Supporting Information

Gold(I)-Catalyzed Homologation of Aryl Aldehydes with Trimethylsilyldiazomethane

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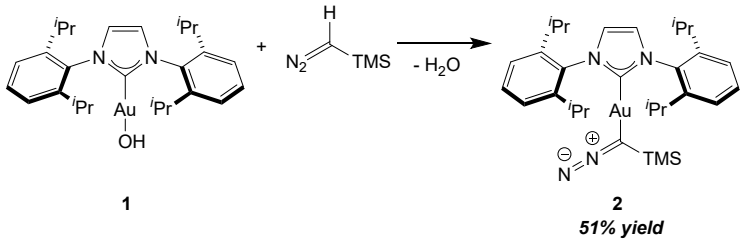
1. General Information

All reactions involving complex **2** were carried out inside a nitrogen-filled glovebox. Gold starting materials were purchased from Strem. Aryl aldehydes and other reagents for the syntheses reported in this article were purchased from Oakwood Chemicals, Combi-Blocks, TCI America, and Sigma Aldrich, and were used without further purification unless otherwise noted. $TMSCHN_2$ was purchased from Oakwood Chemicals as 2M solution in hexanes and used without further purification. The solvents were purchased from Fisher Scientific or Sigma Aldrich and stored over activated 4A molecular sieves. The silica gel (particle size 40-63 μm, 230-400 mesh) that was used for flash column chromatography and thin layer chromatography plates (250 μm thickness) were purchased from SiliCycle. Column chromatography was conducted using Teledyne Isco CombiFlash® Rf+ Lumen with disposable silica columns (RediSep Rf, Teledyne Isco). The ^{1}H NMR spectra were recorded on a JEOL 400 SS 400 MHz spectrometer and are calibrated to the residual monoprotio solvent peak ($CHCl_3$ @ 7.26 ppm). ^{13}C NMR spectra were collected on the same instrument at 100 MHz and calibrated to the deuterated solvent peak ($CDCl_3$ @ 77 ppm). High-resolution mass spectra (HRMS, TOF-ESI) were recorded on a VG 7070E spectrometer (VG Analytical Ltd., Altrincham, Cheshire, England, UK) or a SX102a mass spectrometer (JEOL, Tokyo, Japan).

2. Synthesis and Characterization of Complex 2



Scheme S1. Synthesis of Complex **2**.

In an aluminum foil-wrapped round bottom flask, [IPrAu(OH)] (**1**)[1] (50 mg, 0.083 mmol) in 3 mL anhydrous diethyl ether was cooled to -35 ℃ before a solution of TMS diazomethane (2M solution in hexanes, 42 μL) in 1 mL anhydrous diethyl ether was added. The reaction mixture was stirred for 1 h at -35 ℃ and then filtered through a pre-cooled short column of Celite. All volatiles were removed at ambient temperature while it was protected from the ambient light. The residue was then dissolved in 2 mL anhydrous toluene, and it was filtered through a syringe filter into a 5 mL vial. The filtrate was placed in a -35 ℃ freezer inside a glovebox. After 2 days, yellow crystals of complex **2** were isolated and dried under vacuum to furnish 33 mg of complex **2** (0.042 mmol, 51% isolated yield). Anal. Calcd for $C_{38}H_{53}AuN_4Si$: C, 57.71; H, 6.75; N, 7.08. Found: C 57.98, H 6.84, N 7.21. IR (solid ATR): 3024, 2960, 2924, 2868, 1984, 1549, 1495, 1462, 1458, 1412, 1383, 1363, 1326, 1242, 1241, 1179, 1057, 946, 944, 874, 827, 804, 758, 729, 694, 624. ^{1}H NMR (400 MHz, C_6D_6) δ 7.17–7.13 (4 H, m), 7.08–7.04 (6 H, m), 6.27 (2 H, s), 2.54 (4 H, hept, J = 6.8), 2.11 (3 H, s), 1.42 (12 H, d, J = 6.9), 1.05 (12 H, d, J = 6.8), 0.20 (9 H, s). ^{13}C NMR (101 MHz, C_6D_6) δ 172.77, 145.50, 137.58, 134.64, 130.39, 129.02, 125.38, 124.00, 121.99, 28.72, 24.30, 23.71, 4.25. ^{29}Si NMR (79 MHz, C_6D_6): δ 211.5.

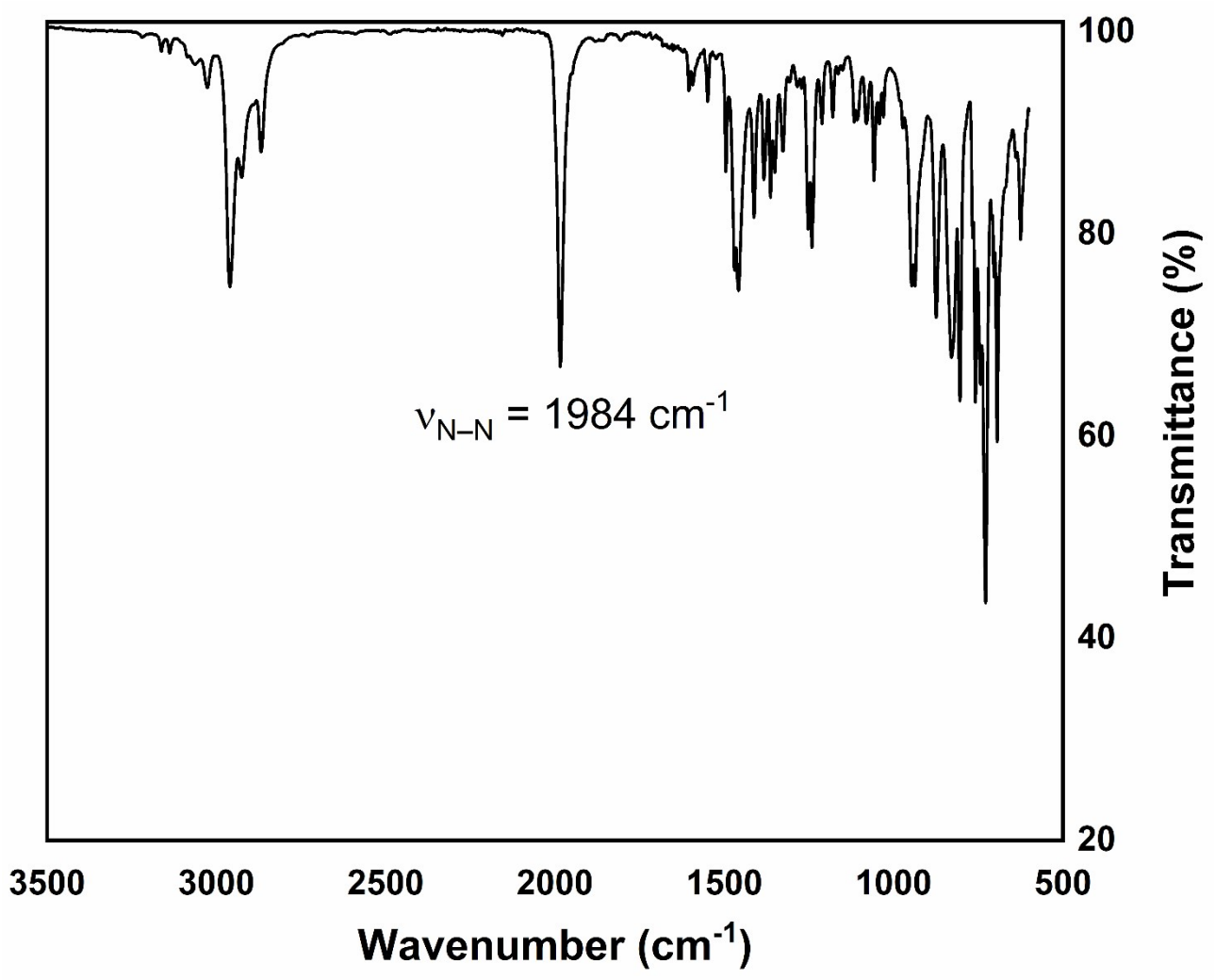


Figure S1. IR spectrum of complex **2**.

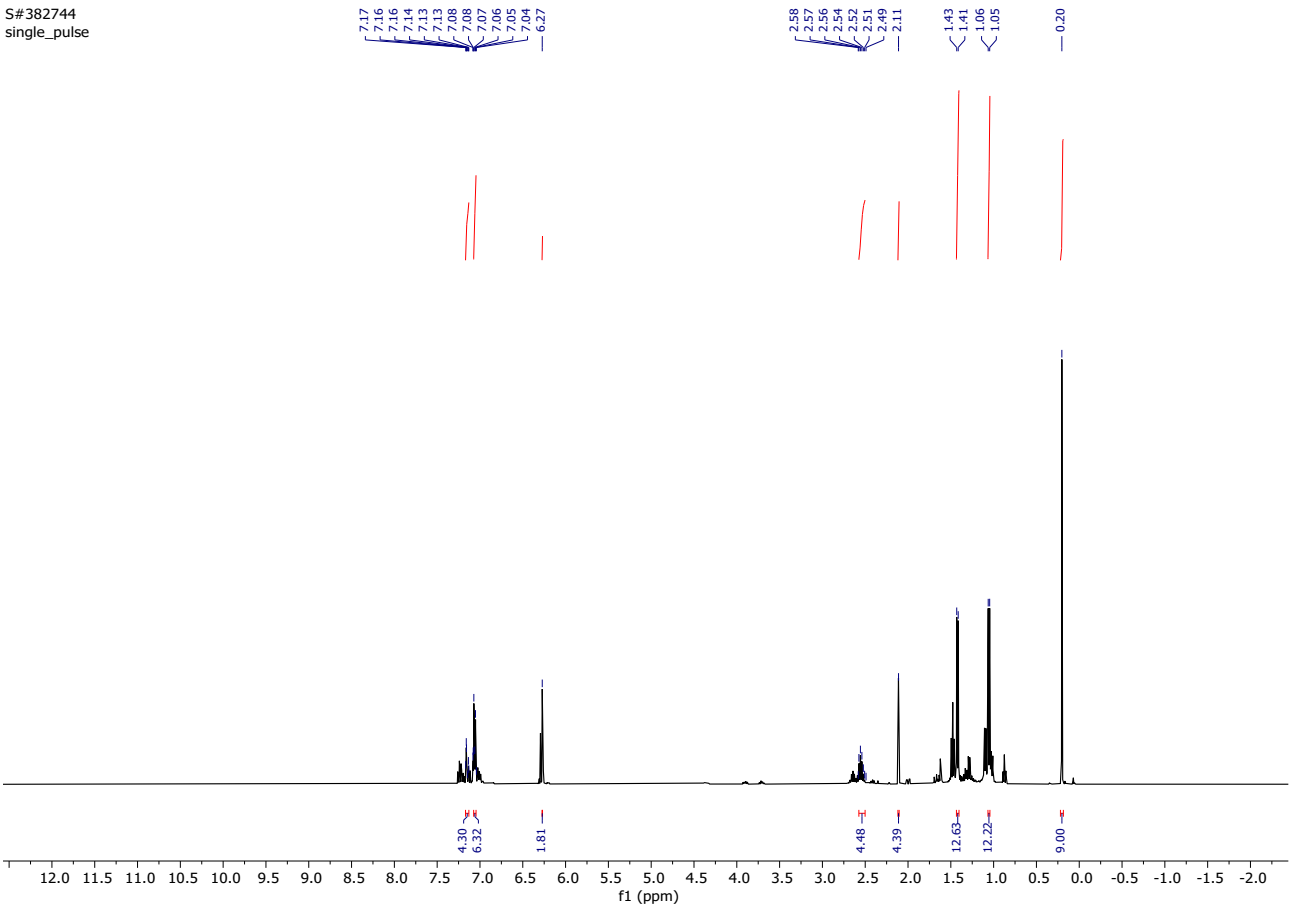


Figure S2. ^{1}H NMR spectrum (400 MHz, C_6D_6) of complex **2**.

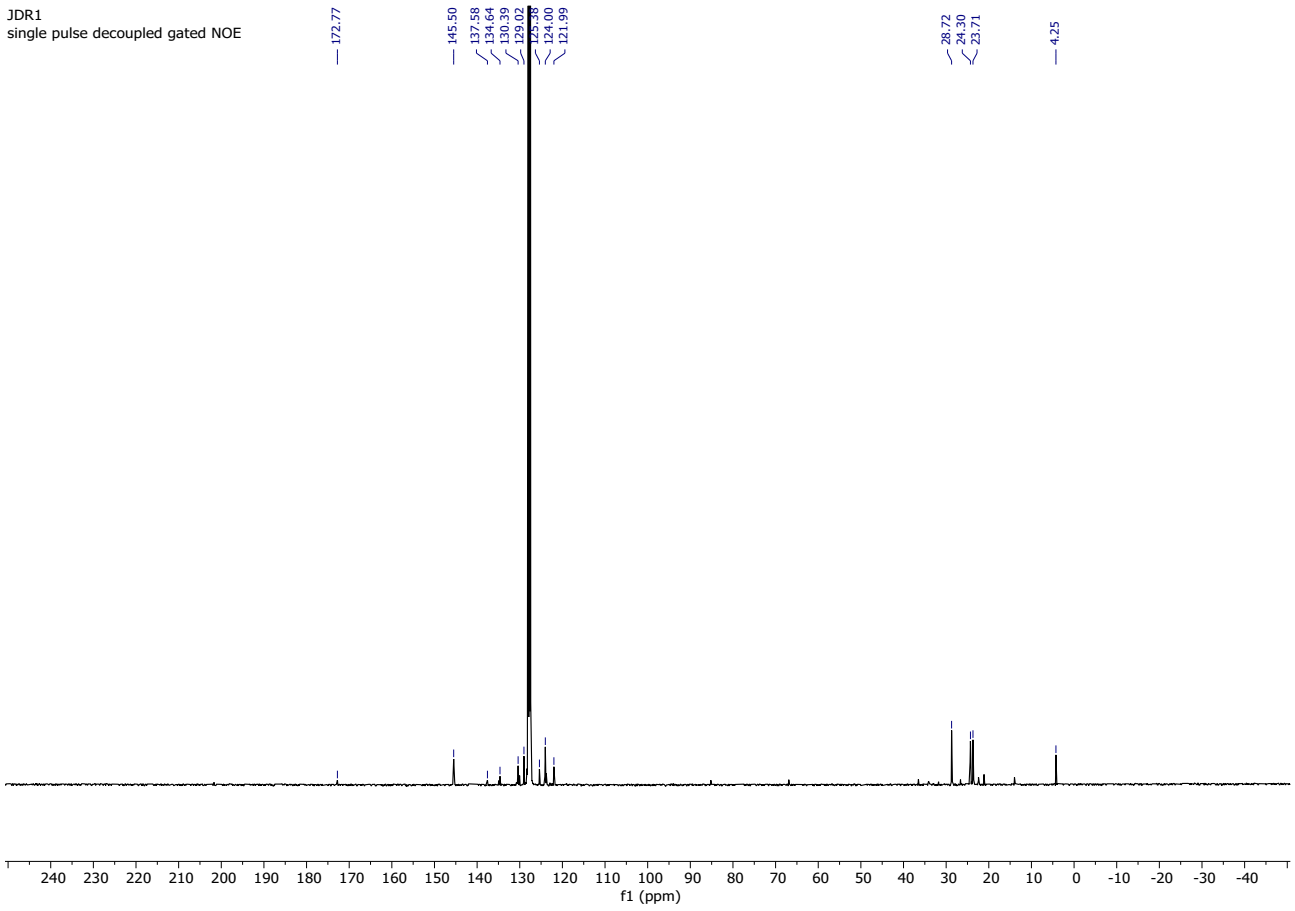


Figure S3. ^{13}C NMR spectrum (101 MHz, C_6D_6) of complex **2**.

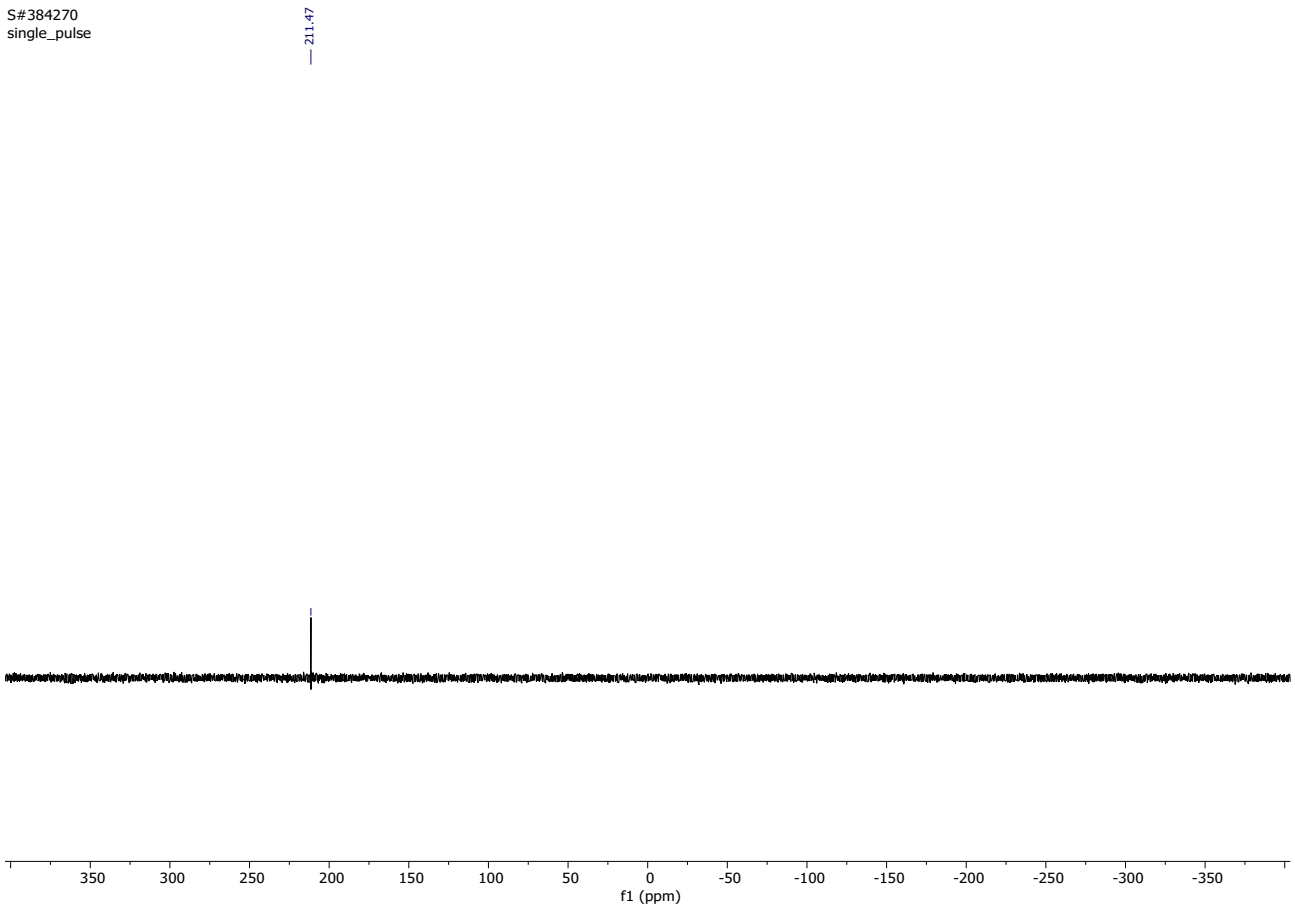


Figure S4. ^{29}Si NMR spectrum (79 MHz, C_6D_6) of complex **2**.

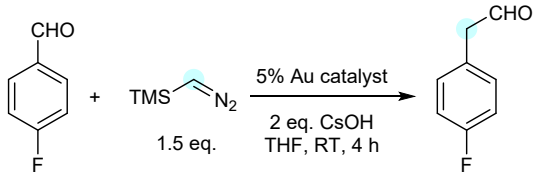
3. General Procedure for the Au-Catalyzed Homologation of Aryl Aldehydes

To a stirred solution of [IPrAu][NTf_2][2] (10 mg, 0.012 mmol) in anhydrous THF (5 mL) was added CsOH (52 mg, 0.346 mmol) and the mixture was allowed to stir at room temperature for 30 minutes. TMS diazomethane (0.278 mmol, 2.0 M in hexanes, 139 μL) in anhydrous THF (1 mL) at room temperature was added and the mixture was stirred for another 30 minutes in the dark. Aryl aldehyde (0.232 mmol) was added slowly over 10 minutes. Vigorous gas evolution was observed right away. Monitoring the reaction with TLC indicated the full consumption of the aryl aldehyde after 2-4 h. At this point 2M HCl in diethyl ether (5 mL) was added to the same reaction mixture and the biphasic reaction mixture was stirred for an additional 4 h. Then ethyl acetate was added, and the organic layer was separated via separatory funnel and all organics were dried over $MgSO_4$. The crude product was The crude material was purified by column chromatography on silica gel (eluent hexanes : EtOAc – 10:1 (v:v) or hexanes : Et_2O – 9:1 (v:v)). All yields were calculated on the basis of isolated products.

4. Screening Tables for Reaction Optimization

Optimization of the reaction conditions was performed on the same scale as described in the general procedure section. *p*-Fluorobenzaldehyde was used as the substrate and the yield of the reaction was calculated based on the ^{1}H-NMR in $CDCl_3$ in the presence of 1,2,4,5-tetrabromobenzene as the standard. The results of the optimization conditions are presented below.

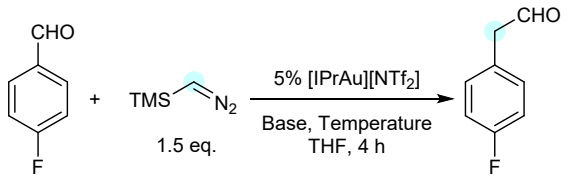
Table S1. Optimization of Reaction Conditions with Various Au Catalyst.



entry	Au source	% yield (NMR)
1	[IPrAu(OH)]	31%
2	[IPrAu][NTf_2]	36%
3	[IPrAu(cbz[a])][3]	Trace
4	{[IPrAu]$_2$[OH]}BF_4[4]	Trace
5	[IPrAu(MeCN)][BF_4][5]	9%
6	[IPrAuCl]	19%
7	Au(tht)Cl	Trace
8	Au(SMe_2)Cl	Trace
9	[Au(PPh_3)$_3$]Cl	11%
10	[Au(PPh_3)]NO_3 [6]	6%

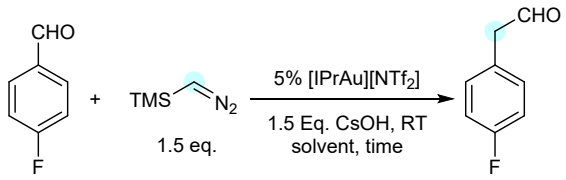
[a]cbz = 9*H*-carbazol-9-yl

Table S2. Optimization of Reaction Conditions with Various Base/Temperature.



entry	Base (equiv.)	temperature	% NMR Yield
1	CsOH (0.5)	RT	13%
2	CsOH (1.0)	RT	21%
3	CsOH (1.5)	RT	43%
4	CsOH (2)	RT	36%
5	CsOH (2.5)	RT	29%
6	CsOH (5)	RT	14%
7	CsOH (0.5)	40 °C	8%
8	CsOH (1.0)	40 °C	16%
9	CsOH (1.5)	40 °C	22%
10	CsOH (2)	40 °C	19%
11	CsOH (2.5)	40 °C	11%
12	CsOH (5)	40 °C	Trace
13	TBAOH (1.0)	RT	9%
14	TBAOH (1.5)	RT	18%
15	TBAOH (2.0)	RT	17%
16	TBAOH (1.0)	40 °C	21%
17	TBAOH (1.5)	40 °C	18%
18	TBAOH (2.0)	40 °C	13%
19	Li_2CO_3 (1.5)	RT	Trace
20	Na_2CO_3 (1.5)	RT	Trace
21	K_2CO_3 (1.5)	RT	7%
22	LiOH (1.5)	RT	16%
23	NaOH (1.5)	RT	23%
24	KOH (1.5)	RT	31%

Table S3. Optimization of Reaction Conditions with Various Solvents and Reaction Times.



entry	Solvent	Reaction Time	% NMR Yield
1	THF	30 min	8%
2	THF	1 h	16%
3	THF	2 h	28%
4	THF	4 h	43%
5	THF	8 h	39%
6	THF	24 h	21%
7	Et_2O	30 min	Trace
8	Et_2O	1 h	Trace
9	Et_2O	2 h	Trace
10	Et_2O	4 h	Trace
11	Et_2O	8 h	Trace
12	Et_2O	24 h	Trace
13	Dioxane	30 min	7%
14	Dioxane	1 h	13%
15	Dioxane	2 h	14%
16	Dioxane	4 h	22%
17	Dioxane	8 h	17%
18	Dioxane	24 h	13%
19	DME	4 h	16%
20	Acetone	4 h	Trace
21	EtOAc	4 h	11%
22	DCM	4 h	Trace
23	DMF	4 h	Trace
24	DMSO	4 h	Trace

5. Limitation of the Current Aryl Aldehyde Homologation

The following substrates were screened in our methodology, and they gave none or trace amount of desired product. We did not pursue the identification of the produced product(s).

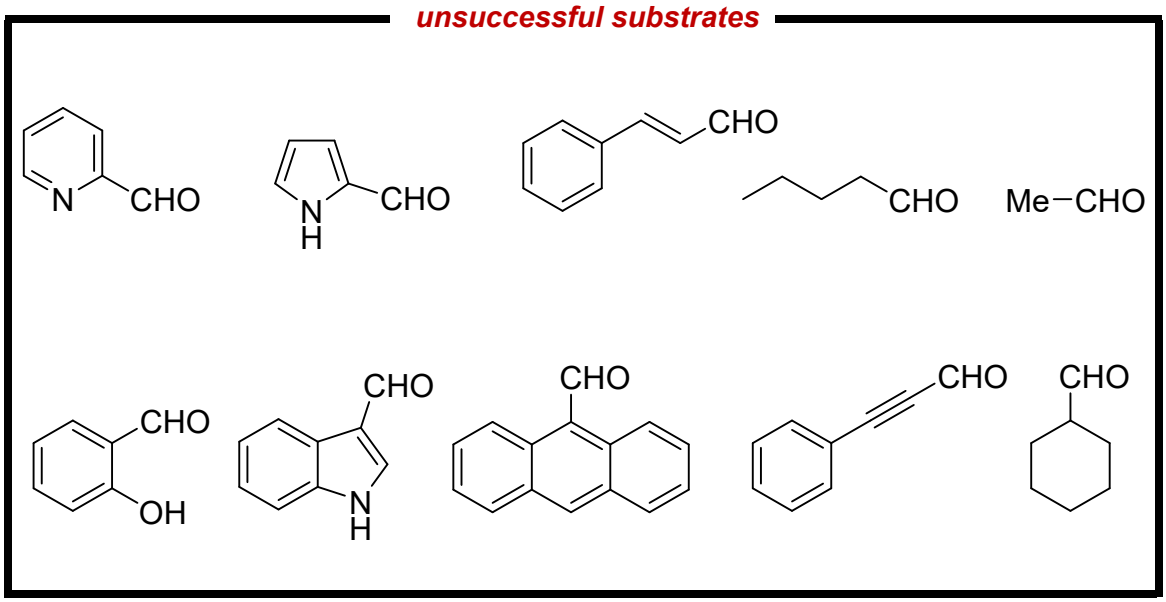


Figure S5. Unsuccessful substrates in this methodology.

6. Preliminary Mechanistic Studies

To obtain insight into the mechanism of this transformation, some preliminary experiments were conducted, and the results are presented in this section. It must be noted that further studies are required to fully elucidate the mechanism of this transformation.

To confirm the formation of the transient Au(I) carbenoid [IPrAuCTMS], complex 2 (25 mg, 0.036 mmol) was reacted with styrene (40 µL, 0.36 mmol, 10 equiv.) in 5 mL anhydrous THF under an atmosphere of dinitrogen and the reaction mixture was stirred at room temperature for 4 hours. Then, the reaction mixture was passed through a short column filled with SiliaMetS Thiol (SH) Metal Scavenger (SiliCycle Inc.) to remove the gold-containing complexes and side products before the NMR study ($CDCl_3$). The Crude NMR is presented below:

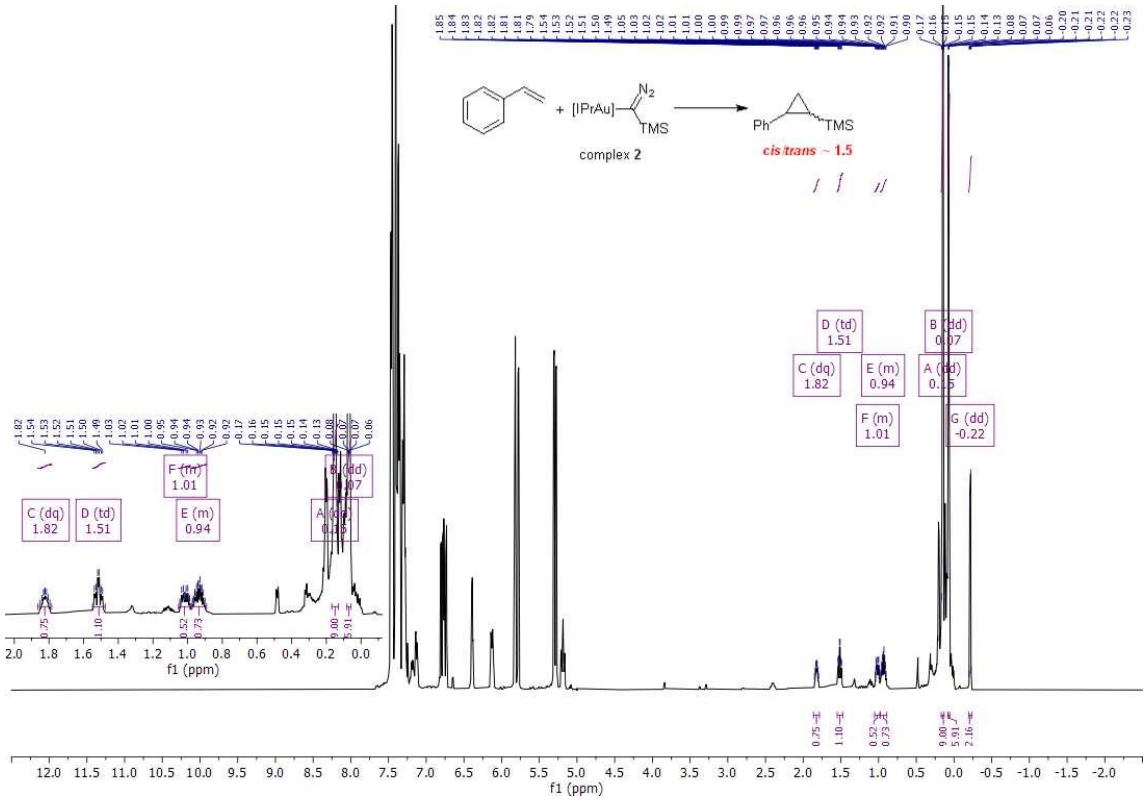


Figure S6. Crude ^1H NMR ($CDCl_3$) of excess styrene with complex **2**.

Several attempts were made to isolate a TMS enol-ethers from the current methodology however, they were not successful in many cases. In most cases, the TMS enol-ethers did not survive the column chromatography. However, in the ^{1}H NMR of the crude reaction mixtures the presence of the TMS enol-ether was verified.

In an example experiment, the reaction between benzaldehyde and $TMSCHN_2$ under the current catalytic system was conducted as presented earlier in section 3, page S7. After 4 h, the reaction mixture was passed through *SiliaMetS Thiol (SH) Metal Scavenger* (SiliCycle Inc.) to remove any gold-containing compounds before the NMR study (THF-d_8). The NMR spectrum can be found below.

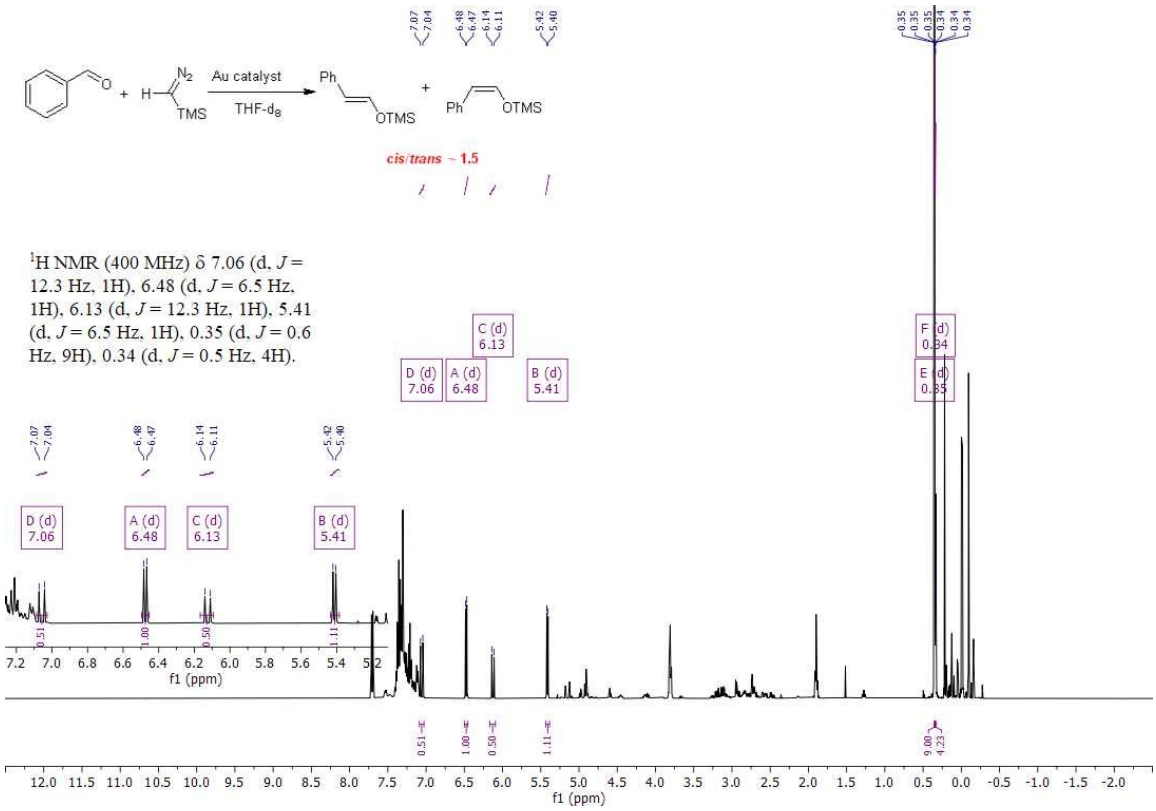
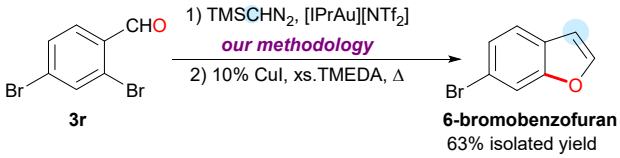


Figure S7. Crude ^{1}H NMR ($CDCl_3$) reaction between benzaldehyde and $TMSCHN_2$ as described in section 3 before the acidic work-up.

It must be noted that control experiments were performed, and no product was observed in the absence of [IPrAuNTf$_2$] catalyst. In the absence of CsOH, only trace amount of the product was detected via GC/MS analysis.

7. Further Transformations of Arylacetaldehydes

6.1. Synthesis of 6-Bromobenzofuran



Scheme S2. Synthesis of 6-bromobenzofuran from 2,4-dibromobenzaldehyde (**3r**).

2,4-Dibromobenzaldehyde (**3r**) was subjected to our homologation and corresponding 2-(2,4-dibromophenyl)acetaldehyde (**4r**) was obtained by following the general procedure. After work up, the obtained **4r** (208 mg, 0.75 mmol) was dissolved in 10.0 mL of anhydrous DMF inside a glovebox under an atmosphere of N_2. This solution was then transferred under an atmosphere of N_2 into a 20 mL scintillation vial containing 14 mg (0.075 mmol, 10 mol%) of CuI and 2 mL of TMEDA (13.3 mmol) in 1.0 mL of DMF. The reaction mixture was heated at 70 ℃ for 2 h. The reaction mixtures was cooled down to room temperature and then diluted with 100 mL of 1:1 mixture of hexanes/ethyl acetate. The mixture was then washed with 50 mL of saturated NH_4Cl solution. The organic layer was separated, and aqueous layer was extracted with 1:1 mixture of hexanes/ethyl acetate (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was concentrated under reduced pressure and the crude material was purified by flash column chromatography on silica gel eluting with hexanes to yield 93 mg (0.47 mmol, 63%) of the title compound as a faint yellow oil.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.69 (td, *J* = 1.2, 0.5 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.44 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.73 (dd, *J* = 2.2, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 155.36, 145.63, 126.58, 126.27, 122.21, 117.66, 114.98, 106.64. GCMS: *m*/*z* calcd for C_8H_5BrO 196.0, found 196.0.

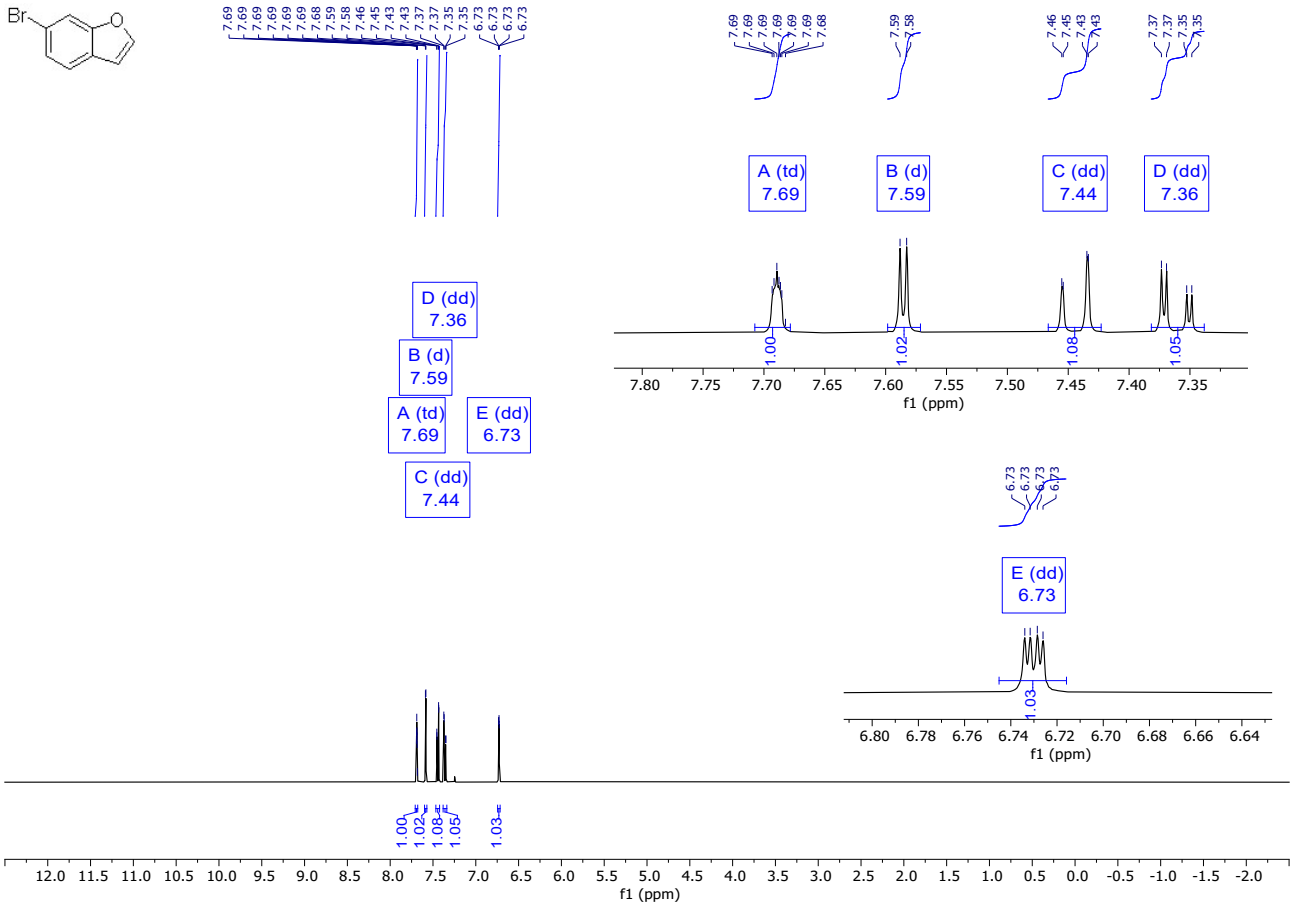


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of 6-bromobenzofuran.

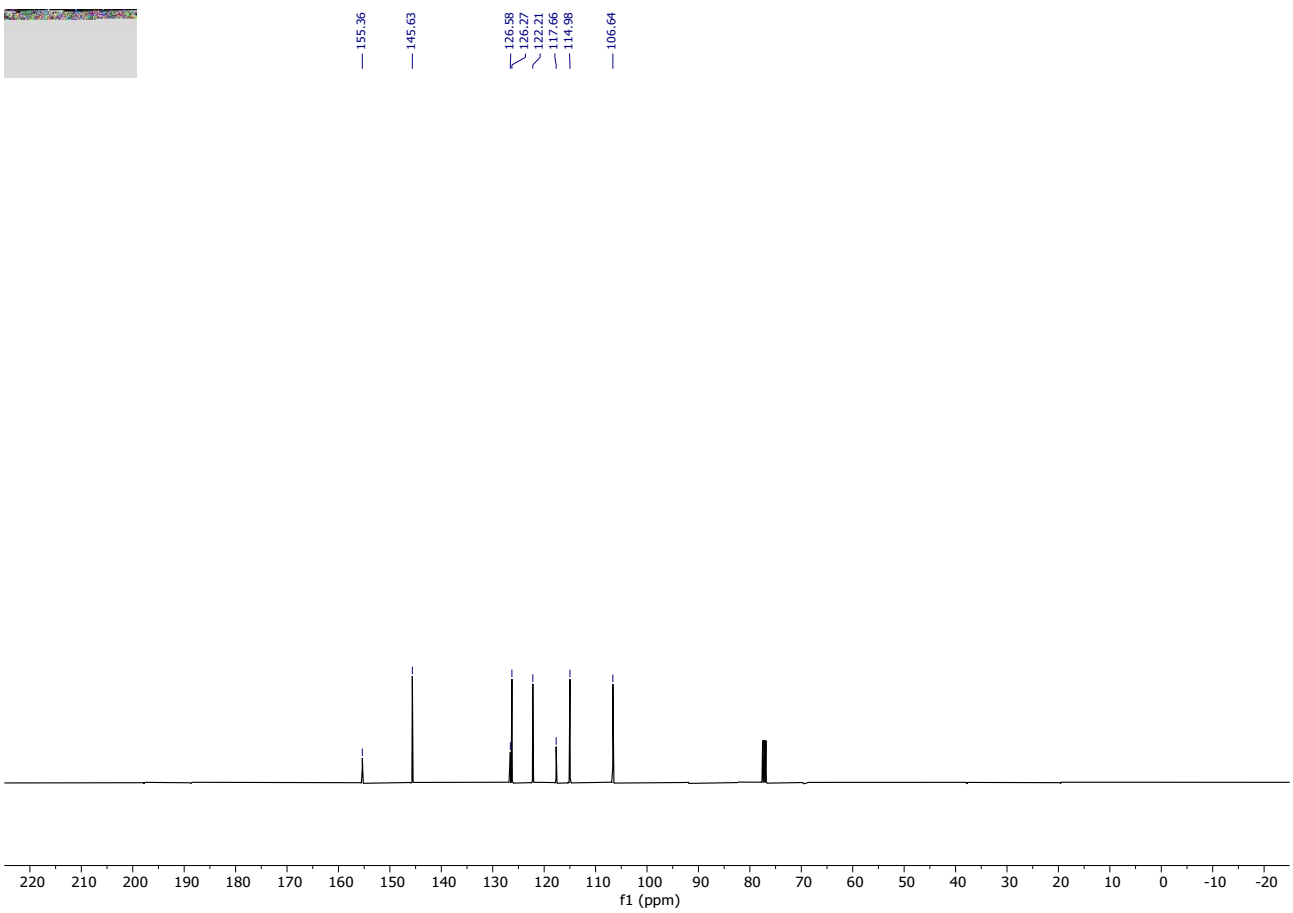
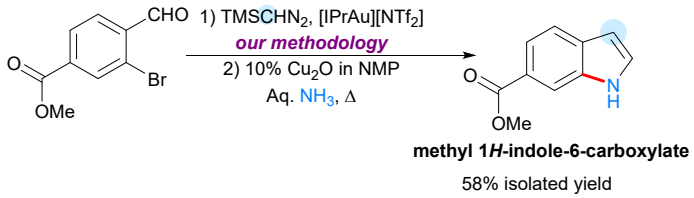


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) of 6-bromobenzofuran.

6.2. Synthesis of Methyl 1*H*-indole-6-carboxylate



Scheme S3. One-pot synthesis of methyl 1*H*-indole-6-carboxylate.

The corresponding aldehyde methyl 3-bromo-4-(2-oxoethyl)benzoate was prepared following the general procedure and using methyl 3-bromo-4-formylbenzoate as the starting material. After work-up and without any purification, the obtained crude material (86 mg, 0.33 mmol) was dissolved in 2.0 mL of NMP under an atmosphere of N_2 inside a glovebox. The solution was transferred into a 25 mL scintillation vial and subsequently charged with 3.5 mL of aqueous NH_4OH (25% in water). To this mixture 5 mg (0.033 mmol, 10 mol%) of cuprous oxide were added and the reaction mixture was stirred at 50 °C for 4 h. The reaction mixture was then quenched with 50 mL of saturated solution of NH_4Cl and extracted with ethyl acetate (3 x 30 mL). The combined organic fractions were dried over anhydrous Na_2SO_4. The volume of the crude product was reduced under vacuum and the crude mixture was purified by flash column chromatography on silica gel (hexanes/EtOAc, 9:1 to 4:1) to give 34 mg (0.19 mmol, 58%) of methyl 1*H*-indole-6-carboxylate as a brownish oil.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.63 (s, 1H), 8.18 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.66 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.46 – 7.13 (m, 1H), 6.59 (ddd, *J* = 3.1, 2.0, 1.0 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 168.45, 135.23, 131.69, 127.75, 123.69, 120.91, 120.40, 113.64, 103.05, 52.11. LR MS: *m*/*z* calcd for $C_{10}H_{10}NO_2$ ($[M + H]^+$) 175.1, found 175.1.

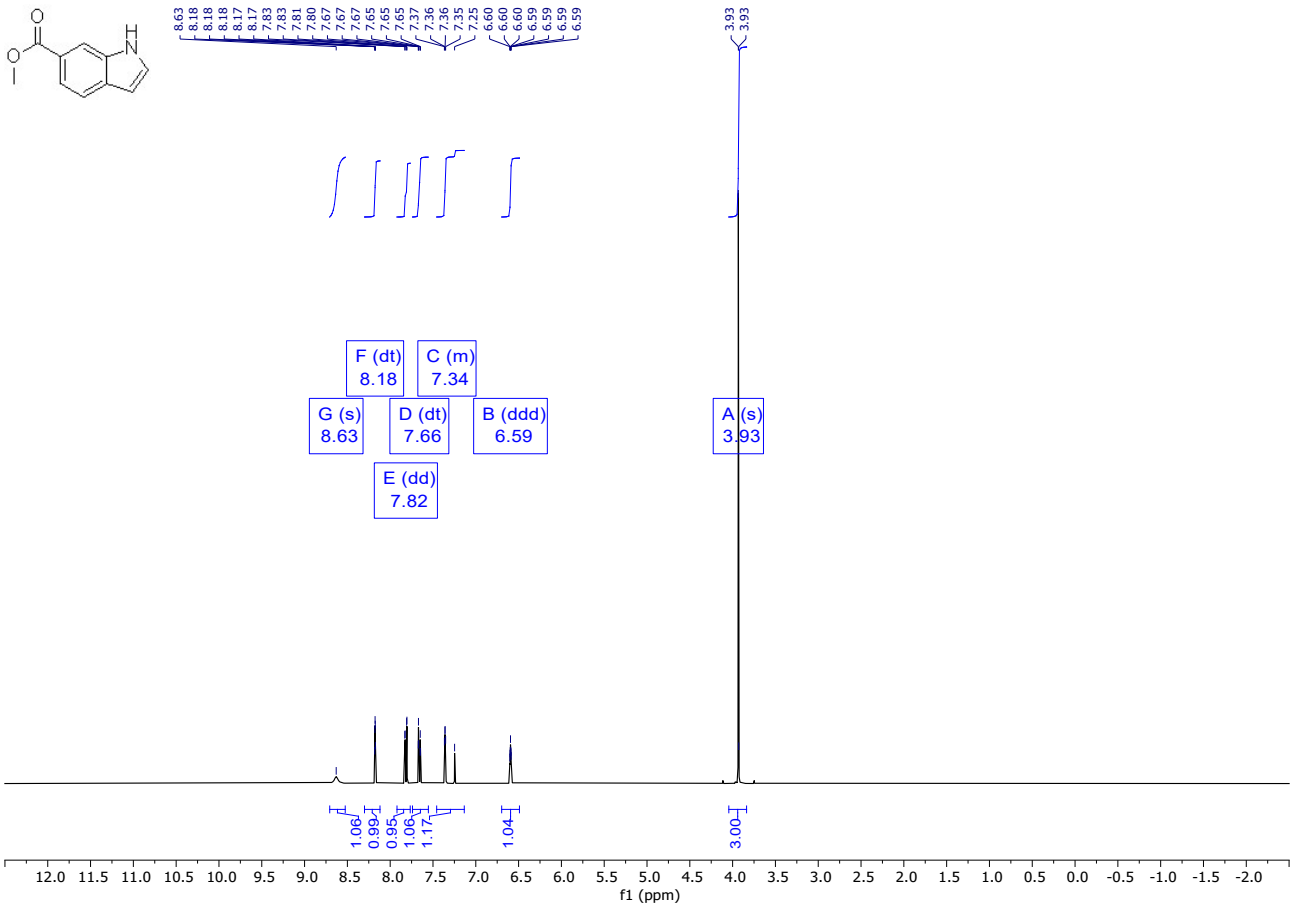


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 1*H*-indole-6-carboxylate.

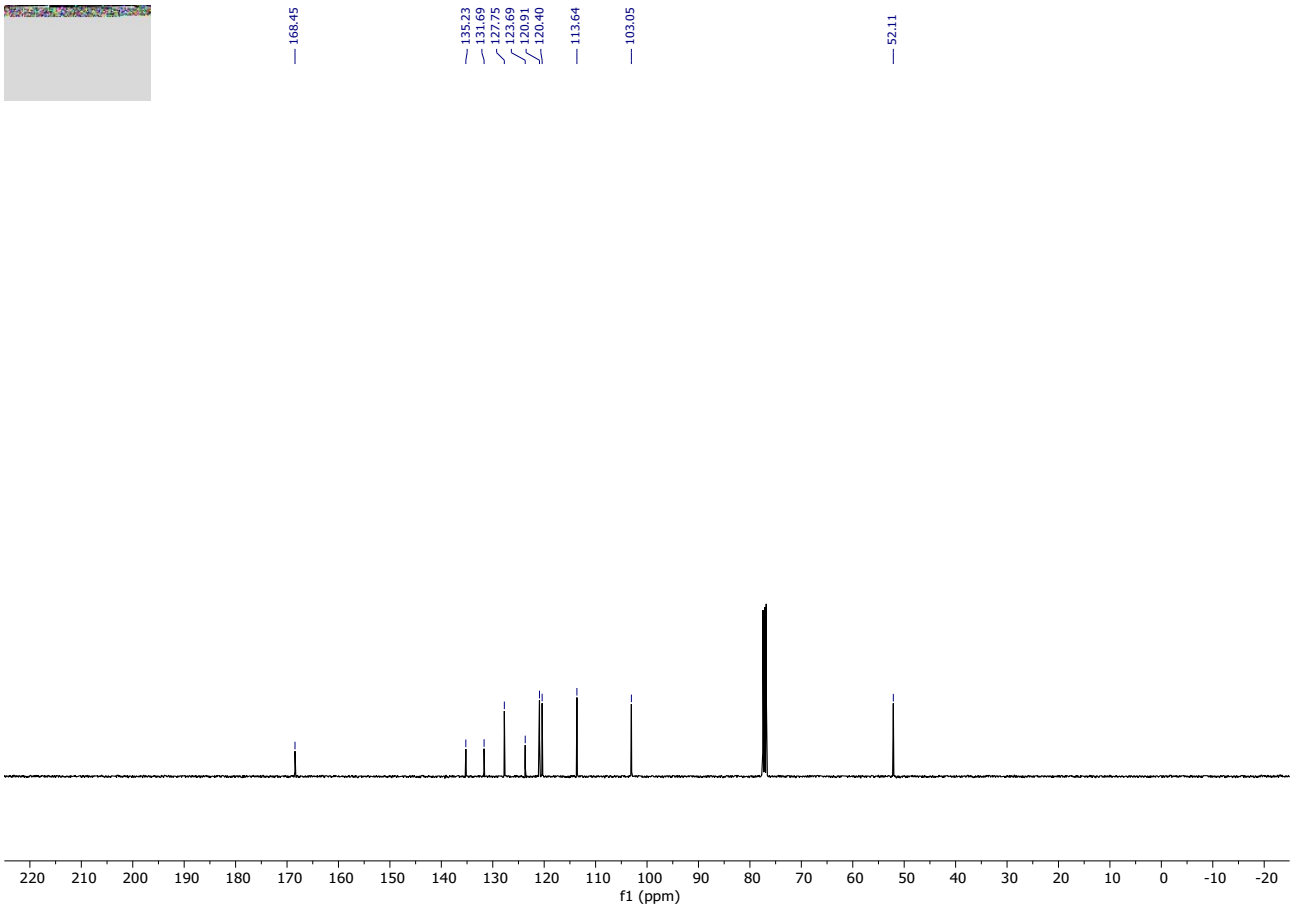


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) of methyl 1*H*-indole-6-carboxylate.

8. X-ray Crystallography Details

Single crystal of compound **2** (CCDC 2329446) was mounted under degassed and pre cooled mineral oil on a pre cooled glass slide and immediately placed under a cold nitrogen stream at 100(2) K prior to data collection. Data were collected on a Bruker D8 Quest equipped with a Photon100 CMOS detector and a Mo ImS source (λ = 0.7107 Å). Data were integrated with the Bruker SAINT program (Bruker 2012, Bruker AXS Inc., Madison, Wisconsin, USA). Structure solutions were performed using the SHELXTL/PC suite.[7] Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS.[8] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions.

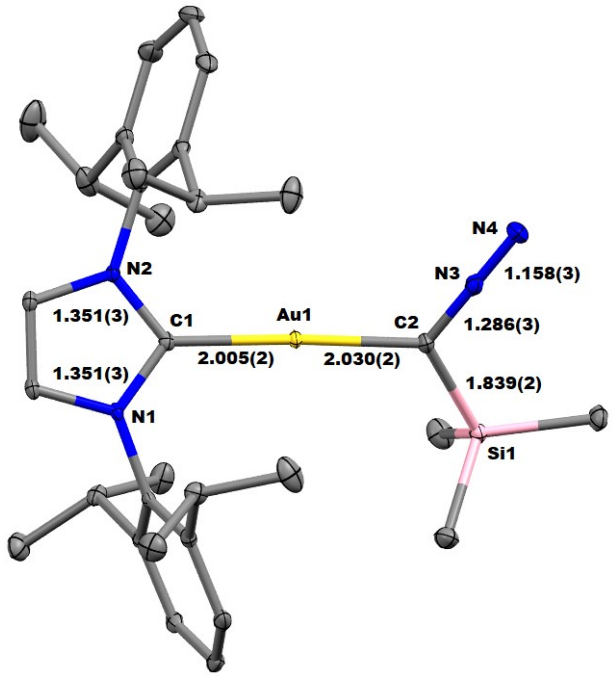
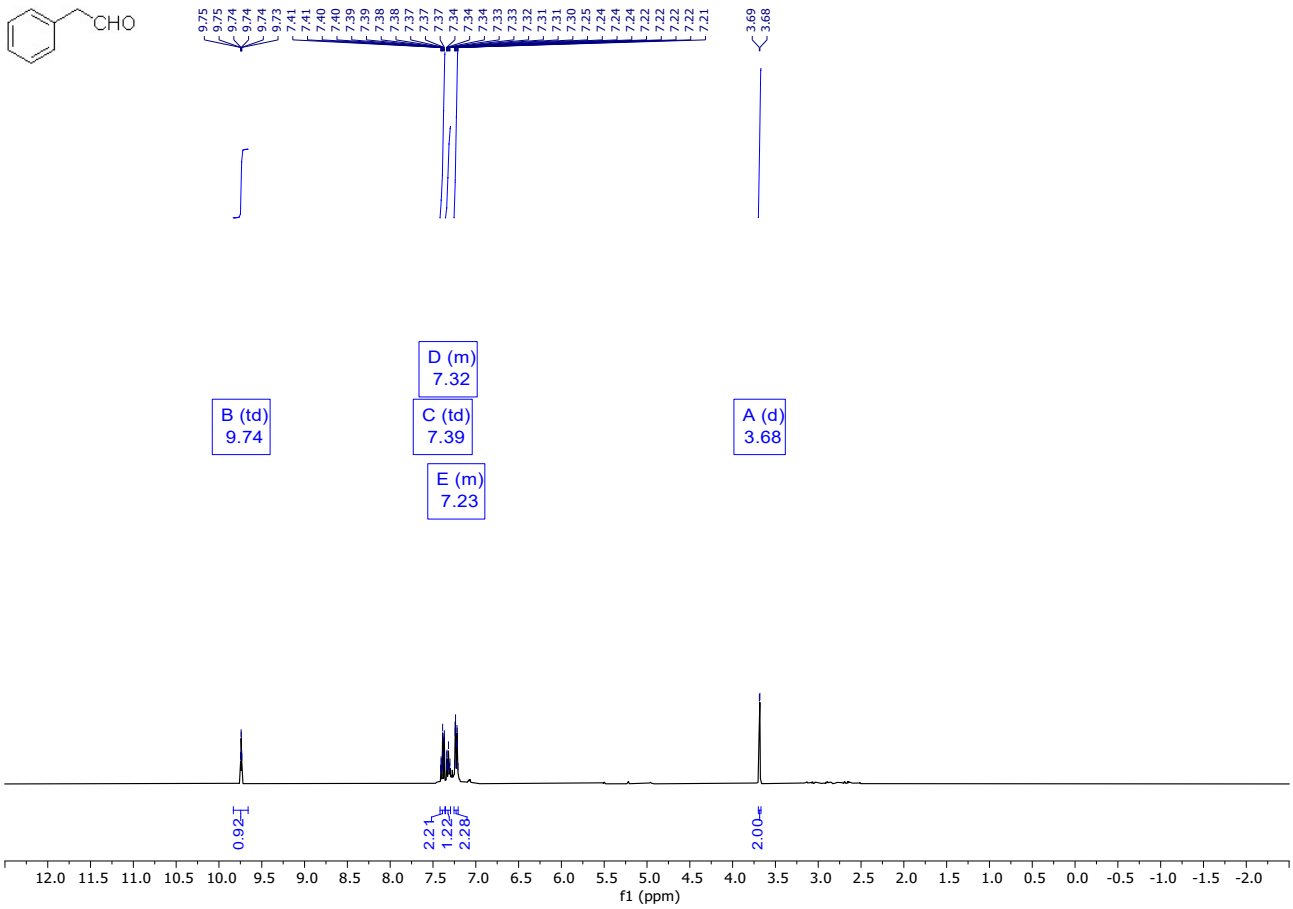


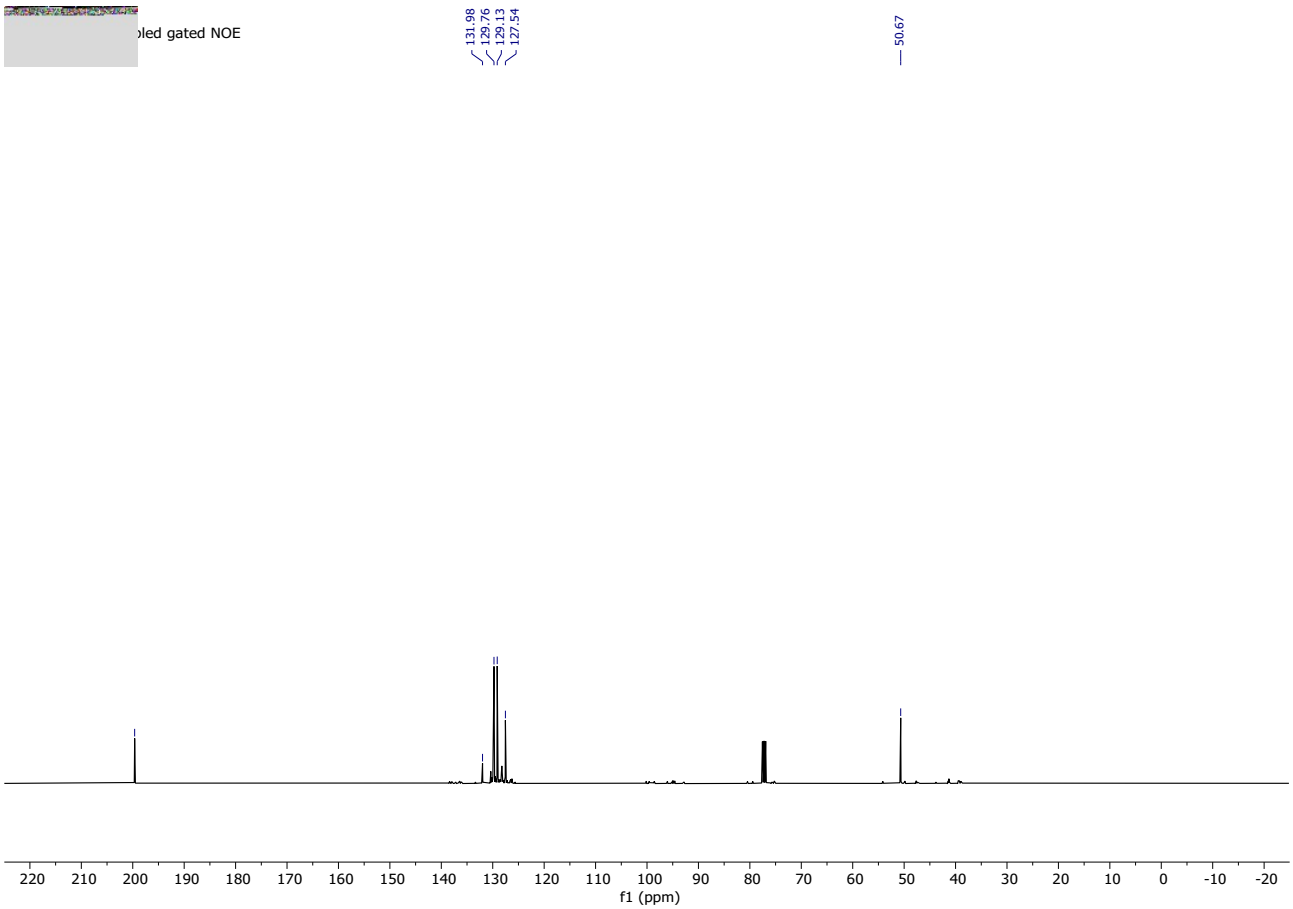
Figure S12. X-ray crystal structure of [IPrAu(C(N_2)TMS)] (**2**) plotted at 50% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°), for **2**: Au1–C1 2.005(2), Au1–C2 2.030(2), C2–N3 1.286(3), N3–N4 1.158(3), C1–Au1–C2 177.18(9), C2–N3–N4 179.3(3).

9. NMR Spectra of Characterized Compounds

2-phenylacetaldehyde (4a). This compound was isolated using flash column chromatography and gave 4a as a colorless oil. Spectral data is in accordance with the literature.[9]

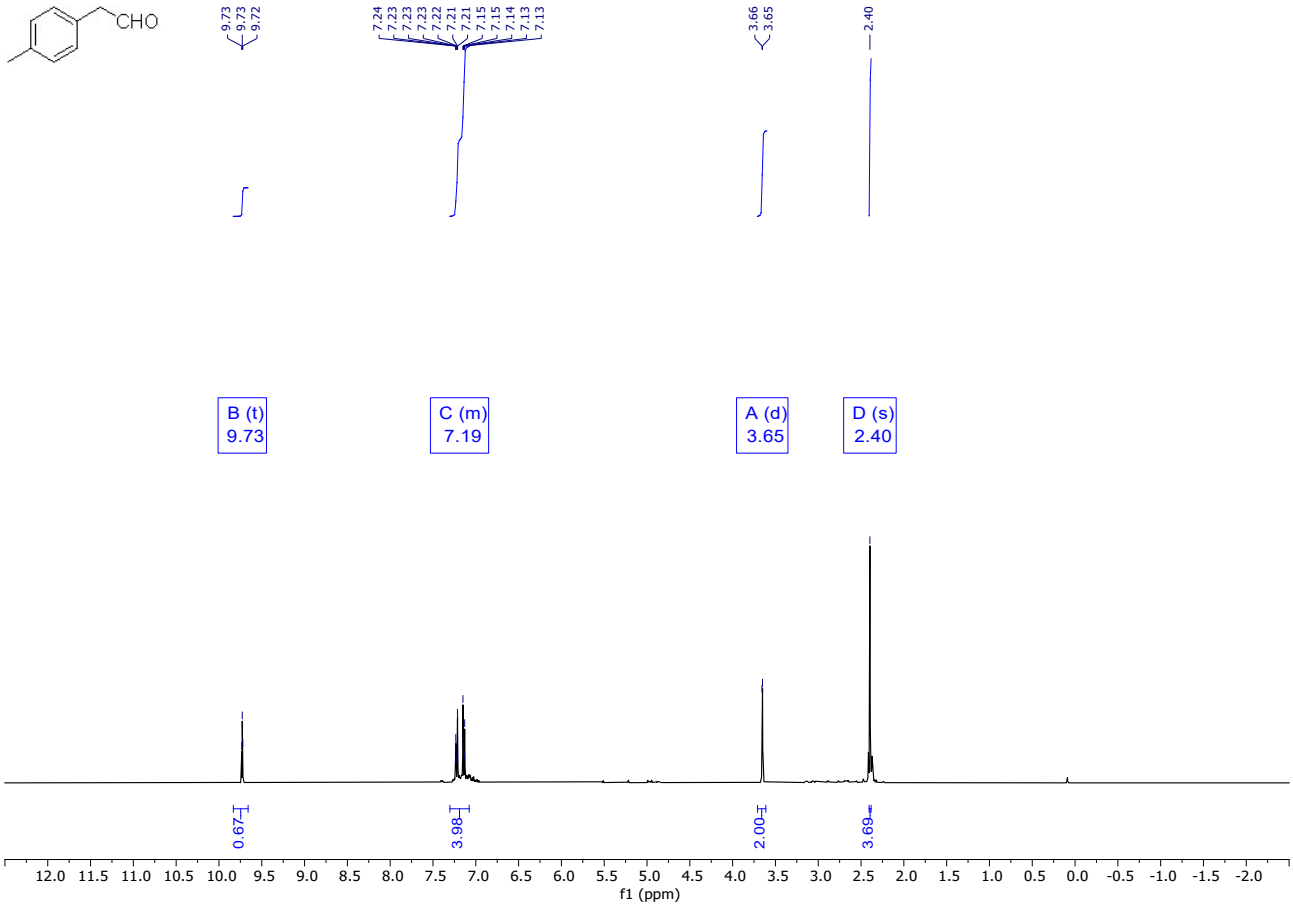
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.74 (td, J = 2.4, 0.8 Hz, 1H), 7.39 (td, J = 7.1, 1.0 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.25 – 7.21 (m, 2H), 3.68 (d, J = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.63, 131.98, 129.76, 129.13, 127.54, 50.67.

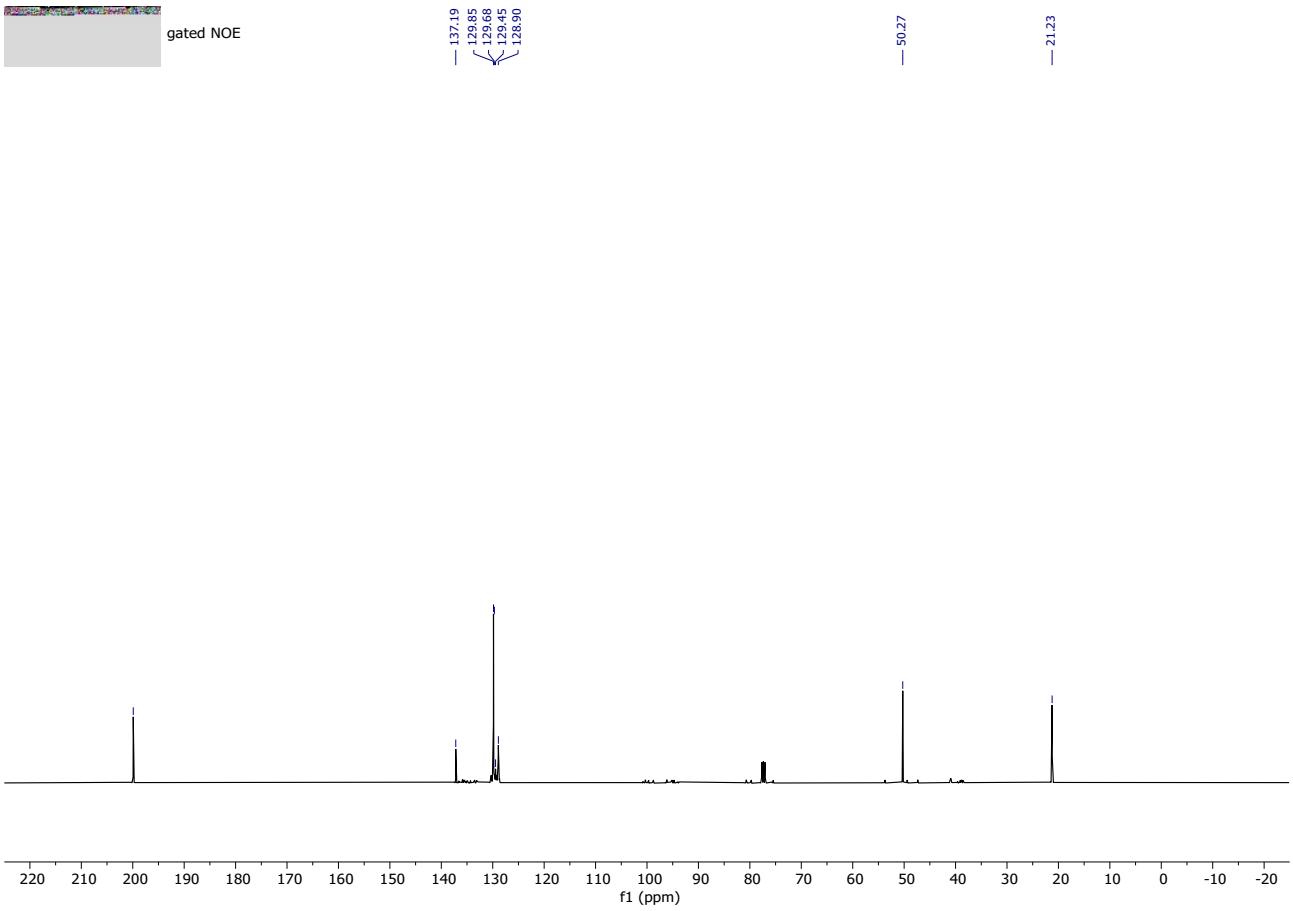



oled gated NOE
131.98
129.76
129.13
127.54
50.67
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(*p*-tolyl)acetaldehyde (4b). This compound was isolated using flash column chromatography and gave 4b as a colorless oil. Spectral data is in accordance with the literature.[9]

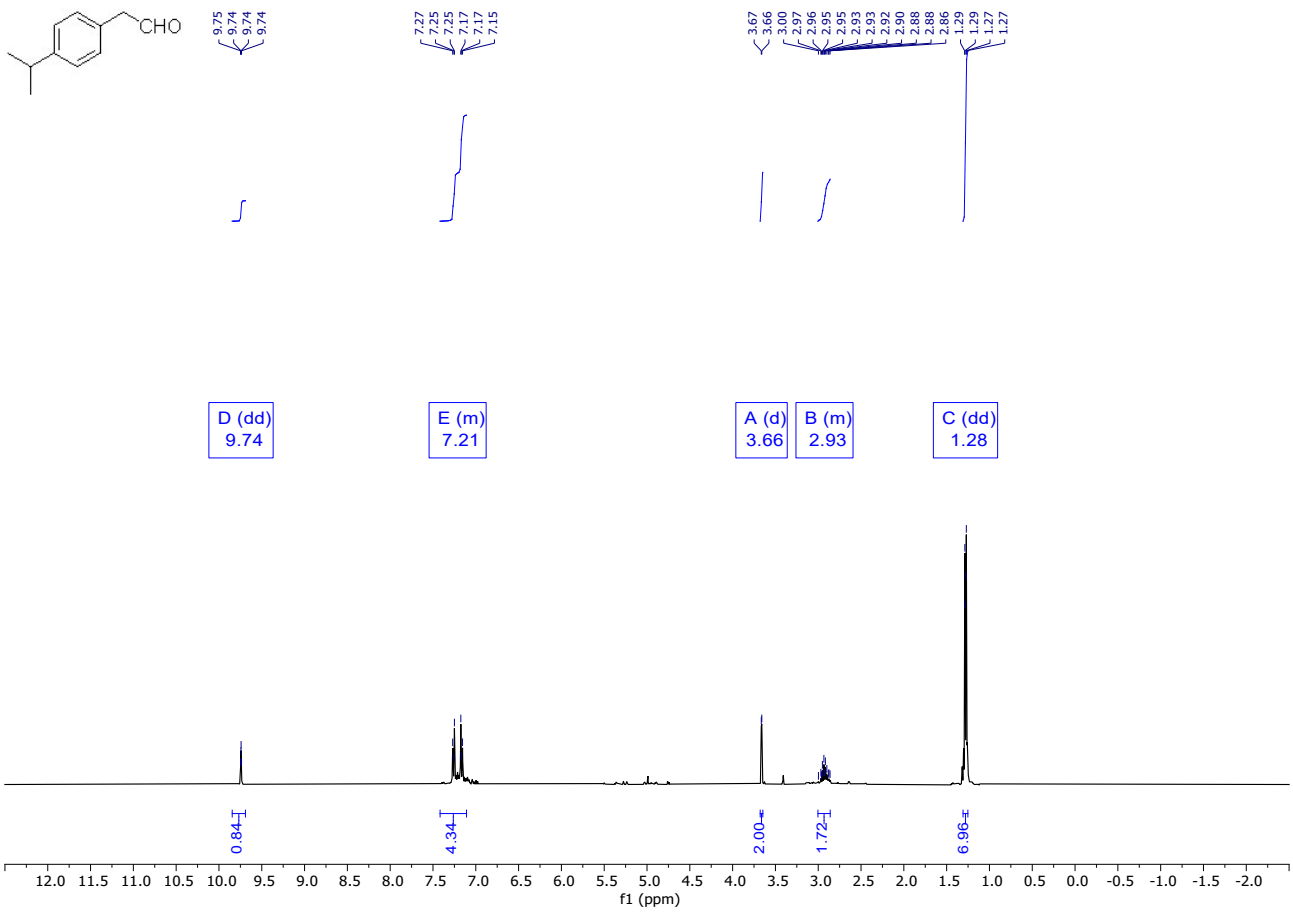
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.73 (t, J = 2.4 Hz, 1H), 7.30 – 7.08 (m, 4H), 3.65 (d, J = 2.5 Hz, 2H), 2.40 (s, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.90, 137.19, 129.85, 129.68, 129.45, 128.90, 50.27, 21.23.

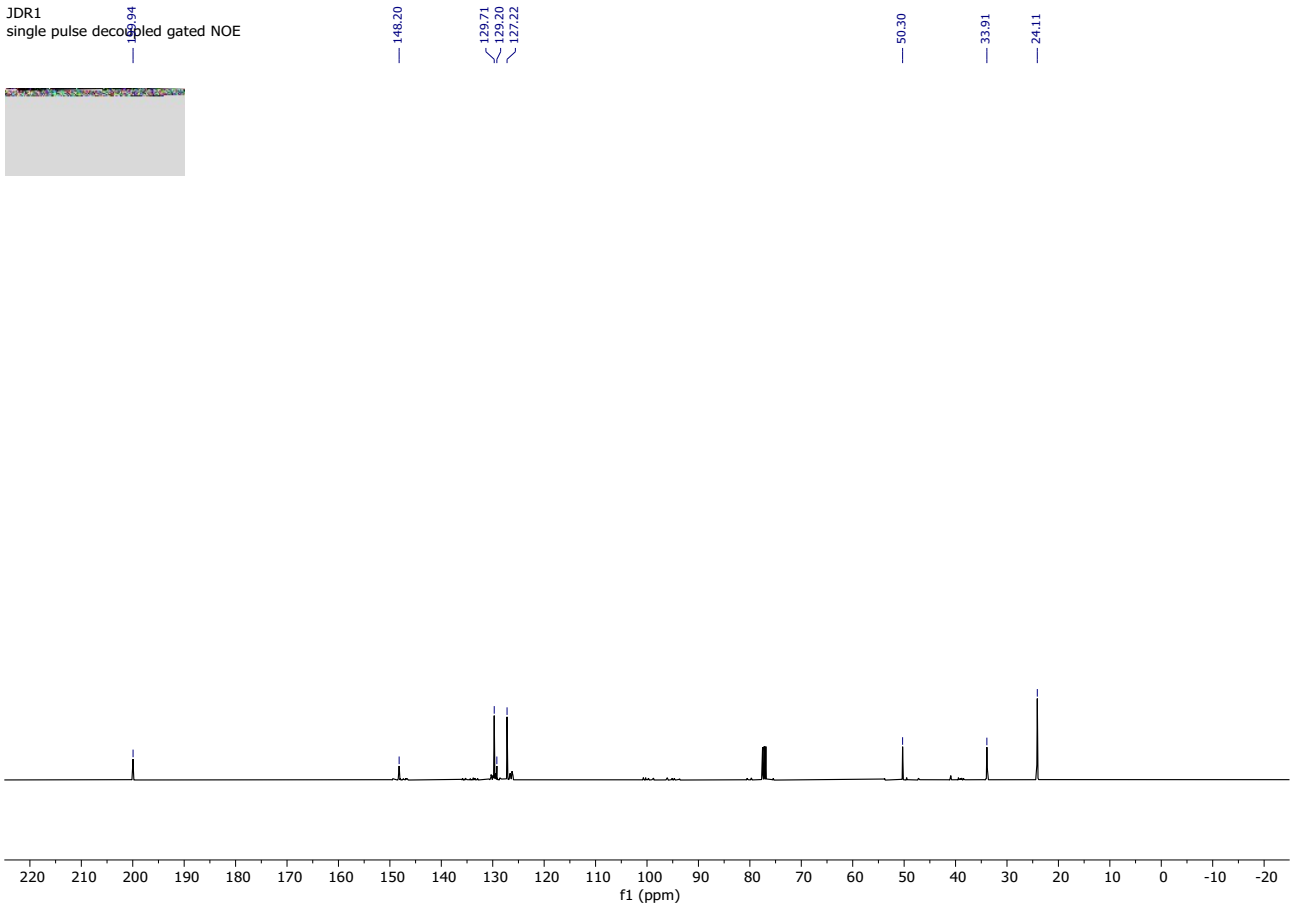



gated NOE
137.19
129.85
129.68
129.45
128.90
50.27
21.23
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(4-isopropylphenyl)acetaldehyde (4c). This compound was isolated using flash column chromatography and gave 4c as a colorless oil. Spectral data is in accordance with the literature.[9]

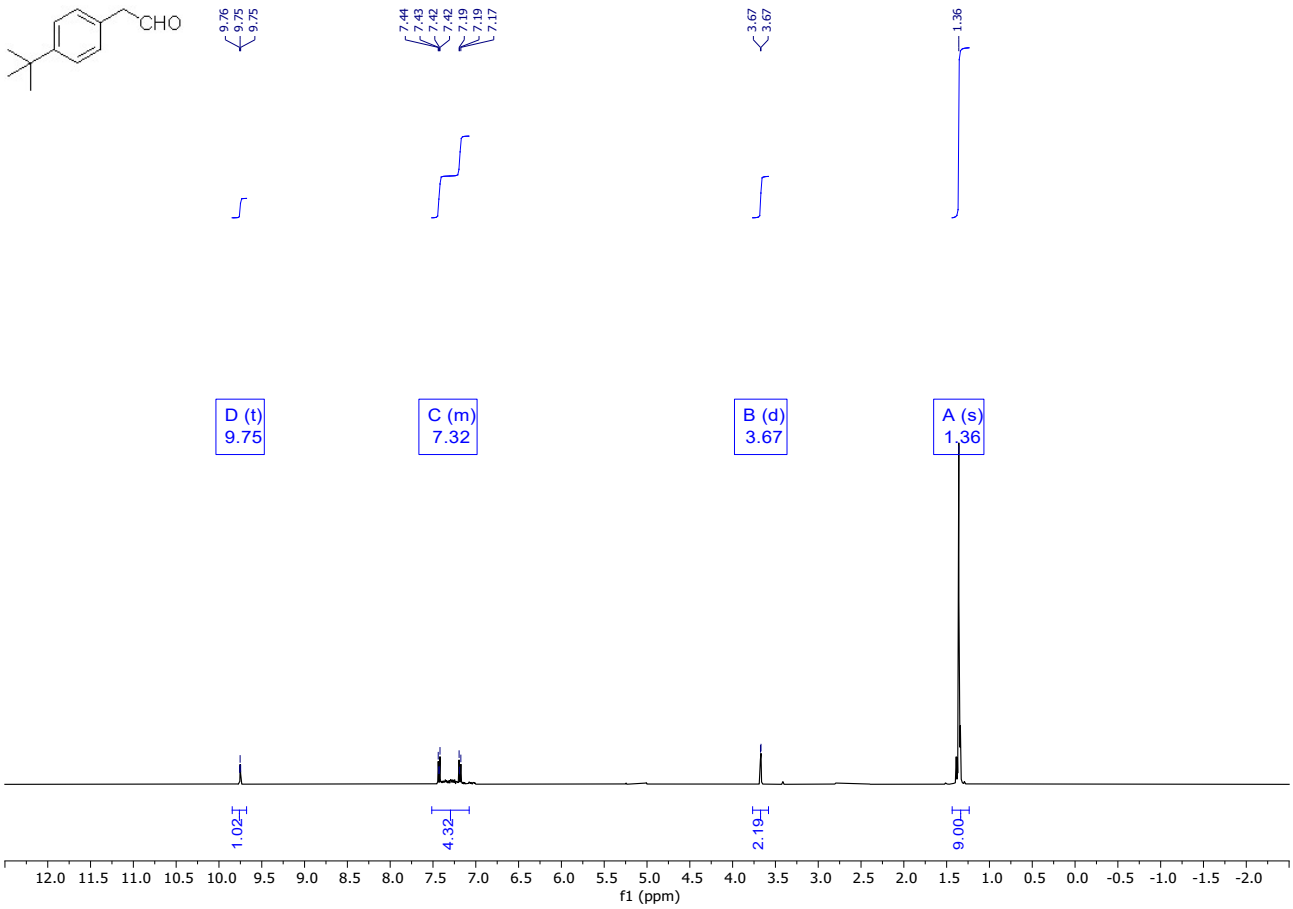
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.74 (dd, J = 2.7, 2.1 Hz, 1H), 7.42 – 7.11 (m, 4H), 3.66 (d, J = 2.5 Hz, 2H), 3.00 – 2.86 (m, 2H), 1.28 (dd, J = 7.0, 0.7 Hz, 7H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.94, 148.20, 129.71, 129.20, 127.22, 50.30, 33.91, 24.11.

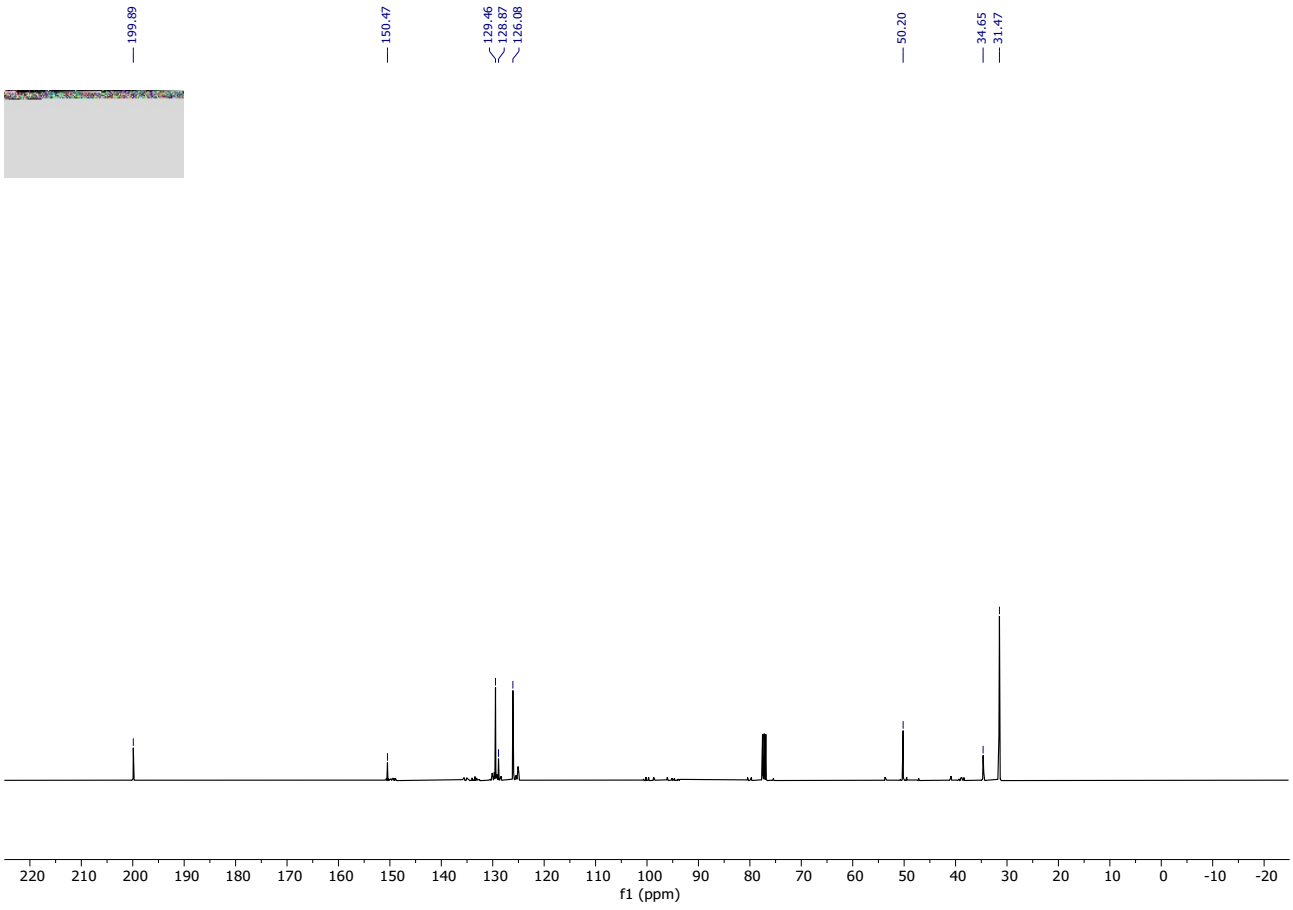



JDR1
single pulse decoupled gated NOE
199.94
148.20
129.71
129.20
127.22
50.30
33.91
24.11
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(4-(tert-butyl)phenyl)acetaldehyde (4d). This compound was isolated using flash column chromatography and gave 4d as a colorless oil. Spectral data is in accordance with the literature.[9]

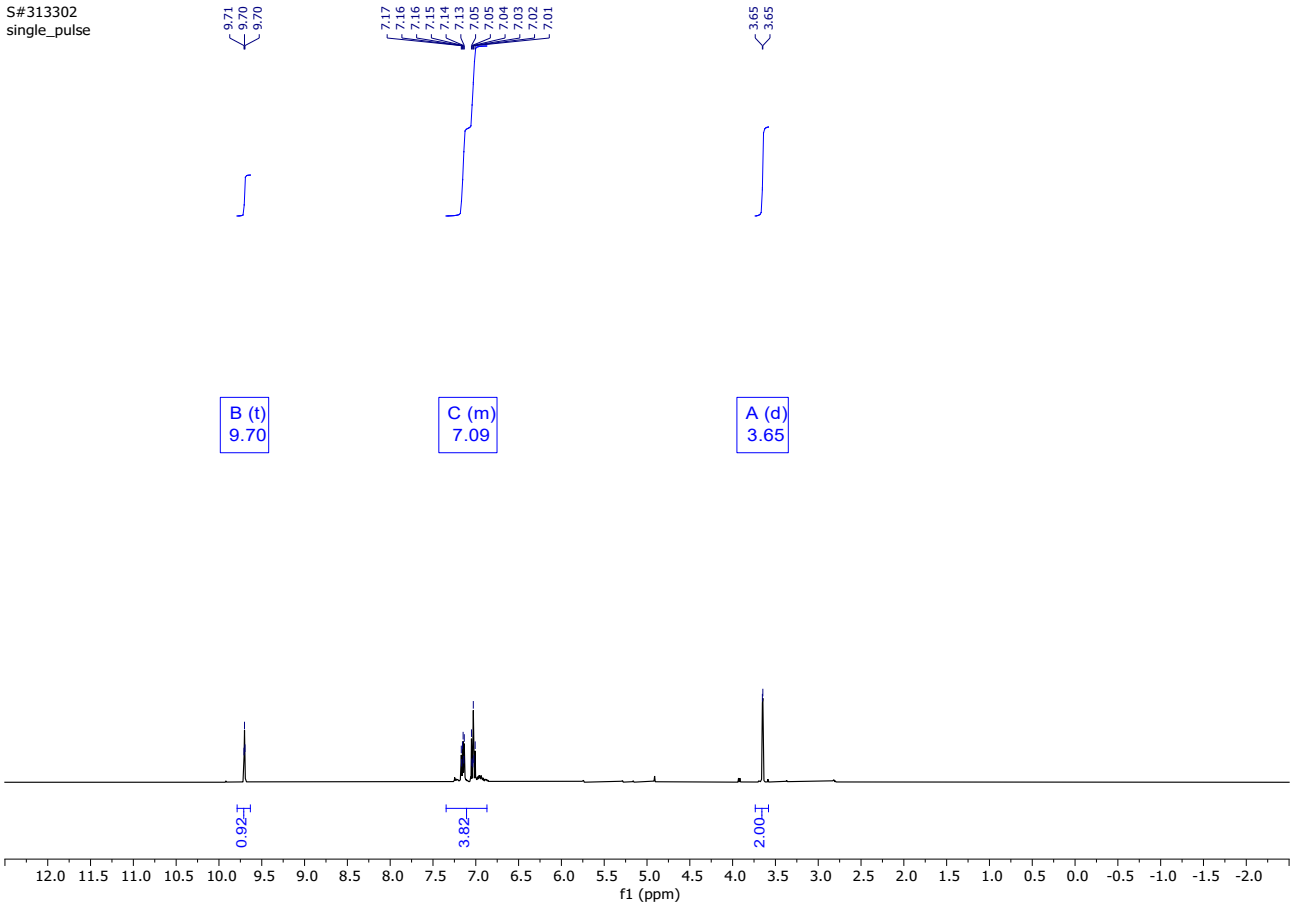
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.75 (t, *J* = 2.4 Hz, 1H), 7.51 – 7.08 (m, 4H), 3.67 (d, *J* = 2.5 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.89, 150.47, 129.46, 128.87, 126.08, 50.20, 34.65, 31.47.

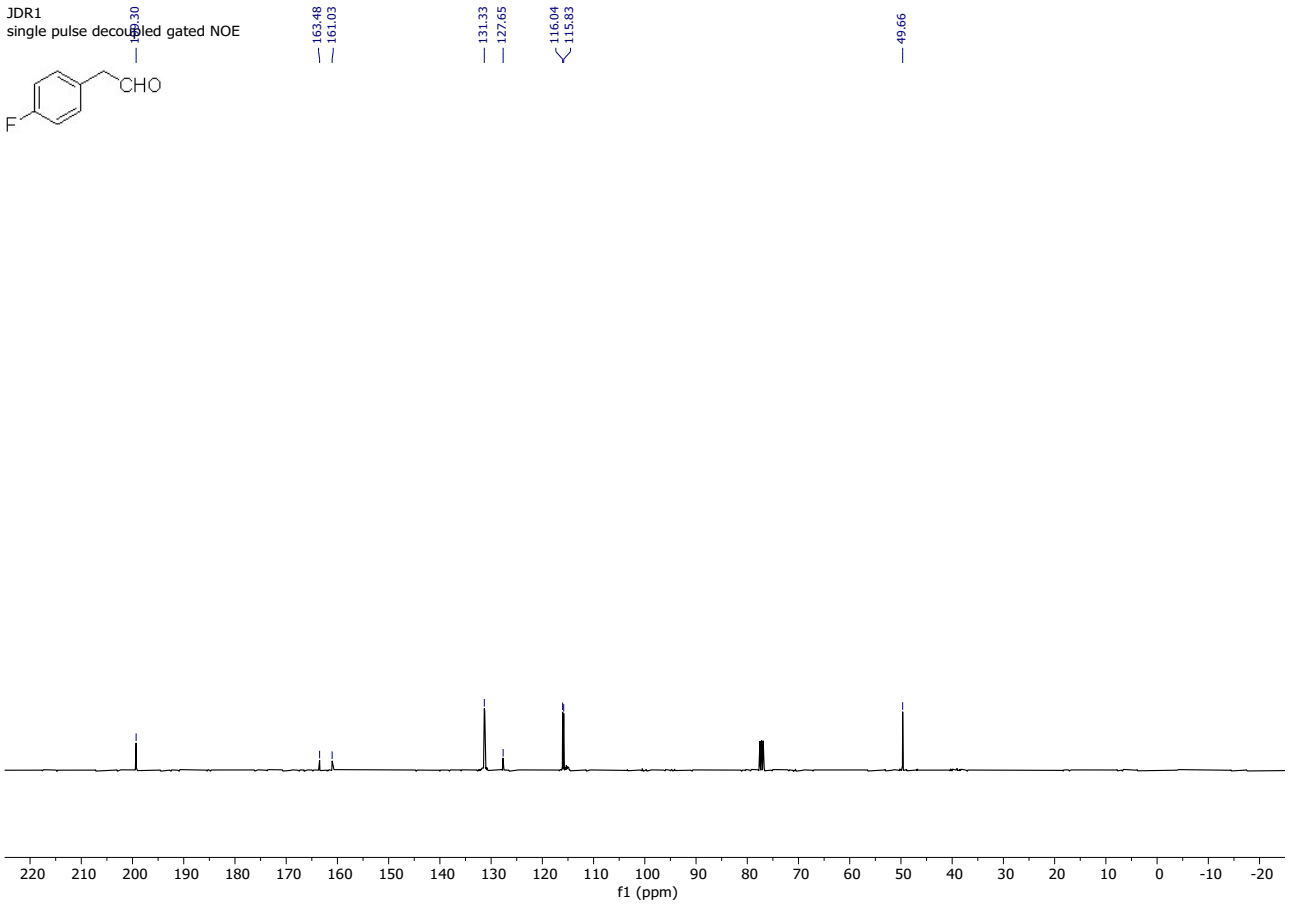


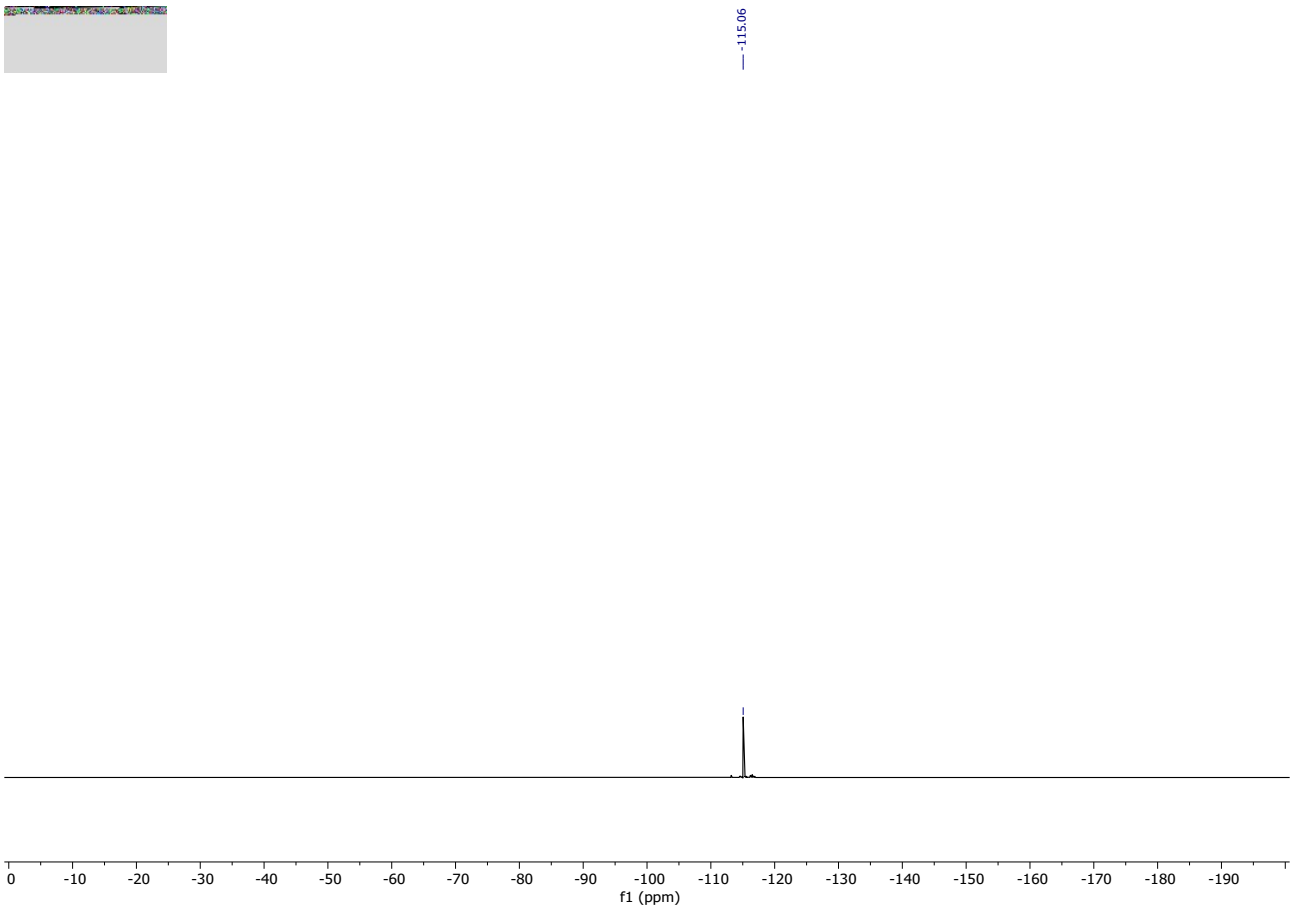

199.89
150.47
129.46
128.87
126.08
50.20
34.65
31.47
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(4-fluorophenyl)acetaldehyde (4e). This compound was isolated using flash column chromatography and gave 4e as a colorless oil. Spectral data is in accordance with the literature.[10]

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.70 (t, J = 2.2 Hz, 1H), 7.35 – 6.87 (m, 4H), 3.65 (d, J = 2.2 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.30, 163.48, 161.03, 131.33, 127.65, 116.04, 115.83, 49.66. ^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ -115.06.

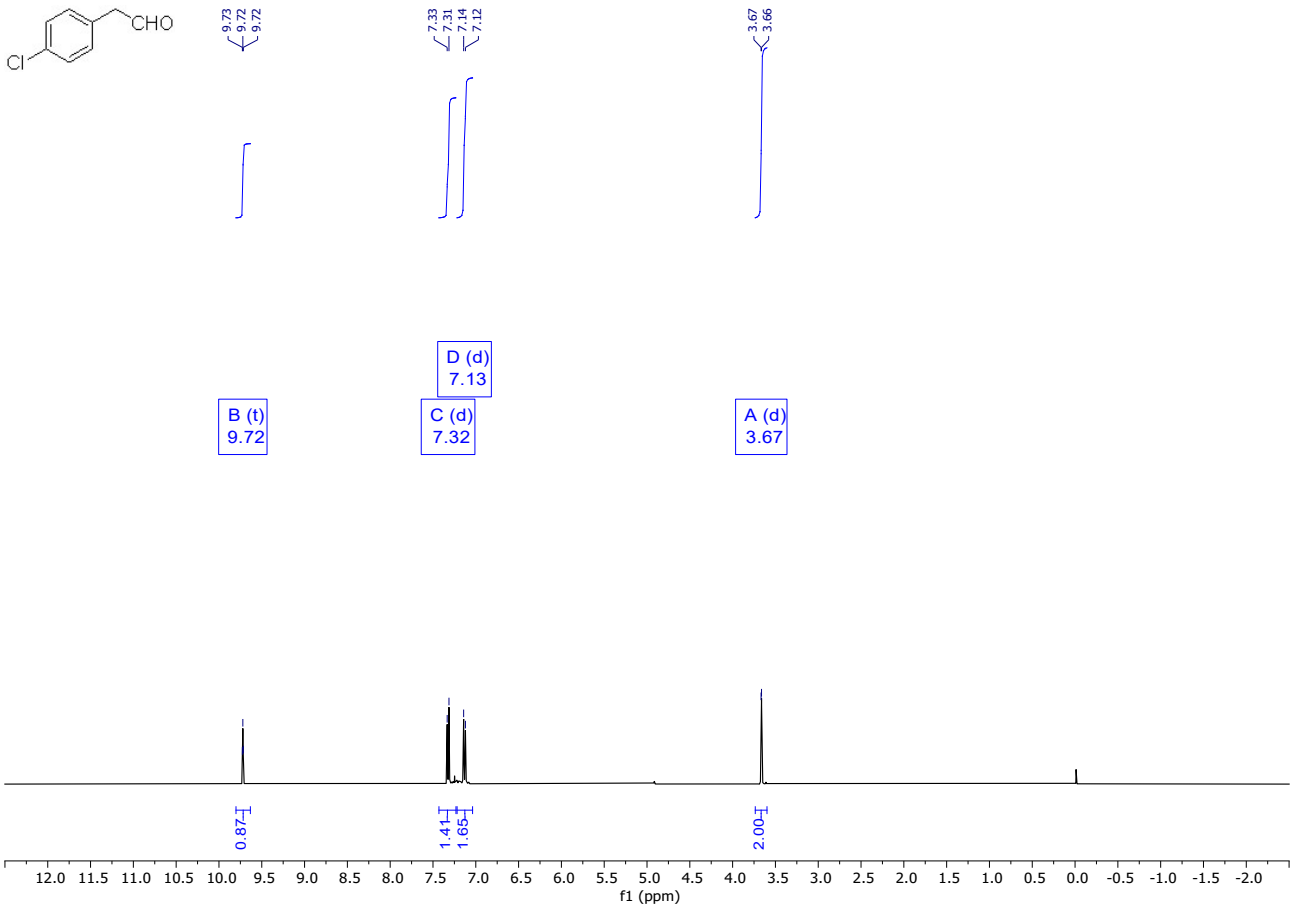


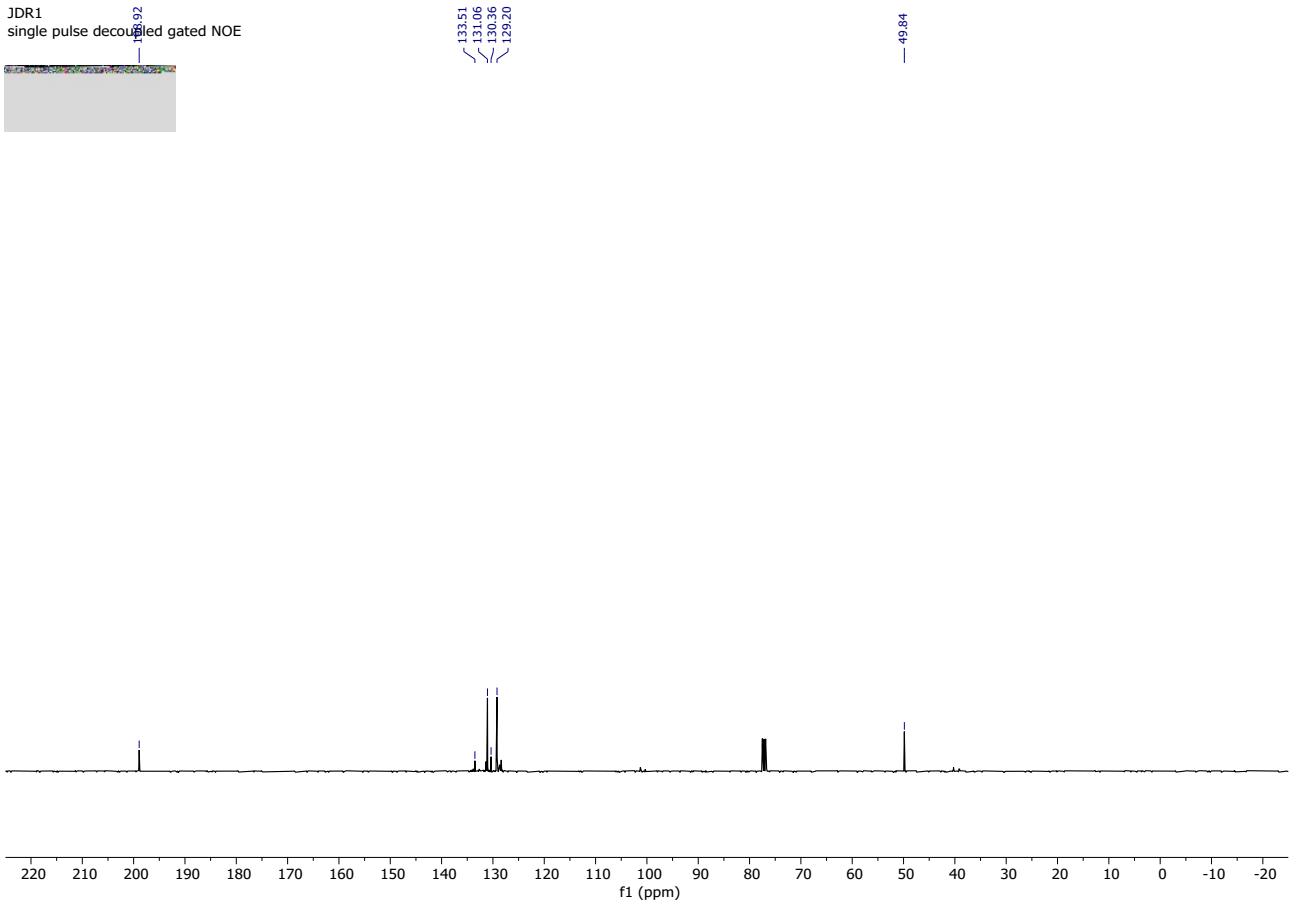

JDR1
single pulse decoupled gated NOE
190.30
163.48
161.03
131.33
127.65
116.04
115.83
49.66
CHO
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-115.06
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

2-(4-chlorophenyl)acetaldehyde (4f). This compound was isolated using flash column chromatography and gave 4f as a colorless oil. Spectral data is in accordance with the literature.[11]

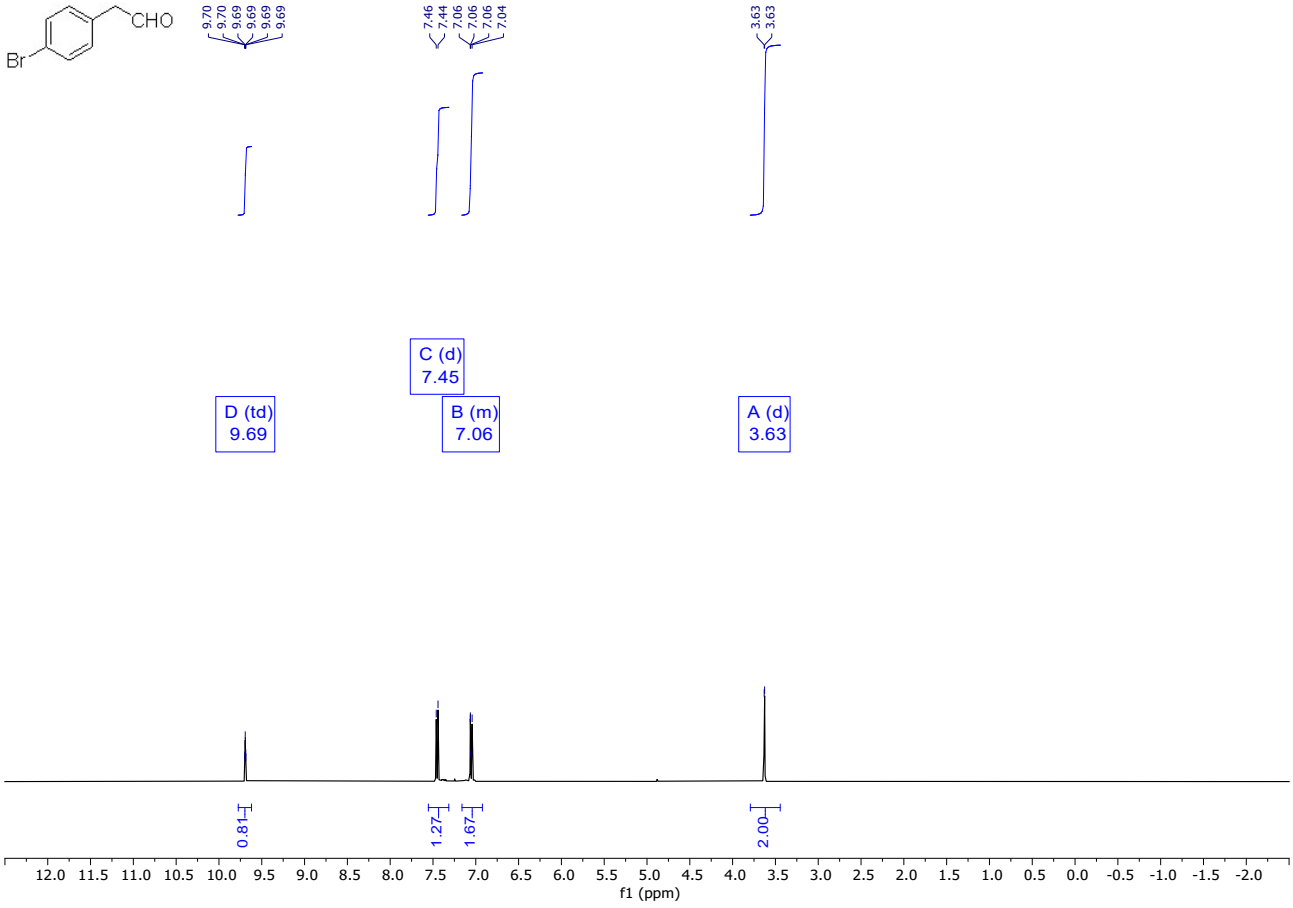
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.72 (t, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.67 (d, *J* = 2.1 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.92, 133.51, 131.06, 130.36, 129.20, 49.84.

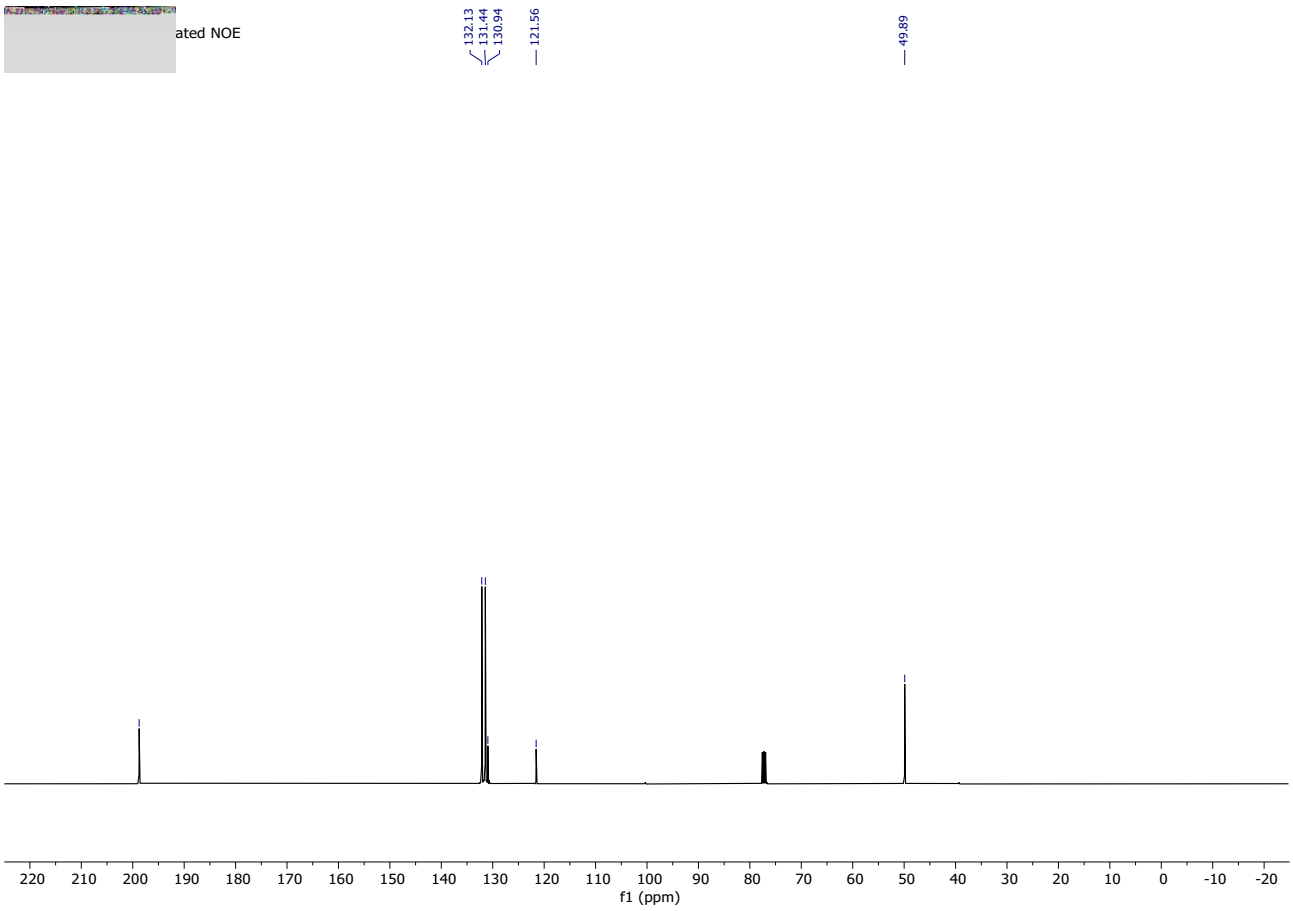



JDR1
single pulse decoupled gated NOE
199.92
133.51
131.06
130.36
129.20
49.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(4-bromophenyl)acetaldehyde (4g). This compound was isolated using flash column chromatography and gave 4g as a colorless oil. Spectral data is in accordance with the literature.[12]

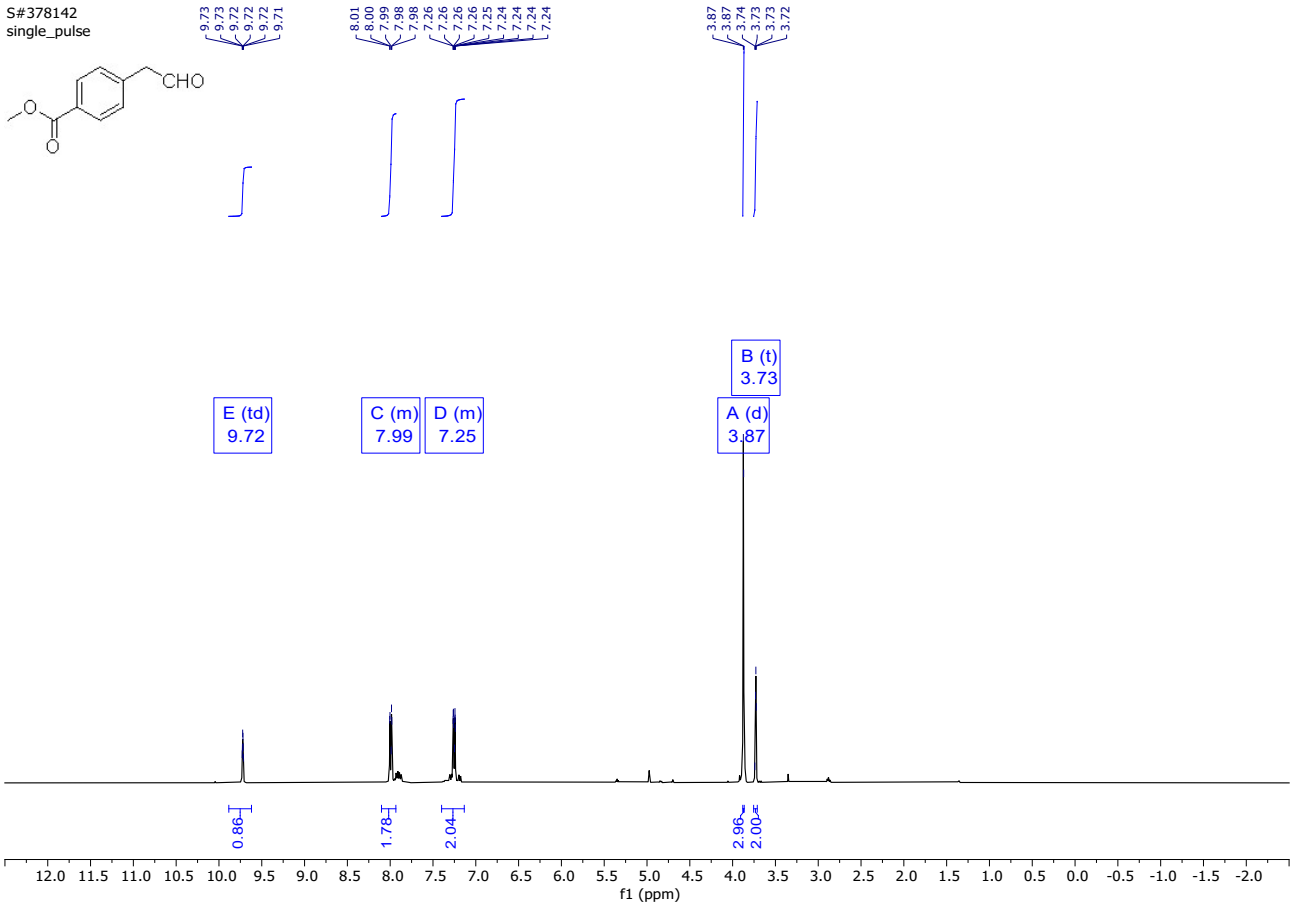
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.69 (td, J = 2.1, 0.6 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.16 – 6.92 (m, 2H), 3.63 (d, J = 2.1 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.75, 132.13, 131.44, 130.94, 121.56, 49.89.

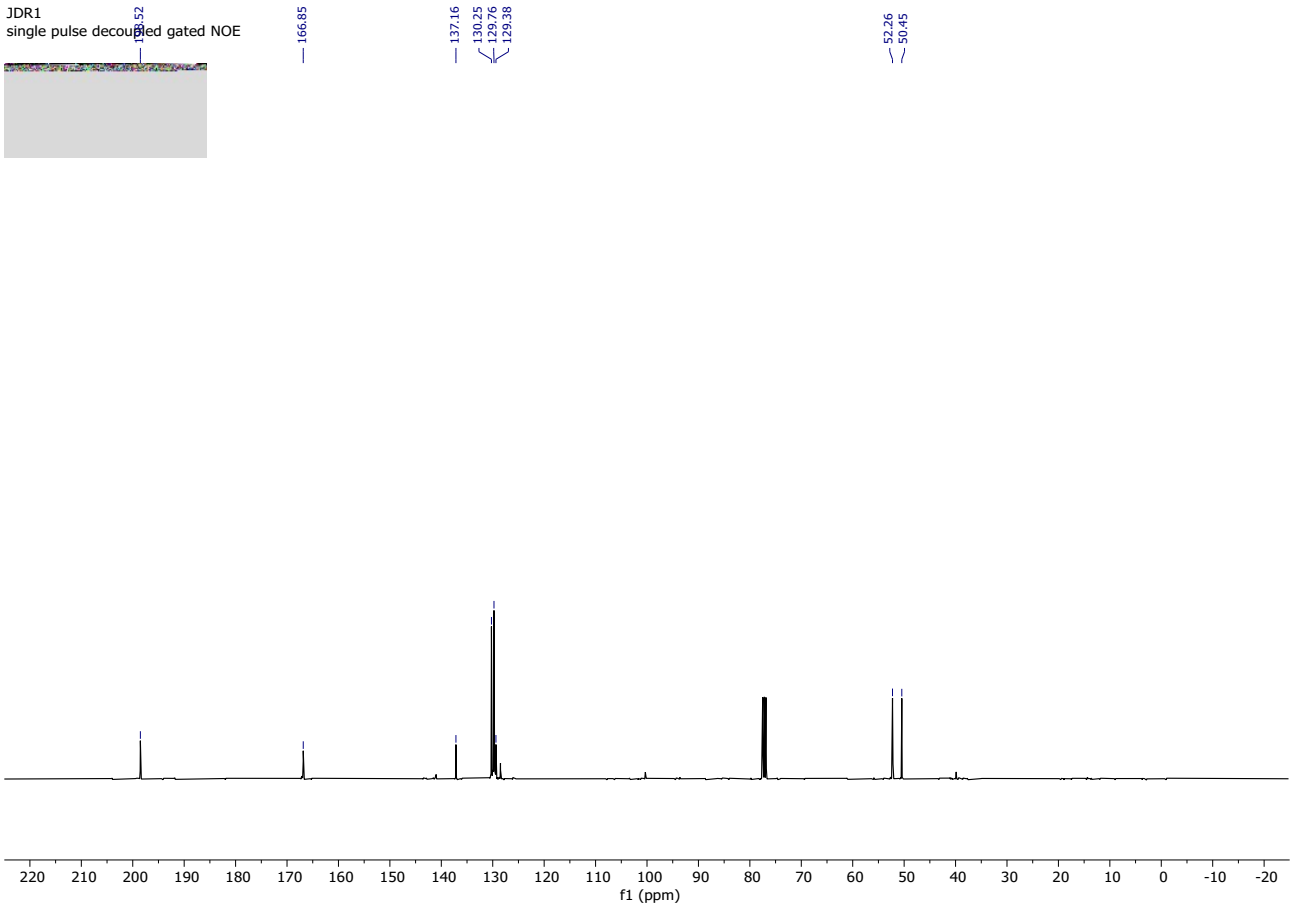



ated NOE
132.13
131.44
130.94
121.56
49.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

methyl 4-(2-oxoethyl)benzoate (4h). This compound was isolated using flash column chromatography and gave 4h as a white solid. Spectral data is in accordance with the literature.[13]

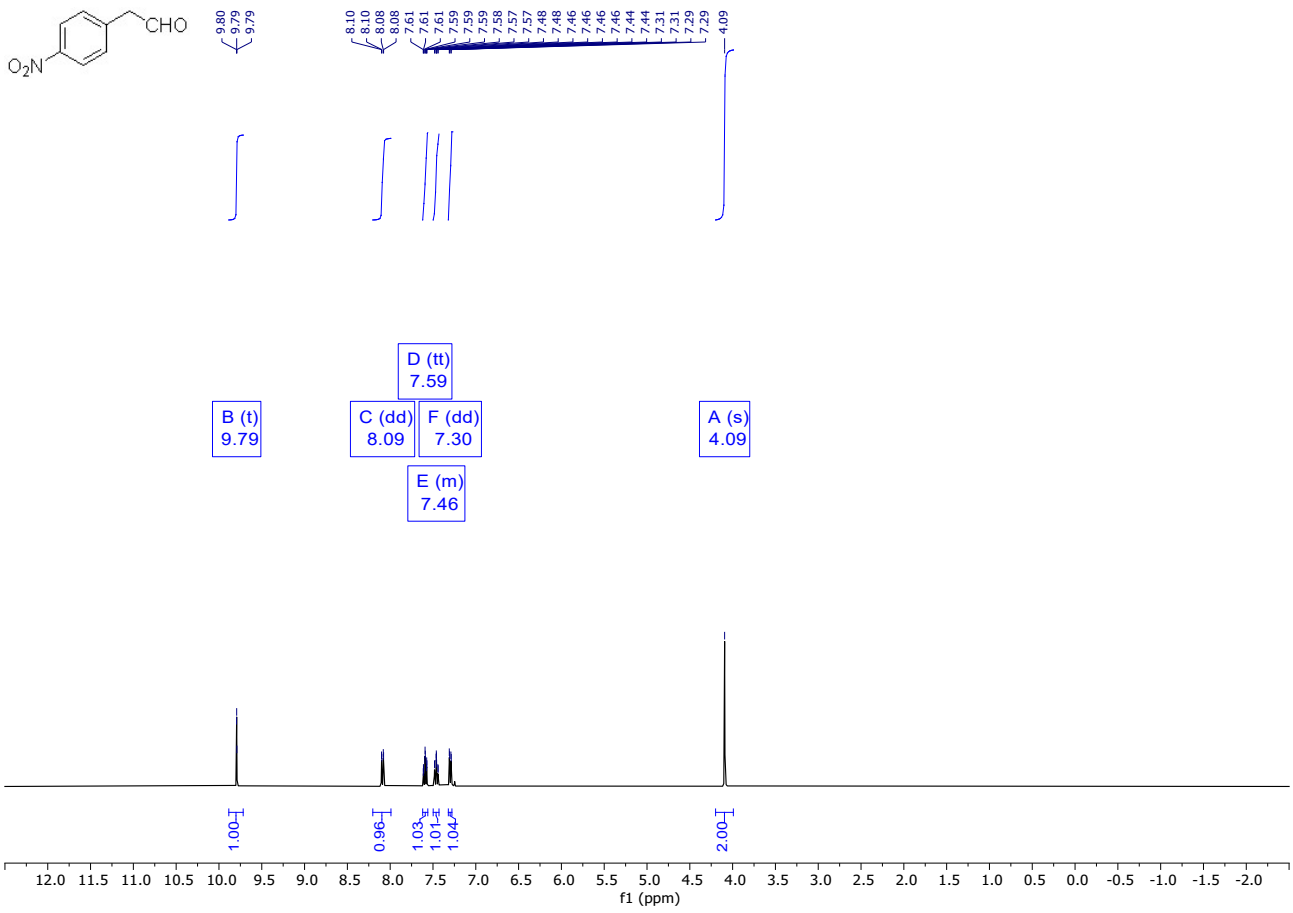
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.72 (td, J = 2.0, 1.2 Hz, 1H), 8.10 – 7.93 (m, 2H), 7.40 – 7.13 (m, 2H), 3.87 (d, J = 1.4 Hz, 3H), 3.73 (t, J = 1.7 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.52, 166.85, 137.16, 130.25, 129.76, 129.38, 52.26, 50.45.

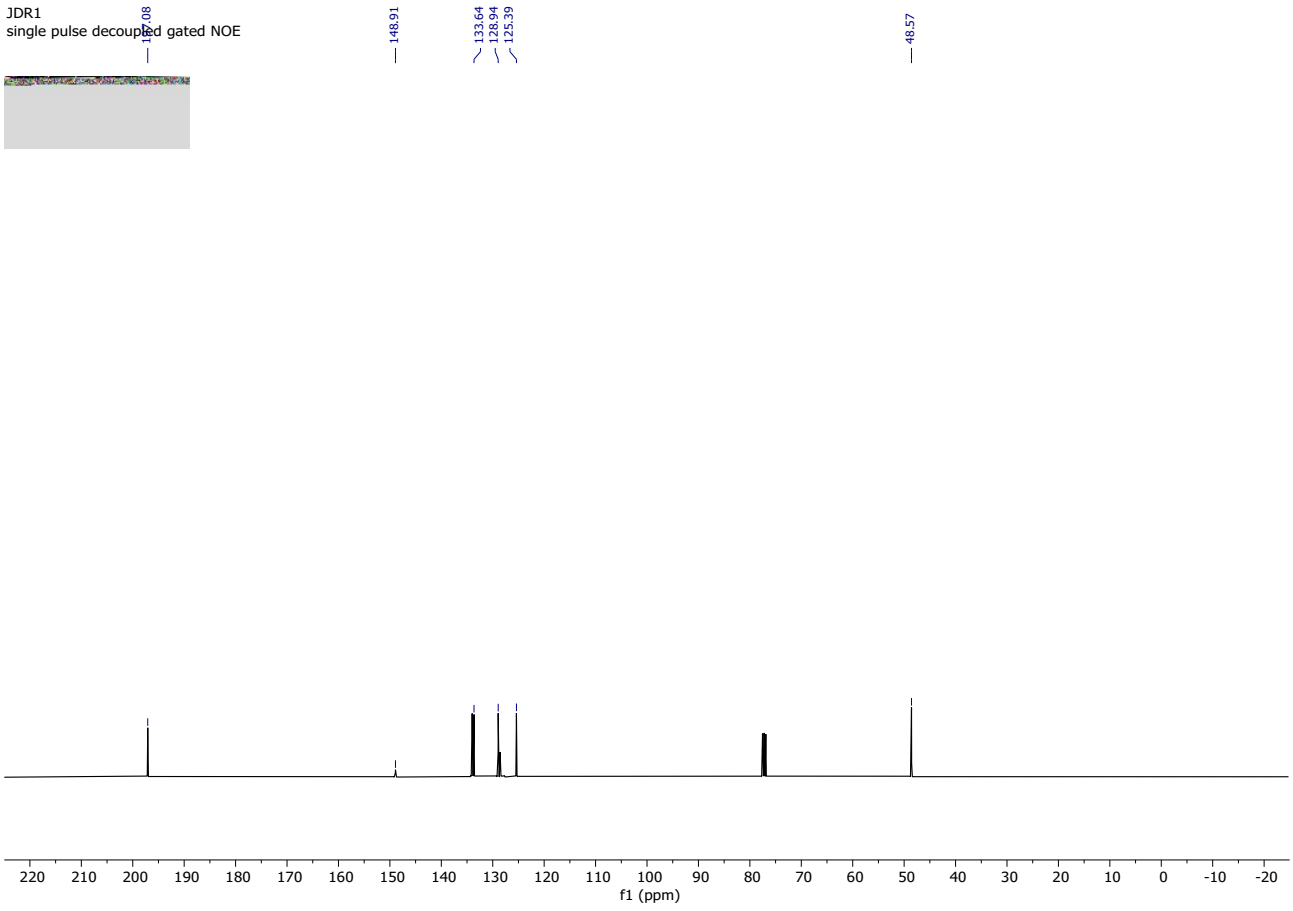



JDR1
single pulse decoupled gated NOE
199.52
166.85
137.16
130.25
129.76
129.38
52.26
50.45
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(4-nitrophenyl)acetaldehyde (4i). This compound was isolated using flash column chromatography and gave 4i as a white crystalline solid. Spectral data is in accordance with the literature.[10]

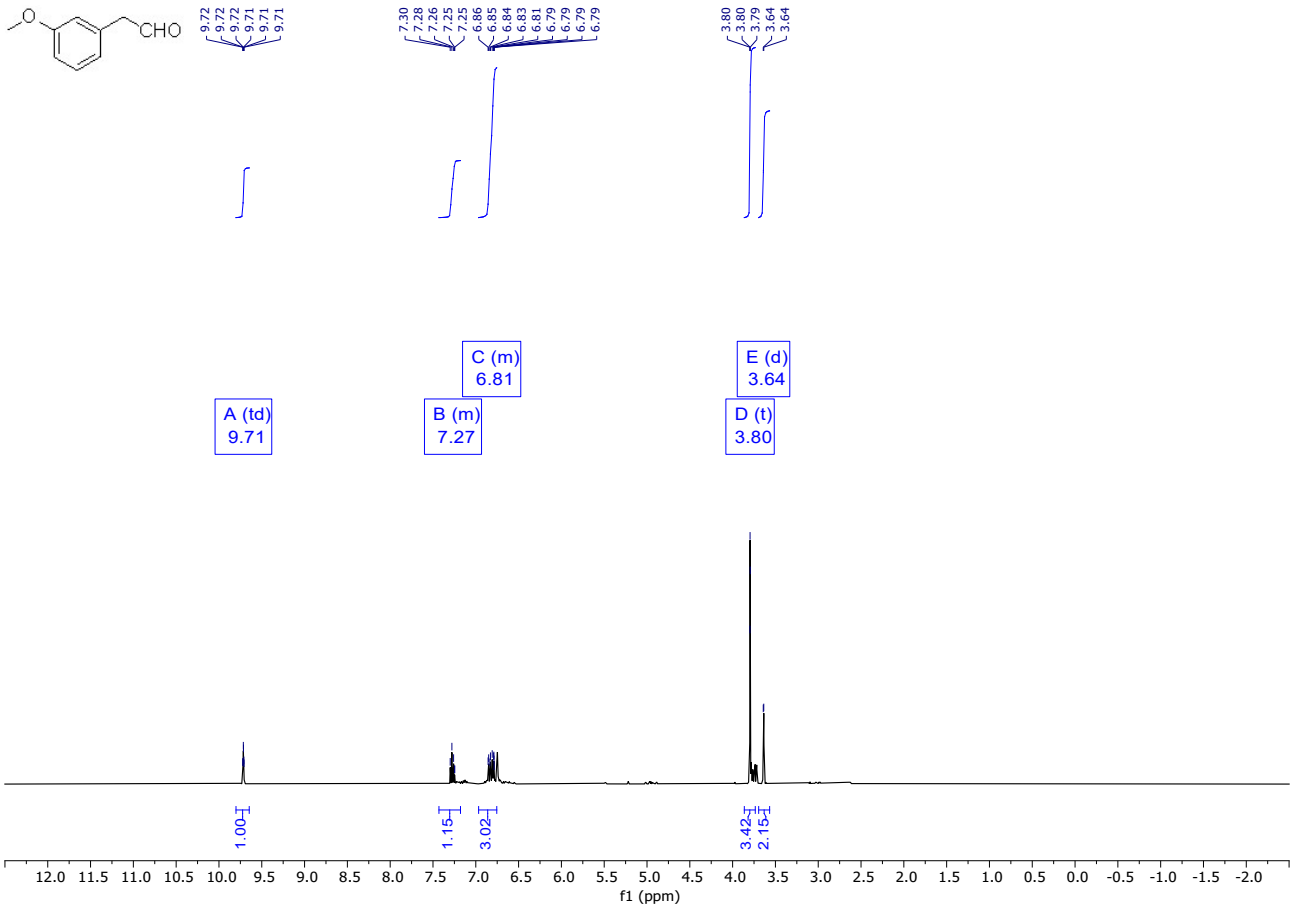
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.79 (t, J = 0.9 Hz, 1H), 8.09 (dd, J = 8.2, 1.4 Hz, 1H), 7.59 (tt, J = 7.5, 1.0 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.30 (dd, J = 7.6, 1.5 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.08, 148.91, 133.64, 128.94, 125.39, 48.57.

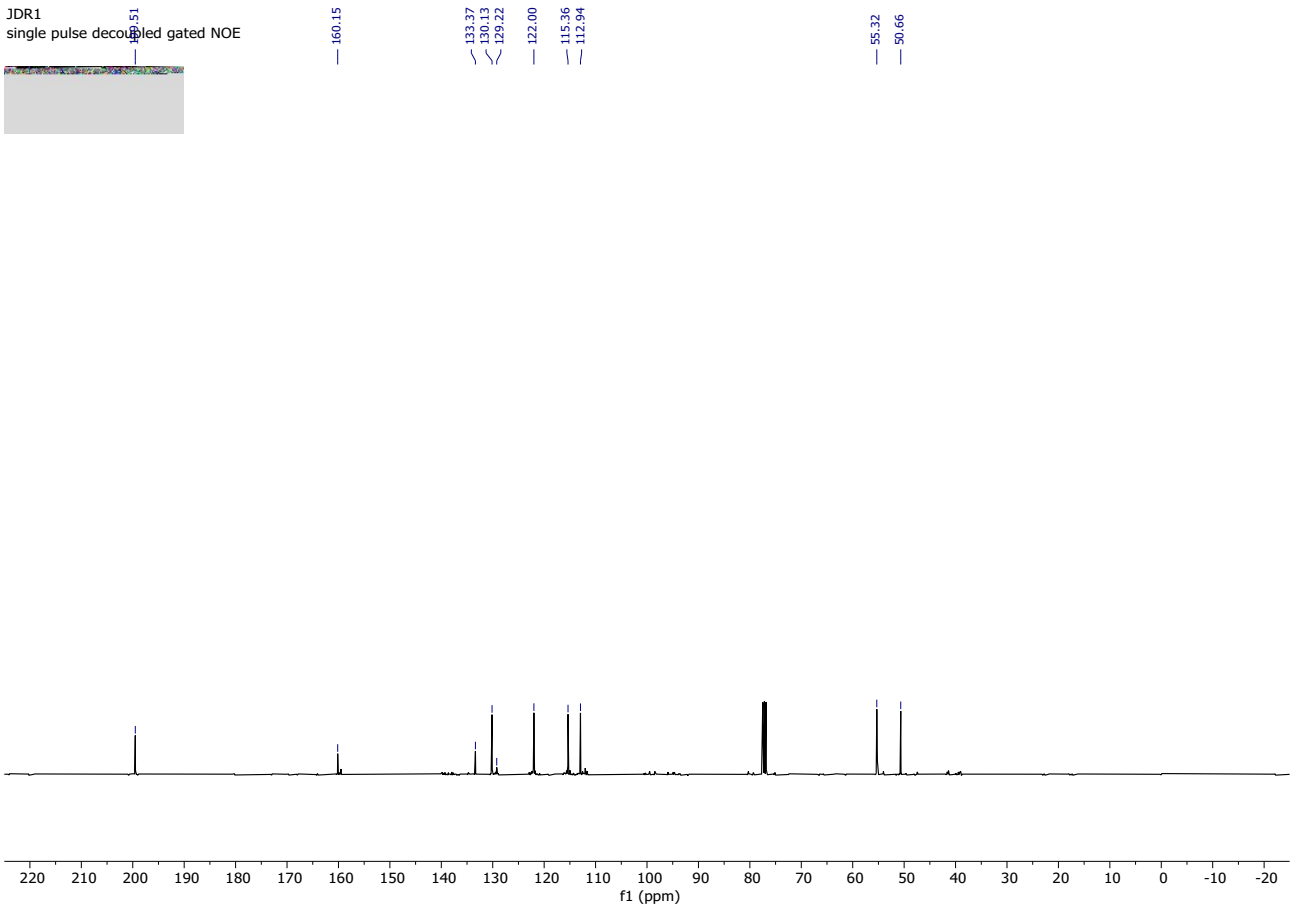



JDR1
single pulse decoupled gated NOE
197.08
148.91
133.64
128.94
125.39
48.57
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(3-methoxyphenyl)acetaldehyde (4j). This compound was isolated using flash column chromatography and gave 4j as a yellow oil. Spectral data is in accordance with the literature.[9]

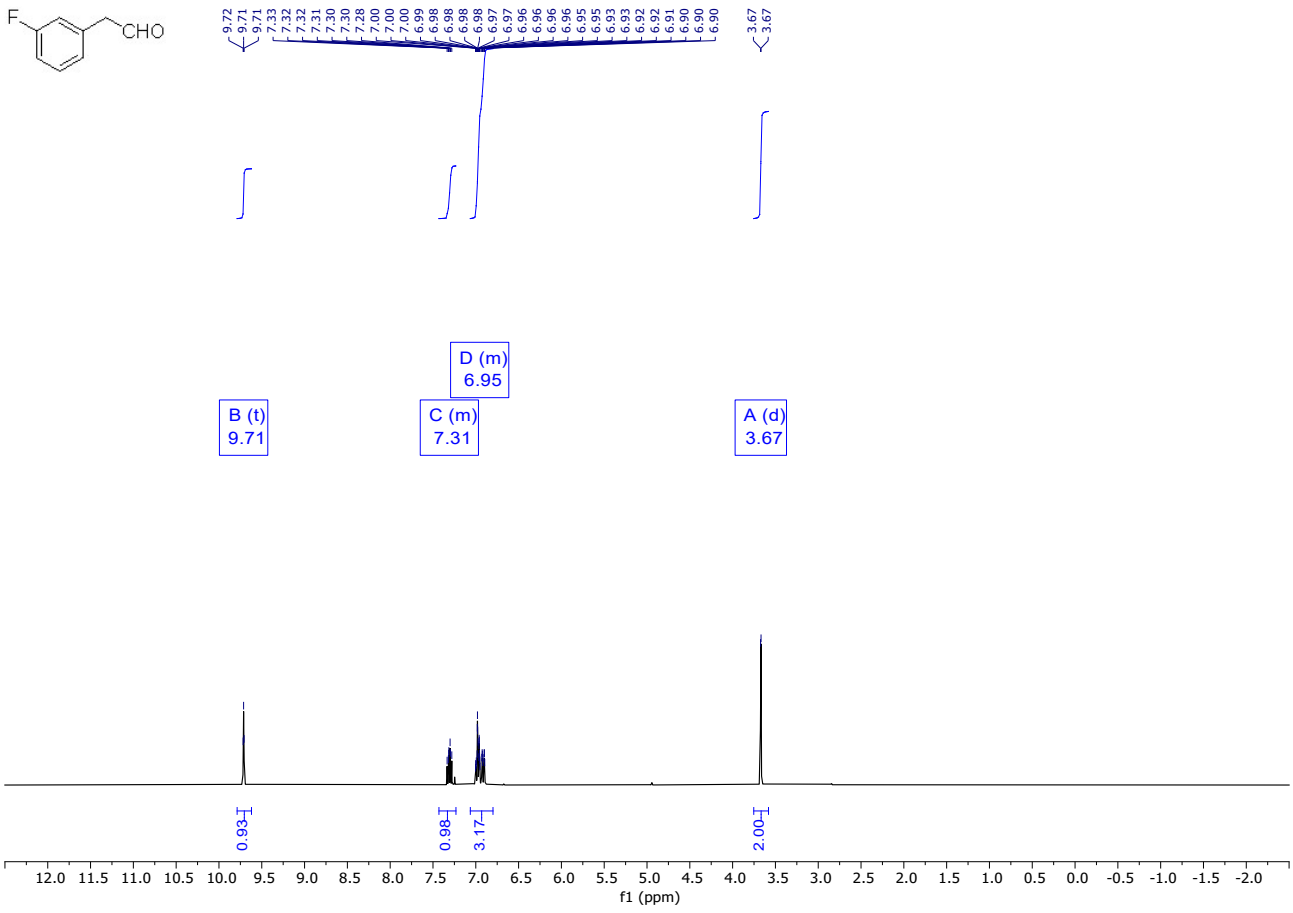
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.71 (td, J = 2.4, 0.7 Hz, 1H), 7.43 – 7.18 (m, 1H), 6.97 – 6.75 (m, 3H), 3.80 (t, J = 0.7 Hz, 3H), 3.64 (d, J = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.51, 160.15, 133.37, 130.13, 129.22, 122.00, 115.36, 112.94, 55.32, 50.66.

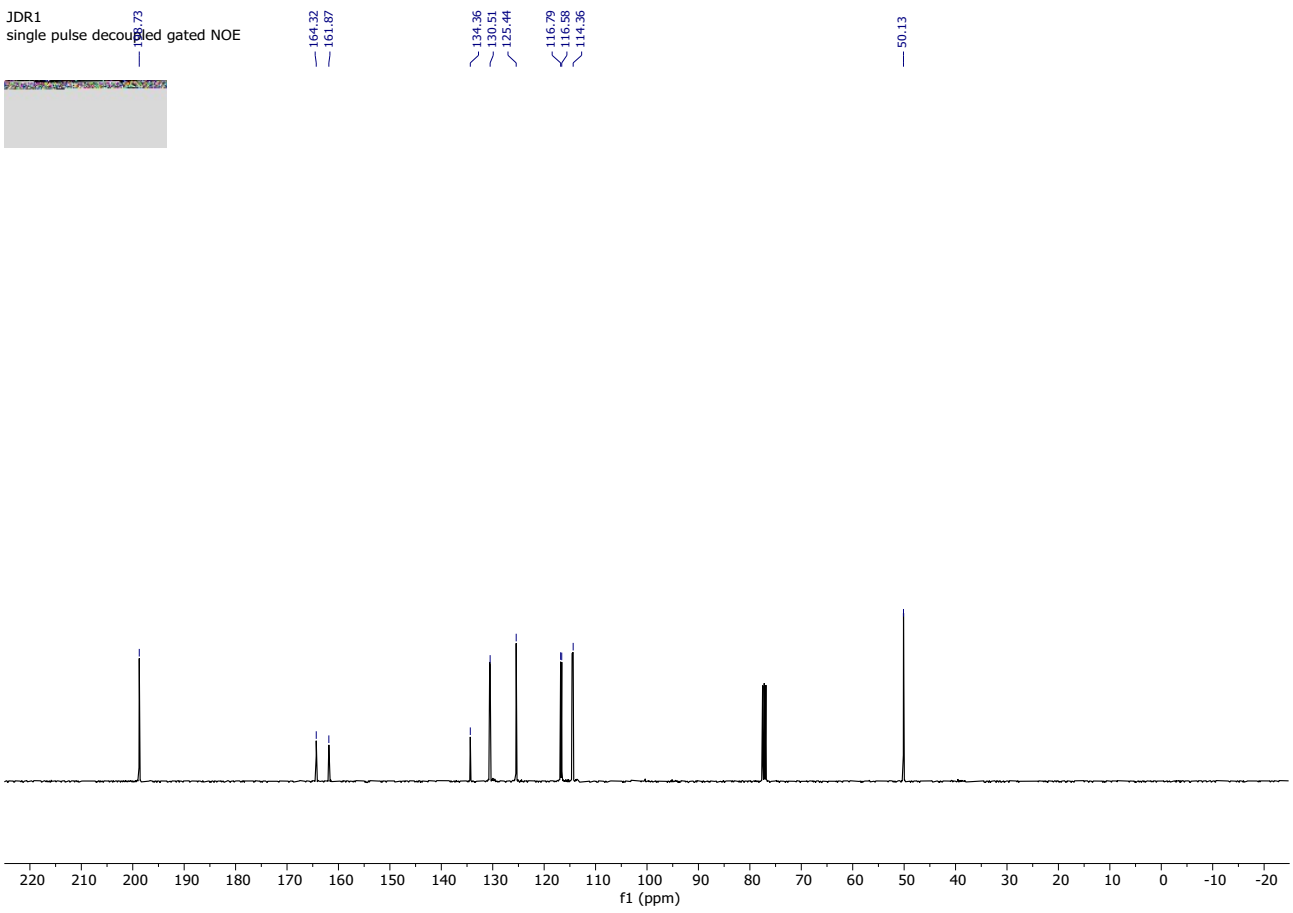


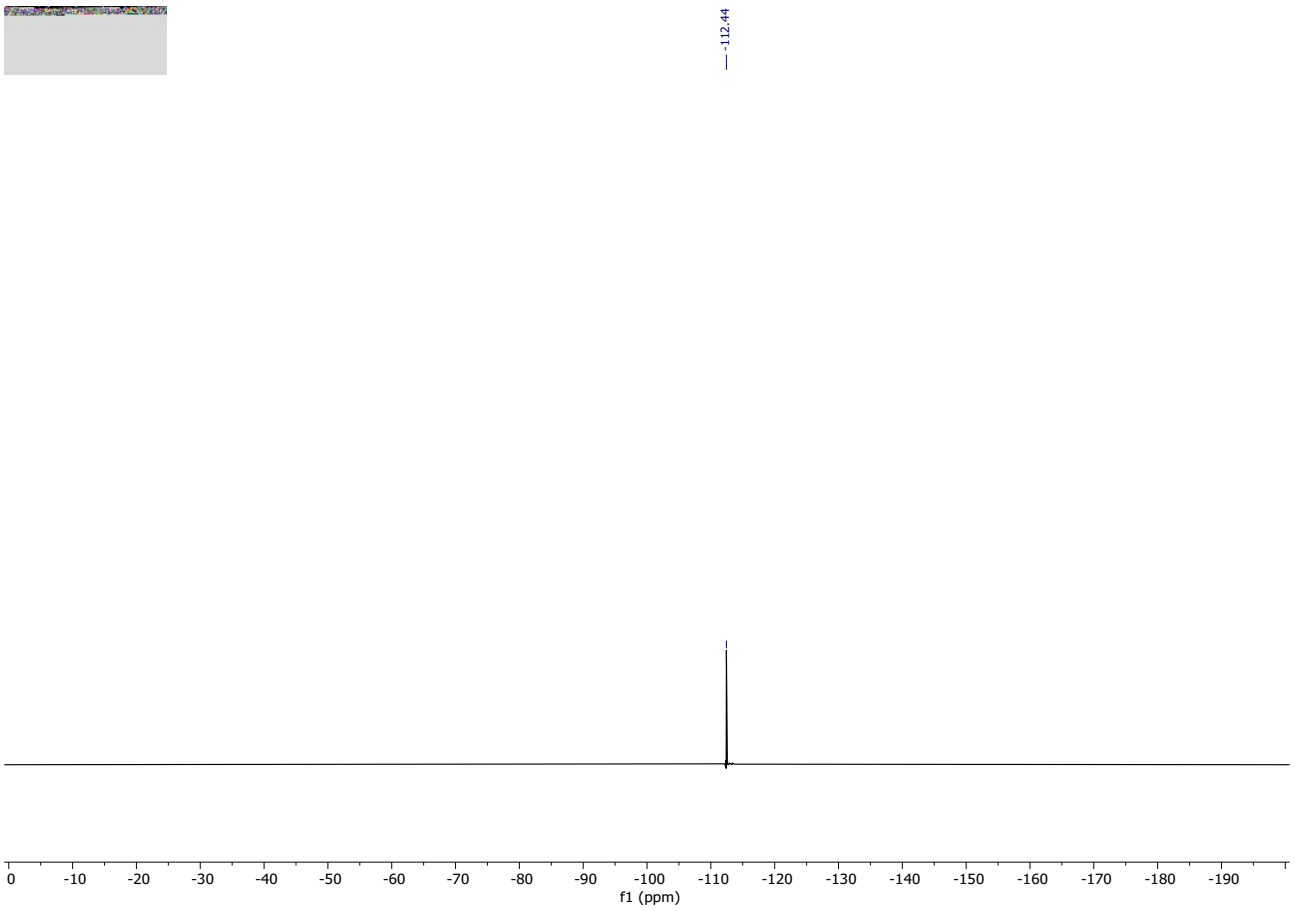

JDR1
single pulse decoupled gated NOE
199.51
160.15
133.37
130.13
129.22
122.00
115.36
112.94
55.32
50.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(3-fluorophenyl)acetaldehyde (4k). This compound was isolated using flash column chromatography and gave 4k as yellow oil. Spectral data is in accordance with the literature.[9]

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.71 (t, J = 2.1 Hz, 1H), 7.43 – 7.23 (m, 1H), 7.06 – 6.80 (m, 3H), 3.67 (d, J = 2.1 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.73, 164.32, 161.87, 134.36, 130.51, 125.44, 116.79, 116.58, 114.36, 50.13. ^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ -112.44.

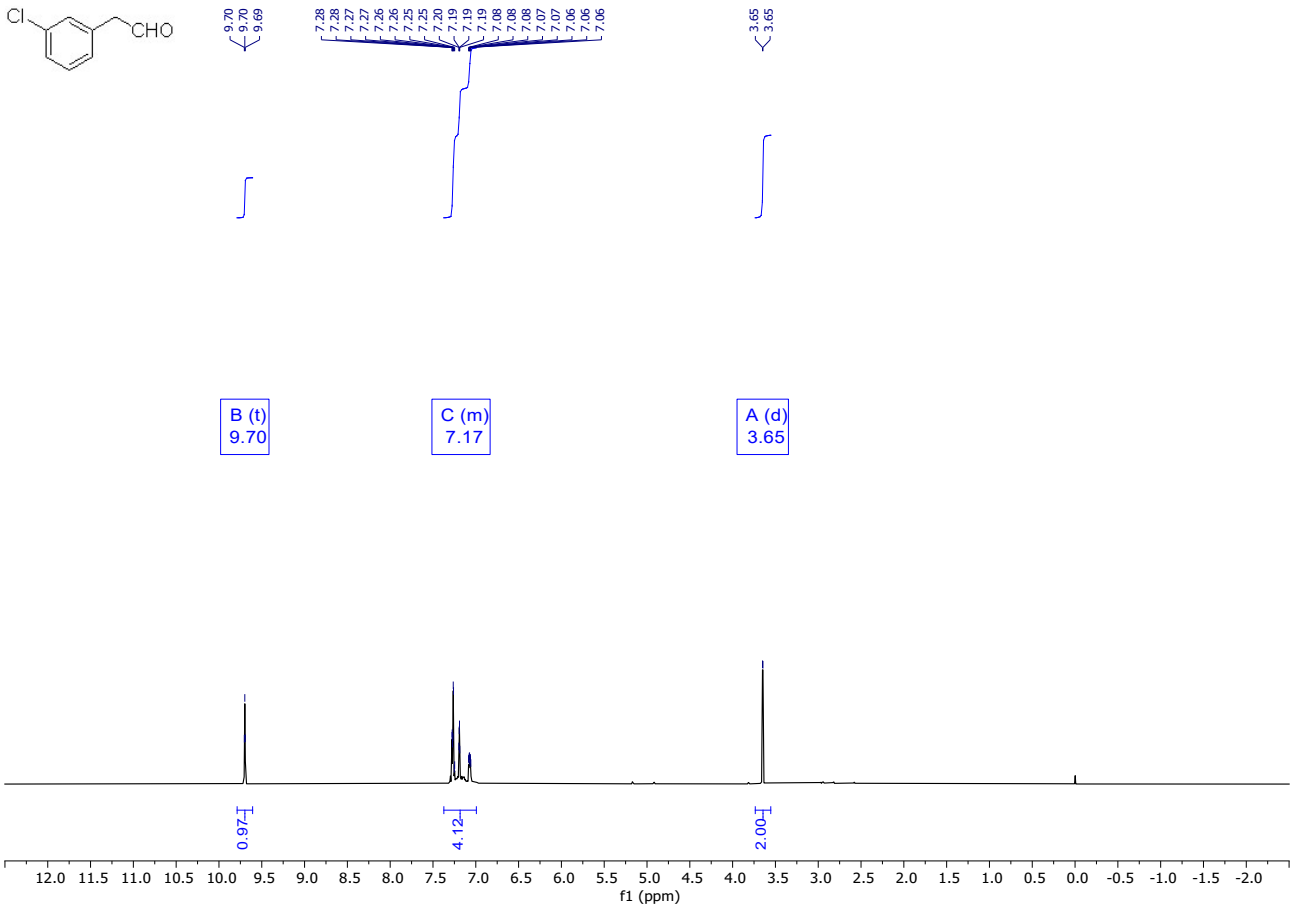


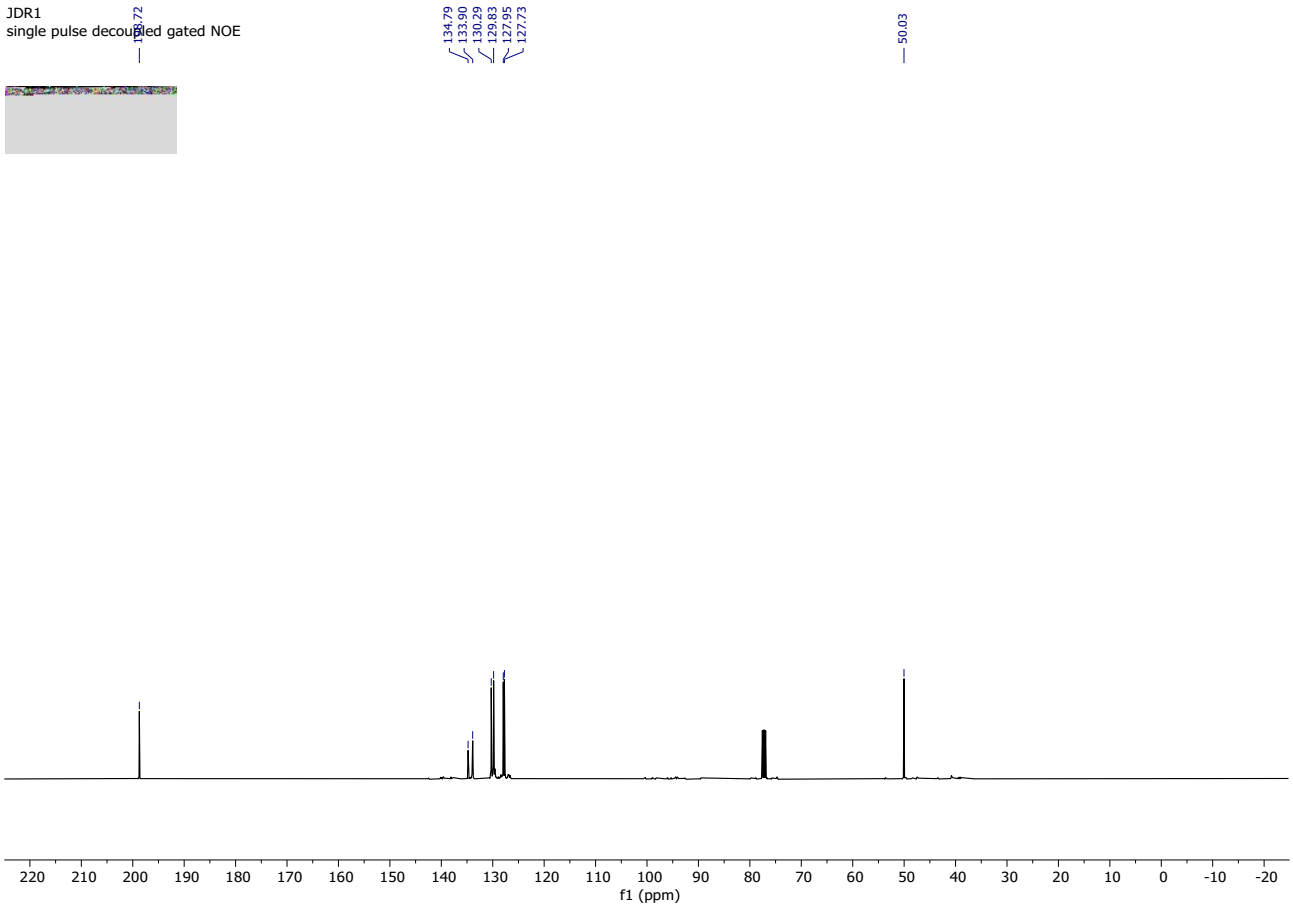

JDR1
single pulse decoupled gated NOE
199.73
164.32
161.87
134.36
130.51
125.44
116.79
116.58
114.36
50.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


-112.44
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

2-(3-chloroophenyl)acetaldehyde (4l). This compound was isolated using flash column chromatography and gave 4l as a yellow oil. Spectral data is in accordance with the literature.[9]

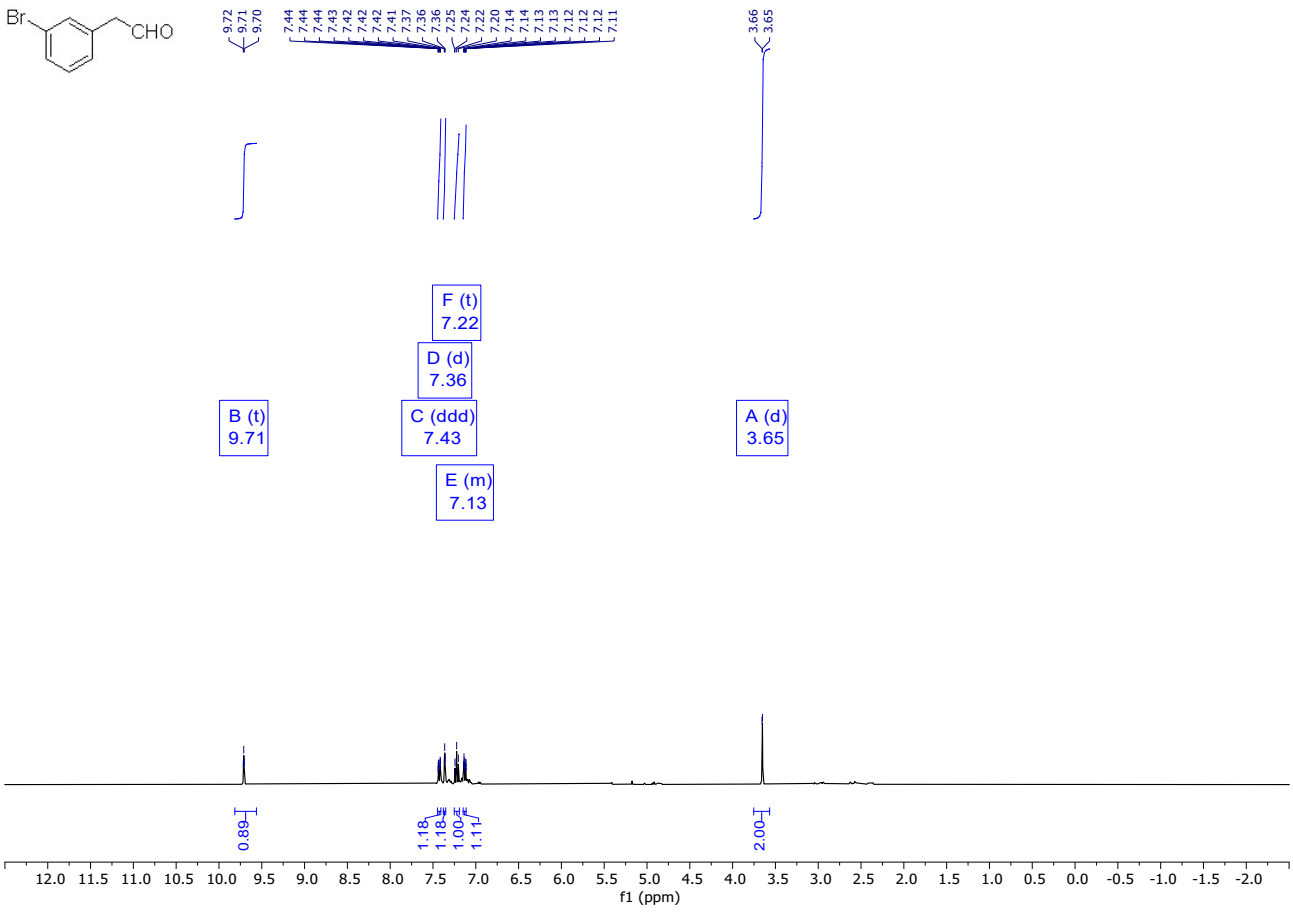
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.70 (t, J = 2.1 Hz, 1H), 7.37 – 6.99 (m, 4H), 3.65 (d, J = 2.1 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.72, 134.79, 133.90, 130.29, 129.83, 127.95, 127.73, 50.03.

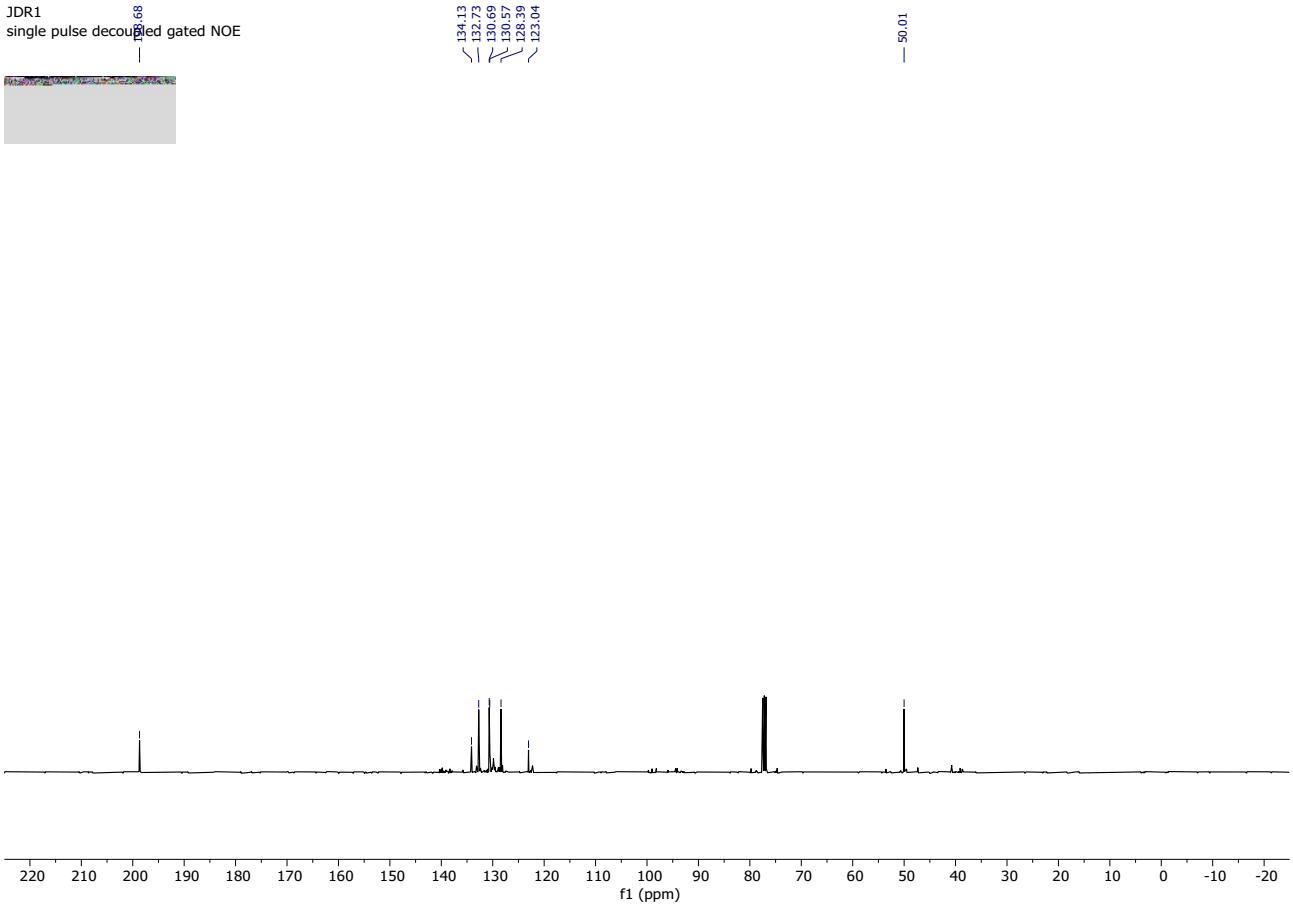



JDR1
single pulse decoupled gated NOE
197.72
134.79
133.90
130.29
129.83
127.95
127.73
50.03
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(3-bromoophenyl)acetaldehyde (4m). This compound was isolated using flash column chromatography and gave 4m as a yellow solid. Spectral data is in accordance with the literature.[9]

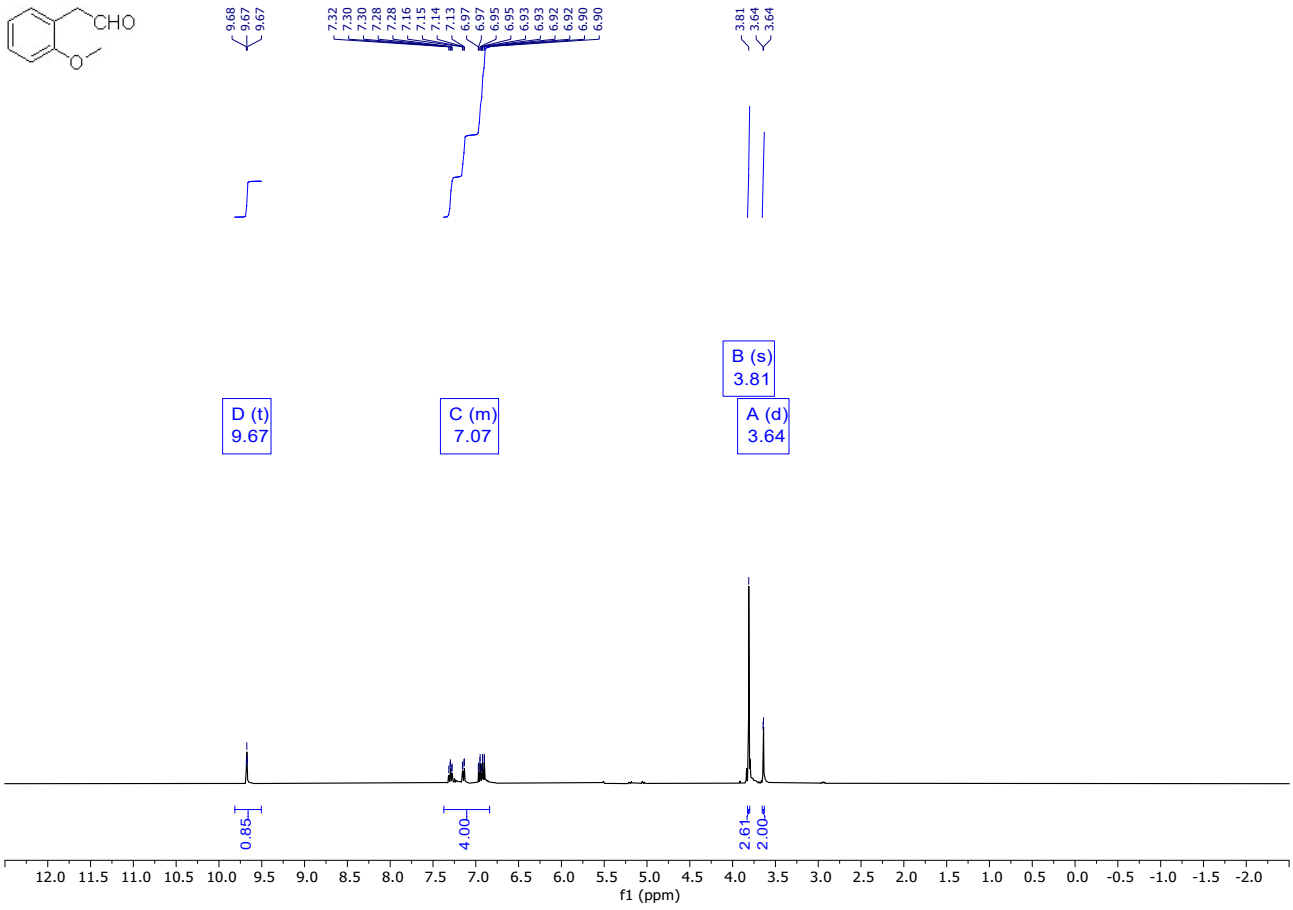
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.71 (t, J = 2.1 Hz, 1H), 7.43 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.15 – 7.11 (m, 1H), 3.65 (d, J = 2.2 Hz, 2H).
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.68, 134.13, 132.73, 130.69, 130.57, 128.39, 123.04, 50.01.

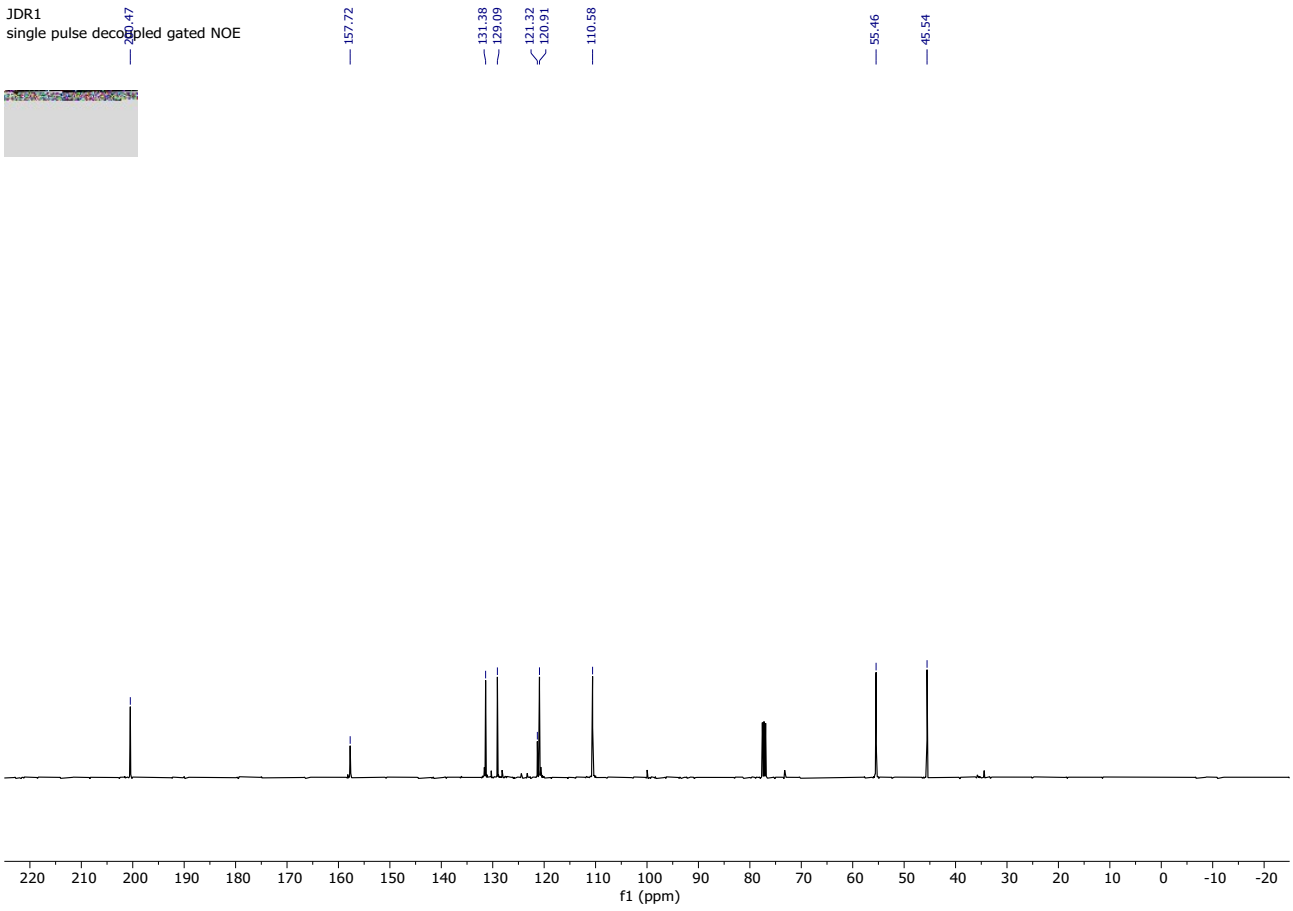



JDR1
single pulse decoupled gated NOE
199.68
134.13
132.73
130.69
130.57
128.39
123.04
50.01
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(2-methoxyphenyl)acetaldehyde (4n). This compound was isolated using flash column chromatography and gave 4n as a yellow oil. Spectral data is in accordance with the literature.[9]

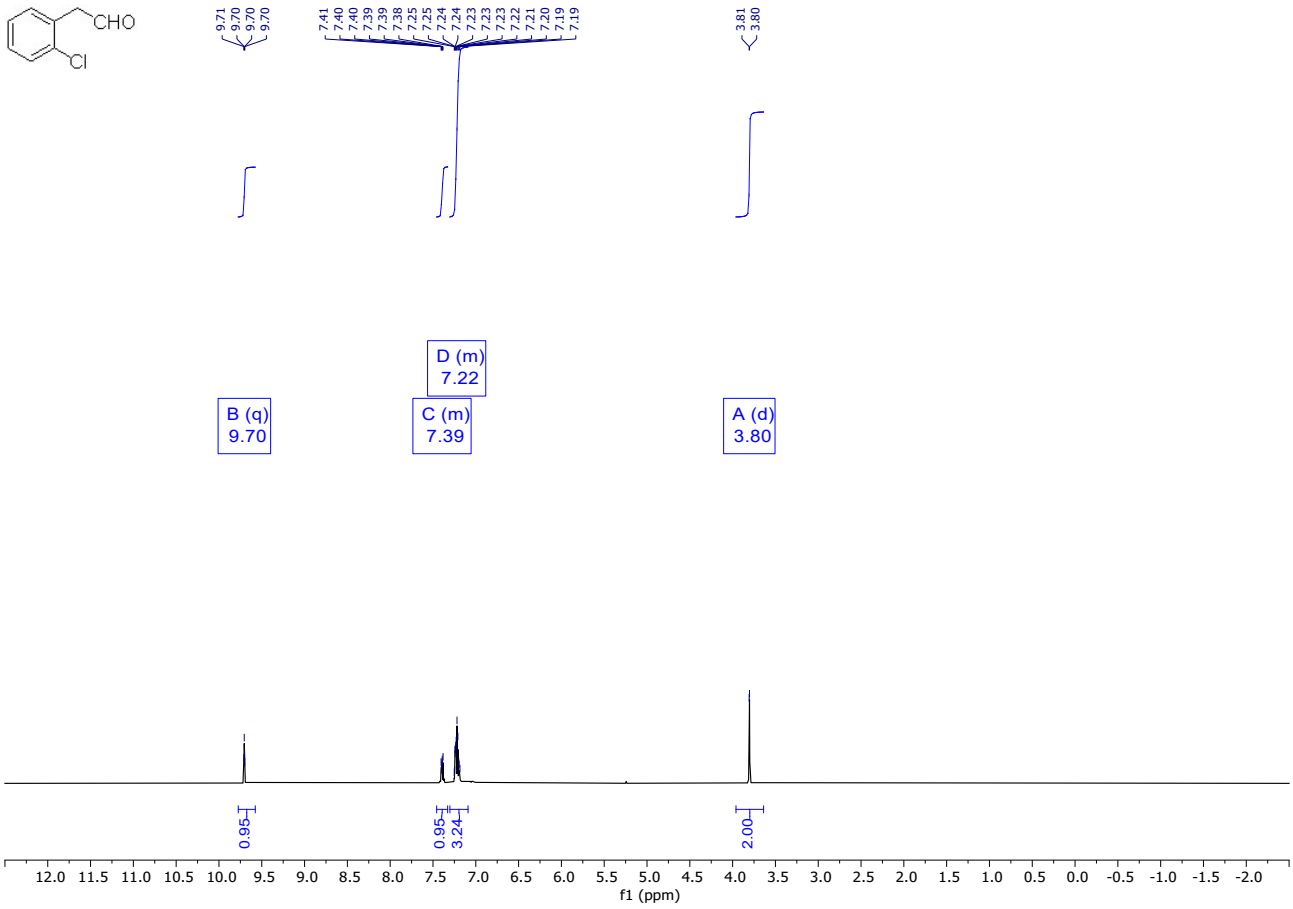
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.67 (t, J = 2.1 Hz, 1H), 7.37 – 6.84 (m, 4H), 3.81 (s, 3H), 3.64 (d, J = 2.2 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 200.47, 157.72, 131.38, 129.09, 121.32, 120.91, 110.58, 55.46, 45.54.

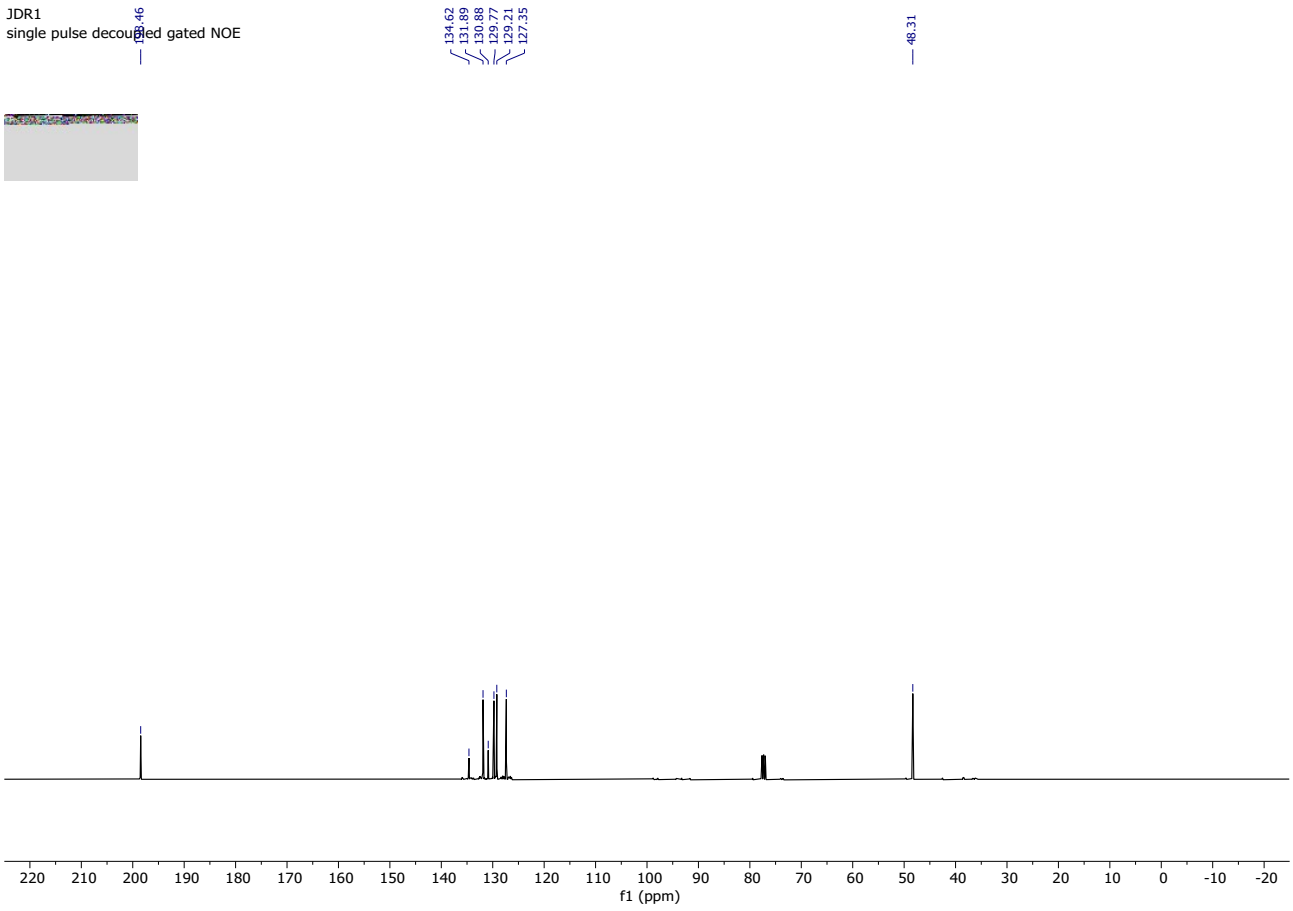



JDR1
single pulse decoupled gated NOE
200.47
157.72
131.38
129.09
121.32
120.91
110.58
55.46
45.54
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(2-chlorophenyl)acetaldehyde (4o). This compound was isolated using flash column chromatography and gave 4o as a yellow oil. Spectral data is in accordance with the literature.[9]

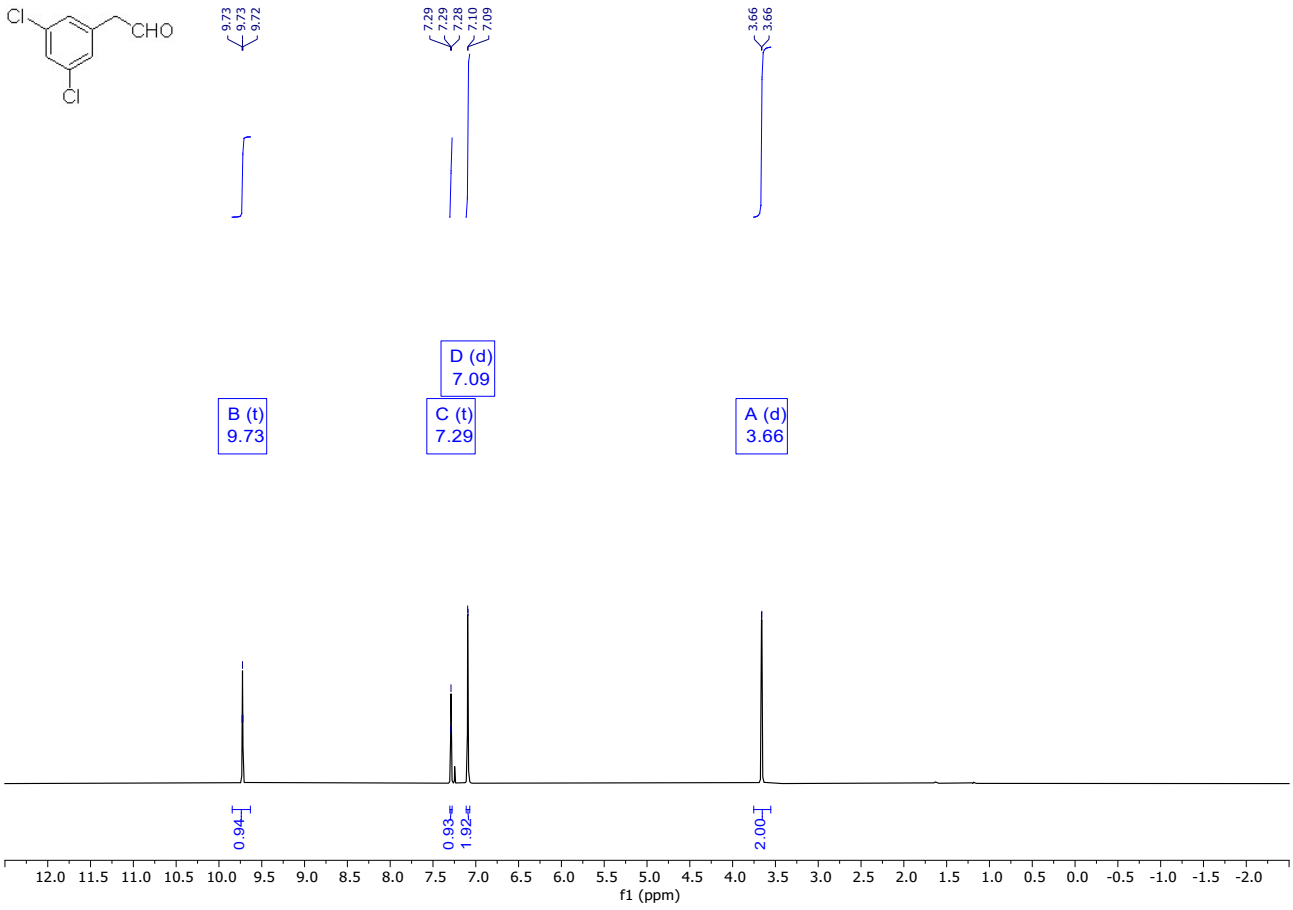
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.70 (q, J = 1.3 Hz, 1H), 7.46 – 7.33 (m, 1H), 7.30 – 7.09 (m, 3H), 3.80 (d, J = 1.7 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 198.46, 134.62, 131.89, 130.88, 129.77, 129.21, 127.35, 48.31.

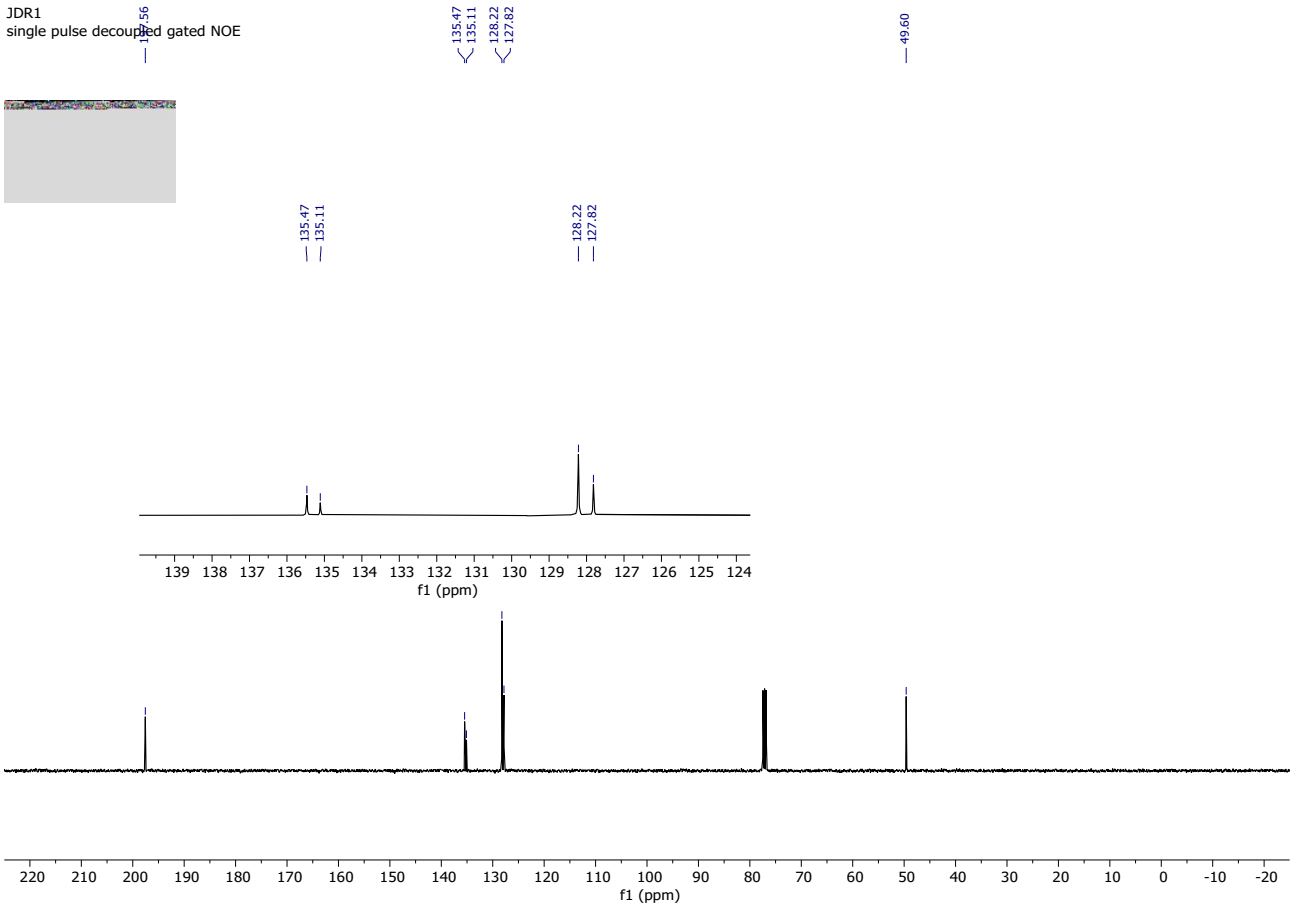



JDR1
single pulse decoupled gated NOE
200.46
134.62
131.89
130.88
129.77
129.21
127.35
48.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(3,5-dichlorophenyl)acetaldehyde (4p). This compound was isolated using flash column chromatography and gave 4p as a yellow solid. Spectral data is in accordance with the literature.[9]

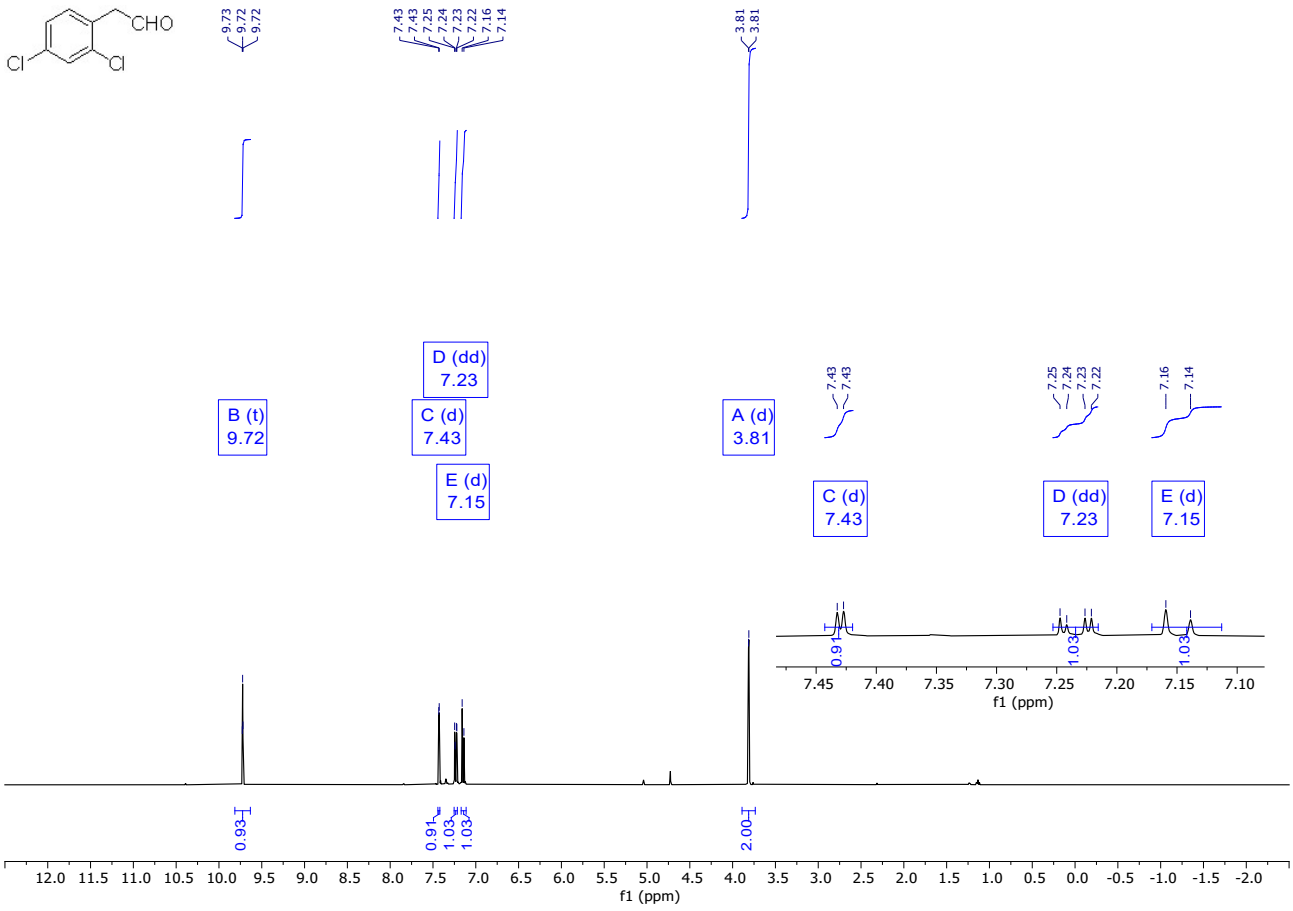
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.73 (t, J = 1.9 Hz, 1H), 7.29 (t, J = 1.9 Hz, 1H), 7.09 (d, J = 1.9 Hz, 2H), 3.66 (d, J = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.56, 135.47, 135.11, 128.22, 127.82, 49.60.

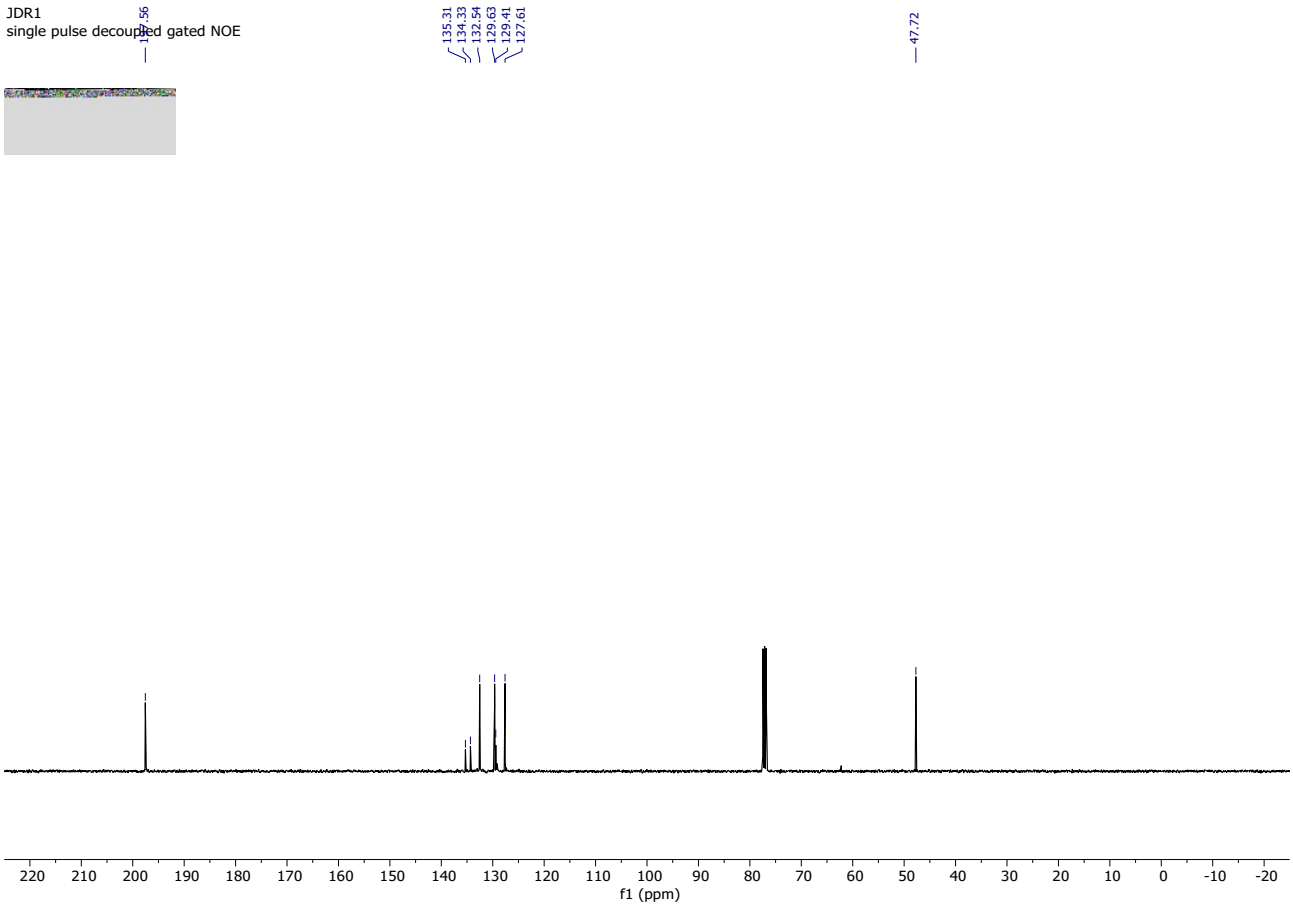



JDR1
single pulse decoupled gated NOE
135.47
135.11
128.22
127.82
49.60
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(2,4-dichlorophenyl)acetaldehyde (4q). This compound was isolated using flash column chromatography and gave 4q as a yellow solid.

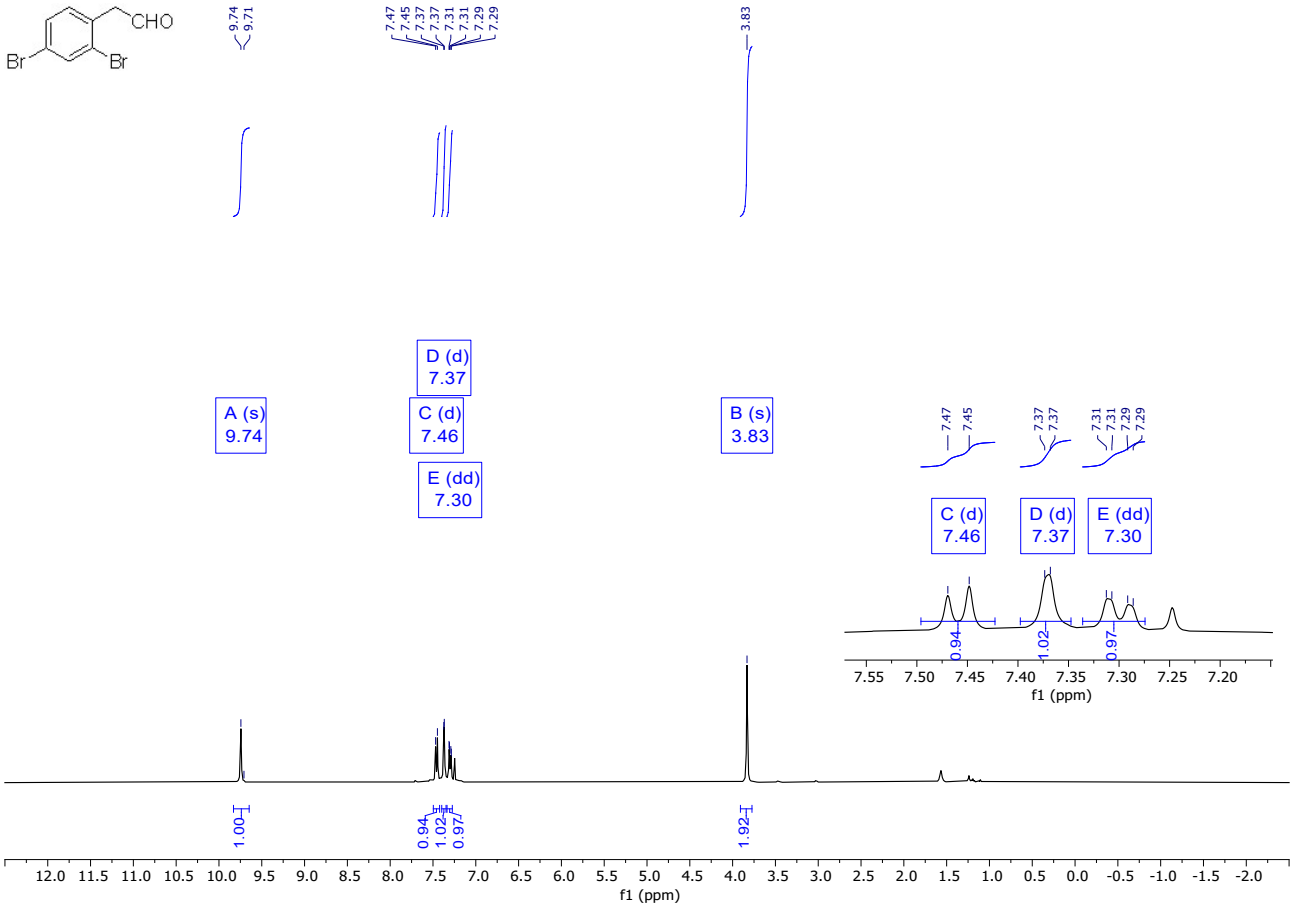
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.72 (t, J = 1.6 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 7.23 (dd, J = 8.2, 2.2 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 3.81 (d, J = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.56, 135.31, 134.33, 132.54, 129.63, 129.41, 127.61, 47.72. HRMS (EI): calcd for $C_8H_7Cl_2O$: 188.9874 ($[M + H]^+$), found: 188.9878.

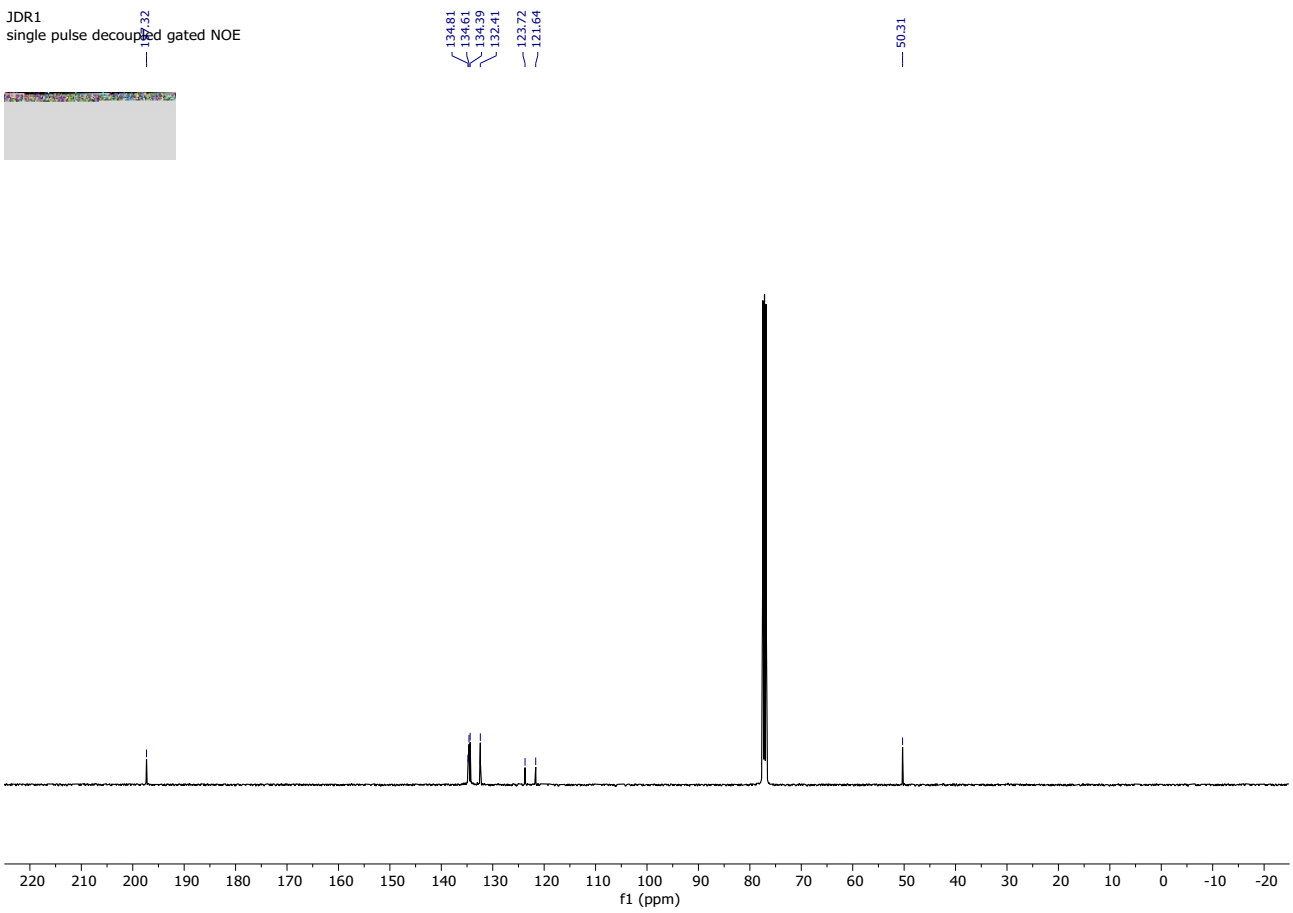



JDR1
single pulse decoupled gated NOE
197.56
135.31
134.33
132.54
129.63
129.41
127.61
47.72
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(2,4-bromophenyl)acetaldehyde (4r). This compound was isolated using flash column chromatography and gave 4r as a yellow solid.

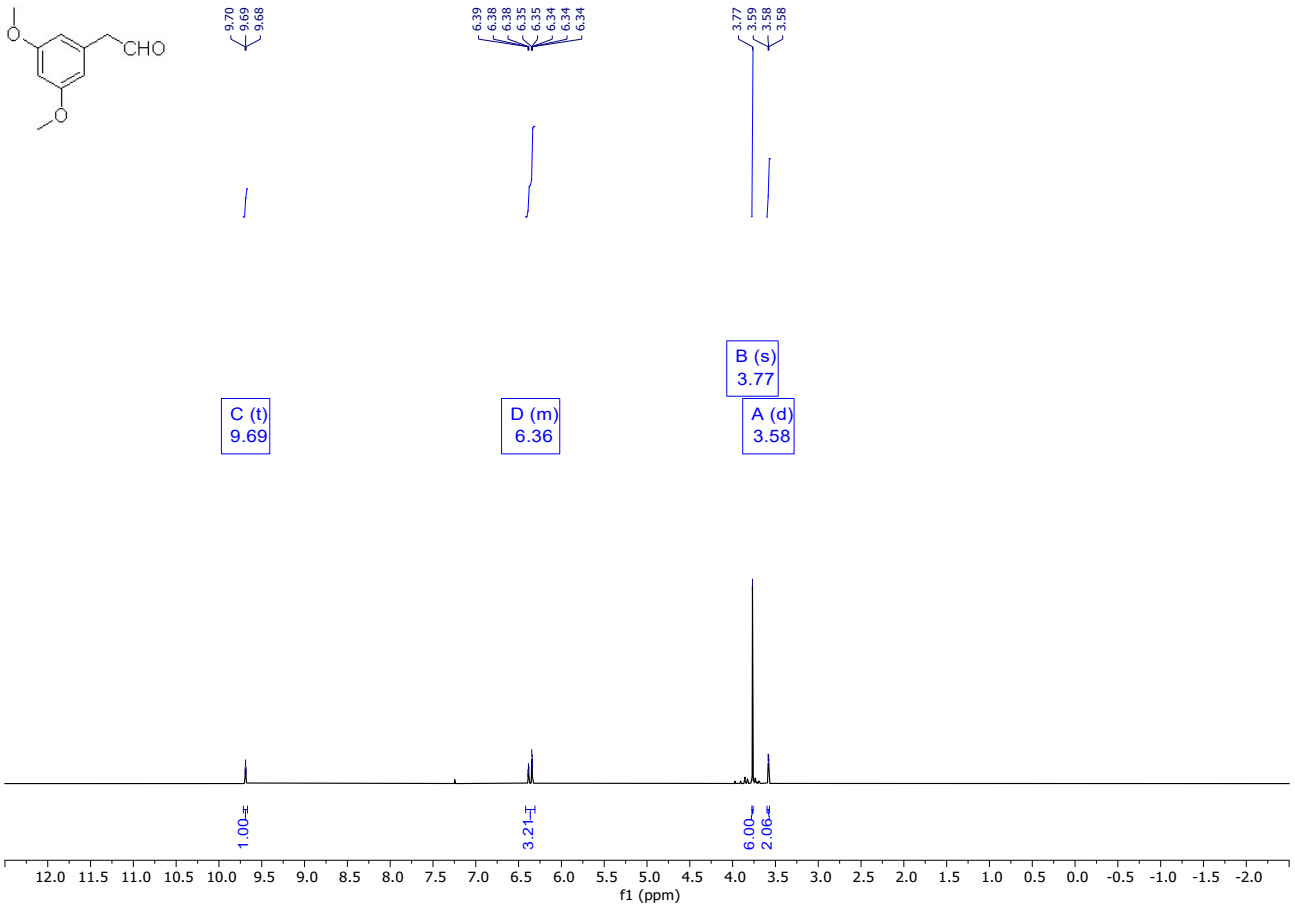
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.74 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.32, 134.81, 134.61, 134.39, 132.41, 123.72, 121.64, 50.31. $C_8H_7Br_2O$: 278.8843 ($[M + H]^+$), found: 278.8848.

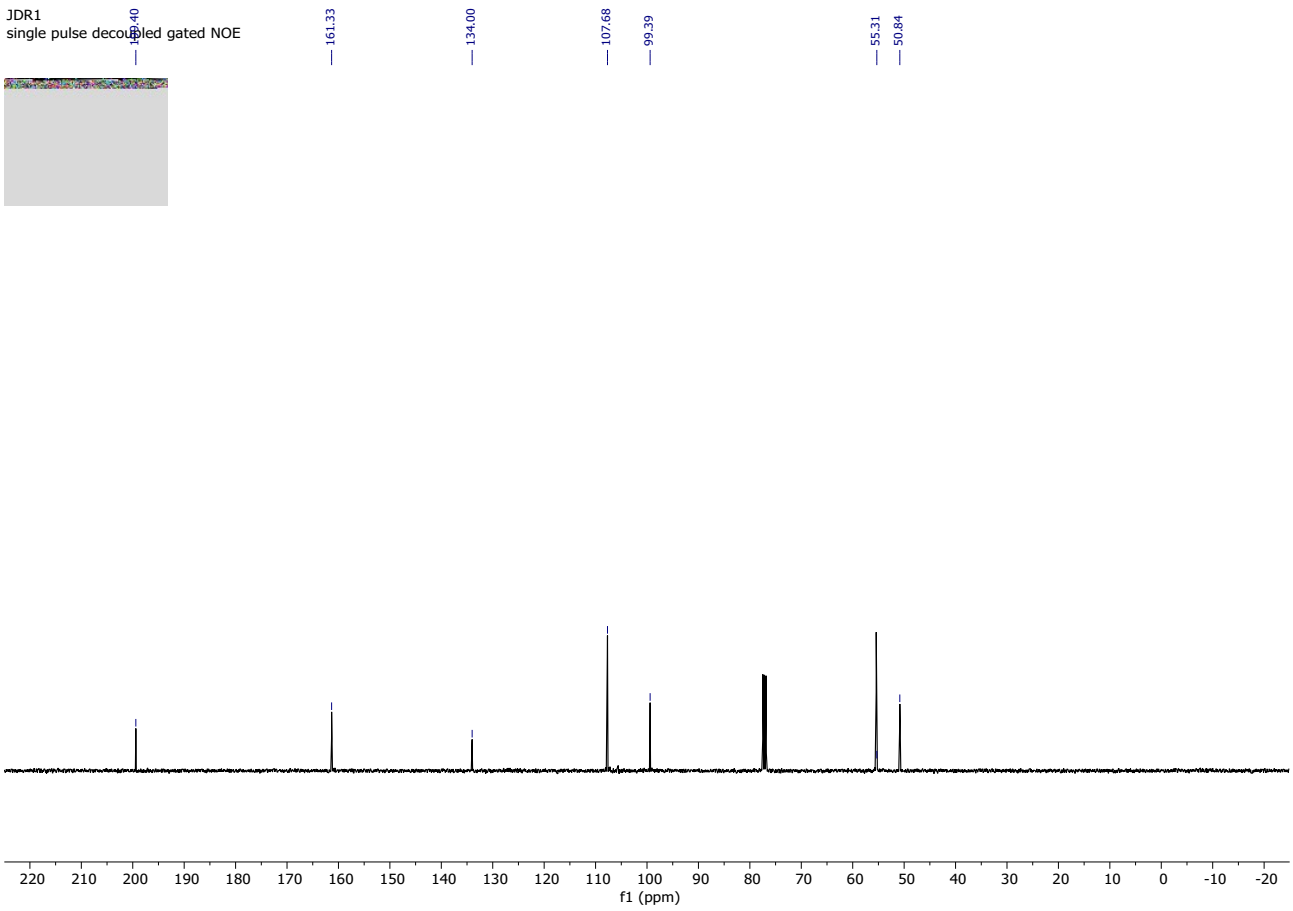



JDR1
single pulse decoupled gated NOE
197.32
134.81
134.61
134.39
132.41
123.72
121.64
50.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(3,5-dimethoxyphenyl)acetaldehyde (4s). This compound was isolated using flash column chromatography and gave 4s as a yellow solid. Spectral data is in accordance with the literature. [13]

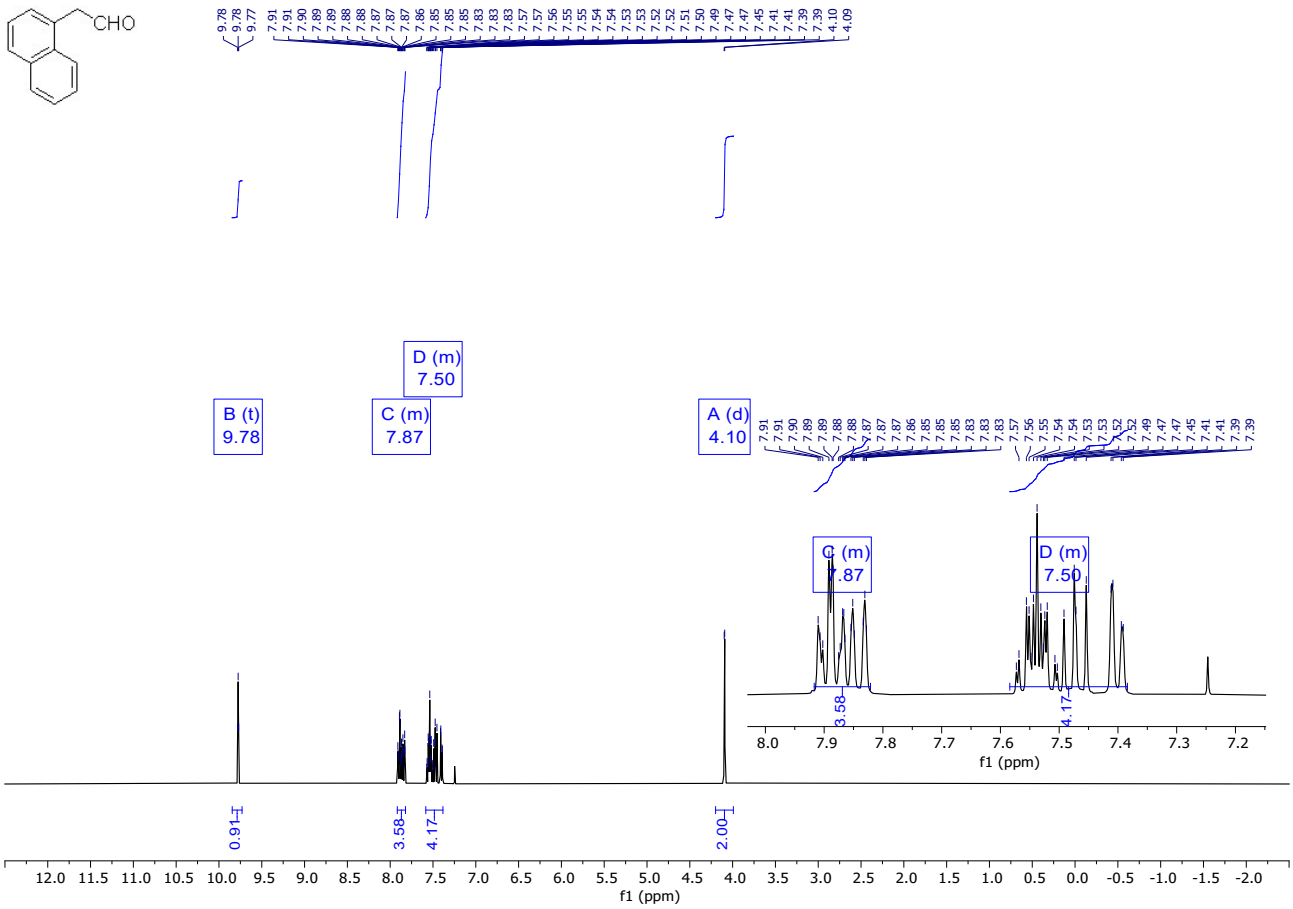
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.69 (t, J = 2.4 Hz, 1H), 6.42 – 6.31 (m, 3H), 3.77 (s, 6H), 3.58 (d, J = 2.5 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.40, 161.33, 134.00, 107.68, 99.39, 55.31, 50.84.

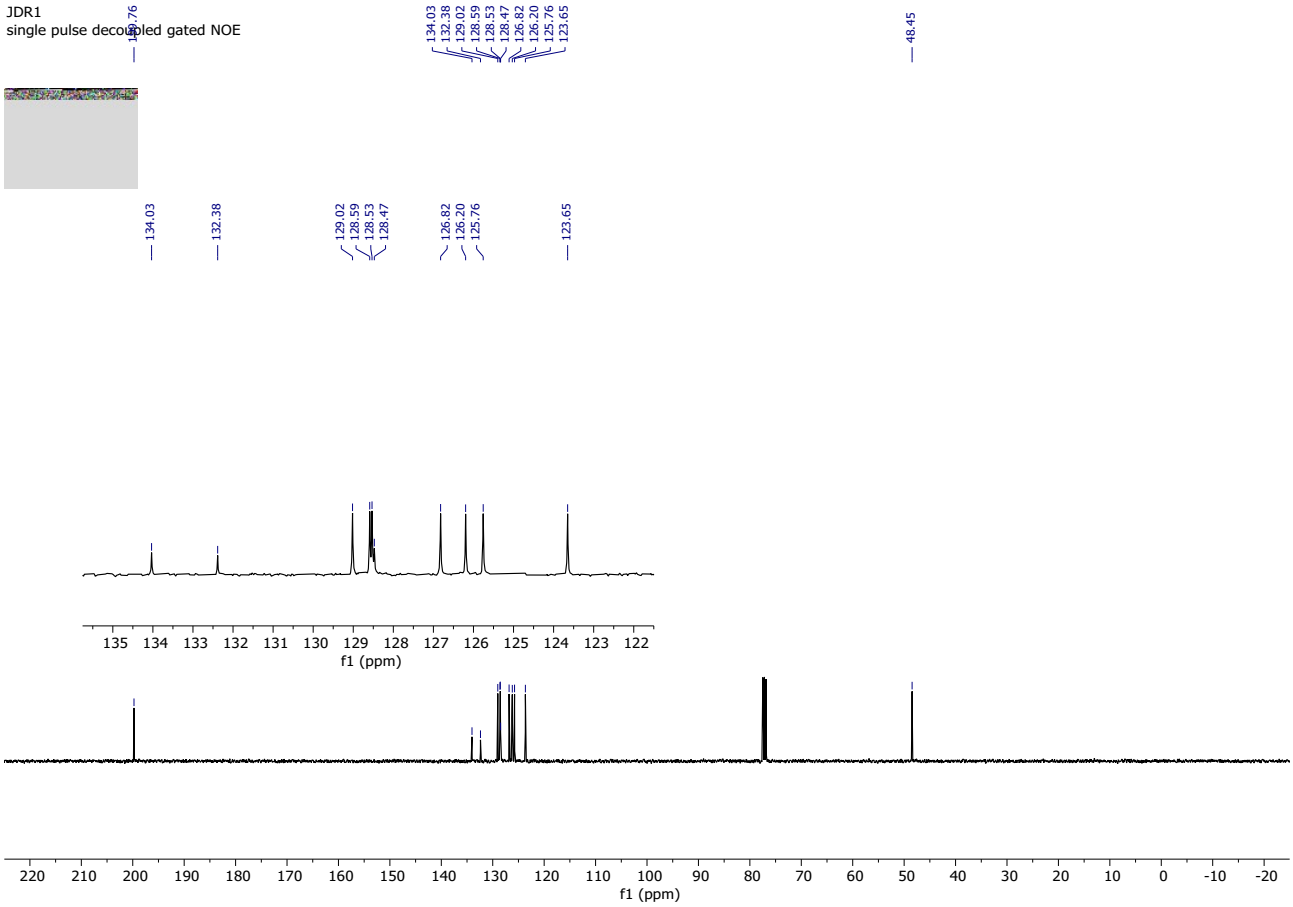



JDR1
single pulse decoupled gated NOE
200.40
161.33
134.00
107.68
99.39
55.31
50.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(naphthalen-1-yl)acetaldehyde (4t). This compound was isolated using flash column chromatography and gave 4t as a yellow solid. Spectral data is in accordance with the literature. [9]

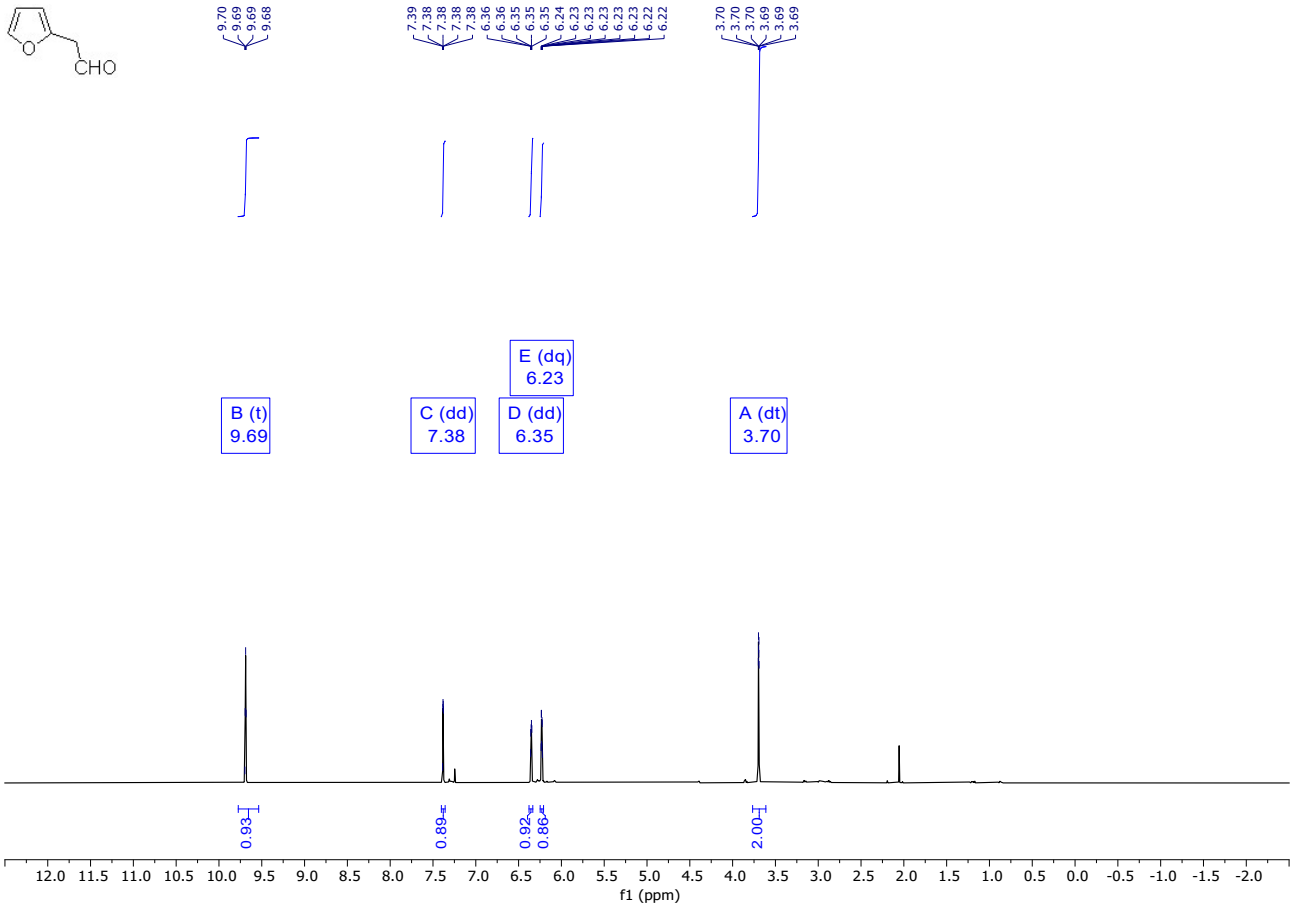
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.78 (t, J = 2.4 Hz, 1H), 7.92 – 7.82 (m, 4H), 7.58 – 7.38 (m, 4H), 4.10 (d, J = 2.5 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 199.76, 134.03, 132.38, 129.02, 128.59, 128.53, 128.47, 126.82, 126.20, 125.76, 123.65, 48.45.

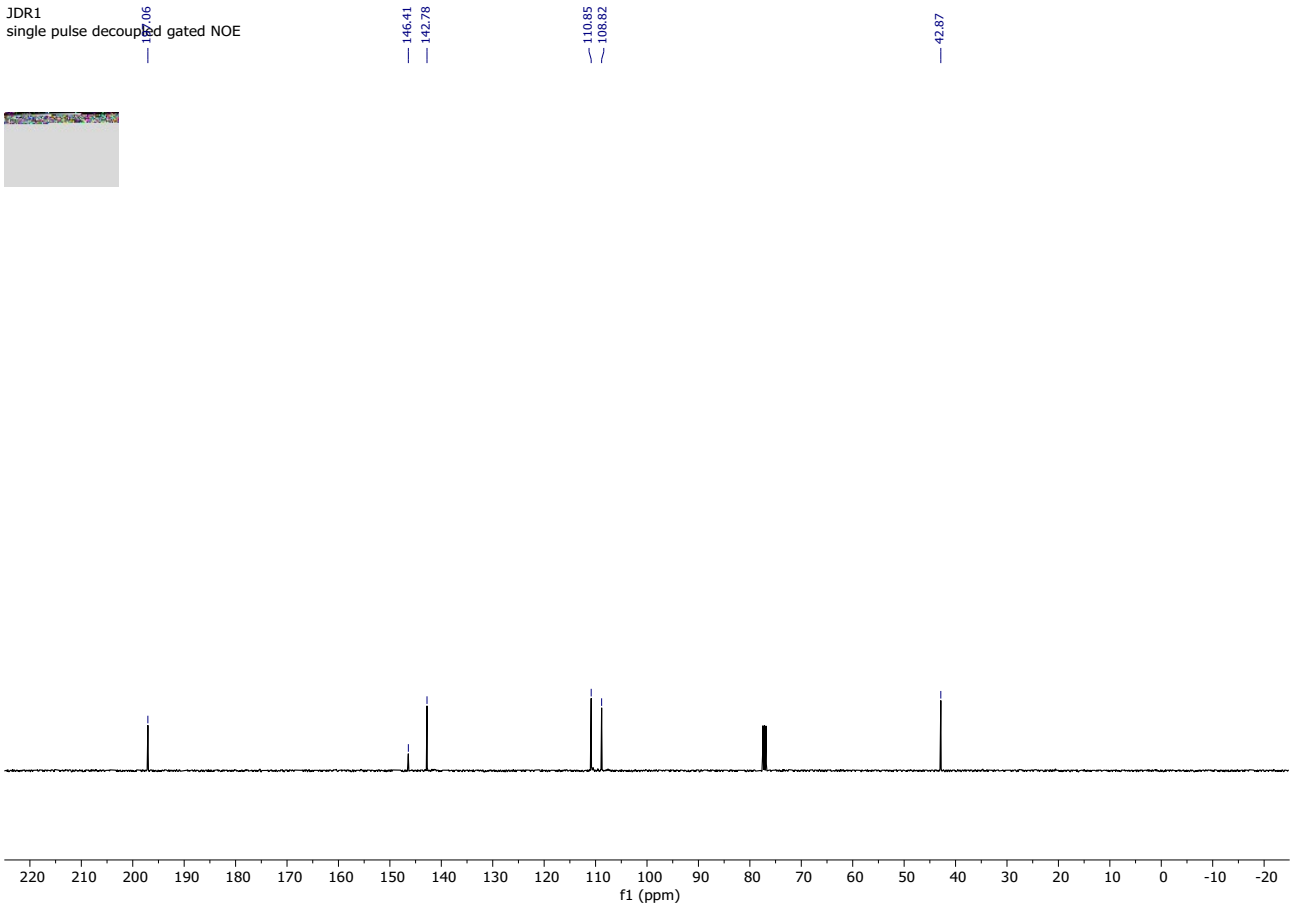



JDR1
single pulse decoupled gated NOE
200.76
134.03
132.38
129.02
128.59
128.53
128.47
126.82
126.20
125.76
123.65
48.45
135 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

2-(furan-2-yl)acetaldehyde (4u). This compound was isolated using flash column chromatography and gave 4u as a yellow oil. This compound is extremely light and temperature sensitive and all manipulations and analysis was performed quickly to avoid degradation.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.69 (t, J = 2.1 Hz, 1H), 7.38 (dd, J = 1.9, 0.8 Hz, 1H), 6.35 (dd, J = 3.3, 1.9 Hz, 1H), 6.23 (dq, J = 3.2, 0.8 Hz, 1H), 3.70 (dt, J = 2.1, 0.6 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 197.06, 146.41, 142.78, 110.85, 108.82, 42.87.




JDR1
single pulse decoupled gated NOE
197.06
146.41
142.78
110.85
108.82
42.87
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)

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