Cycloisomerization of dienes and enynes catalysed by a modified ruthenium carbene species

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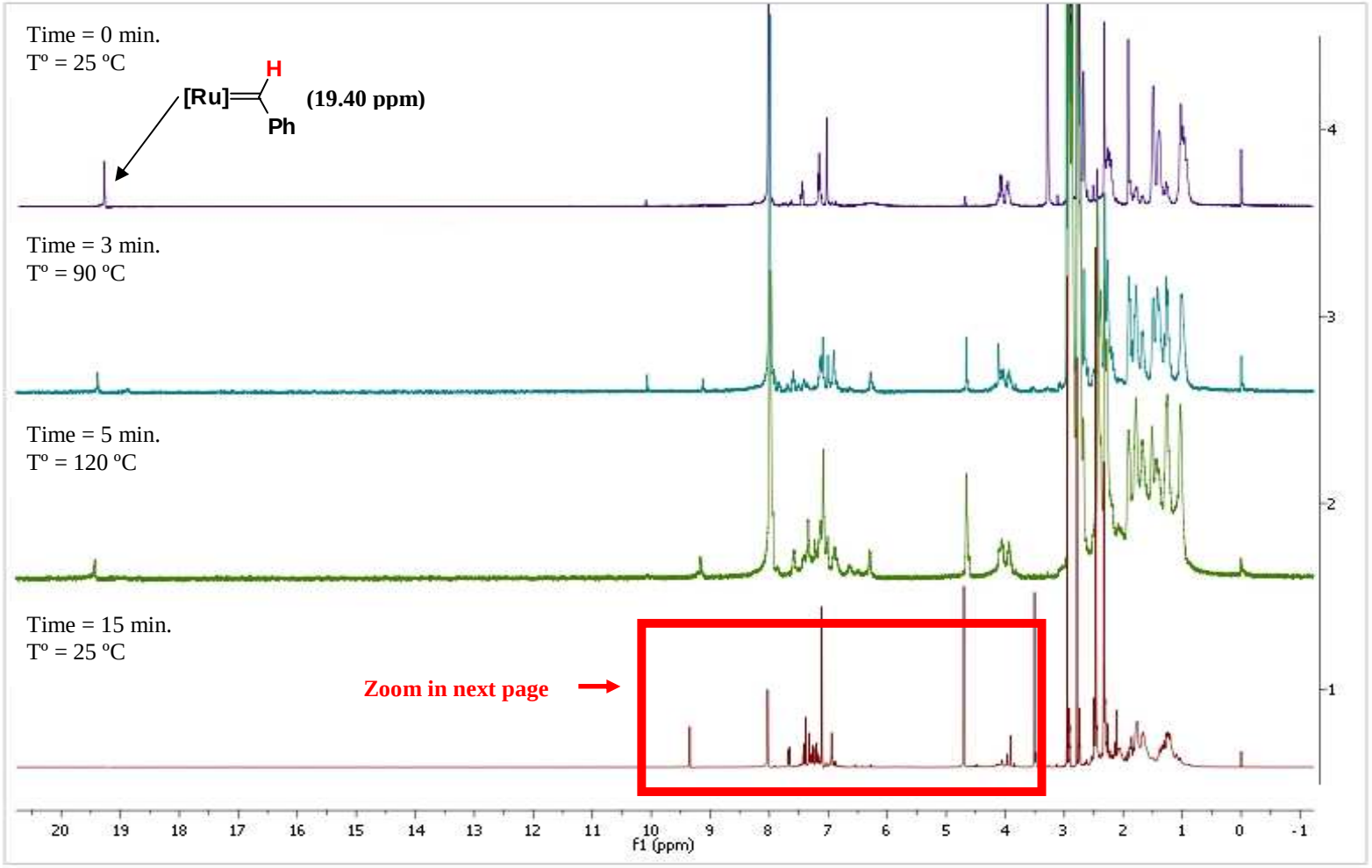
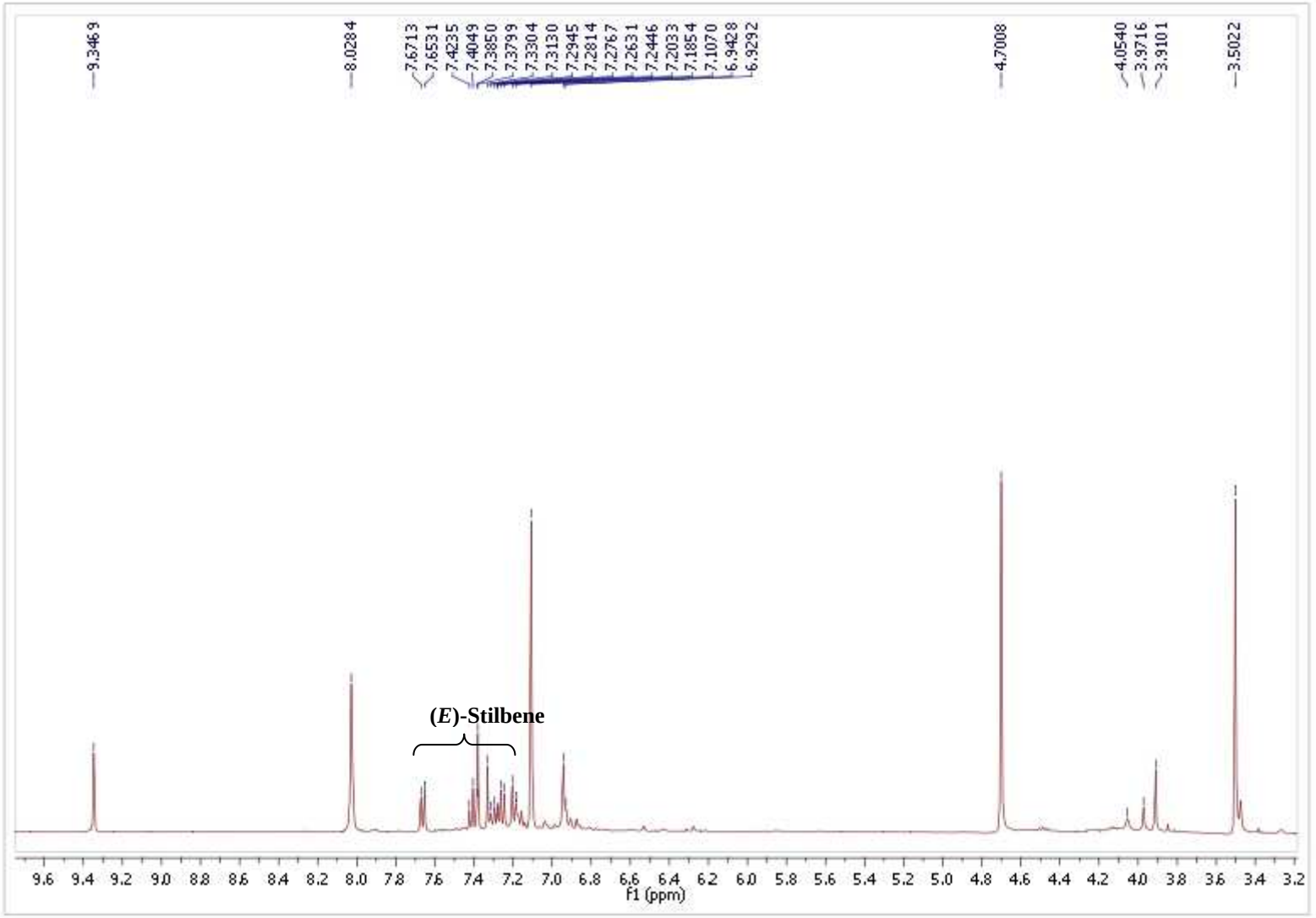
Supplementary material 2

