# SUPPORTING INFORMATION

# CO-free, Aqueous Mediated, Instant and Selective Reduction of Nitrobenzene via Robustly Stable Chalcogen Stabilised Iron carbonyl Clusters ($Fe_3E_2(CO)_9$, E= S, Se, Te)

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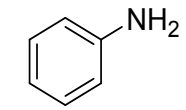
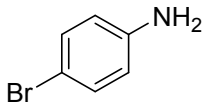
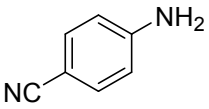
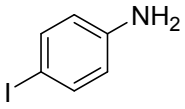
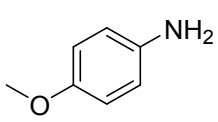
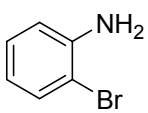
**Experimental Details:** The $^1H$, $^{13}C$ $\{^1H\}$ NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for $^1H$ and 100 MHz for $^{13}C$).

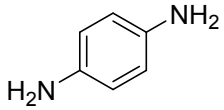
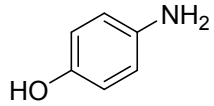
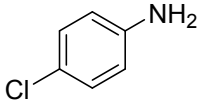
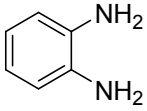
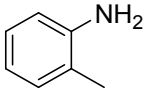
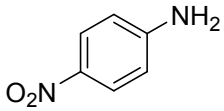
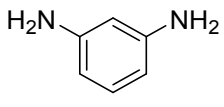
**Chemicals and reagents:** Reactants, reagents, chemicals and solvents available commercially within the country were used.

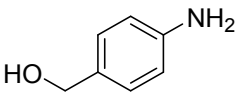
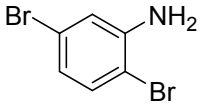
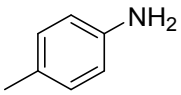
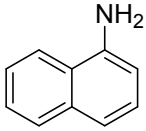
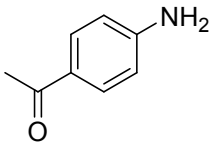
## Experimental Section

In a clean reaction tube, take $Fe_3Se_2(CO)_9$ catalyst (3 mol%) and derivative of nitroarenes (1 mmol). To this added hydrazine hydrate (2 mmol) and water as a reaction medium. Above mixture is heated at 110°C for 15 min. Through TLC monitoring product formation was investigated. After that reaction mixture was cooled at room temperature, by adding water and EtOAc the organic layer was extracted. By using anhydrous $Na_2SO_4$ extracted layer was dried. Under reduced pressure solvent was evaporated to get the crude product. Finally, the product was purified through column chromatography.

**Characterisation Data**

| | |
|---|---|
|  | **Aniline**[1]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.23-7.18 (m, 2H), 6.82-6.79 (t, 1H), 6.72-6.70 (t, 2H), 3.63 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 146.33, 129.42, 118.70, 115.03 |
|  | **4-Bromoaniline**[2]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.11-7.07 (m, 2H), 6.51-6.48 (m, 2H), 5.21 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 148.52, 131.85, 116.34, 106.68 |
|  | **4-Aminobenzonitrile**[3]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.38-7.34 (m, 2H), 6.63-6.60 (m, 2H), 4.25 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 150.76, 133.77, 113.97, 99.95 |
|  | **4-Iodoaniline**[4]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.41-7.37 (m, 2H), 6.51-6.44 (m, 2H), 3.53 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 145.56, 137.83, 117.25, 78.87 |
|  | **4-methoxyaniline**[5]<br>**1H NMR (400MHz, CDCl3)**: δ = 6.76-6.72 (m, 2H), 6.65-6.61 (m, 2H), 3.73 (s, 3H), 3.42 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 152.88, 140.12, 116.51, 114.92, 55.33 |
|  | **2-Bromoaniline**[6]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.29-7.27 (m, 1H), 7.03-6.98 (m, 1H), 6.76-6.73 (m, 1H), 6.44-6.40 (m, 1H), 5.23 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 146.28, 132.62, 128.80, 117.85, 115.92, 107.95 |

| | |
|---|---|
|  | **Benzene-1,4-diamine**[7]<br>**1H NMR (400MHz, CDCl3)**: δ = 6.55 (s, 4H), 3.28 (s, 4H)<br>**13C NMR (100MHz, CDCl3)**: δ = 138.85, 116.42 |
|  | **4-Aminophenol**[8]<br>**1H NMR (400MHz, CDCl3)**: δ = 8.30 (s, 1H), 6.44-6.36 (m, 4H), 4.35 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ =148.73, 141.16, 116.04, 115.74 |
|  | **4-Chloroaniline**[1]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.10-7.08 (m, 2H), 6.60-6.57 (m, 2H), 3.65 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 144.50, 129.42, 123.16, 115.80 |
|  | **Benzene-1,2-diamine**[7]<br>**1H NMR (400MHz, CDCl3)**: δ = 6.73-6.68 (m, 4H), 3.32 (s, 4H)<br>**13C NMR (100MHz, CDCl3)**: δ = 134.82, 120.37, 116.84 |
|  | **o-Toluidine**[7]<br>**1H NMR (400MHz, CDCl3)**: δ = 7.05-7.01 (t, 2H), 6.72-6.66 (m, 2H), 3.59 (s, 1H), 2.14 (s, 3H)<br>**13C NMR (100MHz, CDCl3)**: δ = 144.12, 130.88, 126.82, 121.69, 119.09, 113.97, 18.09 |
|  | **4-Nitroaniline**[7]<br>**1H NMR (400MHz, CDCl3)**: δ = 8.07-8.05 (d, 2H), 6.63-6.59(m, 2H), 4.35 (s, 4H)<br>**13C NMR (100MHz, CDCl3)**: δ = 152.11, 139.15, 126.16, 113.18 |
|  | **Benzene-1,3-diamine**[7]<br>**1H NMR (400MHz, CDCl3)**: δ = 6.95-6.91 (t, 1H), 6.12-6.10 (m, 2H), 6.02-6.01 (d, 1H)<br>**13C NMR (100MHz, CDCl3)**: δ = 147.61, 130.29, 105.55, 102.27 |

| | |
|---|---|
|  | **(4-Aminophenyl)methanol[4]**<br>**1H NMR (400MHz, CDCl3)**: δ = 7.16-7.13 (d, 2H), 6.67-6.64 (m, 4H), 4.53 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 146.15, 131.49, 129.11, 114.66, 65.42 |
|  | **2,5-Dibromoaniline[2]**<br>**1H NMR (400MHz, CDCl3)**: δ = 7.24-7.22 (d, 1H), 6.91-6.88 (t, 1H), 6.73- 6.67 (m, 1H), 4.12 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 145.96, 144.49, 133.10, 121.98, 117.25, 108.07 |
|  | **p-Toluidine[4]**<br>**1H NMR (400MHz, CDCl3)**: δ = 6.99-6.97 (d, 2H), 6.63-6.61 (d, 2H), 3.53 (s, 2H), 2.26 (s, 3H)<br>**13C NMR (100MHz, CDCl3)**: δ = 143.94, 129.42, 127.66, 115.37, 20.33 |
|  | **naphthalen-1-amine[2]**<br>**1H NMR (400MHz, CDCl3)**: δ = 7.86-7.80 (m, 2H), 7.51- 7.46 (m, 2H), 7.37-7.31 (m, 2H), 6.80-6.78 (d, 1H), 4.41 (s, 2H)<br>**13C NMR (100MHz, CDCl3)**: δ = 142.21, 134.51, 128.69, 126.56, 125.95, 125.00, 123.69, 120.96, 119.07, 109.73 |
|  | **1-(3-aminophenyl)ethan-1-one**<br>**1H NMR (400MHz, CDCl3)**: δ = 7.31-7.29 (d, 2H), 7.24-7.19 (m, 2H), 6.86-6.84 (m, 1H), 3.82 (s, 2H), 2.54 (s, 3H)<br>**13C NMR (100MHz, CDCl3)**: δ = 198.81, 146.73, 137.84, 129.43, 119.47, 114.26, 99.56, 26.60 |

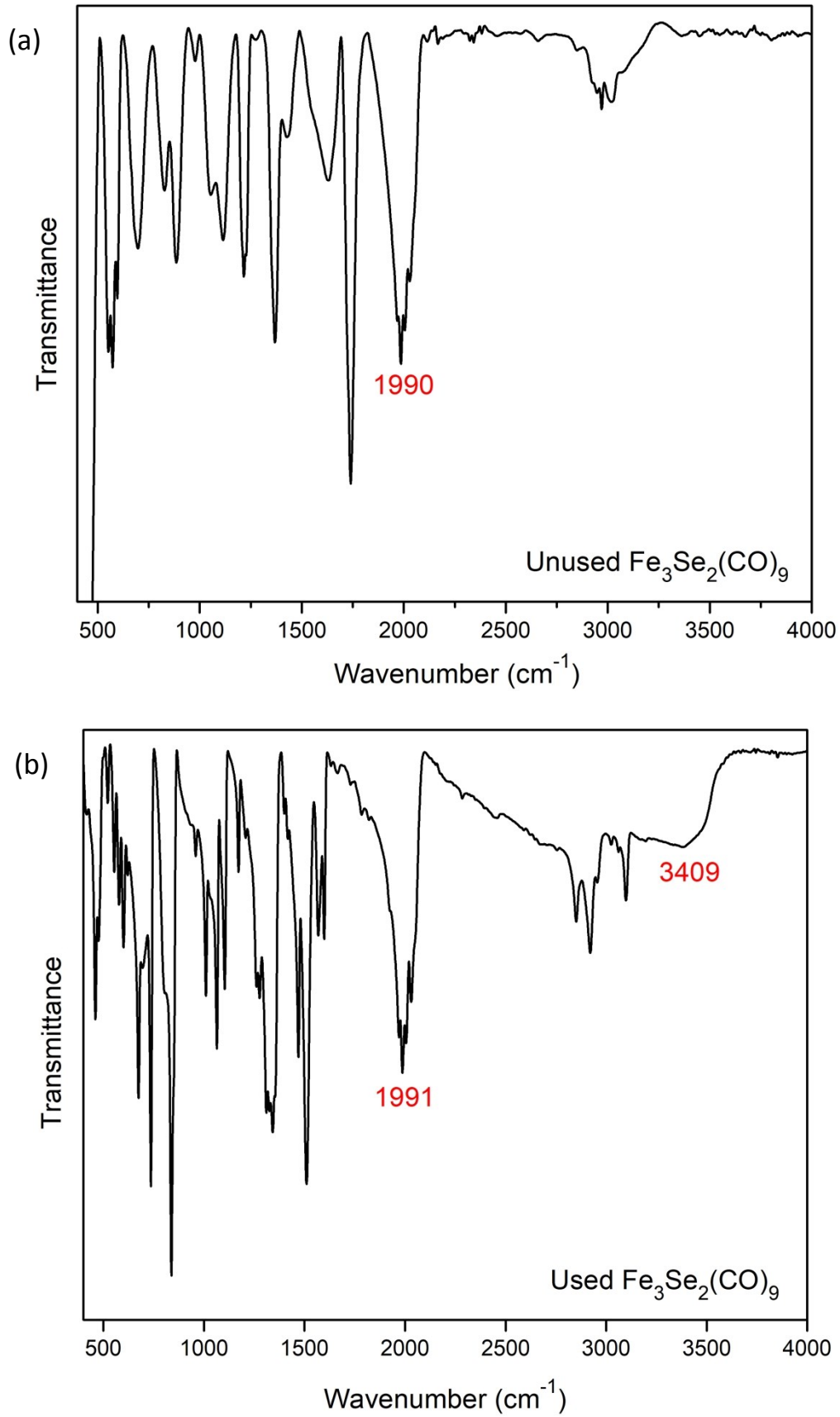
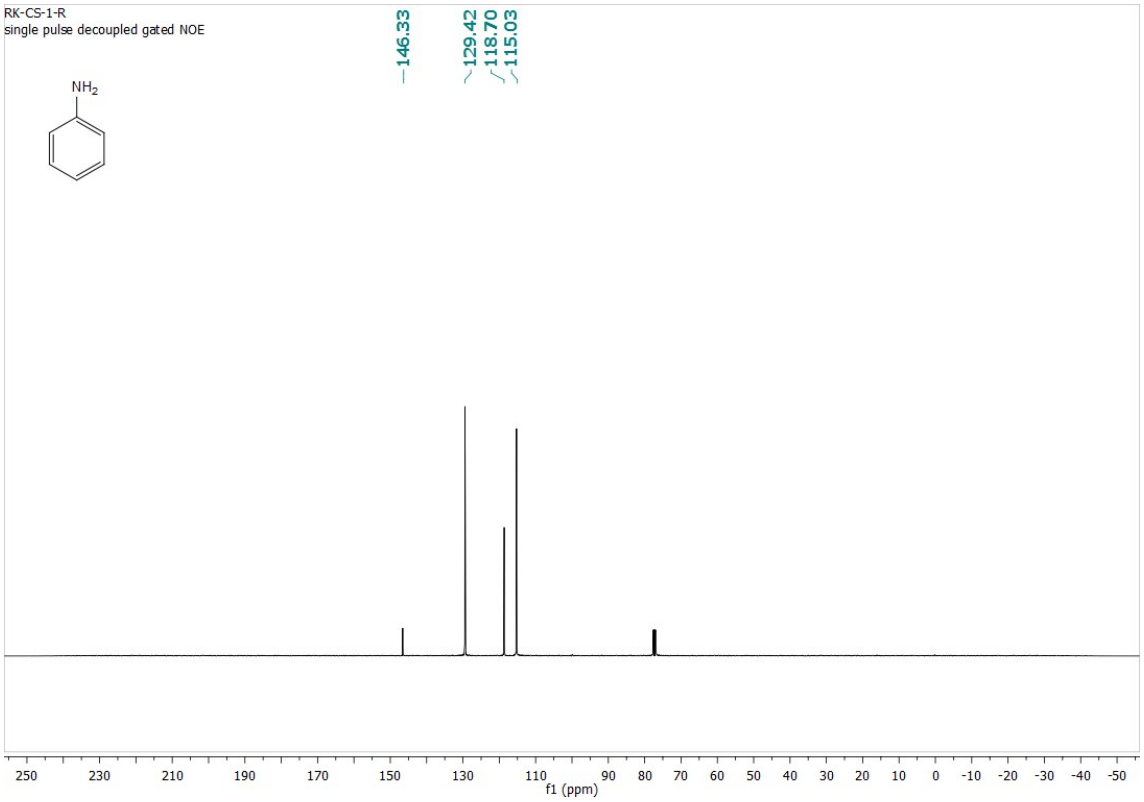
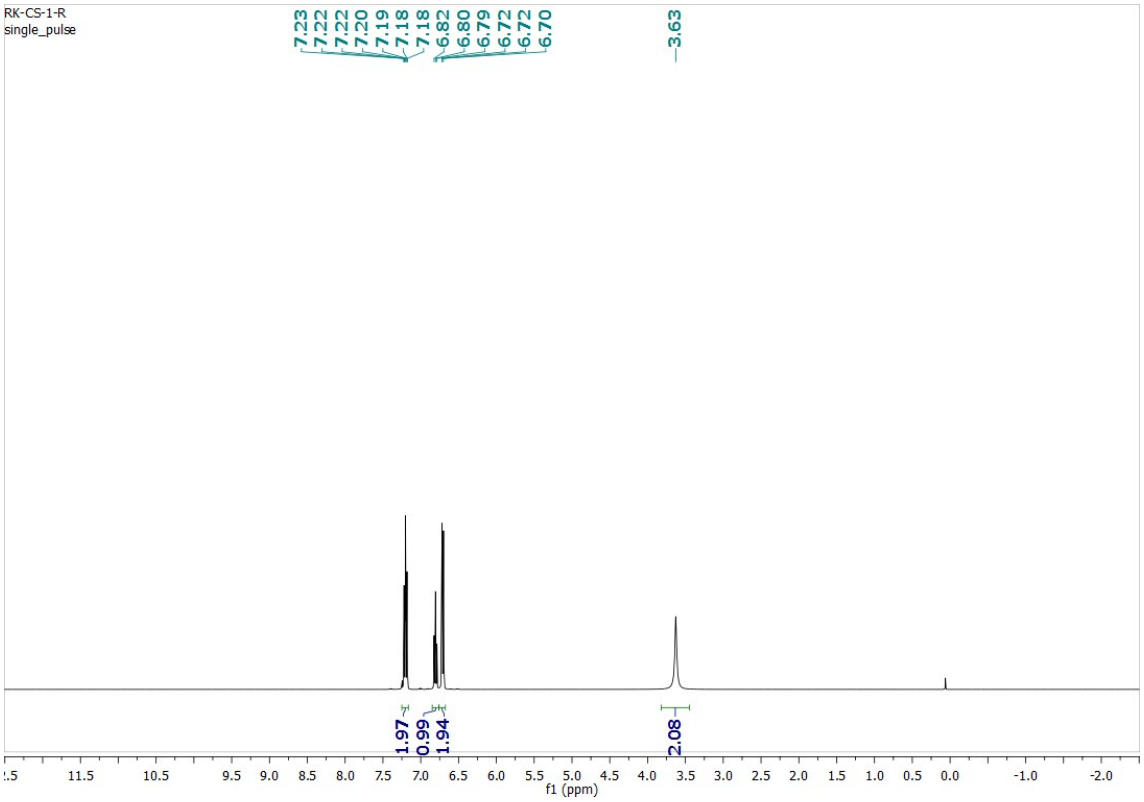
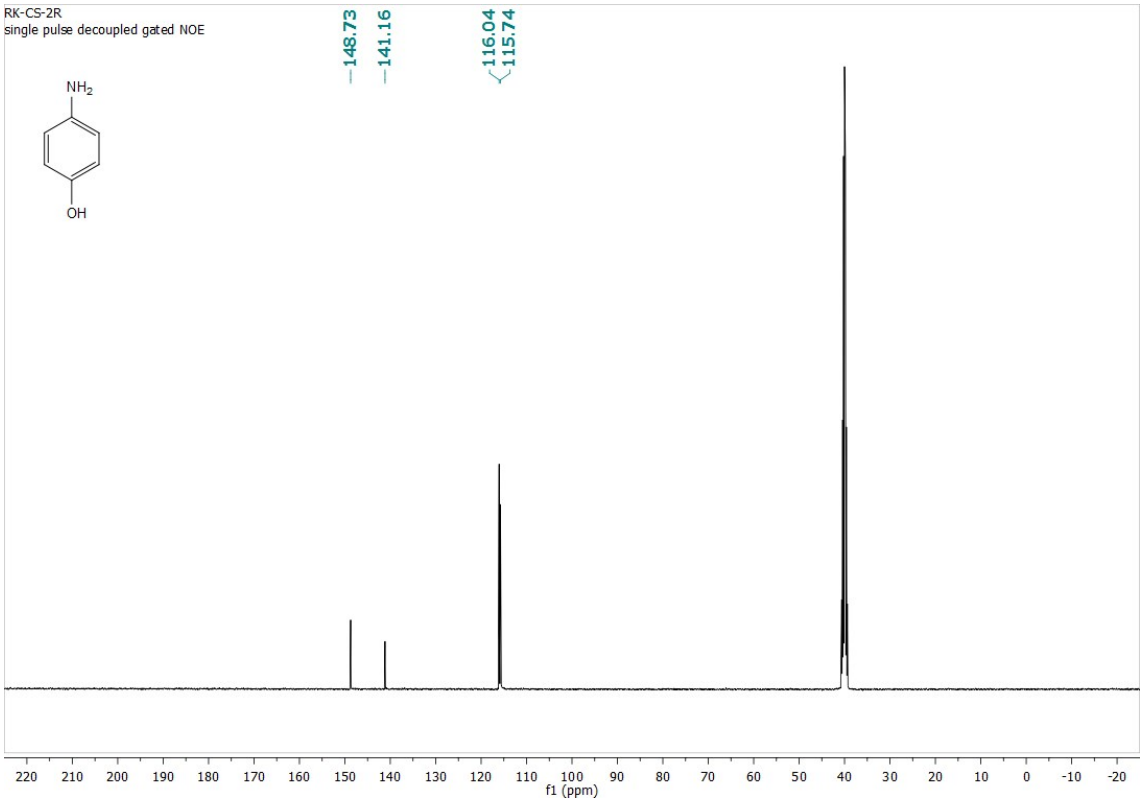
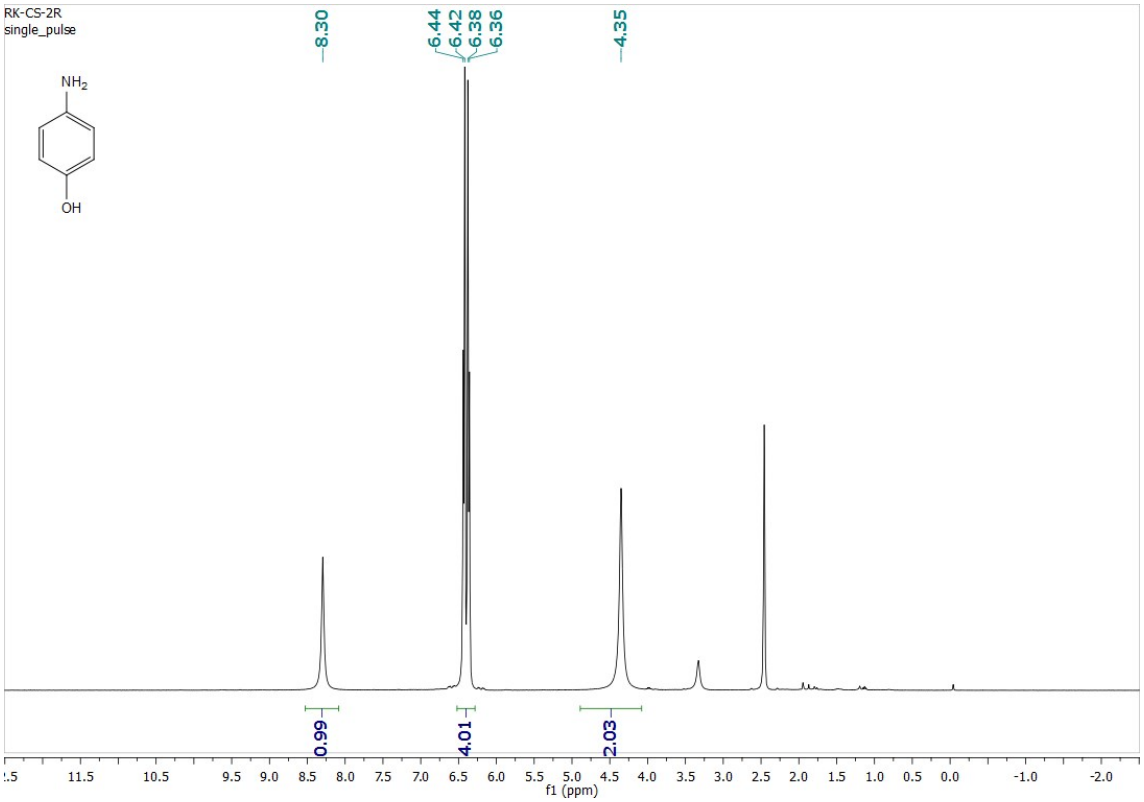


