Supplementary Information

Cyclopentadienyl Nickel (II) N,C-Chelating Benzothiazolyl NHC Complexes: Synthesis, Characterization and Application in Catalytic C-C Bond Formation Reactions

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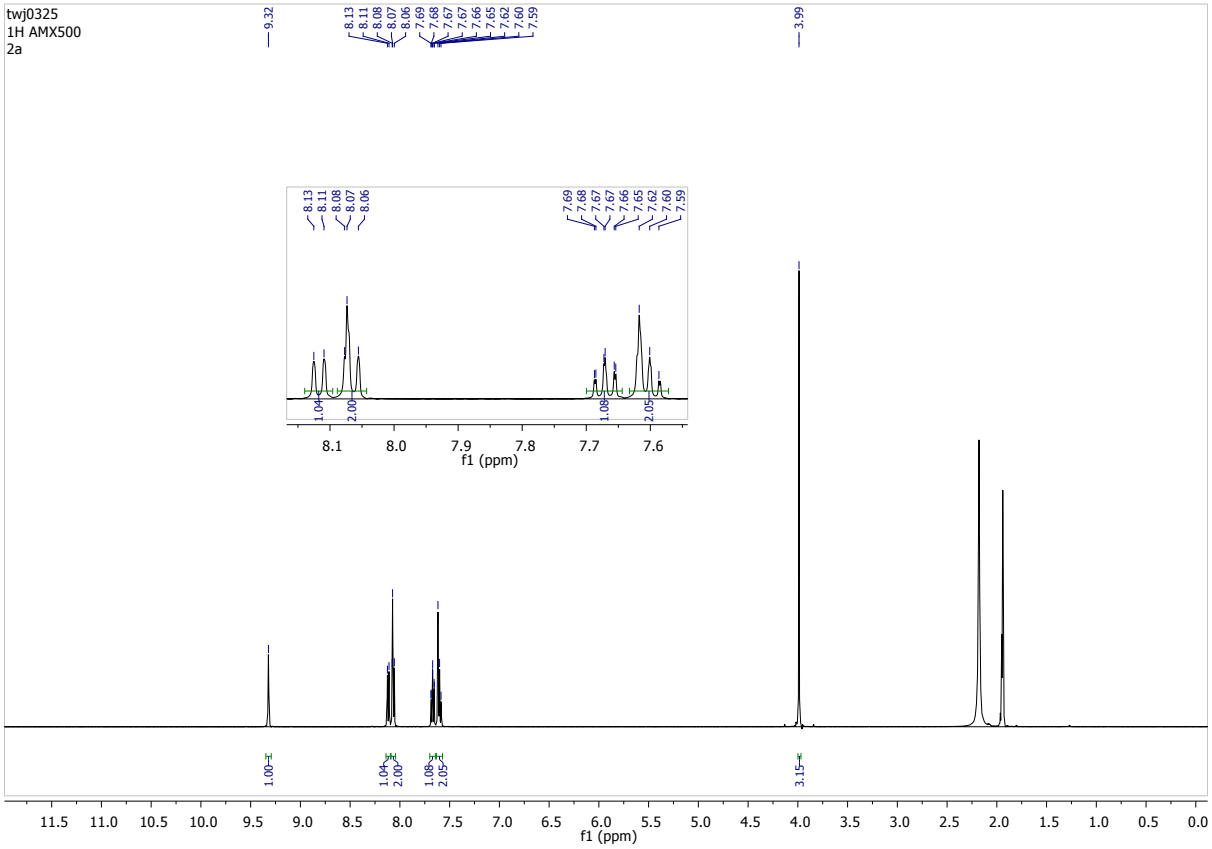
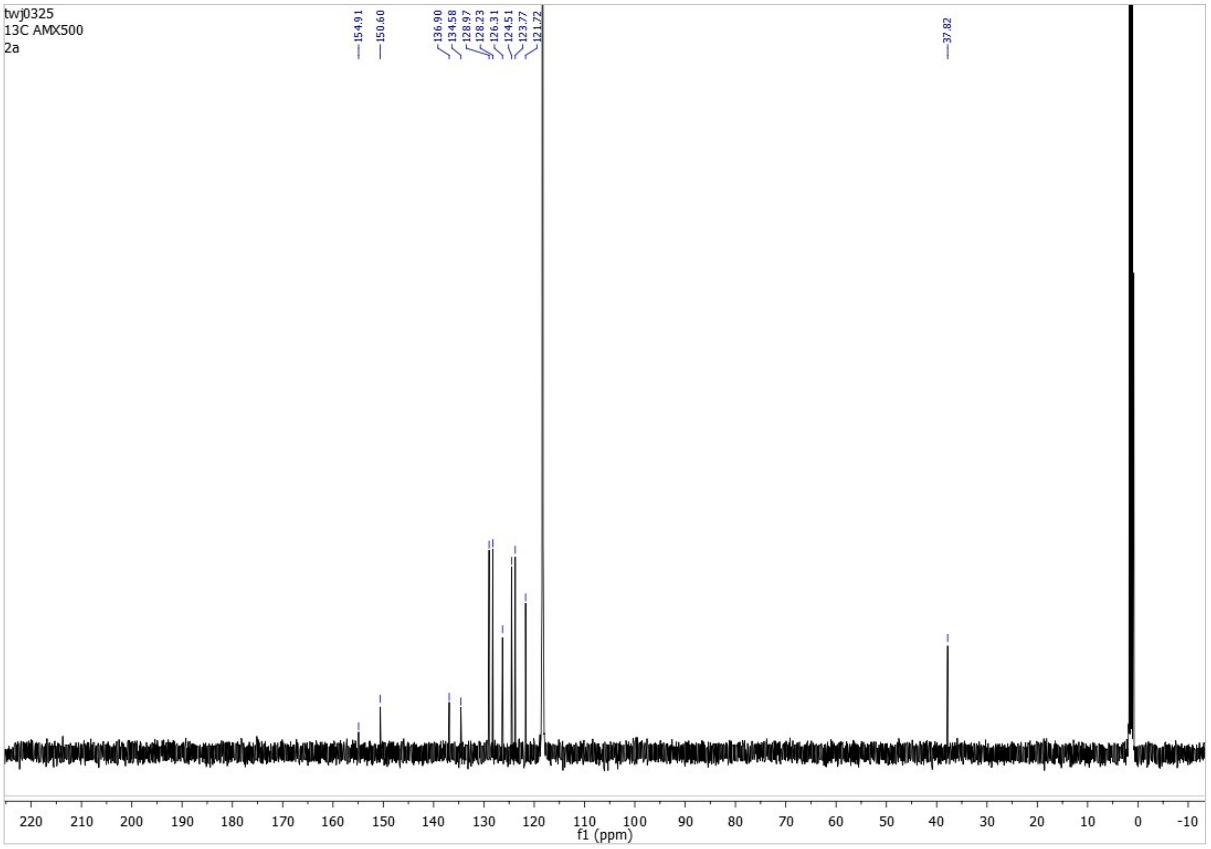
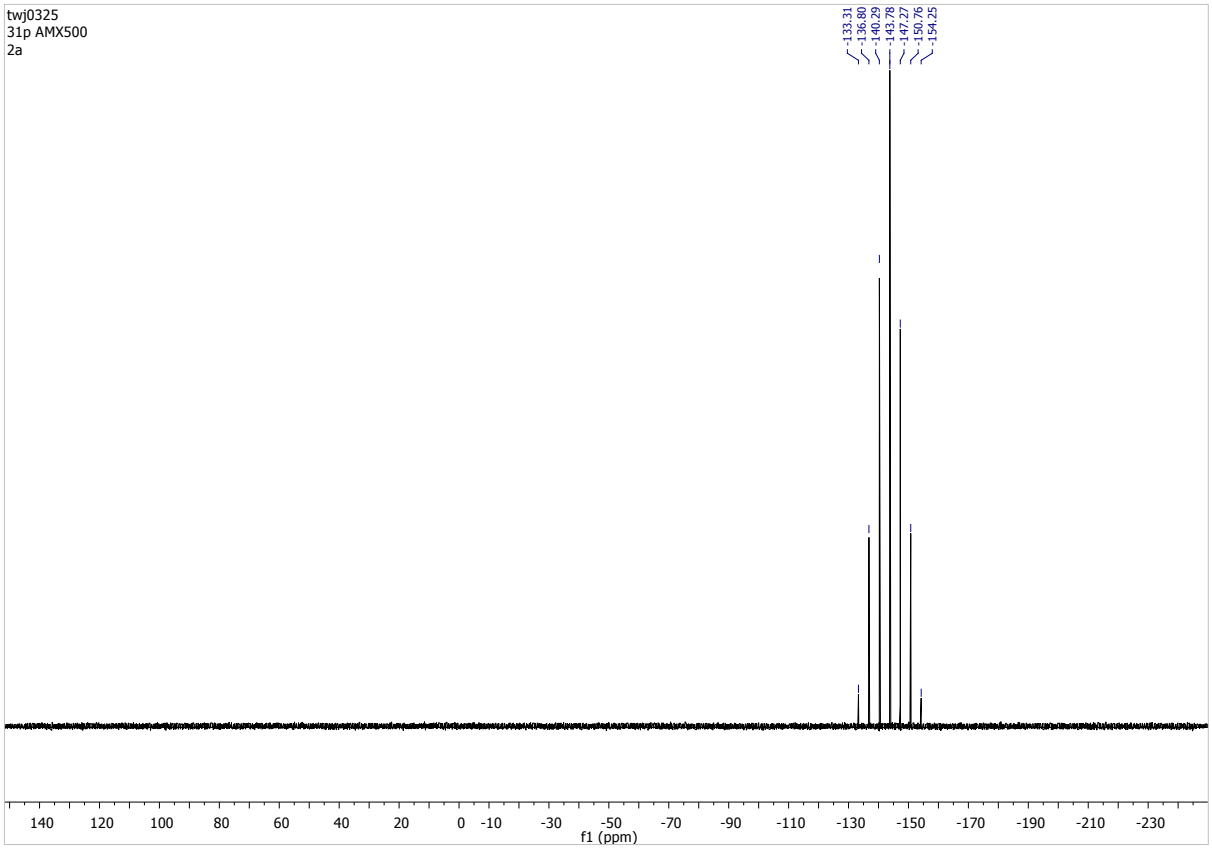
I. ^{1}H, ^{13}C and ^{31}P NMR spectra of ligands **2a-2c**

2a



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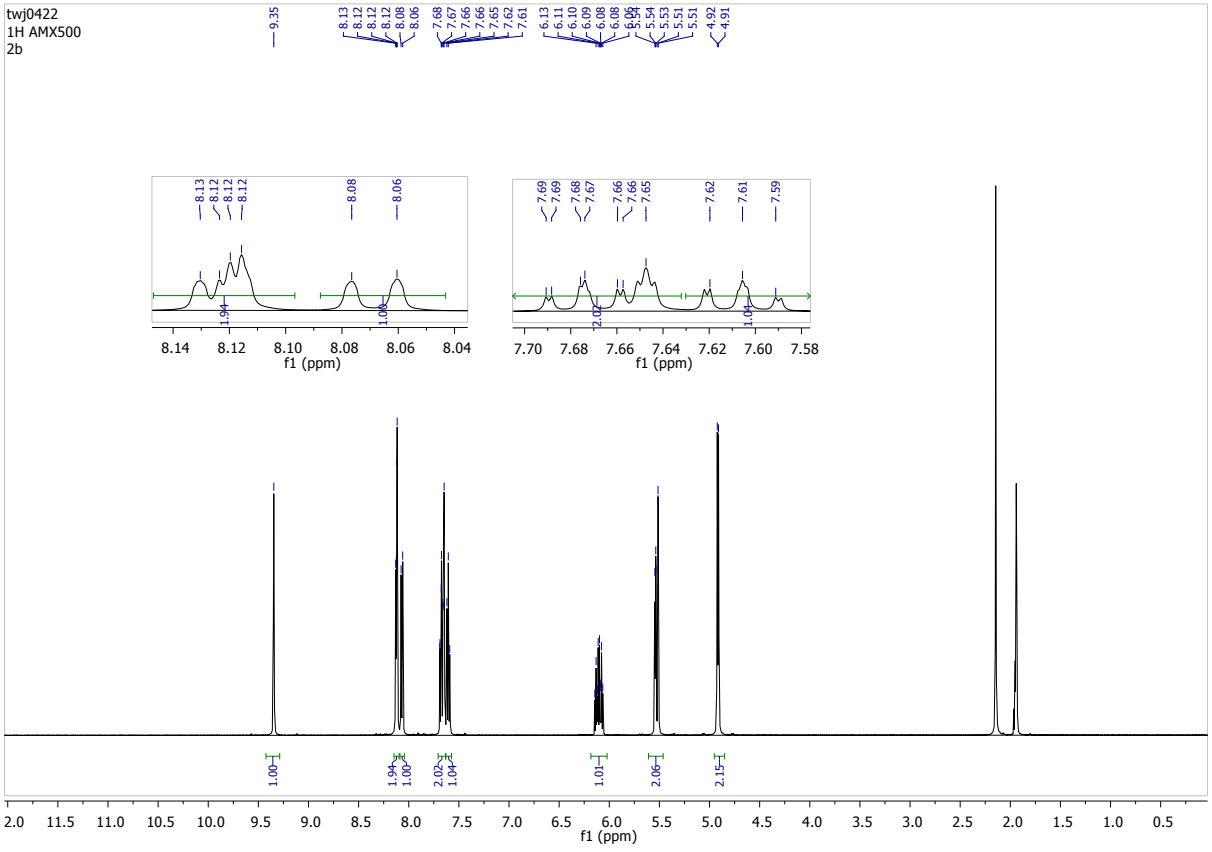
-150.76
-154.25
f1 (ppm)