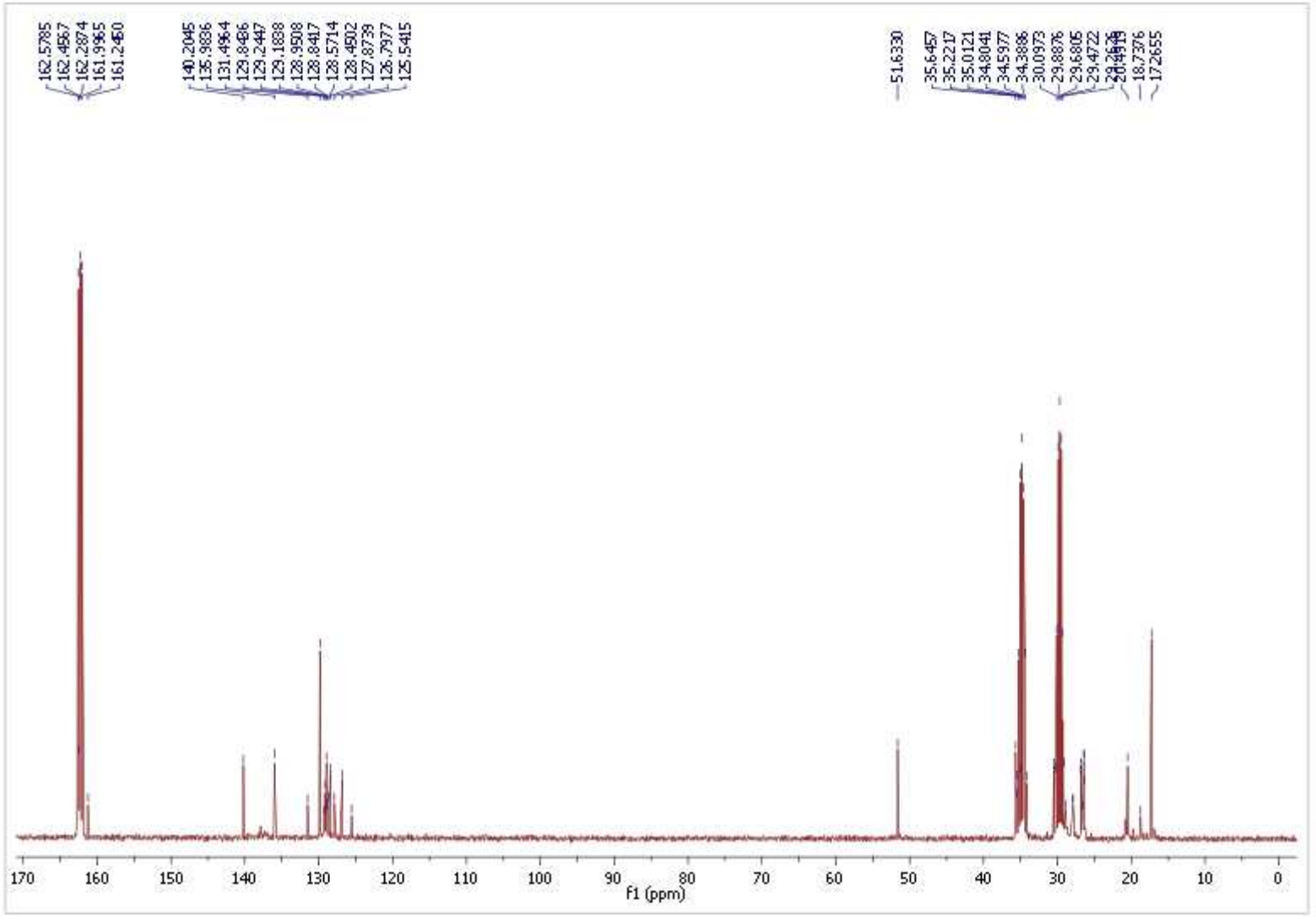
^{1}H Kinetics experiment with [Ru]-II (DMF-d_7) (400 MHz):

