7; IR υ_{max} (cm^{-1}) 3448, 1716, 1686; ESIMS *m/z* 404 [$M+H^+$]; HRMS (ESI) for $C_{24}H_{24}N_2O_4Na$ $[M+Na]^+$ calcd: 427.1634, found: 427.1674.



6m

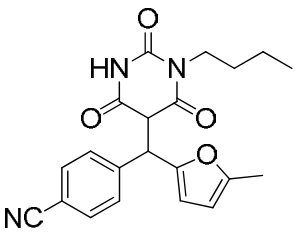
Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 95% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (br d, 1H), 7.28 (d, *J* = 7.0 Hz, 4H), 5.95 (dd, *J* = 3.5, 13.0 Hz, 1H), 5.89-5.91 (m, 1H), 5.02-5.03 (m, 1H), 4.11 (dd, *J* = 4.5, 8.0 Hz, 1H), 3.66-3.77 (m, 2H), 2.25 (s, 3H), 1.38-1.45 (m, 2H), 1.19-1.27 (m, 2H), 0.88-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.5, 167.3, 167.2, 152.3, 152.2, 150.3, 150.0, 150.0, 135.9, 135.7, 134.2, 134.2, 130.3, 130.6, 129.0, 129.0, 110.0, 109.9, 106.8, 53.3, 47.3, 47.24, 47.23, 45.0, 41.5, 30.03, 29.98, 20.2, 20.1, 13.9, 13.8, 13.70; IR υ_{max} (cm^{-1}) 3448, 1717, 1686; ESIMS *m/z* 389 [$M+H^+$]; HRMS (ESI) for $C_{20}H_{21}N_2O_4ClNa$ $[M+Na]^+$ calcd: 411.1088,

found: 411.1105.



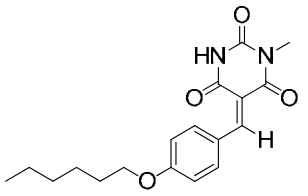
6n

Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 95% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (br d, 1H), 7.43-7.46 (m, 2H), 7.20-7.24 (m, 2H), 5.95 (dd, *J* = 3.5, 13.0 Hz, 1H), 5.90-5.93 (m, 1H), 5.01-5.02 (m, 1H), 4.11 (dd, *J* = 4.5, 7.0 Hz, 1H), 3.70-3.76 (m, 2H), 2.25 (s, 3H), 1.39-1.45 (m, 2H), 1.20-1.25 (m, 2H), 0.88-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.54, 167.47, 167.46, 167.08, 167.05, 167.00, 169.99, 152.3, 152.24, 150.18, 150.15, 150.13, 149.9, 149.8, 136.4, 136.3, 132.08, 132.05, 132.02, 131.98, 131.96, 130.99, 130.95, 130.90, 130.88, 122.39, 122.38, 110.1, 110.0, 106.86, 106.84, 106.81, 105.0, 53.2, 47.34, 47.28, 45.0, 41.6, 30.04, 29.98, 20.17, 20.15, 13.9, 13.8, 13.7; IR υ_{max} (cm^{-1}) 3447, 1717, 1685; ESIMS *m/z* 433 $[M+H^+]$; HRMS (ESI) for $C_{20}H_{21}N_2O_4BrNa$ $[M+Na]^+$ calcd: 455.0582, found: 455.0575.



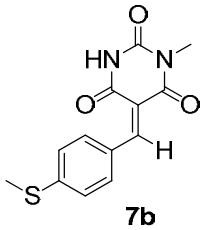
6o

Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.4; 98% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (br d, 1H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 5.99 (dd, *J* = 2.5, 11.0 Hz, 1H), 5.92 (br s, 1H), 5.15 (br s, 1H), 4.07 (t, *J* = 3.5 Hz, 1H), 3.71-3.80 (m, 2H), 2.24 (s, 3H), 1.41-1.48 (m, 2H), 1.24-1.27 (m, 2H), 0.89-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 167.04, 166.96, 166.6, 152.7, 150.1, 150.0, 148.81, 148.79, 143.6, 143.4, 132.50, 132.49, 130.1, 130.0, 129.9, 118.7, 111.97, 111.95, 110.5, 110.4, 106.97, 106.96, 106.94, 61.0, 53.07, 53.05, 53.03, 53.01, 47.24, 47.21, 47.0, 46.9, 41.7, 30.03, 29.97, 21.3, 20.2, 20.1, 14.4, 13.9, 13.74, 13.65; IR υ_{max} (cm^{-1}) 3448, 2230, 1718, 1686; ESIMS *m/z* 380 $[M+H^+]$.



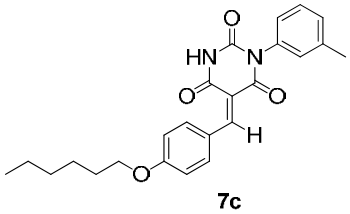
7a *E* / *Z* mixture

Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 95% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61-8.64 (br s, 1H), 8.53 (s, 1H), 8.39 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.39 (s, 3H), 1.79-1.84 (m, 2H), 1.46-1.48 (m, 2H), 1.35-1.36 (m, 4H), 0.90-0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.3, 161.86, 160.88, 160.2, 150.6, 138.9, 125.4, 114.8, 113.5, 68.8, 45.0, 31.7, 29.2, 28.6, 25.83, 22.79, 14.2; IR υ_{max} (cm^{-1}) 3421, 1726, 1699, 1648; ESIMS *m/z* 331 [M+H$^+$]; HRMS (ESI) for $C_{18}H_{23}N_2O_4$ [M+H]$^+$ calcd: 331.1658, found: 331.1642.



7b *E* / *Z* mixture

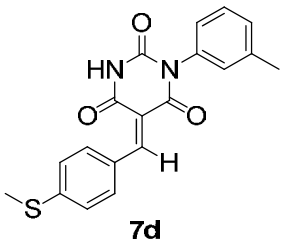
Yellow solid, analytical TLC (silica gel 60) (ethyl acetate) R_f = 0.2; 82% isolated yield; ^{1}H NMR (500 MHz, d^6-DMSO) δ 8.25 (d, *J* = 14.0 Hz, 1H), 8.16-8.20 (t, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.32 (s, 3H), 3.15 (d, *J* = 15 Hz, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO) δ 163.9 (162.9), 162.0 (161.4), 155.5 (154.9), 151.1 (151.0), 146.5 (146.4), 135.0, 129.1 (129.0), 124.81 (124.78), 117.8 (117.7), 28.2 (27.7), 14.30; IR υ_{max} (cm^{-1}) 3421, 1717, 1689; ESIMS *m/z* 277 [M+H$^+$].



7c *E* / *Z* mixture

Yellow crystal, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 41% isolated yield; M.p. 172.2-175.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.39 (d, *J* = 7.0 Hz, 2H), 8.67 (br s, 1H), 7.41 (t, *J* = 6.0 Hz, 1H), 7.27-7.29 (m, 2H), 7.07-7.09 (m, 2H), 6.91 (d, *J* = 7.0 Hz, 2H), 4.04 (t, *J* = 5.0 Hz, 2H), 2.49 (s, 3H), 1.77-1.82 (m, 2H), 1.43-1.46 (m, 2H), 1.33-1.34 (m, 4H), 0.88-0.92 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9, 164.2, 163.0, 161.9, 160.8, 160.7, 160.2, 150.0, 139.7, 139.6, 139.4, 139.0, 134.6, 134.3,

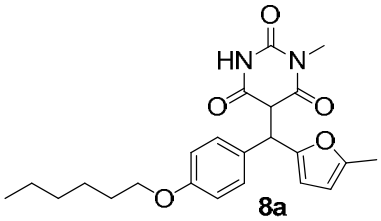
130.2, 130.1, 129.5, 129.41, 129.38, 129.2, 125.8, 125.7, 125.4, 125.3, 114.9, 114.8, 113.5, 113.4, 68.83, 68.80, 31.70, 31.68, 29.2, 29.1, 25.1, 25.78, 22.76, 22.7, 21.54, 21.52, 14.2; IR υ_{max} (cm^{-1}) 3416, 1738, 1689, 1667; ESIMS *m/z* 407 [M+H^+]; HRMS (ESI) for $C_{24}H_{27}N_2O_4$ $[M+H]^+$ calcd: 407.1971, found: 407.1965.



7d

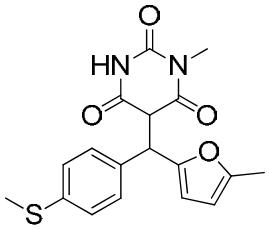
E / *Z* mixture

Yellow solid, analytical TLC (silica gel 60) (ethyl acetate) R_f = 0.2; 53% isolated yield; M.p. 219.4-222.6 ^oC; ^1H NMR (500 MHz, d^6-DMSO) δ 8.28 (d, *J* = 35.0 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.30-7.38 (m, 3H), 7.22-7.24 (m, 1H), 7.11 (m, 2H), 2.55 (d, *J* = 19.0 Hz, 3H), 2.34, (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO) *δ* 163.9 (163.2), 161.9 (161.7), 155.5 (155.3), 150.74 (150.66), 146.61 (146.55), 138.64 (138.62), 136.0(135.7), 135.1 (135.0), 130.0 (129.9), 129.4 (129.3), 129.07 (129.04), 128.95, 126.7 (126.5), 124.83 (124.75), 118.2 (118.0), 21.27, 21.26, 14.31, 14.29; IR υ_{max} (cm^{-1}) 3448, 1731, 1697, 1675; ESIMS *m/z* 353 [M+H^+]; HRMS (ESI) for $C_{19}H_{17}N_2O_3S$ $[M+H]^+$ calcd: 353.0960, found: 353.0970.



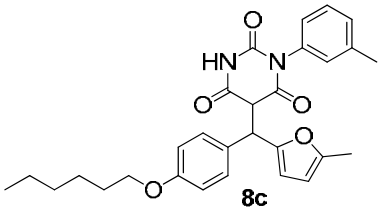
8a

Brown oil, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.5; 20% isolated yield; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.96 (br s, 1H), 7.17-7.22 (m, 2H), 6.81-6.84 (m, 2H), 5.97 (dd, *J* = 2.8, 8.4 Hz, 1H), 5.90 (br s, 1H), 4.91-4.93 (m, 1H), 4.19 (dd, *J* = 3.6, 15.2 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.13 (s, 3H), 2.26 (d, *J* = 4.8 Hz, 3H), 1.73-1.80 (m, 2H), 1.45-1.47 (m, 2H), 1.33-1.35 (m, 4H), 0.89-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 168.1, 167.6, 159.1, 159.0, 151.8, 150.6, 150.4, 150.1, 129.9, 129.8, 128.1, 127.6, 114.6, 109.6, 109.5, 106.5, 106.4, 68.0, 53.8, 53.6, 48.0, 47.9, 31.6, 29.2, 27.64, 27.56, 25.7, 22.6, 14.0, 13.1; IR υ_{max} (cm^{-1}) 3415, 1719, 1690; ESIMS *m/z* 413 [M+H^+]; HRMS (ESI) for $C_{23}H_{28}N_2O_5Na$ $[M+Na]^+$ calcd: 435.1896, found: 435.1911.



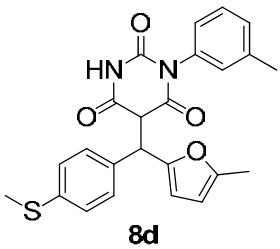
8b

Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.5; 20% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (br s, 1H), 7.21-7.28 (m, 4H), 5.99 (dd, *J* = 3.0, 9.5 Hz, 1H), 5.92 (br s, 1H), 4.97-4.99 (m, 1H), 4.19 (dd, *J* = 3.5, 16.0 Hz, 1H), 3.16 (d, *J* = 3.5 Hz, 3H), 2.49 (s, 3H), 2.28 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.8, 167.1, 166.7, 152.2, 150.3, 150.19, 150.17, 150.1, 139.1, 138.9, 133.6, 1331, 129.5, 129.4, 126.62, 126.58, 110.0, 109.9, 106.74, 106.69, 53.7, 53.0, 48.0, 47.9, 45.0, 27.9, 27.9, 21.3, 15.8, 15.7, 14.4, 13.8; IR υ_{max} (cm^{-1}) 3428, 1717, 1688; ESIMS *m/z* 359 [$M+H^+$].



8c

Brown oil, analytical TLC (silica gel 60) (25% ethyl acetate in *n*-hexane) R_f = 0.3; 46% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (br d, 1H), 7.20-7.34 (m, 4H), 6.66-6.89 (m, 4H), 5.99 (dd, *J* = 3.0, 15.0 Hz, 1H), 5.92 (dd, *J* = 2.5, 9.0 Hz, 1H), 5.01 (dd, *J* = 3.5, 9.0 Hz, 1H), 4.32 (t, *J* = 3.0 Hz, 1H), 3.93-3.97 (m, 2H), 2.35 (s, 3H), 2.27-2.31 (d, *J* = 14.0 Hz, 3H), 1.74-1.82 (m, 2H), 1.46 (m, 2H), 1.33-1.35 (m, 4H), 0.89-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 167.7, 167.4, 166.9, 159.5, 159.4, 152.1, 152.1, 150.8, 150.7, 150.0, 139.6, 133.4, 130.4, 130.34, 130.29, 129.4, 129.0, 128.2, 128.0, 125.4, 114.91, 114.86, 110.0, 106.8, 106.7, 68.3, 54.2, 54.1, 48.6, 48.3, 31.8, 29.5, 29.4, 26.0, 25.9, 22.8, 21.5, 14.2, 13.9, 13.8; IR υ_{max} (cm^{-1}) 3416, 1698; ESIMS *m/z* 488 [$M+H^+$]; HRMS (ESI) for $C_{29}H_{32}N_2O_5Na$ $[M+Na]^+$ calcd: 511.2209, found: 511.2218.



8d

Yellow oil, analytical TLC (silica gel 60) (50% ethyl acetate in *n*-hexane) R_f = 0.6; 75%

isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (br d, 1H), 7.21-7.33 (m, 6H), 6.67-6.78 (m, 2H), 6.00 (dd, *J* = 3.0, 21.0 Hz, 1H), 5.92-5.94 (m, 1H), 5.03-5.04 (m, 1H), 4.29 (t, *J* = 4.0 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 2.28 (d, *J* = 13.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.7, 152.31, 152.30, 150.31, 150.26, 149.9, 139.7, 139.2, 139.1, 133.5, 133.4, 130.3, 129.8, 129.7, 129.4, 129.99, 128.97, 126.70, 126.66, 125.4, 110.2, 106.9, 106.8, 60.7, 54.0, 53.9, 48.3, 48.2, 45.0, 21.5, 21.5, 21.3, 15.8, 15.7, 14.4, 13.9, 13.8; IR υ_{max} (cm^{-1}) 3420, 1755, 1701; ESIMS *m/z* 435 $[M+H^+]$; HRMS (ESI) for $C_{24}H_{22}N_2O_4SNa$ $[M+Na]^+$ calcd: 457.1198, found: 457.1184.

^{1}H NMR Kinetics Study of Conjugate Addition of 5a[1]

All reactions were conducted with 0.025 mmol of benzylidene barbiturate **5a**, 0.25 mmol of 2-methylfuran, 0.03 mmol of internal standard dichloromethane and 20 mol % HB-DAD organocatalysts. Stock solutions of **5a** (0.083 M; 0.05 mmol of **5a** in 0.6 mL of $CDCl_3$) and the HB-DAD organocatalysts (0.05 M; 0.01 mmol of HB-DAD organocatalysts in 0.2 mL of $CDCl_3$) were prepared in 2 mL vials. A NMR tube was charged with 0.3 mL of **5a** stock solution followed by 0.1 mL of HB-DAD organocatalysts stock solution and 1.98 μL of CH_2Cl_2. The mixture was made up to 0.5 mL with $CDCl_3$. After adding 22.3 μL of 2-methylfuran, the first NMR spectrum was taken 5 min after the addition. Additional NMR spectra were recorded every 5 min for a total of 120 min.

The methylene peak of CH_2Cl_2 (5.3, singlet, 2H) was monitored with the ratio of product signal (4.91, multiplet, 1H) that was calibrated as 1. The number of mole of product was calculated based on the known number of mole of internal standard CH_2Cl_2 in the reaction using:

A) Calculation of Concentration of Products

No. of mmol of product = [mmol of CH_2Cl_2 x 2 / Ratio of CH_2Cl_2 signal]

[Concentration of product] = No. of mmol of product/ 0.5mL

B) Plot of ln [Concentration of 5a]) vs time.

With a 10-fold excess of 2-methylfuran, all conjugate additions of **5a** were pseudo-first-order, and the corresponding rate constant k_{obs} were determined the slope of the plot of the ln (0.05 – [Concentration of product]) vs time.

C) Calculation of Relative Rate Constants (k_{rel}), k_{cat} and k_{uncata}

1a-catalyzed reaction: $k_{obs(\mathbf{1a})} = 0.00015466\ s^{-1}$

Uncatalyzed reaction: $k_{obs(background)} = k_{uncata} = 0.00003766\ s^{-1}$

$k_{cat} = k_{obs(\mathbf{1a})} - k_{uncata}$

= 0.00015466-0.00003766

$= 0.00011700\ s^{-1}$

$k_{rel} = k_{cat} / k_{uncata}$

= 0.00011700/ 0.00003766

= 3.12 at 20 mol% of **1a**

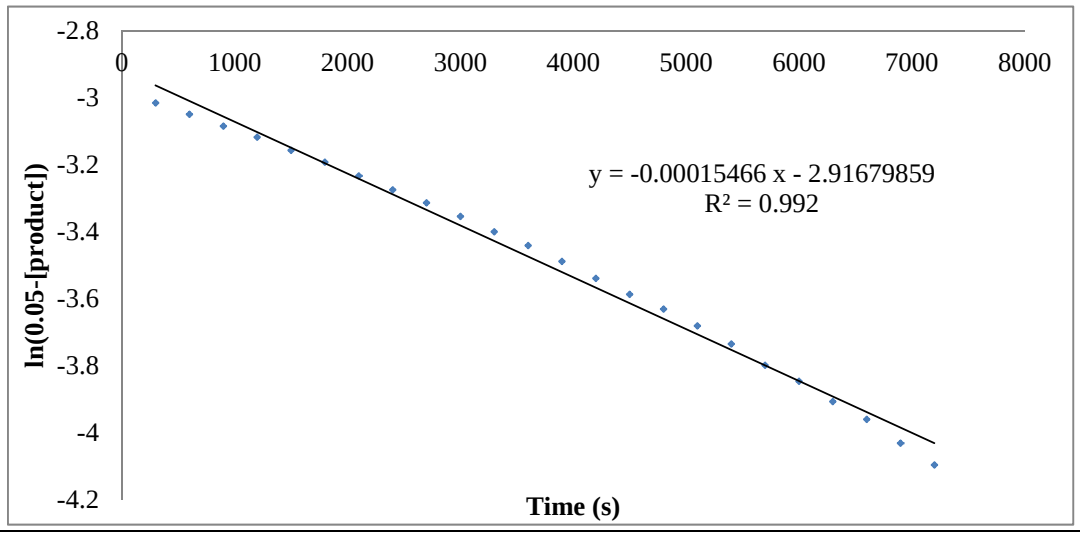
Table S6. Rate constants determinations with ^{1}H NMR studies

Catalysts	k_{obs} x 10^{-4} (s^{-1})	k_{cat} x 10^{-4} (s^{-1})	k_{rel}
-----	0.4288	k_{uncata} = 0.4288	1.0
-----	0.3244	k_{uncata} = 0.3244	1.0
1a	1.5466	1.17	3.10
1a	1.4221	1.0455	2.77
1b	1.0437	0.6671	1.77
1b	1.0548	0.6782	1.80
1c	0.3662	-0.0104	-0.027
2a	1.2174	0.8408	2.23
2a	1.2239	0.8473	2.25
2b	0.9275	0.5509	1.46
2b	0.8725	0.4959	1.33
3a	0.8178	0.4412	1.17

Reference of Kinetics Study:

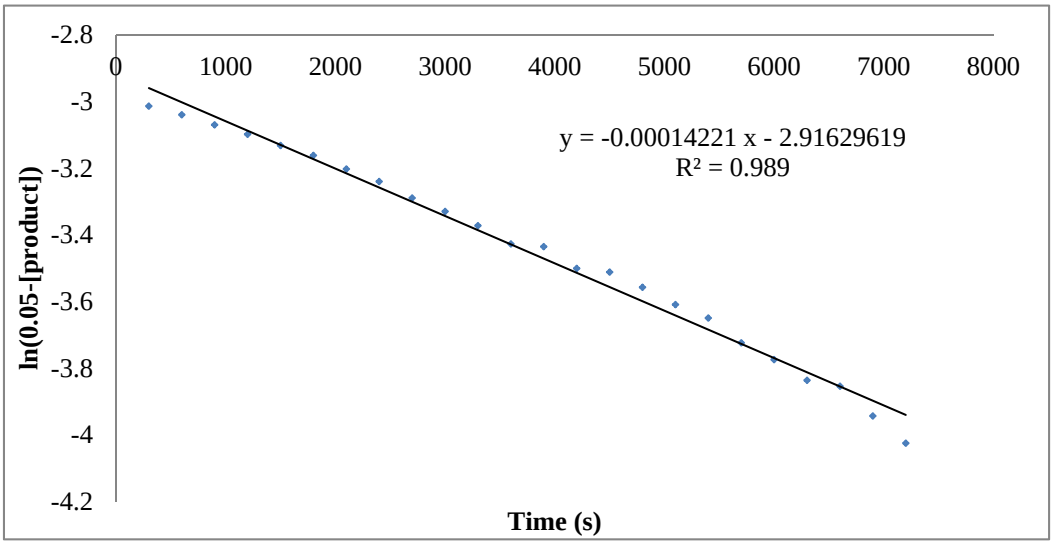
[1] a) A. Wittkopp, P. R. Schreiner, *Chem. Eur. J.* 2003, **9**, 407; b) P. N. H. Huynh, R. R. Walvoord, M. C. Kozlowski, *J. Am. Chem. Soc.* 2012, **134**, 15621.

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1a** (0.005 mmol); $CDCl_3$(0.5 mL)]



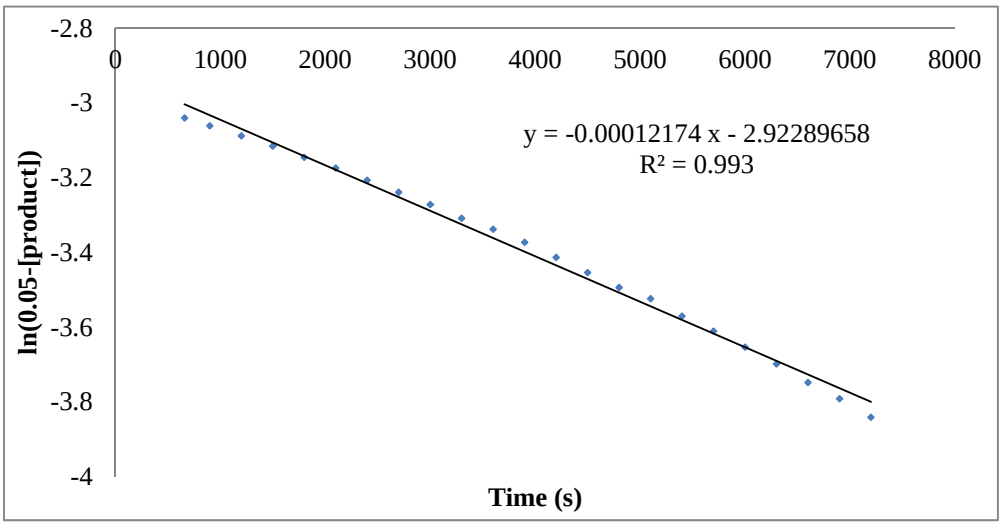
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	137.608	0.00044	1.7	0.0009	0.0491	-3.013
10	600	56.381	0.00106	4.3	0.0021	0.0479	-3.039
15	900	33.776	0.00178	7.1	0.0036	0.0464	-3.069
20	1200	20.943	0.00286	11.5	0.0057	0.0443	-3.117
25	1500	16.149	0.00372	14.9	0.0074	0.0426	-3.157
30	1800	13.483	0.00445	17.8	0.0089	0.0411	-3.192
35	2100	11.359	0.00528	21.1	0.0106	0.0394	-3.233
40	2400	9.863	0.00608	24.3	0.0122	0.0378	-3.275
45	2700	8.819	0.00680	27.2	0.0136	0.0364	-3.313
50	3000	7.976	0.00752	30.1	0.0150	0.0350	-3.354
55	3300	7.220	0.00831	33.2	0.0166	0.0334	-3.400
60	3600	6.684	0.00898	35.9	0.0180	0.0320	-3.441
65	3900	6.173	0.00972	38.9	0.0194	0.0306	-3.488
70	4200	5.729	0.01047	41.9	0.0209	0.0291	-3.539
75	4500	5.381	0.01115	44.6	0.0223	0.0277	-3.586
80	4800	5.108	0.01175	47.0	0.0235	0.0265	-3.630
85	5100	4.842	0.01239	49.6	0.0248	0.0252	-3.680
90	5400	4.596	0.01306	52.2	0.0261	0.0239	-3.734
95	5700	4.351	0.01379	55.2	0.0276	0.0224	-3.798
100	6000	4.192	0.01431	57.3	0.0286	0.0214	-3.846
105	6300	4.016	0.01494	59.8	0.0299	0.0201	-3.906
110	6600	3.880	0.01546	61.9	0.0309	0.0191	-3.959
115	6900	3.723	0.01611	64.5	0.0322	0.0178	-4.030
120	7200	3.598	0.01668	66.7	0.0334	0.0166	-4.096

Second Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1a** (0.005 mmol); $CDCl_3$(0.5 mL)]



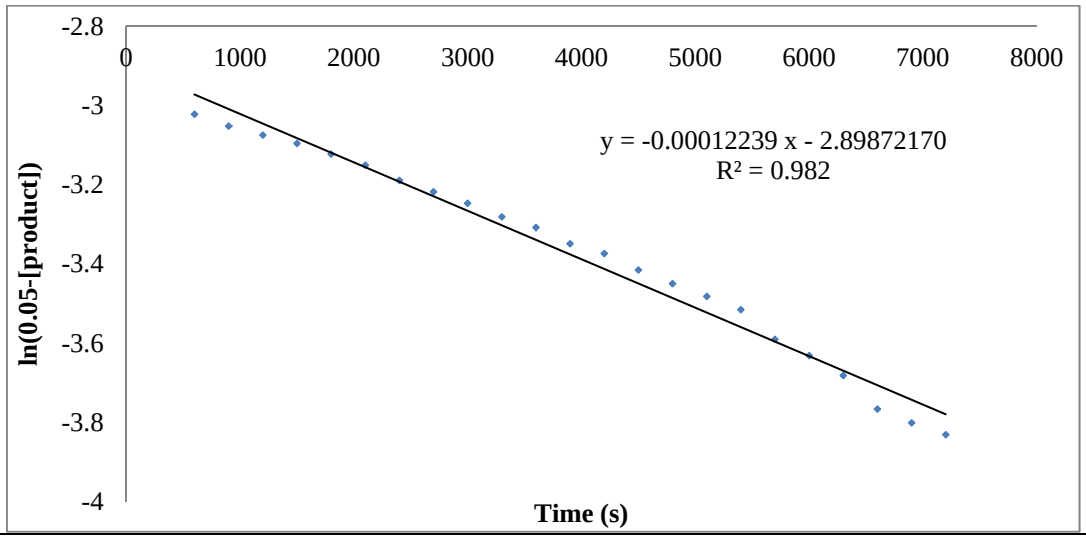
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	137.608	0.00044	1.7	0.0009	0.0491	-3.013
10	600	56.381	0.00106	4.3	0.0021	0.0479	-3.039
15	900	33.776	0.00178	7.1	0.0036	0.0464	-3.069
20	1200	24.711	0.00243	9.7	0.0049	0.0451	-3.098
25	1500	18.949	0.00317	12.7	0.0063	0.0437	-3.131
30	1800	15.761	0.00381	15.2	0.0076	0.0424	-3.161
35	2100	12.889	0.00466	18.6	0.0093	0.0407	-3.202
40	2400	11.096	0.00541	21.6	0.0108	0.0392	-3.239
45	2700	9.441	0.00636	25.4	0.0127	0.0373	-3.289
50	3000	8.466	0.00709	28.3	0.0142	0.0358	-3.329
55	3300	7.653	0.00784	31.4	0.0157	0.0343	-3.372
60	3600	6.856	0.00875	35.0	0.0175	0.0325	-3.427
65	3900	6.750	0.00889	35.6	0.0178	0.0322	-3.435
70	4200	6.056	0.00991	39.6	0.0198	0.0302	-3.500
75	4500	5.958	0.01007	40.3	0.0201	0.0299	-3.511
80	4800	5.587	0.01074	43.0	0.0215	0.0285	-3.557
85	5100	5.235	0.01146	45.8	0.0229	0.0271	-3.609
90	5400	5.002	0.01200	48.0	0.0240	0.0260	-3.649
95	5700	4.641	0.01293	51.7	0.0259	0.0241	-3.724
100	6000	4.436	0.01352	54.1	0.0270	0.0230	-3.774
105	6300	4.222	0.01421	56.8	0.0284	0.0216	-3.836
110	6600	4.165	0.01441	57.6	0.0288	0.0212	-3.854
115	6900	3.919	0.01531	61.2	0.0306	0.0194	-3.944
120	7200	3.734	0.01607	64.3	0.0321	0.0179	-4.025

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **2a** (0.005 mmol); $CDCl_3$(0.5 mL)]



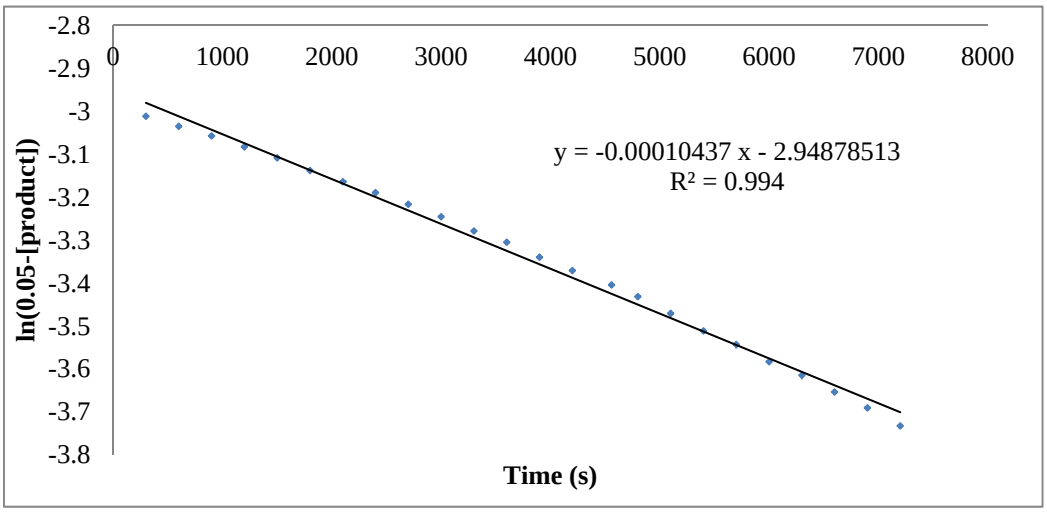
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
11	660	55.682	0.00108	4.3	0.0022	0.0478	-3.040
15	900	37.982	0.00158	6.3	0.0032	0.0468	-3.061
20	1200	27.212	0.00220	8.8	0.0044	0.0456	-3.088
25	1500	21.283	0.00282	11.3	0.0056	0.0444	-3.115
30	1800	17.254	0.00348	13.9	0.0070	0.0430	-3.146
35	2100	14.687	0.00409	16.3	0.0082	0.0418	-3.174
40	2400	12.634	0.00475	19.0	0.0095	0.0405	-3.206
45	2700	11.124	0.00539	21.6	0.0108	0.0392	-3.239
50	3000	9.957	0.00603	24.1	0.0121	0.0379	-3.272
55	3300	8.942	0.00671	26.8	0.0134	0.0366	-3.308
60	3600	8.285	0.00724	29.0	0.0145	0.0355	-3.338
65	3900	7.642	0.00785	31.4	0.0157	0.0343	-3.373
70	4200	7.038	0.00852	34.1	0.0170	0.0330	-3.413
75	4500	6.532	0.00919	36.7	0.0184	0.0316	-3.454
80	4800	6.122	0.00980	39.2	0.0196	0.0304	-3.493
85	5100	5.853	0.01025	41.0	0.0205	0.0295	-3.523
90	5400	5.494	0.01092	43.7	0.0218	0.0282	-3.570
95	5700	5.228	0.01148	45.9	0.0230	0.0270	-3.610
100	6000	4.982	0.01204	48.2	0.0241	0.0259	-3.653
105	6300	4.756	0.01262	50.5	0.0252	0.0248	-3.698
110	6600	4.540	0.01322	52.9	0.0264	0.0236	-3.748
115	6900	4.374	0.01372	54.9	0.0274	0.0226	-3.791
120	7200	4.207	0.01426	57.1	0.0285	0.0215	-3.841

Second Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **2a** (0.005 mmol); $CDCl_3$(0.5 mL)]



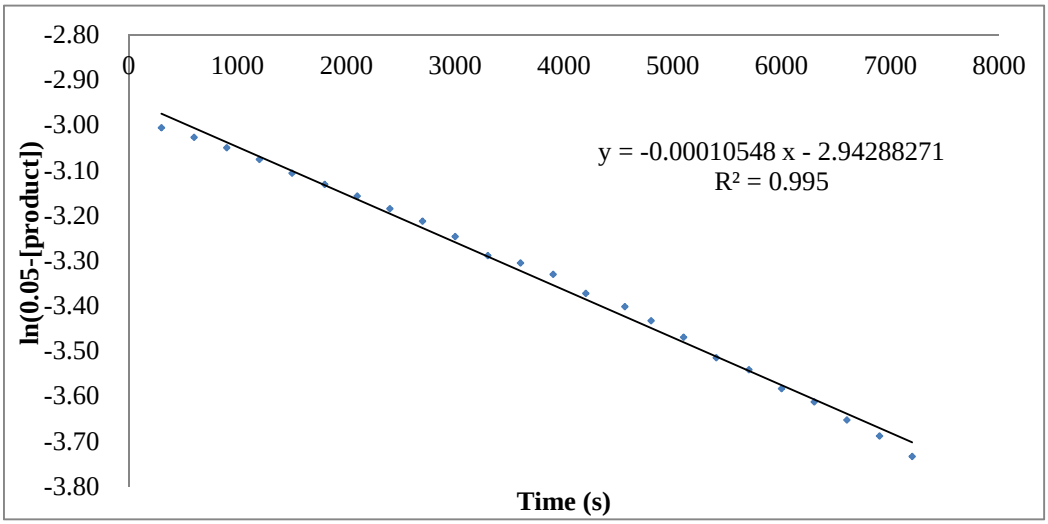
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	242.841	0.00025	1.0	0.0005	0.0495	-3.006
10	600	92.072	0.00065	2.6	0.0013	0.0487	-3.022
15	900	44.052	0.00136	5.4	0.0027	0.0473	-3.052
20	1200	31.731	0.00189	7.6	0.0038	0.0462	-3.074
25	1500	25.261	0.00238	9.5	0.0048	0.0452	-3.096
30	1800	20.107	0.00298	11.9	0.0060	0.0440	-3.123
35	2100	16.723	0.00359	14.4	0.0072	0.0428	-3.151
40	2400	13.651	0.00440	17.6	0.0088	0.0412	-3.189
45	2700	12.061	0.00497	19.9	0.0099	0.0401	-3.218
50	3000	10.807	0.00555	22.2	0.0111	0.0389	-3.247
55	3300	9.668	0.00621	24.8	0.0124	0.0376	-3.281
60	3600	8.956	0.00670	26.8	0.0134	0.0366	-3.308
65	3900	8.065	0.00744	29.8	0.0149	0.0351	-3.349
70	4200	7.628	0.00787	31.5	0.0157	0.0343	-3.374
75	4500	7.001	0.00857	34.3	0.0171	0.0329	-3.416
80	4800	6.576	0.00912	36.5	0.0182	0.0318	-3.450
85	5100	6.231	0.00963	38.5	0.0193	0.0307	-3.482
90	5400	5.922	0.01013	40.5	0.0203	0.0297	-3.515
95	5700	5.353	0.01121	44.8	0.0224	0.0276	-3.591
100	6000	5.100	0.01176	47.1	0.0235	0.0265	-3.632
105	6300	4.834	0.01241	49.7	0.0248	0.0252	-3.682
110	6600	4.466	0.01343	53.7	0.0269	0.0231	-3.767
115	6900	4.338	0.01383	55.3	0.0277	0.0223	-3.802
120	7200	4.237	0.01416	56.6	0.0283	0.0217	-3.832

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1b** (0.005 mmol); $CDCl_3$(0.5 mL)]



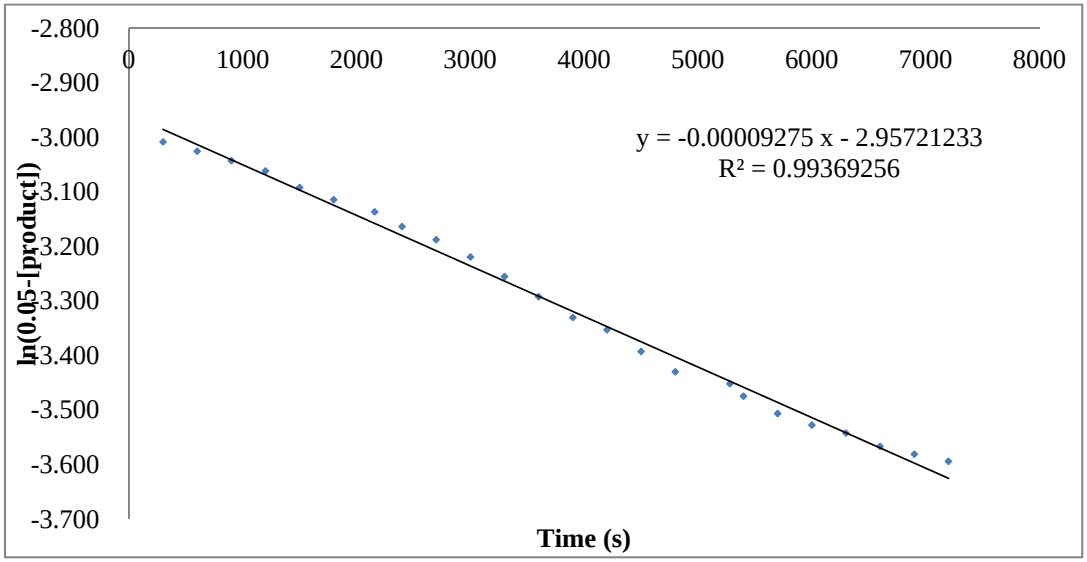
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	154.393	0.00039	1.6	0.0008	0.0492	-3.011
10	600	62.603	0.00096	3.8	0.0019	0.0481	-3.035
15	900	40.411	0.00148	5.9	0.0030	0.0470	-3.057
20	1200	28.940	0.00207	8.3	0.0041	0.0459	-3.082
25	1500	22.553	0.00266	10.6	0.0053	0.0447	-3.108
30	1800	18.152	0.00331	13.2	0.0066	0.0434	-3.138
35	2100	15.512	0.00387	15.5	0.0077	0.0423	-3.164
40	2400	13.650	0.00440	17.6	0.0088	0.0412	-3.189
45	2700	12.135	0.00494	19.8	0.0099	0.0401	-3.216
50	3000	10.870	0.00552	22.1	0.0110	0.0390	-3.245
55	3300	9.741	0.00616	24.6	0.0123	0.0377	-3.279
60	3600	9.035	0.00664	26.6	0.0133	0.0367	-3.304
65	3900	8.247	0.00728	29.1	0.0146	0.0354	-3.340
70	4200	7.678	0.00781	31.3	0.0156	0.0344	-3.371
76	4560	7.161	0.00838	33.5	0.0168	0.0332	-3.404
80	4800	6.798	0.00883	35.3	0.0177	0.0323	-3.431
85	5100	6.352	0.00945	37.8	0.0189	0.0311	-3.470
90	5400	5.961	0.01006	40.3	0.0201	0.0299	-3.511
95	5700	5.698	0.01053	42.1	0.0211	0.0289	-3.543
100	6000	5.405	0.01110	44.4	0.0222	0.0278	-3.583
105	6300	5.204	0.01153	46.1	0.0231	0.0269	-3.614
110	6600	4.980	0.01205	48.2	0.0241	0.0259	-3.653
115	6900	4.795	0.01251	50.1	0.0250	0.0250	-3.690
120	7200	4.604	0.01303	52.1	0.0261	0.0239	-3.732

Second Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1b** (0.005 mmol); $CDCl_3$(0.5 mL)]



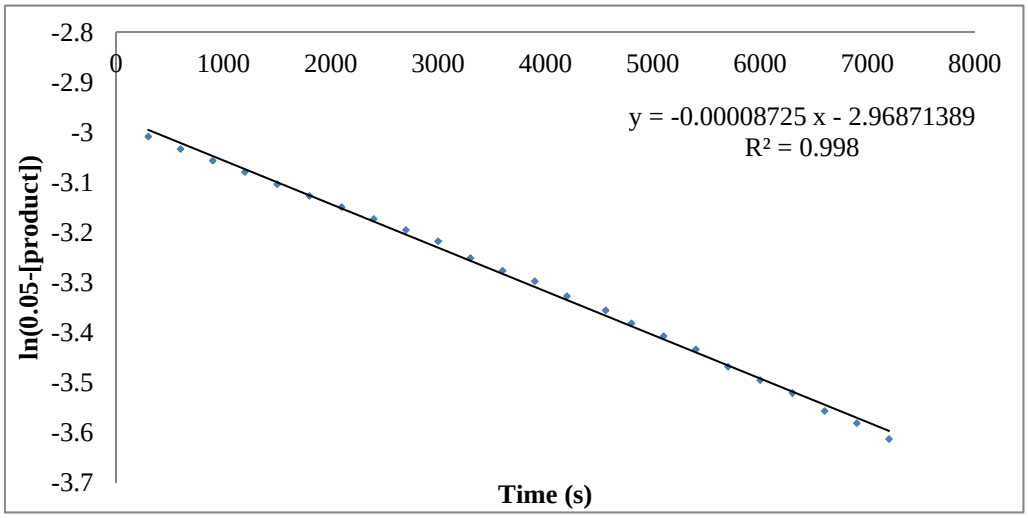
Time(min)	Time(s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	241.987	0.00025	1.0	0.0005	0.0495	-3.006
10	600	77.849	0.00077	3.1	0.0015	0.0485	-3.027
15	900	45.425	0.00132	5.3	0.0026	0.0474	-3.050
20	1200	31.206	0.00192	7.7	0.0038	0.0462	-3.076
25	1500	22.889	0.00262	10.5	0.0052	0.0448	-3.107
30	1800	18.958	0.00316	12.7	0.0063	0.0437	-3.131
35	2100	16.114	0.00372	14.9	0.0074	0.0426	-3.157
40	2400	13.918	0.00431	17.2	0.0086	0.0414	-3.185
45	2700	12.299	0.00488	19.5	0.0098	0.0402	-3.213
50	3000	10.812	0.00555	22.2	0.0111	0.0389	-3.247
55	3300	9.446	0.00635	25.4	0.0127	0.0373	-3.289
60	3600	9.011	0.00666	26.6	0.0133	0.0367	-3.305
65	3900	8.436	0.00711	28.4	0.0142	0.0358	-3.330
70	4200	7.646	0.00785	31.4	0.0157	0.0343	-3.372
76	4560	7.190	0.00835	33.4	0.0167	0.0333	-3.402
80	4800	6.772	0.00886	35.4	0.0177	0.0323	-3.433
85	5100	6.357	0.00944	37.8	0.0189	0.0311	-3.470
90	5400	5.923	0.01013	40.5	0.0203	0.0297	-3.515
95	5700	5.704	0.01052	42.1	0.0210	0.0290	-3.542
100	6000	5.399	0.01111	44.5	0.0222	0.0278	-3.584
105	6300	5.211	0.01151	46.1	0.0230	0.0270	-3.613
110	6600	4.982	0.01204	48.2	0.0241	0.0259	-3.653
115	6900	4.801	0.01250	50.0	0.0250	0.0250	-3.689
120	7200	4.598	0.01305	52.2	0.0261	0.0239	-3.734

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **2b** (0.005 mmol); $CDCl_3$(0.5 mL)]



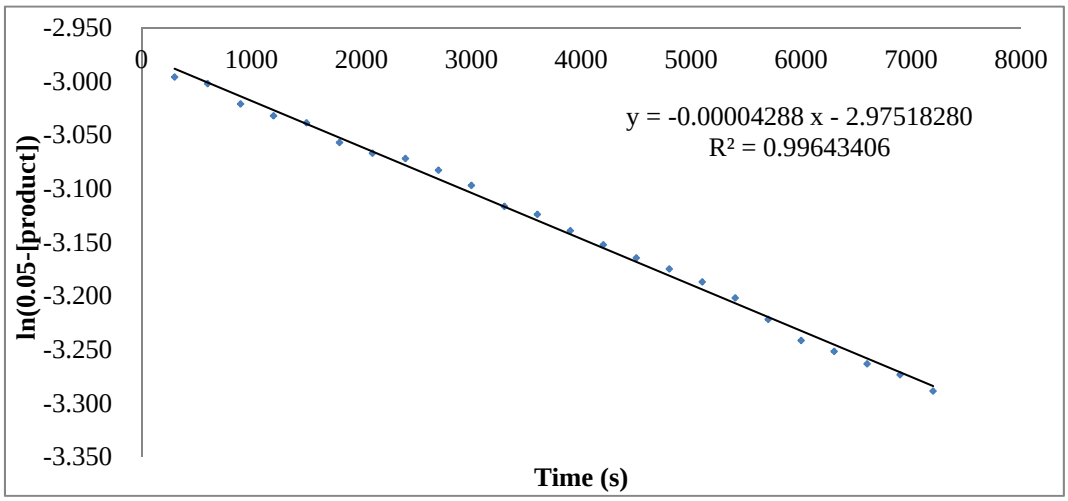
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	195.361	0.00031	1.2	0.0006	0.0494	-3.008
10	600	82.549	0.00073	2.9	0.0015	0.0485	-3.025
15	900	52.693	0.00114	4.6	0.0023	0.0477	-3.042
20	1200	37.759	0.00159	6.4	0.0032	0.0468	-3.061
25	1500	26.193	0.00229	9.2	0.0046	0.0454	-3.092
30	1800	21.500	0.00279	11.2	0.0056	0.0444	-3.114
36	2160	18.286	0.00328	13.1	0.0066	0.0434	-3.136
40	2400	15.552	0.00386	15.4	0.0077	0.0423	-3.163
45	2700	13.757	0.00436	17.4	0.0087	0.0413	-3.187
50	3000	11.985	0.00501	20.0	0.0100	0.0400	-3.219
55	3300	10.512	0.00571	22.8	0.0114	0.0386	-3.255
60	3600	9.361	0.00641	25.6	0.0128	0.0372	-3.292
65	3900	8.445	0.00710	28.4	0.0142	0.0358	-3.330
70	4200	7.996	0.00750	30.0	0.0150	0.0350	-3.353
75	4500	7.329	0.00819	32.7	0.0164	0.0336	-3.392
80	4800	6.819	0.00880	35.2	0.0176	0.0324	-3.430
88	5280	6.557	0.00915	36.6	0.0183	0.0317	-3.452
90	5400	6.309	0.00951	38.0	0.0190	0.0310	-3.474
95	5700	6.003	0.00999	40.0	0.0200	0.0300	-3.506
100	6000	5.822	0.01031	41.2	0.0206	0.0294	-3.527
105	6300	5.702	0.01052	42.1	0.0210	0.0290	-3.542
110	6600	5.520	0.01087	43.5	0.0217	0.0283	-3.566
115	6900	5.419	0.01107	44.3	0.0221	0.0279	-3.581
120	7200	5.332	0.01125	45.0	0.0225	0.0275	-3.594

Second Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1a** (0.005 mmol); $CDCl_3$(0.5 mL)]



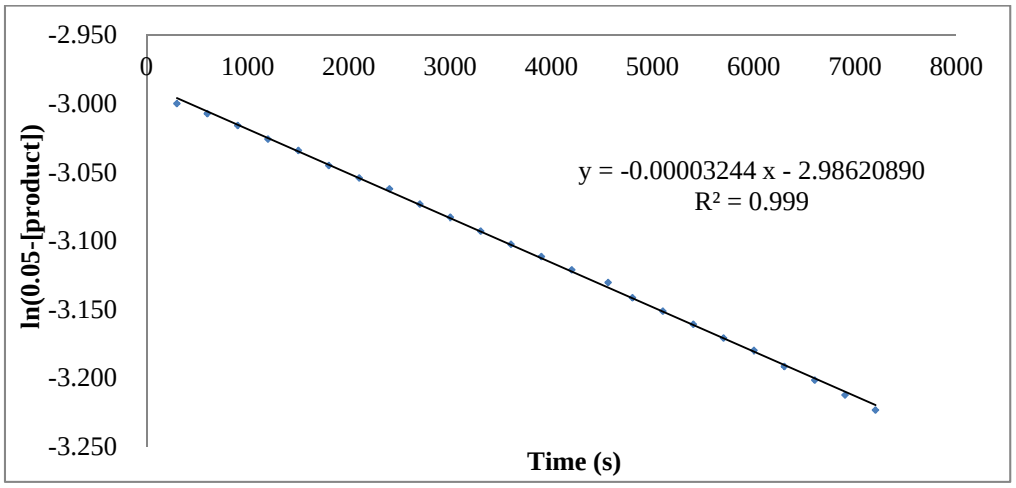
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	194.663	0.00031	1.2	0.0006	0.0494	-3.008
10	600	65.329	0.00092	3.7	0.0018	0.0482	-3.033
15	900	40.720	0.00147	5.9	0.0029	0.0471	-3.056
20	1200	30.016	0.00200	8.0	0.0040	0.0460	-3.079
25	1500	23.477	0.00256	10.2	0.0051	0.0449	-3.104
30	1800	19.556	0.00307	12.3	0.0061	0.0439	-3.127
35	2100	16.861	0.00356	14.2	0.0071	0.0429	-3.149
40	2400	14.775	0.00406	16.2	0.0081	0.0419	-3.173
45	2700	13.278	0.00452	18.1	0.0090	0.0410	-3.195
50	3000	12.074	0.00497	19.9	0.0099	0.0401	-3.217
55	3300	10.657	0.00563	22.5	0.0113	0.0387	-3.251
60	3600	9.813	0.00611	24.5	0.0122	0.0378	-3.276
65	3900	9.213	0.00651	26.0	0.0130	0.0370	-3.298
70	4200	8.508	0.00705	28.2	0.0141	0.0359	-3.327
76	4560	7.943	0.00755	30.2	0.0151	0.0349	-3.356
80	4800	7.498	0.00800	32.0	0.0160	0.0340	-3.382
85	5100	7.114	0.00843	33.7	0.0169	0.0331	-3.407
90	5400	6.766	0.00887	35.5	0.0177	0.0323	-3.434
95	5700	6.375	0.00941	37.7	0.0188	0.0312	-3.468
100	6000	6.104	0.00983	39.3	0.0197	0.0303	-3.495
105	6300	5.877	0.01021	40.8	0.0204	0.0296	-3.521
110	6600	5.589	0.01073	42.9	0.0215	0.0285	-3.557
115	6900	5.416	0.01108	44.3	0.0222	0.0278	-3.581
120	7200	5.210	0.01152	46.1	0.0230	0.0270	-3.613

First Trial– Background–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); $CDCl_3$(0.5 mL)]



