Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

C-H activation in Ir^{III} and N-demethylation in Pt^{II} complexes with mesoionic carbene ligands: examples of monometallic, homobimetallic and heterobimetallic complexes

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General Procedures.

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were distilled by standard procedures prior to use. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE 500 spectrometer or JEOL ECS 400 or JEOL ECP 500 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for $^{1}H,^{1}H$ couplings unless mentioned otherwise. Mass spectra were obtained with Agilent 6210 ESI-MSD TOF. Compound bistriazolium salt **1**[1] was prepared as described in the literature. $K_2[PtCl_4]$, KI, pyridine were purchased from commercial sources and were used as received without further purification.

Compound [2] and [3].

To a mixture of bistriazolium salt **1**[1] (0.020 g, 0.036 mmol), K_2CO_3 (0.045 g, 0.036 mmol), $K_2[PtCl_4]$ (0.030 g, 0.073 mmol) and KI (excess) was added pyridine (5 mL). The resulting suspension was stirred for 48 h at 84 °C. The pyridine was removed in *vacuo* and the crude mixture was extracted with dichloromethane (15 mL). The solvent was removed and the yellow residue was loaded onto a silica gel column. Elution with dichloromethane followed by dichloromethane:acetone (10:1; v:v) mixture gave compounds [**2**] and [**3**].

Compound [**2**]: Yield: 0.016 g (0.012 mmol, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89−8.84 (m, 4H, H_{Py}), 8.03 (s, br, 4H, H_{Ar}), 7.52−7.48 (m, 2H, H_{Py}), 7.20−7.09 (m, 4H, H_{Py}), 4.85 (q, ^3J = 7.2 Hz, 4H, N−CH_2), 3.97 (s, 6H, N−CH_3), 1.71 (t, ^3J = 7.2 Hz, 6H, N−CH_2−CH_3), ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$:CD_2Cl_2; 3:2) δ = 151.9 (C_{Py}), 143.8 (C_{trz}−Ar), 137.1 (C_{Py}), 130.7 (C_{Ar}−H), 129.0 (C_{Ar}−C_{trz}), 124.9 (C_{Py}), 124.9 (C_{trz}−Pt), 50.2 (N−CH_2), 37.7 (N−CH_3), 14.5 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 1374.7840 (calcd for $[[\mathbf{2}]+Na]^+$ 1374.7958), 1216.7014 (calcd for $[[\mathbf{2}]-2Py+Na]^+$ 1216.7112.

Compound [**3**]: Yield: 0.013 g (0.016 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99−8.97 (m, 2H, H_{Py}), 8.04−8.00 (m, 4H, H_{Ar}), 7.88 (s, 1H, H_{trz}), 7.67 (tt, ^4J = 1.50 Hz, ^3J = 7.5 Hz, 1H, H_{Py}), 7.28−7.25 (m, 2H, H_{Py}), 4.96 (q, ^3J = 7.5 Hz, 2H, N−CH_2), 4.52 (q, ^3J = 7.42 Hz, 2H, N−CH_2), 4.01 (s, 3H, N−CH_3), 1.81 (t, ^3J = 7.5 Hz, 3H, N−CH_2−CH_3), 1.65 (t, ^3J = 7.5 Hz, 3H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 153.9 (C_{Py}), 147.2 (C_{trz}−Ar), 144.1(C_{trz}−Ar), 137.2 (C_{Py}), 131.9 (C_{Ar}−C_{trz}), 131.1 (C_{Ar}−H), 127.2 (C_{trz}−Ar), 125.8 (C_{Ar}−H), 124.9 (C_{Py}), 123.8 (C_{trz}−Pt), 119.6 (C_{trz}−H), 50.3 (N−CH_2), 45.6 (N−CH_2), 37.5 (N−CH_3), 15.7 (N−CH_2−CH_3), 15.5 (N−CH_2−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 832.9613 (calcd for $[[\mathbf{3}]+Na]^+$ 832.9651), 753.9229 (calcd for $[[\mathbf{3}]-Py+Na]^+$ 753.9192.

Compound [4].

To a mixture of bistriazolium salt **1**[1] (0.020 g, 0.036 mmol), K_2CO_3 (0.011 g, 0.080 mmol), $[Ir(Cl)_2Cp^*]_2$ (0.017 g, 0.021 mmol), NaOAc (0.003 g, 0.037 mmol) and KI (excess) was added acetonitrile (6 mL). The resulting suspension was stirred for 20 h at 84 °C. The acetonitrile was removed in *vacuo* and the crude mixture was loaded onto a silica gel column. Elution with dichloromethane:methanol (90:10; v:v) mixture gave compound [**4**]. Yield: 0.021 g (0.024 mmol, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.69 (s, 1H, $H_{triazolium}$), 7.79 (d, ^4J = 1.8 Hz, 1H,

H_{Ar}), 7.51 (d, ^3J = 7.9 Hz, 1H, H_{Ar}), 7.24 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, H_{Ar}), 5.0 (q, ^3J = 7.6 Hz, 2H, N−CH_2), 4.52−4.44 (m, 2H, N−CH_2), 4.33 (s, 3H, N−CH_3), 4.27 (s, 3H, N−CH_3), 1.87 (s, 15H, Cp*−CH_3), 1.77 (t, ^3J = 7.6 Hz, 3H, N−CH_2−CH_3), 1.66 (t, ^3J = 7.6 Hz, 3H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 159.0 (C_{Ar}−Ir), 154.4 (C_{trz}−C_{Ar}), 152.9 (C_{trz}−Ir), 144.3 ($C_{triazolium}$−C_{Ar}), 140.0 (C_{Ar}−$C_{trz/triazolium}$), 139.0 (C_{Ar}−H), 129.2 ($C_{trazolium}$−H), 123.3 (C_{Ar}−H), 120.6 (C_{Ar}−H), 120.2 (C_{Ar}−$C_{trz/triazolium}$), 91.1 (C_{Cp*}), 50.3 (N−CH_2), 47.9 (N−CH_2), 39.0 (N−CH_3), 37.6 (N−CH_3), 15.5 (N−CH_2−CH_3), 15.0 (N−CH_2−CH_3), 10.6 (Cp*−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 751.1591 (calcd for $[[\mathbf{4}]-I]^+$ 751.1598).

Compound [5].

To a mixture of complex [**4**] (0.0168 g, 0.019 mmol), K_2CO_3 (0.0053 g, 0.038 mmol), $PdCl_2$ (0.0037 g, 0.021 mmol) and KI (excess) was added pyridine (3 mL). The resulting suspension was stirred for 24 h at 84 °C. The pyridine was removed in *vacuo* and the crude mixture was loaded onto a silica gel column. Elution with dichloromethane:acetone (98:2; v:v) mixture gave compound [**5**]. Yield: 0.012 g (0.010 mmol, 53%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.99 (m, 2H, H_{Py}), 7.79 (dd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H, H_{Ar}), 7.76 (d, ^4J = 1.5 Hz, 1H, H_{Ar}), 7.64 (m, 1H, H_{Py}), 7.56 (d, ^3J = 7.6 Hz, 1H, H_{Ar}), 7.23 (m, 2H, H_{Py}), 4.98−4.84 (m, 2H, N−CH_2), 4.48 (q, ^3J = 7.1 Hz, 2H, N−CH_2), 4.32 (s, 3H, N−CH_3), 3.94 (s, 3H, N−CH_3), 1.87 (s, 15H, Cp*−CH_3), 1.81 (t, ^3J = 7.1 Hz, 3H, N−CH_2−CH_3), 1.66 (t, ^3J = 7.6 Hz, 3H, N−CH_2−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 157.1 (C_{Ar}−Ir), 155.5 (C_{trz}−C_{Ar}), 154.1 (C_{Py}), 152.3 (C_{trz}−Ir), 144.9 (C_{trz}−C_{Ar}), 140.6 (C_{Ar}−H), 137.4 (C_{Ar}−C_{trz}), 137.3 (C_{Py}), 130.9 (C_{trz}−Pd), 124.2 (C_{Py}), 126.6 (C_{Ar}−H), (C_{Ar}−C_{trz}), 124.6 (C_{Ar}−H), 124.2 (C_{Py}), 119.9 (C_{Ar}−H), 90.8 (C_{Cp*}), 51.4 (N−CH_2), 47.7 (N−CH_2), 37.8 (N−CH_3), 37.2 (N−CH_3), 15.6 (N−CH_2−CH_3), 14.5 (N−CH_2−CH_3), 10.7 (Cp*−CH_3) ppm. HRMS (ESI, positive ions): *m/z* = 982.9516 (calcd for $[[\mathbf{5}]-Py-I]^+$ 982.9600).

X-ray Crystallography.