Catalyst **[Ru]-II** (20 mg, 0.023 mmol) was loaded in an NMR tube and anhydrous DMF-d_7 (99.5 atom % D) (0.7 mL) and one drop of anhydrous DMF was added. The tube was filled with argon, closed and the temperature was progressively increased (30 ºC/minute) and ^{1}H was adquired every min. After 15 min the NMR tube was removed and quickly ice-cooled in order to stop the reaction. The last ^{1}H spectra was the acquired at 25 ºC.

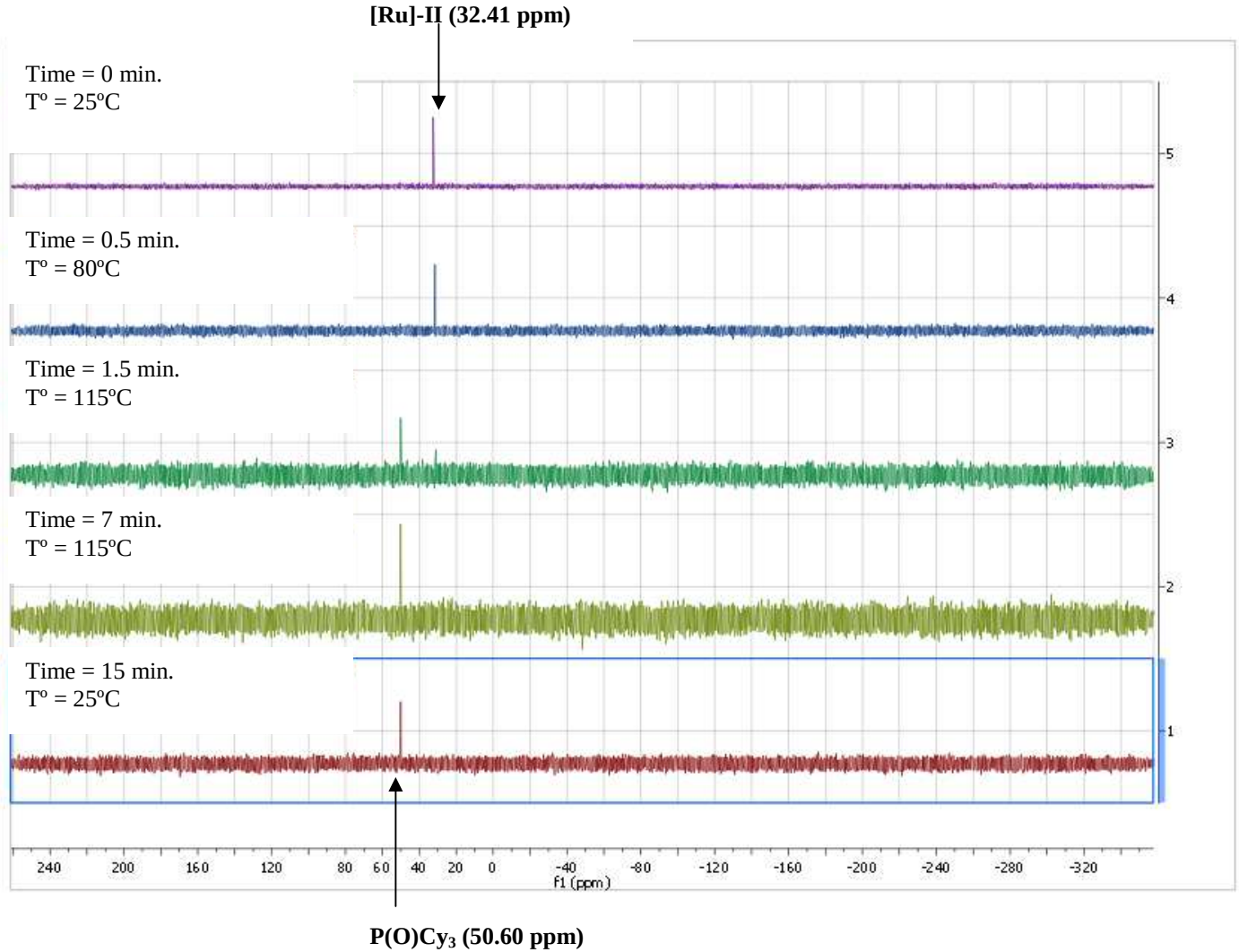




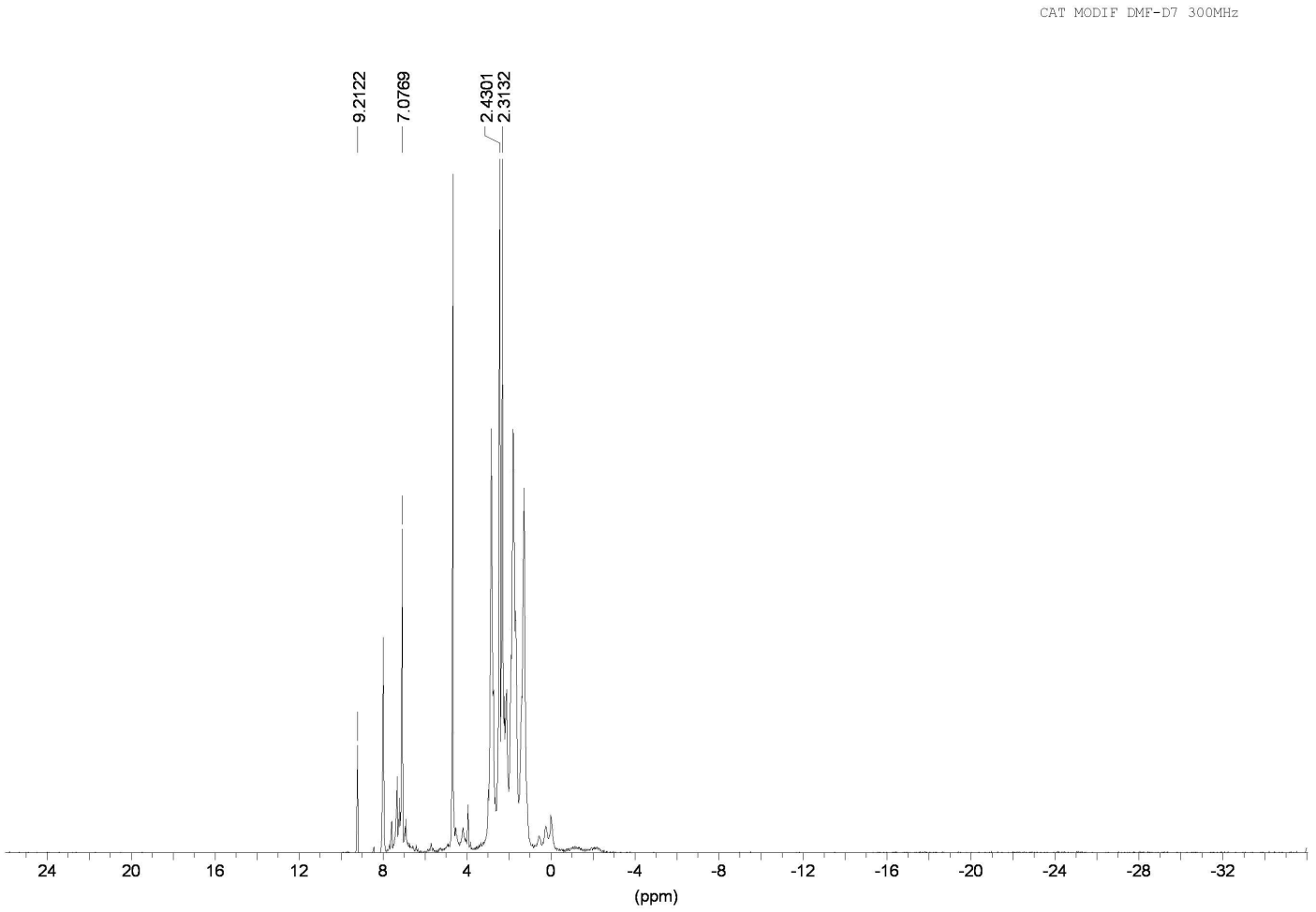
^{13}C spectrum of catalyst [Ru]-II modification reaction mixture after 15 min: (DMF-d_7) (400 MHz):



