Supporting Information

Two birds with one stone: One-pot simultaneous synthesis of 2,2,2-trifluoroethylphenanthridines and benzochromenones featuring with utilization of the byproduct of Togni's reagent

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Contents

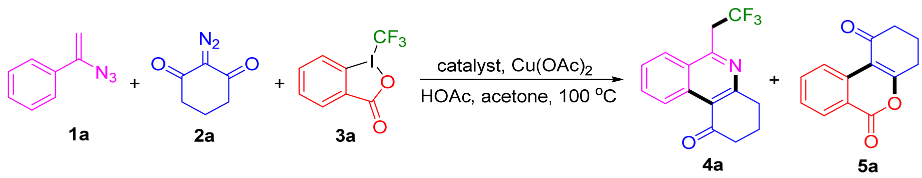
I. General experimental information

Commercial reagents were used without further purification. Vinyl azides (**1**),[1] cyclic α-diazo carbonyl compounds (**2**),[2] the derivatives of Togni's reagent (**3**)[3] and $[RhCp^*Cl_2]_2$[4] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Study on the effect of different transition metal complexes/salts as possible catalyst

Table S1. Effect of different transition metal complexes/salts as catalyst



entry	catalyst	Yield (%)[a,b]	
		4a	**5a**
1	$[IrCp^*Cl_2]_2$	30	11
2	$[Ir(cod)Cl]_2$	ND	ND
3	$[Rh(cod)Cl]_2$	trace	trace
4	$[RhCp^*(CH_3CN)_3][SbF_6]_2$	51	28
5	$[RhCp^*(OAc)_2]_2$	69	47
6	[Ru(*p*-cymene)$Cl_2]_2$	ND	ND
7	$[Ru(cod)Cl_2]$	ND	ND
8	$Co(OAc)_2$	ND	ND
9	$RhCl_3 \cdot 3H_2O$	ND	ND
10	$Pd(OAc)_2$	ND	ND

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), **3a** (0.2 mmol), catalyst (0.01 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), acetone (2 mL), 100 °C, 3 h. [b] Isolated yield.

2. General synthetic procedure and spectroscopic data of products 4, 5, 7 and 8

To a reaction tube equipped with a stir bar were charged with vinyl azide (**1**, 0.3 mmol), cyclic α-diazo carbonyl compound (**2**, 0.6 mmol), Togni's reagent (**3**, 0.2 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol) and acetone (2 mL). The resulting mixture was then stirred at 100 °C under air for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/acetone (20:1) as eluent to afford products **4** and **5**. Products **7** and **8** were obtained in a similar manner from the reaction of **1a** with **6** and **3a**.

6-(2,2,2-Trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4a)

White solid (40.2 mg, 72%), mp: 125-126 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 2.26-2.30 (m, 2H), 2.84 (t, J = 6.0 Hz, 2H), 3.36 (t, J = 6.0 Hz, 2H), 4.17 (q, J = 10.2 Hz, 2H), 7.66-7.69 (m, 1H), 7.86-7.88 (m, 1H), 8.15 (d, J = 8.4 Hz, 1H), 9.49 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.7, 33.6, 40.3 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 40.4, 120.9, 125.2 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 125.5, 126.6, 126.9, 127.5, 132.9, 134.6, 155.3 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 159.8, 200.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.47. HRMS calcd for $C_{15}H_{13}F_3NO$: 280.0944 $[M+H]^+$, found: 280.0943.

9-Methyl-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4b)

White solid (39.9 mg, 68%), mp: 110-111 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 2.14-2.18 (m, 2H), 2.51 (s, 3H), 2.72 (t, J = 6.6 Hz, 2H), 3.23 (t, J = 6.0 Hz, 2H), 4.03 (q, J = 10.2 Hz, 2H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 9.18 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.7, 22.6, 33.6, 40.2 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 40.7, 120.6, 125.2 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 125.30, 125.33, 125.6, 129.5, 134.9, 144.0, 154.9 (q, $^3J_{C\text{-}F}$ = 3.2 Hz), 159.9, 200.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.55. HRMS calcd for $C_{16}H_{15}F_3NO$: 294.1100 $[M+H]^+$, found: 294.1103.

9-(*tert*-Butyl)-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4c)

White solid (42.2 mg, 63%), mp: 138-139 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.47 (s, 9H), 2.24-2.28 (m, 2H), 2.83 (t, J = 6.6 Hz, 2H), 3.34 (t, J = 6.6 Hz, 2H), 4.13 (q, J = 10.2 Hz, 2H), 7.75 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 9.53 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.8, 31.0, 33.7, 35.8, 40.2 (q, $^2J_{C-F}$ = 29.6 Hz), 40.8, 120.9, 121.8, 125.17, 125.24, 125.3 (q, $^1J_{C-F}$ = 276.8 Hz), 126.2, 134.9, 154.7 (q, $^3J_{C-F}$ = 3.3 Hz), 156.5, 160.0, 201.0. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.51. HRMS calcd for $C_{19}H_{21}F_3NO$: 336.1570 $[M+H]^+$, found: 336.1575.

9-Methoxy-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4d)

White solid (34.0 mg, 55%), mp: 166-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.20-2.27 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 3.30 (t, J = 6.4 Hz, 2H), 4.00 (s, 3H), 4.06 (q, J = 10.4 Hz, 2H), 7.24 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 8.00 (d, J = 9.2 Hz, 1H), 8.97 (d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.7, 33.9, 40.4 (q, $^2J_{C-F}$ = 29.6 Hz), 40.8, 55.7, 104.6, 120.0, 120.1, 122.6, 125.3 (q, $^1J_{C-F}$ = 276.6 Hz), 127.3, 137.2, 154.3 (q, $^3J_{C-F}$ = 3.3 Hz), 161.0, 163.3, 201.0. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.61. HRMS calcd for $C_{16}H_{15}F_3NO_2$: 310.1049 $[M+H]^+$, found: 310.1051.

1-Oxo-6-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydrophenanthridin-9-yl acetate (4e)

Yellow solid (34.4 mg, 51%), mp: 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21-2.27 (m, 2H), 2.38 (s, 3H), 2.80 (t, J = 6.4 Hz, 2H), 3.32 (t, J = 6.4 Hz, 2H), 4.12 (q, J = 10.0 Hz, 2H), 7.42 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 8.13 (d, J = 9.2 Hz, 1H), 9.24 (d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.1, 21.6, 33.6, 40.4 (q, $^2J_{C-F}$ = 29.6 Hz), 40.5, 118.1, 120.5, 122.9, 125.0, 125.1 (q, $^1J_{C-F}$ = 276.8 Hz), 127.2, 128.4, 130.1, 133.4, 135.8, 154.1 155.1 (q, $^3J_{C-F}$ = 3.3 Hz), 160.7, 169.1, 200.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.48. HRMS calcd for $C_{17}H_{15}F_3NO_3$: 338.0999 $[M+H]^+$, found: 338.1005.

9-Fluoro-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4f)

White solid (34.5 mg, 58%), mp: 101-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.20-2.26 (m, 2H), 2.80 (t, J = 6.6 Hz, 2H), 3.32 (t, J = 6.6 Hz, 2H), 4.11 (q, J = 10.2 Hz, 2H), 7.38-7.42 (m, 1H), 8.14 (dd, J_1 = 9.6 Hz, J_2 = 6.0 Hz, 1H), 9.21 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.6, 33.6, 40.4, 40.5 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 111.1 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 117.8 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 120.5 (d, $^4J_{C\text{-}F}$ = 5.4 Hz), 124.2, 125.1 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 128.5 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 136.6 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 155.0 (q, $^3J_{C\text{-}F}$ = 2.3 Hz), 161.0, 165.2 (d, $^1J_{C\text{-}F}$ = 252.6 Hz), 200.3. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.53, -102.28. HRMS calcd for $C_{15}H_{12}F_4NO$: 298.0850 $[M+H]^+$, found: 298.0853.

9-Chloro-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4g)

White solid (45.1 mg, 72%), mp: 122-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.15-2.19 (m, 2H), 2.73 (t, J = 7.2 Hz, 2H), 3.25 (t, J = 6.6 Hz, 2H), 4.02 (q, J = 10.2 Hz, 2H), 7.50 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 9.45 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.6, 33.7, 40.4 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 40.5, 119.9, 125.0 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 125.1, 125.8, 127.0, 128.5, 135.3, 139.9, 155.2 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 161.0, 200.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.54. HRMS calcd for $C_{15}H_{12}ClF_3NO$: 314.0554 $[M+H]^+$, found: 314.0546.

9-Bromo-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4h)

White solid (49.3 mg, 69%), mp: 140-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.15-2.20 (m, 2H), 2.73 (t, J = 6.0 Hz, 2H), 3.26 (t, J = 6.0 Hz, 2H), 4.03 (q, J = 10.2 Hz, 2H), 7.65 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 9.63 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.6, 33.7, 40.4 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 40.5, 119.7, 125.1 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 125.3, 126.9, 128.9, 129.1, 131.1, 135.4, 155.4 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 160.9, 200.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.53. HRMS calcd for $C_{15}H_{12}BrF_3NO$: 358.0049 $[M+H]^+$, found: 358.0050.

8-Chloro-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4i)

White solid (37.6 mg, 60%), mp: 141-142 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.16-2.21 (m, 2H), 2.74 (t, J = 6.6 Hz, 2H), 3.26 (t, J = 6.0 Hz, 2H), 4.02 (q, J = 10.2 Hz, 2H), 7.69 (dd, J_1 = 9.6 Hz, J_2 = 2.4 Hz, 1H), 7.99 (d, J = 1.8 Hz, 1H), 9.38 (d, J = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.6, 33.5, 40.3 (q, $^{2}J_{C-F}$ = 29.6 Hz), 40.5, 120.7, 124.3, 125.0 (q, $^{1}J_{C-F}$ = 276.8 Hz), 127.7, 128.5, 132.9, 133.61, 133.63, 154.4 (q, $^{3}J_{C-F}$ = 3.3 Hz), 160.0, 200.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.48. HRMS calcd for $C_{15}H_{12}ClF_3NO$: 314.0554 $[M+H]^+$, found: 314.0557.

6-(2,2,2-Trifluoroethyl)-3,4-dihydrobenzo[*j*]phenanthridin-1(2*H*)-one (4j)

Yellow solid (37.5 mg, 57%), mp: 185-186 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.28-2.33 (m, 2H), 2.87 (t, J = 6.6 Hz, 2H), 3.38 (t, J = 6.0 Hz, 2H), 4.29 (q, J = 10.2 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.70 (s, 1H), 10.08 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.7, 33.7, 40.56, 40.61 (q, $^{2}J_{C-F}$ = 28.8 Hz), 119.9, 124.9, 125.2 (q, $^{1}J_{C-F}$ = 276.8 Hz), 125.8, 126.2, 127.0, 128.4, 128.8, 129.1, 129.4, 131.4, 135.7, 157.3 (q, $^{3}J_{C-F}$ = 3.3 Hz), 158.8, 200.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.09. HRMS calcd for $C_{19}H_{15}F_3NO$: 330.1100 $[M+H]^+$, found: 330.1104.

6-(2,2,2-Trifluoro-1-phenylethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4k)

Brown oil (34.1 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24-2.31 (m, 2H), 2.82 (t, J = 6.4 Hz, 2H), 3.42 (td, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 2H), 5.63 (q, J = 8.8 Hz, 1H), 7.31-7.36 (m, 3H), 7.50-7.56 (m, 3H), 7.73-7.76 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 9.44 (d, J = 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.8, 34.0, 40.7, 53.1 (q, $^{2}J_{C-F}$ = 27.3 Hz), 120.3, 124.2, 125.4 (q, $^{1}J_{C-F}$ = 278.9 Hz), 125.7, 126.8, 127.3, 128.7, 128.8, 130.0, 132.4, 133.3, 134.7, 158.5, 159.8, 200.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -64.88. HRMS calcd for $C_{21}H_{17}F_3NO$: 356.1257 $[M+H]^+$, found: 356.1254.

6-(1-(3,4-Dimethoxyphenyl)-2,2,2-trifluoroethyl)-8,9-dimethoxy-3,4-dihydrophenanthridin-1(2*H*)-one (4l)

Yellow oil (45.6 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22-2.28 (m, 2H), 2.79-2.82 (m, 2H), 3.30-3.42 (m, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 3.92 (s, 3H), 4.05 (s, 3H), 5.38 (q, J = 8.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 7.02 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.15 (s, 1H), 7.20 (s, 1H), 9.01 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 22.0, 34.0, 40.9, 53.1 (q, $^2J_{C-F}$ = 26.3 Hz), 55.7, 55.8, 56.0, 56.2, 102.8, 105.5, 111.0, 112.9, 119.2, 122.0, 122.6, 125.5 (q, $^1J_{C-F}$ = 280.1 Hz), 126.0, 132.1, 149.1, 149.37, 149.42, 154.4, 156.0, 158.8, 201.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -64.94. HRMS calcd for $C_{25}H_{25}F_3NO_5$: 476.1679 $[M+H]^+$, found: 476.1676.

3,3-Dimethyl-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4m)

White solid (34.4 mg, 56%), mp: 101-103 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.20 (s, 6H), 2.70 (s, 2H), 3.26 (s, 2H), 4.16 (q, J = 10.2 Hz, 2H), 7.66-7.69 (m, 1H), 7.85-7.88 (m, 1H), 8.15 (d, J = 8.4 Hz, 1H), 9.51 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 28.2, 32.8, 40.3 (q, $^2J_{C-F}$ = 29.6 Hz), 47.6, 54.3, 119.9, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.4, 126.4, 126.8, 127.4, 132.9, 134.3, 155.7 (q, $^3J_{C-F}$ = 3.3 Hz), 158.3, 201.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.48. HRMS calcd for $C_{17}H_{17}F_3NO$: 308.1257 $[M+H]^+$, found: 308.1252.

2,2-Dimethyl-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4n)

White solid (25.2 mg, 41%), mp: 100-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.22 (s, 6H), 2.04 (t, J = 6.6 Hz, 2H), 3.28 (t, J = 6.0 Hz, 2H), 4.09 (q, J = 10.2 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 9.29 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 24.5, 29.7, 35.0, 40.1 (q, $^2J_{C-F}$ = 28.5 Hz), 42.9, 120.1, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.6, 126.6, 127.0, 127.5, 132.9, 135.2, 154.9 (q, $^3J_{C-F}$ = 3.2 Hz), 157.8, 205.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.51. HRMS calcd for $C_{17}H_{17}F_3NO$: 308.1257 $[M+H]^+$, found: 308.1257.

3-Phenyl-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4o)

White solid (48.3 mg, 68%), mp: 111-112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.89-3.03 (m, 2H), 3.43-3.46 (m, 1H), 3.50-3.56 (m, 2H), 4.03-4.08 (m, 2H), 7.18-7.21 (m, 1H), 7.25-7.30 (m, 4H), 7.56-7.58 (m, 1H), 7.75-7.78 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 9.43 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 39.4, 40.3 (q, $^2J_{C-F}$ = 29.6 Hz), 41.2, 47.5, 120.3, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.5, 126.5, 126.7, 126.9, 127.1, 127.6, 128.9, 133.1, 134.4. 142.7, 155.8 (q, $^3J_{C-F}$ = 3.3 Hz), 159.1, 199.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.40. HRMS calcd for $C_{21}H_{17}F_3NO$: 356.1257 $[M+H]^+$, found: 356.1257.

3-(4-Fluorophenyl)-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4p)

White solid (45.5 mg, 61%), mp: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94-3.11 (m, 2H), 3.45-3.64 (m, 3H), 4.11-4.19 (m, 2H), 7.06 (t, J = 8.8 Hz, 2H), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 9.51 (d, J = 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 38.8, 40.3 (q, $^2J_{C-F}$ = 29.6 Hz), 41.4, 47.6, 115.7 (d, $^2J_{C-F}$ = 20.9 Hz), 120.3, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.5, 126.5, 127.0, 127.7, 128.2 (d, $^3J_{C-F}$ = 8.7 Hz), 133.1, 134.4, 138.5 (d, $^4J_{C-F}$ = 3.3 Hz), 155.9 (q, $^3J_{C-F}$ = 3.3 Hz), 158.8, 161.8 (d, $^1J_{C-F}$ = 243.9 Hz), 199.6. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.43, -115.64. HRMS calcd for $C_{21}H_{16}F_4NO$: 374.1163 $[M+H]^+$, found: 374.1160.

3-(4-Chlorophenyl)-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4q)

White solid (53.7 mg, 69%), mp: 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94-3.10 (m, 2H), 3.45-3.64 (m, 3H), 4.10-4.19 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.87 (t, J = 8.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 9.51 (d, J = 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 38.9, 40.4 (q, $^2J_{C-F}$ = 29.6 Hz), 41.1, 47.3, 120.3, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.5, 126.5, 127.0, 127.7, 128.1, 129.0, 132.8, 133.1, 134.4, 141.2, 155.9 (q, $^3J_{C-F}$ = 3.3 Hz), 158.7, 199.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.42. HRMS calcd for $C_{21}H_{16}ClF_3NO$: 390.0867 $[M+H]^+$, found: 390.0869.

3-(4-Bromophenyl)-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4r)

White solid (57.2 mg, 66%), mp: 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.94-3.11 (m, 2H), 3.48-3.64 (m, 3H), 4.11-4.19 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.48-7.52 (m, 2H), 7.66-7.70 (m, 1H), 7.85-7.89 (m, 1H), 8.14 (d, J = 8.4 Hz, 1H), 9.51 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 38.9, 40.4 (q, $^2J_{C-F}$ = 29.6 Hz), 41.0, 47.3, 120.3, 120.9, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.5, 126.5, 127.0, 127.7, 128.5, 132.0, 133.1, 134.4, 141.7, 155.9 (q, $^3J_{C-F}$ = 3.3 Hz), 158.7, 199.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.42. HRMS calcd for $C_{21}H_{16}BrF_3NO$: 434.0362 $[M+H]^+$, found: 434.0358.

3-(4-Methoxyphenyl)-6-(2,2,2-trifluoroethyl)-3,4-dihydrophenanthridin-1(2*H*)-one (4s)

White solid (45.4 mg, 59%), mp: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.93-3.10 (m, 2H), 3.47-3.63 (m, 3H), 3.81 (s, 3H), 4.10-4.18 (m, 2H), 6.89-6.93 (m, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 9.51 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 38.7, 40.3 (q, $^2J_{C-F}$ = 29.6 Hz), 41.5, 47.8, 55.3, 114.2, 120.3, 125.2 (q, $^1J_{C-F}$ = 276.8 Hz), 125.4, 126.5, 126.9, 127.6, 127.7, 133.0, 134.4, 134.9, 155.8 (q, $^3J_{C-F}$ = 3.3 Hz), 158.6, 159.1, 200.0. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.41. HRMS calcd for $C_{22}H_{19}F_3NO_2$: 386.1362 $[M+H]^+$, found: 386.1364.

3,4-Dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5a)

White solid (22.3 mg, 52%), mp: 165-167 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.16-2.20 (m, 2H), 2.65 (t, J = 6.6 Hz, 2H), 2.93 (t, J = 6.6 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.0, 29.0, 38.9, 111.6, 119.8, 126.0, 128.4, 129.5, 134.0, 135.6, 160.5, 169.5, 197.0. HRMS calcd for $C_{13}H_{10}NaO_3$: 237.0522 $[M+Na]^+$, found: 237.0528.

3,3-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5b)

White solid (26.6 mg, 55%), mp: 135-137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.20 (s, 6H), 2.54 (s, 2H), 2.82 (s, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.80-7.83 (m, 1H), 8.30-8.31 (m, 1H), 9.06 (d, J = 8.4 Hz, 1H). ^{13}C

NMR (150 MHz, $CDCl_3$) δ: 28.2, 32.0, 42.6, 52.9, 110.6, 119.8, 125.9, 128.4, 129.6, 133.9, 135.7, 160.8, 168.0, 197.0. HRMS calcd for $C_{15}H_{14}NaO_3$: 265.0835 $[M+Na]^+$, found: 265.0832.

2,2-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5c)

White solid (10.7 mg, 22%), mp: 110-112 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 1.16 (s, 6H), 1.96 (t, J = 6.4 Hz, 2H), 2.94 (t, J = 6.4 Hz, 2H), 7.60-7.64 (m, 1H), 7.87-7.91 (m, 1H), 8.19 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.94 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 24.5, 25.7, 33.2, 42.0, 109.8, 120.1, 126.2, 128.3, 129.7, 134.5, 135.6, 160.7, 167.5, 201.8. HRMS calcd for $C_{15}H_{14}NaO_3$: 265.0835 $[M+Na]^+$, found: 265.0830.

3-Phenyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5d)

White solid (34.2 mg, 59%), mp: 115-117 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 2.80-2.89 (m, 2H), 3.06-3.13 (m, 2H), 3.47-3.52 (m, 1H), 7.22-7.25 (m, 3H), 7.31-7.33 (m, 2H), 7.46-7.49 (m, 1H), 7.72-7.75 (m, 1H), 8.22 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 9.01 (d, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.4, 38.0, 45.9, 111.4, 119.8, 126.0, 126.6, 127.6, 128.6, 129.1, 129.7, 133.8, 135.8, 141.4, 160.5, 168.6, 196.1. HRMS calcd for $C_{19}H_{14}NaO_3$: 313.0835 $[M+Na]^+$, found: 313.0824.

3-(4-Fluorophenyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5e)

White solid (32.7 mg, 53%), mp: 191-193 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 2.82-2.92 (m, 2H), 3.11 (d, J = 7.8 Hz, 2H), 3.52-3.57 (m, 1H), 7.07 (t, J = 8.4 Hz, 2H), 7.26-7.28 (m, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 9.02 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.4, 37.3, 45.9, 111.3, 115.9 (d, $^2J_{C-F}$ = 21.9 Hz), 119.8, 125.9, 128.2 (d, $^3J_{C-F}$ = 7.7 Hz), 128.6, 129.6, 133.7, 135.7, 137.2 (d, $^4J_{C-F}$ = 2.1 Hz), 160.2, 162.0 (d, $^1J_{C-F}$ = 245.0 Hz), 168.5, 195.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -114.80. HRMS calcd for $C_{19}H_{13}FNaO_3$: 331.0741 $[M+Na]^+$, found: 331.0740.

3-(4-Chlorophenyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5f)

White solid (33.7 mg, 52%), mp: 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.82-2.96 (m, 2H), 3.14 (d, *J* = 8.0 Hz, 2H), 3.51-3.60 (m, 1H), 7.21-7.25 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.79-7.83 (m, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 9.07 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.2, 37.4, 45.7, 111.4, 119.9, 126.0, 128.0, 128.7, 129.2, 129.7, 133.4, 133.7, 135.8, 139.9, 160.3, 168.3, 195.6. HRMS calcd for $C_{19}H_{13}ClNaO_3$: 347.0445 $[M+Na]^+$, found: 347.0448.

3-(4-Bromophenyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5g)

White solid (39.0 mg, 53%), mp: 42-44°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.81-2.90 (m, 2H), 3.09-3.11 (m, 2H), 3.49-3.55 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.48-7.52 (m, 3H), 7.76 (t, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 9.00 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.1, 37.4, 45.6, 111.3, 119.7, 121.3, 125.9, 128.4, 128.7, 129.6, 132.1, 133.6, 135.7, 140.5, 160.2, 168.3, 195.6. HRMS calcd for $C_{19}H_{13}BrNaO_3$: 390.9940 $[M+Na]^+$, found: 390.9941.

3-(4-Methoxyphenyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5h)

White solid (35.9 mg, 56%), mp: 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.82-2.95 (m, 2H), 3.13 (d, *J* = 8.0 Hz, 2H), 3.48-3.56 (m, 1H), 3.81 (s, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 9.09 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.7, 37.2, 46.2, 55.4, 111.4, 114.4, 119.9, 126.0, 127.6, 128.6, 129.7, 133.5, 133.9, 135.8, 158.9, 160.5, 168.7, 196.2. HRMS calcd for $C_{20}H_{16}NaO_4$: 343.0941 $[M+Na]^+$, found: 343.0937.

8-Methyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5i)

White solid (19.6 mg, 43%), mp: 176-177 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.15-2.19 (m, 2H), 2.46 (s, 3H), 2.65 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 7.60 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 8.09 (d, *J* = 0.6 Hz, 1H), 8.93 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.1, 21.2, 28.9, 38.9, 111.7, 119.9, 126.0, 129.3, 131.5, 136.9, 138.7, 160.7, 168.7, 197.0. HRMS calcd for $C_{14}H_{12}NaO_3$: 251.0679 $[M+Na]^+$, found: 251.0681.

8-Fluoro-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5j)

White solid (16.7 mg, 36%), mp: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15-2.22 (m, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.95 (t, J = 6.4 Hz, 2H), 7.48-7.53 (m, 1H), 7.93 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 9.12 (dd, J_1 = 9.2 Hz, J_2 = 5.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.0, 28.8, 38.8, 111.2, 115.1 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 122.0 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 123.6 (d, $^{2}J_{C\text{-}F}$ = 20.7 Hz), 129.0 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 130.6 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 159.6 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 161.8 (d, $^{1}J_{C\text{-}F}$ = 249.3 Hz), 168.8, 196.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.19. HRMS calcd for $C_{13}H_9FNaO_3$: 255.0428 $[M+Na]^+$, found: 255.0434.

8-Chloro-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5k)

White solid (21.8 mg, 44%), mp: 171-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08-2.14 (m, 2H), 2.59 (t, J = 6.8 Hz, 2H), 2.87 (t, J = 6.4 Hz, 2H), 7.65 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.16 (d, J = 2.4 Hz, 1H), 8.96 (t, J = 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.9, 28.9, 38.8, 111.2, 121.4, 127.9, 128.9, 132.5, 134.5, 135.8, 159.4, 169.6, 196.7. HRMS calcd for $C_{13}H_9ClNaO_3$: 271.0132 $[M+Na]^+$, found: 271.0140.

8-Bromo-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (5l)

White solid (28.0 mg, 48%), mp: 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15-2.21 (m, 2H), 2.66 (t, J = 6.4 Hz, 2H), 2.93 (t, J = 6.4 Hz, 2H), 7.87 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.40 (d, J = 2.4 Hz, 1H), 8.97 (d, J = 8.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.9, 29.0, 38.8, 111.2, 121.5, 122.3, 128.0, 132.0, 132.8, 138.6, 159.2, 169.7, 196.6. HRMS calcd for $C_{13}H_9BrNaO_3$: 314.9627 $[M+Na]^+$, found: 314.9627.

5-(2,2,2-Trifluoroethyl)-7,8,9,10-tetrahydro-11*H*-cyclohepta[*c*]isoquinolin-11-one (7)

White solid (36.3 mg, 62%), mp: 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90-2.01 (m, 4H), 2.84 (t, J = 6.0 Hz, 2H), 3.23 (t, J = 6.0 Hz, 2H), 4.13 (q, J = 10.4 Hz, 2H), 7.59-7.63 (m, 1H), 7.70-7.74 (m, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 22.9, 24.1, 35.7, 40.1 (q,

$^{2}J_{C-F}$ = 29.6 Hz), 42.6, 124.8, 125.3, 125.4 (q, $^{1}J_{C-F}$ = 276.8 Hz), 126.5, 127.3, 129.1, 131.4, 133.6, 151.9, 152.3 (q, $^{3}J_{C-F}$ = 3.3 Hz), 208.4. ^{19}F NMR (564 MHz, $CDCl_3$) δ: -62.78. HRMS calcd for $C_{16}H_{15}F_3NO$: 294.1100 $[M+H]^+$, found: 294.1100.

7,8,9,10-Tetrahydrocyclohepta[*c*]isochromene-5,11-dione (8)

White solid (21.9 mg, 48%), mp: 66-67 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.85-1.86 (m, 4H), 2.78 (t, J = 6.8 Hz, 2H), 2.93 (t, J = 6.4 Hz, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.83-7.87 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.18 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 22.4, 23.1, 32.3, 43.0, 116.4, 119.7, 124.6, 128.3, 129.7, 134.5, 135.3, 161.2, 163.6, 202.7. HRMS calcd for $C_{14}H_{12}NaO_3$: 251.0679 $[M+Na]^+$, found: 251.0678.

3. Gram-scale preparation of 4a and 5a

To a reaction tube equipped with a stir bar were charged with (1-azidovinyl)benzene (**1a**, 7.5 mmol), 2-diazocyclohexane-1,3-dione (**2a**, 15 mmol), Togni's reagent (**3a**, 5 mmol), $Cu(OAc)_2$ (10 mmol), HOAc (5 mmol), $[Cp^*RhCl_2]_2$ (0.25 mmol) and acetone (50 mL). The resulting mixture was then stirred at 100 °C under air for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated brine, and extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/acetone (20:1) as eluent to afford product **4a** (68%) and **5a** (50%).

III. Mechanism studies

1. Competition experiment (I)

To a reaction tube equipped with a stir bar were charged with (1-azidovinyl)benzene (**1a**, 0.3 mmol), 2-diazocyclohexane-1,3-dione (**2a**, 0.6 mmol), Togni's reagent (**3a**, 0.2 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), TEMPO (0.4 mmol) and acetone (2 mL). The resulting mixture was then stirred at 100 °C under air for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated brine, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/acetone (20:1) as eluent to afford **5a** in 50% yield. Meanwhile, **4a** was formed only in trace amount.

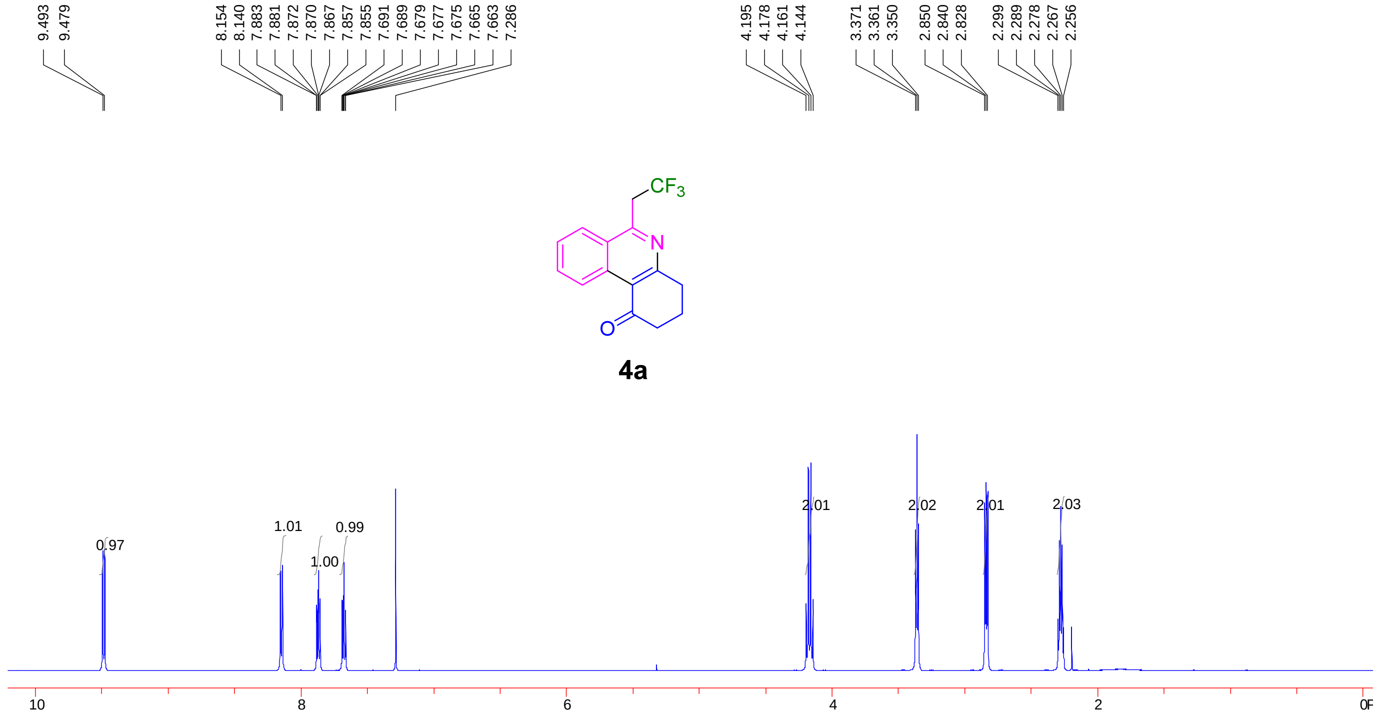
2. Competition experiment (II)

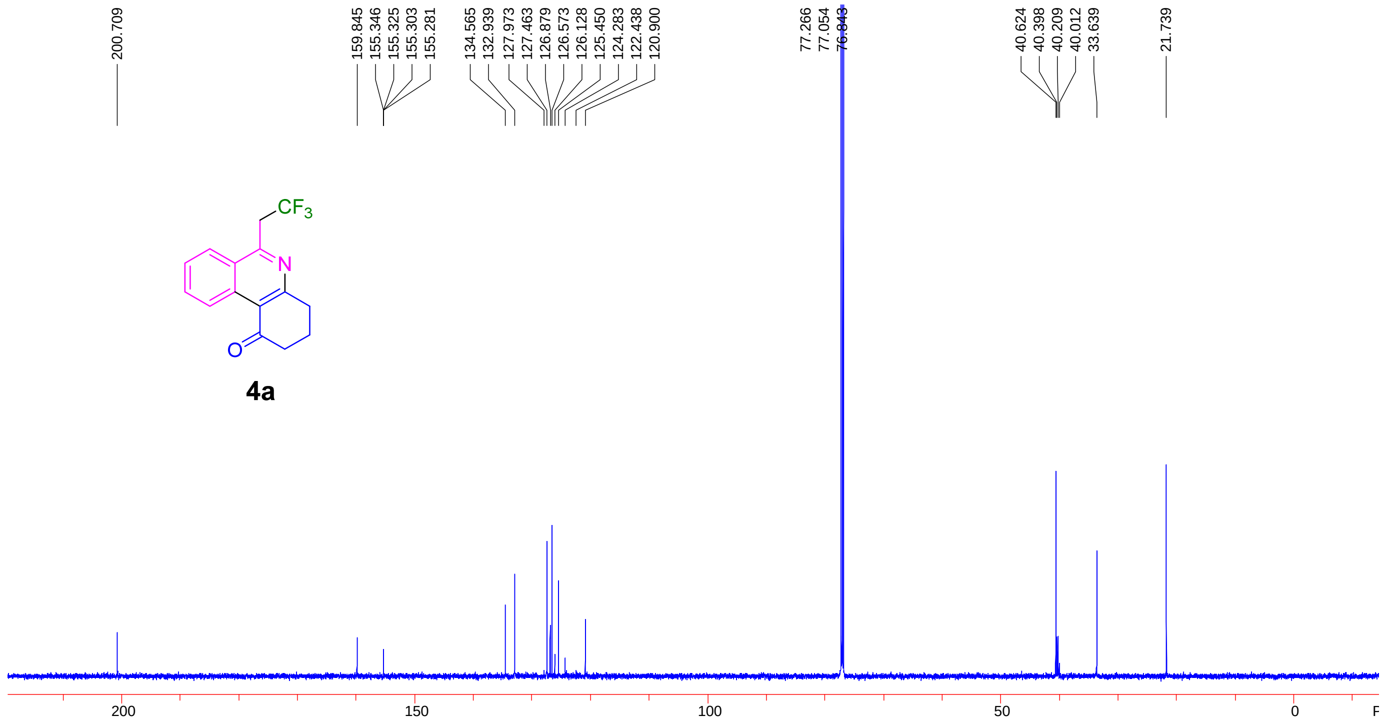
To a reaction tube equipped with a stir bar were charged with 2-iodobenzoic acid (0.2 mmol), 2-diazocyclohexane-1,3-dione (**2a**, 0.22 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol) and acetone (2 mL). The resulting mixture was then stirred at 100 °C under air for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated brine, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/acetone (20:1) as eluent to afford **5a** in 48% yield.

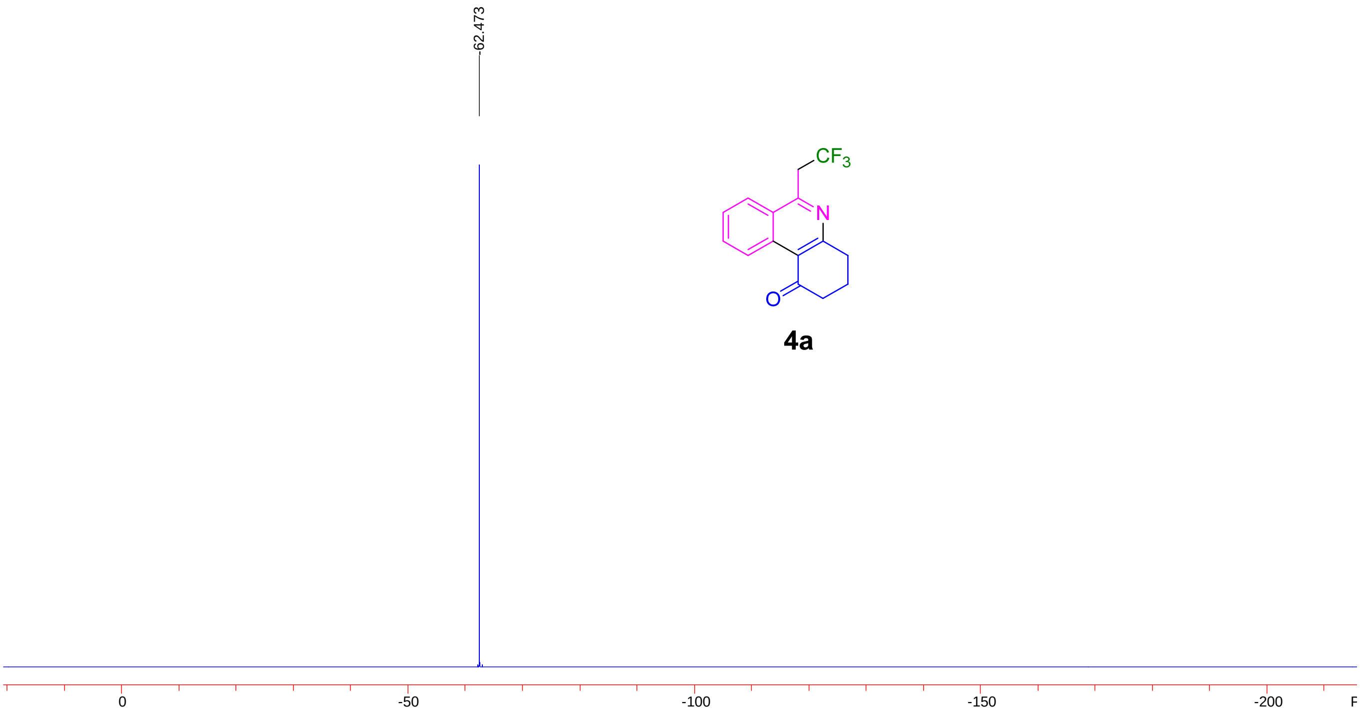
3. Competition experiment (III)

To a reaction tube equipped with a stir bar were charged with benzoic acid (0.2 mmol), 2-diazocyclohexane-1,3-dione (**2a**, 0.22 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol) and acetone (2 mL). The resulting mixture was then stirred at 100 °C under air for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated brine, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/acetone (20:1) as eluent to afford **5a** in 65% yield.