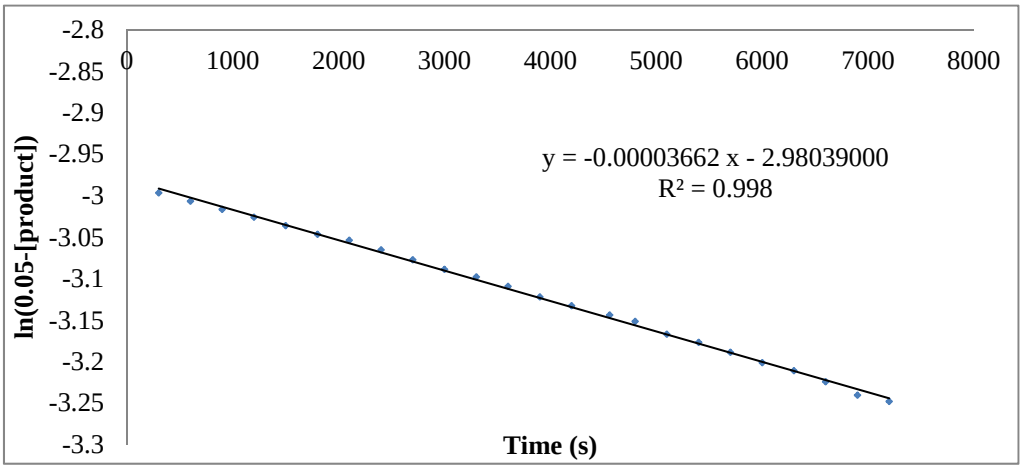
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	32149.684	0.00000	0.0	0.0000	0.0500	-2.996
10	600	391.334	0.00015	0.6	0.0003	0.0497	-3.002
15	900	96.300	0.00062	2.5	0.0012	0.0488	-3.021
20	1200	67.580	0.00089	3.6	0.0018	0.0482	-3.032
25	1500	57.306	0.00105	4.2	0.0021	0.0479	-3.039
30	1800	40.436	0.00148	5.9	0.0030	0.0470	-3.057
35	2100	34.956	0.00172	6.9	0.0034	0.0466	-3.067
40	2400	32.764	0.00183	7.3	0.0037	0.0463	-3.072
45	2700	28.844	0.00208	8.3	0.0042	0.0458	-3.083
50	3000	24.967	0.00240	9.6	0.0048	0.0452	-3.097
55	3300	21.106	0.00284	11.4	0.0057	0.0443	-3.116
60	3600	19.957	0.00301	12.0	0.0060	0.0440	-3.124
65	3900	17.979	0.00334	13.3	0.0067	0.0433	-3.139
70	4200	16.574	0.00362	14.5	0.0072	0.0428	-3.152
75	4500	15.463	0.00388	15.5	0.0078	0.0422	-3.164
80	4800	14.648	0.00410	16.4	0.0082	0.0418	-3.175
85	5100	13.793	0.00435	17.4	0.0087	0.0413	-3.187
90	5400	12.888	0.00466	18.6	0.0093	0.0407	-3.202
95	5700	11.867	0.00506	20.2	0.0101	0.0399	-3.222
100	6000	11.016	0.00545	21.8	0.0109	0.0391	-3.241
105	6300	10.634	0.00564	22.6	0.0113	0.0387	-3.252
110	6600	10.226	0.00587	23.5	0.0117	0.0383	-3.263
115	6900	9.898	0.00606	24.2	0.0121	0.0379	-3.273
120	7200	9.452	0.00635	25.4	0.0127	0.0373	-3.289

Second Trial– Background–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); $CDCl_3$(0.5 mL)]



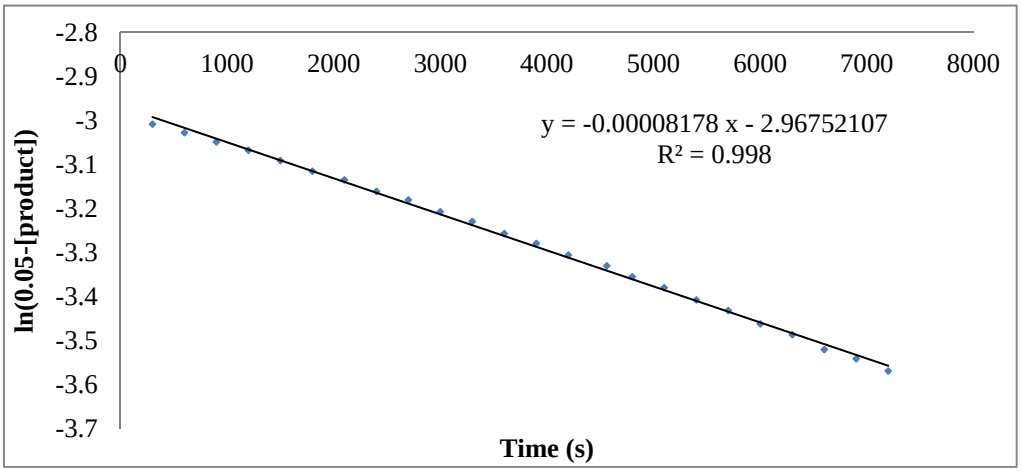
Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	575.814	0.00010	0.4	0.0002	0.0498	-3.000
10	600	210.331	0.00029	1.1	0.0006	0.0494	-3.007
15	900	120.639	0.00050	2.0	0.0010	0.0490	-3.016
20	1200	81.136	0.00074	3.0	0.0015	0.0485	-3.026
25	1500	63.773	0.00094	3.8	0.0019	0.0481	-3.034
30	1800	49.850	0.00120	4.8	0.0024	0.0476	-3.045
35	2100	42.290	0.00142	5.7	0.0028	0.0472	-3.054
40	2400	37.384	0.00160	6.4	0.0032	0.0468	-3.062
45	2700	32.203	0.00186	7.5	0.0037	0.0463	-3.073
50	3000	28.821	0.00208	8.3	0.0042	0.0458	-3.083
55	3300	25.938	0.00231	9.3	0.0046	0.0454	-3.093
60	3600	23.709	0.00253	10.1	0.0051	0.0449	-3.102
65	3900	21.975	0.00273	10.9	0.0055	0.0445	-3.111
70	4200	20.373	0.00295	11.8	0.0059	0.0441	-3.121
76	4560	19.067	0.00315	12.6	0.0063	0.0437	-3.130
80	4800	17.712	0.00339	13.6	0.0068	0.0432	-3.141
85	5100	16.676	0.00360	14.4	0.0072	0.0428	-3.151
90	5400	15.773	0.00380	15.2	0.0076	0.0424	-3.161
95	5700	14.941	0.00402	16.1	0.0080	0.0420	-3.171
100	6000	14.278	0.00420	16.8	0.0084	0.0416	-3.180
105	6300	13.494	0.00445	17.8	0.0089	0.0411	-3.192
110	6600	12.907	0.00465	18.6	0.0093	0.0407	-3.201
115	6900	12.324	0.00487	19.5	0.0097	0.0403	-3.212
120	7200	11.792	0.00509	20.4	0.0102	0.0398	-3.223

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **1c** (0.005 mmol); $CDCl_3$(0.5 mL)]



Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	2814.067	0.00002	0.1	0.0000	0.0500	-2.997
10	600	218.620	0.00027	1.1	0.0005	0.0495	-3.007
15	900	116.964	0.00051	2.1	0.0010	0.0490	-3.016
20	1200	80.702	0.00074	3.0	0.0015	0.0485	-3.026
25	1500	60.503	0.00099	4.0	0.0020	0.0480	-3.036
30	1800	48.430	0.00124	5.0	0.0025	0.0475	-3.047
35	2100	42.585	0.00141	5.6	0.0028	0.0472	-3.054
40	2400	35.740	0.00168	6.7	0.0034	0.0466	-3.065
45	2700	30.681	0.00196	7.8	0.0039	0.0461	-3.077
50	3000	27.006	0.00222	8.9	0.0044	0.0456	-3.089
55	3300	24.711	0.00243	9.7	0.0049	0.0451	-3.098
60	3600	22.356	0.00268	10.7	0.0054	0.0446	-3.109
65	3900	20.226	0.00297	11.9	0.0059	0.0441	-3.122
70	4200	18.771	0.00320	12.8	0.0064	0.0436	-3.133
76	4560	17.451	0.00344	13.8	0.0069	0.0431	-3.144
80	4800	16.638	0.00361	14.4	0.0072	0.0428	-3.152
85	5100	15.251	0.00393	15.7	0.0079	0.0421	-3.167
90	5400	14.492	0.00414	16.6	0.0083	0.0417	-3.177
95	5700	13.674	0.00439	17.6	0.0088	0.0412	-3.189
100	6000	12.918	0.00464	18.6	0.0093	0.0407	-3.201
105	6300	12.403	0.00484	19.4	0.0097	0.0403	-3.211
110	6600	11.748	0.00511	20.4	0.0102	0.0398	-3.224
115	6900	11.057	0.00543	21.7	0.0109	0.0391	-3.240
120	7200	10.769	0.00557	22.3	0.0111	0.0389	-3.248

First Trial–[**5a** (0.025 mmol); 2-methylfuran(0.25 mmol); **3a** (0.005 mmol); $CDCl_3$(0.5 mL)]

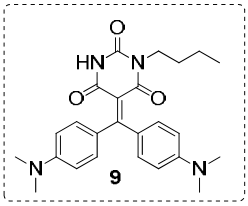


Time (min)	Time (s)	Integration	mmol	NMR Yield (%)	[product]	0.05-[product]	ln(0.05-[product])
5	300	194.764	0.00031	1.2	0.0006	0.0494	-3.008
10	600	76.885	0.00078	3.1	0.0016	0.0484	-3.027
15	900	46.615	0.00129	5.1	0.0026	0.0474	-3.049
20	1200	34.786	0.00172	6.9	0.0034	0.0466	-3.067
25	1500	26.536	0.00226	9.0	0.0045	0.0455	-3.091
30	1800	21.372	0.00281	11.2	0.0056	0.0444	-3.115
35	2100	18.515	0.00324	13.0	0.0065	0.0435	-3.135
40	2400	15.788	0.00380	15.2	0.0076	0.0424	-3.161
45	2700	14.266	0.00421	16.8	0.0084	0.0416	-3.180
50	3000	12.618	0.00475	19.0	0.0095	0.0405	-3.207
55	3300	11.541	0.00520	20.8	0.0104	0.0396	-3.229
60	3600	10.459	0.00574	22.9	0.0115	0.0385	-3.256
65	3900	9.732	0.00617	24.7	0.0123	0.0377	-3.279
70	4200	9.013	0.00666	26.6	0.0133	0.0367	-3.305
76	4560	8.457	0.00709	28.4	0.0142	0.0358	-3.330
80	4800	7.964	0.00753	30.1	0.0151	0.0349	-3.354
85	5100	7.536	0.00796	31.8	0.0159	0.0341	-3.379
90	5400	7.118	0.00843	33.7	0.0169	0.0331	-3.407
95	5700	6.799	0.00882	35.3	0.0176	0.0324	-3.431
100	6000	6.446	0.00931	37.2	0.0186	0.0314	-3.461
105	6300	6.194	0.00969	38.7	0.0194	0.0306	-3.486
110	6600	5.885	0.01020	40.8	0.0204	0.0296	-3.520
115	6900	5.714	0.01050	42.0	0.0210	0.0290	-3.541
120	7200	5.505	0.01090	43.6	0.0218	0.0282	-3.568

UV / Vis. Titration Binding Study of Benzylidene Barbiturate Chromophore

with Amide-Based HB-DAD Organocatalysts

Barbiturate **9** was synthesized and characterized according to literature reports.[2-3]



(A) Preparation of Stock Solution of 9

2 x 10^{-4} M (2 x 10^{-2} mmol of barbiturate **9** in 100.0 mL of CH_2Cl_2)

(B) Preparation of Stock Solution of HB-DAD Organocatalysts

9.67 x 10^{-3} M (9.67 x 10^{-2} mmol of HB-DAD organocatalysts in 10.0 mL of CH_2Cl_2)

(C) Preparation of Samples of HB-DAD Organocatalysts and Barbiturate 9 Mixture[3]

Ten graduated flasks (5 mL) were treated with 0.5 mL of stock solution of barbiturate **9** (final concentration: 2 x 10^{-5} M) and 0, 20, 40, 80, 160, 320, 640, 1260, 2560, 3000 μL (corresponding to a 2-290 fold excess) of a stock solution of HB-DAD organocatalysts, and filled up to 5 mL with CH_2Cl_2. The change in absorbance was monitored and evaluated by linearized Scatchard plot (S1). The given values of K_A were the average of two runs.

(D) Linearized Scatchard Plot

$$\frac{\Delta A}{d \cdot [R]} = -\frac{\Delta A \cdot K}{d} + K \cdot \Delta\varepsilon \cdot [S] \qquad \text{(S1)}$$

[S]: Concentration of benzylidene barbiturate chromophore
[R]: Concentration of amide-based HB-DAD organocatalysts
K: Binding Constant
ΔA: Change of absorbance
Δε: Molar absorptivity
In Scatchard Plot
K = - (slope)
Δε = (x-intercept) / [S]

Table S7. Binding constant determinations with UV / Vis. titration method

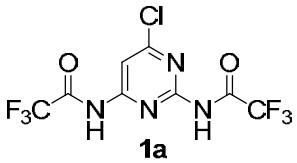
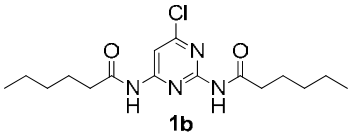
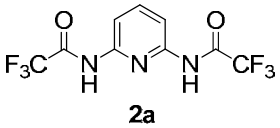
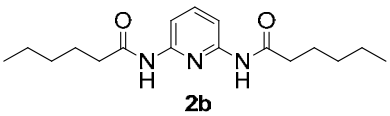
Entry	HB-DAD Organocatalysts	1st Trial K_A (M^{-1})	2nd Trial K_A (M^{-1})	Averaged K_A (M^{-1})
1	 **1a**	8575	9298	8936 (±723)
2	 **1b**	6264	6631	6447 (±380)
3	 **2a**	7557	7937	7747 (±367)
4	 **2b**	5404	4385	4895 (±1019)

Table S8. The rate constants and binding constants of HB-DAD organocatalysts

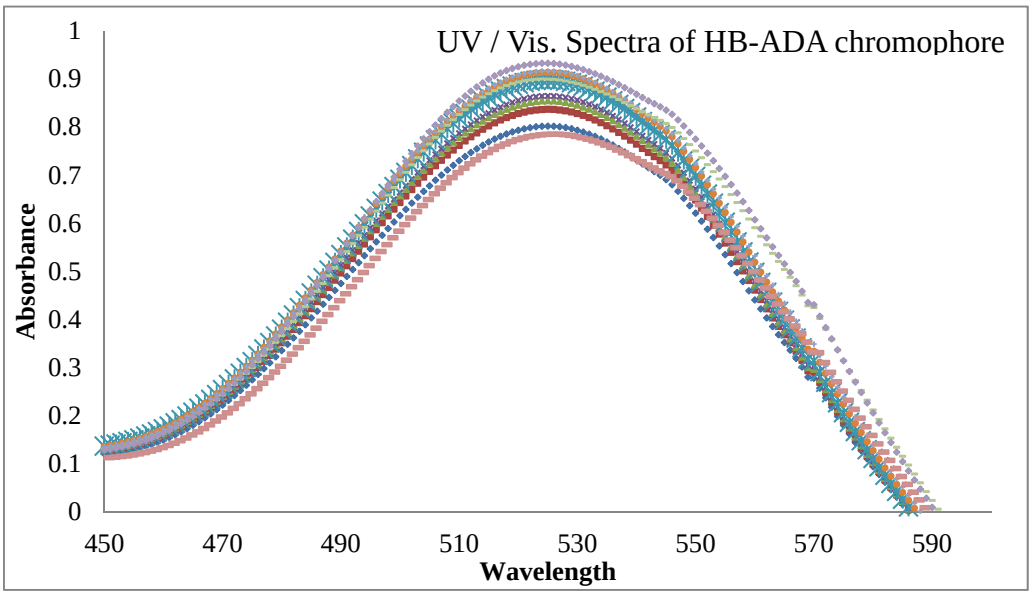
Entry	Catalysts	K_A (M^{-1})	lnK_A	k_{rel}	lnk_{rel}
1	**1a**	8936	9.10	2.94	1.08
2	**1b**	6447	8.96	1.79	0.58
3	**2a**	7747	8.77	2.24	0.80
4	**2b**	4895	8.50	1.39	0.33

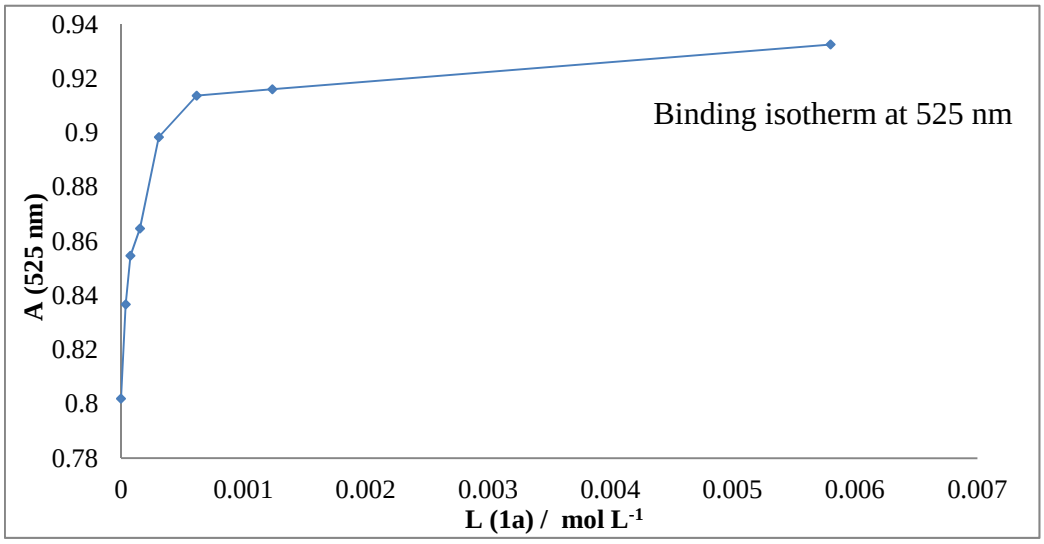
Reference of UV / Vis. Titration Experiment

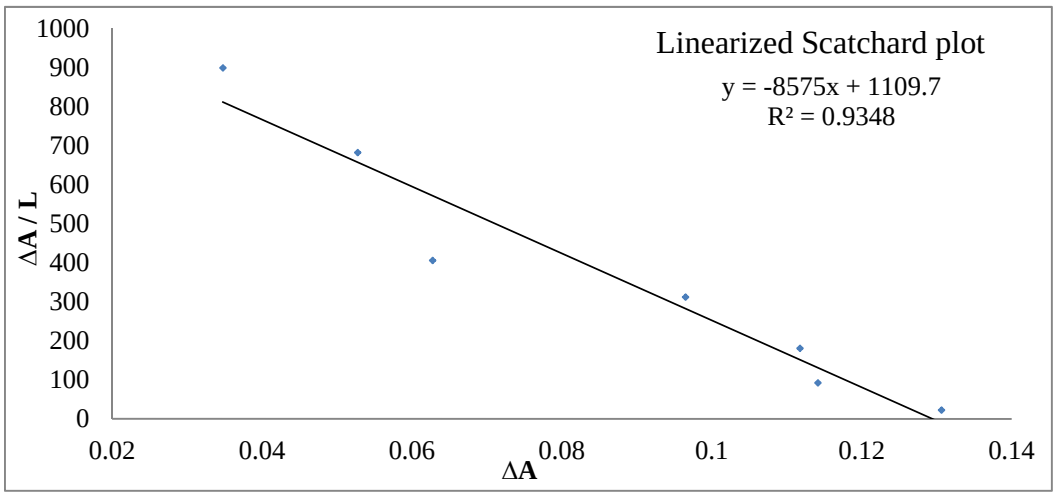
[2] a) K. A. Connors, *Binding Constants: The Measurement of Molecualar Complex Stability*, Wiley-VCH, Weinheim, 1987; b) C. W. Davies, *Ion association*, Butterworths, Washington, 1962, Ch. 4.

[3] M. Bauer, S. Spange, *Angew. Chem. Int. Ed.* 2011, **50**, 9727.

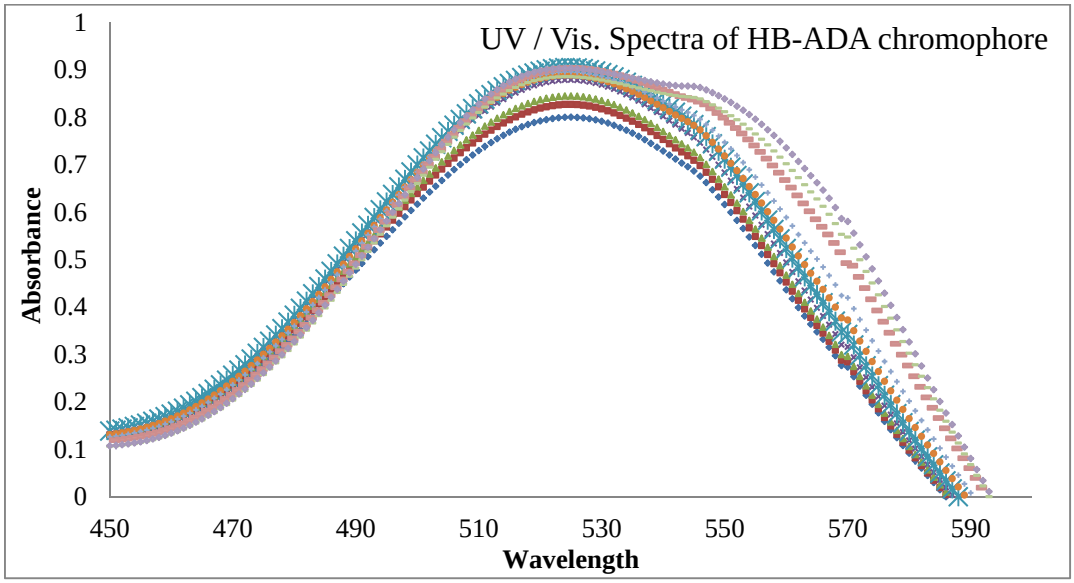
First Trial of Binding Constant of **1a** with **9**

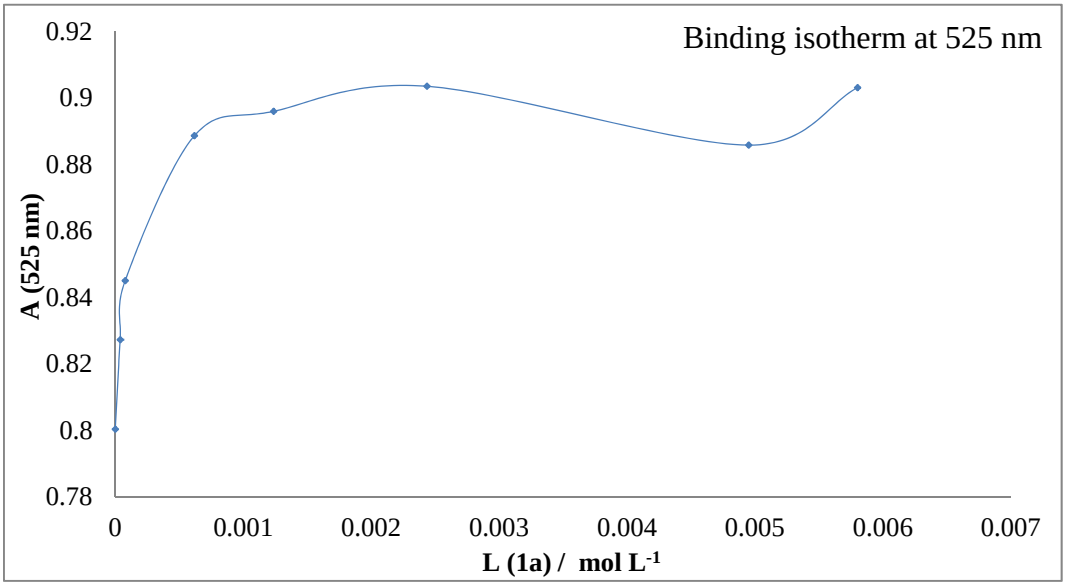


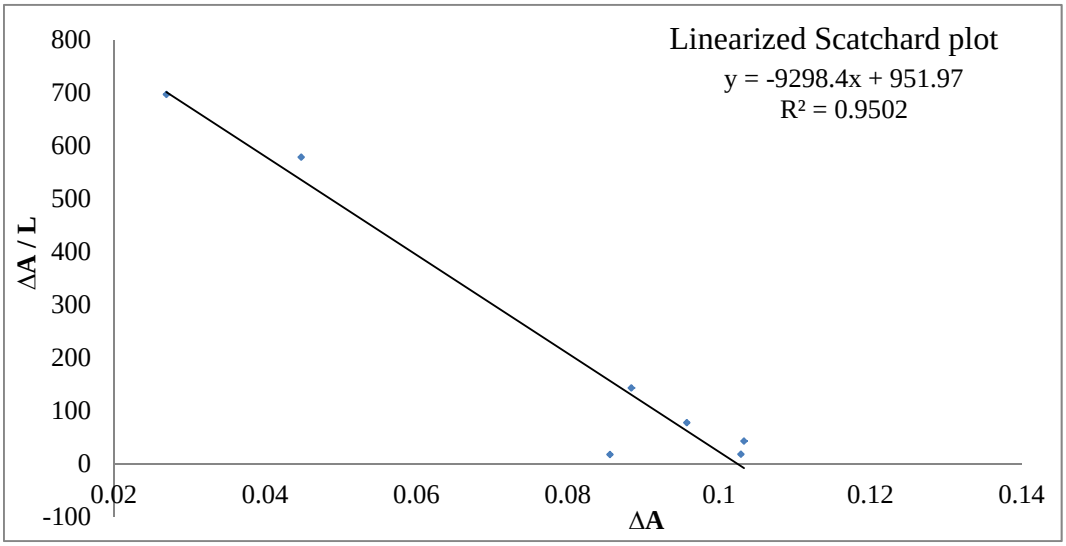




Second Trial of Binding Constant of **1a** with **9**

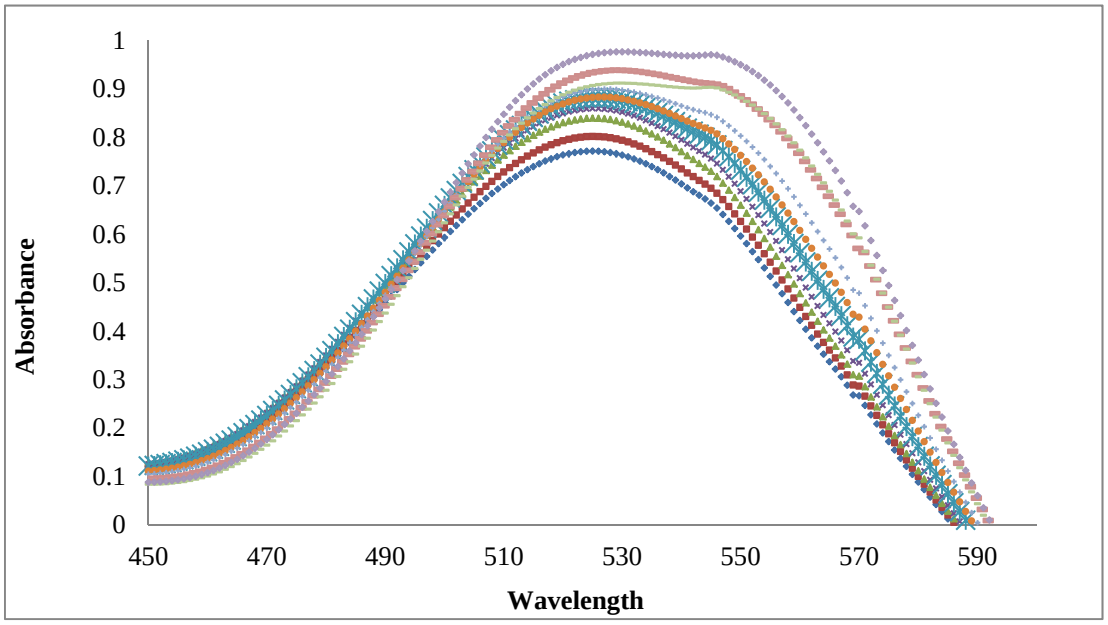


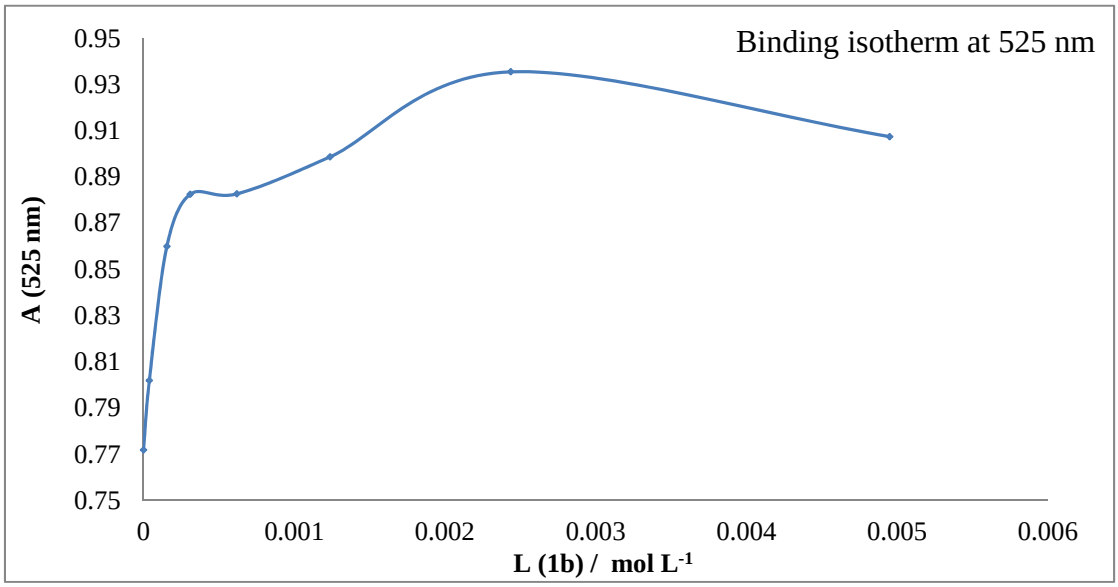


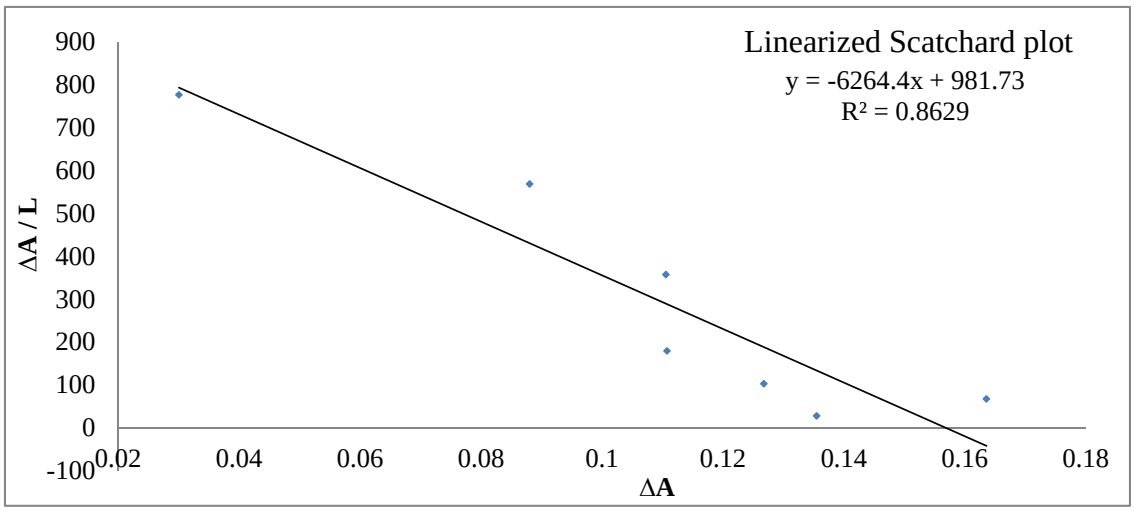


First Trial of Binding Constant of **1b** with **9**

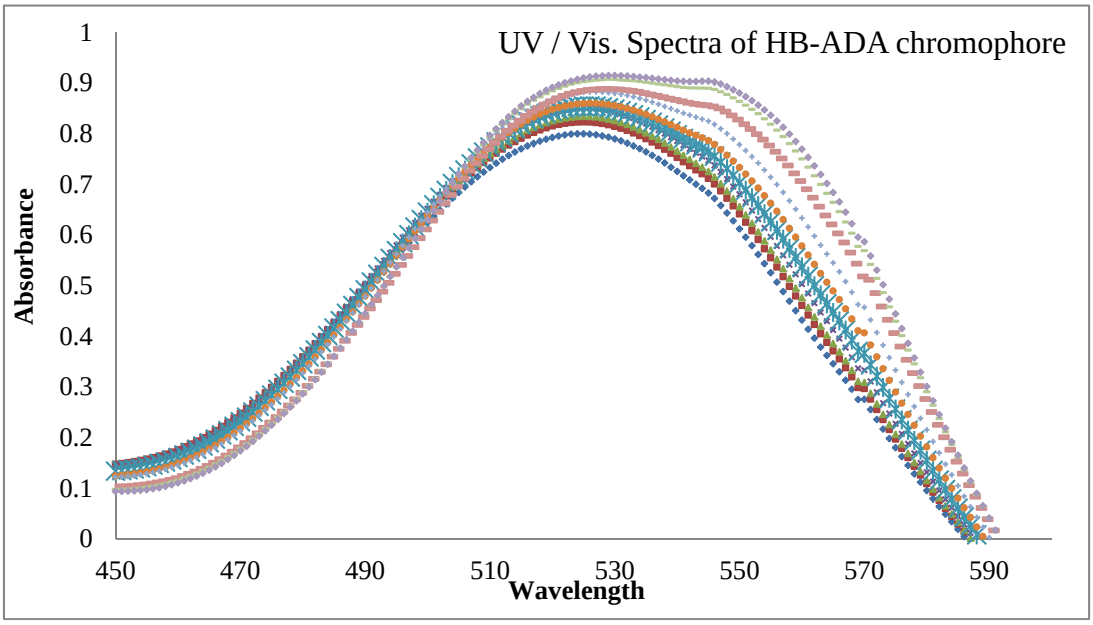
UV / Vis. Spectra of HB-ADA chromophore

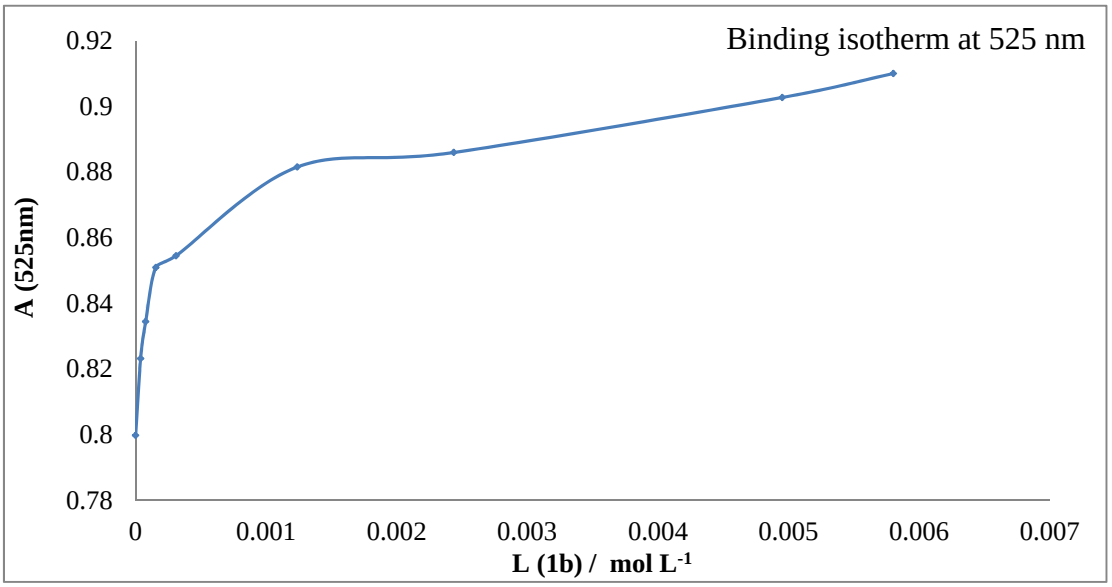


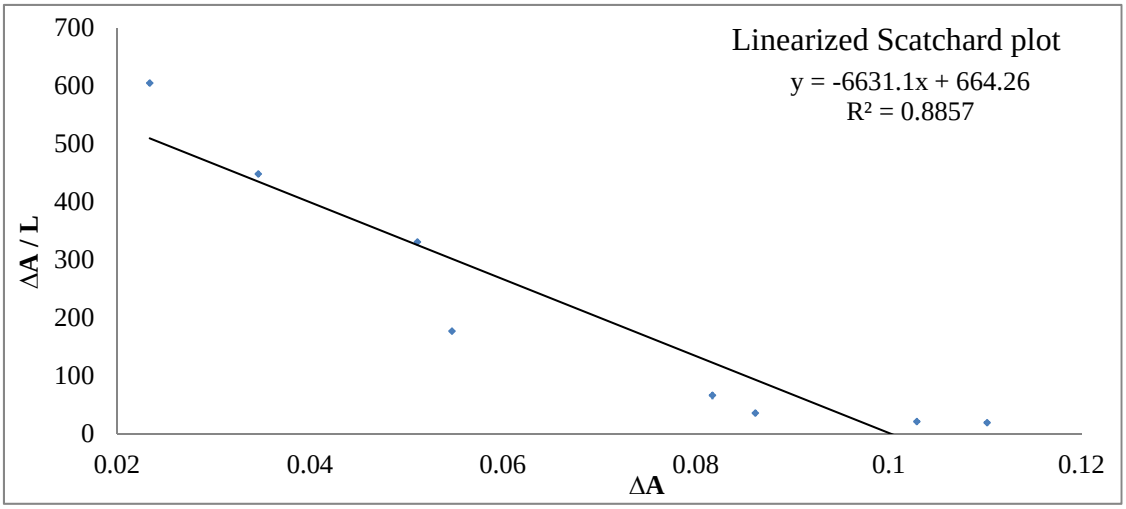




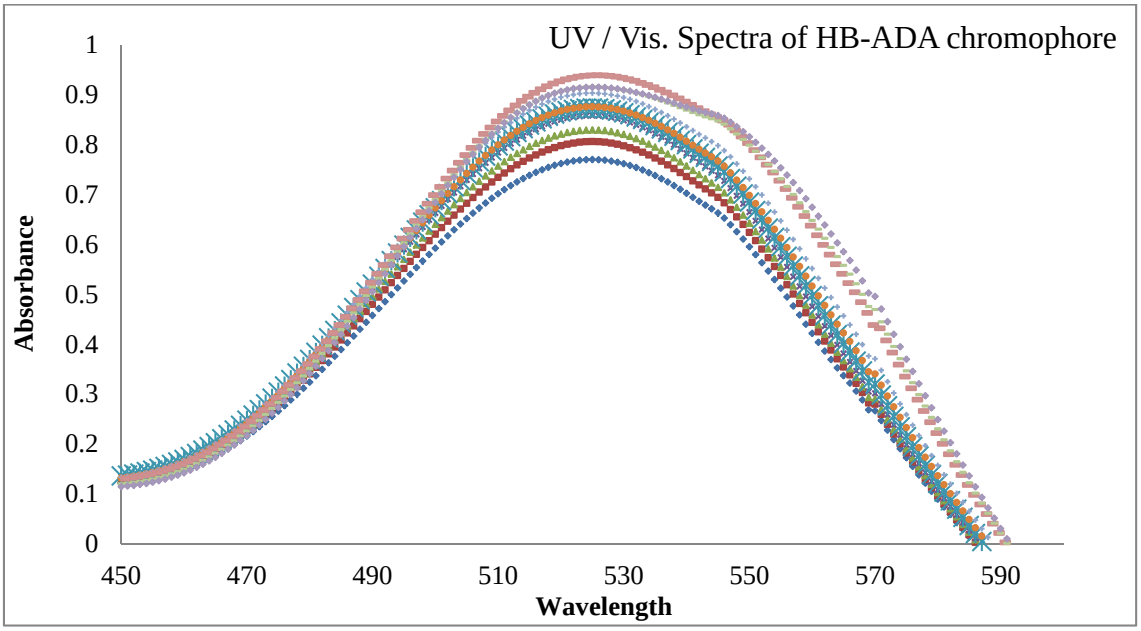
Second Trial of Binding Constant of **1b** with **9**

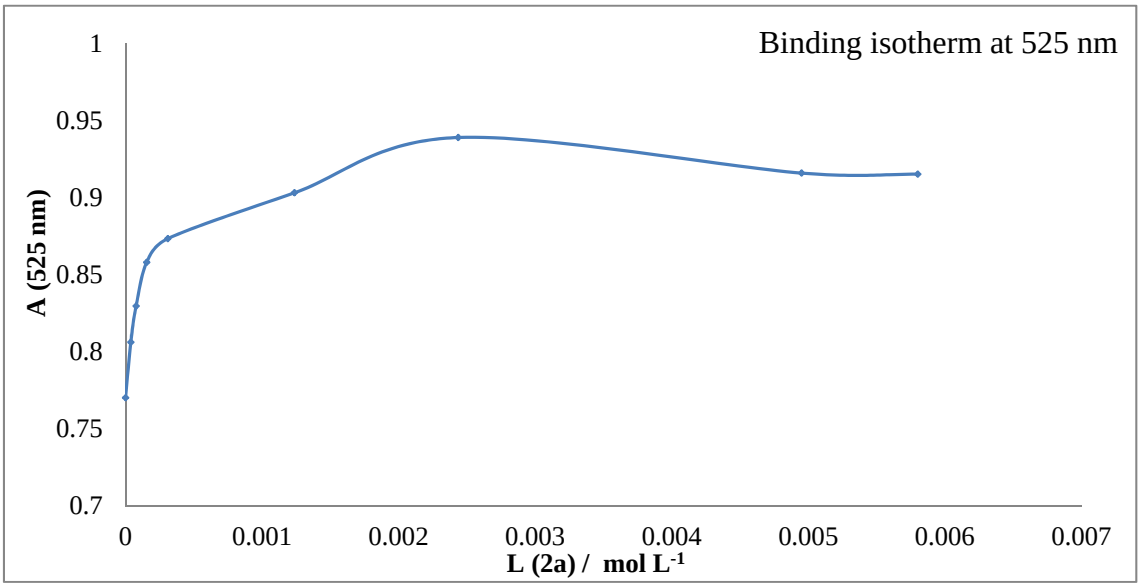


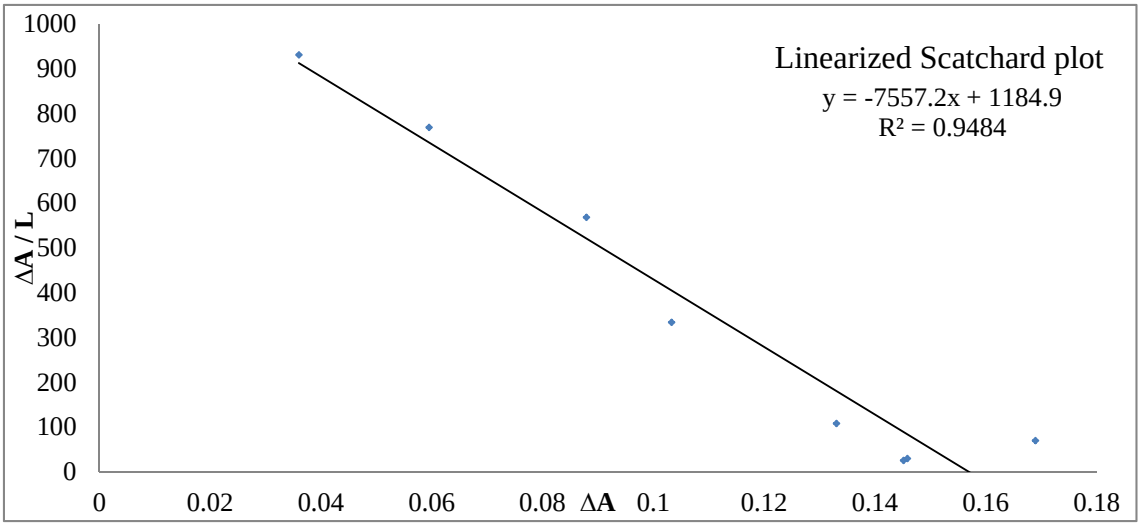




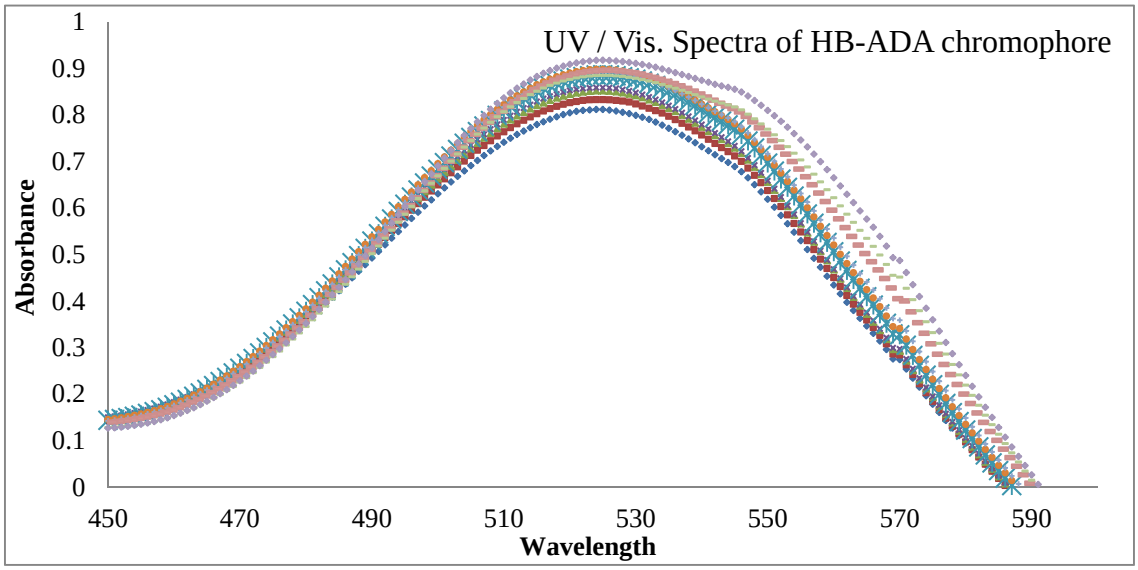
First Trial of Binding Constant of **2a** with **9**

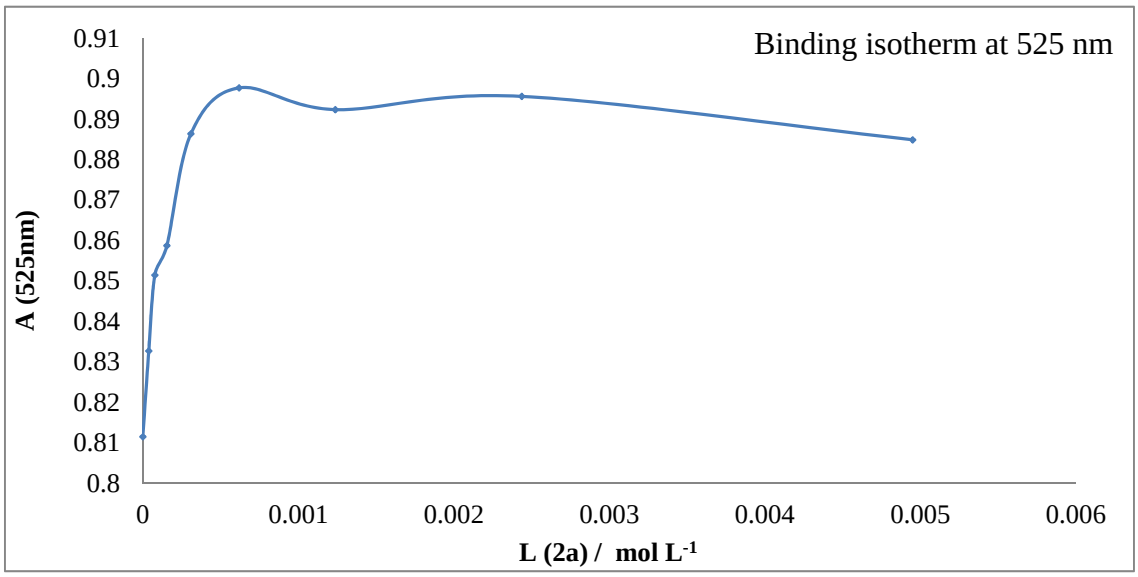


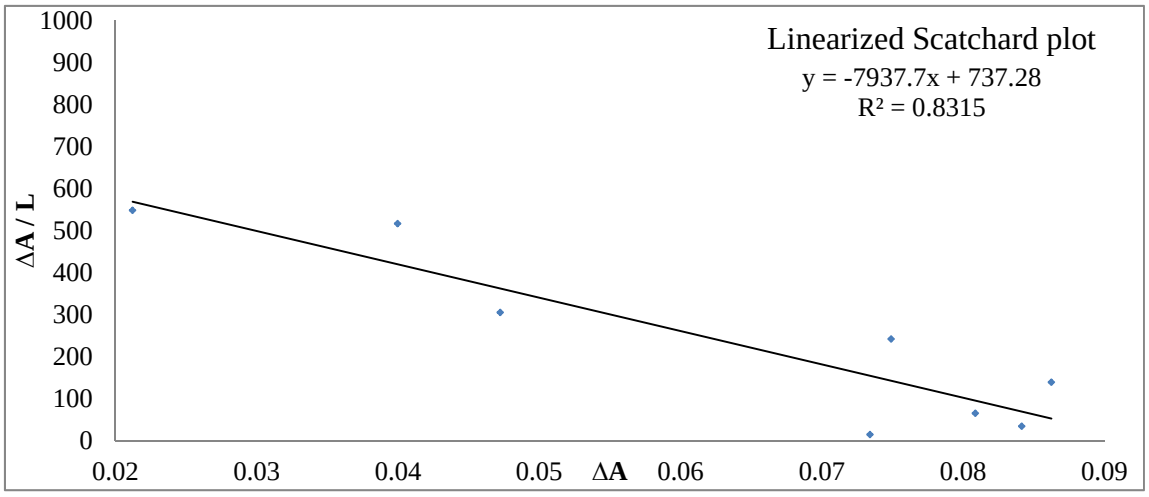




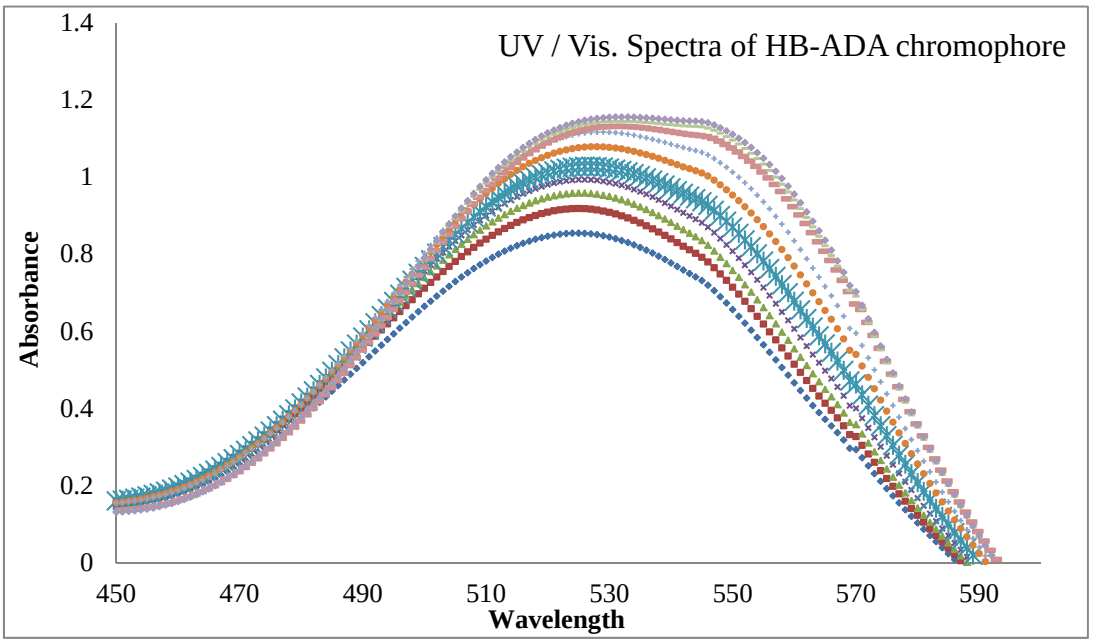
Second Trial of Binding Constant of **2a** with **9**

