

Supplementary Information

Label-Assisted Mass Spectrometry for the Acceleration of Reaction Discovery and Optimization

Jaime R. Cabrera-Pardo,¹ David I. Chai,¹ Song Liu,¹ Milan Mrksich² and Sergey A. Kozmin*¹

Chicago Tri-Institutional Center for Chemical Methods and Library Development

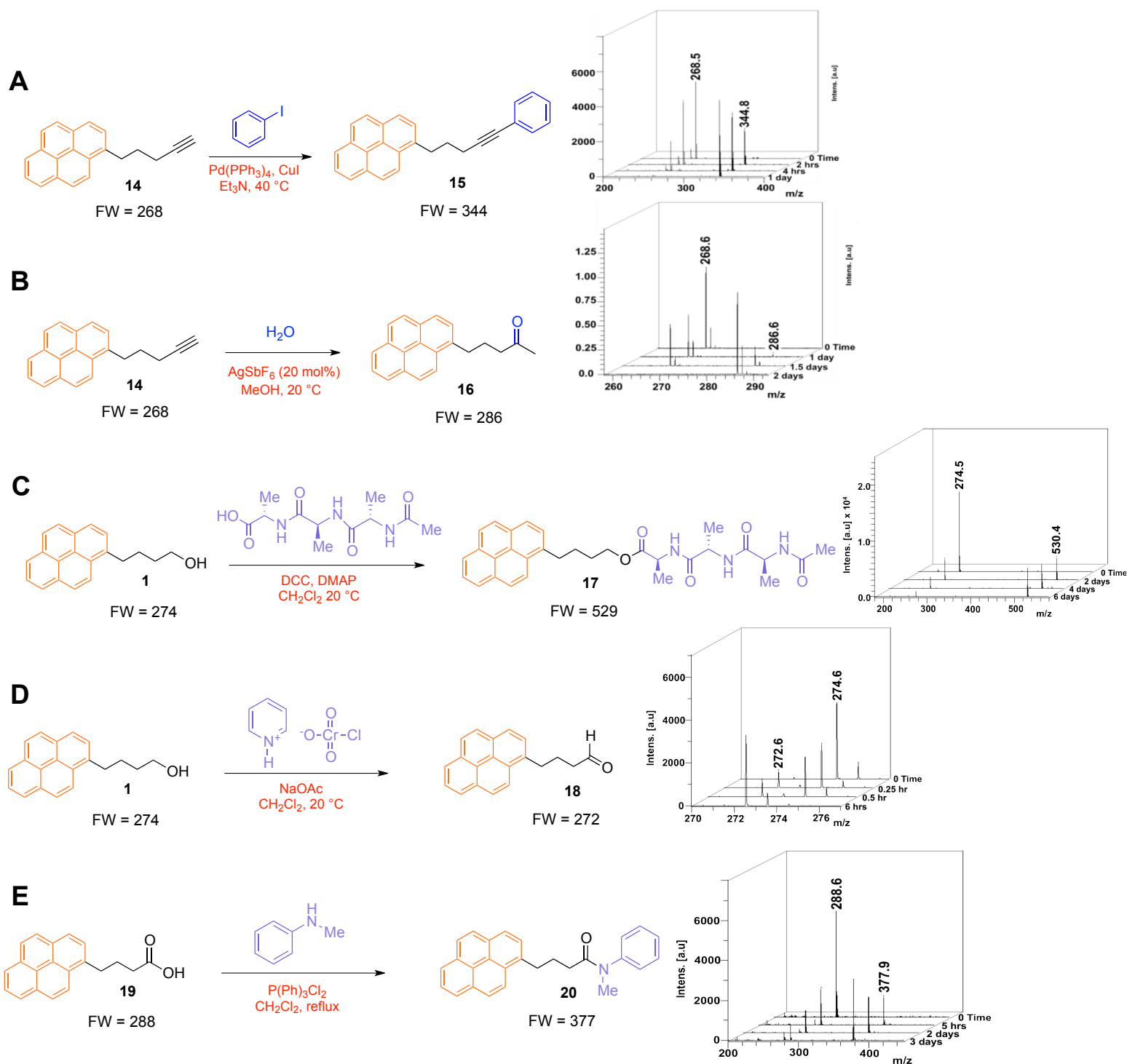
¹Department of Chemistry, University of Chicago, Chicago, IL 60637, USA

²Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

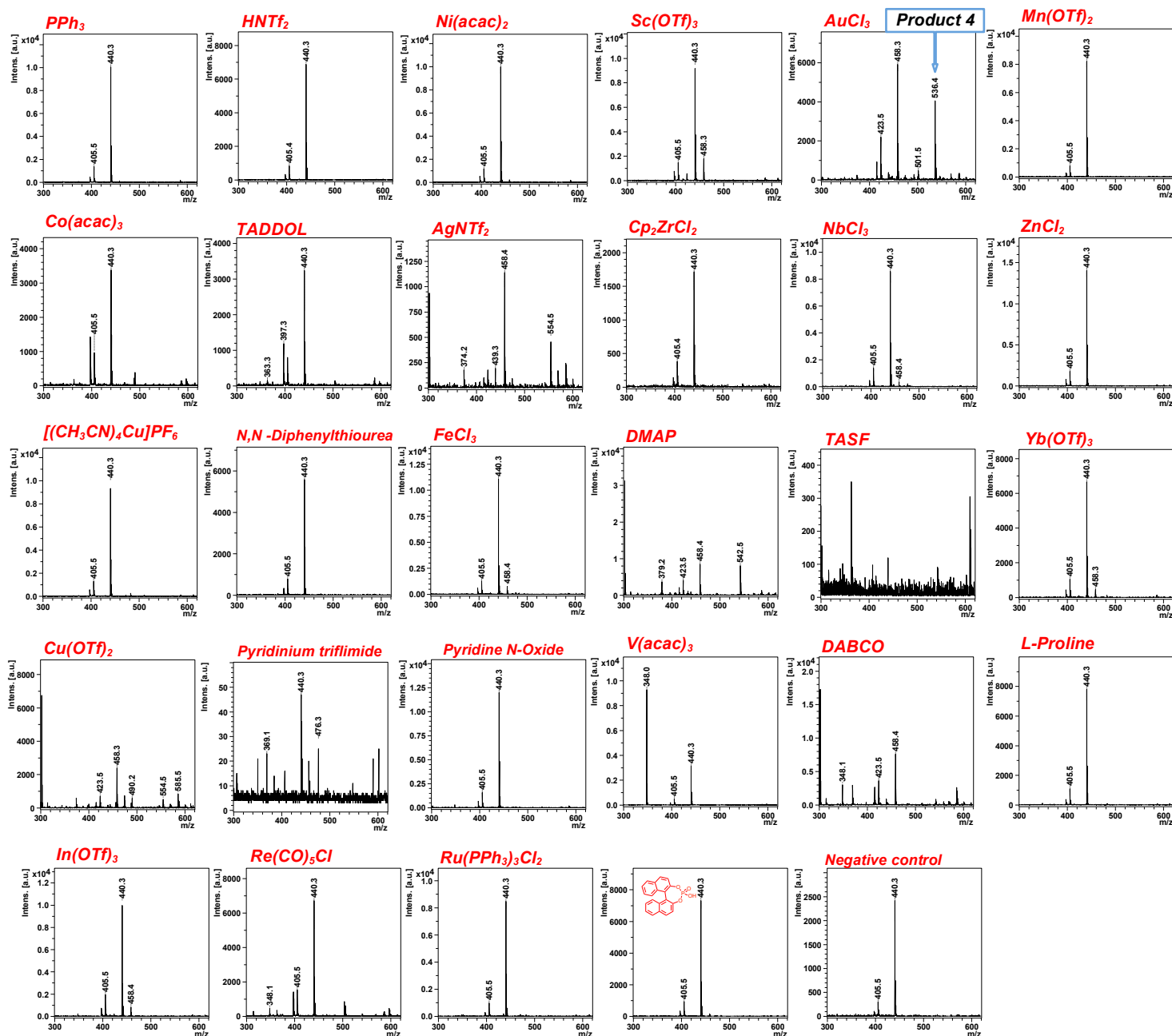
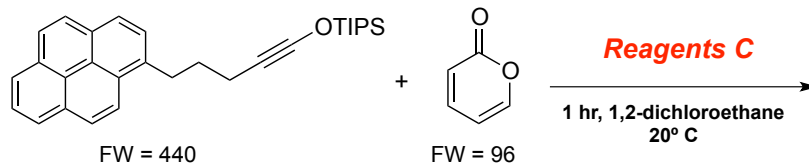
*e-mail: skozmin@uchicago.edu

Table of Contents

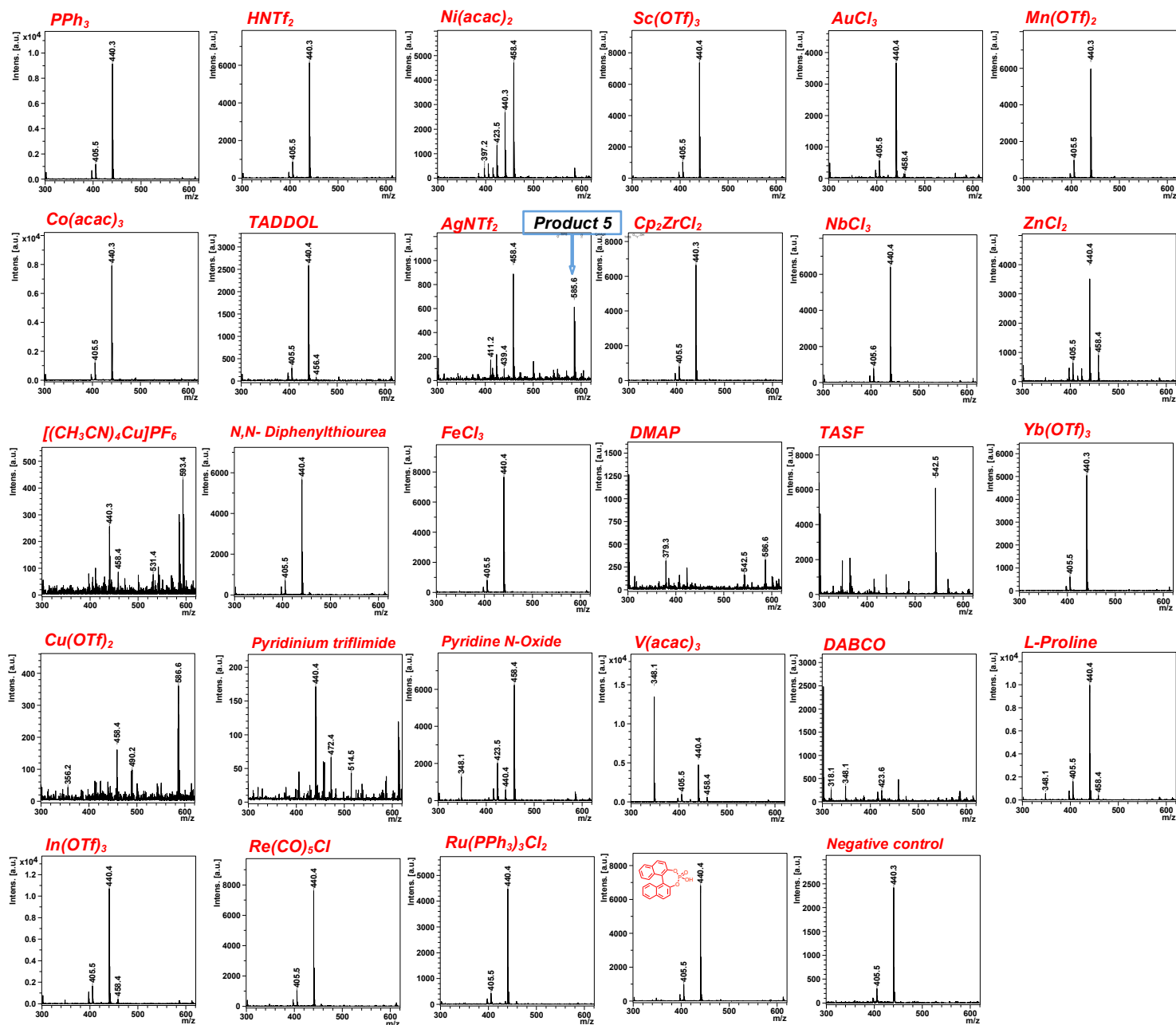
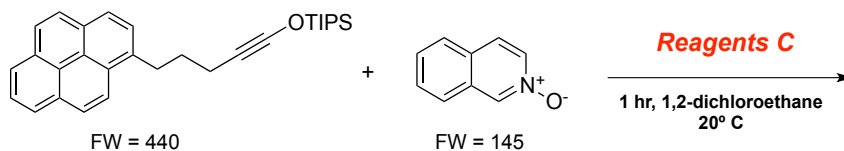
Supplementary Figures	3
Supplementary Tables	6
Supplementary Methods	
General procedures for organic synthesis	8
Experimental procedures and compound characterization	8
Supplementary References	19
Supplementary Data	
NMR data	20
X-Ray crystallographic data	55



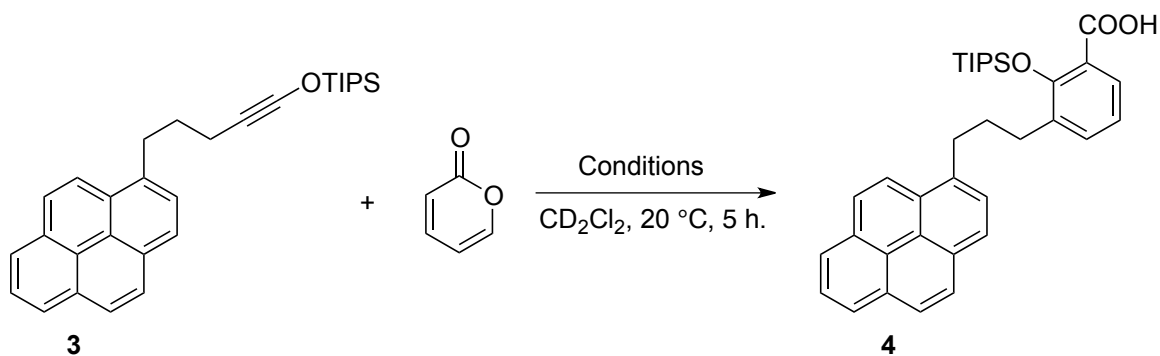
Supplementary Figure S1. Use of LA-LDI-TOF-MS to monitor progress of known reactions. A, Reaction scheme and MS spectra for conversion of terminal alkyne **14** to Sonogashira product **15**. **B,** Reaction scheme and MS spectra for conversion of terminal alkyne **14** to ketone **16**. **C,** Reaction scheme and MS spectra for conversion of terminal alcohol **1** to ester **17**. **D,** Reaction scheme and MS spectra for conversion of terminal alcohol **1** to aldehyde **18**. **E,** Reaction scheme and MS spectra for conversion of carboxylic acid **19** to amide **20**.



Supplementary Figure S2. Representative mass spectrometry data. Reaction scheme and MS spectra for each of the 28 reagents and negative solvent control. Formation of product 4 observed using AuCl_3 .



Supplementary Figure S3. Representative mass spectrometry data. Reaction scheme and MS spectra for each of the 28 reagents and negative solvent control. Formation of product 5 observed using AgNTf₂.



Entry	Catalyst	Catalyst Loading	Conversion (%) ^a	Conversion (%) ^b
1	AuCl ₃	3 mol%	20.5	19.9
2	PPH ₃ AuNTf ₂	3 mol%	1.63	1.66
3		1 mol%	0.0	0.0
4		1 mol%	48.9	50.0
5 ^c		1 mol%	81.0	80.9

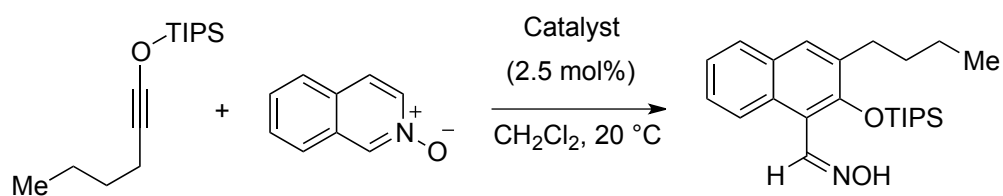
Siloxy alkyne concentration 0.1 M.

^a Conversion to **4** calculated by LA-LDI-MS.

^b Conversion to **4** calculated by analysis of the crude reaction mixtures using ¹H NMR spectroscopy.

^c Further optimization of the reaction gave 2.5 mol% of **8** and 0.3 M of siloxy alkyne as the best conditions. (> 95 % yield determined by 500 MHz ¹H NMR using an internal standard).

Supplementary Table S1. Catalyst screen of benzannulation reaction between siloxy alkyne and 2-pyrone.

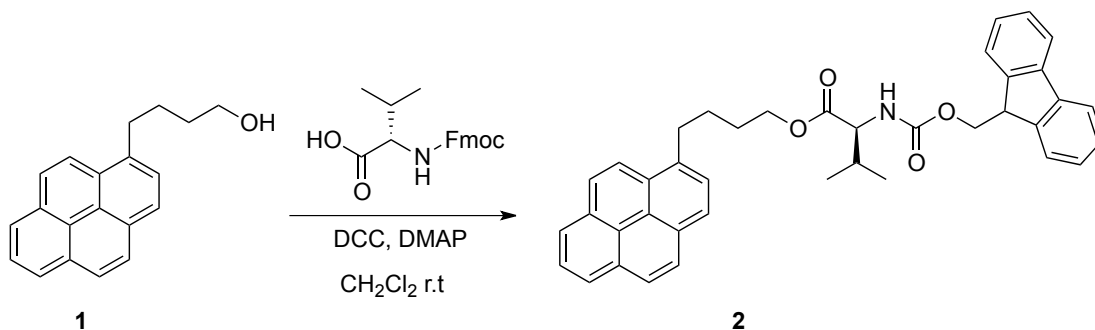


Entry	Catalyst	Concentration of siloxy alkyne	Yield, % ^a
1	AgNTf ₂	0.10 M	63
2	AgSbF ₆	0.10 M	34
3	AuCl ₃	0.10 M	47
4	Ph ₃ PAuNTf ₂	0.10 M	12
5		0.10 M	42
6		0.10 M	59
7		0.10 M	76
8		0.30 M	89

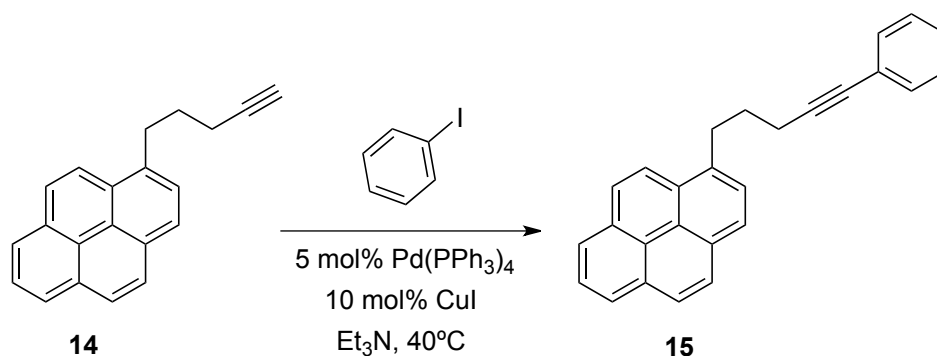
^a Isolable yield.

Supplementary Table S2. Catalyst screen of benzannulation reaction between siloxy alkyne and Isoquinoline *N*-oxide.

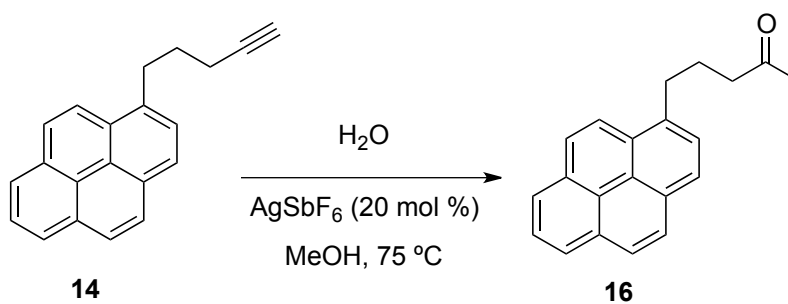
General procedures for organic synthesis. Hexanes (ACS grade) and ethyl acetate (ACS grade) were purchased from Fisher Scientific and used without further purification. Dichloromethane was distilled over calcium hydride under a positive pressure of nitrogen. Unless otherwise noted, all reactions were performed under an inert atmosphere of nitrogen in flame-dried vials equipped with a stirbar and a cap with PTFE insert. Other commercially available reagents were obtained from Sigma-Aldrich, Strem or Alfa Aesar and were used without further purification unless otherwise noted. For siloxy alkyne synthesis, triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) was distilled under reduced pressure over calcium hydride and hexamethyldisilazane (HMDS) was distilled under positive pressure of nitrogen over calcium hydride. Solution-phase reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Column chromatography was performed by CombiFlash[®] using Silicycle silica gel column (12g, 230-400 mesh). NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, tt = triplet of triplets, q = quartet, ddd = doublet of doublet of doublets, br = broad, m = multiplet) and coupling constants in Hertz (Hz). ¹H and ¹³C NMR spectra were recorded on a Bruker DMX-500 instrument and chemical shifts are reported in ppm using residual solvent peaks as internal standards. High resolution mass spectra were recorded with a Waters Q-TOF Ultima tandem quadrupole/time-of-flight instrument. Siloxy alkynes were prepared according to the known procedure¹. (E,E)-1,4-diphenyl-1-aza-buta-1,3-diene and (p-tolyl-meth-(E)-ylidene)pyridin-2-yl-amine) were synthesized by established methods^{2,3}. 4-chloro-2H-pyran-2-one and 4-phenyl-2H-pyran-2-one were prepared according to the known methods^{4,5}. Isoquinolines N-oxides were synthesized by known methods^{6,7,8}.



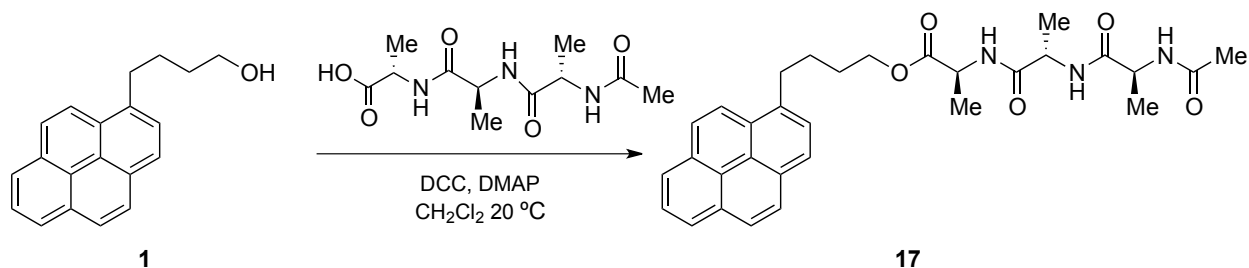
Under a nitrogen atmosphere, a solution of 1-pyrenebutanol **1** (50 mg, 0.182 mmol) and Fmoc-Val-OH (61.77 mg, 0.182 mmol) in dichloromethane (5 mL) was treated with N,N'-dicyclohexylcarbodiimide (37.55 mg, 0.182 mmol), N,N-dimethylpyridin-4-amine (2.22 mg, 0.0182 mmol) and stirred at room temperature. Immediately after adding N,N-dimethylpyridin-4-amine, 1 μ L of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. Additional LDI-MS data of the reaction were taken over time. After 4 days product **2** was isolated as a white solid (93%, 101.7 mg) by silica gel flash chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.22 (1H, d, J = 9.5 Hz), 8.14 (2H, d, J = 7.5 Hz), 8.08 (2H, d, J = 9.5 Hz), 8.00 (2H, s), 7.97 (1H, t, J = 7.5 Hz), 7.83 (1H, d, J = 7.5 Hz), 7.73 (2H, d, J = 7.0 Hz), 7.56 (2H, t, J = 7.0 Hz), 7.37 (2H, t, J = 5.5 Hz), 7.28 (2H, t, J = 8.0 Hz), 5.28 (1H, d, J = 9.5 Hz), 4.37 (2H, dd, J = 7.5, 4.0 Hz), 4.30 (1H, dd, J = 9.5, 5.0 Hz), 4.21-4.19 (3H, m), 3.36 (2H, t, J = 8.0 Hz), 2.15-2.11 (1H, m), 1.94-1.91 (2H, m), 1.83-1.80 (2H, m), 0.93 (3H, d, J = 6.5 Hz), 0.85 (3H, d, J = 7.0 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 156.4, 144.0, 143.9, 141.4, 136.2, 131.5, 131.0, 130.0, 128.7, 127.8, 127.6, 127.5, 127.3, 127.2, 126.8, 126.0, 125.2, 125.18, 125.11, 124.99, 124.93, 123.3, 120.1, 67.2, 65.3, 59.2, 47.3, 33.1, 31.5, 28.7, 28.2, 19.1, 17.7. HRMS-ES⁺ calc'd for C₄₀H₃₈NO₄ [M+H]⁺ 596.2801, found [M+H]⁺ 596.2806.



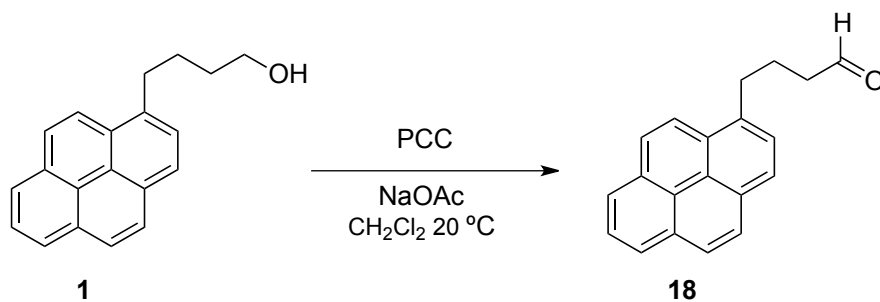
A solution of $\text{Pd(PPh}_3)_4$ (17.3 mg, 0.015 mmol), CuI (5.7 mg, 0.03 mmol) and iodobenzene (44.6 μL , 0.4 mmol) in triethylamine (10 mL) was treated dropwise with a solution of **14** (80 mg, 0.3 mmol) in triethylamine (5 mL) over 10 min. Immediately after complete addition of alkyne **14**, 1 μL of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. The reaction was then warmed up to 40 $^\circ\text{C}$ and stirred under nitrogen atmosphere. Additional LDI-MS data of the reaction were taken over time. After 24 hours, the crude reaction was diluted with dichloromethane (50 mL) followed by an aqueous work up. Purification by silica gel flash chromatography afforded **15** as a white solid (80%, 82.2 mg). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.35 (1H, d, $J = 10$ Hz), 8.15 (2H, dd, $J = 7.5, 2.5$ Hz), 8.10 (2H, t, $J = 10$ Hz), 8.01 (2H, d, $J = 2.5$ Hz), 7.97 (1H, t, $J = 7.5$ Hz), 7.91 (1H, d, $J = 7.5$ Hz), 7.46 (2H, dd, $J = 7.5, 2.0$ Hz), 7.332-7.289 (3H, m), 3.53 (2H, t, $J = 8.0$ Hz), 2.53 (2H, t, $J = 7.0$ Hz), 2.16 (2H, tt, $J = 8.0, 7.0$ Hz). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 136.1, 131.7, 131.6, 131.1, 130.1, 128.9, 128.4, 127.8, 127.7, 127.6, 127.5, 126.8, 126.0, 125.3, 125.2, 125.08, 125.01, 124.9, 124.1, 123.58, 90.0, 81.6, 32.6, 30.8, 19.4. HRMS- EI^+ calc'd for $\text{C}_{27}\text{H}_{20}$ $[\text{M}]^+$ 344.15650, found $[\text{M}]^+$ 344.15745.



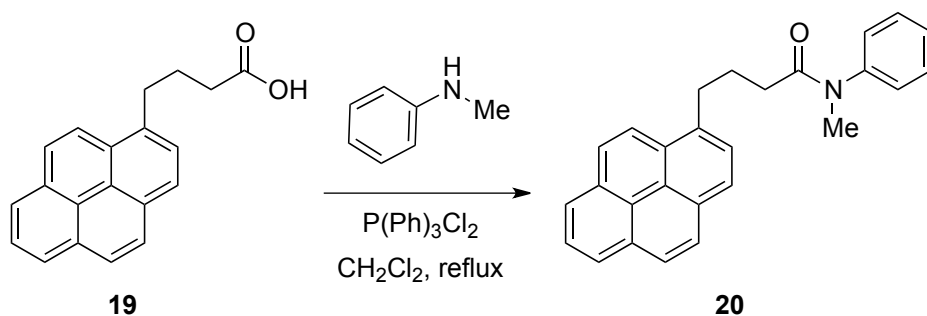
A solution of **14** (20 mg, 0.074 mmol) in 1.5 mL of a mixture of $\text{MeOH}/\text{H}_2\text{O}$ (10/1) was prepared. The resulting mixture was treated with AgSbF_6 (5.08 mg, 0.015 mmol). Immediately after adding AgSbF_6 , 1 μL of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. The reaction was then warmed up to 75 $^\circ\text{C}$ and stirred under a nitrogen atmosphere. Additional LDI-MS data of the reaction were taken over time. After 2 days, the solvent was evaporated and product **16** was isolated as a white solid (45%, 9.4 mg) by silica gel flash chromatography. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.29 (1H, d, $J = 9.0$ Hz), 8.15 (1H, d, $J = 5.5$ Hz), 8.13 (1H, d, $J = 4.5$ Hz), 8.10 (1H, d, $J = 3.5$ Hz), 8.08 (1H, d, $J = 2.5$ Hz), 8.01 (2H, d, $J = 1.0$ Hz), 7.97 (1H, t, $J = 7.5$ Hz), 7.82 (1H, d, $J = 7.5$ Hz), 3.34 (2H, t, $J = 7.5$ Hz), 2.53 (2H, t, $J = 7.0$ Hz), 2.14-2.11 (5H, m). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 208.9, 136.1, 131.6, 131.1, 130.1, 129.0, 127.6, 127.59, 127.52, 126.9, 126.0, 125.2, 125.19, 125.11, 124.99, 124.97, 123.5, 43.1, 32.7, 30.2, 25.7. HRMS- EI^+ calc'd for $\text{C}_{21}\text{H}_{18}\text{O}$ $[\text{M}]^+$ 286.13577, found $[\text{M}]^+$ 286.13519.



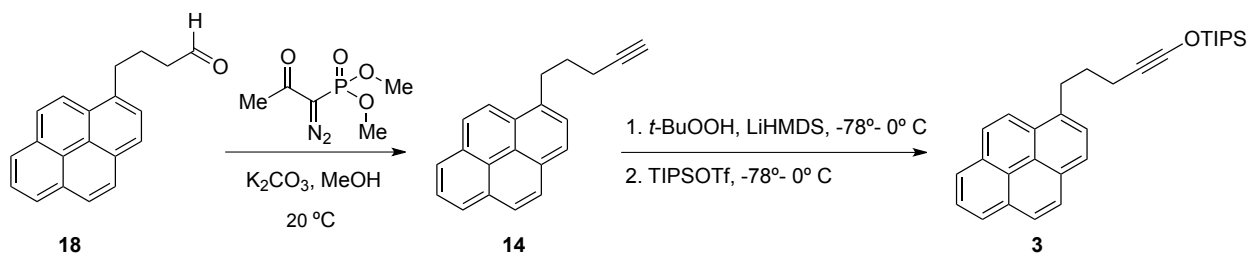
Under a nitrogen atmosphere, a solution of 1-pyrenebutanol **1** (10 mg, 0.036 mmol) and N-acetyl-Ala-Ala (9.8 mg, 0.036 mmol) in dichloromethane (2 mL) was treated with N,N'-dicyclohexylcarbodiimide (7.43mg, 0.036 mmol), N,N-dimethylpyridin-4-amine (0.44 mg, 0.0036 mmol) and stirred at room temperature. Immediately after adding N,N-dimethylpyridin-4-amine, 1 μL of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. Additional LDI-MS data of the reaction were taken over time. After 6 days, product **17** was isolated as a white solid (69%, 13.1 mg) by silica gel flash chromatography. ^1H NMR (500 MHz, CDCl_3) δ 8.20 (1H, d, $J = 9.0$ Hz), 8.12 (2H, dd, $J = 7.5, 3.5$ Hz), 8.08 (1H, s), 8.06 (1H, t, $J = 2.5$ Hz), 7.99 (2H, s), 7.96 (1H, t, $J = 7.5$ Hz), 7.80 (1H, d, $J = 8.0$ Hz), 7.17 and 7.16 (1H, d, $J = 7.0$ Hz), 7.10 and 7.04 (1H, d, $J = 7.0$ Hz), 6.70 and 6.55 (1H, d, $J = 7.0$ Hz), 4.63-4.48 (3H, m), 4.20-4.13 (2H, m), 3.33 (2H, t, $J = 7.5$ Hz), 1.97 and 1.95 (3H, s), 1.92-1.85 (2H, m), 1.82-1.74 (2H, m), 1.36-1.31 (9H, m). ^{13}C NMR (125 MHz, CDCl_3) δ (173.0, 172.9), (172.45, 172.43), (171.8, 171.7), (170.3, 170.1), 136.2, 131.6, 131.0, 130.0, 128.7, 127.6, 127.5, 127.4, 126.8, 126.0, 125.2, 125.18, 125.14, 125.0, 124.95, 123.3, (65.54, 65.51), (49.2, 49.02), (49.00, 48.93), (48.39, 48.36), 33.1, 28.7, 28.1, 23.2, (19.3, 19.1), (19.0, 18.7), (18.4, 18.3). HRMS-ES $^+$ calc'd for $\text{C}_{31}\text{H}_{36}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 530.2655, found $[\text{M}+\text{H}]^+$ 530.2664.



Under a nitrogen atmosphere, a solution of 1-pyrenebutanol **1** (20 mg, 0.072 mmol) and pyridinium chlorochromate (31.04 mg, 0.144 mmol) in dichloromethane (1.0 mL) was treated with sodium acetate (11.8 mg, 0.144 mmol) and stirred at room temperature. Immediately after adding sodium acetate, 1 μL of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. Additional LDI-MS data of the reaction were taken over time. After 6 hours product **18** was isolated as a yellowish solid (70%, 13.7 mg) by silica gel flash chromatography. ^1H NMR (500 MHz, CDCl_3) δ 9.73 (1H, s), 8.23 (1H, d, $J = 10$ Hz), 8.16 (2H, dd, $J = 7.5, 2.5$ Hz), 8.08 (2H, dd, $J = 9.0, 6.5$ Hz), 8.01 (2H, s), 7.98 (1H, t, $J = 7.5$ Hz), 7.78 (1H, d, $J = 8.0$ Hz), 3.29 (2H, t, $J = 7.5$), 2.47 (2H, td, $J = 7.0, 1.5$ Hz), 2.12 (2H, tt, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 202.2, 135.5, 131.4, 130.9, 130.0, 128.7, 127.56, 127.53, 127.3, 126.8, 125.9, 125.1, 125.07, 125.04, 124.9, 124.8, 123.2, 43.4, 32.6, 23.9. HRMS-EI $^+$ calc'd for $\text{C}_{20}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 272.12012, found $[\text{M}]^+$ 272.12080.

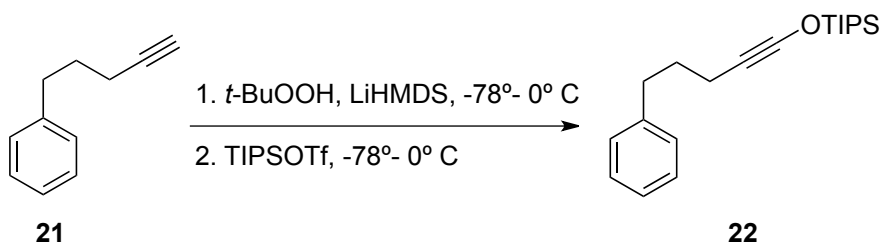


A solution of 1-pyrenebutyric acid **19** (100 mg, 0.347 mmol) and N-methylaniline (45.1 μL , 0.416 mmol) in dichloromethane (10 mL) was treated with dichlorotriphenylphosphorane (277.6 mg, 0.833 mmol) and stirred under a nitrogen atmosphere. Immediately after adding dichlorotriphenylphosphorane, 1 μL of the crude reaction mixture was manually loaded onto a MALDI plate, dried at room temperature for 5 min and then analyzed by LDI-MS. The reaction was then warmed up to reflux. Additional LDI-MS data of the reaction were taken over time. After 5 days, product **20** was isolated as a white solid (55%, 71.4 mg) by silica gel flash chromatography. ^1H NMR (500 MHz, CDCl_3) δ 8.22 (1H, d, $J = 10$ Hz), 8.13 (2H, dd, $J = 7.5, 3.0$ Hz), 8.05 (1H, d, $J = 10$ Hz), 8.01 (1H, d, $J = 10$ Hz), 7.98 (2H, s), 7.96 (1H, t, $J = 10$ Hz), 7.72 (1H, d, $J = 7.5$ Hz), 7.19 (2H, t, 7.0 Hz), 7.13 (1H, d, $J = 7.5$ Hz), 7.02 (2H, d, $J = 6.0$ Hz), 3.27-3.24 (5H, m), 2.19 (2H, t, $J = 6.5$ Hz), 2.11 (2H, tt, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 144.1, 136.3, 131.5, 131.0, 129.9, 129.7, 128.8, 127.7, 127.6, 127.39, 127.37, 127.34, 126.7, 125.9, 125.19, 125.15, 124.9, 124.86, 124.84, 123.7, 37.4, 33.9, 33.0, 27.5. HRMS-ES⁺ calc'd for $\text{C}_{27}\text{H}_{24}\text{NO}$ $[\text{M}+\text{H}]^+$ 378.1858, found $[\text{M}+\text{H}]^+$ 378.1863.