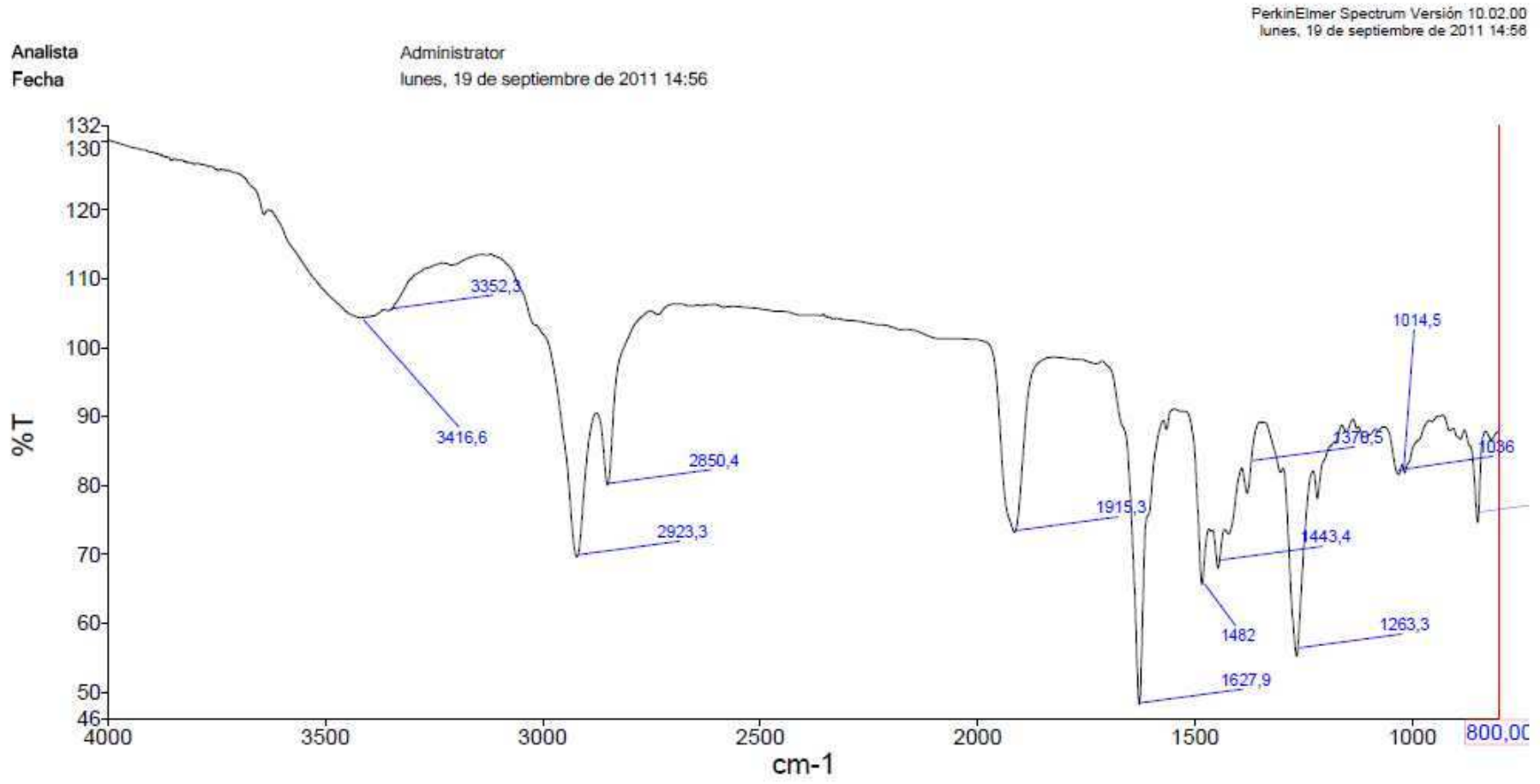
^{31}P Kinetics experiment with [Ru]-II (DMF-d_7) (300 MHz):