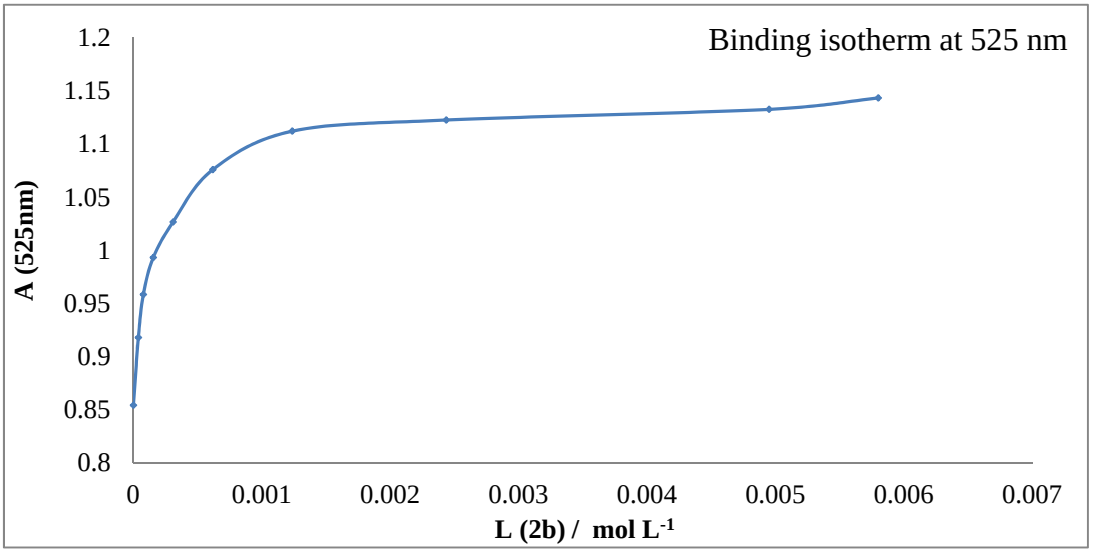


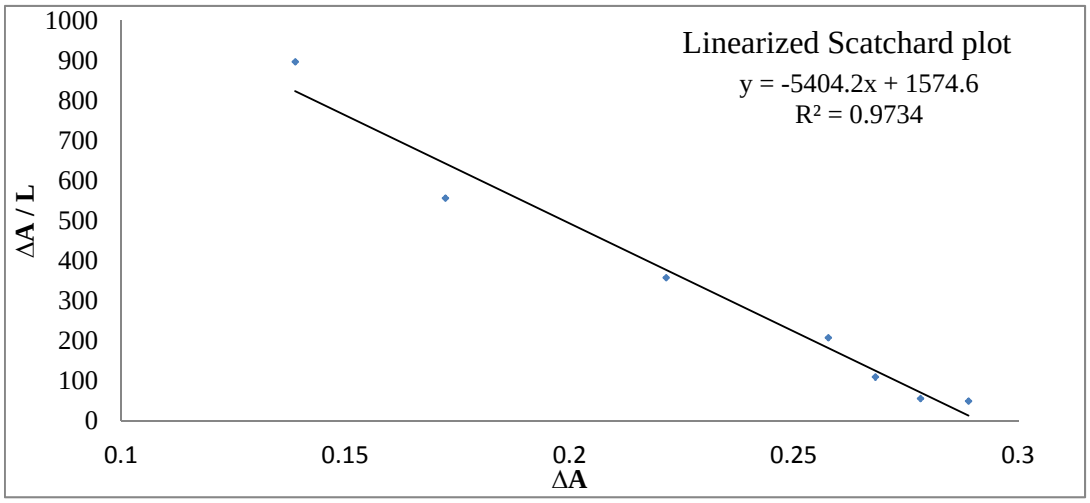




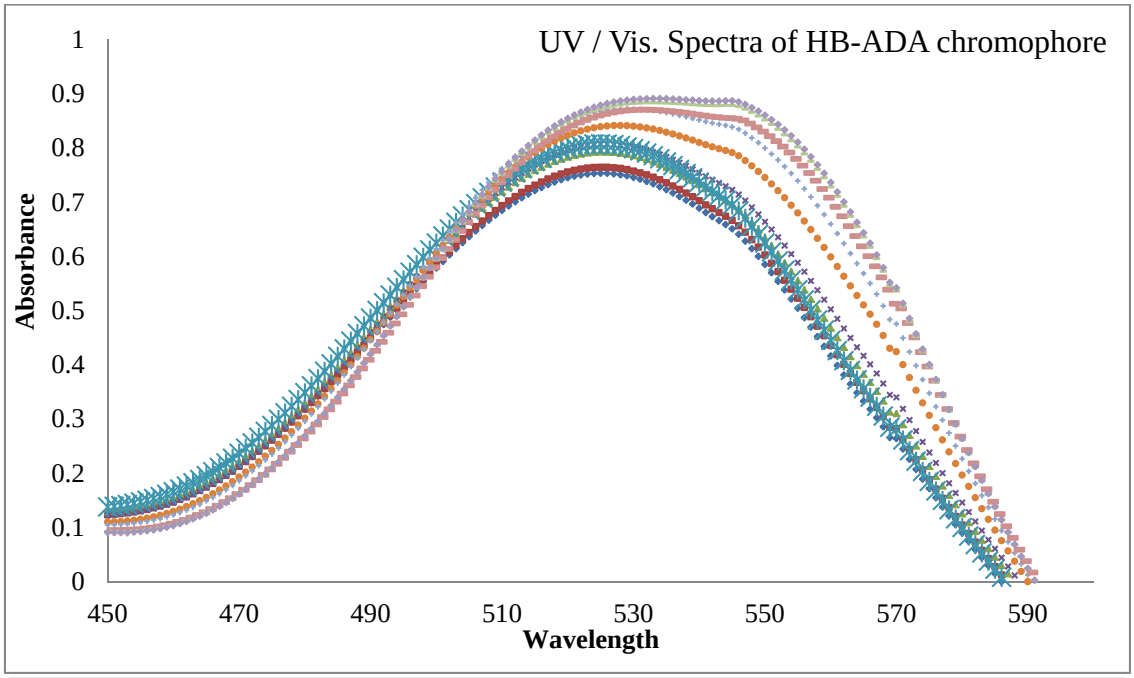
First Trial of Binding Constant of **2b** with **9**

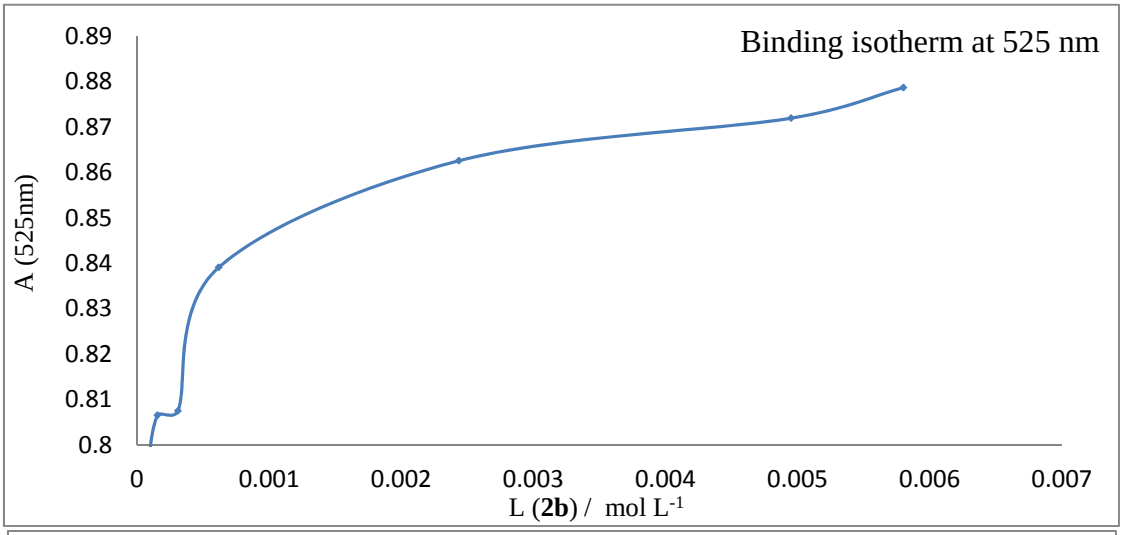


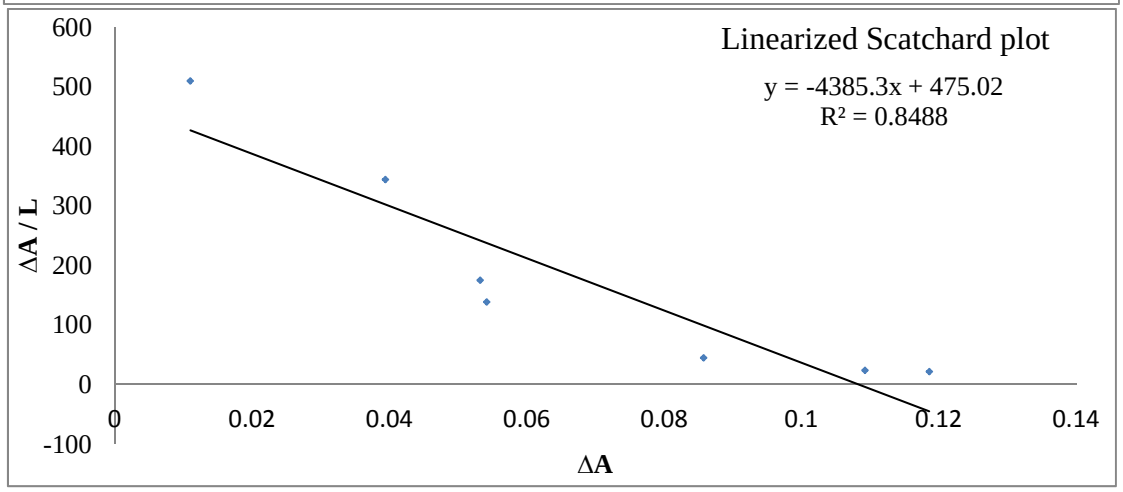


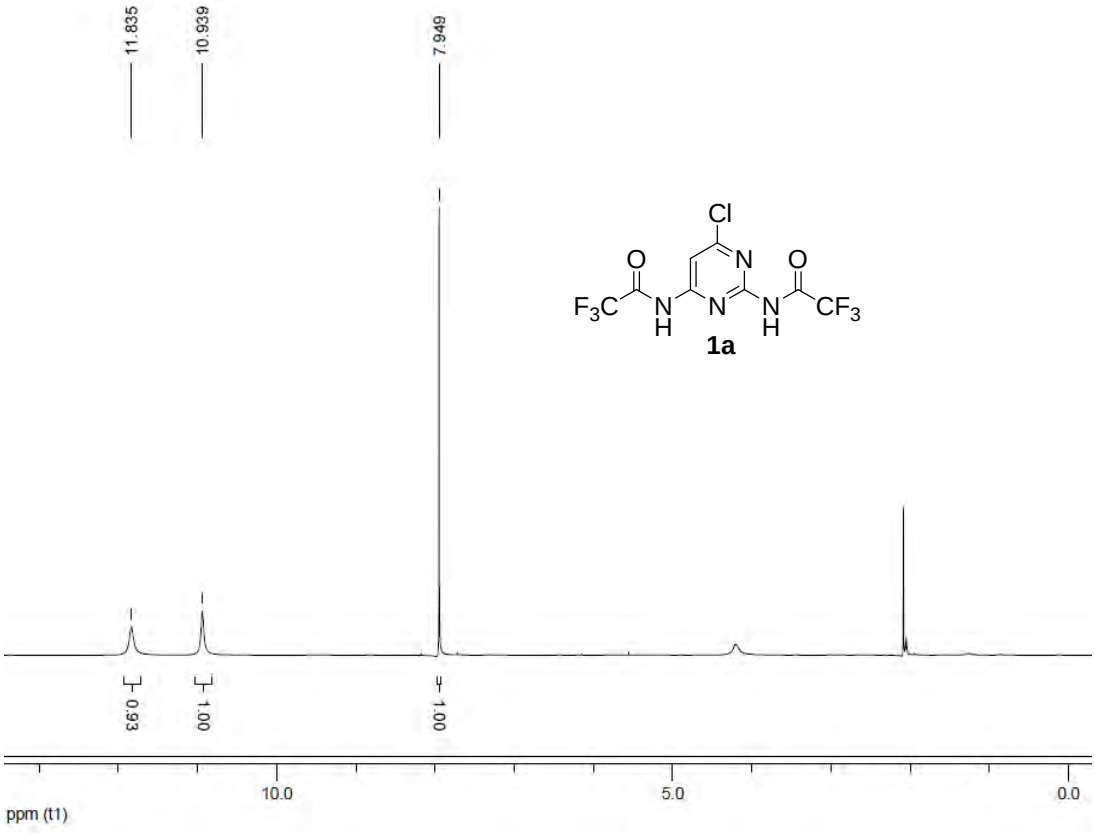


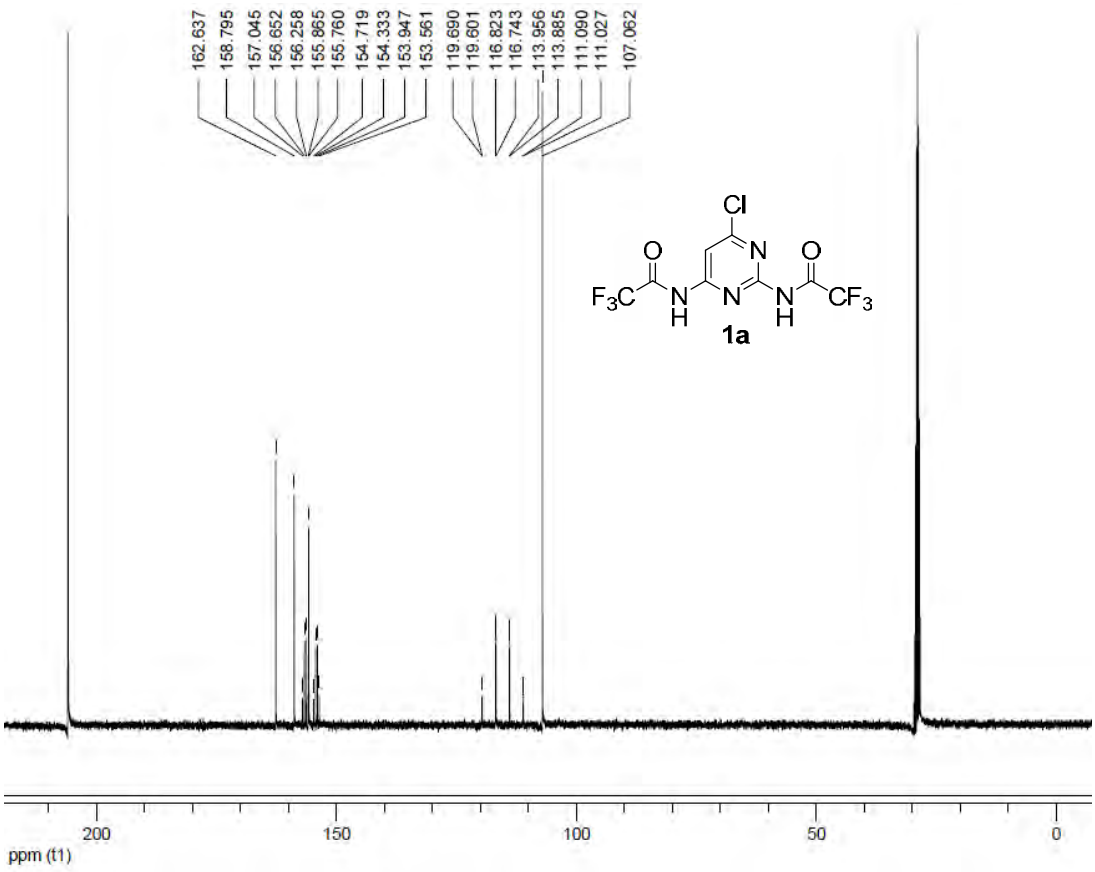
Second Trial of Binding Constant of **2b** with **9**

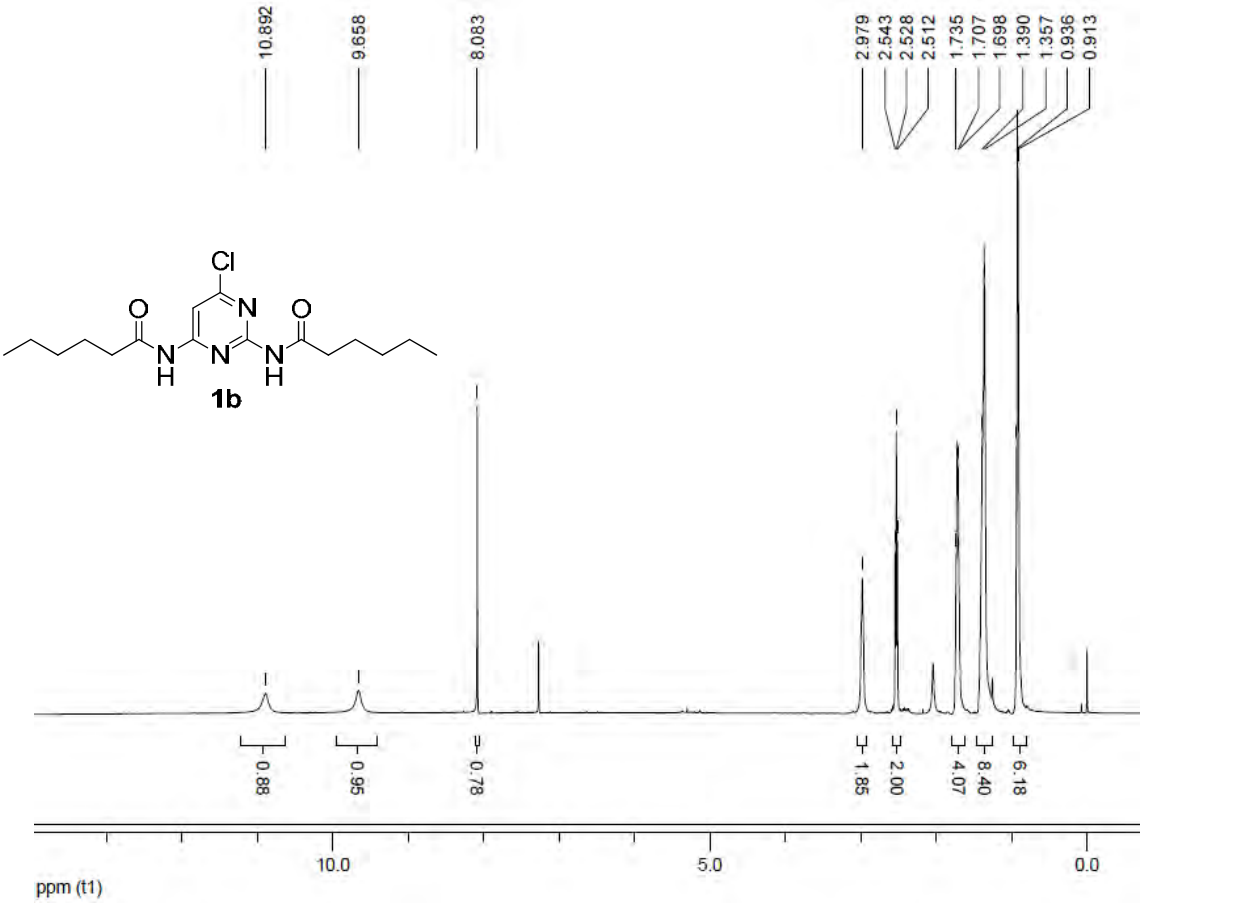

UV / Vis. Spectra of HB-ADA chromophore
Absorbance
Wavelength
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
450
470
490
510
530
550
570
590

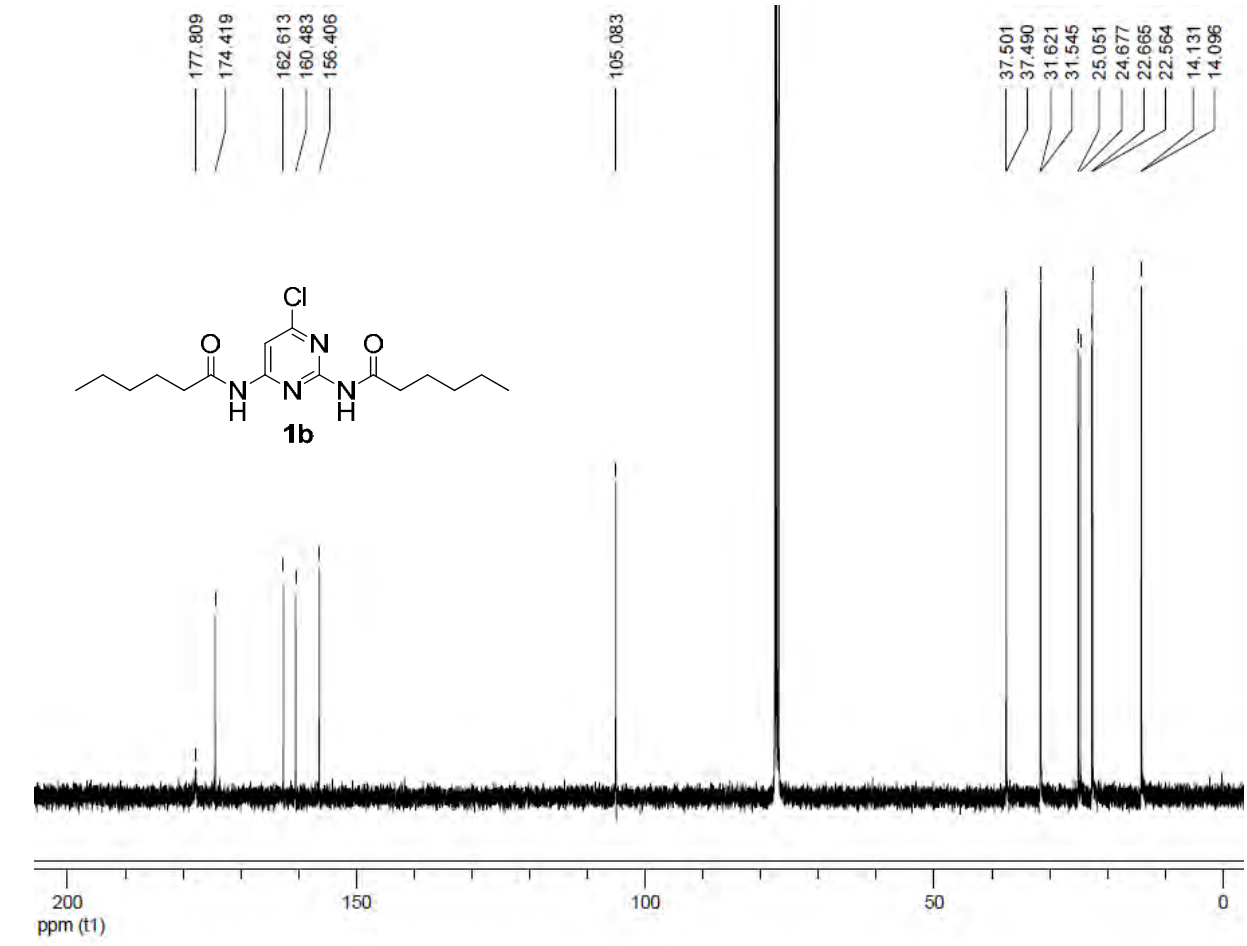

Binding isotherm at 525 nm
A (525nm)
L (2b) / mol L-1
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
0.8
0
0.001
0.002
0.003
0.004
0.005
0.006
0.007

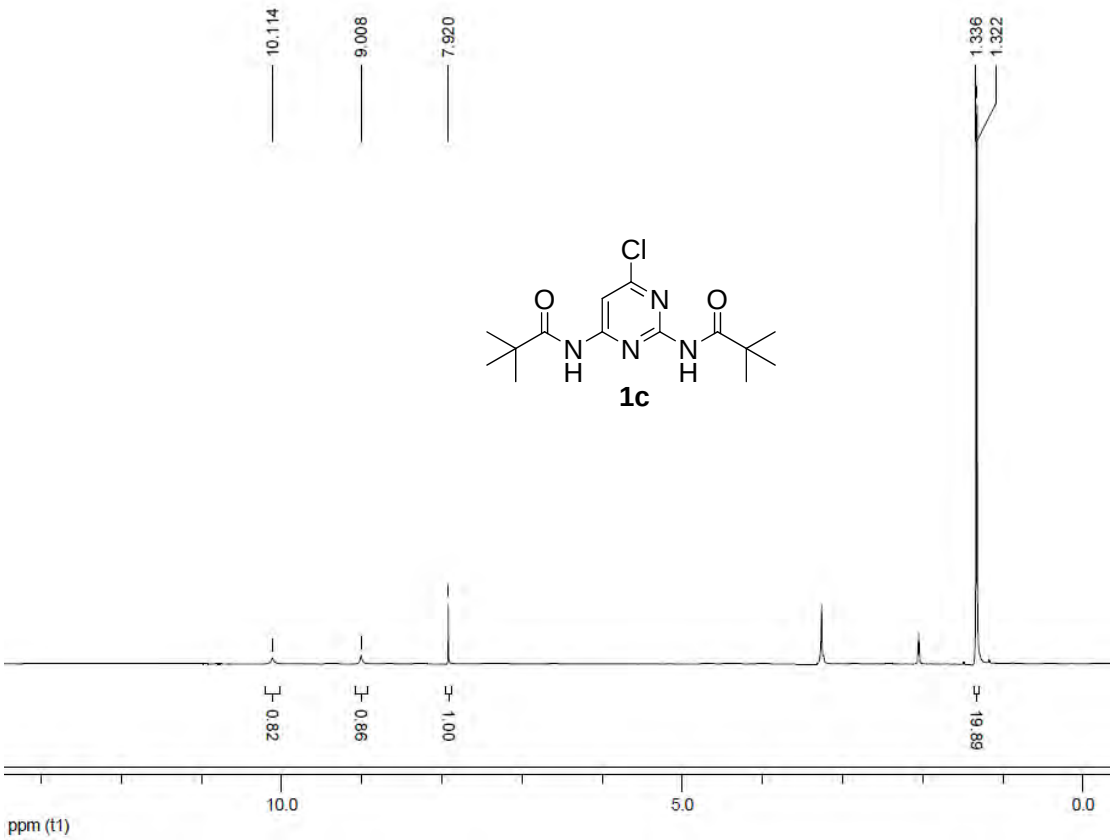

Linearized Scatchard plot
y = -4385.3x + 475.02
R² = 0.8488
ΔA / L
ΔA
600
500
400
300
200
100
0
-100
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14

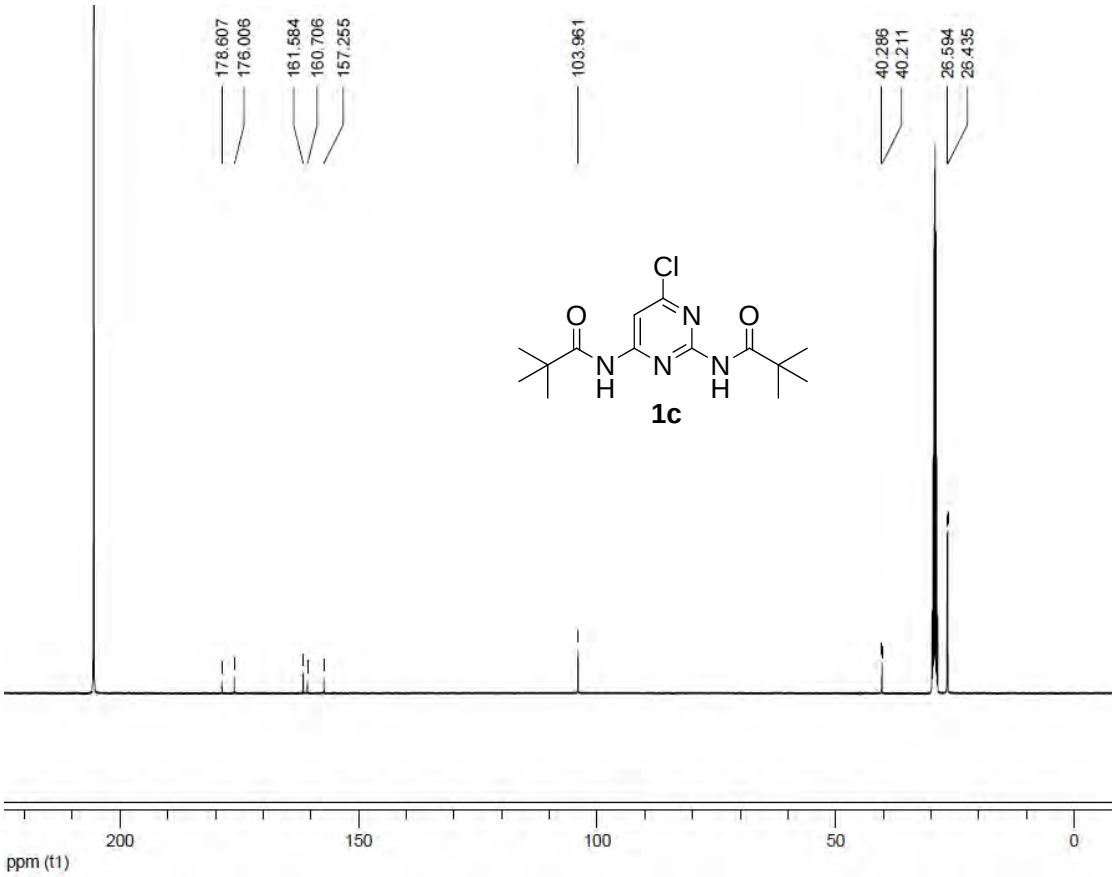

11.835
10.939
7.949
Cl
O
N
O
F3C
N
H
N
N
H
CF3
1a
0.93
1.00
1.00
10.0
5.0
0.0
ppm (t1)

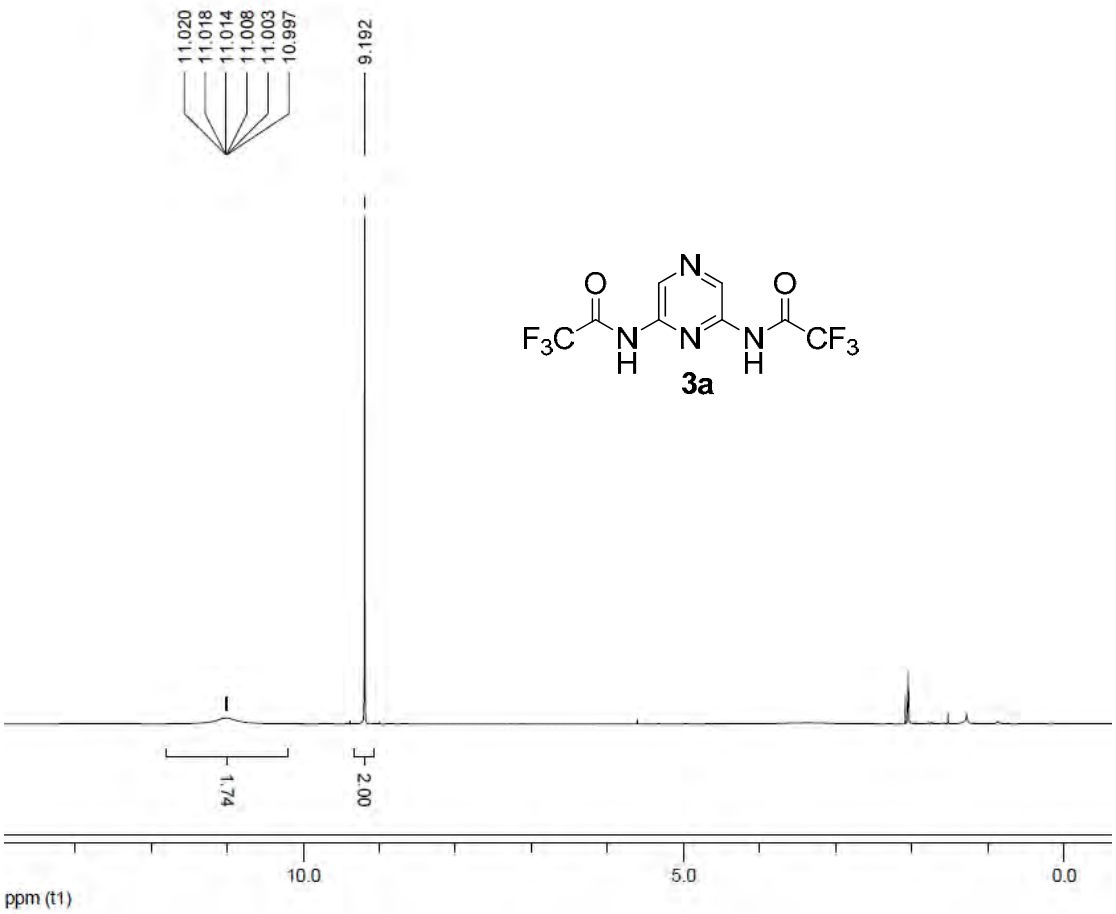

162.637
158.795
157.045
156.652
156.258
155.865
155.760
154.719
154.333
153.947
153.561
119.690
119.601
116.823
116.743
113.956
113.885
111.090
111.027
107.062
Cl
O
N
O
F3C
N
H
N
N
H
CF3
1a
200
150
100
50
0
ppm (t1)


10.892
9.658
8.083
2.979
2.543
2.528
2.512
1.735
1.707
1.698
1.390
1.357
0.936
0.913
Cl
O
N
O
N
H
N
N
H
1b
0.88
0.96
0.78
1.85
2.00
4.07
8.40
6.18
10.0
5.0
0.0
ppm (t1)

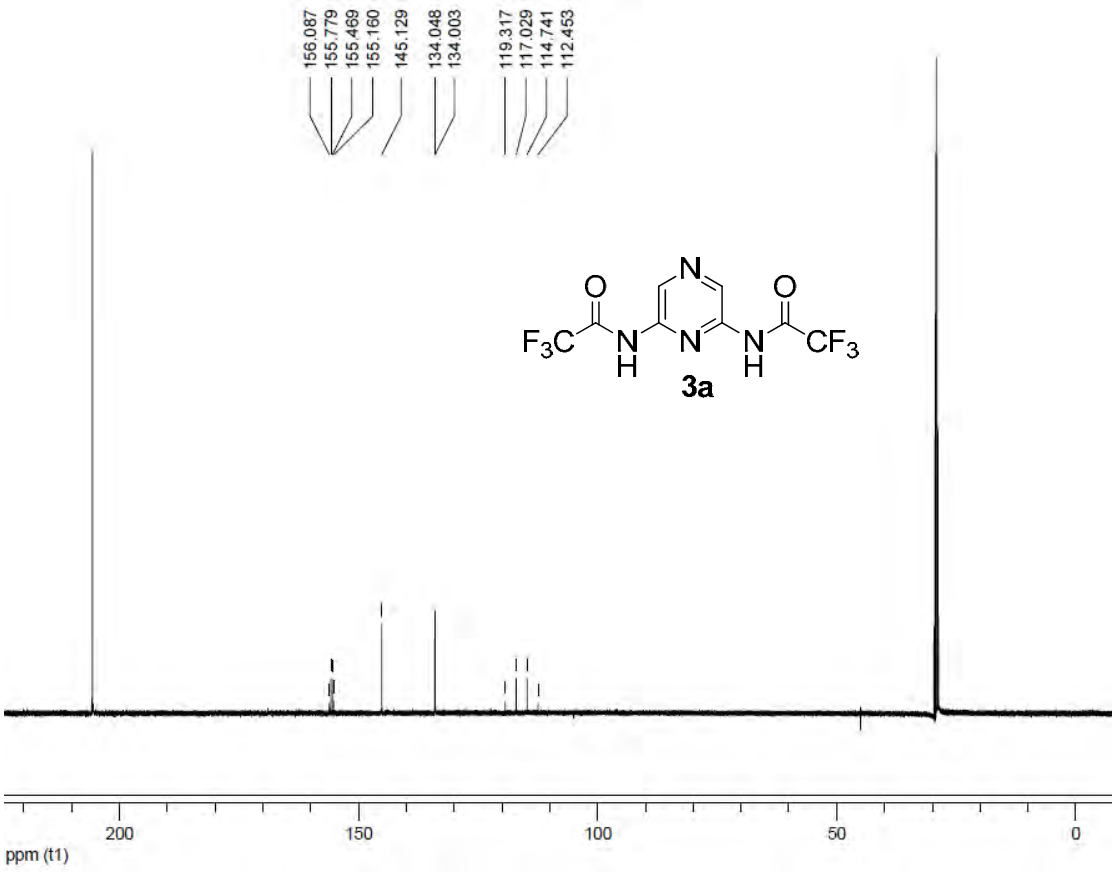

177.809
174.419
162.613
160.483
156.406
105.083
37.501
37.490
31.621
31.545
25.051
24.677
22.665
22.564
14.131
14.096
Cl
O
N
O
N
H
N
N
H
1b
200
150
100
50
0
ppm (t1)


10.114
9.008
7.920
1.336
1.322
Cl
O
N
O
N
H
N
N
H
1c
0.82
0.86
1.00
19.89
10.0
5.0
0.0
ppm (t1)

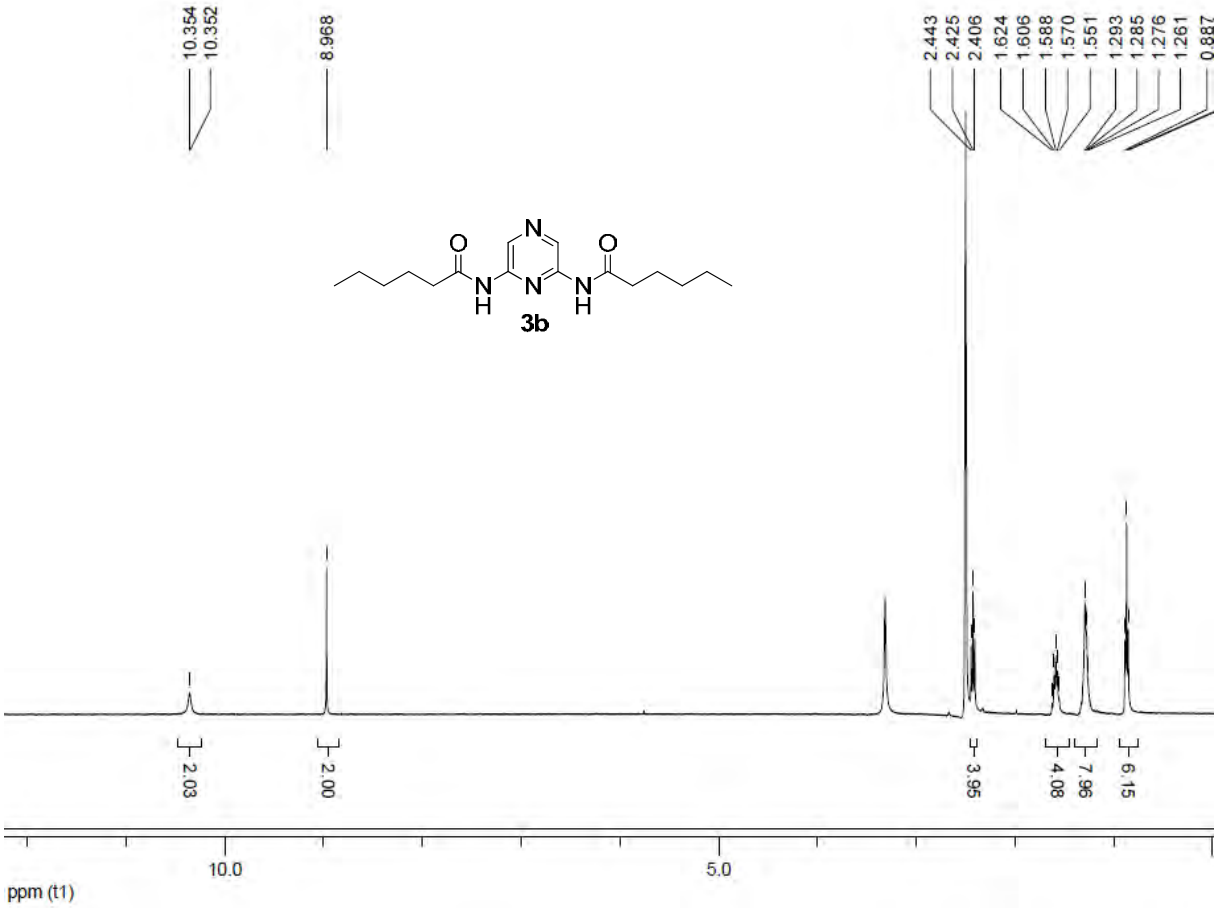

178.607
176.006
161.584
160.706
157.255
103.961
40.286
40.211
26.594
26.435
Cl
O
N
O
N
H
N
N
H
1c
200
150
100
50
0
ppm (t1)

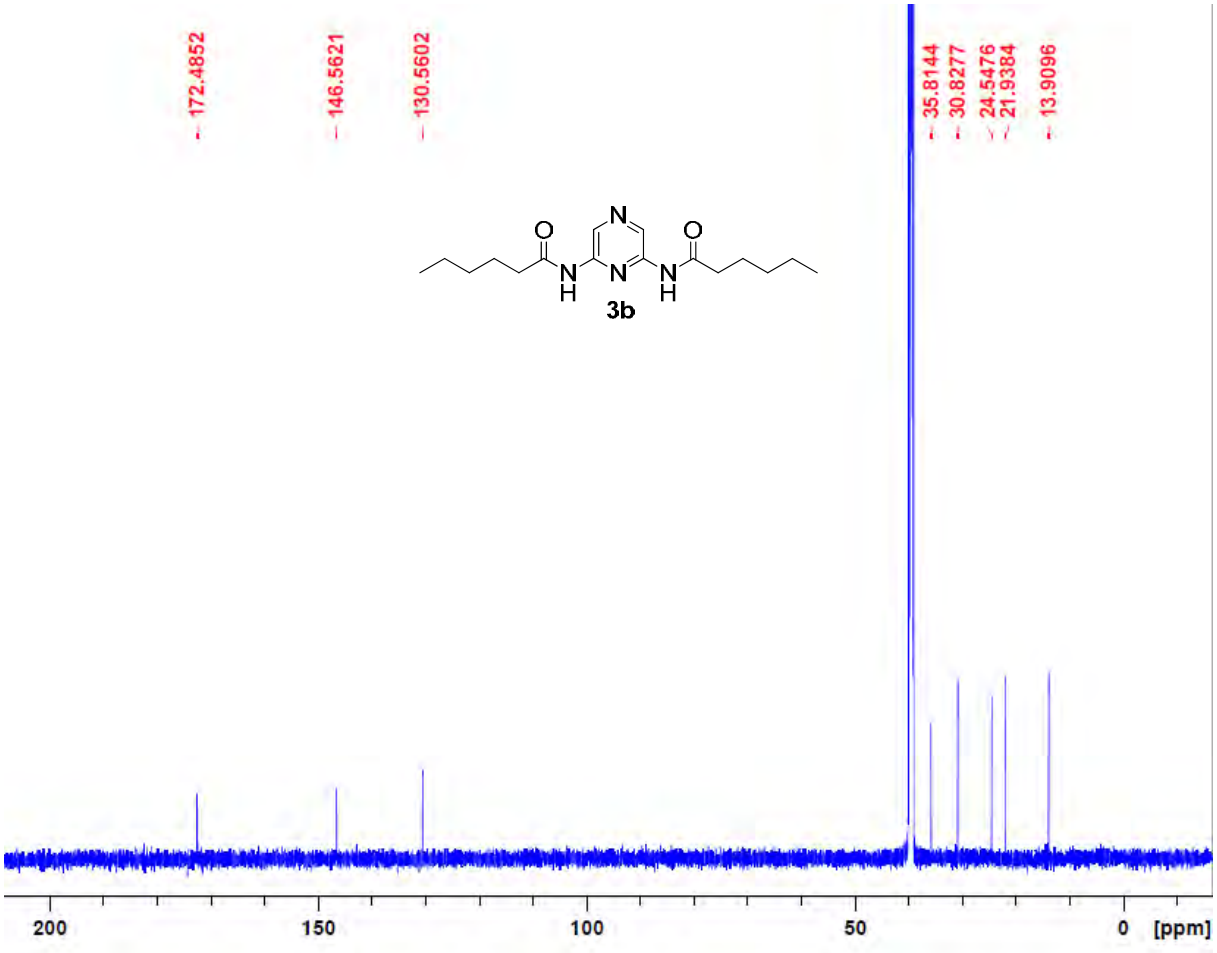

11.020
11.018
11.014
11.008
11.003
10.997
9.192
1.74
2.00
10.0
5.0
0.0
ppm (t1)

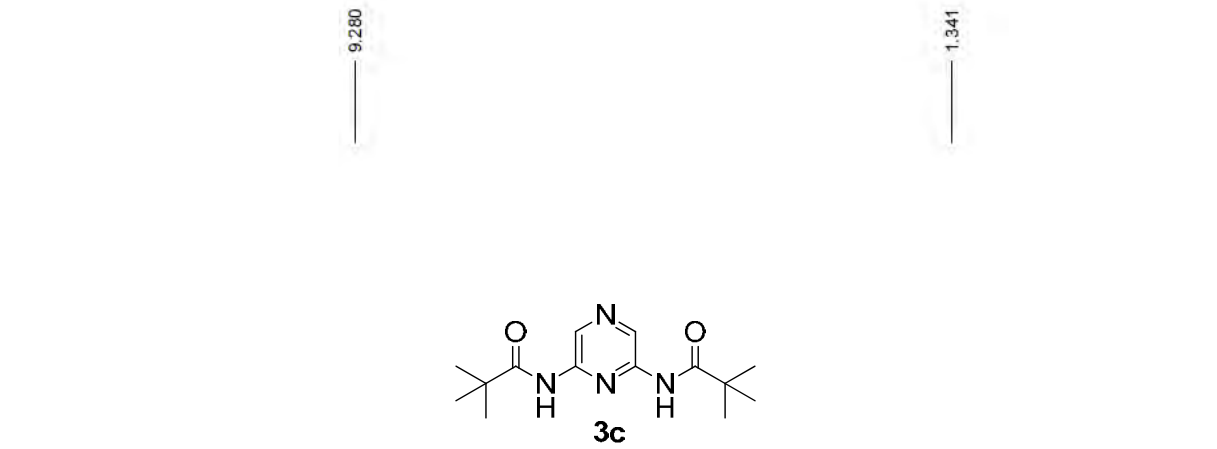
F3C
CF3
3a

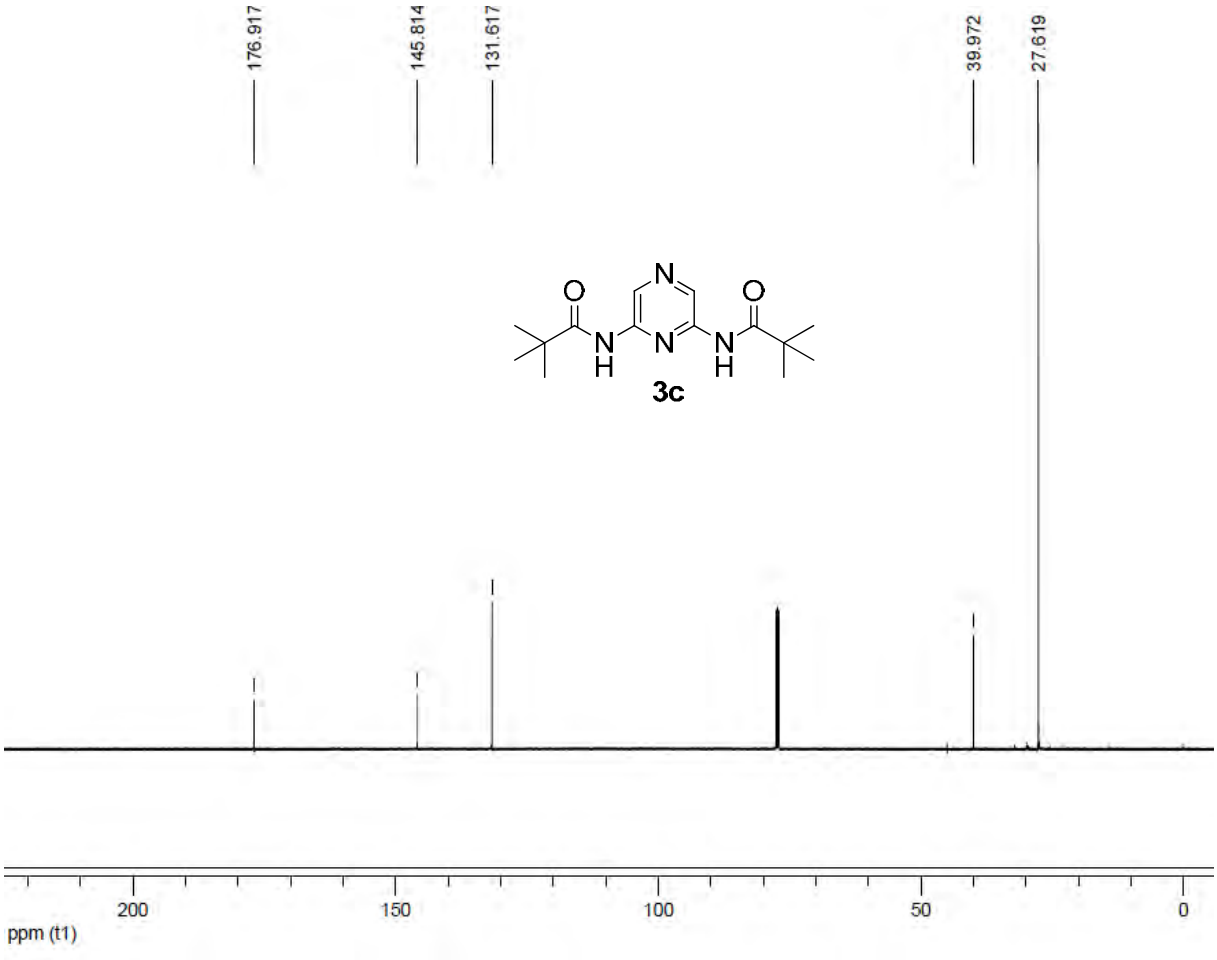

156.087
155.779
155.469
155.160
145.129
134.048
134.003
119.317
117.029
114.741
112.453
200
150
100
50
0
ppm (t1)

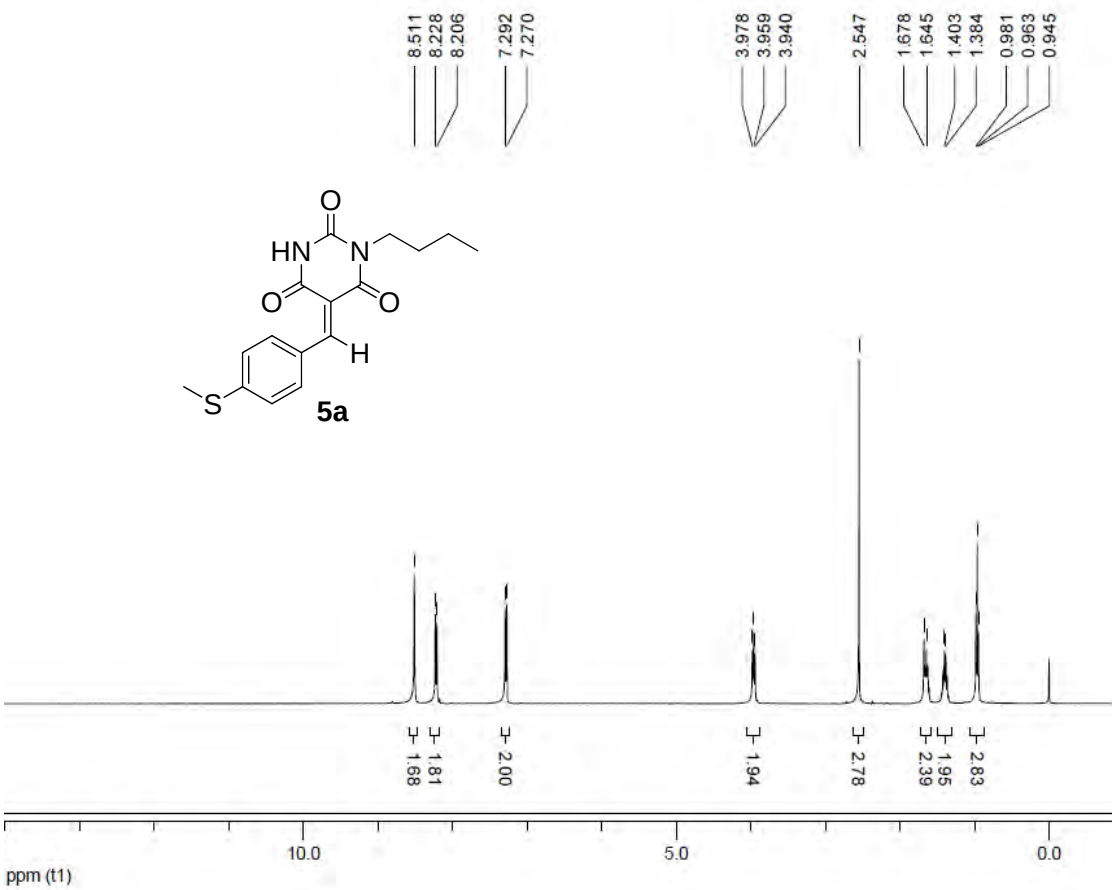
F3C
CF3
3a

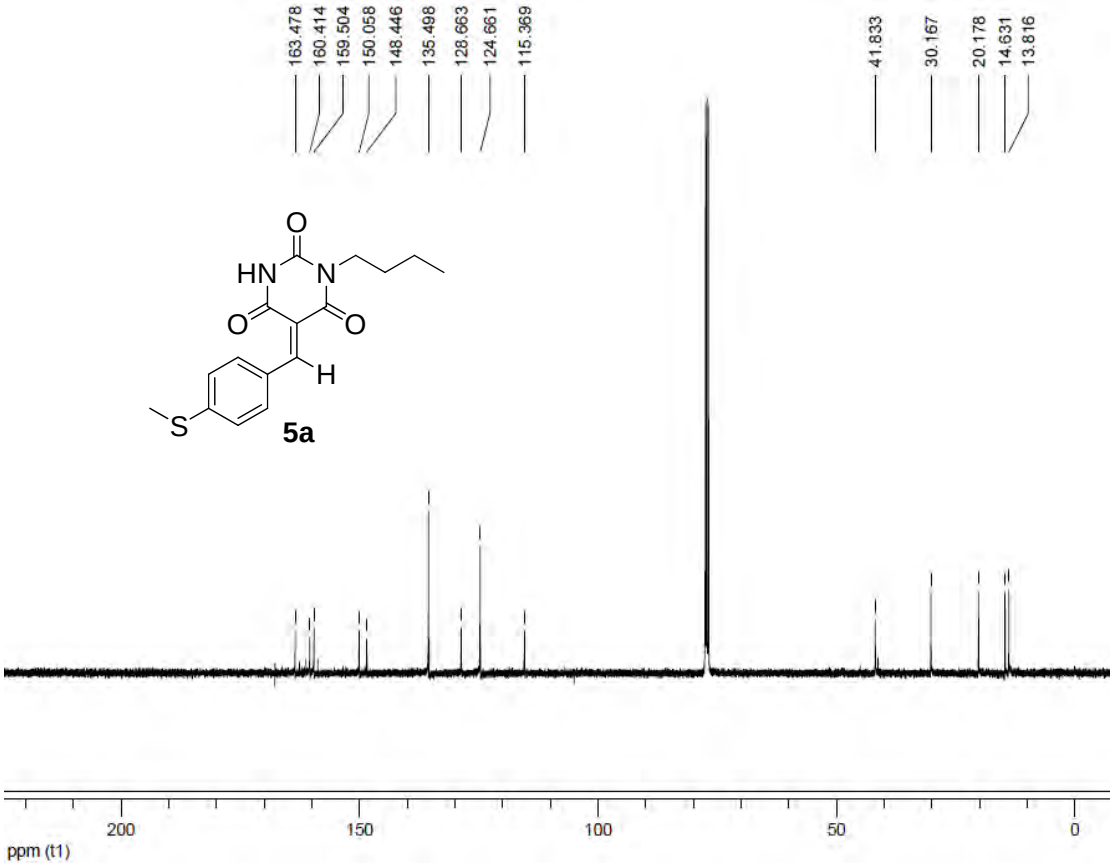

10.354
10.352
8.968
2.443
2.425
2.406
1.624
1.606
1.588
1.570
1.551
1.293
1.285
1.276
1.261
0.887
3b
2.03
2.00
3.96
4.08
7.96
6.15
10.0
5.0
ppm (t1)

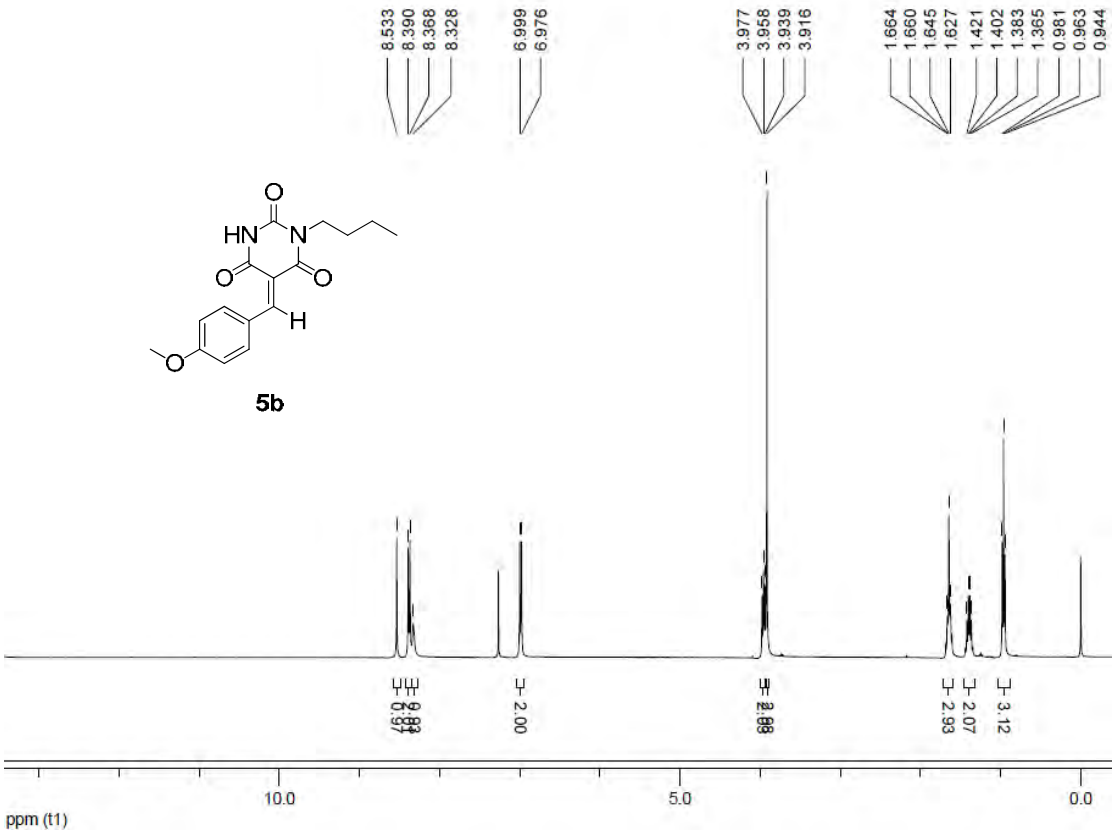

172.4852
146.5621
130.5602
35.8144
30.8277
24.5476
21.9384
13.9096
3b
200
150
100
50
0
[ppm]

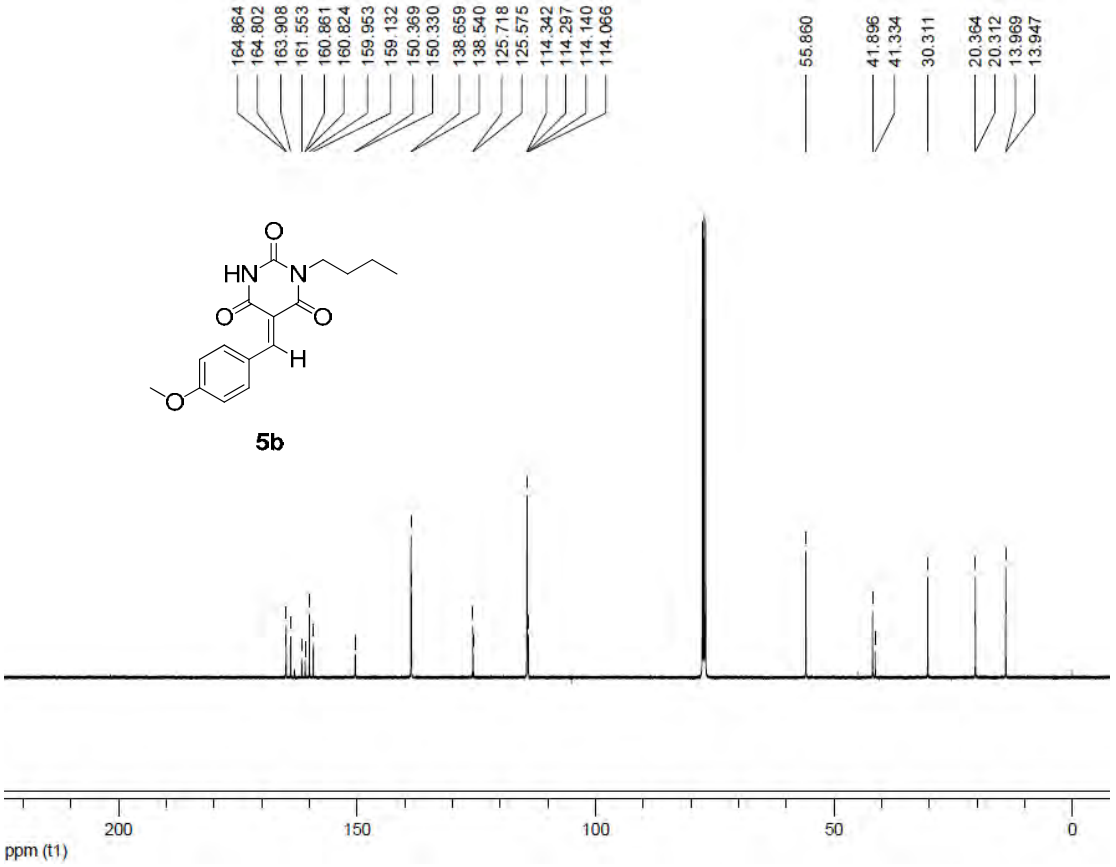

9.280
1.341
3c
2.00
18.20
10.0
5.0
0.0
ppm (t1)

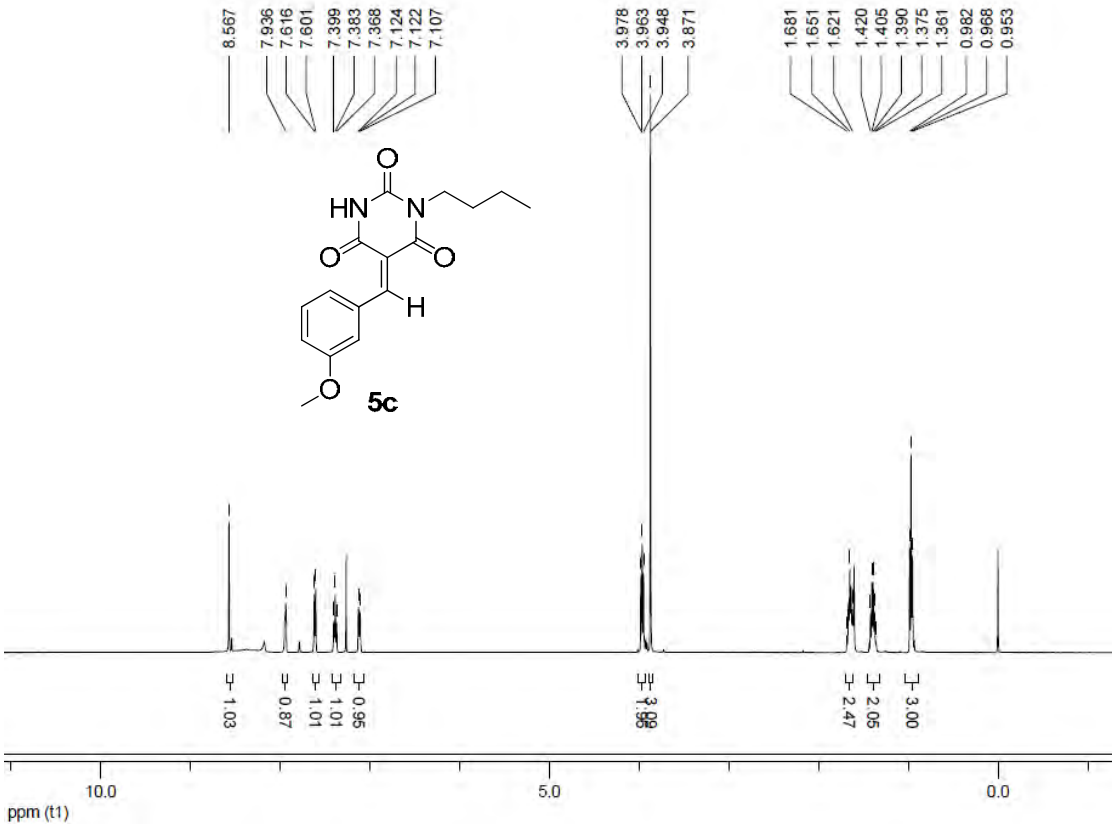

176.917
145.814
131.617
39.972
27.619
3c
200
150
100
50
0
ppm (t1)

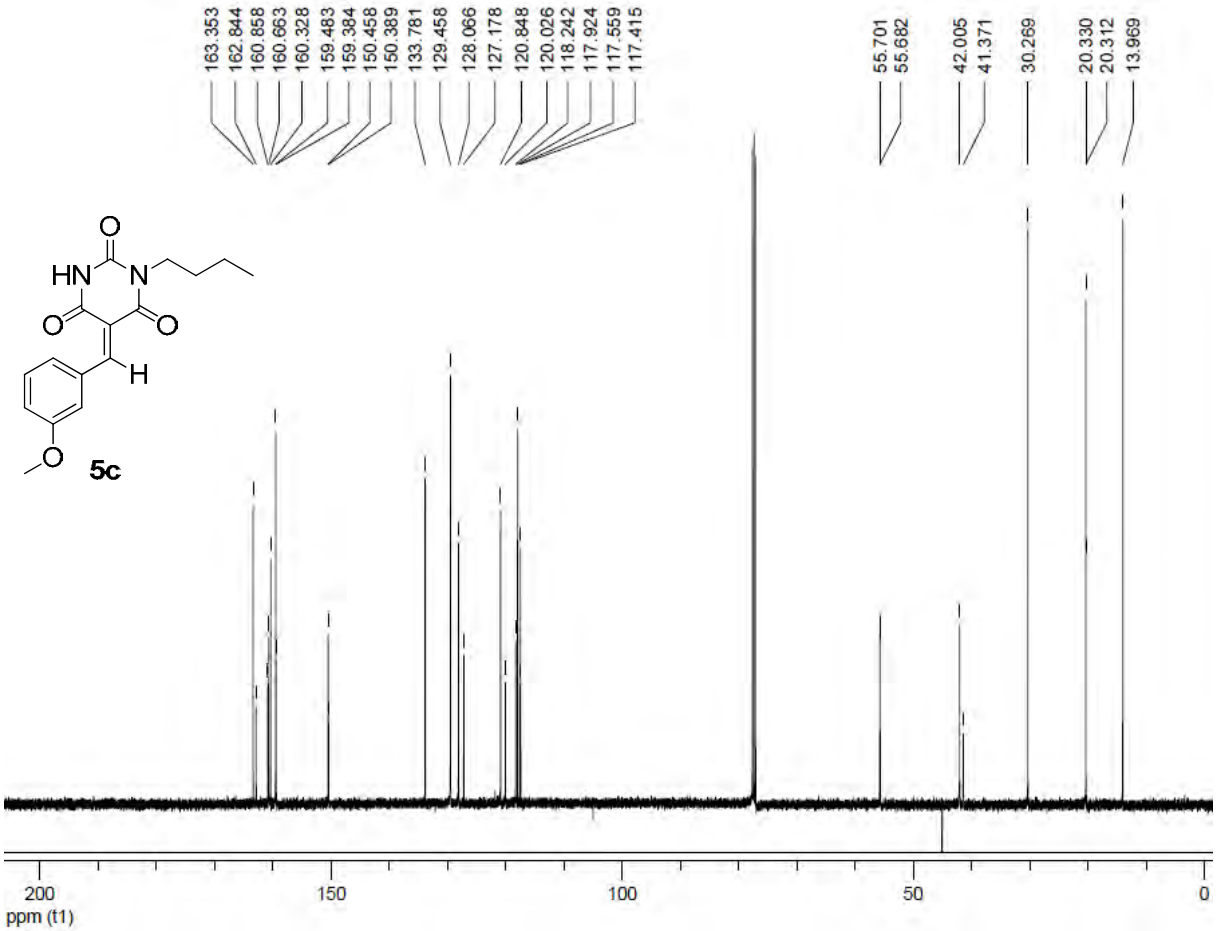

8.511
8.228
8.206
7.292
7.270
3.978
3.959
3.940
2.547
1.678
1.645
1.403
1.384
0.981
0.963
0.945
O
HN
N
O
O
H
S
5a
1.68
1.81
2.00
1.94
2.78
2.39
1.95
2.83
10.0
5.0
0.0
ppm (t1)

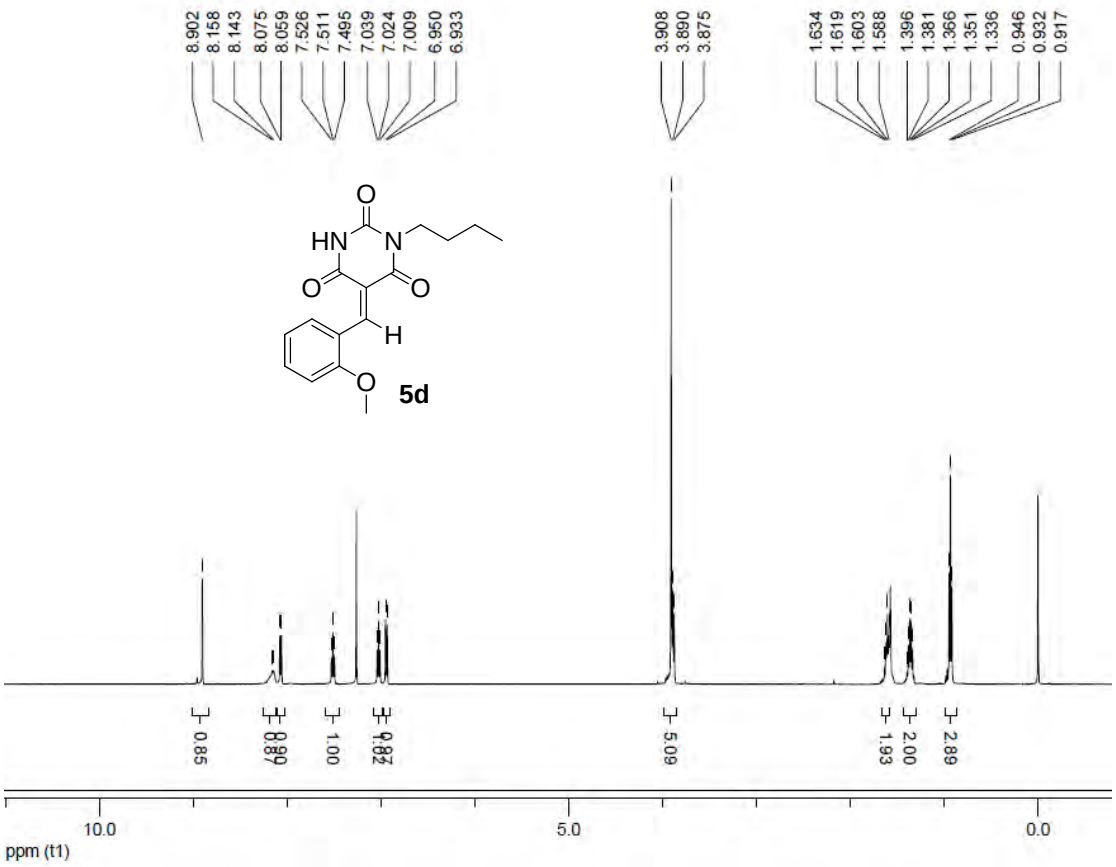

163.478
160.414
159.504
150.058
148.446
135.498
128.663
124.661
115.369
41.833
30.167
20.178
14.631
13.816
O
HN
N
O
O
H
S
5a
200
150
100
50
0
ppm (t1)

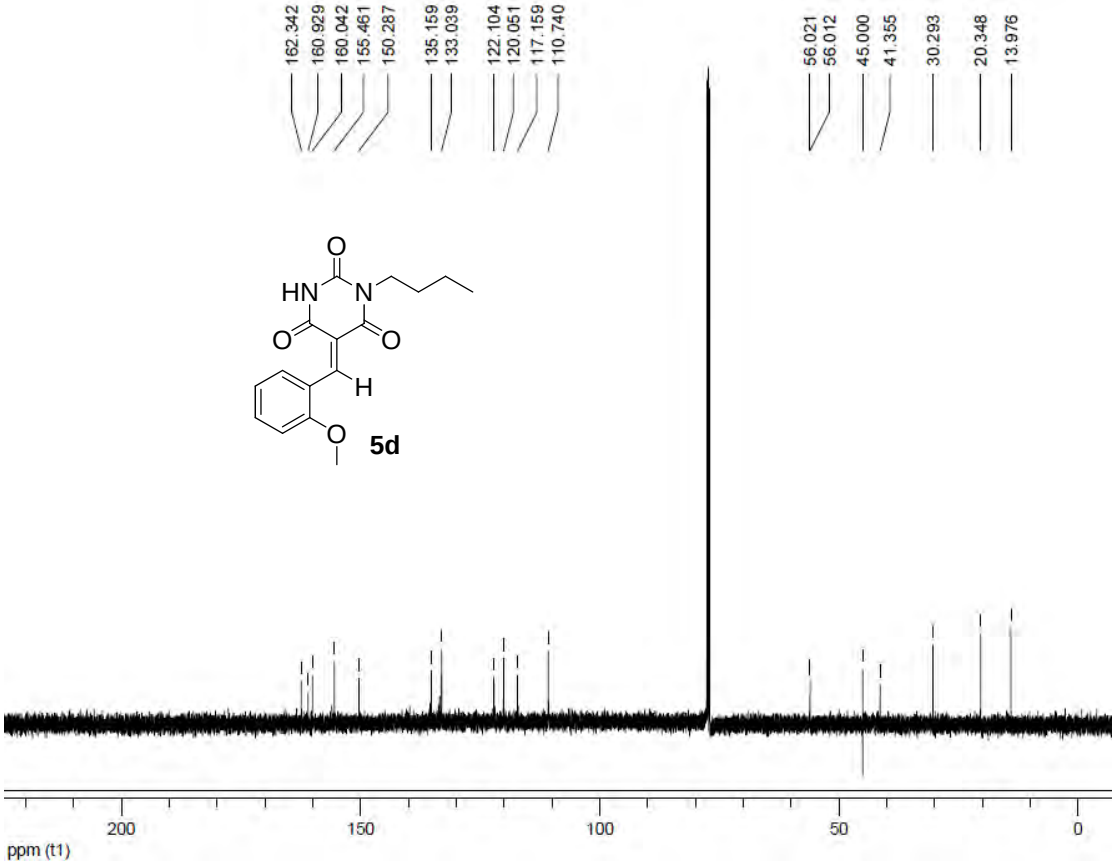

8.533
8.390
8.368
8.328
6.999
6.976
3.977
3.958
3.939
3.916
1.664
1.660
1.645
1.627
1.421
1.402
1.383
1.365
0.981
0.963
0.944
HN
N
O
O
O
H
O
5b
2.00
2.98
2.07
3.12
10.0
5.0
0.0
ppm (t1)

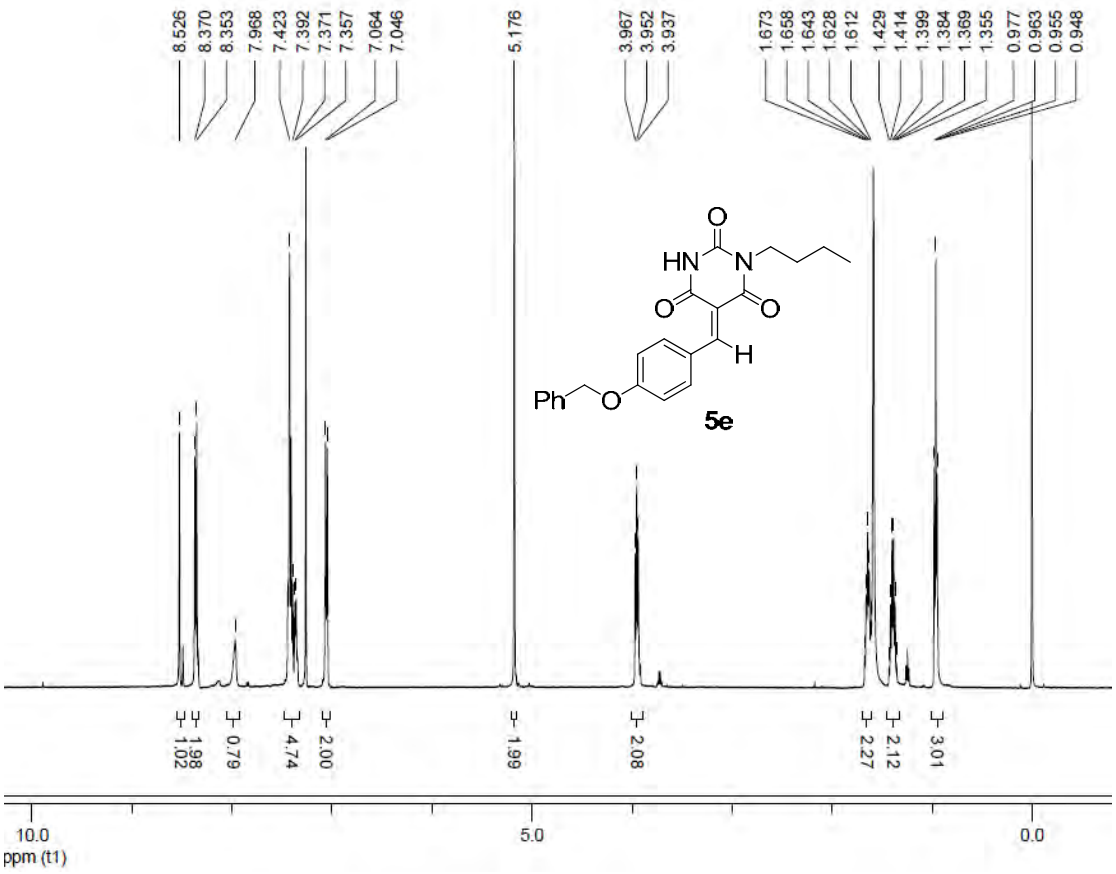

164.864
164.802
163.908
161.553
160.861
160.824
159.953
159.132
150.369
150.330
138.659
138.540
125.718
125.575
114.342
114.297
114.140
114.066
55.860
41.896
41.334
30.311
20.364
20.312
13.969
13.947
HN
N
O
O
O
H
O
5b
200
150
100
50
0
ppm (t1)


8.567
7.936
7.616
7.601
7.399
7.383
7.368
7.124
7.122
7.107
3.978
3.963
3.948
3.871
1.681
1.651
1.621
1.420
1.405
1.390
1.375
1.361
0.982
0.968
0.953
HN
N
O
O
O
H
O
5c
1.03
0.87
1.01
1.01
0.96
3.00
2.06
2.47
10.0
5.0
0.0
ppm (t1)


163.353
162.844
160.858
160.663
160.328
159.483
159.384
150.458
150.389
133.781
129.458
128.066
127.178
120.848
120.026
118.242
117.924
117.559
117.415
55.701
55.682
42.005
41.371
30.269
20.330
20.312
13.969
HN
N
O
O
O
H
O
5c
200
150
100
50
0
ppm (t1)


8.902
8.158
8.143
8.075
8.059
7.526
7.511
7.495
7.039
7.024
7.009
6.950
6.933
3.908
3.890
3.875
1.634
1.619
1.603
1.588
1.396
1.381
1.366
1.351
1.336
0.946
0.932
0.917
HN
N
O
O
O
O
H
O
5d
0.85
0.89
0.89
1.00
1.82
2.80
5.09
1.93
2.00
2.89
10.0
5.0
0.0
ppm (t1)


162.342
160.929
160.042
155.461
150.287
135.159
133.039
122.104
120.051
117.159
110.740
56.021
56.012
45.000
41.355
30.293
20.348
13.976
HN
N
O
O
O
O
H
O
5d
200
150
100
50
0
ppm (t1)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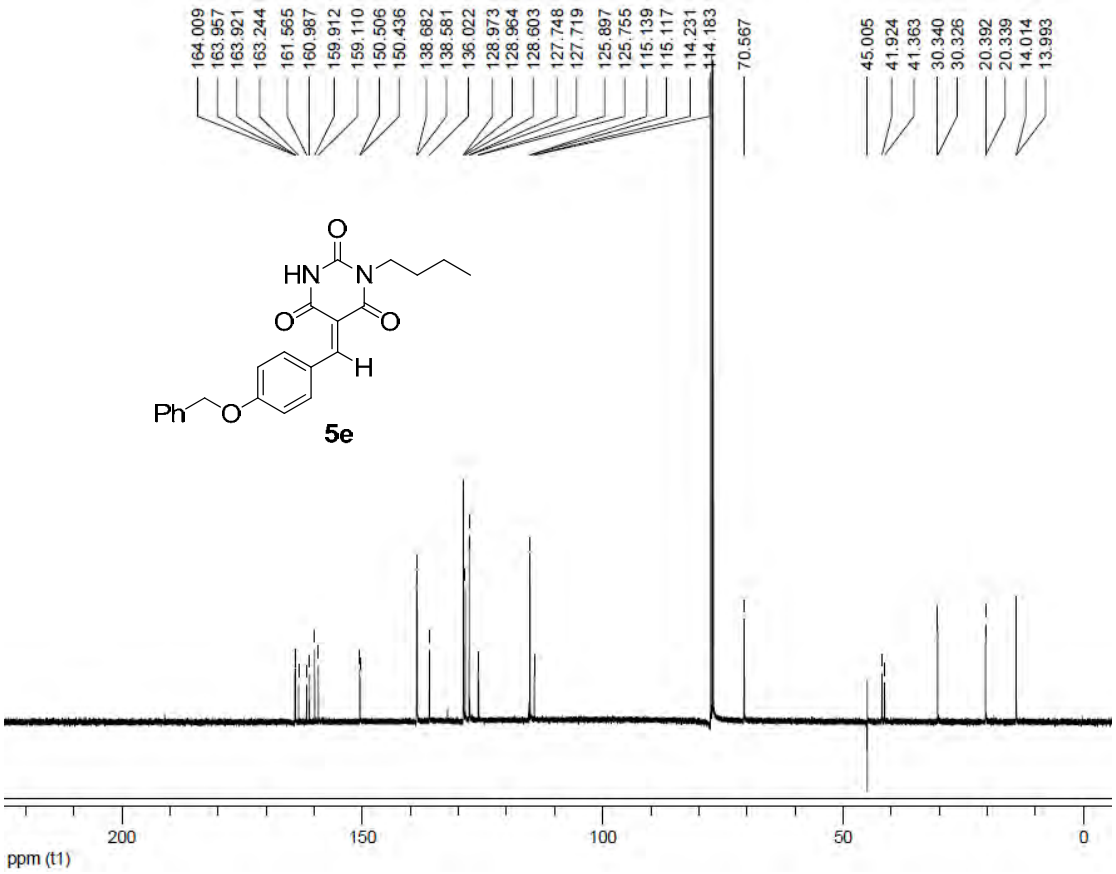
8.353
7.968
7.423
7.392
7.371
7.357
7.064
7.046
5.176
3.967
3.952
3.937
1.673
1.658
1.643
1.628
1.612
1.429
1.414
1.399
1.384
1.369
1.355
0.977
0.963
0.955
0.948
1.02
1.98
0.79
4.74
2.00
1.99
2.08
2.27
2.12
3.01
10.0
5.0
0.0
ppm (t1)
HN
N
O
O
O
H
Ph
O
5e


164.009
163.957
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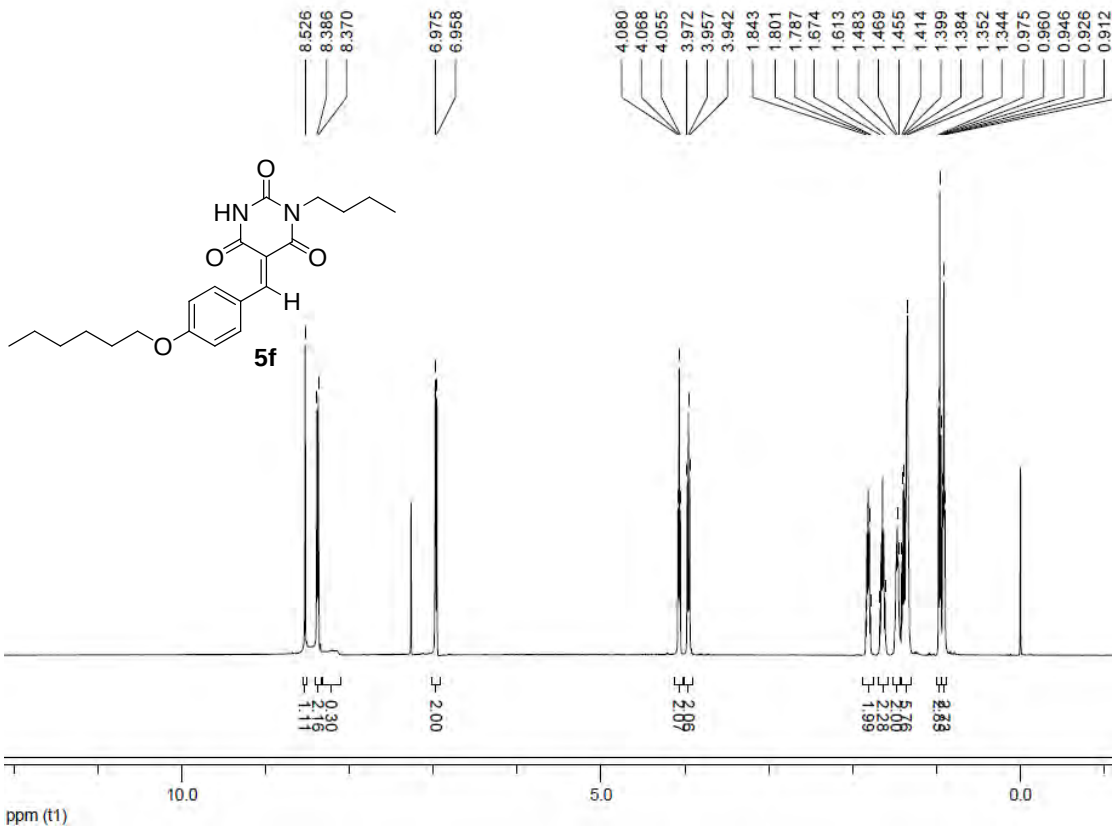
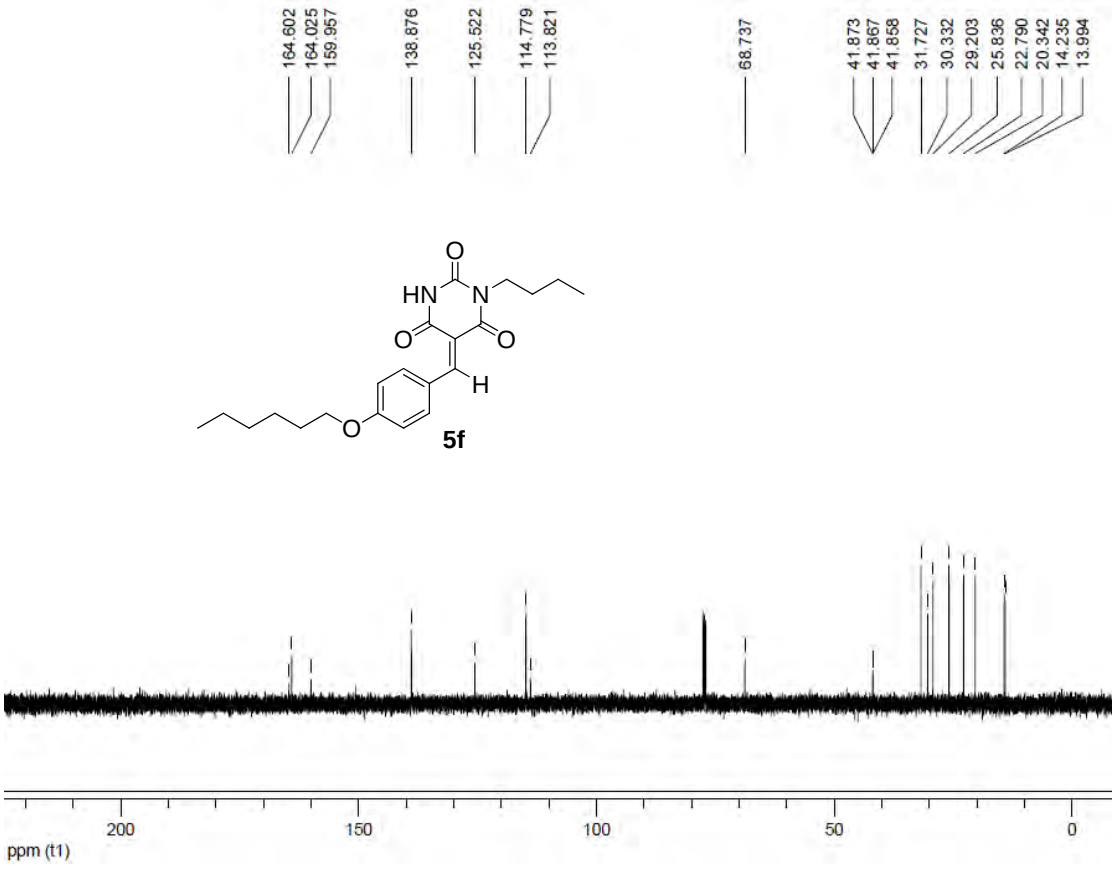
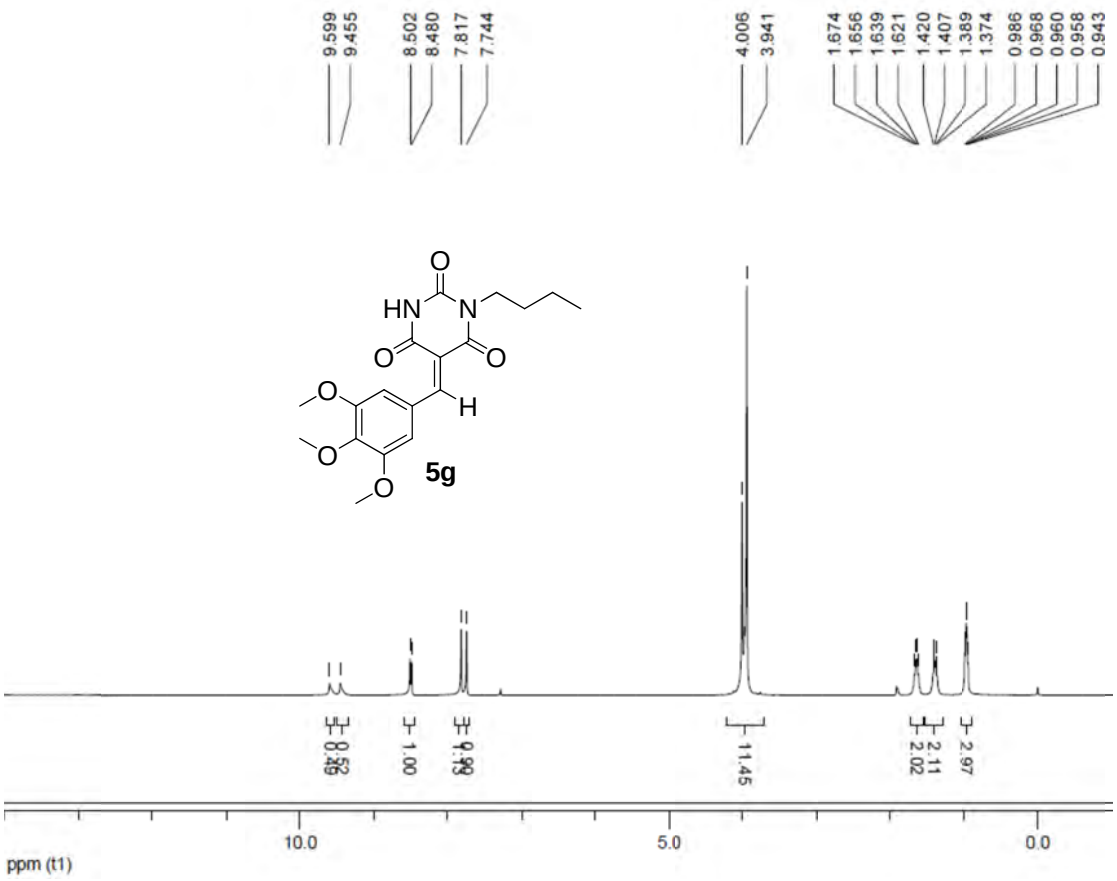
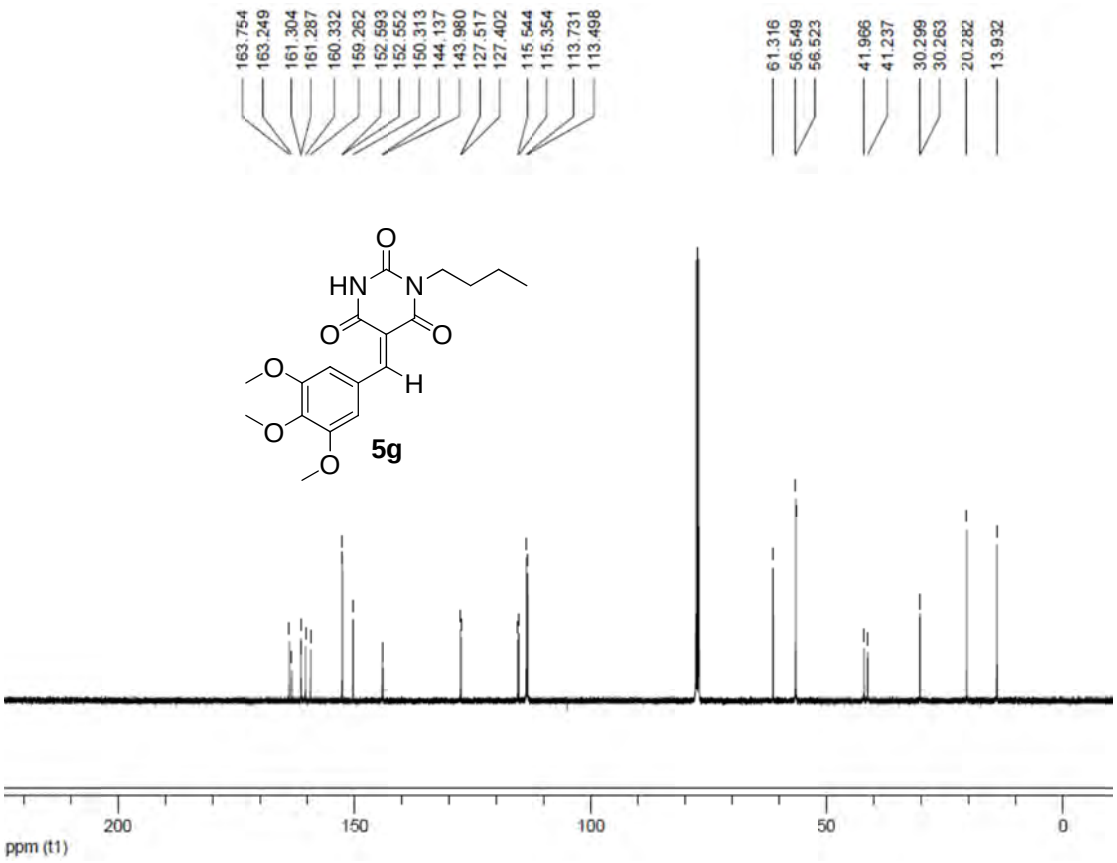
163.244
161.565
160.987
159.912
159.110
150.506
150.436
138.682
138.581
136.022
128.973
128.964
128.603
127.748
127.719
125.897
125.755
115.139
115.117
114.231
114.183
70.567
45.005
41.924
41.363
30.340
30.326
20.392
20.339
14.014
13.993
200
150
100
50
0
ppm (t1)
HN
N
O
O
O
H
Ph
O
5e


8.526
8.386
8.370
6.975
6.958
4.080
4.068
4.055
3.972
3.957
3.942
1.843
1.801
1.787
1.674
1.613
1.483
1.469
1.455
1.414
1.399
1.384
1.352
1.344
0.975
0.960
0.946
0.926
0.912
HN
N
O
O
O
H
O
5f
2.11
2.30
2.00
2.06
1.99
2.08
2.76
3.03
10.0
5.0
0.0
ppm (t1)


164.602
164.025
159.957
138.876
125.522
114.779
113.821
68.737
41.873
41.867
41.858
31.727
30.332
29.203
25.836
22.790
20.342
14.235
13.994
HN
N
O
O
O
H
O
5f
200
150
100
50
0
ppm (t1)


9.599
9.455
8.502
8.480
7.817
7.744
4.006
3.941
1.674
1.656
1.639
1.621
1.420
1.407
1.389
1.374
0.986
0.968
0.960
0.958
0.943
5g
1.00
1.45
2.02
1.12
2.97
10.0
5.0
0.0
ppm (t1)


163.754
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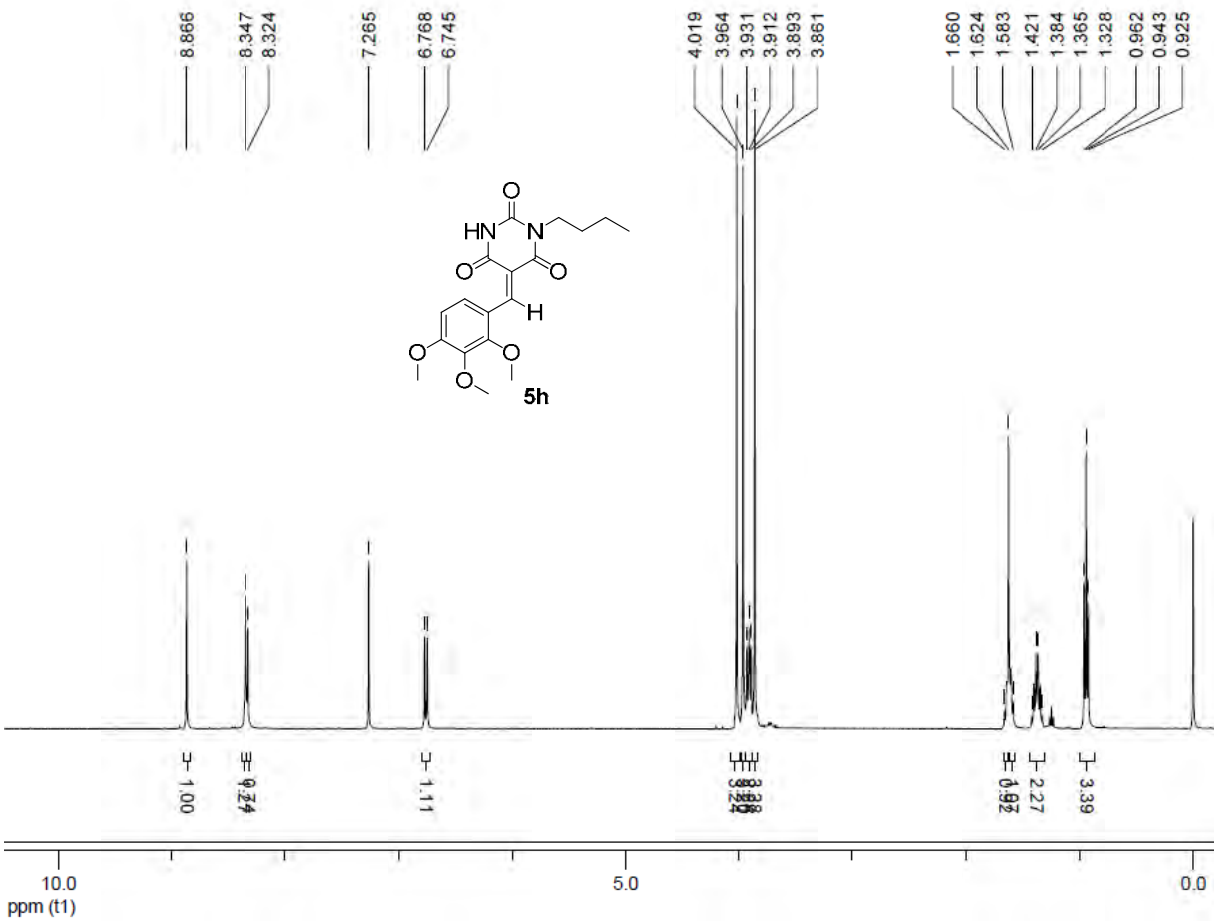
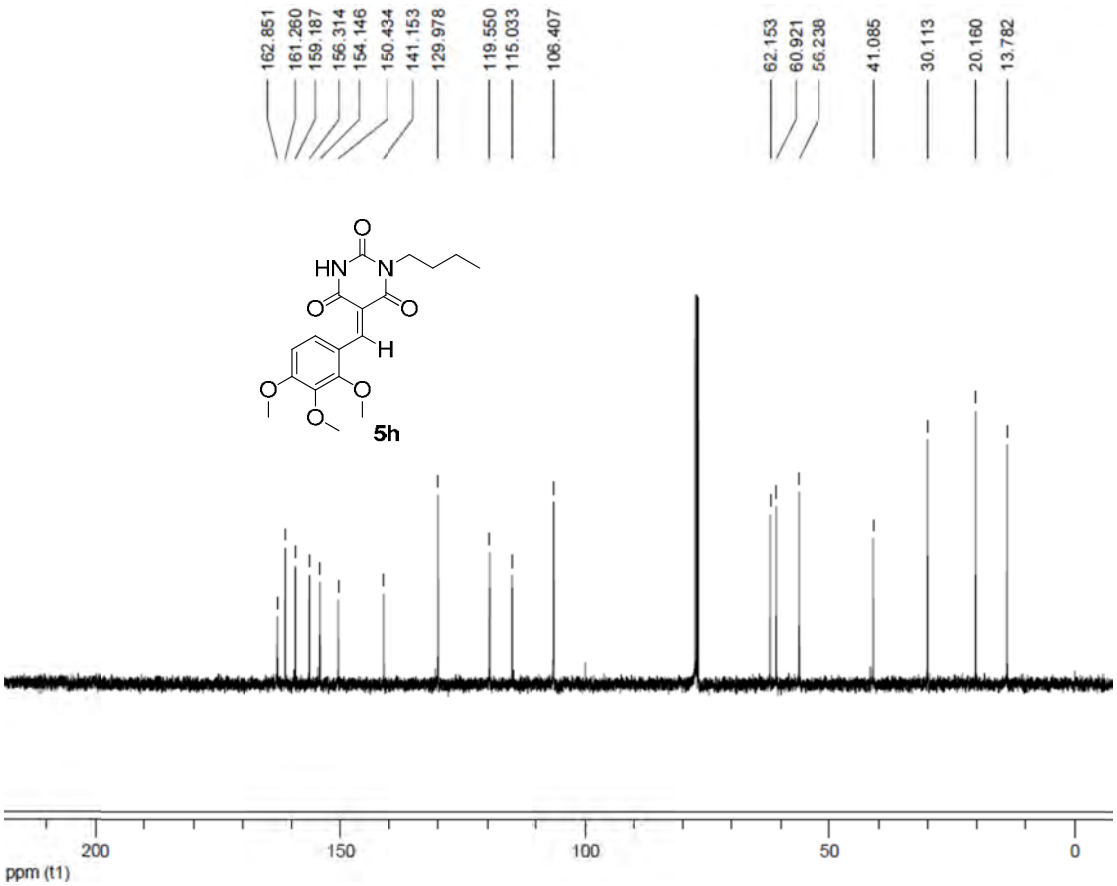
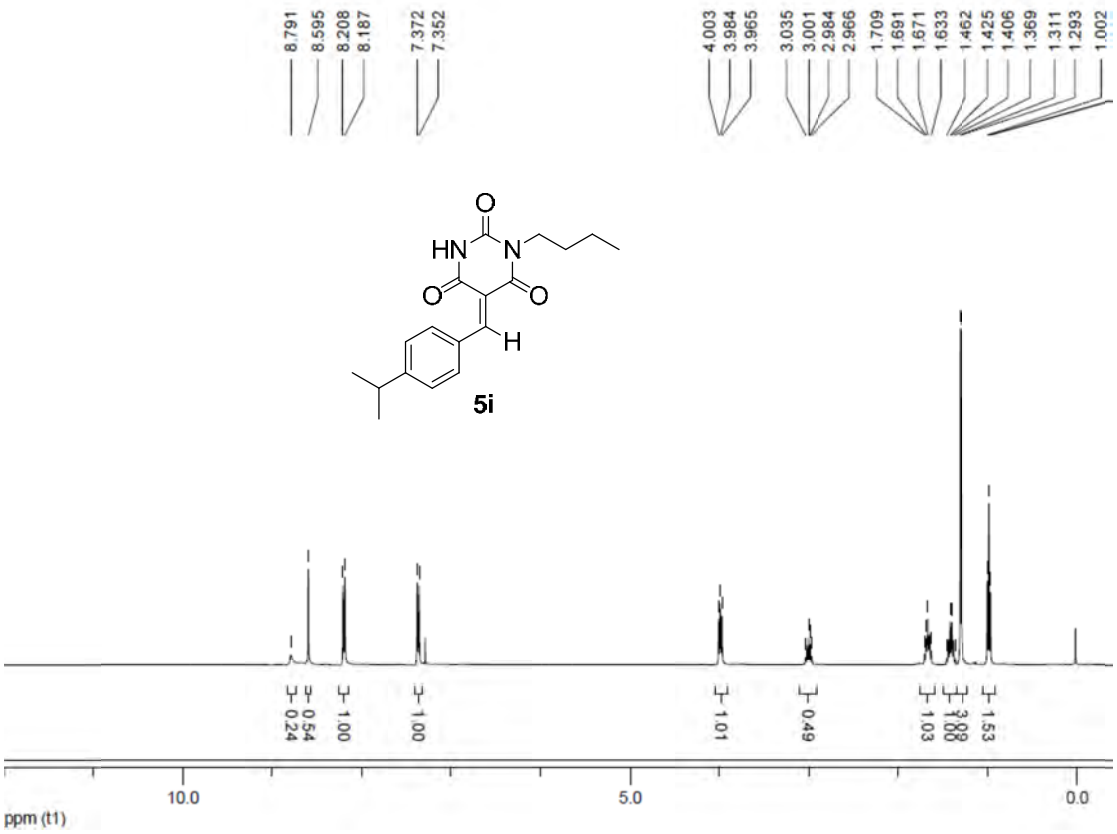
159.262
152.593
152.552
150.313
144.137
143.980
127.517
127.402
115.544
115.354
113.731
113.498
61.316
56.549
56.523
41.966
41.237
30.299
30.263
20.282
13.932
5g
200
150
100
50
0
ppm (t1)


8.866
8.347
8.324
7.265
6.768
6.745
4.019
3.964
3.931
3.912
3.893
3.861
1.660
1.624
1.583
1.421
1.384
1.365
1.328
0.962
0.943
0.925
HN
N
O
H
5h
1.00
0.24
1.11
9.39
6.92
2.27
3.39
10.0
5.0
0.0
ppm (t1)


162.851
161.260
159.187
156.314
154.146
150.434
141.153
129.978
119.550
115.033
106.407
62.153
60.921
56.238
41.085
30.113
20.160
13.782
HN
N
O
H
5h
200
150
100
50
0
ppm (t1)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3.984
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3.035
3.001
2.984
2.966
1.709
1.691
1.671
1.633
1.462
1.425
1.406
1.369
1.311
1.293
1.002
HN
N
O
O
O
H
5i
0.24
0.54
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1.00
1.01
0.49
1.03
3.00
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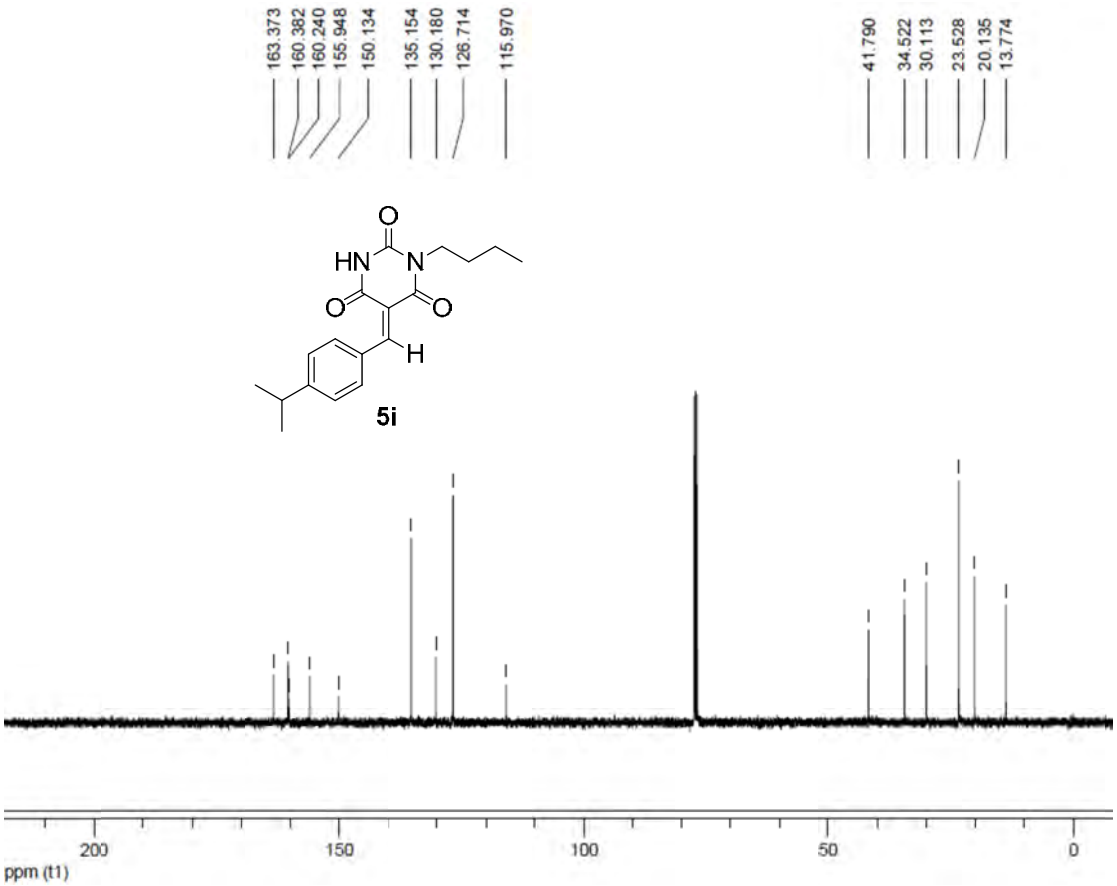
5.0
0.0
ppm (t1)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160.240
155.948
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135.154
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126.714
115.970
41.790
34.522
30.113
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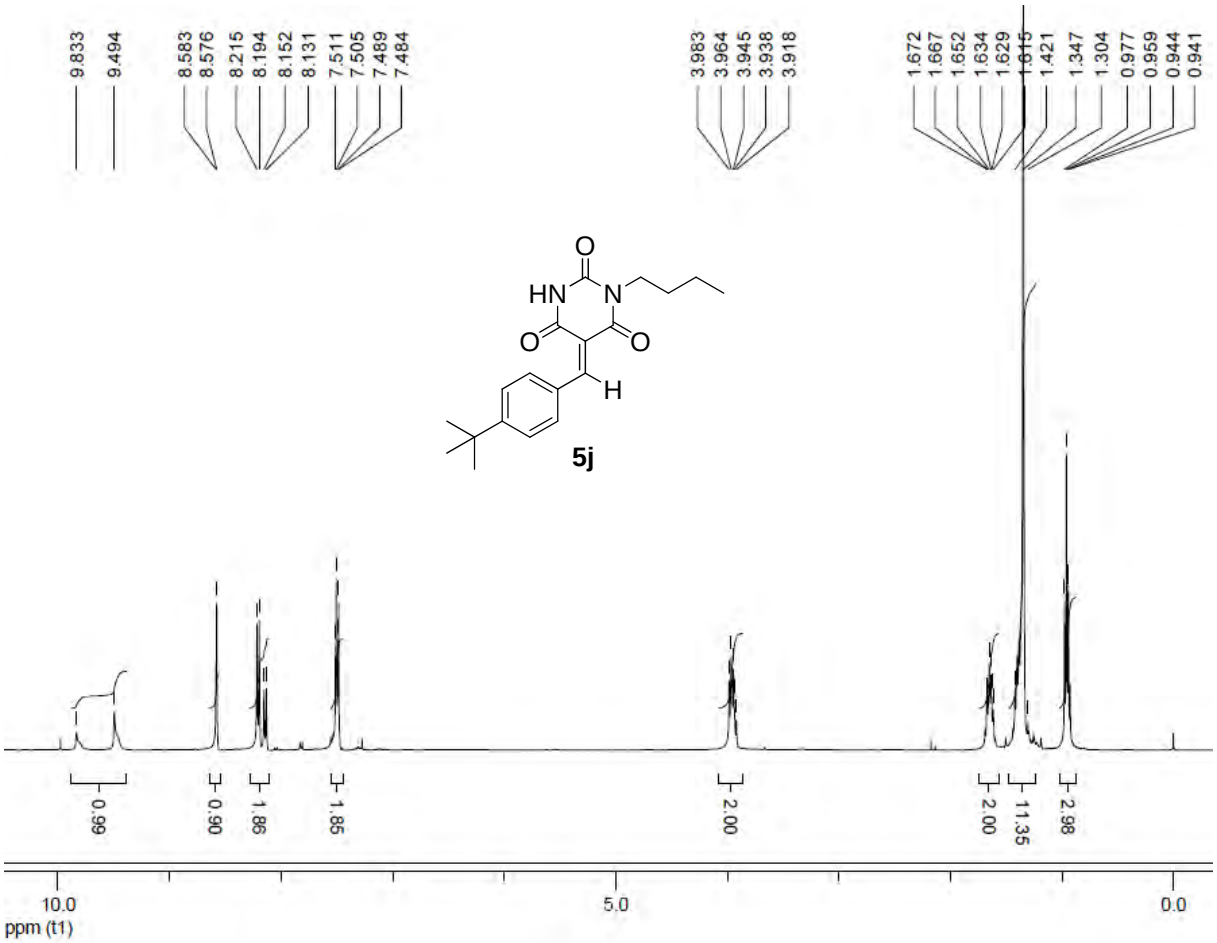
20.135
13.774
HN
N
O
O
O
H
5i
200
150
100
50
0
ppm (t1)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8.576
8.215
8.194
8.152
8.131
7.511
7.505
7.489
7.484
3.983
3.964
3.945
3.938
3.918
1.672
1.667
1.652
1.634
1.629
1.615
1.421
1.347
1.304
0.977
0.959
0.944
0.941
HN
N
O
O
O
H
5j
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1.86
2.00
2.00
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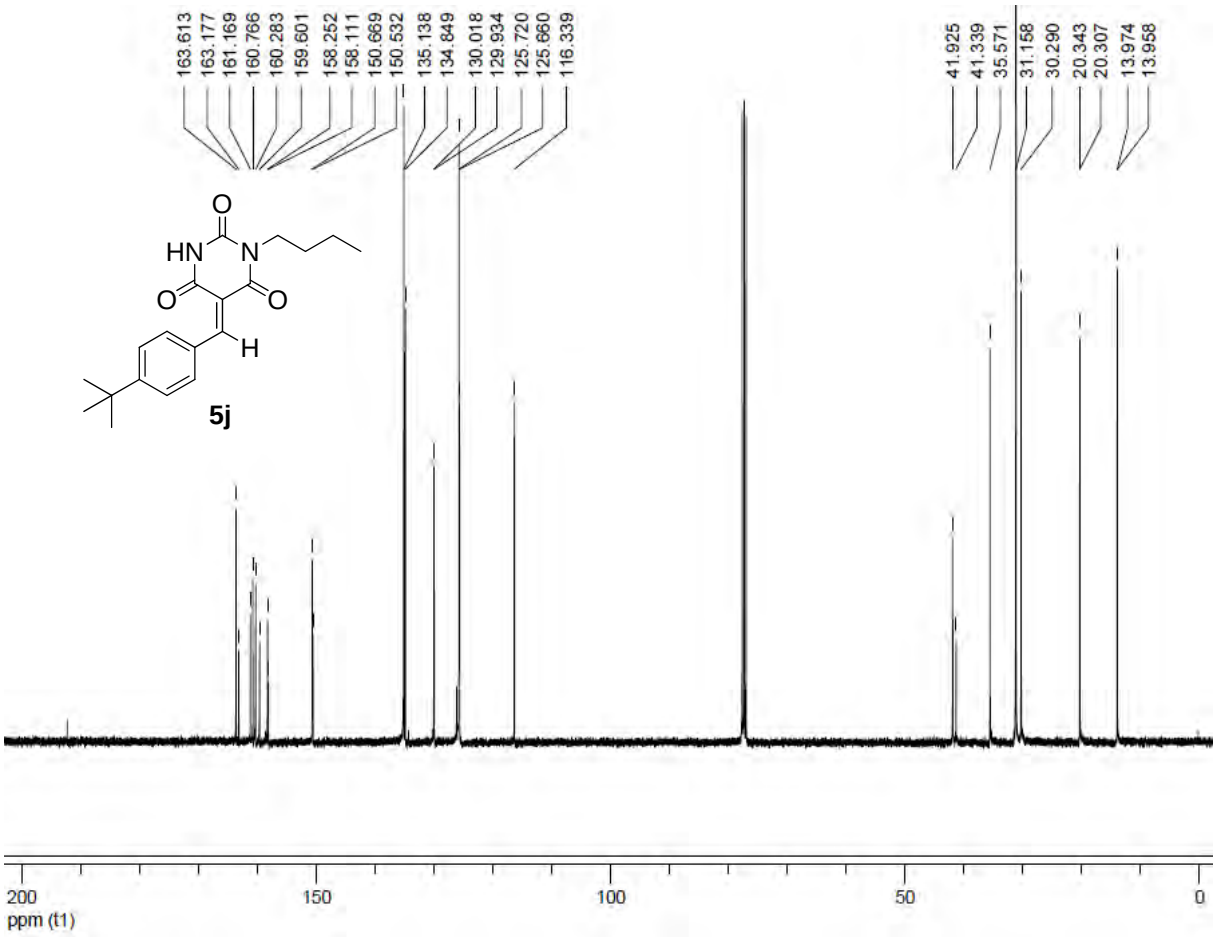
ppm (t1)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158.111
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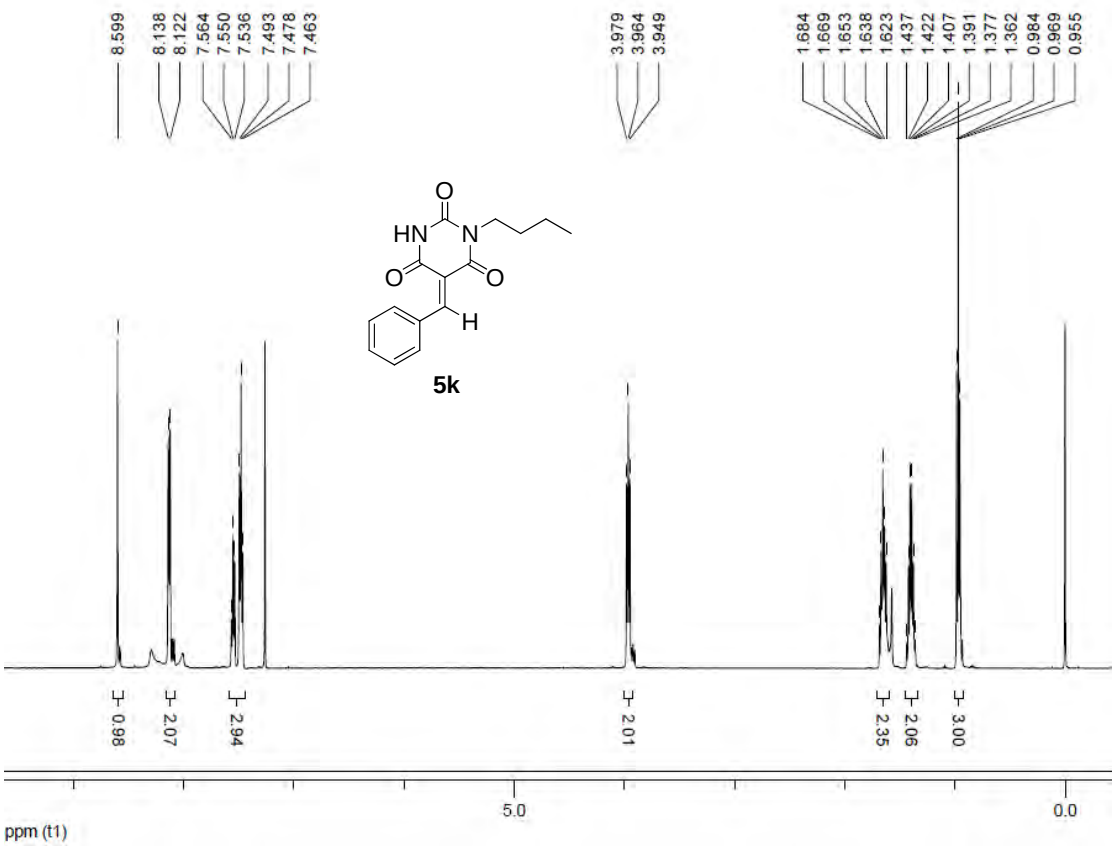
150.532
135.138
134.849
130.018
129.934
125.720
125.660
116.339
41.925
41.339
35.571
31.158
30.290
20.343
20.307
13.974
13.958
HN
N
O
O
O
H
5j
200
150
100
50
0
ppm (t1)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8.138
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7.550
7.536
7.493
7.478
7.463
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3.964
3.949
1.684
1.669
1.653
1.638
1.623
1.437
1.422
1.407
1.391
1.377
1.362
0.984
0.969
0.955
HN
N
O
O
O
H
5k
0.98
2.07
2.94
2.01
2.35
2.06
3.00
5.0
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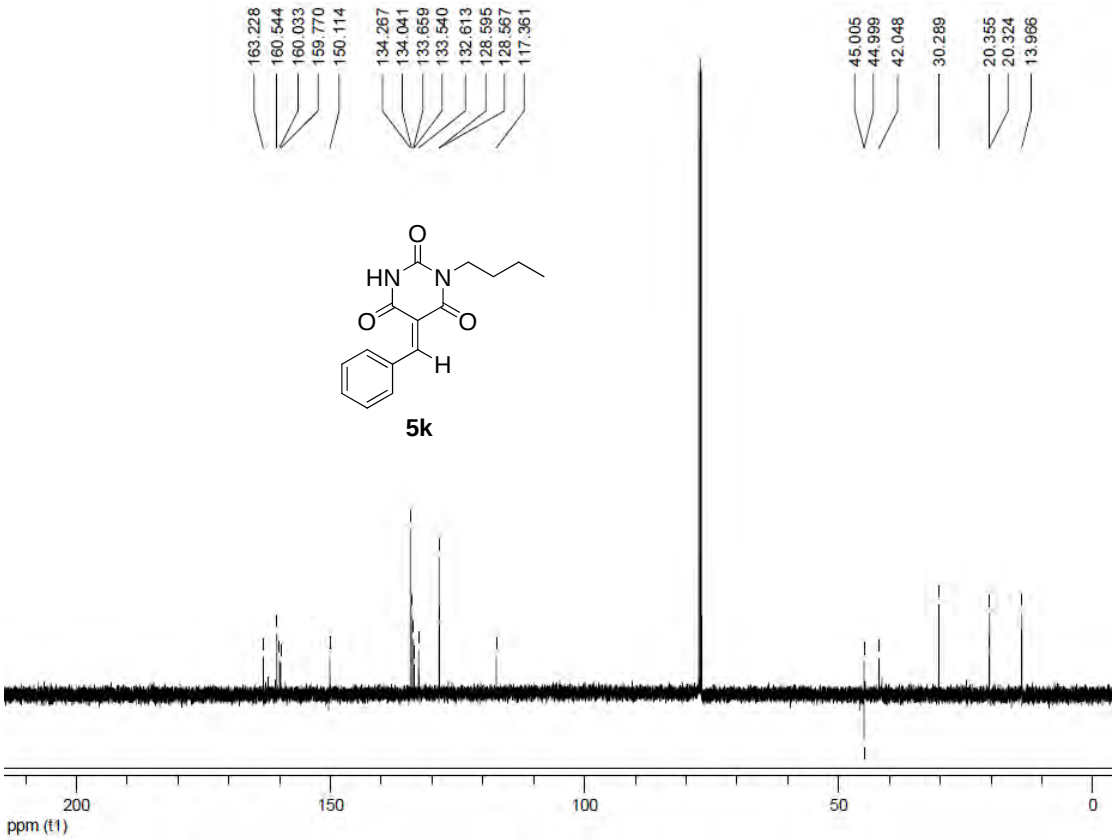
ppm (t1)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128.595
128.567
117.361
45.005
44.999
42.048
30.289
20.355
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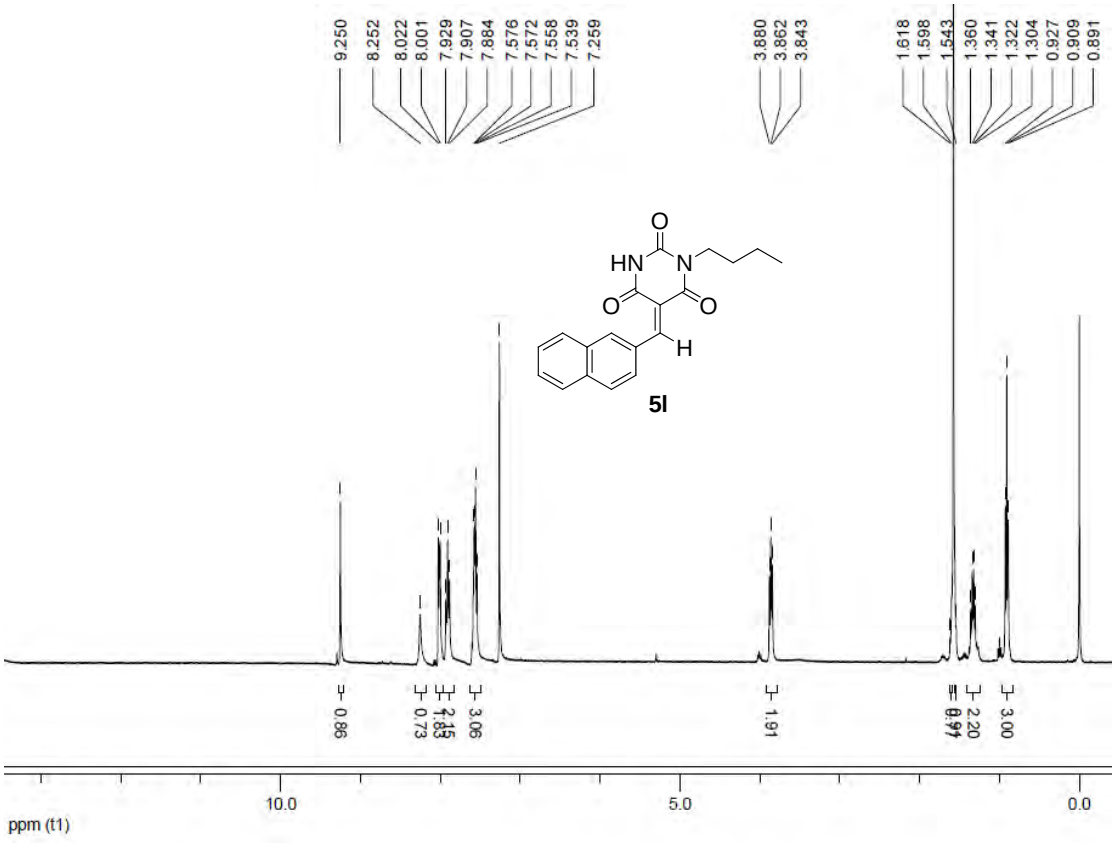
13.966
HN
N
O
O
O
H
5k
200
150
100
50
0
ppm (t1)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7.576
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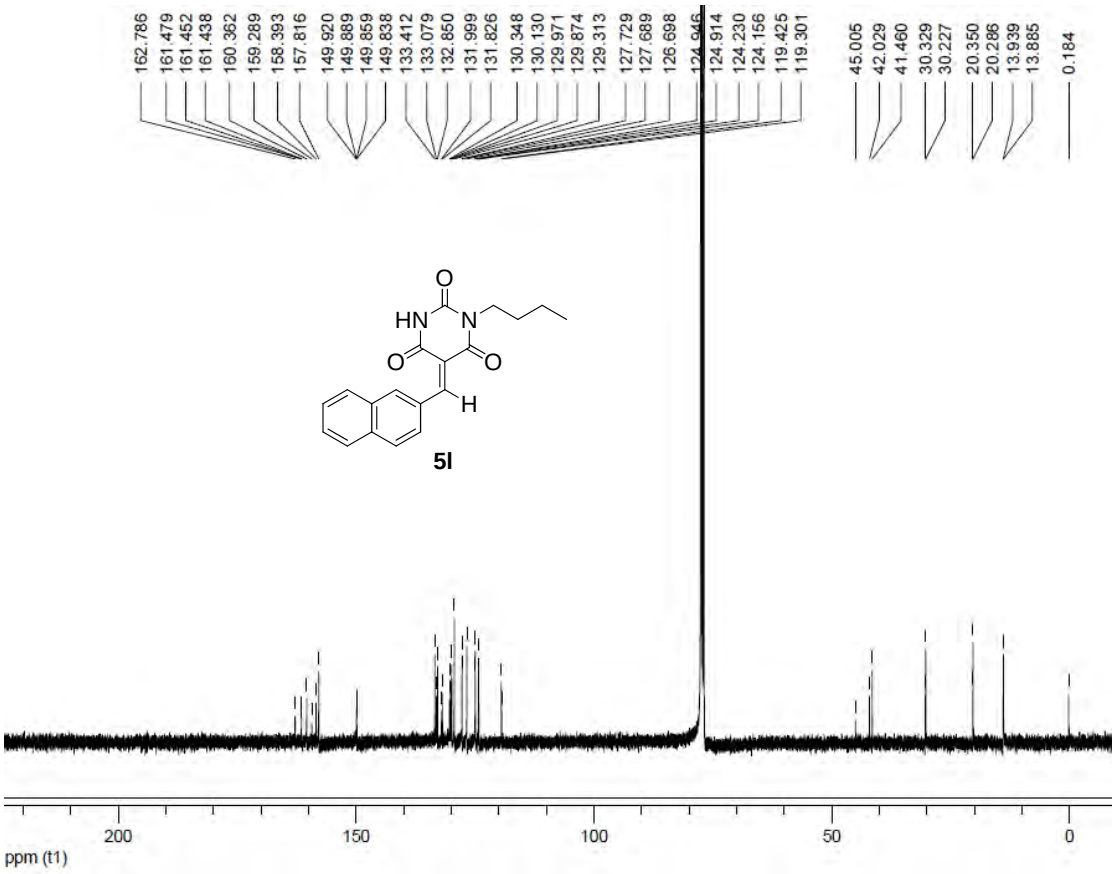
7.558
7.539
7.259
3.880
3.862
3.843
1.618
1.598
1.543
1.360
1.341
1.322
1.304
0.927
0.909
0.891
HN
N
O
O
O
H
5l
0.86
0.73
1.83
2.13
3.06
1.91
8.97
2.20
3.00
10.0
5.0
0.0
ppm (t1)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133.412
133.079
132.850
131.999
131.826
130.348
130.130
129.971
129.874
129.313
127.729
127.689
126.698
124.946
124.914
124.230
124.156
119.425
119.301
45.005
42.029
41.460
30.329
30.227
20.350
20.286
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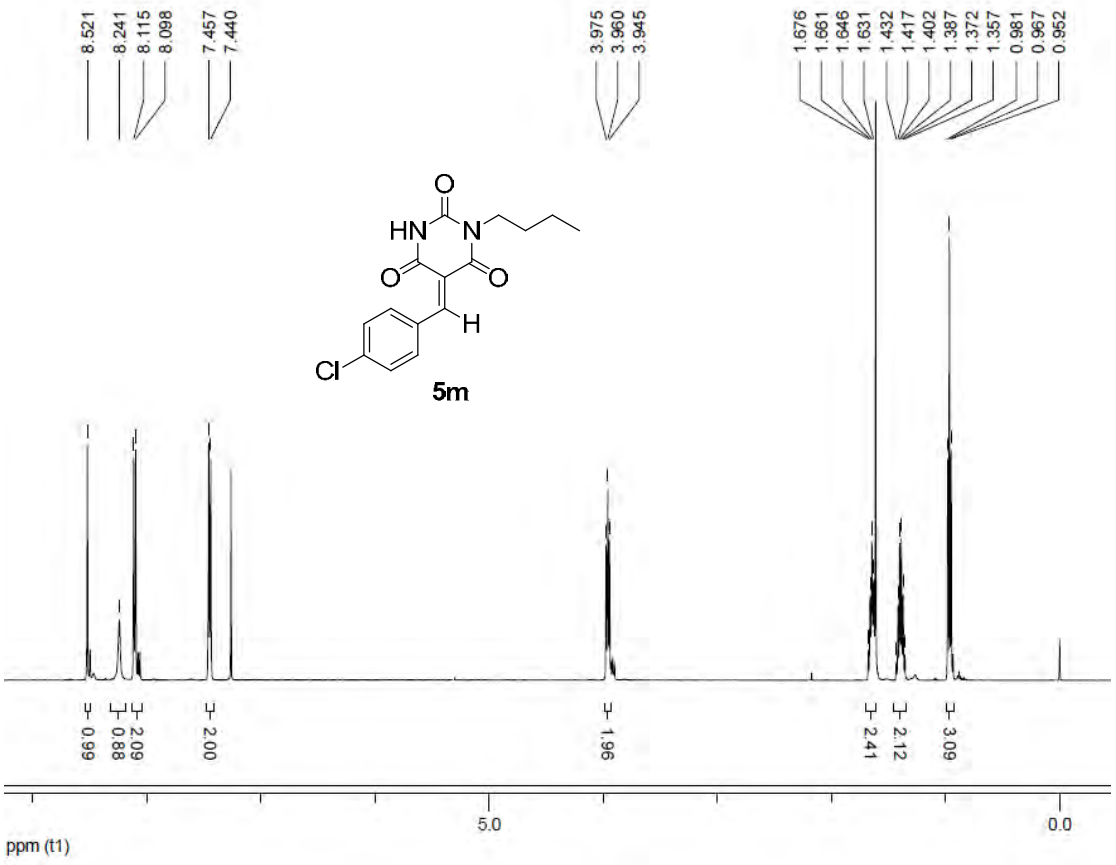
0.184
HN
N
O
O
O
H
5l
200
150
100
50
0
ppm (t1)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8.115
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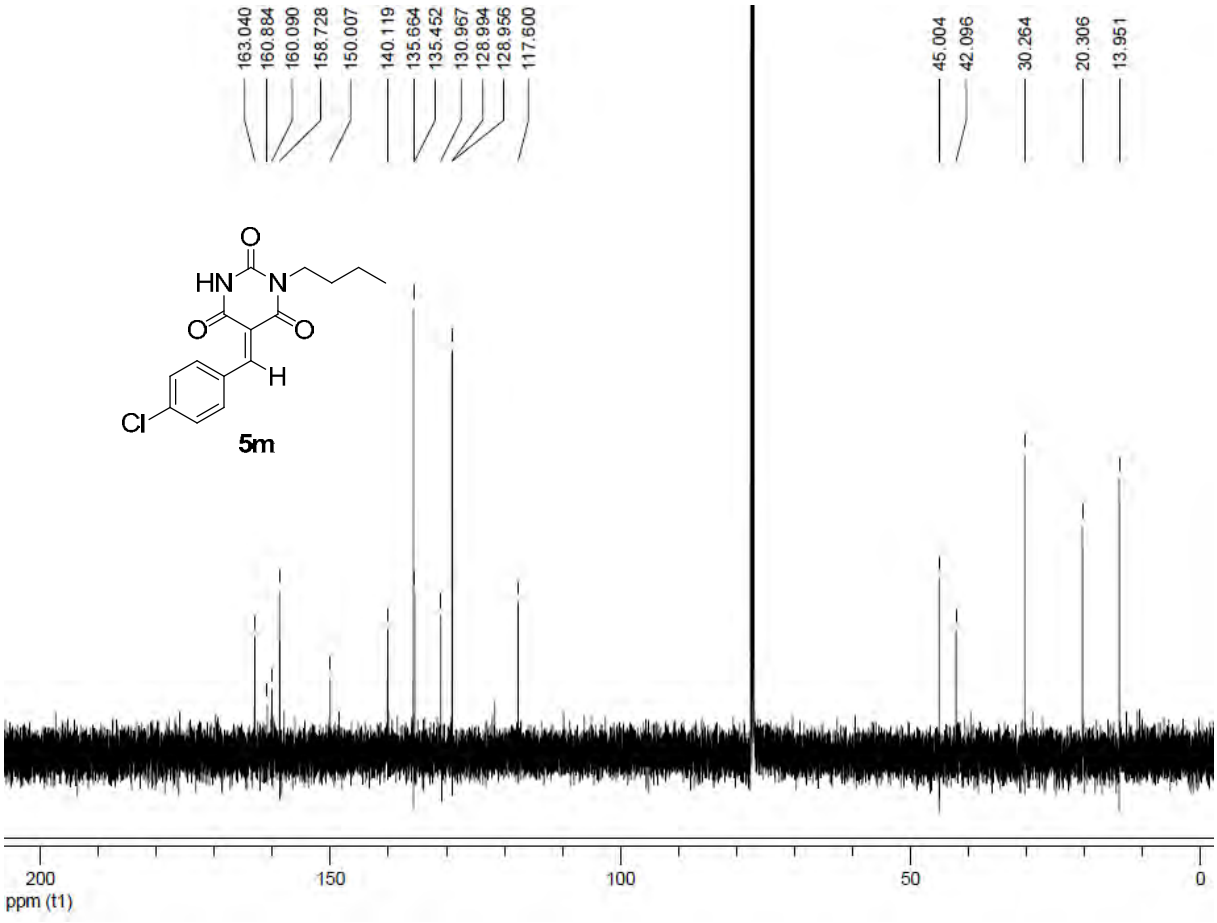
7.457
7.440
3.975
3.960
3.945
1.676
1.661
1.646
1.631
1.432
1.417
1.402
1.387
1.372
1.357
0.981
0.967
0.952
HN
N
O
O
O
H
Cl
5m
0.99
0.88
2.09
2.00
1.96
2.41
2.12
3.09
5.0
0.0
ppm (t1)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135.664
135.452
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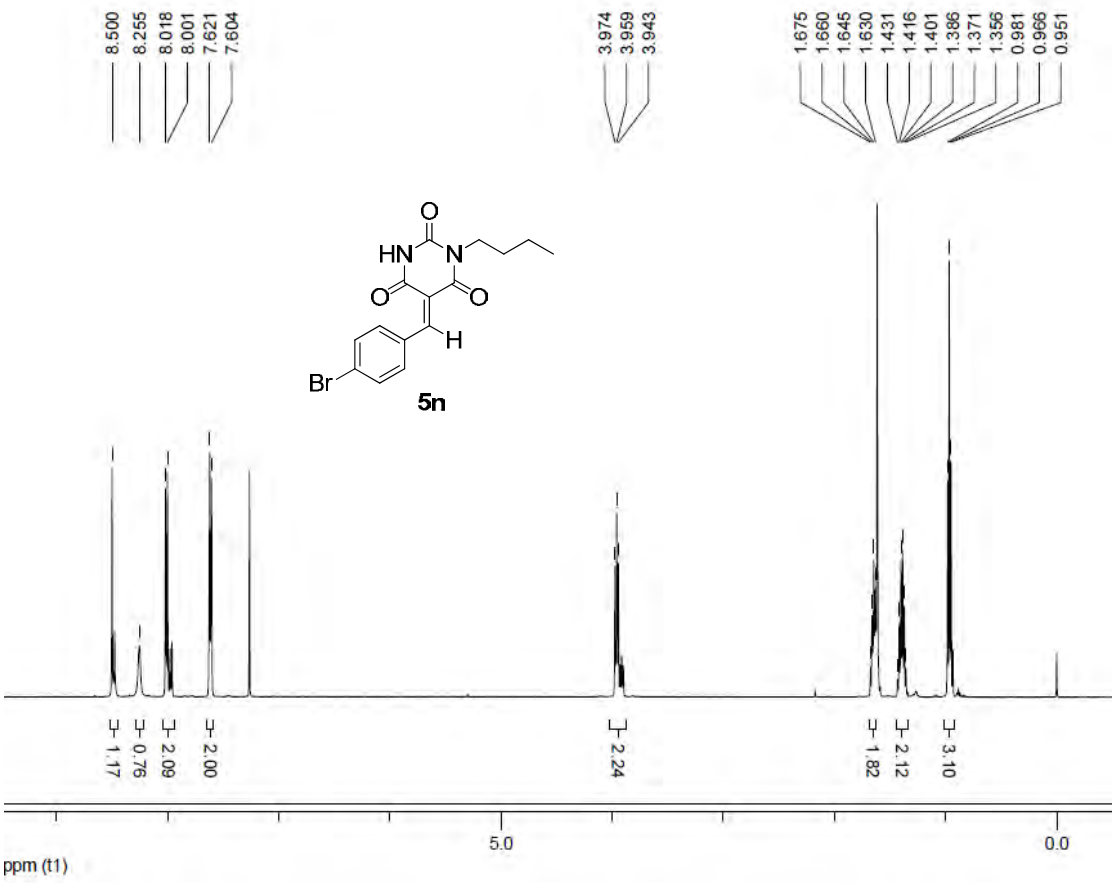
128.956
117.600
45.004
42.096
30.264
20.306
13.951
HN
N
O
O
O
H
Cl
5m
200
150
100
50
0
ppm (t1)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8.001
7.621
7.604
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3.959
3.943
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1.660
1.645
1.630
1.431
1.416
1.401
1.386
1.371
1.356
0.981
0.966
0.951
HN
N
O
O
O
H
Br
5n
1.17
0.76
2.09
2.00
2.24
1.82
2.12
3.10
5.0
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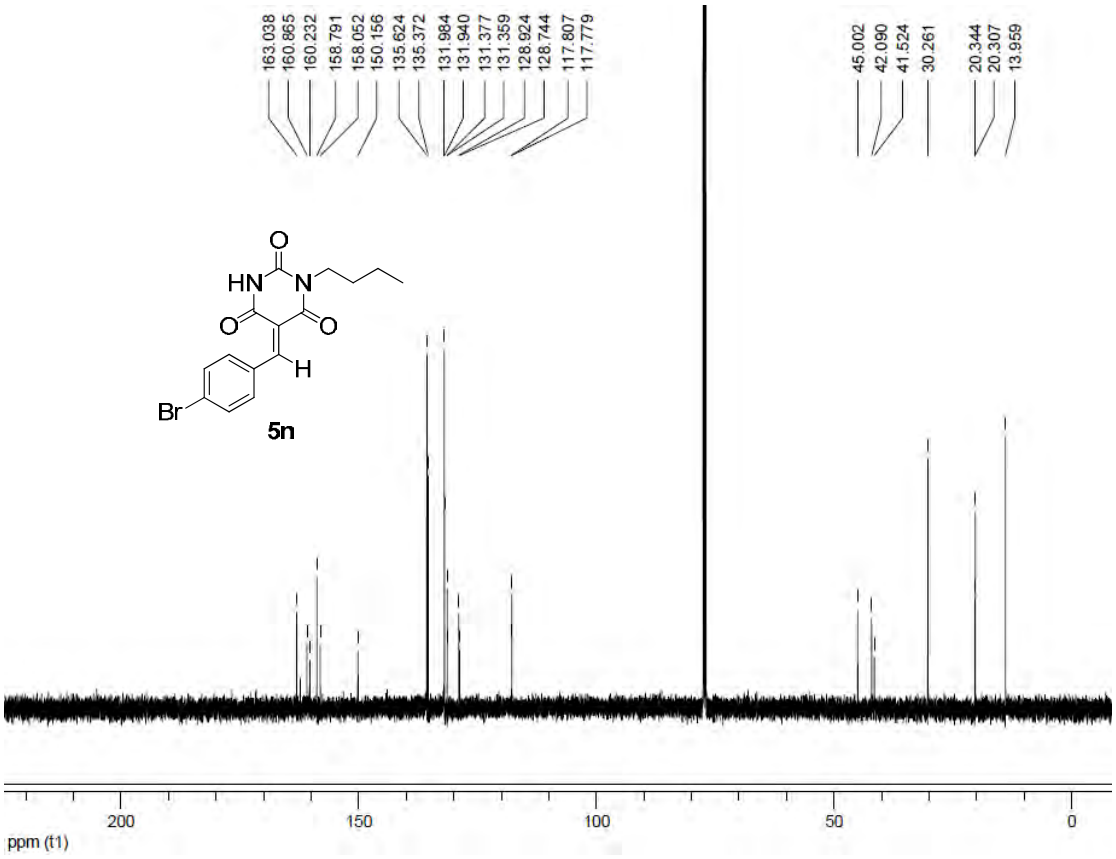
ppm (t1)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135.372
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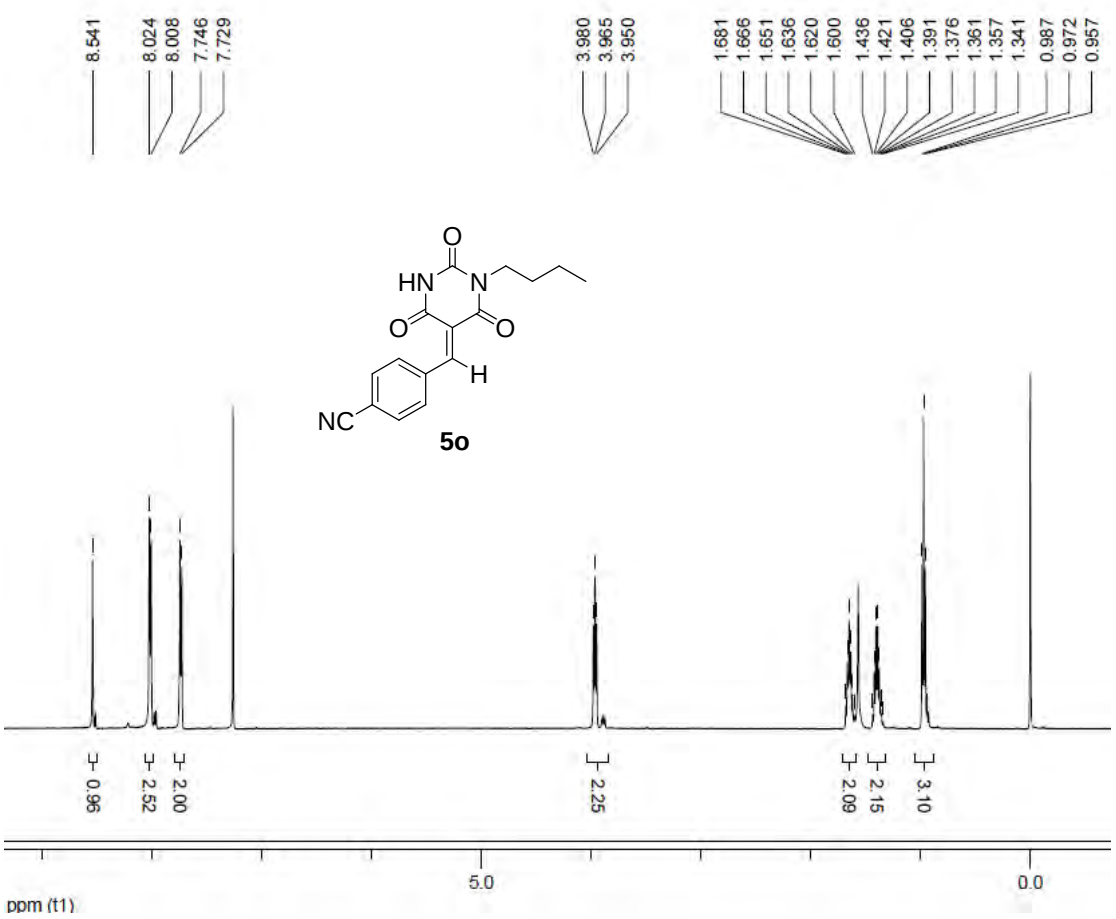
131.940
131.377
131.359
128.924
128.744
117.807
117.779
45.002
42.090
41.524
30.261
20.344
20.307
13.959
HN
N
O
O
O
H
Br
5n
200
150
100
50
0
ppm (t1)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3.950
1.681
1.666
1.651
1.636
1.620
1.600
1.436
1.421
1.406
1.391
1.376
1.361
1.357
1.341
0.987
0.972
0.957
HN
O
N
O
O
H
NC
5o
0.96
2.52
2.00
2.25
2.09
2.15
3.10
5.0
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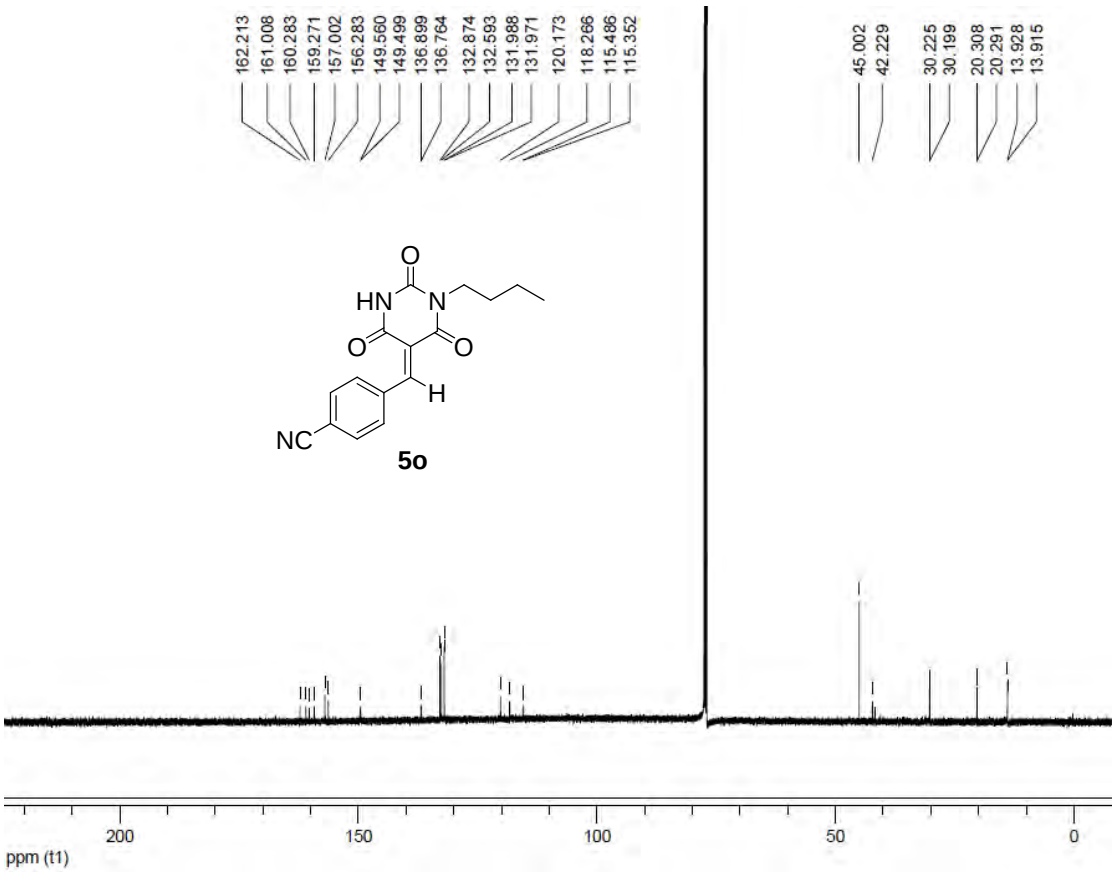
ppm (t1)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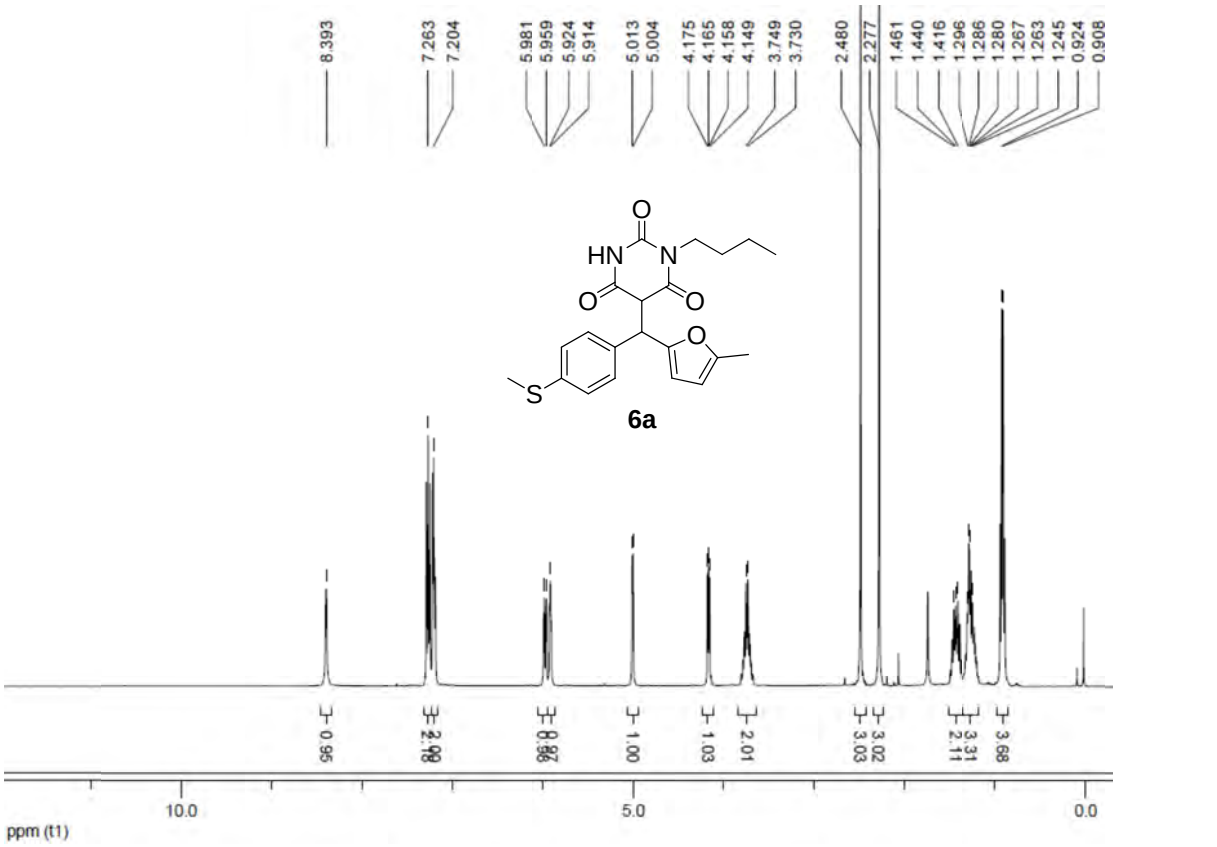
149.560
149.499
136.899
136.764
132.874
132.593
131.988
131.971
120.173
118.286
115.486
115.352
45.002
42.229
30.225
30.199
20.308
20.291
13.928
13.915
HN
O
N
O
O
H
NC
5o
200
150
100
50
0
ppm (t1)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4.158
4.149
3.749
3.730
2.480
2.277
1.461
1.440
1.416
1.296
1.286
1.280
1.267
1.263
1.245
0.924
0.908
HN
N
O
O
O
O
S
6a
0.96
2.98
0.86
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3.03
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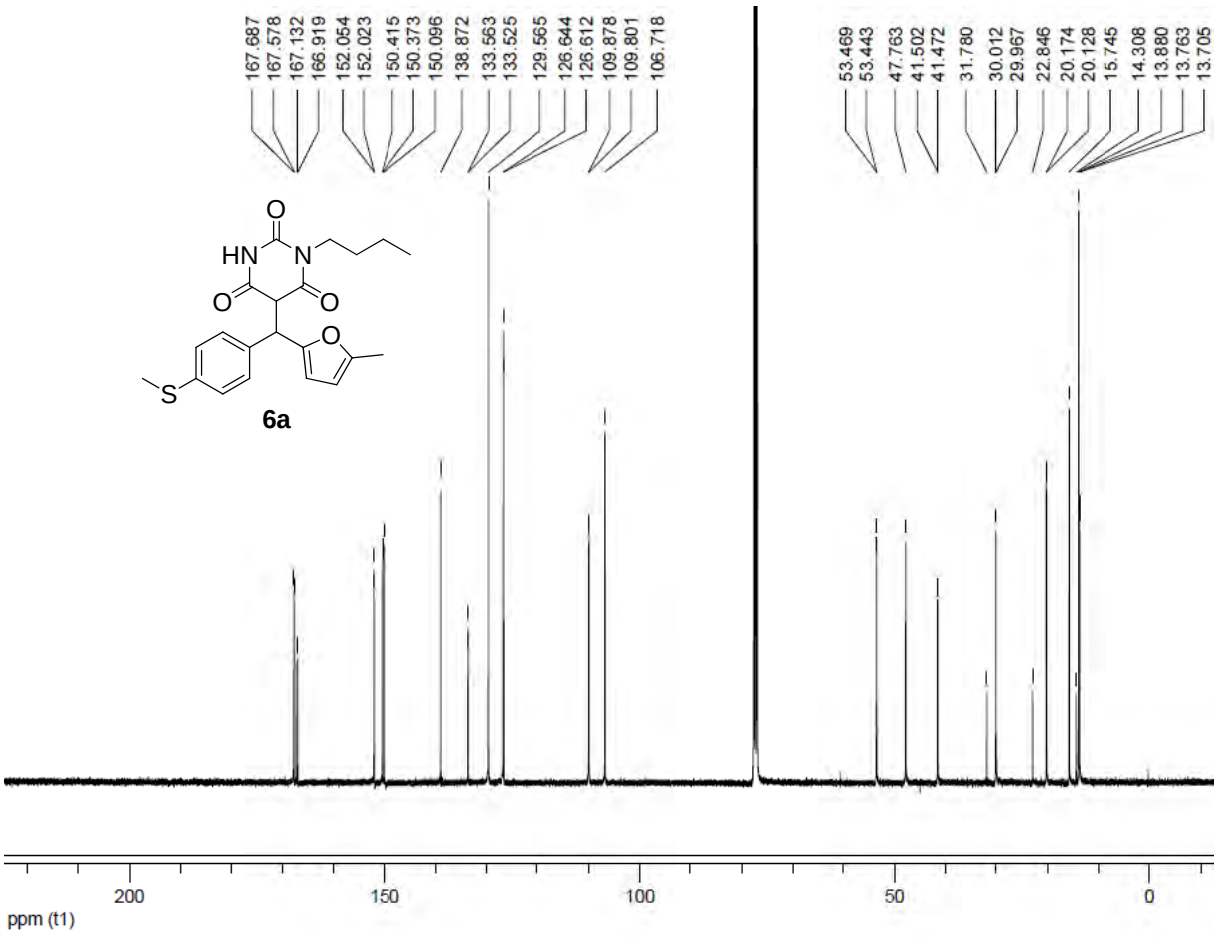
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129.565
126.644
126.612
109.878
109.801
106.718
53.469
53.443
47.763
41.502
41.472
31.780
30.012
29.967
22.846
20.174
20.128
15.745
14.308
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13.763
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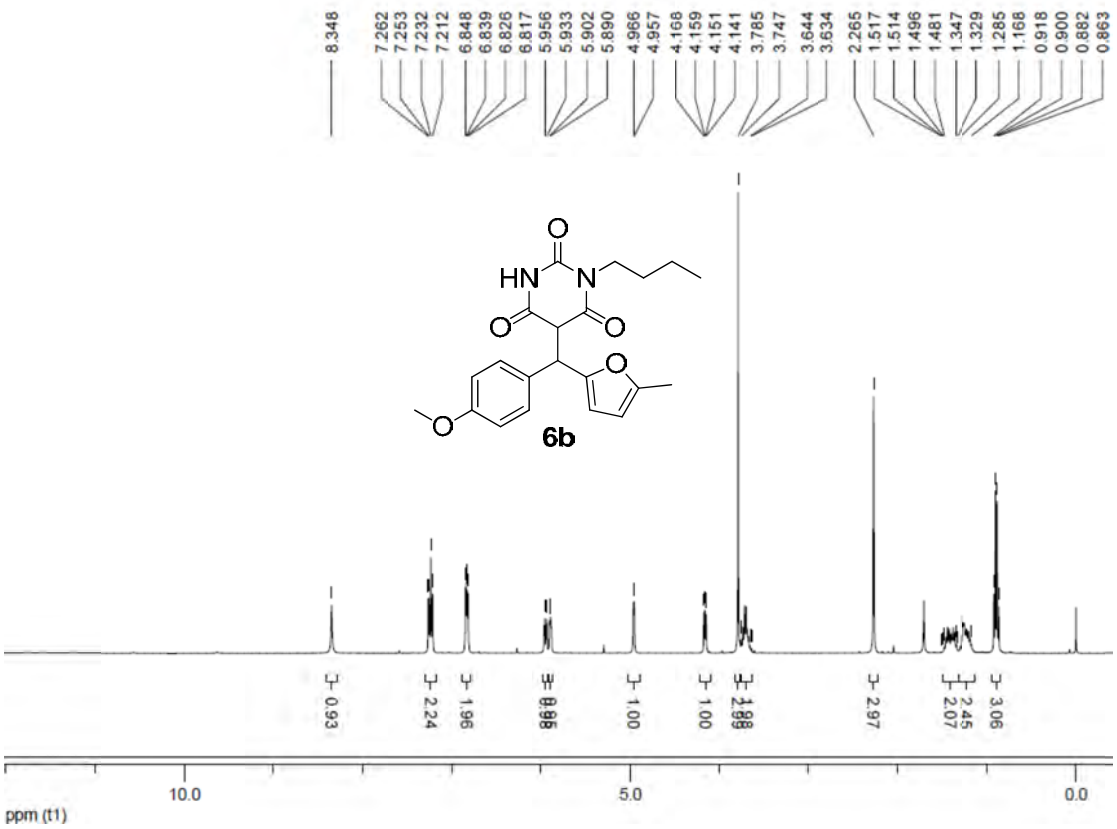
HN
N
O
O
O
O
S
6a
200
150
100
50
0
ppm (t1)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6.826
6.817
5.956
5.933
5.902
5.890
4.966
4.957
4.168
4.159
4.151
4.141
3.785
3.747
3.644
3.634
2.265
1.517
1.514
1.496
1.481
1.347
1.329
1.285
1.168
0.918
0.900
0.882
0.863
HN
N
O
O
O
O
O
6b
0.93
2.24
1.96
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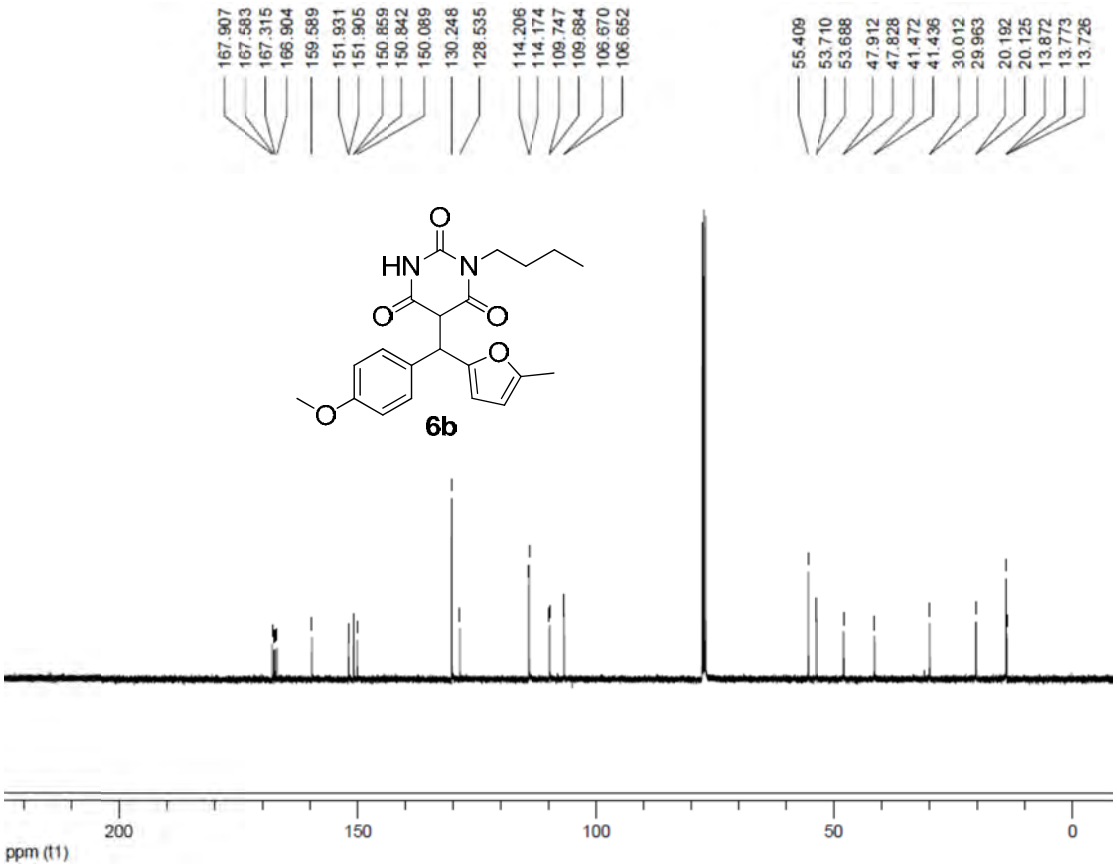
ppm (t1)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114.206
114.174
109.747
109.684
106.670
106.652
55.409
53.710
53.688
47.912
47.828
41.472
41.436
30.012
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20.192
20.125
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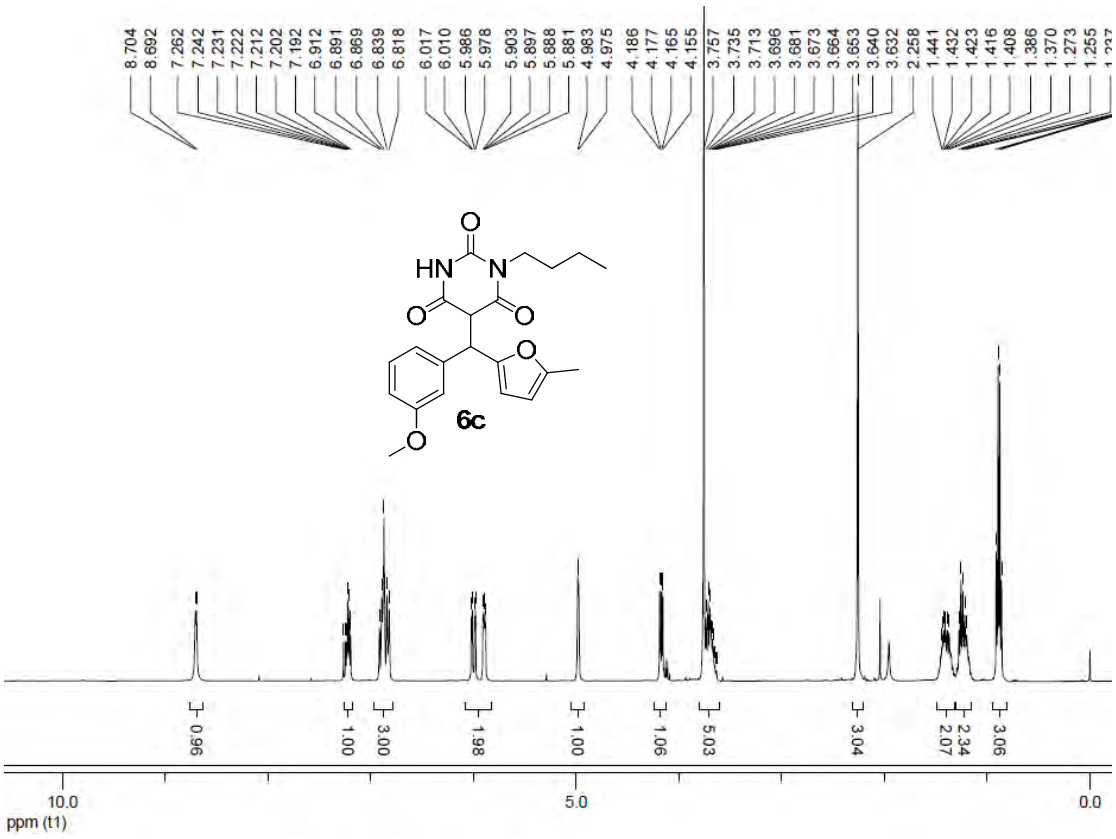
HN
N
O
O
O
O
O
6b
200
150
100
50
0
ppm (t1)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6.017
6.010
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5.903
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4.177
4.165
4.155
3.757
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3.696
3.681
3.673
3.664
3.653
3.640
3.632
2.258
1.441
1.432
1.423
1.416
1.408
1.386
1.370
1.273
1.255
HN
N
O
O
O
O
O
6c
0.96
1.00
3.00
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5.03
3.04
2.07
2.34
3.06
10.0
5.0
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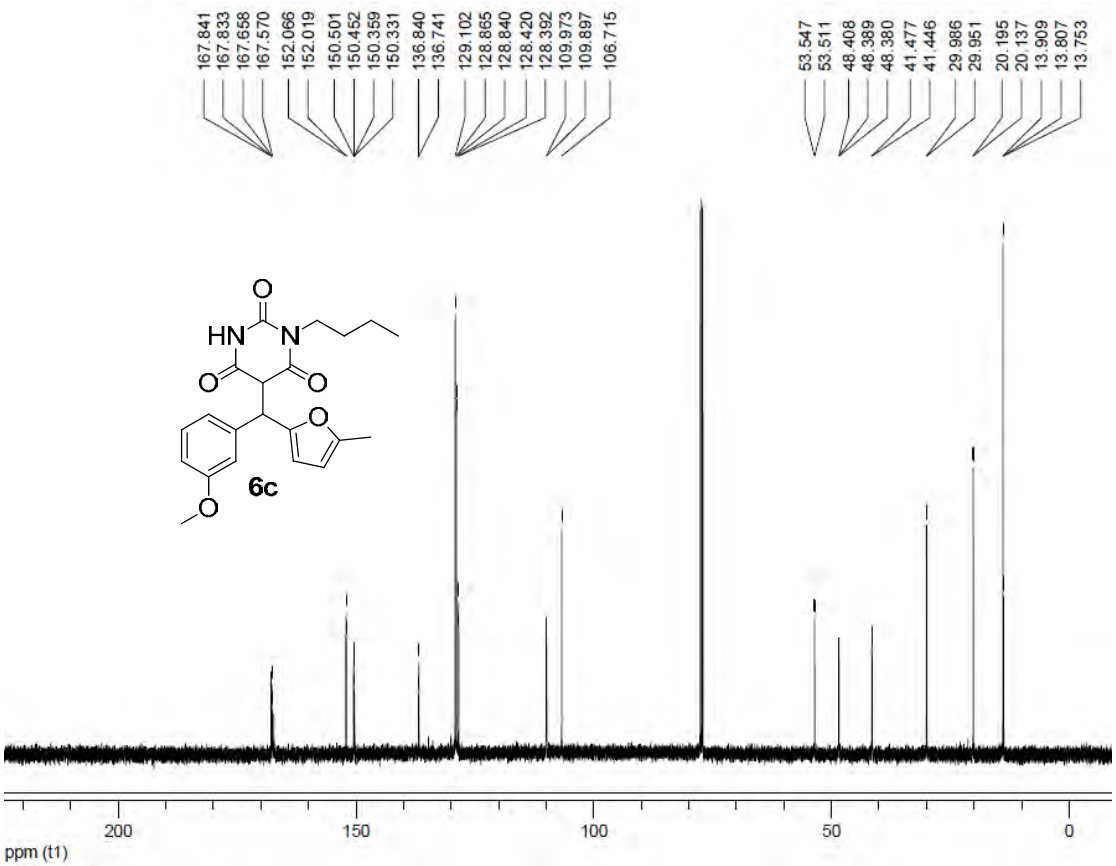
ppm (t1)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48.380
41.477
41.446
29.986
29.951
20.195
20.137
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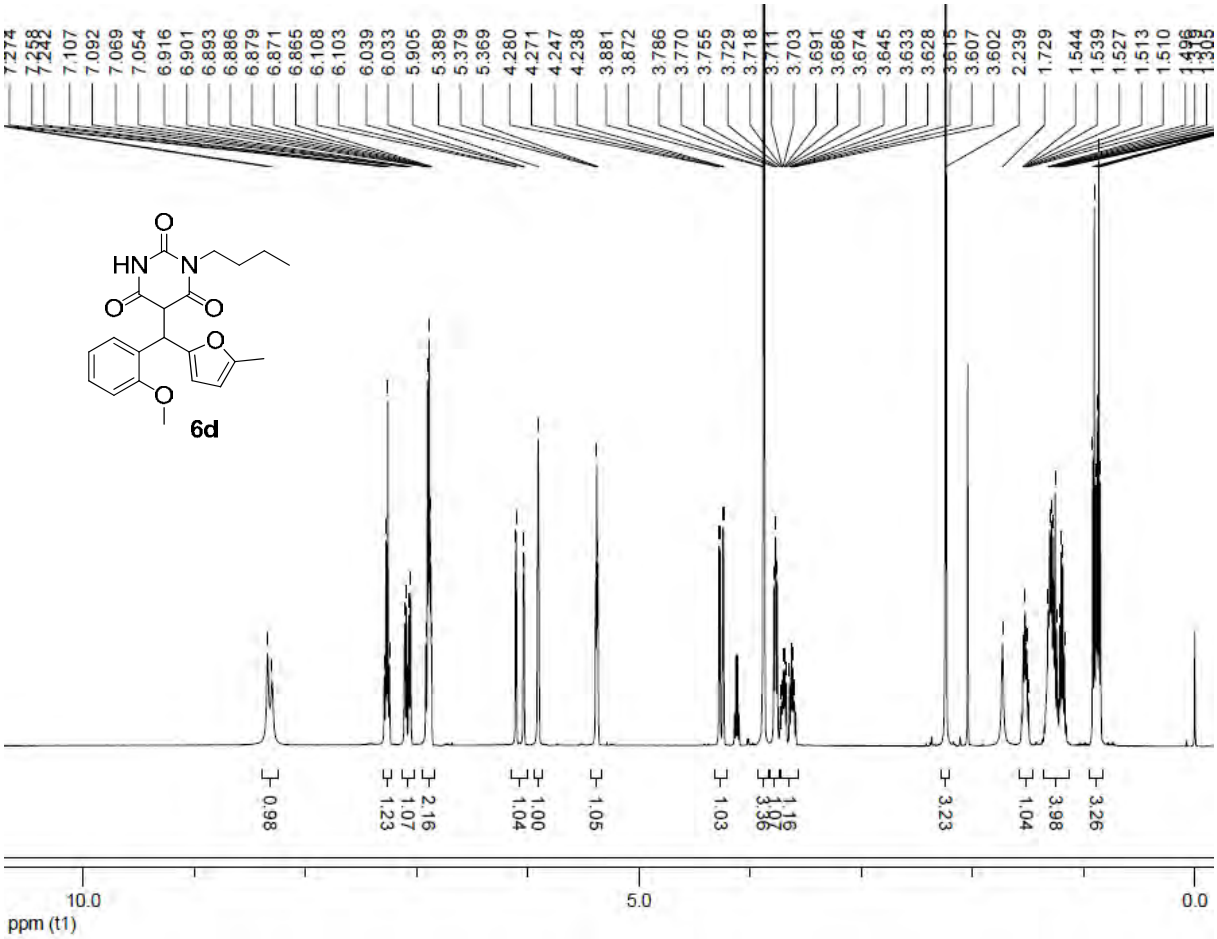
N
O
O
O
O
O
6c
200
150
100
50
0
ppm (t1)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6.886
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6.871
6.865
6.108
6.103
6.039
6.033
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5.389
5.379
5.369
4.280
4.271
4.247
4.238
3.881
3.872
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3.770
3.755
3.729
3.718
3.711
3.703
3.691
3.686
3.674
3.645
3.633
3.628
3.615
3.607
3.602
2.239
1.729
1.544
1.539
1.527
1.513
1.510
0.98
1.23
1.07
2.16
1.04
1.00
1.05
1.03
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3.98
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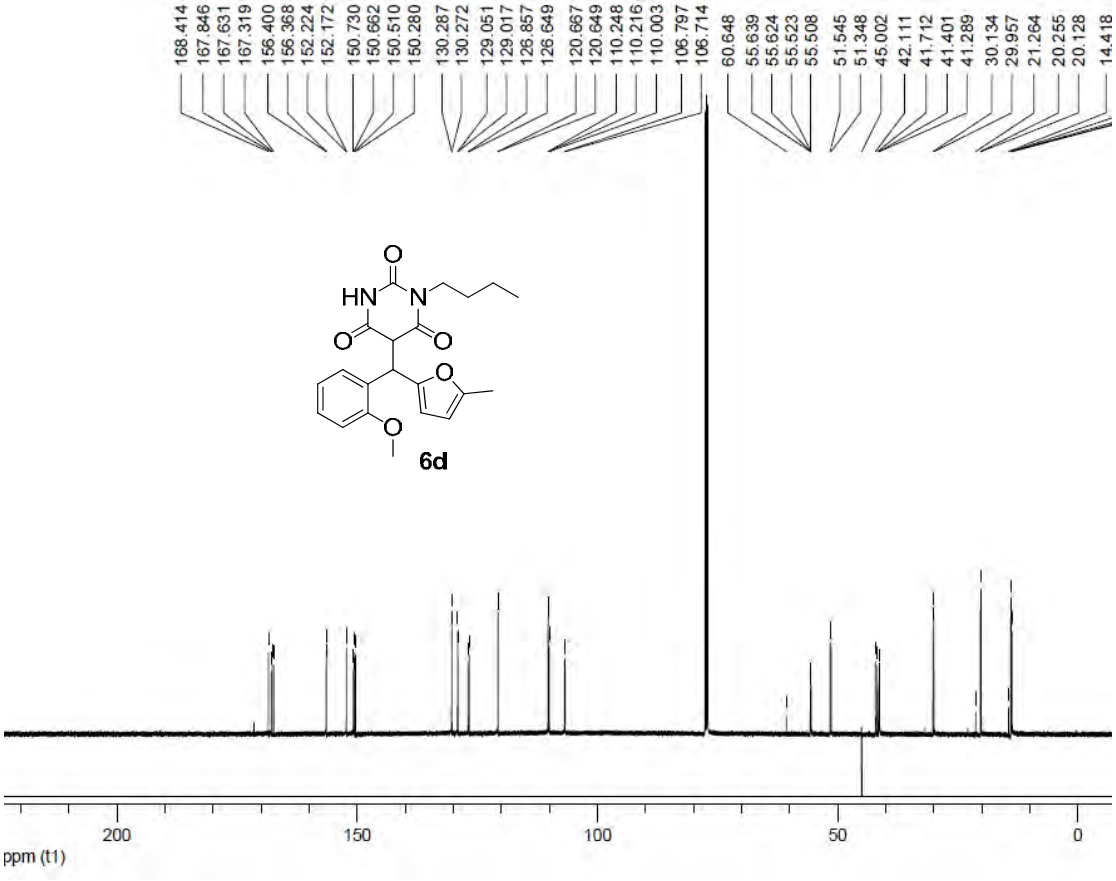
6d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150.280
130.287
130.272
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129.017
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126.649
120.667
120.649
110.248
110.216
110.003
106.797
106.714
60.648
55.639
55.624
55.523
55.508
51.545
51.348
45.002
42.111
41.712
41.401
41.289
30.134
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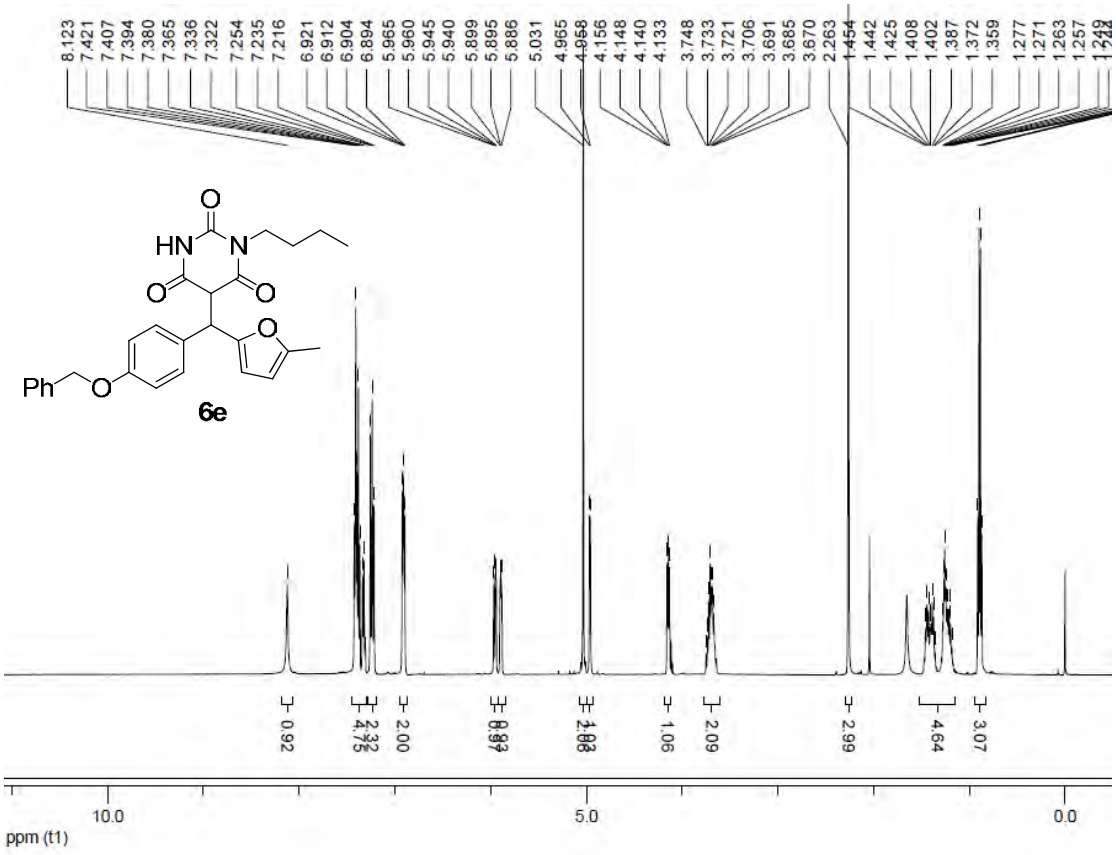
21.264
20.255
20.128
14.418
200
150
100
50
0
ppm (t1)
6d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6.894
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5.960
5.945
5.940
5.899
5.895
5.886
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4.965
4.958
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4.133
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3.733
3.721
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1.442
1.425
1.408
1.402
1.387
1.372
1.359
1.277
1.271
1.263
1.257
HN
N
O
O
O
O
Ph
O
6e
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1.08
1.06
2.09
2.99
4.94
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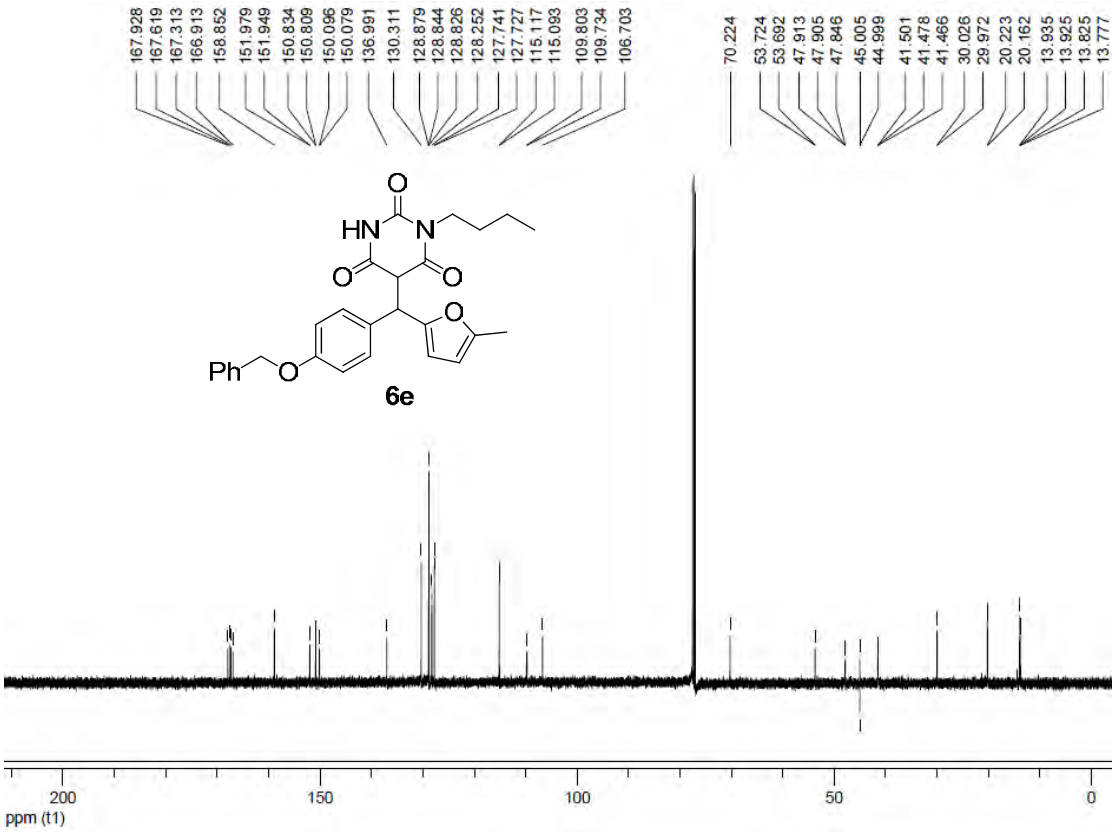
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128.826
128.252
127.741
127.727
115.117
115.093
109.803
109.734
106.703
70.224
53.724
53.692
47.913
47.905
47.846
45.005
44.999
41.501
41.478
41.466
30.026
29.972
20.223
20.162
13.935
13.925
13.825
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O
O
O
O
Ph
O
6e
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50
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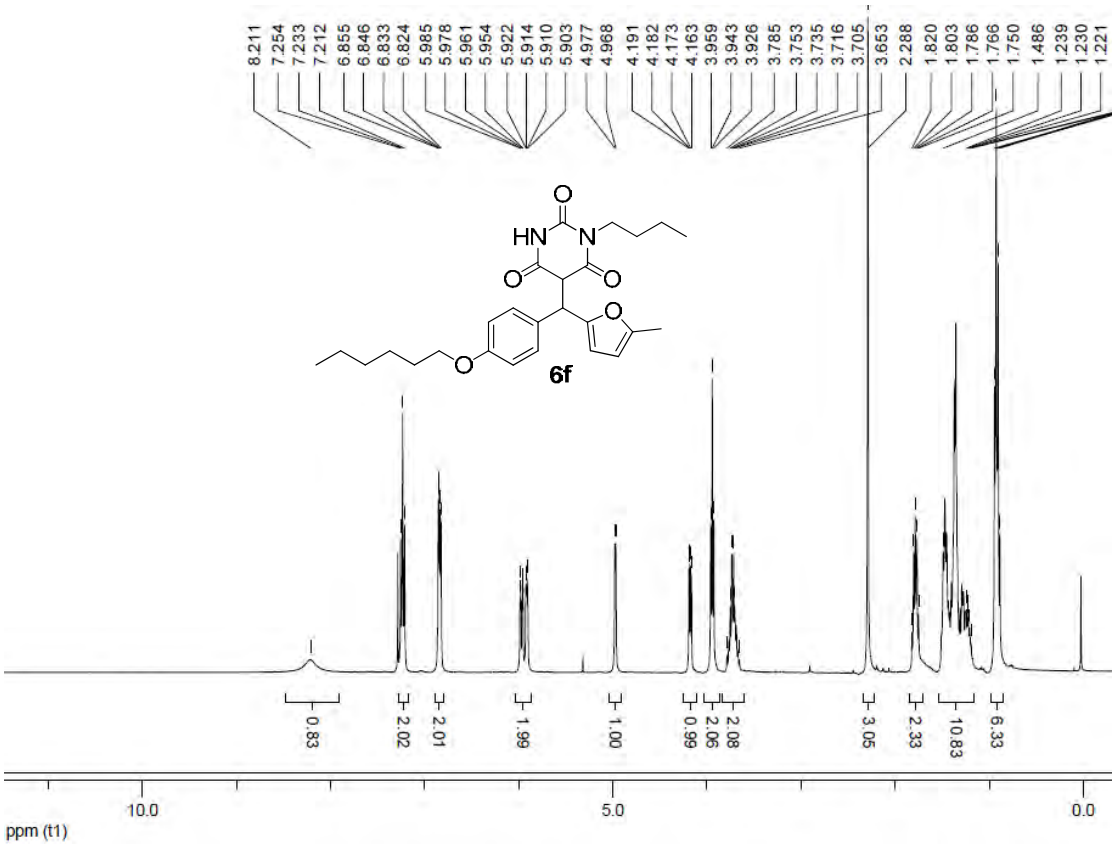
ppm (t1)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6.824
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5.961
5.954
5.922
5.914
5.910
5.903
4.977
4.968
4.191
4.182
4.173
4.163
3.959
3.943
3.926
3.785
3.753
3.735
3.716
3.705
3.653
2.288
1.820
1.803
1.786
1.766
1.750
1.486
1.239
1.230
1.221
HN
N
O
O
O
O
O
6f
0.83
2.02
2.01
1.99
1.00
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2.08
3.05
2.33
10.83
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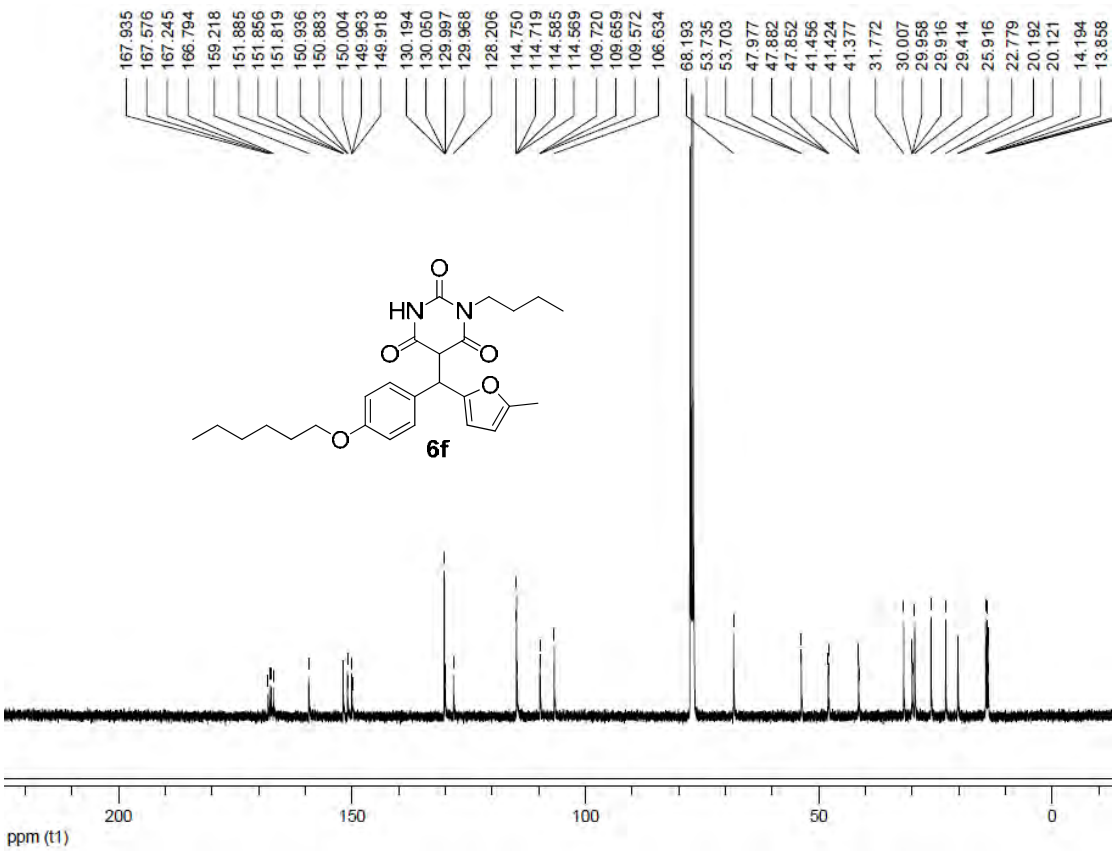
ppm (t1)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47.882
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41.456
41.424
41.377
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29.916
29.414
25.916
22.779
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O
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O
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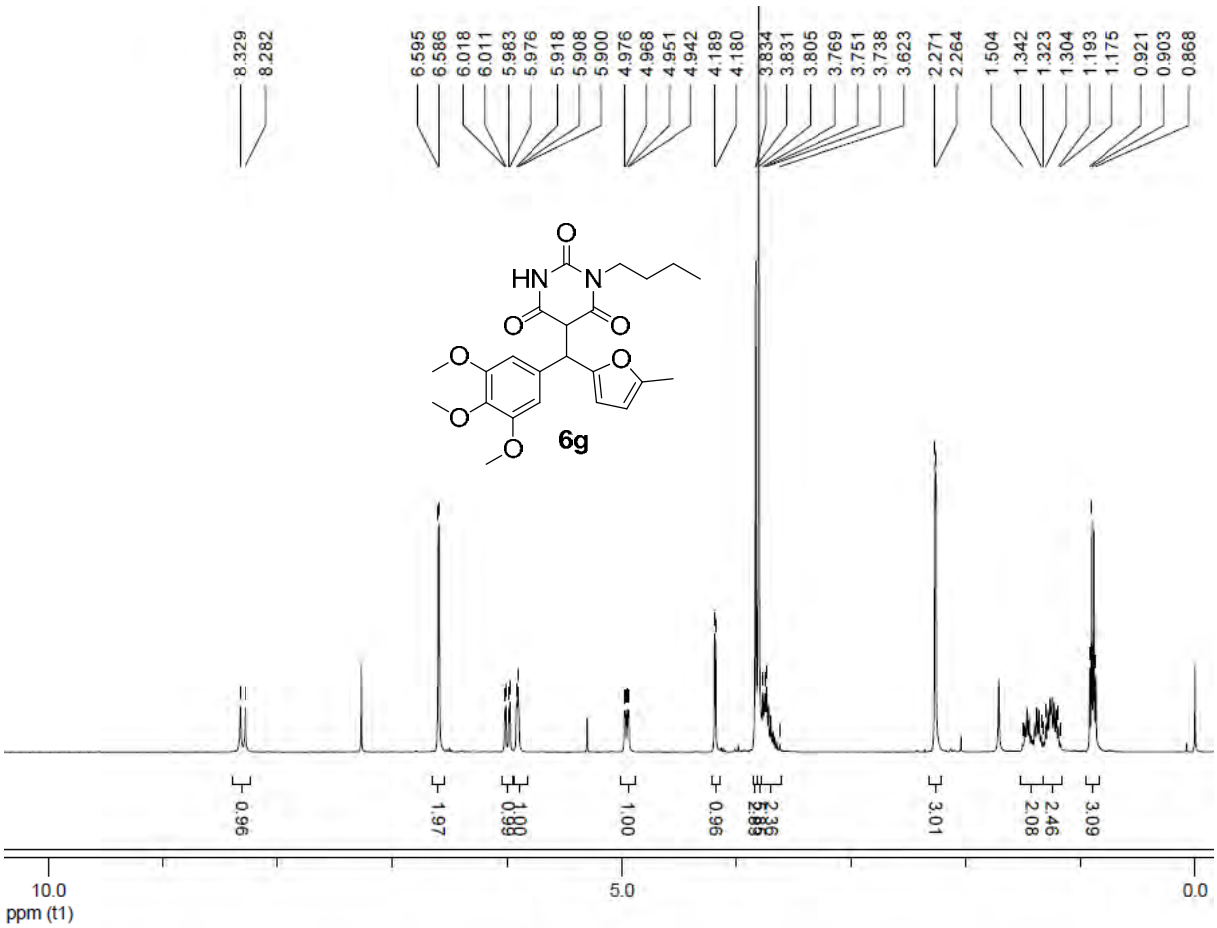
ppm (t1)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5.976
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5.908
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4.976
4.968
4.951
4.942
4.189
4.180
3.834
3.831
3.805
3.769
3.751
3.738
3.623
2.271
2.264
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1.342
1.323
1.304
1.193
1.175
0.921
0.903
0.868
HN
N
O
6g
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1.97
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0.96
3.01
2.08
2.46
3.09
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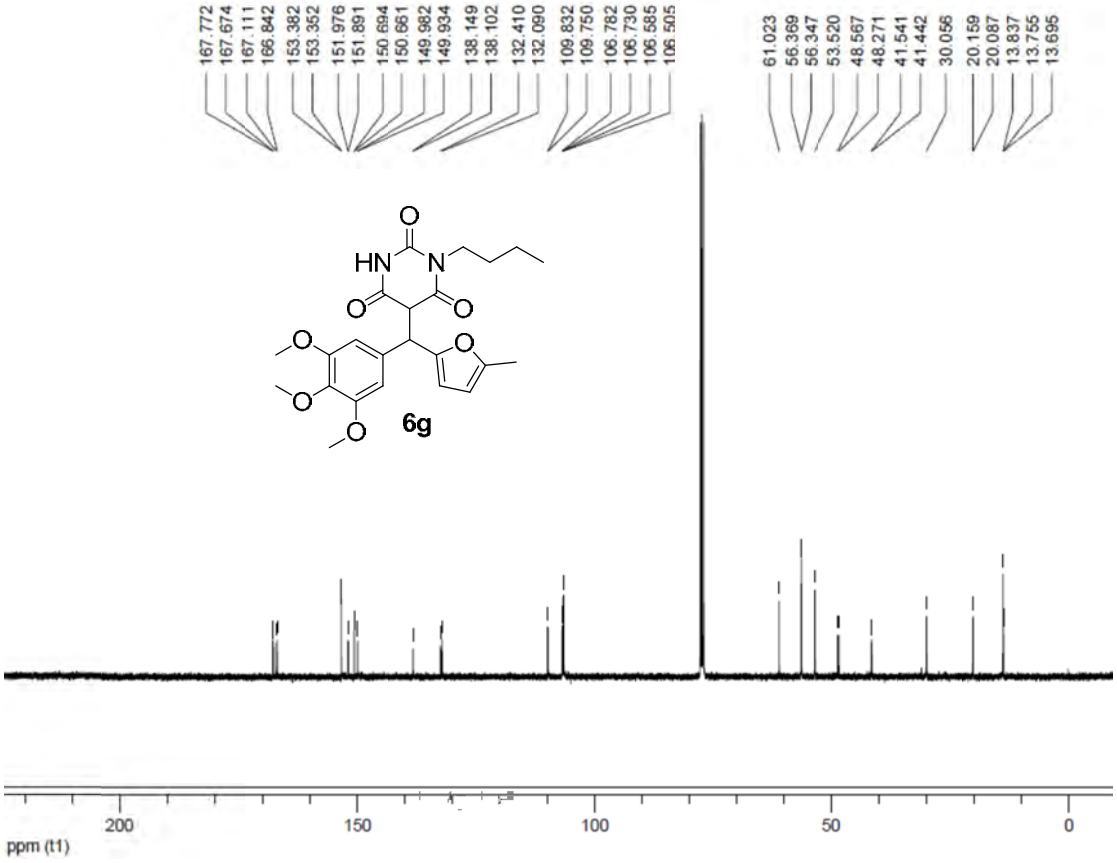
ppm (t1)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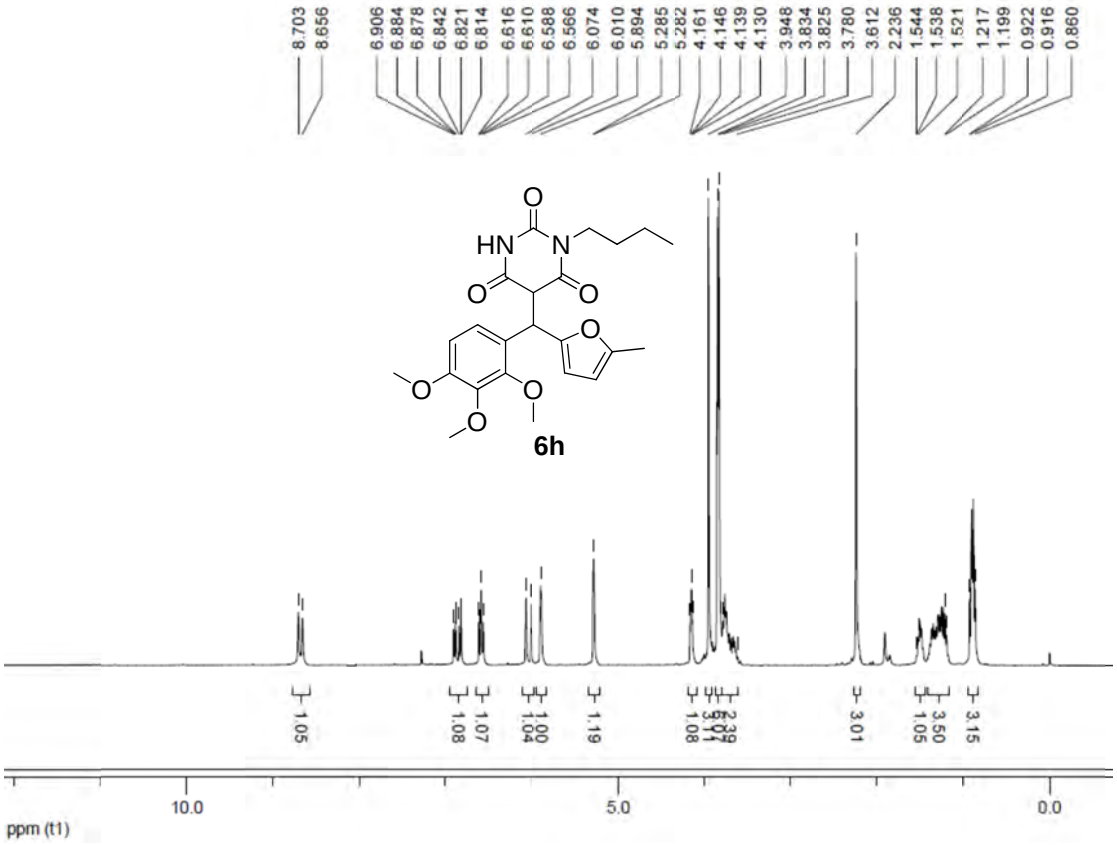
ppm (t1)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6.588
6.566
6.074
6.010
5.894
5.285
5.282
4.161
4.146
4.139
4.130
3.948
3.834
3.825
3.780
3.612
2.236
1.544
1.538
1.521
1.217
1.199
0.922
0.916
0.860
HN
N
O
6h
1.05
1.08
1.07
1.00
1.04
1.19
1.08
3.01
1.05
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10.0
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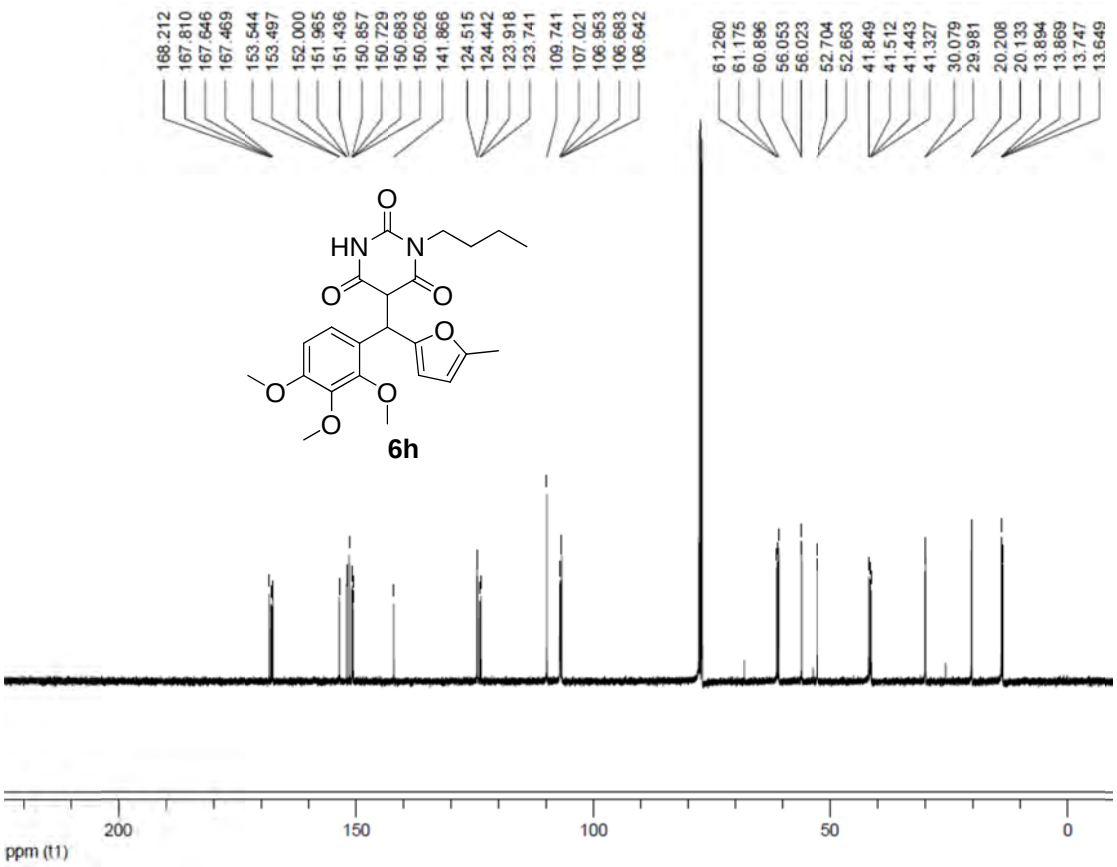
ppm (t1)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150.626
141.866
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124.442
123.918
123.741
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107.021
106.953
106.683
106.642
61.260
61.175
60.896
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20.208
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6h
200
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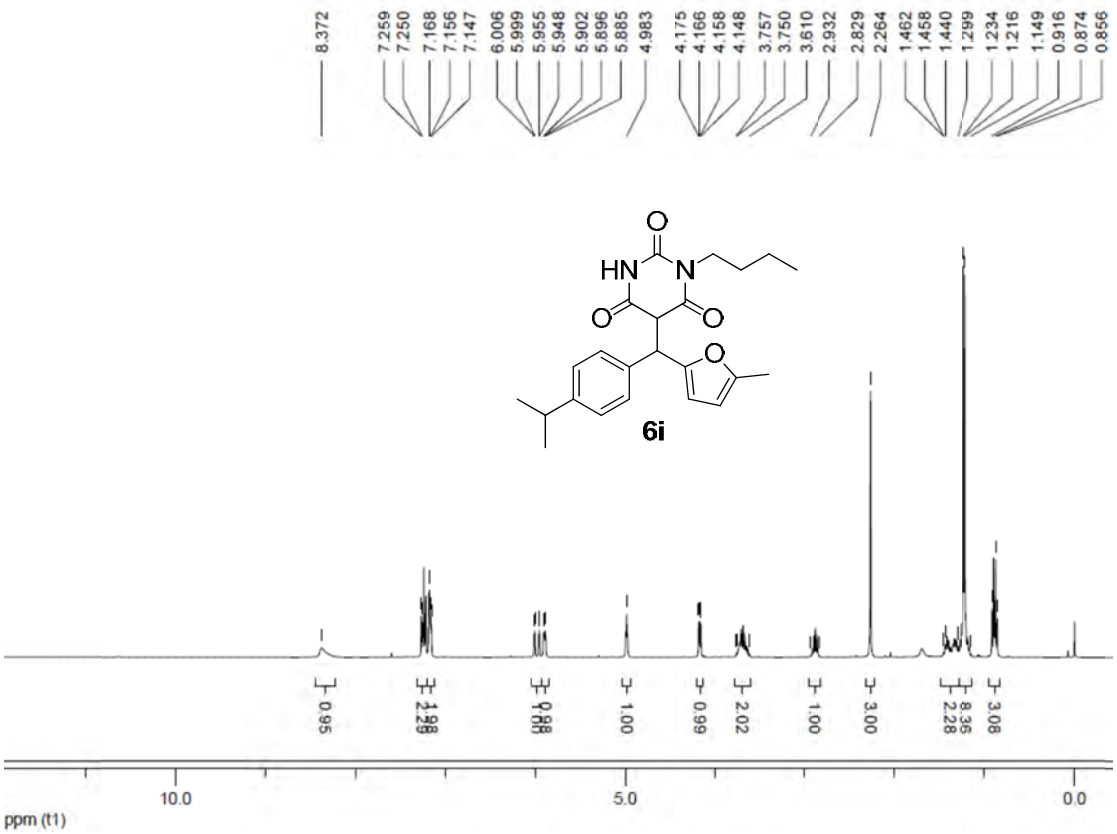
100
50
0
ppm (t1)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5.948
5.902
5.896
5.885
4.983
4.175
4.166
4.158
4.148
3.757
3.750
3.610
2.932
2.829
2.264
1.462
1.458
1.440
1.299
1.234
1.216
1.149
0.916
0.874
0.856
HN
N
O
O
O
O
6i
0.95
2.28
0.88
1.00
0.99
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1.00
3.00
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2.28
3.08
10.0
5.0
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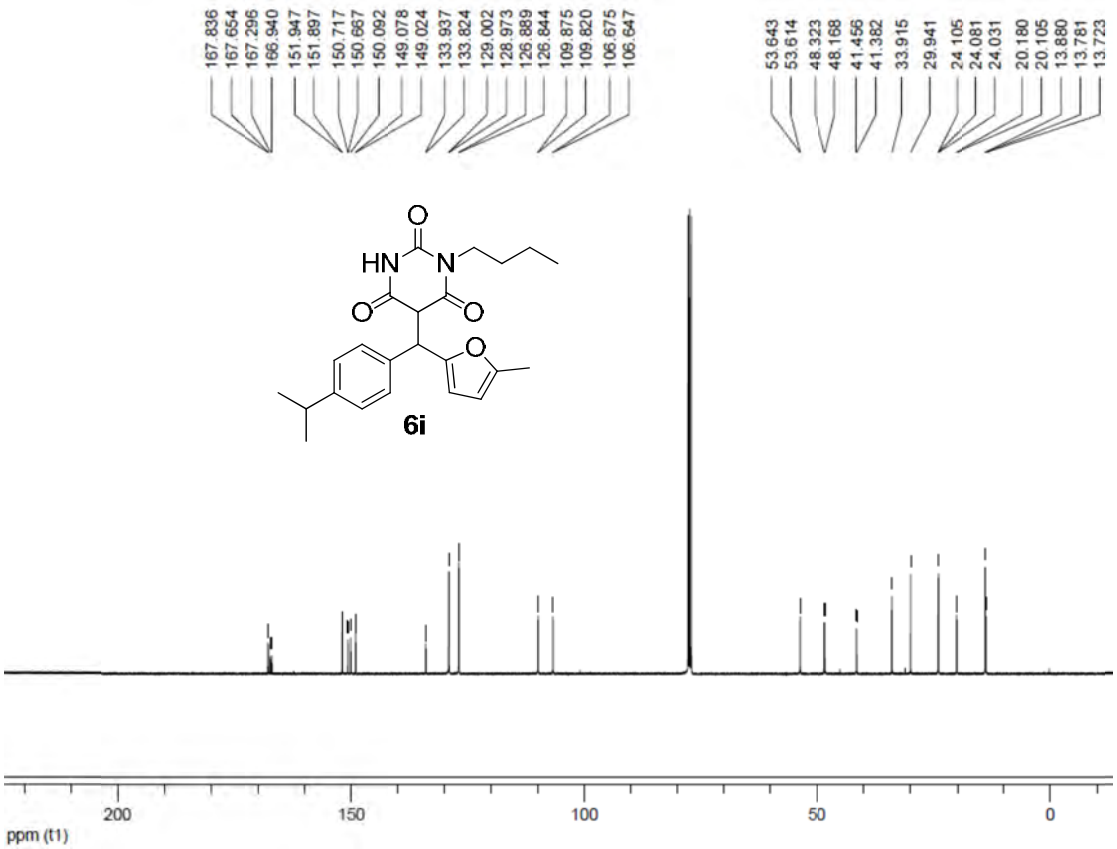
ppm (t1)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109.820
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106.647
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48.168
41.456
41.382
33.915
29.941
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24.031
20.180
20.105
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HN
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O
O
O
6i
200
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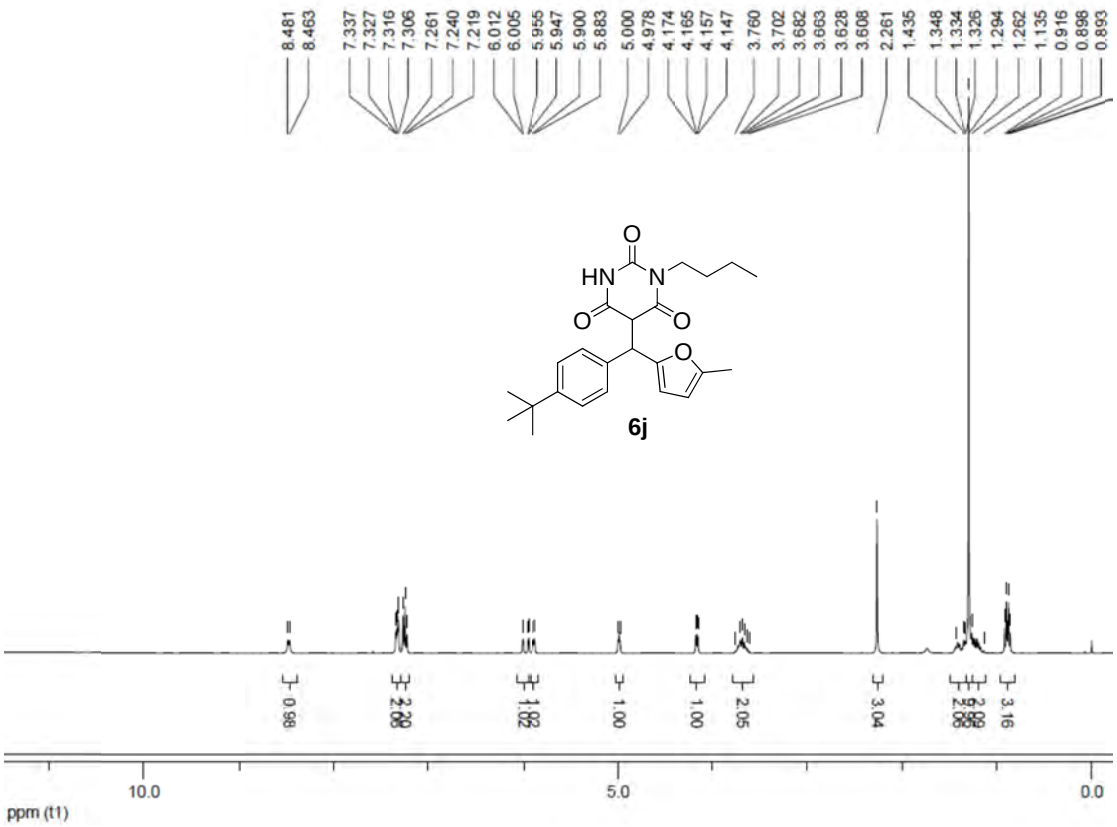
100
50
0
ppm (t1)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5.883
5.000
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4.147
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3.663
3.628
3.608
2.261
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1.348
1.334
1.326
1.294
1.262
1.135
0.916
0.898
0.893
HN
N
O
O
O
O
6j
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2.02
2.01
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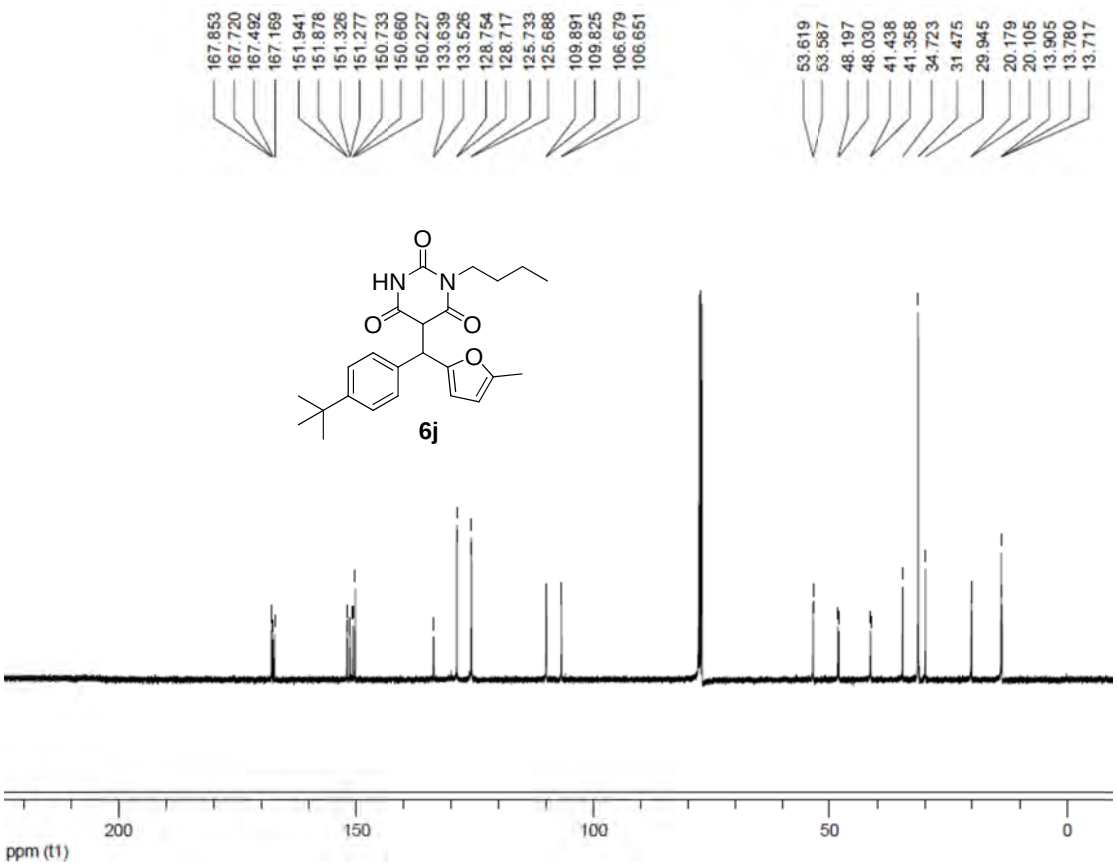
ppm (t1)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133.526
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128.717
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125.688
109.891
109.825
106.679
106.651
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53.587
48.197
48.030
41.438
41.358
34.723
31.475
29.945
20.179
20.105
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HN
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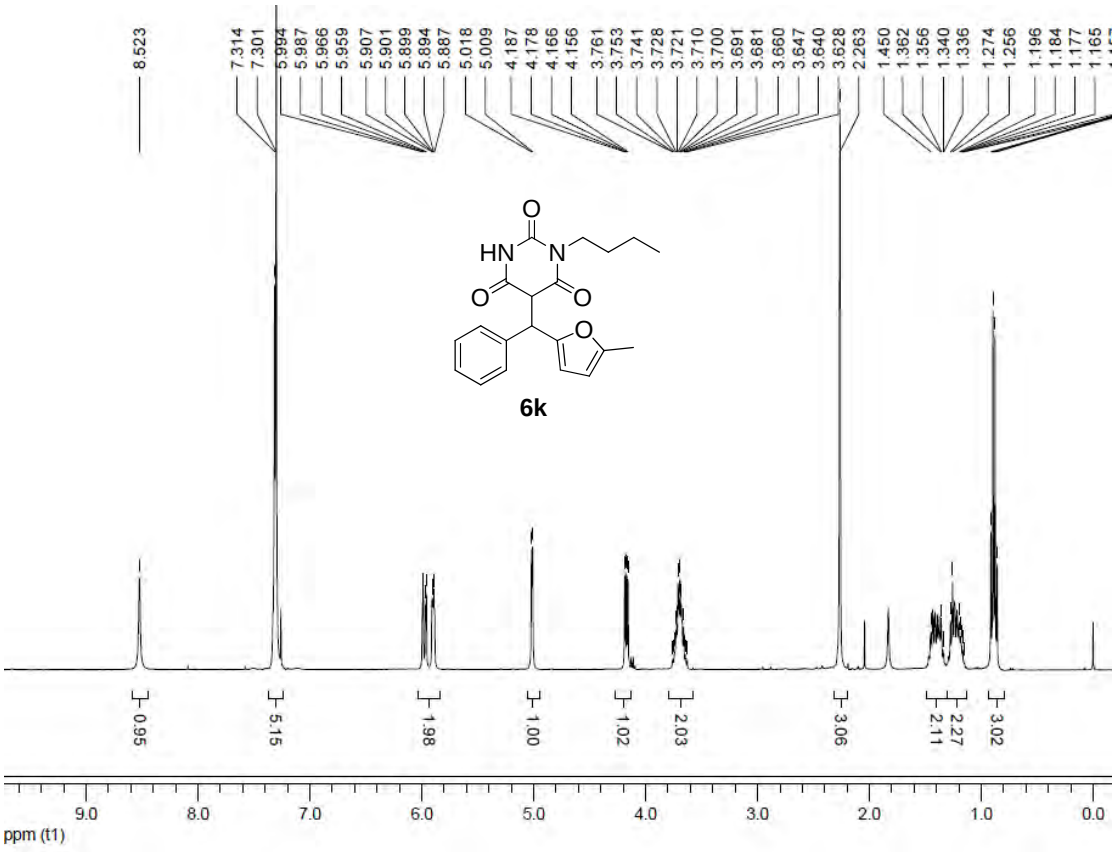
O
O
O
O
6j
200
150
100
50
0
ppm (t1)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4.178
4.166
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3.753
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3.728
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3.681
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1.340
1.336
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1.184
1.177
1.165
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N
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O
O
O
6k
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1.02
2.03
3.06
2.11
2.27
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2.0
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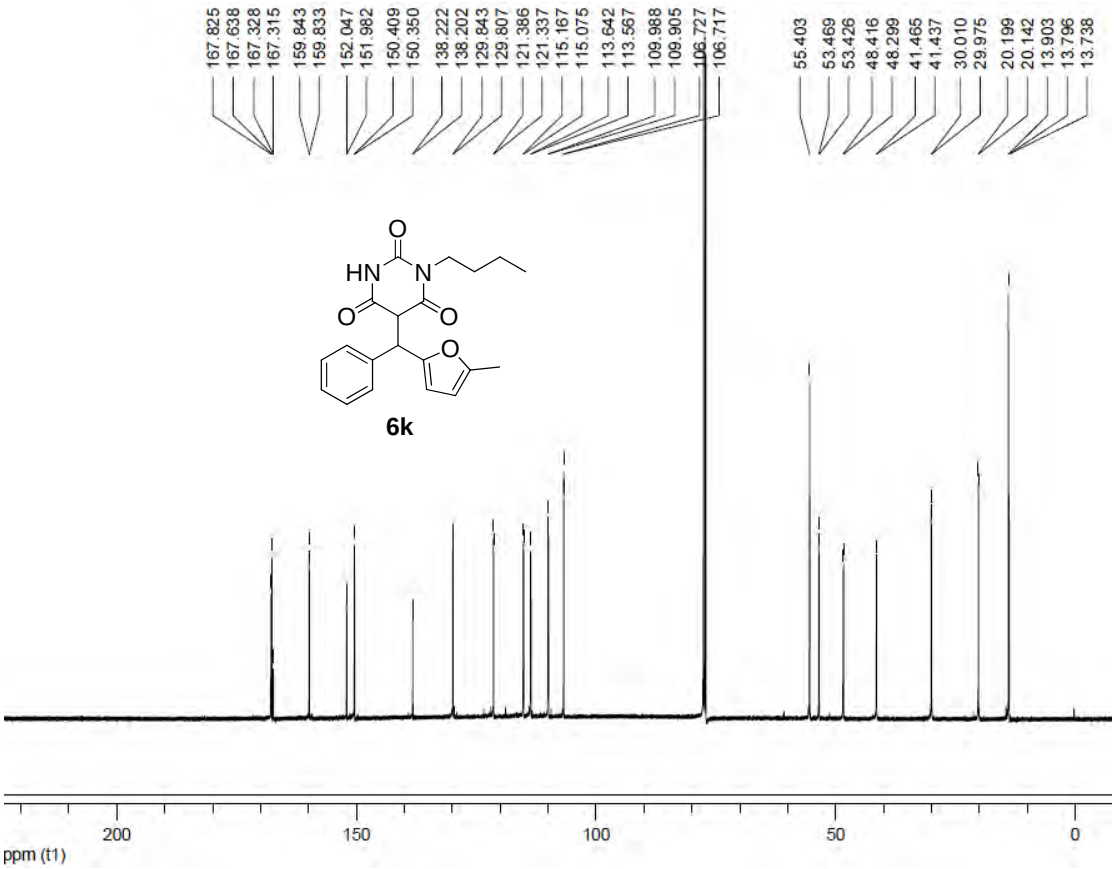
ppm (t1)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115.075
113.642
113.567
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109.905
106.727
106.717
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41.437
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20.142
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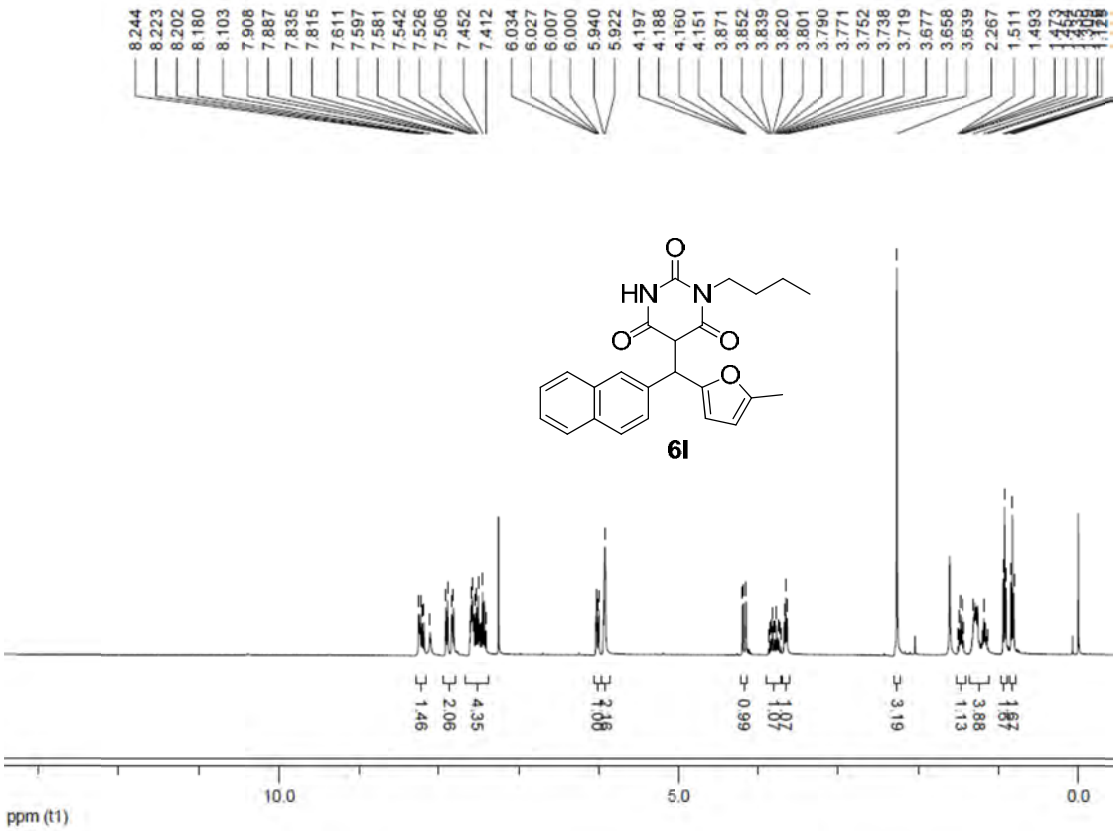
50
0
ppm (t1)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7.526
7.506
7.452
7.412
6.034
6.027
6.007
6.000
5.940
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HN
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O
O
O
6l
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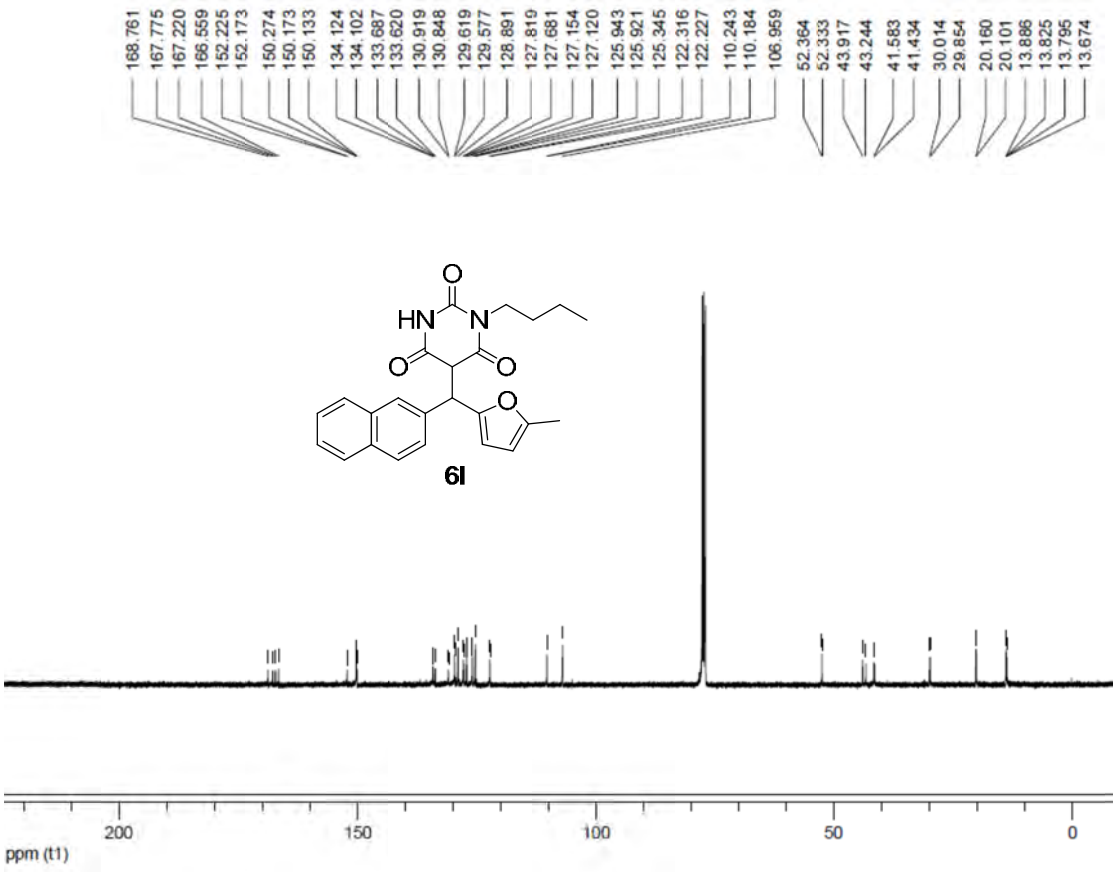
ppm (t1)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125.345
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43.917
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41.583
41.434
30.014
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O
O
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6l
200
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50
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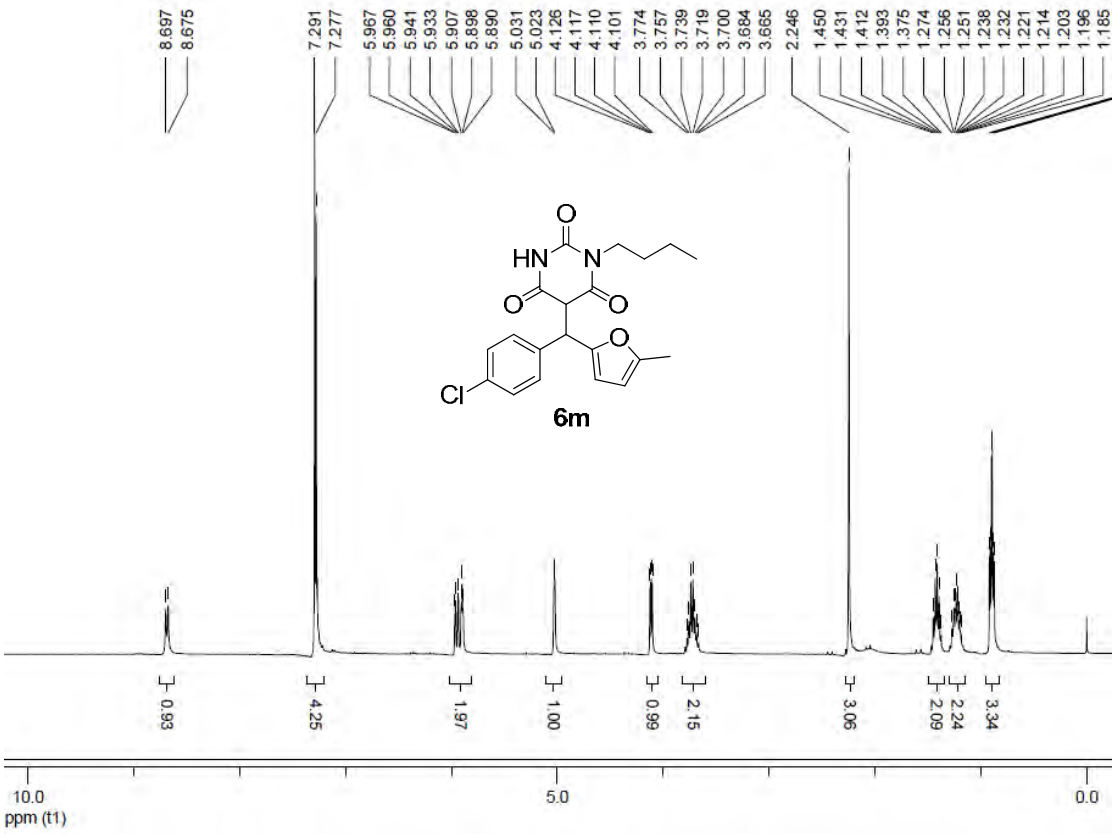
ppm (t1)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5.023
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4.110
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3.774
3.757
3.739
3.719
3.700
3.684
3.665
2.246
1.450
1.431
1.412
1.393
1.375
1.274
1.256
1.251
1.238
1.232
1.221
1.214
1.203
1.196
1.185
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O
O
O
Cl
6m