2b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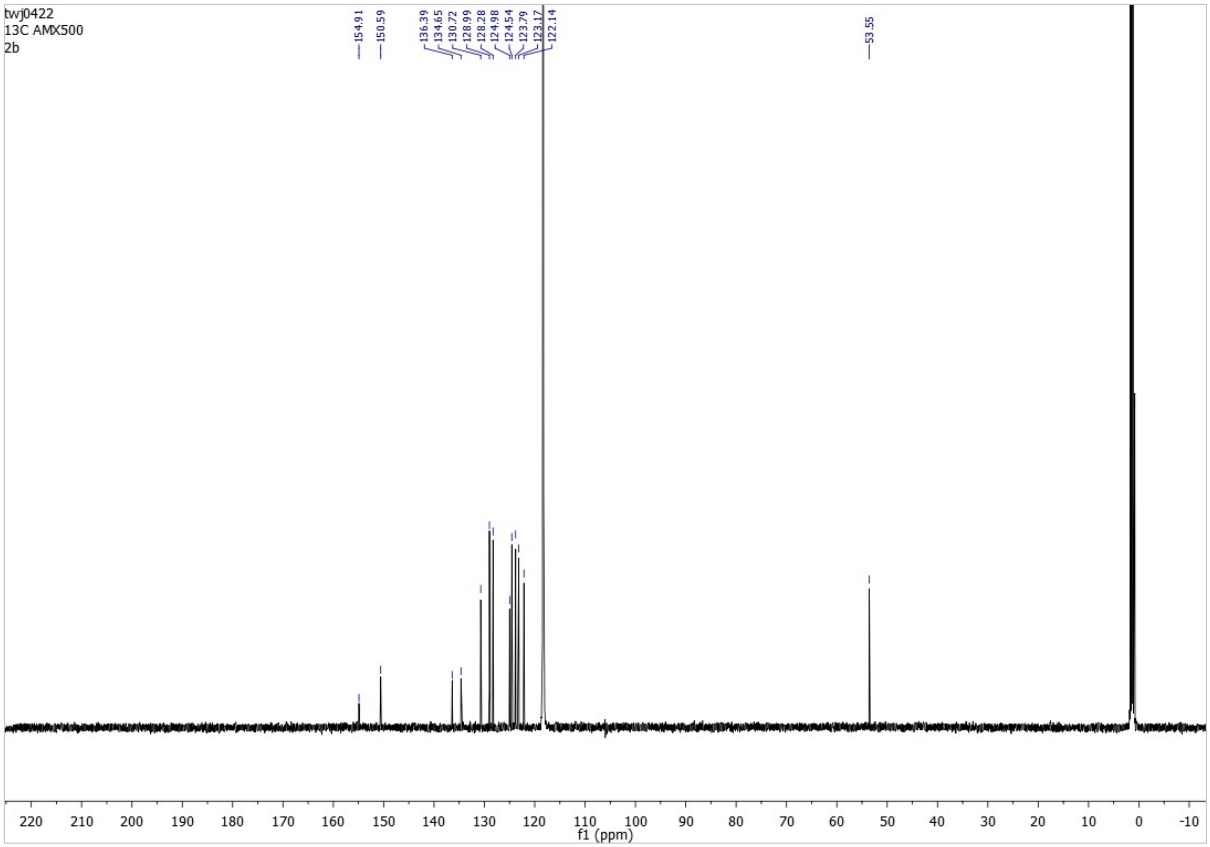
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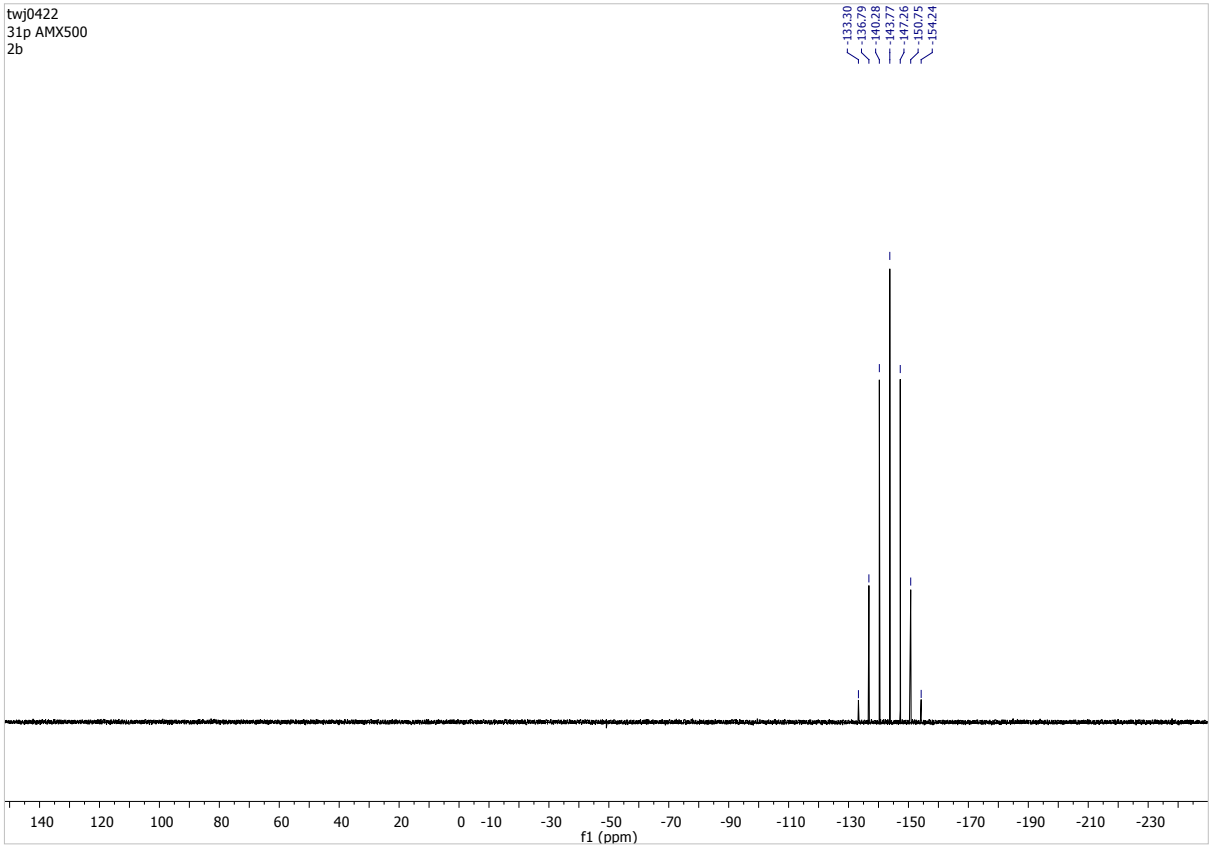
123.17
122.14
53.55
f1 (ppm)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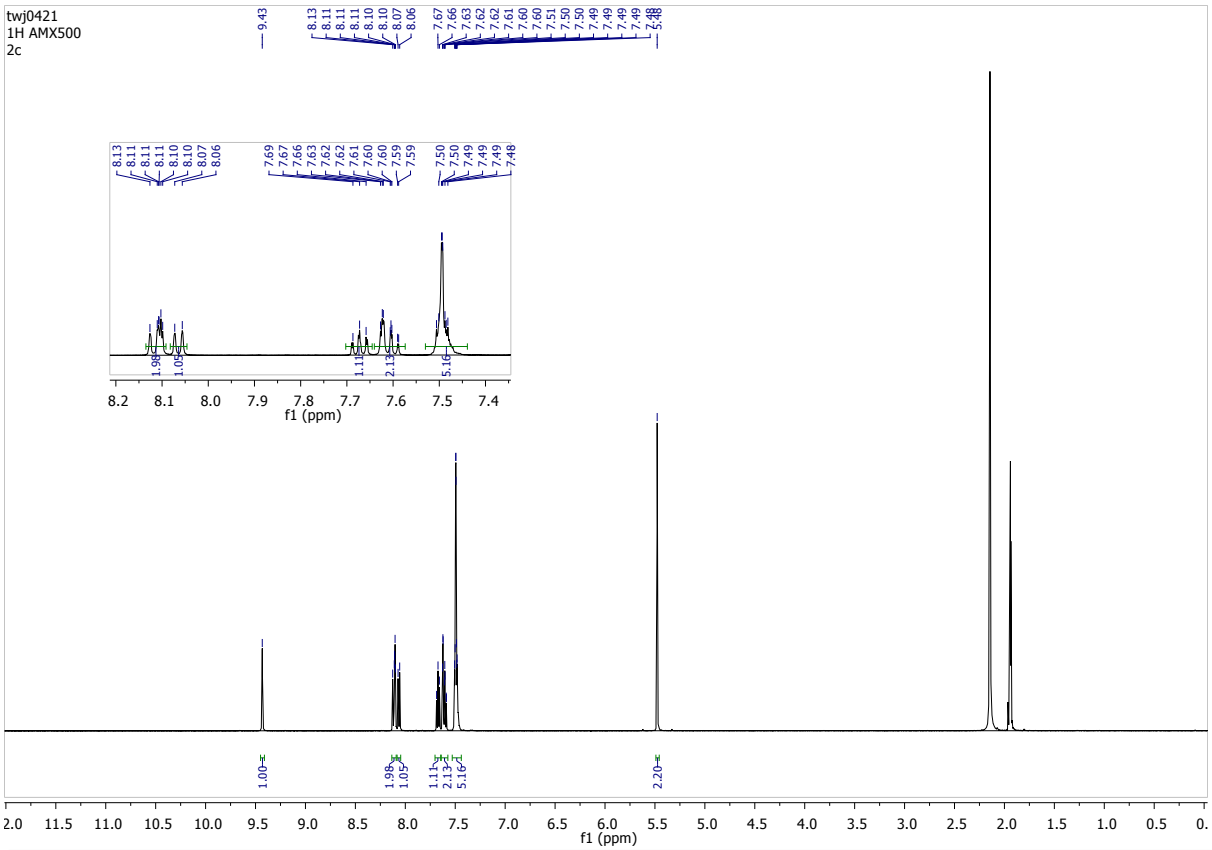
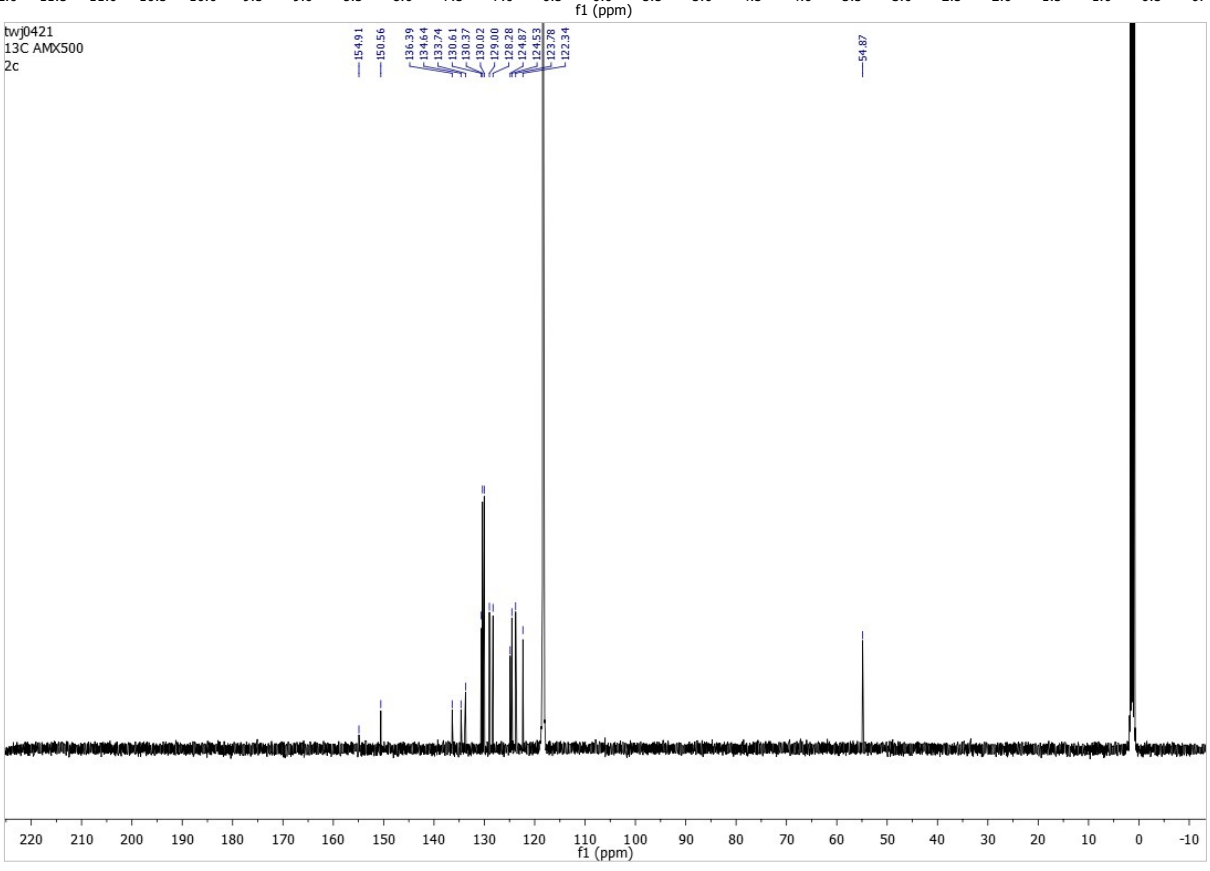
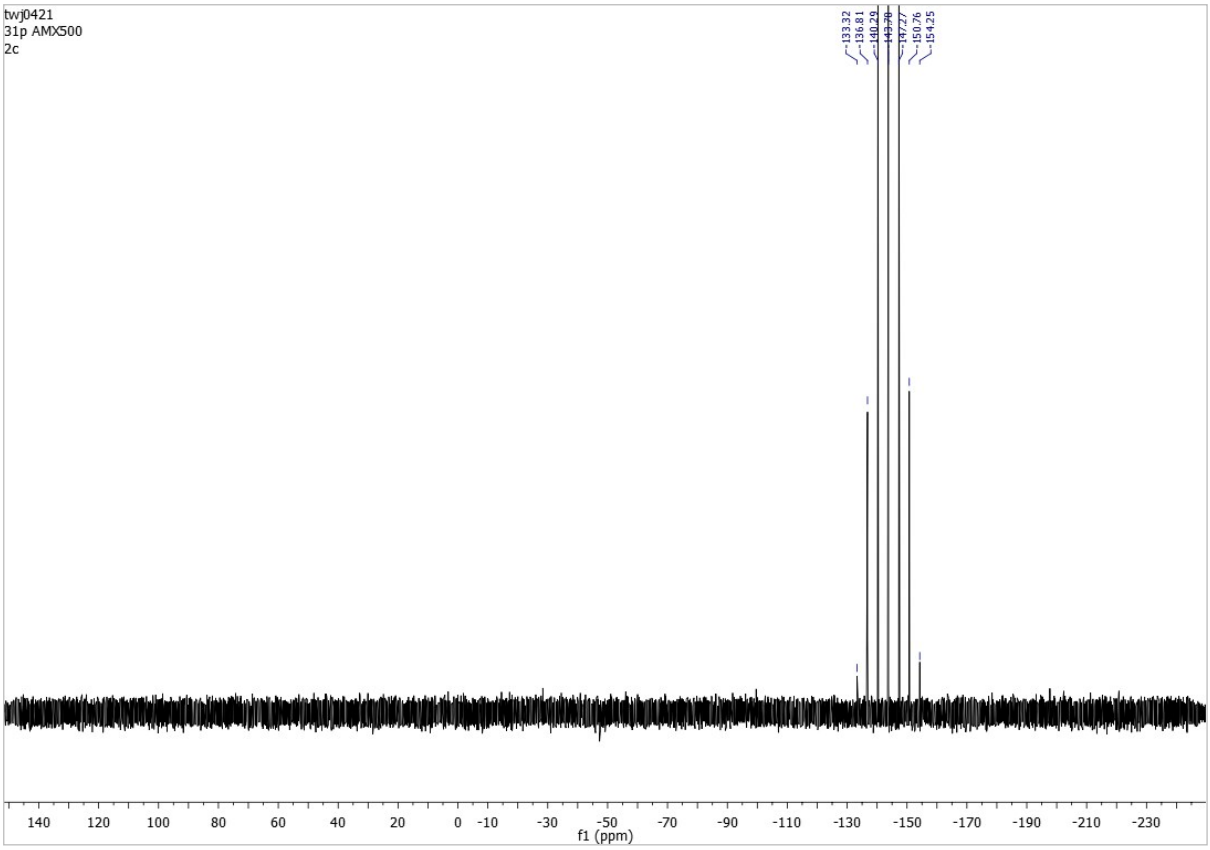
2c