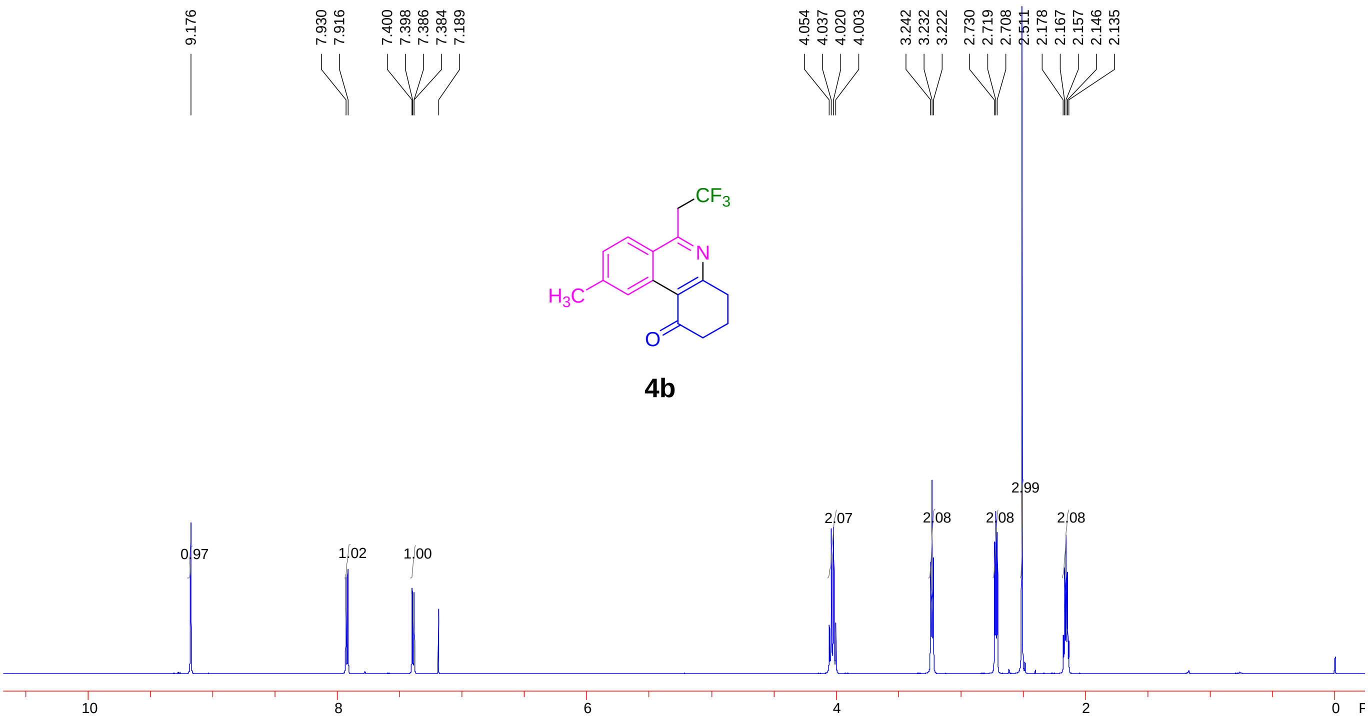
IV. Copies of ^{1}H and ^{13}C NMR spectra of 4a-4s







4a



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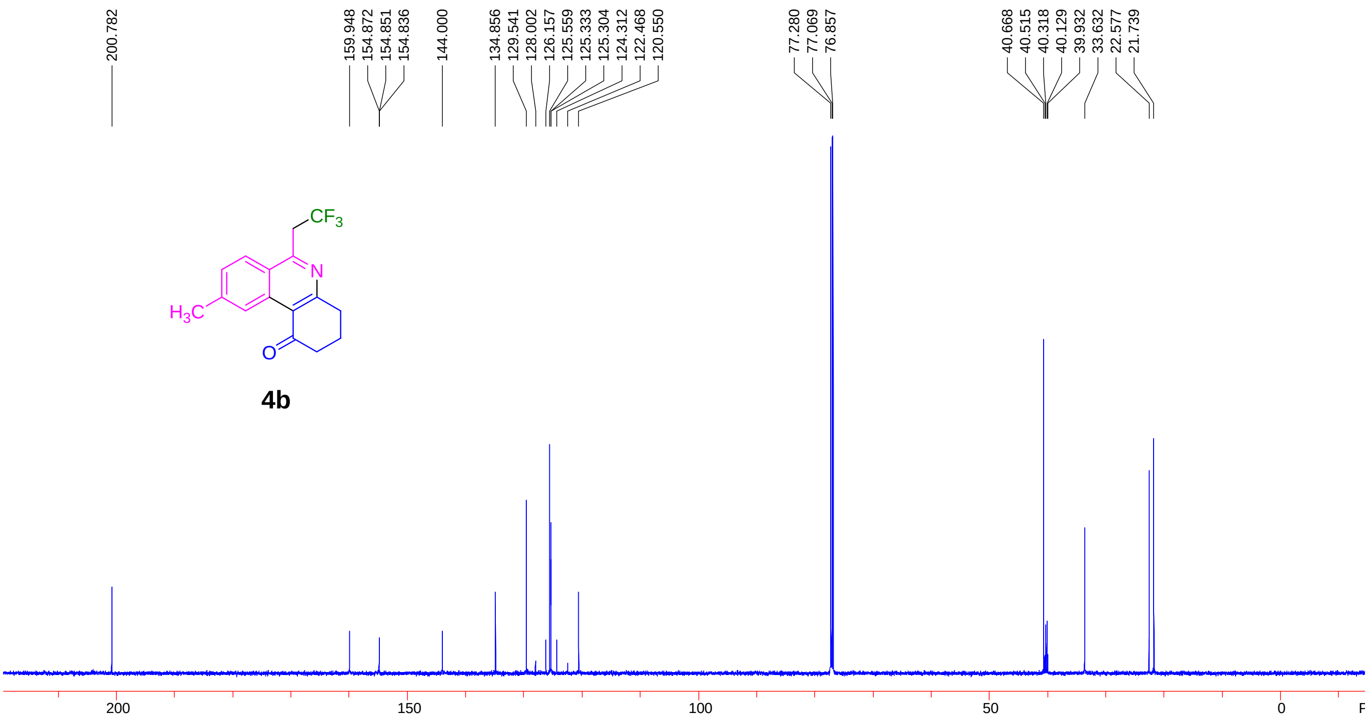

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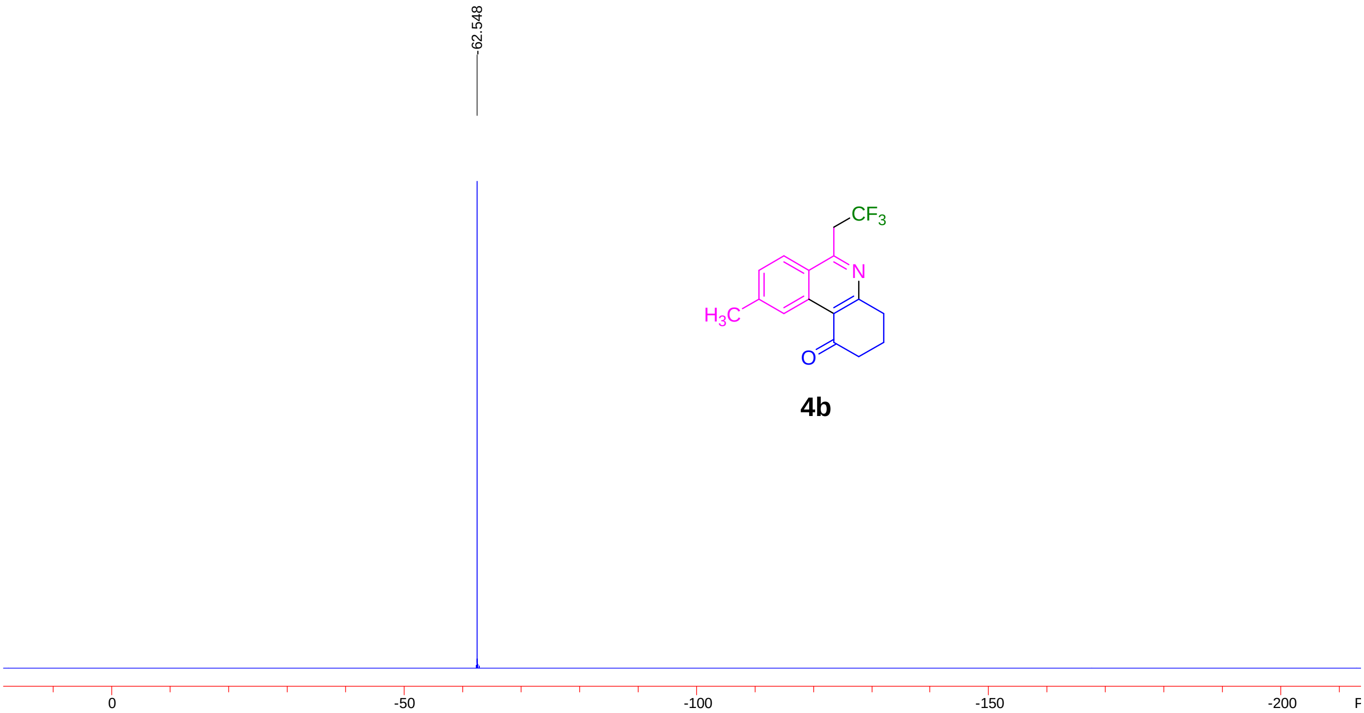
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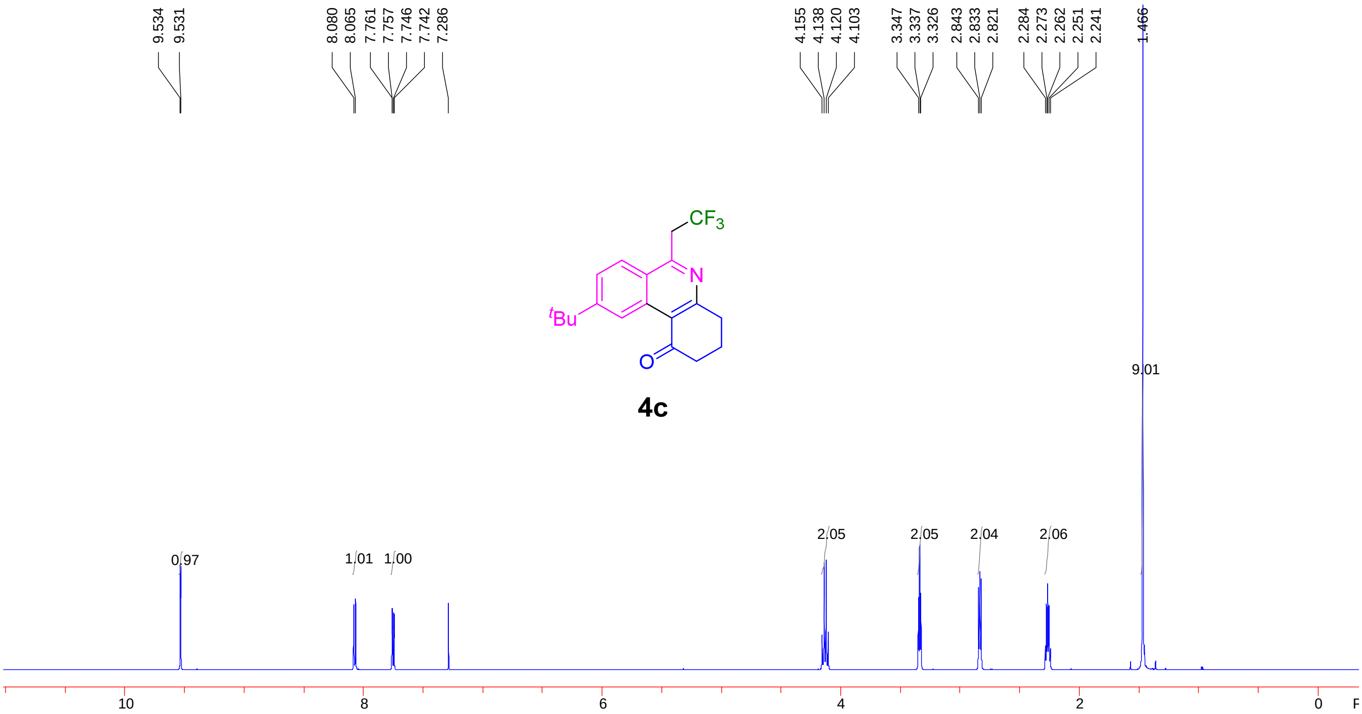
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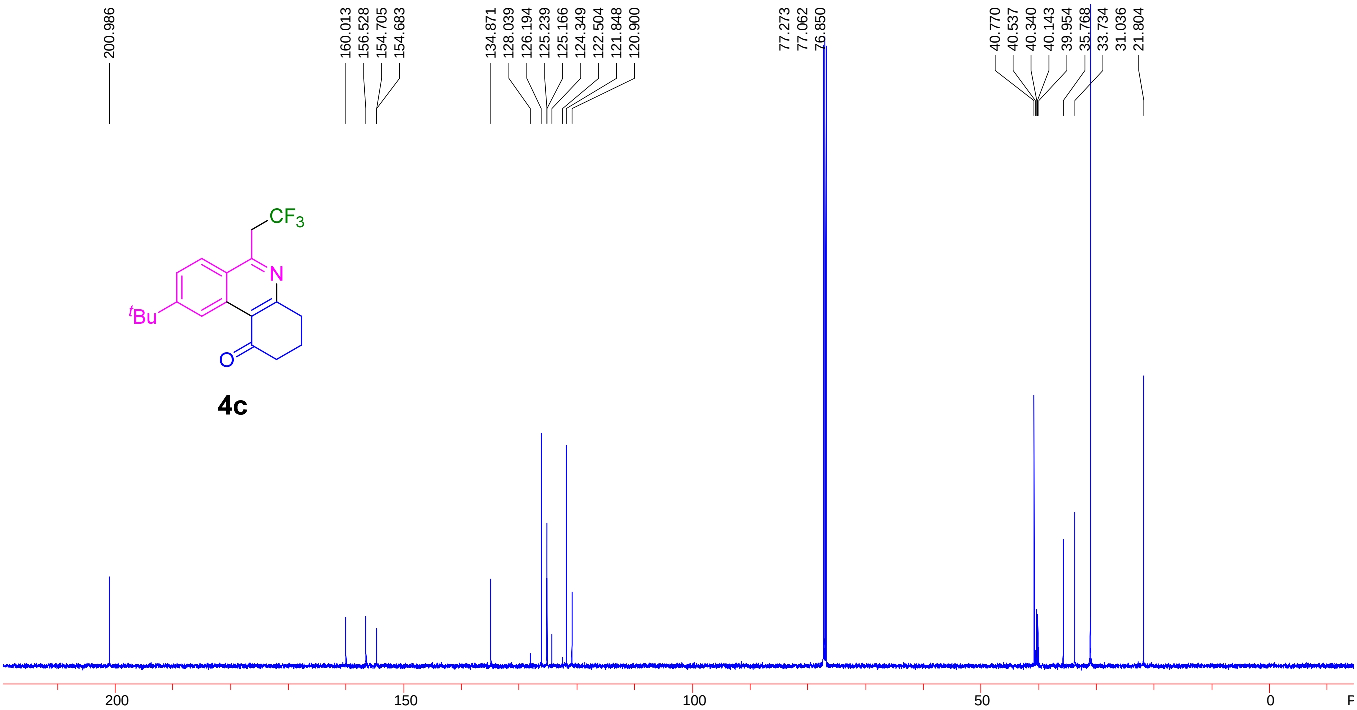
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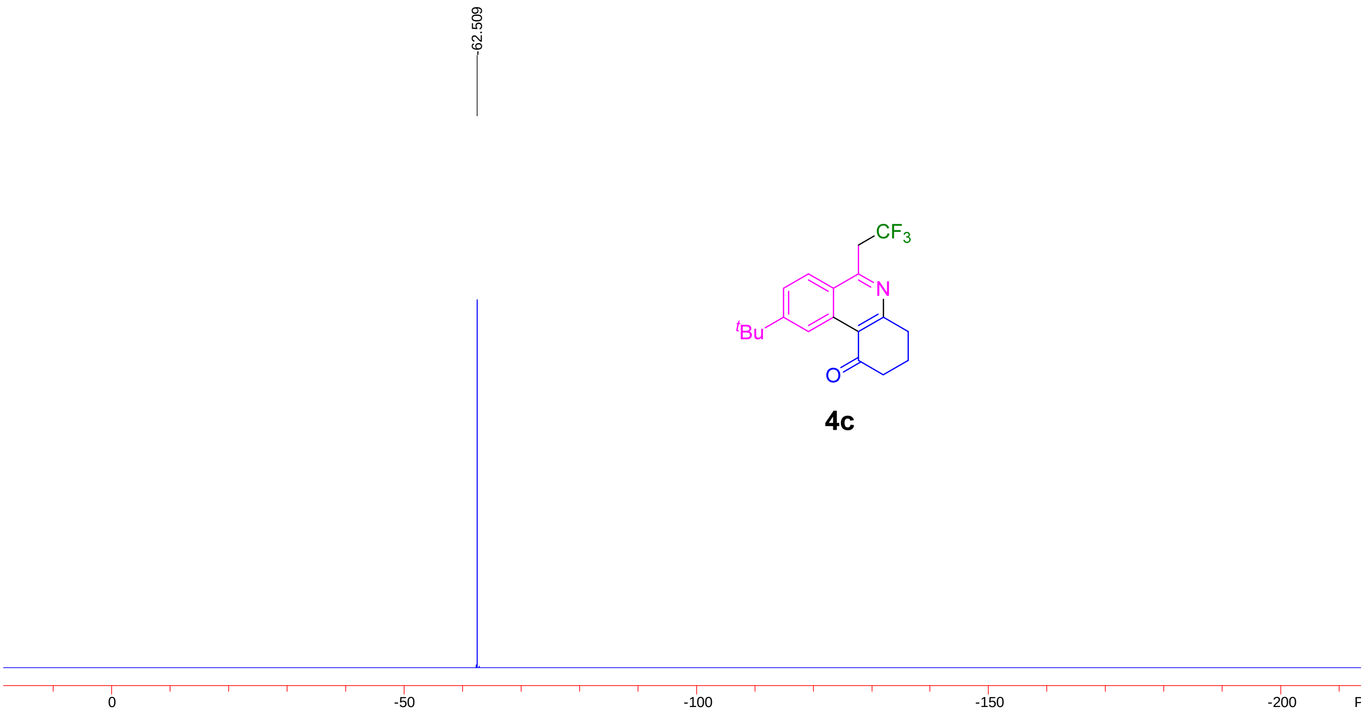

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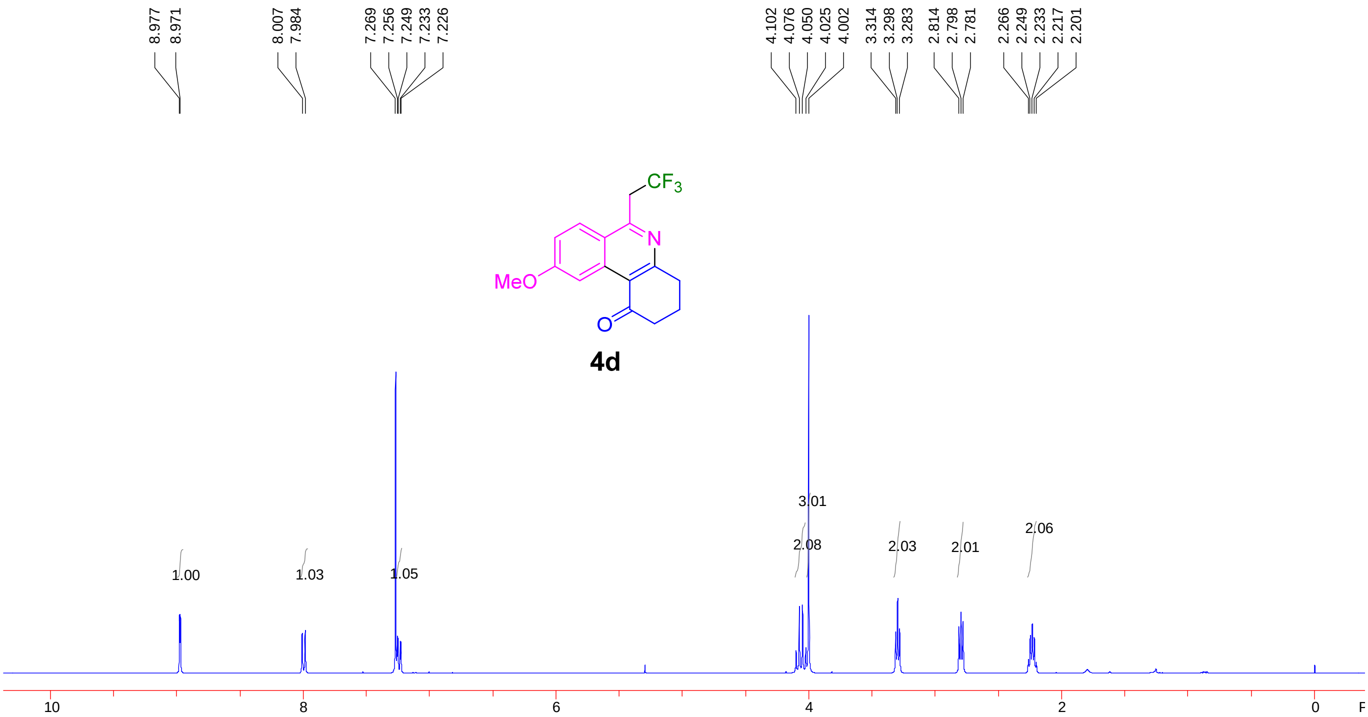
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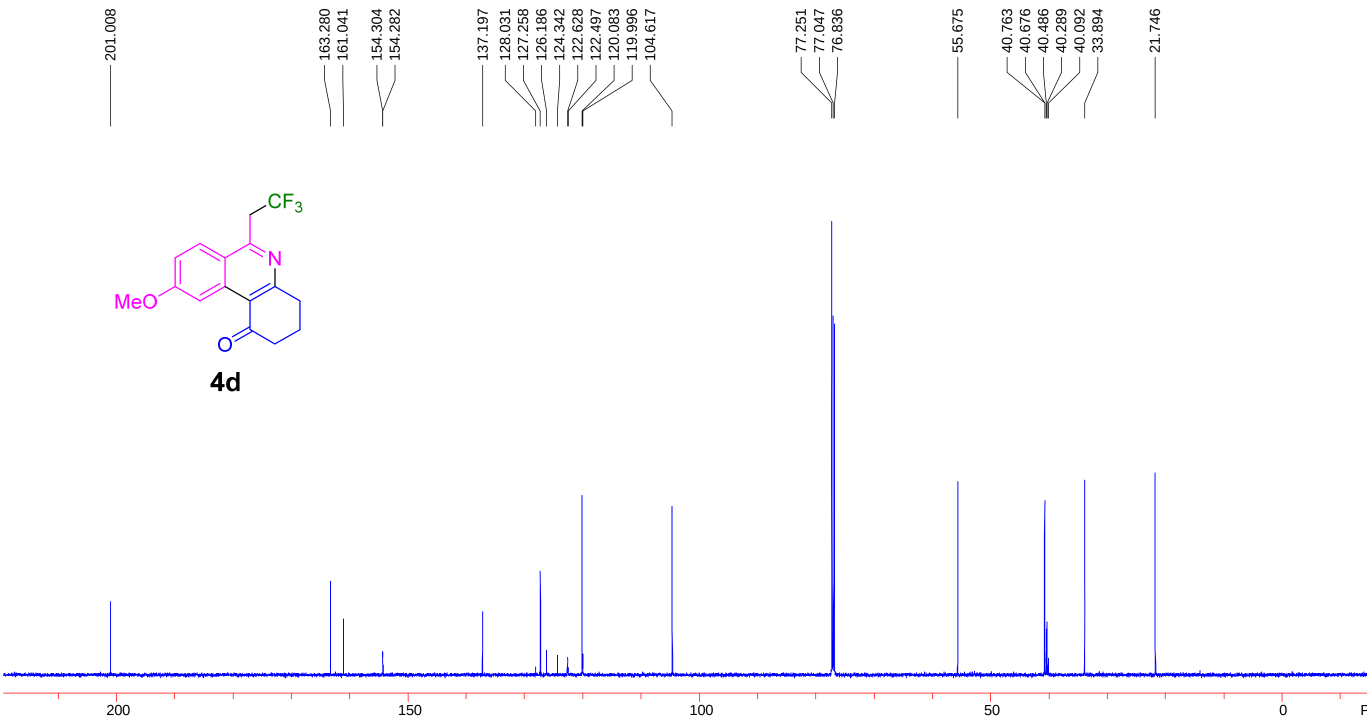
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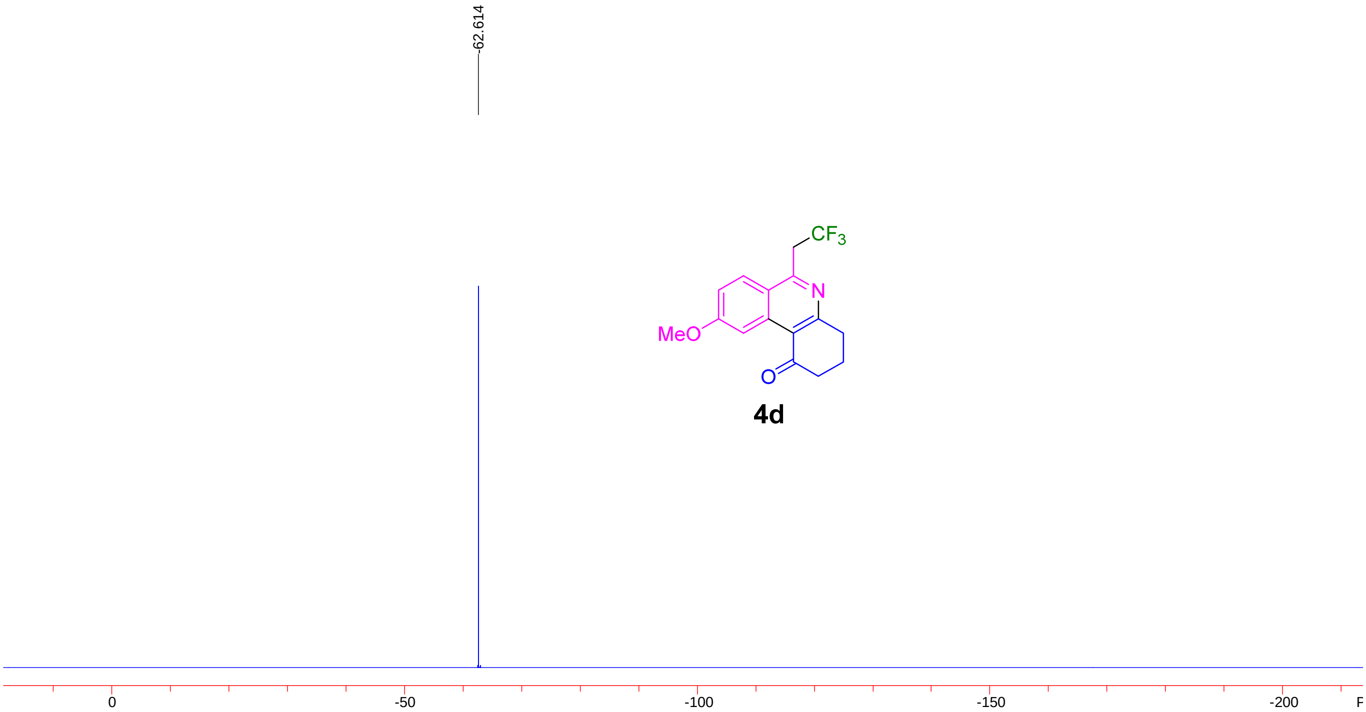

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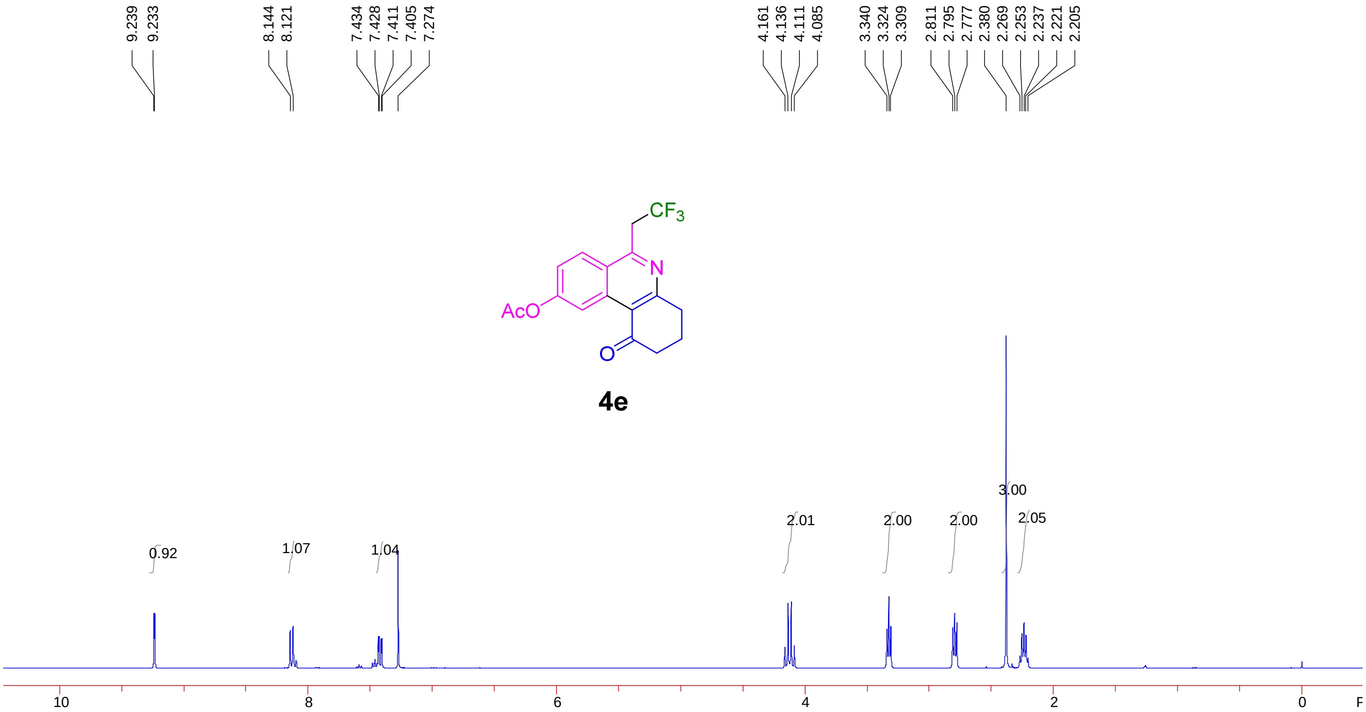
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2.269
2.253
2.237
2.221
2.205
CF3
N
AcO
O
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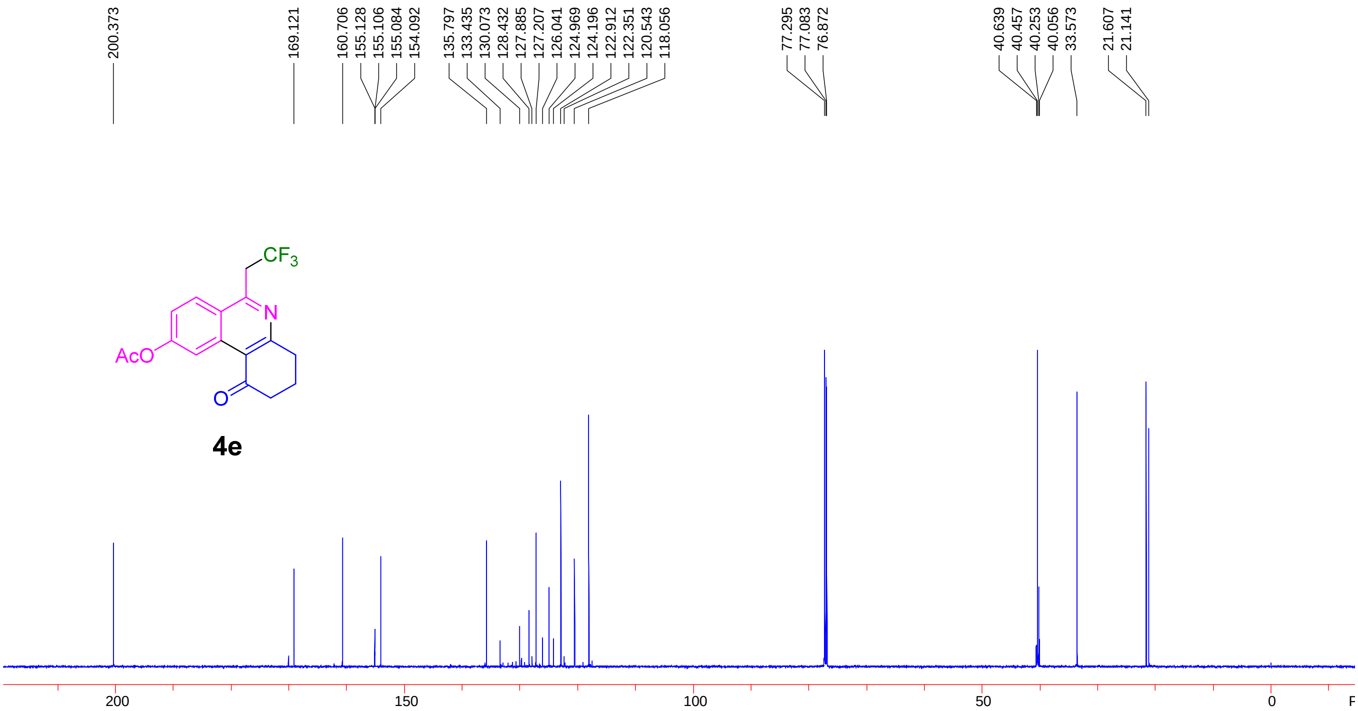
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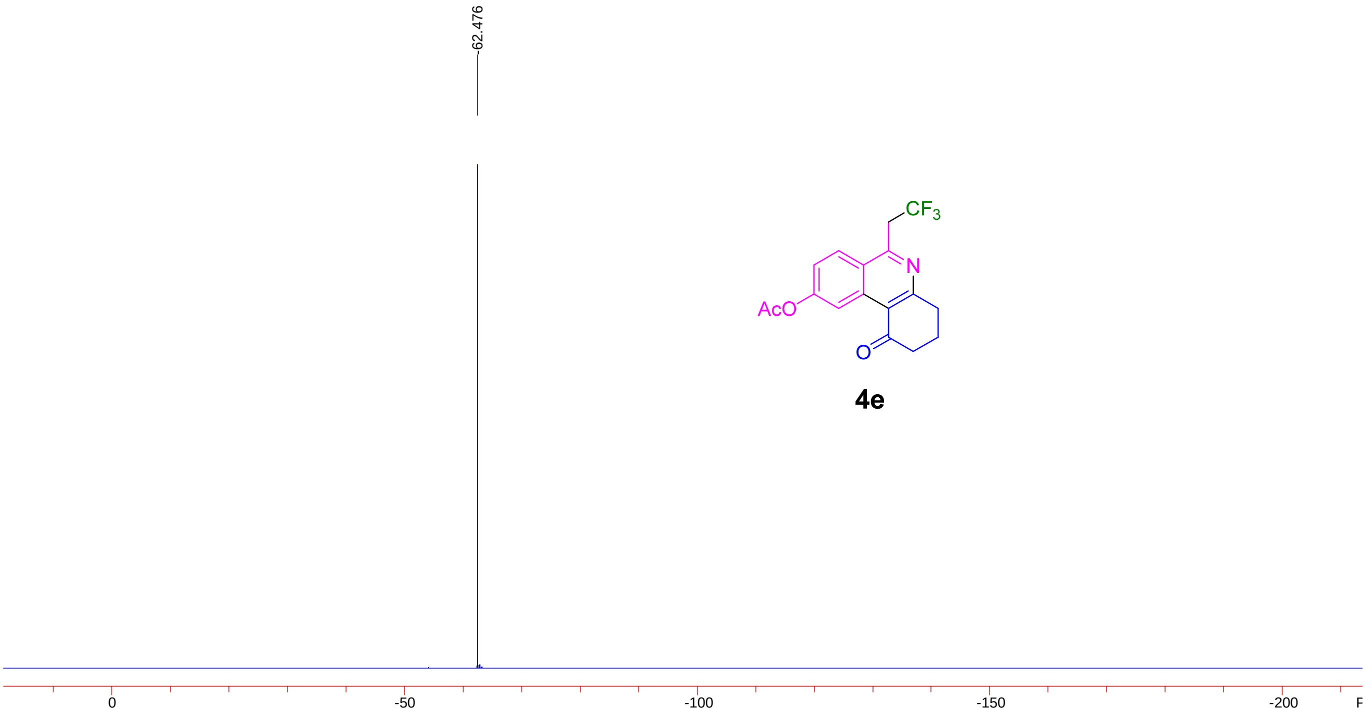

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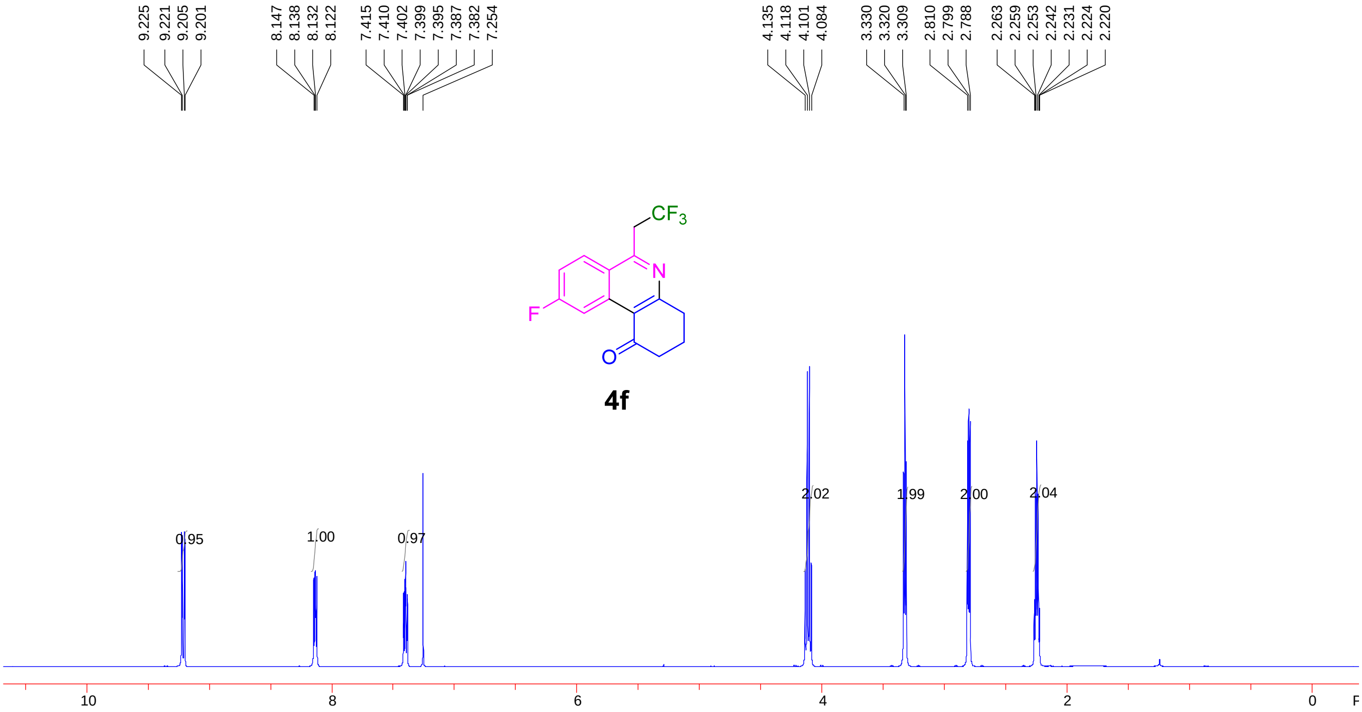

