Rapid Access to 1-Methyleneindenes via Palladium-Catalyzed Tandem Reactions of 1-(2,2-Dibromovinyl)-2-alkynylbenzenes with Arylboronic Acids

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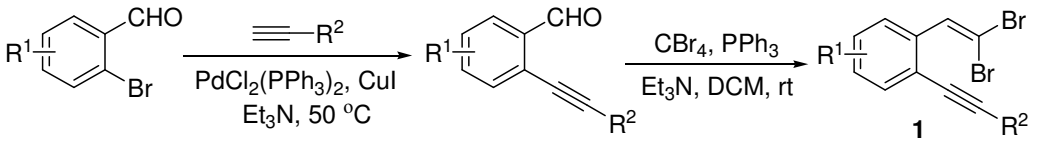
Supporting Information

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.

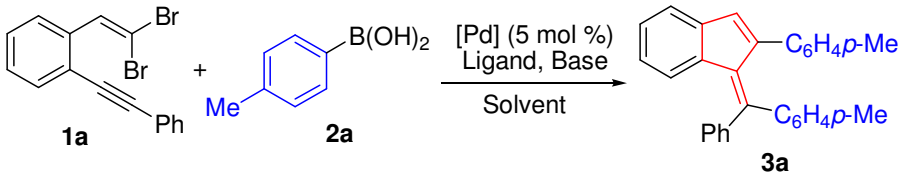
*General procedure for the synthesis of 1-(2,2-dibromovinyl)-2-alkynylbenzene **1.***



2-Alkynylbenzaldehyde was synthesized via Sonogashira coupling according to the literature report (Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 86.).

CBr_4 (2.5 mmol) was added to a solution of PPh_3 (4.5 mmol) and Et_3N (1.1 mmol) in DCM (10 mL) slowly. Subsequently, 2-alkynylbenzaldehyde (1 mmol) was added to the mixture. This mixture was stirred at room temperature under the air for 3h. Then the reaction was quenched with water (20 mL), and extracted with ethyl acetate (20 mL x 2). The combined organic layers were washed with brine (20 mL x 2), dried with Na_2SO_4, and evaporated under reduced pressure. After purification by flash column chromatography (hexane/ethyl acetate = 20:1), the pure 1-(2,2-dibromovinyl)-2-alkynylbenzene **1** could be obtained.

Initial Studies for palladium-catalyzed reaction of 1-(2,2-dibromovinyl)-2-alkynyl-benzene **1a** with 4-methylphenylboronic acid **2a**.

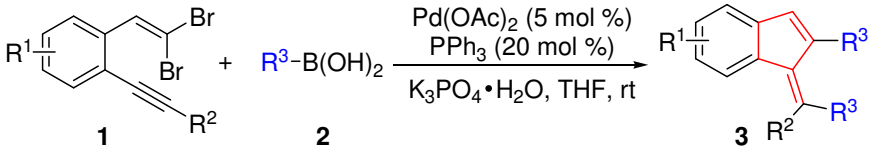


Entry	Pd catalyst	Ligand/%	Base/equiv	Solvent	Temp	Yield[a]
1	$Pd(OAc)_2$	PPh_3/20	K_3PO_4/6	THF	r.t.	63%
2	$Pd(PPh_3)_4$	PPh_3/20	K_3PO_4/6	THF	r.t.	53%
3	$PdCl_2$	PPh_3/20	K_3PO_4/6	THF	r.t.	59%
4	$Pd_2(dba)_3$	PPh_3/20	K_3PO_4/6	THF	r.t.	62%
5	$PdCl_2(PPh_3)_2$	PPh_3/20	K_3PO_4/6	THF	r.t.	55%
6	$PdCl_2$(dppf)	PPh_3/20	K_3PO_4/6	THF	r.t.	62%
7	$Pd(OAc)_2$	PPh_3/20	K_2CO_3/6	THF	r.t.	55%
8	$Pd(OAc)_2$	PPh_3/20	Cs_2CO_3/6	THF	r.t.	47%
9	$Pd(OAc)_2$	PPh_3/20	$NaHCO_3$/6	THF	r.t.	Trace
10	$Pd(OAc)_2$	PPh_3/20	KOH/6	THF	r.t.	57%
11	$Pd(OAc)_2$	PPh_3/20	LiOH/6	THF	r.t.	Trace
12	$Pd(OAc)_2$	PPh_3/20	NaOAc/6	THF	r.t.	Trace
13	$Pd(OAc)_2$	PPh_3/20	t-BuOK/6	THF	r.t.	Trace
14	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	THF	r.t.	86%
15	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	Toluene	r.t.	Trace
16	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	MeCN	r.t.	Trace
17	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	DMAc	r.t.	Trace
18	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	1,4-dioxane	r.t.	65%
19	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	DCE	r.t.	71%
20	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4\cdot H_2O$/6	DMF	r.t.	Trace
21	$Pd(OAc)_2$	BINAP/10	$K_3PO_4\cdot H_2O$/6	THF	r.t.	Trace
22	$Pd(OAc)_2$	PCy_3/20	$K_3PO_4\cdot H_2O$/6	THF	r.t.	Trace
23	$Pd(OAc)_2$	DPPF/10	$K_3PO_4\cdot H_2O$/6	THF	r.t.	64%
24	$Pd(OAc)_2$	DPPP/10	$K_3PO_4\cdot H_2O$/6	THF	r.t.	Trace

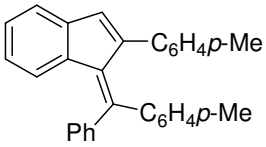
25	$Pd(OAc)_2$	JohnPhos/20	$K_3PO_4·H_2O$/6	THF	r.t.	Trace
26	$Pd(OAc)_2$	XPhos/20	$K_3PO_4·H_2O$/6	THF	r.t.	22%
27	$Pd(OAc)_2$	CyJohnPhos/20	$K_3PO_4·H_2O$/6	THF	r.t.	10%
28	$Pd(OAc)_2$	$(2\text{-furyl})_3P$/20	$K_3PO_4·H_2O$/6	THF	r.t.	51%
29	$Pd(OAc)_2$	$P(o\text{-tolyl})_3$/20	$K_3PO_4·H_2O$/6	THF	r.t.	10%
30	$Pd(OAc)_2$	S-Phos/20	$K_3PO_4·H_2O$/6	THF	r.t.	Trace
31	$Pd(OAc)_2$	Xantphos/10	$K_3PO_4·H_2O$/6	THF	r.t.	Trace
32	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4·H_2O$/6	THF	r.t.	62%
33	$Pd(OAc)_2$	PPh_3/10	$K_3PO_4·H_2O$/6	THF	r.t.	70%
34	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4·H_2O$/5	THF	r.t.	59%
35	$Pd(OAc)_2$	PPh_3/20	$K_3PO_4·H_2O$/6	THF	60°C	78%

[a] Isolated yield based on 1-(2,2-dibromovinyl)-2-alkynylbenzene **1a**

*General procedure for palladium-catalyzed tandem reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzene **1** with arylboronic acid **2**.*

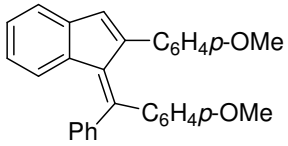


1-(2,2-Dibromovinyl)-2-alkynylbenzene **1** (0.2 mmol, 1 equiv) was added to a solution of $Pd(OAc)_2$ (5 mol %), PPh_3 (20 mol %), $K_3PO_4·H_2O$ (1.2 mmol, 6 equiv) and arylboronic acid **2** (0.6 mmol, 3 equiv) in THF (2.0 mL). The solution was then stirred at room temperature. After completion of reaction as indicated by TLC, the reaction was quenched with water (5.0 mL), extracted with EtOAc (2 x 10 mL), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the product **3**.



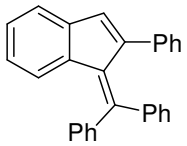
(*Z*)-1-(Phenyl(*p*-tolyl)methylene)-2-*p*-tolyl-1*H*-indene **3a**

Yield: 86%; red solid, melting point: 177-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.18 (s, 3H), 6.35 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.76–6.80 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.89 (s, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.38–7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.0, 120.4, 123.3, 124.5, 126.9, 127.5, 127.8, 128.5, 128.7, 130.9, 132.3, 133.1, 134.8, 135.2, 136.9, 137.9, 138.2, 138.5, 142.2, 143.0, 144.0, 149.5; HRMS (ESI) calcd for $C_{30}H_{25}$ $(M + H)^+$ 385.1956, found 385.1938. Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29; Found: C, 93.65; H, 6.42. (Solvent used for recrystallization: ethyl acetate/*n*-hexane)



(*Z*)-2-(4-Methoxyphenyl)-1-((4-methoxyphenyl)(phenyl)methylene)-1*H*-indene **3b**

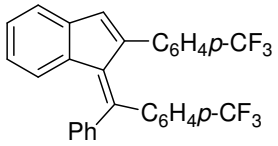
Yield: 75%; red solid ; melting point: 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.67 (s, 3H), 6.32 (d, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 6.77 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 6.87 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.37–7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 55.2, 112.4, 112.9, 120.2, 123.2, 124.4, 126.7, 128.5, 128.8, 129.7, 130.7, 131.0, 132.5, 133.8, 133.9, 136.3, 138.2, 142.1, 143.0, 143.4, 149.1, 157.4, 159.6; HRMS (ESI) calcd for $C_{30}H_{25}O_2$ $(M + H)^+$ 417.1855, found 417.1844. Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81; Found: C, 86.33; H, 5.88.



1-(Diphenylmethylene)-2-phenyl-1*H*-indene **3c**

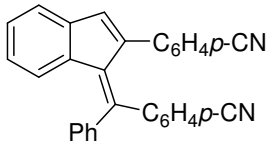
Yield: 80%; red solid ; melting point: 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42

(d, *J* = 7.8 Hz, 1H), 6.84–6.98 (m, 10H), 7.05–7.08 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.44–7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.5, 123.4, 124.8, 125.4, 126.9, 127.1, 127.2, 127.9, 128.6, 128.8, 130.8, 132.4, 134.0, 137.2, 138.1, 138.2, 141.3, 142.1, 142.9, 143.9, 149.5; HRMS (ESI) calcd for $C_{28}H_{21}$ $(M + H)^+$ 357.1643, found 357.1625.



(*Z*)-1-(Phenyl(4-(trifluoromethyl)phenyl)methylene)-2-(4-(trifluoromethyl)phenyl)-1*H*-indene **3d**

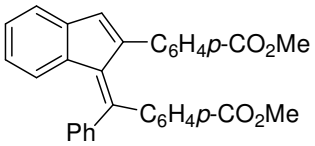
Yield: 70%; yellow solid; melting point: 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.99 (s, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.15–7.19 (m, 3H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.37–7.40 (m, 2H), 7.44–7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.1, 123.6 (q, $^1J_{CF}$ = 269.8 Hz), 123.7, 123.9 (d, $^3J_{CF}$ = 2.8 Hz), 124.0 (q, $^1J_{CF}$ = 270.8 Hz), 124.1 (d, $^3J_{CF}$ = 2.8 Hz), 125.7, 127.8, 128.0 (q, $^2J_{CF}$ = 32.4 Hz), 128.8, 128.9, 129.3, 130.0(q, $^2J_{CF}$ = 32.4 Hz), 130.7, 132.3, 135.8, 137.7, 138.5, 141.5, 141.7, 141.8, 144.6, 147.4; HRMS (ESI) calcd for $C_{30}H_{19}F_6$ $(M + H)^+$ 493.1391, found 493.1382.



(*Z*)-2-(4-Cyanophenyl)-1-((4-cyanophenyl)(phenyl)methylene)-1*H*-indene **3e**

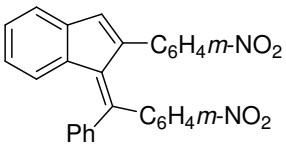
Yield: 72%; yellow solid; melting point: 259-260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.16–7.21 (m, 3H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.46–7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.4, 111.6, 118.0, 118.5, 121.4, 123.7, 126.1, 128.1, 129.0, 129.6, 130.7,

130.8, 131.2, 132.8, 137.2, 137.7, 138.8, 140.9, 141.2, 141.5, 142.6, 145.7, 146.8; HRMS (ESI) calcd for $C_{30}H_{18}N_2$: 429.1368 (M + $Na^{+)}$, found: 429.1357. Anal. Calcd for $C_{30}H_{18}N_2$: C, 88.64; H, 4.46; Found: C, 88.72; H, 4.58.



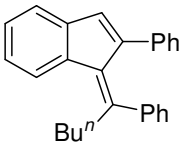
(*Z*)-2-(4-(Methoxycarbonyl)phenyl)-1-((4-(methoxycarbonyl)phenyl)(phenyl)methylene)-1*H*-indene **3f**

Yield: 74%; yellow solid; melting point: 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.84 (s, 3H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 7.00 (s, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.44–7.53 (m, 5H), 7.58 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 52.0, 121.0, 123.6, 125.5, 127.1, 127.6, 128.2, 128.4, 128.6, 128.8, 129.1, 129.2, 130.7, 132.2, 135.7, 137.9, 138.3, 141.8, 141.9, 142.3, 142.7, 145.7, 148.0, 166.4, 166.8; HRMS (ESI) calcd for $C_{32}H_{25}O_4$ (M + $H)^+$ 473.1753, found 473.1737. Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12; Found: C, 81.51; H, 5.15.



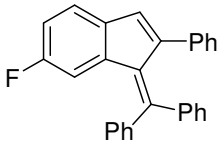
(*Z*)-2-(3-Nitrophenyl)-1-((3-nitrophenyl)(phenyl)methylene)-1*H*-indene **3g**

Yield: 88%; yellow solid; melting point: 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (d, *J* = 7.8 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 7.08 (s, 1H), 7.10–7.21 (m, 3H), 7.27–7.34 (m, 3H), 7.49–7.57 (m, 5H), 7.66 (s, 1H), 7.73–7.76 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.7, 121.4, 122.6, 123.5, 123.8, 126.1, 127.2, 128.2, 128.3, 128.6, 129.0, 129.3, 129.7, 130.3, 131.2, 134.3, 137.0, 137.3, 137.5, 139.0, 139.4, 140.0, 141.0, 141.5, 142.6, 146.0, 147.0, 147.2; HRMS (ESI) calcd for $C_{28}H_{18}N_2O_4$: 469.1164 (M + $Na^{+)}$, found: 469.1170.



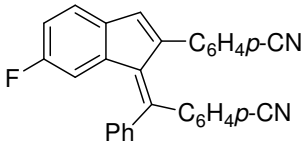
(*Z*)-2-Phenyl-1-(1-phenylpentylidene)-1*H*-indene **3h**

Yield: 62%; yellow solid; melting point: 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.43–1.49 (m, 2H), 1.55–1.63 (m, 2H), 3.16 (t, *J* = 7.3 Hz, 2H), 6.73 (s, 1H), 6.83–6.90 (m, 8H), 6.98–7.00 (m, 2H), 7.24–7.27 (m, 2H), 7.31–7.33 (m, 1H), 7.81 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 23.2, 30.1, 37.8, 120.9, 123.7, 125.1, 125.2, 126.9, 127.0, 127.2, 128.6, 130.1, 132.5, 135.8, 137.1, 138.8, 142.2, 142.4, 144.3, 152.4; HRMS (ESI) calcd for $C_{26}H_{25}$ $(M + H)^+$ 337.1956, found 337.1943.