Single crystals suitable for X-ray diffraction studies were obtained for the complex [**2**]·$2CH_2Cl_2$ by slow evaporation of the solvents from concentrated dichloromethane:chloroform mixture. X-ray diffraction data were collected at T = 140 K with a Bruker Smart AXS diffractometer equipped with a rotation anode using graphite-monochromated Mo-K*α* radiation (λ = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD or Smart software. The data were collected by the standard 'phi-omega scan techniques'. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[2] Crystallographic details are given in Table S1.

CCDC 1415685 contains the cif file of complexes [**2**]·2CH_2Cl_2. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_requests/cif.

Table S1. Crystallographic details

	[**2**]·2CH_2Cl_2
Chemical formula	$C_{28}H_{34}Cl_4I_4N_8Pt_2$
M_r	1522.21
Crystal system	Triclinic
Space group	*P-1*
a (Å)	9.5699(19)
b (Å)	10.094(2)
c (Å)	12.494(3)
α (°)	101.63(3)
β (°)	104.74(3)
γ (°)	110.90(3)
V (Å^3)	1031.7(4)
Z	1
Densitiy (g cm^{-3})	2.450
F(000)	694
Radiation Type	Mo K_α
μ (mm^{-1})	10.055
Crystal size	0.25 x 0.1 x 0.09
Meas. Refl.	11236
Indep. Refl.	3657
Obsvd. [$I > 2\sigma(I)$] refl.	3267
R_{int}	0.0201
R [$F^2 > 2\sigma(F^2)$]	0.0251
wR(F^2)	0.0664
S	1.040
$\Delta\rho_{max}$ (e Å^{-3})	2.618
$\Delta\rho_{min}$ (e Å^{-3})	-1.188

Table S2. Selected bond lengths in Å

Atoms	[**2**]·2CH_2Cl_2
Pt1 – I1	2.5975(9)
Pt1 – I2	2.6034(9)
Pt1– N4	2.094(4)
Pt1 – C1	1.971(5)
N1 – N2	1.331(6)
N2 – N3	1.312(6)
N1 – C1	1.351(7)
N3 – C2	1.364(7)
C1 – C2	1.396(7)

Table S3. Selected bond angles in °

Atoms	[**2**]·2CH_2Cl_2
I1 – Pt1 – I2	174.998(13)
I1 – Pt1 – N4	91.12(14)
I1 – Pt1 – C1	89.37(16)
I2 – Pt1 – C1	87.79(16)
C1 – Pt1 – N4	178.10(19)
C2 – C1 – N1	103.1(5)

References

1. R. Maity, S. Hohloch, M. van der Meer, B. Sarkar, *Chem.−Eur. J.* 2014, **20**, 9952−9961.

2. *SHELXS-97*, *SHELXL-97* and G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112−122.

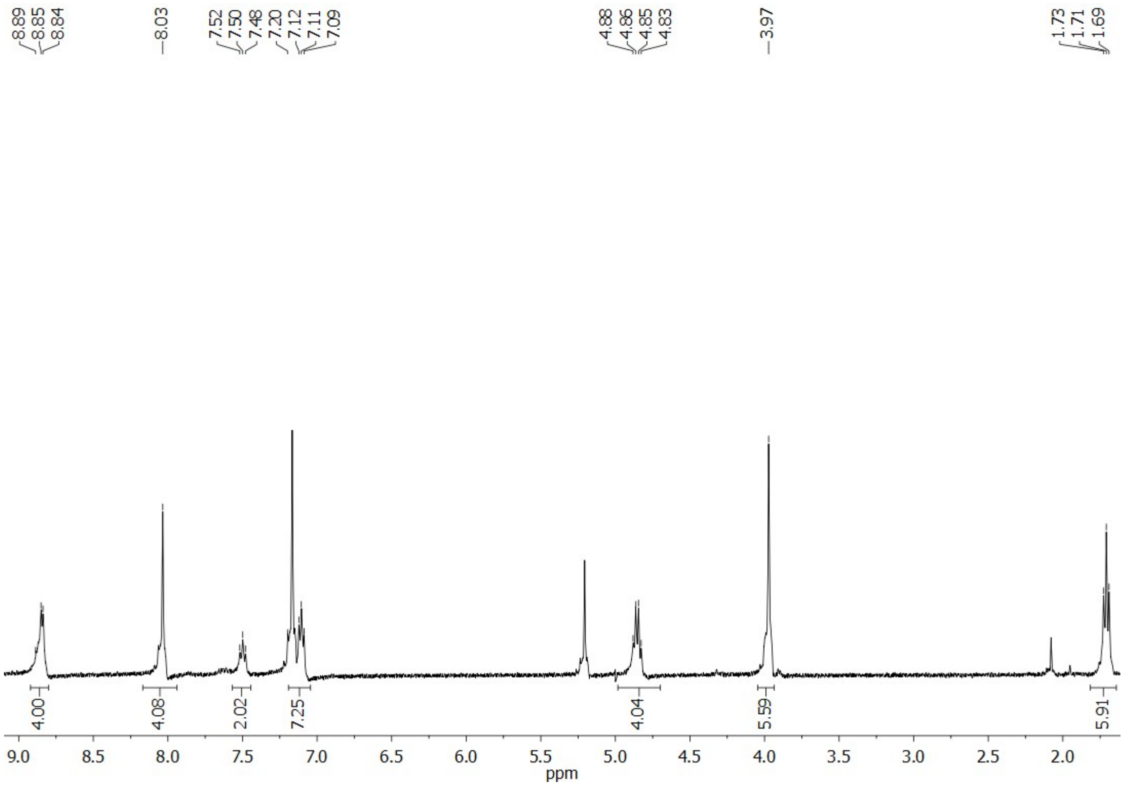

Figure S1. ^{1}H NMR spectrum of [**2**] in $CDCl_3$.

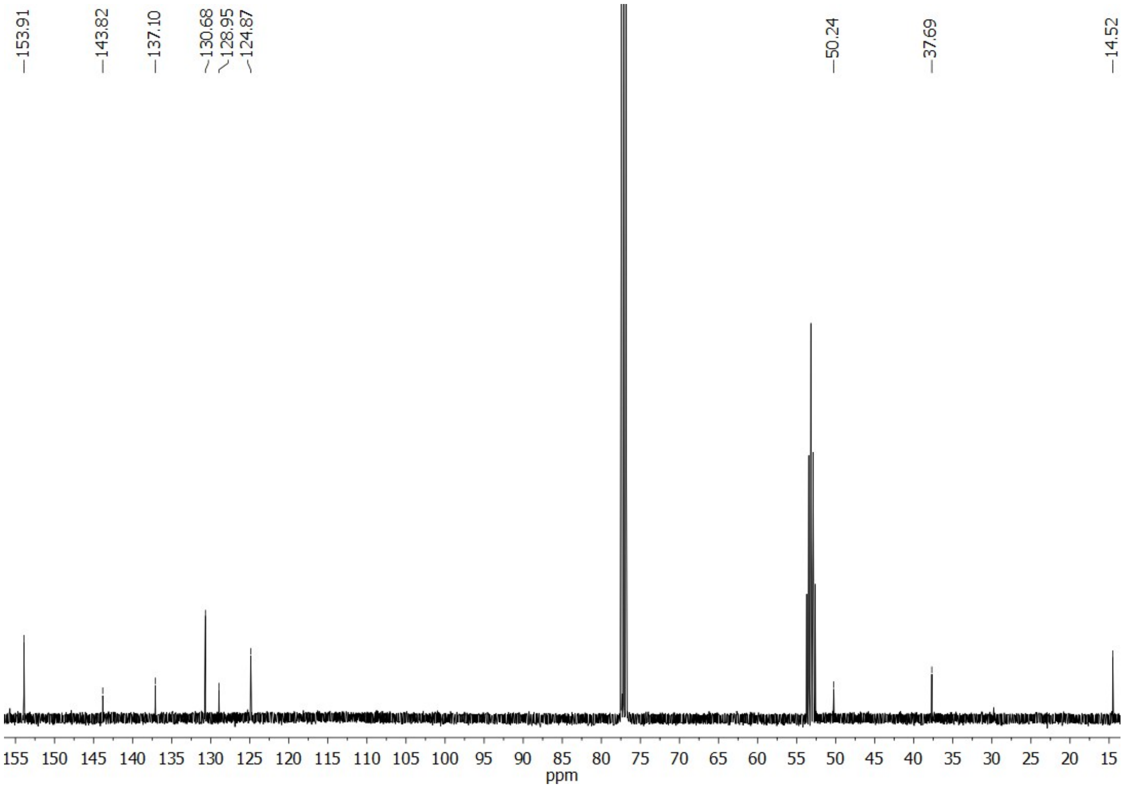

Figure S2. ${}^{13}C\{{}^1H\}$ NMR spectrum of [**2**] in $CDCl_3$:CD_2Cl.

