Electronic Supplementary Material (ESI) for ChemComm.

Modification of Fulleropyrazolines Modulates Their Cleavage by Light

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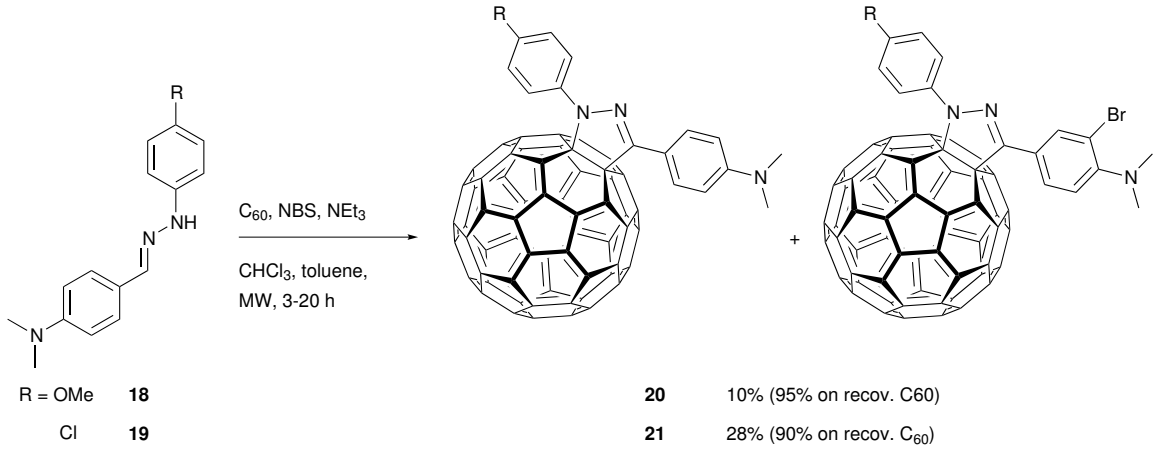
Contents

1 Supplementary Discussion

1.1 Synthetic Scope

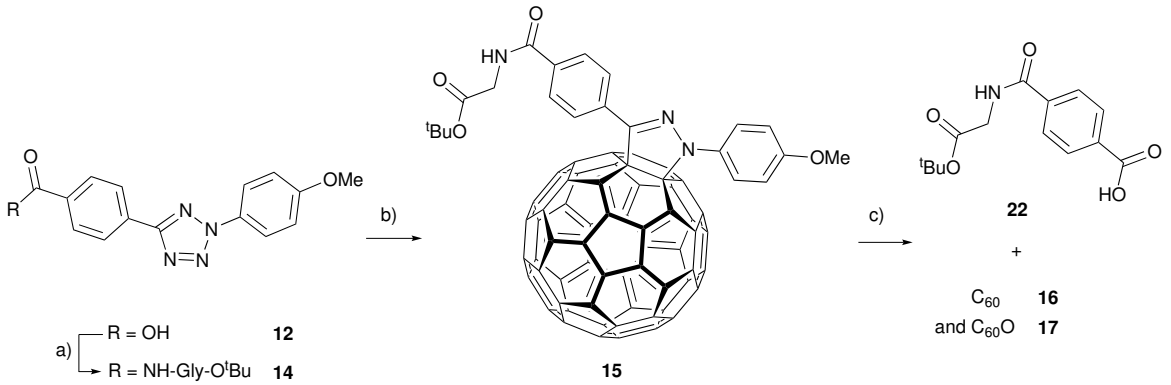
A broader substrate scope applicable to the photocleavage reaction was examined. Attempted synthesis of fulleropyrazolines bearing a simple benzyl or alkyl chain were unsuccessful. For example, heptanal formed an acetal and could not be condensed to give the requisite hydrazone. Reaction between benzaldehyde and *para*-methoxyphenylhydrazine gave an unstable hydrazone[1] which could not be used in the following fulleropyrazoline synthesis.
Furthermore, problems occurred during the synthesis of pyrazolines with electron donating substituted hydrazones like **5**, **18**, and **19**. When using *N*-bromosuccinimide (NBS) for the generation of the 1,3-dipole in the fulleropyrazoline synthesis of **20** and **21** we isolated an inseparable mixture of products (Scheme S1). Monobromination occurred *ortho* to the dimethyl amino group. For the synthesis of **10** we used the mild halogenating agent (diacetoxyiodo)benzene[2] to avoid formation of a similar byproduct.



Scheme S1: Reagents and conditions: hydrazone (1 eq.), NBS (1.5 eq.), $CHCl_3$ [7 mM], r.t., 30 min; then C_{60} (1 eq.), NEt_3 (3 eq.), toluene [5.2 mM], microwave.

1.1.1 Photocleavage of Functionalised Fulleropyrazoline 15

The carboxylic acid group on the benzyl moiety of the fulleropyrazoline system was introduced as a putative handle for further modification. We synthesised an amino acid coupled derivative (**15**) and subjected it to light (Scheme S2). The photocleavage was successful in organic solvents such as chloroform and benzonitrile and in their aqueous emulsions (1:1). The cleavage products were evaluated directly from the solvent mixture $CDCl_3/D_2O$ 1:1 by NMR, IR, mass spectrometry and HPLC. Besides the release of benzoic acid **22** two oxidised *p*-anisole derivatives were formed in the ratio **22**/**23**/**24** 2.5:1.9:1. The product formation is discussed in Section 1.4.1 for the photocleavage of fulleropyrazoline **7**.



Scheme S2: Reagents and conditions: a) tetrazole **12** (1 eq.), H-Gly-O^{t}Bu (1.5 eq.), HATU (2 eq.), DIPEA (2 eq.), DMF [60 mM], r.t., 1 h, 67%; b) C_{60} (5 eq.), toluene [1 mM], hν = 313 nm, 5.5 h, 25%; c) medium pressure Hg-lamp, solvents [1 mM], r.t.

1.2 Reverse Phase HPLC

The photocleavage reaction was followed by t.l.c. and reverse phase high pressure liquid chromatography (RP-HPLC) on a Waters® 2795 AllianceHT using a TSKgel ODS 80TM column ($150 \cdot 4.5\ mm, 5\ \mu m$) and a gradient of hexane in ^{i}PrOH 20%→50% over 10 minutes.[3,4,5] Samples (10 μL, 1 mg/mL) were injected and elution products monitored by UV/vis absorption over a spectrum ($220\ nm < \lambda < 400\ nm$). The retention times were as follows: C_{60} $t_R = 9.1\ min$; $C_{60}O$ $t_R = 8.7\ min$; presumed $C_{60}O_2$ $t_R = 8.3\ min$; presumed $C_{60}O_3$ $t_R = 8.0\ min$; fulleropyrazolines $t_R \approx 6\ min$ (*e.g.* **7** has a retention time of $t_R = 6.0\ min$). Alkenes could not be detected; the retention times were found to be similar to the injection peak ($t_R = 2.0\ min$). For quantitative analysis we looked at chromatograms of $\lambda = 254\ nm$; peak integration was undertaken manually.

Figure S1: HPLC chromatogram of the reaction of **7** (1 eq.), maleic anhydride (30 eq.), toluene [1 mM], medium pressure Hg-lamp, 20 min. Retention times: $t_R(toluene) \sim 2\ min$, $t_R(intermediate) = 5.0\ min$, $t_R(\mathbf{7}) = 6.0\ min$, $t_R(C_{60}O) = 8.5\ min$, $t_R(C_{60}) = 8.9\ min$. Green line – solvent gradient

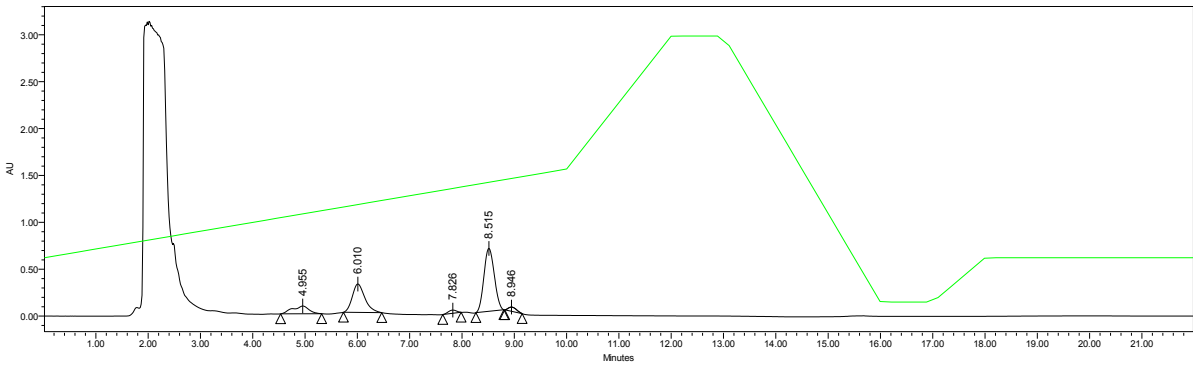
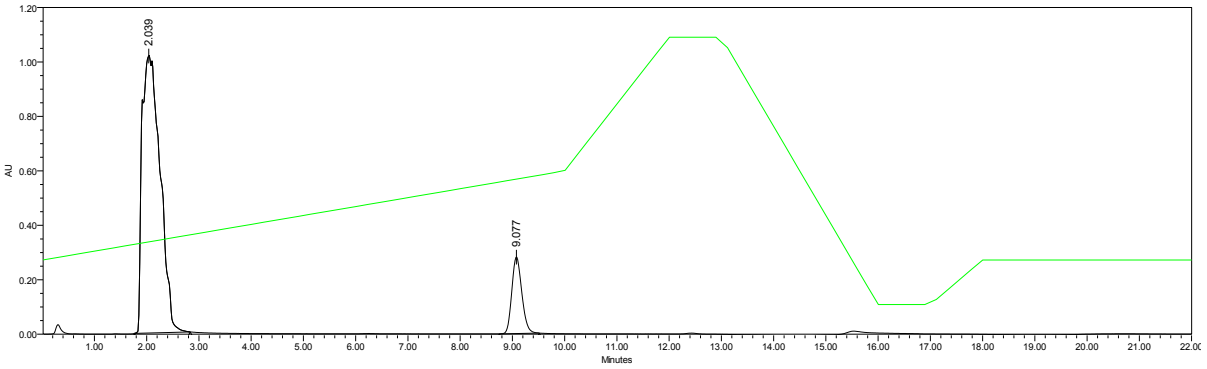
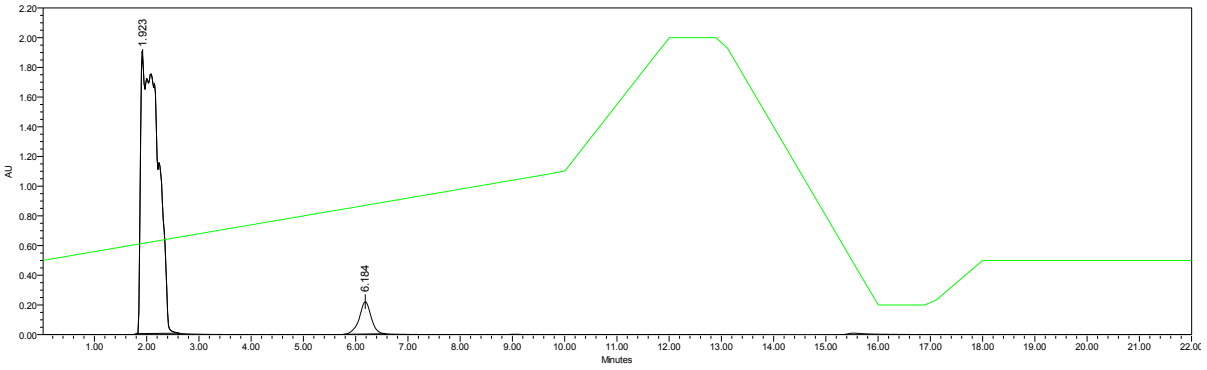


Figure S2: HPLC chromatograms of C_{60} (a), fulleropyrazoline **7** (b), fulleropyrazoline **8** (c), and **10** (d) with the retention times $t_R(toluene) \sim 2\ min$, $t_R(C_{60}) = 9.0\ min$, $t_R(\mathbf{7}) = 6.0\ min$, $t_R(\mathbf{8}) = 6.2\ min$, $t_R(\mathbf{10}) = 5.9\ min$. Green line – solvent gradient

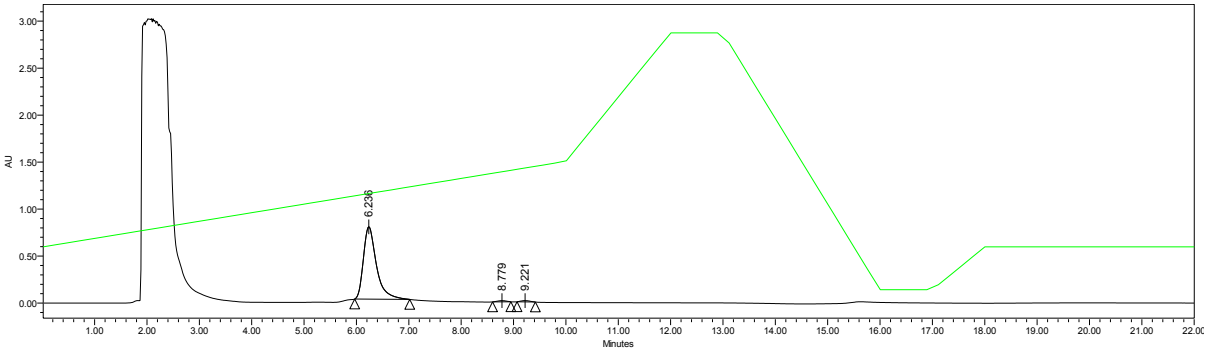
(a)



(b)



(c)



(d)

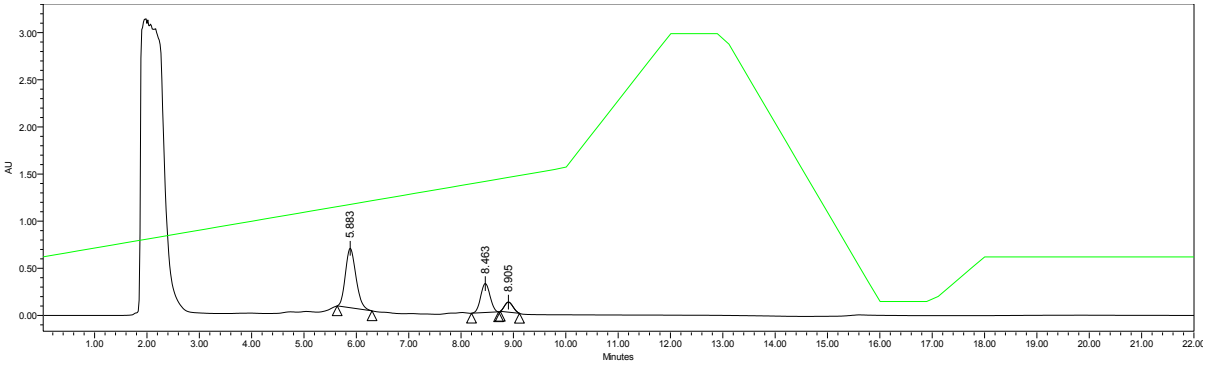
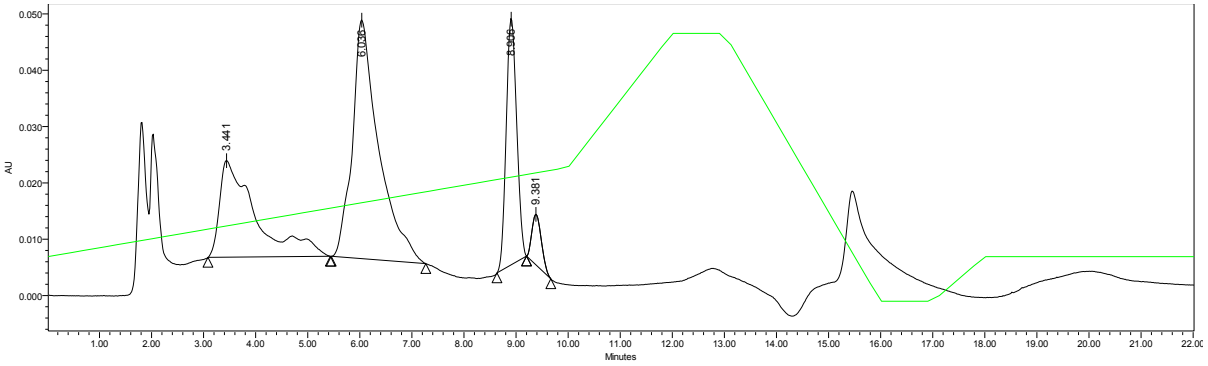
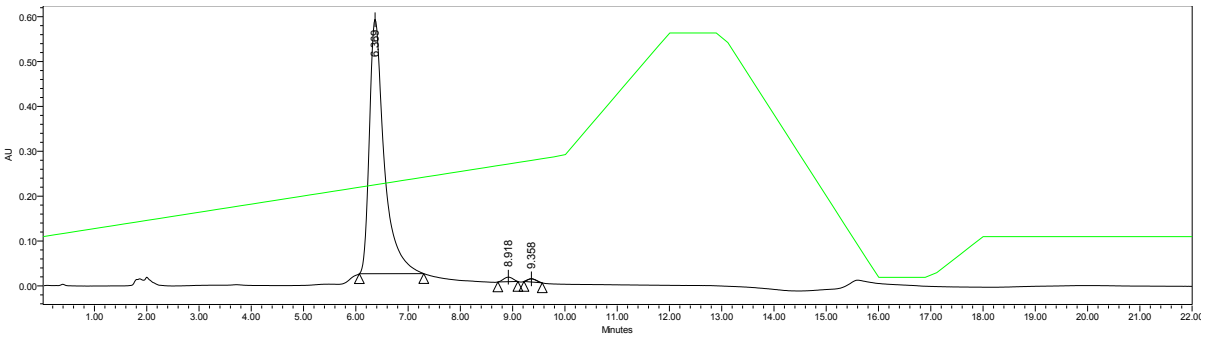


Figure S3: HPLC chromatograms of **11** (a), **13** (b), and fulleropyrazoline **15** (c) with the retention times $t_R(toluene) \sim 2\ min$, $t_R(\mathbf{11}) = 6.0\ min$, $t_R(\mathbf{13}) = 6.4\ min$, $t_R(\mathbf{15}) = 3.2\ min$. Compounds **10** and **11** already show cleavage products when setting up the reaction. Green line – solvent gradient

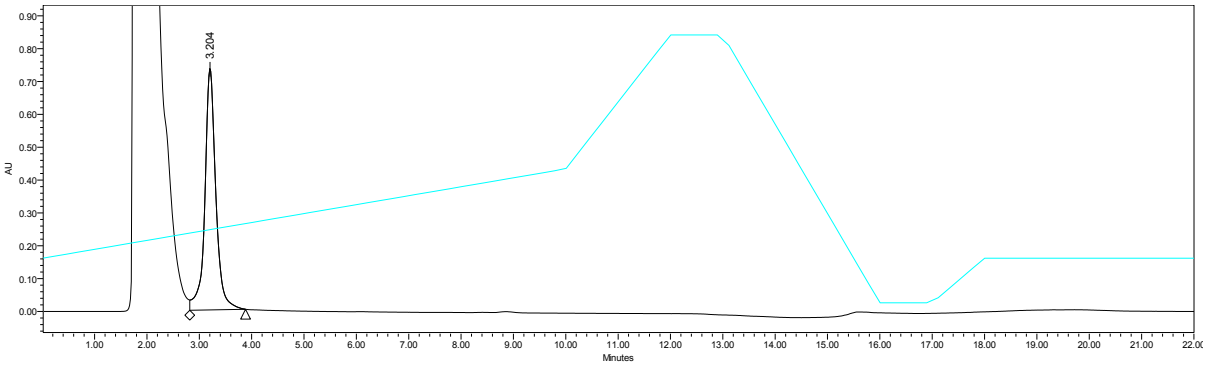
(a)



(b)



(c)



Reaction Progress The photocleavage of the fulleropyrazolines was followed by HPLC (*e.g.* Figure S4). The overall yields of the reactions were obtained by combining the yields of C_{60} and $C_{60}O$ (ratios of C_{60}:$C_{60}O$ are shown in Table S1). No obvious trends in the ratios were observed. The side products formed under photocleavage were also analysed and are discussed in Section 1.4.1.

Figure S4: Photocleavage of **7** monitored by HPLC. Reagents and conditions: maleic anhydride (20 eq.), toluene [1 mM], medium pressure Hg-lamp, 2.5 h. Black dot: intermediate at t=4.9 min; green square: fulleropyrazoline **7**; red cross: C_{60}; blue triangle: $C_{60}O$.