1-(Diphenylmethylene)-6-fluoro-2-phenyl-1*H*-indene **3i**

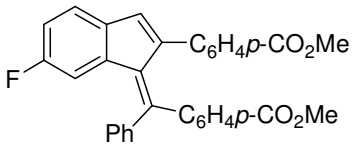
Yield: 82%; yellow solid; melting point: 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 8.7 Hz, 1H), 6.79–6.94 (m, 10H), 6.97–7.00 (m, 2H), 7.14–7.17 (m, 1H), 7.36–7.39 (m, 2H), 7.43–7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.1 (d, $^2J_{CF}$ = 25.7 Hz), 113.5 (d, $^2J_{CF}$ = 22.9 Hz), 120.8 (d, $^3J_{CF}$ = 8.6 Hz), 125.5, 126.9, 127.2, 128.1, 128.5, 128.8, 129.2, 130.7, 132.4, 133.1, 136.6, 137.8, 138.0, 140.0 (d, $^3J_{CF}$ = 8.6 Hz), 140.9, 142.3, 143.7, 150.6, 161.2 (d, $^1J_{CF}$ = 239.3 Hz); HRMS (ESI) calcd for $C_{28}H_{20}F$ $(M + H)^+$ 375.1549, found 375.1571.



(*Z*)-2-(4-Cyanophenyl)-1-((4-cyanophenyl)(phenyl)methylene)-6-fluoro-1*H*-indene **3j**

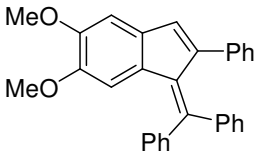
Yield: 74%; yellow solid; melting point: 242-243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 8.3 Hz, 1H), 7.00 (s, 1H), 7.03 (d, *J* = 8.3 Hz,

2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.21–7.28 (m, 5H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.49–7.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.6, 111.5 (d, $^2J_{CF}$ = 26.7 Hz), 111.9, 114.7 (d, $^2J_{CF}$ = 22.9 Hz), 118.0, 118.5, 121.9 (d, $^3J_{CF}$ = 8.6 Hz), 128.9, 129.3, 130.1, 130.6, 130.9, 131.3, 132.8, 136.4, 137.5, 138.2, 139.7, 140.6 (d, $^3J_{CF}$ = 8.6 Hz), 140.8, 142.2, 145.4, 148.0, 161.8 (d, $^1J_{CF}$ = 242.2 Hz); HRMS (ESI) calcd for $C_{30}H_{18}FN_2$ $(M + H)^+$ 425.1454, found 425.1471.



(*Z*)-2-(4-(Methoxycarbonyl)phenyl)-1-((4-(methoxycarbonyl)phenyl)(phenyl)methylene)-6-fluoro-1*H*-indene **3k**

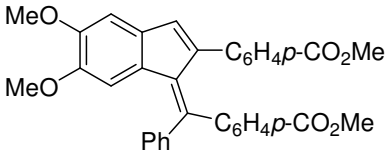
Yield: 75%; yellow solid ; melting point: 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.84 (s, 3H), 6.06 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 8.3 Hz, 1H), 6.95 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 7.12–7.20 (m, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.46–7.53 (m, 5H), 7.58 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 52.0, 111.3 (d, $^2J_{CF}$ = 25.8 Hz), 114.1 (d, $^2J_{CF}$ = 22.9 Hz), 121.4 (d, $^3J_{CF}$ = 9.5 Hz), 127.2, 128.2, 128.3, 128.7, 129.0, 129.4, 129.6, 130.6, 132.1, 134.8, 137.6, 137.8, 139.8 (d, $^3J_{CF}$ = 8.6 Hz), 141.3, 142.2, 142.3, 145.3, 149.2, 161.5 (d, $^1J_{CF}$ = 240.3 Hz), 166.3, 166.7; HRMS (ESI) calcd for $C_{32}H_{24}FO_4$ $(M + H)^+$ 491.1659, found 491.1648. Anal. Calcd for $C_{32}H_{23}FO_4$: C, 78.35; H, 4.73; Found: C, 78.46; H, 4.86.



1-(Diphenylmethylene)-5,6-dimethoxy-2-phenyl-1*H*-indene **3l**

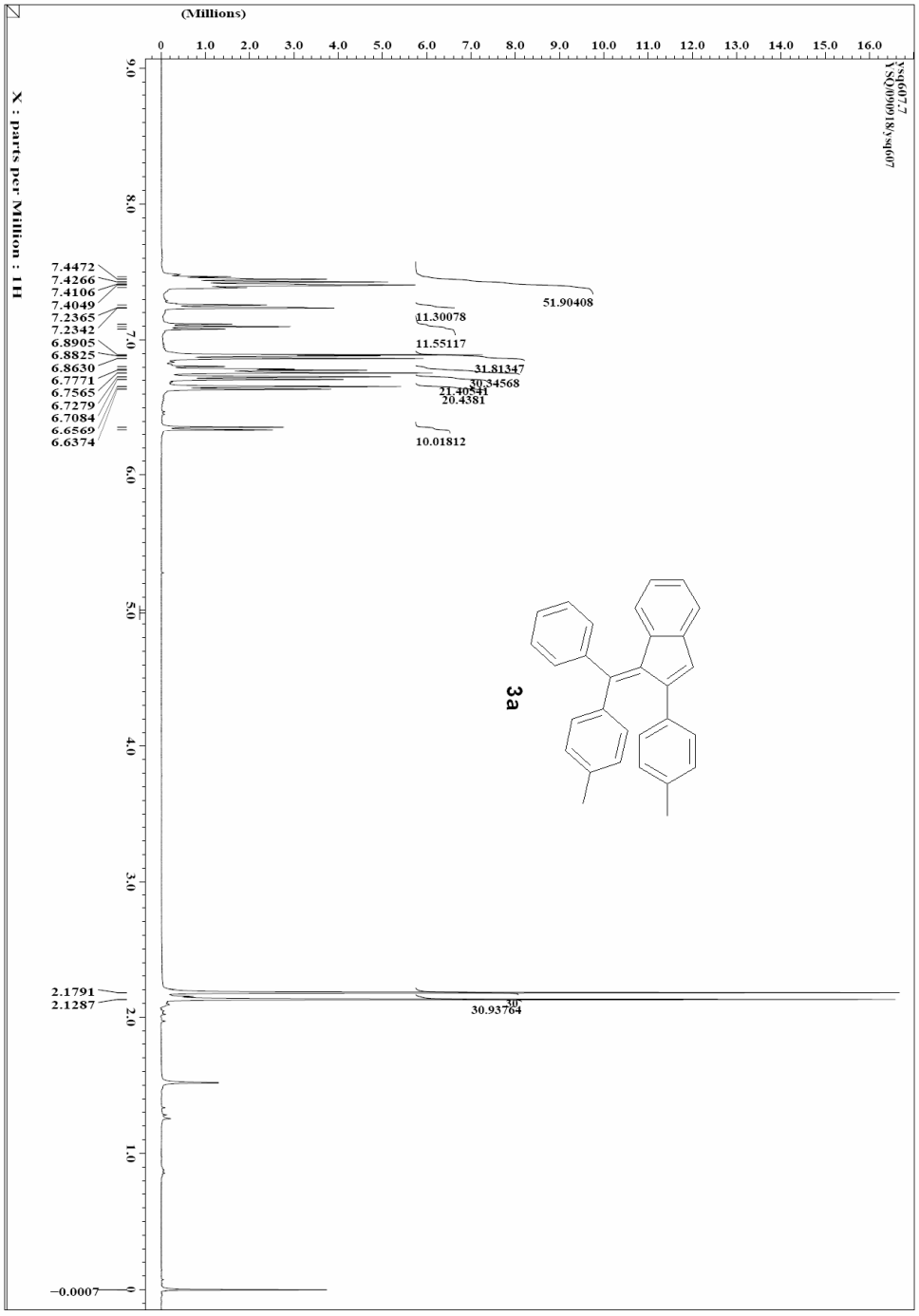
Yield: 95%; red solid ; melting point: 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.88 (s, 3H), 5.91 (s, 1H), 6.81–7.01 (m, 12H), 7.42–7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 56.0, 103.9, 108.0, 125.2, 126.9, 127.2, 127.8, 128.5,

128.6, 128.7, 130.7, 130.8, 132.4, 133.6, 135.5, 137.4, 138.2, 140.9, 142.4, 142.9, 146.4, 148.0, 148.6; HRMS (ESI) calcd for $C_{30}H_{25}O_2$ $(M + H)^+$ 417.1855, found 417.1834.



(*Z*)-2-(4-(Methoxycarbonyl)phenyl)-1-((4-(methoxycarbonyl)phenyl)(phenyl)methylene)-5,6-dimethoxy-1*H*-indene **3m**