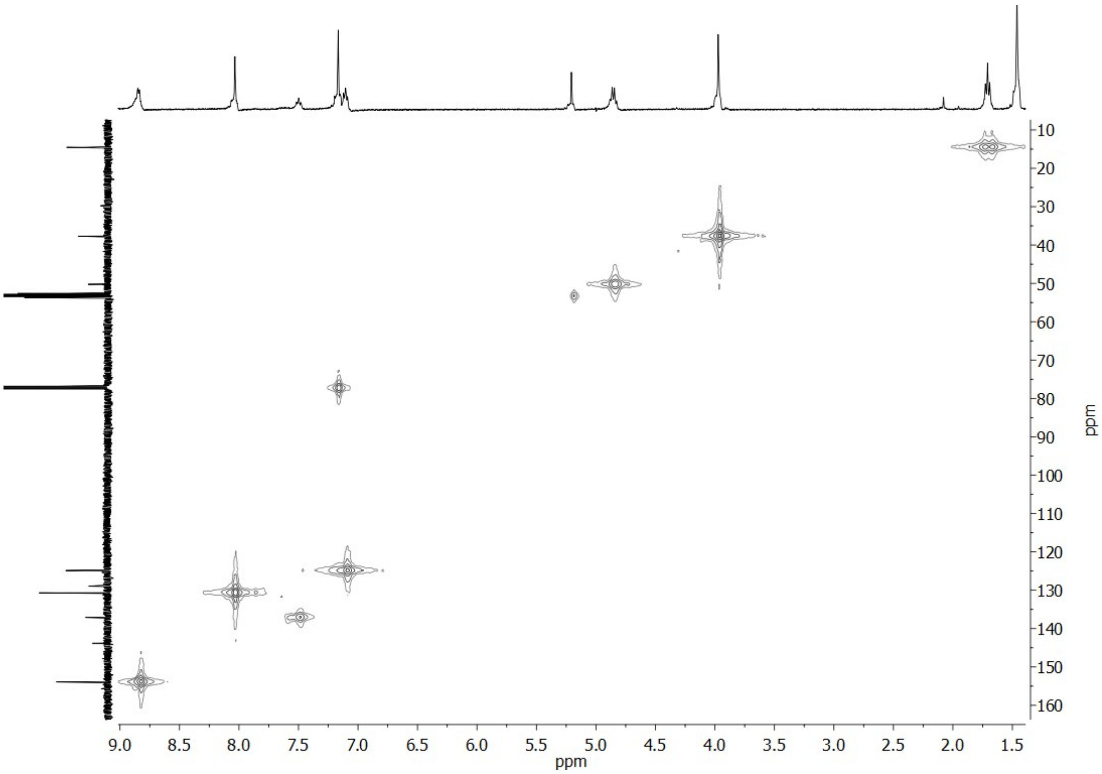

Figure S3. HMQC NMR spectrum of [**2**] in $CDCl_3$:CD_2Cl_2.

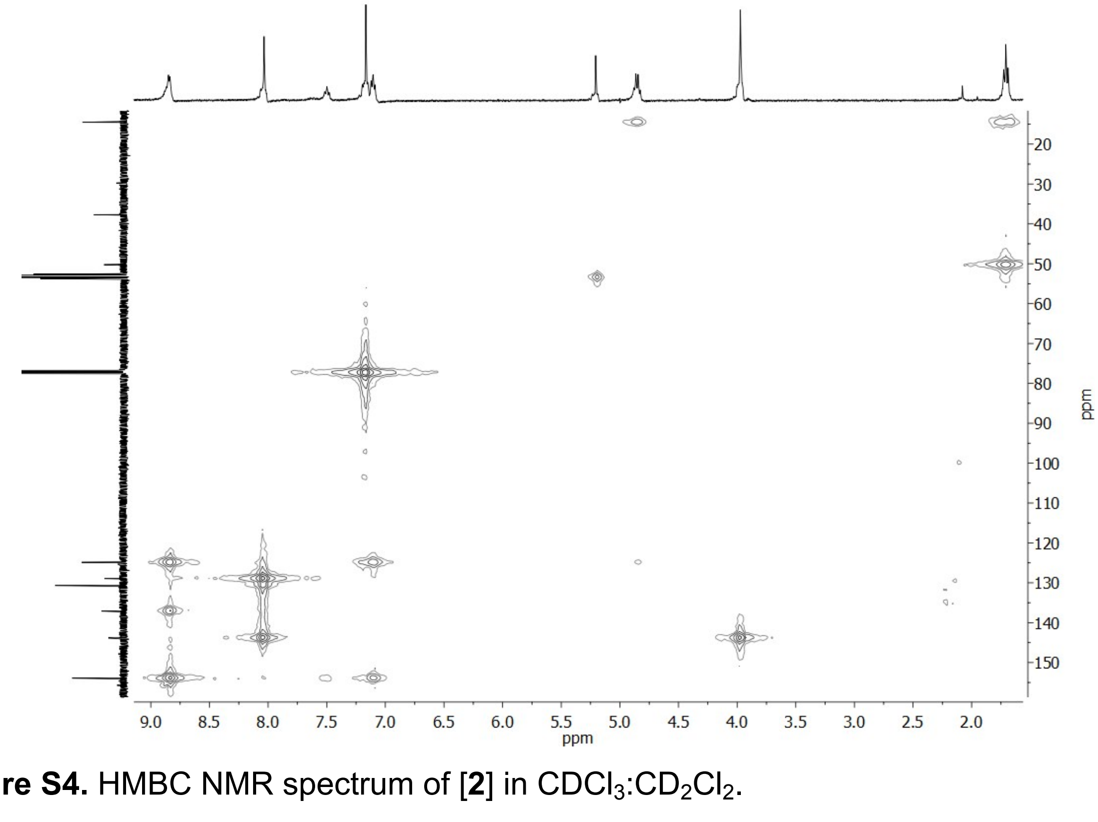

Figure S4. HMBC NMR spectrum of [**2**] in $CDCl_3$:CD_2Cl_2.

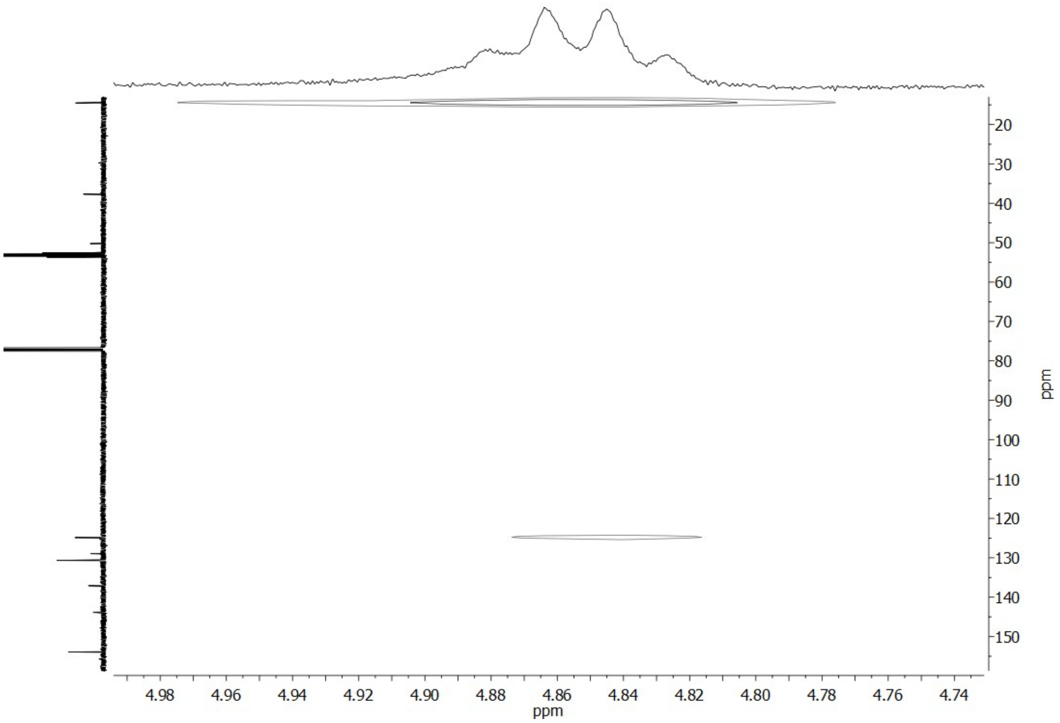

Figure S5. HMBC NMR spectrum of [**2**] in $CDCl_3$:CD_2Cl_2(only carbene correlation peaks are shown).