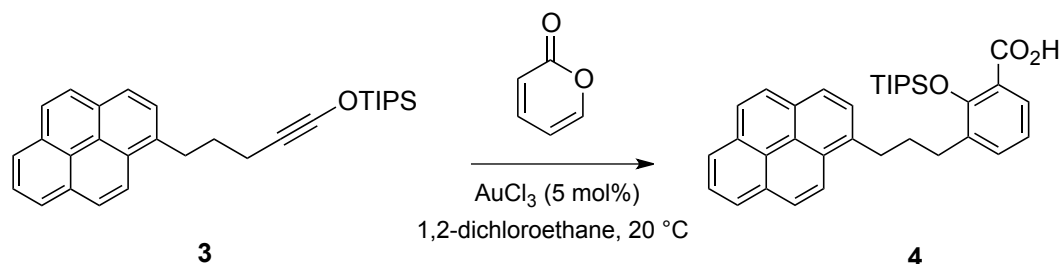


Alkyne 14. A solution of **18** (365 mg, 1.342 mmol) and K_2CO_3 (371 mg, 2.68 mmol) in MeOH (36 mL, anhydrous) was treated with dimethyl (1-diazo-2-oxopropyl)phosphonate (242 μL , 1.61 mmol) and stirred under nitrogen atmosphere at room temperature. After complete consumption of starting material as indicated by TLC, the crude reaction was diluted with ether (50 mL) and washed with saturated aqueous solution of NaHCO_3 (2 times, 50 mL). The organic layer was washed with brine and dried over MgSO_4 . After evaporation of the solvent and isolation by silica gel flash chromatography product **14** was afforded as a white solid (77%, 278.6 mg). ^1H NMR (500 MHz, CDCl_3) δ 8.29 (1H, d, $J = 10$ Hz), 8.15 (2H, dd, $J = 7.5, 3$ Hz), 8.10 (1H, s), 8.09 (1H, d, $J = 2$ Hz), 8.01 (2H, d, $J = 2$ Hz), 7.97 (1H, t, $J = 7.5$ Hz), 7.88 (1H, d, $J = 7.5$ Hz), 3.46 (2H, t, $J = 7.0$ Hz), 2.31 (2H, td, $J = 7.0, 2.5$ Hz), 2.07 (2H, tt, $J = 7.0$ Hz), 2.07 (1H, t, 2.5 Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 135.8, 131.5, 131.0, 130.0, 128.8, 127.6, 127.49, 127.45, 126.8, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 123.4, 84.4, 69.1, 32.3, 30.4, 18.4. HRMS-EI⁺ calculated for $\text{C}_{21}\text{H}_{16}$ $[\text{M}]^+$ 268.12520, found $[\text{M}]^+$ 268.12616.

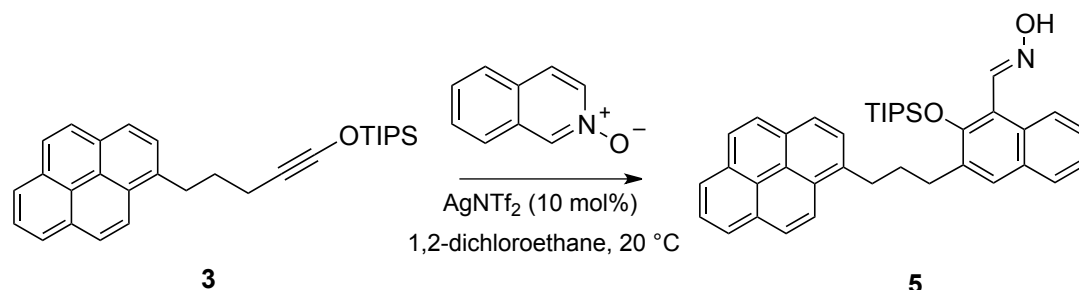
Siloxy alkyne 3. A 100 mL three-necked flame dried round bottomed flask, fitted with rubber septa and a nitrogen line, was charged with tetrahydrofuran (15 mL) and **14** (996.7 mg, 3.72 mmol). The resulting solution was cooled down to -78 °C and treated with *t*-BuOOH (708 μ L, 5.78 M solution in nonane, 4.092 mmol) (CAUTION! OXIDANTS AND OXIDABLES MAY VIOLENTLY REACT). Freshly prepared LiHMDS (9.672 mL, 1M, 9.672 mmol) was added to the reaction via a syringe pump over 30 min. The reaction mixture was warmed up to 0 °C in an ice water bath and stirred for 2.25 hours. Then, the reaction mixture was cooled down to -78 °C and TIPSOTf (1.1 mL, 4.092 mmol) was added dropwisely over 10 min and stirred at -78 °C for 5 min. Finally, the reaction mixture was warmed up again to 0 °C and allowed to stir for 40 min. The crude mixture was diluted with hexanes (25 mL), transferred to a separatory funnel and washed with a saturated solution of NaHCO₃ (2 x 100 mL). The organic layer was then collected and washed with a saturated solution of Na₂S₂O₃ (100 mL) followed by brine (100 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. By products were removed by Kugelrohr distillation (60 °C, 1 hour) and siloxy alkyne **3** was obtained after purification over basic alumina flash chromatography giving a yellowish oil (54%, 877.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.32 (1H, d, J = 10 Hz), 8.15 (2H, t, J = 5 Hz), 8.09 (2H, t, J = 10 Hz), 8.01 (2H, d, J = 5 Hz), 7.98 (1H, t, J = 5 Hz), 7.88 (1H, d, J = 5 Hz), 3.44 (2H, t, J = 10 Hz), 2.25 (2H, t, J = 10 Hz), 1.99 (2H, tt, J = 10 Hz), 1.31 (3H, m, J = 5 Hz), 1.17 (18H, d, J = 5 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 136.7, 131.5, 131.0, 129.9, 128.8, 127.6, 127.4, 127.2, 126.6, 125.8, 125.2, 125.1, 124.91, 124.90, 124.7, 123.6, 87.6, 32.7, 32.1, 30.3, 17.6, 17.5, 12.0. HRMS-EI⁺ calc'd for C₃₀H₃₆OSi [M]⁺ 440.25355, found [M]⁺ 440.25276.



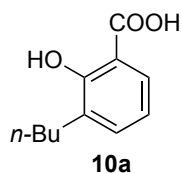
Siloxy alkyne 22. A 500 ml three-necked flamed dried round bottomed flask, fitted with a rubber septa and a nitrogen line was filled with tetrahydrofuran (100 mL) and **21** (5.26 mL, 34.66 mmol). The resulting solution was then cooled down to -78 °C and treated with *t*-BuOOH (6.6 mL, 5.78 M solution in nonane, 38.13 mmol) (CAUTION! OXIDANTS AND OXIDABLES MAY VIOLENTLY REACT). Freshly prepared LiHMDS (90.12 mL, 1M, 90.12 mmol) was added to the reaction via a syringe pump over 30 min. The reaction mixture was warmed up to 0 °C in an ice water bath and stirred for 2.25 hours. Then, the reaction mixture was cooled down to -78 °C and TIPSOTf (10.25 mL, 38.13 mmol) was added dropwisely over 10 min and stirred at -78 °C for 5 min. Finally, the reaction mixture was warmed up again to 0 °C and allowed to stir for 40 min. The crude mixture was then diluted with hexanes (150 mL), transferred to a separatory funnel and washed with a saturated solution of NaHCO₃ (2 x 150 mL). The organic layer was then collected and washed with a saturated solution of Na₂S₂O₃ (150 mL) followed by brine (150 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The siloxy alkyne **22** was purified by Kugelrohr distillation as a clear oil (85%, 9.29 gr). ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.28 (2H, m), 7.22-7.20 (3H, m), 2.73 (2H, t, J = 5.0 Hz), 2.14 (2H, t, J = 5 Hz), 1.77 (2H, tt, J = 5 Hz), 1.33-1.28 (3H, m), 1.17 (18H, d, J = 10 Hz). ¹³C NMR (125 MHz, CDCl₃) δ 142.4, 128.6, 128.4, 125.8, 87.3, 35.1, 31.9, 30.2, 17.5, 17.0, 12.0. HRMS-ES⁺ calc'd for C₂₀H₃₃OSi [M+H]⁺ 317.2301, found [M+H]⁺ 317.2302



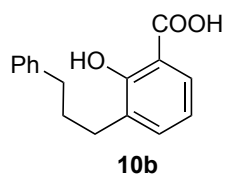
Carboxylic Acid 4. A solution of 2-pyrone (12.04 μL , 0.15 mmol) and catalyst AuCl_3 (2.27 mg, 0.0075 mmol) in 1,2-dichloroethane (0.2 mL) was prepared in a dram vial. The resulting mixture was treated with a solution of siloxyalkyne **3** (99 mg, 0.225 mmol) in 1,2-dichloroethane (0.3 mL). The mixture was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure and the carboxylic acid **4** was purified by column chromatography. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 11.3 (1H, s), 8.13 (1H, d, $J = 9.5$ Hz), 8.03 (2H, dd, $J = 7.5, 1.5$ Hz), 7.99 (1H, d, $J = 8.0$ Hz), 7.96 (1H, D, $J = 9.5$ Hz), 7.92 – 7.85 (3H, m), 7.79 (1H, d, $J = 8.0$ Hz), 7.66 (1H, dd, $J = 8.0, 2.0$ Hz), 7.24 (1H, dd, $J = 7.0, 1.0$ Hz), 6.71 (1H, t, $J = 7.5$ Hz), 3.31 (2H, t, $J = 8.0$ Hz), 2.79 (2H, t, $J = 7.5$ Hz), 2.11 (2H, quintet, $J = 8.0$ Hz), 1.33 (3H, septet, $J = 7.5$ Hz), 1.05 (18H, d, $J = 7.5$ Hz). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 169.8, 159.6, 135.8, 134.7, 130.4, 129.9, 129.4, 128.7, 127.6, 127.6, 126.5, 126.1, 126.0, 125.4, 124.6, 124.0, 124.0, 123.7, 123.7, 123.5, 122.4, 117.3, 112.1, 32.3, 30.4, 28.8, 16.7, 11.0. HRMS-EI calc'd for $\text{C}_{35}\text{H}_{40}\text{O}_3\text{Si}$ [M^+] 536.27468, found [M^+] 536.27408.



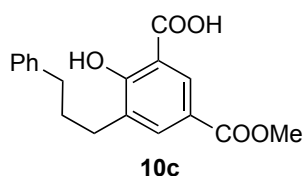
Oxime 5. A solution of isoquinoline *N*-oxide (21.7 mg, 0.15 mmol) and catalyst AgNTf_2 (5.82 mg, 0.015 mmol) in 1,2-dichloroethane (0.2 mL) was prepared in a dram vial. The resulting mixture was treated with a solution of siloxyalkyne **3** (99 mg, 0.225 mmol) in 1,2-dichloroethane (0.3 mL). The mixture was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure and the oxime **5** was purified by column chromatography. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 11.5 (1H, s), 9.32 (1H, s), 8.31 (1H, d, $J = 9.0$ Hz), 8.19 (2H, d, $J = 7.5$ Hz), 8.16 (1H, d, $J = 7.5$ Hz), 8.11 (1H, d, $J = 9.0$ Hz), 8.06 (2H, d, $J = 5.5$ Hz), 8.03 (2H, dd, $J = 10.0, 2.0$ Hz), 7.79 (1H, d, $J = 7.5$ Hz), 7.73 (1H, d, $J = 7.5$ Hz), 7.68 (1H, s), 7.50 (1H, dt, $J = 6.5, 1.0$ Hz), 7.36 (1H, dt, $J = 7.0, 0.5$ Hz), 3.51 (2H, t, $J = 7.5$ Hz), 3.09 (2H, t, $J = 7.5$ Hz), 2.38 (2H, quintet, $J = 8.0$ Hz), 1.41 (3H, m), 1.22 (18H, d, $J = 7.5$ Hz). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 157.0, 153.4, 136.9, 131.4, 131.2, 130.9, 130.9, 129.8, 128.7, 128.4, 128.2, 127.5, 127.2, 127.1, 126.5, 126.5, 125.8, 125.1, 125.0, 124.8, 124.8, 124.6, 123.5, 123.4, 120.0, 106.8, 100.0, 33.4, 31.2, 30.6, 17.9, 11.9. HRMS-EI calc'd for $\text{C}_{39}\text{H}_{43}\text{NO}_2$ [M^+] 585.30631, found [$\text{M}^+ + 2\text{H}$] 587.31884.



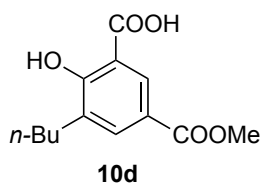
Carboxylic Acid **10a** was prepared in 89% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 10.6 (1H, s), 7.72 (1H, dd, $J = 8.0, 1.5$ Hz), 7.30 (1H, dd, $J = 7.5, 1.0$ Hz), 6.8 (1H, t, $J = 7.5$ Hz), 2.60 (2H, t, $J = 7.5$ Hz), 1.53 (2H, quintet, $J = 7.5$ Hz), 1.32 (2H, sextet, $J = 7.5$ Hz), 0.87 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 175.3, 160.4, 137.0, 131.5, 128.4, 118.9, 110.6, 31.6, 29.3, 22.5, 14.0. HRMS-EI calc'd for $\text{C}_{11}\text{H}_{14}\text{O}_3$ [M^+] 194.0943, found [M^+] 194.09349.



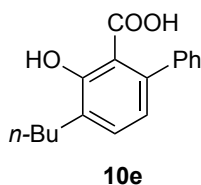
Carboxylic Acid **10b** was prepared in 80% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 10.6 (1H, br s), 7.72 (1H, dd, $J = 8.0, 1.5$ Hz), 7.30 (1H, d, $J = 7.0$ Hz), 7.21 (2H, t, $J = 7.5$ Hz), 7.12 (3H, m), 6.78 (1H, t, $J = 7.5$ Hz), 2.65 (2H, t, $J = 7.5$ Hz), 2.62 (2H, t, $J = 8.0$ Hz), 1.90 (2H, quintet, $J = 8.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 160.5, 142.3, 137.0, 130.9, 128.6, 128.4, 128.3, 125.7, 118.9, 110.8, 35.7, 30.9, 29.4. HRMS-EI calc'd for $\text{C}_{16}\text{H}_{16}\text{O}_3$ [M^+] 256.10995, found [M^+] 256.10921.



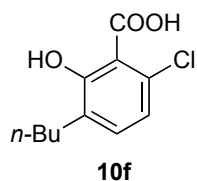
Carboxylic Acid **10c** was prepared in 65% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.7 (1H, s), 8.42 (1H, d, $J = 2.0$ Hz), 7.91 (1H, d, $J = 2.0$ Hz), 7.21 (2H, m), 7.10 (3H, m), 3.82 (3H, s), 2.67 – 2.60 (4H, m), 1.90 (2H, quintet, $J = 8.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 166.5, 164.0, 142.1, 136.3, 130.9, 130.9, 128.4, 128.3, 125.7, 120.4, 111.7, 52.0, 35.7, 30.8, 29.3. HRMS-ESI calc'd for $\text{C}_{18}\text{H}_{18}\text{O}_5$ [M^+] 314.1154, found [$\text{M}+\text{H}^+$] 315.1229.



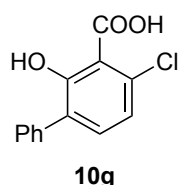
Carboxylic Acid **10d** was prepared in 70% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 12.0 (1H, s), 8.39 (1H, d, $J = 2.0$ Hz), 7.89 (1H, d, $J = 1.0$ Hz), 3.81 (3H, s), 2.60 (2H, t, $J = 7.5$ Hz), 1.54 (2H, quintet, $J = 8.0$ Hz), 1.32 (2H, sextet, $J = 7.5$ Hz), 0.87 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 172.7, 166.4, 163.9, 135.9, 131.2, 130.6, 120.1, 112.0, 51.8, 31.3, 29.1, 22.4, 13.9. HRMS-ESI calc'd for $\text{C}_{13}\text{H}_{16}\text{O}_5$ [M^+] 252.0998, found [$\text{M}+\text{H}^+$] 253.1083.



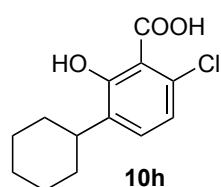
Carboxylic Acid **10e** was prepared in 83% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.3 (1H, brs), 7.28 - 7.18 (6H, m), 6.62 (1H, d, $J = 7.5$ Hz), 2.61 (2H, t, $J = 8.0$ Hz), 1.56 (2H, quintet, $J = 7.5$ Hz), 1.34 (2H, sextet, $J = 7.5$ Hz), 0.88 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 160.4, 142.8, 142.7, 134.1, 130.4, 128.5, 127.7, 126.8, 122.0, 110.4, 31.5, 29.6, 22.6, 14.0. HRMS-ESI calc'd for $\text{C}_{17}\text{H}_{18}\text{O}_3$ [M^+] 270.1256, found [$\text{M}+\text{H}^+$] 271.1342.



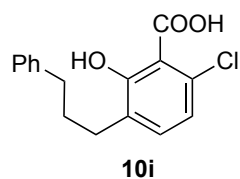
Carboxylic Acid **10f** was prepared in 98% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.3 (1H, brs), 7.15 (1H, d, $J = 8.0$ Hz), 6.87 (1H, d, $J = 8.0$ Hz), 2.56 (2H, t, $J = 7.5$ Hz), 1.50 (2H, quintet, $J = 8.0$ Hz), 1.30 (2H, sextet, $J = 7.5$ Hz), 0.87 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 162.2, 135.4, 132.2, 130.9, 122.1, 109.6, 31.2, 29.4, 22.5, 13.9. HRMS-EI calc'd for $\text{C}_{11}\text{H}_{13}\text{ClO}_3$ [M^+] 228.05533, found [M^+] 228.05598.



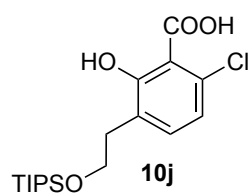
Carboxylic Acid **10g** was prepared in 53% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 12.2 (1H, brs), 7.46 (2H, d, $J = 7.5$ Hz), 7.35 (2H, t, $J = 7.5$ Hz), 7.27 (2H, m), 6.95 (1H, d, $J = 8.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 172.2, 160.7, 136.9, 134.7, 134.4, 129.3, 129.1, 128.1, 127.4, 122.2, 112.4. HRMS-EI calc'd for $\text{C}_{13}\text{H}_9\text{ClO}_3$ [M^+] 248.02403, found [M^+] 248.02470.



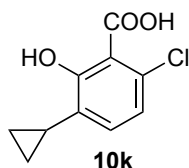
Carboxylic Acid **10h** was prepared in 94% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.9 (1H, brs), 7.09 (1H, d, $J = 8.0$ Hz), 6.82 (1H, d, $J = 8.5$ Hz), 2.87 (1H, t, $J = 12.0$ Hz), 1.77 (4H, t, $J = 13.0$ Hz), 1.67 (1H, d, $J = 13.0$ Hz), 1.40 – 1.32 (2H, m), 1.28 – 1.15 (4H, m). ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 161.1, 134.8, 132.1, 131.1, 121.8, 111.3, 36.5, 32.7, 26.9, 26.3. HRMS-EI calc'd for $\text{C}_{13}\text{H}_{15}\text{ClO}_3$ [M^+] 254.07098, found [M^+] 254.07040.



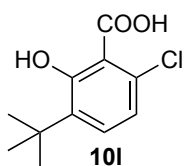
Carboxylic Acid **10i** was prepared in 93% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.2 (1H, s), 7.21 (2H, m), 7.13 (4H, m), 6.86 (1H, d, $J = 8.0$ Hz), 2.60 (4H, t, $J = 7.5$ Hz), 1.86 (2H, quintet, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 173.8, 162.2, 142.1, 135.4, 132.6, 130.3, 128.4, 128.3, 125.8, 122.2, 109.8, 35.6, 30.6, 29.5. HRMS-EI calc'd for $\text{C}_{16}\text{H}_{15}\text{ClO}_3$ [M^+] 290.07098, found [M^+] 290.07192.



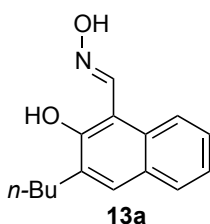
Carboxylic Acid **10j** was prepared in 93% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.0 (1H, brs), 7.18 (1H, d, $J = 8.0$ Hz), 6.86 (1H, d, $J = 8.0$ Hz), 3.86 (2H, t, $J = 6.5$ Hz), 2.83 (2H, t, $J = 6.0$ Hz), 1.00 (3H, m), 0.96 (9H, d, $J = 6.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 172.8, 160.8, 136.1, 132.7, 127.0, 122.0, 111.9, 62.9, 33.9, 17.9, 11.9. HRMS-ESI calc'd for $\text{C}_{18}\text{H}_{29}\text{ClO}_4\text{Si}$ [M^+] 373.1602, found [$\text{M}+\text{H}^+$] 373.1597.



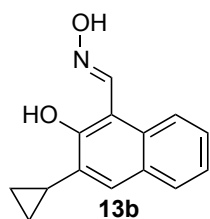
Carboxylic Acid **10k** was prepared in 97% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.8 (1H, brs), 6.78 (2H, m), 2.07 (1H, m), 0.87 (2H, m), 0.54 (2H, m). ^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 162.5, 131.9, 130.8, 129.7, 121.7, 111.2, 9.4, 7.3. HRMS-EI calc'd for $\text{C}_{10}\text{H}_9\text{ClO}_3$ [M^+] 212.02403, found [M^+] 212.02462.



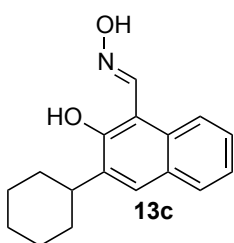
Carboxylic Acid **10l** was prepared in 67% yield according to a general procedure for benzannulation of siloxy alkynes and 2-pyrones. ^1H NMR (500 MHz, CDCl_3) δ 11.7 (1H, s), 7.29 (1H, d, $J = 8.5$ Hz), 6.87 (1H, d, $J = 8.0$ Hz), 1.33 (9H, s). ^{13}C NMR (125 MHz, CDCl_3) δ 174.0, 163.4, 137.5, 132.7, 132.6, 121.8, 109.9, 35.0, 29.1. HRMS-EI calc'd for $\text{C}_{11}\text{H}_{13}\text{ClO}_3$ [M^+] 228.05533, found [M^+] 228.05626.



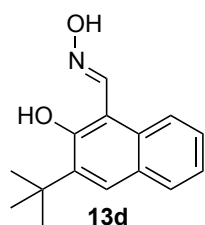
Oxime **13a** was prepared in 92% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 11.17 (1H, s), 9.16 (1H, s), 7.94 (1H, d, $J = 8.5$ Hz), 7.74 (1H, d, $J = 8.0$ Hz), 7.64 (1H, s), 7.49 – 7.44 (1H, m), 7.41 (1H, s), 7.37 – 7.33 (1H, m), 2.86 – 2.79 (2H, m), 1.76 – 1.67 (2H, m), 1.49 – 1.40 (2H, m), 0.98 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 156.54, 150.22, 132.11, 131.36, 130.84, 128.35, 128.26, 126.53, 123.41, 119.87, 106.32, 31.55, 30.18, 22.65, 14.01. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{18}\text{NO}_2$ [$\text{M}+\text{H}$] 244.1338, found [$\text{M}+\text{H}$] 244.1339.



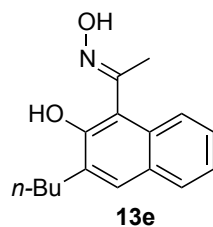
Oxime **13b** was prepared in 78% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.16 (1H, s), 7.92 (1H, d, $J = 8.5$ Hz), 7.70 (1H, d, $J = 8.0$ Hz), 7.52 – 7.44 (1H, m), 7.39 (1H, s), 7.38 – 7.32 (1H, m), 2.33 – 2.28 (1H, m), 1.06 – 1.00 (2H, m), 0.80 – 0.77 (2H, m). ^{13}C NMR (125 MHz, CDCl_3) δ 157.17, 149.81, 132.70, 130.49, 128.41, 128.22, 127.73, 126.66, 123.58, 119.86, 106.11, 10.15, 7.25. HRMS-ESI calc'd for $\text{C}_{14}\text{H}_{14}\text{NO}_2$ [$\text{M}+\text{H}$] 228.1025, found [$\text{M}+\text{H}$] 228.1029.



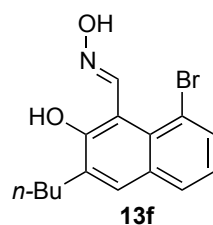
Oxime **13c** was prepared in 89% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.17 (1H, s), 7.93 (1H, d, $J = 8.5$ Hz), 7.76 (1H, d, $J = 8.5$ Hz), 7.67 (1H, s), 7.52 – 7.42 (1H, m), 7.38 – 7.31 (1H, m), 3.15 – 3.11 (1H, m), 2.03 – 2.01 (3H, m), 1.91 – 1.88 (2H, m), 1.82 – 1.80 (1H, m), 1.55 – 1.44 (3H, m), 1.33 – 1.26 (1H, m). ^{13}C NMR (125 MHz, CDCl_3) δ 156.12, 150.29, 136.99, 130.54, 128.73, 128.61, 128.35, 126.59, 123.37, 119.77, 37.14, 33.09, 27.01, 26.44. HRMS-ESI calc'd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ [$\text{M}+\text{H}$] 270.1494, found [$\text{M}+\text{H}$] 270.1484.



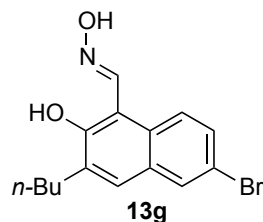
Oxime **13d** was prepared in 77% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.19 (1H, s), 7.91 (1H, d, $J = 8.5$ Hz), 7.77 – 7.76 (2H, m), 7.48 – 7.47 (1H, m), 7.36 – 7.34 (1H, m), 1.53 (9H, s). ^{13}C NMR (125 MHz, CDCl_3) δ 157.88, 150.60, 138.83, 130.94, 129.05, 128.97, 127.97, 126.81, 123.33, 119.49, 106.92, 35.36, 29.56. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{18}\text{NO}_2$ [M+H] 244.1338, found [M+H] 244.1335.



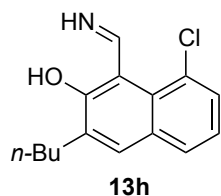
Oxime **13e** was prepared in 60% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 8.84 (1H, s), 7.73 (1H, d, $J = 8.0$ Hz), 7.62 (1H, d, $J = 8.5$ Hz), 7.59 (1H, s), 7.42 – 7.38 (1H, m), 7.31 (1H, dd, $J = 11.0, 4.0$ Hz), 2.82 – 2.77 (2H, m), 2.44 (3H, s), 1.74 – 1.66 (2H, m), 1.48 – 1.41 (2H, m), 0.97 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 158.91, 151.62, 131.81, 130.51, 129.95, 128.89, 128.07, 125.75, 123.91, 123.24, 114.25, 31.69, 30.64, 22.65, 17.47, 14.02. HRMS-ESI calc'd for $\text{C}_{16}\text{H}_{20}\text{NO}_2$ [M+H] 258.1494, found [M+H] 258.1490.



Oxime **13f** was prepared in 93% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.73 (1H, s), 7.75 (1H, d, $J = 7.5$ Hz), 7.65 (1H, d, $J = 7.5$ Hz), 7.56 (1H, s), 7.13 (1H, t, $J = 7.5$ Hz), 2.83 – 2.74 (2H, m), 1.73 – 1.64 (2H, m), 1.42 (2H, m), 0.96 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 157.51, 152.45, 133.36, 133.03, 131.79, 130.64, 128.36, 124.00, 116.54, 106.89, 31.31, 30.18, 22.62, 13.99. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{17}\text{BrNO}_2$ [M+H] 322.0443, found [M+H] 322.0444.

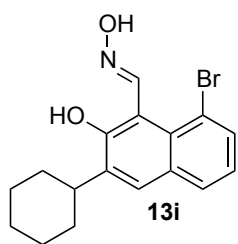


Oxime **13g** was prepared in 92% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 11.18 (1H, s), 9.06 (1H, s), 7.86 (1H, s), 7.76 (1H, d, $J = 9.0$ Hz), 7.51 (s, 1H), 7.49 (2H, d, $J = 10.5$ Hz), 2.84 – 2.77 (2H, m), 1.72 – 1.65 (2H, m), 1.48 – 1.42 (2H, m), 0.97 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 156.68, 149.75, 133.53, 130.21, 130.20, 129.56, 129.50, 129.35, 121.70, 116.93, 106.48, 31.38, 30.14, 22.60, 13.97. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{17}\text{BrNO}_2$ [M+H] 322.0443, found [M+H] 322.0440.

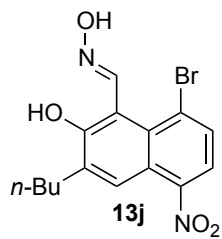


[M+H] 262.0995.

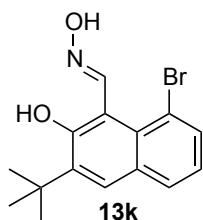
A crude mixture of oxime **13h** (0.5 mmol) and zinc powder (1.5 mmol) acetonitrile (10 mL, anhydrous) was treated with MoCl_5 (70 mol%). After reaction completion, the imine was isolated by flash chromatography (81%, 106 mg over three steps). ^1H NMR (500 MHz, CDCl_3) δ 12.58 (1H, s), 9.60 (1H, d, $J = 9.0$ Hz), 7.42 – 7.39 (3H, m), 7.07 (1H, t, $J = 8.0$ Hz), 6.47 (1H, s), 2.66 – 2.59 (2H, m), 1.64 – 1.59 (2H, m), 1.45 – 1.39 (2H, m), 0.96 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 183.80, 157.51, 139.53, 136.11, 130.84, 130.54, 129.22, 127.90, 126.32, 123.01, 105.86, 30.92, 29.57, 22.77, 14.03. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{17}\text{ClNO}$ [M+H] 262.0999, found



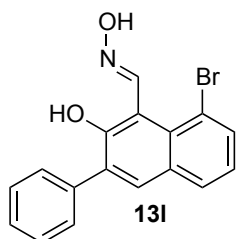
Oxime **13i** was prepared in 90% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.72 (1H, s), 7.76 (1H, d, $J = 7.5$ Hz), 7.68 (1H, d, $J = 8.0$ Hz), 7.59 (1H, s), 7.14 – 7.10 (1H, m), 3.10 – 3.07 (1H, m), 2.04 – 2.01 (2H, m), 1.88 – 1.86 (2H, m), 1.80 – 1.75 (1H, m), 1.45 – 1.37 (m, 4H), 1.35 – 1.24 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 157.00, 152.57, 137.85, 133.34, 130.79, 129.48, 129.18, 128.60, 123.95, 116.48, 37.29, 32.94, 26.94, 26.39. HRMS-ESI calc'd for $\text{C}_{17}\text{H}_{19}\text{BrNO}_2$ $[\text{M}+\text{H}]$ 348.0599, found $[\text{M}+\text{H}]$ 348.0608.



Oxime **13j** was prepared in 95% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 11.27 (1H, s), 9.45 (1H, s), 8.13 (1H, s), 7.82 (1H, d, $J = 8.5$ Hz), 7.69 (1H, d, $J = 8.5$ Hz), 7.43 (1H, s), 2.86 – 2.78 (2H, m), 1.72 – 1.62 (2H, m), 1.48 – 1.37 (2H, m), 0.96 (3H, t, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 157.82, 151.56, 146.90, 136.87, 131.55, 131.08, 125.38, 122.37, 121.66, 120.53, 107.60, 31.15, 30.71, 22.58, 13.90. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{16}\text{BrN}_2\text{O}_4$ $[\text{M}+\text{H}]$ 367.0293, found $[\text{M}+\text{H}]$ 367.0296.



Oxime **13k** was prepared in 85% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.70 (1H, s), 7.76 (1H, d, $J = 7.5$), 7.74 – 7.67 (2H, m), 7.13 (1H, t, $J = 8.0$ Hz), 1.50 (9H, s). ^{13}C NMR (125 MHz, CDCl_3) δ 158.37, 152.62, 139.60, 133.47, 130.38, 129.83, 129.57, 128.89, 123.92, 116.13, 107.53, 35.35, 29.47. HRMS-ESI calc'd for $\text{C}_{15}\text{H}_{17}\text{BrNO}_2$ $[\text{M}+\text{H}]$ 322.0443, found $[\text{M}+\text{H}]$ 322.0452.



Oxime **13l** was prepared in 91% yield according to a general procedure for benzannulation of siloxy alkynes and isoquinoline *N*-oxides. ^1H NMR (500 MHz, CDCl_3) δ 9.75 (1H, s), 7.88 – 7.81 (1H, m), 7.78 (1H, s), 7.77 – 7.73 (1H, m), 7.64 (2H, dd, $J = 5.0, 3.0$ Hz), 7.53 – 7.46 (2H, m), 7.46 – 7.39 (1H, m), 7.19 (1H, t, $J = 8.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 156.20, 152.16, 136.89, 134.22, 133.29, 132.24, 130.62, 130.36, 129.47, 129.07, 128.26, 127.89, 124.46, 116.61, 107.72. HRMS-ESI calc'd for $\text{C}_{17}\text{H}_{13}\text{BrNO}_2$ $[\text{M}+\text{H}]$ 342.0130, found $[\text{M}+\text{H}]$ 342.0123.

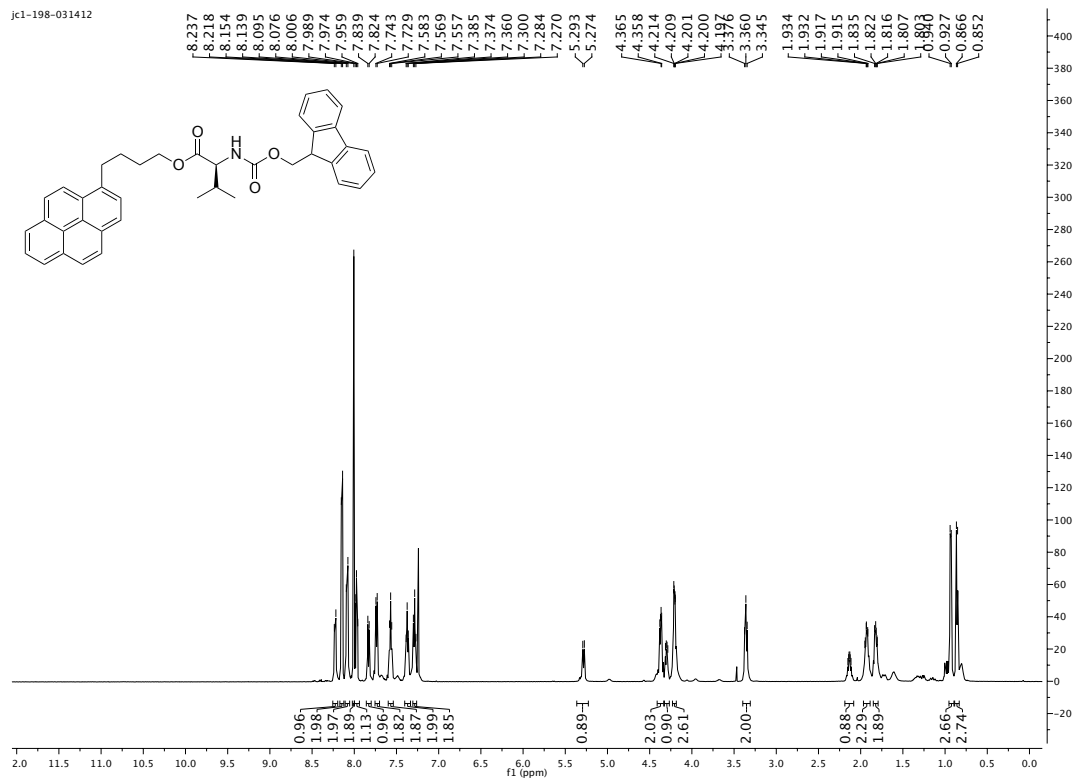
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1. Schramm, M. P.; Shubinets, V. Kozmin, S. A. Preparation and [2+2] Cycloaddition of 1-Triisopropylsiloxy-1-hexyne with Methyl Crotonate: 3-Butyl-4-methyl-2-triisopropylsiloxy-cyclobut-2-enecarboxylic Acid Methyl Ester. *Org. Synth.* **87**, 253-263 (2010)
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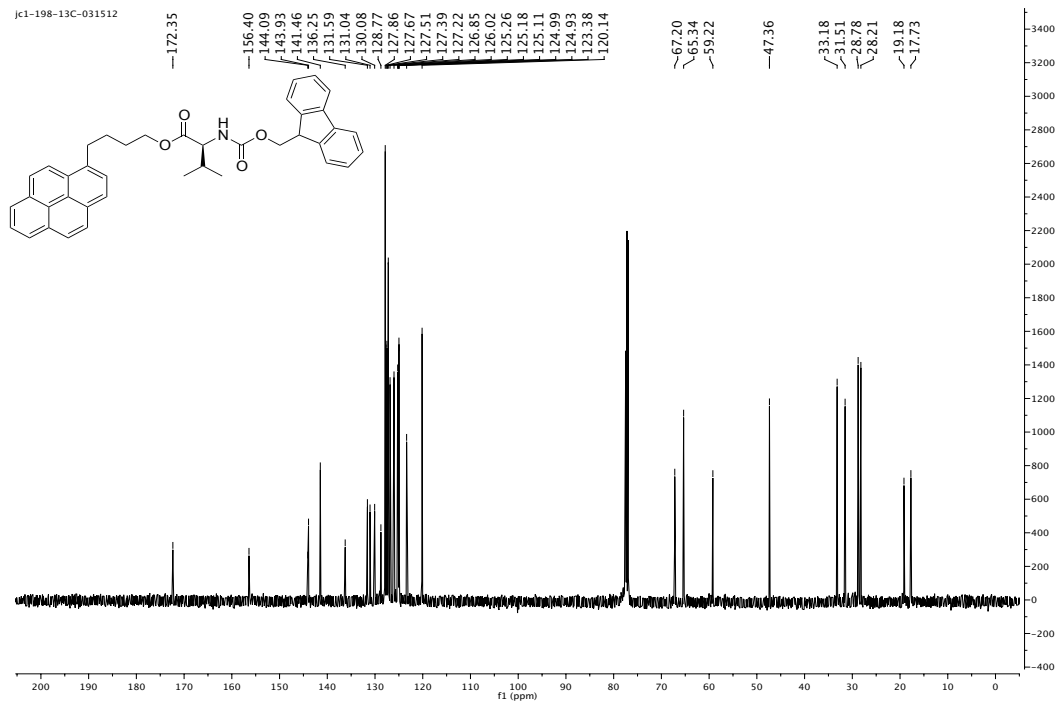
NMR spectra of new compounds