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7.254
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4.084
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3.320
3.309
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2.259
2.253
2.242
2.231
2.224
2.220
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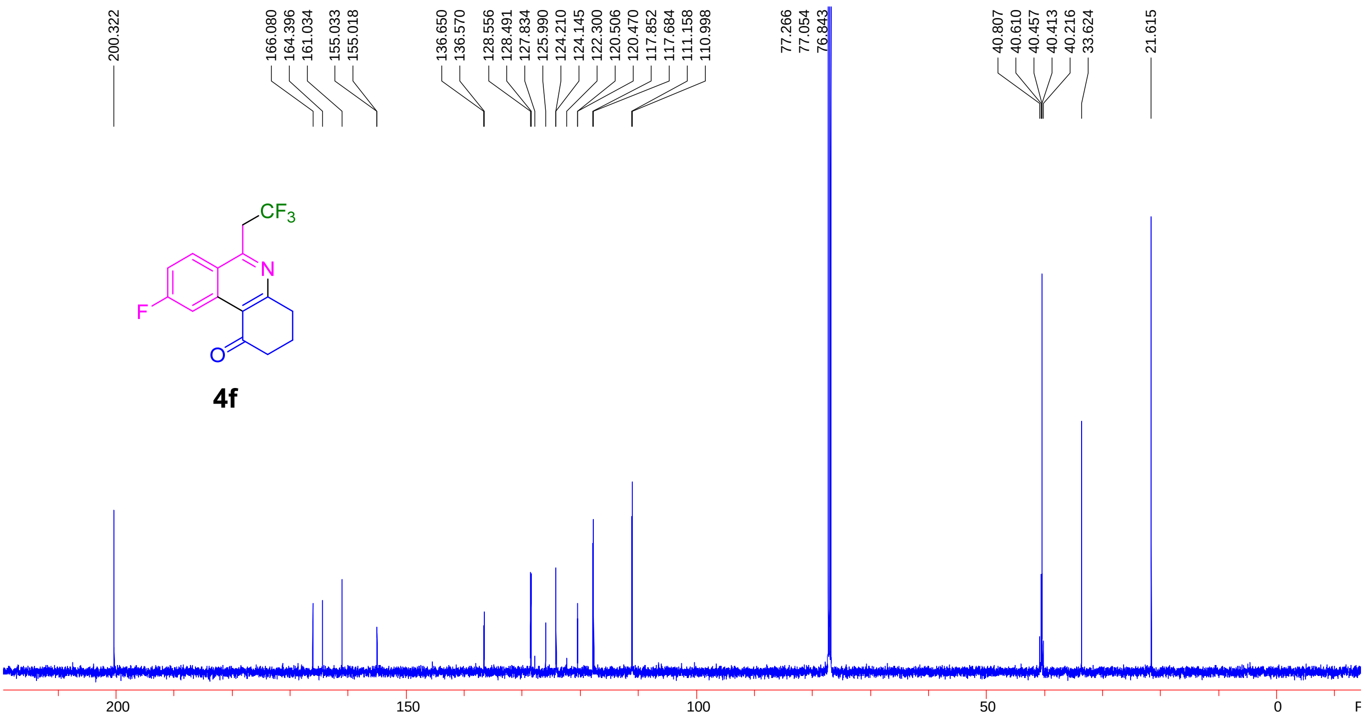

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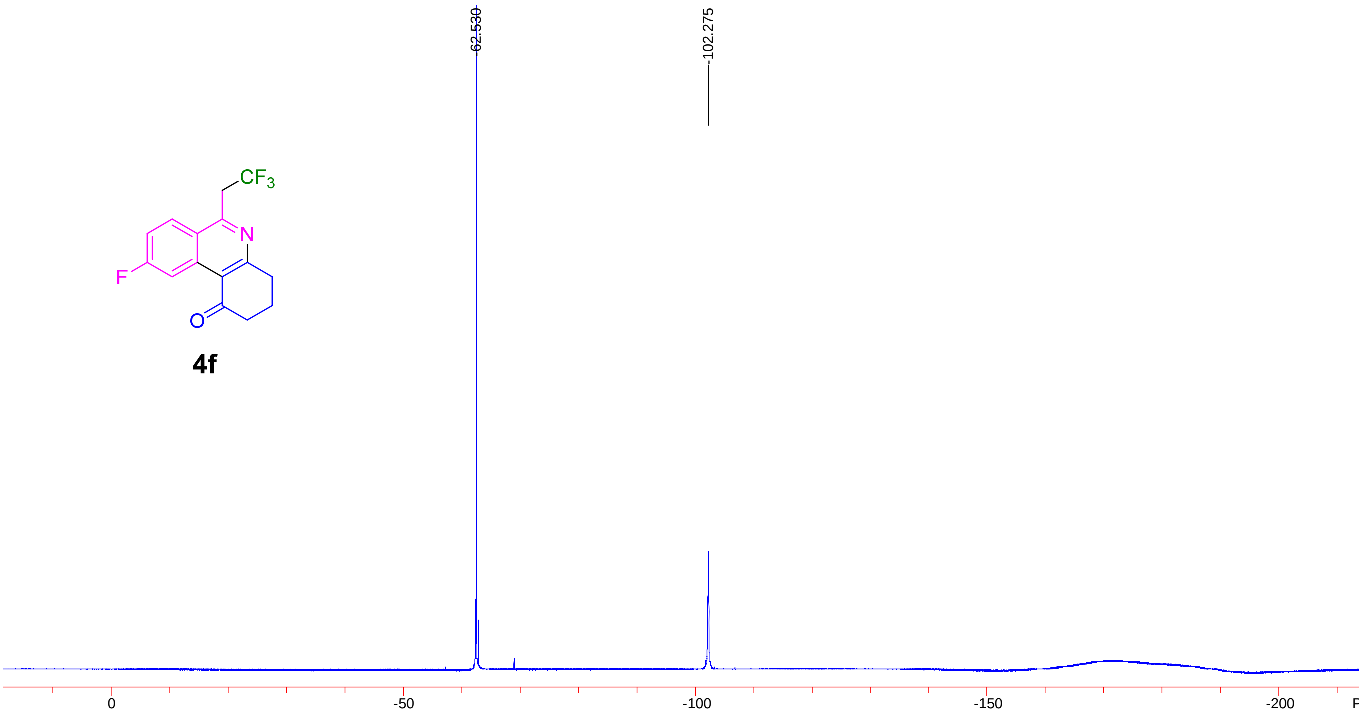

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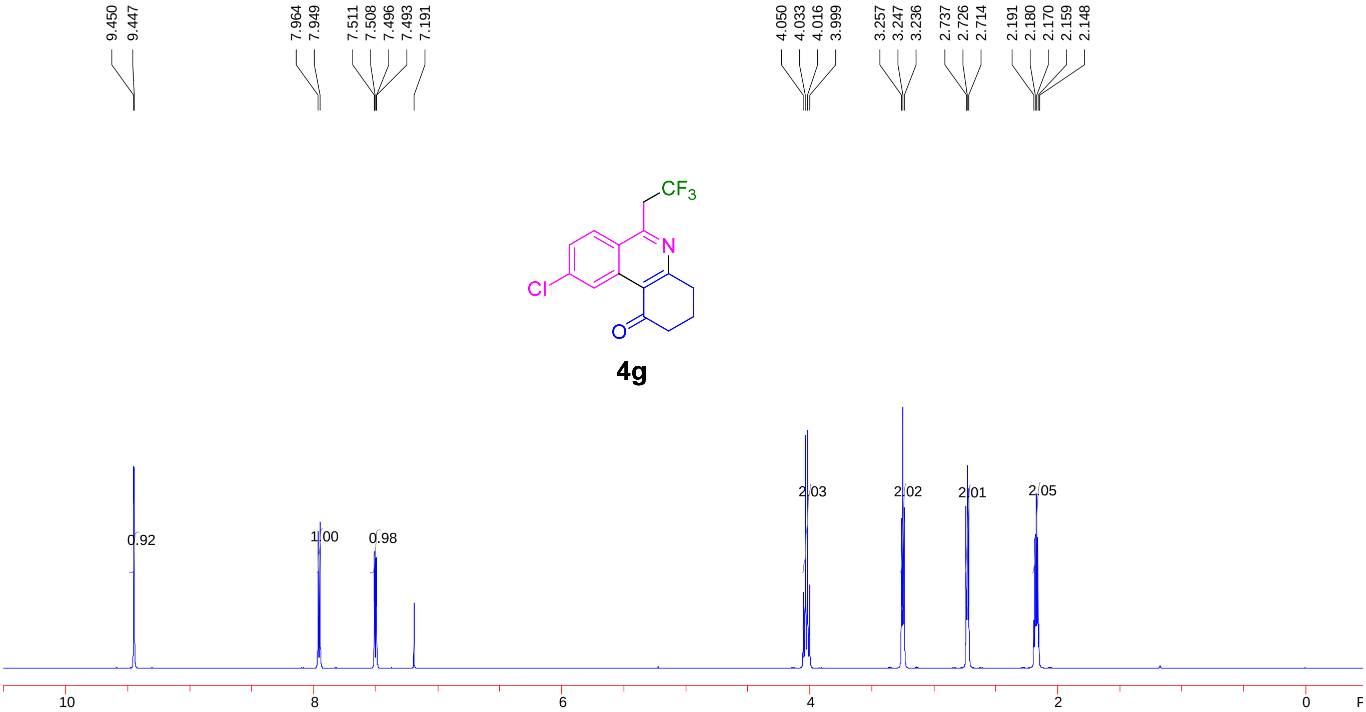
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3.247
3.236
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2.191
2.180
2.170
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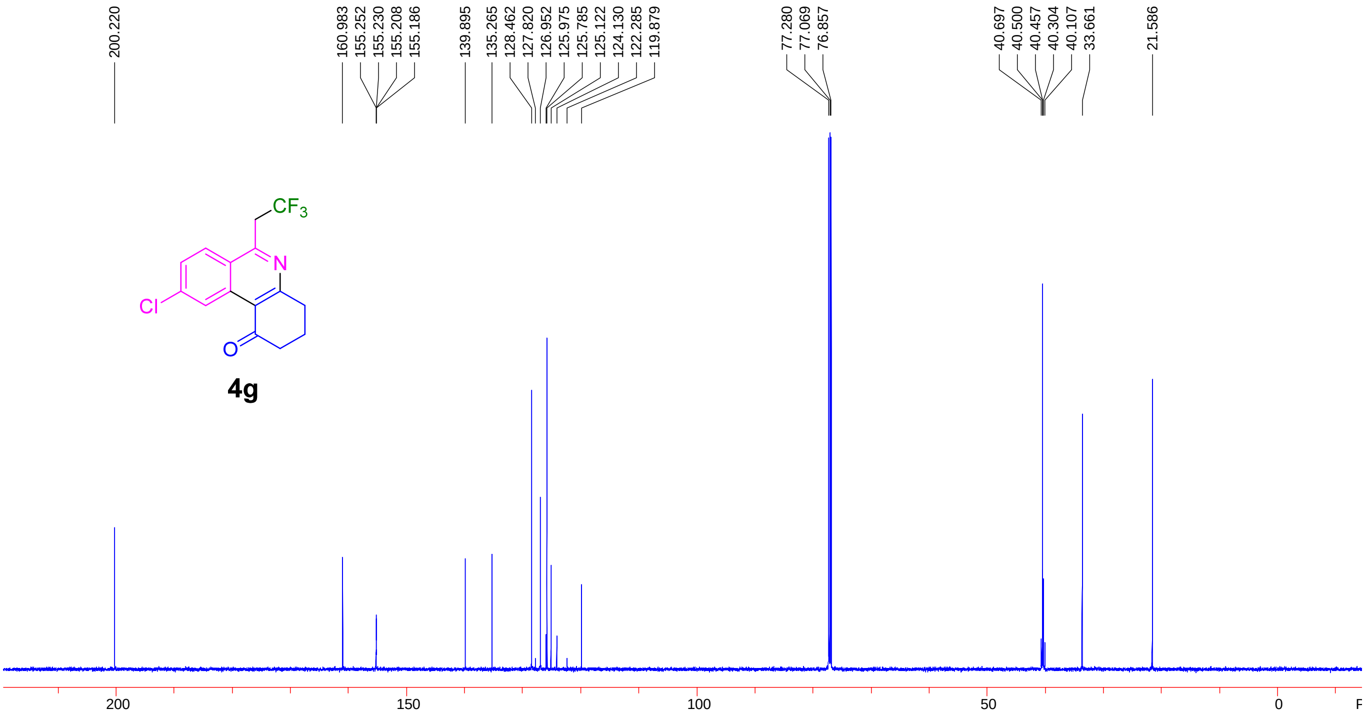
4g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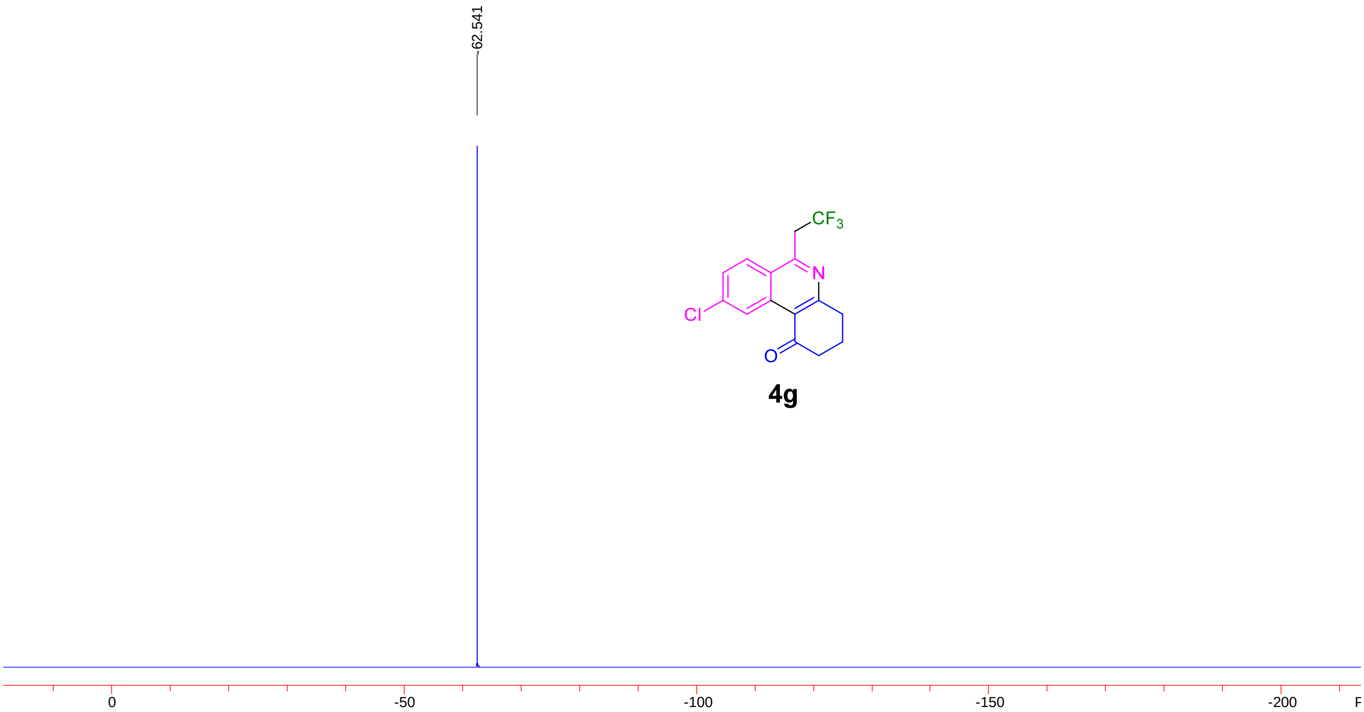
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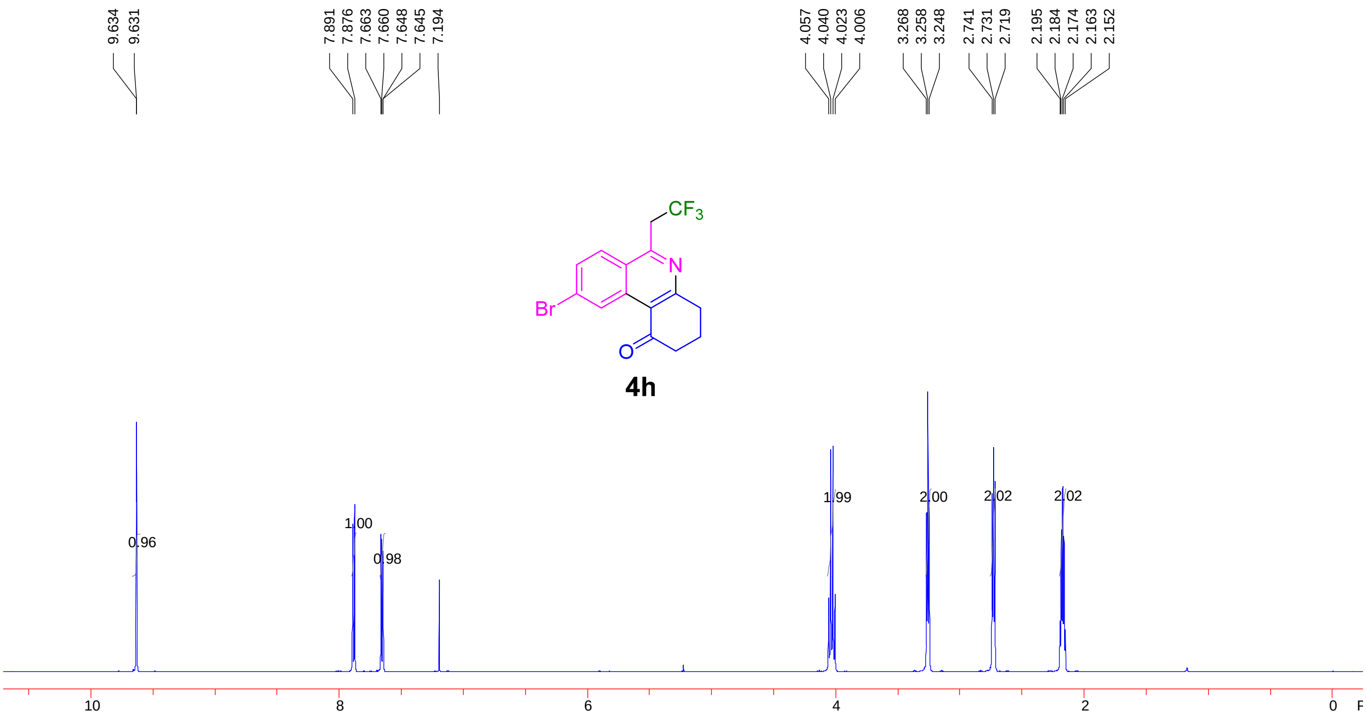
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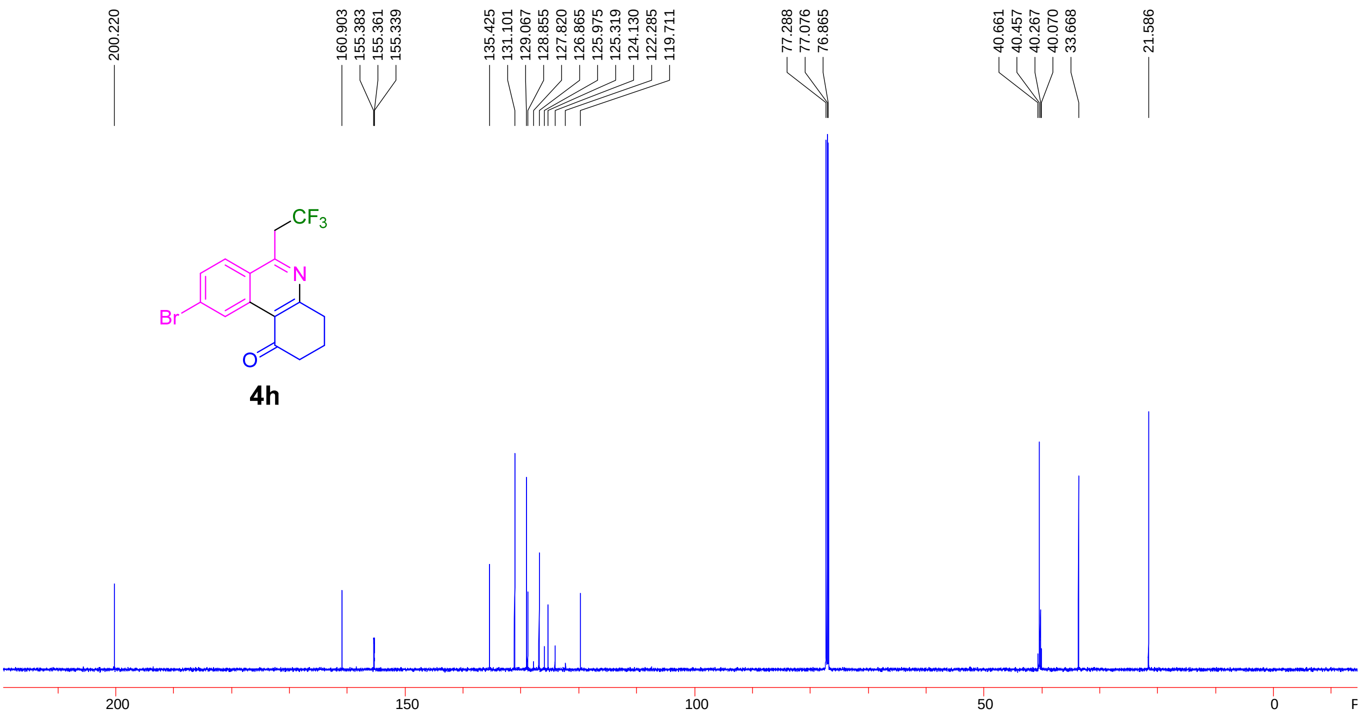
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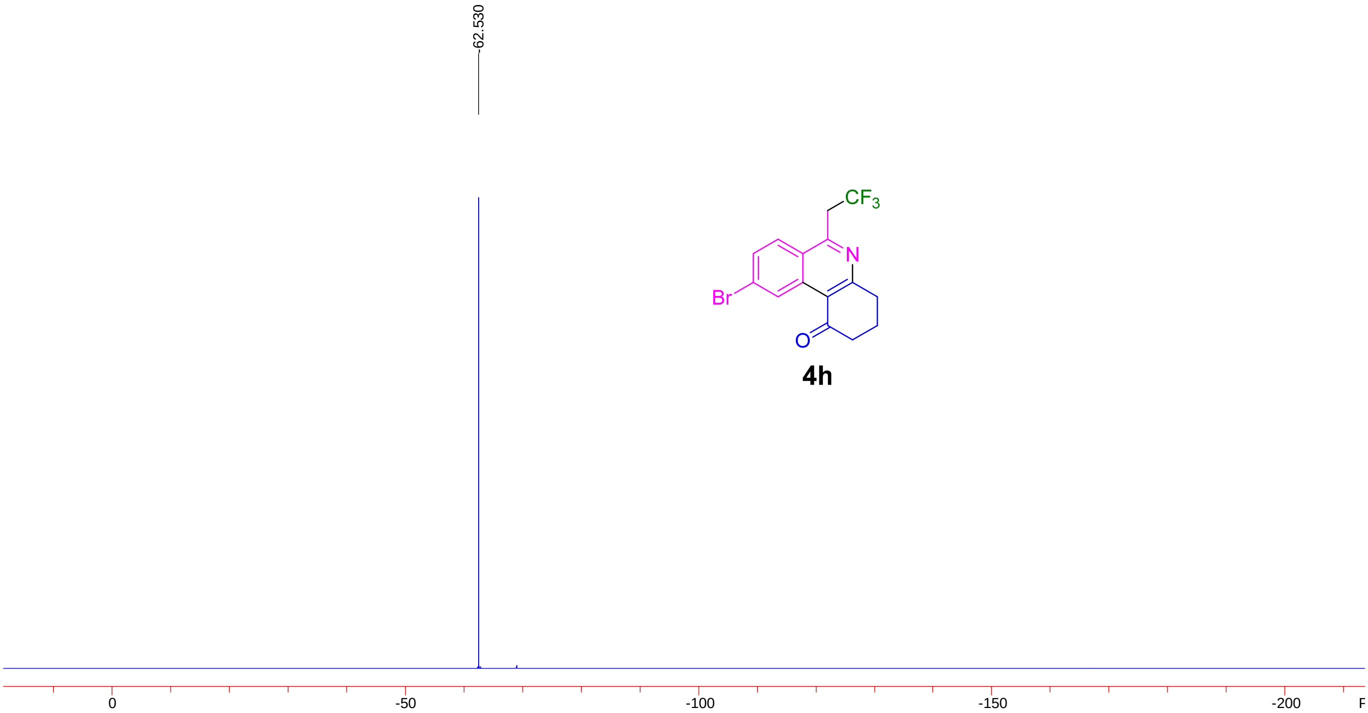
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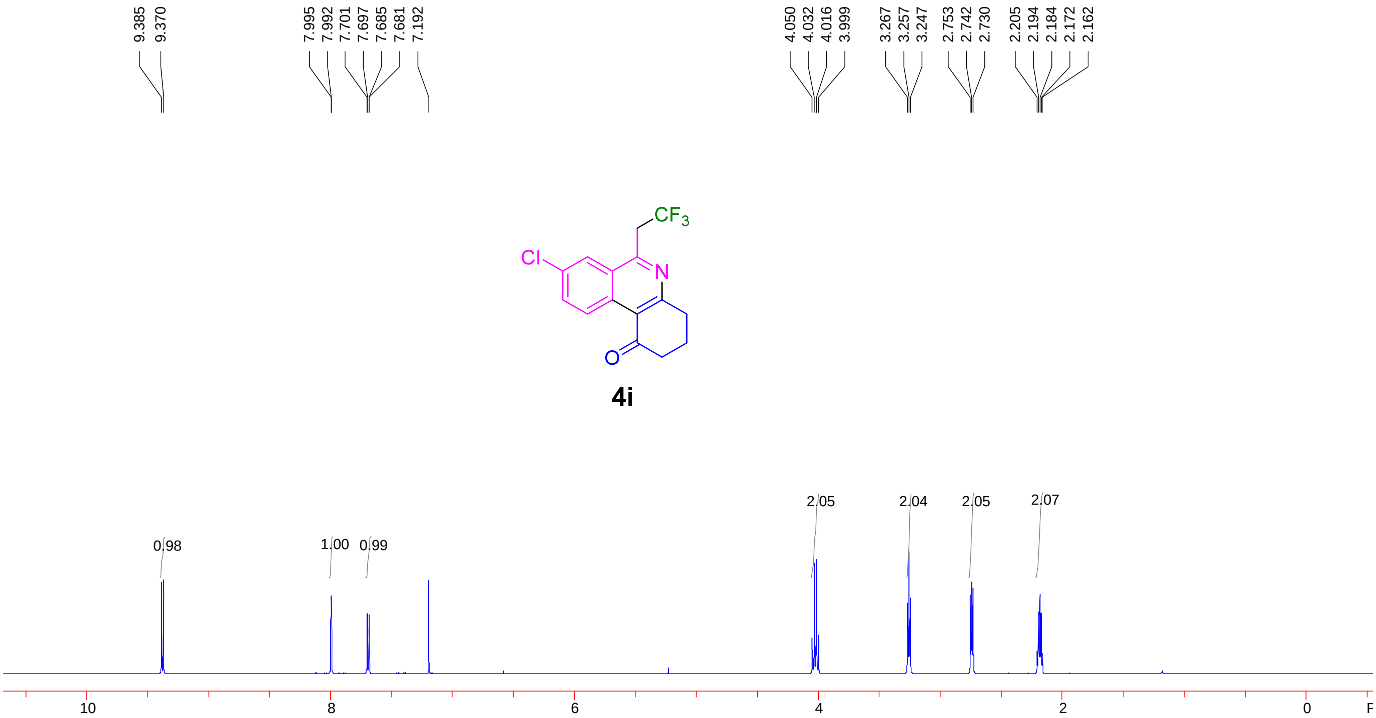
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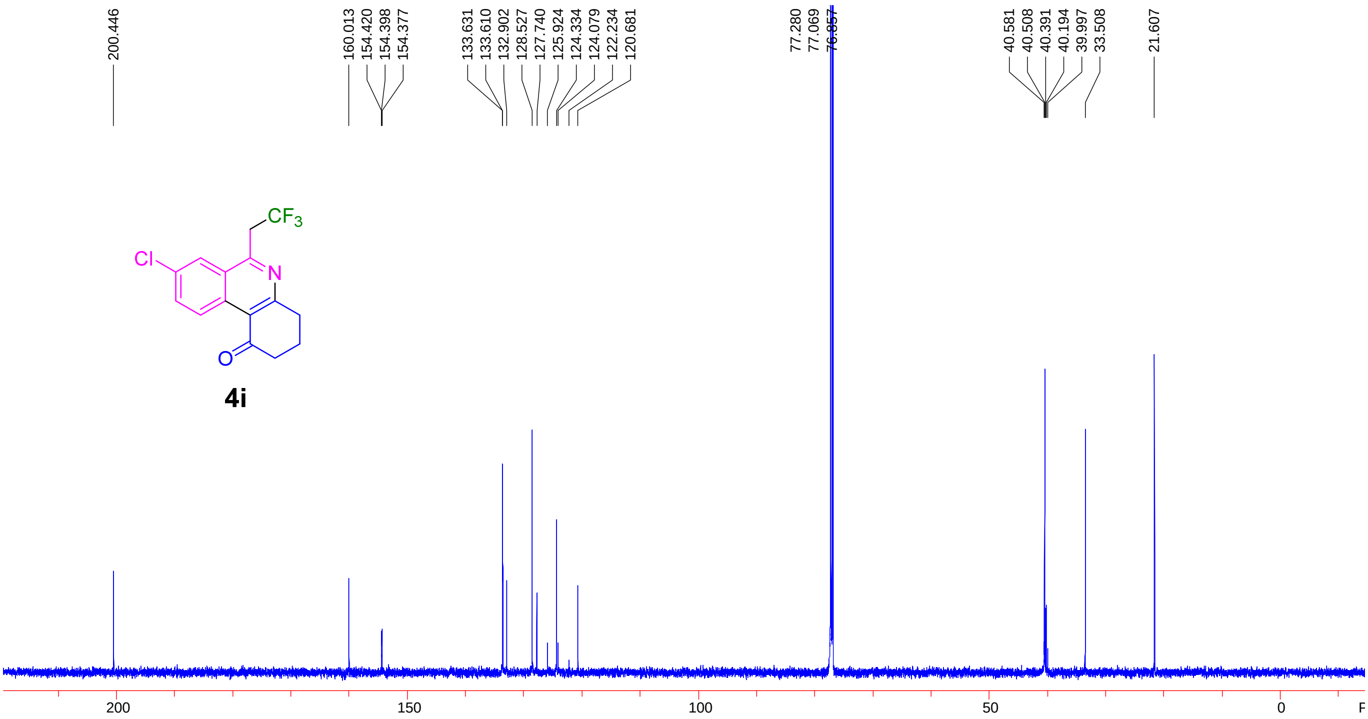
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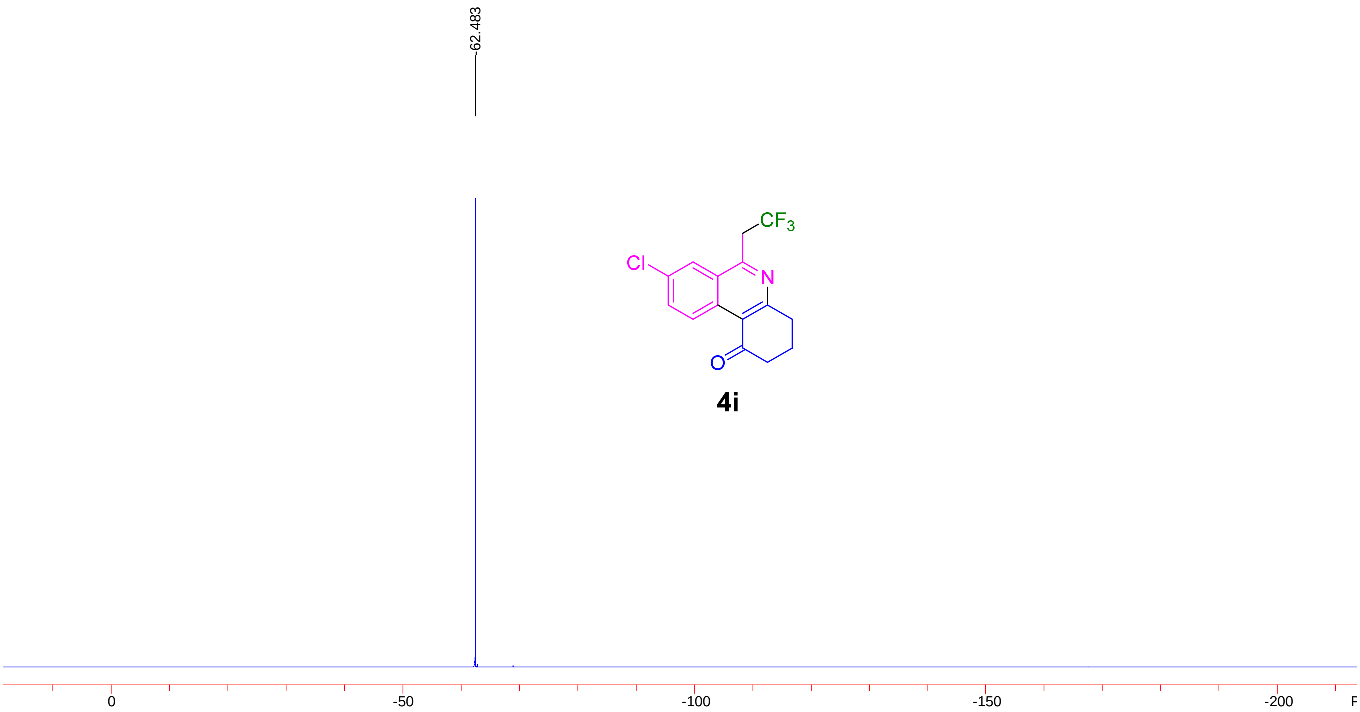