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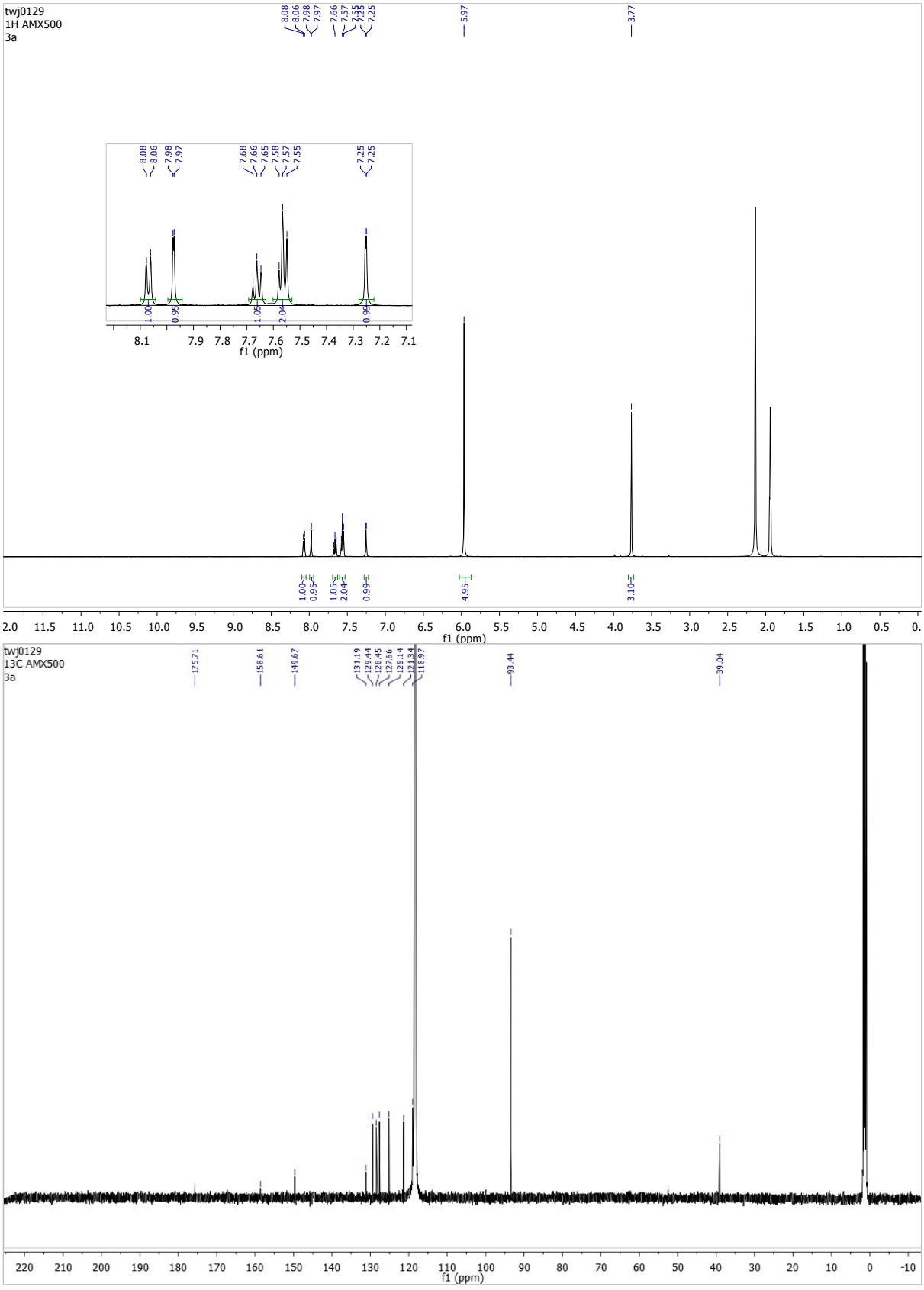
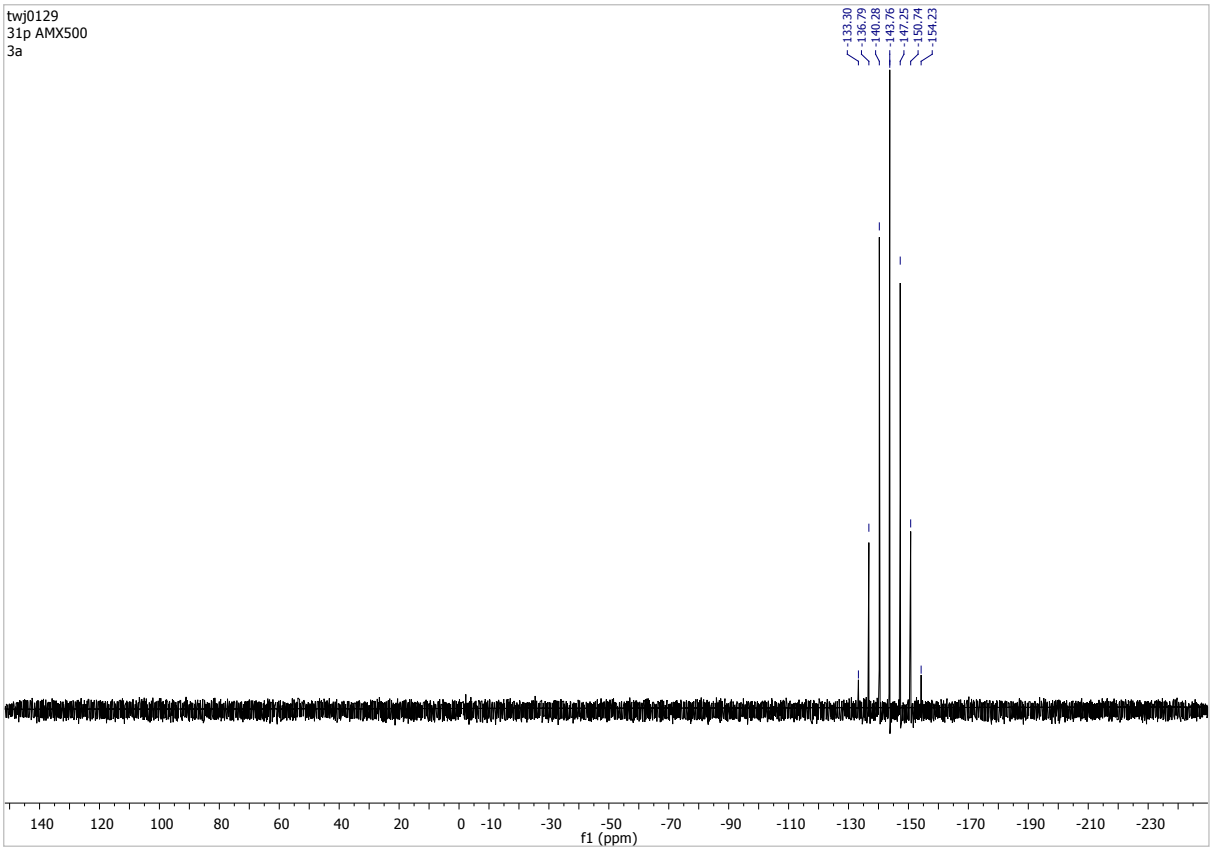
150.76
154.25
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

II. ^{1}H, ^{13}C and ^{31}P NMR spectra of complexes **3a-3c**

3a

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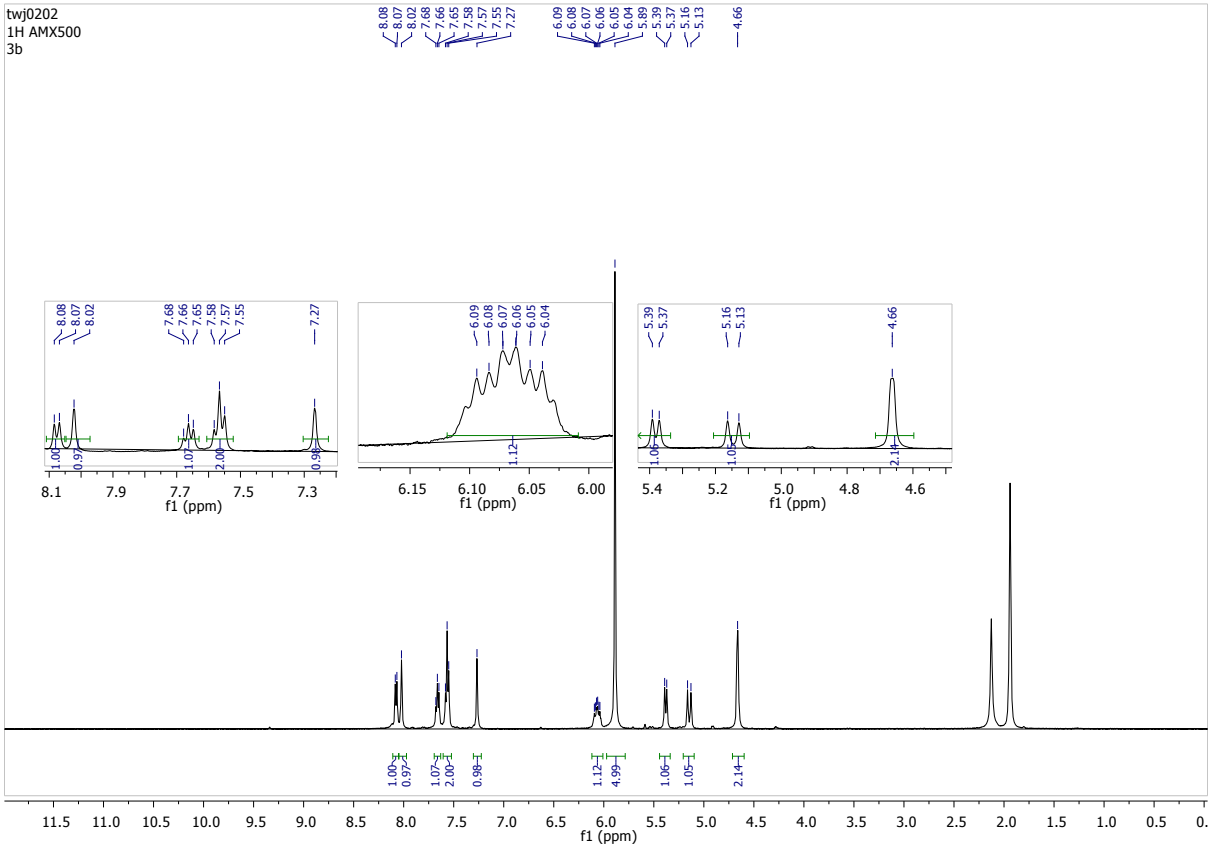
f1 (ppm)

3b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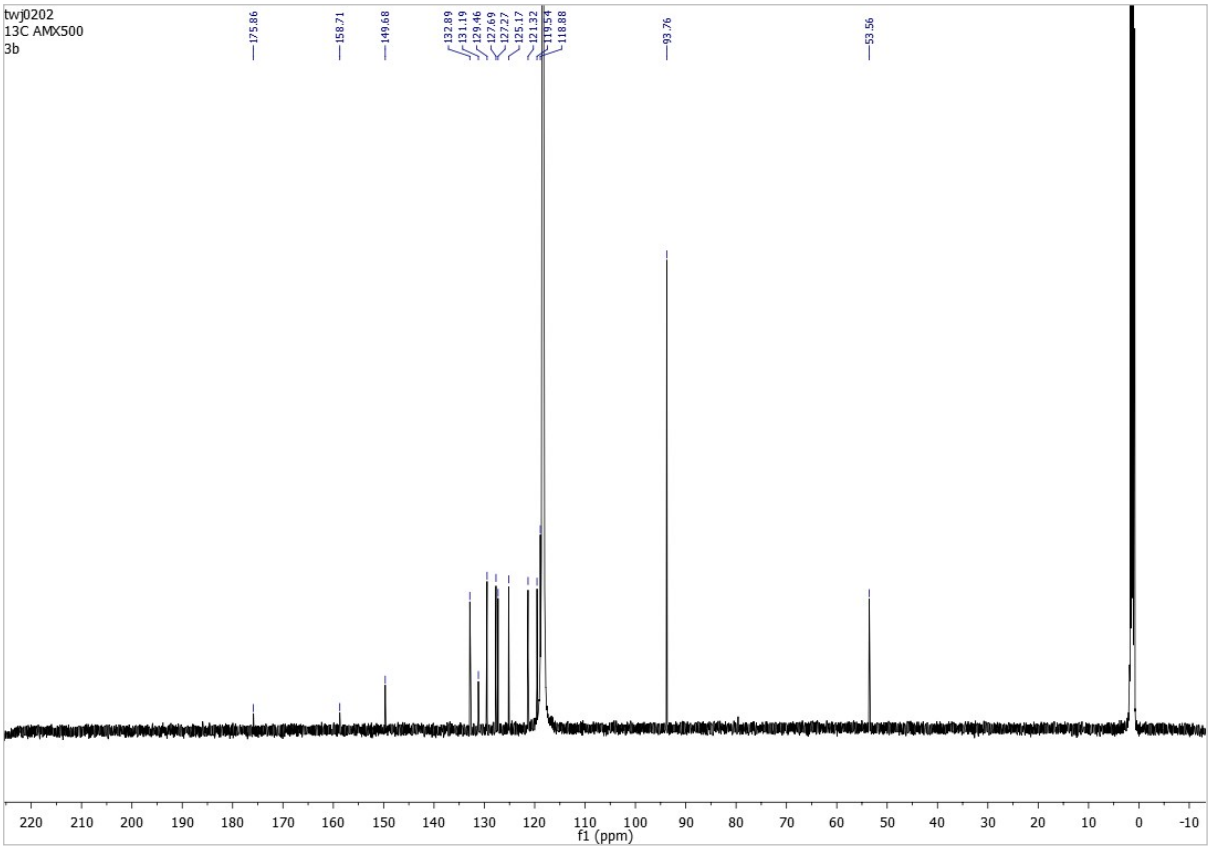
3b
f1 (ppm)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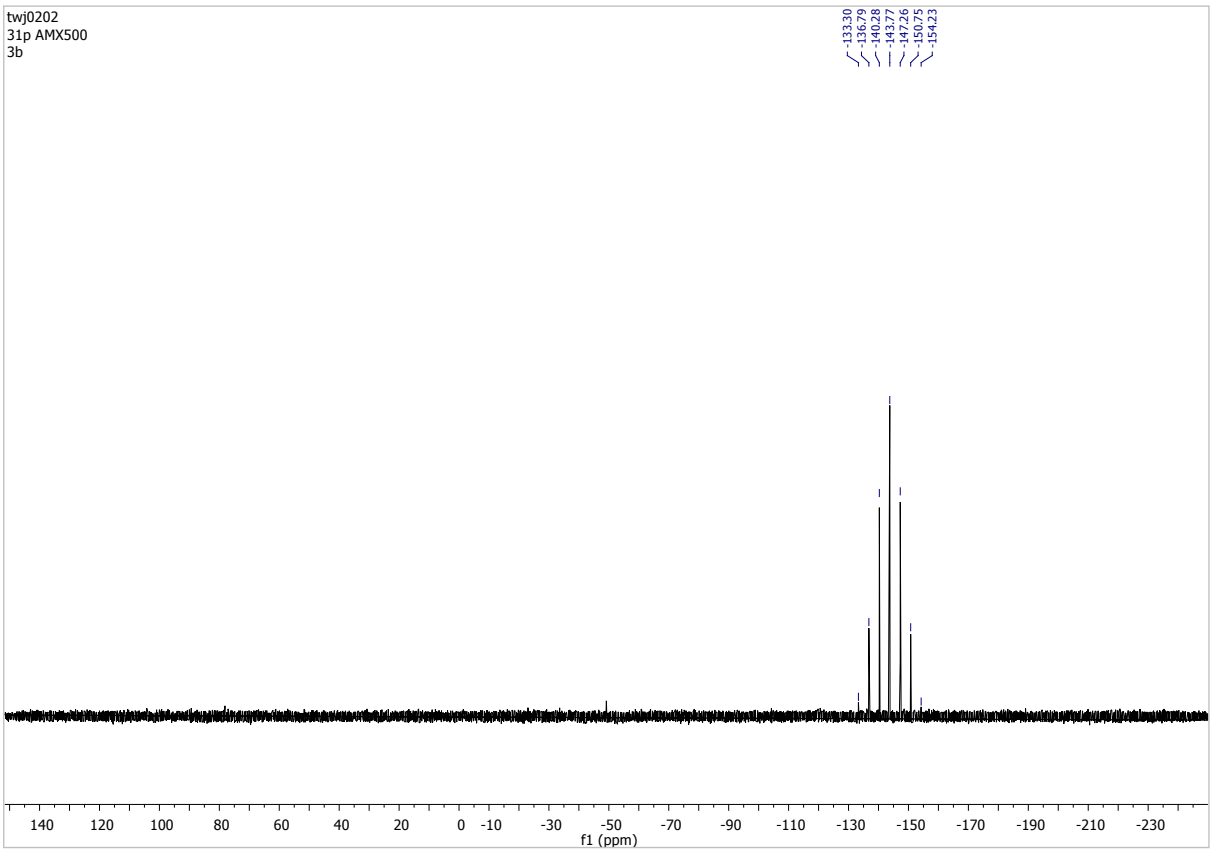
121.32
119.54
118.88
93.76
53.56
f1 (ppm)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31p AMX500
3b
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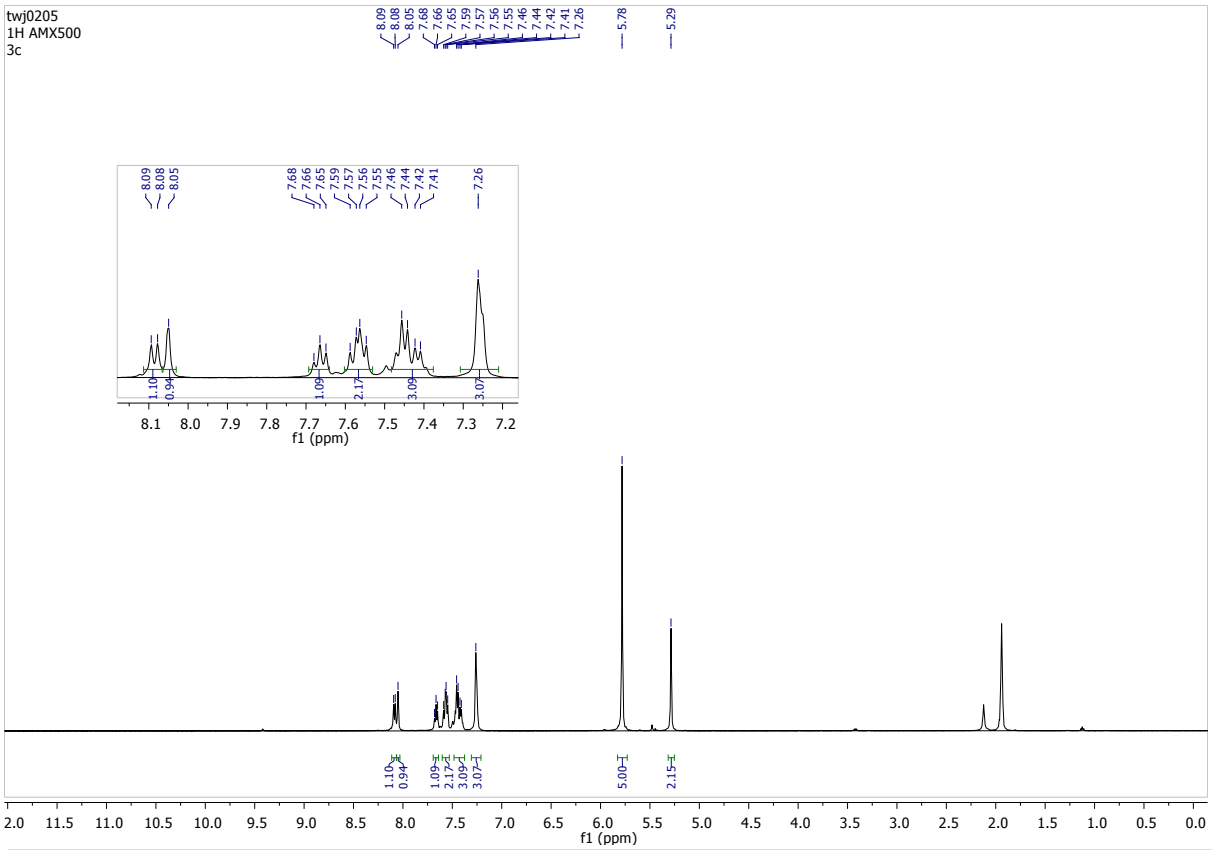
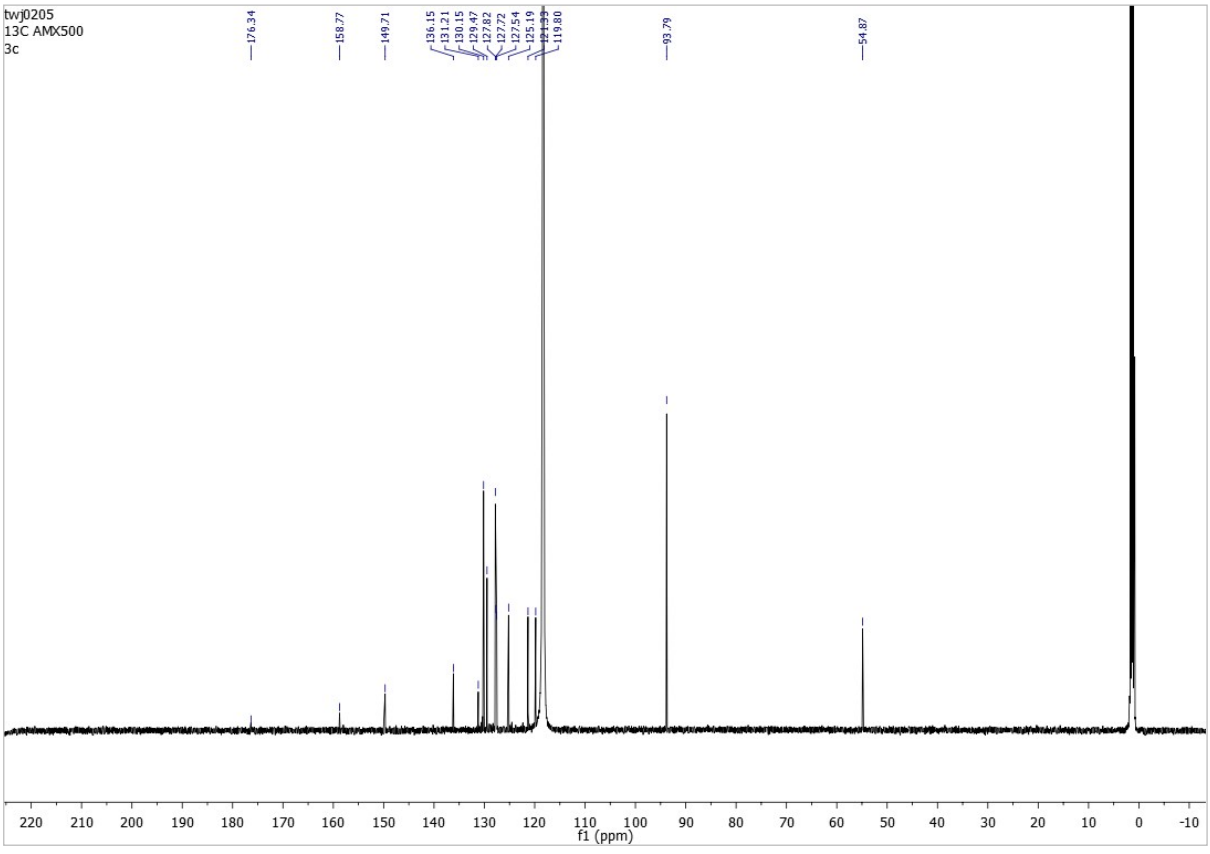
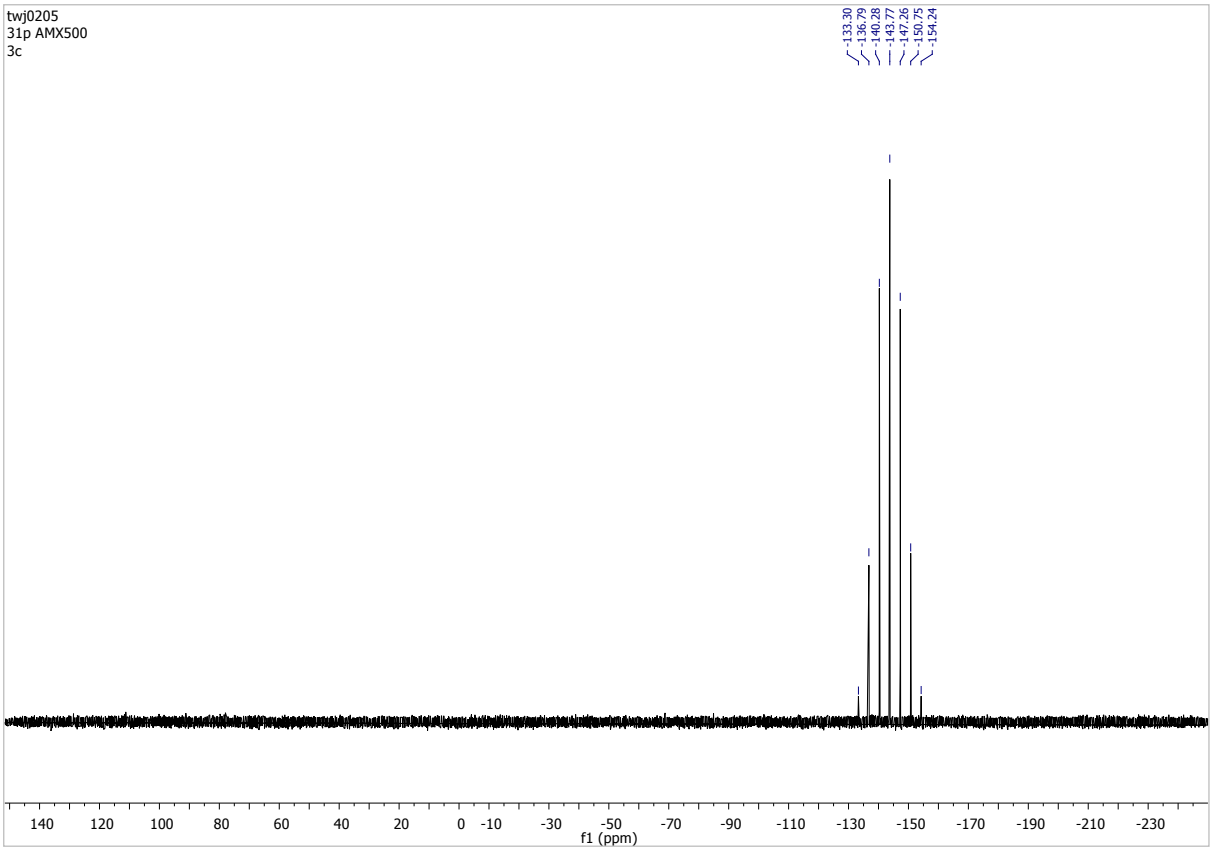
f1 (ppm)