Compound 2

jc1-198-031412

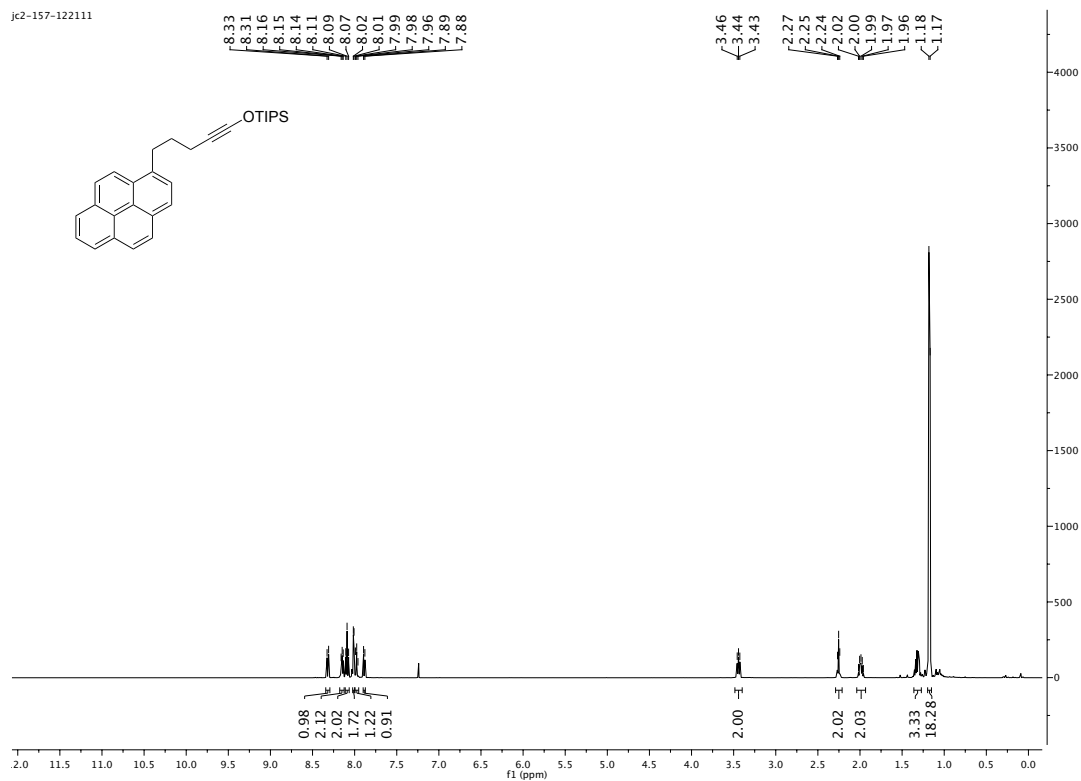


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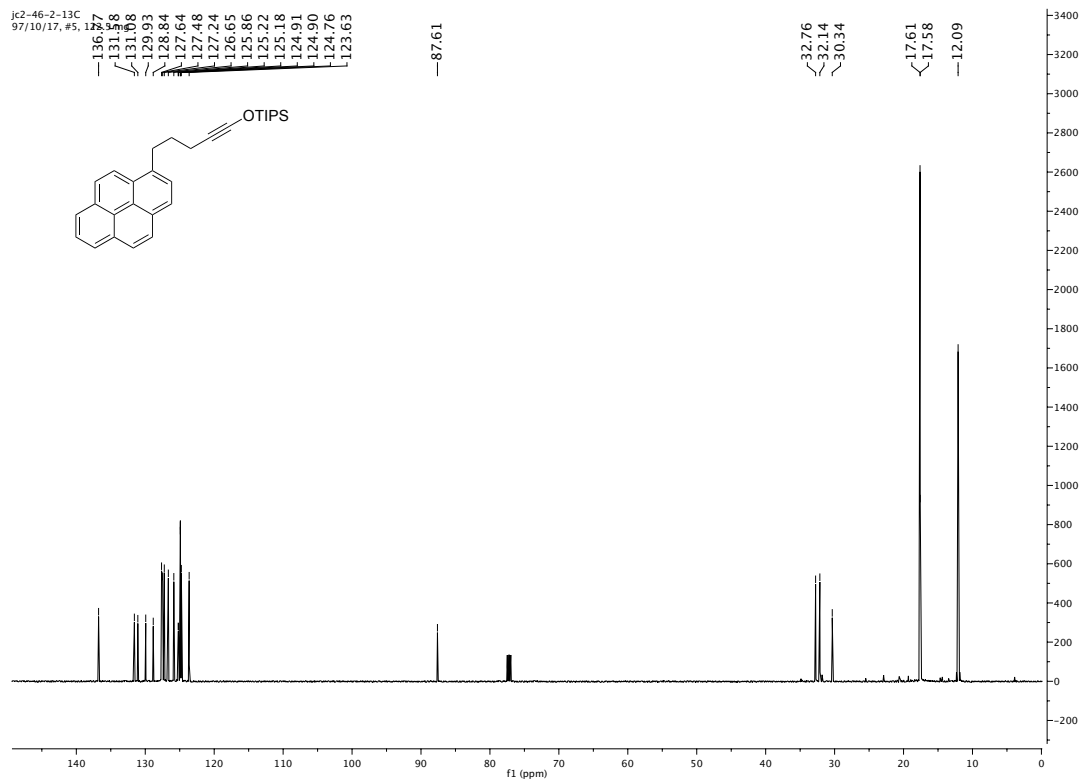