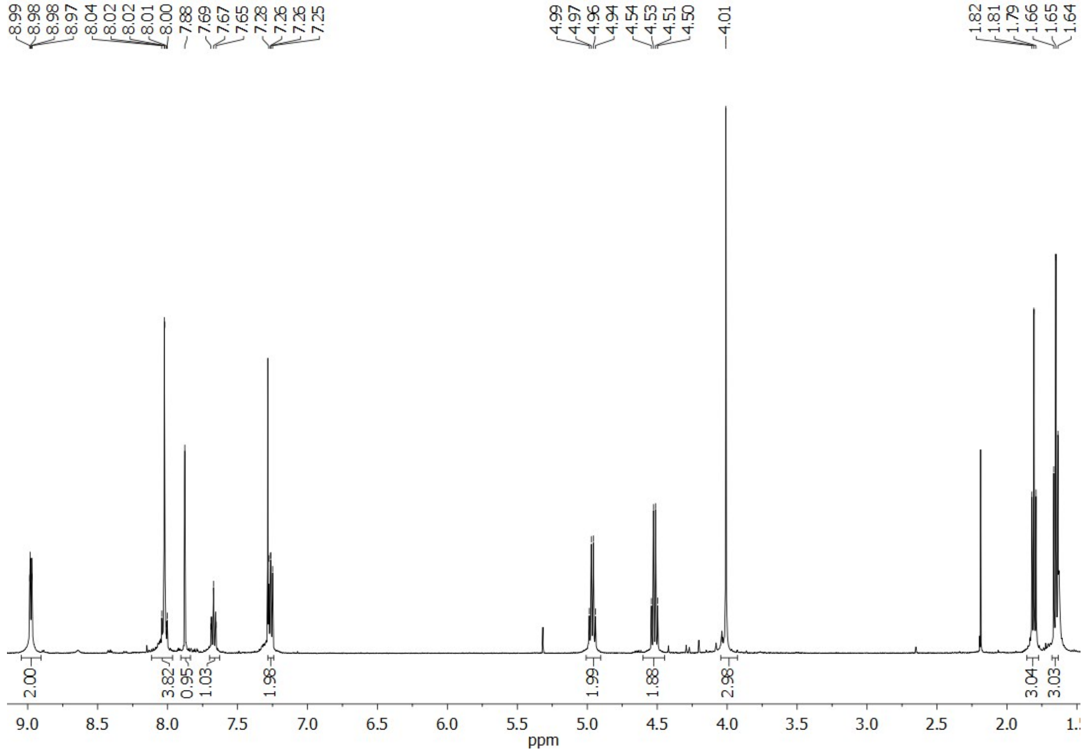

Figure S6. ^{1}H NMR spectrum of [**3**] in $CDCl_3$.

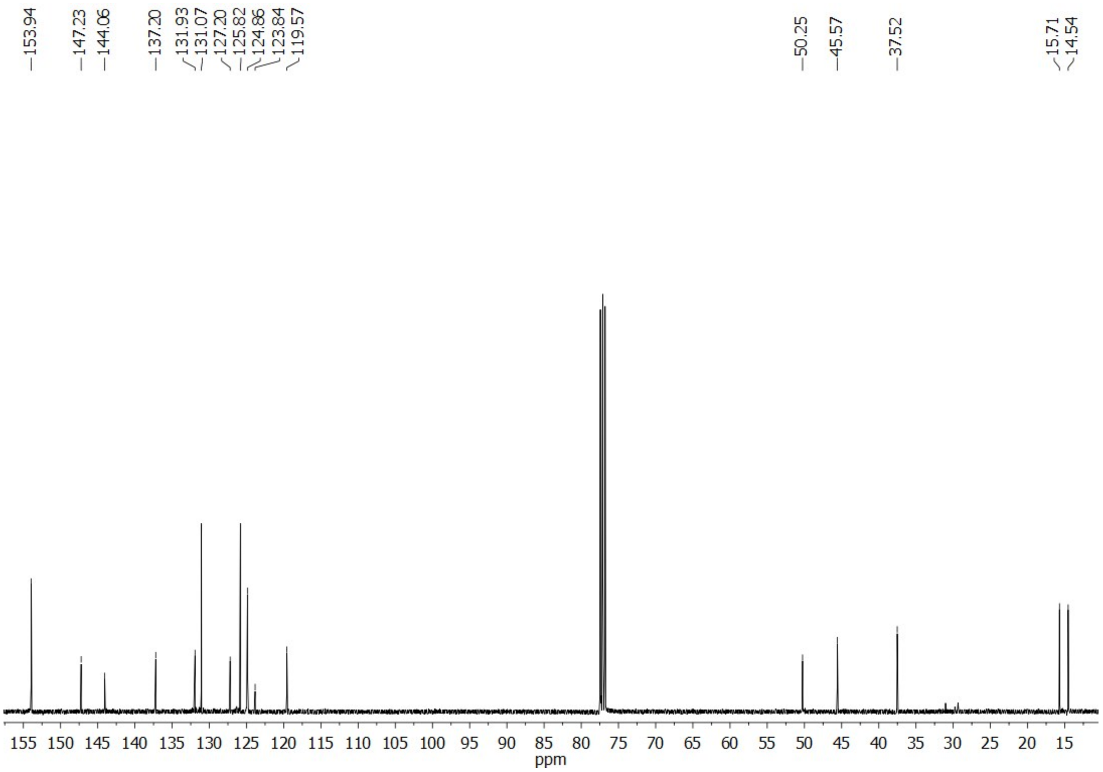

Figure S7. $^{13}C\{^1H\}$ NMR spectrum of [**3**] in $CDCl_3$.

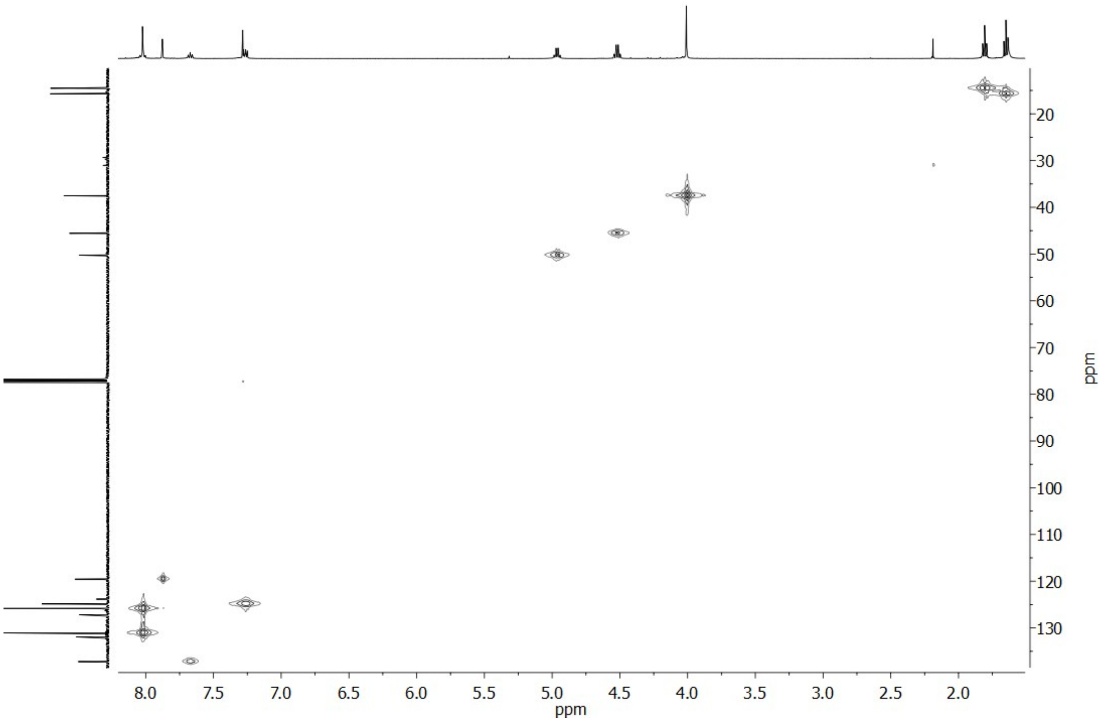

Figure S8. HMQC NMR spectrum of [**3**] in $CDCl_3$.