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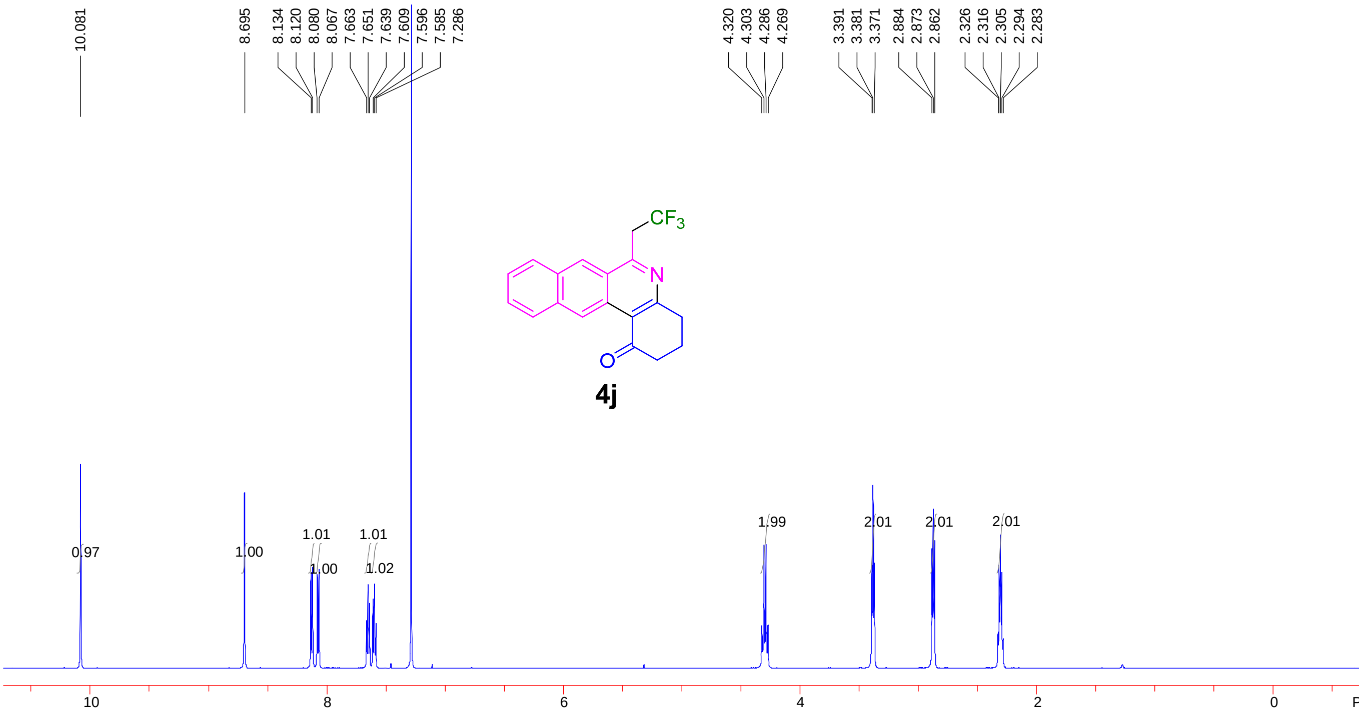
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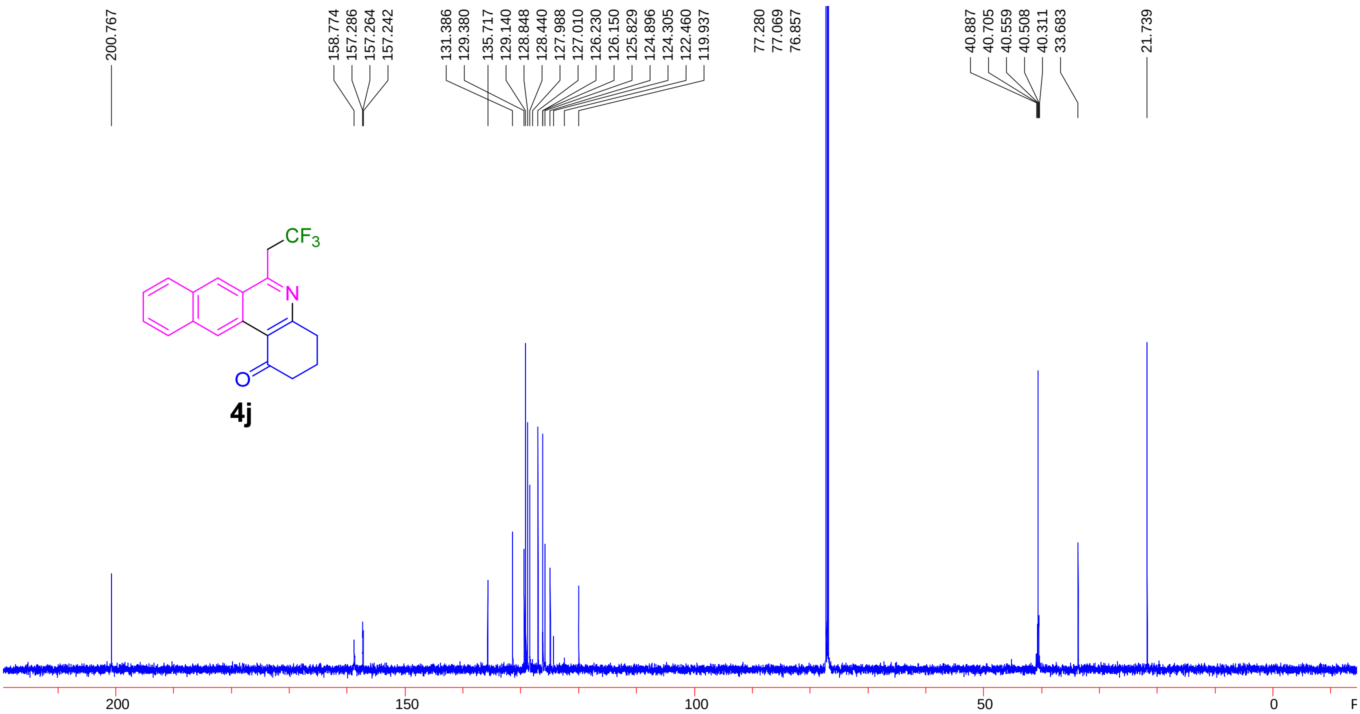
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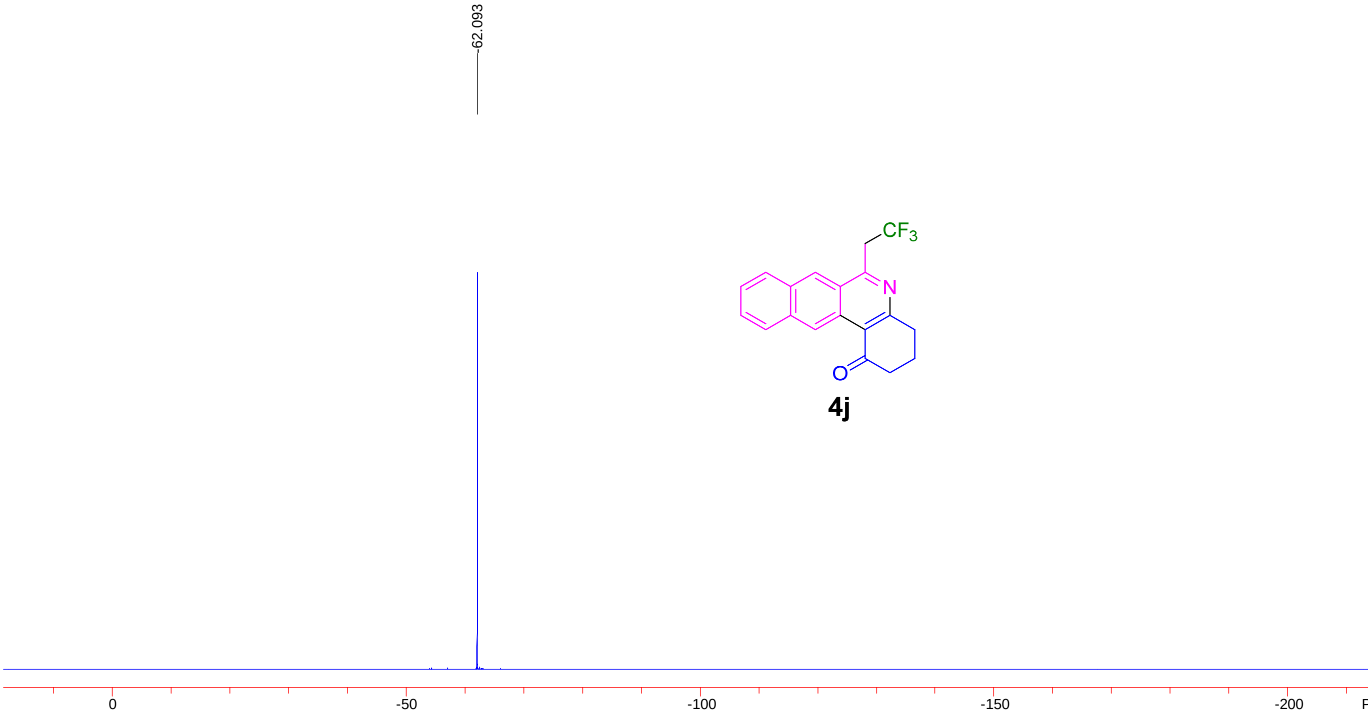

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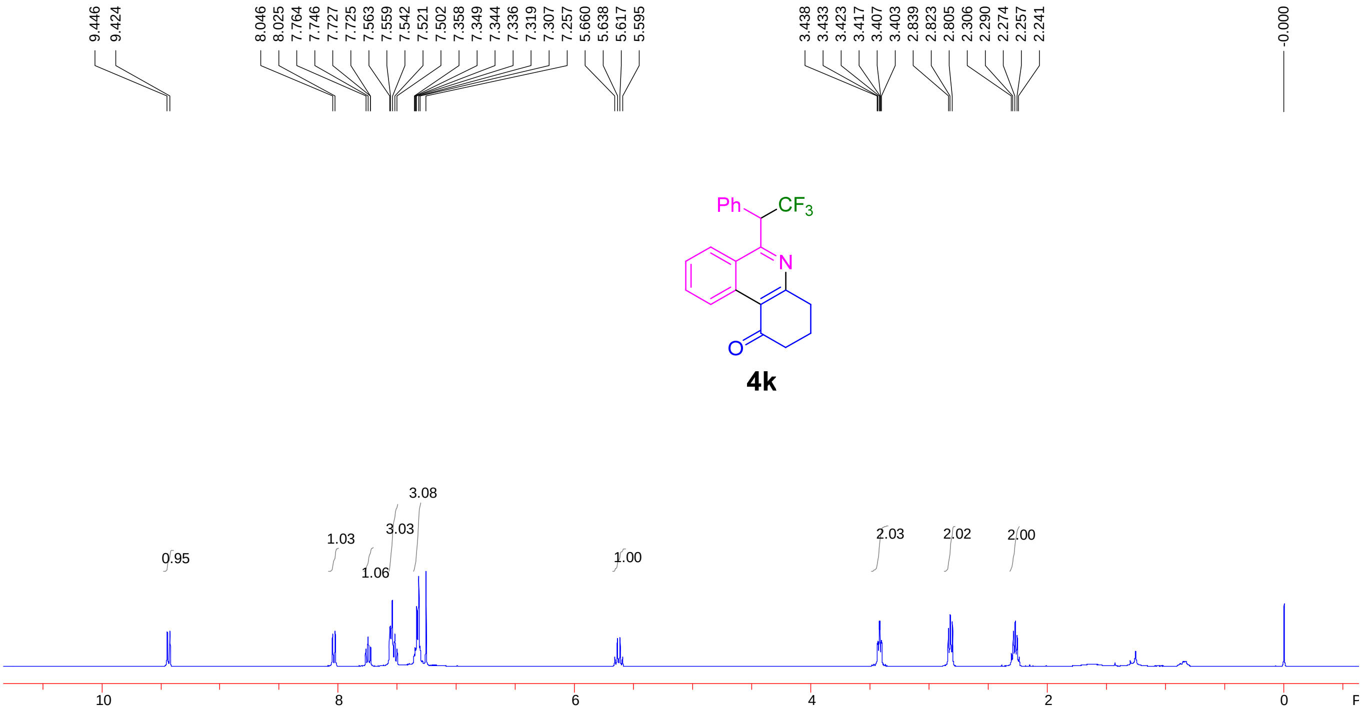
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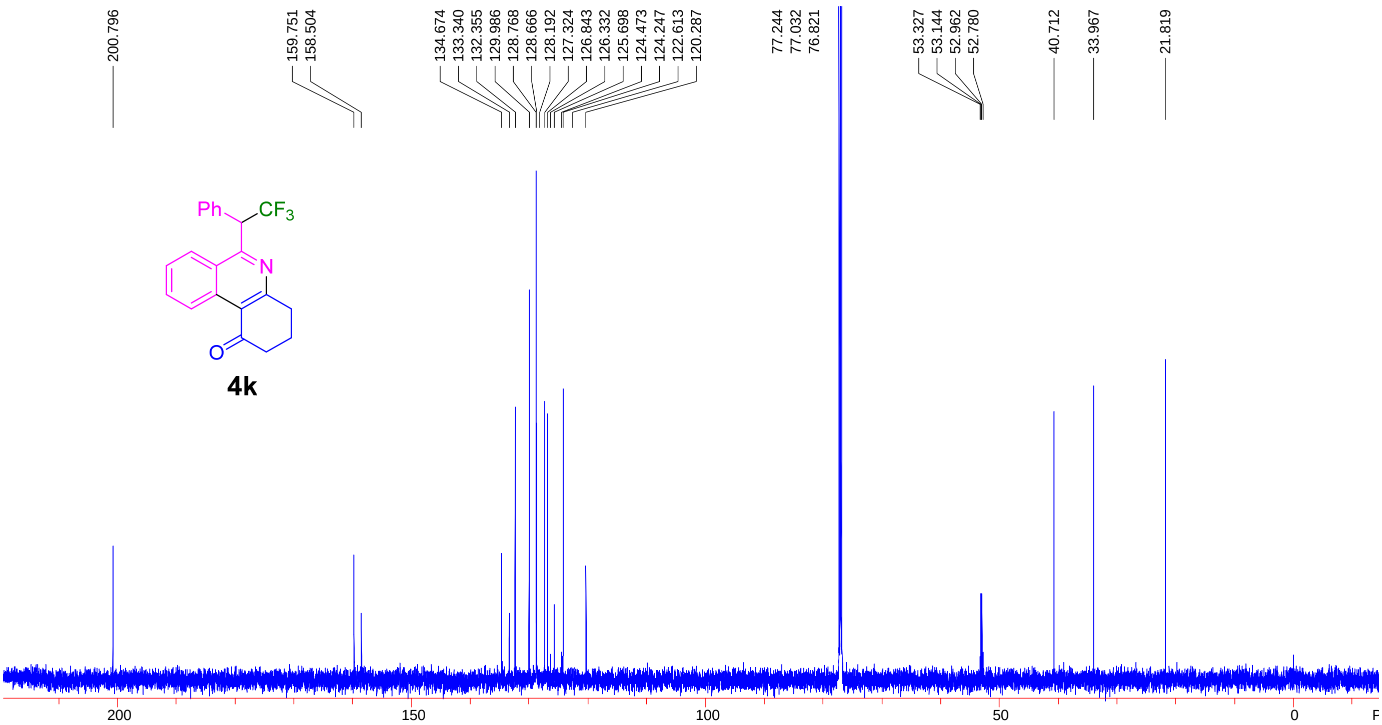
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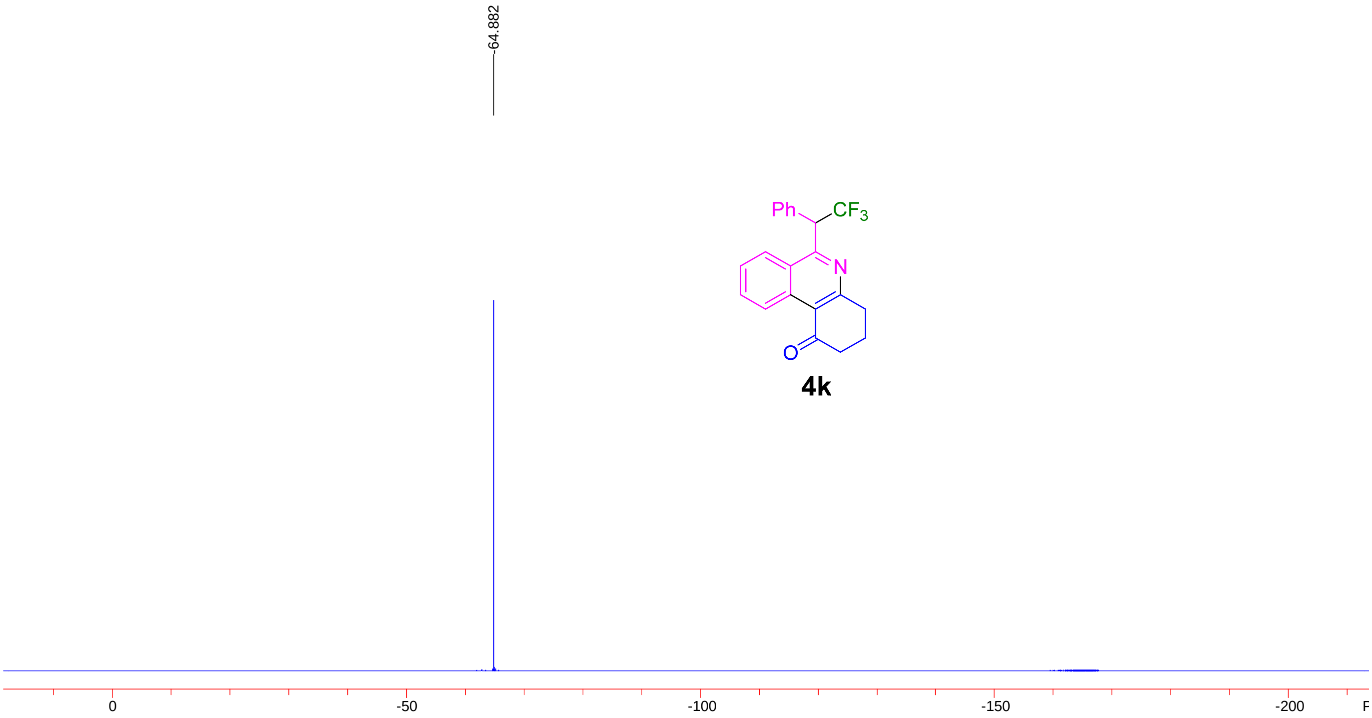
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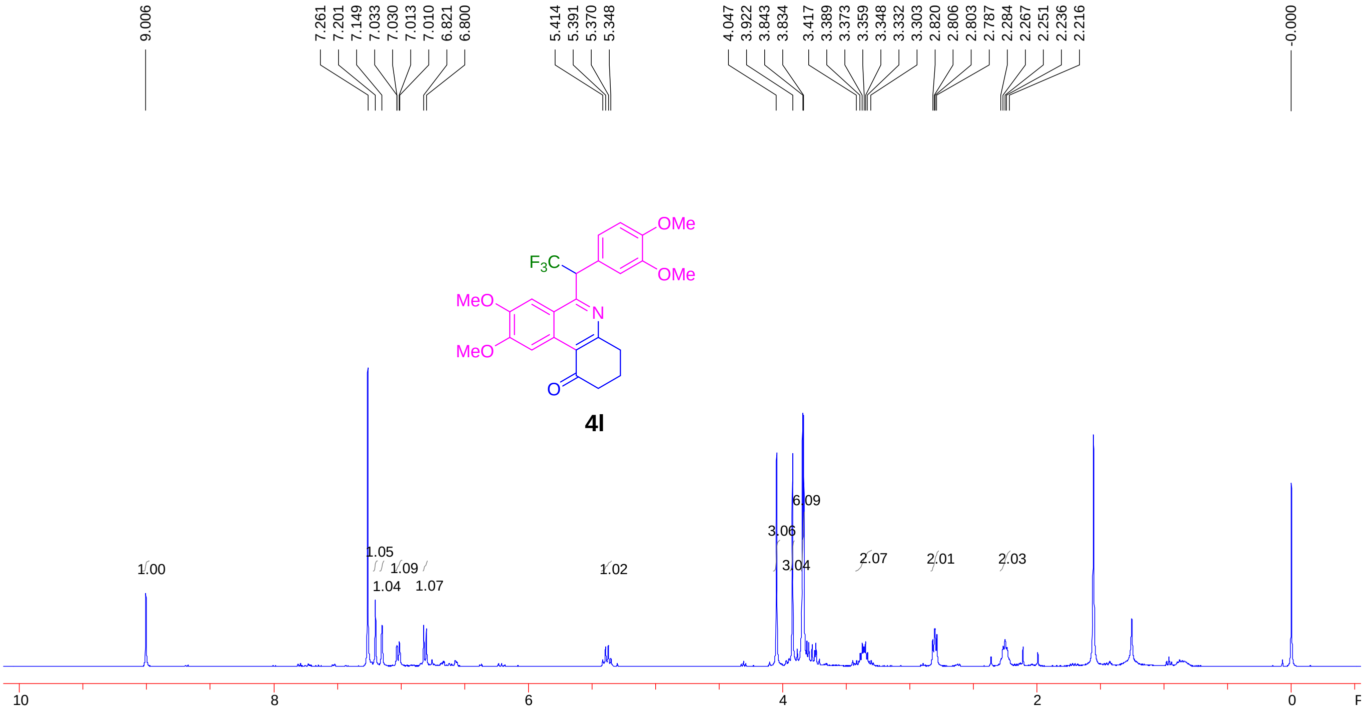
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F_3C
OMe
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O
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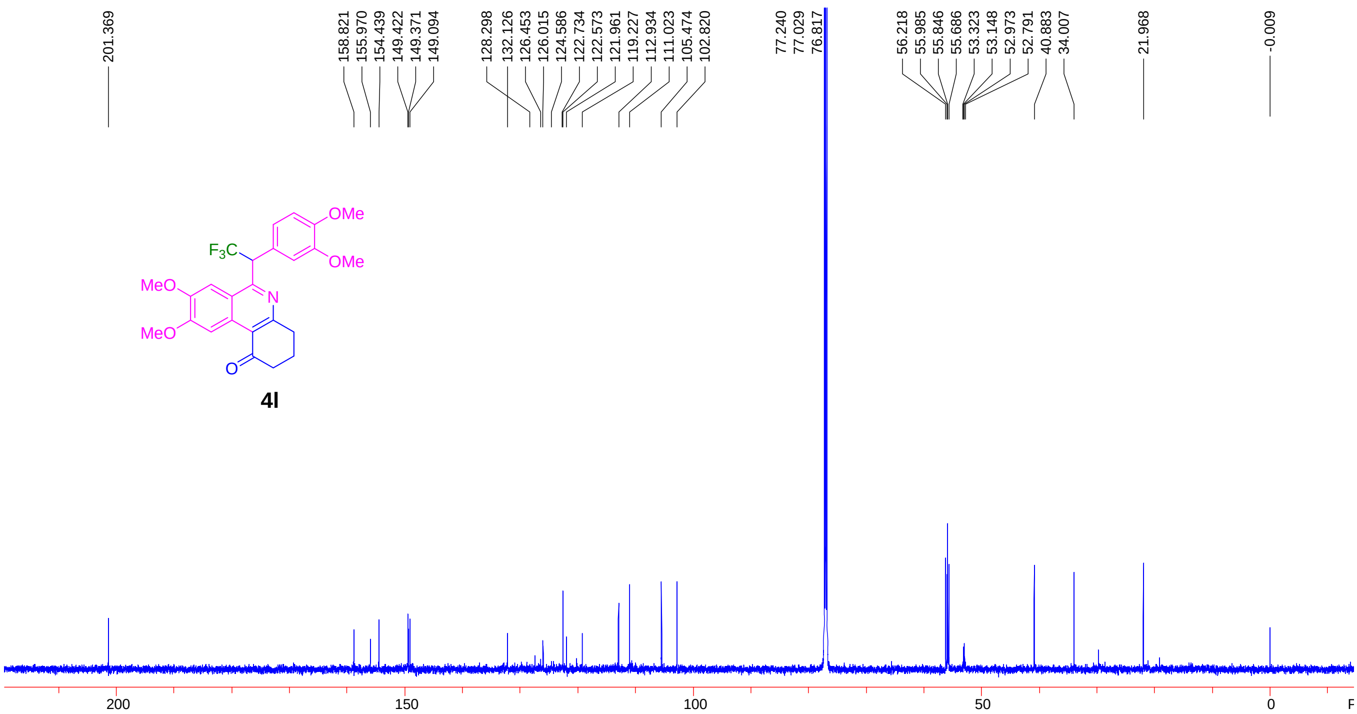
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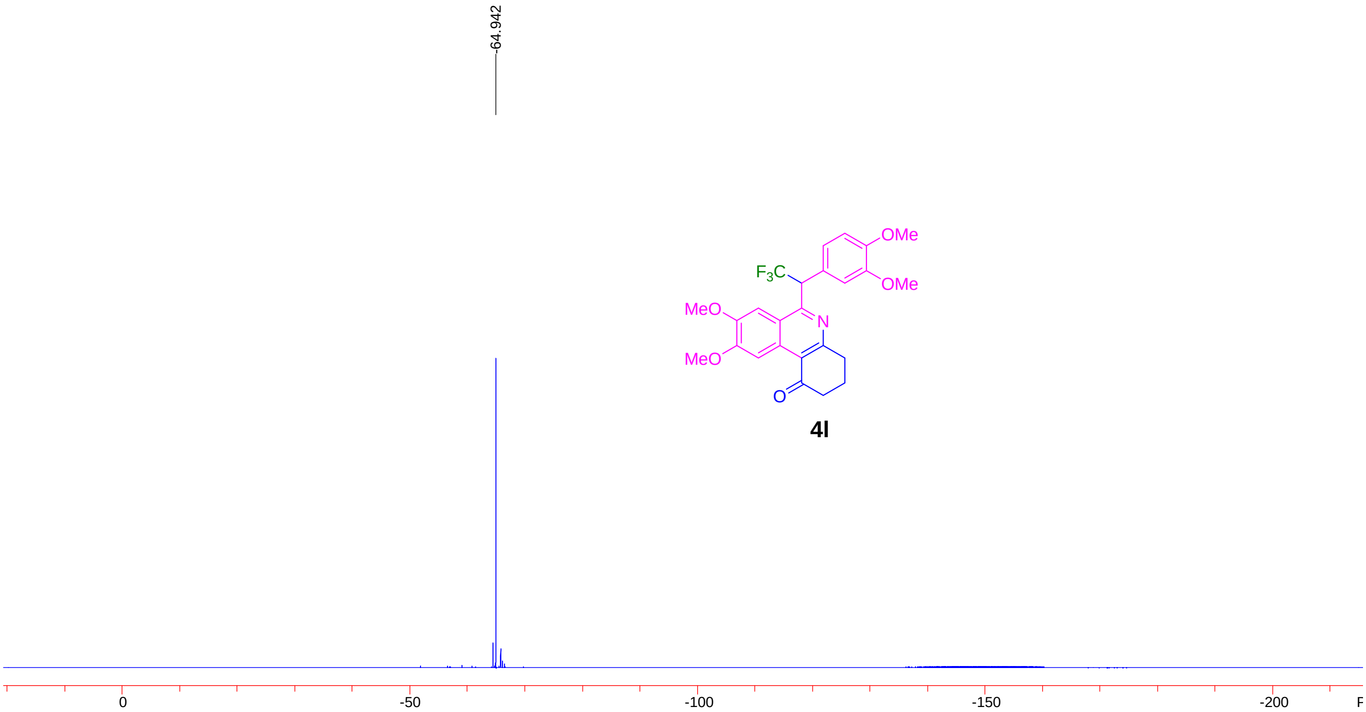

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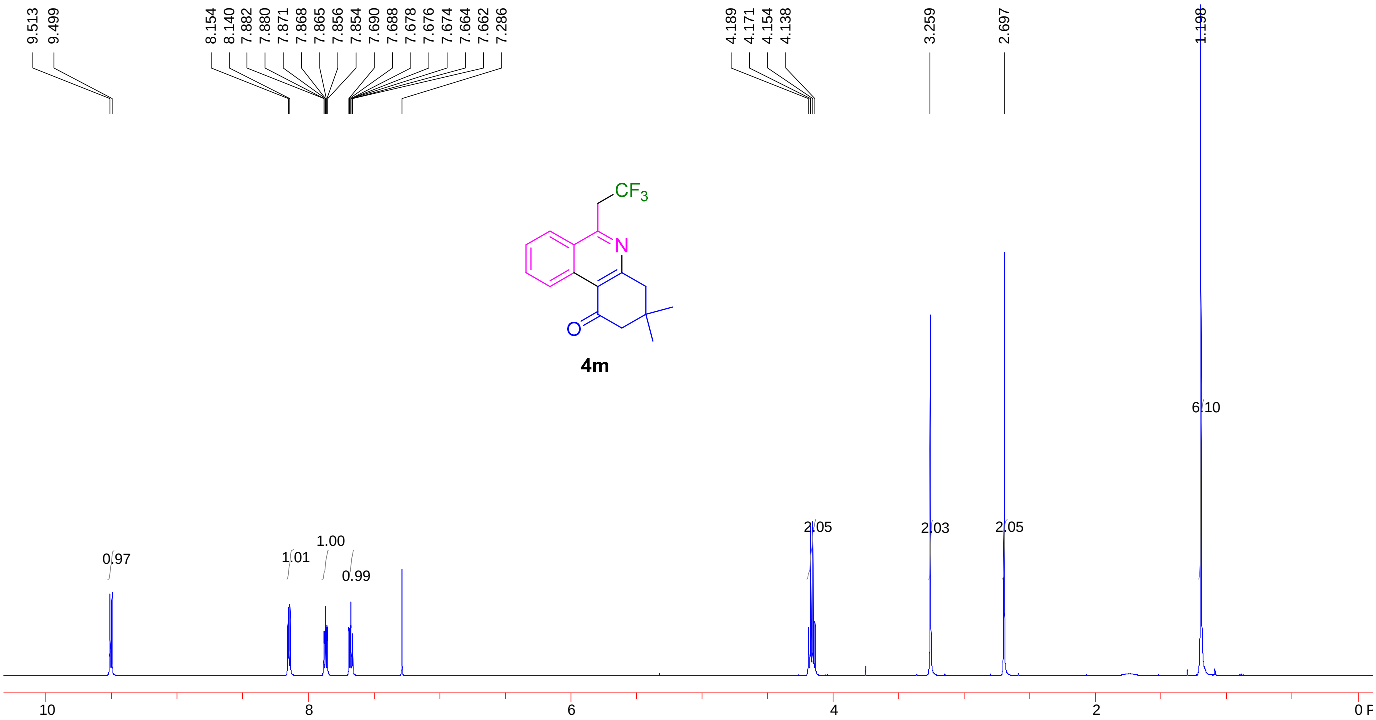
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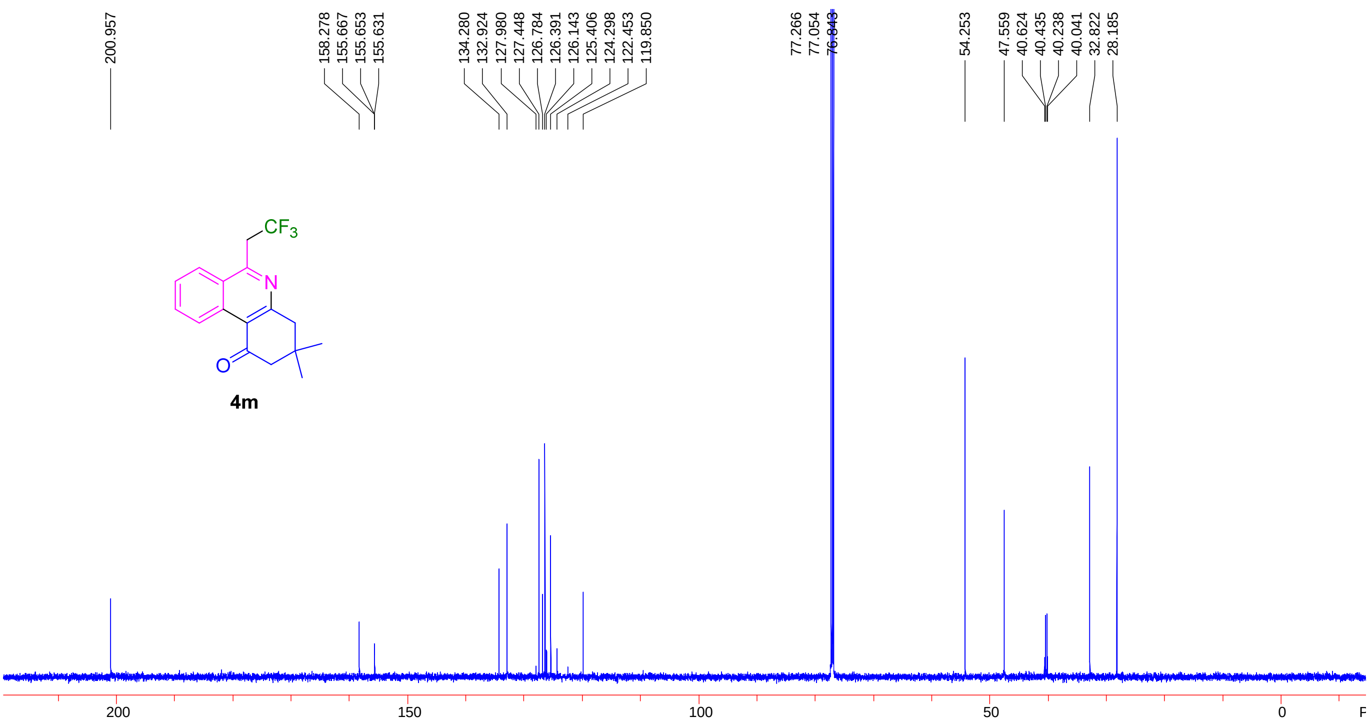
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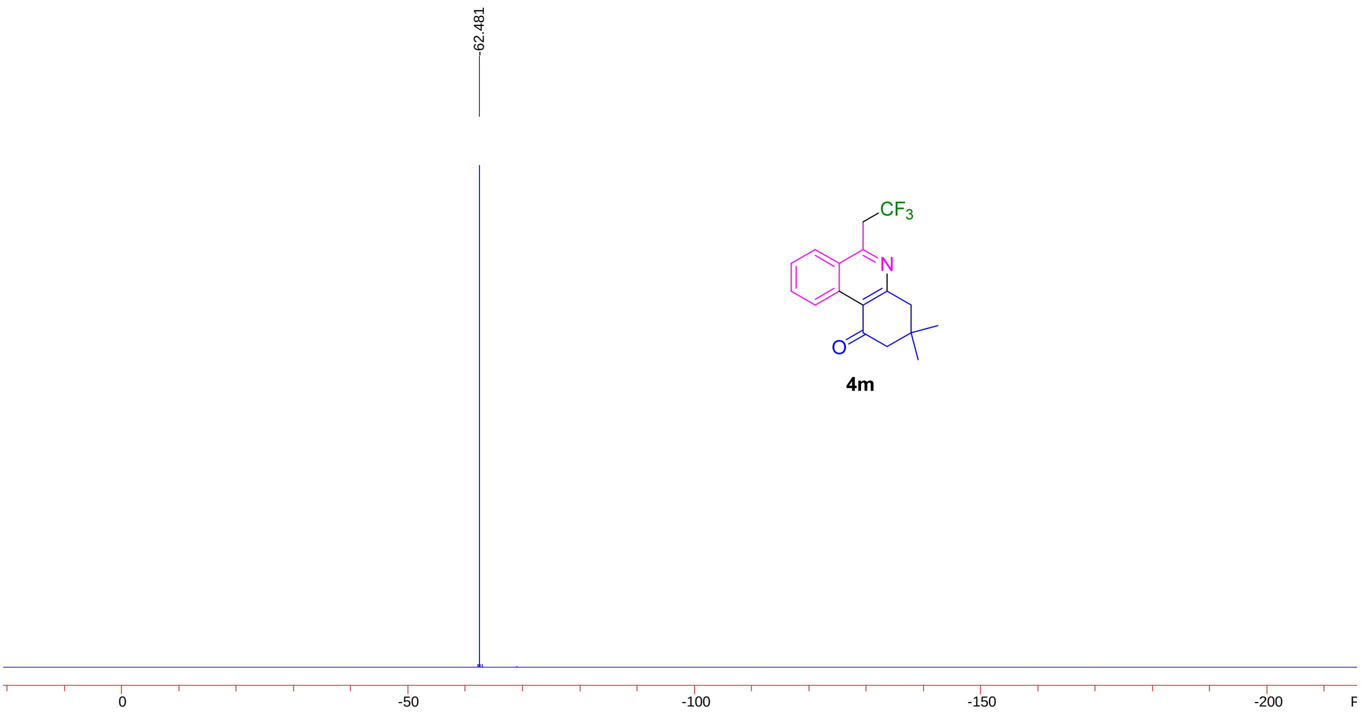
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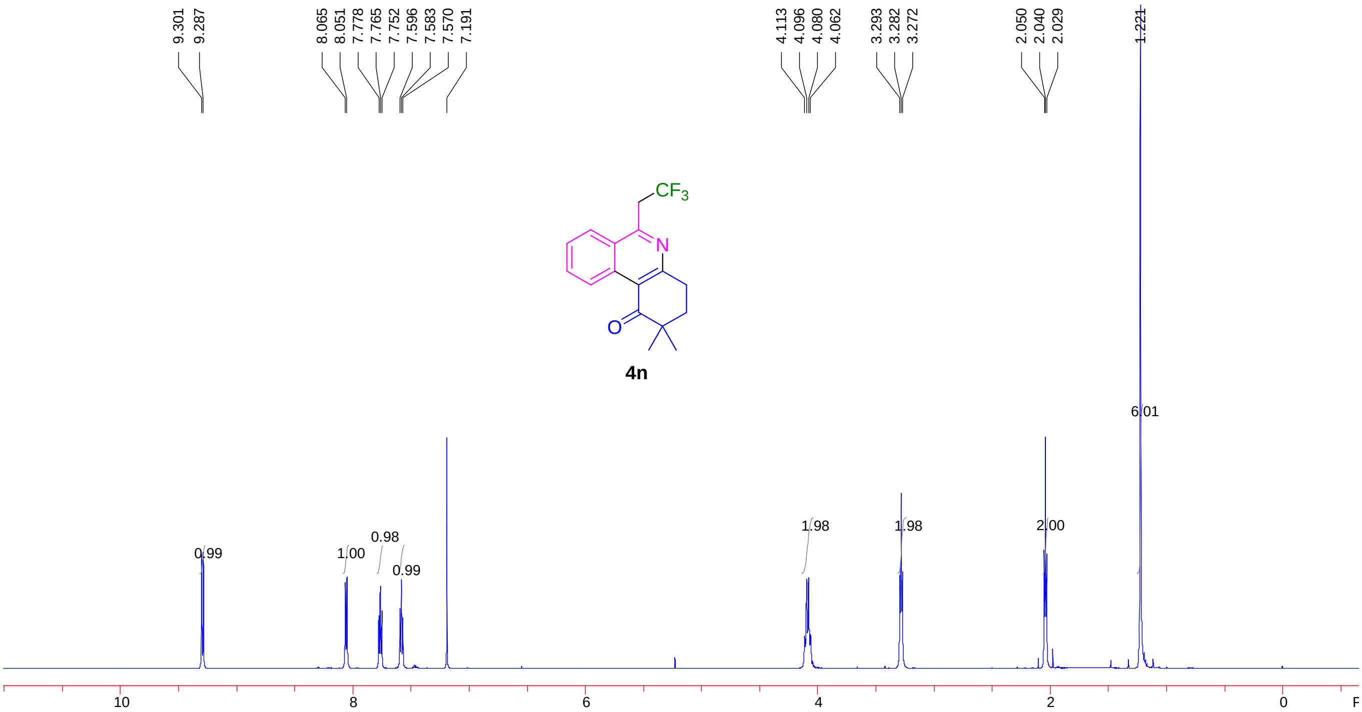

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7.596
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4.096
4.080
4.062
3.293
3.282
3.272
2.050
2.040
2.029
1.221
CF3
N
O
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1.98
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1.00
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0.99
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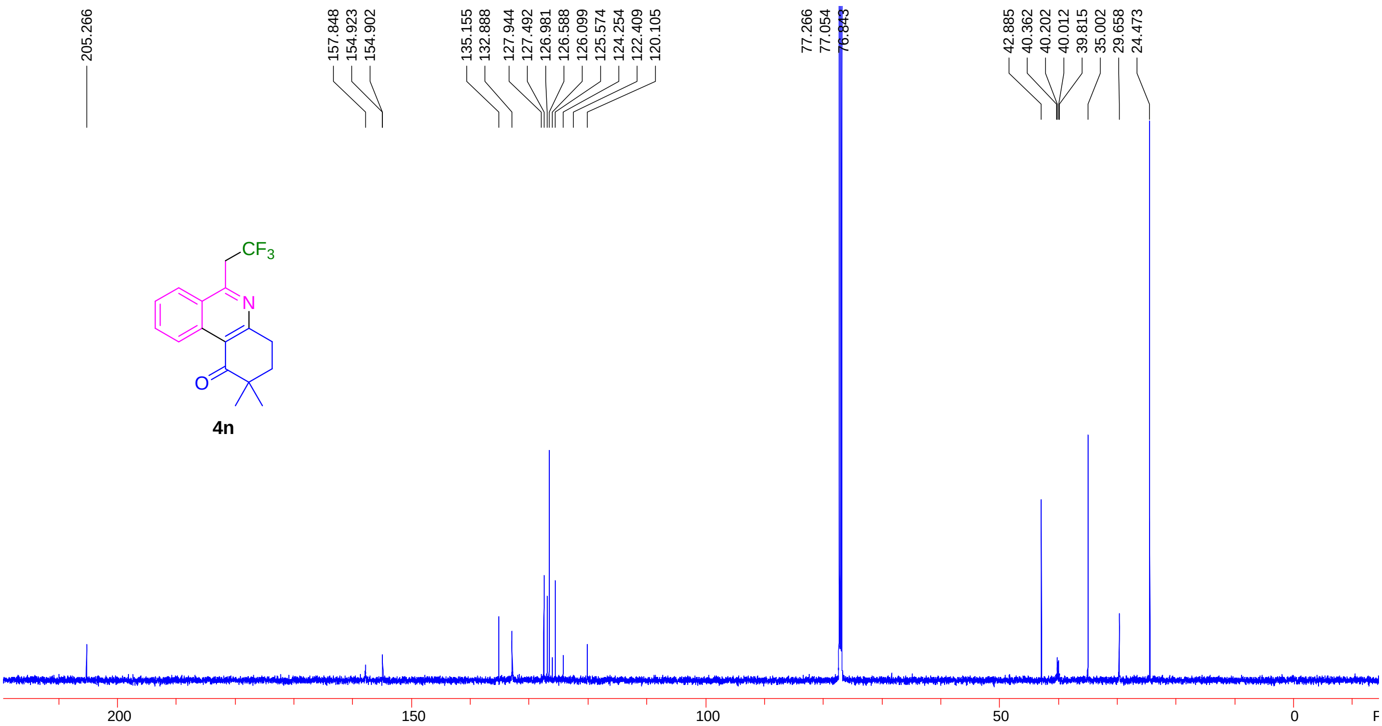