Yield: 72%; red solid ; melting point: 273-274 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 3.89 (s, 3H), 5.94 (s, 1H), 6.83 (s, 1H), 6.90 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.41–7.43 (m, 2H), 7.48–7.53 (m, 5H), 7.57 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 52.0, 55.3, 56.0, 104.3, 108.1, 126.9, 128.2, 128.3, 128.7, 128.9, 129.0, 129.1, 130.7, 132.2, 135.3, 135.4, 138.6, 140.9, 142.0, 142.8, 145.5, 146.6, 146.9, 149.0, 166.5, 166.9; HRMS (ESI) calcd for $C_{34}H_{28}O_6$: 555.1784 $(M + Na^{+})$, found: 555.1774.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6.8630
6.7771
6.7565
6.7279
6.7084
6.6569
6.6374
2.1791
2.1287
-0.0007
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30.34568
21.40541
20.4381
10.01812
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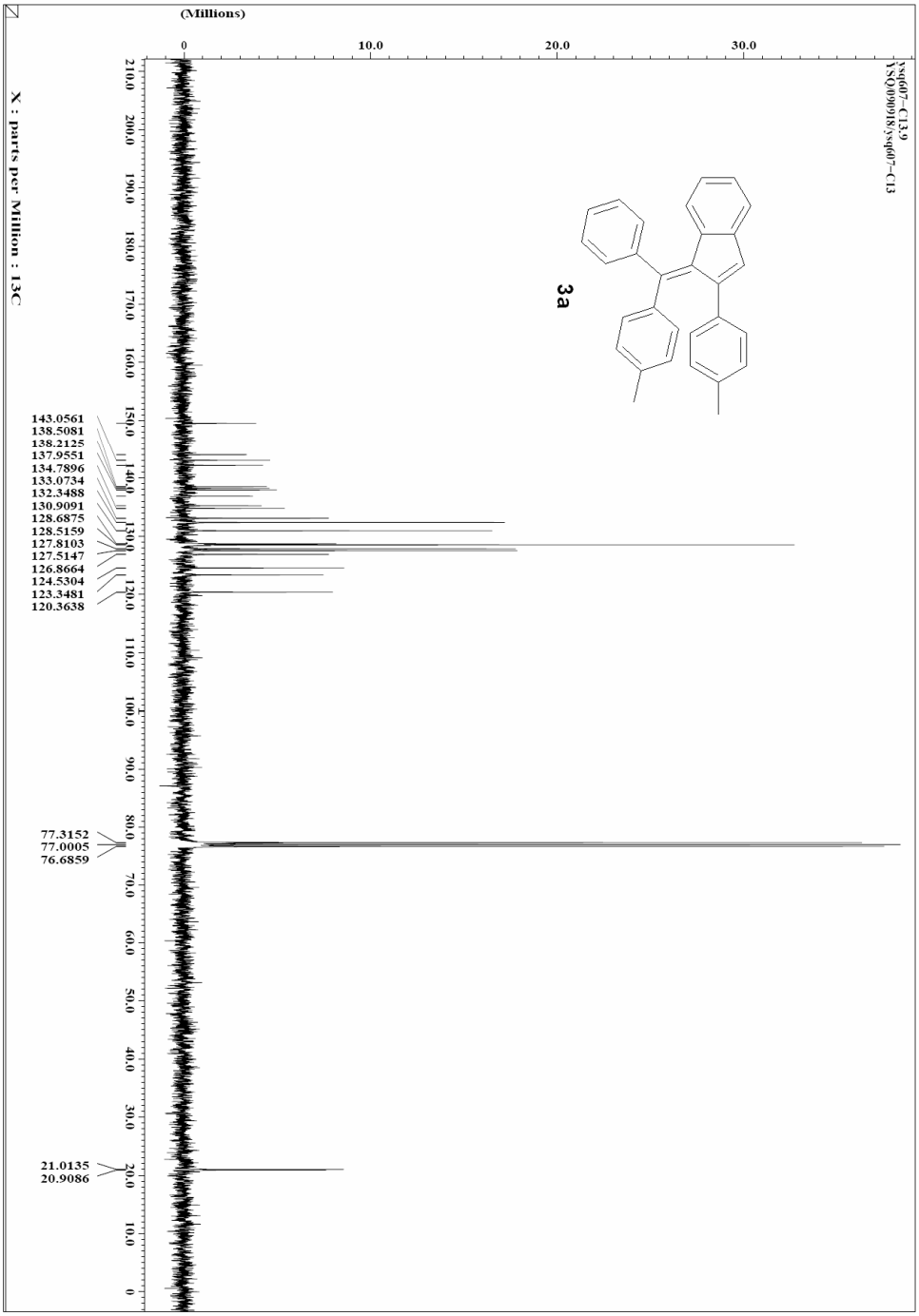
3a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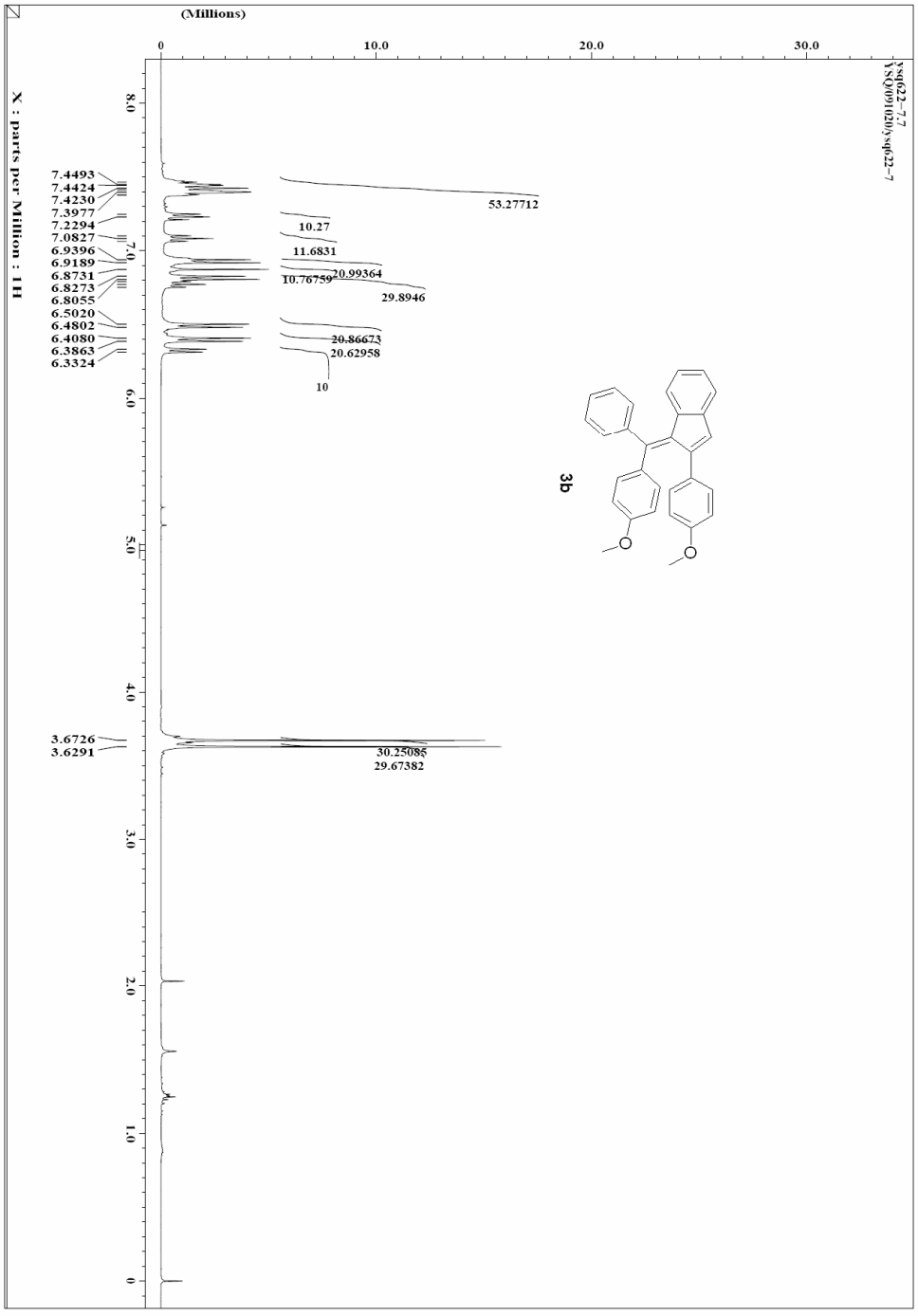
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7.3977
7.2294
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6.9189
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6.4080
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3.6726
3.6291
53.27712
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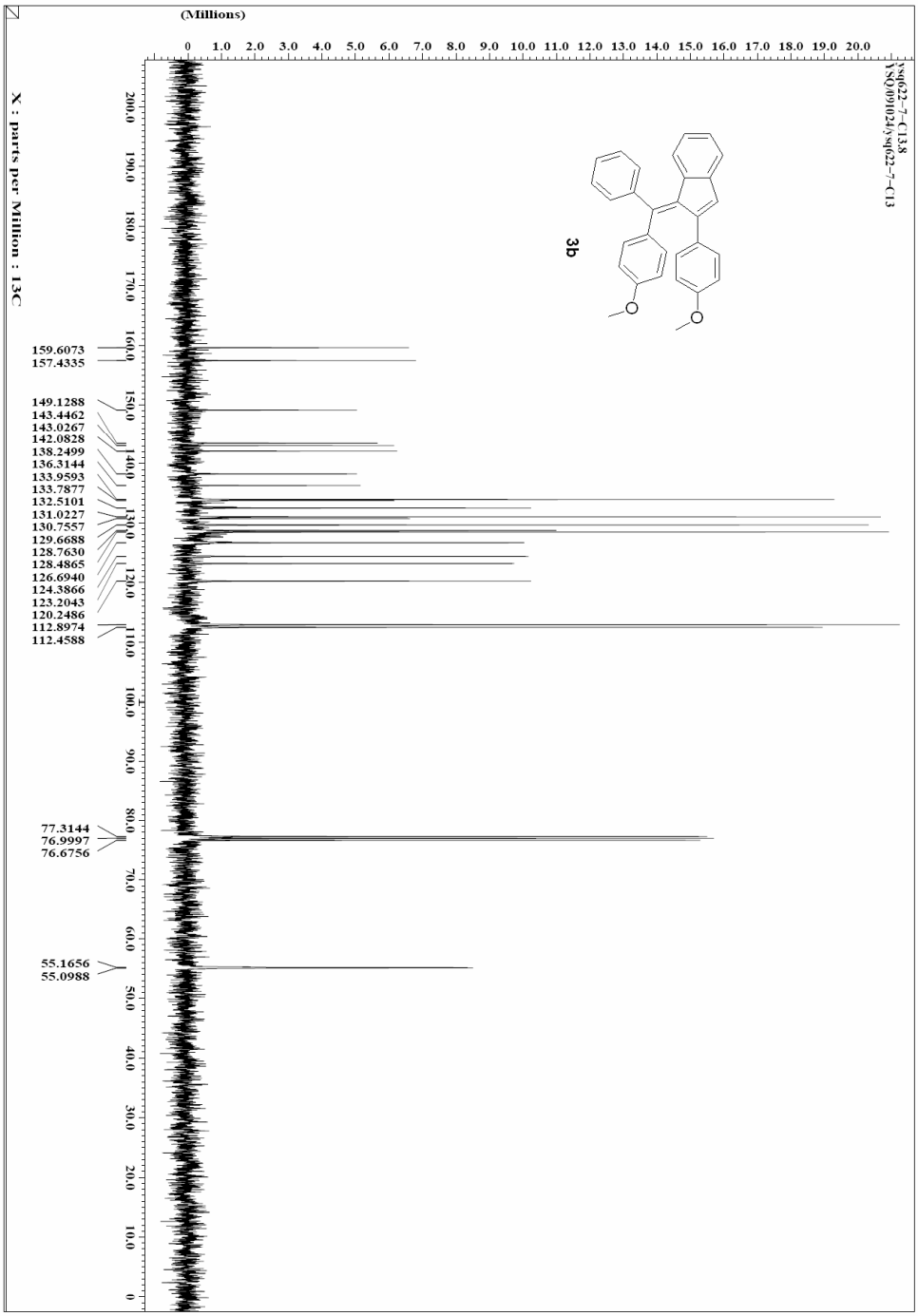
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133.7877
132.5101
131.0227
130.7557
129.6688
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128.4865
126.6940
124.3866
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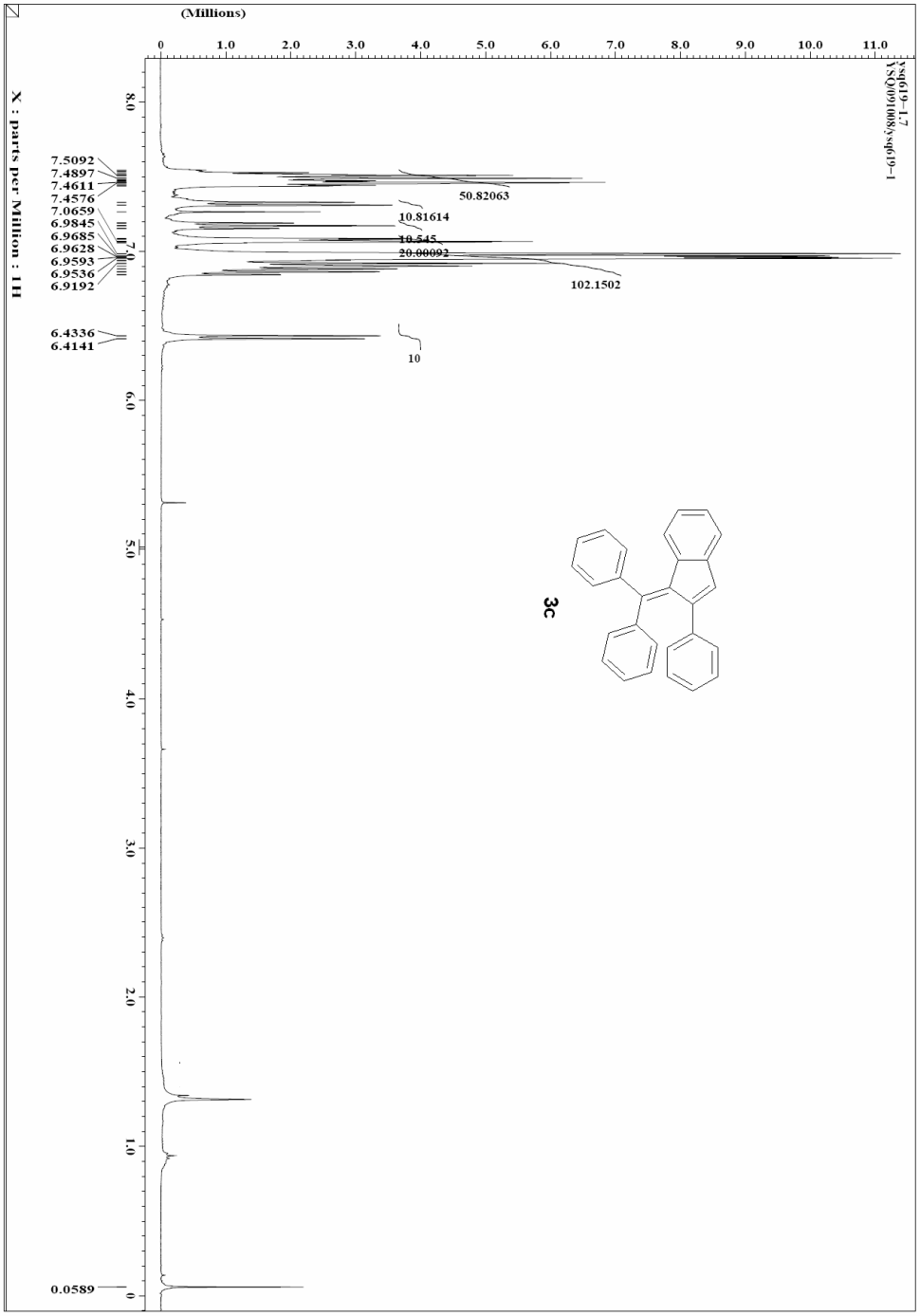
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6.9536
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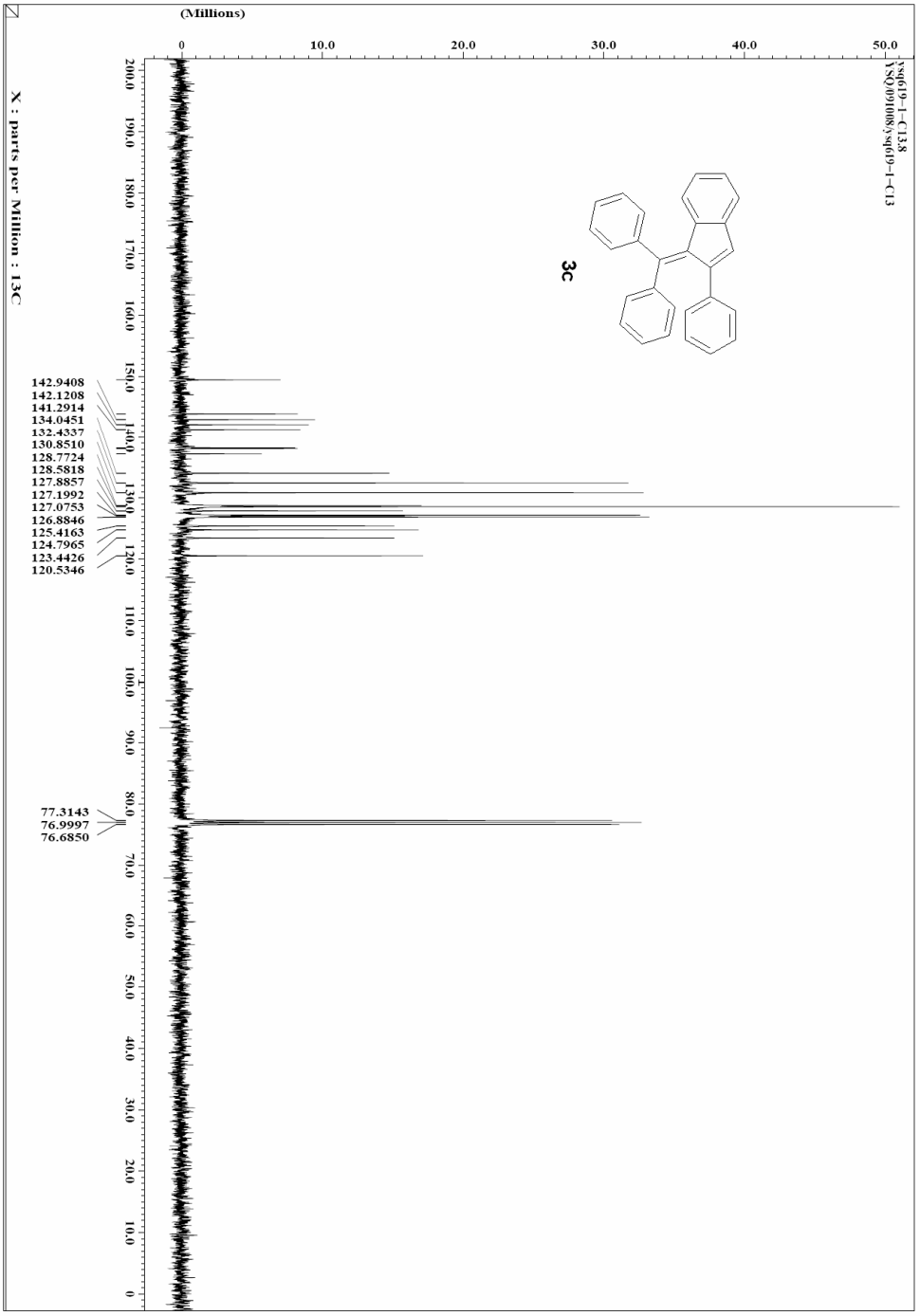
10
3c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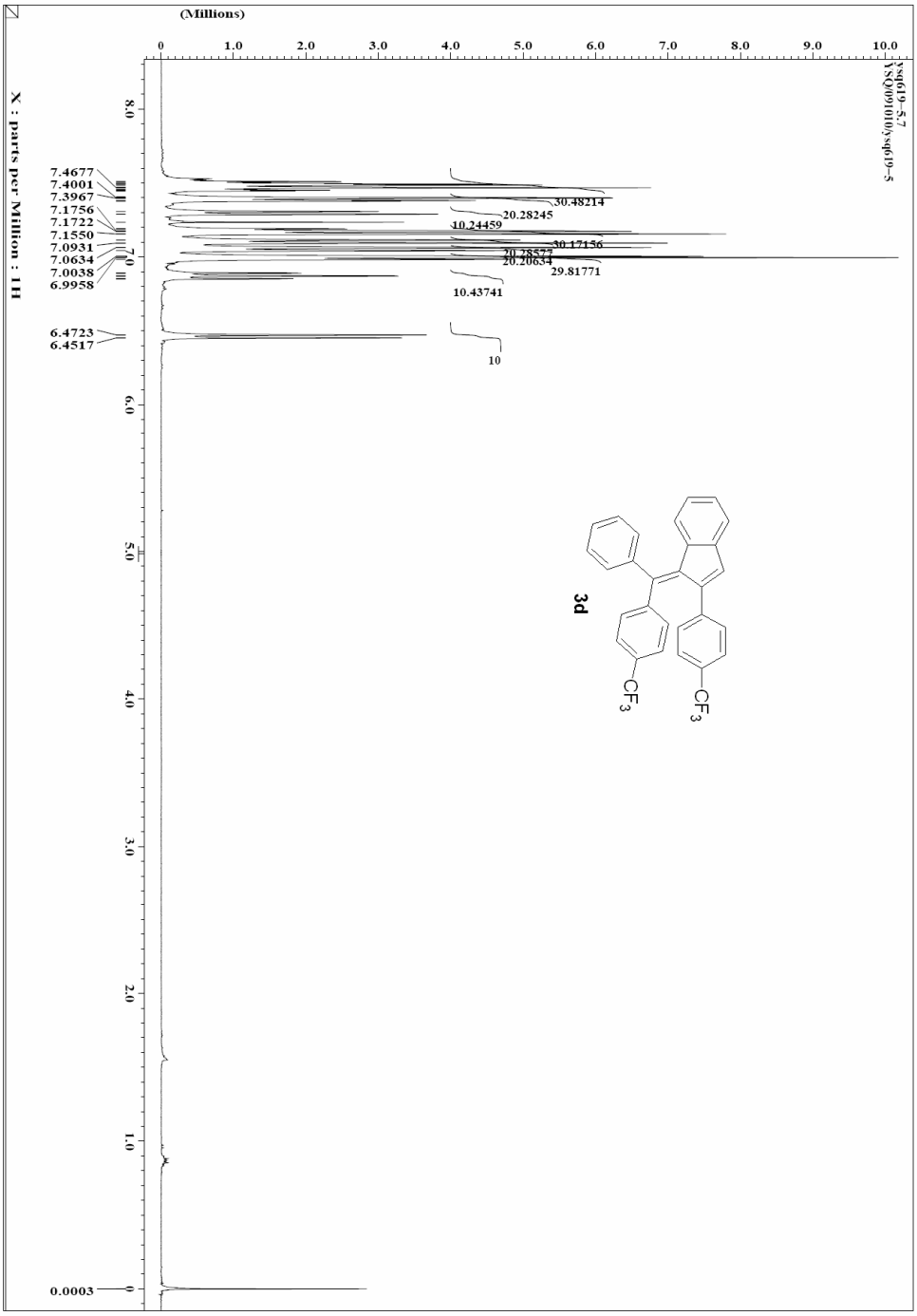
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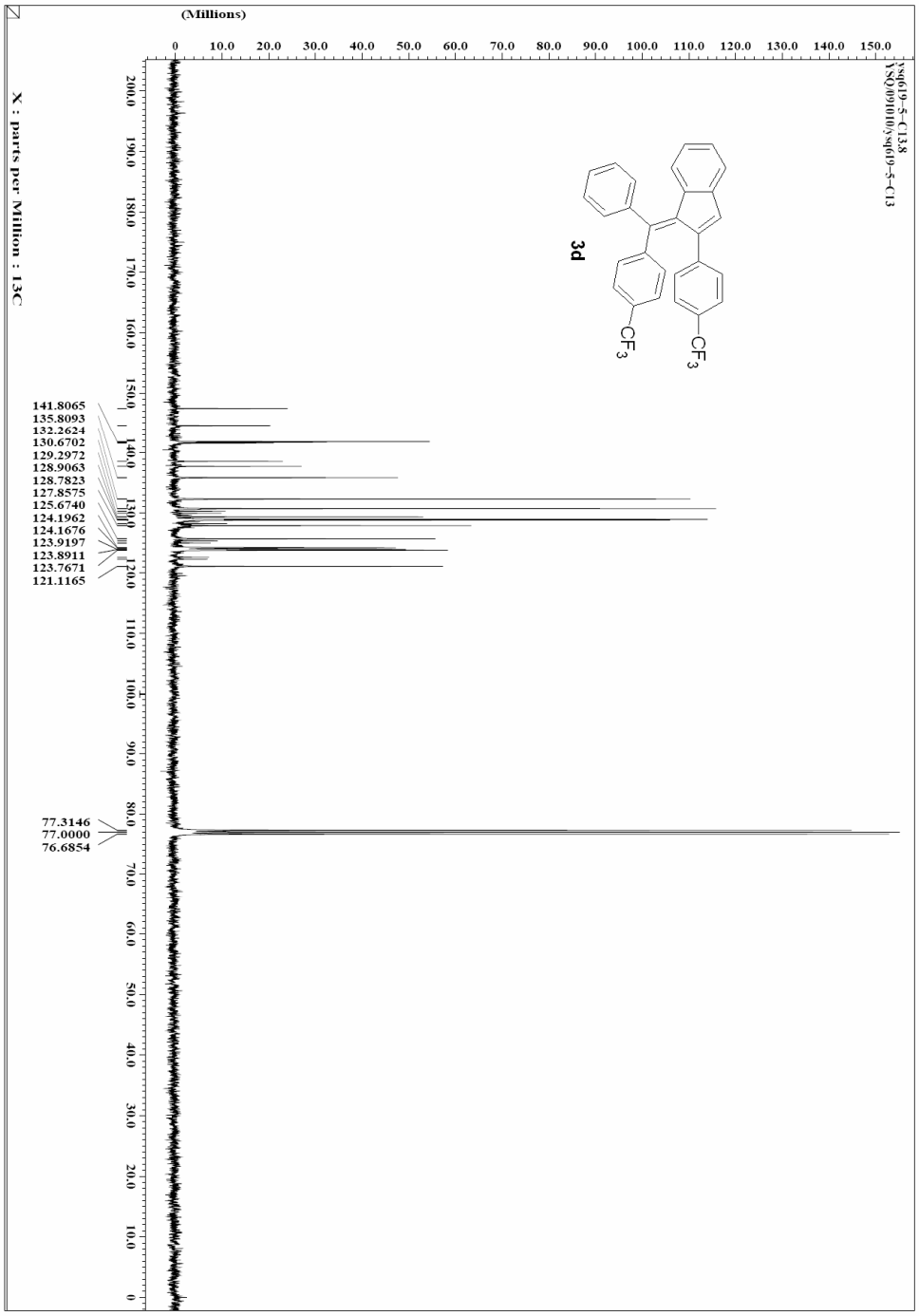
10
3d
CF3
CF3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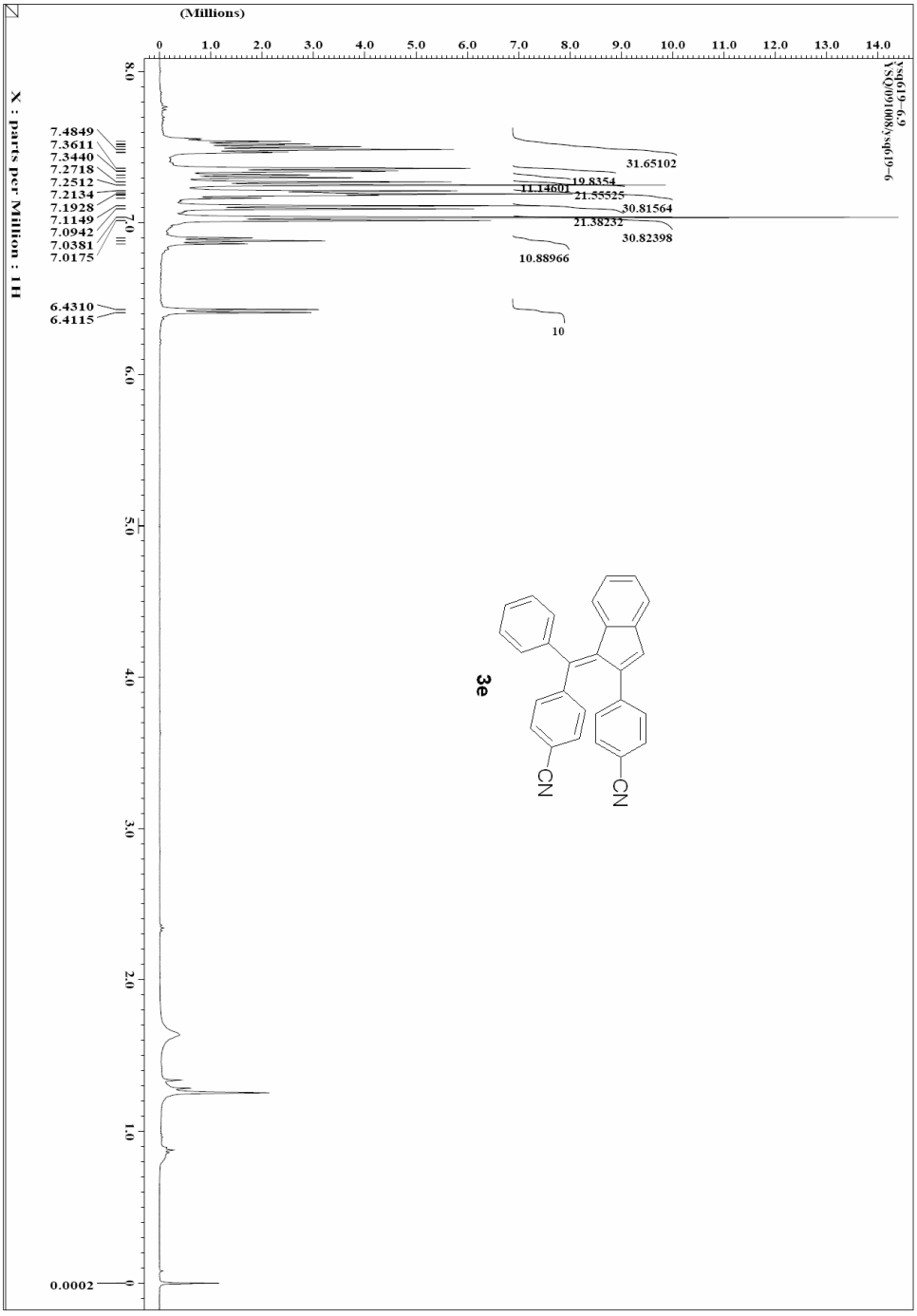
CF3
CF3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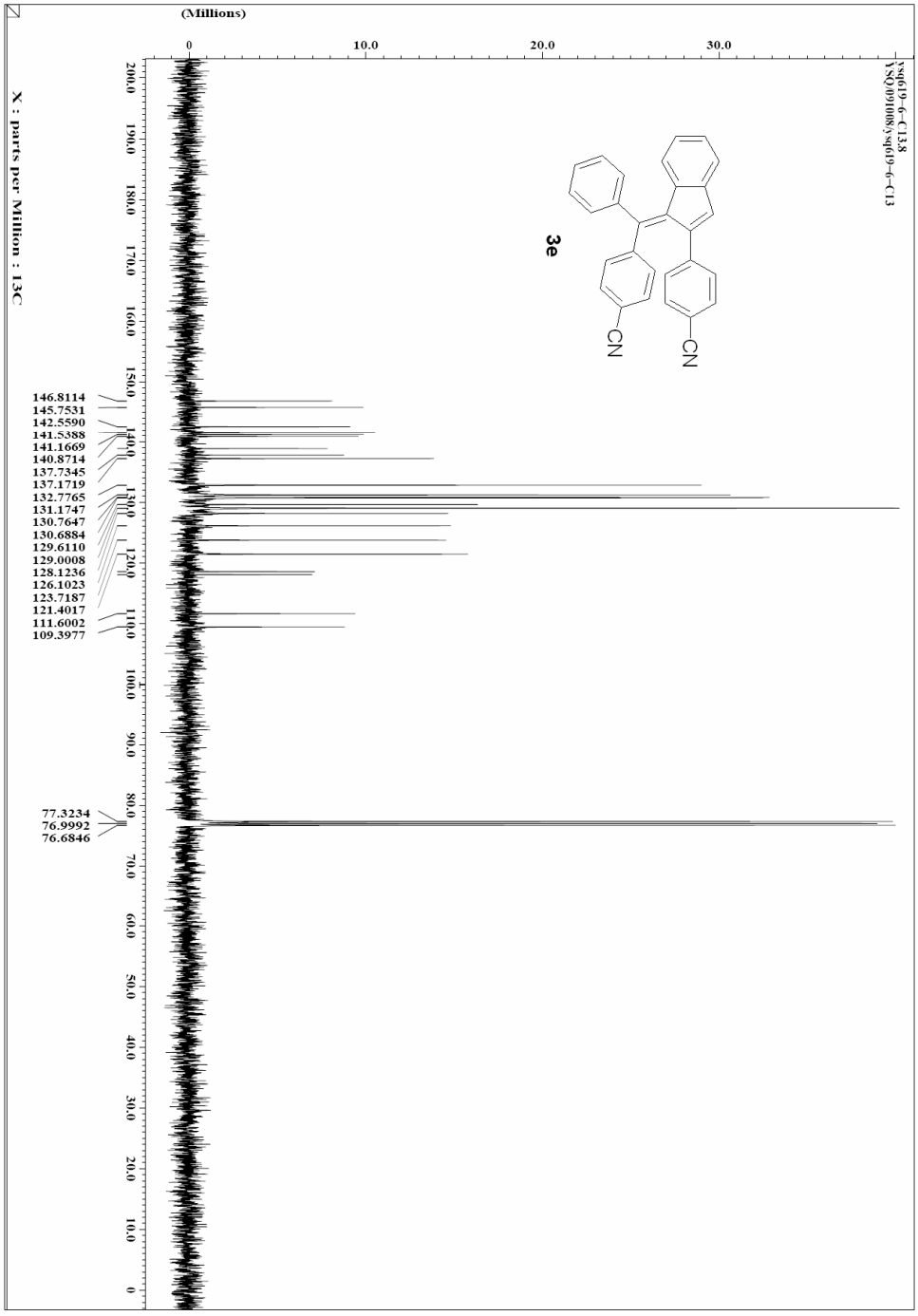
CN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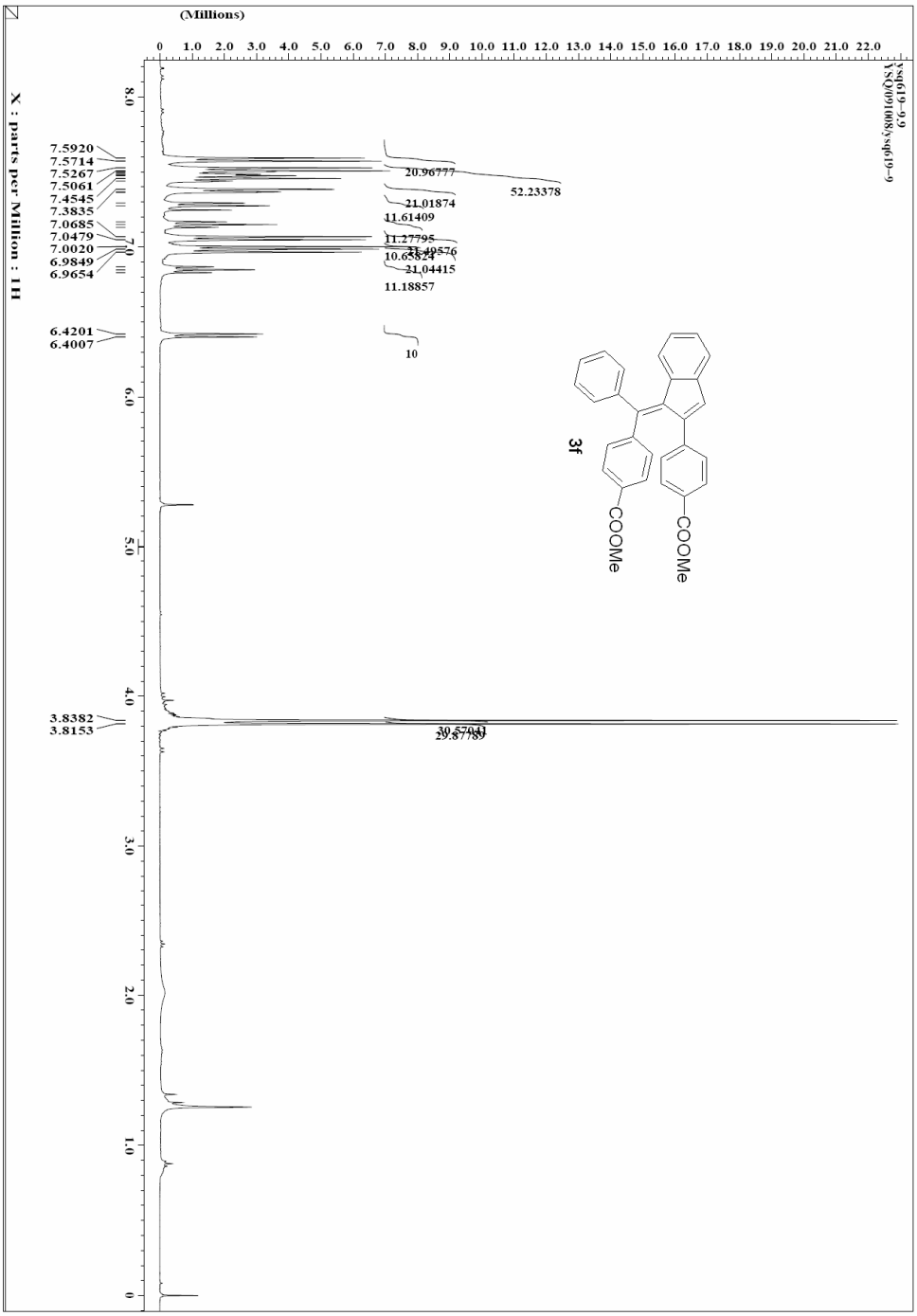
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3.8153
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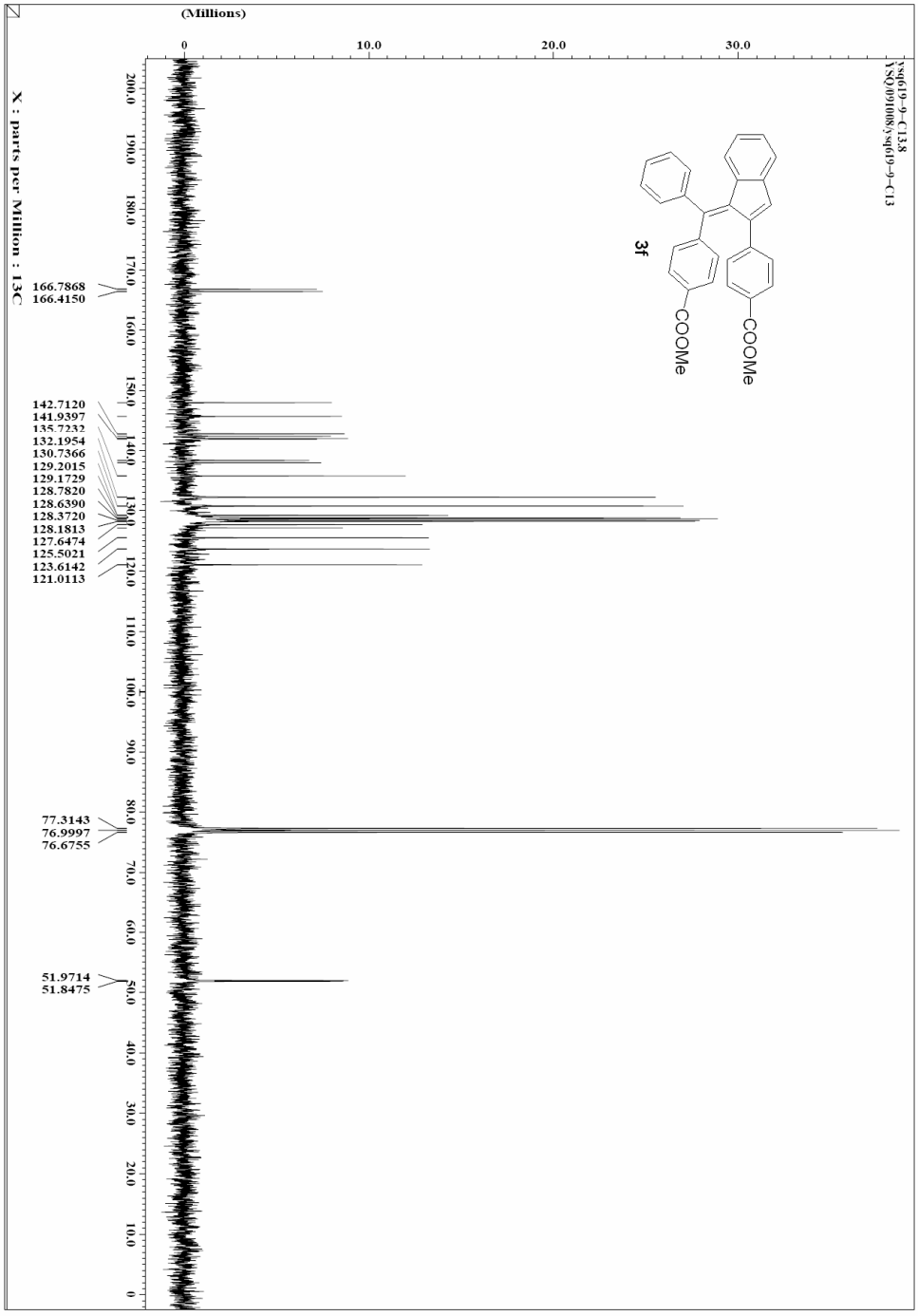
COOMe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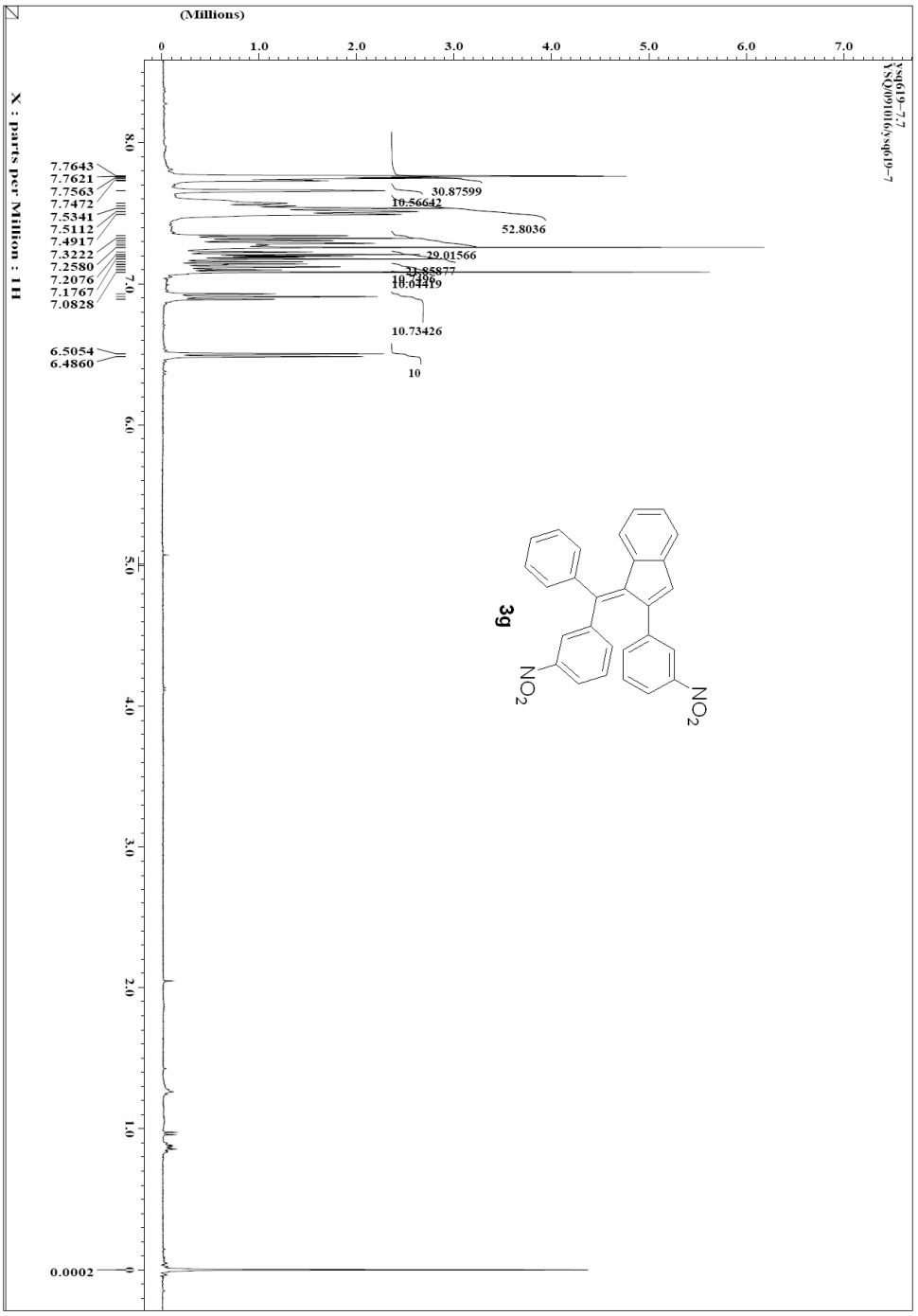
COOMe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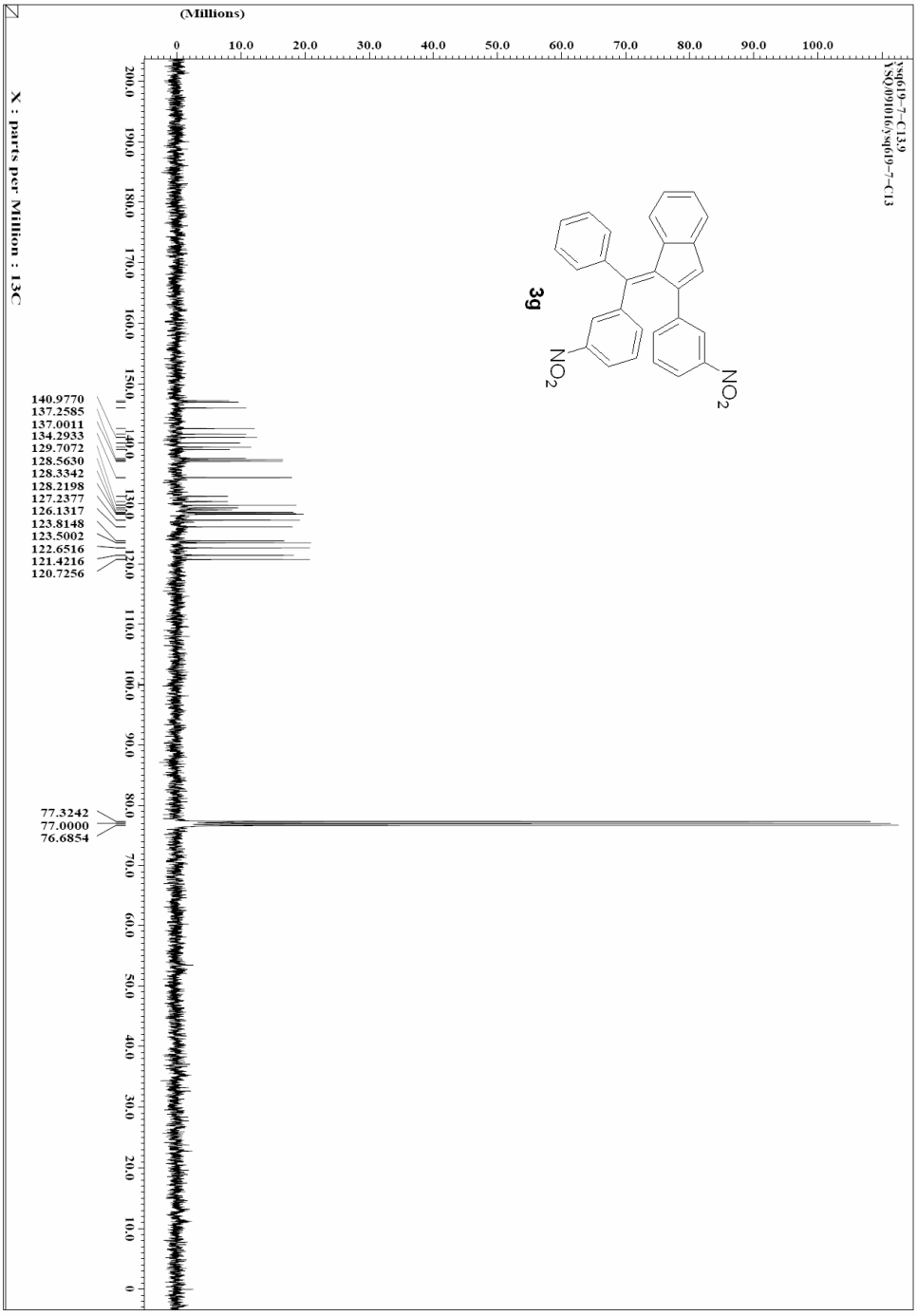
NO2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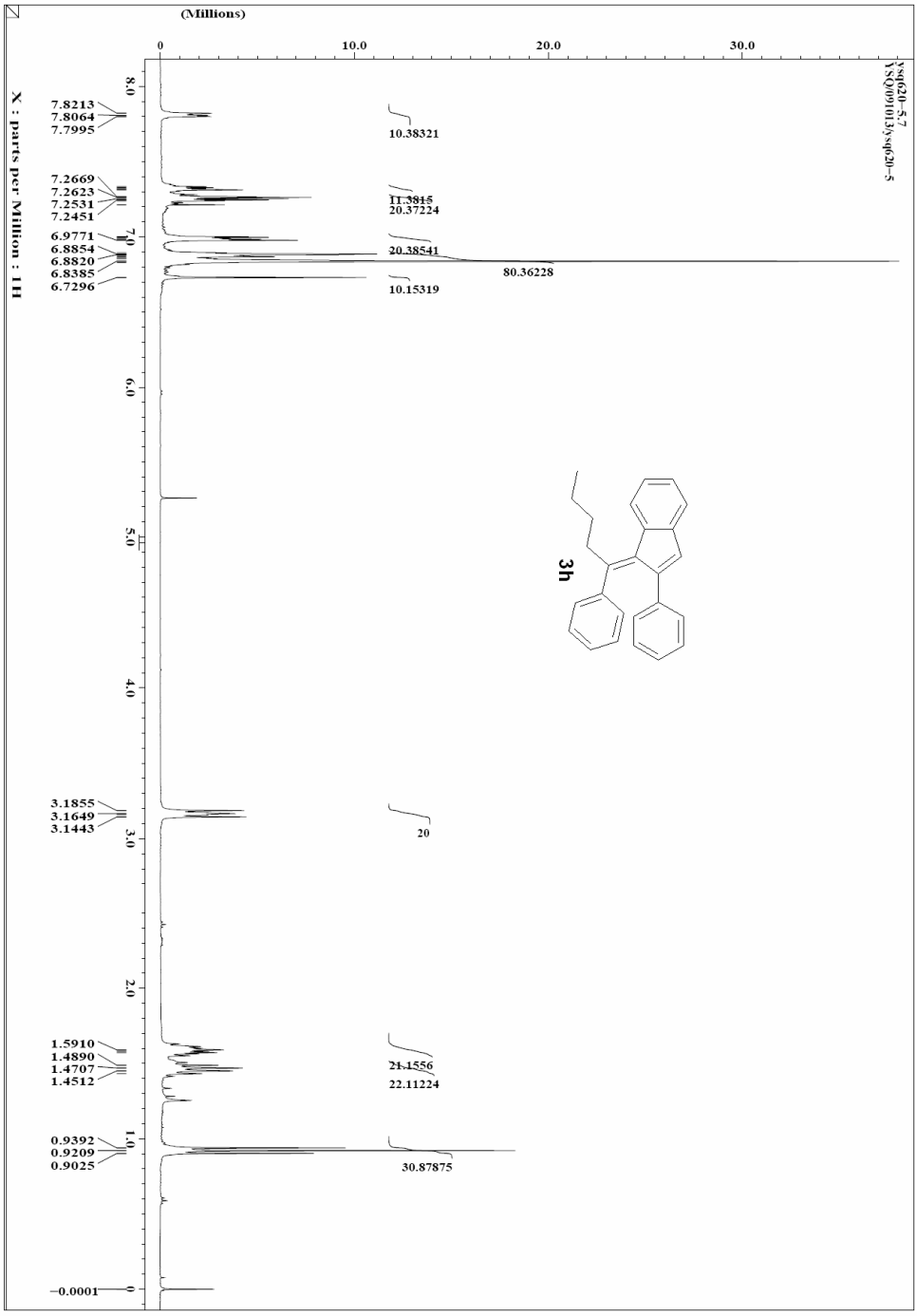
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6.8385
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20
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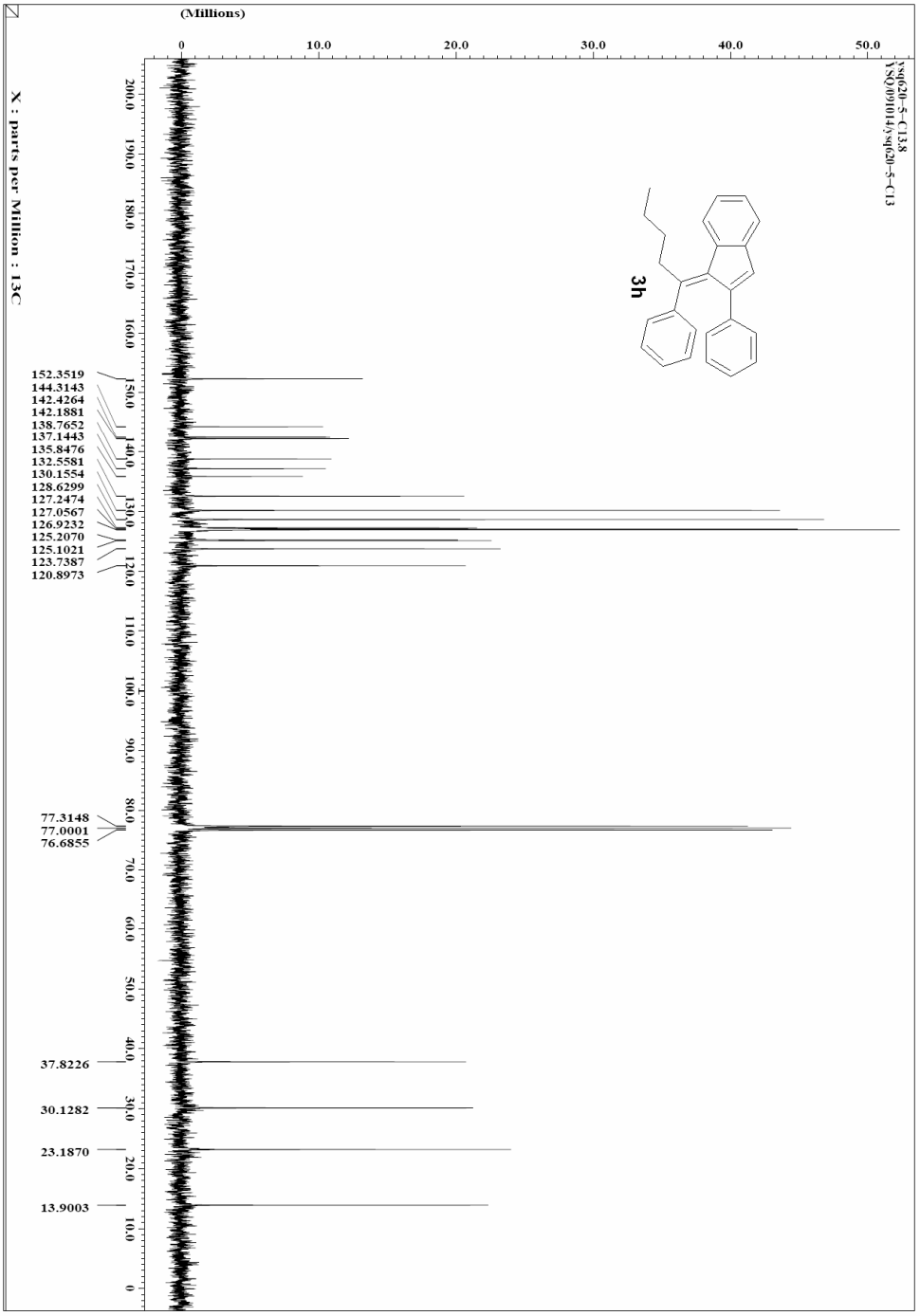
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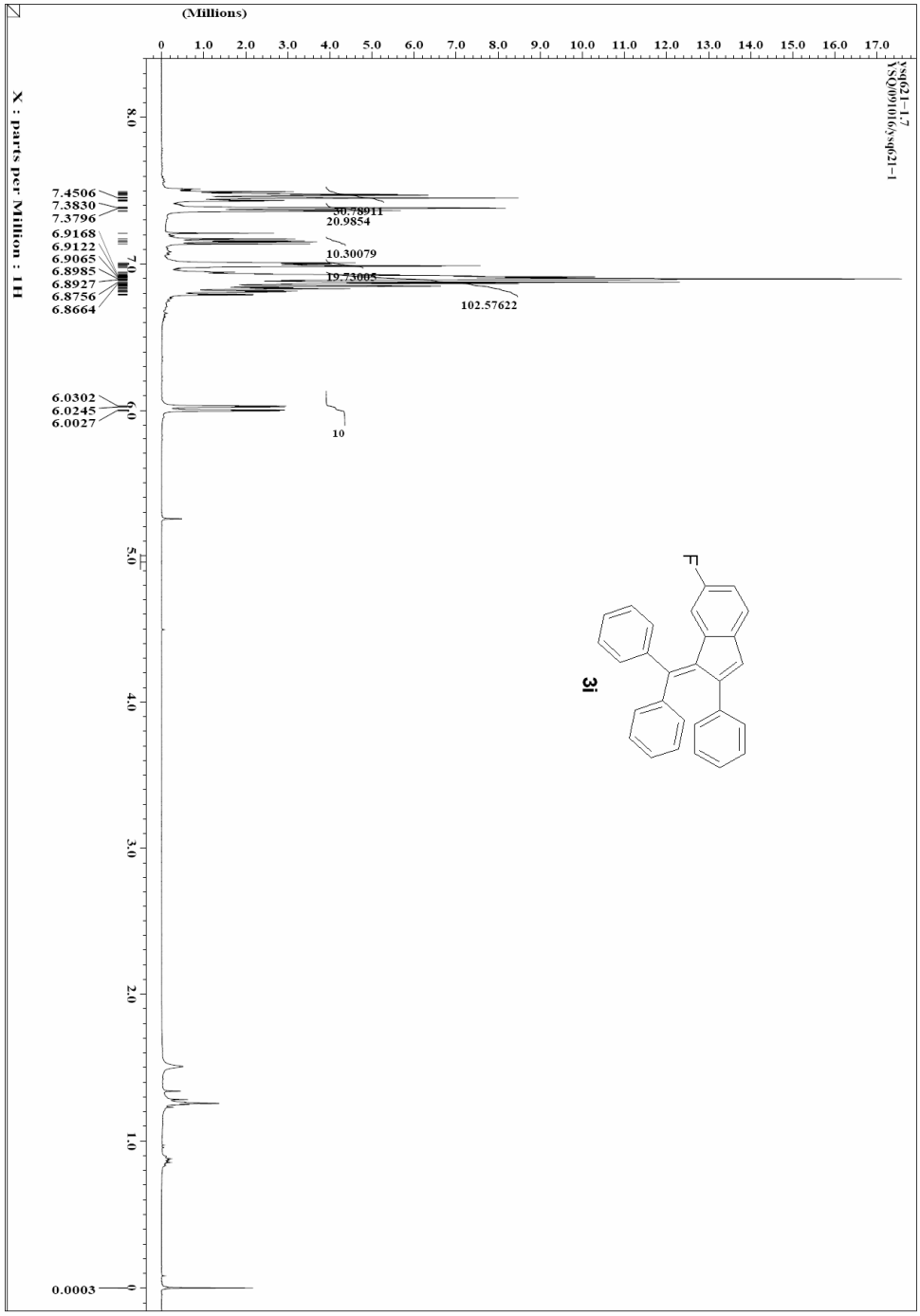
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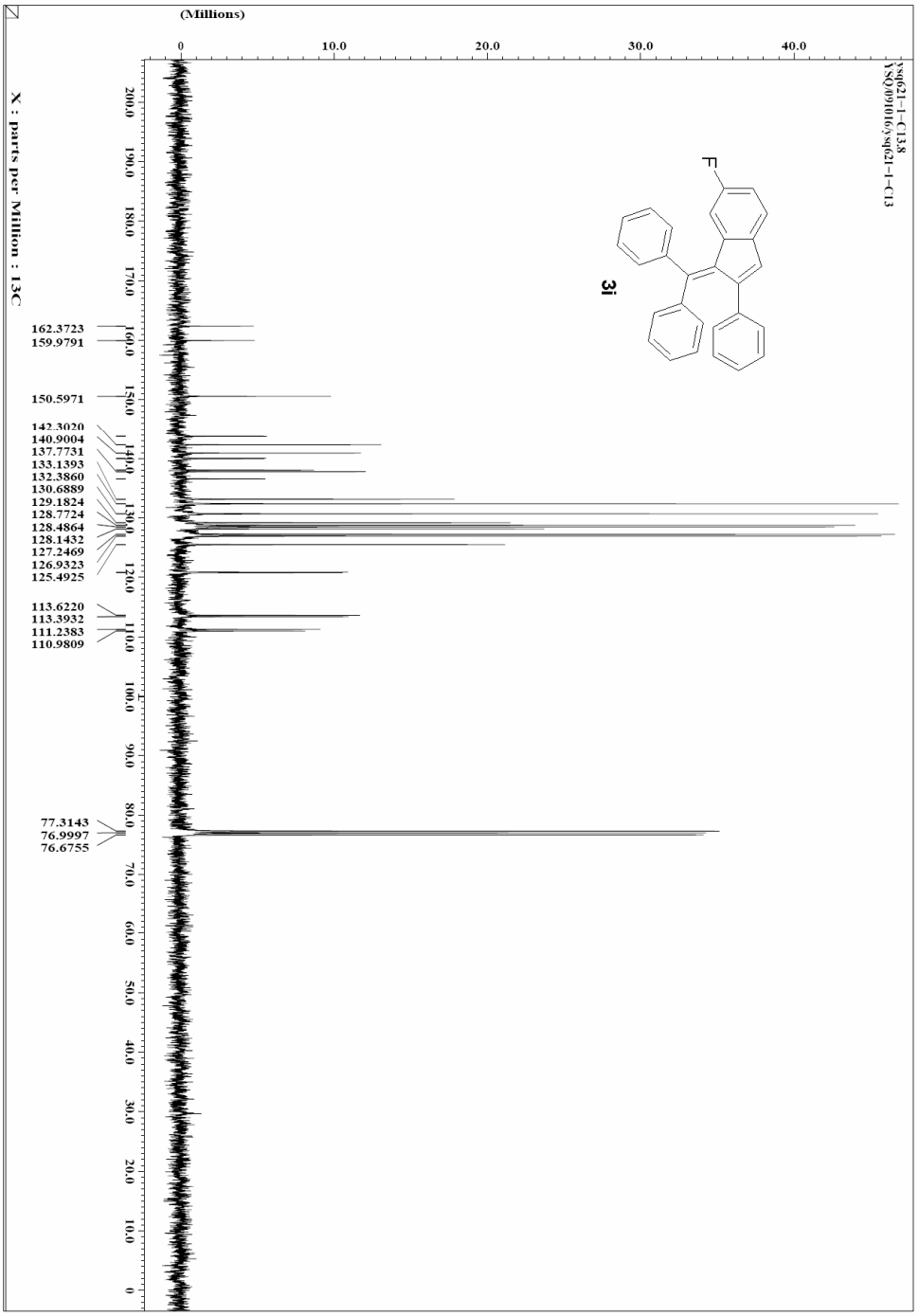
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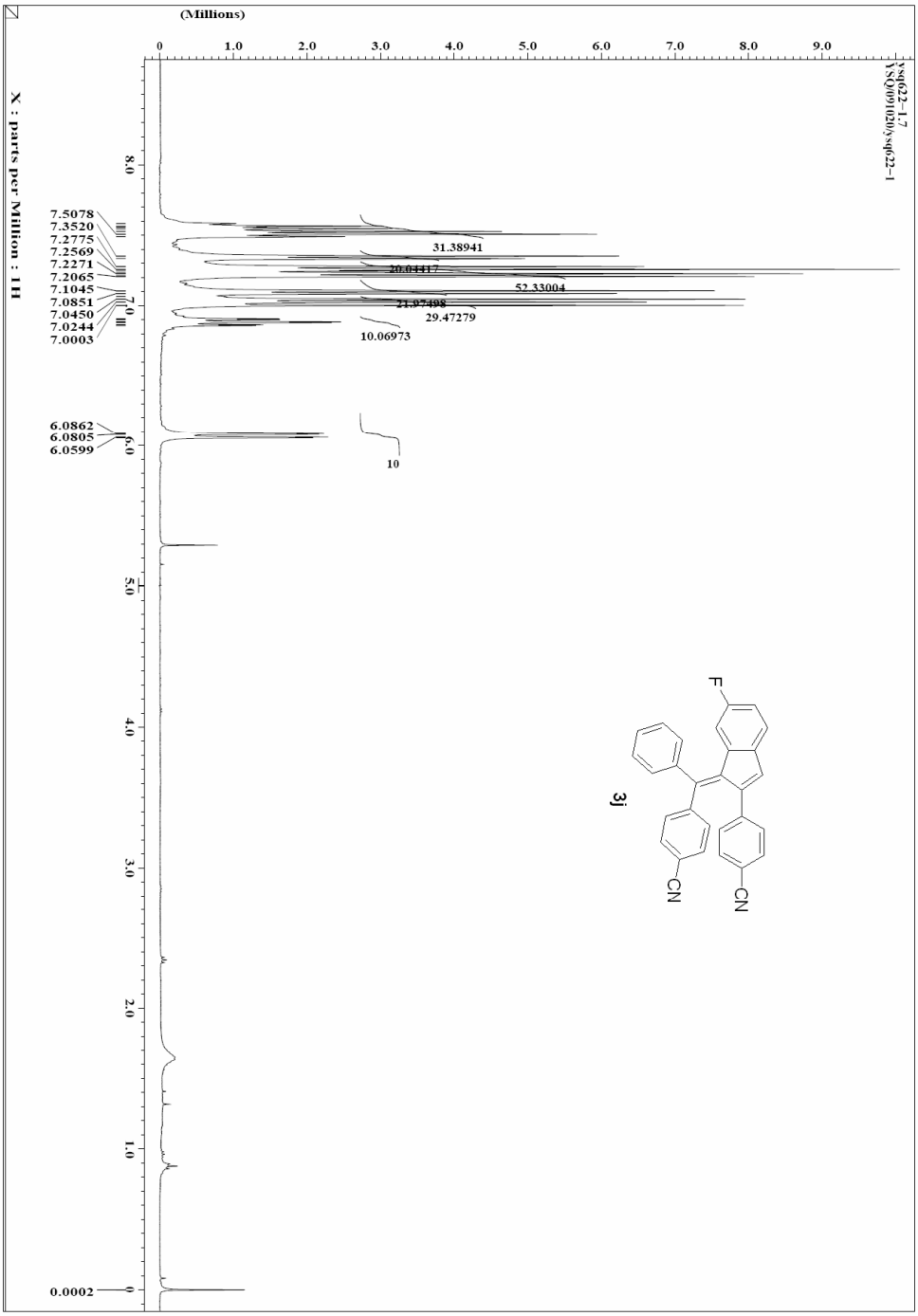
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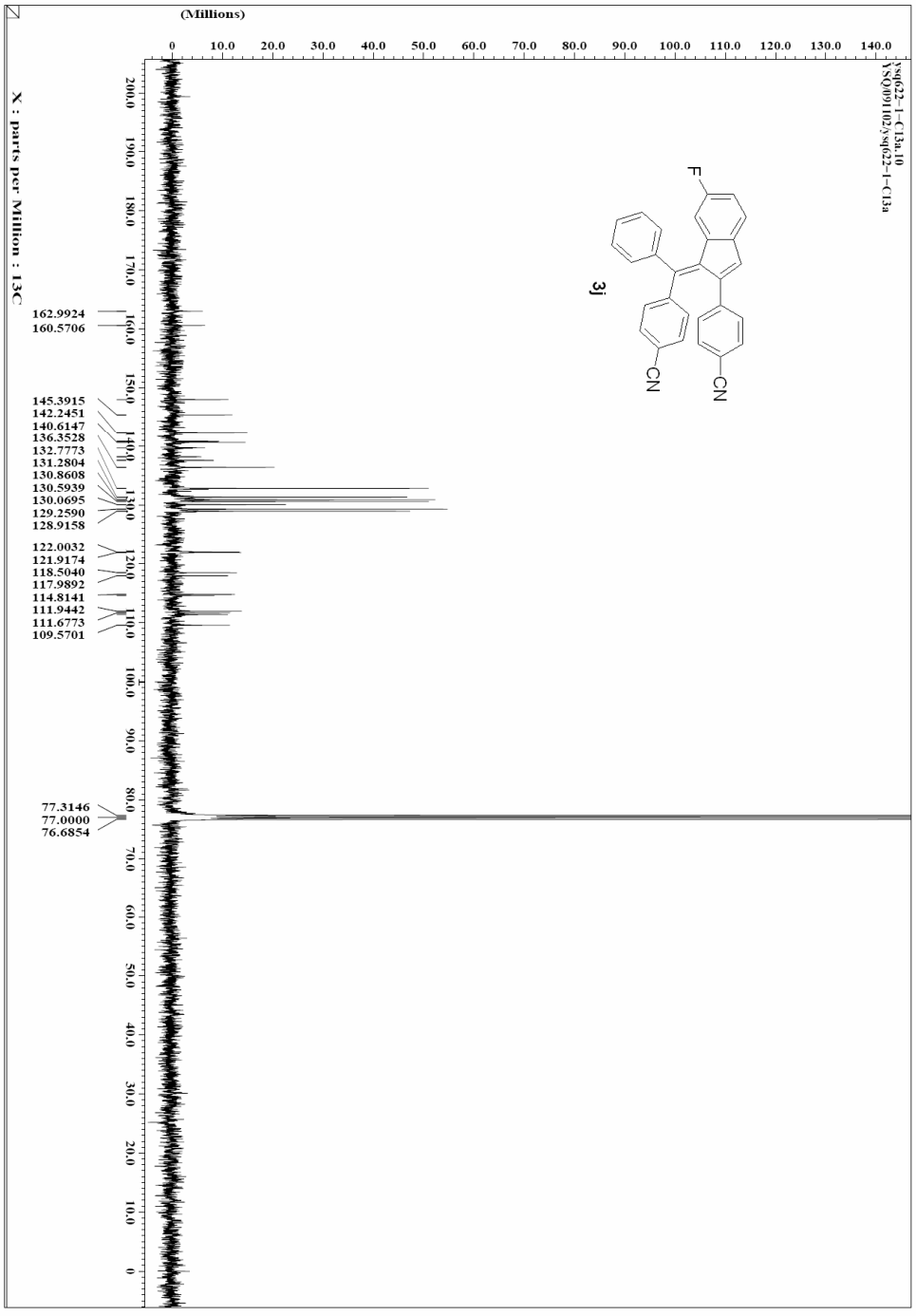
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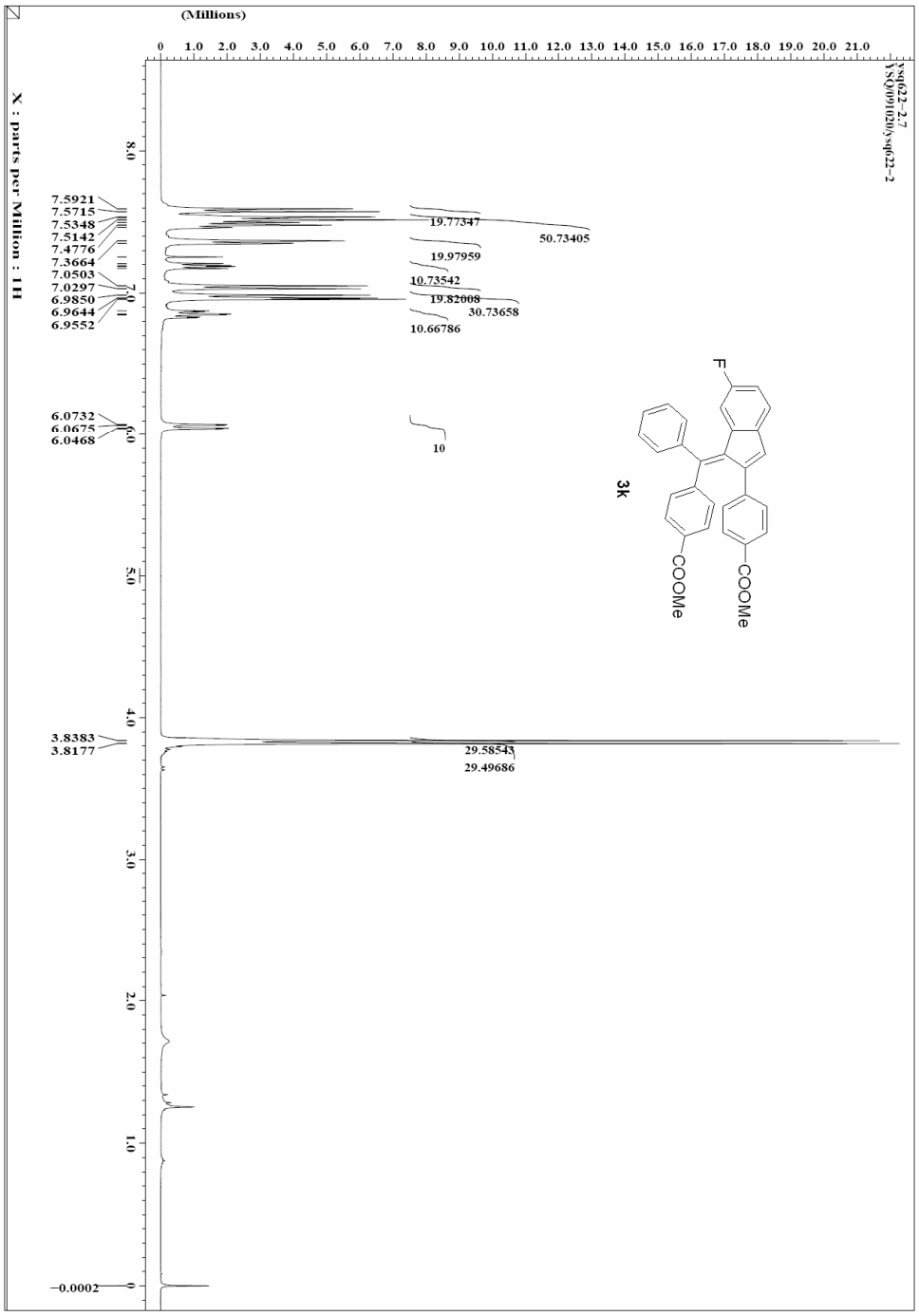
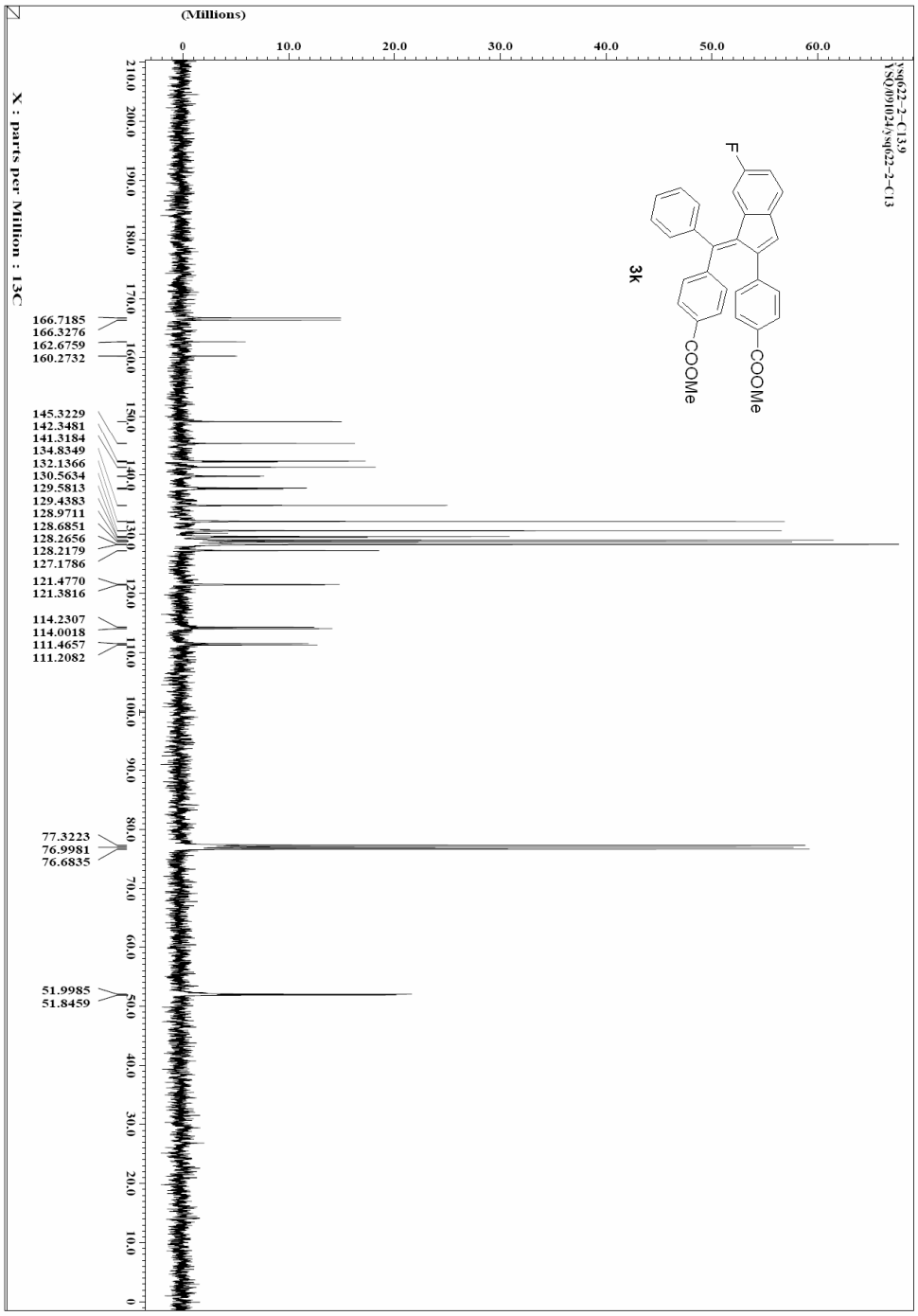
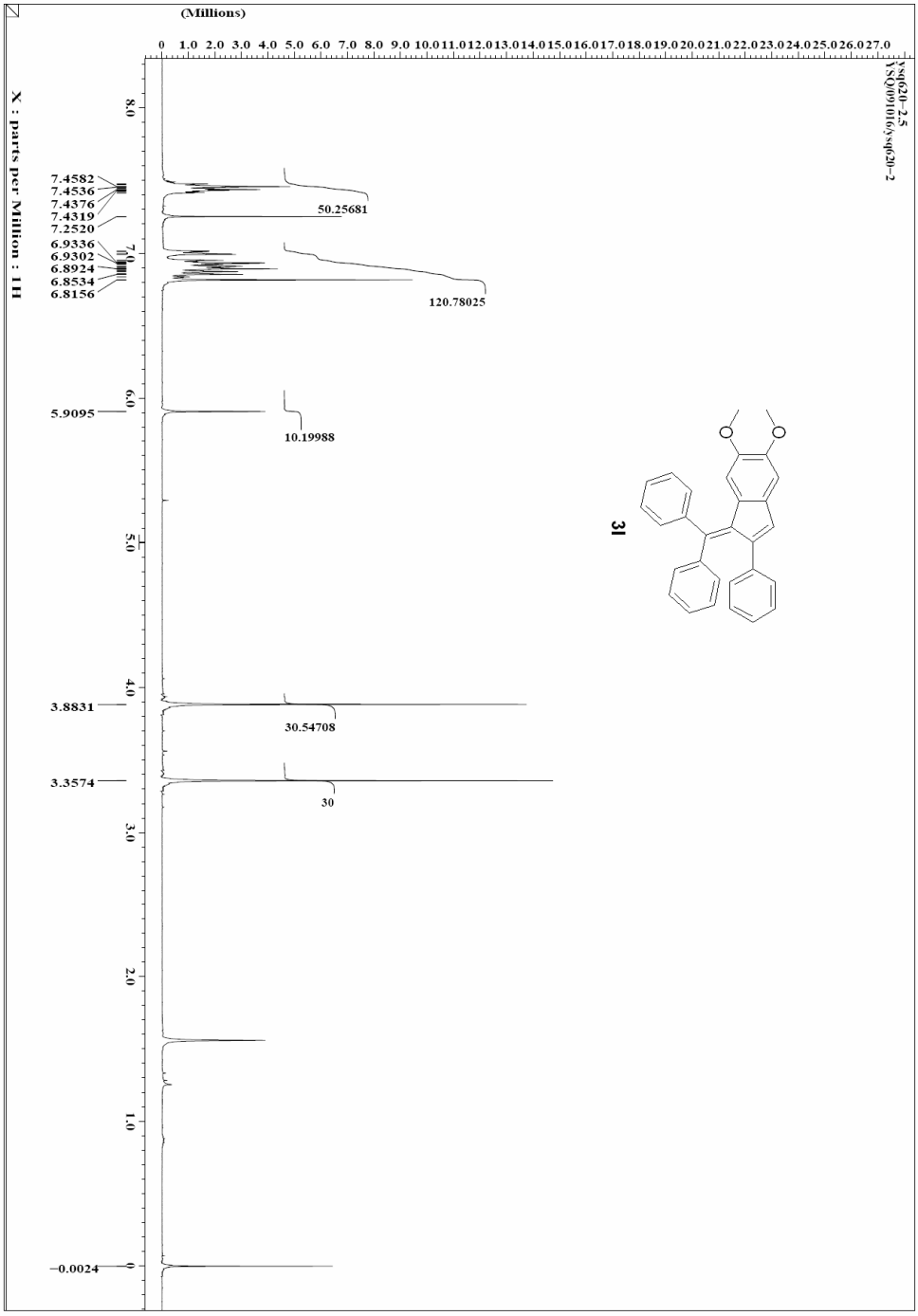
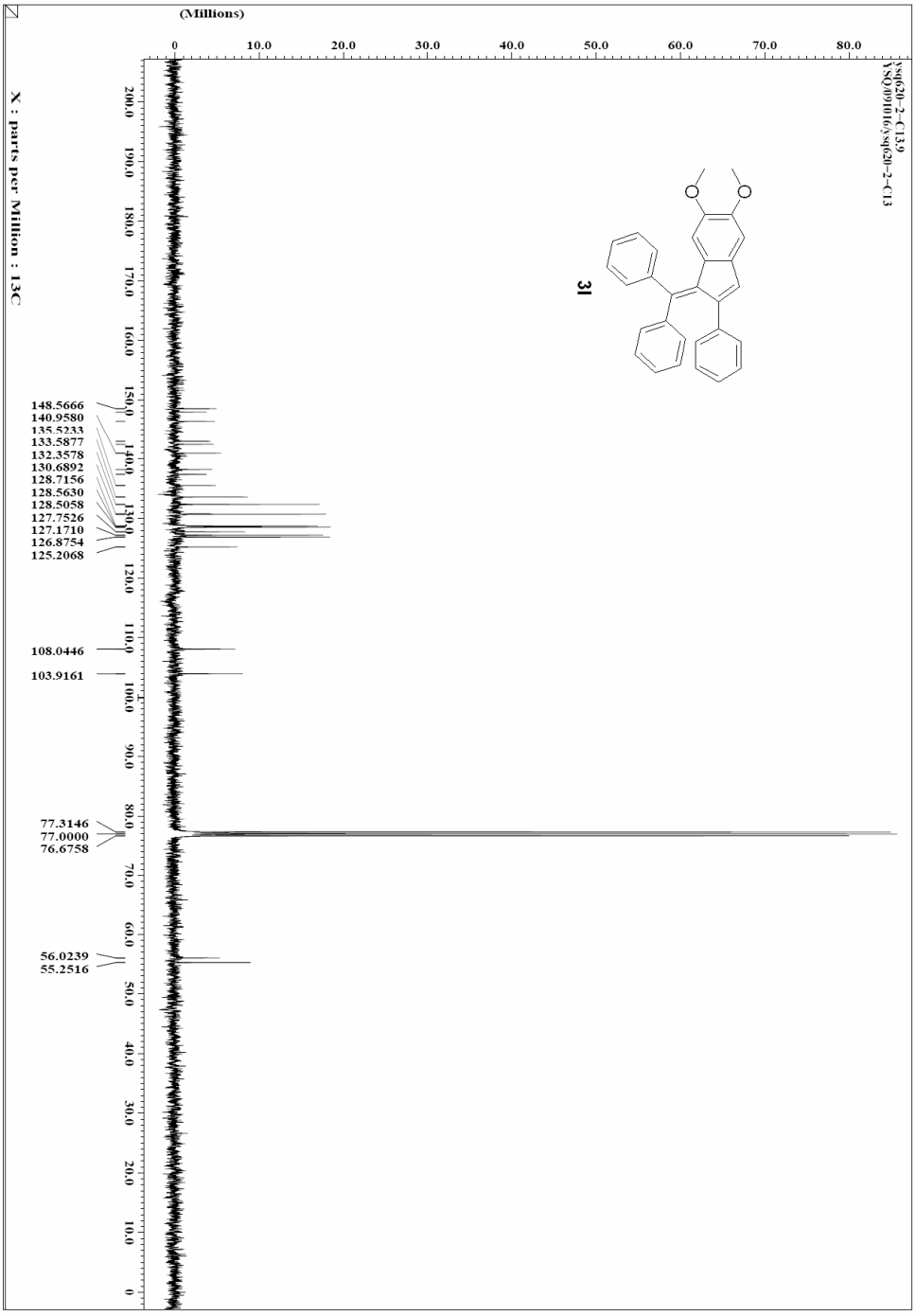
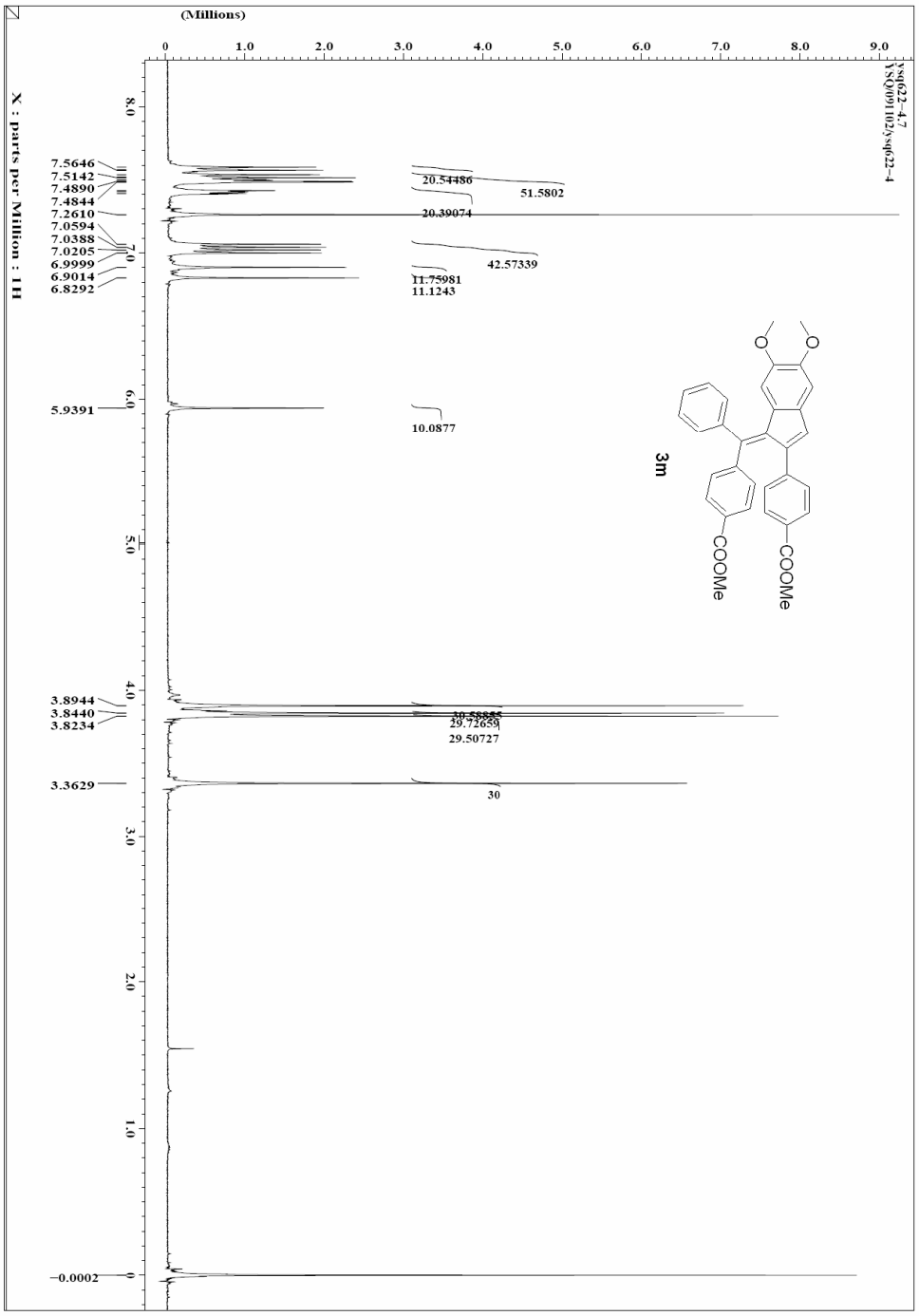
122.0032
121.9174
118.5040
117.9892
114.8141
111.9442
111.6773
109.5701
77.3146
77.0000
76.6854
F
CN
CN
3j