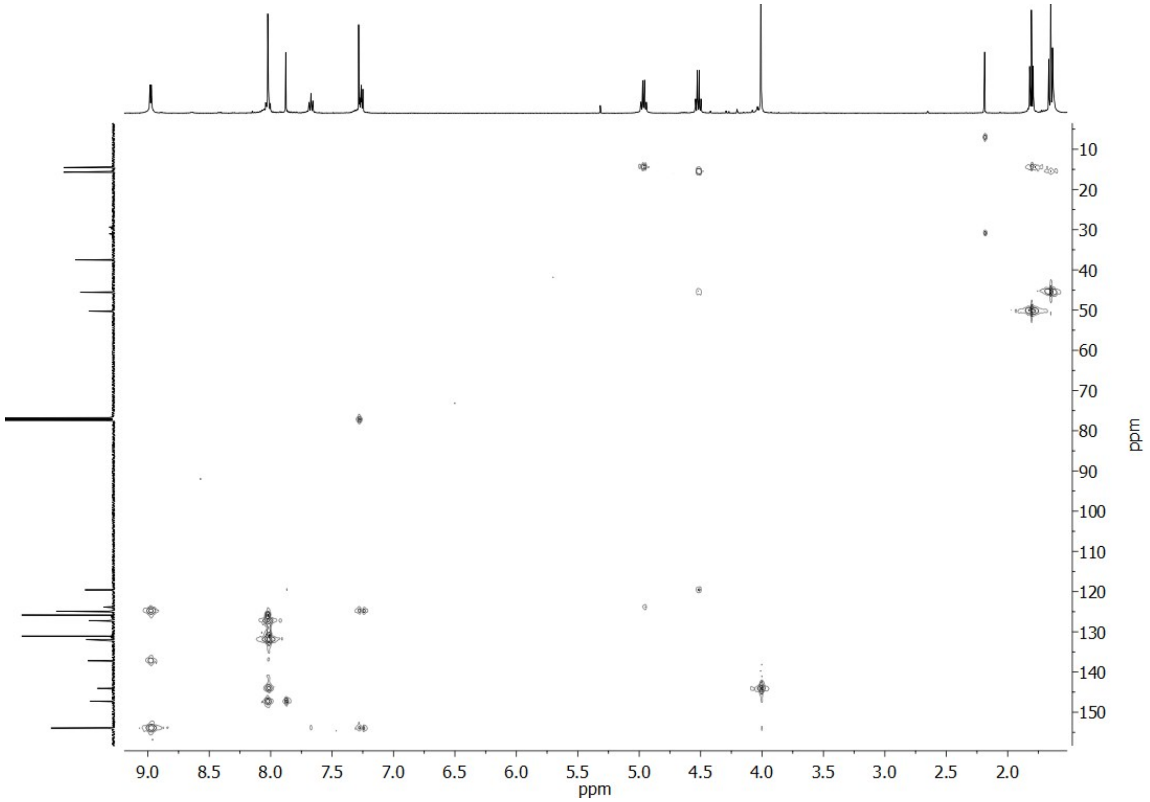

Figure S9. HMBC NMR spectrum of [**3**] in $CDCl_3$.

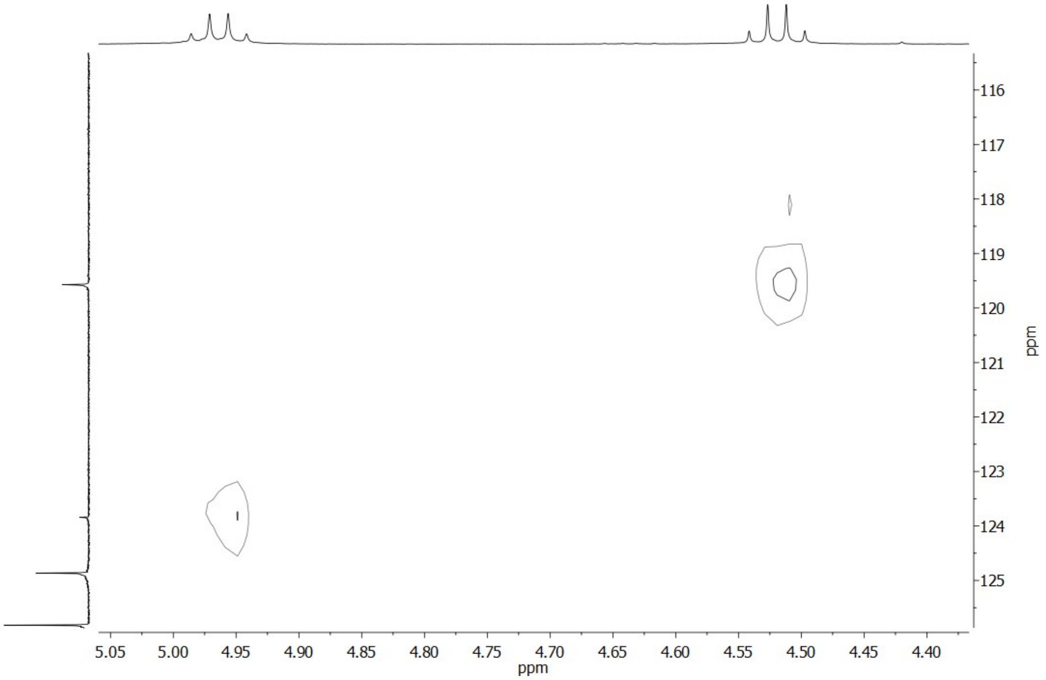

Figure S10. HMBC NMR spectrum of [**3**] in $CDCl_3$ (only carbene correlation peaks are shown).

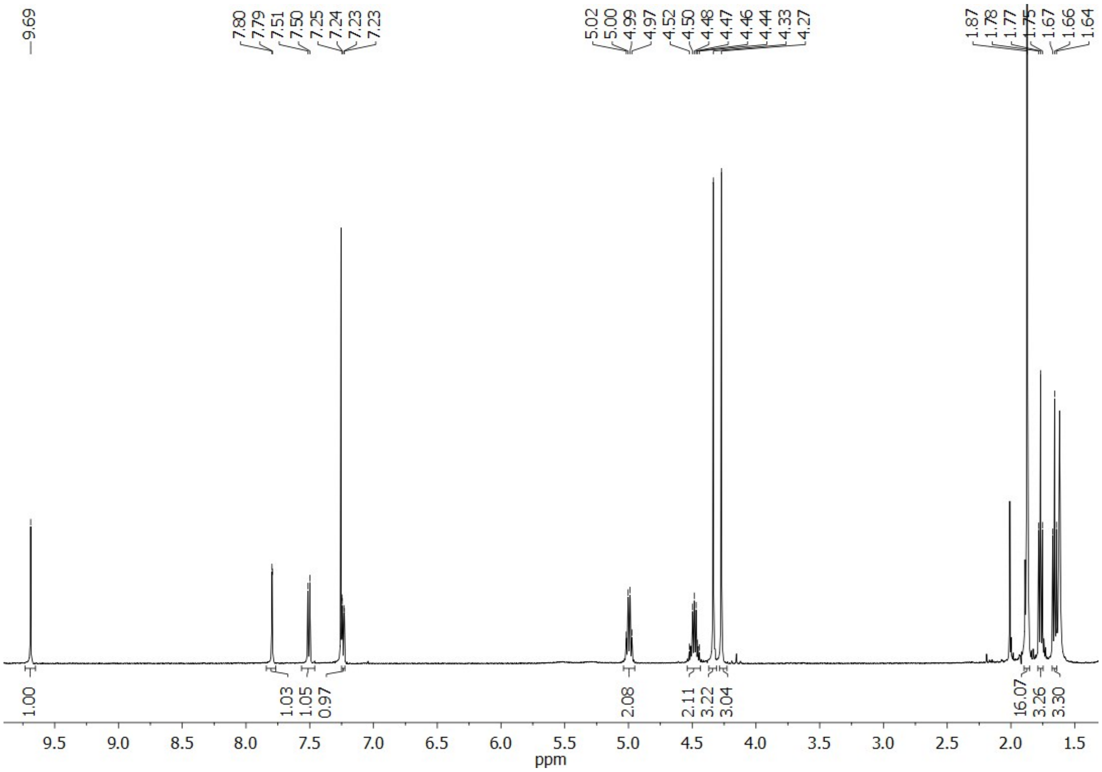

Figure S11. ^{1}H NMR spectrum of [**4**] in CDCl$_3$.

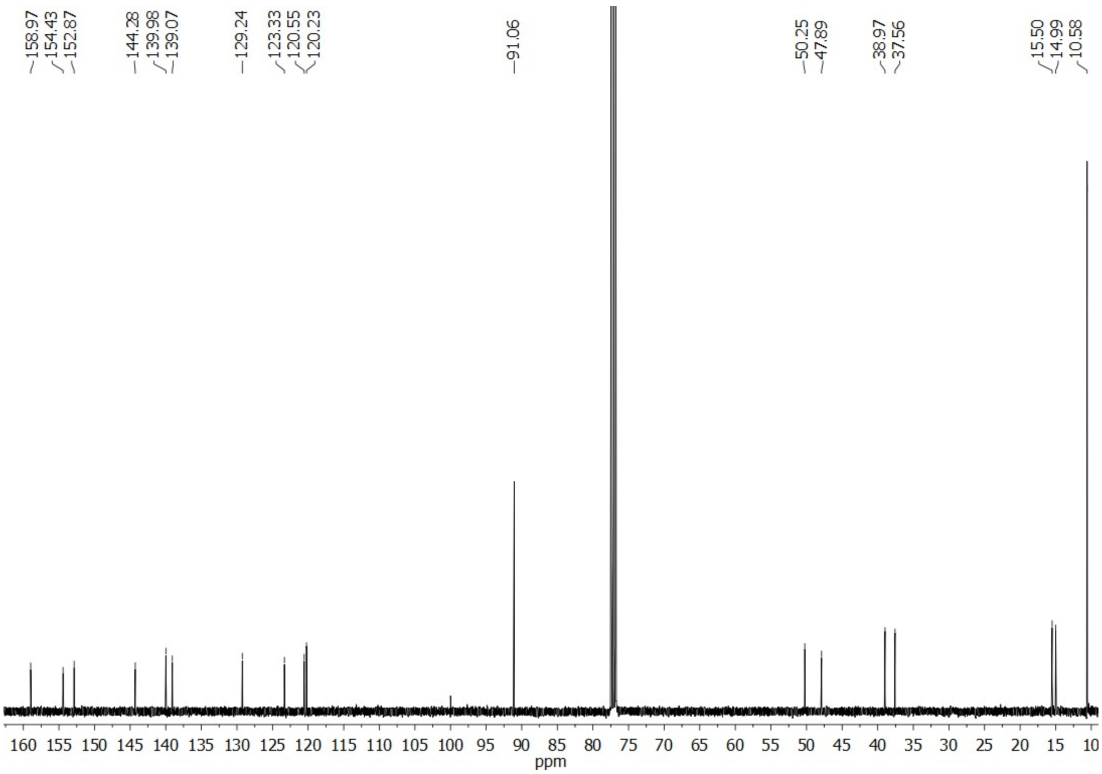

Figure S12. ^{13}C{^{1}H} NMR spectrum of [**4**] in CDCl$_3$.