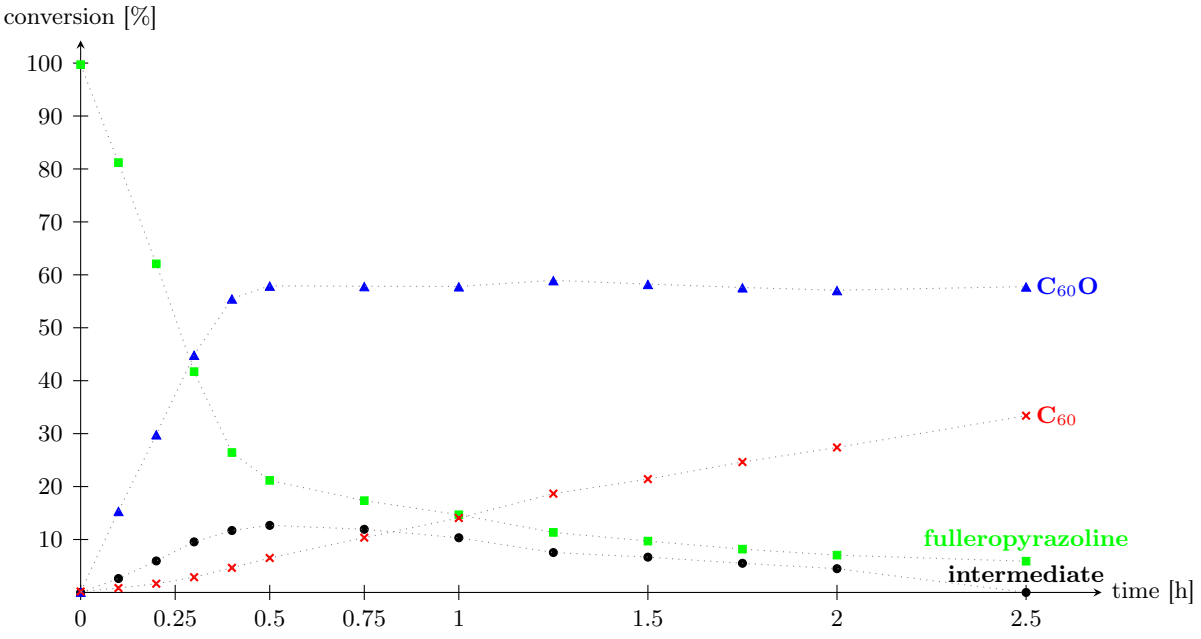


Table S1: Photocleavage of fulleropyrazolines (**7** if not stated otherwise) resulted in a mixture of C_{60} and $C_{60}O$. Ratios were recorded after 2 h irradiation time with a medium pressure Hg-lamp (unless otherwise stated) and normalised to 1 for C_{60}

Entry	Alkene	eq.	solvent	Remarks	$C_{60}O$
1	maleic anhydride	5	toluene	$\lambda = 313nm$ irradiation	15.50
2	maleic anhydride	5	toluene	$\lambda = 350nm$ irradiation	21.00
3	maleic anhydride	5	toluene	$\lambda = 254nm$ irradiation	3.00
4	maleic anhydride	5	toluene	$\lambda = 365nm$ irradiation	31.00
5	maleic anhydride	5	toluene	halogen lamp	24.67
6	coumarin	5	toluene		1.75
7	allylamine	5	toluene		0.00
8	allylbromide	5	toluene		0.00
9	dimethylallylbromide	5	toluene		0.00
10	dimethylallylbromide	5	toluene		0.08
11	dimethylallylbromide	5	$CHCl_3$		0.41
12	allylchloride	5	toluene		1.06
13	chlorostyrene	5	toluene		0.19
14	maleic anhydride	30	toluene	degassed solvent	9.50
15	maleic anhydride	30	$CHCl_3$	degassed solvent	0.98
16	maleic anhydride	30	toluene		9.57
17	maleic anhydride	30	toluene		1.85
18	maleic anhydride	20	toluene		4.19
19	maleic anhydride	10	toluene		0.66

Entry	Alkene	eq.	solvent	Remarks	$C_{60}O$
20	maleic anhydride	5	toluene		0.43
21	maleic anhydride	5	toluene		0.00
22	maleic anhydride	1	toluene		0.47
23	maleic anhydride	1	toluene		8.29
24	–		toluene		0.44
25	–		toluene		2.23
26	maleic anhydride	5	toluene	anhydrous solvent	24.67
27	–		toluene	anhydrous solvent	3.00
28	maleic anhydride	5	toluene	1-phenylnaphthalene (10 eq.)	5.18
29	maleic anhydride	5	toluene	1-phenylnaph. (10 eq.), anhyd.	4.92
30	maleic anhydride	5	toluene	2-methylbut-2-ene (10 eq.)	8.13
31	maleic anhydride	5	toluene	DABCO (10 eq.)	–
32	maleic anhydride	5	$CHCl_3$	photocleavage of compound **8**	0.43
33	maleic anhydride	5	$CHCl_3$	photocleavage of compound **8**	0.69
34	–		$CHCl_3$	photocleavage of compound **8**	0.37
35	–		$CHCl_3$	photocleavage of compound **8**	0.72
36	maleic anhydride	5	toluene	photocleavage of compound **8**	1.40
37	maleic anhydride	5	toluene	degassed solvent, compound **10**	3.14
38	–		$CHCl_3$	photocleavage of compound **11**	0.50
39	–		$CHCl_3$	photocleavage of compound **13**	1.44
40	–		$CHCl_3$	photocleavage of compound **13**	1.38
41	–		$CHCl_3$	photocleavage of compound **15**	4.54
42	–		PhCN/H_2O 1:1	photocleavage of compound **15**	2.36
43	–		$CHCl_3$		1.56
44	–		$CHCl_3$		1.50
45	–		$CHCl_3$		1.33
46	maleic anhydride	5	DMSO		0.07
47	–		DMSO		–
48	maleic anhydride	5	DMSO/H_2O 1:1		–
49	maleic anhydride	5	DMSO/toluene 1:1		0.14
50	maleic anhydride	5	PhCN		2.45
51	–		PhCN/H_2O 1:1		0.68
52	–		PhCN/H_2O 1:1	gentisic acid (10 eq.)	1.69
53	–		PhCN/H_2O 1:1	ascorbic acid (10 eq.)	0.65
54	–		PhCN/H_2O 1:19		1.17
55	–		$CDCl_3$	gentisic acid (10 eq.)	0.04
56	–		$CDCl_3$	acrylamide (10 eq.)	0.05

1.3 Dependency on Alkene Equivalents for Trapping

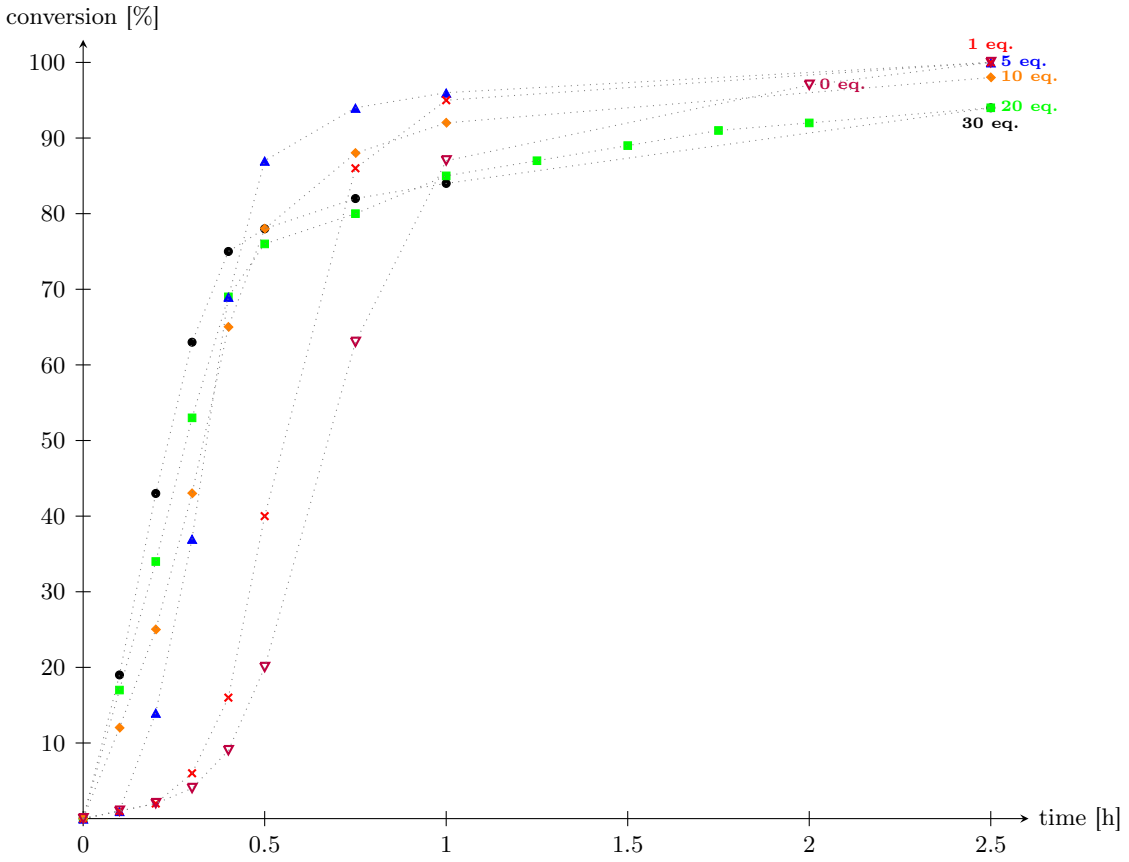
The use of excess maleic anhydride as trapping alkene gave large quantities of precipitation which we reasoned may be due to polymerisation. Lowering the equivalents of maleic anhydride from 30 to 1 led to complete photocleavage after 2.5 h (Figure S5). Higher quantities of alkene gave

faster initial reaction rates but incomplete conversion. The addition of maleic anhydride to an ongoing reaction after 1 h did not cause acceleration of the reaction. Further analysis indicated that an alkene was not required for the reaction to occur (Table S2).

Table S2: Alkenes used during photocleavage of fulleropyrazoline **7**. Reaction conditions: alkene (20 eq.), toluene [1 mM], irradiation with a medium pressure Hg-lamp

Entry	Alkene	Reaction time	yield (based on HPLC)
1	maleic anhydride	2.5 h	94%
2	3,3-dimethylallylbromide	45 min	97%
3	*p*-chlorostyrene	45 min	90%
4	allylbromide	2 h	97%
5	allylchloride	3 h	75%
6	coumarin	4 h	67%
7	allylamine	10 h	58%
8	–	2 h	97%

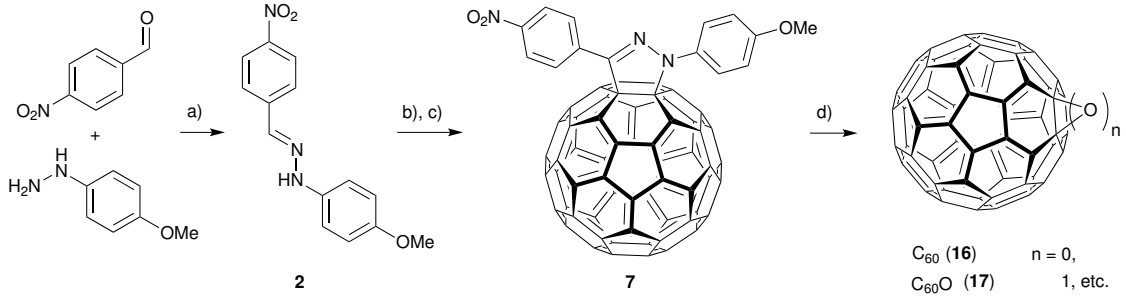
Figure S5: Time dependent photocleavage of fulleropyrazoline **7** in toluene [1 mM] in the presence of varying concentrations of maleic anhydride as a trapping agent. Black dot: 30 eq.; green square: 20 eq.; orange rhombus: 10 eq.; blue triangle: 5 eq.; red cross: 1 eq.; purple triangle: 0 eq.



1.4 Mechanistic Experiments

To gain a deeper insight into the reaction mechanism we evaluated the products formed upon photocleavage by monitoring the reaction mixture directly in deuterated solvents by NMR. Products of the reaction were also isolated after standard work-up and purification by flash column chromatography on silica gel.

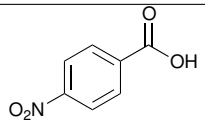
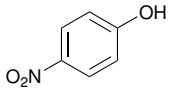
1.4.1 Product Analysis



Scheme S3: Reagents and conditions: a) 4-nitrobenzaldehyde (1 eq.), 4-methoxybenzylhydrazine (1.5 eq.), AcOH (cat.), EtOH [0.3 M], reflux, 25 min, 56%; b) hydrazone (1 eq.), NBS (1.5 eq.), $CHCl_3$ [7 mM], r.t., 30 min; c) C_{60} (1 eq.), NEt_3 (3 eq.), toluene [5.2 mM], reflux, 2 h, 40% (70% based on recovered C_{60}); d) hν, (alkene), solvent [1 mM].

The photocleavage was conducted in deuterated solvent in NMR tubes under irradiation with a medium pressure mercury lamp. Once the photocleavage reaction was complete (1 h in $CDCl_3$, 5 h in toluene-d_8, and 2 h in toluene-d_8/CS_2 10:1), the products were analysed by NMR, IR and mass spectrometry. Various *para*-substituted aromatic species were formed under the reaction conditions as would be expected from the starting fulleropyrazoline. High resolution mass spectrometry of the crude mixture revealed the putative hydrolysed products *para*-nitrobenzoate **25** and *para*-nitrophenol **26** (Table S3).

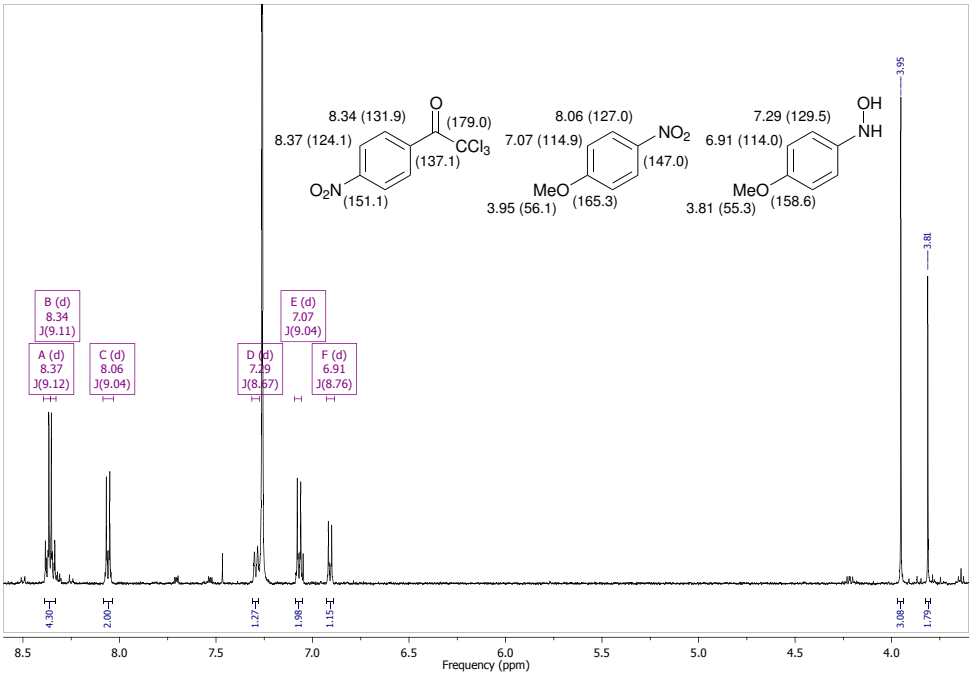
Table S3: High resolution mass spectrometry analysis (electron spray) of the crude reaction mixture of the photocleavage of fulleropyrazoline **7** revealed the hydrolysed compounds

Entry	Structure	compound	calc. mass	found
1		**25**	166.0146 ($-H^+$),	166.0135 (–),
2		**26**	138.0197 ($-H^+$)	138.0200 (–)

The IR spectrum of a crude reaction mixture in $CDCl_3$ showed peaks at 1704 (C_{aryl}-COO), 1601, 1528 (NO_2), 1421, 1345 (NO_2), 1259, 1106, and 800 which are characteristic for *para*-nitrobenzoic acid.[6,7]

During the photocleavage reaction we did not observe the starting hydrazone **2** (Scheme S3). Depending on the solvent and therewith the irradiation time we observed different product distributions. In $CDCl_3$ we observed three major aryl compounds and two methoxy substituents, whereas in toluene-d_8 a mixture of seven *para*-substituted aryl products were observed of which two were identical with the ones found in $CDCl_3$ (Figure S6-S8). Comparison with the previously reported chemical shifts[8,9,10,11] suggests that the products shown in Figure S6 were formed during the reaction.

Figure S6: Irradiation of fulleropyrazoline **7** in $CDCl_3$ [1 mM] with a medium pressure Hg-lamp for 1 h with the possible products indicated.



The photocleavage in toluene-d_8/carbon disulfide 9:1 showed an acceleration of the reaction rate and decrease in the number of products to two major products which appear to be similar to those formed in $CDCl_3$. These observations suggest that different solvent dependent mechanisms may occur.

The product mixture arising from the photocleavage of **7** in $CHCl_3$ [1 mM] was subjected to flash column chromatography ($CHCl_3$/MeOH 4:1). The collected fractions contained mixtures of up to seven *para*-substituted aromatic products of which three were previously observed in the crude reaction mixture. This indicates the formation of reactive intermediates which react further during work-up and purification. One new substrate was tentatively assigned as *para*-nitrobenzoic ethyl ester (**27**) by ^{1}H-,^{13}C-, COSY, HSQC, and HMBC NMR (Figure S9).[12]

Figure S7: Irradiation of fulleropyrazoline **7** in toluene-d_8 [1 mM] with a medium pressure Hg-lamp for 5 h.

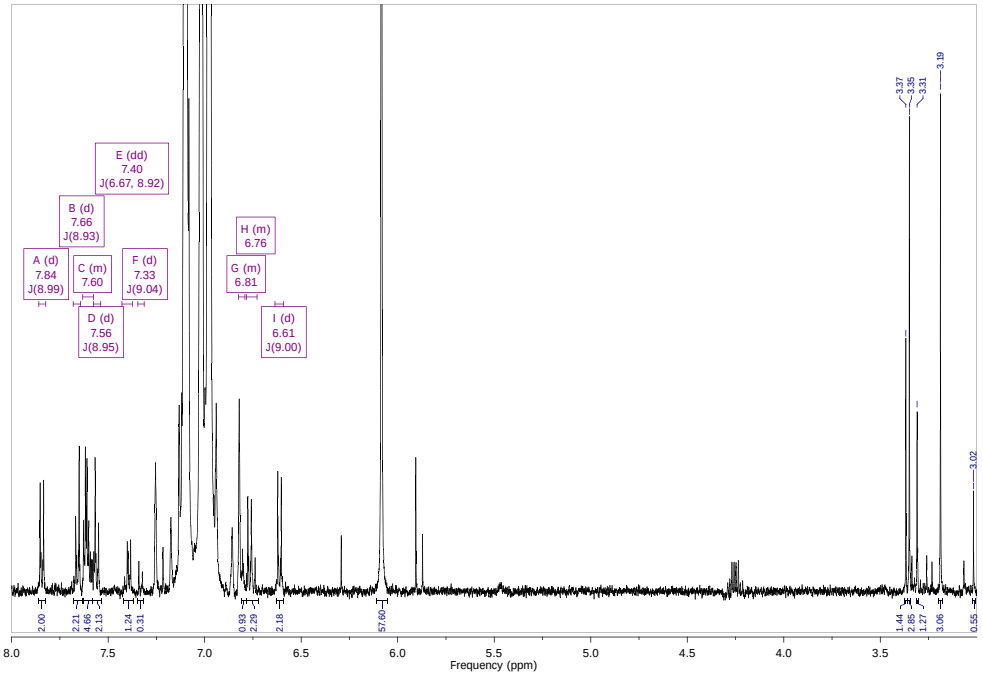


Figure S8: Irradiation of fulleropyrazoline **7** in toluene-d_8/CS_2 10:1 [1 mM] with a medium pressure Hg-lamp for 2 h with the possible products indicated.

