ELECTRONIC SUPPORTING INFORMATION

Au@Zirconium-Phosphonate Nanoparticles as Effective Catalytic System for the Chemoselective and Switchable Reduction of Nitroarenes

Francesco Ferlin,[a] Matteo Cappelletti,[a] Riccardo Vivani,[b] Monica Pica,*[b] Oriana Piermatti,*[a] and Luigi Vaccaro*[a]

[a]Laboratory of Green S.O.C. – Dipartimento di Chimica, biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, 06123 – Perugia – Italia; E-mail: luigi.vaccaro@unipg.it; Web: www.dcbb.unipg.it/greensoc

[b] Dipartimento di Scienze Farmaceutiche, Università di Perugia, Via del Liceo, 1, 06123 Perugia, Italy

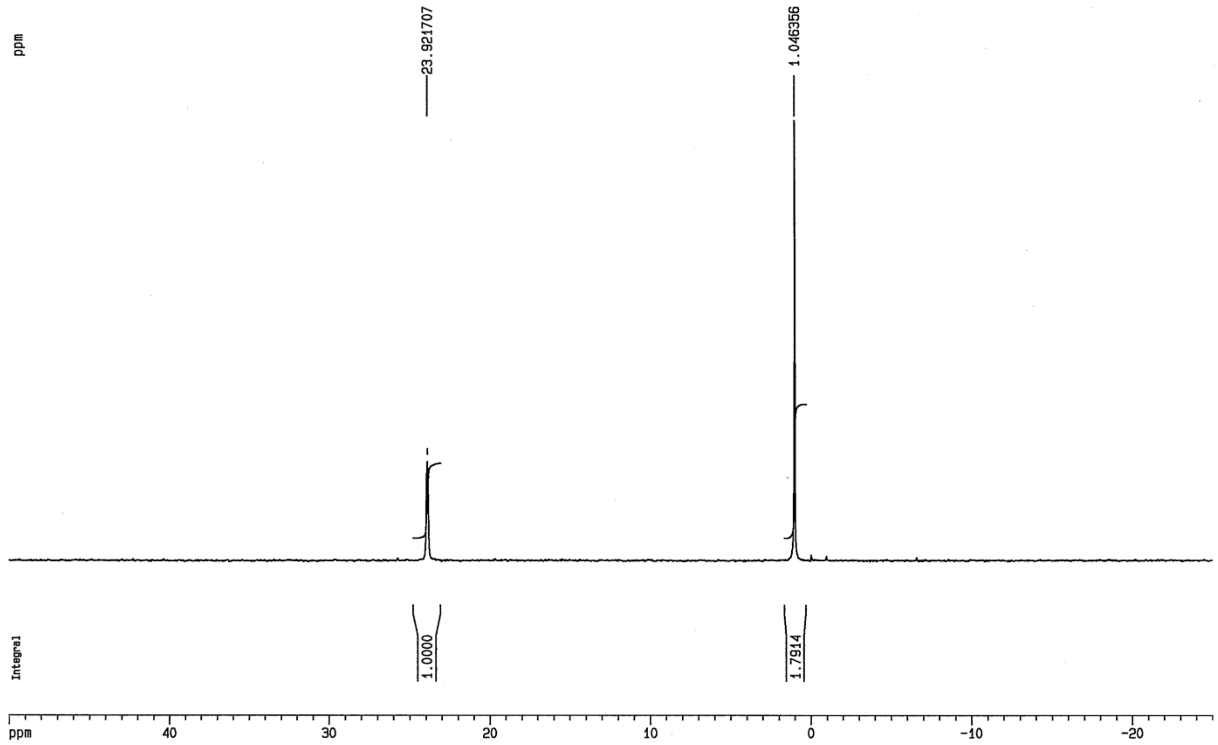


Figure S1a. ^{31}PNMR spectra of ZP(AEP)$_{0.72}$

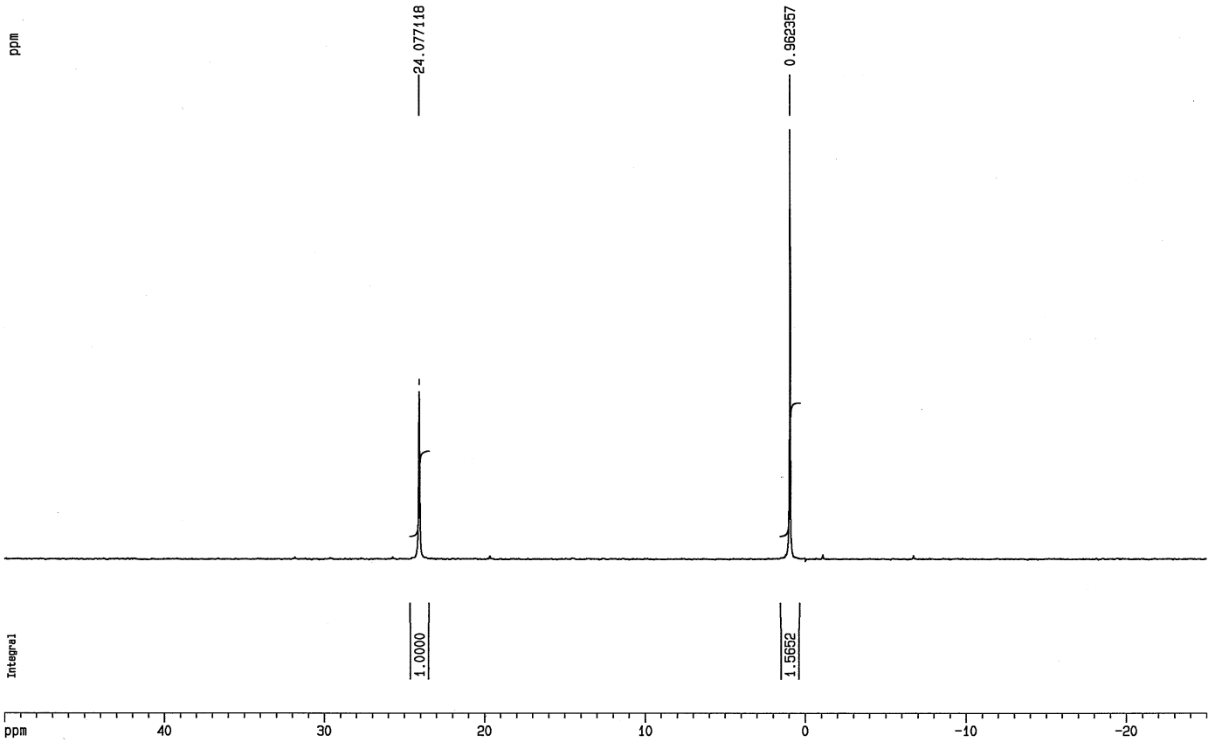


Figure S1b. ^{31}PNMR spectra of ZP(AEP)$_{0.78}$

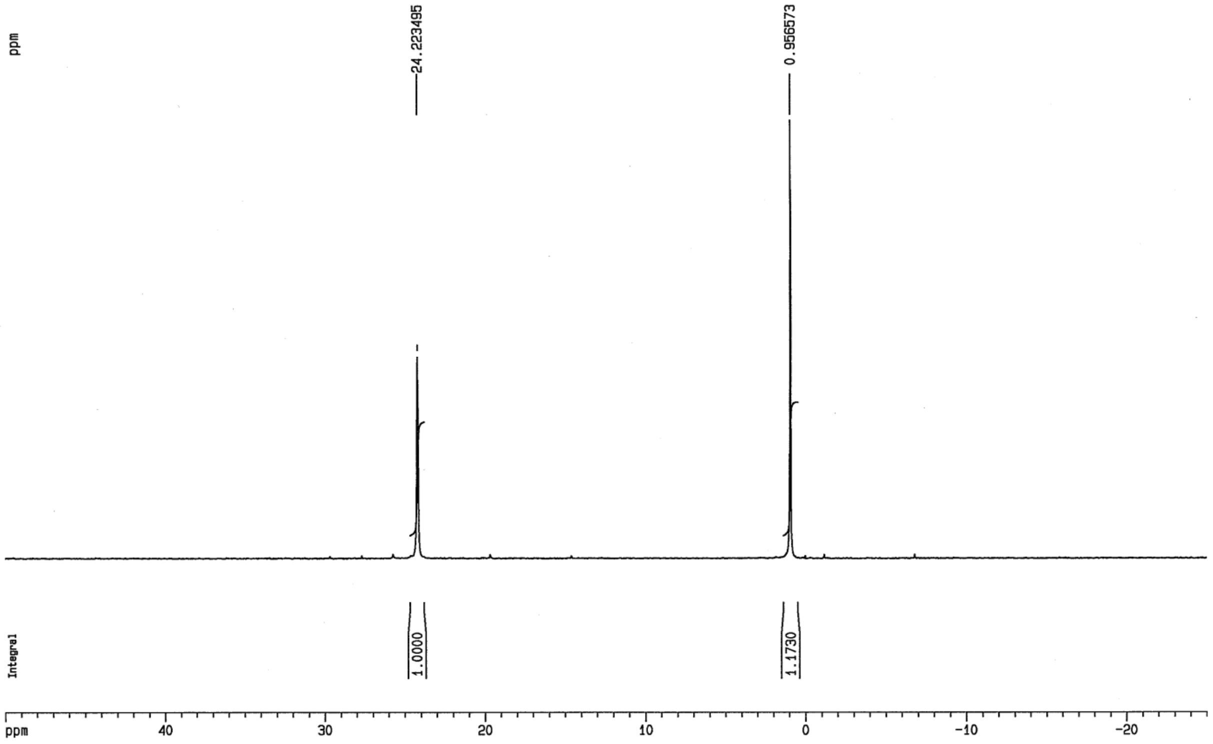


Figure S1c. ^{31}PNMR spectra of ZP(AEP)$_{0.92}$

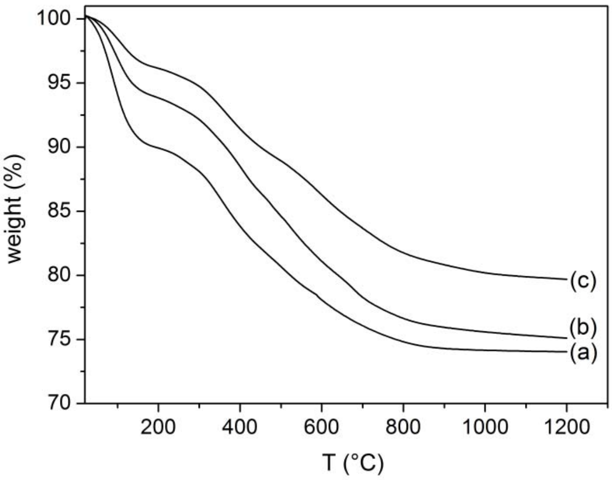


Figure S2. Thermogravimetric curves of ZP(AEP)$_{0.72}$ (a); ZP(AEP)$_{0.78}$ (b); ZP(AEP)$_{0.93}$ (c)

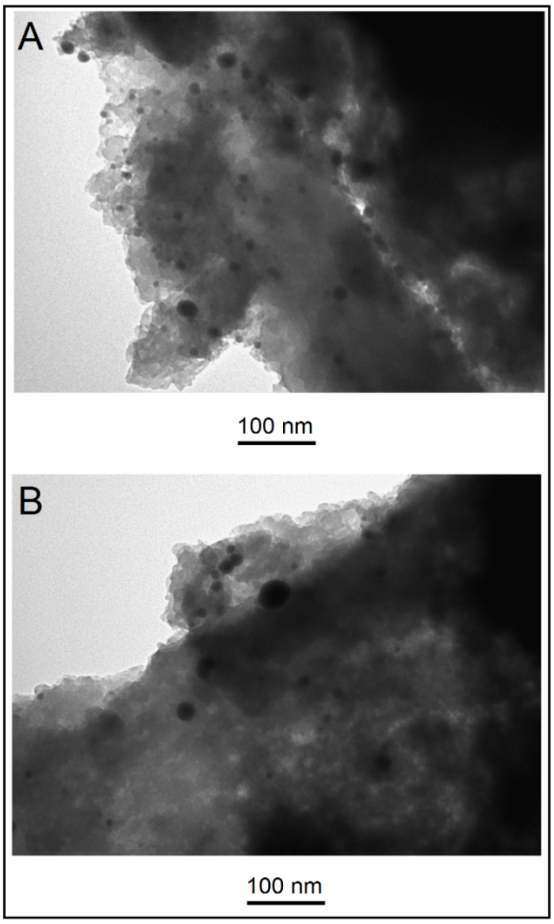
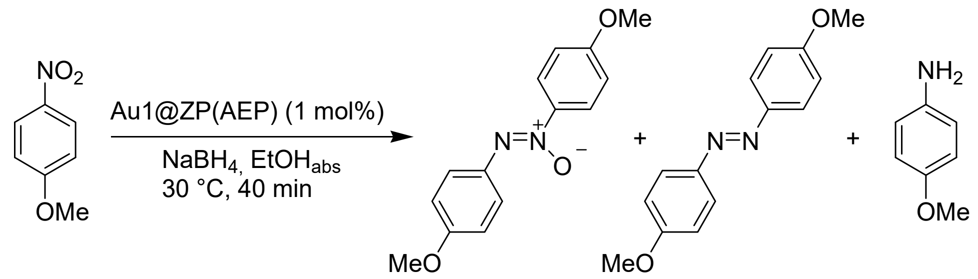


Figure S3. Representative TEM image of Au1@ZP(AEP) after five runs in EtOH 96 % (A) and EtOH abs (B) under batch conditions.

Table S1. Recovery and reuse of catalyst in $EtOH_{abs}$ at 30 °C for a reaction time of 40 min.



1a **2a** **3a** **4a**

Entry[a]	**Run**	**Medium**	**C (%)**[b]	**2:3:4 ratio**[b]
1	Run 1	$EtOH_{abs}$	95	3:1:96
2	Run 2	$EtOH_{abs}$	94	7:1:92
3	Run 3	$EtOH_{abs}$	95	11:1:88
4	Run 4	$EtOH_{abs}$	95	14:1:85
5	Run 5	$EtOH_{abs}$	94	19:1:80

[a] Reaction condition: **1** (0.1 mmol), Au1@ZP(AEP) (1 mol%), $NaBH_4$ (6 eq), reaction medium: $EtOH_{abs}$ (1.8 mL), at 30 °C for 40 min. [b] Conversion and product ratios determined by GLC analyses.

Typical procedure for a sustainable protocol for the preparation of 4a under flow conditions

A premixed mixture of **1a** (1.53 g, 10 mmol), $NaBH_4$ (1.13 g, 3 eq) and and EtOH abs. (40 mL)) was charged into a glass column functioning as a reservoir. The equipment was connected, by using the appropriate valves, to a pump and installed into a box thermostated at 30 °C. The reaction mixture was continuously pumped (flow rate: 0.1 mL·min-1; residence time: 50 min) through the catalyst column (15 cm, stainless steel HPLC column) equipped with a 120 psi back pressure regulator, and the reaction was monitored by GC. Product was collected in fractions and gold content in the EtOH solution was periodically measured by ICP-OES analysis. After completion 20 mL of EtOH was used to wash the catalyst inside the reactor. After removal and recovery of the solvent via distillation (90% of solvent recovered) the product was separated simple by washing the residue with cyclopenthyl methyl ether (3 x 15 mL). The solvent was evaporated by distillation (95% of solvent recovered) obtaining the pure product (yield of **4a** 97%). The catalyst inside the column was dried under N_2 flow at 180 °C and reused in the next cycle.

E-factor calculation for product **4a** (yield 97%): E-factor = [1.5 g (4-nitroanisole, **1a**) + 1.13 g ($NaBH_4$) + 32 g (EtOH) + 39 g (CPME) – 1.2 g (4-methoxyaniline, 4**a**) – 29 g (recovered EtOH)] – 37 g (recovered CPME)] / 1.2 g (4-methoxyaniline, **4a**) = 5.4

Typical procedure for a sustainable protocol for the preparation of 2a under flow conditions

A premixed mixture of **1a** (2,29 g, 15 mmol), $NaBH_4$ (1.7 g, 3 eq) and and EtOH 96 %. (60 mL)) was charged into a glass column functioning as a reservoir. The equipment was connected, by using the appropriate valves, to a pump and installed into a box thermostated at 30 °C. The reaction mixture was continuously pumped (flow rate: 0.1 mL·min-1; residence time: 50 min) through the catalyst column (15 cm, stainless steel HPLC column) equipped with a 120 psi back pressure regulator, and the reaction was monitored by GC. Product was collected in fractions and gold content in the EtOH solution was periodically measured by ICP-OES analysis. After completion 20 mL of EtOH was used to wash the catalyst inside the reactor. After removal and recovery of the solvent via distillation (90% of solvent recovered) the product was separated simple by washing the residue with cyclopenthyl methyl ether (3 x 18 mL). The solvent was evaporated by distillation (95% of solvent recovered) obtaining the pure product (yield of **2a** 90%). The catalyst inside the column was dried under N2 flow at 180 °C and reused in the next cycle.