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125.574
124.254
122.409
120.105
77.266
77.054
76.843
42.885
40.362
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39.815
35.002
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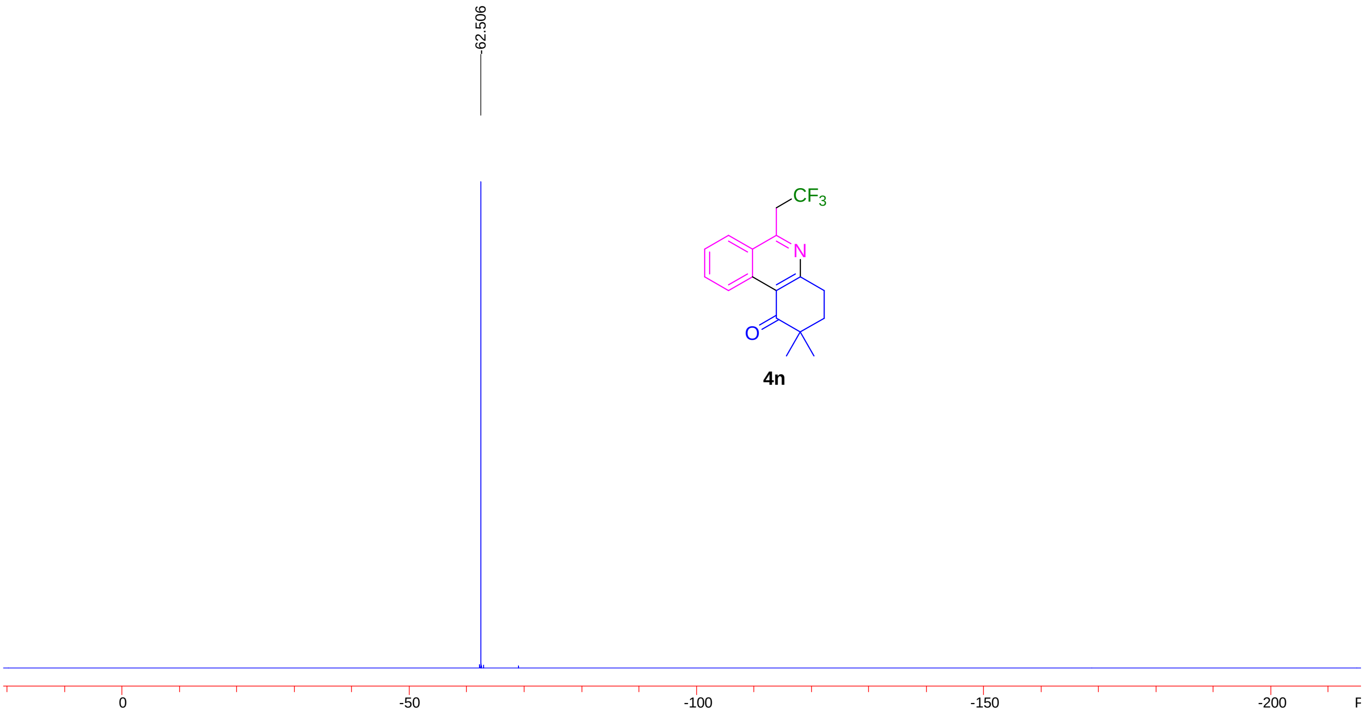
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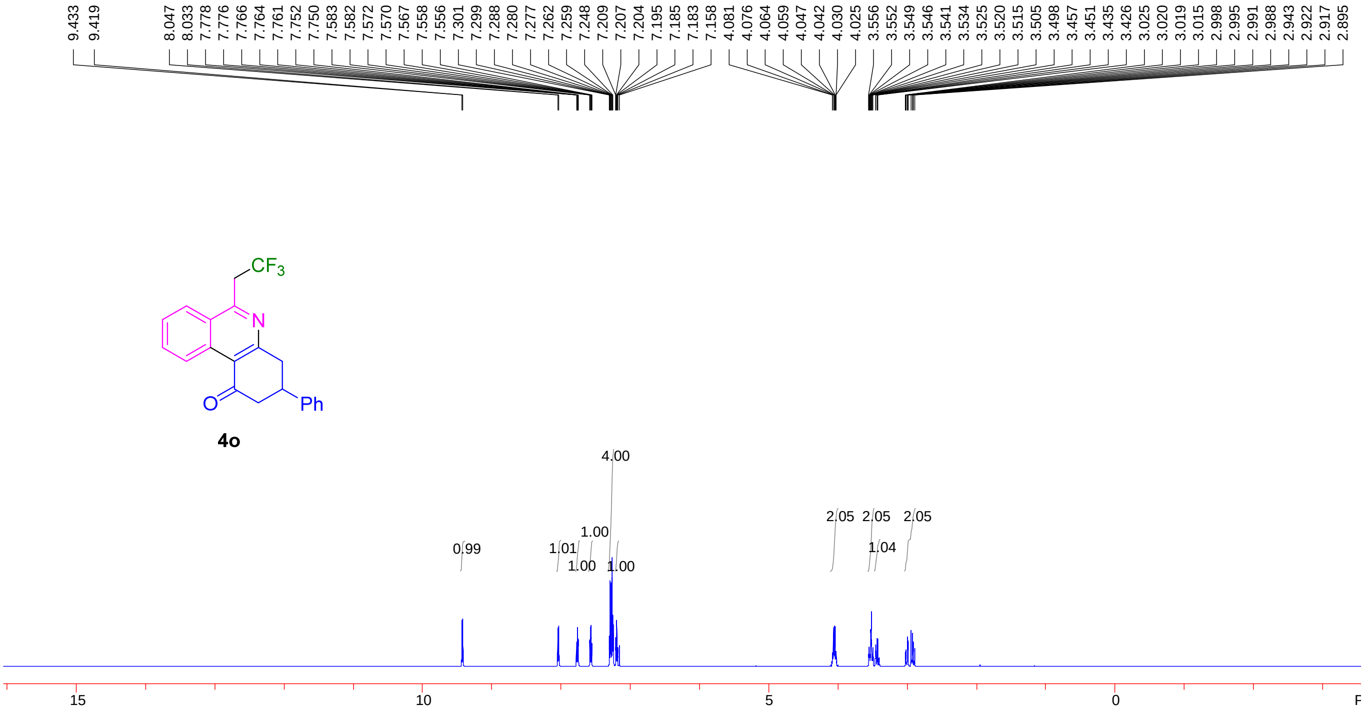
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CF3
N
O
Ph
4o
0.99
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1.00
1.00
4.00
1.00
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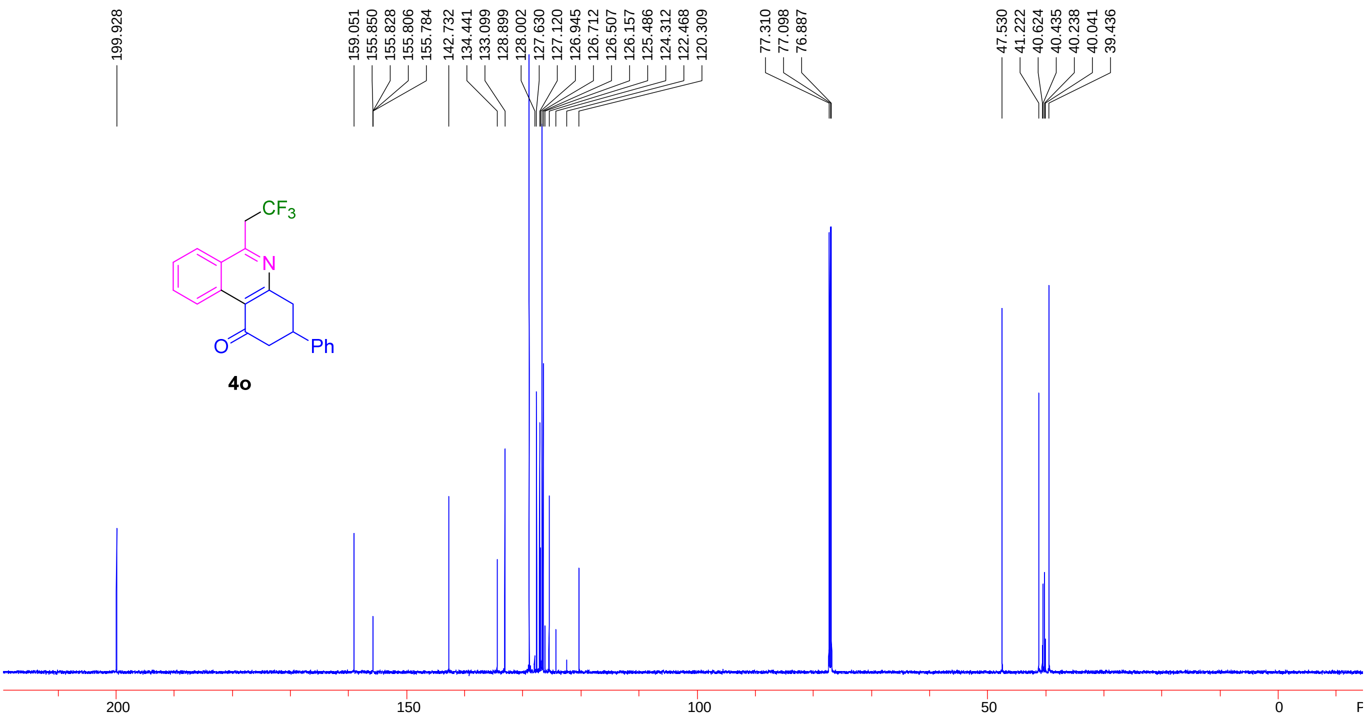
2.05
2.05
1.04
15
10
5
0
F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159.051 155.850 155.828 155.806 155.784 142.732 134.441 133.099 128.899 128.002 127.630 127.120 126.945 126.712 126.507 126.157 125.486 124.312 122.468 120.309
77.310 77.098 76.887
47.530 41.222 40.624 40.435 40.238 40.041 39.436
CF3
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Ph
4o
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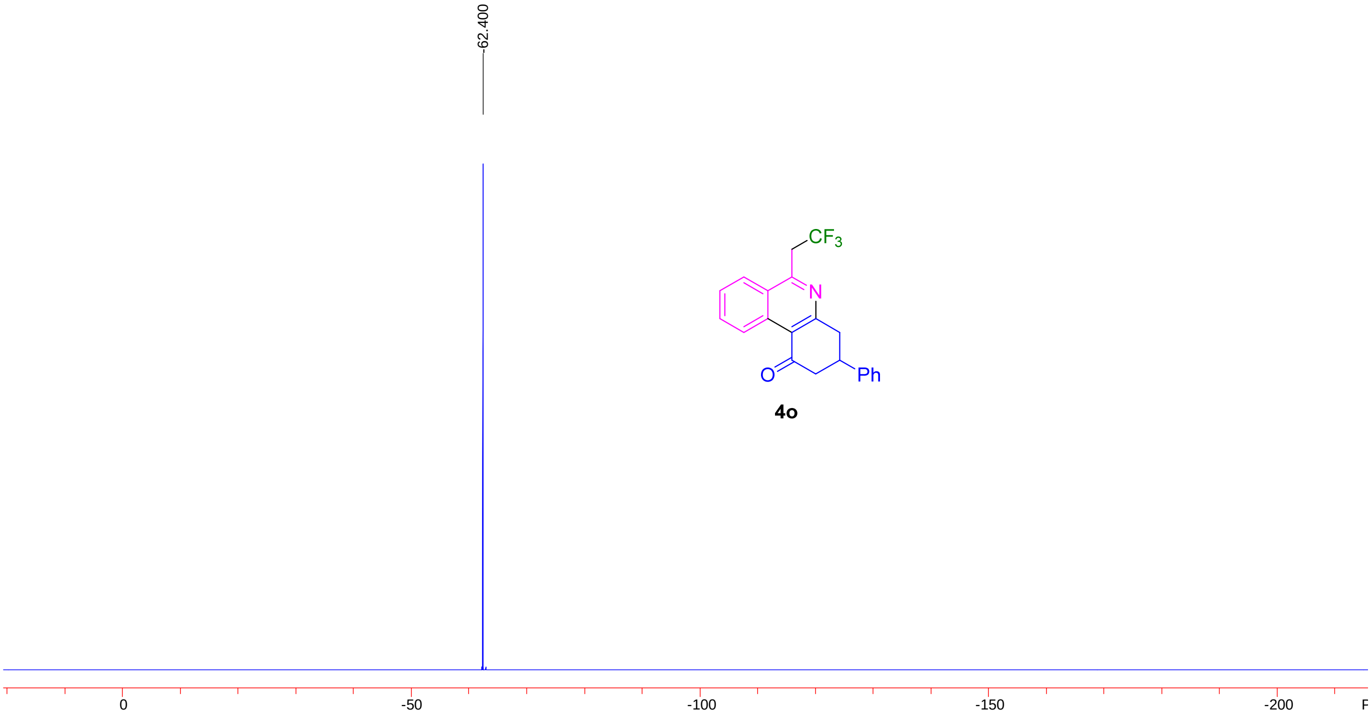
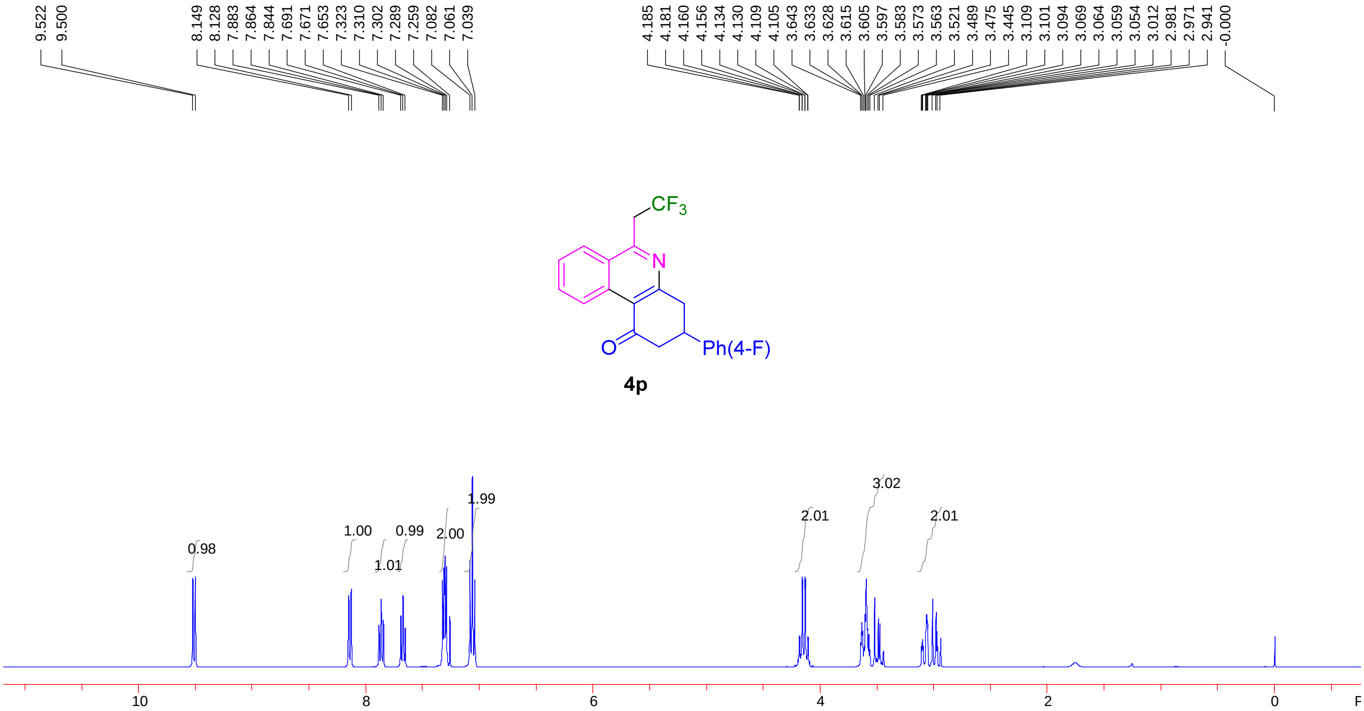


4o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7.302
7.289
7.259
7.082
7.061
7.039
4.185
4.181
4.160
4.156
4.134
4.130
4.109
4.105
3.643
3.633
3.628
3.615
3.605
3.597
3.583
3.573
3.563
3.521
3.489
3.475
3.445
3.109
3.101
3.094
3.069
3.064
3.059
3.054
3.012
2.981
2.971
2.941
-0.000
CF3
N
O
Ph(4-F)
4p
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2.01
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2
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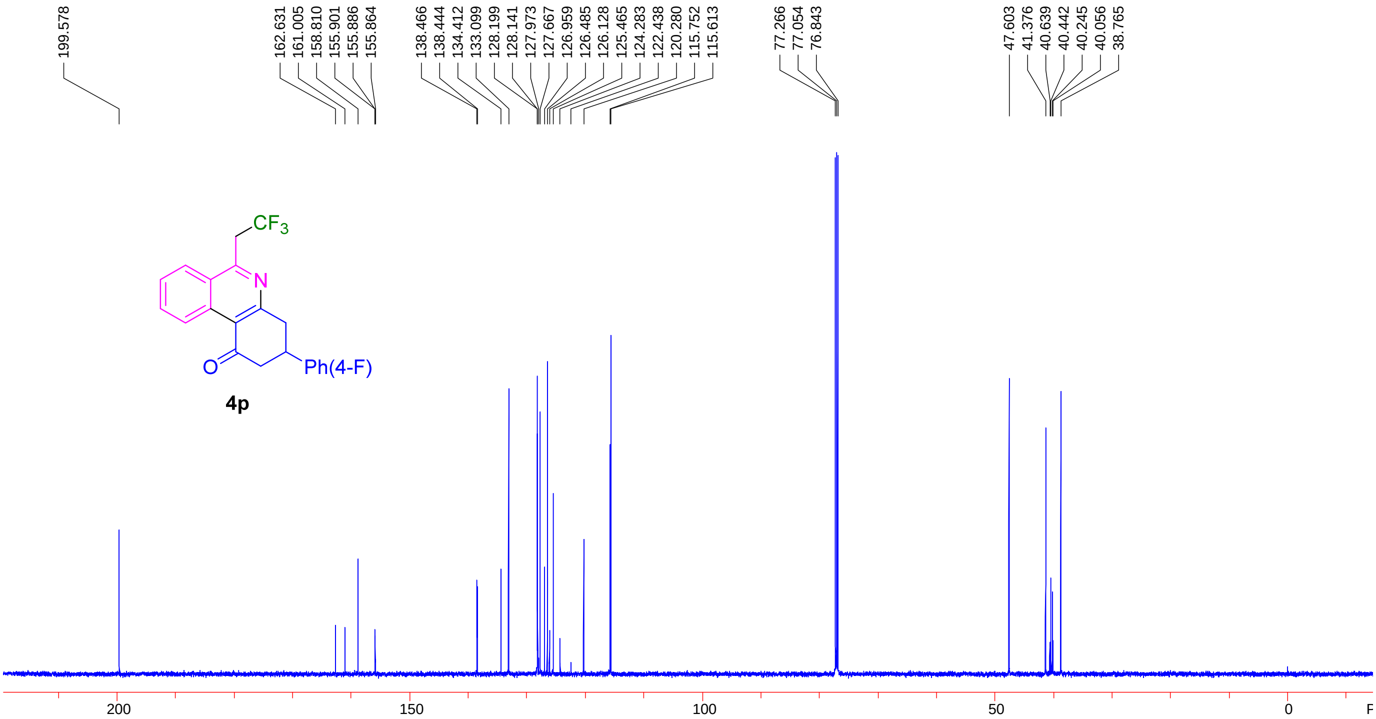
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158.810
155.901
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155.864
138.466
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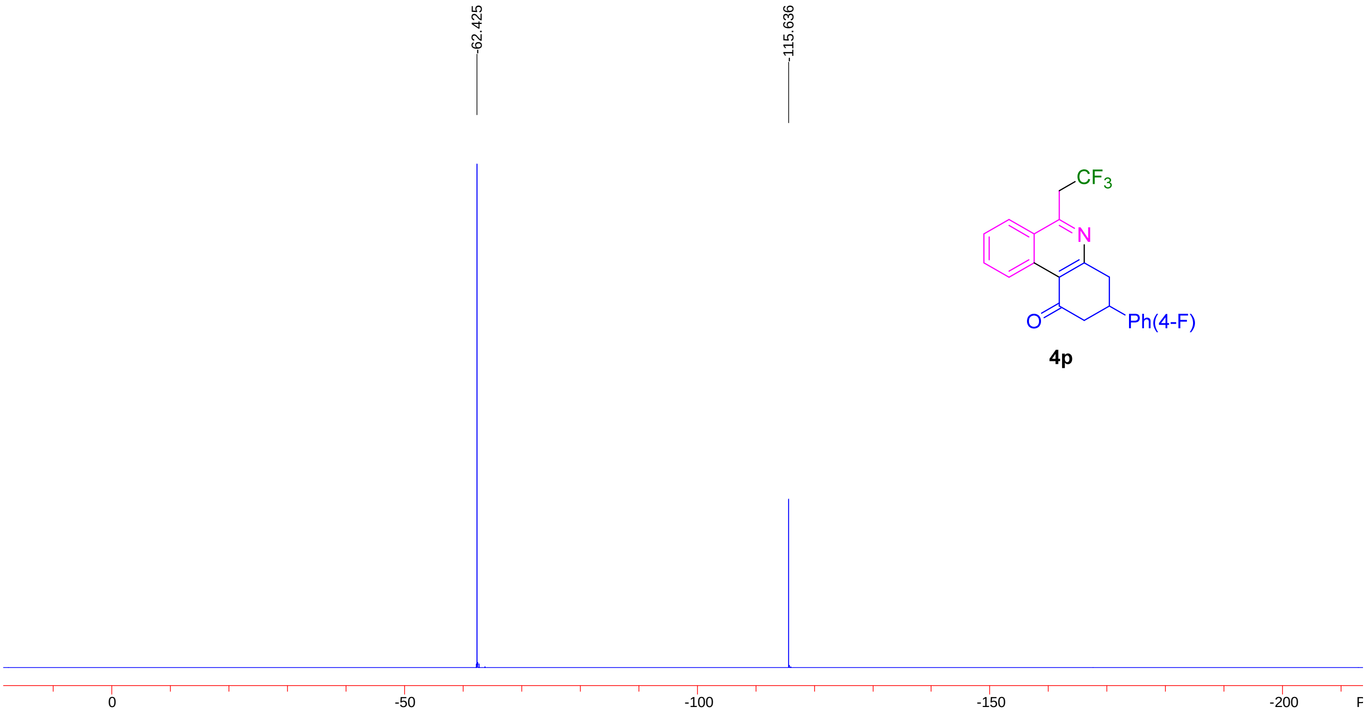
134.412
133.099
128.199
128.141
127.973
127.667
126.959
126.485
126.128
125.465
124.283
122.438
120.280
115.752
115.613
77.266
77.054
76.843
47.603
41.376
40.639
40.442
40.245
40.056
38.765
CF3
N
O
Ph(4-F)
4p
200
150
100
50
0



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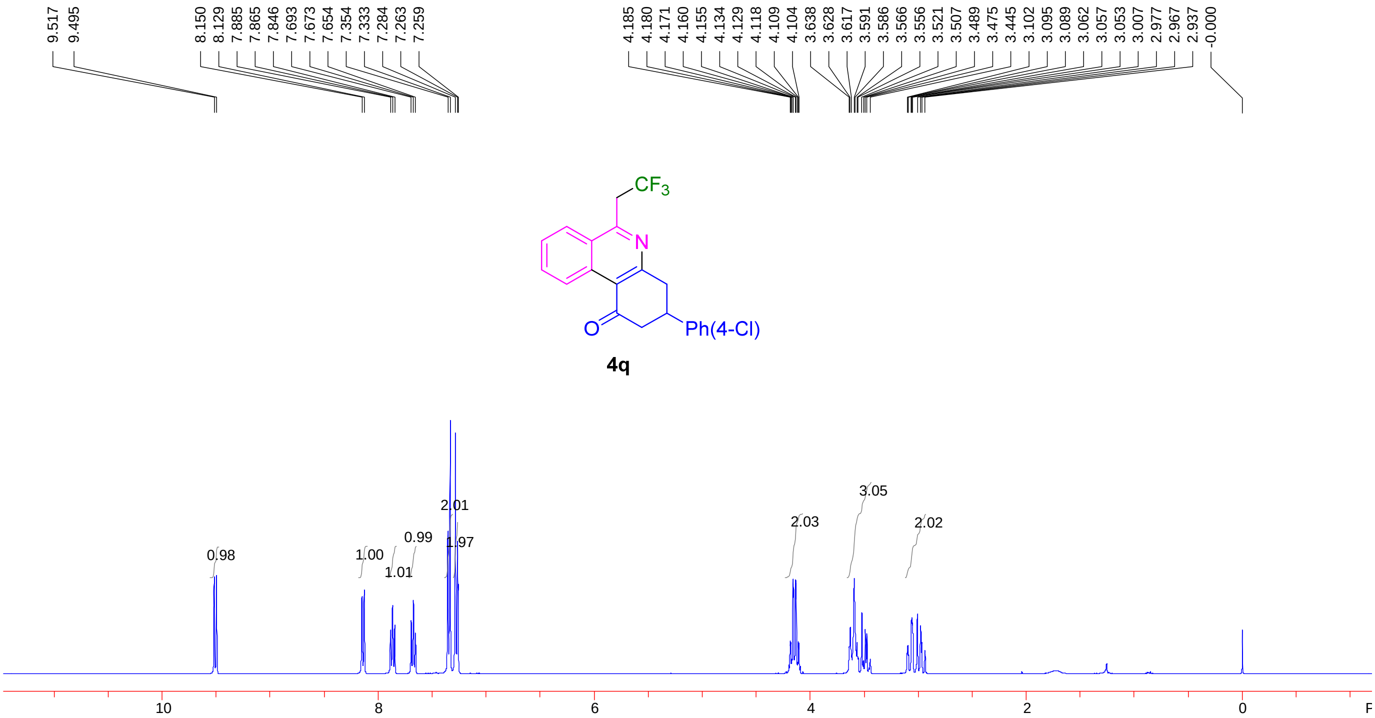
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7.846
7.693
7.673
7.654
7.354
7.333
7.284
7.263
7.259
4.185
4.180
4.171
4.160
4.155
4.134
4.129
4.118
4.109
4.104
3.638
3.628
3.617
3.591
3.586
3.566
3.556
3.521
3.507
3.489
3.475
3.445
3.102
3.095
3.089
3.062
3.057
3.053
3.007
2.977
2.967
2.937
-0.000
CF3
N
O
Ph(4-Cl)
4q
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0.99
2.01
1.97
2.03
3.05
2.02
10
8
6
4
2
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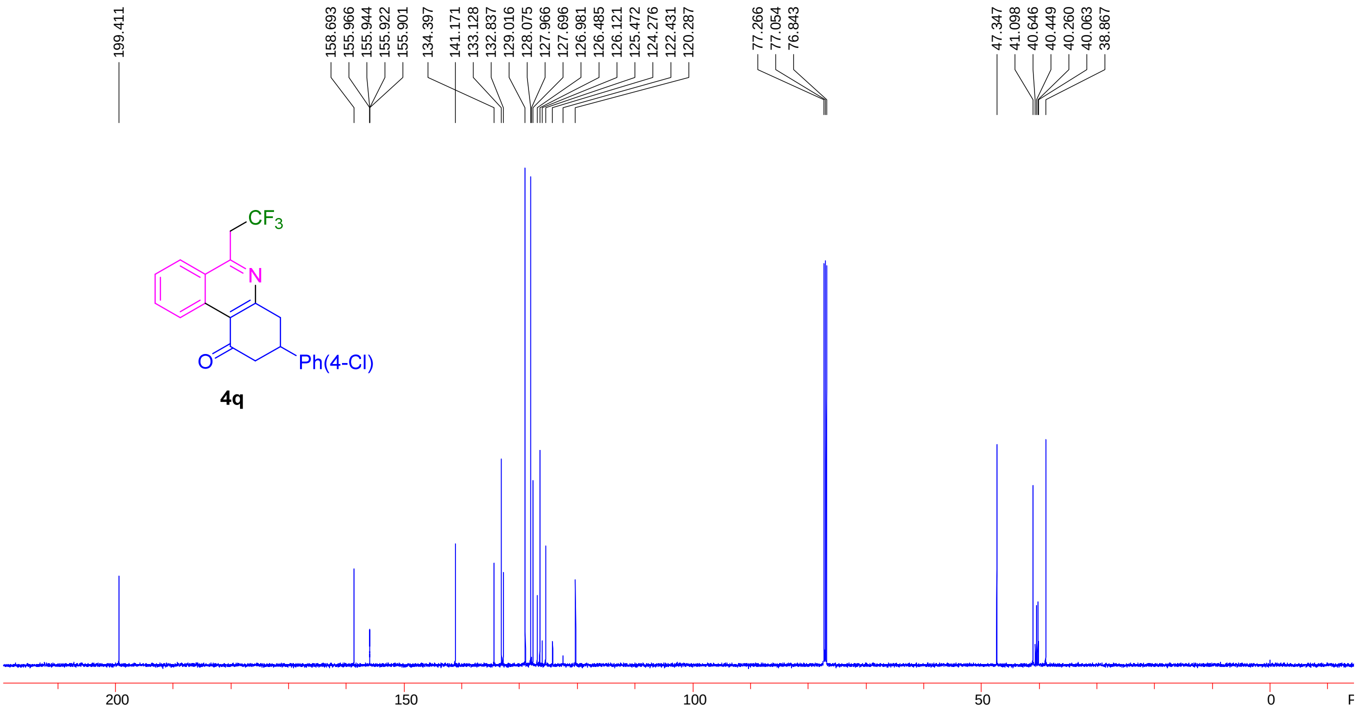
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77.266
77.054
76.843
47.347
41.098
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40.063
38.867
CF3
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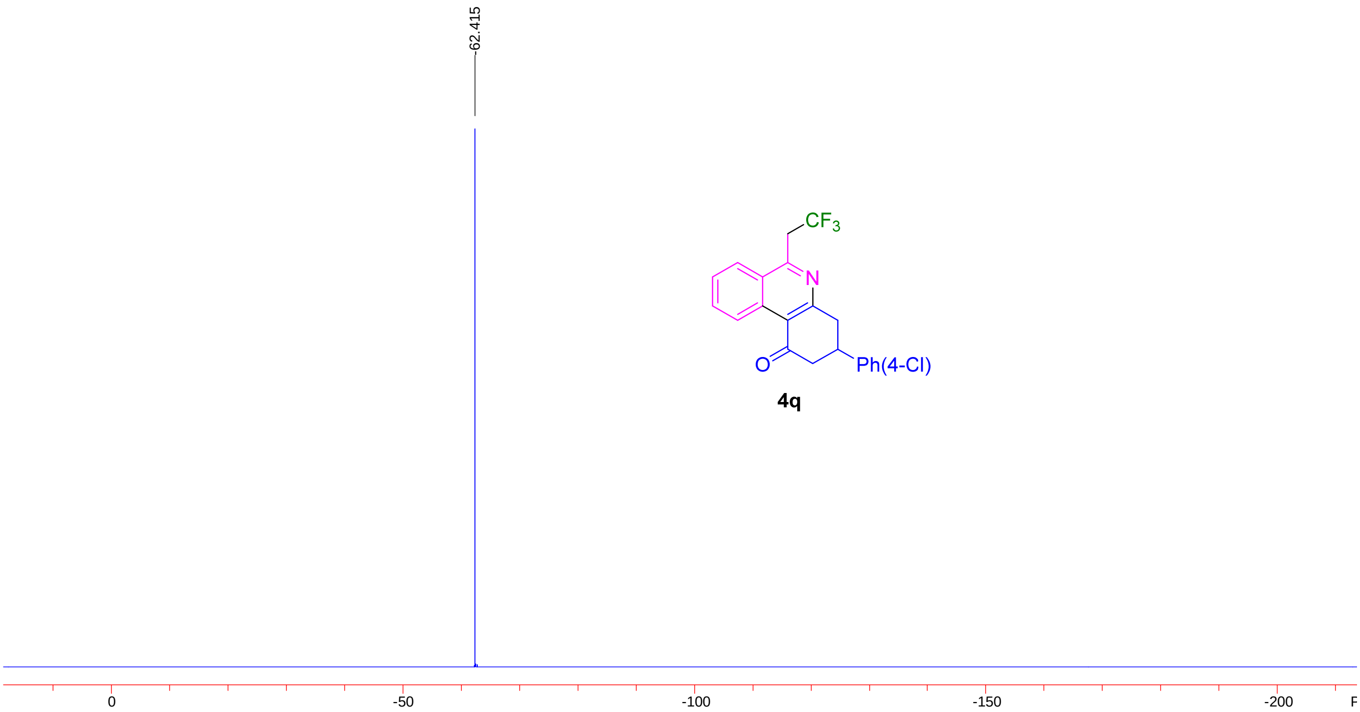
O
Ph(4-Cl)
4q
200
150
100
50
0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O
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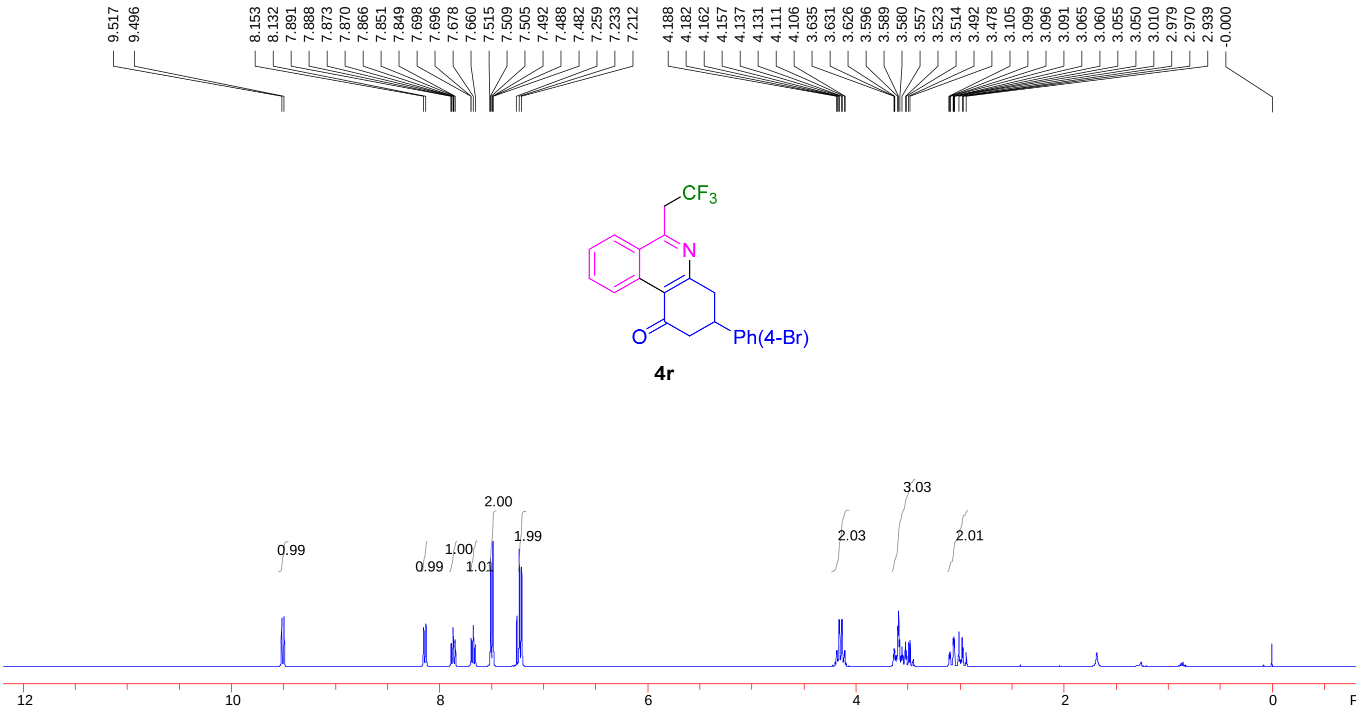
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7.851
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7.698
7.696
7.678
7.660
7.515
7.509
7.505
7.492
7.488
7.482
7.259
7.233
7.212
4.188
4.182
4.162
4.157
4.137
4.131
4.111
4.106
3.635
3.631
3.626
3.596
3.589
3.580
3.557
3.523
3.514
3.492
3.478
3.105
3.099
3.096
3.091
3.065
3.060
3.055
3.050
3.010
2.979
2.970
2.939
-0.000
CF3
N
O
Ph(4-Br)
4r
0.99
0.99
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2.00
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2.03
3.03
2.01
12
10
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6
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2
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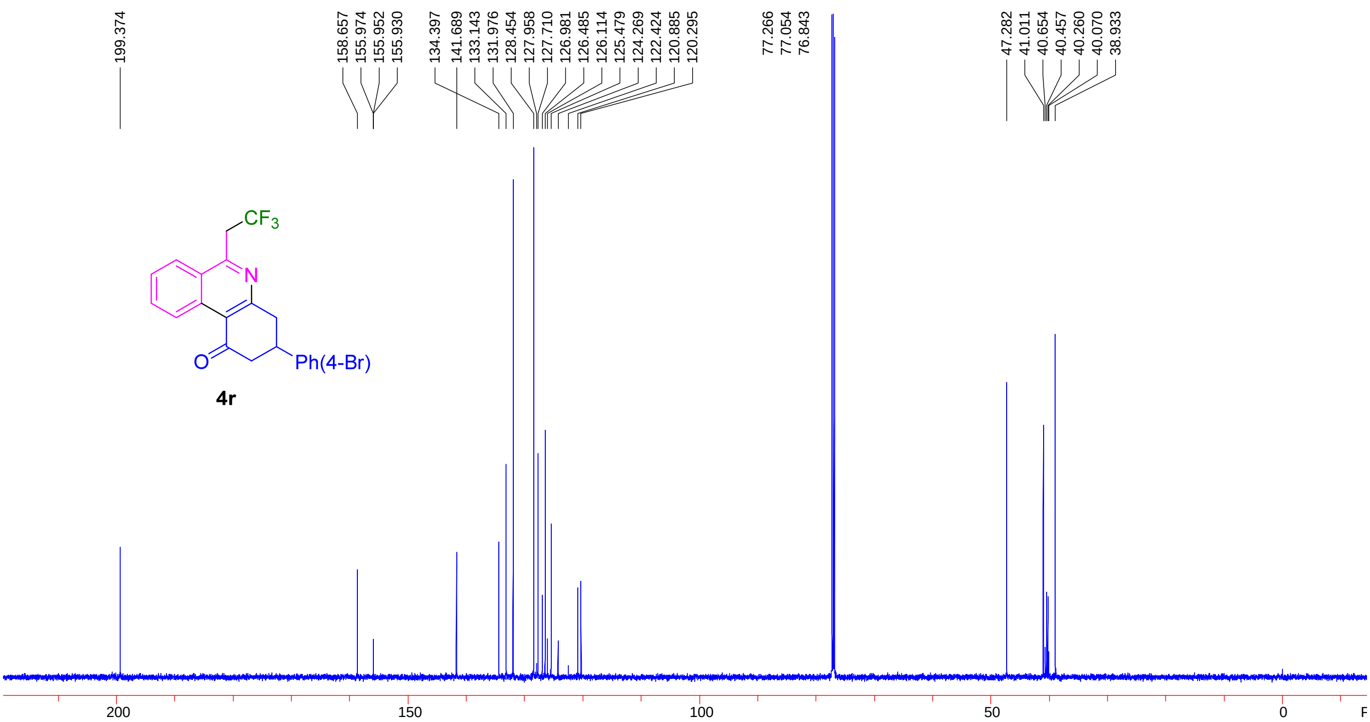
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133.143
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126.981
126.485
126.114
125.479
124.269
122.424
120.885
120.295
77.266
77.054
76.843
47.282
41.011
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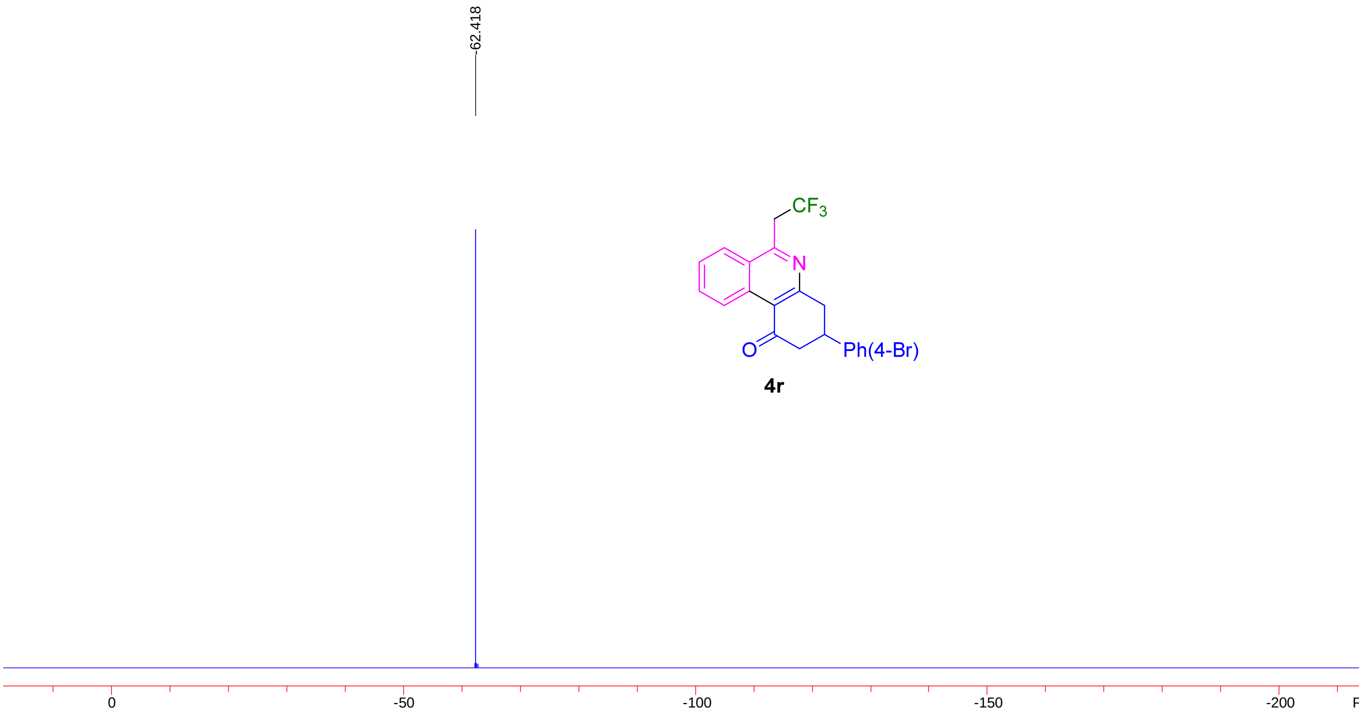
40.457
40.260
40.070
38.933
CF3
N
O
Ph(4-Br)
4r
200
150
100
50
0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O
Ph(4-Br)
4r
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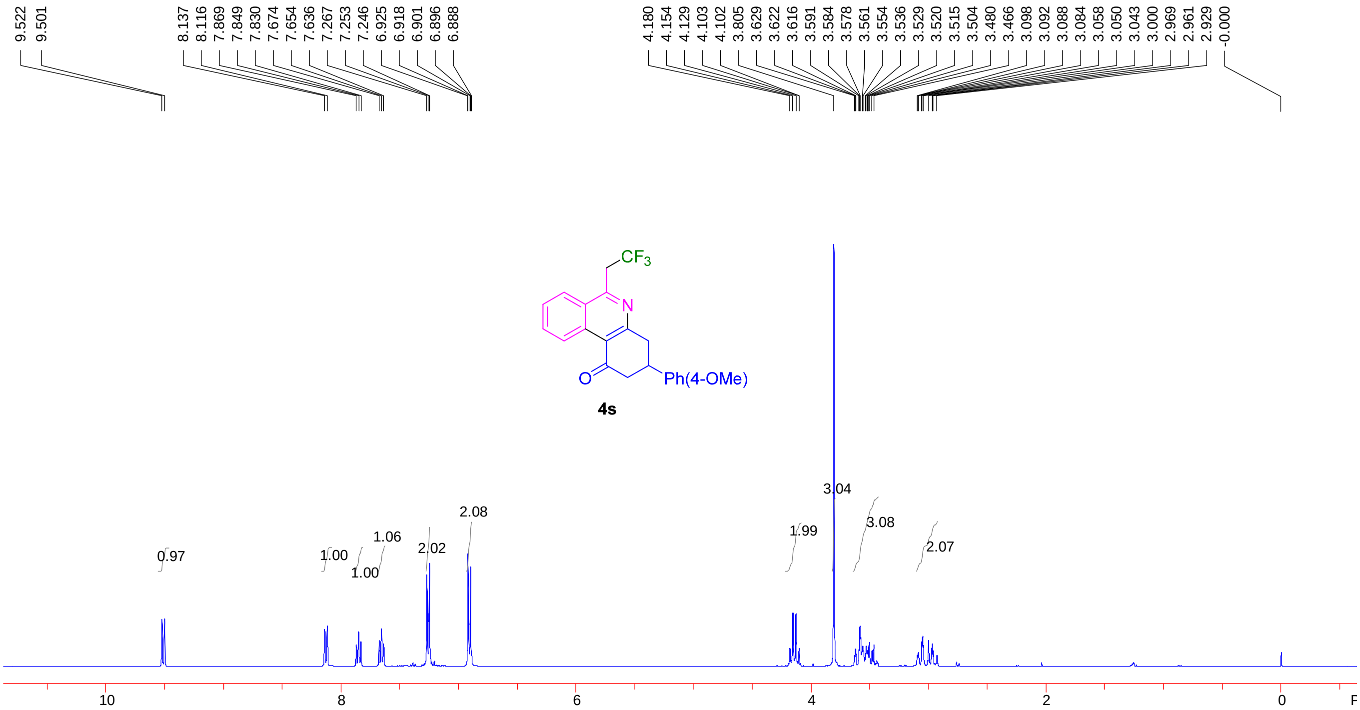
-100
-150
-200
F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7.674
7.654
7.636
7.267
7.253
7.246
6.925
6.918
6.901
6.896
6.888
4.180
4.154
4.129
4.103
4.102
3.805
3.629
3.622
3.616
3.591
3.584
3.578
3.561
3.554
3.536
3.529
3.520
3.515
3.504
3.480
3.466
3.098
3.092
3.088
3.084
3.058
3.050
3.043
3.000
2.969
2.961
2.929
-0.000
CF3
N
O
Ph(4-OMe)
4s
0.97
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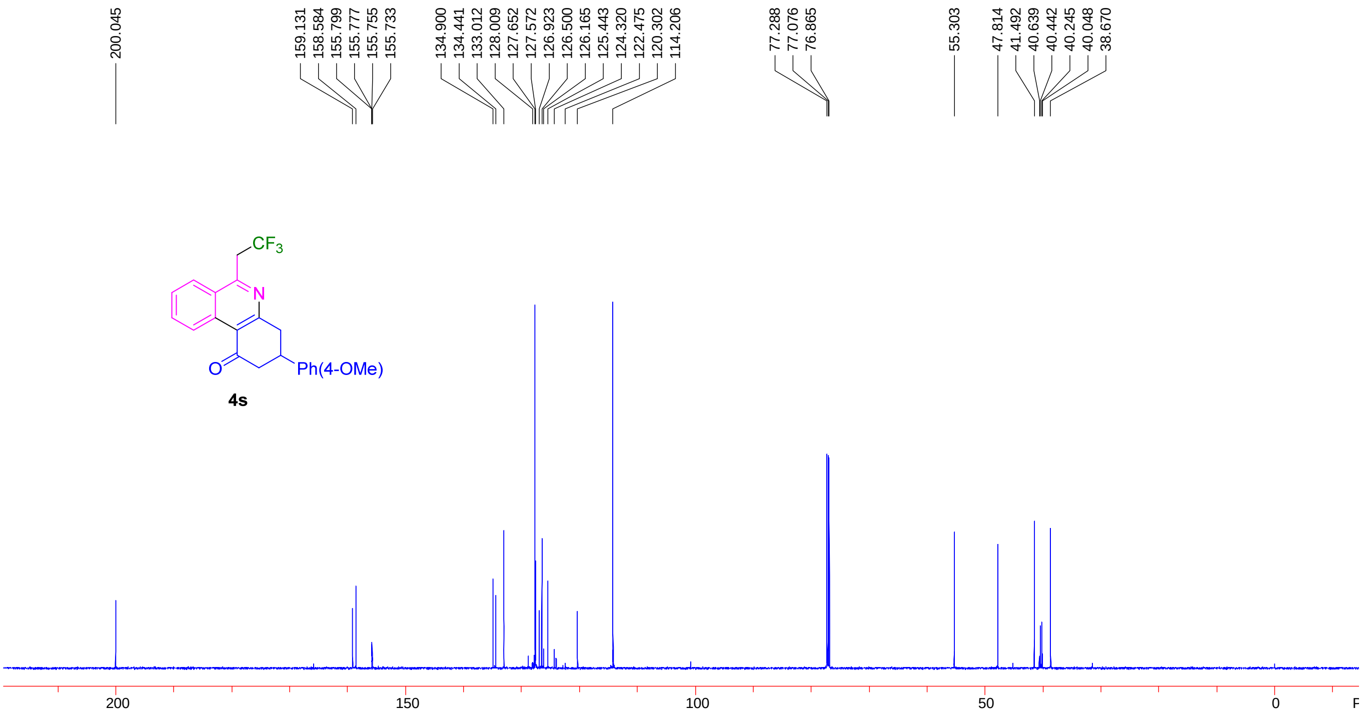
1.00
1.06
2.02
2.08
1.99
3.04
3.08
2.07
10
8
6
4
2
0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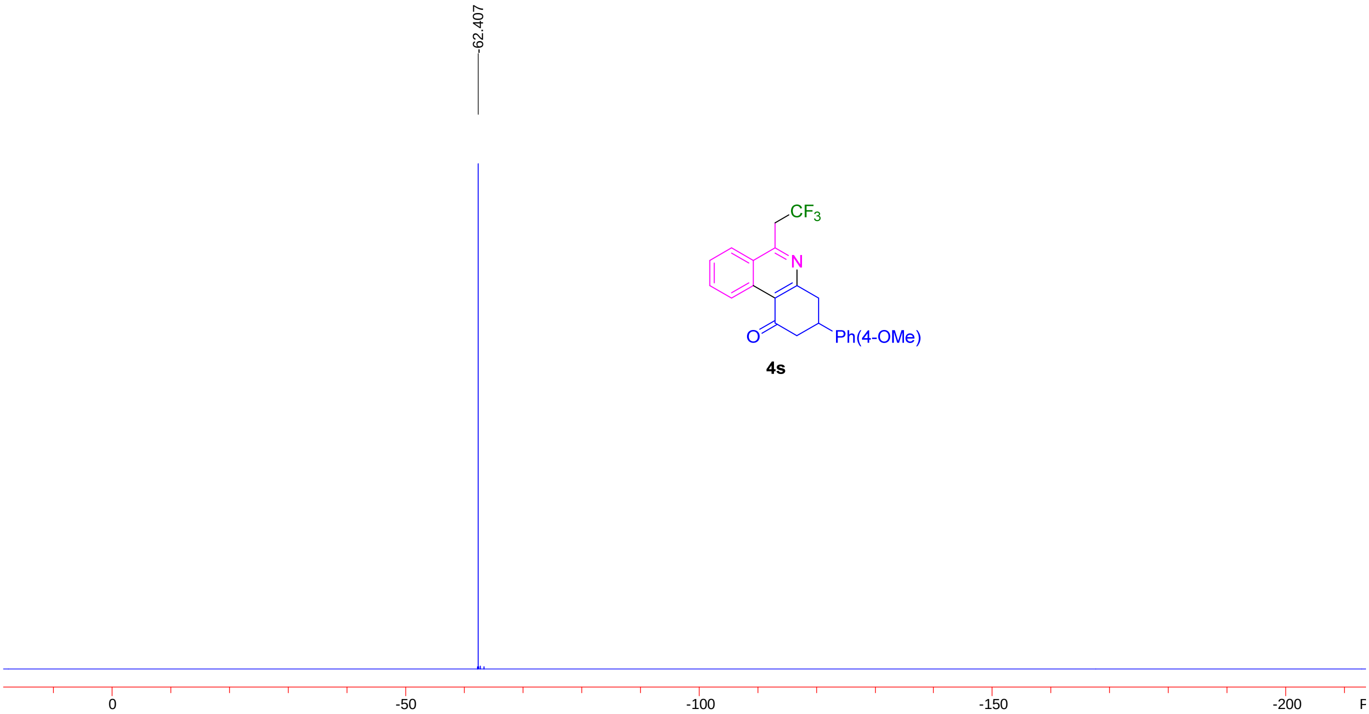
127.572
126.923
126.500
126.165
125.443
124.320
122.475
120.302
114.206
77.288
77.076
76.865
55.303
47.814
41.492
40.639
40.442
40.245
40.048
38.670
CF3
N
O
Ph(4-OMe)
4s
200
150
100
50
0