3c



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154.24
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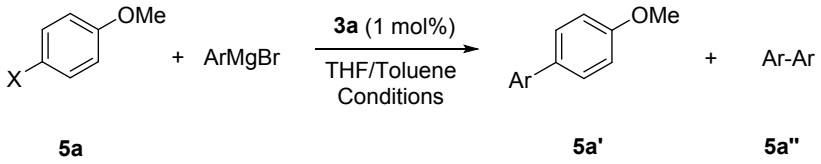
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

III. Results for catalytic C-C bond formation reactions

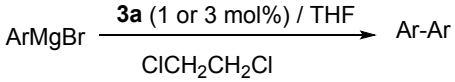
Table S1. Kumada-Tamo-Corriu reactions catalysed by **3a**[a]



Entry	X	Ar	Temperature	Time (h)	Yield of **5a'** [b] (%)	Yield of **5a''**[b,c] (%)
1	Br	Ph	r.t	1	40	50
2	Cl	Ph	100 °C	1	32	13
3	Br	*p*-Tolyl	r.t	1	22	44
4	Cl	*p*-Tolyl	100 °C	4	42	22
5	F	*p*-Tolyl	100 °C	4	19	13

[a]Reaction conditions: ArMgBr (0.6 mmol, 1.0 M in THF) was added dropwise within 30 min to the mixture of **3a** (0.005 mmol, 1 mol%) and 4-bromoanisole (0.5 mmol) in toluene (1 mL) and stirred at r.t. for 1 h. [b]Isolated yield. [c]Based on the amount of ArMgBr .

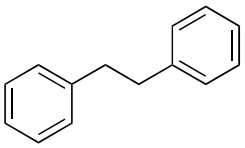
Table S2. Oxidative homo-coupling of aryl Grignard reagent catalysed by **3a**[a]



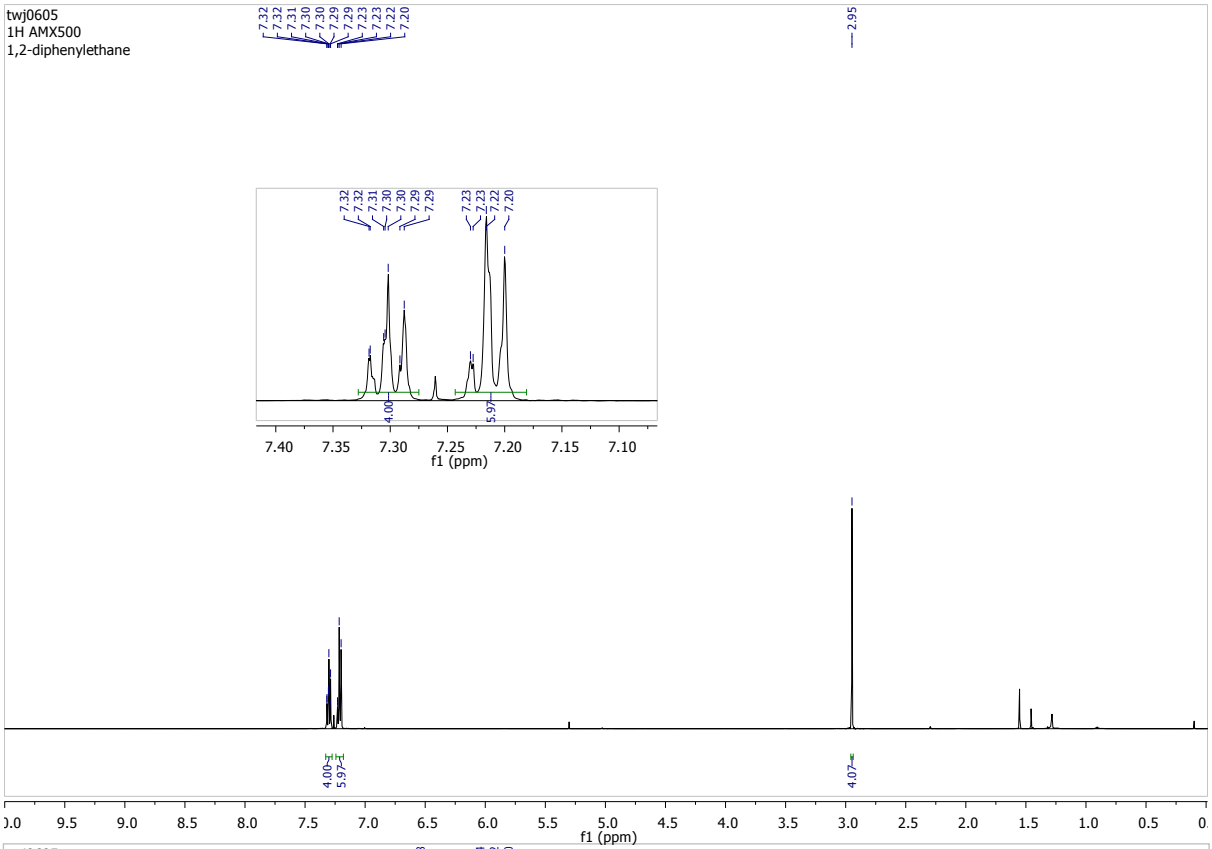
Entry	Ar	Catalyst loading/Temperature/Time	Yield[b] of Ar-Ar (%)
1	*p*-Tolyl	1 mol% / r.t / 1h	49
2	*p*-Tolyl	1 mol% / r.t / 4h	73
3	*p*-Tolyl	1 mol% / reflux / 1h	64
4	*p*-Tolyl	3 mol% / r.t / 1h	81
5	2-Mesityl	3 mol% / r.t / 1h	45

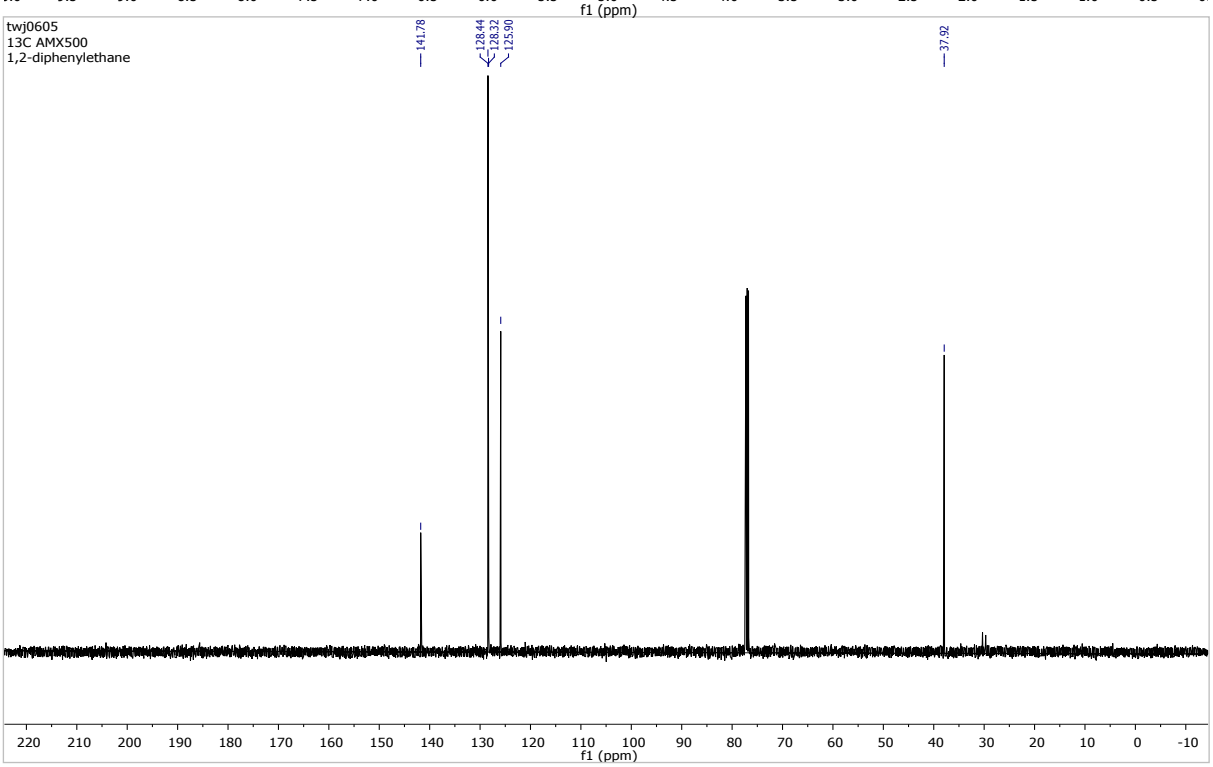
[a]Reaction conditions: ArMgBr (0.5 mmol, 1.0 M in THF) was added to the mixture of **3a** (1 or 3 mol%) and 1,2-dichloroethane (0.62 mmol) in THF (2 mL). [b]Isolated yield.