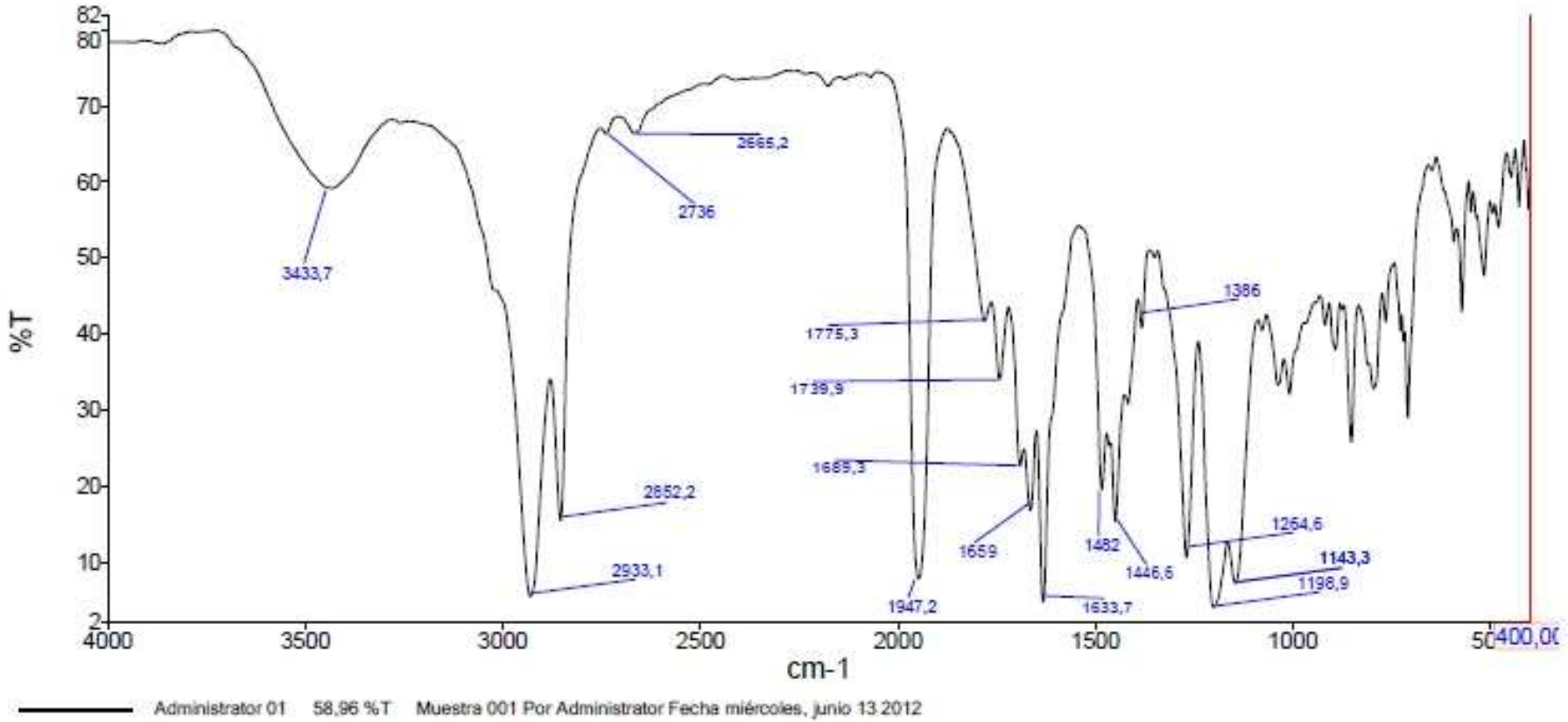
^{1}H of crude modified species conducted down to -35 ppm (DMF-d_7) (300 MHz):



IR spectrum of catalyst [Ru]-II modification reaction mixture after 7 min:



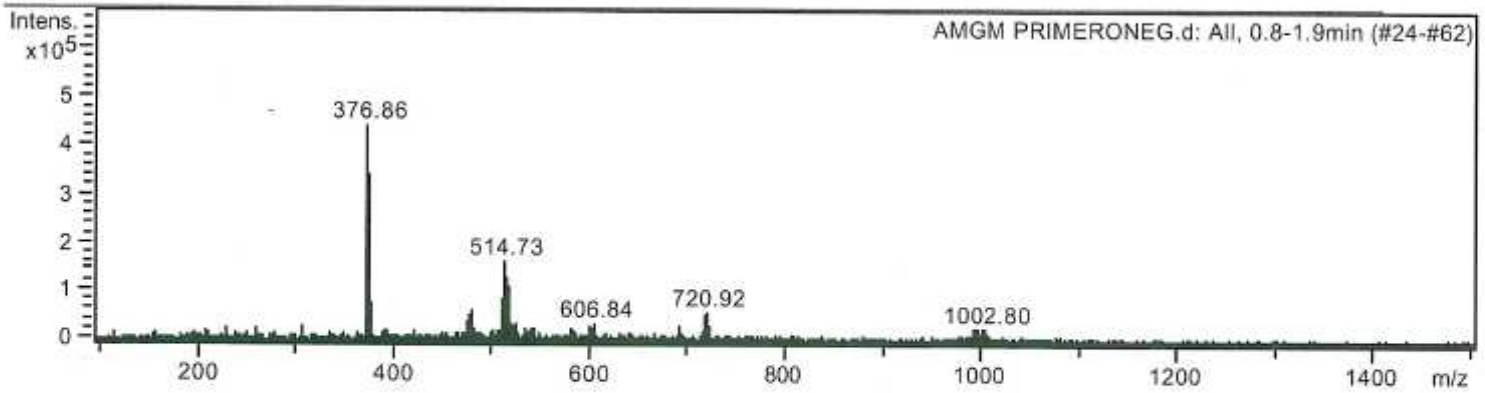
IR spectrum of catalyst [Ru]-II modification reaction mixture after 15 min:



MS spectrum of catalyst [Ru]-II modification reaction mixture after 7 min and 15 min:

Acquisition Parameter

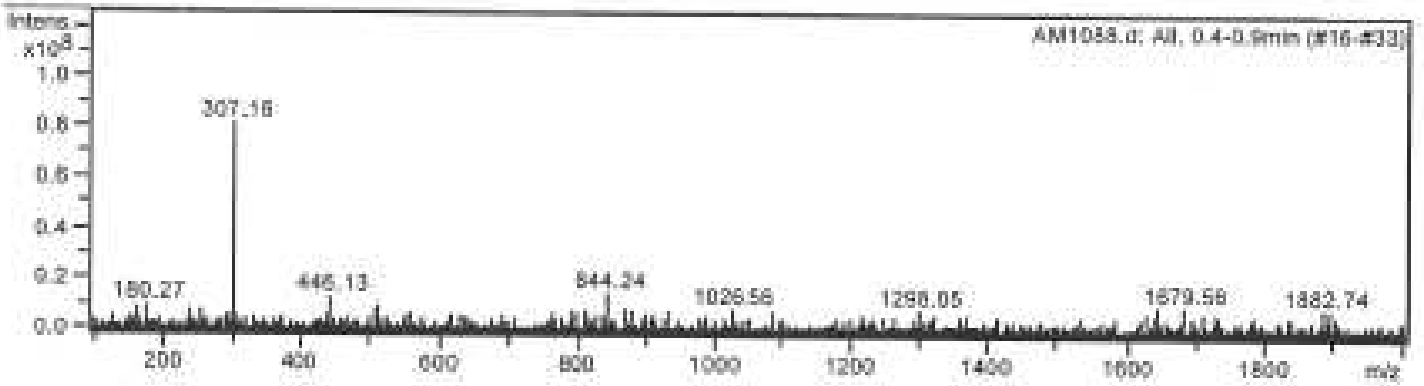
Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	100 m/z	Scan End	1500 m/z
Capillary Exit	-84.9 Volt	Skim 1	-17.4 Volt	Trap Drive	48.2
Accumulation Time	100000 µs	Averages	8 Spectra	Auto MS/MS	off



#	m/z	I	I %
1	376.86	432528	100
2	377.84	97711	23
3	378.86	337628	78
4	379.83	73423	17
5	482.75	59099	14
6	513.69	81880	19
7	514.73	162090	37
8	515.69	108420	25
9	516.67	125141	29
10	518.73	105765	24