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4s
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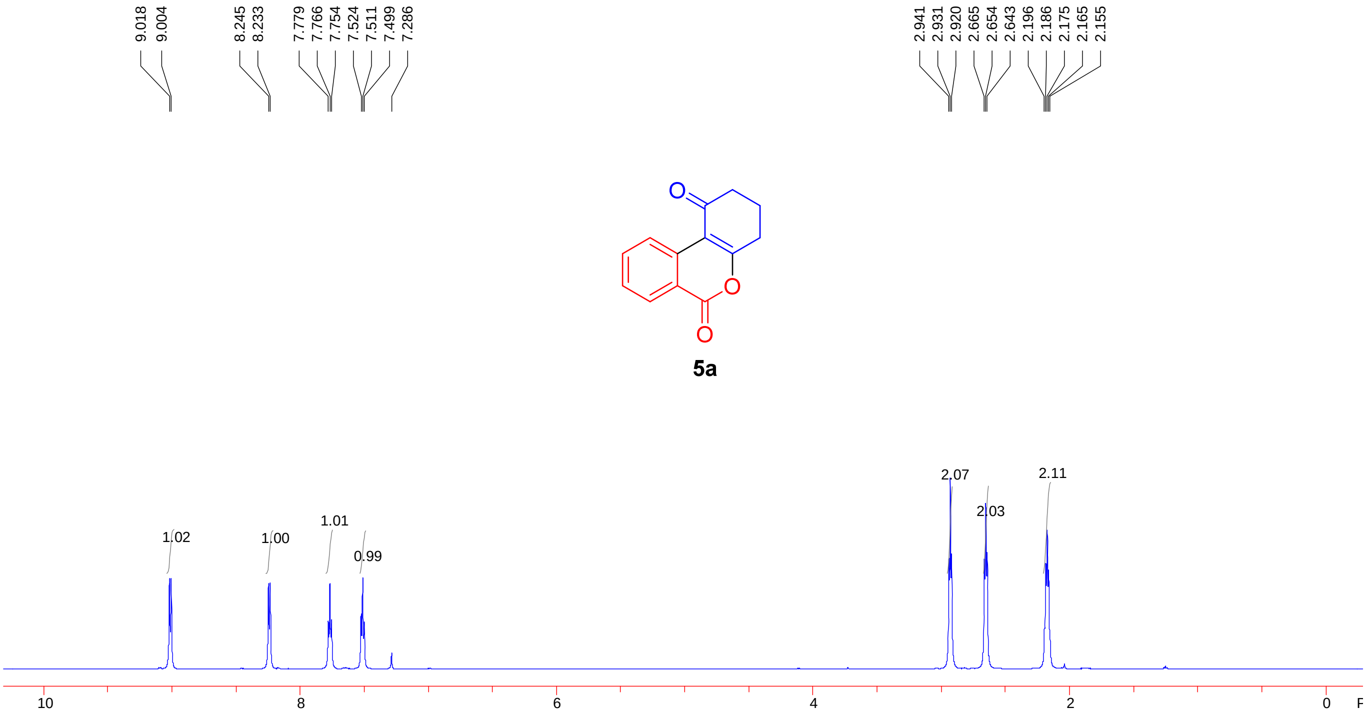
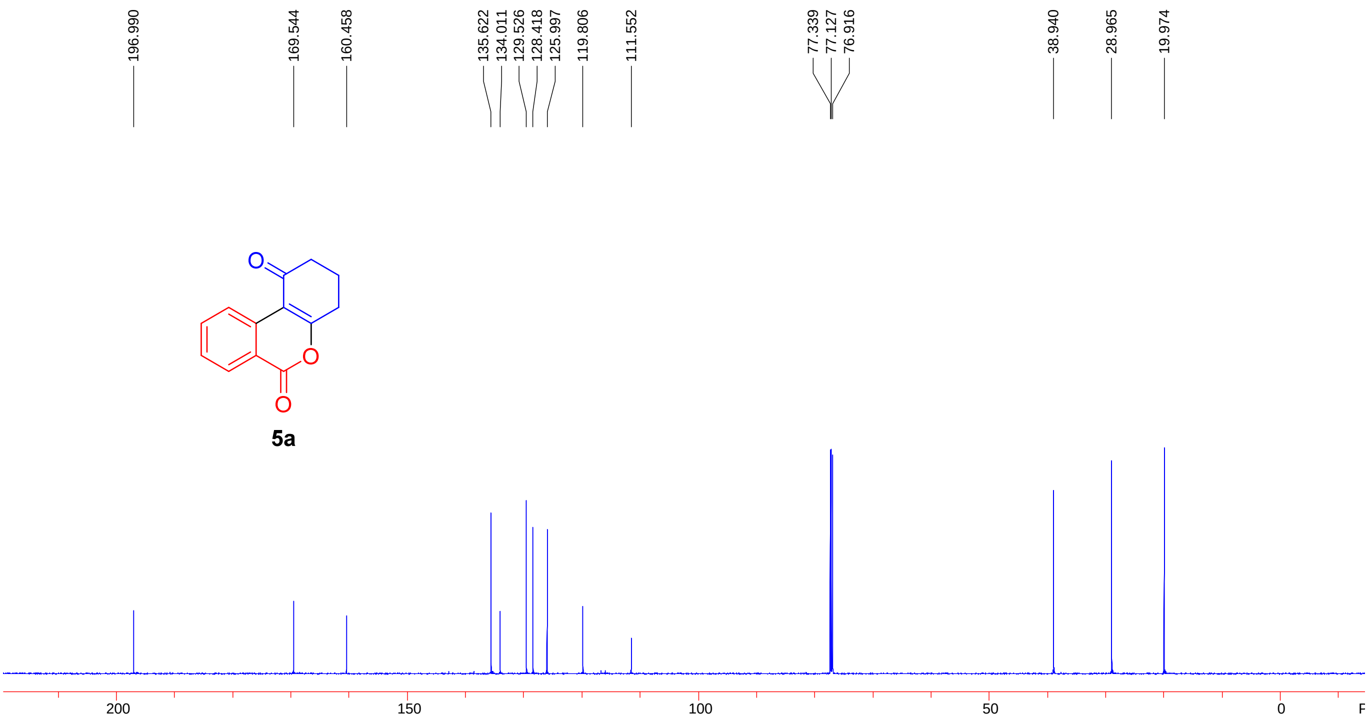
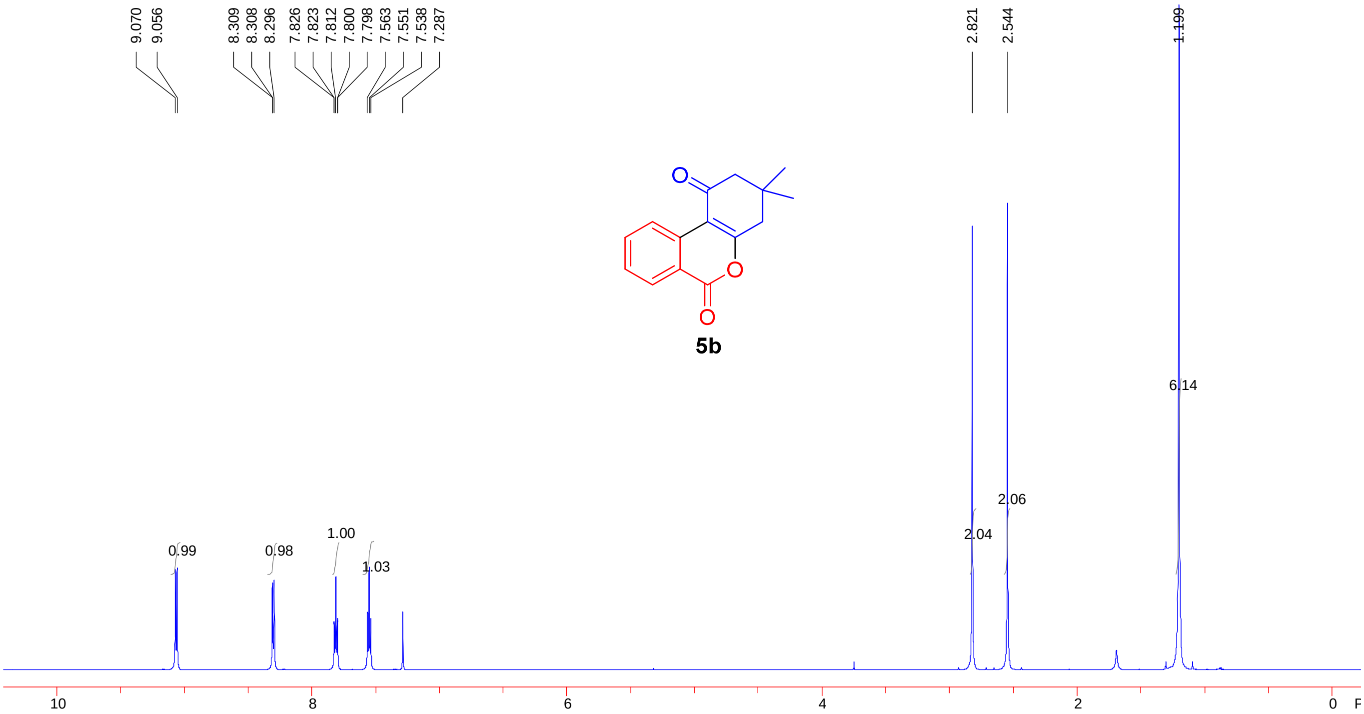
-200

V. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5l



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7.798
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7.551
7.538
7.287
2.821
2.544
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0.98
1.00
1.03
2.04
2.06
6.14
10
8
6
4
2
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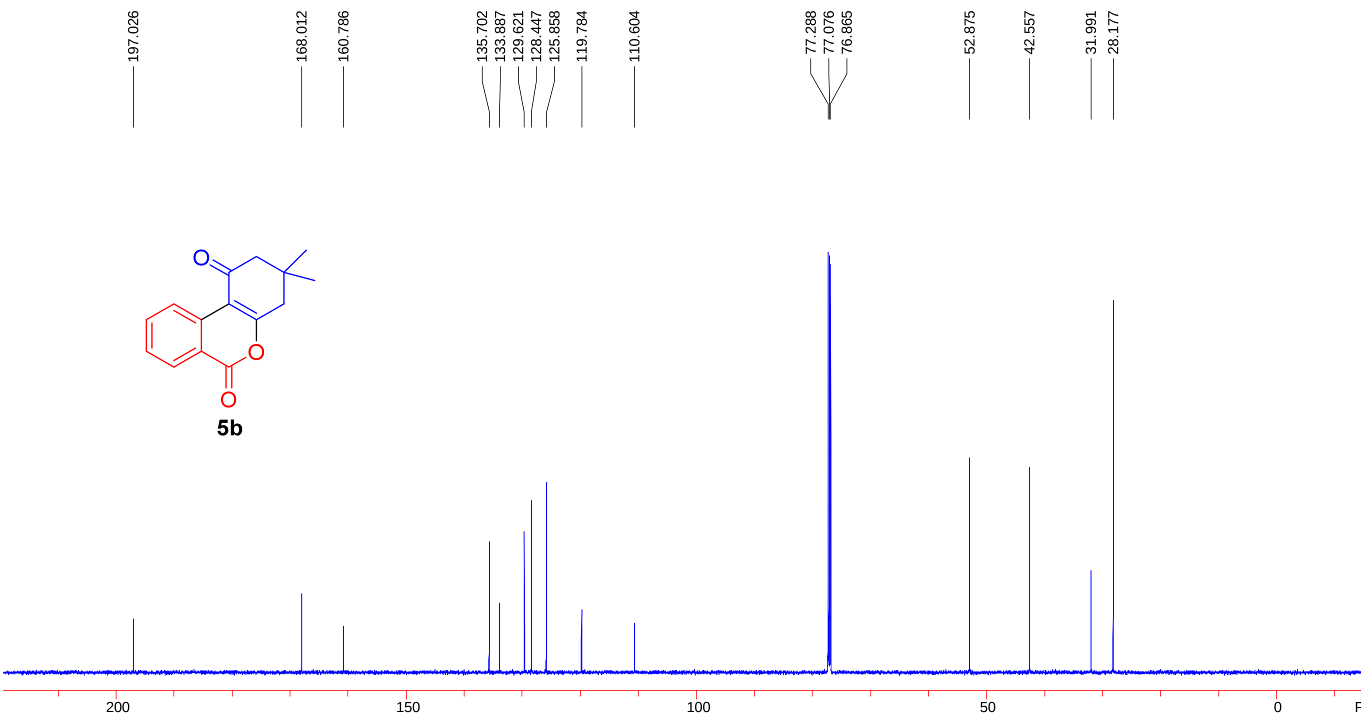
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76.865
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28.177
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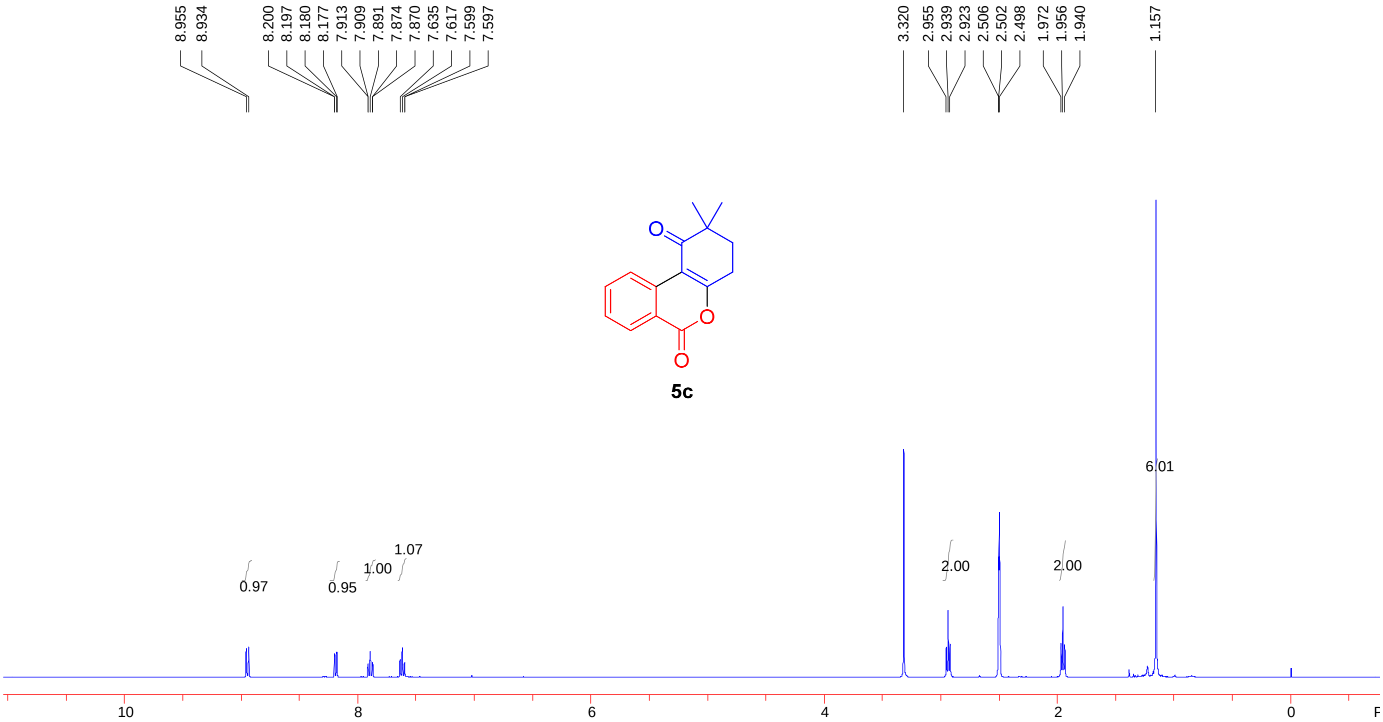
150
100
50
0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7.909
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7.874
7.870
7.635
7.617
7.599
7.597
3.320
2.955
2.939
2.923
2.506
2.502
2.498
1.972
1.956
1.940
1.157
5c
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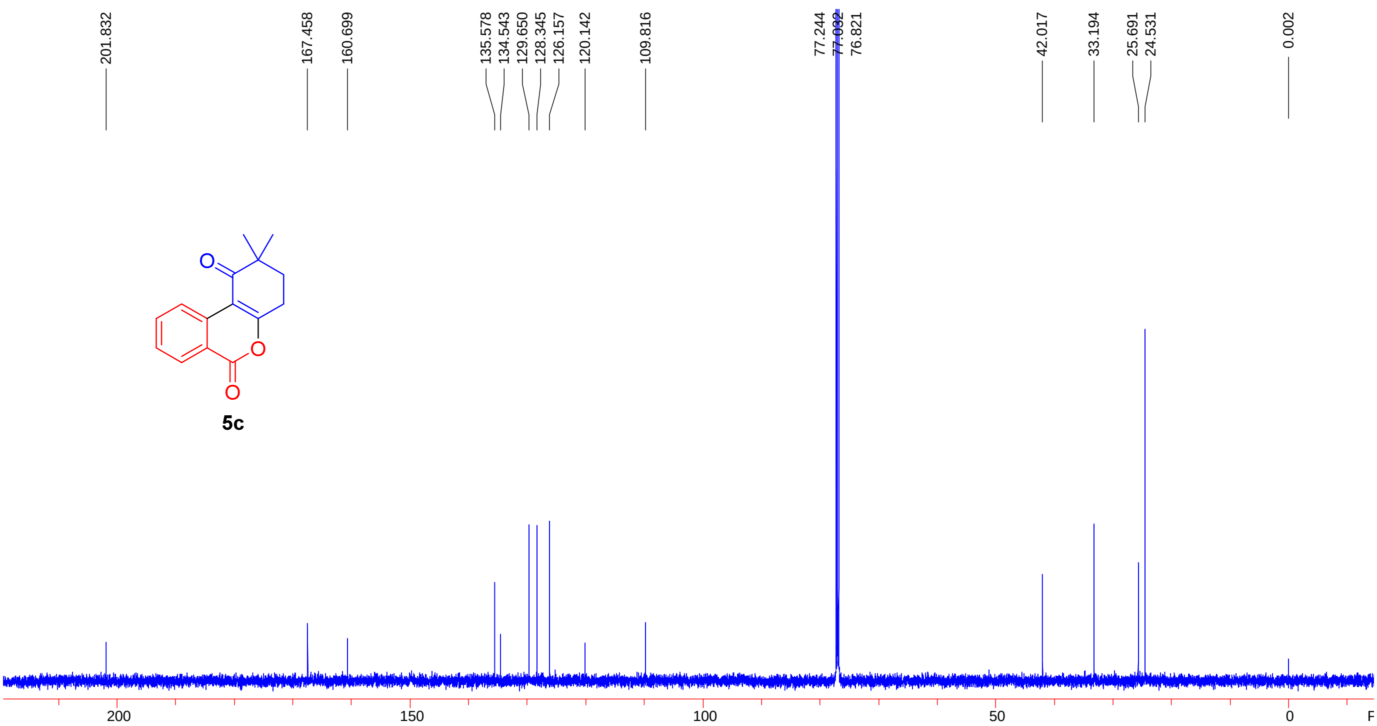
0.95
1.00
1.07
2.00
2.00
6.01
10
8
6
4
2
0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109.816
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200
150
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50
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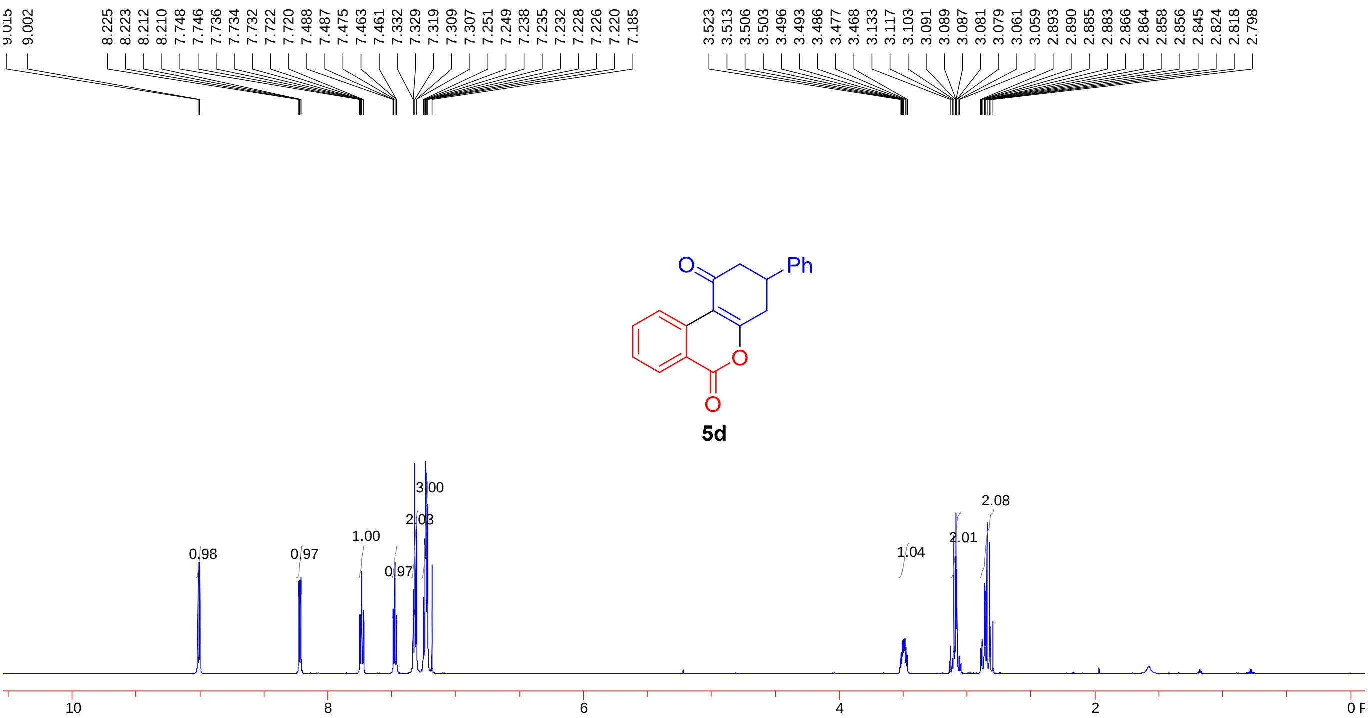
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7.734
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7.722
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7.487
7.475
7.463
7.461
7.332
7.329
7.319
7.309
7.307
7.251
7.249
7.238
7.235
7.232
7.228
7.226
7.220
7.185
3.523
3.513
3.506
3.503
3.496
3.493
3.486
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3.468
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3.103
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3.089
3.087
3.081
3.079
3.061
3.059
2.893
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2.883
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2.864
2.858
2.856
2.845
2.824
2.818
2.798
O
Ph
O
O
5d
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0.97
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3.00
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2.08
10
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4
2
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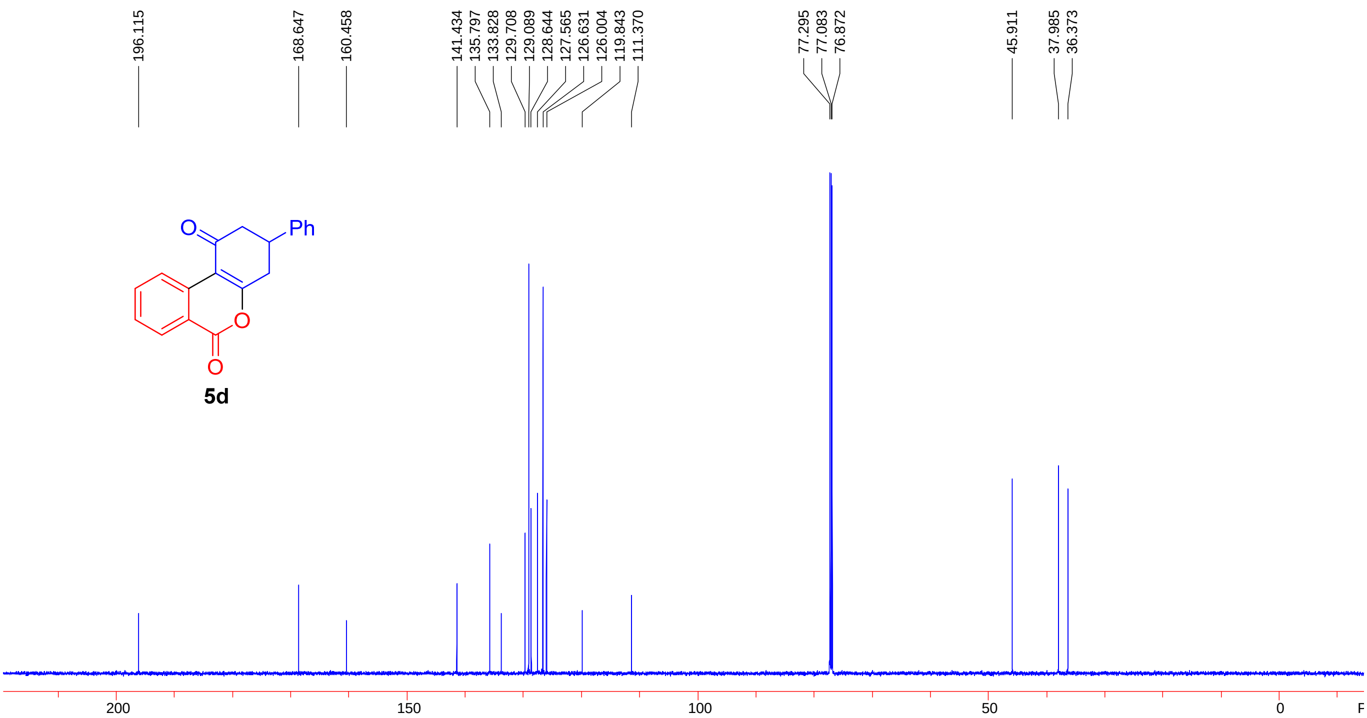
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111.370
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O
Ph
O
O
5d
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150
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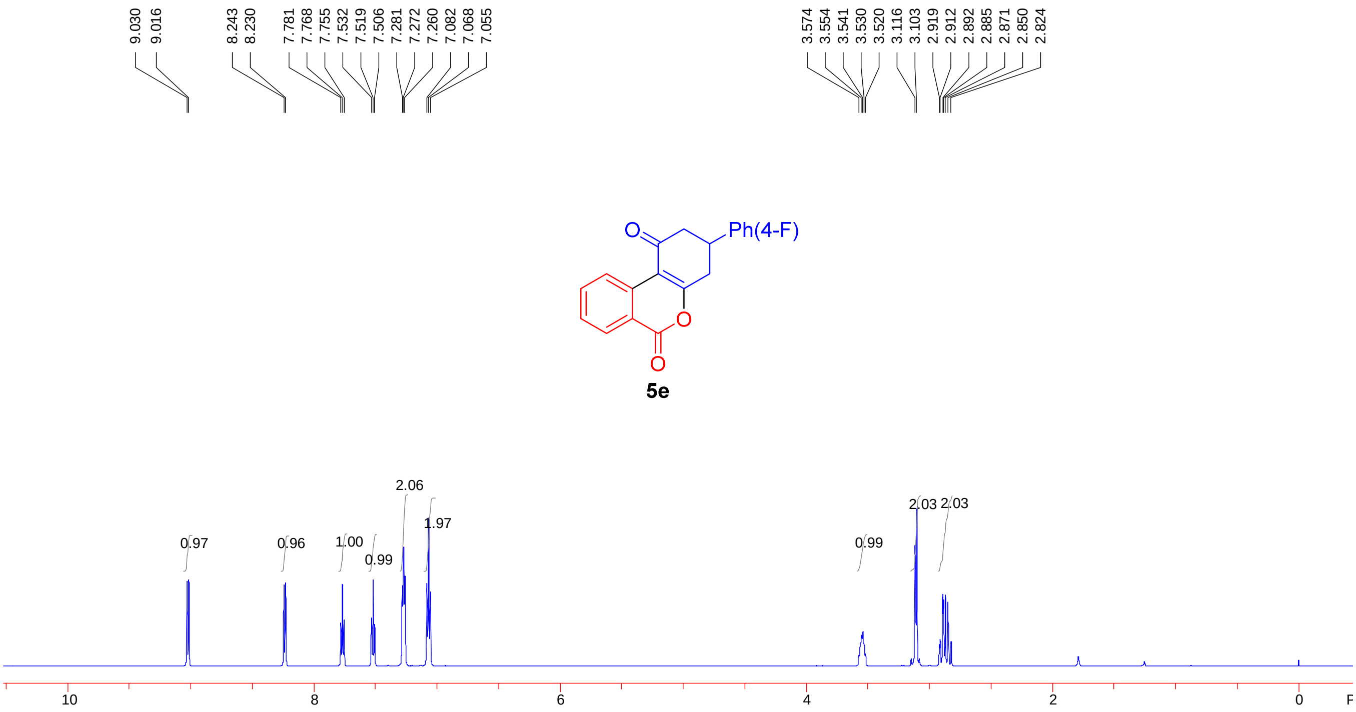
50
0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7.755
7.532
7.519
7.506
7.281
7.272
7.260
7.082
7.068
7.055
3.574
3.554
3.541
3.530
3.520
3.116
3.103
2.919
2.912
2.892
2.885
2.871
2.850
2.824
Ph(4-F)
5e
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0.99
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2.03
2.03
10
8
6
4
2
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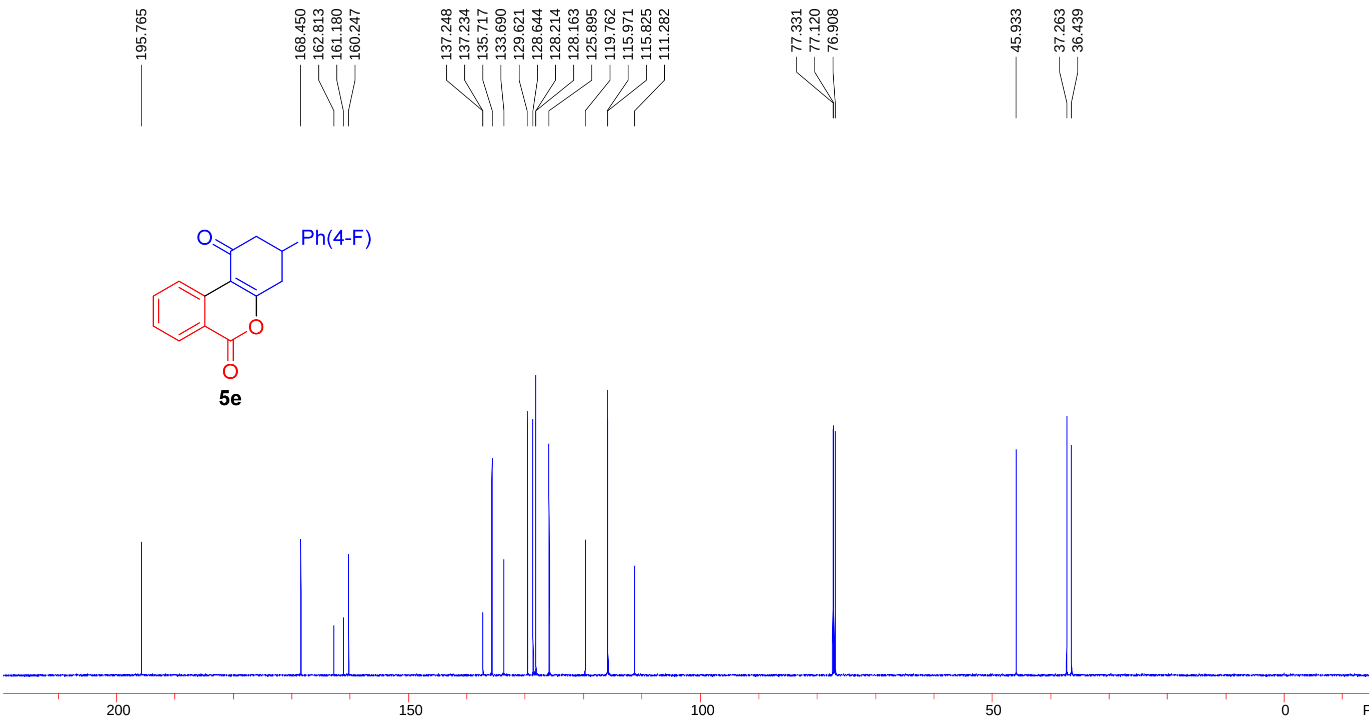
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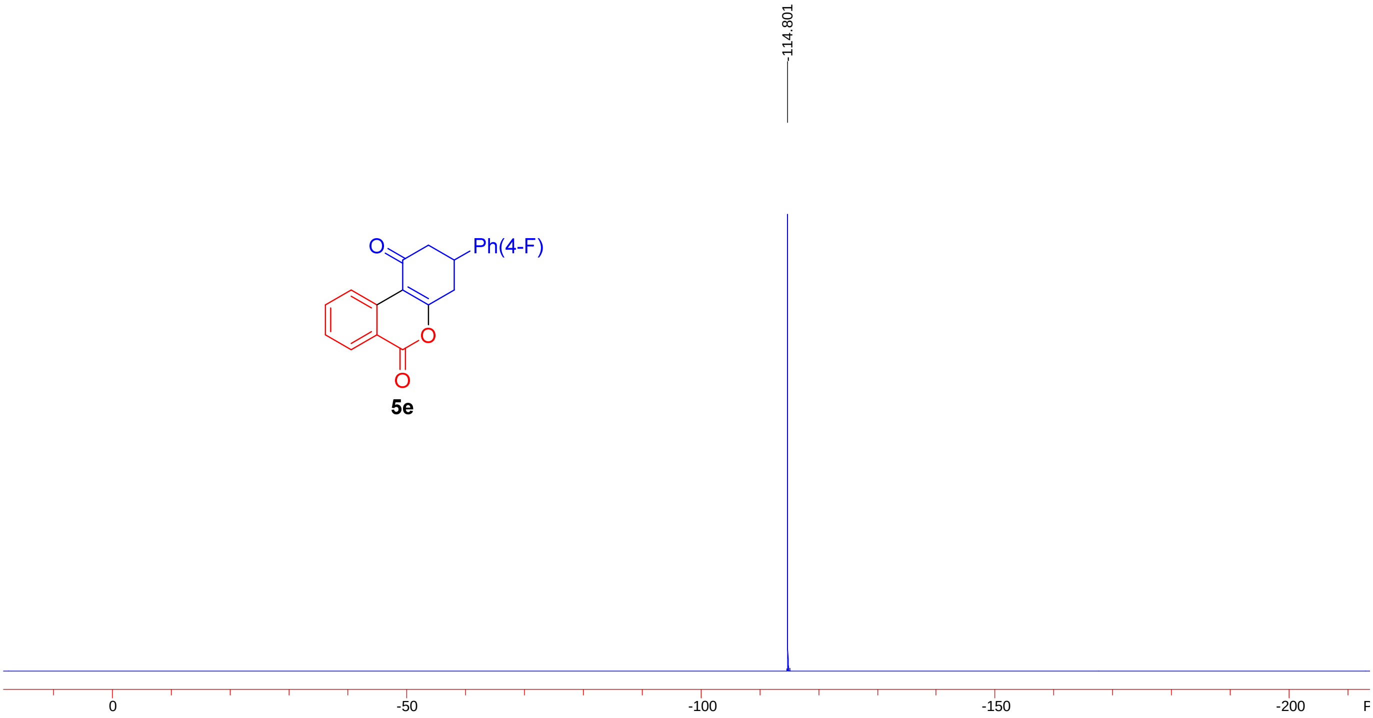
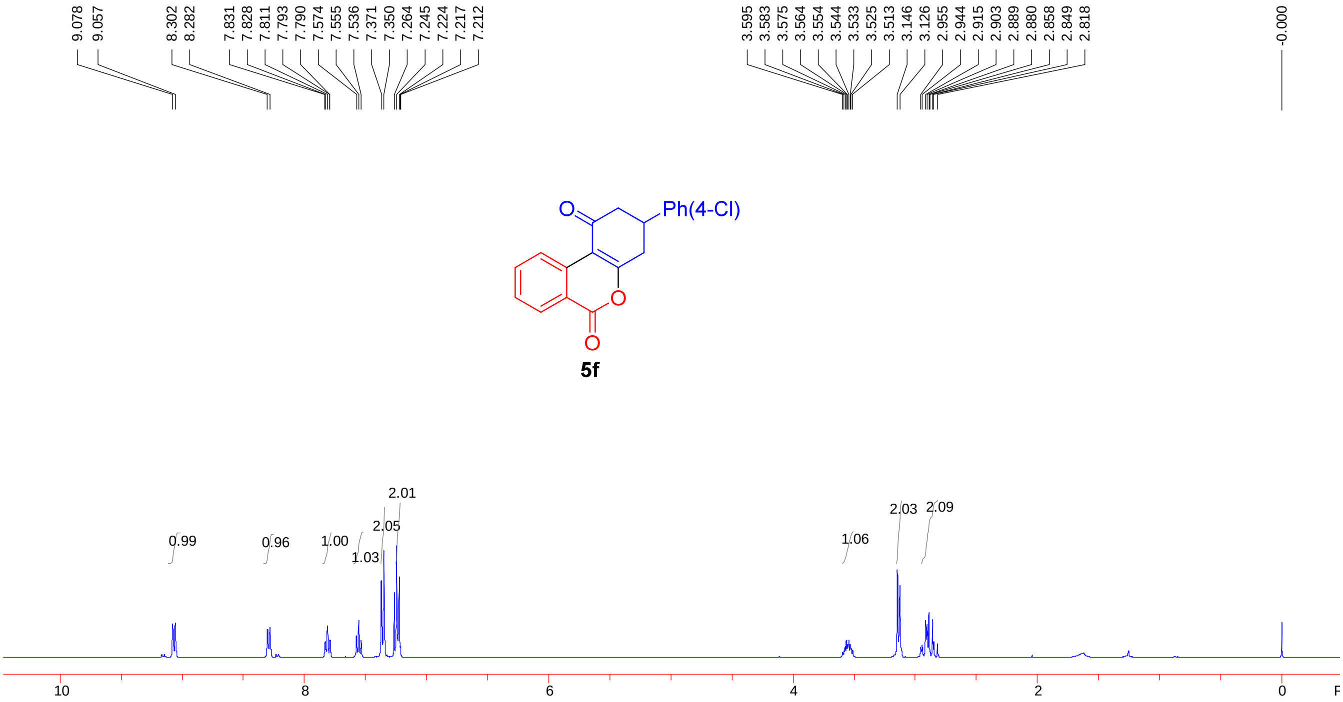
5e
200
150
100
50
0