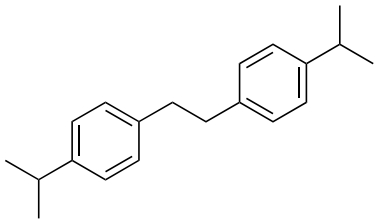
IV. ^{1}H, ^{13}C NMR data and spectra of the bibenzyl products



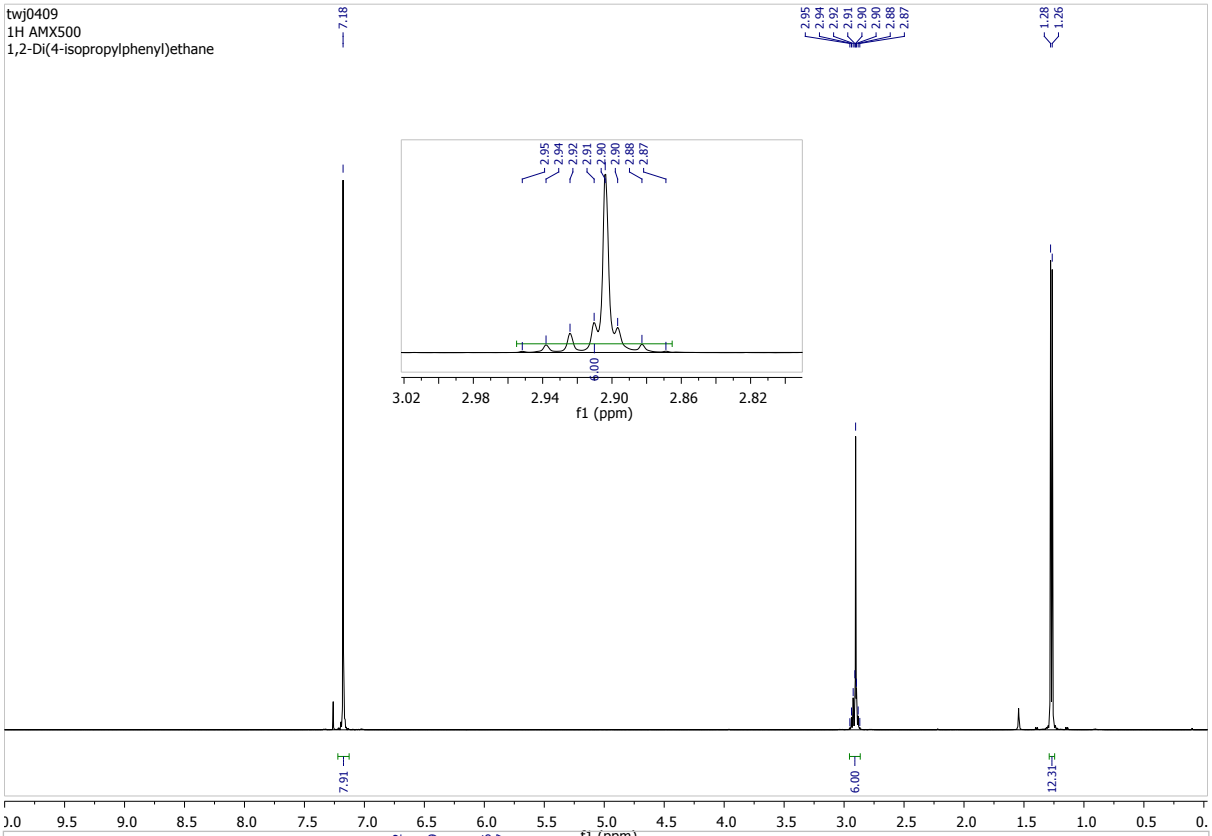
1,2-Diphenylethane[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.32-7.29 (m, 4H), 7.23-7.20 (m, 6H), 2.95 (s, 4H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 141.78, 128.44, 128.32, 125.90, 37.92.

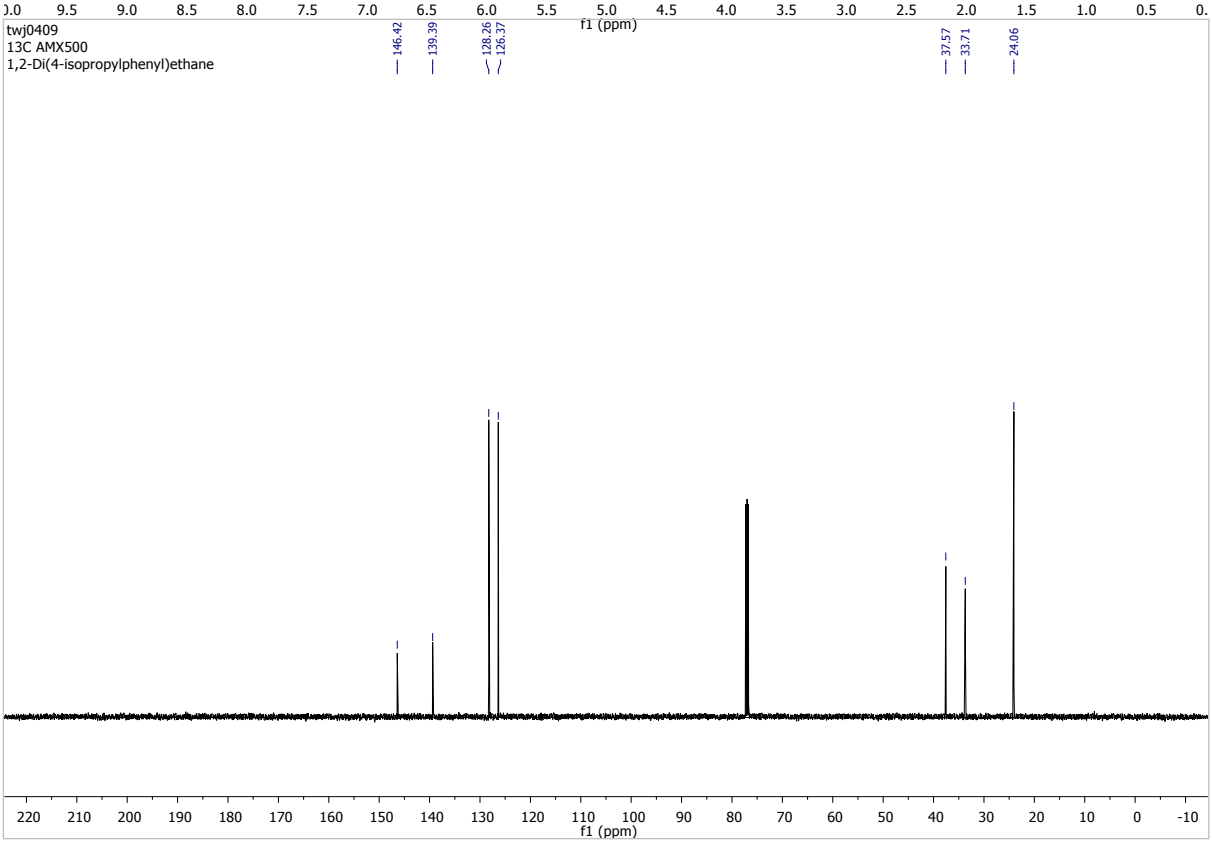


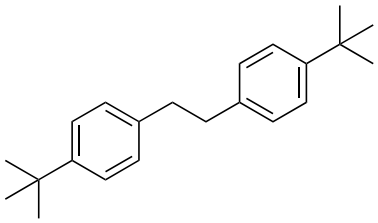




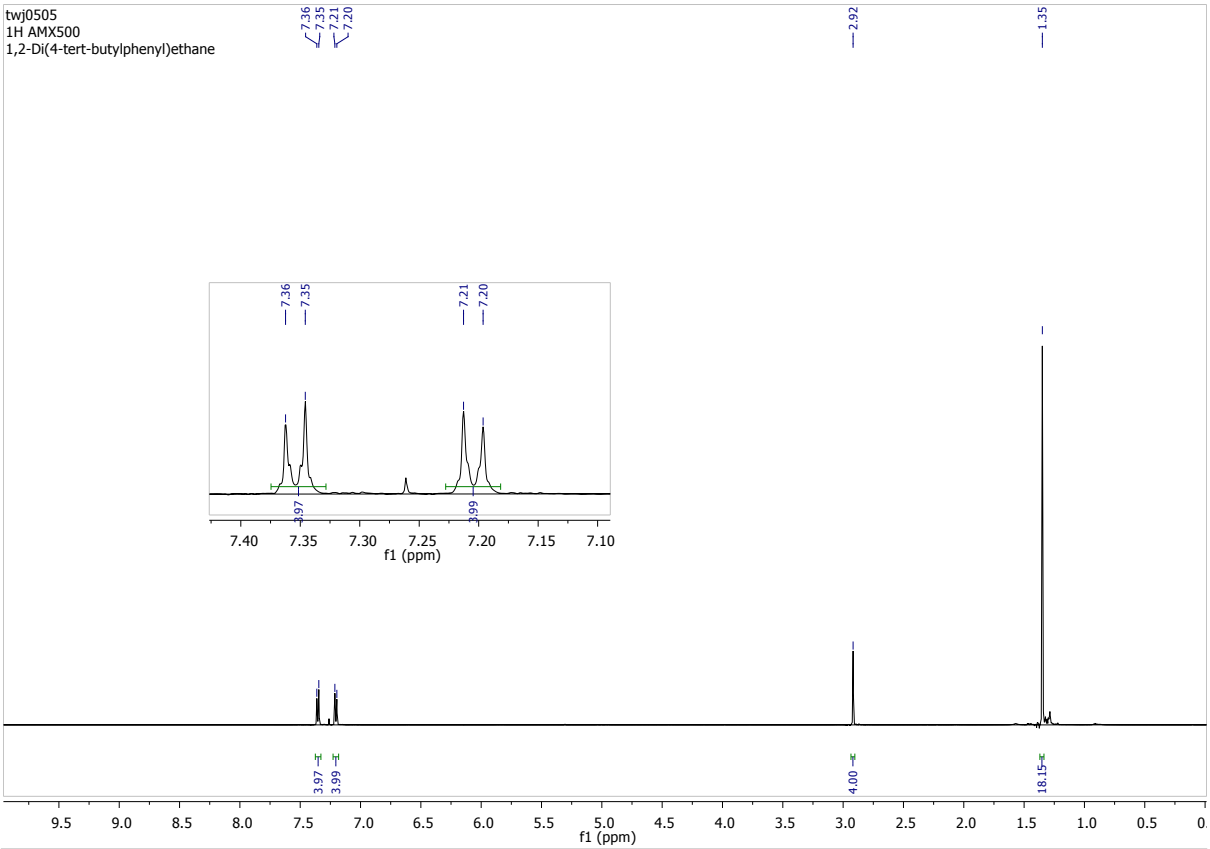
1,2-Di(4-isopropylphenyl)ethane[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.18 (s, 8H), 2.95-2.87 (m, 6H), 1.27 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 146.42, 139.39, 128.26, 126.37, 37.57, 33.71, 24.06.

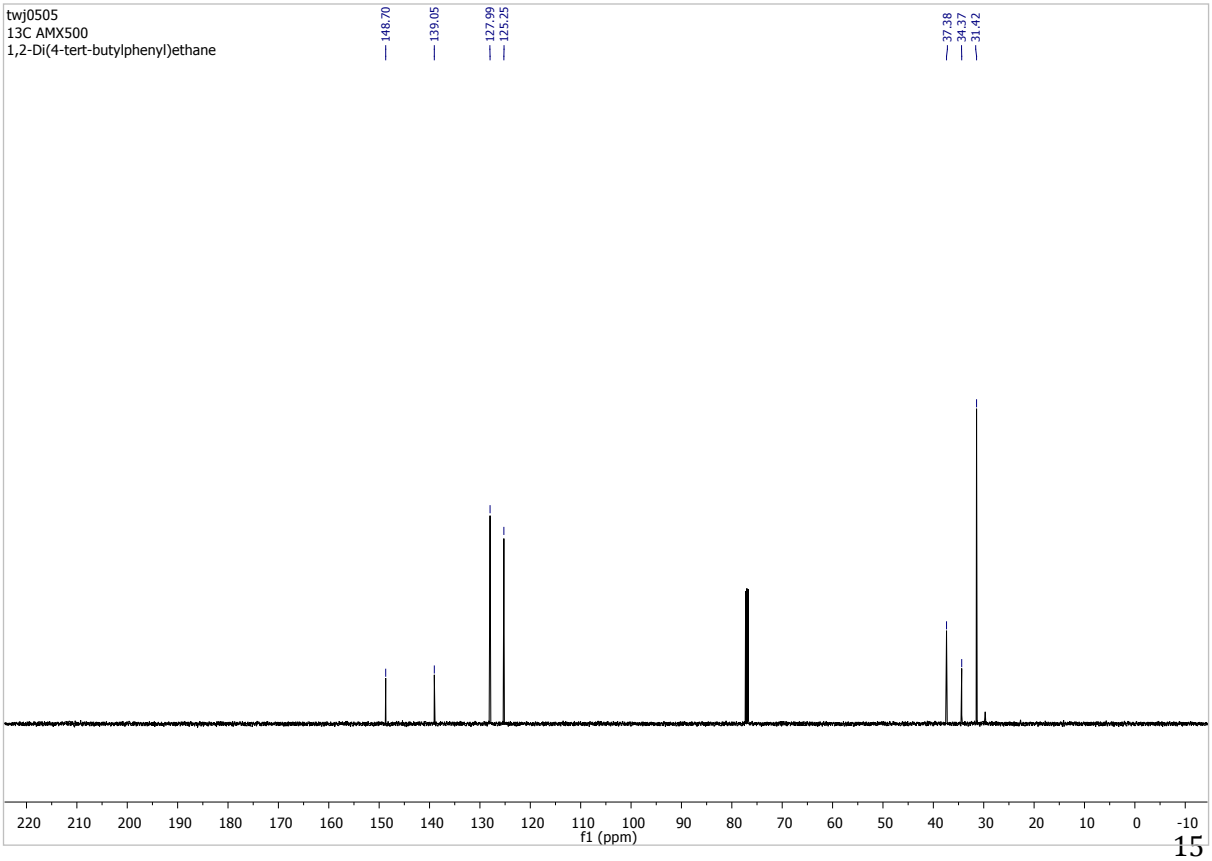


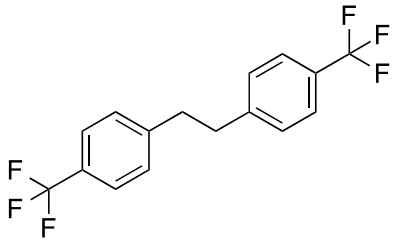




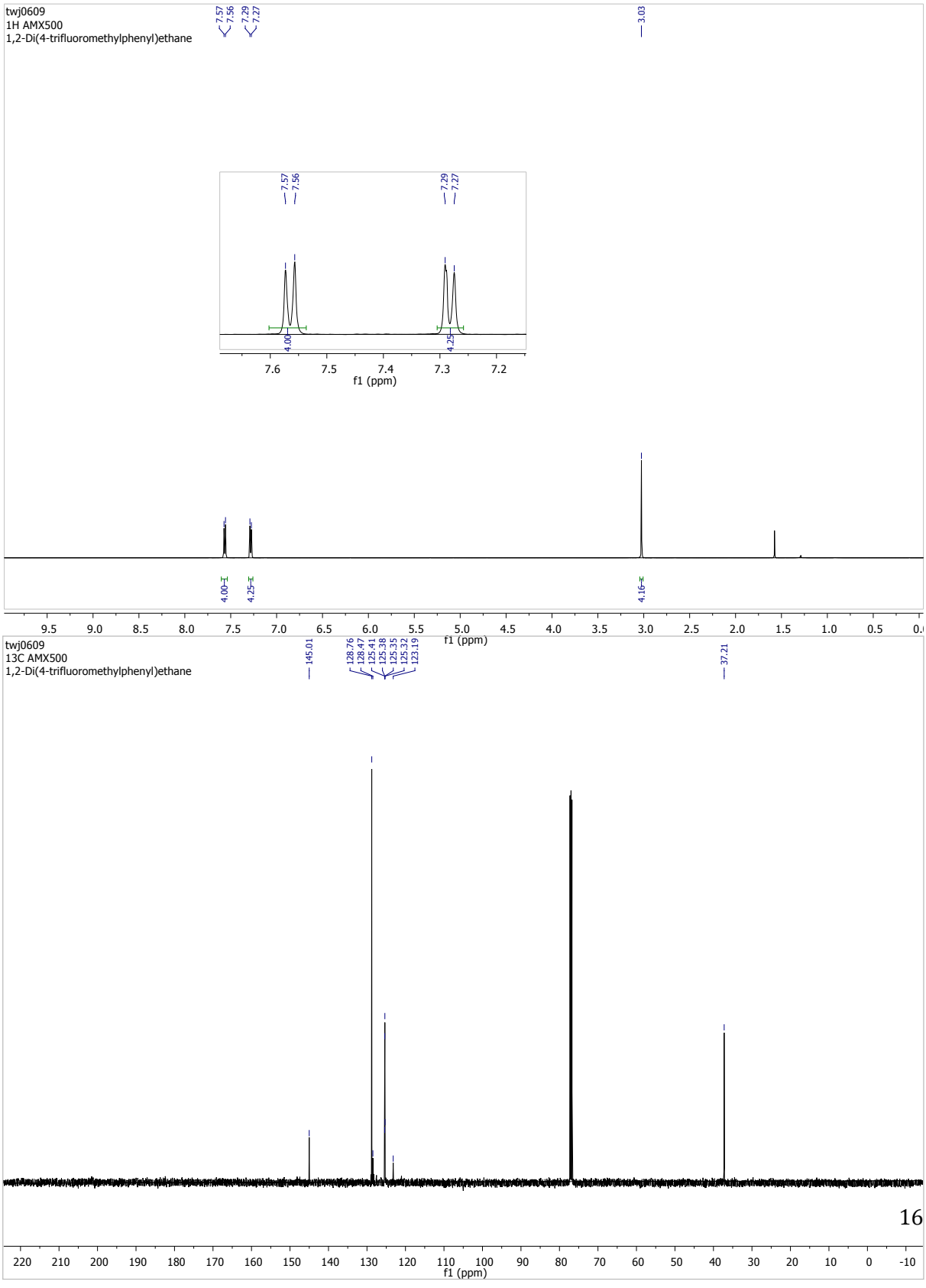
1,2-Di(4-tert-butylphenyl)ethane[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.36 (d, *J* = 8.3 Hz 4H), 7.21 (d, *J* = 8.3 Hz 4H), 2.92 (s, 4H), 1.35 (s, 18H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 148.70, 139.05, 127.99, 125.25, 37.38, 34.37, 31.42.

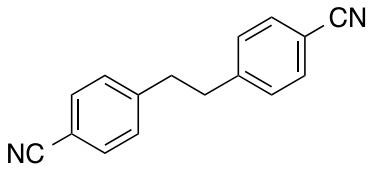




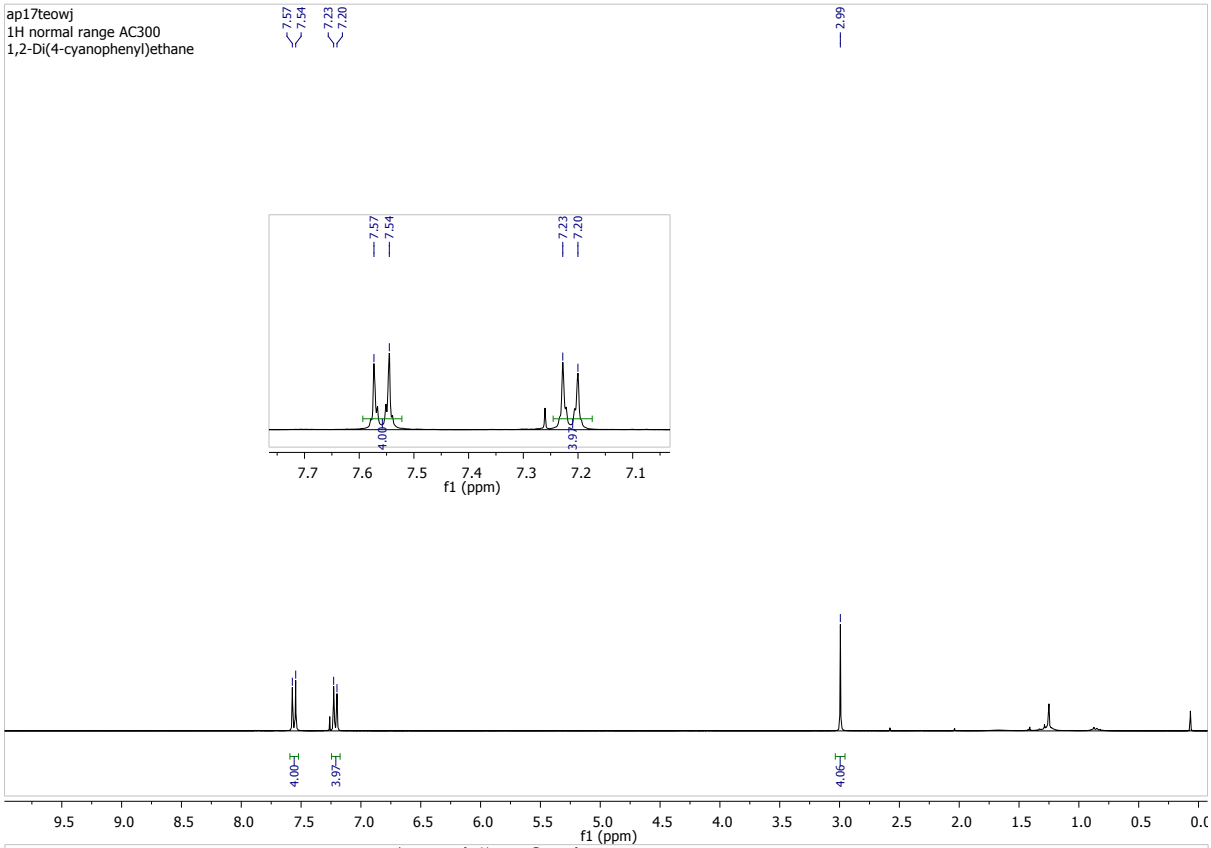


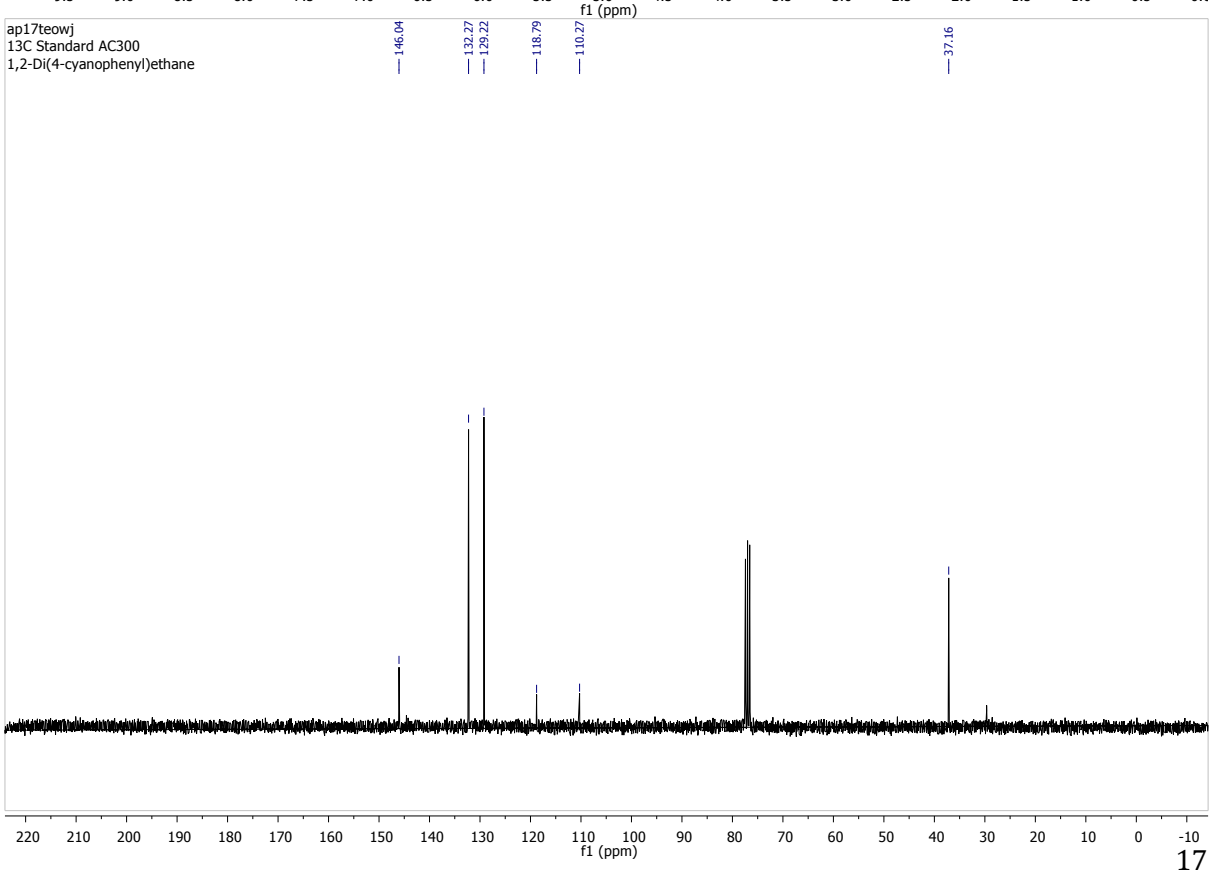
1,2-Di(4-trifluoromethylphenyl)ethane[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.57 (d, *J* = 8.2 Hz 4H), 7.28 (d, *J* = 8.2 Hz 4H), 3.03 (s, 4H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 145.01, 128.76, 128.47, 125.37 (q, *J* = 3.6 Hz), 123.19, 37.21.

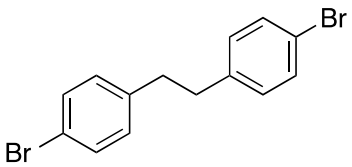




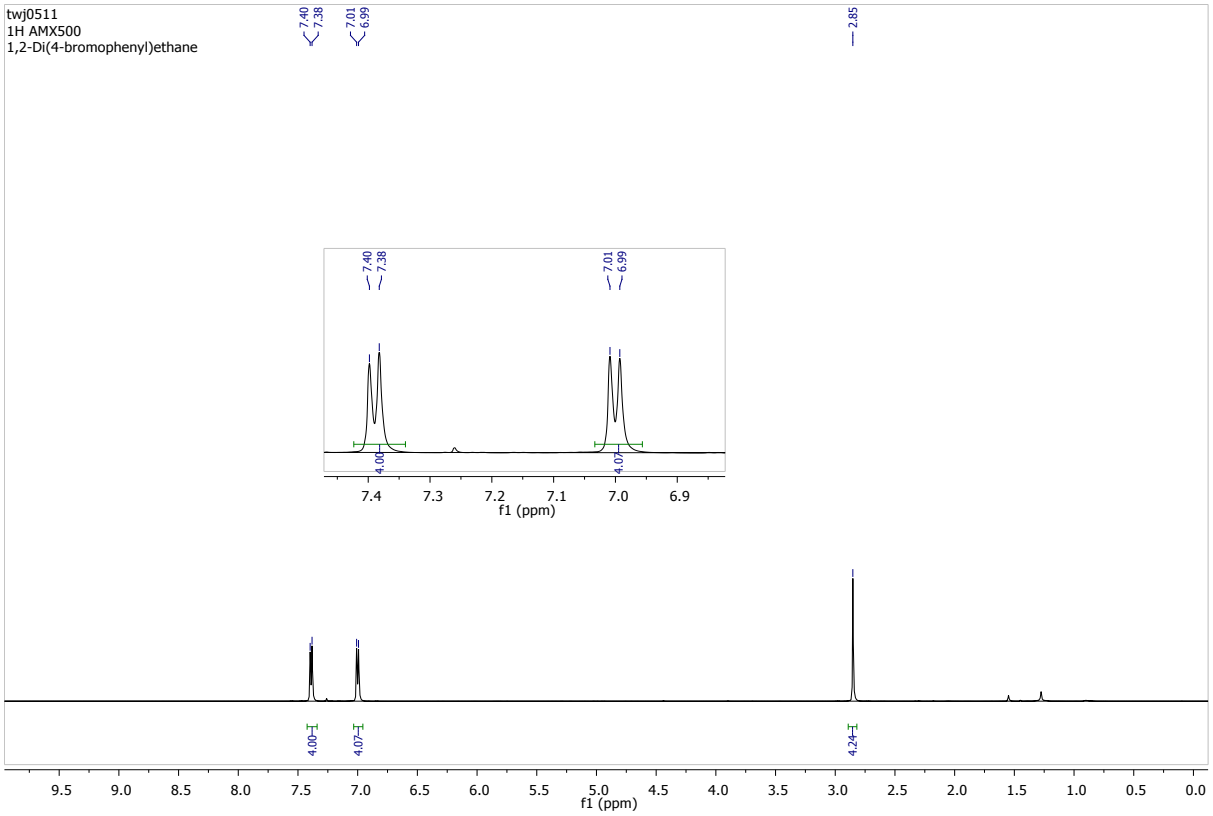
1,2-Di(4-cyanophenyl)ethane[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.56 (d, *J* = 8.4 Hz 4H), 7.22 (d, *J* = 8.4 Hz 4H), 2.99 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 146.04, 132.27, 129.22, 118.79, 110.27, 37.16.