Acquisition Parameter

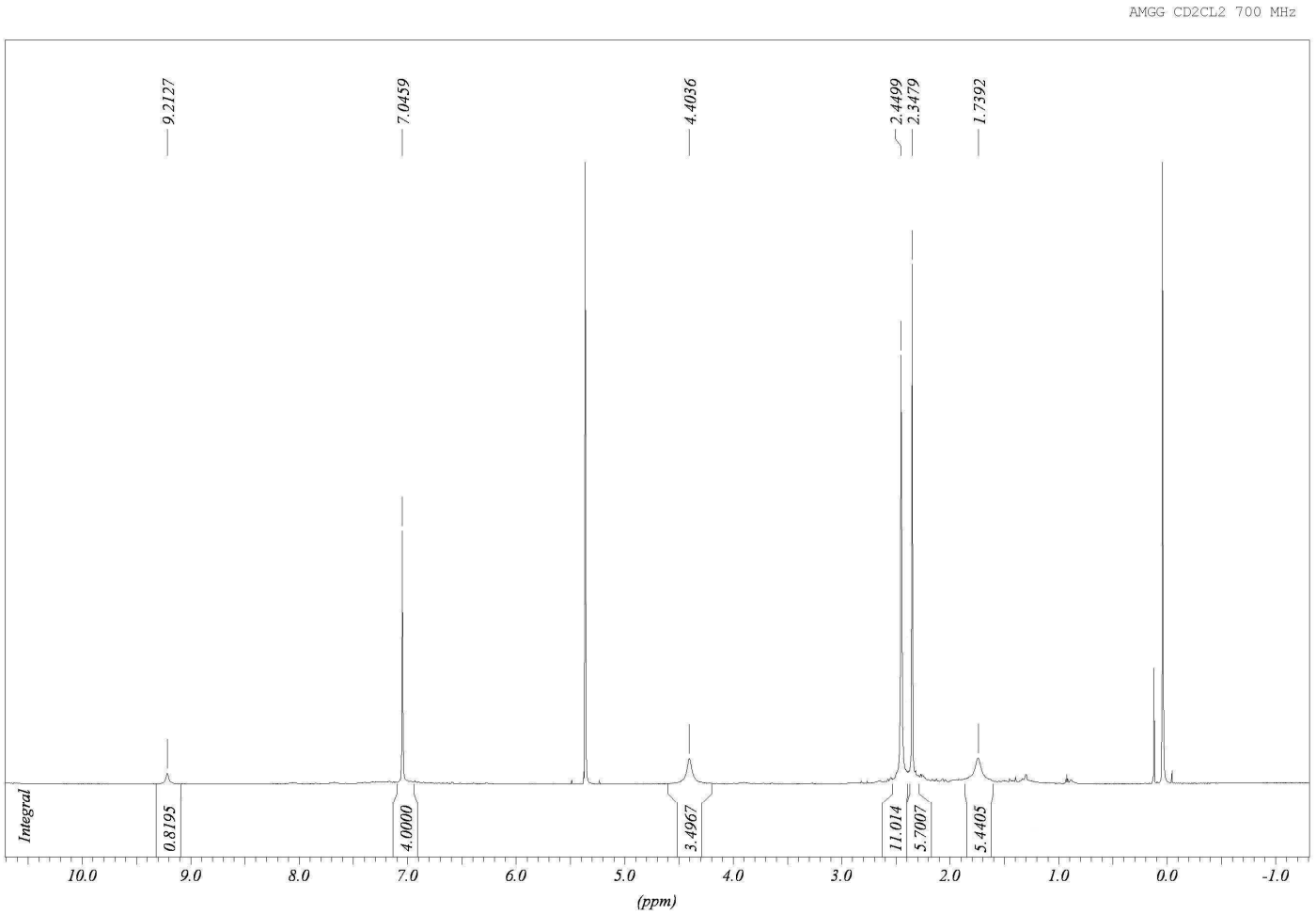
Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	108 m/z	Scan End	2000 m/z
Capillary Exit	91.8 Volt	Skim 1	22.9 Volt	Trap Drive	56.5
Accumulation Time	103 µs	Averages	8 Spectra	Auto MS/MS	off



#	m/z	I	I %
1	180.27	8914214	11
2	307.16	86015434	100
3	308.19	18408679	21
4	446.13	12341977	15
5	513.48	9301282	12
6	844.24	14321343	16
7	1640.05	9989929	12
8	1679.56	10028928	13
9	1882.74	8938813	11
10	1892.38	8929759	11

Isolation of 1,3-*bis*-(2,4,6-trimethylphenyl)imidazolinium chloride: Catalyst **[Ru]-II** (80 mg, 0.094 mmol) was placed in a flame-dried two-necked flask, and two cycles of vacuum-argon were performed. Anhydrous DMF (2 mL) was added and the suspension was heated at 130 ºC for 12 min. The solvent was eliminated under reduced pressure (1 mbar, 80 ºC), the dark oily residue was cooled to 4 ºC and solved in cold toluene (0.8 mL). Cold hexane was added until a black oily residue precipitated and the supernatant was removed. The oil was washed twice with toluene (0.5 mL), hexane (2 mL) and dried under vacuum, affording 21 mg of a black oil. ^{1}H NMR (700 MHz, CD_2Cl_2) δ9.21 (bs, 1H), 7.04 (s, 4H), 4.40 (bs, 4H), 2.45 (s, 12H), 2.35 (s, 6H); ^{13}C NMR (175 MHz, CD_2Cl_2) δ160.7, 140.6, 135.0, 130.2, 130.0, 53.5, 21.1, 18.3.

1,3-*bis*-(2,4,6-trimethylphenyl)imidazolinium chloride ^{1}H RMN spectrum:



1,3-*bis*-(2,4,6-trimethylphenyl)imidazolinium chloride ^{13}C RMN spectrum: