Synthesis of 1-methyleneindenes via palladium-catalyzed tandem reactions

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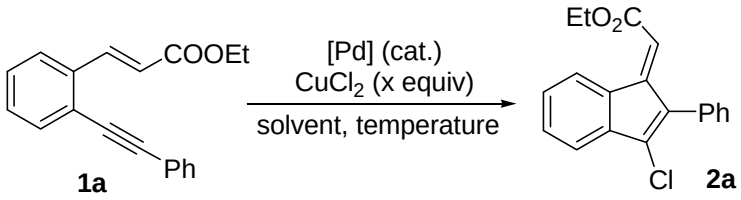
Supporting Information

General experimental methods:

All reactions were performed in reaction tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35°C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

Table 1. Initial Studies for Pd-Catalyzed Reaction of (*E*)-Ethyl 3-(2-(2-phenyl-ethynyl)phenyl)acrylate **1a**



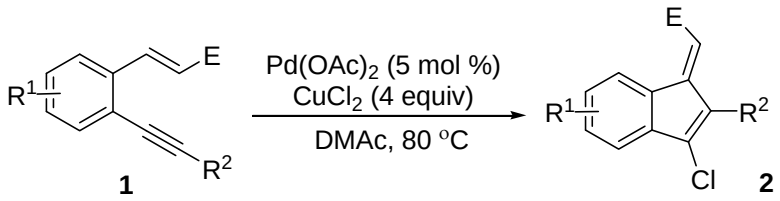
1a **2a**

entry	[Pd]	$CuCl_2$ (equiv)	Solvent / T (°C)	time (h)	yield (%)[a]
1	$PdCl_2$ (10 mol %)	2.0	DMAc / 120	6	40
2	$PdCl_2$ (10 mol %)	2.0	DMAc / 80	6	41
3	$PdCl_2$ (10 mol %)	2.0	DMAc / 50	72	40
4	$PdCl_2$ (10 mol %)	2.0	DMAc / rt	72	trace
5	$PdCl_2$ (10 mol %)	2.0	toluene / 80	12	trace
6	$PdCl_2$ (10 mol %)	2.0	dioxane / 80	12	8
7	$PdCl_2$ (10 mol %)	2.0	MeCN / 80	12	11
8	$PdCl_2$ (10 mol %)	2.0	DCE / 80	12	25
9	$PdCl_2$ (10 mol %)	2.0	THF / 80	12	trace
10	$PdCl_2$ (10 mol %)	2.0	DMF / 80	12	39

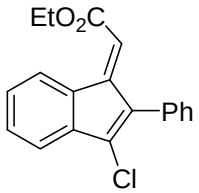
11	$PdCl_2$ (10 mol %)	2.0	DME / 80	12	20
12	$PdCl_2$ (10 mol %)	2.0	NMP / 80	6	36
13	$PdCl_2$ (10 mol %)	2.0	DMSO / 80	12	NR
14	$PdCl_2$ (10 mol %)	4.0	DMAc / 80	3	57
15	$PdCl_2$ (10 mol %)	6.0	DMAc / 80	7	54
16	-	4.0	DMAc / 80	24	NR
17	$PdCl_2$ (5 mol %)	4.0	DMAc / 80	5	58
18	$PdCl_2(PPh_3)_2$ (5 mol %)	4.0	DMAc / 80	24	53
19	$Pd(OAc)_2$ (5 mol %)	4.0	DMAc / 80	3	66
20	$Pd(TFA)_2$ (5 mol %)	4.0	DMAc / 80	3	57
21	$PdCl_2$(dppf) (5 mol %)	4.0	DMAc / 80	12	33
22	$Pd(OAc)_2$ (2 mol %)	4.0	DMAc / 80	12	55

[a]Isolated yield based on (*E*)-ethyl 3-(2-alkynylphenyl)acrylate **1a**

General procedure for Pd-catalyzed reaction of 2-alkenylphenylacetylene 1 in the presence of $CuCl_2$.

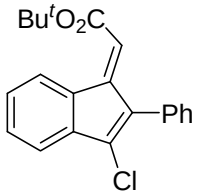


2-Alkenylphenylacetylene **1** (0.25 mmol) was added to a solution of $Pd(OAc)_2$ (0.0125 mmol, 5 mol %) and $CuCl_2$ (1 mmol, 4 equiv) in DMAc (1.0 mL). The solution was then stirred at 80 °C. After completion of reaction as indicated by TLC, the reaction was quenched with aqueous HCl (1.0 M), extracted with EtOAc (2x10 mL), dried by anhydrate Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the product **2**.



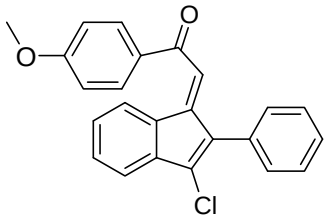
(*E*)-Ethyl 2-(3-chloro-2-phenyl-1*H*-inden-1-ylidene)acetate (2a)

Yield: 66% (51 mg), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.18 (s, 1H), 7.31-7.49 (m, 8H), 8.64 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 60.9, 119.0, 120.5, 127.0, 128.1, 128.2, 128.4, 130.3, 130.5, 131.5, 131.7, 136.2, 137.6, 140.8, 149.4, 165.9; IR (KBr): ν_{max}/cm^{-1} 3060, 2979, 1713, 1619, 1449; MS (ESI): *m/z* 311 (M^++1), 333 (M^++Na); HRMS (ESI) calcd for $C_{19}H_{15}ClNaO_2$ (M + Na^+) 333.0658, found 333.0668.



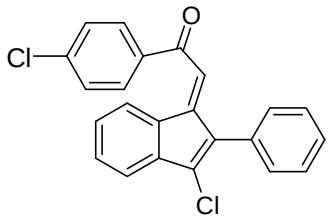
(*E*)-*tert*-Butyl 2-(3-chloro-2-phenyl-1*H*-inden-1-ylidene)acetate (2b)

Yield: 60% (51 mg), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 9H), 6.13 (s, 1H), 7.30 - 7.50 (m, 8H), 8.56 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 81.6, 118.9, 122.7, 126.7, 127.9, 128.2, 128.3, 130.0, 130.5, 131.6, 131.9, 135.5, 137.6, 140.7, 147.7, 165.5; IR (KBr): ν_{max}/cm^{-1} 3060, 2974, 1713, 1445, 1367; MS (ESI): *m/z* 339 (M^++1), 361 (M^++Na); HRMS (ESI) calcd for $C_{21}H_{19}ClNaO_2$ (M + Na^+) 361.0971, found 361.1007.



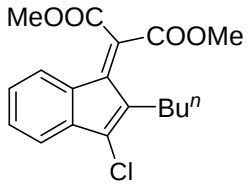
(*E*)-2-(3-Chloro-2-phenyl-1*H*-inden-1-ylidene)-1-(4-methoxyphenyl)ethanone (2c)

Yield: 90% (84 mg), red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.98 (s, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.45 (m, 3H), 7.48 – 7.52 (m, 4H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 114.0, 119.0, 125.1, 127.3, 127.6, 128.2, 128.4, 129.7, 130.3, 130.4, 131.3, 131.8, 131.9, 135.0, 137.0, 140.6, 145.5, 164.1, 191.8; IR (KBr): ν_{max}/cm^{-1} 3056, 2924, 1658, 1596, 1444; MS (ESI): *m/z* 373 (M^++1); HRMS (ESI) calcd for $C_{24}H_{18}ClO_2$ (M + H^+) 373.0995, found 373.1025.



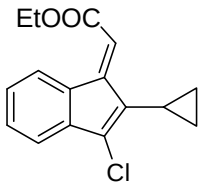
(*E*)-2-(3-Chloro-2-phenyl-1*H*-inden-1-ylidene)-1-(4-chlorophenyl)ethanone (2d)

Yield: 71% (67 mg), red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.35 – 7.52 (m, 9H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ 119.2, 125.3, 125.7, 127.9, 128.3, 128.5, 129.1, 130.1, 130.2, 130.4, 131.6, 131.7, 135.8, 136.1, 137.1, 140.1, 140.7, 147.3, 191.5; IR (KBr): ν_{max}/cm^{-1} 3056, 2928, 1666, 1593, 1445; MS (ESI): *m/z* 377 (M^++1); HRMS (ESI) calcd for $C_{23}H_{15}ClO_2$ (M + H^+) 377.0500, found 377.0524.



Dimethyl 2-(2-butyl-3-chloro-1*H*-inden-1-ylidene)malonate (2e)

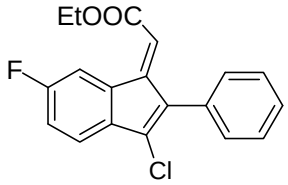
Yield: 95% (79 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.33 – 1.38 (m, 2H), 1.41 – 1.47 (m, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 3.88 (s, 3H), 3.94 (s, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.8, 165.3, 25.7, 31.3, 52.9, 53.2, 118.7, 123.5, 127.2, 130.1, 132.7, 135.6, 139.9, 140.0, 143.2, 165.0; IR (KBr): ν_{max}/cm^{-1} 2951, 2874, 1724, 1600, 1460; MS (ESI): *m/z* 335 (M^++1); HRMS (ESI) calcd for $C_{18}H_{20}ClO_4$ (M + H^+) 335.1050, found 335.1075.



(*E*)-Ethyl 2-(3-chloro-2-cyclopropyl-1*H*-inden-1-ylidene)acetate (2f)

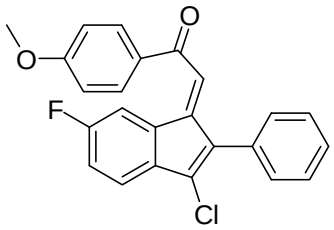
Yield: 54% (37 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 – 0.81 (m, 2H), 0.96 – 1.00 (m, 2H), 1.38 (t, *J* = 7.6 Hz, 3H), 1.50 – 1.56 (m, 1H), 4.32 (q, *J* = 7.6 Hz, 2H), 6.70 (s, 1H), 7.22 – 7.25 (m, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 8.52 (d, *J* = 7.3

Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.8, 6.2, 14.3, 60.8, 117.9, 118.4, 126.8, 127.7, 130.0, 131.5, 136.4, 137.0, 141.2, 150.1, 166.1; IR (KBr): ν_{max}/cm^{-1} 3072, 2975, 2940, 1717, 1631, 1449; MS (ESI): *m/z* 275 (M^++1); HRMS (ESI) calcd for $C_{16}H_{16}ClO_2$ (M + H^+) 275.0839, found 275.0839.



(*E*)-Ethyl 2-(3-chloro-6-fluoro-2-phenyl-1*H*-inden-1-ylidene)acetate (2g)

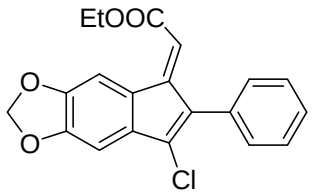
Yield: 55% (45 mg), red solid, melting point: 58.5-59.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 6.21 (s, 1H), 7.09 (dt, *J* = 2.0, 8.3 Hz, 1H), 7.30 (dd, *J* = 5.0, 8.3 Hz, 1H), 7.35 – 7.36 (m, 2H), 7.42 (t, *J* = 7.5, 1H), 7.47 – 7.49 (m, 2H), 8.49 (dd, *J* = 2.0, 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 61.1, 115.7 (d, $^2J_{CF}$ = 28.1 Hz), 116.3 (d, $^2J_{CF}$ = 24.0 Hz), 119.7 (d, $^3J_{CF}$ = 7.8 Hz), 121.4, 128.3, 128.4, 130.4, 131.5, 133.3 (d, $^3J_{CF}$ = 9.9 Hz), 135.6, 136.8, 137.5, 148.7, 163.3 (d, $^1J_{CF}$ = 243.7 Hz), 165.7; IR (KBr): ν_{max}/cm^{-1} 3107, 2975, 1717, 1584, 1460; MS (ESI): *m/z* 329 (M^++1); HRMS (ESI) calcd for $C_{19}H_{15}ClFO_2$ (M + H^+) 329.0745, found 329.0742. Elem. Anal. Calcd for $C_{19}H_{14}ClFO_2$: C, 69.41; H, 4.29; Found: C, 69.46; H, 4.14.



(*E*)-2-(3-Chloro-6-fluoro-2-phenyl-1*H*-inden-1-ylidene)-1-(4-methoxyphenyl)ethanone (2h)

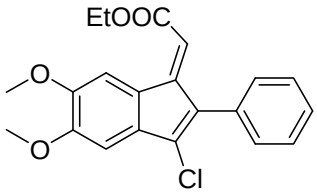
Yield: 64% (63 mg), red solid, melting point: 124.1-124.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.04 (dt, *J* = 2.3, 8.7 Hz, 1H), 7.06 (s, 1H), 7.30 (dd, *J* = 5.0, 8.3 Hz, 1H), 7.43 – 7.53 (m, 5H), 7.76 (dd, *J* = 2.3, 9.6 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 113.6 (d, $^2J_{CF}$ = 26.7 Hz), 114.0, 116.0 (d, $^2J_{CF}$ = 22.9 Hz), 119.7 (d, $^3J_{CF}$ = 8.6 Hz), 127.9, 128.3,

128.5, 130.3, 130.4, 131.3, 131.7, 133.6 (d ,$^{3}J_{CF}$ = 9.5 Hz), 134.6, 136.5, 136.9, 145.1, 162.9 (d, $^{1}J_{CF}$ = 245.0 Hz), 164.1, 191.0; IR (KBr): ν_{max}/cm^{-1} 3106, 2932, 2835, 1650, 1592, 1456; MS (ESI): *m/z* 391 (M^{+}+1); HRMS (ESI) calcd for $C_{24}H_{17}ClFO_2$ (M + H^{+}) 391.0901, found 391.0930. Elem. Anal. Calcd for $C_{24}H_{16}ClFO_2$: C, 73.75; H, 4.13; Found: C, 73.55; H, 3.97.



(*E*)-Ethyl 2-(7-chloro-6-phenyl-5*H*-indeno[5,6-*d*][1,3]dioxol-5-ylidene)acetate (2i)

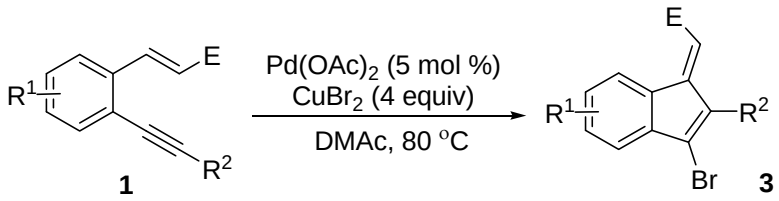
Yield: 72% (64 mg), red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.1 Hz, 3H), 4.25 (q, *J* = 7.1 Hz, 2H), 6.01 (s, 2H), 6.09 (s, 1H), 6.86 (s, 1H), 7.33 – 7.34 (m, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.44 – 7.47 (m, 2H), 8.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 60.8, 100.8, 101.7, 109.2, 119.8, 125.4, 128.0, 128.3, 130.5, 131.7, 135.0, 136.5, 136.6, 147.6, 149.1, 165.9; IR (KBr): ν_{max}/cm^{-1} 3115, 2986, 2924, 1716, 1588, 1460; MS (ESI): *m/z* 355 (M^{+}+1); HRMS (ESI) calcd for $C_{20}H_{16}ClO_4$ (M + H^{+}) 355.0737, found 355.0767.



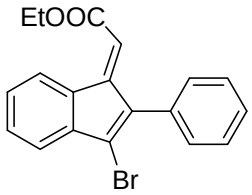
(*E*)-Ethyl 2-(3-chloro-5,6-dimethoxy-2-phenyl-1*H*-inden-1-ylidene)acetate (2j)

Yield: 78% (72 mg), red solid, melting point: 113.3-113.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.3 Hz, 3H), 3.98 (s, 3H), 3.99 (s, 3H), 4.25 (q, *J* = 7.3 Hz, 2H), 6.11 (s, 1H), 6.92 (s, 1H), 7.34 – 7.48 (m, 5H), 8.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 56.1, 56.3, 60.7, 102.7, 112.1, 119.3, 123.9, 128.0, 128.2, 130.5, 131.8, 134.8, 135.5, 136.3, 148.5, 150.1, 150.7, 166.1; IR (KBr): ν_{max}/cm^{-1} 3122, 3048, 2932, 2831, 1713, 1600, 1483; MS (ESI): *m/z* 371 (M^{+}+1); HRMS (ESI) calcd for $C_{21}H_{20}ClO_4$ (M + H^{+}) 371.1050, found 371.1076. Elem. Anal. Calcd for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16; Found: C, 68.02; H, 4.96.

General procedure for Pd-catalyzed reaction of 2-alkenylphenylacetylene 1 in the presence of $CuBr_2$.

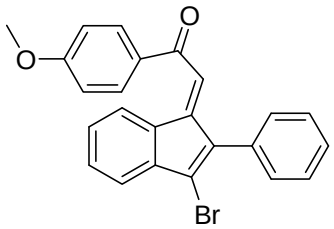


2-Alkenylphenylacetylene **1** (0.25 mmol) was added to a solution of $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), and $CuBr_2$ (1 mmol, 4.0 equiv) in DMAc (1.0 mL). The solution was then stirred at 80 °C. After completion of reaction as indicated by TLC, the reaction was quenched with aqueous HCl (1.0 M), extracted with EtOAc (2 x 10 mL), dried by anhydrate Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the product **3**.



(*E*)-Ethyl 2-(3-bromo-2-phenyl-1*H*-inden-1-ylidene)acetate (3a)

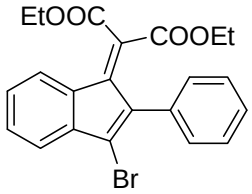
Yield: 72% (64 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.17 (s, 1H), 7.30 – 7.48 (m, 8H), 8.61 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 60.9, 120.3, 120.5, 126.9, 127.4, 128.0, 128.2, 128.3, 130.3, 130.4, 131.7, 132.8, 141.2, 142.0, 149.9, 166.0; IR (KBr): ν_{max}/cm^{-1} 3060, 2983, 1717, 1623, 1445; MS (ESI): *m/z* 355 (M^++1); HRMS (ESI) calcd for $C_{19}H_{16}BrO_2$ ($M + H^+$) 355.0334, found 355.0344.



(*E*)-2-(3-Bromo-2-phenyl-1*H*-inden-1-ylidene)-1-(4-methoxyphenyl)ethanone (3b)

Yield: 60% (63 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.92 (d,

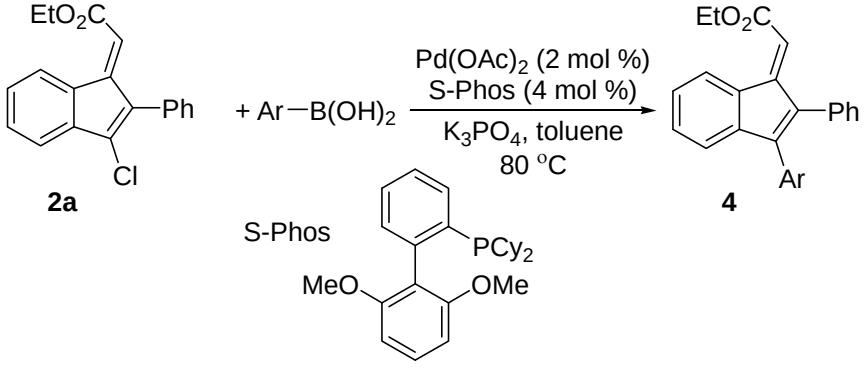
J = 8.9 Hz, 2H), 6.96 (s, 1H), 7.16 – 7.19 (m, 1H), 7.35 – 7.37 (m, 2H), 7.43 – 7.52 (m, 5H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 114.0, 120.3, 124.9, 126.1, 127.4, 127.6, 128.3, 128.4, 129.8, 130.4, 131.3, 132.1, 132.9, 140.6, 141.8, 146.0, 164.1, 191.8; IR (KBr): ν_{max}/cm^{-1} 3060, 2932, 2835, 1654, 1592, 1507; MS (ESI): *m/z* 417 (M^++1); HRMS (ESI) calcd for $C_{24}H_{18}BrO_2$ ($M + H^+$) 417.0490, found 417.0515.



Diethyl 2-(3-bromo-2-phenyl-1*H*-inden-1-ylidene)malonate (3c)

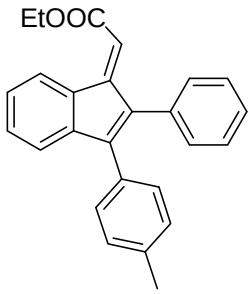
Yield: 84% (90 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 3.39 (q, *J* = 7.1 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.41 (m, 7H), 7.64 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 13.8, 61.6, 62.3, 120.9, 123.7, 126.3, 127.7, 127.8, 127.9, 129.0, 130.3, 131.5, 132.9, 133.9, 138.7, 141.0, 143.9, 163.8, 164.7; IR (KBr): ν_{max}/cm^{-1} 3064, 2979, 1724, 1600, 1445; MS (ESI): *m/z* 427 (M^++1); HRMS (ESI) calcd for $C_{22}H_{20}BrO_4$ ($M + H^+$) 427.0545, found 427.0562.

General procedure for Pd-catalyzed cross couplings of 3-chloro-1-methyleneindene 2a with arylboronic acids.



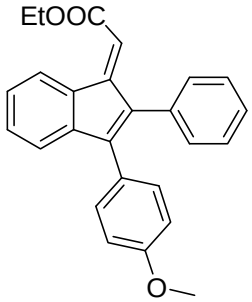
3-Chloro-1-methyleneindene **2a** (0.2 mmol) was added to a solution of arylboronic acids (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2 mol %), S-Phos (4 mol %), and K_3PO_4 (0.4 mmol, 2equiv) in toluene (1 mL). The solution was then stirred at 80 °C. After

completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified on silica gel provided the desired product **4**.



(*E*)-Ethyl 2-(2-phenyl-3-p-tolyl-1*H*-inden-1-ylidene)acetate (4a)

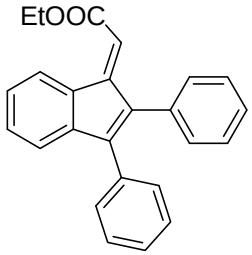
Yield: 92% (67 mg), yellow solid, melting point: 147.7-147.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.16 (s, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.16 (m, 4H), 7.25 – 7.31 (m, 6H), 8.70 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 21.3, 60.6, 119.8, 120.4, 126.9, 127.2, 127.3, 128.1, 128.9, 129.1, 129.7, 130.8, 130.9, 133.3, 134.2, 137.6, 139.0, 144.4, 144.9, 152.2, 166.4; IR (KBr): ν_{max}/cm^{-1} 3052, 2917, 2854, 1716, 1611, 1452; MS (ESI): *m/z* 367 (M^++1); HRMS (ESI) calcd for $C_{26}H_{23}O_2$ (M + H^+) 367.1698, found 367.1727. Elem. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05; Found: C, 84.99; H, 5.99.



(*E*)-Ethyl 2-(3-(4-methoxyphenyl)-2-phenyl-1*H*-inden-1-ylidene)acetate (4b)

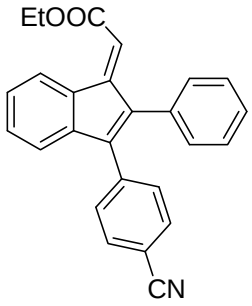
Yield: 70% (54 mg), yellow solid, melting point: 133.7-134.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.77 (s, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.16 (s, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 7.15 – 7.19 (m, 4H), 7.26 – 7.32 (m, 6H), 8.71 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 55.1, 60.6, 113.7, 119.5, 120.4, 126.0, 126.9, 127.2, 127.3, 128.1, 129.7, 130.6, 131.0, 133.3, 134.2, 138.7, 144.4, 144.5, 152.2, 159.2, 166.5; IR (KBr): ν_{max}/cm^{-1} 3056, 2959, 2835, 1709, 1608, 1507,

1449; MS (ESI): *m/z* 383 (M^++1); HRMS (ESI) calcd for $C_{26}H_{23}O_3$ (M + H^+) 383.1647, found 383.1679. Elem. Anal. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80; Found: C, 81.48; H, 5.50.



(*E*)-Ethyl 2-(2,3-diphenyl-1*H*-inden-1-ylidene)acetate (4c)

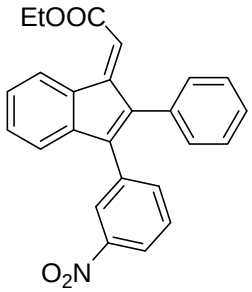
Yield: 99% (69.7 mg), yellow solid, melting point: 123.1-123.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 6.19 (s, 1H), 7.14 – 7.16 (m, 2H), 7.21 – 7.30 (m, 11H), 8.71 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 60.7, 120.2, 120.4, 127.0, 127.3, 127.8, 128.1, 128.2, 129.2, 129.8, 130.9, 133.2, 133.8, 133.9, 139.4, 144.3, 144.9, 152.0, 166.4; IR (KBr): ν_{max}/cm^{-1} 3052, 2978, 1717, 1623, 1456; MS (ESI): *m/z* 353 (M^++1); HRMS (ESI) calcd for $C_{25}H_{21}O_2$ (M + H^+) 353.1542, found 353.1563. Elem. Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72; Found: C, 85.40; H, 5.51.



(*E*)-Ethyl 2-(3-(4-cyanophenyl)-2-phenyl-1*H*-inden-1-ylidene)acetate (4d)

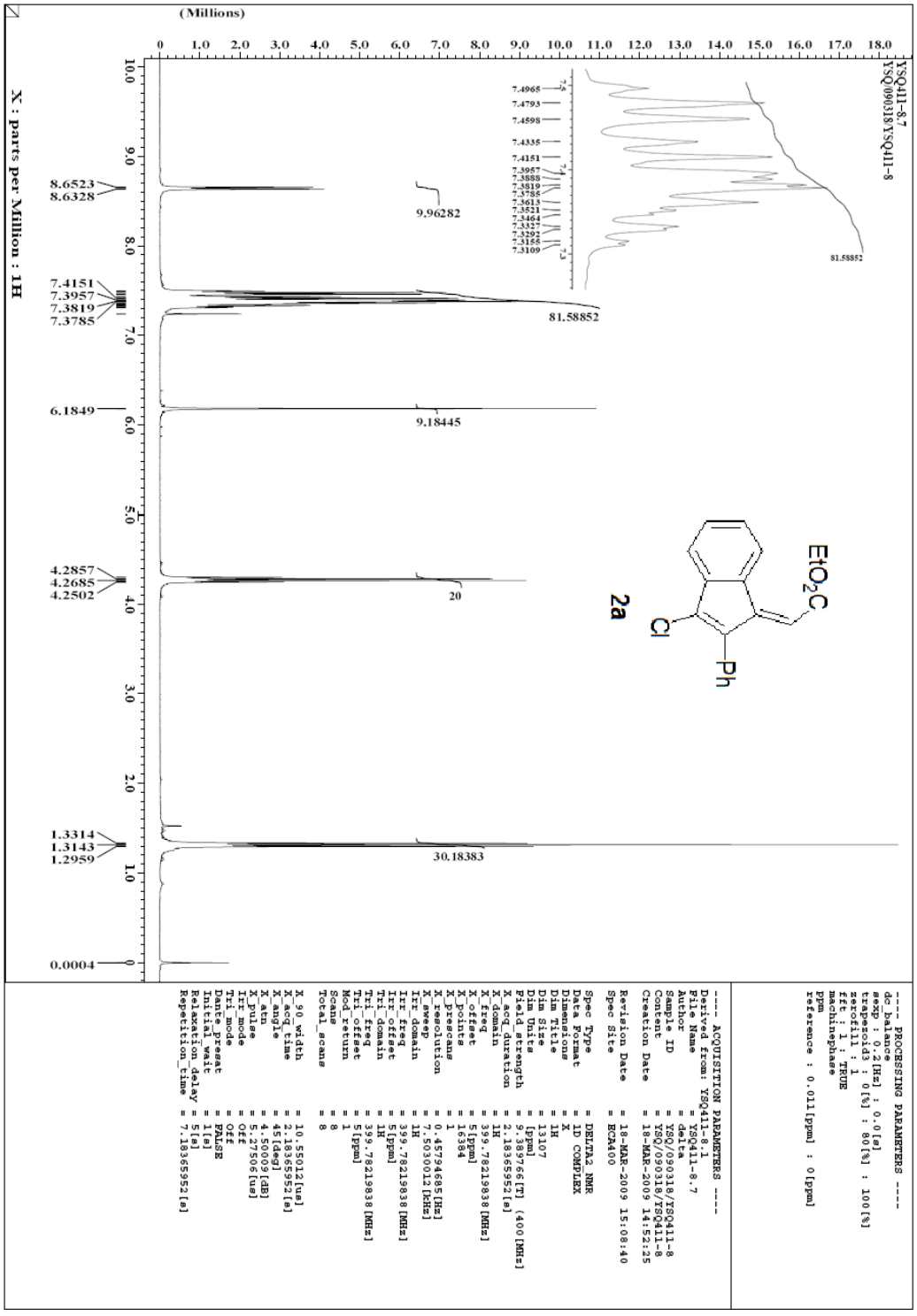
Yield: 74% (56mg), yellow solid, melting point: 158.3-159.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.22 (s, 1H), 7.10 – 7.12 (m, 2H), 7.19 – 7.20 (m, 1H), 7.30 – 7.35 (m, 7H), 7.57 (d, *J* = 8.3 Hz, 2H), 8.71 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 60.9, 111.4, 118.6, 119.9, 121.6, 127.4, 127.6, 127.9, 128.4, 129.9, 130.0, 130.7, 132.0, 132.9, 133.0, 138.8, 141.1, 142.7, 143.2, 151.3, 166.1; IR (KBr): ν_{max}/cm^{-1} 3056, 2928, 2225, 1717, 1623, 1449; MS (ESI): *m/z* 378 (M^++1), 400 (M^++Na); HRMS (ESI) calcd for

$C_{26}H_{19}NNaO_2$ (M + Na^+) 400.1313, found 400.1346. Elem. Anal. Calcd for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71; Found: C, 82.80; H, 4.77; N, 3.77.



(*E*)-Ethyl 2-(3-(3-nitrophenyl)-2-phenyl-1*H*-inden-1-ylidene)acetate (4e)

Yield: 76% (61 mg), yellow solid, melting point: 167.7-167.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.1 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.22 (s, 1H), 7.14 – 7.15 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.36 (m, 5H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.17 (s, 1H), 8.73 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 60.9, 119.8, 121.7, 122.6, 124.0, 127.5, 127.7, 128.0, 128.4, 129.2, 130.0, 130.7, 132.9, 133.0, 135.3, 135.7, 141.3, 142.1, 143.2, 148.2, 151.3, 166.1; IR (KBr): ν_{max}/cm^{-1} 3062, 2982, 1717, 1627, 1530, 1455; MS (ESI): *m/z* 398 (M^++1); HRMS (ESI) calcd for $C_{25}H_{20}NO_4$ (M + H^+) 398.1392, found 398.1425. Elem. Anal. Calcd for $C_{25}H_{19}NO_4$: C, 75.55; H, 4.82; N, 3.52; Found: C, 75.66; H, 4.56; N, 3.49.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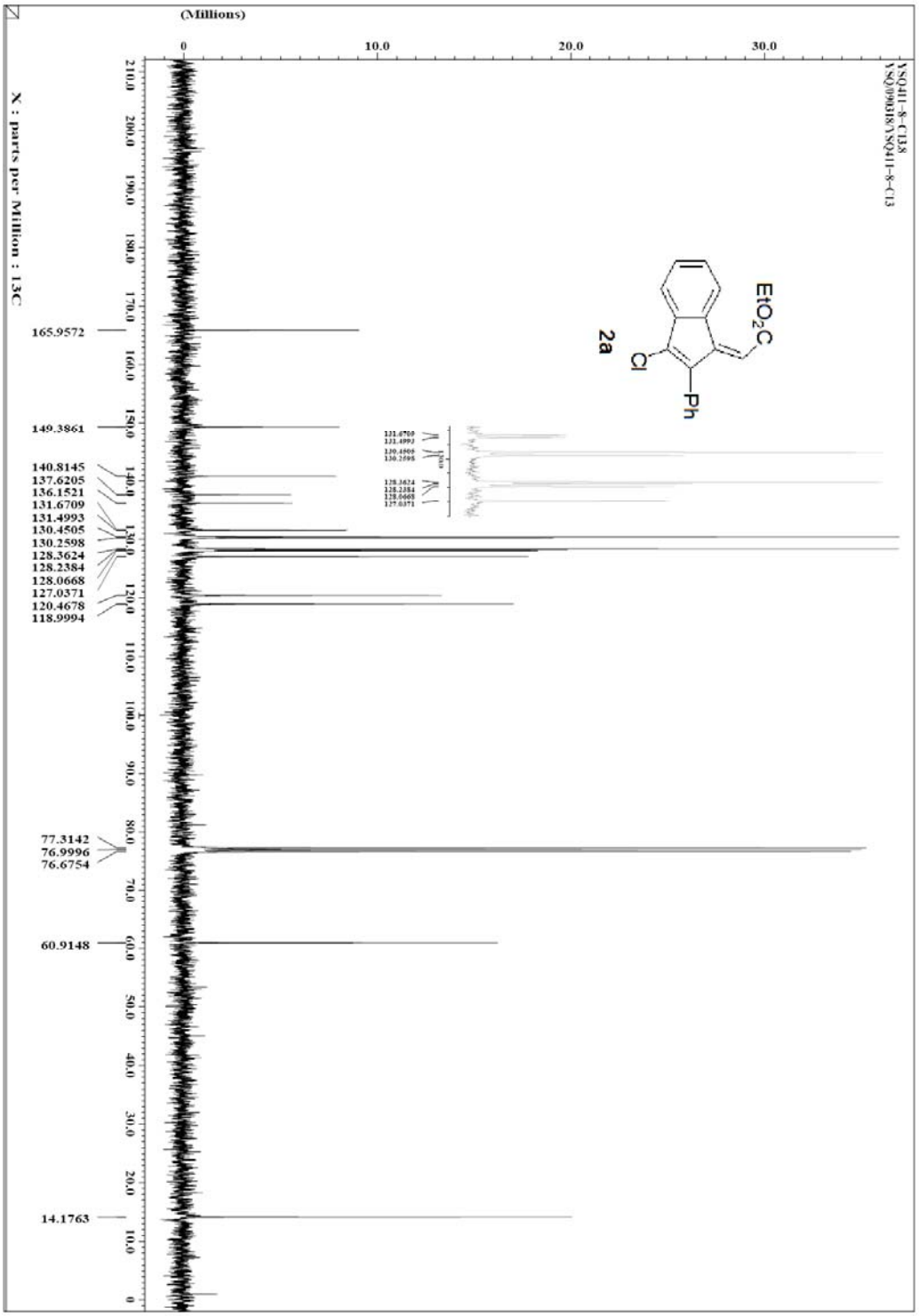
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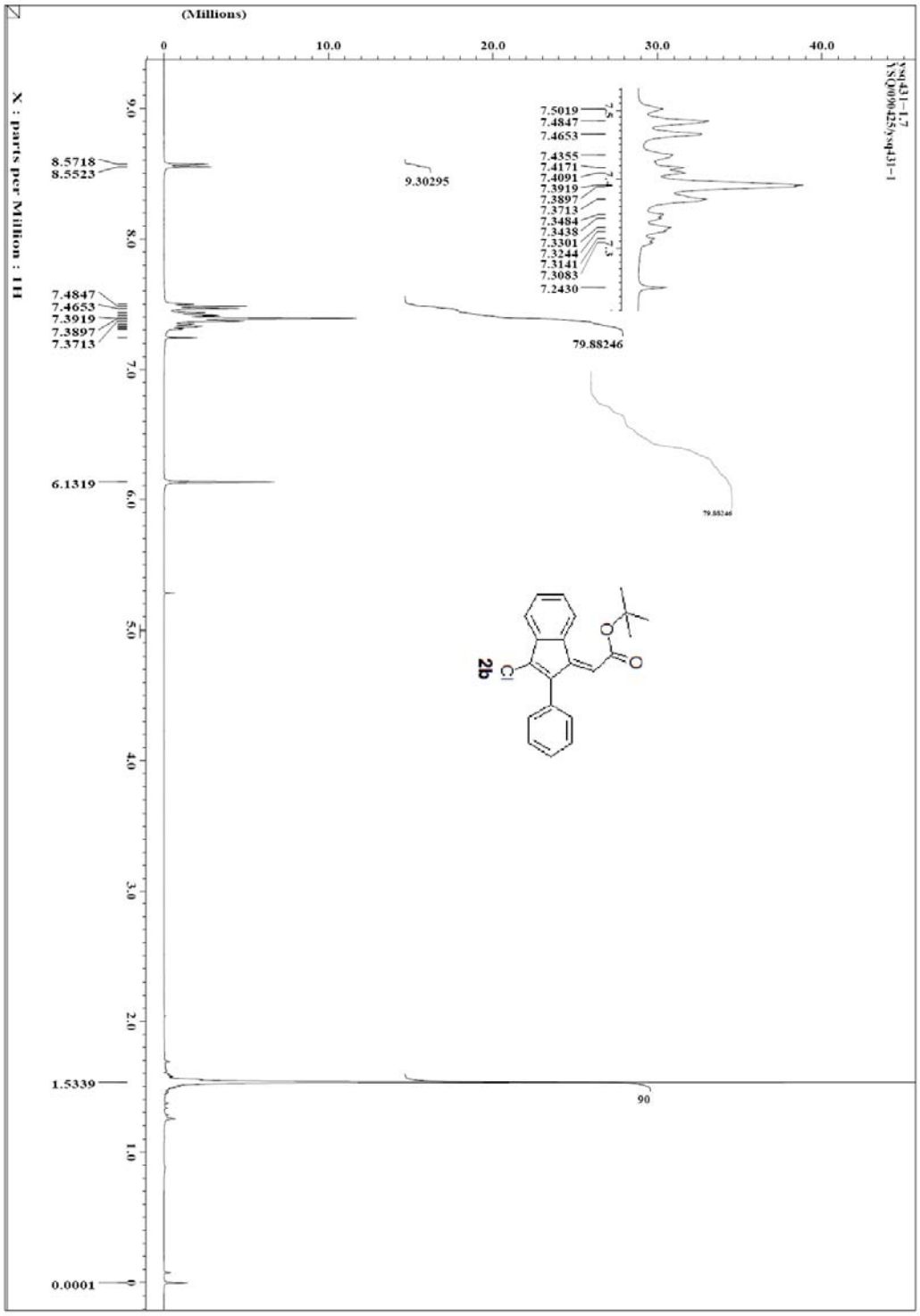
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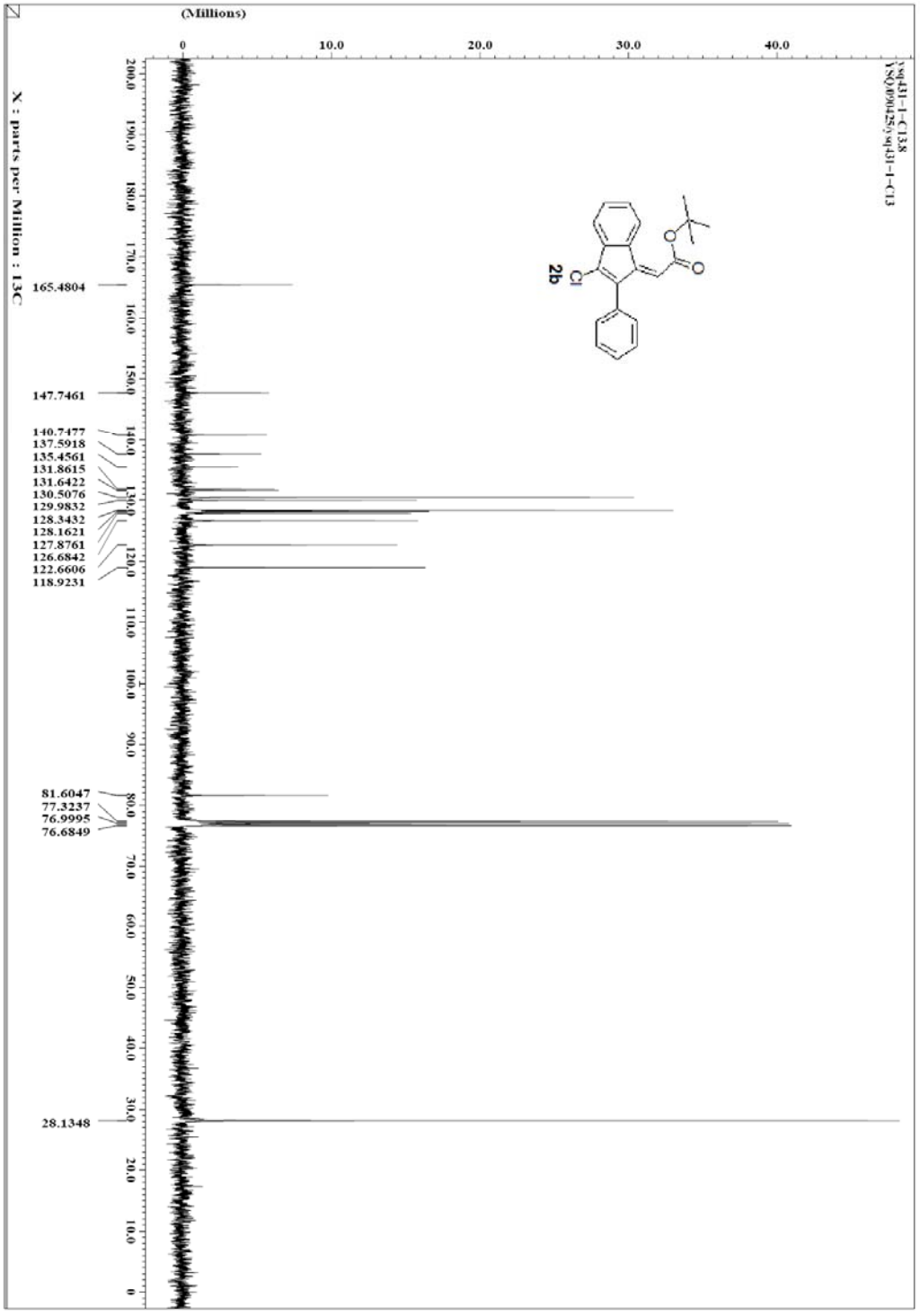
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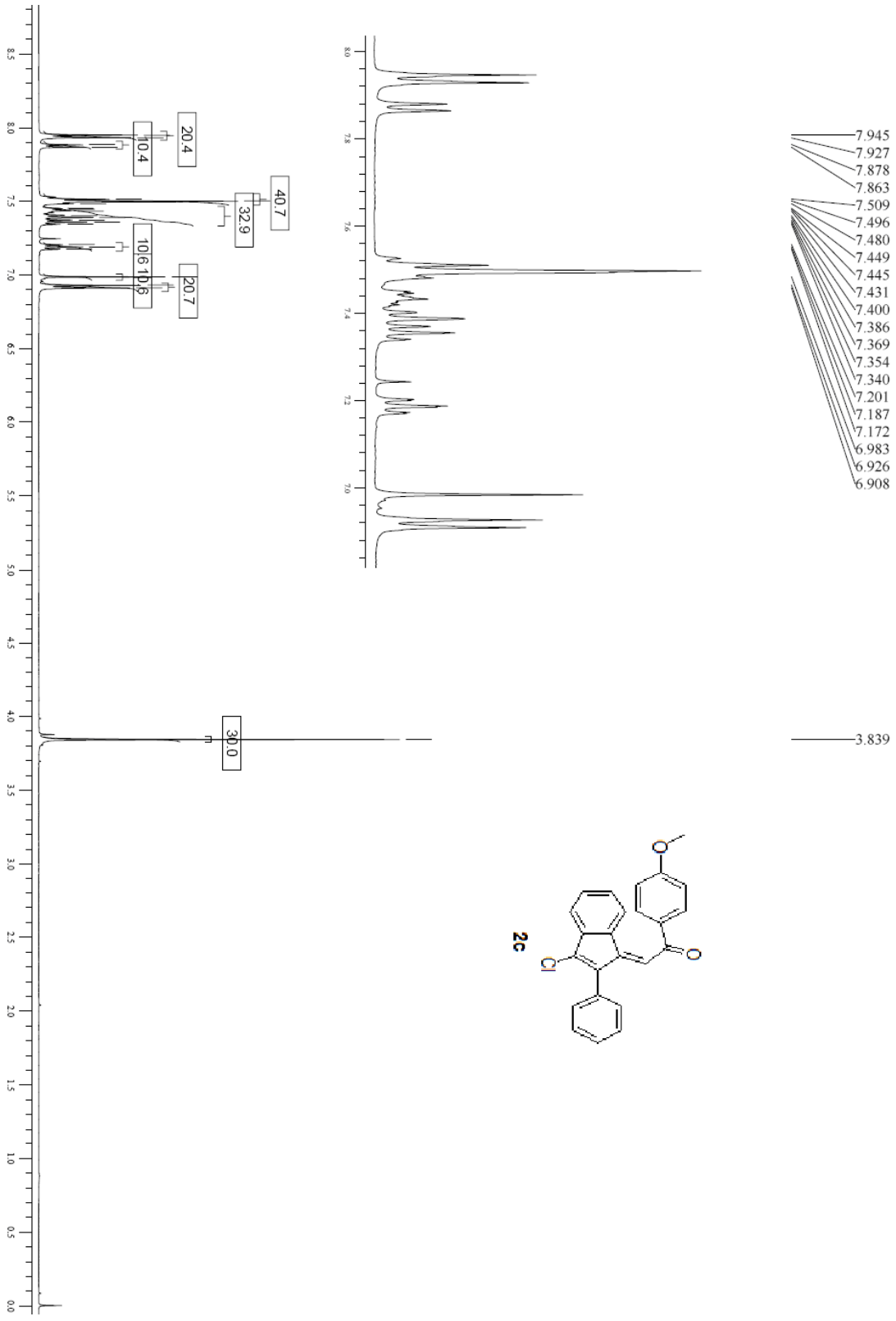
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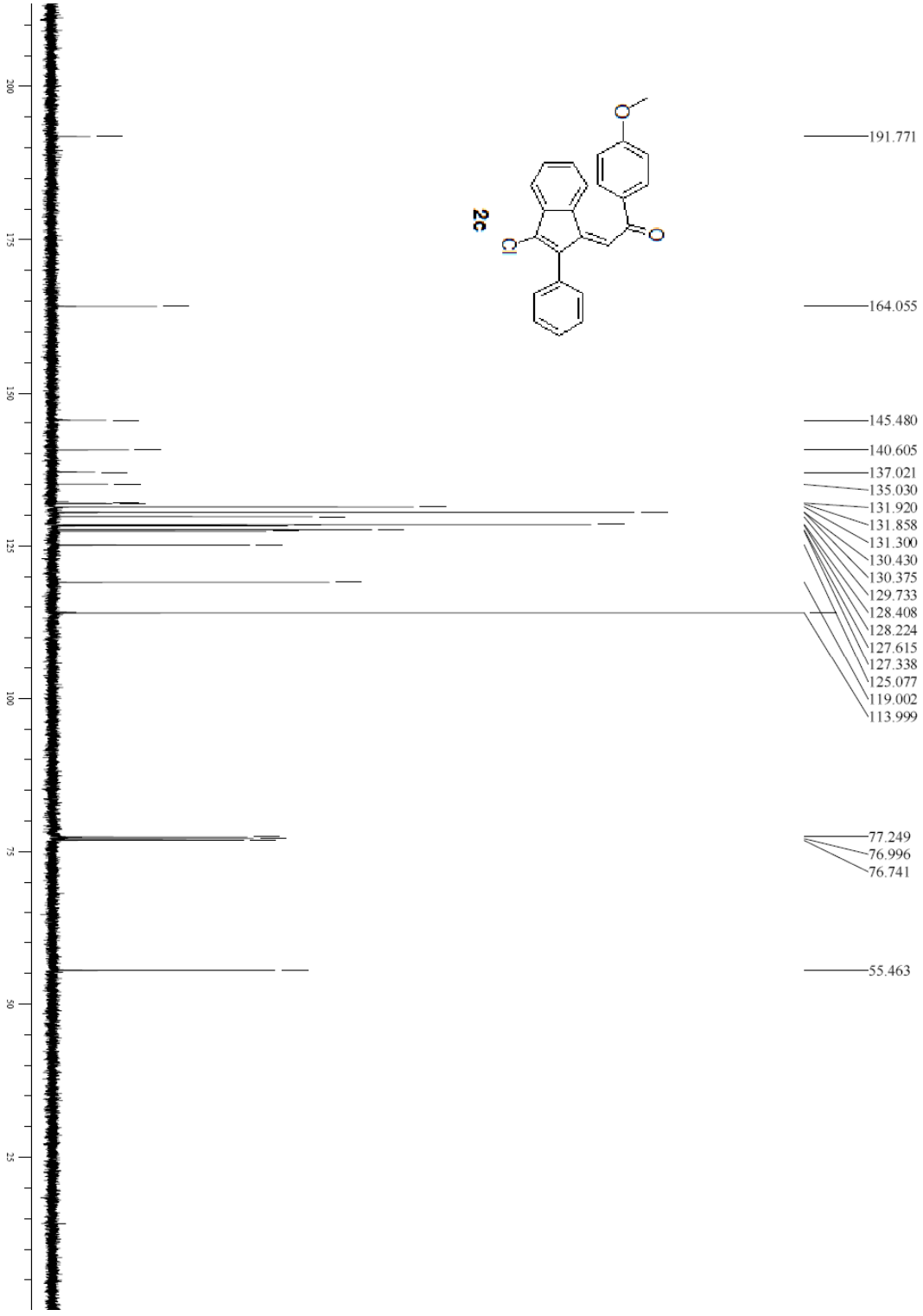
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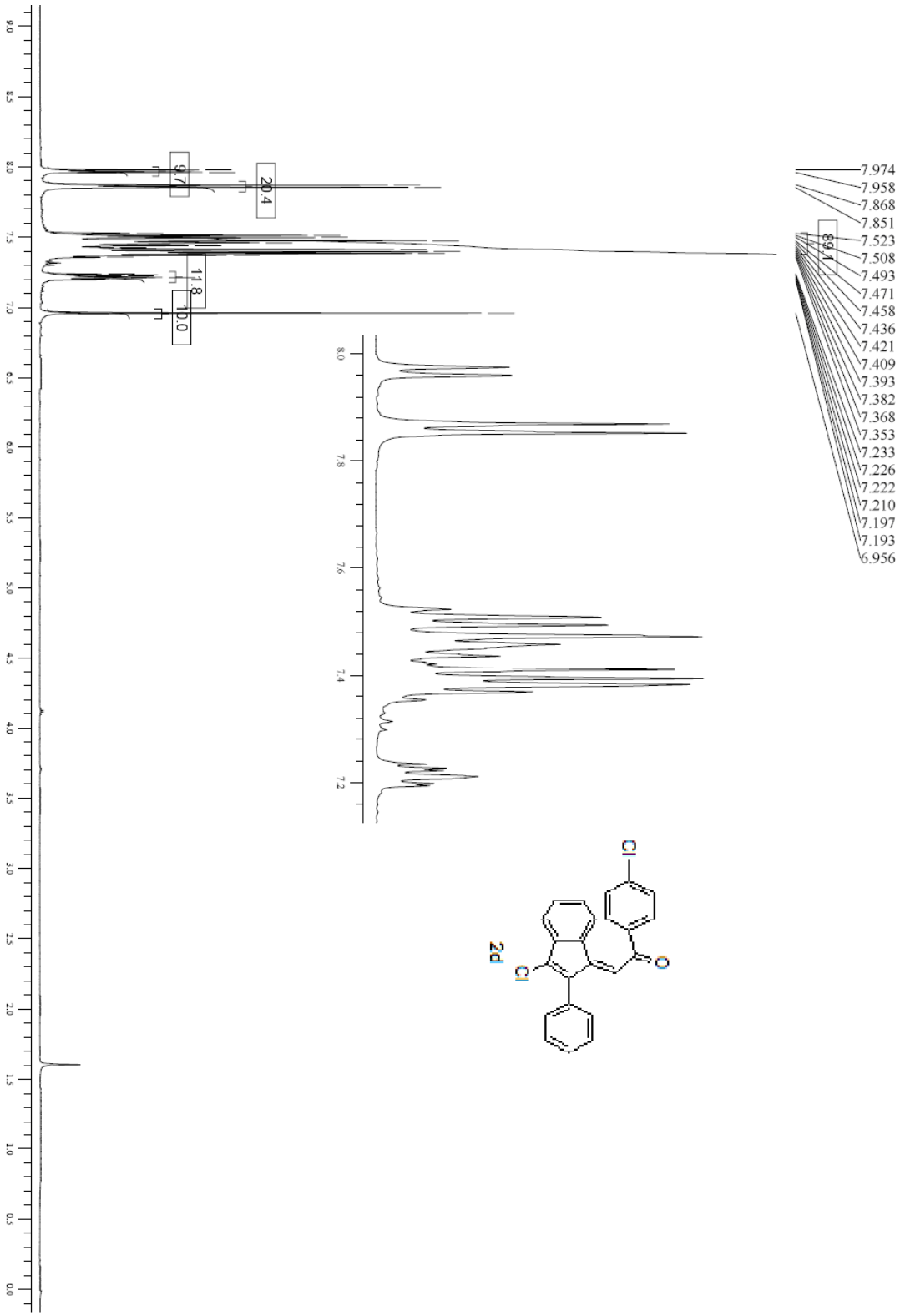
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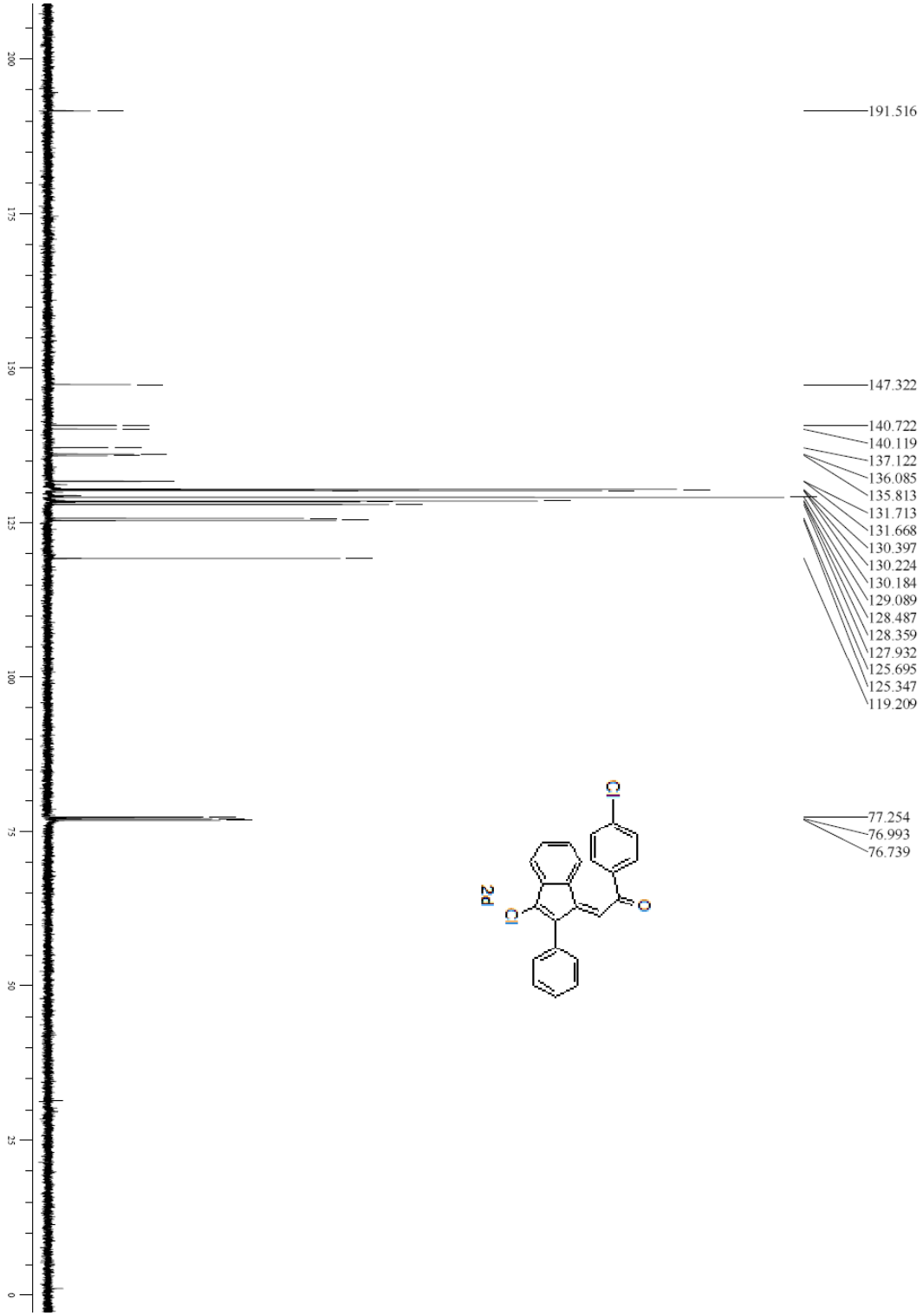
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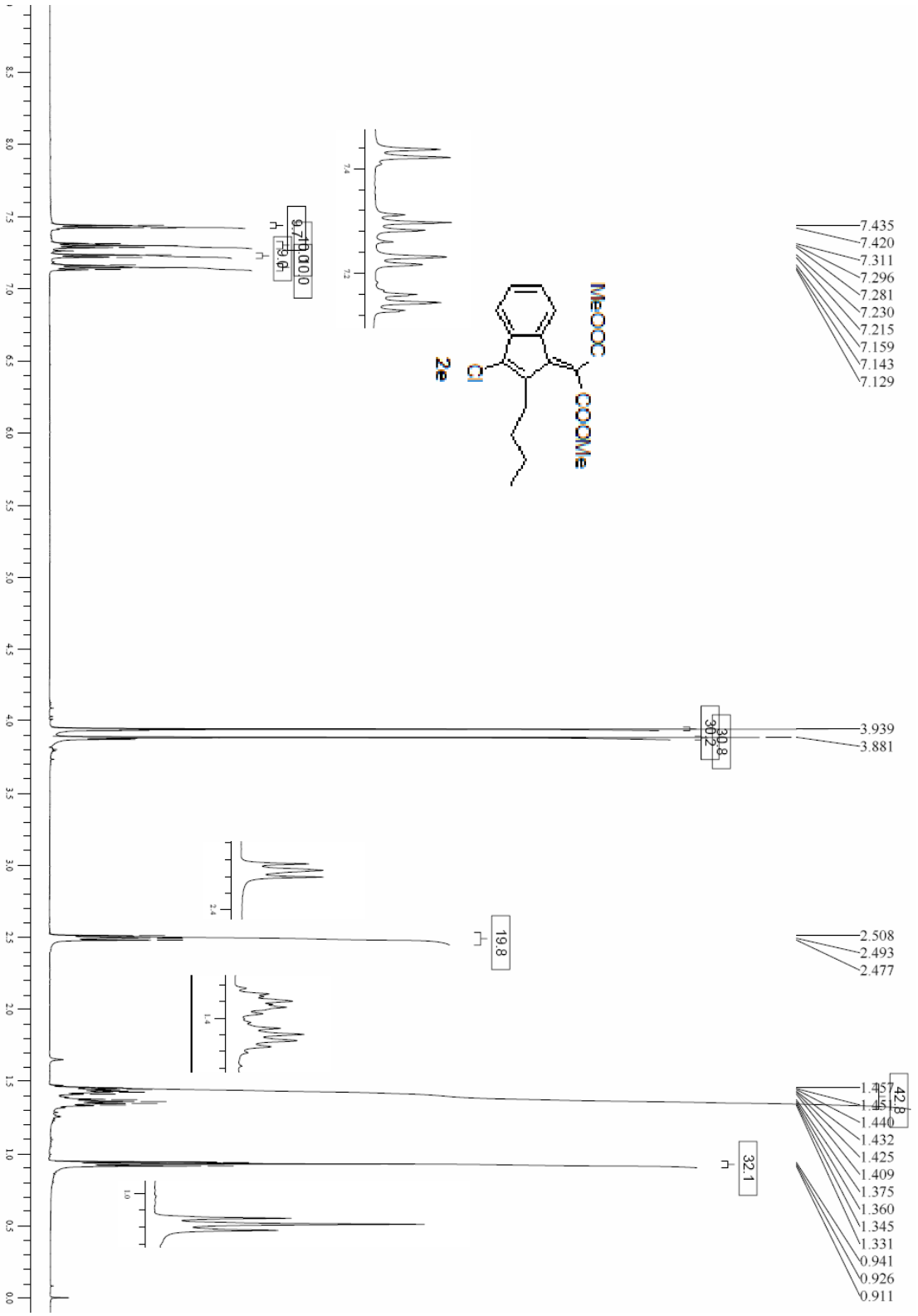
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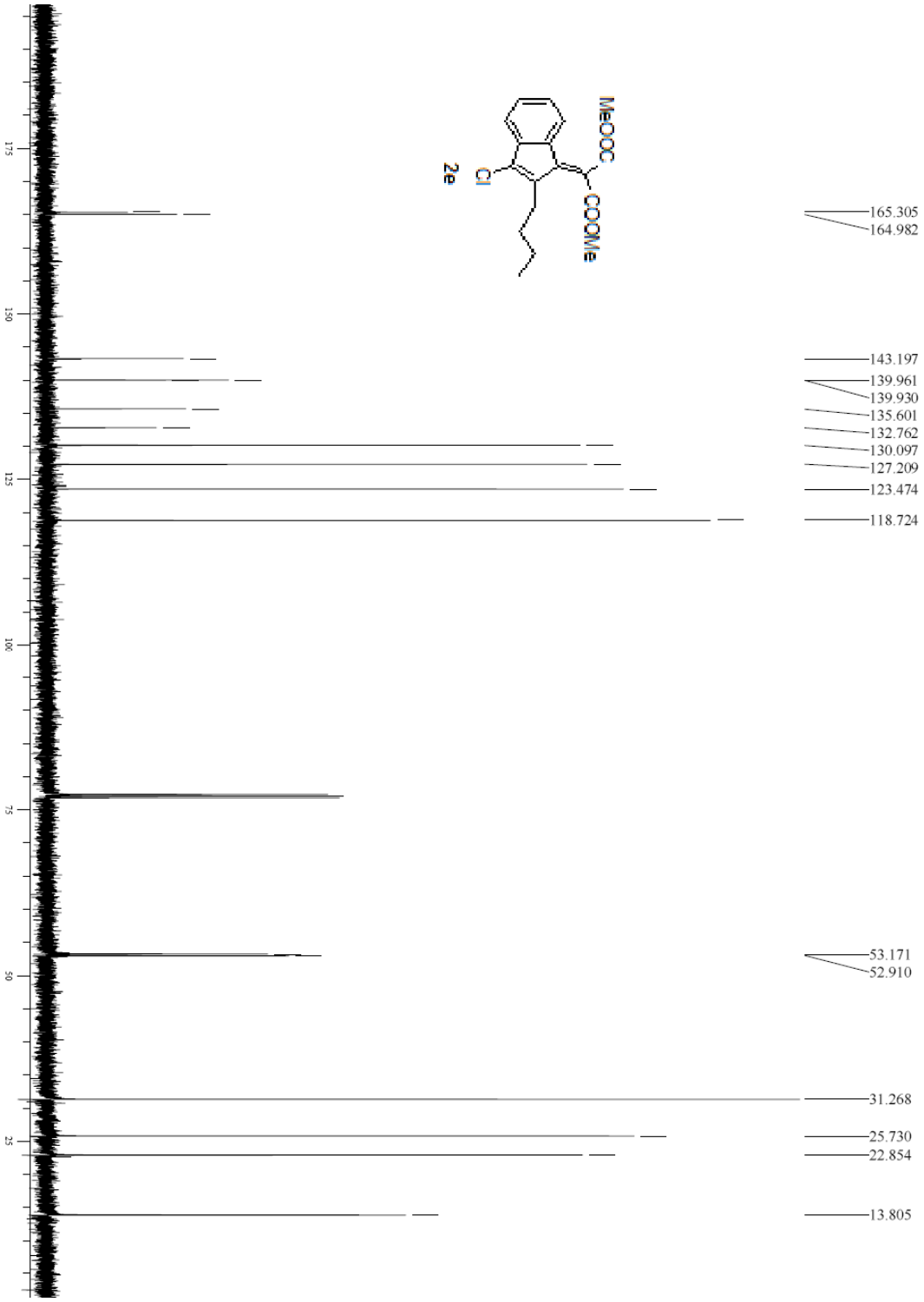
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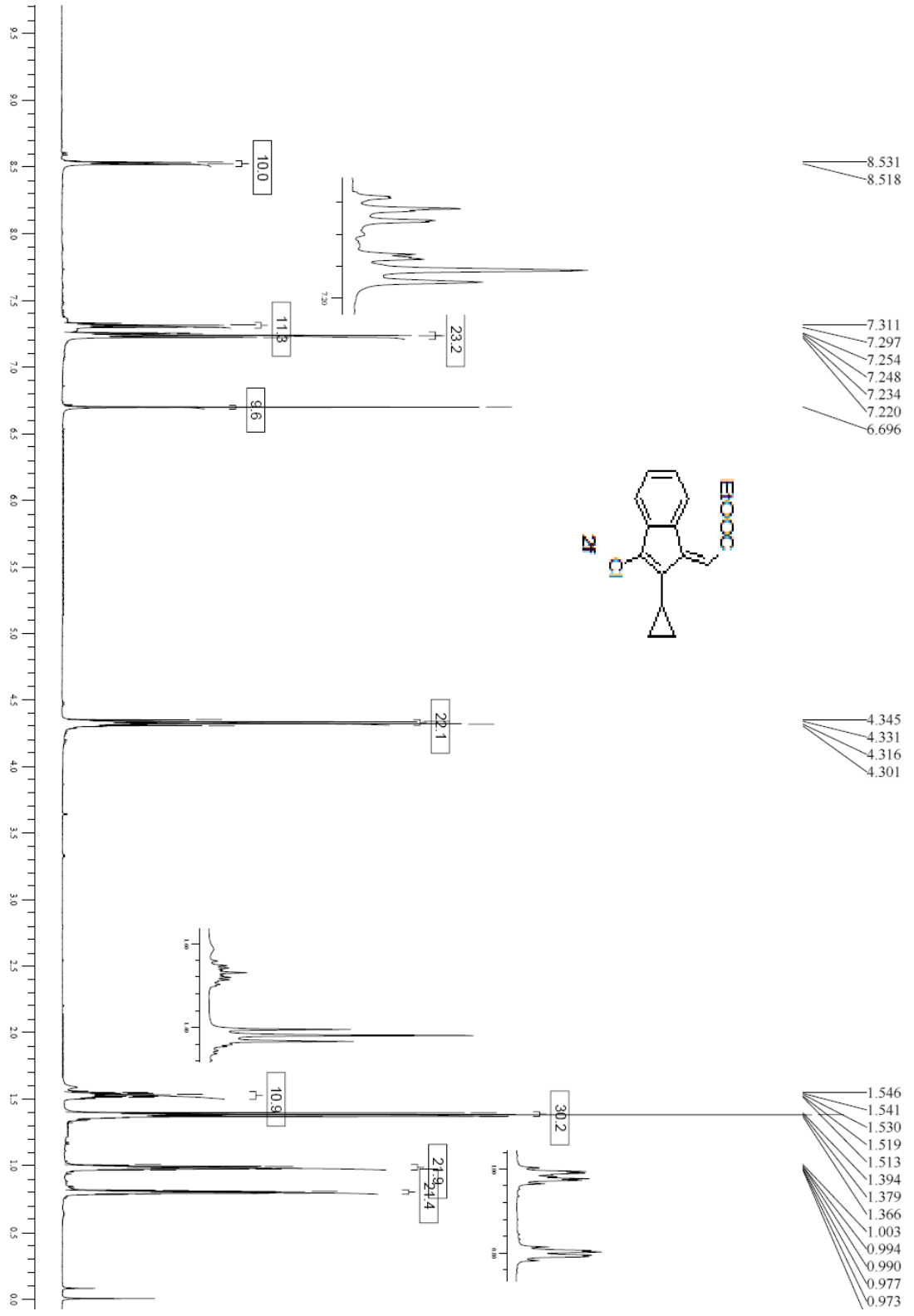
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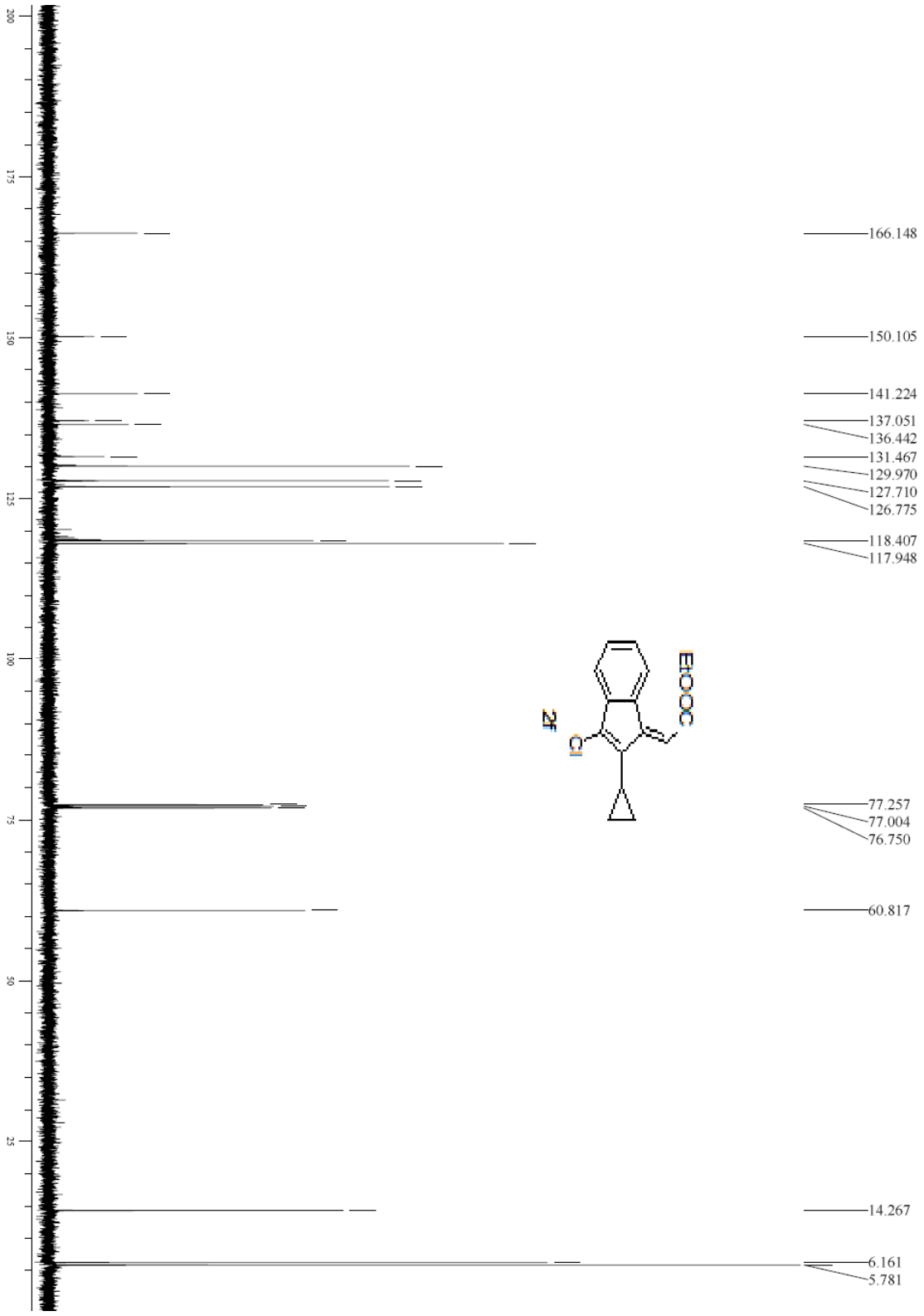
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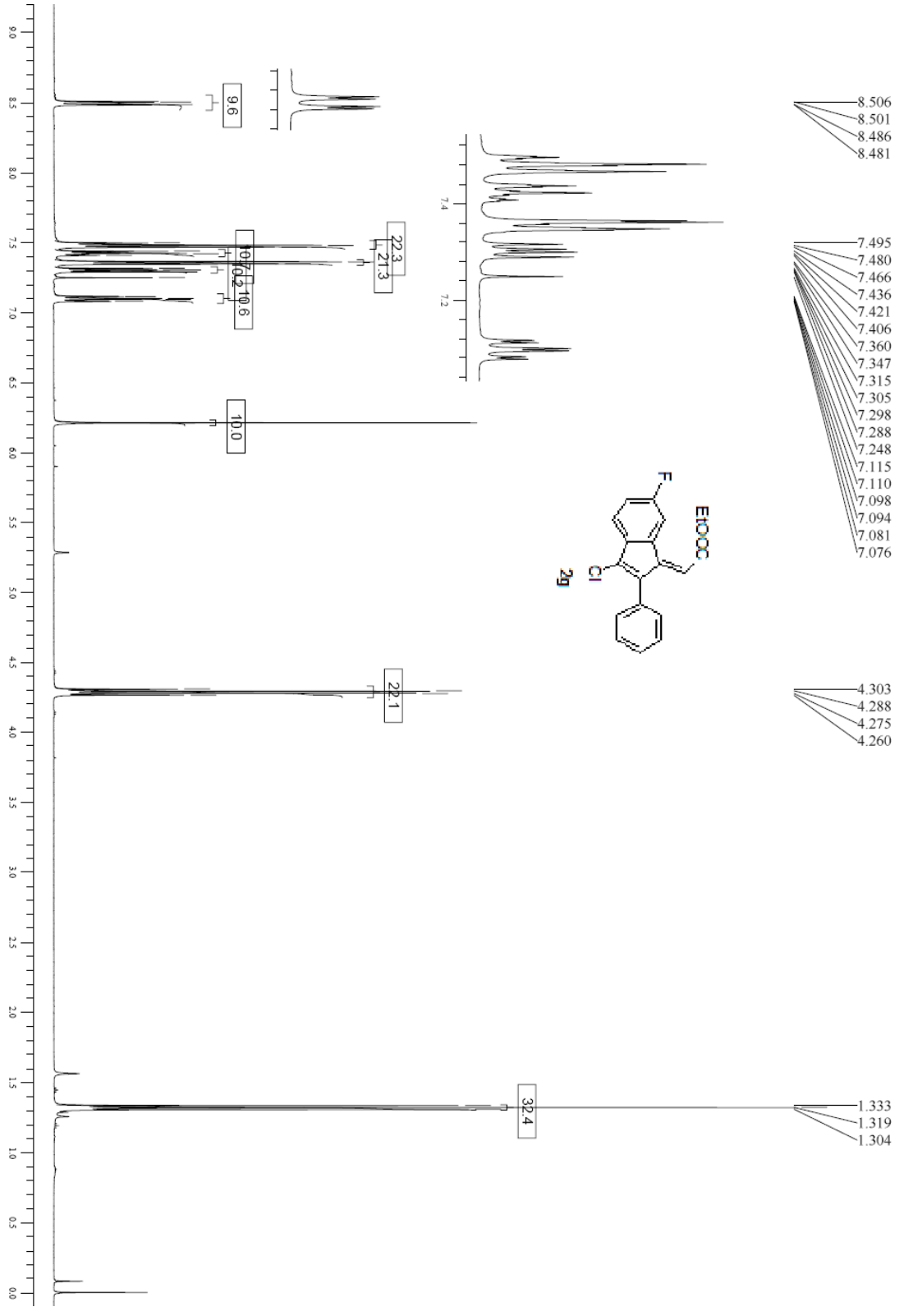
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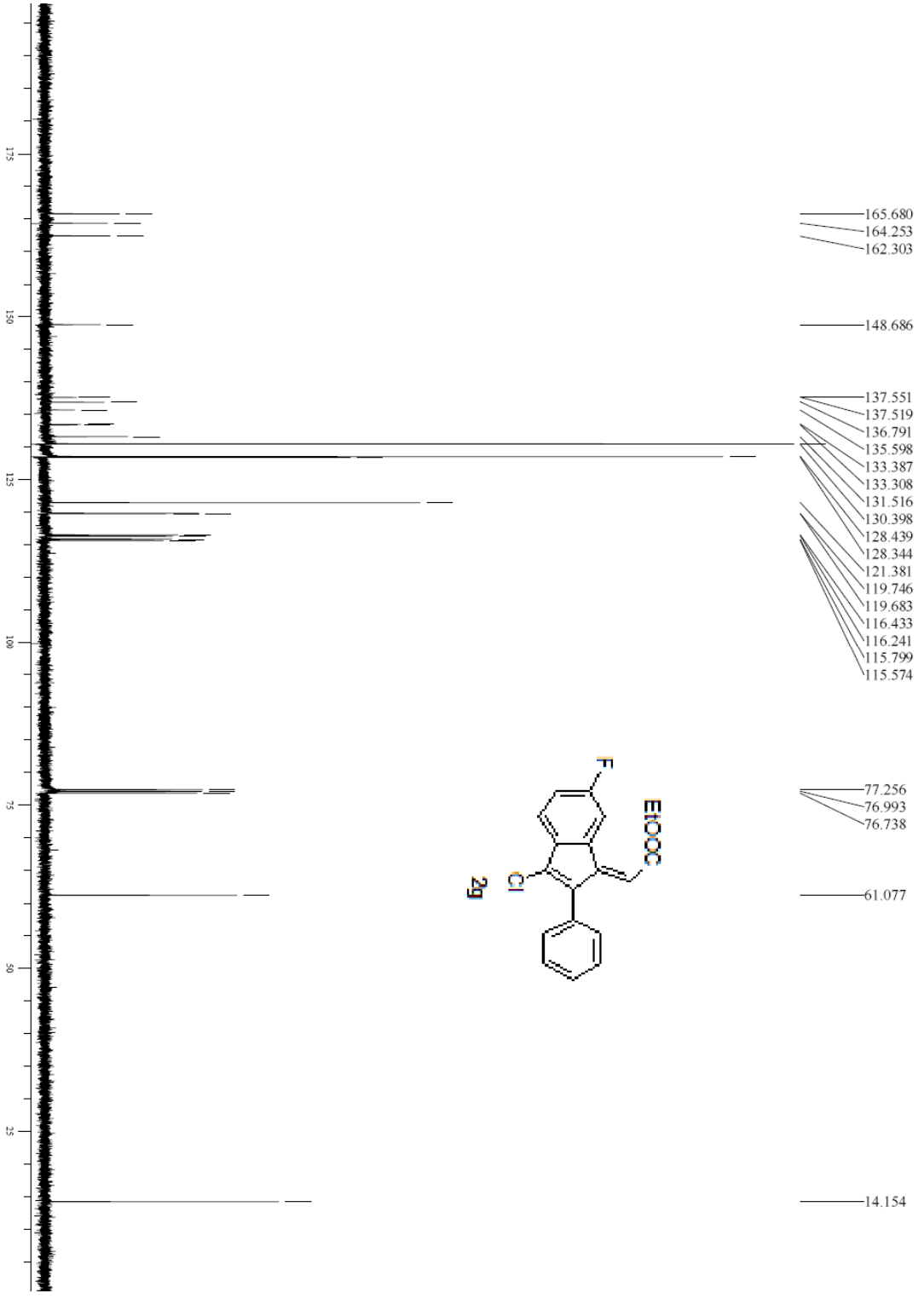
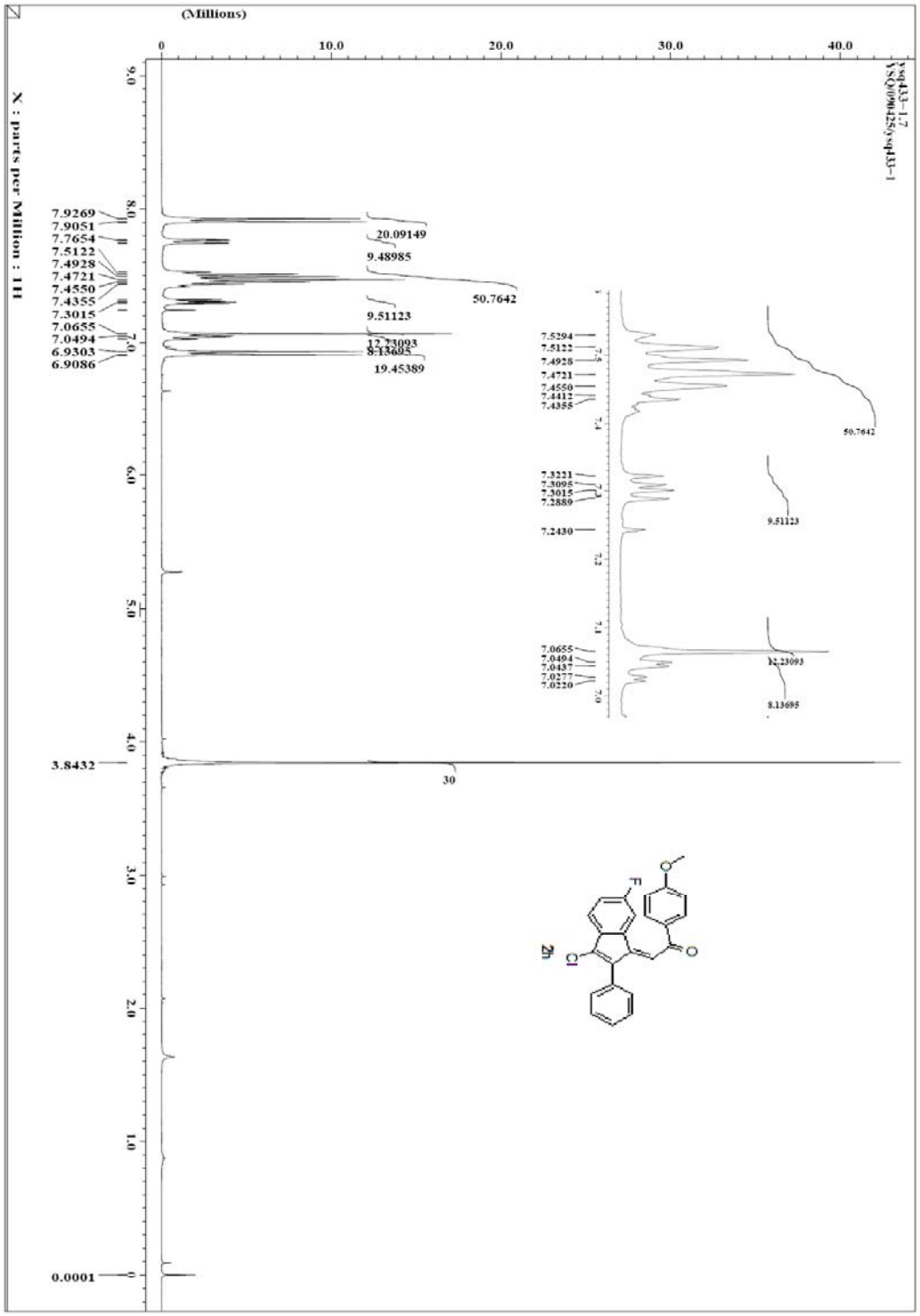
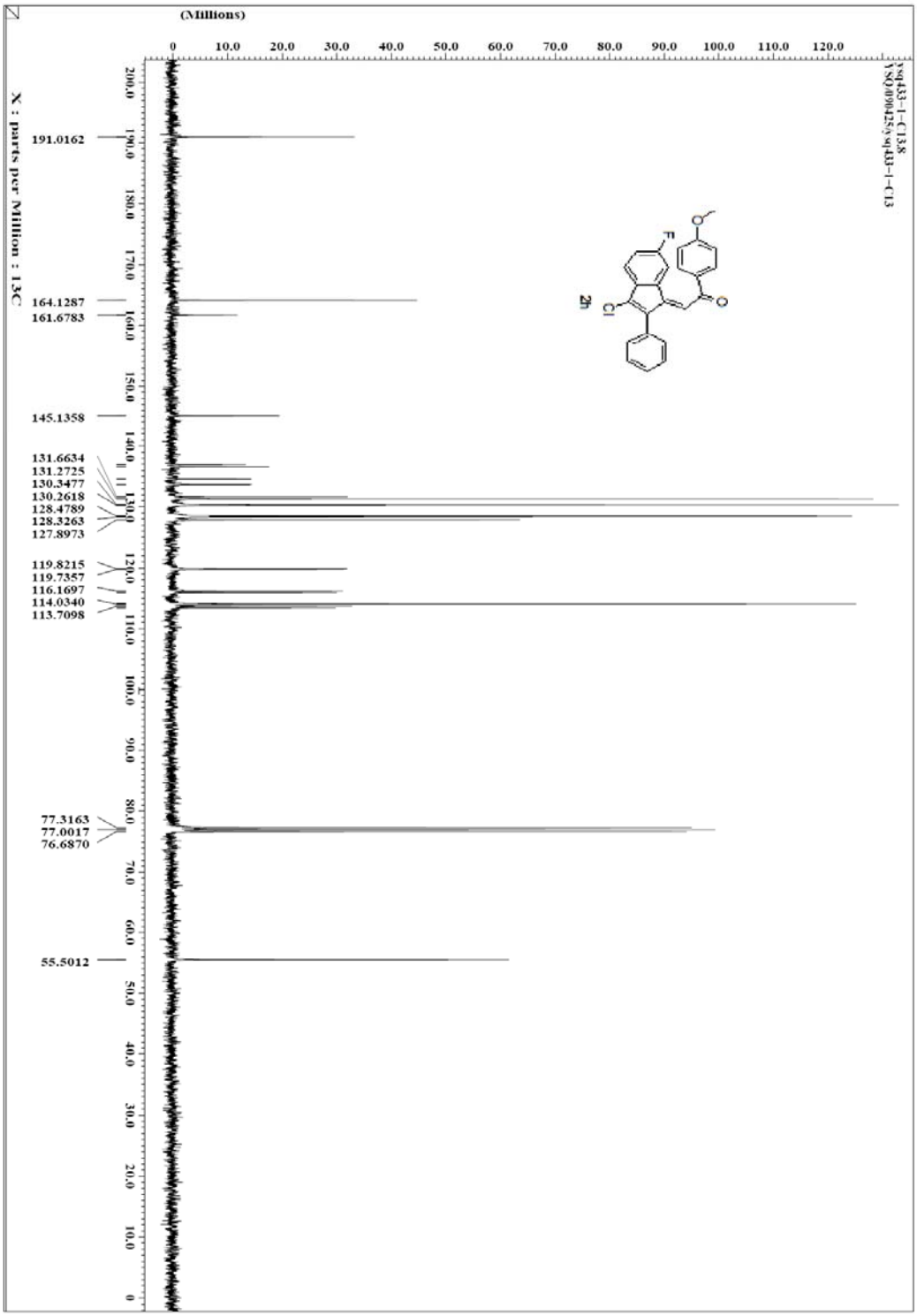
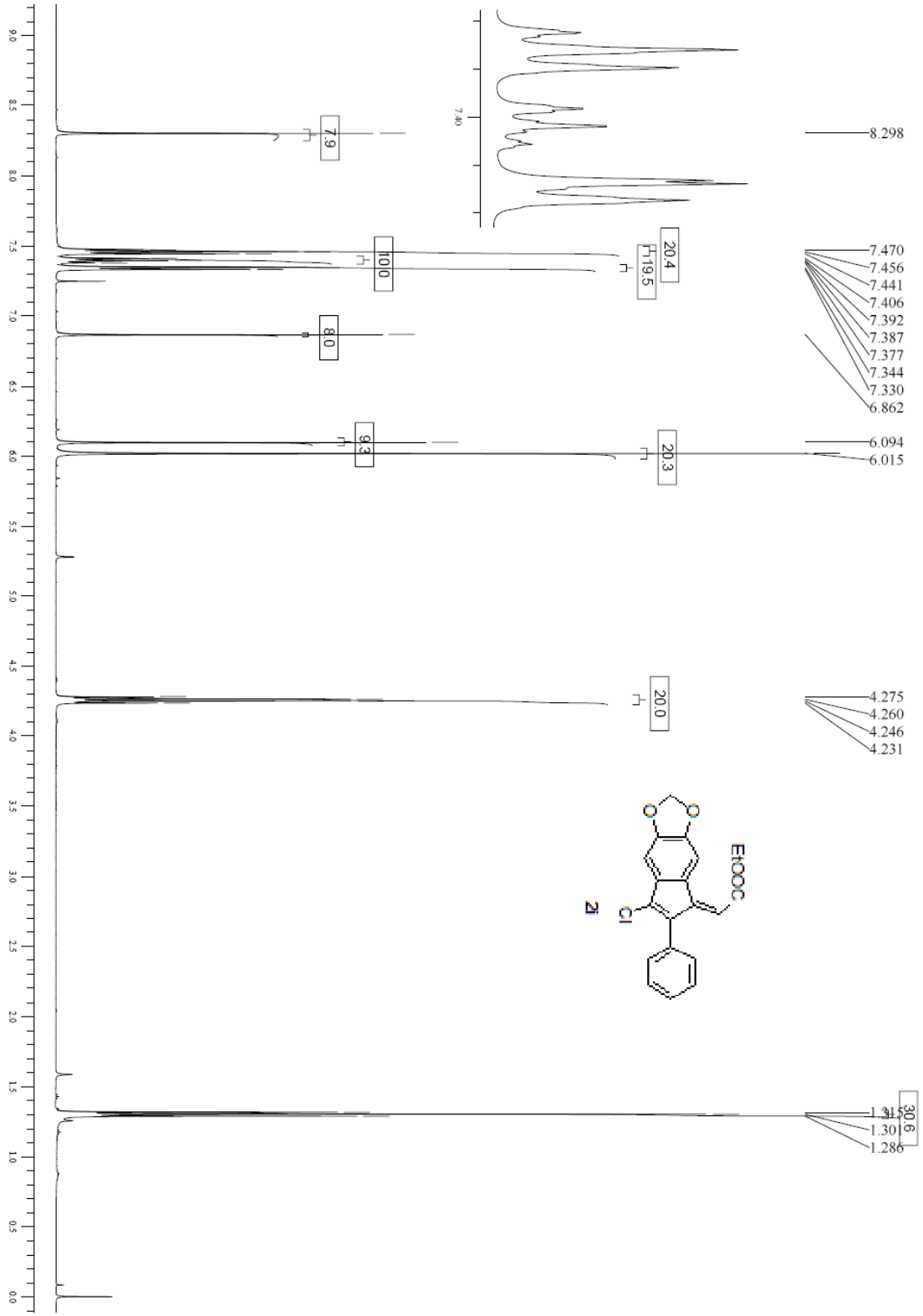
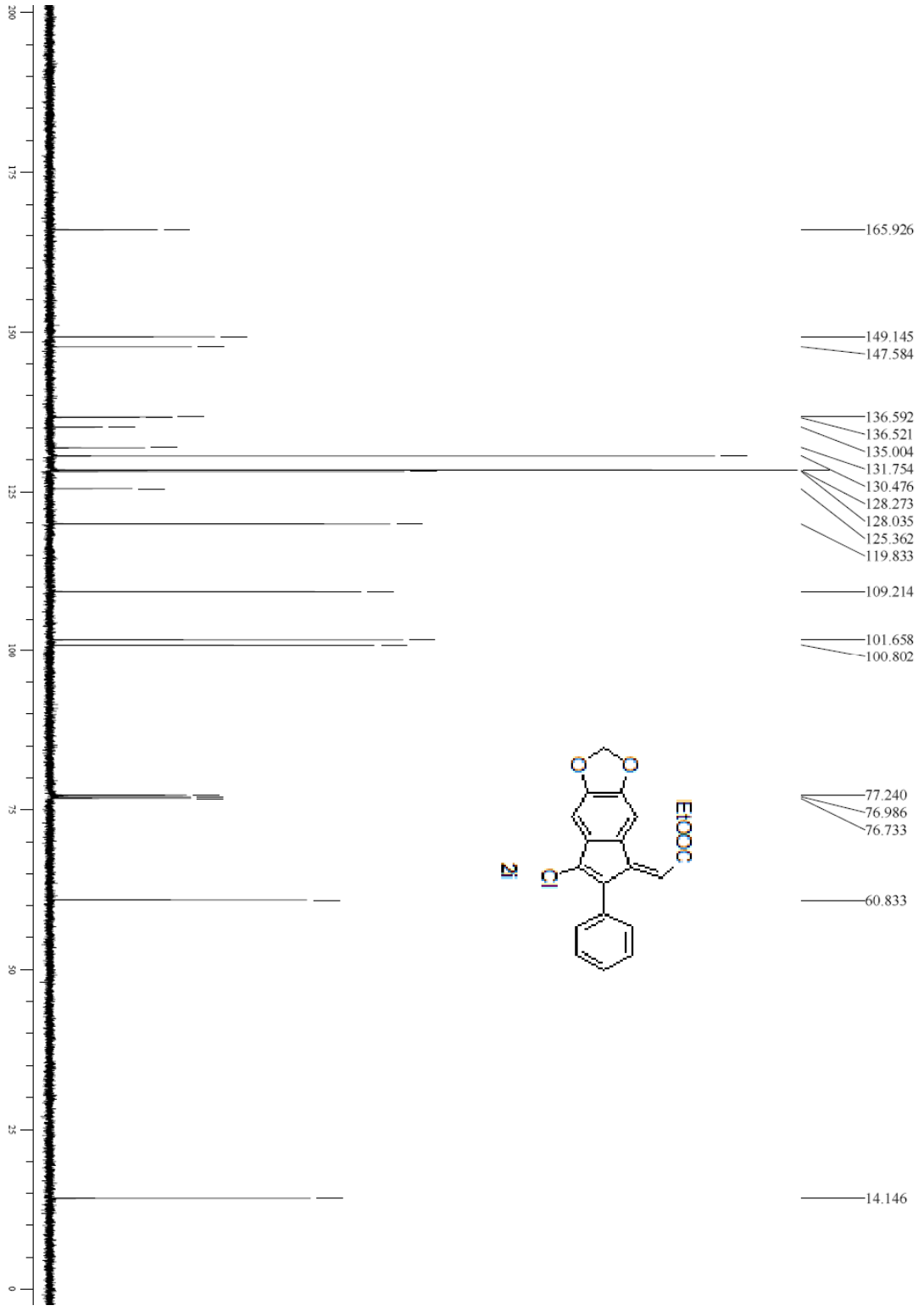
Cl
2g