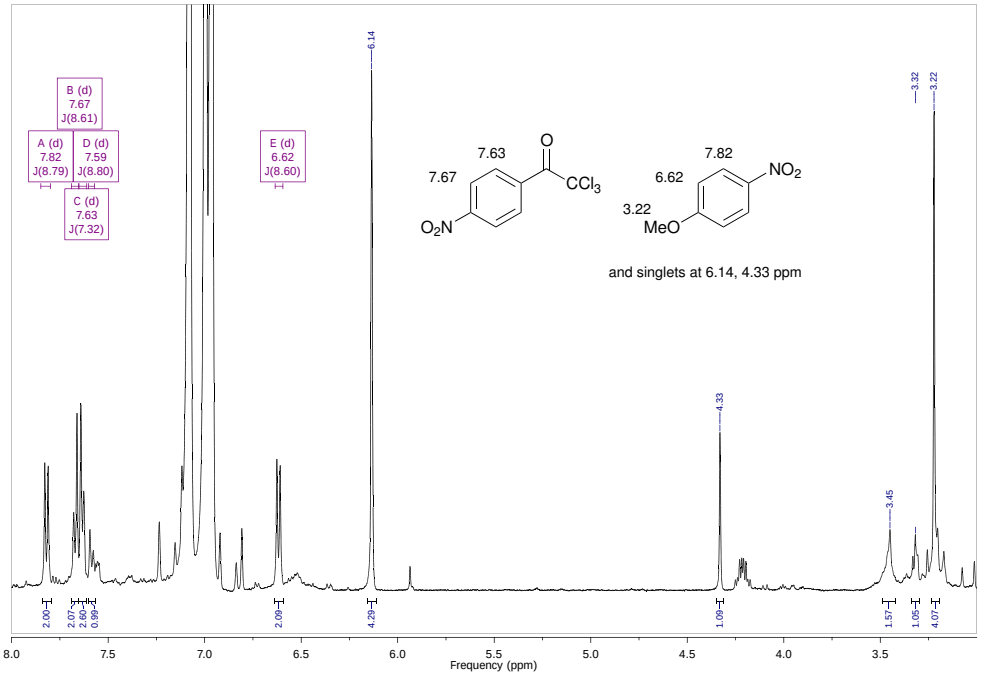
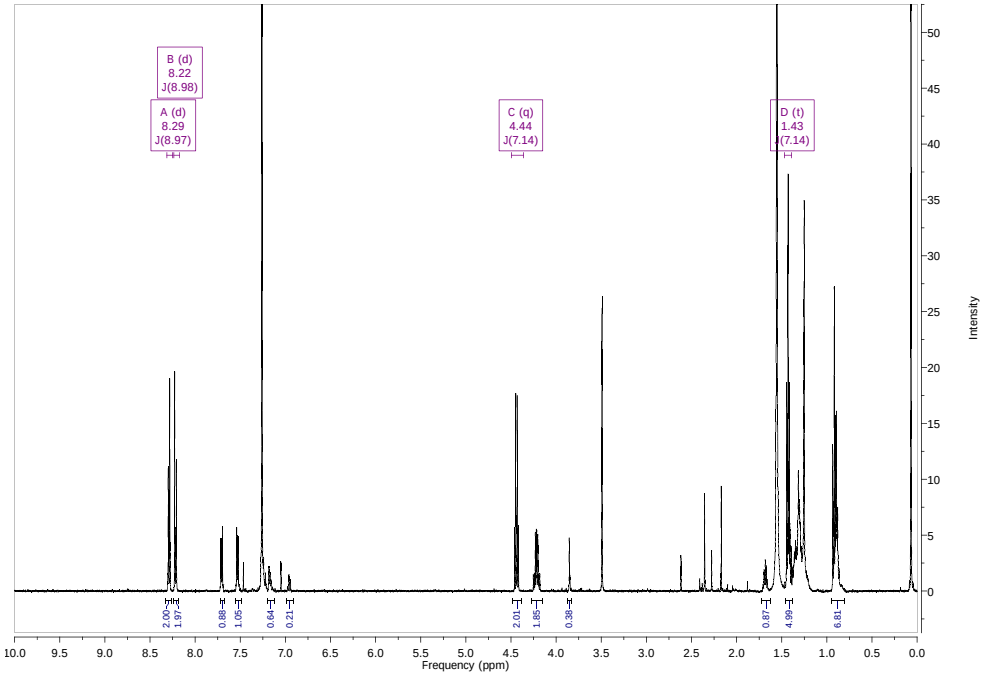


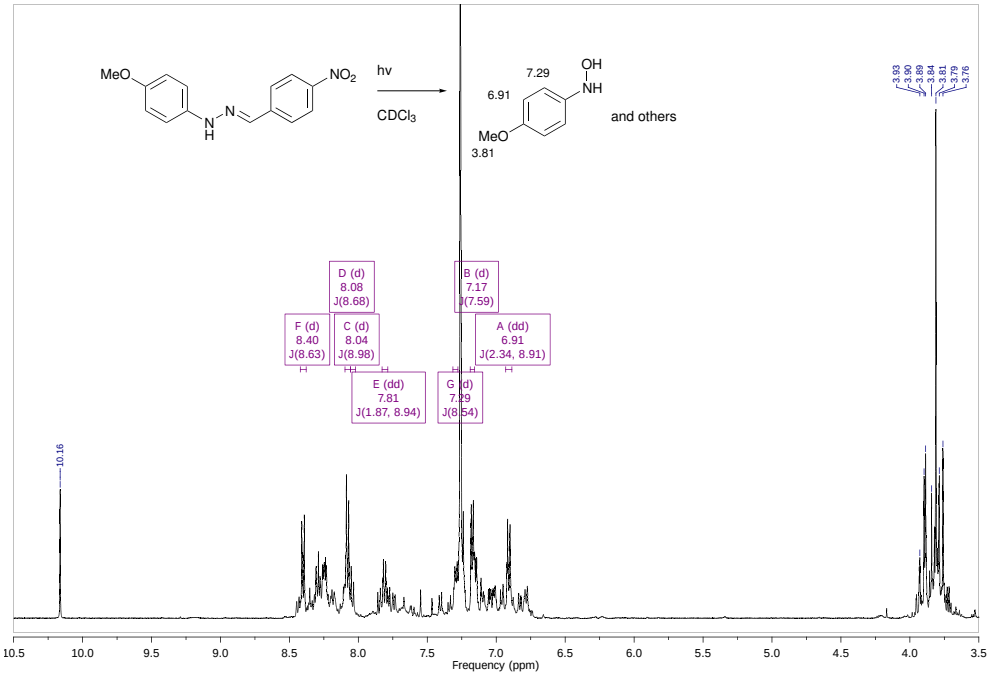
Figure S9: Mixture of products isolated by column chromatography from the photocleavage reaction of fulleropyrazoline **7** in $CHCl_3$ [1 mM] with a medium pressure Hg-lamp.



It has been reported that hydrazones can either undergo autoxidation in the presence of oxygen followed by a breakdown *via* a radical mechanism[1,13] or directly cleave under UV irradiation to give the aminyl and iminyl radical species.[14] Assuming a retrocycloaddition, breakdown of the fulleropyrazoline to a diradical hydrazone species could lead to similar breakdown pathways. However, the products formed in the photocleavage under oxygen free reaction conditions were identical to those formed in undegassed solvent. We conclude from this finding that the breakdown of the species might not be due to autoxidation and cleavage of the hydrazone intermediate.[1,13]

Hydrazone **2** was subjected to irradiation in $CDCl_3$. Complete consumption of **2** was observed after 1 h and numerous unidentifiable products were formed. Amongst these we observed one which corresponds to the photocleavage product of fulleropyrazoline **7** (Figure S10).

Figure S10: Irradiation of hydrazone **2** in $CDCl_3$ [1 mM] with a medium pressure Hg-lamp for 1 h.



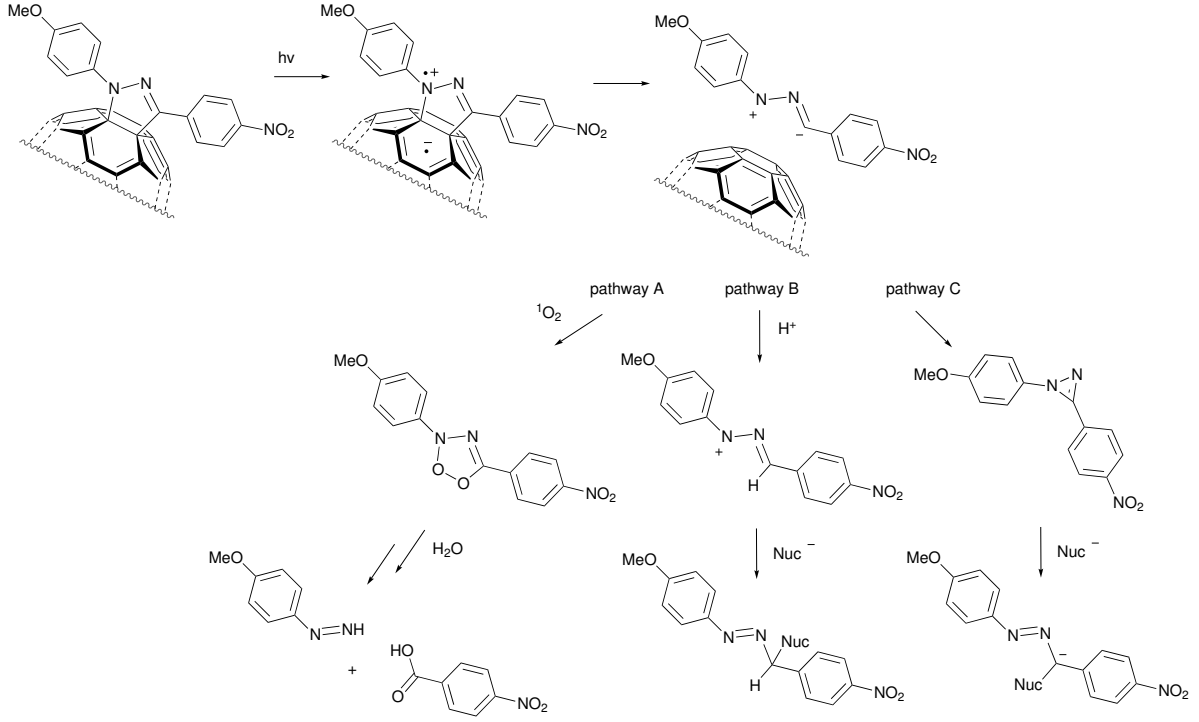
1.4.2 Influence of the Solvent

To further investigate the mechanism of the photocleavage various solvents were used. The solubility of the fulleropyrazoline limited the choice of solvents. We observed that the concentration has a significant impact on the reaction rate. The more concentrated the reaction mixture the slower the cleavage. Results indicate that organic solvents may be used for the photocleavage reaction. Mixtures of toluene, chloroform, or benzonitrile with water in various ratios undergo photocleavage, and the rate of reaction tends to increase in the two solvent systems compared to the pure organic solvent. This effect may result from increased nucleophilicity or H-bonding as confirmed by the increased reaction rate of the photocleavage in toluene/MeOH 1:1 (30 min, Table S4). The decrease of reaction time of the photocleavage with increasing water content suggests either stabilisation of the intermediate by H-bonding or trapping of the intermediate. The reaction rate is additionally influenced by the presence of protic solvent and acidic additives. This observation suggests the formation of a zwitterionic intermediate which is better stabilised under polar conditions (Scheme S4). Furthermore, electron transfer from the pyrazoline moiety to the C_{60} sphere is enhanced by the basic character of the sp^3-nitrogen of the pyrazoline due to the stabilising effect of the electron donating *para*-methoxyphenyl group.[2]

Table S4: Reversible cleavage of fulleropyrazoline **7** under irradiation with a medium pressure Hg-lamp was achieved without a trapping alkene in various undegassed solvents [1 mM]

Entry	Solvent	Dipol moment[15]	Reaction time	Remarks
1	toluene	0.37	3 h	
2	toluene/H_2O 1:1		>1.5 h	
3	toluene/MeOH 1:1		30 min	
4	$CHCl_3$	1.04	10-45 min	as received or alumina neutralised
5	$CHCl_3$/H_2O 1:4		30 min	
6	PhCN	4.18	1 h	
7	PhCN/H_2O 1:1		45 min	
8	PhCN/H_2O 1:19		20 min	
9	DMF	3.82	3 h	rapid decomposition[a)]
10	DMF/H_2O 1:1		5 h	no reaction
11	DMSO	3.96	3 h	no reaction
12	DMSO/H_2O 1:1		3 h	no reaction
13	DMSO/toluene 1:1		2 h	66% cleavage
14	pyridine	2.21	5 h	no reaction
15	1,1,2,2-Tetrachloroethane	1.32	20 min	
16	Tetrachloromethane	0	>2 h	cleavage very slow
17	H_2O	1.85	11 h	not soluble, no reaction

[a)] starting fulleropyrazoline was consumed in 30 min, but no C_{60} product was formed.



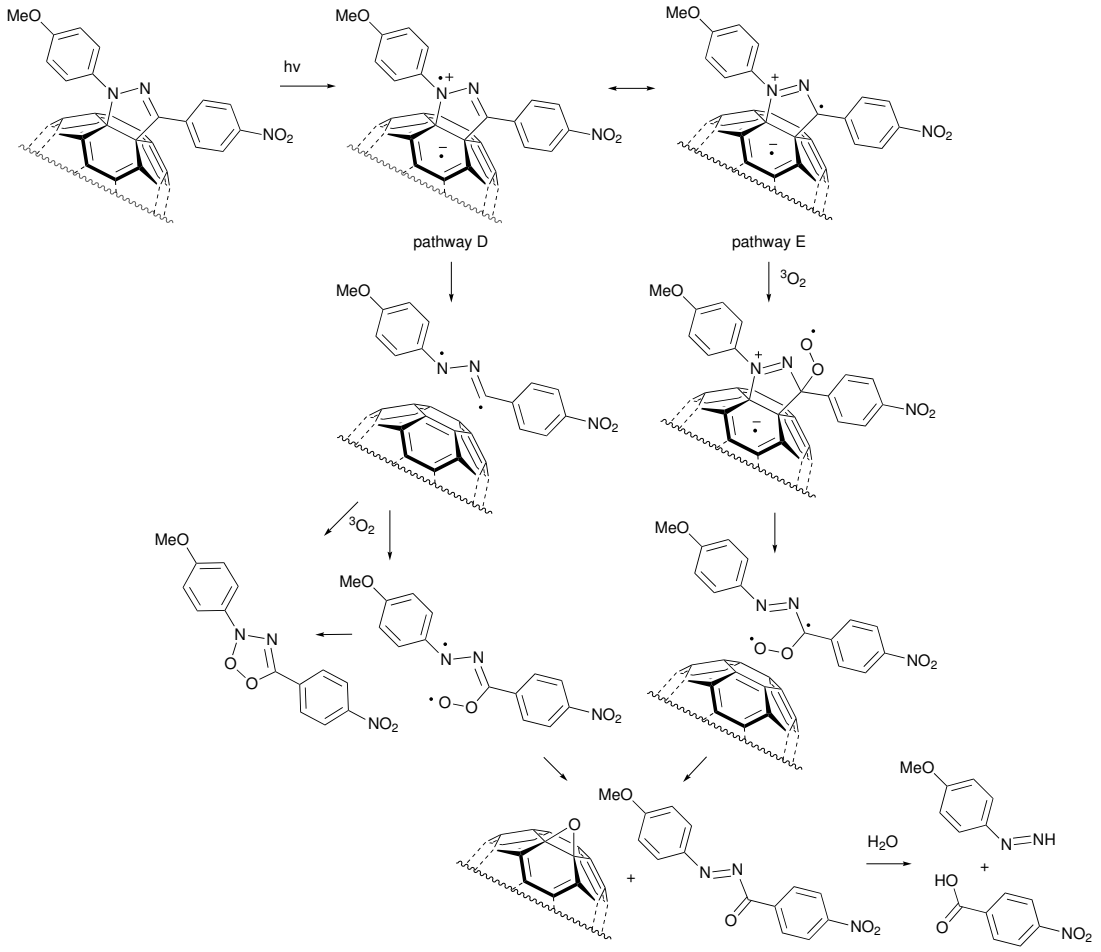
Scheme S4: Potential breakdown mechanism of the photocleavage of fulleropyrazoline **7** with the zwitterionic diradical forming a reactive 1,3-dipole stabilised by the polar solvent. Breakdown pathway A might occur since in undegassed solvent systems the photocleavage rate is increased. Pathway B appears more likely given the large increase in rate in the presence of proton donors. The reactive intermediate formed might undergo hydrolysis or radical cleavage. Pathway C may result in the same reaction products.

1.4.3 Scavengers

We have analysed the photocleavage reaction of fulleropyrazoline **7** in the presence of various scavengers. We used naphthalene 2-methylbutene, 1-phenylnaphthalene or DABCO as a singlet oxygen quencher.[16,17,18] The latter suppressed the photocleavage completely whereas the other two compounds slowed the reaction only marginally. The effect of DABCO could also be ascribed to its basicity and therewith its propensity to undergo electron transfer to the C_{60} species present.[19,20] This finding was confirmed when the photocleavage was undertaken in pyridine or in the presence of NEt_3. Amine bases suppress the photocleavage. Gentisic acid, sodium ascorbate, or acrylamide were added as radical scavengers[21,22] to the photocleavage reaction in either chloroform or benzonitrile/water 1:1 mixture. In the biphasic system these additives had no effect on the reaction rate. The presence of 2,5-dihydroxybenzoic acid or acrylamide in chloroform led to acceleration in the reaction rate. Radical breakdown pathways as suggested in Scheme S5 could lead to the oxidised product species. The addition of scavenging additives revealed interesting results that suggest the reaction is inhibited by the presence of a base while accelerated by acid. The rate acceleration with acid may be due to trapping (protonation) of an intermediate species formed during the photocleavage (pathway B, Scheme S4).

1.4.4 Mechanistic Discussion

Based on the literature precedent,[23] substrate compatibility, and our observations (*vide supra*) we believe that the initial step in the photocleavage is charge separation. According to our observations, various pathways may be envisaged after this stage. Photocleavage *via* the breakdown of the triple state of the fulleropyrazoline (f-$^3C_{60}$*) may be excluded due to the ineffectiveness of oxygen as a quencher. The fact that the trapping alkene is not essential indicates that the breakdown can occur without participation of such species. The acceleration of the reaction rate in polar solvent suggests a polar intermediate (Scheme S4). Furthermore, the electron donating group of the pyrazoline moiety could have a stabilising effect and reinforces the basic character of the sp^3-nitrogen which plays a key role in the charge transfer process.[23] This is supported by the fact that bases inhibit the process, presumably by facile electron transfer.[19,20] In the presence of base the fulleropyrazoline might not be able to form the charged diradical intermediate which leads us to surmise that this step may be essential for the photocleavage reaction. The presence of acidic protons accelerated product formation which indicates that they may be directly involved in the mechanism, *e.g.* by trapping intermediates. Breakdown of the corresponding hydrazone **2** under UV irradiation resulted in formation of various cleavage products and suggested the presence of a similar intermediate during the photocleavage reaction. Apart from these findings the results of the photocleavage in the presences of radical scavengers suggests a concurrent radical breakdown pathway (Scheme S5).



Scheme S5: Potential breakdown mechanism of the photocleavage of fulleropyrazoline **7**. The ionic diradical could breakdown by formation of a diradical species. The presence of radical scavenger resulted in accelerated reaction rate. Presumably the diradical intermediates are quenched to suppress subsequent re-addition. The oxidised species might result from the reaction of oxygen with the intermediate.

2 Experimental

2.1 General

^{1}**H NMR** spectra were recorded at room temperature on the following spectrometers: 200 MHz: Bruker DPX200, 400 MHz: Bruker DQX400 and AV400, 500 MHz: Bruker AV500. Unless reported otherwise, spectra were recorded in $CDCl_3$ solution. Chemical shifts are reported in δ units relative to $CHCl_3$ (δ_H = 7.26). The following abbreviations were used throughout: s =singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, tt = triplet of triplet, q = quartet, quin = quintett, m = multiplet.

^{13}**C NMR** spectra were recorded at room temperature on the following spectrometers: 100 MHz: Bruker DQX400, 125 MHz: Bruker DRX500. Unless reported otherwise, spectra were recorded

in $CDCl_3$ solution. Chemical shifts are reported in δ units relative to $CDCl_3$ ($\delta_C = 77.23$ {central line of triplet}).
HRMS data was determined under conditions of ES^+ on a Micromass Q-Tof mirco (resolution = 4 x 10^{-3} D) using H_3PO_4-clusters as a lock-mass in positive ion mode.
HPLC was performed on a Waters® 2795 Separations Module, AllianceHT with a reversed phase column TSKgel ODS 80TM and a gradient of ^{i}PrOH/hexane 80:20 for 10 min at a flow rate of 1 mg/ml.[5,3,4] Substrates were detected at $\lambda = 254\ nm$ with a Waters® 2996 Photodiode Array Detector. The data was processed with the software Empower Pro, copyright© 2002 Waters Corporation.
MALDI-ToF spectra were recorded on a Waters® Micromass® MALDI micro MX™ Mass Spectrometer in the positive reflectron mode. The data were analysed with MassLynx V4.1.
UV/vis was performed on a NanoDrop® ND-1000 spectrophotometer with a full-spectrum 220-750 nm or a Waters® 2996 Photodiode Array Detector with a spectrum range of 220-400 nm. The sample contained 1 μL and the transmission length is stated as L = 0.1 cm.
Infra-red spectra: Recorded on a Bruker Vector 22 IR spectrometer with the sample being prepared as a thin film between KBr plates or pressed into KBr pellets.
IUPAC names and atom numbering of the compounds described in the experimental section were given using the program CS ChemDraw Ultra 12.0.3.

2.1.1 Reagents and Solvents

All reagents and solvents were obtained from Sigma-Aldrich, Alfa Aesar, Fluka, and Frontier Scientific and were used directly as supplied, unless otherwise reported. Anhydrous solvents are bought from Sigma-Alrich. All non-aqueous reactions were performed in oven or flame dried apparatus under argon or nitrogen atmosphere using anhydrous solvents.

2.1.2 Techniques

Reactions were monitored by thin layer chromatography on pre-coated aluminium-backed plates (Merck Kieselgel 60 with fluorescent indicator UV_{254}). Spots were visualised by quenching of UV fluorescence and/or by staining with potassium permanganate, iodine, ninhydrin, *p*-anisaldehyde or vanillin.
Flash column chromatography was performed according to the method described by Still, Kahn and Mitra[24] with silica gel 60 (0.040 - 0.063 mm) (Geduran® Si 60) applying head pressure by means of manual flushing.

2.2 General Procedure

2.2.1 Hydrazone Formation[25,26]

To a stirred solution of aldehyde (1 eq.) and hydrazine (1 eq.) in EtOH (0.65 M) at 78 °C was added one drop of acetic acid. The solution was heated to reflux until t.l.c. analysis indi-

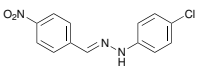
cated complete consumption of the starting material. The reaction mixture was cooled to room temperature and the resultant precipitate was filtered. The crude product was purified by recrystallisation from EtOH to give pure hydrazone as a coloured solid.

2.2.2 Pyrazoline Formation with C_{60}[27,26]

To a stirred solution of hydrazone (1 eq.) in anhydrous $CHCl_3$ (7 mM) at room temperature was added recrystallised NBS (1.5 eq.) under an atmosphere of argon. After stirring for 30 min, at which point t.l.c. analysis indicated complete consumption of starting material, the solvent was removed under reduced pressure. The brown solid was dissolved in anhydrous toluene (5.2 mM). After adding C_{60} (1 eq.) and NEt_3 (3 eq.) the reaction mixture was stirred until t.l.c. analysis indicated complete consumption of starting material. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel (CS_2 →toluene/EtOAc) to give unconsumed C_{60} and the monocycloadduct.