5e



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7.536
7.371
7.350
7.264
7.245
7.224
7.217
7.212
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3.554
3.544
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2.944
2.915
2.903
2.889
2.880
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2.849
2.818
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2.05
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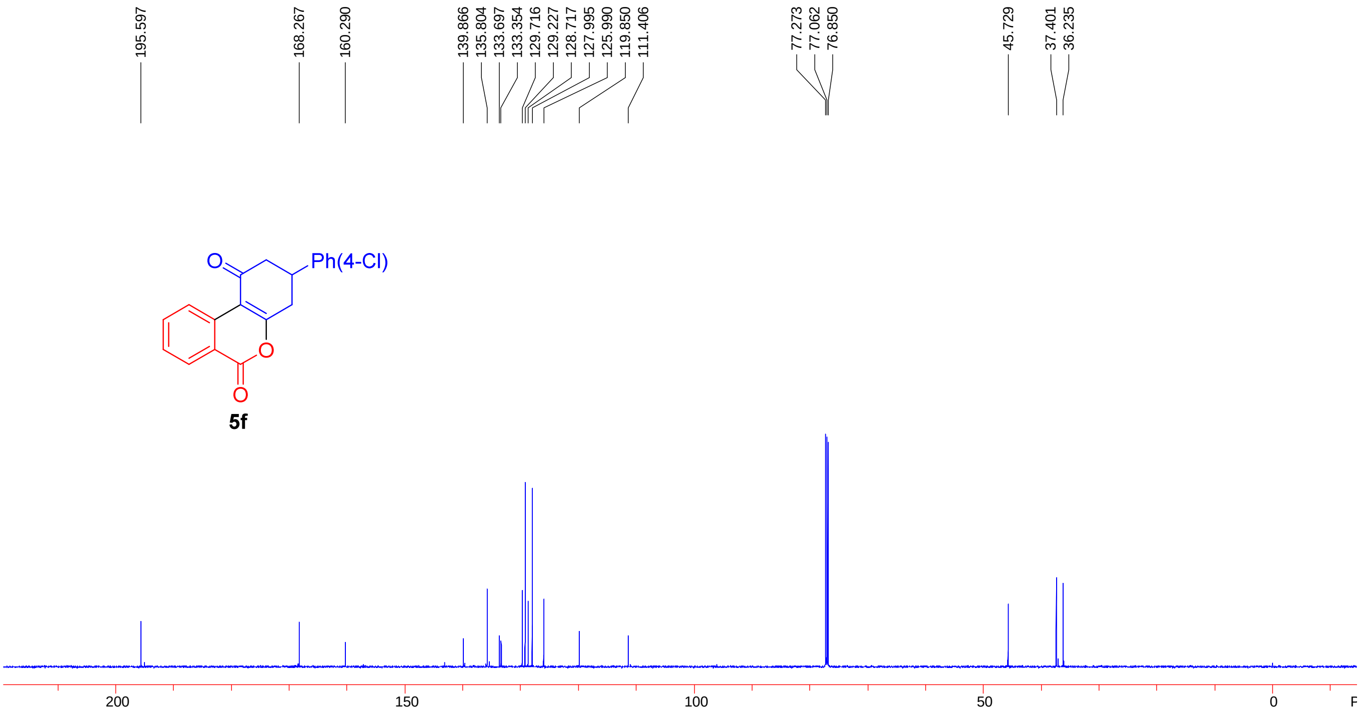
1.06
2.03
2.09



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168.267
160.290
139.866
135.804
133.697
133.354
129.716
129.227
128.717
127.995
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111.406
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77.062
76.850
45.729
37.401
36.235
Ph(4-Cl)
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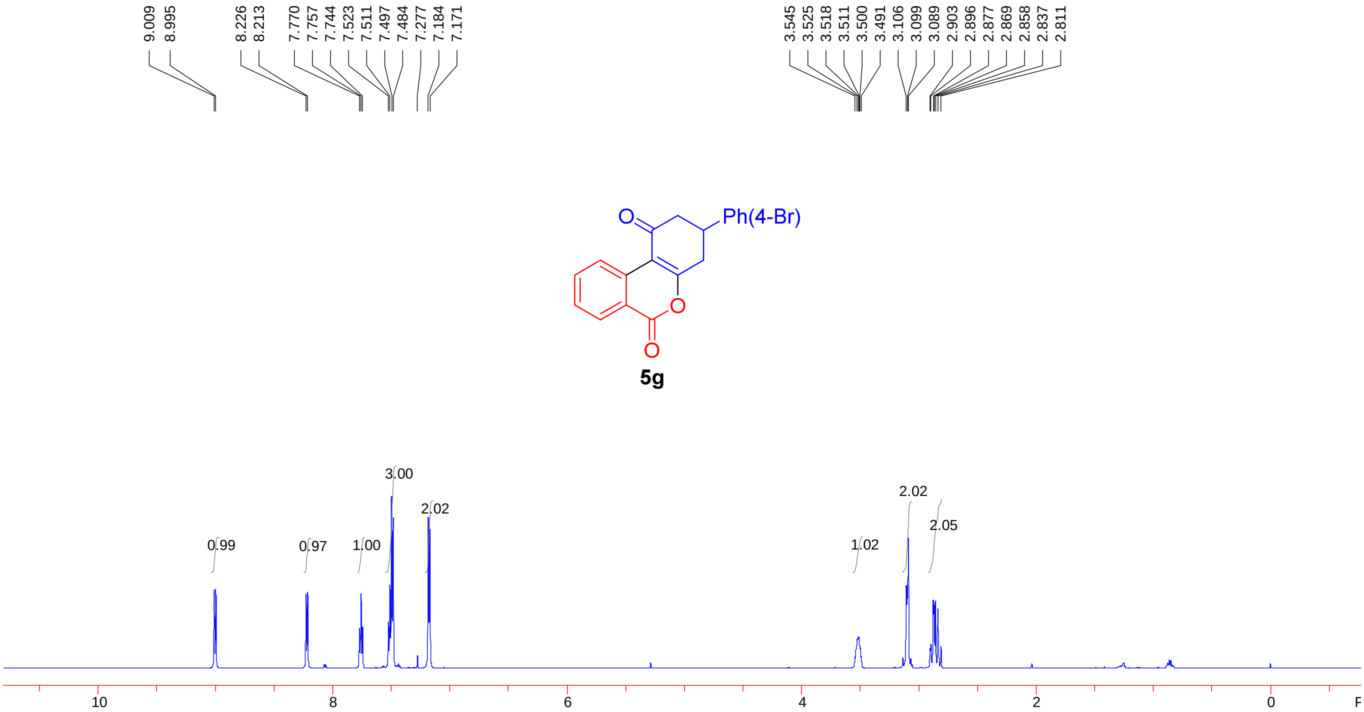
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7.171
3.545
3.525
3.518
3.511
3.500
3.491
3.106
3.099
3.089
2.903
2.896
2.877
2.869
2.858
2.837
2.811
Ph(4-Br)
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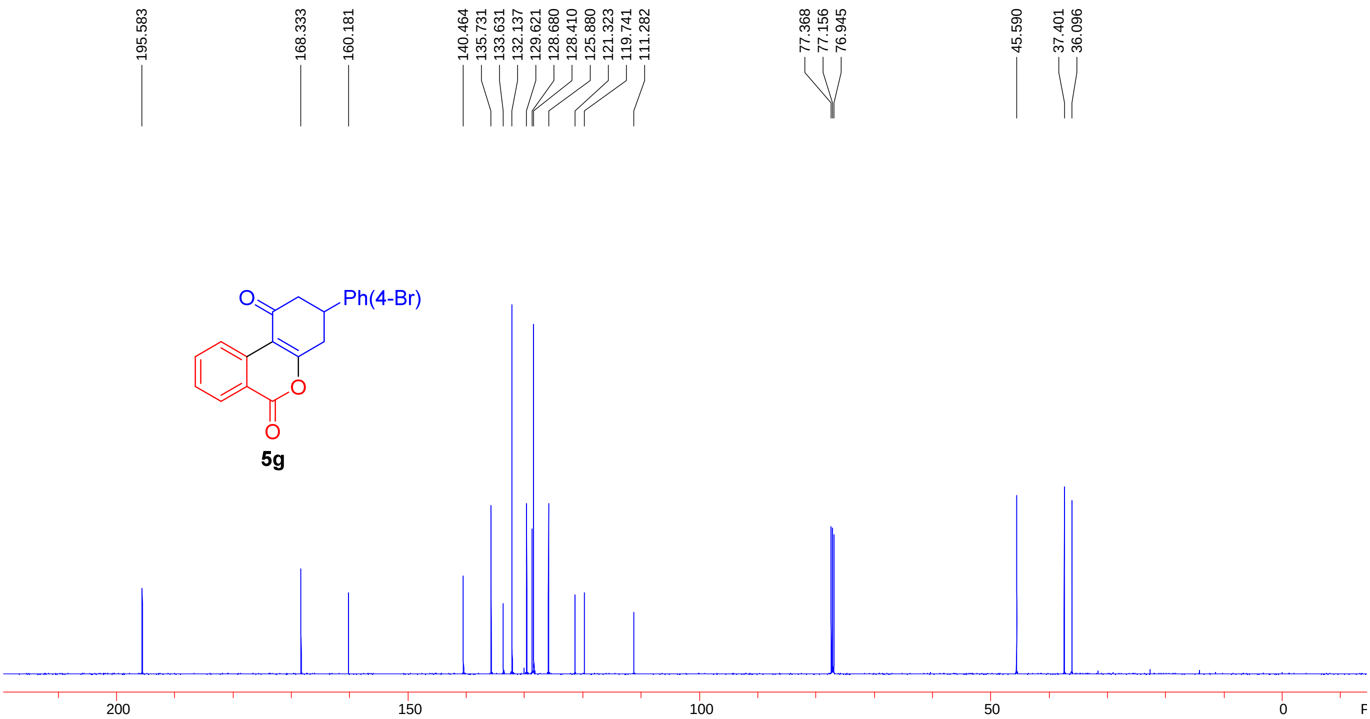
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36.096
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150
100
50
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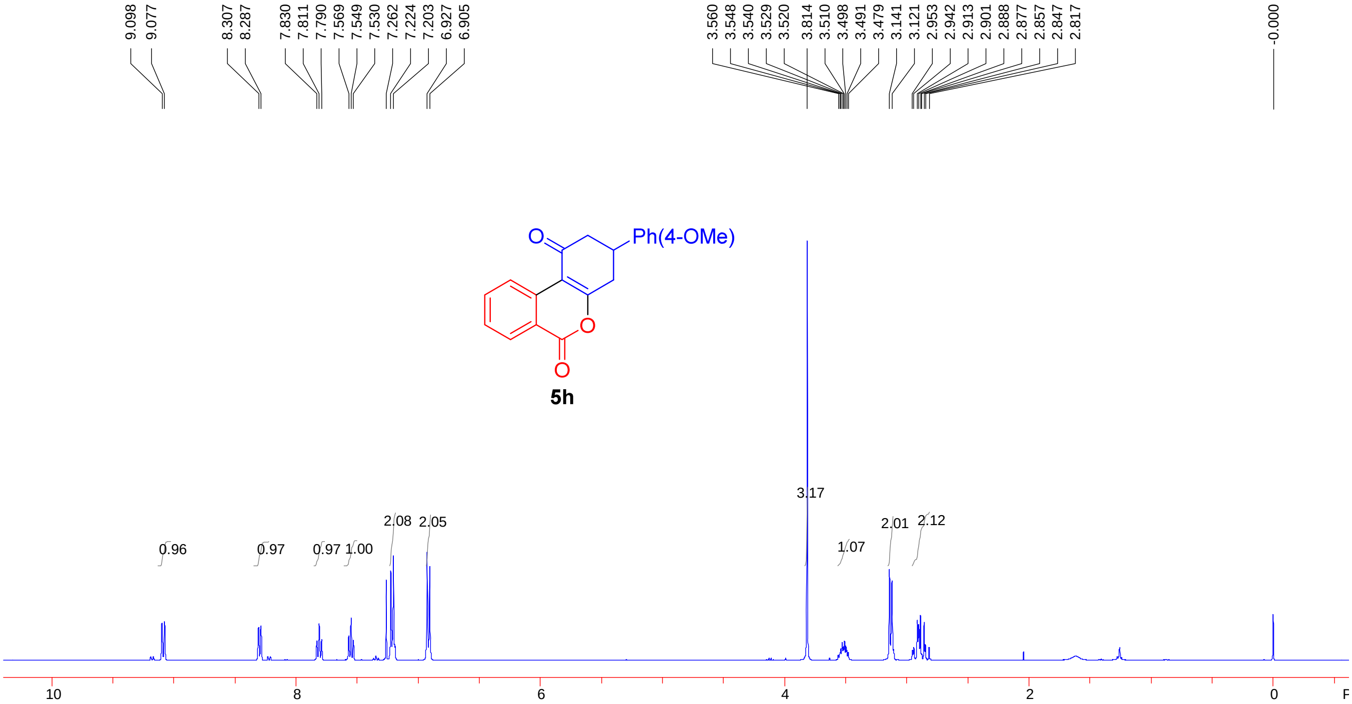
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7.569
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7.203
6.927
6.905
3.560
3.548
3.540
3.529
3.520
3.814
3.510
3.498
3.491
3.479
3.141
3.121
2.953
2.942
2.913
2.901
2.888
2.877
2.857
2.847
2.817
-0.000
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0.96
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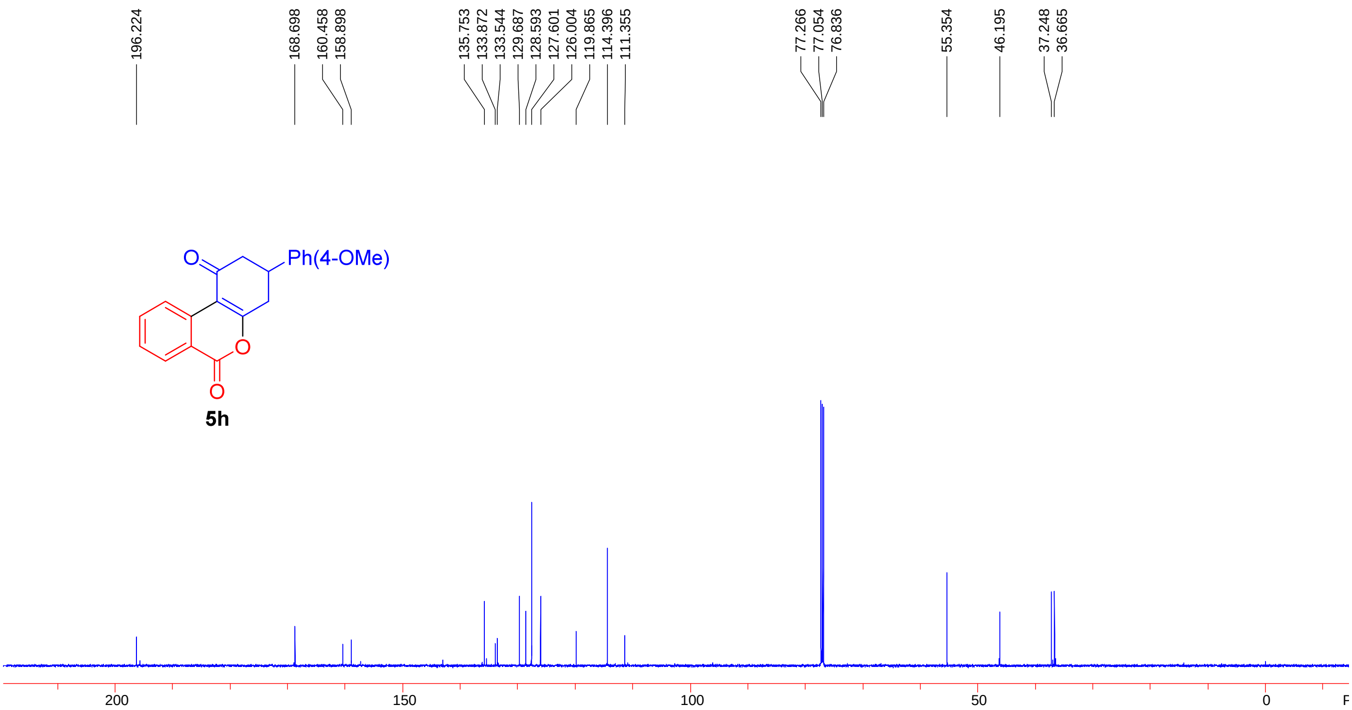
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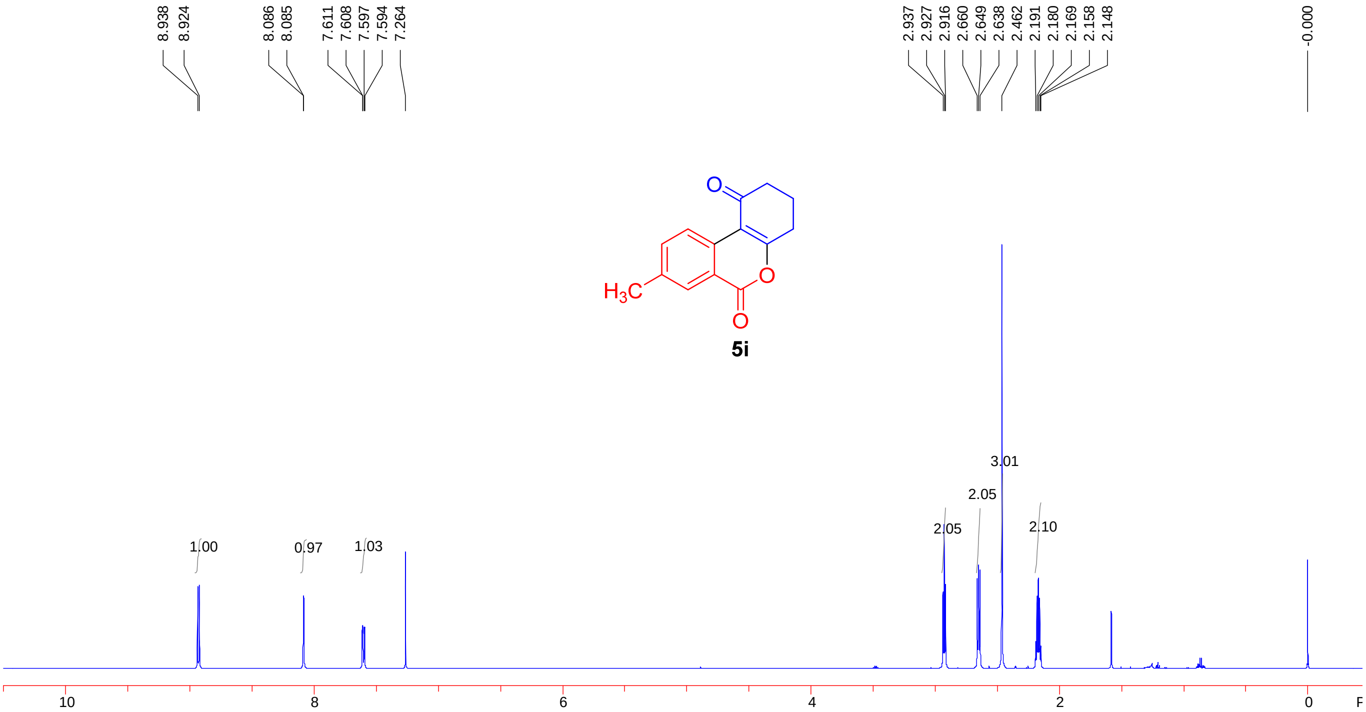
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2.660
2.649
2.638
2.462
2.191
2.180
2.169
2.158
2.148
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H3C
O
O
O
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1.03
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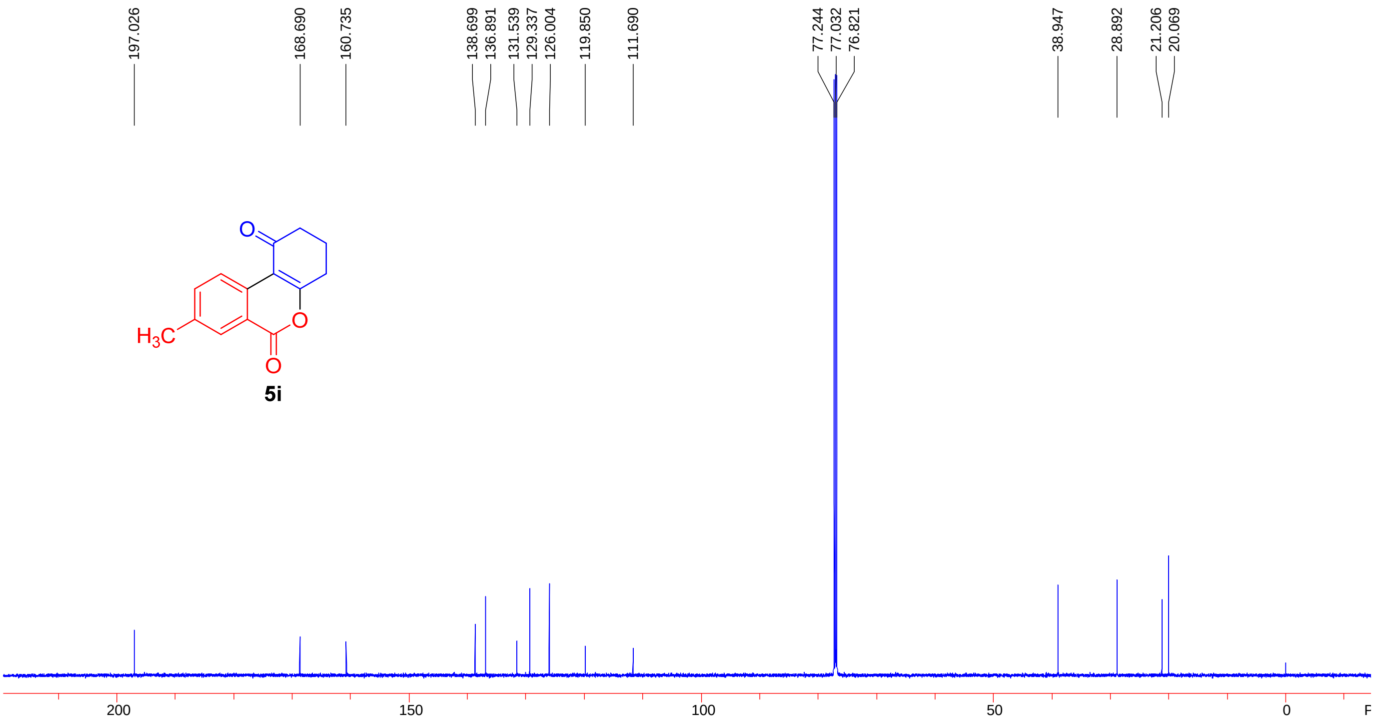
2.05
3.01
2.10
10
8
6
4
2
0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77.032
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28.892
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O
O
5i
200
150
100
50
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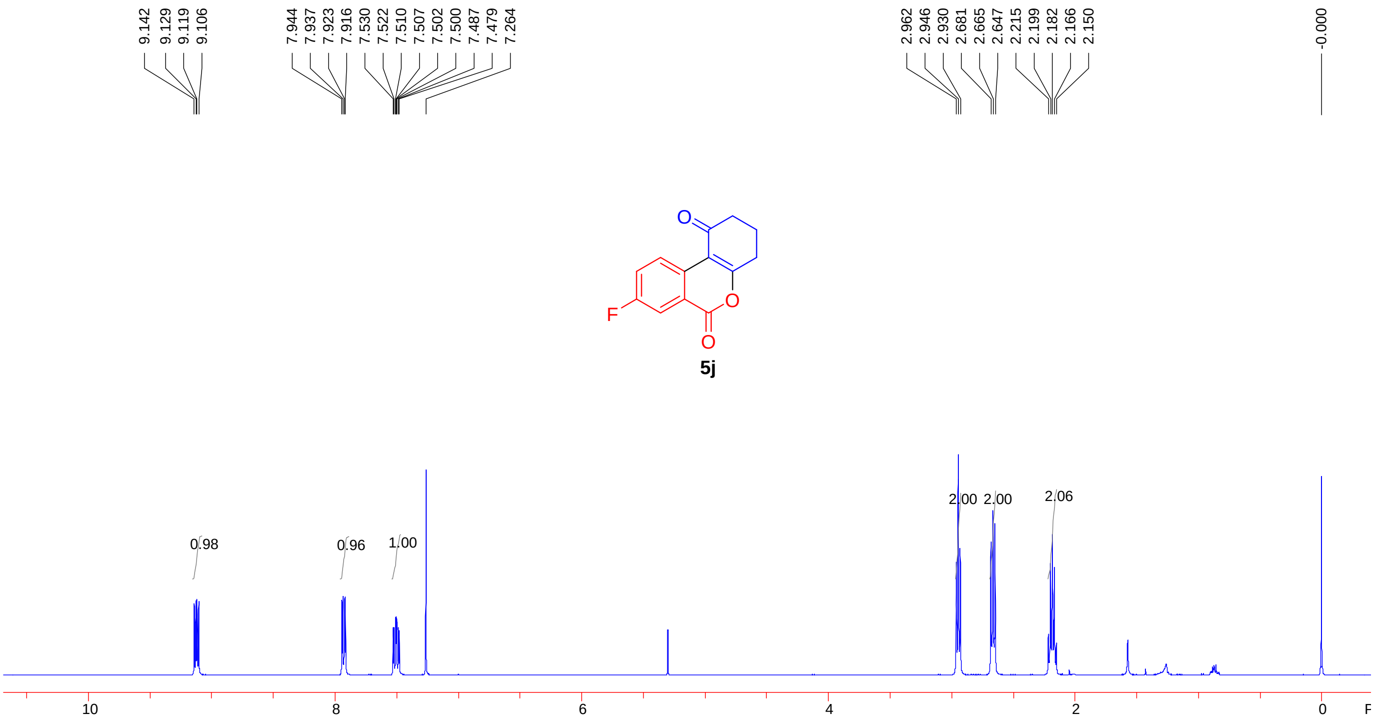
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7.507
7.502
7.500
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10
8
6
4
2
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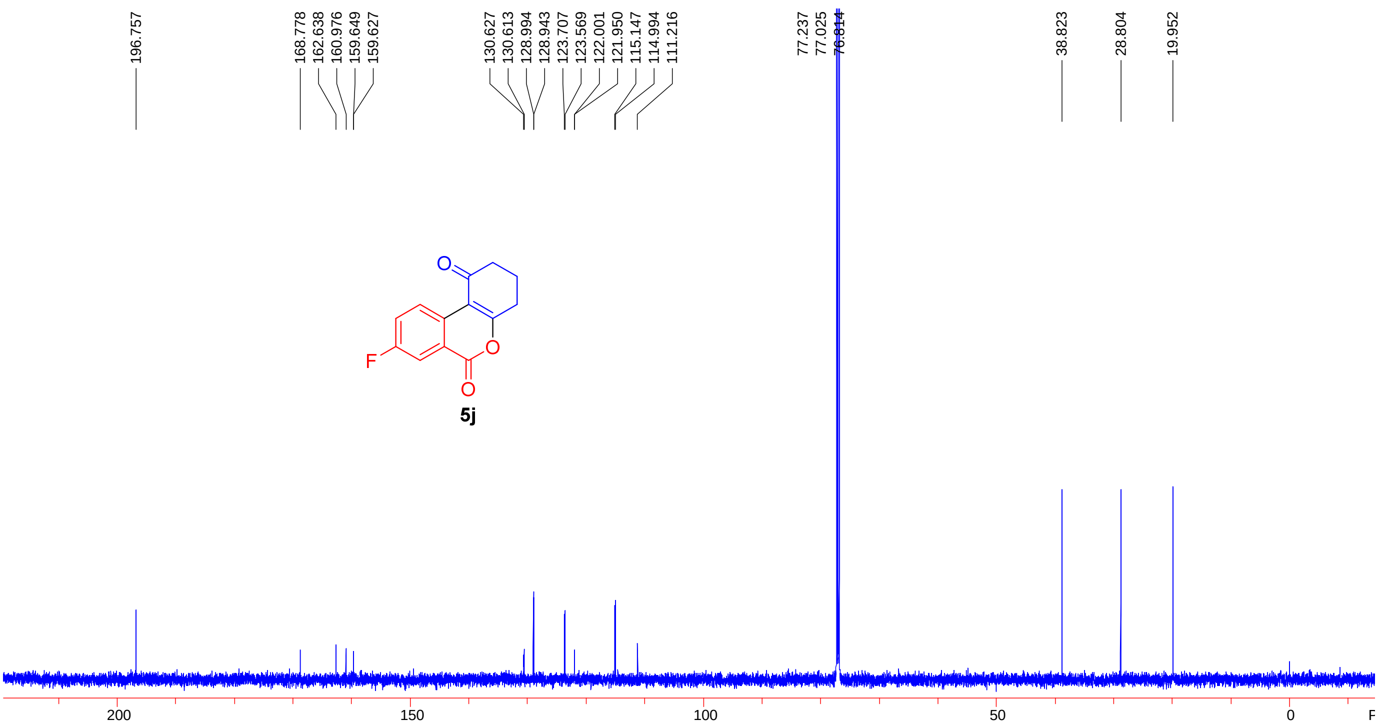
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123.569
122.001
121.950
115.147
114.994
111.216
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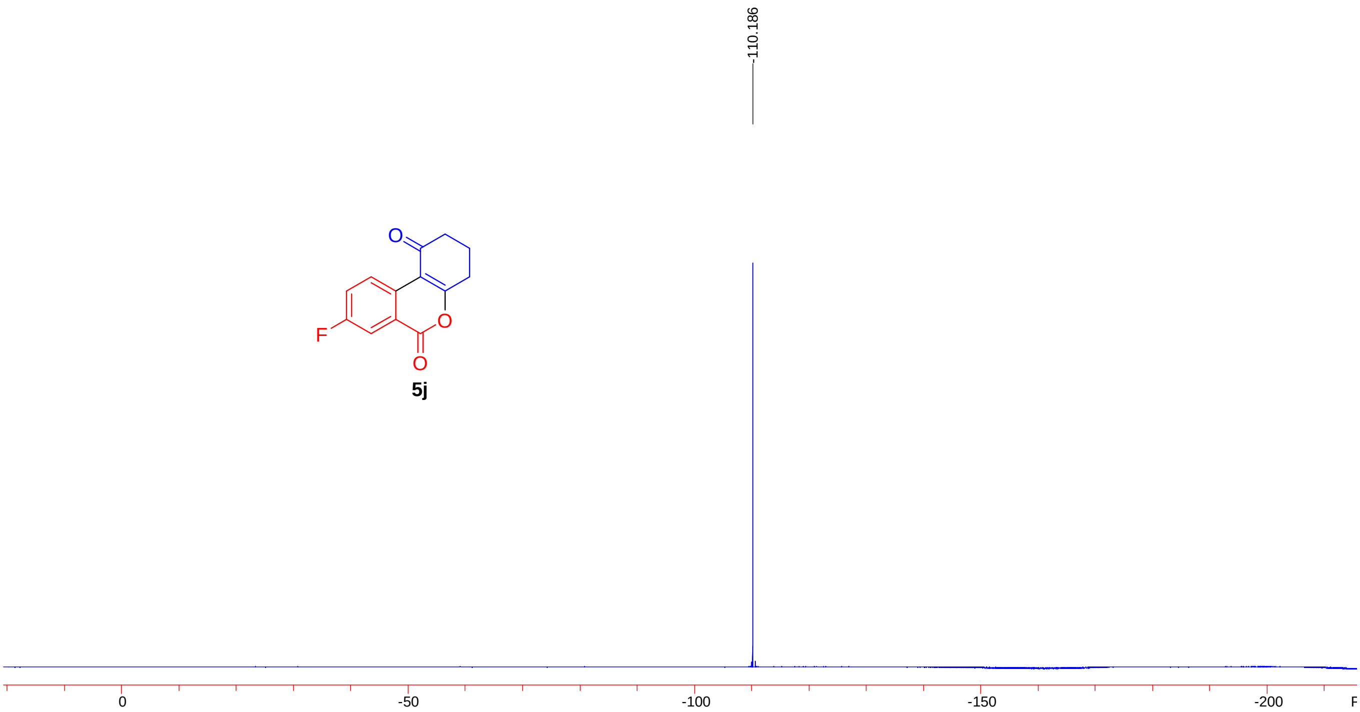
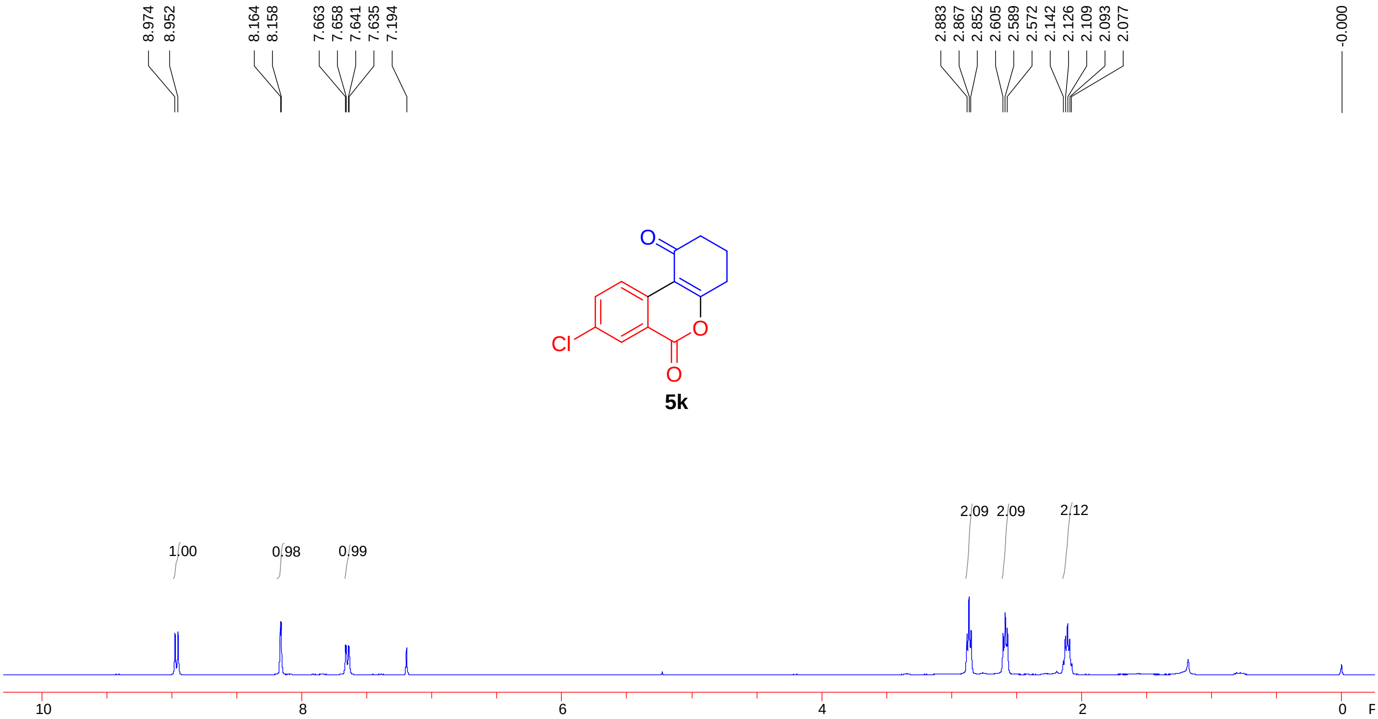
76.814
38.823
28.804
19.952
O
F
O
O
5j
200
150
100
50
0