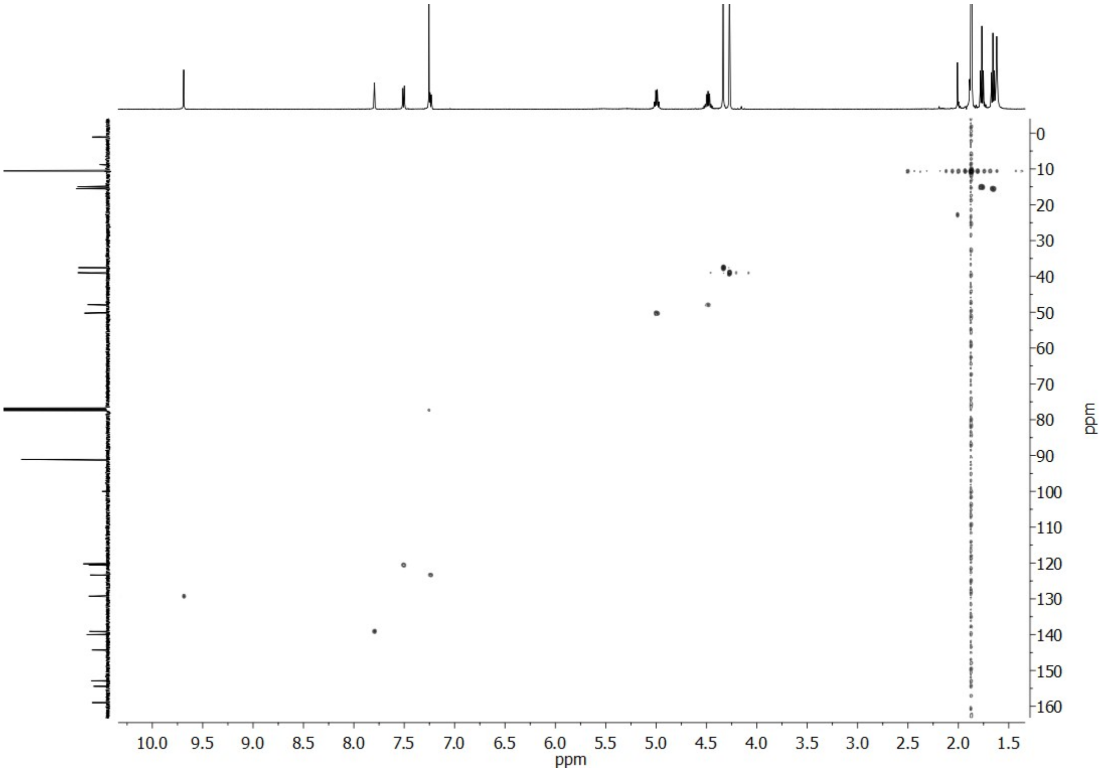

Figure S13. HMQC NMR spectrum of [**4**] in $CDCl_3$.

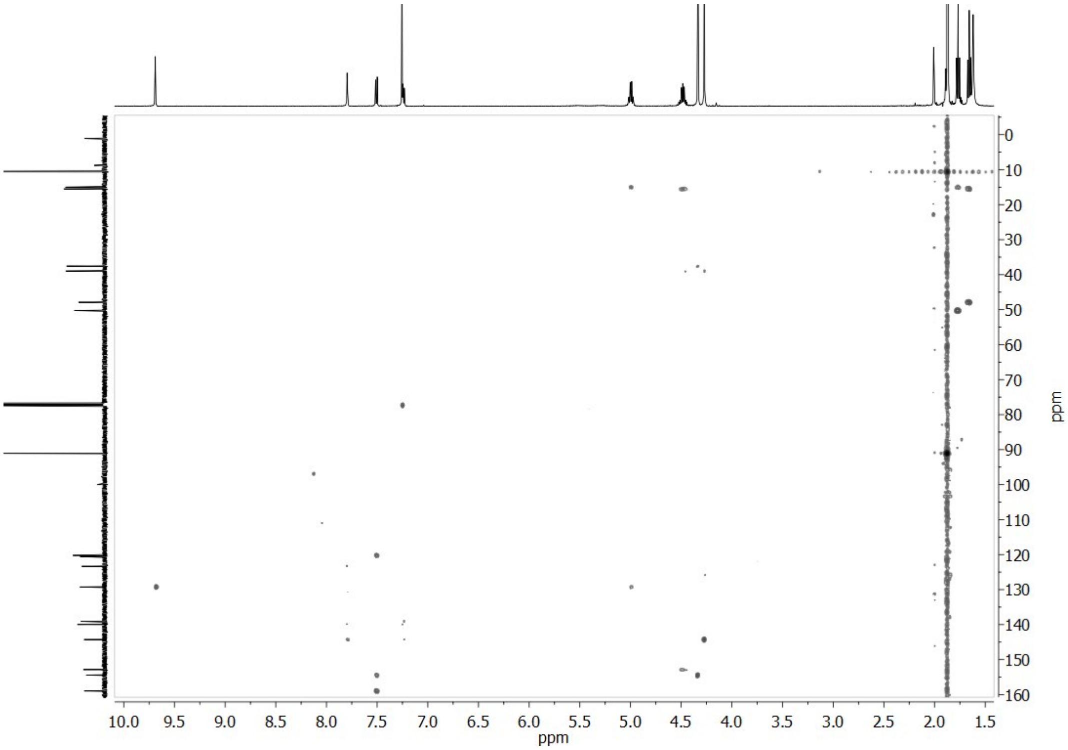

Figure S14. HMBC NMR spectrum of [**4**] in $CDCl_3$.

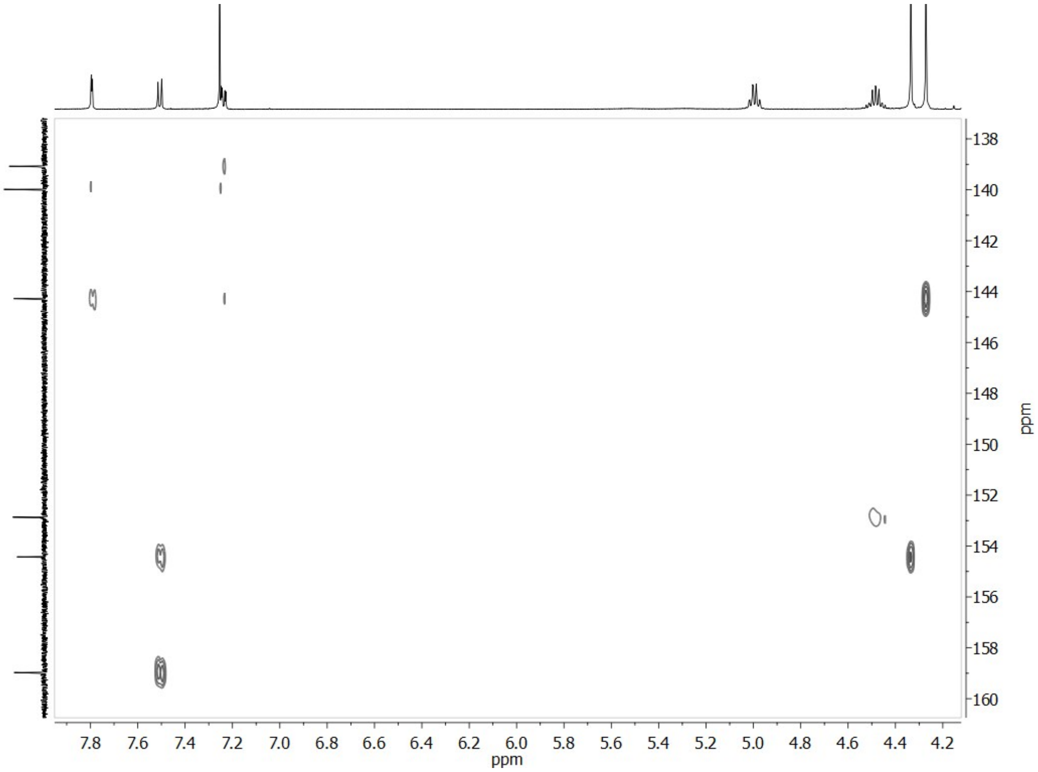

Figure S15. HMBC NMR spectrum of [**4**] in $CDCl_3$.