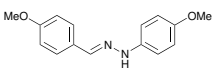
2.3 Hydrazones

2.3.1 (*E*)-1-(4'-Chlorophenyl)-2-(4-nitrobenzylidene)hydrazone (3)



To a stirred solution of *p*-chlorophenyl hydrazine hydrochloride (200 mg, 1.12 mmol, 1 eq.) and NEt_3 (0.14 mL, 1.12 mmol, 1 eq.) in EtOH (1.7 mL, 0.65 M) at 78 °C was added *p*-nitrobenzaldehyde (168.8 mg, 1.12 mmol, 1 eq.) and one drop of acetic acid. The solution turned dark red immediately and was heated at reflux for 20 min until t.l.c. analysis indicated complete consumption of starting material. The reaction mixture was cooled to room temperature and the resultant precipitate was filtered. The crude product was purified by recrystallisation from EtOH to give pure hydrazone **3** as red crystals (284.0 mg, 92%). $\mathbf{R}_f$ 0.40 (toluene); **mp** 161.0-162.2 °C; **UV/vis** λ_{max}(MeOH) [nm] = 413 (ϵ [$dm^3mol^{-1}cm^{-1}$] 42300), 285sh (19400) and 261 (25200); **IR** (film) ν_{max} [cm^{-1}] 3303 (C=C-H), 2856, 15962 (C=C_{arom}), 1565, 1514, 1487, 1410 (CH_2), 1336, 1288, 1259, 1151, 1108, 1090 (C_{aryl}-Cl), 907, 856, 823, 750, 693, 674, 658. 639, 611; **^{1}H NMR** (400 MHz, MeOD) δ_H 7.11 (2H, d, $^3J_{2',3'}$ = 9.3 Hz, H-2', H-6'), 7.21 (2H, d, $^3J_{3',2'}$ = 9.3 Hz, H-3', H-5'), 7.81 (2H, d, $^3J_{2,3}$ = 9.0 Hz, H-2, H-6), 7.81 (1H, s, C*H*=NNH), 8.21 (2H, d, $^3J_{3,2}$ = 9.3 Hz, H-3, H-5); **^{13}C NMR** (100 MHz, MeOD) δ_C 115.0 (C-3', C-5'), 125.0 (C-2', C-6'), 125.7 (C-4'), 127.2 (C-3, C-5), 130.1 (C-2, C-6), 135.3 (C-1', *C*H=NNH), 144.0 (C-1), 148.2 (C-4); **m/z** (FI^+) calc. for $[M]^+$ = 275.0462, found = 275.0456.

2.3.2 (*E*)-1-(4-Methoxybenzylidene)-2-(4'-methoxyphenyl)hydrazone[28] (5)

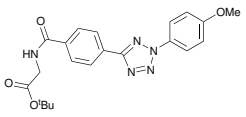


Chopped NaOH pellets (46.0 mg, 1,15 mmol, 1 eq.), *p*-methoxyphenyl hydrazine hydrochloride (200 mg, 1.15 mmol, 1 eq.), silica (115 mg, 10 mmol/g), and NEt_3 (0.15 mL, 1.15 mmol, 1 eq.) were mixed together in an agate mortar. *p*-Methoxybenzaldehyde (0.14 mL, 1.15 mmol, 1 eq.) was added and the mixture subjected

to grinding for 40 min until the powder was dry. The solid was dissolved in CH_2Cl_2 (30 mL) and HCl (12 mL of a 1 M aqueous solution) and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic fractions were washed with $NaHCO_3$ (15 mL of a saturated aqueous solution), brine (15 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by recrystallisation from EtOH to give pure hydrazone **5** as light brown crystals (102.4 mg, 35%). $\mathbf{R}_f$ 0.49 (petrol. ether/EtOAc 3:1); $\mathbf{m}_p$ 125-127 °C (from EtOH); **UV/vis** $\lambda_{max}(CDCl_3)$ [nm] = 355, 312, 260 and 230; **IR** (film) ν_{max} [cm^{-1}] 3310 (amine, C=C-H), 3007, 2957, 2929 ($C_{aryl}H$), 2836 (-OMe), 1608 ($C{=}C_{arom}$), 1569, 1521, 1508, 1477 (amine), 1441, 1417, 1353, 1314, 1295, 1249, 1182, 1167, 1137, 1100, 1032, 945, 905, 827 (C=C-H), 773, 644; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 3.78 (3H, s, OCH_3'), 3.83 (3H, s, OCH_3), 6.86 (2H, d, $^3J_{3',2'}$ = 9.0 Hz, H-3', H-5'), 6.90 (2H, d, $^3J_{3,2}$ = 8.8 Hz, H-3, H-5), 7.05 (2H, d, $^3J_{2',3'}$ = 9.0 Hz, H-2', H-6'), 7.36 (1H, s, CH=NN*H*), 7.58 (2H, d, $^3J_{2,3}$ = 8.8 Hz, H-2, H-6), 7.63 (1H, s, C*H*=NNH); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 55.5 (OCH_3), 55.8 (OCH_3'), 114.1 (C-3', C-5'), 114.2 (C-3, C-5), 114.9 (C-2', C-6'), 127.6 (C-2, C-6), 128.4 (C-1), 137.3 (*C*H=NNH), 139.3 (C-1'), 153.8 (C-4'), 160.0 (C-4); **m/z** (ESI^+) calc. for $[M+Na]^+$ = 279.1104, found = 279.1103.

2.4 Tetrazole

2.4.1 (*tert*)-Butyl 2-(4'-(2"-(4"'-methoxyphenyl)-2*H*-tetrazol-5"-yl)benzamido) acetate (14)

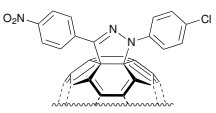


To a stirred solution of tetrazole **12** (50.0 mg, 0.17 mmol, 1 eq.) in anhydrous DMF (2.8 mL, 60 mM) at room temperature was added HATU (128.3 mg, 0.34 mmol, 2 eq.) and DIPEA (58.8 μL, 0.34 mmol, 2 eq.) under an atmosphere of argon. The solution was stirred for 20 min until t.l.c. analysis indicated complete consumption of starting material. To the yellow mixture was added H-Gly-O^{t}Bu (42.4 mg, 0.25 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature for 40 min. The solvent was removed *in vacuo* and the crude product was dissolved in $CHCl_3$ (15 mL) and extracted with H_2O (4 x 15 mL). The combined organic fractions were washed with brine (25 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by flash column chromatography on silica gel ($CHCl_3$) to give tetrazole **14** as white solid (56.4 mg, 67%). $\mathbf{R}_f$ 0.16 ($CHCl_3$); **UV/vis** $\lambda_{max}(CDCl_3)$ [nm] = 260 (ϵ [$dm^3mol^{-1}cm^{-1}$] 42000); **IR** (film) ν_{max} [cm^{-1}] 3335 (amine, C=C-H), 2979, 2934 ($C_{aryl}H$), 1746 (C=O), 1643 (CONH), 1552 (heterocycle), 1512, 1467, 1367, 1305 (N-N=N), 1255, 1224, 1153, 1018 & 998 (heterocycle), 918, 835 (C=C-H), 741, 624; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 1.51 (9H, s, $C(CH_3)_3$), 3.88 (3H, s, OCH_3), 4.16 (2H, d, $^3J_{Gly,NH}$ = 4.9 Hz, H_{Gly}), 6.83 (1H, t, $^3J_{NH,Gly}$ = 4.7 Hz, NH), 7.05 (2H, d, $^3J_{3''',2'''}$ = 9.1 Hz, H-3"', H-5"'), 7.95 (2H, d, $^3J_{3',2'}$ = 8.4 Hz, H-3', H-5'), 8.09 (2H, d, $^3J_{2''',3'''}$ = 9.1 Hz, H-2"', H-6"'), 8.29 (2H, d, $^3J_{2',3'}$ = 8.4 Hz, H-2', H-6'); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 28.2 ($C(\underline{C}H_3)_3$), 42.7 (Gly), 55.8 (OCH_3), 82.8 ($\underline{C}(CH_3)_3$), 114.8 (C-3"', C-5"'), 121.5 (C-2"', C-6"'), 127.2 (C-2', C-6'), 127.8 (C-3', C-5'), 130.4 (C-1"'), 135.5 (C-4'), 160.7 (C-4"'),

164.2 (C-1"), 166.7 (CONH), 169.3 (COO^tBu); **m/z** (ESI^+) calc. for $[M+H]^+$ = 410.1828, found = 410.1816.

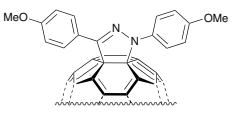
2.5 Fulleropyrazolines

2.5.1 1-(4'-Chlorophenyl)-3-(4-nitrobenzylidene)-4,5-fullerene-pyrazoline (8)



To a stirred solution of hydrazone **3** (10.7 mg, 34.7 μmol, 1 eq.) in anhydrous $CHCl_3$ (5 mL, 7 mM) at room temperature was added recrystallised NBS (9.3 mg, 52.0 μmol, 1.5 eq.) under an atmosphere of argon. The solution was stirred for 30 min until t.l.c. analysis indicated complete consumption of starting material. The solvent was removed under reduced pressure and the brown solid was solved in anhydrous toluene (12 mL, 2.6 mM). After adding C_{60} (25 mg, 34.7 μmol, 1 eq.) and NEt_3 (13.4 μL, 104.0 μmol, 3 eq.) the reaction mixture was stirred at room temperature for 2 h and heated at T = 85 °C for a further 2 h. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel (CS_2 →CS_2/toluene 1:1) to give unconsumed C_{60} (11.6 mg, 46%) and the monocycloadduct **8** (17.8 mg, 51%, 97% based on recovered C_{60}). **UV/vis** λ_{max}(toluene) [nm] = 254 (ϵ [$dm^3mol^{-1}cm^{-1}$] 56600) and 314 (20400); **IR** (film) ν_{max} [cm^{-1}] 2962-2851 (CH_3, CH_2, CH), 1594 (C=C_{arom}), 1544, 1514, 1487, 1405 (CH_2), 1335, 1260, 1219, 1090 (C_{aryl}-Cl), 1017, 850, 797, 773, 689, 667, 621; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.47 (2H, d, $^3J_{2',3'}$ = 8.8 Hz, H-2', H-6'), 7.91 (2H, d, $^3J_{3',2'}$ = 8.8 Hz, H-3', H-5'), 8.37 (2H, d, $^3J_{2,3}$ = 8.9 Hz, H-2, H-6), 8.55 (2H, d, $^3J_{3,2}$ = 8.9 Hz, H-3, H-5); **^{13}C NMR** (125 MHz, $CDCl_3$) δ_C 80.9 (C_{60}-1), 92.6 (C_{60}-2), 124.3 (C-3', C-5'), 125.3 (C-2', C-6'), 129.2 (C-3, C-5), 129.7 (C-2, C-6), 131.4 (*C*H=NN), 136.6, 136.8, 138.8 (1/2C), 140.1, 140.6, 142.0, 142.1, 142.3, 142.3, 142.3, 142.6, 142.6, 142.6 (1/2C), 143.1, 143.1, 144.4, 144.3, 144.4 (2C), 144.9, 145.3, 145.4, 145.5, 145.5, 145.7, 145.8, 146.1, 146.2, 146.2, 146.5, 146.6, 147.5 (1/2C), 147.8 (1/2C), 147.9 (1/2C); **m/z** (MALDI) calc. for [M] = 993.03, found = 993.61 (C_{60} standard m/z = 720.44).

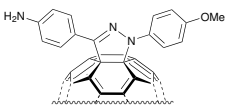
2.5.2 1-(4'-Methoxyphenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline[2] (10)



To a stirred solution of hydrazone **5** (17.8 mg, 69.4 μmol, 1 eq.) and C_{60} (50 mg, 69.4 μmol, 1 eq.) in anhydrous toluene (14 mL, 5 mM) was added (diacetoxyiodo)benzene (33.5 mg, 104.1 μmol, 1.5 eq.) under an atmosphere of argon at 40 °C. The solution was stirred for 3.5 h and the solvent removed quickly under reduced pressure. The crude product was purified by flash column chromatography on silica gel (CS_2 →CS_2/toluene 1:1→toluene) to give unconsumed C_{60} (38.3 mg, 76%) and the monocycloadduct. The solid was washed with MeOH (2 x 1.5 mL) and Et_2O (0.5 mL) to give pure **10** as a brown solid (0.8 mg, 1%, 5% based on recovered C_{60}). $\mathbf{R}_f$ 0.80 ($CHCl_3$/EtOAc 1:19); **UV/vis** λ_{max}(toluene) [nm] = 255 (ϵ [$dm^3mol^{-1}cm^{-1}$] 25300) and 312 (88000); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 3.84 (3H, s, OCH_3'), 3.87 (3H, s, OCH_3), 7.00 (2H, d, $^3J_{3',2'}$ = 8.9 Hz, H-3', H-5'),

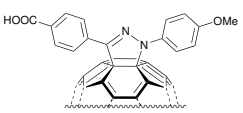
7.03 (2H, d, $^3J_{3,2}$ = 8.8 Hz, H-3, H-5), 7.80 (2H, d, $^3J_{2',3'}$ = 8.9 Hz, H-2', H-6'), 8.23 (2H, d, $^3J_{2,3}$ = 8.8 Hz, H-2, H-6); **^{13}C NMR** product was not sufficiently stable to enable us to record the spectrum; **m/z** (MALDI) calc. for [M] = 974.11, found = 972.81 (C_{60} standard m/z = 718.90).

2.5.3 1-(4'-Aminophenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline[27,29] (11)



To a stirred solution of fulleropyrazoline **7** (32.8 mg, 33.1 μmol, 1 eq.) and tin powder (2.36 g, 19.9 mmol, 600 eq.) in $CHCl_3$ (83 mL, 0.4 mM) was added HCl (33 mL of a 1 M aqueous solution, 1 mM) portionwise at room temperature. The solution was heated at reflux for 6 h, cooled to room temperature and neutralised with $NaOH_{aq}$ to pH 11. The aqueous phase was extracted with $CHCl_3$ (3 x 50 mL), the organic fractions were combined, washed with brine (2 x 50 mL), dried over $MgSO_4$, and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel ($CHCl_3$) to give unconsumed **7** (7.3 mg, 22%) and the monocycloadduct **11** as a brown solid (1.9 mg, 6%, 8% based on recovered **7**). $\mathbf{R}_f$ 0.47 ($CHCl_3$); **UV/vis** λ_{max}(toluene) [nm] = 256 (ϵ [dm^{3}mol^{-1}cm^{-1}] 38900) and 311 (15800); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 3.84 (3H, s, OCH_3), 6.79 (2H, d, $^3J_{3',2'}$ = 8.5 Hz, H-3', H-5'), 6.99 (2H, d, $^3J_{3,2}$ = 8.9 Hz, H-3, H-5), 7.80 (2H, d, $^3J_{2',3'}$ = 8.9 Hz, H-2', H-6'), 8.09 (2H, d, $^3J_{2,3}$ = 8.6 Hz, H-2, H-6); **^{13}C NMR** product was not sufficiently stable to enable us to record the spectrum; **m/z** (MALDI) calc. for [M] = 959.11, found = 959.35 (C_{60} standard m/z = 720.24).

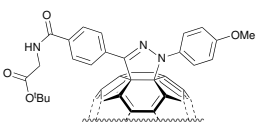
2.5.4 1-(4'-Carboxyphenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline[30,31] (13)



To a stirred solution of tetrazole **12** (3.3 mg, 11.1 μmol, 1 eq.) in toluene (14 mL, 0.8 mM) was added C_{60} (40 mg, 55.5 μmol, 5 eq.) at room temperature. The solution was stirred for 3.5 h under irradiation of a medium pressure mercury lamp. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (toluene/EtOAc 25:1→$CHCl_3$/MeOH 1:20) to give unconsumed C_{60} (27.2 mg, 68%) and the monocycloadduct. The solid was washed with MeOH (3 x 25 mL) to give pure **13** as a brown solid (4.3 mg, 39%). $\mathbf{R}_f$ 0.18 (toluene/EtOAc 4:1); **UV/vis** λ_{max}(toluene) [nm] = 255 (ϵ [dm^{3}mol^{-1}cm^{-1}] 54300) and 317 (18800); **IR** (film) ν_{max} [cm^{-1}] 2961-2851 (CH_3, CH_2, CH), 1507 (C=C_{arom}), 1462, 1409 (CH_2), 1259, 1222, 1086 (C_{aryl}-Cl), 1015, 863, 794, 700, 662; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 3.86 (3H, s, OCH_3), 7.02 (2H, d, $^3J_{3,2}$ = 8.4 Hz, H-3, H-5), 7.82 (2H, d, $^3J_{2',3'}$ = 8.4 Hz, H-2', H-6'), 8.21 (2H, d, $^3J_{2,3}$ = 8.1 Hz, H-2, H-6), 8.45 (2H, d, $^3J_{3',2'}$ = 8.2 Hz, H-3', H-5'); **^{13}C NMR** (125 MHz, $CDCl_3$) δ_C 55.7 (OCH_3), 80.9 (C_{60}-1), 93.2 (C_{60}-2), 114.8 (C-3, C-5), 126.9 (C-2', C-6'), 128.6 (C-3, C-5), 130.8 (C-2, C-6), 136.3 (C-1'), 136.8, 137.5, 137.9, 140.1, 140.4, 141.9, 142.0, 142.3, 142.4, 142.4, 142.5, 142.6, 143.0, 143.0, 143.3, 143.3, 144.4, 144.4, 145.2, 145.3, 145.4, 145.4, 145.6, 145.9, 145.9, 145.9, 146.0, 146.1, 146.1, 146.4, 146.5, 147.4, 147.8, 158.2 (C-4'), 190.1

(COOH); **m/z** (MALDI) calc. for [M] = 988.08, found = 720.80 (C_{60} standard m/z = 720.24).

2.5.5 *tert*-Butyl 2-(4'-(1"-(4"'-methoxyphenyl)-4",5"-fulleropyrazoline)benzamido) acetate[30,31] (15)



To a stirred solution of tetrazole **14** (5.7 mg, 14.0 μmmol, 1 eq.) in toluene (14 mL, 1 mM) was added C_{60} (50.4 mg, 14.0 μmol, 5 eq.) at room temperature. The solution was stirred for 5.5 h under irradiation of a medium pressure mercury lamp at $\lambda = 313nm$. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (toluene→toluene/EtOAc 9:1) to give unconsumed C_{60} (42.0 mg, 83%) and the monocycloadduct **15** as a white solid (3.8 mg, 25%). $\mathbf{R}_f$ 0.4 (toluene/EtOAc 9:1); **UV/vis** λ_{max}(toluene) [nm] = 257 (ϵ [$dm^3mol^{-1}cm^{-1}$] 55200) and 322 (183800); **IR** (film) ν_{max} [cm^{-1}] 3238 (NH), 2955-2852 (CH_3, CH_2, CH), 1737 (C=O), 1669, 1603 (CONH), 1492 (C=C_{arom}), 1459, 1399 (CH_2), 1376, 1363, 1248, 1210, 1190, 1160, 1125, 1082 (C_{aryl}-Cl), 1026, 999, 968, 907, 881, 858, 824, 771; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ_H 1.51 (9H, s, $C(CH_3)_3$), 3.85 (3H, s, OCH_3), 6.69 (1H, t, $^3J_{NH,Gly}$ = 4.7 Hz, NH), 7.02 (2H, d, $^3J_{3''',2'''}$ = 8.9 Hz, H-3"', H-5"'), 7.82 (2H, d, $^3J_{2''',3'''}$ = 8.9 Hz, H-2"', H-6"'), 7.94 (2H, d, $^3J_{3',2'}$ = 8.4 Hz, H-3', H-5'), 8.40 (2H, d, $^3J_{2',3'}$ = 8.2 Hz, H-2', H-6'); ^{13}**C NMR** (150 MHz, $CDCl_3$) δ_C 28.2 ($C(\underline{CH_3})_3$), 42.7 (C_{Gly}), 55.7 (OCH_3), 81.1 (C_{60}-1), 82.9 ($\underline{C}(CH_3)_3$), 93.0 (C_{60}-2), 114.7 (C-3"', C-5"'), 126.9 (C-2"', C-6"'), 127.7 (C-3', C-5'), 128.9 (C-2', C-6'), 134.2 (C-1"'), 136.0 (C-4'), 136.3, 136.7, 137.7 (C-1'), 140.1, 140.4, 142.0, 142.3, 142.4, 142.4, 142.5, 142.6, 143.0, 143.0, 143.3, 144.4 (2C), 145.2, 145.3, 145.5, 145.6, 145.9, 146.0, 146.1, 146.1, 146.4, 146.5, 147.4 (1/2C), 147.8 (1/2C), 158.1 (C-4"'), 166.8 (CONH), 169.3 (COO^tBu); **m/z** (MALDI) calc. for [M] = 1102.07, found = 1103.85 (C_{60} standard m/z = 723.42).

2.6 Light Induced Cleavage

2.6.1 C_{60} (16), $C_{60}O$ (17) and Ethyl 4-nitrobenzoate (27)

To a stirred solution of pyrazoline **7** (2.3 mg, 2.2 μmol, 1 eq.) in freeze-pump-thaw degassed toluene (2.2 mL, 1 mM) at room temperature was added recrystallised maleic anhydride (6.5 mg, 66 μmol, 30 eq.) under an atmosphere of argon. The solution was irradiated with a medium pressure mercury lamp (125 W) for 1 h until t.l.c. analysis indicated complete consumption of starting material. The crude product was purified by flash column chromatography on silica gel (CS_2 →toluene→toluene/EtOAc 25:1) to give an inseparable mixture of C_{60} and $C_{60}O$ (0.9 mg, 56%) and the nitrobenzylethyl ester (0.7 mg, 41%).

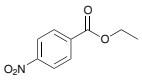
C_{60} (16)

R_f 0.98 (toluene/EtOAc 25:1); **UV/vis** λ_{max}(toluene) [nm] = 256 (ϵ [$dm^3mol^{-1}cm^{-1}$] 16700) and 329 (5000); **^{1}H NMR** (500 MHz, toluene-d_8) δ_H only solvent peaks; **^{13}C NMR** (125 MHz, toluene-d_8) δ_C 143.2; **m/z** (MALDI) calc. for [M] = 720.00, found = 720.42; data consistent with commercial sample.

$C_{60}O$ (17)

R_f 0.98 (toluene/EtOAc 25:1); **UV/vis** λ_{max}(toluene) [nm] = 251 (ϵ [$dm^3mol^{-1}cm^{-1}$] 32800) and 321 (9200); **^{1}H NMR** (500 MHz, toluene-d_8) δ_H only solvent peaks; **^{13}C NMR** (125 MHz, toluene-d_8) δ_C 140.9, 142.1, 142.4, 142.5, 142.7 (1/2C), 143.2, 143.2, 143.2 (C_{60}), 143.7 (1/2C), 144.1, 144.5, 144.5, 145.2 (1/2C), 145.3, 145.4, 145.4; **m/z** (MALDI) calc. for [M+O] = 735.99, found = 736.43 (C_{60} standard m/z = 720.42); data consistent with literature.[32]

Ethyl 4-nitrobenzoate (27)

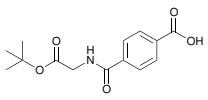


^{1}H NMR (700 MHz, $CDCl_3$) δ_H 1.43 (3H, t, ^3J = 7.2 Hz, $CH_2\underline{CH_3}$), 4.44 (2H, q, ^3J = 7.1 Hz, $\underline{CH_2}CH_3$), 8.22 (2H, d, $^3J_{2,3}$ = 8.7 Hz, H-2, H-6), 8.29 (2H, d, $^3J_{3,2}$ = 8.7 Hz, H-3, H-5); **^{13}C NMR** (150 MHz, toluene-d_8) δ_C 14.4 ($CH_2\underline{CH_3}$), 62.1 ($\underline{CH_2}CH_3$), 123.7 (C-3, C-5), 130.8 (C-2, C-6), 136.0 (C-1), 150.7 (C-4), 164.9 (COO); data consistent with literature.[12]

2.6.2 4-((2'-(*tert*-Butoxy)-2'-oxoethyl)carbamoyl)benzoic acid (22) and oxidised anisidines (23, 24)

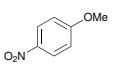
A stirred solution of pyrazoline **15** (1 mg, 0.9 μmol, 1 eq.) in $CDCl_3/D_2O$ 1:1 (1.8 mL, 1 mM) at room temperature was irradiated with a medium pressure mercury lamp (125 W) for 2 h at which point t.l.c. analysis indicated complete consumption of starting material. The crude products were characterised.

4-((2'-(*tert*-Butoxy)-2'-oxoethyl)carbamoyl)benzoic acid (22)



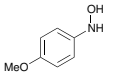
UV/vis λ_{max}($CDCl_3$) [nm] = 258 (ϵ [$dm^3mol^{-1}cm^{-1}$] 35000) and 327 (16500); **IR** (film) ν_{max} [cm^{-1}] 2977-2849 ($C_{aryl}H$), 1702 (C=O), 1653&1601 (CONH), 1541, 1504, 1459, 1421, 1259, 1155, 1142, 1099, 1027, 841 (C=C-H), 802, 669; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 1.51 (9H, s, $C(CH_3)_3$), 4.16 (2H, s, H_{Gly}), 6.83 (1H, t, $^3J_{NH,Gly}$ = 4.9 Hz, NH), 7.95 (2H, d, $^3J_{2,3}$ = 8.3 Hz, H-2, H-6), 8.29 (2H, d, $^3J_{3,2}$ = 8.2 Hz, H-3, H-5); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 28.2 ($C(\underline{CH_3})_3$), 42.5 (Gly), 82.9 ($\underline{C}(CH_3)_3$), 127.7 (C-2, C-6), 131.0 (C-3, C-5), 134.3 (C-4), 138.1 (C-1), 166.7 (COOH), 169.1 (COO^tBu), 180.8 (CONH); **m/z** (ES^+) calc. for $[M-H]^-$ = 278.1034, found = 278.1036.

2.6.3 1-Methoxy-4-nitrobenzene (23)



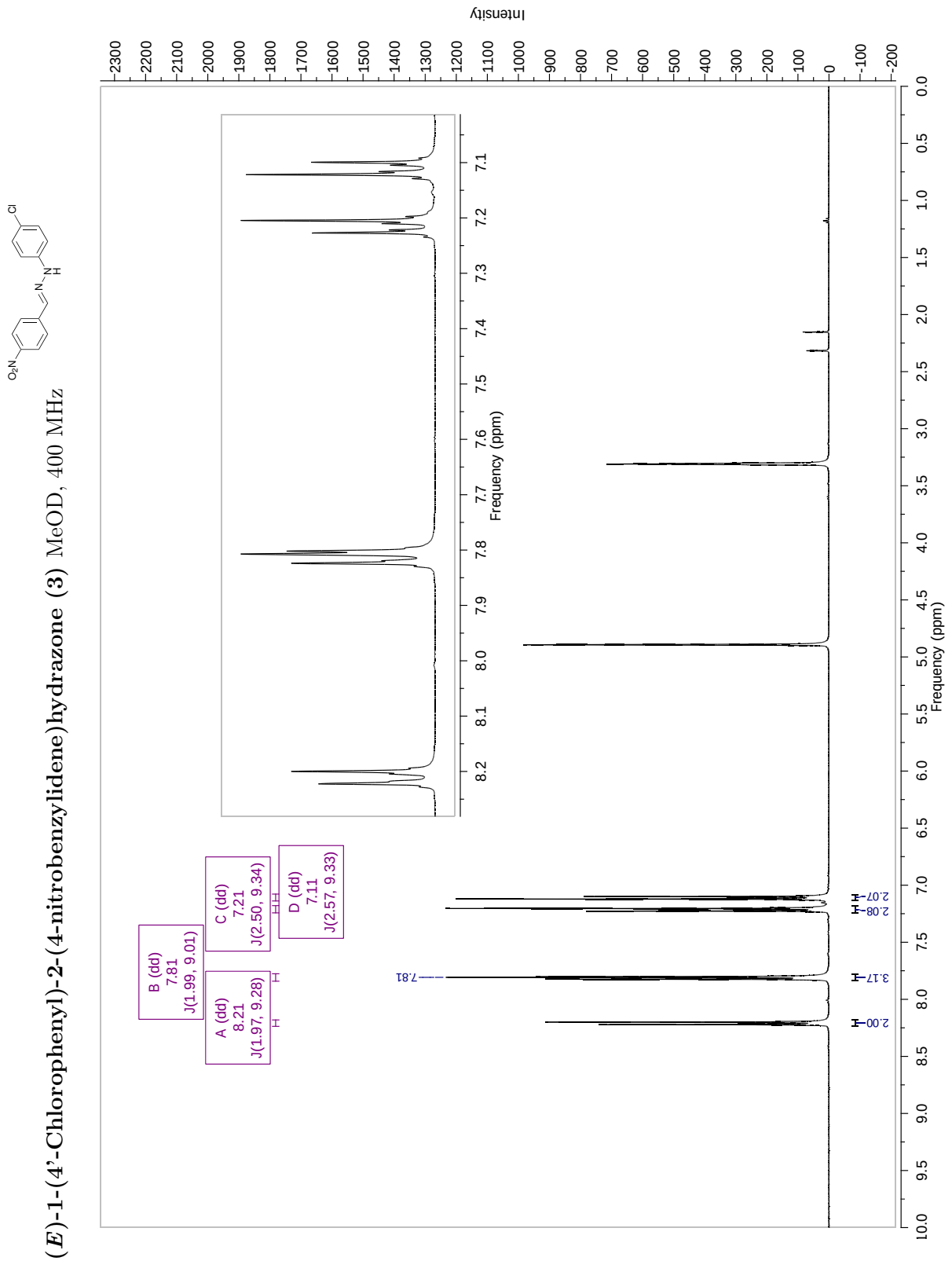
UV/vis λ_{max}($CDCl_3$) [nm] = 258 (ϵ [$dm^3mol^{-1}cm^{-1}$] 35000) and 327 (16500); **IR** (film) ν_{max} [cm^{-1}] 2977-2849 ($C_{aryl}H$), 1702 (C=O), 1653&1601 (CONH), 1541, 1504, 1459, 1421, 1259, 1155, 1142, 1099, 1027, 841 (C=C-H), 802, 669; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 3.95 (3H, s, OCH_3), 7.06 (2H, d, $^3J_{3,2}$ = 8.9 Hz, H-3, H-5), 8.04 (2H, d, $^3J_{2,3}$ = 8.9 Hz, H-2, H-6); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 55.8 (OCH_3), 114.6 (C-3, C-5), 126.5 (C-2, C-6), 164.4 (C-4), 146.7 (C-1); **m/z** (ES^+) calc. for $[M\text{-}MeOH]^-$ = 138.02, found = 138.02.

2.6.4 *N*-(4-Methoxyphenyl)hydroxylamine (24)

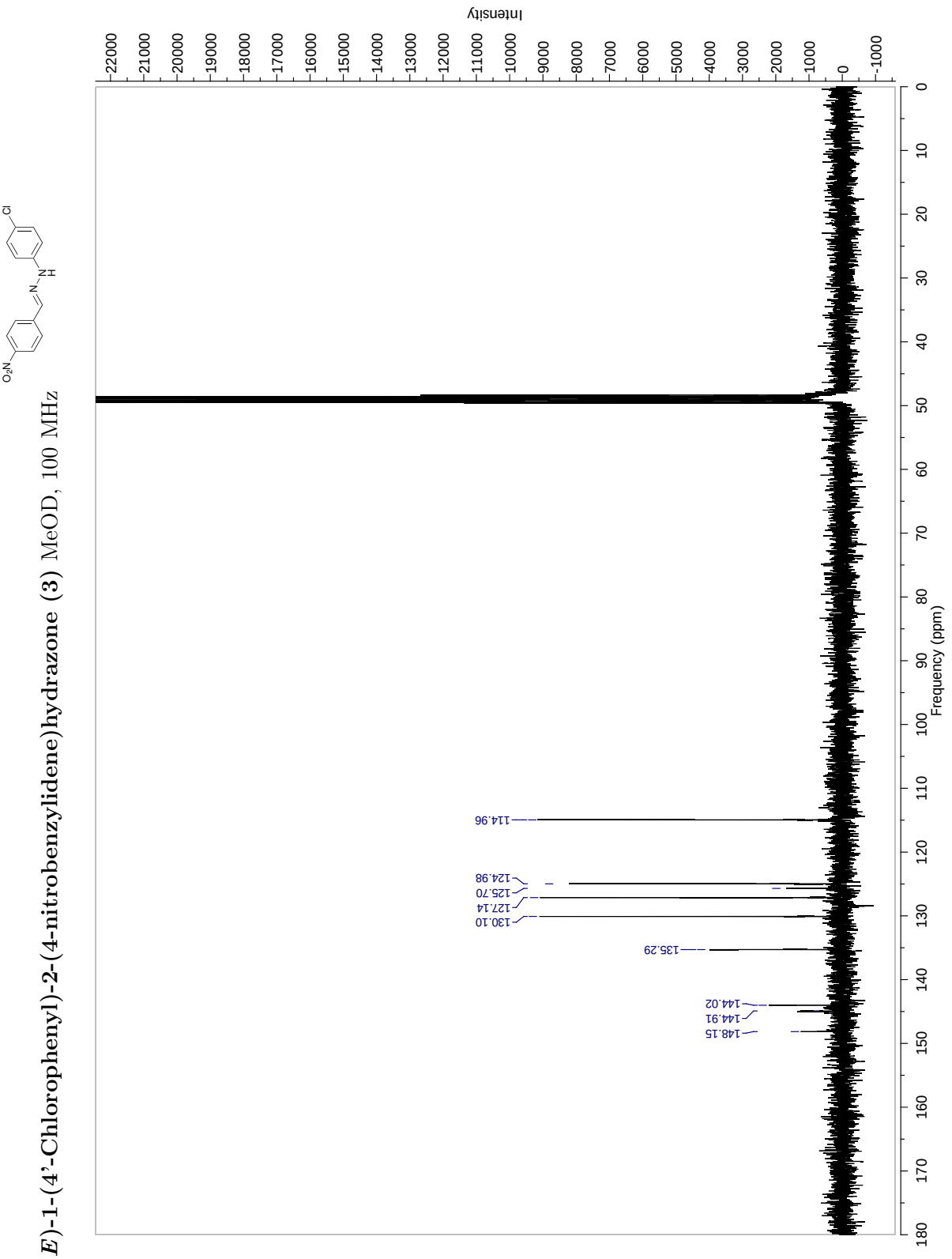


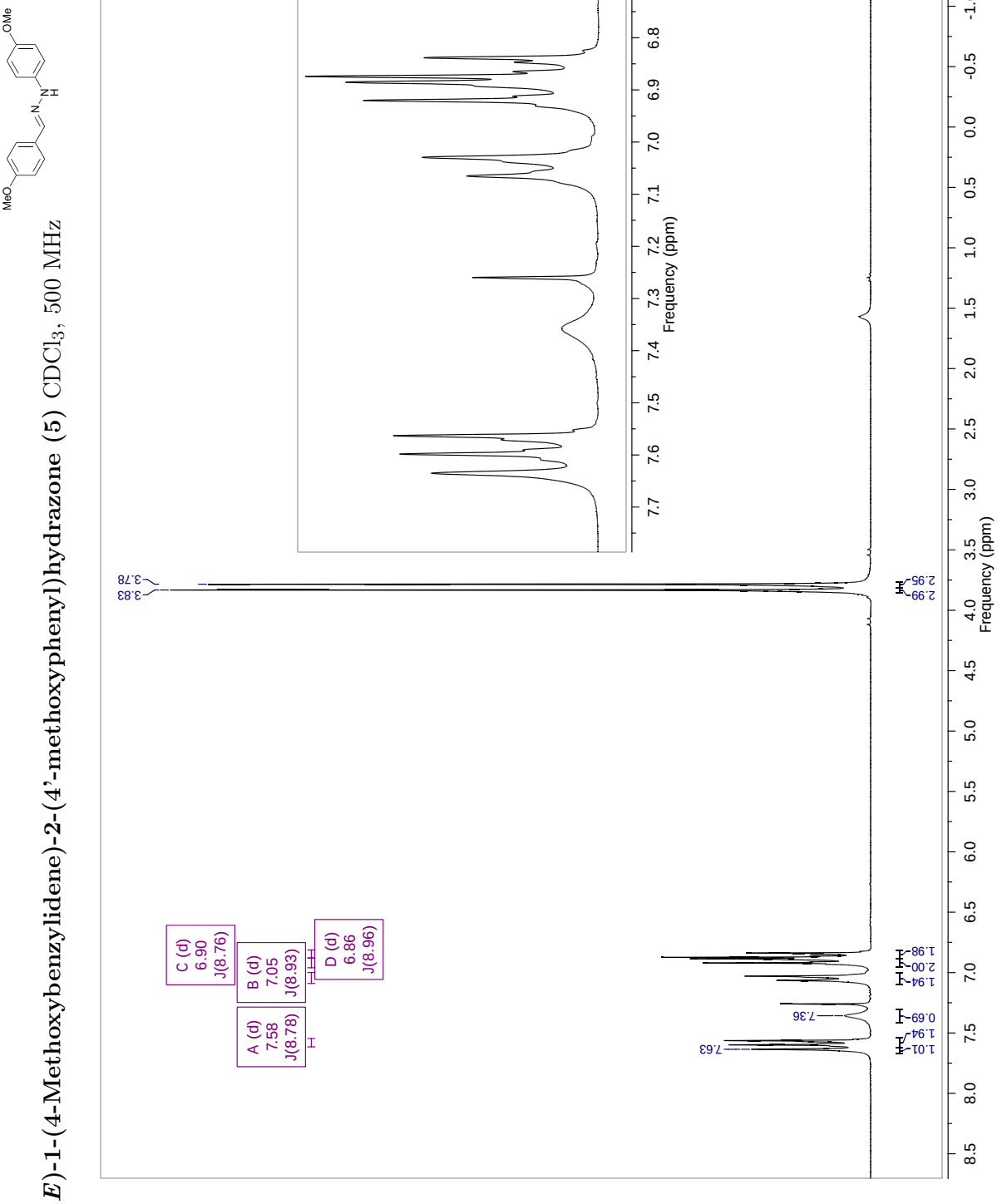
UV/vis λ_{max}($CDCl_3$) [nm] = 258 (ϵ [$dm^3mol^{-1}cm^{-1}$] 35000) and 327 (16500); **IR** (film) ν_{max} [cm^{-1}] 2977-2849 ($C_{aryl}H$), 1702 (C=O), 1653&1601 (CONH), 1541, 1504, 1459, 1421, 1259, 1155, 1142, 1099, 1027, 841 (C=C-H), 802, 669; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 3.81 (3H, s, OCH_3), 6.91 (2H, d, $^3J_{3,2}$ = 8.5 Hz, H-3, H-5), 7.29 (2H, d, $^3J_{2,3}$ = 8.8 Hz, H-2, H-6); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 55.8 (OCH_3), 114.0 (C-3, C-5), 129.5 (C-2, C-6), 158.6 (C-1); **m/z** (ES^+) calc. for $[M\text{-}H]^-$ = 138.06, found = 138.07.

3 Selected Spectra

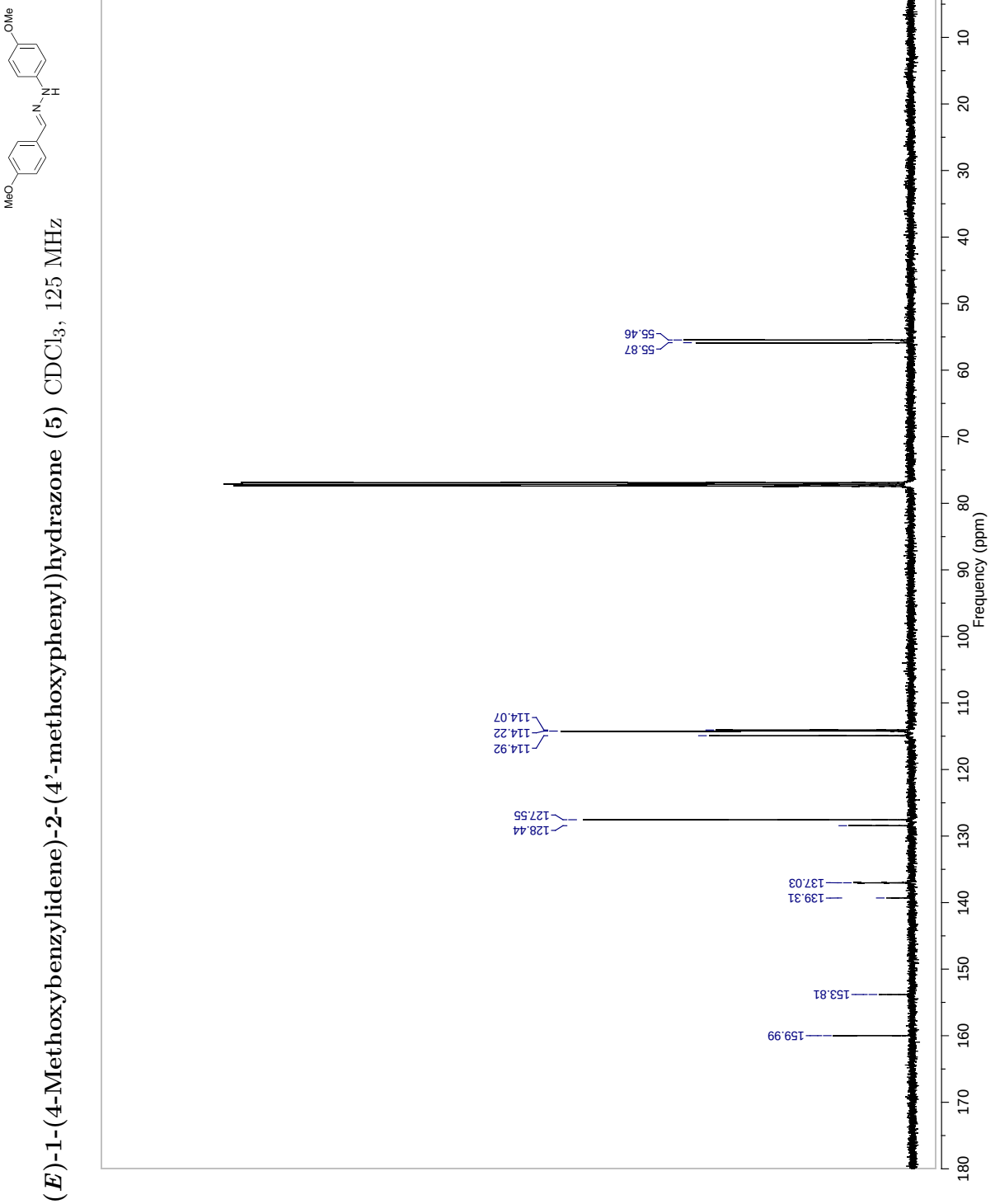


(*E*)-1-(4'-Chlorophenyl)-2-(4-nitrobenzylidene)hydrazone (3) MeOD, 100 MHz

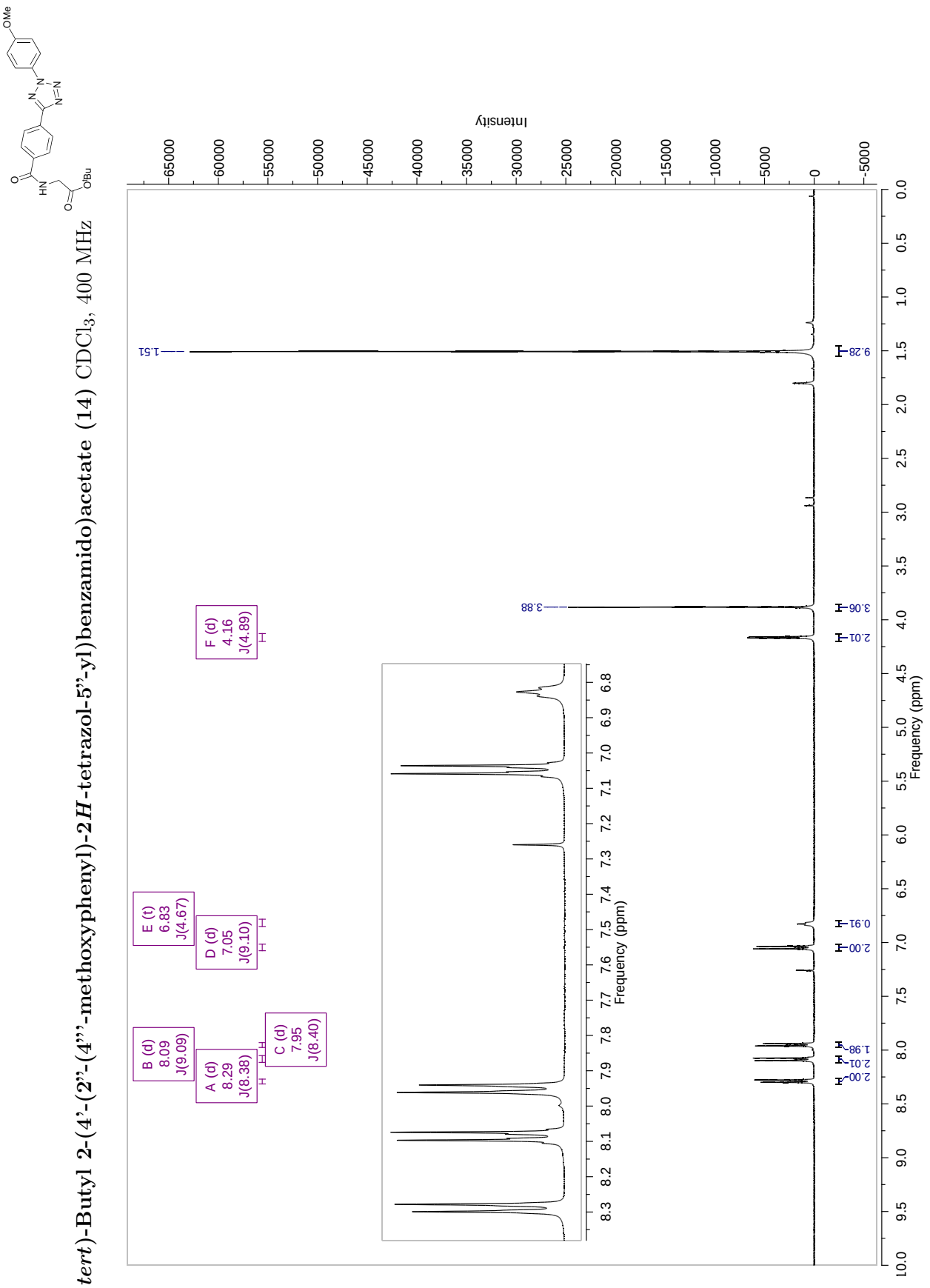




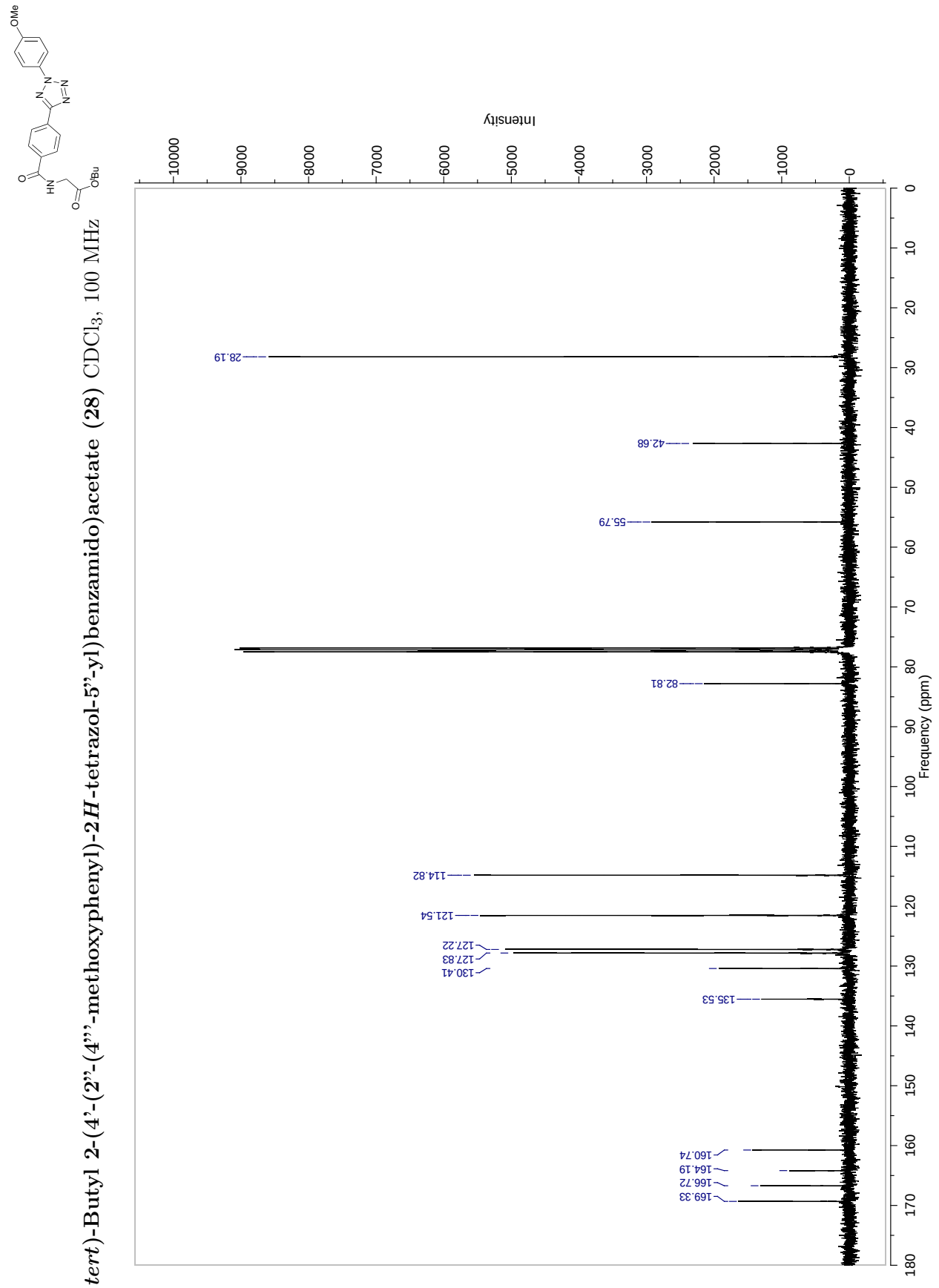
(*E*)-1-(4-Methoxybenzylidene)-2-(4'-methoxyphenyl)hydrazone (5) $CDCl_3$, 500 MHz



(*E*)-1-(4-Methoxybenzylidene)-2-(4'-methoxyphenyl)hydrazone (5) $CDCl_3$, 125 MHz

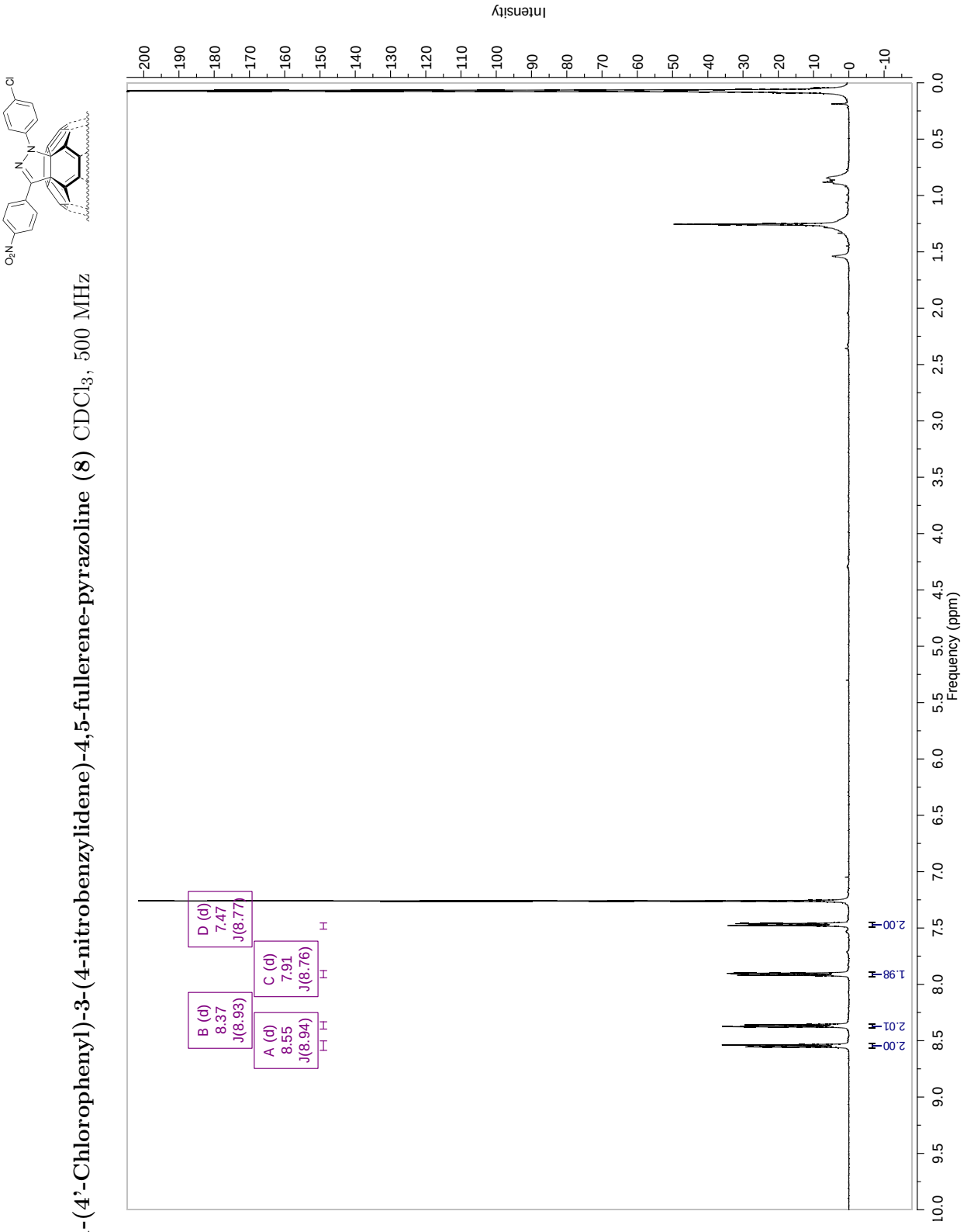


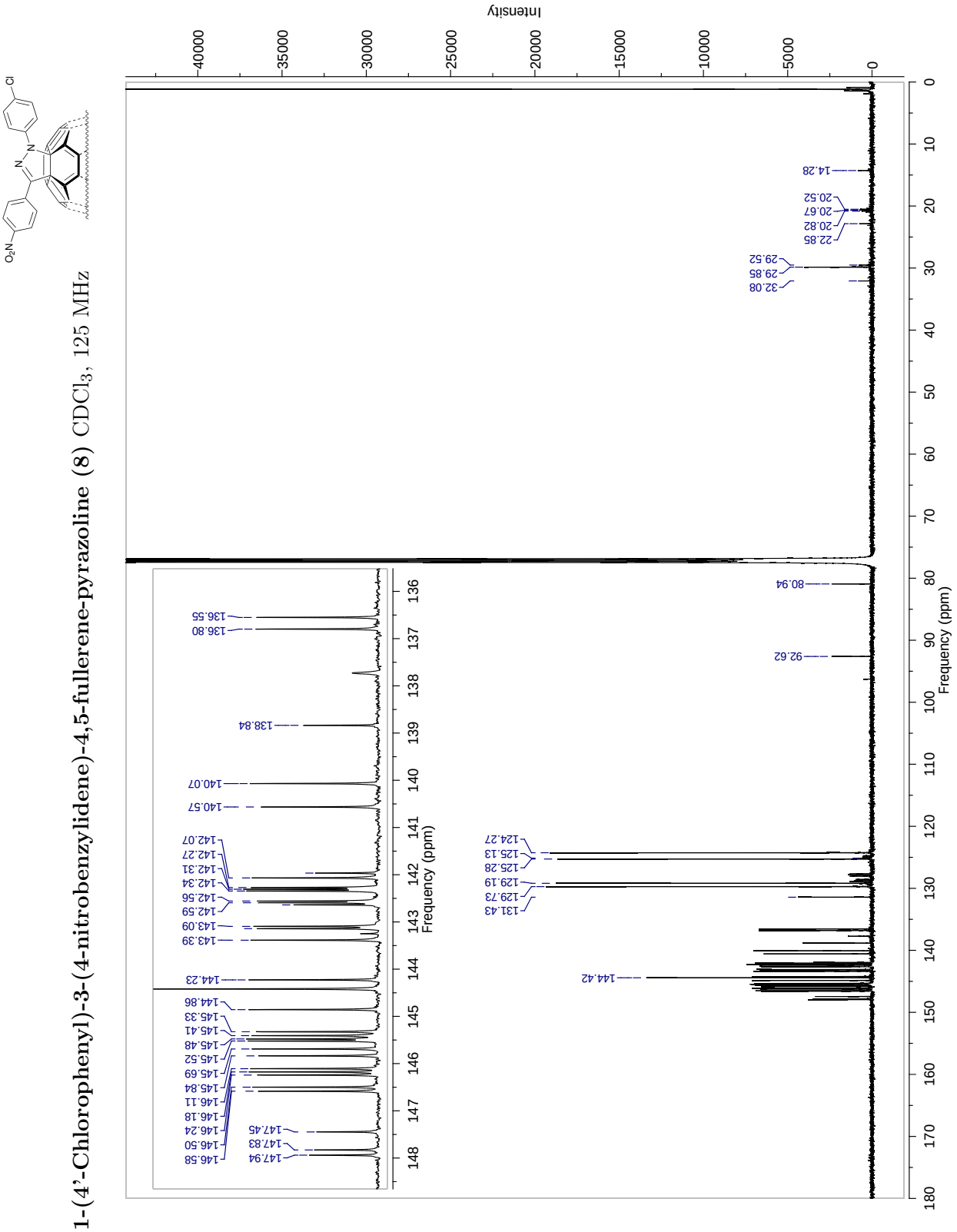
(*tert*)-Butyl 2-(4'-(2''-(4'''-methoxyphenyl)-2*H*-tetrazol-5''-yl)benzamido)acetate (14) $CDCl_3$, 400 MHz



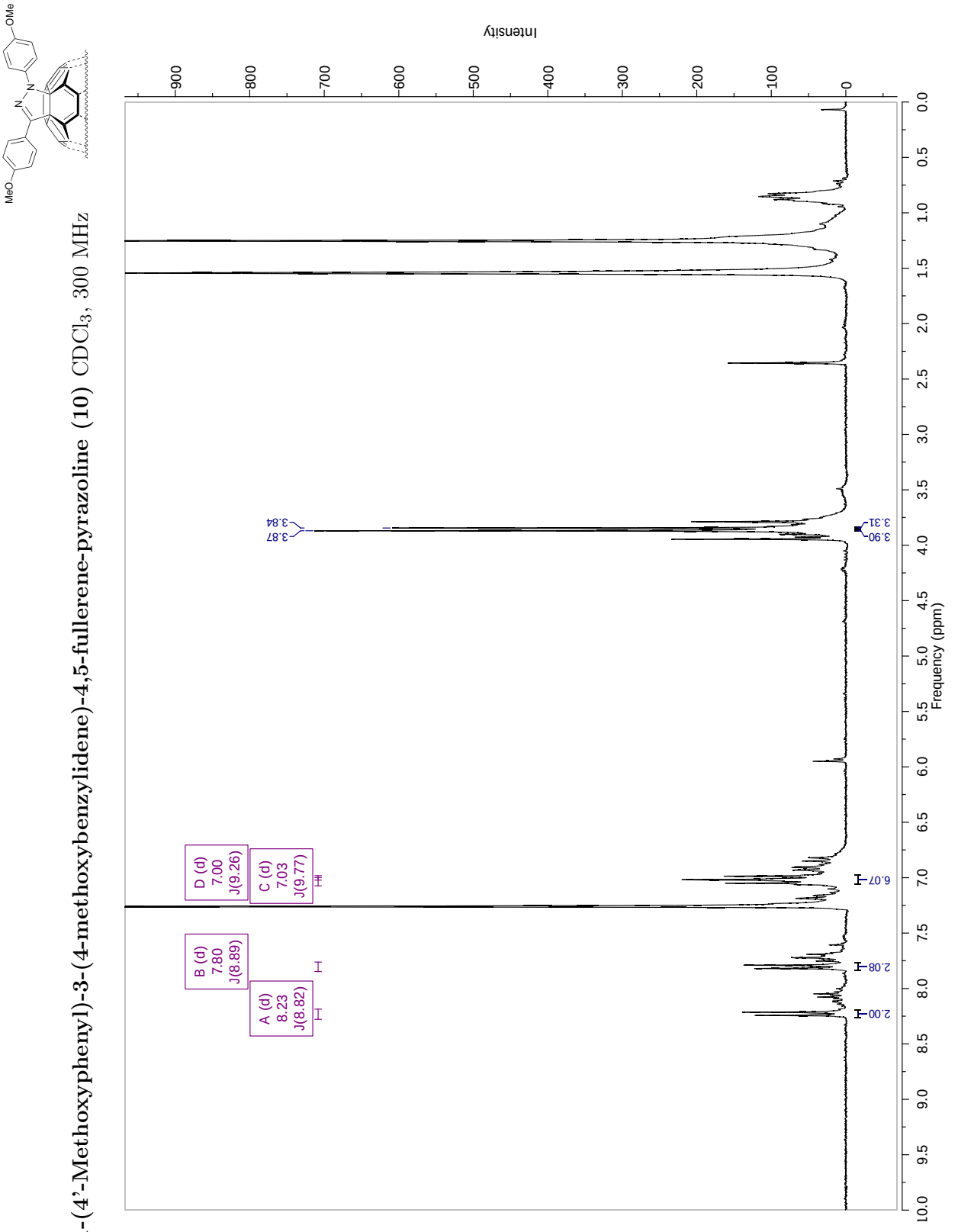
(*tert*)-Butyl 2-(4'-(2''-(4'''-methoxyphenyl)-2*H*-tetrazol-5''-yl)benzamido)acetate (28) $CDCl_3$, 100 MHz

1-(4'-Chlorophenyl)-3-(4-nitrobenzylidene)-4,5-fullerene-pyrazoline (8) $CDCl_3$, 500 MHz

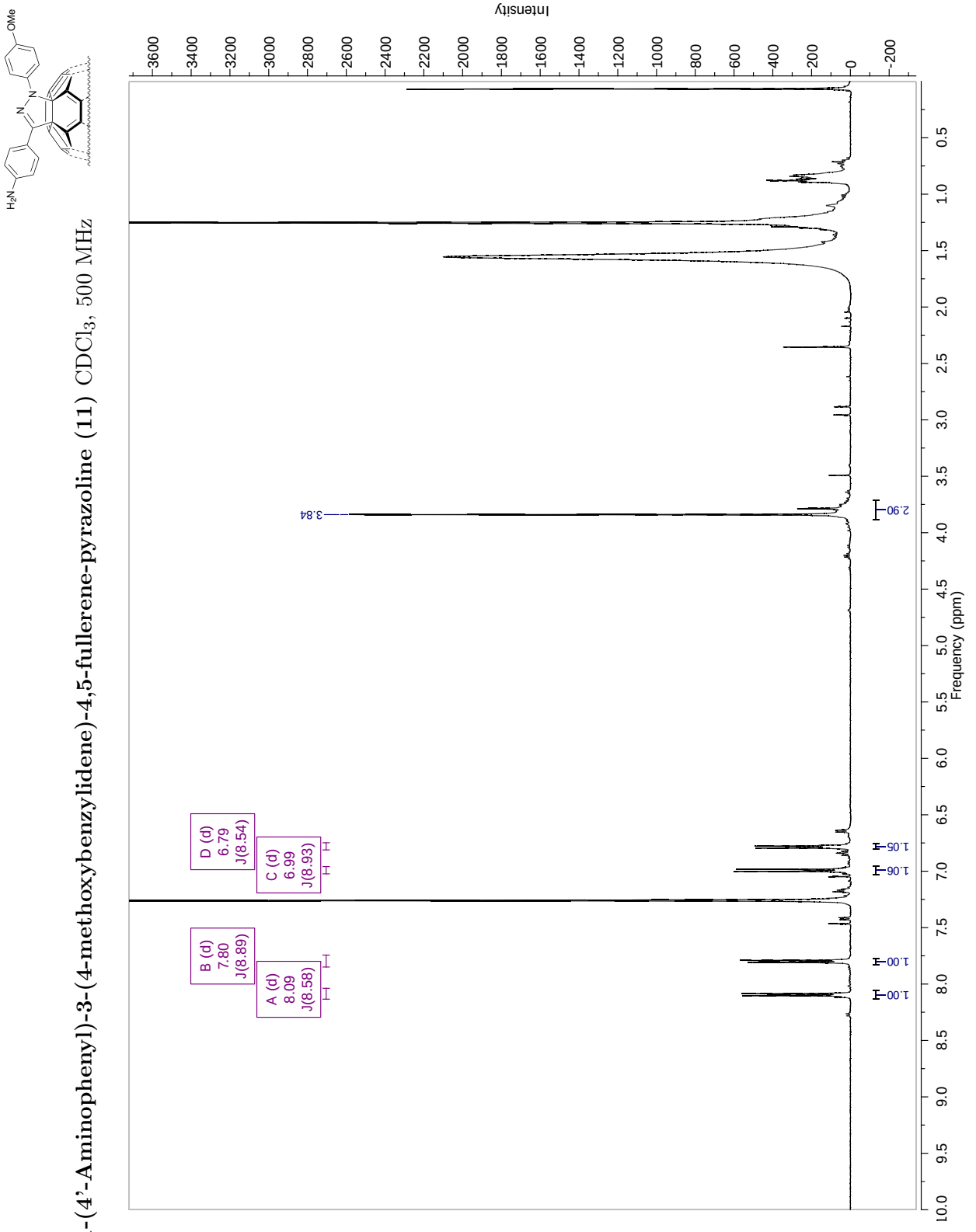




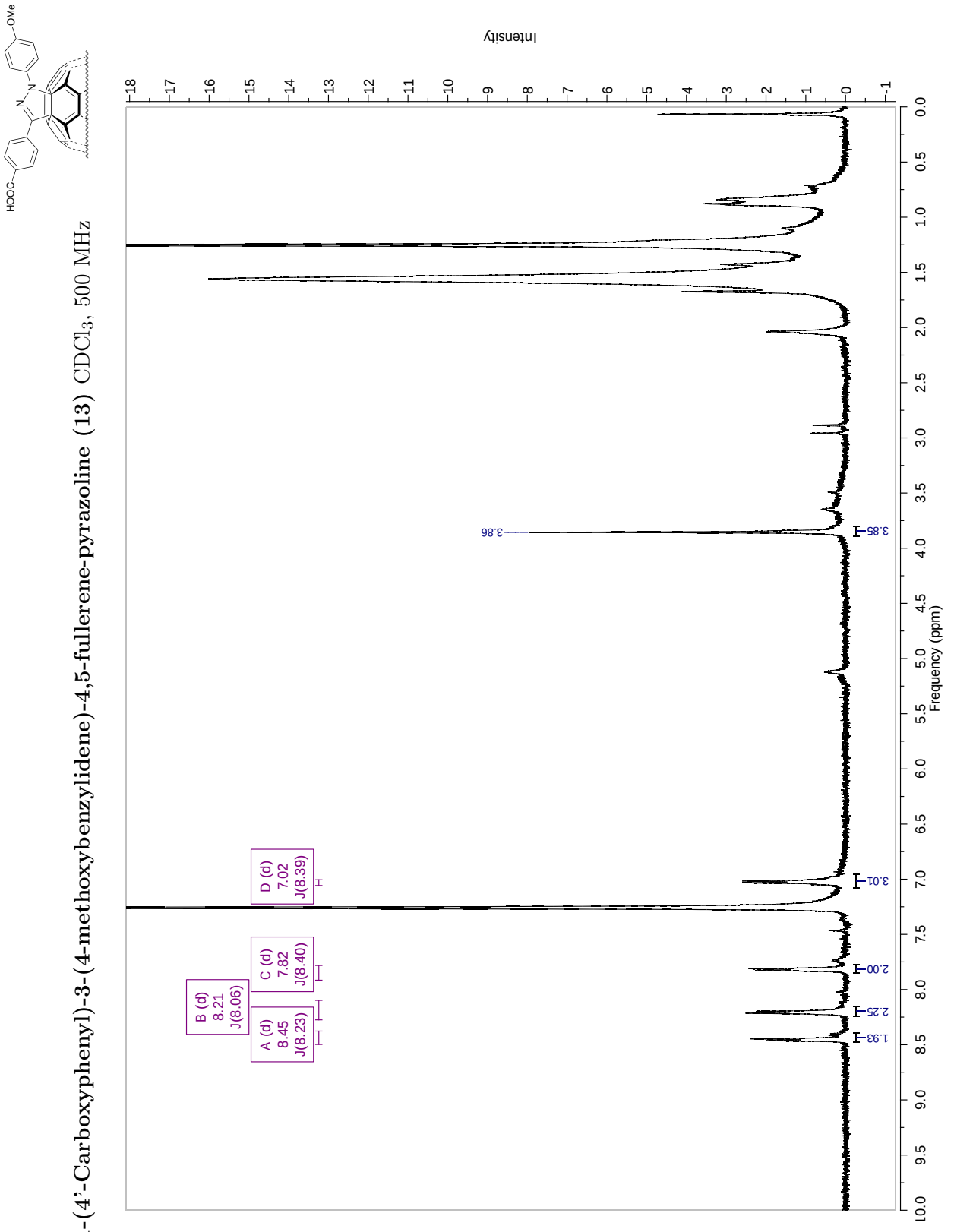
1-(4'-Chlorophenyl)-3-(4-nitrobenzylidene)-4,5-fullerene-pyrazoline (8) $CDCl_3$, 125 MHz



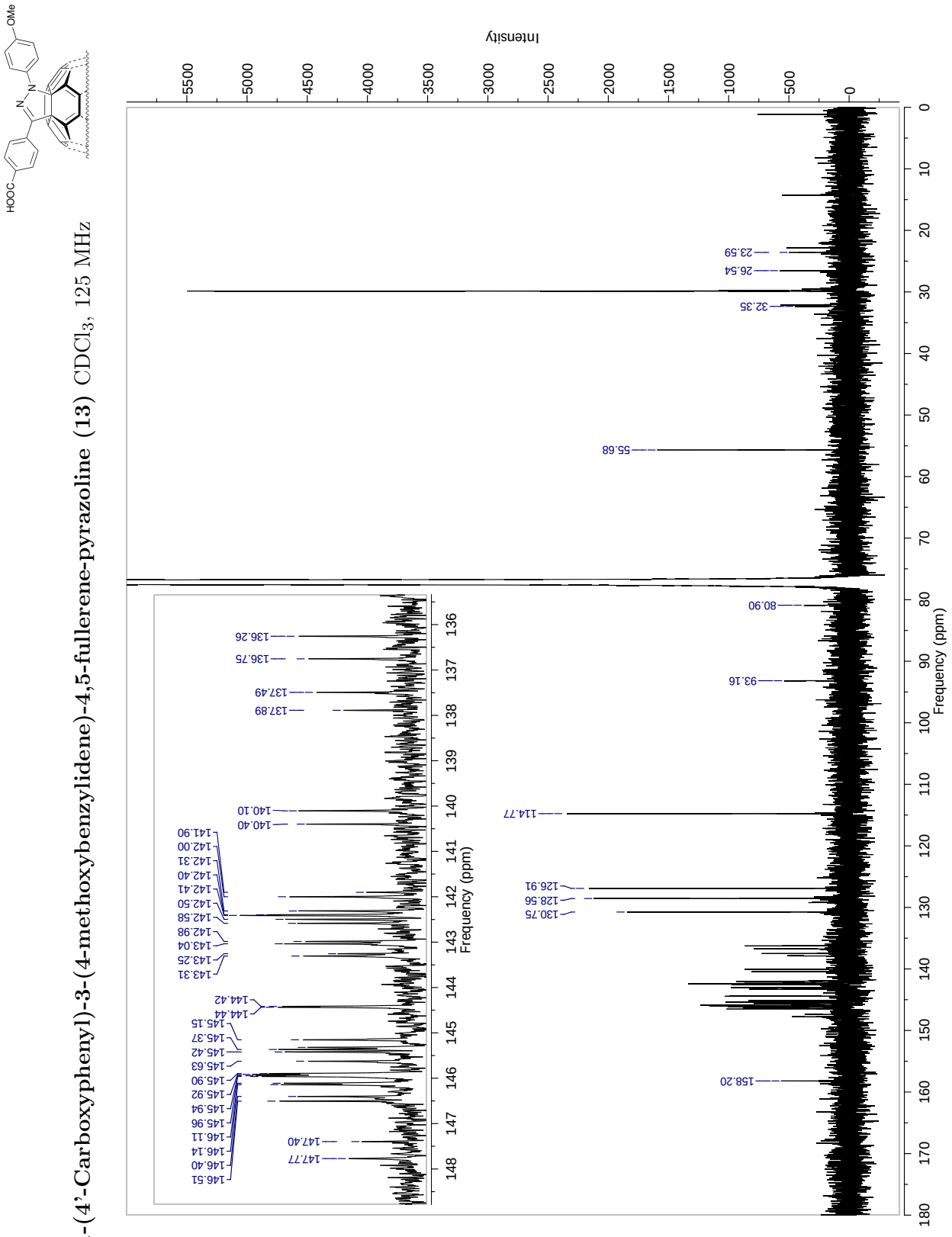
1-(4'-Methoxyphenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline (10) $CDCl_3$, 300 MHz



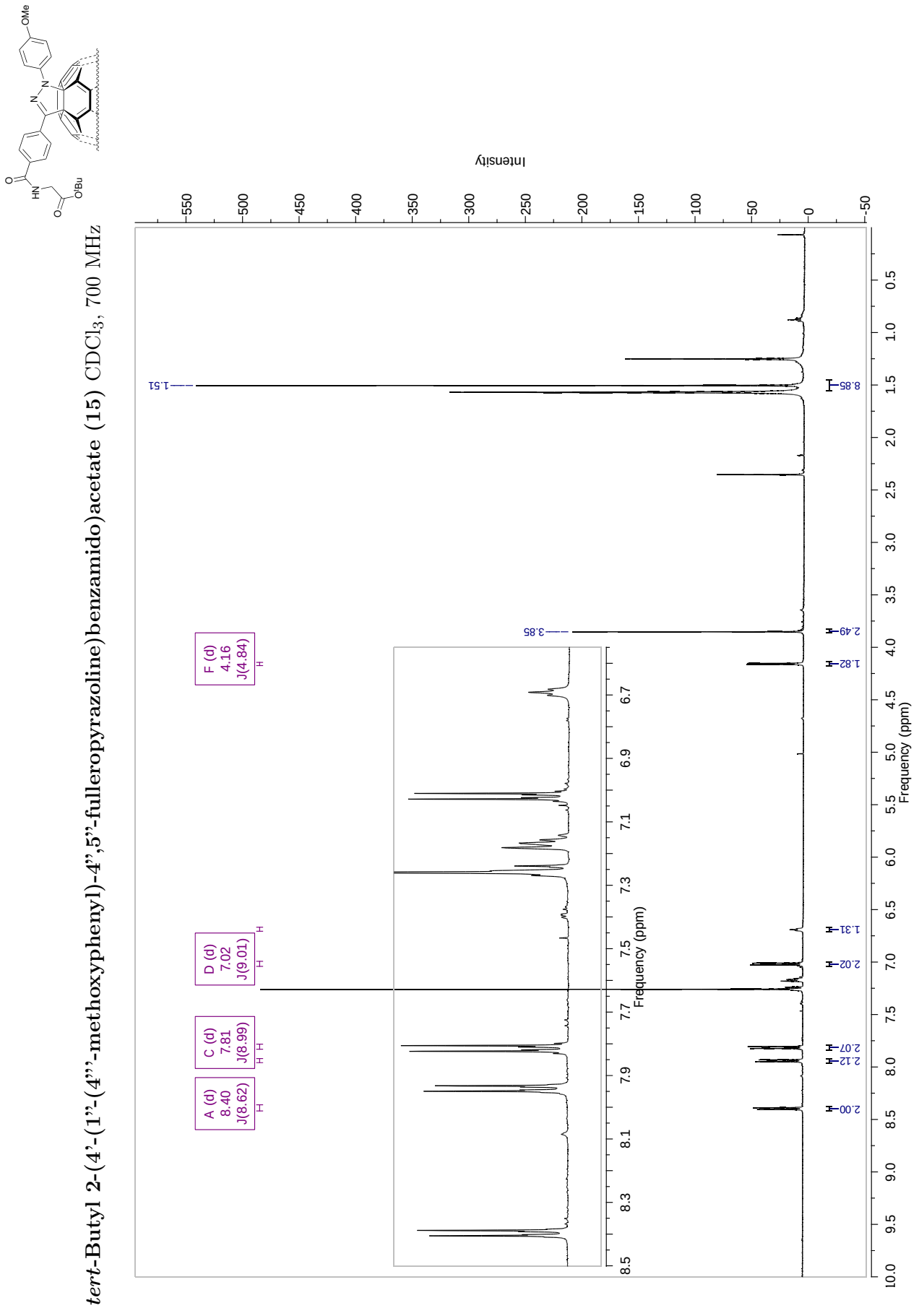
1-(4'-Aminophenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline (11) $CDCl_3$, 500 MHz



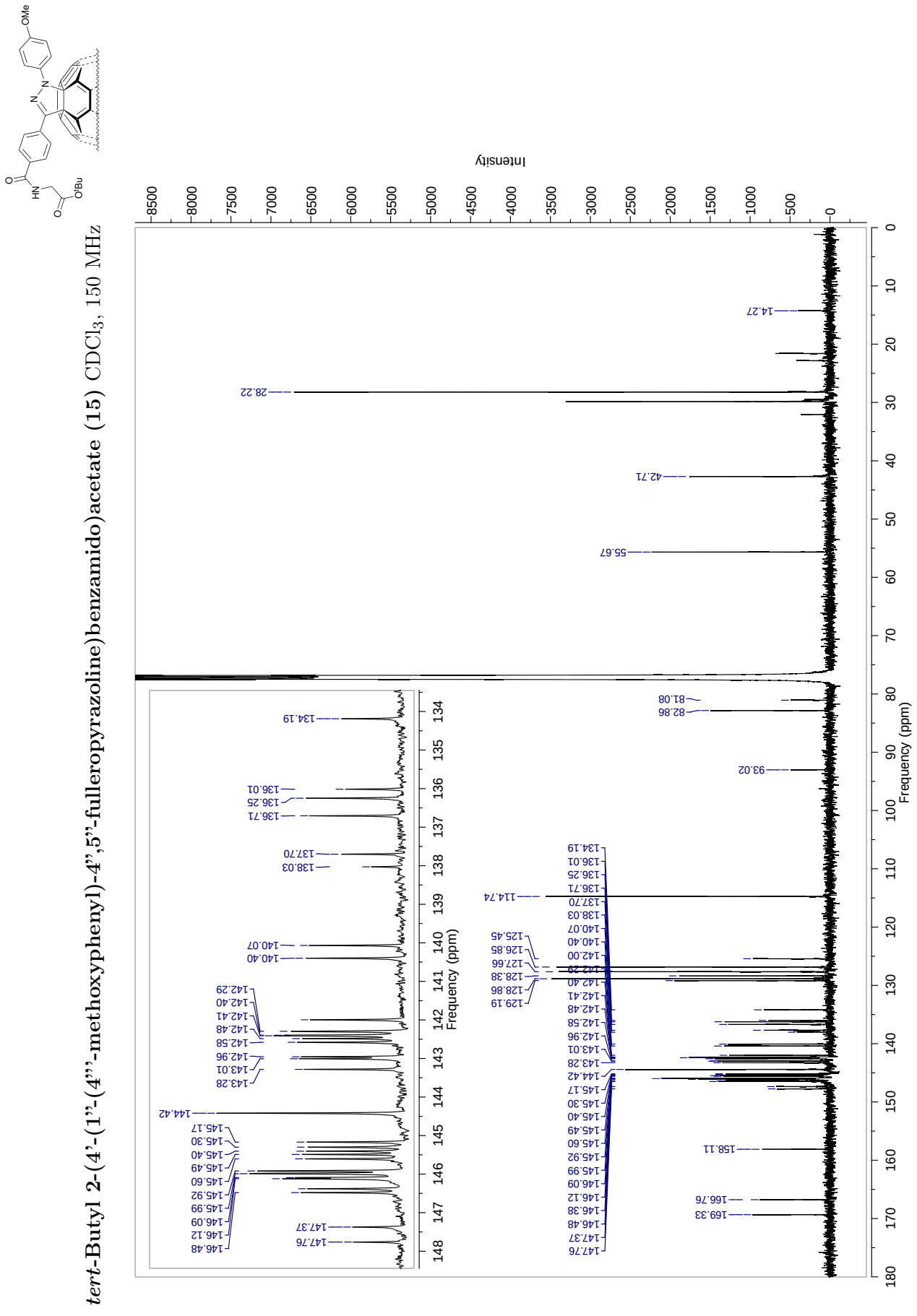
1-(4'-Carboxyphenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline (13) $CDCl_3$, 500 MHz



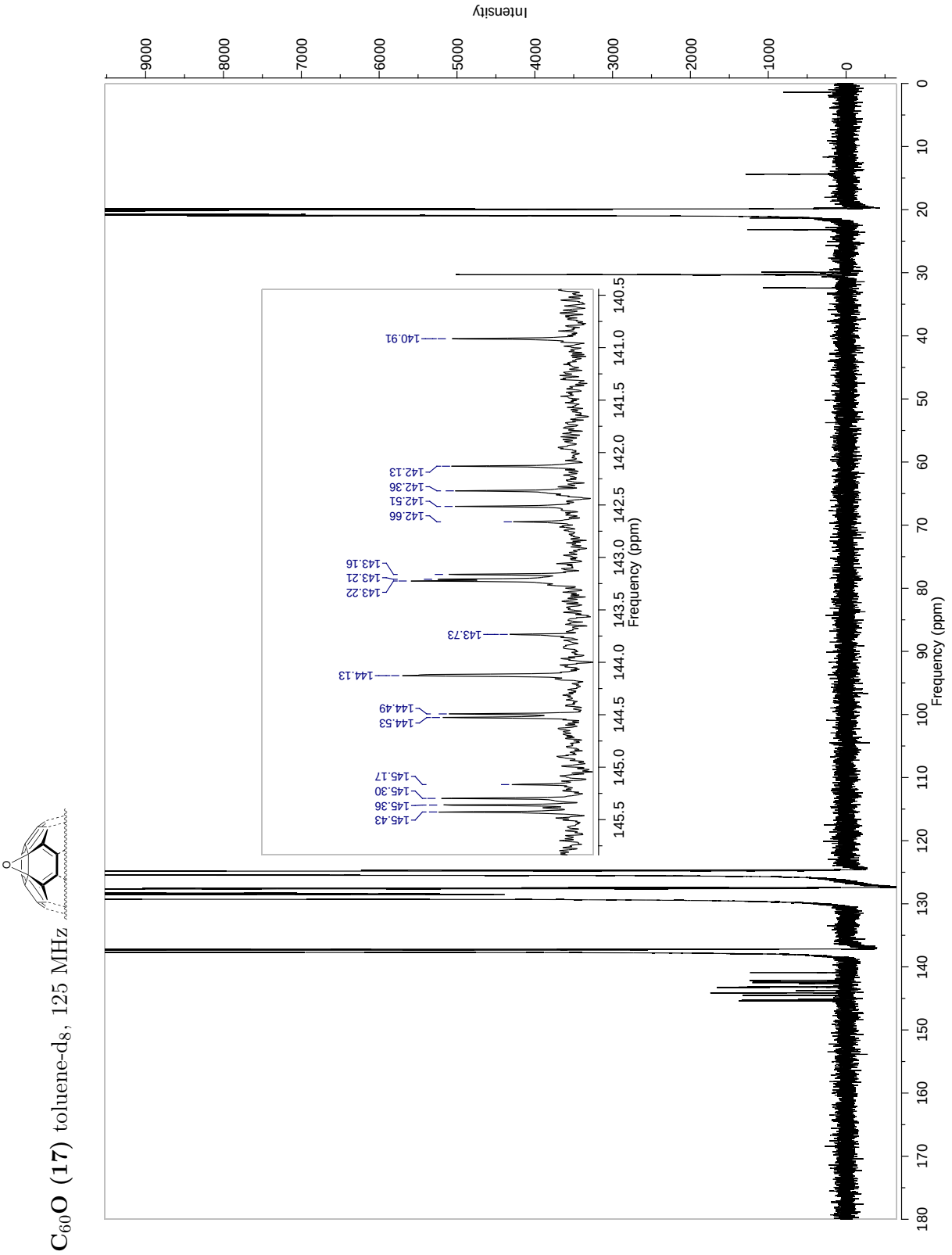
1-(4'-Carboxyphenyl)-3-(4-methoxybenzylidene)-4,5-fullerene-pyrazoline (13) $CDCl_3$, 125 MHz