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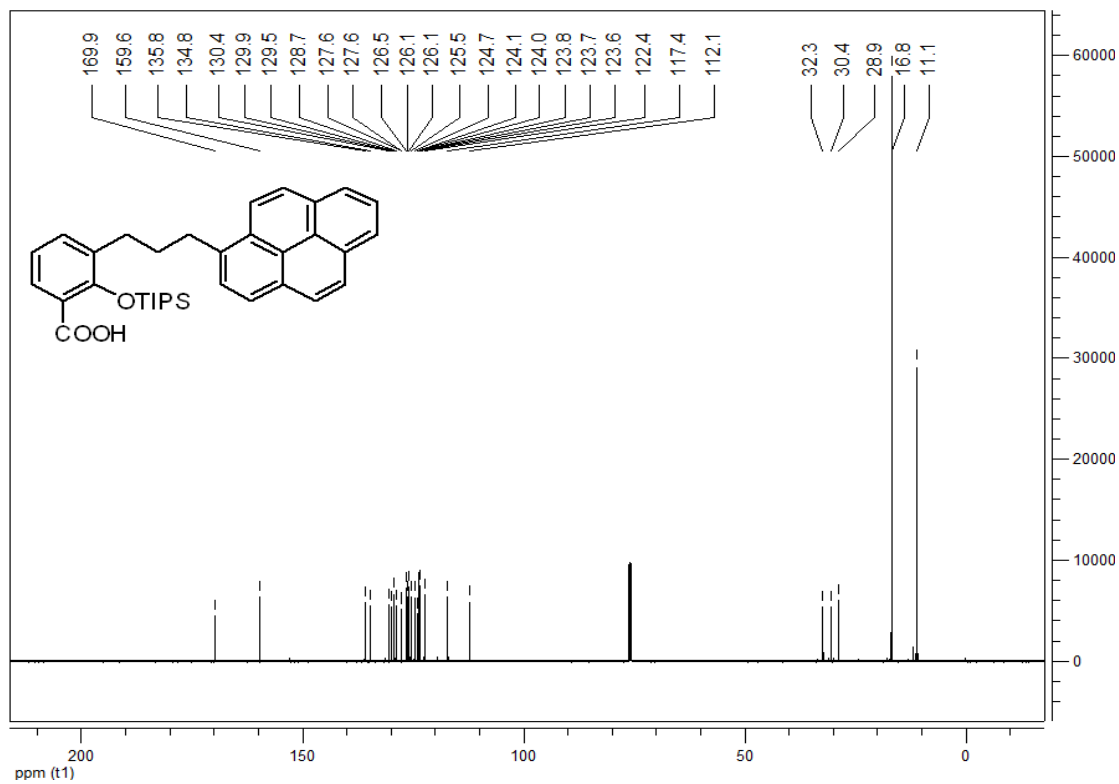
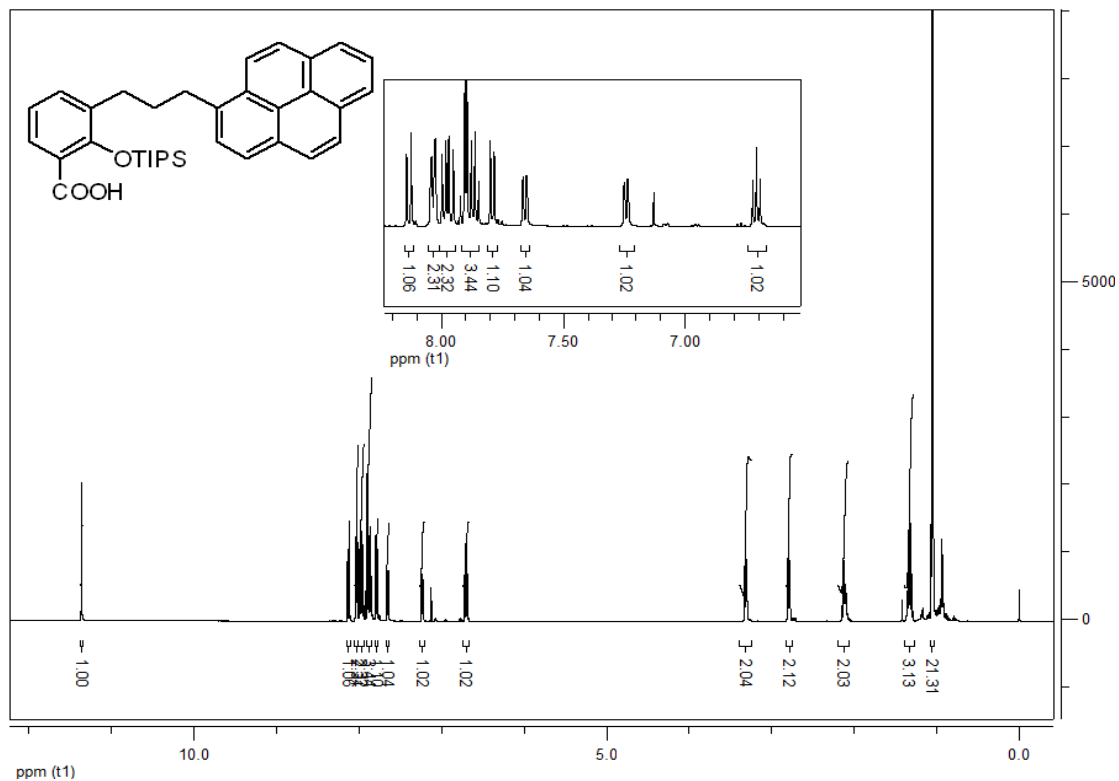
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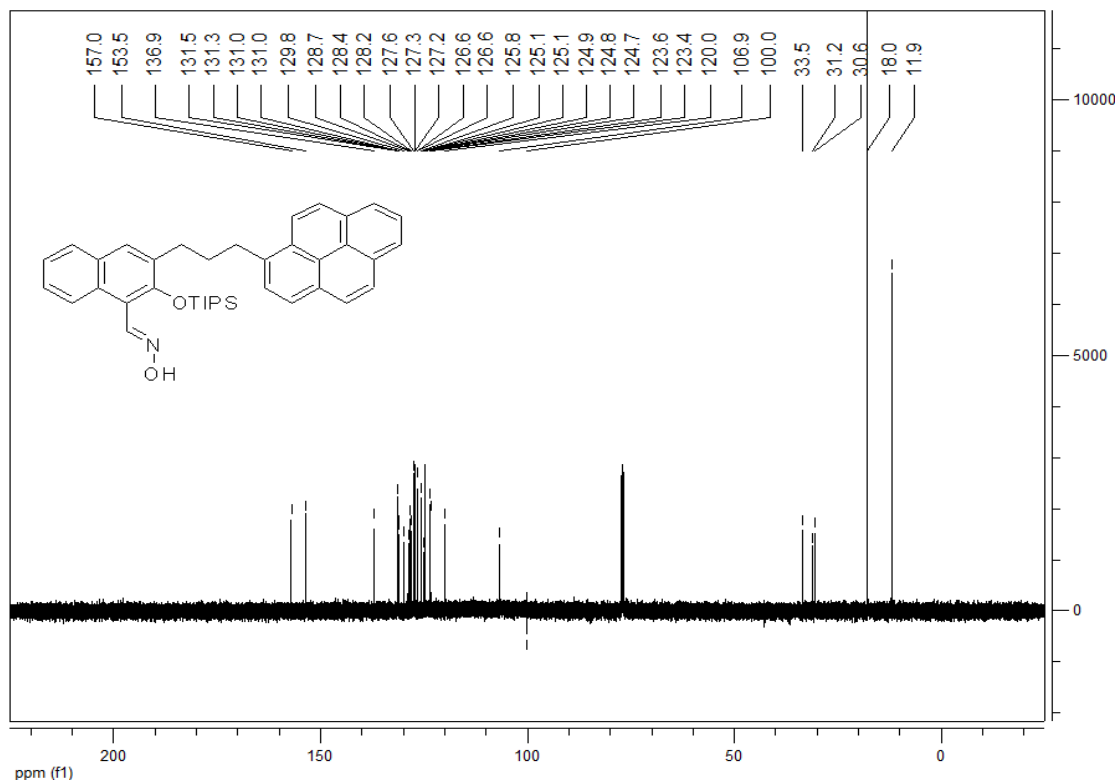
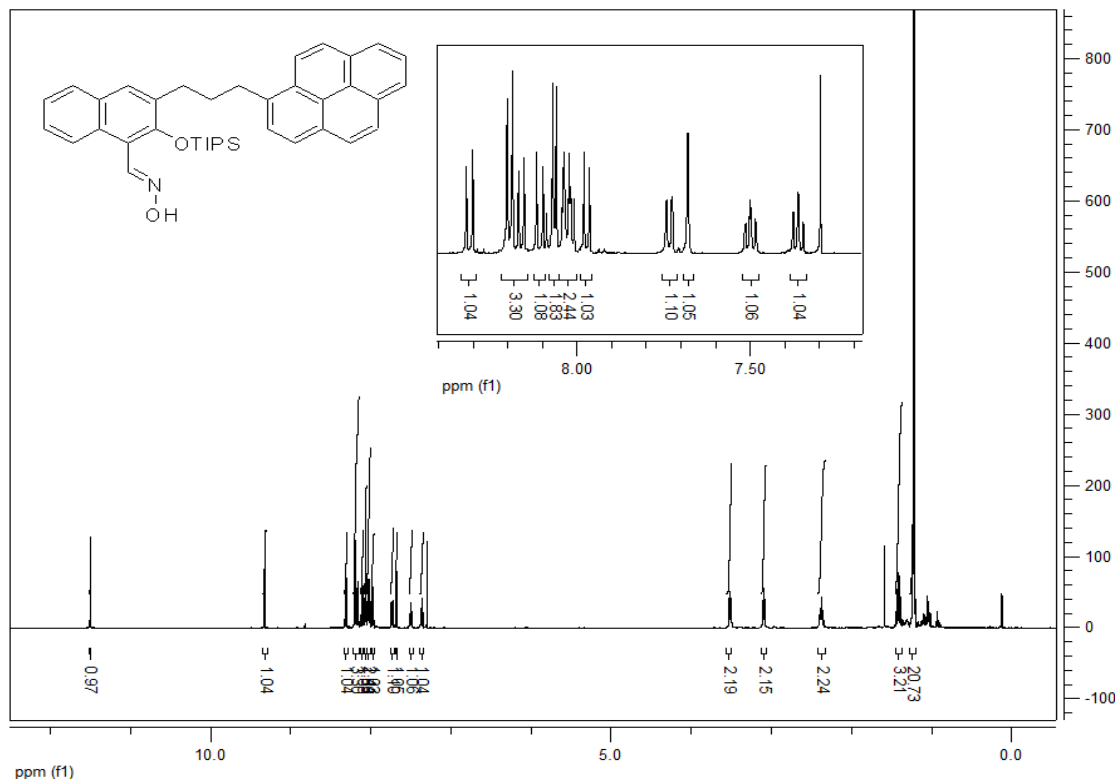
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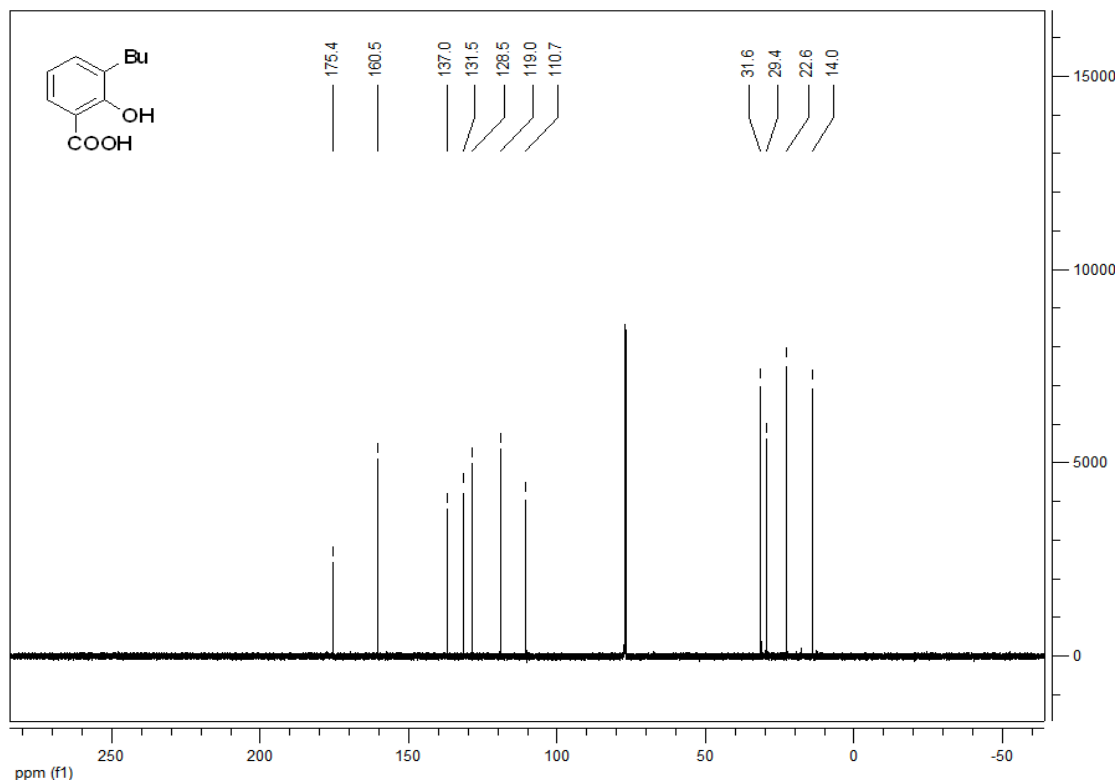
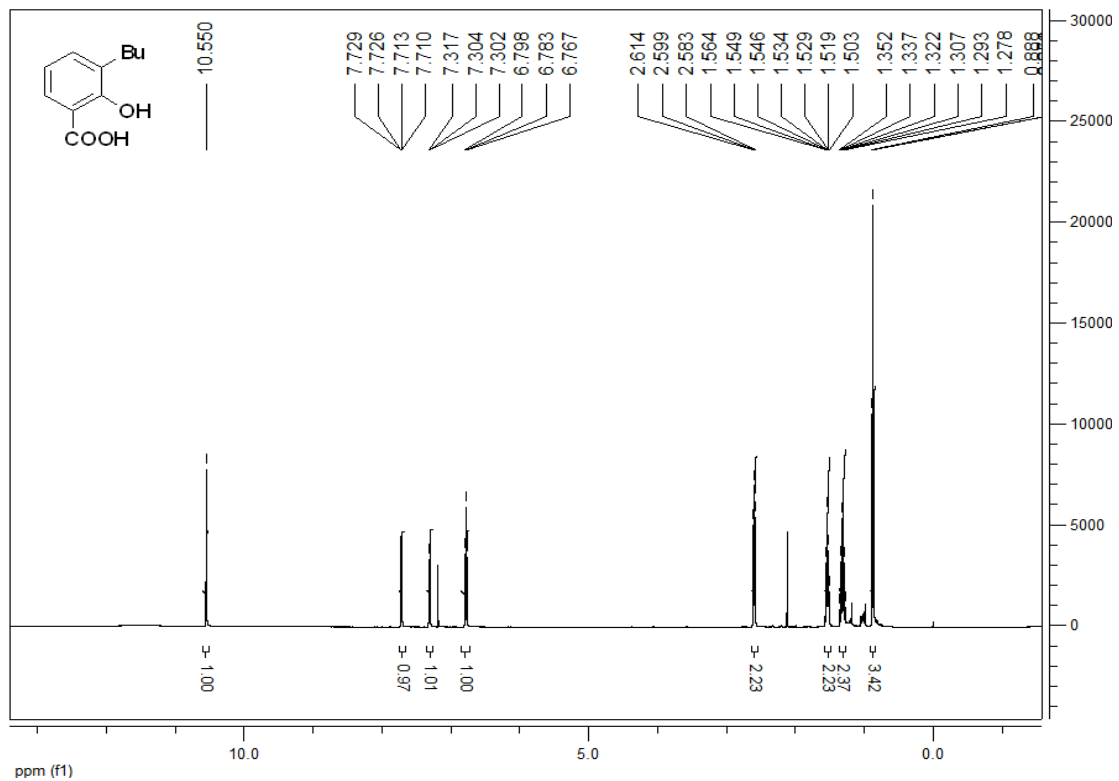
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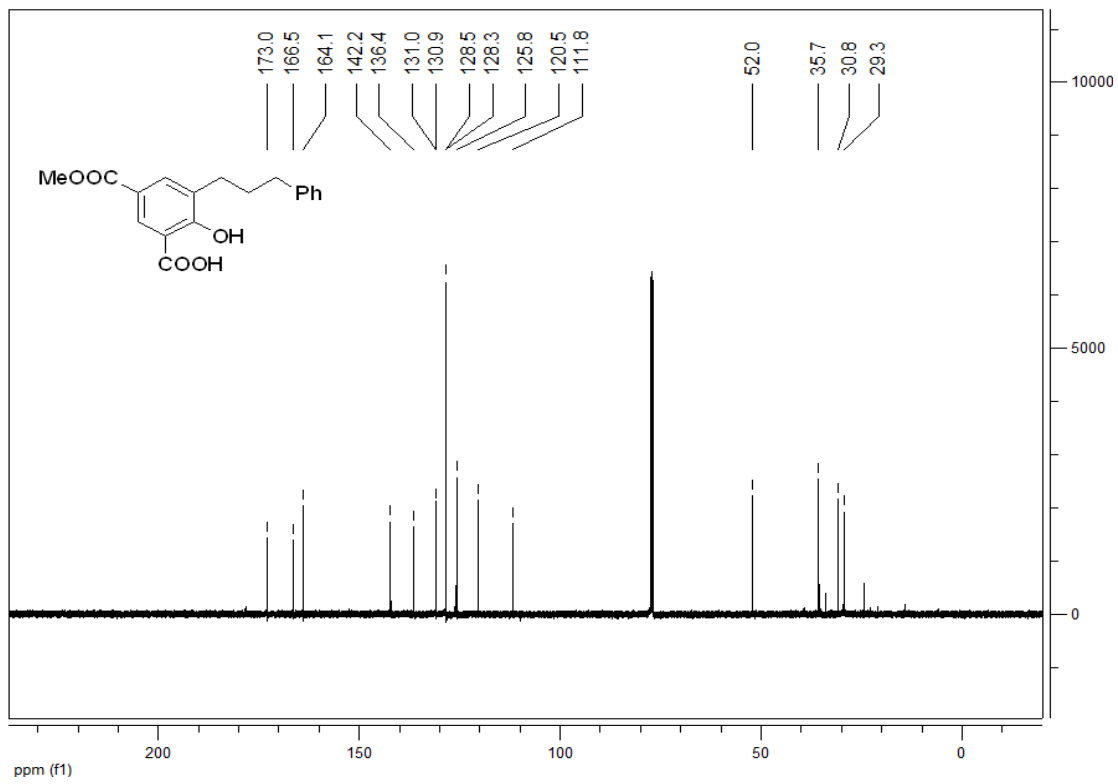
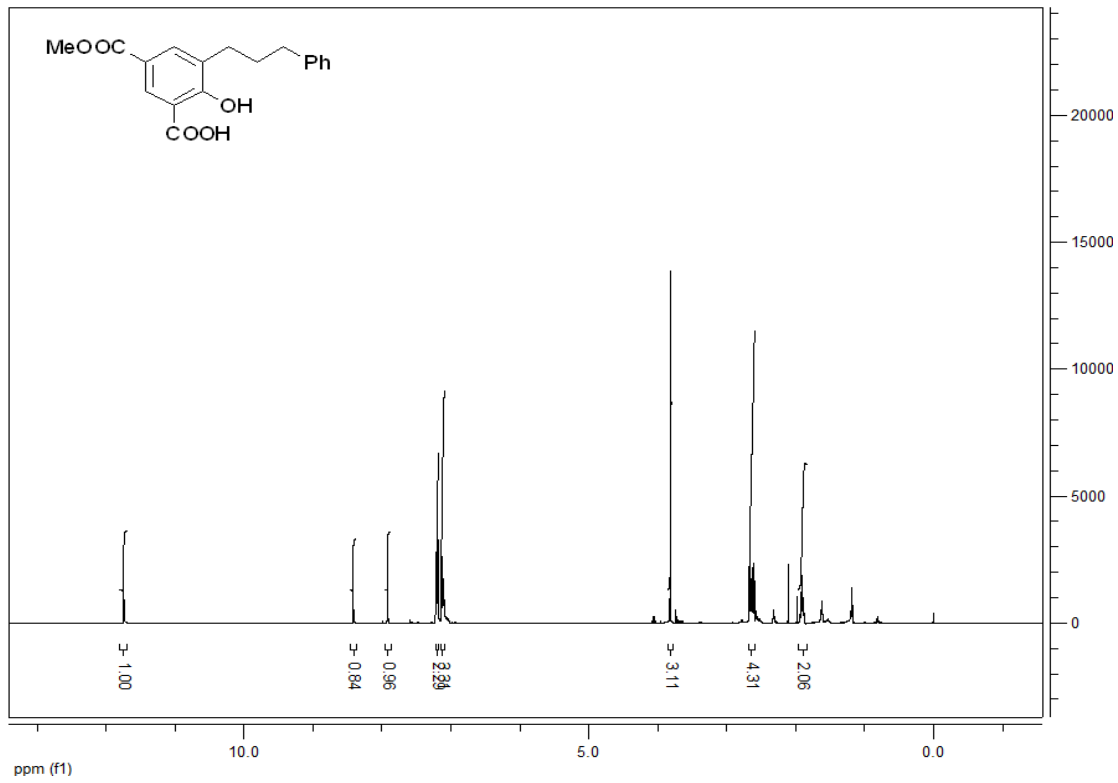
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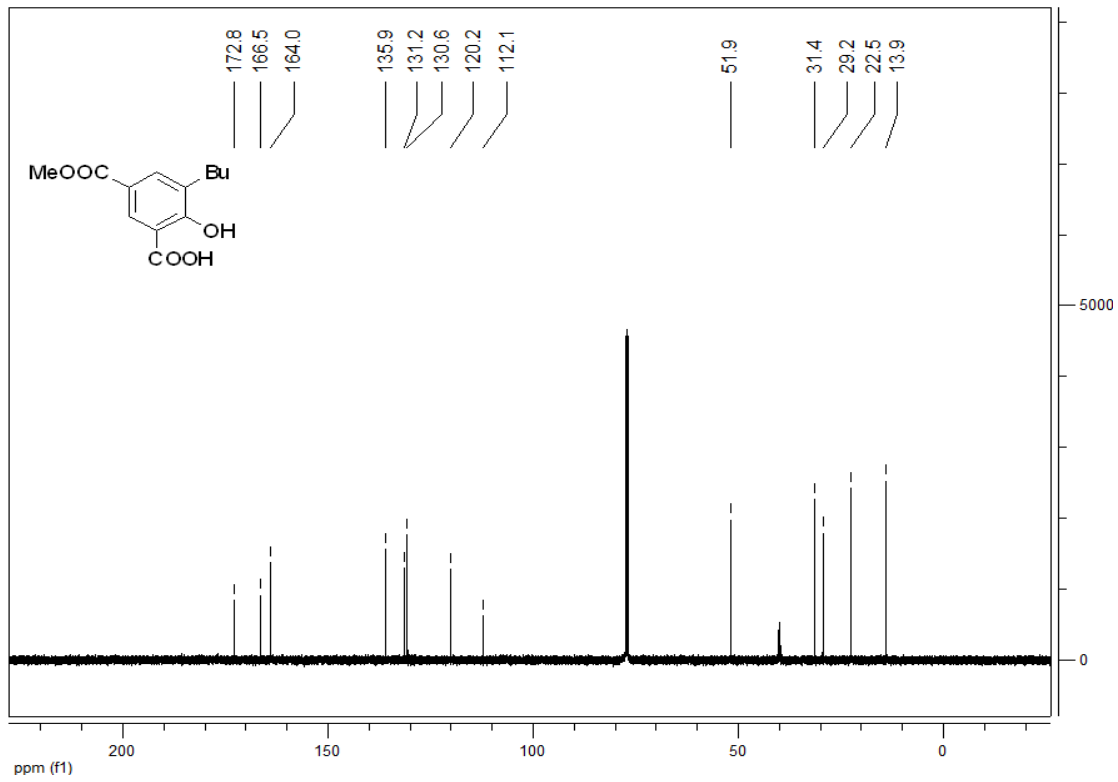
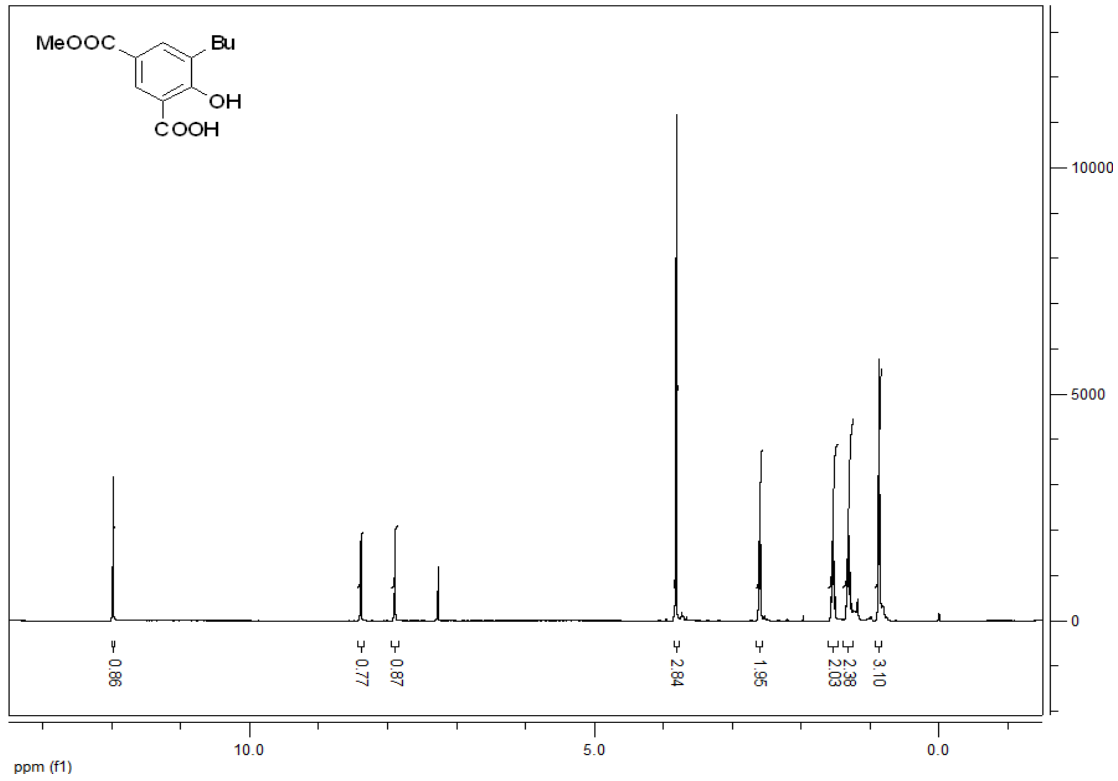
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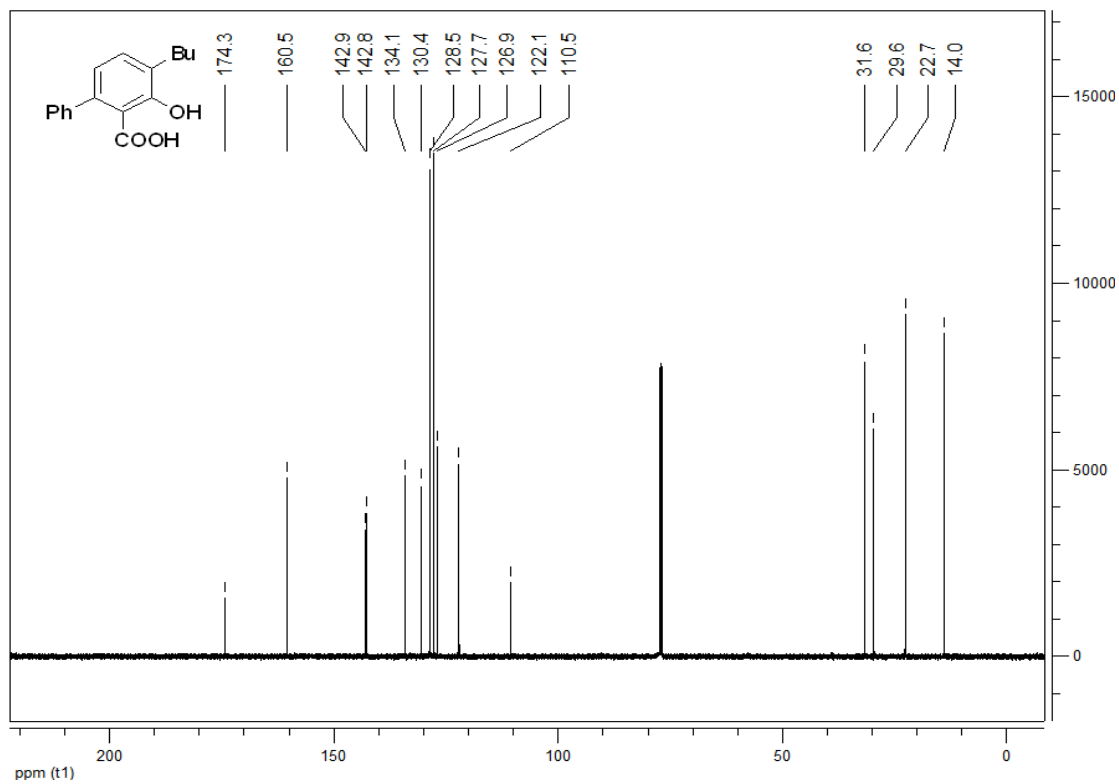
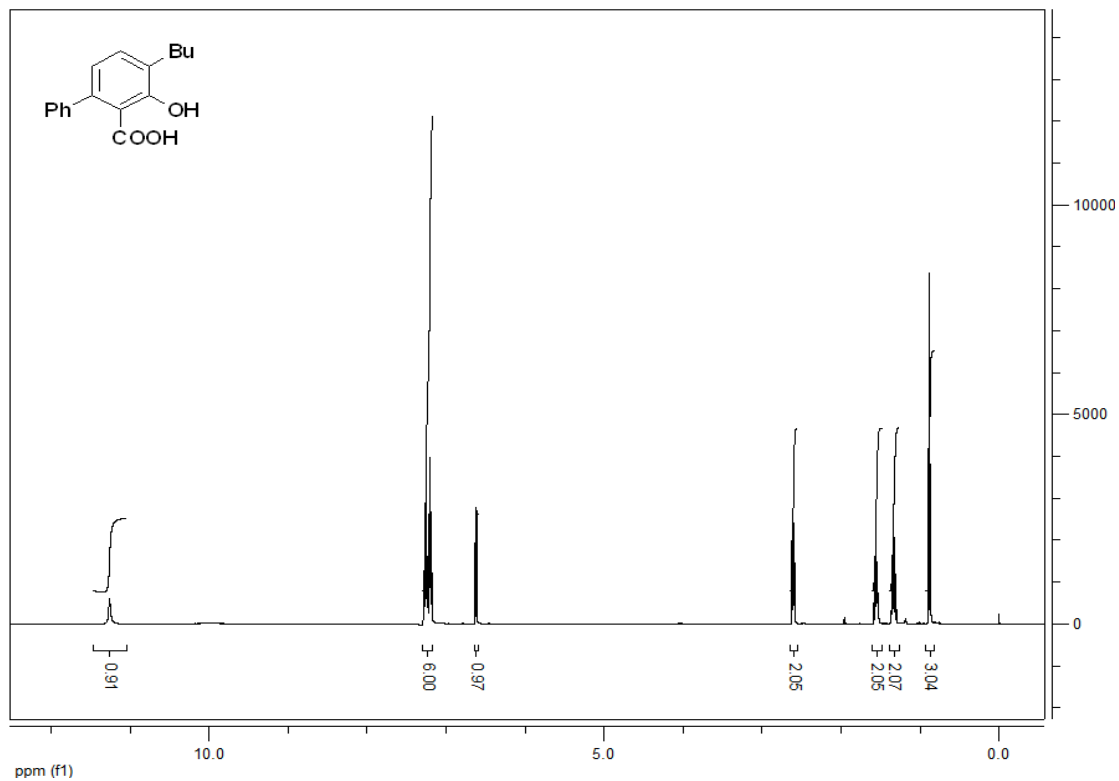
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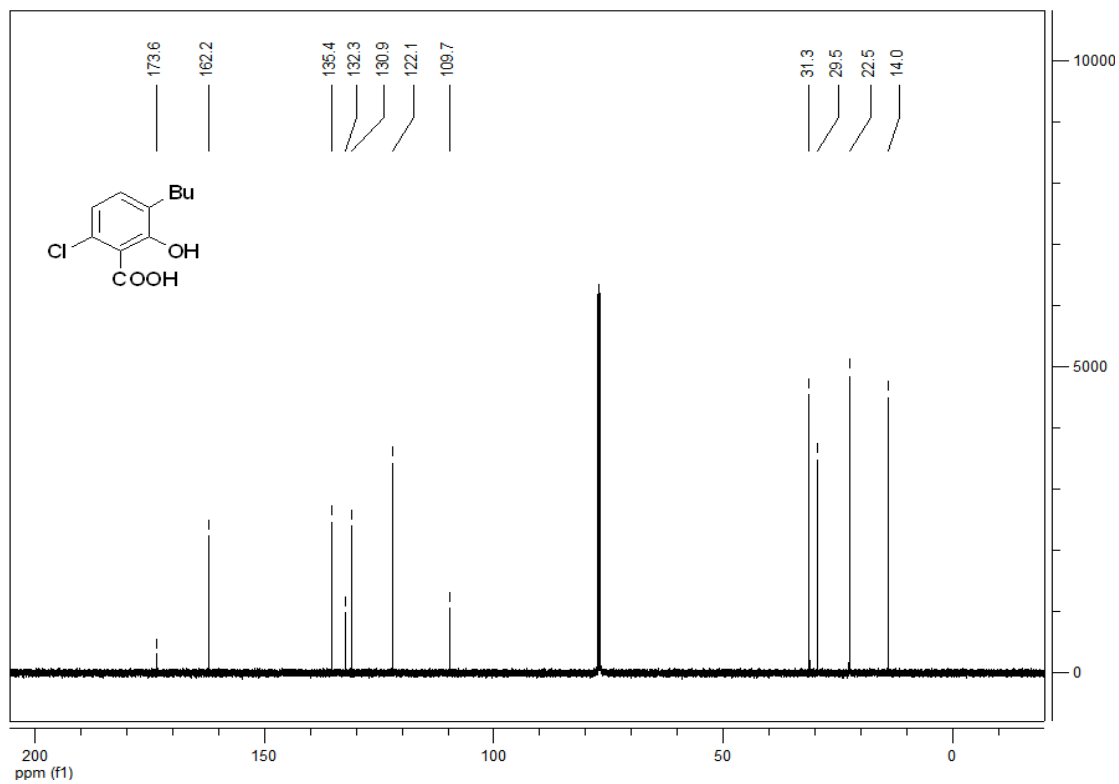
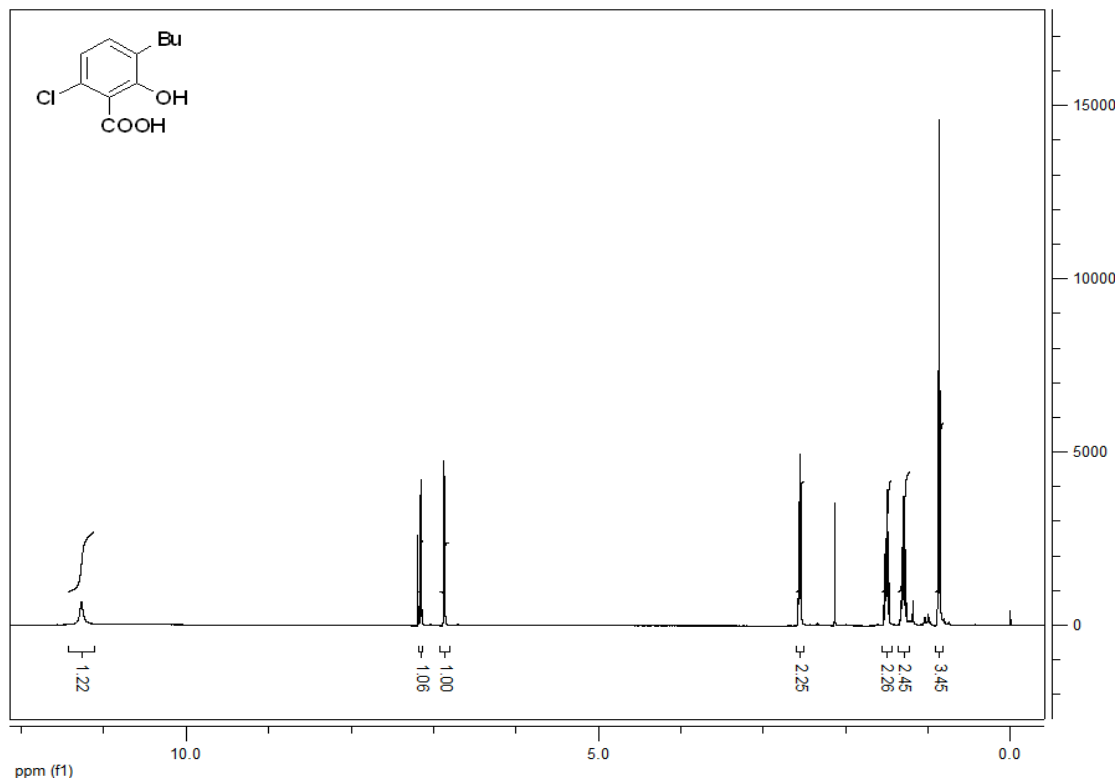
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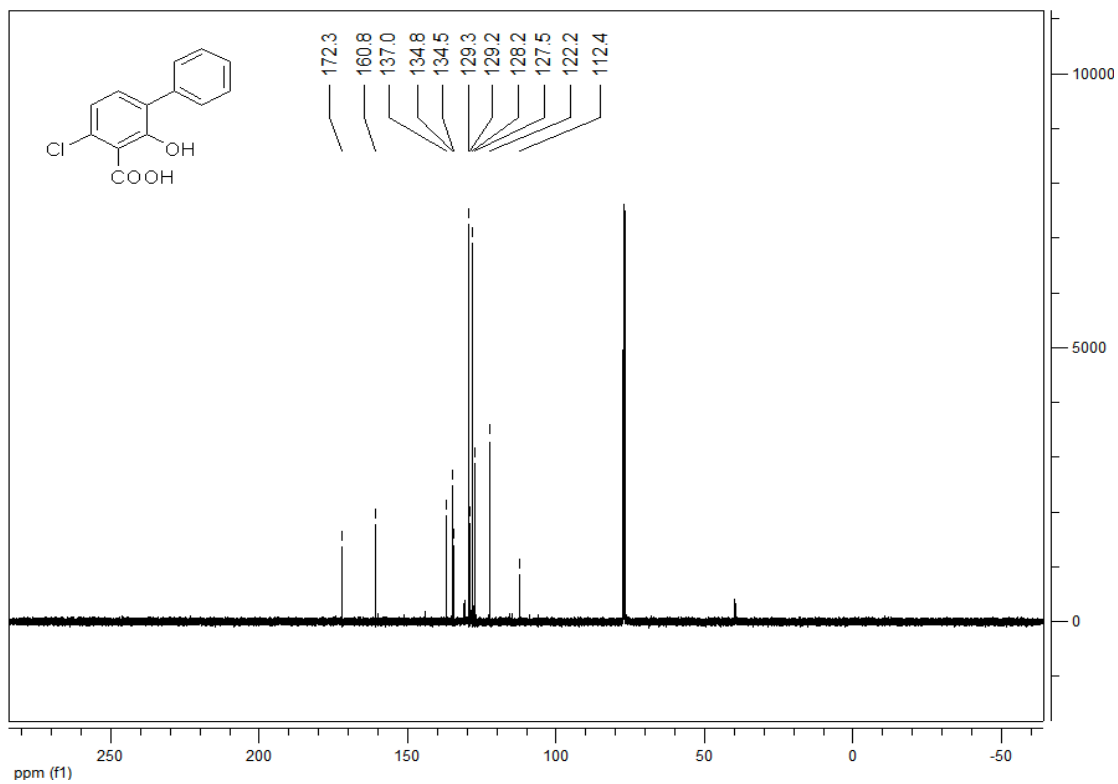
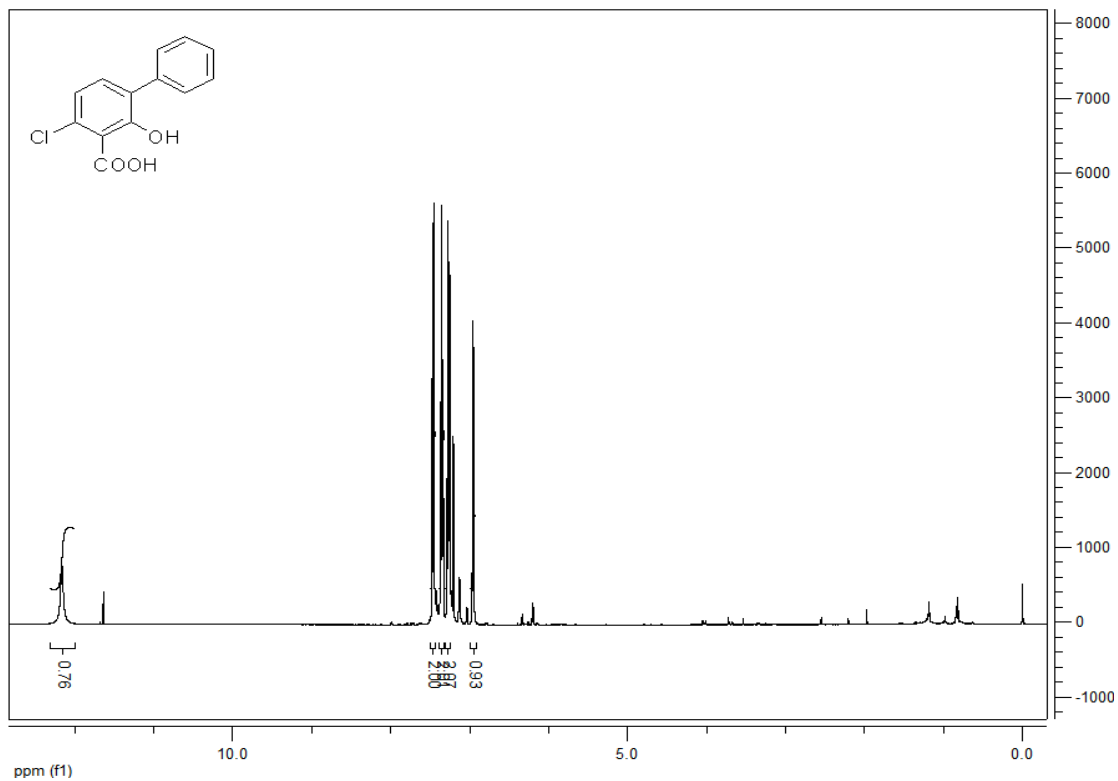
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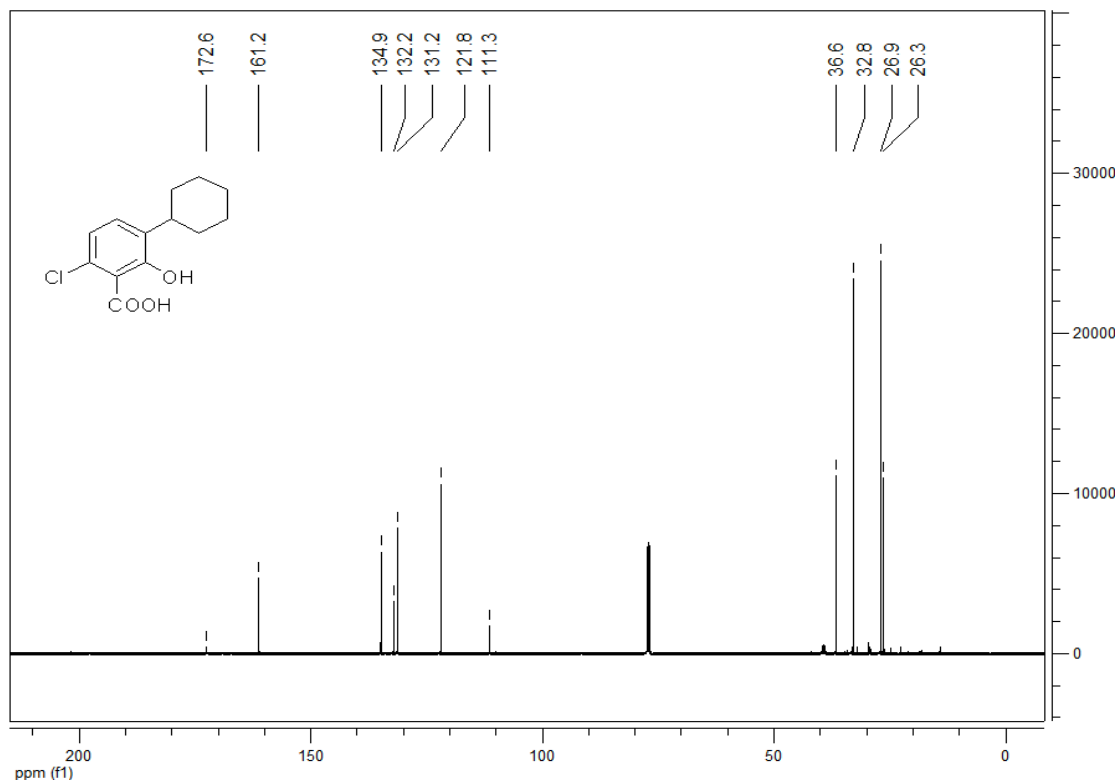
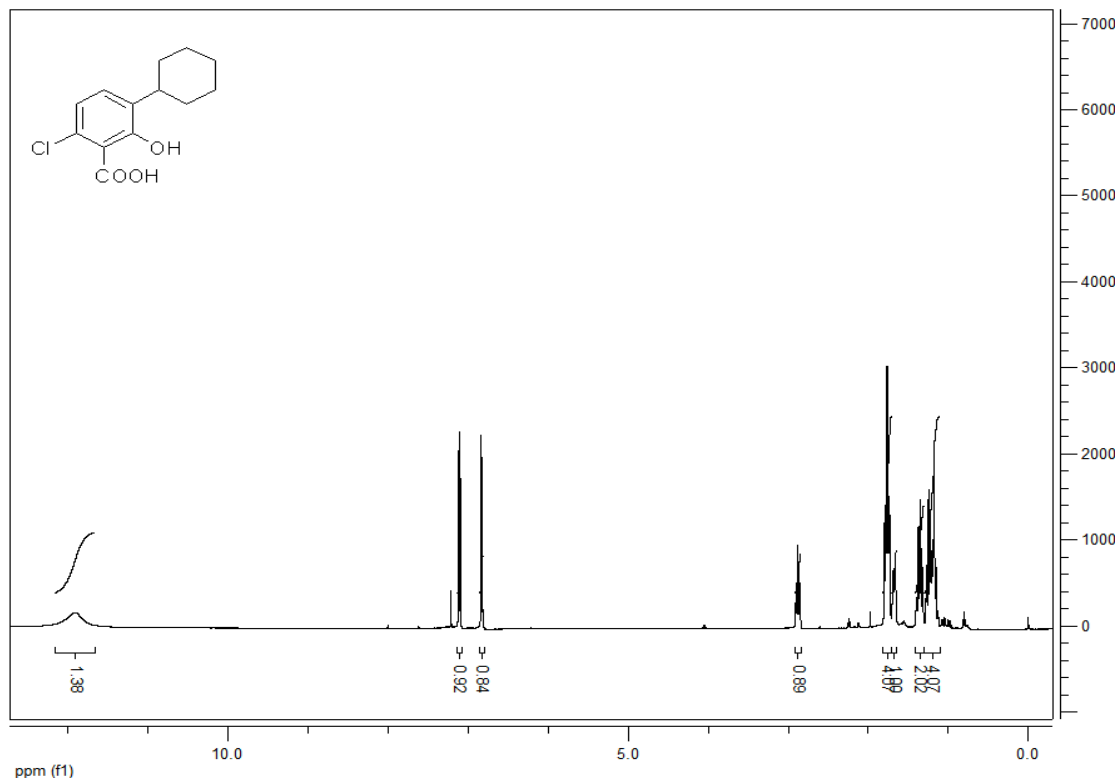
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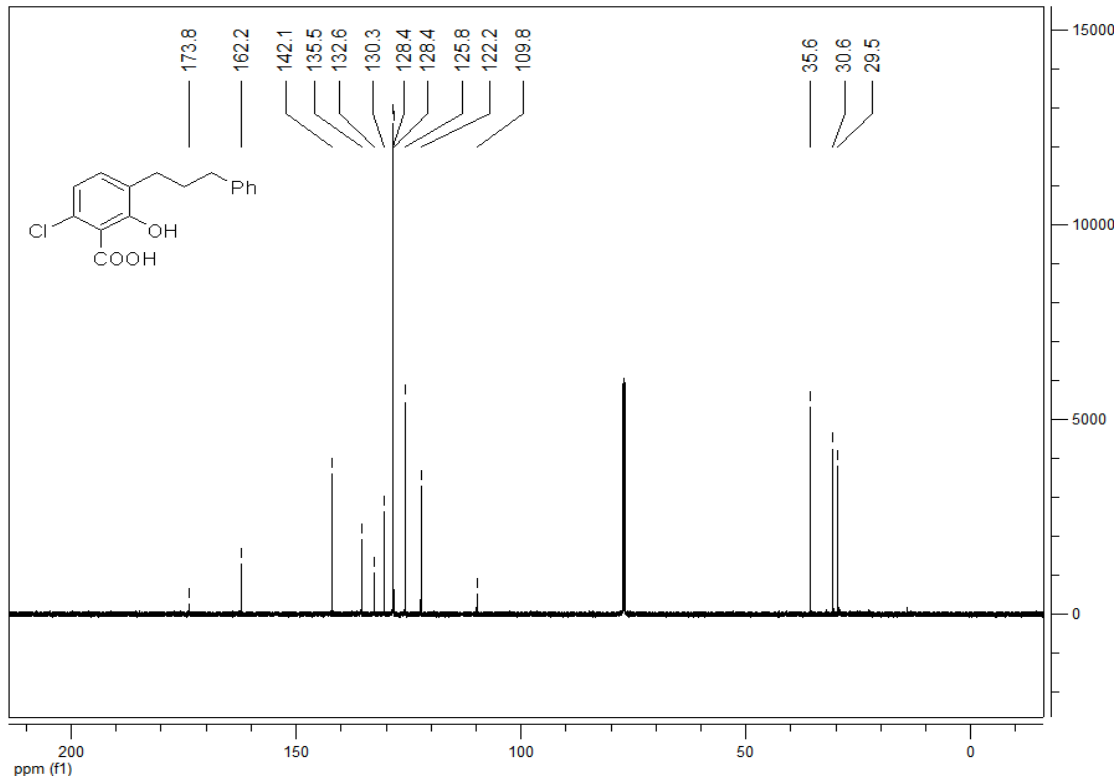
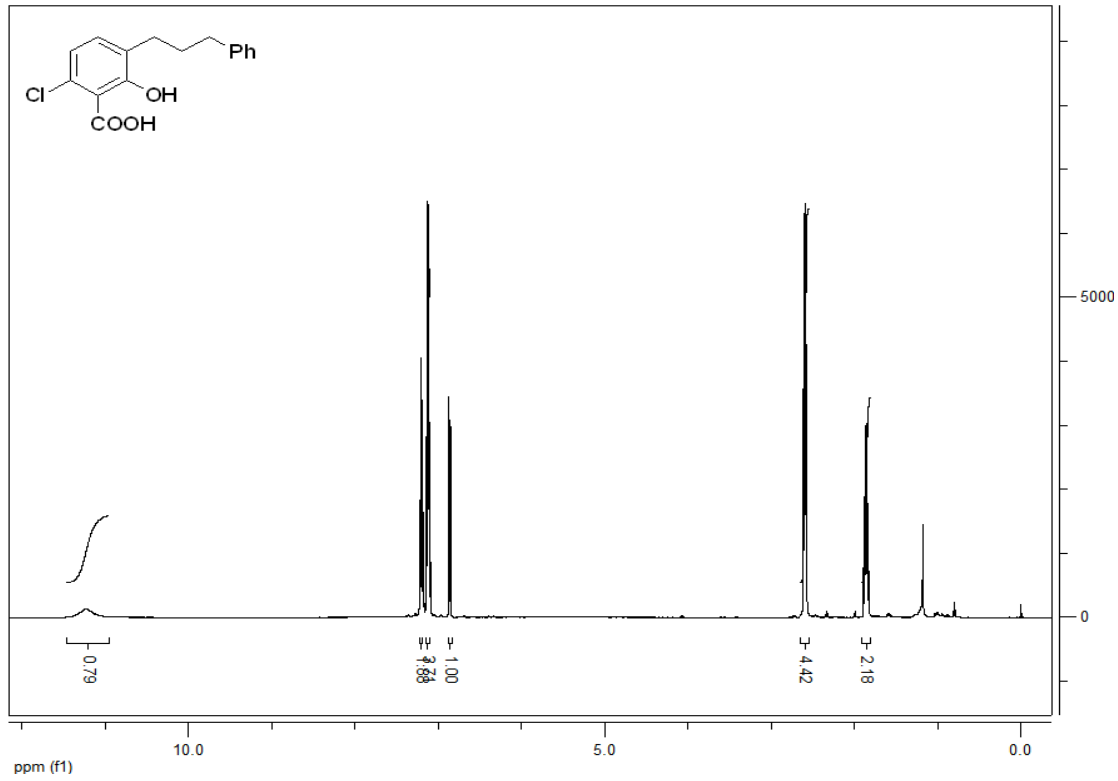
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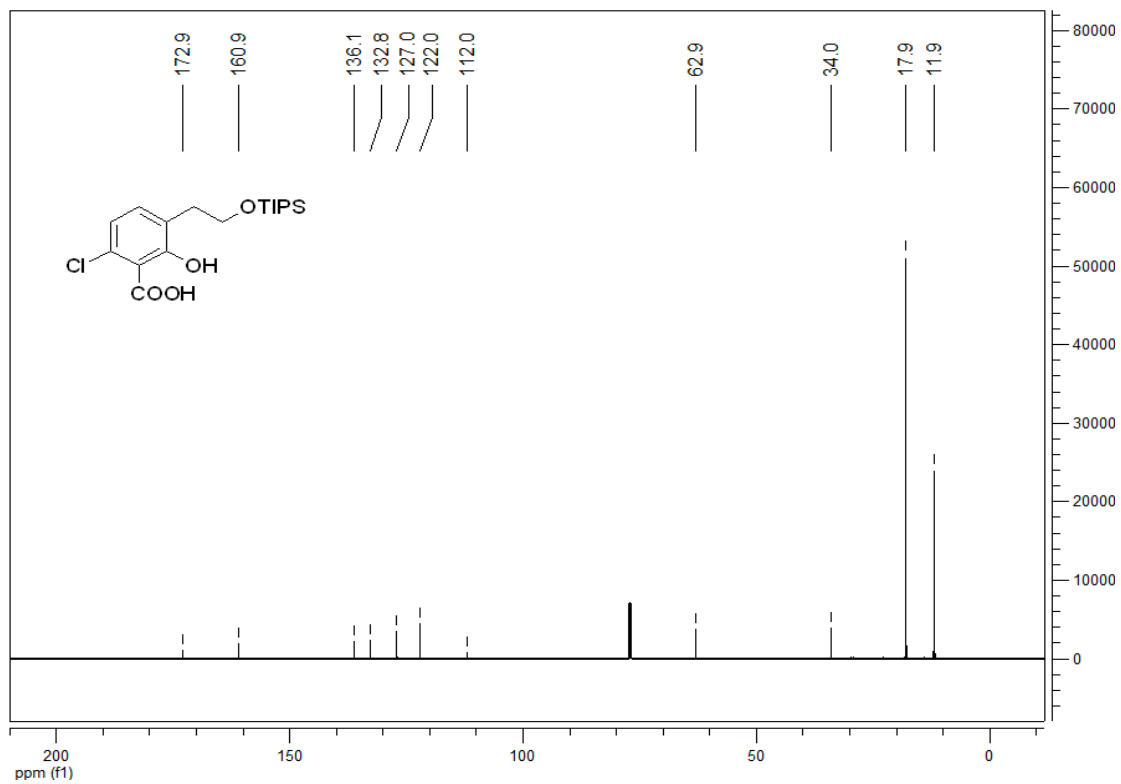
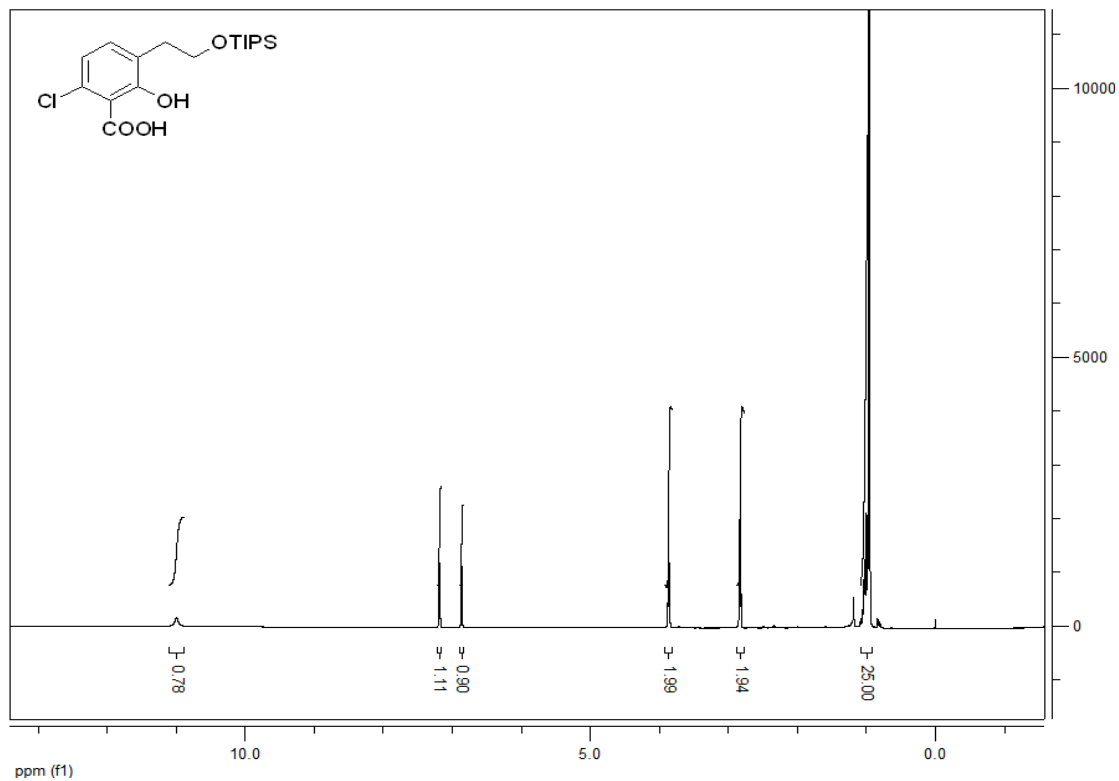
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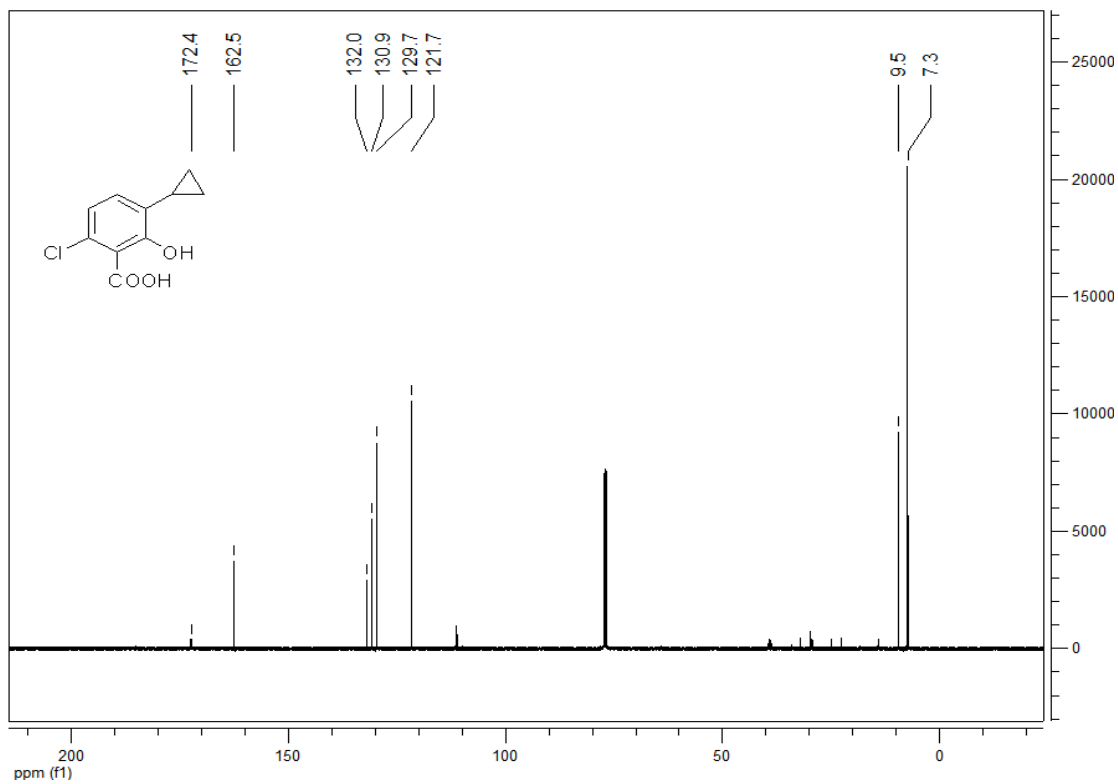
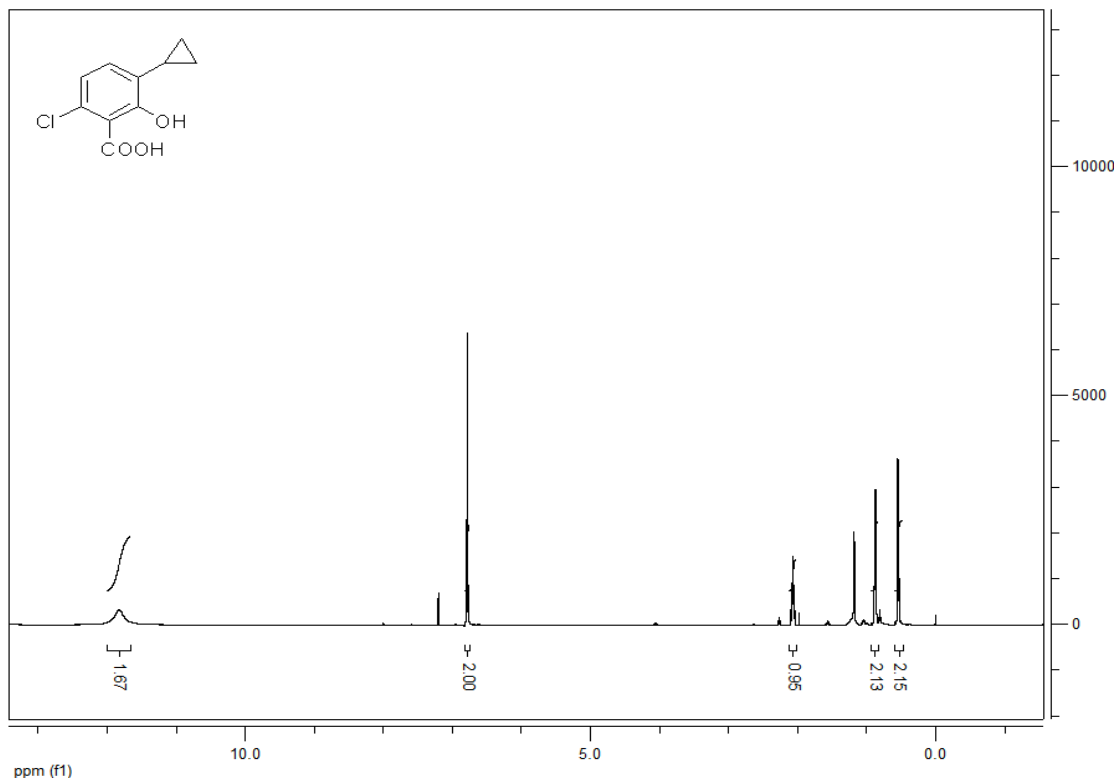
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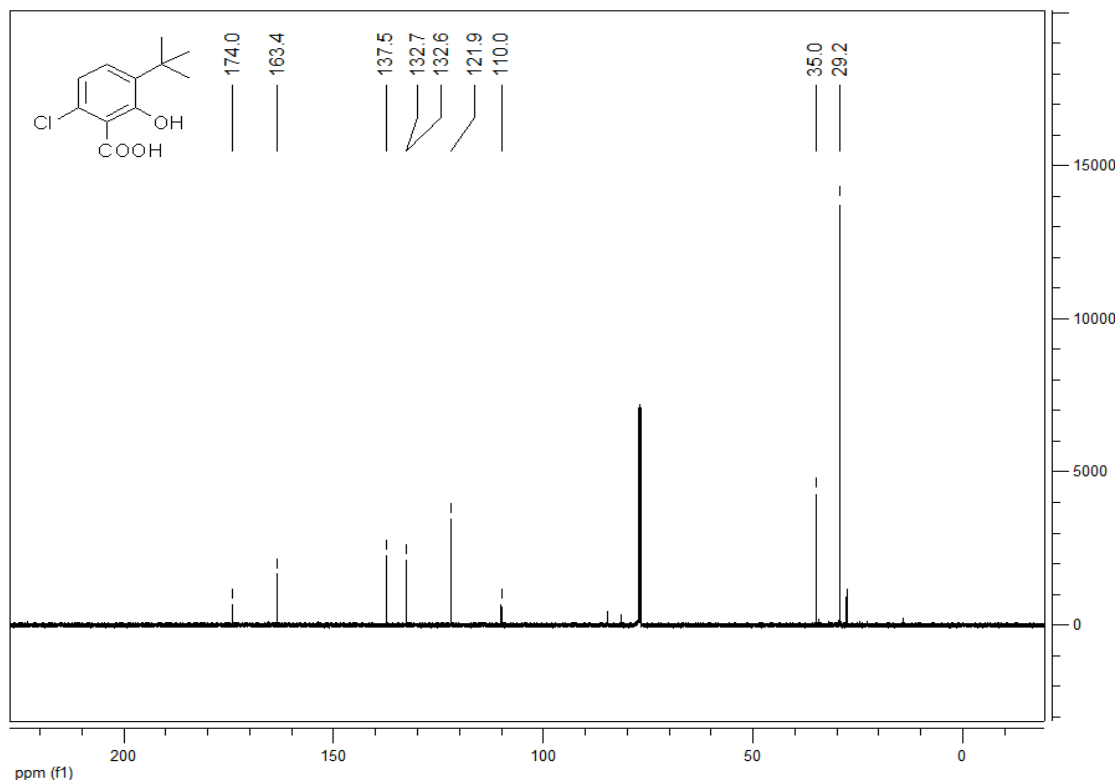
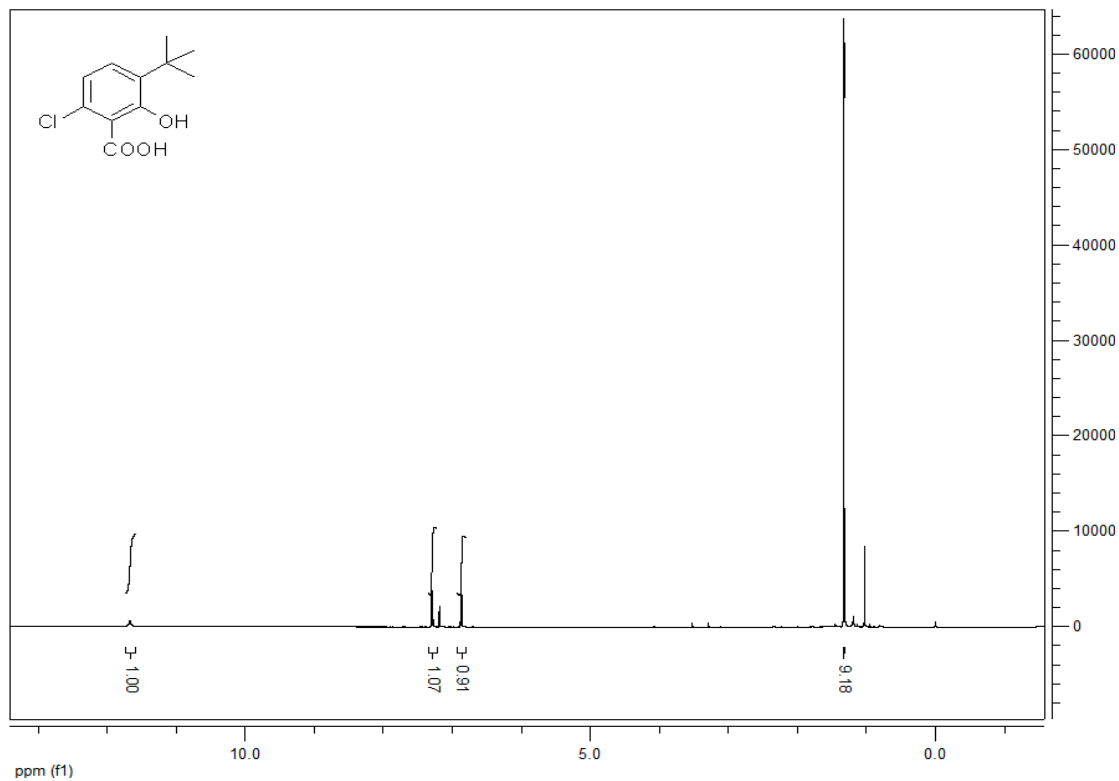
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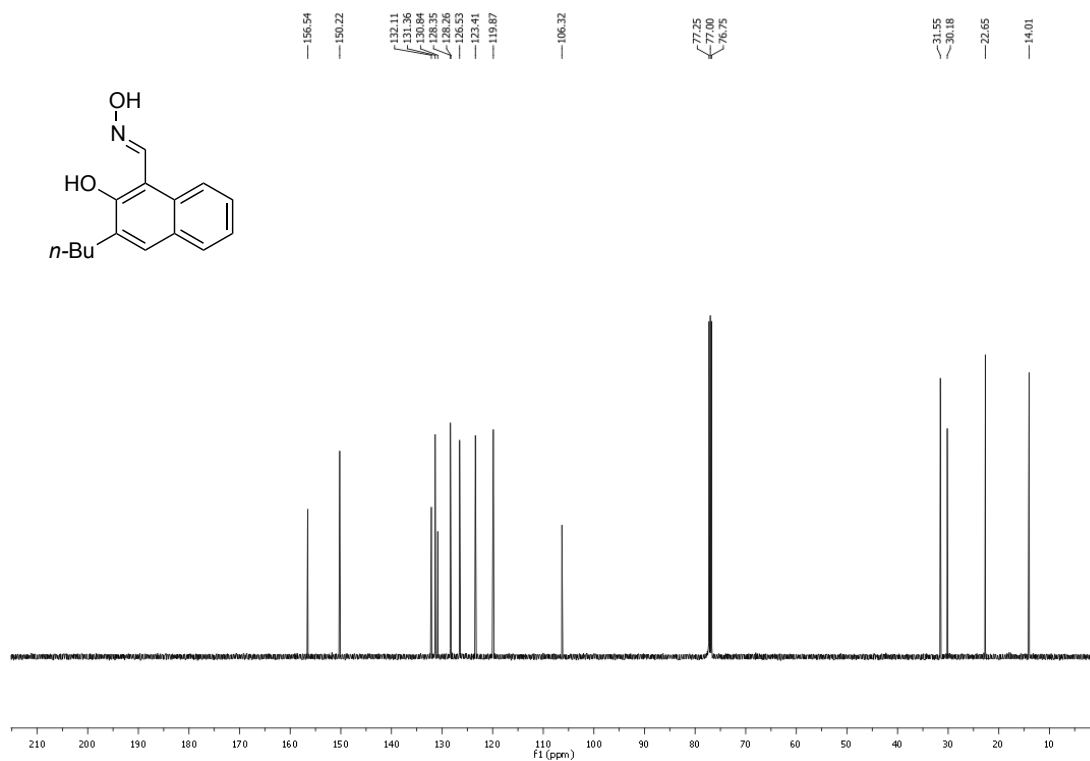
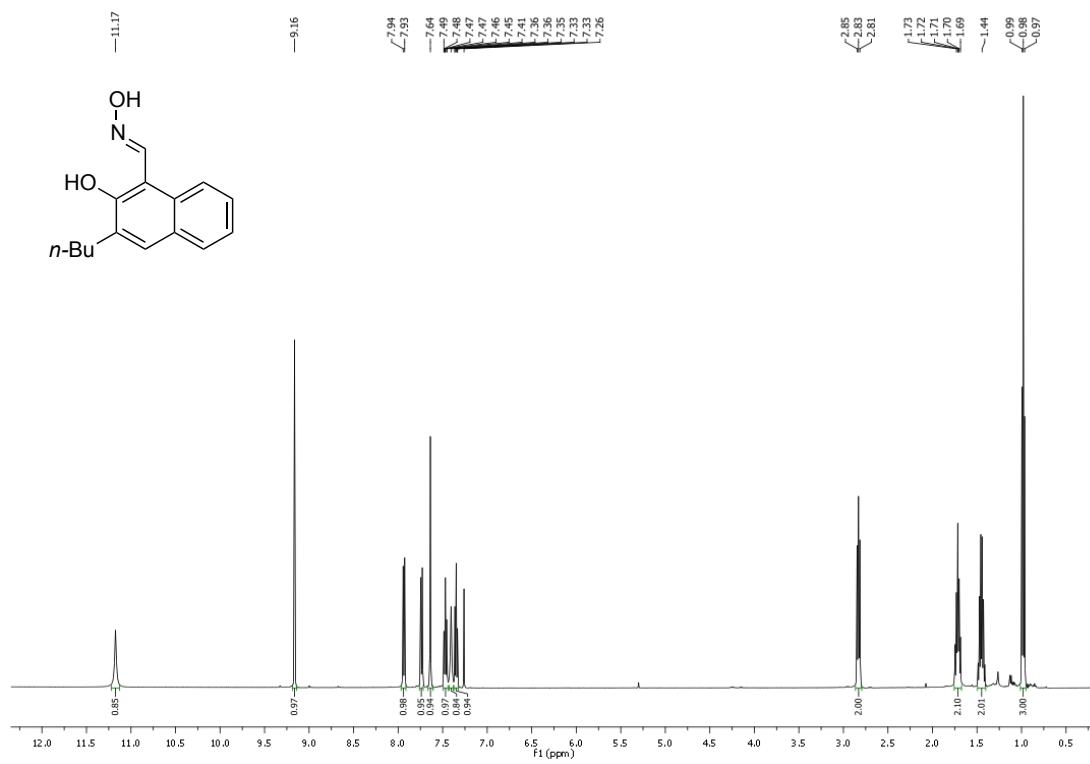
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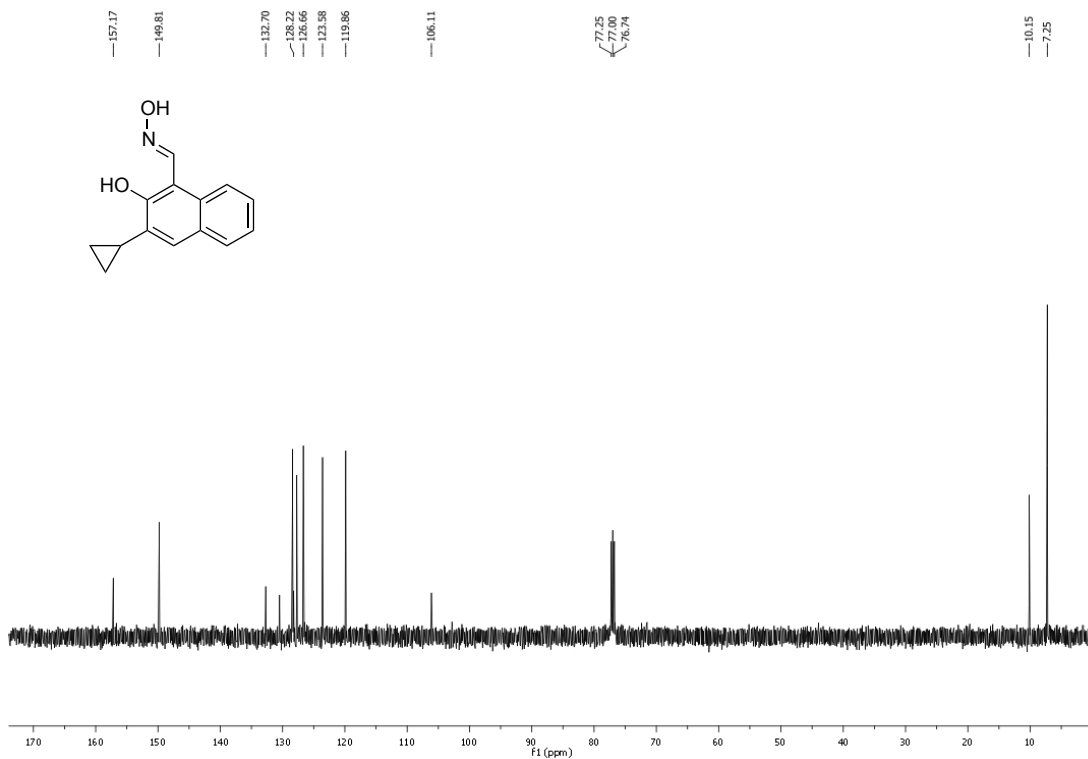
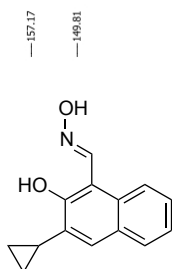
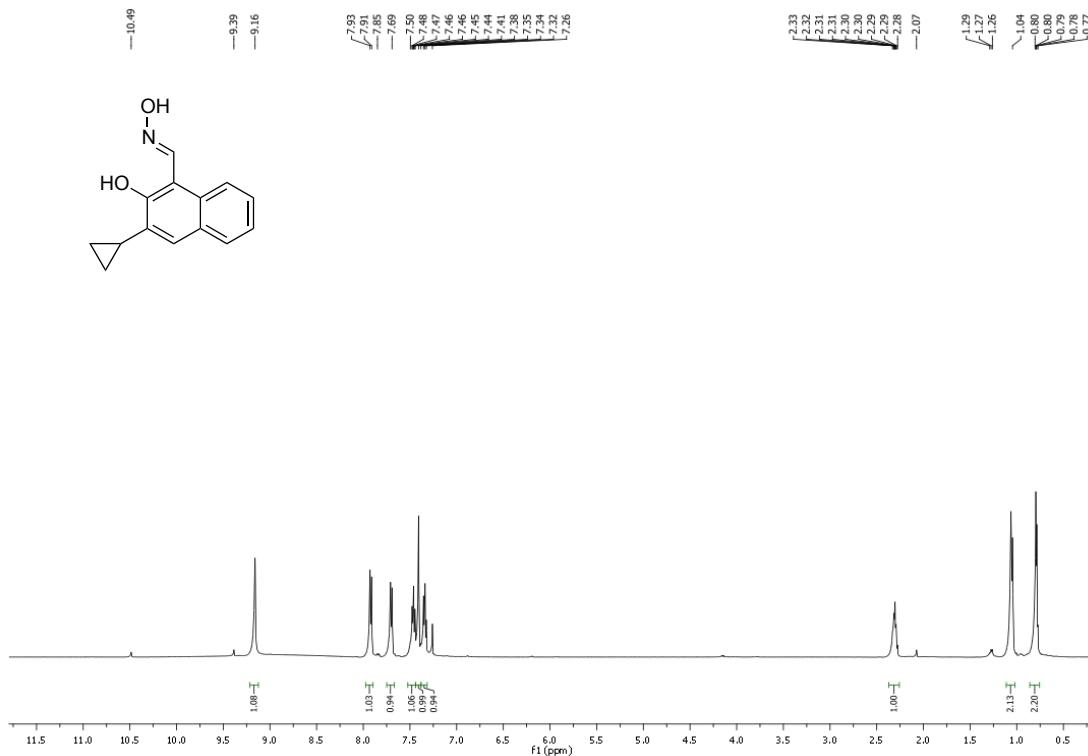
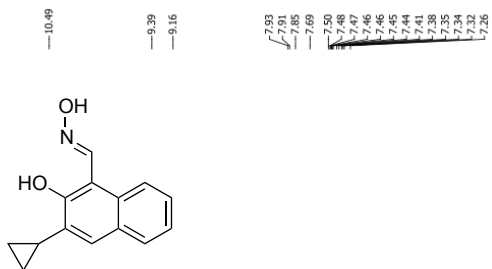
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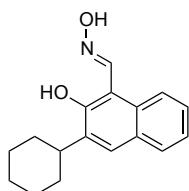
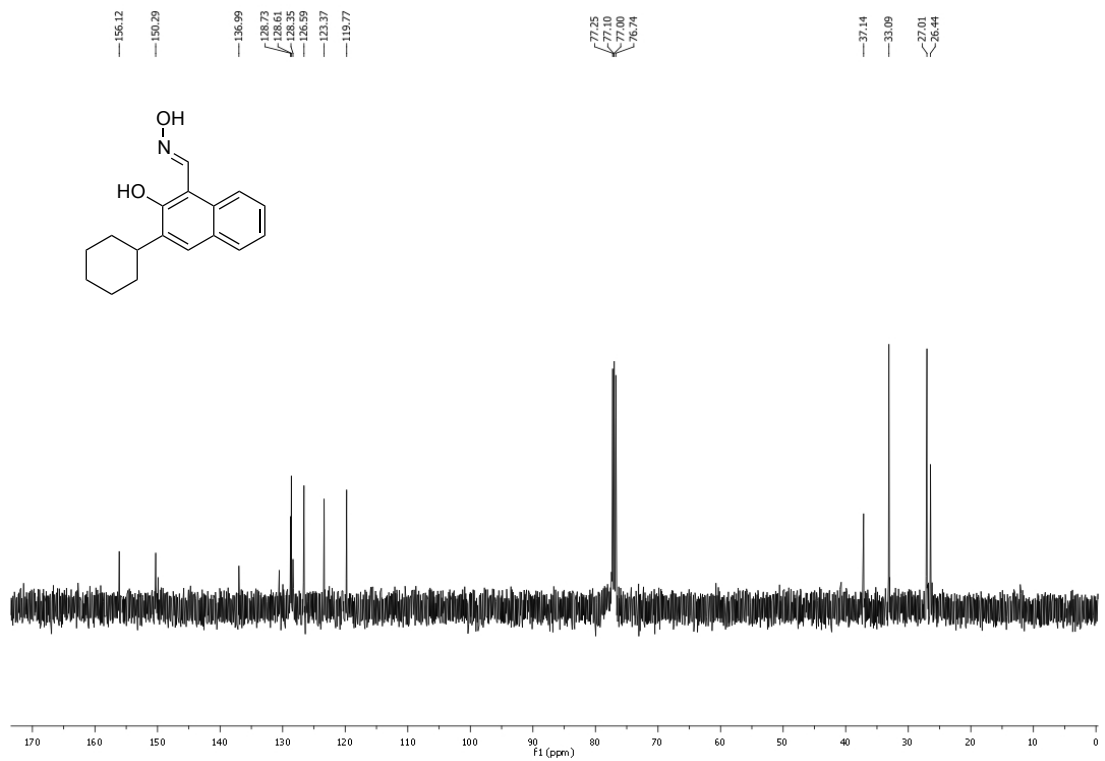
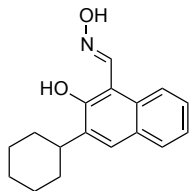
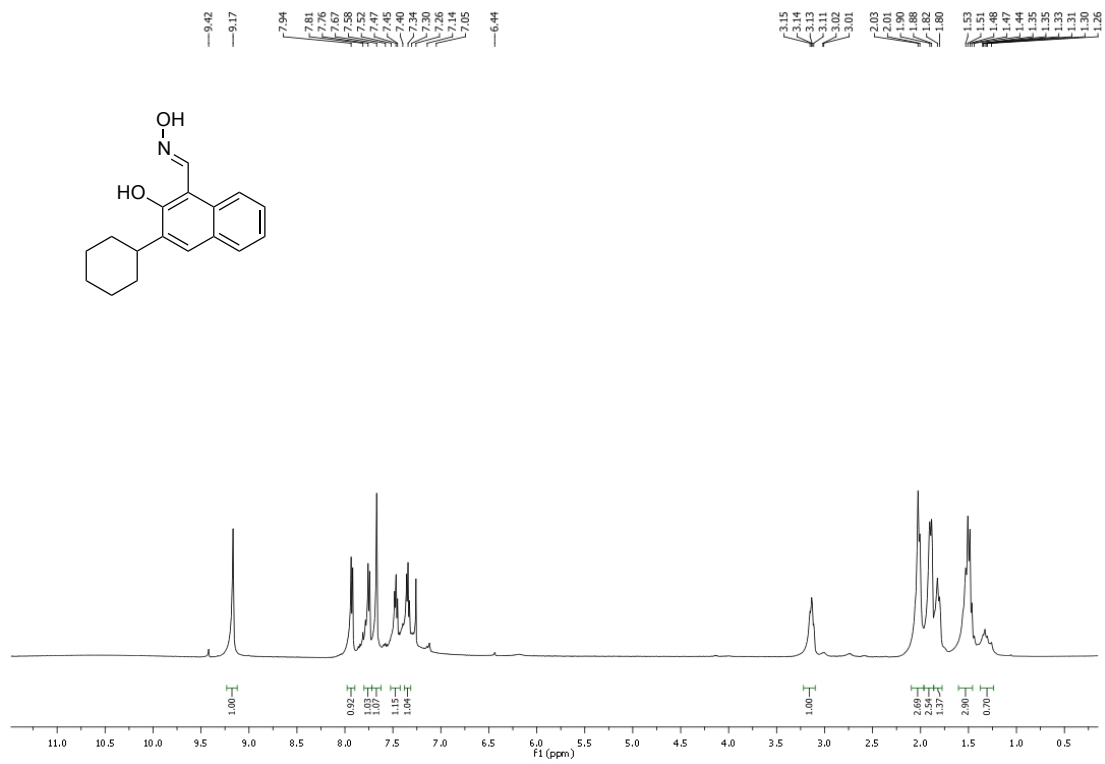
Compound 13a



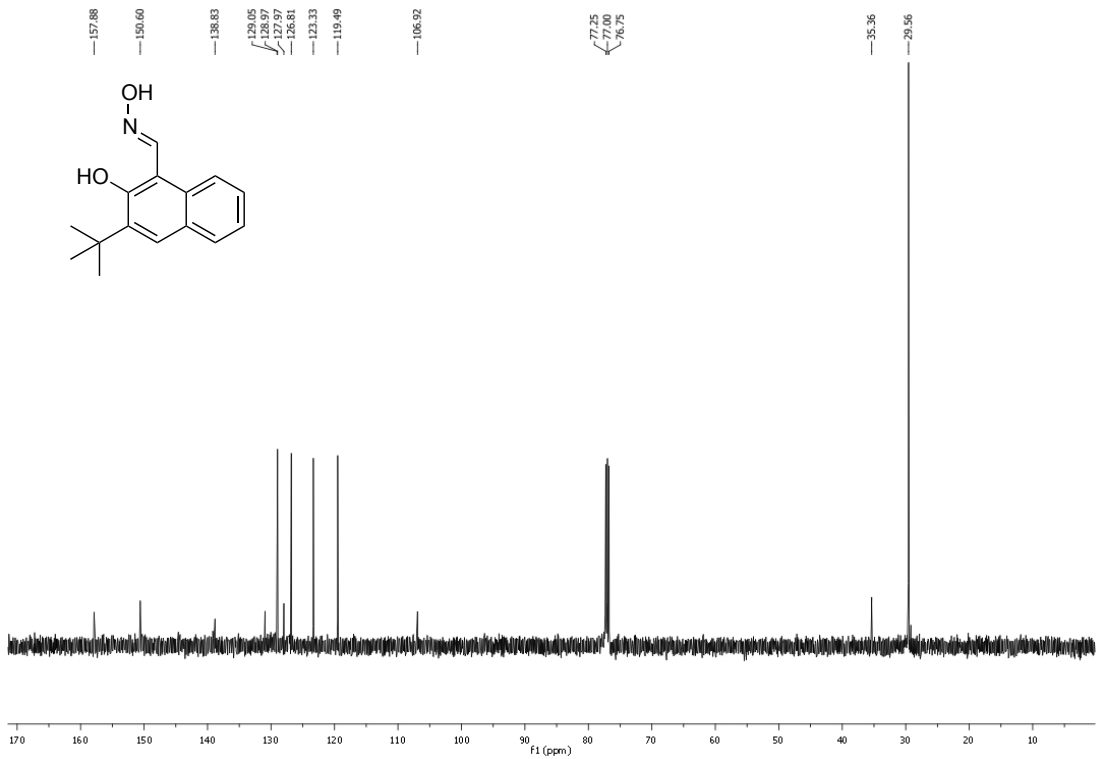
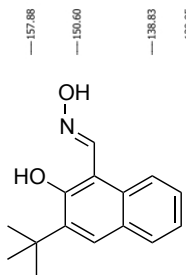
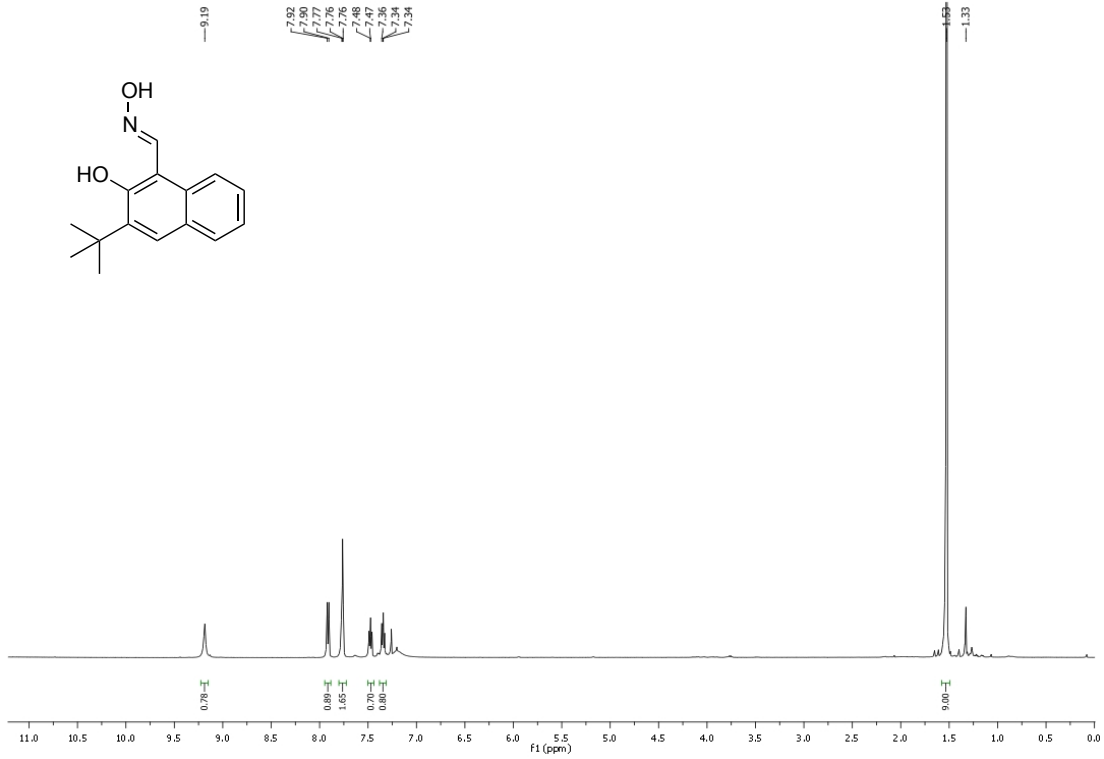
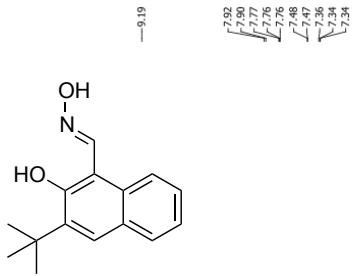
Compound 13b



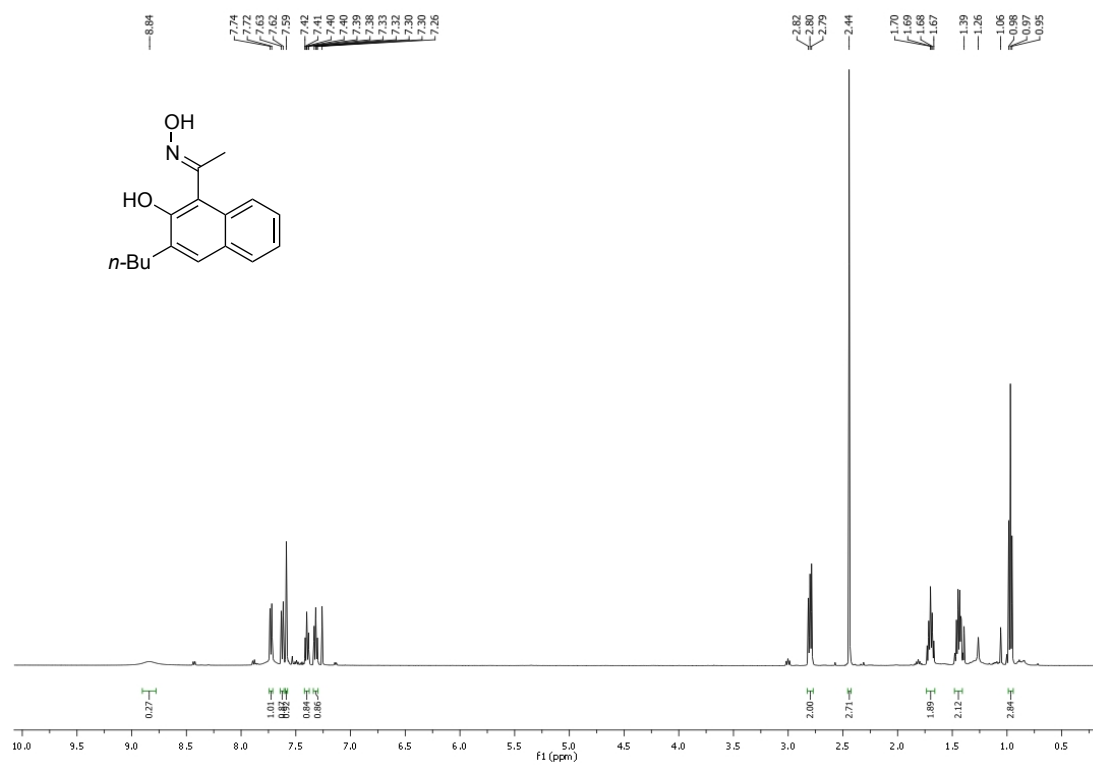
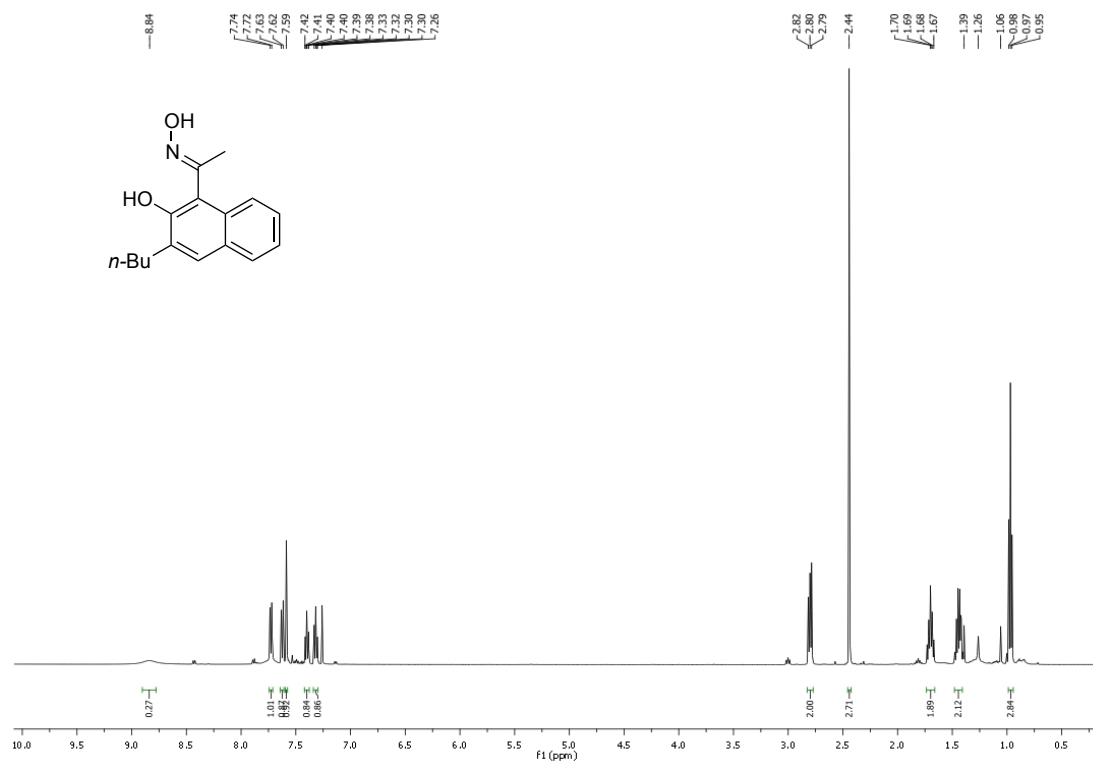
Compound 13c



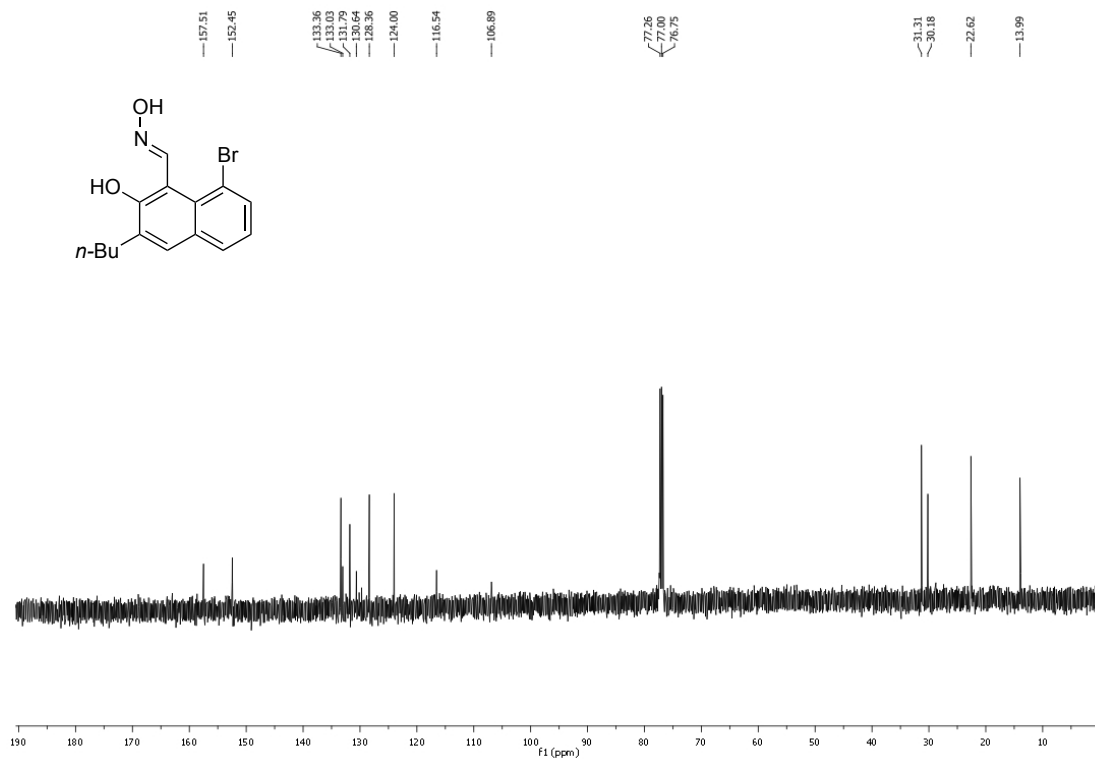
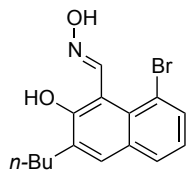
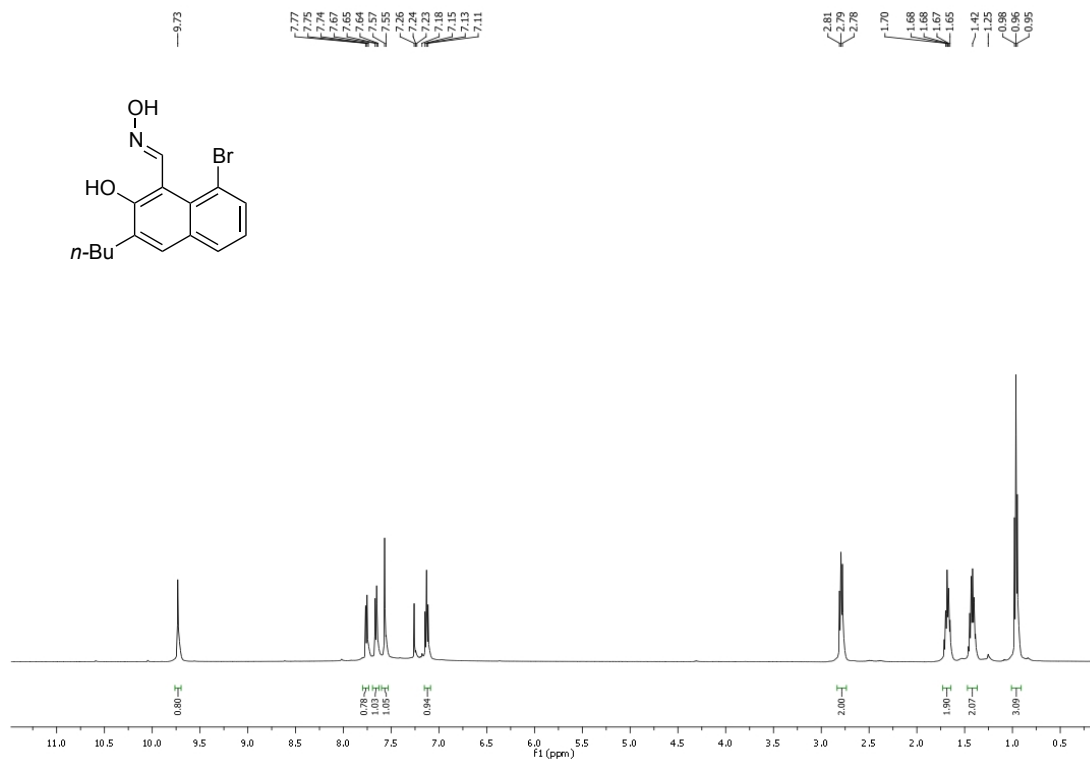
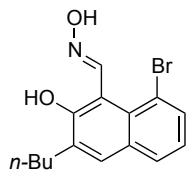
Compound 13d



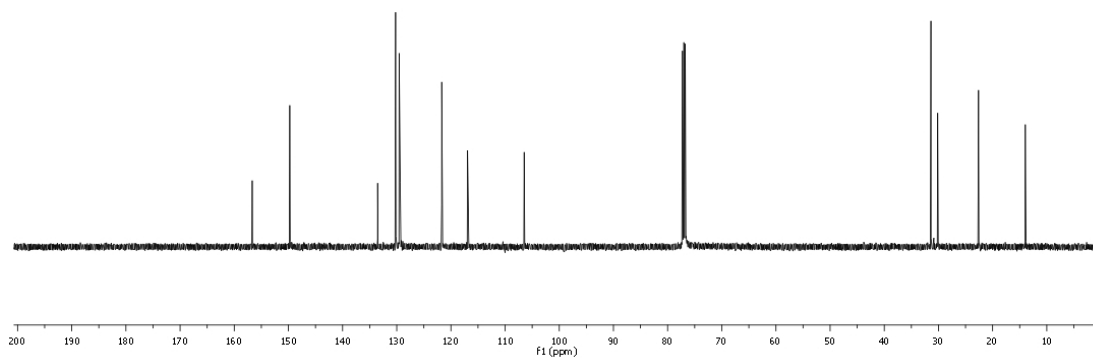
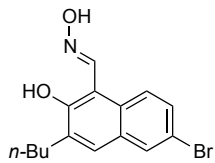
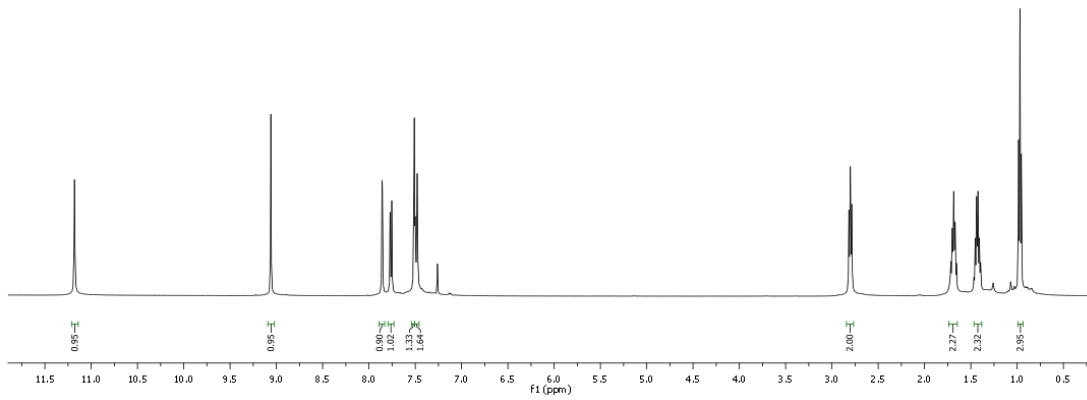
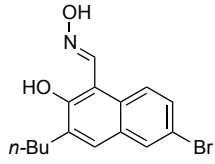
Compound 13e



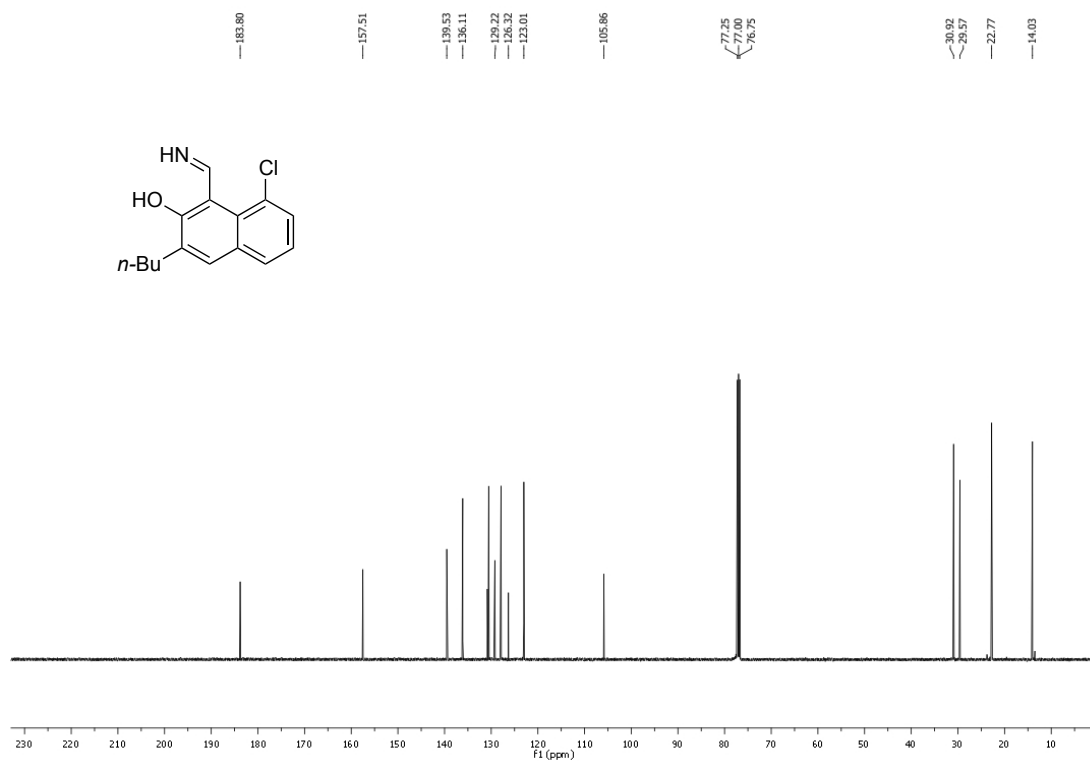
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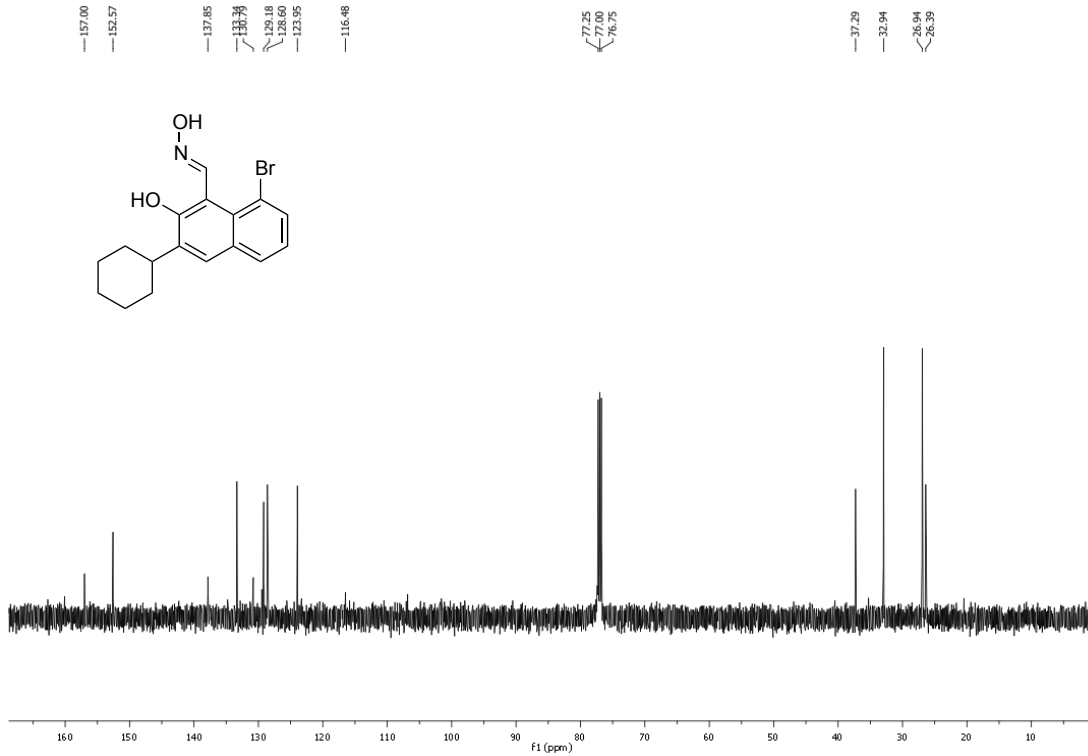
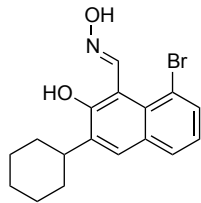
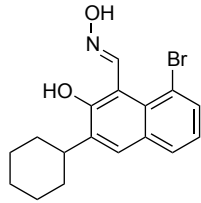
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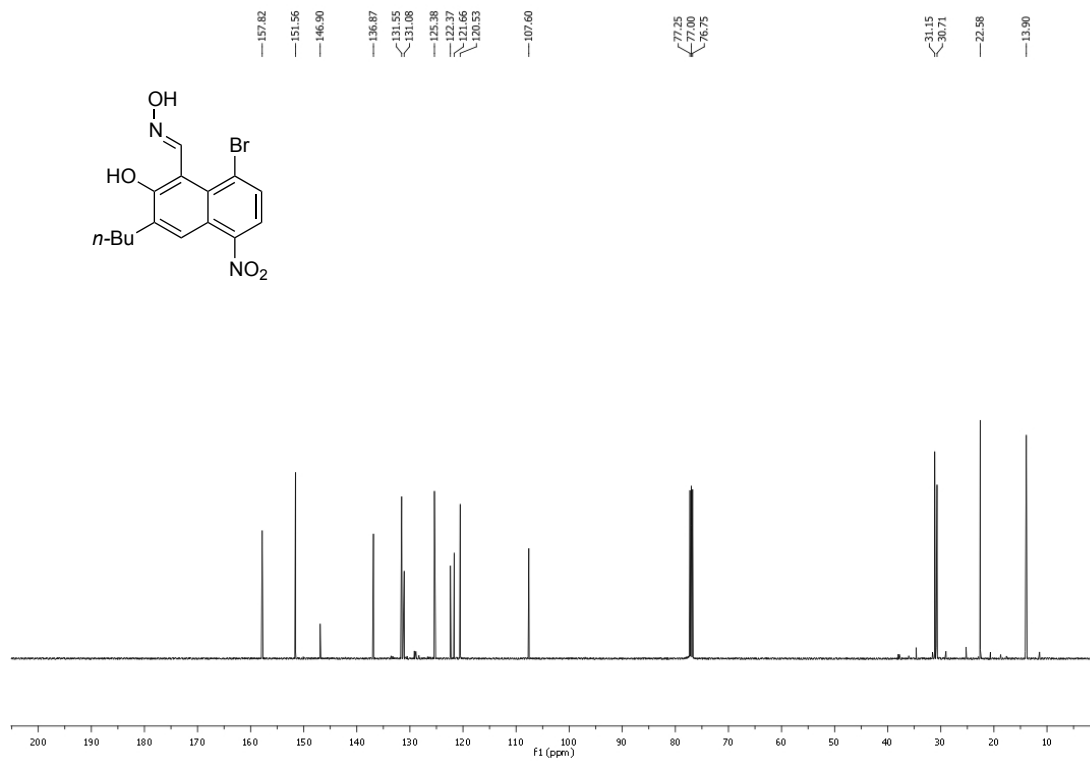
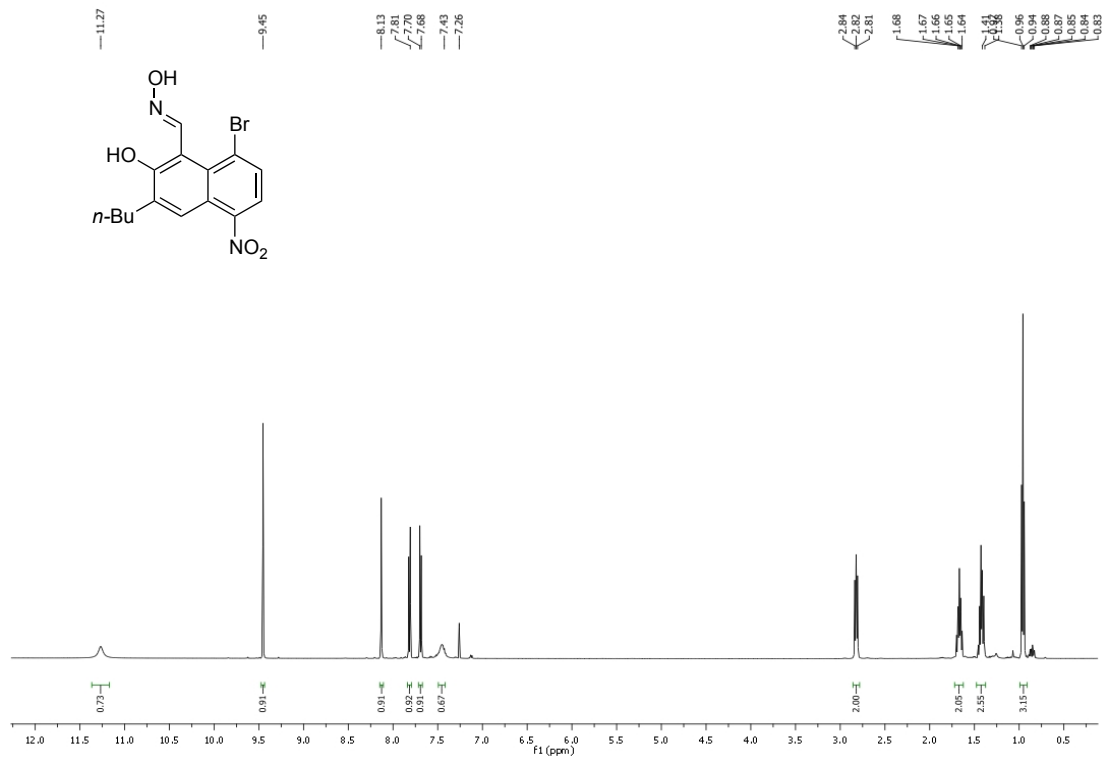
Compound 13h



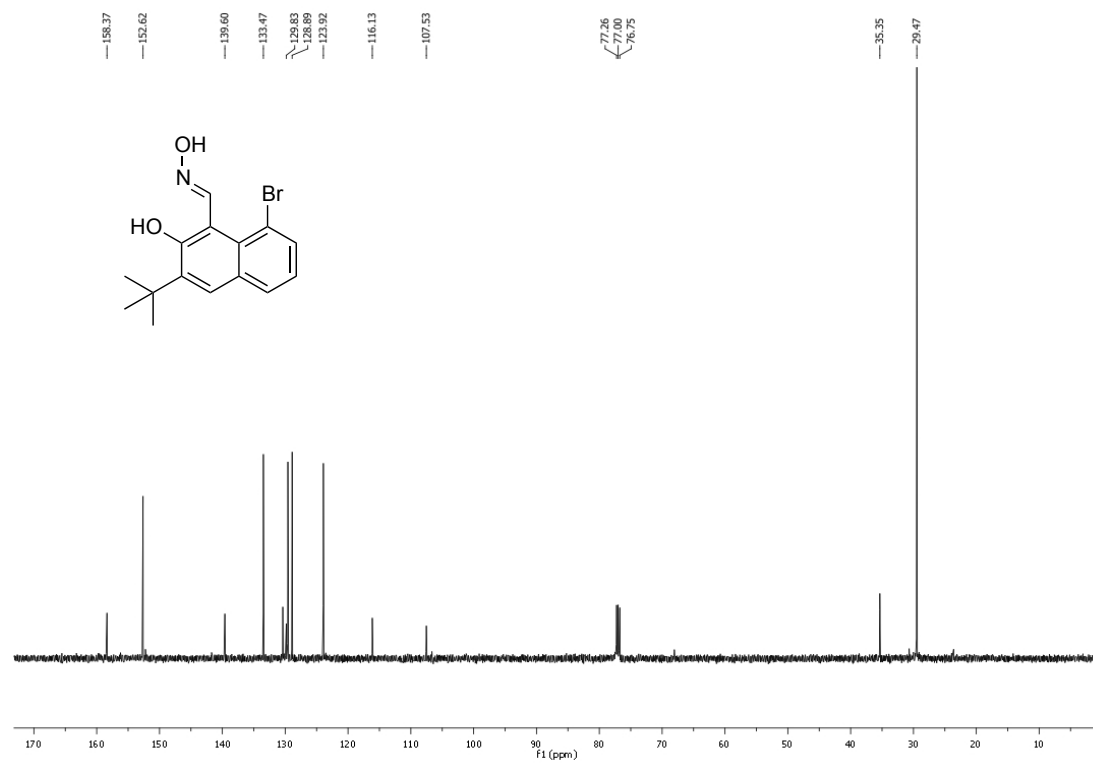
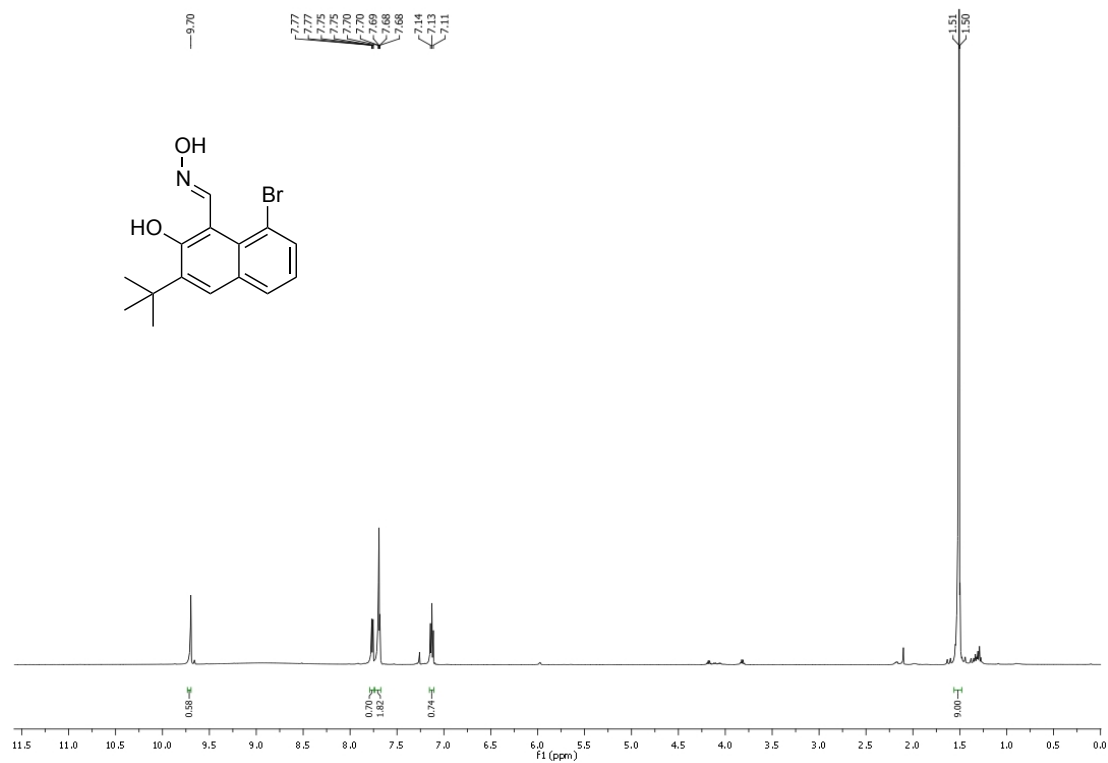
Compound 13i



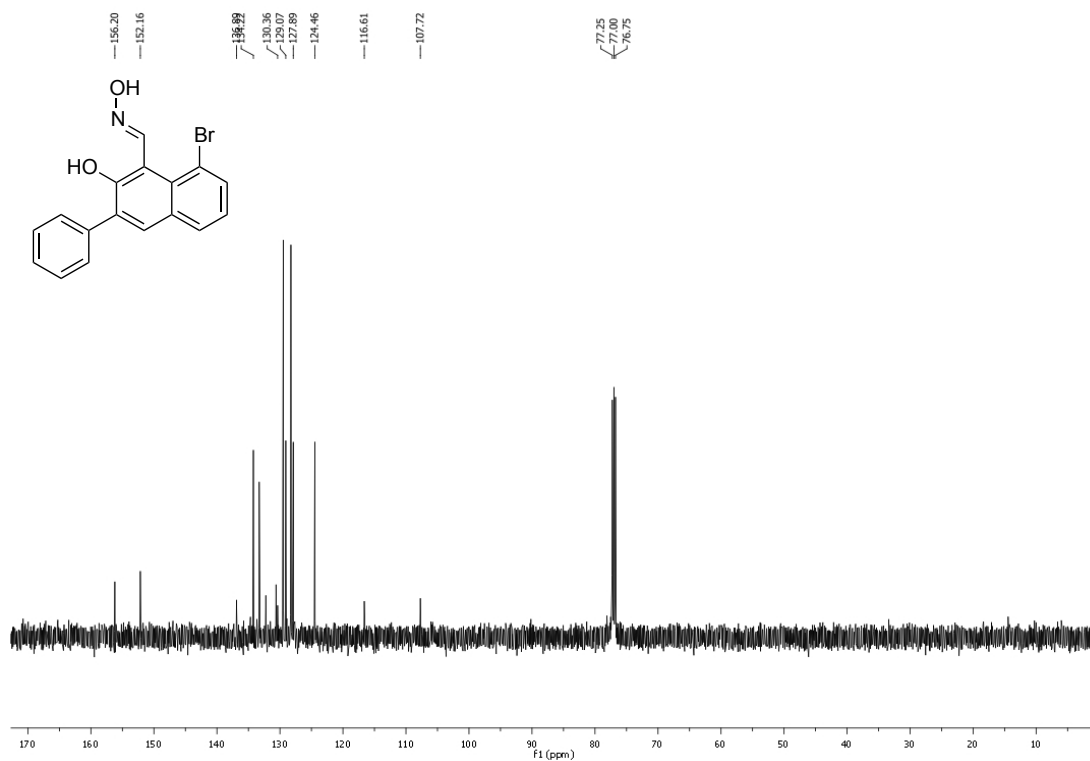
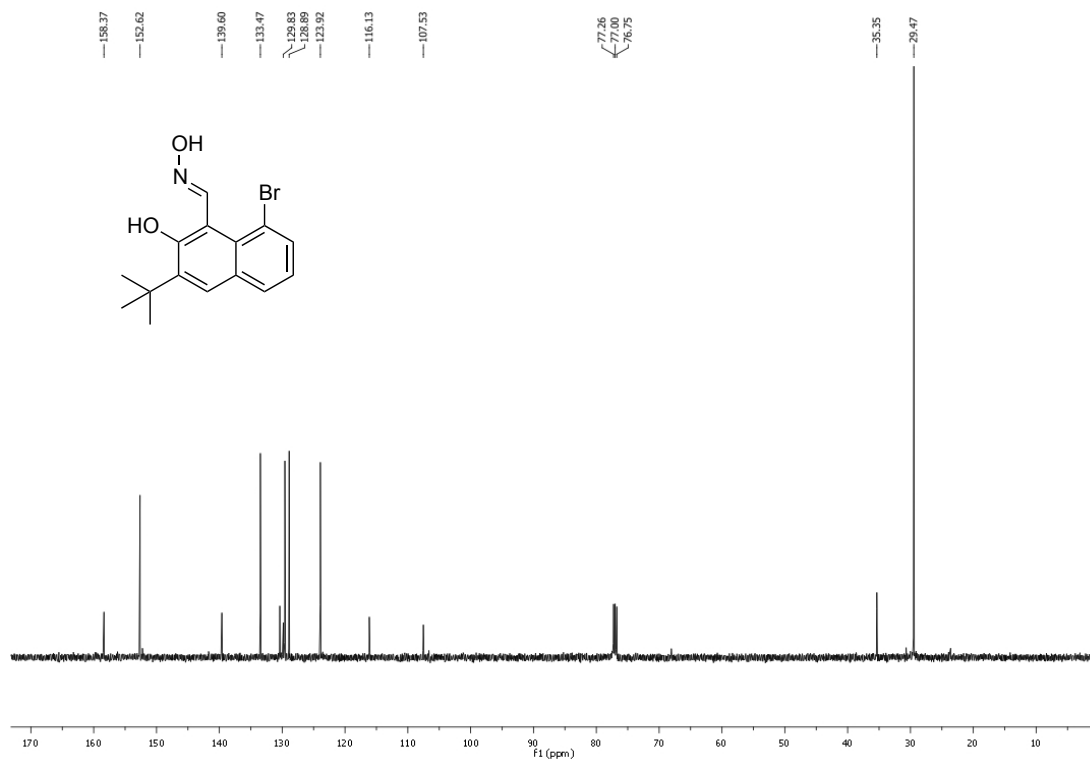
Compound 13j



Compound 13k

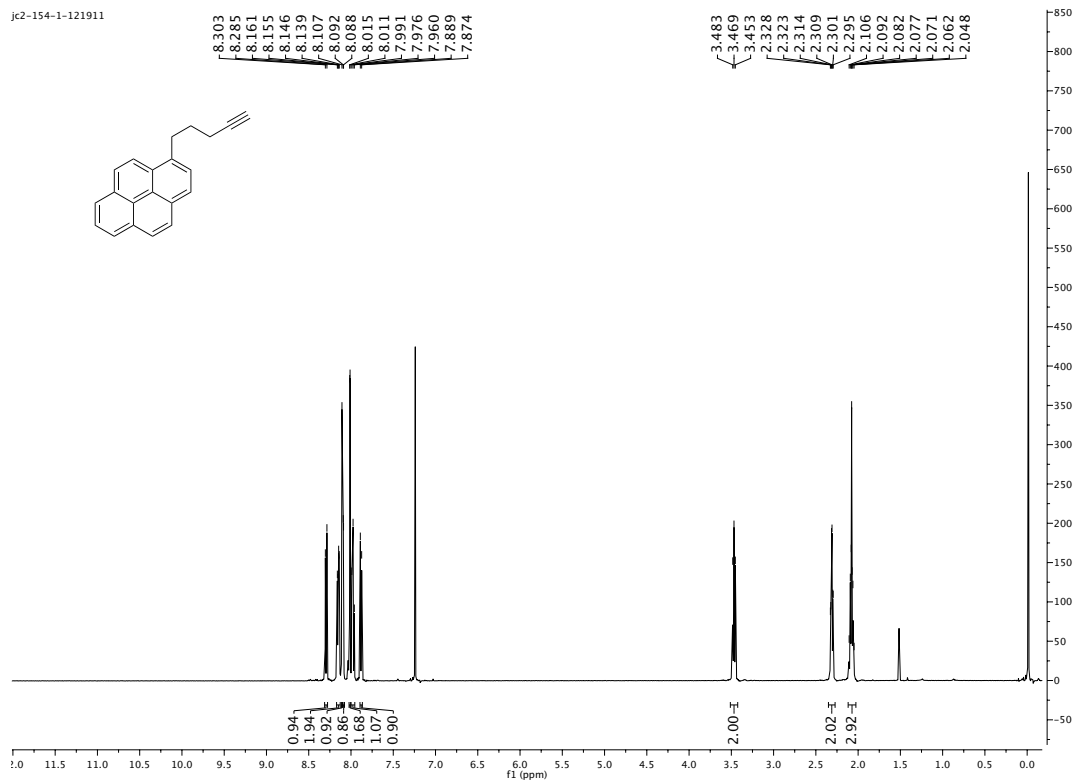


Compound 13I

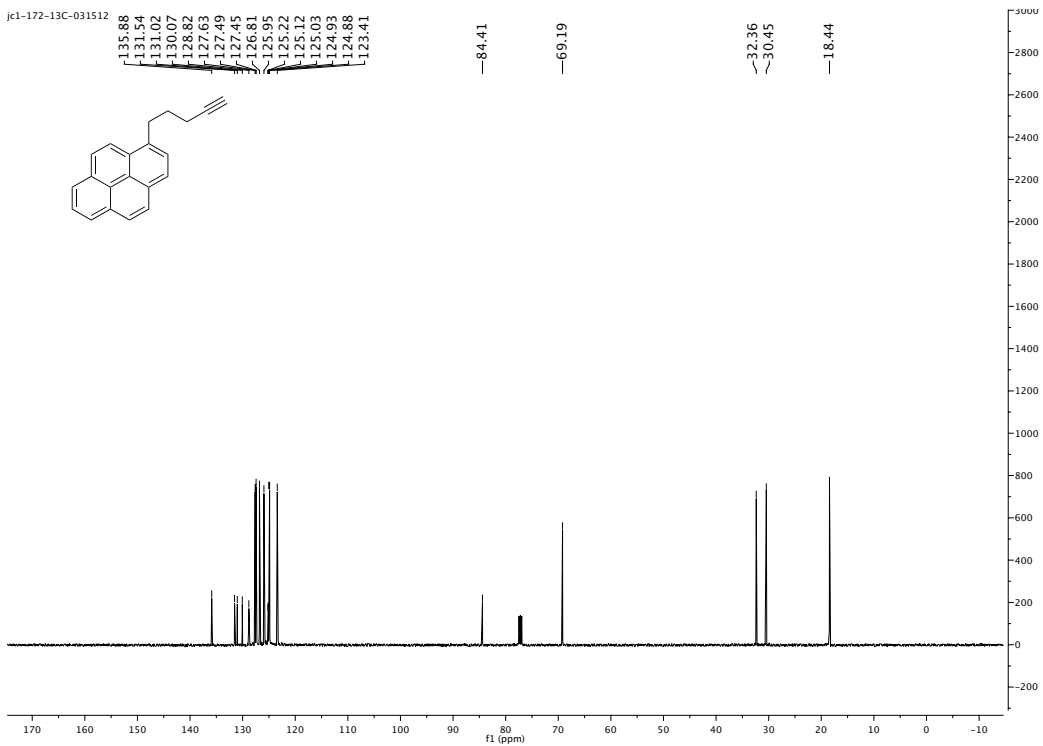


Compound 14

jc2-154-1-121911

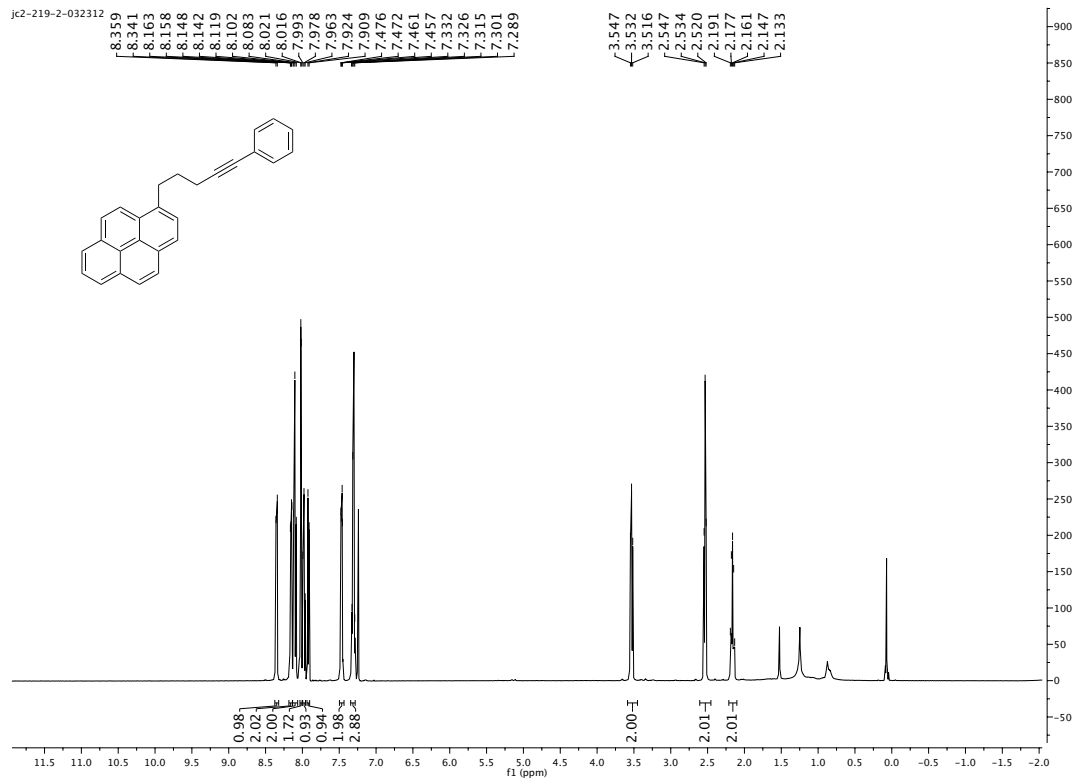


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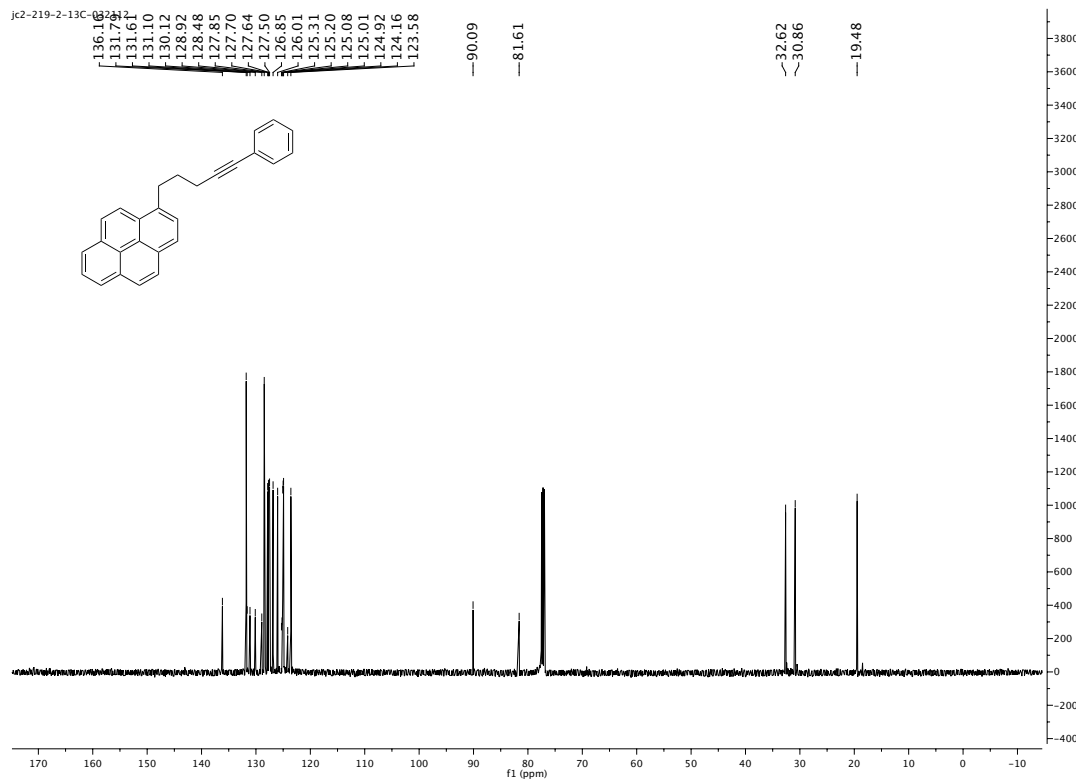


Compound 15

jc2-219-2-032312

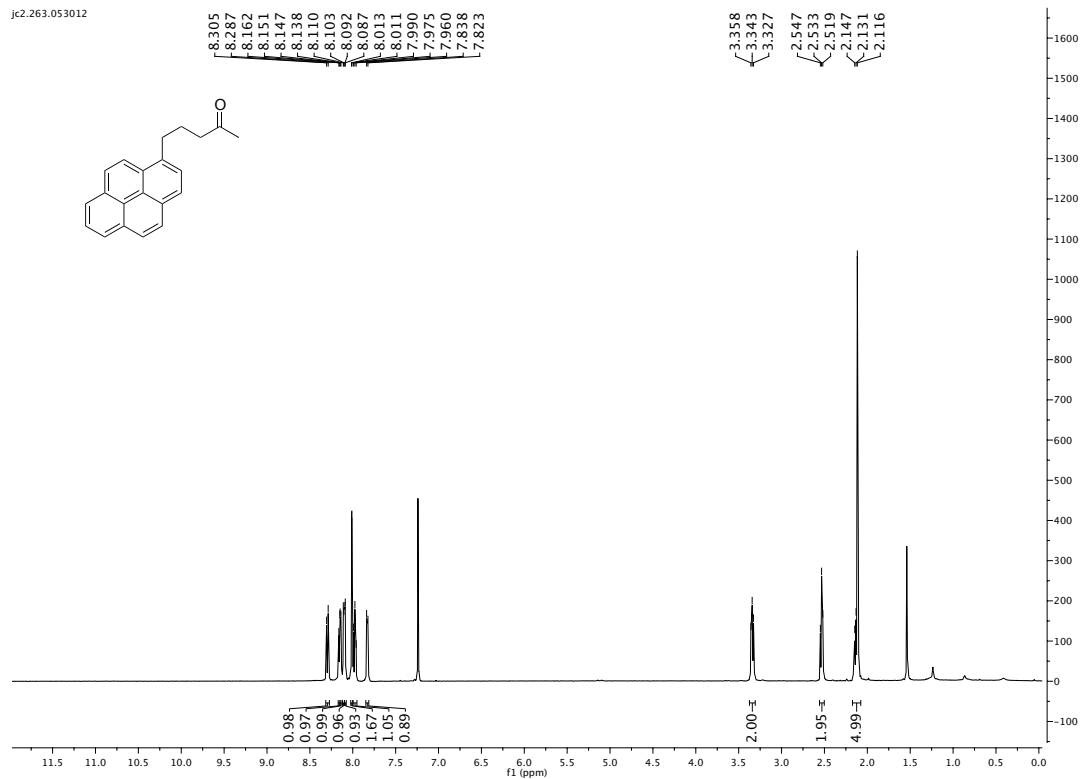


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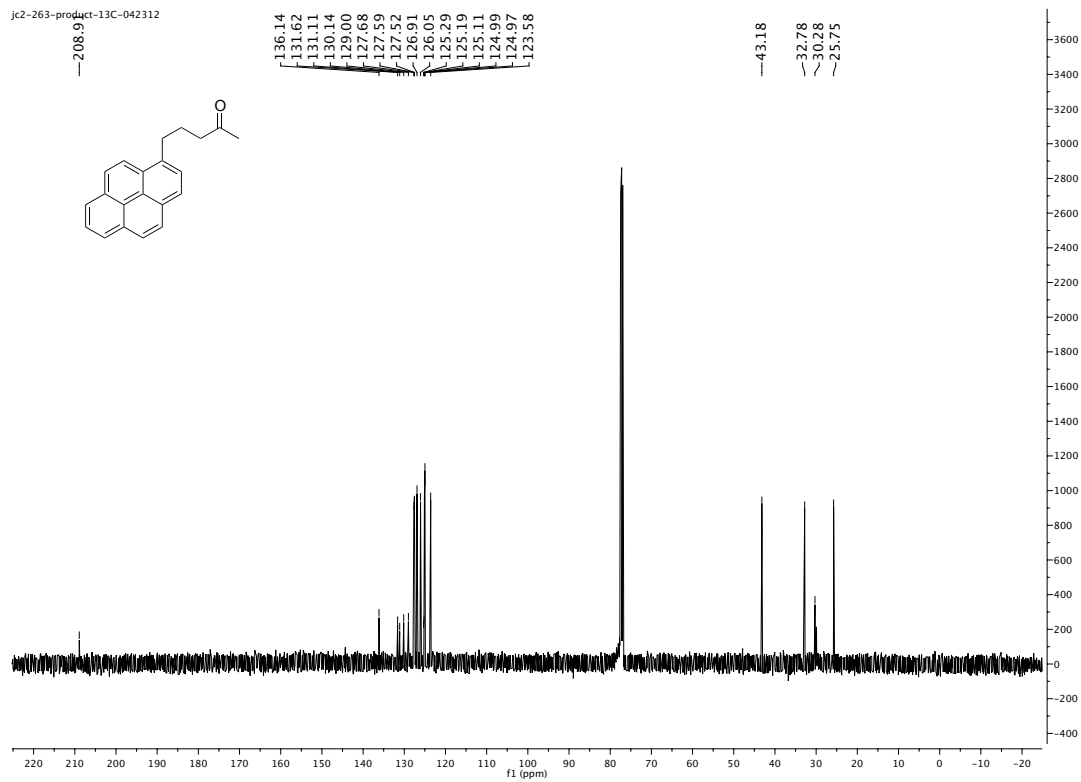


Compound 16

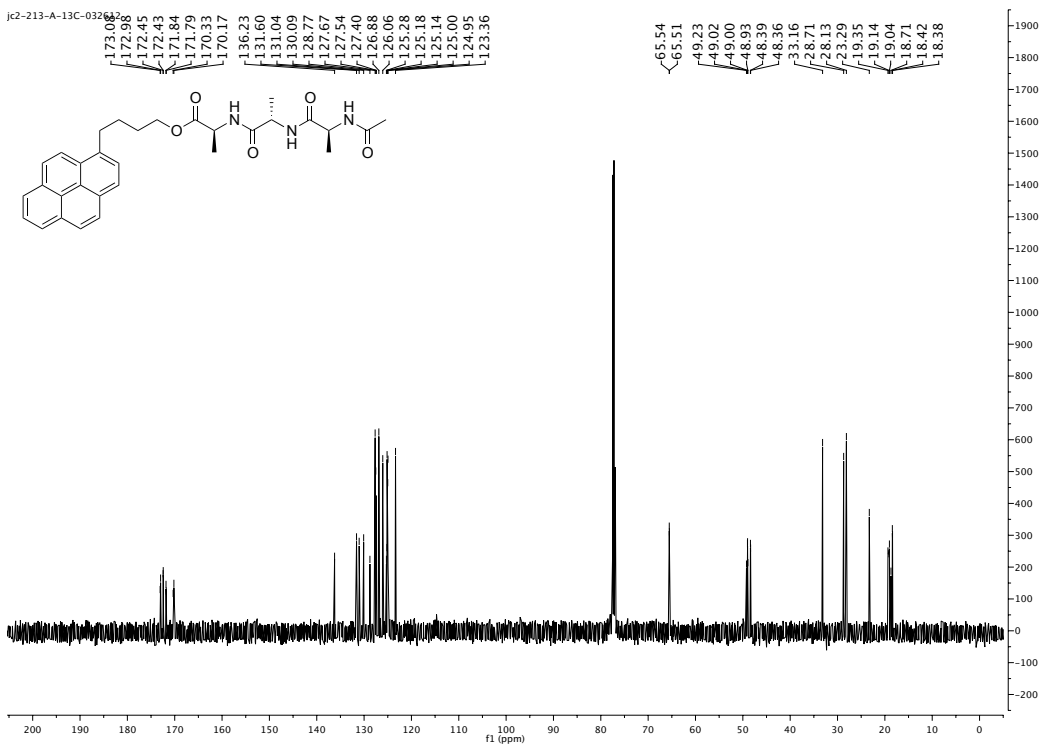
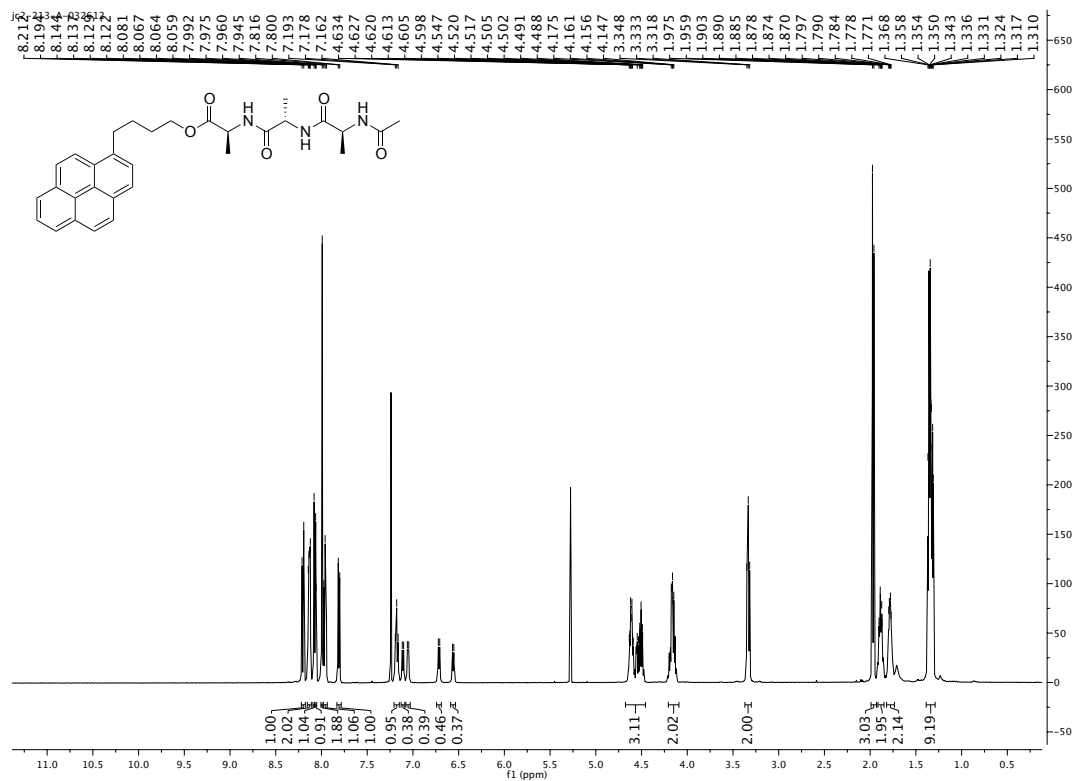
jc2.263.053012