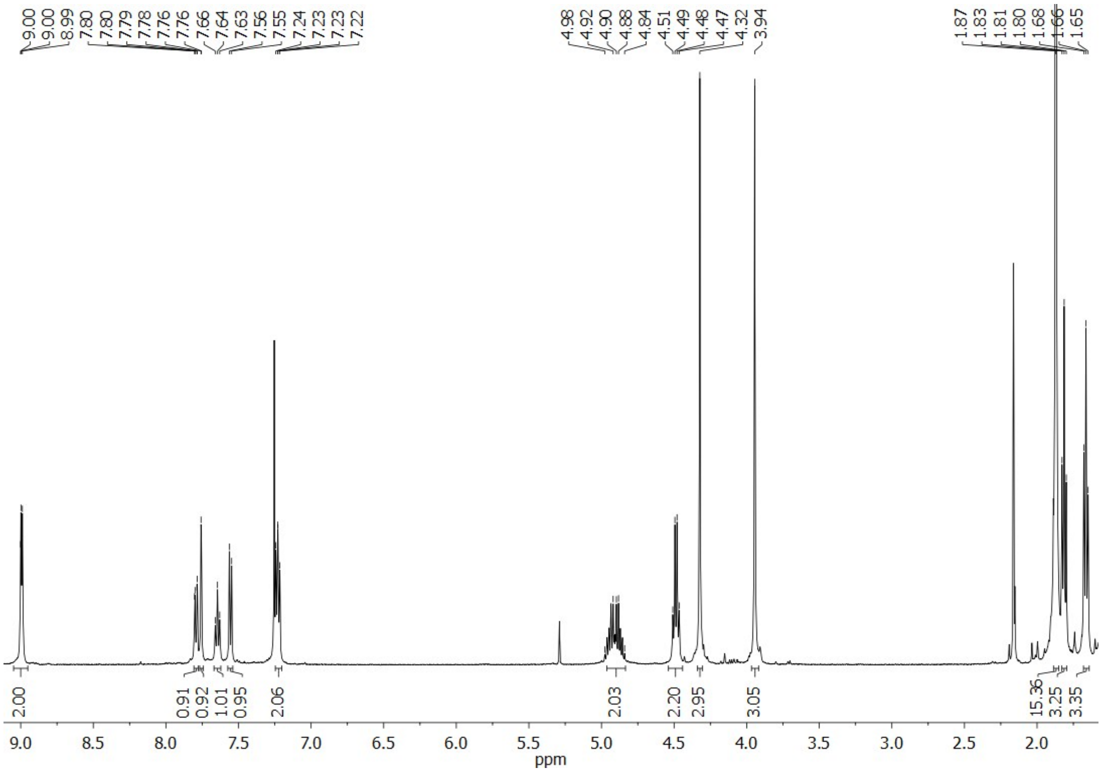

Figure S16. ^1H NMR spectrum of [**5**] in $CDCl_3$.

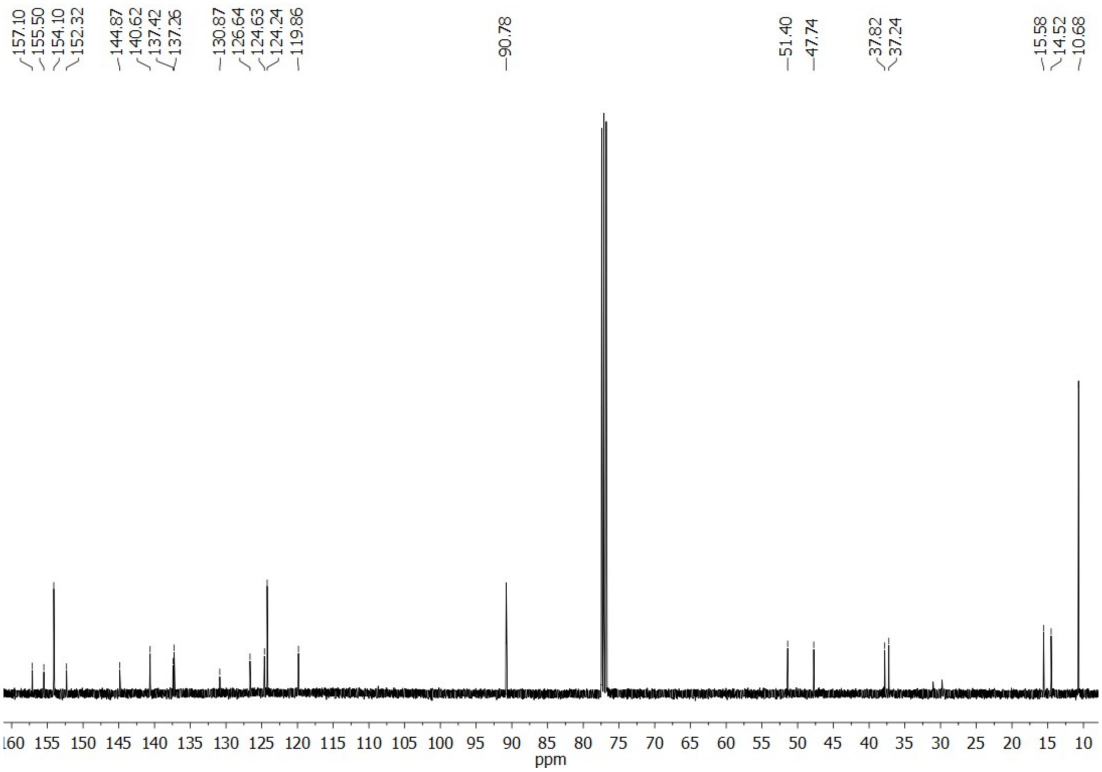

Figure S17. $^{13}C\{^1H\}$ NMR spectrum of [**5**] in CDCl$_3$.

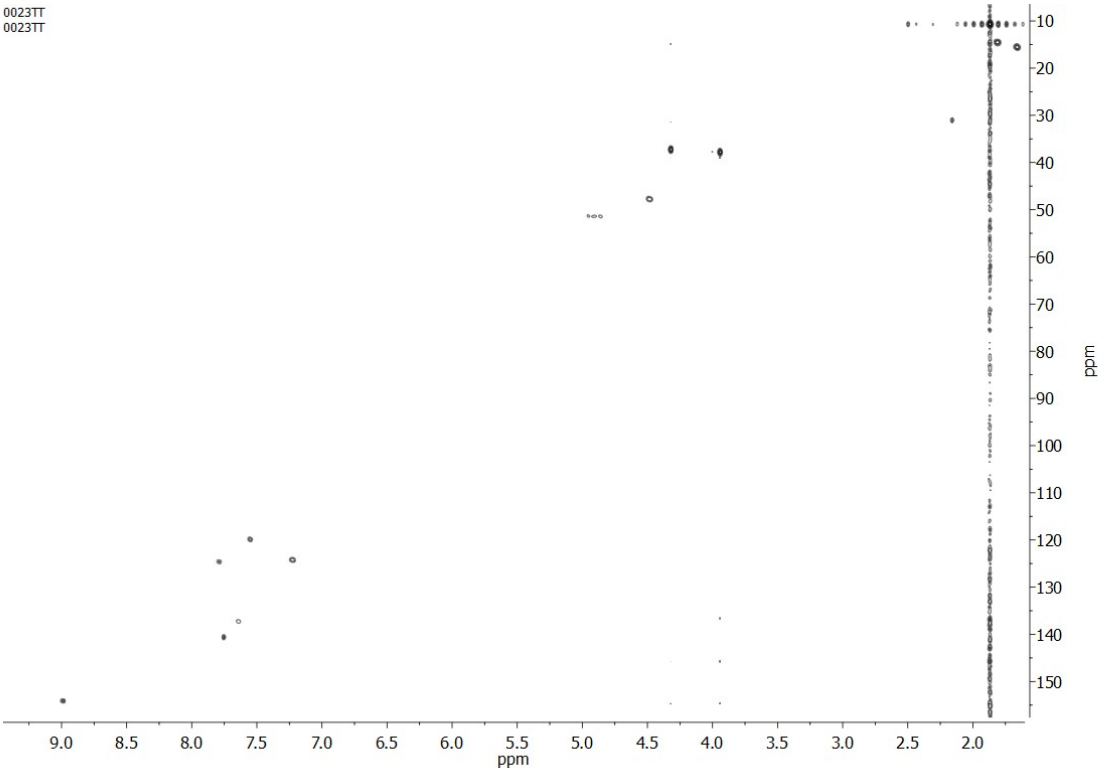

Figure S18. HSQC NMR spectrum of [**5**] in CDCl$_3$.