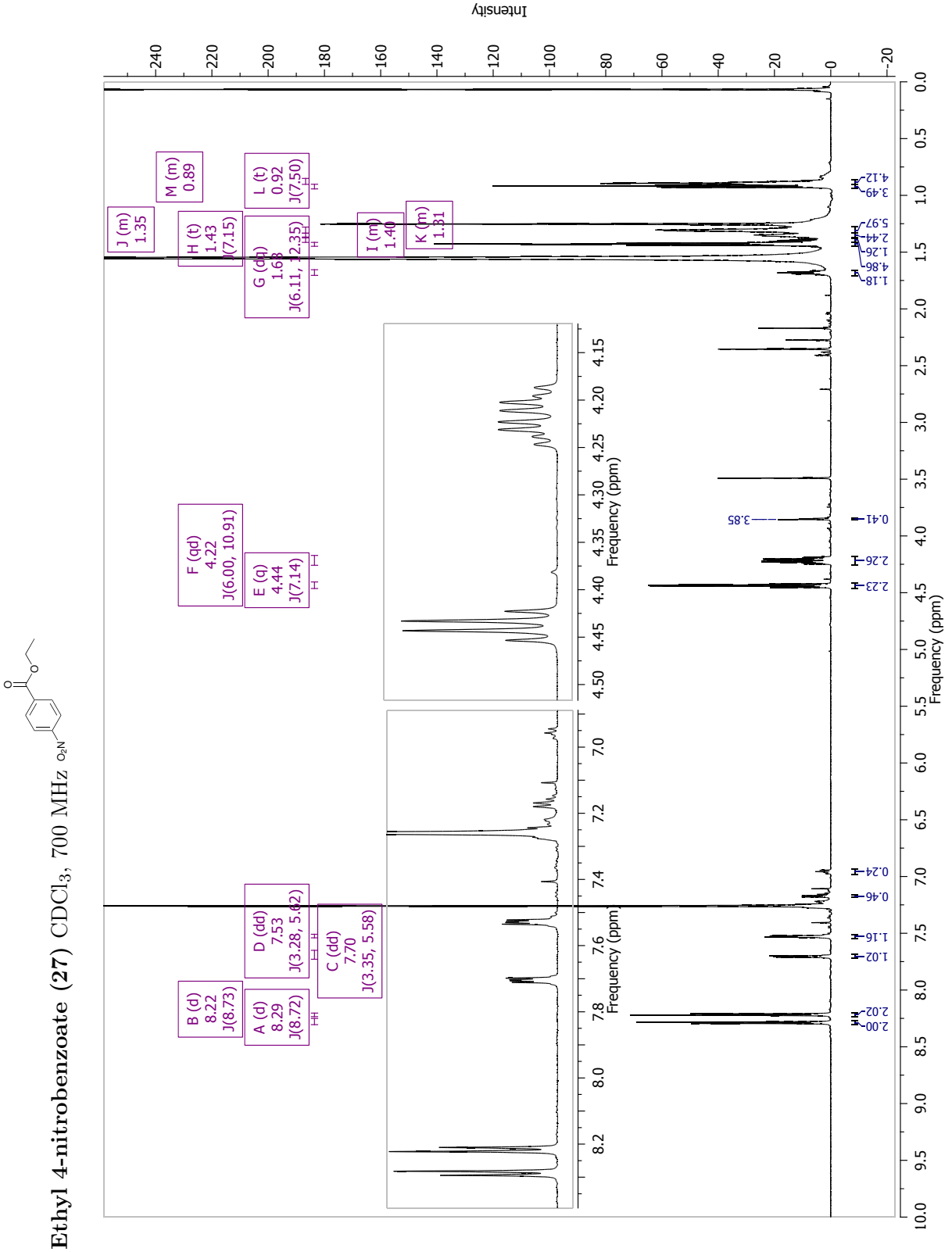


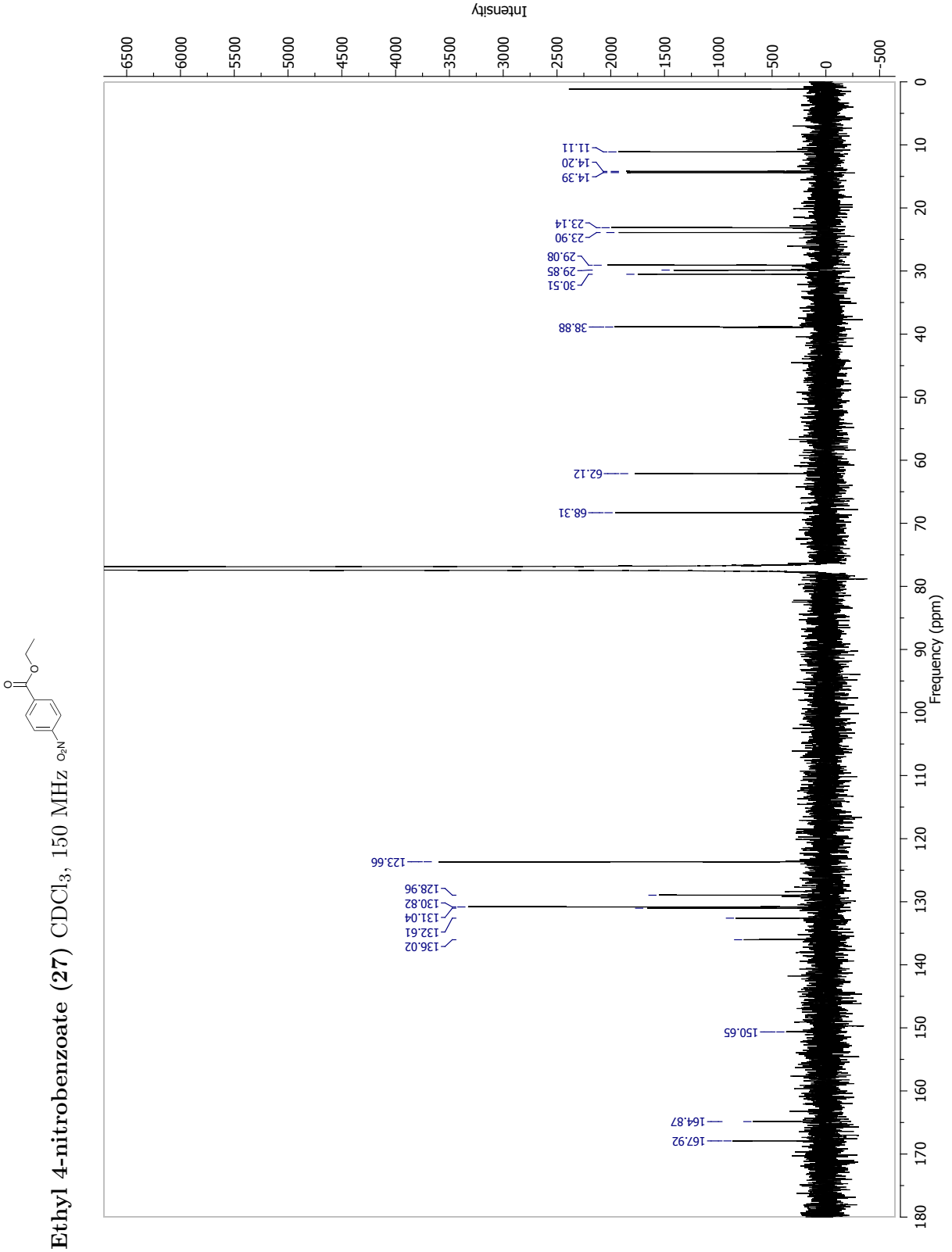
***tert*-Butyl 2-(4'-(1''-(4'''-methoxyphenyl)-4'',5''-fulleropyrazoline)benzamido)acetate (15)** $CDCl_3$, 700 MHz

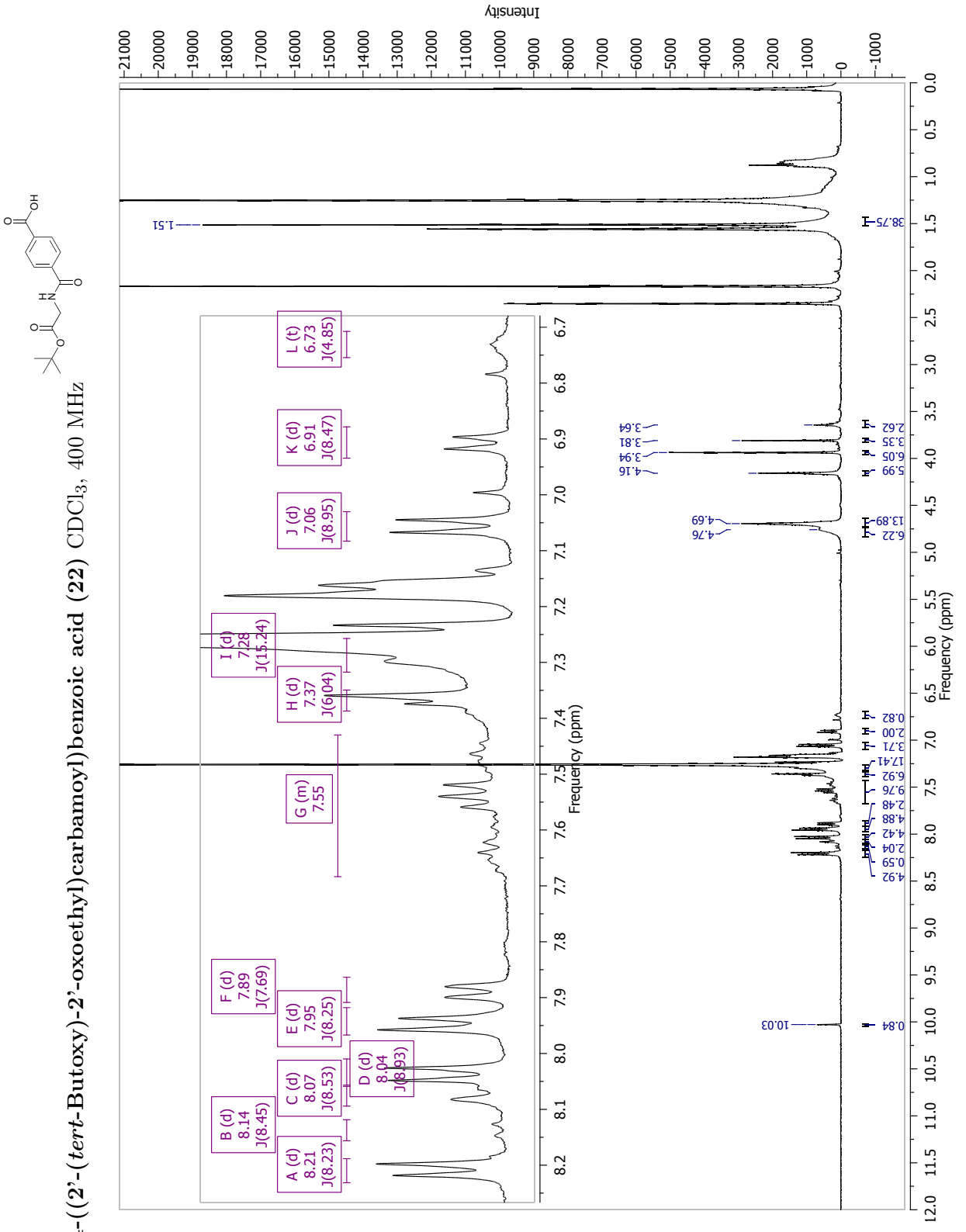


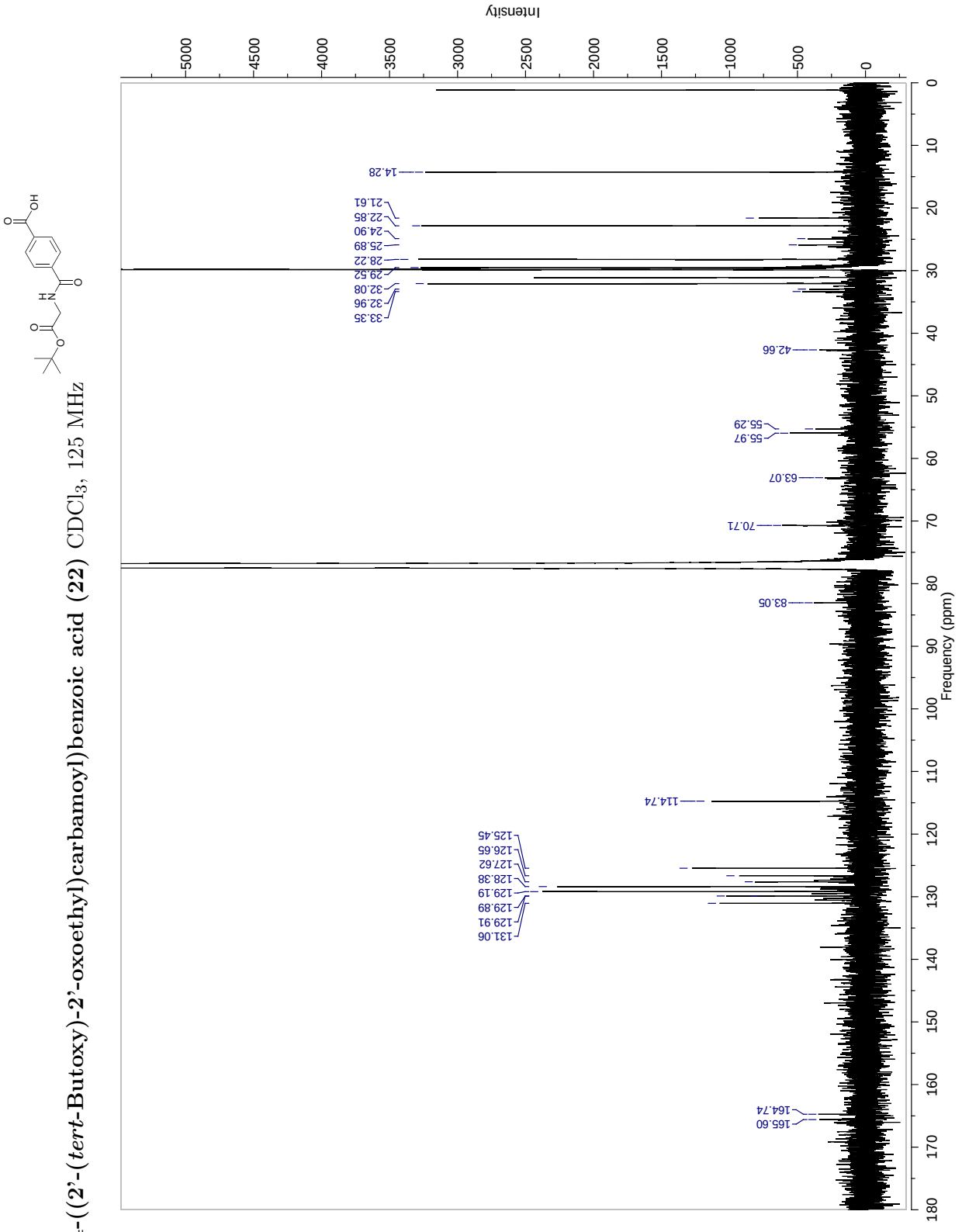
***tert*-Butyl 2-(4'-(1''-(4'''-methoxyphenyl)-4'',5''-fulleropyrazoline)benzamido)acetate (15)** $CDCl_3$, 150 MHz


C60O (17) toluene-d8, 125 MHz
Intensity
Frequency (ppm)
145.43
145.36
145.30
145.17
144.53
144.49
144.13
143.73
143.22
143.21
143.16
142.66
142.51
142.36
142.13
140.91


Ethyl 4-nitrobenzoate (27) CDCl3, 700 MHz
B (d) 8.22 J(8.73)
A (d) 8.29 J(8.72)
D (dd) 7.53 J(3.28, 5.62)
C (dd) 7.70 J(3.35, 5.58)
F (qd) 4.22 J(6.00, 10.91)
E (q) 4.44 J(7.14)
J (m) 1.35
M (m) 0.89
H (t) 1.43 J(7.15)
G (dd) 1.68 J(6.11, 12.35)
L (t) 0.92 J(7.50)
I (m) 1.40
K (m) 1.81
Intensity
Frequency (ppm)


Ethyl 4-nitrobenzoate (27) $CDCl_3$, 150 MHz
Intensity
Frequency (ppm)
167.92
164.87
150.65
136.02
132.61
131.04
130.82
128.96
123.66
68.31
62.12
38.88
30.51
29.85
29.08
23.90
23.14
14.39
14.20
11.11


4-((2'-(tert-Butoxy)-2'-oxoethyl)carbamoyl)benzoic acid (22) CDCl3, 400 MHz
Intensity
Frequency (ppm)
A (d) 8.21 J(8.23)
B (d) 8.14 J(8.45)
C (d) 8.07 J(8.53)
D (d) 8.04 J(8.93)
E (d) 7.95 J(8.25)
F (d) 7.89 J(7.69)
G (m) 7.55
H (d) 7.37 J(6.04)
I (d) 7.28 J(15.24)
J (d) 7.06 J(8.95)
K (d) 6.91 J(8.47)
L (t) 6.73 J(4.85)
1.51
10.03
38.75
0.84
4.92
0.59
2.04
4.42
4.88
2.48
9.76
6.92
17.41
3.71
2.00
0.82
13.89
6.22
4.69
4.76
5.99
6.05
3.35
2.62
4.16
3.94
3.81
3.64



4-((2'-(*tert*-Butoxy)-2'-oxoethyl)carbamoyl)benzoic acid (22) $CDCl_3$, 125 MHz

References

1. K. H. Pausacker. *J. Chem. Res.* **1950**, 3478–3481.
2. B. Lu, J. Zhang, J. Li, J. Yao, M. Wang, Y. Zou, and S. Zhu. *Tetrahedron* **2012**, *68* (43), 8924–8930.
3. T. Santa, D. Koga, and K. Imai. *Biomed. Chromatogr.* **1995**, *9* (2), 110–111.
4. J. R. Deye, A. N. Shiveley, S. A. Oehrle, and K. A. Walters. *J. Chromatogr., A* **2008**, *1181* (1-2), 159–161.
5. L. S. K. Pang and M. A. Wilson. *J. Phys. Chem.* **1993**, *97* (26), 6761–6763.
6. R. Villano, M. R. Acocella, and A. Scettri. *Tetrahedron Lett.* **2014**, *55* (15), 2442–2445.
7. B. Busch, N. Ueberschaar, S. Behnken, Y. Sugimoto, M. Werneburg, N. Traitcheva, J. He, and C. Hertweck. *Angew. Chem. Int. Ed.* **2013**, *52* (20), 5285–5289.
8. D. W. Beistel and W. D. Edwards. *J. Phys. Chem.* **1976**, *80* (18), 2023–2027.
9. S. Dohi, K. Moriyama, and H. Togo. *Eur. J. Org. Chem.* **2013**, *2013* (34), 7815–7822.
10. G. Aridoss and K. K. Laali. *J. Org. Chem.* **2011**, *76* (19), 8088–8094.
11. G. A. Molander and L. N. Cavalcanti. *J. Org. Chem.* **2012**, *77* (9), 4402–4413.
12. D. Giunta, M. P. Masia, M. Marchetti, R. Morrone, and M. Solinas. *Tetrahedron Lett.* **2013**, *54* (3), 5122–5125.
13. H. C. Yao and P. J. Resnick. *J. Org. Chem.* **1964**, *30* (8), 2832–2834.
14. J. R. Hwu, C. C. Lin, S. H. Chuang, K. Y. King, T.-R. Su, and S.-C. Tsay. *Bioorg. Med. Chem.* **2004**, *12* (10), 2509–2515.
15. Properties of Common Laboratory Solvents. `http://cheminfo.chemi.muni.cz/ianua/epr/tab/PropertiesofCommonLaboratorySolvents.pdf`. Accessed: 2014-08.
16. C. Ouannes and T. Wilson. *J. Am. Chem. Soc.* **1968**, *90* (23), 6527–6528.
17. D. M. Guldi, R. E. Huie, P. Neta, H. Hungerbühler, and K.-D. Asmus. *Chem. Phys. Lett.* **1994**, *223* (5-6), 511–516.
18. D. I. Schuster, P. S. Baran, R. K. Hatch, A. U. Khan, and S. R. Wilson. *Chem. Comm.* **1998**, 2493–2494.
19. Y.-P. Sun, B. Ma, and G. E. Lawson. *Chem. Phys. Lett.* **1995**, *233*, 57–62.
20. G. E. Lawson, A. Kitaygorodskiy, and Y.-P. Sun. *J. Org. Chem.* **1999**, *64* (16), 5913–5920.

21. O. Yildirim, Y. Denli, S. Aras, and G. Söylemezoglu. *Biotech. & Biotechnol. Equip.* **2014**, *17* (2), 114–122.

22. R. S. Bodannes and P. C. Chan. *North-Holland Biomedical Press* **1979**, *105* (2), 195–196.

23. N. Armaroli, G. Accorsi, J.-P. Gisselbrecht, M. Gross, V. Krasnikov, D. Tsamouras, G. Hadziioannou, M. J. Gómez-Escalonilla, F. Langa, J.-F. Eckert, and J.-F. Nierengarten. *J. Mat. Chem.* **2002**, *12* (7), 2077–2087.

24. W. C. Still, M. Kahn, and A. Mitra. *J. Org. Chem.* **1978**, *48* (14), 2923–2925.

25. J. L. Delgado, P. de la Cruz, V. López-Arza, F. Langa, Z. Gan, Y. Araki, and O. Ito. *Bull. Chem. Soc. Jpn.* **2005**, *78* (8), 1500–1507.

26. E. Espildora, J. L. Delgado, P. de la Cruz, A. de la Hoz, V. Lopez-Arza, and F. Langa. *Tetrahedron* **2002**, *58*, 5821–5826.

27. J. L. Delgado, P. de la Cruz, V. López-Arza, and F. Langa. *Tetrahedron Lett.* **2004**, *45* (8), 1651–1654.

28. A. R. Hajipour, I. Mohammadpoor-Baltork, and M. Bigdeli. *J. Chem. Res.* **1999**, 570–571.

29. F. Oswald, P. de la Cruz, and F. Langa. *Synlett* **2007**, *7*, 1051–1054.

30. Y. Wang, W. J. Hu, W. Song, R. K. V. Lim, and Q. Lin. *Org. Lett.* **2008**, *10* (17), 3725–3728.

31. W. Song, Y. Wang, J. Qu, and Q. Lin. *J. Am. Chem. Soc.* **2008**, *130* (30), 9654–9655.

32. R. G. Bulgakov, Z. S. Kinzyabaeva, L. M. Khalilov, and V. M. Yanybin. *Russ. J. Org. Chem.* **2011**, *46* (12), 1776–1779.