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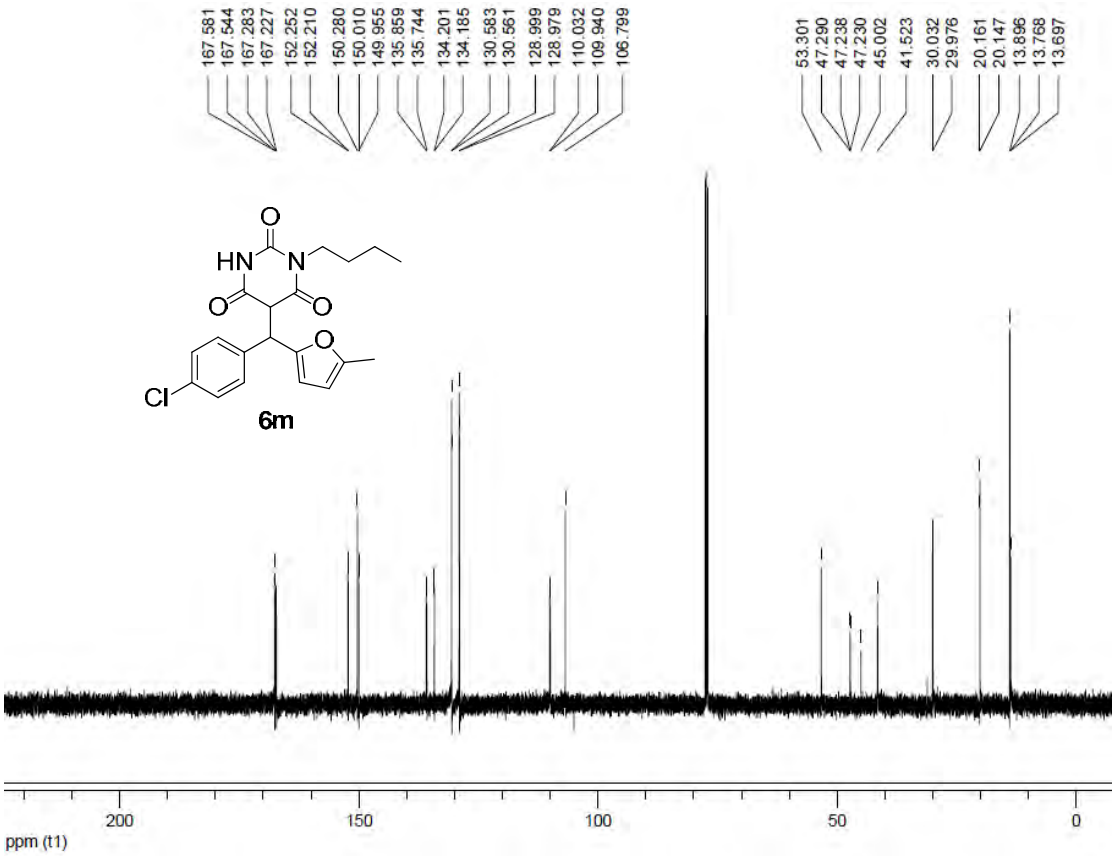
ppm (t1)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47.238
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O
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50
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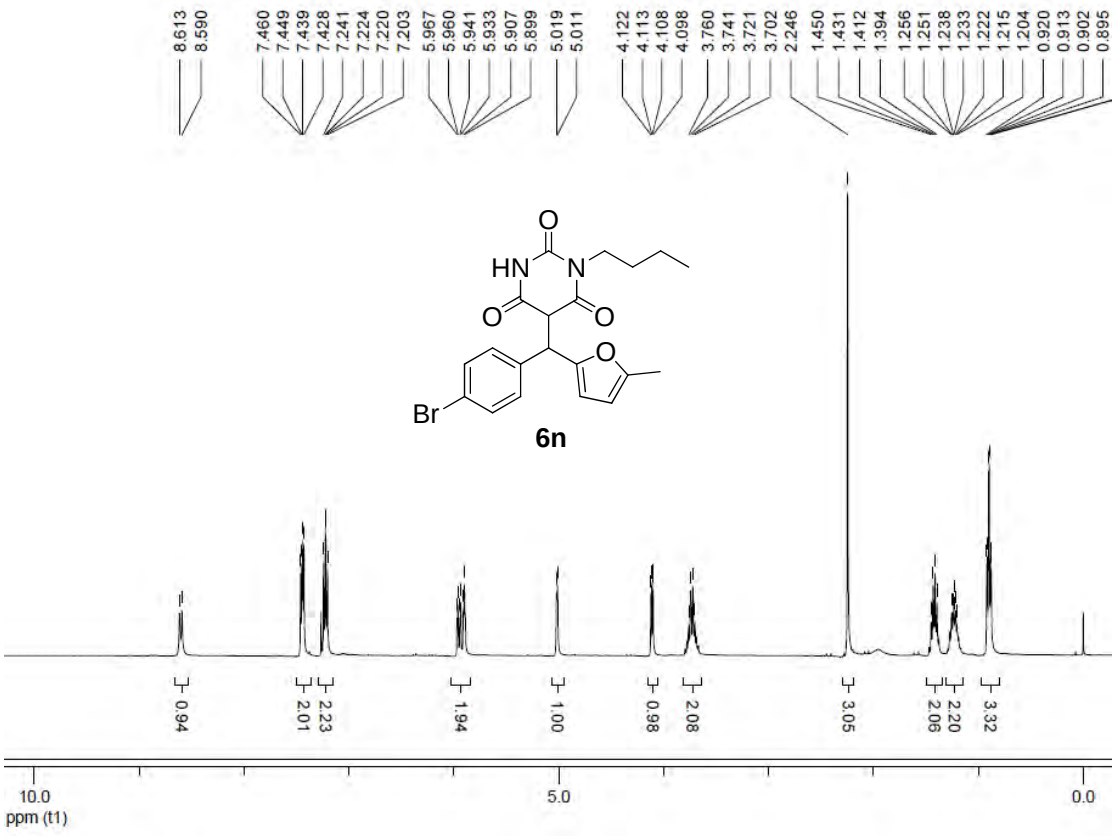
ppm (t1)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3.741
3.721
3.702
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1.412
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1.233
1.222
1.215
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0.913
0.902
0.895
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O
O
O
O
Br
6n
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2.23
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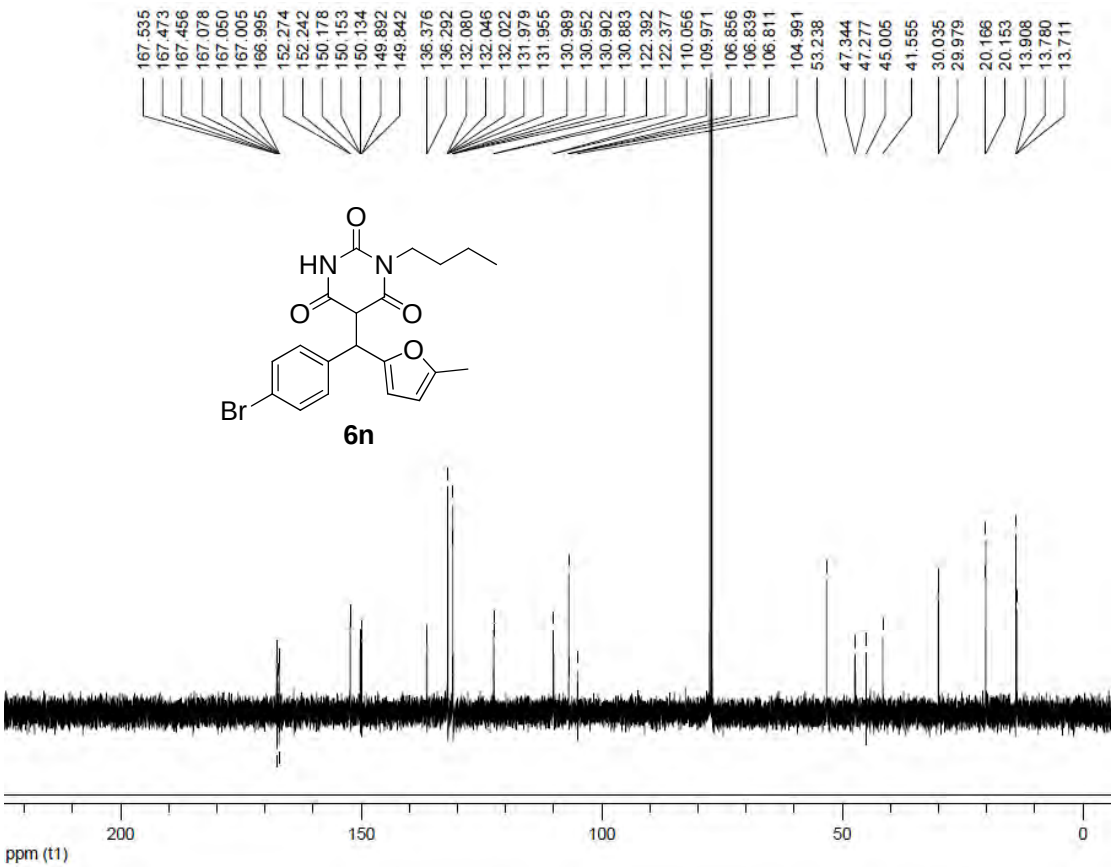
ppm (t1)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106.856
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106.811
104.991
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47.344
47.277
45.005
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30.035
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O
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Br
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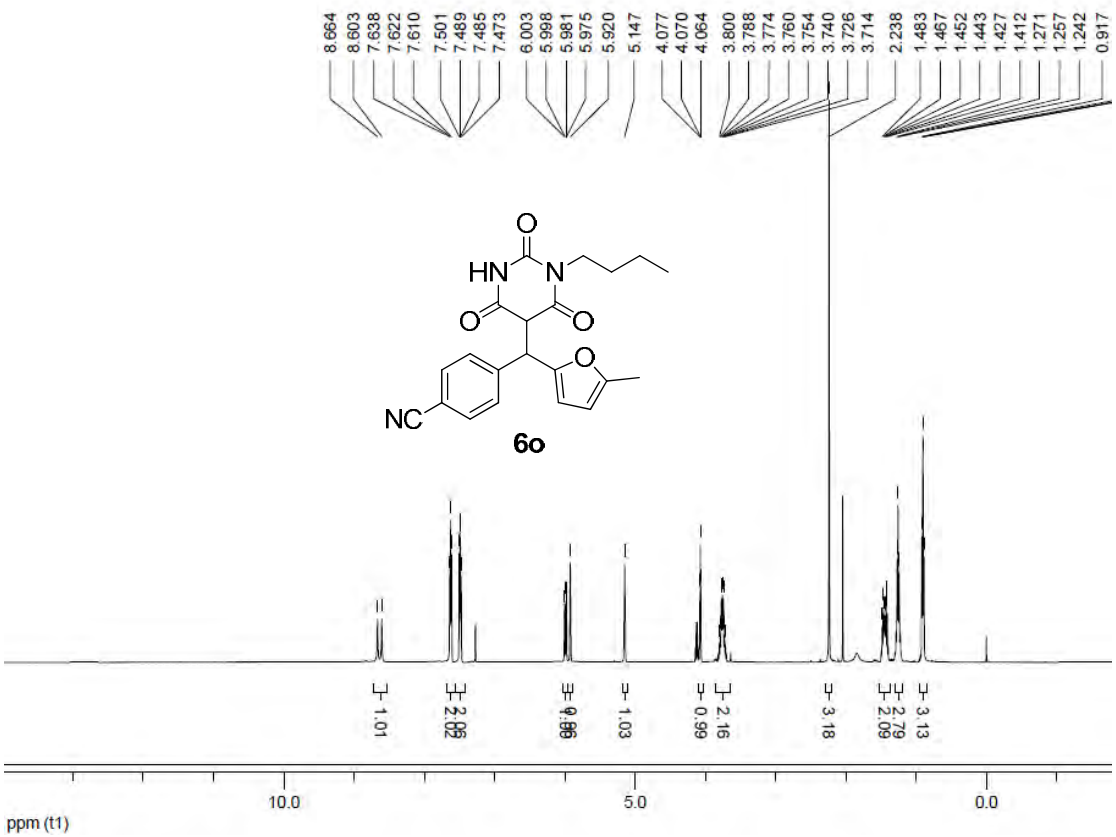
ppm (t1)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3.18
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2.79
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10.0
5.0
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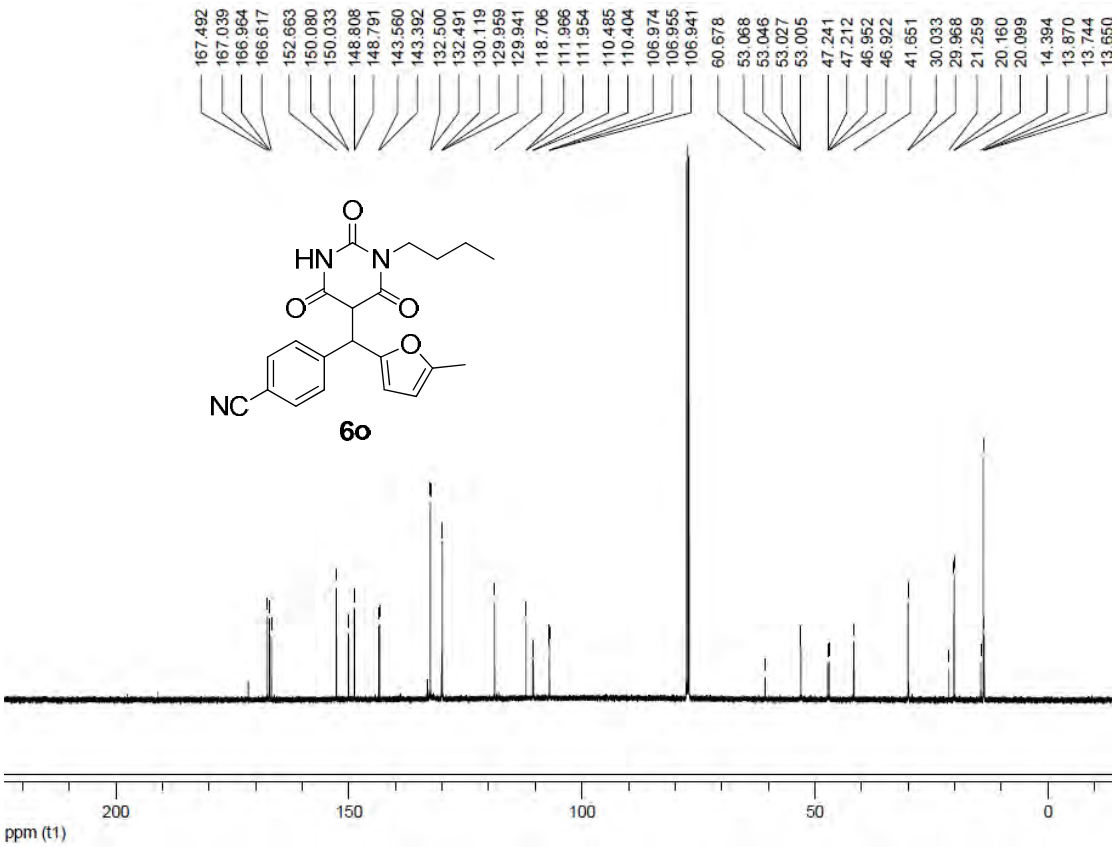
ppm (t1)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132.491
130.119
129.959
129.941
118.706
111.966
111.954
110.485
110.404
106.974
106.955
106.941
60.678
53.068
53.046
53.027
53.005
47.241
47.212
46.952
46.922
41.651
30.033
29.968
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20.160
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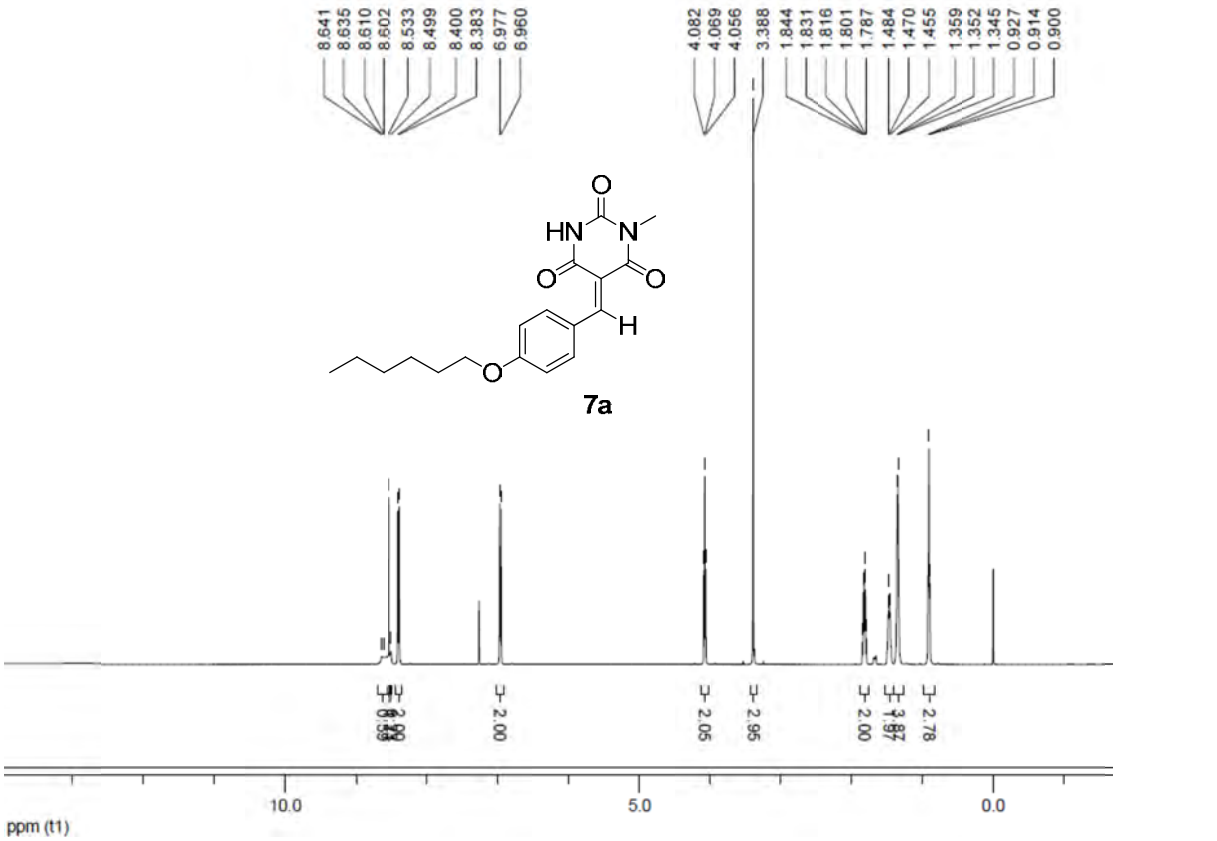
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4.056
3.388
1.844
1.831
1.816
1.801
1.787
1.484
1.470
1.455
1.359
1.352
1.345
0.927
0.914
0.900
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N
O
O
O
H
O
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2.00
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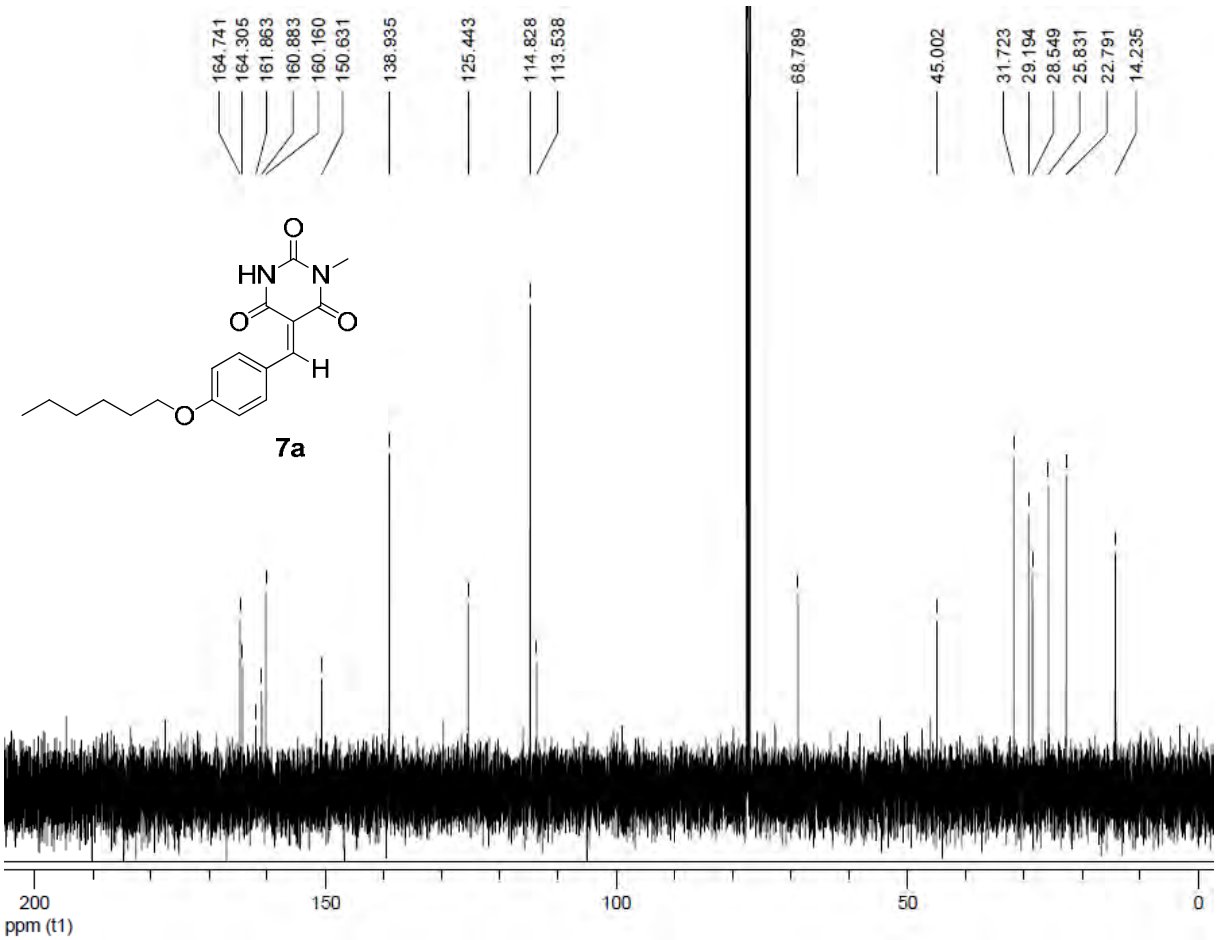
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45.002
31.723
29.194
28.549
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22.791
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H
O
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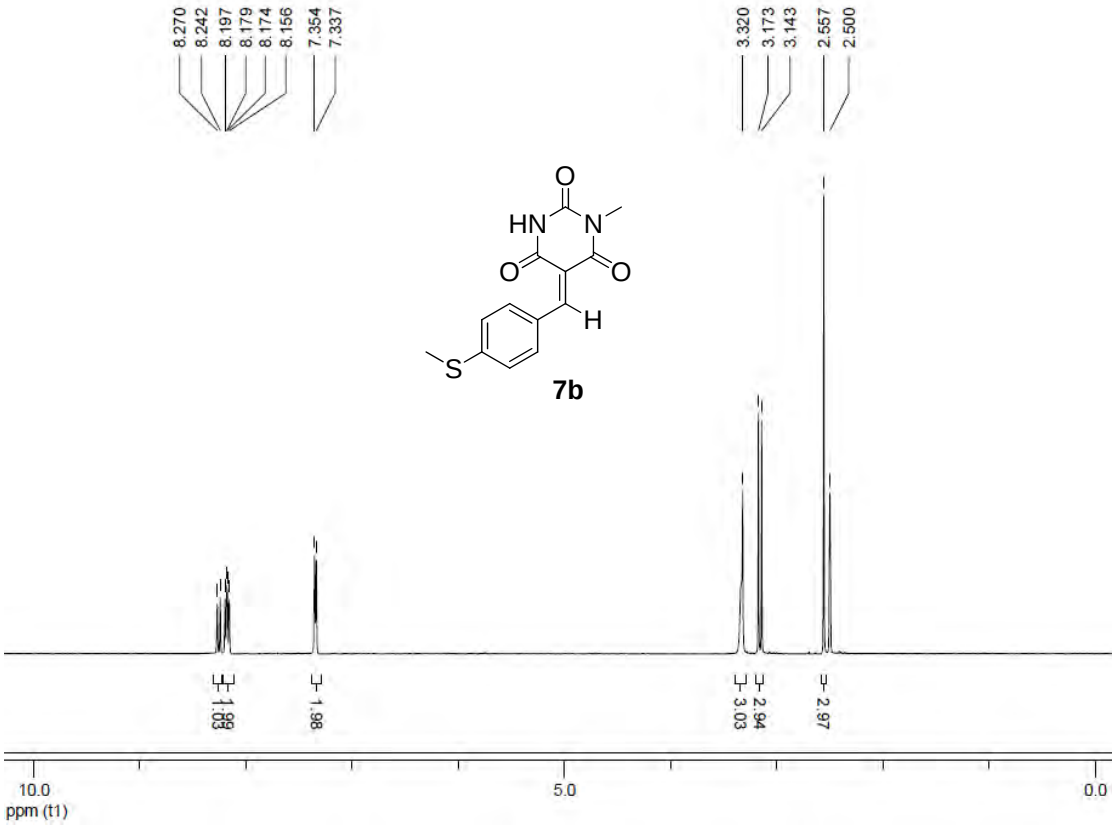
ppm (t1)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3.143
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1.98
3.03
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ppm (t1)
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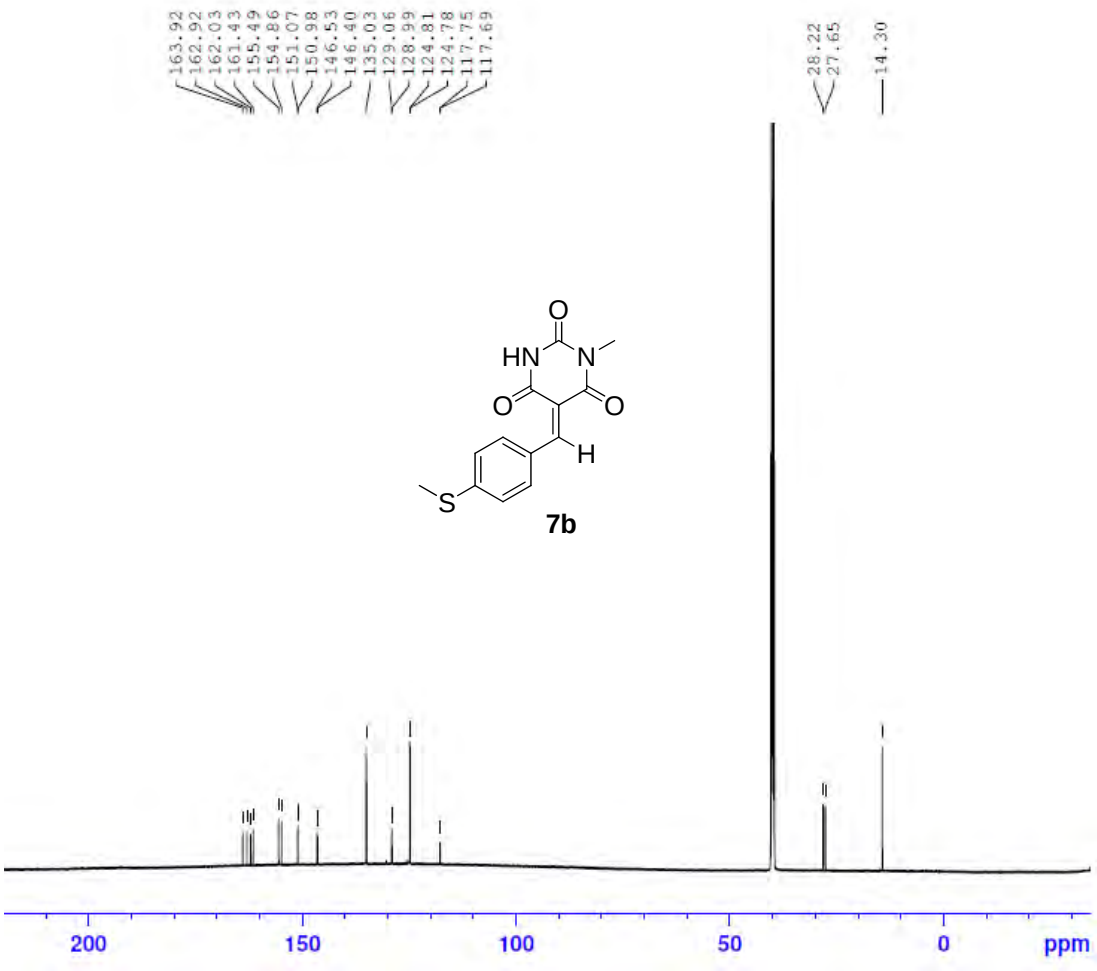
0.0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117.75
117.69
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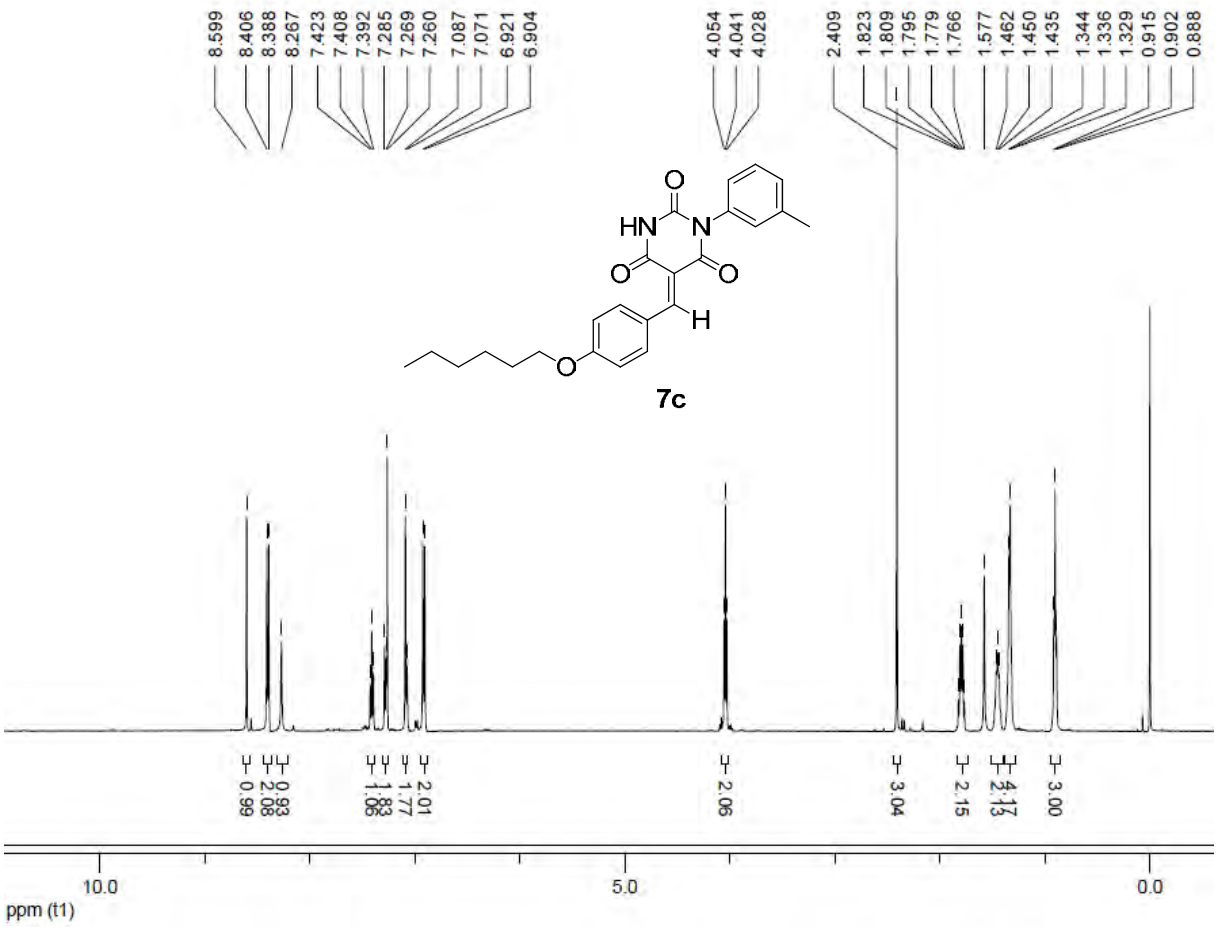
150
100
50
0
ppm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7.285
7.269
7.260
7.087
7.071
6.921
6.904
4.054
4.041
4.028
2.409
1.823
1.809
1.795
1.779
1.766
1.577
1.462
1.450
1.435
1.344
1.336
1.329
0.915
0.902
0.888
HN
N
O
O
O
H
O
7c
0.99
2.08
1.06
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2.06
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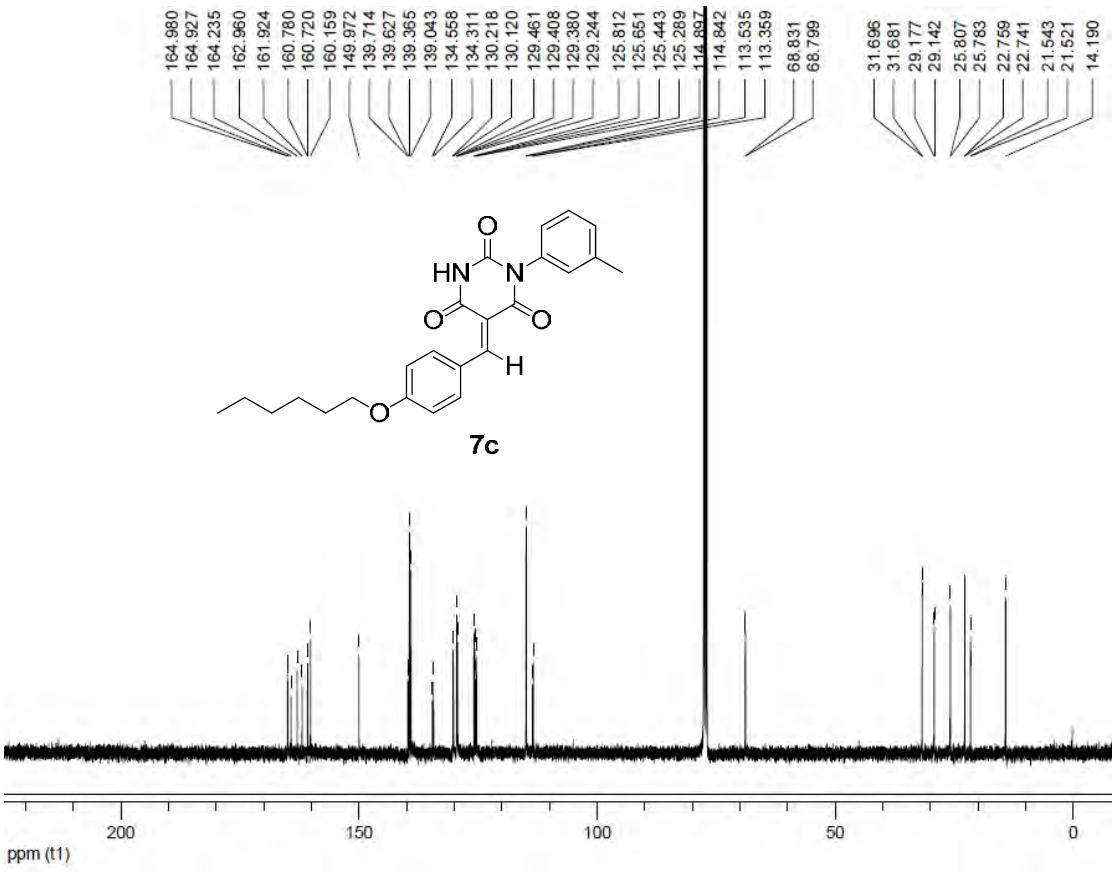
ppm (t1)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139.043
134.558
134.311
130.218
130.120
129.461
129.408
129.380
129.244
125.812
125.651
125.443
125.289
114.897
114.842
113.535
113.359
68.831
68.799
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31.681
29.177
29.142
25.807
25.783
22.759
22.741
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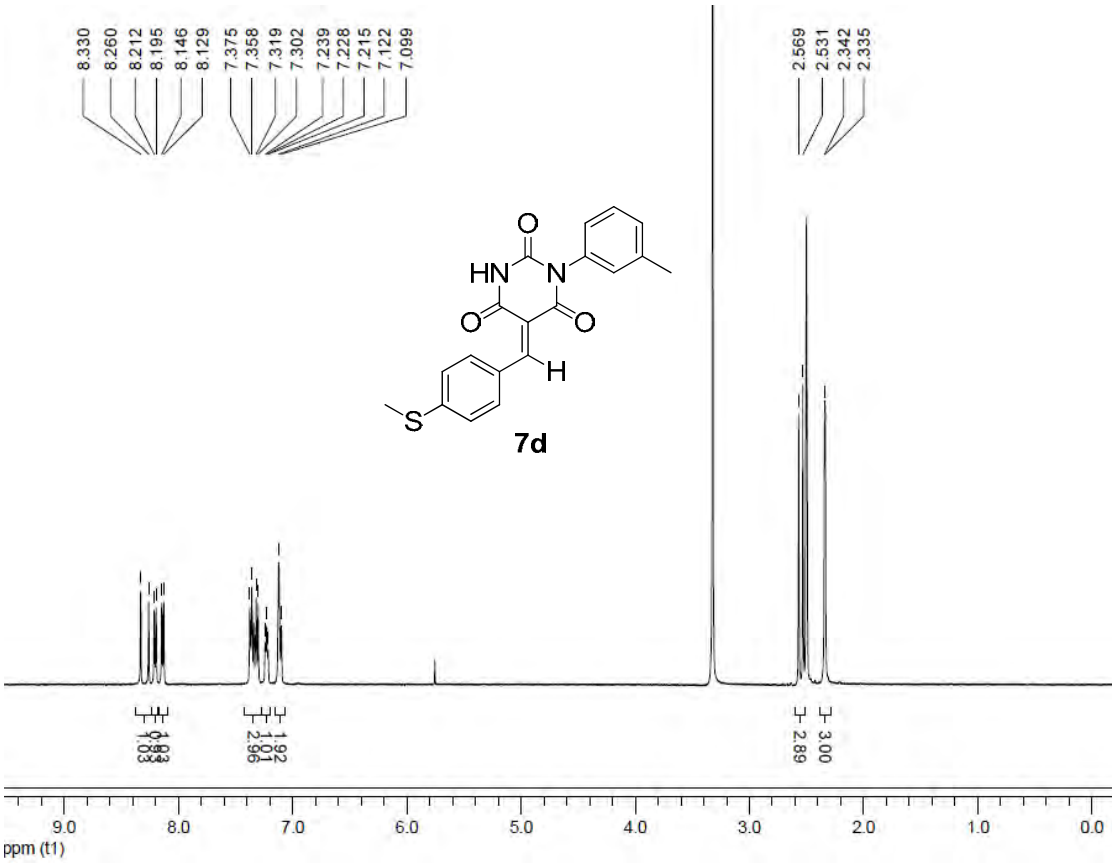
ppm (t1)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7.228
7.215
7.122
7.099
2.569
2.531
2.342
2.335
HN
N
O
O
O
H
S
7d
1.08
1.03
2.96
1.01
1.92
2.89
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7.0
6.0
5.0
4.0
3.0
2.0
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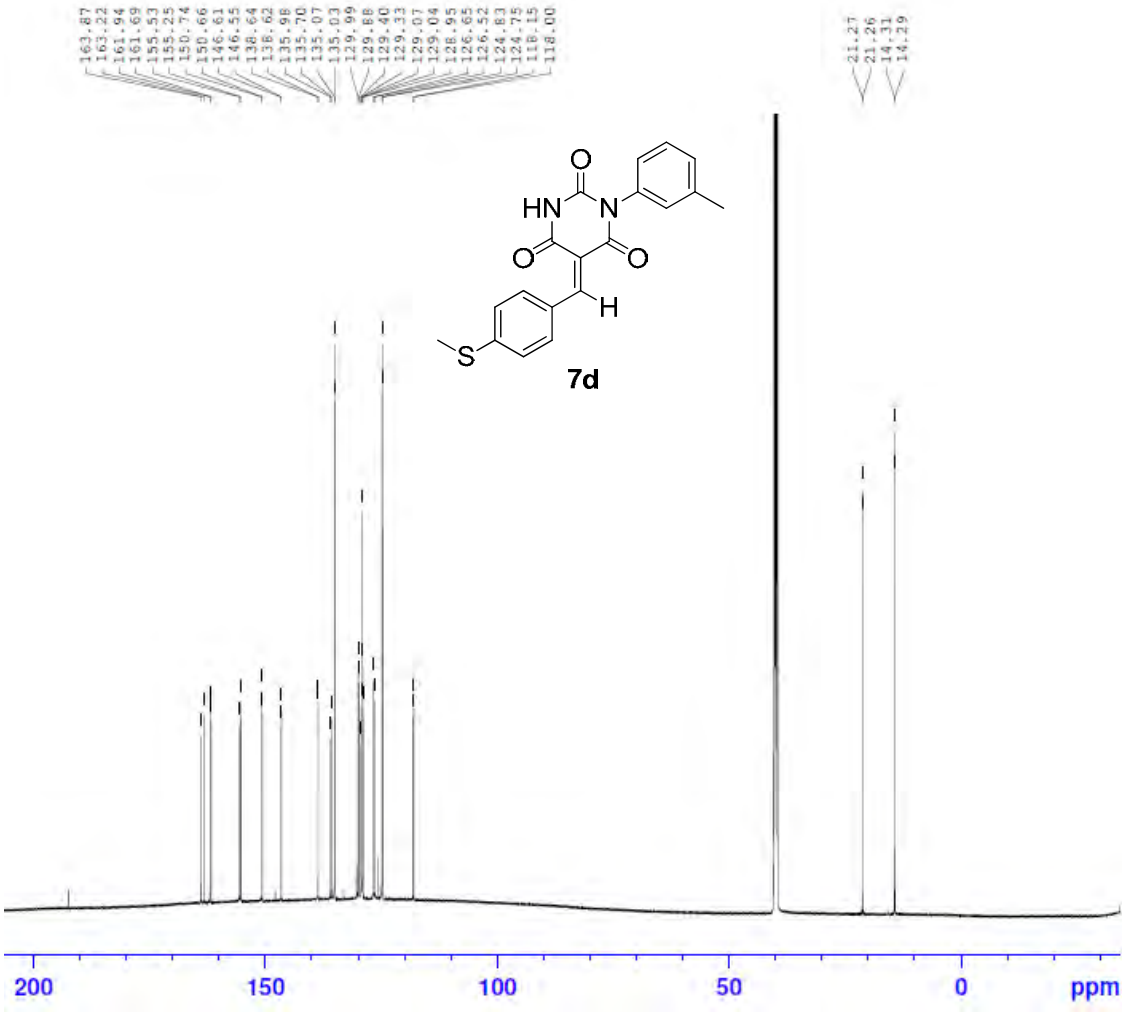
0.0
ppm (t1)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135.70
135.07
135.03
129.99
129.68
129.40
129.33
129.07
129.04
128.95
126.65
126.52
124.83
124.75
118.15
118.00
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14.29
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O
O
H
S
7d
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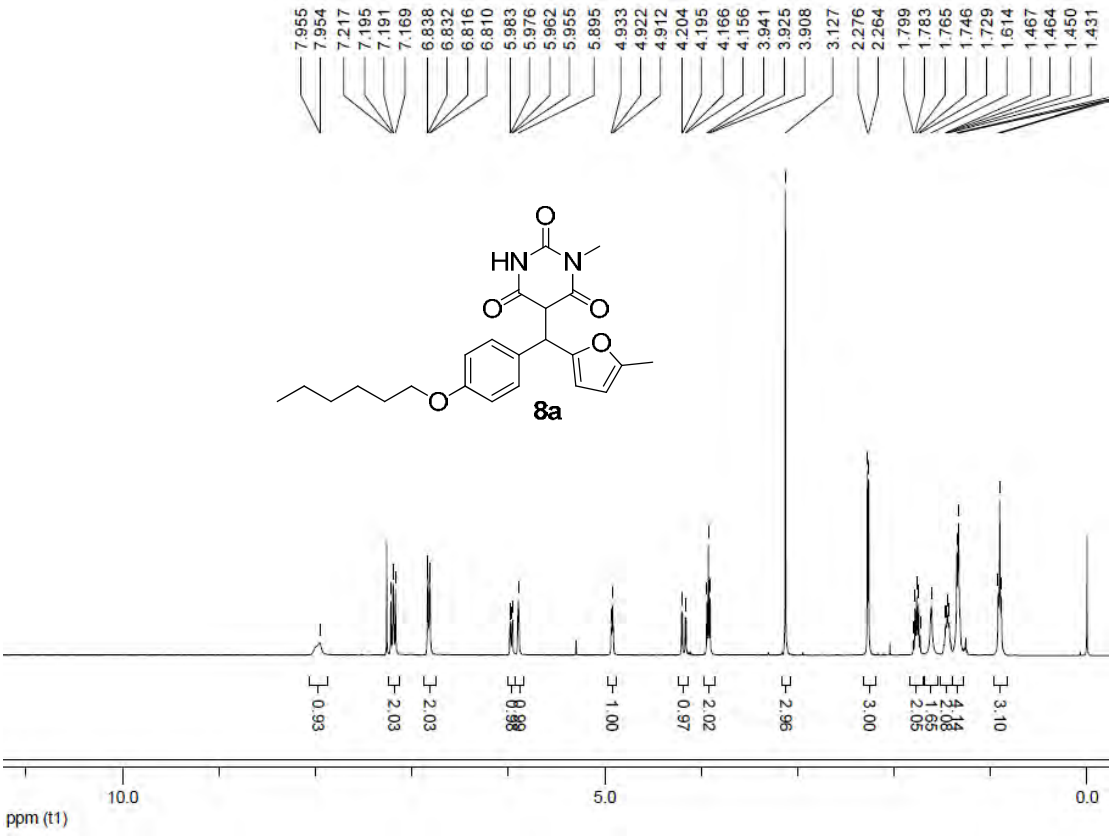
100
50
0
ppm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6.810
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5.962
5.955
5.895
4.933
4.922
4.912
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4.195
4.166
4.156
3.941
3.925
3.908
3.127
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2.264
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1.783
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1.746
1.729
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1.467
1.464
1.450
1.431
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O
O
O
O
O
8a
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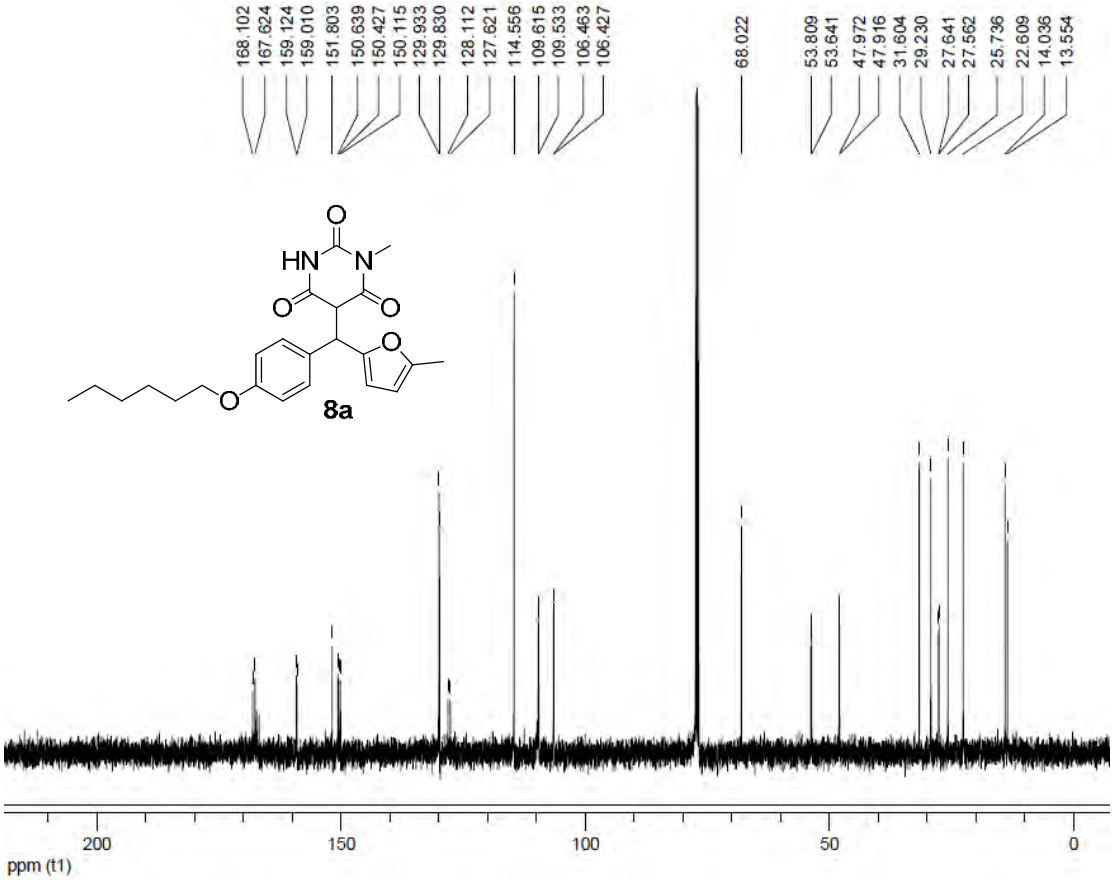
ppm (t1)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109.533
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106.427
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53.641
47.972
47.916
31.604
29.230
27.641
27.562
25.736
22.609
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O
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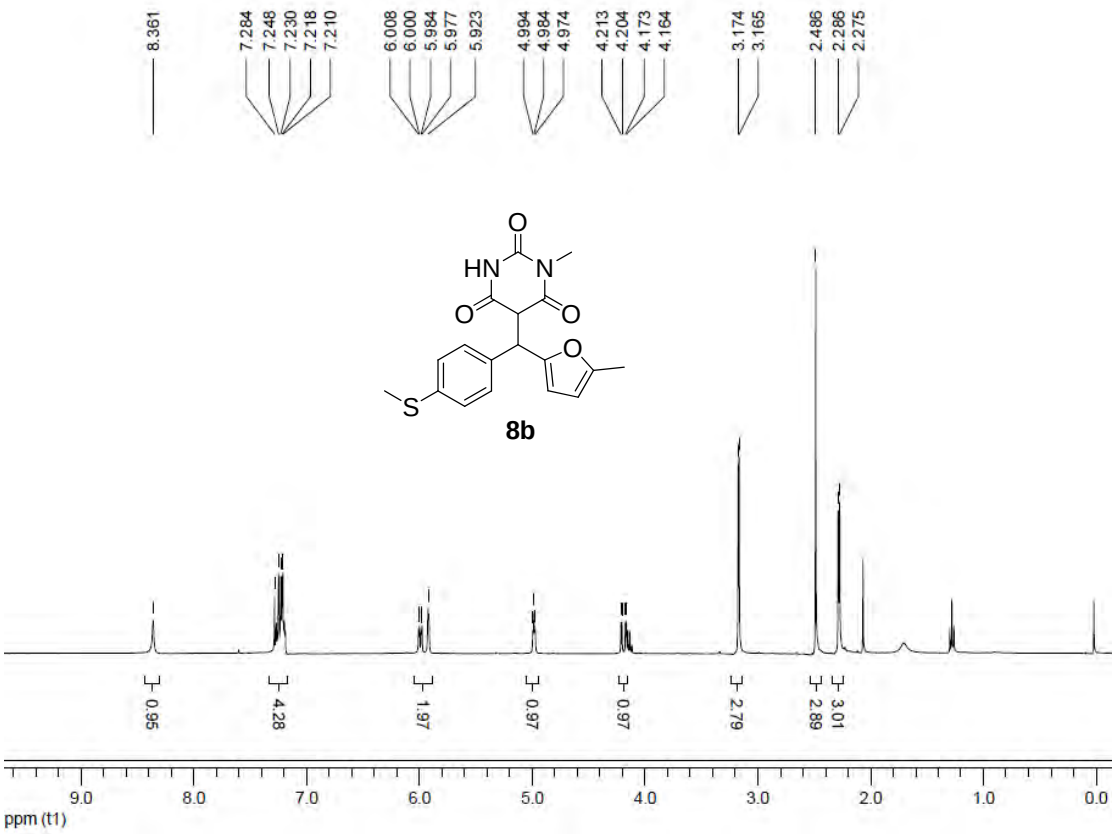
50
0
ppm (t1)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6.000
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5.977
5.923
4.994
4.984
4.974
4.213
4.204
4.173
4.164
3.174
3.165
2.486
2.286
2.275
HN
N
O
O
O
O
S
8b
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4.28
1.97
0.97
0.97
2.79
2.89
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7.0
6.0
5.0
4.0
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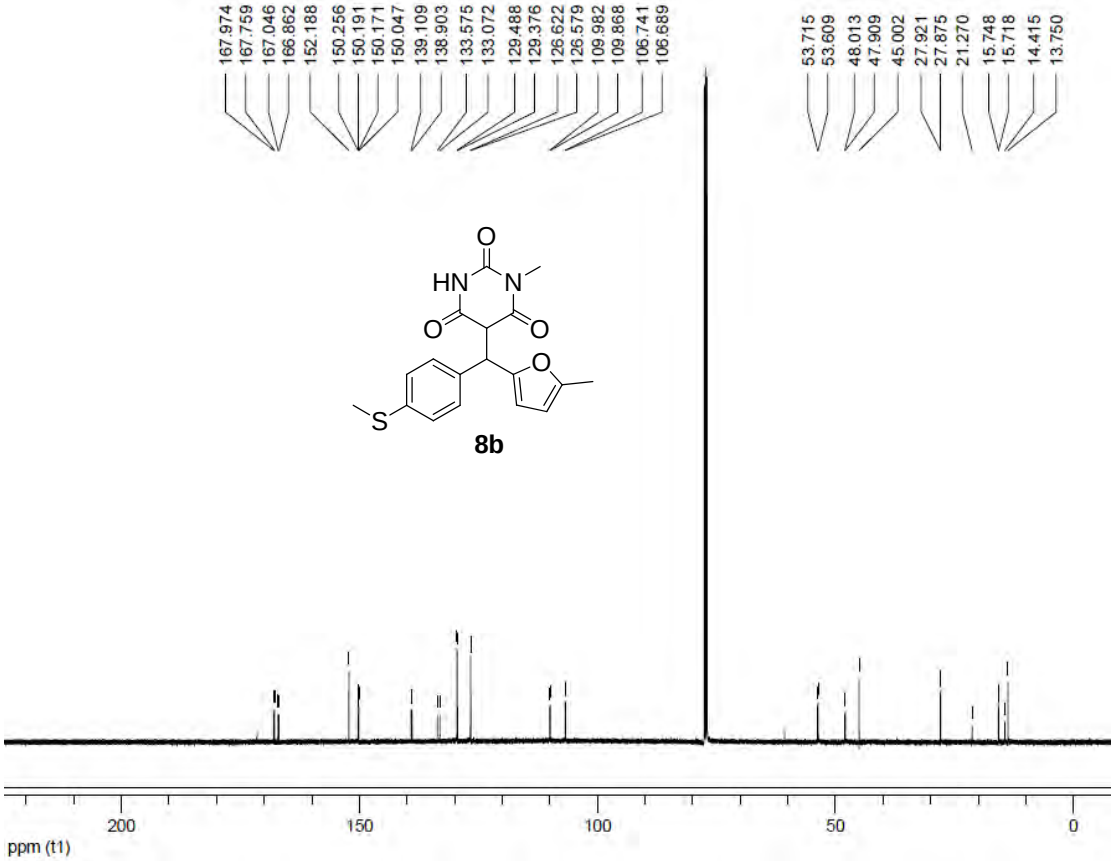
2.0
1.0
0.0
ppm (t1)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150.256
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150.171
150.047
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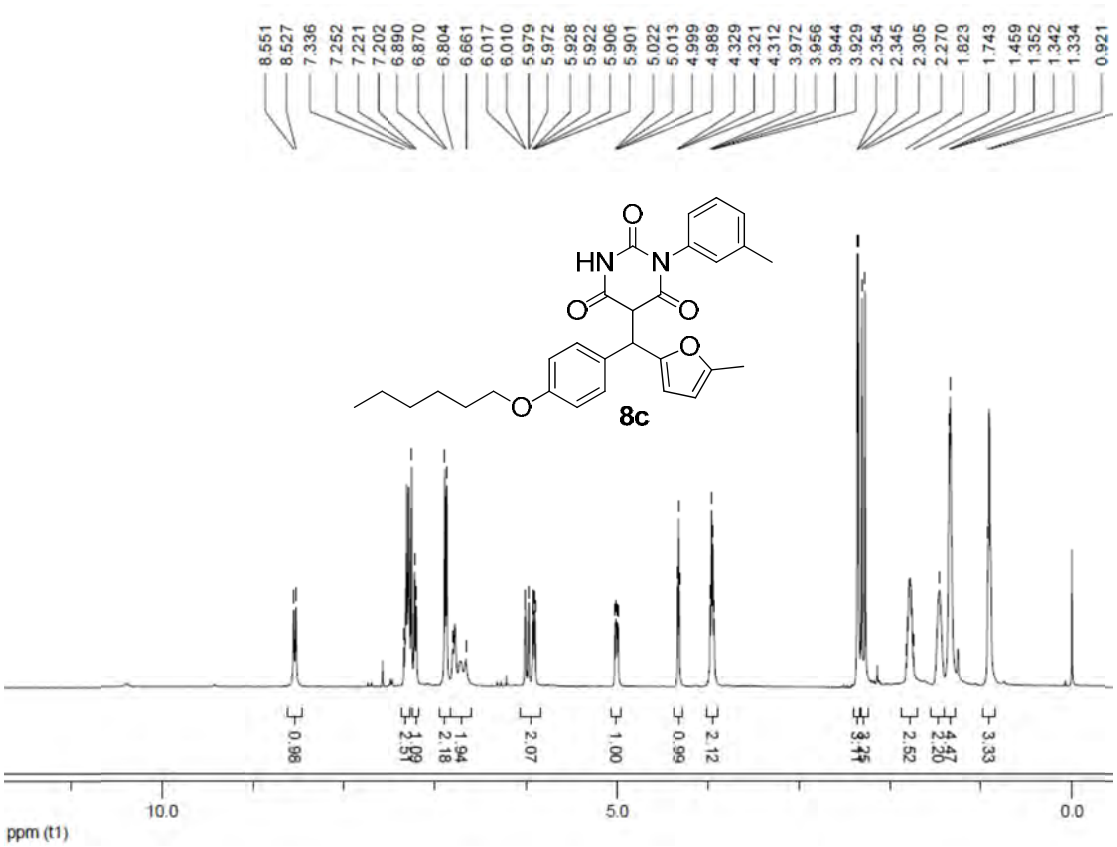
138.903
133.575
133.072
129.488
129.376
126.622
126.579
109.982
109.868
106.741
106.689
53.715
53.609
48.013
47.909
45.002
27.921
27.875
21.270
15.748
15.718
14.415
13.750
HN
N
O
O
O
O
S
8b
200
150
100
50
0
ppm (t1)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5.922
5.906
5.901
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3.929
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1.823
1.743
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O
O
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2.07
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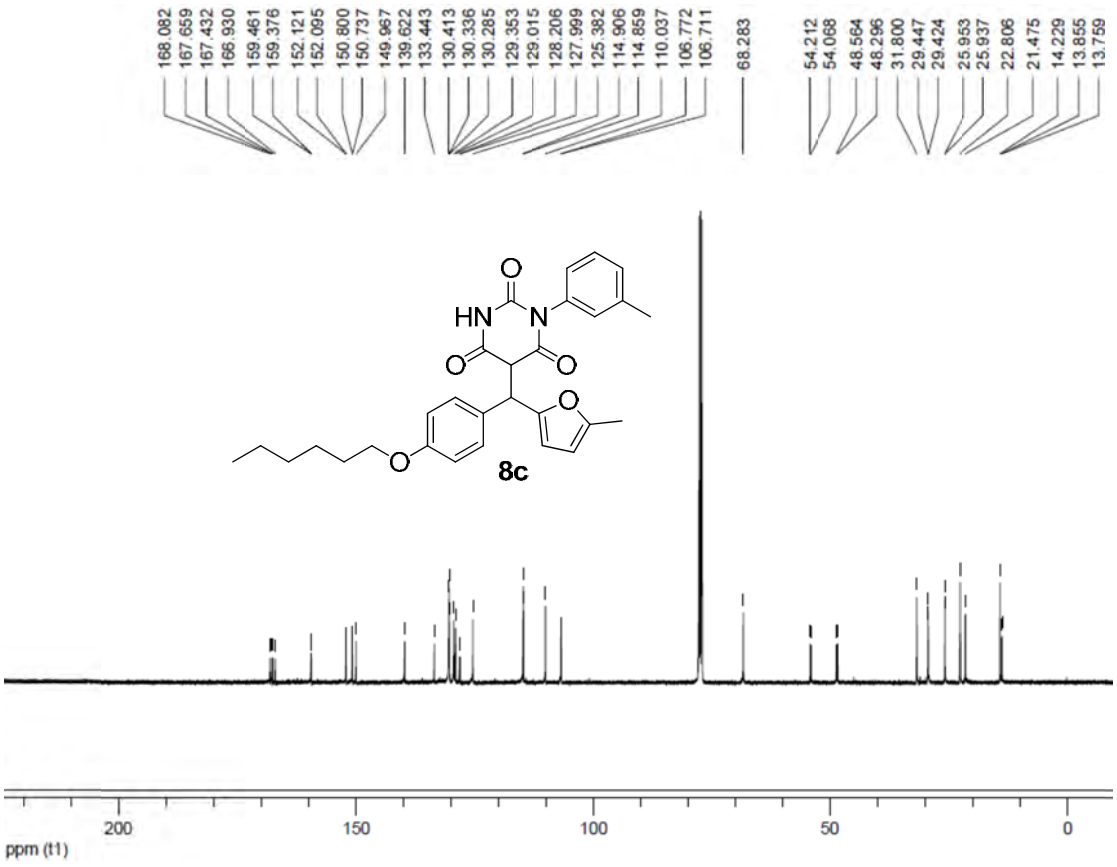
ppm (t1)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114.859
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106.772
106.711
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54.068
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48.296
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29.424
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25.937
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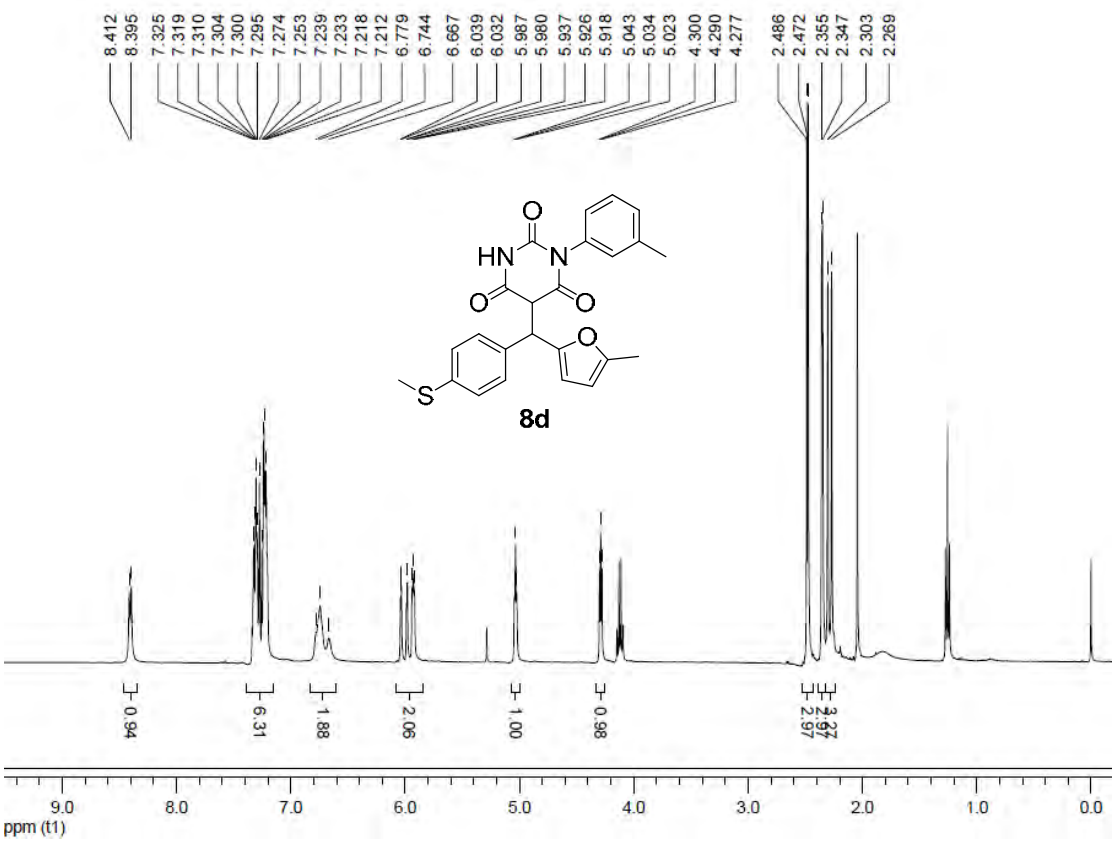
ppm (t1)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7.233
7.218
7.212
6.779
6.744
6.667
6.039
6.032
5.987
5.980
5.937
5.926
5.918
5.043
5.034
5.023
4.300
4.290
4.277
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2.355
2.347
2.303
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HN
N
O
O
O
O
S
8d
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2.06
1.00
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2.97
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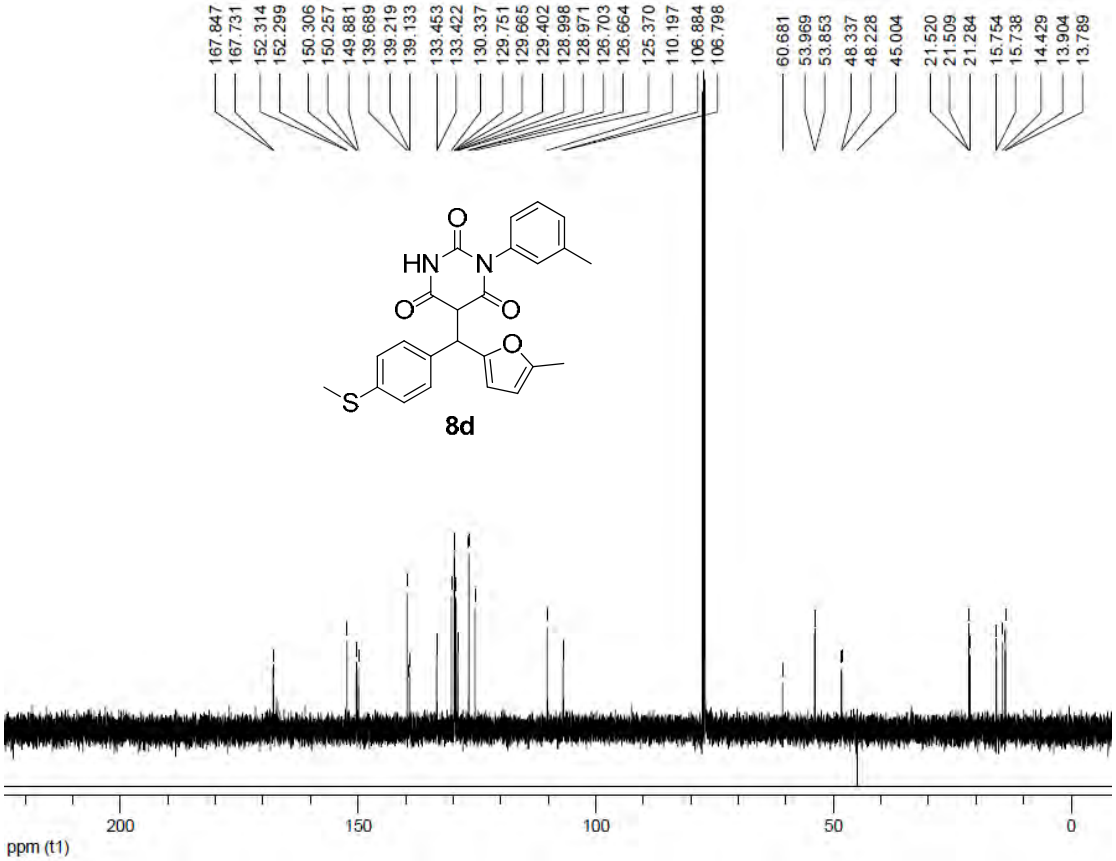
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130.337
129.751
129.665
129.402
128.998
128.971
126.703
126.664
125.370
110.197
106.884
106.798
60.681
53.969
53.853
48.337
48.228
45.004
21.520
21.509
21.284
15.754
15.738
14.429
13.904
13.789
HN
N
O
O
O
O
S
8d
200
150
100
50
0
ppm (t1)