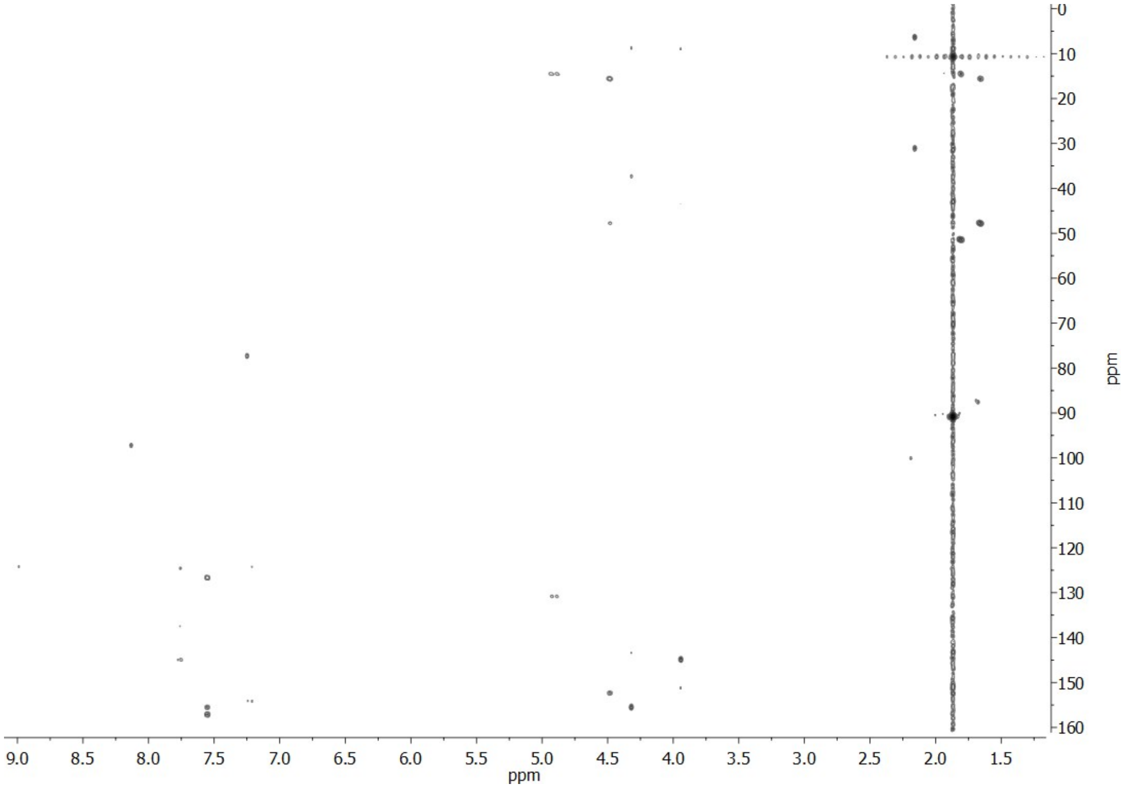

Figure S19. HMBC NMR spectrum of [**5**] in $CDCl_3$.

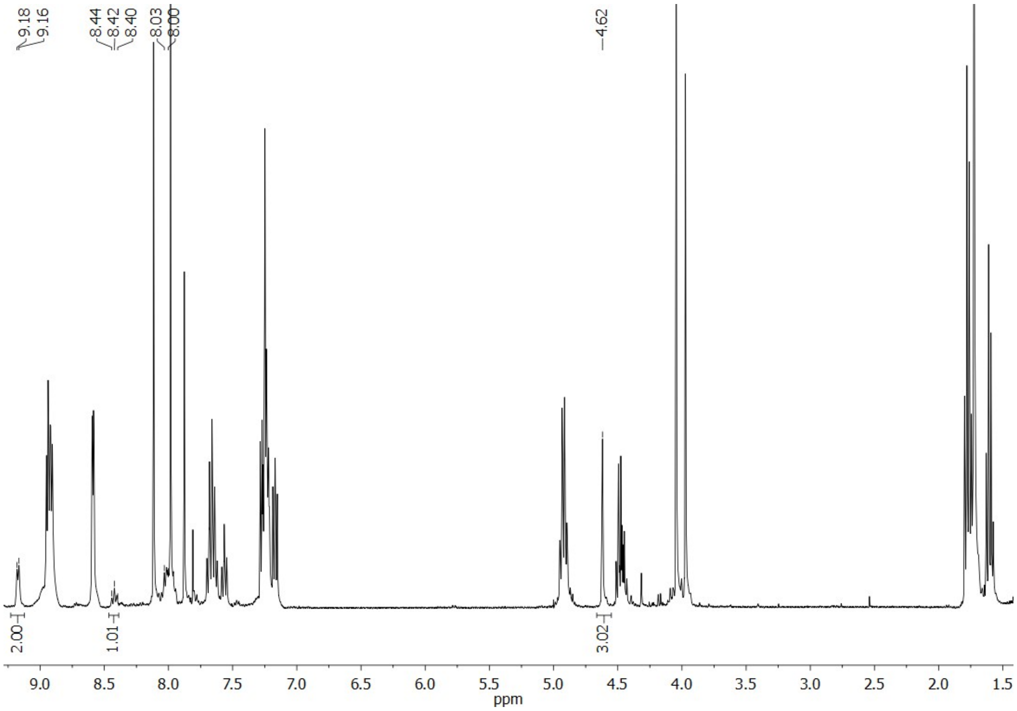

Figure S20. ^1H NMR spectrum (in $CDCl_3$) containing the crude reaction mixture depicted in Scheme 1.

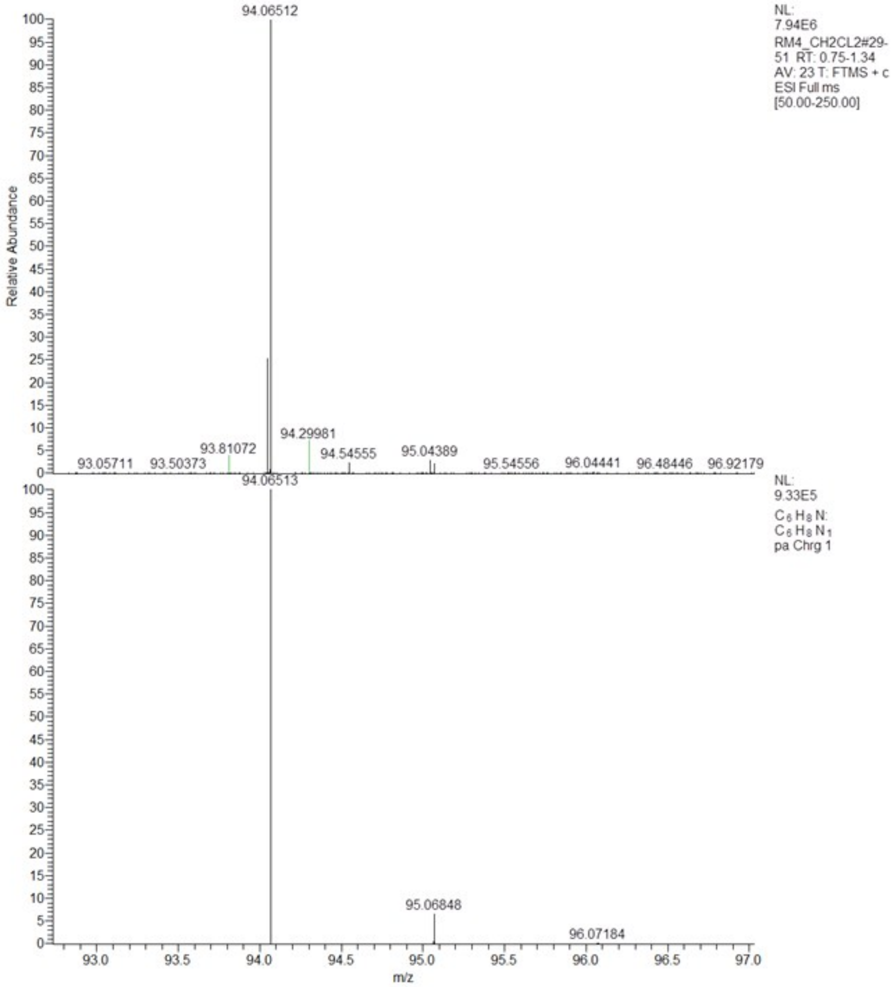

Figure S21. ESI-Mass peak for the cationic 1-methylpyridinium ion obtained from the crude reaction mixture depicted in Scheme 1 (top: experimental spectrum; bottom: calculated isotopic pattern).