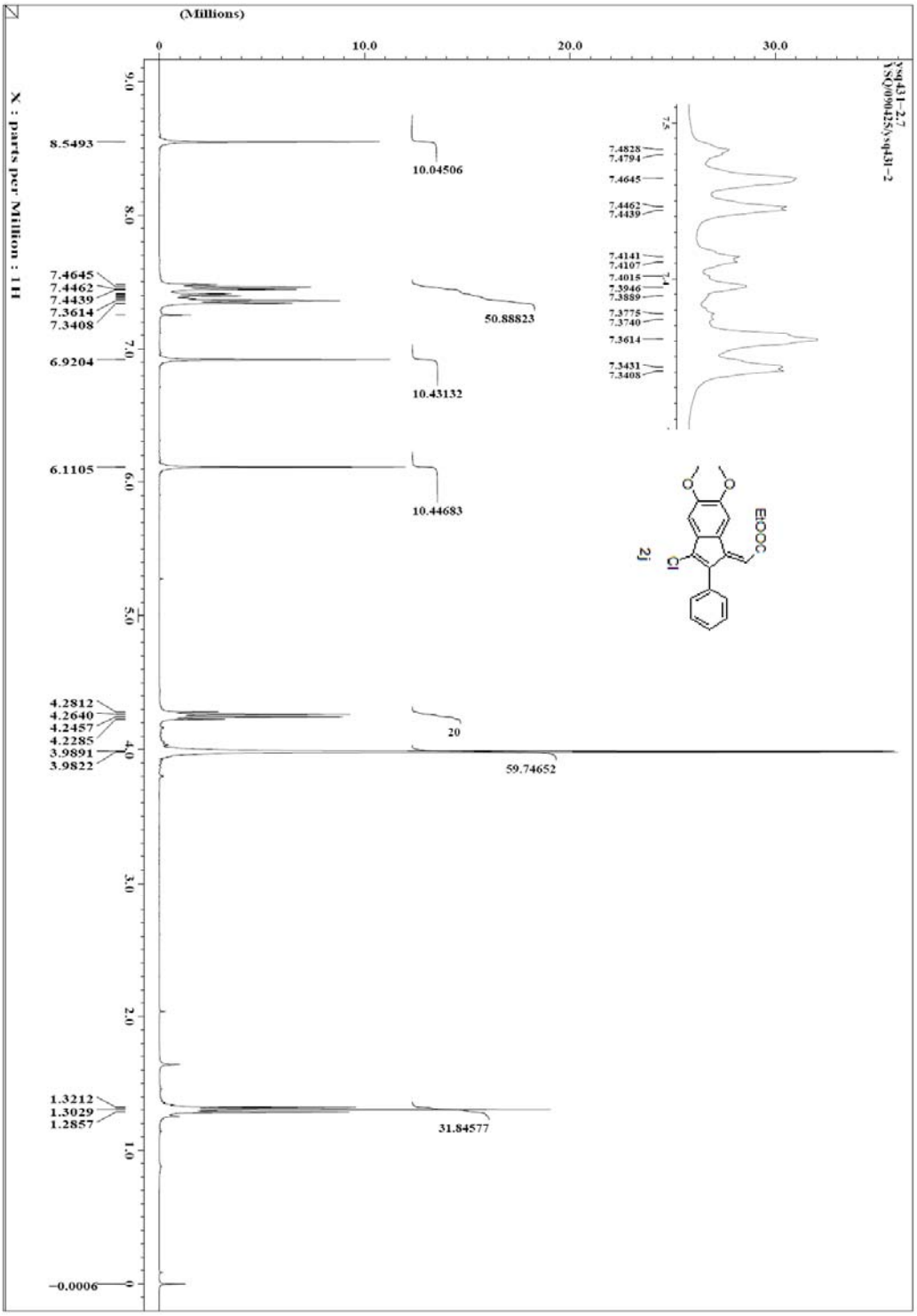

165.680
164.253
162.303
148.686
137.551
137.519
136.791
135.598
133.387
133.308
131.516
130.398
128.439
128.344
121.381
119.746
119.683
116.433
116.241
115.799
115.574
77.256
76.993
76.738
61.077
14.154
F
EtOOC
Cl
2g

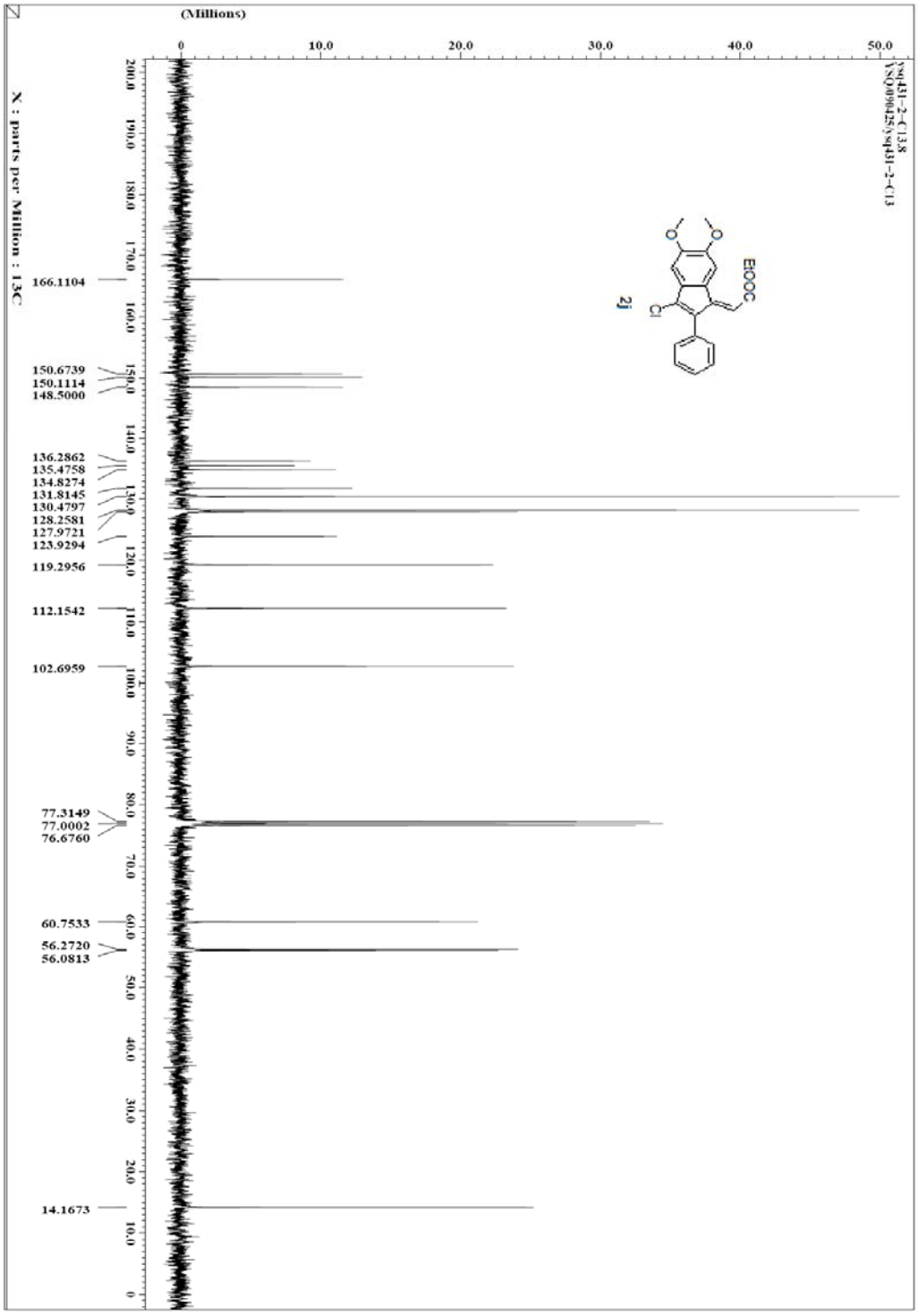

(Millions)
X : parts per Million : 1H
7.9269
7.9051
7.7654
7.5122
7.4928
7.4721
7.4550
7.4355
7.3015
7.0655
7.0494
6.9303
6.9086
20.09149
9.48985
50.7642
9.51123
12.23093
8.13695
19.45389
3.8432
30
0.0001
F
O
O
Cl


(Millions)
X : parts per Million : 13C
191.0162
164.1287
161.6783
145.1358
131.6634
131.2725
130.3477
130.2618
128.4789
128.3263
127.8973
119.8215
119.7357
116.1697
114.0340
113.7098
77.3163
77.0017
76.6870
55.5012
F
O
Cl
O


8.298
7.470
7.456
7.441
7.406
7.392
7.387
7.377
7.344
7.330
6.862
6.094
6.015
4.275
4.260
4.246
4.231
1.315
1.301
1.286
7.9
10.0
20.4
19.5
8.0
9.3
20.3
20.0
30.6
EtOOC
Cl
21


165.926
149.145
147.584
136.592
136.521
135.004
131.754
130.476
128.273
128.035
125.362
119.833
109.214
101.658
100.802
77.240
76.986
76.733
60.833
14.146
O
O
EtOOC
Cl
2i


(Millions)
X : parts per Million : 1H
8.5493
7.4645
7.4462
7.4439
7.3614
7.3408
6.9204
6.1105
4.2812
4.2640
4.2457
4.2285
3.9891
3.9822
1.3212
1.3029
1.2857
-0.0006
10.04506
50.88823
10.43132
10.44683
20
59.74652
31.84577
EtOOC
Cl
2j