5j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8.158
7.663
7.658
7.641
7.635
7.194
2.883
2.867
2.852
2.605
2.589
2.572
2.142
2.126
2.109
2.093
2.077
-0.000
Cl
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O
O
5k
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0.98
0.99
2.09
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2.12
10
8
6
4
2
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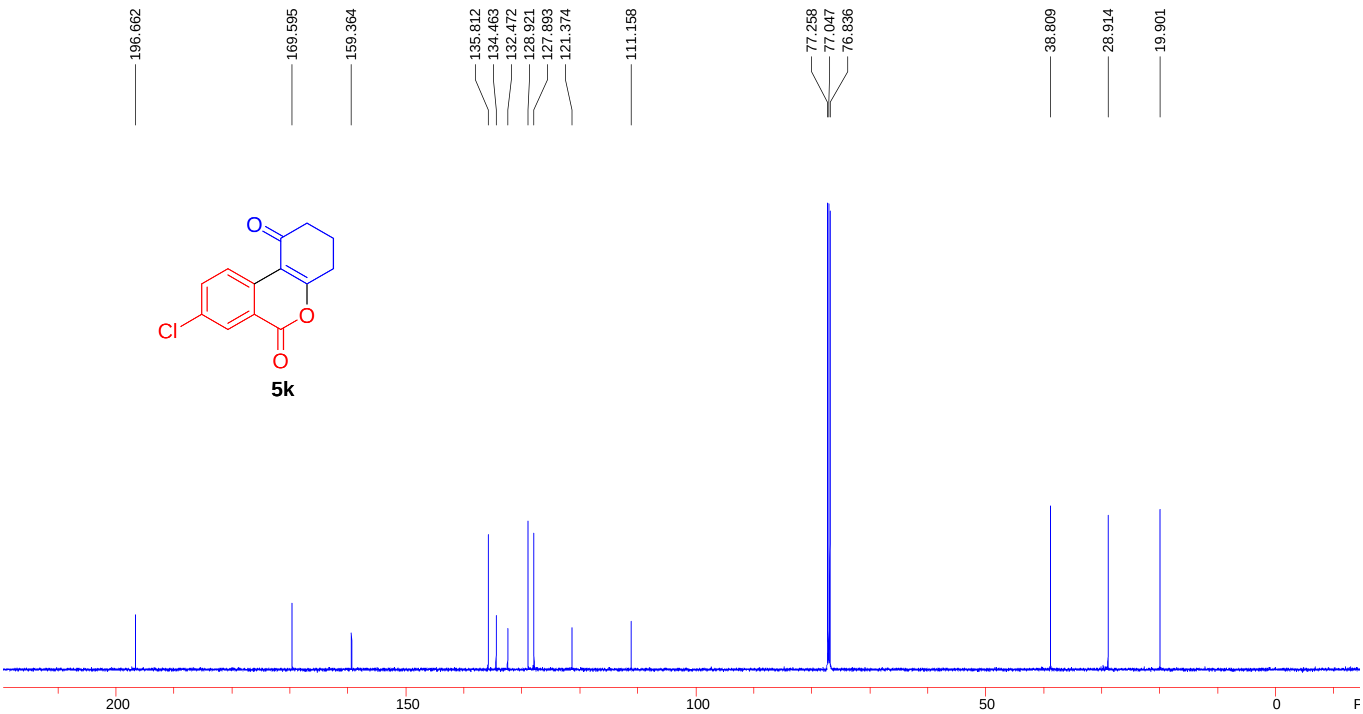
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O
5k
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150
100
50
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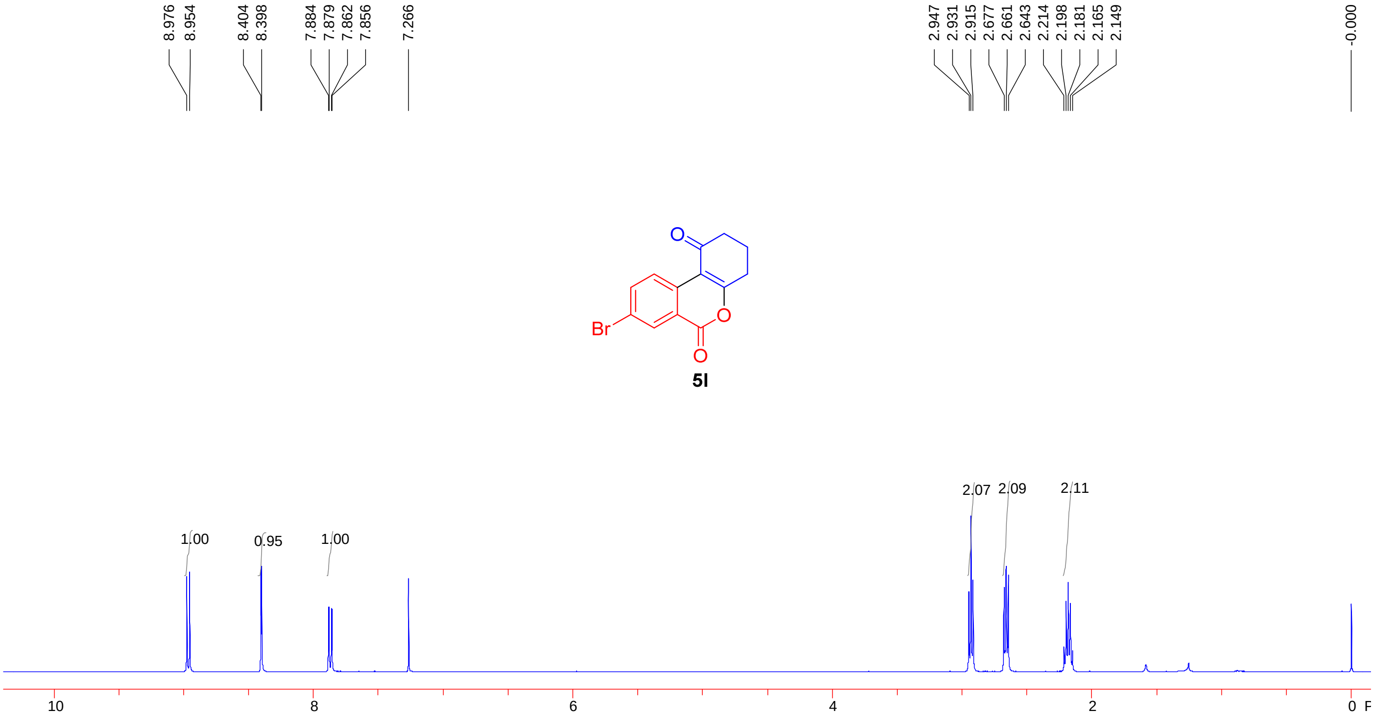
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8.404
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7.884
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7.862
7.856
7.266
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2.915
2.677
2.661
2.643
2.214
2.198
2.181
2.165
2.149
-0.000
O
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O
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5l
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2.11
10
8
6
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2
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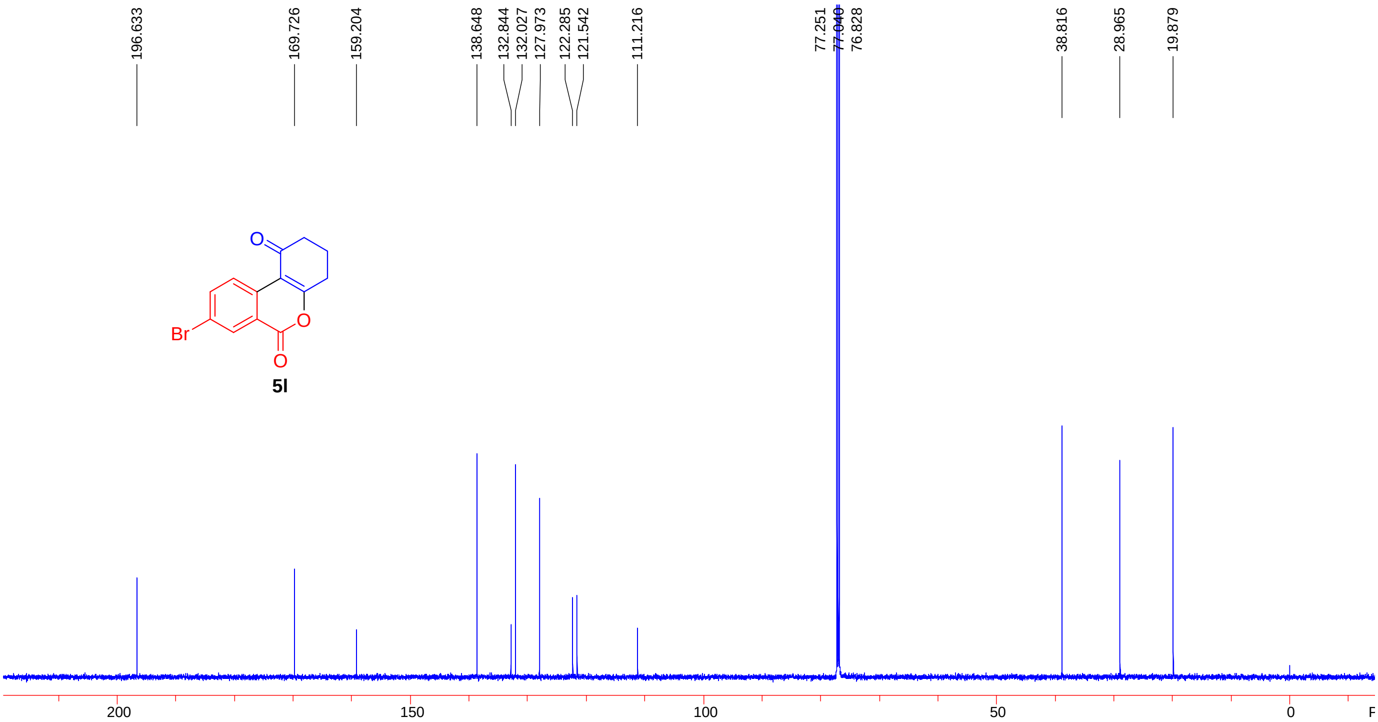
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76.828
38.816
28.965
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Br
O
O
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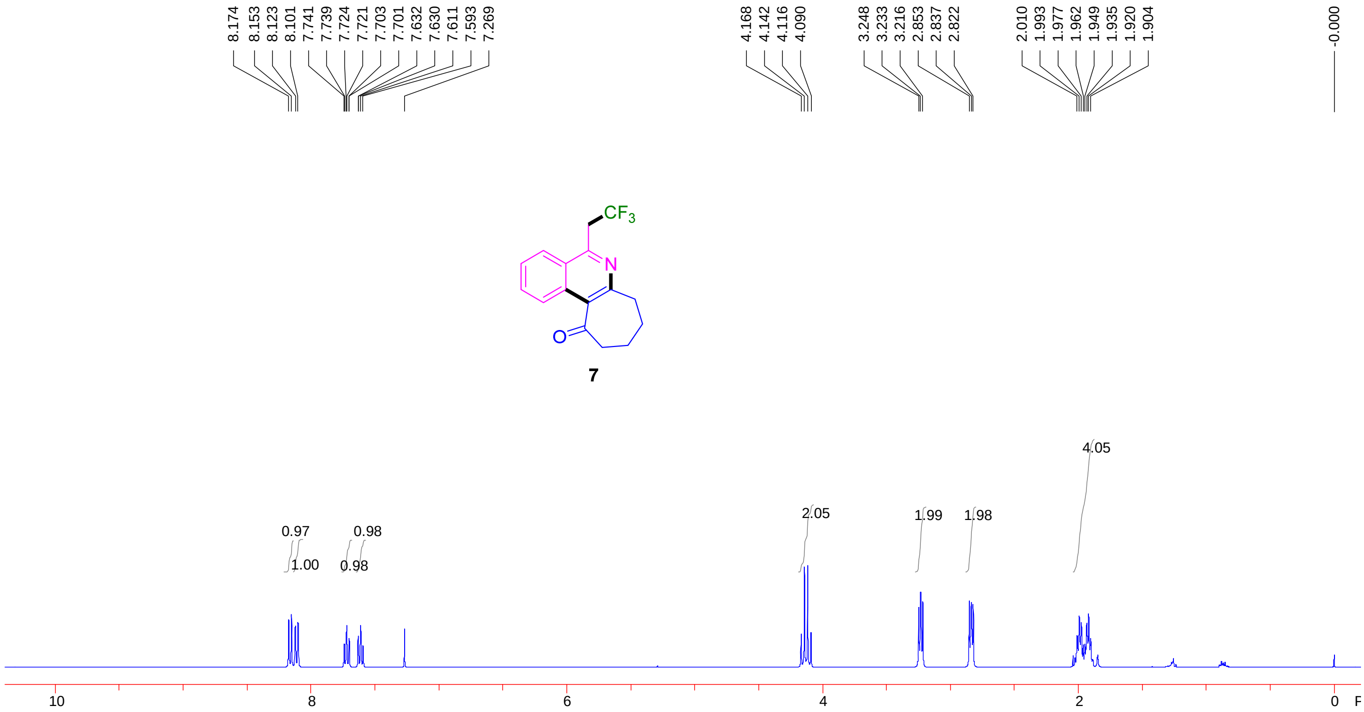
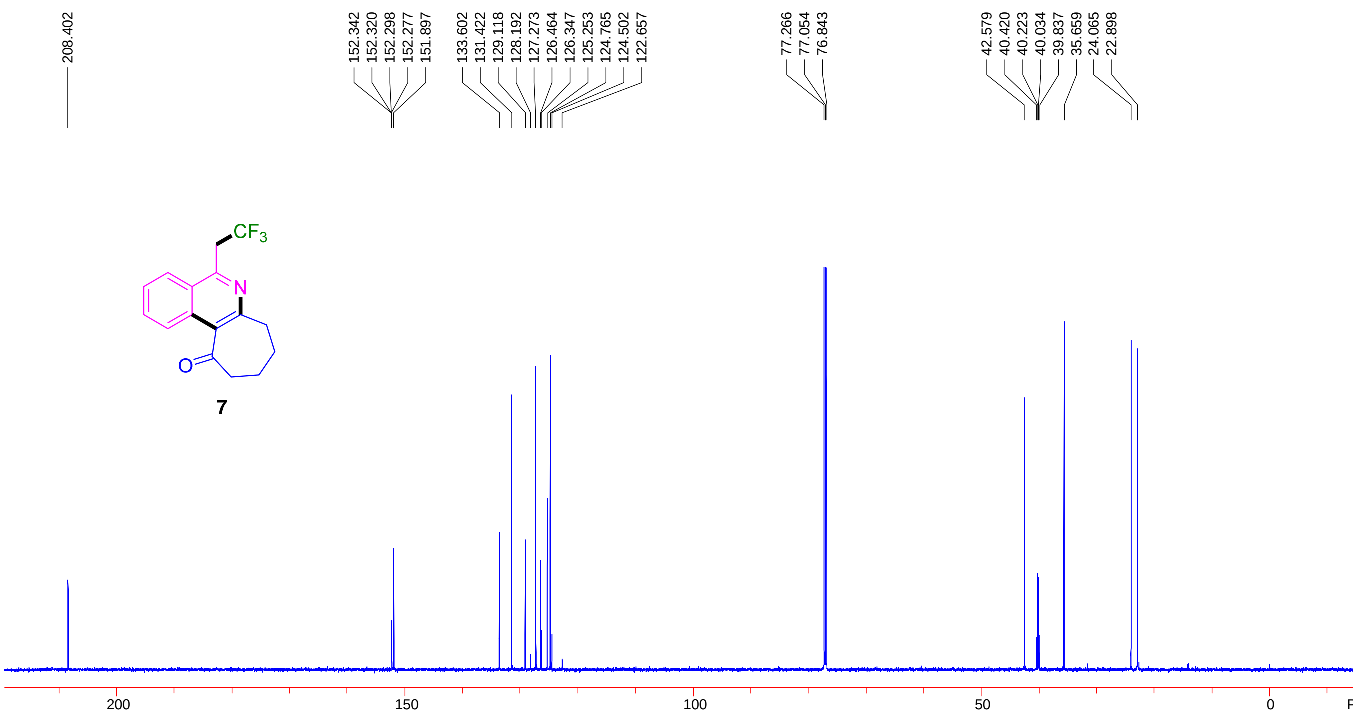
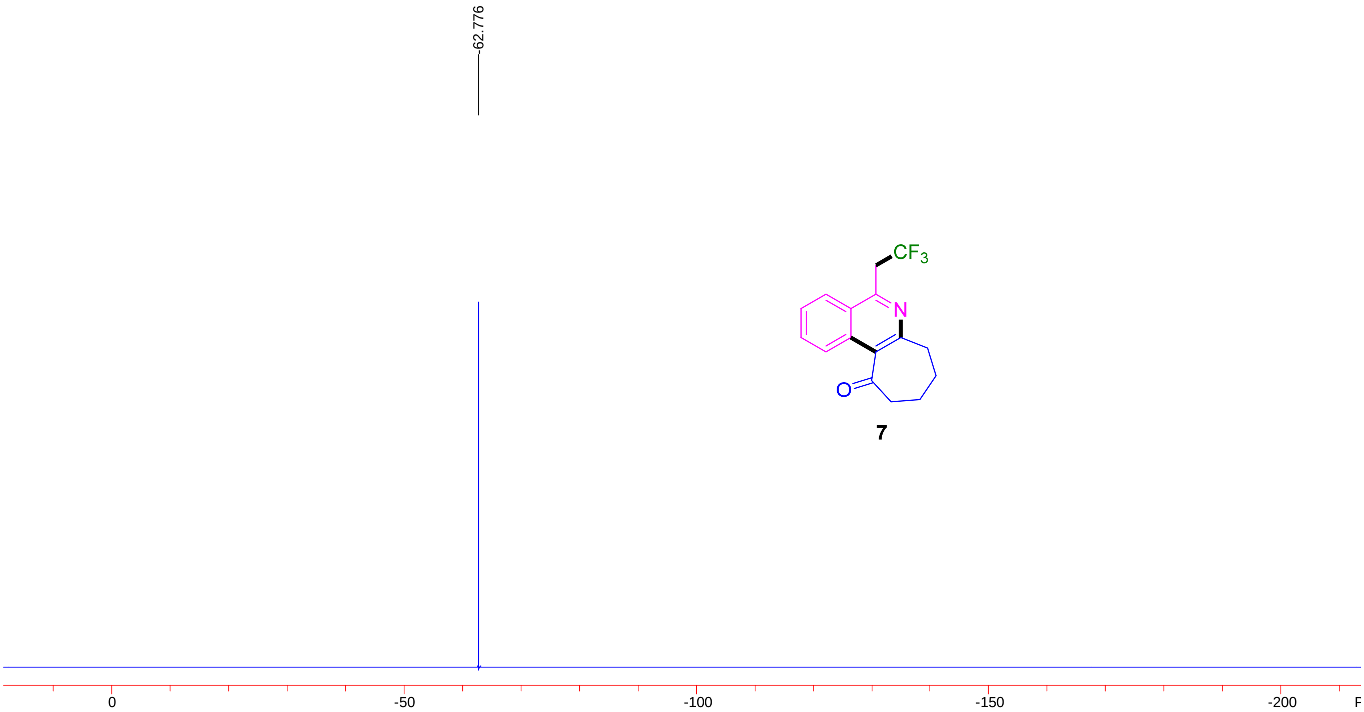
200
150
100
50
0

VI. Copies of ^{1}H and ^{13}C NMR spectra of 7 and 8



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N
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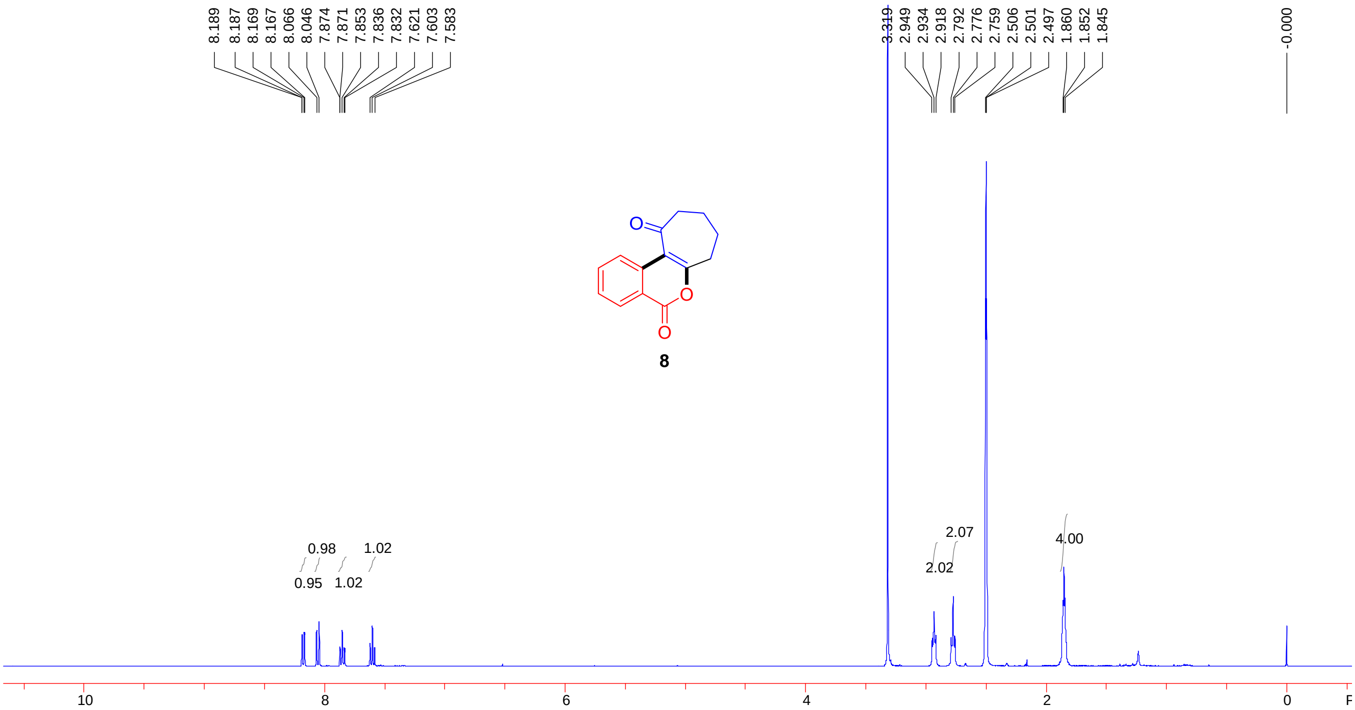
-50
-100
-150
-200
F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7.871
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7.836
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7.603
7.583
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2.949
2.934
2.918
2.792
2.776
2.759
2.506
2.501
2.497
1.860
1.852
1.845
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0.95
1.02
2.07
2.02
4.00
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2
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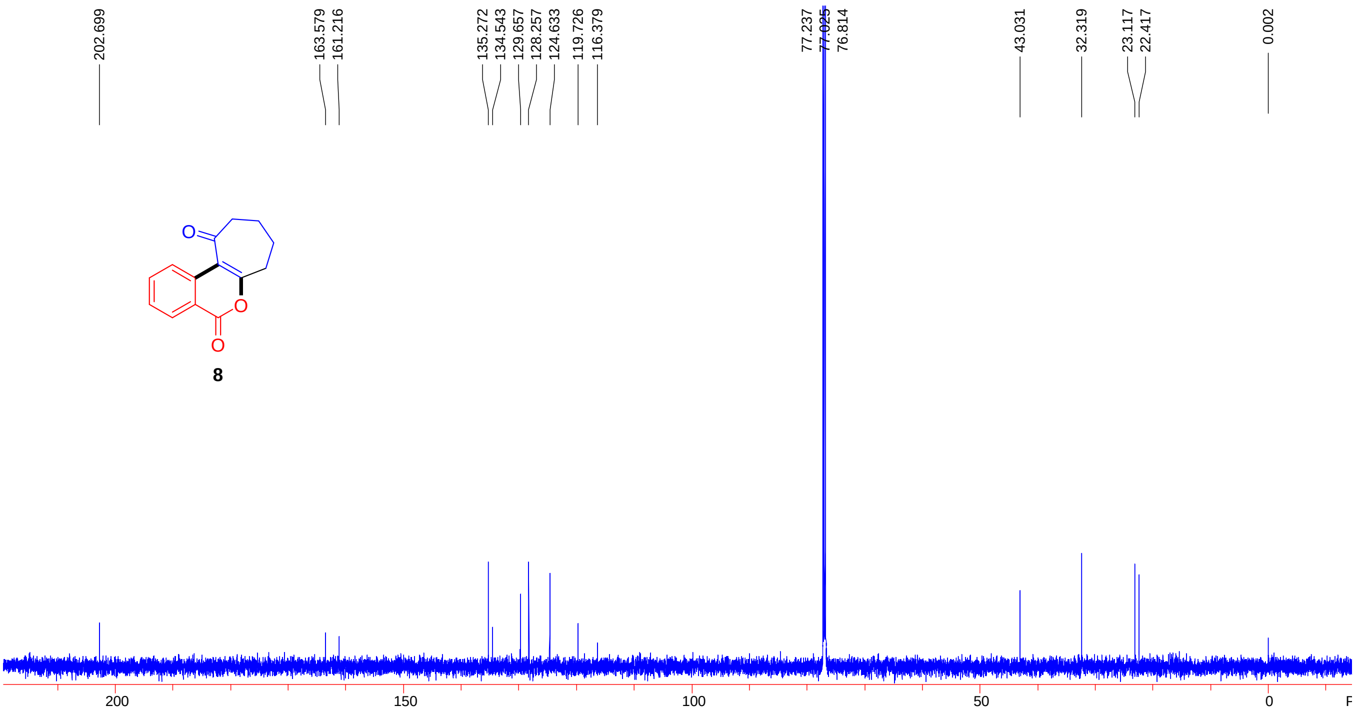
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116.379
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77.025
76.814
43.031
32.319
23.117
22.417
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150
100
50
0

VII. X-ray crystal structure and data of 4j

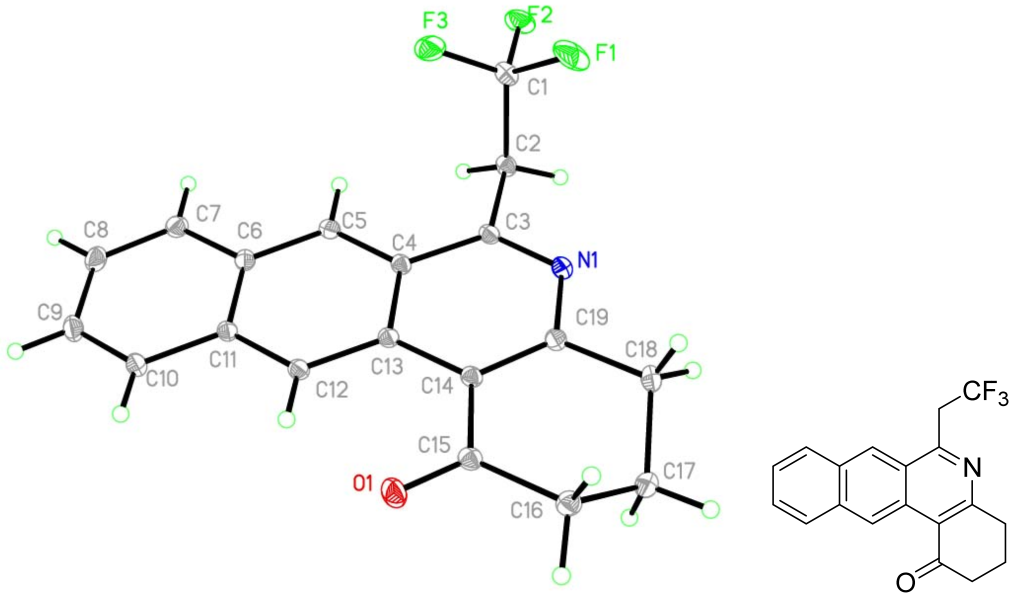

Fig. S1 X-ray structure of **4j** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a chloroform solution of **4j**. Crystal data collection and refinement parameters of **4j** are summarized in Table S2. Intensity data were collected at 170 K on a SuperNova Dual diffractometer using mirror-monochromated CuKα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **4j**

Empirical formula	$C_{19}H_{14}F_3NO$
Formula weight	329.31
Temp, K	169.99(10)
Crystal system	monoclinic
Space group	P21/c

a, Å	9.5181(2)
b, Å	21.4287(4)
c, Å	7.5942(2)
α (°)	90
β (°)	111.404(3)
γ (°)	90
Volume, Å^3	1442.09(6)
Z	4
d_{calc}, g cm^{-3}	1.517
λ, Å	1.54184
μ, mm^{-1}	1.023
No. of data collected	7876
No. of unique data	2760
R_{int}	0.0381
Goodness-of-fit on F^2	1.242
R_1, wR_2 (I> 2σ(I))	0.0527, 0.1379
R_1, wR_2 (all data)	0.0583, 0.1404

VIII. References

(1) H.-T. Qin, S.-W. Wu, J.-L. Liu and F. Liu, *Chem. Commun*., 2017, **53**, 1696.

(2) Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C. M. Park, *Chem. Commun*., 2012, **48**, 3133.

(3) J. Sun, X. Zhen, H. Ge, G. Zhang, X. An and Y. Du, *Beilstein J. Org. Chem*., 2018, **14**, 1452.

(4) K.-I. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto and R. Yamaguchi, *Org. Lett*., 2004, **6**, 2785.