Supporting Information

Iron or boron-catalyzed C-H arylthiation of substituted phenols at room temperature

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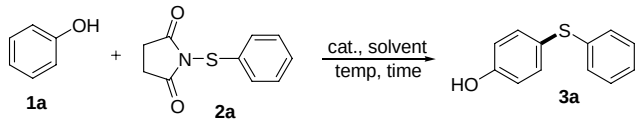
General experimental procedures

All reactions were carried out at room temperature and monitored by TLC. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm) and using tetramethylsilane (TMS) in the solvent of DMSO-d_6 as the internal standard (^{1}H NMR: DMSO-d_6 at 2.50 ppm; ^{13}C NMR: DMSO-d_6 at 39.52 ppm).

Optimization of conditions on reaction of phenol (1a) with 1-(phenylthio)pyrrolidine-2,5-dione (2a)

Table 1 Optimization of conditions on reaction of phenol (**1a**) with 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) leading to 4-(phenylthio)phenol (**3a**)[a]



Entry	Cat. (equiv)	Solvent	Temp (^{o}C)	Time	Yield (%)[b]
1	$FeCl_3$ (0.2)	DCE	RT	10 min	94
2	$BF_3{\cdot}OEt_2$ (0.2)	DCE	RT	10 min	92
3	CuI (0.2)	DCE	RT	10 min	0
4	$CuCl_2$ (0.2)	DCE	RT	10 min	0
5	$Pd(OAc)_2$ (0.2)	DCE	RT	10 min	0
6	AgOAc (0.2)	DCE	RT	10 min	0
7	$RuCl_3$ (0.2)	DCE	RT	10 min	0
8	$ZnCl_2$ (0.2)	DCE	RT	10 min	0
9	$AlCl_3$ (0.2)	DCE	RT	10 min	83
10	TsOH (0.2)	DCE	RT	10 min	42
11	H_2SO_4 (0.2)[c]	DCE	RT	10 min	91
12	-	DCE	RT to 100	16 h	0
13	$FeCl_3$ (0.1)	DCE	RT	3 h	93
14	$BF_3{\cdot}OEt_2$ (0.1)	DCE	RT	3 h	92
15	$FeCl_3$ (0.05)	DCE	RT	3 h	53
16	$BF_3{\cdot}OEt_2$ (0.05)	DCE	RT	3 h	49
17	$FeCl_3$ (0.1)	CH_2Cl_2	RT	3 h	94

18	$BF_3{\cdot}OEt_2$ (0.1)	CH_2Cl_2	RT	3 h	93
19	$FeCl_3$ (0.1)	$CHCl_3$	RT	3 h	85
20	$BF_3{\cdot}OEt_2$ (0.1)	$CHCl_3$	RT	3 h	82
21	$FeCl_3$ (0.1)	MeCN	RT	3 h	64
22	$BF_3{\cdot}OEt_2$ (0.1)	MeCN	RT	3 h	90
23	$FeCl_3$ (0.1)	THF	RT	3 h	52
24	$BF_3{\cdot}OEt_2$ (0.1)	THF	RT	3 h	0
25	$FeCl_3$ (0.1)	DCE	50	3 h	64
26	$BF_3{\cdot}OEt_2$ (0.1)	DCE	50	3 h	62
27	$FeCl_3$ (0.1) + $CuCl_2$ (0.1)	CH_2Cl_2	RT	3 h	94

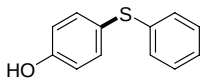
[a] Reaction conditions: phenol (**1a**) (0.3 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) (0.33 mmol), catalyst (0.015-0.06 mmol), anhydrous solvent (2 mL), temperature (RT - 100 ^oC), reaction time (10 mim - 16 h). [b] Isolated yield. [c] 98% H_2SO_4. DCE = 1,2-dichloroethane.

As shown in Table 1, our search for optimized reaction conditions began by treating phenol (**1a**) with 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) in the presence of different catalysts in dichloroethane (DCE) at room temperature (entries 1-11), and $FeCl_3$ (entry 1), $BF_3{\cdot}OEt_2$ (entry 2), $AlCl_3$ (entry 9) and H_2SO_4 (entry 11) gave the higher yields, in which $FeCl_3$ and $BF_3{\cdot}OEt_2$ were most efficient (*the two catalysts showed similar catalytic activity*) (entries 1 and 2). No target product was observed in the absence of catalyst when temperature was changed from room temperature to 100 ^oC (entry 12). Amount of the catalysts were reduced, and 0.1 equiv of catalysts provided similar yields (entries 13 and 14), but 0.05 equiv of catalysts gave lower yields (entries 15 and 16). Other solvents were attempted (entries 17-24), and CH_2Cl_2 was a suitable solvent in this arylthiation of phenol (entries 17 and 18). When temperature was raised to 50 ^oC, yields decreased (entries 25 and 26). In order to check whether trace amount of copper involve in catalysis in the iron-catalyzed arylthiation of phenol, mixed catalysts ($FeCl_3$/$CuCl_2$) were used, and the result showed that addition of $CuCl_2$ did not affect this reaction (entry 27).

General procedure for synthesis of 3a-b'

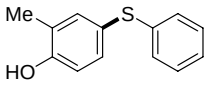
A 10 mL flask was charged with a magnetic stirrer, substituted phenol (**1**) (0.3 mmol) and 1-(substituted phenylthio)pyrrolidine-2,5-dione (**2**) (0.66 mmol for **3n**; 0.33 mmol for others) and dry dichloromethane (2.0 mL). $FeCl_3$ or $BF_3{\cdot}OEt_2$ (0.03 mmol) was added to the flask, and the mixture was stirred at room temperature till the reaction completed (TLC determination). The resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate or dichloromethane/hexane as the eluent to give the desired target product (**3**).

Characterization data of compounds 3a-b'



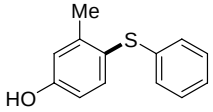
3a

4-(Phenylthio)phenol (3a).[1] Eluent: petroleum ether/ethyl acetate (5:1). Yield: 56 mg (93%) using $FeCl_3$ as the catalyst; 55 mg (92%) using $BF_3{\cdot}OEt_2$ as the catalyst. Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 8.7 Hz, 2H), 7.11 - 7.24 (m, 5H), 6.80 (d, J = 8.7 Hz, 2H), 5.34 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 138.4, 135.6, 129.1, 128.5, 126.0, 124.8, 116.7. EIMS: M^+ m/z 202.2.



3b

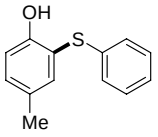
2-Methyl-4-(phenylthio)phenol (3b).[2] Eluent: petroleum ether/ethyl acetate (8:1). Yield: 58 mg (89%) using $FeCl_3$ as the catalyst; 56 mg (87%) using $BF_3{\cdot}OEt_2$ as the catalyst. Light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 - 7.26 (m, 7H), 6.72 (d, J = 8.2 Hz, 1H), 5.17 (s, 1H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 138.7, 136.9, 133.2, 129.0, 128.2, 125.8, 125.4, 124.1, 116.1, 15.8. EIMS: M^+ m/z 216.2.



3c

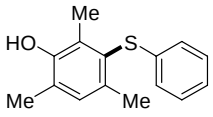
2-Methyl-4-(phenylthio)phenol (3c).[2] Eluent: petroleum ether/ethyl acetate

(8:1). Yield: 62 mg (95%) using $FeCl_3$ as the catalyst; 59 mg (92%) using $BF_3{\cdot}OEt_2$ as the catalyst. Light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.03 - 7.05 (m, 2H), 6.78 (d, *J* = 2.8 Hz, 1H), 6.67 (dd, *J* = 8.2 Hz, 2.8 Hz, 1H), 5.49 (br.s, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 144.2, 138.4, 137.6, 129.0, 127.1, 125.4, 123.0, 117.9, 114.1, 21.0. EIMS: M^+ m/z 216.2.



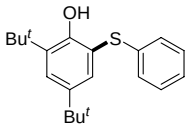
3d

4-Methyl-2-(phenylthio)phenol (3d).[1] Eluent: dichloromethane/hexane (1:3). Yield: 52 mg (81%) using $FeCl_3$ as the catalyst; 52 mg (81%) using $BF_3{\cdot}OEt_2$ as the catalyst. Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, *J* = 1.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.11 - 7.17 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.34 (s, 1H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 137.0, 136.2, 133.1, 130.7, 129.3, 126.9, 126.1, 115.8, 115.4, 20.4. EIMS: M^+ m/z 216.2.



3e

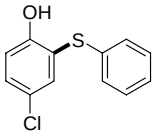
2,4,6-Trimethyl-3-(phenylthio)phenol (3e). Eluent: petroleum ether/ethyl acetate (10:1). Yield: 59 mg (81%) using $FeCl_3$ as the catalyst; 58 mg (79%) using $BF_3{\cdot}OEt_2$ as the catalyst. Light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (t, *J* = 7.3 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.97 (s, 1H), 6.90 - 6.92 (m, 2H), 4.61 (br.s, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8, 138.5, 135.6, 130.2, 129.0, 128.6, 125.6, 124.9, 124.7, 21.3, 16.2, 14.4. EIMS: M^+ m/z 244.1.



3f

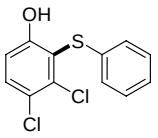
2,4-Di-*tert*-butyl-6-(phenylthio)phenol (3f). Eluent: petroleum ether/ethyl acetate (10:1). Yield: 91 mg (97%) using $FeCl_3$ as the catalyst; 90 mg (96%)

using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 48 - 49 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 - 7.42 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 6.9 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.86 (s, 1H), 1.42 (s, 9H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 142.9, 136.6, 135.9, 131.2, 129.3, 127.0, 126.5, 125.9, 115.8, 35.5, 34.5, 31.7, 29.6. EIMS: M^+ m/z 314.4.



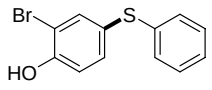
3g

4-Chloro-2-(phenylthio)phenol (3g). Eluent: petroleum ether/ethyl acetate (4:1). Yield: 48 mg (68%) using $FeCl_3$ as the catalyst; 46 mg (65%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 2.3 Hz, 1H), 7.31 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 135.8, 134.9, 132.2, 129.5, 127.6, 126.8, 125.6, 118.3, 116.9. EIMS: M^+ m/z 236.1.



3h

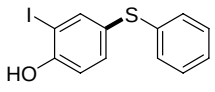
3,4-Dichloro-2-(phenylthio)phenol (3h). Eluent: dichloromethane/hexane (1:1). Yield: 45 mg (55%) using $FeCl_3$ as the catalyst; 47 mg (58%) using $BF_3{\cdot}OEt_2$ as the catalyst. Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, *J* = 9.2 Hz, 1H), 7.25 - 7.29 (m, 2H), 7.18 - 7.22 (m, 1H), 7.10 - 7.13 (m, 2H), 6.99 (d, *J* = 9.2 Hz, 1H), 6.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 138.5, 133.4, 133.0, 129.6, 127.5, 127.0, 124.9, 118.4, 114.7. EIMS: M^+ m/z 270.1.



3i

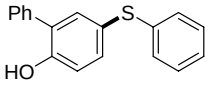
2-Bromo-4-(phenylthio)phenol (3i).[1] Eluent: petroleum ether/ethyl acetate (5:1). Yield: 65 mg (77%) using $FeCl_3$ as the catalyst; 65 mg (77%) using $BF_3{\cdot}OEt_2$ as the catalyst. Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 2.3 Hz, 1H), 7.16 - 7.31 (m, 6H), 6.99 (d, *J* = 8.3 Hz, 1H), 5.63 (br.s, 1H). ^{13}C

NMR ($CDCl_3$, 100 MHz) δ 152.4, 137.3, 136.4, 134.4, 129.3, 129.3, 126.8, 126.6, 117.0, 110.8. EIMS: M^+ m/z 280.2.



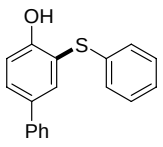
3j

2-Iodo-4-(phenylthio)phenol (3j). Eluent: petroleum ether/ethyl acetate (5:1). Yield: 70 mg (71%) using $FeCl_3$ as the catalyst; 72 mg (73%) using $BF_3{\cdot}OEt_2$ as the catalyst. Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.3 Hz, 2.3 Hz, 1H), 7.16 - 7.28 (m, 5H), 6.96 (d, *J* = 8.3 Hz, 1H), 5.43 (br.s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 142.6, 137.4, 135.5, 129.2, 129.1, 127.1, 126.5, 115.9, 86.3. EIMS: M^+ m/z 328.2.



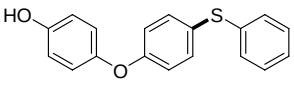
3k

5-(Phenylthio)biphenyl-2-ol (3k). Eluent: petroleum ether/ethyl acetate (15:1). Yield: 70 mg (84%) using $FeCl_3$ as the catalyst; 71 mg (85%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 - 7.46 (m, 7H), 7.19 - 7.23 (m, 4H), 7.11 - 7.15 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 5.40 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.8, 138.3, 136.2, 135.7, 134.8, 129.5, 129.4, 129.1, 128.6, 128.3, 126.0, 124.9, 117.2. EIMS: M^+ m/z 278.3.



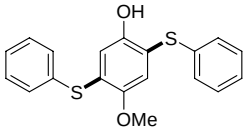
3l

3-(Phenylthio)biphenyl-4-ol (3l). Eluent: dichloromethane/hexane (1:4). Yield: 57 mg (69%) using $FeCl_3$ as the catalyst; 56 mg (68%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 57 - 58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.51 - 7.54 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.11 - 7.15 (m, 4H), 6.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.8, 139.9, 135.8, 135.4, 134.8, 131.1, 129.4, 129.0, 127.2, 127.1, 126.8, 126.4, 116.9, 116.0. EIMS: M^+ m/z 278.3.



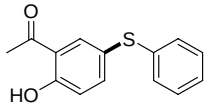
3m

4-(4-(Phenylthio)phenoxy)phenol (3m). Eluent: dichloromethane/hexane (1:4). Yield: 58 mg (66%) using $FeCl_3$ as the catalyst; 57 mg (65%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 56 - 57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.22 - 7.31 (m, 4H), 7.15 - 7.19 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.91 (br.s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 152.2, 149.7, 137.7, 134.6, 129.3, 129.2, 127.2, 126.4, 121.5, 118.3, 116.6. EIMS: M^+ m/z 294.2.



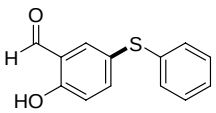
3n

4-Methoxy-2,5-bis(phenylthio)phenol (3n). Eluent: petroleum ether/ethyl acetate (15:1). Yield: 93 mg (91%) using $FeCl_3$ as the catalyst; 97 mg (95%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 - 7.55 (m, 2H), 7.38 - 7.43 (m, 3H), 7.21 - 7.25 (m, 2H), 7.12 - 7.16 (m, 1H), 7.05 - 7.08 (m, 2H), 6.97 (s, 1H), 6.48 (s, 1H), 6.05 (s, 1H), 3.84 (s, 3H),. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 149.7, 136.1, 135.0, 133.1, 131.0, 129.8, 129.4, 129.1, 126.6, 126.2, 117.5, 114.3, 112.2, 56.7. EIMS: M^+ m/z 340.2.



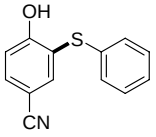
3o

1-(2-Hydroxy-5-(phenylthio)phenyl)ethanone (3o). Eluent: petroleum ether/ethyl acetate (7:1). Yield: 45 mg (62%) using $FeCl_3$ as the catalyst; 49 mg (67%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.4 (s, 1H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.25 - 7.29 (m, 2H), 7.17 - 7.20 (m, 3H), 6.99 (d, *J* = 8.7 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.3, 162.7, 142.1, 137.7, 136.4, 129.3, 128.6, 126.4, 123.2, 120.5, 120.1, 26.8. EIMS: M^+ m/z 244.2.



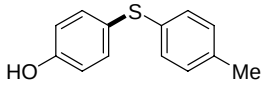
3p

2-Hydroxy-5-(phenylthio)benzaldehyde (3p). Eluent: petroleum ether/ethyl acetate (7:1). Yield: 40 mg (58%) using $FeCl_3$ as the catalyst; 37 mg (54%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 45 - 46 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.1 (s, 1H), 9.85 (s, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.19 - 7.30 (m, 5H), 6.99 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.2, 161.7, 142.1, 138.5, 137.1, 129.4, 129.3, 126.7, 125.1, 121.4, 119.3. EIMS: M^+ m/z 230.2.



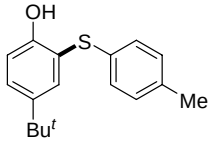
3q

4-Hydroxy-3-(phenylthio)benzonitrile (3q). Eluent: dichloromethane/hexane (1:3). Yield: 35 mg (52%) using $FeCl_3$ as the catalyst; 36 mg (53%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 104 - 105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 2.3 Hz, 1H), 7.61 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.21 - 7.31 (m, 3H), 7.09 - 7.15 (m, 3H), 7.02 - 7.04 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 140.5, 135.7, 133.8, 129.7, 128.3, 127.4, 119.6, 118.3, 116.7, 105.0. EIMS: M^+ m/z 227.2.



3r

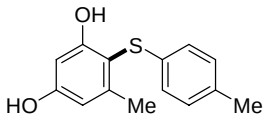
4-(*p*-Tolylthio)phenol (3r).[3] Eluent: petroleum ether/ethyl acetate (8:1). Yield: 59 mg (91%) using $FeCl_3$ as the catalyst; 58 mg (90%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 66 - 67 °C (lit.[3] 64 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.21 (s, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 136.4, 134.5, 134.1, 129.9, 129.6, 126.1, 116.5, 21.1. EIMS: M^+ m/z 216.0.



3s

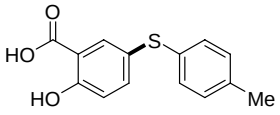
4-*tert*-Butyl-2-(*p*-tolylthio)phenol (3s). Eluent: petroleum ether/ethyl acetate

(15:1). Yield: 73 mg (90%) using $FeCl_3$ as the catalyst; 73 mg (90%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, *J* = 2.3 Hz, 1H), 7.37 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 6.97 - 7.04 (m, 5H), 6.35 (s, 1H), 2.26 (s, 3H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 144.2, 136.1, 133.5, 132.6, 130.1, 129.4, 127.1, 116.1, 115.0, 34.3, 31.6, 21.0. EIMS: M^+ m/z 272.3.



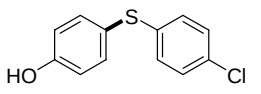
3t

5-Methyl-4-(*p*-tolylthio)benzene-1,3-diol (3t). Eluent: petroleum ether/ethyl acetate (5:1). Yield: 68 mg (93%) using $FeCl_3$ as the catalyst; 67 mg (91%) using $BF_3{\cdot}OEt_2$ as the catalyst. Gray solid, mp 75 - 76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (d, *J* = 7.8 Hz, 2H), 6.98 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 2.3 Hz, 1H), 6.41 (d, *J* = 2.3 Hz, 1H), 5.68 (br.s, 1H), 2.32 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 158.2, 145.9, 135.8, 132.3, 130.1, 126.1, 110.4, 107.8, 99.8, 21.2, 21.0. EIMS: M^+ m/z 246.2.



3u

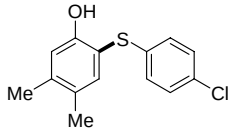
2-Hydroxy-5-(*p*-tolylthio)benzoic acid (3u). Eluent: dichloromethane/hexane/AcOH (1:1:0.001). Yield: 52 mg (67%) using $FeCl_3$ as the catalyst; 51 mg (65%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 247 - 248 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.78 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.10 - 7.15 (m, 4H), 6.93 (d, *J* = 8.7 Hz, 1H), 2.25 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.6, 140.5, 135.7, 133.8, 129.7, 128.3, 127.4, 119.6, 118.3, 116.7, 105.0. ESI-MS: $[M-H]^-$ m/z 259.1.



3v

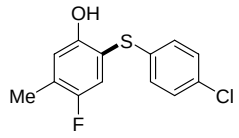
4-(4-Chlorophenylthio)phenol (3v).[4] Eluent: petroleum ether/ethyl acetate (8:1). Yield: 68 mg (96%) using $FeCl_3$ as the catalyst; 66 mg (93%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 32 - 33 °C. ^{1}H NMR ($CDCl_3$, 400

MHz) δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1, 137.1, 135.7, 131.8, 129.6, 129.2, 124.3, 116.7. EIMS: M^+ m/z 236.2.



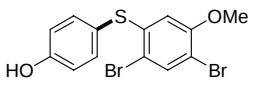
3w

2-(4-Chlorophenylthio)-4,5-dimethylphenol (3w). Eluent: petroleum ether/ethyl acetate (15:1). Yield: 67 mg (84%) using $FeCl_3$ as the catalyst; 68 mg (85%) using $BF_3{\cdot}OEt_2$ as the catalyst. White solid, mp 113 - 114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.87 (s, 1H), 6.19 (s, 1H), 2.25 (s, 3H), 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 142.1, 137.2, 135.3, 131.9, 129.9, 129.3, 127.9, 116.8, 112.1, 20.2, 18.8. EIMS: M^+ m/z 264.0.



3x

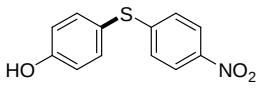
2-(4-Chlorophenylthio)-4-fluoro-5-methylphenol (3x). Eluent: petroleum ether/ethyl acetate (10:1). Yield: 55 mg (69%) using $FeCl_3$ as the catalyst; 52 mg (65%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 94 - 95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 6.4 Hz, 1H), 6.15 (s, 1H), 2.28 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3 (d, *J* = 240.6 Hz), 153.3, 134.2, 132.5, 130.2 (d, *J* = 19.2 Hz), 129.5, 128.4, 121.8 (d, *J* = 24.0 Hz), 117.8 (d, *J* = 4.8 Hz), 113.4 (d, *J* = 7.7 Hz), 15.1 (d, *J* = 2.9 Hz). EIMS: M^+ m/z 268.1.



3y

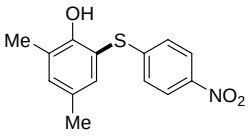
4-(2,4-Dibromo-5-methoxyphenylthio)phenol (3y). Eluent: petroleum ether/ethyl acetate (6:1). Yield: 96 mg (82%) using $FeCl_3$ as the catalyst; 98 mg (84%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.22 (s, 1H),

5.53 (s, 1H), 3.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.0, 155.5, 141.2, 137.2, 136.0, 122.2, 117.1, 111.6, 111.1, 108.7, 56.2. EIMS: M^+ m/z 390.1.



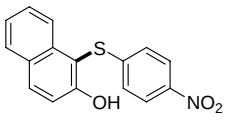
3z

4-(4-Nitrophenylthio)phenol (3z).[5] Eluent: petroleum ether/ethyl acetate (4:1). Yield: 48 mg (65%) using $FeCl_3$ as the catalyst; 47 mg (64%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 153 - 154 °C (lit.[5] 150 - 151 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.5, 150.2, 145.1, 137.6, 125.7, 124.1, 120.5, 117.3. EIMS: M^+ m/z 247.2.



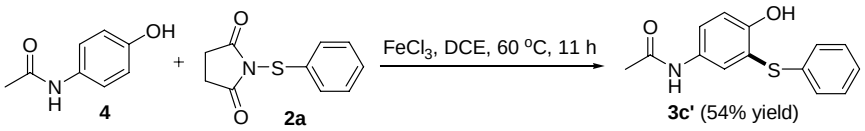
3a'

2,4-Dimethyl-6-(4-nitrophenylthio)phenol (3a'). Eluent: petroleum ether/ethyl acetate (10:1). Yield: 44 mg (53%) using $FeCl_3$ as the catalyst; 47 mg (57%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 130 - 131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.10 - 7.15 (m, 4H), 6.15 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 146.4, 145.8, 135.6, 134.3, 130.8, 126.0, 125.6, 124.3, 112.5, 20.4, 16.6. EIMS: M^+ m/z 275.2.

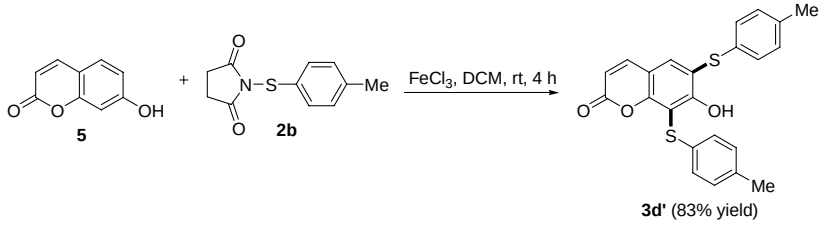


3b'

1-(4-Nitrophenylthio)naphthalen-2-ol (3b'). Eluent: petroleum ether/ethyl acetate (10:1). Yield: 54 mg (61%) using $FeCl_3$ as the catalyst; 53 mg (59%) using $BF_3{\cdot}OEt_2$ as the catalyst. Yellow solid, mp 184 - 185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.51 (t, *J* = 6.9 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.89 (br.s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 145.9, 145.2, 135.0, 134.0, 129.7, 129.0, 128.6, 126.1, 124.5, 124.4, 124.1, 117.3, 105.7. EIMS: M^+ m/z 297.1.

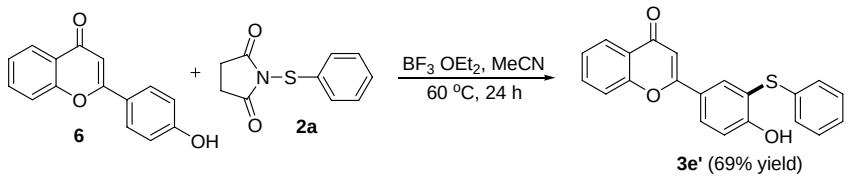


Synthesis of *N*-(4-hydroxy-3-(phenylthio)phenyl)acetamide (3c'). $FeCl_3$ (0.03 mmol, 5 mg), *N*-(4-hydroxyphenyl)acetamide (**4**) (0.3 mmol, 45 mg), 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) (0.36 mmol, 1.2 equiv, 75 mg) and anhydrous dichloroethane (DCE) (2 mL) were added to a 25 mL Schlenk tube charged with a magnetic stirrer, and then the mixture was stirred at 60 ^{o}C for 11 h. After the reaction completed (TLC determination), the resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1 : 1) as the eluent to give *N*-(4-hydroxy-3-(phenylthio)phenyl)acetamide (**3c'**) (42mg, 54%) as a brown oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.65 (d, *J* = 2.8 Hz, 1H), 7.51 (dd, *J* = 8.6 Hz, 2.8 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.42 (s, 1H), 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.5, 154.2, 135.5, 131.3, 129.4, 128.4, 127.4, 126.5, 125.0, 116.9, 115.9, 24.4. EIMS: M^+ m/z 259.2.



Synthesis of 7-hydroxy-6,8-bis(*p*-tolylthio)-2*H*-chromen-2-one (3d'). A 10 mL flask was charged with a magnetic stirrer, 7-hydroxy-2*H*-chromen-2-one (**5**) (0.3 mmol, 49 mg) and 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**2b**) (0.66 mmol, 146 mg) and dry dichloromethane (DCM) (2.0 mL). $FeCl_3$ (0.03 mmol, 5 mg) was added to the flask, and the mixture was stirred at room temperature for 4 h. After the reaction completed (TLC determination), the resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5 : 1) as the eluent to give 7-hydroxy-6,8-bis(*p*-tolylthio)-2*H*-chromen-2-one (**3d'**) (101 mg,

83%) as a white solid, mp 179 - 180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 - 7.46 (m, 3H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.96 - 6.98 (m, 3H), 6.83 (s, 1H), 2.41 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 158.7, 154.8, 140.3, 137.1, 135.3, 134.5, 134.1, 131.3, 131.0, 130.3, 127.9, 127.4, 125.9, 115.5, 114.5, 103.2, 21.5, 21.1. ESI-MS: $[M-H]^-$ m/z 405.1.



Synthesis of 2-(4-hydroxy-3-(phenylthio)phenyl)-4*H*-chromen-4-one (3e'). $BF_3{\cdot}OEt_2$ (0.03 mmol, 4 uL), 2-(4-hydroxyphenyl)-4*H*-chromen-4-one (**6**) (0.3 mmol, 71 mg), 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) (0.36 mmol, 1.2 equiv, 75 mg) and anhydrous MeCN (2 mL) were added to a 25 mL Schlenk tube charged with a magnetic stirrer, and then the mixture was stirred at 60 °C for 24 h. After the reaction completed (TLC determination), the resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using dichloromethane/ methanol (40 : 1) as the eluent to give 2-(4-hydroxy-3-(phenylthio)phenyl)-4*H*-chromen-4-one (**3e'**) (72 mg, 69%) as a yellow solid, mp 235 - 236 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.95 (br. s, 1H), 8.01 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.77 - 7.82 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 1H), 7.37 - 7.39 (m, 2H), 7.29 - 7.30 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 176.8, 162.2, 159.8, 155.5, 134.5, 134.1, 130.9, 129.7, 129.4, 128.1, 126.9, 125.4, 124.7, 123.2, 122.5, 121.0, 118.2, 116.2, 105.2. ESI-MS: $[M+H]^+$ m/z 347.3.

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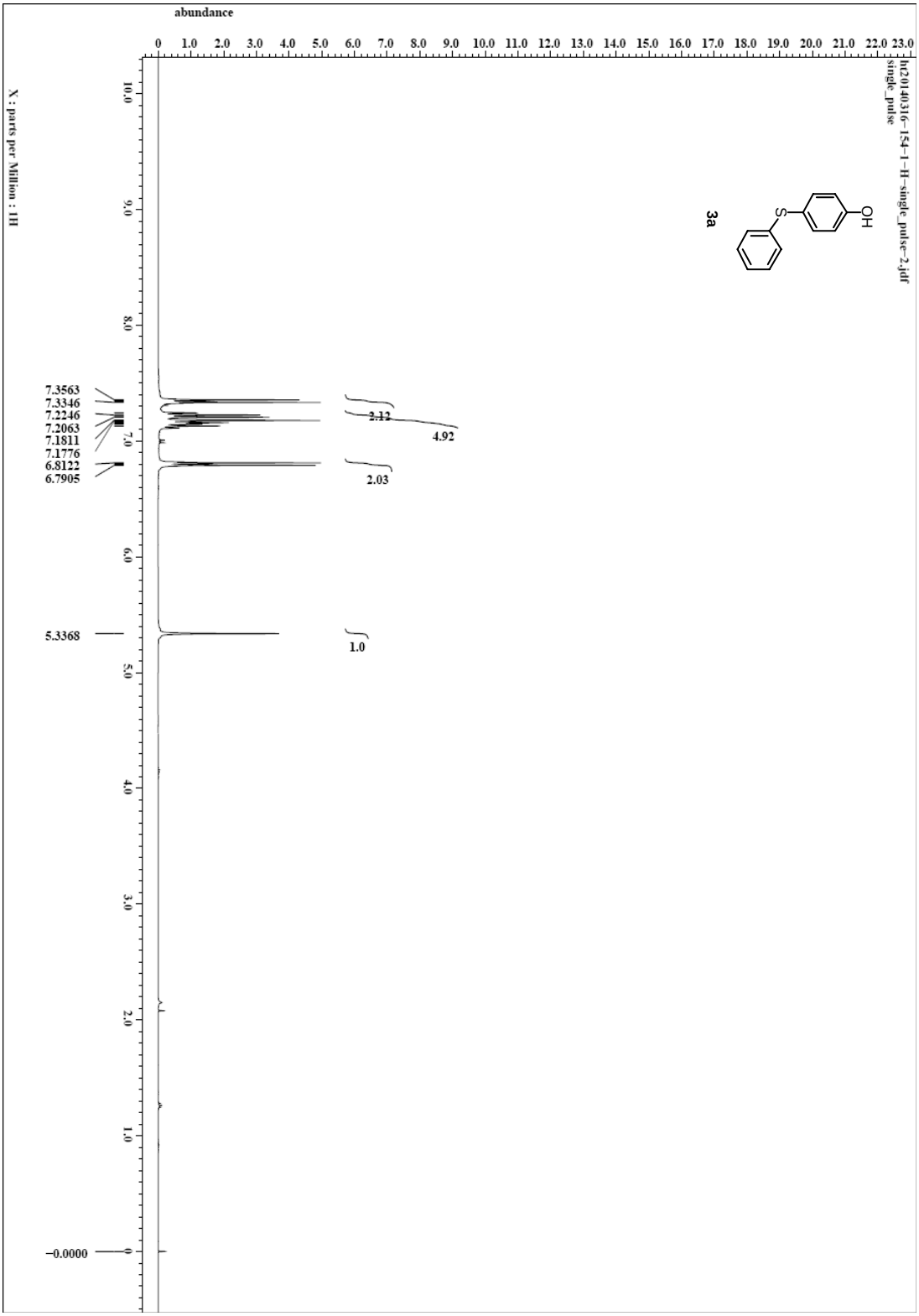
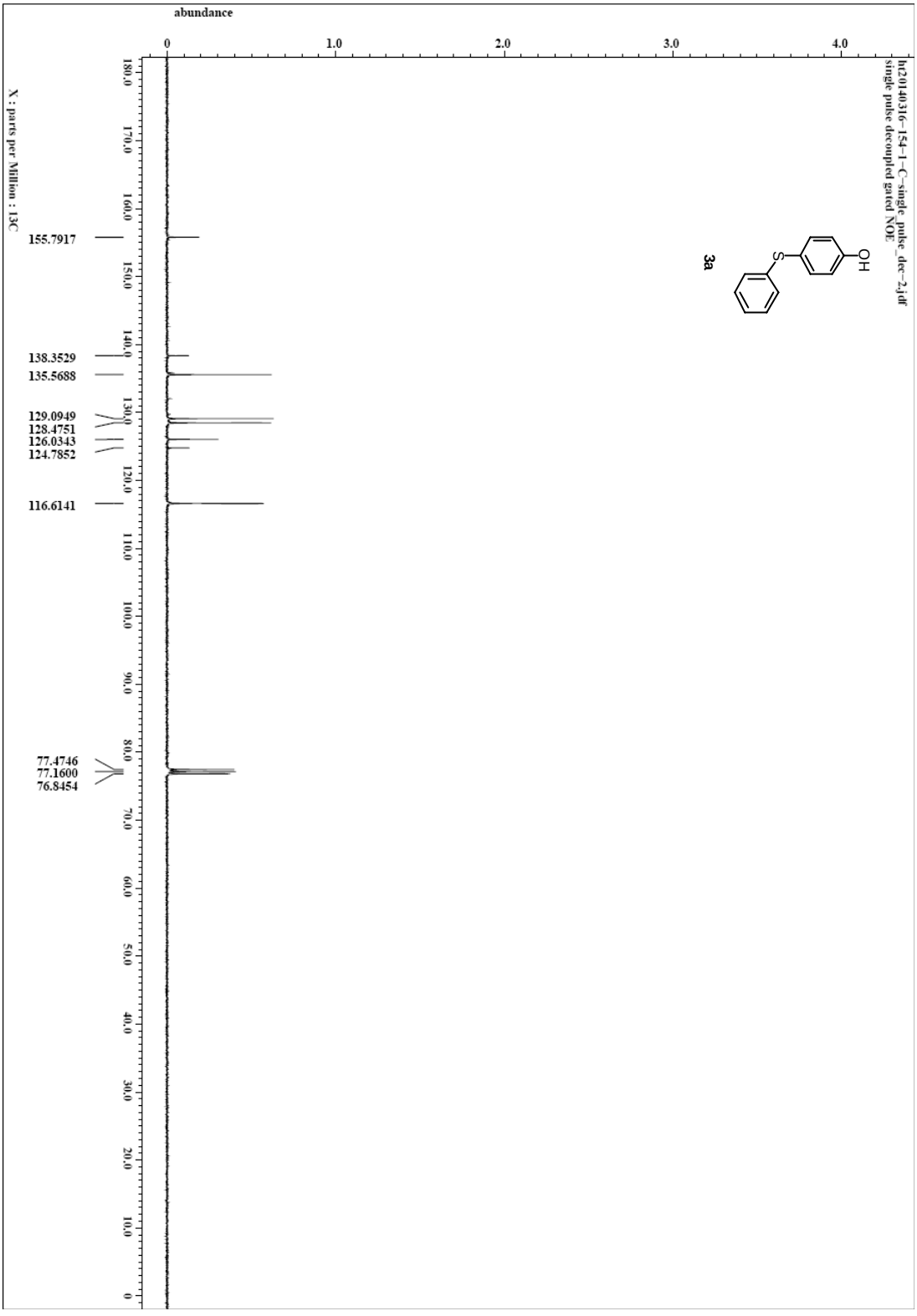
The ^{1}H and ^{13}C NMR spectra of compounds 3a-e'

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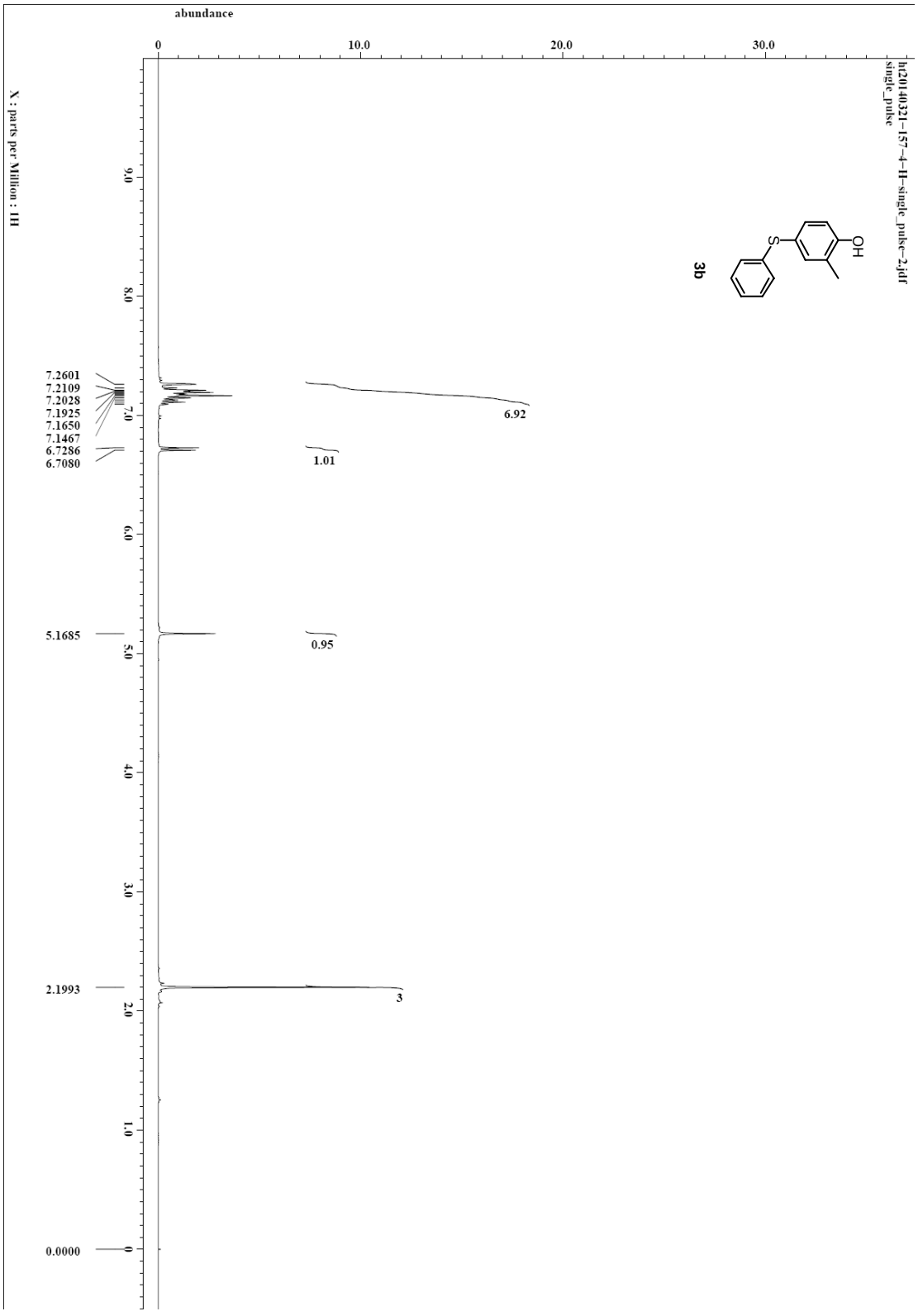
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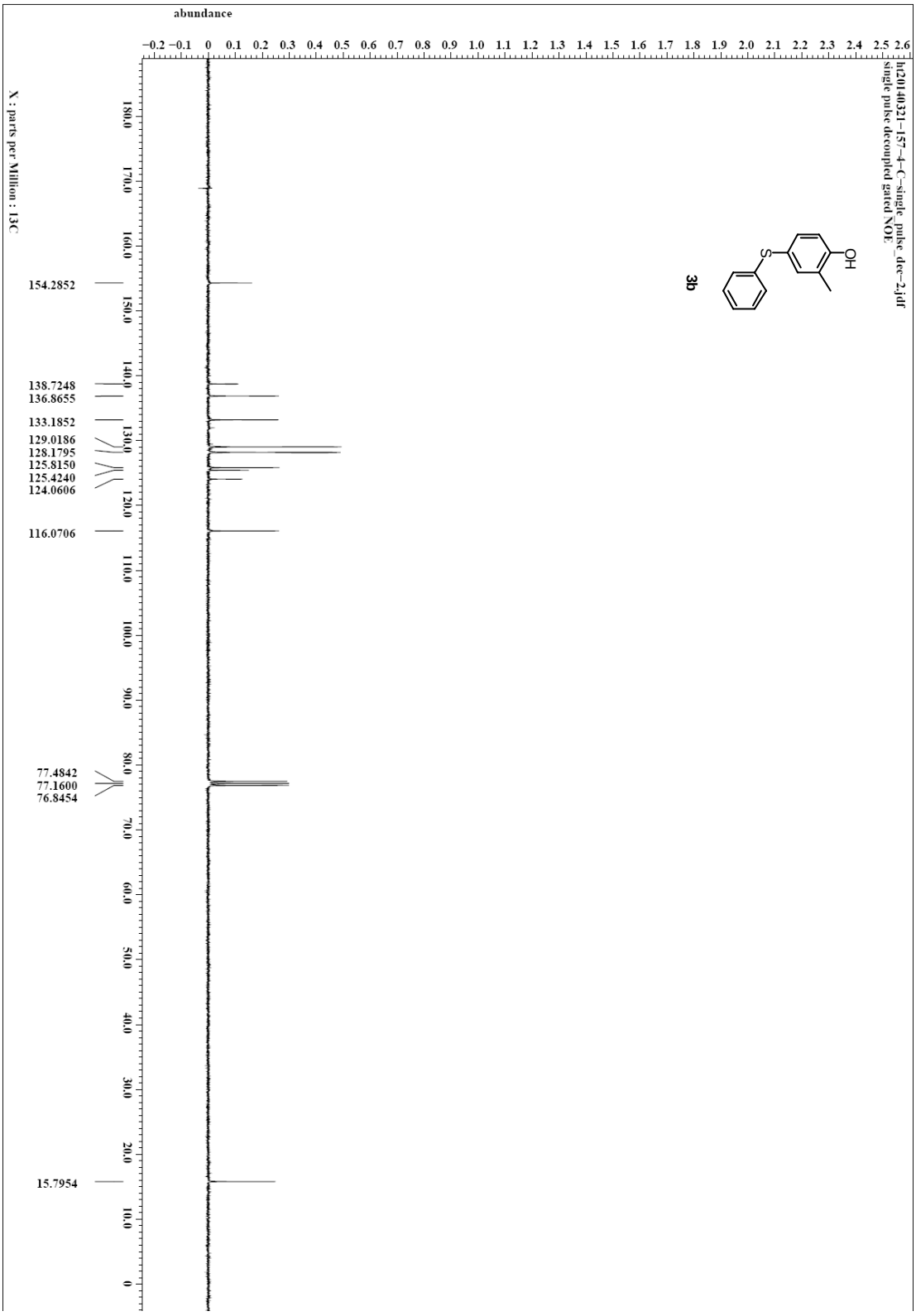
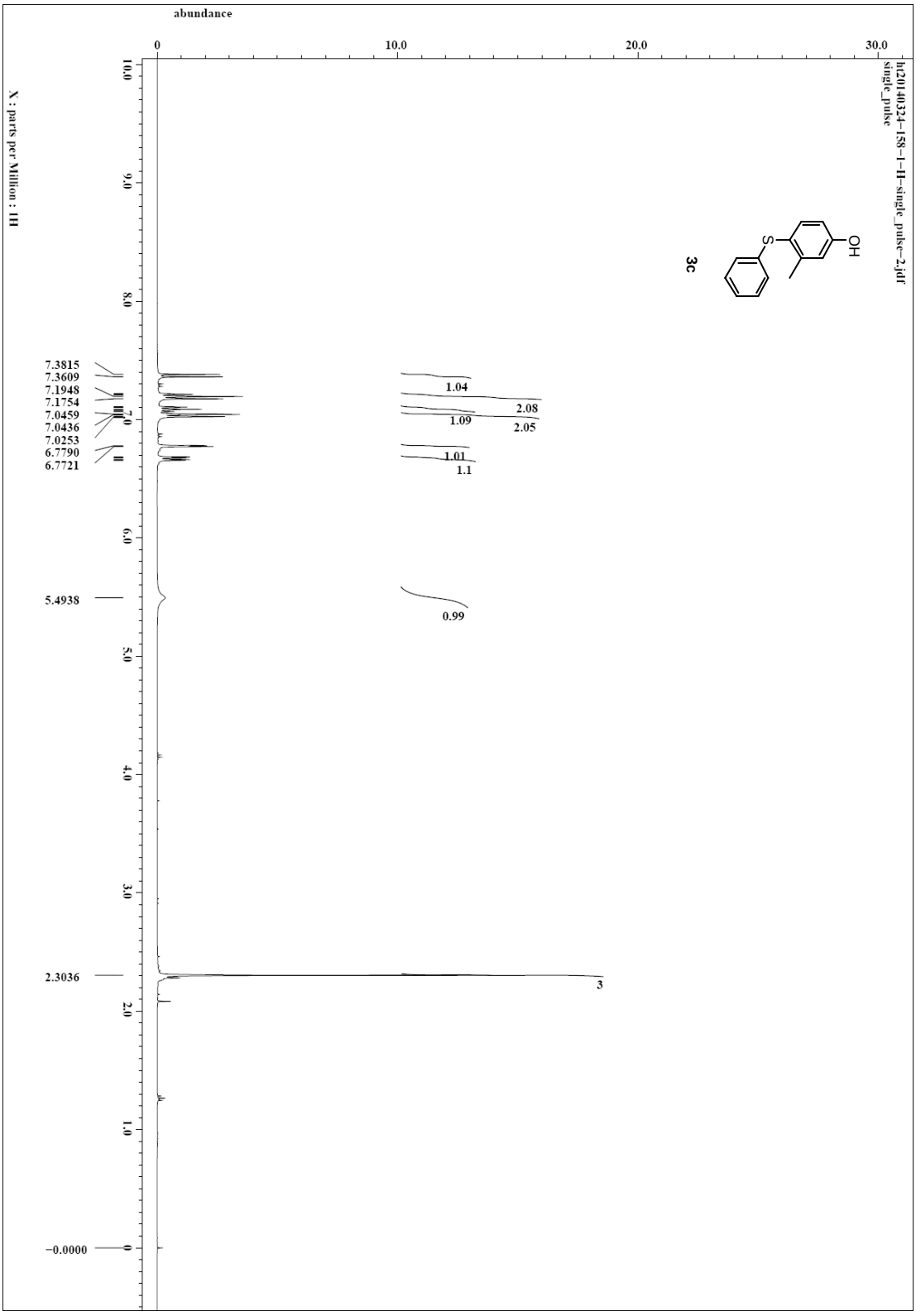
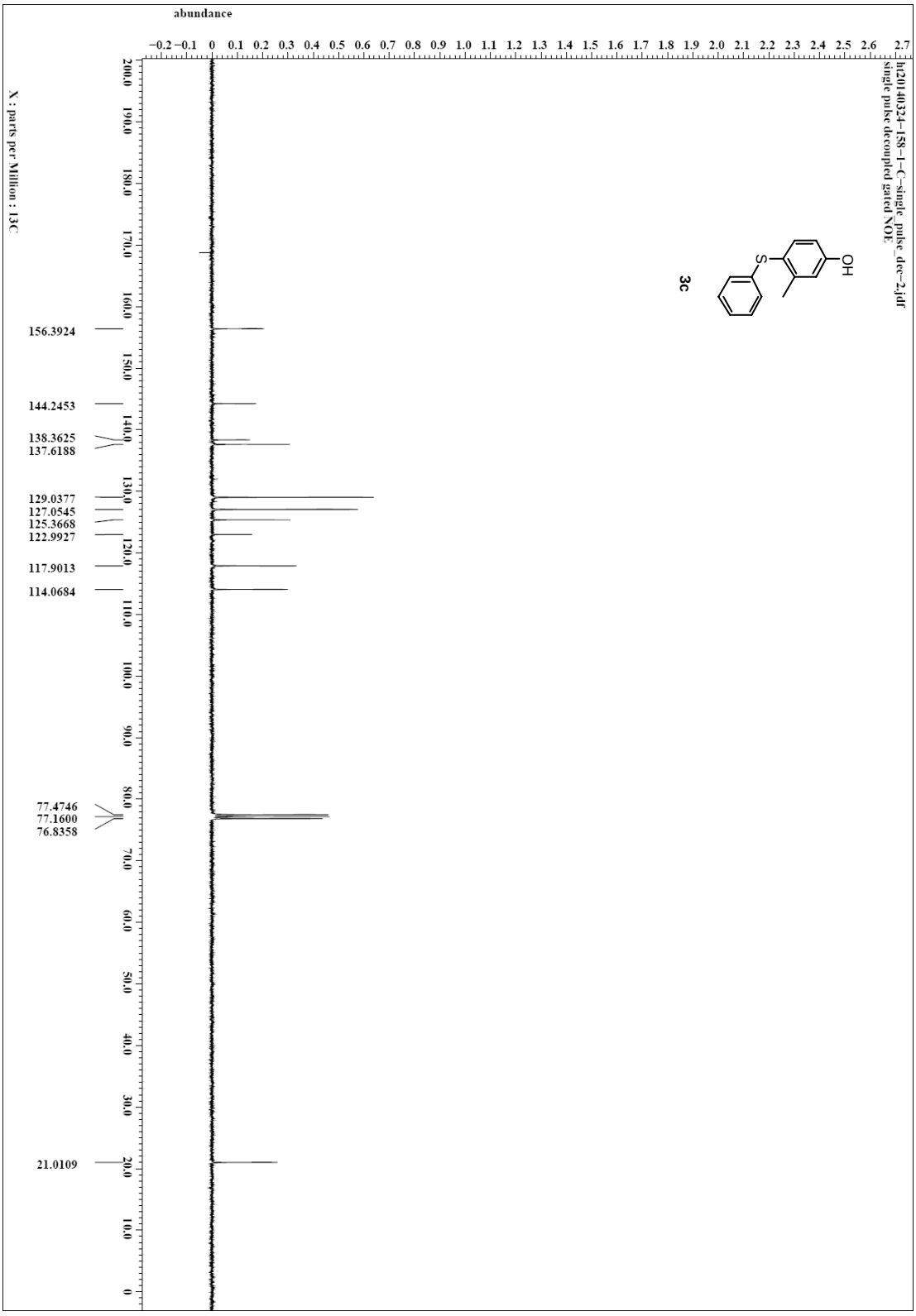
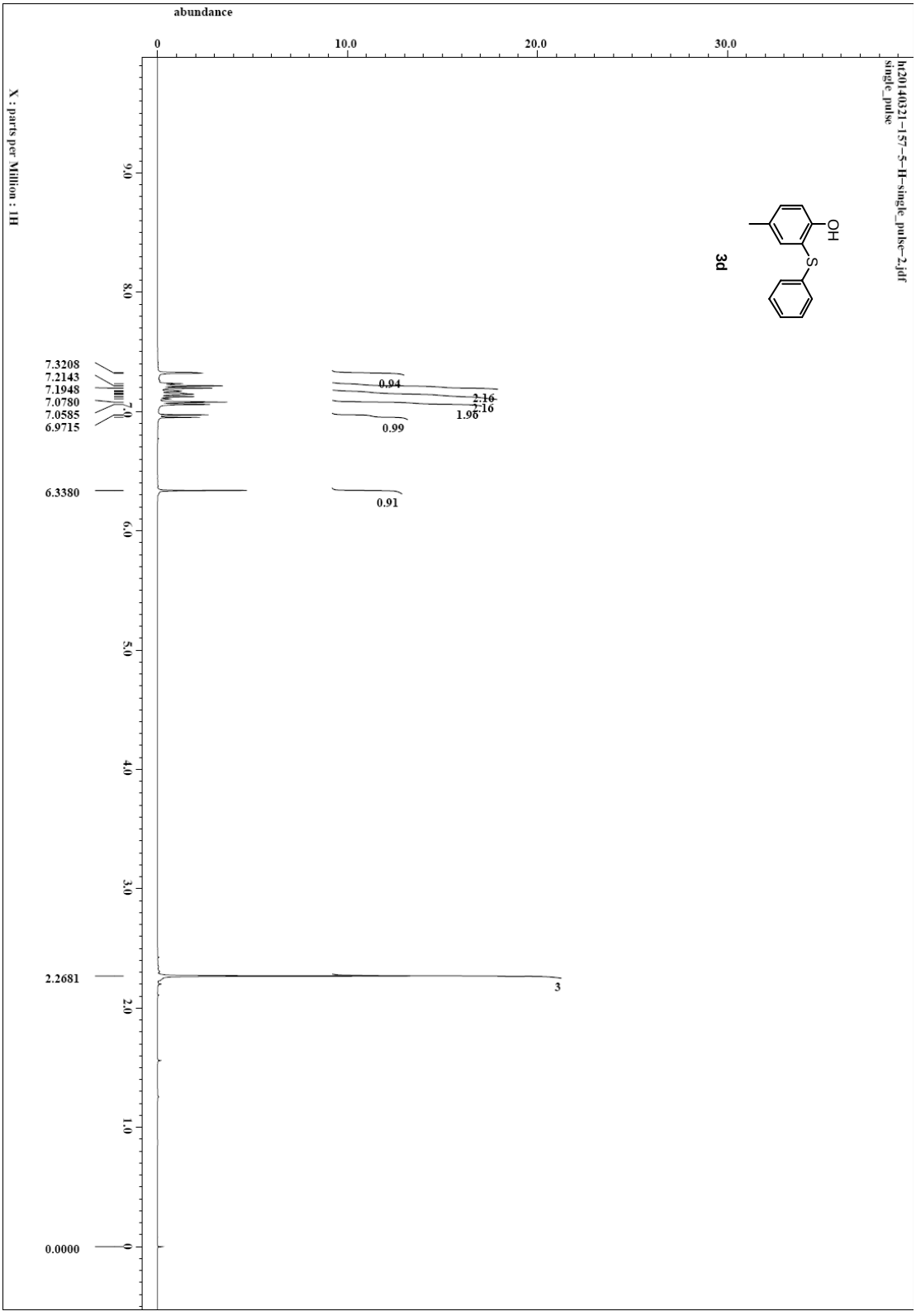
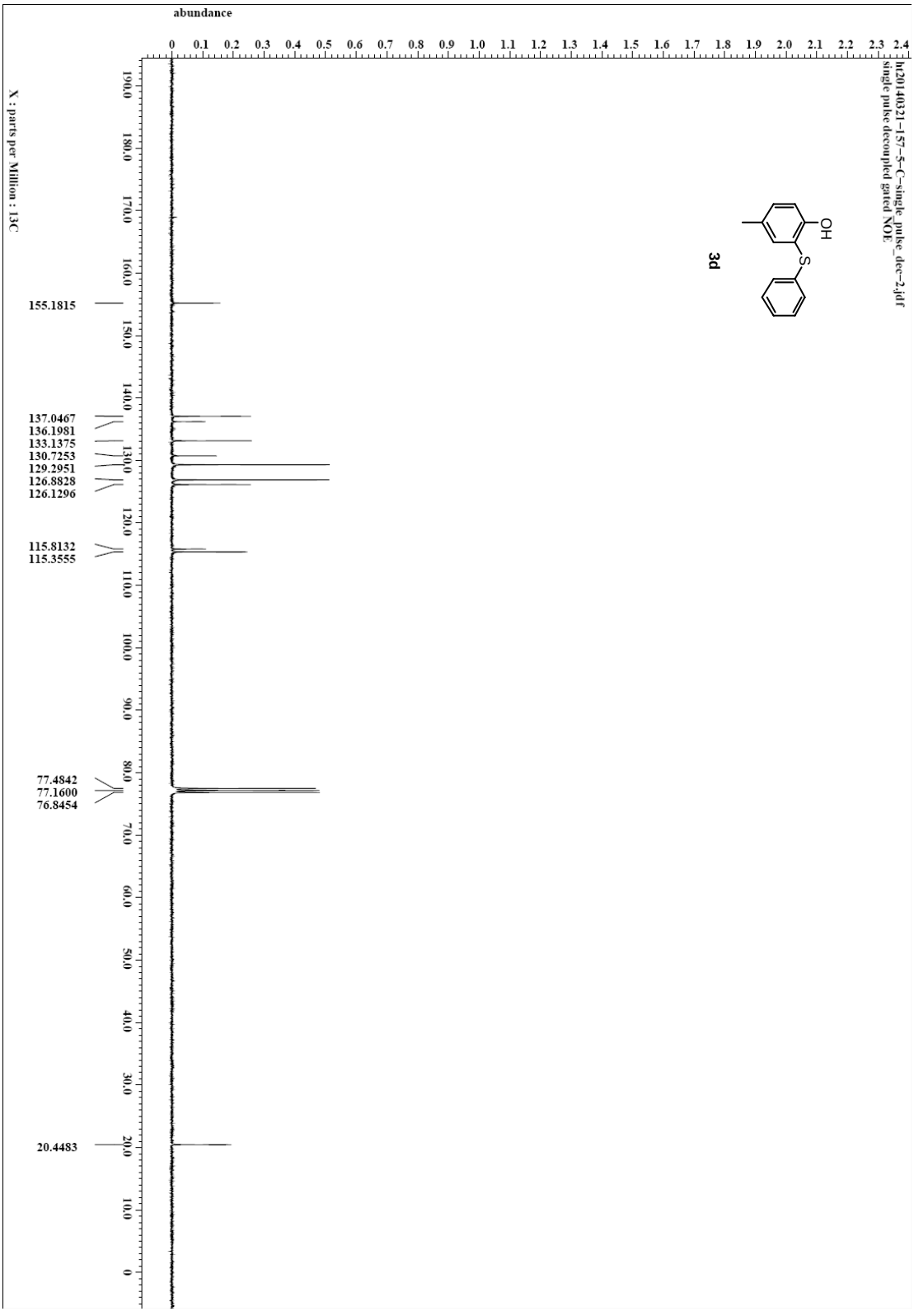
0.95
3
3b
S
OH

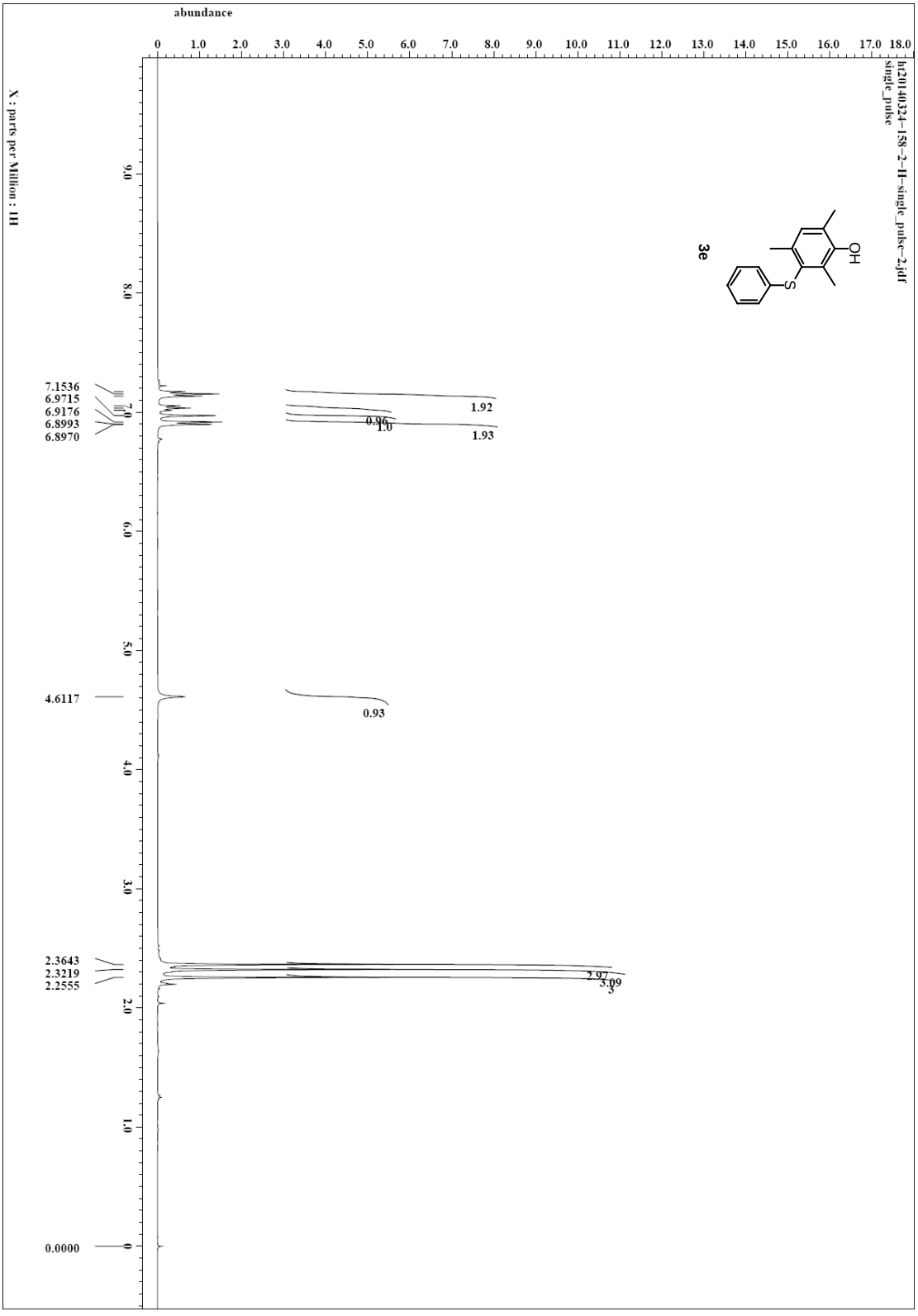

abundance
X : parts per Million : 13C
154.2852
138.7248
136.8655
133.1852
129.0186
128.1795
125.8150
125.4240
124.0606
116.0706
77.4842
77.1600
76.8454
15.7954
3b
OH
S
nt20140321-157-4-C--single_pulse_dec-2.jdf
single pulse decoupled gated NOE

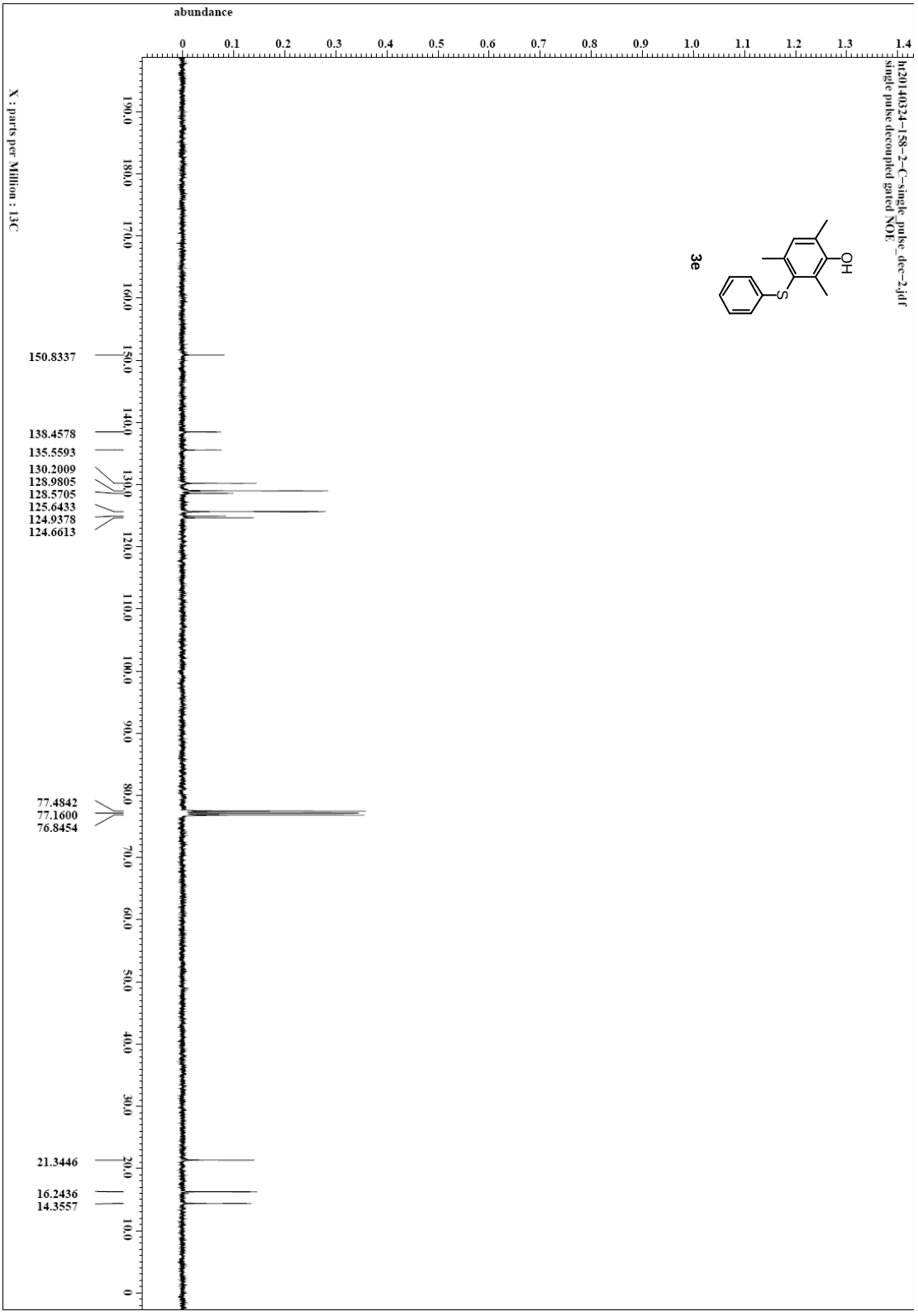

abundance
0
10.0
20.0
30.0
hr20140324-158-1-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3815
7.3609
7.1948
7.1754
7.0459
7.0436
7.0253
6.7790
6.7721
5.4938
2.3036
−0.0000
1.04
2.08
1.09
2.05
1.01
1.1
0.99
3
3c
S
OH

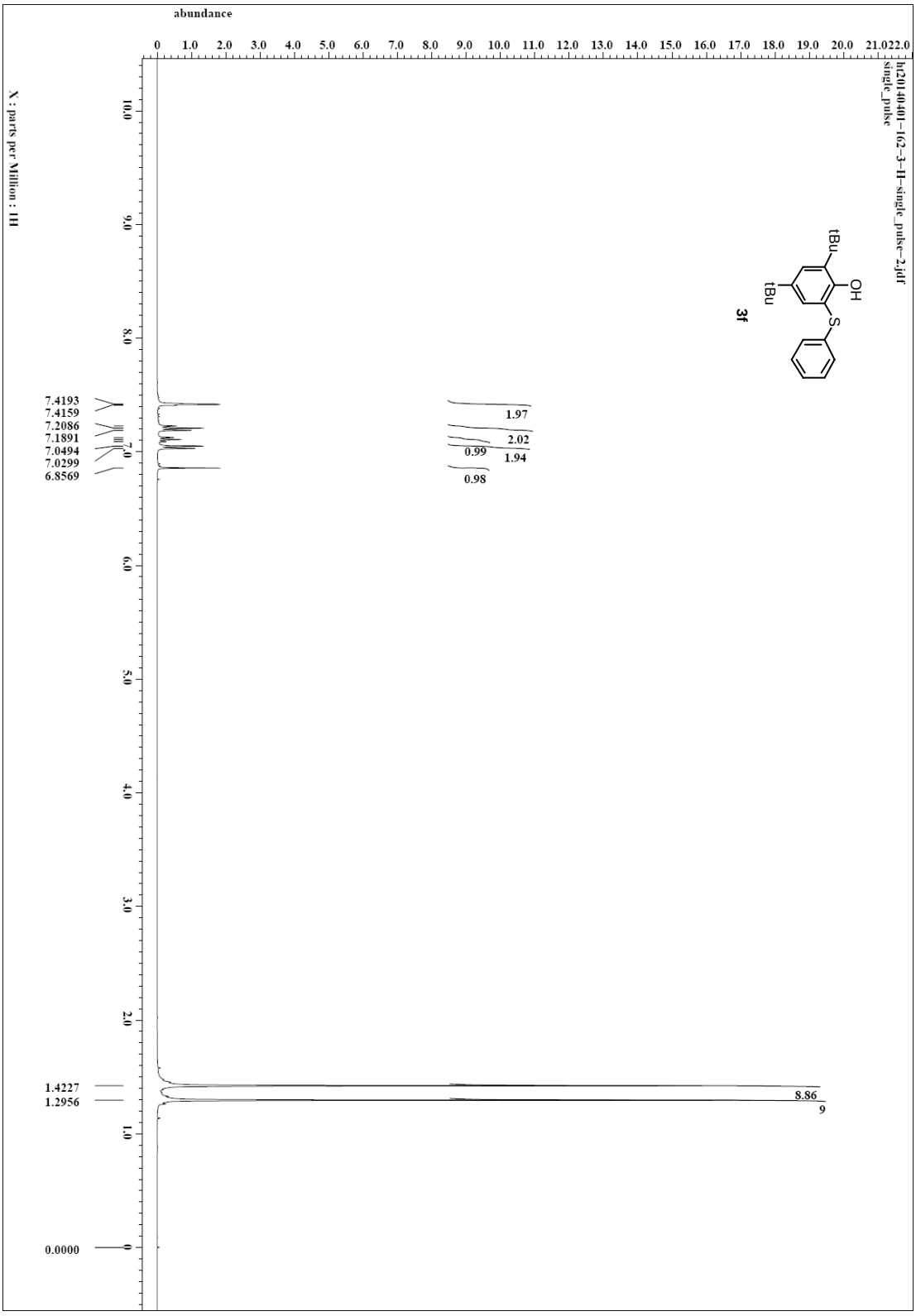

abundance
X : parts per Million : 13C
hz20140324-158-1-C--single_pulse_dec-2.jdf
single pulse decoupled gated NOE
3c
OH
S
156.3924
144.2453
138.3625
137.6188
129.0377
127.0545
125.3668
122.9927
117.9013
114.0684
77.4746
77.1600
76.8358
21.0109

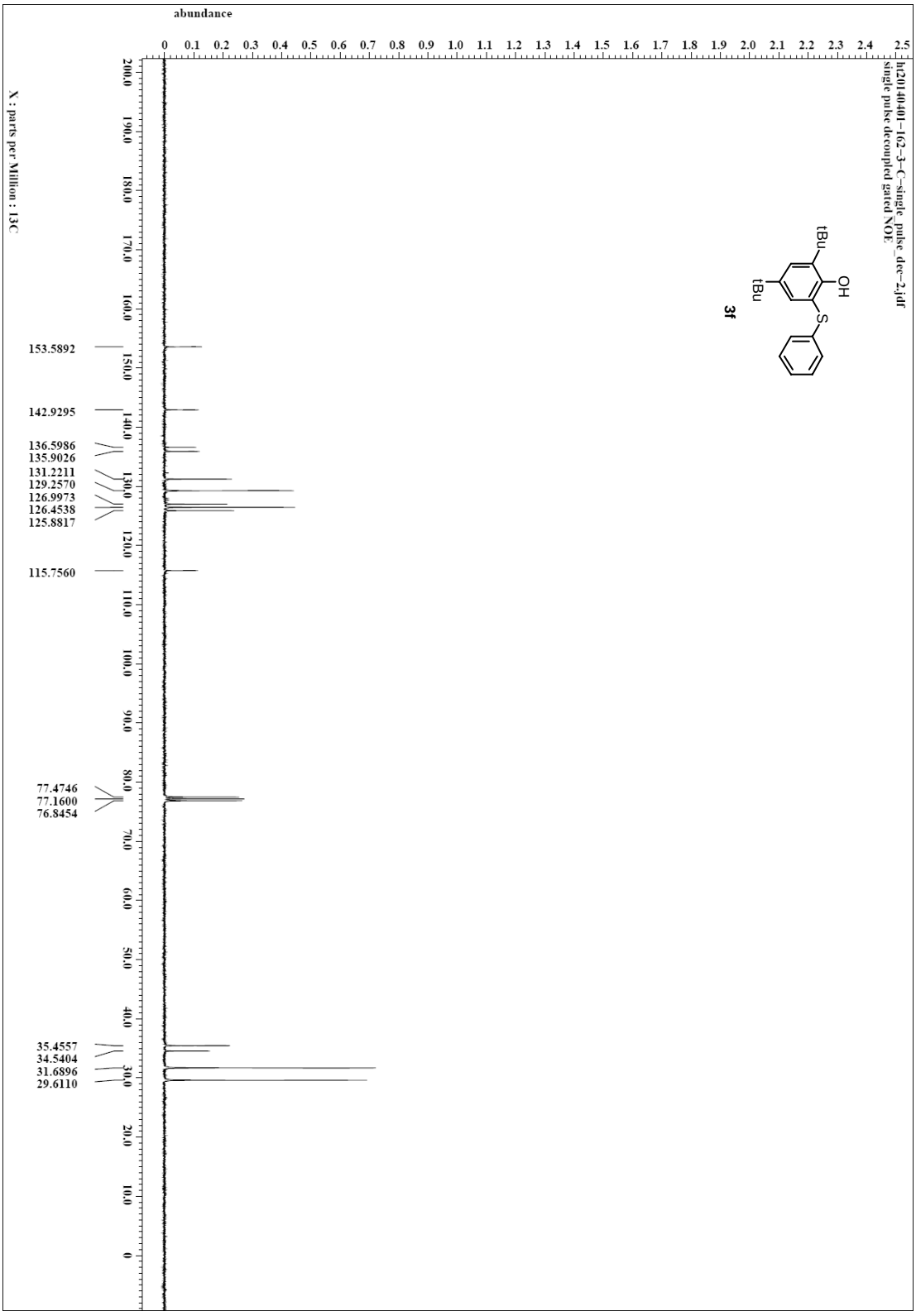

abundance
0
10.0
20.0
30.0
hz20140321-157-5-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3208
7.2143
7.1948
7.0780
7.0585
6.9715
6.3380
2.2681
0.0000
0.94
2.16
2.16
1.96
0.99
0.91
3
OH
S
3d

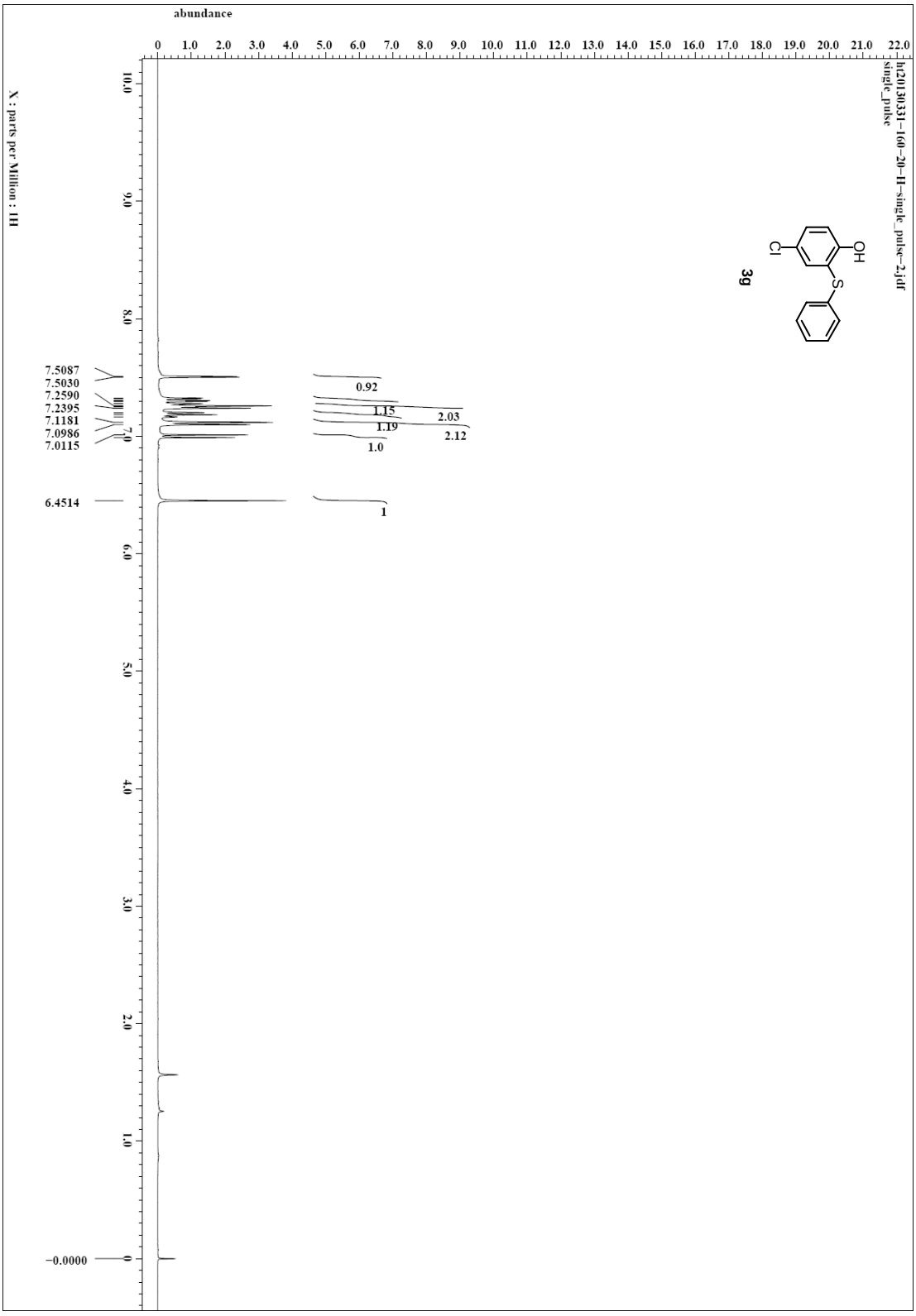

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4
hr20140321-157-5-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
155.1815
137.0467
136.1981
133.1375
130.7253
129.2951
126.8828
126.1296
115.8132
115.3555
77.4842
77.1600
76.8454
20.4483
OH
S
3d

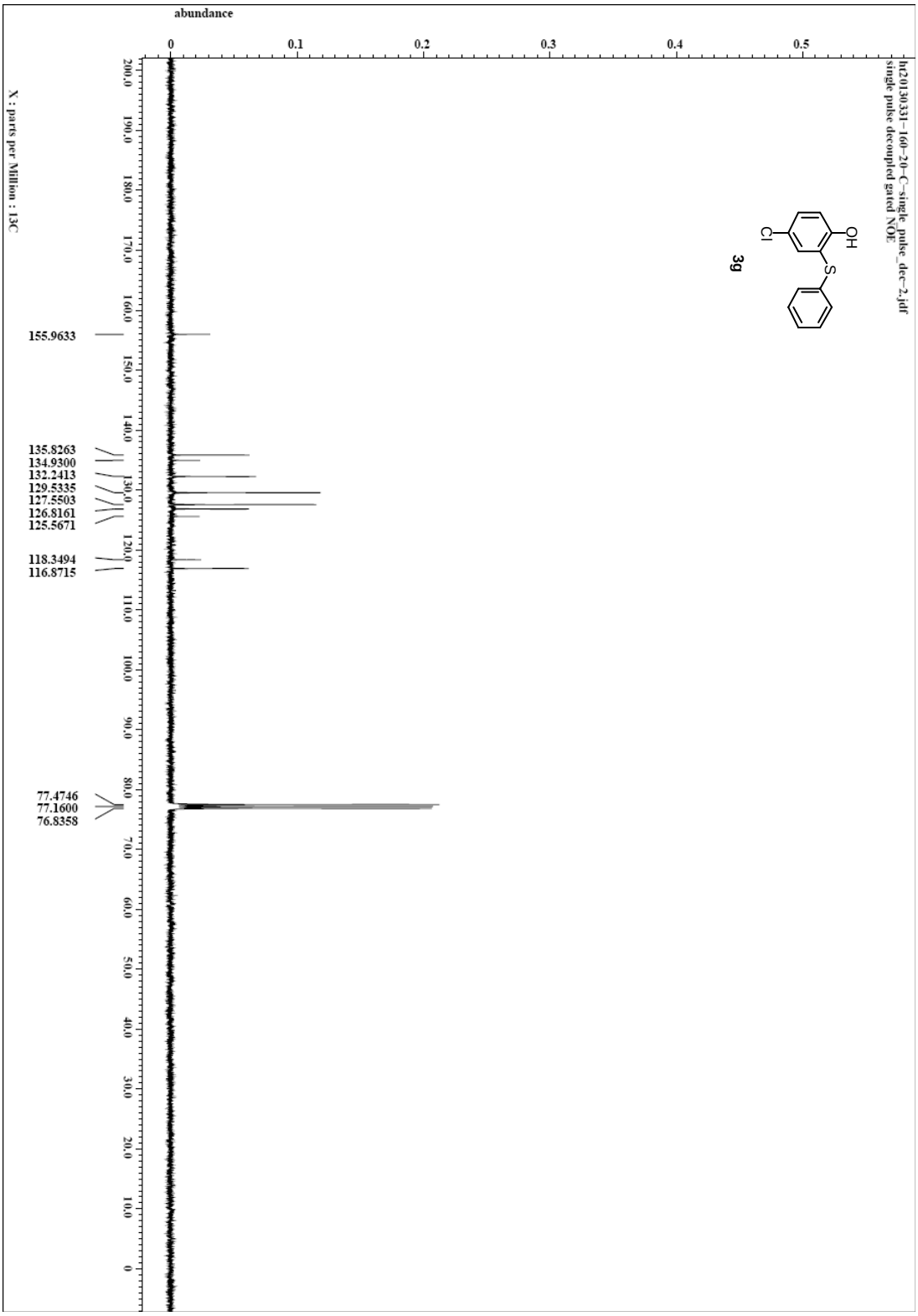

abundance
X : parts per Million : 1H
hz20140324-158-2-1H-single_pulse-2.jdf
single_pulse
3e
OH
S
7.1536
6.9715
6.9176
6.8993
6.8970
4.6117
2.3643
2.3219
2.2555
0.0000
1.92
0.96
1.0
1.93
0.93
2.97
3.09
3

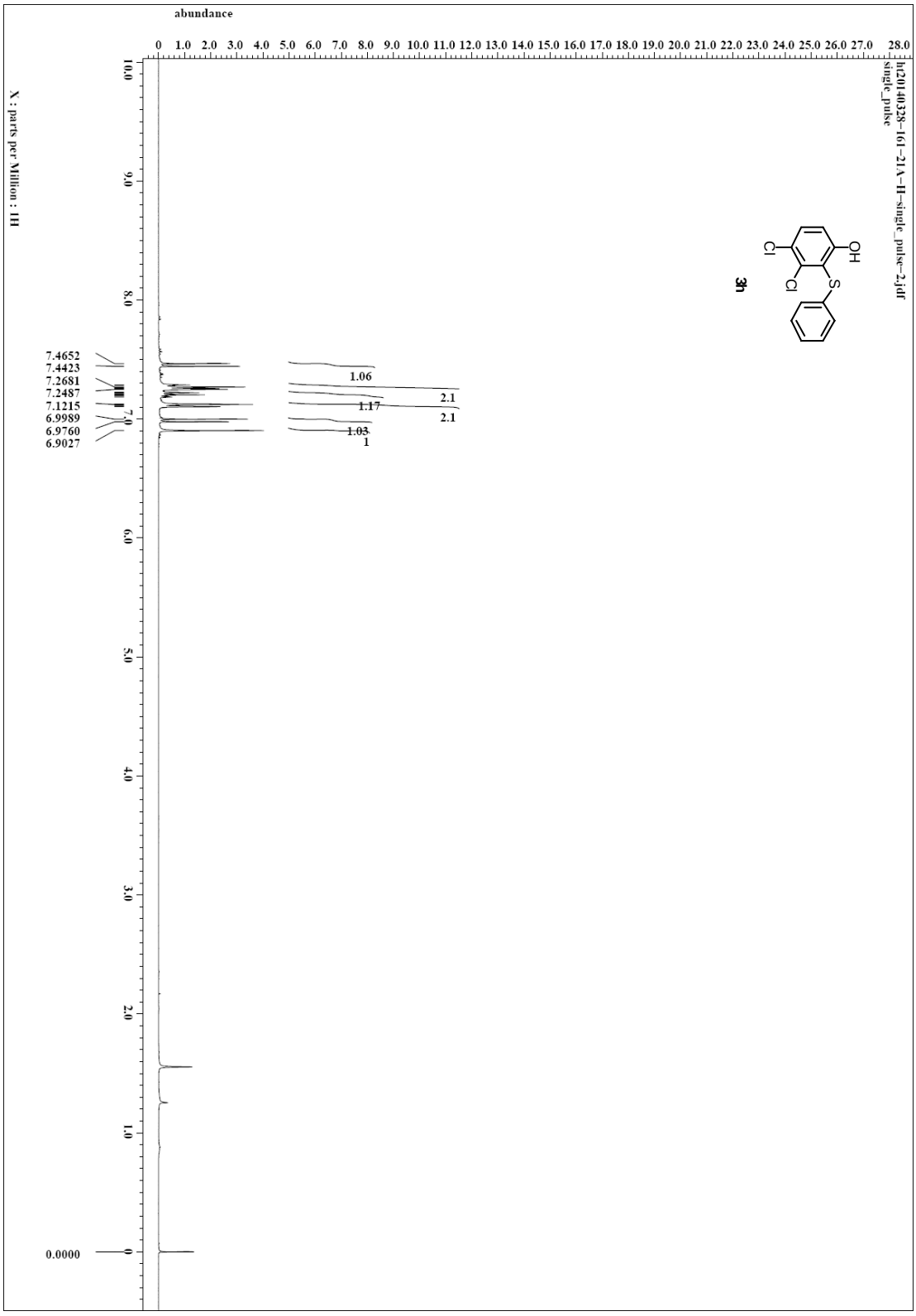

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
h20140324-158-2-C-single_pulse_dec-2.jdf
Single pulse decoupled gated NOE
X : parts per Million : 13C
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.8337
138.4578
135.5593
130.2009
128.9805
128.5705
125.6433
124.9378
124.6613
77.4842
77.1600
76.8454
21.3446
16.2436
14.3557
3e
OH
S

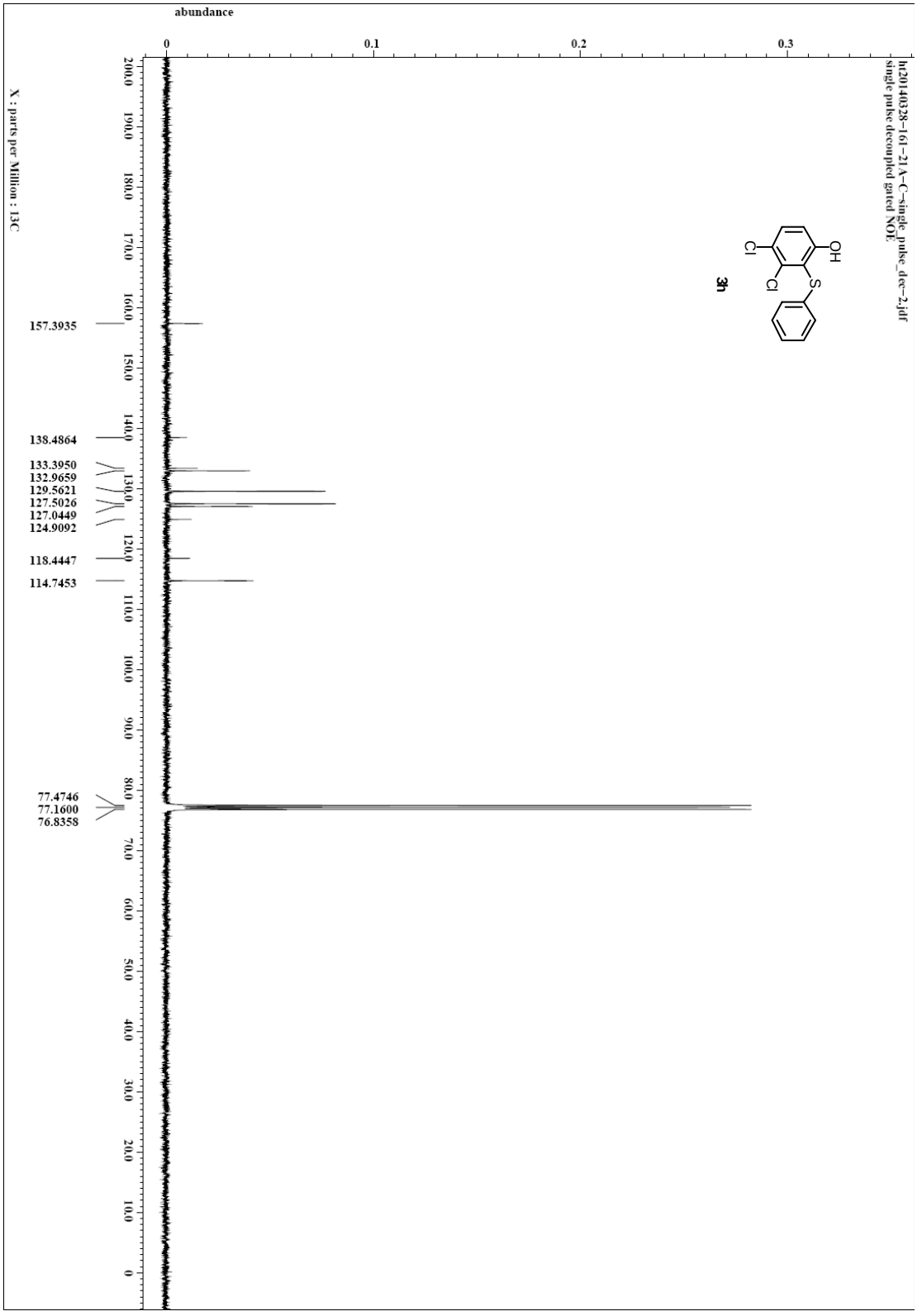

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0
hz20140401-162-3-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.4193
7.4159
7.2086
7.1891
7.0494
7.0299
6.8569
1.97
2.02
0.99
1.94
0.98
1.4227
1.2956
8.86
9
0.0000
tBu
tBu
OH
S
3f

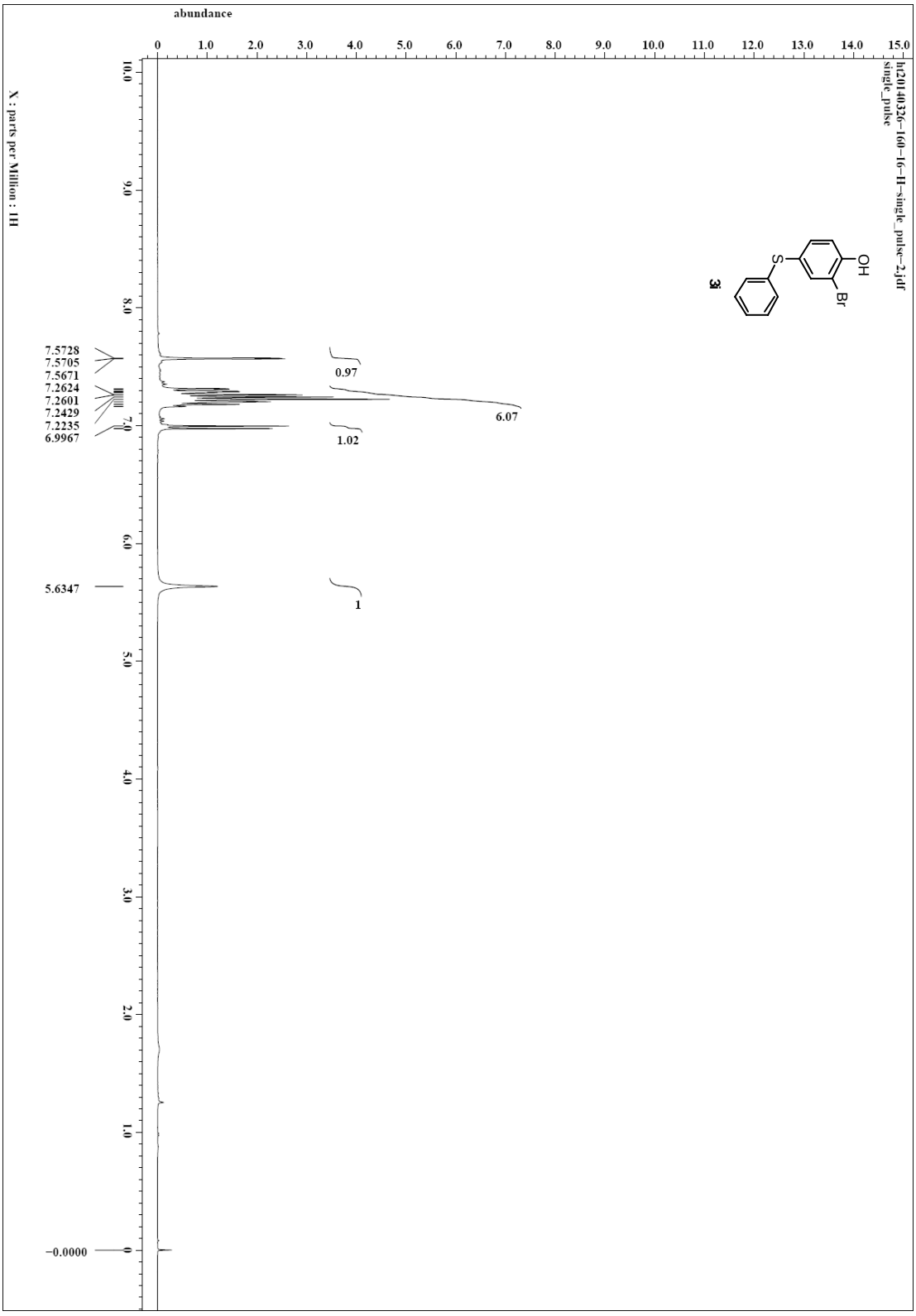

abundance
X : parts per Million : 13C
153.5892
142.9295
136.5986
135.9026
131.2211
129.2570
126.9973
126.4538
125.8817
115.7560
77.4746
77.1600
76.8454
35.4557
34.5404
31.6896
29.6110
tBu
tBu
OH
S
3f

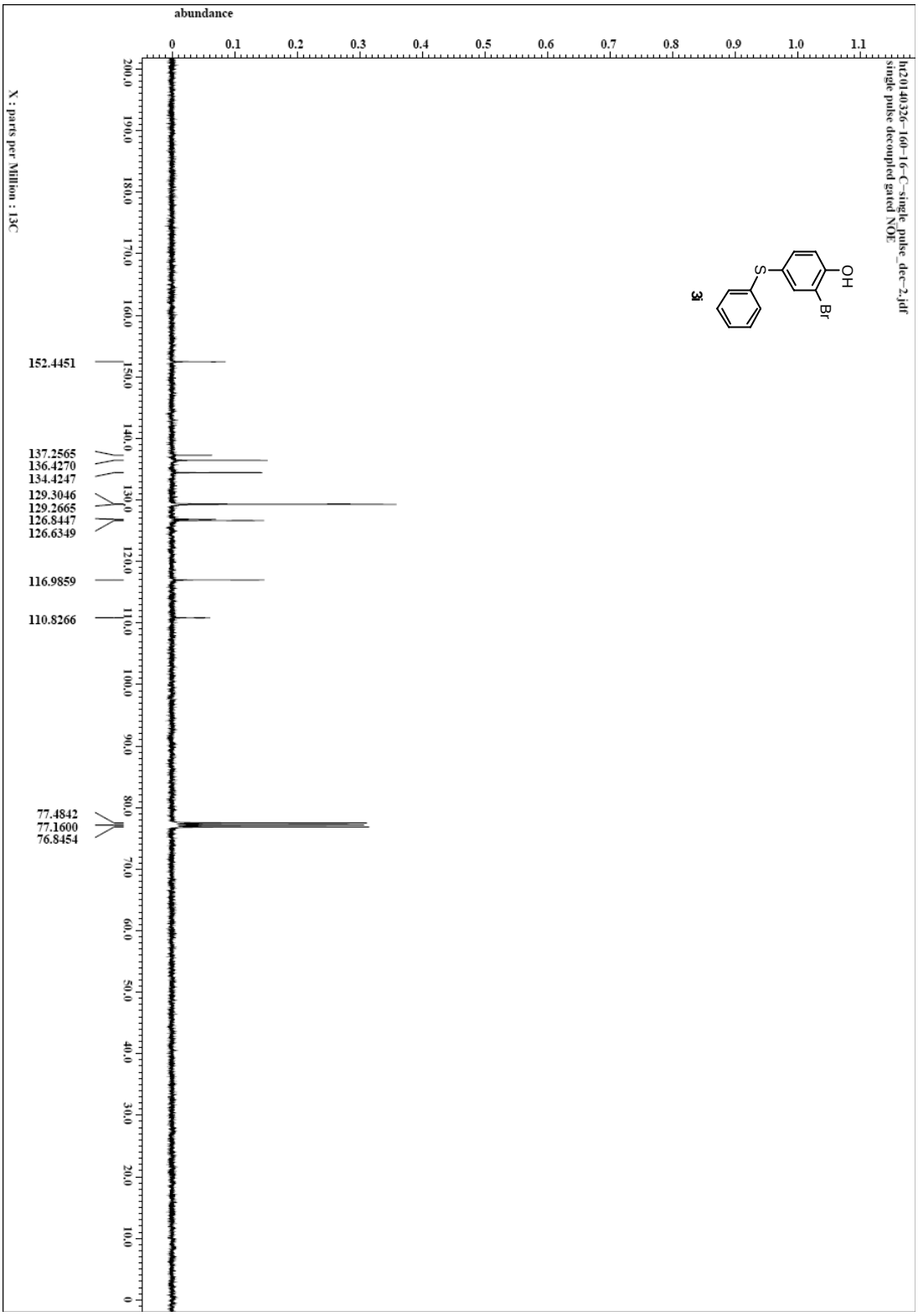

abundance
X : parts per Million : 1H
hr20130331-160-20-1H-single_pulse-2.jdf
single_pulse
3g
Cl
OH
S
7.5087
7.5030
7.2590
7.2395
7.1181
7.0986
7.0115
6.4514
−0.0000
0.92
1.15
2.03
1.19
2.12
1.0
1

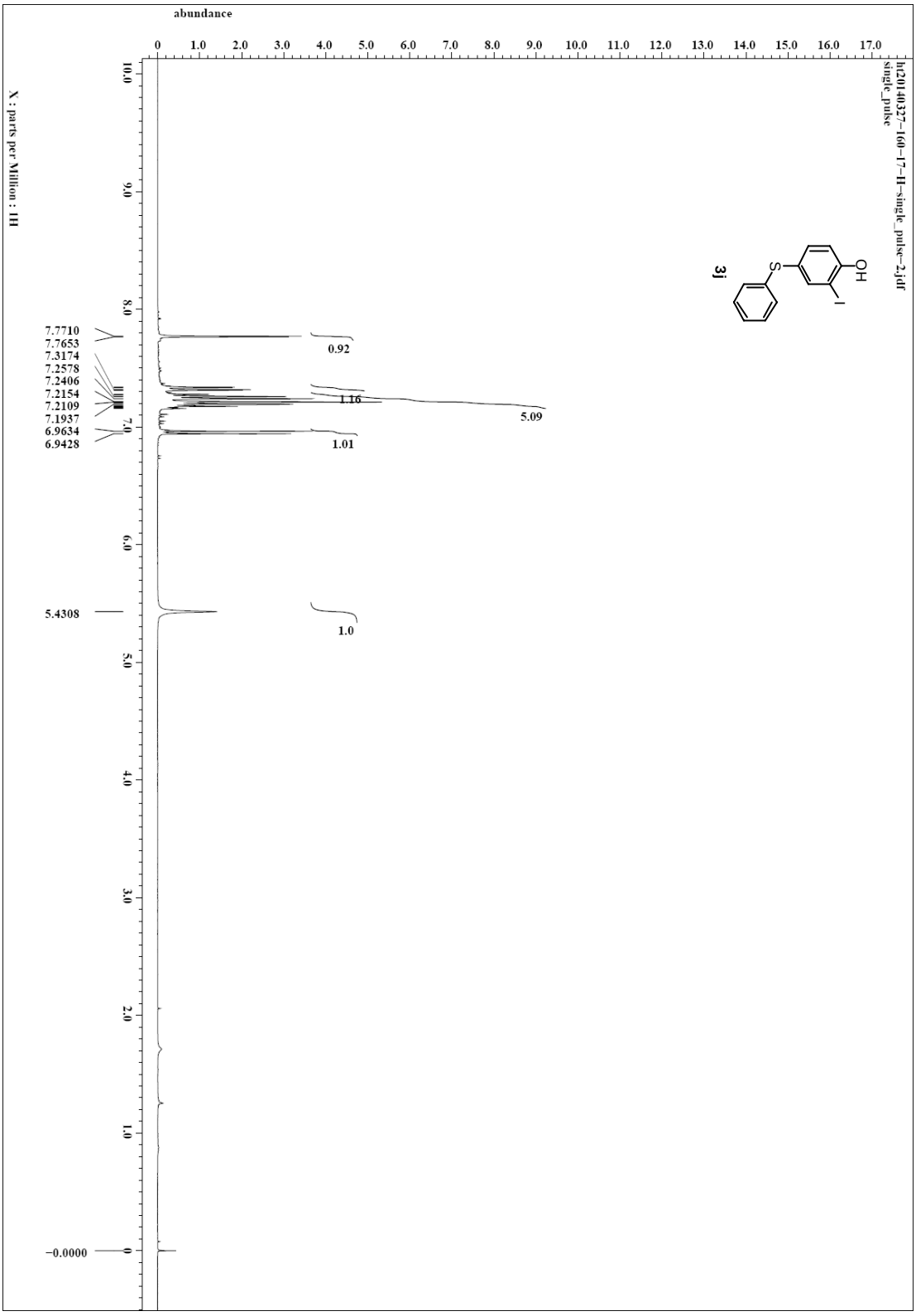

abundance
0
0.1
0.2
0.3
0.4
0.5
hz20130331--160-20--C--single_pulse_dec--2.idf
single pulse decoupled gated NOE
X : parts per Million : 13C
155.9633
135.8263
134.9300
132.2413
129.5335
127.5503
126.8161
125.5671
118.3494
116.8715
77.4746
77.1600
76.8358
Cl
OH
S
3g

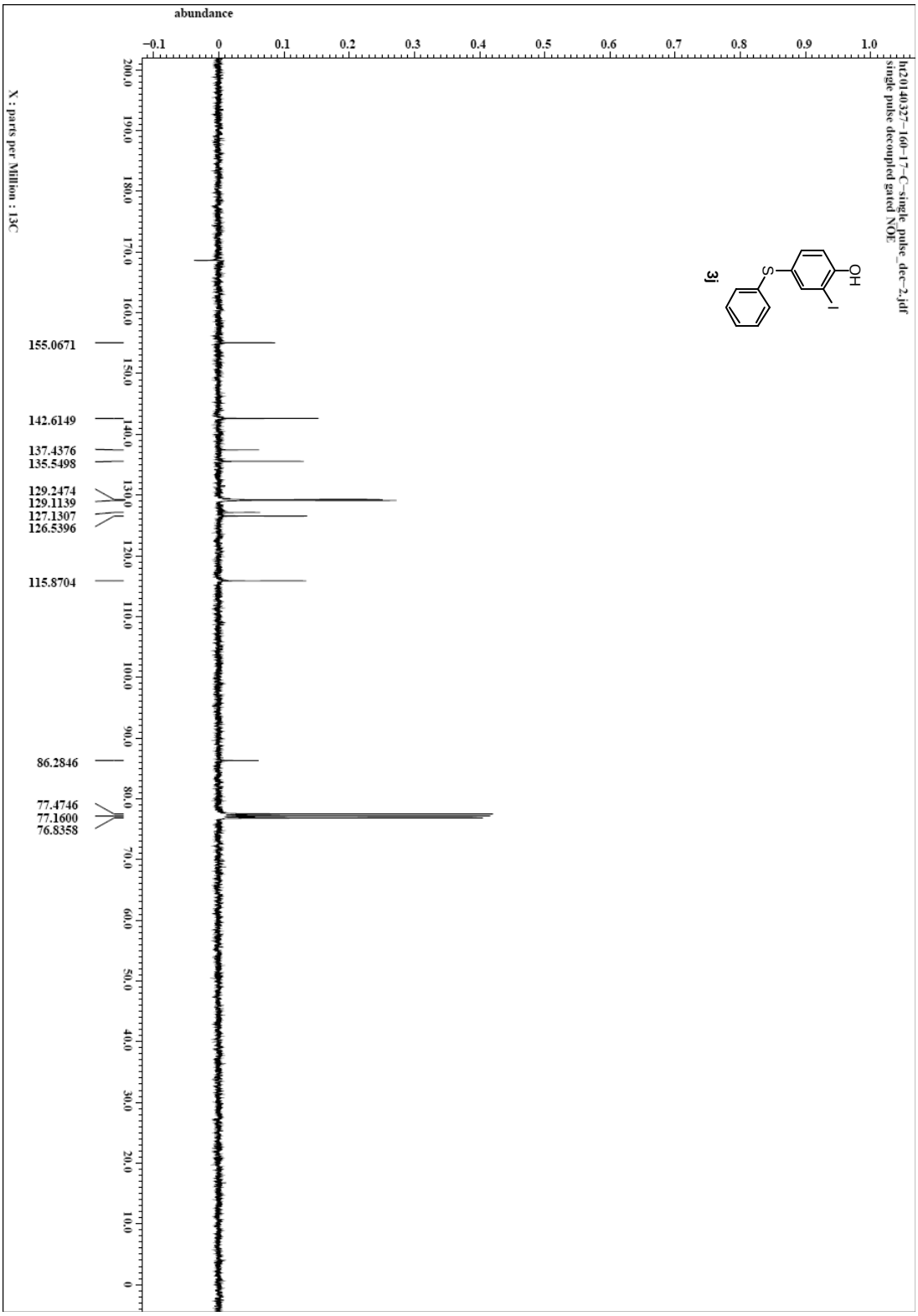

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0
hi20140328-161-21A-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
7.4652
7.4423
7.2681
7.2487
7.1215
6.9989
6.9760
6.9027
0.0000
1.06
2.1
1.17
2.1
1.03
1
3h
Cl
Cl
OH
S

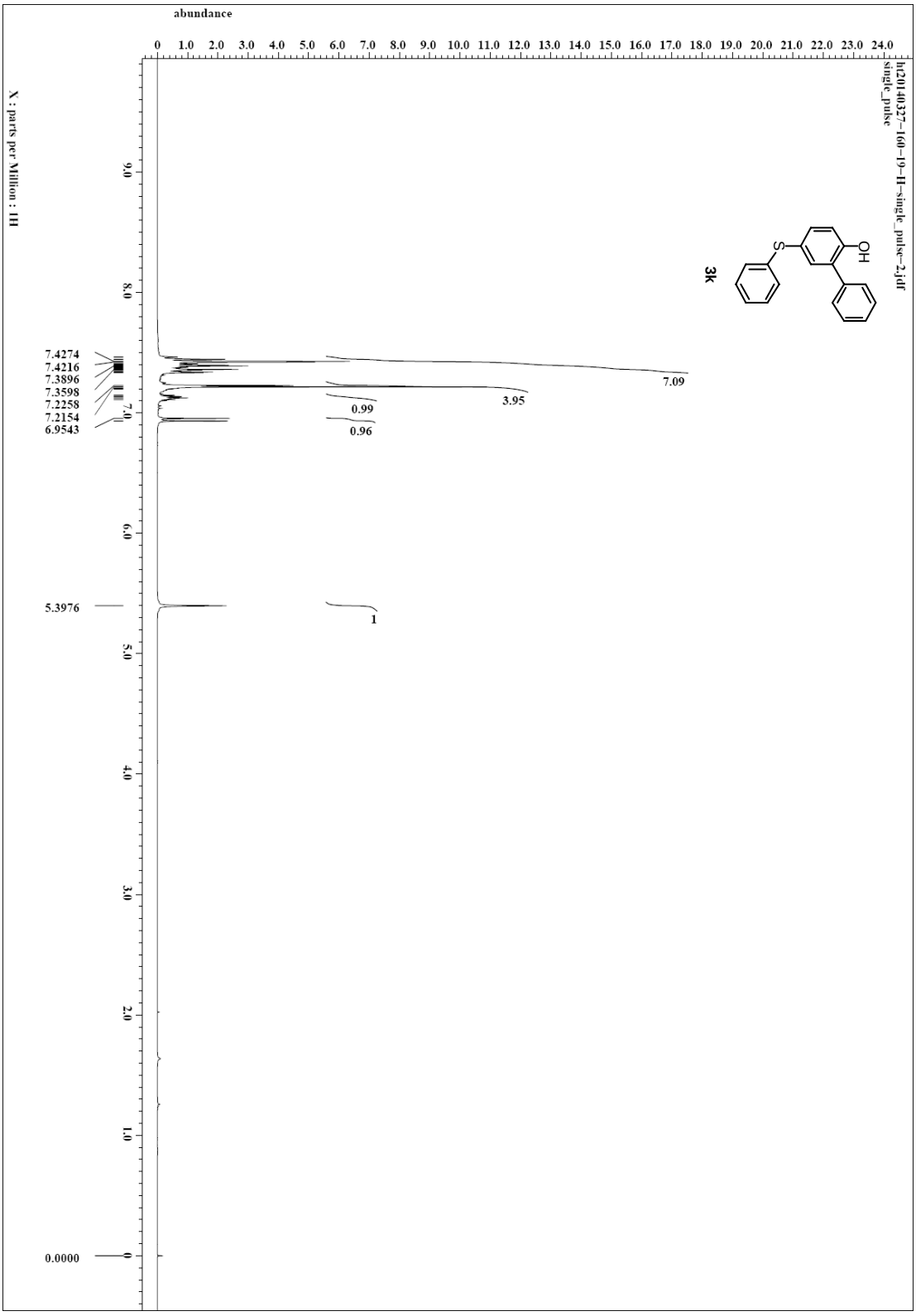

abundance
0
0.1
0.2
0.3
hz20140328-161-21A-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
157.3935
138.4864
133.3950
132.9659
129.5621
127.5026
127.0449
124.9092
118.4447
114.7453
77.4746
77.1600
76.8358
OH
Cl
Cl
S
3n

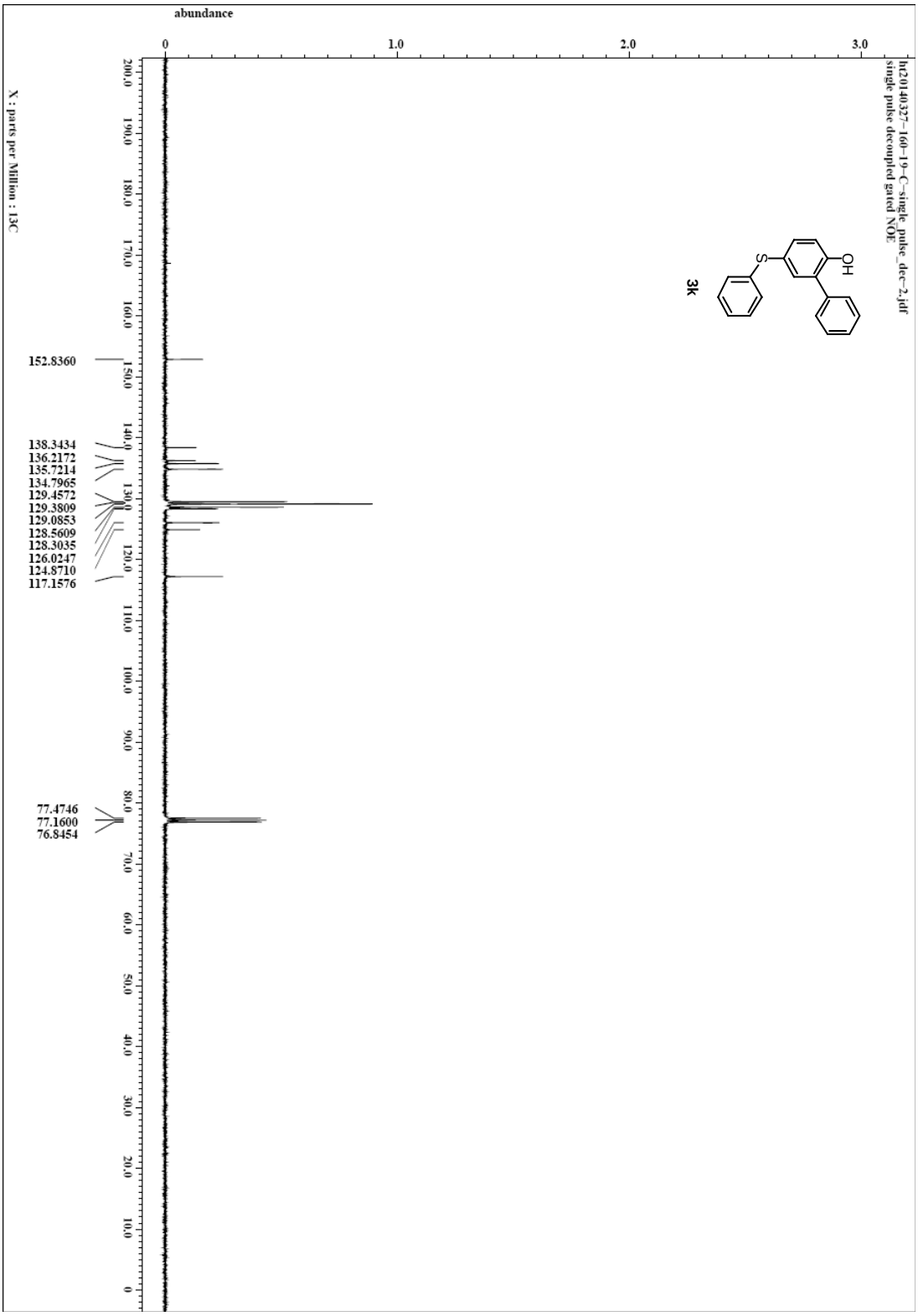

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
h120140326-160-16-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5728
7.5705
7.5671
7.2624
7.2601
7.2429
7.2235
6.9967
5.6347
−0.0000
0.97
6.07
1.02
1
3
S
OH
Br

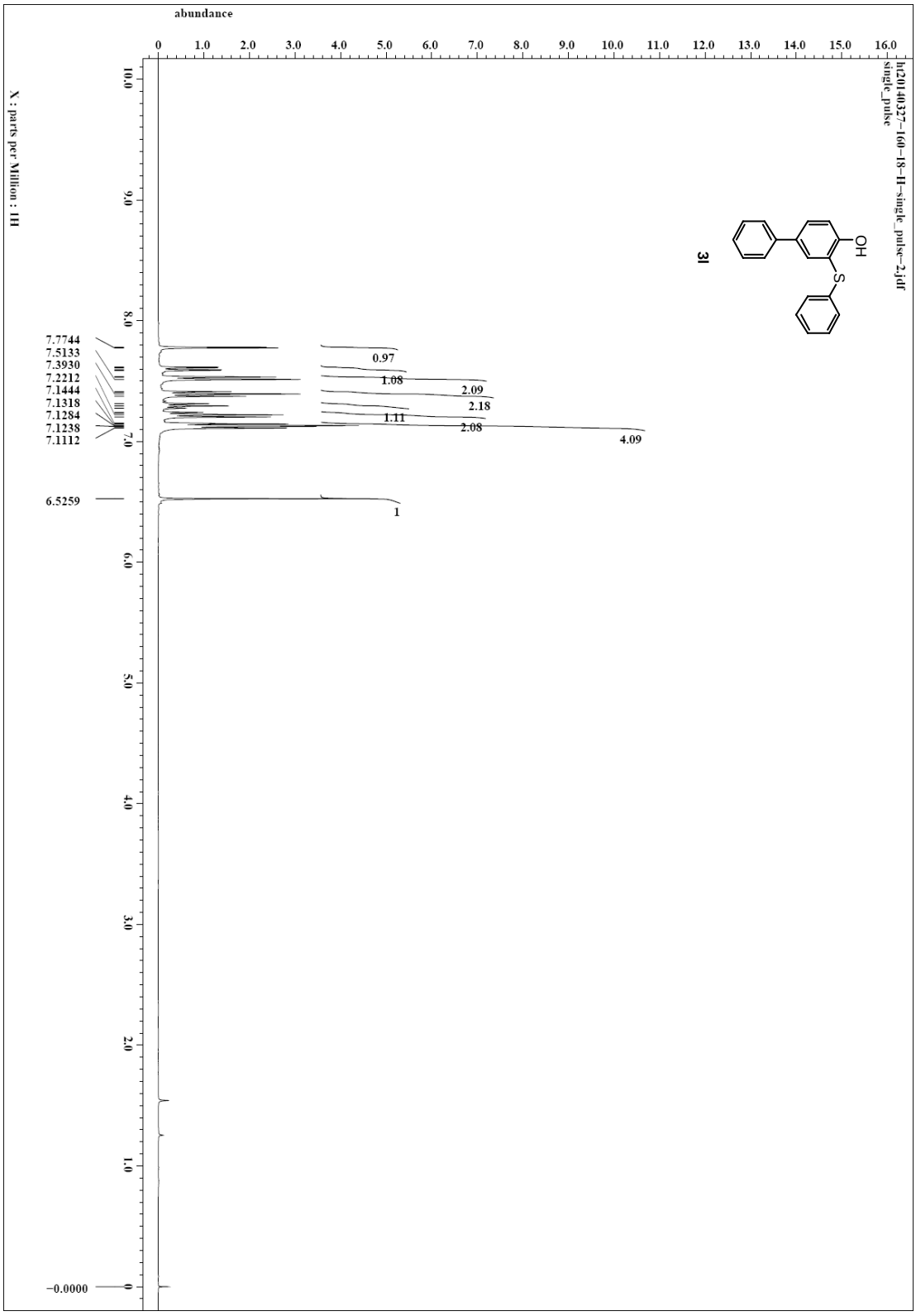

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.4451
137.2565
136.4270
134.4247
129.3046
129.2665
126.8447
126.6349
116.9859
110.8266
77.4842
77.1600
76.8454
OH
S
Br
3l
hz20140326-160-16-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE

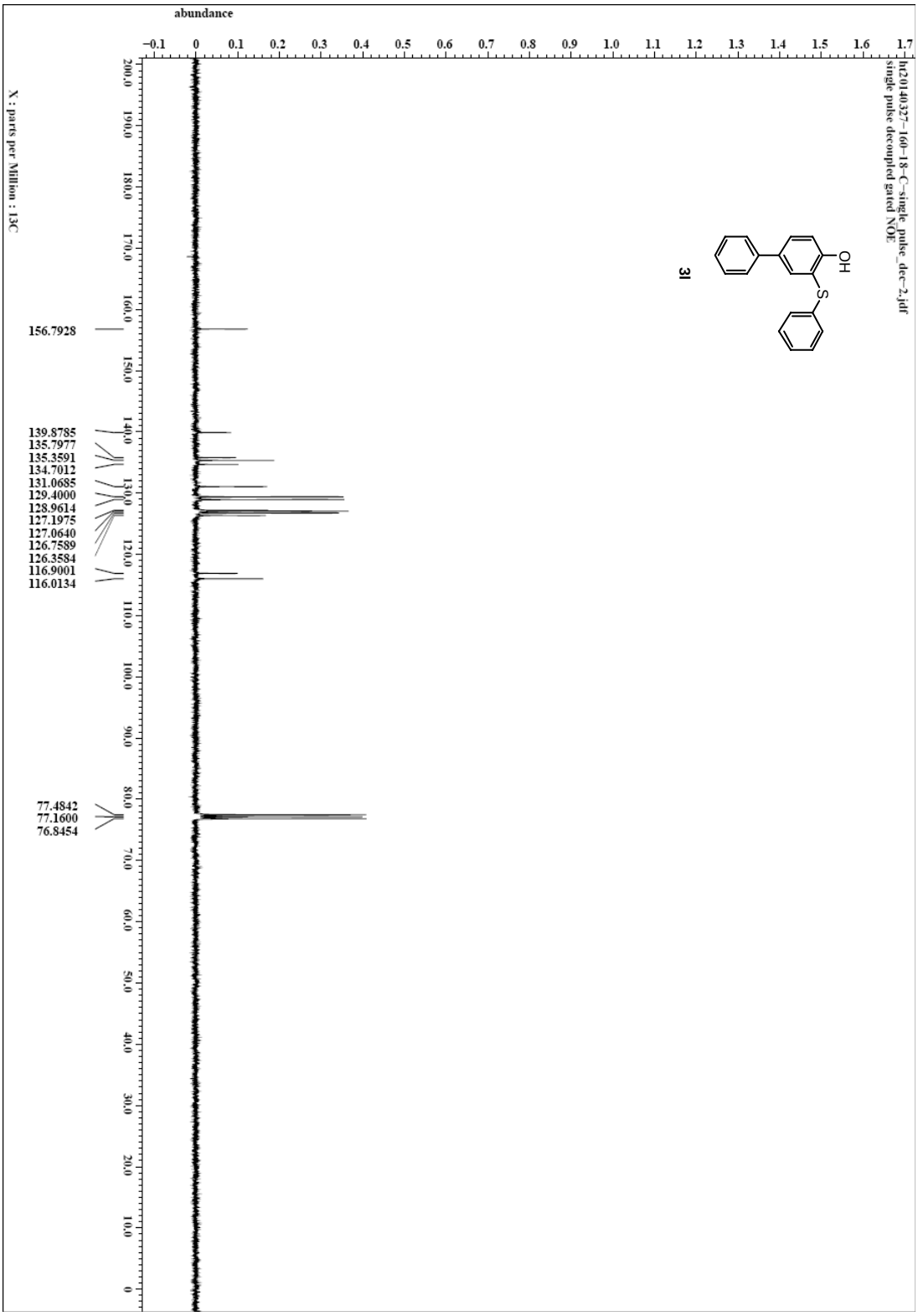

abundance
X : parts per Million : 1H
hr20140327-160-17-1H-single_pulse-2.jdf
single_pulse
3j
7.7710
7.7653
7.3174
7.2578
7.2406
7.2154
7.2109
7.1937
6.9634
6.9428
5.4308
−0.0000
0.92
1.16
5.09
1.01
1.0

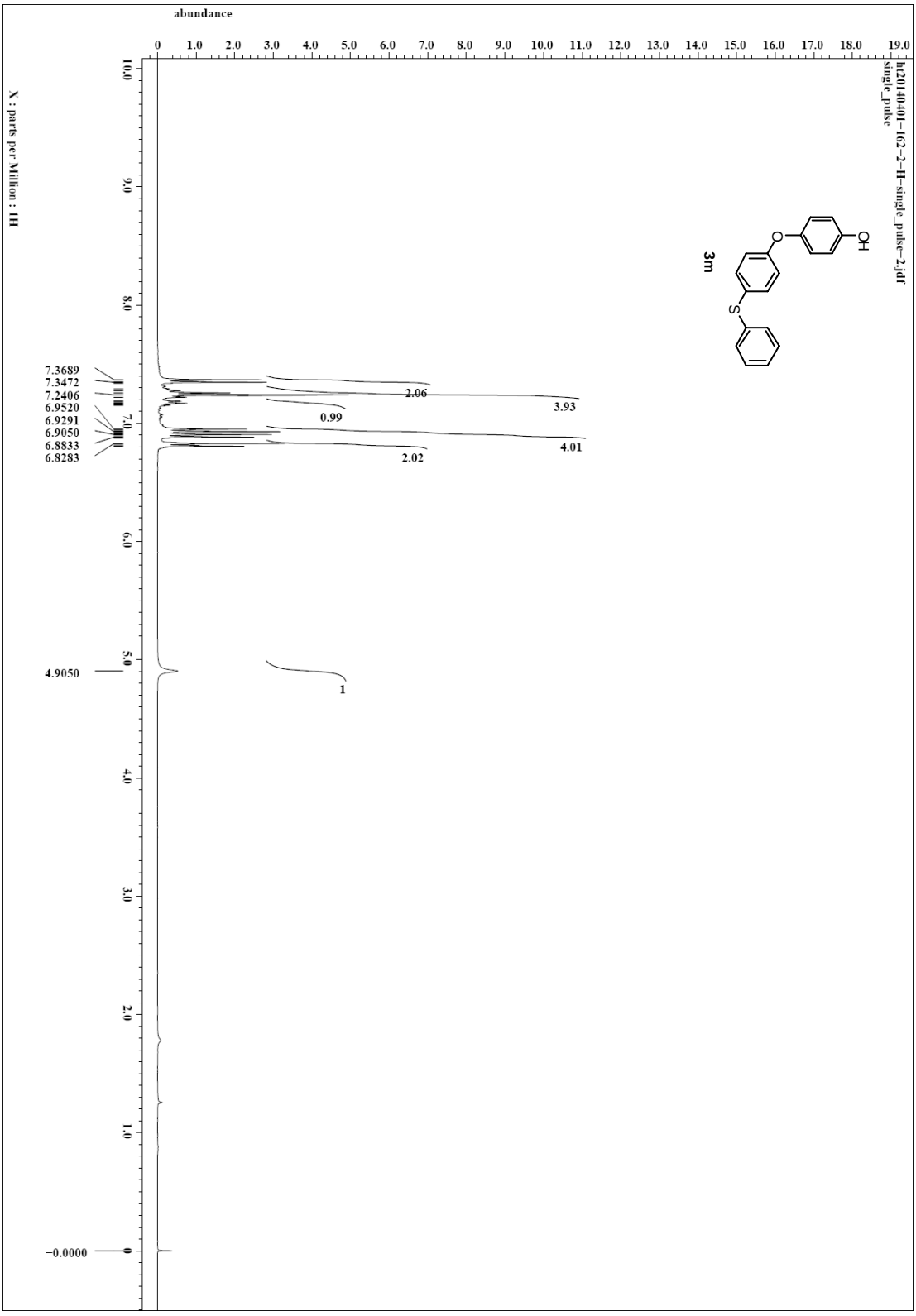

abundance
X : parts per Million : 13C
hz20140327--160--17--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
3j
OH
S
I
155.0671
142.6149
137.4376
135.5498
129.2474
129.1139
127.1307
126.5396
115.8704
86.2846
77.4746
77.1600
76.8358

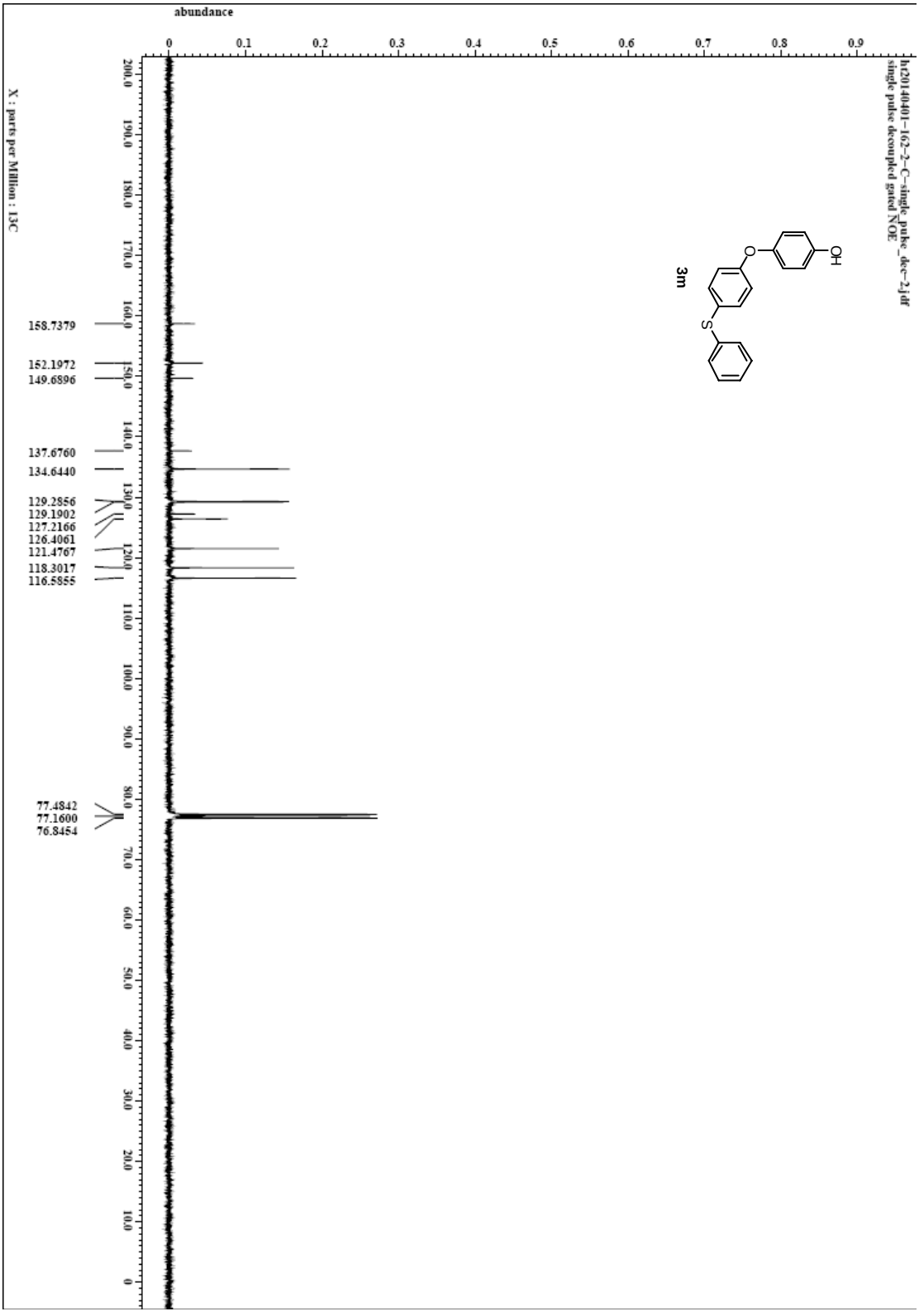

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0
hr20140327-160-19-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
3k
OH
S
7.4274
7.4216
7.3896
7.3598
7.2258
7.2154
6.9543
5.3976
0.0000
7.09
3.95
0.99
0.96
1
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

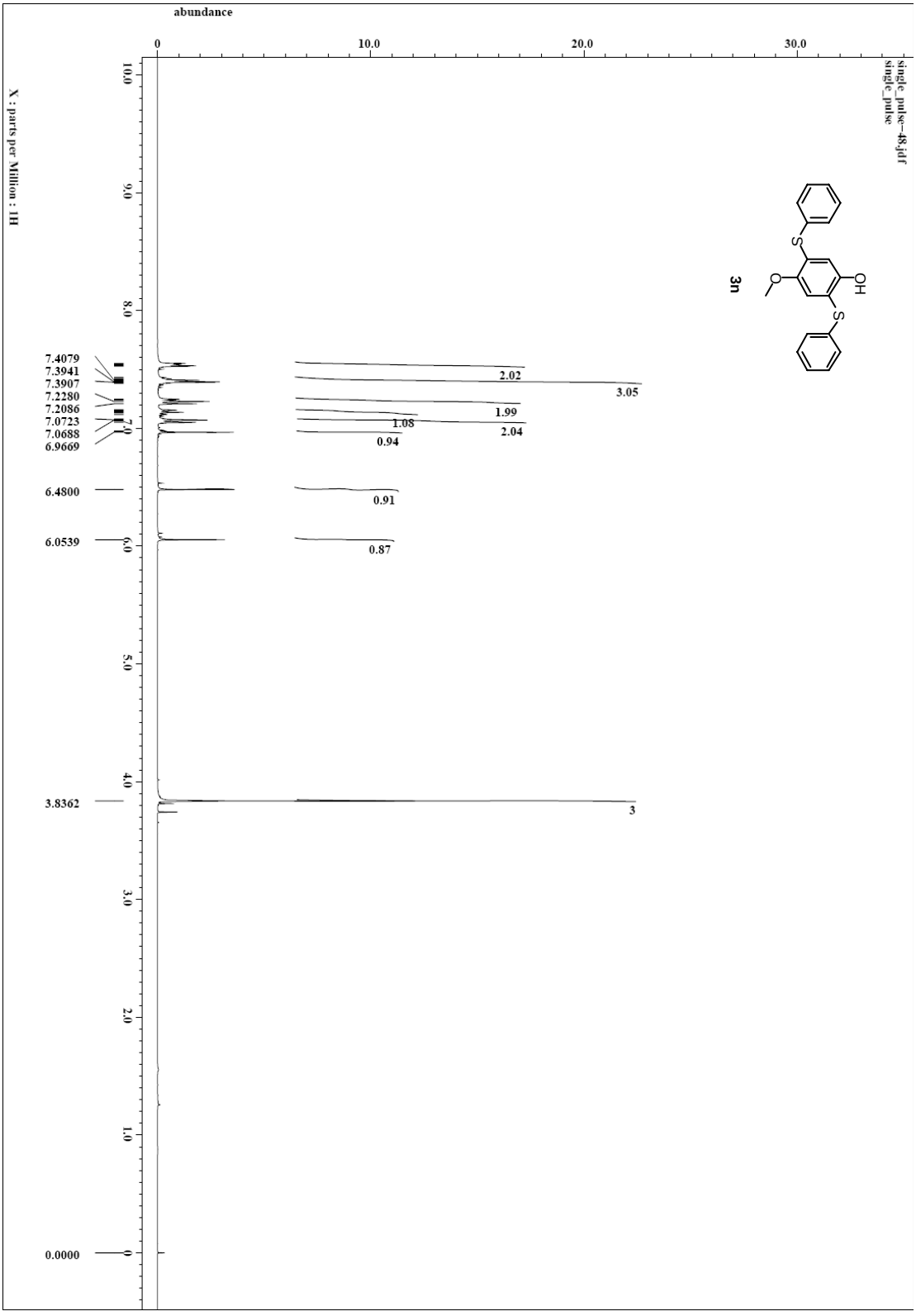

abundance
0
1.0
2.0
3.0
hz20140327--160--19--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.8360
138.3434
136.2172
135.7214
134.7965
129.4572
129.3809
129.0853
128.5609
128.3035
126.0247
124.8710
117.1576
77.4746
77.1600
76.8454
3k
S
OH

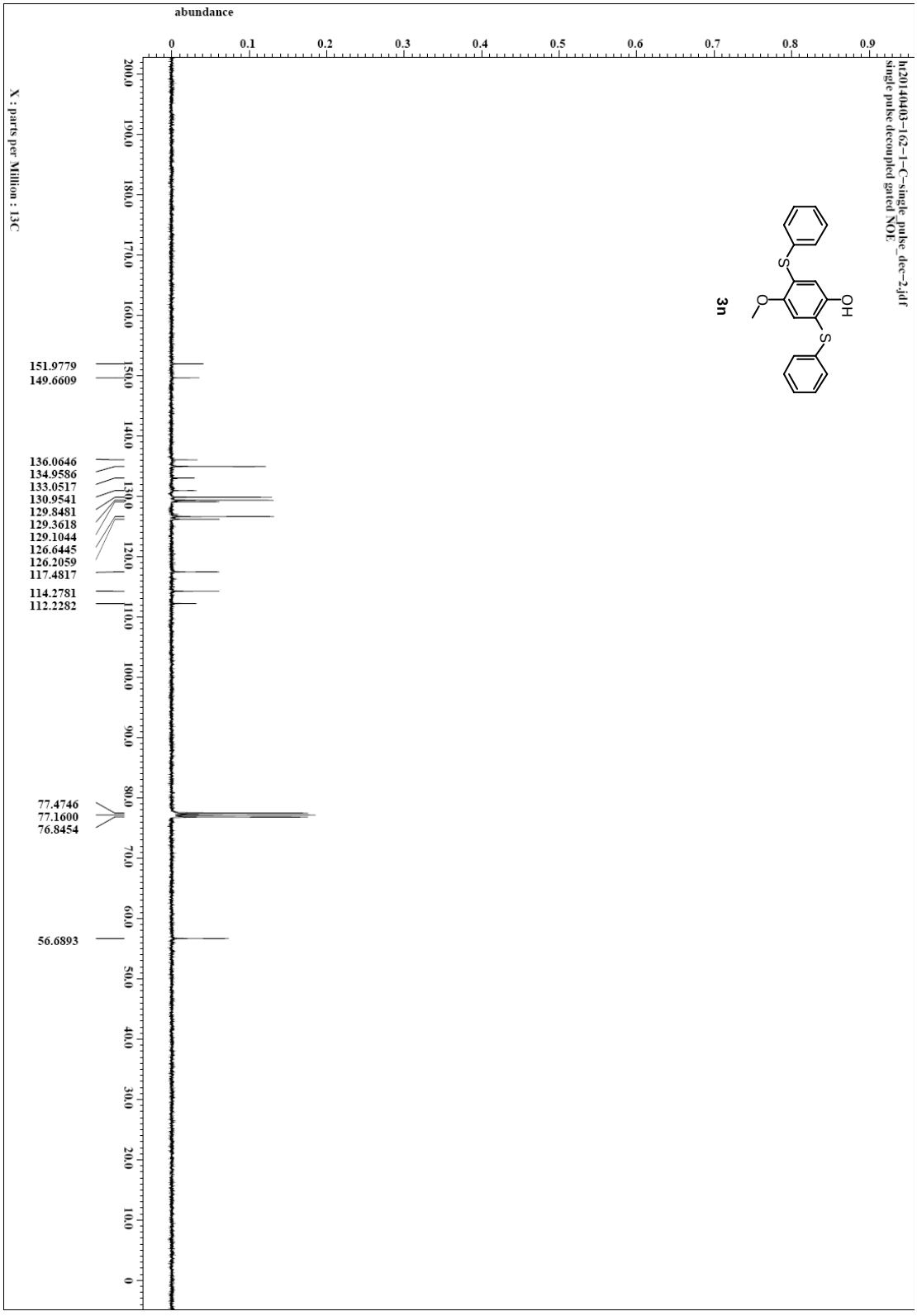

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0
hz20140327-160-18-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −0.0000
7.7744
7.5133
7.3930
7.2212
7.1444
7.1318
7.1284
7.1238
7.1112
6.5259
0.97
1.08
2.09
2.18
1.11
2.08
4.09
1
3l
OH
S

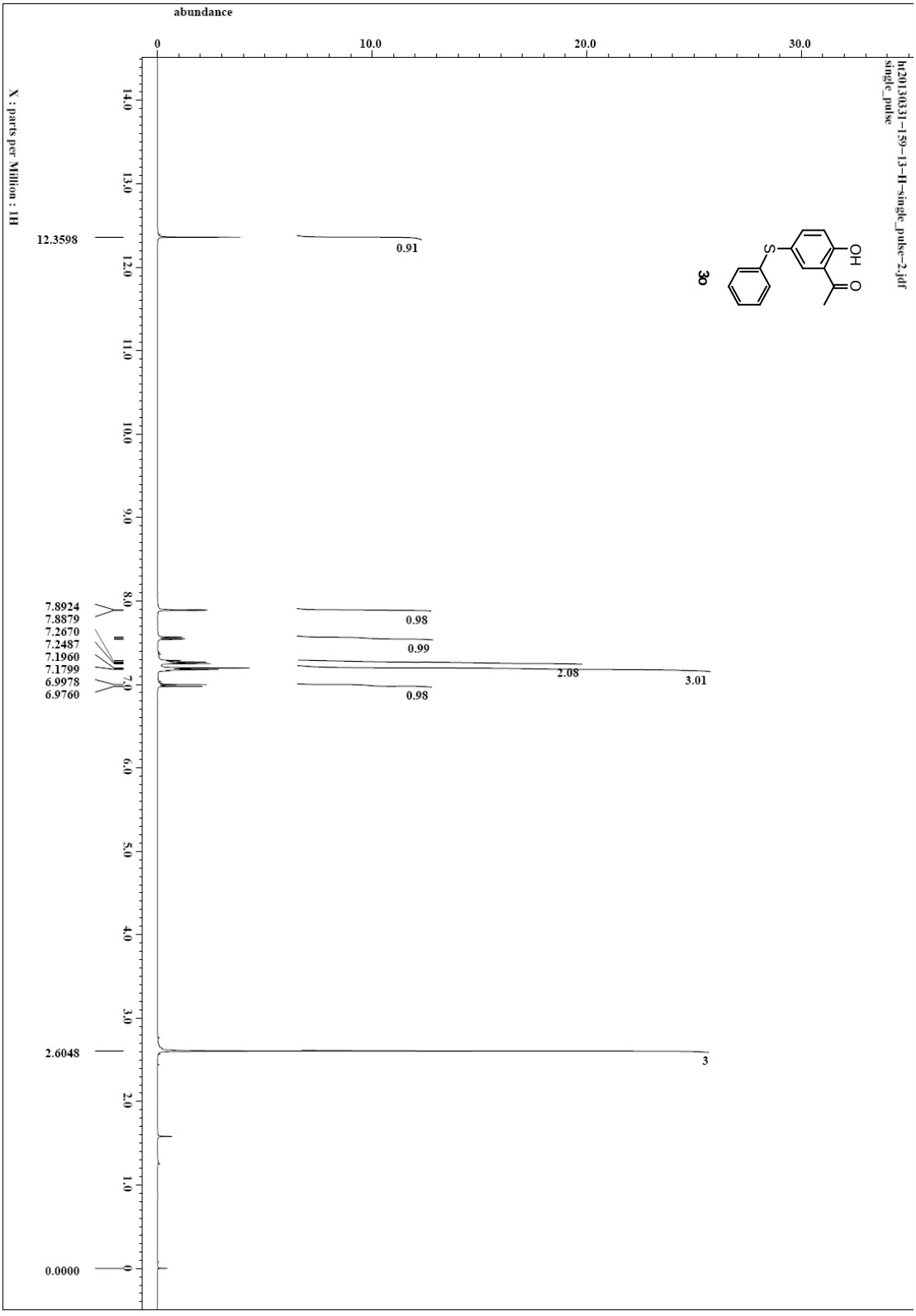

abundance
X : parts per Million : 13C
hz20140327--160--18--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
3l
OH
S
156.7928
139.8785
135.7977
135.3591
134.7012
131.0685
129.4000
128.9614
127.1975
127.0640
126.7589
126.3584
116.9001
116.0134
77.4842
77.1600
76.8454

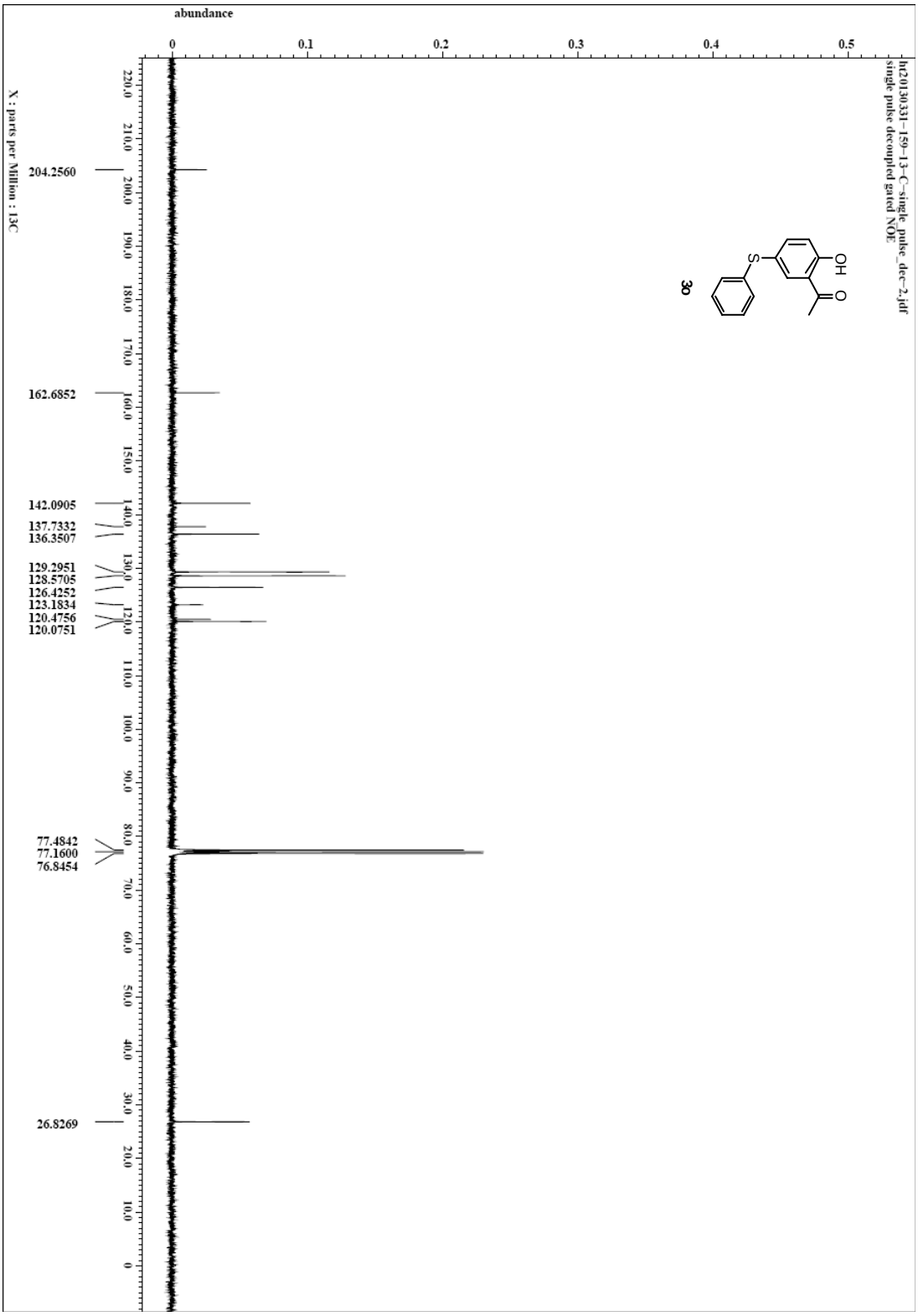

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0
h120140401-162-2-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.3689
7.3472
7.2406
6.9520
6.9291
6.9050
6.8833
6.8283
4.9050
−0.0000
2.06
3.93
0.99
4.01
2.02
1
3m
OH
O
S

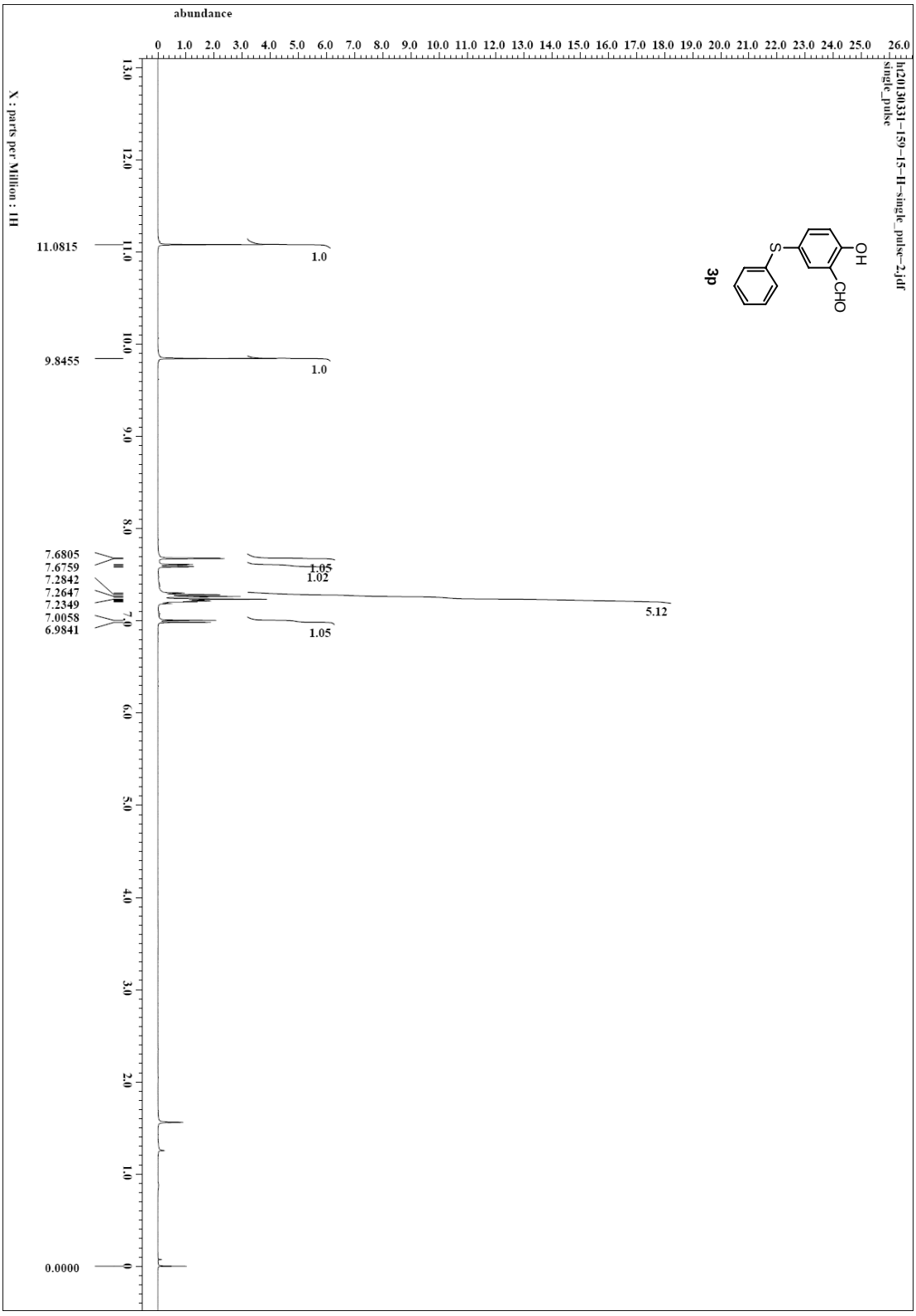

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
hr20140401-162-2-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.7379
152.1972
149.6896
137.6760
134.6440
129.2856
129.1902
127.2166
126.4061
121.4767
118.3017
116.5855
77.4842
77.1600
76.8454
3m
O
OH
S

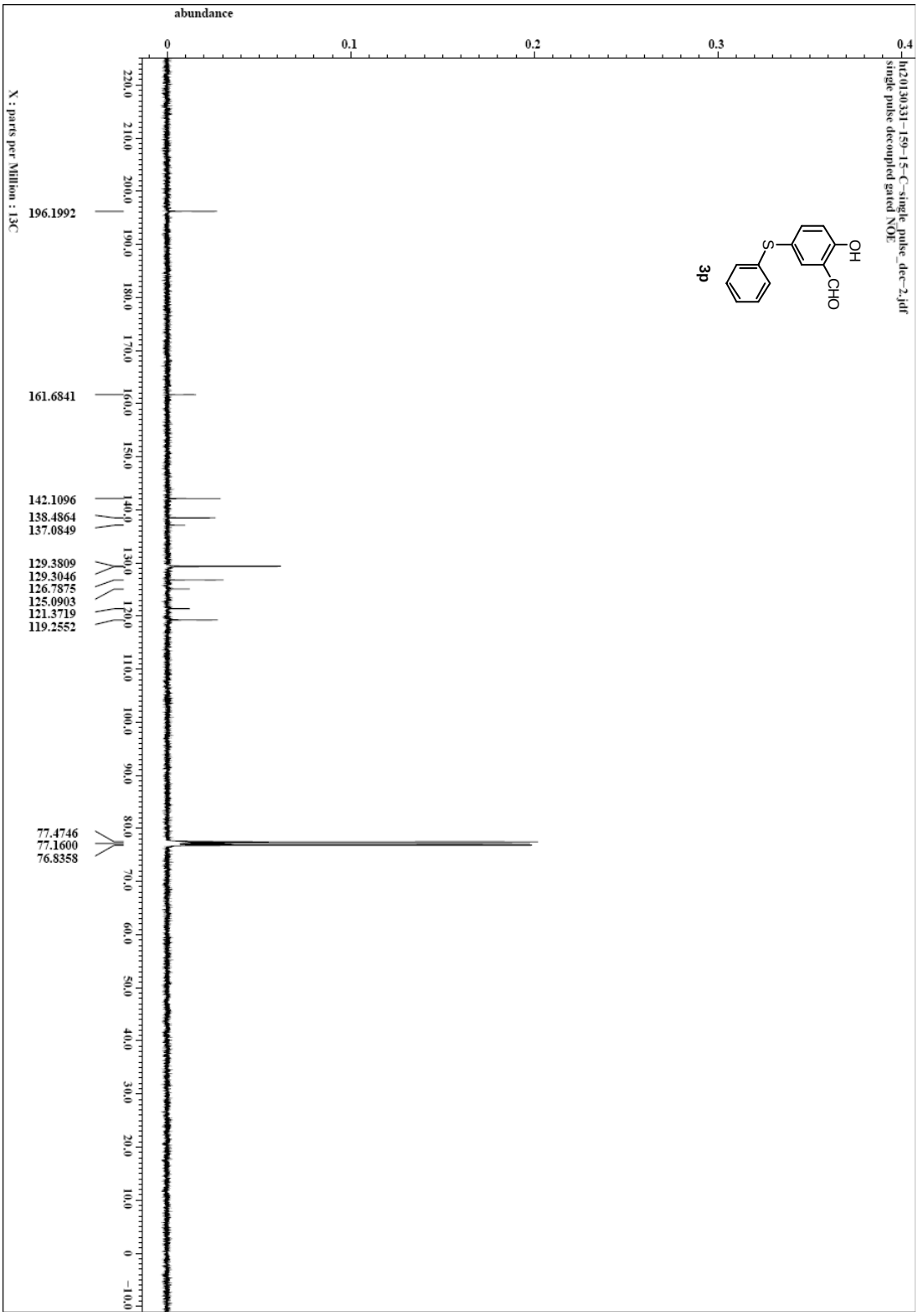

abundance
0
10.0
20.0
30.0
single_pulse~48.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.4079
7.3941
7.3907
7.2280
7.2086
7.0723
7.0688
6.9669
6.4800
6.0539
3.8362
0.0000
2.02
3.05
1.99
1.08
2.04
0.94
0.91
0.87
3
3n
S
O
OH
S

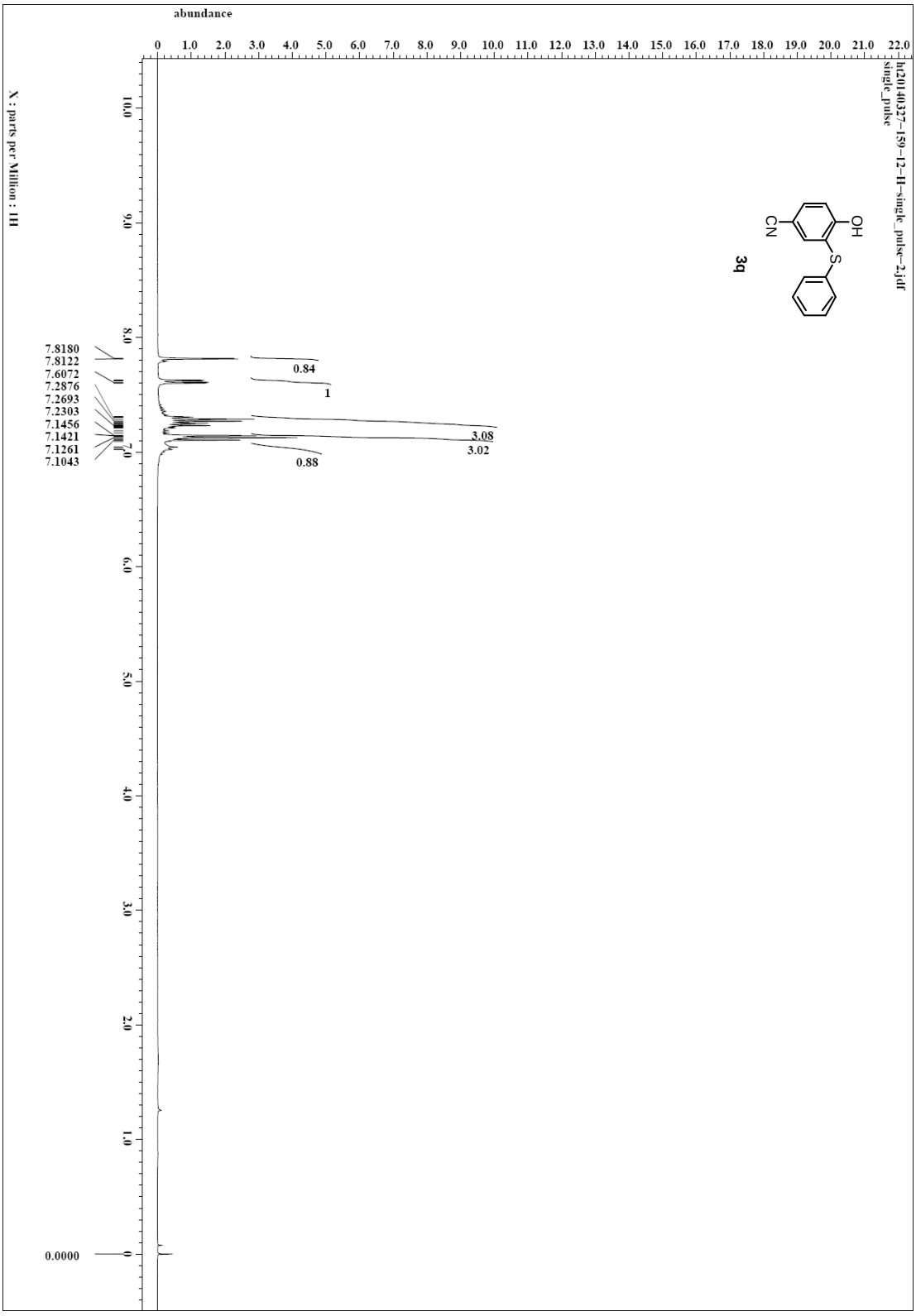

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
h20140403-162-1-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.9779
149.6609
136.0646
134.9586
133.0517
130.9541
129.8481
129.3618
129.1044
126.6445
126.2059
117.4817
114.2781
112.2282
77.4746
77.1600
76.8454
56.6893
3n
S
O
OH
S

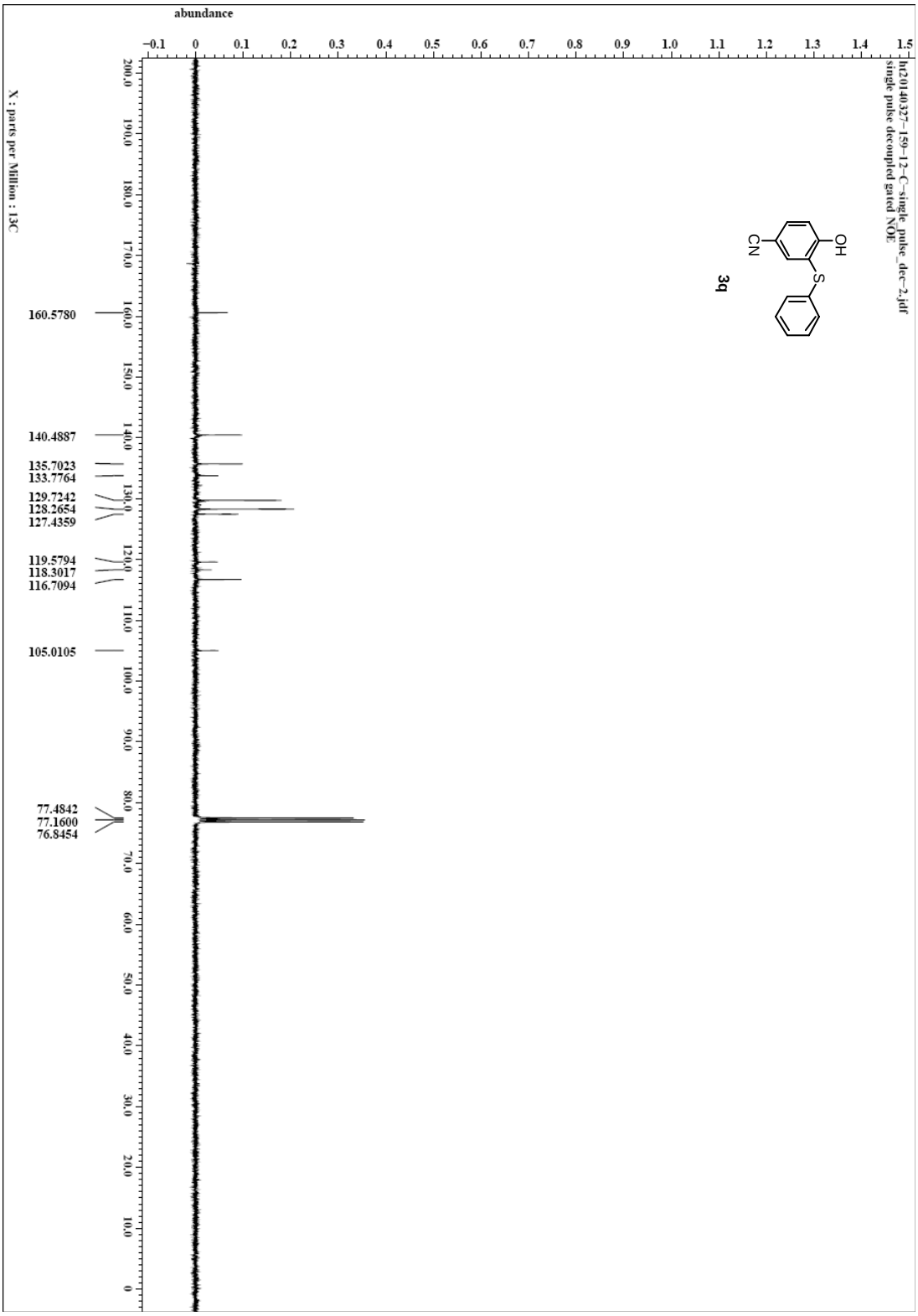

abundance
0
10.0
20.0
30.0
hz20130331-159-13-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
12.3598
7.8924
7.8879
7.2670
7.2487
7.1960
7.1799
6.9978
6.9760
2.6048
0.0000
0.91
0.98
0.99
2.08
3.01
0.98
3
OH
O
S
3o

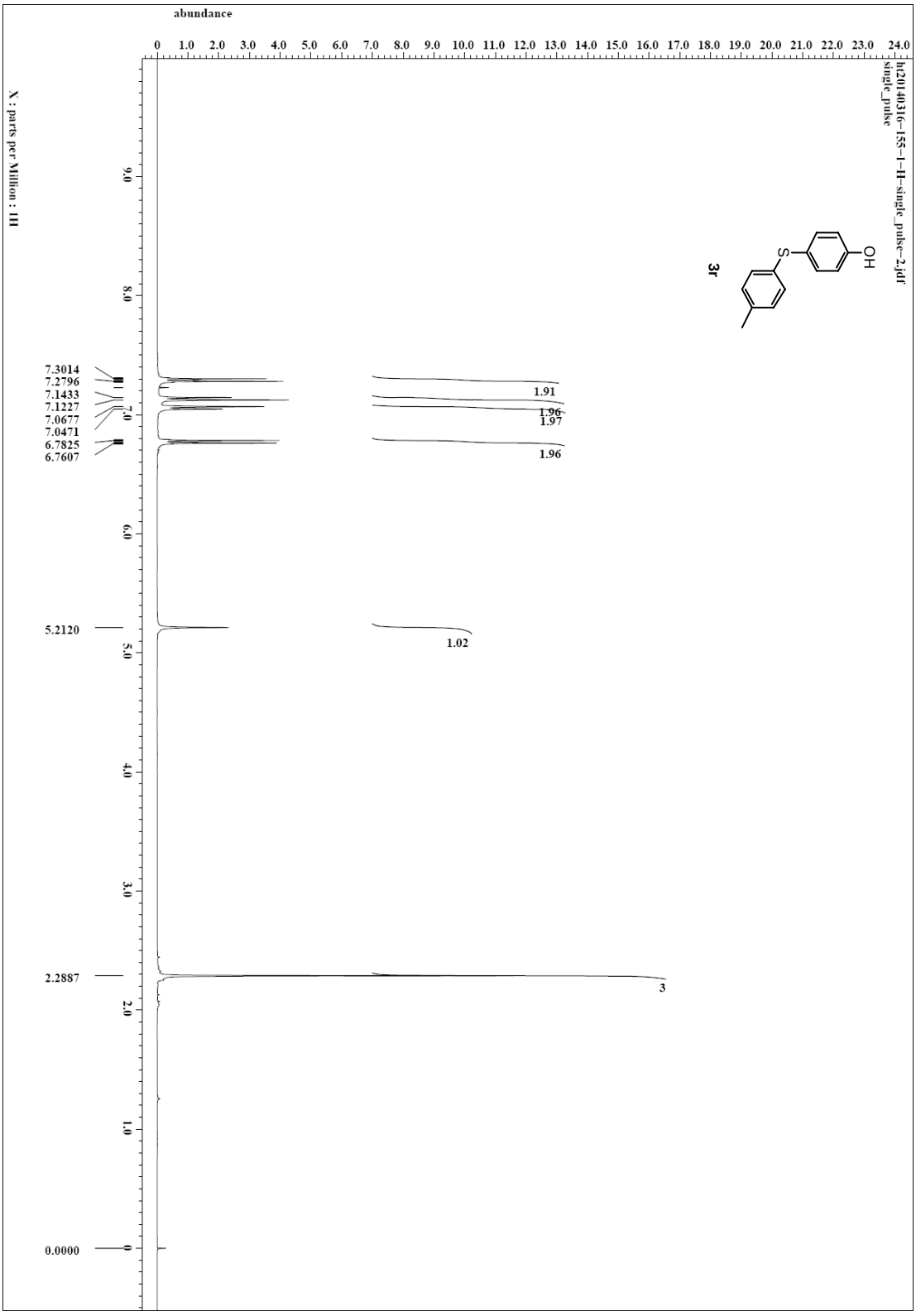

abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : 13C
204.2560
162.6852
142.0905
137.7332
136.3507
129.2951
128.5705
126.4252
123.1834
120.4756
120.0751
77.4842
77.1600
76.8454
26.8269
hz20130331--159-13-C--single_pulse_dec-2.jdf
single pulse decoupled gated NOE
3o
OH
O
S

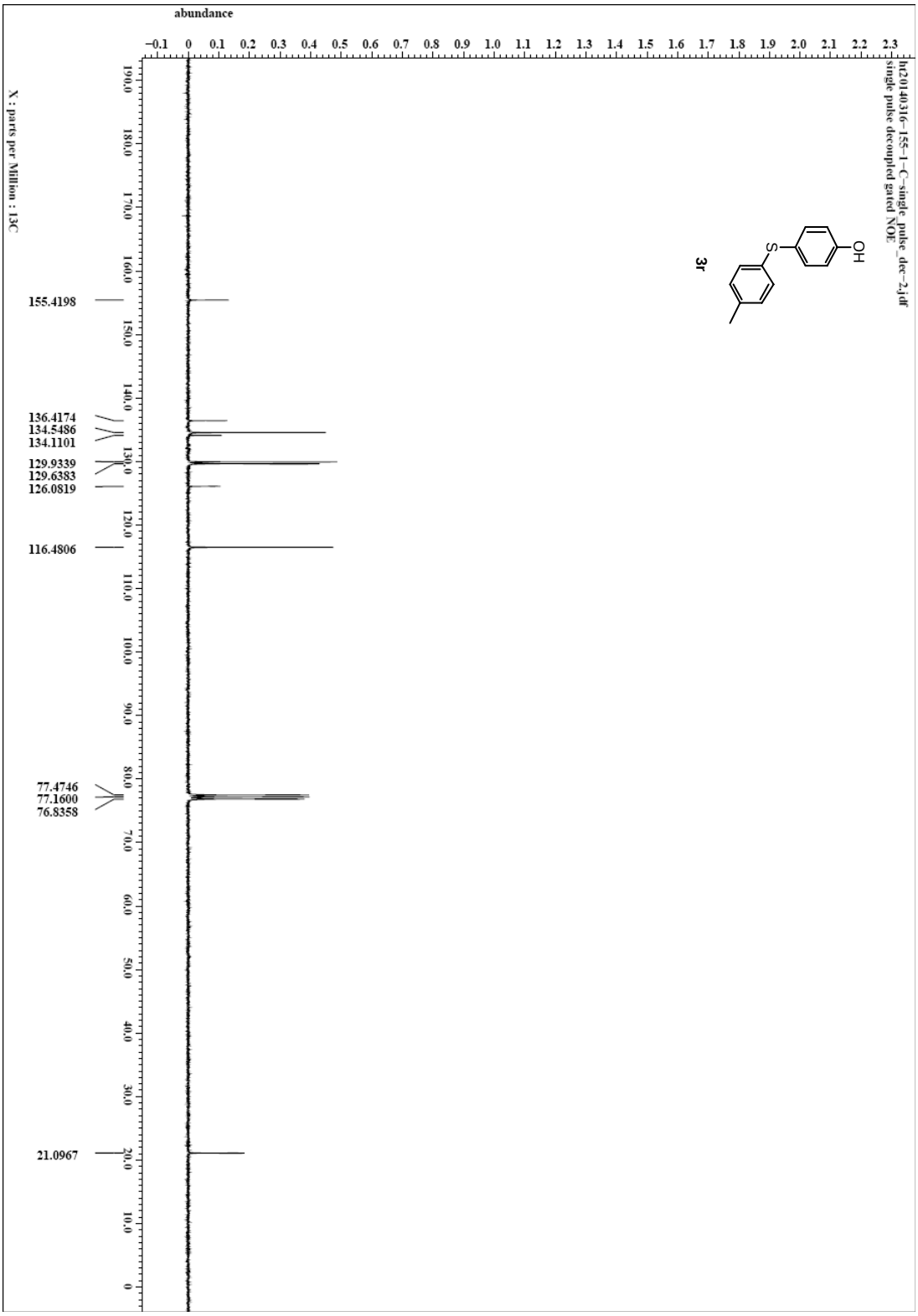

abundance
X : parts per Million : 1H
hr20130331-159-15-1H-single_pulse-2.jdf
single_pulse
11.0815
9.8455
7.6805
7.6759
7.2842
7.2647
7.2349
7.0058
6.9841
0.0000
1.0
1.0
1.05
1.02
5.12
1.05
3p
OH
CHO
S

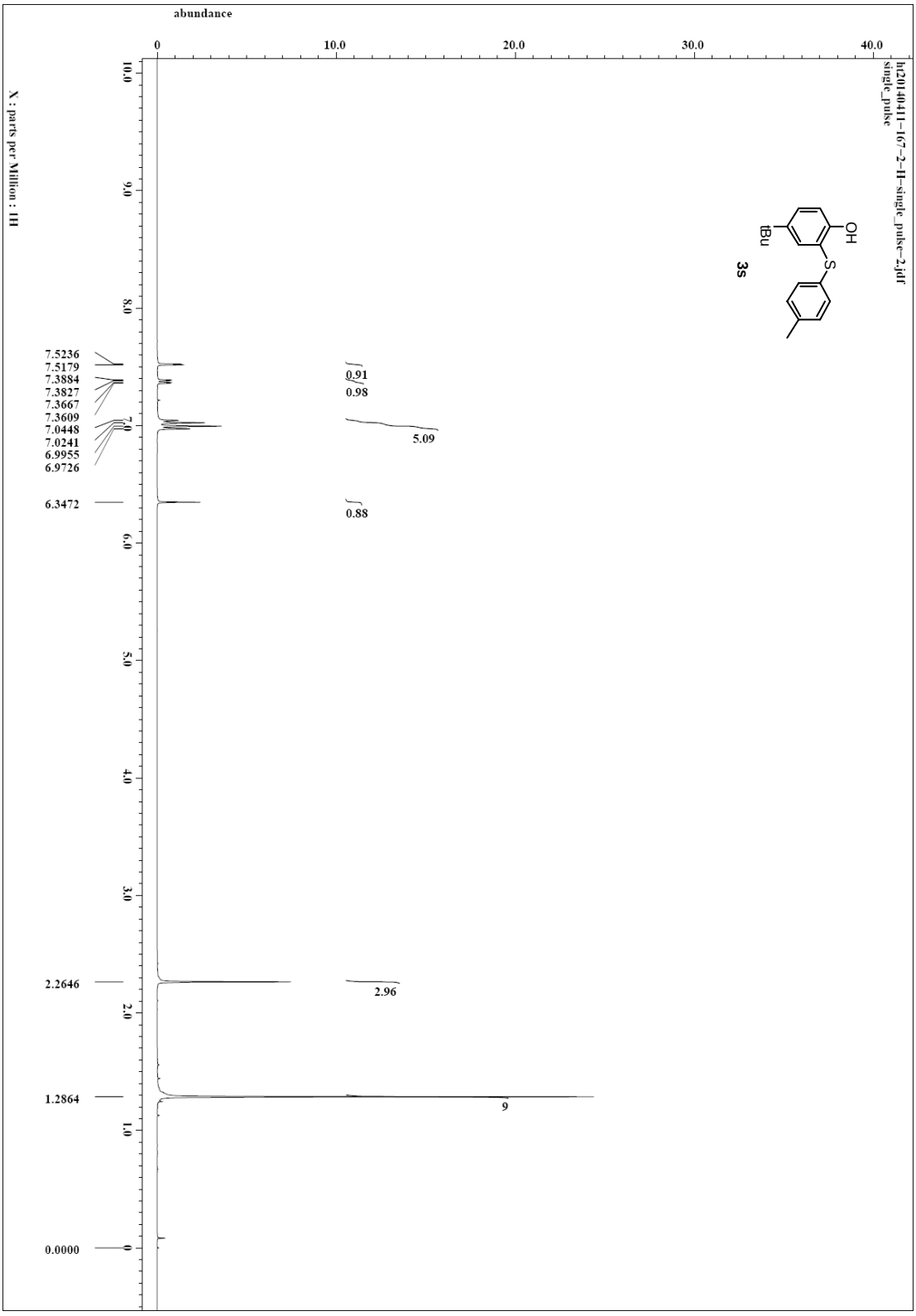

abundance
0
0.1
0.2
0.3
0.4
hz20130331--159-15-C--single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
196.1992
161.6841
142.1096
138.4864
137.0849
129.3809
129.3046
126.7875
125.0903
121.3719
119.2552
77.4746
77.1600
76.8358
3q
OH
CHO
S

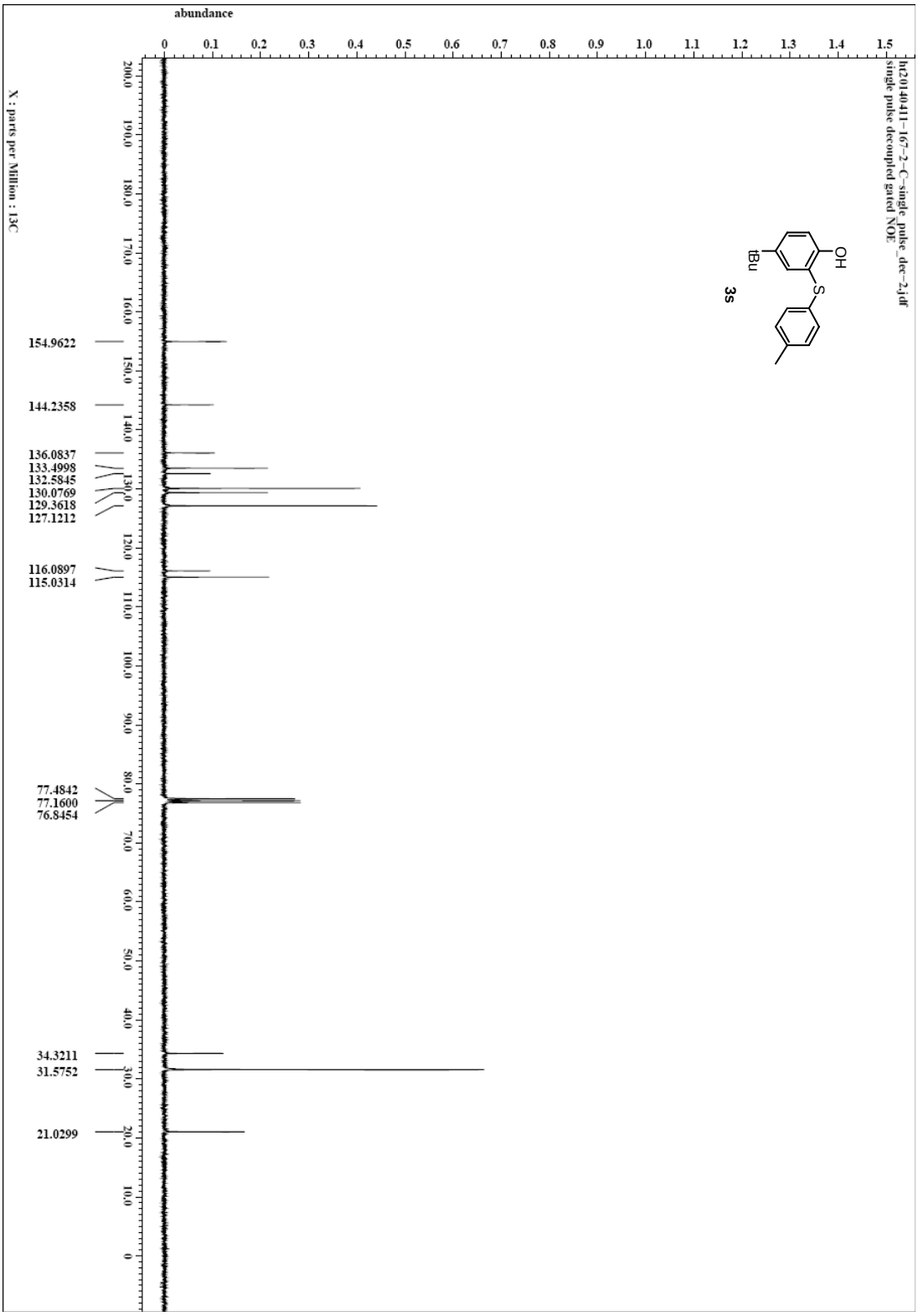

abundance
X : parts per Million : 1H
hr20140327-159-12-H-single_pulse-2.jdf
single_pulse
3a
CN
OH
S
7.8180
7.8122
7.6072
7.2876
7.2693
7.2303
7.1456
7.1421
7.1261
7.1043
0.84
1
3.08
3.02
0.88
0.0000

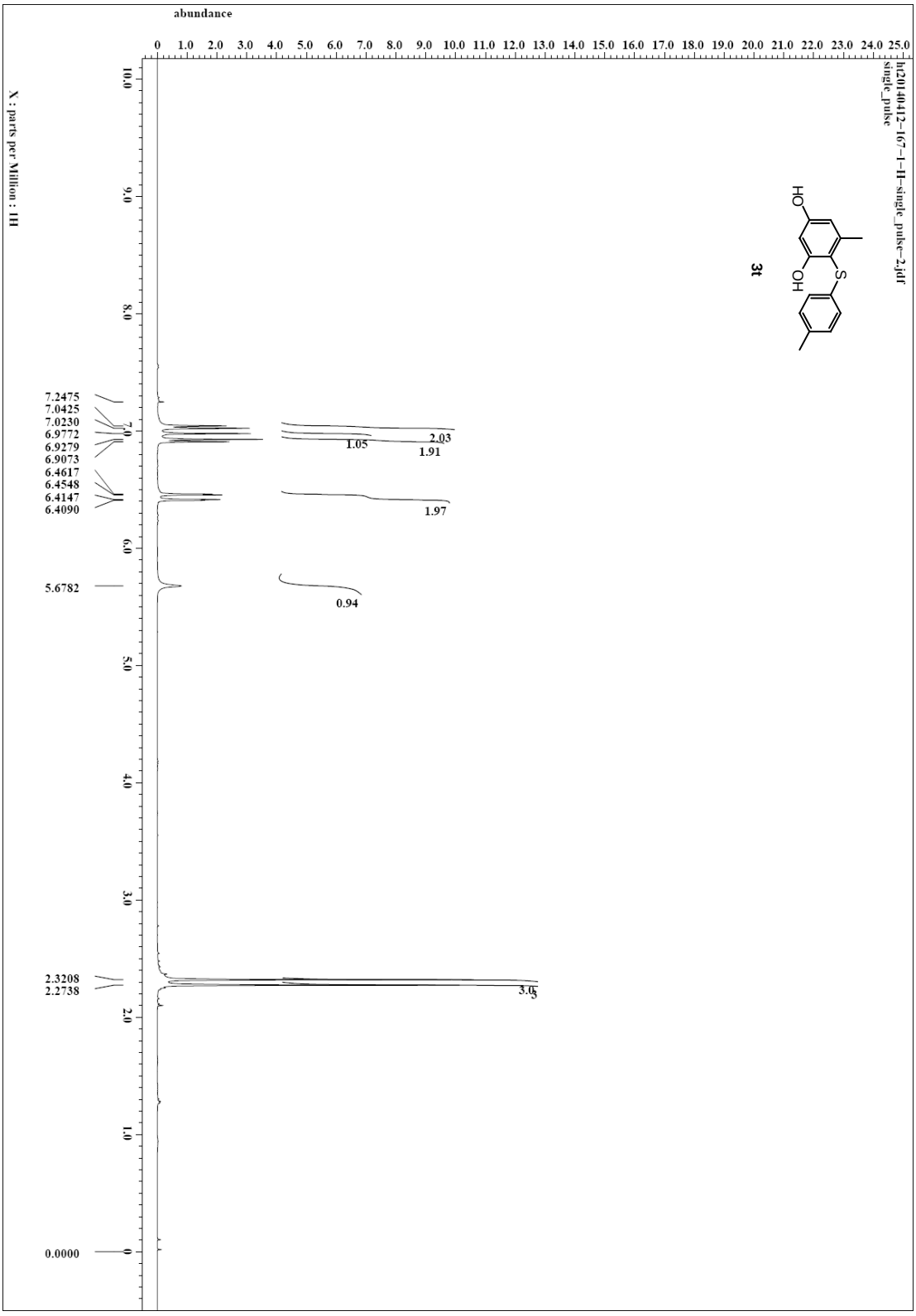

abundance
X : parts per Million : 13C
hz20140327--159-12--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
160.5780
140.4887
135.7023
133.7764
129.7242
128.2654
127.4359
119.5794
118.3017
116.7094
105.0105
77.4842
77.1600
76.8454
CN
OH
S
3q

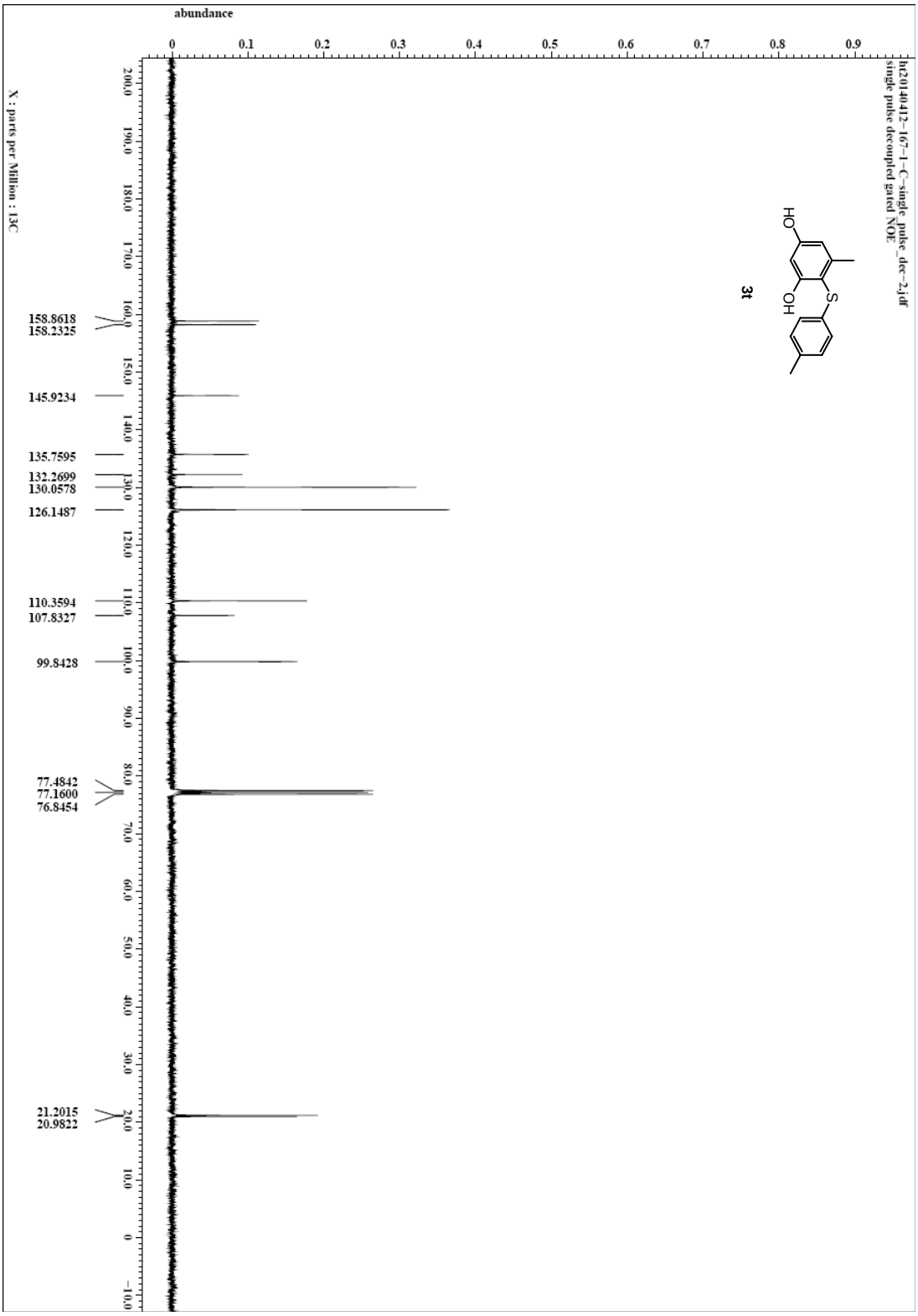

abundance
X : parts per Million : 1H
nt20140316-155-1-H-single_pulse-2.jdf
single_pulse
3r
OH
S
7.3014
7.2796
7.1433
7.1227
7.0677
7.0471
6.7825
6.7607
5.2120
2.2887
0.0000
1.91
1.96
1.97
1.96
1.02
3

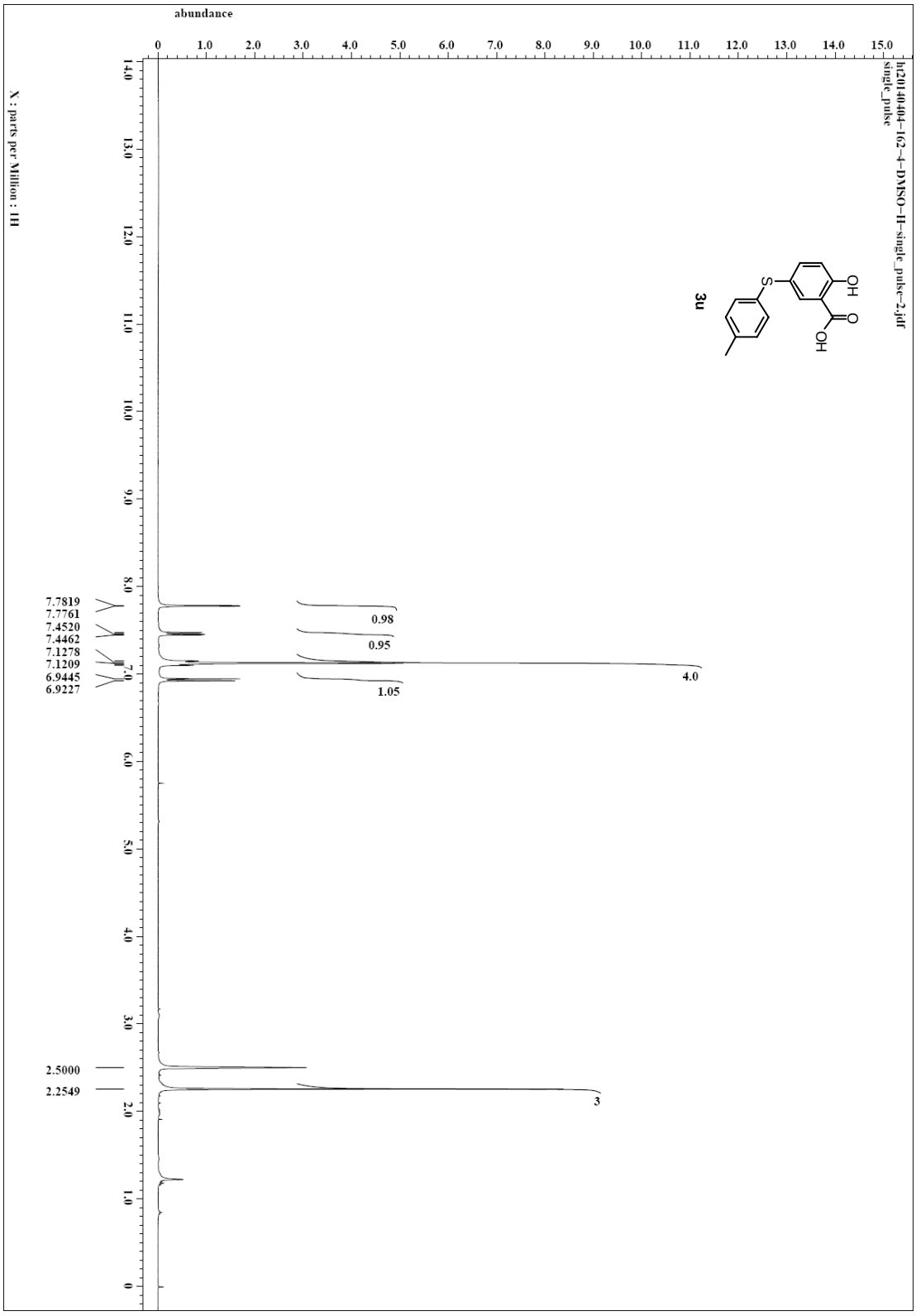

abundance
X : parts per Million : 13C
hz20140316-155-1-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
3r
OH
S
155.4198
136.4174
134.5486
134.1101
129.9339
129.6383
126.0819
116.4806
77.4746
77.1600
76.8358
21.0967

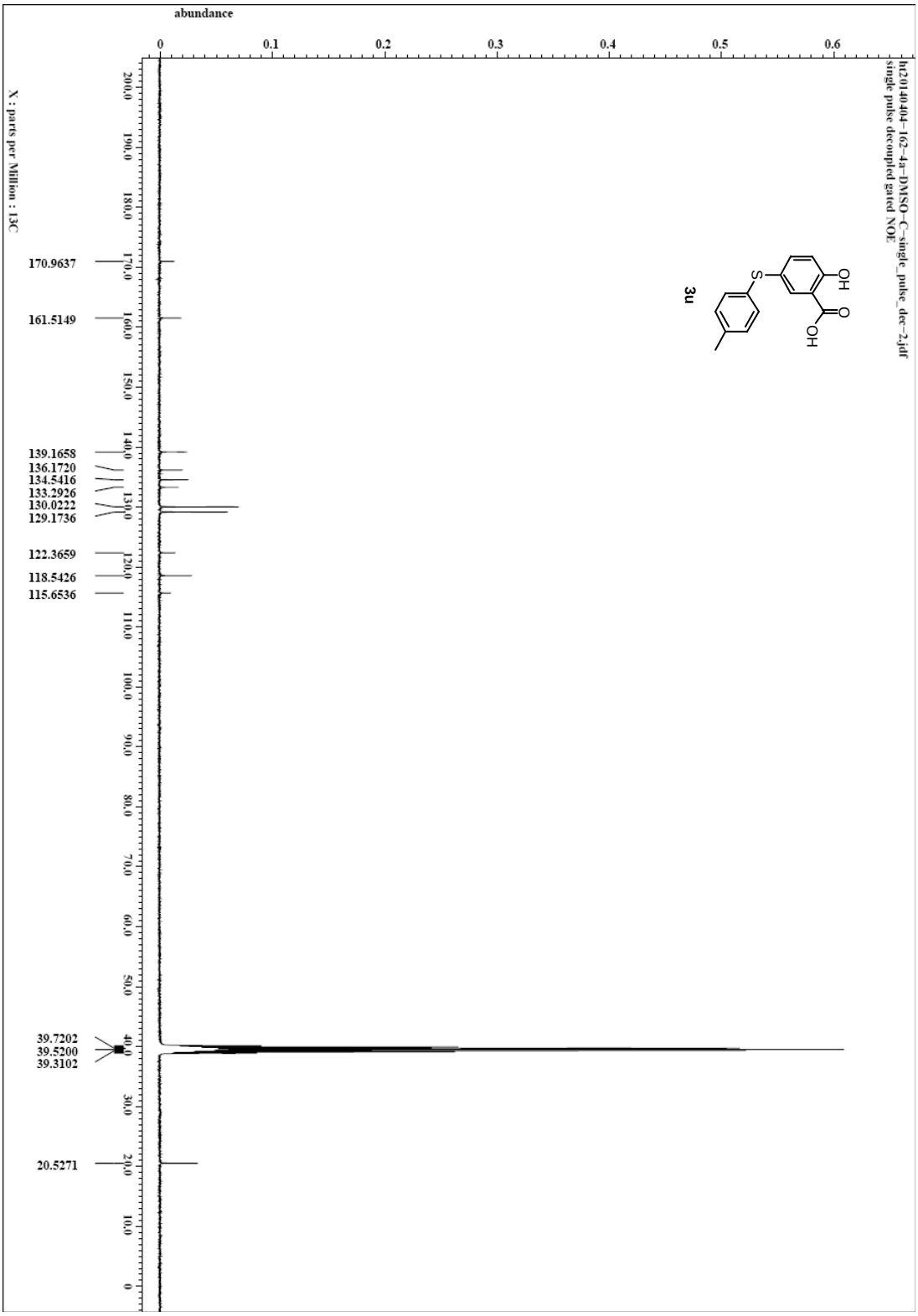

abundance
0
10.0
20.0
30.0
40.0
h120140411-167-2-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5236
7.5179
7.3884
7.3827
7.3667
7.3609
7.0448
7.0241
6.9955
6.9726
6.3472
2.2646
1.2864
0.0000
0.91
0.98
5.09
0.88
2.96
9
OH
tBu
S
3s

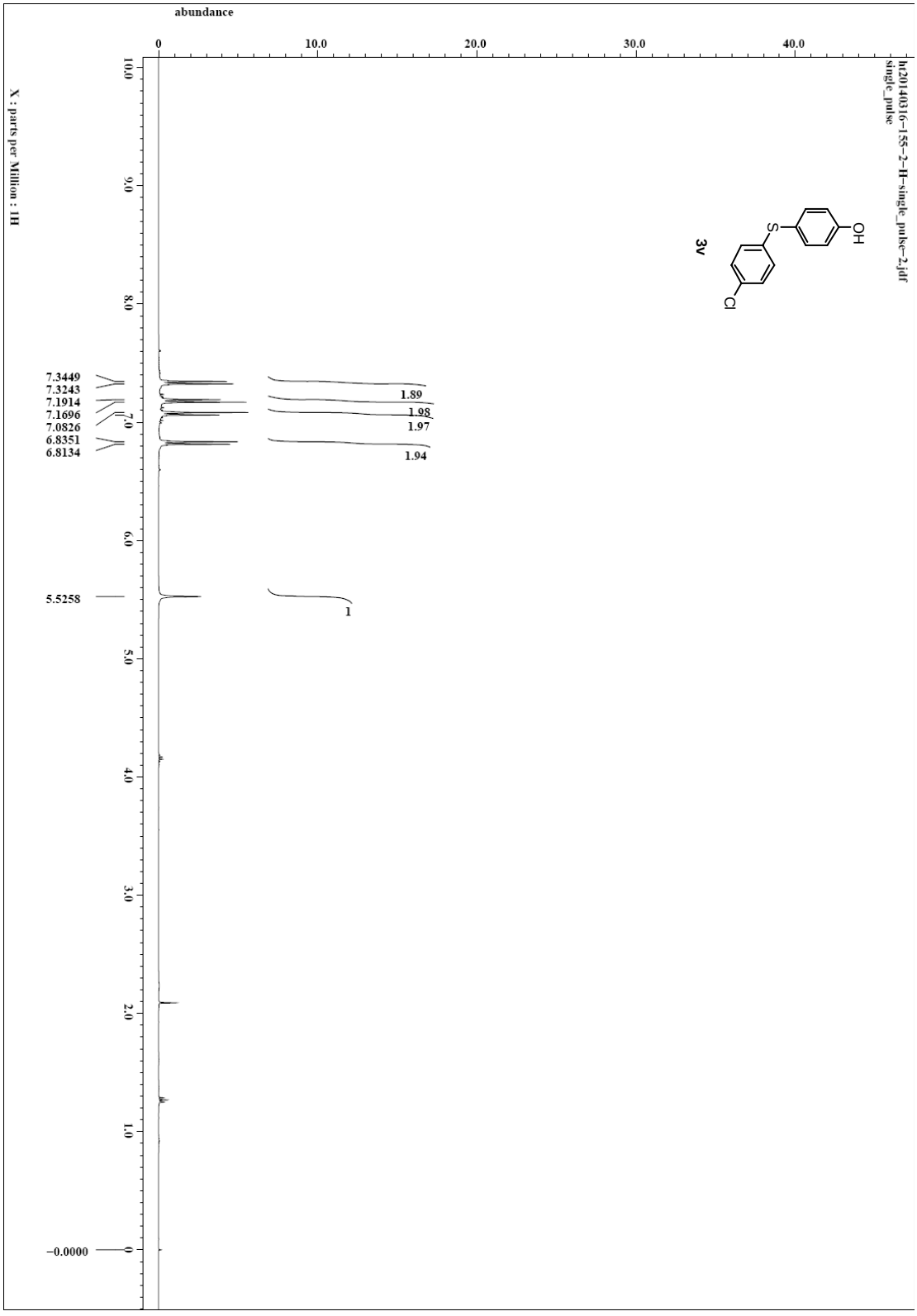

abundance
X : parts per Million : 13C
hz20140411--167--2--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
154.9622
144.2358
136.0837
133.4998
132.5845
130.0769
129.3618
127.1212
116.0897
115.0314
77.4842
77.1600
76.8454
34.3211
31.5752
21.0299
tBu
OH
S
3s

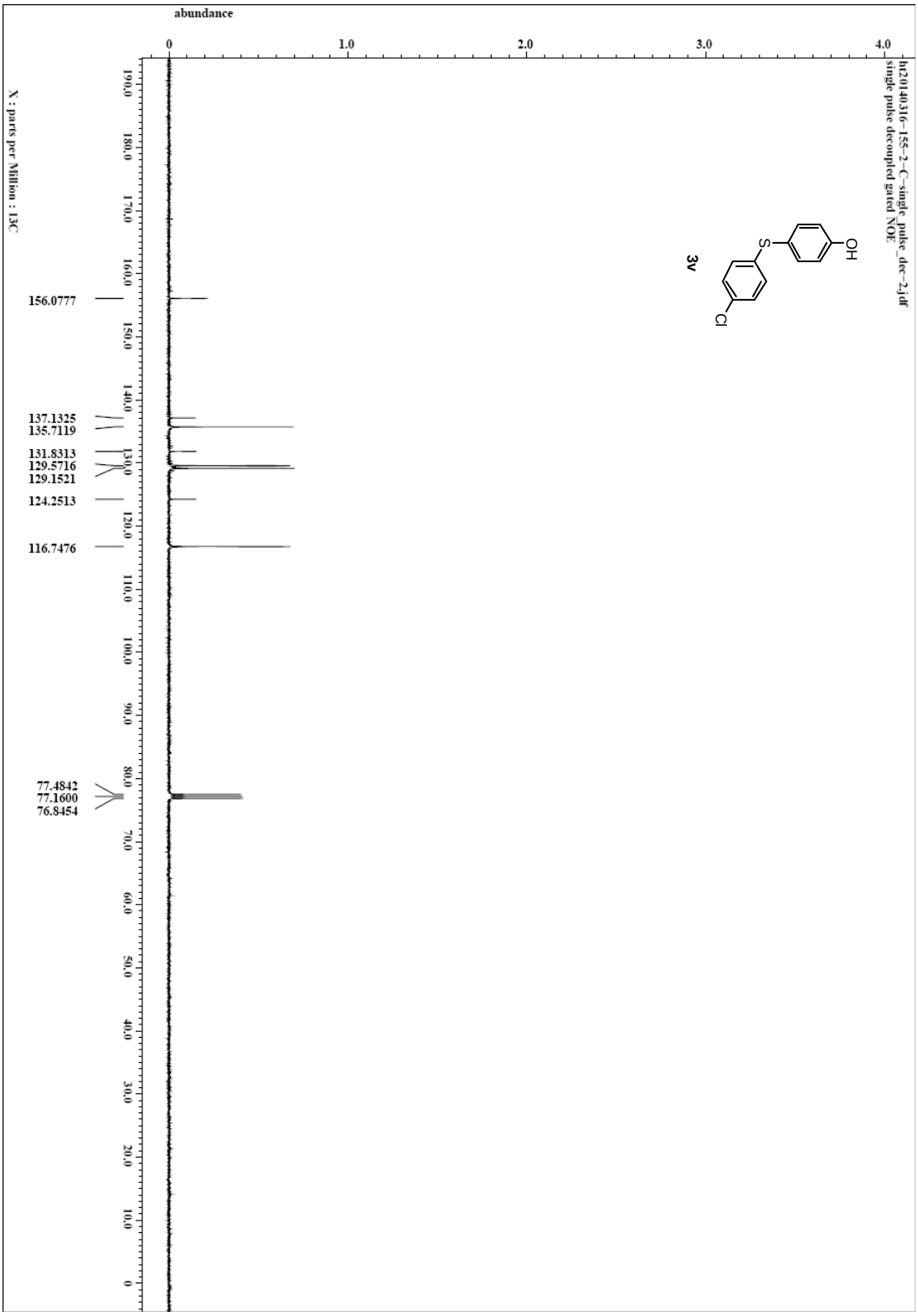

abundance
X : parts per Million : 1H
hi20140412-167-1-H-single_pulse-2.jdf
single_pulse
3t
HO
OH
S
7.2475
7.0425
7.0230
6.9772
6.9279
6.9073
6.4617
6.4548
6.4147
6.4090
5.6782
2.3208
2.2738
0.0000
1.05
2.03
1.91
1.97
0.94
3.05

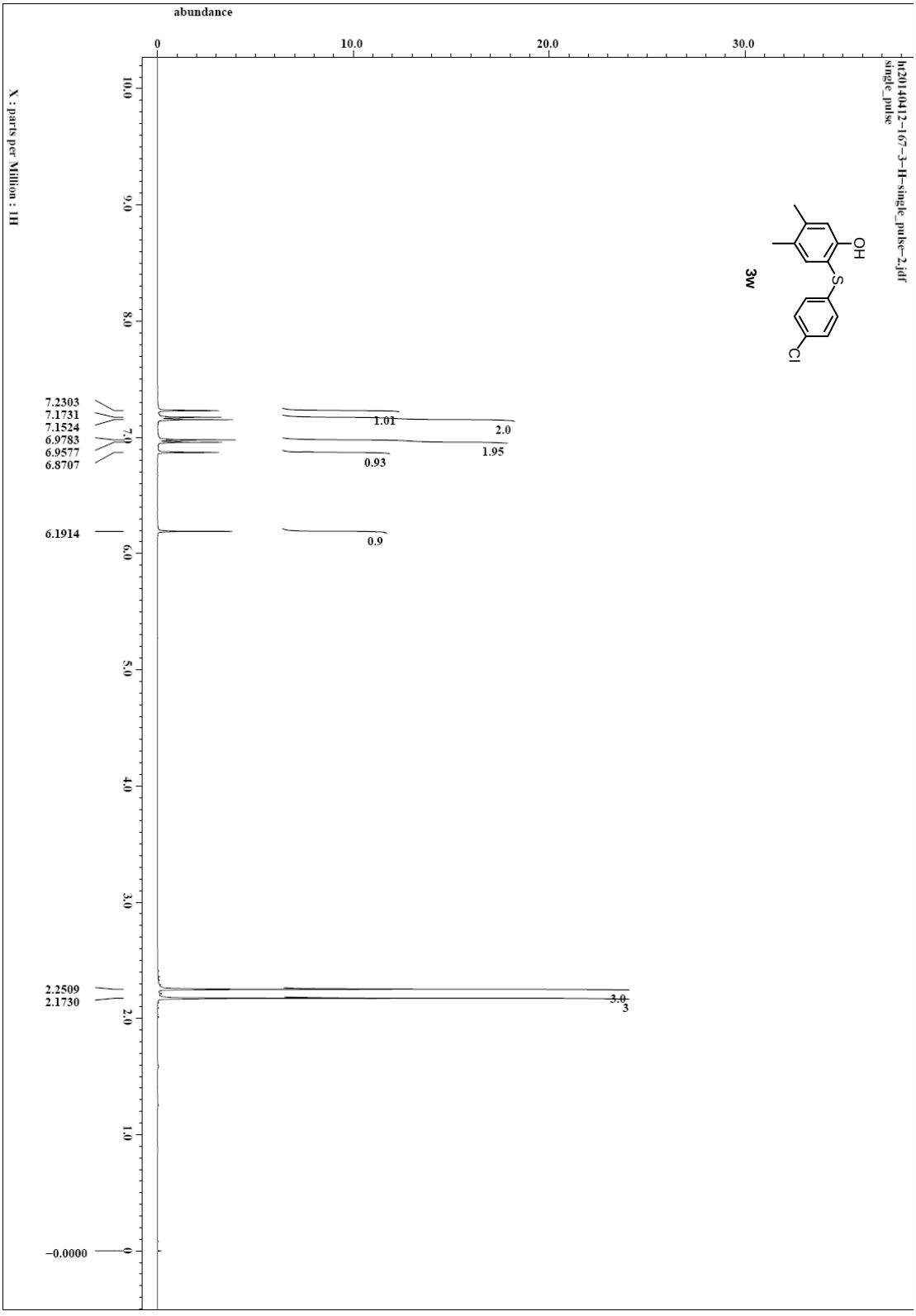

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
hz20140412-167-1-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
158.8618
158.2325
145.9234
135.7595
132.2699
130.0578
126.1487
110.3594
107.8327
99.8428
77.4842
77.1600
76.8454
21.2015
20.9822
3t
HO
OH
S

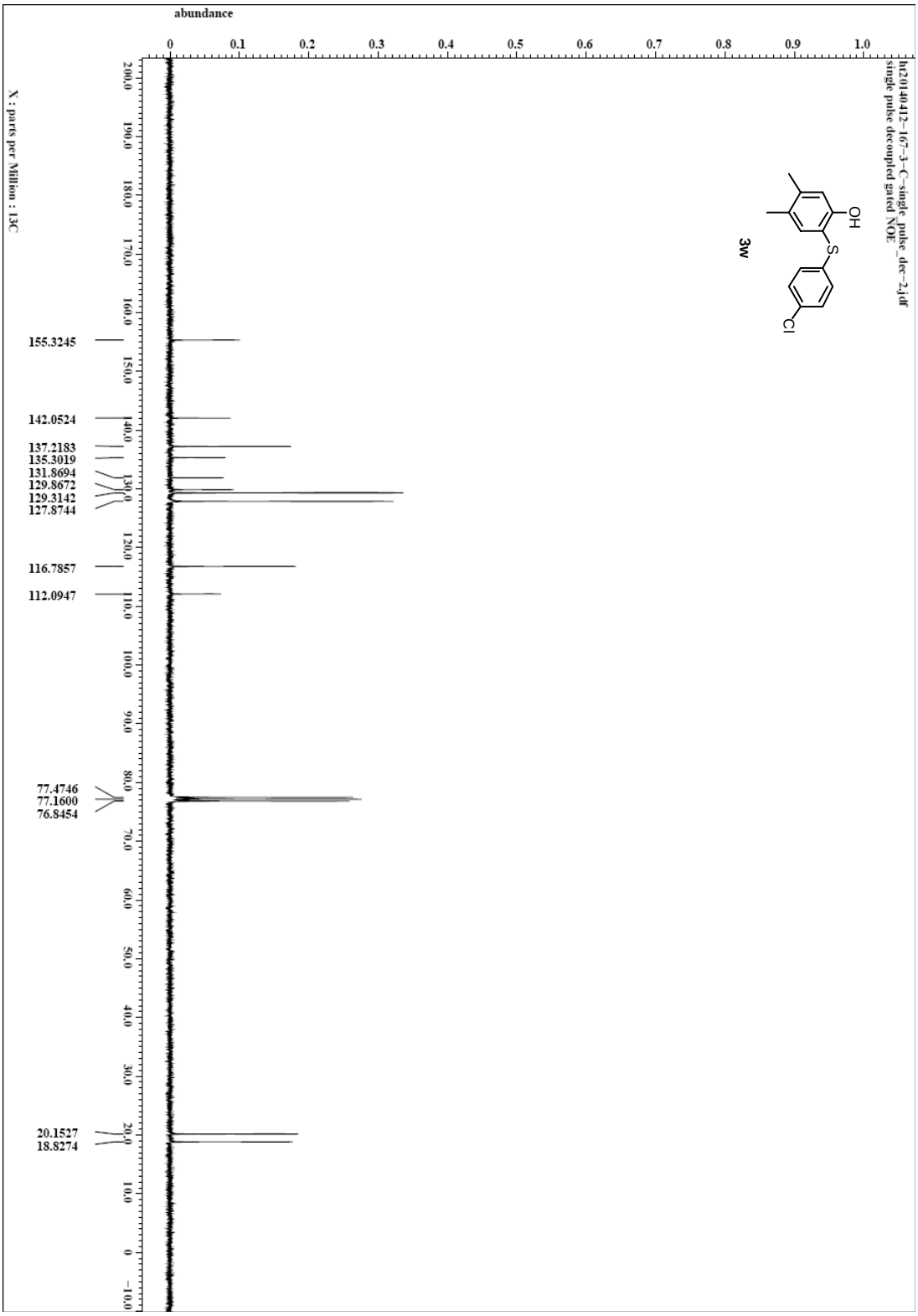

abundance
X : parts per Million : 1H
h20140404-162-4-DMSO-H-single_pulse-2.jdf
single_pulse
3u
OH
O
OH
S
7.7819
7.7761
7.4520
7.4462
7.1278
7.1209
6.9445
6.9227
2.5000
2.2549
0.98
0.95
4.0
1.05
3

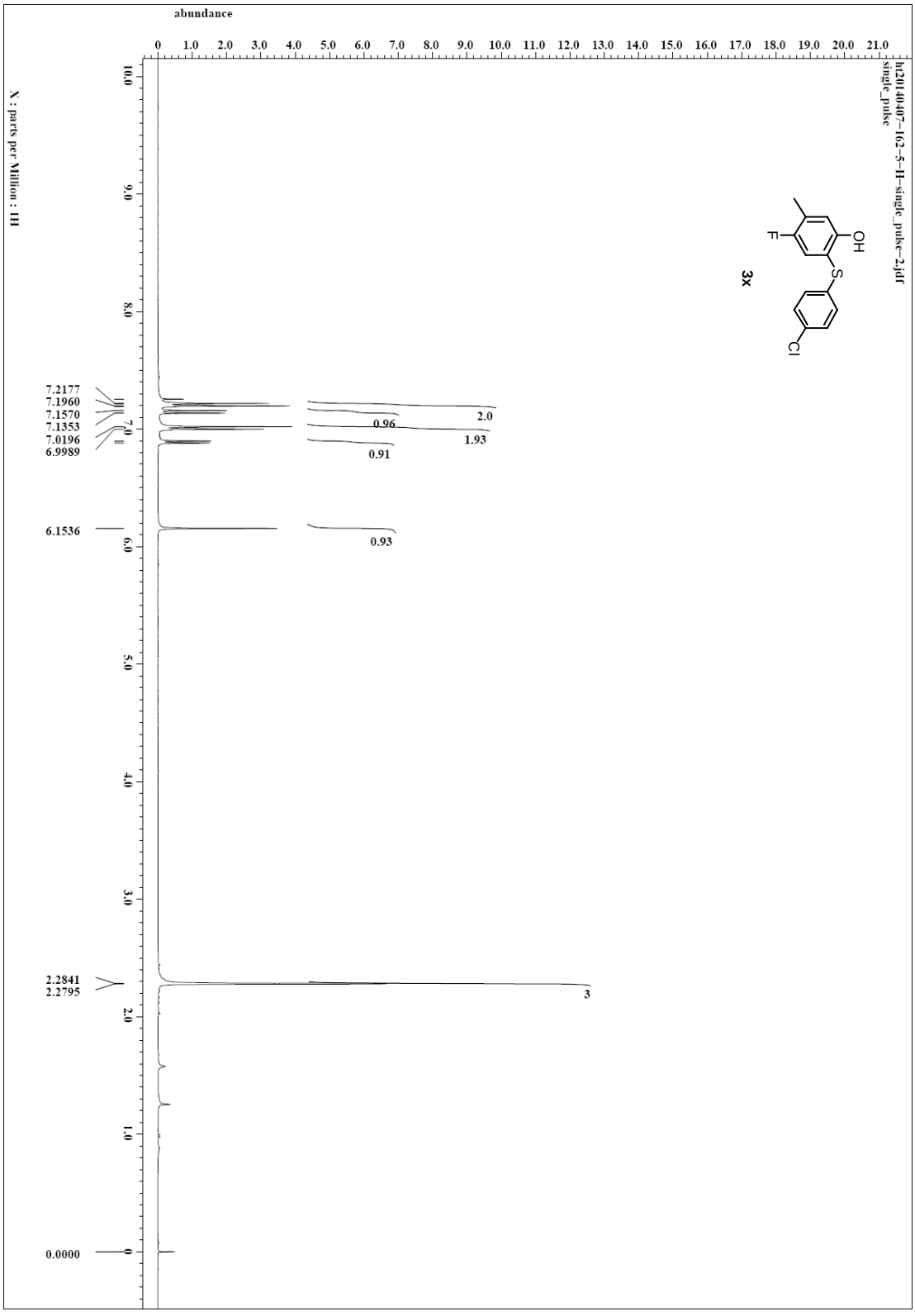

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.9637
161.5149
139.1658
136.1720
134.5416
133.2926
130.0222
129.1736
122.3659
118.5426
115.6536
39.7202
39.5200
39.3102
20.5271
3u
S
OH
O
HO
hz20140404-162-4a-DMSO-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE

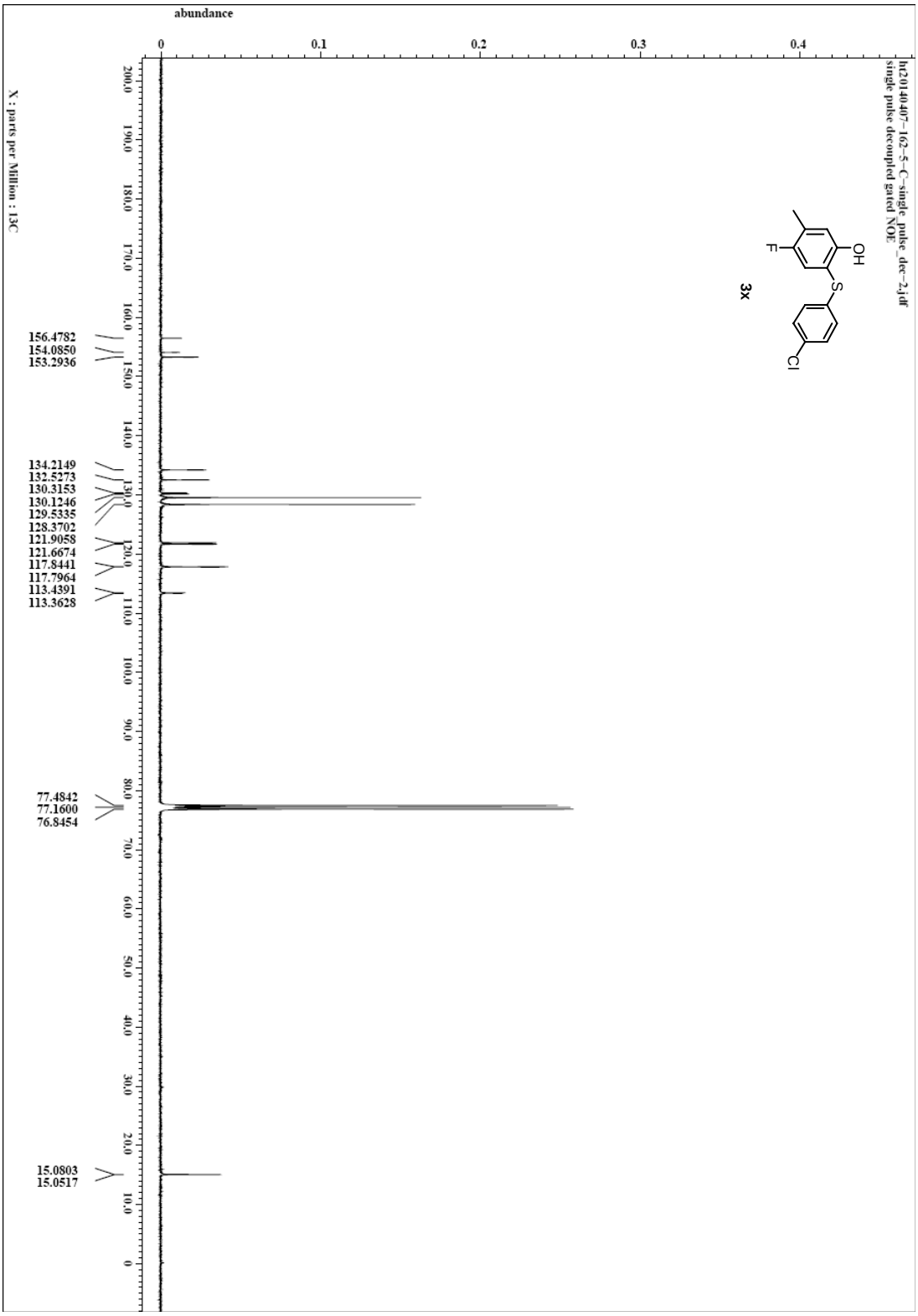

abundance
0
10.0
20.0
30.0
40.0
hz20140316-155-2-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3449
7.3243
7.1914
7.1696
7.0826
6.8351
6.8134
5.5258
−0.0000
1.89
1.98
1.97
1.94
1
3v
S
OH
Cl

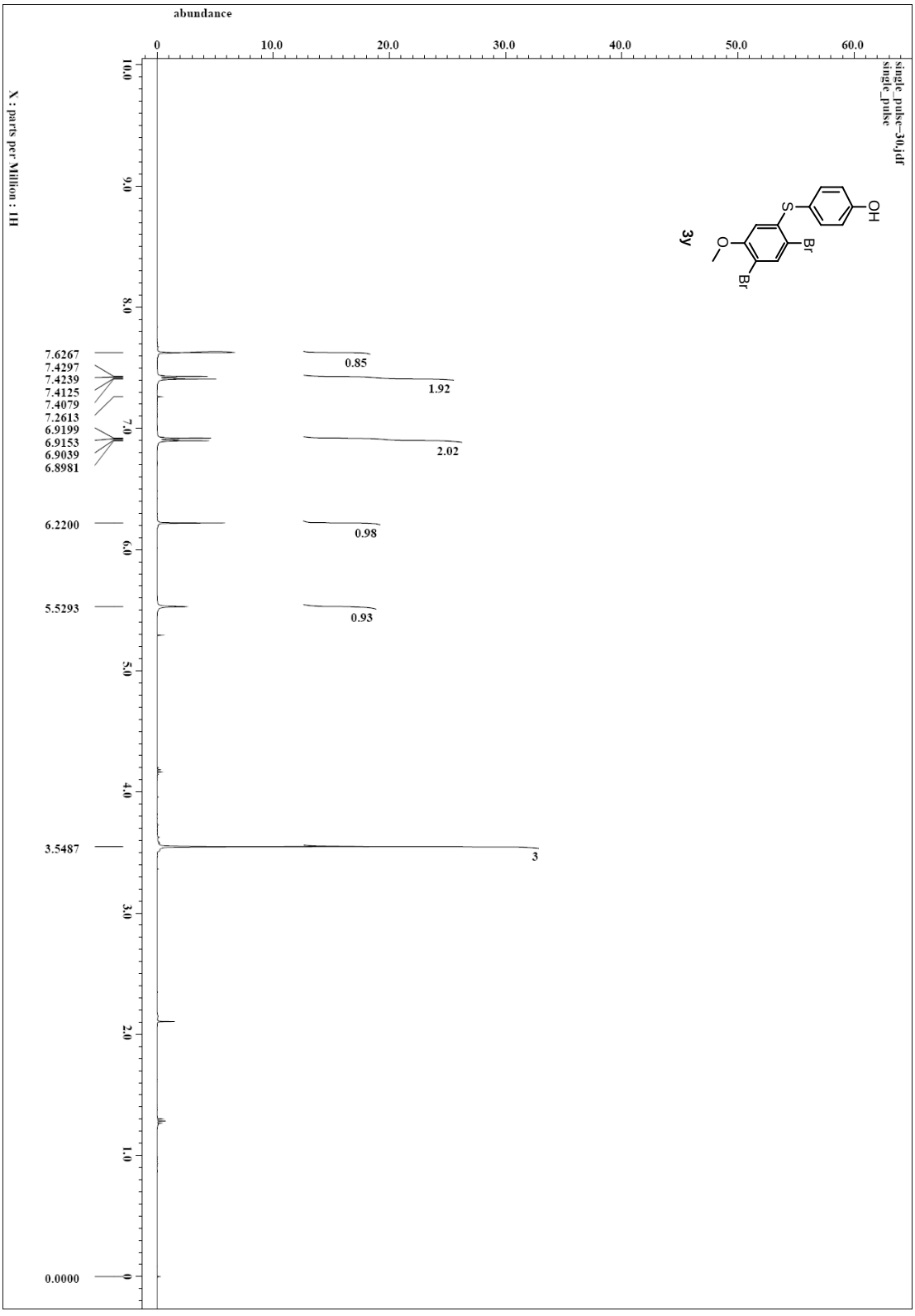

abundance
0
1.0
2.0
3.0
4.0
hz20140316-155-2-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.0777
137.1325
135.7119
131.8313
129.5716
129.1521
124.2513
116.7476
77.4842
77.1600
76.8454
3v
S
OH
Cl

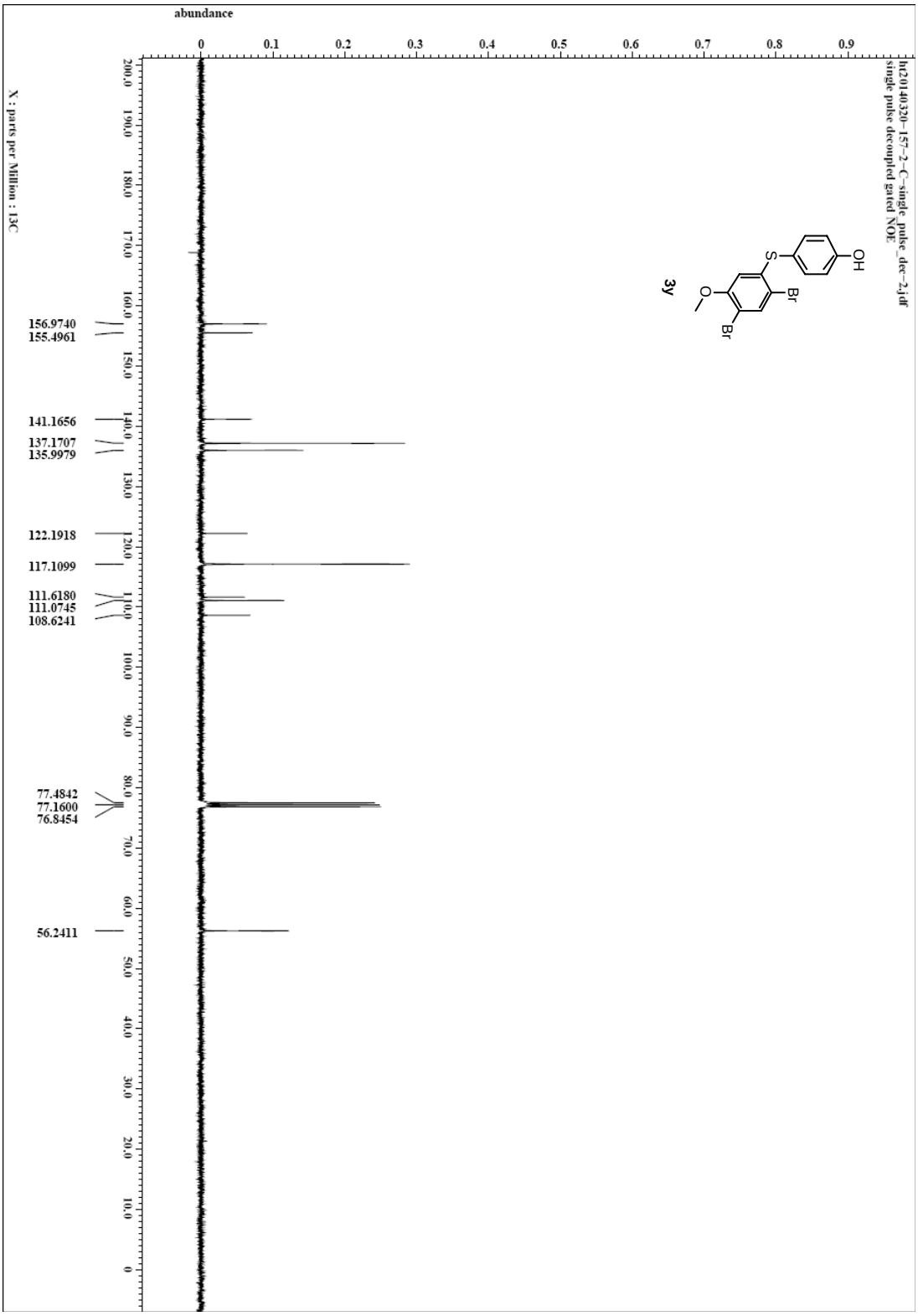

abundance
0
10.0
20.0
30.0
h20140412-167-3-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2303
7.1731
7.1524
6.9783
6.9577
6.8707
6.1914
2.2509
2.1730
−0.0000
1.01
2.0
1.95
0.93
0.9
3.0
3
OH
S
Cl
3w

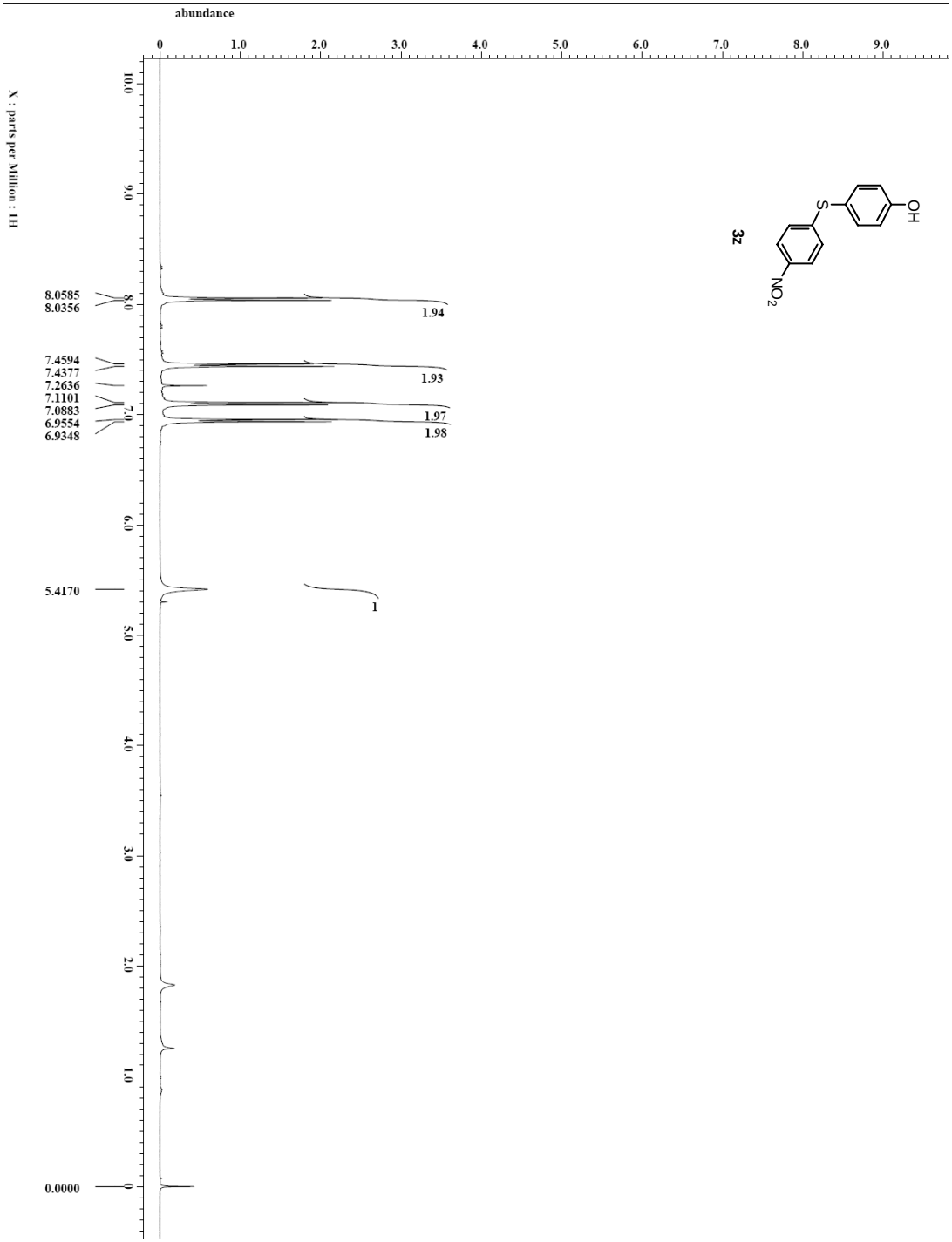

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
hz20140412-167-3-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
155.3245
142.0524
137.2183
135.3019
131.8694
129.8672
129.3142
127.8744
116.7857
112.0947
77.4746
77.1600
76.8454
20.1527
18.8274
OH
S
Cl
3w

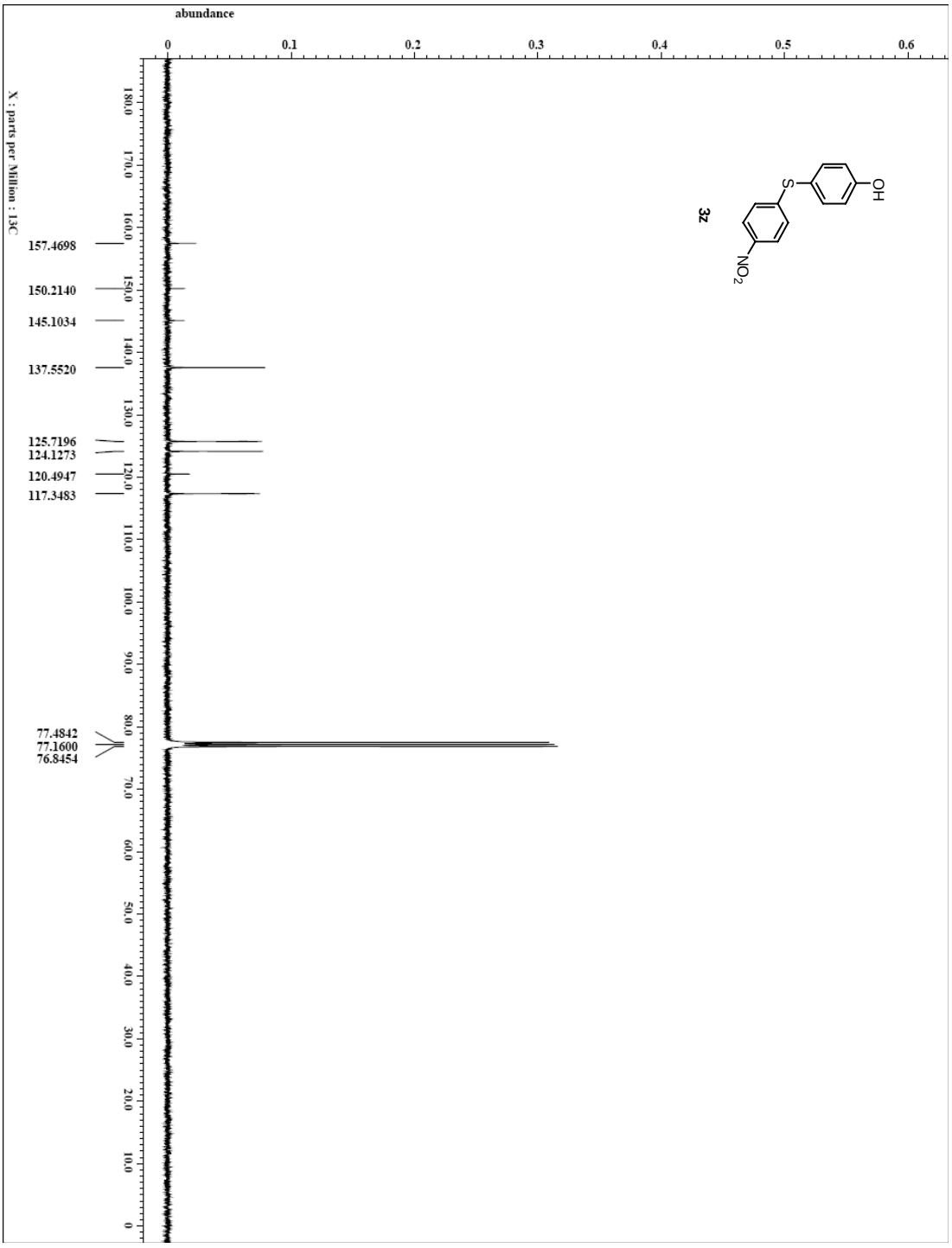

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0
hr20140407-162-5-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.2177
7.1960
7.1570
7.1353
7.0196
6.9989
6.1536
2.2841
2.2795
0.0000
2.0
0.96
1.93
0.91
0.93
3
OH
F
S
Cl
3x

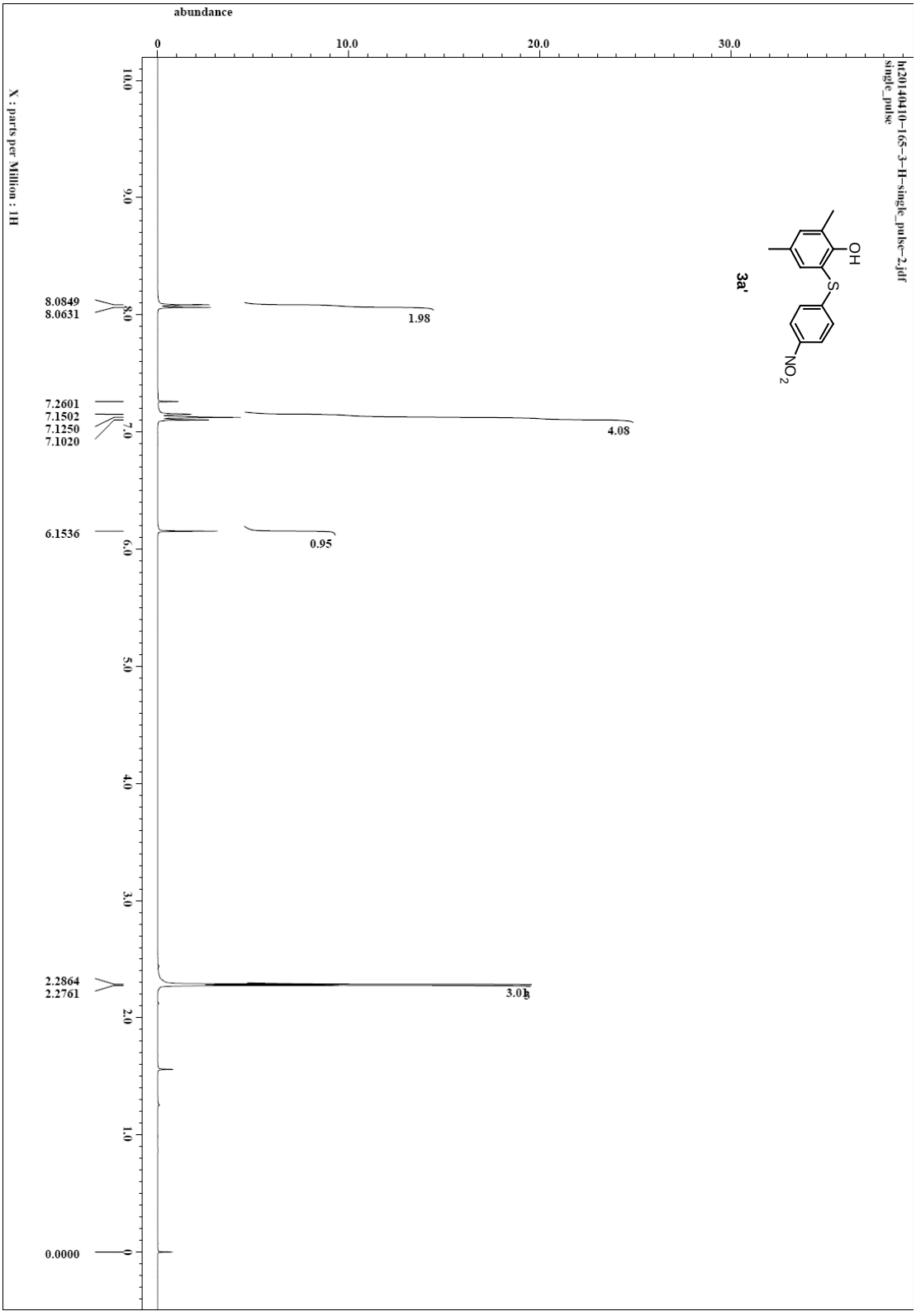

abundance
0
0.1
0.2
0.3
0.4
hz20140407--162--5--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
3x
OH
F
S
Cl
156.4782
154.0850
153.2936
134.2149
132.5273
130.3153
130.1246
129.5335
128.3702
121.9058
121.6674
117.8441
117.7964
113.4391
113.3628
77.4842
77.1600
76.8454
15.0803
15.0517

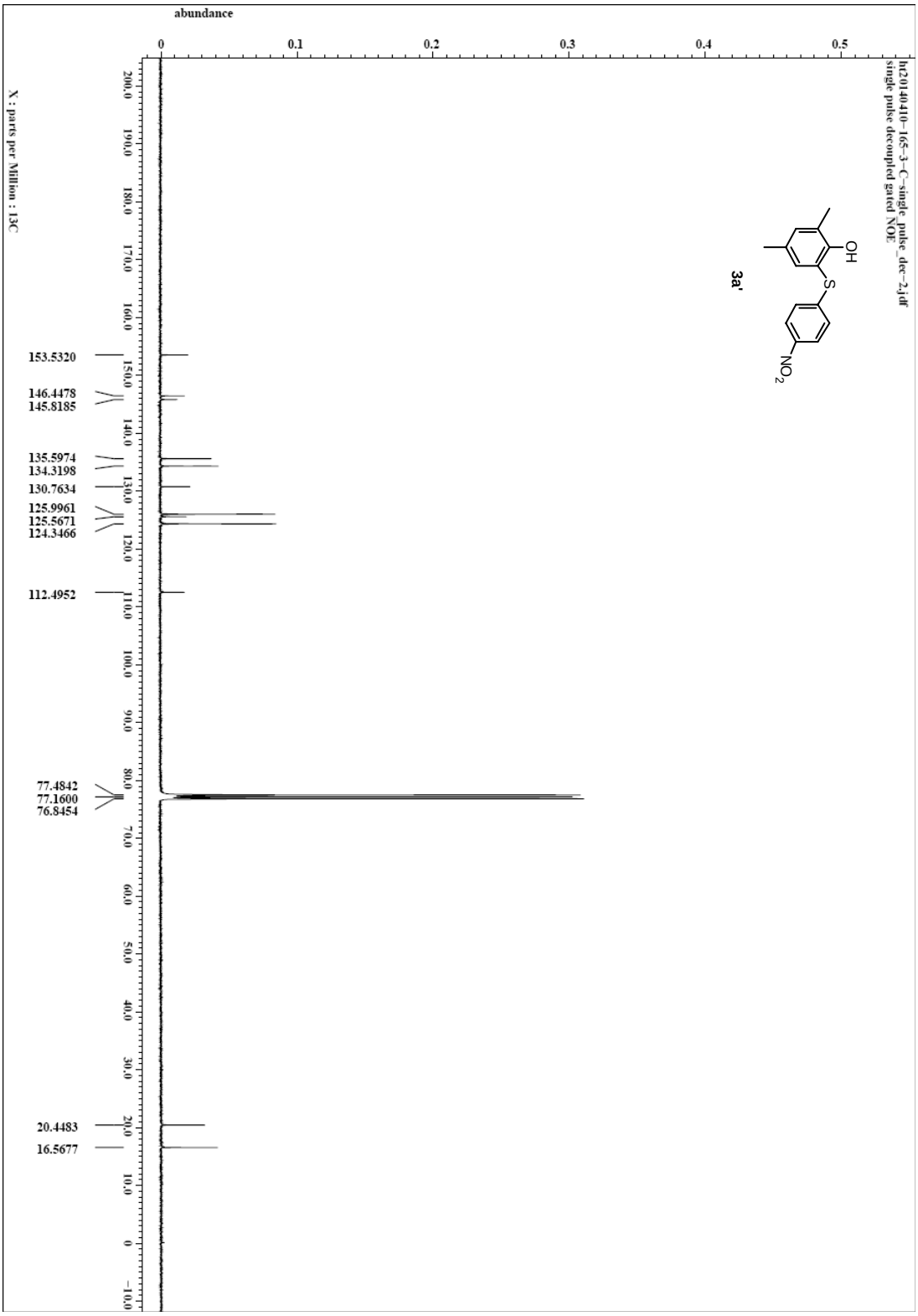

abundance
0
10.0
20.0
30.0
40.0
50.0
60.0
single_pulse
single_pulse-30.jdf
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6267
7.4297
7.4239
7.4125
7.4079
7.2613
6.9199
6.9153
6.9039
6.8981
6.2200
5.5293
3.5487
0.0000
0.85
1.92
2.02
0.98
0.93
3
3y
OH
S
Br
O
Br

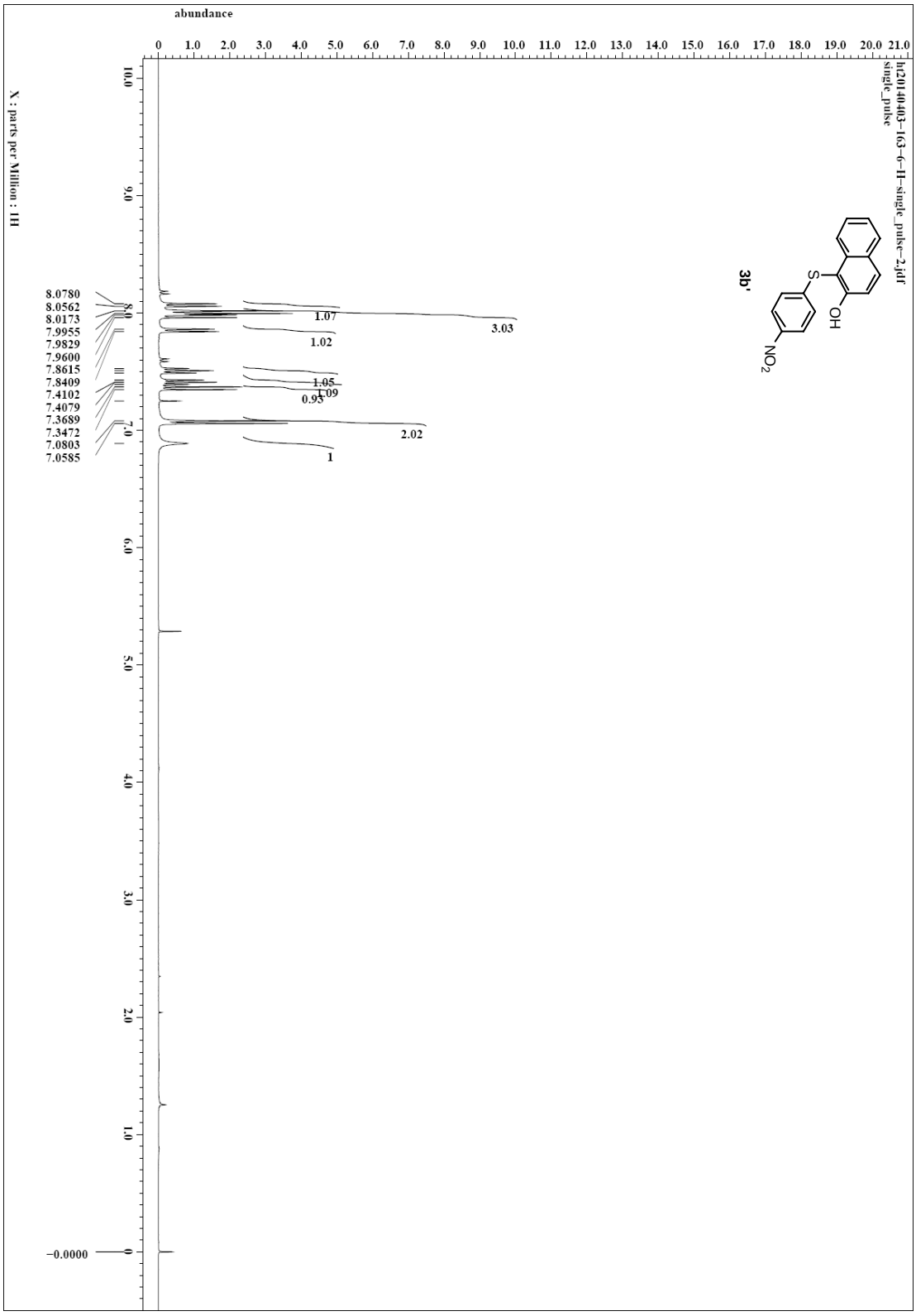

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
hz20140320--157--2--C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.9740
155.4961
141.1656
137.1707
135.9979
122.1918
117.1099
111.6180
111.0745
108.6241
77.4842
77.1600
76.8454
56.2411
3y
OH
S
Br
O
Br

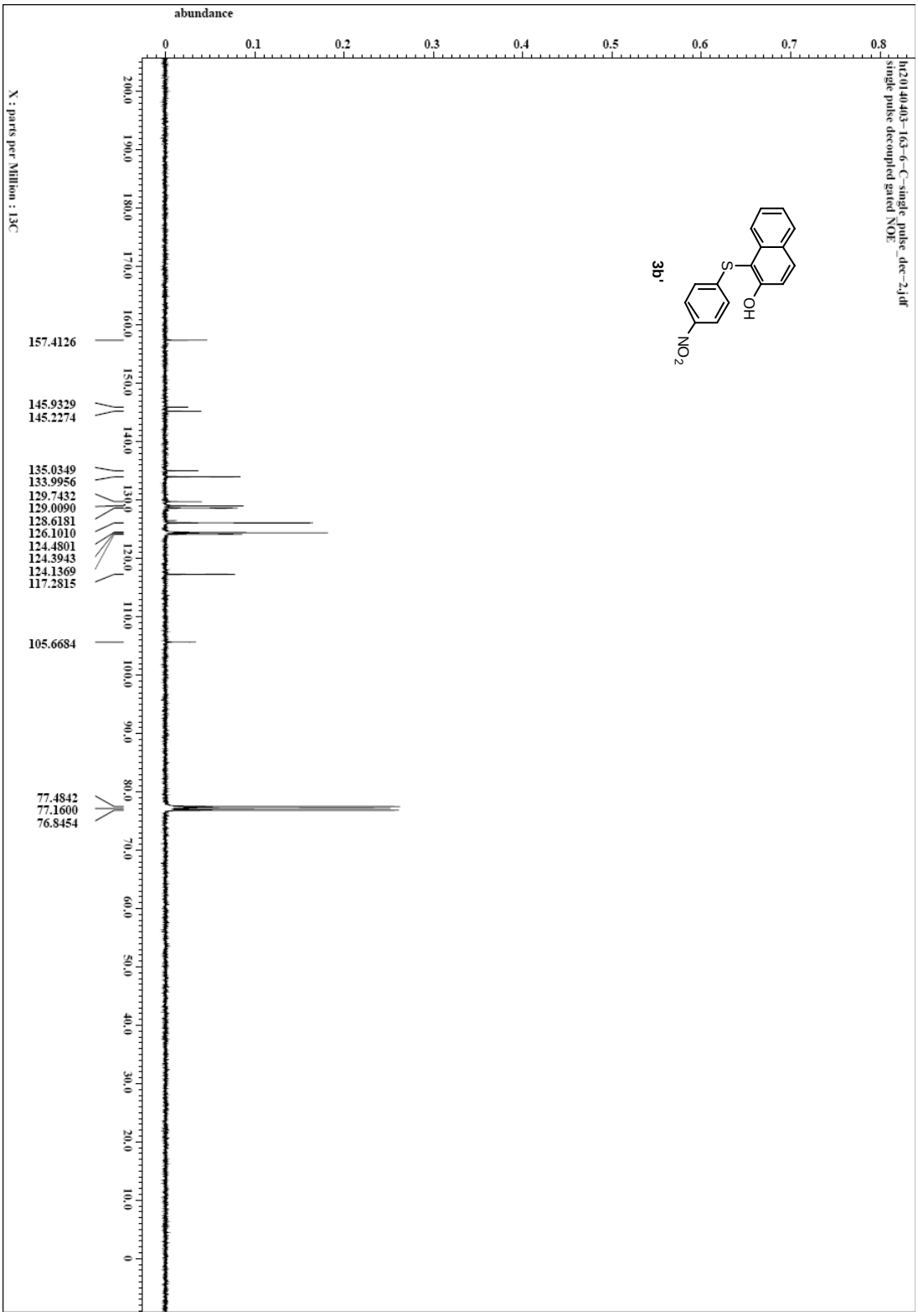

abundance
X : parts per Million : 1H
8.0585
8.0356
7.4594
7.4377
7.2636
7.1101
7.0883
6.9554
6.9348
5.4170
0.0000
1.94
1.93
1.97
1.98
1
3z
OH
S
NO2

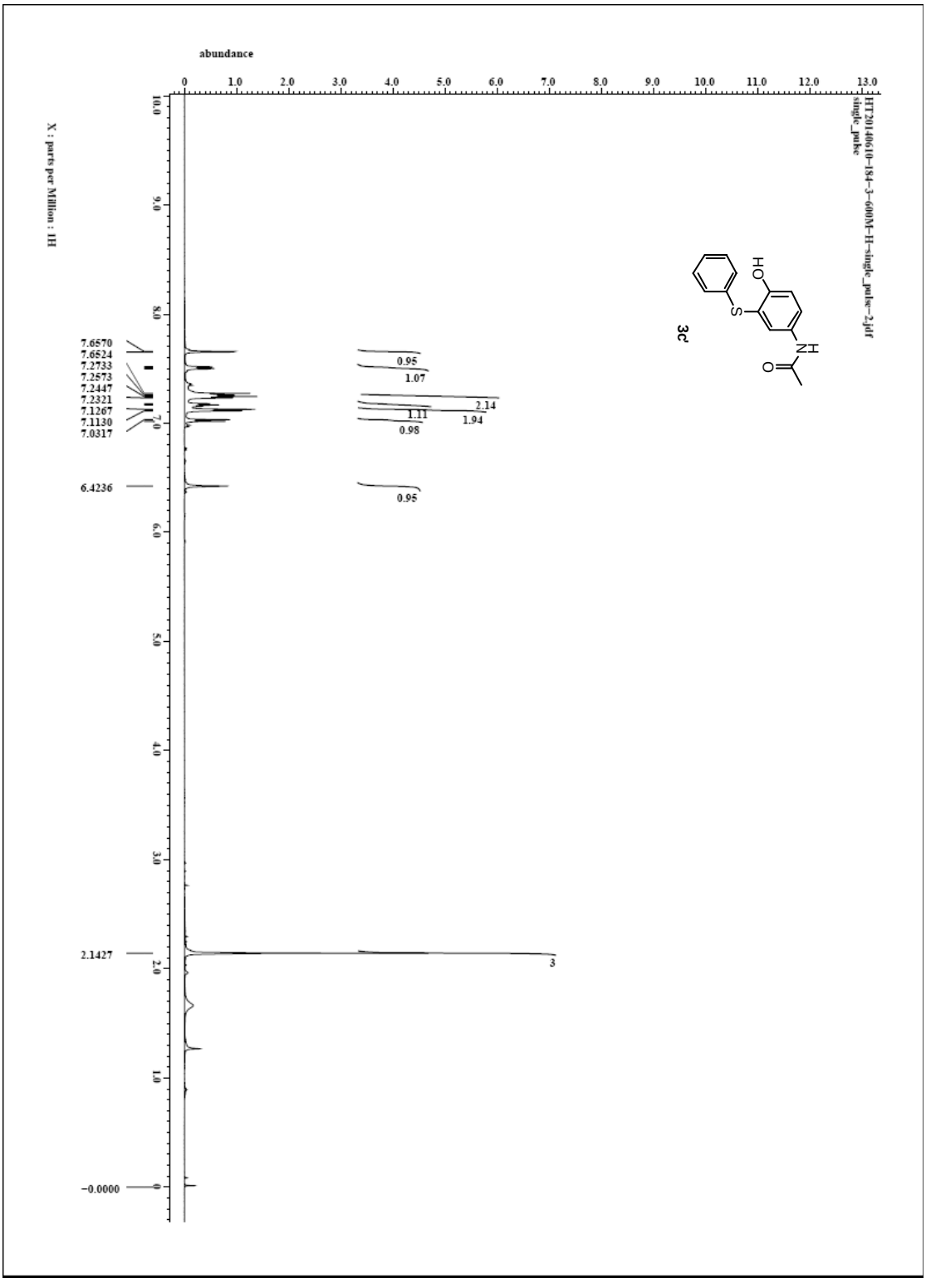

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
X : parts per Million : 13C
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.4698
150.2140
145.1034
137.5520
125.7196
124.1273
120.4947
117.3483
77.4842
77.1600
76.8454
3z
S
OH
NO2

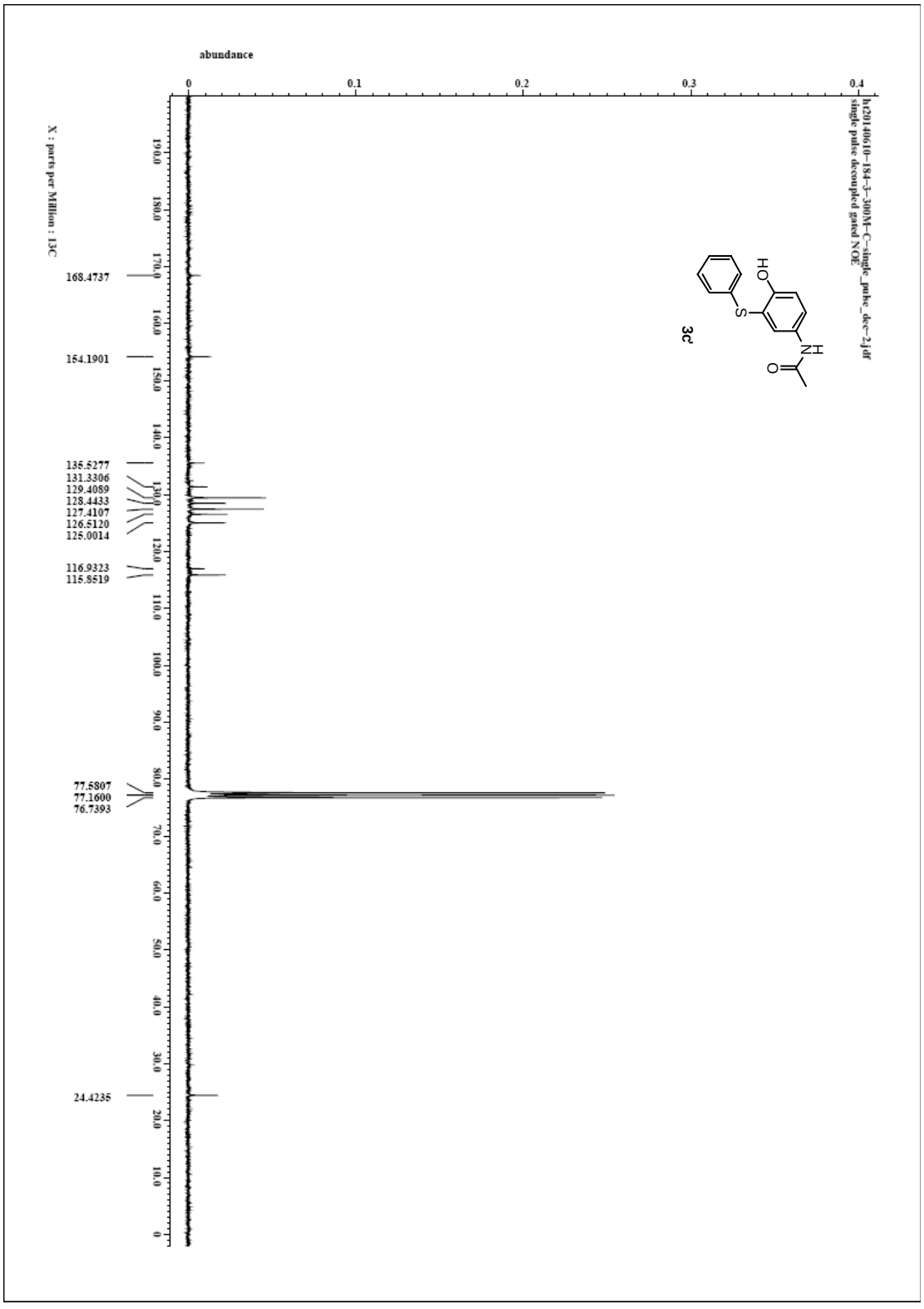

abundance
0
10.0
20.0
30.0
hz20140410-165-3-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.0849
8.0631
7.2601
7.1502
7.1250
7.1020
6.1536
2.2864
2.2761
0.0000
1.98
4.08
0.95
3.01
3a'
OH
S
NO2

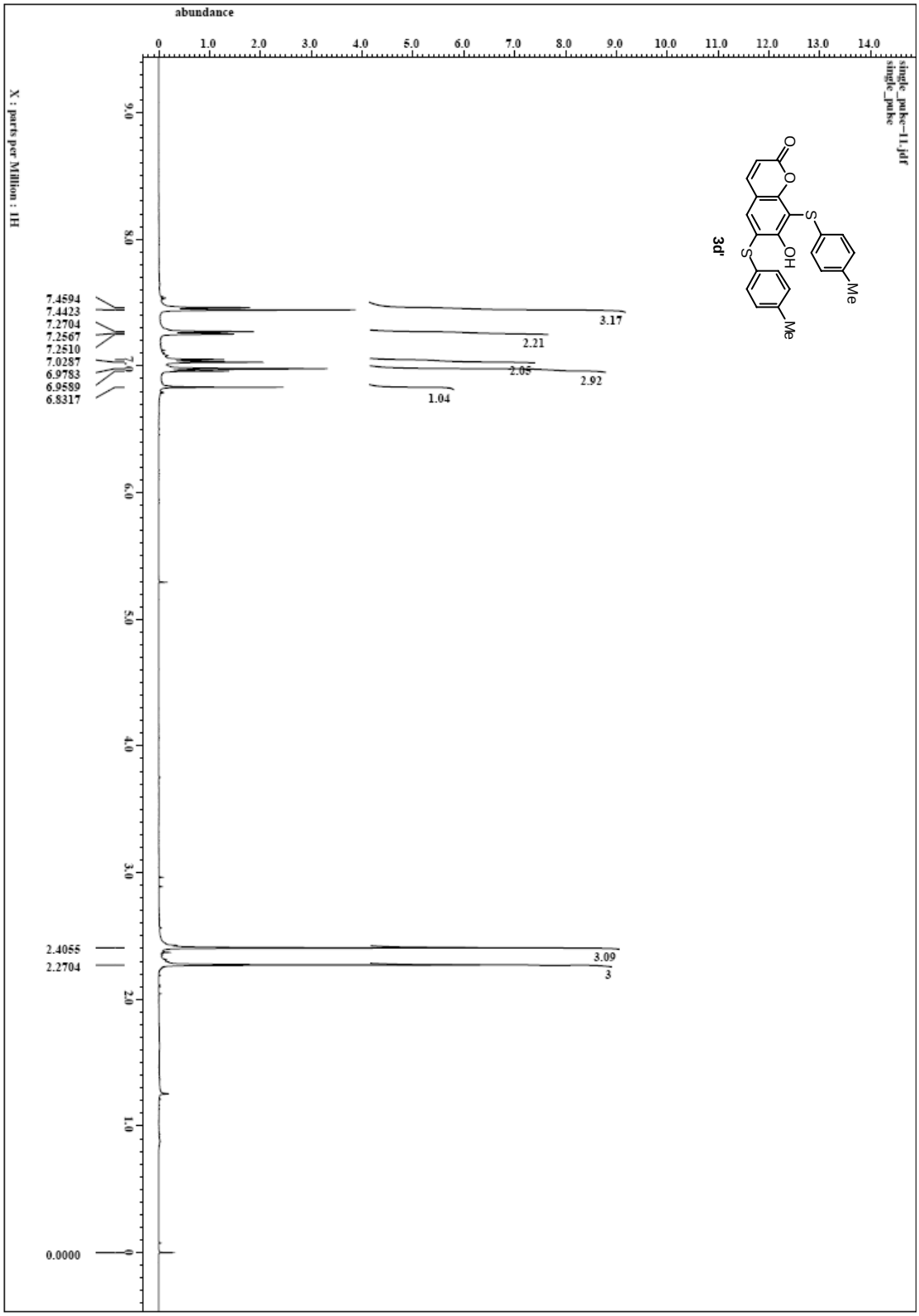

abundance
0
0.1
0.2
0.3
0.4
0.5
hz20140410-165-3-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
153.5320
146.4478
145.8185
135.5974
134.3198
130.7634
125.9961
125.5671
124.3466
112.4952
77.4842
77.1600
76.8454
20.4483
16.5677
OH
S
NO2
3a'

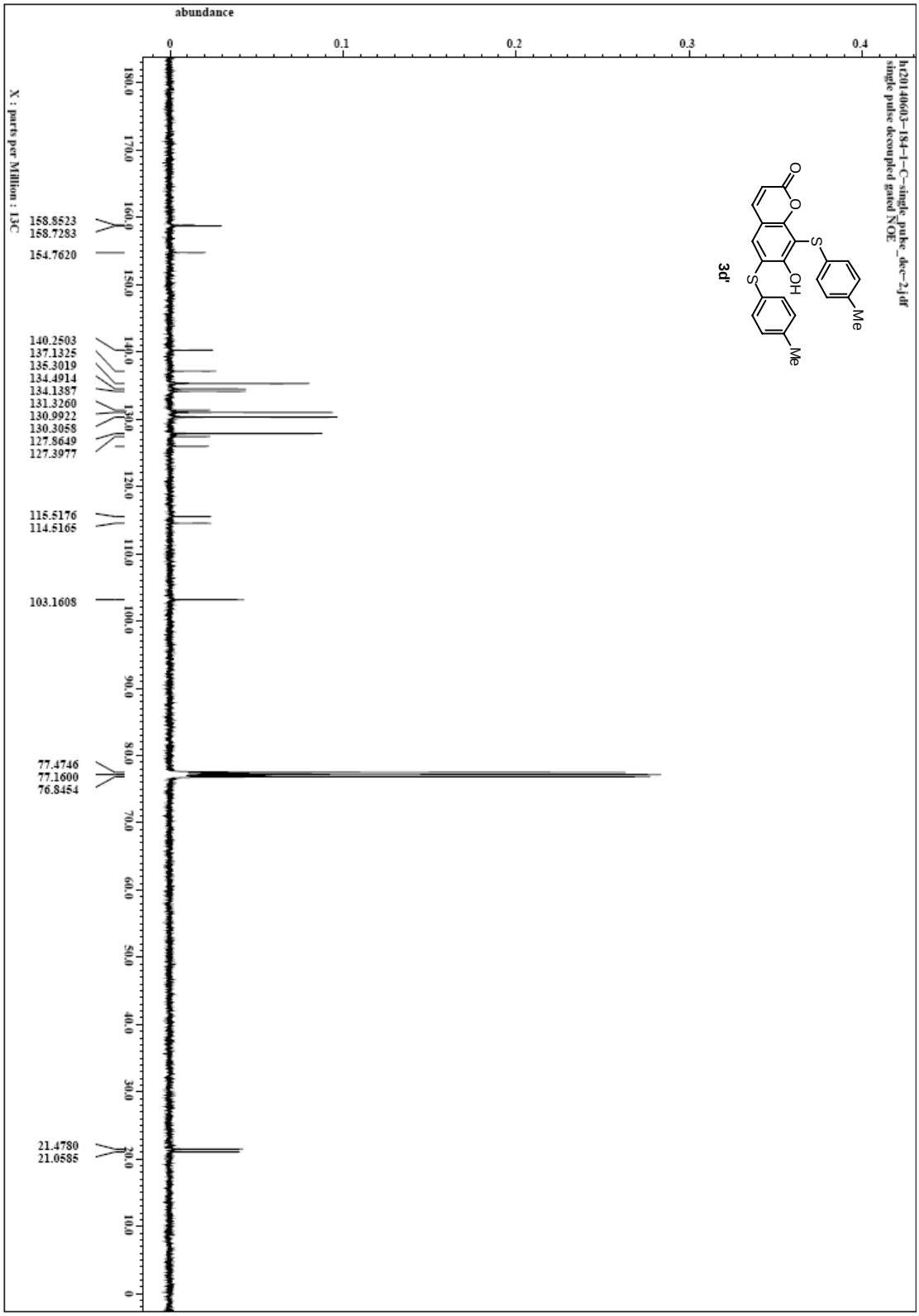

abundance
X : parts per Million : 1H
hz20140403-163-6-H-single_pulse-2.jdf
single_pulse
3b'
8.0780
8.0562
8.0173
7.9955
7.9829
7.9600
7.8615
7.8409
7.4102
7.4079
7.3689
7.3472
7.0803
7.0585
−0.0000
1.07
3.03
1.02
1.05
1.09
0.93
2.02
1
S
HO
NO2

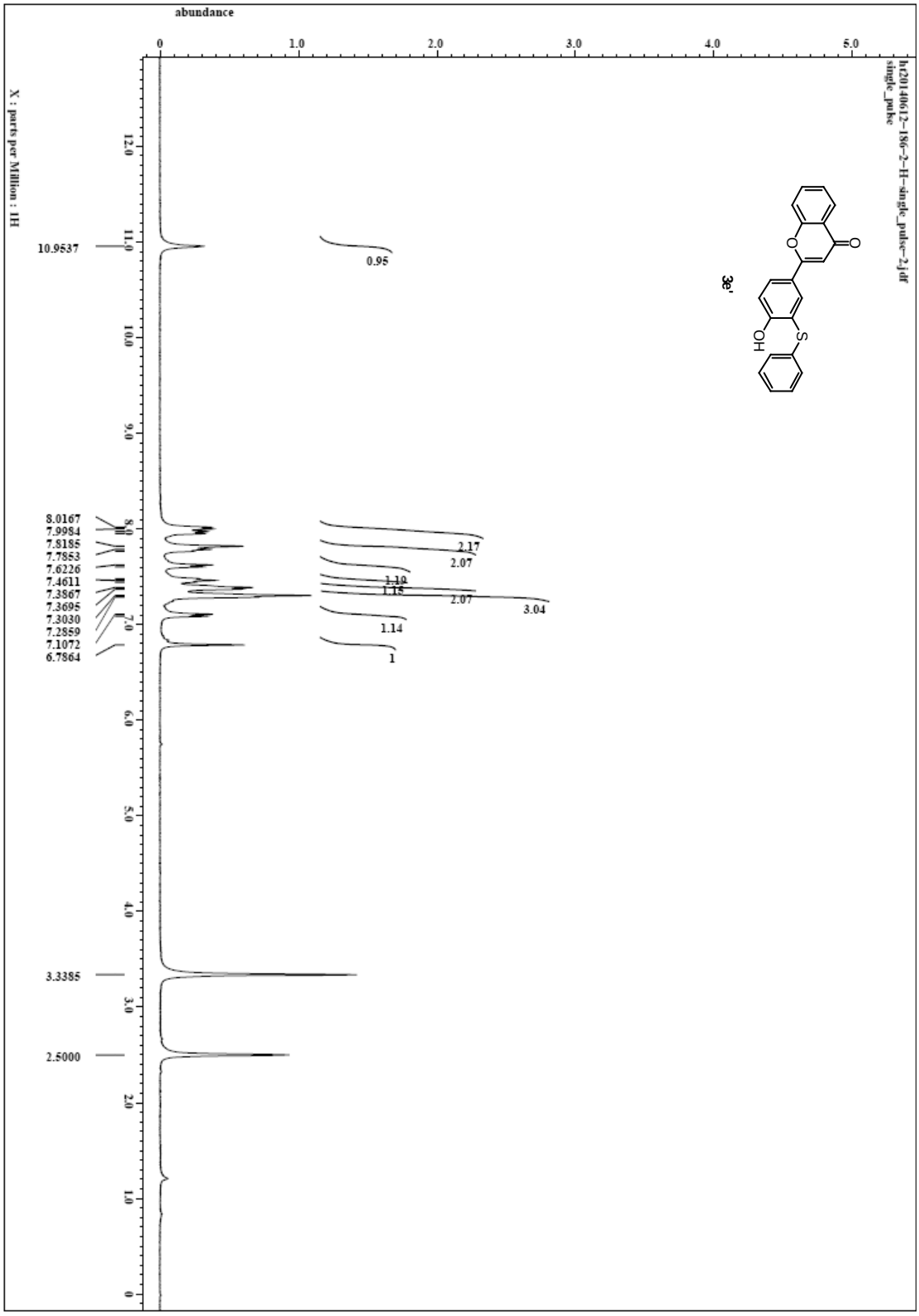

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
hz20140403--163-6-C--single_pulse_dec--2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.4126
145.9329
145.2274
135.0349
133.9956
129.7432
129.0090
128.6181
126.1010
124.4801
124.3943
124.1369
117.2815
105.6684
77.4842
77.1600
76.8454
3b'
S
OH
NO2

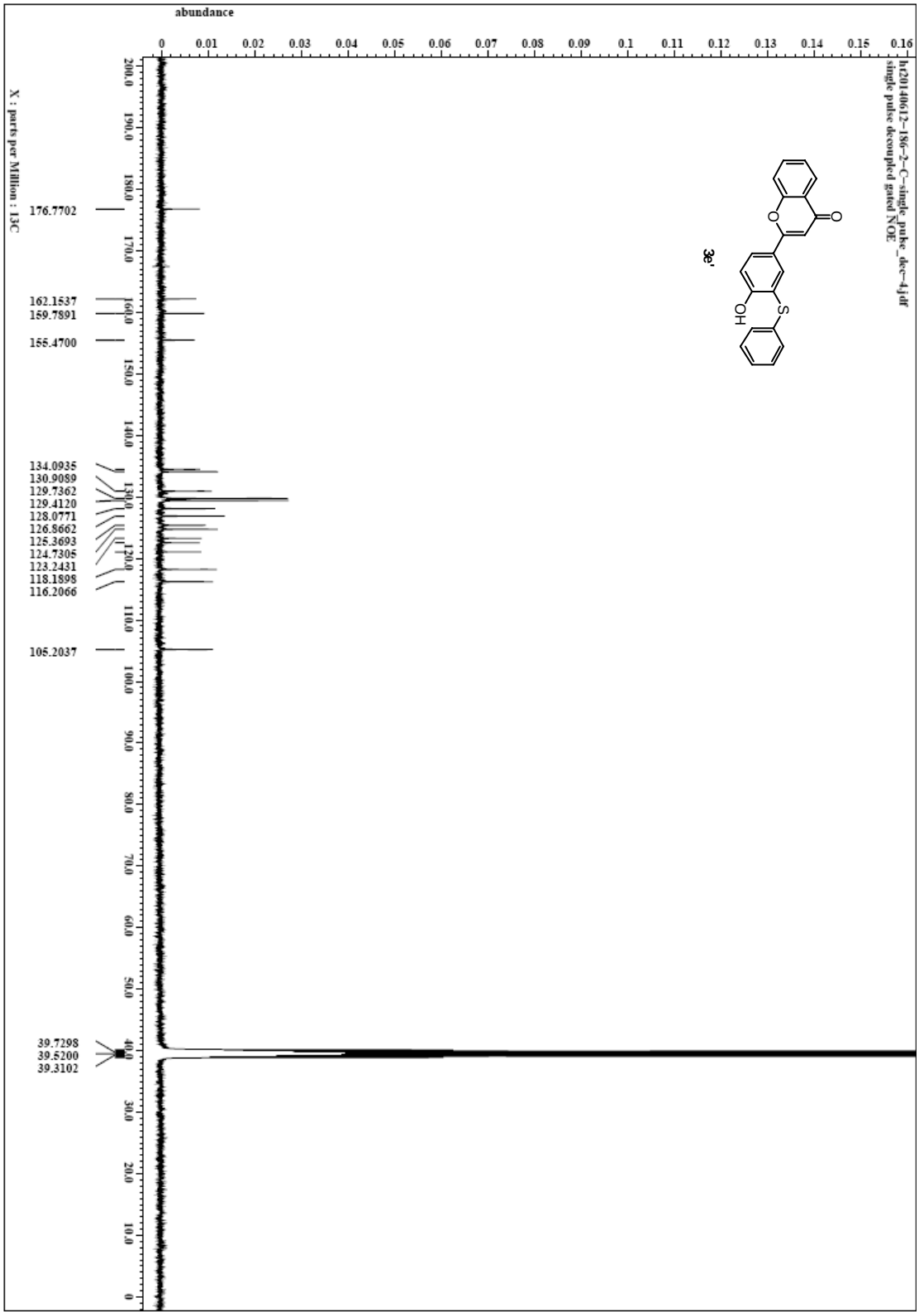

abundance
X : parts per Million : 1H
HT20140610-184-3-600M-H-single_pulse-2.jdf
single_pulse
7.6570
7.6524
7.2733
7.2573
7.2447
7.2321
7.1267
7.1130
7.0317
6.4236
2.1427
−0.0000
0.95
1.07
1.11
2.14
1.94
0.98
0.95
3
3c'


abundance
0
0.1
0.2
0.3
0.4
hr20140610-184-3-300M-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
168.4737
154.1901
135.5277
131.3306
129.4089
128.4433
127.4107
126.5120
125.0014
116.9323
115.8519
77.5807
77.1600
76.7393
24.4235
3c'
OH
S
NH
O


abundance
X : parts per Million : 1H
single_pulse-11.jdf
single_pulse
7.4594
7.4423
7.2704
7.2567
7.2510
7.0287
6.9783
6.9589
6.8317
2.4055
2.2704
0.0000
3.17
2.21
2.05
2.92
1.04
3.09
3
3d'
OH
Me
Me


abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
158.8523
158.7283
154.7620
140.2503
137.1325
135.3019
134.4914
134.1387
131.3260
130.9922
130.3058
127.8649
127.3977
115.5176
114.5165
103.1608
77.4746
77.1600
76.8454
21.4780
21.0585
3d'
OH
S
S
Me
Me
O
O


abundance
0
1.0
2.0
3.0
4.0
5.0
X : parts per Million : 1H
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.9537
8.0167
7.9984
7.8185
7.7853
7.6226
7.4611
7.3867
7.3695
7.3030
7.2859
7.1072
6.7864
3.3385
2.5000
0.95
2.17
2.07
1.10
1.15
2.07
3.04
1.14
1
3e'
O
O
HO
S
hz20140612-186-2-1H-single_pulse-2.jdf
single_pulse


abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
176.7702
162.1537
159.7891
155.4700
134.0935
130.9059
129.7362
129.4120
128.0771
126.8662
125.3693
124.7305
123.2431
118.1898
116.2066
105.2037
39.7298
39.5200
39.3102
hz20140612-186-2-C--single_pulse_dec--4.jdf
single pulse decoupled gated NOE
3e'
O
O
HO
S