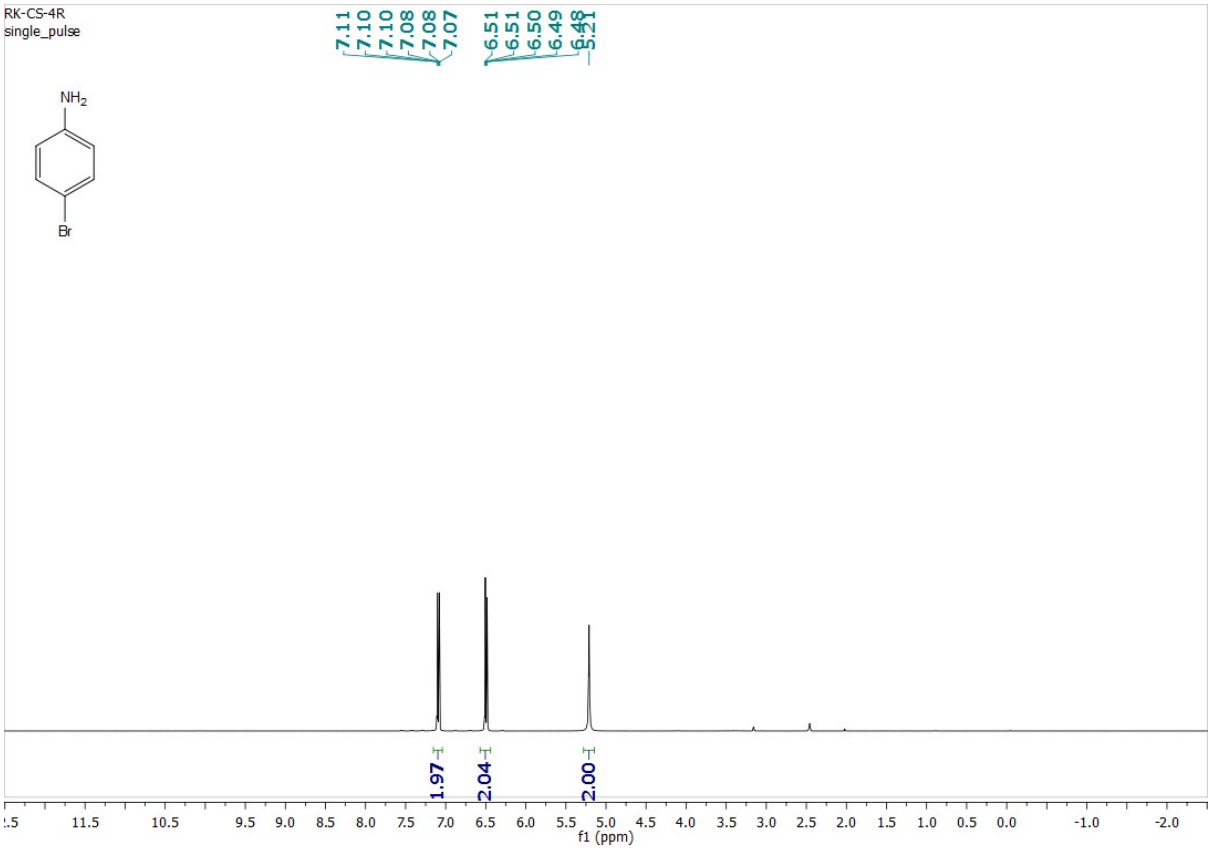

Figure s1: (a) FTIR spectrum of Unused $Fe_3Se_2(CO)_9$, (b) FTIR spectrum of Used $Fe_3Se_2(CO)_9$


RK-CS-1-R
single pulse decoupled gated NOE
NH2
146.33
129.42
118.70
115.03
f1 (ppm)


RK-CS-1-R
single_pulse
7.23
7.22
7.22
7.20
7.19
7.18
7.18
6.82
6.80
6.79
6.72
6.72
6.70
3.63
1.97
0.99
1.94
2.08
f1 (ppm)


RK-CS-2R
single pulse decoupled gated NOE
148.73
141.16
116.04
115.74
NH2
OH
f1 (ppm)


RK-CS-2R
single_pulse
8.30
6.44
6.42
6.38
6.36
4.35
NH2
OH
0.99
4.01
2.03
f1 (ppm)


RK-CS-4R
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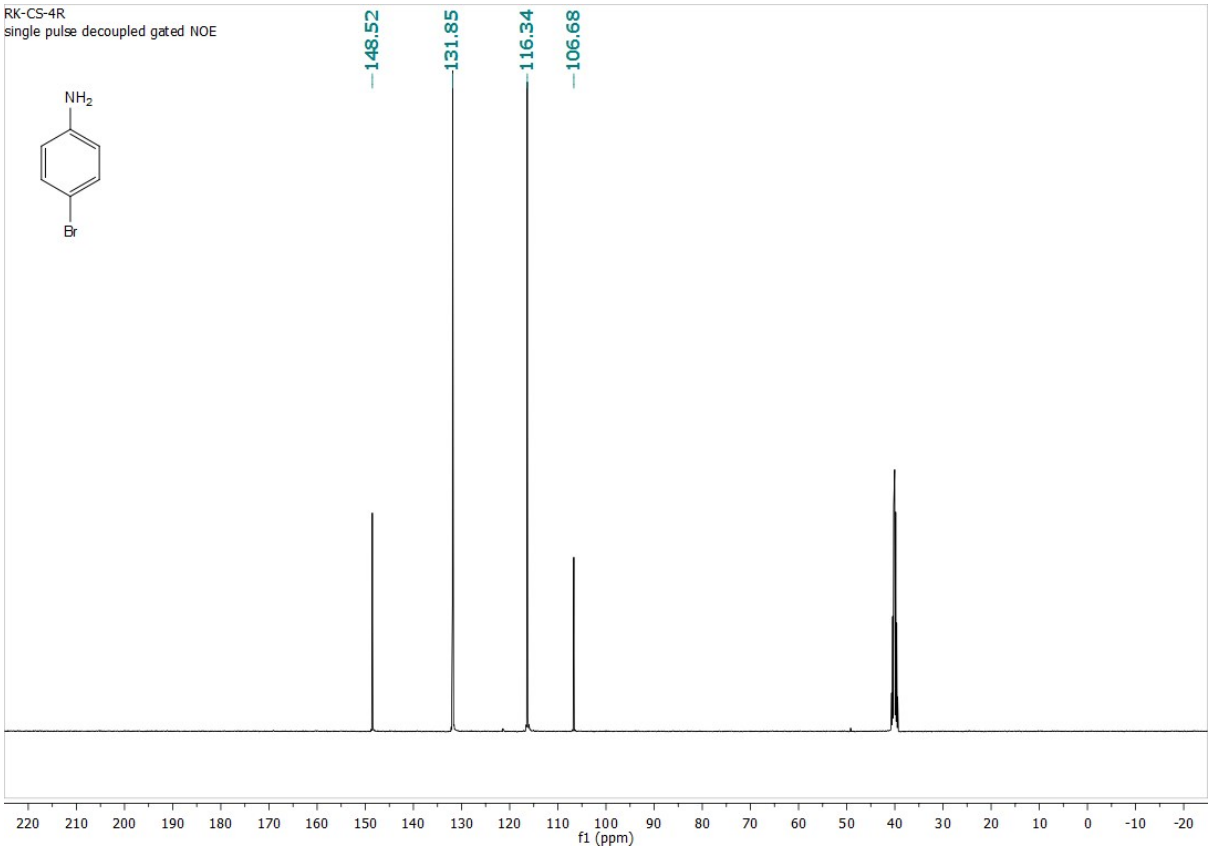
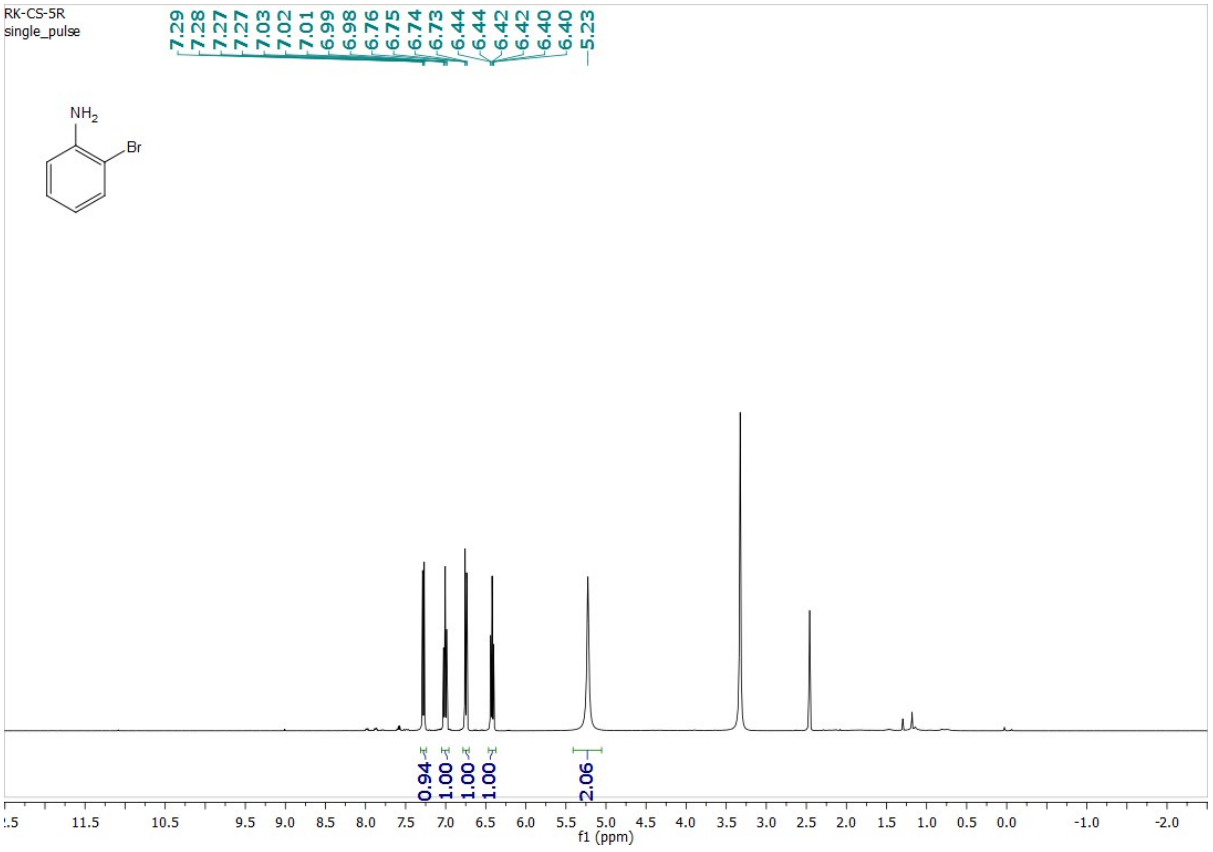
7.11
7.10
7.10
7.08
7.08
7.07
6.51
6.51
6.50
6.49
6.48
5.21
NH2
Br
1.97
2.04
2.00
f1 (ppm)


RK-CS-4R
single pulse decoupled gated NOE
148.52
131.85
116.34
106.68
NH2
Br
f1 (ppm)


RK-CS-5R
single_pulse
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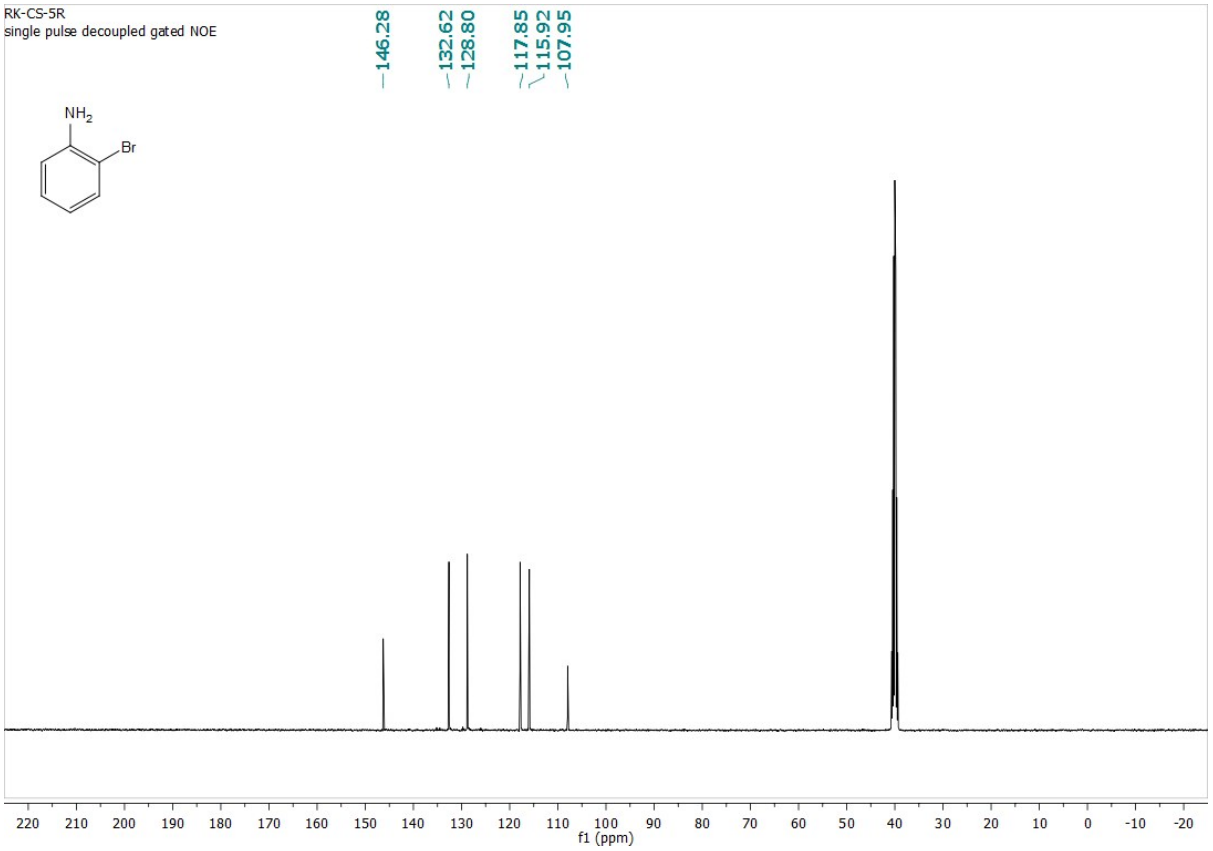
7.28
7.27
7.27
7.03
7.02
7.01
6.99
6.98
6.76
6.75
6.74
6.73
6.44
6.44
6.42
6.42
6.40
6.40
5.23
NH2
Br
0.94
1.00
1.00
1.00
2.06
f1 (ppm)


RK-CS-5R
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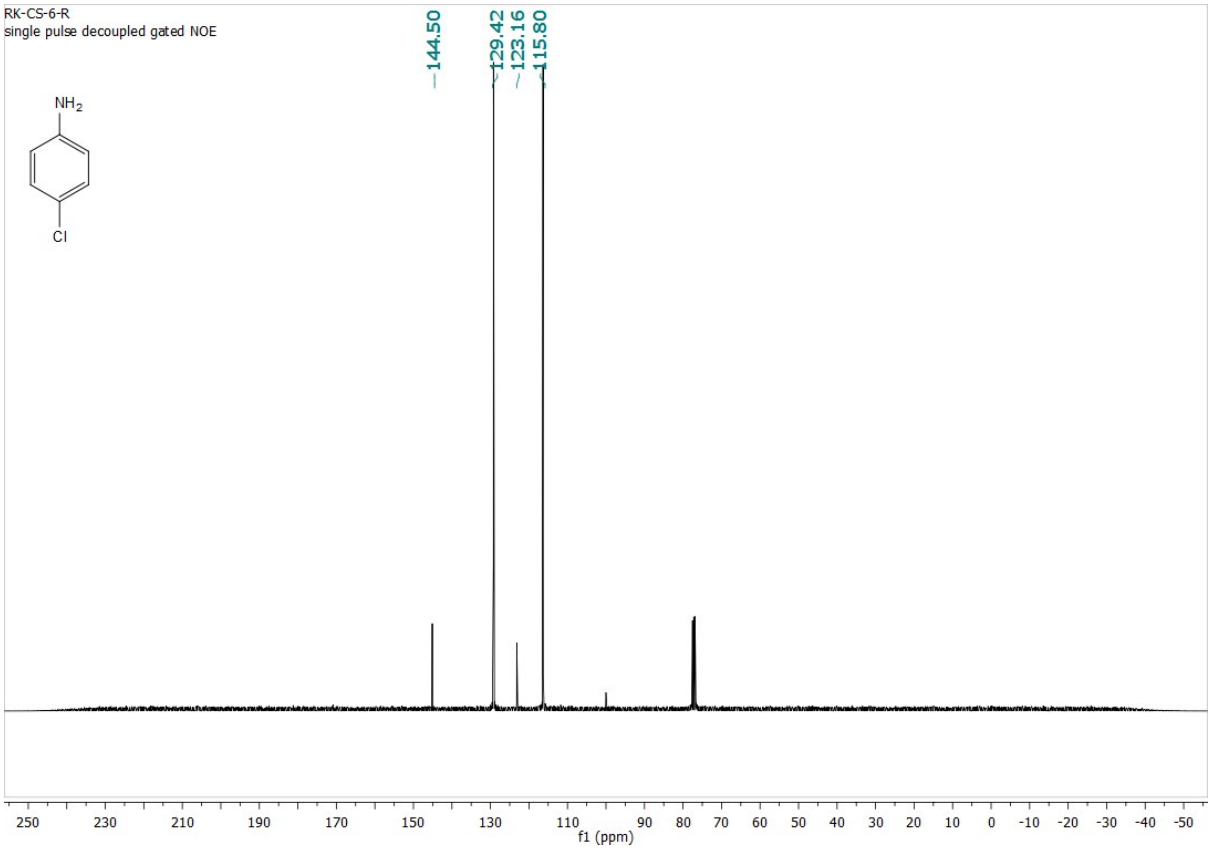
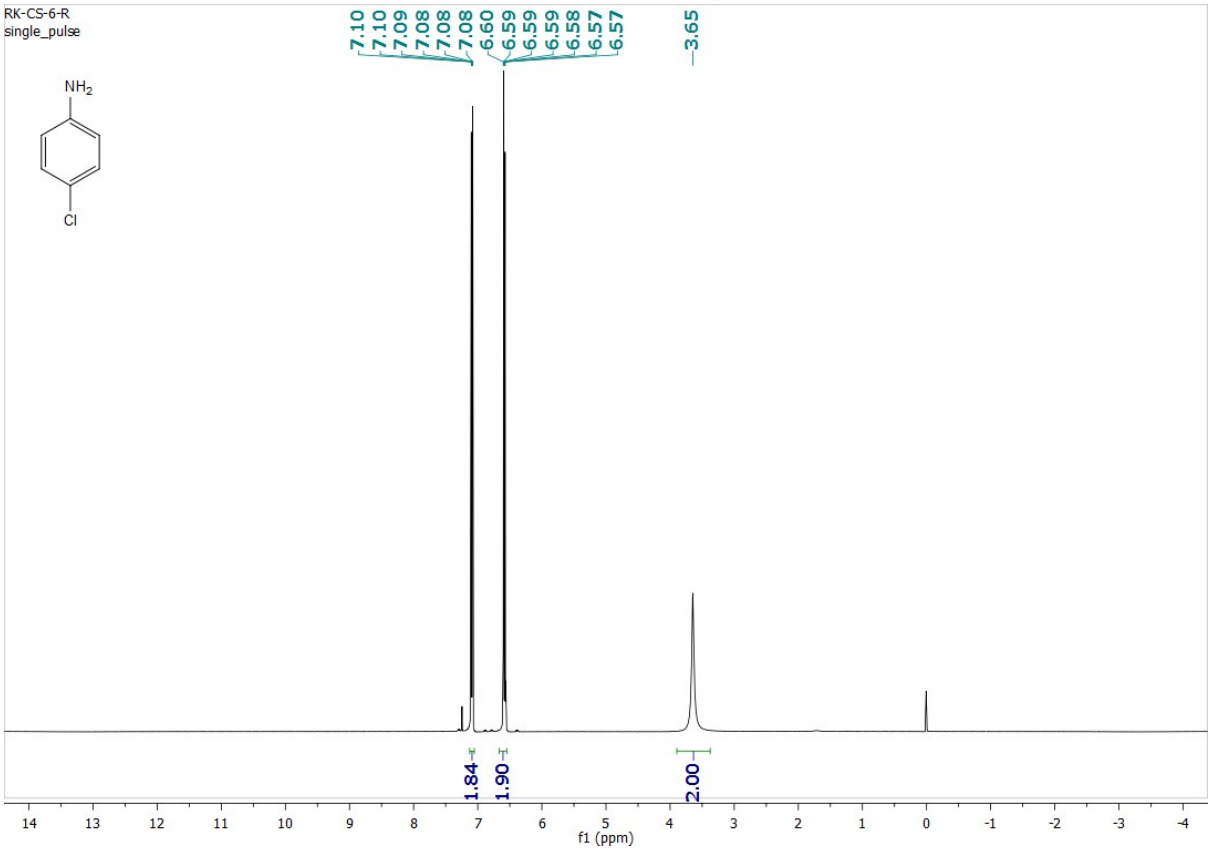
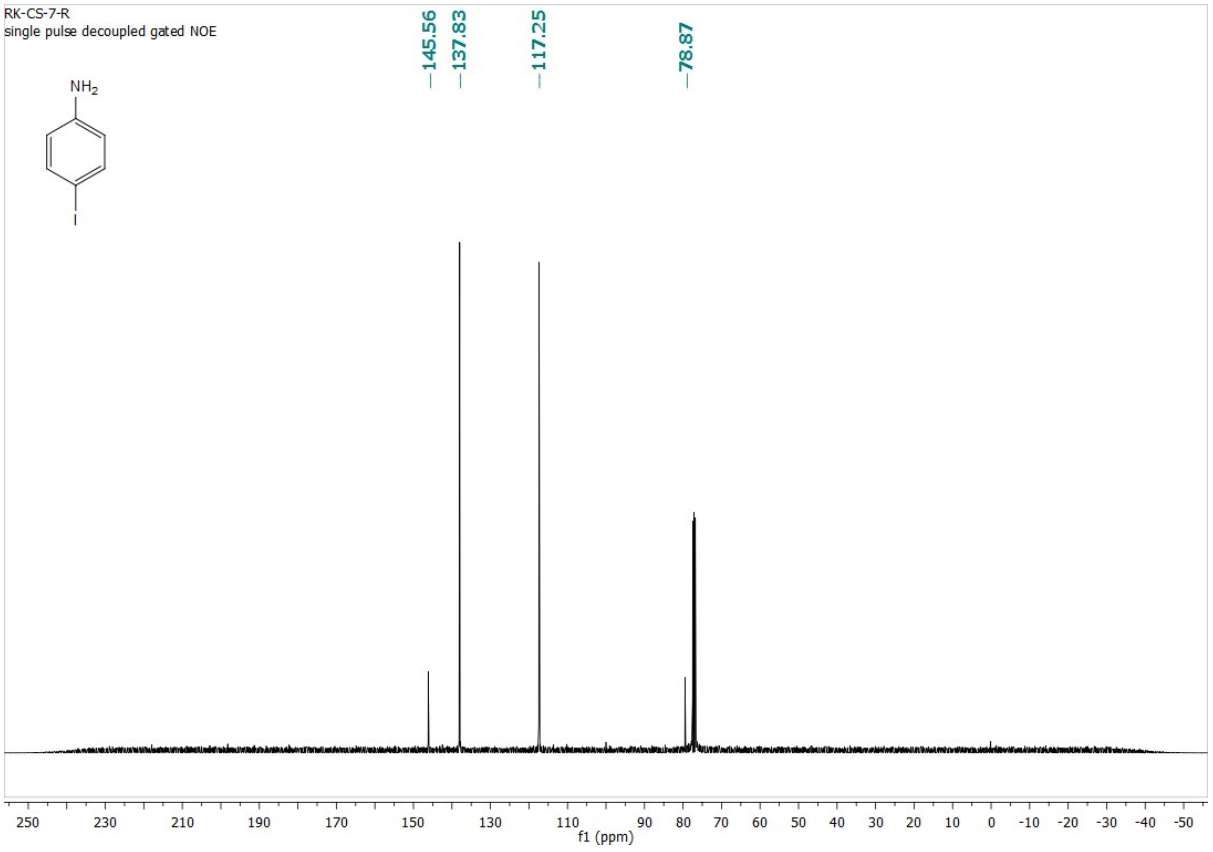
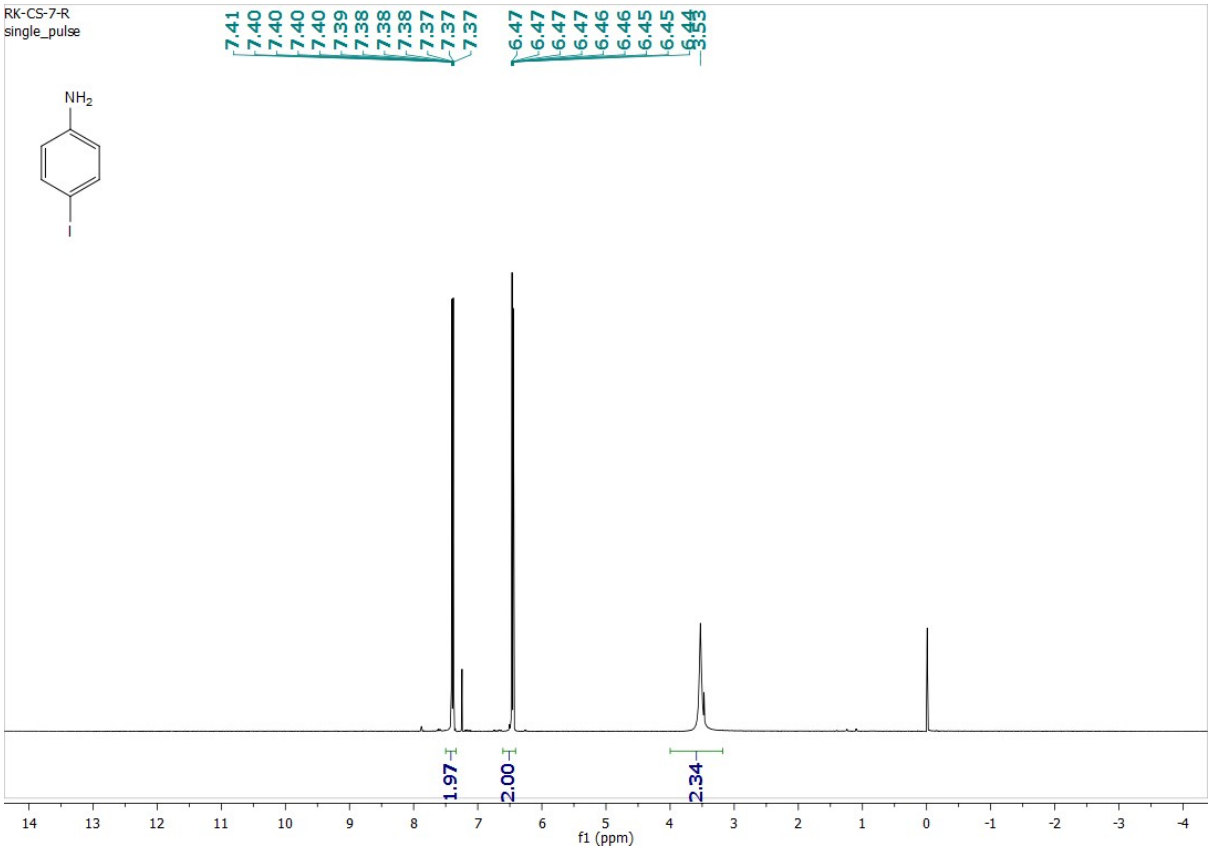
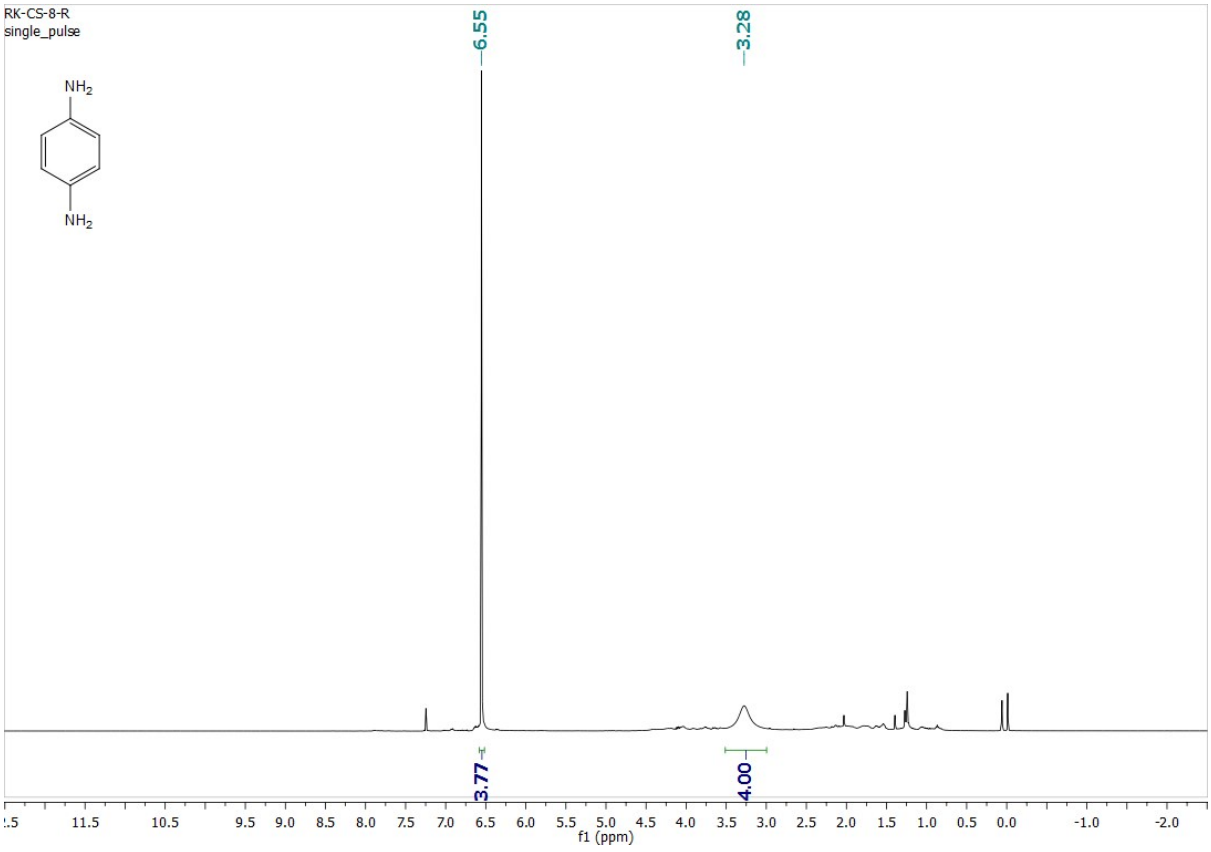
146.28
132.62
128.80
117.85
115.92
107.95
NH2
Br
f1 (ppm)

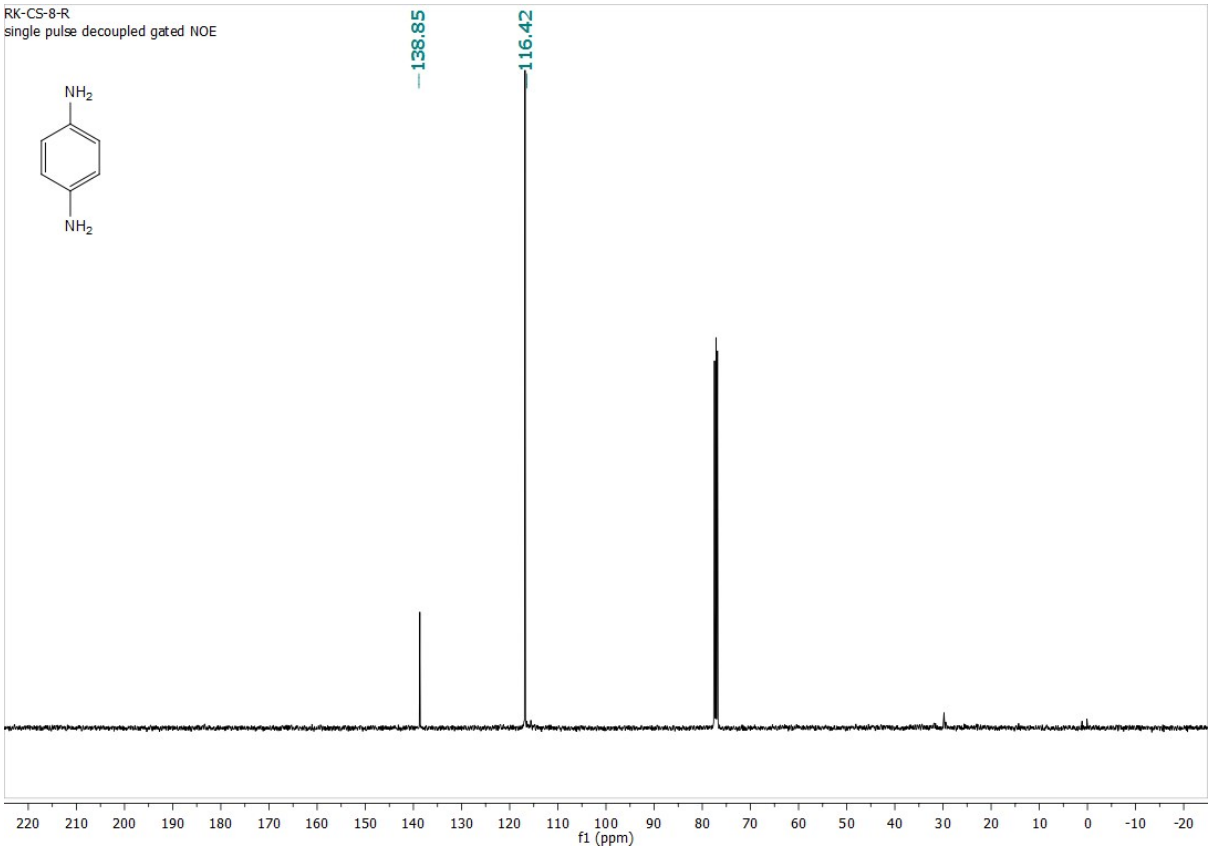

RK-CS-6-R
single pulse decoupled gated NOE
144.50
129.42
123.16
115.80
NH2
Cl
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

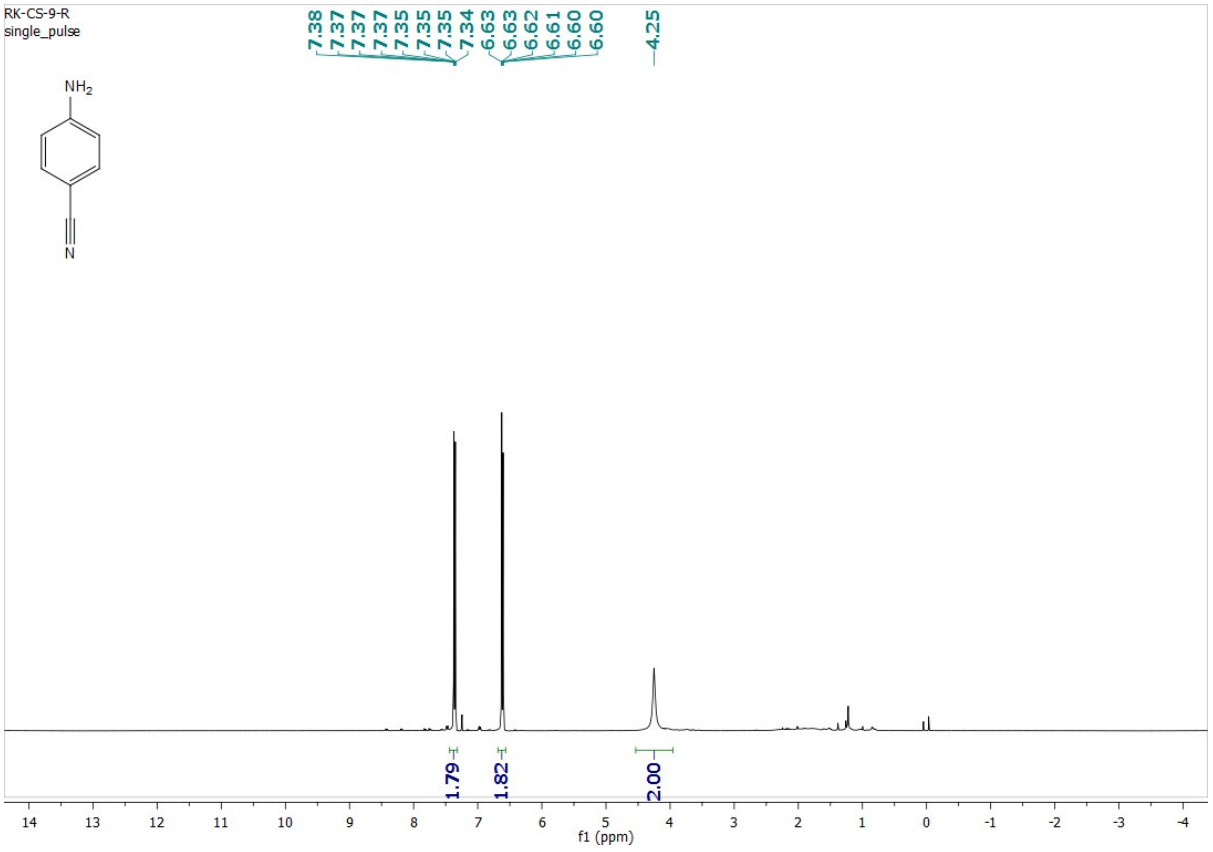

RK-CS-6-R
single_pulse
7.10
7.10
7.09
7.08
7.08
7.08
6.60
6.59
6.59
6.59
6.58
6.57
6.57
3.65
NH2
Cl
1.84
1.90
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

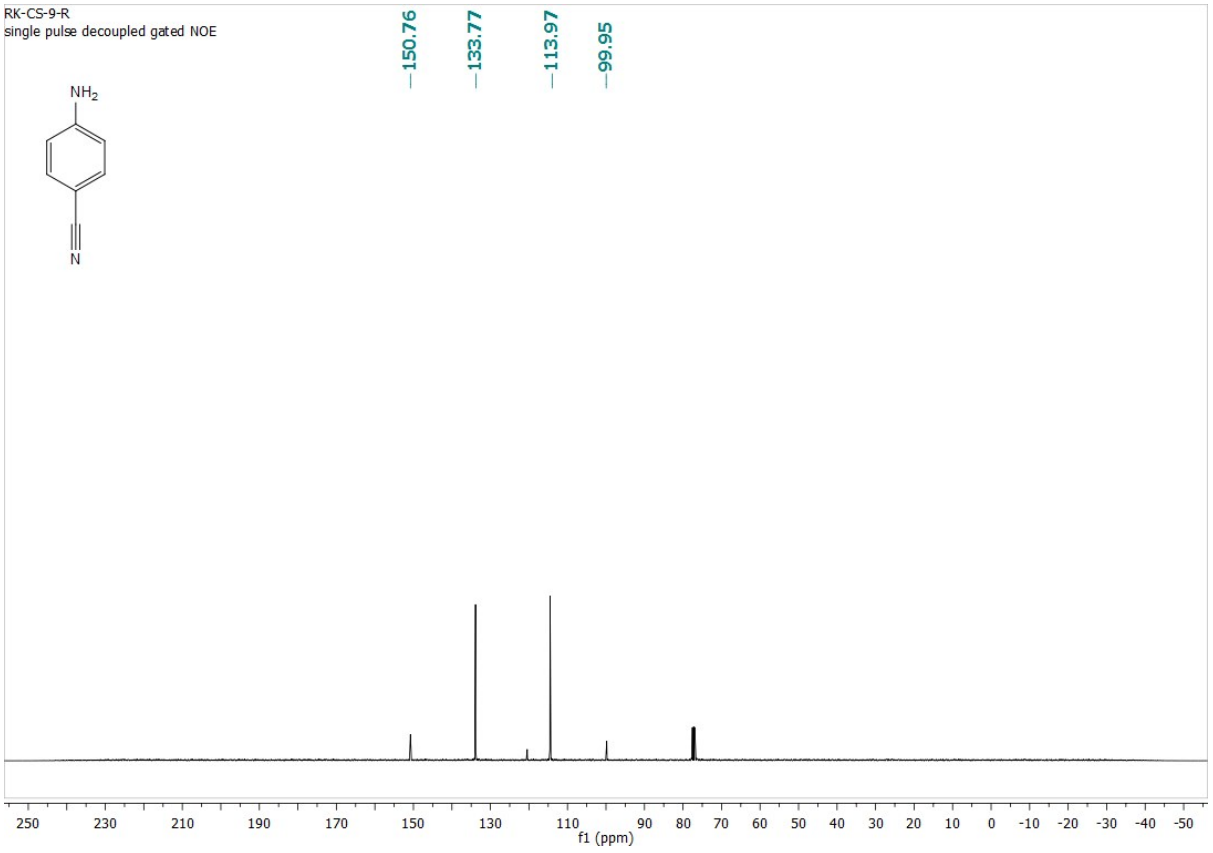

RK-CS-7-R
single pulse decoupled gated NOE
145.56
137.83
117.25
78.87
NH2
I
f1 (ppm)

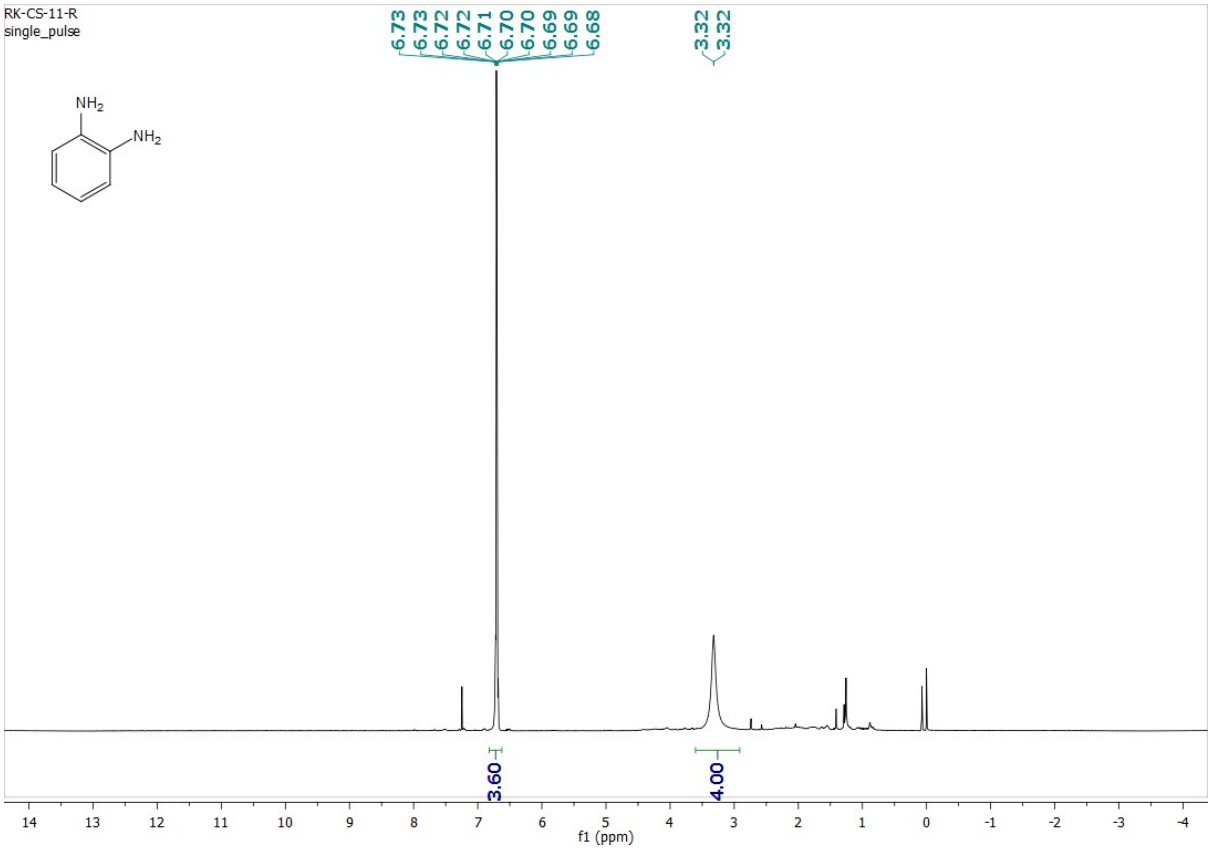

RK-CS-7-R
single_pulse
7.41
7.40
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.37
6.47
6.47
6.47
6.47
6.46
6.46
6.45
6.45
6.44
3.53
NH2
I
1.97
2.00
2.34
f1 (ppm)

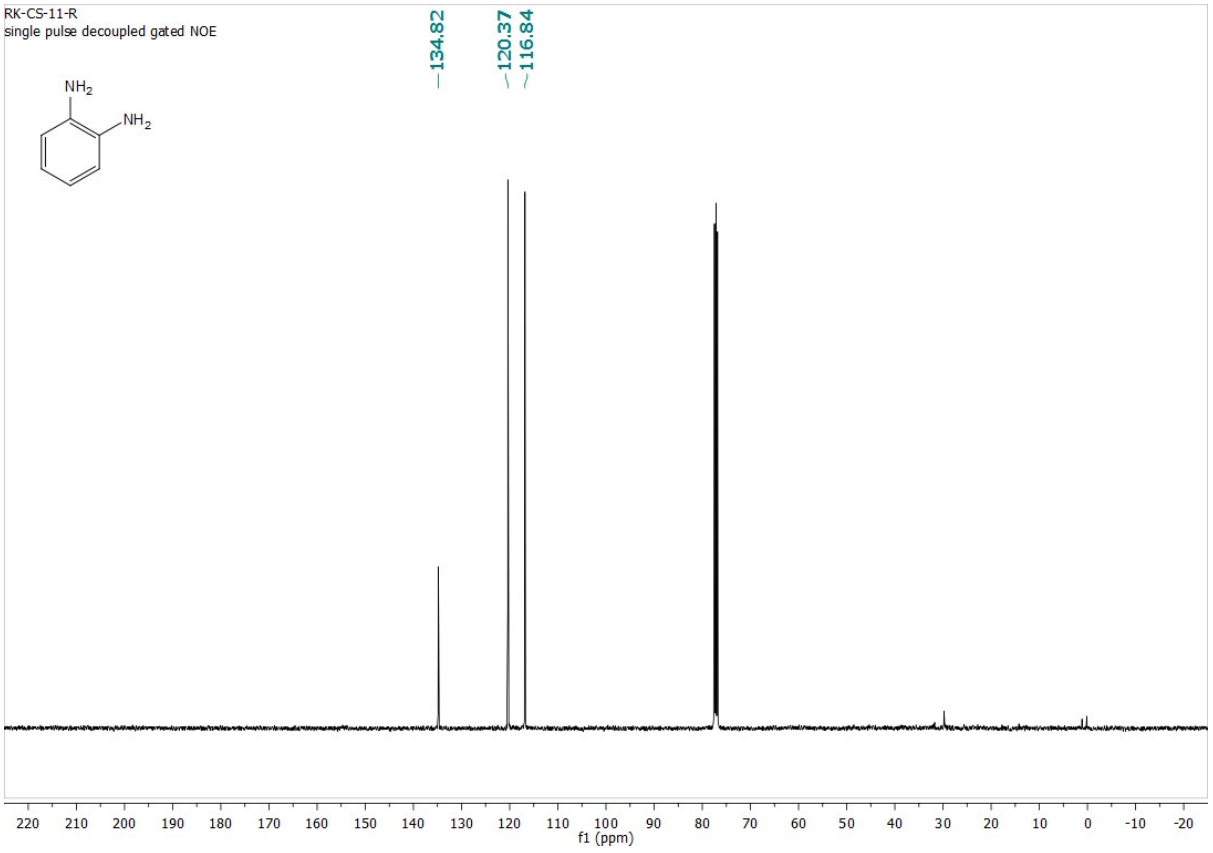

RK-CS-8-R
single_pulse
6.55
3.28
NH2
NH2
3.77
4.00
f1 (ppm)

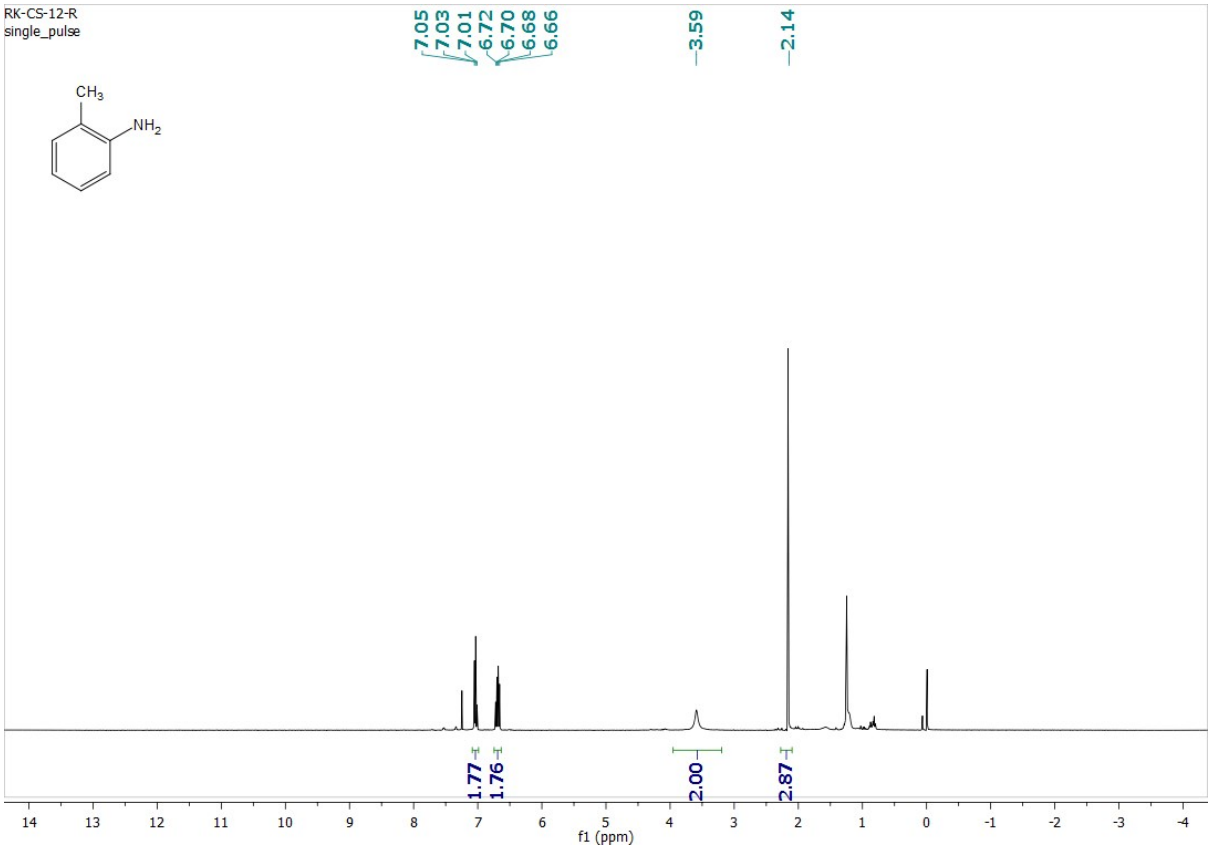

RK-CS-8-R
single pulse decoupled gated NOE
138.85
116.42
NH2
NH2
f1 (ppm)

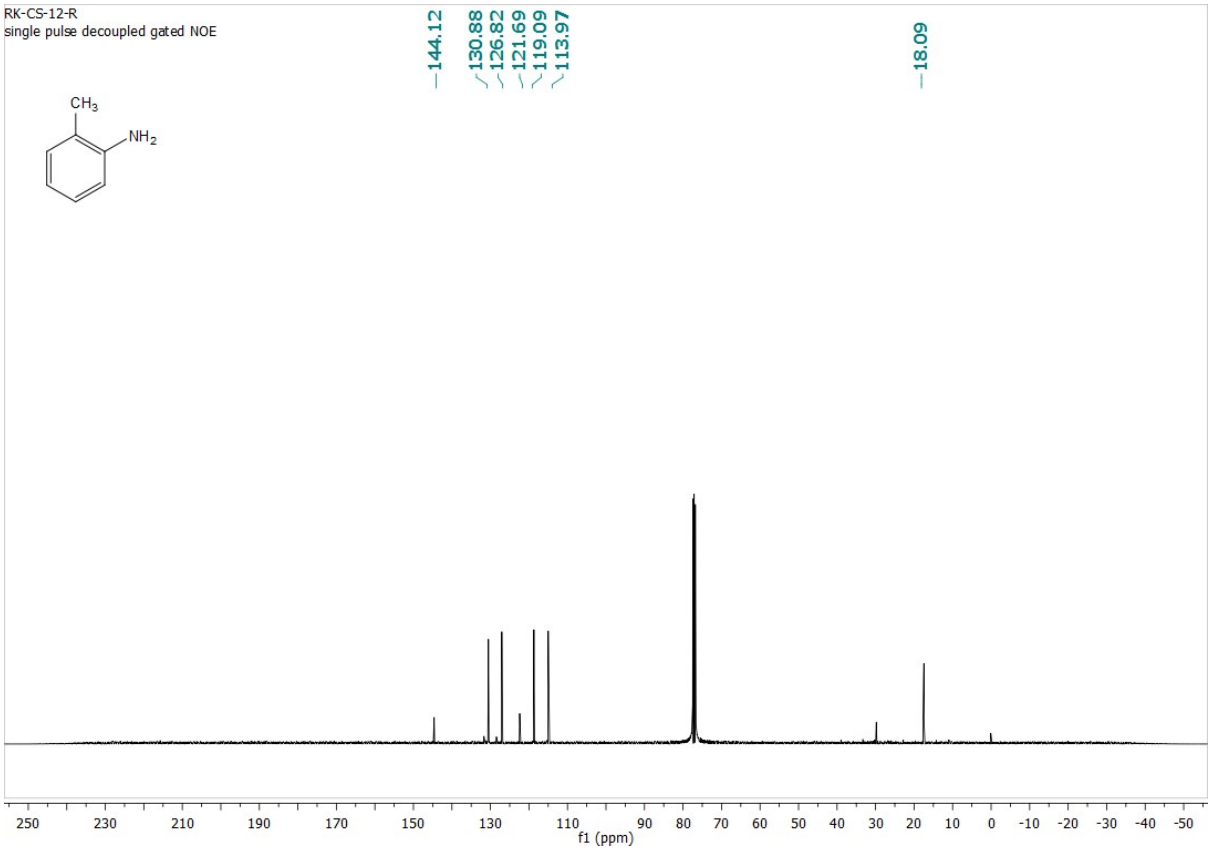

RK-CS-9-R
single_pulse
7.38
7.37
7.37
7.37
7.35
7.35
7.35
7.34
6.63
6.63
6.62
6.61
6.60
6.60
4.25
NH2
N
1.79
1.82
2.00
f1 (ppm)

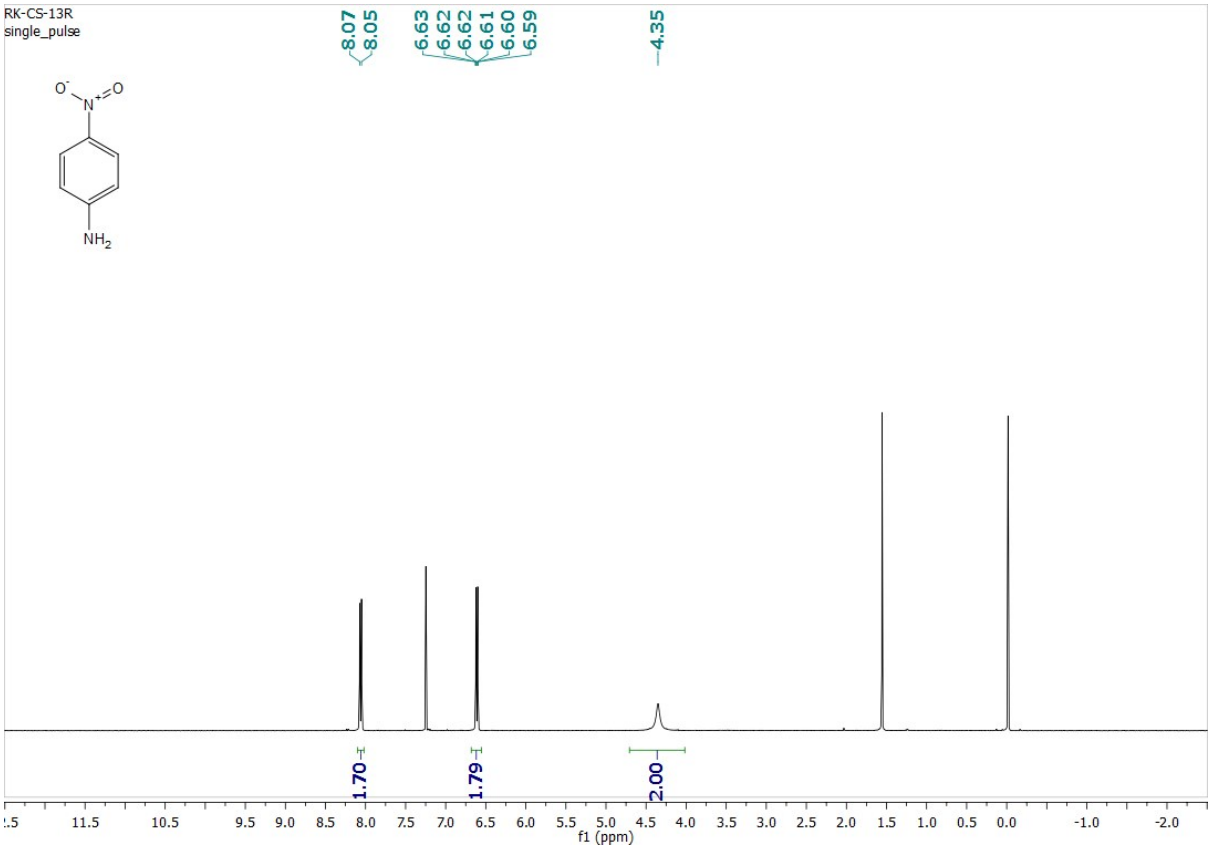

RK-CS-9-R
single pulse decoupled gated NOE
150.76
133.77
113.97
99.95
NH2
N
f1 (ppm)

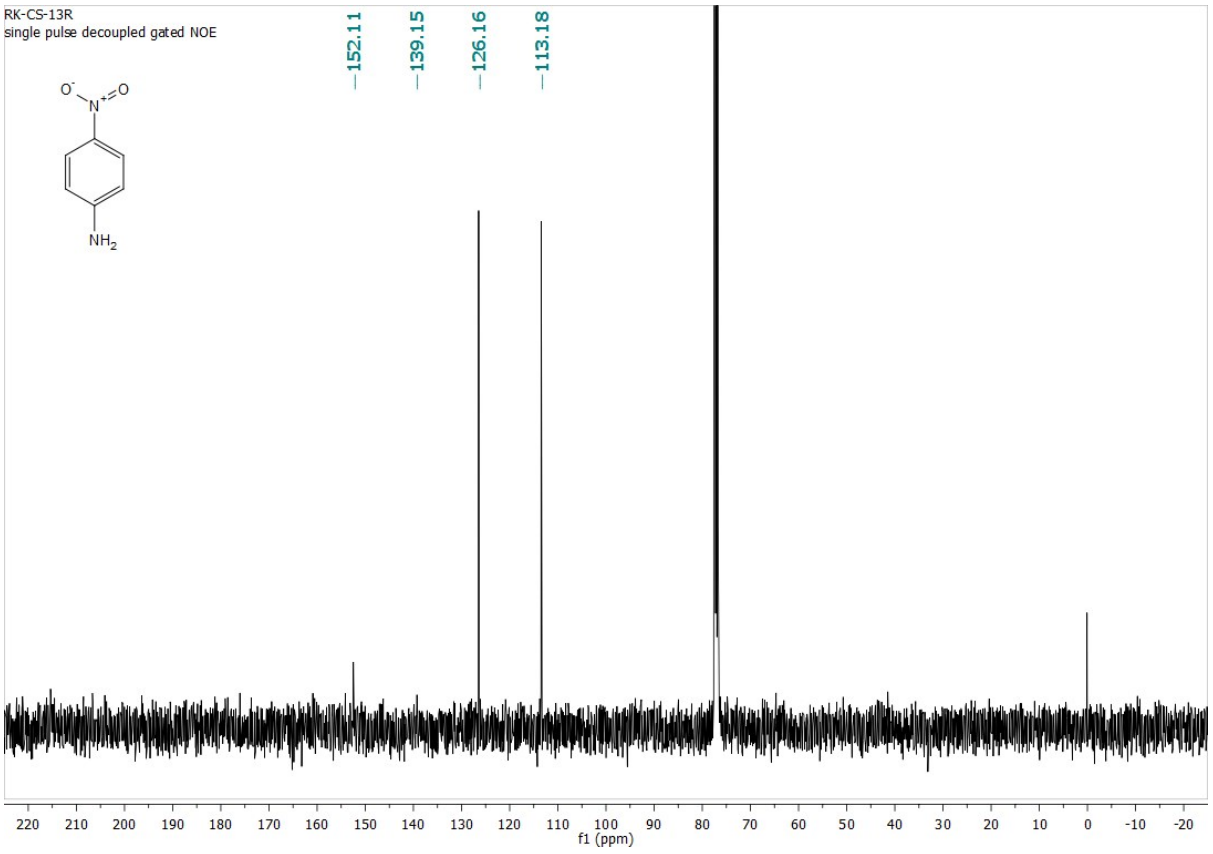

RK-CS-11-R
single_pulse
6.73
6.73
6.72
6.72
6.71
6.70
6.70
6.69
6.69
6.68
3.32
3.32
NH2
NH2
3.60
4.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

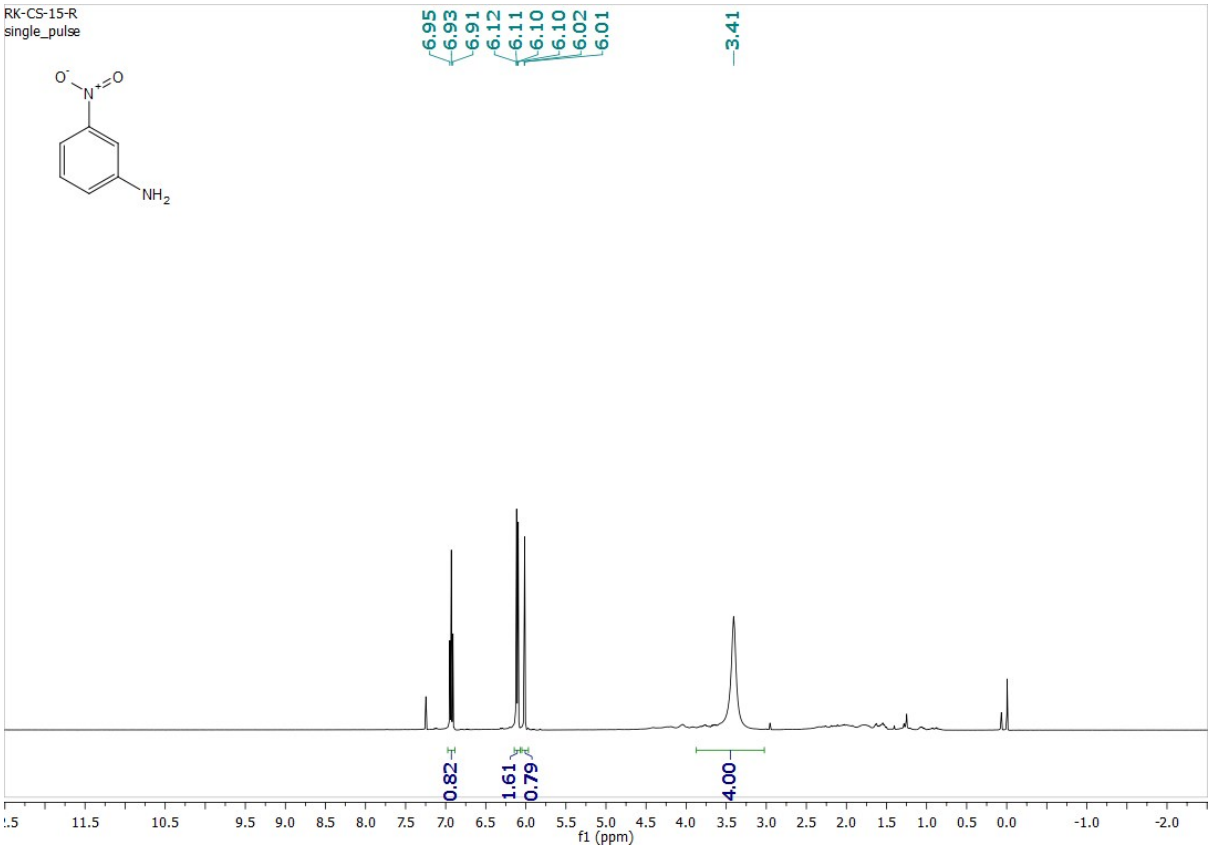

RK-CS-11-R
single pulse decoupled gated NOE
134.82
120.37
116.84
NH2
NH2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

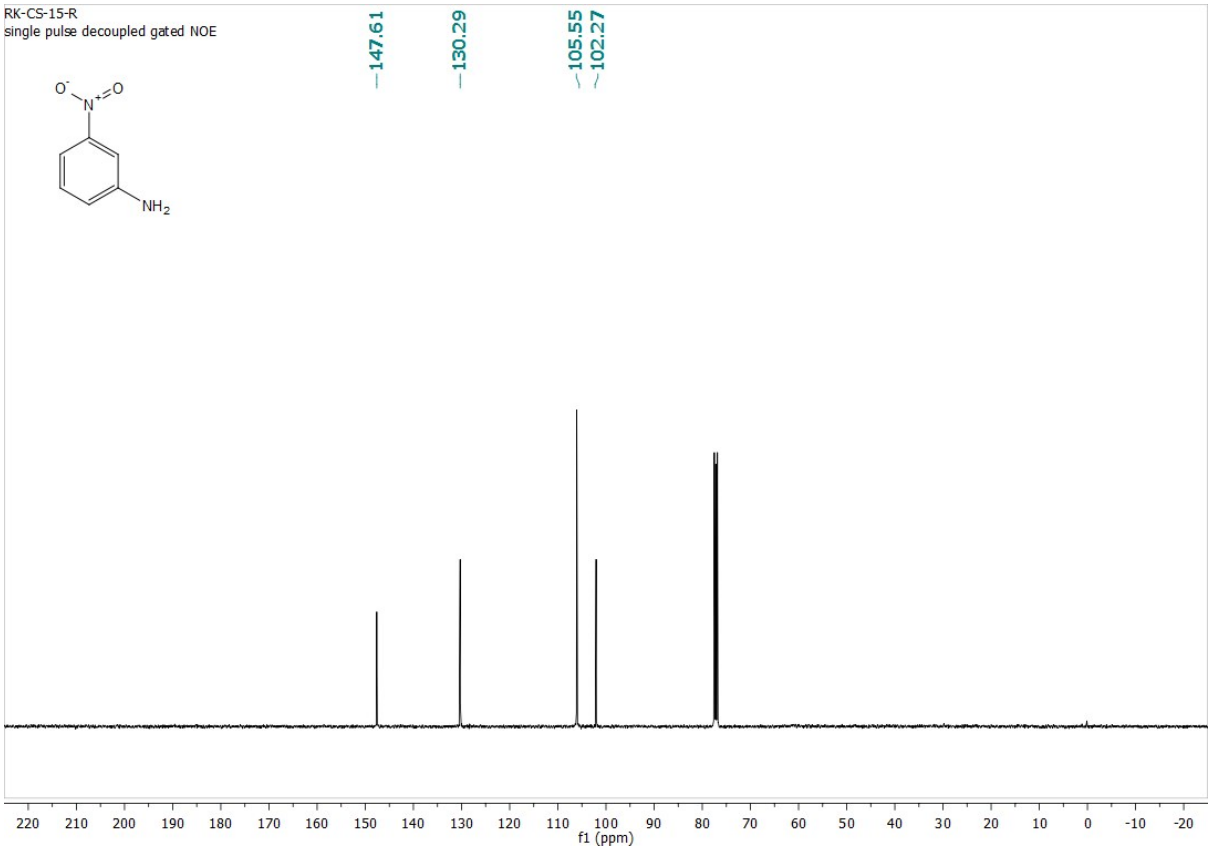

RK-CS-12-R
single_pulse
7.05
7.03
7.01
6.72
6.70
6.68
6.66
3.59
2.14
CH3
NH2
1.77
1.76
2.00
2.87
f1 (ppm)

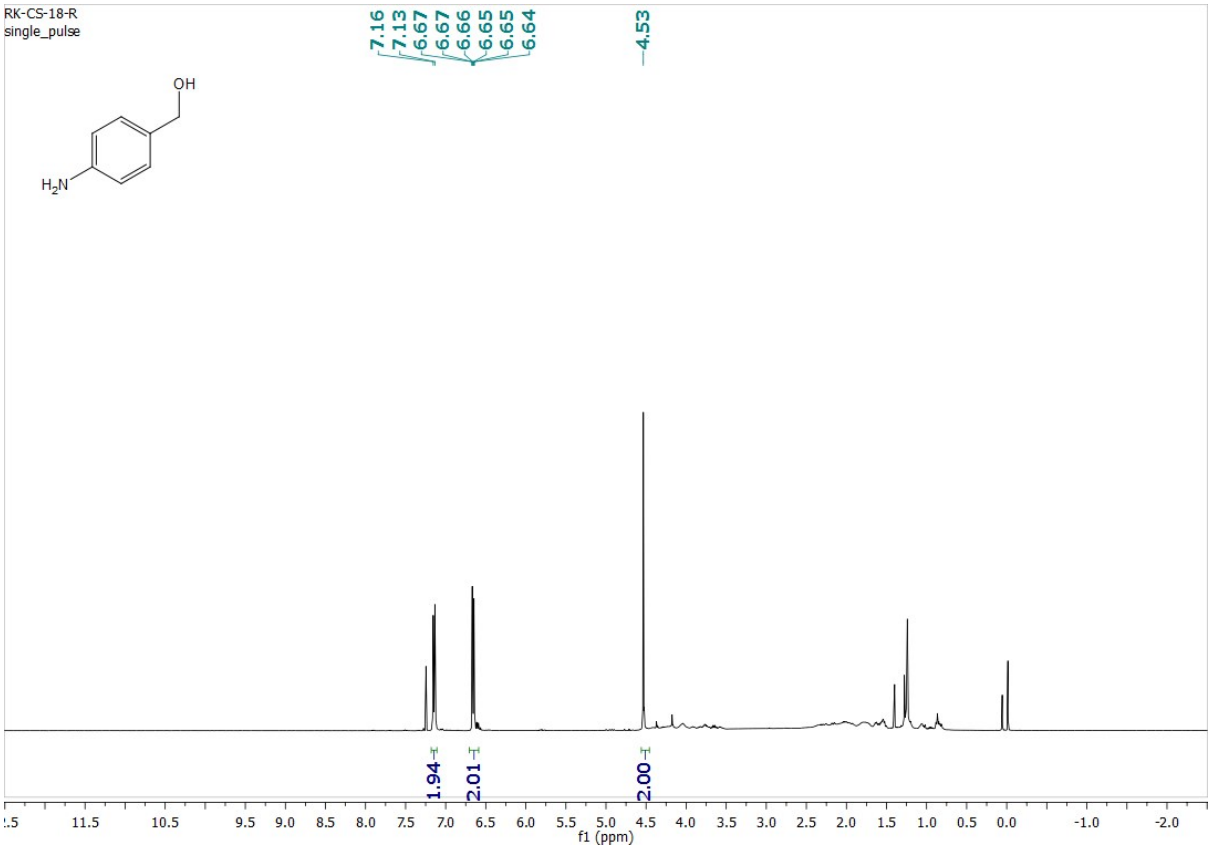

RK-CS-12-R
single pulse decoupled gated NOE
144.12
130.88
126.82
121.69
119.09
113.97
18.09
CH3
NH2
f1 (ppm)

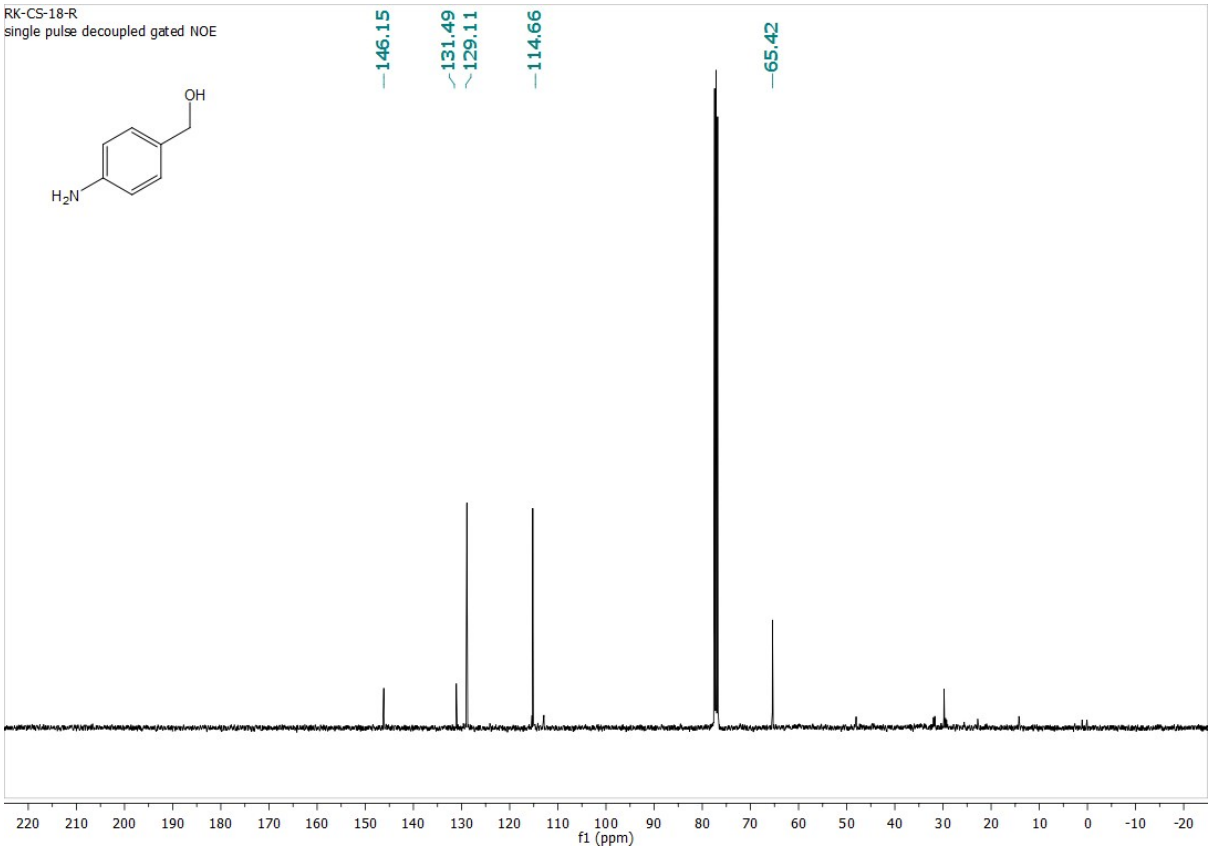

RK-CS-13R
single_pulse
8.07
8.05
6.63
6.62
6.62
6.61
6.60
6.59
4.35
1.70
1.79
2.00
f1 (ppm)

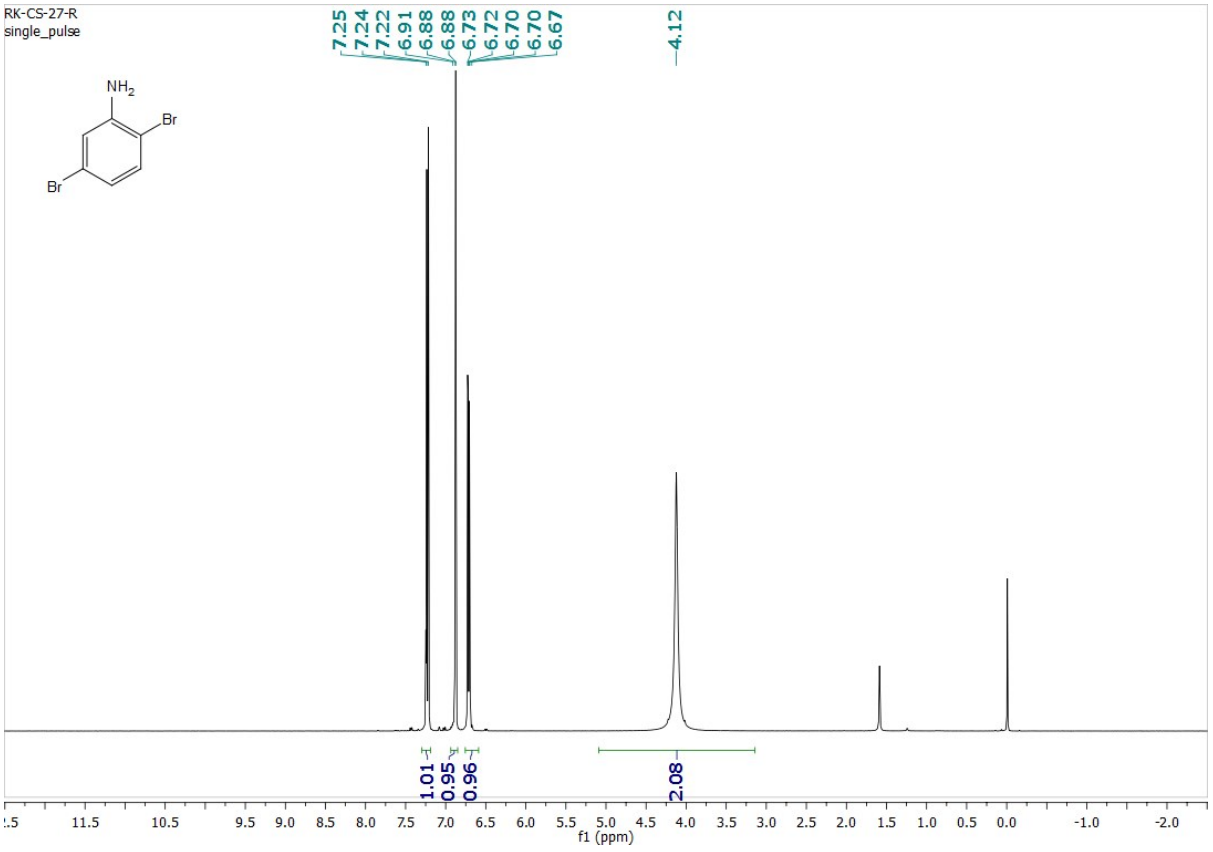

RK-CS-13R
single pulse decoupled gated NOE
152.11
139.15
126.16
113.18
f1 (ppm)

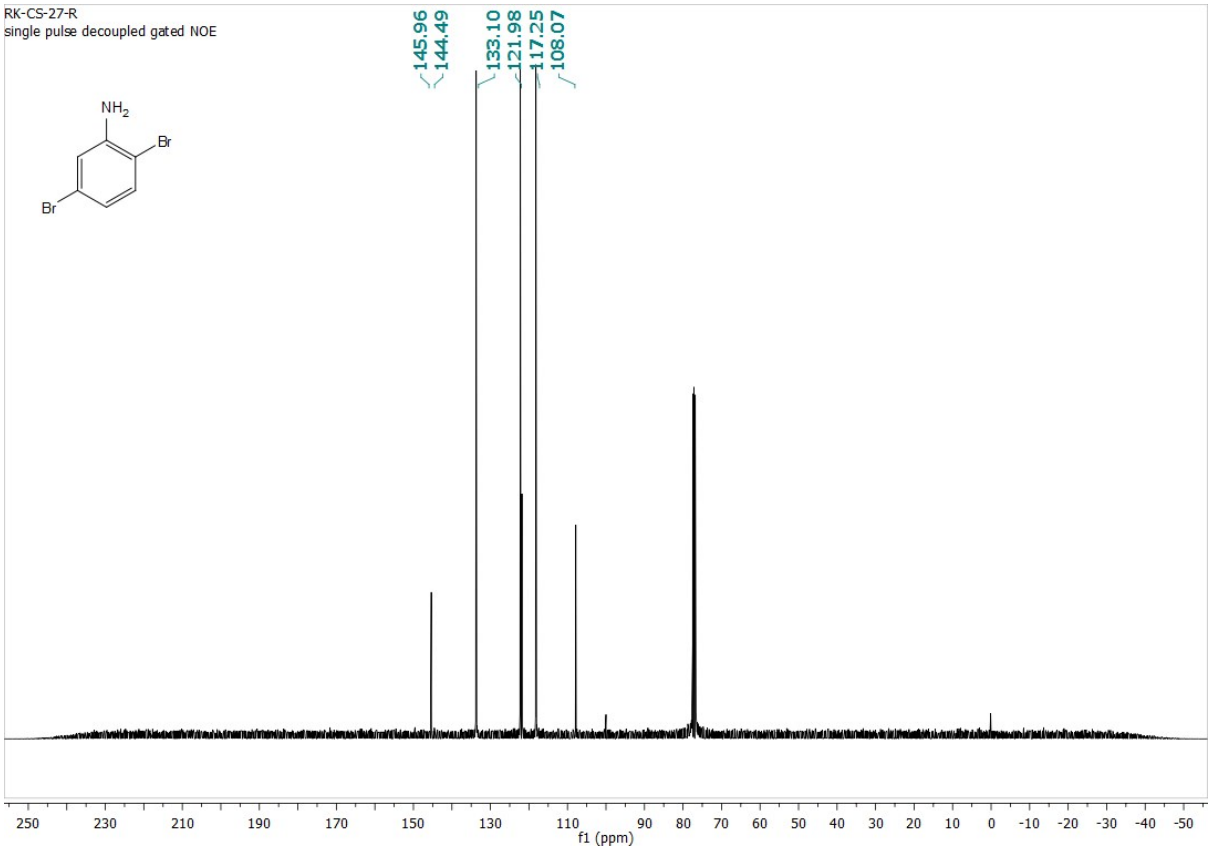

RK-CS-15-R
single_pulse
6.95
6.93
6.91
6.12
6.11
6.10
6.10
6.02
6.01
3.41
0.82
1.61
0.79
4.00
f1 (ppm)

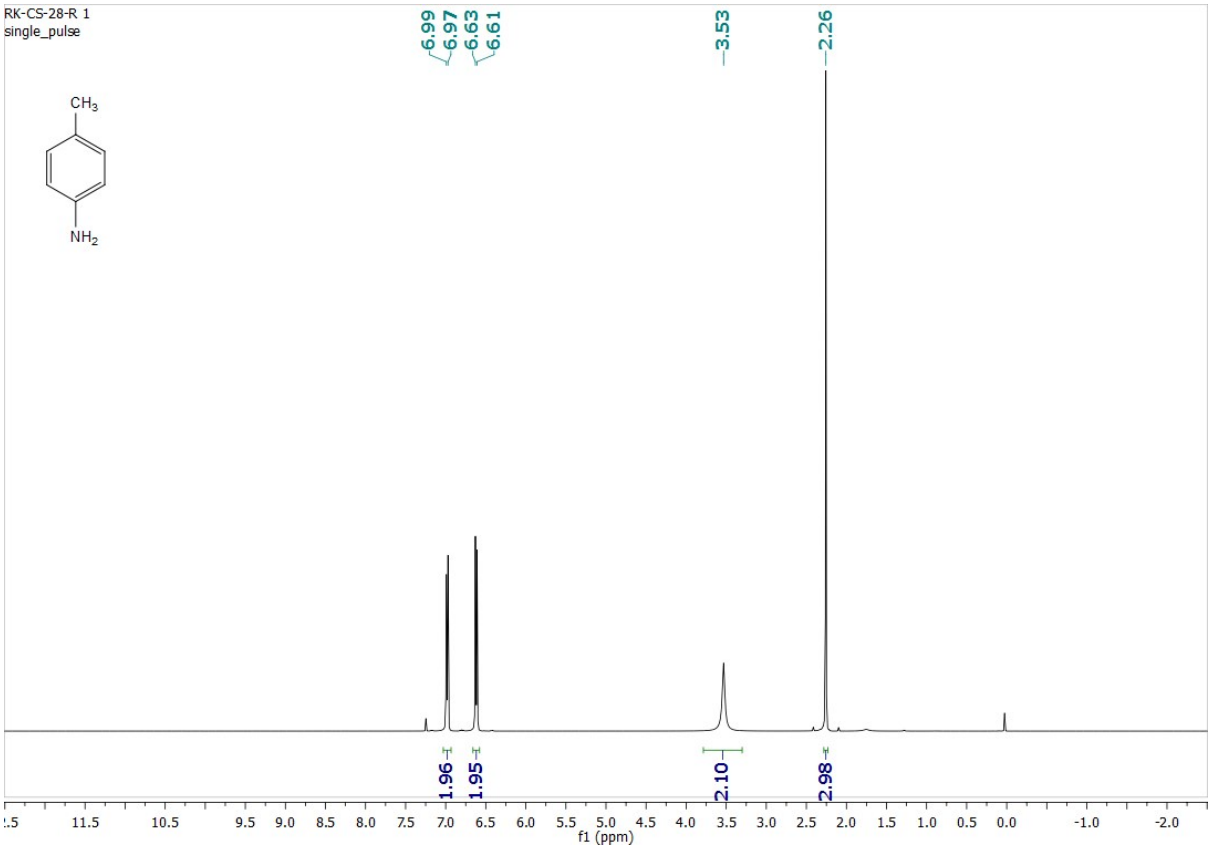

RK-CS-15-R
single pulse decoupled gated NOE
147.61
130.29
105.55
102.27
f1 (ppm)

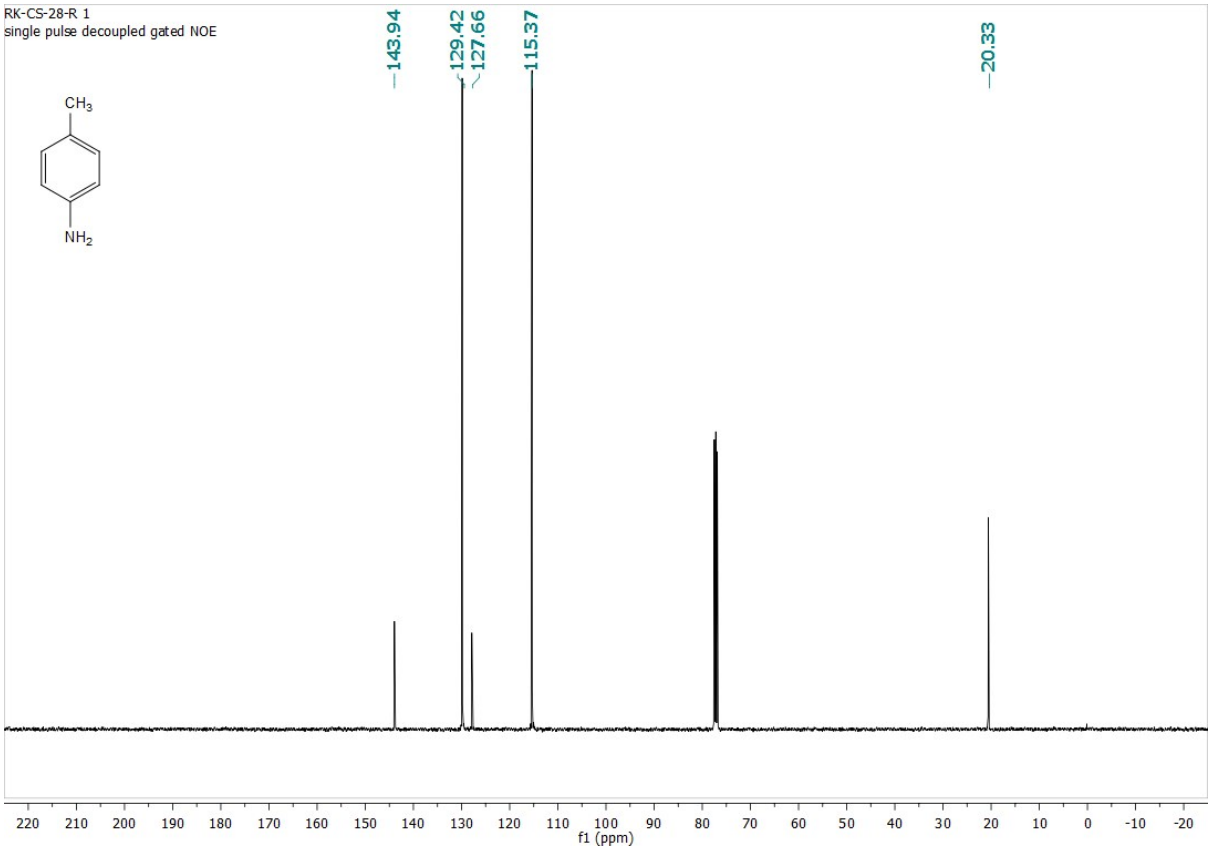

RK-CS-18-R
single_pulse
7.16
7.13
6.67
6.67
6.66
6.65
6.65
6.64
4.53
OH
H2N
1.94
2.01
2.00
f1 (ppm)

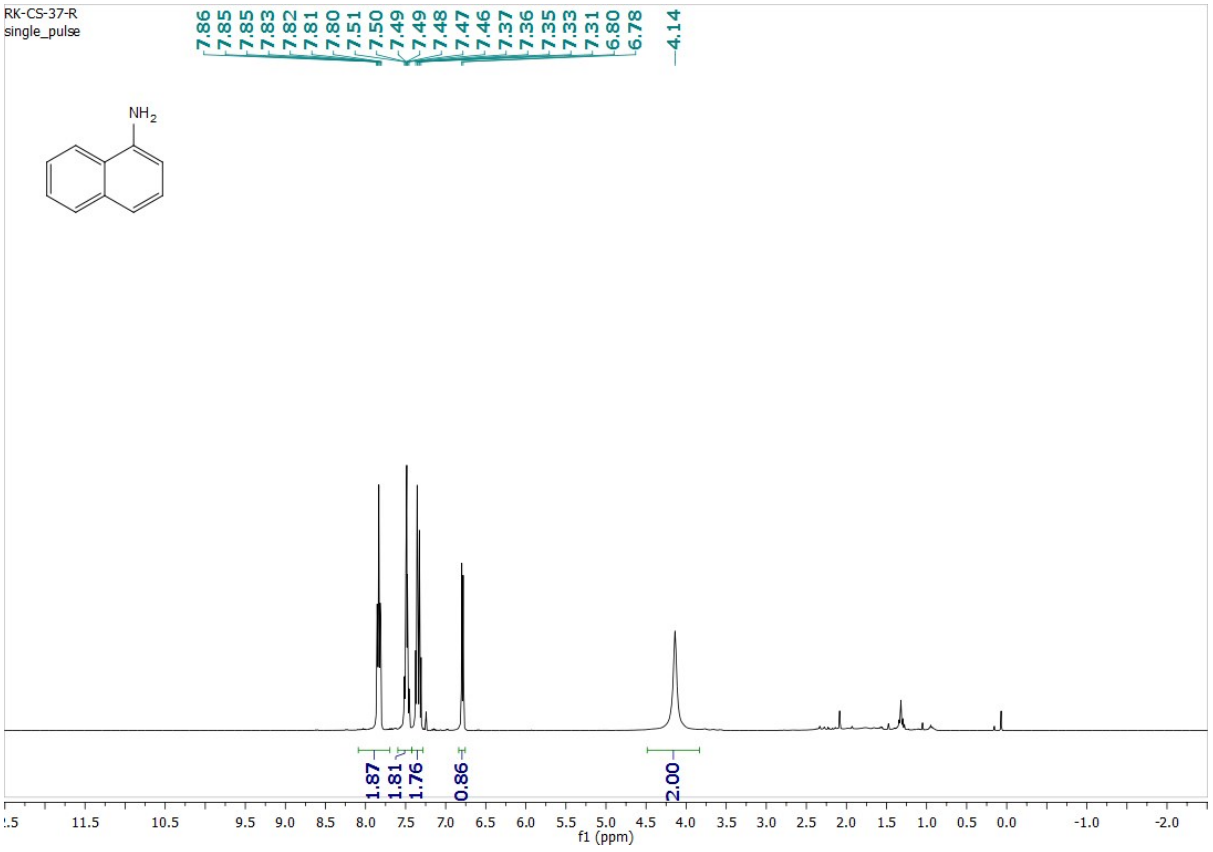

RK-CS-18-R
single pulse decoupled gated NOE
146.15
131.49
129.11
114.66
65.42
OH
H2N
f1 (ppm)

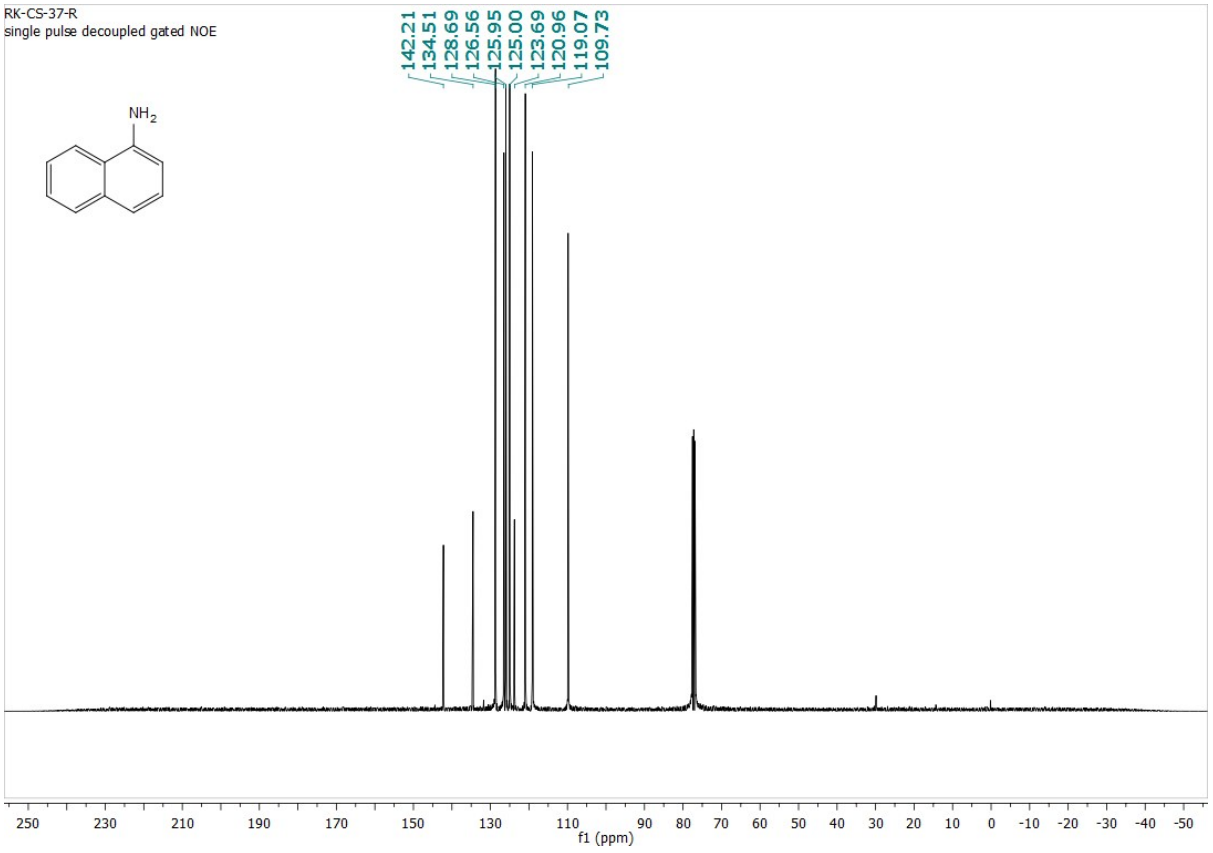

RK-CS-27-R
single_pulse
7.25
7.24
7.22
6.91
6.88
6.88
6.73
6.72
6.70
6.70
6.67
4.12
NH2
Br
Br
1.01
0.95
0.96
2.08
f1 (ppm)

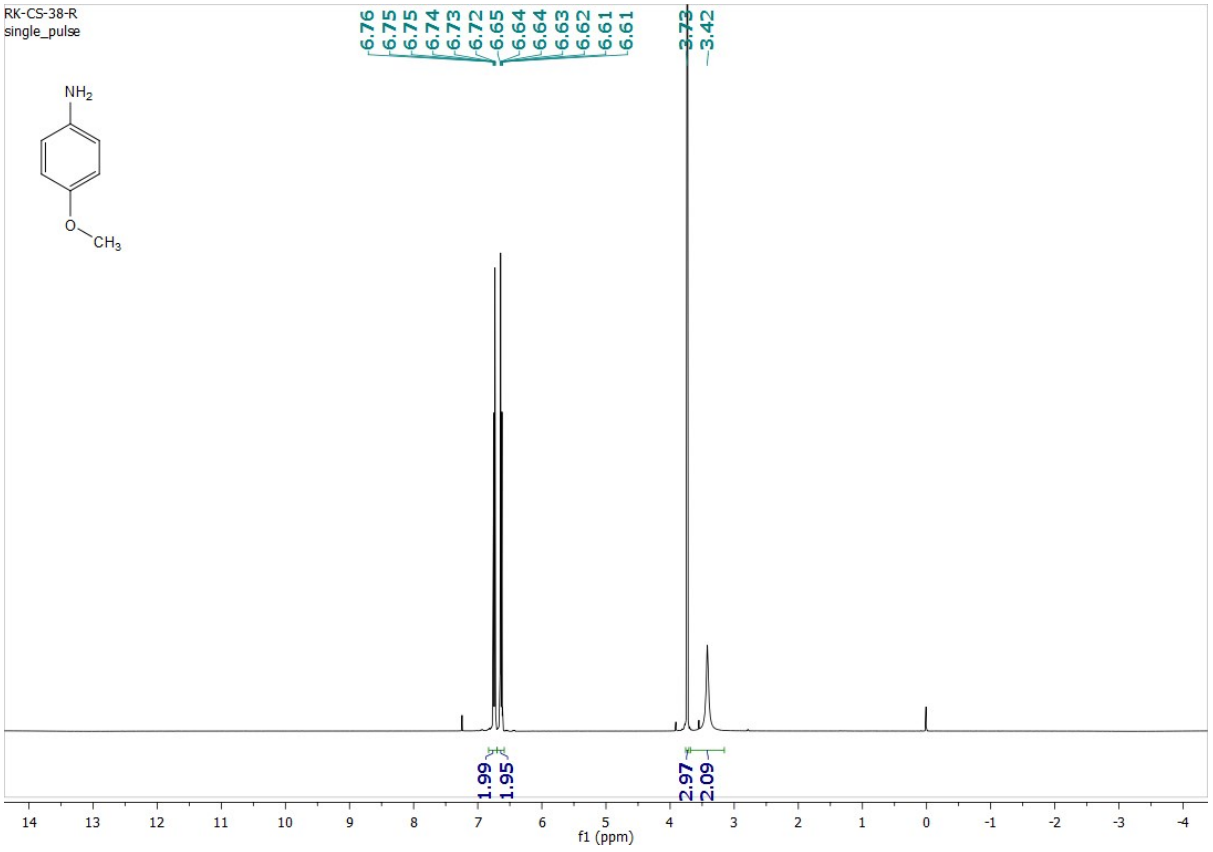

RK-CS-27-R
single pulse decoupled gated NOE
145.96
144.49
133.10
121.98
117.25
108.07
NH2
Br
Br
f1 (ppm)

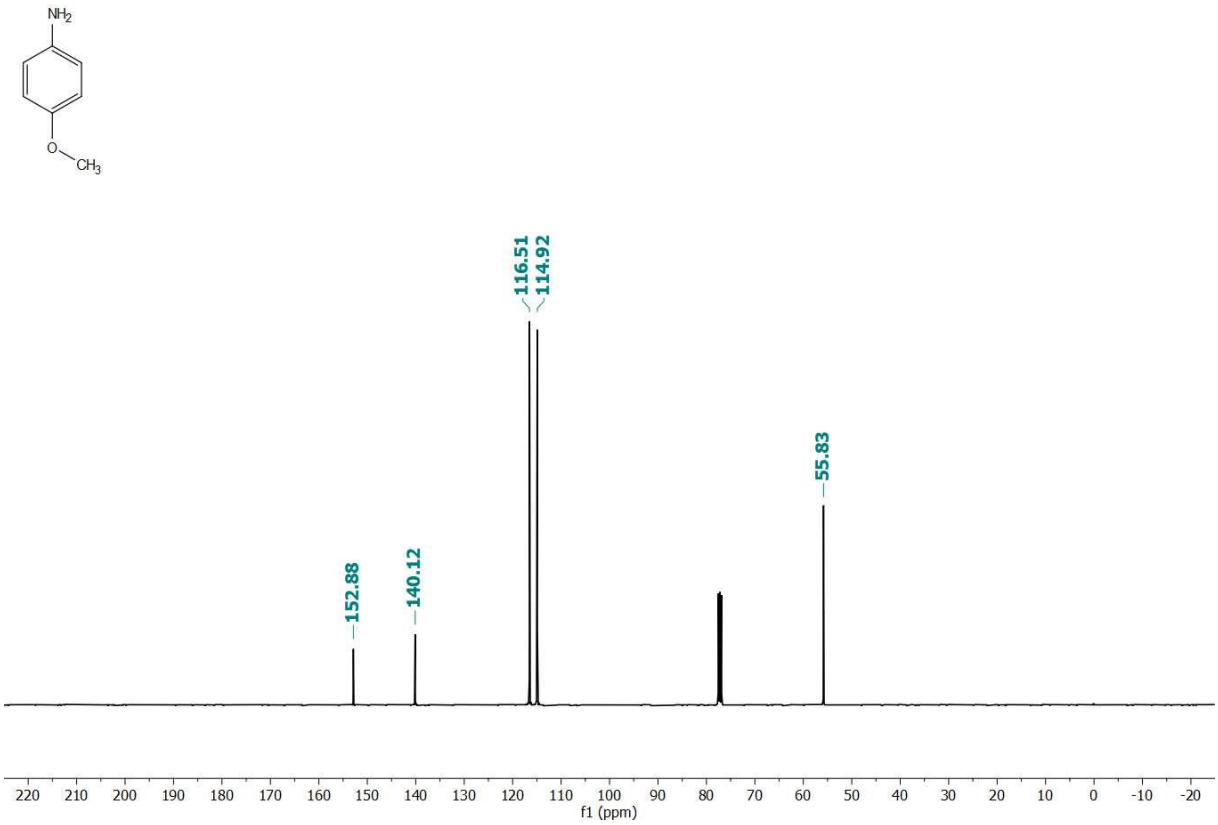

RK-CS-28-R 1
single_pulse
6.99
6.97
6.63
6.61
3.53
2.26
CH3
NH2
1.96
1.95
2.10
2.98
f1 (ppm)

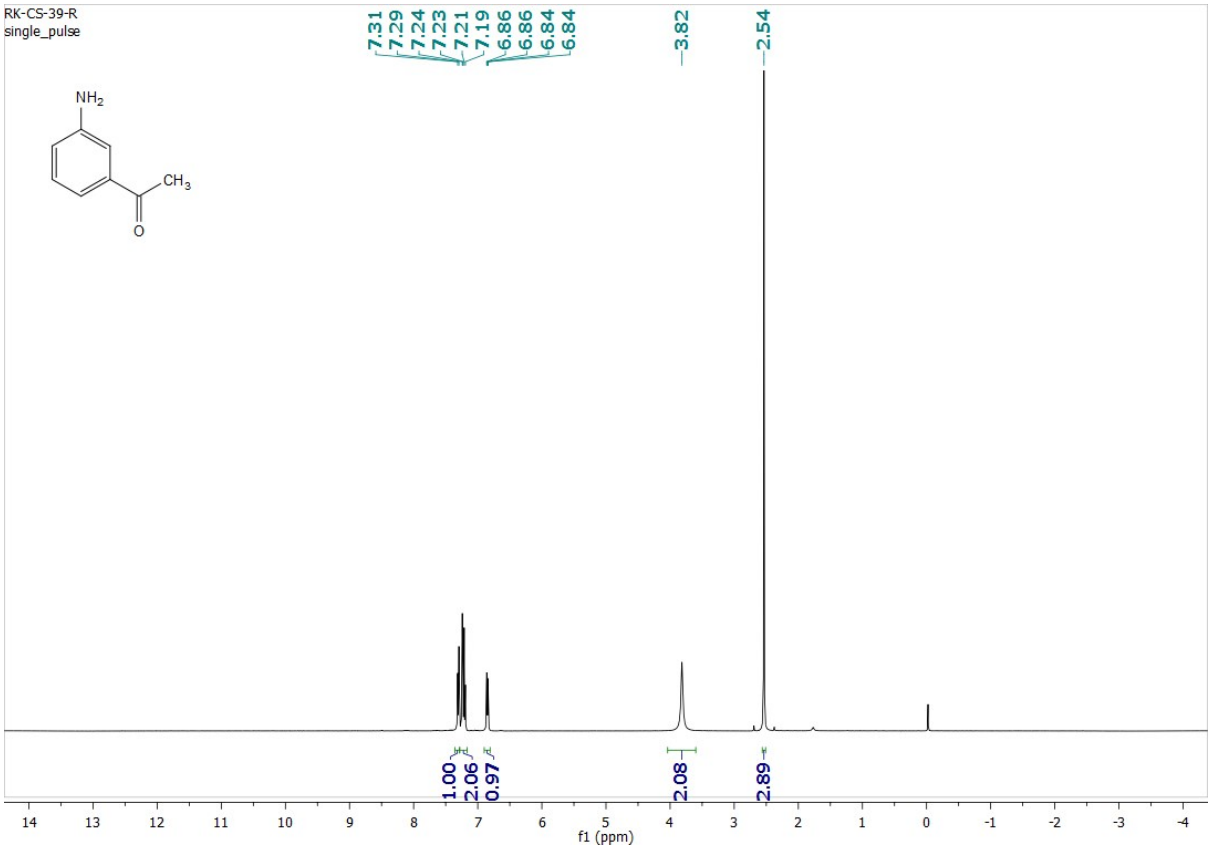

RK-CS-28-R 1
single pulse decoupled gated NOE
143.94
129.42
127.66
115.37
20.33
CH3
NH2
f1 (ppm)

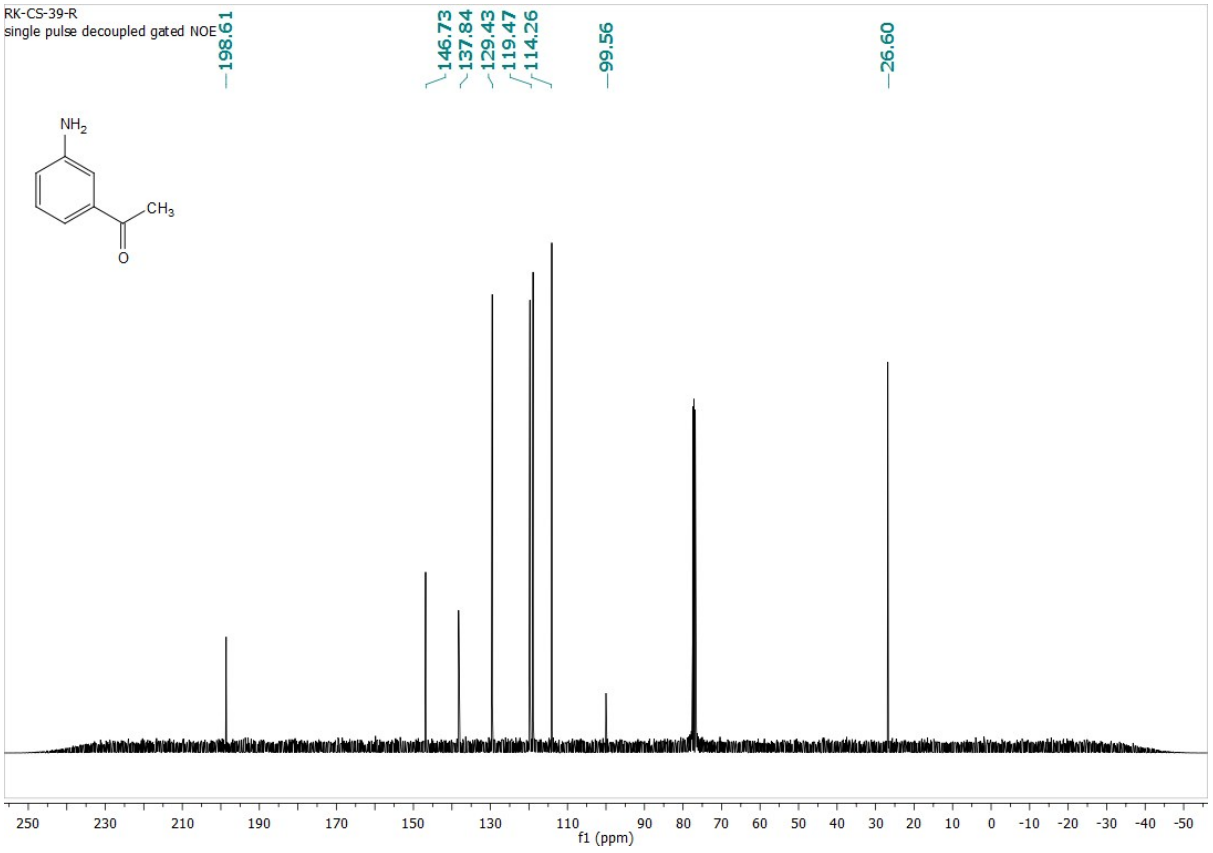

RK-CS-37-R
single_pulse
7.86
7.85
7.85
7.83
7.82
7.81
7.80
7.51
7.50
7.49
7.49
7.48
7.47
7.46
7.37
7.36
7.35
7.33
7.31
6.80
6.78
4.14
NH2
1.87
1.81
1.76
0.86
2.00
f1 (ppm)


RK-CS-37-R
single pulse decoupled gated NOE
142.21
134.51
128.69
126.56
125.95
125.00
123.69
120.96
119.07
109.73
NH2
f1 (ppm)


RK-CS-38-R
single_pulse
6.76
6.75
6.75
6.74
6.73
6.72
6.65
6.64
6.64
6.63
6.62
6.61
6.61
3.73
3.42
NH2
O
CH3
1.99
1.95
2.97
2.09
f1 (ppm)


NH2
O
CH3
116.51
114.92
152.88
140.12
55.83
f1 (ppm)


RK-CS-39-R
single_pulse
7.31
7.29
7.24
7.23
7.21
7.19
6.86
6.86
6.84
6.84
3.82
2.54
NH2
CH3
O
1.00
2.06
0.97
2.08
2.89
f1 (ppm)


RK-CS-39-R
single pulse decoupled gated NOE
198.61
146.73
137.84
129.43
119.47
114.26
99.56
26.60
NH2
CH3
O
f1 (ppm)

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