E-factor calculation for product **2a** (yield 90%): E-factor = [2.3 g (4-nitroanisole, **1a**) + 1.7 g ($NaBH_4$) + 47 g (EtOH) + 46 g (CPME) – 3.5 g (azoxyderivative, 2**a**) – 42 g (recovered EtOH)] – 44 g (recovered CPME)] / 3.5 g (4-methoxyaniline, **2a**) = 2.1

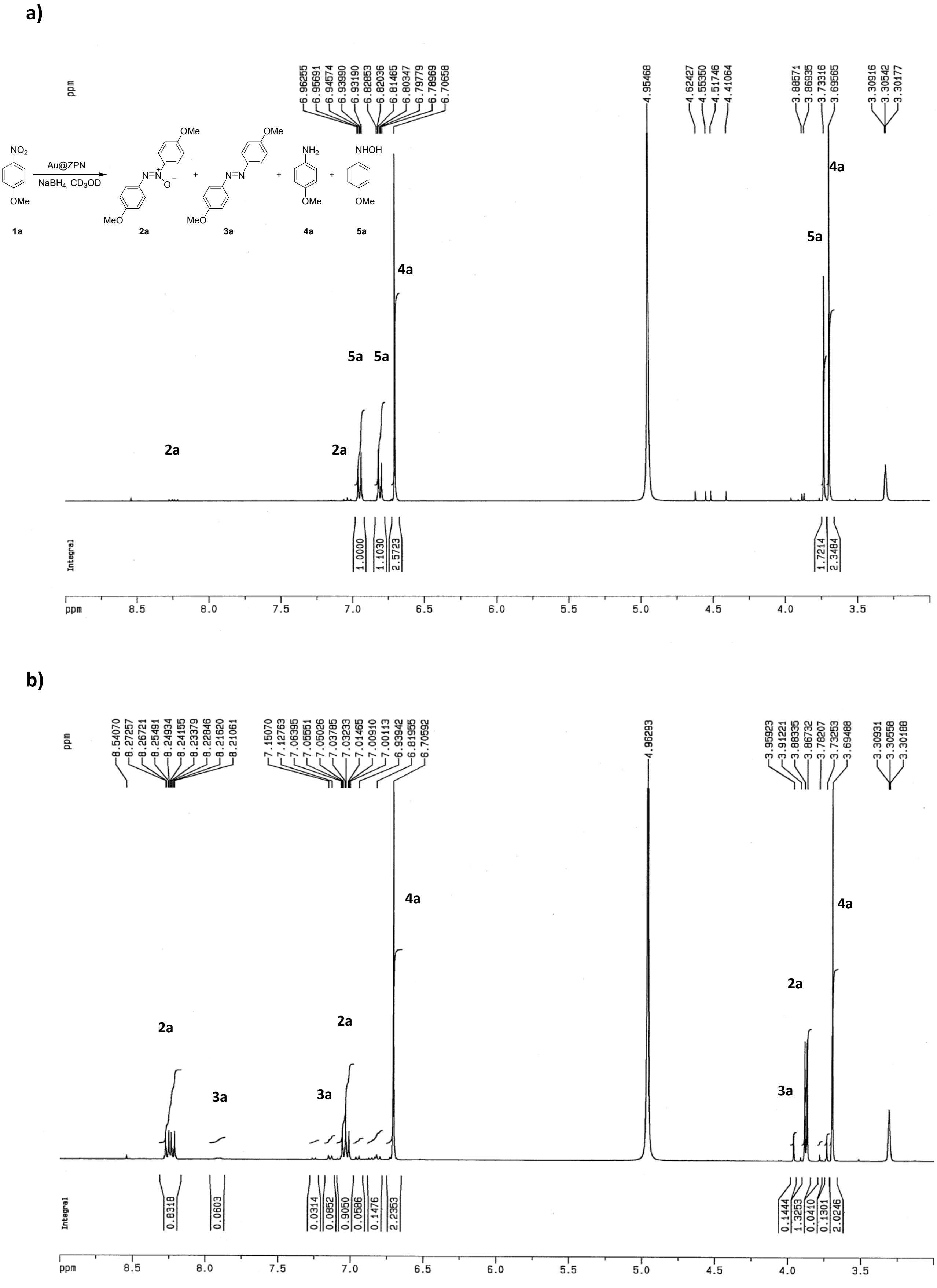
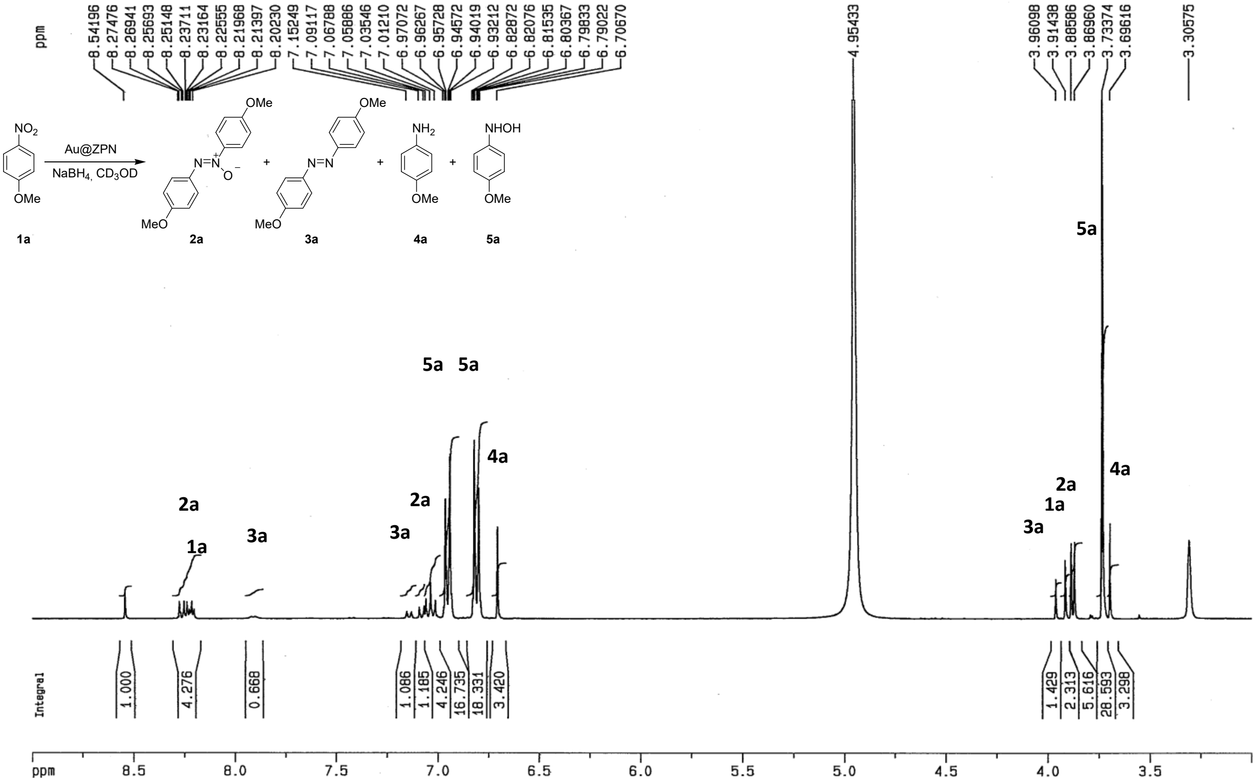
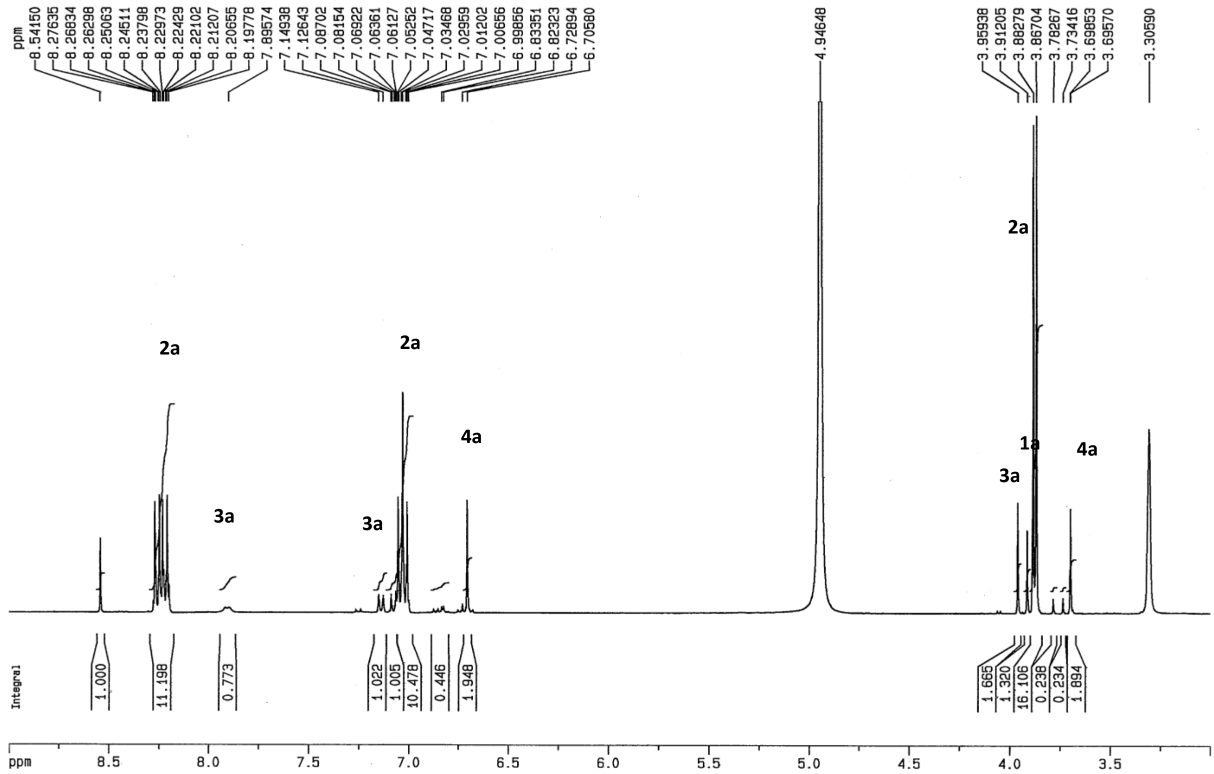


Figure S4: 1H-NMR spectrum of crude mixture of reduction of **1a** in CD_3OD with $NaBH_4$, reaction time 20 min, immediately after filtration on celite (**a**) and after 1h from filtration (**b**)

a)

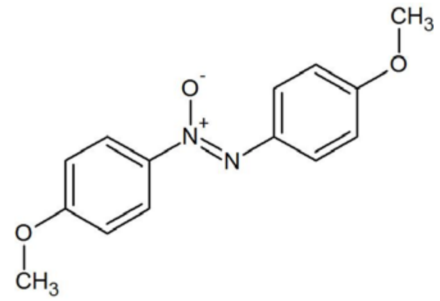

ppm
8.54196
8.27476
8.26941
8.25693
8.25148
8.23711
8.23164
8.22555
8.21968
8.21397
8.20230
7.15249
7.09117
7.06788
7.05886
7.03546
7.01210
6.97072
6.96267
6.95728
6.94572
6.94019
6.93212
6.82872
6.82076
6.81535
6.80367
6.79833
6.79022
6.70670
4.95433
3.96098
3.91438
3.88586
3.86960
3.73374
3.69616
3.30575
NO2
OMe
Au@ZPN
NaBH4, CD3OD
N=N
O
OMe
MeO
N=N
OMe
MeO
NH2
OMe
NHOH
OMe
1a
2a
3a
4a
5a
5a
5a
5a
4a
2a
1a
3a
2a
3a
4a
5a
2a
1a
3a
4a
Integral
1.000
4.276
0.668
1.086
1.185
4.246
16.735
18.331
3.420
1.429
2.313
5.616
28.593
3.298
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

b)


ppm
8.54150
8.27635
8.26834
8.26298
8.25063
8.24511
8.23798
8.22973
8.22429
8.22102
8.21207
8.20655
8.19778
7.89574
7.14938
7.12643
7.08702
7.08154
7.06922
7.06361
7.06127
7.05252
7.04717
7.03468
7.02959
7.01202
7.00656
6.99856
6.83351
6.82323
6.72894
6.70580
4.94640
3.95938
3.91205
3.88279
3.86704
3.78267
3.73416
3.69853
3.69570
3.30590
2a
3a
2a
3a
4a
2a
3a
1a
4a
Integral
1.000
11.198
0.773
1.022
1.005
10.478
0.446
1.948
1.665
1.320
16.106
0.238
0.234
1.894
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

FigureS5: ^{1}H-NMR spectrum of crude mixture of reduction of **1a** in CD_3OD/D_2O (96:4) with $NaBH_4$, reaction time 20 min, immediately after filtration on celite (**a**) and after 1h from filtration (**b**).

4,4'-dimetoxy-azoxybenzene (2a) [1-2]



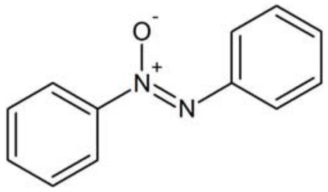
Yellow pale solid, mp 117-119 °C.

^{1}HNMR ($CDCl_3$, 400 MHz) δ: 3.869 (s, 3H), 3.872 (s, 3H), 6.95 (d, 2H, J = 8.9 Hz), 6.97 (d, 2H, J = 8.7 Hz), 8.24 (d, 2H, J = 9.1 Hz), 8.28 (d, 2H, J = 9.1 Hz).

^{13}CNMR ($CDCl_3$, 100.6 MHz) δ: 55.4, 55.6, 113.5 (2C), 113.7 (2C), 123.7 (2C), 127.8 (2C), 137.9, 141.6, 160.1, 161.8.

GC-MS (m/z): 258 (100), 215 (7), 137 (10), 121 (70), 107 (57), 92 (29), 77 (36), 64 (21), 52 (9%).

Azoxybenzene (2b)[1-4]



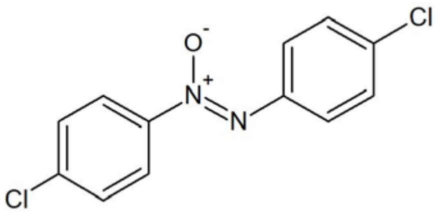
Yellow pale solid, mp 36-37 °C

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.38-7.42 (m, 1H), 7.47-7.59 (m, 5H), 8.17 (d, 2H, J = 7.6 Hz), 8.31 (d, 2H, J = 8.2 Hz).

GC-MS (m/z): 198 (100), 170 (38), 169 (97), 141 (56), 115 (25), 105 (65), 91 (100), 77 (100), 65 (92), 64 (72), 51 (100).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 122.3 (2C), 125.5 (2C), 128.7 (2C), 128.8 (2C), 129.6, 131.6, 143.9, 148.3.

4,4'-dichloro-azoxybenzene (2c) [1-4]



Yellow pale solid, mp 152-155 °C

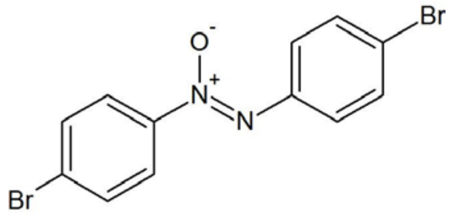
^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.44 (d, 2H, J = 8.8 Hz), 7.48 (d, 2H, J = 8.8 Hz), 8.16 (d, 2H, J = 8.8 Hz), 8.25 (d, 2H, J

= 8.8 Hz).

^{13}C-NMR (CDCl$_3$, 100.6 MHz) δ: 123.7 (2C), 127.1 (2C), 128.9 (2C), 129.0 (2C), 135.2, 138.0, 142.2, 146.5.

GC-MS (m/z): 268 (29), 266 (44), 203 (11), 168 (9), 139 (18), 125 (45), 111 (100), 90 (32), 75 (44), 63 (18), 50 (13).

4,4-dibromo-azoxybenzene (2d) [1-4]



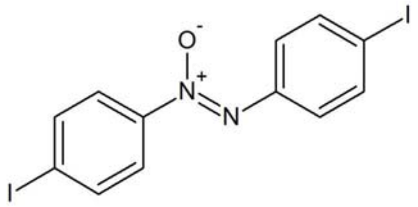
Yellow pale solid, mp 169-171 °C

^{1}H-NMR (CDCl$_3$, 400 MHz) δ: 7.61 (d, 2H, J = 8.8 Hz), 7.66 (d, 2H, J = 9.0 Hz), 8.08 (d, 2H, J = 8.8 Hz), 8.18 (d, 2H, J = 9.0 Hz).

^{13}C-NMR (CDCl$_3$, 100.6 MHz) δ: 123.6, 123.90 (2C), 126.5, 127.2 (2C), 131.98 (2C), 132.04 (2C), 142.6, 147.1.

GC-MS (m/z): 358 (31), 356 (62), 354 (32), 249 (12), 247 (12), 185 (26), 183 (19), 171 (29), 169 (31), 168 (46), 157 (96), 155 (100), 145 (10), 143 (10), 140 (11), 90 (66), 76 (51), 75 (47), 63 (38), 50 (31).

4,4'-diiodo-azoxybenzene (2e) [1,2]



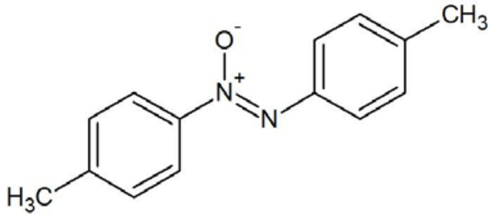
Yellow pale solid, mp 199-200 °C

^{1}H-NMR (CDCl$_3$, 400 MHz) δ: 7.81 (d, 2H, J = 8.8 Hz), 7.5 (d, 2H, J = 8.9 Hz), 7.92 (d, 2H, J = 8.8 Hz), 8.02 (d, 2H, J = 8.9 Hz).

^{13}C-NMR (CDCl$_3$, 100.6 MHz) δ: 95.7, 98.7, 123.9 (2C), 127.2 (2C), 138.0 (2C), 138.1 (2C), 143.1, 147.8.

GC-MS (m/z): 450 (94), 295 (9), 233 (13), 231 (23), 217 (17), 203 (100), 168 (34), 140 (18), 90 (52), 76 (75), 63 (30), 50 (27).

4,4'-dimethyl-azoxybenzene [1-4]



Yellow pale solid, mp 65-68 °C

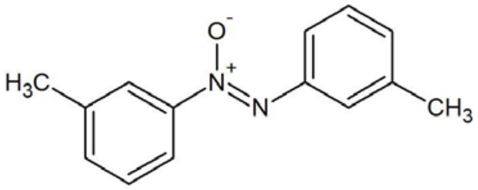
^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.42 (s, 3H), 2.44 (s, 3H), 7.29 (m, 4H), 8.12 (d, 2H, J = 8.4 Hz), 8.19 (d, 2H, J = 8.6 Hz).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 21.3, 21.5, 122.1 (2C), 125.6 (2C), 129.3 (4C), 140.0, 141.8, 141.9, 146.2.

GC-MS (m/z): 226 (48), 198 (47), 183 (21), 155 (8), 119 (9), 105 (24), 104 (38), 91 (100), 79 (34), 77 (35), 65 (50), 51 (11).

3,3'-dimethyl-azoxybenzene [1-4]

$C_{14}H_{14}N_2O$ - 226.274 g/mol - P.f. = liq



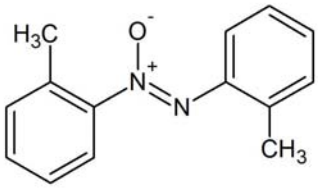
Yellow pale solid, mp 34-36 °C

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.44 (s, 3H), 2.47 (s, 3H), 7.21 (d, 1H, J = 7.4 Hz), 7.35-7.43 (m, 3H), 7.97 (s, 1H), 7.98 (d, 1H, J = 7.4), 8.08-8.11 (m, 2H).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 21.4, 21.5, 119.5, 122.5, 122.8, 126.0, 128.5, 128.6, 130.3, 132.3, 138.4, 139.0, 144.0, 148.4.

GC-MS (m/z): 226 (48), 198 (47), 183 (21), 155 (8), 119 (9), 105 (24), 104 (38), 91 (100), 79 (34), 77 (35), 65 (50), 51 (11).

2,2'-dimethyl-azoxybenzene [1-3]



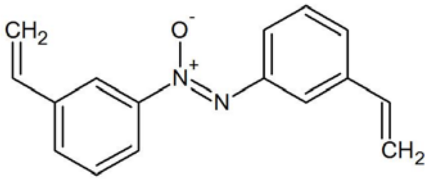
Yellow pale solid, mp 53-56 °C

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.38 (s, 3H), 2.53 (s, 3H), 7.24-7.42 (m, 6H, J = 8.4 Hz), 7.68 (d, 1H, J = 8.7 Hz), 8.04 (d, 1H, J = 7.8 Hz).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 18.39, 18.42, 121.5, 123.6, 126.0, 126.6, 128.6, 130.0, 130.8, 131.2, 131.8, 134.1, 142.8, 149.5 .

GC-MS (m/z): 226 (32), 225 (45), 211 (92), 209 (33), 194 (7), 183 (9), 168 (10), 119 (7), 104 (32), 91 (100), 79 (27), 77 (26), 65 (52), 51 (13).

3,3'-divinyl azoxybenzene [5]



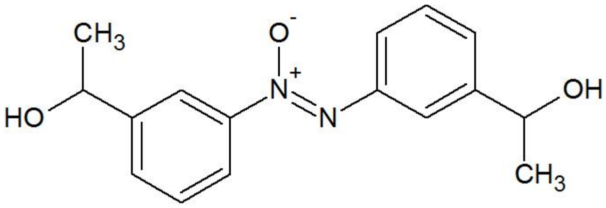
Yellow solid, mp 34-36 °C

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.33 (d, 1H, J = 10.9 Hz), 5.40 (d, 1H, J = 10.9 Hz), 5.84 (d, 1H, J = 17.6 Hz), 5.90 (d, 1H, J = 17.6 Hz), 6.78 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.4 Hz), 6.80 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.4 Hz), 7.40-7.50 (m, 3H), 7.60 (d, 1H, J = 7.6 Hz), 8.09 (m, 1H), 8.18 (m, 1H), 8.20 (s, 1H), 8.34 (s, 1H).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 114.8, 115.9, 119.9, 121.5, 123.4, 124.7, 127.3, 128.8, 128.9, 129.3, 135.5, 136.2, 138.2, 138.6, 144.2, 148.6.

GC-MS (m/z): 250 (75), 222 (33), 221 (100), 208 (2%), 207 (9), 195 (9), 178 (12), 165 (7), 131 (7), 116 (20), 103 (100), 91 (44), 90 (45), 89 (36), 77 (83), 65 (20), 51 (25).

3,3'-di(1-idroxyethyl)azoxybenzene



Yellow pale oil

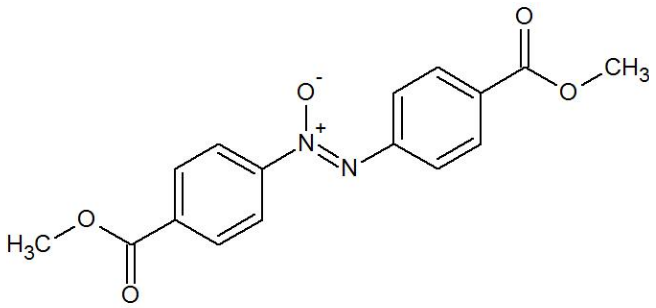
^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.50 (s, 3H), 1.52 (s, 3H), 2.52 (s broad, 2H), 4.94 (m, 2H), 7.37-7.48 (m, 3H), 7.53 (d, 1H, J = 7.6 Hz), 8.04 (d, 1H, J = 7.8 Hz), 8.08 (s, 1H), 8.13 (d, 1H, J = 8.0 Hz), 8.25 (s, 1H).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 25.1, 25.3, 69.7, 70.0, 119.3, 121.2, 122.7, 124.3, 126.7, 128.6, 128.8, 128.9, 143.9, 146.5, 147.1, 148.2.

GC-MS (m/z): 286 (41), 270 (4), 242 (5), 195 (5), 181 (15), 169 (8), 149 (8), 121 (88), 103 (100), 93 (30), 91 (24), 77 (56), 65 (20), 51 (11).

4,4'-(metoxycarbonyl)azoxybenzene [3,4]

$C_{16}H_{14}N_2O_5$ - 314.293 g/mol - P.f. = 197-200 °C



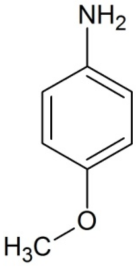
Yellow pale solid, mp 197-200 °C

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.95 (s, 3H), 3.97 (s, 3H), 8.14-8.20 (m, 6H), 8.38 (d, 2H, J = 8.6 Hz).

^{13}C-NMR ($CDCl_3$, 100.6 MHz) δ: 52.3, 52.6, 122.5 (2C), 125.3 (2C), 130.2 (2C), 130.4 (2C), 130.7, 133.3, 146.9, 150.9, 165.7, 166.2.

GC-MS (m/z): 314 (27), 298 (13), 283 (11), 227 (7), 163 (20), 151 (10), 135 (100), 120 (22), 119 (18), 104 (28), 103 (30), 90 (10), 76 (34), 63 (15), 59 (14), 50 (13).

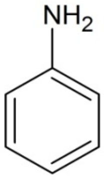
4-metoxyaniline (4a) [6-8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.21 (s broad, 2H), 3.74 (s, 3H), 6.64 (d, 2H, J = 8.8 Hz), 6.75 (d, 2H, J = 8.8 Hz).

GC-MS (m/z): 123 (70%), 109 (7), 108 (100%), 80 (53), 65 (5), 53 (15%).

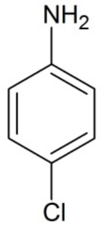
Aniline (4b) [4,6-8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.47 (s broad, 2H), 6.70 (m, 2H), 6.77 (m, 1H), 7.16 (m 1H).

GC-MS (m/z): 93 (100), 77 (7), 66 (35), 65 (21), 61 (10), 51 (10).

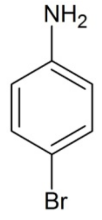
4-chloroaniline (4c) [4, 6-8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.99 (s broad, 2H), 6.61 (d, 2H, J = 8.8 Hz), 7.10 (d, 2H, J = 8.8 Hz).

GC-MS (m/z): 129 (33), 127 (100), 102 (2%), 100 (9), 92 (13), 65 (12), 63 (5%).

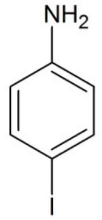
4-bromoaniline (4d) [4,6,8]



^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 3.52 (s broad, 2H), 6.56 (d, 2H, J = 8. 8 Hz), 7.24 (d, 2H, J = 8.8 Hz).

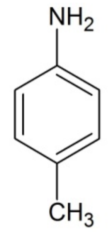
GC-MS (m/z): 173 (100), 171 (100), 145 (11), 143 (11), 119 (8), 117 (8), 92 (100), 91 (42), 74 (14), 66 (31), 65 (100), 64 (44%), 63 (70), 62 (36), 61 (23), 52 (29), 51 (13), 50 (23).

4-iodoaniline (4e) [8]



GC-MS (m/z): 219 (100), 127 (12), 92 (42), 65 (43), 63 (11), 62 (6), 52 (5).

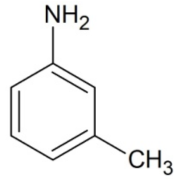
4-methylaniline (4f) [4,7,8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.24 (s, 3H), 3.30 (s broad, 2H), 6.62 (d, 2H, J = 7.9 Hz), 6.97 (d, 2H, J = 7.9 Hz).

GC-MS (m/z): 107 (84), 106 (100), 89 (8), 79 (15), 77 (19), 63 (6), 52 (9), 51 (10).

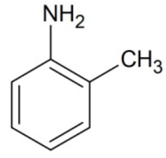
3-methylaniline (4g) [4,8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.26 (s, 3H), 3.49 (s broad, 2H), 6.53-6.62 (m, 3H), 7. 06 (m, 1H)

GC-MS (m/z): 107 (100), 106 (100), 91 (16), 89 (20), 80 (30), 79 (65), 77 (69), 65 (19), 63 (17), 53 (24), 52 (24), 51 (25).

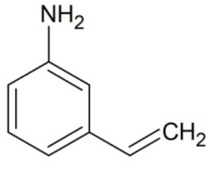
2-methylaniline (4e) [8]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.19 (s, 3H), 3.83 (s broad, 2H), 6.70-6.75 (m, 2H), 7.03-7.07 (m, 2H).

GC-MS (m/z): 107 (100), 106 (100), 91 (4), 80 (10), 79 (16), 77 (24), 63 (6), 53 (10), 52 (12), 51 (12)..

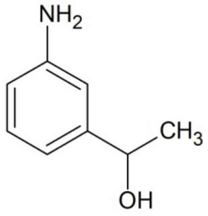
3-vinylaniline (4i) [6,7]



^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.58 (s broad, 2H), 5.20 (dd, 1H, J 10.8, 0.8 Hz), 5.70 (dd, 1H, J = 17.6, 0.9 Hz), 6.58-6.67 (m, 2H), 6.74 (s, broad, 1H), 6.83 (d, 1H, J = 7.6), 7.11 (m, 1H).

GC-MS (m/z): 119 (100), 118 (58), 117 (17), 104 (7), 93 (12), 91 (34), 77 (4), 65 (14), 63 (8), 51 (6%).

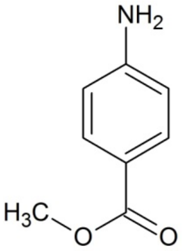
3-(1-idroxyethyl)aniline (4j) [6,7,9]



^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 1.47 (d, 3H, J = 6.4 Hz), 2.73 (s broad, 2H), 4.81 (q, 1H, J = 6.4 Hz), 6.57-6.63 (m, 1H), 6.72-6.77 (m, 2H), 7.14 (m, 1H).

GC-MS (m/z): 137 (44), 122 (23), 94 (100), 93 (17), 91 (6), 77 (26), 65 (15), 51 (5).

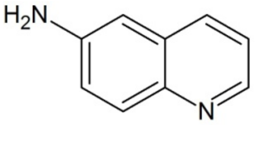
4-(metoxycarbonyl)aniline (4k) [4,6,7]



^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 3.85 (s, 3H), 4.06 (s broad, 2H), 6.63 (d, 2H, J = 8.2 Hz)), 7.85 (d, 2H, J = 8.2 Hz).

GC-MS (m/z): 151 (100), 121 (50), 120 (100), 108 (9), 93 (2), 92 (100), 66 (210, 65 (100%), 63 (37), 52 (18), 51 (6).

6-aminoquinoline (4l) [7]



^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 3,92 (s broad, 2H), 6.89 (d, 1H, J = 2.6 Hz), 7.15 (dd, 1H, J = 9.0, 2.6 Hz), 7.26 (dd, 1H, J = 8.4, 4.2 Hz), 7.89 (dd, 1H, J = 8.4, 1.6 Hz), 7.90 (d, 1H, J = 9.0 Hz), 8.65 (dd, 1H, J = 4.2, 1.6 Hz).

GC-MS (m/z): 145 (100), 144 (100), 127 (8), 118 (53), 117 (100), 116 (100), 91 (27), 90 (100), 89 (100), 72 (46), 63 (75), 52 (32), 51 (21).

References

[1] Y. Liu, B. Liu, A. Guo, Z. Dong, S. Jin, Y. Lu, Molecules 2011, 16, 3563-3568.

[2] Y. Liu, B. Liu, A. Guo, Z. Dong, S. Jin, Y. Lu, *Synth. Commun.* **2012**, *42*, 2201-2206.

[3] N. Sakai, K. Fujii, S. Nabeshima, R. Ikeda, T. Konakahara, *Chem. Commun.* **2010**, *46*, 3173-3175.

[4] X. Liu, S. Ye, H.-Q. Li, Y.-M. Liu, Y. Cao, K.-N. Fan, *Catal. Sci. Technol.* **2013**, *3*, 3200-3206.

[5] J. H. Kim, J. H. Park, Y. K. Chung, K. H. Park, *Adv. Synth. Catal.* **2012**, *354*, 2412-2418.

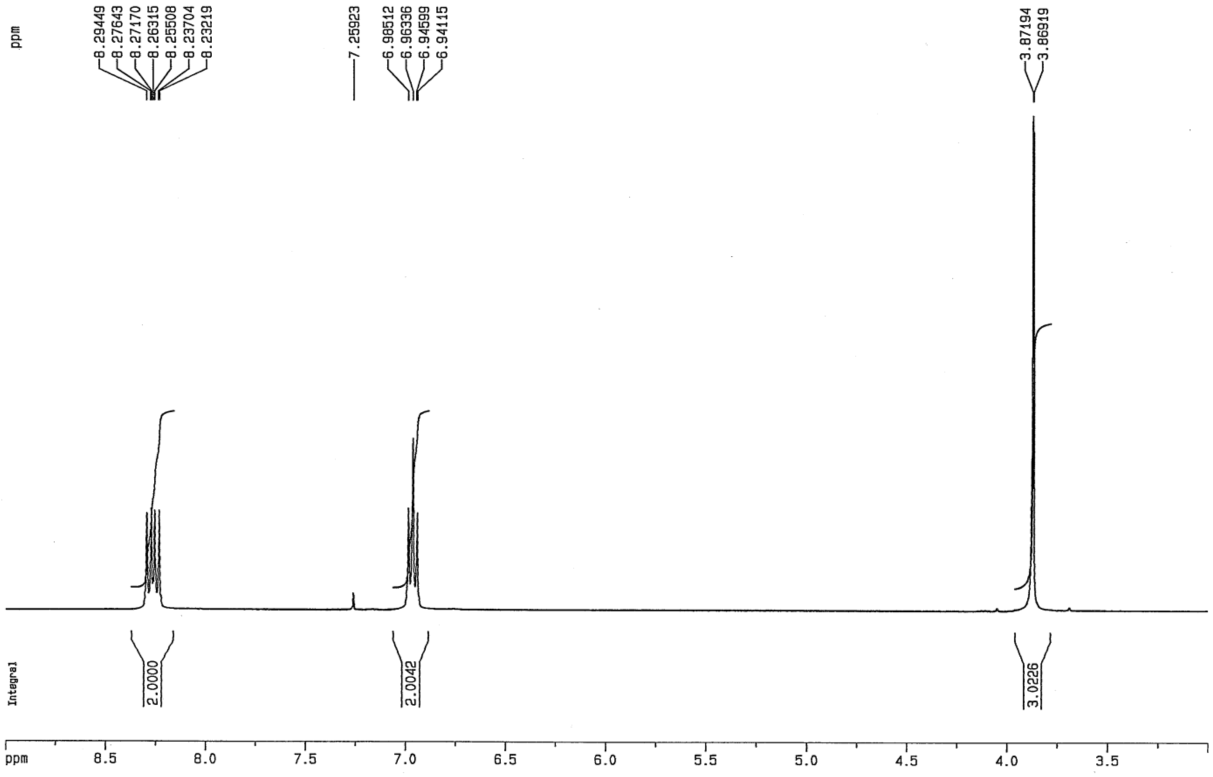
[6] S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas, I. N. Lykakis, *ACS Catal.* **2014**, *4*, 3504-3511

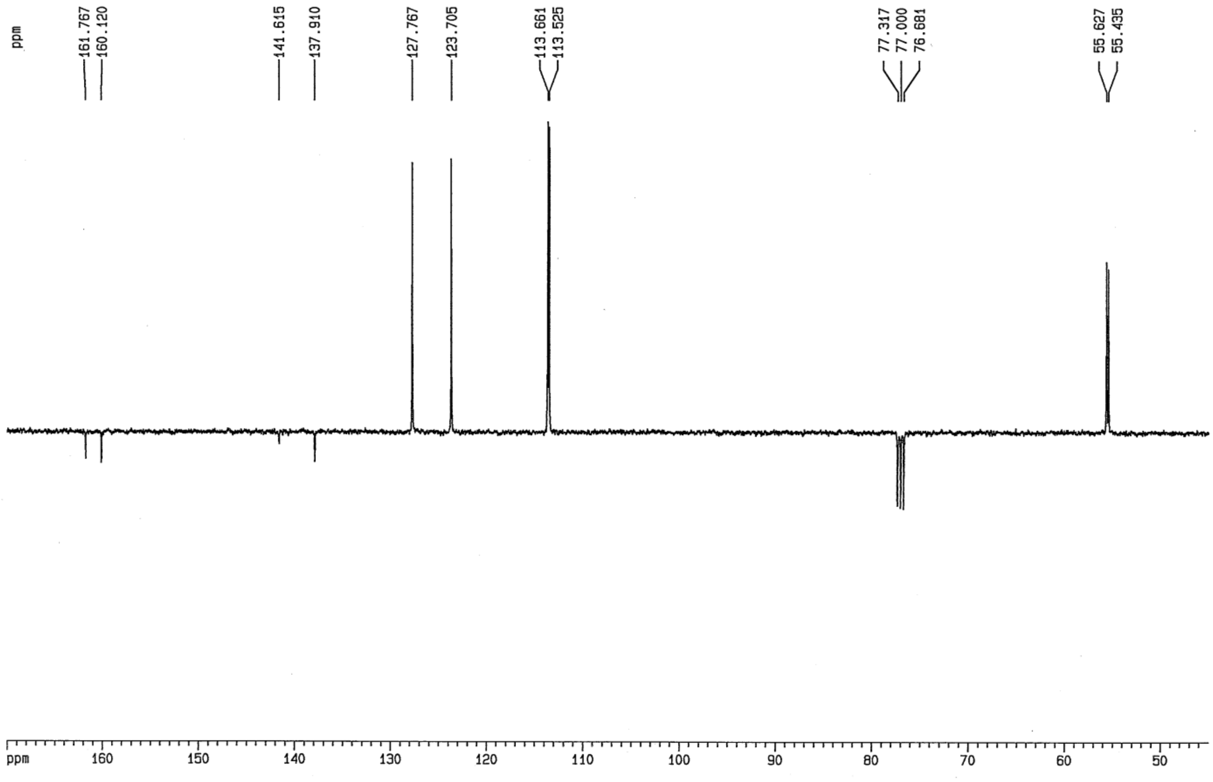
[7] X.-B. Lou, L. He, Y. Qian, Y.-M. Liu, Y. Cao, K.-N. Fan, *Adv. Synth. Catal*. **2011**, *353*, 281-286.

[8] W.-G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, En-H. Sheng, *Organometallics* **2016**, *35*, 503-512.

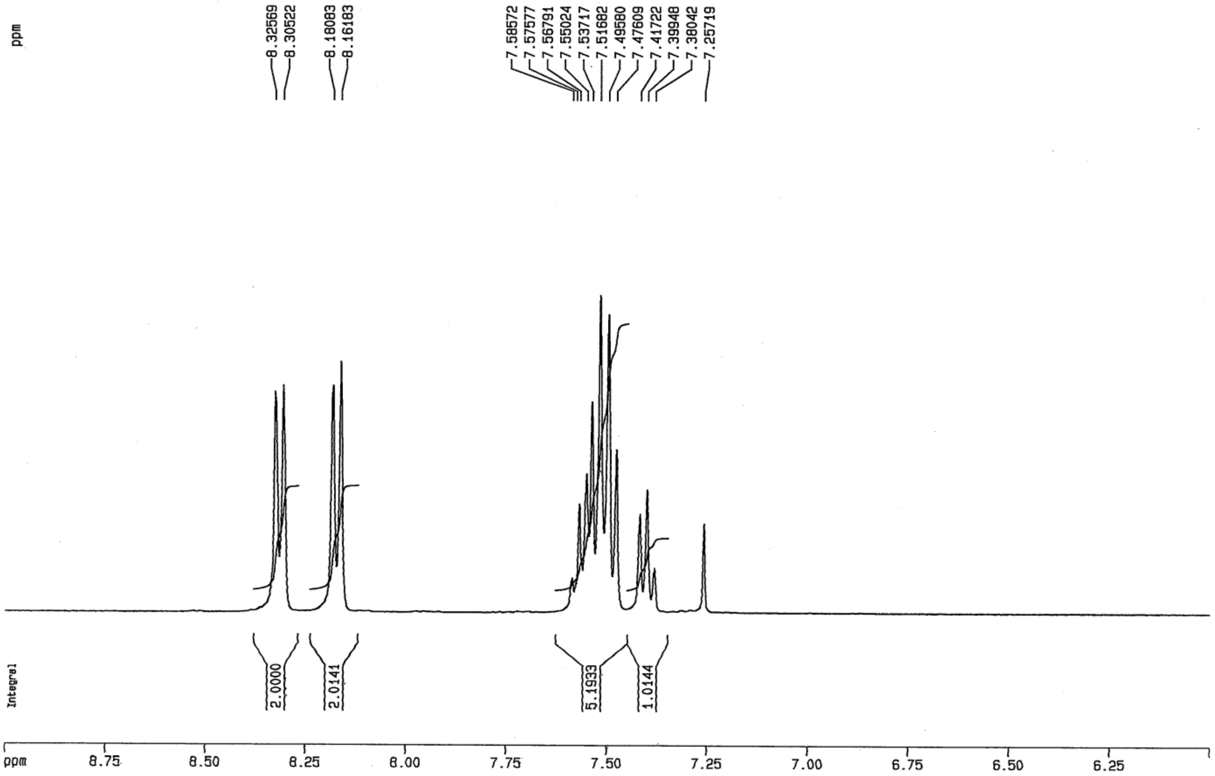
[9] C.-Z. Zhang, H. Yang, D.-L. Wu, G.-Y. Lu, *Cinese J. Chem.* **2007**, *25*, 653-660.