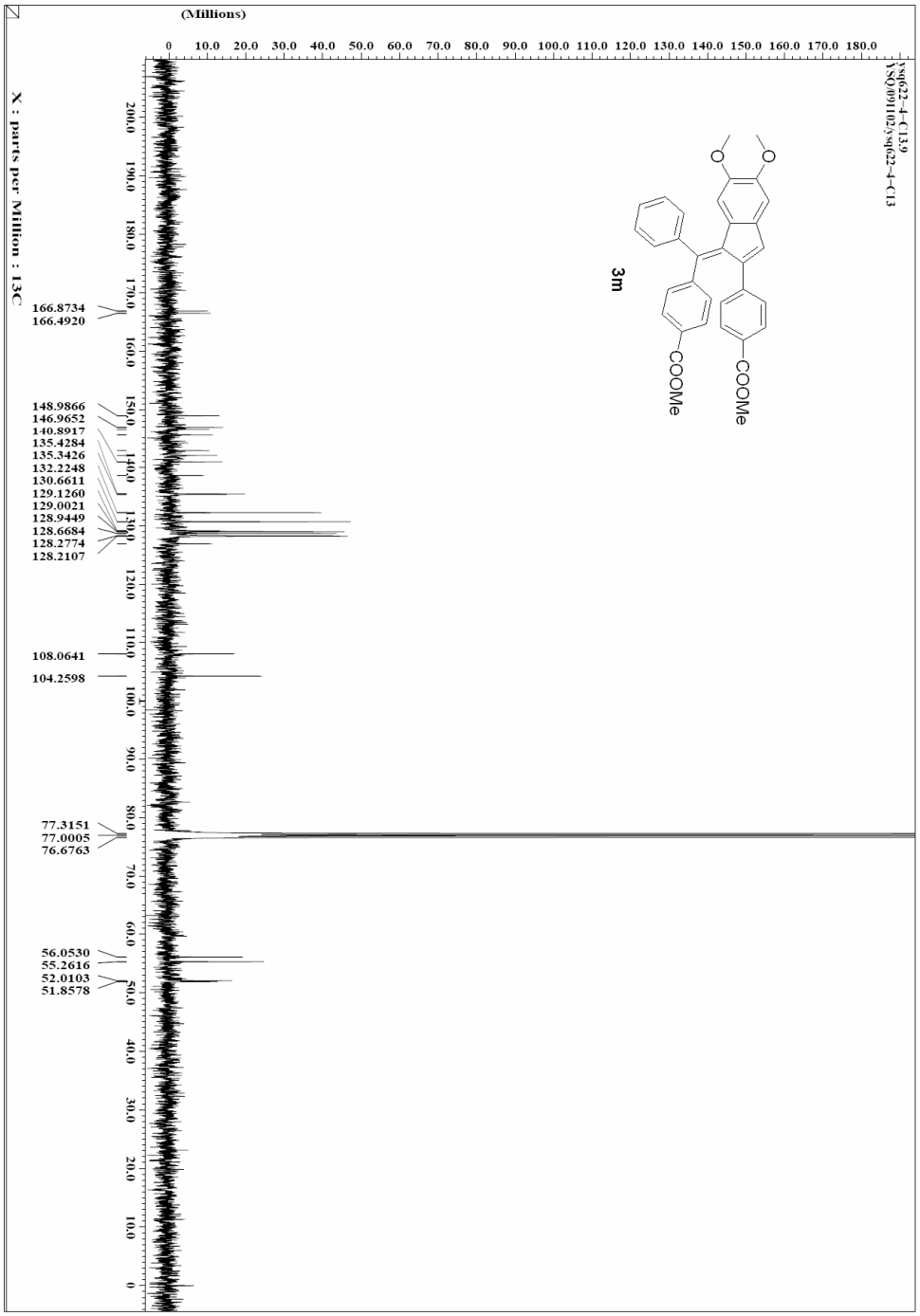

(Millions)
X : parts per Million : 1H
7.5921
7.5715
7.5348
7.5142
7.4776
7.3664
7.0503
7.0297
6.9850
6.9644
6.9552
6.0732
6.0675
6.0468
3.8383
3.8177
−0.0002
19.77347
50.73405
19.97959
10.73542
19.82008
30.73658
10.66786
10
29.58543
29.49686
F
COOMe
COOMe
3k


(Millions)
X : parts per Million : 13C
166.7185
166.3276
162.6759
160.2732
145.3229
142.3481
141.3184
134.8349
132.1366
130.5634
129.5813
129.4383
128.9711
128.6851
128.2656
128.2179
127.1786
121.4770
121.3816
114.2307
114.0018
111.4657
111.2082
77.3223
76.9981
76.6835
51.9985
51.8459
F
COOMe
COOMe
3k


(Millions)
X : parts per Million : 1H
7.4582
7.4536
7.4376
7.4319
7.2520
6.9336
6.9302
6.8924
6.8534
6.8156
5.9095
3.8831
3.3574
−0.0024
50.25681
120.78025
10.19988
30.54708
30
3l


(Millions)
X : parts per Million : 13C
148.5666
140.9580
135.5233
133.5877
132.3578
130.6892
128.7156
128.5630
128.5058
127.7526
127.1710
126.8754
125.2068
108.0446
103.9161
77.3146
77.0000
76.6758
56.0239
55.2516
31


(Millions)
X : parts per Million : 1 H
7.5646
7.5142
7.4890
7.4844
7.2610
7.0594
7.0388
7.0205
6.9999
6.9014
6.8292
5.9391
3.8944
3.8440
3.8234
3.3629
−0.0002
20.54486
51.5802
20.39074
42.57339
11.75981
11.1243
10.0877
29.72659
29.50727
30
3m
COOMe
COOMe


(Millions)
X : parts per Million : 13C
166.8734
166.4920
148.9866
146.9652
140.8917
135.4284
135.3426
132.2248
130.6611
129.1260
129.0021
128.9449
128.6684
128.2774
128.2107
108.0641
104.2598
77.3151
77.0005
76.6763
56.0530
55.2616
52.0103
51.8578
3m
COOMe
COOMe