jc2-263-product-13C-042312

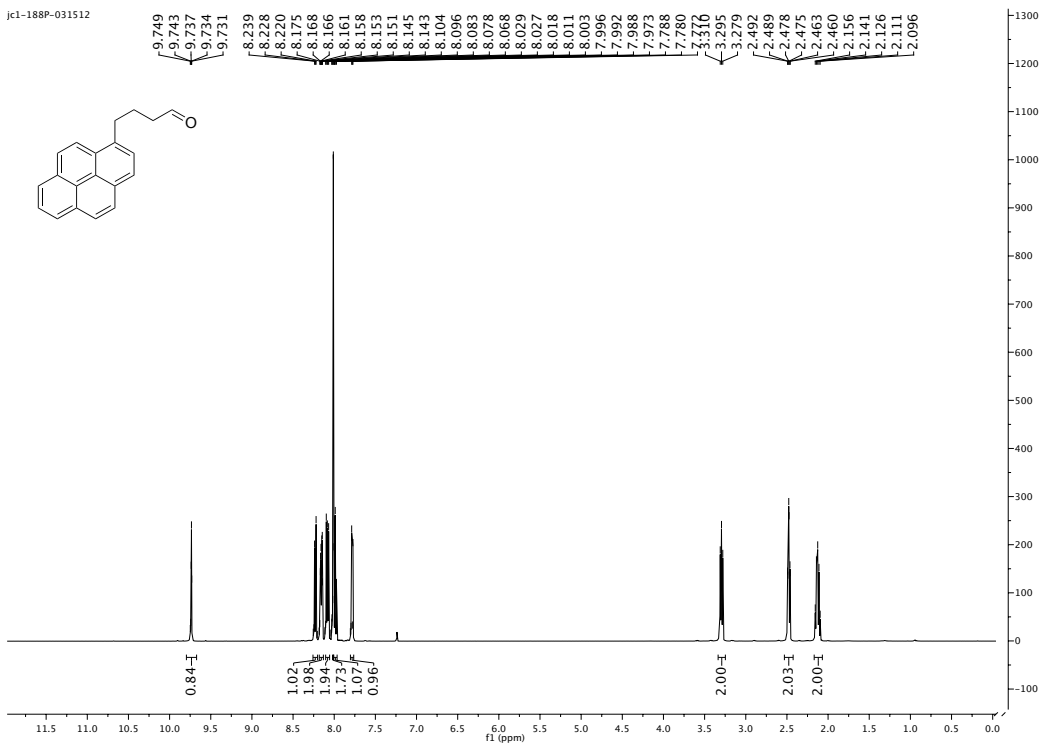


Compound 17

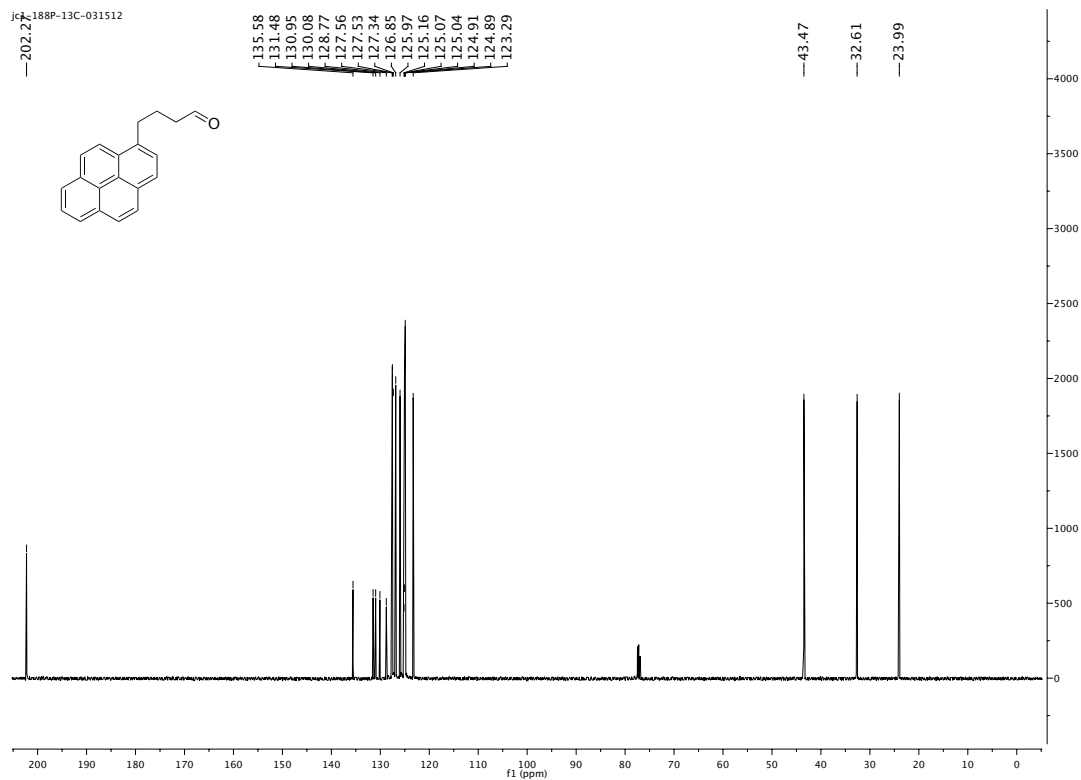


Compound 18

jc1-188P-031512

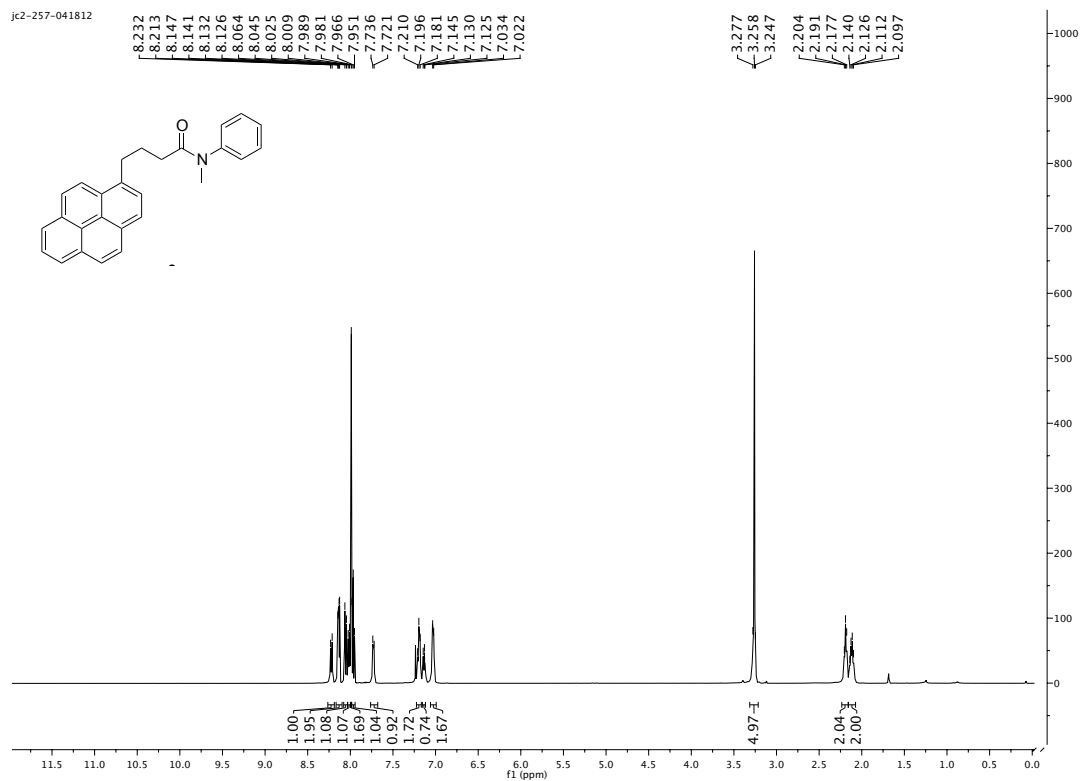


jc1-188P-13C-031512

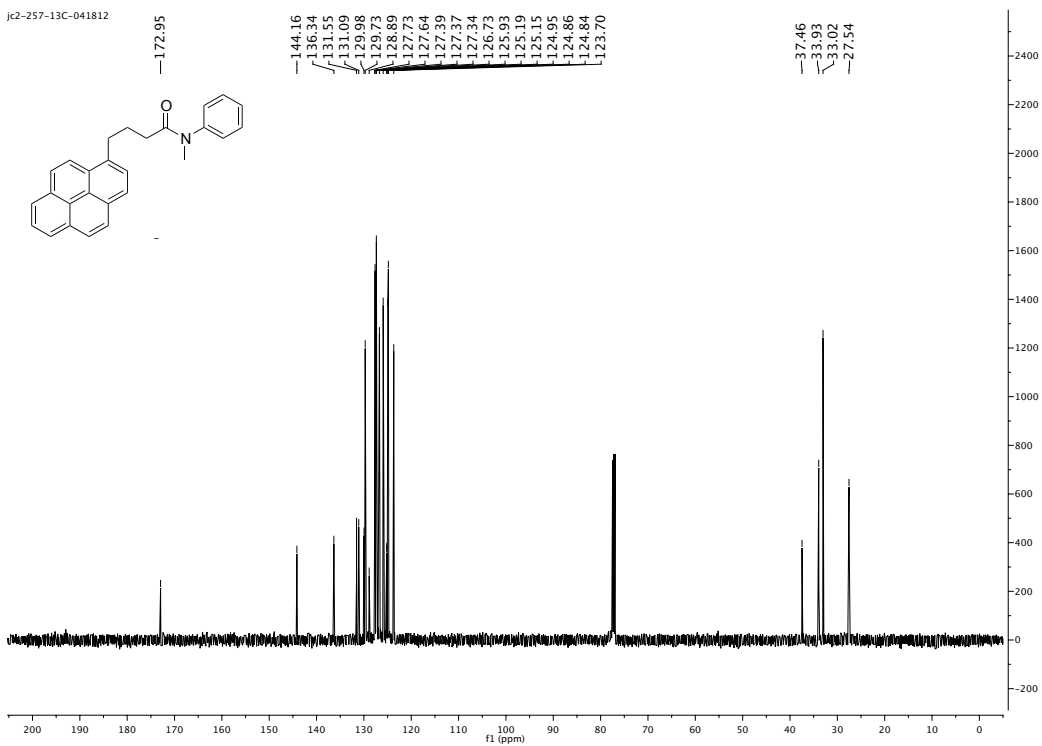


Compound 20

jc2-257-041812

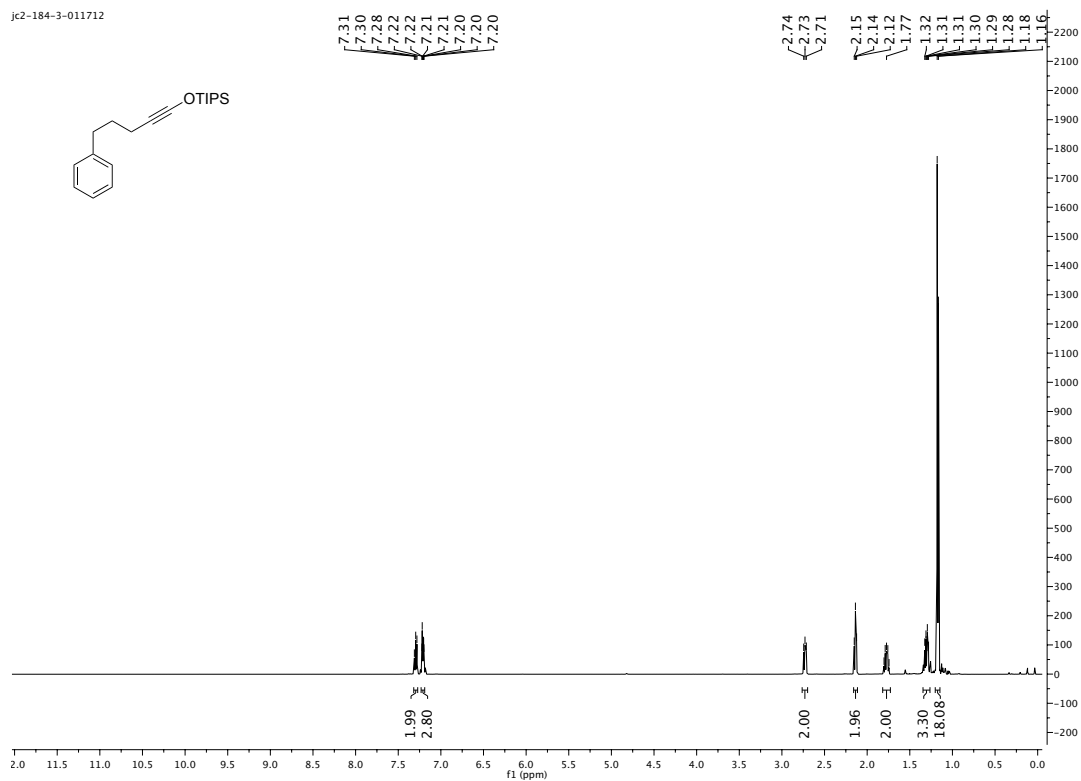


jc2-257-13C-041812

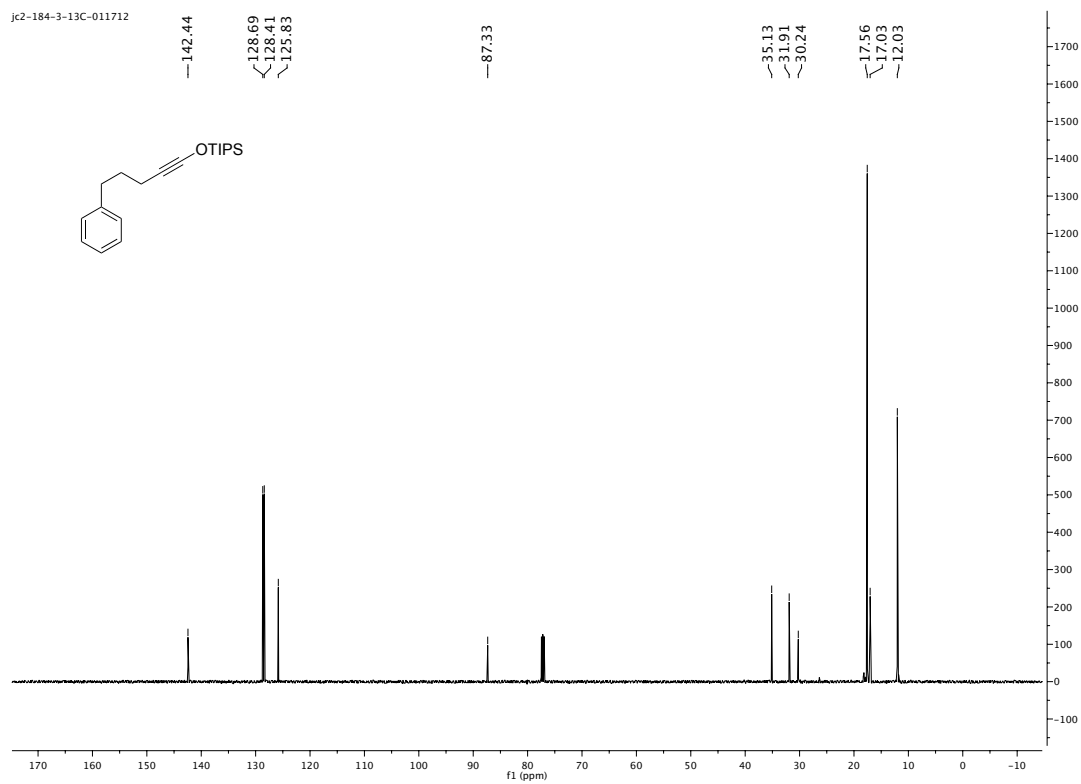


Compound 22

jc2-184-3-011712



jc2-184-3-13C-011712



X-Ray crystal structures

X-ray Crystal Structures for 10a, 10e, 13a, and 13f

Single crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a solution of **10a** and **10e** in DCM/hexanes (Supplementary Figure 4), **13a** and **13f** in Hexanes/EtOAc (Supplementary Figure 5). CCDC 895621, 895622, 895726, 895727 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Data Collection for 10a

An elongate broken fragment (0.48 x 0.20 x 0.12 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained which samples approximately all of reciprocal space to a resolution of 0.84 Å using 0.3° steps in using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Data Collection for 10e

A rod shaped fragment (0.36 x 0.12 x 0.10 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained which samples approximately all of reciprocal space to a resolution of 1.00 Å using 0.3° steps in using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Data Collection for 13a

An irregular broken fragment (0.32 x 0.32 x 0.40 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained which samples approximately all of reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Data Collection for 13f

An irregular rod-shaped fragment (0.48 x 0.20 x 0.16 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

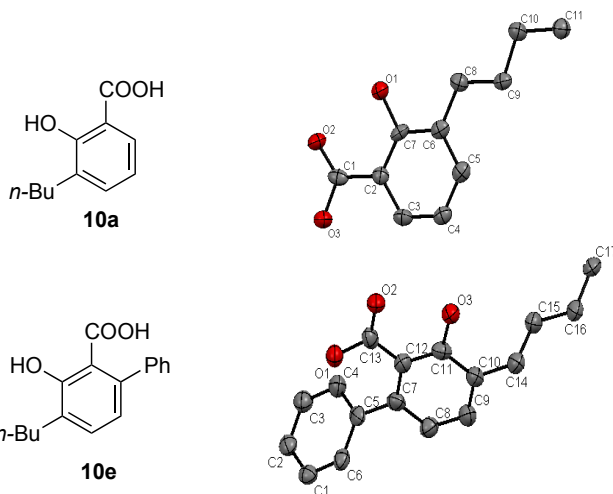
A “full sphere” data set was obtained which samples approximately all of reciprocal space to a resolution of 0.75 Å using 0.3° steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement for 10a, 10e, and 13a

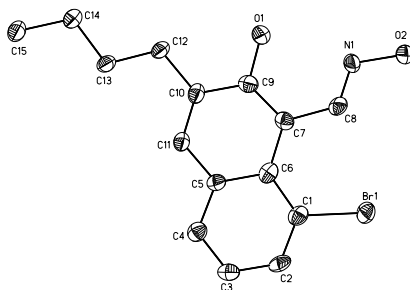
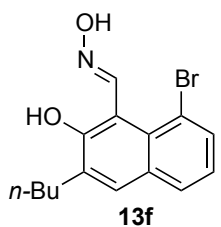
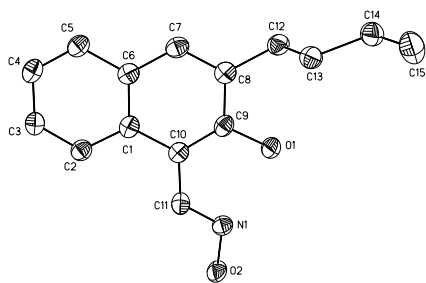
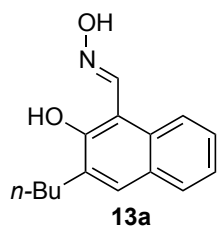
The space group was determined as P2₁/c based on systematic absences and intensity statistics. Direct methods were used to locate most C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C and O atoms. Following anisotropic refinement of the non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for O and C and isotropic riding for H atoms. No anomalous bond lengths or thermal parameters were noted. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Structure solution and refinement for 13f

The space group was determined as P1($\bar{1}$) based on systematic absences and intensity statistics. Direct methods were used to locate the Br and most C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, N and O atoms. Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for all non-H atoms and isotropic riding for H atoms. No anomalous bond lengths or thermal parameters were noted. All ORTEP diagrams have been drawn with 50% probability ellipsoids.



Supplementary Figure S4. X-ray Crystal Structure of 10a and 10e.



Supplementary Figure S5. X-ray Crystal Structure of 13a and 13f.

Supplementary Table S3. Crystal and structure refinement for 10a.

Identification Code	13a	
Empirical formula	$C_{11}H_{14}O_3$	
Formula weight	194.22	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space Group	$P2_1/c$	
Unit cell dimensions	$a = 6.845(4)$ Å	$a = 90.0^\circ$
	$b = 14.765(9)$ Å	$b = 108.061(11)^\circ$

	$c = 9.899(6) \text{ \AA}$	$g = 90.0^\circ$
Volume	951.1(10) \AA^3	
Z	4	
Density (calculated)	1.356 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	416	
Crystal size, color, habit	0.48 x 0.20 x 0.12mm, clear, rod	
Theta range for data collection	2.57 – 25.29 $^\circ$	
Index ranges	$-8 \leq h \leq 8, -17 \leq k \leq 17, -11 \leq l \leq 11$	
Reflections collected	8,963	
Independent reflections	1,704 ($R_{\text{int}} = 0.0504$)	
Reflections with $I > 4s(F_o)$	901	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.379	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = [s^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2 F_c^2)/3, a = 0.0549, b = 0.0, q = 1$	
Data / restraints / parameters	1704 / 0 / 130	
Goodness-of-fit on F^2	0.836	
Final R indices [$I > 2 \text{ sigma}(I)$]	R1 = 0.0643, wR2 = 0.1245	
R indices (all data)	R1 = 0.1198, wR2 = 0.1406	
Largest diff. peak and hole	0.258, -0.219 e\AA^{-3}	

Supplementary Table S4. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 10a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
C(1)	12961(5)	5139(2)	5957(3)	32(1)	
C(2)	11421(5)	5259(2)	6660(3)	29(1)	
C(3)	10774(5)	6118(2)	6897(3)	32(1)	
C(4)	9335(5)	6222(2)	7564(3)	33(1)	
C(5)	8503(5)	5471(2)	8020(3)	35(1)	
C(6)	9097(5)	4599(2)	7805(3)	30(1)	
C(7)	10544(5)	4515(2)	7100(3)	30(1)	
C(8)	8227(5)	3775(2)	8278(3)	33(1)	
C(9)	6727(5)	3908(2)	9090(3)	30(1)	
C(10)	5986(5)	3025(2)	9491(3)	35(1)	
C(11)	4463(5)	3123(2)	10301(3)	37(1)	
O(1)	11067(3)	3656(1)	6878(2)	35(1)	
O(2)	13573(3)	4393(1)	5700(2)	33(1)	
O(3)	13718(3)	5880(2)	5631(2)	35(1)	

Supplementary Table S5. Bond lengths [Å] and angles [°] for 10a.

C(1)-O(2)	1.233(4)
C(1)-O(3)	1.294(3)
C(1)-C(2)	1.443(4)
C(2)-C(7)	1.385(4)
C(2)-C(3)	1.387(4)
C(3)-C(4)	1.354(4)
C(4)-C(5)	1.384(4)
C(5)-C(6)	1.387(4)
C(6)-C(7)	1.382(4)
C(6)-C(8)	1.492(4)
C(7)-O(1)	1.355(3)
C(8)-C(9)	1.501(4)
C(9)-C(10)	1.496(4)
C(10)-C(11)	1.506(4)
O(2)-C(1)-O(3)	121.1(3)
O(2)-C(1)-C(2)	123.7(3)
O(3)-C(1)-C(2)	115.2(3)
C(7)-C(2)-C(3)	118.6(3)
C(7)-C(2)-C(1)	120.5(3)
C(3)-C(2)-C(1)	120.9(3)
C(4)-C(3)-C(2)	120.3(3)
C(3)-C(4)-C(5)	120.2(3)
C(4)-C(5)-C(6)	121.6(3)
C(7)-C(6)-C(5)	116.7(3)
C(7)-C(6)-C(8)	120.2(3)
C(5)-C(6)-C(8)	123.0(3)
O(1)-C(7)-C(6)	115.6(3)
O(1)-C(7)-C(2)	121.9(3)
C(6)-C(7)-C(2)	122.4(3)
C(6)-C(8)-C(9)	117.9(3)
C(10)-C(9)-C(8)	111.9(3)
C(9)-C(10)-C(11)	113.9(3)

Supplementary Table S6. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 10a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	36(2)	26(2)	26(2)	5(2)	0(2)	-5(2)
C(2)	30(2)	29(2)	27(2)	2(1)	8(2)	0(2)
C(3)	35(2)	25(2)	31(2)	0(2)	5(2)	-5(2)
C(4)	36(2)	28(2)	31(2)	-2(2)	6(2)	2(2)
C(5)	35(2)	36(2)	31(2)	-3(2)	7(2)	3(2)
C(6)	30(2)	29(2)	25(2)	-4(2)	0(2)	1(2)
C(7)	37(2)	20(2)	29(2)	-3(2)	6(2)	8(2)
C(8)	36(2)	31(2)	31(2)	2(2)	9(2)	-3(2)
C(9)	32(2)	24(2)	30(2)	0(2)	4(2)	0(2)
C(10)	37(2)	31(2)	37(2)	-1(2)	11(2)	-4(2)
C(11)	41(2)	35(2)	37(2)	0(2)	13(2)	-1(2)
O(1)	39(2)	28(1)	40(2)	1(1)	15(1)	3(1)
O(2)	41(2)	22(1)	37(1)	-1(1)	12(1)	3(1)
O(3)	39(2)	25(1)	42(2)	1(1)	14(1)	-2(1)

Supplementary Table S7. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 10a.

	x	y	z	U(eq)
H(3)	11343	6636	6589	38
H(4)	8894	6812	7719	39
H(5)	7502	5556	8492	42
H(8A)	9388	3410	8876	40
H(8B)	7541	3410	7424	40
H(9A)	7393	4261	9962	36
H(9B)	5536	4261	8503	36
H(10A)	7184	2676	10077	42
H(10B)	5341	2673	8615	42
H(11A)	5107	3448	11191	56
H(11B)	4030	2521	10513	56
H(11C)	3263	3462	9726	56
H(1)	11989	3666	6482	52
H(3A)	14566	5755	5201	53

Supplementary Table S8. Torsion angles [°] for 10a.

O(2)-C(1)-C(2)-C(7)	0.5(5)
O(3)-C(1)-C(2)-C(7)	-178.0(3)
O(2)-C(1)-C(2)-C(3)	-178.9(3)
O(3)-C(1)-C(2)-C(3)	2.6(4)
C(7)-C(2)-C(3)-C(4)	0.9(5)
C(1)-C(2)-C(3)-C(4)	-179.7(3)
C(2)-C(3)-C(4)-C(5)	0.3(5)
C(3)-C(4)-C(5)-C(6)	-0.4(5)
C(4)-C(5)-C(6)-C(7)	-0.6(5)
C(4)-C(5)-C(6)-C(8)	-179.7(3)
C(5)-C(6)-C(7)-O(1)	-178.7(3)
C(8)-C(6)-C(7)-O(1)	0.4(4)
C(5)-C(6)-C(7)-C(2)	1.9(4)
C(8)-C(6)-C(7)-C(2)	-179.0(3)
C(3)-C(2)-C(7)-O(1)	178.6(3)
C(1)-C(2)-C(7)-O(1)	-0.8(5)
C(3)-C(2)-C(7)-C(6)	-2.1(5)
C(1)-C(2)-C(7)-C(6)	178.5(3)
C(7)-C(6)-C(8)-C(9)	177.5(3)
C(5)-C(6)-C(8)-C(9)	-3.4(5)
C(6)-C(8)-C(9)-C(10)	179.9(3)
C(8)-C(9)-C(10)-C(11)	-179.6(2)

Supplementary Table S9. Crystal and structure refinement for 10e.

Identification Code	13e
Empirical formula	C ₁₇ H ₁₈ O ₃
Formula weight	270.31
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space Group	P2 ₁ /c
Unit cell dimensions	$a = 7.612(3) \text{ \AA}$ $\alpha = 90.0^\circ$ $b = 20.668(9) \text{ \AA}$ $\beta = 118.97(2)^\circ$ $c = 9.542(3) \text{ \AA}$ $\gamma = 90.0^\circ$
Volume	1313.4(9) Å ³
Z	4
Density (calculated)	1.367 Mg/m ³
Absorption coefficient	0.093 mm ⁻¹
F(000)	576
Crystal size, color, habit	0.36 x 0.12 x 0.10 mm, clear, rod
Theta range for data collection	1.97 – 20.81 °
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -9 ≤ l ≤ 9
Reflections collected	8,835
Independent reflections	1,377 (R _{int} = 0.0541)
Reflections with I > 4(F _o)	844
Absorption correction	SADABS based on redundant diffractions
Max. and min. transmission	1.0, 0.643
Refinement method	Full-matrix least squares on F ²
Weighting scheme	$w = q [s^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2 F_c^2)/3$, $a = 0.0543$, $b = 0.0$, $q = 1$
Data / restraints / parameters	1377 / 0 / 182
Goodness-of-fit on F ²	0.913

Final R indices [$I > 2 \sigma(I)$] R1 = 0.0683, wR2 = 0.1373

R indices (all data) R1 = 0.1010, wR2 = 0.1495

Largest diff. peak and hole 0.242, -0.270 eÅ⁻³

Supplementary Table S10. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for 10e. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
O(1)	7811(5)	10496(2)	8727(4)	43(1)	
O(2)	8236(5)	9467(2)	9383(4)	43(1)	
O(3)	5316(5)	8787(2)	9060(4)	42(1)	
C(1)	4205(7)	12126(3)	6554(7)	38(2)	
C(2)	4801(7)	12099(3)	5403(7)	41(2)	
C(3)	5055(8)	11511(3)	4894(7)	45(2)	
C(4)	4747(7)	10951(3)	5498(7)	43(2)	
C(5)	4140(7)	10979(3)	6654(7)	37(2)	
C(6)	3906(7)	11573(3)	7163(7)	40(2)	
C(7)	3619(8)	10386(3)	7214(7)	38(2)	
C(8)	1631(8)	10314(3)	6821(6)	42(2)	
C(9)	932(9)	9758(3)	7174(6)	42(2)	
C(10)	2139(8)	9239(3)	7888(7)	40(2)	
C(11)	4176(9)	9306(3)	8323(7)	40(2)	
C(12)	4935(8)	9871(3)	8027(6)	37(2)	
C(13)	7110(9)	9926(3)	8755(7)	39(2)	
C(14)	1383(7)	8633(2)	8230(6)	43(2)	
C(15)	1036(8)	8086(2)	7078(7)	42(2)	
C(16)	269(8)	7494(2)	7478(7)	42(2)	
C(17)	114(7)	6911(2)	6464(7)	44(2)	

Supplementary Table S11. Bond lengths [Å] and angles [°] for 10e.

O(1)-C(13)	1.300(6)
O(2)-C(13)	1.222(6)
O(3)-C(11)	1.344(6)
C(1)-C(6)	1.351(7)
C(1)-C(2)	1.377(7)
C(2)-C(3)	1.356(7)
C(3)-C(4)	1.365(7)
C(4)-C(5)	1.387(7)
C(5)-C(6)	1.364(7)
C(5)-C(7)	1.466(7)
C(7)-C(8)	1.380(7)
C(7)-C(12)	1.409(7)
C(8)-C(9)	1.374(6)
C(9)-C(10)	1.361(7)
C(10)-C(11)	1.405(7)
C(10)-C(14)	1.479(7)
C(11)-C(12)	1.391(7)
C(12)-C(13)	1.457(7)
C(14)-C(15)	1.509(7)
C(15)-C(16)	1.483(6)
C(16)-C(17)	1.513(7)
C(6)-C(1)-C(2)	119.9(5)
C(3)-C(2)-C(1)	118.7(5)
C(2)-C(3)-C(4)	121.7(6)
C(3)-C(4)-C(5)	119.5(5)
C(6)-C(5)-C(4)	118.2(5)
C(6)-C(5)-C(7)	121.2(5)
C(4)-C(5)-C(7)	120.5(5)
C(1)-C(6)-C(5)	122.0(5)
C(8)-C(7)-C(12)	117.5(5)
C(8)-C(7)-C(5)	116.5(5)
C(12)-C(7)-C(5)	125.9(5)
C(9)-C(8)-C(7)	121.9(5)
C(10)-C(9)-C(8)	122.3(5)
C(9)-C(10)-C(11)	116.8(5)
C(9)-C(10)-C(14)	122.5(5)
C(11)-C(10)-C(14)	120.7(5)
O(3)-C(11)-C(12)	123.3(5)
O(3)-C(11)-C(10)	114.6(5)
C(12)-C(11)-C(10)	122.0(5)
C(11)-C(12)-C(7)	119.4(5)
C(11)-C(12)-C(13)	117.1(5)
C(7)-C(12)-C(13)	123.0(5)
O(2)-C(13)-O(1)	121.1(5)
O(2)-C(13)-C(12)	122.6(5)
O(1)-C(13)-C(12)	116.3(5)
C(10)-C(14)-C(15)	115.0(4)
C(16)-C(15)-C(14)	112.5(4)
C(15)-C(16)-C(17)	114.2(4)

Supplementary Table S12. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 10e. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	39(2)	39(2)	50(3)	1(2)	22(2)	-4(2)
O(2)	38(2)	35(2)	56(3)	3(2)	24(2)	4(2)
O(3)	39(2)	38(2)	55(3)	3(2)	26(2)	2(2)
C(1)	29(3)	40(4)	40(4)	-2(3)	12(3)	4(3)
C(2)	29(3)	40(4)	48(4)	5(3)	14(3)	3(3)
C(3)	41(4)	42(4)	52(4)	5(4)	23(3)	3(3)
C(4)	40(4)	42(4)	50(4)	-4(3)	24(3)	-6(3)
C(5)	23(3)	35(4)	44(4)	-3(3)	10(3)	-2(3)
C(6)	28(3)	42(4)	47(4)	8(3)	17(3)	1(3)
C(7)	40(4)	33(4)	43(4)	-9(3)	20(3)	1(3)
C(8)	37(4)	44(4)	45(4)	1(3)	21(3)	3(3)
C(9)	40(4)	40(4)	47(4)	-5(3)	22(3)	-4(3)
C(10)	39(4)	35(4)	46(4)	-5(3)	22(3)	-1(3)
C(11)	46(4)	33(4)	42(4)	2(3)	23(3)	9(3)
C(12)	38(4)	36(4)	40(4)	-1(3)	22(3)	0(3)
C(13)	49(5)	32(4)	41(4)	0(3)	27(4)	-5(3)
C(14)	35(4)	42(4)	52(4)	-4(3)	22(3)	-2(3)
C(15)	42(4)	38(4)	52(4)	2(3)	28(3)	-1(3)
C(16)	32(3)	39(4)	55(4)	-2(3)	21(3)	-3(3)
C(17)	33(4)	41(4)	62(4)	1(3)	27(3)	4(3)

Supplementary Table S13. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 10e.

	x	y	z	U(eq)
H(5)	9495	10492	9656	64
H(3A)	6501	8856	9253	63
H(1)	4005	12533	6918	46
H(2)	5031	12485	4974	49
H(3)	5458	11489	4096	54
H(4)	4945	10544	5131	51
H(6)	3521	11599	7971	47
H(8)	719	10658	6292	50
H(9)	-441	9735	6909	50
H(14A)	102	8727	8221	51
H(14B)	2357	8487	9324	51
H(15A)	60	8227	5980	50
H(15B)	2315	7983	7092	50
H(16A)	-1076	7587	7351	50
H(16B)	1168	7385	8618	50
H(17A)	-756	7015	5331	66
H(17B)	-458	6547	6765	66
H(17C)	1454	6795	6640	66

Supplementary Table S14. Torsion angles [°] for 10e.

C(6)-C(1)-C(2)-C(3)	0.7(7)
C(1)-C(2)-C(3)-C(4)	-0.4(8)
C(2)-C(3)-C(4)-C(5)	0.6(8)
C(3)-C(4)-C(5)-C(6)	-1.0(7)
C(3)-C(4)-C(5)-C(7)	174.3(5)
C(2)-C(1)-C(6)-C(5)	-1.2(8)
C(4)-C(5)-C(6)-C(1)	1.4(8)
C(7)-C(5)-C(6)-C(1)	-173.9(5)
C(6)-C(5)-C(7)-C(8)	62.6(7)
C(4)-C(5)-C(7)-C(8)	-112.6(6)
C(6)-C(5)-C(7)-C(12)	-121.4(6)
C(4)-C(5)-C(7)-C(12)	63.4(8)
C(12)-C(7)-C(8)-C(9)	-1.3(8)
C(5)-C(7)-C(8)-C(9)	175.0(5)
C(7)-C(8)-C(9)-C(10)	-1.9(8)
C(8)-C(9)-C(10)-C(11)	2.8(8)
C(8)-C(9)-C(10)-C(14)	-178.3(5)
C(9)-C(10)-C(11)-O(3)	178.4(5)
C(14)-C(10)-C(11)-O(3)	-0.5(7)
C(9)-C(10)-C(11)-C(12)	-0.6(8)
C(14)-C(10)-C(11)-C(12)	-179.6(5)
O(3)-C(11)-C(12)-C(7)	178.6(5)
C(10)-C(11)-C(12)-C(7)	-2.5(8)
O(3)-C(11)-C(12)-C(13)	-8.7(8)
C(10)-C(11)-C(12)-C(13)	170.3(5)
C(8)-C(7)-C(12)-C(11)	3.4(8)
C(5)-C(7)-C(12)-C(11)	-172.6(5)
C(8)-C(7)-C(12)-C(13)	-169.0(5)
C(5)-C(7)-C(12)-C(13)	15.1(9)
C(11)-C(12)-C(13)-O(2)	11.5(8)
C(7)-C(12)-C(13)-O(2)	-176.0(5)
C(11)-C(12)-C(13)-O(1)	-167.4(5)
C(7)-C(12)-C(13)-O(1)	5.1(8)
C(9)-C(10)-C(14)-C(15)	102.1(6)
C(11)-C(10)-C(14)-C(15)	-79.0(6)
C(10)-C(14)-C(15)-C(16)	-179.7(5)
C(14)-C(15)-C(16)-C(17)	-173.7(4)

Supplementary Table S15. Crystal and structure refinement for 13a.

Identification Code	17a
Empirical formula	C ₁₅ H ₁₇ NO ₂
Formula weight	243.30
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space Group	P2 ₁ /c
Unit cell dimensions	$a = 10.591(4) \text{ \AA}$ $\alpha = 90.0^\circ$ $b = 4.9385(19) \text{ \AA}$ $\beta = 93.823(7)^\circ$ $c = 24.376(9) \text{ \AA}$ $\gamma = 90.00^\circ$
Volume	1272.1(9) Å ³
Z	4
Density (calculated)	1.270 Mg/m ³
Absorption coefficient	0.084 mm ⁻¹
F(000)	520
Crystal size, color, habit	0.32 x 0.32 x 0.40 mm, clear, fragment
Theta range for data collection	1.93 – 25.10 °
Index ranges	-12 ≤ h ≤ 12, -5 ≤ k ≤ 5, -29 ≤ l ≤ 29
Reflections collected	11,501
Independent reflections	2,254 (R _{int} = 0.0603)
Reflections with I > 4σ(F _o)	1,589
Absorption correction	SADABS based on redundant diffractions
Max. and min. transmission	1.0, 0.672
Refinement method	Full-matrix least squares on F ²
Weighting scheme	$w = q [s^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2 F_c^2)/3$, a = 0.0589, b = 0.0, q = 1
Data / restraints / parameters	2254 / 0 / 166
Goodness-of-fit on F ²	0.926

Final R indices [$I > 2 \sigma(I)$] R1 = 0.0496, wR2 = 0.1075

R indices (all data) R1 = 0.0693, wR2 = 0.1142

Largest diff. peak and hole 0.238, -0.160 eÅ⁻³

Supplementary Table S16. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for 13a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
C(1)	7085(2)	1629(4)	1754(1)	27(1)	
C(2)	8204(2)	2795(4)	2007(1)	30(1)	
C(3)	8698(2)	1905(4)	2510(1)	31(1)	
C(4)	8111(2)	-193(4)	2788(1)	32(1)	
C(5)	7032(2)	-1335(4)	2561(1)	30(1)	
C(6)	6485(2)	-466(4)	2040(1)	27(1)	
C(7)	5361(2)	-1673(4)	1806(1)	30(1)	
C(8)	4818(2)	-912(4)	1303(1)	28(1)	
C(9)	5414(2)	1189(4)	1020(1)	27(1)	
C(10)	6522(2)	2459(4)	1223(1)	26(1)	
C(11)	7100(2)	4584(4)	909(1)	30(1)	
C(12)	3629(2)	-2206(4)	1050(1)	31(1)	
C(13)	2439(2)	-489(4)	1099(1)	29(1)	
C(14)	1279(2)	-1619(4)	771(1)	35(1)	
C(15)	105(2)	105(5)	816(1)	48(1)	
N(1)	6592(2)	5362(3)	445(1)	31(1)	
O(1)	4845(1)	1861(3)	519(1)	31(1)	
O(2)	7272(1)	7405(3)	200(1)	39(1)	

Supplementary Table S17. Bond lengths [Å] and angles [°] for 13a.

C(1)-C(6)	1.420(3)
C(1)-C(2)	1.421(3)
C(1)-C(10)	1.448(3)
C(2)-C(3)	1.374(3)
C(3)-C(4)	1.405(3)
C(4)-C(5)	1.359(3)
C(5)-C(6)	1.427(3)
C(6)-C(7)	1.418(3)
C(7)-C(8)	1.371(3)
C(8)-C(9)	1.417(3)
C(8)-C(12)	1.507(3)
C(9)-O(1)	1.365(2)
C(9)-C(10)	1.392(3)
C(10)-C(11)	1.457(3)
C(11)-N(1)	1.279(2)
C(12)-C(13)	1.530(3)
C(13)-C(14)	1.525(3)
C(14)-C(15)	1.517(3)
N(1)-O(2)	1.396(2)
C(6)-C(1)-C(2)	118.00(17)
C(6)-C(1)-C(10)	118.29(17)
C(2)-C(1)-C(10)	123.71(18)
C(3)-C(2)-C(1)	121.00(19)
C(2)-C(3)-C(4)	120.79(18)
C(5)-C(4)-C(3)	119.83(18)
C(4)-C(5)-C(6)	121.17(19)
C(7)-C(6)-C(1)	119.99(17)
C(7)-C(6)-C(5)	120.80(18)
C(1)-C(6)-C(5)	119.20(18)
C(8)-C(7)-C(6)	122.37(19)
C(7)-C(8)-C(9)	117.53(18)
C(7)-C(8)-C(12)	122.53(18)
C(9)-C(8)-C(12)	119.93(17)
O(1)-C(9)-C(10)	121.28(17)
O(1)-C(9)-C(8)	115.38(17)
C(10)-C(9)-C(8)	123.31(18)
C(9)-C(10)-C(1)	118.49(18)
C(9)-C(10)-C(11)	120.80(17)
C(1)-C(10)-C(11)	120.71(17)
N(1)-C(11)-C(10)	120.88(18)
C(8)-C(12)-C(13)	113.81(16)
C(14)-C(13)-C(12)	113.32(16)
C(15)-C(14)-C(13)	113.09(17)
C(11)-N(1)-O(2)	113.33(16)

Supplementary Table S18. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 13a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	28(1)	30(1)	23(1)	-3(1)	4(1)	6(1)
C(2)	32(1)	32(1)	27(1)	1(1)	4(1)	1(1)
C(3)	30(1)	34(1)	28(1)	-2(1)	-1(1)	2(1)
C(4)	34(1)	37(1)	24(1)	1(1)	1(1)	6(1)
C(5)	34(1)	32(1)	26(1)	2(1)	4(1)	3(1)
C(6)	31(1)	27(1)	25(1)	-2(1)	6(1)	4(1)
C(7)	33(1)	30(1)	28(1)	2(1)	7(1)	2(1)
C(8)	30(1)	28(1)	26(1)	-3(1)	5(1)	4(1)
C(9)	32(1)	30(1)	21(1)	-1(1)	2(1)	6(1)
C(10)	28(1)	28(1)	25(1)	-1(1)	4(1)	3(1)
C(11)	27(1)	37(1)	26(1)	0(1)	-1(1)	-1(1)
C(12)	37(1)	30(1)	25(1)	1(1)	2(1)	-2(1)
C(13)	34(1)	31(1)	23(1)	-2(1)	4(1)	-3(1)
C(14)	38(1)	37(1)	29(1)	1(1)	-1(1)	-7(1)
C(15)	37(1)	53(2)	51(2)	-5(1)	-6(1)	-5(1)
N(1)	33(1)	34(1)	26(1)	5(1)	4(1)	-4(1)
O(1)	35(1)	36(1)	23(1)	3(1)	-1(1)	-4(1)
O(2)	38(1)	48(1)	31(1)	15(1)	-3(1)	-11(1)

Supplementary Table S19. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 13a.

	x	y	z	U(eq)
H(2)	8616	4213	1825	36
H(3)	9445	2717	2673	37
H(4)	8468	-812	3133	38
H(5)	6633	-2736	2753	36
H(7)	4969	-3060	2004	36
H(11)	7865	5403	1051	36
H(12A)	3507	-3973	1231	37
H(12B)	3738	-2559	656	37
H(13A)	2255	-366	1491	35
H(13B)	2604	1367	968	35
H(14A)	1465	-1756	379	42
H(14B)	1108	-3468	904	42
H(15A)	-89	239	1203	71
H(15B)	-610	-730	603	71
H(15C)	256	1920	672	71
H(1)	5273	3060	373	47
H(2A)	6824	8088	-61	59

Supplementary Table S20. Torsion angles [°] for 13a.

C(6)-C(1)-C(2)-C(3)	0.6(3)
C(10)-C(1)-C(2)-C(3)	-179.45(17)
C(1)-C(2)-C(3)-C(4)	0.2(3)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(3)-C(4)-C(5)-C(6)	0.8(3)
C(2)-C(1)-C(6)-C(7)	179.44(17)
C(10)-C(1)-C(6)-C(7)	-0.5(3)
C(2)-C(1)-C(6)-C(5)	-0.8(3)
C(10)-C(1)-C(6)-C(5)	179.34(17)
C(4)-C(5)-C(6)-C(7)	179.83(18)
C(4)-C(5)-C(6)-C(1)	0.0(3)
C(1)-C(6)-C(7)-C(8)	0.6(3)
C(5)-C(6)-C(7)-C(8)	-179.23(18)
C(6)-C(7)-C(8)-C(9)	-0.9(3)
C(6)-C(7)-C(8)-C(12)	179.46(17)
C(7)-C(8)-C(9)-O(1)	179.46(16)
C(12)-C(8)-C(9)-O(1)	-0.9(3)
C(7)-C(8)-C(9)-C(10)	1.2(3)
C(12)-C(8)-C(9)-C(10)	-179.13(17)
O(1)-C(9)-C(10)-C(1)	-179.30(16)
C(8)-C(9)-C(10)-C(1)	-1.2(3)
O(1)-C(9)-C(10)-C(11)	1.0(3)
C(8)-C(9)-C(10)-C(11)	179.15(18)
C(6)-C(1)-C(10)-C(9)	0.8(3)
C(2)-C(1)-C(10)-C(9)	-179.15(17)
C(6)-C(1)-C(10)-C(11)	-179.56(17)
C(2)-C(1)-C(10)-C(11)	0.5(3)
C(9)-C(10)-C(11)-N(1)	1.2(3)
C(1)-C(10)-C(11)-N(1)	-178.51(17)
C(7)-C(8)-C(12)-C(13)	102.3(2)
C(9)-C(8)-C(12)-C(13)	-77.3(2)
C(8)-C(12)-C(13)-C(14)	171.63(16)
C(12)-C(13)-C(14)-C(15)	-179.48(17)
C(10)-C(11)-N(1)-O(2)	-179.81(16)

Supplementary Table S21. Crystal and structure refinement for 13f.

Identification Code	17f	
Empirical formula	C ₁₅ H ₁₆ BrNO ₂	
Formula weight	322.20	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space Group	P1(bar)	
Unit cell dimensions	$a = 9.978(5) \text{ \AA}$	$a = 108.600(8)^\circ$
	$b = 14.249(7) \text{ \AA}$	$b = 90.668(8)^\circ$
	$c = 20.322(9) \text{ \AA}$	$\gamma = 94.197(9)^\circ$
Volume	2729(2) Å ³	
Z	8	
Density (calculated)	1.568 Mg/m ³	
Absorption coefficient	3.009 mm ⁻¹	
F(000)	1312	
Crystal size, color, habit	0.48 x 0.20 x 0.16 mm, clear, rod	
Theta range for data collection	1.06 – 28.66 °	
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -26 ≤ l ≤ 27	
Reflections collected	32,769	
Independent reflections	13,094 (R _{int} = 0.0412)	
Reflections with I > 4σ(F _o)	6,422	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.719	
Refinement method	Full-matrix least squares on F ²	
Weighting scheme	$w = q [s^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2F_c^2)/3$, a = 0.0532, b = 0.0, q = 1	
Data / restraints / parameters	13094 / 0 / 697	
Goodness-of-fit on F ²	0.685	
Final R indices [I > 2 σ(I)]	R1 = 0.0566, wR2 = 0.1184	
R indices (all data)	R1 = 0.1054, wR2 = 0.1226	
Largest diff. peak and hole	0.837, -0.516 eÅ ⁻³	

Supplementary Table S22. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 13f. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
Br(1)	10157(1)	9583(1)	751(1)	34(1)	
Br(2)	4509(1)	4382(1)	10619(1)	39(1)	
Br(3)	13923(1)	4122(1)	4324(1)	33(1)	
Br(4)	8918(1)	9275(1)	4338(1)	34(1)	
C(1)	9036(5)	8739(4)	1132(2)	28(1)	
C(2)	8961(5)	7756(4)	731(2)	28(1)	
C(3)	8074(5)	7062(4)	889(2)	27(1)	
C(4)	7248(5)	7381(4)	1429(2)	27(1)	
C(5)	7336(5)	8387(3)	1850(2)	23(1)	
C(6)	8283(5)	9103(4)	1726(2)	24(1)	
C(7)	8359(5)	10107(3)	2220(3)	24(1)	
C(8)	9460(5)	10851(3)	2227(2)	25(1)	
C(9)	7417(5)	10340(3)	2734(3)	26(1)	
C(10)	6468(5)	9625(4)	2853(2)	26(1)	
C(11)	6453(5)	8677(3)	2418(2)	24(1)	
C(12)	5529(5)	9954(3)	3455(2)	26(1)	
C(13)	4520(5)	9154(3)	3524(2)	25(1)	
C(14)	3612(5)	9536(4)	4135(3)	30(1)	
C(15)	2765(5)	8696(4)	4278(3)	35(1)	
C(16)	4081(5)	3008(3)	10485(3)	25(1)	
C(17)	3089(5)	2830(3)	10904(2)	26(1)	
C(18)	2550(5)	1861(3)	10815(2)	27(1)	
C(19)	2987(5)	1099(4)	10297(3)	26(1)	
C(20)	4025(5)	1262(3)	9862(2)	24(1)	
C(21)	4653(5)	2233(3)	9959(2)	23(1)	
C(22)	5738(5)	2321(3)	9513(2)	23(1)	
C(23)	6687(5)	3218(4)	9675(3)	29(1)	
C(24)	6018(5)	1488(4)	8956(3)	26(1)	
C(25)	5362(5)	529(4)	8851(2)	25(1)	
C(26)	4418(5)	440(4)	9304(2)	24(1)	
C(27)	5785(5)	-338(3)	8259(2)	25(1)	
C(28)	4970(5)	-1326(3)	8145(2)	27(1)	
C(29)	5445(5)	-2170(3)	7547(3)	32(1)	
C(30)	4638(5)	-3152(3)	7462(3)	36(1)	
C(31)	12242(5)	3505(4)	4466(2)	25(1)	
C(32)	11988(5)	2551(4)	4029(3)	29(1)	
C(33)	10874(5)	1946(4)	4113(3)	32(1)	
C(34)	10063(5)	2301(3)	4649(2)	27(1)	
C(35)	10297(5)	3274(3)	5112(2)	24(1)	
C(36)	11383(5)	3943(3)	5021(2)	24(1)	
C(37)	11500(5)	4945(3)	5497(2)	23(1)	
C(38)	12352(5)	5747(4)	5371(3)	26(1)	
C(39)	10638(5)	5191(3)	6055(3)	25(1)	
C(40)	9595(5)	4520(3)	6153(2)	24(1)	

C(41)	9453(5)	3592(3)	5675(2)	23(1)
C(42)	8680(5)	4870(3)	6755(2)	26(1)
C(43)	7683(5)	4087(3)	6863(2)	26(1)
C(44)	6890(5)	4446(3)	7521(3)	30(1)
C(45)	6021(5)	3622(4)	7658(3)	34(1)
C(46)	7888(5)	8023(3)	3957(3)	24(1)
C(47)	6855(5)	7880(4)	4377(3)	29(1)
C(48)	6097(5)	6985(4)	4208(3)	28(1)
C(49)	6378(5)	6222(4)	3638(3)	28(1)
C(50)	7406(5)	6341(4)	3198(2)	25(1)
C(51)	8189(5)	7274(3)	3332(2)	25(1)
C(52)	9203(5)	7355(3)	2851(2)	23(1)
C(53)	9844(5)	8307(4)	2833(2)	25(1)
C(54)	9461(5)	6502(3)	2311(2)	23(1)
C(55)	8713(5)	5569(4)	2178(3)	26(1)
C(56)	7701(5)	5527(3)	2615(2)	24(1)
C(57)	9060(5)	4710(3)	1573(2)	28(1)
C(58)	8303(5)	3724(3)	1518(2)	27(1)
C(59)	8816(5)	2868(3)	951(3)	29(1)
C(60)	7973(5)	1884(3)	854(3)	34(1)
N(1)	9353(4)	11774(3)	2533(2)	26(1)
N(2)	7532(4)	3313(3)	9224(2)	31(1)
N(3)	12559(4)	6598(3)	5839(2)	27(1)
N(4)	10931(4)	8346(3)	2520(2)	28(1)
O(1)	7408(3)	11279(2)	3194(2)	31(1)
O(2)	10515(3)	12366(3)	2507(2)	33(1)
O(3)	6963(3)	1536(2)	8499(2)	31(1)
O(4)	8443(4)	4149(2)	9493(2)	36(1)
O(5)	10728(3)	6109(2)	6536(2)	28(1)
O(6)	13271(3)	7300(2)	5591(2)	32(1)
O(7)	10449(3)	6505(2)	1853(2)	27(1)
O(8)	11346(3)	9320(2)	2538(2)	31(1)

Supplementary Table S23. Bond lengths [Å] and angles [°] for 13f.

Br(1)-C(1)	1.927(5)
Br(2)-C(16)	1.903(5)
Br(3)-C(31)	1.904(5)
Br(4)-C(46)	1.915(5)
C(1)-C(2)	1.374(6)
C(1)-C(6)	1.404(6)
C(2)-C(3)	1.394(6)
C(3)-C(4)	1.360(6)
C(4)-C(5)	1.412(6)
C(5)-C(6)	1.424(6)
C(5)-C(11)	1.431(6)
C(6)-C(7)	1.459(6)
C(7)-C(9)	1.389(7)
C(7)-C(8)	1.467(6)
C(8)-N(1)	1.276(5)
C(9)-O(1)	1.367(5)
C(9)-C(10)	1.421(6)
C(10)-C(11)	1.357(6)
C(10)-C(12)	1.522(6)
C(12)-C(13)	1.507(6)
C(13)-C(14)	1.524(6)
C(14)-C(15)	1.519(6)
C(16)-C(17)	1.375(6)
C(16)-C(21)	1.429(6)
C(17)-C(18)	1.400(6)
C(18)-C(19)	1.353(6)
C(19)-C(20)	1.424(6)
C(20)-C(21)	1.429(6)
C(20)-C(26)	1.429(6)
C(21)-C(22)	1.443(6)
C(22)-C(24)	1.402(6)
C(22)-C(23)	1.479(6)
C(23)-N(2)	1.285(6)
C(24)-O(3)	1.345(5)
C(24)-C(25)	1.422(6)
C(25)-C(26)	1.351(6)
C(25)-C(27)	1.514(6)
C(27)-C(28)	1.521(6)
C(28)-C(29)	1.521(6)
C(29)-C(30)	1.522(6)
C(31)-C(32)	1.369(6)
C(31)-C(36)	1.432(6)
C(32)-C(33)	1.402(6)
C(33)-C(34)	1.351(6)
C(34)-C(35)	1.406(6)
C(35)-C(41)	1.405(6)
C(35)-C(36)	1.444(6)
C(36)-C(37)	1.441(6)
C(37)-C(39)	1.399(6)

C(37)-C(38)	1.465(6)
C(38)-N(3)	1.281(6)
C(39)-O(5)	1.357(5)
C(39)-C(40)	1.421(6)
C(40)-C(41)	1.365(6)
C(40)-C(42)	1.509(6)
C(42)-C(43)	1.511(6)
C(43)-C(44)	1.524(6)
C(44)-C(45)	1.507(6)
C(46)-C(47)	1.392(7)
C(46)-C(51)	1.426(6)
C(47)-C(48)	1.375(6)
C(48)-C(49)	1.361(6)
C(49)-C(50)	1.404(6)
C(50)-C(56)	1.421(6)
C(50)-C(51)	1.436(6)
C(51)-C(52)	1.439(6)
C(52)-C(54)	1.396(6)
C(52)-C(53)	1.468(6)
C(53)-N(4)	1.270(6)
C(54)-O(7)	1.365(5)
C(54)-C(55)	1.420(6)
C(55)-C(56)	1.363(6)
C(55)-C(57)	1.498(6)
C(57)-C(58)	1.516(6)
C(58)-C(59)	1.512(6)
C(59)-C(60)	1.536(6)
N(1)-O(2)	1.394(4)
N(2)-O(4)	1.400(5)
N(3)-O(6)	1.408(5)
N(4)-O(8)	1.409(5)
C(2)-C(1)-C(6)	123.3(5)
C(2)-C(1)-Br(1)	113.1(4)
C(6)-C(1)-Br(1)	123.3(4)
C(1)-C(2)-C(3)	120.5(5)
C(4)-C(3)-C(2)	118.9(5)
C(3)-C(4)-C(5)	120.9(5)
C(4)-C(5)-C(6)	121.5(4)
C(4)-C(5)-C(11)	118.4(4)
C(6)-C(5)-C(11)	120.1(4)
C(1)-C(6)-C(5)	114.7(4)
C(1)-C(6)-C(7)	128.1(4)
C(5)-C(6)-C(7)	117.2(4)
C(9)-C(7)-C(6)	118.8(4)
C(9)-C(7)-C(8)	119.0(4)
C(6)-C(7)-C(8)	122.0(4)
N(1)-C(8)-C(7)	121.0(5)
O(1)-C(9)-C(7)	121.3(4)
O(1)-C(9)-C(10)	115.1(4)
C(7)-C(9)-C(10)	123.4(4)
C(11)-C(10)-C(9)	117.4(5)
C(11)-C(10)-C(12)	123.6(4)
C(9)-C(10)-C(12)	119.0(4)

C(10)-C(11)-C(5)	122.6(4)
C(13)-C(12)-C(10)	115.2(4)
C(12)-C(13)-C(14)	112.4(4)
C(15)-C(14)-C(13)	112.0(4)
C(17)-C(16)-C(21)	122.9(4)
C(17)-C(16)-Br(2)	113.7(4)
C(21)-C(16)-Br(2)	123.2(4)
C(16)-C(17)-C(18)	120.7(5)
C(19)-C(18)-C(17)	119.2(5)
C(18)-C(19)-C(20)	121.1(5)
C(19)-C(20)-C(21)	121.4(4)
C(19)-C(20)-C(26)	119.1(4)
C(21)-C(20)-C(26)	119.5(4)
C(20)-C(21)-C(16)	114.3(4)
C(20)-C(21)-C(22)	117.5(4)
C(16)-C(21)-C(22)	128.2(4)
C(24)-C(22)-C(21)	119.3(4)
C(24)-C(22)-C(23)	117.9(4)
C(21)-C(22)-C(23)	122.2(4)
N(2)-C(23)-C(22)	119.9(5)
O(3)-C(24)-C(22)	122.2(4)
O(3)-C(24)-C(25)	115.4(4)
C(22)-C(24)-C(25)	122.4(4)
C(26)-C(25)-C(24)	117.6(5)
C(26)-C(25)-C(27)	123.6(4)
C(24)-C(25)-C(27)	118.8(4)
C(25)-C(26)-C(20)	123.2(5)
C(25)-C(27)-C(28)	115.8(4)
C(29)-C(28)-C(27)	113.5(4)
C(28)-C(29)-C(30)	112.1(4)
C(32)-C(31)-C(36)	122.3(5)
C(32)-C(31)-Br(3)	113.5(4)
C(36)-C(31)-Br(3)	123.9(4)
C(31)-C(32)-C(33)	121.2(5)
C(34)-C(33)-C(32)	119.3(5)
C(33)-C(34)-C(35)	121.1(5)
C(41)-C(35)-C(34)	118.8(4)
C(41)-C(35)-C(36)	119.7(4)
C(34)-C(35)-C(36)	121.5(4)
C(31)-C(36)-C(37)	128.0(4)
C(31)-C(36)-C(35)	114.4(4)
C(37)-C(36)-C(35)	117.6(4)
C(39)-C(37)-C(36)	118.7(4)
C(39)-C(37)-C(38)	118.2(4)
C(36)-C(37)-C(38)	122.6(4)
N(3)-C(38)-C(37)	121.1(5)
O(5)-C(39)-C(37)	121.6(4)
O(5)-C(39)-C(40)	115.0(4)
C(37)-C(39)-C(40)	123.3(4)
C(41)-C(40)-C(39)	117.1(5)
C(41)-C(40)-C(42)	123.6(4)
C(39)-C(40)-C(42)	119.3(4)
C(40)-C(41)-C(35)	123.4(4)

C(40)-C(42)-C(43)	116.0(4)
C(42)-C(43)-C(44)	114.1(4)
C(45)-C(44)-C(43)	112.9(4)
C(47)-C(46)-C(51)	122.4(4)
C(47)-C(46)-Br(4)	113.2(4)
C(51)-C(46)-Br(4)	124.3(4)
C(48)-C(47)-C(46)	120.4(5)
C(49)-C(48)-C(47)	120.1(5)
C(48)-C(49)-C(50)	121.1(5)
C(49)-C(50)-C(56)	120.0(4)
C(49)-C(50)-C(51)	121.2(4)
C(56)-C(50)-C(51)	118.8(4)
C(46)-C(51)-C(50)	114.7(4)
C(46)-C(51)-C(52)	126.9(4)
C(50)-C(51)-C(52)	118.4(4)
C(54)-C(52)-C(51)	118.4(4)
C(54)-C(52)-C(53)	117.5(4)
C(51)-C(52)-C(53)	123.5(4)
N(4)-C(53)-C(52)	121.1(5)
O(7)-C(54)-C(52)	122.1(4)
O(7)-C(54)-C(55)	114.1(4)
C(52)-C(54)-C(55)	123.7(4)
C(56)-C(55)-C(54)	116.6(5)
C(56)-C(55)-C(57)	124.3(4)
C(54)-C(55)-C(57)	119.0(4)
C(55)-C(56)-C(50)	123.7(5)
C(55)-C(57)-C(58)	115.0(4)
C(59)-C(58)-C(57)	112.4(4)
C(58)-C(59)-C(60)	112.4(4)
C(8)-N(1)-O(2)	112.9(4)
C(23)-N(2)-O(4)	112.0(4)
C(38)-N(3)-O(6)	112.4(4)
C(53)-N(4)-O(8)	112.2(4)

Supplementary Table S24. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 13f. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	38(1)	39(1)	26(1)	11(1)	9(1)	-4(1)
Br(2)	46(1)	25(1)	43(1)	8(1)	16(1)	3(1)
Br(3)	28(1)	35(1)	32(1)	7(1)	9(1)	1(1)
Br(4)	43(1)	27(1)	26(1)	3(1)	4(1)	-1(1)
C(1)	31(3)	35(3)	17(3)	8(2)	2(2)	3(2)
C(2)	35(3)	33(3)	15(3)	5(2)	7(2)	10(2)
C(3)	36(3)	23(3)	21(3)	6(2)	1(2)	9(2)
C(4)	29(3)	30(3)	25(3)	11(2)	3(2)	5(2)
C(5)	26(3)	24(3)	20(3)	6(2)	2(2)	4(2)
C(6)	25(3)	34(3)	18(3)	14(2)	-1(2)	5(2)
C(7)	30(3)	19(3)	25(3)	10(2)	0(2)	3(2)
C(8)	32(3)	27(3)	18(3)	11(2)	6(2)	3(2)
C(9)	33(3)	22(3)	22(3)	7(2)	0(2)	3(2)
C(10)	24(3)	31(3)	23(3)	12(2)	2(2)	-1(2)
C(11)	23(3)	26(3)	23(3)	10(2)	3(2)	0(2)
C(12)	32(3)	28(3)	19(3)	7(2)	8(2)	4(2)
C(13)	26(3)	29(3)	20(3)	5(2)	4(2)	3(2)
C(14)	34(3)	32(3)	24(3)	9(2)	6(2)	2(2)
C(15)	45(3)	32(3)	32(3)	14(3)	15(3)	7(3)
C(16)	26(3)	24(3)	24(3)	5(2)	6(2)	4(2)
C(17)	31(3)	25(3)	22(3)	7(2)	7(2)	3(2)
C(18)	31(3)	31(3)	23(3)	15(2)	6(2)	3(2)
C(19)	28(3)	26(3)	27(3)	11(2)	-2(2)	-1(2)
C(20)	23(3)	27(3)	21(3)	7(2)	2(2)	4(2)
C(21)	26(3)	27(3)	17(3)	8(2)	2(2)	5(2)
C(22)	25(3)	23(3)	22(3)	10(2)	1(2)	5(2)
C(23)	32(3)	30(3)	24(3)	5(2)	3(2)	6(2)
C(24)	26(3)	31(3)	25(3)	14(2)	4(2)	7(2)
C(25)	26(3)	30(3)	18(3)	5(2)	2(2)	6(2)
C(26)	23(3)	26(3)	27(3)	12(2)	-3(2)	1(2)
C(27)	28(3)	27(3)	22(3)	11(2)	8(2)	5(2)
C(28)	28(3)	32(3)	24(3)	12(2)	5(2)	7(2)
C(29)	39(3)	29(3)	26(3)	7(2)	10(3)	7(3)
C(30)	50(4)	26(3)	31(3)	7(3)	10(3)	4(3)
C(31)	26(3)	32(3)	19(3)	11(2)	1(2)	3(2)
C(32)	32(3)	35(3)	20(3)	9(2)	4(2)	6(2)
C(33)	35(3)	32(3)	25(3)	4(2)	-3(3)	4(3)
C(34)	29(3)	25(3)	24(3)	6(2)	4(2)	-1(2)
C(35)	30(3)	26(3)	18(3)	8(2)	2(2)	7(2)
C(36)	25(3)	26(3)	21(3)	8(2)	2(2)	8(2)
C(37)	24(3)	27(3)	18(3)	8(2)	-1(2)	5(2)
C(38)	24(3)	31(3)	23(3)	9(2)	4(2)	4(2)
C(39)	29(3)	23(3)	24(3)	9(2)	1(2)	3(2)
C(40)	24(3)	27(3)	24(3)	11(2)	1(2)	1(2)
C(41)	21(3)	27(3)	24(3)	13(2)	0(2)	1(2)
C(42)	28(3)	26(3)	19(3)	2(2)	1(2)	5(2)

C(43)	31(3)	25(3)	21(3)	6(2)	4(2)	2(2)
C(44)	29(3)	31(3)	27(3)	4(2)	7(2)	6(2)
C(45)	34(3)	35(3)	30(3)	8(3)	10(3)	-3(3)
C(46)	30(3)	17(3)	28(3)	9(2)	-2(2)	3(2)
C(47)	36(3)	33(3)	18(3)	7(2)	1(2)	12(3)
C(48)	21(3)	33(3)	32(3)	14(3)	5(2)	7(2)
C(49)	30(3)	30(3)	25(3)	8(2)	0(2)	0(2)
C(50)	30(3)	28(3)	18(3)	5(2)	6(2)	5(2)
C(51)	28(3)	26(3)	22(3)	8(2)	2(2)	8(2)
C(52)	24(3)	23(3)	23(3)	8(2)	3(2)	5(2)
C(53)	27(3)	28(3)	21(3)	7(2)	2(2)	2(2)
C(54)	26(3)	25(3)	22(3)	13(2)	3(2)	6(2)
C(55)	27(3)	28(3)	27(3)	13(2)	2(2)	7(2)
C(56)	27(3)	25(3)	19(3)	8(2)	-3(2)	-3(2)
C(57)	28(3)	29(3)	23(3)	4(2)	5(2)	6(2)
C(58)	27(3)	33(3)	21(3)	7(2)	5(2)	5(2)
C(59)	31(3)	32(3)	24(3)	7(2)	4(2)	6(2)
C(60)	39(3)	36(3)	24(3)	6(3)	9(3)	10(3)
N(1)	29(2)	25(2)	23(2)	8(2)	2(2)	-6(2)
N(2)	32(3)	31(3)	29(3)	10(2)	6(2)	-4(2)
N(3)	24(2)	29(2)	29(3)	11(2)	4(2)	-2(2)
N(4)	33(3)	25(2)	28(3)	10(2)	0(2)	2(2)
O(1)	37(2)	23(2)	31(2)	7(2)	6(2)	-2(2)
O(2)	35(2)	29(2)	29(2)	5(2)	8(2)	-7(2)
O(3)	35(2)	28(2)	31(2)	13(2)	13(2)	-2(2)
O(4)	39(2)	33(2)	31(2)	6(2)	9(2)	-10(2)
O(5)	32(2)	24(2)	25(2)	5(2)	7(2)	-3(2)
O(6)	30(2)	31(2)	38(2)	16(2)	11(2)	-1(2)
O(7)	31(2)	27(2)	25(2)	10(2)	10(2)	0(2)
O(8)	34(2)	22(2)	38(2)	14(2)	10(2)	2(2)

Supplementary Table S25. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 13f.

	x	y	z	U(eq)
H(2)	9518	7547	344	33
H(3)	8047	6378	623	32
H(4)	6603	6921	1524	33
H(8)	10266	10643	2000	30
H(11)	5831	8187	2492	28
H(12A)	6080	10221	3892	31
H(12B)	5035	10503	3398	31
H(13A)	5004	8604	3587	31
H(13B)	3958	8885	3090	31
H(14A)	4173	9908	4555	36
H(14B)	3012	10000	4034	36
H(15A)	2179	8344	3870	52
H(15B)	2213	8970	4679	52
H(15C)	3356	8233	4376	52
H(17)	2766	3370	11258	31
H(18)	1886	1739	11116	32
H(19)	2594	444	10221	32
H(23)	6671	3724	10112	35
H(26)	3994	-201	9248	29
H(27A)	6739	-427	8345	30
H(27B)	5730	-166	7826	30
H(28A)	5021	-1505	8577	32
H(28B)	4016	-1246	8052	32
H(29A)	6406	-2240	7631	38
H(29B)	5364	-2005	7111	38
H(30A)	4708	-3315	7894	54
H(30B)	4993	-3678	7081	54
H(30C)	3692	-3096	7355	54
H(32)	12577	2295	3662	34
H(33)	10692	1294	3797	38
H(34)	9322	1886	4714	32
H(38)	12758	5634	4935	31
H(41)	8747	3138	5726	28
H(42A)	8175	5406	6685	31
H(42B)	9246	5164	7185	31
H(43A)	8172	3516	6881	31
H(43B)	7042	3848	6458	31
H(44A)	7527	4755	7922	36
H(44B)	6313	4963	7480	36
H(45A)	5400	3304	7259	51
H(45B)	5507	3898	8074	51
H(45C)	6591	3129	7730	51
H(47)	6672	8403	4784	35
H(48)	5375	6898	4490	33
H(49)	5870	5599	3535	34

H(53)	9439	8904	3059	30
H(56)	7162	4919	2524	28
H(57A)	10036	4638	1605	33
H(57B)	8880	4865	1140	33
H(58A)	8391	3599	1968	33
H(58B)	7336	3762	1422	33
H(59A)	9760	2794	1067	35
H(59B)	8801	3019	508	35
H(60A)	7974	1735	1292	50
H(60B)	8359	1348	493	50
H(60C)	7047	1941	713	50
H(1)	7947	11666	3070	46
H(2A)	10607	12854	2874	49
H(3A)	7330	2117	8609	46
H(4A)	8976	4191	9185	54
H(5)	11347	6467	6436	42
H(6)	14082	7179	5553	48
H(7)	10828	7081	1948	41
H(8A)	11977	9305	2265	46

Supplementary Table S26. Torsion angles [°] for 13f.

C(6)-C(1)-C(2)-C(3)	2.2(8)
Br(1)-C(1)-C(2)-C(3)	-172.7(4)
C(1)-C(2)-C(3)-C(4)	2.5(7)
C(2)-C(3)-C(4)-C(5)	-3.7(7)
C(3)-C(4)-C(5)-C(6)	0.3(7)
C(3)-C(4)-C(5)-C(11)	-179.1(4)
C(2)-C(1)-C(6)-C(5)	-5.4(7)
Br(1)-C(1)-C(6)-C(5)	169.0(3)
C(2)-C(1)-C(6)-C(7)	174.5(5)
Br(1)-C(1)-C(6)-C(7)	-11.2(7)
C(4)-C(5)-C(6)-C(1)	4.1(7)
C(11)-C(5)-C(6)-C(1)	-176.5(4)
C(4)-C(5)-C(6)-C(7)	-175.7(4)
C(11)-C(5)-C(6)-C(7)	3.7(6)
C(1)-C(6)-C(7)-C(9)	173.1(5)
C(5)-C(6)-C(7)-C(9)	-7.1(6)
C(1)-C(6)-C(7)-C(8)	-12.1(7)
C(5)-C(6)-C(7)-C(8)	167.8(4)
C(9)-C(7)-C(8)-N(1)	-22.7(7)
C(6)-C(7)-C(8)-N(1)	162.4(4)
C(6)-C(7)-C(9)-O(1)	-177.4(4)
C(8)-C(7)-C(9)-O(1)	7.6(7)
C(6)-C(7)-C(9)-C(10)	7.1(7)
C(8)-C(7)-C(9)-C(10)	-167.9(4)
O(1)-C(9)-C(10)-C(11)	-178.9(4)
C(7)-C(9)-C(10)-C(11)	-3.2(7)
O(1)-C(9)-C(10)-C(12)	1.2(6)
C(7)-C(9)-C(10)-C(12)	176.9(4)

C(9)-C(10)-C(11)-C(5)	-0.6(7)
C(12)-C(10)-C(11)-C(5)	179.3(4)
C(4)-C(5)-C(11)-C(10)	179.6(4)
C(6)-C(5)-C(11)-C(10)	0.2(7)
C(11)-C(10)-C(12)-C(13)	-2.2(7)
C(9)-C(10)-C(12)-C(13)	177.7(4)
C(10)-C(12)-C(13)-C(14)	-179.8(4)
C(12)-C(13)-C(14)-C(15)	-170.2(4)
C(21)-C(16)-C(17)-C(18)	-2.3(8)
Br(2)-C(16)-C(17)-C(18)	172.7(4)
C(16)-C(17)-C(18)-C(19)	-2.1(7)
C(17)-C(18)-C(19)-C(20)	2.9(7)
C(18)-C(19)-C(20)-C(21)	0.5(7)
C(18)-C(19)-C(20)-C(26)	-177.7(4)
C(19)-C(20)-C(21)-C(16)	-4.5(7)
C(26)-C(20)-C(21)-C(16)	173.7(4)
C(19)-C(20)-C(21)-C(22)	177.2(4)
C(26)-C(20)-C(21)-C(22)	-4.6(6)
C(17)-C(16)-C(21)-C(20)	5.4(7)
Br(2)-C(16)-C(21)-C(20)	-169.1(3)
C(17)-C(16)-C(21)-C(22)	-176.5(5)
Br(2)-C(16)-C(21)-C(22)	8.9(7)
C(20)-C(21)-C(22)-C(24)	7.8(7)
C(16)-C(21)-C(22)-C(24)	-170.2(5)
C(20)-C(21)-C(22)-C(23)	-163.8(4)
C(16)-C(21)-C(22)-C(23)	18.1(7)
C(24)-C(22)-C(23)-N(2)	16.7(7)
C(21)-C(22)-C(23)-N(2)	-171.5(4)
C(21)-C(22)-C(24)-O(3)	176.0(4)
C(23)-C(22)-C(24)-O(3)	-12.0(7)
C(21)-C(22)-C(24)-C(25)	-6.5(7)
C(23)-C(22)-C(24)-C(25)	165.5(4)
O(3)-C(24)-C(25)-C(26)	179.1(4)
C(22)-C(24)-C(25)-C(26)	1.5(7)
O(3)-C(24)-C(25)-C(27)	1.1(6)
C(22)-C(24)-C(25)-C(27)	-176.6(4)
C(24)-C(25)-C(26)-C(20)	2.0(7)
C(27)-C(25)-C(26)-C(20)	180.0(4)
C(19)-C(20)-C(26)-C(25)	177.9(5)
C(21)-C(20)-C(26)-C(25)	-0.4(7)
C(26)-C(25)-C(27)-C(28)	6.5(7)
C(24)-C(25)-C(27)-C(28)	-175.6(4)
C(25)-C(27)-C(28)-C(29)	-179.6(4)
C(27)-C(28)-C(29)-C(30)	178.2(4)
C(36)-C(31)-C(32)-C(33)	-1.1(7)
Br(3)-C(31)-C(32)-C(33)	172.5(4)
C(31)-C(32)-C(33)-C(34)	-2.2(7)
C(32)-C(33)-C(34)-C(35)	1.7(8)
C(33)-C(34)-C(35)-C(41)	-177.6(5)
C(33)-C(34)-C(35)-C(36)	2.1(7)
C(32)-C(31)-C(36)-C(37)	-177.1(5)
Br(3)-C(31)-C(36)-C(37)	10.0(7)
C(32)-C(31)-C(36)-C(35)	4.5(7)

Br(3)-C(31)-C(36)-C(35)	-168.4(3)
C(41)-C(35)-C(36)-C(31)	174.7(4)
C(34)-C(35)-C(36)-C(31)	-5.0(7)
C(41)-C(35)-C(36)-C(37)	-3.8(7)
C(34)-C(35)-C(36)-C(37)	176.5(4)
C(31)-C(36)-C(37)-C(39)	-172.8(5)
C(35)-C(36)-C(37)-C(39)	5.5(6)
C(31)-C(36)-C(37)-C(38)	15.7(7)
C(35)-C(36)-C(37)-C(38)	-166.0(4)
C(39)-C(37)-C(38)-N(3)	16.7(7)
C(36)-C(37)-C(38)-N(3)	-171.7(4)
C(36)-C(37)-C(39)-O(5)	177.5(4)
C(38)-C(37)-C(39)-O(5)	-10.6(7)
C(36)-C(37)-C(39)-C(40)	-4.0(7)
C(38)-C(37)-C(39)-C(40)	167.9(4)
O(5)-C(39)-C(40)-C(41)	179.0(4)
C(37)-C(39)-C(40)-C(41)	0.4(7)
O(5)-C(39)-C(40)-C(42)	1.2(6)
C(37)-C(39)-C(40)-C(42)	-177.4(4)
C(39)-C(40)-C(41)-C(35)	1.5(7)
C(42)-C(40)-C(41)-C(35)	179.2(4)
C(34)-C(35)-C(41)-C(40)	180.0(4)
C(36)-C(35)-C(41)-C(40)	0.3(7)
C(41)-C(40)-C(42)-C(43)	7.9(7)
C(39)-C(40)-C(42)-C(43)	-174.5(4)
C(40)-C(42)-C(43)-C(44)	173.5(4)
C(42)-C(43)-C(44)-C(45)	-173.4(4)
C(51)-C(46)-C(47)-C(48)	1.5(7)
Br(4)-C(46)-C(47)-C(48)	-174.3(3)
C(46)-C(47)-C(48)-C(49)	1.9(7)
C(47)-C(48)-C(49)-C(50)	-2.4(7)
C(48)-C(49)-C(50)-C(56)	178.5(4)
C(48)-C(49)-C(50)-C(51)	-0.5(7)
C(47)-C(46)-C(51)-C(50)	-4.1(7)
Br(4)-C(46)-C(51)-C(50)	171.3(3)
C(47)-C(46)-C(51)-C(52)	177.9(5)
Br(4)-C(46)-C(51)-C(52)	-6.7(7)
C(49)-C(50)-C(51)-C(46)	3.6(7)
C(56)-C(50)-C(51)-C(46)	-175.4(4)
C(49)-C(50)-C(51)-C(52)	-178.3(4)
C(56)-C(50)-C(51)-C(52)	2.7(7)
C(46)-C(51)-C(52)-C(54)	172.2(4)
C(50)-C(51)-C(52)-C(54)	-5.6(7)
C(46)-C(51)-C(52)-C(53)	-17.0(8)
C(50)-C(51)-C(52)-C(53)	165.2(4)
C(54)-C(52)-C(53)-N(4)	-25.7(7)
C(51)-C(52)-C(53)-N(4)	163.5(5)
C(51)-C(52)-C(54)-O(7)	-176.8(4)
C(53)-C(52)-C(54)-O(7)	11.9(7)
C(51)-C(52)-C(54)-C(55)	4.7(7)
C(53)-C(52)-C(54)-C(55)	-166.6(4)
O(7)-C(54)-C(55)-C(56)	-179.2(4)
C(52)-C(54)-C(55)-C(56)	-0.6(7)

O(7)-C(54)-C(55)-C(57)	0.0(6)
C(52)-C(54)-C(55)-C(57)	178.6(4)
C(54)-C(55)-C(56)-C(50)	-2.7(7)
C(57)-C(55)-C(56)-C(50)	178.2(4)
C(49)-C(50)-C(56)-C(55)	-177.5(5)
C(51)-C(50)-C(56)-C(55)	1.6(7)
C(56)-C(55)-C(57)-C(58)	-6.9(7)
C(54)-C(55)-C(57)-C(58)	174.1(4)
C(55)-C(57)-C(58)-C(59)	-173.1(4)
C(57)-C(58)-C(59)-C(60)	-175.2(4)
C(7)-C(8)-N(1)-O(2)	177.8(4)
C(22)-C(23)-N(2)-O(4)	-173.3(4)
C(37)-C(38)-N(3)-O(6)	-173.1(4)
C(52)-C(53)-N(4)-O(8)	177.3(4)