(Millions)
X : parts per Million : 13C
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150.6739
150.1114
148.5000
136.2862
135.4758
134.8274
131.8145
130.4797
128.2581
127.9721
123.9294
119.2956
112.1542
102.6959
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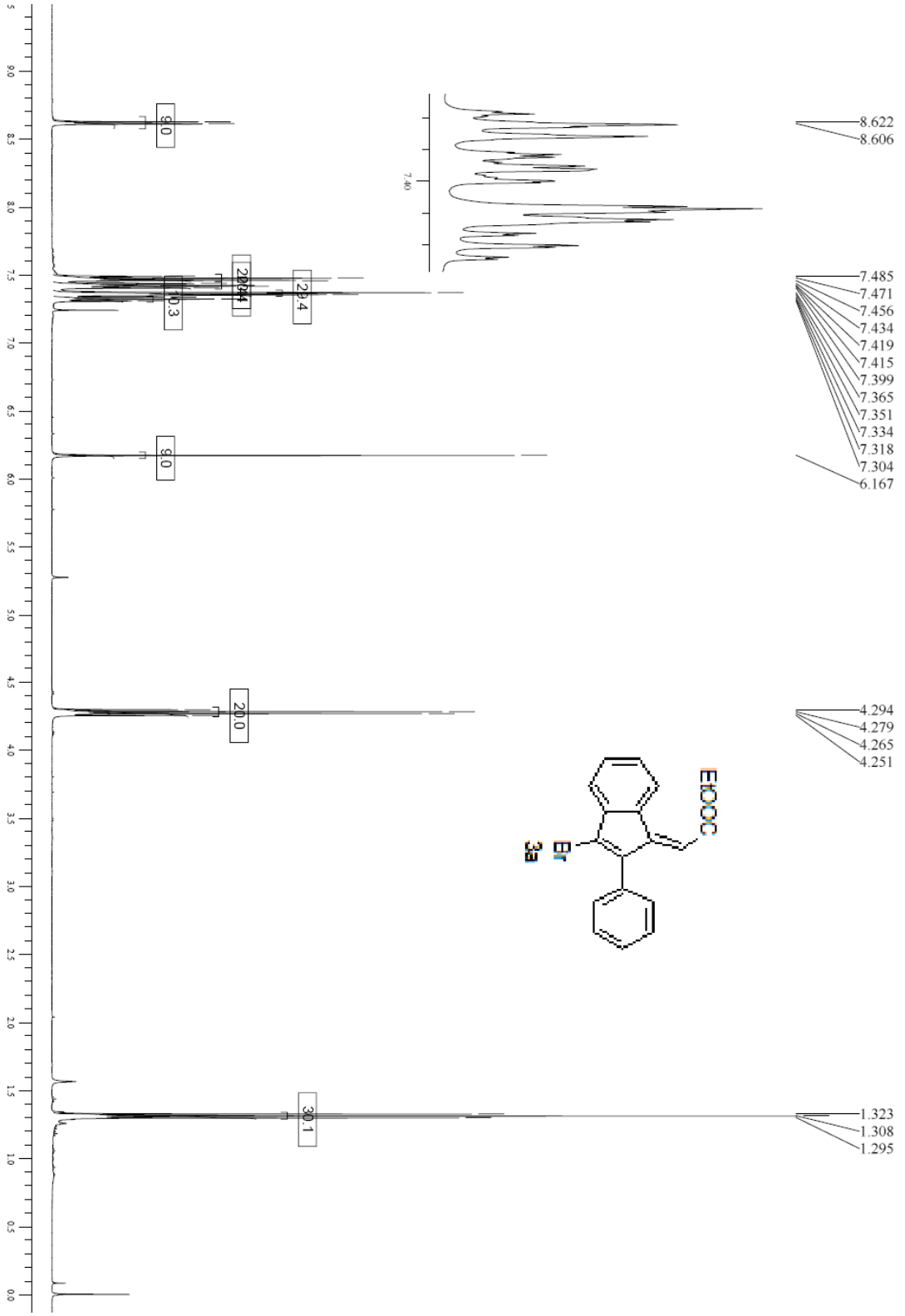
77.0002
76.6760
60.7533
56.2720
56.0813
14.1673
EtOOC
Cl
2j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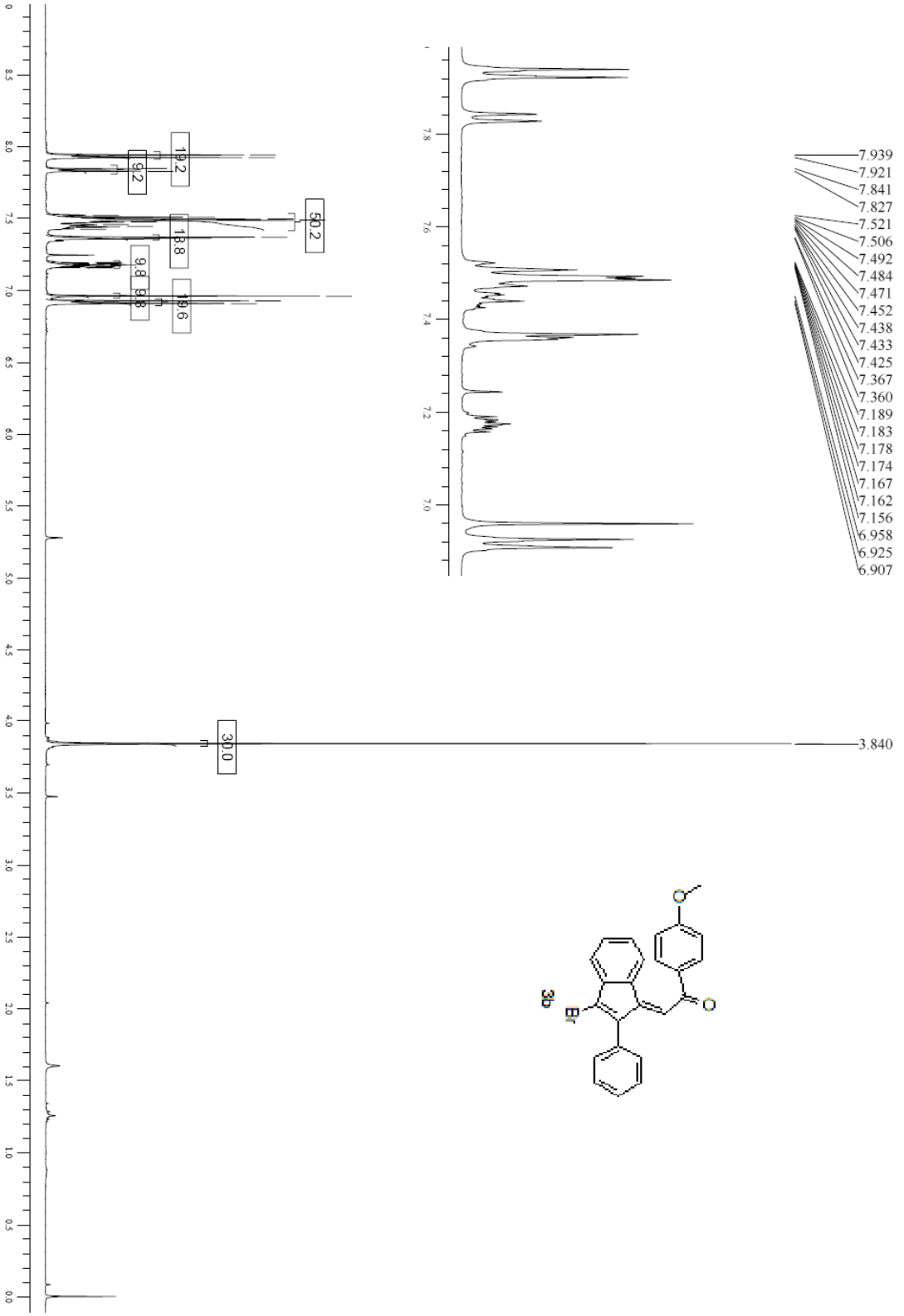
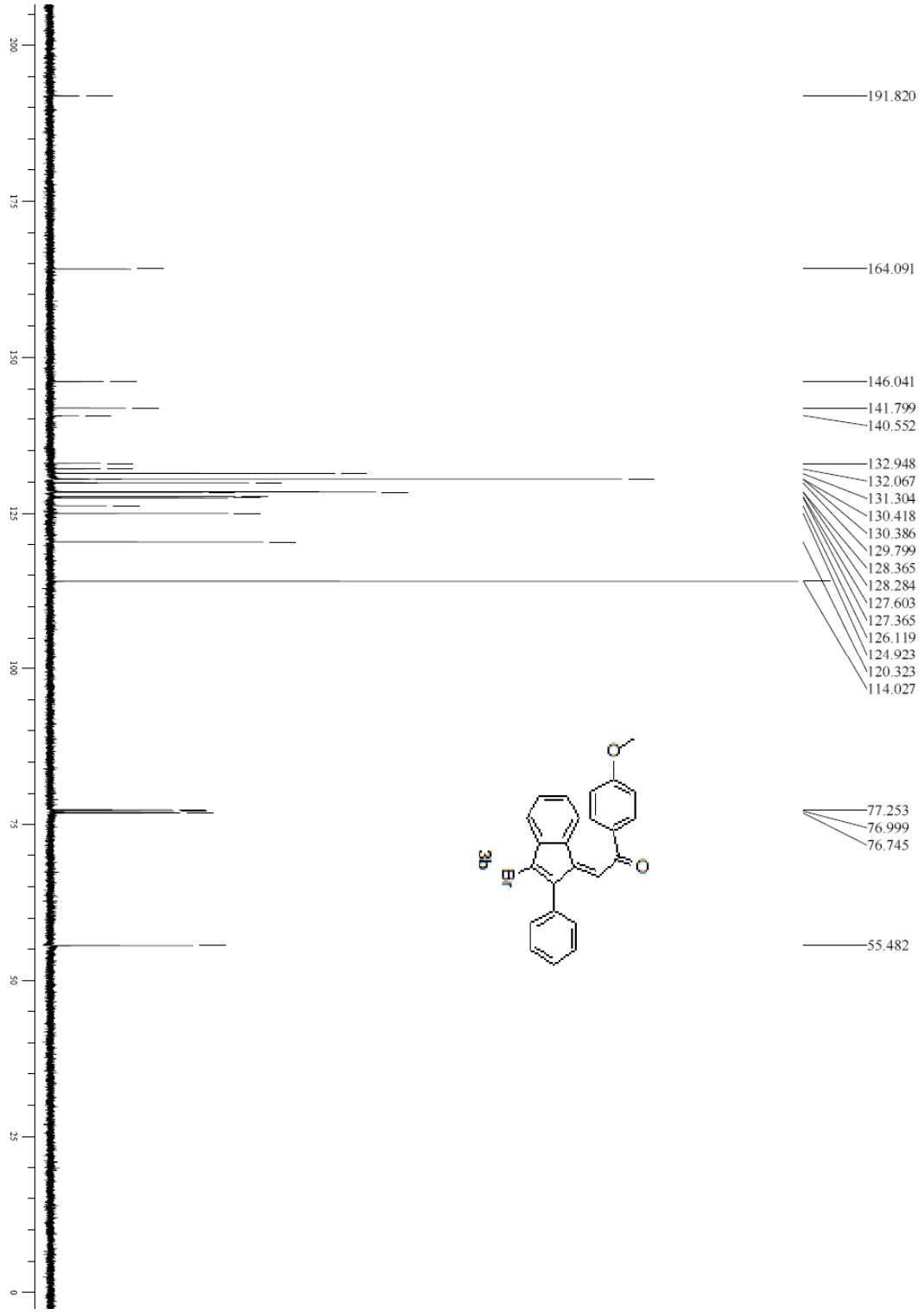
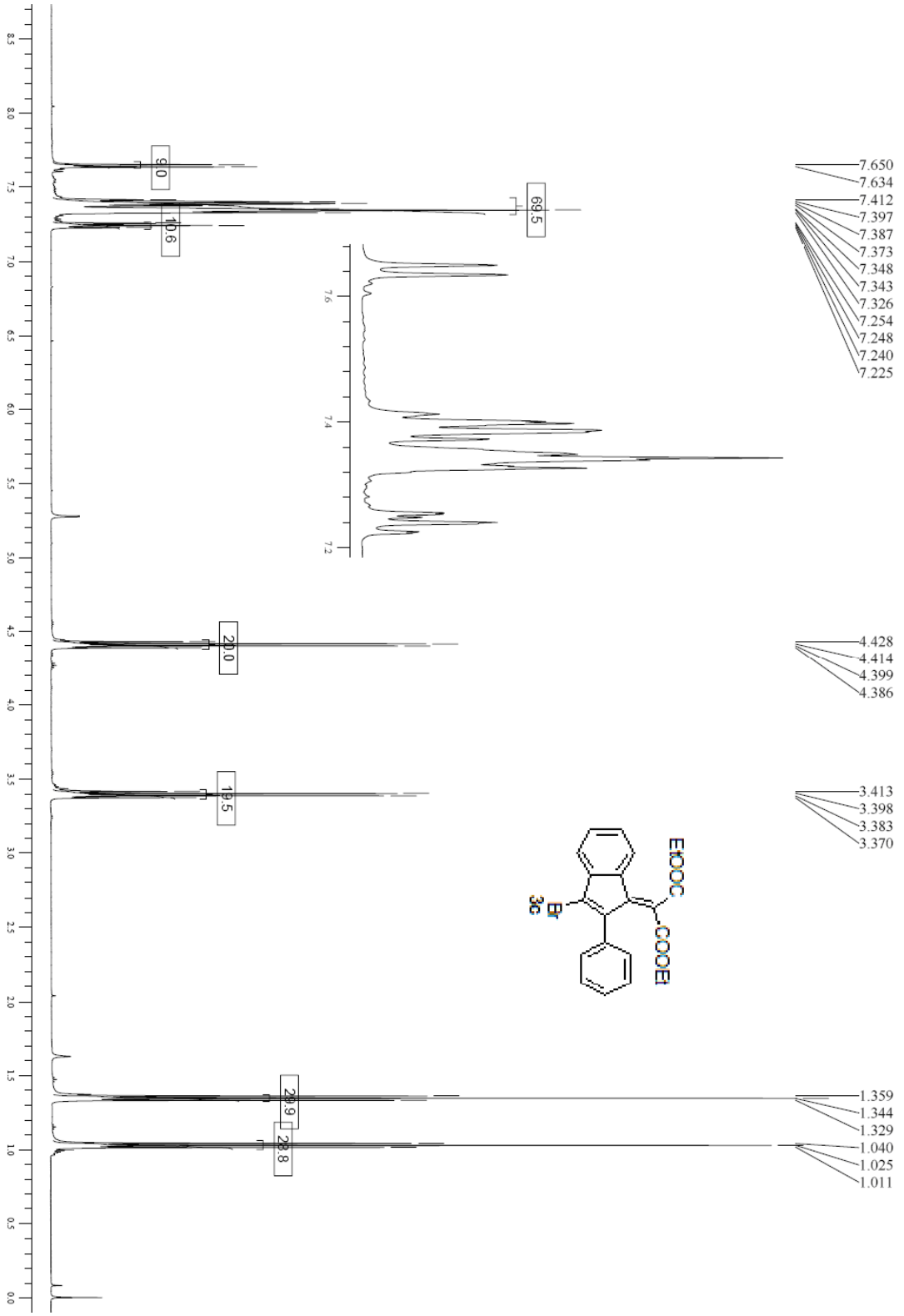
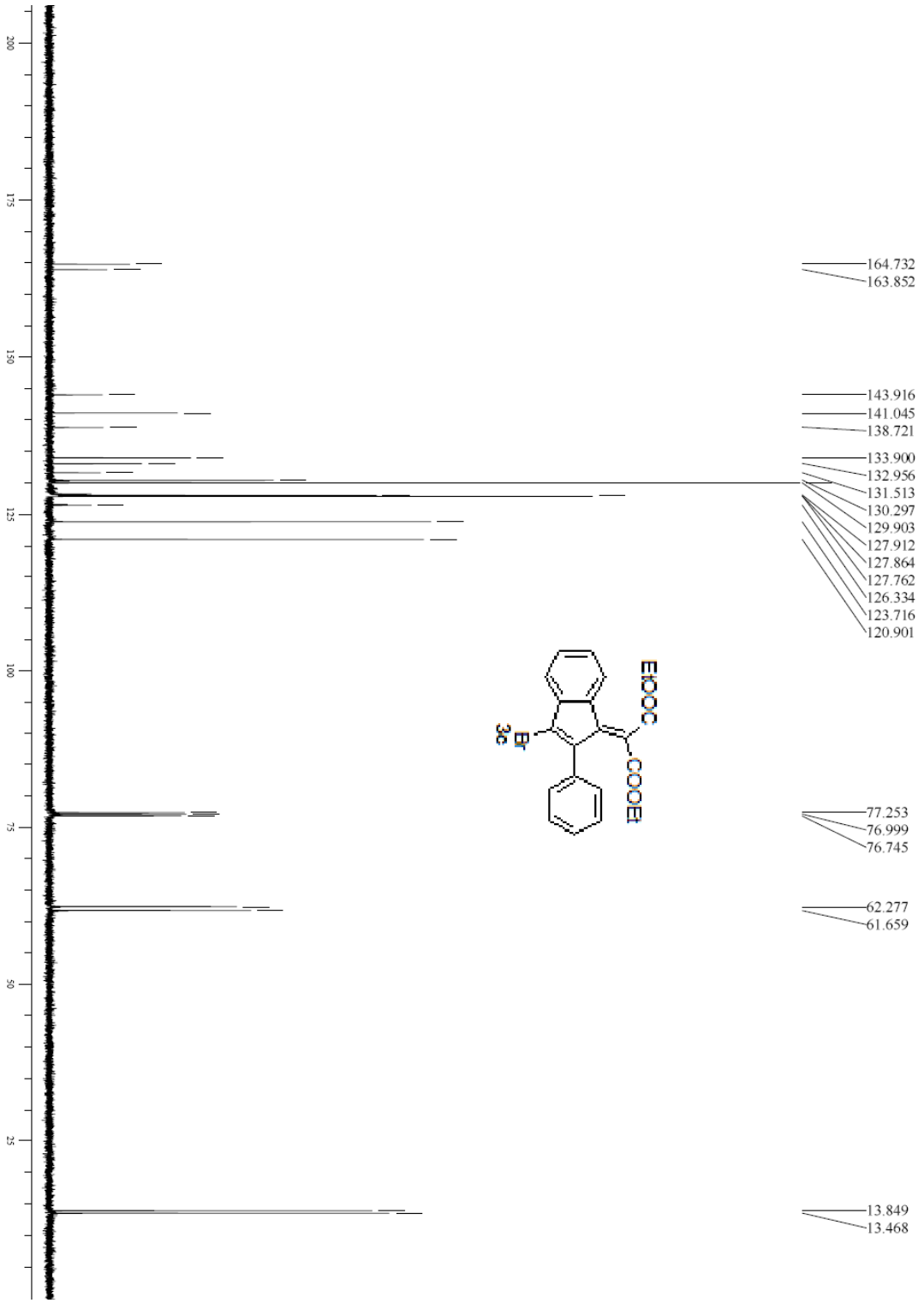
8.606
7.485
7.471
7.456
7.434
7.419
7.415
7.399
7.365
7.351
7.334
7.318
7.304
6.167
4.294
4.279
4.265
4.251
1.323
1.308
1.295
9.0
2.4
10.3
9.0
2.0
30.1
EtOOC
Br
33


165.982
149.891
142.015
141.184
132.768
131.739
130.414
130.309
128.305
128.273
128.027
127.408
126.861
120.522
120.319
77.248
76.995
76.740
60.904
14.162
EtOOC
Et
Et


19.2
9.2
50.2
13.8
9.8
9.8
19.6
30.0
3.840
7.939
7.921
7.841
7.827
7.521
7.506
7.492
7.484
7.471
7.452
7.438
7.433
7.425
7.367
7.360
7.189
7.183
7.178
7.174
7.167
7.162
7.156
6.958
6.925
6.907
O
O
Br
3b


191.820
164.091
146.041
141.799
140.552
132.948
132.067
131.304
130.418
130.386
129.799
128.365
128.284
127.603
127.365
126.119
124.923
120.323
114.027
77.253
76.999
76.745
55.482
Br
O
O


9.0
69.5
10.6
20.0
19.5
29.9
28.8
7.650
7.634
7.412
7.397
7.387
7.373
7.348
7.343
7.326
7.254
7.248
7.240
7.225
4.428
4.414
4.399
4.386
3.413
3.398
3.383
3.370
1.359
1.344
1.329
1.040
1.025
1.011
EtOOC
Br
COOEt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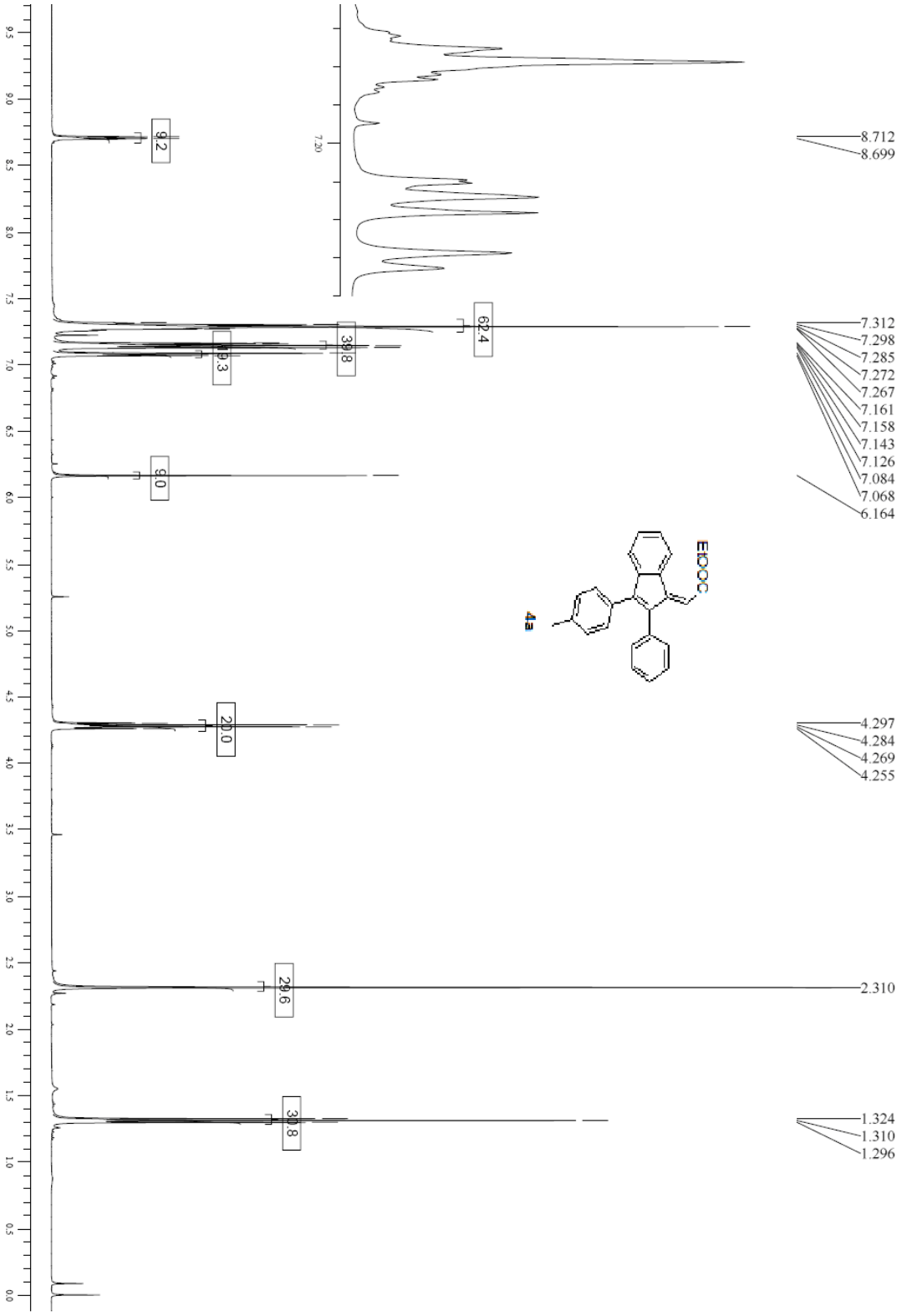
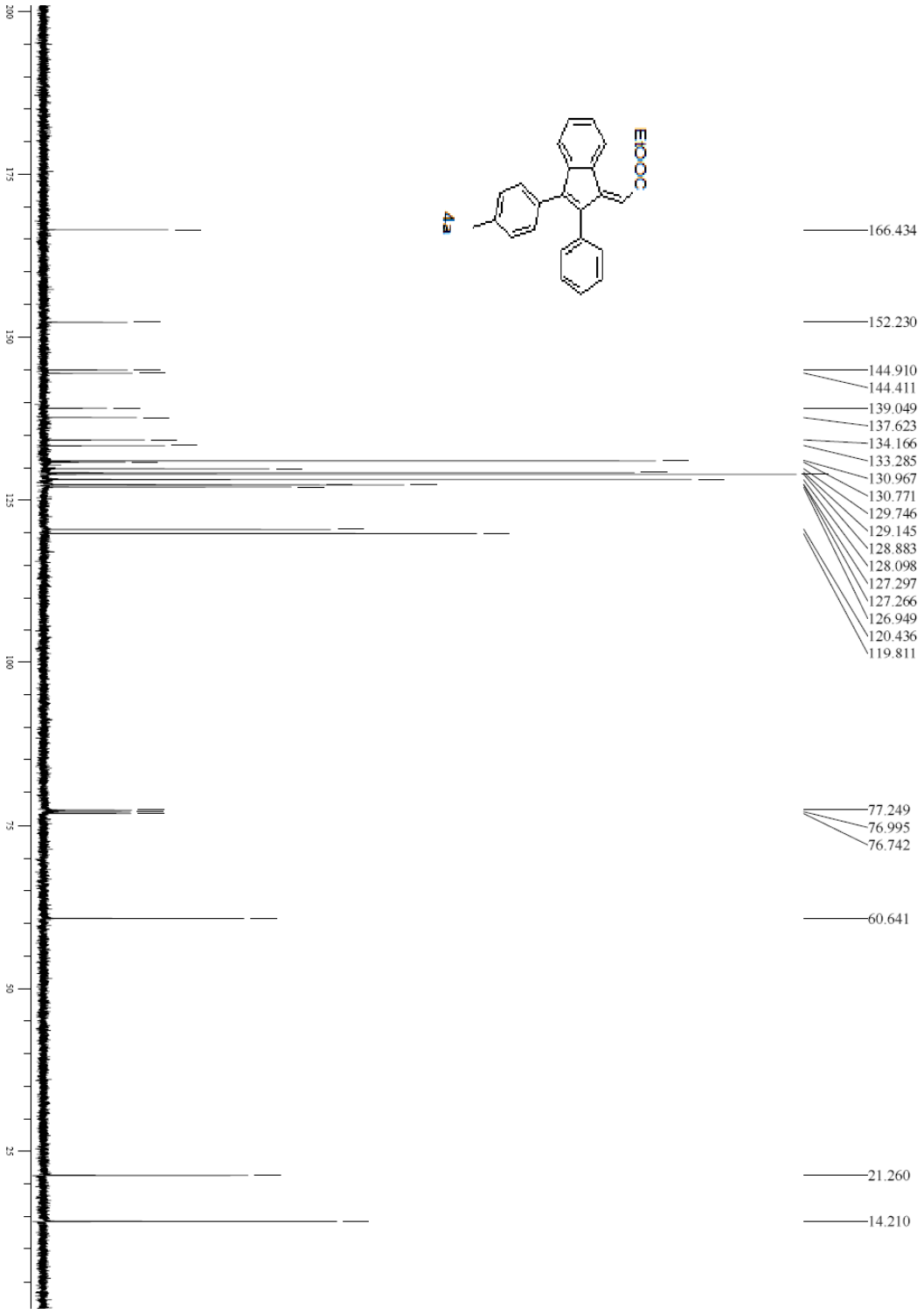
163.852
143.916
141.045
138.721
133.900
132.956
131.513
130.297
129.903
127.912
127.864
127.762
126.334
123.716
120.901
77.253
76.999
76.745
62.277
61.659
13.849
13.468
EtOOC
Et
COOEt


9.2
2.3
39.8
62.4
9.0
20.0
29.6
30.8
8.712
8.699
7.312
7.298
7.285
7.272
7.267
7.161
7.158
7.143
7.126
7.084
7.068
6.164
4.297
4.284
4.269
4.255
2.310
1.324
1.310
1.296
EtOOC
4a


EtOOC
4a
166.434
152.230
144.910
144.411
139.049
137.623
134.166
133.285
130.967
130.771
129.746
129.145
128.883
128.098
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126.949
120.436
119.811
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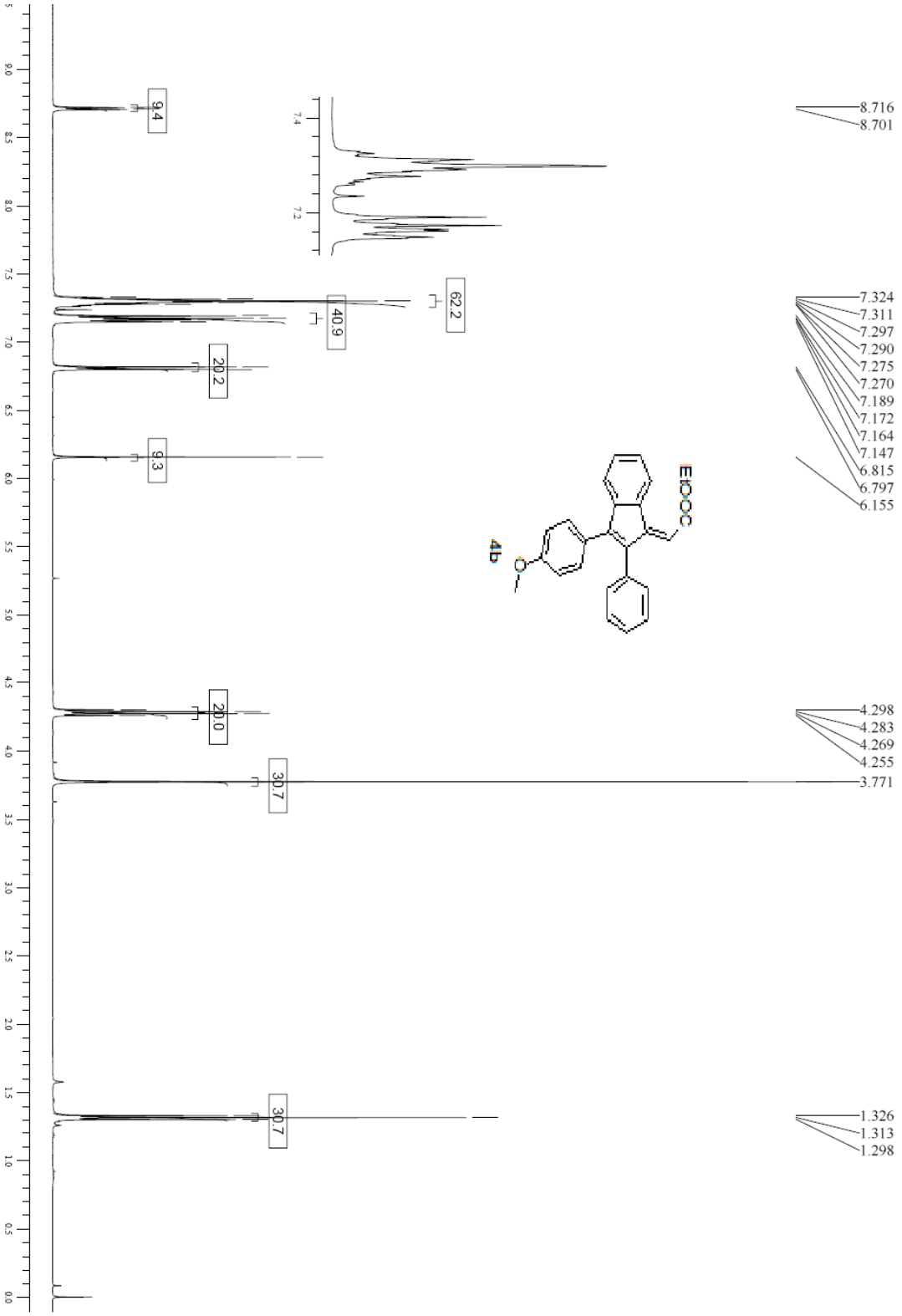
76.995
76.742
60.641
21.260
14.210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62.2
40.9
20.2
9.3
20.0
30.7
30.7
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8.701
7.324
7.311
7.297
7.290
7.275
7.270
7.189
7.172
7.164
7.147
6.815
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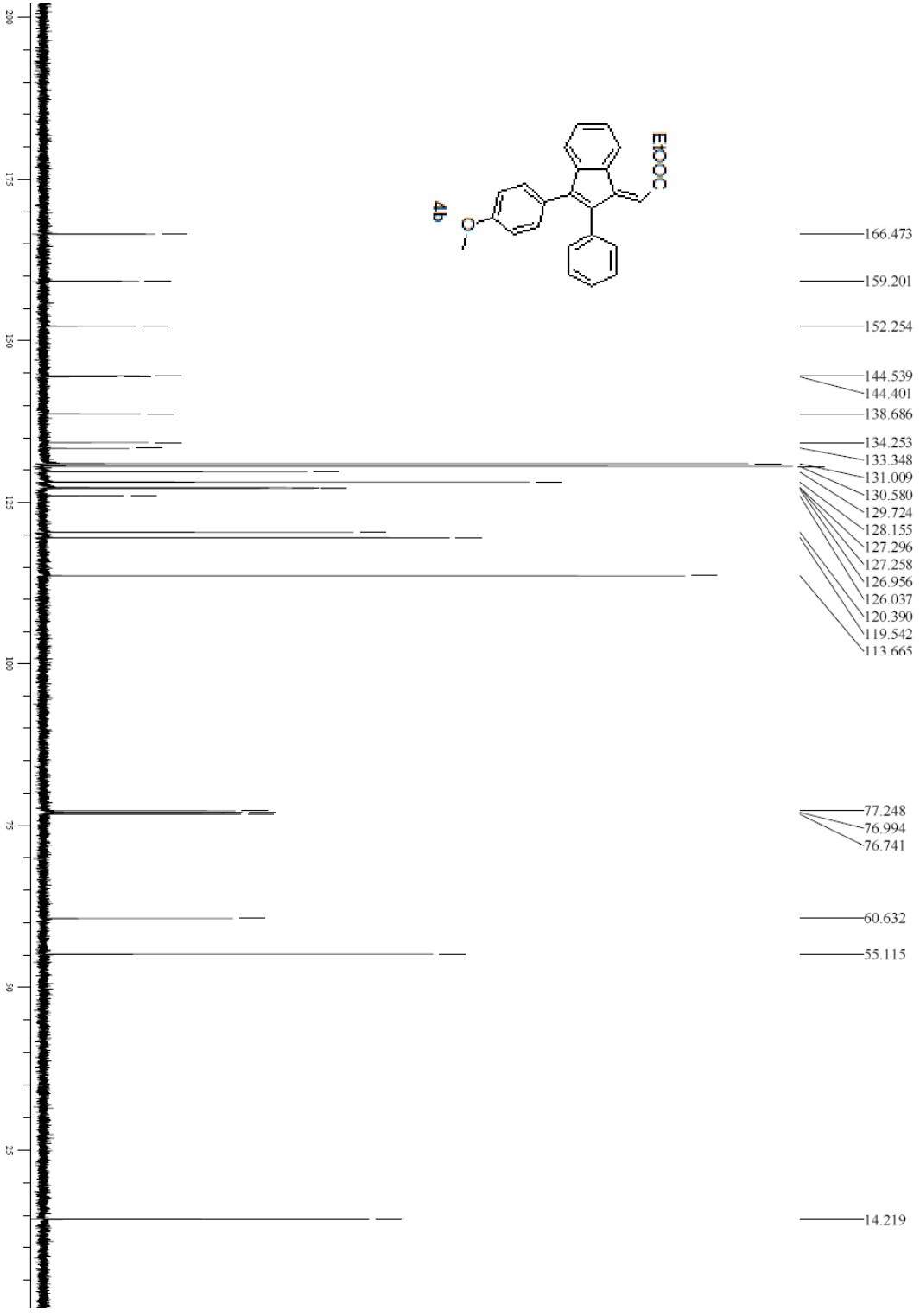
6.155
4.298
4.283
4.269
4.255
3.771
1.326
1.313
1.298
EtOOC
O
4b


4b
EtOOC
O
166.473
159.201
152.254
144.539
144.401
138.686
134.253
133.348
131.009
130.580
129.724
128.155
127.296
127.258
126.956
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120.390
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77.248
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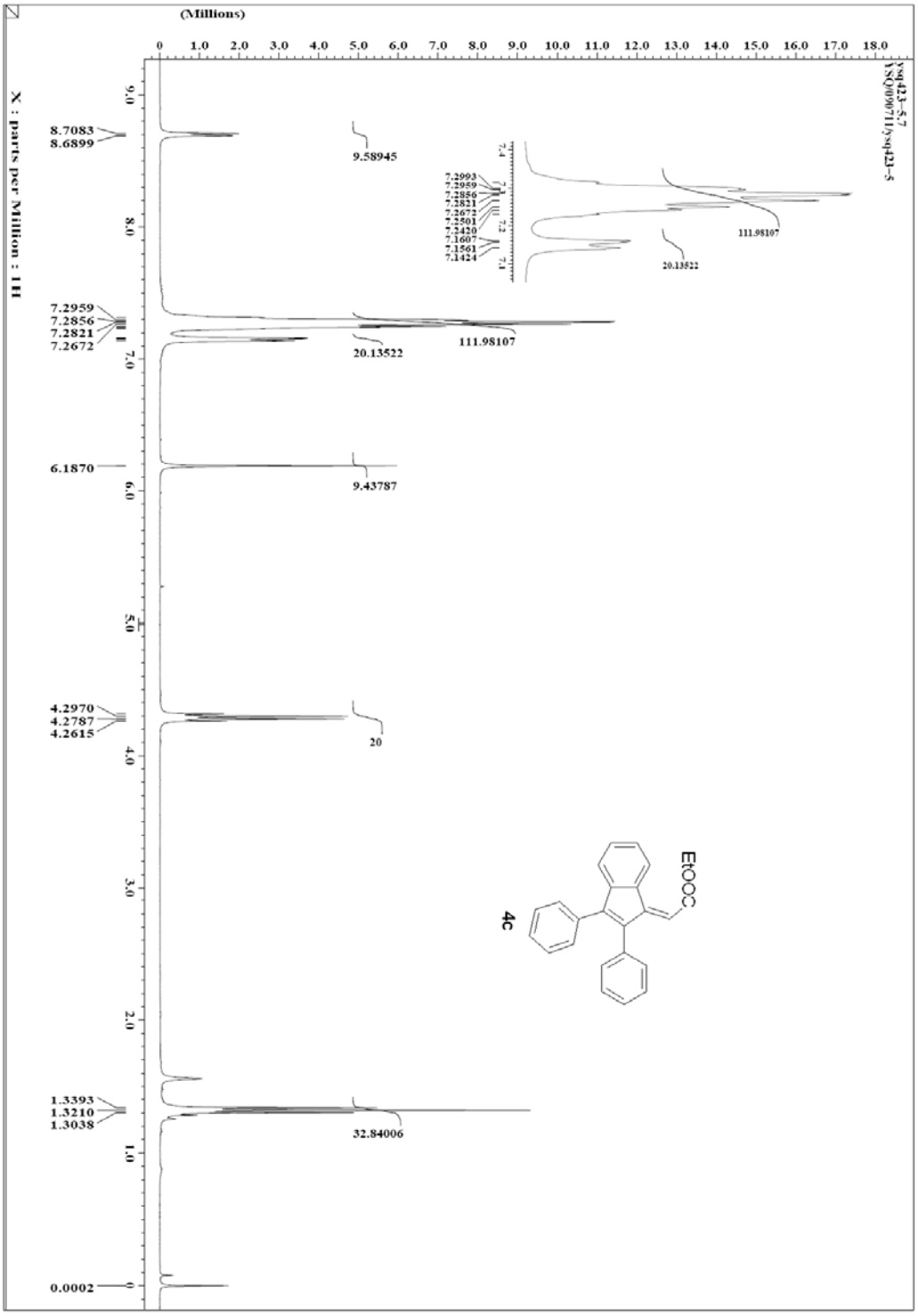
55.115
14.219


(Millions)
X : parts per Million : 1H
8.7083
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7.2856
7.2821
7.2672
20.13522
111.98107
6.1870
9.43787
4.2970
4.2787
4.2615
20
1.3393
1.3210
1.3038
32.84006
0.0002
4c
EtOOC


166.383
152.068
144.897
144.310
139.419
133.946
133.788
133.200
130.950
129.799
129.229
128.150
128.103
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127.008
120.402
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76.744
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14.207
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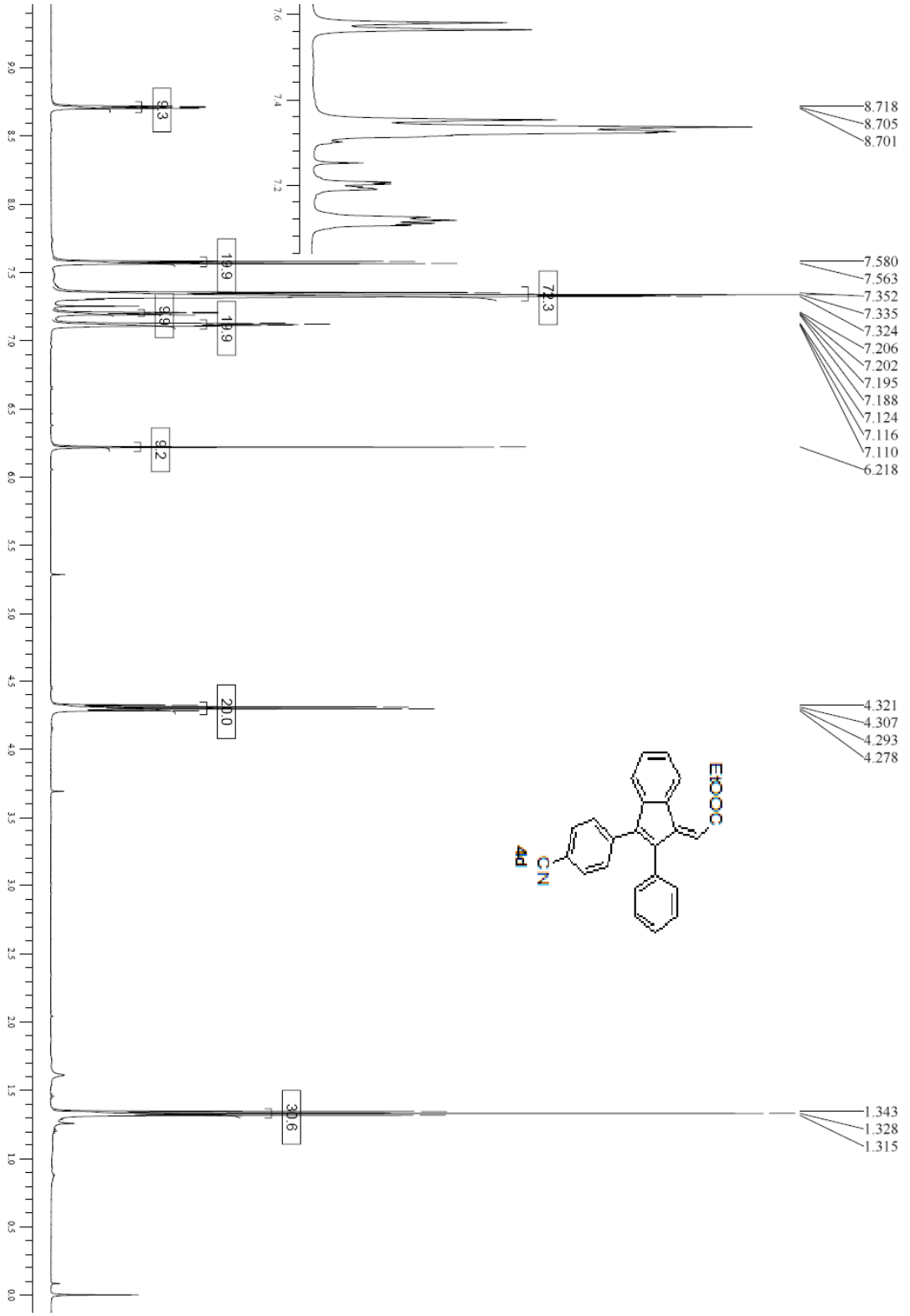
4b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7.335
7.324
7.206
7.202
7.195
7.188
7.124
7.116
7.110
6.218
4.321
4.307
4.293
4.278
1.343
1.328
1.315
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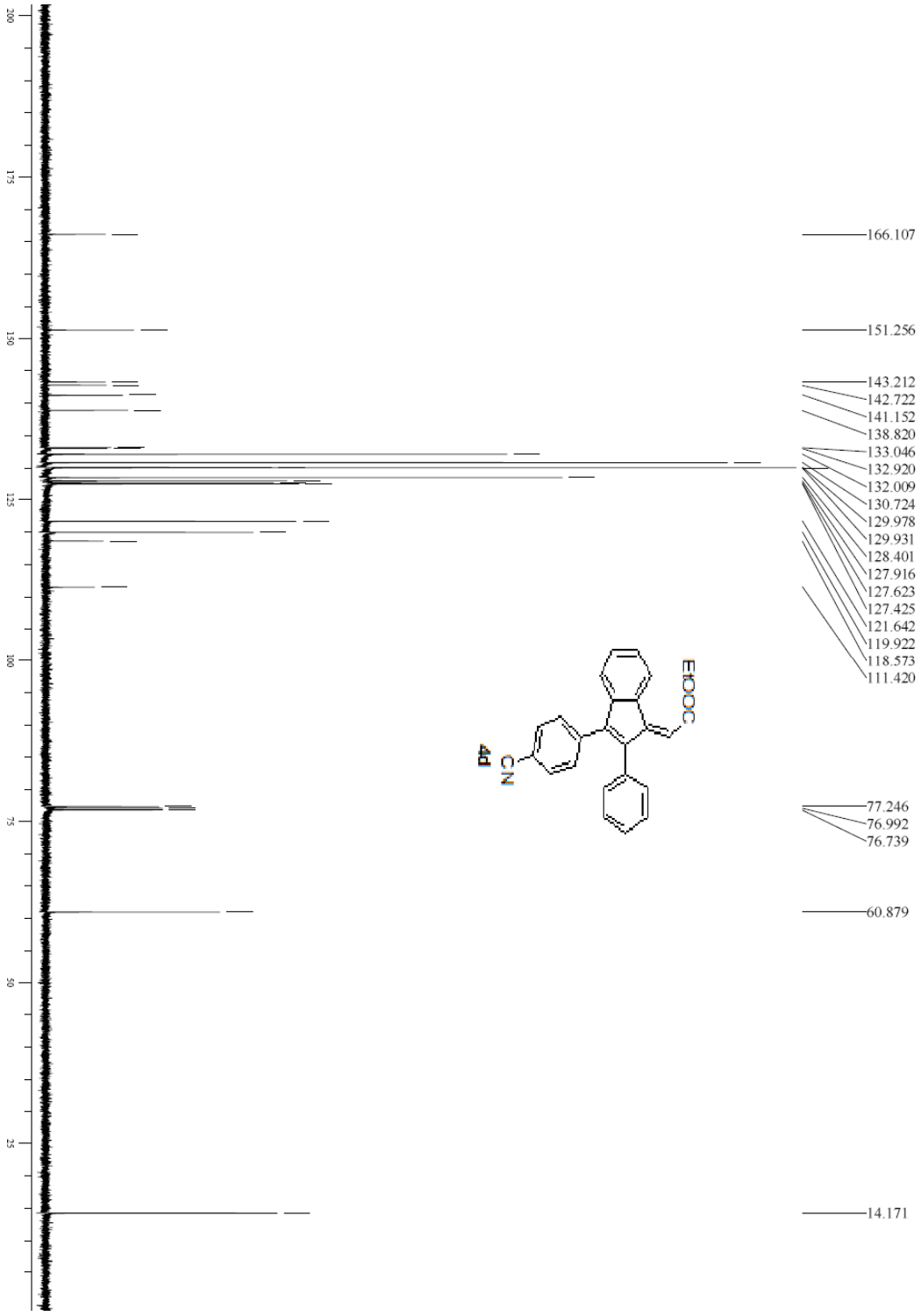
19.9
72.3
9.9
19.9
9.2
20.0
30.6
EtOOC
CN
4d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138.820
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132.920
132.009
130.724
129.978
129.931
128.401
127.916
127.623
127.425
121.642
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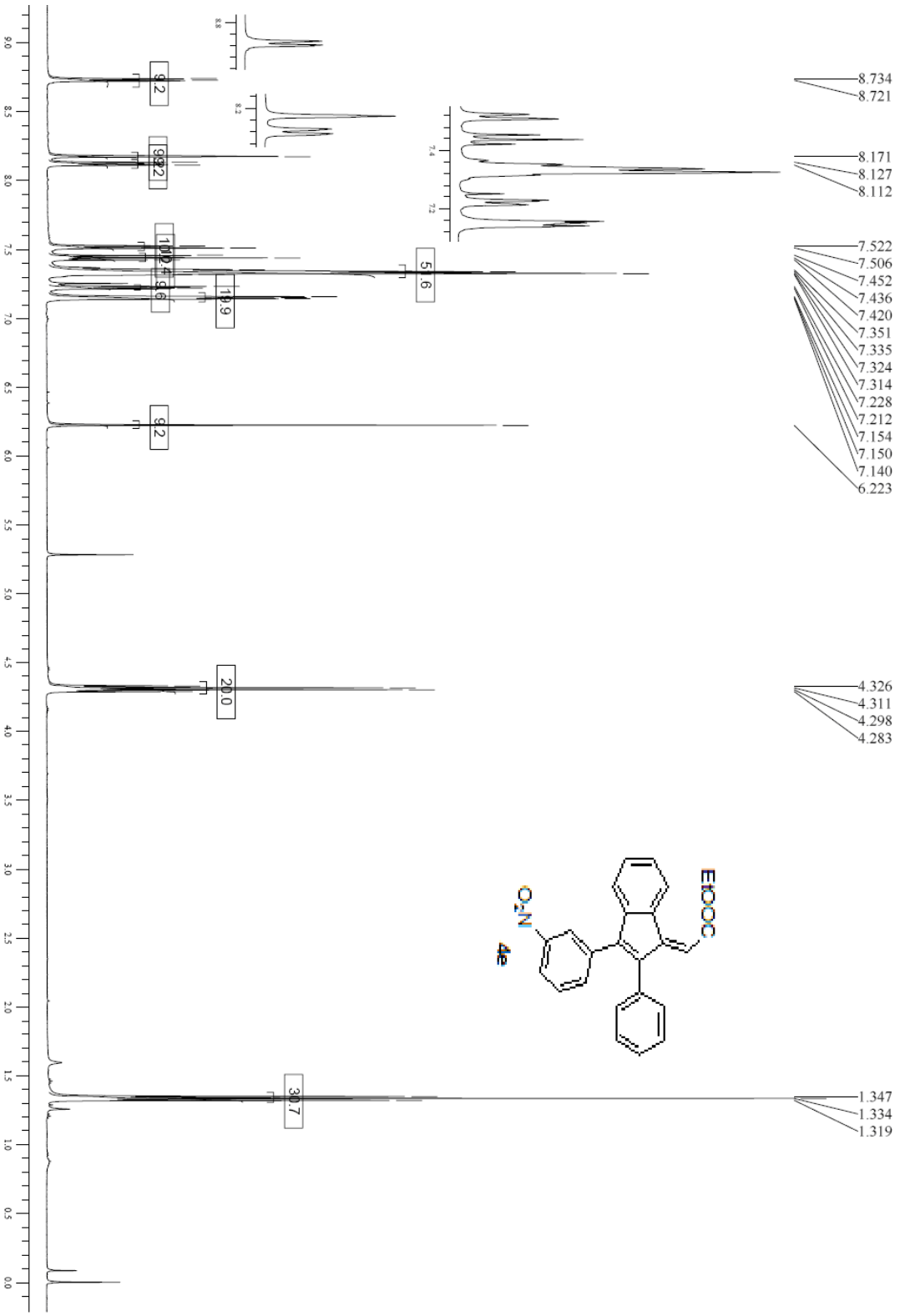
111.420
77.246
76.992
76.739
60.879
14.171
EtOOC
CN
4d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7.324
7.314
7.228
7.212
7.154
7.150
7.140
6.223
4.326
4.311
4.298
4.283
1.347
1.334
1.319
9.2
9.2
9.2
5.6
10.9
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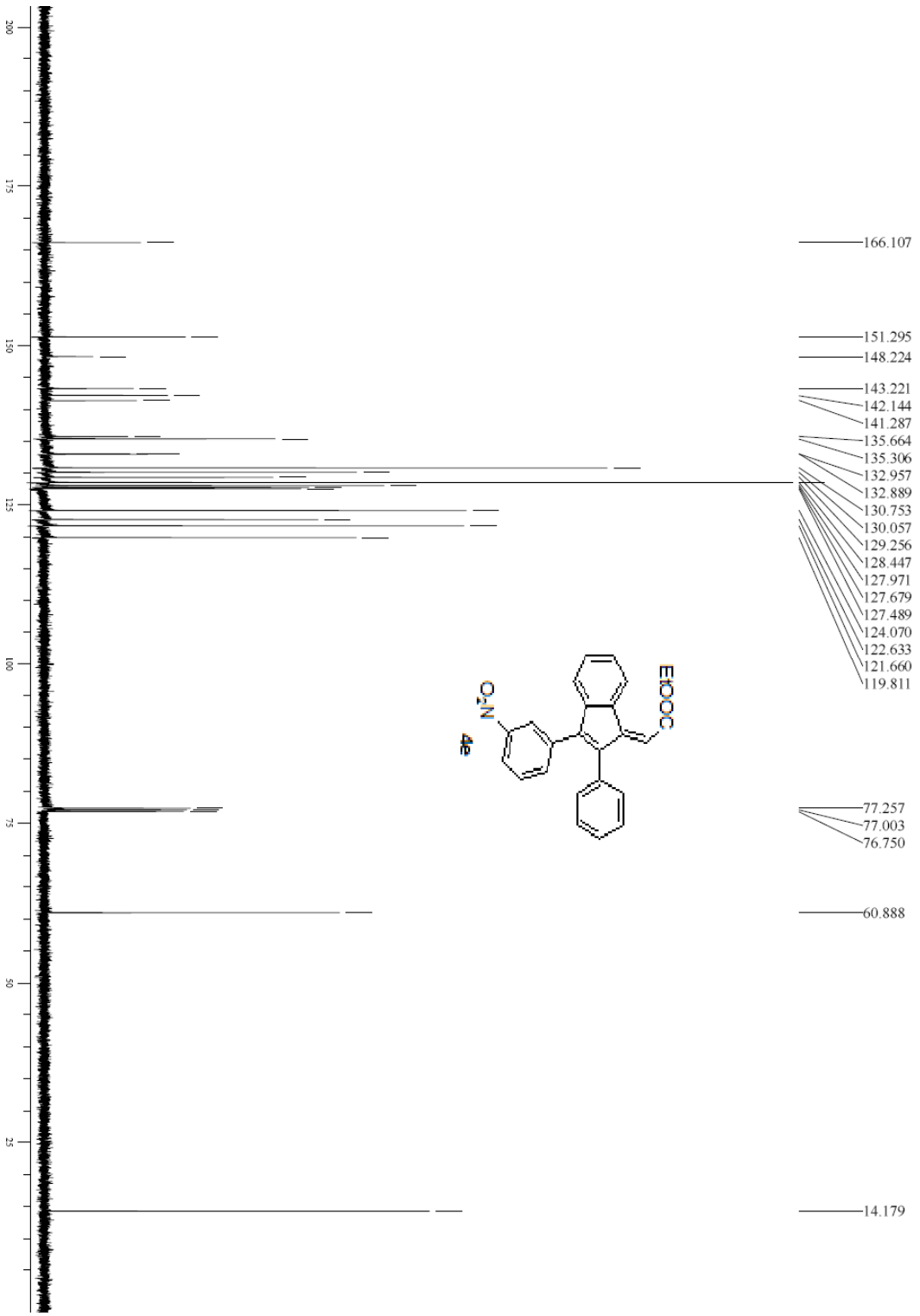
EtOOC
4e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132.889
130.753
130.057
129.256
128.447
127.971
127.679
127.489
124.070
122.633
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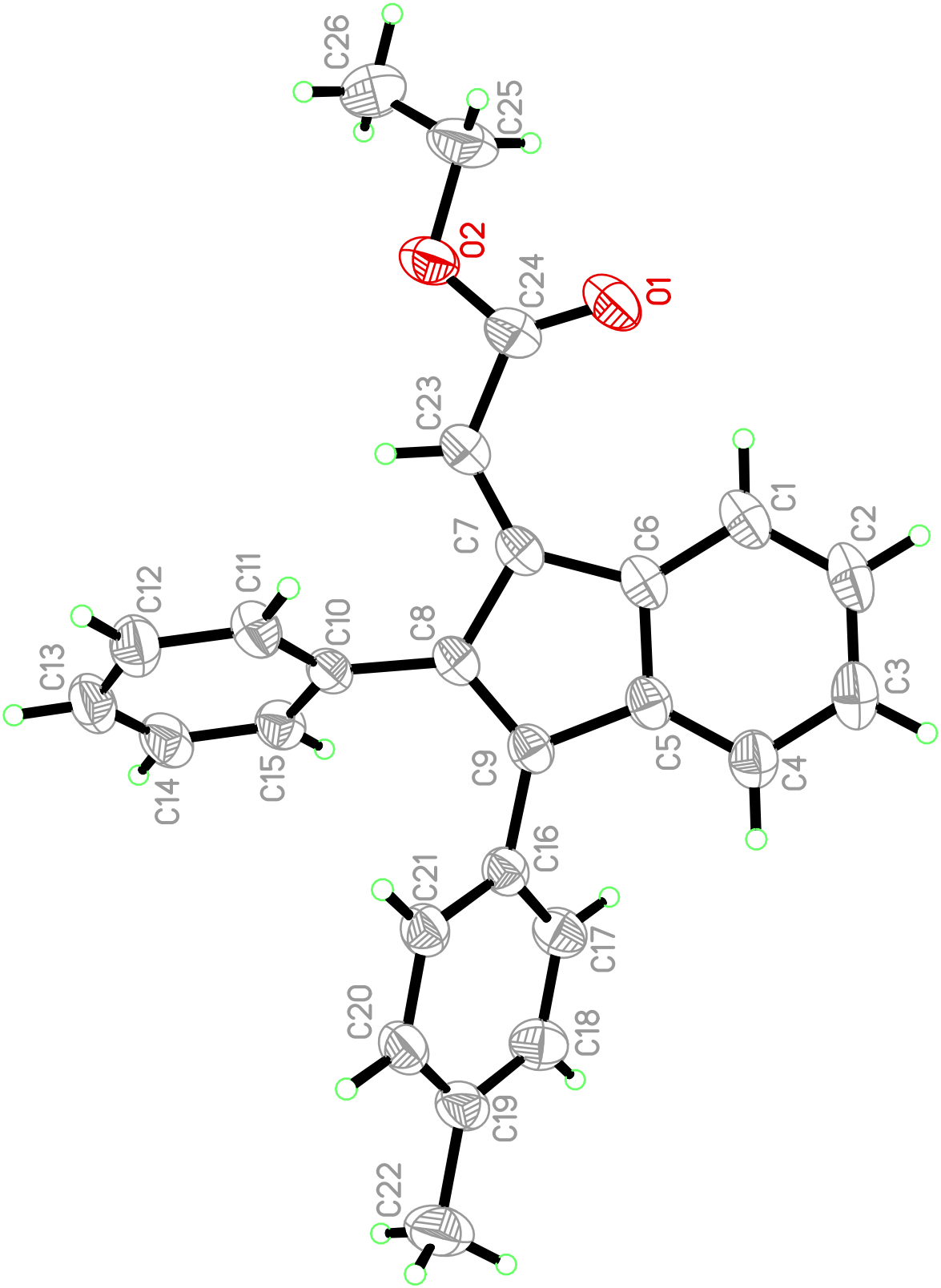
119.811
77.257
77.003
76.750
60.888
14.179
O2N
EtOOC
4e



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: wujie090420_0m

Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=10.1464(3) b=10.1719(3) c=10.4892(3)
alpha=72.943(1) beta=79.827(1) gamma=81.861(1)
Temperature: 296 K

	Calculated	Reported
Volume	1014.04(5)	1014.04(5)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C26 H22 O2	?
Sum formula	C26 H22 O2	C26 H22 O2
Mr	366.44	366.44
Dx,g cm-3	1.200	1.200
Z	2	2
Mu (mm-1)	0.074	0.074
F000	388.0	388.0
F000'	388.17	
h,k,lmax	12,12,12	12,12,12
Nref	3987	3946
Tmin,Tmax	0.963,0.971	0.864,1.000
Tmin'	0.954	

Correction method= MULTI-SCAN

Data completeness= 0.990 Theta(max)= 25.990

R(reflections)= 0.0567(3197) wR2(reflections)= 0.1593(3946)

S = 1.058 Npar= 255

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTM02_ALERT_3_C The ratio of expected to reported Tmax/Tmin(RR') is < 0.90
Tmin and Tmax reported: 0.864 1.000
Tmin(prime) and Tmax expected: 0.954 0.971
RR(prime) = 0.880
Please check that your absorption correction is appropriate.
ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without

```
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as multi-scan
CELLT02_ALERT_1_C  The cell measurement temperature is greater than the
           given melting point of the compound.
           Value of measurement temperature given =   296.000
           Value of melting point given =     0.000
SHFSU01_ALERT_2_C  The absolute value of parameter shift to su ratio > 0.05
           Absolute value of the parameter shift to su ratio given   0.058
           Additional refinement cycles may be required.
PLAT080_ALERT_2_C Maximum Shift/Error ..........................       0.06
PLAT220_ALERT_2_C Large Non-Solvent    C     Ueq(max)/Ueq(min) ...       2.70 Ratio
PLAT061_ALERT_4_C Tmax/Tmin Range Test RR' too Large ............       0.88
PLAT063_ALERT_4_C Crystal Probably too Large for Beam Size .....       0.63 mm
PLAT153_ALERT_1_C The su's on the Cell Axes   are Equal (x 100000)         30 Ang.
PLAT195_ALERT_1_C Missing _cell_measurement_theta_max   datum ....          ?
PLAT196_ALERT_1_C Missing _cell_measurement_theta_min   datum ....          ?
```

Alert level G

```
ABSTM02_ALERT_3_G  When printed, the submitted absorption T values will be
           replaced by the scaled T values. Since the ratio of scaled T's
           is identical to the ratio of reported T values, the scaling
           does not imply a change to the absorption corrections used in
           the study.
           Ratio of Tmax expected/reported      0.971
           Tmax scaled      0.971 Tmin scaled      0.839
PLAT062_ALERT_4_G Rescale T(min) & T(max) by ...................       0.97
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal  (x 10000)        100 Deg.
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3
```

```
   0 ALERT level A = In general: serious problem
   0 ALERT level B = Potentially serious problem
  11 ALERT level C = Check and explain
   4 ALERT level G = General alerts; check

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 09/04/2009; check.def file version of 08/04/2009

Datablock wujie090420_0m - ellipsoid plot