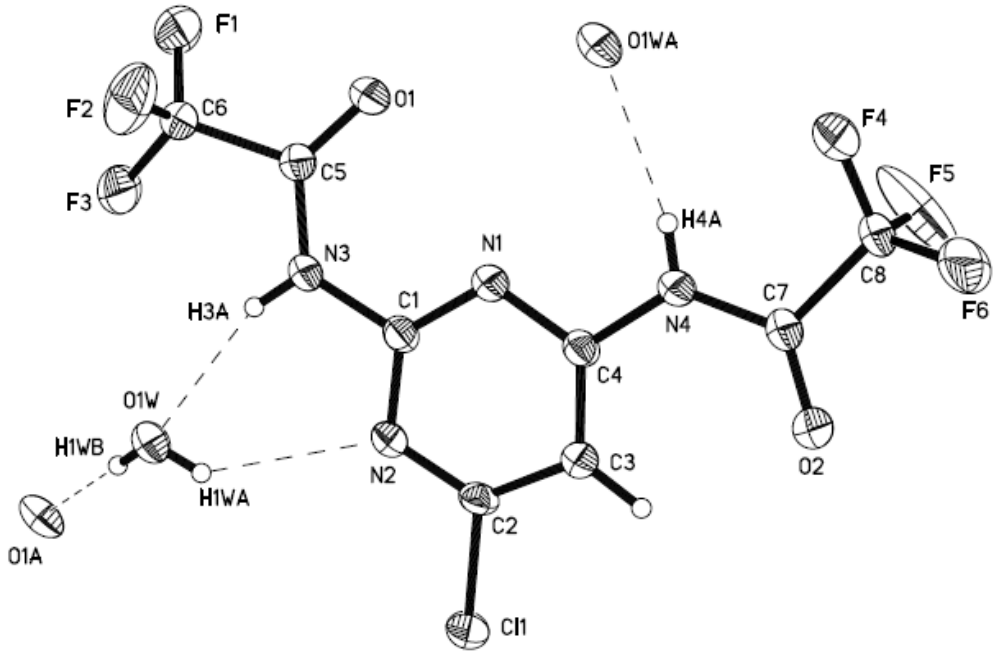
X-Ray Crystallography of 1a

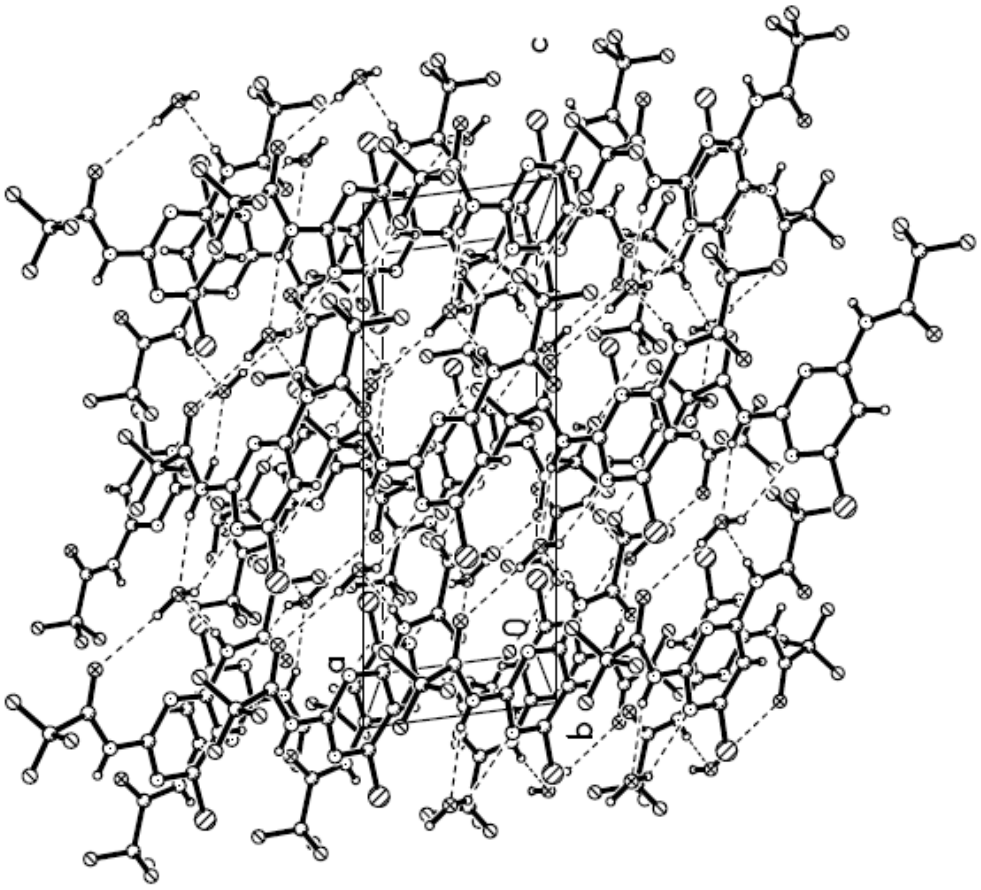
Table 1. Crystal data and structure refinement for BCLKC35 (13 Mar 2013).

Identification code	lkc35	
Empirical formula	$(C_8 H_3 Cl F_6 N_4 O_{3)} .H_2O$	
Formula weight	354.61	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.0503(2) Å	α= 90°.
	b = 18.9742(7) Å	β= 97.537(2)°.
	c = 13.6338(5) Å	γ = 90°.
Volume	1295.18(8) $Å^3$	
Z	4	
Density (calculated)	1.819 Mg/m^3	
Absorption coefficient	0.389 mm^{-1}	
F(000)	704	
Crystal size	0.60 x 0.40 x 0.30 mm^3	
Theta range for data collection	1.85 to 29.27°.	
Index ranges	-6<=h<=6, -25<=k<=25, -18<=l<=18	
Reflections collected	23780	
Independent reflections	3410 [R(int) = 0.0440]	
Completeness to theta = 29.27°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5904	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3410 / 0 / 220	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0844, wR2 = 0.2172	
R indices (all data)	R1 = 0.1113, wR2 = 0.2413	
Extinction coefficient	0.016(2)	
Largest diff. peak and hole	0.797 and -0.558 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for lkc35. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	5384(2)	692(1)	7024(1)	71(1)
O(1W)	-502(4)	2536(1)	7099(1)	56(1)
O(1)	69(5)	2846(1)	3379(2)	64(1)
O(2)	9961(5)	475(1)	3911(2)	66(1)
N(1)	3860(4)	1927(1)	4266(2)	45(1)
N(2)	3011(5)	1665(1)	5914(2)	45(1)
N(3)	749(4)	2560(1)	5032(2)	46(1)
N(4)	6850(5)	1331(1)	3481(2)	48(1)
C(1)	2635(5)	2018(1)	5055(2)	42(1)
C(2)	4830(5)	1159(1)	5945(2)	44(1)
C(3)	6257(5)	993(1)	5179(2)	45(1)
C(4)	5667(5)	1402(1)	4340(2)	42(1)
C(5)	-277(5)	2933(1)	4224(2)	46(1)
C(6)	-2026(7)	3557(2)	4466(2)	58(1)
C(7)	8784(5)	868(2)	3322(2)	48(1)
C(8)	9428(6)	877(2)	2245(2)	54(1)
F(1)	-3935(5)	3679(1)	3735(2)	88(1)
F(2)	-614(6)	4130(1)	4595(2)	109(1)
F(3)	-3169(5)	3446(1)	5266(2)	110(1)
F(4)	8798(6)	1474(2)	1792(2)	138(1)
F(5)	8169(8)	405(2)	1738(2)	173(1)
F(6)	11930(5)	799(2)	2210(2)	109(1)


F1
F2
C6
F3
O1
C5
N3
H3A
O1W
H1WB
H1WA
O1A
C1
N1
N2
C2
Cl1
C3
C4
O1WA
H4A
N4
C7
O2
F4
F5
C8
F6


c
b