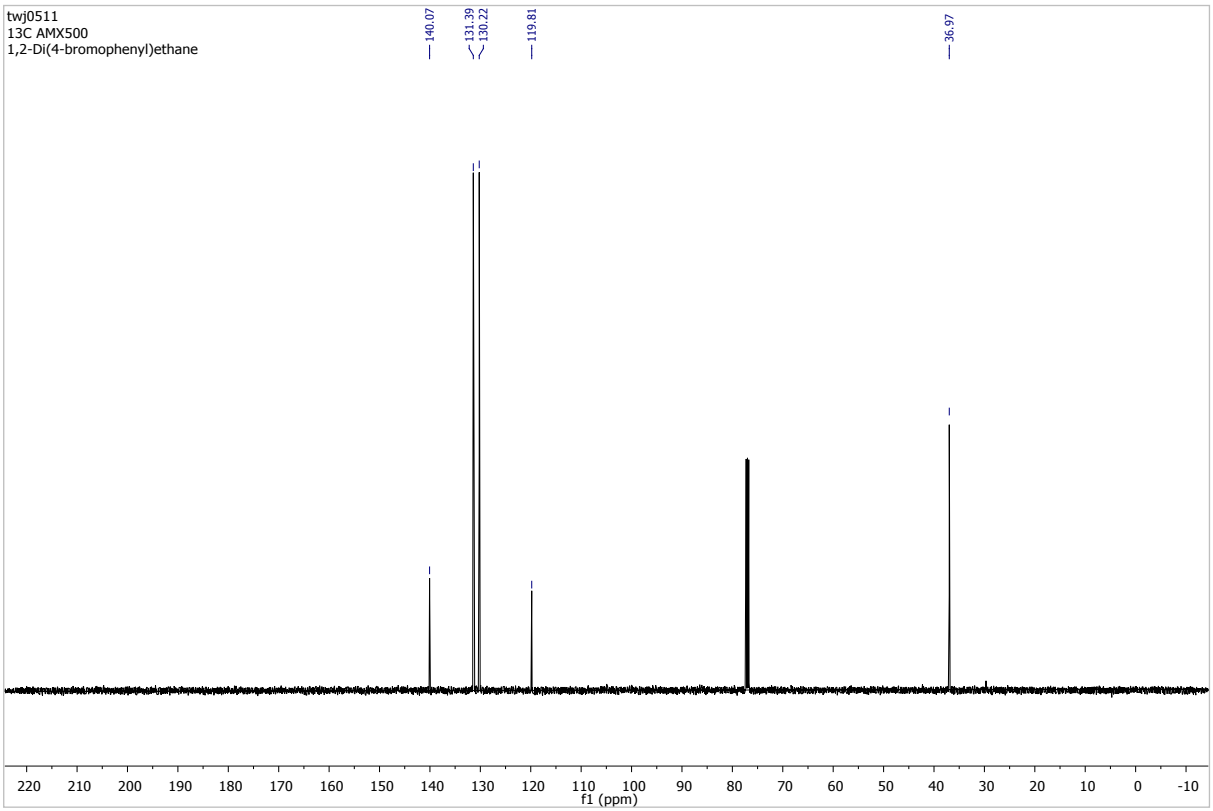


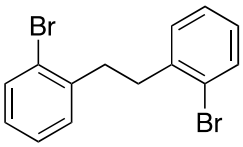




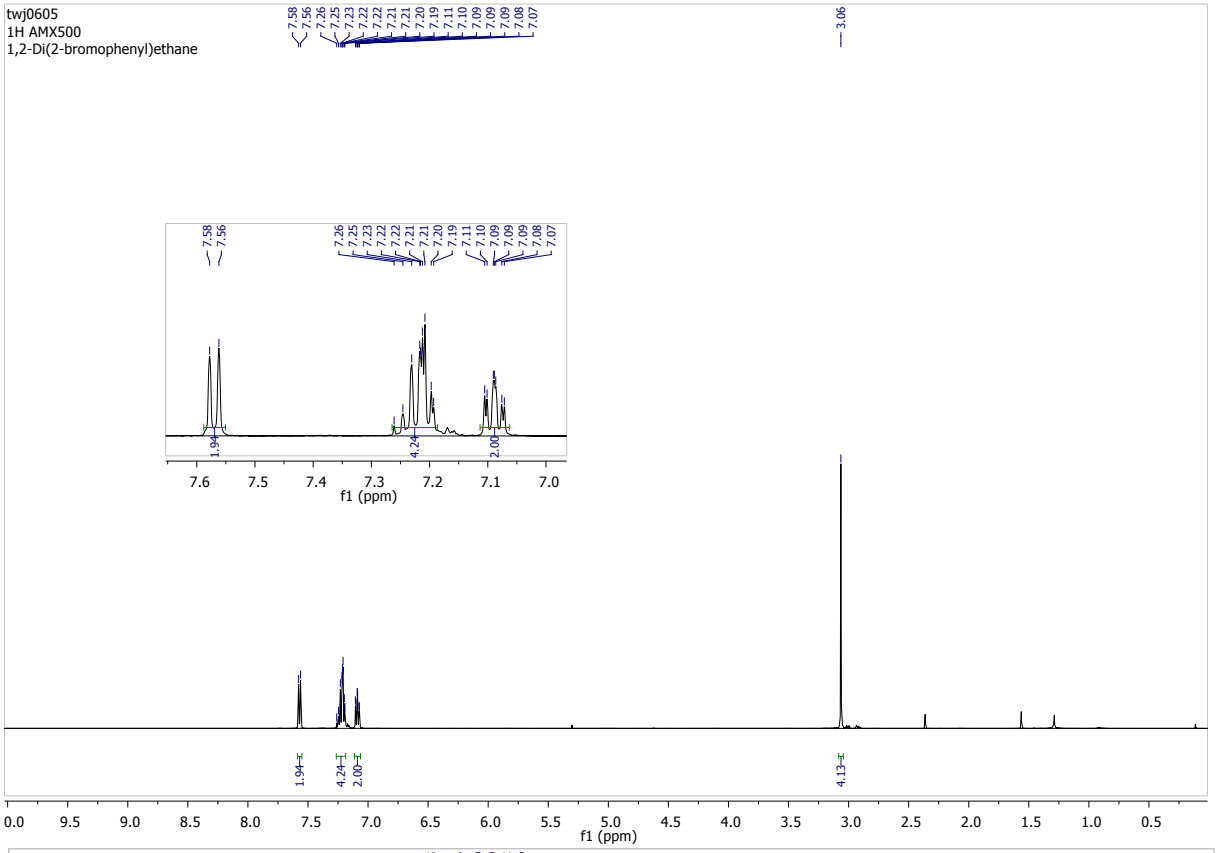
1,2-Di(4-bromophenyl)ethane[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.39 (d, *J* = 8.0 Hz 4H), 7.00 (d, *J* = 8.0 Hz 4H), 2.85 (s, 4H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 140.07, 131.39, 130.22, 119.81, 36.97.

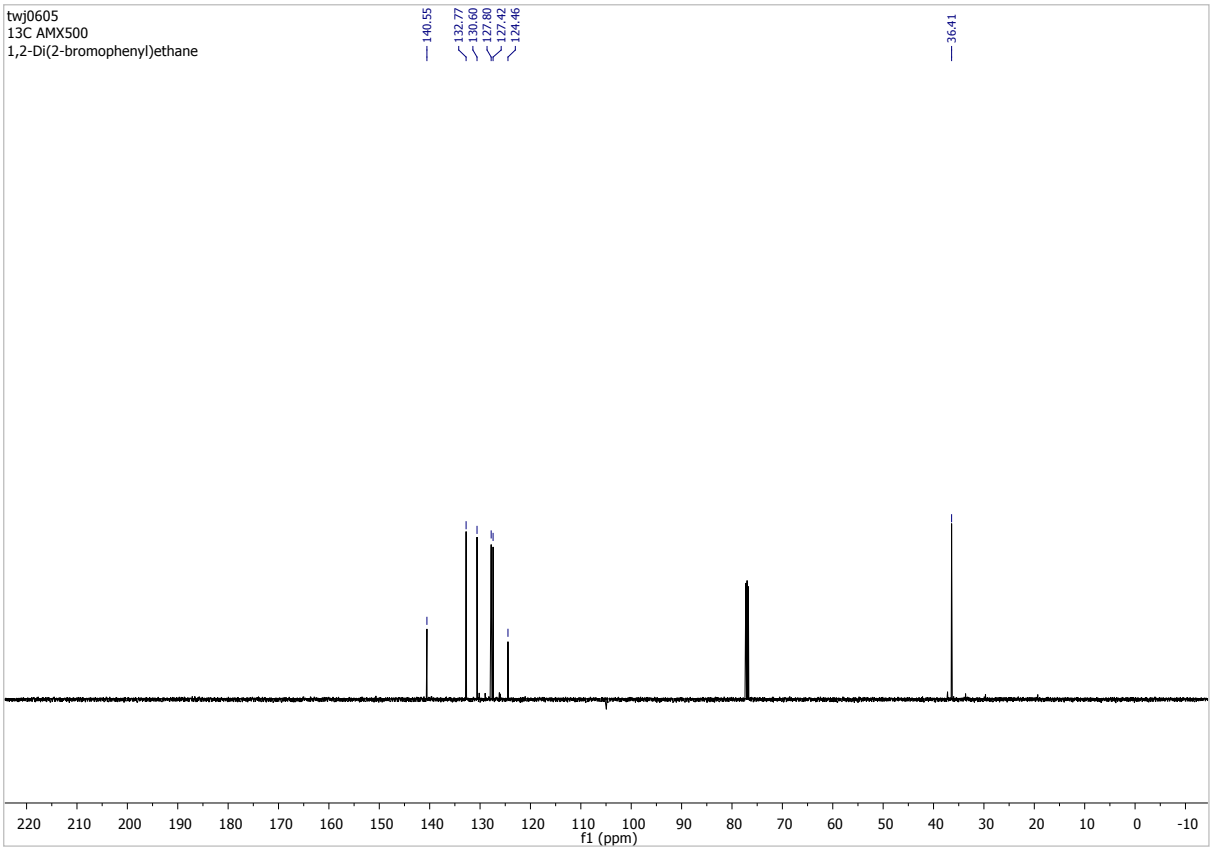


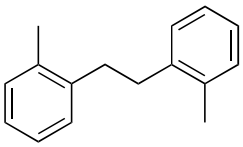




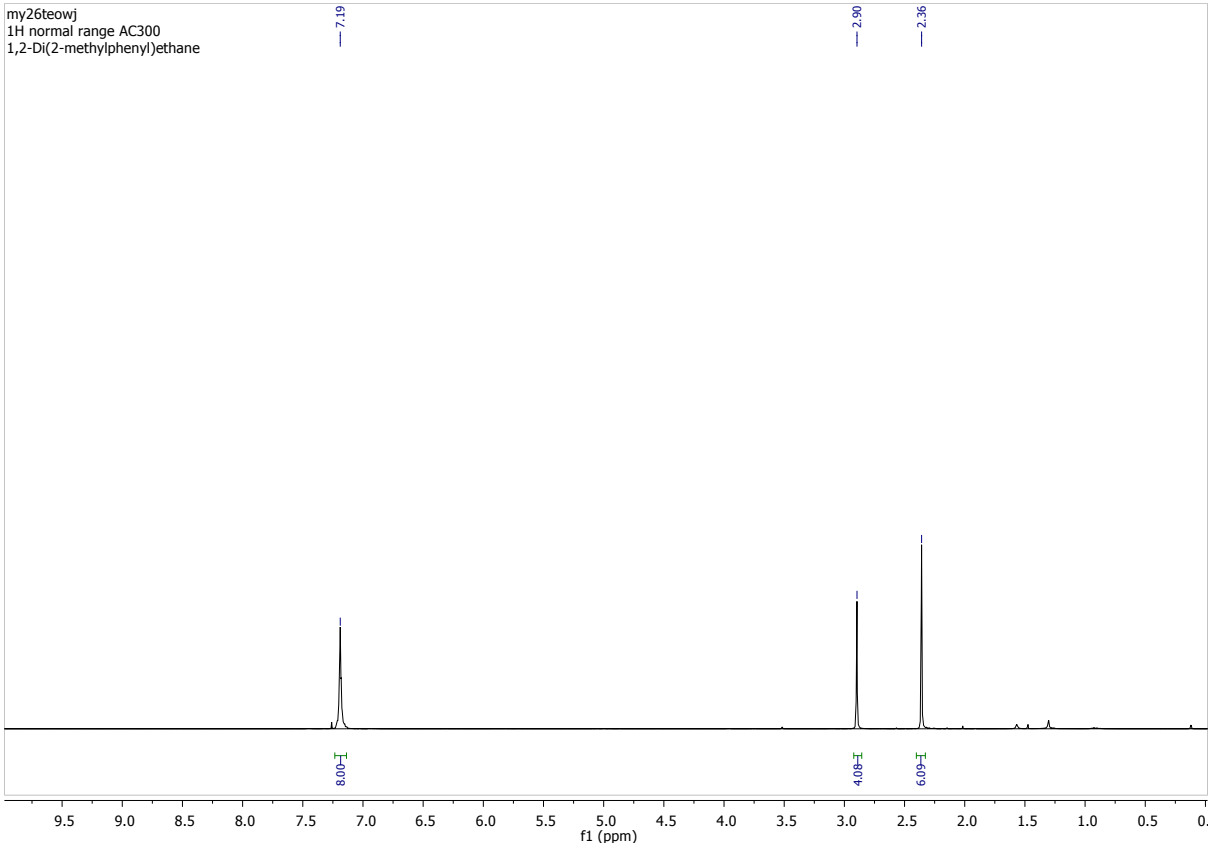
1,2-Di(2-bromophenyl)ethane[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.57 (d, *J* = 8.0 Hz 2H), 7.26-7.19 (m, 4H), 7.11-7.07 (m, 2H), 3.06 (s, 4H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 140.53, 132.77, 130.60, 127.80, 127.42, 124.46, 36.41.

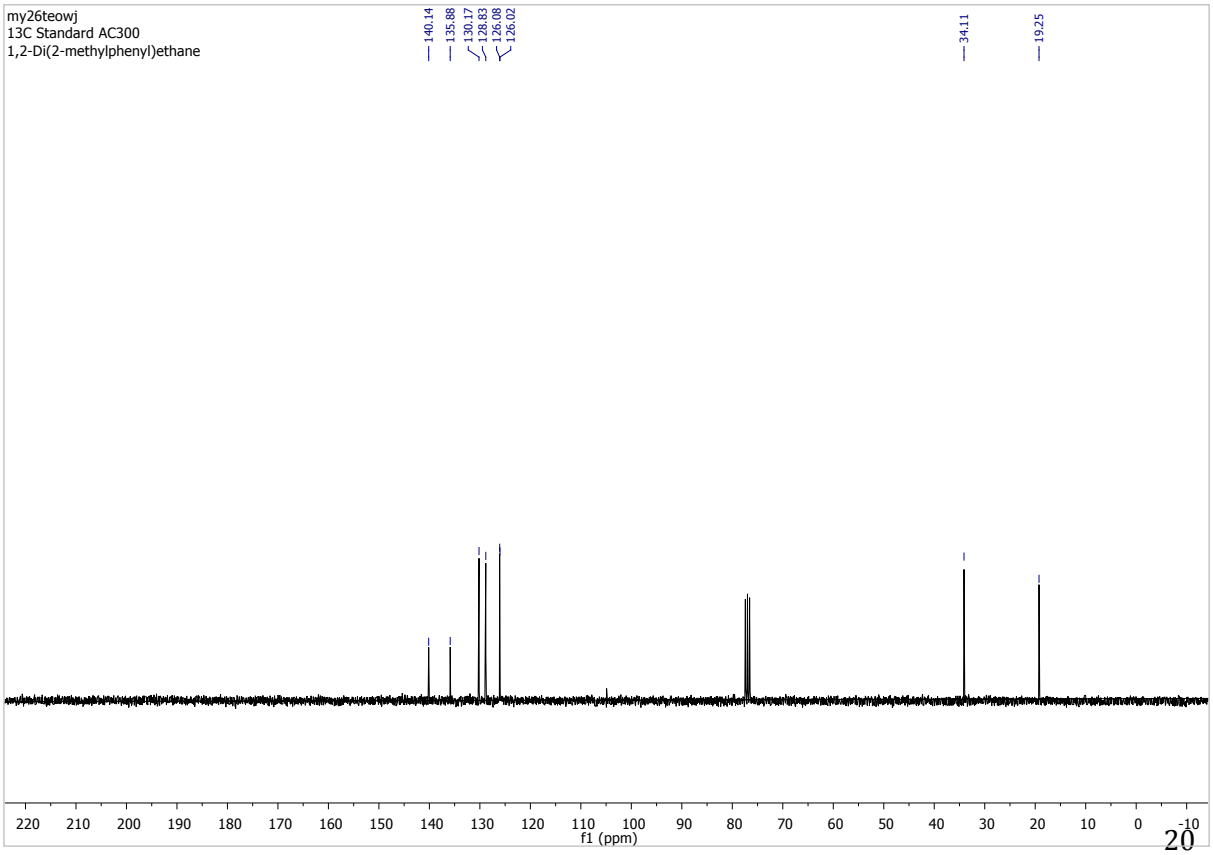


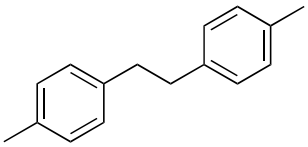




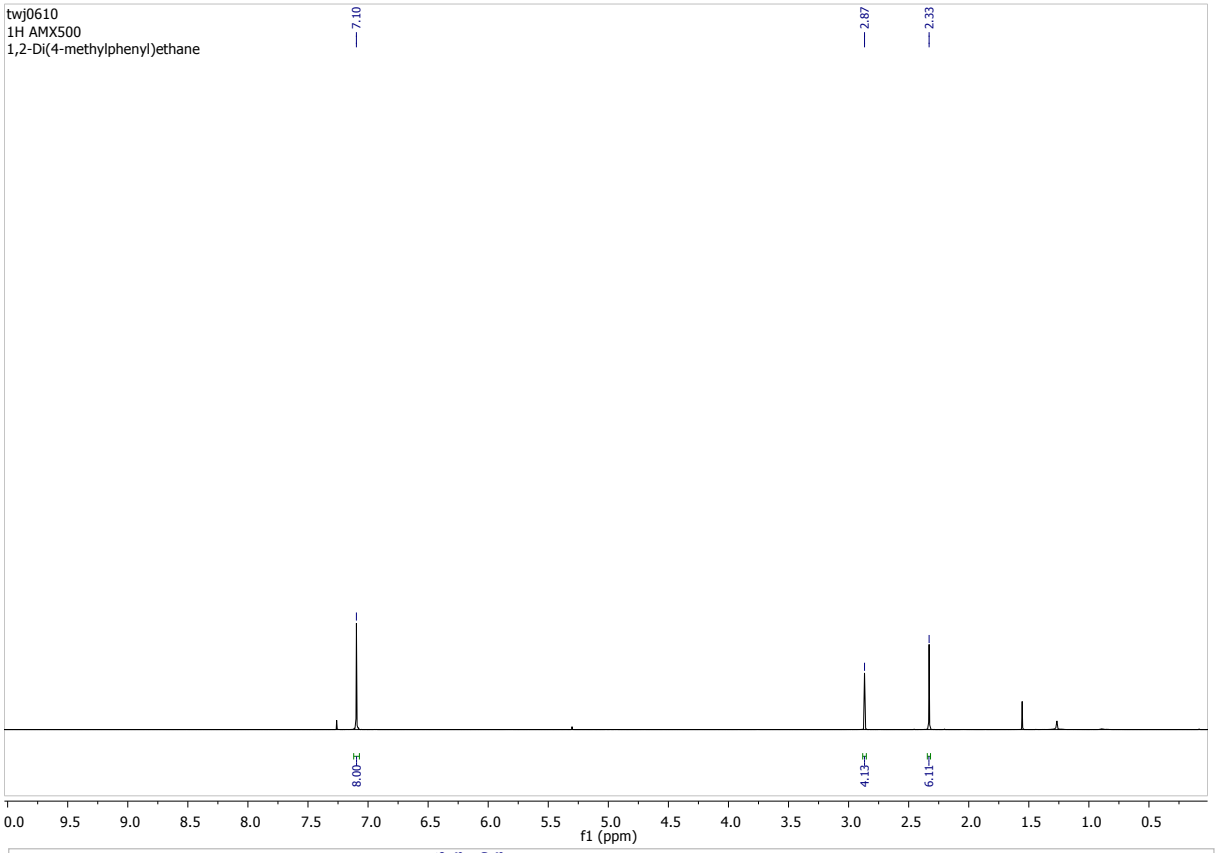
1,2-Di(2-methylphenyl)ethane[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.19 (s, 8H), 2.90 (s, 4H), 2.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 140.14, 135.88, 130.17, 128.83, 126.08, 126.02, 34.11, 19.25.

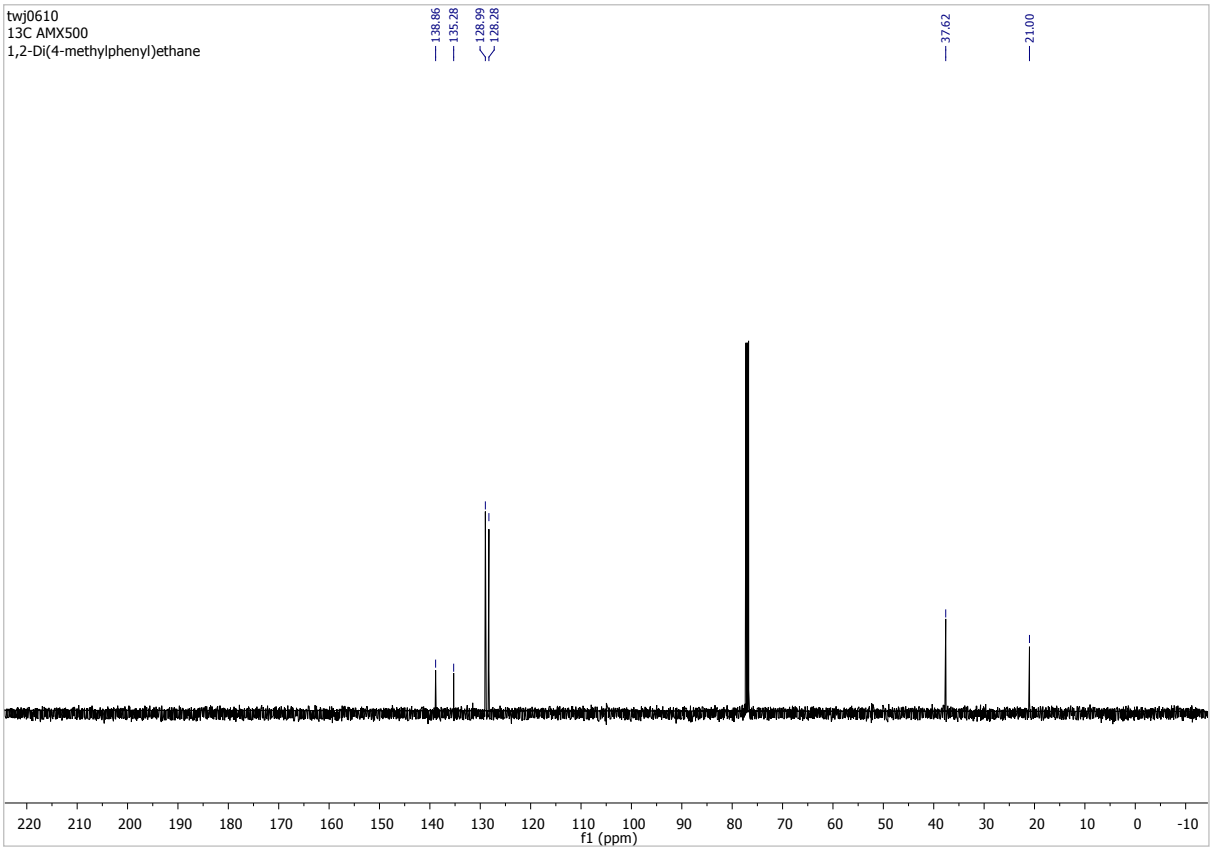


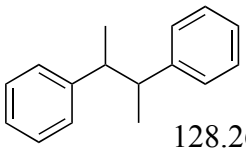




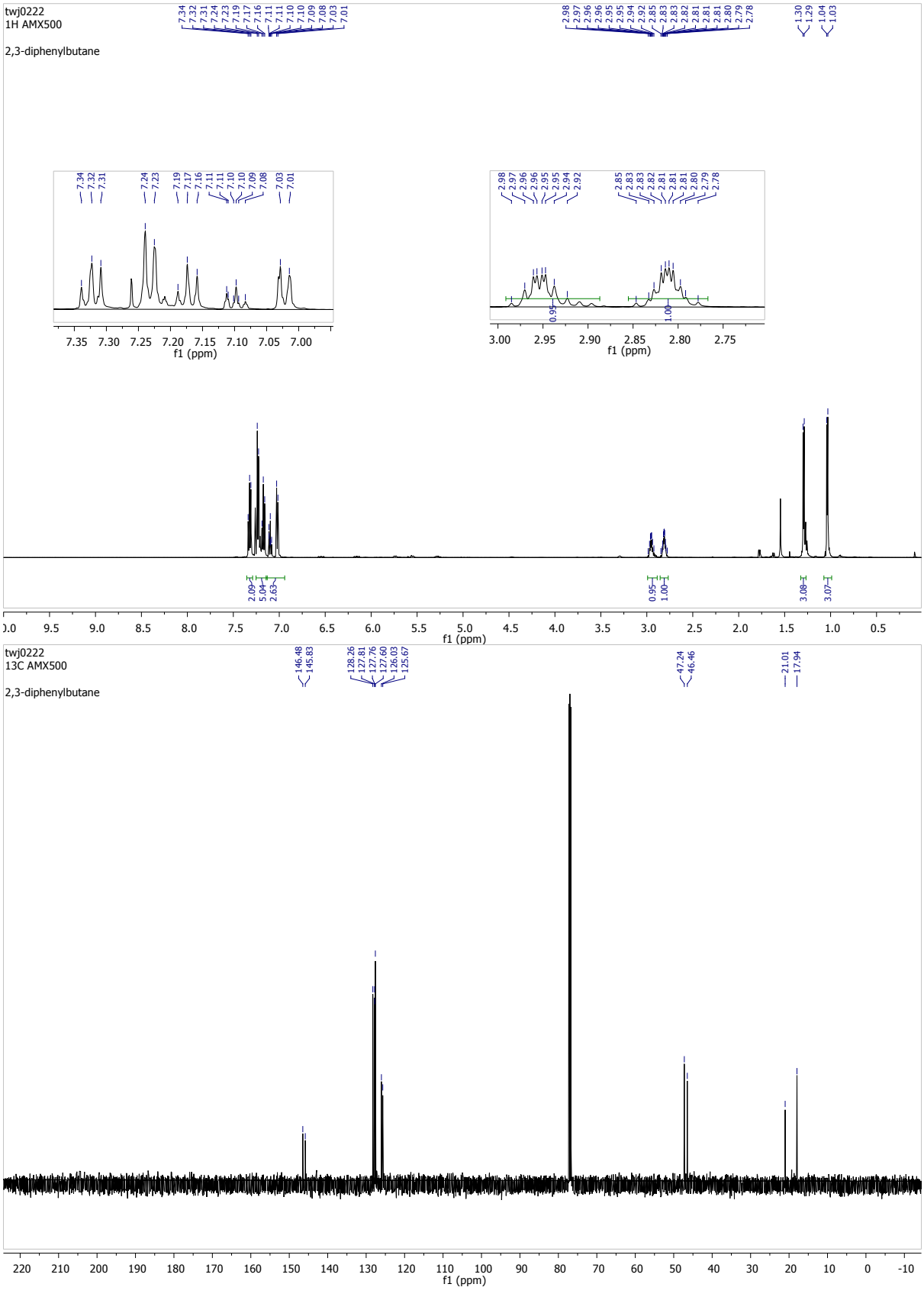
1,2-Di(4-methylphenyl)ethane[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.10 (s, 8H), 2.87 (s, 4H), 2.33 (s, 6H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 138.86, 135.28, 128.99, 128.28, 37.62, 21.00.

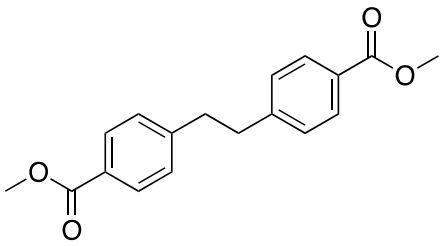




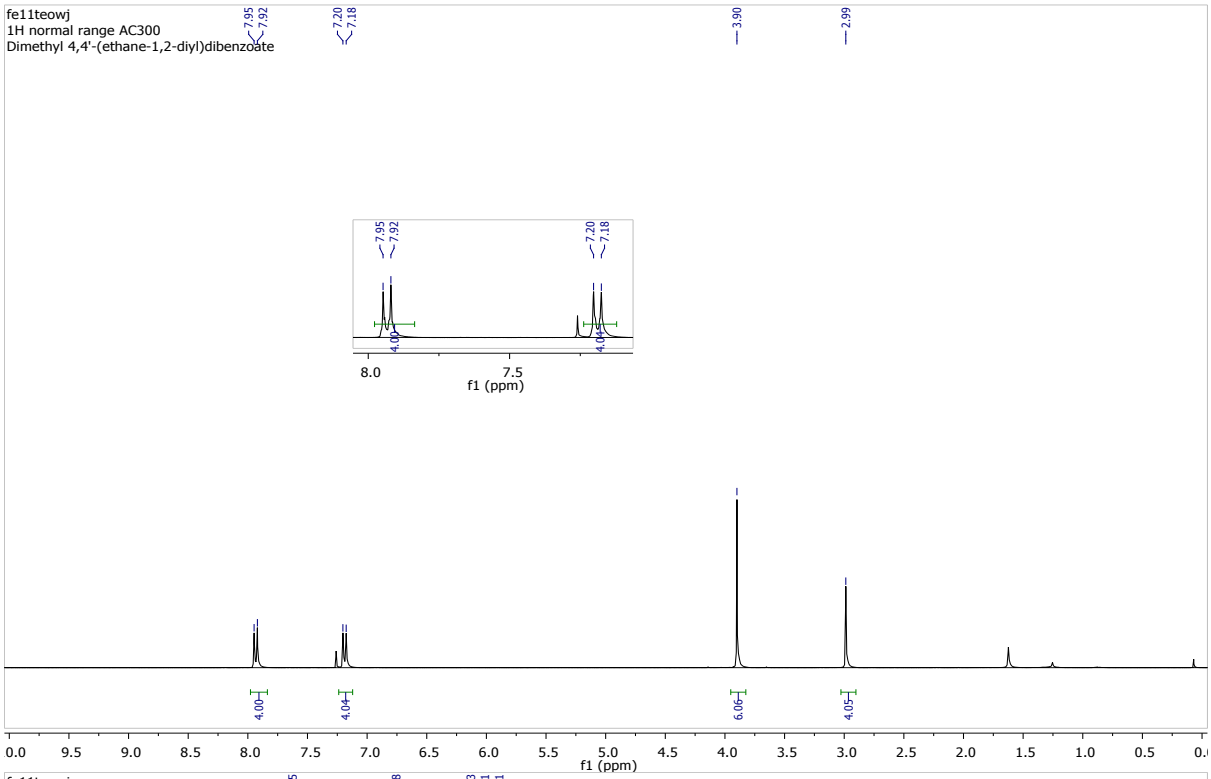


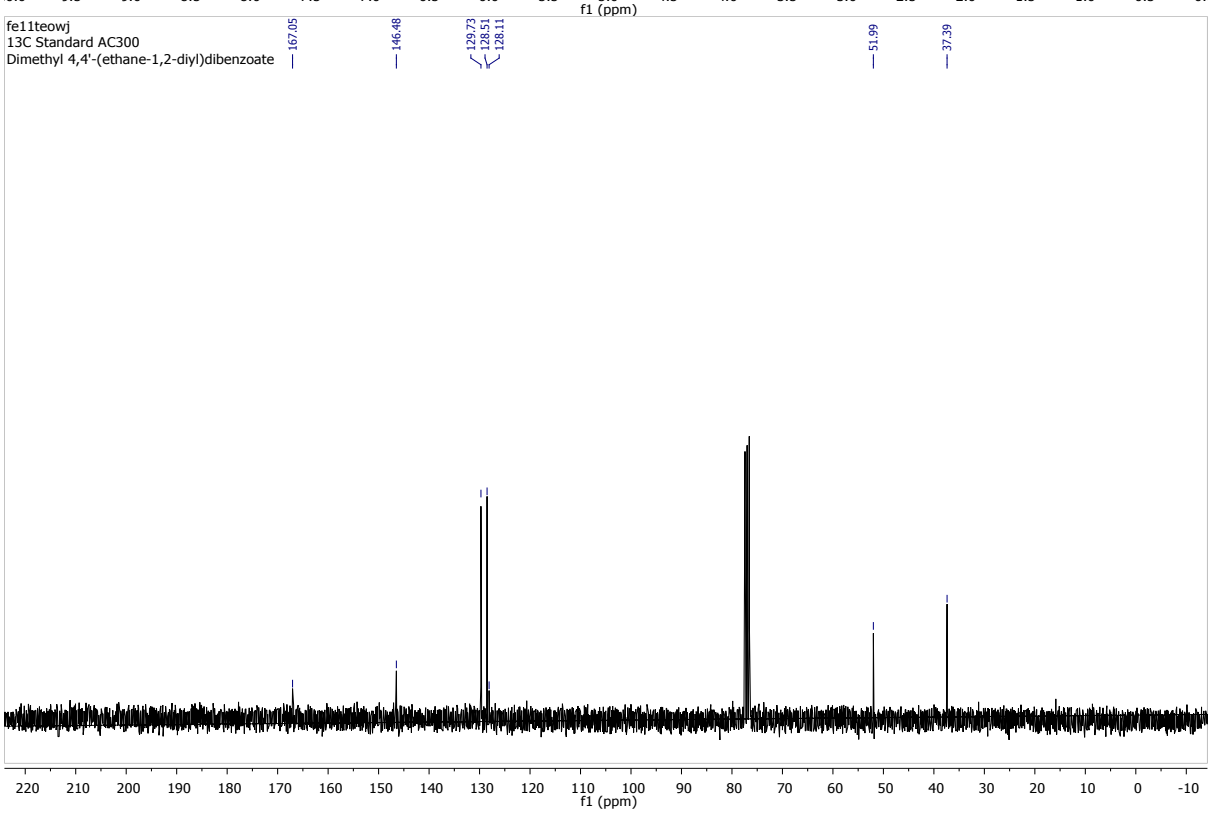
2,3-diphenylbutane[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.34-7.01 (m, 10H), 2.98-2.78 (m, 2H), 1.29 (d, *J* = 6.0 Hz 3H), 1.03 (d, *J* = 6.0 Hz 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ (ppm) = 146.48, 145.83，128.26, 127.81, 127.76, 127.60, 126.03, 125.67, 47.24, 46.46, 21.01, 17.94.





Dimethyl 4,4'-(ethane-1,2'-diyl)dibenzoate[6] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (d, *J* = 8.0 Hz 4H), 7.19 (d, *J* = 8.0 Hz 2H), 3.90 (s, 6H), 2.99 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.05, 146.48, 129.73, 128.51, 128.11, 51.99, 37.39.





V. Crystal data and structure refinement parameters of complexes **3a-3c**

Table S3. Crystal data and structure refinement for complexes **3a-3c**

Complex	**3a**	**3b**	**3c**
Chemical formula	$C_{16}H_{14}F_6N_3NiPS$	$C_{18}H_{16}F_6N_3NiPS$	$C_{22}H_{18}F_6N_3NiPS$
Formula weight	484.04 g/mol	510.08 g/mol	560.13 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Crystal size	0.090 x 0.130 x 0.210 mm	0.100 x 0.120 x 0.600 mm	0.200 x 0.260 x 0.460 mm
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	P n m a	P 1 21/c 1	P b c n
a/Å	14.8278(7)	7.3234(13)	10.8112(12)
b/Å	6.9438(4)	18.776(3)	13.5233(15)
c/Å	17.7673(9)	13.938(2)	30.106(3)
α/°	90	90	90
β/°	90	90.253(4)	90
γ/°	90	90	90
V/Å^3	1829.34(16)	1916.5(6)	4401.6(9)
Z	4	4	8
Density (calculated)	1.758 g/cm^3	1.768 g/cm^3	1.691 g/cm^3
Reflections collected	17118	13566	54601
Independent reflections	2451	4434	5091
R_{int}	0.0406	0.0443	0.0596
Parameters	158	271	307
GOF on F^2	1.048	1.033	1.085
R_1 [I > 2σ(I)]	0.0284	0.0397	0.0459
wR_2 (all data)	0.0645	0.0985	0.1104

VI. References

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