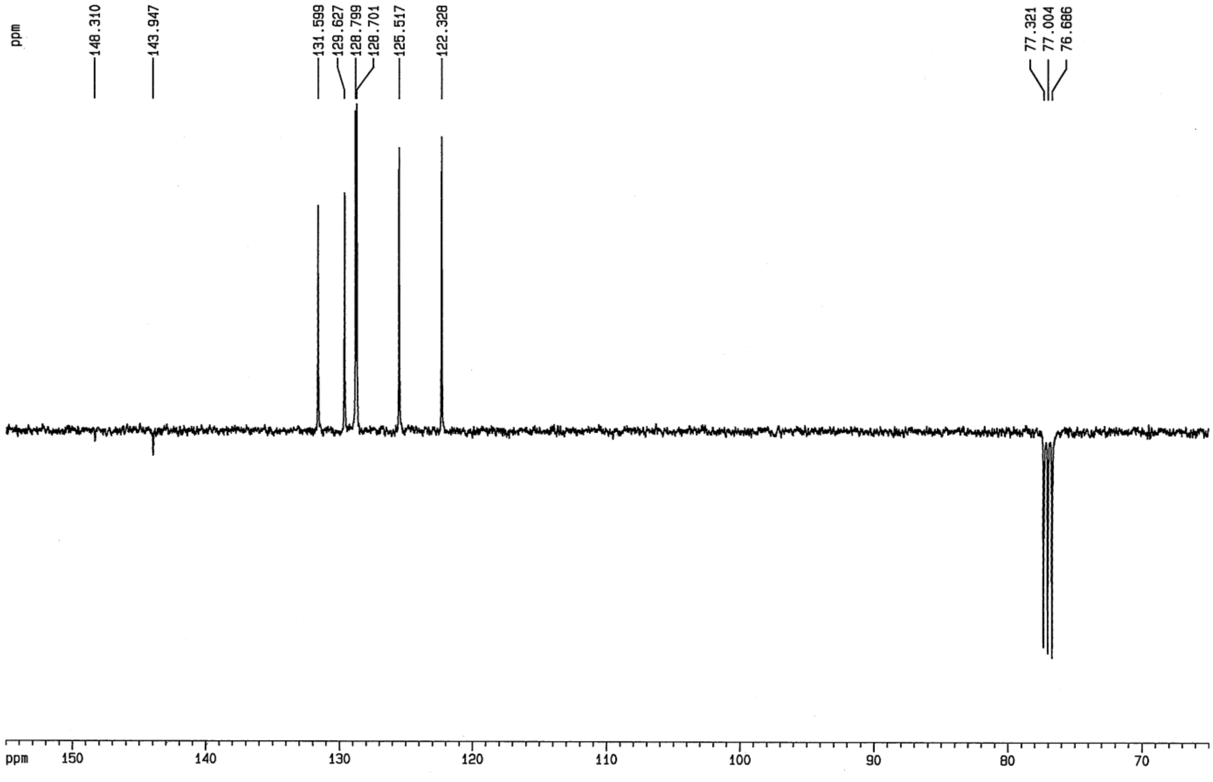
2a: R = 4-OMe


ppm
8.29449
8.27643
8.27170
8.26315
8.25508
8.23704
8.23219
7.25923
6.98512
6.96336
6.94599
6.94115
3.87194
3.86919
Integral
2.0000
2.0042
3.0226
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

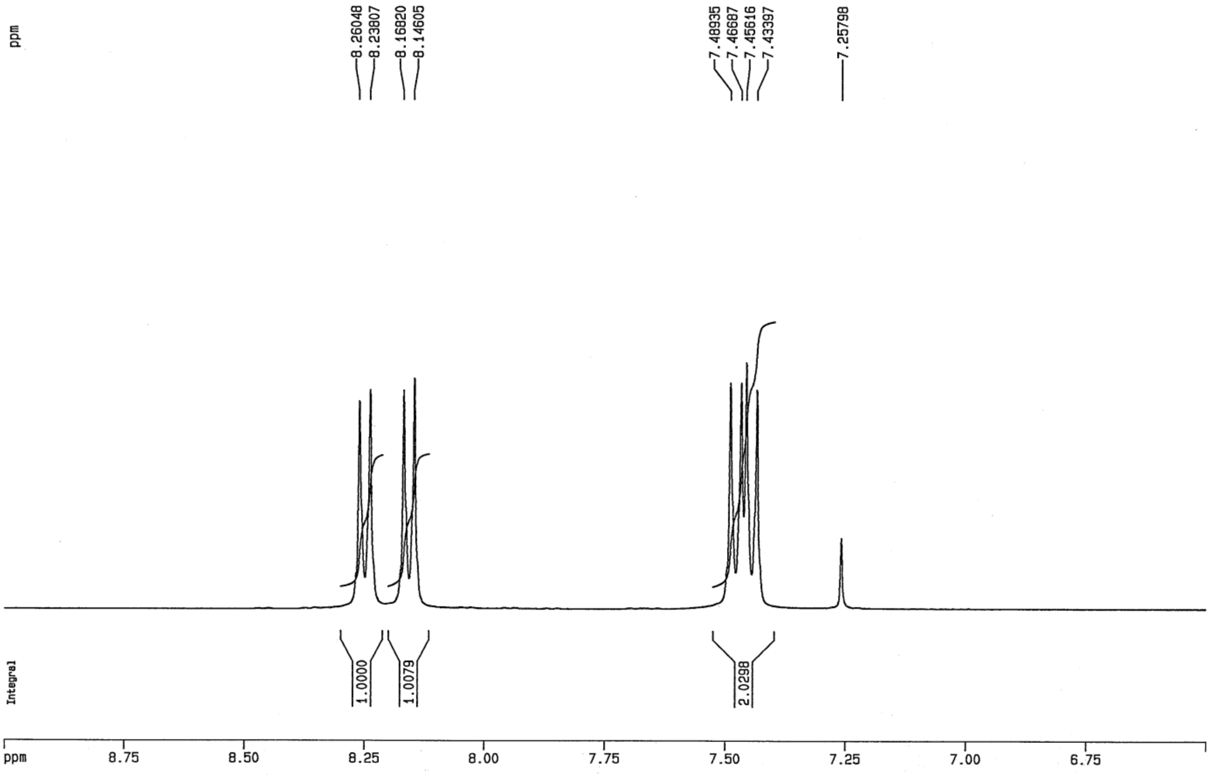

ppm
161.767
160.120
141.615
137.910
127.767
123.705
113.661
113.525
77.317
77.000
76.681
55.627
55.435
ppm
160
150
140
130
120
110
100
90
80
70
60
50

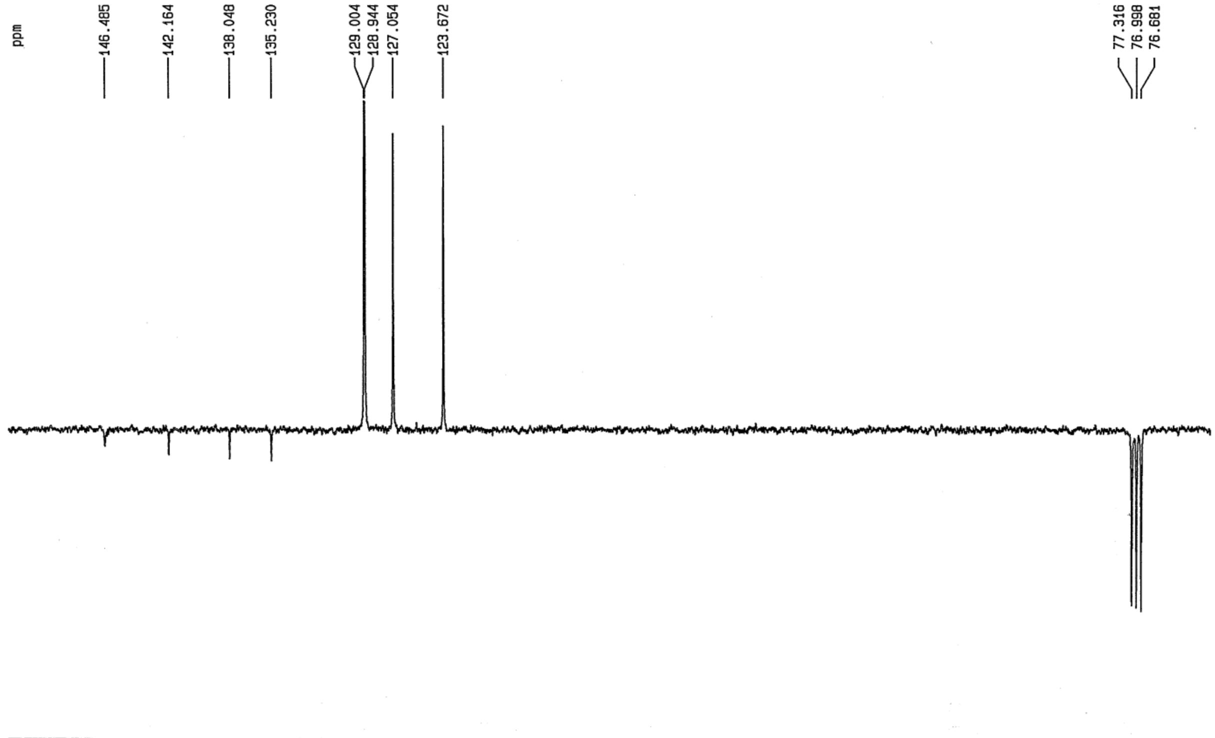
2b: R = H


ppm
8.32569
8.30522
8.18083
8.16183
7.58572
7.57577
7.56791
7.55024
7.53717
7.51682
7.49580
7.47609
7.41722
7.39948
7.38042
7.25719
Integral
2.0000
2.0141
5.1933
1.0144
ppm
8.75
8.50
8.25
8.00
7.75
7.50
7.25
7.00
6.75
6.50
6.25

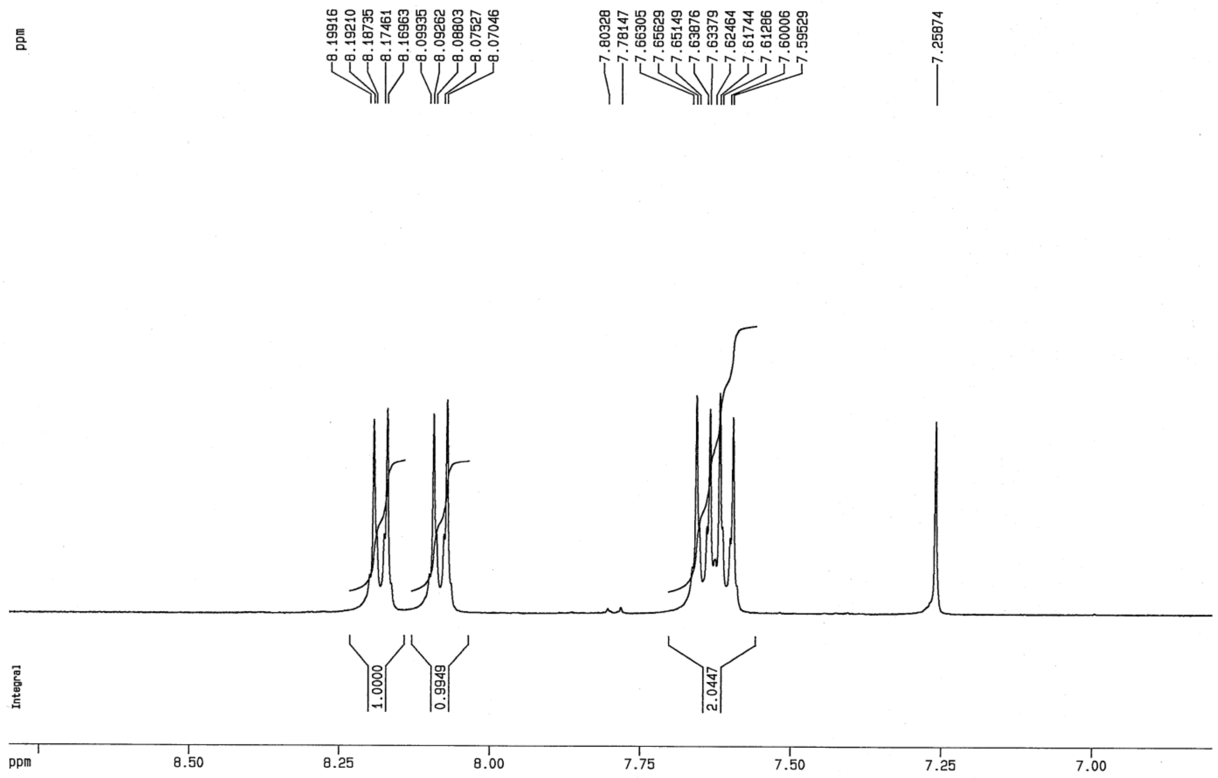

ppm
148.310
143.947
131.599
129.627
128.799
128.701
125.517
122.328
77.321
77.004
76.686
ppm
150
140
130
120
110
100
90
80
70

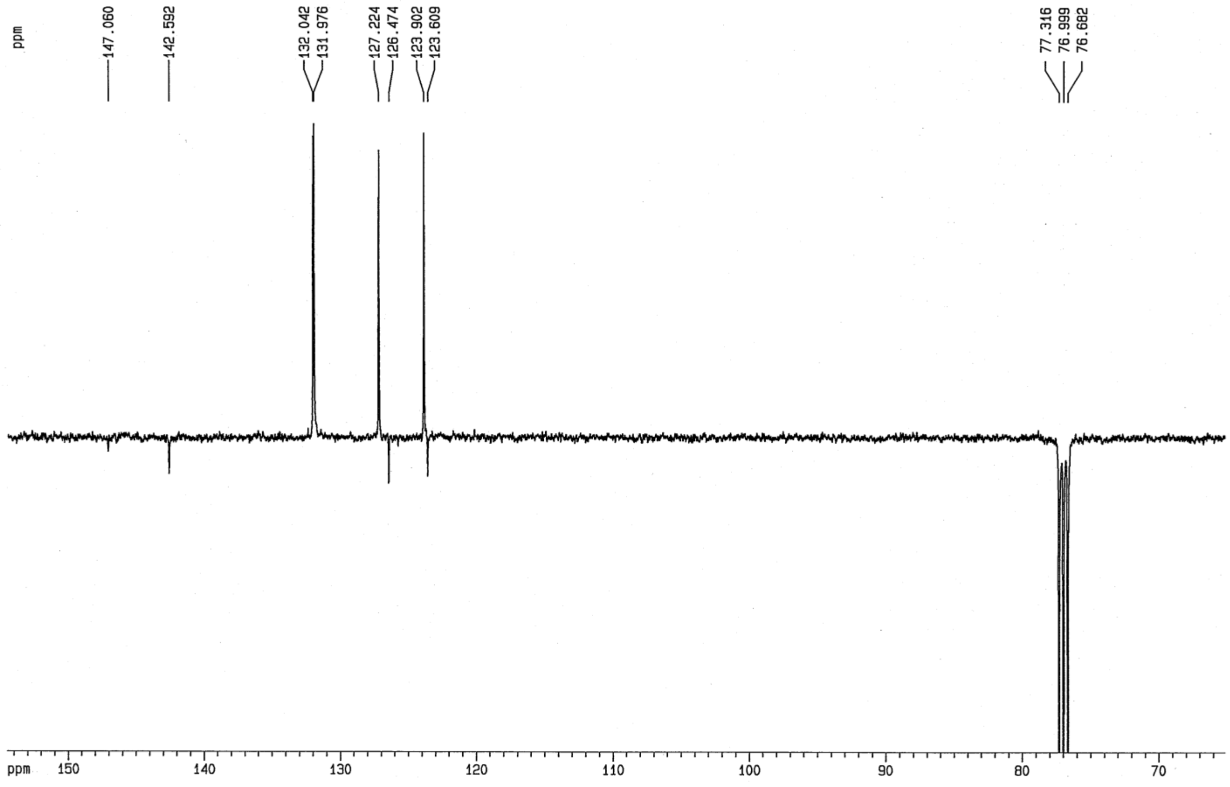
2c: R = 4-Cl


ppm
8.26048
8.23807
8.16820
8.14605
7.48935
7.46687
7.45616
7.43397
7.25798
Integral
1.0000
1.0079
2.0298
ppm
8.75
8.50
8.25
8.00
7.75
7.50
7.25
7.00
6.75

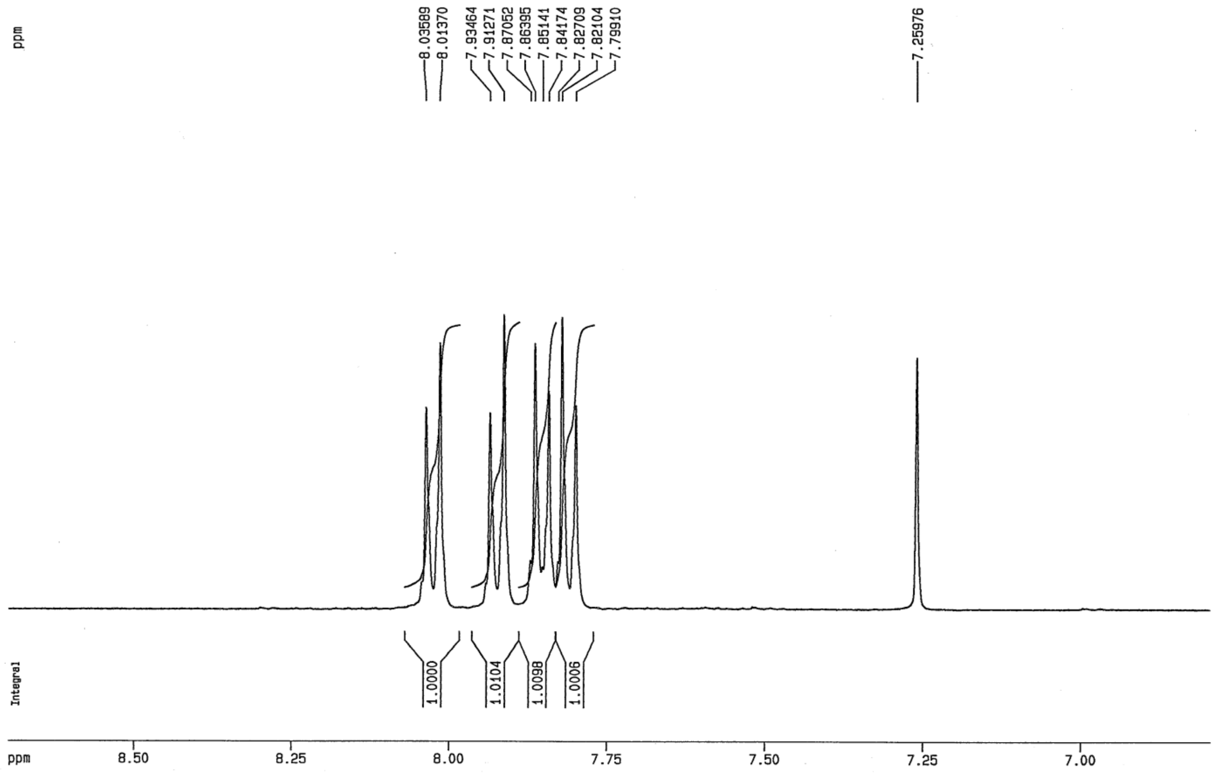

ppm
146.485
142.164
138.048
135.230
129.004
128.944
127.054
123.672
77.316
76.998
76.681
ppm
140
130
120
110
100
90
80

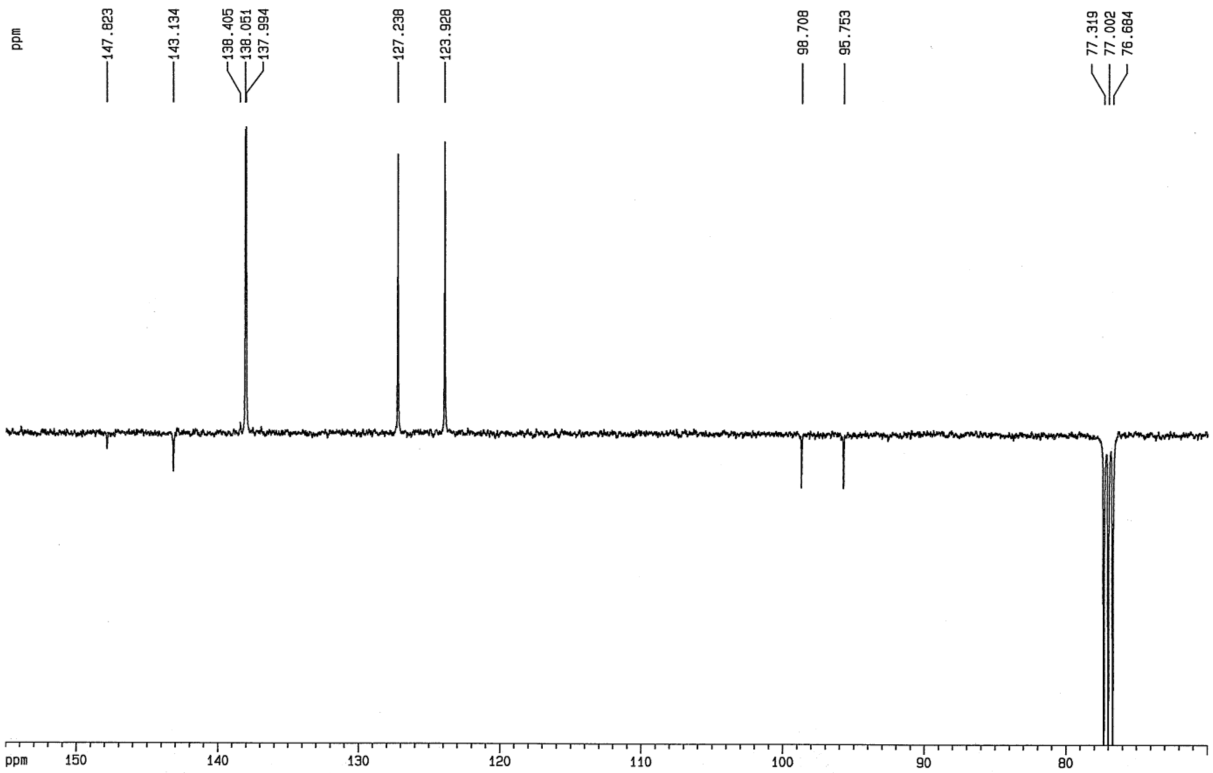
2d: R = 4-Br


ppm
8.19916
8.19210
8.18735
8.17461
8.16963
8.09935
8.09262
8.08803
8.07527
8.07046
7.80328
7.78147
7.66305
7.65629
7.65149
7.63876
7.63379
7.62464
7.61744
7.61286
7.60006
7.59529
7.25874
Integral
1.0000
0.9949
2.0447
ppm
8.50
8.25
8.00
7.75
7.50
7.25
7.00

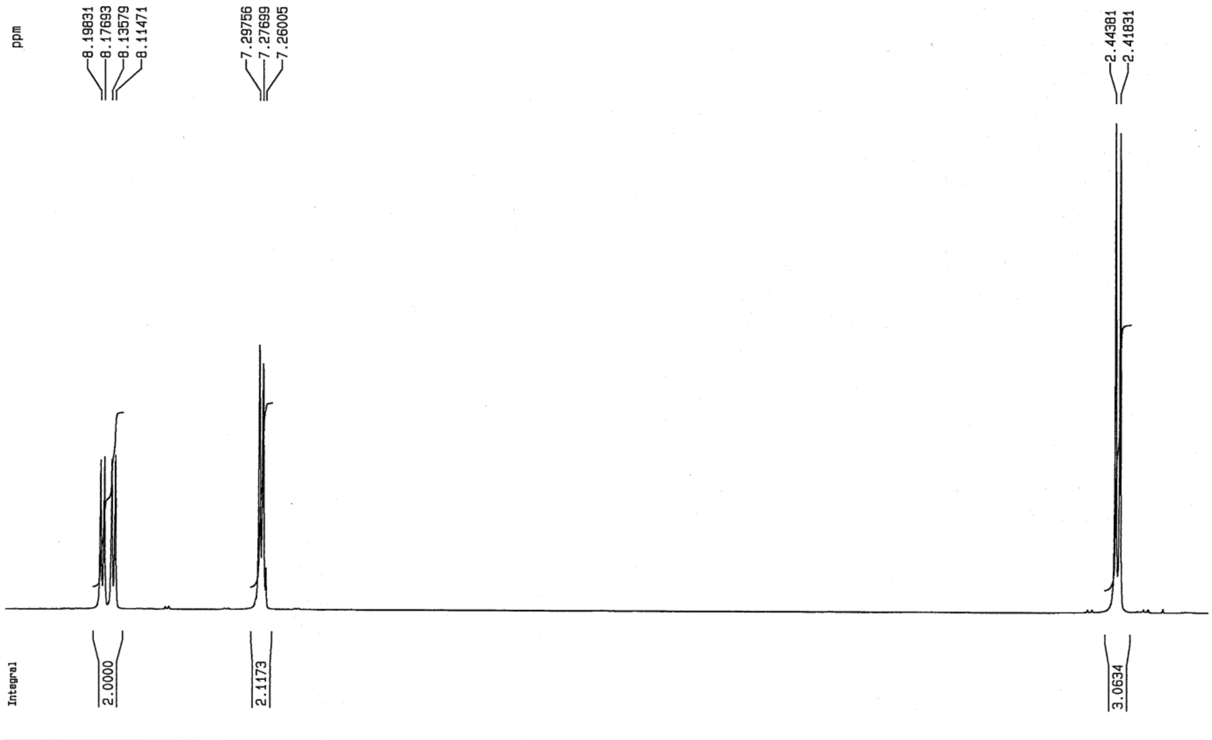

ppm
147.060
142.592
132.042
131.976
127.224
126.474
123.902
123.609
77.316
76.999
76.682
ppm
150
140
130
120
110
100
90
80
70

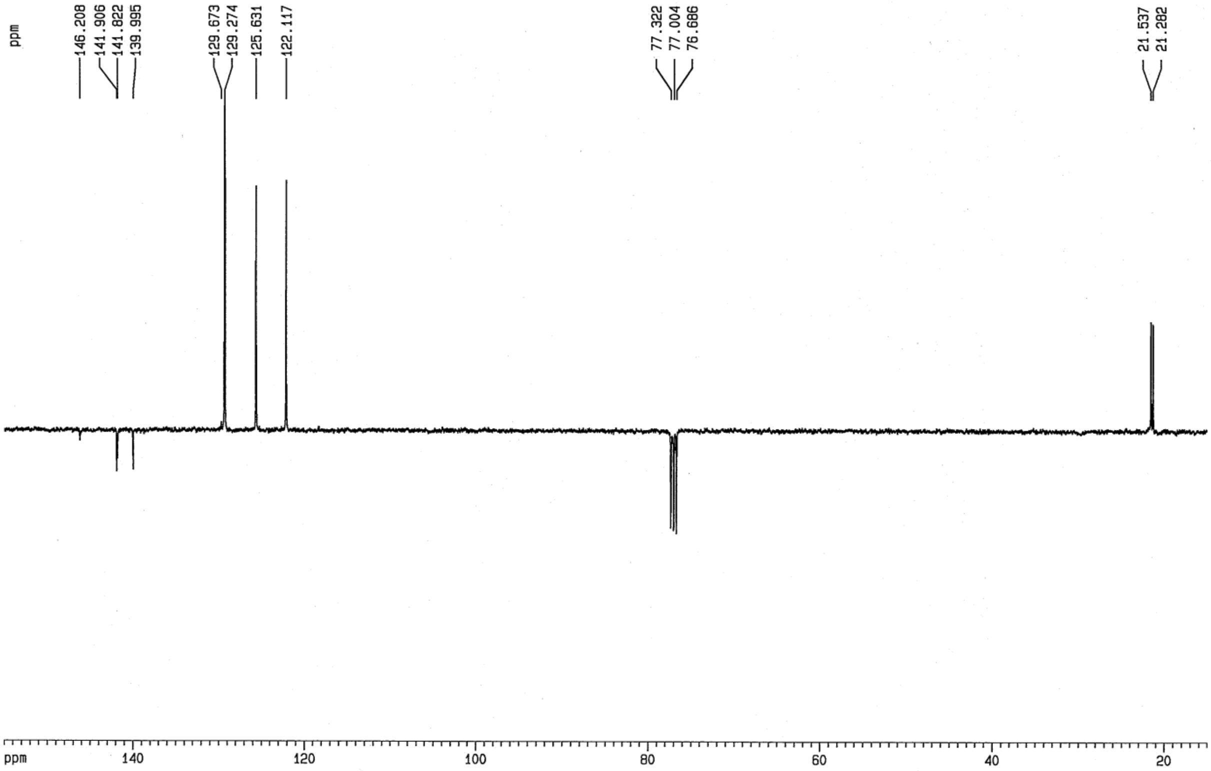
2e: R = 4-I


ppm
8.03589
8.01370
7.93464
7.91271
7.87052
7.86395
7.85141
7.84174
7.82709
7.82104
7.79910
7.25976
Integral
1.0000
1.0104
1.0098
1.0006
ppm
8.50
8.25
8.00
7.75
7.50
7.25
7.00

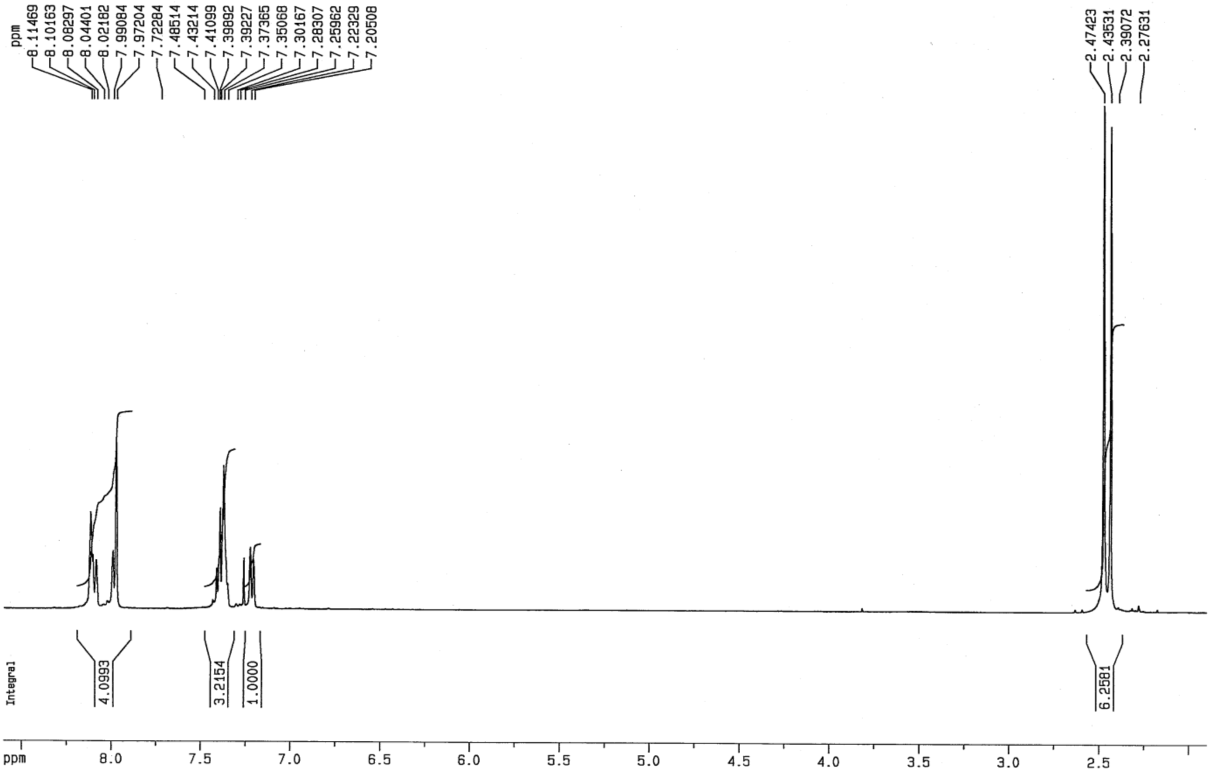

ppm
147.823
143.134
138.405
138.051
137.994
127.238
123.928
98.708
95.753
77.319
77.002
76.684
ppm
150
140
130
120
110
100
90
80

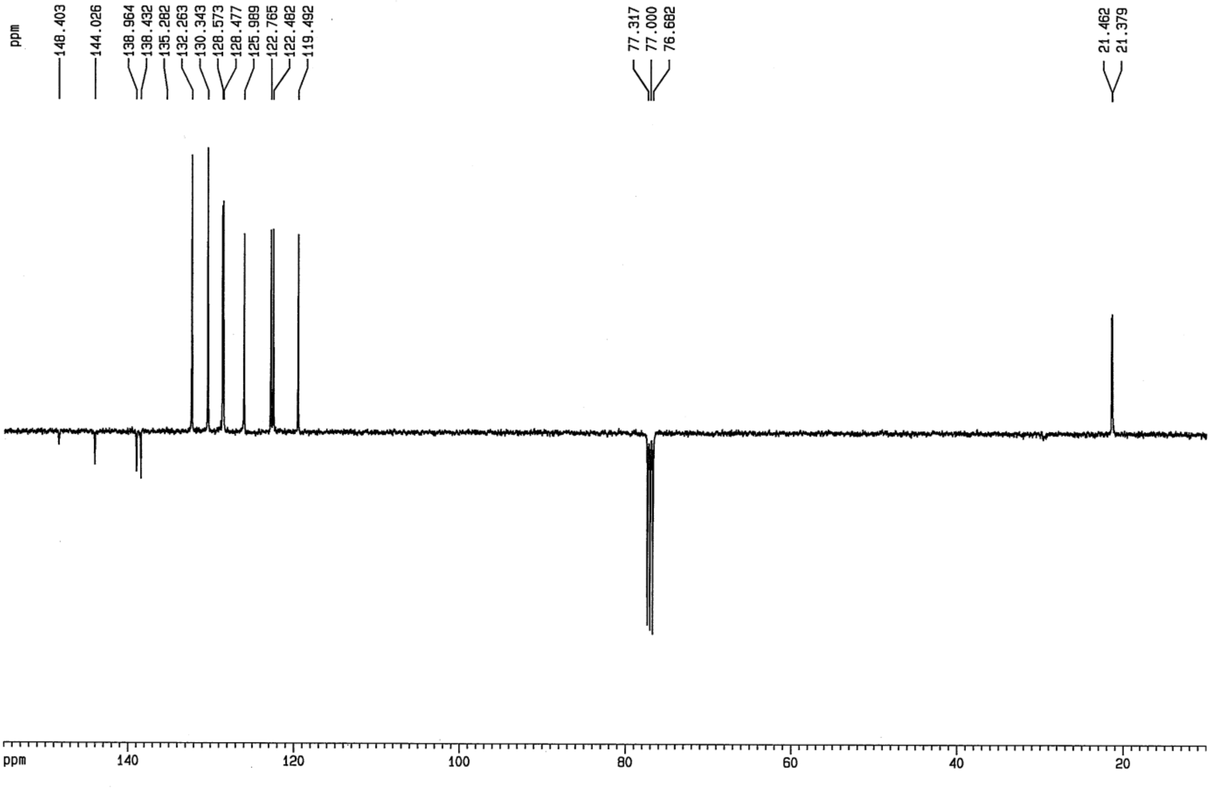
2f: R = 4-Me


ppm
8.19831
8.17693
8.13579
8.11471
7.29756
7.27699
7.26005
2.44381
2.41831
Integral
2.0000
2.1173
3.0634
ppm
8
7
6
5
4
3
2

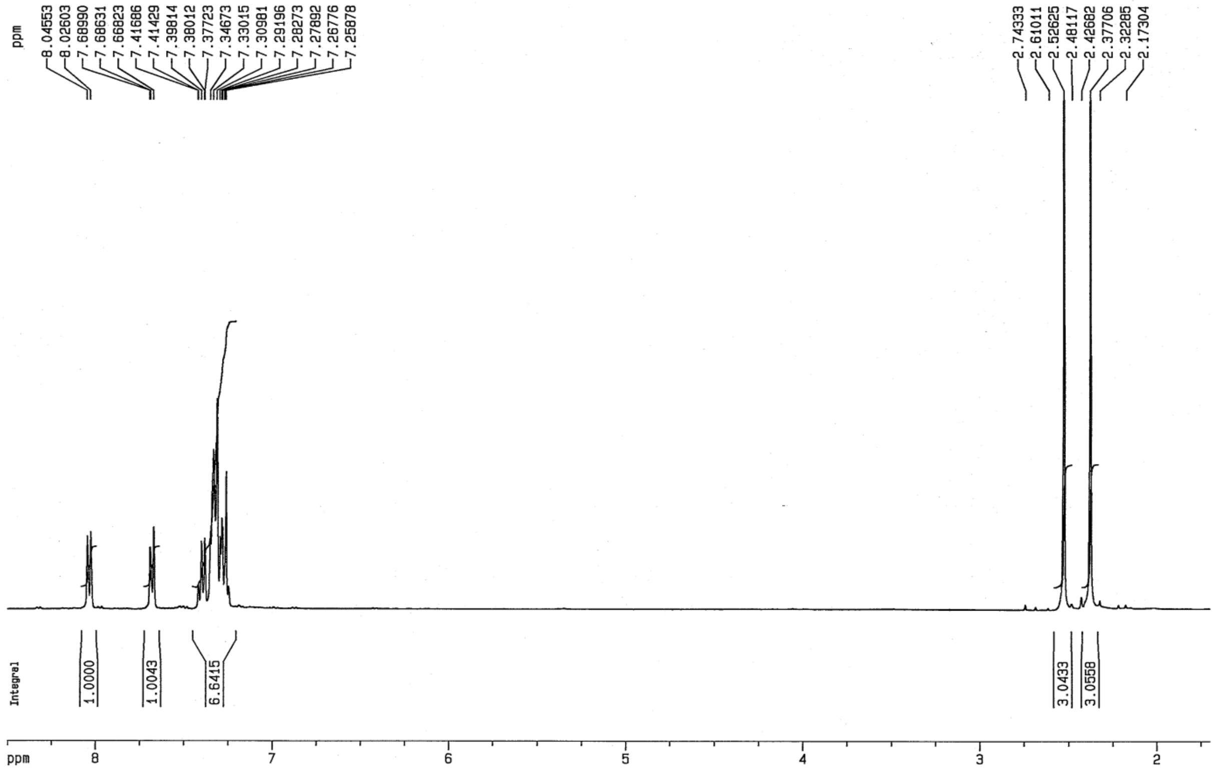

ppm
146.208
141.906
141.822
139.995
129.673
129.274
125.631
122.117
77.322
77.004
76.686
21.537
21.282
ppm
140
120
100
80
60
40
20

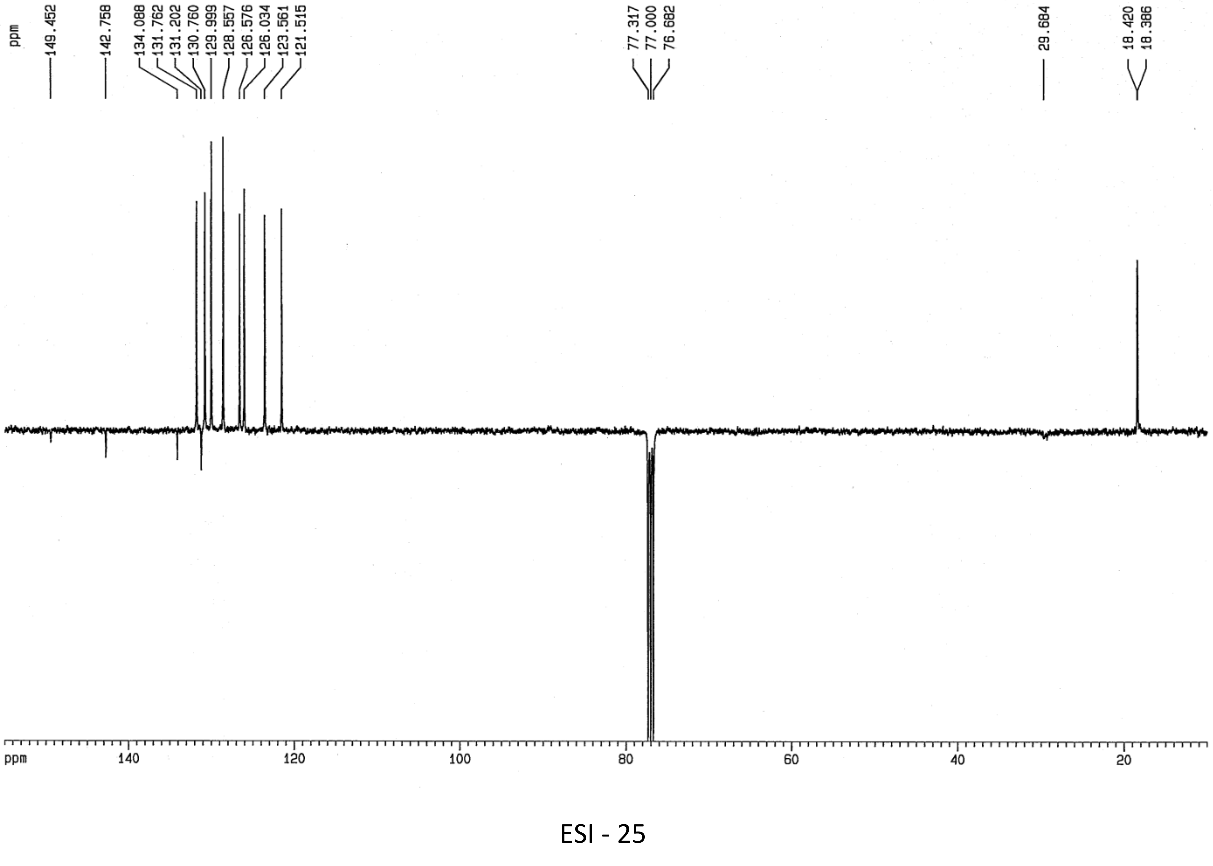
2g: R = 3-Me


ppm
8.11469
8.10163
8.08297
8.04401
8.02182
7.99084
7.97204
7.72284
7.48514
7.43214
7.41099
7.39892
7.39227
7.37365
7.35068
7.30167
7.28307
7.25962
7.22329
7.20508
2.47423
2.43531
2.39072
2.27631
Integral
4.0993
3.2154
1.0000
6.2581
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

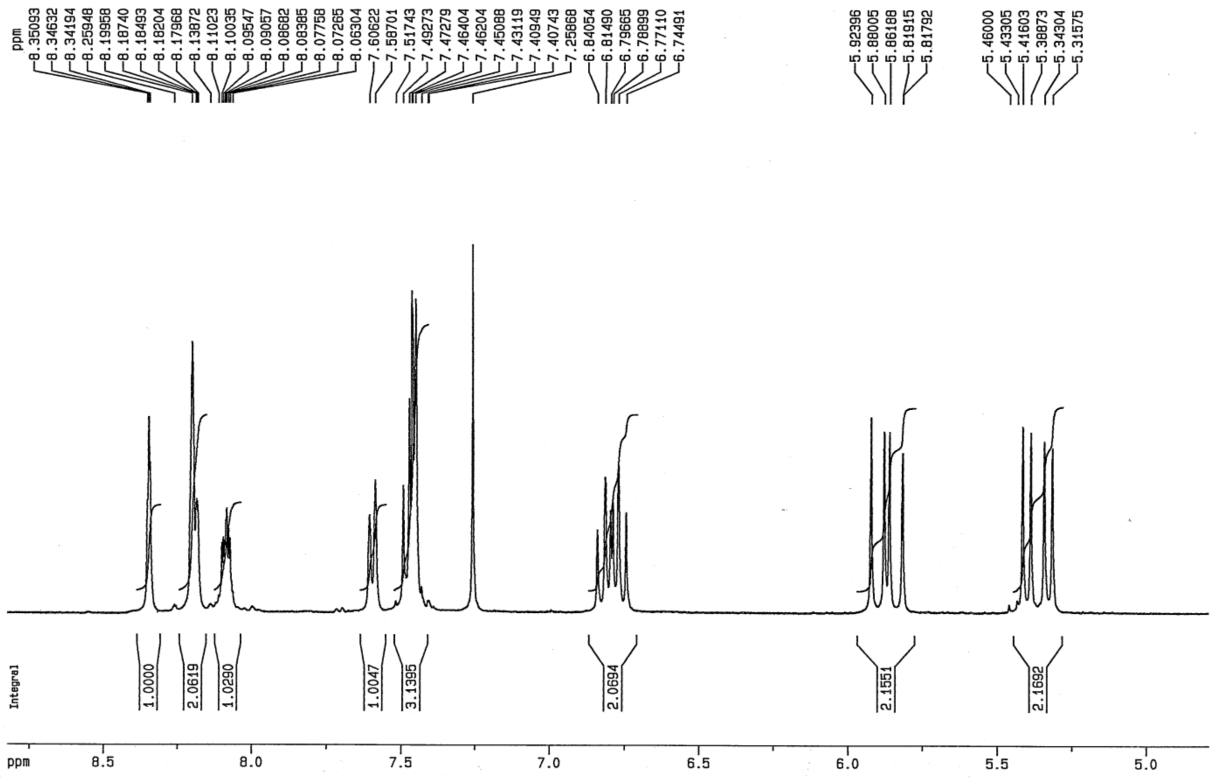

ppm
148.403
144.026
138.964
138.432
135.282
132.263
130.343
128.573
128.477
125.989
122.765
122.482
119.492
77.317
77.000
76.682
21.462
21.379
ppm
140
120
100
80
60
40
20

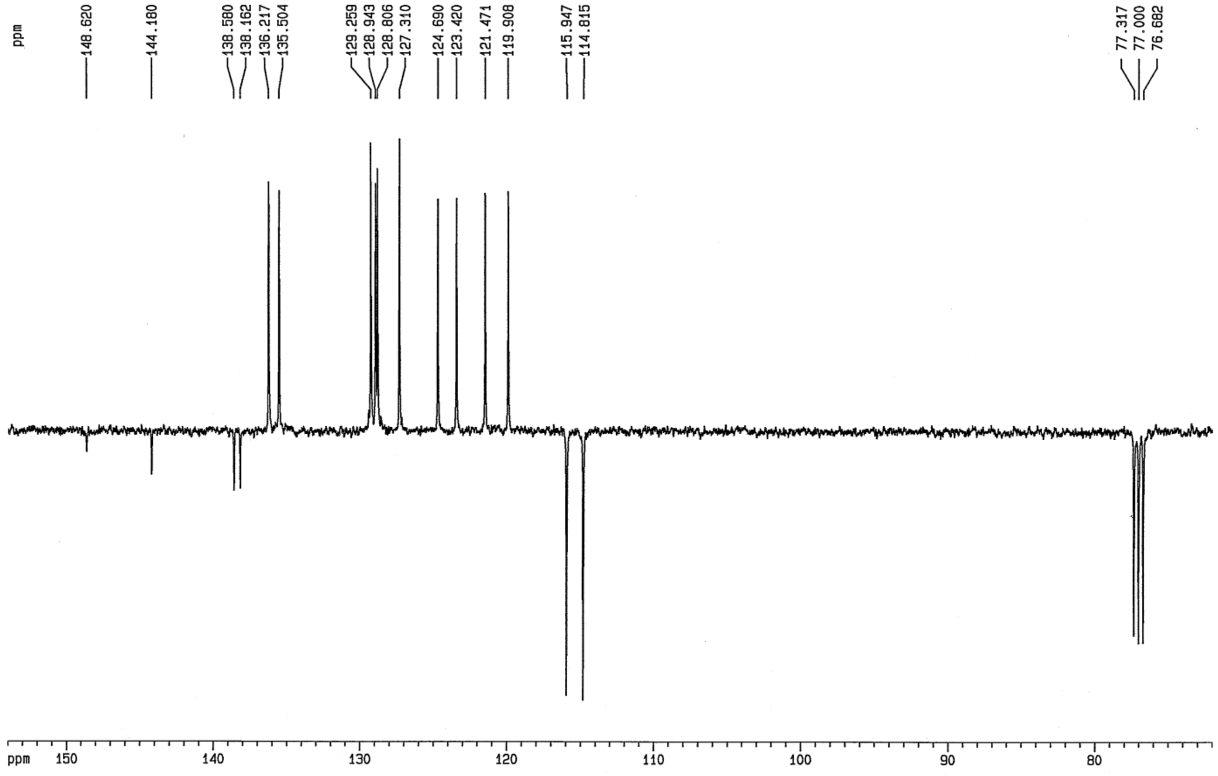
2h: R = 2-Me


ppm
8.04553
8.02603
7.68990
7.68631
7.66823
7.41686
7.41429
7.39814
7.38012
7.37723
7.34673
7.33015
7.30981
7.29196
7.28273
7.27892
7.26776
7.25878
2.74333
2.61011
2.52625
2.48117
2.42682
2.37706
2.32285
2.17304
Integral
1.0000
1.0043
6.6415
3.0433
3.0558
ppm
8
7
6
5
4
3
2

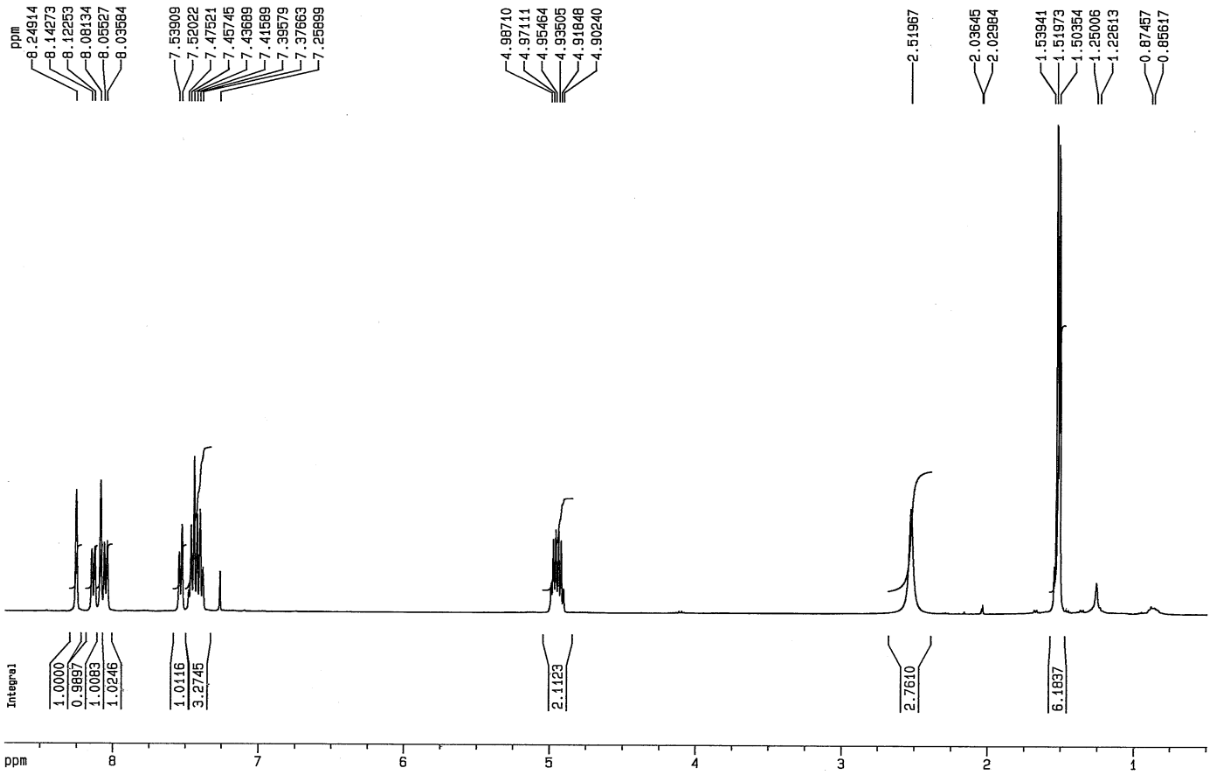

ppm
149.452
142.758
134.088
131.762
131.202
130.760
129.999
128.557
126.576
126.034
123.561
121.515
77.317
77.000
76.682
29.684
18.420
18.386
ppm
140
120
100
80
60
40
20

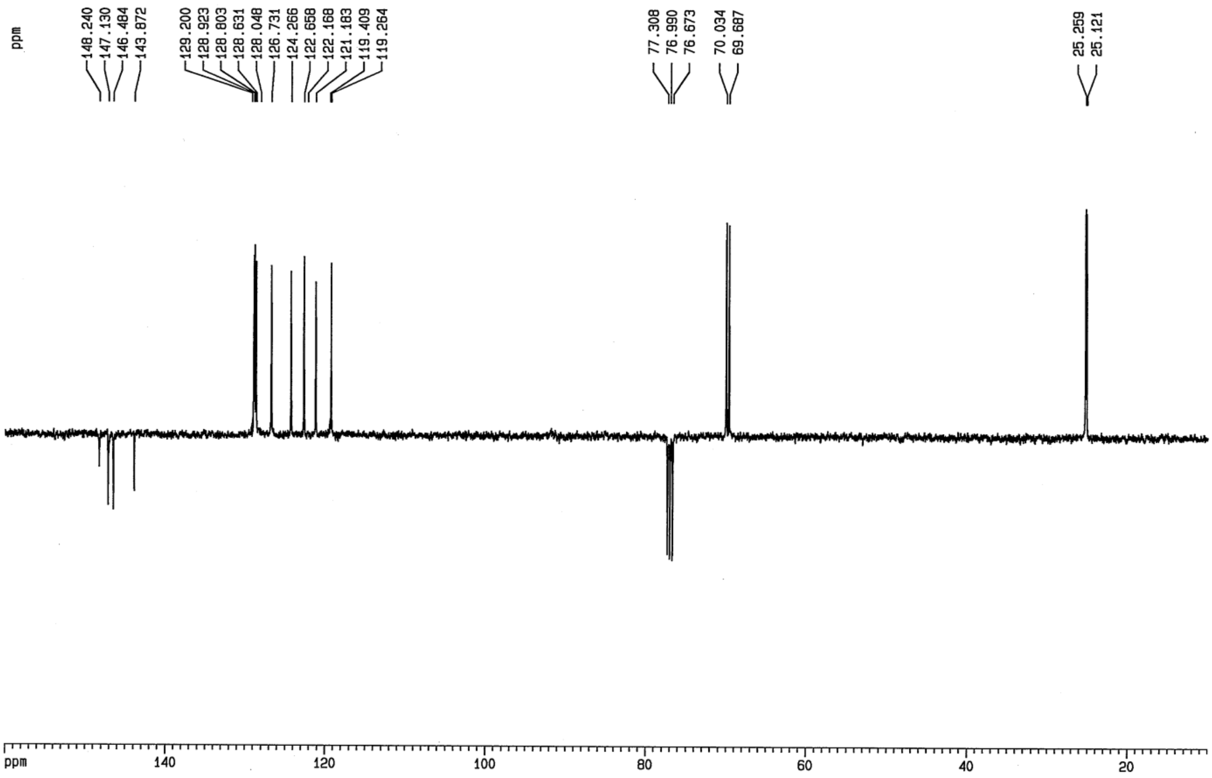
2i: R = 3-CH=CH$_2$


ppm
8.35093
8.34632
8.34194
8.25948
8.19958
8.18740
8.18493
8.18204
8.17968
8.13872
8.11023
8.10035
8.09547
8.09057
8.08682
8.08385
8.07758
8.07265
8.06304
7.60622
7.58701
7.51743
7.49273
7.47279
7.46404
7.46204
7.45088
7.43119
7.40949
7.40743
7.25868
6.84054
6.81490
6.79665
6.78899
6.77110
6.74491
5.92396
5.88005
5.86188
5.81915
5.81792
5.46000
5.43305
5.41603
5.38873
5.34304
5.31575
Integral
1.0000
2.0619
1.0290
1.0047
3.1395
2.0694
2.1551
2.1692
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0

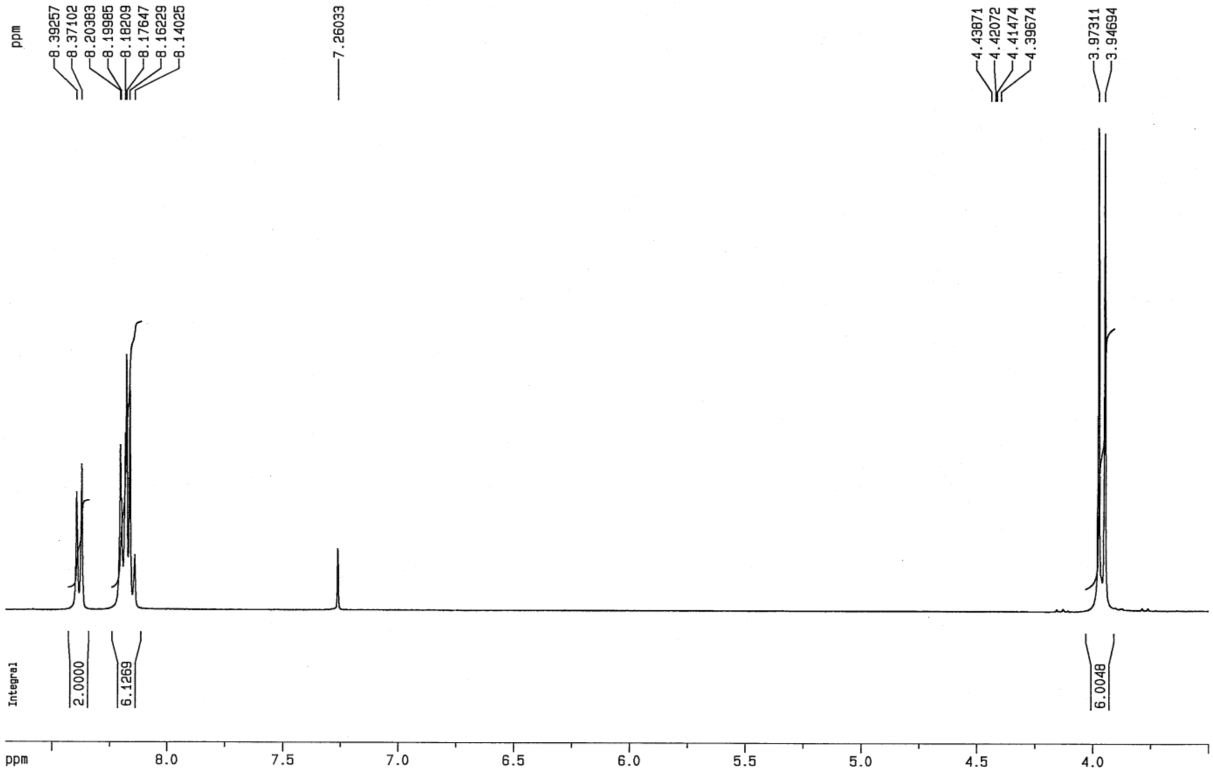

ppm
148.620
144.180
138.580
138.162
136.217
135.504
129.259
128.943
128.806
127.310
124.690
123.420
121.471
119.908
115.947
114.815
77.317
77.000
76.682
ppm
150
140
130
120
110
100
90
80

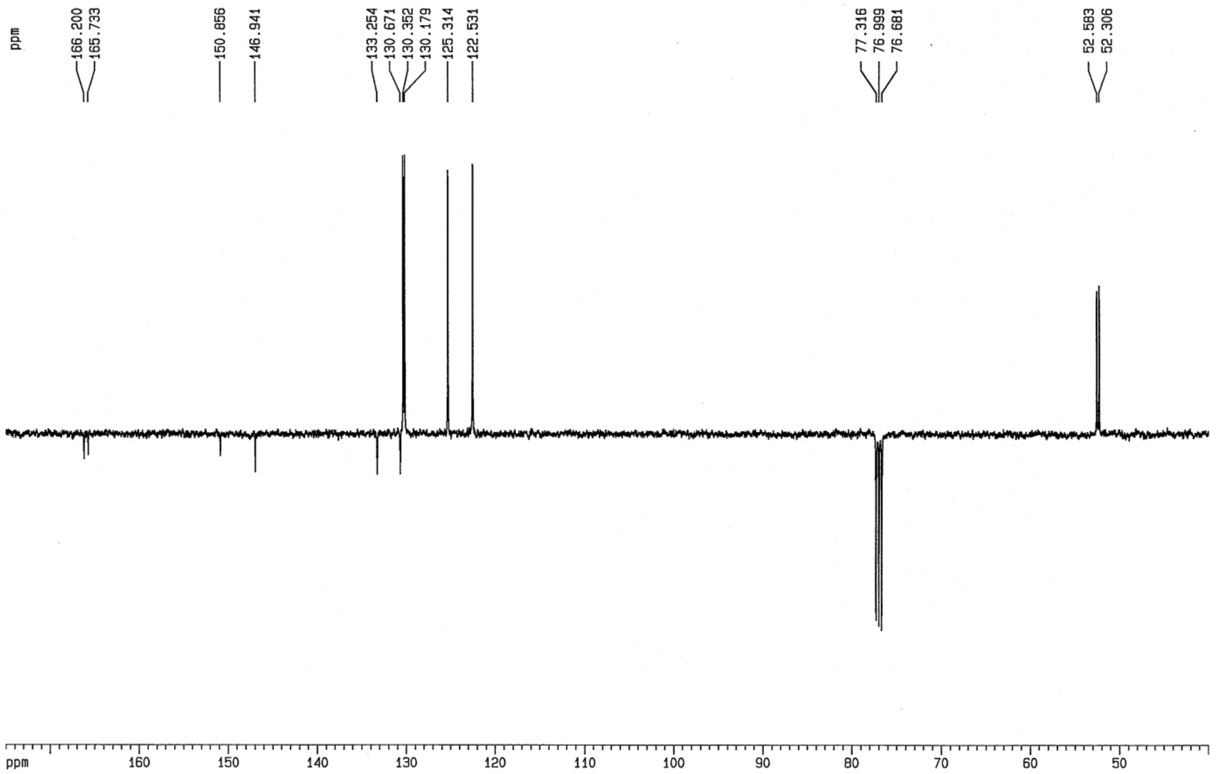
2j: R = 3-CH(OH)Me


ppm
8.24914
8.14273
8.12253
8.08134
8.05527
8.03584
7.53909
7.52022
7.47521
7.45745
7.43689
7.41589
7.39579
7.37663
7.25899
4.98710
4.97111
4.95464
4.93505
4.91848
4.90240
2.51967
2.03645
2.02984
1.53941
1.51973
1.50354
1.25006
1.22613
0.87457
0.85617
Integral
1.0000
0.9897
1.0083
1.0246
1.0116
3.2745
2.1123
2.7610
6.1837
ppm
8
7
6
5
4
3
2
1

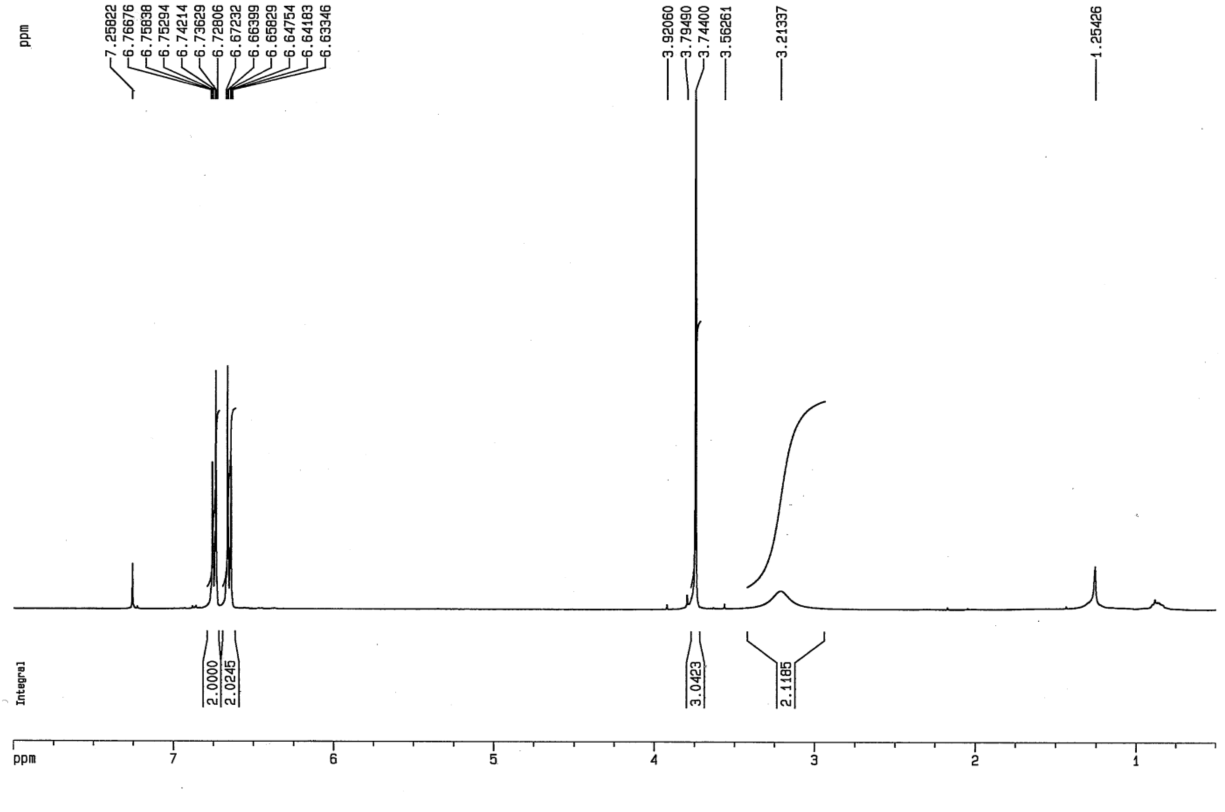

ppm
148.240
147.130
146.484
143.872
129.200
128.923
128.803
128.631
128.048
126.731
124.266
122.658
122.168
121.183
119.409
119.264
77.308
76.990
76.673
70.034
69.687
25.259
25.121
ppm
140
120
100
80
60
40
20

2k: R = 4-COOMe

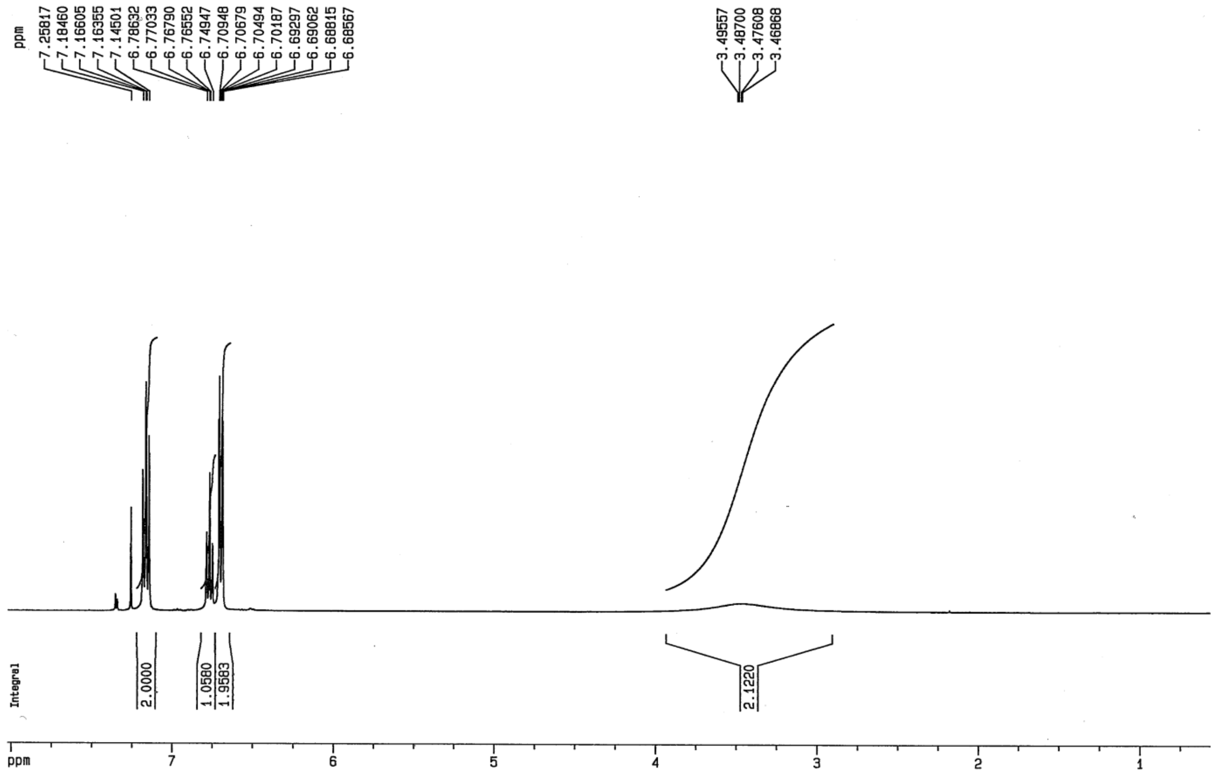

ppm
8.39257
8.37102
8.20383
8.19985
8.18209
8.17647
8.16229
8.14025
7.26033
4.43871
4.42072
4.41474
4.39674
3.97311
3.94694
Integral
2.0000
6.1269
6.0048
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0



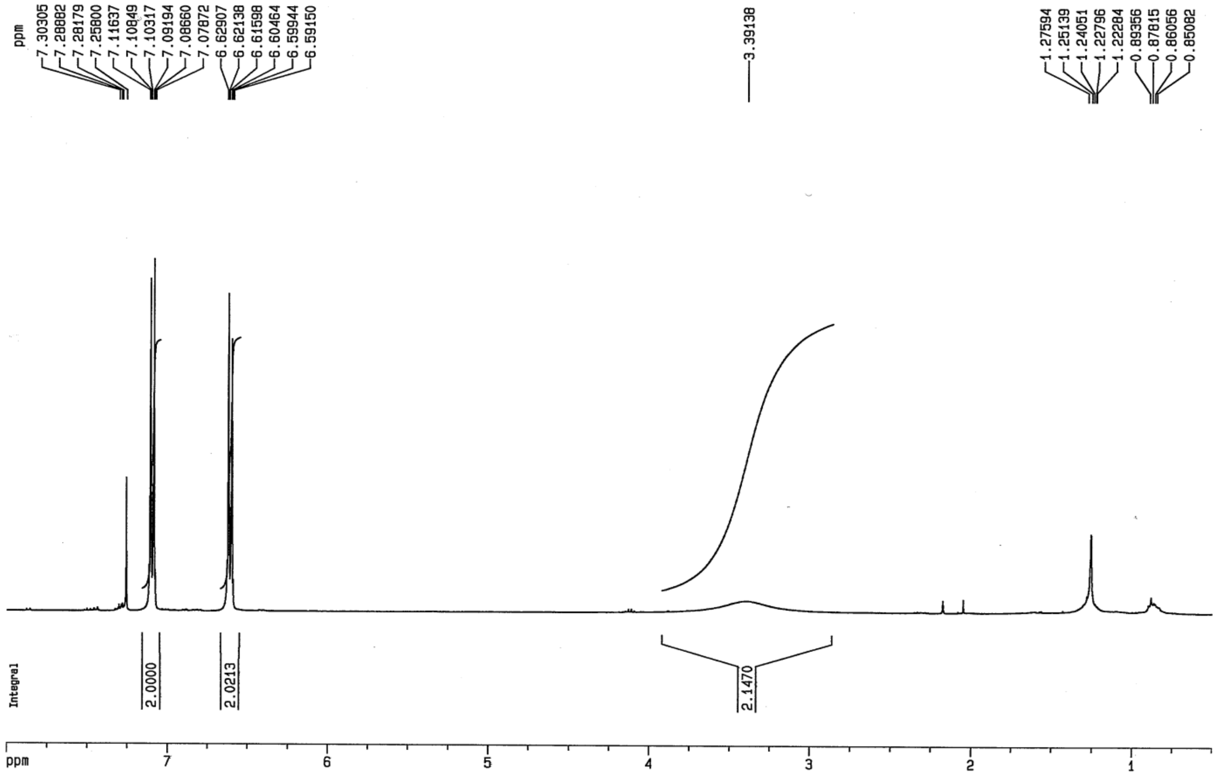
4a: R = 4-OMe



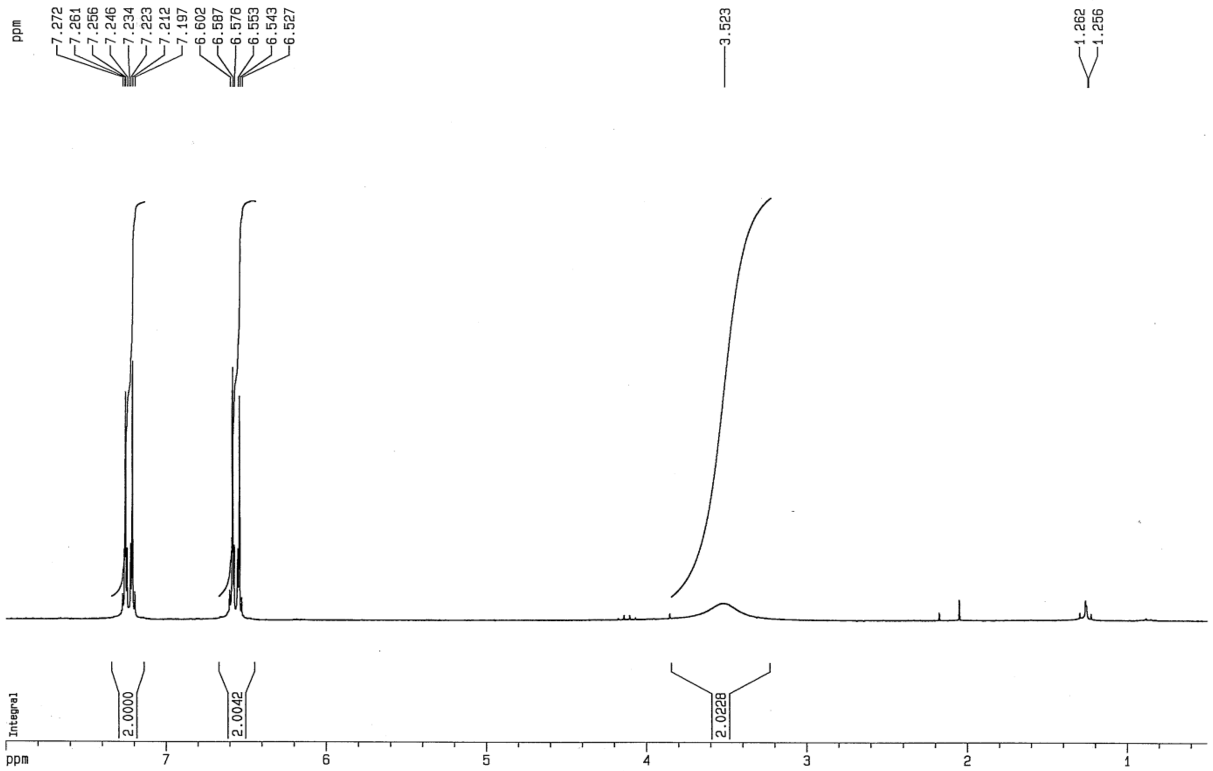
4b: R = H



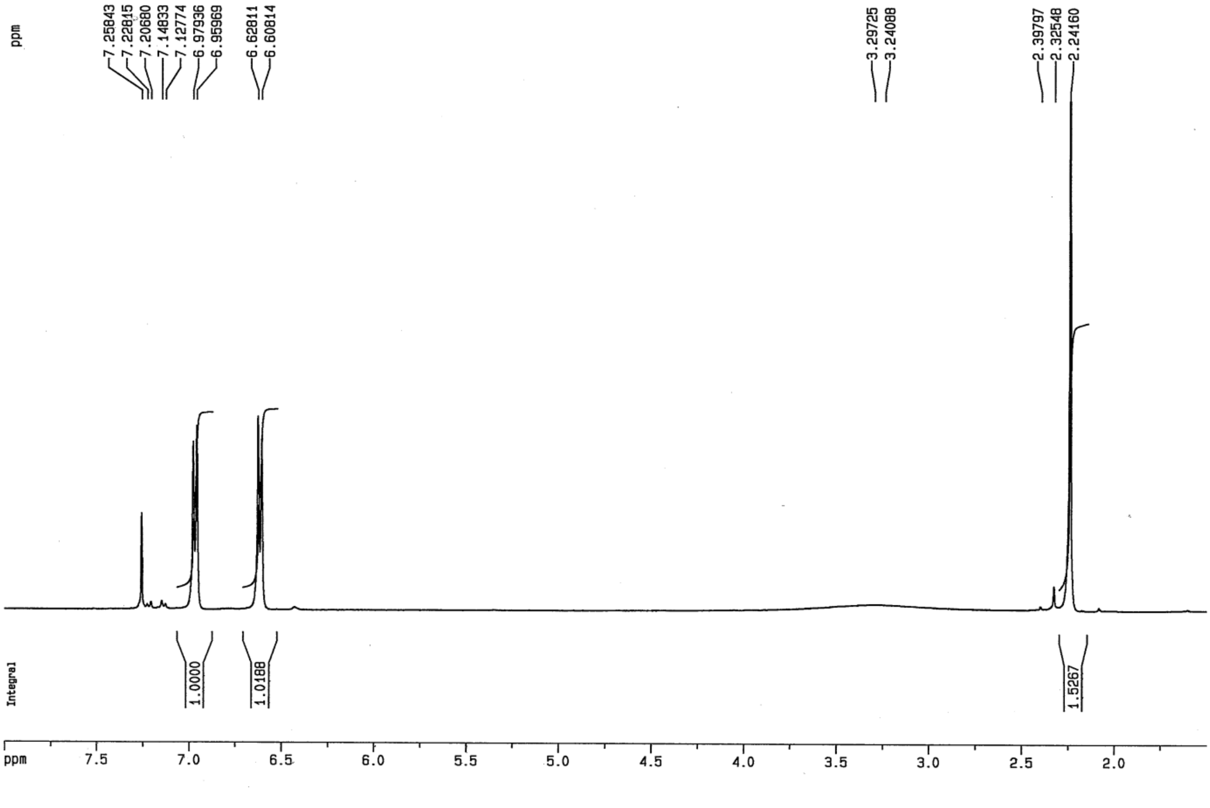
4c: R = 4-Cl



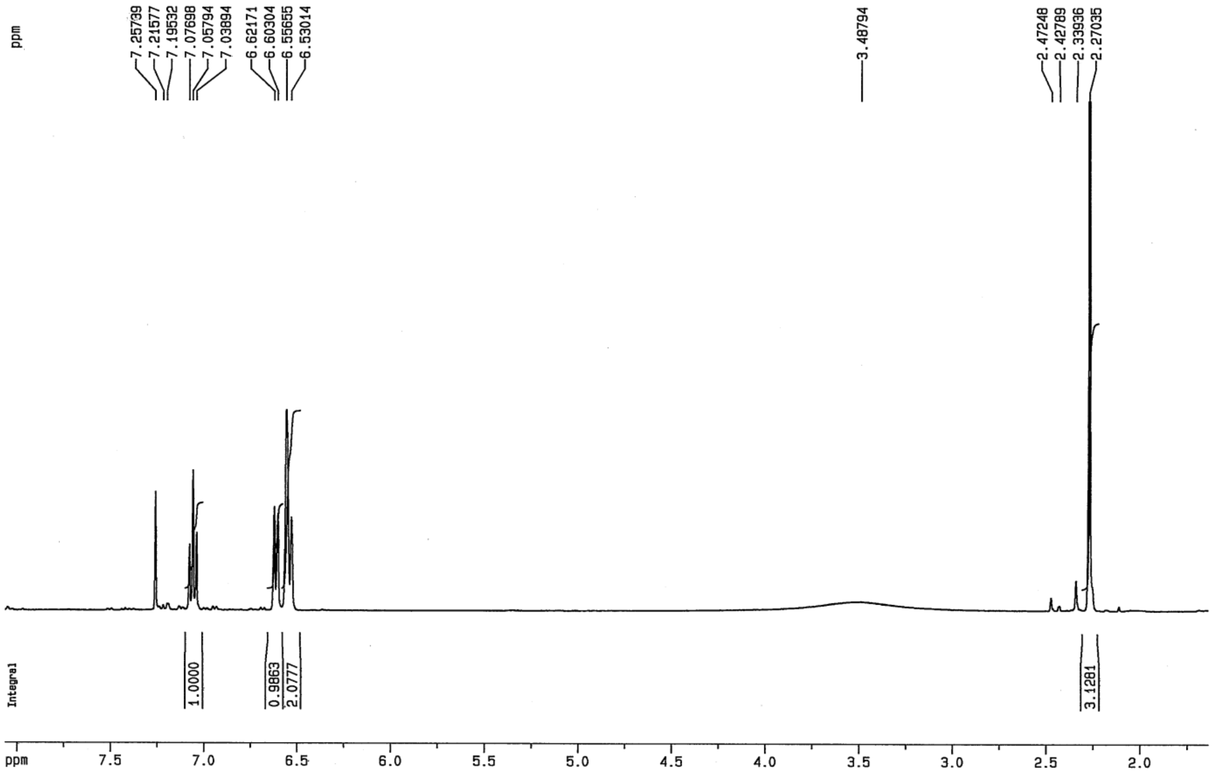
4d: R = 4-Br



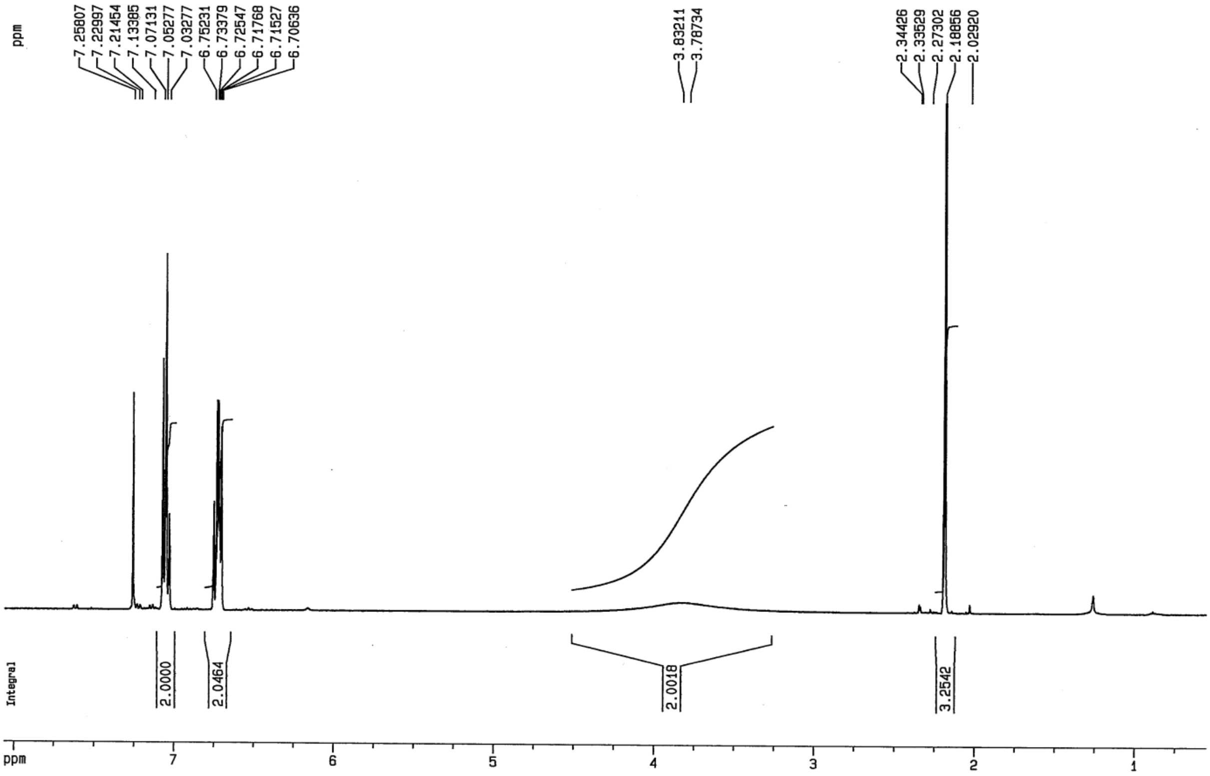
4f: R = 4-Me



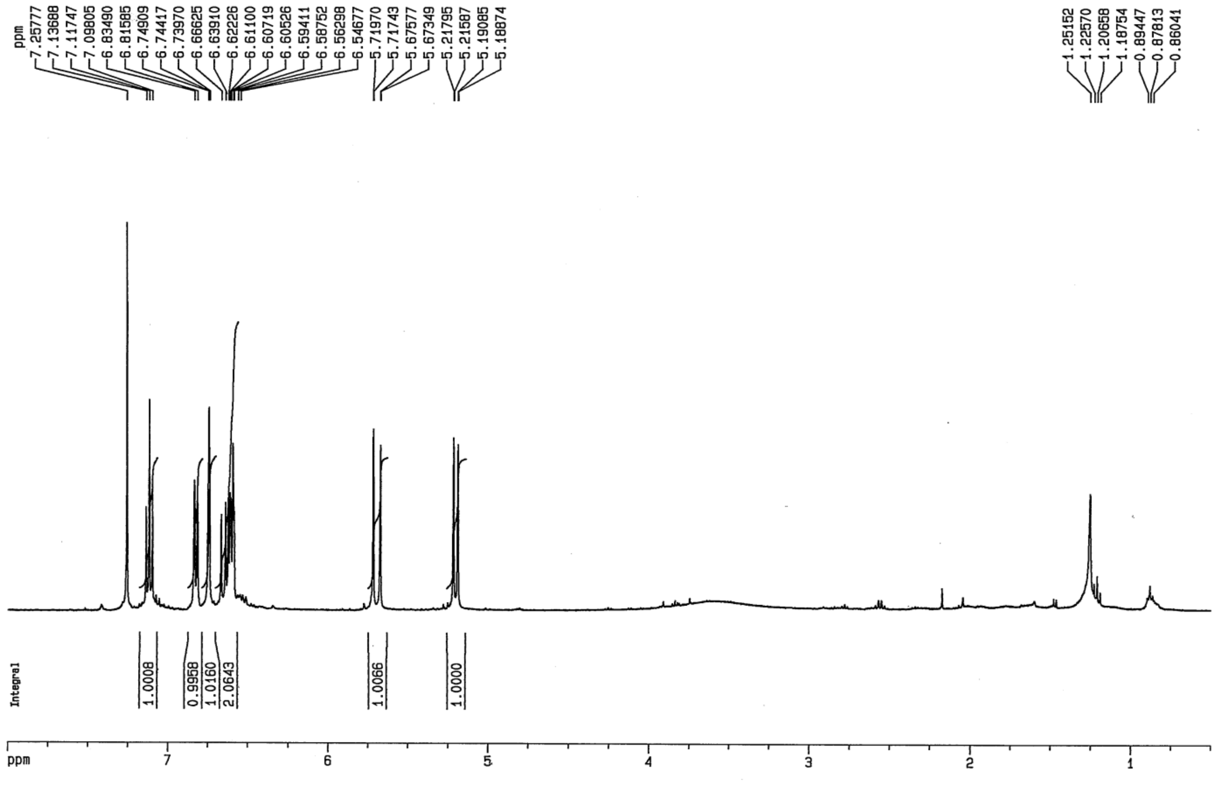
4g: R = 3-Me



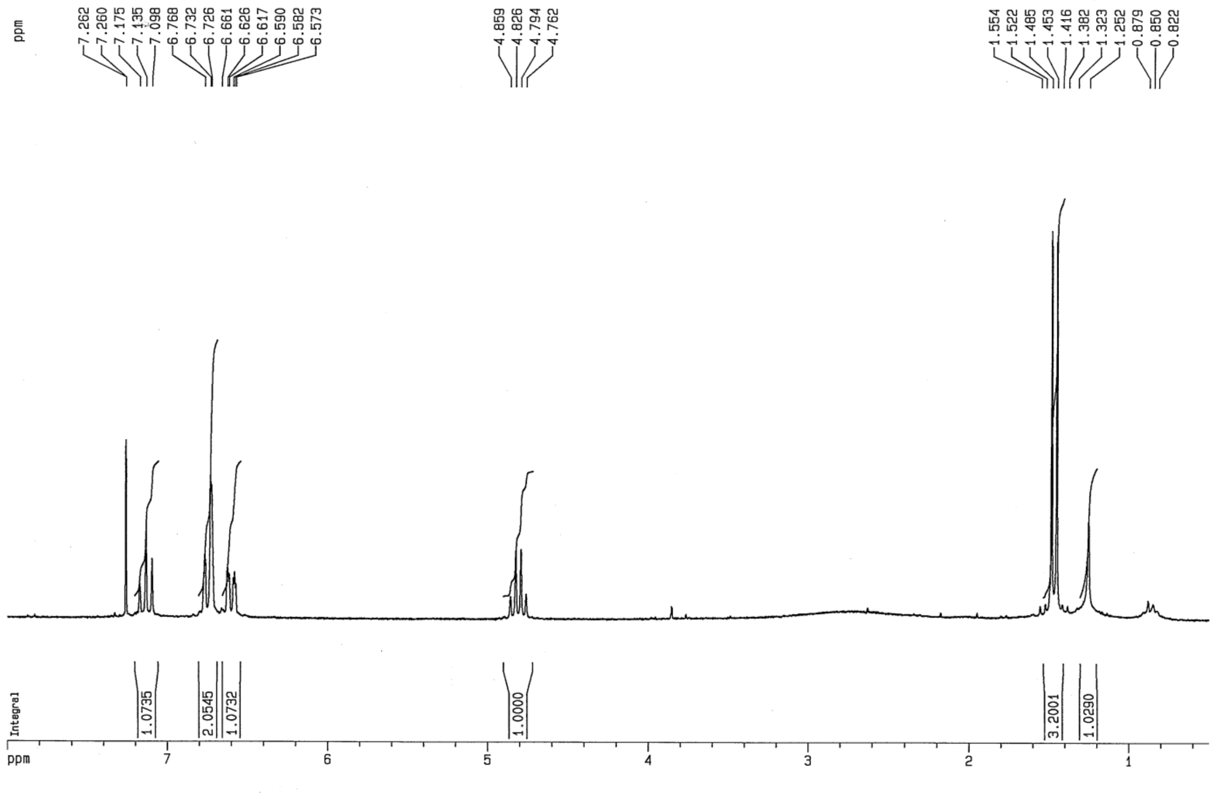
4h: R = 2-Me



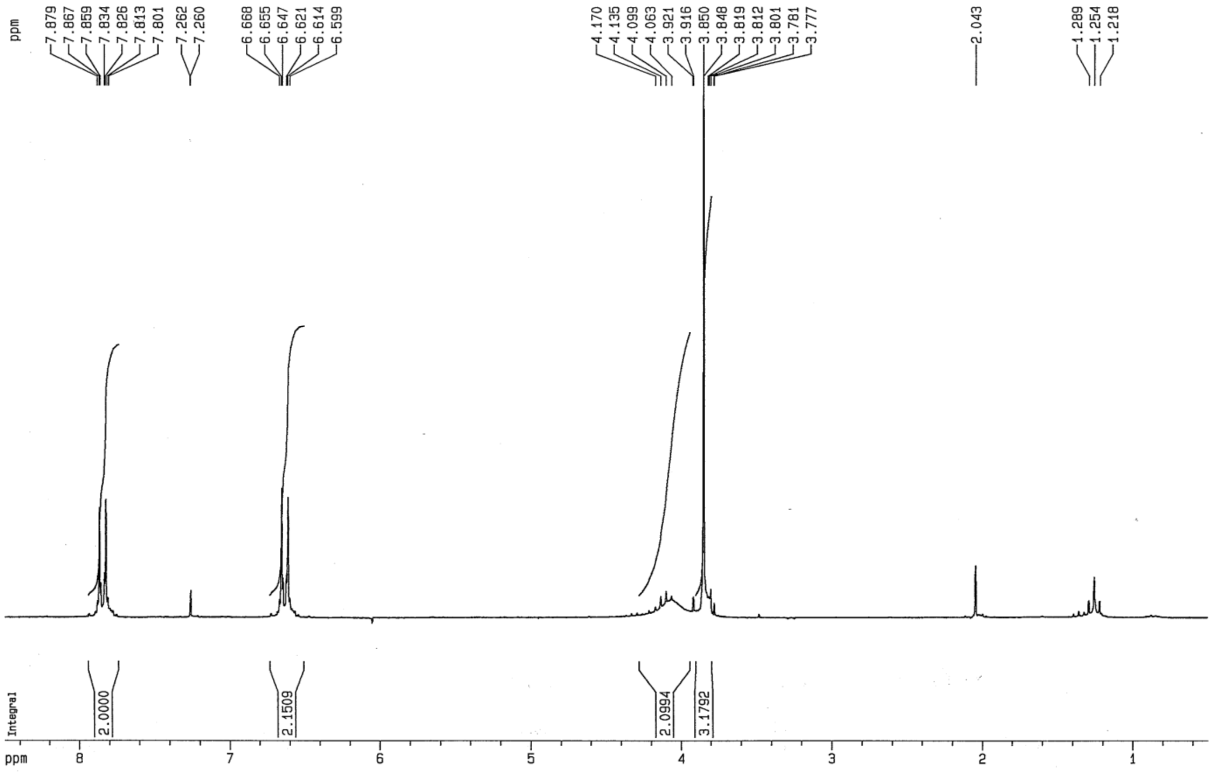
4i: R = 3-CH=CH$_2$



4j: R = 3-CH(OH)Me



4k: R = 4-COOMe



4l: 6-nitroquinoline